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Development of hybrid aluminum-air battery fuel-cell system

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Abstract. Industrial 4.0 accelerates the need to introduce clean energy to accommodate the increase in electricity demand globally without causing environmental issues. Metal-air battery is a new type of energy storage system in which the metal anode is consumed to generate electricity through the electrochemical reaction. Among various types of the metal anode, aluminum is a promising energy carrier. Aluminum-air battery shows advantages such as high capacity, abundance, low cost, and being environmentally friendly. Traditional aqueous aluminum-air battery experiences restriction from application due to its self-corrosion issues. In this study, instead of reducing or limiting the self-corrosion issues, a different approach is proposed so to make use of the self-corrosion issues of the aluminum-air battery. By incorporating an additional hydrogen-air subcell to the aluminum-air battery, this hybrid system turned the self-corrosion issue into a beneficial reaction by utilizing the hydrogen gas produced from the aluminum anode as the fuel to power the hydrogen-air fuel cell and improving the overall power performance. The electrical performance of each system is studied experimentally using potassium hydroxide electrolytes. The hybrid system shows a great improvement as compared to a single system. The maximum power is improved by more than 40%. This study shows that the hybrid design is feasible in enhancing the aluminum-air battery performance and yet, maintaining low cost and low weight in nature.

Keywords: Battery, Aluminum-air battery, Fuel cell, Hydrogen fuel cell, Hybrid

1. Introduction

Fossil fuel, the primary energy source that provides mankind's energy demand worldwide has led to rapid depletion of the resources. To reduce the dependency on fossil fuels, it has promoted the development of the electrochemical energy system (ESS). ESS comprises batteries, electrochemical capacitors, and fuel cells [1]. Batteries are widely utilized in various applications especially in automotive industries due to their reliability and excellent performance and compact design [2]. Metal-air batteries utilizing metal elements as anode and consuming oxygen from the atmosphere in electricity generation have received attention from worldwide researchers. There are many types of metal that can be used as metals anode in a metal air batteries. Some metals include such potassium, lithium, sodium, zinc, tin-, magnesium, and aluminum-air [3]. Aluminum is a promising candidate



among various types of metal anode as it possesses high energy density, can be recycled easily with minimal loss, is safe, environment friendly, and available abundantly on earth. Aluminum-air batteries show a high-theoretical energy density of about 2791 Wh/kg and high theoretical cell voltage (2.7 V) [4]. An electric vehicle installed with aluminum batteries can travel up to eight times the distance traveled by using lithium-ion batteries [5]. In the aluminum-air battery, the aluminum anode will undergo an oxidation reaction and produce electrons. On the other hand, the air cathode takes in oxygen from ambient air and reduces it to hydroxyl ions [6]. This electrochemical process generates electricity. Studies suggested that alkaline solutions such as potassium hydroxide (KOH), and sodium hydroxide (NaOH) performed well as an electrolyte in the aluminum-air battery. The performance of the aluminum-air battery improved with increasing the concentration of the alkaline electrolytes. The peak power density showed an improvement to 45 mW/cm² from 23 mW/cm² as the concentration of NaOH increased from 1M to 5M [7]. However, high concentrations of alkaline electrolytes will cause large amounts of hydrogen to be generated [8]. A similar effect is also observed when KOH electrolyte is used [9, 10]. The parasitic reaction on the surface of the aluminum causes the production of hydrogen gas and cannot be stopped. This will reduce the overall utilization efficiency of the aluminum anode.

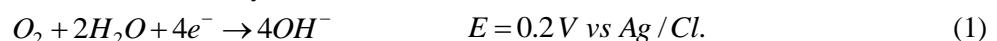
Most of the literature available focused on reducing the corrosion rate of the aluminum anode through alloying the aluminum metal and modification of the electrolyte. In this study, the generated hydrogen during the parasitic reaction is used as a fuel for a fuel cell system to generate electricity. The electrical performance of the hybrid system will be tested experimentally. The hybrid aluminum-air battery-fuel cell design will help to improve the overall electrical performance of the conventional aluminum-air battery. Besides that, this hybrid design also reduce the cost as there is no need to introduce corrosion inhibitors in the electrolyte.

