EUROPEAN COMMISSION – FCH JU

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New Anion Exchange Membrane Electrolysers

GRANT AGREEMENT No. 875024

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.

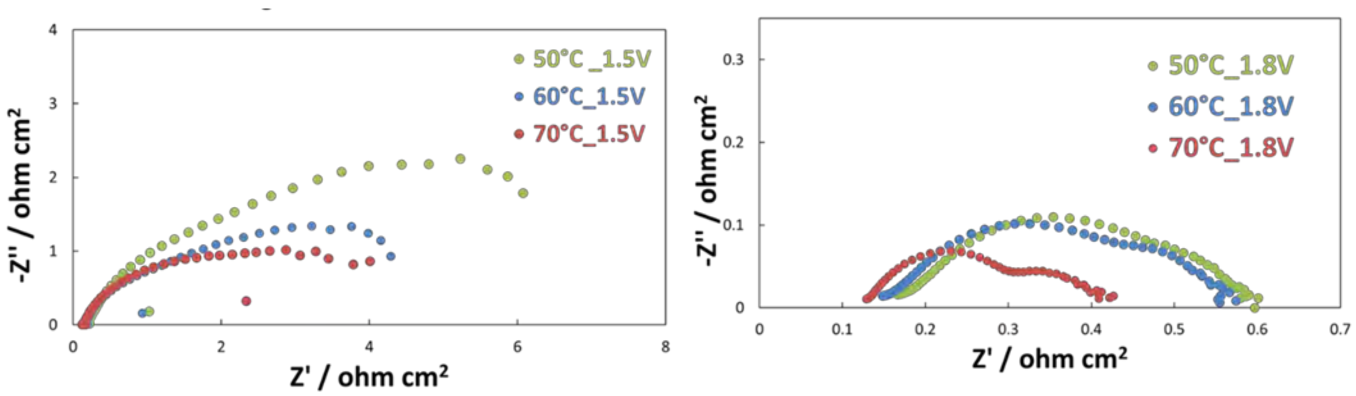

Figure 21. *The EIS of NiCu measured in the temperature range 50-70°C by feeding 1M KOH feed to the anode based on NiFe oxide. Experimental EIS spectra at 1.5 V (a), and at 1.8 V (b)*

The Rs values obtained through the EIS experiments are summarised in table 3. As discussed above, the increase of temperature causes a reduction of 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.

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

Rs	**Ohm cm^2**	**Ohm cm^2**
T°C	**1.5V**	**1.8V**
30°C	0.2297	0.2712
40°C	0.1978	0.2308
50°C	0.1553	0.1664
60°C	0.1361	0.1481
70°C	0.1212	0.1307

Figure 22 shows the durability test of cell mounting based on NiCu as cathode conducted in galvanostatic mode at different current densities. This experiment was conducted at 60 °C.

During this test, the cell showed relevant losses with time although it seems independent from the current density applied to the cell.

Since the membrane was relatively stable in the presence of NiFe oxide anode and Pt/C cathode. This behaviour appears related to the cathode.

