

# High Performance Aluminum-Air Battery for Sustainable Power Generation

Weng Cheong Tan<sup>a</sup>, Lip Huat Saw<sup>a\*</sup>, Ming Chian Yew<sup>a</sup>, Dongyang Sun<sup>b</sup>, Wei-Hsin Chen<sup>c</sup>

<sup>a</sup> Lee Kong Chian Faculty of Engineering and Science, UTAR, Kajang, Malaysia – 43000.

<sup>b</sup> Nanomaterial unit, School of Engineering and Built Environment, Edinburgh Napier University, Edinburgh EH10 5DT, UK.

<sup>c</sup> Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan, ROC

Phone: +603-90860288

Fax: +603-90193886

\*E-mail address: sawlh@utar.edu.my, bernardsaw81@yahoo.com

## Abstract

Metal-air battery is receiving vast attention due to its promising capabilities as an energy storage system for the post lithium-ion era. The electricity is generated through oxidation and reduction reaction within the anode and cathode. Among various types of metal-air battery, aluminum-air battery is the most attractive candidate due to its high energy density and environmentally friendly. In this study, a novel polypropylene-based dual electrolyte aluminum-air battery is developed. Polypropylene pads are used as a medium to absorb the electrolyte, isolate the anode and cathode, control the hydrogen generation in the parasitic reaction. Potassium hydroxide is used as anolyte and sulfuric acid is used as catholyte. Parametric study is conducted to investigate the effect of electrolyte concentration and polypropylene separator thickness on the performance of the battery. The results show that the dual-electrolyte system can boost the open circuit voltage to 2.2 V as compared to the single electrolyte system for 5M of anolyte while maintaining specific discharge capacity of about 1390.92 mAh.g<sup>-1</sup>. The maximum peak power density has improved dramatically from 100 mW.cm<sup>-2</sup> to 350 mW cm<sup>-2</sup> for the dual electrolyte system.

Keywords: Metal-air battery; aluminum-air battery; hydrogen generation; energy storage system; dual-electrolyte system

## **1.0 Introduction**

Global pollution is becoming more severe nowadays due to the rapid development of technology which requires high energy usage. Burning of fossil fuels is still the primary energy extraction method available in the market which led to a severe environmental issue due to the emission of dangerous gas such as carbon dioxide. Hence, a paradigm shift is necessary to reduce the dependency on fossil fuels and replace it with a clean energy harvesting system. In the transportation sector, electrical vehicles (EVs) have gained attention due to their capabilities of reducing greenhouse gasses through eliminating fossil fuels in power generation. The battery is the most popular alternative to replace the internal combustion engine of the vehicle [1]. Some of the most common batteries used in the EV include lithium-ion battery, nickel-cadmium, nickel-metal hydride, and lead-acid battery [2, 3]. The lithium-ion battery is the most popular selection among all the battery types. It has high energy capacity and longer cycle life, but it also suffers from environmental issues as there is no proper solution to recycle the used battery and it is also prone to thermal runaway due to its narrow range of operating temperature [4, 5]. Currently, the performance of the lithium-ion battery is limited by the technology and their energy density is almost at its peak. It is predicted that the energy density of the battery can be increased by only 30% in the future and the travel distance is limited to 500 km [6, 7]. Therefore, it is crucial to explore a new type of battery as a substitution for the lithium-ion battery to extend the travel distance of the EV.

Metal-air batteries are a promising candidate to replace lithium-ion batteries. Studies have shown that metal-air batteries will produce three to ten times more energy density than lithium-ion batteries [8]. Besides that, metal-air batteries offer attractiveness such a low cost

and high energy capacities depending on the metal anode used [9]. There is a wide range of metals available for the metal anodes such as lithium, aluminum, sodium, potassium, and zinc [10]. In metal-air batteries, the metal anode undergoes oxidation and oxygen is reduced at the cathode. This redox reaction generates electrons and produces electricity. Among various types of metal-air batteries, aluminum-air batteries show a vast potential for the future energy storage system [11]. Aluminum-air batteries possess a high energy density of  $8.1 \text{ kWh.kg}^{-1}$  and a high theoretical potential of 2.7 V. This is because aluminum is low cost, easily available, and good electrical properties. Moreover, the recycling process of used aluminum is mature, further encouraging the application of aluminum as a metal anode. However, pure aluminum anode is not an ideal candidate as the anode for the aluminum-air battery as the pure aluminum anode will suffer severe corrosion with formation of  $\text{Al}_2\text{O}_3$  and  $\text{Al}(\text{OH})_3$  layers on the anode surface when reacting with water [12]. This reduces the aluminum utilization efficiency as the oxide layer impedes the reaction and hydrogen gas is generated as a parasitic reaction. This study is supported by the work from Mutlu et al. in which pure aluminum is subjected to high corrosion as compared to aluminum alloy [13]. The corrosion will lead to hydrogen generation which reduces the specific capacity of the aluminum-air battery [14, 15]. Hence, there is a need to reduce the corrosion rate of the pure aluminum anode. One of the solutions is alloying the pure aluminum to reduce the corrosion [16].

