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New Anion Exchange Membrane Electrolysers

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

ANIONE – Public deliverable Report

D5.1 – Engineered membrane electrode assemblies for AEM electrolysis operation

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1.0	10-06-2021	Laila Grahl-Madsen (IRD)	Revision, aligning figure numbers, test etc. Adding summary and conclusion

Disclaimer/ Acknowledgment

D5.1 – Engineered MEAs for AEM electrolysis operation

Summary and conclusion

The presented work concerns the development and characterization of durable and efficient AEM-electrolysis MEAs. The specific AnIone objectives and targets defined for the MEA development are as follows:

1. Develop innovative MEAs for AEM electrolysis based on thin reinforced, perfluorinated anionic Aquivion® or hydrocarbon-type, membranes and ionomers, and nonCRM catalysts based on Ni, Fe, Mn alloys and oxides

2. Assess MEA performance and stability in lab scale and in full-scale cells

3. Achieve a current density for the MEAs >1 A/cm^2 at 1.8 V under optimised operating conditions

4. Demonstrate high durability in single cell tests with degradation rate <5 µV/h under steady state galvanostatic conditions (1 A/cm^2) and <10 µV/h under cycled operation (0.2-1.0 A/cm^2)

5. Develop a robust MEA configuration for operation in a wide temperature range (up to 90°C) under high differential or balanced pressure (≥ 30 bar)

6. Assessment of Faradaic efficiency (>99%) under high differential pressure

The presented work comprises the initial screening analysis that was carried out at the CNR-ITAE of different MEAs based on various precursors and combinations. The MEAs were judged based on polarisation and EIS; long-term test was performed on selected MEAs with encouraging performance.

The work has been concentrated on NiFe-oxide anodes with 33 wt% AEM ionomer and a catalyst loading of 2.5 mg/cm^2. The commercially available Fumatech membrane FAA3-50 has been chosen for this study. Several cathode configurations have been tested. The project performance and durability targets has been obtained for a MEAs with a cathode loading of 1.2 mg$_{Pt}$/cm^2. However, encouraging results have also been obtained with several of the nonPGM cathode catalysts developed within the AnIone project. The AnIone project performance target has been obtained with an AnIone NiMo cathode catalyst on supported Ketjen Black at 50ºC after 2,000 accumulated test hours. Pure hydrogen was produced at the cathode with a faradaic efficiency better than 99%. The Information derived from the screening analysis has been transferred to IRD in order to scale-up the selected formulations for large scale MEA manufacture.

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D5.1 – Engineered MEAs for AEM electrolysis operation

Acronym table

Abbreviation	Explanation
AEM	Anion Exchange Membrane
BET	Brunauer–Emmett–Teller
BoL	Beginning of Life
BoT	Beginning of Test
CAPEX	Capital expenditures
CCM	Catalyst Coated Membrane
CRM	Critical Raw Materials
DT	Durability Tested
EIS	Electrochemical Impedance Spectroscopy
EoL	End of Life
EoT	End of Test
EW	Equivalent Weight
EW	Equivalent Weight
FC	Fuel Cell
GDE	Gas Diffusion Electrode
GDL	Gas Diffusion Layer
HHV	Higher Heating Value
IR	Ohmic potential drop
KB	Ketjen Black
LHV	Lower Heating Value
MEA	Membrane Electrode Assembly
PEM	Proton Exchange Membrane
PFSA	PerFluoroSulfonic Acid
PGM	Platinum-Group Metals
SEM	Scanning Electron Microscope
SoA	State-of-the-Art
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

Introduction

The Anione project aims to further develop and mature the anion exchange membrane (AEM) water electrolysis technology, so it becomes an efficient, cost effective and durable technology.

The WP5 activities of Anione comprise the design of advanced MEAs for AEM electrolysis applications with the overall aim of improving performance and durability while simultaneously reducing cost. The specific WP5 objectives are as follows:

- Develop and manufacture innovative MEAs for AEM electrolysis based on thin, perfluorinated anionic Aquivion® or hydrocarbon-type, membranes and ionomers, and non-CRM catalysts based on Ni, Fe, Mn alloys and oxides

- Develop a robust MEA configuration for operation in a wide temperature range

D5.1 – Engineered MEAs for AEM electrolysis operation

- Achieve a current density for the MEAs ≥1 A·cm^{-2} at 1.8 V under optimised operating conditions in lab scale and in full-scale cells

- Demonstrate high durability in single cell tests with degradation rate <5 μV/h under steady state galvanostatic conditions (1 A/cm^2) and <10 μV/h under cycled operation (0.2-1.0 A/cm^2).

- Assessment of Faradaic efficiency (>99%) under high differential pressure

The initial MEA screening analyses have been carried out at CNR-ITAE. The information and results have been transferred to IRD in order to scale-up the selected formulations for large scale CCM coating.

Electrocatalysts for MEA preparation have been produced by PV3 and CNR-ITAE. Hydrocarbon and perfluorinated membranes produced by POCELLTECH and CNR-ITAE have been used in MEAs. Benchmark Fumatech membranes modified at CNR-ITAE have been widely used to develop MEAs.

Scope

This report summarises the results of the screening analysis carried out at the CNR-ITAE of different MEAs based on various precursors and combinations. The MEAs were judged based on polarisation and EIS; a long-term test was performed on selected MEAs. Information derived from the screening analysis was transferred to IRD in order to scale-up the selected formulations for large scale CCM coating.

Experimental

Details on the Anione catalyst-precursors development is reported in the public Anione deliverable report D4.1[1]. All catalysts, developed within the Anione project and other catalysts utilised within the project are listed in Appendix A. A list of the Anione precursors utilised for the MEA manufacture reported *ibid* is provided in Table 1.

All CCMs are design symmetrically with respect to type and level of ionomer if not stated otherwise.

During the project, material samples have been frequently shipped between partners particular between WP3, WP4 and WP5 partners, cf. Appendix A.

Table 1   Utilised CCM precursors.

ID	Explanation	Comments
FAA3-50	Modified FumaTech polymer	50 μm thick AEM membrane. The polymeric film is delivered in the Br-form from FumaTech. Only lot. No. M35351903 is utilised within the Anione project. This is house modified first to chloride and therefore to hydroxide form (D3.1)
FAA3	Shredded film/ionomer from FumaTech	Ionomer solution preparation reported in ANIONE D3.1 report
Catalyst	Catalysts developed within Anione WP4; Benchmark catalysts from CENmat.	Cf. Anione D4.1 report & Appendix A (*ibid*) Cf. Anione D2.1 report.

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

Membrane treatment

The FumaTech FAA-50 membrane is supplied on the Br$^-$ form and needs to be exchanged to the OH$^-$ form before use. Polymer modifications are reported in D3.1[2].

- All MEA fabrication procedures involving temperatures above 60°C are performed while the membrane is still on the Br$^-$ form.

- When all hot-pressing steps have been performed; the membrane is exchanged to the Cl$^-$ form by inserting the membrane in 1 M NaCl at room temperature for 72 hours. And then rinsed thoroughly with DI water. This can be done in the lab where the MEAs are used, or the membrane can be shipped between partners in the Cl$^-$ form as long as it is kept humidified.

- Immediately before use the membrane should be converted to the OH$^-$ form by exchange in 1 M KOH or 1 M KHCO$_3$ solution at room temperature. This can be done within the test cell, and the electrolyte solution is changed before MEA characterization is started.

Single cell test benches

Single cell hardware for the initial screening of various combinations of electrocatalysts and ionomers differ in terms of active area (5-100 cm^2) and/or operating mode e.g., pressurised or ambient pressure operation. A sketch of the single cell hardware test cell at CNR-ITAE is shown in Fig. 1. The manufacture and tested MEAs at CNR-ITAE are listed in Table 2. The actual test conditions temperature, pressure etc. are listed together with the individual presented results. The MEAs were tested with a supporting electrolyte supply (1ml/min/cm^2) to the anode based on 0.1, 0.5 and 1 M KOH made out of Type I DI water (18.2 M$\Omega\cdot$cm). The anode KOH solution is recirculating in the single cell test. The KOH solution was maintained at the cell temperature or fed at ambient temperature. Electrochemical measurements include polarization curves, electrochemical impedance spectroscopy (EIS), galvanostatic durability tests and cycled test. Hydrogen concentration in the oxygen stream was monitored by an AGILENT micro-GC. The electrochemical results have been obtained at CNR-ITAE.

MEAs were tested in accordance with the harmonised test protocols listed in the Anione delivery report D2.1[3] unless otherwise stated.
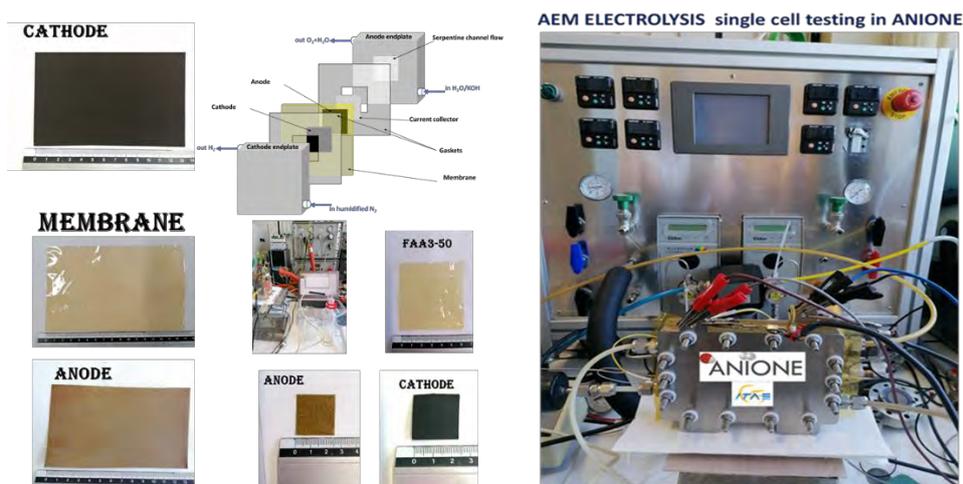
Fig. 1 Single cell hardware configuration at CNR-ITAE.

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[22] Carbone et al. (2021): D3.1 Supply of 1st generation ionomer dispersions, reinforcements, and additives for manufacturing AEM electrolysis membranes.

[3] Arico et al. (2020): D2.1 Harmonised test protocols for assessing AEM electrolysis components, cells, and stacks in a wide range of operating temperature and pressure.

Table 2   MEAs manufactured and tested at CNR-ITAE.

