

**CRITICAL RAW MATERIALS ELIMINATION BY A TOP-DOWN APPROACH TO
HYDROGEN AND ELECTRICITY GENERATION**

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DELIVERABLE REPORT

DELIVERABLE 3.3 – CRM-FREE METAL OXIDES AS OER CATALYSTS: SYNTHESIS, CHARACTERIZATION AND PERFORMANCE IN AEMEL & BMEL

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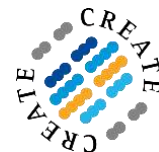
DISSEMINATION LEVEL

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PP	Restricted to other programme participants (including the Commission Services)	
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NATURE OF THE DELIVERABLE

R	Report	X
P	Prototype	
D	Demonstrator	
O	Other	

SUMMARY	
Keywords	oxygen evolution reaction, alkaline media, electrocatalyst, catalyst, critical raw material, iron, nickel
Full Abstract (Confidential)	<p>The report presents the synthesis, activity and stability data for Ni-Zn-Fe oxides obtained as nanoparticles or as nanostructured films on Ni electrode supports in alkaline electrolyte, measured with rotating ring disk electrode and Ni foam electrodes in liquid alkaline electrolyte first. Results obtained in AEMEL are then reported, including durability over 140 h at constant current density.</p> <p>The results show high activity at 2.25 V, high power performance in AEMEL and promising durability during AEMEL operation with Ni-Fe anodes and Pt(Ru)/C cathodes in alkaline electrolyte. The activity at 1.65 V in AEMEL is higher than that obtained with 1.5 mg(IrO₂) cm⁻² state-of-art anodes, while slightly lower performance is seen at high current densities, assigned to poor gas diffusion in Ni foam. The Ni-Zn-Fe oxide catalyst showed slightly lower performance than Ni-Fe anode, assigned to poorer electrical conductivity due to the ionomer interface, and showed lower performance than in rotating ring disk electrode setup.</p>
Publishable Abstract (If different from above)	



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1 INTRODUCTION

The purpose of D3.3 is to demonstrate the preparation of optimized OER catalysts and to characterize them for the oxygen evolution reaction (OER) in alkaline medium first, and then in AEMEL and also in BMEL if a bipolar membrane (BM) with sufficient through-plane conductivity is available at M38 (due date of this deliverable). The goal was to demonstrate a promising path for replacing iridium oxide by anode catalysts based on Earth-abundant elements in AEMEL and/or BMEL, with no or small performance drop when replacing IrO₂ by non-PGM cathodes.

This report presents the synthesis of optimized OER catalysts based on abundant metals: Fe, Ni, Zn (not belonging to the EU-updated list of Critical Raw Materials); their structural characterization, their electrochemical characterization in alkaline electrolyte (activity, selectivity, stability) and then their evaluation at the anode of AEMELs. Due to higher through-plane resistance of bipolar membrane than desired for high power density AEMEL at M38 and issues associated with the preparation of BM with H⁺ and OH⁻ form on each side, testing of BMEL with these anodes has not been performed yet. The promising results obtained with AEMEL with Fe-Ni oxide nanostructured anodes however show that such anodes would also be suitable for BMEL if a proper BM and MEA preparation for BMEL is available in the near future.

2 PROTOCOLS FOR ELECTROCHEMICAL MEASUREMENTS

2.1 EXPERIMENTAL CONDITIONS AND PROTOCOL FOR OER ACTIVITY MEASUREMENT IN LIQUID ELECTROLYTE

The electrochemical experiments were performed with a Biologic SP-300 potentiostat. A three-electrode cell configuration was used for all experiments using 0.1 M KOH as electrolyte solution, a reversible Hg/HgO electrode as a reference, and a graphite rod as counter electrode.

For powder samples, the catalyst ink was deposited on a nickel rotating working electrode. The catalyst ink was prepared with 10 µg/µL (FAA-3, 5% solution in lower alcohols). The ink was ultrasonicated for 30 minutes and a 6 µL aliquot was then deposited with a pipette on the nickel rotating electrode (0.07 cm² disk electrode), so that a catalyst loading of ca 0.84 mg·cm⁻² is obtained. Once the electrode was completely dry, a drop of water was deposited on it to minimise the entrapment of air bubbles during the immersion of the shaft and rotating disk electrode (RDE) tip in the electrolyte. Then, a current interrupt (0.5 mA) is applied with a frequency of 0.2s for 10 times to measure the Ohmic drop. Ar or N₂ is bubbled through the electrolyte for 15-30 min to remove O₂, then inert gas is supplied above the electrolyte; cycling the potential between 1.3 V vs. RHE and 1.7 V vs RHE at 75 mV/s until reproducible, at 1600 rpm. Bubbling O₂ for 30 min or until OCP stabilizes. Polarization curves are measured at 1 mV/s starting from OCP to 1.7 V vs. RHE and back to 1.3 V vs RHE (1 cycle if the positive and negative going scans superimpose, 2 cycles or more otherwise) at 1600 rpm, or without rotation (if not in RDE)

