

Anion Exchange Membrane Electrolyzers Showing 1 A/cm² at Less Than 2 V

R. I. Masel, Z. Liu, and S. D. Sajjad

Dioxide Materials, 3998 FAU Blvd #300, Boca Raton FL, 33431, USA

This paper reports initial data on anion exchange membrane water electrolyzers using Sustainion™ membranes. These are styrene based membranes, that are functionalized with imidazoliums or pyridiniums as described in US patent 9,370,773. Initial work was done with platinum anode catalysts and iridium cathode catalysts. By optimizing the membrane composition and the choice of ionomer initial currents of 1 amp/cm² at 1.69 V and 6 A/cm² at 2.05 V are observed in a cell at 60 C with 1 M KOH. So far we have been able to maintain 1 A/cm² at about 1.7 V for 100 hours. The run is continuing. These results show the advantage of Sustainion™ membranes for water electrolyzers.

Introduction

Alkaline exchange membrane water electrolyzers have the potential to lower the capital cost of a water electrolysis system, but so far advances have been limited due to a lack of suitable membranes, catalysts and ionomers. In recent work we have developed new membranes (1) and ionomers (2) for alkaline exchange membrane CO₂ electrolyzers that show superior performance. For example, a CO₂ electrolysis run using a imidazolium functionalized styrene polymer (0) showed currents up to 600 mA/cm² at 3.25 V at room temperature, and have been run continuously for 6 months at room temperature with no loss of performance.

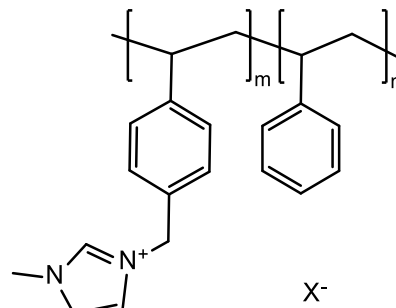


Figure 1. The structure of the membranes used for CO₂ electrolysis.

In this paper we attempted to determine whether similar membranes were stable in 1 M KOH at 60 °C, and whether the membranes were useful for water electrolysis.

Methods

Electrodes were prepared by creating nanoparticle inks and applying them to porous substrates. The cathode ink was made by adding 10 mg of Pt nanoparticles to 0.1 mL of distilled water and 0.2 mL isopropanol and possibly some ionomers. This mixture was sonicated for one minute, then spray painted onto a 2.5 cm x 2.5 cm square cut of carbon

gas diffusion layer (Sigracet 35 BC GDL, Ion Power). IrO₂ anodes were prepared in the same way, but with the addition of 100 μ L of 5% PTFE solution or an ionomer as binder. The anode catalyst was then sintered for one hour at 330 °C.

Electrochemical testing cells were assembled by sandwiching a membrane between a silver cathode and IrO₂ anode such that both electrode catalyst layers were facing the membrane. Each catalyst was surrounded by a layer of gasketing for protection and electrical insulation, and this assembly was then mounted into Fuel Cell Technologies 5 cm² fuel cell hardware with serpentine flow channels.

During the experiments reported here the cell was heated to 60 °C and 1 M KOH was recycled through the anode and cathode the current was fixed, and we measured the cell voltage as a function of time. All of the currents per unit area reported here are based on the area exposed to the KOH solution (5 cm²) and not the area (6.25 cm²) of the cathodes.

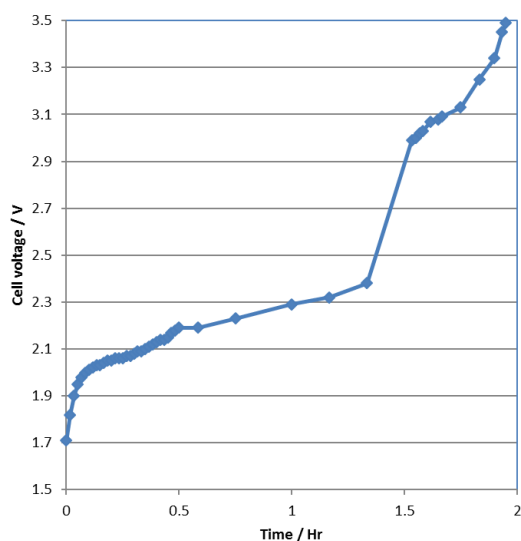


Figure 2. A plot of the voltage as a function of time in a constant current run at 800 mA/cm², using a membrane cast from the polymer in 0. 60 °C, 1 M KOH, IrO₂ anode, Pt cathode

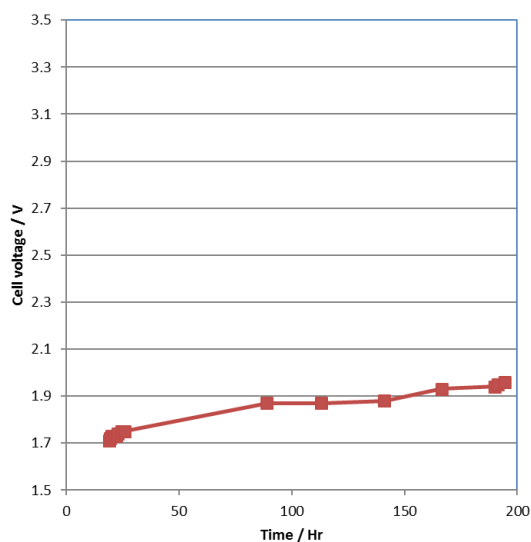


Figure 3. A plot of the voltage as a function of time in a constant current run at 800 mA/cm², using a membrane with a modified imidazolium. 60 °C, 1 M KOH, IrO₂ anode, Pt cathode

