Next-generation anion exchange membrane water electrolyzers operating for commercially relevant lifetimes

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Abstract

Alkaline anion exchange membrane (AEM) water electrolysis has gained increasing attention due to its potential to achieve low-cost, high performance hydrogen production. However, most existing membranes are not durable in industrial settings. Here, we demonstrate good performance relative to industrial parameters using Sustainion® anion exchange membranes. Long-duration tests showed stable performance of 1 A/cm^2 at 1.85 V with a degradation rate of less than 1 μV/hr over 10,000 hours. The projected lifetime is thus over 20 years. Daily on/off cycling performance over the course of 30 years was simulated experimentally through accelerated voltage shock tests, resulting in a performance loss of only 0.15 μV/cycle over 11,000 cycles. As shown through impact and crossover testing, an improvement in performance is achieved by the addition of zirconia to the polymer matrix and mechanically reinforcing the membrane.

Keywords: Water electrolysis; green hydrogen; renewable fuel; anion exchange membranes; electrochemistry

1. Introduction

Today, hydrogen for fuel cell vehicles and industrial applications is primarily produced through steam methane reforming (SMR), a process which emits 12 tons of carbon dioxide per ton of hydrogen. Only about 5% of production is from potentially clean energy sources supplied by water electrolysis.1 However, the number and scale of commercial water electrolyzers have been rapidly increasing in the last few years, as is evident from the 20 MW facilities operated by Air Liquide and 10 MW facility operated by Shell for example.2, 3 The majority of commercially deployed electrolyzers are run in alkaline conditions, but such alkaline electrolyzers have significant drawbacks. An alkaline electrolyzer includes an anode electrode and cathode electrode separated by a thin diaphragm, across which the hydroxide ions migrate. Major drawbacks of Alkaline electrolyzers include limited current density due to limited hydroxide mobility in the liquid phase, the inability to operate at high pressures, the highly corrosive electrolyte employed, and the inability of the thin diaphragm to fully separate hydrogen and oxygen produced at the cathode and

anode, respectively[4]Over the last few years, research has shown the emergence of anion exchange membranes (AEMs) that have the potential to improve alkaline electrolyzers on multiple dimensions such as allowing for a higher current density (i.e. increased H_2 production), increased differential pressure between the anode and cathode to enable electrochemical compression, thereby improving system efficiency and response time, and smaller footprint. This set of features has thus far only been available to proton exchange membrane (PEM) electrolyzers. While PEM electrolyzers offer the aforementioned advantages, there are several disadvantages of PEM electrolyzers. PEM electrolyzes operate in acidic conditions using noble metal catalysts (platinum and iridium), expensive membranes (typically Nafion), and titanium plates due to the corrosive conditions.[5] This results in a significantly higher cost for a PEM electrolyzer compared to an alkaline electrolyzer (roughly 3 times greater in cost for the same hydrogen production rating). Due to the alkaline condition, alkaline electrolyzers can be made of inherently lower-cost materials, such as stainless steel and nickel electrodes.

The main challenge for anion exchange membranes is their chemical and mechanical durability. Research reviews on AEMs have also pointed to other potential drawbacks such as a lack of long-term testing data, limited cycling and failure analysis. [6-8]Here, we experimentally test the long-term durability of an AEM and cycling response to address some of these concerns. A imidazolium functionalized styrene (Sustainion®) membrane is employed, considering it has previously been shown to outperform other available AEMs in terms of stability and current density[9]. Dioxide Materials has shown that their Sustainion® AEM is able to achieve 1 A/cm^2 at 1.85V, which is about three times the current density of modern alkaline systems at the same voltage. The Sustainion® membrane with an ion exchange capacity (IEC) of 1.1 showed significantly lower area specific resistance (ASR) and thus, higher conductivity achieved. Comprehensive information about Sustainion® membrane and comparison with other commercially available membranes can be found in studies published by Kaszur *et al.* [10] and Liu *et al.* [11] in this work we have used well-known experimental techniques to test the long-term durability of the Sustainion® membrane over 10,000 hours of operation, the cycling response over 11,000 cycles simulating daily on/off cycles over the course of 30 years, and we experimentally evaluate a method of reinforcing the membrane to improve mechanical stability without negatively affecting performance.