For surface-decorated Ni foam working electrodes, the catalyst loading was determined by weight difference, before and after the decoration, and then the ionomer ink was deposited on the surface for additional stabilization. An analogous activity protocol was performed, including break-in procedure, by using magnetic stirring.

3 PROTOCOLS FOR ELECTROCHEMICAL MEASUREMENTS

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3.2 EXPERIMENTAL CONDITIONS AND PROTOCOL FOR OER STABILITY MEASUREMENT IN LIQUID ELECTROLYTE

Accelerated stability tests (AST) were performed by comparison between the initial polarization curve (following the procedure described above) and the polarization curve obtained with the same electrode after 5000 potential cycles between 1.3 and 1.7 V vs. RHE. The 5000 cycles were applied either in N₂-saturated or O₂-saturated 0.1 M KOH electrolyte (indicated in figure captions), at a scan rate of 100 $\text{mV}\cdot\text{s}^{-1}$ and without any rotation (AST protocols No. 1 and 2, as defined in Deliverable 2.1, "Definition of Test Protocols" of the project CREATE). For the final polarisation curve, a fresh electrolyte was used, and the same conditions as used for recording the initial polarisation curve were applied.

3.3 MEMBRANE-ELECTRODE-ASSEMBLY PREPARATION AND AEMEL TEST CONDITIONS

Catalyst coated membranes were prepared by a direct spray coating of the OER catalyst ink (as described above) onto the membrane. A hot-pressing procedure at 140°C was implemented to assist with adhesion of the catalyst to the membrane. This was carried out in the bromide form of the FAA-3 ionomer as this is the most stable form under elevated temperature conditions.

Catalyst coated electrodes technique was used for surface-decorated Ni foam working electrodes. In this case, the nano-FeNi/Ni foam supports were sprayed with FAA-3 ionomer and then incorporated to the MEA by mechanical pressing procedure.

3.4 SYNTHESIS OF OER CATALYSTS

NiZnFe-comb catalysts: All reagents were commercially available and used as received. Mixed metal oxides were prepared from metal nitrates, in appropriate ratio, dissolved in 50 mL of distilled water. Glycine was added into the aqueous solution (glycine/metal molar ratio = 1.20) and stirred until total dissolution. Afterwards, the solution was heated up to 200°C until total solvent evaporation and glycine combustion. The resulting porous dark solid was recovered and calcined at 1100°C in a tubular oven for 1

hour. Finally, calcined material was mechanically milled in an Agate ball milling jar (2 Agate balls) at 25 KHz for 15 minutes.

NiZnFe-8.5 catalysts: Metal oxide was obtained by hydrothermal method. Equimolecular amounts of the metal nitrates were dissolved in water (metal concentration 50 mM), and the solution was hydrolyzed with diluted aqueous ammonia until pH 8.5. The solution was introduced in a Teflon cup and mounted in an autoclave at 140°C for 2 hours. After the hydrothermal treatment, the pressure vessel was cooled in air and the product was washed with H₂O and CH₃CH₃OH, and the nanoparticles were collected by centrifugation (Final particle size ~8 nm). In general, for all oxides the yield per batch is ~ 100 mg.

Fe-Zn-Ni nanostructured catalysts on Ni-foam supports: To decorate Ni foam electrodes with nanostructured Fe-Ni oxides we followed a multi-step procedure. First, a piece of commercial Ni foam was dipped into an iron nitrate solution (prepared by dissolving 7.5g Fe(NO₃)₃·9H₂O precursor in 50 mL deionized water) and slowly dried in air. After drying in air, it was then thermally phosphatized in a tube furnace at 450°C. The phosphorus source was 1 g sodium hypophosphite monohydrate (NaH₂PO₂·H₂O), which was put at the upstream of the Ar circulation at around 400°C. This thermal phosphidation forms Fe(PO₃)₂ nanocrystals on top of the Ni₂P surface formed on the Ni foam, during cooling down to room temperature under argon. This immersion/phosphidation process was repeated twice to yield a Fe(PO₃)₂ loading of 3-5 mg·cm⁻².

