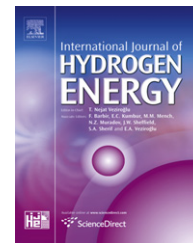




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A comparison of cathodes for zero gap alkaline water electrolyzers for hydrogen production

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ABSTRACT

Selected coatings on nickel or stainless steel micromeshes have been examined as electrocatalysts for hydrogen evolution in conditions mimicking those found in zero gap alkaline water electrolyzers. Voltammetry in 4 M NaOH at a temperature of 333 K, shows that Pt, NiMo and RuO₂ are the coatings of choice giving a superior performance particularly at higher current densities. NiMo and RuO₂ coatings also give stable performance during a 10 day electrolysis in a laboratory, zero gap, alkaline water electrolysis cell with a hydroxide conducting membrane; when combined with a NiFe(OH)₂ coated anode, a current density of 1 A cm⁻² is achieved with a cell voltage of ~2.1 V. Pt catalyses H₂ evolution efficiently at short times of electrolysis but cells with a Pt cathode show an increase in cell voltage from 2.05 V to 2.23 V during the first two days of operation.

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1. Introduction

With limited resources of C-based fuels, hydrogen is expected to provide an essential component to the solution of our needs for a sustainable fuel for our future transport requirements and also an approach to large-scale storage of energy. Presently, 95% of the world's hydrogen is produced by the reformation of hydrocarbons and this is an energy intensive process consuming hydrocarbons and also leading to carbon dioxide. In contrast, water electrolysis provides a clean route to hydrogen without the consumption of fossil fuel or the emission of carbon dioxide. If the electricity comes from renewable energy sources, water electrolysis becomes a truly green technology [1,2]. In consequence, there is presently much interest in new hydrogen technology that is cheaper and consumes less energy.

Existing water electrolysis plants are usually based on cells with an aqueous alkaline electrolyte and a porous separator.

The maximum current density is typically ~0.25 A cm⁻² and its energy efficiency is typically only ~60%. These shortcomings led to the development of solid polymer electrolyte (SPE) water electrolyzers [3,4]. Acidic SPE electrolyzers have a substantial improvement of conversion efficiency and are commercially available in small units. Until now, however, this technology cannot be regarded as low cost because of its heavy dependence on precious metals as catalysts and also using expensive Nafion[®] membranes.

Alkaline SPE water electrolyzers based on a non-perfluorinated, hydroxide ion permeable membrane and non-precious metal catalysts for both oxygen and hydrogen evolution should lead to substantial reductions in the investment cost of cells and also the possibility of lower energy consumption [1]. Overall there would be a significant reduction in the cost of hydrogen production. In our previous paper, we have studied a number of nickel based materials as potential oxygen evolution catalysts under conditions close to

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those in a zero gap alkaline water electrolyser [5]. Several nickel based mixed oxides/hydroxides have been identified as suitable anode catalysts for oxygen evolution.

In this paper, we report studies on cathode catalysts for hydrogen evolution suitable for zero gap alkaline water electrolysers. Hydrogen evolution is probably the most extensively studied electrode reaction [6–9]. The literature, however, seldom addresses the conditions likely to be found in modern, alkaline water electrolysers, namely current densities in the range 0.5–2.0 A cm⁻² and temperatures in the range 323–363 K. We have sought to compare a number of promising candidate cathode materials largely selected from knowledge of cathode performance in chlor alkali cells. The materials selected for study were platinum [9–14] (for comparison), ruthenium dioxide [15–24], nickel and nickel alloys [7,25–44] although cost considerations would lead to a preference for non-precious metal materials in commercial water electrolysis cells.

2. Experimental

The substrates for all the coatings were either Ni mesh (DeXmet Corporation, 4 Ni 6-040, 0.004" nominal thickness, 0.006" strand width, 0.040" long diagonal of the diamond) or stainless steel mesh (DeXmet Corporation, 4SS 5-050, 0.004" nominal thickness, 0.005" strand width, 0.050" long diagonal of the diamond); SEM images of these meshes are shown in Fig. 1. The Pt was deposited onto stainless steel and Ni, NiAl and NiMo coatings onto Ni mesh using magnetron sputtering by Teer Coatings Ltd. using conditions developed in order to produce high surface area coatings [45]. The coatings were ~1.5 μm thick and SEM images are shown in Fig. 1(c)–(f). The Ni/S coating was cathodically deposited onto Ni mesh at 10 mA cm⁻² at 298 K for 30 min in an electrolyte containing 200 g L⁻¹ NiSO₄·7H₂O, 20 g L⁻¹ NaCl, 40 g L⁻¹ H₃BO₃, and 100 g L⁻¹ thiourea as the source of sulphur [46], see Fig. 1(g). The RuO₂ coating was deposited using thermal decomposition of a Ru(III) solution onto the Ni mesh by Permascand AB, Sweden, see Fig. 1(h).

