Preliminary Results of Seawater-Polymer-Electrolyte Metal-Air Battery*

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***Abstract*— This study explores the possibility of using seawater and environmentally friendly materials to create polymer electrolytes for metal-air batteries, a potential energy source. The battery's separator, or polymer electrolyte, was made by doping PVA (polyvinyl alcohol) with NaOH(aq) or untreated seawater. Aluminum and magnesium were used as the anode and copper plate as the cathode. The results are promising. The aluminum-air cell had an open-cell voltage of 1.2 V with electrolytes made from $NaOH_{(aq)}$-doped PVA. The magnesium-air cell had a higher open-cell voltage in the range of 1.3 to 1.4 V with electrolytes made from seawater-doped PVA. The batteries performed consistently over continuous runtimes of 12 or 24 hours, with the magnesium-air battery achieving a 24-hour runtime.**

Keywords*— *Anion-Ion Exchange Membrane; metal-air battery; energy storage

I. Introduction

The global temperature rise is a factor leading to climate change. The temperature rises result in the disappearance of glaciers, unprecedented drought in parts of the world, and extreme weather conditions. Acidification of the ocean also occurs, which threatens the health of the ecosystem. The long-term effects on the coastal water around Japan can be seen as an example and extrapolation to global water [1]. To prevent irreversible and negative impacts on the ecosystem, we must limit the temperature rise to 1.5ºC by 2050 [2]. One strategy to reduce CO_2 emissions is to electrify mobility, using renewable sources to generate electricity. Electrifying mobility has gained momentum as can be seen from the electrical vehicle (EV) sales increased by 26% in 2021 compared to the previous year and further increased by 65% in 2022 compared to 2021. It is reported by IEA [3] one in every eight passenger cars sold in the U.S. was an EV and the rate of EV sales is increasing. The battery will be an important platform that stores electricity generated from renewable sources. However, the lithium global supply will have a challenge meeting the demand for EV manufacturing. Other alternatives need to be explored. One of which is the metal-air battery.

Metal-air batteries are a promising energy source, but practical applications still face challenges [4]. In this study, we used an anion-ion exchange membrane (AEM) that we made in-house. Originally intended for use in an alkaline fuel cell, we discovered that the AEM could also be used as a separator in metal-air batteries. AEMs are considered a low-cost alternative to proton exchange membranes (PEMs or cation ion exchange membranes) in fuel cells. They can achieve performance comparable to PEM fuel cells at a lower cost1. Recent trends in the fabrication of polymer-based high-performance AEMs are

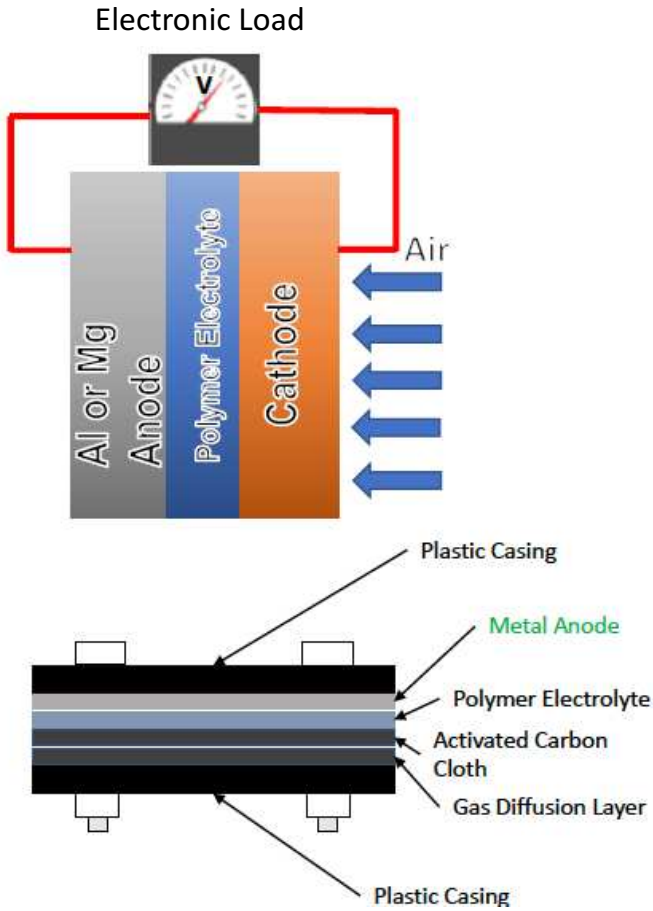

Figure. 1. Schematic of the electrochemical cell.