4 STRUCTURAL CHARACTERIZATION OF NI-ZN-FE OXIDES AND NI-FE/NI FOAM ELECTRODES

4.1 STRUCTURAL CHARACTERIZATION OF NI-ZN-FE OXIDE CATALYSTS

We characterized the Ni-Zn-Fe oxide OER electrocatalysts by HR-TEM images (Figure 1), including electron diffraction. The material is a pure phase cubic M₃O₄ [FD3-MZ]-Space group 227, with lattice parameter $a = 0.8391$ nm.

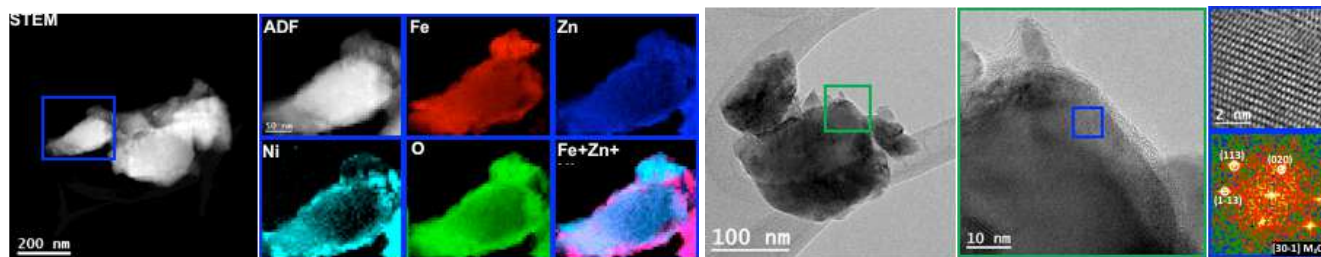


Figure 1. NiZnFeOx HR-TEM data and electron diffraction: (left) EELS chemical composition maps obtained from the blue rectangle area in the ADF-STEM micrograph. Individual Fe (red), Ni (green), Zn (blue), O (indigo) maps and composite maps. (right) Left and Middle: low magnification TEM micrograph shows edge structure of the nanoparticle. Right: magnified detail HRTEM of the blue squared region and the corresponding temperature coloured FFT spectrum, which indicates cubic M₃O₄ [FD3-MZ]-Space group 227, as visualized along the [30 $\bar{1}$] direction.

4.2 STRUCTURAL CHARACTERIZATION OF NANO-NI-FE/NI FOAM ELECTRODES

We characterized the nano-Ni-Fe/Ni foam OER electrodes by HR-TEM images (Figure 2), including electron diffraction. The presence of Fe was detected, but only as amorphous nano-islands, since no structural pattern was observed. The surface material detected is a pure Ni₂P phase the hexagonal Ni₂P, [P6-2M]-Space group 189, with lattice parameters $a = 0.5866$ nm and $c = 0.3385$ nm.