Slow scan voltammetry into the potential region for H₂ evolution has been used to compare the catalytic activities of the coating materials. Electrochemical measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT30 in a small-undivided beaker cell (volume 20 cm³) equipped with a water jacket connected to a Camlab W14 water thermostat. A small piece of coated mesh, a large area platinum gauze and a mercury/mercury oxide electrode (Hg/HgO in 4 M NaOH) were used as working, counter and reference electrodes, respectively. The reference electrode was always at the same temperature as the working electrode. In order to minimise IR drop and hence make more reliable comparison of materials at the high current densities of interest for water electrolysers, the measurements were carried out with small area cathodes. The coated meshes were masked with an insulating polyimide tape, leaving a small area, 0.03 cm², on one face of the mesh exposed to the solution. The working electrode was placed vertically and parallel to the counter electrode. Hydrogen bubbles leaving the cathodes surface are clearly visible and consequent oscillations in

the current are always observed. Even so, while this approach will not totally eliminate the uncompensated IR drop, it appears to allow the recording of reliable comparative data. Prior to testing, all of the coating materials were cleaned by soaking in first acetone and then water, each for 15 min. The catalytic activity of various coating materials for hydrogen evolution was assessed by recording voltammograms at coating electrodes at a temperature of 333 K in 4 M NaOH using a potential scan rate of 1 mV s⁻¹. Throughout the paper, current densities were based on the geometric area of the mesh cathodes used in the experiment.

The electrolyses were carried out at a temperature of 333 K using a zero gap cell with a 160 μm thick, hydroxide ion conducting membrane under development by ITM Power plc, UK. The cell was assembled with the two mesh electrodes (each geometric area, 9 cm²) pressed up against the membrane and 4 M NaOH flowed down the rear of the meshes at a flow rate of 15 cm³ min⁻¹ to prevent gas accumulation. The anode was the fine stainless steel mesh coated with a Ni/Fe hydroxide layer by cathodic electrodeposition [5] and the cathodes were the various coated materials. Prior to recording the cell current versus cell potential curves, electrolysis with a current density of 1 A cm⁻² for 1 h was carried out in order for the cell components to approach their steady state performance. The longevity tests were carried out in the same cell under constant electrolysis at a current density of 1 A cm⁻² at 333 K and ambient pressure.

The surface morphology and composition of the samples were characterized using a JSM-6500F scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) microanalysis (Oxford Inca 300) and operated at an accelerating voltage of 15 kV.

3. Results and discussion

High magnification SEM images of the coatings are reported in Fig. 1. All the coatings can be seen to be uniform. The coatings prepared by magnetron sputtering all have a reflecting metallic appearance by visual observation and exhibit excellent adhesion when tested with sticky tape. The Pt coating, Fig. 1(c), can be seen to have a structure consisting of tightly packed centres with dimensions below 100 nm and these centres are themselves made up of smaller growths. When studied by cyclic voltammetry in 1 M H₂SO₄, the response shows clean peaks for the PtO/Pt couple and H adsorption/desorption [47,48]. Calculation of the charge under the H adsorption peaks indicates that the surface has a roughness factor of 244; this is a high value comparable to that for Pt blacks. The nickel and nickel alloy coatings also all consist of tightly packed centres made up of smaller growths and the dimensions of the centres increase along the series Pt < Ni < NiMo < NiAl. As a result, the NiAl has very much the appearance of a 'standard cauliflower' structure, common in metal deposits. All may be considered high surface area deposits. Indeed, the roughness factor for the nickel as estimated from the charge under the Ni(OH)₂/NiOOH peak on a cyclic voltammogram in 1 M NaOH [49] is 240. EDX analysis gives a Mo and Al content of the alloys of ~20 at. %. The Ni/S coating prepared by electrodeposition is also bright and

