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Performance of polyethylene based radiation grafted anion exchange membrane with polystyrene-b-poly (ethylene/butylene)-b-polystyrene based ionomer using NiCo$_2$O$_4$ catalyst for water electrolysis

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**Highlights**

- Soluble AEM based on SEBS with OH$^-$/H$^+$ conductivity of 0.14 S cm$^{-1}$, IEC 1.9 mmol g$^{-1}$.
- At 10 mg cm$^{-2}$ NiCo$_2$O$_4$ has superior OER activity to IrO$_2$ 2 mg cm$^{-2}$ at 1/200 of cost.
- Electrolyser performance using NiCo$_2$O$_4$, 1.65 V at 100 mA cm$^{-2}$ at 60$^\circ$C & 0.1 M OH.
- Challenges are low pH equivalent of AEM of 11.5 & 100 times slower HER than acid.

**Abstract**

A soluble anion exchange ionomer with high OH$^-$/H$^+$ ion conductivity comparable to that of Nafton is synthesised by chloromethylation of polystyrene-b-poly (ethylene/butylene)-b-polystyrene (SEBS) and used with NiCo$_2$O$_4$ electro-catalyst for water electrolysis. The ionomer has an ion exchange capacity of 1.9 mmol g$^{-1}$ and ionic conductivity of 0.14 S cm$^{-1}$ at 50 $^\circ$C. The cell voltage at 20 $^\circ$C at 100 mA cm$^{-2}$ is 1.77 and 1.72 V in, 0.1 and 1.0 M NaOH, respectively, for an optimum loading of 10 mg cm$^{-2}$ NiCo$_2$O$_4$. At 10 mg cm$^{-2}$ NiCo$_2$O$_4$ electrolyser performance is at least equal to or superior to that of IrO$_2$ at 2 mg cm$^{-2}$ with excellent stability over 1 h. When the catalyst is sprayed on the GDL instead of CCM, the performance is further improved to 1.65 V at 100 mA cm$^{-2}$ at 60 $^\circ$C & 0.1 M KOH. The limited AEM electrolyser performance when operating with deionised water in comparison to PEM and alkaline electrolyser arises from the sluggish OER in the AEM environment equivalent to pH of 11.5 and the two orders of magnitude slower HER activity with respect to acid medium combined with the high Tafel slope of 120 mV dec$^{-1}$.

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### 1. Introduction

In the growing demand of moving towards renewable and sustainable energy sources, one of the main challenges is the storage of the intermittent renewable energy and its transport for use at other locations. One promising candidate for energy storage is hydrogen due to, the highly efficient reversible conversion between H$_2$ and electricity, the good energy density of compressed gas compared to most batteries and the scalability of H$_2$ technologies for grid scale applications. However, 95% of the total H$_2$ generated globally is via reformation of hydrocarbons (steam reforming) [1–3], while around only 5% being generated by electrolysis due to the relatively high cost of the electrical energy and systems. Currently, production of H$_2$ by electrolysis is more expensive than steam reforming: the electricity required to split water into H$_2$ and O$_2$ can account for up to 75% of the total H$_2$ production cost with current costs between 3.7 and 5.4 €/Kg H$_2$ [4]. The capital cost of proton exchange membrane (PEM) electrolyzers is high and is largely dictated by the high material costs of membranes (perfluorinated polymers) amounting to 8% of the cost, precious metal (Pt, Ir, Ru) catalysts amounting to 30% of the cost [5], and the titanium based flow fields. Alkaline electrolyzers use lower...
cost electrode materials based on Ni but have poor gas separation due to the use of porous membrane to embed the KOH liquid electrolyte. Additionally, the high alkaline concentration used causes degradation of the electrodes. It is reported that the current average cost of PEM electrolyser stack is 2090 €/kW in comparison to 1100 €/kW for alkaline electrolyser [6]. However PEM water electrolysis systems offer advantages over alkaline technologies such as ability to operate at differential pressure (H2 compression), higher production rates (current density per unit electrode area), and more compact and flexible design operation. Adopting alkaline anion exchange membranes (AAEM) provides the opportunity to combine the attractions of both electrolyser types, to create lower cost polymer membrane electrolyser systems, through low cost catalyst (non-noble), membrane and bipolar plates. Moreover, AAEM electrolysis is not affected by the presence of cationic species in the feed-water, which can exchange with H+ in PEMs and reduce conductivity. Polymer electrolyte electrolyser also need less operation and maintenance effort and are thus promising for use in small scale applications (residential applications). In comparison to proton conducting polymer based electrolyser the amount of research conducted on alkaline anion exchange membrane polymer electrolyser is relatively small [7–11]. Most of the research is focussed on developing new catalyst for oxygen evolution reaction (OER) due to its sluggish kinetics (high overpotential (η)).