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highlighted and future directions are identified [5]. The durability of the polymers operated in a strong alkaline environment is a critical issue for the development of the AEM fuel cells [5].

The metal-air electrochemical cell (battery), as illustrated in Fig. 1, consists of an anode (Al or Mg in this study), separator (AEM), cathode (Cu plate), and air channel. The anode and cathode reactions can be written by Eqs. (1) and (2):

Anode

$$Al + 3\,OH^- \rightarrow Al(OH)_3 + 3e^-, \text{ or} \quad (1a)$$

$$Mg + 2\,OH^- \rightarrow Mg(OH)_2 + 2e^- \quad (1b)$$

Cathode

$$H_2O + 1/2\,O_2 + 2\,e^- \rightarrow 2OH^- \quad (2)$$

II. Experimental Methods

The AEM separator of the metal-air cell is in-house made from doping polyvinyl alcohol (PVA, CH2CHOH) with $NaOH_{(aq)}$ or seawater. PVA, known as hydroxyethene, is water soluble, hydrophilic, nontoxic, and biodegradable. Different agents were used for crosslinking in PVA to make AEMs for fuel cells and double-layer capacitors [6, 7, 8]. We used a freeze-and-thaw process to prepare the polymer electrolytes with two PVA concentrations (5% and 10%, by weight, dissolved in de-ionized water, denoted 5% wt and 10% wt in the discussion herein).

The first step of the freeze and thaw process is to prepare the PVA solution by dissolving PVA in de-ionized water. The solution was poured into a mold and placed into a freezer that was set to -20 ºC. After a set time, the mold thaw at room temperature. The freeze-and-thaw cycle was repeated 4 times, and a crystalline structure is formed in the PVA film/membrane. Following the fourth cycle, the film was dried at room temperature. The membrane was then placed in two $NaOH_{(aq)}$ solutions with a molarity of 1.0 M or 1.5 M, a process also known as doping. The process results in a membrane that only negatively charged ions (i.e., OH^-) can pass through. This is the property making the PVA membrane become an AEM, i.e., the separator, for the metal-air electrochemical cell. The AEM is an insulator to electrons but a conductor to the OH^- ion that transports across the separator. To assess if seawater can be used to "dope" the membrane, NaOH(aq) was replaced by seawater taken from Corpus Christi Bay by the Texas A&M University-Corpus Christi campus (27.715470, -97.321951). The PVA film/membrane was soaked in seawater and followed the same procedure using $NaOH_{(aq)}$ for preparing the membrane. The active areas of 64 or 72 cm^2 were used for $NaOH_{(aq)}$-doped membranes/polymer electrolytes and 81 cm^2 for seawater-doped membranes.

The experiments were conducted by connecting the cell output (electrodes) to an electronic load (BK Precision 8540) as illustrated in Fig. 1. The in-house design and fabricated electrochemical cell is shown in Fig. 2. The currents were set to 1 mA for NaOH-doped membrane (Cases A and B in Table 1) and 10 mA (Cases B, C, and D in Table 1) for seawater-doped membranes. The active area, current density, open cell voltage, peak voltage, and runtime, are also summarized in Table 1.

Continuous testing of the electrochemical cells was conducted. For NaOH(aq)-doped-AEM aluminum-air cells, the testing time was set to 12 h. For seawater-doped-AEM magnesium-air cells, the continuous testing time was extended to 20 h.

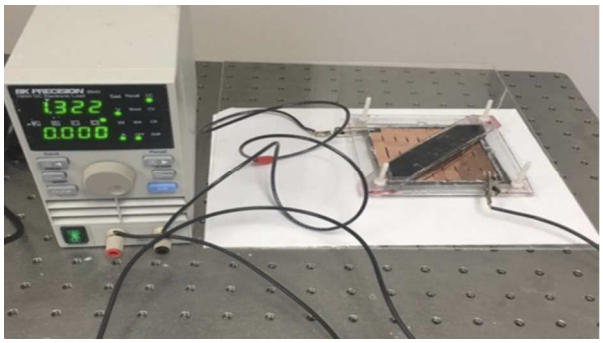

Figure 2. Experimental electrochemical cell.