MEA ID	Anode catalyst	Anode ionomer wt%	Anode loading mg/cm²	Cathode catalyst	Cathode ionomer wt%	Cathode loading mg/cm²	Test results shown in Fig.
120	NiFe-oxide	33	2.5	40% Pt/C	33	1.20	2,3,4,5,6 & 7
112	NiFe-oxide	33	2.5	NiMo	33	4.22	8, 9 & 10
130	NiFe-oxide	33	2.5	NiMo/KB	33	4.50	11, 12, 13, 14, 15, 16 & 17
116	NiFe-oxide	33	2.5	NiCu	33	5.20	18, 19, 20 & 21
122	NiFe-oxide	33	2.5	$Ni_{0.4}Cu_{0.4}Mo_{0.2}$	33	6.50	23 & 24
134	NiFe-oxide	33	2.5	NiAl	33	3.50	25, 26 & 27
111	$NiFeyO_2$ comm.	33	2.3	Mo_2C Comm.	33	4.19	28, 29 & 30
138	NiFe-oxide	33	2.5	Pt/C	33	1.30	34

Results and Discussion

MEAs with NiFe based Anione anodes and PGM-containing cathodes

Preliminary tests were carried out with a cell based on Pt/C as cathode and NiFe-oxide as anode. NiFe-oxide anode was prepared at CNR-ITAE as described in D.4.1. Fig. 2 shows the impedance spectra collected at 2 V and at four different temperatures (i.e., 30°C, 40°C, 50°C and 60°C). All spectra exhibit at least 2 collapsed semicircles in which the high frequency semicircle is mainly due to the hydrogen evolution occurring on the Pt/C electrocatalyst and the low frequency semicircle is associated with the oxygen evolution occurring on the NiFe-oxide electrocatalyst. The increased temperature reduced both the i) series resistances (i.e., the intercept of spectra with x-axis at high frequencies) as a consequence of an enhanced conductivity of the membrane and the ii) total resistance (i.e., the intercept of spectra with x-axis at low frequencies) which is ascribed to better reactions kinetics.
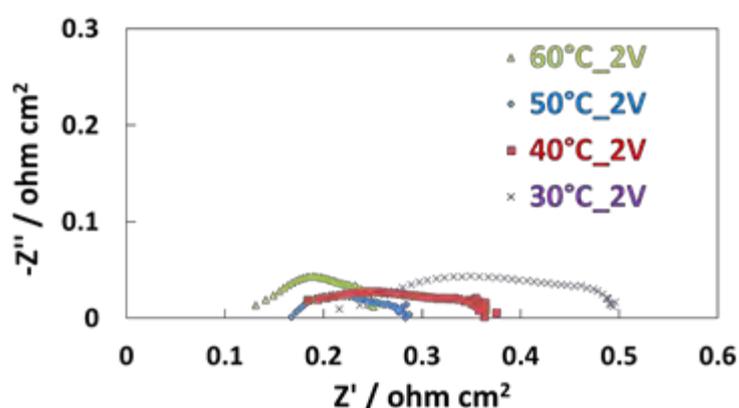
Fig. 2
EIS carried out in the temperature range 30-60°C by feeding 1M KOH at the anode acquired at cell voltages of 2 V for the cell using Pt/C as cathode and NiFe-oxide as anode.
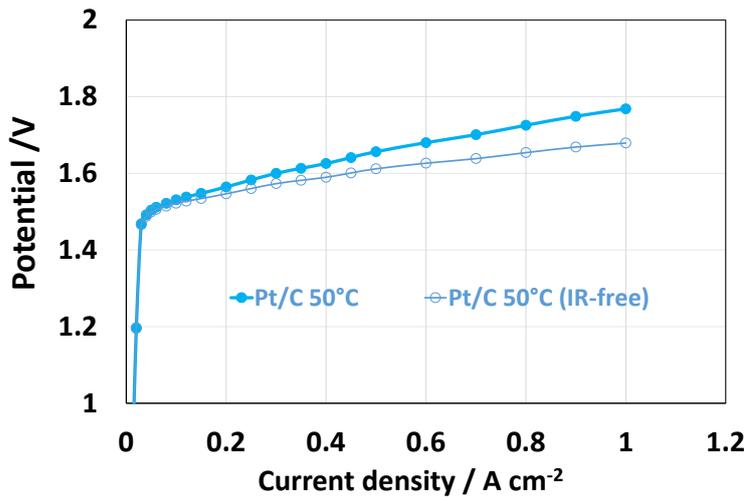
Fig. 3
Polarisation curves carried out by feeding 1M KOH to the anode for the cell using Pt/C as cathode and NiFe-oxide as anode.
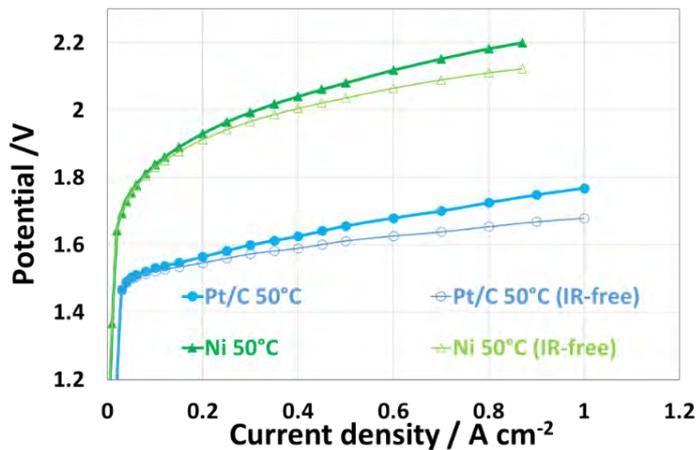
Fig. 4
Polarization curves for Pt/C and metallic Ni cathodes measured at 50°C by feeding 1M KOH to the anode based on NiFe-oxide.

Fig. 3 shows the Polarisation curves carried out by feeding 1M KOH to the anode for the cell using Pt/C as cathode and NiFe-oxide as anode indicating excellent performance of the anode in combination with a Pt cathode and a FAA-3 membrane.

In Fig. 4, the polarisation curves carried out with reference cathode (Pt-based) and Ni are compared. As observed in the Figure, the iV curves of Ni cathode conducted at 50°C show a large activation control of about 400 mV compared to the curve of Pt cathode. Fig. 4**Error! Reference source not found.** also includes the IR-free polarization curves (empty blue symbols). These suggest that ohmic drop is mainly referred to the electrolyte conductivity.

Fig. 5 reports the measure of cell voltage during a life-time test of about 1000 hrs under the galvanostatic operating condition of 1 A cm^{-2}. During this test some interruptions occurred due to external factors e.g., laboratory issues etc. The cell potential rapidly increased in the first hours indicating the occurrence of recoverable losses (mass transfer issues); however, after a steady state was reached the successive behaviour shows continuous decrease of cell potential corresponding to an increase of cell efficiency. Test interruptions and replacement of the KOH solution resulted in a discontinuous behaviour. However, since the cell potential decreased with time no relevant degradation rate was observed in this time span. It is pointed out that in this experiment 1M KOH was supplied to the anode at ambient temperature, whereas the cell was kept at 50°C.
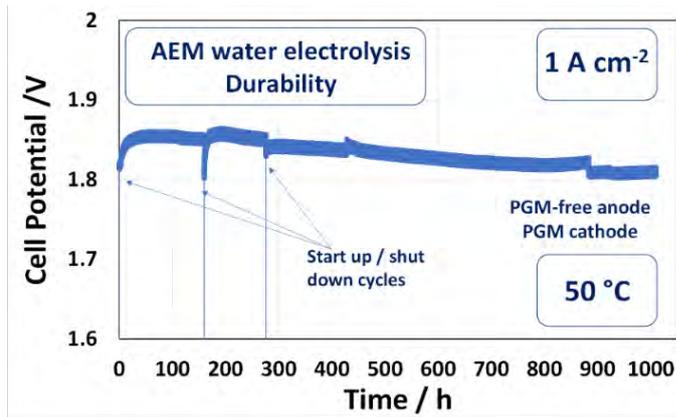
Fig. 5
Lifetime for the cell based on the NiFe-oxide as anode and reference Pt cathode fed with 1M KOH at the anode at ambient temperature. The cell was operated at 50°C.
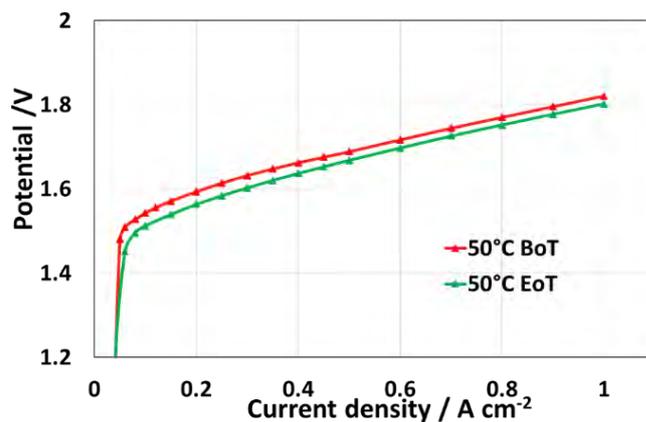
Fig. 6
Comparison of polarisation curves at the beginning and end of the durability test carried out at 50°C for the cell based on the NiFe-oxide as anode and reference Pt cathode fed with 1M KOH at the anode.

Fig. 6 is related to the comparison of iV curves collected at the beginning (BoT) and end (EoT) for this specific durability test and it shows that the performance of cell remains substantially identical without any relevant degradation, albeit the trend shown in the durability test was irregular and suffered from some interruptions (Fig. 5). Nevertheless, a slight improvement in performance was observed at the end of the test and it is essentially ascribed to a lower activation constraint probably associated with the anode reaction (i.e., oxygen evolution). No evidence of membrane degradation was observed since the ohmic slope remained the same after the prolonged test.

The EIS analyses of Fig. 7 shows the different cell response before and after the prolonged test. The spectra consist of 2 semicircles. The semicircle at low frequency could be associated with the reaction characterised by the rate determining step (larger relaxation times) and this semicircle collapses with an increase in the cell voltage. The rate determining step in these experiments is related to the anodic process (i.e., oxygen evolution) being Pt used at the cathode. Moreover, after the durability test, the Impedance spectra showed that:

i) the higher series resistance (R_s-intercept at high frequency with the x-axis) remained the same value indicating that the prolonged test did not affect the membrane conductivity, and

ii) the semicircle appearing at low frequency of spectra collected at 1.5 V was much smaller after prolonged test because of lower activation control for the oxygen evolution mechanism as shown in Fig. 7. This may be related the progressive uptake of hydroxides by the NiFe anode with time.

D5.1 – Engineered MEAs for AEM electrolysis operation
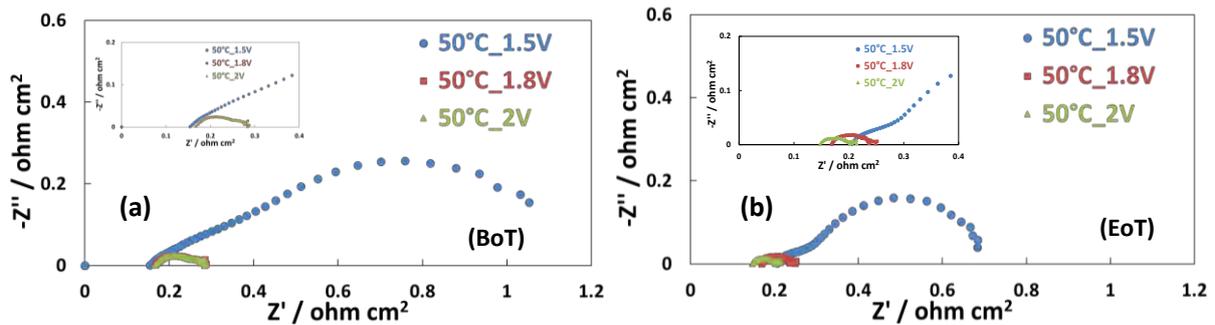
Fig. 7   Comparison of EIS spectra carried out at 50°C at the beginning and end of the durability test for the cell based on NiFe-oxide anode and Pt/C as cathode.
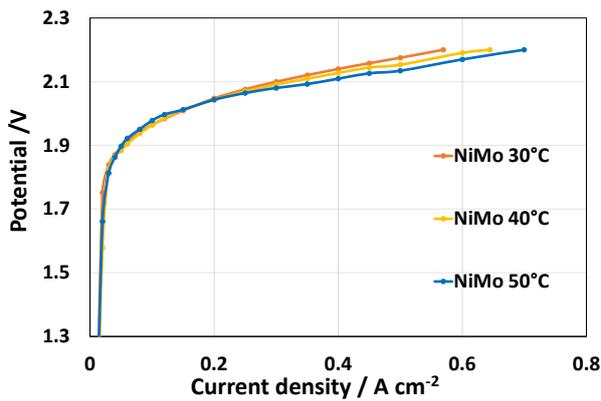
Fig. 8
Comparison of polarization curves carried out with NiMo as cathode and NiFe-oxide as anode in the temperature range 30°C - 50°C.
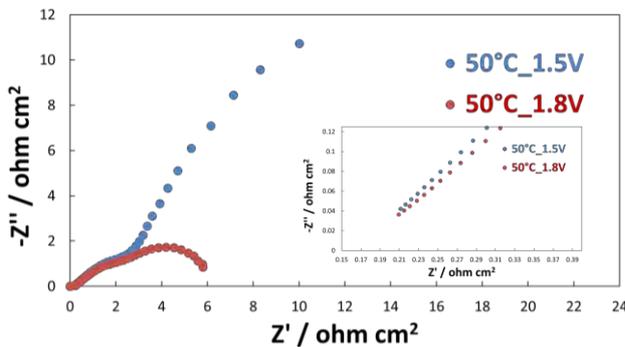
Fig. 9
EIS of cell based on NiMo as cathode and NiFe-oxide as anode measured at 1.5 V and 1.8 V at 50°C

MEAs based on Anione NiFe anodes and Anione unsupported NiMo cathode catalysts

Metallic NiMo cathode electrocatalysts were prepared at CNR-ITAE and tested in single cell using NiFe-oxide as anode and FAA3 Fumatech as electrolyte. As done for the other experiments, also this cell was fed with 1 M KOH to the anode. Fig. 8 compares the polarization curves of this cell investigated in the temperature range 30-50°C and it shows that an increase of temperature does not affect the activation control, albeit the slope of curves changed around 0.3 A cm^{-2} as a consequence of increased conductivity within the electrolyte.

