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## **Short Communication**

# The effect of membrane on an alkaline water electrolyzer



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#### ABSTRACT

Water electrolyzers are being developed as a way of storing renewable energy, as a way to produce hydrogen for fuel cell automobiles, and as a route to renewable fuels and chemicals. In this paper the performance of an alkaline water electrolyzers at 60 °C with 1 M KOH and iron/nickel/cobalt catalysts with several different membranes: Sustainion<sup>®</sup> 37–50, Fumasep FAS-50, Fumasep FAPQ, Neosepta ACM, AMI 7001, Nafion<sup>®</sup> 115, and Celazole<sup>®</sup> PBI. Measured area specific resistances (ASR) at 60 °C with 1 M KOH varied from 0.045  $\Omega$ -cm<sup>2</sup> with Sustainion<sup>®</sup> 37–60 to over 50  $\Omega$ -cm<sup>2</sup> with Neosepta ACM. The current at a cell potential of 1.9 V varied from 1 A/cm<sup>2</sup> with Sustainion<sup>®</sup> 37, 0.5 A/cm<sup>2</sup> with Fumasep FAPQ and less than 0.1 A/cm<sup>2</sup> for Neosepta ACM, AMI 7001, Nafion 115 and Celazole<sup>®</sup> PBI. Constant current runs at 1 A/cm<sup>2</sup> were done with the Sustainion<sup>®</sup> 37 membranes and the Fumasep FAS-50. The cell with the Sustainion<sup>®</sup> 37 membrane was very stable. The voltage to maintain 1 A/cm<sup>2</sup> in the cell with the FAS-50 membrane showed over 200  $\mu$ V/h increase and failed after 200 h.

**One Sentence Summary:** The paper shows that one can double the current output of an alkaline water electrolyzer by using Sustainion<sup>®</sup> 37 membranes.

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#### Introduction

Commercial alkaline water electrolyzers typically use 2-3 mm thick porous layers to minimize gas crossover. Ion transport through the layer is limited, which limits device performance [1]. Many previous investigators have tried to develop "zero gap" electrolyzers [1–6], where the 2–3 mm thick porous layer is replaced by a 50–100  $\mu$ m thick anion exchange membrane.

At this point we do not know which membrane is best. In this paper, we compare the performance of various membranes to determine how the membrane affects performance. We decided to focus on commercially available membranes: Sustainion<sup>®</sup> 37–50, Fumasep FAS-50, Fumasep FAPQ, Neosepta ACM, AMI 7001, Nafion and Celazole PBI (polymenzimidazole) and compare the performance.

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#### Methods

#### Membranes

Sustainion<sup>®</sup> 37–50 came from Dioxide Materials, Fumasep FAS-50 and Fumasep FAPQ-375 were purchased from Fuel Cell store, Neosepta ACM was purchased from Astom, AMI 7001 was purchased from Membranes International, Nafion 115 was purchased from Ion Power, and Celazole PBI was purchased from PBI Performance Products Incorporated.

#### Conductivity measurements

The through-plane conductivity of each membrane was determined in 1 M KOH, by measuring the electrochemical impedance spectrum (EIS) in a 5 cm<sup>2</sup> Fuel Cell technologies (Albuquerque, NM) cell with a platinum cathode, an  $IrO_2$  anode and the membrane to be tested in between the cathode and the anode. Details are given in the supplemental material.

#### Cell testing

The membranes were tested in fuel cell technologies 5 cm<sup>2</sup> cell hardware with 2 mg/cm<sup>2</sup> NiFeCo nanoparticles (US Nano) cathode catalysts deposited onto a Sigracet 39BC GDL carbon paper with a Nafion binder and 2 mg/cm<sup>2</sup> of NiFe<sub>2</sub>O<sub>4</sub> particles (Sigma Aldrich) with a Nafion binder on a 316L sintered stainless steel fiber felt (Bekaert). The anode was 0.5 cm larger than the cathode to simplify alignment. Details are given in the supplemental material.