\[
\begin{align*}
\text{Cathode : } & \quad 2 \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2 \text{OH}^- \quad (E_0) \\
& = \quad -0.83 \text{ V vs. SHE}) \\
\text{Anode : } & \quad 2 \text{OH}^- \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- \quad (E_0) \\
& = \quad 0.403 \text{ V vs. SHE}) 
\end{align*}
\]

A solid state water electrolyser based on AAEM has recently been reported with a cell voltage of 1.59 V at 100 mA cm\(^{-2}\) using DI-water feed at 50 °C using Tokuyama AS-4 ionomer (1.4 mmol g\(^{-1}\)) [10]. The electrolyser however used high loadings of Pt group metal catalysts. Xiao et al. reported a first implementation of an AAEM-based alkaline electrolyser with non-precious metal catalysts based on Ni-Fe (anode) and Ni-Mo (cathode), however with very high loading in excess of 40 mg cm\(^{-2}\) [11]. They obtained cell voltage of 1.7 V at 100 mA cm\(^{-2}\) with use of 1.0 M KOH electrolyte at 70 °C. We have reported previously performance of various Co3O4 based OER catalyst [12–15] in water electrolyser based on a poly(methacrylate quaternary ammonium hydroxide (QPDTH-OH) with IEC 1.3 mmol g\(^{-1}\) and conductivity of 0.059 S cm\(^{-1}\) at 50 °C [12], and good stability over 10 h continuous operation. Using deionised water feed, cell voltage at 100 mA cm\(^{-2}\) was 1.82 V with 3 mg cm\(^{-2}\) Cu0.7Co0.3O4 at 25 °C [13], 1.81 V with 2.5 mg cm\(^{-2}\) Li0.21Co0.79O4 at 45 °C [14] and 1.89 V using 3 mg cm\(^{-2}\) Cu0.6 Mn0.3Co0.1O4 at 40 °C [15]. Pandirajan et al. [16] has recently reported a voltage of 1.7 V at 100 mA cm\(^{-2}\) at 25 °C with 3.5 mg cm\(^{-2}\) Ce0.2MnFe1.8O4.

Very recent reports on the use of NiCo2O4 in AEM reported a cell voltage of 1.8 V at 100 mA cm\(^{-2}\) using 10 mg cm\(^{-2}\) NiCo2O4 at 50 °C using 1.8 M KOH and quaternized polyphenylene oxide ionomer (IEC 1.4 mmol g\(^{-1}\) and conductivity of 0.098 S cm\(^{-1}\)) [17] and 1.95 V was reported for 5 mg cm\(^{-2}\) NiCo2O4 at 100 mA cm\(^{-2}\) at 50 °C using 1.8 M KOH and quaternized bisphenol a polysulfone ionomer (IEC 1.2 mmol g\(^{-1}\) and conductivity of 24.5 S cm\(^{-1}\)) [18].

Low carbonate concentrations (1% K2CO3) in DI-water was used to stabilise AEM. The reported cell voltages were 1.79 V and 1.7 V at 100 mA cm\(^{-2}\) with 2.7 and 7.4 mg cm\(^{-2}\) loading of CuCoOx at 43 °C, respectively [19].

The current status of alkaline anion exchange membrane electrolyser has produced reasonable performance employing non-precious metal catalyst when using high alkaline concentrations (e.g. >1.0 M) KOH solution but poorer performance with demineralised water in the range of 1.7–1.9 V at 100 mA cm\(^{-2}\) [9–19]. Operating AEM with alkaline concentrations above 1.0 M however will result in rapid degradation of the head groups and quick performance loss, on the other hand operation with DI-water and low alkaline concentration will result in much prolonged membrane life over 6 month [20,21] but with relatively poor performance (in comparison with PEMFC).