2. Materials and Methods

2.1. Electrochemical cells and membrane electrode assemblies

The membrane, electrodes, and electrochemical cells were purchased from Dioxide Materials. The anode is made of $NiFe2O_4$ catalyst (US Research Nanomaterials, US) loaded at 2 mg/cm^2 on a stainless-steel gas diffusion layer (Dioxide Materials, US). The cathode is 3 mg/cm^2 of modified Raney nickel (Sigma Aldrich) loaded onto a nickel fiber paper (Dioxide Materials). The Sustainion® X37-50 (Dioxide Materials, US) membrane is used, which is 50-80 µm thick. The X37-50 membrane was released from a PET liner by soaking in 1 M KOH for four hours and transferred to a fresh solution of 1M KOH to allow complete conversion from the chloride form to

the hydroxide form. The membrane was rinsed with deionized water before use. Each electrode is surrounded by a gasket layer for electrical insulation. This assembly is sandwiched into a Fuel Cell Technologies 5 cm^2 cell with serpentine flow channels. The endplates are made of aluminium and the graphite flow fields are replaced with nickel. Carbon paper coated with Pt and Pt/Ru were also purchased from Dioxide Materials and used as the electrodes for hydrogen cross over test.

2.2. Procedures for long-duration test

Long-duration testing was performed using the setup shown in Figure 1. A peristaltic pump meters a 1M KOH solution that is evenly split to both the anode and cathode from a common solution reservoir with two separate gas disengagers. The total pump flowrate is about 10 mL/min. The fluid stream exiting each electrode compartment are separately routed to the corresponding gas disengager, preventing mixture of the two product gases. The cells are heated to 60 °C for 30 minutes before a current is applied. The current was increased to 5 A (1 A/cm^2) and the cell voltage was measured as a function of time.

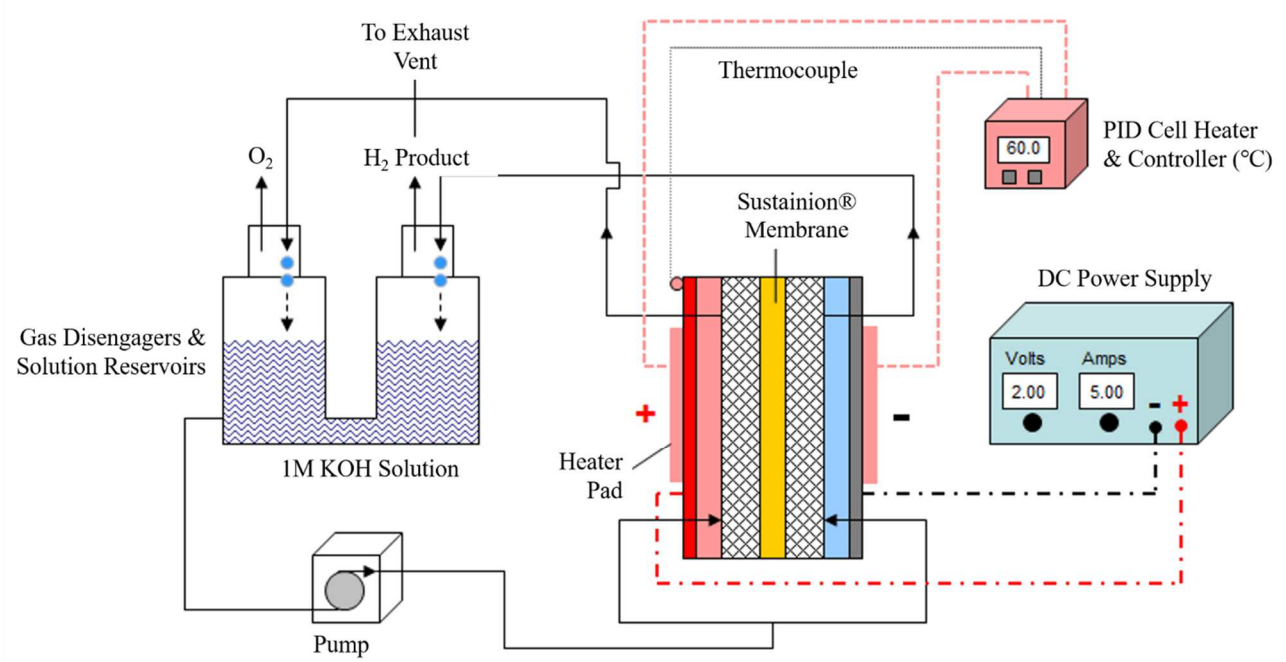

Figure 1. Lab setup of AEM water electrolysis cell testing station.