2. Methodology

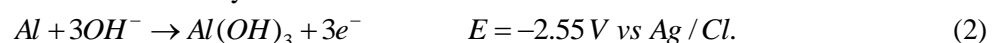
2.1. Discharge mechanisms of the hybrid system

In the aluminum-air battery, the aluminum anode undergoes oxidation while the reduction reaction occurs at the air cathode. This redox reaction generates electricity. The half-cell reaction and the overall reaction undegoes within the cathode and anode in the aluminum-air battery are as described in the equations below [11]. On the other hand, the parasitic reaction occurs at the aluminum anode when the aluminum reacts with hydroxyl ions in the electrolyte.

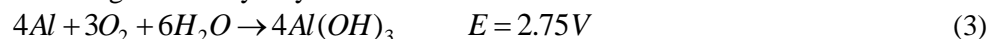
Cathode reaction in aluminum-air battery:



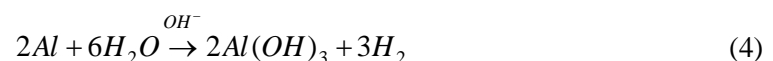
Anode reaction in aluminum-air battery:



The overall reaction of a single electrolyte system:

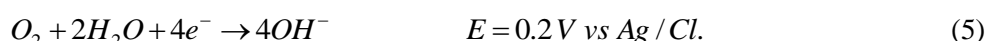


Parasitic reaction at anode:

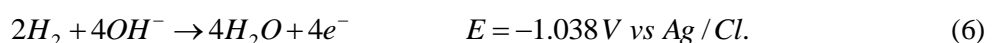


In the hydrogen-air subcell, hydrogen is consumed at the anode and undergoes oxidation to release electrons in the process. Contrarily, the reduction happens at the cathode side to release hydroxyl ions. The reaction is purely non-polluting as the by-product is water.

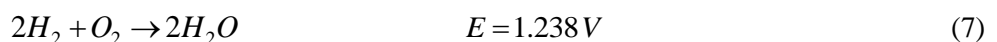
Cathode reaction in fuel cell:



Anode reaction in fuel cell:



Overall reaction in fuel cell:



2.2. Test rigs design

The hybrid system test rig consists of two main components, an aluminum-air subcell, and a hydrogen-air subcell. The aluminum-air subcell is using aluminum foil (Reynolds Consumer Products LLC) as anode and carbon cloth (AvCarb Material Solutions) as air cathode. The hydrogen-air subcell used the same carbon cloth as the anode whereas the cathode is sharing the same cathode with the aluminum-air subcell. The size of the aluminum foil and carbon cloth is 15 mm x 10 mm. The aluminum foil is located at the bottom of the test rig. When a parasitic reaction occurs, the hydrogen gas will float and move upwards to the hydrogen reservoir. A hydrogen compartment is placed on the top and acts as a reservoir for the hydrogen gas. Potassium hydroxide (KOH) is used as the electrolyte in the hybrid system. Figure 1 shows the design and cross-sectional view of the test rig. All the housing was made of Perspex and laser-cut was used to cut the Perspex into the desired shape. The battery case has a dimension of about 80 mm (L) x 80 mm (W) x 15 mm (H). Two slots with a size of 30 mm x 1 mm were used to house the hydrogen anode and carbon cathode. There is a 10 mm space to separate the gas diffusion electrode (GDE) and aluminum foil. This space is filled with KOH electrolytes.