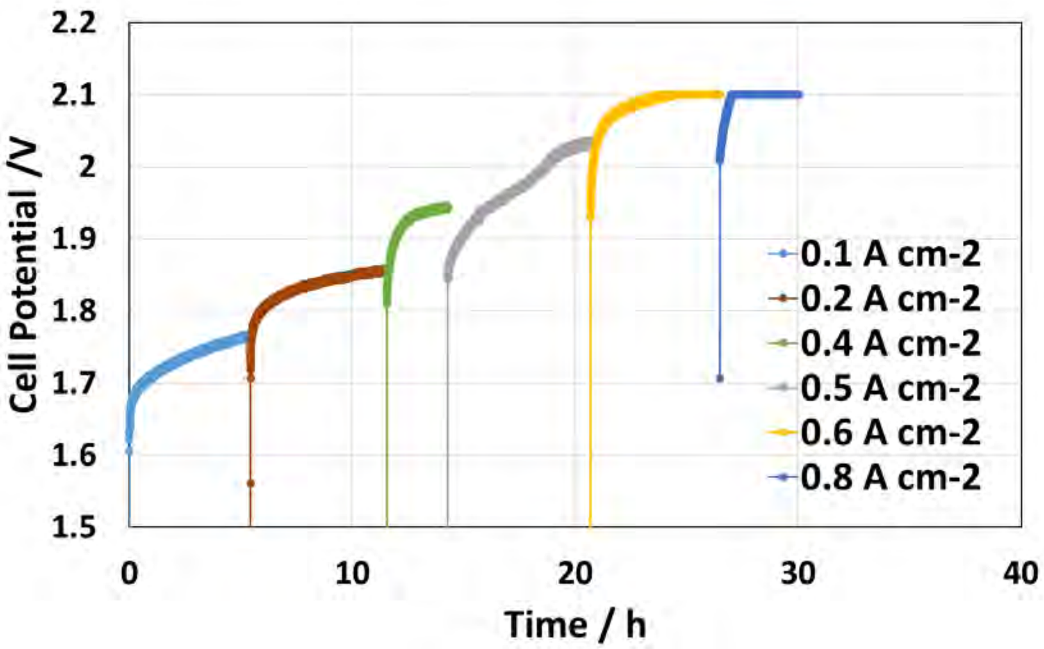

Figure 22. *The durability test was carried out at 60 °C at different current densities circulating in the cell based on NiCu as cathode and NiFe oxide as anode.*

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 figure 23. 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 a Pt cathode. However, the largest losses are related to an increase of polarisation resistance.

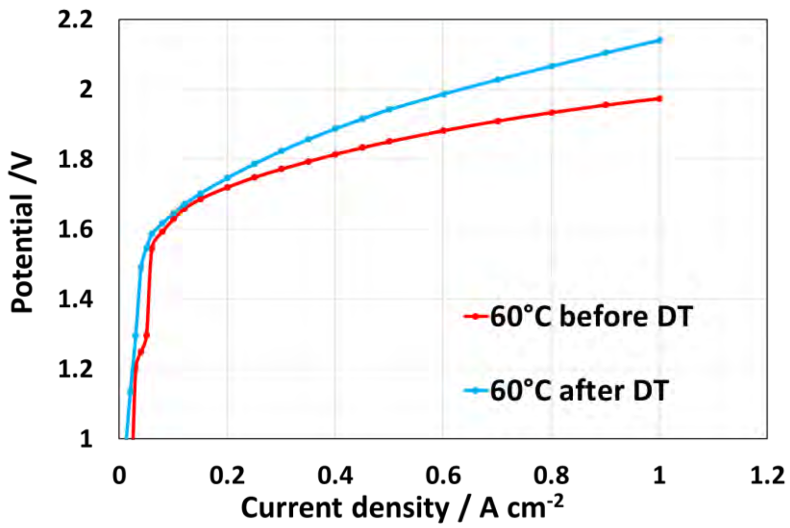

Figure 23. *Comparison of polarisation curves at the beginning and end of the durability test carried out at 60 °C with the cell based on NiCu at the cathode.*

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.

Figure 24 shows, as after the durability test, a large increase of Rs both in the curves collected at 1.5V and 1.8V.