2.3. Testing protocol for cycling experiments

To determine the response behaviour of the membrane electrode assemblies in extreme real-world conditions of on/off duty cycling, an accelerated aging protocol was followed with MEA's containing Sustainion® and MEAs containing reinforced Sustainion. Cells were cycled between 100 mA to 12,000 mA (2.4 A/cm^2) for a total of 11,000 times. The Neware Technologies 4000 series battery testing system was employed to run the automated cycling experiments, with data

acquisition frequency of 10Hz and an accuracy of 0.1%. Due to the relatively small size of the electrolysis cell, the ramp up in current was nearly instantaneous (over 12,000 mA/second) , thus causing a stressful 'voltage shock' on each cycle. The cycle consisted of increasing the current to 12,000 mA, holding the current at 12,000 mA for 2 seconds, then returning the current to 100 mA for 2 seconds. The voltage oscillated between about 1.6 V and 2.1 V in each cycle. The same procedure was used for both virgin and reinforced Sustainion with all other cell components remaining identical.

2.4. Methods used to reinforce membranes

Mechanical properties of polymer membranes can be altered by introducing inorganic materials, thus creating inorganic-organic hybrid networks.[12, 13] Zirconium-based networks or particles have been used in several papers to prepare inorganic-organic hybrid anion exchange membranes and resins due to their stability in a wide range of pH and good hydrophilicity [14-16]. In this work, a sol-gel method was used to synthesize a zirconia and Sustainion® hybrid network to improve the mechanical properties of the final anion exchange membrane. The zirconia sol was prepared as described by Kessman *et al.*[17] Zirconium (IV) propoxide 70% was used as a precursor and mixed with 2-propanol as a solvent. Acetic acid was added dropwise as a chelating agent with a molar ratio of 1:2:15. The alkoxide solution was stirred at room temperature for 2 hours. Nitric acid and water were added as catalysts for hydrolysis and mixed with 2-propanol with a molar ratio of 0.6:1:7.5. The resulting catalyst solution was then added to the precursor solution. The sol solution was stirred for 2 hours at room temperature for a condensation reaction to take place. The zirconia sol solution was blended with Sustainion® in Dowanol. The composition of Zirconia is calculated based on the weight percentage ratio of Zirconium to Sustainion® polymer in solution. The resulting blends were cast using BYK Automatic Film Applicator. The cast films were dried in the oven at 60°C for 40 minutes and then activated in 1 M KOH overnight.

2.5. Procedure for crossover experiments

Crossover current is an effective way of quantifying gas crossover in electrochemical cells. We measured crossover current by a standard electrochemical method using linear sweep voltammetry (LSV). Sustainion® with a thickness of 55 µm and reinforced Sustainion with Zirconia membrane with a thickness of 50 µm was sandwiched between a Pt supported carbon fiber paper cathode and Pt/Ru coated on a carbon fiber paper anode and mounted in 5 cm^2 fuel cell hardware. As shown in the literature,[18] for low hydrogen crossover conditions, removing oxygen traces in the system can be difficult even after long periods of purging. Nonetheless, the cathode was purged with pure hydrogen for 15 minutes to minimize the effect of oxygen reduction, although purging for any duration between 6 minutes to 30 minutes did not result in a difference in the measured crossover current. Humidified hydrogen and nitrogen were fed to the cathode and anode, respectively

The cathode functioned as a counter and reference electrode. Linear sweep voltammograms were conducted from 0.0 V to 0.7 V with a scan rate of 1.5 mVs^{-1} using a potentiostat (Solartron 1255B). The current increases in the voltage range of 0 V to 0.2 V, then reaches a plateau. The current at the plateau, often called a limiting current, is equivalent to the hydrogen crossover current once

normalized by the cross-sectional membrane area (i_x, $A \cdot cm^{-2}$). One can then calculate the hydrogen crossover rate ($\dot{f}$, $mol \cdot cm^{-2} \cdot s^{-1}$) as

$$\dot{f} = \frac{i_x}{zF} \qquad \text{Equation (1)}$$

in which F is Faraday's constant and z is the number of electrons transferred (2).

2.6. Procedure for impact testing

In order to assess the mechanical stability of the membranes, virgin and reinforced Sustainion® were subjected to impact testing as described in ASTM D3420 – 95[19] . This method provides a realistic stress test of abrupt mechanical forces that allow researchers to assess relative mechanical strength of many formulations. The impact strength of membranes was tested using a Leading Instruments FIT-01 Film Impact Tester (see Figure S1 in Supplementary Information) The test method measures the energy required for a weighted pendulum to punch through a sample that is placed between two circular plates with a diameter of 60 mm. The impact strength or impact energy is calculated based on the loss in mechanical energy of the pendulum. More energy lost means a higher impact strength and therefore a more robust membrane.