The EIS analyses reported in Fig. 9 show two well-defined semicircles with the one at lower frequency possibly related to the cathode process in this case. The much larger overpotential compared to Pt causes a large shift in relaxation time. Moreover, the figure shows as the semicircle at low frequency is affected by the different current densities circulating in the cell at 1.5 V and 1.8 V.

D5.1 – Engineered MEAs for AEM electrolysis operation
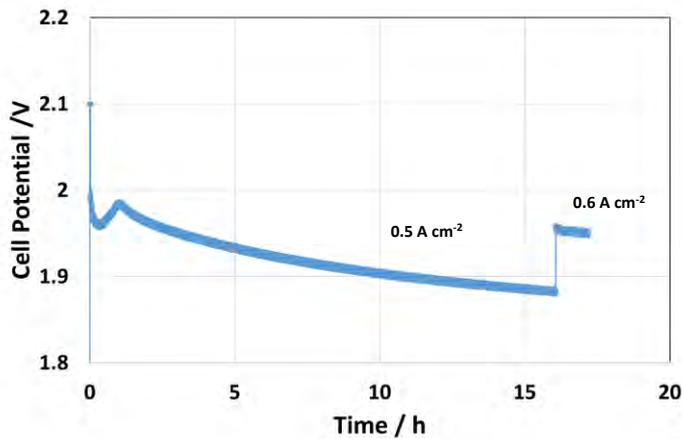
Fig. 10
Short durability test carried out under galvanostatic conditions at 50°C for cell based on NiMo as the cathode and NiFe-oxide as anode.
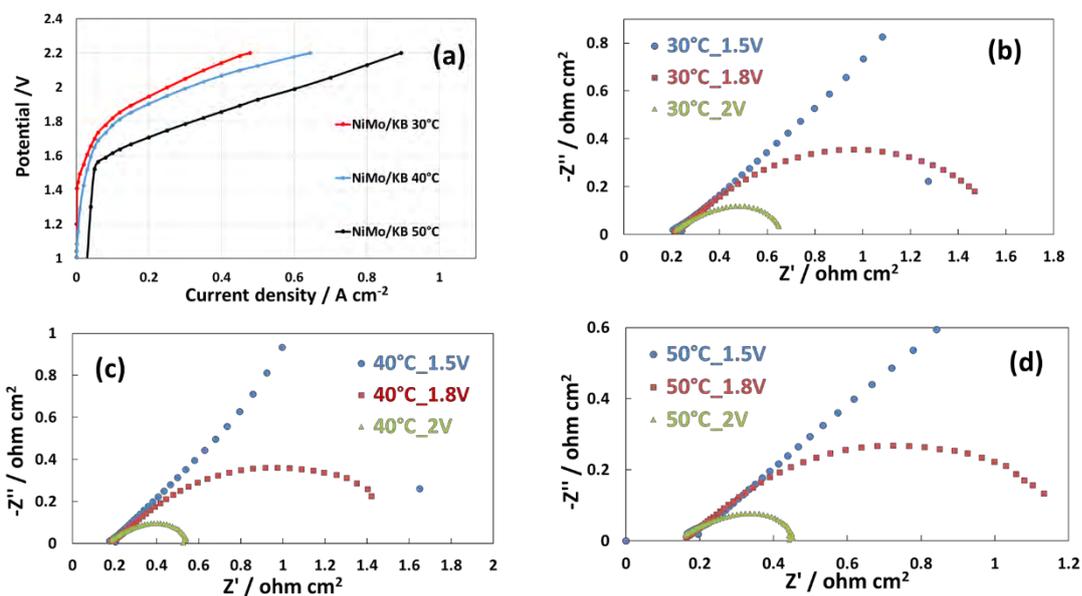
Fig. 11 Polarization curves (a) and EIS (b,c,d) carried out in the temperature range 30-50°C by feeding 1M KOH at the anode acquired at cell voltages of 1.5 V, 1.8 V and 2 V for the cell using NiMo/KB as cathode and NiFe-oxide as anode.

The short galvanostatic test carried out at 50°C (Fig. 10) was sufficient to show as the cell improved its performance with time but the voltage was still high at moderate current densities.

MEAs based on NiFe anodes and NiMo/KB cathode catalysts

Carbon supported metallic NiMo cathode with 40% of metal on carbon was synthesised at CNR-ITAE. Fig. 11 shows the polarisation curves (a) carried out by feeding 1M KOH to the anode for the cell using NiMo/KB as cathode and NiFe-oxide as anode with FAA-3 membrane. Fig. 11b-d show the impedance spectra collected at 1.5-2 V and at three different temperatures (i.e., 30°C, 40°C and 50°C).
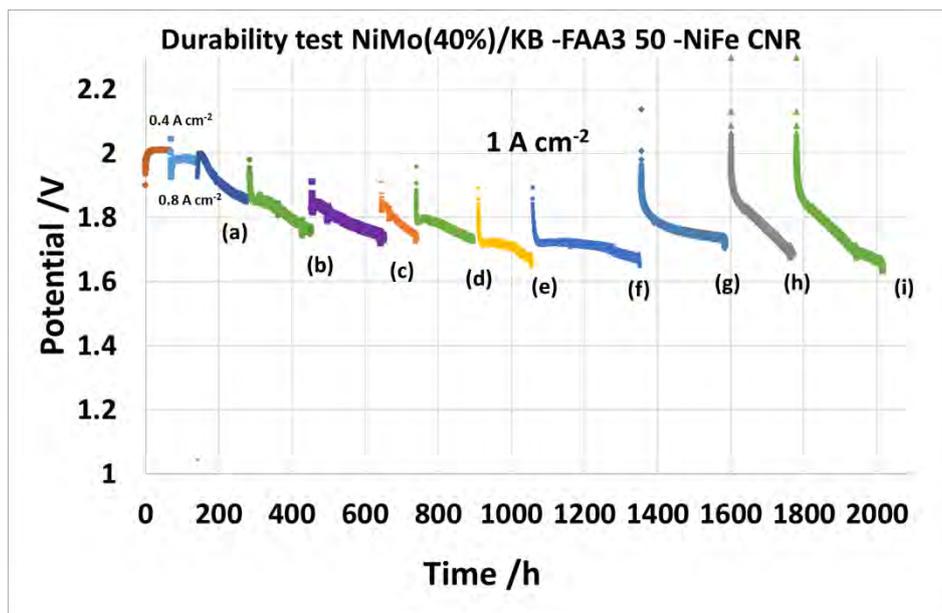
Fig. 12 Durability test carried out under galvanostatic conditions at 50°C for cell based on NiMo/KB as the cathode and NiFe-oxide as anode. Recirculation of 1M KOH at the cell temperature

Initial performance was promising for this non PGM catalysts-based MEA but slightly far from the project target.

Fig. 12 reports the measure of cell voltage during a life-time test of about 2,000 hrs under the galvanostatic operating conditions of the first 150 hrs increasing from 0.4 to 0.8 A cm^{-2}. Thereafter, the current was increased to 1 A cm^{-2}, and kept constant for the remaining 1,850 hrs. To monitor the cell behaviour using electrochemical diagnostics several interruptions were carried out during the test. In this test KOH was preheated at the cell temperature. During this test the cell potential rapidly increased in the first hours indicating the occurrence of recoverable losses (mass transfer issues); thereafter, the cell shows a continuous decrease of cell potential corresponding to an increase of cell efficiency.

A possible explanation for the reversible losses may rely in the carbonation phenomena where the formed carbonates are decomposed during electrolysis operation. In fact, cathode outlet was open to air during shut down periods, causing a possible uptake of CO_2. This aspect is subject to further investigation. Regarding the general improvement of voltage efficiency with time, this appears related to two phenomena possible occurring within the catalysts. Progressive reduction of oxides on the surface of NiMo/C and increased uptake of hydroxides by the Ni-Fe anode.

Faradaic efficiency was determined by measuring the amount of gas production at cathode and the gas composition. Pure hydrogen was produced at the cathode with a faradaic efficiency better than 99% (Fig. 13). This decreased to about 95% at the end of the durability test.
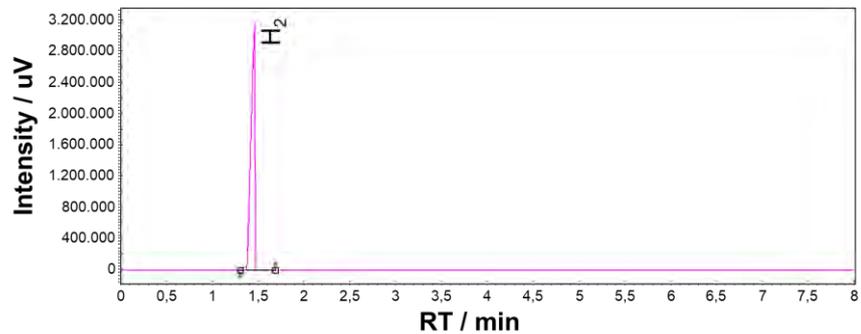
Fig. 13   Set-up for measuring faradaic efficiency based on H₂ flow meter and micro gas chromatograph to study the purity of the hydrogen stream at the cathode.
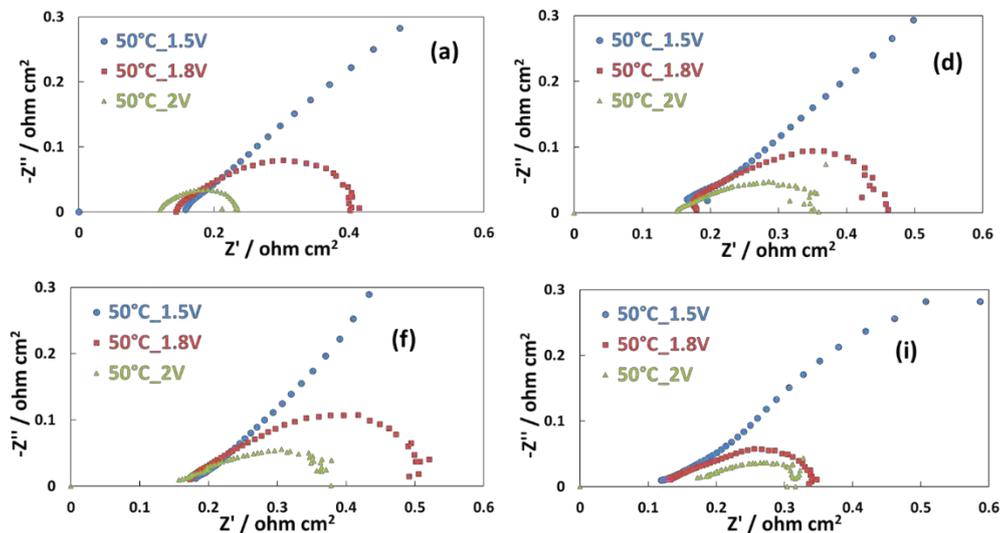
Fig. 14   EIS carried out at 50°C in different steps of the durability test by feeding 1M KOH at the anode acquired at cell voltages of 1.5 V, 1.8 V and 2 V for the cell using NiMo/KB as cathode and NiFe-oxide as anode.

Series resistance remained constant through most of the durability test excluding the spectra collected after 2,000h where it decreased slightly probably due to membrane thinning (Fig. 14). Polarisation resistance was affected by the specific cell condition and related reversible losses when the spectra were collected.