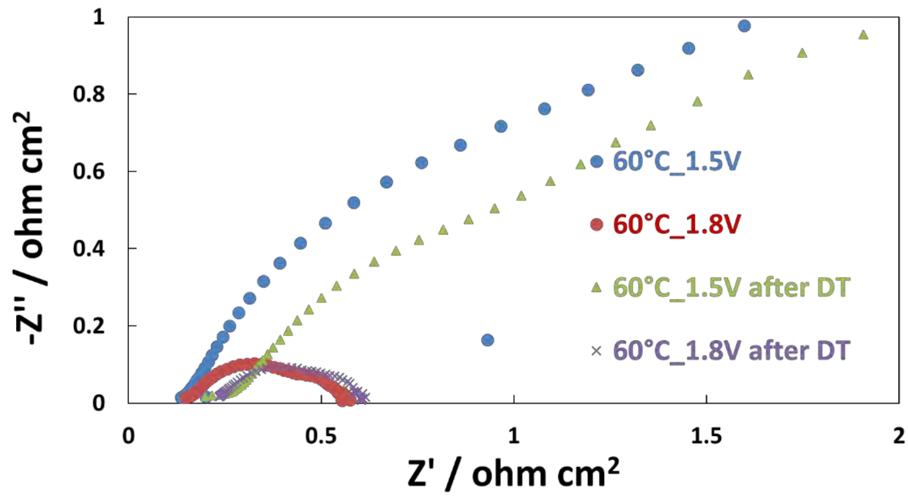

Figure 24. *Comparison of EIS analyses carried out before and after durability test on the cellbased on NiCu as cathode and referred to 1.5 V and 1.8 V.*

To get more insight into the degradation behaviour, a further durability test was carried out by cycling the potential of the cell between 1 V and 1.8 V.

This test is referred to as "potential cycling-based durability test".

The test of figure 25 was conducted at 60 °C for 65 hrs for the cell based on NiCu as cathode and showed limited stability since a decrease of the current density of approximately 25% in 65 hrs was observed.