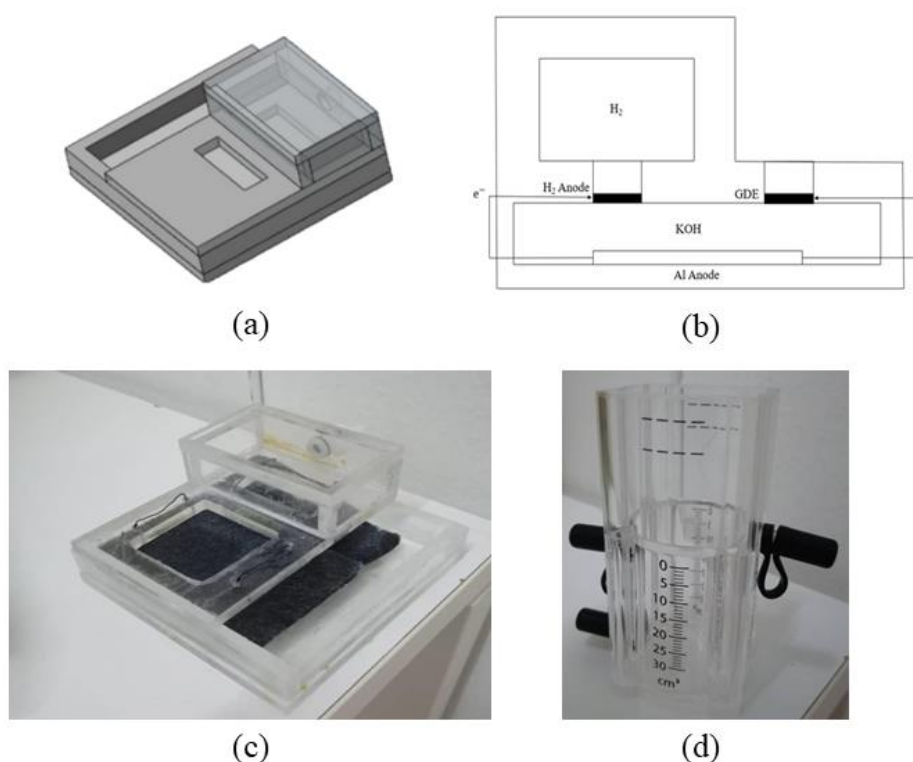


Figure 1. (a) CAD drawing of the hybrid system test rig. (b) Cross-section view of the hybrid system. (c) Prototype of the hybrid system test rig and (d) Hydrogen collection tube

2.3. Experiment Setup

The experiment was conducted using VersaStat 4 Potentiostat/Galvanostat workstation. Linear sweep voltammetry (LSV) was conducted with a scan rate of 10 mV/s ranging from open-circuit voltage to 0 V. Single electrode polarization and two electrode polarization were conducted and compared the performance of the aluminum-air battery subcell and hydrogen-air subcell. The hydrogen generated from the aluminum anode is channeled to the hydrogen collector. It will displace the water-filled in the hydrogen collector as it occupies the space in the hydrogen collector. The rate of hydrogen generation was measured in terms of the water displaced in the unit of $\mu\text{L/s}$. Parafilm was used as a sealant. It can help to prevent hydrogen gas from leaking out from the hydrogen reservoir to the surrounding.

3. Results and Discussion

3.1. Performance of aluminium-air battery subcell

Figure 2(a) shows the polarization curve for the aluminum-air battery subcell. The open-circuit voltage and the short circuit current for the aluminum-air battery are recorded at 1.33 V and 28 mA. The cell reached peak power output at a current of about 15 mA, in which the peak power output reached 6.2 mW. Initially at OCV, the cell experience a sharp drop in voltage to about 0.8 V at a current of 5 mA. This is due to the activation loss as a result of poor cathodic reaction and leads to poor oxygen reduction rate. Next, a proportional drop of voltage with increasing current suggests that the internal resistance of the battery increases. This contributes to the ohmic loss of the battery. Further increasing the current induces a sharp voltage drop again, especially in the high current region. This is caused by poor mass transport capabilities of the cell. The supply of the reactant from the cathode cannot catch up with the demand required by the anode. Hence, a rapid voltage drop occurs as the current is greater than 25 mA.