Fig. 15 shows the comparison of polarization curves collected during durability test. These show that the performance of cell improved with time. The largest improvement was in the first 250 h. Occurrence of reversible losses may have in part affected these polarisation curves.
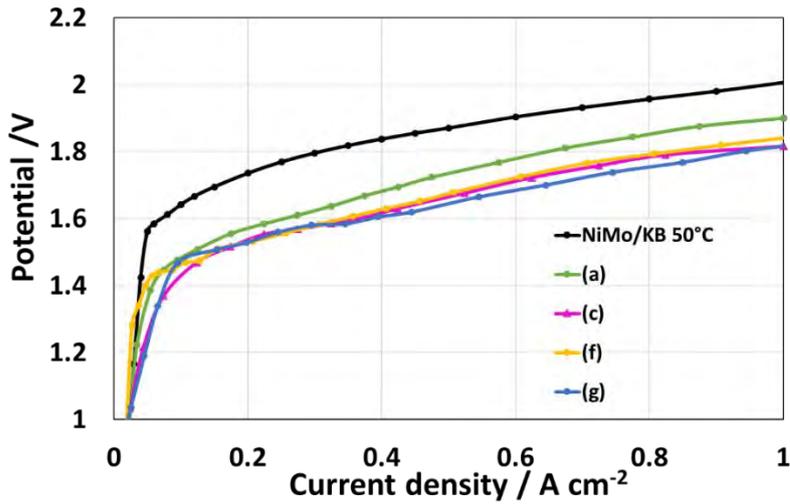
Fig. 15
Comparison of polarization curves carried out at 50°C with NiMo/KB as cathode and NiFe-oxide as anode during the durability test.
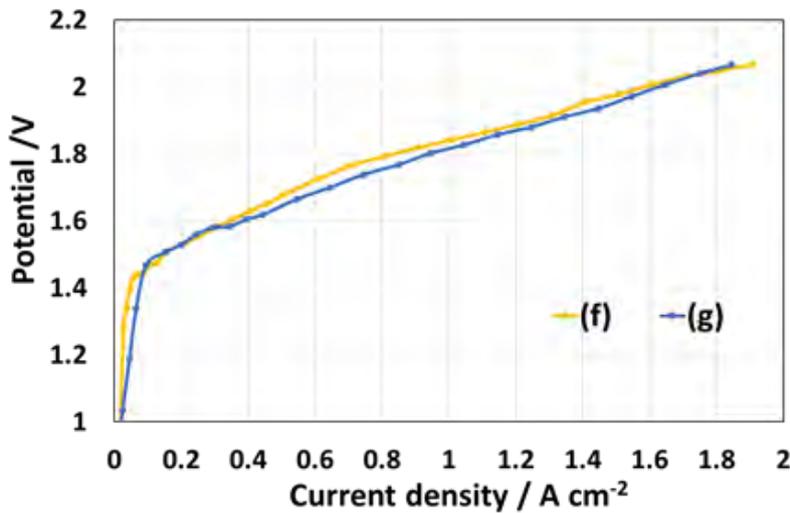
Fig. 16
Comparison of polarization curves carried out with NiMo/KB as cathode and NiFe-oxide as anode at 50°C during the durability test.

Fig. 16 shows some polarization curves collected up to high current density during the durability test. These curves show an ohmic slope at high current density of 0.3 Ohm cm^2.

This MEA formulations also showed proper dynamic behaviour when subjected to current cycling showing stable performance as observed in Fig. 17.

D5.1 – Engineered MEAs for AEM electrolysis operation
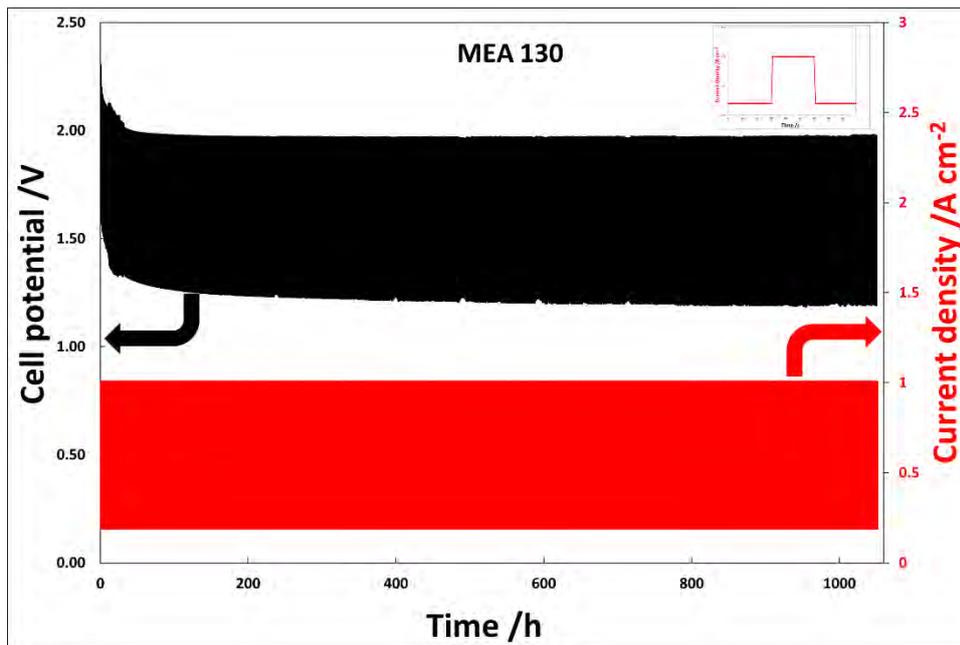
Fig. 17 Current cycling with NiMo/KB as cathode and NiFe-oxide as anode at 50°C 1 min at each current step {0.2 & 1 A/cm², respectively}.
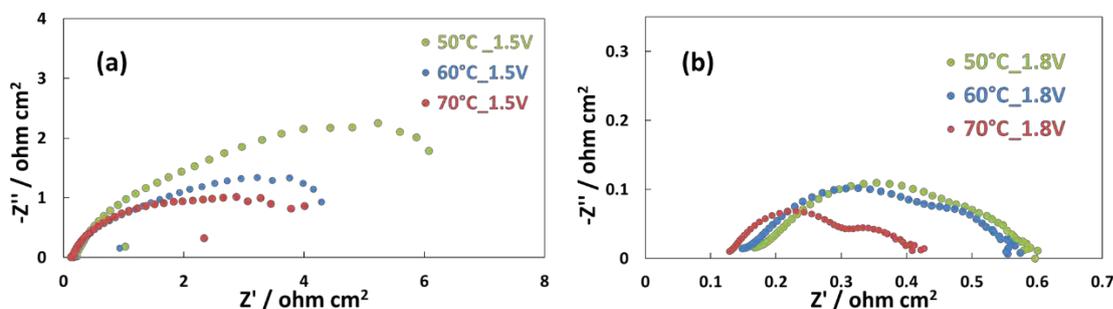
Fig. 18   The EIS of MEA with NiCu based cathodes measured in the temperature range 50-70°C by feeding 1M KOH feed to the anode based on NiFe-oxide. Experimental EIS spectra at 1.5 V (a), and at 1.8 V (b).

MEAs based on Anione NiFe anodes and Anione NiCu cathode catalysts

Metallic unsupported NiCu cathode electrocatalysts were prepared at CNR-ITAE and tested in single cell using NiFe-oxide as anode and FAA3 Fumatech as electrolyte. Also, this cell was fed with 1 M KOH to the anode.

Fig. 18 shows a comparison of EIS spectra collected in the temperature range 50-70°C and at two potentials (i.e., 1.5 V (16a) and 1.8 V (16b)) for the cell based on NiCu cathode and NiFe-oxide anode. At 1.5 V, a large semicircle ascribed to the cathodic reaction is observed incorporating the semicircle of the anodic reaction. Such behaviour is a direct consequence of high activation control of the cathodic reaction and is strictly connected with the low current density circulating in the cell at 1.5 V, albeit the increase of temperature had an effective role in mitigating the activation losses. In fact, the dimension of the semicircles appearing at low frequency was strongly affected by temperature. Two well-defined semicircles were observed with the smaller semicircle appearing at lower frequencies (lower relaxation times). An improved conductivity for the membrane is observed with increased temperature with a shift of Rs to lower values.

Table 3   Rs values versus temperature at 1.5 V and 1.8 V.

T {°C}	Rs @ 1.5 V [ohm cm²]	Rs @ 1.8 V [ohm cm²]
30	0.2297	0.2712
40	0.1978	0.2308
50	0.1553	0.1664
60	0.1361	0.1481
70	0.1212	0.1307
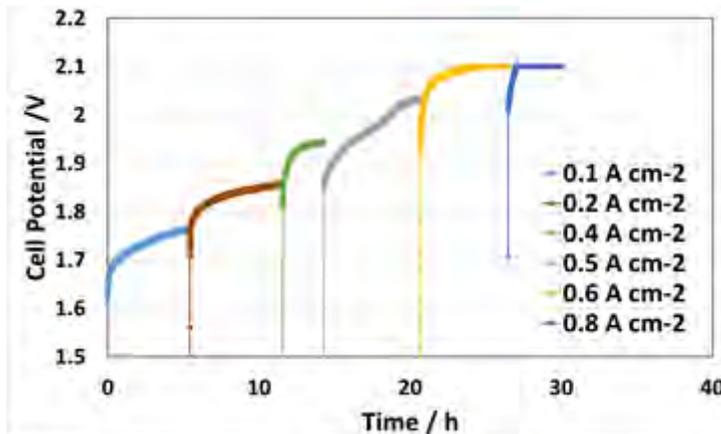
Fig. 19
Durability test at 60°C of a MEA based on NiCu as cathode and NiFe-oxide as anode.

The Rs values obtained through the EIS experiments are summarised in Table 3. As discussed above, the increase of temperature causes a reduction of the Rs values because the ionic conductivity of the membrane is improved. But it is worthy to note that at 1.8 V, Rs is slightly higher than at 1.5 V and this behaviour is essentially related to the increase of current density passing through the cell.

Fig. 19 shows a short galvanostatic durability test of a cell based on NiCu cathode. During this test, the cell showed both reversible and irreversible voltage losses that apparently are independent from the current density applied to the cell. Since the membrane was relatively stable in the presence of a NiFe-oxide anode and Pt/C cathode, this behaviour appears related to the cathode. The rapid deactivation seems to be caused by the simultaneous occurrence of recoverable and irrecoverable losses.

To better understand the effect of the degradation occurring in the cell during the durability test, the polarisation curves before and after the durability test are compared in Fig 18. This figure shows both activation and ohmic losses. The latter may be related to a conductivity decay for the membrane that was not observed with Pt or supported NiMo/C cathodes. However, the largest losses are related to an increase of polarisation resistance.
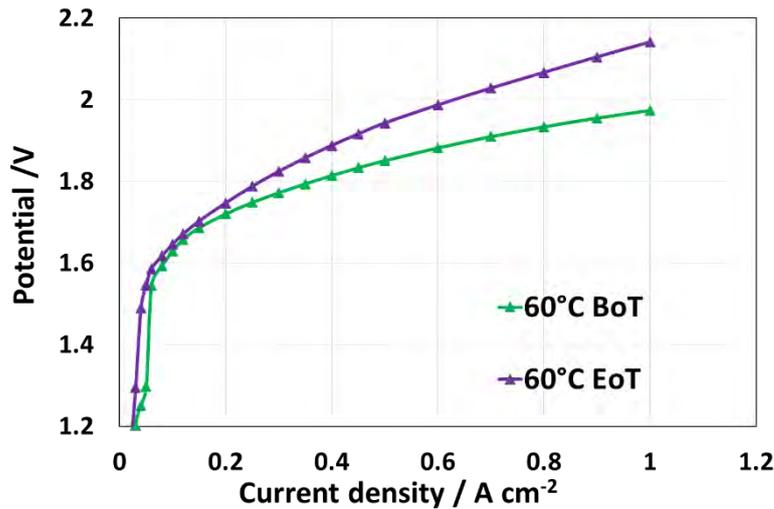
*Fig. 20
Comparison of
polarisation curves at BoL
and EoT of the MEA
durability tested 60°C (cf.
Fig. 19).*
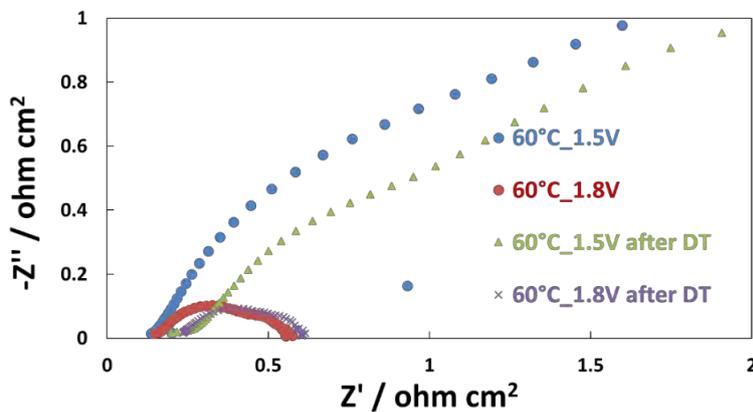
*Fig. 21
Comparison of EIS analyses
carried out before and after the
durability test on the cell based
on NiCu as cathode and referred
to 1.5 V and 1.8 V. (cf. Fig. 19).*

A further prove of a partial loss of conductivity for the membrane was observed by comparing the EIS spectra collected before and after the durability test. Fig. 21 shows, as after the durability test, a large increase of Rs both in the curves collected at 1.5 V and 1.8 V.