3. Results

3.1. Long-duration tests

Figure 2 shows the voltage required to maintain 1 A/cm² over time in an AEM electrolyzer using a 50 µm thick Sustainion® X37-50 and PTFE reinforced Sustainion® (Grade-T) membranes . In order to establish a relative baseline, we ran an identical cell using Fumatech FAS-50, the only other commercially available AEM at the time when testing began (2018). The area specific resistance (ASR) for each cell was measured as it described in study by Liu *et al*. The ASR For Sustainion® Grade-T, Sustainion® X37-50 and cell assembled using Fumatech FAS-50 are 0.08 Ω.cm^2, 0.06 Ω.cm^2 and 0.12 Ω.cm^2 respectively. All three cells were run at a constant current of 5 A and the resulting voltage over time can be translated into a degradation rate. The test for Fumatech FAS-50 was ended at 140 hours once it was obvious that the slope of the degradation line (655 µV/hr) was much steeper than would be acceptable for industrial applications. If a commonly applied threshold of <10% performance loss (i.e. energy efficiency) is applied, then the cell would require replacement after 298 hours, or 12 days, once the voltage increases from 1.950 V to 2.145 V. Table 1 provides comparison to additional membranes from literature. Both cells running with Sustainion® performed much better. The degradation rates are 1.85 V + 0.7 ±0.02 µV/hr and 1.83

V + 0.7 ±0.02 μV/hr in the respective cells. This resulted in a total voltage rise of only ~8 mV in 12,000 hours (over 1 year). The results were essentially within the measurement error of the equipment, i.e. fluctuations in voltage (about ±0.02 V) naturally occur during testing due to minor fluctuations in temperature. These results demonstrate the membranes are stable for thousands of hours in 1 M KOH at 60 °C and can meet industrial performance requirements. If we use the same formula to calculate replacement time when the voltage rises from 1.850V to 2.035V (>10% performance loss), then 1.0 μV/hr degradation would take 185,000 hours, or 21.1 years.

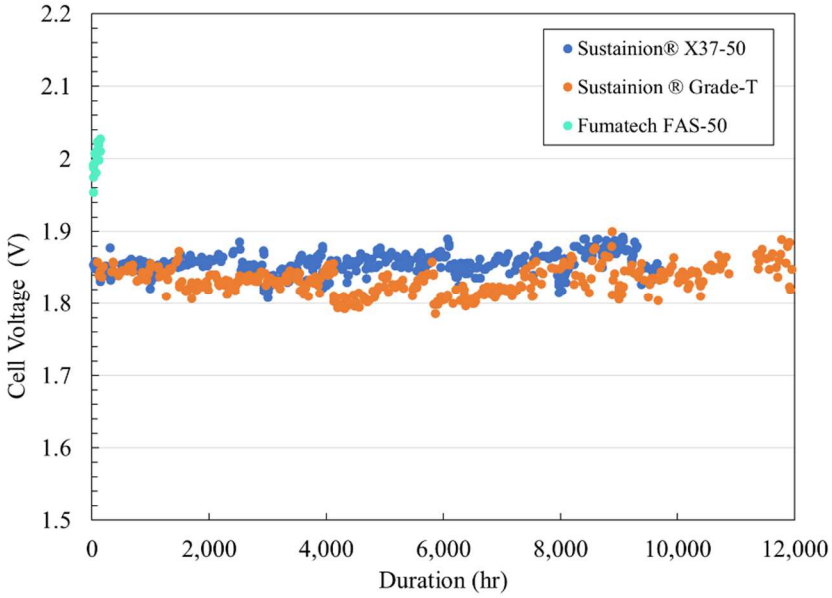

Figure 2. The voltage needed to maintain 1 A/cm² current in an AEM electrolyzer running at 60 °C in 1 M KOH. Dark green and light green points are data from two different cells using Sustainion® membranes. Blue data points are from FAS-50 running in the same conditions.

3.2.Impact strength tests

The effect of introducing zirconia into the Sustainion® matrix on impact resistance of the final membrane was studied by the pendulum impact resistance method described in ASTM D3420 – 95. Multiple reinforced membranes were synthesized with zirconia content varying from 1.5 wt.% to 10 wt.%. The addition of zirconia resulted in a variation in membrane thickness, as shown in Figure 3(a). From Figure 3(b), the highest impact strength was achieved with Sustainion® +2 wt.% zirconia. Increasing the content of zirconia more than 5 wt.% resulted in decreased mechanical integrity and impact strength. This observation may be due to the agglomeration of inorganic content[20] and creating a nonuniformity in the host polymer matrix. Tabulated results are provided in Table S1 of the Supplementary Information.