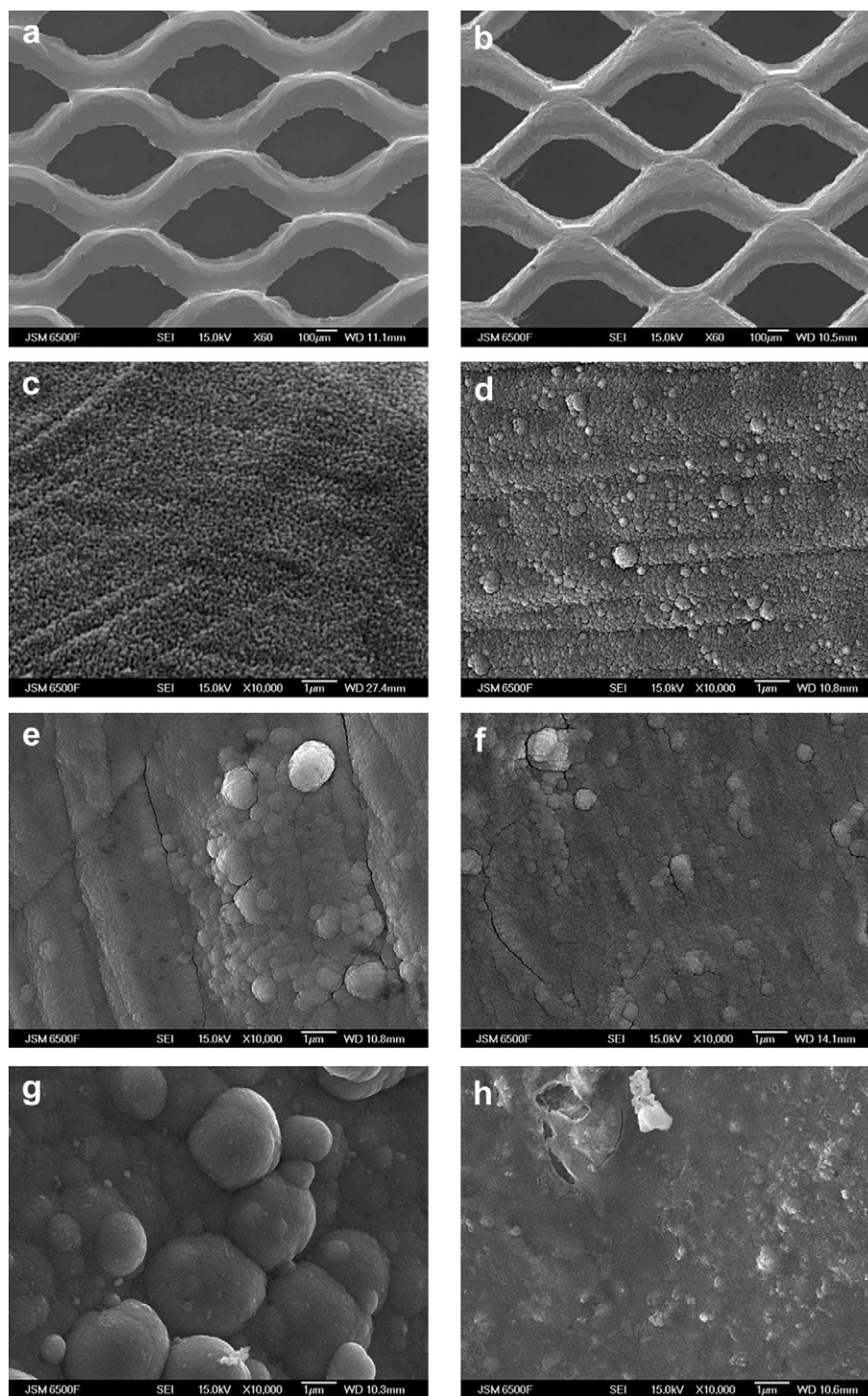


Fig. 1 – Low resolution SEM images of (a) Ni micromesh and (b) stainless steel micromesh, and high-resolution SEM images of the various coatings: (c) Pt; (d) Ni; (e) NiAl; (f) NiMo; (g) NiS; (h) RuO₂.

appears uniform to the eye. The high magnification image also shows a ‘cauliflower’ structure with centres up to a few microns. At a lower magnification, the layer can be seen to be cracked but otherwise uniform. By eye, the RuO₂ coating is black and compact and the high magnification SEM image reveals little about the layer structure. On a lower magnification, the layer again looks uniform but some cracks typical of thermally produced layers can be observed.