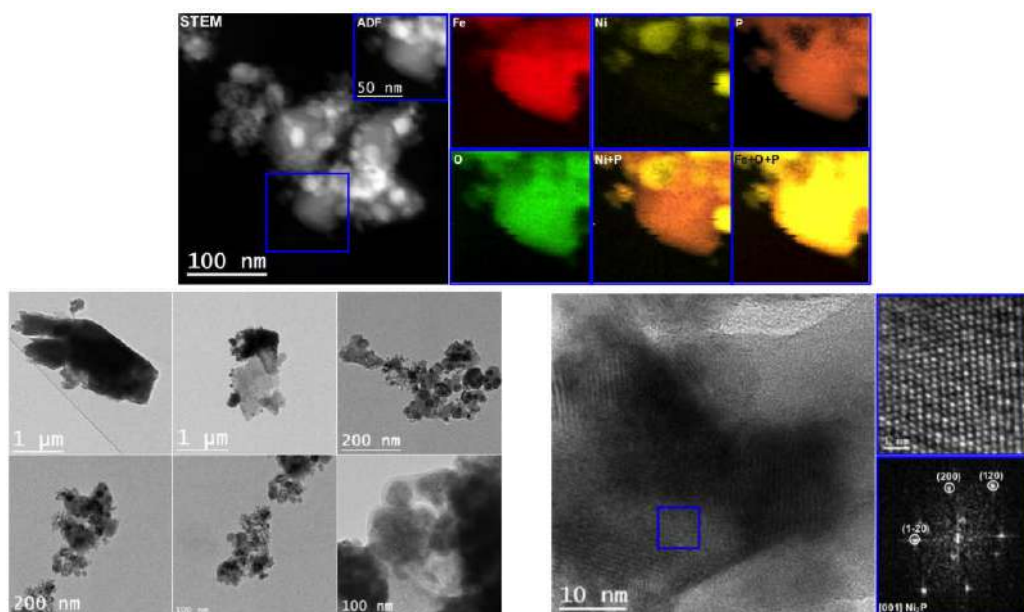


Figure 2. $[\text{Fe}(\text{PO}_3)/\text{Ni}_2\text{P}/ \text{Ni-foam}]$. (top) EELS chemical composition maps obtained from the blue rectangle area in the ADF-STEM micrograph. Individual Fe (red), Ni (yellow), O (green), P (orange) maps and respective composite maps. (bottom left) Low magnification TEM images showing the general morphology of the sample. (bottom right) HRTEM image of the sample, detail of the blue squared region and the corresponding FFT spectrum, which indicates that it is in agreement to the hexagonal Ni_2P , [P6-2M]-Space group 189, with lattice parameters of $a = b = 0.5866 \text{ nm}$, $c = 0.3385 \text{ nm}$, and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ as visualized along the [001] direction.

The electrodes were characterized by scanning electron microscopy (ESEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (Fig. 3) after AST cycles. These data support the evolution of the as-prepared $\text{Fe}(\text{PO}_3)/\text{Ni}_2\text{P}$ species to amorphous Fe-Ni oxide, since metallic Ni is the only structural response from these used electrodes. Therefore, these analyses confirmed the presence, before and after OER, of all different elements on the surface and purity of the crystalline structure. The surfaces do not show visible degradation after the electrochemical testing.

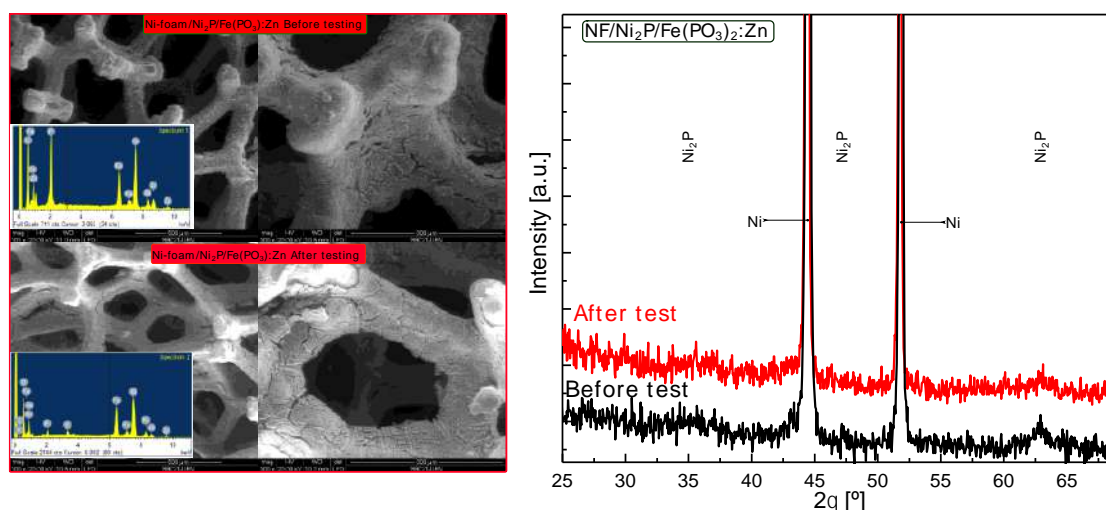


Figure 3. ESEM image and XRD pattern of the Ni-foam decorated with the $\text{Ni}_2\text{P}/\text{meta-phosphate}$ doped with Zn. The characterization was performed before and after the electrochemical tests.

5 STABILITY AND ACTIVITY OF Ni-Zn-Fe OXIDES AND Ni-Fe/Ni FOAM ELECTRODES IN LIQUID ELECTROLYTE

5.1 ELECTROCHEMICAL ACTIVITY

The electrochemical tests were performed in a three-electrode system in 0.1 M KOH electrolyte purged with high-purity oxygen gas continuously. A graphite rod and mercury/mercurous oxide (Hg/HgO) reference were used as the counter and reference electrodes, respectively. The catalysts on Ni foam were used as the working electrode directly. The OER catalytic activity was evaluated using linear sweep voltammetry with a sweep rate of 1 mV/s.

