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New Anion Exchange Membrane Electrolysers

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ANIONE

Anion Exchange Membrane Electrolysis for Renewable Hydrogen Production on a Wide-Scale

ANIONE – Deliverable Report

D 4.1 Data set on catalytic activity, electrochemical performance and stability of enhanced catalysts

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 875024. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme, Hydrogen Europe and Hydrogen Europe research.

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Publishable summary

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Abbreviations

Symbol / Shortname	Full Name
CRM	Critical raw materials
PGM	Platinum group metal
MEAs	Membrane electrodes assemblies
BOL	Beginning of life
EOL	End of life
ASP	Area Specific Resistance
BET	Specific Surface Area measured by the Brauner–Emmett–Teller method
BoT	Beginning-of-Test
d.p.	Decimal precision
DHE	Dynamic Hydrogen Electrode
DMA	Dynamic Mechanical Analysis (Glass transition temperature)
DoA	Description of Action
DSC	DSC Differential Scanning Calorimeter
Ea	Anode Overpotential
Ec	Cathode overpotential
BET	Specific Surface Area measured by the Brauner–Emmett–Teller method

ECSA	ElectroChemical Surface Area
EDX	Energy Dispersive X-ray
EIS	Electrochemical Impedance Spectroscopy
EoT	End-of-Test
EW	Equivalent weight
GC	Gas Chromatography
GDL	Gas Diffusion Layer
ICP	Inductively Coupled Plasma
IEC	Ion Exchange Capacity
OCV	Open Cell Voltage
PEM	Proton Exchangeable Membrane
PTL	Porous Transport Layers

1 Introduction

Anion exchange membrane water electrolysis

Alkaline liquid-electrolyte water electrolysis is currently one of the least costly technologies for water electrolysis. Alkaline electrolysis is a mature technology for hydrogen production up to the megawatt range and it represents one of the most used electrolytic technology at a commercial level worldwide. Alkaline systems are currently characterised by a lower cost of the raw materials among the different electrolysis technologies. This system is comparatively cheap with low cost diaphragm separators, non-precious metals as the electro-catalysts for the hydrogen and oxygen evolution reactions and steel bipolar plates. However, a significant disadvantage is the use of a corrosive alkaline liquid electrolyte, e.g. 7-10 M KOH, in these systems. This makes the electrolyte management and recirculation difficult and it easily reacts with carbon dioxide from the air. The major issues of alkaline electrolysers are essentially the low partial load range, a limited current density, a low operating pressure. In particular, the diaphragm does not completely prevent the product gases from cross diffusing through it, which lowers Coulombic efficiency. Hydrogen diffusion to the oxygen evolution chamber must be avoided to preserve the efficiency, as well as safety.

Proton exchange membrane water electrolysis technology is based on a proton exchange membrane separator. It shows several advantages over conventional alkaline liquid electrolyte electrolysis including significantly higher current density and hydrogen output pressure, greater hydrogen purity, better dynamic behaviour both in terms of fast response and load range. The solid polymer membrane in PEM electrolysis allows for a shorter ionic path between the electrodes than in the alkaline electrolysers. The low gas crossover rate of the polymer electrolyte membrane (yielding higher hydrogen purity), allows the PEM electrolyser to safely work under a wide load range with consequent technical and economic benefits. Protons are characterised by higher mobility than hydroxide ions corresponding to enhanced conductivity and lower ohmic losses.

Beside these advantages, there are severe drawbacks that still limit a large scale deployment of this technology. The acidic environment provided by the proton exchange membrane and ionomer is highly corrosive and requires the use of special and at the same time expensive materials. Only few materials can be selected for this harsh environment. These include noble metal catalysts in particular Ir, Pt, and Ru, and expensive Ti-based diffusion media, current collectors and bipolar plates.

The aim of ANIONE project is to realise breakthroughs in Anion Exchange Membrane water electrolysis in order to favour green hydrogen production from renewables on a wide-scale. This means to combine the advantages of proton exchange membrane-based water electrolysis such as high performance, high energy efficiency, high operating pressures and flexible/dynamic behaviour with those of liquid alkaline electrolyte water electrolysis such as low capital equipment costs and use of non-precious metals as the electrocatalysts. Key aspects to enhance AEM water electrolysis are the development of highly conductive and stable membranes and incorporation of a highly durable ionomers in the catalyst layers composed of active non-PGM electrocatalysts.