In the battery electrochemical reaction, the electrolyte is an important component to facilitate the movement of ions between the anode and cathode. In an aqueous aluminum-air battery system, the electrolyte can be alkaline, acidic, and neutral. Among three different types of electrolytes, alkaline was proved to perform the best in power generation. Wang et al. conducted a comparison of three different types of electrolytes on the performance of the aluminum-air battery [17]. The electrolytes used are sulfuric acid (acid electrolyte), potassium hydroxide (alkaline electrolyte), and potassium nitride (neutral electrolyte). The comparison

indicated that the potassium hydroxide electrolyte had the highest reaction rate of aluminum compared to potassium nitride and sulphuric acid. The maximum energy density achieved by the potassium hydroxide electrolyte is  $72.57 \text{ Wh.kg}^{-1}$  while sulfuric acid electrolyte only can achieve  $9.45 \text{ mWh.kg}^{-1}$ . The open-circuit voltage of the aluminum battery tends to reduce as the pH value decreases [18, 19]. Since alkaline electrolytes performed better than that of acidic and neutral electrolytes, most studies focus on using the alkaline electrolyte for the aluminum-air battery. The most popular alkaline electrolytes are potassium hydroxide (KOH) and sodium hydroxide (NaOH) with the concentration ranging from 0.2M to 4M [20]. The battery capacity tends to increase due to the increasing amount of  $\text{OH}^-$  ions in high concentration of KOH solution. However, high  $\text{OH}^-$  ions also induce a higher corrosion rate. Hence, there is a compromise between electrical performance and hydrogen generation rate in the system. Wang et al. conducted a numerical modelling and concluded that the amount of  $\text{OH}^-$  ions affect the corrosion rate and current density of the aluminum-air battery [21]. To achieve a high current density, the concentration of the electrolyte should be high. However, high concentration of electrolyte used is also associated with high corrosion which is not practical [22].

Tan et al. used polypropylene pad to reduce the corrosion in the aluminum-air battery [23]. In the design, a polypropylene pad is used as a medium to store the KOH electrolyte. The polypropylene pad not only serves as a storage for the electrolyte but also as a separator to isolate the anode and cathode. By increasing the concentration of the KOH, the electrical performance will also improve. To further improve the performance of the aluminum-air battery, a dual electrolyte system is proposed. In this system, two different types of electrolytes are used in anode and cathode respectively with a separator in between to prevent crossover of the electrolyte. Chen et al. combined an alkaline and acid electrolyte to form a dual electrolyte system for the aluminum-air battery [24]. The anolyte was KOH solution while the catholyte was sulfuric acid ( $\text{H}_2\text{SO}_4$ ). This configuration further enhanced the power density by almost

100% from a single electrolyte system which recorded at a peak of  $176 \text{ mW.cm}^{-2}$ . In the other work done by Wen et al. [25], the combination of alkaline-acid electrolyte can improve the open-circuit voltage by 30%. Moreover, a dual electrolyte system was also made possible by adding methanol in the anolyte [26]. The KOH anolyte was mixed with methanol, while the catholyte used was KOH solution. The presence of methanol improved the coulomb efficiency by 74% due to the lower corrosion rate at the anode side. Teabnamang et al. conducted a similar work to study the effect of the amount of water content in the mixture of methanol/KOH in the anolyte of an aluminum-air battery [27]. High water content corresponds to higher maximum power output in the system. The power density improved from  $4.78 \text{ mW.cm}^{-2}$  to  $19.60 \text{ mW.cm}^{-2}$  when the water content increased from 0% to 20% in the methanol/KOH mixture. The effects of reducing the corrosion rate are more significant than that of reducing the battery's internal resistance [28, 29]. Although the electrical performance is improved due to the addition of methanol, it is not widely applied due to its toxicity.

The main problem of the aqueous aluminum-air battery is the requirement of the good sealant of the battery to prevent leakage and electrolyte recirculation system. The issues can be resolved by introducing a paper-based separator to absorb the electrolyte. Wang et al. used paper to absorb a small amount of KOH and NaCl electrolyte and act as a separator [30, 31]. The soaked paper is then sandwiched between the anode and cathode to form an aluminum-air battery. The power density recorded for KOH and NaCl electrolyte were  $21 \text{ mW.cm}^{-2}$  and  $6.7 \text{ mW.cm}^{-2}$ , respectively. The design is small, low cost, and simple as it does not require an electrolyte circulation system to feed the fresh electrolyte to the anode. A maximum voltage output of 13.2 V is achieved when the batteries are connected in series to form a battery pack. On the other hand, paper soaked with KOH electrolyte is also possible with a power density of  $28 \text{ mW.cm}^{-2}$  which is higher than NaOH electrolyte [32]. By using MnO as a catalyst at the air

cathode, the power density can be improved by 40% when a thin porous paper was soaked in the KOH solution which serve as electrolyte in an aluminum-air battery [32].