Figure 4 shows the activity toward OER electro-oxidation for the NiZnFe oxides, as obtained by combustion or hydrothermal methods. The best catalyst in these forms was NiZnFe-8.5, with best activity related to its smaller particle size and larger surface area.

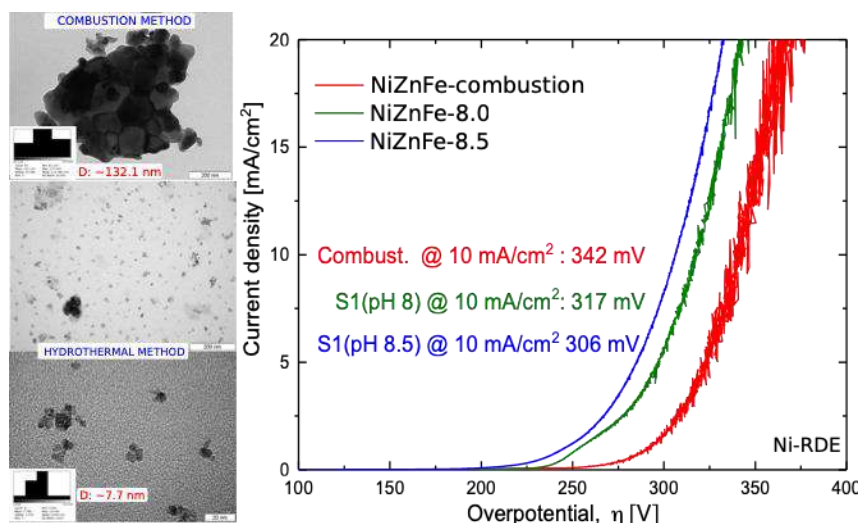


Figure 4. Compared activity for OER electro-oxidation for the three best NiZnFe oxides obtained by combustion, or hydrothermal methods (8.0 and 8.5) in O_2 -saturated 0.1 M KOH electrolyte. The polarisation curves are measured at 1 mV s^{-1} and 1600 rpm of rotation

In Figure 5, we show the comparison of the decorated Ni-foam with different element doping and ratios. At this stage, the best performance was observed for the nano-NiFe/Ni foam doped with Zn (red curve). In contrast, the doping with Ni increased the overpotential (green curve), resulting in a lower activity compared to the initial situation without doping (blue curve).

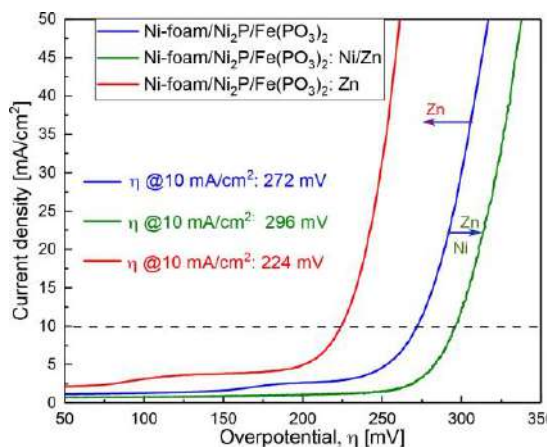


Figure 5. Compared activity for OER electro-oxidation for the nano-NiFe/Ni foam electrodes oxides in O₂-saturated 0.1 M KOH electrolyte with different element doping. The polarisation curves are measured at 1 mV s⁻¹ in a magnetically stirred solution.

5.2 ELECTROCHEMICAL STABILITY

The stability of the catalysts was studied by Accelerated Stability Test (AST).

The NiZnFe-8.5 activity improved during ASTs, so we increased the cycle number up to 15,000 (Figure 6). During this experiment, a continuous increase of the catalytic activity is observed, still occurring between 10 k and 15 k cycles, and reducing the overpotential to deliver 10 mA·cm⁻² from 327 mV initially to only 270 mV after 15 k cycles. This reduction by 57 mV of the overpotential is a strong evidence that the catalyst is not only robust, but even presents increased activity while cycling for long period of time.