PEM water electrolyser that use Nafion usually requires a cell voltage of 1.45 V to produce current density of 100 mA cm\(^{-2}\) with noble metal catalyst [14] which is 150 mV better than AEM with noble metal catalyst and 250–350 mV better than AEM with non-noble metal catalyst at low alkaline concentrations. Considering Tafel slope of 60 mV dec\(^{-1}\) an increase in four orders of magnitude is therefore required in activity to achieve similar performance to PEMF or two orders of magnitude in the case of Tafel slope of 120 mV dec\(^{-1}\). While increasing the non-noble catalyst loading is one strategy to enhance AEM electrolyser performance as reported with loading up to 40 mg cm\(^{-2}\) used in the literature [10] this will only result in an increase by maximum an order of magnitude in activity and require suitable soluble anion exchange ionomer materials with high conductivity (>80 mS cm\(^{-1}\)) comparable to Nafion that can provide good ionic conduction in the catalyst layer. Another strategy can be the use of electro-catalysts which are less pH sensitive, in other words has reaction order close to zero with respect to OH-. Currently most of the non-noble metal catalyst rely on doped Co3O4 spinels with Co3O4 has reportedly a reaction order of 1 with respect to OH- concentration [22]. This means when reducing the alkaline concentration from 1.0 M to 0.01 M, two orders of magnitude decrease in activity will occur. This combined with the high Tafel slope of hydrogen evolution reaction (HER) in alkaline media of ca. 120 mV dec\(^{-1}\) [23–26] explain why AEM employing deionised water is still at least 150 mV lacking behind PEMF using similar loading of precious metal catalyst as reported earlier.

This paper will tackle the three strategies mentioned above, investigate the effect of soluble ionomer with higher conductivity, alkaline concentration and catalyst loading on AEM water electrolyser with view to close the gap between AEM and PEM electrolyser's performances.

2. Experimental

2.1. Catalyst synthesis

Nickel cobalt spinel, NiCo2O4, was prepared by a thermal decomposition following similar procedures we have previously reported for Li and Cu doped Co3O4 [13,15]. A procedure reported in Ref. [27] was followed where Ni (NO3)2:6H2O (14.54 g) and Co (NO3)2:6H2O (29.1 g) were dissolved in methanol (100 mL) and heated at 338 K to evaporate solvent. The dried powder sample was calcined at 648 K for 20 h and ball milled for 12 h.

2.2. Ionomer synthesis

250 mL of chloroform was added to 4 g of polystyrene-b-poly (ethylene/butylene)-b-polystyrene SEBS polymer 60/swt styrene (Kuraray, Japan) in nitrogen purged round flask. The flask was attached to a condenser, a thermocouple and a glass tube for the nitrogen flow. The mixture is stirred. Once the polymer is dissolved, 5.4 g of trioxane was added and the flask was then immersed in ice bath until the temperature of the mixture decreased to 1 °C. 22.8 mL of chloromethylsilane and then 3 mL of
tin chloride was injected with syringe. The mixture was kept stirring at 2–3 °C for 30 min, and then at room temperature for 17.5 h. To stop the reaction at the end of the stirring time, the mixture was poured in a beaker filled with 300 mL of methanol/water (50% each). The mixture was then poured in a separator funnel to separate the two obtained phases, at the bottom the chloroform with the polymer dissolved, at the top the methanol and water and un-reacted reagents. The process of “washing” the chloroform/polymer solution with methanol/water was repeated for a second time to ensure removal of reagents. The chloromethylated SEBS polymer was then obtained by evaporating the chloroform. The chloromethylated SEBS polymer was then immersed in 45%wt trimethylamine (TMA) solution for amination of the chloromethyl group. The schematic for ionomer synthesis is shown in Fig. 1.