Electro-catalysts

The ANIONE project focuses on tailoring anode and cathode catalysts for stable operation at high current density with low overpotential. Advanced non-PGM and non-CRM electrocatalysts for cathode and anode that have a high active surface area and are stable (not susceptible to catalyst poisoning, low degradation rate) are developed. The activity is mainly regarding an increase of catalyst activity and stability by producing supported nanostructured

Ni and Fe oxide (layered double-hydroxides) for the anode and nanosized Ni and Ni-alloys as cathode with specific solid solutions structures. At CNR-ITAE, during the first 10 months of the project, Ni-Fe oxide/hydroxide based anode catalysts, metallic Ni and Ni-Cu based cathode catalysts have been synthesized and investigated for operation in the alkaline environment. For the electrocatalyst assessment, the procedures include specification of catalyst loading in the electrodes, analysis of catalyst properties, methodologies for the determination of crystallite size and active phase dispersion, ex-situ characterization and screening of the catalysts in situ screening of the catalysts in the presence of AEM ionomer and electrolyte. Definition of the measurement protocols for electrochemical testing, for potentiodynamic and steady-state galvanostatic polarization measurements to determine the performance at specific potentials in relevant electrolyte and ionomer systems, temperature and pressure conditions. Identification of electrochemical characterisation protocols for the determination of electrocatalytic parameters. Identification of durability study test protocols such as prolonged operation at high potentials, to evaluate the catalyst degradation.

2 AEM operation environment

The principles of operation of the developed electrochemical reactor working in an alkaline environment are described in **Fig. 1.** H_2 evolution occurs at the cathode over a Ni, NiMo or NiCu-based catalyst whereas oxygen evolution occurs at the anode at a Ni, NiFe-oxide catalyst to complete the electrochemical process. When the anode catalyst only is assessed, a Pt/C cathode can be used since hydrogen evolution occurs on Pt with relatively low polarisation and this can be used as reference and counter electrode and reported as dynamic hydrogen electrode (DHE). This was approximated to the RHE for experiments carried out in single cell since the hydrogen evolution at the Pt cathode is not polarised significantly.

These catalysts are used in the reactor with different mass loading (3 - 5 mg/cm^2). The catalysts are mixed with AEM ionomer deposited onto gas diffusion backing layers to form electrodes. These are separated by an anion exchange membrane based on polymers such as FAA3 from Fumatech that was used in the screening phase. These polymers contain ammonium functional groups allowing the exchange of hydroxyl ions. The membrane avoids the recombination of the reaction products while allowing ionic percolation in the device as needed to complete the electrochemical process.

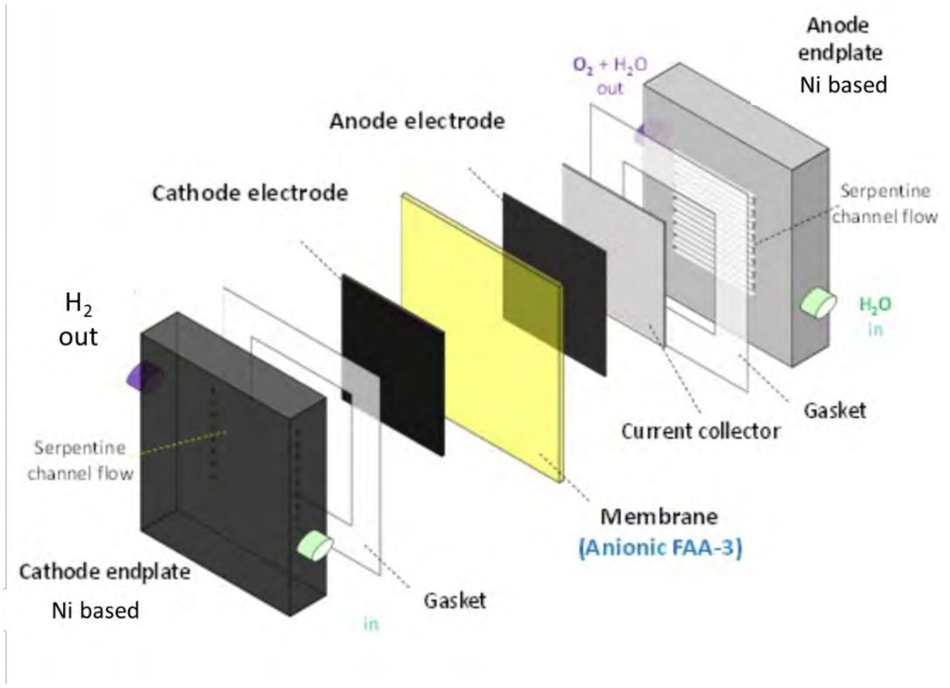

Figure 1. Scheme of a single cell unit used for catalysts screening. For the anode assessment Pt/C is used at the cathode forming a DHE electrode that is assumed to operate similarly to an RHE electrode being not polarised significantly.

The system was characterized in terms of electrochemical properties to investigate the reaction rates at different cell potentials.