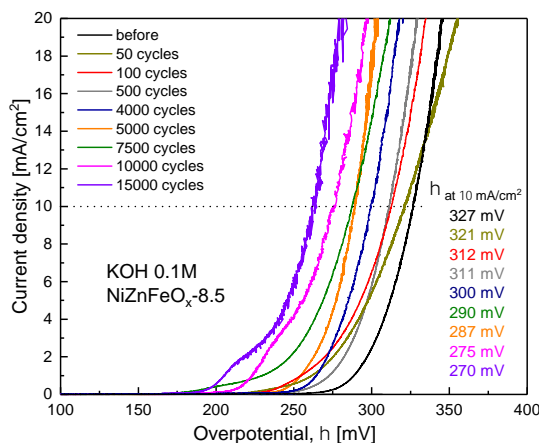


Figure 6. LSV curve after different cycles (AST) for the NiZnFe-8.5 catalyst. Catalyst loading 840 μg cm⁻², FAA-3 as a binder, 1 mV/s, 1600 rpm for initial and final LSV, 800 rpm during AST, 0.1 M KOH

Comparative stability was also determined by chrono-potentiometry 50 h measurements (Figure 7) showing that all OER catalysts exhibit good stability. All of them are able to maintain 10 mA cm⁻² during this time with changes in overpotential < 10 %.

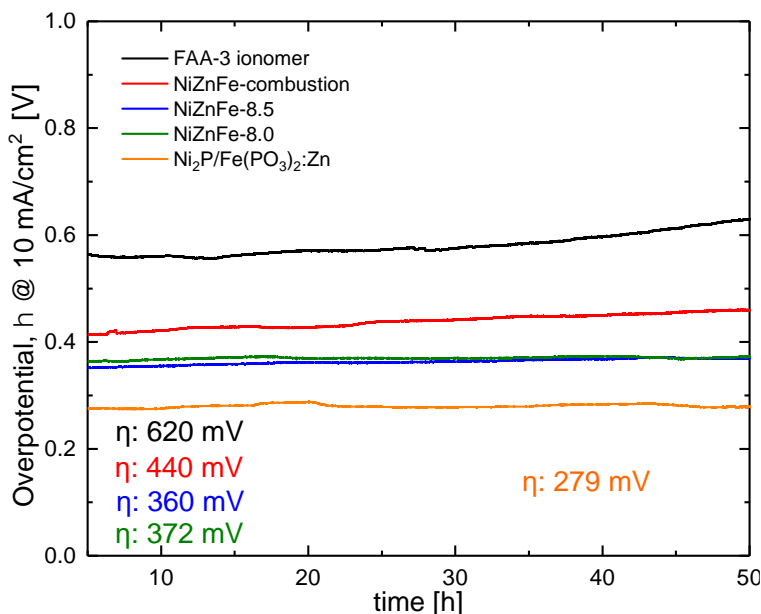


Figure 7. Chrono-potentiometry, comparing the most active catalyst obtained in the first stage of the project. The catalyst was supported directly on Ni-foam, using the FAA-3 ionomer from FUMATECH.

5.3 OPERANDO STUDIES

Changes in the oxidation states of the Ni-Zn-Fe **oxide** during the OER reaction were investigated by *operando* EXAFS-XANES analysis in liquid electrolyte from the partner Northeastern University (Qingying Jia and Sanjeev Mukerjee). The preliminary XAS analysis shows that only Fe changes its oxidation state at potentials relevant to OER (Figure 8). The Fe changes its oxidation state as early as 1.0 V vs RHE, which can probably be related to high OER activity, assuming Fe is the active site. The Ni K-edge and Zn K-edge spectra were also recorded but did not show any change with electrochemical potential (spectra not shown here).

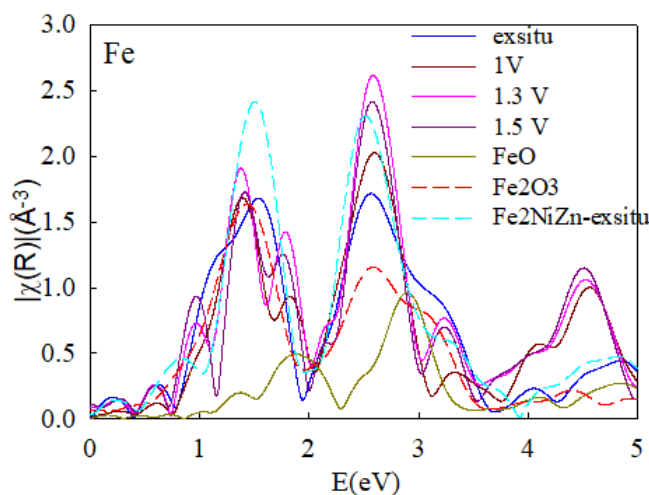


Figure 8. In-operando EXAFS on Fe edge for NiZnFe at potentials of 1.0, 1.3 and 1.5 V vs. RHE, in 0.1 M KOH.