2.3. Membrane synthesis

The radiation grafted Anion Exchange Membrane (AEM) was synthesised as previously reported using low-density polyethylene (LDPE) with vinylbenzyl chloride (VBC) as the graft monomer [28,29]. The LDPE-g-VBC copolymer was prepared by immersing the LDPE films (75 μm thick) in nitrogen purged 31/26/45 by volume VBC/toluene/methanol solution placed in a screw-cap vial. Samples were sent to Synergy Health plc (Wiltshire, UK) for mutual gamma radiation grafting. The irradiation was carried out under a dose rate of 2 kGy/h and total radiation dose of 20 kGy. The grafted membranes obtained were washed thoroughly with acetone to completely remove VBC homopolymers. To produce the anion exchange functionality, Benzyltrimethylammonium groups was obtained by immersing the membrane in trimethylamine (TMA) 45% wt solution in water for 24 h. The counter ion was subsequently exchanged from Cl− to OH− by treating the membrane with fresh 1.0 M KOH solution every 20 min, three times (total OH− exchange time of 1 h) to completely exchange the chloride ions with hydroxide ions. The membrane was then washed with copious amount of deionised water to remove residual hydroxide ions. Removal of excess OH− ions was confirmed by using pH paper. Degree of grafting based on initial weight (DOG) is 65.6% and IEC is 2.3 mmol g−1 with final hydrated membrane thickness of 120 μm and ionic conductivity of 0.09 S cm−1 at 50 °C and 100% RH [20,21].

2.4. XRD diffraction

The crystal structure of the samples were analysed using powder X-ray diffraction (XRD, Bruker, D8 ADVANCE) with Kx radiation (λ = 1.5418 Å). The average crystallite size can be calculated using the Scherer equation as below

$$D = \frac{K\lambda}{\beta\cos(\theta)}$$

where D is the mean size of the crystalline domains, K is called shape factor (usually 0.9), λ is the wavelength of X-ray, β is the line broadening at full width at half maximum intensity, and θ is the Bragg angle.

2.5. Electrochemical measurements

For the oxygen evolution reaction at the anode, titanium fibre felt GDL with thickness of 300 μm (Bekaert S.A. Fibre Technologies, Netherlands) with 78% porosity using 20 μm titanium fibres was used. The titanium mesh was cut into an area of 1.2 cm2. The anode electrode was prepared by either coating the catalyst ink directly on the membrane (CCM) method or by spraying the anode catalyst directly on the Ti GDL (spray) method with ionomer content of 10% wt (40% vol), 2, 10, 20 & 30 mg cm−2 NiCo2O4 loading were studied and compared with 2 mg cm−2 of commercial catalysts namely: IrO2 and Co3O4 (Johnson Matthey) and CuO-Co2O3 (Acta Spa 3030).

As for the hydrogen evolution reaction electrode, non-wet proofed carbon GDL with MPL (Freudenberg Germany) is used at the cathode. The carbon mesh is cut into 13 mm diameter circle. For
experiment to test the performance of different OER catalyst, 0.4 mg cm$^{-2}$ 20% Pt on carbon was selected as the standard HER catalyst. The catalyst ink, consists of 20% Pt on C, 28 wt% ionomer and THF, was prepared and sprayed directly on the carbon GDL/MPL (Cathode). Autolab Potentiostats/Galvanostats (Model PGSTAT302 N) instrument was used to conduct the electrochemical analysis. The experiment was run at different concentration of alkaline solution from 0.01 M, 0.1 M, to 1.0 M NaOH and a temperature range from 20 °C to 80 °C. A schematic of the electrochemical setup is shown in supplementary information (Fig. S2).

3. Characterisation of SEBS ionomer

3.1. Measurement of the ion-exchange capacity (IEC)

The OH$^-$ exchanged membranes were immersed in a known volume of 1.0 M NaCl solution and were left to stand overnight. The liberated hydroxide ions were titrated with 0.10 M H$_2$SO$_4$ solution using a Titrette GMBH bottle-top digital burette and the endpoint was determined visually using methyl red indicator. After titration, the membranes were washed with deionised water to completely remove the salt and dried using a MTI Model DZF-6020-FP vacuum oven. Measurements of the weight were performed until no change in the dry weight was achieved. The IECs were computed using the amount of OH$^-$ ions neutralised, expressed in mmol, divided by the dry weight of the membranes, in grams.