The electrochemical procedures were regarding:

a) Polarization curves: the current is directly proportional to the reaction rate. The operating cell voltage at each current density provides information on overpotential and voltage efficiency.

b) Ac-impedance: this is an electrochemical diagnostic tool that allows to deconvolute the ohmic contribution, e.g. due to the membrane resistance (high frequency intercept on the real axis), from the polarisation contribution (charge transfer and mass transfer) corresponding to the low frequency intercept on the x-axis of the Nyquist plot subtracted by the high frequency intercept. Very low frequency response is indicative of strong mass transport constraints. To distinguish between kinetic and mass transfer limitations, ac-impedance spectra are collected at different potentials and currents.

c) Steady state chrono-potentiometric studies at constant current (time studies), or constant potential preceded by a specific conditioning procedure, allow to understand the degradation behaviour at a specific voltage efficiency of reaction rate.

d) Cycled operation: voltage cycling between 1 V and 1.8 V can provide information about degradation during intermittent operation.

Specific protocols and procedures for the electrochemical and physico-chemical assessment of the electrocatalysts are discussed in D2.1.

2.1 Experimental conditions

During the first screening phase, the anode electrocatalysts have been first characterised ex-situ using the following methods:

- ✓ Structure was determined from XRD
- ✓ Crystallite size was determined from XRD

- ✓ Morphology was determined by SEM
- ✓ Particle size and related dispersion were determined from TEM
- ✓ For the nano-sized catalysts, crystalline structure and atomic arrangement were determined from HR-TEM
- ✓ Surface area, pore size and cumulative pore volume from BET

3 Methods and Results

3.1 Preparation and physico-chemical properties of non-precious catalysts for AEM electrolysis

3.1.1 Catalysts preparation at CNR-ITAE

The raw cathode and anode catalysts were prepared according to the synthetic procedure referred to as “oxalate method” (Patent WO2004049491). Metallic nitrates were dissolved in distilled water and mixed with a solution of oxalic acid neutralised at pH 6.5 with NaOH. The molar ratio between the chelating agent and metals was 10. A complex was formed and then decomposed at 80 °C with hydrogen peroxide to form a precipitate. The precipitate was filtered, washed and dried at 100 °C for 24 hrs. The powder was then calcined in air a temperature range between 200° and 350 °C for 120 min. Figure 2a is referred to the diffraction X-ray pattern (XRD) and transmission electron microscopy (TEM) of NiCu-based oxide sample carried out at CNR. The typical reflections of a cubic spinel structure due to $NiCuO_x$ (referred to the JCPDS card n° 00-001-1110) were observed in the specimen. Figure 2b is referred to the structural and morphology properties of the NiFe-oxide catalysts. The sample shows an Ni hydroxide hydrate structure.

Ni and NiCu alloys were formed after a treatment in diluted H_2 between 200° and 350 °C. The TEM imaging shows fine particles with a crystallite average size of approximately 7 nm (Fig. 3) but the catalysts are significantly agglomerated (Fig. 4).

Successively, preparation of a binary or ternary NiMo or NiCuMo catalysts was achieved by incipient wetness of the precursor oxide catalysts with $NH_4Mo(H_2O)O_2PO_4$ and successive thermal decomposition in reducing environment.

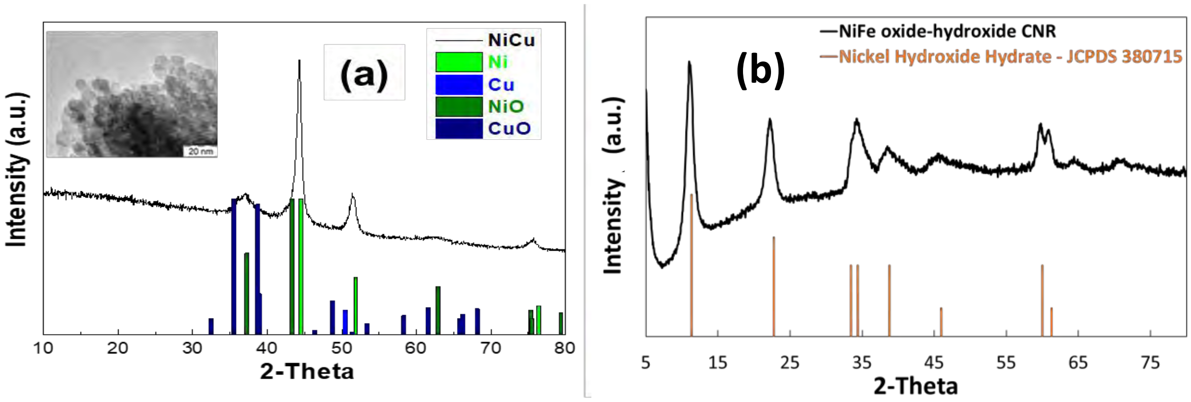

Figure 2. *X-ray diffraction patterns and TEM micrographs of the CNR NiCuO$_x$ cathode precursors (a) and NiFe oxide-hydroxide (b) anode catalysts*