III. Results and Discussion

The test results of alumina-air cells are plotted in Figs. 3 and 4. The results show that the in-house prepared polymer electrolytes, i.e., PVA doped with $NaOH_{(aq)}$ can be used as the separator of aluminum-air batteries. The test results showed that the open cell voltage of the aluminum-air cell was 1.2 V, which is substantially lower than the theoretical open cell of 2.7 V [9] but is slightly lower than the reported practical open cell voltage of 1.4 to 1.6 V [10]. When a current density of 0.0138 mA/cm^2 was applied (or 1 mA set at the electronic load), the cell voltage dropped to 0.856 V at 1 hour of continuous runtime and it peaked to 1.025 V at 8 hours of continuous runtime, cf. Fig. 3. The cell performance increased when the AEM was prepared by doping PVA with $NaOH_{(aq)}$ of 1.5 M, i.e., test condition of Case B of Table 1. The open cell voltage remained the same (1.2 V). The cell voltage first decreased to 0.8 V at a runtime of 1 h and gradually increased and approached the open cell voltage of 1.2 V as shown in Fig. 4.

The test results of the magnesium-air cell are summarized in Figs. 5, 6, and 7. Figure 5 shows that the measured open cell voltage is 1.4 V, which is substantially lower than the theoretical open cell voltage of 3.1 V [11] but is slightly lower than the reported open cell voltage of 1.6 V [11]. When a current density of 0.1230 mA/cm^2 was set (or 1 mA set at the electronic load), the cell voltage dropped to 0.62 V at 1 hour of continuous runtime. The cell voltage then increased and

maintained at around 0.95 V for the remainder of the test run. Similar results can be seen for the test run reported in Fig. 6. The initial voltage drop was 0.68 V and maintained at around 0.85 V for the test runtime of 5 to 12 hours. The most encouraging results are the test run of Case E, Fig. 7. We were able to run the cell for a period of 24 hours. The open cell voltage was 1.32 V. The initial cell voltage dip was 0.67 V at 1 hour of runtime and "recovered" to around 0.9 V and then decreased to 0.524 V at runtime of 24 hours, cf. Fig. 7. As shown in Table 1, the magnesium-air cell was operated at a current density about an order of magnitude higher than the aluminum-air cell.

The test results showed that a sustained cell operation of 12 hours was achieved for the aluminum-air cells with $NaOH_{(aq)}$-doped membranes and up to 24 hours of the runtime was achieved for the magnesium-air cells with (untreated) seawater-doped membranes. The magnesium-air cells with seawater-doped membranes outperformed the aluminum-air cells with $NaOH_{(aq)}$-doped membranes.

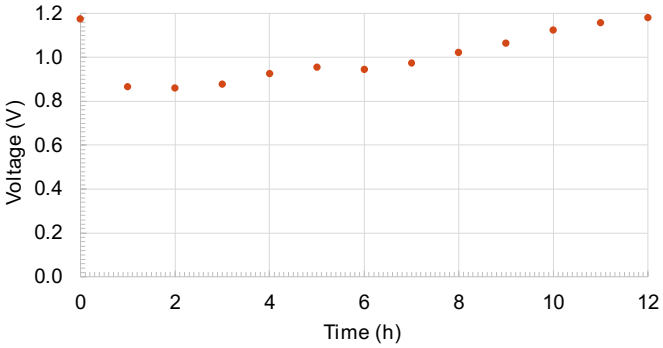

Figure 4. Cell voltage v. runtime of aluminum-air cell with AEM separator prepared by PVA doped with 1.5 M $NaOH_{(aq)}$, current density set to 0.0156 mA/cm^2, active area of 68 cm^2, and total runtime of 12 hours; Case B, Table 1.