Figure 3(a) shows the results obtained for the single electrode polarization of the aluminum-air battery. Silver/silver chloride (Ag/AgCl) is used as the reference electrode. From equations (1) and (2), the standard potential for anode and cathode are -2.5 V and 0.2 V respectively. In this study, the potential for Al anode is recorded to be -1.33 V. There is a large deviation from the theoretical value, 2.5 V. The difference is about 1.18 V. This is because of the effect of overpotential. The parasitic reaction and activation loss are the factors attributed to the overpotential. The aluminum anode tends to self-corrupt to produce hydrogen gas when reacting with the water in the KOH electrolyte, which reduces the amount of aluminum anode available in the electrochemical reaction which generates electrons in the process. Moreover, the activation loss is caused by the formation of $\text{Al}(\text{OH})_3$. As time passes, $\text{Al}(\text{OH})_3$ will accumulate along the surface of the aluminum anode and hinder fresh aluminum to be consumed in the electrochemical reaction and hence, reduce the electrical performance. During the electrochemical reaction, the potential of Al reduces from -1.33 V to -0.62 V. The negative potential obtained indicated that oxidation occurs at the aluminum anode. The voltage tends to shift from a more negative value to a less negative value indicating the activity of OH^- ions start to decrease. The weak performance obtained in the experiment may be due to the poor cathode used in the study. The cathode does not provide a sufficient oxygen reduction reaction. Hence, it limits the movement of fresh OH^- ions to be fed to the anode. A good oxygen reduction electrocatalyst can help to enhance the electrical performance. In this study, the carbon cloth used has a pore diameter of 10 μm . This structure allows the oxygen from the atmosphere to move freely to the cathode. However, due to its porous structure and large pore size, the area of the carbon cloth decreases. This leads to a poor specific surface area and reduces the catalytic activity and eventually, reduces the performance of the battery [12].

3.2. Performance of hydrogen-air subcell

In the hydrogen-air subcell, the anode receives the hydrogen as fuel from the aluminum-air battery. Due to the irregular amount of hydrogen generated from the parasitic reaction at the aluminum anode, the supply of hydrogen fuel to the hydrogen-air subcell is not consistent. This may affect the performance of the hydrogen-air subcell. At the cathode, the oxygen is reduced to OH^- ions. The hydrogen-air subcell at the cathode side shares the same reduction mechanisms as the cathode of the aluminum-air battery. The polarization performance of the hydrogen-air subcell is as indicated in Figure 2(b). The curve is almost identical to the aluminum-air battery in which there is a sharp drop of voltage at low current and high current while maintaining a linear drop in voltage at intermediate current. The explanation for the phenomenon is identical to the aluminum-air battery. Generally, the hydrogen-air subcell perform weaker than aluminum-air battery in polarization study. This can be proven by observing the OCV and short circuit current in the polarization curve which was recorded at 0.8 V and 15 mA respectively. At a current of about 9.1 mA, a peak power of 2.73 mW is recorded. The disturbance on the curve is due to the inconsistent of hydrogen fuel from the aluminum-air battery.

The result for single electrode polarization is plotted in Figure 3(b). The theoretical voltage against Ag/AgCl is as shown in Equation (5) and Equation (6). From the experiment results, the

activation loss for both the anode and the cathode is about 0.2 V and 0.4 V respectively. At the anode, the half cell undergoes oxidation while reduction occurs at the cathode. The anode potential moves from -0.8 V to -0.44 V while there is a shift from -0.2 V to -0.44 V for the cathode of the hydrogen-air subcell.

By combining the electrical performance of the aluminum-air battery and hydrogen-air subcell, it can be seen that the peak power output improved. The standalone design suggests that the peak power output of the aluminum-air battery and hydrogen-air subcells are 6.20 mW and 2.73 mW respectively. When the peak power output is measured by combining these two systems, the power output is increased by 44 % to 8.93 mW. This improvement is due to the usage of generated hydrogen from the aluminum anode in the aluminum-air battery. Instead of wasting the generated hydrogen, it is converted into energy which in turn enhances the anode utilization.

