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Performance of polyethylene based radiation grafted anion exchange membrane with polystyrene-b-poly (ethylene/butylene)-b-polystyrene based ionomer using $NiCo_2O_4$ catalyst for water electrolysis

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HIGHLIGHTS

- Soluble AEM based on SEBS with OH^- conductivity of 0.14 S cm^{-1}, IEC 1.9 mmol g^{-1}.
- At 10 mg cm^{-2} $NiCo_2O_4$ has superior OER activity to IrO_2 2 mg cm^{-2} at 1/200 of cost.
- Electrolyser performance using $NiCo_2O_4$, 1.65 V at 100 mA cm^{-2} at 60 °C & 0.1 M OH.
- Challenges are low pH equivalent of AEM of 11.5 & 100 times slower HER than acid.

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ABSTRACT

A soluble anion exchange ionomer with high OH^- ion conductivity comparable to that of H^+ conductivity of Nafion is synthesised by chloromethylation of polystyrene-b-poly (ethylene/butylene)-b-polystyrene (SEBS) and used with $NiCo_2O_4$ 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^{-2} at 50 °C. The cell voltage at 20 °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} $NiCo_2O_4$. At 10 mg cm^{-2} $NiCo_2O_4$ electrolyser cell 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 °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 lower HER activity with respect to acid medium combined with the high Tafel slope of 120 mV dec^{-1}.

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 electrolysers 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) electrolysers 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 electrolysers use lower

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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 electrolysers [6]. However PEM water electrolysis systems offer advantages over alkaline technologies such as ability to operate at differential pressure (H_2 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 electrolysers 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 electrolysers the amount of research conducted on alkaline anion exchange membrane polymer electrolysers 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)).

$$\text{Cathode}:\ 2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^- \quad (E_0 = -0.83\ \text{V vs. SHE}) \tag{1}$$

$$\text{Anode}:\ 2\,OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \quad (E_0 = 0.403\ \text{V vs. SHE}) \tag{2}$$

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 Co_3O_4 based OER catalyst [12–15] in water electrolyser based on a polymethacrylate quaternary ammonium hydroxide (QPDTB-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} $Cu_{0.7}Co_{2.3}O_4$ at 25 °C [13], 1.81 V with 2.5 mg cm^{-2} $Li_{0.21}Co_{2.79}O_4$ at 45 °C [14] and 1.89 V using 3 mg cm^{-2} $Cu_{0.6}Mn_{0.3}Co_{2.1}O_4$ 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} $Ce_{0.2}MnFe_{1.8}O_4$.

Very recent reports on the use of $NiCo_2O_4$ in AEM reported a cell voltage of 1.8 V at 100 mA cm^{-2} using 10 mg cm^{-2} $NiCo_2O_4$ 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} $NiCo_2O_4$ 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 mS cm^{-1}) [18].

Low carbonate concentrations (1% K_2CO_3) 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 $CuCoO_x$ at 43 °C, respectively [19].

The current status of alkaline anion exchange membrane electrolysers 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 PEMFC 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 Co_3O_4 spinels with Co_3O_4 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 PEMFC 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 electrolysers' performances.

2. Experimental

2.1. Catalyst synthesis

Nickel cobalt spinel, $NiCo_2O_4$, was prepared by a thermal decomposition following similar procedures we have previously reported for Li and Cu doped Co_3O_4 [13,15]. A procedure reported in Ref. [27] was followed where Ni $(NO_3)_2 \cdot 6H_2O$ (14.54 g) and Co $(NO_3)_2 \cdot 6H_2O$ (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%wt 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 was 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