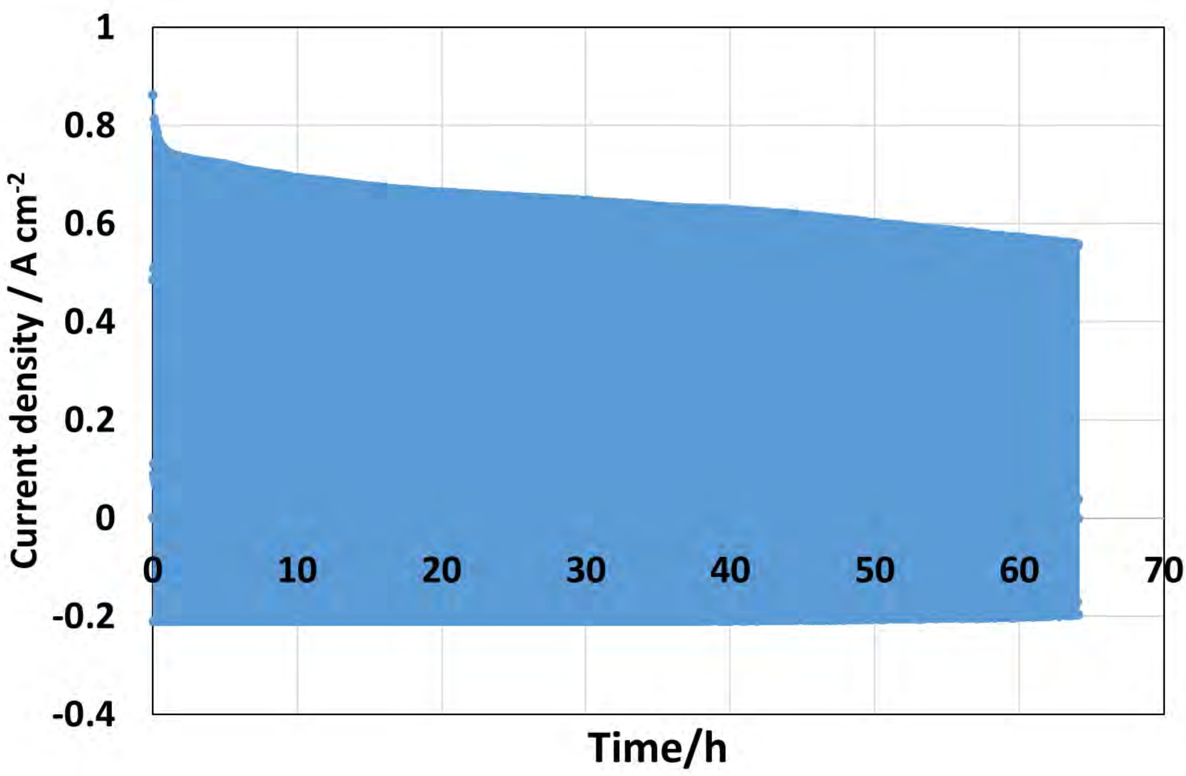

Figure 25. *Potential cycling test (1-1.8V) at 60°C for the cell based on NiCu as cathode – NiFE oxide anode and by recycling 1M KOH at the anode.*

Figure 26 compares the I-V curves collected before and after the potential-cycling test.

Cell degradation appears related to a strong increase of activation losses and ohmic resistance at the end of durability test.

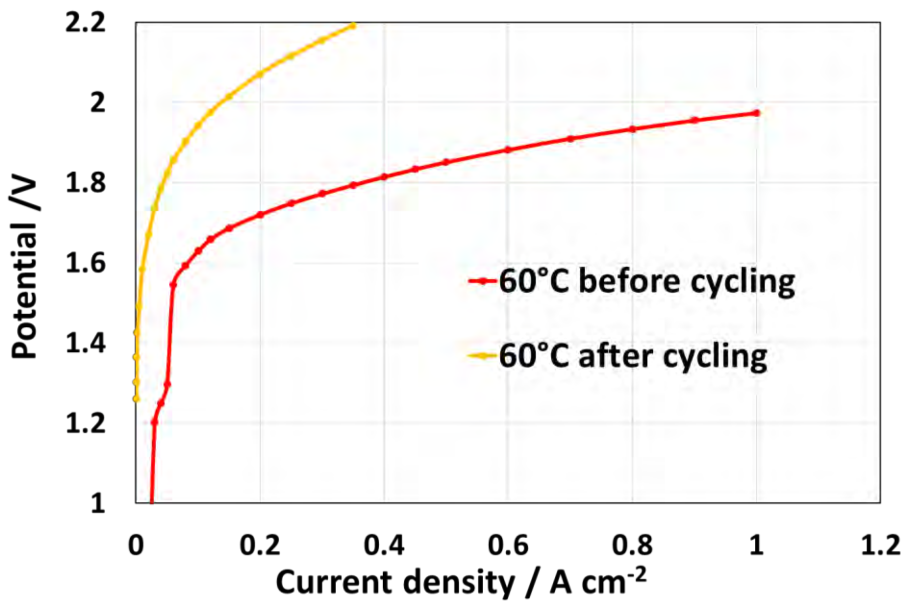

***Figure 26**. Comparison of polarization curves at the beginning and end of the potential cycling test (1-1.8V) at 60 °C with the cell based on NiCu at the cathode.*

3.1.5 Benchmarking CNR catalysts vs. commercial catalysts

In order to compare the performance and stability of CNR catalysts versus the state of the art catalysts CENmat catalysts were used as reference for comparison. First experiments regarded the assessment of the commercial catalyst Mo_2C (CENmat) provided by IRD and PV3. In the experiments conducted at CNR-ITAE, Mo_2C was used as a cathode coated onto gas-diffusion layer (GDL-Sigracet).

The experiments regarded a complete MEA incorporating a FUMATECH alkaline membrane and a Ni foam coated with NiFe oxide (CNR) at the anode.

The tests were carried out by circulating and recycling 1M KOH at the anode.

In the preliminary tests, the effect of temperature on the electrochemical characteristics was investigated.

Figure 27 compares the I-V curves carried out in the temperature range 30-50 °C and shows that the activation control is strongly related to the temperature.

A high cell voltage was recorded at low current density. The electrochemical performance was much lower than NiCu CNR catalyst. In particular, at 0.5 A cm-2 and 50°C the cell based on the CENmat catalysts showed 2.2. V cell voltage whereas CNR NICU catalyst showed 1.85 V.