MEAs based on Anione NiFe anodes and unsupported NiCuMo cathode catalysts

In one experiment it was opted to combine Cu and Mo as promoters of Ni. The role of Cu is to mitigate to crystallite growth during the high temperature reduction process whereas the role of Mo is to promote H_2 evolution.

The next experiments are related to the investigation of unsupported $Ni_{0.4}Cu_{0.4}Mo_{0.2}$ cathode. In Fig. 22, the polarisation curves of the cell using this electrocatalyst as cathode are reported. As shown, the best performance was observed at 50°C that was an optimal compromise between the lower activation overpotential and better conductivity of membrane. A further increase of current density was achieved vs. NiMo but the performance was still lower than NiCu. As can be seen at 60°C an iV curve with lower performance was achieved. Moreover, durability issues were observed as in the case of NiCu.
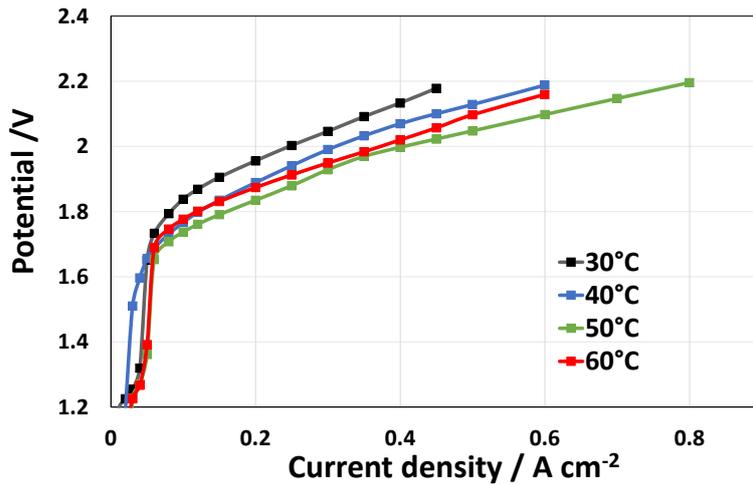
Fig. 22
Comparison of polarization curves carried out on the cell with $Ni_{0.4}Cu_{0.4}Mo_{0.2}$ as cathode and NiFe-oxide as anode in the temperature range 30°C - 60°C.
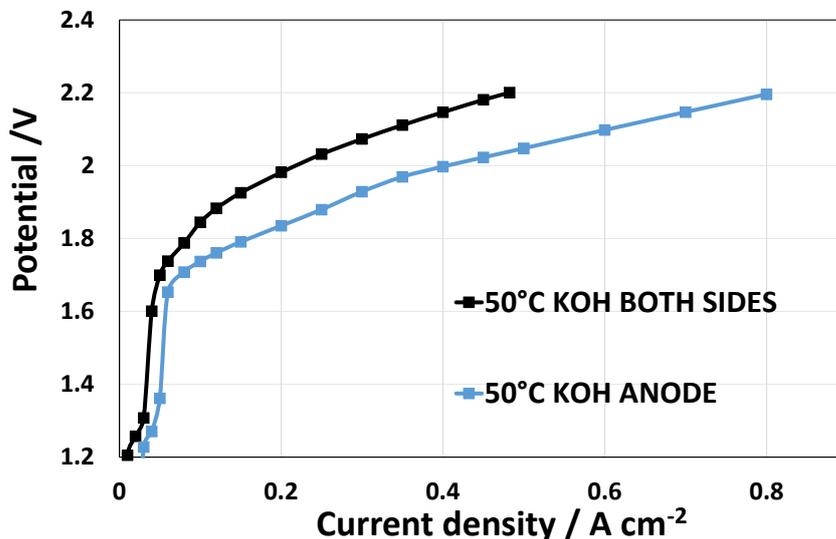
Fig. 23
A comparison of polarization curves carried out on the cell based $Ni_{0.4}Cu_{0.4}Mo_{0.2}$ as cathode and NiFe-oxide as anode at 50°C by feeding KOH on one or both sides of cell.

In order, to evaluate the effect of KOH feed to the cathode according to the reaction stoichiometry an investigation was conducted with a KOH feed at both electrodes. Fig. 21 compares the results of this new approach with the performance of the cell investigated in a conventional configuration (i.e., by feeding KOH to the anode). As observed, the presence of KOH on both sides of cell worsened the performances in terms of both activation and ohmic overpotentials. This may be related to an increase of mass transfer issues. H_2 is released more easily when no solution is recirculated at the cathode.

The EIS reported in Fig. 24 shows as the presence of KOH fed on both sides of cell caused an increase of the semicircle appearing at low frequencies. Thus, hydrogen evolution is negatively affected by the presence of KOH at the cathode.

D5.1 – Engineered MEAs for AEM electrolysis operation
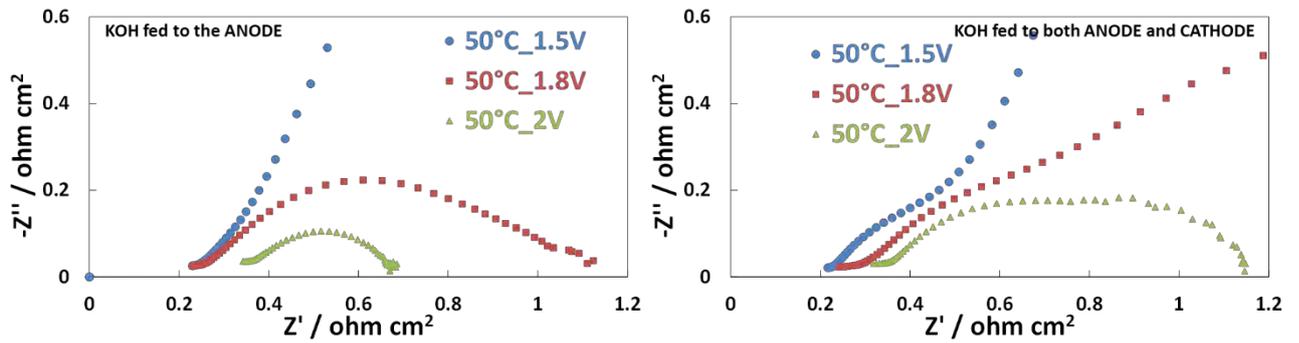
Fig. 24 The EIS of cell based $Ni_{0.4}Cu_{0.4}Mo_{0.2}$ as cathode and NiFe-oxide as anode measured at 50°C by feeding KOH at one or both sides of cell.
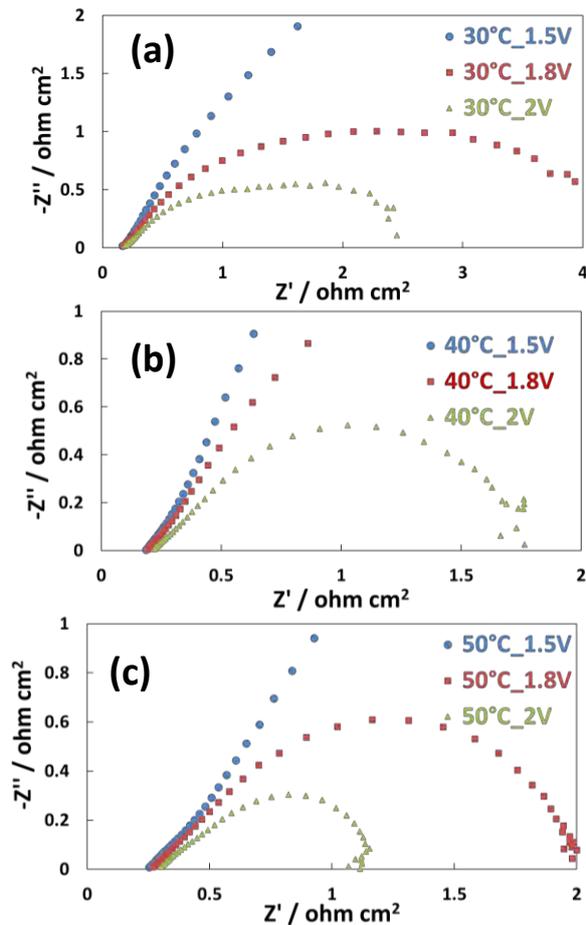
Fig. 25
EIS of a cell based NiAl as cathode and NiFe-oxide as anode measured at 30-50°C by feeding KOH.

MEAs based on ANIONE NiFe anodes and ANIONE NiAl cathode catalyst

The next experiments are related to the investigation of unsupported NiAl cathode prepared by FTP (PV3) in combination with NiFe oxide prepared by CNR-ITAE and Fumatech membrane. In Fig. 26, the polarisation curves of the cell using this electrocatalyst as cathode are reported. As shown, the best performance was observed at 50°C after 120°C. At 1.5 V, a large semicircle ascribed to the cathodic reaction is observed incorporating the semicircle of the anodic reaction. Such behaviour is a direct consequence of high activation control of the cathodic reaction and is strictly connected with the low current density circulating in the cell at 1.5 V, albeit the increase temperature had an effective role in mitigating the activation losses. In fact, the dimension of the semicircles appearing at low frequency was strongly affected temperature.
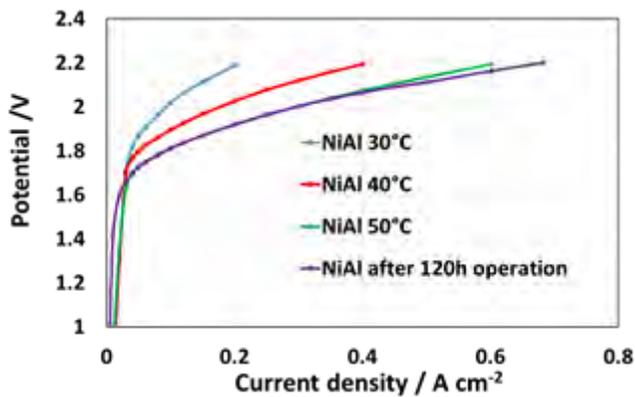
Fig. 26
A comparison of polarization curves carried out on the cell based NiAl as cathode and NiFe-oxide as anode at 50°C by feeding KOH.
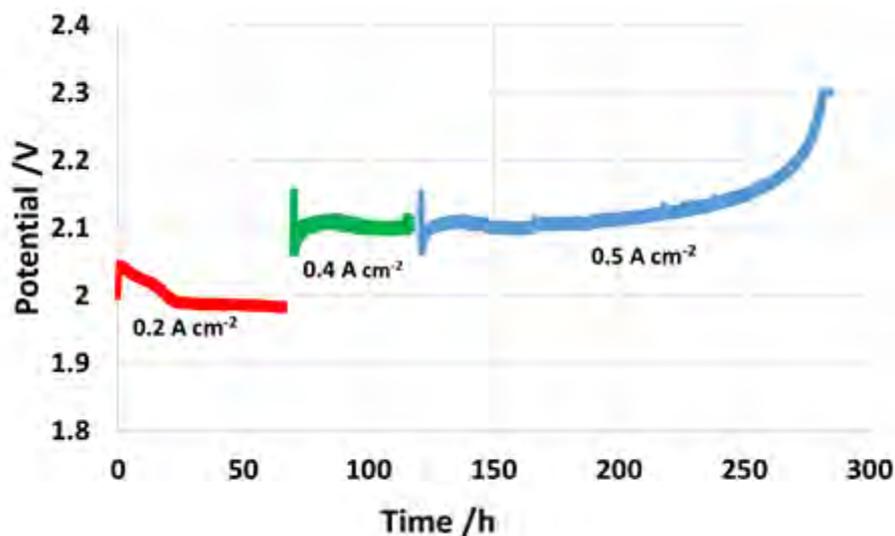
Fig. 27
Durability test carried out under galvanostatic conditions at 50°C for cell based on NiAl as the cathode and NiFe-oxide as anode.