During the experiments, 1 M KOH was recirculated through the anode and cathode at a rate of 2 ml/min. The temperature of the cell was raised to 60 °C, the current was set at a fixed value, and the cell voltage was measured as a function of time. We use a closed loop system, where the anode and cathode output solutions are mixed in a sealed holding tank to minimize carbonate buildup in the system. Additional details are given in the supplemental materials.

#### Results

Fig. 1 compares the low imaginary Z ( $Z_{\rm im})$  portion of the impedance spectra of Sustainion  $^{\circledast}$  37–50, Fumasep FAS-50,

Fumasep FAPQ, AMI 7001, Nafion 115 and Celazole PBI. We also tried to measure the impedance of Neosepta ACM, but the membrane degraded so quickly in 1 M KOH that we were not able to get any reliable measurements. Notice that the impedance spectra are all similar, but there is a large variation in the intercept of the curves. The Sustainion<sup>®</sup> 37–50 membrane shows an intercept of 0.074  $\Omega$ . All of the other curves showed higher intercepts.

We have calculated the area specific resistance (ASR) for all of the membranes from:

#### $ASR = (intercept \Omega)^*5 \text{ cm}^2$

Table 1 shows the results. Notice that the ASR varies tremendously with the membrane composition.

We have also measured the temperature dependence of the conductivity of the Sustainion<sup>®</sup> 37–50 membrane as a function of temperature in several supporting electrolytes. The results are shown in Fig. 2. Notice that the conductivity in 1 M KOH varies from 80 at 30 °C to 140 mS/cm at 80 °C. It is lower in other supporting electrolytes, but still quite high.

#### Alkaline electrolyzer performance

Next we tested the performance of each of the membranes in an alkaline water electrolyzer, with NiFe<sub>2</sub>O<sub>4</sub> anode catalysts and NiFeCo cathode catalysts. In all cases the cell was run at 60 °C with 1 M KOH fed into both the anode and cathode.

Fig. 3 compares a linear sweep voltammogram taken with each membrane after 15–30 min on stream. At a cell potential of 1.9 V, the Sustainion<sup>®</sup> 37–50 membrane shows about 1 A/ cm<sup>2</sup>, the Fumatech FAS-50 shows about 0.5 A/cm<sup>2</sup>, the FAPQ shows 0.16 A/cm<sup>2</sup>, the AMI-7001 shows 0.11 A/cm<sup>2</sup>, the Nafion 115 shows 0.1 A/cm<sup>2</sup>, and the PBI shows 0.05 A/cm<sup>2</sup>. We could not detect any electrolyzer current with the Neosepta ACM.

Next, measurements were done by holding the cell current at 1 A/cm<sup>2</sup>, and measuring the voltage as a function of time. Fig. 4 shows the results. We were able to maintain 1 A/cm<sup>2</sup> only with the Sustainion<sup>®</sup> 37–50 membrane and the FAS-50 membrane. The voltage to maintain 1 A/cm<sup>2</sup> was stable with the Sustainion<sup>®</sup> membrane. The initial data showed an



Fig. 1 – The portion of the electrochemical impedance spectrum near  $Z_{im}$ =0 at 60 °C in 1 M KOH measured in a cell with a 5 cm<sup>2</sup> active area for the membranes considered here.

Table 1 $-$ The ASR measured for several membranes at 60 $^\circ$ C in 1 M KOH.							
Membrane	Sustainion <sup>®</sup> 37-50	FAS-50	Nafion 115	FAPQ	AMI-7001	PBI	ACM
Thickness ASR Ω-cm <sup>2</sup>	50 μm 0.045	50 μm 0.3783	125 μm 0.52	75 μm 0.83	450 μm 2.0	50 μm 8.3	110 μm >50



Fig. 2 – The conductivity of Sustainion<sup>®</sup> X-37 membranes measured by impedance spectroscopy as described in the supplemental material.