3.2. Measurement of the ionic conductivity

The through-plane ionic conductivity of each of the functionalised membranes was measured following the same procedure previously reported [21] using the following formula:

$$\sigma = \frac{4L}{R(\pi d^2)}$$

where $\sigma$ is the hydroxide ion conductivity, L is the membrane thickness, R is the resistance derived from the impedance value at zero-phase angle and d is the diameter of the membrane test area.

3.3. Solution Nuclear magnetic resonance spectroscopy

$^1$H NMR spectra of the initial and chloromethylated SEBS polymer solutions in Tetrahydrofuran-d$_8$ were obtained using a Bruker 500 Avance III HD NMR spectrometer operating at 500 MHz for $^1$H with TMS as the chemical shift reference. All NMR spectra were processed using MestReNova 11.0 (Mestrelab Research S.L.) software. FTIR spectra were recorded using a Varian 800 FT-IR spectrometer system.

4. Results and discussion

4.1. SEBS based ionomer

Fig. 2 (a) shows the obtained $^1$H NMR spectra for both pristine and chloromethylated SEBS. The peak at 0 ppm is that of the reference material (TMS) used, while the peaks at 1.63 and 3.48 ppm are from THF (solvent). The H methanediyl group ($-$CH$_2$-) can be found at 1.62 ppm and that of the methanetriyl group (CH) at 2.37 ppm (styrene). The H attached to aliphatic

Fig. 2. (a) $^1$H- NMR spectra of pristine and chloromethylated SEBS, (b) Ionic conductivity of SEBS with respect to temperature.
with the structure reported in literature for NiCo$_2$O$_4$ [33]. No other peaks from impurity were observed. The average crystallite size of the catalyst was calculated by using the Scherer equation (4) and annealed Si was taken as the standard in order to eliminate instrumental error. The average crystallite size was ~110 nm. The relatively large average particle size is expected for the synthesis method used due to the long 20 h calcination period required at 648 K.

4.3. Effect of the catalyst loading

The initial testing of the NiCo$_2$O$_4$ was to find out the effect of the catalyst loading on the cell over potential in order to obtain the best performance and thus different loading in the range of 2 mg cm$^{-2}$ to 30 mg cm$^{-2}$ were chosen. The lowest loading of 2 mg cm$^{-2}$ was chosen for easier comparison to the literature data as 2 mg cm$^{-2}$ was the most widely used loading composition. The higher loading was chosen in line with some reports in the literature [11] and was still economical since the cost of iridium is more than 200 times to that of nickel and cobalt. Fig. 4 shows the polarisation curves obtained for NiCo$_2$O$_4$ catalyst with different catalyst loading in 1.0 M NaOH solution at 20 °C. It can be clearly seen that with the increase of loading from 2 mg cm$^{-2}$ to 10 mg cm$^{-2}$, the voltage decreased from 1.78 to 1.72 V at 100 mA cm$^{-2}$. This improvement in the electrolyser performance could be seen over the entire potential window studied. However, as the loading was further increased to 20 mg cm$^{-2}$ and 30 mg cm$^{-2}$, there was increase in the cell voltage to 1.74 V and 1.82 V at 100 mA cm$^{-2}$, respectively. This increase in the cell voltage with the loading can be related to the thickness of the catalyst layer that can induce higher resistance resulting in decreased conductivity and thus decreased performance. There is an optimum for the catalyst layer thickness balancing the requirement of reducing ohmic loss (due to ionic transport in the catalyst layer) with the requirement to reduce mass transport losses due to water diffusion and gases evolution. The former favouring activity close to membrane surface and the latter favouring activity away from the membrane and closer to the flow channel. As we move away from the optimum thickness, the slope of the polarisation curve will become worse as mass transport and ohmic losses will increase. The catalyst layer thickness increased from ~29 µm to ~59 µm—~87 µm for 10 mg cm$^{-2}$, 20 mg cm$^{-2}$ and 30 mg cm$^{-2}$ loadings, respectively.