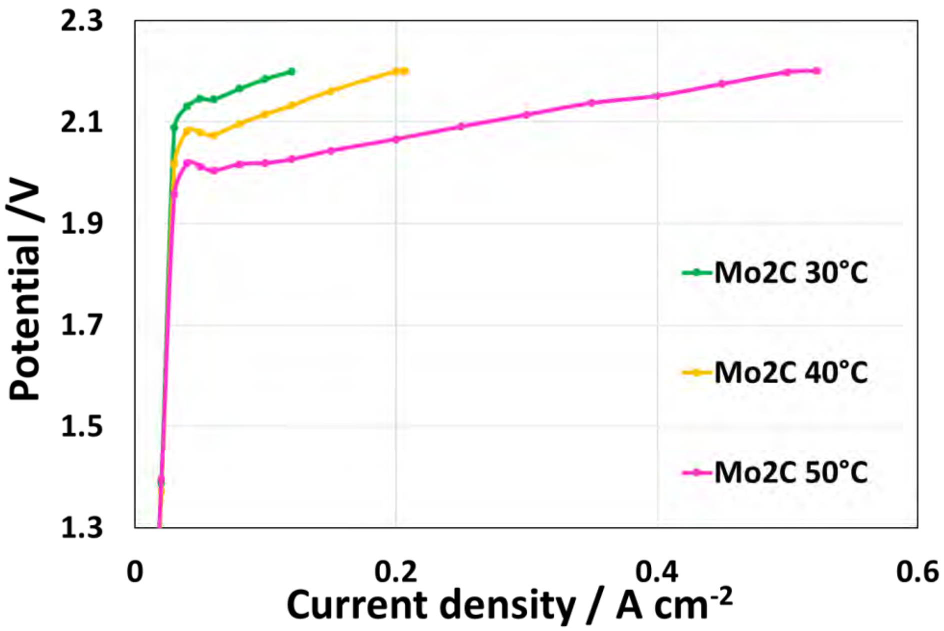

Figure 27. *Comparison of polarization curves carried out for the cell with Mo_2C as cathode and NiFe* oxide *as anode in the temperature range 30 °C - 50 °C.*

The EIS analyses carried out at 1.5V and 1.8 V on the cell based on Mo_2C as cathode are reported in the next figures for each temperature investigated. Figures 28 shows as the potential strongly affected the dimension of the semicircle appearing at low frequencies. Such behaviour is strictly connected with the large activation overpotential observed also in the polarisation curves of figure 27. It may be also expected a modification of the typical relaxation time for hydrogen evolution at these catalysts. As expected, the series resistance (high frequency intercept with the x-axis) slightly decreased with the temperature as a consequence of an enhanced conductivity of membrane. Curiously the series resistance is 0.21 Ohm cm^2 at 50°C for the cell based on Mo_2C compared to 0.13 Ohm cm^2 for NiCu catalyst.

