ICE 2017

International Conference on Electrolysis

1st International Conference on Electrolysis

12 – 15 June 2017

Book of abstracts

Sponsor:

EWII

Venue: Axelborg, Copenhagen, Denmark
http://ice2017.net

Idea and Scope for the ICE series

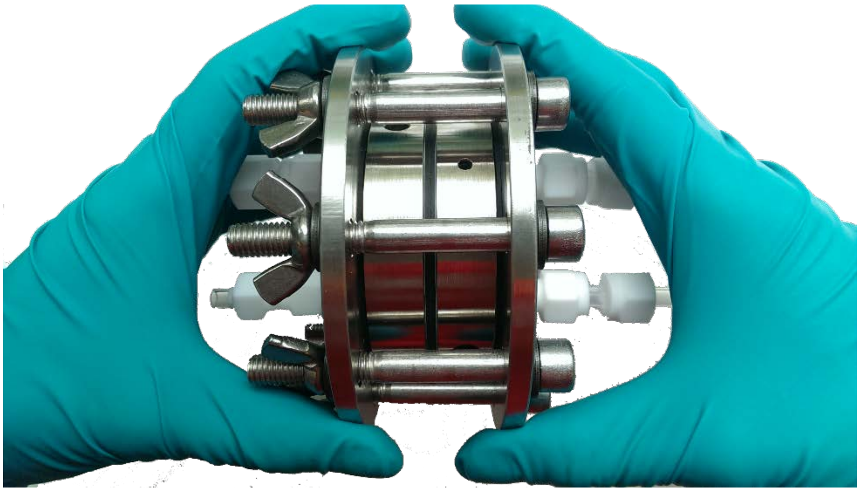
Electrolyzer events are rare and real conference series perhaps non-existing. Electrolyzers are equivalent to fuel cells, but while conferences devoted to fuel cells are plentiful, electrolyzer conferences are certainly not. Scientific and technical exchange of knowledge regarding electrolyzers are typically taking place in sub-sessions of fuel cell conferences or overarching hydrogen conferences like the WHEC. You may have joined one-at-a-time workshops or thematic meetings on electrolysis, but full-blown international conference series where the growing community can gather, network and share the latest findings in a regular manner remain to be seen.

Research in all the aspects of electrolysis for energy conversion is growing, and the awareness that the conversion from electrical energy to storable and portable matter - fuels - is an inevitable part of the green transition from a fossil based energy infrastructure to a sustainable one. Fuel cells are expected to play a vital role in this transition too, but they compete with proven and well-established technologies, while electrolyzers bridge a gab for which no other alternative is obvious. On this background it is even more striking that we have not yet managed to put up a designated conference series on electrolysis for energy conversion.

***The aim of this initiative** is to start a conference series devoted to electrolysis for energy conversion. Let us make a forum in which electrolysis is the main theme and not a sub-topic among many others. We prepared the setting for the fist event in a nice venue, but only the participants can ensure the success – now and for the years to come.*

Welcome at ICE2017 in Copenhagen

Jens Oluf Jensen
Chair of ICE2017



Invited Speakers

Everett B. Anderson – *Proton OnSite* (US)

Antonino Arico – *CNR* (IT)

Peter Blennow – *Haldor Topsoe A/S* (DK)

Oliver Borm– *Sunfire* (DE)

Tianshan Chen – *Purification Equipment Research Institute of CSIC* (CN)

Nick van Dijk – *ITM* (UK)

Steven Holdcroft – *Simon Fraser University* (CA)

John Irvine – *University of St. Andrews* (UK)

Nikolaos Lymperopoulos– *FCH Joint Undertaking* (B)

Pierre Millet – *Université Paris Sud* (FR)

Mogens B. Mogensen – *DTU Energy* (DK)

Bryan Pivovar – *NREL* (US)

Thomas J. Schmidt – *PSI* (CH)

Bjørn Simonsen – *NEL Hydrogen* (NO)

Carl Stoots – *Idaho National Laboratory* (US)

Jan Vaes – *Hydrogenics* (B)

Manfred Waidhas – *Siemens* (DE)

Hui Xu– *Giner Inc.* (US)

International Scientific Committee

Dmitri Bessarabov - ***HySA Infrastructure at North-West University* (ZA)**

Marcelo Carmo - ***Forschungszentrum Jülich* (DE)**

EunAe Cho - ***Korea Advanced Institute of Science and Technology* (KR)**

John T. S. Irvine - ***University of St Andrews* (UK)**

Jürgen Mergel - ***Forschungszentrum Jülich* (DE)**

Pierre Millet - ***Université Paris Sud* (FR)**

Bryan Pivovar - ***National Renewable Energy Laboratory* (US)**

Yang Shao-Horn - ***Massachusetts Institute of Technology* (US)**

Tom Smolinka - ***Fraunhofer ISE* (DE)**

Carl Stoots - ***Idaho National Laboratory* (US)**

Magnus Thomassen - ***SINTEF* (NO)**

Local Organising Committee

Jens Oluf Jensen - ***DTU Energy***

Mogens Bjerg Mogensen - ***DTU Energy***

Anne Hauch - ***DTU Energy***

Laila Grahl Madsen - ***EWII Fuel Cells***

Søren Knudsen Kær - ***Aalborg University***

Lars Nilausen Cleemann - ***DTU Energy***

David Aili - ***DTU Energy***

Lene Christensen - ***DTU Energy***

Jens Q Adolphsen - ***DTU Energy***

Christodoulos Chatzichristodoulou - ***DTU Energy***

Ming Chen - ***DTU Energy***

Katrine Elsøe - ***DTU Energy***

Filippo Fenini - ***DTU Energy***

Li Han - ***DTU Energy***

Mikkel Rykær Kraglund - ***DTU Energy***

Sebastian Molin - ***DTU Energy***

Aleksey Nikiforov - ***DTU Energy***

Carsten Brorson Prag - ***DTU Energy***

Saher Al Shakhshir - ***Aalborg University***

Shahid Ali - ***Aalborg University***

Samuel Simon Araya - ***Aalborg University***

Steffen Frensch - ***Aalborg University***

Saeed Sadeghi Lafmejani - ***Aalborg University***

Anders Olesen - ***Aalborg University***

Programme Overview

	Mon 12	Tue 13	Wed 14	Thu 15
08:00	Arrival+reg.			
08:30		Arrival+reg.	Arrival+reg.	Arrival+reg.
09:00	Opening	Talks PEMFC	Talks SOEC	Talks AEC
09:20	Talks Other			
09:40				
10:00				
10:20				
10:40	Coffee	Coffee	Coffee	Coffee
11:00	Talks PEMEC	Talks AEC	Talks PEMEC	Talks SOEC
11:20				
11:40				
12:00				
12:20				
12:40	Lunch	Lunch	Lunch buffet and Poster II EWII presentation 14:30	Lunch
13:00				
13:20				
13:40	Talks AEC	Talks SOEC		Talks PEMEC
14:00				
14:20				
14:40				
15:00			Harbour tour 15.30-16.30	
15:20	Coffee	Coffee		Coffee
15:40	Talks SOEC	Talks PEMEC		Talks AEC
16:00				
16:20				
16:40				Closing
17:00				
17:20	Welcome reception Poster I	Coffee	Free	
17:40		Talks Other		
18:00			Drink	
18:20				
18:40				
19:00			Dinner Axelborg	
19:20		Sci. Committee Meeting		
19:40				
20:00				
20:20				
20:40				
21:00				
21:20				
21:40				
22:00				
22:20				
22:40				
23:00				

Programme Monday 12/6

08:30	**Registration, Coffee**		
09:00-10:40	**Session 1. Special**	**Chair: Laila Grahl Madsen**	No.
09:00	**Welcome, opening remarks**	**Jens Oluf Jensen** DTU Energy Denmark	
09:20	Application of Potentially Inexpensive Ceramics in Electrolysis Cells	**Mogens B. Mogensen (INVITED)** DTU Energy Denmark	1
09:40	Overview of FCH JU support to Electrolysis for energy applications	**Nikolaos Lymperopoulos (INVITED)** FCH-JU, Energy Pillar Belgium	2
10:00	Efficient seawater electrolyzer based on Nickel Iron layered double hydroxide as selective Oxygen evolution reaction catalyst	**Sören Dresp** Technische Universität Berlin Germany	3
10:20	Corrosion-resistant materials for use in unconventional molten carbonate electrolysis environments: evaluation of Al-diffusion coatings for stainless steel protection in a ternary LiNaK carbonate melt at 500°C under CO_2 gas	**Stefano Frangini** ENEA Italy	4
10:40	**Coffee break**		
11:00-12:40	**Session 2. PEMEC**	**Chair: Marcelo Carmo**	No.
11:00	Advancing PEM Electrolysis for Current and Future Hydrogen Markets	**Everett B. Anderson (INVITED)** Proton OnSite USA	5
11:20	Key Performance Indicators for MW-scale PEM water electrolyzers	**Pierre Millet (INVITED)** Universite Paris Sud France	6
11:40	Business Opportunities for MW electrolysis and related Requirements	**Manfred Waidhas (INVITED)** Siemens AG Germany	7
12:00	Stack design for a Megawatt scale PEM electrolyser, and overview of the FCH-JU project MEGASTACK	**Magnus Thomassen** SINTEF Norway	8
12:20	Techno-Economic Modeling of Renewable Energy Hydrogen Supply Systems based on Water Electrolysis	**Øystein Ulleberg** Institute for Energy Technology Norway	9
12:40	**Lunch**		

Monday 12/6 (*Continued*)

13:40-15:20	**Session 3. AEC**	**Chair: Karel Bouzek**	No.
13:40	The Oxygen Evolution Reaction: The Enigma in Water Electrolysis	**Thomas J. Schmidt (INVITED)** Paul Scherrer Insitute Switzerland	10
14:00	Oxygen Evolution Reaction on Perovskites: A Combined Experimental and Theoretical Study of Their Structural, Electronic, and Electrochemical Properties	**Xi Cheng** Paul Scherrer Institut Switzerland	11
14:20	Electrocatalysis of Oxygen-Evolution on Well-Defined Mass-Selected NiFe nanoparticles	**Claudie Roy** Technical University of Denmark Denmark	12
14:40	Raney-Ni electrodes for the alkaline electrolysis of water	**Christian Müller** Fraunhofer IFAM Germany	13
15:00	Raney Nickel alloy electrodes for alkaline water electrolysis	**Syed-Asif Ansar** German Aerospace Center Germany	14
15:20	**Coffee break**		
15:40-17:20	**Session 4. SOEC**	**Chair: John Irvine**	No.
15:40	Roles for High Temperature Electrolysis in the Rapidly Changing US Energy Market	**Carl Stoots (INVITED)** Idaho National Laboratory USA	15
16:00	Solid Oxide Electrolysis for Grid Balancing: Recent Achievements and Future Challenges	**Ming Chen** DTU Energy Denmark	16
16:20	Operation and performance of tubular proton ceramic electrolysers	**Einar Vøllestad** University of Oslo Norwawy	17
16:40	Fabrication and Characterization of Metal-supported Solid Oxide Electrolysis Cells	**Feng Han** German Aerospace Center (DLR) Germany	18
17:00	Solid Oxide Electrolyzer Cells oxygen electrode based on infiltrated nanocomposite mesoporous materials	**Elba Hernández** Catalonia Institute for Energy Research-IREC Spain	19
17:20-19:40	**Poster session I**	**With welcome reception**	

Tuesday 13/6

08:30	**Registration, Coffee**		
09:00-10:40	**Session 5. PEMEC**	**Chair: Magnus Thomassen**	**No.**
09:00	The development and implementation of Ir based nanowires as oxygen evolution electrocatalysts	**Bryan Pivovar (INVITED)** NREL USA	20
09:20	The oxygen evolution at IrxRu1-xO2 produced by hydrolysis synthesis	**Svein Sunde** NTNU Norway	21
09:40	Study of the Physical Morphology and Electrochemical Characteristics of Oxygen Evolution Reaction (OER) Iridium Based Electrocatalyst Synthesized with a Polyol Method for PEM Water Electrolysis	**Brant A Peppley** Queen's University Canada	22
10:00	Anode catalysts for PEM electrolyzers: Synthesis, Activity and Degradation Aspects with Ex Situ and In Situ Characterization	**Li Wang** German Aerospace Center (DLR) Germany	23
10:20	On the design and optimization of a bimetallic (Co,Mn)-based catalyst for hydrogen evolution in acidic medium	**Ali Shahraei** TU Darmstadt Germany	24
10:40	**Coffee break**		
11:00-12:40	**Session 6. AEC**	**Chair: Thomas J. Schmidt**	**No.**
11:00	Hydrogen reaching fossil parity around the world	**Bjørn Simonsen (INVITED)** Nel Hydrogen Norway	25
11:20	PERIC’s development on AEL and SPE technology	**Tianshan Chen (INVITED)** Purification Equipment Research Institute of CSIC China	26
11:40	Alkaline Water Electrolyzers With Base Metal Catalysts Showing 1 A/cm^2 At 1.75 V	**Richard I Masel** Dioxide Materials USA	27
12:00	A unique approach for high intensity alkaline water electrolysis using a membraneless Divergent-Electrode-Flow-Through (DEFT TM) electrolyser	**Malcolm Gillespie** Hydrox Holdings Ltd. South Africa	28
12:20	High temperature alkaline electrolysis	**Christodoulos Chatzichristodoulou** DTU Energy Denmark	29
12:40	**Lunch**		

Tuesday 13/6 (*Continued*)

13:40-15:20	**Session 7. SOEC**	**Chair: Carl Stoots**	**No.**
13:40	Tailoring electrode interfaces for conversion	**John T.S. Irvine (INVITED)** University of St Andrews UK	30
14:00	Degradation Behavior of (La,Sr)(Fe,Co)O3 Solid Oxide Cell Oxygen Electrodes During Reversible Electrolysis and Fuel Cell Operation	**Scott Barnett** Northwestern University USA	31
14:20	Eliminating degradation and repairing damage in solid oxide cell and stack fuel electrodes	**Theis Skafte** DTU Energy Denmark	32
14:40	Post-test analysis of a solid oxide electrolysis cell operated for 23000 h	**Qingxi Fu** EIFER Germany	33
15:00	Regenerating the performance of solid oxide electrolyzers by periodic treatments to extend lifetime	**Christopher Graves** DTU Energy Denmark	34
15:20	**Coffee break**		

15:40-17:20	**Session 8. PEMEC**	**Chair: Bryan Pivovar**	**No.**
15:40	Megawatt scale dual stack PEM electrolysis development for enhancing renewable energy integration by providing grid services during hydrogen generation	**Jan Vaes (INVITED)** Hydrogenics Belgium	35
16:00	Increasing PEM water electrolysis energetic efficiency by a surface modification of Ti gas diffusion layer	**Karel Bouzek** University of Chemistry and Technology Prague Czech Republic	36
16:20	Materials and coatings for PEM water electrolysers	**Alejandro Oyarce** SINTEF Norway	37
16:40	Flow field design for high-pressure PEM electrolysis cells	**Anders Olesen** Aalborg University Denmark	38
17:00	Protective coatings for low-cost bipolar plates and current collectors of proton exchange membrane electrolyzers	**Philipp Lettenmeier** German Aerospace Center Germany	39
17:20	**Coffee break**		

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17:40-19:20	**Session 9. Special**	**Chair: Søren Knudsen Kær**	No.
17:40	EU Harmornised Test Protocols for Electrolysis Applications	**Georgios Tsotridis** Joint Research Centre Netherlands	40
18:00	Catalytic and Photochemically-Assisted Electroreduction of Carbon Dioxide	**Pawel Kulesza** University of Warsaw Poland	41
18:20	Impact of the design on performance loss in photo-driven water electrolysers	**Fredy Nandjou** EPFL/LRESE Switzerland	42
18:40	SO2 depolarized electrolyser- Enhanced H2 production with SiC foam flow layer	**Annukka Santasalo-Aarnio** Aalto University Finland	43
19:00	Sputtered Pt-containing electrocatalysts for SO_2(aq) electrolysis	**Anzel Falch** North-West University South Africa	44
19:20	**Scientific Committee meeting**		

Wednesday 14/6

08:30	**Registration, Coffee**		
09:00-10:40	**Session 10. SOEC**	**Chair: Anne Hauch**	No.
09:00	Steam Electrolysis as the Core Technology for Sector Coupling in the Energy Transition	**Oliver Borm (INVITED)** Sunfire GmbH Germany	45
09:20	Electrochemical Tailoring of Syngas	**Severin Foit** Forschungszentrum Jülich Germany	46
09:40	System design and operation of a solid oxide electrolyzer	**Ligang Wang** EPFL Switzerland	47
10:00	Solid oxide electrolyzes system development	**Richard Schauperl** AVL Austria	48
10:20	Electrochemical Characterization of a 10 layer Solid Oxide Electrolysis Stack operated under pressurized conditions	**Marc Riedel** German Aerospace Center Germany	49
10:40	**Coffee break**		
11:00-12:40	**Session 11. PEMEC**	**Chair: Pierre Millet**	No.
11:00	The Development of Accelerated Stress Tests for PEM Electrolysers	**Nicholas van Dijk (INVITED)** ITM Power UK	50
11:20	Benchmarking Catalyst Activity and Durability for Water Electrolysis	**Hui Xu (INVITED)** Giner Inc. USA	51
11:40	Operation of low-temp electrolyzers at very high current densities: a pipe dream or an opportunity?	**Krzysztof Lewinski** 3M USA	52
12:00	Membranes for recombination and electro-oxidation of permeated hydrogen in PEM electrolysis	**Dmitri Bessarabov** HySA at North-West University South Africa	53
12:20	Physical factors affecting gas-leakage from PEMWE	**Kohei Ito** Kyushu University Japan	54
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15:00	**Departure for Copenhagen Harbour tour**	
15:30-16:30	**Copenhagen Harbour tour**	

18:00	**Drink**	
19:00-23:00	**Conference Dinner**	

Thursday 15/6

08:30	**Registration, Coffee**		
09:00-10:40	**Session 12. AEC**	**Chair: Christodoulos Chatzichristodoulou**	**No.**
09:00	Polyaromatic, Solid Polymer Electrolytes for Acidic and Alkaline Electrolyzers	**Steven Holdcroft (INVITED)** Simon Fraser University Canada	55
09:20	Recent developments in alkaline pressure electrolysis with anion-conductive membrane (AEM)	**Ulrich Fischer** Brandenburg University of Technology Germany	56
09:40	Anion selective membranes based laboratory-scale alkaline water electrolysis stack	**Jaromír Hnát** University of Chemistry and Technology Prague Czech Republic	57
10:00	High Temperature Membraneless Alkaline Electrolysis	**Jeremy Hartvigsen** Missouri S&T USA	58
10:20	Alkaline membrane electrolysis with PEM-level electrochemical performance	**Mikkel Rykær Kraglund** DTU Energy Denmark	59
10:40	**Coffee break**		
11:00-12:40	**Session 13. SOEC**	**Chair: Scott Barnett**	**No.**
11:00	CO from CO2 – on-site carbon monoxide generation	**Peter Blennow (INVITED)** Haldor Topsoe A/S Denmark	60
11:20	Thermodynamic constraints in operating a solid oxide electrolysis stack on dry carbon dioxide gathered from the Mars atmosphere	**Joseph Hartvigsen** Ceramatec, Inc. USA	61
11:40	Development and flight qualification of a solid oxide CO2 electrolysis stack for the Mars2020 MOXIE project	**Jessica Elwell** Ceramatec, Inc USA	62
12:00	Synthetic methane production from CO2 methanation: process integration with SOEC electrolyser and reaction kinetics on hydrotalcite-derived catalyst and	**Andrea Lanzini** Politecnico di Torino Italy	63
12:20	Performance and durability of four 6-cell solid oxide electrolyser stacks for hydrogen and syngas production	**Mikko Kotisaari** VTT Finland	64
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13:40-15:20	**Session 14. PEMEC**	**Chair: Dmitri Bessarabov**	**No.**
13:40	Effect of catalyst loading on performance and durability of a PEM water electrolysis cell based on an Aquivion® perfluorosulfonic acid (PFSA) membrane	**Antonino S. Arico' (INVITED)** CNR-ITAE Italy	65
14:00	Aging of PEMWE catalyst coated membranes during dynamic operation: Electrochemical and microscopic study	**Georgios Papakonstantinou** Max Planck Institute for Dynamics of Complex Technical Systems Germany	66
14:20	Durability of PEMEC MEAs	**Laila Grahl-Madsen** EWII Fuel Cells Denmark	67
14:40	Towards selective test protocols for accelerated in situ degradation of PEM electrolysis cell components	**Thomas Lickert** Fraunhofer ISE Germany	68
15:00	Mechanical characterisation and durability of sintered bodies for PEM electrolysis	**Elena Borgardt** Research Center Juelich Germany	69
15:20	**Coffee break**		
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15:40	Complex of cobalt and molybdenum carbide nanoparticles for efficient oxygen evolution reaction in alkaline electrolytes	**Eunae Cho** KAIST Republic of Korea	70
16:00	Gold-Metal Oxide Core-Shell Nanoparticles As Electrocatalysts for Water Oxidation	**Maria Escudero-Escribano** University of Copenhagen Denmark	71
16:20	Modified carbon nanomaterials as highly active electrocatalysts for water-splitting	**Mohammad Tavakkoli** Aalto University Finland	72
16:40-17:00	**Closing**	**Jens Oluf Jensen** DTU Energy Denmark	

Monday 12/6 - POSTER SESSION

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	Nickel/Tungsten-Carbide Composite Catalysts for Oxygen Evolution in Alkaline Water Electrolysis	**Donghoon Song** KAIST Republic of Korea	103
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	A Facile Synthesis of Nano-sized IrO_2 and RuO_2 Catalysts for the Oxygen Evolution Reaction in Alkaline Medium	**Günther G. A. Scherer** TUM CREATE Singapore Switzerland	105
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	A 3-D micro porous Co-Fe-P catalyst for oxygen and hydrogen evolution reactions in alkaline water electrolysis	**Hyowon Kim** KAIST Republic of Korea	107
	Process intensification of alkaline water electrolysis by using 3-D electrodes	**Quentin De Radiguès** Université catholique de Louvain Belgique	108
	Don Quichote: Demonstration of How to Produce Hydrogen Using Wind Energy	**Ahmed Aly** FAST Italy	109
	Materials and coatings for PEM water electrolysers	**Alejandro Oyarce** SINTEF Norway	110
	From Polyelectrolytes to Robust, Highly Proton Conducting Hydrocarbon Membranes for PEM Fuel Cell and PEM Electrolysis Applications	**Andreas Münchinger** Max-Planck-Institute for Solid State Research Germany	111
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	Experimental analysis of local effects in a 50 cm PEM water electrolysis cell	**Christoph Immerz** Leibniz Universität Germany	115
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	Polymer functionalized carbon nanotubes as highly active bifunctional electrocatalysis for full water splitting	**Fatemeh Davodi** Aalto university Finland	122
	Spinel-structured materials as catalyst support/current collector materials for PEM electrolysis cells	**Filippo Fenini** DTU Energy Denmark	123
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	Development of SOEC stacks at DTU Energy	**Henrik Lund Frandsen** DTU Energy Denmark	135
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	Specific electrical conductivity in solid and molten CsH_2PO_4 and $Cs_2H_2P_2O_7$ – a potentially new electrolyte for water electrolysis at ~225-400 °C	**Aleksey Nikiforov** DTU Energy Denmark	140
	Oxygen Evolution Reaction Performance of $PrBaCo_2O_{5+\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{2+\delta}$ in Carbonated Electrolyte for Water Electrolysis	**Baejung Kim** Paul Scherrer Institut Switzerland	141
	The catalysis of the electrolytic production of H_2O_2	**Ifan Stephens** DTU Physics Denmark	142
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Wednesday 14/6 - POSTER SESSION

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	Hydrogen production from photovoltaic via “zero gap” alkaline electrolysis	**Jirina Polakova** UJV Rez, a. s. Czech Republic	202
	Mathematical model and experimental validation of a 15-kW alkaline electrolyzer	**Mónica Sánchez** Centro Nacional del Hidrógeno Spain	203
	Activity of plasma vapour deposited $Pt_xNi_yAl_z$ as anode electrocatalyst for (membraneless) alkaline water electrolysis	**Roelof Jacobus Kriek** North-West University South Africa	204
	Small-scale systems for alkaline water electrolysis	**Ulrich Vogt** Empa Switzerland	205
	New separator concepts for a radical improvement of the gas quality in alkaline water electrolysis (AWE)	**Wim Doyen** VITO Belgium	206
	Control and energy efficiency of alkaline and PEM water electrolyzers in renewable energy systems	**Joonas Koponen** Lappeenranta University of Technology Finland	207
	The effect of line frequency and forced commutation on the losses of the electrolyzer stack and the power supply unit	**Vesa Ruuskanen** Lappeenranta University of Technology Finland	208
	Hydrogen production as a part of P-to-X system	**Antti Kosonen** Lappeenranta University of Technology Finland	209
	Detection and modelling of hydrogen crossover in PEM electrolysers using EIS	**Julio César García-Navarro** German Aerospace Center Germany	210
	Demonstration of Impedance Spectroscopy as a Method to Evaluate Losses of Polymer Electrolyte Membrane Electrolysis Cells during Water Electrolysis	**Katrine Elsøe** DTU Energy Denmark	211
	Engineering of high temperature PEMWE	**Kohei Ito** Kyushu University Japan	212

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	The HyBalance Project will demonstrate how hydrogen can be used as mean to store energy which in turn will be used for Industry and fuel-cell vehicles	**Louis Sentis** Air Liquide Advanced Business France	213
	Advances in PEM Electrolyzer Components	**Madeleine Odgaard** EWII Fuel Cells Denmark	214
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Abstract No. 1 (INVITED)

Application of Potentially Inexpensive Ceramics in Electrolysis Cells

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Summary. The aims of this presentation are: 1) to give an overview of inexpensive ceramics already used for cell components like electrodes, porous membranes and diaphragms for liquid electrolyte immobilization, and supports for electrocatalysts and cells; 2) to outline strategies for search of stable and efficient electro-ceramics for electrolysis.

Abstract. It seems generally agreed that the whole world will need electrolysis of water and CO_2 for storing renewable energy in a relatively near future. Also a need for electrolysis type of cells for production of chemicals and fuels are appearing, and R&D activities have been started. However, there is a main problem for these applications, namely the costs.

Commercial electrolysis cells exist. Cells such as alkaline electrolysis cells for production of high purity hydrogen for industrial purposes, and cells for chlor-alkali and chlorate processes have been commercially available during more than a century [1,2]. Even though these types of cells are technically excellent for hydrogen production, they are too expensive for the energy sector. A lot may be learned from these old technologies, but the costs must be decreased significantly.

Some main types of electrolysis cells, AEC (alkaline electrolysis cell) [3,4,5], PEMEC (polymer electrolyte membrane electrolysis cell) [3, 6], MCEC (molten carbonate electrolysis cell) [7] and SOEC (solid oxide electrolysis cell)[5,8,9] will be reviewed with respect to state of the art materials and performance, followed by considerations on possible strategies to decrease the costs by improving cell performance and durability of cells based on non-precious elements with emphasis on ceramic materials.

Finally, possible interrelationships between structure, stability, conductivity and catalytic activity of oxides will be outlined.

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Abstract No. 2 (INVITED)

Overview of FCH JU support to Electrolysis for energy applications

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Summary. An overview of the support provided by the FCH JU to the development and demonstration of electrolysers is presented along with the success of the sector in reaching respective Key Performance Indicators.

Abstract. The Fuel Cells and Hydrogen Joint Undertaking is a Public Private partnership between the European Commission and European Industry and Researchers, its aim being to help hydrogen energy technologies reach market readiness by 2020. Out of the 728MEuro of support provided by the FCH JU since its launch, 93 MEuro (13%) were provided to 36 projects on Hydrogen Production topics and out of those 69 MEuro (9.5%) to 23 projects on electrolysers. Electrolysers are thus the workhorse for renewable hydrogen production and indeed have the lowest CO2 footprint ($27g_{CO2}/kWh_{H2}$) and highest TRL (7-8) compared to other routes like biogas reforming ($203g_{CO2}/kWh_{H2}$, TRL 8), biomass gasification ($162g_{CO2}/kWh_{H2,}$ TRL 7), concentrated solar for the thermal dissociation of water (TRL 5) or photo-electrochemical devices (TRL 3).

PEM electrolysers have received half of FCH JU electrolysis support (35.6MEuro) with two large demonstration projects (Hybalance and H2Future) accounting for 20MEuro. Solid Oxide electrolysers have received 20MEuro for research projects as this technology is at lower TRL levels. Alkaline electrolysers being the most mature technology have received 9MEuro for Research plus one large demonstration (Demo4Grid).

This type of support has led to Alkaline and PEM electrolysers meeting some of the Key Performance Indicators set by the FCH JU as can be seen in the table below where the international State of the Art is also shown.

	FCH JU project results 2015		MAWP target		non-European
	PEME	AE	2017		SoA
CAPEX, M€/(t/d)	⚠	✓	<	3.7	1.7-3.5 @ 1 MW / 500 kg/d
Energy consumption, kWh/kg	⚠	⚠	<	55	65
Efficiency degradation, %/y	✓	✓	<	2	1.1
Min load, % of nominal capa.	✓	-	<	5	0
Max load, % of nominal capa.	⚠	-	>	150	100
Hot start, seconds	✓	✓	<	10	10
Cold start, seconds	⚠	⚠	<	120	300

Besides support to technology development and demonstration, the FCH JU is supporting the European electrolysis sector through studies like the “Commercialisation of Energy Storage in Europe” study that identified a long term (2050) potential of 170GW of electrolysers in Germany if H2 costs of 2Euro/kg can be reached. The findings of a study on “Early business cases for Hydrogen in Energy Storage” will be available in Spring 2017 and will be included in the present publication.

Abstract No. 3

Efficient seawater electrolyzer based on Nickel Iron layered double hydroxide as selective Oxygen evolution reaction catalyst

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Summary. An efficient alkaline membrane based seawater electrolyzer was investigated by using NiFe-layered double hydroxide as selective seawater Oxygen evolution reaction catalyst

Abstract. In times of energy revolution, renewable energy saving plays an ever-increasing role. Commonly used water electrolysis for hydrogen production requires precleaned or easily available freshwater sources. The direct use of seawater could promote sustainable energy technology in areas of scarce fresh water but easily accessible seawater. To realize a seawater electrolyzer, a selective Oxygen evolution reaction (OER) catalyst that simultaneously suppresses the Chlorine evolution reaction (ClER) is required.

Based on a seawater electrolysis design criterion[1], highly crystalline Nickel Iron layered double hydroxides (NiFe-LDH) was identified and prepared to be tested in a membrane based electrolyzer using anion exchange membranes. The crystallinity was confirmed by using X-ray diffraction (XRD) and elemental composition by using inductively coupled plasma -optical emission spectrometry (ICP-OES). The catalyst materials were tested in artificial seawater (0.5 M NaCl) and different KOH concentrations. A current drop was determined when adding NaCl to the electrolyte, while increasing the KOH concentration counteracted the loss in current density. To explore this effect, the anion exchange membranes (AEM) were further investigated regarding their Ion conductivity at different KOH and NaCl concentrations using a four-electrode set-up. Long-term stabilities were further tested galvanostatically and as load alternating day/night measurements. After reapplying a potential, a strong "recovery effect" was discovered that could help increase overall activity and efficiency.

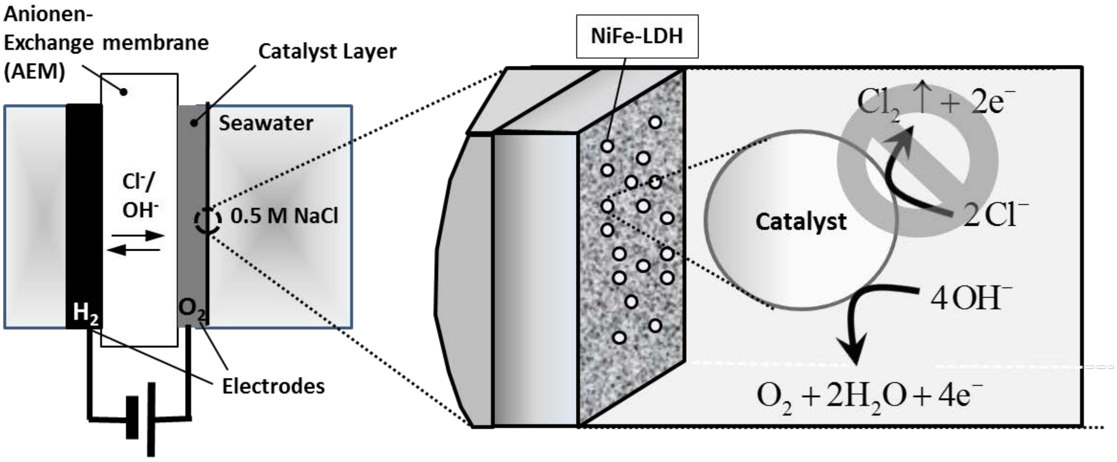

Figure 1:Simplified model of membrane based alkaline seawater electrolyzer and the corresponding anode reactions

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Abstract No. 4

Corrosion-resistant materials for use in unconventional molten carbonate electrolysis environments: evaluation of Al-diffusion coatings for stainless steel protection in a ternary LiNaK carbonate melt at 500°C under CO_2 gas

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Summary. A new steam electrolysis process in eutectic molten carbonate electrolytes is under investigation. Adequate corrosion-resistant materials need to be identified for a successful implementation of the electrolysis process. Corrosion stability of Al-diffusion coatings in a ternary LiNaK molten carbonate has been studied at 500°C under CO_2 gas.

Abstract. According to several scenario-based projections, high temperature steam electrolysis (HTSE) is expected to play an important role in the near future either for chemical energy storage applications or for sustainable production of H_2 by renewable energy sources. Although most current research focuses on temperatures > 750°C and solid oxide electrolyzers for maximum conversion efficiency, we have recently started the study of a novel steam electrolysis process at intermediate temperatures, that is at around 500°C, which is optimal for use of heat and electricity produced in Concentrating Solar Power plants. The proposed solar-powered electrolysis process uses a ternary eutectic molten carbonate electrolyte with a melting point of 397°C. Although the steam is supplied to the cathode side mixed with CO_2, only steam is subjected to electrolysis reactions in the operating conditions, whereas the role of CO_2 is to keep a stable molten carbonate electrolyte composition and to assist the cathode reaction. Due to the unconventional corrosive environment, studies with small-scale electrolytic cells are currently in progress to identify suitable electrode and structural materials for process optimization, cell design and scale-up. In this context, experience from the Molten Carbonate Fuel Cell (MCFC) technology indicates that Al-diffusion coatings can offer stable protection against stainless steel molten carbonate corrosion, although lower temperatures and higher content of the CO_2 corrosive gas are present in the electrolysis process as compared to MCFC. Therefore, the corrosion behavior of Al-diffusion coatings in molten carbonates has been rechecked under more appropriate electrolysis conditions. For this purpose, a 316L stainless steel sample was aluminized by pack cementation and then pre-oxidized in air at 750°C for improving its corrosion resistance. Finally, the aluminized sample was immersed for half of its size in eutectic Li/Na/K carbonate salt at 500°C under pure CO_2 gas for a 48 h period. The corrosion resistance of the Al-diffusion coating in the different zones of the sample was evaluated by SEM/EDX analysis. Results of the corrosion test will be reported at the time of the Conference.

Abstract No. 5 (INVITED)

Advancing PEM Electrolysis for Current and Future Hydrogen Markets

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Summary. PEM Electrolysis has been satisfying industrial applications for hydrogen for more than 20 years and is now poised to leverage that same successful commercial track record for the emerging renewable energy and mobility markets for hydrogen.

Abstract. Hydrogen is an important industrial gas, representing a 10 million metric tons/year industry worth $100 billion. Currently over 95% of that hydrogen is made from fossil fuels: natural gas reforming or coal gasification. Close to 50% of the world's annual hydrogen production is used for ammonia generation and oil refining, with the hydrogen generation being the highest energy and highest emission subcomponent of ammonia generation. In addition, 2% of U.S. energy currently goes through hydrogen as an intermediate, a number that will increase substantially when hydrogen-fuelled vehicles become widespread. To meet the Climate Action Plan goals of 80% reduction in greenhouse gas emissions by 2050, net zero carbon pathways for hydrogen production are therefore critical.

There are several pathways to generating hydrogen from renewable sources, but one of the most advanced is membrane-based water electrolysis powered by solar, wind, or hydropower. While electrolysis has been demonstrated at megawatt scale, there is still significant promise for further improvement. Several countries are already committed to advancing this technology, and are working on the critical materials issues that drive cost and efficiency. Longer term technologies such as photoelectrochemical water splitting or thermochemical routes may provide lower cost pathways in the end, but need to build from technologies that have already been developed at relevant scale.

The "perfect" technology to address the energy challenge will always be 20 years away. As new concepts move from basic principles to bench-scale experiments and beyond, the pitfalls become clearer. At the same time, dismissing existing commercial technologies because of limitations which might become relevant at multi-gigawatt or terawatt scale prevents us from maximizing early impact on sustainability. Commercial proton exchange membrane (PEM)-based electrolysis has advanced to larger and larger scale over the last twenty years, progressing from systems of 1 kg H_2/day or less to several hundred kg/day. While leveraging the same basic manufacturing processes and technology, scale up has driven down the capital cost per kg of hydrogen by over 80%. PEM electrolysis also has tremendous potential for continuing cost reduction, leveraging system and manufacturing scaling laws as well as leveraging advancements in PEM fuel cell materials, manufacturing, and analysis tools. Order-of-magnitude improvements in some of the highest cost elements are easily achievable. The technology elements are known, but need to be refined and validated in a manufacturing environment, including modifications in materials and methods of fabrication. This presentation will focus on the need to leverage existing clean energy technologies in the near term to serve the megawatt and gigawatt scale, as building blocks and bridges to future technologies.


H Series
C Series
M Series
1 MW Process Skid
S Series
Lab Gas Generators
2 MW Process Skid

Proton OnSite's Line of Commercial PEM Electrolysis Products

Abstract No. 6 (INVITED)

Key Performance Indicators for MW-scale PEM water electrolyzers

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Summary. Emerging water electrolysis markets are calling for systems of increasing size. Compared to hydrogen from methane (via SMR, even when CCS is included), electrolytic hydrogen is penalized by a higher energy cost which, on MW systems and above, is expected to account as much as 80% of the production cost. Access to low cost kWh is therefore a key factor to make water electrolysis cost competitive. In the frame of the energy transition, increasing amounts of intermittent electric power are expected to transit on national electricity grids. Grid services and the energy trade market are expected to increase significantly. Opportunities to purchase low cost electrical kWh (including at negative price) are appearing but from the engineering viewpoint, the resulting constraint is the need for more flexible and more reactive water electrolysis plants. This could in turn have deleterious effect on process efficiency, safety, durability and cost. The situation might be even worse if the electrolysis plant is directly powered by more intermittent wind or solar power sources. Among three main water electrolysis technologies (alkaline, PEM and steam electrolysis), proton exchange membrane (PEM) is considered as very promising and very capable to satisfy these new operating constraints. The purpose of this communication is to discuss a set of key performance indicators that can be used for the qualification of MW-scale PEM water electrolysers for grid services.

Abstract. There are currently three main markets of different maturity for electrolytic (from water) hydrogen: (i) H_2 as a chemical for miscellaneous applications in the industry; (ii) H_2 as an energy-vector for mobility applications (via on-board power generation by electrochemical combustion of hydrogen in air using fuel cells); (iii) H_2 as an energy-vector for power-to-gas and large scale energy storage. Whereas commercial activities are mostly supported by the H2-chemical market, mobility applications seem and endless short-term reality and power-to-gas a promising El Dorado for technology manufacturers.

Considering the fact that, for large water electrolysers, the cost of the H2-kg is increasingly determined by the cost of electricity, expected progress in process efficiency, although highly desirable, will not be sufficient to make electrolytic hydrogen cost competitive with incumbent technologies. Cheap kWh is required, as has always been. The energy transition and the massive irruption of intermittent electricity might offer some determining opportunities to those who will be able to put on the market appropriately large and flexible technologies. Also, downstream operating constraints (e.g. periodical production of compressed hydrogen) may interfere with input power constraints, requiring customized technologies that still need to be developed. Whereas most commercial PEM water electrolysis applications are designed for stationary operation, a higher flexibility that would not penalize efficiency, safety, durability and cost poses some interesting challenges to the electrochemical engineer in charge of R&D activities. Here, the water electrolysis plant as a whole (including the electrochemical reactor but also a set of ancillary equipment such as the water purification unit, the gas purification unit, etc.) needs adaptation.

The purpose of this communication is first to review the opportunities and constraints imposed by emerging grid services, then to present and discuss key performance indicators (KPI) that can be used for the characterization of MW-scale PEM water electrolyzers wishing to operate on such markets. The first KPI of interest is the efficiency in transient conditions of operation. A detailed description of efficiency calculation in varying T,P conditions will be presented. The second KPI is process flexibility, i.e. the ability of the water electrolysis plant as a whole to operate on demand to any power load set between zero (off-grid) and maximum power (full on-grid). The third KPI is process reactivity, i.e. the rate at which the setting power can be reached. The fourth KPI is the safety of operation. Ramp-up and ramp-down load profiles are expected to change gas composition and to induce accelerated ageing processes. Both may raise safety issues during operation. The fifth KPI is durability, i.e. the ability of the water electrolysis plant to operate in a flexible way on a sufficiently long period of time to maintain capex aligned with market requirements.

Some results that demonstrate the potential of PEM water electrolysis for such applications will be presented and finally, some development challenges (in terms of material but also in terms of water electrolysis plant as a whole) will be highlighted.

Abstract No. 7 (INVITED)

Business Opportunities for MW electrolysis and related Requirements

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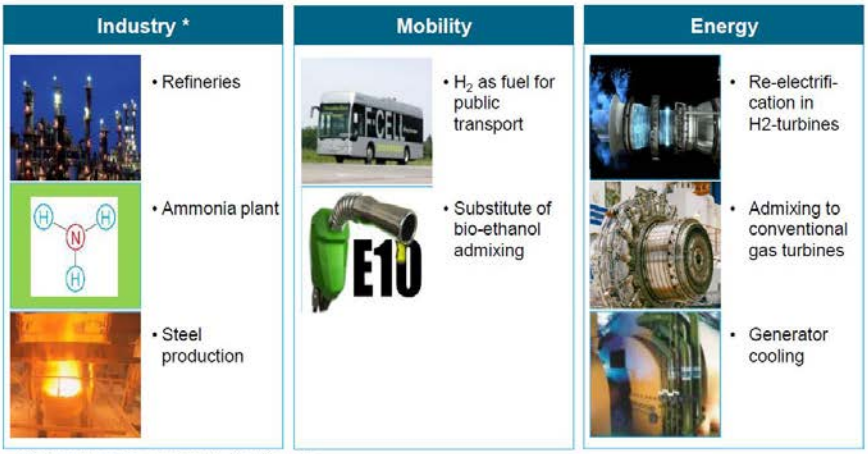
Summary. Hydrogen is an enabler to push forward the energy transition in an economically viable manner. Siemens view on this topic is provided and some examples along its roadmap are described.

Abstract. If the worldwide commitment to CO_2- reduction remains vivid the forced extension of renewable energies (RE) is mandatory. The big challenge in this context is the volatile character of its power generation leading to an increasing mismatch between generation and demand. The storage of excess production will become essential in the future in order to enable viable business cases. The estimated storage demand in many countries with related CO_2 reduction plans will be in the TWh range.

Among the three options for large-scale storage – pumped hydro, compressed air and hydrogen - hydrogen is the only viable option to address capacities >10 GWh. Moreover, it is a multifunctional chemical energy carrier. It provides the option to be re-electrified without CO_2 emissions. But it is also a valuable raw material in chemical industry with a market volume of approx. 100 billion USD.

Coupling the Energy sector with the industrial and mobility world is the relevant key to proceed in the energy transition and to make it affordable. Enabling component of the hydrogen storage concept is the electrolyzer system. It must – among a number of other features – be reliable under industrial working conditions and its overall efficiency must be optimized for intermittent operation. With the intention to provide solutions for future energy grids Siemens developed the PEM system called "SILYZER".

The presentation will point out relevant technical requirements and necessary frame condition for a competitive market environment. Information is given on the modular Silyzer 200 system, successfully operated at 'Energiepark Mainz' and the new Silyzer 300 development. It is modular as well and planned to cover the power range of approx. 10 to 100 MW.



* Besides these: glass, semiconductor, food&beverage

Fig: Green hydrogen has a broad variety of potential applications

Abstract No. 8

Stack design for a Megawatt scale PEM electrolyser, and overview of the FCH-JU project MEGASTACK

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Summary. The FCH-JU project MEGASTACK is developing a PEM electrolyser stack design for MW-sized water electrolysers. This presentation will give an update of the main achievements and results from the MEGASTACK project from fundamental aspects of transport in porous titanium sinters, two phase flow modelling to design and cost elements of the final stack design.

Abstract. In the MEGASTACK project we take advantage of the existing PEM electrolyser stack designs of ITM power as well as novel solutions in the low-cost stack design concepts developed and further refined in the FCH-JU projects NEXPEL and NOVEL. In order to successfully up-scale the design concept from a 10-50 kW to a MW-sized stack, an integrated two-phase flow and structural mechanics modelling approach has been applied together with optimization of stack components such as MEAs, current collectors and sealings which are important for stack scale up. The development activities have focused on existing solutions, already proven in kW-sized electrolyser stacks, rather than aiming to use completely new, unproven concepts and materials. The stack design will have ease of manufacture and stack assembly as a major goal, with necessary quality control processes and robust supply chains for components.

To reach these ambitious objectives, MEGASTACK has developed and will demonstrate an enhanced stack design essential for cost-competitive, efficient and dynamic PEM electrolysis systems through the following key concepts:

- The stack design process will have an integrated approach, involving stack manufacturers, component and MEA suppliers as well as PEM electrolyser experts from research institutes.
- Evaluation and adaptation of existing solutions and commercially available components for use in large format stacks and increased ease of stack assembly by the reduction of stack part count.
- Advanced multiphase flow modelling coupled with multiphysics models for electrochemical kinetics, heat and momentum transport will be used as detailed design tools for cell and stack components.
- Implementation of quality control measures and supply chain evaluation of all components will be performed in order to reduce costs and minimise technology and manufacturing risks

Abstract No. 9

Techno-Economic Modeling of Renewable Energy Hydrogen Supply Systems based on Water Electrolysis

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Summary. There is a growing interest for using renewable power to run water electrolyzers for on-site production of hydrogen for supply to various energy, industrial, and transport applications. How can such systems become cost-efficient? A techno-economic modelling tool has been developed in order to try to answer this question.

Abstract. On-site small water electrolyzer systems are modular, and can be developed for many different sizes and capacities. Several international companies supply on-site hydrogen production system, and the technology readiness level is high (TRL 7-9). However, on a system level it is still necessary to develop more energy and cost-efficient solutions. In order to achieve this it will be necessary to both reduce the amount of materials used in the key components (e.g. cells and stacks) and to develop more efficient overall balance of plants (e.g. drying, compression, and storage, and electrical systems).

A simplified equation based techno-economic modelling tool has been developed in EES (Engineering Equation Solver program). This program can adjusted and used to access the techno-economics of a wide range of renewable power based water electrolyzers systems, including hydrogen compression, storage and dispensing systems. The models are based on up-to-date technical performance data obtained from leading PEM and alkaline water electrolyzer and other hydrogen technology suppliers around the world, and cost data collected in various projects conducted at IFE over the past few years.

The modelling tool has been applied in to evaluate the economic viability (*business case*) for both large-scale (4-5 MW) and small-scale (150-200 kW) hydro-electric power based water electrolysis systems. The techno-economic viability of a system (Figure) connected to a small-scale hydro-electric power plant in Norway is presented.

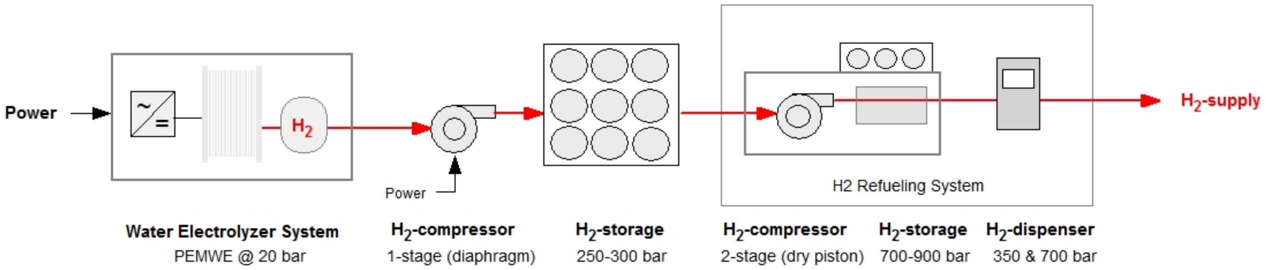

Figure – System schematic of the water electrolyzer and hydrogen supply system evaluated in this study

Abstract No. 10 (INVITED)

The Oxygen Evolution Reaction: The Enigma in Water Electrolysis

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Summary. In order to gain better mechanistic understanding for the oxygen evolution reaction in both acidic and alkaline environment, nanoscaled oxides are investigated by electrochemical methods and by operando x-ray absorption spectroscopy. Important insights could be gained on the surface self-assembly of the catalyst surface responsible for high activity.

Abstract. Oxygen electrodes are playing a key role in electrochemical energy conversion devices such as fuel cells and water electrolyzers. In both acidic and alkaline environment, both the oxygen reduction and oxygen evolution reaction (ORR and OER), respectively, are limiting the overall energy/voltage efficiency due to its sluggish kinetics. [1, 2]

Whereas in acidic environment, mainly precious metal oxides are used to catalyze the OER (e.g., IrO_2), the variety of possible catalysts in alkaline electrolyte is significantly increased and many metal oxide based systems can be employed. Generally the oxygen evolution mechanism is only partly understood independent of the electrolyte environment and material used. In order to help to understand the underlying mechanism for the OER and to support the experimental results, very often computational methods are used, mainly using density functional theory (DFT) calculations. Similar approaches are also used for gaining insights into catalyst stabilities under operational conditions.

In this talk, some of your recent findings on noble and non.noble metal catalysts, i.e., nanoscaled IrO2 and nanoscaled perovskites will be presented. By employing operando X-ray absorption spectroscopy (both XANES and EXAFS), important insights could be gained with respect to the oxide electronic structure and the local catalyst structure helping to better understand the underlying mechanism for the OER.

Acknowledgement. This work is supported by the Swiss National Science Foundation, the Swiss Competence Center for Energy Research (SCCER) Heat & Electricity Storage, the Swiss Federal Office of Energy and the Competence Center Energy & Mobility Switzerland.

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Abstract No. 11

Oxygen Evolution Reaction on Perovskites: A Combined Experimental and Theoretical Study of Their Structural, Electronic, and Electrochemical Properties

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Summary. The correlation between the OER activity with one physico-chemical materials property presents always some deviation points, indicating the limit of the 2-Dimension correlation. Hence, we try to correlate the OER activity with several physico-chemical materials properties at the same time and leading to a 3-Dimension correlation.

Abstract. Perovskite Oxides (ABO_3) with alkaline or rare-earth cations in the A-site and first row transition metal cations in the B-site have shown the potentials of being viable oxygen electrode catalysts in alkaline solution [1]. Furthermore, it was demonstrated that their physical-chemical properties as well as their catalytic activity can be significantly influenced by substitution or partial substitution of the A and/or B-site by other elements giving $(A_xA'_{1-x})(B_yB'_{1-y})O_3$ compositions. However, it is a difficult task to find the most active oxides among the many different families of perovskites. A descriptor-based analysis can provide a promising approach to predict and identify the most active materials, since it correlates the prospective electrocatalytic activity to other, simpler properties.

In the present work, the crystallographic structure, bulk electronic structure, conductivity and electrochemical activity toward the oxygen evolution reaction for two perovskite series ($La_{1-x}Sr_xCoO_3$[2] with x=0, 0.2, 0.4, 0.6, 0.8, 1 and $LaBO_3$ with B=Cr, Mn, Fe, Co, Ni) are investigated experimentally and theoretically. Experimental characterizations (XRD, XAS, neutron diffraction, ex-situ electronic conductivity and OER measurements) demonstrate that the varying of the A-site and B-site delivers several changes in the physicochemical properties of the considered oxides. But by combining experiments with density-functional theory calculations, we show that it is possible to reliably relate some simple physico-chemical materials properties including the electronic structure to the observed activity towards the oxygen evolution reaction. However, the correlation between the OER activity with one physico-chemical materials property presents always some deviation points, indicating the limit of the 2-Dimension correlation. Hence, we try to correlate the OER activity with several physico-chemical materials properties at the same time and leading to a 3-Dimension correlation. This correlation might facilitate the search and design of highly active oxygen evolution catalysts, in the quest for efficient anodes in water electrolyzers.

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Abstract No. 12

Electrocatalysis of Oxygen-Evolution on Well-Defined Mass-Selected NiFe nanoparticles

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Summary. Electrocatalysis of oxygen-evolution on well-defined Mass selected NiFe(O_x) nanoparticles was investigated in 1 M KOH. Results obtained show a turnover frequency among the highest in alkaline media. This well-defined system provides key insight towards the optimization of the electrocatalytic activity of the NiFe system.

Abstract. Water electrolysis can provide a means to produce hydrogen using renewable electricity. The storage of energy using hydrogen as fuel is hindered by the sluggish kinetic of the oxygen evolution reaction. In order for these devices to be developed on a large scale, more active catalysts are needed. NiFe oxy-hydroxides are the current state-of-the-art catalysts for oxygen evolution. The origin of their activity is currently under intense debate. For example, there is uncertainty whether the bulk or the surface is active. In order to improve the catalysis of this reaction, it is important to gain further understanding of the factors controlling the intrinsic activity. To this end, in our current study, we investigated well-characterized model systems of NiFe nanoparticles[1-3]. We deposited mass-selected NiFe nanoparticles with different sizes on polycrystalline gold substrates to create well-defined model-systems. Our laboratory previously this approach to elucidate oxygen reduction[4] and hydrogen evolution[5].