Table 1. Summary of Test Conditions

Case	Polymer Electrolyte Doping	Cathode Metal	Active Area (cm^2)	Current Density (mA/cm^2)	Open Cell (V)	Run Time (h)	Peak Voltage (V)
A	NaOH - 1.0 M	Aluminum	72	0.0138	1.2	12	1.0
B	NaOH - 1.5 M	Aluminum	64	0.0156	1.2	12	1.2
C	Seawater	Magnesium	81	0.1230	1.4	12	0.9
D	Seawater	Magnesium	81	0.1230	1.3	12	0.9
E	Seawater	Magnesium	81	0.1230	1.3	24	0.9

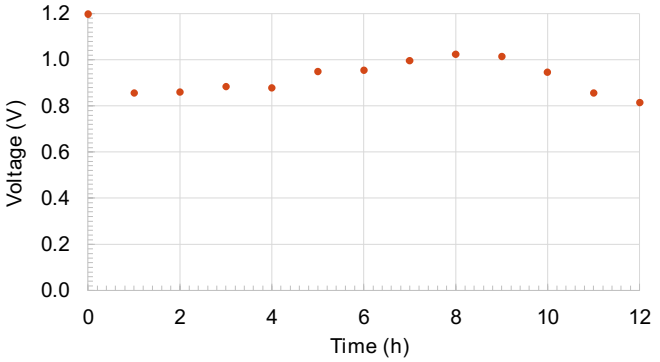

Figure 3. Cell voltage v. runtime of aluminum-air cell with AEM separator prepared by PVA doped with 1.0 M $NaOH_{(aq)}$, current density set to 0.0138 mA/cm^2, active area of 72 cm^2, and total runtime of 12 hours; Case A, Table 1.

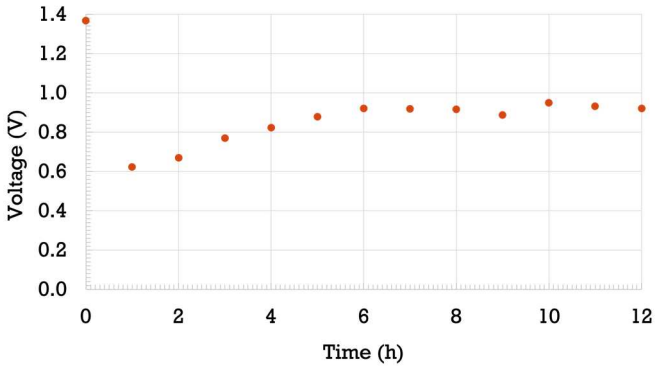

Figure 5. Cell voltage v. runtime of magnesium-air cell with AEM separator prepared by PVA doped with seawater, current density set to 0.123 mA/cm^2, active area of 81 cm^2, and total runtime of 12 hours; Case C, Table 1.

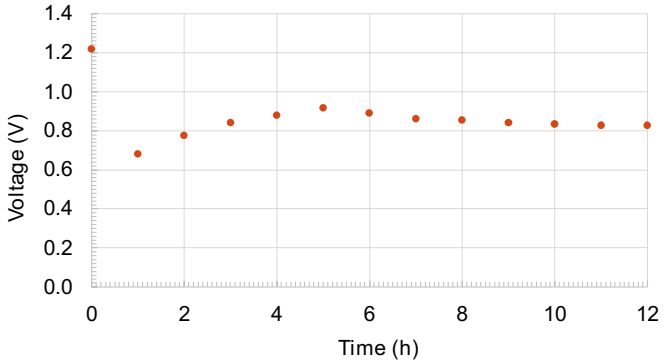

Figure 6. Cell voltage v. runtime of magnesium-air cell with AEM separator prepared by PVA doped with seawater, current density set to 0.123 mA/cm^2, active area of 81 cm^2, and total runtime of 12 hours. (Case D, Table 1)

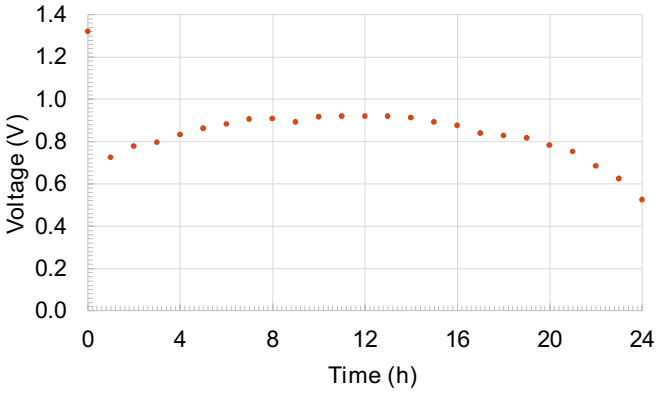

Figure 7. Cell voltage v. runtime of magnesium-air cell with AEM separator prepared by PVA doped with seawater, current density set to 0.123 mA/cm^2, active area of 81 cm^2, and total runtime of 24 hours. (Case E, Table 1)