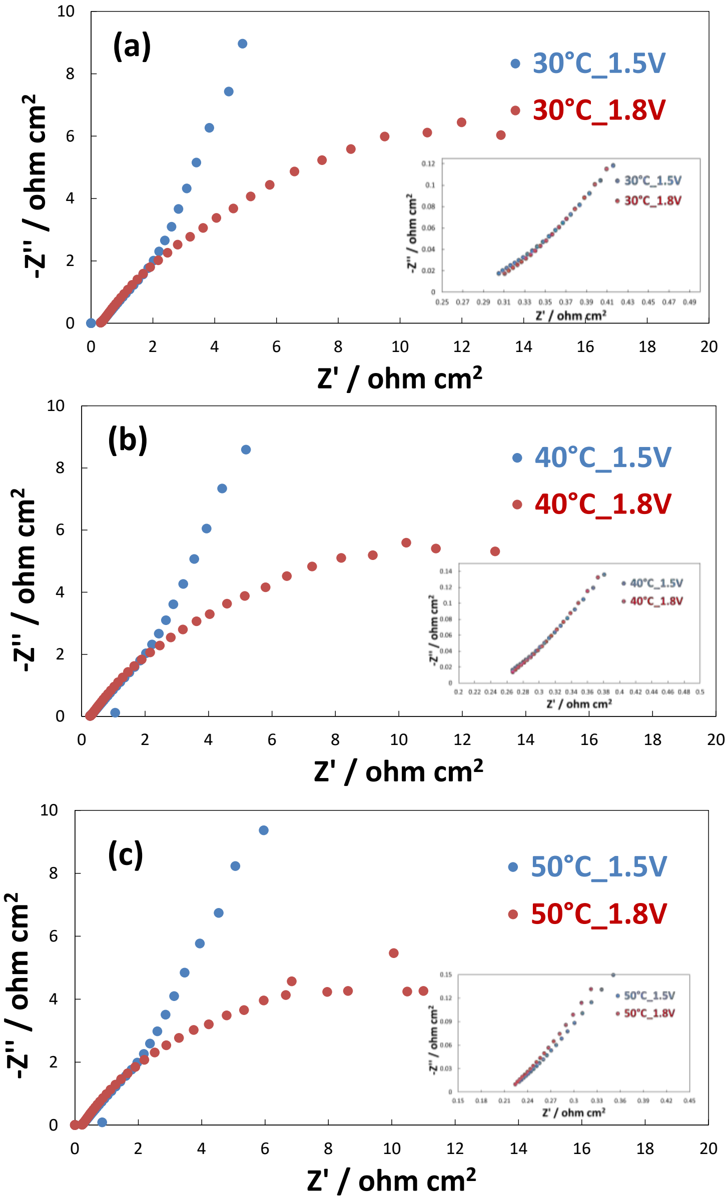

Figure 28. *EIS of the cell based on* Mo_2C *as cathode and NiFe* oxide *as anode measured at 1.5 V and 1.8 V at 30 °C (a), 40 °C (b) and 50 °C (c).*

A further investigation of the commercial Mo_2C (CENmat) provided by IRD as cathode was investigated in the presence of commercial $NiFeyO_2$ (CENmat) as anode and FUMATECH alkaline membrane. Also in this case, the cell was operated by recycling 1M KOH at anode.

Figure 29 shows the comparison between the I-V curves of this cell operating in the temperature range 30-50°C and as shown, the performances were definitely worse than that observed in the figure 27 related to cell using the CNR NiFe oxide as anode since less current density was achieved at the same cell potential.