A wide range of techniques was used to characterize our model system: X-ray Photoelectron Spectroscopy, Ion Scattering Spectroscopy, X-ray diffraction, Secondary Electron Microscopy and Transmission Electron Microscopy. We tested the catalysts electrochemically for oxygen evolution in 1 M KOH using a rotating ring disk electrode set-up. The activity as function of particle size and interparticle distances was evaluated, as well as measuring the stability against corrosion. Our results show that the particles have among the highest intrinsic activity of non-noble alkaline oxygen evolution catalyst reported.

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Abstract No. 13

RANEY-NI ELECTRODES FOR THE ALKALINE ELECTROLYSIS OF WATER

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Summary. Raney-Ni electrodes were produced via a powder metallurgical route and electrochemically characterized. The results suggest that the formation of nickel hydrides is a crucial issue for the degradation of Raney-Ni electrodes. An operating instruction is given to minimize the degradation of Raney-Ni electrodes.

Abstract.

The growing energy consumption and the shortage of the fossil energy sources necessitate the search for alternative energy carriers. In this regard, hydrogen is a safe and versatile energy carrier which can be produced via water electrolysis using renewable energy sources (“green hydrogen”). For a commercial H_2-based energy cycle (mobile application) the production costs of green hydrogen must drop below 6 €/Nm³. Therefore, the CAPEX as well as the OPEX of electrolysers has to be improved by developing more active and stable electrode materials for the hydrogen evolution reaction (HER).

In this contribution we report on 3-dimensional Raney-Ni electrodes, which were produced and characterized under industrial relevant conditions (see Figure 2). Ni meshes were employed as a porous substrate material. The porosity of the electrode is decisive to manage the flow of evolved gas bubbles to the backside of the electrode. A powder metallurgical route was deployed to produce the Raney-Ni electrodes, including the following steps: deposition of Al-powder, formation of the Raney-Ni phases (heat treatment) and leaching in KOH solution at 353 K. Different powder/mesh ratios (PMR) were tested and the corresponding electrochemical properties were studied. The galvanostatic measurements (GS) indicate that a high Al-powder mesh ratio (PMR) is necessary to receive a stable Raney-Ni layer. Also the HER-activity of the electrode increases dramatically with the PMR value. This is mainly due to the formation of a very high electrochemically active surface area (determined with cyclic voltammetry (CV)), which gives rise to very high number of reaction sites for the HER. Ex-situ investigations of the cross section of the electrodes reveal that the main deactivation path of the Raney-Ni electrodes is the delamination of the catalyst layer. Linear sweep voltammetry (LSV) experiments suggest that during the HER the formation of nickel-hydrides occurs (see Figure 2 b)), which is accompanied with the volumetric expansion of the Raney-Ni layer. This, in turn, might lead to the delamination of the Raney-Ni layer. In the presentation the results are discussed in more detail and an operating instruction is given to minimize the degradation of Raney-Ni electrodes.

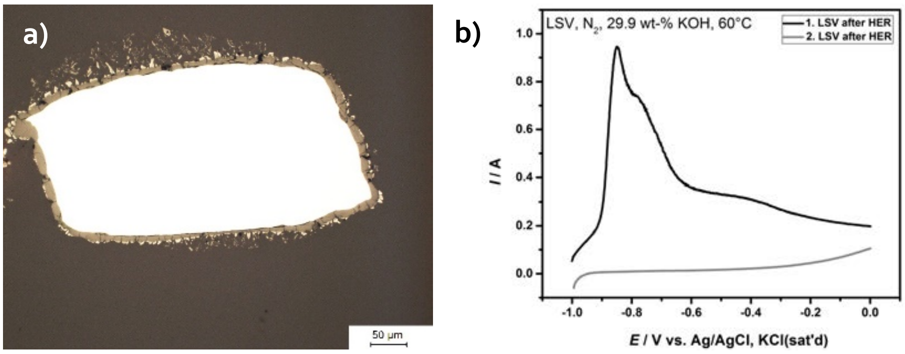

Figure 2: a) cross section of a Raney-Ni electrode and b) linear sweep voltammogram of a Raney-Ni electrode after HER.

Abstract No. 14

Raney Nickel alloy electrodes for alkaline water electrolysis

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Summary. Alkaline electrolysis anodes and cathodes of high efficiency and stability were developed using vacuum and atmospheric plasma spraying. Low cost materials and a simplified coating process allow for cost reductions.

Abstract. Alkaline water electrolysis for hydrogen production is a well-established technique available commercially in a wide power range. Hydrogen production by electrolysis is increasingly studied as a way to smoothen the fluctuating power output of renewable energy sources in oversupply situations. However, some technological issues regarding the coupling of alkaline water electrolysis and Renewable Energy Sources (RES) remain unaddressed. The presented research aims at improving present electrolysers for the specifics of direct coupling to fluctuating power operation. Due to the cost-effective hydrogen production by steam reforming as competition the importance of electrolyser cost reduction and improving efficiency is paramount. One of the aspects is to develop high-efficient electrolysers with superior current density that can tolerate periods of idling without degradation. Electrodes with low cost coatings for this purpose are presented here.

Efficient electrodes are prepared by vacuum plasma spray deposition of catalyst powders at DLR onto plain nickel electrodes. The electrodes with Raney-nickel-alloy coatings give an overpotential reduction of 330 mV compared to uncoated electrodes thus showing high performance with low cost materials. Long term on-off tests were performed in half cells. Considering only the electrode potentials of anode and cathode together an excellent stability was demonstrated: after 1100 on-off cycles 98% of the initial efficiency was retained. Electrodes were tested in half cells and in a 300 cm^2 alkaline single cell.

To further reduce the costs for electrode coating atmospheric pressure plasma spraying is tested. First results of this seem quite promissing reaching the same performance level as for vacuum plasma spraying.

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° [278732] 10, project RESelyser. See also www.reselyser.eu. Furthermore support by the Ministerium für Finanzen und Wirtschaft Baden-Württemberg (MFW) in Leuchtturmprojekt „Power-to-Gas" is gratefully acknowledged.

Abstract No.15 (INVITED)

Roles for High Temperature Electrolysis in the Rapidly Changing US Energy Market

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Summary. The United States energy market has changed dramatically over the past decade. Although the drivers and implementation strategies for water-splitting-based hydrogen production have changed, there still remains significant interest and need for advanced hydrogen production technologies.

Abstract. The United States Department of Energy (DOE) established the Nuclear Hydrogen Initiative in the year 2003 to study how nuclear energy (in particular, high temperature gas-cooled nuclear reactors) could be diversified beyond baseload electricity generation power water-splitting for large-scale hydrogen production. At that time, the motivation was primarily energy security. US policy makers had been concerned about the US dependence upon imported energy since World War II. These concerns were highlighted in the 1970s when the US experienced sharply rising oil prices, which in turn led to economic recessions and inflation. Furthermore, energy pundits began to worry about a concept called “Peak Oil.” First put forward by M. King Hubbert, this concept suggests that oil production follows a steep bell curve, where production rises and then enters a permanent decline. His theory suggested that US oil production would peak sometime in the late 1960s and then decline – which ended up being partially correct. Dropping US oil production was thought to potentially cause the US to be increasingly dependent on other producers, leading to issues of domestic energy security. By introducing a second energy currency that could be sustainably produced domestically, the US government hoped to avoid over-dependency upon foreign, and potentially hostile, entities for energy.

However, instead of US oil production continuing to drop, production began to rise steadily in 2009 due to new advanced drilling technologies (horizontal drilling / hydraulic fracturing) and hence new access to previously inaccessible reserves of shale oil and gas. Fracking has had a profound impact upon the US energy market. The HIS Markit estimated that fracking “increased disposable income by an average of $1200 per US household in 2012” and an average reduction in electricity costs of 10%. In parallel to the growth of fracking, the US has also been experiencing an explosion of renewable energy, primarily wind and solar. Both coal and nuclear power are traditionally large, baseload, electricity generators which experience increased costs and maintenance when forced to cycle in response to renewable (nondispatchable) energy availability. Nuclear operators in the US are now struggling to stay open, more than six nuclear reactors have recently shut down, and 15 to 20 more plants are at risk of premature shutdown in the next decade due to natural gas economics. And coal-based electricity production has dropped from 53% of the US energy mix in 1993 to 33% in 2015.

Despite the dramatic changes in the US energy portfolio, hydrogen via high temperature water splitting is still considered an important long-term energy strategy and continues to generate interest at the US DOE. Technologies such high temperature electrolysis can be linked to nuclear reactors to enhance their economic competitiveness via diversification beyond baseload electricity generation. High temperature electrolysis can enhance grid stability by absorbing excess electricity via hydrogen production and storage. The same technology can provide additional electricity generation capacity when renewables are not available. High temperature electrolysis can provide hydrogen to upgrade oil, and convert low value carbon sources to higher value carbon products (synfuels, plastics, etc.). Ultimately, hydrogen from water is being studied as the next major transportation fuel, powering fuel cell vehicles.

Abstract No. 16

Solid Oxide Electrolysis for Grid Balancing: Recent Achievements and Future Challenges

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Summary.

Solid oxide electrolysis is a promising technology for energy storage and synthetic fuel production and it has a unique potential for grid regulation in the Danish power system. In this presentation results from the recent ForskEL projects coordinated by DTU Energy on developing the SOEC technology will be presented.

Abstract.

Globally the amount of electricity generated from renewable energy sources is increasing. To integrate high amount of fluctuating energy into the existing energy grid, efficient and cost competitive conversion of electricity into other kinds of energy carriers is needed. Solid oxide electrolysis (SOE) has the potential to become a key technology in enabling this integration. With solid oxide electrolysis cells (SOECs), electrical energy can be converted to chemical energy and stored as H_2 or synthesis gas (syngas, $CO+H_2$) via high temperature electrolysis of steam or co-electrolysis of steam and CO_2. H_2 and syngas can be further processed to a variety of synthetic fuels, which may be stored and later either reconverted into electricity or used in the transportation sector. Within the last decade, DTU Energy coordinated and participated in a number of ForskEL projects funded by Energinet.dk, on developing the SOEC technology together with Haldor Topsoe A/S. In this presentation results from the recent ForskEL projects (ForskEL 2013-1-12013 “Solid Oxide Electrolysis for Grid Balancing” and ForskEL 2015-1-12276 “Towards Solid Oxide Electrolysis Plants in 2020”) will be given. The focus will be on performance and durability of different generations of SOEC cells and stacks, together with post-mortem analysis results. Latest results on using SOEC stacks for grid balancing based on real-world wind profile will be highlighted. Potential problems in terms of life time limiting degradation phenomena in SOEC operation (both at the cell level and at the stack level) will be discussed in detail based on own findings as well as literature. Finally, some of the challenges faced in the future development of SOEC cells, stack components and stacks will be presented.

Abstract No. 17

Operation and performance of tubular proton ceramic electrolysers

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Summary. Tubular proton ceramic cells based on Y-doped Ba(Zr,Ce)O_3 are developed with a novel double perovskite steam electrode ($Ba_{1-x}Gd_{0.8}La_{0.2+x}O_{6-\delta}$). State-of-the-art performance is achieved at 600°C with a total cell resistance of 3.5 Ωcm^2 and a total electrode resistance of 1.5 Ωcm^2. Optimization of the electrolyte layer and adhesion between electrolyte and electrode layers should give room for further improvement of these cells to achieve the required total cell resistances well below 1 Ωcm^2.

Abstract.

With the recent introduction of hydrogen-fuelled vehicles in major markets there is an increased demand to develop new cost-efficient technologies for clean and renewable hydrogen production. High temperature electrolysers (HTEs) may produce H_2 efficiently utilising electricity from renewable sources and steam from solar, geothermal, nuclear, or industrial plants. The traditional solid oxide electrolyser (SOE) leaves wet H_2 at the steam side. In contrast, proton ceramic electrolysers (PCEs) can pump out and pressurize dry H_2 directly. Further, the danger of delamination of oxygen electrodes due to O_2 bubbles in SOECs is alleviated in PCECs. Literature reports on the use of various solid solutions of the $BaZrO_3$-$BaCeO_3$ system (BZCY) as the electrolyte, with promising current densities. However, relatively high polarization resistance of the O_2/H_2O-electrode and non-faradaic electronic leakage currents are challenges that are not properly understood or quantitatively described.

In this contribution, we investigate a cathode-supported tubular proton ceramic electrolyser cell using a 30 µm $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$ electrolyte with a Ni-BZCY composite as the cathode (H_2-electrode) and the double perovskite $Ba_{1-x}Gd_{0.8}La_{0.2+x}O_{6-\delta}$ (x = 0-0.5) as the anode (H_2O-O_2 electrode). Current-voltage characteristics and hydrogen production rates are measured as a function of steam pressure (pH_2O = 0.5-4 bar) and pO_2 in the temperature range 500-700°C. Combined with electrochemical impedance spectroscopy under electrolysis operation we are able to describe the functional dependencies of the electrodes and the electrolyte separately.

The best performance at 600°C was achieved using a $Ba_{0.7}Gd_{0.8}La_{0.5}O_{6-\delta}$ electrode, and operating the cell at 1.4 V for a current density of 250 $mAcm^{-2}$ with 4 bar steam in the anode compartment. This is the best PCE performance reported in literature to date. With a total electrode polarization resistance of 1.5 Ωcm^2, most of the voltage drop through the cell is due to ohmic resistances in the electrolyte and current collectors, which should be central in further improvement of PCEs.

Acknowledgments

Financial support by the Spanish Government (Grants SEV-2012-0267 and ENE2014-57651) and by the EU FP7 Fuel Cells and Hydrogen (FCH) Joint Technology Initiative (JTI) under grant agreement n° 621244 ("ELECTRA").

Abstract No. 18

Fabrication and Characterization of Metal-supported Solid Oxide Electrolysis Cells

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Summary.

Metal-supported solid oxide electrolysis cell

$La_{0.1}Sr_{0.9}TiO_{3-\alpha}$ (LST) composite fuel electrode

Gadolinium doped ceria (GDC)/yttrium-stabilized zirconia (YSZ) bilayer thin-film electrolyte

Abstract. Solid oxide electrolysis cells (SOECs) belong to the most efficient and cost-effective electrochemical devices for the energy storage application via power to gas (P2G) concept. Intermittent energy in form of electricity or heat from renewable sources can be stored long-termly in the magnitude of GWh level as chemical energy in H_2 and CO through the electrolysis process occurs in SOEC systems. In comparison to conventional anode-supported and electrolyte-supported full ceramic cells, metal supported cells has many advantages, such as reduced manufacturing and maintenance cost, fast start-up features, excellent mechanical, thermal and redox cycle stability, and etc. In this work, novel metal-supported cells were fabricated on robust porous ferritic steel. Nickel free composite made of $La_{0.1}Sr_{0.9}TiO_{3-\alpha}$ (LST) and gadolinium doped ceria (GDC) was applied as fuel electrode material. 3 μm thick thin-film bilayer electrolyte of GDC/yttrium-stabilized zirconia (YSZ) was prepared by a combination of physical vapour deposition (PVD) and wet ceramic processing. The fuel electrode and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) air electrode were both deposited by screen printing. The gas-tightness of the electrolyte was monitored by differential air leakage tests at room temperature. Half cells with low leakage rate were selected and loaded with nickel nanoparticles as catalysts into the LST-GDC backbones to improve the electrochemical performance of the fuel electrode. Cells were tested under fuel cell mode and electrolysis mode, respectively. Performance and aging characteristics during operation were analysed by electrochemical impedance spectroscopy (EIS) and chronopotentiometry. Subsequently, the post mortem analysis was applied to facilitate the understanding of the degradation features and mechanisms specific to the electrolysis operation of the metal-supported cells.

Abstract No. 19

Solid Oxide Electrolyser Cells oxygen electrode based on infiltrated nanocomposite mesoporous materials

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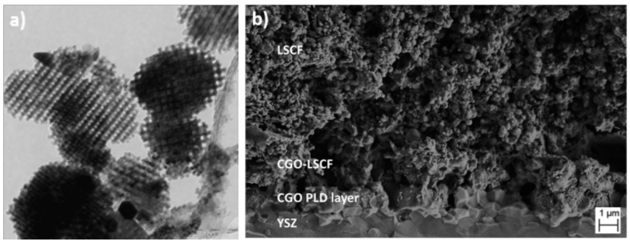
Summary. Oxygen electrode functional active layers for Solid Oxide Electrolysis Cells (SOEC) supported on fuel electrode were fabricated employing mesoporous $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO) material as ceramic scaffold infiltrated with $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$(LSCF) as the catalytic active phase. Electrolysis and co-electrolysis atmosphere compositions were used for testing its performance and stability.

Abstract. The conditions of SOEC operation are demanding in terms of electrode materials performance and stability. For this reason the attention of the present work has been focused in the development of functional layers for oxygen electrodes, based on nanostructured composite materials which present a high density of triple phase boundary (TPB) that will lead to better long term stability and catalytic activity [1]. Mesoporous nanocomposites are presented as an alternative material for electrodes functional layer because they present high surface active area, thermal stability at intermediate temperatures (500-750°C) and the interpenetration between the ionic conductive ceramic scaffold and the active compounds, ensuring the percolation between both nets [2]. In this work, fuel electrode supported cells (Ni-YSZ) with YSZ electrolyte were tested using oxygen electrodes based on CGO mesoporous materials infiltrated with LSCF generating mixed ionic-electronic conductors (MIEC) electrodes [3]. CGO mesoporous material was synthetized and characterized by different techniques as scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET). The attachment temperature of mesoporous CGO to zirconia electrolyte was optimized by electrochemical EIS measurements of symmetrical cells. An automatic airbrushing system has been used to deposit CGO mesoporous material by wet power spraying technique. Fabricated mesoporous oxygen electrode based SOEC were tested under different electrolysis and co-electrolysis atmospheres and characterised by electrochemical measurements. Produced mixtures of gases were analysed by gas chromatography and the microstructures were studied as fabricated and post operation by SEM techniques. The results of the mesoporous based nanocomposite characterisation and of the SOEC cells are used for demonstrating the improvement in performance and stability of SOEC based on mesoporous materials.



Figures: (a) TEM image of dopped-Ce mesoporous powder (b) SEM image of cross section showing the composition of characteristic layers constituting the fuel supported cell based on LSCF infiltrated CGO mesoporous oxygen electrode.

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Acknowledgements

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Abstract No. 20 (INVITED)

The development and implementation of Ir based nanowires as oxygen evolution electrocatalysts

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Summary. Ir based nanowires have shown promise for their potential to enable lower cost PEM electrolyzers by having higher performance and mass activity compared to traditional Ir nanoparticles.

Abstract. Water electrolysis offers extraordinary potential as a route to couple renewable (sustainable) resources with transportation and industrial needs. Not only would hydrogen produced renewable help improve societal issues such as greenhouse gas emissions and air/water quality, but it would also provide benefits in power generation load/demand mismatch and resiliency/reliability, while decreasing water requirements of the entire energy system. Additionally, such systems enable domestic energy sources to be more widely employed. Often these issues are considered only as a single advantage, however the positive attributes of water electrolysis are more favourable when viewed across energy sectors for their synergistic advantages. In order to improve the commercial competitiveness of hydrogen from water electrolysis, capital cost reductions of systems are a key concern. PEM electrolyzers offer significant potential, but require relatively high loadings of Ir (a metal with even lower natural abundance than Pt). While alternatives to Ir may be possible and being pursued, improvements upon Ir could allow very low amounts to be required.

We have investigated Ir nanowires synthesized from Ni and Co nanowire templates for their applicability as advanced electrolysis candidates. This work has built on previous studies of our group developing Pt nanowires for fuel cell applications.[1] We have found that Ir based nanowires offer significant benefit in terms of activity (~10x improvement) and durability compared to Ir nanoparticles. While most of our efforts have focused on catalyst development and ex-situ testing, the performance advantages of these systems has also been shown in electrolysis cell testing. This presentation will focus on the optimization of IrCo nanowires and a comparison between IrCo and IrNi nanowires using commercial Ir nanoparticle catalysts as baseline comparison materials.

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Abstract No. 21

The oxygen evolution at $Ir_xRu_{1-x}O_2$ produced by hydrolysis synthesis

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Summary.

Reaction orders were obtained for the oxygen-evolution reaction for solid solutions of iridium and ruthenium oxide made by the hydrolysis method. The results were fully consistent with the electrochemical oxide path.

Abstract.

Due to the highly acidic environment to which electrocatalysts are exposed in PEM water electrolysers, possible catalysts for the oxygen evolution reaction (OER) are in practice quite limited. The catalysts exhibiting the highest activity towards the OER are RuO_2 and IrO_2, ruthenium oxide being more active than iridium oxide, but also more unstable[1]. Mixing of these two oxides is therefore often performed in order to achieve both an active and stable catalyst[1-4]. A significant issue in this context is how and to which degree the various elements, for example Ir and Ru, in these catalysts interact.

We found in a previous work[3] that the electrocatalytic activity of $Ir_xRu_{1-x}O_2$ solid solutions appear to be additive, i.e. the activity is simply the sum of the iridium activity multiplied by x and the ruthenium activity multiplied by 1-x. However, such an interpretation rests on an appropriate interpretation of the polarization curves, which is frequently compounded by gas evolution at the electrodes. However, the more accurate the model for the reaction mechanism the better the interpretation of activity data for bimetallic oxides for catalysis of the OER in PEM water electrolysers. To distinguish between the large number of mechanisms proposed for the OER[5-7] under these circumstances, reaction orders are a useful supplement to Tafel slopes for the analysis.

In this work we present the results of a mechanistic study of the oxygen evolution reaction (OER) performed for $Ir_xRu_{1-x}O_2$, x=1, 0.6, 0.3 and 0, prepared by the hydrolysis synthesis. The oxides were characterized by X-ray diffraction, cyclic voltammetry and steady state polarization measurements. The electrolyte pH was varied in order to obtain the reaction order with respect to protons.

The polarization curves recorded could were fitted to a model derived for the electrochemical oxide path with the oxidation of adsorbed hydroxyl ions being the rate determining step (rds). The expected trends for this mechanism with the indicated rate-determining step with respect to potential and pH was fully consistent with the experimental data. The models emerging from this work will be important in analysing the interaction between elements in solid solution electrocatalysts for the OER, and appear to be able to reconcile observed differences in trends in the catalytic activity of $Ir_xRu_{1-x}O_2$ with composition.

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Abstract No. 22

Study of the Physical Morphology and Electrochemical Characteristics of Oxygen Evolution Reaction (OER) Iridium Based Electrocatalyst Synthesized with a Polyol Method for PEM Water Electrolysis

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Summary. A number of supported and un-supported OER iridium based electrocatalysts were synthesized using a polyol method. The electrocatalysts and the supports were characterized using a wide range of physical and electrochemical methods. The effect of morphological characteristics of the OER electrocatalyst and the support on the OER activity was studied.

Abstract. The effect of heat treatment (calcination temperature) on the morphology and OER activity of Ir/ATO electrocatalyst synthesized using the polyol method was studied. It was observed that the iridium electrocatalyst synthesized with the polyol method, consisted of 1-5 nm particles for calcination temperatures below 400ºC and had an amorphous structure. The iridium calcined at these lower temperatures also had an average oxidation state less than +4. Calcining the catalyst at temperatures above 400 ºC up to 700ºC: 1) increased the size of the iridium particles to 30 nm, 2) changed the structure of iridium particles from amorphous to crystalline, 3) increased the iridium oxidation state to +4 (IrO_2), 4) reduced the electrochemically active surface area by approximately 50%, and 5) reduced the OER activity by approximately 25%; however, it had no significant effect on the physical and chemical morphology of the ATO support.

Potential support materials: Tantalum Carbide (TaC), Niobium Oxide (Nb_2O_5), Niobium Carbide (NbC), Titanium Carbide (TiC) and Tungsten Carbide (WC) were also studied. These materials were used as supports for the iridium OER electrocatalysts and compared to the ATO supported catalyst. TaC was found to be a promising support, and increasing its surface area by 4% improved the OER performance of the final supported catalyst by approximately 50%. The maximum mass specific activity for the TaC supported iridium catalyst was occurred at a loading of 5 wt% iridium.

Abstract No. 23

Anode catalysts for PEM electrolyzers: Synthesis, Activity and Degradation Aspects with Ex Situ and In Situ Characterization

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Summary. In this presentation, our strategies toward developing high performance oxygen evolution reaction (OER) catalysts will be summarized; as-developed catalysts were investigated from nano scale to system level; in operando near-ambient pressure XPS technique was applied for electrocatalysis mechanism exploration.

Abstract. Proton exchange membrane (PEM) water electrolysis is considered as one of the most promising technologies for hydrogen production from renewable energies, which has a potential to penetrate the market in near future and enable the P2G application on a wider scale. However, one of the main hurdle for PEM electrolysis is the anode catalyst because of the sluggish OER kinetics and its insufficient durability due to the highly corrosive working environment.[1] To date, Ir-based catalyst is still the only feasible option to promote OER in the anode of a PEM electrolyzer due to its high activity and considerable stability. Not only the high cost of the precious metal, but also the scarcity of Ir in the earth crust are barriers on the road to commercialization of PEM electrolyzers. Therefore, highly active and stable OER catalysts in acid electrolyte with ultra-low Ir loading are required to address this issue.

Generally, there are two approaches to improve an electrocatalyst activity: i) increasing the intrinsic activity of each active site; ii) increasing the number of active sites on a given electrode. Under this frame, amorphous IrO_x nanoparticles are prepared to achieve a high intrinsic activity, it displays five-fold higher OER activity than commercial Ir-black.[2] In addition, a highly active Ir electrocatalyst derived from amorphous $IrRuO_x$ via an electrochemical way was developed, which demonstrates 13 times higher OER activity compared to the rutile phase of $IrRuO_2$. The stability was evaluated by PEM electrolyzer measurements, showing no cell potential decrease during ca. 400 h test. With the second approach, DLR takes electro-conductive ceramics as supporting materials to increase the active sites number, thus achieve an improved Ir utilization. First, IrO_x was deposited on Magnéli phase Ti_4O_7 showing a better OER activity in terms of Ir mass relative to Ir-black.[3] Further on, SnO_2:Sb aerogel (developed by Armines) was introduced as a support. By taking advantage of the highly porous structure of the aerogel support, Ir/SnO_2:Sb-aerogel allows a decrease of more than 70 wt.% precious metal usage in the catalytic layer, while keeping the same activity and significantly enhancing the stability compared to its unsupported counterpart.[4]

The advanced in operando technique, near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), is applied to provide insight into the potential-dependent specific chemical state of the catalysts surface and explore their electrocatalysis and stabilization mechanisms. RuO_2 and $IrRuO_2$ were investigated under water splitting condition in the form of the Aquivion-based membrane electrode assemblies (MEA), demonstrating that unstable hydrous Ru(IV) oxide formed on the surface already before the OER region mainly contributes to the fast dissolution of RuO_2, while its formation was hindered by the presence of Ir in the case of $IrRuO_2$.[5] Furthermore, the surface analysis of amorphous IrO_x compared to the rutile phase of IrO_2 under the same conditions will also be discussed.

Acknowledgement. The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for Fuel Cell and Hydrogen Joint Technology Initiative under Grant No. 621237 (INSIDE).

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Abstract No. 24

On the design and optimization of a bimetallic (Co,Mn)-based catalyst for hydrogen evolution in acidic medium

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Summary. In the current work the effect of metal species in bimetallic (Co,Mn)-N-C catalysts with predominately MeN_4 sites for the HER was investigated. Our results indicate that with the optimization of the metal ratio and sulfur content within the synthesis a highly active catalyst for the hydrogen evolution reaction (HER) is obtained.

Abstract. Hydrogen produced by water electrolysis is positioned among the key solution of a transition to clean energy as it can be used as energy carrier within the transportation sector. Nevertheless, regarding a long-term ambition of hydrogen to encourage the global investment, there are several compelling challenges. Herein, clean hydrogen production technologies, specifically electrolysers, attract significant attention during past years. However, the most crucial is to find cheap catalysts for water splitting in order to replace cost-intensive precious metals.

Liang et al.[1] recently reported Co-N-C catalysts which were active toward HER, and where the activity was assigned to CoN_4 active centers. In our recent work, several Me-N-C catalysts with various different metal species were studied in order to elucidate the nature of HER activity experimentally and theoretically. Bimetallic (Co,Me)-N-C (Me = Mo, Mn) have been presented as the most active and stable catalysts in this work.

In this contribution, we will present a systematic variation of the Co:Mn ratio in (Co,Mn)-N-C catalysts with and without additional sulfur modification. Sulfur comes into play for two main reasons: (i) recently, we showed that sulfur addition is beneficial to improve the number of MeN_4 sites that remain intact during the preparation[2,3] and (ii) in case of hydrogen evolution early results by Tributsch[4] and later others showed the good performance of metal sulfides for HER.

In this work, we will discuss the impact of the aforementioned parameters on the hydrogen evolution reaction with astonishing stability.

Acknowledgement

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Abstract No.25 (INVITED)

Hydrogen reaching “fossil parity” around the world

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Summary.

With the falling prices of renewable energy, renewable hydrogen from water electrolysis is gradually becoming more and more competitive with both liquid fossil fuels and hydrogen from steam-methane reforming. With the technology presently available from Nel Hydrogen, “fossil parity” is already a fact several places in the world.

Abstract.

Renewable energy is being exploited at an increasing scale around the world, both due to climate and environmental reasons, but also energy security. Lately, renewable energies have also become cost competitive with fossil alternatives in many regions across the world. Most of the new, renewable generation capacity being installed is solar and wind, which result in hourly, daily and seasonal changes in the electricity production. This leads to challenges for the electricity grid, since the electricity consumption and production is gradually being more decoupled. For energy producers this results in highly fluctuating electricity prices, and a general trend of falling spot prices.

In order to capture and store electricity in periods of excess, and create added value, energy companies can convert this electricity into high-value hydrogen, which has a wide range of applications, and can provide electricity at a later time and different place than when and where it was produced.

Large quantities of hydrogen is already used in the industrial sector today, mainly for ammonia production and in refineries. The source of this hydrogen is from from natural gas, oil and coal today, and up until recently, hydrogen produced via electrolysis has not been able to compete with fossil hydrogen, neither on a CAPEX-base compared to steam methane reformers, nor on an OPEX base, electricity compared to natural gas. However, with the prices of renewable falling at a steady rate, and large scale electrolyser plants, based on a new plant design by Nel, fossil parity will also be reached within the industrial sector.

Nel Hydrogen has developed hydrogen production technology based on water electrolysis since 1927, and built several of the largest electrolysis-based hydrogen production plants in history. 90 years after the start, the technology is more relevant than ever, providing the world with a flexible and clean energy carrier, a simple and effective way of storing energy, increasing the value and amount of renewable energy which can be implemented in the energy system.

Renewable hydrogen can and will be produced practically all over the world, outcompete fossil liquid fuels at the pump, and eventually also hydrogen generated from steam-methane reforming for the industry sector, opening up a very large and existing market for electrolysis, while reducing associated carbon emissions drastically.

Abstract No. 26 (INVITED)

PERIC's development on AEL and SPE technology

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Summary. With the research and development on alkaline-type electrolyzer and SPE technology for more than 50 years, PERIC has been succeeding in both large-scale hydrogen gas generation with pressurization and low power consumption features. This is also beneficial to the users of PERIC's products.

Abstract. Belonging to China Shipbuilding Industry Corporation, Purification Equipment Research Institute of CSIC, China (Hereinafter called as PERIC) was founded in 1966. Since its establishment, PERIC has focused on the research and development, design and production, technical services for military and civilian industries. Up to now, there have been more than 500 different kinds of products with high reliability and advanced technology to be successfully supplied for both domestic and international customers in civilian and militaries industries. The main technologies researched and developed by PERIC are the followings: application chemistry, high-energy chemistry engineering, H2-O2 gas generation by water electrolysis, hydrogen elimination for nuclear power plant, gas purification and analysis, electronics special-type gas, catalyst, safety guard system, etc.

As one of the most successful technologies and products, hydrogen generation technology and products by water electrolysis has been worldwide marketed and used for all sorts of civilian industries since 1970s. As of now, the H2 gas capacity ranges from 0.5Nm^3/hr to 1000Nm^3/hr from a single alkaline-type electrolyzer with rated operating pressure 1.50MPa (g), 0.10Nm^3/hr to 10Nm^3/hr from a single PEM-type electrolyzer with rated operating pressure 4.0MPa (g); the key features of the alkaline-type electrolyzer are tight lye-sealing, low power consumption and long-term operating life, etc. .


Electrolyzers with different H2 capacity

2 capacity : 0.5Nm^3/hr ~ 1000Nm^3/hr

ated pressure : 1.50MPa (g);

ated temperature : 90 Deg.C;

2 content in H2 : less than 0.2%;

2 content in O2 : less than 0.8%;

DC power consum.: less than 4.3kWh/Nm^3 H2


A corner of PERIC's workshop

In order to satisfy the diverse requirements from different customers, there have been four kinds of hydrogen generation system as shown in the pictures.

PERIC will keep its steps forward continuously on research and development, innovation and improvement on electrolyzers, to satisfy the multipurpose from a varity of customers.

Abstract No. 27

Alkaline Water Electrolyzers With Base Metal Catalysts Showing 1 A/cm^2 At 1.75 V

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Summary. Alkaline water electrolyzers with base metal catalysts and Sustainion™ membranes show $1A/cm^2$ at 1.75 V in 1 M KOH at 80 °C.

Abstract.

This paper will describe the performance of Dioxide Materials' new Sustainion™ membranes in alkaline water electrolyzers with base metal catalysts. Figure 1 shows the conductivity of the membranes. Notice that the conductivity is a factor of 2-4 higher than the closest competitor. the conductivity is stable for thousands of hours at 60 °C in 1 M KOH.

Dioxide Materials has done testing of the membranes in Alkaline water electrolyzers. Figure 2 shows a run at 60 °C in 1 M KOH using commercial nanoparticles from Sigma Aldrich as catalysts. We observe stable performance for 1000 hour with a average voltage loss of only 10 µV/hr.

Figure 3 shows a short run done with an optimized catalyst. This catalyst shows $1A/cm^2$ at 1.75 V.

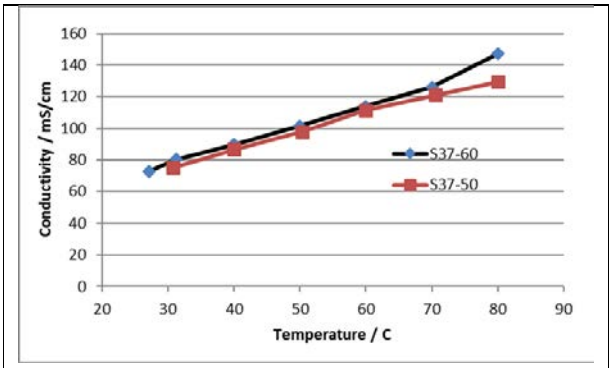

Figure 1 The measured conductivity of Dioxide Materials' Sustainion™ membranes in 1 M KOH

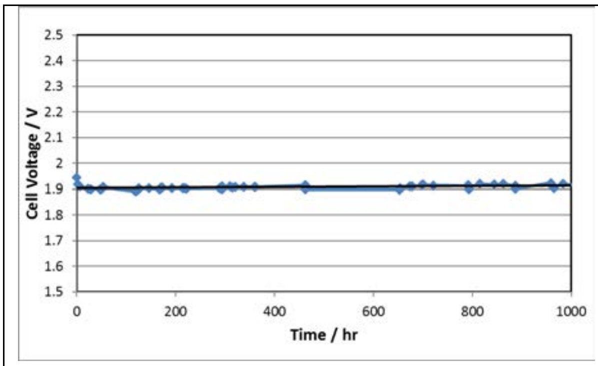

Figure 2 The stability of an electrolyzer with $NiFeO_4$ anode catalysts and NiFeCo cathode catalysts at 60 °C and 1 M KOH. In this case, the current was maintained at 1 A/cm^2 and the voltage to maintain the current was measured as a function of time

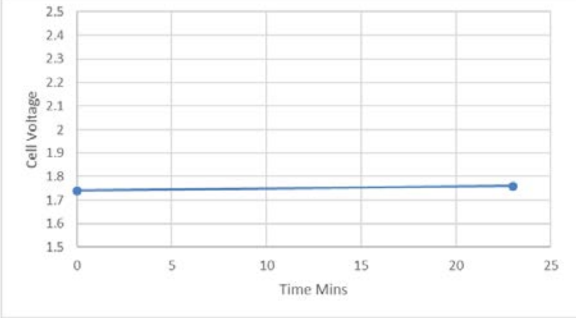

Figure 3 A short run with an improved catalyst at 80 °C and 1 M KOH. In this case, the current was maintained at 1 A/cm^2 and the voltage to maintain the current was measured as a function of time

Abstract No. 28

A unique approach for high intensity alkaline water electrolysis using a membraneless Divergent-Electrode-Flow-Through (DEFT^{TM}) electrolyser

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Summary. A membraneless alkaline water electrolysis technology, that manipulates the flow of electrolyte in opposing directions, which achieves (i) separation of the constituent gases, (ii) simplification of the electrolyser design, and (iii) elimination of key limitations of conventional alkaline water electrolysers, e.g. low current densities.

Abstract. Alkaline water electrolysers are hindered by cross-diffusion of gases across the membrane/diaphragm, limited current densities and low operating pressures. It remains a well developed technology with a number of advantages extending to an environment that allows the use of inexpensive materials of construction, however, it remains capital intensive due to low operating current densities [1]. Proton Exchange Membrane (PEM) electrolysers overcome some of the weaknesses associated with alkaline systems by allowing efficient performance at high current densities, pressurised operation and production of superior gas purities. The aggressive acidic regime, however, requires the use of distinct construction materials that are scarce and expensive [1].

The Divergent-Electrode-Flow-Through (DEFT^{TM}) solution captures some key advantages from both alkaline and PEM systems (Figure 1). Uninterrupted flow of an alkaline electrolyte flows through two close proximity circular porous electrodes, of limited diameter (~30mm) and electrode gap (>2mm), therefore eliminating the need for a membrane. For this configuration flow is the only requirement for continuous high purity gas separation (98.98 vol% H_2 and 97.60 vol% O_2 at a flow velocity of 0.075 m.s^{-1}). This is a reliable and simple approach capable of achieving stable current densities as high as 3.5 A.cm^{-2} at reasonable cell potentials employing optimal catalysts [2]. The current focus is on scaling the DEFT^{TM} technology to successfully produce elevated quantities of hydrogen gas.

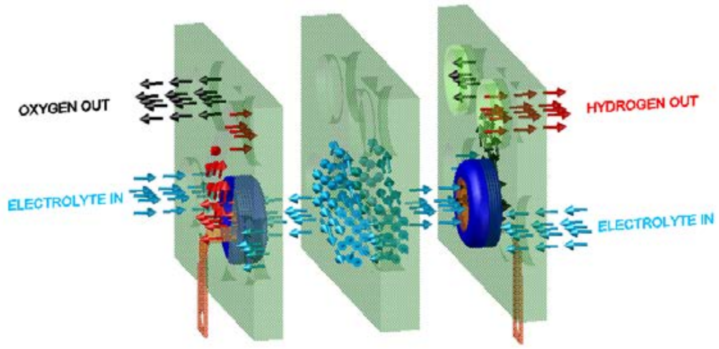

Figure 3: Operating principle of a pole pair of electrodes from a membraneless DEFT^{TM} electrolyser stack

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Abstract No. 29

High temperature alkaline electrolysis

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Summary. High temperature and pressure alkaline electrolysis cells have been demonstrated at current densities of up to 3.75 A cm^{-2} at a cell voltage of 1.75 V at 200 °C and 20 bar, corresponding to an electrical efficiency of 85 %, with relatively stable performance over 400 h, thereby promising a drastic cost reduction in electrolytic H_2 production.

Abstract. Alkaline electrolysis is a proven technology with several large scale facilities for hydrogen production realized and operated reliably for decades. Nevertheless, its broader deployment is hindered by the relatively high cost for hydrogen production. To overcome this obstacle, it is necessary to improve cell efficiency, increase the production rate, and decrease capital cost. Since conventional alkaline electrolysis technology has reached maturation, only small incremental improvements can be expected. To achieve a drastic step forward, we have developed a new generation of alkaline electrolysis cells that can operate at elevated temperature and pressure, producing pressurized hydrogen at high rate and high electrical efficiency.

The concept relies on the development of corrosion resistant high temperature diaphragms, based on mesoporous ceramic membranes where aqueous KOH is immobilized by capillary forces, in combination with gas diffusion electrodes that overcome mass transport limitations at large production rates. Raising the operating temperature offers a means to drastically improve performance, as both ionic transport and reaction kinetics are exponentially activated with temperature. Indeed, we have demonstrated alkaline electrolysis cells operating at 200-250 °C and 20-50 bar at very high efficiencies and power densities. This enables high production rates near the thermoneutral voltage, thereby overcoming the need for cooling.

This work will provide an overview of the exploratory technical studies undertaken so far. Three electrochemical test stations have been established to carry our experiments at elevated pressures (up to 99 bar) and temperatures (up to 300 °C). The conductivity of aqueous KOH was investigated at elevated temperatures to establish the optimum concentration at 200-250 °C. An optimum value of 0.84 S cm^{-1} was established at 200 °C for 45 wt% aqueous KOH immobilized in mesoporous $SrTiO_3$. Gas diffusion electrodes were developed using metal foams loaded with different non-precious metal electrocatalysts in order to reduce the overpotentials for oxygen and hydrogen evolution. Small cells have been fabricated and operated at current densities of up to 1.75 A cm^{-2} and 3.75 A cm^{-2} at cell voltages of 1.5 V and 1.75 V at 200 °C at 20 bar, corresponding to electrical efficiencies of almost 99 % and 85 %, respectively. Long-term operation at 200 °C was successfully demonstrated for 400 h, suggesting relatively stable cell performance. Finally, low-cost production methods have been utilized for a first scale-up of the cell size from 1 cm^2 to 25 cm^2. Efforts are currently directed towards the investigation of the intrinsic activity of mixed oxides for the oxygen evolution reaction at elevated temperatures and pressures, and towards the development of high surface area electrodes for testing of full cells at 25 cm^2 size.

Abstract No.30 (INVITED)

Tailoring electrode interfaces for conversion

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Summary. The electrochemical reactions in fuel cells and electrolysers occur at the interface between electrodes and electrolyte. Here we look at attempts to nanoengineer this interface to enhance performance and also probe the changes in local structure that relate to activation or ageing during operation.

Abstract. The development of new and renewable sources of energy is essential to meet global energy needs and to reduce the emissions of pollutants that contribute to the reduction of air quality and to net greenhouse gas production. The intermittency of renewable electricity produced from in particular wind, is a major barrier to further expansion and can result in significant periods when grid balancing is required to maintain integrity of supply.

High temperature steam electrolysis (HTSE) is a highly efficient process for hydrogen production and is carbon-neutral provided that the electricity comes from a renewable source[1]. Electricity and heat are combined within a solid oxide electrolysis cell (SOEC) for the electrochemical reduction of steam to hydrogen plus oxide ions at the hydrogen electrode (cathode), followed by oxide ion migration across a solid electrolyte to the oxygen electrode (anode) where oxygen is evolved. Recent interest in steam electrolysis has been largely concerned with performance, stability and degradation issues relating to highly developed SOFC materials[2]. These have formed a starting point for SOEC development; however recent work on exsolution SOEC cathodes has yielded enhanced performances in robust systems[3]. Besides steam electrolysis, CO_2 electrolysis using SOECs has also attracted increasing research efforts worldwide due to the emission of greenhouse gases into the atmosphere and the resulting climate change[4]. A key advantage of both steam and CO_2 high temperature electrolysis processes is that electrical energy demand significantly decreases as temperature increases, with thermal energy providing the additional energy for the process. This can be provided by Joule heating capitalising on ohmic losses in the SOEC stacks. Autothermal operation, where ohmic losses and entropic energy demands match is often considered as an appropriate mode of operation.

Here we present the growth of a finely dispersed array of anchored metal nanoparticles on an oxide electrode through electrochemical poling of a SOC at 2 V for a few seconds, yielding a sevenfold increase in fuel cell maximum power density. These new electrode structures are capable of delivering high performances in both fuel cell and electrolysis mode (e.g. 2 W cm^{-2} in humidified H_2 and 2.75 A cm^{-2} at 1.3 V in 50% H_2O/N_2, at 900 °C). Both the nanostructures and corresponding electrochemical activity show no degradation over 150 hours of testing. These results not only prove that *in operando* treatments can yield emergent nanomaterials, which in turn deliver exceptional performance, but also provide proof of concept that electrolysis and fuel cells can be unified in a single, high performance, versatile and easily manufacturable device. This opens exciting new possibilities for simple, quasi-instantaneous production of highly active nanostructures for reinvigorating SOC cells during operation

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Abstract No. 31

Degradation Behavior of (La,Sr)(Fe,Co)O_3 Solid Oxide Cell Oxygen Electrodes During Reversible Electrolysis and Fuel Cell Operation

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Summary. Most prior studies of oxygen electrode degradation during electrolysis have focused on (La,Sr)MnO_3 (LSM) – less is known about (La,Sr)(Fe,Co)O_3 (LSCF). Here we report results showing that LSCF degrades by a different mechanism than LSM, due to a lower overpotential under typical operating conditions.

Abstract. Previous work on reversible solid oxide electrolysis has focused on LSM-YSZ oxygen electrodes,[1-3] where degradation at the electrode-electrolyte interface leading to cracking and delamination has been observed. A similar mechanism is observed during DC electrolysis, although degradation is more rapid than in current switching.[2] Degradation rates $\lesssim$ 1 %/khr have been reported during reversing current operation for LSM-YSZ,[1] but only for low current densities/overpotentials[1] or for current switching with very low electrolysis duty fractions.[4] Thus, it is important to determine whether other oxygen electrode materials can provide low degradation rates at a higher current density j than in LSM-YSZ. Furthermore, energy storage involving co-electrolysis is predicted to be substantially more efficient and economical if the SOC operates at lower operating temperatures,[5] so low temperature electrodes are of particular interest.

Here we present life tests on symmetric LSCF/GDC/LSCF cells operating under current switching, showing the effect of varied j and overpotentials η on degradation. This is the first detailed study of LSCF electrode degradation during current switching, to our knowledge. Symmetric cells have the advantage of isolating degradation of the oxygen electrode, without the need to deconvolute from a fuel electrode. These cells allow focus to be placed on degradation in the LSCF and at the LSCF/GDC interface; since there is no YSZ electrolyte, there are no LSCF-YSZ reactions. Microstructural evaluation is presented and compared with the electrochemical degradation in order to observe the nature of the degradation mechanisms.

Current switching life tests of LSCF on GDC symmetric cells were performed in ambient air at 700 ^{o}C for about 1000 h at 0.7, 0.9, 1.0, and 1.5 A/cm^2. The cell resistance degradation rate increased with increasing j. Most of the resistance increase was attributed to the electrode polarization resistance R_P. The cell operated at 0.7 A/cm^2 had a relatively slow degradation rate of 0.6 ± 0.4 %/kh. On the other hand, at 1.5 A/cm^2 the degradation was very rapid over the first ~ 500 h, increasing R_P by 0.1 Ωcm^2, but leveled off during the remaining 500 h. All degradation occurred at $\eta \leq 0.1$ V, below the value predicted to cause GDC electrolyte delamination due to oxygen bubble formation, and indeed there were no significant changes observed in the electrolyte microstructure or the ohmic resistance. 3D tomography using FIB-SEM was performed on cells after life testing at j = 0, 0.7, and 1.5 A/cm^2 showing that the LSCF structure coarsened at the highest j values. However, the microstructural changes did not appear sufficient to explain the observed R_P increase, based on Adler-Lane-Steele (ALS) model calculations. It is suggested that high j operation might also cause degradation by accelerating cation transport in the electrode, *e.g.* Sr surface segregation. The ALS model calculations indicate that a decrease in oxygen surface exchange rate by a factor of ~ 4, similar to that observed previously due to Sr segregation,[6] accounts for most of the degradation. Results on Sr segregation will be reported.

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Abstract No. 32

Eliminating degradation and repairing damage in solid oxide cell and stack fuel electrodes

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Summary. The fuel electrode of commercial solid oxide electrolysis cells and stacks are shown to be repairable by employing wet infiltration in a novel manner. Performance prior to otherwise fatal damage was entirely regained and long-term degradation over the course of thousands of hours is eliminated.

Abstract. The solid oxide cell (SOC) could play a vital role in energy storage when the share of intermittent electricity production is high. However, the wide-scale commercialization of the technology is still hindered by limited lifetime. Here, we address this issue by examining the potential for repairing various failure and degradation mechanisms occurring in the fuel electrode, thereby extending the potential lifetime of a SOC system. We successfully infiltrated the nickel and yttria-stabilized zirconia cermet (Ni-YSZ) electrode in commercial cells with Gd-doped ceria (CGO) after operation. By this method we fully repaired the fuel electrode after simulated reactant starvation, carbon formation and thousands of hours of steady degradation. The potential for entirely eliminating the degradation of the fuel electrode was proven by infiltrating after microstructural stabilization had occurred. Moreover, we demonstrated scalability of the concept by repairing an 8-cell stack based on a commercial design.

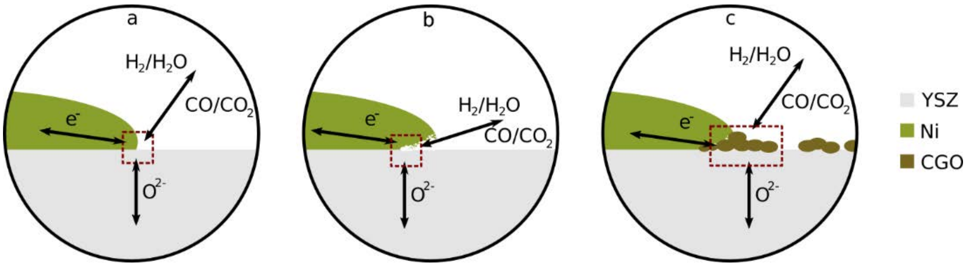

__Figure 4 | Illustration of one suggested degradation mechanism and how infiltration repairs the damage. a__, electrons supplied by the Ni particle, oxygen ions supplied by the YSZ particle and gas meets in the reaction zone at the triple-phase-boundary (3PB). __b__, as local delamination takes place, the reaction zone moves and the 3PB shrinks. For particles with poor connection, complete delamination can occur. __c__, the delamination is filled by infiltrated nanoparticles and the reaction zone is extended.

Abstract No. 33

Post-test analysis of a solid oxide electrolysis cell operated for 23000 h

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Summary. The present work presents the microstructural and compositional change of an electrolyte supported solid oxide cell operated in the steam-electrolysis mode for a duration of more than 23000 h with a current density of up to -0.9 A cm^{-2}.

Abstract. An electrolyte supported solid oxide cell with an active area of 45 cm^2 was operated in the steam-electrolysis mode for a duration of more than 23000 h, of which 20000 h with a current density of j = -0.9 A cm^{-2} and a steam conversion of 51%. The cell is composed of a scandia/ceria-stabilized zirconia (6Sc1CeSZ) electrolyte of about 130 μm thickness, gadolinia-substituted ceria (CGO) diffusion-barrier/adhesion layers between electrolyte and electrodes, a lanthanum strontium cobalt ferrite (LSCF) oxygen electrode, and a Ni/CGO steam/hydrogen electrode. In the galvanostatic operation period with j = -0.9 A cm^{-2}, the cell voltage increased at a rate of 7.4 mV / 1000 h (0.6% / 1000 h). In-situ electrochemical impedance spectroscopy revealed that the cell degradation was dominated by the increasing ohmic resistance, which can be attributed mainly to the decay of the ionic conductivity of the electrolyte. In addition, a small increase of the polarization resistance caused by an increasing loss from the interfacial charge transfer process was identified [1].

Except the delamination of a small fraction of the oxygen electrode, the cell showed no mechanical damage after being dismounted from the test rig. In order to understand better the degradation mechanism, post-test analysis of the cell has been conducted using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). At the steam/hydrogen electrode, Si-accumulation was observed at the interface between the Ni/CGO layer and the CGO adhesion layer (Figure 1). The amount of Si decreases from the centre to the outer edge of the cell. It is speculated that Si originating from the water supply system is carried by the steam/hydrogen stream to the cell and deposits then at the proximity of reaction sites. Si-accumulation could contribute to the observed increase of both ohmic and charge-transfer resistances. At the oxygen electrode, formation of $SrZrO_3$ at the CGO/6Sc1CeSZ interface as a result of Sr-migration from the LSCF electrode through the CGO diffusion-barrier layer was observed, which should also lead to an increasing ohmic resistance of the cell. At the surface of the oxygen electrode, a foreign phase rich in P and Sr was identified, which can be correlated to the observed surface darkening, caused most probably by the impurities in the compressor air used as the purge gas at the oxygen electrode.

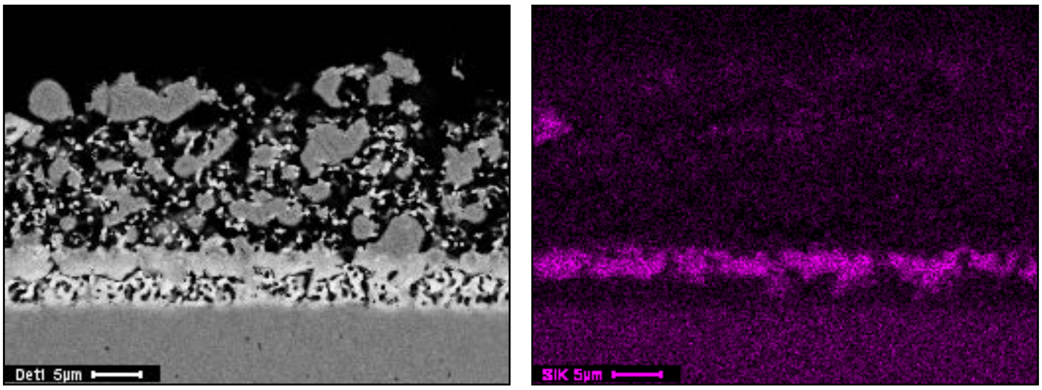

Figure 1: Elemental mapping of the steam/hydrogen electrode, showing accumulation of Si.