4.2. NiCo$_2$O$_4$ characterisation

Fig. 3 shows the XRD pattern of the NiCo$_2$O$_4$ catalyst synthesised by thermal decomposition method. All the diffraction peaks in the full spectra agreed well with the spinel NiCo$_2$O$_4$ phase (JCPDF No. 20-0781) with a face-centred cubic structure. This is in agreement with the structure reported in literature for NiCo$_2$O$_4$ [33].
4.4. Effect of alkaline concentration

Fig. 5 shows the polarisation curves of different OER catalyst at 20 °C in different concentrations of NaOH. From Fig. 5 (a), it can be clearly seen that at room temperature, the performance in very dilute solutions close to DI-water conditions (0.01 M NaOH) was generally poor. Fig. 5(b) compares the performance of 2 and 10 mg cm⁻² NiCo₂O₄ loadings with IrO₂ catalyst with a loading of 2 mg cm⁻². It can be seen that performance at least comparable to, or superior to IrO₂ can be obtained from NiCo₂O₄ when using higher loadings of 10 mg cm⁻² (5 times the typically used IrO₂ loading) over the entire alkaline concentration studied (0.01–1.0 M). For example when using 1.0 M alkaline concentration at 20 °C in the electrolyte, cell voltage was 1.72 V at 100 mA cm⁻² for both 10 mg cm⁻² NiCo₂O₄ and 2 mg cm⁻² IrO₂, respectively.

Using the same amount of catalyst loading of 2 mg cm⁻², IrO₂ showed the best cell performance among the studied catalysts followed by NiCo₂O₄, Co₃O₄ (commercial from Johnson Matthey) and Cu₀-γCo₂-γO₄ (commercial from Acta). The cell voltage using catalyst loading of 2 mg cm⁻² at 100 mA cm⁻² in (0.01 M) was 1.9 V (IrO₂), 2.02 V (NiCo₂O₄), 2.19 V (Co₃O₄), whereas Cu₀-γCo₂-γO₄ did not even reach the 100 mA cm⁻² current density over the tested range of voltage up to 2.2 V.

The effect of alkaline concentration on catalyst activity was tested at three conditions namely 0.01, 0.1 and 1.0 M NaOH. Alkaline concentration has two impacts on the electrolyser performance, firstly on the ionic conductivity of the ionomer and membrane and secondly on the electrocatalyst activity (exchange current density increases for reaction order >0 with respect to OH). Furthermore, assuming OER is the major contributor of the activation losses at 100 mA cm⁻², a potential shift of ca. 60 mV per pH unit at room temperature of OER onset potential is expected from Nernst equation. At 0.01 M concentration the ionic conductivity of the solution is too low in comparison to that of the membrane/
activity increase (assuming reaction order of 1 and Tafel slope of 60 mV dec\(^{-1}\) as discussed above.) The low equivalent pH of AEM running on DI-water of 11.5 in comparison to pH values used in alkaline electrolysers in the range of 14.5, will result in anode potential shift of 360 mV, 180 mV (from Nernst potential shift) and another 180 mV (assuming reaction order of 1 (OH) and Tafel slope of 60 mV dec\(^{-1}\)) and explains why AEM electrolysers have poor performance when using DI-water and inferior performance to traditional liquid electrolyte alkaline electrolysers. However, if the right selection of catalyst is made where the catalyst OER activity is almost pH independent for example cobalt phosphides [36] this challenge can be overcome.

A challenge remains to find suitable catalyst for HER with improved Tafel slope and exchange current density with respect to platinum. While HER activity on platinum in alkaline solution is two order of magnitude lower than acid (Nafion) [24] the increase in Tafel slope for HER on platinum from 30 to 120 mV per decade is especially challenging [24]. This means that when we are moving from acid to alkaline solutions, to increase the current density by two orders of magnitudes (to reach similar activity in acid system) this will result in an additional cathode overpotential of 240 mV (Tafel slope - 120 mV dec\(^{-1}\)).