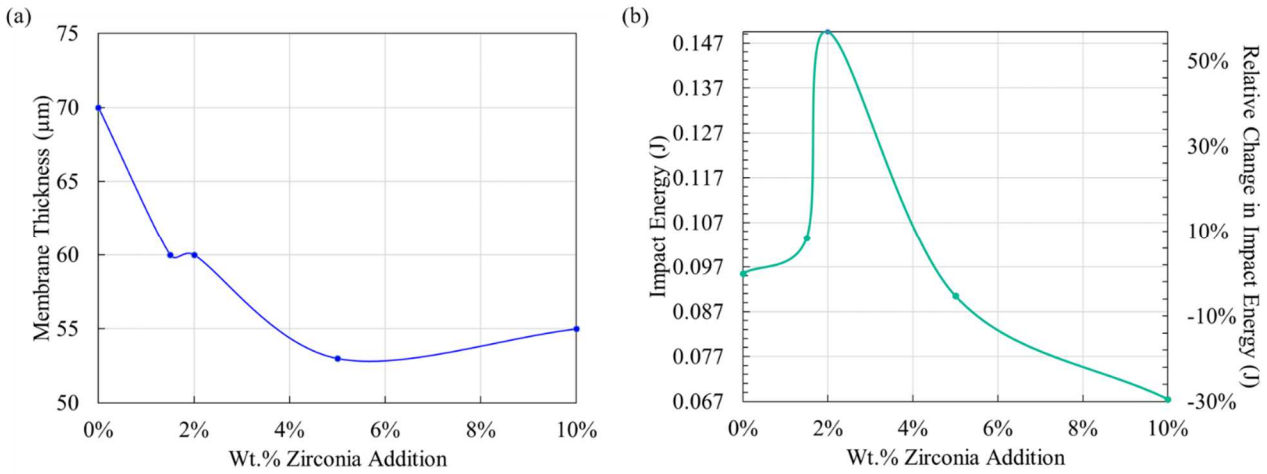

Figure 3. Effects of zirconia doping of Sustainion® X37-50 on (a) membrane thickness and (b) impact energy. Change in impact energy is relative to impact energy with 0% zirconia addition.

3.3. Cycle tests

Cycling current or voltage has been employed as a fast and informative method of testing MEA durability in various electrochemical applications.[21] The durability of Sustainion® and zirconia-reinforced Sustainion was tested by cycling the current between 100 mA and 12,000 mA for 11,000 cycles to simulate abusive conditions through rapid voltage spikes. As Figure 4 shows, reinforced Sustainion required a higher range of voltage (2.11 V – 2.14 V), to achieve 12,000mA in each cycle than did virgin Sustainion® (2.09 V – 2.11 V). This can be explained by a decrease in the functional group density of Sustainion® resulting from blending with 2 wt.% zirconia. However, as can be seen in Figure 4(a), the rate of increase in voltage per cycle for zirconia-reinforced Sustainion® is only 1.65 μV/cycle and 0.15 μV/cycle for the virgin membrane. In both cases, the increase in voltage is likely due to higher resistance resulting from degradation. Nonetheless, the degradation rates are very low, indicating that both membranes are stable under these abusive conditions.