[1] J. Schefold, A. Brisse, H. Poepke, Int. J. Hydrogen Energy, 2017, in press

Abstract No.34

Regenerating the performance of solid oxide electrolyzers by periodic treatments to extend lifetime

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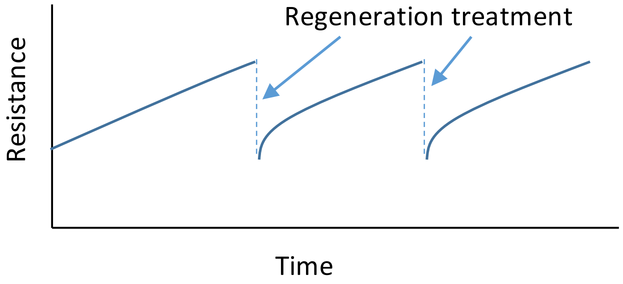
Summary. Solid oxide electrolyzers can produce fuels using renewable electricity with higher energy efficiency than other types of electrolyzers, but they are known to suffer from shorter operating lifetimes. We present several ways that device lifetime can be extended by applying periodic treatments to regenerate the performance.

Abstract. Due to their high temperature operation, solid oxide electrolyzers (SOEs) are able to split H_2O into H_2 and O_2, and CO_2 into CO and O_2, or even both H_2O and CO_2 directly into CH_4 and O_2, with nearly 100% energy efficiency. This makes the technology of great interest for large-scale renewable electricity storage and transportation fuel production. However, the demonstrated SOE operating lifetime is shorter than that of commercial alkaline electrolyzers, which results in a higher capital cost. Ongoing R&D in cell and stack designs has yielded considerable improvements in lifetime for steady-state electrolysis operation.

We have been investigating new, alternative ways to extend lifetime by periodically subjecting the cell or stack to treatments that restore performance. These include *ex situ* treatments – where the device is cooled down, repaired, and heated back up to resume operation – and *in situ* treatments – where the applied voltage or gas composition is briefly adjusted to induce a boost in performance. We have demonstrated *ex situ* repair by infiltration of cells and a stack with precursor solutions that produce electrocatalyst nanoparticles in the nickel-based fuel electrode, which was the source of performance degradation during thousands of hours of operation, and found that performance could be regained to the initial level. One *in situ* treatment is the exposure of certain fuel-electrodes to oxidizing gasses and then back to fuel gasses, which results in restoration of nano-structured electrode surface features that were lost by coarsening processes. Another is the application of short controlled pulses of high cathodic polarization, which we found can similarly produce nano-structured interfaces that improve electrode performance.

The presentation will also summarize our current knowledge of the mechanisms by which these regeneration treatments work, limitations of the treatments, the time periods for how long the re-activation lasts until the treatment must be used again, and some examples from literature that are relevant to this new strategy for lifetime extension.



Abstract No. 35 (INVITED)

Megawatt scale dual stack PEM electrolysis development for enhancing renewable energy integration by providing grid services during hydrogen generation

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Summary. Hydrogenics has developed an outdoor electrolyser that is able to convert 2.5 MW peak power into hydrogen. The unit was conceived with a dual stack set-up, in order to achieve a high operational flexibility and to minimize total cost of ownership for the project owner. The unit will be installed in Hobro, Denmark, and will be fully operational in 2017. The site owner is aiming at generating additional revenues by offering operational flexibility to the electricity grid.

Abstract. Hydrogen has a long standing history as a feedstock gas or process medium in industrial applications. Electrolytic hydrogen generation is a good option whenever small to medium flows are required, and is also often the technology of choice when high purity streams are needed. Currently there is an increased demand for electrochemical hydrogen because it gives an answer to the growing practical issues related to the integration of renewable energies in today's energy mix. In the power-to-gas concept, that provides a realistic route for a carbon-free economic future, water electrolysis is the key technology to store renewable energy surpluses, allowing the crossover between different energy vectors; electricity on the grid, natural gas as chemical energy storage and fuel for transport applications.

This contribution presents the PEM based electrolyser development in the Hybalance project. This FCH-JU and Energynet.dk co-funded project illustrates how PEM water electrolysis, complimented with additional hydrogen compression and transportation technologies, demonstrates different hydrogen applications in real life when a number of important boundary conditions are met. The consortium partners in the project are Air Liquide, Neas energy, Hydrogen Valley and the Copenhagen Hydrogen Network (CHN).

In the Hybalance project, electricity in converted by pressurized water electrolysis into hydrogen and further compressed and transported at high pressure for Hydrogen delivery to the fueling stations operated by CHN in Denmark. The 500 kg per day production unit is based on Hydrogenics 1500 cm^2 PEM platform and is a next iteration of the previously demonstrated single stack units. During this development a number of challenges have been tackled. The FCH-JU efficiency target was put forward as a design criterion and in addition the commercial operation of the plant for a minimum of fifteen years required a very reliable, available installation with low degradation rate of the efficiency. With these conditions defining the process window in terms of stack current density, operational temperature and redundant components, additional constraints in terms of harmonic distortion on the electrical grid and noise emission in a residential area had to be met. Finally, special attention had to be given to the operational flexibility of the electrolyser, allowing for a demand side (hydrogen) or supply side (excess of cheap electricity) control of the hydrogen production rate, in order to achieve the lowest cost of ownership for the entire plant.

Abstract No. 36

Increasing PEM water electrolysis energetic efficiency by a surface modification of Ti gas diffusion layer

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Summary. A state of art gas diffusion layer for PEM water electrolysis anode is usually based on porous Ti. However, too extensive passivation layer of Ti increases surface contact resistance and consequently energetic losses. Appropriate surface modification of Ti leads to improved and stable performance of water electrolyser.

Abstract. Proton exchange membrane (PEM) water electrolysis attracts a lot of attention as an important part of Hydrogen Economy Concept. While the process can be operated with high efficiency, space-time yield and flexibility, there are several issues limiting severely its practical applicability on a larger scale. The most important ones are connected with stability of materials on the anode part of the cell where high electrode potential is combined with low pH. Such conditions are detrimental for majority of electron-conducting materials. For example, only Ti or Ta can be efficiently used for a gas diffusion layer construction. While thermodynamically highly unstable under the mentioned conditions, their stable and intact passivation layer efficiently protects bulk of the metal from further dissolution. On the other hand, presence of the passivation layer increases surface contact resistance and consequently decreases energetic efficiency of the electrolysis process especially when operated at high intensity. Common, though not often mentioned solution is coating of the gas diffusion layer with metals like Pt. This, however, further increases already high investment cost of the whole process.

In this study an attempt is reported to understand more deeply processes occurring on the Ti surface during polarisation under the conditions relevant to the PEM water electrolysis. On the base of the knowledge obtained an attempt was made to solve the issue and to decrease the surface contact resistance by appropriate surface modification of the Ti gas diffusion layer. A promising approach represented etching of the Ti in an appropriate acid solution. It led not only to a large reduction of energy losses during water electrolysis related to the contact resistance but also to a decrease of performance degradation rate. The observed effect was, in more details, studied using techniques such as Secondary Ion Mass Spectrometry, X-ray photoelectron spectroscopy or classical electrochemical methods. In the presentation, the results will be discussed in context of the (sub)surface layer composition and passivation layer thickness related to the anode performance and degradation rate.

Acknowledgement

Financial support of this study by the Grant Agency of the Czech Republic with the framework of the project No. 15-02407J is gratefully acknowledged.

Abstract No. 37

Materials and coatings for PEM water electrolysers

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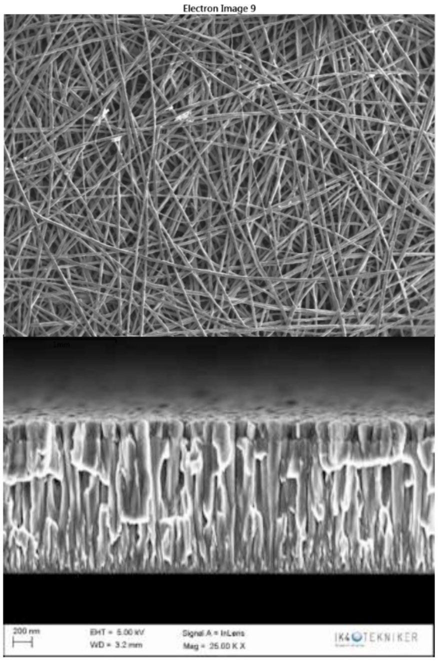
Summary. PEM electrolyzers coupled with renewable energy sources (wind and solar) represent one of the most promising candidates for clean hydrogen production. Bipolar plates (BPP) could be exposed to acidic environment, but also must withstand high overvoltage (up to 2V) in the anodic side of a PEM eletrolyzer. These factors strongly reduce the material candidates for BPP fabrication. Titanium (Ti) is considered as the state-of-the-art material. On the other hand, Ti tends to form an insulating passive oxide layer that increases interfacial contact resistance (ICR) and diminishes electrolyzer cell efficiency as electrolyzer ages. Therefore, electrolyzer manufacturers usually apply expensive conductive coatings.

Abstract.

In this study, an extensive characterization of a promising novel coating for BPP protection deposited on Ti is presented. The coating (Ta_ITO) is made of a tantalum layer (Ta) acting as an anti-corrosion barrier followed by a thin indium tin oxide (ITO) conductive film. Ta layer was deposited by High Power Pulsed Magnetron Sputtering Technology (HPPMS) that produces dense and low-defect microstructure films. Several ITO layers deposited by pulsed DC magnetron sputtering (PMS) were investigated both ex-situ and in-situ.



The corrosion resistance of different Ta_ITO coatings was investigated using potentiostatic and potentiodynamic measurements in simulated PEM electrolyzer anodic environment. The effect of the substrate was also analysed. The samples were immersed in a 0.1M Na_2SO_4 solution that had been pH adjusted by addition of 1m M H_2SO_4. Temperature, potential and length of the potentiostatic polarization were varied, to study the effect this would have on both the substrates and the Ta_ITO coatings. Before and after each polarization, the ICR was measured in a setup similar to the one described by Lædre et al. [1], with the plate to be tested placed with a GDL on top between two gold coated copper plates (soft contact ICR).

In addition, porous titanium transport layers, PTLs, (or sinters) from BEKAERT were also coated with the most promising coatings. These were tested as both anode and cathode PTLs in an electrolyzer using commercially available MEAs and electrolyzer hardware. Polarization curves, EIS and ICR measurements were performed before and after an AST protocol developed in-house and the results were compared against uncoated Ti, as well as noble metal coated Ti PTLs.

[1] Lædre, S., et al., The effect of pH and halides on the corrosion process of stainless steel bipolar plates for proton exchange membrane fuel cells. International Journal of Hydrogen Energy, 2012. 37(23): p. 18537-18546.

Abstract No. 38

Flow field design for high-pressure PEM electrolysis cells

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Summary. To study the electrochemical behaviour of full-scale, flow field designs of high-pressure PEM electrolysis cells, a computational fluid dynamics model has been developed. For a set of specific operating conditions, different flow fields are investigated in terms of their ability to handle gas and heat management.

Abstract. With the increasing interest in producing hydrogen through water electrolysis, the importance of understanding the transport phenomena governing its operation increases. To ensure optimal operating conditions for PEM electrolysis, it is particularly important to understand how the liquid feed-water distributes. Water not only serves a reactant, it also aids in cooling due to its high specific heat capacity. The movement of liquid water at the anode is difficult to model, since it is highly coupled to the formation of gas bubbles. To capture the complex two-phase flow behaviour that takes place within micro-channels and porous media, our research group has developed an Euler-Euler model in the computational fluid dynamics modelling framework of ANSYS CFX. In addition to two-phase flow, the model accounts for turbulence, species transport in the gas phase, heat transport in all three phases (i.e. solid, gas and liquid), as well as charge transport of electrons and ions. Our recent improvements have focused on the models ability to account for phase change and electrochemistry as well as the modelling of two-phase flow regimes.

For comparison, an interdigitated and parallel channel flow field will be investigated with regard to how well they distribute gas and heat. To obtain a high durability when operating at high current densities, it is essential that liquid water and temperature is evenly distribution over the entire active surface area. In Figure 1, a contour plot of the temperature distribution within an interdigitated flow field is presented as an example. The axis-symmetric simulation shows that the formation of hot spots in the order of 8°C above the inlet temperature can occur for a current density of 3 A/cm^2 and a water stoichiometry of 350. These spots are primarily located underneath the outlet channels. To avoid them, an in-depth design and simulation study is necessary.

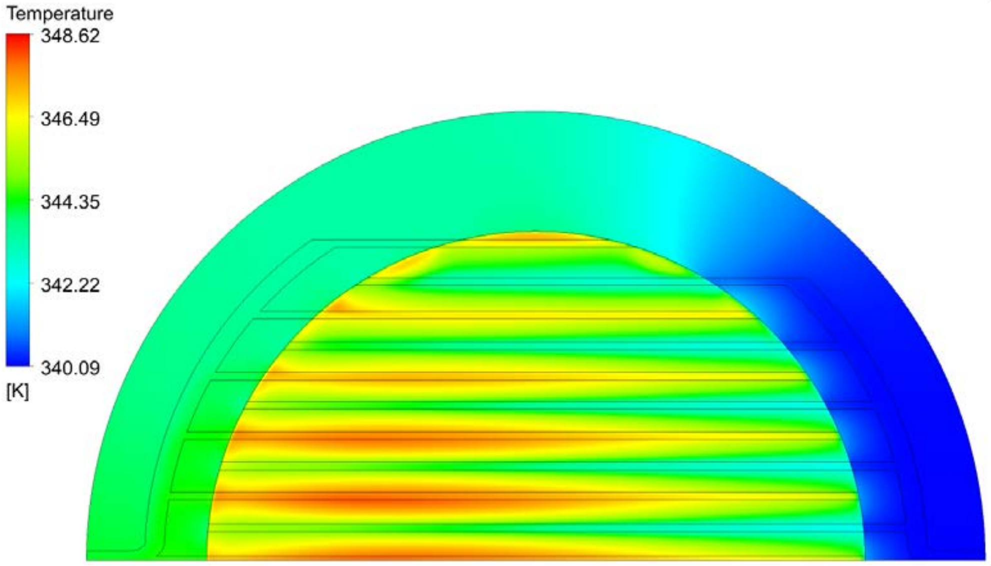

Figure 5: Contour plot of the temperature distribution for an interdigitated flow field at a current density of 3 A/cm^2 and a water stoichiometry of 350.

Abstract No. 39

Protective coatings for low-cost bipolar plates and current collectors of proton exchange membrane electrolyzers

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Summary.

Vacuum plasma spraying, a versatile applicable technology to apply various types of coatings to a wide range of surfaces, is used to produce highly stable and multifunctional coatings for cost effective interconnectors of proton exchange membrane (PEM) electrolyzers.

Abstract.

Hydrogen produced by PEM electrolysis technology is a promising solution for energy storage, integration of renewables, and power grid stabilization for a cross-sectorial green energy chain. The most expensive components of the PEM electrolyzer stack are the bipolar plates (BPP) and porous transport layers (PTL). These components account together for 50 to 70 % of the stack cost depending on the design. The high cost is due to the fact that the employed materials need to withstand corrosion at 2 V in acidic environment. Currently only titanium is the material of choice for the anode side. Yet, a semi-conductive oxide layer grows its surface over a long period of time.[1] In this context, a lucrative solution is to replace the Ti BPPs by coated stainless steel.

We use vacuum plasma spraying (VPS) technology to apply highly stable coatings of titanium (Fig. 1a) and niobium to protect stainless steel BPPs from the oxidative conditions on the anode side.[2] The latter is able to decrease the interfacial contact resistance and improves the long term stability of the electrolyzer. Furthermore, porous transport layers (PTL) can be realized by VPS as well. These coatings can be produced on existing titanium current collectors acting as macro porous layers (MPL).[3] Lastly, free standing multifunctional structures (Fig. 1b) with optimized tortuosity, capillary pressure and gradient porosity are used as current collectors. The coatings and porous structures developed by VPS enable the reduction of the required material and costs without performance losses.

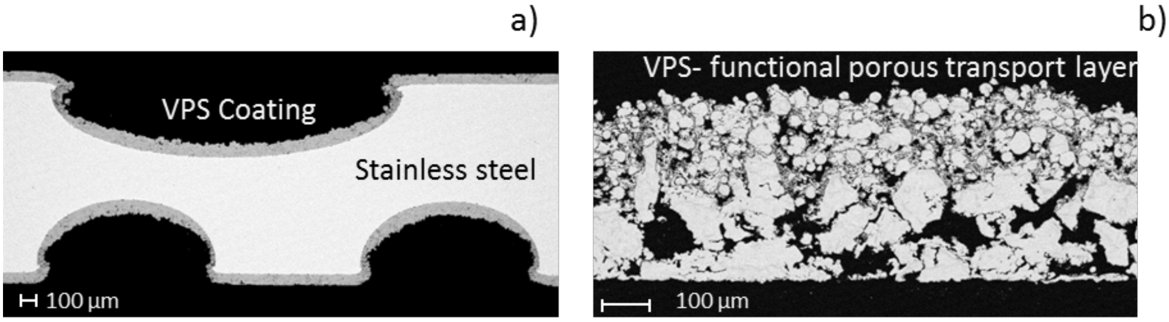

Figure 1: a) VPS coated stainless steel bipolar plate with flow field; b) VPS produced functional porous transport layer with gradient pore size distribution and optimized contact surface to the electrode.

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Abstract No. 40

EU Harmornised Test Protocols for Electrolysis Applications

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Summary.

The objective of this paper is to present a set of harmonised operating conditions, testing protocols and procedures for assessing performance, durability and grid connectivity of Low Temperature Water Electrolysis application for allowing fair comparison of test results from various projects and laboratories.

Abstract.

The Energy Union Strategy is built on the ambition to achieve, in a cost-effective way, a fundamental transformation of Europe's energy system, moving to more sustainable, secure and competitive ways of delivering energy affordably to consumers. It is also committed to transforming its transport and energy sector as part of a future low carbon economy. It is recognised that Fuel Cell and hydrogen technologies hold great promise for energy and transport applications from the perspective of meeting Europe’s energy, environmental and economic goals and are part of the Strategic Energy Technologies (SET) Plan - , which was adopted by the European Union in 2008.

Water electrolysis plays a key role in almost all scenarios for the widespread roll-out of hydrogen for mobility, industry or energy storage. It is the dominant and most efficient route to hydrogen production from renewable electricity sources and hence the most proven of the options for generation of ultralow-carbon hydrogen. Electrolysis also has the added advantage of being very flexible, and hence potentially advantageous for electricity grids, where rapidly responding loads can meet the needs for a variety of grid services in a world of increasing intermittent renewable generation.

The objective of this paper is to present a set of harmonised operating conditions, testing protocols and procedures for assessing performance of Low Temperature Water Electrolysis applications for allowing fair comparison of test results from various projects and laboratories. The document also deals with assessment of efficiency, durability and dynamic behaviour of various electrolysis systems. Durability is evaluated through endurance testing by applying various load profiles to the cell/stack and also to systems for assessing the grid connectivity capabilities.

Abstract No. 41

Catalytic and Photochemically-Assisted Electroreduction of Carbon Dioxide

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Summary. There has been growing interest in the electrochemical conversion of carbon dioxide to useful carbon-based fuels or chemicals. The reaction products are of potential importance to energy technology, food research, medical applications and fabrication of plastic materials.

Abstract. Because CO_2 molecule is very stable, its electroreduction processes are characterized by large overpotentials. It is often postulated that, during electroreduction, the rate limiting step is the protonation of the adsorbed CO product to form the CHO adsorbate. In this respect, the proton availability and its mobility at the photo(electro)chemical interface has to be addressed. On the other hand, competition between such parallel processes as hydrogen evolution and carbon dioxide reduction has also to be considered.

Recently, we have concentrated on the development of hybrid materials by utilizing combination of metal oxide semiconductors thus capable of effective photoelectrochemical reduction of carbon dioxide. For example, the combination of titanium (IV) oxide and copper (I) oxide has been considered before and after sunlight illumination. Application of the hybrid system composed of both above-mentioned oxides resulted in high current densities originating from photoelectrochemical reduction of carbon dioxide mostly to methanol (CH_3OH) as demonstrated upon identification of final products. Among important issue is intentional stabilization, activation, and functionalization of the mixed-metal-oxide-based photoelectrochemcal interface toward better long-term performance and selectivity production of small organic molecules (C1-C4) and other chemicals. In this respect, ultra-thin films of conducting polymers (simple or polyoxometallate-derivatized) and supramolecular complexes (with nitrogen containing ligands and certain transition metal sites), sub-monolayers of metals (Cu, Au), networks of noble metal (Au, Ag, Pd) nanoparticles or layers of robust bacterial biofilms have been considered.

We are also going to demonstrate that the photoinduced electron from semiconductor conduction band is capable of activation of the active center of the metalo-enzyme molecule. Here the.nanostructured silicon material has been chosen as the substrate for the enzyme adsorption. In this case the p-type Si(111) was etched toward formation of the bunched steps on the surface. The photo-biocathode with Cu-containing enzyme has induced the reduction of not only oxygen but carbon dioxide as well, under illuminations with photon energies higher than silicon band gap.

In the presentation, special attention will be paid to mechanistic aspects of electroreduction of carbon dioxide, fabrication and characterization of highly selective and durable semiconductor photoelectrode materials and to the reaction conditions permitting effective electrolysis of carbon dioxide.

Abstract No. 42

Impact of the design on performance loss in photo-driven water electrolysers

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Summary. In this study, we develop a degradation model in order to predict the performance loss in photo-driven water electrolysers. It appears that the durability highly depends on device design choice, on irradiation intensity in the photoabsorber, as well as on the current density in the electrolyser.

Abstract.

Photo-driven water electrolysis is an attractive and clean method to store the solar energy directly in the form of hydrogen. As illustrated in Figure 1.a, photo-driven water electrolysis consists of directly coupling a semiconductor (photoabsorber) to an electrolyser, without need of further power converters or electronics. Compared to the separate photovoltaic and electrolyser configuration, it has the potential to increase energy conversion efficiency and to reduce hydrogen cost. When facing the problem of large scale implementation, the question arises of how to design the integrated electrolyser in order to maximize the cumulated amount of the produced hydrogen during the device's lifetime. Indeed, for a given photovoltaic cell, the design of the electrolyser will highly impact on the solar to hydrogen efficiency, as well as on the degradation.

Here, we discuss the impact of the photo-driven electrolyser design and operating conditions on performance loss. A physics-based model, which uses degradation rates of the device components, is used to predict the performance loss in four different illustrative device designs. One fundamental difference between commercial electrolysers and electrolysers operating with photoabsorbers is the operating current density. While the former operate at current densities around 1 A/cm^2, the latter operate at around 10 mA/cm^2. Cost advantages are usually observed for larger current densities (reduced use of components). In order to control current densities, radiation and/or current concentration can be applied [1]. Examples of i-V curves obtained during the first 30'000 operating hours of the device for four different cases, using or not using radiation concentration in the photoabsorber and/or current concentration in the electrolyser, are presented in Figure 1.b. The operating point of the device, which determines the amount of the produced hydrogen, is the intersection between the photoabsorber and electrolyser curves. Thus, a tradeoff between electrolyser undersizing compared to the photoabsorber and durability can be found. Furthermore, the instabilities caused by the solar profile induce extreme dynamics in the device, which are known to accelerate the degradation of the electrolyser. Heat and water management, device maintenance, and component replacement can help in mitigating degradation and the corresponding effects on device performance.

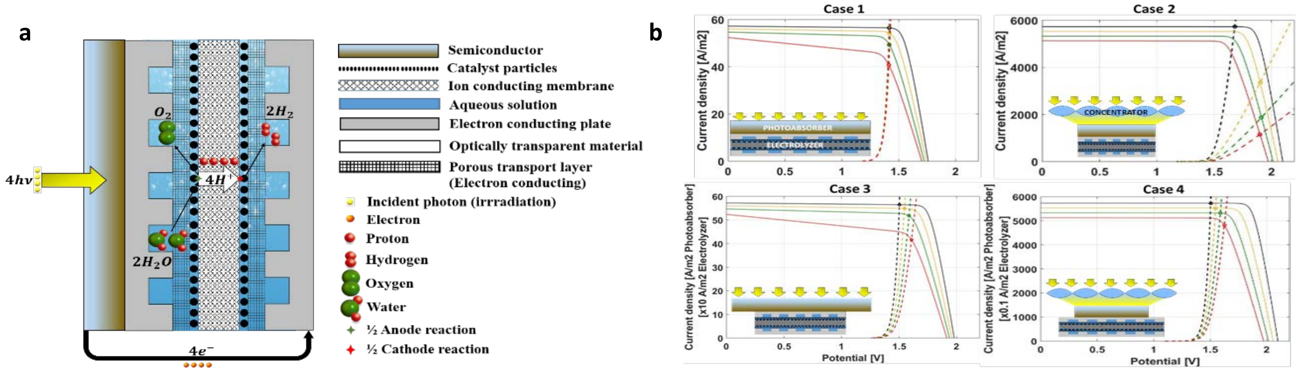

Figure 1. a. Photo-driven water electrolyser - **b.** Evolution of the i-V curves during the first 30'000 operating hours of the device for four different cases, using or not using radiation and/or current concentration [2].

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Abstract No. 43

SO_2 depolarized electrolyser- Enhanced H_2 production with SiC foam flow layer

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Summary. SO_2 depolarized electrolyzer can produce H_2 economically with reduced overvoltage and cheaper cell components than traditional PEM water electrolyzers. In this work it was confirmed that use of SiC foam provides highly improved mixture in anolyte, leading to higher current densities, suppressing formation of parasitic products.

Abstract. For economical, technical and environmental sustainability water electrolysis powered by renewable power sources is traditionally considered technique. It requires however high overvoltage (theoretical E^0 = 1.23 V vs. practical 1.7-2.2 V), and therefore leads to lower efficiency, higher hydrogen costs and use of expensive PGM catalysts. Alternative process - sulfur dioxide depolarized electrolysis (SDE) - has been developed, where SO_2 is added to the anode space and is oxidized electrochemically to sulfuric acid followed by hydrogen evolution at cathode. Such overall reaction requires only E^0 ~0.16 V, i.e. several times reduced voltage vs. H_2O splitting [1]. Nevertheless, one of the obstacles for commercialization is the SO_2 carry-over to cathode with formation of parasitic products (elemental sulfur or H_2S) [2].

For SDE, materials designed for water electrolysis are currently used (such as polymer flow field plates), but they are efficient when liquid carry-over phenomenon is not present. In this study, chemically resistant SiC foam (EngiCer SA) was tested for it effect on flow properties in a bench-scale SDE system (Aalto). The results confirmed increased current densities in comparison to traditional inserts. In addition, SiC foam was found to clearly reduce the SO_2 carry-over, hindering sulfur particles growth and facilitating the process control. To confirm the experimental findings, CFD calculations for foam model (below) were made indicating that velocities and their gradients have been indeed improved by several times, giving more efficient mixing and therefore SO_2 mass transport.

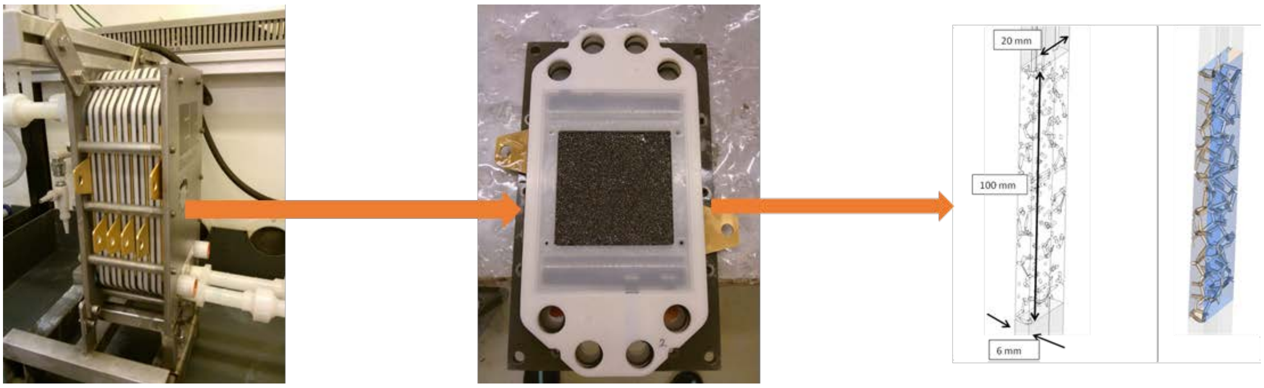

Figure 1. Five Cell SDE stack (Aalto) having SiC foam (Erbicer) as a flow field material, and the model developed of the foam (Enginsoft).

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Acknowledgement.
The research leading to these results was supported by the European Union's Seventh Framework Programme (FP7), the Fuel Cell and Hydrogen Joint Undertaking, under grant agreement n° 325320 of the SOL2HY2 project.
Visit: https://sol2hy2.eucoord.com/

Abstract No. 44

Sputtered Pt-containing electrocatalysts for SO_2(aq) electrolysis

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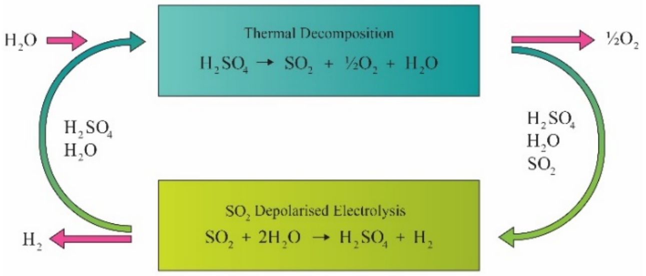
Summary. Pt_3Pd_2 and $Pt_{40}Pd_{57}Al_3$ thin film combinations were identified, by employing a high-throughput and combinatorial (HTC) approach, as potential contenders to compete with pure Pt that is currently being employed as the anode material in the hybrid sulphur (HyS) cycle for SO_2 electrolysis.

Abstract.

The hybrid sulphur cycle (Figure 1a), a thermo-electrochemical water splitting process that includes the electrochemical oxidation of SO_2, serves as a means of producing hydrogen in a usable form without emitting any harmful pollutants. Interest in the non-carbon-based HyS cycle as a potential large scale hydrogen production process results from the fact that, whereas the anodic reaction for regular water electrolysis occurs at a standard potential of 1.23 V (SHE), the anodic reaction in the SO_2 depolarised electrolyser (SDE) occurs at a standard potential of 0.17 V (SHE), which translates into an energy gain of more than one volt that makes the HyS cycle more favourable. An aspect that can improve the SDE performance and economic viability is improving the anodic reaction of electrochemically oxidising aqueous SO_2. This can be achieved by improving the electrocatalyst for the anodic reaction.

Combinatorial sputtering, high-throughput screening, and traditional methods were employed to investigate various thin film electrocatalyst combinations containing varying ratios of platinum (Pt), palladium (Pd) and aluminium (Al), towards the electro-oxidation of aqueous SO_2 [1]. The combinatorial sputtering approach, based on magnetron enhanced plasma sputtering and photolithography, was developed and employed in the syntheses of the thin film electrocatalysts. A multi-channel potentiostat, connected to a custom manufactured multi-working electrode electrochemical cell, allowed for high-throughput parallel screening of the deposited electrocatalysts towards the electro-oxidation of aqueous SO_2. Employing onset potential and current output as the screening criteria together with stability tests and the results obtained from physical characterisation, thin films exhibiting satisfactory performance were identified. A Pt_3Pd_2 thin film, annealed at 800 °C [2], and a ternary combination of $Pt_{40}Pd_{57}Al_3$, annealed at 900 °C [3], were identified as potential contenders to compete with pure Pt that is currently being employed as the anode material. Both Pt_3Pd_2 and $Pt_{40}Pd_{57}Al_3$ thin films contain less Pt than a pure Pt thin film (Figure 1b), while exhibiting increased electrocatalytic activity, and can serve as a basis for future studies.



a) b)

Figure 1: a) The hybrid sulphur (HyS) cycle and b) correlation of current density (mA.mg Pt^{-1}) with Pt content (%) [3]

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Abstract No. 45 (INVITED)

Steam Electrolysis as the Core Technology for Sector Coupling in the Energy Transition

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Summary. The steam electrolysis with its superior efficiency due to the utilisation of waste heat is the core technology to connect the electrical sector with the oil & gas sector. This leads eventually to a decarbonisation of all sectors and the achievement of the 2°C target until 2050.

Abstract.

The decarbonisation of the power sector alone is not sufficient to reach the 2°C target in 2050, as only up to 25% of energy is consumed as electricity. The increased installed renewable power leads to an increasing volatility in the power production, and due to that to a necessary overcapacity in installed power. This pushes the electricity grid under heavy load and leads to an increasing amount of curtailed power, especially from large wind farms. Instead of curtailing this renewable energy, it should be shifted into the oil & gas sector in an efficient manner. This enables also a seasonal storage of renewable energy in large quantities.

The efficient hydrogen production by renewable electricity is the first and most important step in the sector coupling. The electrical efficiency of the steam electrolysis is up to 20% higher than common water electrolysis technologies, due to the utilisation of waste heat for the steam generation. Waste heat at a relatively low temperature level of roughly 150°C is needed, and is typically available in industrial surroundings, like refineries, chemical and metal industries. Thus, the decentralised hydrogen production via steam electrolysis in order to mitigate CO_2 emissions from Steam Methane Reformer (SMR) is economically favourable in those environments.

In addition to that, the hydrogen production is the core of all Power-to-Gas and Power-to-Liquid applications. In those processes, the exothermic reaction enthalpy is used for the steam generation, which makes a combination of steam electrolysis and synthesis of drop-in fuel (synthetic natural gas, diesel, gasoline, kerosene, etc.) most promising.

Hence, the steam electrolysis is the optimal technology to connect the electrical sector with the oil & gas sector. This leads eventually to a decarbonisation of all sectors and the achievement of the 2°C target until 2050.

Abstract No. 46

Electrochemical Tailoring of Syngas

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Summary: The present work is focused on syngas production by high-temperature co-electrolysis. By modification of reaction conditions, specific syngas compositions can be tailored. In this respect, polarization curve, impedance spectra and product analysis of the performance of single cells are compared and investigated in detail.

Abstract: In the energy system transition (German: *Energiewende*) a major role is foreseen for the high-temperature co-electrolysis of carbon dioxide and water vapour to syngas by usage of renewably generated electricity. Syngas is used on a large scale for the production of basic chemicals like ammonia and methanol, but can be used also for the synthesis of synthetic fuels, like Fischer-Tropsch diesel and oxymethylenether [1]. In the Solid Oxide Electrolysis Cell (SOEC) the direct reduction of water vapour, of carbon dioxide and the reverse water-gas shift reaction are the underlying mechanisms. In the framework of the German Kopernikus project 'Power-to-X' the co-electrolysis process in SOECs is investigated and further developed to meet the requirements for the subsequent hydrocarbon synthesis, i.e. 'tailoring' of the syngas compositions. Commercially available fuel electrode supported cells (CeramTec) composed of a LSCF anode, a CGO barrier-layer, an 8YSZ electrolyte and a Ni/8YSZ cathode were used in these investigations. These were examined by the combination of electrochemical methods (I/V-performance, EIS) and an all-embracing quantitative product analysis. Experiments under varying conditions (temperature, current density, pure or mixed gases) were performed and conclusions about the competitive fundamental reactions have been drawn by comparison and calculation.

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Abstract No. 47

System design and operation of a solid oxide electrolyzer

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Summary. From the overall system perspective, the thermoneutral and exothermic operation of a solid oxide electrolyzer achieves similar efficiency while exothermic operation with an allowable temperature gradient allows for much larger operating current, thus a larger fuel production rate and thus possibly a lower production cost.

Abstract. Compared with the best available alkaline electrolyzer (2.0 V, 0.2 A/cm^2) and PEM electrolyzer (1.8 V, 1.0 A/cm^2), a solid oxide electrolyzer (SOEC) can operate at a rather low voltage (1.25-1.4 V) with a reasonable current density (0.2 to 0.8 A/cm^2), achieving thus intrinsically higher electrolysis efficiency and moderate equipment size (cost). For the operation of the SOEC itself, thermoneutral operation has been preferred, under which the consumed power satisfies the electrolysis requirement and keeps the operating temperature nearly unchanged. However, from the perspective of system design, thermoneutral operation is questioned, as 1) the operating current density is low at thermoneutral voltage, and 2) a feasible heat exchanger design is expected to heat up the gas feeds with the available heat from the electrolyzer outlet. Considering these two points, exothermic operation at a voltage higher than the thermoneutral one may offer a better choice. Due to the excess potential, the additional power consumed may establish a certain temperature gradient along the flow direction in the electrolyzer. The temperature increase along the flow direction increases the average operating current density. More importantly, the temperature difference between the electrolyzer outlet and inlet enables better feasible designs for the heat exchange. In this paper, the thermoneutral and exothermic operation modes of SOEC are investigated and compared to quantify the benefits from an exothermic operation point of view and to find the best exothermic operating points.

As most experimental data on the SOEC performance are at constant operating temperature, the performance of the exothermic operation should be predicted by modelling to a reasonable precision. A quasi 2D model considering mass transfer along electrodes by the dusty gas model, current-density distribution along the gas channels and detailed overpotential calculation, has been developed and calibrated with experimental data for SOLIDPower SOEC of steam electrolysis with a feed composition (H_2O/H_2: 0.9/0.1) at both atmospheric and elevated pressures and co-electrolysis with various feed compositions ($H_2O/H_2/CO_2$: 0.8/0.1/0.1, $H_2O/H_2/CO_2$: 0.65/0.1/0.25, $H_2O/H_2/CO_2$: 0.45/0.1/0.45) at atmospheric pressure. The calibrated model could predict the experimental electrolysis performance with good accuracy. It is hence assumed that this model provides a reasonable performance prediction for exothermic operation.

As is known, for SOEC the steam cannot be converted to very high rates to avoid degradation, thus its utilization factor is recommended to lie in the range of 60-80%. The higher this utilization factor, the higher the overall system efficiency will be. For thermoneutral operation at 700 C and a utilization factor of 80%, the operating voltage, average current density and feed flowrate are calculated as 1.28 V, 0.3695 A/cm^2 and 3.59 NmLPM/cm^2, respectively. While for the exothermic operation at the same utilization factor (80%), a feed temperature of 700 °C and a temperature difference of 110 °C between the electrolyzer outlet and inlet, the operating voltage, current density and feed flowrate are calculated as 1.339 V, 0.716 A/cm^2, 6.94 NmLPM/cm^2. It can be shown that with the same utilization factor the thermoneutral and exothermic operation of a solid oxide electrolyzer can achieve the same system efficiency, while the exothermic operation allows a significantly larger operating current, thus a larger fuel production rate and thus possibly a lower production cost. Particularly, for the same area of electrolyer, the total power stored is doubled by exothermic operation with an outlet-inlet temperature difference of 110 °C, compared with thermoneutral operation. Thus, exothermic operation can be recommended for cost-effective design and operation of a standalone SOEC system.

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 621173, SOPHIA.

Abstract No. 48

Solid oxide electrolyzes system development

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Summary.

Various advantageous system concepts for SOEC, Co-SOEC and rSOEC systems including all components which are necessary to operate the high temperature electrolysis stack, were identified. Validated system concepts on the test rig will be presented, reaching electrical to chemical energy conversion efficiencies up to 80%.

Abstract.

Power-to-Gas-to-Power technologies offer strong potentials for energy markets with highly stochastic energy production from renewable sources, such as wind and PV. Electrical energy can be stored in chemical energy by producing molecular hydrogen or syngas. This happens via electrolysis of steam or co-electrolysis of steam and carbon dioxide. These energy carriers can either be used as a buffer for fluctuating energy production, or used as transport fuels. The synthetic fuels are potentially carbon neutral, when the electricity comes from renewable energy production.

Increasing efficiencies and cost effectiveness are key issues in state of the art solid oxide electrolyzes systems and still a major challenge. A very cost effective solution is using instead of two separate units that operate alternately for gas or power production, a reversible SOE system (rSOE). The rSOEC system can switch between these two operation modes, which results in a more compact system that can be operated almost full time. Additionally, the system can be highly efficient operated with a whole range of different fuels, which increases the technologies flexibility and usability.

This multiuse and multifuel character of SOE systems leads to very particular challenges in the development. A feasible concept has to combine all necessary BoP components and control mechanisms allowing all modes of operation, while keeping efficiencies and cost effectiveness. One particular challenge for the system design is heat management. A method was developed that promises best possible use of heat recirculation in all modes, while being minimal in design and regulation requirements. For the first time dynamic simulations for all operating conditions e.g. start-up, shut-down, stand-by and mode-switching processes, including all relevant mass and energy flows are currently developed. This strongly supports the system development by making them more effective, since iterative development circles and thus development time and hardware costs were reduced.

The project “Hydrocell” (2013-2016) demonstrated the usability of these simulation methods. A Proof-of-Concept SOEC system has been developed and tested with electricity to H_2 (LHV) conversion efficiencies above 80%el.

Within the current project “AuRora”, various system designs for a fully autonomous rSOE system were identified. The concepts are switchable between H_2O electrolysis, H_20+CO_2 co-electrolysis with system integrated catalytic methanation and multifuel SOFC operation. System concepts are developed with conversion efficiencies above 80%el* for H_2 production and CH_4 production. Based on the simulation results, including CFD, a 1kWel Proof-of-Concept will be realized on the testrig in 2017.

Within the presentation, the theoretical background, different SOE and rSOE systems designs, optimized operation conditions, as well as system measurements performed in the project “Hydrocell” and “AuRora” will be explained. This includes steam-electrolysis, H_2O + CO_2 co-electrolysis with system integrated catalytic methanation, SOFC operation with H_2, as well as multifuel operation with system integrated fuel reformation.

* based on LHV energy content

Abstract No. 49

Electrochemical Characterization of a 10 layer Solid Oxide Electrolysis Stack operated under pressurized conditions

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Summary.

A commercially available planar 10 layer solid oxide electrolysis stack with electrolyte supported cells was characterized in an operating pressure range between 1.4 and 8 bar. Current-voltage characteristics and impedance spectroscopy were carried out by varying reactant gas composition, steam utilization and operating temperature.

Abstract.

The major part of the prospective power supply system will be based on solar and wind energy. The associated intermittency of energy supply due to varying weather conditions requires flexible storage and usage options. Converting electrical into chemical energy could be an essential constituent in this challenge. One promising path is the solid oxide electrolysis cell (SOEC) technology which can highly efficiently provide chemicals like hydrogen or derived hydrocarbons from electricity. These products can be used as fuels in mobility, for the chemical process industry, for conversion back to electricity or heating.

SOECs offer a great potential for a highly efficient energy conversion due to their high operating temperature. Fast kinetics of electrochemical reactions lead to reduced electrochemical losses. Additionally, previous studies have shown that the efficiency of solid oxide cells can be significantly improved by operating at elevated pressure [1, 2]. A further reason for pressurization is the use of pressurized hydrogen in downstream processes like storage or fuel synthesis.

Experimental results of a SOEC stack operated under pressurized conditions in water electrolysis mode are presented. For a parameter study a commercially available planar stack consisting of 10 electrolyte supported cells was used. The stack was operated in a pressure range between 1.4 and 8 bar. Parameter sensitivities were examined by varying reactant gas composition (x_{H2O}=0.80…0.98), steam utilization (0.60…0.85) and operating temperature (750…850 °C). Pressure influence on open-circuit voltage (OCV) and reachable power density was examined on the basis of current-voltage curves. Impedance spectroscopy was carried out for further investigations to distinguish between different electrochemical phenomena. Whereas the impedance measurements show strong influences on several electrochemical and physical processes, current-voltage curves show only small changes due to the comparably low current densities reachable with electrolyte supported cells.

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Abstract No. 50 (INVITED)

The Development of Accelerated Stress Tests for PEM Electrolysers

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Summary. An understanding of degradation mechanisms of key materials (catalyst, membrane and bipolar plates) in PEM electrolysers is important to get innovations to market faster. Along with mechanisms, the accelerated stress tests developed to test these will be discussed.

Abstract. In a world in which fossil fuel energy is becoming ever more scarce and expensive and countries are struggling to meet their carbon reduction obligations, hydrogen solutions have finally reached the top of energy agendas. The only industrially applicable zero carbon method to produce hydrogen is via electrolysis utilizing renewable sources of electricity.

ITM Power is at the very heart of the initiatives and programmes to adopt hydrogen technology that will reduce both carbon footprints and energy costs. Using its technology and know-how, ITM is aiming to be the world leading supplier of both infrastructure for the production of green hydrogen transport fuel, and products for the generation and storage of hydrogen fuel from intermittent renewable energy sources.

PEM electrolysers have a lifetime of 5-10 years; as such there is difficulty in getting new materials to market. In order to get innovations to market faster the failure mechanisms need to be well understood and methods to accelerate degradation, based on real failure mechanisms need to be developed.

The first step is to understand the mode of operation of electrolysers in the field. The key is electrolysers (almost independent of application) need to be off for long periods of time and need to be able to respond on a subsecond basis. This very different to how most electrolysers are tested in the laboratory steady state and intermittent load following are common practice. The reasons behind this will be explained in more detail.

In addition, the stack failure mechanisms will be discussed and how these are measured in the laboratory. In one such example ITM have used an in-situ reference electrode (developed in collaboration with the National Physical Laboratory) to help understand catalyst degradation within the cell. This approach enables separation of the relative contributions of anode and cathode to the overall reaction. During shut down periods, it was observed that the cathode contributes more to changes in the open circuit voltage. This knowledge has been used to show that the majority of the degradation is occurring on the cathode catalyst, which is in contrast to the perceived thought which assumes the anode degrades faster. Changes in the electrochemically active surface area of the platinum cathode as a result of potential cycling were determined in-situ via hydrogen underpotential cyclic voltammetry. Scanning electron microscopy and X-ray tomography were used to correlate changes in catalyst morphology with performance degradation of both carbon-supported and unsupported platinum catalysts. These experiments have led to the development of accelerated stress tests, based on cycling of the electrode potential, for PEM electrolyser catalysts. Other such examples will be presented.

Acknowledgement

This project has received funding from the FCH JU and European Union's Horizon 2020 research and innovation programme under grant agreement No 700008. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and Hydrogen Europe and N.ERGHY.

Abstract No. 51 (INVITED)

Benchmarking Catalyst Activity and Durability for Water Electrolysis

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Summary. Giner Inc. (Giner) has been a world leader in researching, developing and manufacturing low temperature water electrolyzers. Advanced catalysts have been developed to enhance the performance of water electrolyzers while lowering their capital cost. Benchmark water electrolysis catalyst performance and durability will be established.

Abstract. The utilization of renewable energy has substantially driven investments into water electrolysis. As renewable energy emerges and penetrates further into the energy market, the storage of surplus “off peak” electricity has received widespread attention. An electrolyzer can utilize “off peak” electricity from solar or wind farms to produce hydrogen (H_2). This hydrogen can then be operated in a fuel cell mode to generate electricity when needed. It is estimated that the water electrolyzer market can rise up to 300 GW over the next two decades. The power to gas market alone is poised to become a multi-billion dollar market for on-site water electrolysis systems over the next decade.

However, current hydrogen production from electrolysis comprises only a small fraction of the global hydrogen market due to the high cost that results from expensive materials even if “free” electricity from renewable energy can be acquired. Giner has been a world leader in researching, developing and manufacturing low temperature water electrolyzers and reversible fuel cells. We have been striving to address the challenges of these materials (catalyst, membrane, and bipolar) to improve electrolyzers’ performance, extend their lifetime, and lower their capital cost. These efforts include: 1) lowering platinum-group metal (PGM) catalyst loading; 2) discovering non-precious metal catalysts; 3) improving membrane durability; 4) reducing H_2 crossover across membrane; 5) increasing corrosion resistance of separators and other hardware.

In Particular, catalyst activity and durability play an essential role for the cost and viable commercialization of water electrolysis. In the field of proton exchange membrane electrolysis, Giner develops advanced Ir nanoparticle catalysts that, in a comparison with commercial catalyst, has successfully lowered the Ir loading by an order of magnitude while retaining a similar performance. The stability of the advanced Ir nano-catalyst has also been examined, which is founded to be tremendously impacted by processing conditions amid catalyst synthesis. In the field of alkaline membrane electrolysis, Giner has developed bifunctional oxygen reduction reaction (ORR)/oxygen evolution reaction (OER), Co_3O_4 supported on corrosion-resistant carbon tubes, which enables the operation of reversible fuel cells with extended hours.

Unlike the well-established catalyst benchmarks of fuel cells, the performance and durability of water electrolyzer catalyst have not been thoroughly studied. We aim to establish benchmark catalyst performance and durability for low temperature water electrolysis. For this purpose, a series of oxygen evolution reaction (OER) catalysts, which includes commercial Ir black and various Ir nanostructures, will be evaluated under test protocols established at Giner Inc. These approaches include high-voltage hold (>1.8 V), voltage cycling (1.4 to 2.0 V), and constant low-current operations. The polarization curves of the MEAs will be obtained after each test. The morphology and structure of MEAs after durability tests will be characterized to correlate to their performance and durability.

Some of these advances have been applied in our electrolyzer products, from small lab hydrogen generators to MW stacks. The performance and efficiency of our electrolyzers are thus tremendously improved. The development and deployment of these MW electrolyzer stacks will cultivate the large-scale storage and application of a variety of renewable energy.

Abstract No. 52

Operation of low-temp electrolyzers at very high current densities: a pipe dream or an opportunity?

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Abstract. Recently introduced 3M NSTF-based electrolyzer specific catalysts and CCMs were shown to be excellent performers in electrolysis mode, particularly at the very high current density ranges, with current densities approaching as high as 20 A/cm^2 were reported(1) In addition to the excellent performance these catalysts are able to achieve this performance with unrivalled low PGM use, typically around 1/10th of the typical catalyst loadings used in conventional PEM electrolyzers. Surprisingly, the performance at these low loadings seem to have no ill effects on durability of CCMs based on these catalysts as demonstrated in recent presentations(2,3), even when the operating temperature of the cell was raised to 80°C and beyond.

These advances may open the way to successfully address global energy storage markets where sizable penetration of renewable energy generating sources start to introduce stress on the existing power grids(4). By coupling the electrolyzers to the renewable energy generators (wind, solar, tide, etc.) one can decouple generation and storage (via hydrogen storage in tanks, caverns, gas fields, etc.) and better match energy supply to energy demand. To successfully do that however, relatively inexpensive electrolyzers may need to be used, as they are predicted to be utilized only in the fraction of the day when electricity prices are depressed by overproduction from renewable sources (hence relatively higher per kW capital costs). We believe the best way to lower the capital cost of the electrolyzer is to operate one at high current density range (large dynamic window), thus eliminating the need for multiple electrolyzer units.

Can this be achieved? Or is this just a pipe dream?

Our presentation will discuss results where 3M NSTF electrolyzer CCMs were evaluated at relatively high current densities under a durability test, including operation as high as 10A/cm2 for 5000 hours. We'll also take the opportunity to introduce our collaboration with Dioxide Materials and present new and interesting data on high performance electrolysis in alkaline environments.

All PEM data to be presented were/will have been obtained with Ir-NSTF and Pt-NSTF electro-catalyst on the anode and cathode sides respectively. A fuel cell technology hardware with graphite cathode and Ti made anode with 50 cm^2 active membrane area was used in all the experiments.

1. Krzysztof A. Lewinski, Sean M. Luopa, (invited) "High Power Water Electrolysis as a New Paradigm for Operation of PEM Electrolyzer" (abstract 1948), Spring ECS Meeting, Chicago, IL, May 2015.
2. Krzysztof A. Lewinski, Dennis van der Vliet, and Sean M. Luopa, "NSTF Advances for PEM Electrolysis - the Effect of Alloying on Activity of NSTF Electrolyzer Catalysts and Performance of NSTF Based PEM Electrolyzers" (Abstract 1457), Fall ECS Meeting, Phoenix, AZ, Oct 2015.
3. Krzysztof A. Lewinski, Dennis van der Vliet, and Sean M. Luopa, "NSTF Advances for PEM Electrolysis - the Effect of Alloying on Activity of NSTF Electrolyzer Catalysts and Performance of NSTF Based PEM Electrolyzers", (10.1149/06917.0893ecst), ECS Transactions, 69 (17) , p. 893-917 (2015).
4. Bryan Pivovar, "H2 NREL Workshop at Scale: Enhance the U.S. energy portfolio through sustainable use of domestic resources, improvements in infrastructure, and increase in grid resiliency.", NREL Workshop, November 16, 2016 (https://energy.gov/sites/prod/files/2016/12/f34/fcto_h2atscale_workshop_pivovar_2.pdf)

Abstract No. 53

Membranes for recombination and electro-oxidation of permeated hydrogen in PEM electrolysis

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Summary. Recombination and electro-oxidation of permeated hydrogen will result in reduction of its concentration in the anode compartment of PEM electrolysers. In order to achieve this hydrogen concentration reduction, PFSA-based membranes were modified by depositing platinum nanoparticles within the membrane structure.

Abstract. The origin of the hydrogen in the anode section of PEM electrolyser is due to the permeation occurring from the cathode compartment. This talk will provide some data and theoretical analysis on the use of platinum (Pt) nanoparticles within the PFSA membrane matrix to reduce hydrogen concentration during PEM water electrolysis.

Deposition of platinum particles was achieved by proprietary electro-less reduction technique.

Commercially available PFSA-based membranes were used. The membrane structure was modified by platinum nanoparticles. All-titanium made electrolysis cell with 25 cm^2 active membrane area was used in all the experiments. The permeation rate of hydrogen from cathode to anode compartment was measured by gas chromatography method. The effect of Pt presence within the membrane structure on the concentration of hydrogen in the oxygen stream was assessed. Temperatures as well as water supply rate and current densities were also used as experimental variables.