The catalytic activities of the cathodes were compared by recording voltammograms in 4 M NaOH as the electrolyte and at a temperature of 333 K. It was recognised that at the current densities of interest for water electrolyzers (up to 2 A cm⁻²), IR distortion of the voltammograms would be inevitable particularly with the high volume of gas being evolved. In this work, data are always presented as potentials and we are reluctant to discuss the results in terms of overpotentials or more

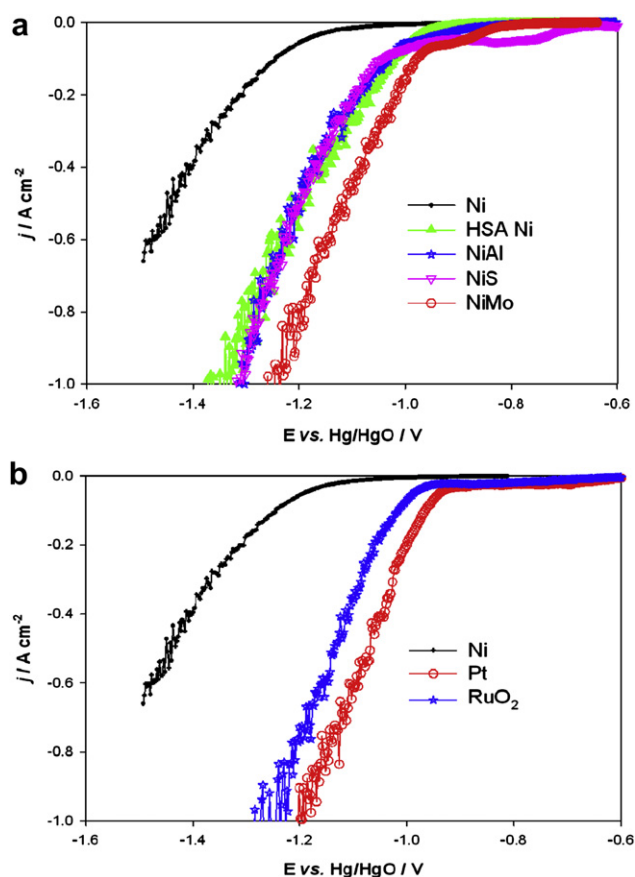


Fig. 2 – Steady state polarization curves recorded for hydrogen evolution at various coating materials in 4 M NaOH at 333 K with a potential sweep rate of 1 mV s^{-1} : (a) Ni mesh, high area Ni, NiAl, NiS and NiMo coatings; (b) Ni mesh, Pt and RuO₂ coatings.

fundamental factors because of the inclusion of IR drops in all the measured potentials. This IR distortion of the data was minimised by using a small area cathode and positioning the electrode so that the hydrogen gas left the working-counter electrode gap as rapidly as possible. With these precautions, it

was believed that the comparison of materials would be sound.

Fig. 2 shows voltammograms recorded at 1 mV s^{-1} and all show increasing current densities for hydrogen evolution negative to -0.95 V vs. the Hg/HgO reference electrode. Data from the responses are also summarised in Table 1. It can be seen that all the coatings studied lead to hydrogen evolution at a substantially less negative potential than uncoated Ni mesh. Fig. 2(a) reports the responses for the Ni based materials and it can be seen that the high surface area Ni, the NiAl and Ni/S give very similar voltammograms, The aluminium and sulphur are probably dissolving by corrosion and anodic dissolution (to give Al(III) in solution or surface film) and cathodic reduction (to give sulphide in solution) to give more porous and higher area layers than the as-prepared coatings. The presence of molybdenum in the nickel alloy leads to a significant further improvement in performance. It appears that Mo acts as a genuine catalyst as well as increasing the active areas [1]. Variation of the Mo content between 20 and 50 at. % did not lead to discernable changes to the electro-catalytic activity. Fig. 2(b) compares the voltammograms for Pt and RuO₂ with uncoated Ni. The performance of the RuO₂ is very comparable to that of the NiMo. In this short timescale experiment, however, Pt shows the best performance.

The data in Table 1 shows a further interesting feature. For a current density of 0.1 A cm^{-2} , the potentials of all the coatings fall in the narrow range, -0.97 V to -1.04 V , close to the equilibrium potential for the H₂O/H₂ couple estimated as -0.93 V vs. the Hg/HgO reference electrode [50] in the experimental conditions. But when the current density had the higher value of 0.5 A cm^{-2} , the coatings showed a greater divergence in performance and Pt, RuO₂ and NiMo appear to be superior. This division in performance becomes more marked if the voltammograms were continued to even higher current densities.

