Cathode Composition in a Saltwater Metal-Air Battery

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Abstract

Metal-air batteries consist of a solid metal anode and an oxygen cathode of ambient air, typically separated by an aqueous electrolyte. Here, simple saltwater-based models of aluminum-air and zinc-air cells are used to determine the differences between theoretical cell electric potentials and experimental electric potentials. A substantial difference is observed. It is also found that the metal cathode material is crucial to cell electric potential, despite the cathode not participating in the net reaction. Finally, the material composition of the cathode appears to have a more significant impact on cell potential than the submerged surface area of the cathode.

Keywords: Saltwater battery, metal-air battery, electric potential, electrochemical cell

I. INTRODUCTION

Recent research from the energy sector has focused on the development of metal-air batteries for their high specific energy density in comparison to common methods of energy storage[1-4]. For instance, the aluminum-air car battery has been calculated to generate enough power to match gasoline-powered cars in driving range and acceleration[3]. A metal-air battery is an electrochemical cell that uses an metal anode and an external cathode of ambient air, and typically an aqueous electrolyte[4]. Oxygen is usually reduced by a metal-based electrode that henceforth will also be referred to as the cathode.

Saltwater electrochemical cells, which are used as a classroom demonstration of electro-chemistry, function on the same principles as a commercial metal-air battery. The theoretical electric potential ($E°_{cell}$) generated by any voltaic cell under standard conditions (electrolyte concentrations of 1 mole per liter and pressures of 1 atmosphere at 25°C) is calculated by subtracting the standard reduction potential ($E°_{red}$) of the anodic oxidation half-reaction from the $E°_{red}$ of the cathodic reduction half-reaction. Such half-cell reactions are based on the half-cell galvanic cell model and comprise of equilibrium equations in which electrodes interact with ions of the same chemical species. However, because an empirical potential difference measurement is only possible for a complete circuit of two electrodes, all $E°_{red}$ values are relative to the standard hydrogen electrode half-cell,

$$2\ H^+\ (aq) + 2\ e^- \rightarrow H_2\ (g) \qquad (1)$$

conventionally defined as zero. As $E°_{cell}$ becomes more positive, the maximum theoretical voltage of the cell increases.

In a saltwater electrochemical cell, the metal cathode receives electrons from the external circuit and passes them on to dissolved oxygen gas in the electrolyte, according to the equation below. This, and all other standard theoretical cell potentials, assumes an electrolyte

concentration of 1M, whereas the maximum equilibrium amount of dissolved oxygen in water at 25°C is 0.00026 M:[5]

$$O_{2(aq)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)} \quad (2)$$
$$E°_{red} = 0.40 \text{ V}$$ [6]

The anode serves as the site of oxidation, and gives up electrons to the external circuit[6]:

$$Al_{(s)} + 3OH^-_{(aq)} \rightarrow Al(OH)_{3(s)} + 3e^- \quad (3)$$
$$E°_{oxidation} = -2.30 \text{ V}$$

The net cell potential of an aluminum-air cell is $E°$ = (0.40 V) – (–2.30 V) = 2.70 V

In electrochemical cells using zinc anodes, the most likely anodic oxidation reaction, by energetic favorability, is predicted to be[7]:

$$Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^- \quad (4)$$
$$E°_{oxidation} = 1.25 \text{ V}$$

The net cell potential of a zinc-air cell is $E°$ = (0.40 V) – (–1.25 V) = 1.65 V

Saltwater serves merely as a conductive medium to complete the circuit. Any conductive liquid could serve as an electrolyte, and special ones have been engineered for commercial metal-air cells. The electric potential produced with a regular NaCl saltwater electrolyte is expected to be significantly lower than the theoretical potential of the cell as saltwater does not contain 1 mole of dissolved oxygen per litre at atmospheric pressure and room temperature.

Here, the difference between theoretical standard potentials and experimentally achievable electric potentials of an NaCl saltwater cell with a single, aqueous electrolyte at equilibrium was measured. In addition, the impact of cathode surface area and cathode composition on electric potential was investigated.

II. METHODS

Two copper (Cu), carbon (C), zinc (Zn), and aluminum (Al) electrodes were obtained. A container was filled with 1000 mL water and mixed with 35 g salt to create a saltwater solution. Pairs of electrodes were attached to a multimeter set at 2000 mV, as shown in Figure 1. Electric potential was measured after submerging both electrodes for 5 seconds, ensuring that the alligator clips did not come into contact with the electrolyte. Electrode pairs (Zn/Cu, Zn/C, Al/Cu, Al/C) were tested in the saltwater electrolyte in an alternating fashion until 10 measurements were made for each pair. All electrode pairs were then tested in electrolytes of varying concentrations.