Fig. 27 shows a galvanostatic durability test of a cell based on NiAl as cathode. During this test, the cell showed irreversible voltage losses that apparently are dependent from the current density applied to the cell. This behaviour appears related to the cathode. The rapid deactivation seems to be caused by the corrosion of aluminium and relative leaching from the electrode at cathode.

MEAs based on commercial anode and cathode benchmark catalysts

Full benchmark MEAs have been manufactured and tested in accordance to the agreement between the three FCH JU projects Anione, Channel and Newly.[4] These benchmark MEAs are founded on commercial Mo_2C (CENmat) cathode catalysts and a commercial $NiFe_yO_2$ (CENmat) anode catalysts and FUMATECH FAA-50 AEM membrane. Also in this case, the cell was operated by recycling 1 M KOH at anode.

Fig. 28 shows the comparison between the curves of this cell operating in the temperature range 30-50°C and as shown, the performances were definitely worse than cell using the CNR-ITAE NiFe-oxide as anode (see D4.1) since less current density was achieved at the same cell potential.

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[4] Arico et al. (2020): D2.1 Harmonised test protocols for assessing AEM electrolysis components, cells and stacks in a wide range of operating temperature and pressure.
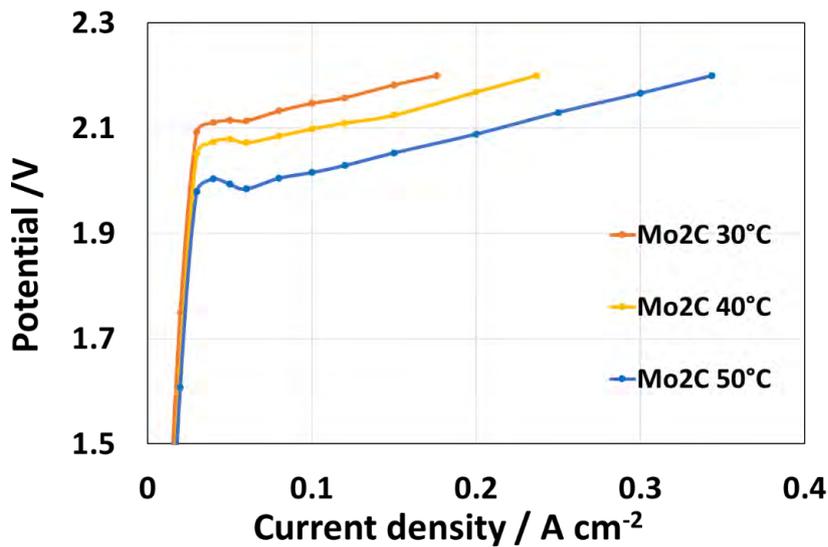
Fig. 28
Comparison of polarization
based on Mo₂C as cathode
and NiFeyO₂ as anode in the
50°C.
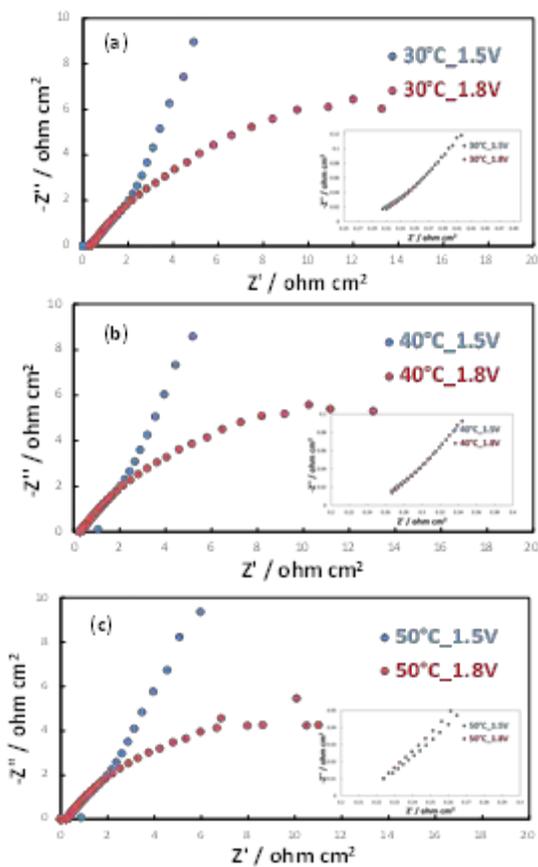
Fig. 29
EIS of cells based on Mo₂C as cathode and NiFeyO₂
and 1.8 V at 30°C (a), 40°C (b) and 50°C (c).

The EIS analyses of this cell is shown in Fig. 29. A large semicircle at low frequency was observed and this was only partially mitigated by the increased temperature. The short-term durability test under galvanostatic conditions (i.e., 0.3 A cm⁻²) at 50°C (Fig. 30) a very low current density was selected to avoid reaching the cut-off potential. Fig. 30 shows a short durability test (just 17 hrs) but it was evident a much lower performance if compared with the performance achieved with ANIONE catalysts. In the specific case of this cell a stationary condition was approximately obtained after 10 hrs.

D5.1 – Engineered MEAs for AEM electrolysis operation
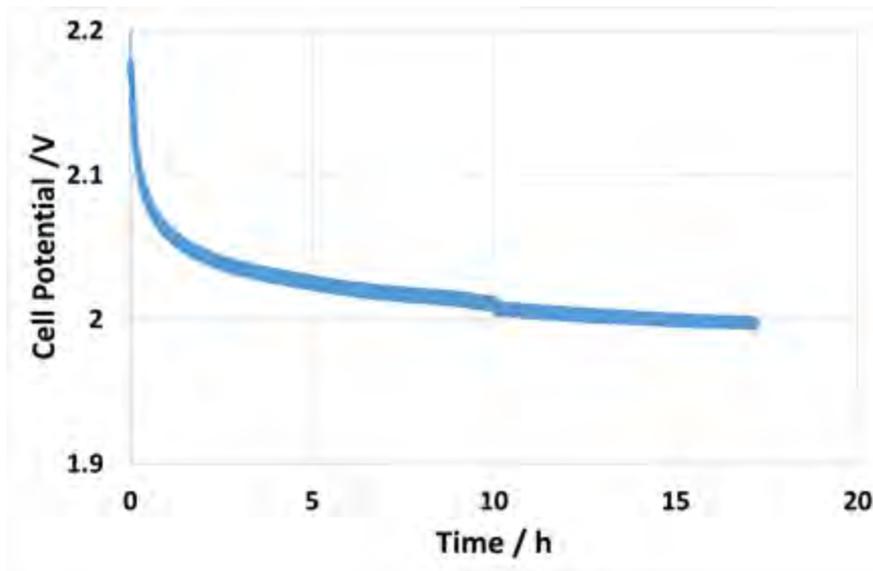
*Fig. 30
Short durability test carr
galvanostatic conditions
the cell based on comme
NiFeyO₂ as anode.*

Comparison of MEAs based on different catalysts

Fig. 31 shows a comparison between different nonCRM cathode electrocatalysts and Pt/C as cathode. As observed in the Fig. 31, the Ni cathodes showed a higher activation control compared to Pt excluding supported NiMo/C after 280 h operation. The latter showed about 120 mV performance gap at 1 Acm^{-2}. This decreased considerably during the 2,000 hrs testing as shown previously.
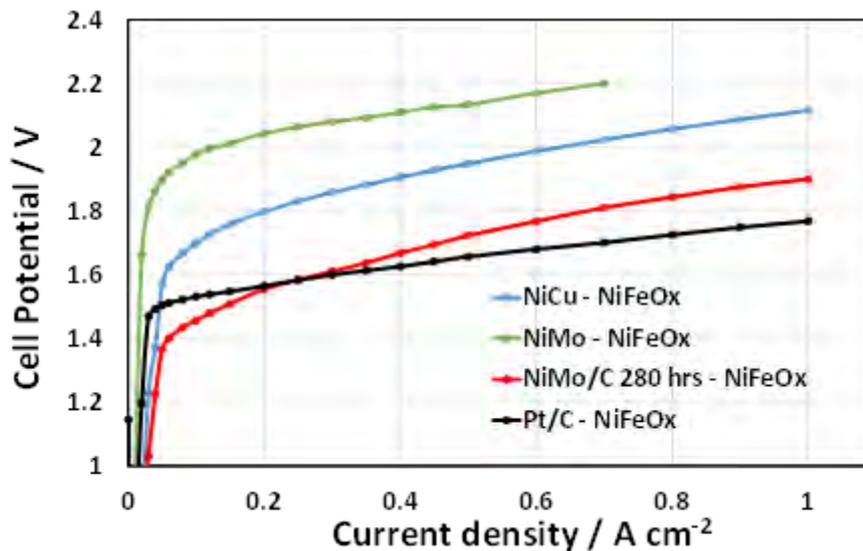
*Fig. 31
Polarization curves
of MEAs based on
different cathode
catalysts
measured at 50°C
by feeding 1M
KOH feed to the
anode based on
NiFe-oxide.*

Commercial catalysts obtained from CENMAT appear less performing than the ANIONE catalyst in the specific Anione' operating conditions (Fig.32).

D5.1 – Engineered MEAs for AEM electrolysis operation
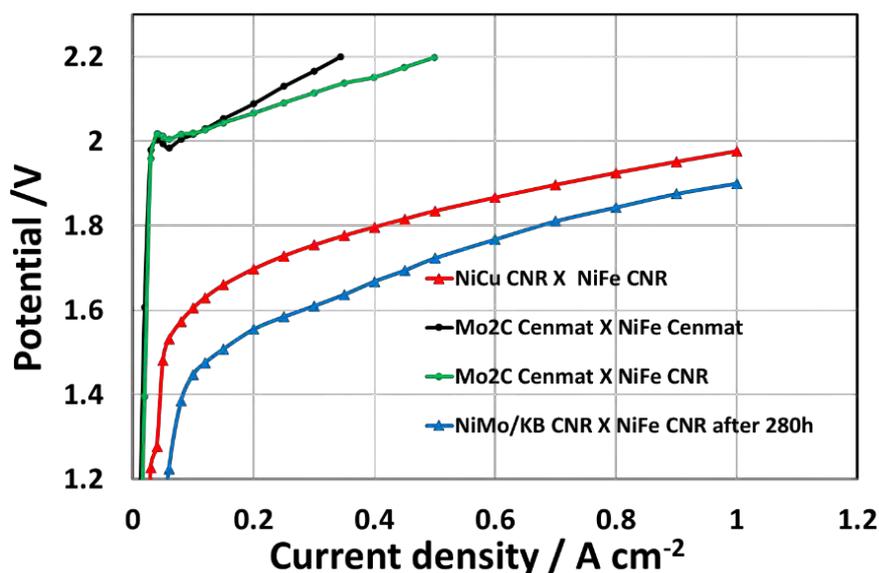
Fig. 32 Comparison of polarization curves at 50°C for the cell based on non PGM CNR-ITAE catalysts and the cell based on commercial catalysts.