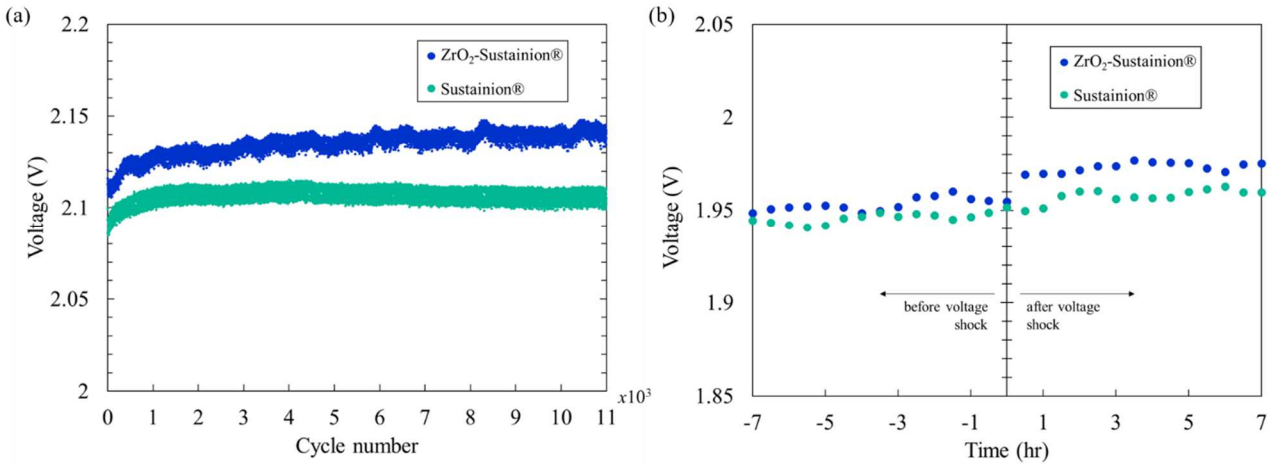

Figure 4. (a) Voltage at each cycle of virgin (green) and 2 wt.% zirconia-reinforced (blue) Sustainion® X37-50. Cycle number is by the thousands. (b) Steady-state performance of virgin (green) and 2 wt.% zirconia-reinforced (blue) Sustainion® X37-50 for the 7 hours before and after cycling experiments.

Figure 4(b) also shows the stability before and after the 11,000 cycles. The voltage for the cell using virgin Sustainion® X37-50 operated at 5 A (1 A/cm^2) was 1.95 V for the 7-hour period leading up to the voltage shock experiments and upon resuming steady-state operation stabilized at 1.96 V. The cell with the zirconia-reinforced membrane showed a voltage increase about twice as high of 0.02 V from 1.95 V to 1.97 V. Both cells also showed a slight increase in impedance of ~0.005 ohms after the cycling tests, most likely due to membrane degradation.

3.4. Hydrogen crossover tests

Hydrogen crossover can lead to an increased degradation rate, pinhole formation, and reduction in efficiency.[22] Figure 5 shows that reinforcing Sustainion® by blending with 2% of Zirconia resulted in a decrease in hydrogen cross over current from 0.075 mA/cm^2 to 0.033 mA/cm^2. This corresponds to a 56% reduction in hydrogen crossover flux from 3.9×10^{-10} to 1.7×10^{-10} $mol/(cm^2 \cdot s)$ for the reinforced Sustainion® membrane. Long term testing creates a major tension and distresses for membranes in through-plane direction. This fact magnifies the importance of studying the impact resistance in comparison with tensile resistance.

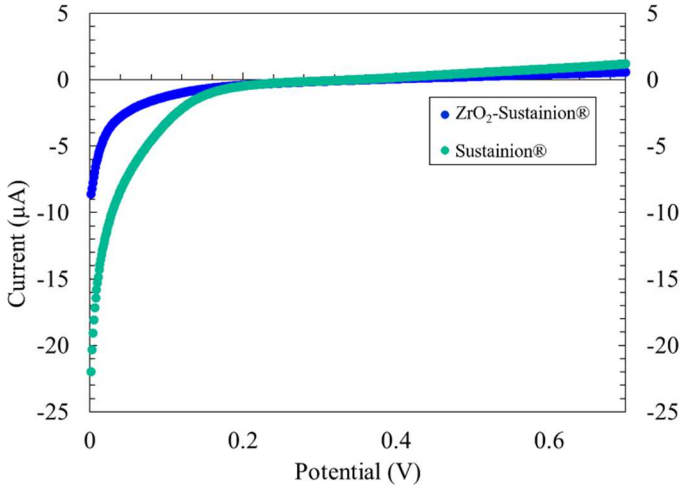

Figure 5. Current vs. Potential plot from crossover experiments for Sustainion® X37-50 and zirconia doped Sustainion® X37-50 membranes.

4. Discussion

The commercial viability of electrolyzers depends on many performance characteristics. First and foremost, the economics dictate that the process must be energy efficient. The cost of operating the system must be balanced with the initial capital cost. Most commercial electrolyzers operate around 2 V for this reason. There is a trade-off with multiple conditions that define when a system is running at "economically optimal" conditions. In electrochemical cells, this roughly takes the shape of the I/V curve where it is desirable to run at the lowest possible voltage (primary driver for electricity and therefore operational costs) and highest current density of the cell (primary driver for cell/stack capital cost). This paper will not go into the detailed economics and instead refer to detailed models and techno-economic analyses such as the H2A model published by the National Renewable Energy Laboratory (NREL)[23]. Relative to PEM electrolyzers, cell and stack costs can be significantly reduced by replacing the platinum and iridium catalysts with base metals by operating in alkaline conditions. Alkaline systems are therefore much lower cost, but currently cannot reach high current density and are thus fundamentally limited to how low the capital cost can go. AEMs offer a unique combination of low voltage and high current density. The next set of factors influencing operational costs are maintenance, in particular, replacement costs incurred by component failure. Many electrochemical cells using AEMs in literature run for about 300 hours to show "stable" performance, but often do not calculate degradation rates.