Current density vs. cell potential were recorded for each of the coatings in a zero gap electrolysis cell where two mesh electrodes were pressed up against a hydroxide conducting membrane and each was fed with 4 M NaOH at 333 K, see Fig. 3. Data taken from these responses are also reported in Table 1. In all cases the anode was a NiFe(OH)₂ coating on stainless steel mesh as described in an earlier paper [5] and

Table 1 – (a) Potentials from voltammograms for the evolution of hydrogen at a current density of 0.1 and 0.5 A cm^{-2} . (b) Cell potential for a zero gap water electrolysis cell at a current density of 0.1, 0.5 and 1.0 A cm^{-2} . (c) Cell potential for a zero gap water electrolysis cell after electrolysis at a current density of 1.0 A cm^{-2} for 10 days (* except for uncoated Ni and high area Ni when the electrolysis were discontinued after 2 days). 4 M NaOH. 333 K.

Cathode	(a) E vs. Hg/HgO/V		(b) E _{cell} /V			(c) E _{cell} /V after 10 days electrolysis at 1 A cm^{-2}
	0.1 A cm^{-2}	0.5 A cm^{-2}	0.1 A cm^{-2}	0.5 A cm^{-2}	1.0 A cm^{-2}	
Uncoated Ni	-1.25	-1.44	2.00	2.23	2.42	2.48*
High area Ni	-1.02	-1.19	1.83	2.07	2.28	2.37*
NiAl	-1.03	-1.20	1.83	2.06	2.24	2.33
NiS	-1.04	-1.20	1.75	1.95	2.16	2.32
NiMo	-0.98	-1.12	1.71	1.90	2.04	2.14
RuO ₂	-1.02	-1.14	1.67	1.86	2.02	2.06
Pt	-0.97	-1.07	1.61	1.80	2.00	2.23

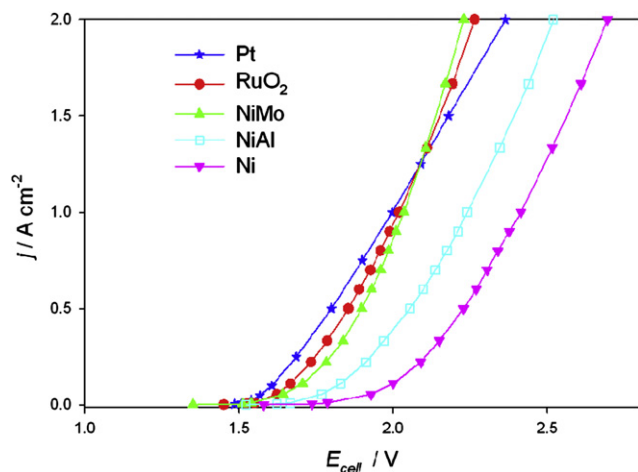


Fig. 3 – Cell current vs. cell voltage plots for the zero gap, alkaline water electrolyser with various coating materials as cathode and NiFe hydroxide as anode pressed up against the hydroxide ion exchange membrane in 4 M NaOH at 333 K (electrode areas 9 cm^2).

the cell was run at 1 A cm^{-2} for 1 h prior to recording the response in order to stabilise the cell components. It can be seen that with this cell configuration, water electrolysis commences with a cell voltage close to 1.5 V and it is possible to achieve very high current densities, at least 2 A cm^{-2} with moderate cell voltages, despite a probable significant contribution from IR drop. Again the best catalysts appear to be Pt, RuO_2 and NiMo when the cell voltages for current densities of 0.1 , 0.5 and 1 A cm^{-2} are $\sim 1.7 \text{ V}$, $< 1.9 \text{ V}$ and $< 2.1 \text{ V}$ respectively, see data in Table 1. It can also be seen that the Pt coating appears superior below 1 A cm^{-2} but loses its advantage at even higher current densities.

The same cell was used to examine the longer term performance of the cells and the cell voltages were monitored during continuous electrolyses carried out for a period of 10 days with a current density of 1 A cm^{-2} ; in fact these data were recorded following the recording of the cell current vs. cell voltage responses discussed above. Fig. 4 shows the results for the three preferred electrocatalysts while cell voltages for all the coatings are reported in Table 1. At least some of the small variations in cell voltage arise as a result of periodic maintenance of the system, e.g. addition of water and overnight, small changes to temperatures. Clearly, however, the cell with the Pt cathode catalyst showed an increase in cell voltage from an initial value of 2.07 V to a steady state value of 2.23 V during the first two days. After the 10 day electrolysis with this cell, the operating current was stepped between 1 A cm^{-2} and zero at 4 hour intervals; on recommencing the electrolysis, the cell voltage always returned immediately to 2.23 V. The Pt surface is undergoing a rather rapid and irreversible decay in performance and this probably results from the adsorption of trace organics in the system, e.g. from the membrane. The cell with the NiMo catalysed cathode also showed a smaller but rapid increase voltage, settling down at 2.14 V while the cell with the RuO_2 catalysed cathode