4.5. Stability of the catalyst

Fig. 6 shows the short term performance of the different catalyst studied in different concentration of NaOH solution at 20 °C by potentiostatic hold at 2 V for 1 h. It can be seen that the best performing catalyst i.e. IrO\(_2\) degrades faster in all the concentrations and reaches a current density similar or even lower than NiCo\(_2\)O\(_4\) after 1 h. The degradation rate of all the spinel structure i.e. NiCo\(_2\)O\(_4\), Co\(_3\)O\(_4\), Cu\(_0\)γCo\(_2\)γO\(_4\) was either negligible or very low suggesting that they were very stable under the tested conditions. The current density at 2 V increased initially and stabilised afterwards for NiCo\(_2\)O\(_4\) at lower concentration of 0.01 M (0.082 e 0.093 A cm\(^{-2}\)) and 0.1 M (0.21 – 0.22 A cm\(^{-2}\)), this was due to the activation of the catalyst over time to form the hydrated CoOOH [13,14]. Whereas, the current density for IrO\(_2\) dropped significantly from 0.133 to 0.091 A cm\(^{-2}\) and 0.258 to 0.224 A cm\(^{-2}\) in 0.01 M and 0.1 M NaOH, respectively. The other commercial catalyst of Co\(_3\)O\(_4\) and Cu\(_0\)γCo\(_2\)γO\(_4\) showed very negligible degradation over time with different concentrations of NaOH. However, their current densities were lower than that of NiCo\(_2\)O\(_4\) at all studied conditions.

To test the long-term durability of the NiCo\(_2\)O\(_4\) catalyst, the
catalyst was potentiostatically held at 2 V for 12 h in 1.0 M NaOH solution at two different temperatures of 40 °C and 80 °C and polarisation curves were recorded before and after the test as shown in Fig. 7. At 2 V the current density decreased from initially 0.743 A cm⁻² to 0.415 A cm⁻² at 40 °C after 12 h, whereas for 80 °C it decreased from initially 1.16 A cm⁻² to 0.43 A cm⁻² after 12 h operation. Another observation was that the area specific resistance did not change for the catalyst tested at both the temperature i.e. 40 °C (0.15 Ω cm²) and 80 °C (0.07 Ω cm²), suggesting that the membrane was intact during the course of test. Given the high ionic conductivity of the 1.0 M OH⁻ used in the test changes in ionomer conductivity, if any, will have negligible effect on the performance too.

Similar degradation in performance over 12 h was observed for the commercial catalyst Acta 3030 (Fig. 51). Acta 3030 has shown good stability over 1000 h test and negligible loss of performance over 12 h period [19]. This suggests that the most probable reason for performance loss detected within this relatively short time span of 12 h is the catalyst detachment from the electrode/membrane interface. Rapid gas evolution results in catalyst detachment where

Fig. 6. Chronoamperometry of the different catalysts at 2 V in (a) 0.01 M, (b) 0.1 M and (c) 1.0 M NaOH solution at 20 °C.

Fig. 7. Polarisation curves of NiCo₂O₄ catalyst (loading - 10 mg cm⁻²) after holding at 2 V for 12 h in 1.0 M NaOH solution at (a) 40 °C and (b) 80 °C.
catalyst agglomerates could be seen in the circulating electrolyte as time evolved. The rate of degradation was faster at higher temperatures due to the higher current densities obtained (faster rate of gas bubbles formation) as well as the softening and excess swelling of the ionomer/membrane at elevated temperatures. As the catalyst was sprayed directly on the membrane in dry state and when the membrane was submerged in aqueous alkaline solutions to exchange the Cl\(^-\) ions to OH\(^-\), this will result in swelling of almost 50–70% [20]. This is significant swelling, which is an undesired property associated with the high conductivity and IEC required (almost double that's of 0.91 mmol g\(^{-1}\) for Nafion). This is needed to achieve similar ionic conductivity since the diffusion coefficient of hydroxide ions in dilute solutions is almost half that of proton. Another way of making electrodes needs to be explored in order to minimise this problem as well as new electrodes architecture and binders. One approach is to spray (deposit) the catalyst on the Titanium GDL followed by sandwiching the membrane electrodes assembly on already swollen and hydrated membrane via cold pressing to minimise excessive swelling of the catalyst layer, minimise mechanical stress and improve the interface between the catalyst and the AEM membrane as will be discussed in the next section.