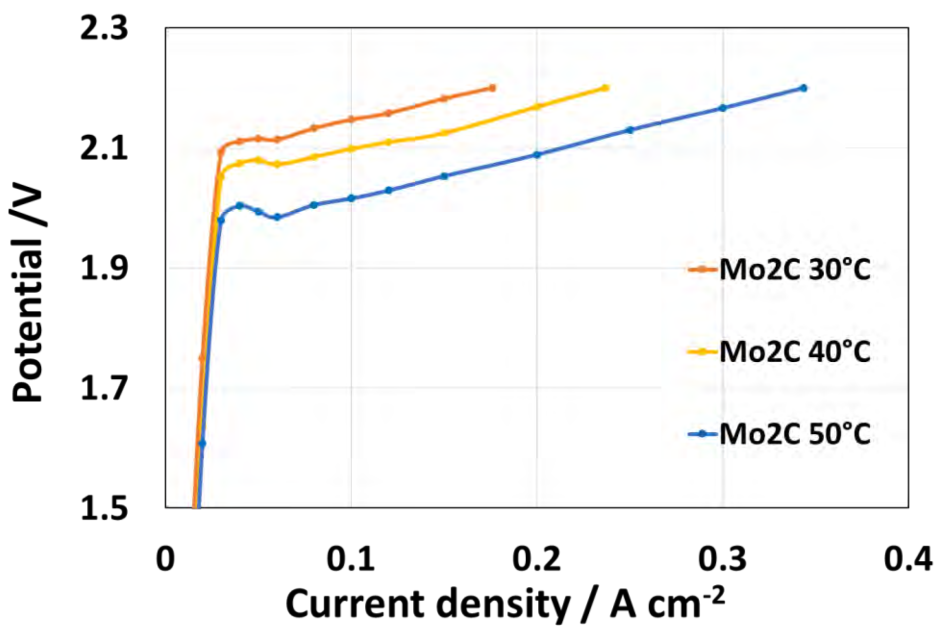

Figure 29. *Comparison of polarization curves carried out on the cell based on Mo_2C as cathode and $NiFeyO_2$ as anode in the temperature range 30 °C - 50 °C.*

The EIS analyses of this cell are shown in figure 30. A large semicircle at low frequency was observed and this was only partially mitigated by the increased temperature.

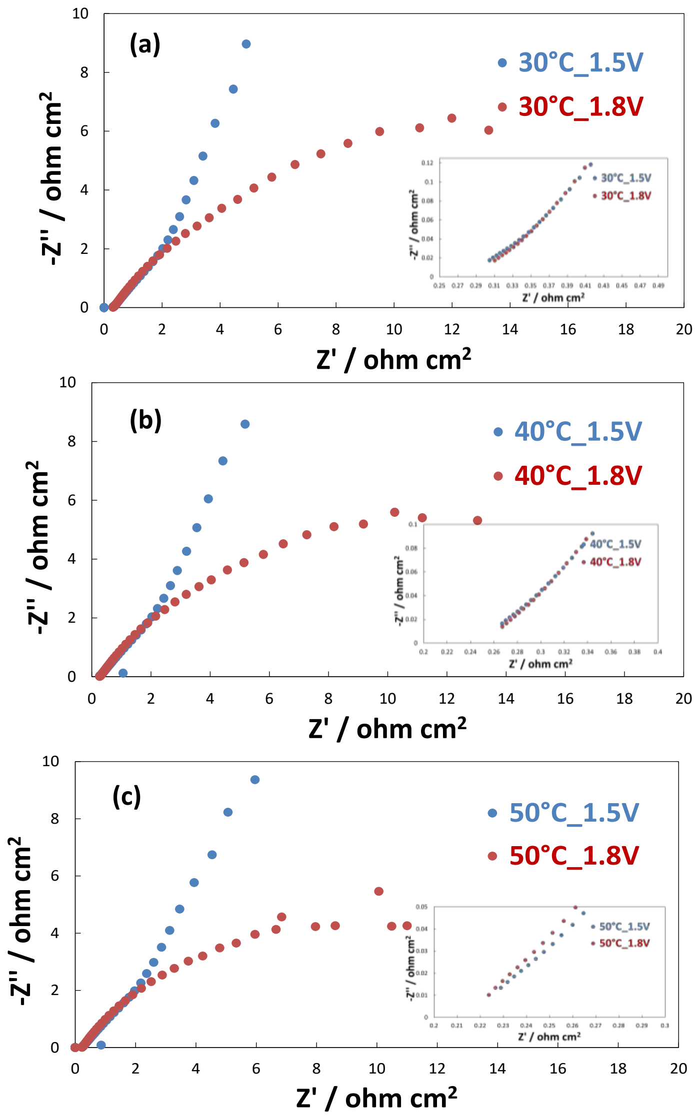

Figure 30. *EIS of cellbased on Mo_2C as cathode and $NiFeyO_2$ as anode measured at 1.5 V and 1.8 V at 30 °C (a), 40 °C (b) and 50 °C (c).*

Then, the cell equipped with Mo_2C as anode and *$NiFeyO_2$* as anode was placed under galvanostatic conditions (i.e. 0.3 A cm^{-2}) at 50 °C to evaluate the stability.