Fig. 3 – A comparison of the current produced in the cell as a function of voltage for each of the membranes considered here measured via linear sweep voltammography at 60 °C with 1 M KOH. In all cases the cell had NiFe<sub>2</sub>O<sub>4</sub> anode catalysts and NiFeCo cathode catalysts at loadings of 2 mg/cm<sup>2</sup>.

upward slope of 10  $\mu$ V/h, but the voltage increase completely recovered when we replaced the KOH solution at the 1670 h point. The average increase was only 5  $\mu$ V/h over a 1950 h run. By comparison the FAS-50 membrane showed an initial



Fig. 4 – The steady state voltage to maintain 1 A/cm<sup>2</sup> current with the Sustainion<sup>®</sup> 37–50 membrane and the FAS-50 membrane at 60 °C with 1 M KOH. In all cases the cell had NiFe<sub>2</sub>O<sub>4</sub> anode catalysts and NiFeCo cathode catalysts with catalyst loadings of 2 mg/cm<sup>2</sup>.

average increase of about 400  $\mu$ V/h, but leveled off to about 200  $\mu$ V/h after 180 h. We tested the cell with the FAS-50 membrane for leakage current at the 200 h point. The cell showed 0.2 A/cm<sup>2</sup> of leakage current at 1.23 V indicating that the membrane had failed, so we stopped the test.

We also tested the cell with the Sustainion<sup>®</sup> anion membrane for leakage current. We did not observe significant leakage current at any time during the run. More detailed measurements shown in the supplemental material show that the cell with Sustainion<sup>®</sup> 37–50 membrane showed less than 1  $\mu$ A/cm<sup>2</sup> leakage current at 60 °C.

We have now completed multiple 1000 h runs with the Sustainion<sup>®</sup> anion membranes. We found that as the carbon flow-fields aged after multiple runs and started to leak. When we replaced the carbon flow fields with nickel flow fields, everything was stable. One of the runs showed a decrease in the voltage to maintain 1 A/cm<sup>2</sup> of 20  $\mu$ V/h. Others showed increases of 0.8, 3, 5 and 10  $\mu$ V/h.

### Discussion

The results here demonstrate that the choice of membrane can make a tremendous difference to electrolyzer performance. The current at 1.9 V shown in Fig. 3 varies by more than an order of magnitude according to which membrane is used. The Sustainion<sup>®</sup> 37–50 and the FAS-50 both show industrially relevant currents at 1.9 V, while the other membranes show much lower currents.

Unfortunately, the voltage needed to maintain 1 A/cm<sup>2</sup> in the cell with FAS-50 increases by 200–400  $\mu$ V/h under the conditions tested. Further, the FAS-50 failed after 200 h. The Sustainion<sup>®</sup> membrane is stable.

The stability of the Sustainion<sup>®</sup> anion membrane was surprising. Hugar et al. [7] Coates et al. [8] found that methylsubstituted imidazoliums are not particular stable. Instead one needs to graft phenyl groups onto the imidazolium ring to produce an alkaline stable membrane. Here we find that the tetramethyl-imidazolium functionalized styrene membrane is stable. Evidently, the styrene is able to act like phenyls to protect the membrane from hydroxyl attack.

There is also a surprising lack of influence of  $CO_2$  poisoning. Parrondo et al. [9] saw rapid degradation of their electrolyzer due to traces of  $CO_2$  in their system. We observe a small effect in Fig. 4, where the cell potential dropped by 20 mV when we replaced the KOH solution at 1660 h. But this is a much smaller effect than seen previously [9].

Another surprise was that the Fumasep FAS-50 degraded so quickly, since it is supposed to be stable at pH 14. Evidently, the combination of temperature and pH lead to membrane degradation.

A third surprise was that the results do not simply scale as the membrane conductivity. Nafion 115 is reasonably conductive in 1 M KOH, but the cell with the Nafion 115 membrane produced very little current, presumably because Nafion 115 conducts cations (e.g.  $K^+$ ) but not anions.

Similarly, the FAPQ membrane shows lower current than one would expect from the conductivity, presumably because the FAPQ membrane is degrading at the conditions tested. (FAPQ is not recommended above a pH of 10).

Of the membranes tested, only the Sustainion<sup>®</sup> 37–50 membrane showed the needed combination of high currents, and stable performance.