The results are promising regarding the use of aluminum-air and magnesium-air batteries as alternative energy sources. Aluminum and magnesium are abundant in the earth's crust; they are the third (aluminum) and eighth (magnesium) most abundant elements in the earth's crust. However, there are challenges with the current cell configuration. Experiments showed that deposits formed on both aluminum and magnesium anodes, e.g., see Fig. 8. They appear to be hydroxides of aluminum and magnesium.

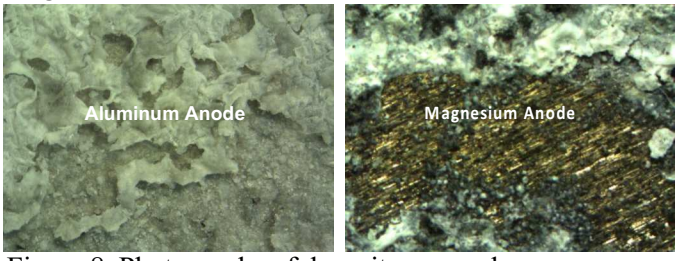

Figure 8. Photographs of deposits on anodes.

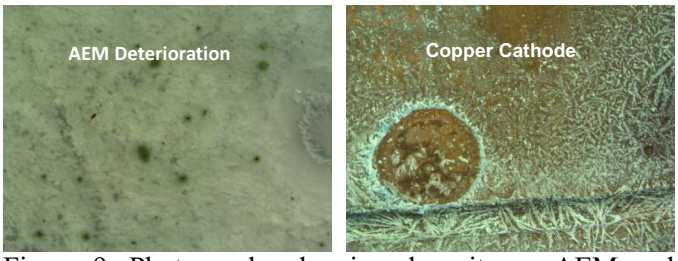

Figure 9. Photographs showing deposits on AEM and "fibrous" structures formed on copper cathode after the test runs.

The test results also showed the deterioration of the polymer electrolyte separator, Fig. 9, suggesting that the AEM prepared by the method described and used in the experiments may not be practical for use as a separator for metal-air batteries. Effective removal of the products formed at the electrodes will be needed. To address this requirement, we are exploring a flow-battery configuration for the metal-air battery.

IV. Conclusion and Recommendation for Future Study

The exploratory investigation reported in this paper shows that doping polyvinyl alcohol (PVA, CH2CHOH) with $NaOH_{(aq)}$ and untreated seawater via the freeze-and-thaw process was successful in preparing the anion-ion-exchange membranes. The $NaOH_{(aq)}$ concentration used to prepare the polymer electrolyte affects the aluminum-air cell performance. The aluminum-air cell with the 1.5M-$NaOH_{(aq)}$ doped PVA has a higher electrochemical cell performance than the cell with the 1.0M-$NaOH_{(aq)}$ doped PVA. The results of the magnesium-air cell with (untreated) seawater-doped PVA are encouraging. Magnesium is the eighth most abundant element on earth and PVA is biodegradable PVA.

For future experiments, it is suggested to first use the synthetic seawater to prepare the PVA-based AEM and to conduct characterization experiments (e.g., ionic conductivity and SEM micrographs) on the fabricated AEM. Following the synthetic seawater, filtered seawater with known concentration and other properties be used, and characterization experiments be conducted. The PVA-based AEM can also be used for alkaline fuel cells.

The exploratory experiments also showed that metal-air electrochemical cells hold the potential as an alternative energy source. Research along this line could be an important endeavor as we are experiencing the rising demand for electric vehicles at a time when the global lithium production capacity is limited. However, to make the metal-air cell an alternative energy source, effectively removing the byproducts formed at the anode and cathode is needed. Challenges to the low AEM ionic conductivity and the AEM deterioration must also be addressed should

AEM separators be used, or an alternative battery form factor, e.g., the flow-battery configuration, be explored.

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