6 PERFORMANCE OF NI-FE/NI FOAM ANODES IN AEMEL

6.1 AEMEL PERFORMANCE WITH NANO-NI-FE/NI FOAM ANODES AND COMPARISON TO IRIIDIUM OXIDE

Polarisation curves recorded at 60°C for the best performing AEMEL cells are shown in Figure 9. The main difference appears to be the lower Ohmic resistance for the cell using IrO_x which is at least partly due to the use of a thinner membrane for this test. Hence, the Fe-Ni-Ox/Ni foam catalyst can be considered to be a good replacement for PGM catalysts at the anode.

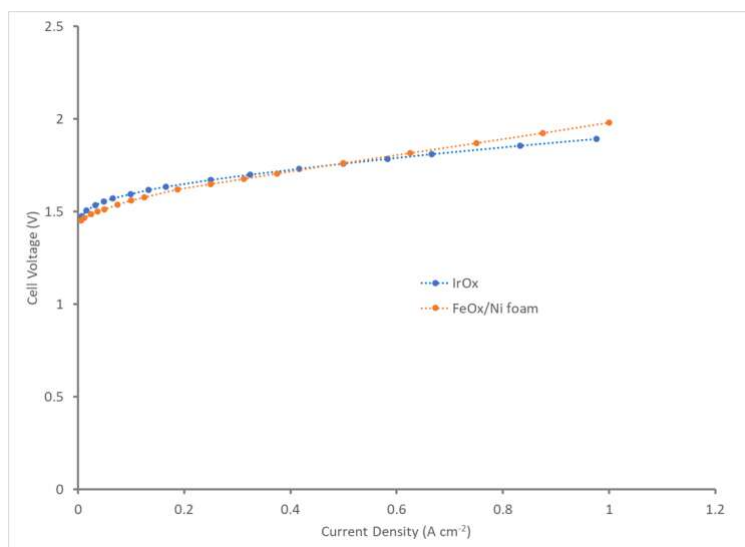


Figure 9. Polarisation curves recorded at 60°C using fumapem[®] VM-FAA- 3-50 membranes. 1.47 mg cm⁻² IrO_x on Ti felt 1wt% K₂CO₃ and 2.7 mg cm⁻² Fe-Ni-Ox/Ni foam anode. Cathode Pt/C 0.2 mg cm⁻² loading.

6.2 PERFORMANCE AND DURABILITY OF NANO-NI-FE/NI FOAM IN AEMEL WITH ALKALINE ELECTROLYTE

Figure 10 shows the results obtained in a AEMEL equipped with a MEA prepared with a fumapem[®] VM-FAA-3-50 membrane with 6.3 mg cm⁻² Fe-Ni-Ox/Ni foam anode and 0.23 mg cm⁻² Pt/C cathode. The fumion[®] FAA-3 ionomer was used to process both electrodes. Testing was performed at 45°C and 60°C. Figure 11 shows the results obtained with analogous architecture but with lower loadings of 1.4 mg cm⁻² Fe-Ni-Ox/Ni foam anode and 0.01 mg cm⁻² PtRu/C cathode. In this case, a fumion[®] AE resin was used at the cathode. Testing was performed at 45°C and 60°C. These results show that high performance can be achieved with an ultra-low CRM AEMEL, using the non-CRM nano-Fe-Ni-Ox/Ni foam anodes. A steady state test at 45°C and 0.5 A cm⁻² is shown in Figure 12.

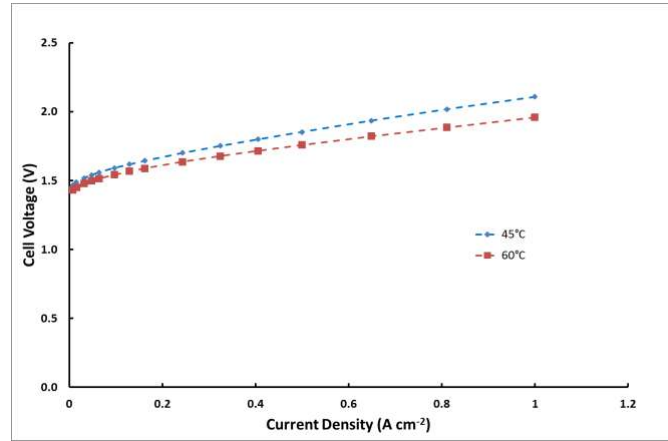


Figure 10. Polarisation curves for an 8 cm² AEMEL cell with 6.3 mg cm⁻² Fe-Ni-Ox/Ni foam anode, a 0.23 mg cm⁻² Pt/C cathode, and a fumapem® VM-FAA-3-50 membrane. Measurements were performed at 45°C and 60°C.