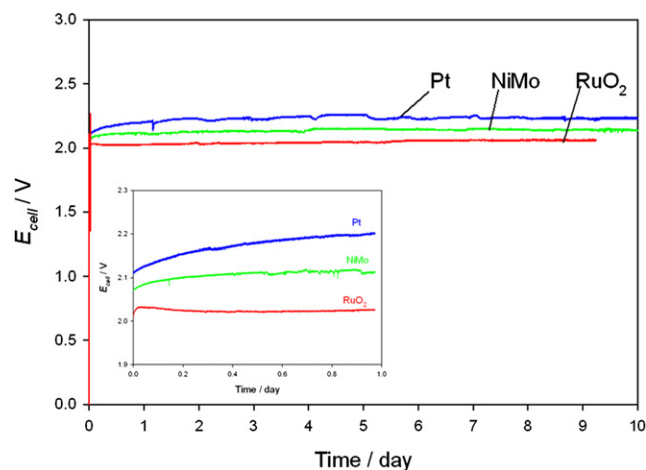


Fig. 4 – Cell voltage for the zero gap, alkaline water electrolyser during 10 days of electrolysis with the three preferred cathode coatings. The inset shows an expansion of the behaviour during the first day.

maintained a steady voltage of 2.06 V. For comparison, it should be noted that the cell with an uncoated Ni cathode had a cell voltage of 2.48 V. As a further demonstration of the stability of the cell performances, the cell current vs. cell

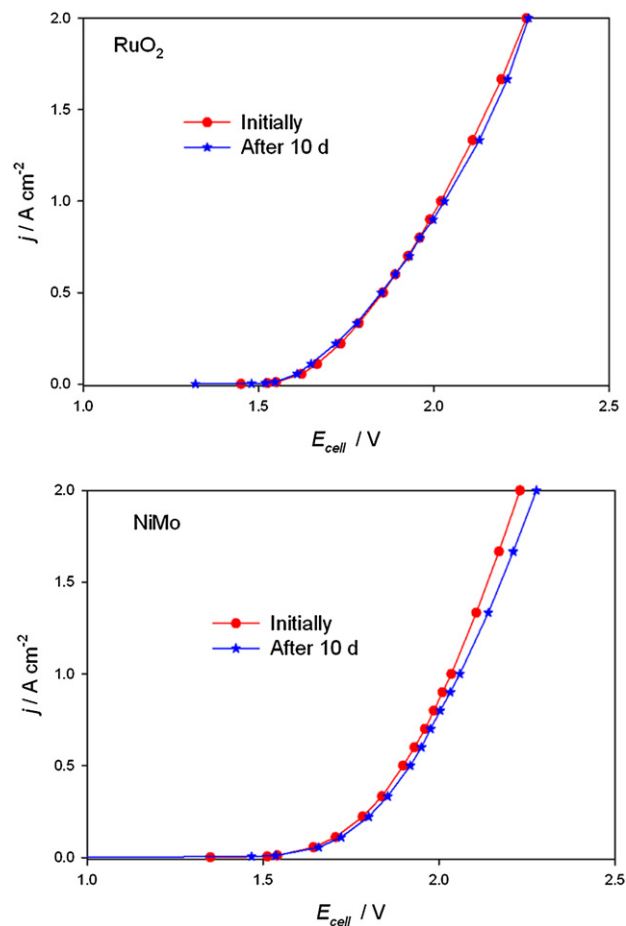


Fig. 5 – Cell current vs. cell voltage curves recorded before and after the 10 days electrolysis with RuO_2 and NiMo coatings as cathode.

voltage responses were recorded at the end of the 10-day electrolysis. The results for RuO₂ and NiMo are shown in Fig. 5 where it can be seen that the change is very small.

4. Conclusions

Throughout this paper, the approach has been to compare practical electrocatalysts for the cathode reaction in zero gap alkaline water electrolyzers. It is clear that both RuO₂ and NiMo are stable coatings that can support very high current densities in alkaline media. Indeed, they seem to be very promising materials for zero gap alkaline water electrolyzers, a technology likely to become more important in the near future.

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