Hu and Cui showed that the paper has a low resistance of about  $1 \Omega \cdot \text{sq}^{-1}$  [33] and possesses good electrical conductivity and mechanical flexibility when coated with a layer of carbon nanotubes [34]. Avoundjian et al. designed a  $9 \text{ cm}^2$  aluminum-air battery with paper as the separator [35]. It can be used to provide a total power of 3 mW. A microfluidic aluminum-air battery with paper separator was introduced by Shen et al [36]. The battery can produce an energy density of  $2900 \text{ Wh} \cdot \text{kg}^{-1}$  while maintaining a specific capacity of  $2750 \text{ Ah} \cdot \text{kg}^{-1}$ . However, most of the aluminum-air batteries with solid electrolyte still suffer from low performance. Although aqueous electrolyte system shows a promising result, the aqueous system required electrolyte recirculation system and bulky and lack of portability.

In the view above, this study introduced a dual electrolyte aluminum-air battery using polypropylene separator to increase the performance of the conventional aqueous electrolyte battery and facilitate compact design of the battery. Polypropylene pad will be used to store the catholyte and anolyte. Current design is simple and low cost as it does not require a complicated electrolyte recirculation system. The performance of the aluminum-air battery will be evaluated using different concentrations of anolyte and catholyte as well as separator thickness and polypropylene pad thickness. Then, the performance of the battery will be compared with a single electrolyte aluminum-air battery. Next, SEM and XRD analysis were conducted to investigate the changes in the microstructure of the aluminum anode and identify the composition presence in the battery after the reaction. The paper is arranged as follows: Section 2 discusses the mechanisms of the electrochemical reaction, the design of the battery, and the experimental procedure. This paper is followed by section 3 which presents the experimental results and discussions of the study under the effect of different parameters. Finally, based on the findings obtained, conclusions are concluded in section 4.

## 2. Methodology

### 2.1 Electrochemical reaction of aluminum-air battery

The electrochemical reactions of a single electrolyte system aluminum-air battery for the anode and cathode are illustrated in Equation 1 and Equation 2. An oxygen reduction reaction occurs (ORR) at the cathode side. The oxygen in the atmosphere is consumed and reduced into hydroxyl ions ( $\text{OH}^-$ ). The aluminum anode undergoes oxidation by releasing electrons to form aluminum ions at the anode side. These aluminum ions react with the hydroxyl ions to form aluminum hydroxide as a by-product during the reaction. Electricity generated through the movement of electrons in the battery correlated to the redox reaction by releasing the electron. Equation 3 shows the overall reaction of an aluminum-air battery with single electrolyte system [37].

Cathode reaction in an alkaline electrolyte:



Anode reaction in an alkaline electrolyte:



The overall reaction of a single electrolyte system:

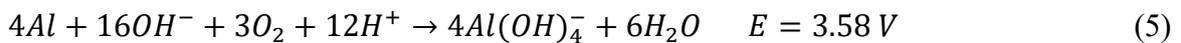


Whereas for a dual electrolyte system, an acidic electrolyte is used at the cathode side and the reduction reaction is shown in Equation. 4 [37].

Cathode reaction in an acidic electrolyte:



The overall reaction of a dual electrolyte system:



There is about 30% increase in the theoretical voltage of the dual electrolyte system compared to a single electrolyte system. However, both designs suffered from parasitic

reactions at the aluminum anode. The aluminum anode starts to corrode and react with alkaline electrolyte to form aluminum hydroxide and hydrogen gas. This reaction does not contribute to the electrical performance but reduces the anodic efficiency. The parasitic reaction is a major problem in the aluminum-air batteries. The formation of the aluminum hydroxide on the aluminum anode due to the parasitic reaction will hinder the movement of the ions in the electrolyte. Equation 6 shows the parasitic reaction in occurs at the anode.