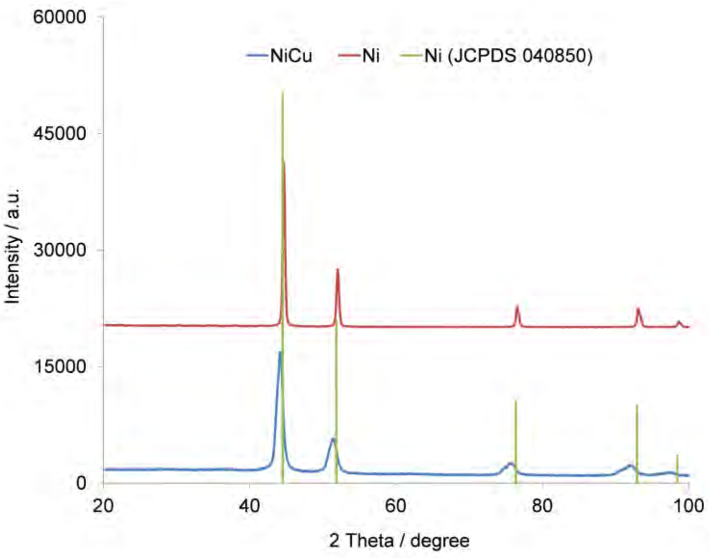

Figure 3. *X-ray diffraction patterns and TEM micrographs of the CNR metallic Ni and NiCu cathode catalysts*

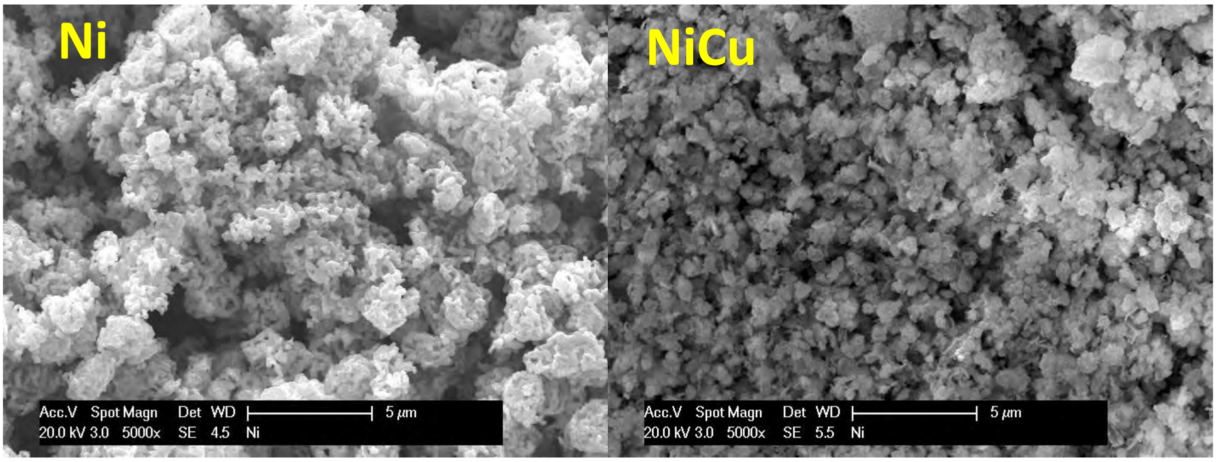

Figure 4. *Morphology of CNR metallic Ni and NiCu cathode catalysts*

3.1.2 Analysis and Characterisation of Nickel-based catalysts at PV3

To get a better understanding of chemical, morphological, structural properties four main Ni-based anode and cathode catalysts for AEM electrolysis, synthesised by CNR-ITAE, have been characterised by PV3 Technologies using XRD, SEM and EDS analysis techniques. A short summary of these catalysts is listed in Table 1. Preliminary results from CNR-ITAE have reported promising performance for NiFe anode catalyst, however NiCu(Mo) cathode catalysts have exhibited poor performance. Further characterisation of these materials discussed within this report can help to understand the performance behaviour of these materials.

Table 1. Summary of Ni-based anode and cathode catalysts.

Alloy	Electrode	Expected Ratio	Heat treatment
NiFe oxide-hydroxide	Anode	Ni:Fe 5.7 : 1	None
NiFeOx	Anode	Ni:Fe 5.7 : 1	Calcined at 200 ^{o}C
NiCu	Cathode	Ni:Cu 1 : 1	Reduced at 350 ^{o}C
NiMo	Cathode	NiMo 3 : 1	Reduced at 350 ^{o}C
NiCuMo	Cathode	NiCu:Mo 2 : 1	Reduced at 350 ^{o}C