Abstract No. 54

Physical factors affecting gas-leakage from PEMWE

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Summary.

Sealing technology is critical to commercialize high pressure PEMWE. Representative parameters to determine sealing performance is experimentally examined with TAGUCHI method. Among the parameters, cathode packing material, surface roughness of PEM and O-ring hardness are dominant factors to determine the sealing performance.

Abstract.

Sealing to highly pressurized gas in PEMWE is generically difficult. Different from conventional sealing in metallic piping and its joints, the sealing materials embedded in PEWEM faces different kinds of material, and the gas leakage occurs at the interface between the materials. One of the materials is supposed to be polymer electrolyte membrane (PEM). PEM shrinks and expands in rather large extent, according to degree of hydration. In addition, the surface of PEM has a roughness, which is predicted to worse sealing performance. Moreover, PEM indicates high acid nature, which suggests corrosion-resistive material as sealing material. These specific characteristic cause difficulty in developing adequate sealing method for PEMWE.

This study picks up physical factors, which are predicted to affect gas-leakage, and evaluates the impact of the each factor on the gas-leakage from PEMWE cell. Seven factors, such as O-ring hardness and PEM, are picked up. Gas-tightness test, in which the cell is composed of a specific pair of the factors, is executed and repeated. The test identifies which factor significantly impacts on gas-leakage. Taguchi method is introduced to give an efficiency, which reduces the number of times under different pair of factor for the gas-tightness test. In addition, the load imposed on O-ring are measured with pressure-sensitive-film. The load to O-ring is thought to directly determine path of gas leakage and thus the flow rate of the gas leakage. Furthermore, impact of sealing factor on contact electrical resistance is evaluated. Inappropriate sealing manner, such as too large wire diameter of O-ring and too low tightening pressure, causes a gap between cell components, resulting in an increase of the contact resistance. Through the above successive evaluations, dominant factors and proper sealing method is discussed.

Abstract No. 60 (INVITED)

Polyaromatic, Solid Polymer Electrolytes for Acidic and Alkaline Electrolyzers

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Summary. Are durable hydrocarbon proton- and hydroxide-conducting solid polymer electrolytes attainable?

Abstract. Perfluorinated proton-exchange polymers form the basis of standard high-performance PEM electrolyzers but difficult synthetic chemistry hampers further materials development. Hydrocarbon proton-exchange materials, on the other hand, are founded on well-established and versatile synthetic chemistry that allows for rapid materials development, and offer a less expensive alternative to perfluorinated polymers. In the corollary case of Anion Exchange Membrane electrolyzers, the search continues for an alkaline-stable, polymeric hydroxide-conducting medium. Solutions to these challenges require the undertaking of rigorous systematic studies on model polymers and representative materials of known and controllable molecular structure and preferred nano-morphology. In this presentation, the properties of unique proton- and hydroxide-conducting polymers will be described.

Abstract No. 56

Recent developments in alkaline pressure electrolysis with anion-conductive membrane (AEM)

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Summary. An overview of recent developments in alkaline pressure electrolysis with anion-conductive membrane (AEM) and the advantages and disadvantages of the technology is given. The targets of our current research project in this field are introduced.

Abstract. Research in alkaline membrane electrolysis with an anion-conductive membrane (AEM) has experienced increased attention in the last years due to its perspective to combine positive features of both the common alkaline and PEM-water electrolysis [1-3]. The AEM electrolysis uses an anion-conductive membrane which acts as separator and electrolyte simultaneously. Many advantages result from this specific property. It is possible to introduce a zero gap design with the working electrodes adhered directly to the membrane which in turn decreases the overvoltages and increases the current density. Furthermore only a weak lye or even pure water is necessary instead of a hazardous strong lye. Distilled water has to be fed only to the low pressure anode side. There are lower requirements concerning the feed water quality in comparison to PEM-electrolysis. No water circuit is necessary at the cathode side and high pressure hydrogen up to 30 bar is released with a very low water vapor content in the range of a few ppm [4]. In comparison to the PEM electrolysis a wider range of non-noble catalysts is applicable [5]. The more compact and simple system design with cheap materials can significantly reduce manufacturing costs. Beside these advantages the compact design offers the possibility to apply higher working pressures and to gain an additional benefit in concern of energy consumption [6].

But there is yet research effort necessary to improve the insufficient stability of the available anion-selective membranes under the conditions of water electrolysis. Membranes have to fulfill various requirements concerning high ionic conductivity and long-term mechanical and chemical stability. The operation is still restricted to temperatures below 70°C. The membranes which contain positively charged ionic groups for the ionic conductivity exhibit insufficient mechanical stability yet if the number of ionic groups is too high.At our Hydrogen Research Centre a project was started with focus on the application of anion-conductive membranes in pressure electrolysis. In the course of the project AEL-MALFE (alkaline electrolysis with solid anion conductive electrolyte) the setup of a new test cell is aimed. The design and construction of the test facility is based on operational expertise from a pressurised alkaline electrolyser and a single cell test rack. Different concepts of cell design and different material combinations will be evaluated.

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Abstract No. 57

Anion selective membranes based laboratory-scale alkaline water electrolysis stack

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Summary. Laboratory-scale alkaline water electrolysis stack was developed, constructed and operated under different conditions utilising different types of ion selective polymer membranes. Influence of the type of the polymer membrane and operational conditions on the electrolysis voltage/current efficiency and gases purity were followed.

Abstract. Water electrolysis represents the most widely used method of water splitting under hydrogen and oxygen evolution. It separates the overall reaction into two half-cell reactions in which hydrogen and oxygen are released from molecule of water by individual electrode reactions. Such separation is necessary in order to reach high product purity and process efficiency, as well as to operate the process safely. Process efficiency is strongly related to the cell voltage needed to run the process under desired intensity. Theoretical decomposition voltage of water of 1.23 V at 25 °C is under real conditions shifted to the operational value of 1.7 – 2.0 V. The reason for this increase is two-fold: (i) ohmic voltage loss and (ii) electrode reactions overvoltage. PEM water electrolysis utilizes proton exchange membrane (PEM) as a separator of cathode and anode compartments and a polymer electrolyte in one. It allows using “zero-gap” cell design reducing thus impact of the first reason of increased voltage. It is because it reduces interelectrode distance and eliminates danger of gas phase accumulation in the space between the electrodes. Unfortunately, similar materials are not generally available for the case of alkaline water electrolysis. Thus, a porous separator (diaphragm) is typically used. The application of porous inorganic or organic diaphragm as separator of the electrodes compartments has several negative consequences. It includes, besides increased ohmic drop, a need to use significant volumes of highly concentrated KOH solution as an electrolyte. It is therefore desirable to replace diaphragm by anion selective polymer electrolyte separator. Such a setup allows utilizing of the zero-gap resulting in KOH electrolyte concentration reduction also in the case of the alkaline water electrolysis. This change increases safety and flexibility of the process. At the same time, due to the reduced conductivity of the liquid electrolyte, importance of the parasitic currents is in contrast to the traditional stack arrangement reduced. Additionally, it is possible to use the electrodes modified by the suitable catalytic layer, utilizing anion selective materials as binders and thus achieve further voltage losses reduction.

The present study is focused on development of the laboratory scale zero-gap alkaline water electrolysis stack utilizing ion conductive membrane. Electrodes of the geometrical active surface area of 25 cm^2 were used. Mathematical model evaluating influence of the distribution channels and flow plate design on the electrode chambers flooding and occurrence of the parasitic currents was developed. It was based on calculation of the one phase flow in order to get the primary information on the liquid electrolyte distribution in the each cell of the laboratory scale stack. At this level model supposes the inertial forces to be negligible and calculates on the basis of the mass and kinetic energy balance. Efficiency of the produced gas phase removal was optimised experimentally. Voltage/current characteristics and purity of the gasses produced by the designed stack were followed for heterogeneous and homogeneous anion selective polymer membrane. The results were compared to the commercially available Nafion cation selective membrane. Achieved results of the experimental part showed the potential to achieve industrial values of the electrolysis voltage efficiency under milder conditions (lower temperature and KOH concentration) and high current efficiency even at relatively low current densities.

Acknowledgement

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Abstract No. 58

High Temperature Membraneless Alkaline Electrolysis

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Summary. Performance of a high temperature membraneless alkaline electrolysis. Increasing the operating temperature allows for the use of non-precious metal catalysts, while increasing overall performance.

Abstract. Recent work has been performed on membraneless and high temperature alkaline electrolysis. This work builds on previous work done by changing the materials of construction in order to reach higher temperatures.

The activity of nickel electrodes above 150 °C is a dramatic improvement over operation at 80 °C where most commercial electrolyzers operate. The typical limiting factor in increasing temperature is the membrane. A novel flow-based product separation is used to prevent product mixing. Previous results have shown that this mixing can be minimized to levels comparable with standard alkaline membranes. By increasing the temperature further to 200-250°C the system can operate at or near the thermal neutral voltage. This reduced the cooling load needed for the electrolyte, as well as reducing the overall energy consumption. Performance in this region is the focus of the work presented.

Abstract No. 59

Alkaline membrane electrolysis with PEM-level electrochemical performance

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Summary. Alkaline electrolysis reaching more than 2 A/cm^2 at 2 V is unusual. Using polymeric membranes (*m*-PBI) with liquid KOH electrolyte, we achieve polarization performance surpassing those of state-of-the-art PEM reference cells.

Abstract. We have employed potassium hydroxide doped poly(2,2’-(*m*-phenylene)-5,5’-bibenzimidazole) (*m*-PBI) membranes as separators in alkaline electrolysis. This class of membranes have shown high ionic conductivity in 20-25 wt% KOH.[1],[2] The membranes reduce ohmic losses compared to traditional porous separators and enable high current densities when combined with active electrodes.[3]

The electrodes use a classic perforated plate electrode geometry. A vacuum plasma sprayed Raney-nickel-molybdenum cathode[4] and an uncoated nickel anode is assembled in a zero-gap configuration with a pre-doped membrane. This configuration allow for very good gas-liberation properties, but most likely does not represent the optimum use of electrode and membrane area. Nonetheless, we are able to reach more than 2 A/cm^2 at 2 V after 12 hour break-in, see Figure 1.
While the membranes show good chemical stability in up to 25 wt% KOH, but have shown some increased in-cell degradation, the extend of this is unknown.[5] We demonstrate a lifetime of up to two weeks depending on thickness. Cell failure is caused by membrane degradation, while performance decrease appear to be caused by electrode degradation, which was previously shown to be stable.[6]

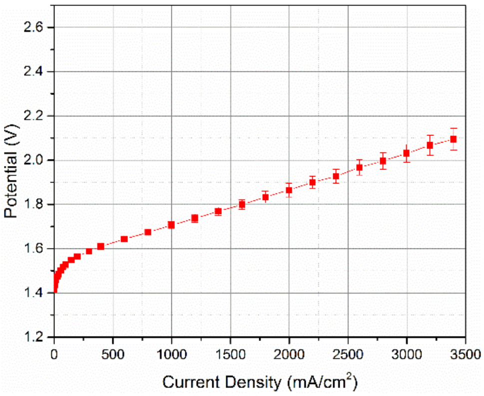

Figure 6: Polarization curve of the cell: *Raney-NiMo cathode | m-PBI/KOH electrolyte | Nickel anode*. [KOH] = 24 wt%, T = 80°C.

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Abstract No. 60 (INVITED)

CO from CO_2 – on-site carbon monoxide generation

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Summary. A plant producing pure CO from a source of CO_2 via solid oxide electrolysis. The plant works on-site and is cost-competitive.

Abstract. This presentation will cover the technical and commercial features of Haldor Topsoe's CO from CO_2 technology. Haldor Topsoe's eCOs is a solid oxide electrolysis cell (SOEC) technology that allows the safe, efficient, and cost-competitive production of carbon monoxide directly at the site of facilities where the gas is needed. The CO-generation device uses feedstock carbon dioxide and electrical power to produce CO in quantities ideal for most operations that today rely on cylinder or tube trailer supply. The modular containerized design allows for a compact design and a foot print that in many cases is comparable to the tube trailer loading bay.

An eCOs plant is delivered as a stand-alone unit with power, CO_2 and product gas connections. Furthermore, the plant ensures high levels of purity, producing CO at 99.5% assay with minimal contaminants and CO_2 as the main contaminant. An eCOs solution can also be customized to produce CO at 99.999% purity.

On site CO generation is a significant development to the medical, pharmaceutical, metallurgy, electronics and specialty chemicals industries, which require carbon monoxide in their processes. The eCOs technology ensure security of supply, eliminates the need to transport hazardous gas, and drastically reduce costs related to storage, rentals and connections. In the longer run, this technology opens up for a whole new segment of green and sustainable chemicals from renewable carbon sources.

Abstract No. 61

Thermodynamic constraints in operating a solid oxide electrolysis stack on dry carbon dioxide gathered from the Mars atmosphere.

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Summary. Electrolysis of dry CO_2 by high temperature electrolysis encounters challenges at both extremes of the pO_2 range seen at the cathode. The nickel cermet cathode can be oxidized by pure CO_2, while CO produced by electrolysis can be further electrolyzed to carbon. Avoiding electrode oxidation and carbon formation by CO reduction are essential to sustained operation of MOXIE on Mars.

Abstract. Ceramatec has developed the solid oxide electrolysis stack to demonstrate oxygen production from Mars atmosphere CO_2 in the MOXIE[1] instrument on the Mars 2020 rover. There are no process utilities such as air, hydrogen, nitrogen, or water available to MOXIE. MOXIE can only take in filtered Mars atmosphere, and in an unattended operation, produce oxygen from the CO_2 in the atmosphere. The nickel cermet cathode is oxidized by pure CO_2 at 800°C which results in a loss of conductivity and a disruption of the microstructure due to volume expansion on oxidation.

Mars atmosphere, which is about 96% CO_2, is supplied to the solid oxide electrolysis stack by means of a scroll compressor. The scroll pump is a fixed displacement device, so the delivered flow rate of CO_2 will depend on atmospheric density, which varies as a function of landing site elevation as well as seasonal and diurnal atmosphere cycles. The landing site has not yet been selected, but even at a given site the density will vary over a wide range. Therefore, MOXIE must be capable of operating over a wide range of feedstock rates. The MOXIE system and operating strategy must be designed to protect against cathode oxidation and carbon deposition as there are no provisions to recover from either event.

The thermodynamic and resulting electrochemical boundaries have been mapped analytically and used to develop system configurations and operating strategies to protect against cathode oxidation and CO reduction to carbon. These approaches have been and continue to be validated experimentally with increasing degrees of system integration. The MOXIE stack process integration and operational development path and results will be presented.

Acknowledgment: This material is based on work supported by NASA through JPL's prime contract under JPL subcontract number 1515459. The authors would like to acknowledge the contributions of Michael Hecht (MIT, MOXIE Principal Investigator, PI), Jeff Hoffman (MIT, MOXIE Deputy PI), Jeff Mellstrom (JPL, MOXIE Project Manager), Carl Guernsey (JPL, SOXE Contract Technical Manager), Gerald Voecks (JPL, SOXE lead) in support of the Ceramatec role in the MOXIE.

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Abstract No. 62

Development and flight qualification of a solid oxide CO_2 electrolysis stack for the Mars2020 MOXIE project

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Summary. The NASA Mars2020 mission will land a Curiosity class rover on Mars with a set of seven new science instruments.[2] One of these instruments, MOXIE, the Mars Oxygen ISRU (In Situ Resource Utilization) Experiment, will demonstrate oxygen production by solid oxide electrolysis of Mars atmosphere CO_2. Ceramatec has developed and qualified the Solid OXide Electrolysis (SOXE) device for MOXIE.

Abstract. Renewed interest in manned exploration of Mars is turning attention back to the application of solid oxide electrolysis for production of oxygen from CO_2. The Martian atmosphere is 96% CO_2, making it a valuable resource for extraction of oxygen for life support. An even greater oxygen requirement is for ascent vehicle propellant enabling a return to earth. The fundamental operating principles and materials of the Mars ISRU application are no different than for the more common terrestrial hydrogen and synfuel applications. However, the environments the device will be subjected to in reaching Mars, and while operating on the Martian surface, create the need for some unique and highly rigorous qualification testing.

The thermal and mechanical environment requirements imposed on MOXIE are extreme. MOXIE must demonstrate that it can reach Mars intact. This qualification effort includes subjecting the stack and thermal insulation system to multi-axis shock and vibration to simulate the loads of launch, entry, descent and landing. Since the stack will operate with a nominal 1 bar internal pressure against a Mars ambient pressure that varies around 10 mbar, seals are critical. The stack is held in compression to counteract the internal pressure, as well as to secure it within the thermal insulation package, requiring the demonstration of the mechanical load capability of the stack.

The rover is energy limited, and MOXIE will require nearly the full Sol's (Mars day) energy budget for a 2-4 hour operating cycle. It may be weeks between operating cycles while other experiments are being conducted. As a result, the system will be exposed to extremes of cold between operational cycles.

Ceramatec stacks has successfully met operating targets for oxygen production and oxygen purity after undergoing mechanical compression, shock and vibration, cold cycling to as low as -65°C, and through over 20 thermal/operating cycles. The MOXIE stack development and qualification process history will be presented.

Acknowledgment: This material is based on work supported by NASA through JPL's prime contract under JPL subcontract number 1515459. The authors would like to acknowledge the contributions of Michael Hecht (MIT, MOXIE Principal Investigator, PI), Jeff Hoffman (MIT, MOXIE Deputy PI), Jeff Mellstrom (JPL, MOXIE Project Manager), Carl Guernsey (JPL, SOXE Contract Technical Manager), Gerald Voecks (JPL, SOXE lead) in support of the Ceramatec role in the MOXIE.

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[2] http://mars.nasa.gov/mars2020/mission/instruments/

Abstract No. 63

Synthetic methane production from CO_2 methanation: process integration with SOEC electrolyser and reaction kinetics on hydrotalcite-derived catalyst and

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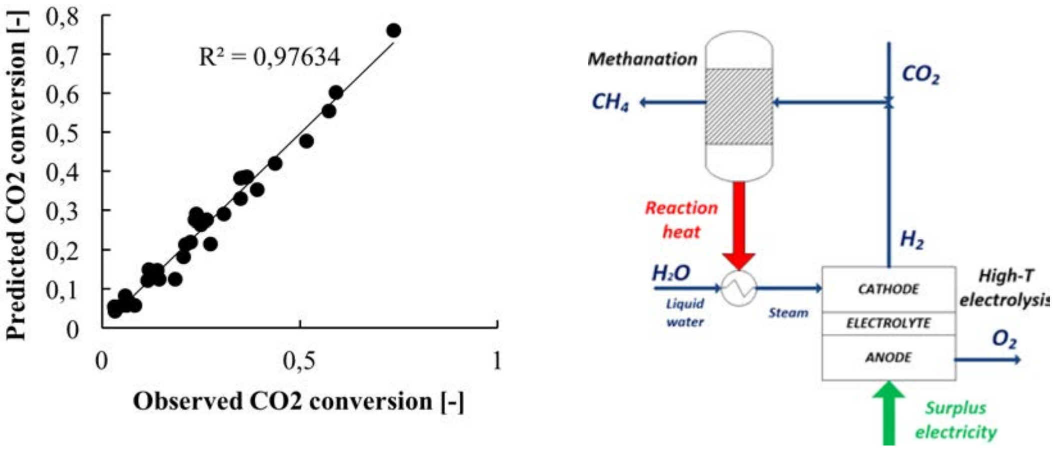
Summary. Recycling waste CO_2 with electrolytic H_2 to produce synthetic fuels is a promising solution to reduce the use of fossil fuels. We present experiments and the reaction kinetics equation for a hydrotalcite-derived Ni catalyst used for CO_2 methanation. The methanation reactors' design and process integration with the SOEC is also provided.

Abstract. This work analyses the energy performance and reactor engineering aspects of the integration of an SOEC with a downstream methanation section, which comprises a series of two inter-condensed reactors. The proposed configuration is able to produce an outlet syn-gas with 95 mol.% of CH_4. One of the main challenges is represented by the reactor thermal management because CO_2 hydrogenation is a strongly exothermic reaction and may lead to a hot spot (and thus to catalyst thermal degradation), especially within the first reactor. To avoid the risk of overheating, part of carbon dioxide bypasses the first reactor to feed directly the second one. The steam produced from the reactor cooling system can be used as a reactant in the solid oxide electrolyser (SOEC). Such strong thermal integration among the methanation section and the SOEC lead to a higher efficiency than obtained through power-to-gas systems based on conventional low-temperature electrolysis. A micro-reactor configuration has been used to evaluate the catalytic activity of a hydrotalcite-derived Ni catalyst for CO_2 methanation. Experiments have carried out at different temperatures (within the range 270-390 °C), H_2/CO_2 feed ratios and flow rates. The impact of the reaction products on the reaction rate has been also evaluated by co-feeding reactants with H_2O and CH_4. Different kinetic models have been evaluated starting from experimental results. Power law, power law with the inhibition influence of adsorbed water or hydroxyl, and finally a Langmuir-Hinshelwood (LH) approach have been compared. The overall process was first modelled by considering the Sabatier reaction. Then, the reverse water-gas shift (RWGS) reaction was also added to the simulation to take into account the presence of CO. A nonlinear regression analysis was performed to evaluate the kinetic parameters. Results show a better fitting of experimental data using the LH and the power law with the inhibition term approaches. The reaction kinetics equation has been then used in 1D plug flow model that simulates the thermal and chemical performance of an evaporating water-cooled multi-tubular methanation reactor.



(Left) Parity plot considering a power law with the hydroxyl inhibition term for both the methanation and the RWGS reactions. (Right) Integrated SOEC methanation plant.

Abstract No. 64

Performance and durability of four 6-cell solid oxide electrolyser stacks for hydrogen and syngas production

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Summary. Performance and durability of four SOE stacks operated with different gas compositions and in different temperatures was analysed in order to estimate their suitability for fuel synthesis with co-electrolysis powered by intermittent electricity supply.

Abstract. The 6-cell stack prototypes were produced by SOLIDPower. The operation temperature range was 700-800 °C and the CO_2 fraction in the cathode inlet 0.00-0.45, representative of cases in which the electrolyser would be combined with a fuel synthesis process and produce hydrocarbons with different hydrogen-to-carbon ratios. Characterization methods were iV curves, load cycling and gas chromatography of the cathode outlet gas. The performance of all stacks was found to depend primarily on the operation temperature and only to a small extent on the inlet gas composition. Gas analysis of the cathode outlet indicated that the measured compositions were in line with the compositions calculated from thermodynamical equilibrium. This indicates that the water gas shift reaction was at equilibrium in the tested range.

Moreover, durability tests were performed at 750 °C in steam electrolysis and co-electrolysis conditions, test hours of all the stacks reaching cumulatively 5800 h. The degradation results are diverse. Several periods of voltage decrease were recorded, the longest being 1500 h steam electrolysis with a voltage decrease of 9 mV/kh. The reason behind the decreasing voltage, the apparent activation, is not clearly understood. Although complex, the results are encouraging and indicate that this type of stack is a suitable candidate for co-electrolysis operation for hydrogen and syngas production.

This research has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement No 621173 and from European Union’s Horizon 2020 Research and Innovation Programme under grant agreement No 731224.

Abstract No. 65 (INVITED)

Effect of catalyst loading on performance and durability of a PEM water electrolysis cell based on an Aquivion® perfluorosulfonic acid (PFSA) membrane

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Summary.

Abstract. One of the main problems that a future energy system must address is the excess of renewable energy which cannot be transferred to the grid when demand is low and thus must be curtailed by the grid operators. This problem can be conveniently addressed by converting the intermittent surplus of electrical energy into hydrogen and storing the energy chemically. Electrolysis of water using renewable energy sources is one of the most promising chemical processes to produce ‘‘green” hydrogen economically with the high purity needed for fuel cell based electric vehicles. Membrane-electrode assemblies (MEAs) designed for polymer electrolyte membrane (PEM) water electrolysis, based on Aquivion®, perfluorosulfonic acid (PFSA) membrane, with various cathode and anode noble metal loadings, were investigated in terms of both performance and durability. Utilizing a nanosized Ir-Ru oxide solid solution anode catalyst and a supported Pt/C cathode catalyst, in combination with the Aquivion® membrane, gave excellent electrolysis performances exceeding 3.2 $A\cdot cm^{-2}$ at 1.8 V terminal cell voltage (~80 % efficiency) at 90 °C in the presence of a total catalyst loading of 1.6 $mg\cdot cm^{-2}$. A very small loss of efficiency, corresponding to 30 mV voltage increase, was recorded at 3 $A\cdot cm^{-2}$ using a total noble metal catalyst loading of less than 0.5 $mg\cdot cm^{-2}$. Steady-state durability tests, carried out for >3000 h at 3 $A\cdot cm^{-2}$, showed excellent stability for the MEA with low noble metal catalyst loading (cell voltage increase ~5-10 µV/h). Therefore operation at very high current densities is possible in the presence of low catalyst loading and a reduction of capital costs may be achieved without compromising significantly the stack durability [1].

Acknowledgment

The research leading to these results has received funding from the European Community’s H2020 Programme. Work performed was supported by the Fuel Cells and Hydrogen Joint Undertaking in the context of project HPEM2GAS G.A. 700008.

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Abstract No. 66

Aging of PEMWE catalyst coated membranes during dynamic operation: Electrochemical and microscopic study

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Summary. The dynamic operation, mimicking fluctuating power, of PEMWE single cell, induced significant structural and morphological alterations of the amorphous Ir hydroxide containing anode catalyst layer without affecting the electrochemical response. The observed effects question the use of low Ir loadings under technical conditions.

Abstract. The environmental impact of fossil fuels usage is pushing the interest towards sustainable energy systems. The increasing share of renewable electricity requires the development of technologies able to store the excessive energy produced during the off-peak demand periods, i.e. during the night or weekend. H_2O electrolysis is a suitable technology with high thermodynamic efficiency for H_2 production and can be used to at least temporarily store the surplus energy in the chemical energy of H_2. Among the known H_2O electrolysis processes, the polymer electrolyte membrane (PEM) H_2O electrolysis is particularly attractive because it can cope with the intermittent and fluctuating nature of renewable electricity. However, the harsh oxidative and corrosive environment (low pH and high electrochemical potential) necessitates the use of expensive corrosion resistant materials in the anode, such as noble metals as catalysts and Ti based current collectors and separator plates. Additionally, the sluggish anode reaction kinetics, even with the currently state-of-the-art Ir based catalysts in terms of both activity and stability, require high loadings increasing significantly the cost, especially in view of the scarcity of Ir in earth's crust. Therefore, the system durability is of essential interest, since extended lifetime can partially compensate for the high cost.

HYDRion catalyst coated membrane (CCM) of circular geometry (63.5 cm^2 active area), consisted of Ir based anode, Pt based cathode and N117 membrane, was placed in commercial Ti based PEMWE single cell (Sylatech). Porous Ti layer (PTL, 1 mm thickness, 80% porosity), made of sintered Ti fibres, in the anode and hydrophobised carbon paper (H2315 I6, Freudenberg, 210 µm thickness) in the cathode were serving as current collectors and diffusion media. Ti grid (Dexter, 1 mm thickness) was used as spacer in the anode instead of flow channels to facilitate the reactants/products distribution. The effect of dynamic operation, consisting of ramp (100 mV/s) / hold (2.5 min and 15 min) between 1.4 and 1.8 V at 60 °C and ambient pressure, applied for ca. 750 h, on the cell performance was examined by in-situ electrochemical diagnostic techniques, such as polarisation simultaneously with impedance measurements and cyclic voltammetry (CV). The microstructural alterations induced by the experimental protocol were identified by post-test microscopic investigations, including scanning and scanning transmission electron microscopies, complemented by electron diffraction and x-ray photoelectron spectroscopies.

The cell performance at technical current densities was heavily dictated by the oxygen evolution reaction (OER) kinetics and high ohmic resistance, with 50 % share at 1 A/cm^2 and 60 °C. It was estimated that ca. 50% of the ohmic resistance can be assigned to the anode catalyst layer (ACL) resistance and the contact resistance between the ACL and Ti PTL, signifying the importance of the catalyst conductivity and the ACL-Ti PTL interface. The cell performance was enhanced during the first 100 h of testing and thereafter was declining with average degradation rate of ca. 30 µV/h at 0.75 A/cm^2. Both performance variations were majorly dictated by the ohmic resistance variation, providing iR free degradation rate lower than 10 µV/h. CV indicated no significant alterations of the apparent electrochemical active surface, contradicting the strong structural and morphological alterations evidenced by post-test analysis. The latter revealed Ir dissolution with formation of a sparse band inside the membrane and close to the membrane-ACL interface with Ir containing particles, Ir mass loss from the back of the ACL and respective concentration at the membrane-ACL interface forming large agglomerates, and formation of rutile type platelets well embedded within the originally present amorphous Ir hydroxide catalyst phase.

Abstract No. 67

Durability of PEMEC MEAs

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One of the main challenges for a more widespread utilisation of PEM electrolysis is related to the present high cost of particular the flow-field plates (machined titanium plates) and the electrodes that are equipped with a high noble metal catalyst loading. The state-of-the-art catalyst cost of the PEMEC MEA is ≈10% of the total stack cost[3]. However, particular the OER catalyst (iridium-oxide) draw in an important R&D effort as iridium defines a limited resource being the rarest element on the earth crust. Consequently will an increasing use of iridium possesses a potential future cost issue. The R&D efforts are related towards novel catalysts e.g. Ir-Ru-oxides and/or lower catalyst loadings. The state-of-the-art PEM electrolysis MEA do possess a durable long lifetime potential (Fig. 1), but this may be altered for low catalyst loaded MEAs. Presented is long-time single cell durability data of PEM electrolysis MEAs equipped with different catalysts and variated catalyst loadings. Microstructural post-mortem characterisation has been performed on selected MEAs. The influence of low catalyst loadings and alternative OER catalysts on the durability is discussed.

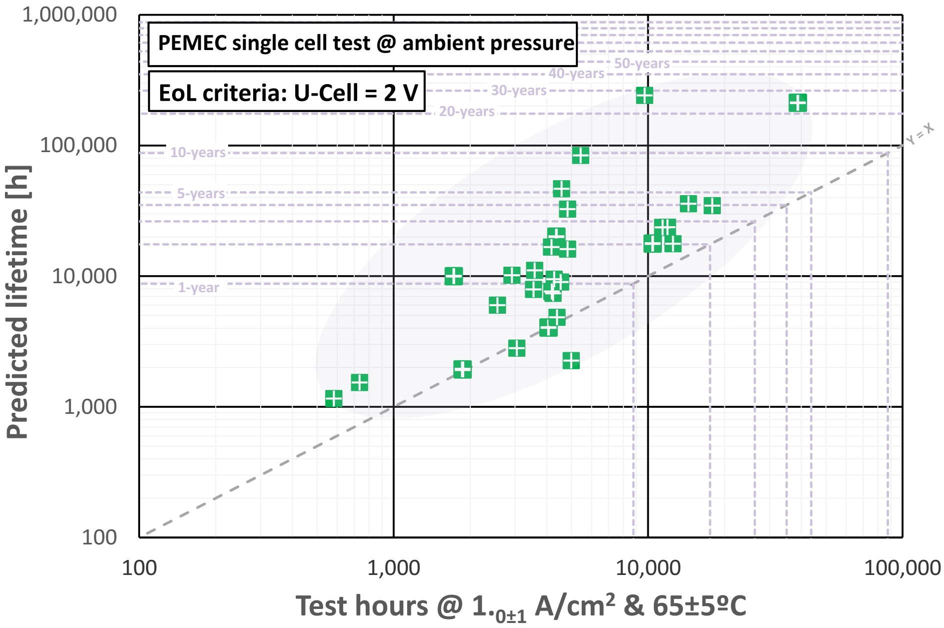

Fig. 1
'Steady state' operational hours versus the calculated lifetime.

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Abstract No. 68

Towards selective test protocols for accelerated in situ degradation of PEM electrolysis cell components

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Summary. Time and cost consuming tests for degradation analysis make the acceleration of these necessary. Currently, such accelerated test protocols are not in existence in the field of electrolysis. Herein, we present the first step towards selective in situ degradation tests of different components of a PEM electrolysis cell.

Abstract. The understanding of degradation effects within polymer electrolyte membrane water electrolysis cells (PEMWE) is an important issue for life time prediction and component development for commercial PEMWE stack manufacturers. Since life-time tests are time and cost consuming, accelerated stress tests (AST) are required to gain the same amount of information within a fraction of time. In a first step, the development of testing procedures for degradation studies of individual components is addressed to be able to distinguish between the influences originating from different parameters during operation. In other words, what is degrading the membrane, the catalyst layers, the titanium components and how. For example, when coupling renewables with a PEM electrolyser, like wind or solar systems, fluctuating power is usual. These fluctuations are under suspicion to degrade the catalyst layer more than the membrane.

In a second step, the acceleration of the underlying processes will be investigated. In this contribution, the work on selective degradation testing protocols will be presented. Different current/voltage profiles were tested in a 25 cm^2 laboratory test cell with Au coated flow channels, commercial membrane electrode assemblies (MEA) and Au reference electrodes for separation of anodic and cathodic contributions to the voltage decay. Electrochemical impedance spectroscopy (EIS) (see Figure 2) and steady-state polarisation curves (see Figure 1) were used for in situ characterisation. Scanning electron microscopy (SEM) and an in-house developed test measurement for interfacial contact resistances (ICR) were employed as ex situ characterisation to investigate membrane thinning and titanium oxide formation.

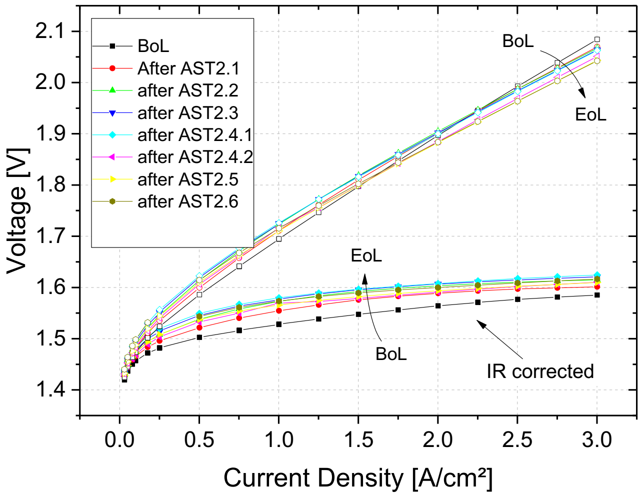

Figure 7: Polarisation curves (+ IR-correction) at Various points in time during the AST

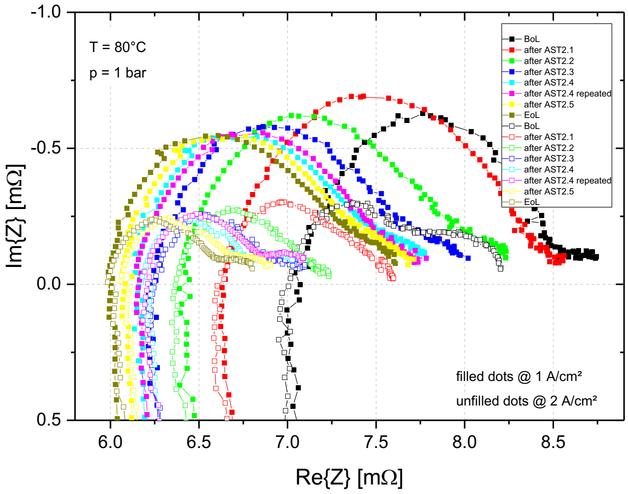

Figure 8: Impedance spectra at 1 A/cm² and 2 A/cm² at various points in time during the AST

Abstract No. 69

Mechanical characterisation and durability of sintered bodies for PEM electrolysis

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Summary. In differential pressure electrolysis, the mechanical durability of current collectors must be ensured. In order to withstand recurring differential pressure, a high plasticity of the titanium body is crucial. It was studied how plasticity can be influenced by varying sintering temperature and by possible contamination of the material.

Abstract. Differential pressure electrolysis offers the potential for increasing the efficiency of compression of hydrogen from electrolysis. Due to the differential pressure acting within the cell, the anode-side current collector is subjected to high stresses. If the mechanical strength of the current collector is not sufficient and thus the component fails, the catalyst-coated membrane (CCM) is no longer stabilized. Thus failure of the sintered body leads to a failure of the CCM and finally to failure of the hole cell. For safety reasons, the mechanical stability of the current collector must be ensured. Current collectors for PEM electrolysis are typically prepared by thermal sintering of titanium powder. These porous titanium transport layers ensure a good electron conductivity and corrosion resistance [1]. The mechanical properties of pure titanium are significantly influenced by even a small amount of impurities. In particular, the amount of oxygen, nitrogen and carbon led to brittleness and lowered ductility [2].

The mechanical and dynamic mechanical behaviour of sintered titanium sheets have been investigated via stress-strain curves and periodic loads in test cell, respectively. Experiments were carried out with samples of powders which differ in shape and in their chemical composition. Samples with sintering temperatures in the range of 800-1200 °C were available for each powder. Samples made of spherical powder were in a porosity range of 33-10 % and samples of shapeless powder in a range of 55-10 %.

In the stress-strain diagrams, it was found that higher sintering temperature and lower porosity were associated with higher tensile strength and higher deformability. It was noticeable that samples from spherical powders had a considerable increase in the ductility from a sintering temperature of 1000 °C onwards, whereas samples from shapeless powders showed no great increase in ductility at elevated sintering temperature. The materials exhibiting the greatest plastic deformability were able to withstand the greatest differential pressure in the test cell. Also it has been shown in the durability test that samples with a low sintering temperature cannot guarantee sufficient fatigue strength.

None of the samples with porosity above 25 % showed sufficient mechanical stability for a flow field width of 4 mm. A high porosity as well as high static and dynamic strength for a flow field width of 3 mm could only be demonstrated by one of the samples tested here. However, there is a risk that impurities, which enter during the sintering process, lead to embrittlement and thus to the failure of the current collector.

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Abstract No. 70

Complex of cobalt and molybdenum carbide nanoparticles for efficient oxygen evolution reaction in alkaline electrolytes

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Summary. We report a complex of Co and Mo_2C nanoparticles as an efficient electrocatalyst for alkaline OER. Chemical coupling of Co with Mo_2C leads to increase in OH^- affinity and oxygen binding energy on Co surface. These changes significantly diminish kinetic barrier for OER on Co surface, resulting in high OER activity in alkaline electrolytes.

Abstract. Increasing demand for clean energy have triggered researches on alternative energy sources and devices to reduce use of fossil fuel. Hydrogen has been considered as one of the most promising energy source for future due to its high energy density and no air pollutant emission. Splitting water into hydrogen and oxygen is an environmentally friendly method for producing hydrogen gas. This technology can store excess electric energy in the form of chemical bond of hydrogen, which can resolve an issue about surplus electric power of present renewable energy systems caused by irregular energy source such as airflow and sunlight.

Water electrolysis reaction is divided into two half reactions; hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). High overpotentials of both HER and OER are the most significant problems to hamper reaction rate and overall efficiency of water electrolysis, especially OER has much higher overpotential than HER. Therefore, recently major efforts have been devoted to exploring active catalysts for the OER in water electrolysis cell.

Herein, we report novel catalysts, which composed of Co and molybdenum carbide (Mo_2C) nanoparticles (Co-Mo_2C), as efficient OER catalysts for alkaline water electrolysis Mo_2C has very similar electronic structure with platinum (Pt) group metal. Therefore, it can be expected that Co-Mo_2C can have high OER activity in alkaline electrolytes by chemical coupling effect of two materials (Co, Mo_2C) at their interfaces. We synthesized Co-Mo_2C by using a simple solution based process. g-C_3N_4 was used as a carbon source for carburizing reaction of Mo. The synthesized Co-Mo_2C exhibited enhanced activity compared with Co and RuO_2 catalysts in alkaline electrolytes (0.1 and 1 M KOH). From, XPS and DFT calculation results, high OER activity is ascribed to increase in OH^- affinity and oxygen binding energy on Co surface by chemical coupling of Co and Mo_2C. Moreover, we tried to additionally modify the electronic structure of Co-Mo_2C by incorporating other transition metals into Co, such as iron (Fe), manganese (Mn), nickel (Ni). Fe-doped Co-Mo_2C exhibited higher activity for OER compared than Co-Mo_2C and ruthenium dioxide (RuO2) catalysts in alkaline media (0.1 and 1 M KOH). But, other transition metal-doped Co-Mo_2C have lower OER activity than undoped materials.

Abstract No. 71

Gold-Metal Oxide Core-Shell Nanoparticles As Electrocatalysts for Water Oxidation

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Summary. We present the synthesis, characterisation and electrochemical performance of Au-core metal oxide-shell (Au@M_xO_y where M=Ni, Co, Fe, and CoFe) catalysts with enhanced activity for the oxygen evolution reaction in alkaline electrolyte.

Abstract. Water oxidation, or the oxygen evolution reaction (OER), is a key half reaction of many electrochemical processes for sustainable energy conversion and storage technologies such as water splitting, reduction of carbon dioxide and metal-air batteries. Renewable energy can be converted into high purity hydrogen by electrochemical water splitting. The main problem of water electrolysers is the slow kinetics of the OER. Although transition metal oxides have shown high OER activity and stability in alkaline media [1], high overpotentials are still required. Au supports can enhance the OER activity for many transition metal oxides in alkaline media [2,3].

Herein, we present the chemical synthesis, characterisation and performance of Au-core metal oxide-shell (Au@M_xO_y where M=Ni, Co, Fe, and CoFe) catalysts for the OER. Particle morphology and composition were analysed by transmission electron microscopy (TEM), scanning TEM energy dispersive spectroscopy (STEM-EDS), scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS). Electrochemical activity and stability were evaluated in a three electrode rotating disk arrangement in Fe-free conditions for non-Fe based catalysts. All Au@M_xO_y core-shell nanoparticles demonstrated enhanced activity with Au [4]. Our results demonstrate that the Au-core transition metal alloy oxide-shell structure is a promising strategy to achieve high performance OER catalysts.

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Abstract No. 72

Modified carbon nanomaterials as highly active electrocatalysts for water-splitting

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Summary. Herein, the process of synthesis of carbon nanotubes (CNTs) is modified to grow carbon-encapsulated iron nanoparticles as efficient catalysts for hydrogen evolution reaction (HER) in acidic media. Then, a simple electrochemical modification is applied to make these catalyst materials active for oxygen evolution reaction (OER) in alkaline media.

Abstract.

Electrochemical water splitting can be divided into two half reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). For HER, efficient and stable non-precious catalysts are required. Furthermore, the efficiency of water electrolysis is severely limited by the large anodic overpotential and sluggish reaction rate of OER. Therefore, the development of efficient electrocatalysts for OER has also drawn much attention.

For HER, single-shell carbon-encapsulated iron nanoparticles (SCEINs) decorated on single-walled carbon nanotubes (SWNTs) have shown ultra-high activity and stability for HER in acidic media, comparable to that of platinum based electrocatalysts (Figure 1a) [1]. The SCEIN/SWNT sample is synthesized by a novel fast and low cost aerosol chemical vapor deposition method in a one-step synthesis [1]. In SCEINs, the single carbon layer does not prevent desired access of the reactants to the vicinity of the iron nanoparticle but protects the active metallic core from oxidation and dissolution in acidic media.

For OER, as a critical reaction in electrochemical water splitting and rechargeable metal–air batteries, the structure of carbon-encapsulated iron nanoparticles (CEINs) decorated on carbon nanotubes (CNTs) is changed to high quality crystalline maghemite (γ-Fe_2O_3) nanoparticles decorated on CNTs (γ-Fe_2O_3/CNT) through a simple electrochemical method (Figure 1b) [2]. The γ-Fe_2O_3/CNT sample is reported as a highly active and durable catalytic material for OER in alkaline media [2].

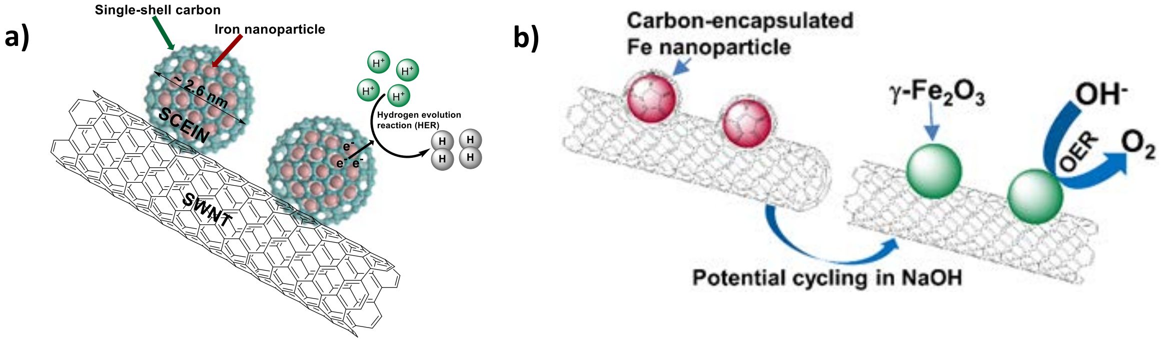

Figure 1. a, Schematic representation of the SCEIN/SWNT sample and HER on the SCEINs. **b,** Schematic representation for transformation of CEIN/CNT to γ-Fe_2O_3/CNT as an active electrocatalyst for OER .

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Abstract No. 101

Influence of geometry and kinetic of hydrogen and oxygen evolution on the current density distribution and electrode potentials in bipolar electrolyzers.

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Summary. The secondary current distribution in an electrolizer with bipolar electrodes was theoretically determined by means of an own algorithm that allows performing the potential distribution from a fixed applied current. Analysis of current and potential distribution were performed taking into account kinetics of oxygen and hydrogen and cell geometry from industrial conditions. Mains figures of merit were evaluated.

Abstract. The bipolar electrolyzer consist of a series of identical cells. Each cell is in the form of a vertical channel of a circular or rectangular cross section. The major attractions of the bipolar reactor are easy construction, saving in space that a compact design allows, and the lower cost of the electrical equipment. The main disadvantage of the reactor is the presence of parasitic electrical currents (bypass) at the lower and upper parts of the electrode stack. This results in an electrical efficiency loss, a non-uniform potential and current distribution and consequently, an increase in possible corrosion rates of electrodes. Bypass currents can be reduced by increasing the electrical resistance of the channels and manifold, but at the same time, increasing the overall electrolytic power cost due to increasing cell resistance.

In the past, many authors have investigated in a simplified way current distribution in bipolar reactors using electrical analogy [1] or by solving Laplace equation and assuming anodic and cathodic overpotentials [2] or imposing a fixed potential (independent of kinetics) in bipolar electrodes [3]. From experimental data it was shown that simplified models are not accurate due to non-linear cell current-voltages results are obtained when conductivity of electrolyte is high enough, as in alkaline electrolyzers (80 °C and 30 % KOH), and it is due to the fact that the electric field inside the reactor is not sufficient high to polarize completely bipolar electrodes [4].

The objective of this communication is to conduct a simulation study of the electrochemical processes involve in this kind of systems from real kinetic data, to gain insights into the presence of bypass currents existing in bipolar alkaline electrolysers, and to provide suggestions that aid in design considerations. Kinetics parameter were obtained for Nickel and Nickel Raney at 25 and 80 °C in KOH 6 M as supporting electrolyte using Ag/AgCl as reference electrode.

In the mathematical model some assumptions are made: The metal phase in the electrodes is isopotential; the effect of gases generated at the electrodes on the electrolyte resistivity can be disregarded. The effect of kinetic parameters on potential and current distribution of terminal and bipolar electrodes were analysed, also molar energy consumption and overall electrolytic power cost were evaluated for different geometries and, as consequence, bypass currents. Showing that when leakage current increase, also cell potential decreases. Helping to reach, In the case of catalyst resistant to corrosion, a lower overall electrolytic power cost and in some cases a slightly lower molar energy consumption.

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Abstract No. 102

Ion-solvating polymer electrolytes for alkaline water electrolysis

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Summary. Polybenzimidazole membranes imbibed with aqueous KOH show excellent performance in alkaline water electrolysis. This contribution describes the fundamental physicochemical properties of such membranes and extends to a discussion about stability concerns and degradation mitigation strategies.

Abstract. Poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole) (*m*-PBI) belongs to a large family of polymers with benzimidazole groups as a part of the polymer repeat unit. It is the most thoroughly studied polybenzimidazole derivative and is recognized for its excellent thermo-mechanical properties, chemical stability and good film-forming characteristics. It is highly hydrophilic and due to its amphoteric nature it strongly interacts with and absorbs aqueous acids and bases, such as potassium hydroxide (Figure 1).

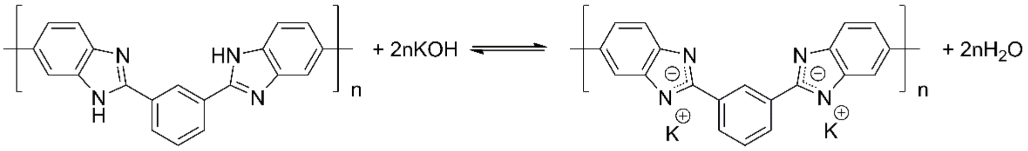

Figure 1 The chemical structure of *m*-PBI in the neutral pristine form (left) and in the potassium poly(benzimidazolide) (right).

When equilibrated in 15-25 wt% aqueous KOH it forms a ternary *m*-PBI/KOH/H_2O electrolyte system with a total polymer weight fraction of less than half the total weight.[1] The absorbed aqueous KOH supports remarkably high ion conductivity, which makes it suitable as electrolyte and electrode separator in alkaline water electrolyzers.[2, 3] By further development of electrodes and cells, such systems are now approaching performances that are comparable with that of the proton exchange membrane electrolyzers.[4]

This contribution describes the fundamental physicochemical properties of polybenzimidazole-based ion-solvating polymer electrolytes, which strongly depend on the concentration of the surrounding solution. It extends to a discussion about long-term stability concerns in aqueous KOH[5] as well as under operational conditions[3] and briefly presents strategies for mitigating degradation.[6]

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Abstract No. 103

Nickel/Tungsten-Carbide Composite Catalysts for Oxygen Evolution in Alkaline Water Electrolysis

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Summary.

Nickel/Tungsten-carbide (Ni/WC) composite catalysts for oxygen evolution reaction were synthesized using WC as a parent material, and Ni for an active catalyst material. The OER activity of the Ni/WC (η @ 10 mA/cm^2) showed only 324 mV, and this performance was mainly attributed to its property change originated from the bimetallic interface.

Abstract.

Hydrogen, produced by electrolysis, is one of the most promising systems to store electricity coming from renewables and to solve its intermittency. Due to the increase of global electricity share from renewable energy sources, large-scale storage systems are required. Alkaline electrolysis can be a suitable solution for the large-scale energy storage system. However, high overpotential and slow kinetics, particularly of the oxygen evolution reaction (OER), still limit the efficiency of the system. To enhance the efficiency of alkaline electrolysis cells, catalysts with high electrocatalytic activity for OER should be developed.

One suggested method to increase the catalytic activity of a catalyst is to make bimetallic interface, and modify properties of materials. In this study, nickel/tungsten-carbide (Ni/WC) composite with large bimetallic interface was synthesized to increase the OER catalytic activity. Tungsten carbide was used as a host material, and nickel was chosen as a metal layer for an active material. Ni/WC showed superior catalytic activity than Ni nanoparticle and WC (Figure 1). The overpotential of Ni/WC for OER at 10 mA/cm^2 was only 324 mV, and it was lower OER activity than that of commercial Ir/C catalyst. In addition, Ni/WC showed excellent stability in 1 M KOH solution (Figure 2).

To investigate the origin of the outstanding performance of Ni/WC, various techniques such as TEM, XPS, and electrochemical experiments were employed, and this performance was probably due to a change in the nickel characteristics resulting from the bimetallic interface.

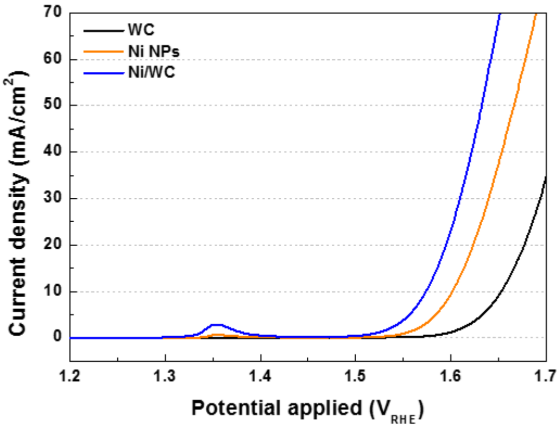

Figure 1. OER activity of WC, Ni, and Ni/WC catalysts in Ar-saturated 1 M KOH solution

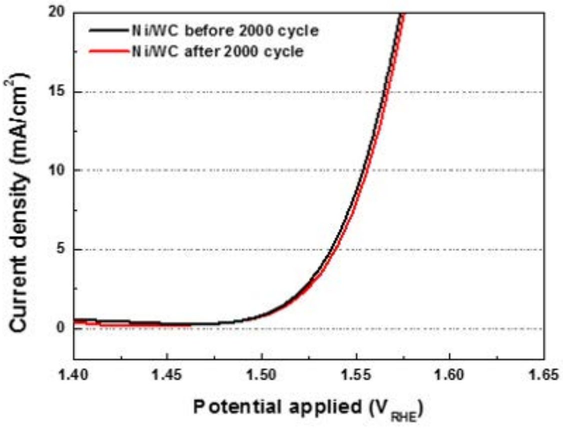

Figure 2. Durability test for Ni/WC in Ar-saturated 1 M KOH solution

Abstract No. 104

Bubble characterization in an electrolysis cell using a flow visualization system

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Summary. The velocity and size of individual bubbles inside an alkaline water electrolysis cell have been studied using a flow visualization system. The bubbles diameter has been measured at different currents, temperatures and flow rates to determine the influence of operating conditions. The results were adjusted to different statistical distributions.

