

Development of novel High Temperature and Pressure Alkaline Electrolysis Cells (HTP-AEC)

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Introduction

Background

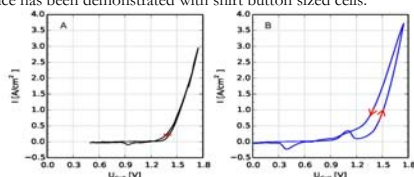
- A HTP-AEC with gas diffusion electrodes (metal foams) and an aqueous KOH electrolyte immobilized in a mesoporous ceramic matrix structure has been developed at DTU Energy.

- Very high current density and performance has been demonstrated with shirt button sized cells:

Record data from earlier work [1]:

3.75 A/cm^2 at 1.75 V with

$\eta_a = 85\%$ (200°C , 20 bar) [1]



Motivation

- High temperatures (200°C) increase the activity of the electrodes and the conductivity of the electrolyte significantly.

- A cell that allows for high efficiency and current density simultaneously using non-noble metals.

Challenges

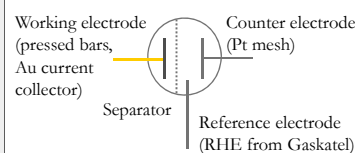
- Corrosion issues at the oxygen electrode. Identification of more stable materials, which also show sufficiently high catalytic activity towards the oxygen evolution reaction.
- Processing of cell layers with optimized microstructure using a low cost & scalable processing method.

The experiments

Electrode materials for the oxygen electrode

- Electrode materials (electrocatalysts) based on La, Ni and Fe for the oxygen evolution reaction (OER) have been identified and evaluated.
- The electrochemical activity of the materials has been tested at room temperature and pressure conditions in N_2 atmosphere using densely sintered pellets polished down to $1 \mu\text{m}$ roughness.
- The chemical stability of the powder, immersed in $45 \text{ wt}\%$ KOH, and heated in an autoclave to 200°C has been examined comparing XRD patterns before and after.

Three-electrode setup for electrochemical characterization

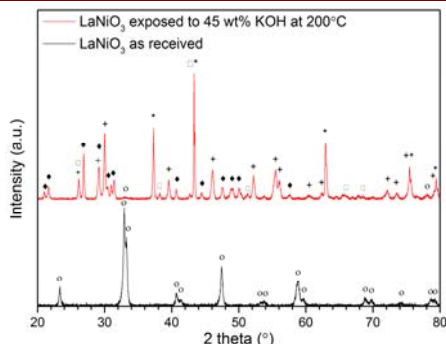
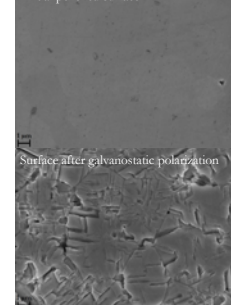


Chemical stability assessment

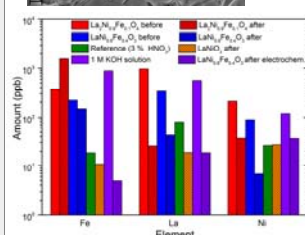


Results – chemical stability

$\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ pellet surface before and after $\sim 20 \text{ h}$ electrochemical testing.

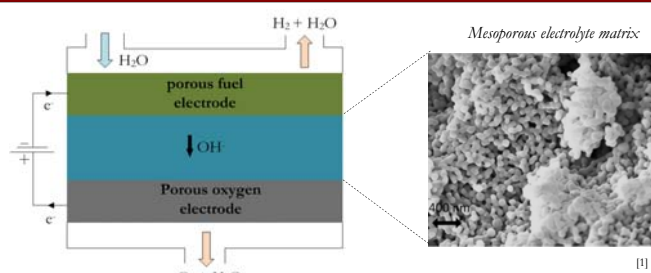


XRD patterns of the as-received LaNiO_3 powder and the same powder after exposure to $45 \text{ wt}\%$ KOH at 200°C for 9 days. The symbols represent the following phases: $\circ \text{LaNiO}_3$, $\blacklozenge \text{LaO(OH)}$, $\square \text{NiO(OH)}$, $\ast \text{La}_2\text{O}_3$, $\ast \text{NiO}$. The $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ and $\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_4$ powder showed similar decomposition behaviour though at a slower rate.