Comparison of MEAs based on different membranes

Fig. 33 shows a comparison of MEAs based on different membranes. The anionic Aquivion membrane showed a worst performance compared to Fumatech and POcelltech alkaline polymers. However, it is important to mention that the anionic Aquivion membrane is still in a developmental phase and the synthesis process needs proper amelioration. POcelltech (Hydrolite) and Fumatech membrane are more similar in performance. Optimisation of MEAs based on the Hydrolite membrane are still undergoing.
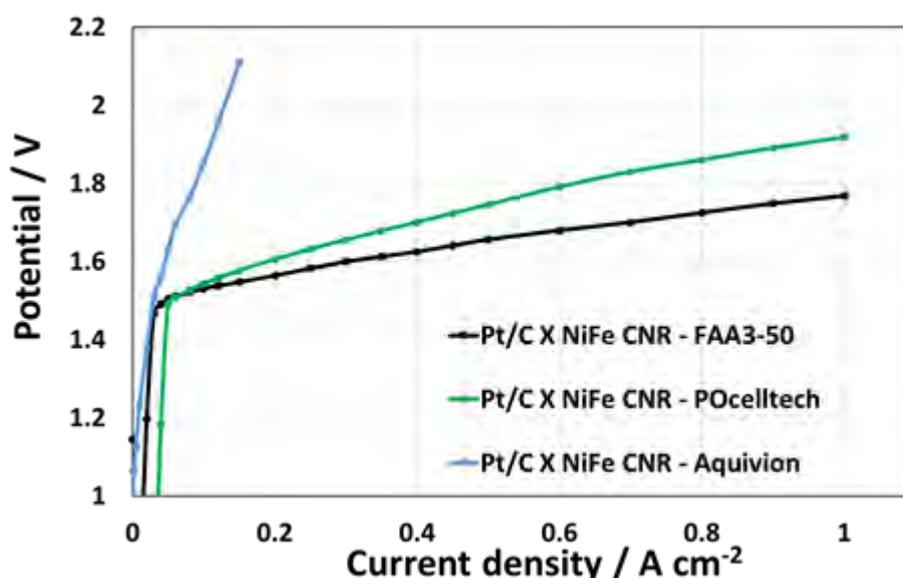
Fig. 33 Comparison of polarization curves at 50°C for the cell based on CNR-ITAE catalysts and different membranes.

Fig. 34 shows a comparison of the curves of cell operating with AQUIVION anionic membrane using Pt/C at cathode and NiFeOx at anode. The tests have been carried out in the temperature range 30-90°C and as shown, the performances were definitely worse than the cell using hydrocarbon membranes.

D5.1 – Engineered MEAs for AEM electrolysis operation
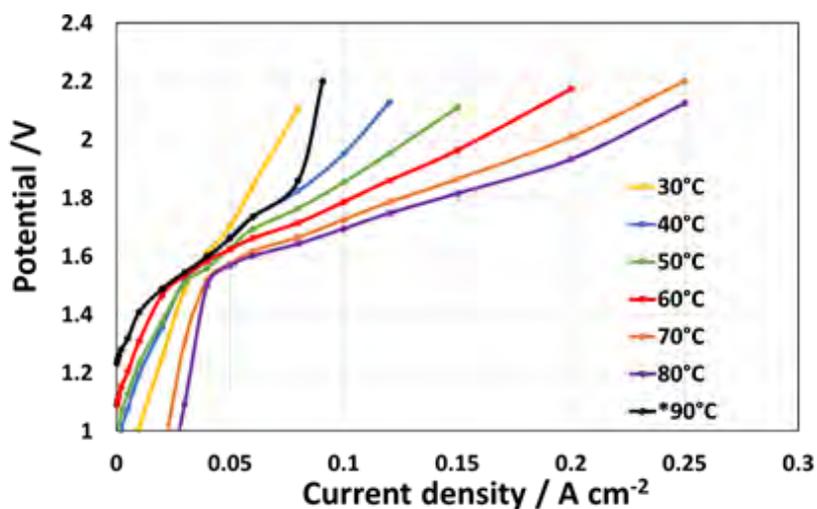
*Fig. 34
Comparison of
polarization
curves 30- 90°C
for the cell
based on CNR-
ITAE catalysts
and Aquivion
membrane.*

The assessment in single cell of recast membranes with and without a scavenger using a FAA ionomer indicates that these are less performing than the bare extruded FAA membrane showing a larger slope in the high current density range. Since the thickness is similar (about 50 µm), this may be related to a lower ion conductivity (Fig. 35). Durability tests indicate that most of the performance gap is recovered for the scavenger based MEA after 180 hours operation at 1 A cm^{-2}. Similar evidence was observed for the recast membrane (Fig. 36). Thus, the initial gap is essentially due to the presence of impurities, affecting conductivity; these are in part removed during electrolysis operation resulting in an in-situ purification. Unfortunately, for the radical scavenger-based MEA, there was a problem occurring with the test station after 450 hrs and this has not allowed to continue the durability test.
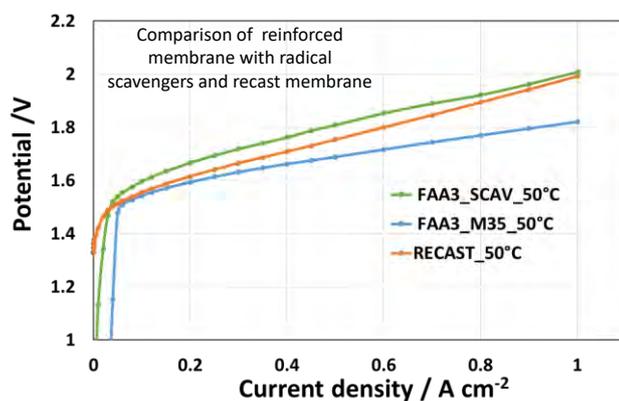
Fig. 35 Comparison of BoT polarization curves for MEAs containing recast, radical scavenger-based and bare extruded FAA membranes.

D5.1 – Engineered MEAs for AEM electrolysis operation
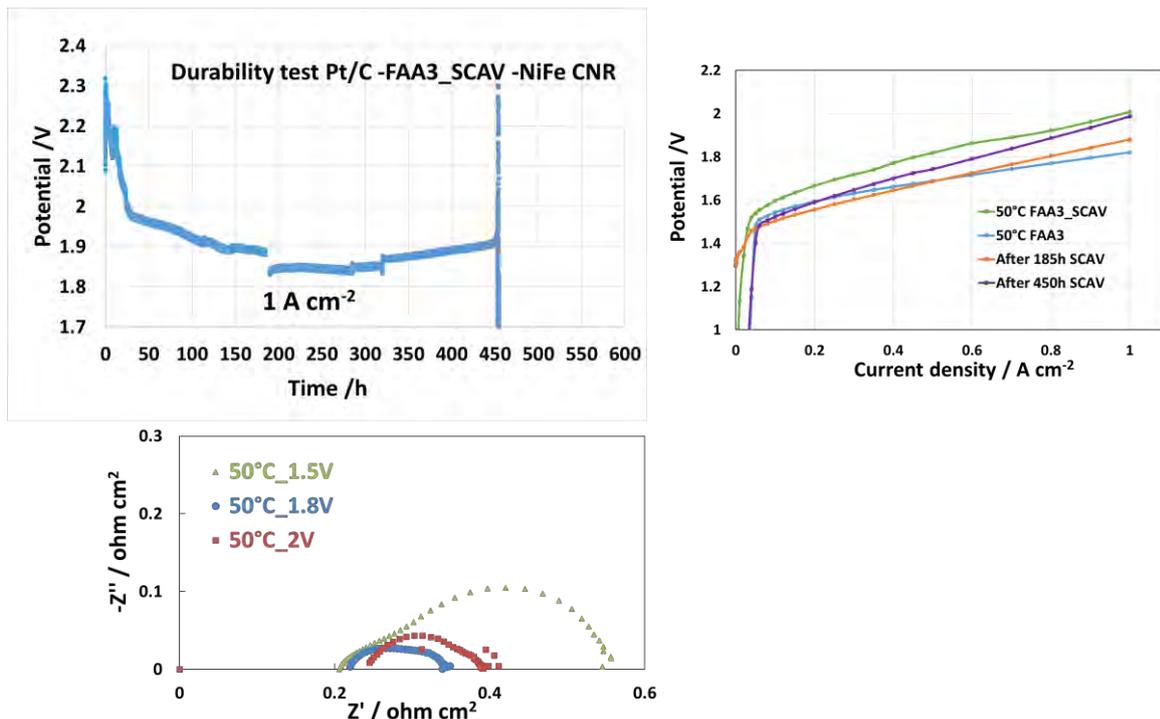
Fig. *36* *Durability and polarisation curves versus time for an MEA containing radical scavenger-based FAA membrane (top). Ac impedance spectra for an MEA containing radical scavenger-based FAA membrane (bottom)*

Impedance tests for the scavenger-based MEA after 180 hrs indicate a low series resistance of 0.2 Ohm cm^2 and low polarisation resistance about 0.4 Ohm cm^2 at 1.8 V cell voltage (Fig. 36 bottom). A comparison of performance and impedance response of scavenger-based and recast membrane during electrolysis operation is shown in Fig. 37 indicating similar characteristics.

D5.1 – Engineered MEAs for AEM electrolysis operation
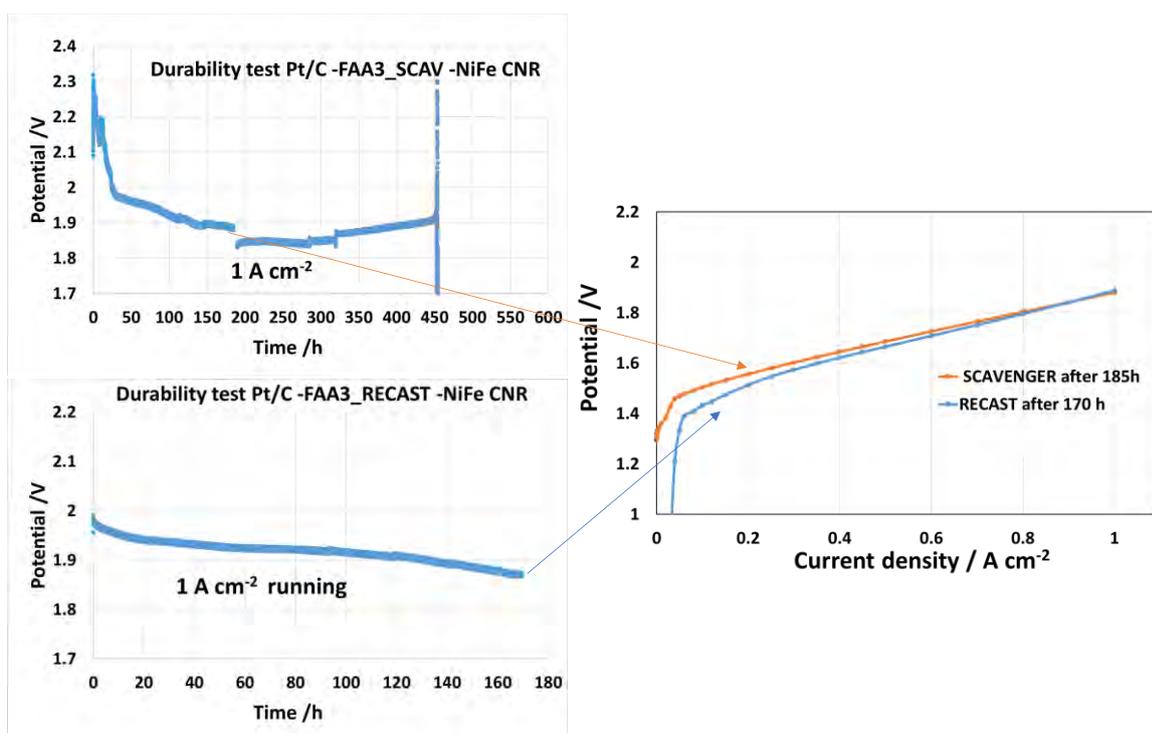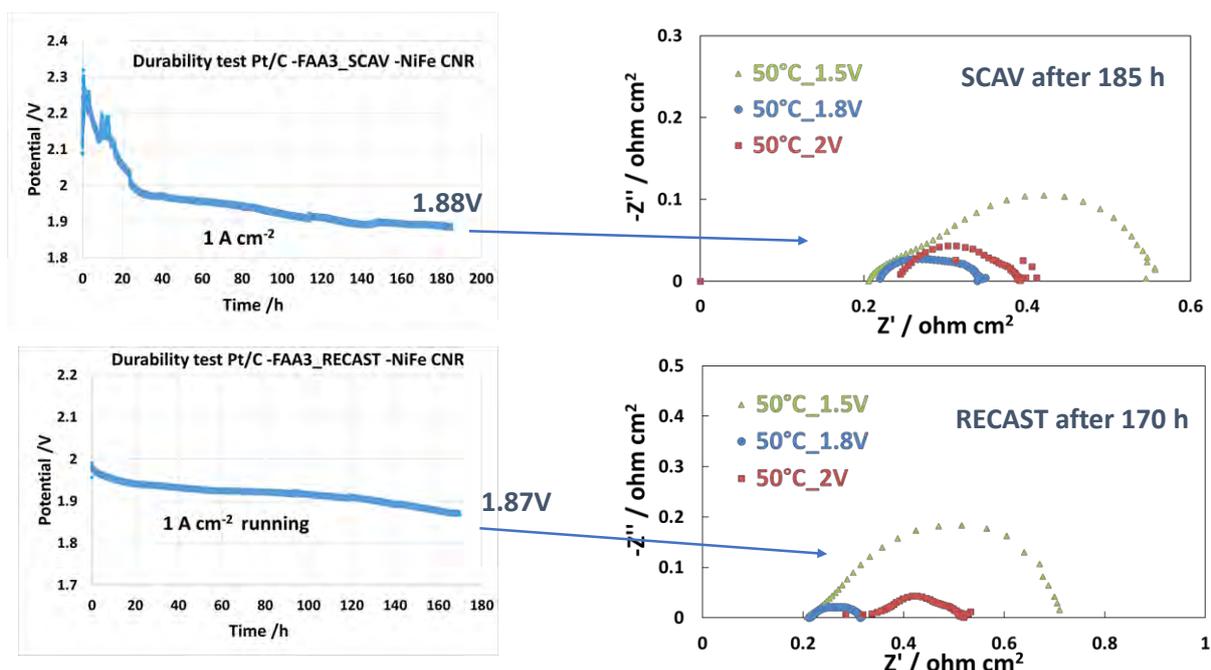
Fig. *37* *Performance and impedance response of scavenger-based and recast membrane during electrolysis operation.*