Abstract. Figure 1a shows the experimental alkaline water electrolysis set-up used in this study. As can be appreciated in Figure 1c, the electrolysis cells (ELECTROCELL, Micro Flow Cell) have been modified to include a 10 mm transparent window (PMMA frame) between electrodes and diaphragm. A PIV (*Particle Image Velocimetry*) system, provided by DANTEC Dynamics, consisting of a Nd:YAG laser and a CMOS camera (1000 fps) allows the flow visualization and the characterization of the gas bubbles generated during electrolysis inside the cell (Figure 1b). Direct visualization of bubbles within a transparent container has been used previously by others authors [1, 2].

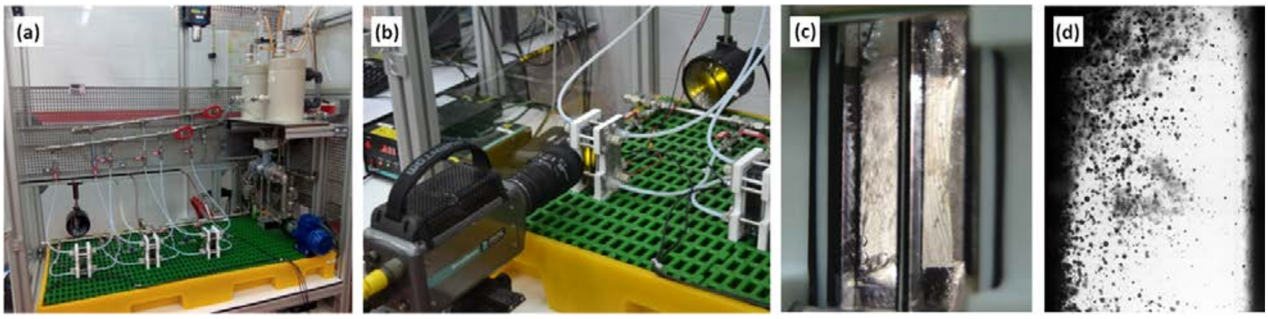

Figure 1. Experimental set-up: (a) cell electrolysis test bench; (b) PIV system; (c) transparent cell; (d) gas bubbles inside a cell

The hydrogen bubble diameter has been determined by capturing 200 images in 196 ms (Figure 1d) for each of the current densities investigated (5-300 mA/cm^2). However, there is a density current value (depending on experimental conditions) above which, the cell is filled with gas and the flow visualization system cannot clearly distinguish individual bubbles. This procedure has been repeated at different flow rates (natural convection-2.8 l/min) and temperatures (30-70 °C) to determine the influence of experimental conditions on particle size distribution. Also, the polarization curve and the Faraday efficiency were measured and compared in all tests [3].

The bubbles size data have been adjusted to different statistical distributions (Figure 2a). Later, the Kolmogorov-Smirnov test was used to determine the best statistical distribution in this study. According to the experimental data, the mean bubble diameter increases with current (Figure 2b) and it decreases with higher flow rates (Figure 2c).

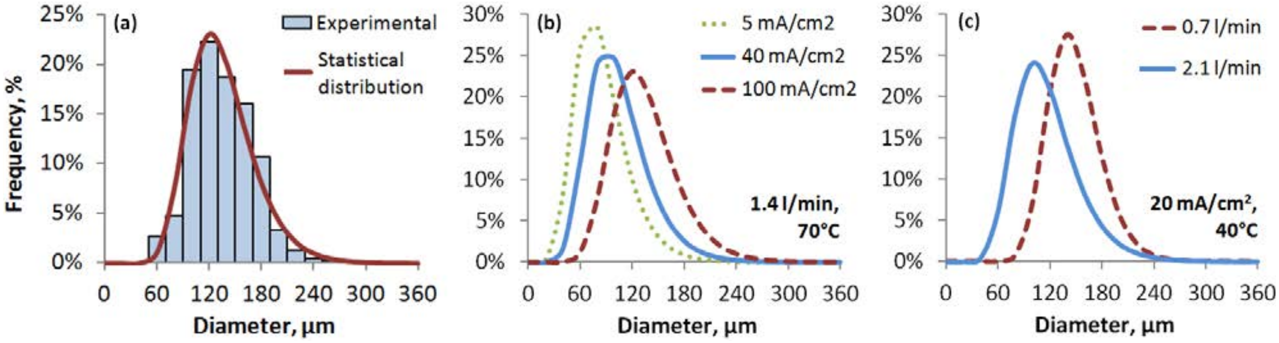

Figure 2. Bubble diameter: (a) experimental and statistical distribution; (b) at different current densities; (c) at different flow rates

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Abstract No. 105

A Facile Synthesis of Nano-sized IrO_2 and RuO_2 Catalysts for the Oxygen Evolution Reaction in Alkaline Medium

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Summary. A facile wet-chemical method for synthesizing IrO_2 and RuO_2 nanoparticles (NPs) for the oxygen evolution reaction in alkaline medium.

Abstract.

The efficiency of the water electrolysis process is mainly restricted by the sluggish kinetics of the oxygen evolution reaction (OER). Many catalysts have been developed to improve the kinetics of the OER and therefore the overall efficiency of the water electrolysis. Among of them, IrO_2 and RuO_2 are two of the most effective catalysts for OER. Due to the high cost and low elemental abundance, IrO_2 and RuO_2 in form of nanoparticles are often used to optimize the mass efficiency. However, finding an effective synthetic method to produce small size IrO_2 and RuO_2 NPs still remains challenging. In this report, a facile wet-chemical method for synthesizing IrO_2 and RuO_2 nanoparticles (NPs) for the OER was introduced. The nanoparticles were synthesized by reducing metal chlorides in ethylene glycol in the presence of polyvinylpyrrolidone, followed by annealing in air at different temperatures to control the particle size. The activity of IrO_2 and RuO_2 NPs supported on carbon black (acetylene carbon) was investigated by cyclic voltammetry (CV) in alkaline (0.1 M KOH) electrolyte. As-synthesized IrO_2 and RuO_2 NPs indicated high catalytic activity for the OER. The IrO_2 NPs exhibited a specific activity of up to 3.5 (± 1.6) $\mu A/cm^2_{oxide}$ at 1.53 V (vs. RHE), while the RuO_2 NPs achieved a value of 124.2 (± 8) $\mu A/cm^2_{oxide}$. For mass activity, RuO_2 NPs showed a value up to 102.6 (±10.5) A/g_{oxide} at 1.53 V (vs. RHE), representing the highest value reported in the literature to date. Moreover, a correlation between specific activity and crystal orientation of IrO_2 and RuO_2 NPs was also observed, which can be considered as one of the main governing factors for the OER activity.

Abstract No. 106

DFT studies of doped Cobalt and Nickel Oxyhydroxide Catalysts for Oxygen Evolution

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Summary. Using density functional theory we study the complex interplay between catalyst structure, activity, electronic conductivity and stability for doped and un-doped cobalt and nickel oxyhydroxide catalysts for the oxygen evolution reaction.

Abstract. We use Density Functional Theory to study Nickel and Cobalt oxyhydroxides as catalysts for the oxygen evolution reaction (OER) in neutral and alkaline media. We investigate the activity of model oxide edge and terrace terminations on bulk and 2D nano sheets catalysts.

We find the OER takes place on oxygen lattice sites through the $^*OH$, $^*O$, $^*OOH$, and $^*O_{vac}$ intermediates, and that while the activity of cobalt oxyhydroxides increases substantially from bulk structures to nanosheets, the activity of nickel oxyhydroxides is rather insensitive to the structure.

We investigate the changes in catalyst activity and electronic conductivity induced by 25 different dopants stable at alkaline conditions. From our analysis, we identify Cr and Fe doped cobalt oxyhydroxide, and V, Fe, Ru, Ir and Rh doped nickel oxyhydroxide, as the best catalysts, with Rh doped Ni ox-hys exhibiting the highest activity. The electronic conductance of the doped oxyhydroxides changes as a function of the dopant atom's valence, which is a function of the applied potential; e.g. Fe^{4+} is a conductive species compared to non-conductive Fe^{3+}.

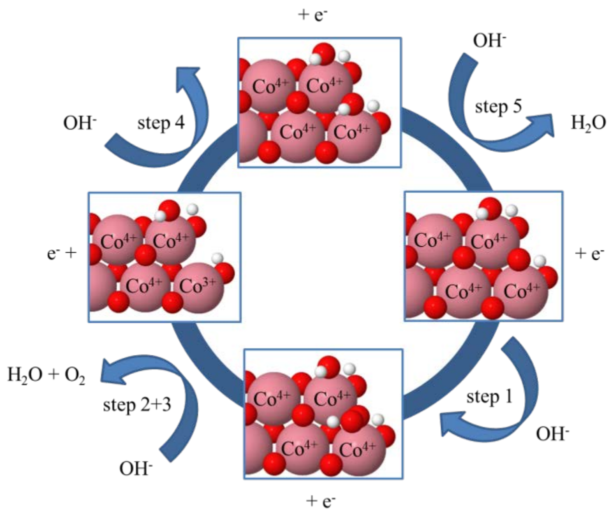

Figure: OER intermediates on a cobalt oxyhydroxide nanosheet.

This work was supported by the Horizon 2020 framework, grant number 646186.

Abstract No. 107

A 3-D micro porous Co-Fe-P catalyst for oxygen and hydrogen evolution reactions in alkaline water electrolysis

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Summary. A 3-D micro porous Co-Fe-P foam catalyst was fabricated by electrodeposition method on a Cu foam substrate. Overpotential of the Co-Fe-P foam catalyst at 10 mA/cm^2 was 294 mV for OER and 73 mV for HER in the 1 M KOH, which was superior to the noble metal catalysts.

Abstract. Recently, hydrogen energy has been attracting attention owing to depletion of fossil fuels and global warming. Hydrogen can be produced by water electrolysis without consumption of fossil fuels. However, high overpotential is required for decomposing water in the actual water electrolysis reaction and efficiency of the electrolysis is around 60 %. Therefore, researches on electrochemical catalysts have been carried out to reduce the overpotential of the electrolysis reactions. Transition metal phosphide catalysts have been studied as catalysts for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) in an alkaline environment. In the previous studies, most of the catalysts were synthesized via multi-step processes invoking high cost, time-consumption and use of toxic chemical problems. In this study, a 3-D micro porous Co-Fe-P foam catalyst was fabricated by optimized Co-Fe-P electrodeposition on a Cu foam structure. The Co-Fe-P foam with thickness of about 15 μm was electrodeposited without clogging the pore. Overpotential of the Co-Fe-P foam catalyst at 10 mA/cm^2 was 294 mV for OER and 73 mV for HER in the 1 M KOH. In addition, toward HER, the Co-Fe-P foam catalyst exhibited overpotential of 70 mV in the 0.5 M H_2SO_4. These results demonstrate that the Co-Fe-P foam catalyst had excellent HER and OER activity, superior to the noble metal catalysts. The improved performance of Co-Fe-P foam was attributed to low charge transfer resistance and high electrochemical active surface area (ECSA) caused by highly porous foam structure.

Abstract No. 108

Process intensification of alkaline water electrolysis by using 3-D electrodes

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Summary. In this presentation we will show how 3D electrodes and a forced electrolyte flow will allow to achieve the necessary process intensification (P.I.) for alkaline water electrolysis. The second part will show how this technology can be scaled up in a pilot plant set-up of representative industrial scale.

Abstract. Hydrogen is a promising and well-accepted energy vector to store electricity produced by intermittent sources, such as solar panels and wind turbines. In order to be cost effective, the water electrolysis needs to be intensified (higher production in smaller units) and scaled up to the match the power of electricity sources

The current work focuses on a simple way to increase the efficiency of water electrolysis by the use of 3-D electrodes and forced electrolyte flow. Such macro-porous electrodes allow to reduce the cathodic overpotential compared to state of the art 2-D plate electrodes. Under natural convection the produced gas bubbles tend to block the 3-D structure reducing its benefit. Thanks to the forced flow, the gas bubbles are forced out of the 3-D electrodes.

A typical result is shown in Figure 1. According to the electrokinetic Butler-Volmer equation, a higher current density requires a higher overpotential. Therefore, since for the same applied current the current density decreases with increasing specific electrode area, the required (over-)potential to drive the macroscopic current will be lower for the 3-D electrode compared to a 2-D electrode. For this reason the use of 3-D electrodes will reduce the cell voltage for a given applied current as it can be seen in Figure 1.

In Figure 2, we can see the influence of the catholyte flow rate on the cell voltage. At lower flow rate (v1) the produced hydrogen bubbles tend to block the 3-D structure of the electrode, reducing the surface area in contact with the electrolyte. Increasing the flow rate (v3 to v9) will force de bubbles out of the electrode allowing to take full advantage of their high surface area.

Figures 1 and 2 were obtained in a benchtop laboratory experiment. Future work will focus on implementation of these results in a pilot plant setup. The latter has a size representative for an industrial production equipment. Our presentation will show the results of this scale-up.

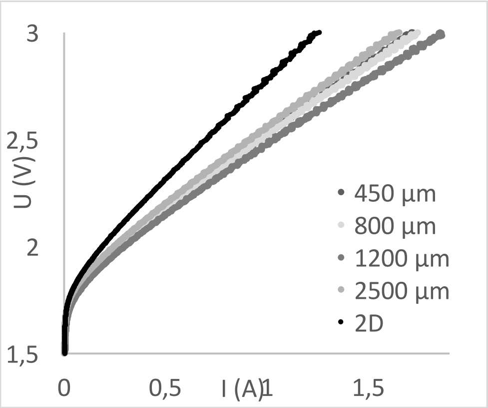

Figure 9: Cell voltage vs the applied current for a 2-D electrode and various 3-D electrodes of different pore size.

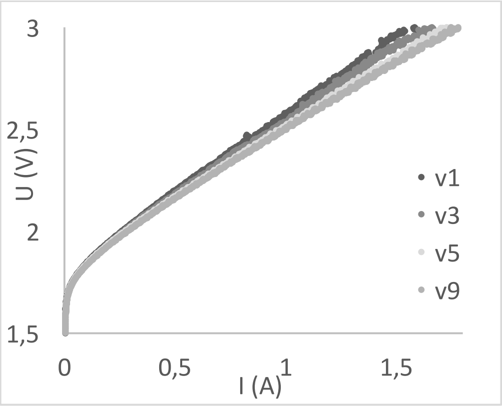

Figure 10: Influence of the catholyte flow rate on the cell voltage for a 3-D electrode of 800 µm pore size.

Abstract No. 109

Don Quichote: Demonstration of How to Produce Hydrogen Using Wind Energy

G. Tagliabue*, A. Essam Aly* , W. van der Laak** - J. Vaes***
*FAST – Federazione Associazioni Scientifiche e Tecniche, Milano
** WaterstofNet
*** Hydrogenics
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Summary. The Don Quichote project, an EU-funded demonstration project, is proving the commercial viability of an integrated hydrogen storage system linked to a refuelling facility, directly connecting intermittent renewable electricity to transport applications.

With a complete hydrogen-based energy system established at a commercial site near Brussels, the Don Quichote team is using electricity from solar panels and a wind turbine to generate hydrogen through electrolysis that is then used for back-up power supply and to refuel fuel cell-powered forklift trucks and other vehicles. The system proved to be a success – both in terms of efficiency and costs.

Index Terms – hydrogen, fuel cell technology, hydrogen storage, renewable energy

Abstract. Under the co-ordination of Hydrogenics Europe, the participants in the project are Hydrogen Efficiency Technologies, WaterstofNet vzw, Establishment Franz Colruyt NV, TUV Rheinland Industrie Service GmbH, JRC-Joint Research Centre-European Commission, PE International AG, Icelandic New Energy Ltd and FAST.

Don Quichote is co-financed by the FCH JU (July 2012-June 2017) and want to demonstrate the technical and economic feasibility of hydrogen storage for electricity from renewable energy.

Hydrogen storage plays an important role because it allows the achievement of European carbon reduction. This project results in much more efficiency, but the complexity and the costs of these solutions have prevented large-scale demonstrations.

II. OBJECTIVES AND CONTENTS

This project brings innovations and demonstrations as:

- Extensive testing of the existing system, focused on dynamic behavior, efficiencies, and availability
- Doubling the hydrogen capacity by adding a very efficient and dynamic PEM-electrolyser (storage 130 kg/day)
- Developing, testing, demonstration and validation of direct coupling between wind turbine (1, 5 MW) and solar panels (1050 kW) and the electrolyser technology

The demonstrations programs consist of three phases, everyone is long twelve months (8000 hours per phase), in total 24000 hours.

- Phase 1: Adaptation of existing hydrogen fuel system (electrolyser, compressor, storage, fueling fork lifts)
- Phase 2: Research, additional storage and a fuel cell system, the latest for active balancing the grid
- Phase 3: Research, development and build of a new system for efficient, compact, modular compression and expansion of hydrogen.

Abstract No. 110

Designing Megawatt size PEM water electrolysers

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Summary. The EU-funded project MEGASTACK (FCHJU) aims at reducing the cost of megawatt size PEM electrolysers by designing and producing large area megawatt sized PEM water electrolysers. However, in order to achieve maximum performance and long lifetime, it is important to have a clear understanding of the processes occurring within each cell in a stack and to translate this understanding into tools that can aid in cell and stack design. As part of the MEGASTACK project, significant effort has been made in the development of mathematical models for different scales. This paper presents the current status of the efforts within the MEGASTACK project, and in particular, the efforts made in developing a two phase flow models for investigation of the liquid and gas transport in the anode flow field of a large scale PEM electrolysis cell.

Abstract.

The two-phase flow model is based on the volume of fluid (VOF) model in ANSYS/Fluent 16.2 and implements a sub-grid scale models for water electrolysis as a set of user-defined functions. These sub-grid scale models include, gas nucleation, gas-liquid mass transfer and bubble coalescence and breakup phenomena on sub-grid length scales. Experiments using a transparent cell in combination with a high-speed digital camera as well as numerical image processing was used to quantify temporal and spatial gas distribution and flow velocities.

The experimental results are compared to the two-phase flow model results and the validity and implications of the model are discussed. It is clear from both the modelling work and experimental results, that inlet and outlet manifolds, as well as the flow resulting from specific choices for current collector greatly impacts the water distribution of the electrolyser stack and therefore also on the gas distribution within the cell.

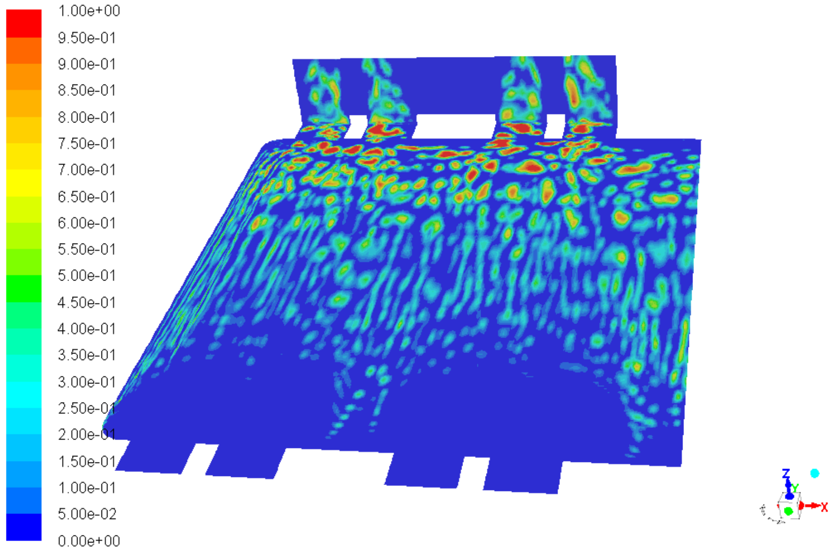

Fig 1. Two-phase flow simulation showing the Oxygen volume fraction of a large area (1000 cm^2) water electrolyser at 1.5 A cm^{-2}.

Abstract No. 111

From Polyelectrolytes to Robust, Highly Proton Conducting Hydrocarbon Membranes for PEM Fuel Cell and PEM Electrolysis Applications

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Abstract. Here, we present a family of membranes making use of the amazing properties of highly sulfonated poly (phenylene sulfone)s as their key constituent. It is the particular electronic structure of this polyelectrolyte and its high density of ionic groups which leads to a combination of high chemical stability [1,2], superior proton conductivity [3-5] and low electroosmotic water drag [3]. Since pure sulfonated poly (phenylene sulfone)s show salt-like behaviour, i.e. brittleness in the dry state and exaggerated swelling or even dissolution in water [2-5], we have used these polyelectrolytes as constituents of polymer blends for forming robust membranes.[6,7] These membranes combine the advantageous properties of pure poly (phenylene sulfone)s with mechanical robustness needed for their application in PEM fuel cells and PEM electrolyzers. As compared to PFSA membranes (e.g. Nafion), they may be considered to be high-T membranes with higher activation enthalpy for all transport coefficients, low gas-crossover even at high temperature and mechanical properties which are almost independent of temperature (T < 180°C).

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Abstract No. 112

Investigation on porous transport layers for PEM electrolysis

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Summary: This work investigates porous transport layers using in- and ex-situ measurements techniques to understand mass transport limitation. The influence of permeability is studied in cell designs with and without flow field. A new quantity, namely the gas transportability is established, which corresponds to mass transport limitation.

Abstract:

Porous transport layer (PTL) plays an essential role in PEM electrolysis cells to transport gas and water and electrical current. The mass transport limitation is observed at high current densities in PEM electrolysis cell [1], which has given comparatively less concern in literature to date. To analyse the phenomena of mass transport limitation, we have started to build up a fundamental understanding by comprehensive ex-situ and in-situ characterisation. To study pore size distribution and porosity mercury intrusion porosimetry is used. Capillary flow porometry (CFP) is used to investigate through-plane gas permeability and pore size and permeatry is used to determine in-plane absolute water and gas permeability. Besides these standard methods we used the CFP to developed a new method to investigate capillary pressure versus liquid saturation relation and to get access to contact angle inside PTL structures. In-situ measurements were carried out in a special designed 25 cm² electrolysis test cell. **Error! Reference source not found.** shows the methodology used for the investigation. Results of polarisation curves in Figure 12 are compared against results of ex-situ characterisation. It is found that for cell designs without flow field the in-plane permeability plays a crucial role regarding mass transport limitation. A new quantity is established, which is name gas transportability, which explains the ability of PTL to transport gas from catalyst layer to the flow channel at a given current density. An increase in gas transportability of wetted PTL reduces voltage loss due to mass transport limitation in the polarization curve. Using the proposed technique, the applicability of any PTL can be quantified for PEM electrolysis cells with flow field.

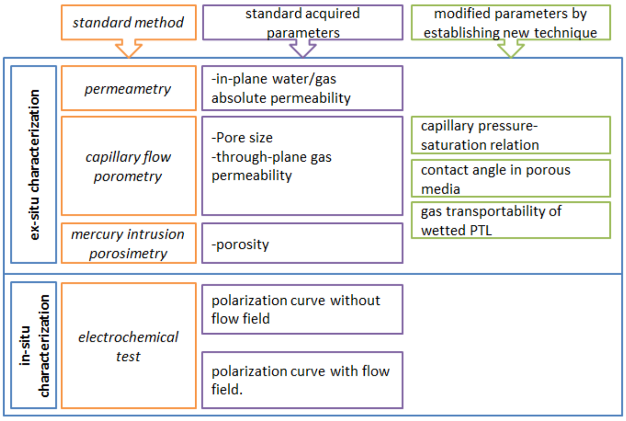

Figure 11: Approached methodology

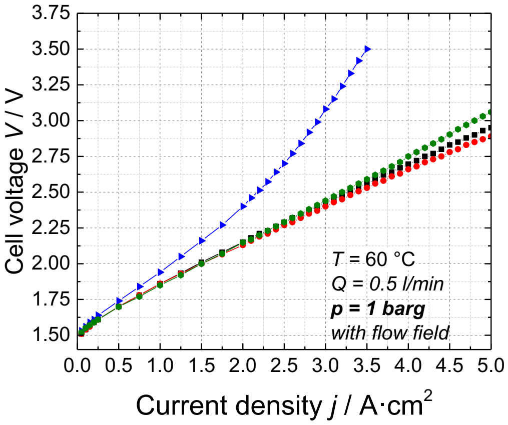

Figure 12: Polarization curves without flow field for different porous transport layers.

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Abstract No. 113

Accelerated stress tests for efficient degradation studies on iridium-based mixed metal oxide catalysts for PEM-electrolysis

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Summary.

Recently proposed accelerated stress tests (ASTs) are applied to gain new insight into factors governing catalyst stability during electrochemical water oxidation.

Abstract.

Due to the intermittent nature of renewable energies, current endeavors in sustainable energy are strongly dependent on reliable energy storage solutions.[1] Storing energy in the chemical bonds of molecular hydrogen produced from (photo)-electrochemical water splitting has proven to be one of the promising strategies to counteract this drawback.[2] While several water splitting technologies (liquid or solid electrolyte, pressurized, low and high temperature, etc.) have emerged, and whole catalyst families have been investigated, with respect to activity, much remains unknown about the mechanism of water splitting, especially the oxygen evolution reaction (OER) at the anode side.[3] Even more so, potential factors determining stability of suitable OER catalysts have been mostly disregarded and in contrast to fuel cell research standardized protocols and common figures of merit are missing. There are several other stability issues to address in PEM-Electrolysis but together with the need for cost-reduction and lower catalyst-loadings, finding reliable iridium-based mixed metal oxide catalysts has become crucial.[4]

Recently, we have proposed a series of accelerated stress test (AST) protocols and figures of merit for OER catalysts to advance comparability – and progress – in OER research.[5] In this study we report the application of these AST protocols to test performance and durability of iridium-based mixed metal oxide catalysts for the OER in PEM water electrolysis devices. Thorough physicochemical characterization combined with nondestructive pre-/post-catalysis screening of catalyst composition and online analysis of catalyst decomposition are used to identify and monitor stability-governing factors.

Identifying the degradation mechanisms during OER may open the way towards new catalyst designs that could break the inverse relation between catalyst activity and stability. New catalysts with comparable activity to pure iridium oxide catalysts but with increased stability and reduced cost would improve further commercialization of PEM-Electrolysis.

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Abstract No. 114

Direct membrane deposition – a simple and cost effective fabrication method for polymer electrolyte membrane electrolysis cells

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Summary. Direct membrane deposition is presented as a novel manufacturing approach. It is an inversion of the state-of-the-art fabrication method and allows an optimized catalyst utilization and a simplified fabrication procedure for polymer electrolyte membrane fuel cells (PEMFCs) (Figure 1a).

Abstract. For PEMFCs the advantages of direct membrane deposition have already been shown in several publications [1,2]. As stated, the direct deposition of the membrane in liquid form onto the electrodes provides a better contact between catalyst layer and polymer electrolyte membrane (Figure 1b) [3]. Additional to a lower contact resistance, this method yields a lower mass transport resistance.

We present the transfer of this concept to polymer electrolyte membrane water electrolysis cells. The challenge hereby is to fabricate smooth and homogeneous electrodes on titanium based porous transport layers for the anode side in order to get a membrane layer without crossover and internal electrical shorting (Figure 1c). The membrane ionomer is deposited in liquid form onto these electrodes for example by inkjet-printing. This method also enables a simple fabrication of composite membranes with nanoparticles or electrospun nanofibers to increase mechanical and chemical stability [4,5].

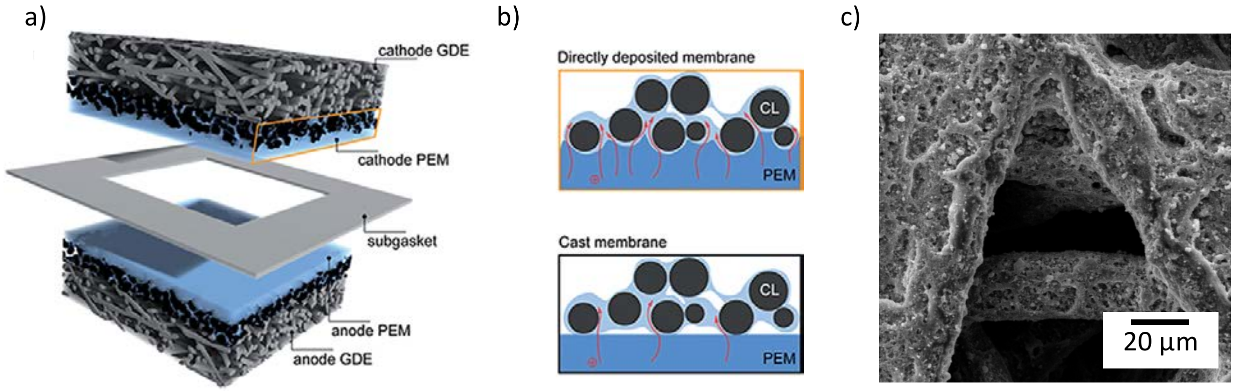

Figure 13 a) A schematic of a fuel cell fabricated with direct membrane deposition. b) DMD provides a better contact between catalyst layer (CL) and polymer electrolyte membrane (PEM). c) Titanium fiber substrate coated with IrO_2 to form a catalyst layer.

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Abstract No. 115

Experimental analysis of local effects in a 50 cm PEM water electrolysis cell

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Summary. This contribution provides results of an experimental analysis of the current and temperature distribution in a single-channel PEM water electrolysis with a length of 50 cm.

Abstract. PEM electrolysis is a promising technology to provide a coupling between the three main energy sectors heat, electric power and mobility in the prospective decarbonized energy system. State-of-the-art PEM water electrolysis cells are mainly known on a laboratory scale. Fabricated PEM water electrolysis cells in MW-scale are so far mainly installed for demonstration purposes with high potentials in the kinetic, thermodynamic and flow dynamic optimization. The present contribution gains better understanding of the detailed behavior of scaled up PEM water electrolysis cells.

For this purpose a single-channel PEM water electrolysis cell of 50 cm length is observed. The cell is divided into 250 measurement segments, allowing to detect the distribution of current density and temperature along the channel. Such local measurements provide additional information about the cell performance that are far beyond the integral information obtained from normal integral measurements. Identification of local temperature hot spots or inhomogeneous current density distributions, leading to faster degradation and losses in cell performance, get visible.

This work focuses on the experimental influences of the operation parameters mean current density $\bar{\imath}$, cell voltage U_{cell} the anode and cathode temperatures $T^{\mathrm{A\backslash C}}$ and the feed water flux $\dot{m}^{\mathrm{A}}_{\mathrm{H2O,in}}$ on the integral cell performance in general and on the distribution of current density and temperature along the channel in particular.

First results show that these investigations can give important additional information about the cell performance:

- Feed water flux variation influences the homogeneity of local current density distribution along the channel.
- Inhomogeneity of current density and temperature shows no clear correlation with integral cell overvoltage, e.g. despite low integral voltage high inhomogeneity of current density and temperature is possible.
- Characteristic current density profiles of a CCM change with time enabling the identification of activation or degradation processes.
- Very low feed water fluxes change water consumption rates locally and dynamically.
- Current density profiles are highly influenced by electrical contacting, e.g. differences of CCM or CCE design.

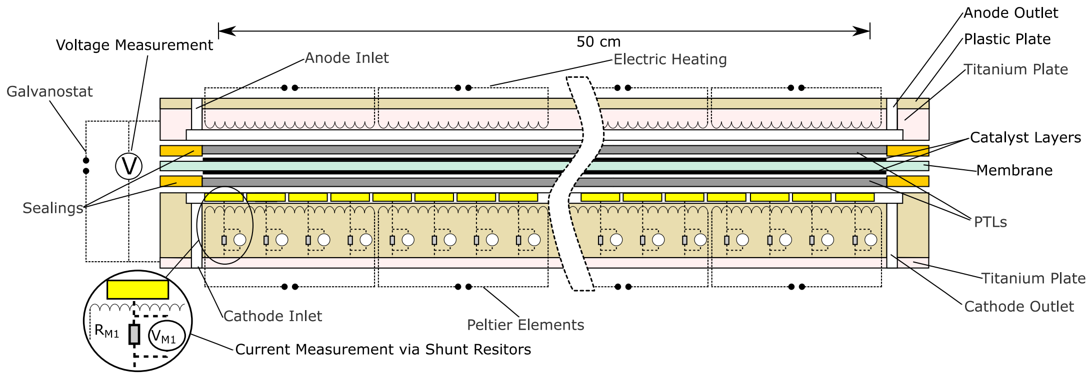

Figure 1: Schedule of experimental PEMEC for segmented current density and temperature measurement

Acknowledgements: Financial support by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) within the framework of the project grant HA 6841/2-1 and the Grant Agency of the Czech Republic within the framework of the Project No. 15-02407J is gratefully acknowledged.

Abstract No. 116

Modelling and Simulation Activities on PEM Water Electrolysis

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Summary. A detailed review of PEM electrolysis modelling and simulation is presented. Starting from early approaches based upon polarization curve to micro and nanoscale modelling of porous transport layer, a chronological study is carried out. Different activities have been compared and research gaps are identified.

Abstract. PEM electrolysis as a method of producing hydrogen by using electrical energy from renewable sources has received much attention recently. Research in PEM water electrolysis domain is still in its early stages as compared to research in fuel cells. As with any other engineering research, this also involves theoretical approaches and experimentation. Modelling and simulation of PEM electrolyzer systems started nearly two decades ago and it has gotten significant traction in the past few years. This involves simple analytical equations to 3D flow simulation, steady state models to dynamic models, component level models to system level models or models integrating photo-voltaic systems. It is therefore essential to present the research community a good overview of the activities that have taken place over time. A comprehensive review of PEM electrolysis systems in general has been reported by Carmo et al. [1]. Bensmann and Hanke-Rauschenbach [2] have also reported a brief study on the modeling of PEM water electrolysis systems. Here we aim to provide further details into this subject. We have compared activities carried out by different groups and provided valuable insight to the current state of the art. It is found instance that Onda et al. [3] reported one of the earliest modelling approaches. Nie and Chen [4] have reported a three dimensional computational fluid dynamics simulation of flow in the flow field plates. However, no such activities have been reported after 2010. In addition, Oliveira et al. [5] have utilised micro and nanoscale models for porous electrodes and the catalyst layer modelling. We have also critically observed that modelling of porous electrodes and catalyst layer still requires further development.

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Abstract No. 117

Investigation of advanced components in a high pressure single-cell electrolyser for the development of a HP-PEM-ELY stack as part of a Regenerative Fuel Cell System

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Summary. The objective of the presented work is the performance and tolerance evaluation of selected components and materials for the development of a High Pressure, Polymer Electrolyte Membrane (PEM) Electrolyser (HP-PEM-ELY) Stack, aiming to operate at 80 bar with a performance output of 0.3 A/cm^2 at 1.6 V.

Abstract. Regenerative fuel cells offer significant advantages over rechargeable batteries as energy storage devices, especially in applications where high specific energy density is required as in the case of telecommunication satellites. A closed loop regenerative PEM fuel cell system (RPEMFCS) operates as a high pressure PEM electrolyser when excess power is available from the solar array (charging mode/reactant regeneration) and as a PEM fuel cell when the solar array does not generate power i.e. when the satellite is in eclipse (discharge mode). It has to be mentioned that operation of an electrolyser at high pressure is advantageous due to (i) reduction of internal cell resistance, (ii) reduction of volume of gas bubbles, which facilitates the transportation of liquid water and (iii) production of compressed H_2 and O_2, which makes the electrolyser to perform at the same time as a gas compressor. In this way, the installment of external compressors can be avoided, which finally improves and simplifies the whole system`s integration. Regenerative fuel cells, of a discrete or a unitized design, have been considered as potential energy storage solution for future space missions [1], as well as for terrestrial applications. The ultimate objective of the current activity is the research and development of a regenerative PEM fuel cell (RPEMFC) system for space applications, targeting at (a) large telecommunication platforms in geostationary orbit, GEO (Commercial application), (b) planetary exploration missions (Science application) and last but not least (c) terrestrial (Commercial and Science) applications. Based on the materials research and development, which has been carried out up to now, two stacks (a high-pressure PEM electrolyser and a high-temperature PEM fuel cell) are under manufacturing and preliminary testing, aiming to be incorporated in a regenerative fuel cell test bench for further evaluation [2]. Complete testing of the whole system will be performed under a predefined load profile in accordance to the needs of a telecom platform in GEO orbit. In the presented work, an extensive study was performed on a single-cell high pressure PEM electrolyser manifold, leading to a list of materials with suitable properties and engineering solutions towards specific operation requirements. This investigation provided the necessary feedback for the design and manufacture of a prototype HP-PEM-ELY stack, which is also discussed.

Acknowledgments

The research leading to these results has received funding from the European Space Agency (ESA) under the projects GTF2065: “Regenerative PEM Fuel Cells” (Contract No. 22329/09/NL/CBI) and “Development of a Closed Loop Regenerative HT-PEM Fuel Cell System” (Contract No. 4000109578/13/NL/SC).

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Abstract No. 118

Permeation and Recombination of Hydrogen under PEM electrolysis conditions

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Summary. Recombination of hydrogen reduces its concentration in the anode compartment of PEM electrolysers. The origin of the hydrogen in the anode section of PEM electrolyser is due to the permeation taking place from the cathode compartment. This talk will provide some data and theoretical analysis on the use of platinum (Pt) within the anode electrode structure to reduce hydrogen concentration during PEM water electrolysis.

Abstract. 3M NSTF CCMs were used as permeation barrier in PEM electrolyser. They were coated with Ir and Pt NSTF electro-catalyst on the anode and cathode sides respectively. All-titanium made cell with 25 cm^2 active membrane area was used in all the experiments. In one set of experiments Ti-based platinised GDL was used and in the other set of experiments gold-coated titanium-based GDL was used on the anode. The permeation rate of hydrogen from cathode to anode compartment was measured by gas chromatography method to analyse the effect of Pt presence within the GDL structure on the concentration of hydrogen in the oxygen stream. Temperatures as well as water supply rate and current densities were also used as variables.

Abstract No. 119

Design of Reference Electrode for Polymer Electrolyte Membrane Electrolyzer

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Integrating hydrogen-based energy technologies are an effective strategy to decarbonize the electricity market. Hydrogen can be produced by electrolyzing water and stored as an energy carrier. Polymer Electrolyte Membrane Electrolysers (PEMEs) are a power-to-gas technology, which is well suited to converting intermittent electricity from renewable sources into pure hydrogen and oxygen, due to their fast response and ability to accept large input power surges [1]. Adding PEMEs into the electricity grid as an energy storage technology will help to improve the reliability and stability [2-3]. The majority of the electrode research for PEM electrolysis has focussed on the oxygen evolution reaction at the anode. The contribution to polarization losses from the hydrogen-producing cathode has received much less attention. This may be, in part, due to issues with implementing a stable and reliable reference electrode (RE). Several configurations of internal and external type REs were investigated to separate the contribution of the anode and cathode to overall cell polarization. RE efficacy was assessed by comparing the agreement between the overall cell potential and the sum of the electrode potentials. Using a stable RE, we have been able to show that the overpotential of the cathode is significantly affected by the crossover of oxygen through the Nafion membrane. Furthermore, the kinetic and ohmic parameters of the membrane electrode assembly (MEA) were calculated from the polarization curves. The contribution of cathode polarization to cell performance is clearly shown to be sensitive to the partial pressure of oxygen at the anode, Figure 1. In addition, the cathodic polarization decreases with temperature in a way that can be related to the solubility of oxygen in water. The implications of controlling oxygen crossover polarization to overall PEME performance and lifetime will be discussed.

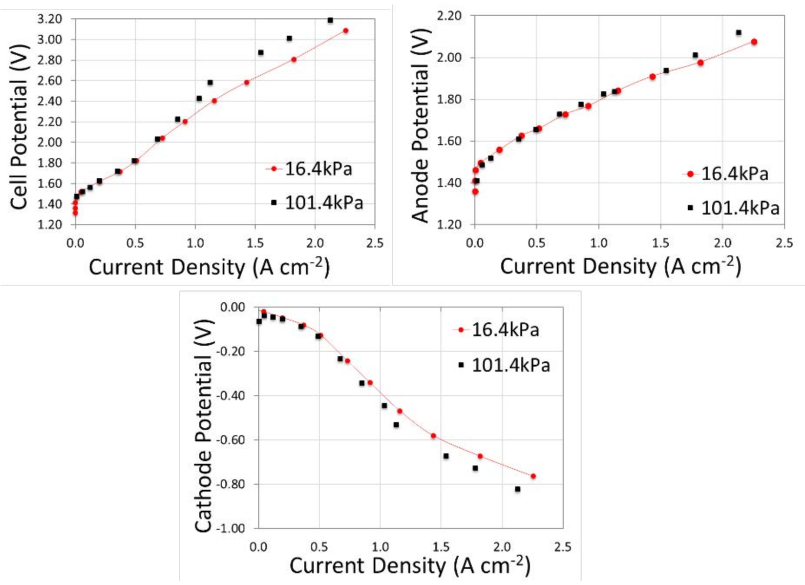

Figure. 1. Reference electrode polarization curves for anode, cathode, and cell at operating pressures: -85kPa and 101kPa.

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Abstract No. 120

Electrospun-TiO_2 Supporting materials for Oxygen Evolution Reaction in Acidic conditions

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Summary. Metal doped-TiO_2 supporting materials (M-doped TiO_2) were prepared by using electrospinning method for oxygen evolution reaction in acidic conditions. Ir/M-doped TiO_2 was synthesized and evaluated by linear sweep voltammetry. Prepared Ir/M-doped TiO_2 catalyst showed better OER activity than Ir black.

Abstract. Polymer electrolyte membrane electrolytic cells (PEMECs) is one of appropriate energy storage systems connected with renewable energy due to high drive current and endurance under road fluctuation. In water electrolysis, oxygen evolution reaction (OER) occurs under acidic and high potential. So, the large amount of precious metal catalyst is needed for performance and stability. Introduction of supporting materials could reduce the amount of precious metal catalyst without performance degradation. Titanium oxide (TiO_2) is one of few materials which shows good stability under acidic and high potential conditions. Also low electronic conductivity of TiO_2 (~10^{-6} S/cm) can overcome with introduction of appropriate doping element into TiO_2.

In this work, various metal elements were doped into TiO_2 supporting materials. M-doped TiO_2 were prepared by electrospinning method. Figure 1 (a) is a SEM image of prepared nanofiber TiO_2. M-doped TiO_2 were characterized to study physical and chemical properties. Then, iridium catalysts on M-doped TiO_2 support (Ir/M-doped TiO_2) were synthesized by polyol method and were electrochemically evaluated. OER activity of prepared catalysts was measured by linear sweep voltammetry in oxygen-saturated 0.5 M H_2SO_4, respectively. As shown in fig. 1 (b), polarization curves for each catalysts were changed as variation of doping elements. Ir/M-doped TiO_2 shows higher OER activity than iridium black. From these results, it was obtained that introduction of dopant into TiO_2 change the characteristics of TiO_2 and this change contribute to improvement OER activity. Ir/M-doped TiO_2 could be suggested OER catalyst to reduce the amount of precious metal catalyst without performance degradation.

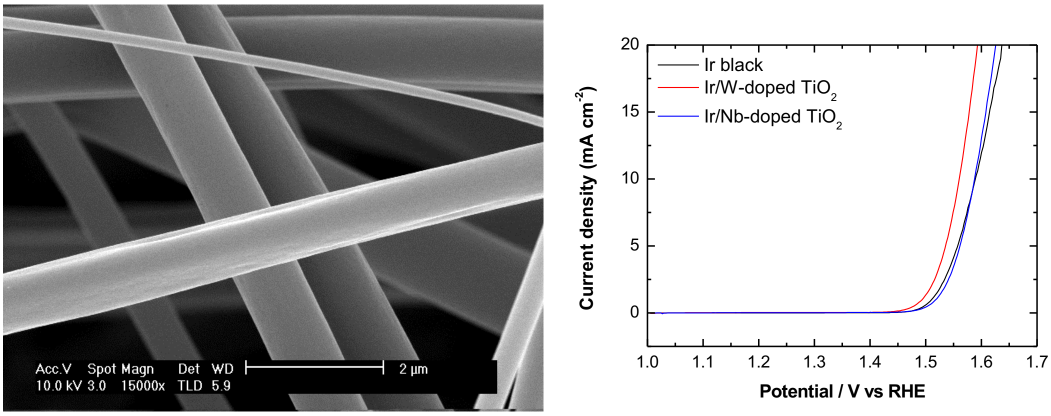

Fig 1. (a) SEM images of electrospun TiO_2 nanofiber, (b) Polarization curves of prepared catalysts and commercial Ir black measured in O_2-saturated 0.5 M H_2SO_4 solution at room temperature with rotation speed of 1600 rpm and scan rate of 5 mV/sec

Abstract No. 121

PEM-Electrode drying

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Summary. A new method to investigate selective drying processes of catalyst dispersions was set up. The variation of drying conditions and catalyst dispersion composition and its influence on the layer formation during the manufacturing of membrane electrode assemblies is studied.

Abstract. The establishment of a fully renewable energy system is predicated on the use of hydrogen as a fuel. Polymer electrolyte membrane (PEM-) water electrolyzers for hydrogen generation and (PEM-) fuel cells for its reconversion will be essential components of such a system. To become economically feasible, their costs have to be reduced drastically. The quantity of expensive materials utilized for the construction of cells, including platinum, iridium or titanium must be reduced and overall efficiency increased. The efficiency of these devices is depending on the electrochemical processes that take place in the electrodes and is strongly influenced by their structure. The structure can be affected by controlling various steps in the manufacturing progress. Aside from the chemical composition of the wet coat (consisting of the supported catalyst, Nafion®, solvents and additives) the drying plays a significant role during the self-organization progress in the catalyst layer. Therefore, the drying aspect is one of the main focuses of interest.

In the manufacture of membrane electrode assemblies (MEA) the used catalyst dispersions are commonly based on a mixture of organic solvents. To monitor the drying process a test station was developed measuring the evaporation of the solvents selectively using FT-IR-spectroscopy and is validated to be accurate within a few percent. The difference in the drying rates for each solvent results in a change of the catalyst dispersion composition. The composition can be determined as a function of time (fig. 1). Therefore, chemical and physical properties are varying over time. Consequently the generated catalyst layers will differ widely if either the drying conditions (e.g. temperature, overflow rate …) or the starting composition are adjusted (fig. 2).

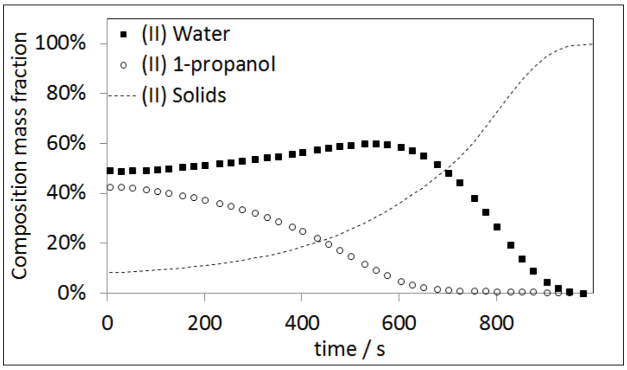

Figure 1: Dispersion composition as a function of time

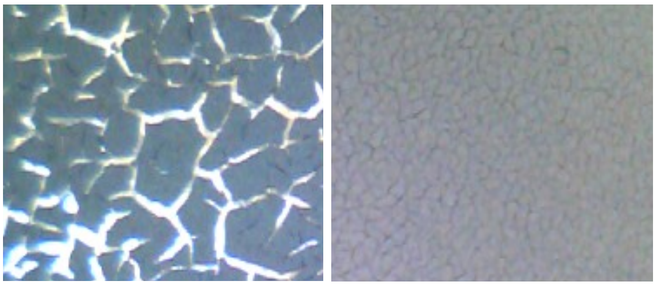

Figure 2: Same-sized microscopic images resulting from different drying curves

Abstract No. 122

Polymer functionalized carbon nanotubes as highly active bifunctional electrocatalysis for full water splitting

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Summary. We have developed a facile and scalable method for synthesizing the bifunctional nitrogen functionalized carbon nanotubes (NMWNTs) for full water splitting.

Abstract. Among different methods to produce hydrogen as the future clean energy carrier, electrochemical water splitting is a promising straightforward method. However, efficient and low-cost electrocatalyst for hydrogen and oxygen evolution reactions (HER and OER) on cathode and anode of an electrochemical electrolyzer respectively are required. Consequently, new alternative catalyst materials must be introduced so that electrochemical electrolyzers can be adopted. For HER and OER efficient non-noble metal and metal free electrocatalysts have been introduced recently.

The unique structure and intrinsic properties of carbon nanotubes (CNTs) such as high-surface area, high-chemical stability, and high electrical conductivity make them extremely attractive as catalyst supports for heterogeneous catalysis. Thus, synthesis of composite materials of CNTs has been selected in this study as a promising approach to fabricate efficient and low-cost electrocatalysts. Functionalization of CNTs with low-cost polymers is a novel and relatively simple method to fabricate metal free catalysts for HER and OER in electrochemical water electrolysis. The fabricated composite materials, based on the combination of CNTs and polymers, have shown properties of the individual components with synergistic effects [5]. These metal free electrocatalysts show catalytic properties toward both HER in acidic media and OER in alkaline environment comparable to those of commercial noble metal based electrocatalysts. This work opens new avenues for the functionalization of CNT with polymers in order to synthesize new catalyst materials for the electrochemical hydrogen production.

Abstract No. 123

Spinel-structured materials as catalyst support/current collector materials for PEM electrolysis cells

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Summary. Corrosion stability test conducted on different spinel-structured oxides will be shown and the effect of different doping levels and types will be correlated to the stability of the materials, together with conductivity measurement showing the impact of doping on the materials properties.

Abstract. PEM electrolysis cells can play an important role in the future energy scenario as efficient device for renewably-produced intermittent energy harvesting, due to their flexibility and fast response [1]. Cost still hinders a wider utilization of this technology, not only due to high price of the catalyst used at the oxygen electrode but also due to costly components and poor catalyst utilization due to lack of a proper support. Ceramic materials could match the characteristics required for the application, due to their inherent stability toward further oxidation, tuneable electrical properties and surface area. Specifically, both theoretical and experimental evidence has been found that Cr-based spinel-structured materials could be tailored to possess high conductivity at low temperature by proper doping [2,3]; moreover, the corrosion stability of those is suggested also by the materials being found in the passivation layer of stainless steels [4].

Different formulations of spinel-structured materials were investigated. The materials were synthesized by solid state route, calcined and pressed into pellets to prepare samples for the corrosion test. Harsh corrosion testing was performed on the materials simulating cell operation conditions by exposing the materials to an aqueous oxidizing and acid environment at 85 °C. The mass loss after 24 hours of exposure was negligible, suggesting the materials being stable in the conditions required by the application. The effects of different levels and type of doping on electrical and stability properties will be shown. The doping appears to influence the corrosion stability of the materials, possibly because of the internal structural stress caused by the substituent ions, particularly at higher doping levels. Conductivity measurements in the application temperature range will be presented and correlated to occupancies of A and B sites determined by Rietveld refinement (where A and B are the tetrahedral and octahedral sites respectively in a spinel structure with general formula AB_2O4).

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Abstract No. 124

Hydrogen production from short-chain alcohols using polymeric proton conductors

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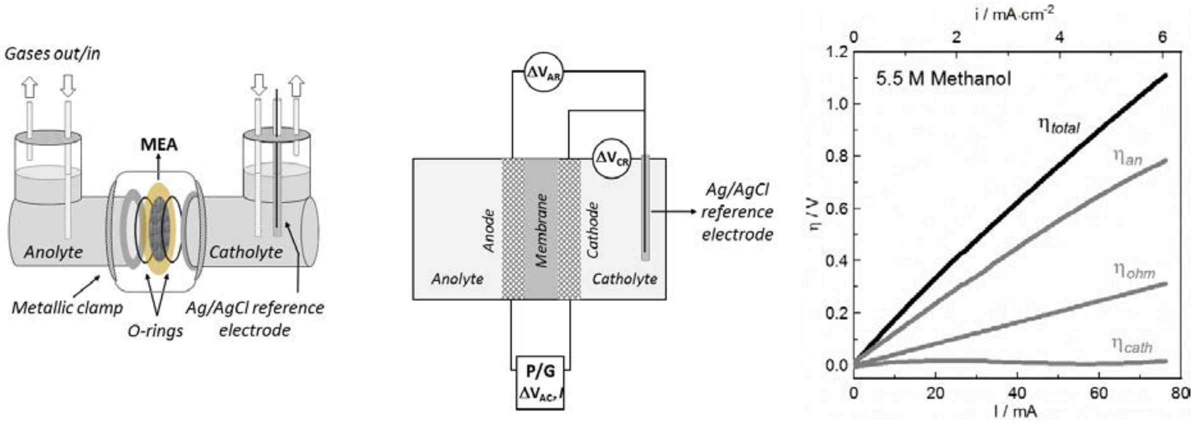
Summary. Gas diffusion electrodes interfaced to polymeric H^+ conductors were used for producing H_2 through the electrolysis of C1-C3 alcohols and their mixtures. An alternative reactor design allowed us to quantify individual potential losses. The role of the anolyte solution's pH on the overall performance was examined.

Abstract. A promising approach for hydrogen production using polymeric electrolytes has emerged lately, named alcohol electrolysis or electrochemical reforming of alcohols. The power demands for this process are significantly lower compared to water electrolysis, thus this technology can offer remarkably reduced operational costs.

We investigated the electrolysis of C1-C3 alcohols and their mixtures using an alternative reactor design, appropriate for fundamental investigations. Membrane-electrode assemblies separated the two chambers of an electrochemical reactor (fig. 1a), filled with aqueous alcohol and H_2SO_4 solutions. The half-reactions which take place upon polarization are the alcohols electrooxidation at the anode and the hydrogen evolution at the cathode. The aqueous phase allows the utilization of a standard Ag/AgCl reference electrode for monitoring the individual overpotentials (fig. 1b).

As shown in figure 1c, the deconvolution of the overpotential components indicated that the overall performance is mainly (~75%) affected by the sluggish anodic reaction (i.e. alcohol electrooxidation). Proton transport through the electrolytic membrane has a smaller contribution while the cathodic overpotential is negligible in all cases. Cell currents under standard applied potentials were found to decrease as the number of C-atoms in the alcohol increases, due to the formation of strongly adsorbed intermediates and to the need for breaking the C-C bond. When using alcohol mixtures, the heaviest alcohol dictates the cell performance. Changes in the pH of the anolyte solution within the acidic regime affect the anodic half-reaction, in a way that the presence of ionic agents in the solution extends the reaction zone and thus increases reaction rates.