To further advance the state of AEM electrolysers, we conducted long-term tests on two separate cells. The results showed a degradation rate of ~1 µV/hr. Figure 6(a) shows degradation rates of similar cells, with additional details provided in Table 1. The low degradation rate was maintained for more than 10,000 hours (Figure 6b), while all other similar AEMs were run for less than an order of magnitude in duration. The results presented herein are several orders of magnitude better than previous results, in terms of degradation rate. When calculating the impacts of equipment

downtime and component replacement costs, it becomes obvious that frequent maintenance will make the process less economically attractive to operate. We can further employ a practical calculation to convey the importance of a low degradation rate. Operational parameters are often set to remain at a threshold of ~10% performance loss to stay within specification. If we assume that a commercially deployed system must maintain >90% of initial performance, then 1 μV/hr degradation (from 1.85 V to 2.035 V) would take 185,000 hours, or 21.1 years. A span of 20-30 years is commonly used to calculate amortization costs on large capital projects like chemical plants. This rate only refers to cell degradation. Most PEM systems have shown cell lifetimes of about 40,000 hours.[5] Therefore, the MEAs tested here are now on-par with commercially available PEM technology in terms of lifetime. Future research on AEMs should also conduct longer-term testing under actual operating conditions. Thus far, many results presented in the literature show a simple I/V curve which conveys impressive current densities at low voltage, but the key for industrial applications will be to maintain > 1 A/cm^2 over multiple years.

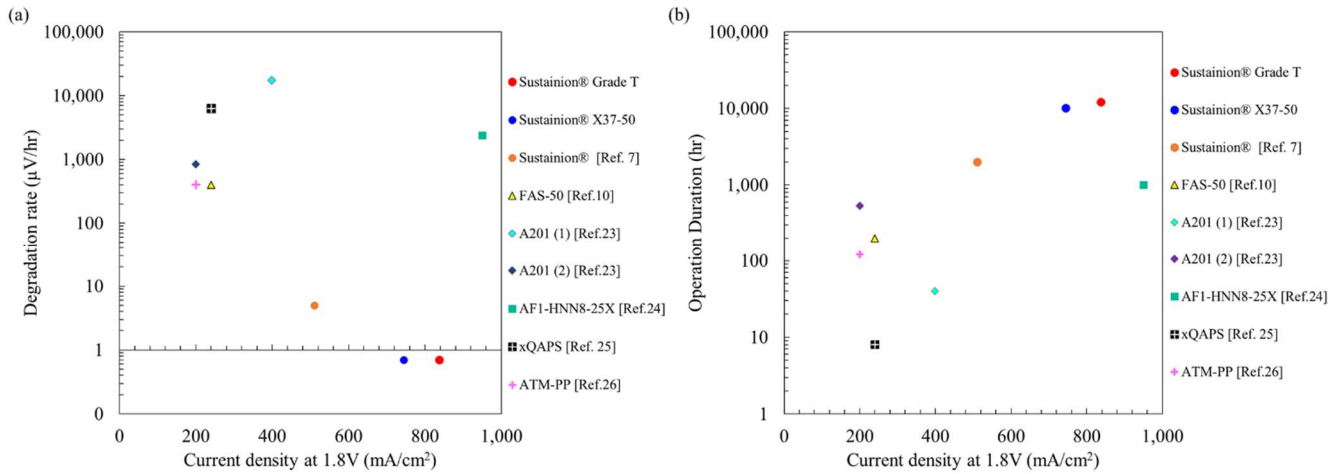

Figure 6. Performance of various anion exchange membranes at a voltage of 1.8 V, with respect to (a) maximum testing duration and (b) degradation rate of the membrane.

285 Table 1. Comparison of Anion Exchange Membranes.

AEM	Anode [loading (mg/cm^2)]	Cathode [loading (mg/cm^2)]	Current density at 1.8V (mA/cm^2)	Degradation rate (μV/hr)	Set test current (mA/cm^2)	Total test duration (hr)	Ref.
Sustainion Grade T	NiFe2O4 (1.8)	Raney nickel (14.5)	837	0.7	1000	12,180	This work
Sustainion X37-50	NiFe2O4 (1.8)	Raney nickel (2.7)	744	0.7	1000	10,100	This work
Sustainion	NiFe2O4 (1.8)	NiFeCo (2.7)	510	5	1000	2,000	Ref. 7
FAS-50	Ni2FeO4 (1.8)	NiFeCo (2.7)	240	400	1000	200	Ref. [11]
A201	IrO2 (2.9)	Pt (3.2)	399	17500	200	40	Ref. [24]
A201	IrO2 (2.6)	Pt (2.4)	200	840	200	535	Ref. [24]
AF1-HNN8-25X	IrO2 (3.8)	Pt (1)	950	>2390	500	1,000	Ref. [25]
xQAPS	NiFe (n/a)	NiMo (40)	240	6300	400	8	Ref. [26]
ATM-PP	IrO2 (3.0)	Pt (3.0)	200	400	200	120	Ref. [27]