Percolation study

A percolation study was carried out using the NiAl catalyst cathode catalyst prepared at TFP (PV3), the FAA-3 membrane and ionomer and the NiFe anode catalyst prepared at CNR. Electrodes were manufactured at IRD. Different ionomer concentrations were investigated i.e. 20, 25 and 33%. The latter is assumed as a limit for a good electronic percolation. An increase of ionomer content increases the ionic percolation but decreases the electronic one. The NiAl catalyst cathode was designed with the aim of achieving a progressive leaching during cell operation to assure a highly porous Ni cathode. The same conditioning period was adopted for all these electrodes. The best results are shown for the composition with the higher ionomer loading (Fig. 38). This does not just reflect a higher ionic percolation but also a larger hydrophilicity resulting in a better uptake of hydroxyl ions.

The low performance of the 25% ionomer based MEA seems to be related to some conditioning issues. After an additional condition period of 100 h achieves a performance comparable to the MEA containing 33% ionomer (Fig. 39).

D5.1 – Engineered MEAs for AEM electrolysis operation
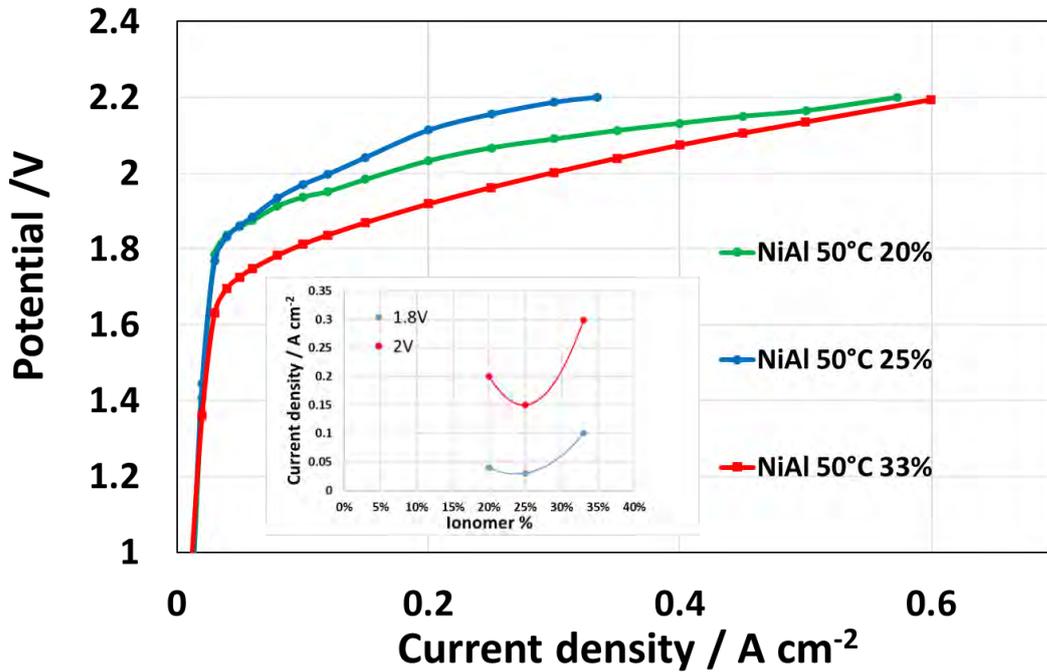
*Fig. **38** Percolation study for MEAs using NiAl cathode and FAA membrane.*
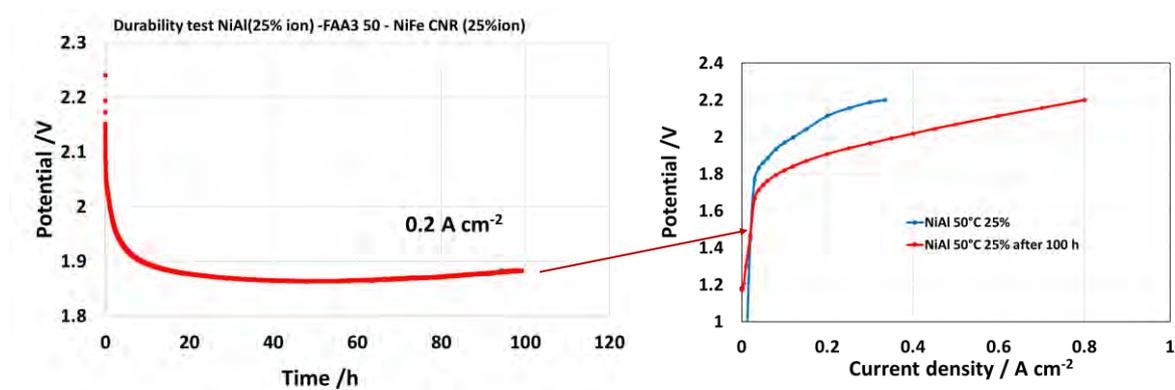
*Fig. **39** Conditioning effect for a 20% ionomer-based MEA using a NiAl cathode and FAA membrane.*

Effect of KOH feed concentration on electrolysis performance

An analysis of cell performance variation as function of the concentration of recirculating KOH solution is presented in Fig. 40. Experiments were carried out using an MEA based on NiMo/C cathode, Fumatech membrane and NiFe anode. This comparison was carried out after a short conditioning period of about 100 h. The investigated concentrations were 0.1, 0.5 and 1 M KOH. The performance achieved with 0.1 M KOH was definitively lower than with higher concentrations of the recirculating solution. Interestingly, at low current densities, operation with 0.5 M KOH provided a performance better than with 1 M KOH. At high current densities, the better conductivity achieved with 1 M KOH provided an enhanced performance i.e., a lower cell voltage at 1 A cm^{-2} that is the target operation of this project.

D5.1 – Engineered MEAs for AEM electrolysis operation
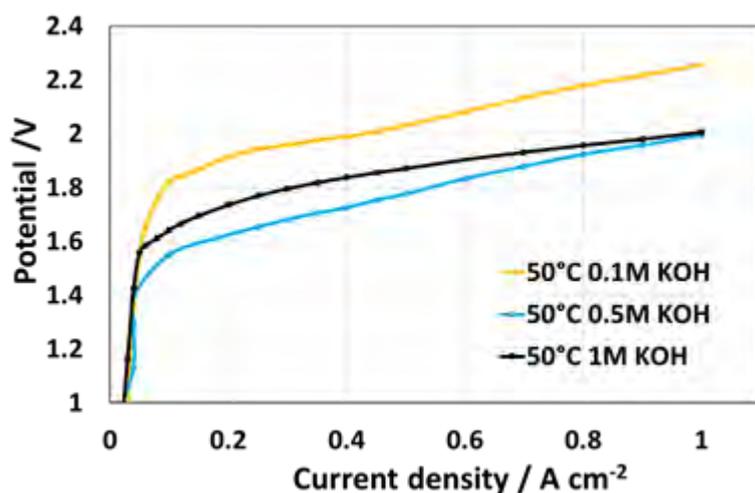
*Fig. **40***
Comparison of polarization curves at 50°C for the cell based on CNR-ITAE catalysts and Fumatech membrane in different KOH concentration.

Acknowledgement

The author(s) would like to thank the partners in the project for their valuable comments on previous drafts and for performing the review.

Project partners:

#	Partner	Partner Full Name
1	CNR-ITAE	CONSIGLIO NAZIONALE DELLE RICERCHE
2	CNRS	CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE
2.1	UM	UNIVERSITE DE MONTPELLIER
3	HydroLite (formerly PoCellTech)	HYDROLITE
4	TFP	PFP Hydrogen Products (former PV3 TECHNOLOGIES LTD)
5	IRD	IRD FUEL CELLS A/S
6	HYDROGENICS	HYDROGENICS EUROPE NV
7	UNR	UNIRESEARCH BV

D5.1 – Engineered MEAs for AEM electrolysis operation

Appendix A – Exchange of Materials in relation to WP5

Related deliverable/ Milestone	Requesting Organisation	Country of Requesting Org. (EU/other)	Providing Organisation	Country of Providing Org. (EU/other)	Material	Quantity	Date requested	Date sent
D5.1	CNR-ITAE	IT (EU)	IRD	DK (EU)	NiCo-spinel, from C-tech	10 g	feb-20	03-mar-20
D5.1	CNR-ITAE	IT (EU)	IRD	DK (EU)	MMO (minus 20 µm prior to calcination at 350ºC); from C-tech	10 g	feb-20	03-mar-20
D5.1	CNR-ITAE	IT (EU)	IRD	DK (EU)	NiCo-spinel, from C-tech	3 g	04-jun-20	08-jun-20
D5.1	IRD	DK (EU)	CNR-ITAE	IT (EU)	2*A4 sheets of FAA3-50 (Lot no. M35351903) in the Cl- form		jun-20	17-jun-20
D5.1	IRD	DK (EU)	CNR-ITAE	IT (EU)	FAA3 shredded film (Br-form)	5 g	jun-20	17-jun-20
D5.1	IRD	DK (EU)	CNR-ITAE	IT (EU)	NiFe LDH catalyst	2.6 g	jun-20	17-jun-20
D5.1	IRD	DK (EU)	CNR-ITAE	IT (EU)	Ni-catalyst	5.1 g	jun-20	27-jun-20
D5.1	CNRS	F (EU)	IRD	DK (EU)	NiCo-spinel, from C-tech	3 g	jun-20	08-jun-20
D5.1	CNR-ITAE	IT (EU)	IRD	DK (EU)	NiFe-catalyst from CENmat	2 g	jun-20	31-aug-20
D5.1	CNR-ITAE	IT (EU)	IRD	DK (EU)	Mo_2C from CENmat	2 g	jun-20	31-aug-20
D5.1	IRD	DK (EU)	CNR-ITAE	IT (EU)	NiCu	1.9 g	Oct-20	Oct-20
D5.1	IRD	DK (EU)	CNR-ITAE	IT (EU)	NiFe LDH catalyst	5 g	jan-21	18-jan-21
D5.1	IRD	DK (EU)	CNR-ITAE	IT (EU)	NiCu	5 g	jan-21	
D5.1	IRD	DK (EU)	TFP Hydrogen	UK (nonEU)	NiAl	2*10 g	jan-21	26-feb-21

D5.1 – Engineered MEAs for AEM electrolysis operation