To assess the impact of cathode surface area, sheets of graphite (carbon), aluminum, zinc, and copper were cut into the following dimensions: 12 × 1 cm, 12 × 3 cm, 12 × 5 cm, and 12 × 10 cm. Saltwater cells were set up with anodes of constant material and dimensions, while cathodes of differing materials and dimensions were systematically submerged in

Figure 1. The experimental setup with a Zn anode | Cu cathode pair.

the electrolyte. Similarly, another group of saltwater cells was set up with cathodes of constant material and dimensions, while anodes of differing materials and dimensions were systematically submerged in the electrolyte. Electric potential was measured until 5 trials had been recorded for each anode/cathode combination. (Complete data can be found at www.isjos.org/pdfs/ISJOS_v11_p5-Data.pdf).

III. RESULTS AND DISCUSSION

As expected, the saltwater electrochemical cells generated substantially less electric potential than the theoretical voltage predicted by the two half reactions. As seen in Figure 2, the aluminum anode cells produced an experimental mean of 0.77V for the Al/C cell and 0.56V for the Al/Cu cell, compared to a theoretical 2.70 volts. T-tests comparing the mean experimental value for each cathode material with the theoretical value produced p-values of <0.001. The zinc anode cells produced an experimental mean of 1.08V for the Zn/C cell and 0.83V for the Zn/Cu cell, compared to a theoretical 1.65 volts. T-tests gave p-values of <0.001.

Although the theoretical maximum electric potential of an aluminum-based metal-air cell is greater than that of the zinc-based metal-air cell, the saltwater cells with aluminum anodes produced a lower voltage than the saltwater cells with zinc anodes on average, as can be seen in Figure 2. Interestingly, the cathode material appears to be of central importance, despite the cathode not participating in the reaction, with the carbon cathode producing a higher potential than the copper cathode for both the zinc and aluminum anode cells.

A possible explanation for these observations is that the structure of carbon is more porous than that of copper, and therefore better facilitates the oxidation of dissolved oxygen gas as a result of greater exposed surface area. It is generally known that surface area of the electrodes may impact the total current produced by the cell as more atoms will react with one another per second, but potential difference is expected to depend only on the chemical identities of the cathode and anode. Testing showed no statistically significant effect of either anode or cathode surface area on potential difference. For consistency with the other research described in the literature, current was not measured.

In summary, although the choice of cathode material is ignored in calculating theoretical saltwater cell potentials, the cathode material has a large effect on the experimental cell potential measured, possibly because the cathode acts as a catalyst for the reduction of oxygen.

One issue that needs to be addressed in future is that, although temperature and pressure were assumed to be standard, the Nernst equation could not be applied to adjust the theoretical standard electric potentials for electrolyte concentration because equipment was not sufficient to measure the equilibrium oxygen

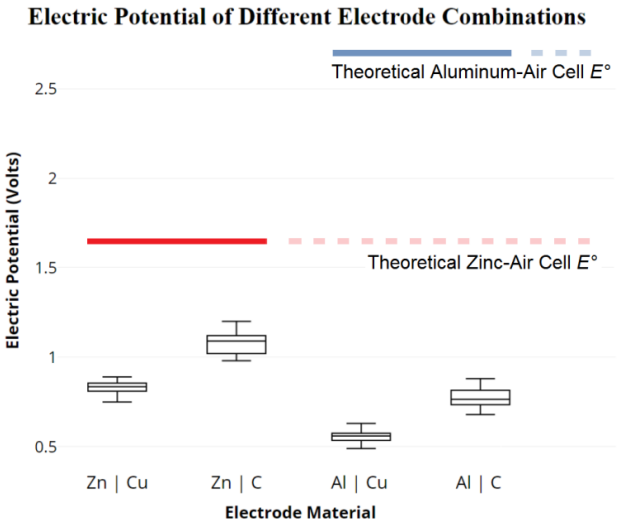

Figure 2. The experimental and theoretical electric potential (volts) produced by aluminum- and zinc-based saltwater cells. Note the variation associated with the cathode material used.

concentration in the saltwater. Further research into optimizing cathode material for maximum electric potential output is suggested, as well as measuring total electric current output of varying cathode and anode materials and surface areas.

IV. CONCLUSION

Although saltwater batteries are common electrochemistry demonstrations in general chemistry courses worldwide, little research has been published on the molecular mechanisms by which they operate. This paper has shown a statistically significant difference of up to threefold between experimental electric potential measurements and those predicted by standard cell potential calculations for simple metal-air batteries.

The cathode material composition in a saltwater cell was found to affect electric potential as much as anode material. These results indicate that the choice of both electrode materials matters in experimental voltage measurements, while only anode material was seen as a variable in the theoretical cell potential calculations.

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