286

287 Electrolyzers must perform adequately under real-world conditions. For many cases, this will
288 involve on/off cycling as hydrogen production follows electricity produced by variable renewable
289 resources like wind and solar. To examine the stability of the Alchemr's MEAs, we cycled the cells
290 from 100 mA (limited by the Neware tester as an "off" condition) to 12,000 mA (2.4 A/cm^2) over
291 11,000 cycles. This was the largest voltage shock allowed by our testing equipment and represents
292 severe abuse conditions since the system-level parameters would not vary current from 2% to 240%
293 of nominal conditions in 2-second cycles. While the testing protocol was harsh, it accelerated
294 membrane degradation substantially and allowed for a relative comparison between our baseline
295 and zirconia-reinforced membranes. The rate of increase in voltage per cycle for Sustainion® is
296 only 0.15 μV/cycle compared with 1.65 μV/cycle for the zirconia-reinforced membrane. Both
297 degradation rates are very low, so the trade-off will more likely be between the reduced energy
298 efficiency and improved mechanical stability. The 11,000-cycle test on a 5 cm^2 cell is clearly not a
299 substitution for real-world testing, but it provides a valuable set of data that will be used to inform
300 future testing and techno-economic models. If the system were cycled on and off once per day, this
301 testing protocol would represent 30 years of data.

302

303 Mechanical stability is additionally imperative to the commercially viability of water electrolyzer
304 membranes. We have achieved a 57% improvement in impact strength by reinforcing Sustainion®
305 membranes with zirconia. This result is particularly relevant to industry, since the construction and
306 assembly of MEAs and inserting them into stacks poses a risk of the membrane being punctured.

Improving mechanical stability reduces the opportunity for accidental punctures leading to short circuits. In addition to a need to improve mechanical stability, we explored methods of reducing gas crossover of the commercially available Sustainion® membranes. Reduced crossover is important because it improves the overall energy efficiency of the cell and, especially in multi-cell stacks, improves safety. The danger arises in the mixing of gas bubbles containing H_2 and O_2, considering the lower explosion limit of hydrogen-oxygen mixtures is only ~4 mol% H_2. Zirconia-reinforced membranes performed exceptionally well in this arena as well.

5. Conclusions

We have demonstrated that Alchemr's water electrolyzer cells employing the Sustainion® membrane and Dioxide Material's catalysts meet multiple commercially relevant performance metrics. Previously, steady-state performance of AEMs in the literature were limited to only a few hundred hours of operation. Herein, we showed stable performance of ~1 μV/hr over 10,000 hours of testing, resulting in a projected MEA lifetime of over 20 years. We have also shown that harsh voltage shock tests, to simulate accelerated daily on/off cycling, results in a performance loss of only 0.15 μV/cycle over 11,000 cycles. Currently, comparative AEM literature is not available, but we hope that future experimentalists will take a similar approach in voltage shock tests to measure realistic performance of AEMs. Additionally, we have shown increased mechanical stability of a Sustainion® membrane through blending with Zirconia. We hope the scientific community continues to push the limits of AEM, and test under longer and harsher conditions to help advance AEMs to commercially relevant performance such that AEM water electrolyzers can serve as a significant method of hydrogen production.

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Author Contributions
B.M. conducted the cycling and membrane reinforcement experiments; Z.L. conducted the long-duration experiments; All authors contributed to data analysis and writing the manuscript.

Declaration of Interests
The authors have submitted US Patent 9,982,353 and several continuing patents based on the results reported in this paper. There are also several patents on the membranes and cell designs used for the work here including US9,370,773, US9,481,939, US9,580,824, US9,815,021, US9,982,353, and US9,943,841. The authors and Dioxide Materials have a financial interest in these patents. Dioxide Materials is offering all the research materials used here (membranes, cells, catalysts, etc.) for sale to other research groups so that they can reproduce and build on the findings. The authors associated with Dioxide Materials declare a financial interest in these sales.

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