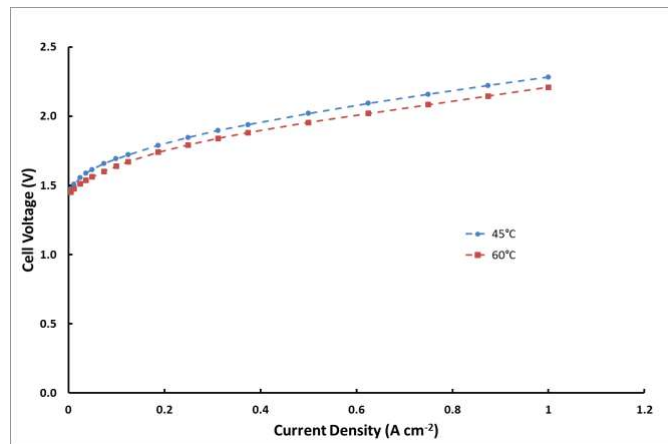


Figure 11. Polarisation curves for an 8 cm² AEMEL cell with 1.4 mg cm⁻² Fe-Ni-Ox/Ni foam anode, a 0.01 mg cm⁻² PtRu/C cathode and a fumapem® VM-FAA-3-50 membrane. Measurements were performed at 45°C and 60°C.

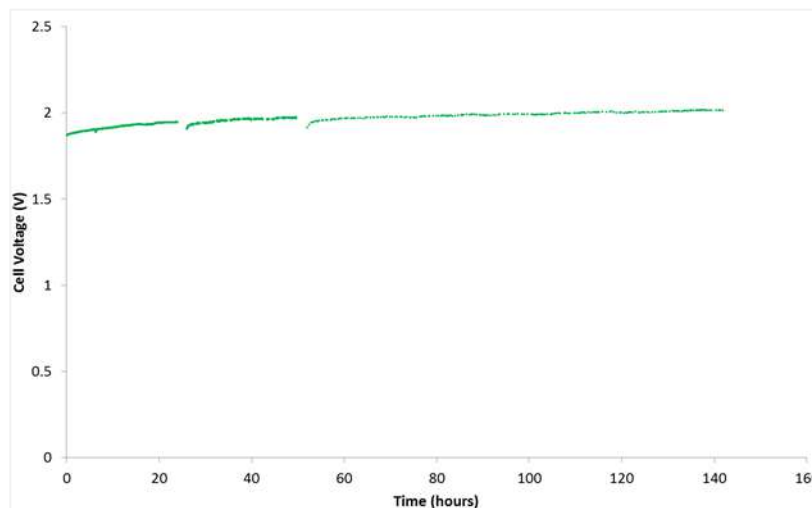


Figure 12. Steady state test at 45°C, 0.5Acm⁻² with 7.0 mg cm⁻² (Ni₂P/Fe(PO₃)₂) anode, 0.23 mg cm⁻² Pt cathode, fumapem® VM-FAA-3-50, 0.1M NaOH

7 CONCLUSIONS

In the first stage, several material options based on non-CRM elements were explored for the anode, using just Ni, Zn and Fe but of different compositions and morphologies. After a careful analysis, also taking into account the crystalline structure observed after accelerated stress tests, we decided to use a nanostructured NiZnFe catalyst with 1/1/1 atomic ratio for further integration and testing in AEMEL configuration in WP5. At this stage, we found outstanding results in liquid electrolyte with very low overpotential around 270 mV to deliver $10 \text{ mA}\cdot\text{cm}^{-2}$, above the internal CREATE target defined for OER activity, and of course, free of precious materials such as Ir, Ru, etc... However, this high activity for the nanostructured NiZnFe-8.5 material did not result in outstanding performance in AEMEL configuration, with problems arising with performance stability.

We therefore translated the same synthesis strategy to the direct decoration of Ni foam supports with Ni-Fe oxides via a phosphidation process. In this case, the Fe-Ni-Ox/Ni foam catalyst showed the highest activity in liquid alkaline electrolyte, providing a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ at 1.449 V vs. RHE ($\eta=220 \text{ mV}$). These electrodes also offered exceptional performance in AEMEL configuration, which a current density of 0.5 A cm^{-2} at 1.98 V, cell temperature of 45°C , using ca 2% PtRu/C at the cathode ($0.01 \text{ mg}_{\text{PGM}} \text{ cm}^{-2}$). These results are above the previously best reported results for a non-PGM anode catalyst in AEMEL.