4.6. CCM vs GDL spraying

Fig. 8 shows the polarisation curves of the NiCo\(_2\)O\(_4\) catalyst prepared using spraying on the GDL and CCM method in 0.1 M NaOH solution at different temperatures. An improvement in performance i.e. 40 mV at 60 °C at a current density of 100 mA cm\(^{-2}\) can be seen for the samples prepared by spraying directly on the GDL. The main improvement can be seen in the slope of the polarisation curve which suggests reduced ohmic losses through improved interfacial contact (ASR decreased from 0.18 to 0.15 ohm cm\(^2\) at 40 °C using 0.1 M OH). This improvement was similar to the improvement that can be seen when increasing the concentration of NaOH by an order of magnitude from 0.1 to 1.0 M. Thus, the new method of spraying directly on the GDL can help to achieve the same performance in lower concentration of NaOH solution. The voltage required to obtain a current density of 100 mA cm\(^{-2}\) at 60 °C in 0.1 M NaOH using the two methods was 1.65 V (GDL-spraying) and 1.69 V (CCM) which is better than the values reported for different non-noble catalyst in literature in the range of 1.7–1.9 V [11–18]. This performance is very promising considering it is carried out at very low alkaline concentration of 0.1 M. To close the remaining gap of 200 mV with PEM (at 100 mA cm\(^{-2}\)), future improvements can focus on new synthesis methods to produce OER catalyst with smaller particle size (from 100 to 10 nm) improving the surface area and consequently the activity by order of magnitude which translates to 60 mV only (60 mV dec\(^{-1}\) Tafel slope) or pH independent OER catalyst (possible saving of up to 180 mV provided the activity and Tafel slope remain comparable to NiCo\(_2\)O\(_4\) at 0.1 M). As suggested earlier there is much more room for improvements from increasing the activity of HER catalyst through new materials, where a saving of 120 mV is achieved for every order of magnitude increase in activity, (Tafel slope 120 mV dec\(^{-1}\)). An additional saving of 120 mV and more can be achieved by producing new HER catalyst materials with Tafel slope of 60 mV dec\(^{-1}\) and below.

5. Conclusion

A polystyrene based soluble anion exchange ionomer with high OH\(^-\) ion conductivity of 0.14 S cm\(^{-1}\) comparable to that of H\(^+\) conductivity of Nafion was synthesised by chloromethylation of polystyrene-b-poly (ethylene/butylene)-b-polystyrene and used as ionomer with NiCo\(_2\)O\(_4\) electro-catalyst for water electrolysis. When this ionomer was coupled with the NiCo\(_2\)O\(_4\), it was found that there was a limit to the amount of catalyst which can be used to improve the performance with an optimum loading of 10 mg cm\(^{-2}\). The catalyst was compared to commercial catalysts like IrO\(_2\), CuO\(_2\) and CuO\(_2\) :O\(_4\) and it showed an improved performance at different concentrations of NaOH at an optimum loading of 10 mg cm\(^{-2}\) and lowest cell voltage of 1.72 V for NiCo\(_2\)O\(_4\) was obtained at 1.0 M NaOH solution which was same as that for IrO\(_2\) at 100 mA cm\(^{-2}\). The degradation studies at 2 V using loadings of 2 mg cm\(^{-2}\) showed that NiCo\(_2\)O\(_4\) was very stable over the 1 h test period, while IrO\(_2\), despite having higher activity at the beginning of the test, has reached the same current density after 1 h to that of NiCo\(_2\)O\(_4\) using the same loading. The long-term durability of the catalyst was influenced by catalyst detachment and wash off from the electrode due to swelling of the membrane. A new method of spraying directly on the GDL resulted in an improved performance by bringing the voltage down to 1.65 V to reach a current density of 100 mA cm\(^{-2}\) at 60 °C. Our best AEM performance running on low alkaline or deionised water still lacks behind PEM electrolyser by at least 200 mV. The low equivalent pH of 11.5 of AEM in comparison to traditional liquid alkaline electrolyser create an overvoltage of 180 mV in comparison to liquid alkaline electrolyser. In addition, the two order of magnitude slower HER in alkaline environment in comparison to PEM with Tafel slope of 120 in comparison to 30 mV dec\(^{-1}\) will result in additional 240 mV loss.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2017.07.026.
Reference