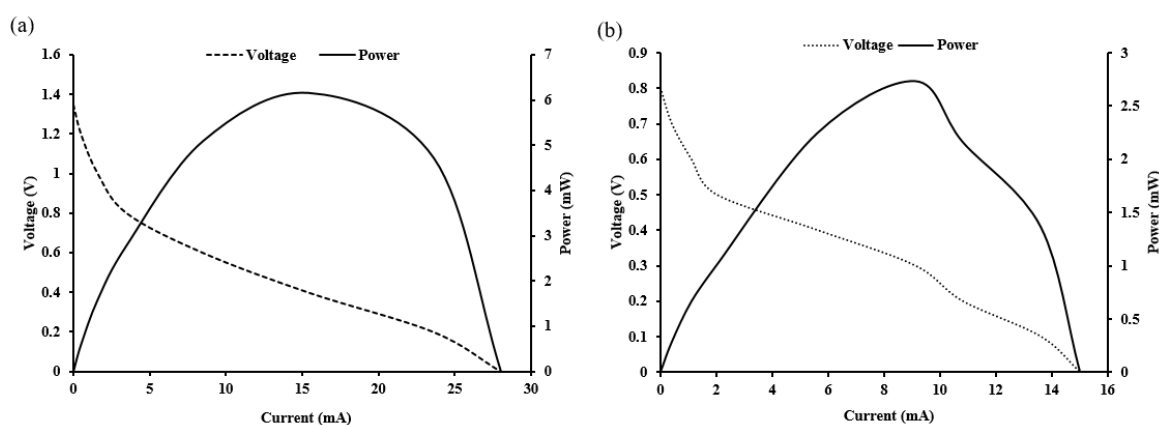


Figure 2. Polarization curve of (a) Aluminum-air battery subcell and (b) Hydrogen-air subcell

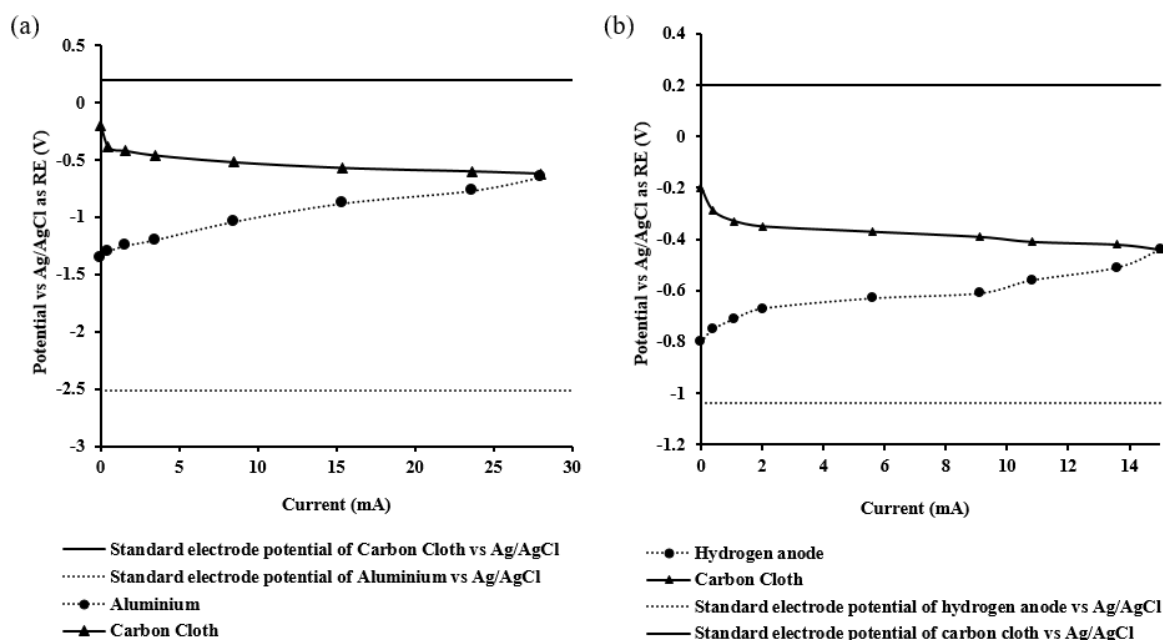


Figure 3. Single electrode polarization of (a) Aluminum-air battery subcell and (b) Hydrogen-air subcell vs Ag/AgCl as reference electrode.

4. Conclusion

An aluminum-air battery is undoubtedly an interesting energy storage system with a simple design and low cost. However, the parasitic reaction restricts the application of the aluminum-air battery. To

overcome its limitation, an aluminum-air battery and a hydrogen-air fuel cell is combined to form a hybrid system. This system is low cost and simple as the anode is made of aluminum kitchen foil and carbon cloth as the cathode. To further improve the performance of the aluminum-air battery, the hydrogen generated from the self corrosion of the aluminum anode is fed to the hydrogen-air fuel cell for electricity generation. A single system of the aluminum-air battery can only provide a power of 6.2 mW. Through the introduction of the hybrid hydrogen-air fuel cell, the peak power is improved by 44% to 8.93 mW. The hybrid design helps to increase the anode utilization rate as compared to the traditional aluminum-air battery.

Acknowledgements

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