Results

Our first test was to determine whether the membrane cast from the polymer in 0 was useful in an anion exchange water electrolyzer. 0 shows a case where we cast the polymer 0 into a membrane, mounted the membrane into a cell, heated the cell to 60 °C, circulated 1 M KOH through the anode and cathode, fixed the current at 800 mA/cm² and measured the cell voltage as a function of time. The cell started out reasonably: initially we were able to obtain 800 mA/cm² at 1.7 volts, but the needed voltage rose very quickly. We stopped the run after 2 hours when the voltage had already passed 3.5 V. Analysis of the membrane at the end of the run indicated that the membrane conductivity had decreases from about 0.07 S/cm in the beginning of the run to virtually zero at the end of the run. This is consistent with the work of Shia et al. (3), Wang et al. (4) and Ye at al (5) who found that 1-methyl-imidazole is quickly degraded in 1 M KOH.

Next we replaced the methyl-imidazolium in the membrane with a substituted imidazolium to improve the membrane stability. The details will appear in a future patent. In this case we observed more stable performance. See Figure 3. The run went 200 hours with no issues, but failed when power went out.

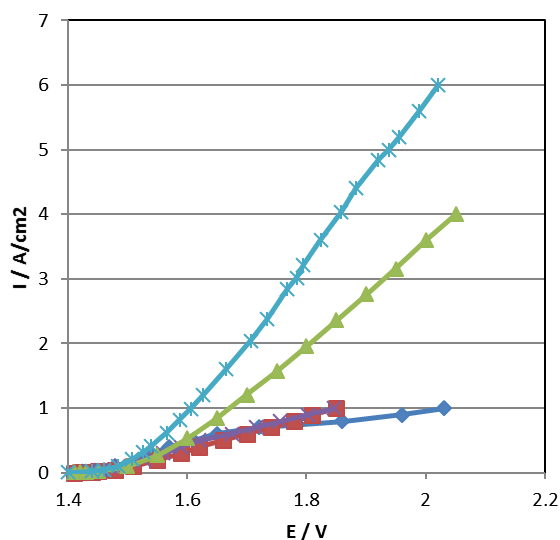


Figure 4. The effect of binder on the polarization curve of the electrolyzer. 60 °C, 1 M KOH, IrO₂ anode, Pt cathode. ◆ = Teflon binder. ■ = Sustainion™ XC cathode binder, ▲ = optimized anode binder, X = optimized anode and cathode binder.

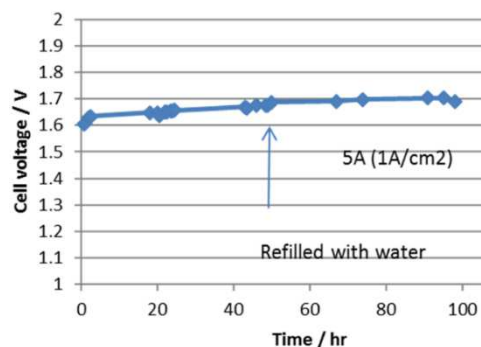


Figure 5. A 100 hour constant current run (1 A/cm²) with an electrolyzer with an optimal binder. 60 °C, 1 M KOH, IrO₂ anode, Pt cathode

Next we varied the binder to see how the binder affects the catalyst performance. 0 shows how the binder changed the performance of the electrolyzer. The blue line in the figure had Teflon in the anode and cathode. The other lines were generated by replacing the Teflon with various polymer electrolytes. Notice that we were able to achieve initial currents of 6 A/cm² at 2.05 V by using an electrolyte in the anode and cathode layer.

We also did a 100 hour constant current run at 1 A/cm² with an optimized anode and

cathode ionomer. The results are shown in Figure 5. Notice that we can obtain 1 A/cm² at 1.7 V.

Summary

In this paper we have shown that Sustainion™ membranes show promise for water electrolyzers. We observe currents of 1 A/cm² at 1.7 V and 6 A/cm² at 2.05 V.

Competing Financial Interests

The authors have U.S. Patents and patent applications which claim the membranes and electrolyzer designs discussed here. Dioxide Materials™ is planning to offer improved versions of these membranes for sale. The authors all have a financial stake in the outcome of this sale.

Acknowledgement

Parts of this work were supported by ARPA-E under contract DE-AR0000684 and by 3M. The opinions here are those of the authors and may not reflect the opinions of ARPA-E or 3M. Assistance from colleagues, collaborators and friends from 3M are gratefully acknowledged.

Literature cited

1. R. I. Masel, Q. Chen, Z. Liu and R. Kutz, Ion-Conducting Membranes, U.S. Patent 9,370,773 (2016)
2. R. I. Masel, Z. Liu, R. Kutz and S. D. Sajjad, Catalyst Layers and Electrolyzers, U. S. Patent Application 15/158,227 (2016)
3. Z. Si, L. Qiu, H. Dong, F. Gu, Y. Li and F. Yan, *ACS Appl. Mater. Interfaces*, **6**, 4346 (2014).
4. W. Wang, S. Wang, X. Xie, Y. Lv and V. K. Ramani, *J. Membr. Sci.*, **462**, 112 (2014).
5. Y.-S. Ye and Y. A. Elabd, *Macromolecules*, **44**, 8494 (2011).