(a) (b) (c)

Figure 1. (a) Schematic representation of the reactor. (b) The corresponding electrical circuits. (c) Effect of the current on the total cell overpotential and on the anodic, cathodic and ohmic overpotentials during methanol electrolysis.

Acknowledgements: This project has received funding from the European Union's Horizon 2020 research and innovation programme "CritCat" under grant agreement No 686053 and from Synfuels China Technology Co. Ltd.

Abstract No. 125

Single crystal studies to evaluate the structure sensitivity of the Oxygen Evolution Reaction (OER) under acidic conditions

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Summary. In the presented work, we introduce a new approach to study well-defined model catalysts for the OER based on electrochemistry and Raman spectroscopy. Combining oxide stripping with Raman spectroscopy, we correlate the structure of Pt single crystals with their OER activity.

Abstract. From fundamental point of view, the Oxygen Evolution Reaction (OER) is the decisive process in electrolysers. The efficiency of the device is mainly limited by this reaction, which exhibits a large overpotential on all known catalysts. Over the last years many efforts have been addressed to develop more stable and active catalysts. However, most of these studies involved nanostructured catalysts deposited on different types of supports, while just a few works tried to understand the fundamentals of this reaction. Such investigation can be used to improve actual catalysts, but they are also an important link between theory and experiment. One of the main issues that still wait to be experimentally explored is the structure sensitivity of the OER. Usually such studies are done with single crystal electrodes of different surface orientations. However, there are many drawbacks in the use of this approach for studying the OER. The main challenge is that the surface loses its order once overpotential is driven to higher values and metal oxides start to form. This process is inevitable since the oxide is an intermediate in the reaction mechanism, while surface reorganisation cannot be easily avoided. Despite these intrinsic limitations, we have been able to retain structural information developing an investigation approach based on electrochemical and spectroscopic techniques. This approach allowed us to investigate the structure sensitivity of the OER on Pt single crystals and hopefully soon can be applied to more relevant systems.

Abstract No. 126

Impact of Dynamic Load from Renewable Energy Sources on PEM Electrolyzer Lifetime

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Summary. Determining the lifetime of electrolysers is challenging, especially under dynamic load as will occur with varying energy supply by renewable energy sources. This paper discusses Accelerated Stress Testing procedures allowing prediction of durability of the electrolyser components under realistic dynamic mode conditions.

Abstract. The paper discusses a PEM electrolyser test protocol for gaining insight into the degradation behavior of the electrolyser specifically under dynamic load patterns as might occur by varying energy supply of renewable energy. PEM electrolyser are able to achieve 40 000 hours of lifetime or more. However, this lifetime literally comes at a cost. Long lifetimes can only be achieved using expensive materials. Degradation can be limited by using high catalyst loadings, thicker membranes, complex fabrication technology for the separator plate, etc. But the use of these materials adds excessively to the cost of the electrolyser stack. Durability has thus a double impact on the electrolyser economics. Reduced lifetime increases the capital cost because of depreciation is done over a shorter period of time but also because of the need to go to more expensive materials. In addition PEM fuel cell development has extensively shown that degradation may be much quicker under impact of rapid load changes, start-stop cycles and operation close to open cell voltage. Although there are a number of important differences between fuel cells and electrolysers, durability needs to be assessed both under full-load and under transient and off-design conditions. In particular if the electrolyser is used to manage a varying supply of renewable energy, it will be operated under varying loads. How these will vary, depends on the application.

Determining durability is challenging, especially when dynamic load patterns are used. It is time-consuming to do a single lifetime measurement and the time required to determine the impact of several variables rapidly becomes a challenging task. The “holy grail” regarding the issue lifetime is to be able to accelerate degradation in such a way that it allows prediction of the durability of components under real conditions (Accelerated Stress Testing (ASR)). Operating at a higher temperature, a higher impurity level or higher current density will accelerate degradation. There is a clear need for this type of testing, as illustrated by the set of research priorities as presented by Hydrogenics.

In this paper suggestions for ASR test protocols will be given based on an extensive study on degradation mechanisms both experimentally and from literature.

Abstract No. 127

Research and Demonstration of Solid Polymer Electrolysis Technology in China

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Summary. Solid polymer electrolyte (SPE) electrolysis water technology has the characteristics of high efficiency and high purity, and has become one of the effective technologies for preparing high purity hydrogen. In this topic, the research status and commercial applications of SPE electrolysis technology in China is reviewed from four aspects: catalyst, membrane electrode assembly, separator and modelling.

Abstract.

Due to the increasingly prominent problem of environmental pollution, hydrogen as the cleanest energy has been widely concerned. SPE electrolysis water technology with its low energy consumption and high efficiency become a hot topic of concern.

Since 1987, China began the SPE electrolysis of water technology research. Purification Equipment Research Institute of CSIC, Tsinghua University, Tianjin University, Beijing Institute of Technology, Dalian Institute of Chemical Physics, Chinese Academy of Sciences and other research institutions carried out a large number of catalysts, membrane electrode assembly and other aspects of research work. After years of hard work, a large-scale SPE water electrolysis was produced in 2010. However, compared with alkaline water electrolysis, the high manufacturing costs limit its pace of industrialization. Up to now, there are few examples of large-scale application of SPE electrolysis technology in China, the potential market is that the researchers do not stop the need for further research.

In order to reduce the cost of hydrogen production of the SPE, the cost of electricity must first be reduced. To achieve this, the SPE electrolysis water technology and renewable energy should be combined with the comprehensive utilization of renewable energy. With the strong support of the Chinese government and the government of the Kingdom of Denmark, our research team, Purification Equipment Research Institute of CSIC, Tsinghua University, North University of China, North China Electric Power University and the Technical University of Denmark jointly are doing: research and demonstration of storage system for hydrogen production by SPE, which electricity from the abandoned wind. The research should start from three aspects, one is to prepare low-cost, excellent performance and long life of the proton exchange membrane; the second is the development of high catalytic activity of non-precious metal catalyst; third is to optimize the collector, separator and hydrogen system structure design, further reduce energy consumption and cost.

Acknowledgments

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Abstract No. 128

Progress of the European Project Efficient Co-Electrolyser for Efficient Renewable Energy Storage - ECo

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Stefan Diethelm[f], Frédéric Mercier[g], Jacobo Rubio Fernandez[h], and Marco Lindemann-Lino[i]

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Summary. The ECo Project aims at utilizing electricity from renewable sources for production of storage media via electrolysis of steam & CO_2 in SOEC (Solid Oxide Electrolysis Cells). The challenge is approached from cell, stack, and system level.

Abstract. The concept of the ECo project includes the development of improved SOECs, the investigation of durability under realistic co-electrolysis operating conditions, the design of a plant to integrate the co-electrolysis with fluctuating electricity input and catalytic processes for hydrocarbon production, the transfer of knowledge to and test of a co-electrolysis system under realistic conditions, the demonstration of the economic viability for the overall process, and a life cycle assessment. Highlights from the first project year will be presented.

Improvement of the SOEC performance is based on micro structural tuning. This was achieved specifically for the oxygen electrode by two approaches: backbone manufacturing and infiltration of the LSC or LSCF phase on one side, and particle size optimisation for screen printing of the LSCF/CGO electrode on the other.

For the mapping of the performance and durability of initially state-of-the-art SOEC, a comprehensive test matrix was identified, which is based on previous activities of harmonisation of SOFC/SOEC testing in Europe, for example the EU SOCTESQA project, and was extended by the relevant parameters such as co-electrolysis and test under higher pressures. The tests are combined with comprehensive micro structural pre- and post-test analysis. Furthermore, the results are substantiated by a detailed model that accounts for electrochemical processes for a given micro structure.

System models for the assessment of different power-to-gas and power-to-liquid scenarios were established. These scenarios include different options for the SOEC co-electrolysis input (e.g., CO_2 sources such as cement industry, electricity sources such as wind turbines) and output (potential, desired hydrocarbon products such as methane or methanol). The aim is to identify the most promising cases and to benchmark them with state-of-the-art technologies and with routes via steam electrolysis.

Abstract No. 129

Comparative degradation study of a Ni-YSZ supported Solid Oxide Fuel Cell under electrolysis and co-electrolysis operations

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Summary.

anode supported solid oxide electrolysis cell

degradation study under electrolysis and co-electrolysis operations

chronopotentiometry and electrochemical impedance spectroscopy

Abstract. Production of renewable energies through the combination of different natural sources and promising technologies is of critical importance. Hydrogen production from steam water using solid oxide electrolysis cells (SOEC) is part of this so called “energy mix”. In the present study, commercial anode supported solid oxide fuel cells (SOFC) were tested under electrolysis and co-electrolysis conditions. The cell consisted of Ni-yttrium-stabilized zirconia (Ni-YSZ) as fuel electrode, gadolinium-doped ceria (GDC)/yttrium-stabilized zirconia (YSZ) as electrolyte and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) as O_2 electrode. Operations under electrolysis and co-electrolysis modes lasted for 2500 hours and 1500 hours, respectively, with an applied current density of -1.0 A/cm^2. Evolution of the cell degradation profiles were followed with time through the use of chronopotentiometry and electrochemical impedance spectroscopy (EIS). Thus, analysis of the post-mortem characterization by SEM/EDX, along with the electrochemical testing results, aims at distinguishing the cell changes specifically associated to degradation under co-electrolysis operation.

Abstract No. 130

Performance and degradation of a SOEC stack with different air electrodes

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Summary. A 4-cell stack in F10-design from Forschungszentrum Jülich GmbH was tested in SOFC and SOEC mode. Mid-term stationary operation was conducted. The performance and the degradation behavior were monitored via EIS and DRT analysis was applied to improve quality and reliability of the equivalent circuit fitting.

Abstract. The world is running out of fossil energy. Therefore it is essential to raise the share of renewable energy in power production. Renewable energies cannot be regulated to meet demand, so mankind has to come up with a possibility to store energy. Hydrogen is not only the feedstock for the petrochemical industry and ammonia production, but also an environmentally friendly energy carrier. A promising method to produce hydrogen is high temperature water electrolysis with solid oxide electrolysis stacks.

In this poster a 4-cell-SOEC stack in standard F10-design (see Figure 1.a) from Forschungszentrum Jülich GmbH is presented. The materials used for the cells are an 8YSZ electrolyte with a GDC barrier layer and Ni/8YSZ as substrate and fuel electrode. The stack is equipped with two different types of air electrodes, namely $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF).

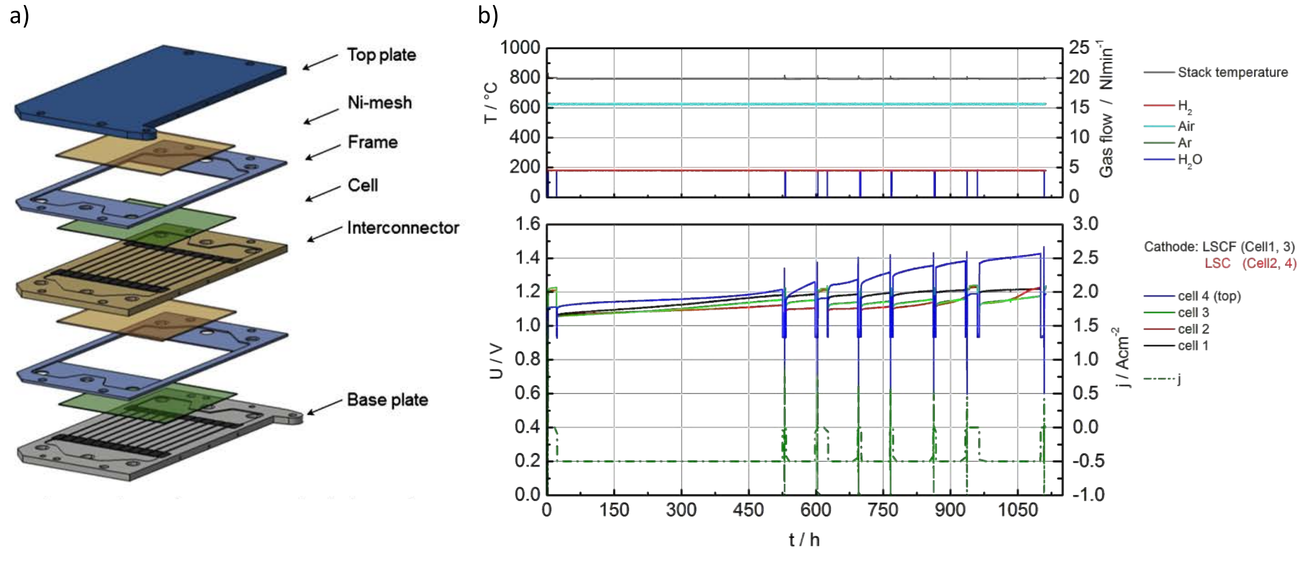

Figure 14: a) Jülich F10-design for two cells.[1] *b) Stationary SOEC operation at 800°C, 50% humidified H_2, -0.5 A·cm^{-1}, 50% steam utilisation.*

The performance of the stack was monitored both in SOFC and SOEC mode at 700-800°C. A mid-term stationary operation at -0.5 A·cm^{-1} and steam conversion of 50% at 800°C was conducted to show durability (see Figure 1.b). All cells show obvious degradation, but loss of activity for cells equipped with LSC is higher compared to cells with LSCF electrodes. Electrochemical Impedance Spectroscopy (EIS) was utilized to study the electrochemical performance as well as the degradation behaviour during mid-term electrolysis. To improve the quality and reliability of the equivalent circuit fitting, a Distribution of Relaxation Times (DRT) analysis was applied. Post-test analysis was used to reveal reasons for decreasing activity in electrolysis.

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Abstract No. 131

Synergies between Solid Oxide Electrolyser Cells and Catalytic Methanisation

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Summary. This poster presents the first data from a pilot plant combining catalytic methanisation and Solid Oxide Electrolyser Cells. Carbon dioxide in biogas is upgraded to pure methane. Important synergies include excess heat recovery, reuse of waste water and biogas pretreatment.

Abstract. Catalytic methanisation is a highly exothermal reaction. The excess heat and generated water provides multiple synergies when coupled with Solid Oxide Electrolyzer Cells. This study verifies these synergies in a 10 Nm3/h pilot plant upgrading biogas using a 50kW SOEC as hydrogen source. Data from 1000 production hours is presented. The gas quality produced can replace natural gas and provides a promising future for highly efficient power-to-gas conversion.

Abstract No. 132

Techno-economic study of a Reversible Solid Oxide Cell (SOC) system for industrial hydrogen production and grid support applications

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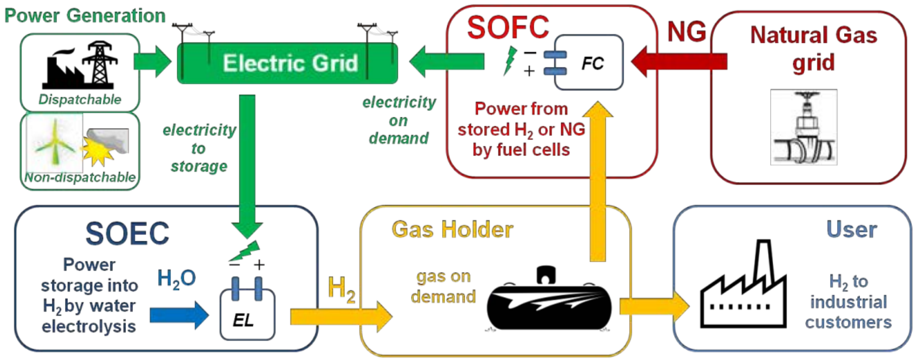
Summary. The effectiveness of arbitrage strategies for decreasing the cost of the hydrogen produced from SOEC electrolysis is investigated through a techno-economic analysis at the system level. Different solutions for the reversible operation of a solid oxide cell (R-SOC) system in a grid-connected industrial environment are analyzed and discussed.

Abstract. The Electrical Energy Storage (EES) into chemical energy through reversible Solid Oxide Cells (RSOCs) is one of the most promising solutions for large-scale EES that allows the storage of electrical energy into hydrogen – a flexible multi-purpose energy carrier. The produced hydrogen produced from the high-temperature electrolysis plant is stored either for deferred electricity production, thus operating the SOC in fuel cell mode, or it used as a commodity in different applications (industry or automotive sectors, or even for the injection in the natural gas grid). Especially, industrial hydrogen holds a huge market potential that is currently covered mostly by steam methane reforming (SMR) (48% of total demand [1]).

To reach competitive costs with hydrogen production by SMR, SOEC systems could exploit the flexibility of reversible systems, which can also produce electricity from the stored hydrogen, or NG from the grid. In this way, it is possible to maximize all the possible integrations of the SOEC with the industrial users (especially by recovering available heat and steam flows).

The present work addresses the techno-economic analysis of different options for increasing the competitiveness of SOEC hydrogen production under an arbitrage strategy. In fact, electricity is imported from the grid depending on the hourly market price. SOFC operation is allowed by using either the stored hydrogen or natural gas from the grid. The levelized cost of the produced hydrogen is evaluated in the analysis by taking into account the cost of plant equipment, maintenance and electricity/gas supply (net of the revenues obtained by selling electricity to the grid). The analysis includes realistic technological constraints of the R-SOC system (i.e., load ramp rates, SOEC-SOFC switching time) and applies optimization procedures to identify the electricity price for changing the operation mode from SOEC to SOFC which allows to minimize the production cost of hydrogen on different time scales (year, month and week). The impact of different electricity price and hydrogen demand profiles on the levelized cost of hydrogen are investigated. The potential for integration opportunities of RSOC systems with industrial processes are finally assessed.



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Abstract No. 133

Solid oxide electrolysis at Forschungszentrum Jülich

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Summary. Solid oxide electrolysis for energy storage – the other side of a sustainable energy future. Status and perspectives from Jülich's point of view.

Abstract. Solid oxide fuel cells (SOFC) able to operate in the reversed solid oxide electrolysis cell mode (SOEC) are a very promising technology for buffering surpluses in energy supply. In case of steam electrolysis the produced hydrogen gas could be stored and later converted back to electrical power when needed. Given a cheap heat source (e.g. waste heat), the SOEC can be operated in an endothermal mode and electrical-to-hydrogen conversion efficiencies of or even above 100% may become feasible. The co-electrolysis of steam and carbon dioxide offers even more potential for applications since the produced syngas (CO and H_2) can be converted into a variety of useful chemicals which may not only be used for later power generation.

For SOEC application there is not yet as much knowledge as for the conventional fuel cell mode available. This applies in particular for complete stacks and systems, which exclude the application of many analytical techniques that are readily available for single cells, half cells or individual electrodes. Common expectations are that degradation mechanisms in SOEC mode and in particular co-electrolysis mode are different. Accordingly, current experiences point towards a decreased operational stability than in SOFC mode.

An introduction into the degradation phenomena specific to the SOEC mode will be given. The aim is to apply the existing knowledge in designing, assembling, operating and characterizing anode supported SOFC stacks to extend the corresponding knowledge for the SOEC and co-electrolysis modes. This contribution shall present and discuss the current state and the ongoing research activities at Forschungszentrum Jülich concerning the development of SOECs based on the anode-supported SOFC design, focusing on testing of whole stacks.

Abstract No. 134

3D printed electrolytes for Solid Oxide Electrolyser devices with complex hierarchical geometries

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Summary. 3D printing technology is presented as a new method for the fabrication of complex structures for Solid Oxide Electrolyser Cells (SOEC) and monolithic stacks by stereolithography (SLA) and YSZ as printing material.

Abstract. Solid Oxide Electrolysis Cells (SOEC) devices offer an efficient technology for energy storage through the power to gas and power to liquid routes. These routes are presented as the most efficient solution for the renewable energy storage, solving the mismatch between consumption and demand delays with a close to zero carbon cycle. SOEC devices convert steam in highly pure hydrogen operated under electrolysis mode or mixtures of steam and carbon dioxide in syngas ($CO+H_2$) under co-electrolysis mode [1]. One of the problems of these devices is the fabrication costs due to the high number of manufacturing steps [2]. The main objective of the present work is to fabricate YSZ pieces by SLA ceramic 3D printing new technology to be used as SOEC electrolytes where different 3D surface geometries are printed. The resulting complex geometries allow increasing between the active area per volume of the electrolyser. At the same time 3D printing enables manufacturing monolithic jointless devices that ease the fabrication process of the SOC stacks, avoiding the typical sealing problems of the standard ones. It also permits to directly link catalytic reactors for synthetic fuels fabrication. The improvement on the fabrication costs of these devices directly results on a more cost efficient produced or stored energy [3]. In the present work complex geometries of SLA 3D printed electrolyte, as the ones presented in figure 1, are proposed and tested as a SOEC device.

Figures: Complex 3D printed geometries for SOEC electrolytes.

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Acknowledgements

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Abstract No. 135

Development of SOEC stacks at DTU Energy

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Summary. DTU Energy has initiated the development of SOEC stacks for hands-on-experience with the challenges of the stack technology. The aim is to develop distinct stacks, which addresses the known challenges of the technology. Starting from scratch (and not from an SOFC stack) some interesting design choices can be made.

Abstract. In this presentation, the design choices made for the first SOEC stack design at DTU Energy are shown and explained. Focus has been on optimizing the cost both through choice of materials and processes, but mainly by increasing the durability of the stacks. The intention is both to minimize the degradation of the electro-chemical performance, and to improve the mechanical integrity of the stacks.

To decrease the degradation of the Ni containing cathode, this is exposed to a relatively dry mixture of steam and hydrogen to minimize the Ni-coarsening and migration occurring at high partial vapour pressures. To avoid starvation of the cell, the dry gas mixture is overblown (flown in higher degree than stoichiometrically needed) by increasing the flow rate over the cell. The dry mixture can be achieved by partially re-using the fuel and adding vapour for each pass.

Hereby the temperature of the stack can also be controlled by supplying convective heat of a warmer vapour hydrogen mixture to balance the endothermic electro-chemical process. In SOFC stacks this is typically done by overblowing air over the air electrode. Thus, relatively larger gas-channels are needed on the fuel side by this type of operation, rather than on the air side. Avoiding air-side overblowing also implies that the produced oxygen can be extracted and utilized by supplying a small under-pressure without diluting it with air or another carrier gas. The oxygen is in the current design sucked through the sides perpendicular to the flow direction of steam and hydrogen, see Figure 15. Hereby a cross-flow type of flow-field is achieved, but with the thermal advantages of a co-flow, as there is no gradient of the oxygen partial pressure on the anode side (pure oxygen).

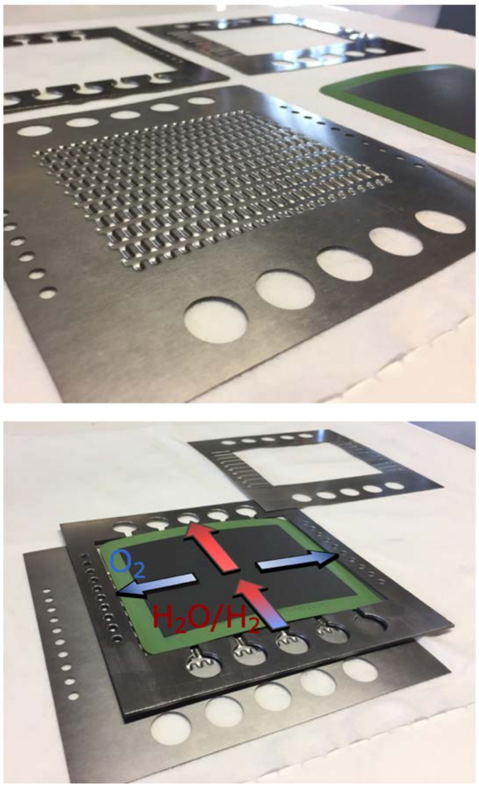

Figure 15 Stack components from the first DTU Energy SOEC stack.

The flow field does thus provide an almost linear thermal profile, which is beneficial to minimize the mechanical stresses. This is true both for the stresses in the cell plane, and for the vertical stresses, which tends to induce loss of contact between the cell and the interconnect. To further enhance the durability of the stack with respect to this particular failure mode, flexible contact components have been introduced on either electrode. Furthermore, on the oxygen side a noble in-situ reaction bonding contact layer has been utilized. This has shown to be mechanically superior to the conventional contact layers. Using these flexible contact layers also enables the use of thin seals, as thick seals usually are employed to accomodate the variations of the thickness of the layers, which naturally occurs in the production. Thinner seals are also an advantage to minimizes the risk of mechanical failures.

The cells are furthermore sealed internally to a frame, whereby it can be avoided to cut holes for manifolds in the cells. Internally cut holes can act as point from which cracks propagates due to temperature gradients and flaws from the cutting process. This also minimizes the leakage of the stacks, as the porous layers are not going all the way to the edge of the stack.

Abstract No. 136

Measurement of effective diffusion for Ni/YSZ material used for SOFC/SOEC with a Wicke-Kallenbach setup and assessment of concentration profiles during CO_2- and co-electrolysis.

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Summary. Measurement of the effective diffusion with a Wicke-Kallenbach setup has been conducted to determine the effective diffusion for the Ni/YSZ electrode. Based on the measurement, the resulting concentration profiles during electrolysis has been modelled. Especially the risk of carbon formation has been investigated.

Abstract. In order to model the gas diffusion in solid oxide cells, the porosity, tortuosity, permeability and pore diameter must be known. The porosity and pore size distribution can easily be measured with mercury intrusion porosimetry [1,2], the tortuosity can be calculated using data obtained with focused ion beam–scanning electron microscopy (FIB–SEM) [3], or from correlations with the porosity [4] and, the permeability can be measured with permeametry where a pressure difference is used to cause a flow [5]. However, in diffusion models the tortuosity is typically used as a fitting parameter and includes not only the pore orientation effects (measured with FIB-SEM), but also the effect of non-cylindrical pores and pores with dead ends [6,7]. To fit the diffusion models it is therefore necessary to measure the effective diffusion [2] or calculate it from polarisation resistance [8].

To directly measure the effective diffusion and subsequently calculate the tortuosity, a Wicke-Kallenbach diffusion cell has been used. The effective diffusion was measured for fuel electrode material supplied by Haldor Topsoe.

Using an extension of a previously reported model for gas diffusion in SOEC cathodes [9], the concentration profiles resulting from the effective diffusion measurement for CO2- and co-electrolysis are reported. The concentration profiles showed that there is a risk of carbon formation via the Boudouard reaction, due to high concentrations of CO, if the operation conditions are not chosen carefully.

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Abstract No. 137

Orbital Physics of Active Perovskites for Oxygen Catalysis

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Summary. In order to find an explanation for the different performance of complex oxides in oxygen electrocatalyis, we perform ab initio calculations to correlate activity in relation to the corresponding magnetic and electronic state. We try to unravel the orbital physics of the transition metals that are particularly relevant to oxygen electro-catalysis.

Abstract. Cobaltites and Manganites are among the most active families of perovskites in oxygen catalysis, in general, with activities comparable to (and in some cases, greater than) noble metals. Activity seems to be related to the paramagnetic nature of the ↑O=O↑ molecule, and with the presence of specific exchange interactions in the catalyst. For example, the catalytic activity of cobaltites in combustion reactions is associated with three conflicting electronic states: low-spin (LS) $t_{2g}^{6}e_{g}^{0}$, high-spin (HS) $t_{2g}^{4}eg^{2}$ and intermediate-spin (IS) $t_{2g}^{5}e_{g}^{1}$; each of these states competing in stability.[1] The electronic structure of the perovskite will depend on the dominant orbital configuration; our recent ab initio calculations try to unravel the orbital physics of the transition metals, particularly relevant in the fundaments of oxygen electro-catalysis.[2]

Our in-depth study of the magnetic structure within the most active Cobaltites for Oxygen Evolution Reaction shows that conflicting orbital interactions between localized spins helps in the extraction of electrons by ferromagnetic interactions: High Spin Entropy.[3][4] On the other hand, the electronic properties of Manganites, good catalysts for the Oxygen Reduction Reaction, agree with polarised density of states, ferromagnetic half-metals, with a Curie temperature above operation conditions: Low Spin Entropy. The implications of such observations are discussed in terms of exchange interactions, because usually in the chemistry of paramagnetic O_2 reactants and products do not preserve spin, and effective catalysts can speed up the reactions if it is able to appropriately use the magnetic degeneracies.

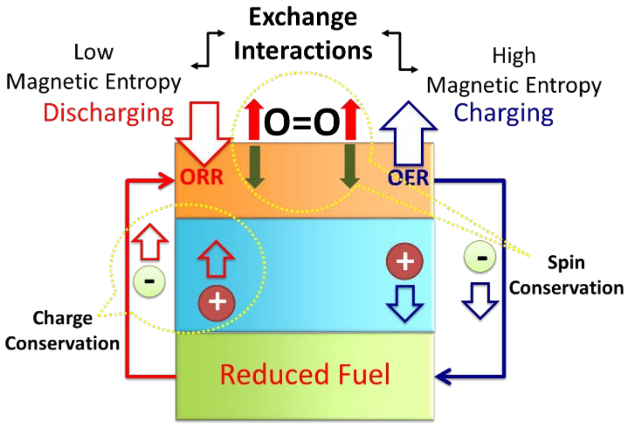

Figure 1. Role of exchange interactions in the design principles of OER and ORR catalysts.

In agreement with the experimental data, we note that in the most active catalysts the electron mobility is linked with high or low entropy per electron. Consequently, we discuss the contribution of the electronic degeneracies, entropy, to the kinetics of OER and ORR on the basis of transition state theory. We thus find that the magnetic phase is actually an important factor in the best ORR catalysts. Our findings can be immediately applied in the fundamental understanding of oxygen electro-catalysis.

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Abstract No. 138

Determining the fracture energy for oxygen electrode and contact layer interfaces in SOECs stacks

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Summary. Interface fracture is a key issue for reliable long-term operation of SOEC stacks. Effective bonding between interconnects and electrodes is required. Conventional interface bonding strength between oxygen electrodes (LSC-CGO) and contact layers (LSC, LSM, LSC-LSM, LNF) were investigated in this study, and a bonding method using CuMn foam showed significant improvement compared with other methods.

Abstract. SOEC stacks have a high market value for converting electricity directly into storable fuel with one of the highest efficiencies among other technologies. It shows a great promise for a highly efficient method for energy conversion and storage. A big challenge for SOEC stack is to achieve high durability and stability under large electrical currents, gas/fuel corrosions, and thermal cycles. This is because in an operational stack, high concentrations of stresses are introduced by temperature gradients and thermal expansions. For stresses perpendicular to the cell planes, the weakest spots in a SOEC stack are at the interfaces between metallic interconnects, ceramic contact layers, and ceramic oxygen electrodes.

In this study, we systematically tested and analyzed the fracture energy for oxygen electrode and contact layer interfaces in SOEC stacks. The tests covered popular contact layer materials including $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC), $(La_{0.8}Sr_{0.2})_{0.98}$ $MnO_{3-\sigma}$ (LSM), LSC-LSM, and $LaNi_{0.6}Fe_{0.4}O_3$ (LNF), as well as oxygen electrode material LSC-CGO. A bonding method using CuMn foam was additionally used and investigated.

The fracture energy release rate was measured by modified 4-point bending method using Charalambides type of geometry, where the fracture energy was calculated from the load-displacement plateau at crack propagation. Also the fracture mechanisms were investigated by microscopy. It was found that chemical bonding and mass diffusion have significant influence to the fracture energy of the interfaces.

A bonding method using CuMn foam showed an improved bonding strength to both the oxygen electrode and interconnects, where the significantly higher fracture energy was obtained. This is explained by the observed effective chemical reaction and bonding.

Abstract No. 139

High temperature electrolyser with proton conducting ceramic tubular cells

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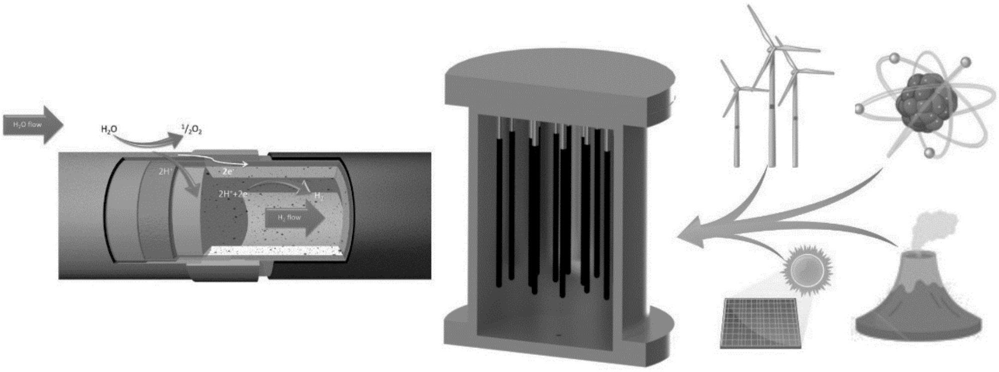
Summary. Multi-tube high temperature electrolyser which allows monitoring and controlling of individual modules at working conditions has been designed. The tubular electrolysis cell comprises a proton conducting electrolyte with LSM/BCZY27 60/40 vol.% anode composite infiltrated with Pr-Ce 50 vol.% nanocatalysts.

Abstract

High temperature electrolysis technology offers high conversion efficiency of renewable and peak electricity to H_2 and may increase performance further by utilising available sources of heat and steam from solar, geothermal, or nuclear plant. In contrary to solid oxide electrolysers (SOECs), which operate at around 800 °C and the hydrogen is produced on the steam feed side, proton conducting electrolysers (PCECs) generate pressurized dry H_2 what significantly enhances total efficiency.

The main objective of ELECTRA project is to develop and demonstrate scalable fabrication of tubular high temperature electrolyser (HTE) cells with proton conducting electrolyte. In order to produce 250 Ln/h of H_2 (pressurized at >10 bara) from 1 kW of electrical power, multi-tube reactor has been designed.



ELECTRA utilises a novel generic tubular module holding single-end closed tubes. The tubular cells are mounted with patented solution allowing then to be inserted, fastened, sealed, monitored and controlled at working conditions of individual tubes, from a cold accessible side. High pressure steam is fed to the outside of each tube, and pure H_2 is collected inside. The electrochemical performance and system durability have been studied by electrochemical impedance spectroscopy (EIS) and gas chromatography methods. The measurements were performed in the temperature range 800 - 600 °C and up to 30 bar of pressure of humidified air (75% of steam).

Related to the anode development, $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) composite material has been deposited on proton-conducting $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ (BCZY27) electrolyte and studied in symmetric cells to investigate the anode microstructure and electrochemical performance. To enhance anode kinetic reaction, the LSM/BCZY27 60/40 vol.% composite was infiltrated with Pr-Ce 50 vol.% nanocatalysts.

Finally, ELECTRA aims to demonstrate proof-of-concept CO_2 and steam co-electrolysis, where compared to SOECs, pressurised steam and CO_2 are fed on separate sides of the cell in the PCEC in co-ionic conduction mode, which may be advantageous for economical syngas production.

Acknowledgements

Spanish Government (SEV-2012-0267 and ENE2014-57651), Polish Government (Diamentowy D12013 003243) and by the EU FP7 Fuel Cells and Hydrogen (FCH) Joint Technology Initiative (JTI) under GA n° 621244 ("ELECTRA").

Abstract No. 140

Specific electrical conductivity in solid and molten CsH_2PO_4 and $Cs_2H_2P_2O_7$ – a potentially new electrolyte for water electrolysis at ~225-400 °C

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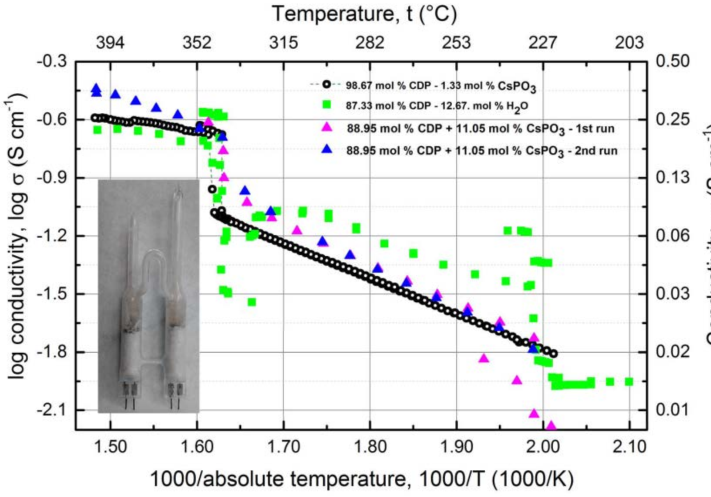
Summary. Conductivity of solid state and molten CsH_2PO_4 was carefully examined in the temperature interval 220 - 400 °C with 2 °C steps and under its own vapor pressure of H_2O in a sealed ampule system. Additionally, conductivities of mixtures composed of CsH_2PO_4 and different contents of water and $CsPO_3$ were examined and compared with values corresponding to pure CsH_2PO_4.

Abstract. An H-cell fabricated from quartz was used to evaluate the conductivity of synthesized CsH_2PO_4 (CDP) and its mixtures with water or $CsPO_3$. The melting point of the CsH_2PO_4 under its own water vapor pressure was determined to be ~345 °C, which was proved by differential scanning calorimetry (DSC), and Raman spectroscopy (RS) analysis, where the latter technique gave information on the different structures of CDP at 3 temperatures: 25 ℃, 250 ℃ and 300 ℃.

During the melting process, the following reactions take place in open air [1-4]:

$$2\ CsH_2PO_4 \leftrightarrow Cs_2H_2P_2O_7 + H_2O \leftrightarrow 2/n\ (CsPO_3)n + 2\ H_2O \quad (n = 1, 2, 3, \ldots.) \qquad (1)$$

Molten CsH_2PO_4 above 347 °C and under its own vapor pressure represents a liquid with a high conductivity of 0.2 S cm^{-1}, and increasing from that temperature it reaches values above 0.25 S cm^{-1} at 400 °C. A jump in the conductivity from below 0.1 S cm^{-1} to 0.25 S cm^{-1} opens new perspectives for possible applications of this electrolyte in energy conversion systems at elevated temperatures. The conductivity data are given as polynomial functions of temperature and composition. The results show that molten CDP has a significant potential as electrolyte in intermediate temperature electrolysis systems, essentially in those, where an excess of water is unavoidable. X-ray diffraction (XRD), differential scanning calorimetry (DSC), and Raman spectroscopy (RS) analysis were used to identify and characterise the formed compounds. The figure shows the conductivity results obtained. The photo insert shows the ampoule with the frozen salts after end of measurements.



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Abstract No. 141

Oxygen Evolution Reaction Performance of $PrBaCo_2O_{5+\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{2+\delta}$ in Carbonated Electrolyte for Water Electrolysis

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Summary. OER activities and stabilities of reputable perovskite oxides, $PrBaCo_2O_{5+\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{2+\delta}$, are assessed under a condition that better resemble practical application operation, which the electrolyte is in a quasi-neutral pH. Observations are explicated in thermodynamic standpoint based on DFT calculations.

Abstract. Development of energy storage systems is absolutely necessary to mediate the variable nature of energy generation from renewable resources in the course of supplanting fossil-fuel based energy technologies. The development of water electrolysis technologies has been the centre of the spotlight owing to its capability to store a large amount of energy. The water splitting reaction which underlies the performance of water electrolysis requires effective electrocatalysts to facilitate efficient oxygen evolution reaction (OER), which suffers from a high overpotential. Among cost viable electrocatalysts, perovskite oxides composed of abundant transition metals, in particular $PrBaCo_2O_{5+\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{2+\delta}$, are gaining much attention for their high activities toward OER in alkaline water electrolyze. Up to date, however, only their performance under alkaline conditions (pH 13 – 14) have been extensively studied without considering the pH changes toward a neutral value upon the contact of carbon dioxide from the atmosphere. In this investigation, we first compare and assess the OER activities of nano-scaled $PrBaCo_2O_{5+\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{2+\delta}$ prepared via flame synthesis to those prepared via a conventional sol-gel method in alkaline conditions. Thereafter, we assess the OER activities of electrocatalysts prepared via flame spray synthesis under an intentionally carbonated environment to understand their electrocatalytic features under conditions that have better resemblance of a practical operation. We further elucidate on their electrocatalytic performances with DFT based Pourbaix diagrams, which provides further insights into their thermodynamic stabilities in varying pH scale. Overall, we highlight the importance of understanding OER activity under a practical operating condition and evaluating the electrocatalytic performance on the basis of thermodynamic stability.

Abstract No. 142

The catalysis of the electrolytic production of H_2O_2

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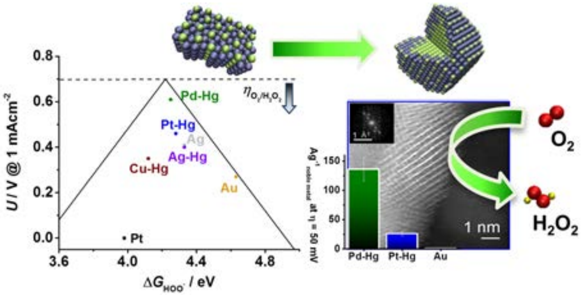
Summary. A survey of electrolytic H_2O_2 production: acid versus basis and model studies versus real devices.



Left: Experimental measurement of potential required for a partial current density for H_2O_2 production of 1 mAcm^{-2}, as a function of HOO* binding energy. Right: Mass activity of Pd-Hg/C and Pt-Hg/C nanoparticles, relative to Au/C.

Abstract. H_2O_2 is a valuable commodity chemical, with an annual global production exceeding 3 million tons. At present, it is synthesised by the anthraquinone route, a complex, batch process, conducted in large scale facilities from H_2 and O_2. H_2O_2 is transported high concentrations, although the end users often only need low concentrations. On-site electrolytic production of H_2O_2 would mitigate current safety concerns related to its transportation at high concentrations. Moreover, it would be more inexpensive than the anthraquinone process and circumvent the need for molecular H_2. The viability of electrolytic H_2O_2 production is dependent on the catalyst at the cathode: not only should it exhibit high activity, but also high selectivity to H_2O_2 over H_2O.

We discovered a new set of electrocatalysts that showed an unprecedented combination of these two desired properties: alloys of Pt, Ag or Pd with Hg.[1, 2] In our earlier papers, we tested these catalysts using rotating ring disk electrode (RRDE) experiments in 0.1 M $HClO_4$.[1, 2] In the current contribution, we also test these compounds in 0.1 M KOH. We find that both the activity and stability follow vastly different trends from acid. We will also compare performance of these catalysts in a RRDE assembly to a real device based on a polymer electrolyte membrane electrode assembly.

Our studies incorporate electrochemical measurements, ultra-high vacuum based surface science methods, electron microscopy and density functional theory calculations.

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Abstract No. 143

Bioreactor with in situ water electrolysis for protein production

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Summary. Water electrolysis can be applied in cultivation of hydrogen-oxidizing bacteria by performing electrolysis directly in a bioreactor. The bacteria use hydrogen as an energy source and accumulate CO_2 into biomass. Bacterial biomass has high protein content and it could be used as an ingredient in animal feed or human food.

Abstract. Hydrogen-oxidizing bacteria (e.g. *Cupriavidus necator*, *Rhodococcus opacus*, and *Hydrogenobacter thermophilus*) are capable of autotrophic growth by using hydrogen as an electron donor and oxygen as an electron acceptor to fix carbon dioxide to build up their biomass [1]. Hydrogen and oxygen can be supplied for the bacteria by performing electrolysis directly in the bioreactor, where the bacteria are cultivated. In situ water electrolysis allows efficient substrate utilization by the bacteria, due to better mass transfer of gas to aqueous solution, than in the case of external gas supply. Also flammable mixtures in the reactor headspace can be avoided. In addition to H_2 and O_2, CO_2 and nutrients needed for growth are supplied to the reactor.

Bacterial biomass has high protein content (50–83 %), and it can be used as an ingredient in human and animal nutrition. An electricity-to-biomass efficiency of 54 % has been achieved by applying direct electrolysis in a bioreactor, which would correspond to approximately 10 % solar-to-biomass efficiency (assuming 18 % efficiency for photovoltaics) [2]. For comparison, the annual average efficiency of crops do not typically exceed 1 %, and efficiencies during the growing seasons can reach only 3.5–4.3 % [3]. Bacteria have also very fast growth rate. Their biomass doubling time is typically 20-120 minutes, while e.g. soybean has doubling time 1–2 weeks.

Due to high conversion efficiency and fast growth, bacterial protein production requires significantly less water and land area compared to the conventional protein sources. By applying direct air capture (DAC) of CO_2 by adsorption/desorption process, bacterial protein can be produced basically only from electricity, air water and some nutrients, making the production very independent on place and climate. The concept is still in research stage, but in the future, it may provide a solution to environmental impacts of conventional agriculture, such as greenhouse gases, fresh water use, land use, and pollution caused by fertilizers and pesticides. Optimization of electrode materials, cultivation medium and conditions, bioreactor construction, and process modeling and control are under research by the authors.

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Abstract No. 201

Development of oxygen evolution electrocatalysts and electrodes for High Temperature and Pressure Alkaline Electrolysis Cells (HTP-AEC)

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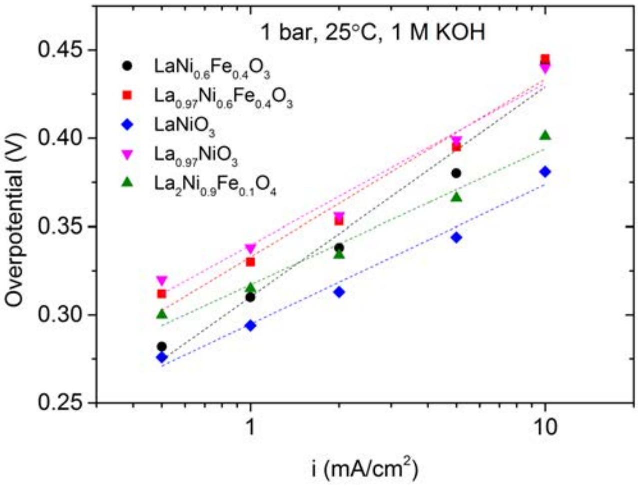
Summary. A new alkaline electrolysis cell concept, HTP-AEC, with cells operated at ~ 200°C and ~ 45 bar in concentrated KOH (45 wt%), offers the potential of a 10-fold increase in current density and of increasing the electrical efficiency.

Abstract. A new alkaline electrolysis cell concept with cells operated at high temperature (~ 200°C) and pressure (~ 45 bar) in concentrated KOH (45 wt%), offers the potential of a 10-fold increase in current density while increasing the cell efficiency as well. One challenge lies in identifying ceramic materials, which are electrocatalytically active for the oxygen evolution reaction and chemically stable under operation. Perovskite type materials, consisting of La, Ni (and Fe), with compositions $LaNi_{0.6}Fe_{0.4}O_3$, $La_{0.97}Ni_{0.6}Fe_{0.4}O_3$, $La_2Ni_{0.9}Fe_{0.1}O_4$ and a multiphase material containing $LaNiO_3$, have been identified as potential candidates for the oxygen electrode. The compositions are $LaNi_{0.6}Fe_{0.4}O_3$, $La_{0.97}Ni_{0.6}Fe_{0.4}O_3$, $La_2Ni_{0.9}Fe_{0.1}O_4$ and a multiphase material containing $LaNiO_3$. Their electrocatalytic activity has been measured at STP in 1 M KOH showing similar performance as state-of-the-art electrocatalysts, such as IrOx, $Ni_{1-y}Fe_y O_x$, and $PrBaCo_2O_{5+x}$. Their chemical stability, tested at 200°C, 15 bar pressure in 45 wt% KOH, was found to be inadequate. $LaNi_{0.6}Fe_{0.4}O_3$ was selected for processing porous oxygen electrodes, aiming to reveal the microstructure-performance correlations that will lead to electrode optimization. A microstructurally optimized oxygen electrode will be integrated into our alkaline electrolysis cell concept. The project, hence, aims at demonstrating the feasibility of this cell concept by full cell testing at 5x5 cm^2 cell size.



Material	b (V/dec)	η (V) @ 10 mA/cm^2
$LaNiO_3$	0.079	0.38
$La_{0.97}NiO_3$	0.092	0.44
$LaNi_{0.6}Fe_{0.4}O_3$	0.12	0.44
$La_{0.97}Ni_{0.6}Fe_{0.4}O_3$	0.10	0.45
$La_2Ni_{0.9}Fe_{0.1}O_4$	0.077	0.40
IrO_x [1]	-	0.32
$Ni_{0.9}Fe_{0.1}O_x$ [2]	0.030	0.34
$PrBaCo_2O_{5+x}$ [3]	~0.07	~0.38

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Abstract No. 202

Hydrogen production from photovoltaic via “zero gap” alkaline electrolysis

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Summary. The water electrolysis connected with the renewably energy sources represents a promising way of hydrogen production without CO_2 footprint. However, currently used alkaline electrolyzers are not suitable for intermittent operation required for this type of application. The concept of zero-gap alkaline electrolysis with ion conduction membrane appears suitable for this application.

Abstract. The process of alkaline water electrolysis is one of the candidate technologies for producing hydrogen on a large scale from renewable energy, because it does not require application of precious metals, like platinum, ruthenium etc., as compared to proton exchange membrane electrolysis. However, this system has limited ability to respond to fluctuations in electrical power, which is commonly required in conjunction with renewable energy sources. The paper deals with the design of an innovative concept of alkaline electrolysis which is able to overcome this restriction. The design of the electrolyzer is based on a zero gap bipolar cell construction. For achieving this target it was necessary to develop a non-platinum electrocatalyst, which is necessary to accelerate electrode reactions, and an alkaline polymer material, which is able to fulfil the role of an anion conducting electrolyte. Also, structure and geometry of the individual electrolytic cell were designed and optimized.

The final electrolytic stack has the electrical power input of 1 kW and operating conditions were 60 °C, 4 barg and 10 - 30 wt% solution of KOH as electrolyte. The cells were made of hydroxide ion conducting membranes based on polyethylene, and nickel foam as electrodes with different electrocatalysts for both anode and cathode side. The different types of membranes were tested. In general, the performance of laboratory membrane was similar to an industry membrane at 30 wt% KOH electrolyte; nevertheless, at 10 wt% KOH electrolyte the laboratory membrane achieved considerably higher performance in comparison with the industry membrane. The concept was verified in real operational conditions; the results are shown in figure 1. The alkaline electrolyzer responds very quickly to the fluctuations in electric power supplied by a photovoltaic plant. The suggested design of electrolyzer is suitable for production of hydrogen from renewable sources.

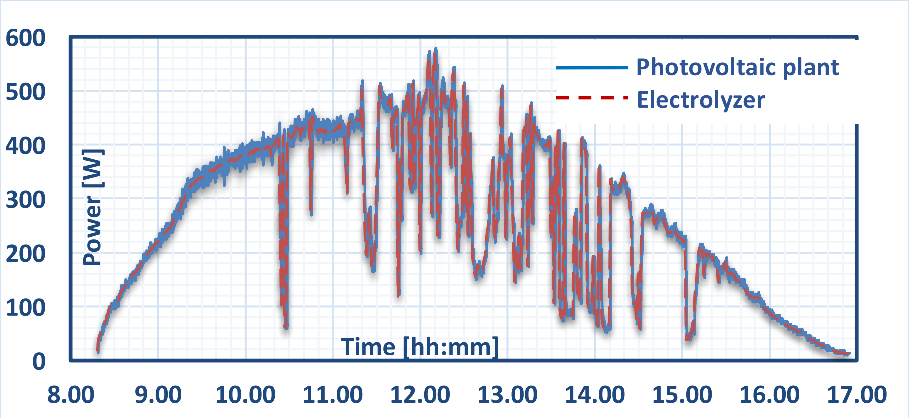

Fig. 1 Real performance of alkaline electrolyzer operated according to the power of photovoltaic panels during the day

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Abstract No. 203

Mathematical model and experimental validation of a 15-kW alkaline electrolyzer

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Summary. The objective of this work is to develop a semi-empirical mathematical model that predicts the voltage and the Faraday efficiency of an electrolyzer as a function of the current. This model has been fitted with the experimental data obtained with a 15 kW alkaline electrolyzer at different temperatures, pressures and electrolyte concentrations.

Abstract. The electrochemical behaviour of an electrolyzer can be modelled using a semi-empirical current-voltage model. One of the most widely used models is the one proposed by Ulleberg [1], which describes the voltage of an electrolyzer according to the parameters “s” (V) and “t” (m^2/A) related to activation overpotentials and “r” ($\Omega \cdot m^2$) for the ohmic overpotentials. However, in this model the parameters only depend on the temperature (T). In order to obtain a wider model, the equation has been modified to include pressure (p) and electrolyte concentration (M). For this purpose, two additional parameters have been incorporated in the model: “j” and “d” ($\Omega \cdot m^2$) which represent the variation in the ohmic overpotentials according to the electrolyte concentration and pressure, respectively.

$$U = U_{rev} + s \cdot log[t \cdot i + 1] + (r + j + d) \cdot i \Longrightarrow$$

$$U = U_{rev} + s \cdot log[(t_1 + t_2 \cdot T^{-1} + t_3 \cdot T^{-2})i + 1] + (r_1 + r_2 \cdot T + j_1 + j_2 \cdot M + j_3 \cdot M^2 + d_1 + d_2 \cdot p) \cdot i$$

Regarding Faraday efficiency, it has been modelled using the equation proposed in [1], including a linear relation for temperature (“f_1”, “f_2”). The pressure and electrolyte concentration have not been included due to its slight influence:

$$\eta_F = [f_1 + i^2]^{-1} \cdot i^2 \ \cdot f_2 \Longrightarrow \eta_F = [(f_{11} + f_{11} \cdot T) + i^2]^{-1} \cdot i^2 \cdot (f_{21} + f_{22} \cdot T)$$

Figure 1. 15-kW electrolysis test bench

A 15-kW alkaline electrolysis test bench developed by CNH2 [2] has been used for carrying out the experimental tests (Figure 1). For this purpose, a 12-bipolar cell stack of 1000 cm^2 surface area with a nominal production rate of 2 Nm^3/h hydrogen (@ 400 A) has been characterized at different temperatures (55, 65, 75 °C), pressures (5, 7, 9 bar) and electrolyte concentrations (28, 35, 42 % w/w KOH). In each of these tests the polarization curve, the purity of the gases produced and the Faraday efficiency have been studied. A standard procedure has been followed to ensure the repeatability and reproducibility of the experimental data.