It is useful to compare these results to those in the previous literature. Previous alkaline water electrolyzers with base metal catalysts ran at currents below 0.35 A/cm<sup>2</sup> at 2 V [1-4,10-13] and 60 °C. And even precious metal catalysts have had trouble obtaining our measured performance. Cho et al. [14] for example reported currents of about 0.3 A/cm<sup>2</sup> at 50 °C with platinum/IrO<sub>2</sub> catalysts. Ahn et al. reported a cell current of 0.25 A/cm<sup>2</sup> at 1.9 V using platinum doped nickel catalysts [5]. Leng et al. [6] were able to demonstrate alkaline cells running at 0.9 A/cm<sup>2</sup> at 2 V, but only when they used 2 mg/cm<sup>2</sup> of precious metals: iridium oxide anodes and platinum cathodes. Notice that our data in Figs. 3 and 4 show higher current than that of Leng et al., Cho et al. or Ahn et al., even though we are using base metal catalysts while Leng et al. Cho et al. and Ahn et al. used precious metals.

The stability of our cell is also much better than the cells reported previously. For example, Fig. 4 shows a voltage rise of only 5  $\mu$ V/h compared to about 150  $\mu$ V/h in Fig. 4 in Pavel et al. [15]. There is one paper that demonstrated similar currents to ours [16]. That work was done at 80 °C using very high catalyst loadings.

It is also useful to compare these results to those in PEM electrolyzers. Fig. 4 shows that we can obtain 1 A/cm<sup>2</sup> at 60  $^{\circ}$ C

and 1.9 V cell potential. In contrast, PEM electrolyzers with precious metal catalysts are often reported to show 1 A/cm<sup>2</sup> at about 1.7 V at 60 °C and 1.65 V at 80 °C [17]. Note, however, that in many papers the reported voltage is the initial voltage seen with the electrolyzer, and not the voltage after 1000 h or more of steady operation. Most PEM electrolyzers considered in the literature are not as stable as the one in Fig. 4. For example, Rakousky et al. [18] reported a degradation rate of about 200 µV/ hr for a typical cell (See Rakousky et al. Figs. 1 and 2). Rakousky et al. succeeded in lowering the degradation rate to 12  $\mu$ V/h by electrodepositing the platinum onto the titanium current collector instead of using a standard MEA. But that is not typical. If a cell starts at 1.7 V and degrades at 200  $\mu\text{V/hr}$  then the cell will reach 1.9 V at about 1000 h, and 2.1 V at 2000 h. In contrast, Fig. 4 shows a potential of about 1.9 V over the entire run. So over time, there is very little difference in the voltage needed to maintain 1 A/cm<sup>2</sup> using the design reported here, with base metal catalysts, and PEM electrolyzers with precious metal catalysts.

#### Conclusions

These results show that many of the commercially available membranes are not suitable for use in alkaline water electrolyzers. Either they have too high of an area specific resistance (ASR) or degrade too quickly under the conditions tested here. Sustainion<sup>®</sup> 37–50 membranes are an exception. An alkaline water electrolyzer running at 60 °C in 1 M KOH using nickel/ iron/cobalt catalysts and a Sustainion<sup>®</sup> 37–50 membrane operates at 1 A/cm<sup>2</sup> at about 1.9 V for 2000 h. While the initial voltage is higher than a typical PEM electrolyzer with platinum/ iridium catalysts, the stability is better, so after 1000 h or so, the performance is quite similar. This presents the possibility of one replacing rare materials such as platinum/iridium with iron and nickel, and still maintaining high currents.

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#### **Conflict of interest statement**

The authors have submitted several patents on the membranes and designs disclosed here including US 9,370,773, US 9,481,939, US 9,580,824, and applications 15/400,775, 15/ 406,909, 15/411,831. The authors have a financial interest in these patents. Dioxide Materials is offering all of our research materials (membranes, catalysts etc.) for sale to other research groups so that they can reproduce and build on the findings. The authors declare a financial interest in these sales.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.ijhydene.2017.10.050.

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