A very low current density was selected to avoid reaching the cut-off potential. Figure 31 shows a short durability test (just 17 hrs) but it was evident a much lower performance if compared with the performance achieved with Pt/C and NiCu. In the specific case of this cell a stationary condition was approximately obtained after 10 hrs.

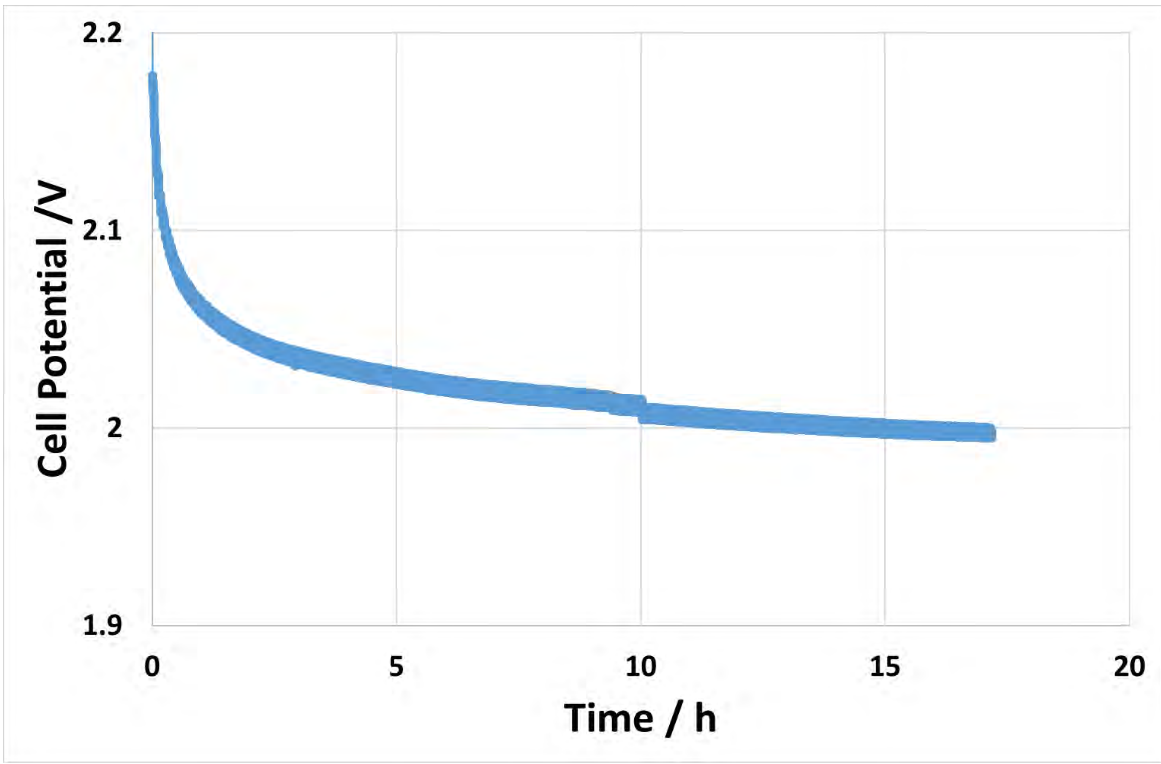

Figure 31. Durability test   carried out under galvanostatic conditions (0.3 A cm^{-2}) at 50 °C for the cell based on commercial Mo_2C as cathode and $NiFeyO_2$ as anode.

3.1.6 NiMo-based catalysts prepared at CNR

Metallic NiMo cathode electrocatalysts were prepared at CNR 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 1M KOH to the anode. Figure 29 compares the polarization curves of this cell investigated in the temperature range 30-50 °C and it shows that an increased 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. This is an unusual behaviour. However, the current density here achieved for the the NiMo catalyst was higher than that of the corresponding Mo/C commercial catalyst.