The model constants have been calculated by means of a non-linear regression using MATLAB, according to a previously established procedure [3]. To do this, the experimental data obtained for the polarization curve and the Faraday efficiency have been used. The prediction accuracy of the model can be verified by comparing simulated and measured values for the polarization curves at different temperatures, pressures and electrolyte concentrations (see Figure 2). Also the RMS error has been evaluated with a result of 6.18 mV (voltage cell) and 0.53% (Faraday efficiency).

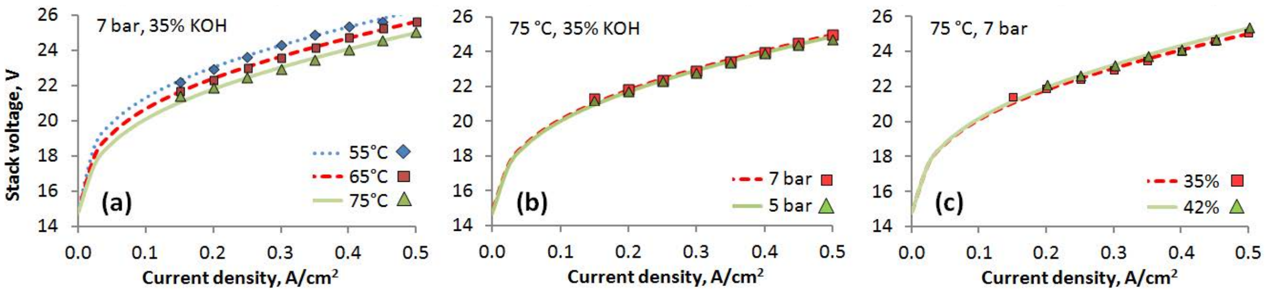

Figure 2. Calculated (line) vs. measured (dot) voltage at different temperatures (a), pressures (b) and electrolyte concentrations (c)

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[1] Int. J. Hydrogen Energy 2003 28 pp.21; [2] M. Sánchez et al. Iberconappice. Barcelona 2014; [3] Int. J. Hydrogen Energy 2014 39(25) pp. 13063

Abstract No. 204

Activity of plasma vapour deposited $Pt_xNi_yAl_z$ as anode electrocatalyst for (membraneless) alkaline water electrolysis

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Summary. $Pt_9Ni_{56}Al_{35}$, in the form of a plasma vapour deposited (PVD) thin film, greatly enhances the oxygen evolution reaction (OER) in alkaline media on both a laboratory scale (deposited onto glassy carbon disk inserts) as well as on a pilot scale that consists of a divergent electrode flow-through (DEFT™) membraneless electrolyser.

Abstract. The two predominant water electrolysis technologies are alkaline electrolysis (AEL) and acid or proton exchange membrane electrolysis (PEMEL). AEL is the more mature technology and is the current standard for large industrial scale production of hydrogen (in the MW range). It is a fairly robust technology and commonly makes use of nickel coated steel electrodes. AEL technology, however, suffers from low current densities and a limited ability to respond to fluctuations in electrical input, which is crucial when trying to integrate renewables such as wind and solar. PEMEL, on the other hand, can operate at higher current densities, but it comes at a huge cost as the electrodes predominantly contain noble metals such as platinum, iridium and ruthenium. It is as a result of this fact that PEMEL does not operate in the MW range and is predominantly employed in the decentralised onsite production of hydrogen, such as hydrogen refuelling stations. Cost effective and high(er) efficiency AEL water splitting technology is therefore needed that operates at high(er) current densities, but without high noble metal content.

While the current OER electrocatalysts consist of pure metal such as Ni, or exotic materials such as RuO_2 and/or IrO_2, our newly developed OER electrocatalyst consists of a thin metal film, in the form of highly active $Pt_9Ni_{56}Al_{35}$, which is co-deposited onto the electrode by means of plasma vapour deposition. On glassy carbon disk inserts $Pt_9Ni_{56}Al_{35}$, as well as other $Pt_xNi_yAl_z$ ratios, outperform pure Ni, Pt and Ni_yAl_z (Figure 1). On a pilot DEFT™ membraneless alkaline water electrolysis facility $Pt_9Ni_{56}Al_{35}$ increases current density between 50 and 100% (Figure 2).

Figure 1 Linear polarisation scans of PVD electrocatalysts on glassy carbon (0.1M KOH)

Figure 2 Current densities on a DEFT™ membraneless electrolyser for different electrocatalysts

Abstract No. 205

Small-scale systems for alkaline water electrolysis

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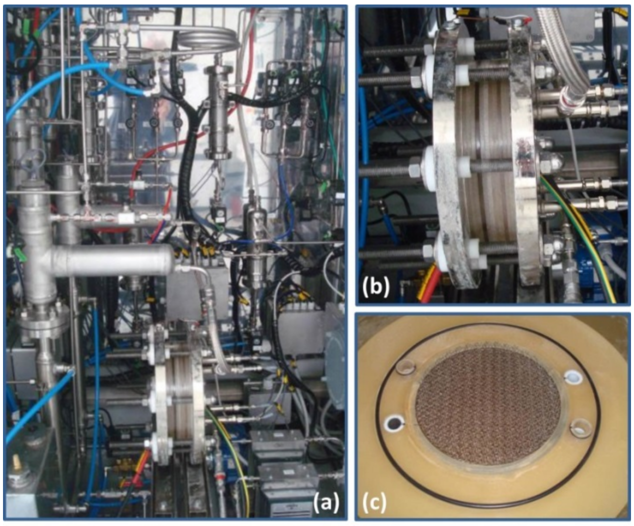
Summary. Due to the increasing amount of renewable electricity, water electrolysis attracts accretive interest as an environmental friendly hydrogen production technology. Besides polymer electrolyte membrane electrolysis (PEME), alkaline electrolysis (AE) is of high interest for megawatt systems due to its robust quality and long-life experience.

Abstract. In order to make alkaline electrolysis more attractive, the energy consumption for water splitting in alkaline electrolysis has to be reduced and the power density increased. While the electrocatalytic activity of electrode materials is frequently studied in this context, system parameters like operation temperature, working pressure, cell design and process parameters like electrolyte flow or gas bubble management are also of high importance for improving the electrolyser efficiency. Experimental studies on such parameters are scarce, as laboratory equipment for realistic alkaline electrolysis conditions is hardly available.

For these reasons we have acquired two different small-scale water electrolysis systems: A lab-pilot electrolyser VOLTIANA, based on a stack of 5 to 10 cells with 500-1000 cm^2 active area, and a custom-made laboratory electrolyser Electra IV, based on one cell of 20 cm^2. We discuss how these electrolysers can be used for material testing and process optimisation of both, system properties and fundamental studies. We present results applying standard electrodes and cost-effective composite diaphragms. The diaphragms are prepared in-house by a phase inversion process and are composed of polysulfone (PSF) as binder combined with barite ($BaSO_4$) as particle filler.



Lab-pilot electrolyzer VOLTIANA: Electrolyzer cabinet (a), 7 cell stack (b), and single cell design (c).

Laboratory electrolyser Electra IV with cell compartment.

Abstract No. 206

New separator concepts for a radical improvement of the gas quality in alkaline water electrolysis (AWE)

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Keywords: Advanced Alkaline Water Electrolysis, AWE, Hydrogen generation, Technology, Material

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Summary. Poor gas quality at low current density and at very high pressure is a major drawback of Alkaline Water Electrolysis (AWE). This limitation can be substantially mitigated with a new separator membrane concept especially tailored for this purpose.

Abstract. Advanced Alkaline Water Electrolysis technology (AWE) using thin separator has a lot of advantages over PEM electrolysis technology: it is well established, with systems up to MW scale already commercial and it is the cheapest technology. However, the AWE technology suffers from poor gas quality at a current density below 0.2 A/cm² and/or at very high pressure (above 50 bar).

Vito is developing new separator concepts to solve this disadvantage. Different approaches are being used. One of the new separator membrane concepts recently developed is the e-by-pass separator. It features an internal electrolyte circulation (an electrolyte bypass).

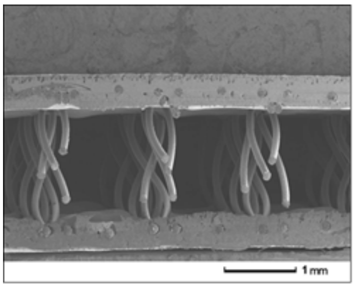

Figure 1: cross-section of the double-layer "e-bypass" separator

This e-bypass separator is constructed around a dedicated 3D-textile structure (a weft-type of PPS spacer-fabric), which is used in the same time as a support structure and as a spacer material. This PPS spacer-fabric is coated on its both sides with a Zirfon® separator layer, resulting in a "double-layer separator" which comprises the afore mentioned internal electrolyte channel. The internal channel forms a third compartment in the electrolyser between the anolyte and the catholyte compartments. With this separator concept and novel cell design (adapted to improve mass transfer) HTO values below 0.1% have been achieved at 0.150 A/cm² ([1]) vs. 0.8% HTO for state-of-the-art AWE.

Other separator concepts are being engineered, also targeting HTO values below 0.8%.. The presentation will give an overview of the potential for improvement of gas quality with these novel separator concepts, as well as their limitations. Preliminary results and research prospects will be discussed as well.

Acknowledgements: This work has been partly carried out within the project Elyntegration. This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 671458. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and Spain, Belgium, Germany, Switzerland. The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° [278732], project RESelyser. The authors gratefully acknowledge fruitful discussions with Elyntegration project partners: FHA (Spain), IHT (Switzerland), Fraunhofer IFAM (Germany), INYCOM (Spain), IAEW (Germany); and with RESelyser project partners: DLR, Hydrogenics Europe (Belgium) and DTU (Denmark).

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[1] Public final report RESelyser, http://www.fch.europa.eu/project/hydrogen-res-pressurised-alkaline-electrolyser-high-efficiency-and-wide-operating-range

Abstract No.207

Control and energy efficiency of alkaline and PEM water electrolyzers in renewable energy systems

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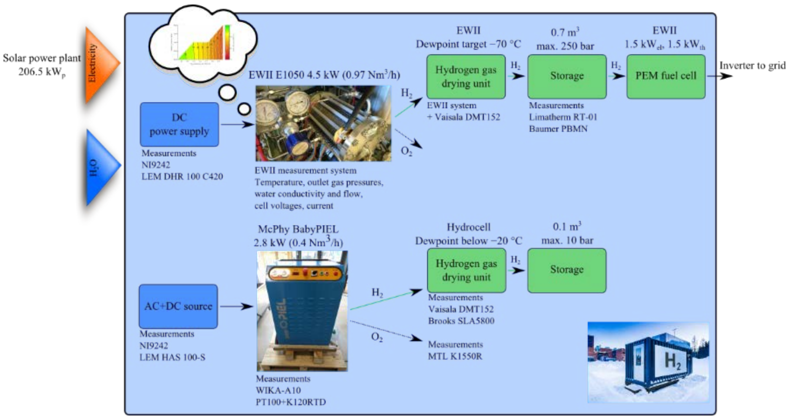
Summary. Water electrolyzers require DC power and their operation depends on electric conditioning. Experimental setup including a small-scale alkaline and PEM electrolyzer is built in order to identify factors from the viewpoint of power electronics affecting the specific energy consumption of these two water electrolysis processes.

Abstract. In order to reach a net zero-emission society, the whole energy system—including electricity, transportation, and direct industrial fuel use—has to be restructured. This would practically require CO_2 free power generation, bridges between different areas of energy systems, and efficient means of energy storage. To support the global energy transition, renewable hydrogen and recycled CO_2 are required. Therefore, the technical and economic performance of water electrolysis processes will be in a key role.

The Faraday efficiency is determined as a ratio of the actual and ideal hydrogen production rates; the ideal hydrogen production is proportional to the mean of the current supplied to the electrodes, while the actual hydrogen production rate might be lower due to process inefficiencies. The Faraday efficiency may decrease notably from unity due to hydrogen gas crossover into the anode compartment, stray currents, or reduction in the active cell area as the cell ages. The essential difference between PEM and alkaline water electrolyzers is the lack of liquid electrolyte, which enables the more compact system design for PEM electrolyzers. The compact design and structure allows PEM electrolyzers to operate at differential pressures, where the cathode compartment pressure can be maintained at notably higher pressures, e.g. by a factor of 25. Direct production of high-pressure hydrogen is tempting, since the volumetric energy density of hydrogen gas is low and the main synthetization routes for hydrogen and carbon (di)oxide, such as chemical methanation or the Fischer-Tropsch process, require elevated pressures. However, the differential pressure operation further induces the adverse hydrogen gas crossover and sets a limitation on the minimum safe load for the electrolyzer.

Industrial water electrolyzers, a category dominated by the conventional alkaline technology, are characterized by high DC currents. Therefore, the rectifiers in conventional industrial water electrolyzers are typically based on thyristors and diodes, which switch according to the line frequency. Use of more modern power electronic converters could decrease the harmonic content and the resultant heat losses introduced by line frequency switching. However, semiconductors using forced commutation would require modular conversion structures to moderate the supplied current to suitable levels. The effect of current and voltage harmonics on the specific energy consumption of water electrolysis processes—a quantity, where Faraday efficiency should be included—is yet to be thoroughly studied. Line frequency switching in the power supply also exposes the electrolyzer stack to continuous highly dynamic operation.

A Power-to-Hydrogen laboratory setup is built in a shipping container to study both the alkaline and PEM water electrolysis processes. The electrolyzers employed are a 2.8 kW BabyPIEL alkaline electrolyzer manufactured by McPhy and a 4.5 kW PEM electrolyzer by EWII. The studied PEM electrolyzer operates at anode and cathode compartment pressures of 150–250 kPa and 1500–5000 kPa, respectively. The hydrogen laboratory setup is also virtually connected to a 206.5 kW_p solar PV power plant to study control optimization strategies from both electricity production and stack performance point of view. Measurements are stored using a Windows PC running LabVIEW.



Abstract No. 208

The effect of line frequency and forced commutation on the losses of the electrolyzer stack and the power supply unit

Vesa Ruuskanen[a], Joonas Koponen[a], Antti Kosonen[a], Markku Niemelä[a] and Jero Ahola[a]

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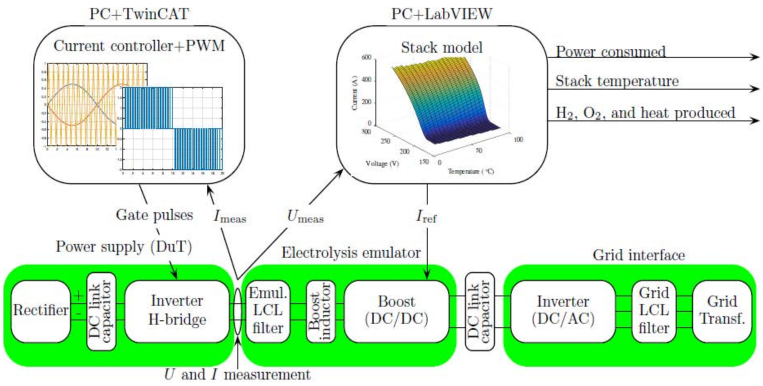
Summary. To study the effect of power quality on the electrolyzer stack performance, a programmable DC+AC power supply unit using a commercially available frequency converter hardware is implemented. A power-hardware-in-loop (PHIL) simulator with nominal current of 405 A is built to test industrial-scale electrolyzer supply power electronics under realistic load conditions.

Abstract. Owing to the requirement for high DC currents, the rectifiers in conventional industrial water electrolyzers are typically based on thyristors and diodes. However, switching according to the line frequency generates high amplitude harmonics to the supplied current and voltage. The harmonics generate additional heat losses in the water electrolysis process, and can cause premature aging of the electrolyzer stack. Using passive filters, especially on the MW scale, can be unfavorable because of the high amplitude and low-frequency harmonics introduced by the rectification. Application of more modern power electronic converters may be beneficial, but would require modular conversion structures to share the supplied currents to suitable levels for semiconductors using forced commutation.

A transistor-based power supply for water electrolyzer system is developed to add the desired AC frequency content to the electrolyzer stack supply voltage. The power supply is based on a commercially available industrial three-phase frequency converter. The inverter is equipped with a modified controller board allowing custom pulse-width modulator (PWM) implementation and high bandwidth voltage/current reference tracking through EtherCAT fieldbus interface. The load is connected between two inverter phase legs forming an H-bridge to allow three voltage levels (0, +U_{DC}, and -U_{DC}). The currents of inverter legs are used as a feedback signal for a current controller setting the DC current to a desired value. At the same time, voltage harmonics are added directly to the controller output voltage reference signal.

The voltage waveforms, emulating pure DC supply and line frequency switching power electronics with high harmonic content are generated to study the effect of the frequency content of DC power on the performance of the electrolyzer stack. The stack efficiency of the Baby McPhy alkaline electrolyzer, with hydrogen production capability of 0.4 Nm^3 and the maximum electrical power consumption of 2.8 kW, is measured. The typical DC current and voltage values of the electrolyzer are 35 A and 65 V.

A PHIL simulator is implemented using commercially available water cooled converters to fast and safely test electrolyzer power supply electronics. The PHIL simulation enables testing of industrial scale power electronics under realistic load conditions emulating the different electrolyzer stacks without hardware changes. The PHIL simulator is capable of handling continuous current up to 405 A and more than 600 V of voltage, producing a power of 250 kW. The PHIL simulator is modular and can be divided into three operational parts.



The power supply module is the actual device under test (DuT) supplying DC current to the electrolyzer. The electrolyzer emulator acts as a variable impedance to control the emulator interface current based on the measured electrolyzer interface voltage. The emulator has a boost converter and an LCL filter between the boost converter and the power supply unit. The grid interface returns the electric energy safely back to the grid.

Abstract No. 209

Hydrogen production as a part of P-to-X system

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Summary. PEM electrolyser is tested in a P-to-X system, where electricity is produced from solar PV, CO_2 captured from air, and the hydrogen and CO_2 are supplied to a Fischer-Tropsch (FT) reactor. The pilot system set limitations for the dynamics, pressure levels, production rate, and storage used in hydrogen production of a PEM electrolyser.

Abstract. EU has set targets for 2050 to cut carbon emissions to 80% below 1990 levels in the EU. To achieve this stringent target, the whole energy system shall be restructured so that it is more based on renewable electricity. Depending on the local conditions renewable energy production based on solar and wind power may become one of the key technologies enabling this change. In this case, we need an efficient means of energy storage as well as a bridge between electricity and the transportation fuel sector. This link can be realized through a hydrocarbon acting as an energy storage. In the future, the carbon is recycled and it can be captured back to fuels. “Re-carbonized” energy system in 2050 is illustrated in Fig. 1.

Fig. 1. “Re-carbonized” energy system.

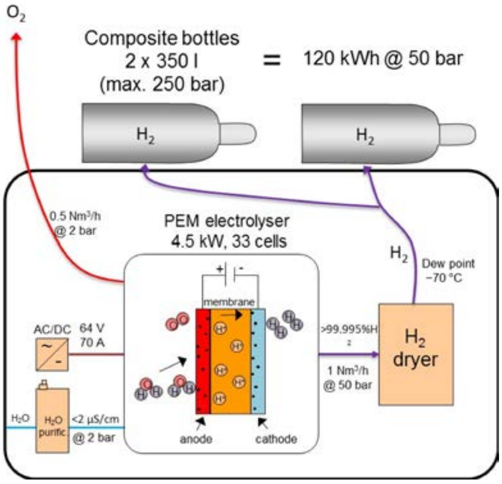

Fig. 2. PEM electrolyser container.

Power-to-X concept arise as a synergic solution for storing the energy from intermittent renewable energy sources such as wind and solar, and for CO_2 mitigation. The electrical energy produced by these energy sources is converted to hydrogen through electrolysis of water, which can be further converted to carbon based chemicals. Electric power can be converted to several products collectively called as Power-to-X, in which “X” can refer to gas or liquid depending on the applications. The combination of renewable electrical and heat power and captured CO_2 as inputs for the PtX could lead to a potentially carbon neutral fuel cycle, and truly sustainable synthetic fuels.

The pilot demonstration system to be built consists of four sea containers and a solar power plant. Each container includes individual sub-systems. The containers include hydrogen production based on PEM water electrolyser technology, a direct air capture (DAC) system, synthesis, and buffer storage systems. These are connected together to form an energy conversion system that can be utilized for example as an SNG filling station.

The hydrogen container includes a 4.5 kW PEM electrolyser (33 cell stacks) with additional devices (a power supply, water purification, a hydrogen dryer, two 350 l composite bottles for hydrogen storage) that are necessary from the operation point of view. The schematic of the container is illustrated in Fig. 2.

Abstract No. 210

Detection and modelling of hydrogen crossover in PEM electrolysers using EIS

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Summary. We investigate hydrogen crossover in a PEM electrolyser with varying pressure difference. EIS shows pseudo-inductive behaviour in the low frequency range. We use surface relaxation impedance to model the pseudo-inductive effect. We find evidence of relation between surface relaxation and hydrogen crossover.

Abstract. Detection of hydrogen crossover in proton exchange membrane (PEM) electrolysers, utilizing electrochemical impedance spectroscopy (EIS) has been scarcely studied, despite having a potentially measurable effect. In this work, we study the hydrogen crossover as a function of pressure difference, from 0 to 9 bar, with a membrane electrode assembly (MEA) made of Nafion 115. The EIS was carried out at 1.5 Acm-2 and 65°C. We find a low frequency pseudo-inductive behaviour, attributed to a competition between hydrogen oxidation reaction (HOR) and oxygen evolution reaction (OER), the former fuelled by hydrogen crossing over from the cathode to the anode. We modelled the competition using surface relaxation impedance, having two components: resistance and time. The probability of competition increases with hydrogen crossover rate, detected in EIS spectra as a rise in the low frequency pseudo-inductive behaviour, and it was confirmed by a proportional relationship between surface relaxation resistance and hydrogen crossover rate.

Abstract No. 211

Demonstration of Impedance Spectroscopy as a Method to Evaluate Losses of Polymer Electrolyte Membrane Electrolysis Cells during Water Electrolysis

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Summary.

Electrochemical impedance spectroscopy (EIS) is in this talk demonstrated as a tool to investigate processes contributing to limitations in the polymer electrolyte membrane electrolysis cell (PEMEC) performance during electrolysis of water at ambient pressure and at 61 ˚C. A hypothesis describing the processes limiting the cell performance is suggested based on the EIS measurements, cyclic voltammetry and iV-characteristics.

Abstract.

In combination with other techniques such as scanning electron microscopy, cyclic voltammetry or XPS, just to mention a few examples, electrochemical impedance spectroscopy is a valuable electrochemical method used to characterize processes contributing to impedance losses in electrochemical cells.

The technology has successfully been demonstrated on solid oxide cells, but literature resolving impedance spectra of PEMECs is sparse. This presentation demonstrates the experimental approach ADIS (Analysis of Differences in Impedance Spectra) (Jensen et al., 2007) known from solid oxide cell research to resolve the impedance of operating PEMECs. The EIS results, some of which are shown in figure 1, reveal two dependent processes with summit frequencies of approximately 0.4 and 100 Hz significantly contributing to the overall performance loss of the operating PEMEC. Cyclic voltammetry and iV-characteristics measured on the cells are accompanying the EIS measurements and a hypothesis trying to explain the observed electrochemical results of the three methods is given.

Reference.

S. H. Jensen et al. (2007). A Method to Separate Process Contributions in Impedance Spectra by Variation of Test Conditions. *Journal of The Electrochemical Society*, 154 (12), B1325-B1330.

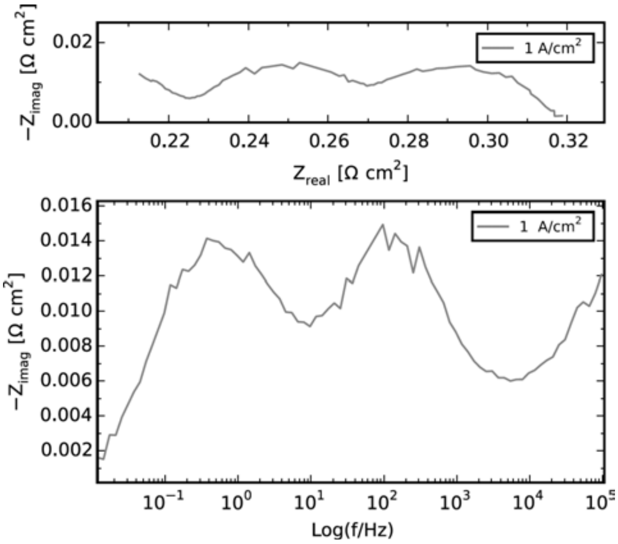

Figure 16. Electrochemical impedance data obtained on a PEMEC operating at ambient pressure, 61 ˚C and 1 A/cm^2 represented in a Nyquist plot (upper graph) and in a Bode plot (lower graphs).

Abstract No. 212

Engineering of high temperature PEMWE

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Summary.

High temperature PEMWE is optimized, in engineering manner, in term of operation condition, current collector, and flow field pattern. Electrochemical characterization reveals that these engineering parameter impact on overpotential through water behaviour in cell, and an optimized pair of the parameter can reach 1.69@2A/cm^2, 120 °C, 0.3 MPa.

Abstract.

High temperature operation is a possible solution to reduce the cost of PEMWE. Increasing temperature generally results in a decrease of activation overpotentials, especially in oxygen evolution reaction process. Less overpotential introduced by raising temperature enables to operate PEMWE under a high current density condition with smaller amount of catalyst, resulting in less cost. However, as a trade-off, the high temperature operation tends to cause dehydration of polymer electrolyte membrane (PEM), and raises ionic resistance (ohmic resistance), resulting in decreasing the performance of PEMWE.

This study elucidates overpotential in PEMWE under high temperature condition with changing operation parameters and embedded components, and challenges to reduce electrolysis voltage. In addition to the ohmic overpotential directly caused by the PEM dehydration, the other overpotential, such as activation and concentration overpotential, is carefully addressed with electrochemical characterization. Changing operation parameters, such as pressure and flow rate of supplied water, has effect on the water behaviour and overpotential, and adequate choice of parameters to suppress the overpotential is explored. Also, different structures of current collector and flow field pattern, which is expected to change the water behaviour, are embedded into a PEMWE cell, and try to minimize electrolysis voltage and to maximize electrolysis performance.

On the effect of operation parameters on electrolysis performance, electrochemical characterization reveals that simply elevating temperature causes a significant increase of concentration overpotential and a rather small increase of ohmic overpotential. In addition to increasing water flow rate as usually treated, raising operating pressure is found to suppress the concentration overpotential. This finding suggests that coexistence of vapour and liquid phases in cell by increasing operating pressure is key when operation temperature is elevated.

The structure of anode current collectors (ACC) are optimized to minimize overpotentials. Hydrophilicity (contact angle) and thickness of the ACC impact the electrolysis voltage through concentration and ohmic overvoltages. Smaller contact angle and thinner ACC in the range of 0-120° and 200-300µm, respectively, enhance water supply to anode catalyst layer and decreases the concentration and ohmic overpotentials. In addition, an optimized pore diameter in ACC is suggested to be 21µm, which can minimize the electrolysis voltage.

Flow field pattern and flow configuration are also examined under high temperature condition. Among cascade, parallel, and serpentine pattern, the cascade pattern minimizes the concentration overpotential. The flow configuration (counter and parallel flow) has little impact on the electrolysis performance. Different from PEM fuel cell, water supply performed in PEMFC distributes water in homogeneous manner, and this nature trivialize the effect of flow configuration.

Abstract No. 213

The HyBalance Project will demonstrate how hydrogen can be used as mean to store energy which in turn will be used for Industry and fuel-cell vehicles

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Summary. HyBalance is a project that will demonstrate the use of hydrogen in the energy systems. The hydrogen will be produced from water electrolysis, enabling the storage of cheap renewable electricity from wind turbines. It will thus help balance the grid and the green hydrogen will be used for clean transportation and in the industrial sector.

Abstract. In a world where the reduction of carbon emissions is a daily challenge for everyone, Air Liquide is working on developing innovative technologies and solutions for reducing carbon emissions during the hydrogen production process. Although hydrogen is mainly used today for industrial purposes in chemistry and refinery, it is increasingly used in other sectors, such as clean transportation.

Clean Hydrogen can be produced through water electrolysis. Air Liquide is demonstrating the advantages of this technology by leading a major project in Denmark, HyBalance. This project is a technology showcase for sustainable development pathways in Europe. For this reason, it receives both European and Danish support, through the European Fuel Cells and Hydrogen Joint Undertaking and the Danish ForskEL programs.

HyBalance will demonstrate the complete value chain, from energy storage through the production of hydrogen from renewable sources (wind turbines) to its distribution for applications in clean transportation and the industrial sector.

The facility will also provide services to the power grid. Energinet.dk, the grid operator, also coordinator of the ForskEL program, manages the highest shares in Europe of intermittent wind energy in a domestic power mix. Wind power is fluctuating and requires adequate flexibility operations to ensure balance in the electricity grid. Dynamic water electrolysis offers such flexibility using electricity when the prices are low or when there is a need for balancing by tuning the power consumption in a prompt and reliable manner.

The HyBalance project will develop a model in which the operation of the hydrogen plant is triggered as function of the power prices, the power balancing service prices and the hydrogen demand forecasts.

HyBalance will use a Proton Exchange Membrane (PEM) electrolyser, delivered and maintained by Hydrogenics and producing up to 230 Nm3 of hydrogen per hour. The project will demonstrate the highly dynamic operations of the PEM technology to provide grid services together with the requirements of an industrial environment: a high efficiency commitment of the complete process from power to pure hydrogen, low noise emissions, limited power factor and the reliability and maintainability of the whole system. HyBalance is designed for 15 years of operation and will be supplying industrial customers. For that purpose, Hydrogenics has designed built and tested a customized product.

HyBalance facility will be capable of supplying a fleet of more than 1000 Fuel Cell Electric Vehicles (FCEVs). More than 60 FCEVs are already on the road today and Air Liquide is operating a network of five stations in Denmark through Copenhagen Hydrogen network. FC buses projects are also being developed. Thanks to HyBalance, these vehicles will be able to be fueled with renewable hydrogen.

The facility is now being built in Hobro, in the northern part of Jutland in Denmark. The start of the operations is planned for October this year.

Abstract No. 214

Advances in PEM Electrolyzer Components

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Summary. The step from small-scale prototype manufacturing to real products is a major challenge in the effort of making PEM electrolysers a commercial success. The status of novel components and the challenges related to their materials and processing by a design approach is addressed in the presentation.

Abstract. Due to the increasing energy demand of the world, the need for clean and renewable energy sources is rising. Hydrogen coming from water electrolysis using renewable energy sources like wind, sun and waves is one of the cleanest alternatives to fossil fuels. Polymer electrolyte membrane electrolyser cell (PEMEC) technology makes this option possible. However, there are several major market challenges for PEMEC in the competition with other technologies. One of them is the product scale required by grid owners. Multi-MW electrolyser systems are needed to balance the grid. In order to actualise that, the electrochemically active area, the operating current density and the pressure have to be increased. This will lead to significantly higher hydrogen crossover and to a new demand for suppliers of membrane–electrode assemblies (MEAs) to change their current production method to cope with the required increase in the active area. Multi-MW systems with a few large MW stacks are already available from several suppliers. The present MW stacks are designed with large cell areas up to 1 m^2. In this presentation, the challenges of scaling up the catalyst-layer manufacture while maintaining a high-performing MEA are discussed. The tackling of the various challenges through the development of new technology and advanced products is treated. Thus, light is shed upon the manufacture of large-scale MEAs with areas on the 1-m^2 scale with a focus on components integrity as well as on compliance with the OEM requirements for further improvement of performance, durability and cost.

Abstract No. 215

Determination of the bipolar plate aging under PEM electrolysis operation

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Summary.

Investigation of various bipolar plate materials via electrochemical (in situ) and contact resistance (ex situ) measurements as well as the concentration analysis of the process water indicate the level of corrosion development. By the usage of stainless steel as bipolar plate material and a thin gold coating the corrosion development is reducible.

Abstract.

The intention to reduce Germany's CO2 emissions over the long term will be fosterned by the expansion of renewable energy sources, such as wind power. Since the network coverage of such systems is strongly dependent on weather conditions and will therefore entail fluctuation in their energy supply, it will be necessary to integrate suitable storage systems so that potential bottlenecks in the electricity supply may be bridged. One storage option is the generation of hydrogen, which can be conducted by means of using renewable power to drive water electrolysis. Due to its dynamic operation mode, the polymer electrolyte membrane (PEM) electrolysis is particularly suitable, because it can react rapidly to varying input capacities. One important cell component is the metallic bipolar plate (BPP), which is responsible for the electrical connectivity along the stack and the distribution of the liquid and gaseous media inside the cell. The state-of-the-art bipolar plate material is Titanium [1].

In the context of our work we investigate commercially available and in the industry well-known corrosion stable materials to be used due to their suitability as bipolar plate material in PEM water electrolysis. The aim is to identify alloys that are stable in the long term, or material combinations that are characterized by low corrosion with good electrical contact properties. An evaluation of the corrosion that develops is carried out by using the experimental investigations in outsourcing corrosion and single cell tests through analysis of the metal ion emission, as well as the increase in contact resistance that results from the strain, influenced by the cell potential, temperature and pH value of the operating water [2].

Using both, analytical electric and electrochemical methods, the selection of possible substrate and coating materials could be limited to a few metals within the PSE. In a preselection various alloys were characterize under simulated PEM electrolysis conditions to find out more stable materials. Subsequent continuous and long-term tests under real PEM electrolysis conditions have shown that a combination of stainless steel substrate and a thin gold layer already results in significantly lower metal ion emissions and virtually no increase in contact resistance compared to the benchmark.

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Abstract No. 216

H2FUTURE, Hydrogen from electrolysis for low carbon steelmaking

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Summary. This contribution will introduce and explain the H2FUTURE project. The project will operate a 6 MW state-of-the-art PEM electrolyser within an integrated steelworks to deliver green hydrogen for low carbon steelmaking. In addition, the unit will serve within a pool of demand-response units to provide services for grid balancing.

Abstract. Novel electrolysers are the technological cornerstone that will make hydrogen sufficiently affordable in the future to act as an energy carrier in a low-carbon energy system, and to enable decarbonisation of several main industrial processes, such as steelmaking and fertilizer production. The H2FUTURE[1] project aims to make a significant contribution to this development. In a 4.5-year, €18 million field demonstration project, a consortium, led by Austrian-based electricity company VERBUND, will construct and test one of the world's largest proton exchange membrane (PEM) electrolysis plants for producing green hydrogen.

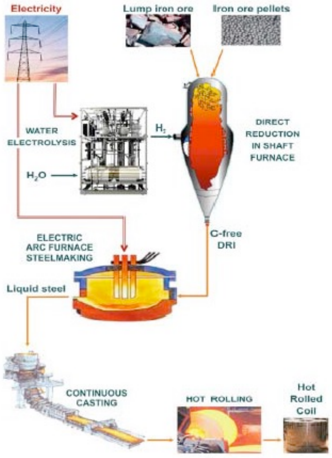

Figure 17 Steel plant based on direct reduced iron production with pure hydrogen from electrolysis.

A 6 MW state-of-the-art Siemens electrolyser will be built and operated on the premises of voestalpine in Linz, Austria, and the hydrogen produced will be integrated into regular operations at the steelworks. As such, the project is a new step in the development of a route for steelmaking using pure hydrogen, where iron ore is directly reduced by hydrogen in a shaft furnace. The resulting direct reduced iron (DRI, also called sponge iron) is further treated in an electric arc furnace (EAF) to produce steel. By producing hydrogen from water electrolysis and using renewable electricity for both electrolysis and the EAF, this process scheme offers a promising route to low-carbon or even carbon-free steelmaking.

As part of the project, VERBUND will also implement the unit within a pool of demand-response units to test its capabilities to provide grid balancing services, such as primary, secondary or tertiary reserve power. Deployment will take place based on commercial contracts with the Austrian transmission system operator APG, which is also a partner in the project.

The capital cost reduction of electrolysers is one of the major challenges when putting large-scale installations into economic operation. The target of the demonstration is to reach €1000/kW for the electrolyser system at nominal power, including power supply. The achievement of this and other technical, economic and environmental performance targets will be analysed and assessed by knowledge institutes ECN and K1-MET in conjunction with the other partners. This will be done based on data resulting from an extensive pilot plant test programme and an 18 month quasi-commercial operational period that are foreseen within the project. The results will be used for the development of a business plan to continue operation of the unit after the project period. In addition, the results will form the basis of rollout scenarios which describe the technical and economic conditions under which electrolysis becomes a viable solution for the steel industry. This will involve an economic and environmental impact assessment for the case that EU28-wide implementation of the demonstrated solution takes place, including an assessment of the impact on the electricity system.

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[1] This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 735503. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and Hydrogen Europe and N.ERGHY.

Abstract No. 217

Iron sulfides as low-cost bioinspired cathode catalysts for proton exchange membrane electrolyzers

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Summary. We present the syntheses and characterisations of different iron sulfides and their performances as cathode catalysts in proton exchange membrane electrolysers. We found a fairly good activity for pyrite FeS2, showing a 400 mV overpotential at 2 A cm^{-2} compared to standard Pt/C and high stability over 100 h.

Abstract. Several electrocatalysts based on non-noble metal sulfides, phosphates or phosphides have recently been reported for their high activity toward hydrogen evolution reaction (HER).[1] Given the ubiquity of iron sulfide minerals in nature, such as Pyrite, which is the most abundant mineral on Earth's surface, we propose iron sulfides as a new materials for HER.[2,3]

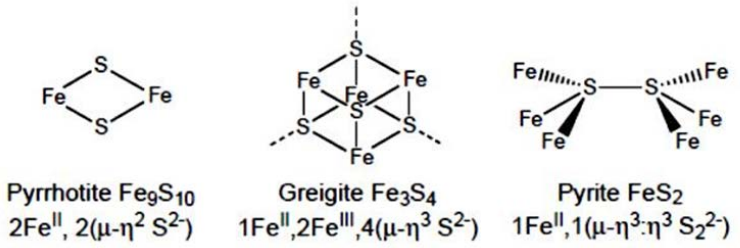

Figure 1: *Iron and Sulfur formal oxidation states.*

In order to investigate the influence of iron and sulfur oxidation states and crystal structure on the HER, we have synthesized FeS nanoparticles of different stoichiometry: pyrrhotite Fe_9S_{10}, greigite Fe_3S_4 and pyrite FeS_2 (figure 1) using a soft chemistry route, the polyol method. The nanoparticles crystalline structure and morphology were characterized by XRD and SEM and TEM. Mössbauer spectroscopy was used to probe the iron oxidation and magnetic states in each material. Composite catalyst layers made of FeS nanoparticles, carbon and Nafion were coated on glassy carbon electrodes to measure electrochemical performances. The materials show overpotentials between 200 and 300 mV, their durability and robustness was assessed by controlled-potential electrolysis. Quantitative (≥0.99) Faradic yield for hydrogen evolution was confirmed by GC and volumetric measurements. EXAFS and XANES spectra were recorded on the composite films in-operando in an electrochemical cell at the Fe and S K-edges to follow the evolution of the materials structure during the HER. The FeS nanoparticles were also tested as cathode catalysts in an electrolyzer. Pyrite was found to be the most active compared with greigite and pyrrhotite, and showed a 400 mV overpotential at 2 A cm^{-2} compared to standard Pt/C and high stability over 100 h.

[1] C. Morales-Guio, L.-A. Stern, X. Hu, *Chem. Soc. Rev.* 2014, 43, 6555

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Abstract No. 218

Tungsten Carbide Support Materials for the Hydrogen Evolution Reaction Produced by the Self-Propagating High-Temperature Synthesis Method

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Summary. We present the synthesis of tungsten carbide and other relevant ceramic materials for use as catalyst supports in electrolysers for the hydrogen evolution reaction, using the self-propagating high-temperature synthesis method which allows for rapid and upscalable synthesis.

Abstract. Tungsten carbide (WC) shows promise as an alternative platinum support material in PEM electrolysers, due to its co-catalytic ability towards the hydrogen evolution reaction (HER) and its improved stability in comparison to more traditional carbon materials [1,2]. The development of high-surface area WC materials could lead to reduction in platinum loading and increased lifetime of electrolyser cathodes [3].

Formation of WC through the use of self-propagating high-temperature synthesis (SHS) is possible by reacting a mixture containing a tungsten precursor with a reductant in the presence of carbon. Once ignited, the exothermic reaction results in the formation of pure tungsten. To facilitate the conversion of tungsten to tungsten carbide, the reaction is carried out in a pressurised reactor.

Our research is focused on developing the SHS method towards the formation of WC and WC-based materials with the properties desired for catalyst supports in PEM electrodes. This includes testing of various precursors, carbon types, and compositions of the reactant mixture while observing the effects on particle size, morphology of the product, and electrochemical activity.

With this presentation, we hope to illuminate the potential of the SHS method, which allows for the rapid and upscalable synthesis of a plethora of ceramic materials that show potential for use in electrochemical energy conversion technology. At the same time, we hope to present our own work on the synthesis of WC and similar materials by this method.

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Abstract No. 219

Current density impact on hydrogen permeation during PEM water electrolysis

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Summary. This contribution presents experimental data that emphasizes the strong effect of current density on hydrogen permeation. For example, a current density of 0.55 A/cm^2 can causes similar permeation rates as a hydrogen pressure of 10 bar. The second part of this contribution shows a theoretical explanation of this effect.

Abstract. Hydrogen permeation is an important phenomena for PEM water electrolyzers, due to the three main reasons safety issues, degradation and efficiency losses. The present contribution shows hydrogen volume fraction measurements within the anode product gas during PEM water electrolysis for different temperatures and cathode pressures. Especially, at high cathode pressures the hydrogen volume fractions are close to the lower explosion limit of hydrogen in oxygen (≈4 vol.%) (Fig. 1(a)). Consequently, this safety issue limits the range of operation conditions.

With the experimental hydrogen volume fraction data (Fig. 1(a)) it is difficult to predicate the course of the hydrogen permeation rate with increasing current density. Therefore, the experimental date is converted into the hydrogen permeation rate (Fig. 1(b)).

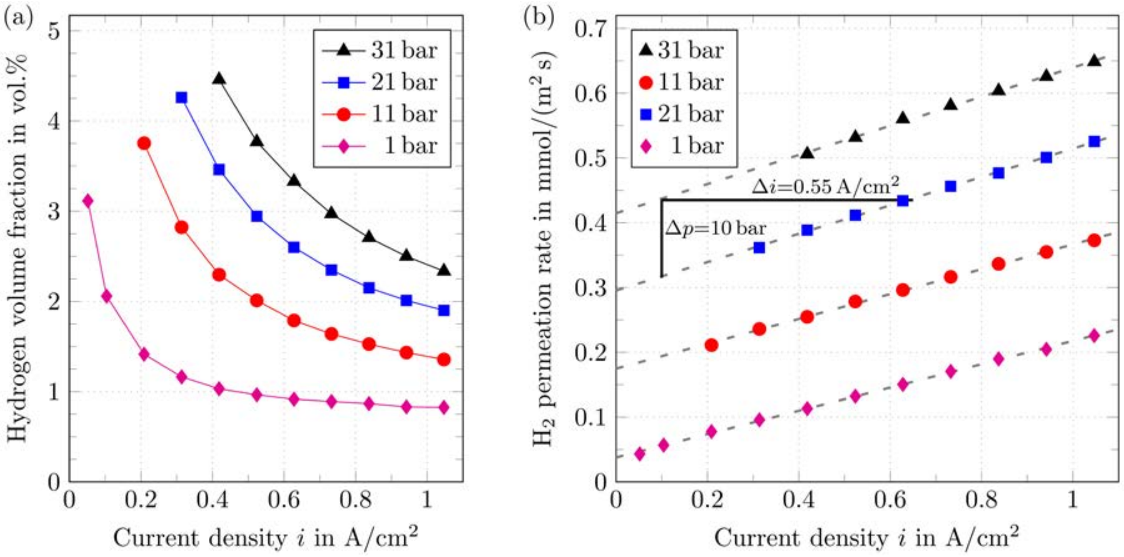

Fig. 1: Cathode pressure effect at T =60 °C on: (a) hydrogen volume fraction and (b) hydrogen permeation rate versus the current density.

In Fig. 1(b) it can be seen that hydrogen permeation increases linear with increasing current density. The impact of current density on the hydrogen permeation is very strong in comparison e. g. a current density increase of 0.55 A/cm^2 can cause a permeation increase like a cathode pressure increase of 10 bar.

This strong and surprising effect is theoretically discussed in the second part of this contribution. Different possible explanations, such as temperature and pressure increases with increasing current density are evaluated. The most probable explanation is that due to mass transfer limitations a supersaturation of dissolved gas within the catalyst ionomer film arises that causes this strong investigated increase in permeation.

Acknowledgements. The authors gratefully acknowledge the financial support by the Federal Ministry of Education and Research of Germany (BMBF) in the framework of PowerMEE (project number 03SF0536B).

Abstract No. 220

Highly Active Iridium Nanoparticles for Anodes of Proton Exchange Membrane (PEM) Electrolyzers

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Summary.

Addressing the large scale introduction of PEM Electrolyzer in a CO_2 neutral energy chain, the reduction of precious metal content is one of the main challenges. Due to the fact, that iridium is the rarest metal in the earth crust, the enhancement of the activity, accompanied by the reduction of electro catalytic material for OER is a bottle neck.

Abstract.

Proton exchange membrane (PEM) water electrolysis is one of the most promising technologies for a sustainable and emission-free hydrogen production due to its high power density and high efficiency. However, the current precious metal content for MEAs (between 2 and 4 mg cm^{-2}) is a drawback which might become critical in case of large market introduction in the GW range. Therefore the reduction of iridium, the rarest metal in the earth crust, as an oxygen evolution reaction catalyst is going to be a bottle neck.

Proton exchange membrane (PEM) water electrolysis is one of the most promising technologies for a sustainable and emission-free hydrogen production due to its high power density and high efficiency.[1] High amounts of expensive noble metals, such as platinum and iridium for cathode and anode side respectively, contribute significantly to the high investment cost of the stack. Therefore, lower loadings of platinum group metals can reduce significantly the overall cost of PEM electrolysis. In this work we synthesise nano-sized iridium particles by reducing $IrCl_3$ in anhydrous C_2H_6O at room temperature.[2] Transmission electron microscopy (TEM) images show Ir clusters with a uniform particle size distribution (Figure 1a). X-ray diffraction (XRD) analysis reveals a cubic face centred structure of the Ir nanoparticles with a crystallite size of approx. 1.8 nm – 2 nm. XPS confirms the metallic properties of the Ir particles covered with a very thin oxide layer. The synthesized catalyst shows a nine-fold higher activity towards oxygen evolution reaction (OER) than Ir black at 1.51 V and 25°C (Figure 1b). The effect of thermal treatment, synthesis quality and electrochemical performance of the catalysts in the PEM electrolyser are discussed as well.

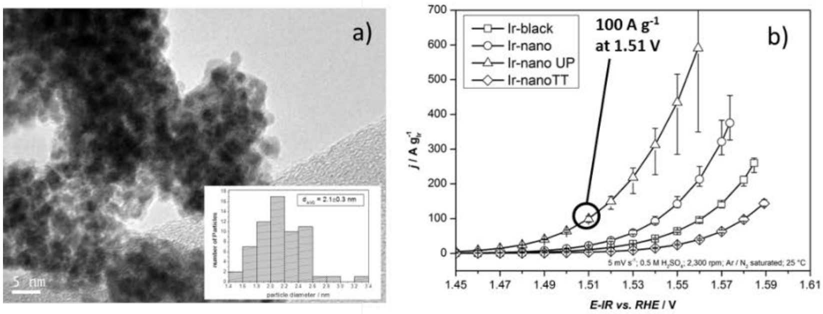

Figure 1: a) TEM image with particle size distribution of Ir nanoparticles and, b) mass activity characteristics for OER measured at 5 mV s^{-1} in 0.5 M H_2SO_4. The rotation speed of the electrode is 2500 rpm and the temperature 25 °C.

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Abstract No. 221

Degradation mechanisms of PEM electrolyzer MEAs operating at high current densities

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Summary.

Accelerating stress tests (ASTs) enable the analysis of degradation in adequate time. Here we present the aging characterization of three 8 cell short stacks of 120 cm² active surface area, running different AST protocols. By in- and ex-situ analysis we study the effects of catalyst amount, catalyst type and degradation at high current densities.

Abstract.

The fluctuating behaviour of renewable energy sources hinders their widespread integration into a reliable electricity grid. Presumably, the wide operation range and rapid response of proton exchange membrane (PEM) electrolyzers can stabilize the grid, yet the degradation effects are not fully understood. The results presented here show no decrease in performance over several thousand hours, operating constant and dynamically a 8-cell stack (120 cm² active area) at up to 4 A cm^{-2}, with commercial membrane electrode assemblies (MEA). The maximum electrolyzer efficiency is achieved at constant 1.7 A cm^{-2}. The efficiency only decreases less than 3% when doubling the current density.

Based on EIS analysis, a semi empirical and simplified model was created to quantify the degradation effects of each individual impedance and over potential. We were able to observe a decrease of ohmic resistance as the main aging behaviour, if the bipolar plates are protected against corrosion and oxidation, properly. This increases the efficiency by enhanced proton conductivity through the membrane but on the other hand also the water and gas cross over which decreases the dynamic properties.[1] Furthermore, we observed different degradation behaviour for Ir-metal based catalysts and Ir-oxides, where latter stays fairly constant during the ATS but metallic Ir-catalysts diffuse into the membrane and loose intrinsic activity over time.[2]

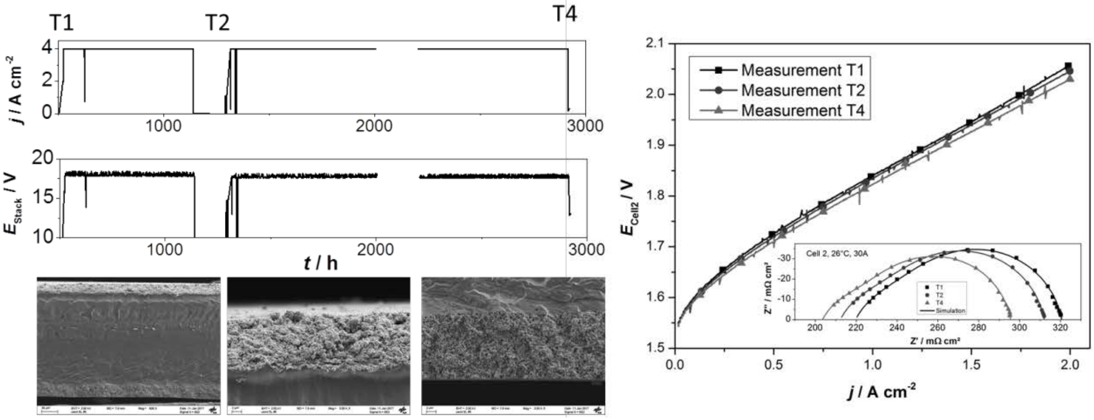

Figure 1: AST: > 2000 h at 2 A cm-2; SEM post mortem analysis of MEAs; Polarisation curve before AST (T1), in between (T2), and after AST (T4) and corresponding EIS measurement as Nyquist diagram (inset)

References

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Abstract No. 222

Experimental analysis of gas-liquid flow in PEM water electrolyser mini-channels using a permeable wall

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Summary. In this paper, gas-liquid flow in mini-channels of an inter-digitated bi-polar plate of a PEM water electrolysis is analysed.

Abstract. Converting surplus of fluctuating electricity generated from renewable energy to hydrogen for long term (more than an hour) storage is a key component for closing the loop of the renewable energy system. PEM water electrolyser converts water to oxygen and high pressure hydrogen using electricity with a fast response rate that suits to damp grid fluctuations. One of the issues within these electrolysers is their high cost. One means of reducing the cost is to increase production from the existing cells by increasing the current density from 1 (A/cm^2) (at the existing conventional cells) to 5 (A/cm^2). At high current densities, due to high rate of oxygen generation and concentrated heat generation in the cell, issues related to heat and bubble management come up which must get managed. In this study, an experimental setup is made of plexiglass, Titanium-felt (Ti-felt) and microporous ceramic. The setup demonstrates a similar gas-liquid flow encounters in PEM water electrolysis channels and anode porous media. The microporous ceramic plate simulates generating small bubbles simulating the real membrane electrode assembly (MEA). The movement of bubbles upward in the mini-channel at a specific stoichiometric number is analysed and its multiphase flow regime is identified.

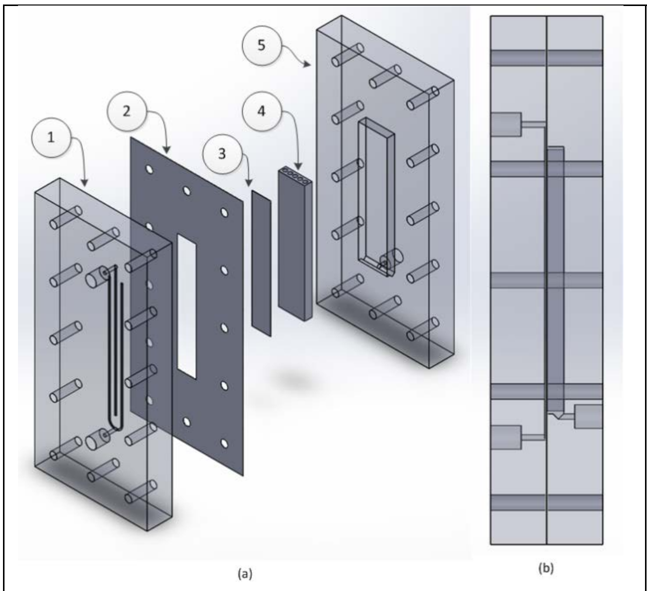

Fig.1: Geometry of the transparent test case.