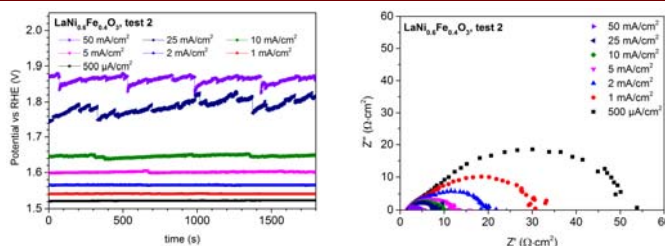
ICP analysis of supernatants from the KOH solution used for the chemical stability testing. The concentration of La, Ni and Fe ions are generally decreasing after compared to before testing. This indicate that there is a net consumption of the metal ions most likely consumed by the decomposition products (cf. the XRD pattern above)

The cell concept

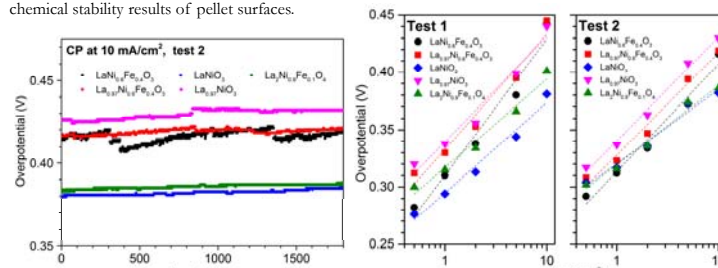


The mesoporous electrolyte matrix contains the KOH electrolyte. The porous electrodes will allow some infiltration of the electrolyte into the electrode to increase the surface area where the electrochemical reactions take place.

Results - Electrochemical activity towards the OER



The iR-corrected galvanostatic polarization of $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ and the Nyquist plot of the EIS measurements performed after each galvanostatic polarization. Current densities are based on geometric surface areas. Test 2 is performed on the same sample as test 1 so it is not a newly polished sample; cf. chemical stability results of pellet surfaces.



Comparison of the of galvanostatic polarizations performed at 10 mA/cm^2 .

The tafel plot of the measurements. The fit is from $0.5 \sim 10 \text{ mA/cm}^2$. There is a slight increase in the tafel slope above 2 mA/cm^2 , which is then not accounted for.

The calculated Tafel fit parameters ($E = a + b \log(i)$) from the tafel plot, test 1 together with the overpotential, η , at 10 mA/cm^2 . The state-of-the-art, IrO_x , and two of the best performing non-noble oxygen evolution catalysts are also included as benchmarking.

Material	b (mV/dec)	a	R ²	η (V) @ 10 mA/cm^2
LaNiO_3	79	0.30	0.97	0.38
$\text{La}_{0.97}\text{NiO}_3$	92	0.34	0.97	0.44
$\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$	119	0.31	0.95	0.44
$\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$	101	0.33	0.97	0.45
$\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_4$	77	0.32	0.98	0.40
IrO_x [2],[3]	-49	-	-	0.32/0.54
$\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_x$ [3],[4]	30/30	-	-	0.34/0.28
$\text{PrBaCo}_2\text{O}_{5+x}$ [5]	~ 70	-	-	~ 0.38

Outlook

Processing of porous oxygen electrodes

Based on the electrochemical screening, $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ is going to be used as oxygen evolution electrocatalyst. The microstructure of the oxygen electrode is going to be optimized using the processing method screen printing. The thickness, porosity and pore size distribution of the electrode will be varied during this optimization process.

Successful fabrication and electrochemical characterization of up-scaled cells ($5 \times 5 \text{ cm}^2$) with the microstructurally optimized oxygen electrode is the expected outcome of the project.