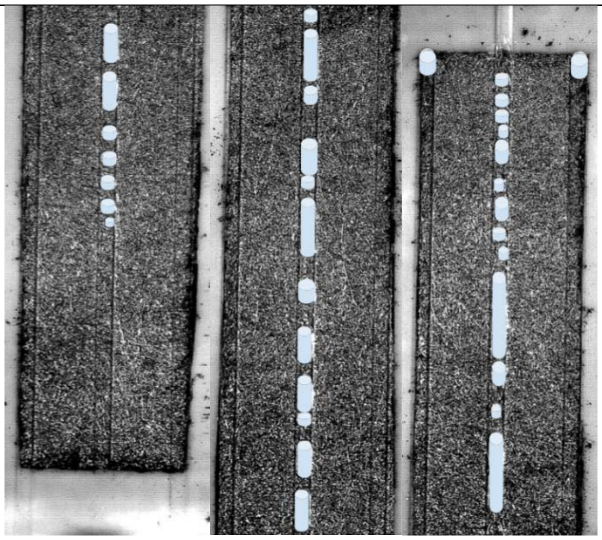

Fig.2: Gas-liquid flow in the cell mini-channels.

1st International Conference on Electrolysis
Copenhagen, 12-15 June 2017

Abstract No. 223

Experimental study on the influence of clamping pressure on proton exchange membrane water electrolyzer (PEMWE) cell's characteristics

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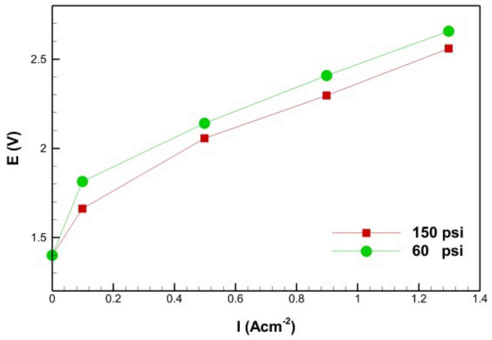
Summary. PEMWE's clamping pressure has to be optimized to avoid membrane damage as it is pressurized against the metallic titanium filt and not to reduce electrical conductivity between the cell components. Thus clamping pressure influence on cell performance, electrical conductivity, and hydrogen and water cross-over is demonstrated in this work.

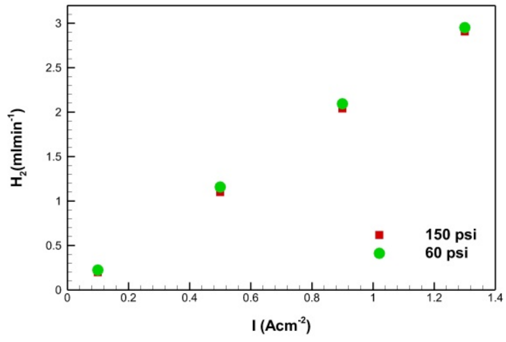
Abstract. Energy transition can be led by more hydrogen production. Hydrogen offers a clean, sustainable, and flexible option for overcoming different obstacles that face the low-carbon economy [1]. PEMWE is one of the most promising candidate technologies to produce hydrogen from renewable energy sources. PEMWE cell splits water into hydrogen and oxygen when an electric current is passed through it. Electrical current forces the positively charged ions to migrate to negatively charged cathode, where hydrogen is reduced. Meanwhile, oxygen is produced at the anode side electrode and escapes as a gas with the circulating water.

In the recent few years, PEMWE's R&D has inched towards; operating conditions; such as increased operating temperature and cathode-anode high differential pressure operation, flow field design, stack development, and numerical modelling [2,3]. In this work the effect of clamping pressure on the PEMWE cell characteristics'; performance, conductivity, hydrogen and water cross-over through the membrane electrode assembly (MEA) is studied. A 50 cm^2 active area PEMWE cell with double serpentine flow field channels for the anode and cathode side is used. Measurements are carried out at constant cell temperature (70°C) and atmospheric pressure.

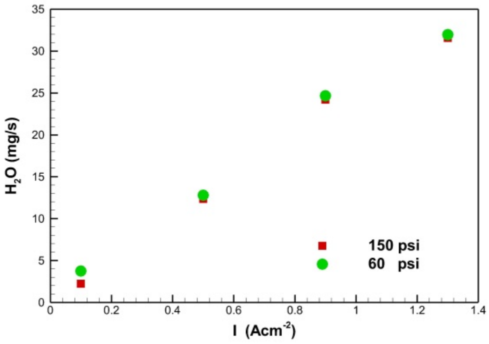
Early results for IV curve predict that the PEMWE cell performance increases with increasing the clamping pressure at fixed temperature and current density. This can be elucidated by the EIS measurements which predict an increment in ohmic and activation resistance at lower clamping pressure values at the same temperature and current density. Furthermore, early results have not shown any significant change in the amount of hydrogen crossing-over from cathode to anode and water from anode to cathode. This might be attributed to the membrane properties which might not be changed significantly with changing the clamping pressure.



IV curves at different clamping pressures cell temperature of 70°C.



Hydrogen cross-over from cathode to anode at different clamping pressures cell temperature of 70°C.



Water cross-over from anode to cathode at different clamping pressures cell temperature of 70°C.

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Abstract No. 224

Fabrication of porous Co-P foam by electrodeposition for an efficient hydrogen and oxygen evolution reactions

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Summary.

A high-performance bifunctional Co–P foam catalyst was successfully synthesized by facile one-step electrodeposition at a high cathodic current density. It exhibits excellent HER (η @10 mA cm^2, 0.5 M H_2SO_4: 50 mV) and OER activity (η @10mA cm^2, 1 M KOH: 300 mV).

Abstract.

A high-performance bifunctional Co–P foam catalyst was successfully synthesized by facile one-step electrodeposition at a high cathodic current density. The synthetic approach includes fast generation of hydrogen bubbles as well as fast deposition of Co–P, which played a key role in forming a porous Co–P foam structure. The Co–P foam exhibits remarkable electrocatalytic activity and stability in both acidic and alkaline solution. It's HER activity was recorded with an overpotential of 50 mV in 0.5 M H_2SO_4 and 131 mV in 1 M KOH at 10 mA cm^2, which is comparable to that of commercial Pt/C (η @10 mA cm^2 0.5 M H_2SO_4: 33 mV, η 10 mA, 1 M KOH: 80 mV). The Co–P foam (η @10mA cm^2: 300 mV) exhibits better OER activities than Ir/C (η @10 mA cm^2: 345 mV) and RuO_2 (η @10 mA cm^2: 359 mV) in 1 M KOH solution. The excellent performance of the Co–P foam as an HER and OER catalyst can be attributed to the charge separation between Co and P in Co–P foam as well as the porous foam structure providing a large electrochemically active surface area (ECSA). The ECSA of the Co–P foam was calculated to be 118 cm^2, which was 2.4 times higher than that of a Co–P film (49 cm^2).

Abstract No. 225

A PEM water electrolyser based on metallic iridium electrocatalyst, Pt/C and an Aquivion membrane

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Summary. Advanced membrane and electro-catalysts were developed for water electrolysis. The electrochemical activity was investigated in a single cell PEM electrolyser consisting of a Pt/C cathode, Ir metallic anode and an Aquivion membrane.

Abstract. An Iridium black nanosized anode electrocatalyst was coupled to an Aquivion short-side chain perfluoro-sulfonic acid membrane (90 µm; EW: 980 g/eq) for operation in a PEM electrolyser. Iridium black powder has been synthesized by chemical reduction of $H_2IrCl_6x6H_2O$ using $NaBH_4$ as chemical reducer according to Ref. [1]. The electrocatalyst has been evaluated in a single cell polymer electrolyte membrane water electrolyser (PEMWEs) of 5 cm^2, based on Aquivion® membrane and 30% Pt/C as cathode catalyst [2, 3].

The single cell was investigated by using linear sweep voltammetry, electrochemical impedance spectroscopy and chrono-potentiometric measurements. The electrochemical activity of this MEA was analyzed in a temperature range from 25° to 90°C. The properties of this electrocatalyst have been investigated with the help of both ex-situ characterization and in-situ electrochemical diagnostics.

Acknowledgements

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Abstract No. 226

Conceptual Degradation Model for a PEM Water Electrolyzer

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Summary. This poster presents the conceptual approach of a lifetime model for a PEM water electrolyzer. A performance model is extended with degradation phenomena to predict the lifetime of the electrolyzer under various operational parameters.

Abstract. The expected lifetime of a PEM electrolyzer is a crucial measure for market maturity and financial competitiveness. However, laboratory work on degradation is time-consuming and accelerated stress tests are yet to be defined and validated. Simulations can support lifetime evaluations. Two approaches for the development of a mathematical model for lifetime prognosis are conceivable. First, a mechanistic model based on physical degradation mechanisms of crucial components such as membrane and catalyst layers. Second, a model based on empirical data for voltage decay rates. The approaches are illustrated in figure 1. This work suggests a way to construct such a model and gives first indications on whether certain operation parameters such as temperature and input current affect cell degradation. Based on the application, operation can be optimized according to the simulation outcomes.

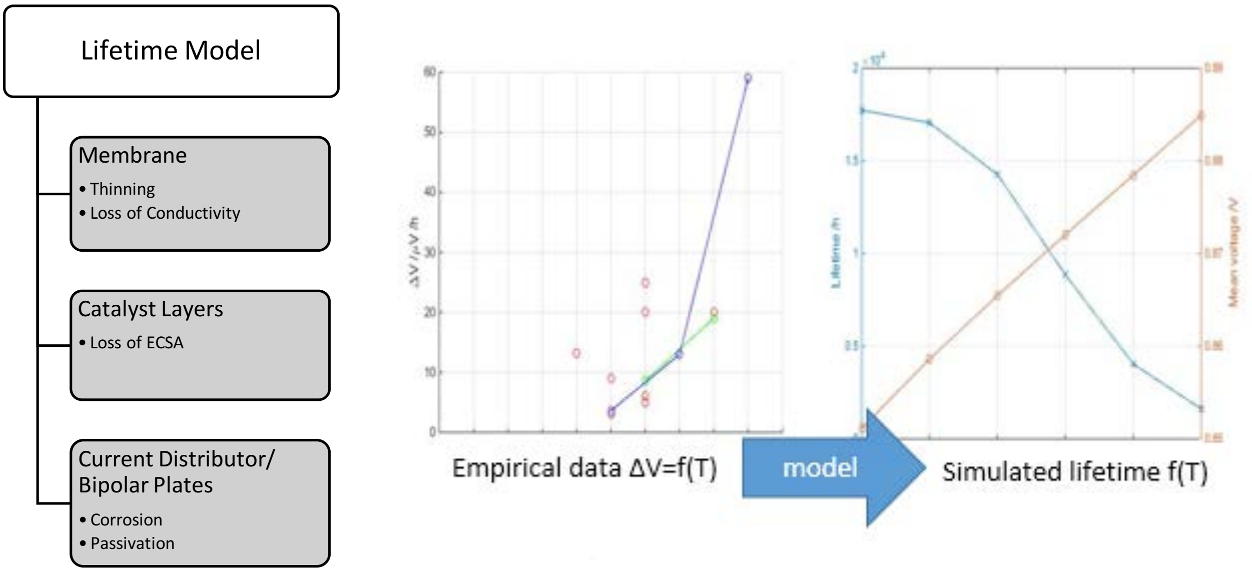

Figure 18: Mechanistic approach (l.) and empirical approach (r.)

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Abstract No. 227

Analysis of Porous Transport Layers for Proton Exchange Water Electrolysis

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Summary. The study focuses on the impact of porous transport layers (PTL) on the performance of proton exchange water electrolysis (PEWE). Properties of titanium based PTLs are characterized by X-ray tomography using a micro CT. Furthermore performance tests are conducted to enable a correlation with ex-situ based PTLs structure analysis.

Abstract. Electrochemical production of hydrogen has been investigated for over a century. State of the art proton exchange water electrolyze reaches a maximum voltage efficiency of 82%$_{HHV}$ [1]. The high efficiency, as the sustainable and dynamic operation makes PEWE a suitable technique to face the global energy demand and environmental problems of these days.

The minimization of potential losses in PEWE is the essential requirement for designing efficient systems. The main losses within an electrolyser can be related to kinetic, ohmic and mass transport losses. In contrary to kinetic and ohmic losses, the origin of mass transport losses is still not fully understood. More fundamental studies have to be conducted to isolate the governing resistance for the two phase transport in the cell.

A possible source is the porous transport layer. The anodic porous media is in general based on Ti substructures such as fibres or particles enabling the water and gas management between the catalyst layer and flow fields and providing thermal and electrical conductivity. It is known that the morphology of PTLs affects the performance of PEWE. This study focuses on the link between PTL parameters analysed by the ex-situ method X-ray tomographic microscopy (XTM) and performance measurements. Different PTL types are analysed to isolate the governing parameters for PEWEs.

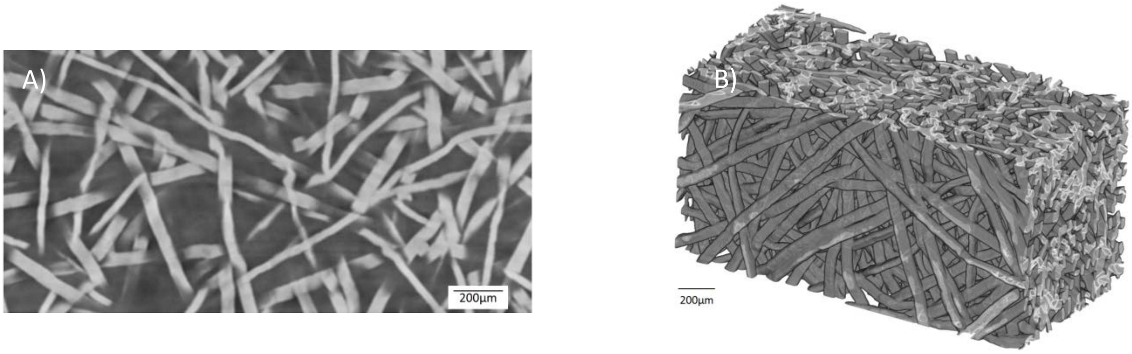

Figure 19. Image A) shows 1000x2000µm CT-slice of a fibre based Ti PTL. The 3D structure of the segmented PTL is visualized in image B) ; both featuring a voxel edge length of 2µm.

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Abstract No. 228

Plasma-chemical technologies for PEM electrolyzers catalysts and protective coatings

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Summary. Physical - plasma-chemical technologies were developed for catalysts and protective coatings synthesis. Anode and cathode catalyst with particles size 2-20 nm with high activity and stability were obtained. Protective coatings with different structure and specific surface demonstrated their efficiency at high operating pressure.

Abstract. Physical - plasma-chemical technologies (ion implantation and magnetron sputtering) were developed for catalysts and protective coatings synthesis. Nanostructural Pt-based electrocatalysts (Pt, Pd, Pt-Pd, Pt-Ni, Pd-Ni on nanostructured carbon carriers) with catalyst particles dimensions 2-10 nm on nanostructured carbon carriers were synthesized for electrolyzer cathodes. Average particle size could be easier varied due to ion current density, pulsed mode of sputtering and time of sputtering. Pt catalyst with average particle size about 4-6 nm (specific surface up to 60 m^2/g) demonstrated same activity at lower Pt loadings as catalysts synthesized by traditional technology – liquid phase reduction by boron hydride or ethylene glycol. Pt-Pd, Pt-Ni demonstrated the same and even higher (Pt-Ni) activity but after some additional anode polarization. As anode catalyst Ir oxide and mixed Ru-Ir oxides deposited on carbon particles by the same technologies with further carbon removal by oxidation in air at elevated (300-400^{o}C) were used. In this case particle size was larger (8-20 nm) due to thermal treatment. Such catalysts had higher specific surface and activity in comparison with the catalysts of the same composition obtained by thermal decomposition of the proper precursors. Oxygen evolution catalysts base on mixed oxides demonstrated high activity (same activity as for iridium and even higher) with decreased (about 30%) of Ir loading in case of Ir-Ru oxides and good stability (tests during 500 hours).

Magnetron-ion sputtering of Pt and Pd was also used for bipolar plates and electrolyzer current collectors protection from oxidation and hydrogen saturation (for titanium components). Different sputtering modes (sputtering at a constant current, sputtering at a constant current with pulsed negative potential bias of the sputtered current collector/bipolar plate and pulsed sputtering at low frequencies were tested. It was demonstrated that coatings with different structure (density, porosity and so on) could be obtained at different sputtering modes. For protective coatings the sputtering at a constant current with pulsed negative potential bias (50-100 V) of the sputtered current collector/bipolar plate permitted to get the most dense and stable coating. The pulsed sputtering at low frequencies permitted to get coatings with a high specific surface (roughness factor more than 20 in case of porous current collectors). The combination of the two modes mentioned above was very efficient for production of current collectors with good stability and an increased surface catalytic activity. Such an activity permitted to decrease the cathode catalyst loading for 20%.

Application of current collectors with high specific Pt surface also provided an efficient hydrogen-oxygen recombination at anode (hydrogen was diffused from cathode) at elevated operating pressure (up to 150 bar). The efficiency was comparable with modification of the anode catalyst composition by Pt nanoparticles and resulted in oxygen purity increase (for example from 96-97% to 97-98% at 130 bar) as hydrogen reaction with oxygen was rather efficient at the current collector surface. It was shown that Pt dissolution from anode protective coating is one of he reasons of electrolysis cell degradation and additional ion implantation by Ar ions permitted to increase the protective coating stability about 2 times.

Acknowledgements. This research was executed with financial support of the Russian Scientific Foundation (project No. 14-29-00111) in NRC “Kurchatov Institute”.

Abstract No. 229

Modified NiO/GDC cermets as possible cathode electrocatalysts for H_2O electrolysis & H_2O/CO_2 co-electrolysis processes in SOECs

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Summary. The present work deals with physico-chemical characterization of commercially available NiO/GDC powder, modified with Au, Mo and BaO. Selected electrodes were kinetically studied for the RWGS reaction. Finally, single SOEC measurements were also performed in order to investigate their performance for the H_2O electrolysis process.

Abstract. H_2O electrolysis constitutes a promising method for the production of pure-H_2 and O_2 by using electrical energy. One characteristic and recent application of this technology is electrolysis at high temperatures, by using Solid Oxide Electrolysis Cells (SOECs). Specifically, the electrical energy that is required for the high temperature (600-1000 °C) H_2O electrolysis process, is much lower than the energy required at low temperatures (<100 °C), which as a result yields significantly higher efficiency and performance in the former case [1]. Although this technological application has considerable advantages, it confronts many problems that prevent the widespread use and commercialization. One of the most important is the deactivation of the fuel electrodes (H_2O/H_2), which is usually ascribed to nickel re-oxidation and/or agglomeration during H_2O electrolysis, or/and carbon deposition during H_2O/CO_2 co-electrolysis [2]. Another disadvantage is the degradation/delamination of the oxygen electrodes. Consequently, recent research activities focus on the development and investigation of new, tolerant fuel (H_2O/H_2) and air electrodes. The aim of this work is the development and study of ceramo-metallic electrocatalysts/electrodes, which are based on commercial NiO/GDC powder (Marion Technologies). This powder is modified with chemical methods by the addition of Ba, Au or/and Mo. The Au or/and Mo modified electro-catalysts have been extensively studied, from our research group, as electrodes in Solid Oxide Fuel Cells (SOFCs) applications [3,4] and their use in SOECs, as H_2/H_2O electrodes (cathodes), is also very interesting. Furthermore, the modification with Ba aims to the protection of the Ni properties, towards the potential limitation of fast re-oxidation or/and agglomeration. All cermets were investigated through physicochemical characterization with the methods of BET, XRD, XPS, TGA-MS, H_2-TPR, O_2-TPO, including specific redox stability measurements under various H_2O-H_2 feed conditions. The powders were also used for the preparation of appropriate paste, which was deposited on solid YSZ electrolytes with the method of screen printing. The prepared/calcined electrodes were kinetically studied, in the form of half cells, for their catalytic activity for the Reverse Water Gas Shift Reaction in the temperature range of 800-900 °C with simultaneous analysis of products/reactants using gas chromatography. Electrocatalytic measurements with Electrochemical Impedance Spectra (EIS) analysis were also performed in single solid oxide cells, within the same temperature range, under H_2O electrolysis conditions by applying different pH_2O/pH_2 ratios.

Acknowledgments.
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Abstract No. 230

In operando Raman spectroscopy for investigation of solid oxide electrolysis cells

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Summary. How can in operando Raman spectroscopy increase our understanding of degradation and activation processes in solid oxide electrolysis cells? Recent experimental results are reported, including experiments showing remarkable polarisation induced compositional changes in infiltrated perovskite electrodes.

Abstract. Traditional evaluation of solid oxide electrolysis cell (SOEC) durability and performance relies on electrochemical methods including voltammetry and impedance spectroscopy. In operando electrochemical studies are then followed by post mortem investigations of changes in microstructure and elemental composition. As a supplement to these well-established characterization methods various in situ and in operando spectroscopies have received increased attention in the solid oxide cell community during the last decades[1-2] and may offer a great potential for improving the understanding of degradation processes in solid oxide electrolysis cells. The advantage of these in situ and operando techniques is they may *reveal changes in elemental electrode compositions in real time as the changes occur.*

For solid oxide cells in operando spectroscopy is defined as spectroscopy with the three operating parameters: 1) Temperature, 2) Atmosphere and 3) Electrical polarization, held at values similar to those experienced during real operation of the cells. Previous work using operando Raman spectroscopy to study solid oxide cells and materials has examined coking by carbon containing fuels[3] as well as changes in a material's oxidation state[4] under atmospheric pressures and at temperatures as high as 800 °C.

In the present poster, a number of recent cases are presented, where Raman spectroscopy has been applied in situ and in operando to study solid oxide cells and solid oxide materials. Special emphasis is put on an experiment applying in operando Raman spectroscopy on an air electrode prepared by BaO infiltration of LSM ($(La_{0.85}Sr_{0.15})_{0.9}Mn_{3\pm j}$) , as this experiment led to several interesting observations[5]. The first surprising discovery was that the BaO had formed a secondary $Ba_3Mn_2O_8$ phase due to reaction with the LSM. This phase was likely the cause of a decreased polarization resistance observed at OCV conditions. Secondly, this $Ba_3Mn_2O_8$ phase reversibly decomposed with electrical polarization with Mn changing its oxidation state sequentially from 5+ to 2+ (MnO). When the electrical polarization was removed, the MnO was transformed back into $Ba_3Mn_2O_8$. These findings emphasize the need to directly observe material changes in high temperature solid oxide electrodes under realistic working condition, especially electrodes prepared by infiltration.

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Abstract No. 231

Oxygen evolution reaction kinetics on LSM electrode doped by Pt

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Summary: LSM is proven electrode material for oxygen electrode in the high temperature water electrolysis. Its electrocatalytical activity can be promoted by addition of platinum. Various level of Pt loading was evaluated in symmetrical cell.

Abstract. High temperature water electrolysis represents intensively studied technology. In contrast to the well-known established technologies, like alkaline and PEM water electrolysis, the high operating temperature brings several advantages. The main of them are lower reversible cell voltage, fast electrode reactions kinetics and their high reversibility. Therefore both operating modes, i.e. fuel cell (SOFC) and electrolysis (SOEC), are possible with the same unit. It makes high temperature electrolysis attractive way for buffering the fluctuation of electric energy production generated by alternative power sources. Although significant progress was made during last decade, several issues remain still unresolved. The main of them is durability of the system. The undesired morphology changes of electrodes, formation of inactive compounds and layers delamination can be mentioned as typical examples.

Non-stoichiometric oxides with perovskite structure are usually used as oxide electrode. Most widely used material is $LaMnO_3$ doped with Sr, which is typically referred to as LSM. Beside electron conductivity it has also ionic conductivity. But ionic conductivity is rather poor. Another drawback of pure LSM as the oxygen electrode represents its insufficient mechanical stability and its potential degradation at the phase interface with Y-stabilized ZrO_2 (YSZ) electrolyte. It is typically due to its delamination. Therefore, LSM is preferably used in a mixture with YSZ (or other ionic conducting material) in order to maximize occurrence of the three phase boundary in the electrode body. At the same time it improves mechanical stability of the electrode and its adhesion to the electrolyte surface. The optimal ratio between YSZ and LSM is crucial for proper oxygen electrode performance.

Beside the non-stoichiometric oxides, the platinum metal catalyst is accepted as the best catalyst for SOFC/SOEC. Platinum possesses several important advantages, like it doesn't tend to form nonconductive compounds on the phase interfaces. The most important drawback is, however, its high price. The compromise is the use of LSM with small addition of platinum for enhancing catalytic properties. As it was found by several authors [1, 2], addition of already 0.5 wt.% of transition metals into the cathode enhances the SOFC performance significantly. Low content of Pt ensures higher Pt utilization in comparison to the low temperature PEM systems.

Present works deals with determination of influence of the Pt addition to the LSM on the resulting electrode properties. Synthetized Pt powder was added directly to the LSM/YSZ mixture. LSM/YSZ ratio was kept 50:50 in all experiments. Prepared electrode mixtures were deposited by screen printing on the YSZ substrates and sintered at 1150°C. Symmetrical cell based on LSM electrodes on both sides of the electrolyte were prepared. The symmetrical cell operated in oxygen pump mode. Impact of the oxygen partial pressure and operational temperature were studied. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were used to characterize the system. The IR corrected curves were fitted by one-dimensional macrohomogeneous model of single SOEC cell to obtain real kinetics parameters of the electrode. Exchange current density and charge transfer coefficient was determined with respect to the Pt content.

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Abstract No.232

Experimental loop of high temperature electrolysis in coupling of high temperature process

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Summary. European Union wants the energy sector to be shifted towards the low-carbon technologies (H_2, renewable energy). When H_2 will be used in wider scale (energetics, mobility), its production only from electricity surplus will not be sufficient and a central H_2 production will be necessary. Therefore, the HT-electrolysis in cogeneration with other processes is investigated in Centrum výzkumu Řež (CVŘ).

Abstract.

High-temperature electrolysis is especially profitable when the waste heat is used. This heat can be produced e.g. by the planned fourth-generation nuclear reactor, so called high-temperature gas reactor (HTGR). Hydrogen production with HTGR that can produce a large amount of hydrogen could be one of the promising systems for a future hydrogen economy, but HTGR reactor is not yet available. Therefore, the paper investigates the co-generation of high-temperature electrolysis with the industrially-available technologies.

Within the sustainable European project SUSEN, SUStainable ENergy, an experimental facility for hydrogen generation by high-temperature water electrolysis (HTE) was built. The objective of the loop (fig.1) is to experimentally validate the thermodynamic coupling of HTE with HTGR (high temperature gas-cooled reactor) and other high temperature processes. The central component is the heat exchanger for gas and water steam. The gas side of the heat exchanger simulates a high-temperature process. It is also possible to test the combination with different high-temperature processes, e.g. heat from steel fabrication, refinery, pyrolysis and other industrial processes. The test will be conducted on approx. 1 kW_{el} electrolysis stack.

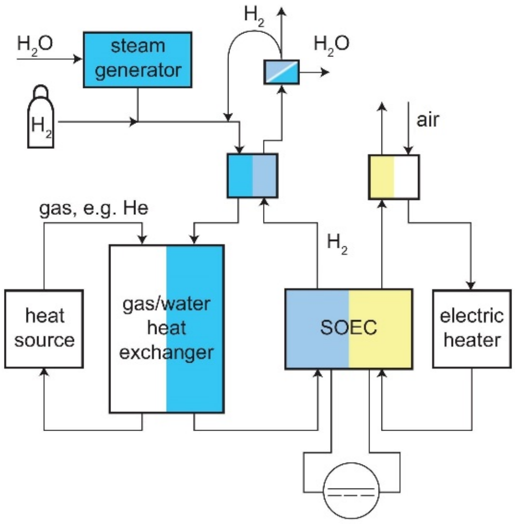

Fig.1: scheme of High-temperature electrolysis loop

Acknowledgement

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Abstract No. 233

Distribution of relaxation times – tool for the analysis of impedance spectra

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Summary. In this work usefulness of DRT analysis will be discussed.

Abstract. Impedance spectroscopy is a standard tool for investigation of electroceramic devices like fuels cells or electrolyzers. It allows investigating ohmic and polarization resistances and potentially link the polarization resistance with the limiting electrochemical process. However, frequently the electrochemical processes have very similar characteristic frequency and pointing the exact process is very challenging. Therefore, recently a distribution of relation times (DRT) is used to analyze the impedance spectra and better separate the processes [1,2]. This analysis is especially useful for the analysis of solid oxide electrolyzer cells (SOECs), for which more than 6 electrochemical processes can be foreseen. Although, the analysis is rather complicated, analysis tools start to be available on-line [3].

In this work usefulness of DRT analysis will be discussed. Especially, the limitation of DRT analysis will be pointed and issues related to data discretization and selection of DRT parameters will be analyzed. The examples of DTR analysis will be provided and connected with exact DRT solutions of standard electrochemical processes. The data will be linked with results obtained on solid oxide electrolyzers. Issues related to polarization resistance analysis based on DRT plot will be discussed.

Acknowledgement:

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Abstract No.234

In-situ upgrading of bio-oil using solid oxide electrolysis process

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Summary. Bio-oil from fast pyrolysis of woody biomass is a potential source of green fuel. Presently, bio-oil requires centralized hydrodexoygenation process to lower its high oxygen content but instability of bio-oil makes it a challenge for storage and transportation. A partial or full deoxygenation process using solid oxide electrolysis process in investigated as a potential low cost, low CO_2 footprint alternative.

Abstract. Biomass can be converted to liquid fuels via bio-oil production by fast pyrolysis. Typical pyrolyzer operation produces bio-oil as a mixture of oxygenated organic compounds and is biphasic. Only the organic phase is processed by hydrodeoxygenation, leaving behind valuable carbon-containing material in the aqueous phase.

Bio-oil properties such as low heating value, incomplete volatility, acidity, instability, and incompatibility with standard petroleum fuels significantly restrict its application.[1] The undesirable properties of pyrolysis oil result from the chemical composition of bio-oil that mostly consists of different classes of oxygenated organic compounds. The elimination of oxygen is thus necessary to transform bio-oil into a liquid fuel that would be broadly accepted and economically attractive. Hydrodeoxygenation (HDO) or hydrotreating involves high-temperature, high-pressure processing in the presence of hydrogen and catalyst to remove oxygen.[2] HDO suffers from significant challenges such as coking, polymerization of various compounds in bio-oil before deoxygenation, deactivation of HDO catalysts by the presence of water in the pyrolysis oil, requirement of significant quantities of hydrogen to remove oxygen, economic availability of hydrogen at distributed smaller scale suitable for biomass conversion and significant process exotherm due to high oxygen removal requirement (25% by mass). Thus, there are numerous challenges that prevent commercialization of bio-oil upgrading to hydrocarbons process. An alternative economically feasible, less hydrogen dependent and decentralized process is required to convert bio-oil to refinery ready hydrocarbons.

A process of deoxygenation of bio-oil using solid-state, oxygen conductor based electrochemical cell is under investigation. The cell is operated at 500 – 550 °C to match the typical pyrolysis temperature for both physical and process integration of the two operations. The electrolysis process removes oxygen from the oxygenated organic molecule as well from steam to produce hydrogen in-situ. Thus, relatively small quantities of external hydrogen is needed for deoxygenation, allowing for a distributed, small scale integrated upgrading unit. Mixtures of model compounds were tested using button cells and short stacks. The product from the electrochemical cell contained a suite of compounds with significantly lower oxygen content. Integrated testing of short stacks at the Pacific Northwest National Laboratory using a slip stream from the pyrolyzer shows that the product composition is similar to catalytic pyrolysis process. Additional tests are planned using improved electrode materials.

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Abstract No. 235

Infiltrated Solid Oxide Cell Oxygen Electrodes: Degradation During Reversible Current-Switching Operation

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Summary. We report results showing good stability of symmetrical solid oxide cells operated reversibly at 1 Acm^{-2}, utilizing electrode materials produced by infiltration of the mixed-conducting oxides (Sm,Sr)CoO_3 (SSC) into Gd-doped Ceria (GDC) and La_2NiO_4 (LNO) into (La,Sr)(Ga,Mg)O_3 (LSGM) scaffolds.

Abstract. Many prior studies have shown that solid oxide cells (SOCs) with LSM-based oxygen electrodes degrade during electrolysis or reversing current operation at sufficiently high current density and/or electrode overpotential. Reduction in the electrode overpotential, at a given current density, is one way to reduce the high effective oxygen pressure at the electrode/electrolyte interface. It may also be useful to reduce the cell operating temperature, since this will reduce cation transport kinetics that enable degradation by, *e.g.,* void formation on electrolyte grain boundaries. Reduced overpotential and/or reduced temperature can be enabled through the use of mixed-ionically- and electronically-conducting (MIEC) electrodes such as (La,Sr)(Fe,Co)O_3 (LSCF). Further improvements are possible by utilizing nano-scale MIEC electrodes, such as those obtained by wet-chemical infiltration.

Here we report reversible current-switching life test results on symmetrical cells with electrodes prepared by infiltration of MIEC materials into porous ionically-conducting scaffolds. Two cell types are reported – the perovskite (Sm,Sr)CoO_3 (SSC) infiltrated into a porous Gd-doped Ceria (GDC) scaffold with GDC electrolyte, and the Ruddlesden-Popper phase La_2NiO_4 (LNO) infiltrated into a porous (La,Sr)(Ga,Mg)O_3 (LSGM) with LSGM electrolyte. Life tests carried out at 650 °C in air, with the current density of 1.0 or 2.0 A cm^{-2} switched abruptly every 6 h, for a cycle period of 12 h. Each life test was run for ~ 1000 h, *i.e.,* ~ 80 complete cycles. Impedance spectroscopy measurements were taken periodically at zero current. At 1.0 A cm^{-2}, corresponding to an initial electrode overpotential of ~ __ V, both cells showed a continuous but relatively low degradation rate of __ %/kh. At 2.0 A cm^{-2}, corresponding to an initial electrode overpotential of ~ __ V, both cells showed continuous but much larger degradation at a rate of ~ __%/kh. The increase in cell resistance was approximately equally split between the electrolyte and the electrode in each case. Post-measurement evaluation of the cells using scanning electron microscopy showed no obvious microstructural changes, even at the higher current density. Results on Sr segregation measurements will be reported for the SSC electrodes.

Abstract No. 236

Protective coatings for interconnects for solid oxide cell stacks

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Summary. Long term operation of solid oxide cell stacks with low degradation requires use of protective interconnect coatings with low chromium permeation and high electrical conductivity. This work summarizes research and development efforts in the field of protective coatings carried out at DTU Energy.

Abstract. High temperature corrosion of steel interconnects (IC) is an important degradation issue of solid oxide cell stacks. Due to a continuous growth of relatively poorly conductive oxides, resistance of the interconnect increases over time [1], contributing to increasing stack losses. In addition, on the oxygen side of the IC, evaporation of Cr species can occur and poison the electrodes further lowering stack performance. On the hydrogen side, interdiffusion of Cr, Fe and Ni can occur and cause austenitization [2,3] of the alloy and change of its thermal expansion and carbon solubility. For mitigation of these negative phenomena protective coatings can be used. This work summarizes coating solutions currently used at DTU Energy.

For the oxygen side, protective coatings include Mn-Co spinels, which have been proven to block chromium diffusion, have high electronic conductivity and good thermal expansion coefficient match to other stack components. These coatings, typically ~10 µm thick, are prepared by the electrophoretic deposition method, allowing covering large shaped ICs. In addition to the spinel, thin reactive elements coatings based primarily on yttria are considered for even further lowering corrosion rates. When used together with the spinel, these coatings offer synergistic effect of slow oxide growth and low Cr diffusion on the oxygen side.

For the hydrogen side, coatings based on yttria and doped ceria are being considered. They can slow the oxide growth and block interdiffusion between the alloy and the hydrogen electrode.

By combining coatings both for the oxygen side and for the hydrogen side, an advanced and effective coating solution can be achieved.

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Abstract No. 237

Power to Gas/Liquid - biomass gasification and SOEC combined system

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Summary. A very promising route for the production of biomass-derived transport fuel can be obtained by combining gasification and electrolysis units with a fuel synthesis reactor. The methanol or methane produced in this way could be 120-170% of the biomass input energy [1, 2]

Abstract. Many different technologies have been considered for large-scale storage of renewable electricity e.g. hydro storage which is technically very mature but limited possible sites. Electrochemical storage is also possible but batteries are very bulky, expensive and have limited operational life. Then there is chemical energy storage in the form of hydrogen. Hydrogen production is another option which has unlimited production prospect and can be converted back to electricity using fuel cell (though not preferred because of very poor round-trip efficiency). It can be used as a valuable feedstock for chemical industry e.g. production of ammonia, ethylene and synthesis of alternative energy carriers such as Synthetic natural gas (SNG), methanol, Dimethyl ether (DME) etc. by combining with CO_2 and N_2. This addition of external hydrogen will upgrade the existing biomass gasification process thereby extending the biomass resources.

The overall purpose of the SYNFUEL project is “to produce sustainable fuels: Using surplus electricity from e.g. wind power to produce hydrogen by steam electrolysis and upgrade it to gasified biomass thereby extending the biomass resources. By combining electrolysis and thermal gasification with a catalytic converter it becomes possible to synthesize methane, SNG or liquid fuel such as DME, FT (Fischer-Tropsch) and methanol”. The hydrogen addition meets the required stoichiometry and allows a nearly complete utilization of the carbon contained in the biomass [3]. Another advantage of such combined system is - the oxygen produced in the electrolysis can be used in oxygen-blown gasification process which has the advantage of avoiding feedstock from nitrogen dilution [4].

A gasification model of LT-CFB (Low temperature circulating fluidized bed) using oxygen as gasifying agent instead of air has been developed, it is a novel methodology and hardly any experience with these systems exist in practice. Similarly, a model for solid oxide electrolysis (SOE) has been developed and combined with gasification for the production of both methanol and methane. Different analyses have been performed on the complete system model e.g. Recycle ration effect on the methanation, temperature and pressure effect on syngas composition and final product etc. Currently, working on the SOE model to modify it for higher pressures, compares to the already developed state of the art systems to make it more compatible with the gasification process and especially for methanol synthesis. Later, the whole system will be optimized by heat integration using pinch analysis and heat exchanger network synthesis.

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Abstract No. 238

LSCF and LSC infiltrated LSCF electrode for high temperature steam electrolysis

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Summary: The present work is focused on $La_{0.58}Sr_{0.4}CoO_{3-\delta}$ (LSC) infiltrated $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) electrodes for solid oxide electrolysis cell (SOEC) aimed at efficient hydrogen production. In this respect, polarization curves and impedance spectra of both symmetrical as well as single cells are compared and investigated in detail.

Abstract: Solid oxide electrolysis cells (SOECs) have attracted considerable interest in the attainment of high purity hydrogen production. The most common electrolyte and hydrogen electrode materials for SOEC are yttria stabilized zirconia (YSZ) and Ni-YSZ respectively, exhibiting good electrochemical performance and stability. In terms of oxygen electrode materials LSM, LSCF and their composite with GDC or YSZ have been reported. Nevertheless, the electrochemical and thermo-mechanical stability of these materials during SOEC operation still requires further investigation.

Recently several researchers have focused their work on the degradation mechanism during SOEC operation. In short term (during first few hours) of ageing, the formation of Sr- and/or Co-rich particles on the top surface of dense LSCF samples has been reported by the authors while only surface Sr-enrichment is usually observed in aged porous oxygen electrode without microstructural changes [1, 2]. When it is kept for long duration at operating condition then particularly the delamination of oxygen electrode at the electrode/electrolyte interface is the most common mode of failure [3, 4]. According to Virkar [3], the oxygen evolution reaction at the oxygen electrode leads to a locally high partial pressure of oxygen (pO_2) in the electrode and at the electrode/electrolyte interface in SOEC mode, further leads to increase in electrode overpotential. So, the pO_2 and overpotential (η) at the electrode/electrolyte interface are the governing factors and should be treated carefully considering the specific interface structure. One way to avoid these problems could be to increase the ionic conductivity at the electrode/electrolyte interface.

Our current research work is focused on the oxygen electrode to avoid such kind of delamination by increasing the activity of oxygen electrode using infiltration of very active LSC material. The electrochemical performance of LSC infiltrated LSCF oxygen electrode is investigated for steam electrolysis and compared with blank LSCF electrode. Furthermore it is also tried to investigate at which overpotential the delamination of oxygen electrode starts. In this respect the symmetrical half-cell as well as single cell containing LSCF oxygen electrode with and without LSC infiltration are characterized using electrochemical impedance spectroscopy in the temperature range 750-900 °C. The symmetrical half-cells "8YSZ//CGO//LSCF" are characterized in a three electrode set up using a reference electrode with the aim to obtain detailed information on the different electrochemical processes and degradation mechanisms. The polarization resistance (R_p) values obtained for symmetrical half-cells with and without infiltration are 24 $m\Omega.cm^2$ and 32 $m\Omega.cm^2$ respectively, at 800 °C. The behavior of Ni-YSZ supported single cells "Ni-YSZ//8YSZ//CGO//LSCF is also investigated from 750-900 °C temperature range under both SOFC and SOEC modes. A maximum current density value of 1.48 $A.cm^{-2}$ is obtained at 800 °C under an applied electrolysis voltage of 1.5 V. Moreover, a decrease in the slope of I-V curve is noticed when temperature increases from 750 to 900 °C, which means that lower electrolysis voltage is required for hydrogen production at higher temperature. The investigation of LSC infiltrated LSCF single cell is under progress. The comparison of electrochemical properties of symmetrical half-cells and single cells with and without infiltration will be presented and discussed in detail.

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Abstract No. 239

Understanding and Tailoring Activity and Stability of Perovskite and Manganese Oxides for the Oxygen Evolution Reaction

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Summary. Using density functional theory calculations we endeavour to understand and disentangle the complex interplay between magnetic, electronic and geometric factors and their influence on the: structure stability, electronic conductivity and catalytic activity. Exploiting this knowledge we identify several promising oxygen evolving catalysts.

Abstract. The oxygen evolution reaction (OER) is a bottleneck in direct solar and electrocatalytic water splitting cells, and rechargeable aqueous metal-air batteries. Improving the cost-efficiency of these devices requires development of efficient and cheap oxygen evolving catalysts. A good catalyst material should fulfil several important criteria: the composition and structure should be stable at conditions of interest, it should be able to conduct electrons from the active site, and it should be sufficiently active to catalyze water oxidation to oxygen. Furthermore, it should be cheap, easy to handle and preferentially non-toxic.

We explore two different oxide classes: pristine and doped perovskite oxides (ABO_3, where A is the alkaline earth or lanthanide metal and B the 1st row transition metal) and several MnO_2 polymorphs.

Stability and the electronic conductivity of doped materials are assessed and compared to pristine catalysts by computing formation energies and analysing the electronic structure of bulk crystals, respectively. After selecting stable dopants, we calculate the relevant surface termination and deduce the reaction overpotential from the energetically most favourable reaction mechanism.

For the perovskite oxides, we observe an inverse correlation between the OER activity and stability such that the most catalytically active $LaCrO_3$ and $CaFeO_3$ oxides are not sufficiently stable and will readily dissolve under operating conditions. We identify Fe^{4+}, Co^{3+}(IS), Ni^{3+} and Mn^{3+}/Mn^{4+} pairs as electronically conductive species and distinguish among three different electron conduction types: intrinsic conductance (Fe^{4+} and Ni^{3+}), electron polaron hoping along the Metal-Oxygen-Metal chains (Mn^{3+}/Mn^{4+} and Cr^{3+}/Cr^{2+}) and conduction via oxygen holes in the valence band. Although, the intrinsic stabilities of La perovskites are rather low, they are likely to be the most stable catalysts in open systems because they do not form carbonates, which, otherwise, are readily formed with alkaline earth metals. From a combinatorial analysis on La perovskites, we identify Cu doped $LaMnO_3$, Mn doped $LaCuO_3$ and $LaCoO_3$ and Ni doped $LaCoO_3$ as the most promising oxygen evolving catalysts.

We find that the oxygen evolution activity of MnO_2 polymorphs reduces in the $\alpha MnO_2 > \beta MnO_2 > \gamma MnO_2$ sequence. We choose αMnO_2 as the most active catalyst and subsequently investigate whether its performance can be furthered by doping. The electronic conductance is greatly improved by creating Mn^{3+} sites, i.e. Mn^{3+}/Mn^{4+} pairs. This can be achieved by intercalating electrolyte ions (e.g. Na^+ or K^+) in large αMnO_2 holes or introducing oxygen defects/foreign atoms in the structure. From the catalytic analysis, we identify Pd doped αMnO_2 as the most active catalyst for oxygen evolution.

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Abstract No. 240

INSIDE – In-situ Diagnostics in Water Electrolysers

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Summary. An in-situ tool for online monitoring of operating conditions is developed for PEMWE, AE, and AEMWE.

Abstract. In this joint R&D project supported by the EU Fuel Cell and Hydrogen Joint Undertaking, an electrochemical in-situ diagnostics tool for the monitoring of locally resolved current densities in polymer electrolyte membrane fuel cells is adapted to three different water electrolysis technologies: based on proton exchange membranes (PEMWE), on anion exchange membranes (AEMWE), and alkaline water electrolysis (AE). The developed tools allow correlating performance issues and ageing processes with local anomalies. The corresponding mechanisms are investigated with ex-situ analytics.

INSIDE consortium:
- Deutsches Zentrum für Luft- und Raumfahrt e.V., Stuttgart, Germany (Coordination, polymer electrolyte membrane based water electrolysis)
- NEL Hydrogen AS, Notodden, Norway (Alkaline water electrolysis)
- Heliocentris Italy S.r.l., Crespina, Italy (Anion exchange membrane based water electrolysis)
- Centre National de la Recherche Scientifique, France (Ex-situ analytics)
- Université de Strasbourg, Strasbourg, France (Ex-situ analytics)
- Hochschule Esslingen, Esslingen, Germany (Ex-situ analytics)

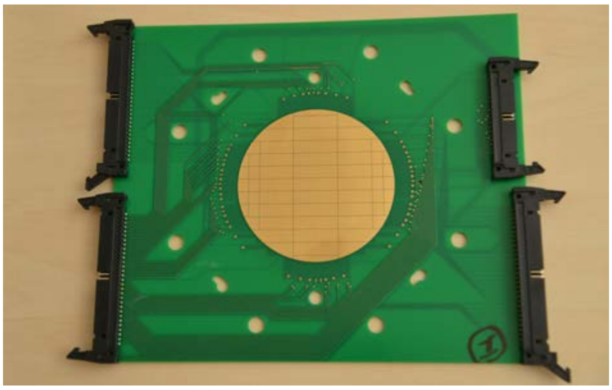

Fig. 1. 1st prototype for AEMWE has been constructed

The patented segmented printed circuit board (PCB) for the monitoring of current density distributions in PEM based fuel cells is used and continuously improved for e.g. the investigation of specific mechanisms or systematic optimisation.

The embedding of an in-situ diagnostics tool in water electrolysis system enables:
- monitoring of performance and local anomalies during operation
- revealing systematical deficiencies not detectable with off-line diagnostics
- correlating degradation mechanisms and system parameters
- identifying and preventing critical operation
- systematically improving the efficiency of water electrolysis

Abstract No. 241

Innovative photoelectrochemical cells based on polymeric membrane electrolytes and suitable porous photoanodes

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Summary. We have developed and evaluated a novel photoelectrochemical cell with polymeric electrolytes influenced by the design of PEM electrolysers, which operates with cheap and abundant photoanode materials. This innovative design allows us to enable novel operation modes for H_2 generation via water or alcohol electrolysis.

Abstract. Photoelectrochemical (PEC) splitting of water by the direct use of sunlight is an ideal, renewable method of hydrogen production. The majority of PEC cell studies utilize aqueous solutions as both the electrolyte and the photoanode reactants. Only few studies have attempted to separate the two half reactions compartments with a polymeric electrolyte membrane (PEM). In most of these cases acidic and alkaline solutions are used as anode reactants, but little work has been done with gaseous feedstock for the anode. In our study we used solid-state electrolytes in conjunction with gaseous reactants in a PEM-PEC cell. Such system shows potential advantages over the liquid ones such as operation at higher temperatures and pressures (for improving the electrode kinetics), direct production of compressed H_2, compact and robust design besides the separation of the products at the electrode compartments. Moreover, it allows a water "neutral" operation, in which water is captured from the humidity in the ambient air.

Typically in PEM-PEC studies the powder photocatalyst is dispersed on the porosity of carbon supports (to ensure electronic conductivity). This choice presents two main disadvantages: (i) the formation of many photogenerated species recombination pathways at the powder grain boundaries and (ii) poor stability after prolonged operation, since the photocatalytic powder may become unbound to the substrate. To overcome these issues, we have successfully demonstrated an alternative design for PEM-PEC photoelectrodes, which utilizes a Ti-web of microfibers as starting material. Electrochemical anodization of this substrate has led to the fabrication of TiO_2 nanotubes arrays. In order to enhance the scope of application of our system to the visible domain of sun light, we chose to modify our TiO_2 electrodes with lower band-gap semiconductors. It has been shown in the literature that the addition of a WO_3 layer on TiO_2 leads to an increase of the current along with a redshifted light absorption. Furthermore it is also well known that $WO_3/BiVO_4$ association leads to some of the most visible light active photoanodes.

We have developed photoanodes which are based on the double junction $TiO_2/WO_3/BiVO_4$. Since the porous nature of the titanium substrate prevents the use of conventional techniques such as spin coating, an alternative fabrication method was developed. The protocol involves sputtering of W, followed by anodization and then by successive ionic layer adsorption and reaction (SILAR) method for BiVO4 deposition. In this way we were able to create the desired double junction and the synergies between the different layers were studied by photoelectrochemistry. The performances of the TiO_2/WO_3 and $TiO_2/BiVO_4$ assemblies at pH=1 remained quite limited with a maximum photocurrent of 0.1 mA/cm2 at 1.2V. But the full association $TiO_2/WO_3/BiVO_4$ gave a significant magnification of the current to reach ~1 mA/cm2 at 1.2V (Figure 1).

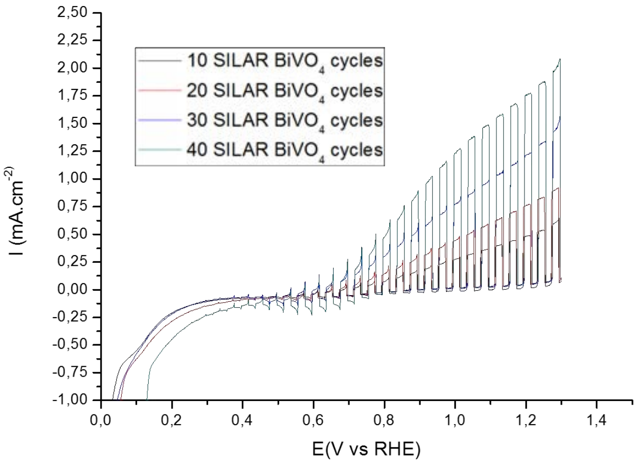

Figure 1: Effect of $BiVO_4$ loading on TiO_2/WO_3 substrate under simulated AM1.5 solar light at the chopped (On/Off) light condition at pH=1.

Abstract No. 242

Electrolysers based on CsH_2PO_4 to work at high pressures and moderate temperatures

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Summary. Electrolysers able to work at high pressures and moderate temperature were developed using CsH_2PO_4 as electrolyte base. The electrodes electrocatalytic activity was tailored by using different metals and electrode configurations. Stable production of hydrogen was obtained during steam electrolysis with high Faradic efficiencies.

Abstract. CsH_2PO_4 is a new-generation electrolyte for fuel cells that enable operation at intermediate temperature (200 - 300 ºC) [1]. CsH_2PO_4 transforms into cubic phase showing superprotonic conductivity when the temperature is increased above 230 ºC [2]. Unlike high temperature electrochemical cells, the low operation temperature of CsH_2PO_4 allows the possibility to use cheap materials for the stack construction, reducing the cost of the device and increasing the lifetime. Moreover, due to the higher operation temperature, compared with polymeric membrane fuel cells (80 ºC), different catalysts instead of platinum can be employed, increasing the possibilities of the cell.

Usually, the same material can be used as electrolyte in a fuel cell or electrolyser cell, but the reactions involved are the reverse. This premise was taken into account and CsH_2PO_4 was tested as electrolyte material in a fuel cell and electrolyser mode.

Different cell configurations were studied for the optimization of the cell performance. Firstly, symmetrical cells supported on the electrolyte were manufactured by employing the same electrode material for cathode and anode. Carbon Gas Diffusion Layer (GDL) was employed as electrode backbone and different catalysts as Cu, Zn and Pt were infiltrated. Some improvements were performed as to enlarge the triple phase boundary and composite electrodes were designed. CsH_2PO_4 was selected as proton phase whereas carbon powder impregnated with different metals was used as electronic conductor material. Secondly, the electrolyte thickness was reduced by supporting the cell on different supports: steel or nickel porous supports, reducing the thickness of the electrolyte from 1.8 mm to 100 µm. Further studies were performed in order to improve the mechanical stability of the sample. The addition of an epoxy in the electrolyte [3] allowed working with a system pressure of 20 bar. Different ratios of CsH_2PO_4 and epoxy were studied in order to obtain good conductivity and good mechanical stability.

Furthermore, the influence of total pressure was tested for the different cells, and results showed that increasing the pressure in the system, the performance increased in more than six times. The results highlighted the big influence of the system pressure and operation temperature. During the time that a constant current was applied to the system in the steam electrolysis mode, the composition of the outlet stream was analysed by a mass spectrometer and a gas chromatograph. Stable production of H_2 was observed and the Faraday's efficiency achieved values around 100 %.

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