Parasitic reaction at the anode [11]:



## 2.2 Dual electrolyte battery design

Figure 1 illustrated the design of the dual electrolyte polypropylene-based aluminum-air battery. A dry filter paper (Smith, Qualitative filter paper, medium speed with pore size 8-10  $\mu\text{m}$ ) was used as a separator to isolate the anode from the cathode. The filter paper has low diffusion rate which can help to reduce the diffusion of the anolyte or catholyte in the aluminum-air battery. In the long-term operation, only a limited amount of  $\text{H}_2\text{SO}_4$  or  $\text{KOH}$  might diffuse to the opposite direction. However, small amount of diffusion will not affect the performance of the battery as large amounts of the anolyte and catholyte are still present in the polypropylene absorbent pad. Besides that, the presence of  $\text{H}_2\text{SO}_4$  will not affects the reaction at the anode as it does not involve in the electrochemical reaction of the aluminum-air battery as shown in equation 3. Acrylic board was used to construct the battery body to contain the electrodes and separator. The aluminum anode used in this study was commercial grade aluminum alloy 6061 (2 mm thickness). Polypropylene absorbent pad from Crisben with a thickness of 2 mm (100% Polypropylene) was used as the absorbent for the anolyte and catholyte. Two breathing windows of 40 mm x 45 mm were cut on the acrylic board at the cathode side to supply oxygen to the battery and the cathode is made of graphite plate. The rubber gasket is used as a sealant and houses the anode and air cathode in the battery and is not

involved in the electrochemical reaction. This design eliminates the need of an electrolyte recirculation system and limit the self-corrosion at the anode by controlling the amount of electrolyte absorbed by the polypropylene pad. Potassium hydroxide (KOH) electrolytes with different molarities were prepared by dissolving a potassium hydroxide pellet (System Chemicals) with distilled water. A total of 4 ml of KOH electrolyte was absorbed by the polypropylene pad and used as a solid electrolyte at the anode side. On the other hand, sulfuric acid with different concentrations was prepared by diluting a concentrated sulfuric acid (Merck). A total of 2 ml of H<sub>2</sub>SO<sub>4</sub> was absorbed by polypropylene pad and used as solid electrolyte at the cathode. A layer of activated carbon and manganese oxide (MnO) (HmbG Chemicals) is deposited on the graphite surface to act as an electrocatalyst. The carbon black and MnO mass ratio are fixed at 1:1 [38].

### **2.3 Experimental Procedures**

The experiment was conducted by investigating the effects of different KOH and H<sub>2</sub>SO<sub>4</sub> electrolyte concentrations and discharge current on the battery's performance. The open-circuit voltage (OCV) was measured using an electrochemical workstation (VersaSTAT 4, Ametek). The polarization curve of the battery was obtained by conducting the linear sweep voltammetry test. The OCV of the battery is swept through 0 V using a scan rate of 5 mV.s<sup>-1</sup>. The discharge performance of the battery is investigated by changing the concentration of the electrolytes and discharge current. To ensure consistency of the results, all the tests were performed three times. After each test, the aluminum anode was removed, and the weight was measured. The surface morphologies of the anode after the discharging process were analyzed using SEM. Next, X-Ray diffraction (XRD) analysis was used to examine the composition present on the anode. It is conducted by using a scan rate of 2° per minute for a scan range from 5 to 85 degrees. The XRD spectrum is then analyzed using X'Pert HighScore Plus.

### **3. Results and Discussions**

#### **3.1 Effects of the separator thickness**

The performance of the current aluminum-air battery design is affected by several factors such as thickness of the separator, concentration of the anolyte and catholyte and thickness of the polypropylene pad. The role of the separator is to isolate the polypropylene pad at the anode and polypropylene pad at the cathode and reduce the mixing of anolyte and catholyte in the battery but allow the ions transfer to occur. Mixing of anolyte and catholyte is unfavourable as it can reduce the battery's performance. Individual thickness of the filter paper is 0.2 mm. Filter papers are stacked to produce separator with three different thickness of the separator which is 0.2 mm, 0.4 mm and 0.6 mm. Although a thin separator will reduce the ionic resistance, it will also cause mixing of anolyte and catholyte and affect the performance of the battery. The dual electrolyte battery will behave like a single electrolyte battery. Hence, there is a need to optimize the separator thickness to ensure the power output of the battery is always at its peak.

As shown in Figure 2 of the battery's performance using discharge current of 10 mA, the discharge duration for the 0.2 mm thick separator is about 30 mins. As time passes, infiltration of the electrolyte will occur and cause mixing of anolyte and catholyte. Increasing the thickness of the separator to 0.6 mm helps to prevent the mixing and reduce the movement of  $\text{OH}^-$  ions. Hence, the voltage is generally lower than using a 0.4 mm thick separator. Besides that, the discharge duration is also shorter than that of the separator with 0.4 mm thickness. The best performance is achieved by using the thickness of 0.4 mm; it achieved an optimum setting for the ion transfer process and infiltration of the electrolytes. As a result, it can provide higher voltage and longer discharge duration. This observation is coherent with the study by Wang et al. on the aqueous dual electrolyte system [31]. Since only 4 ml of electrolyte is added to the anolyte and catholyte, the discharge duration is limited to about 1 hour. By providing

extra electrolyte to both anolyte and catholyte, the discharge duration of the battery can be improved.

The thickness of the filter paper plays an important role in affecting the movement of  $\text{OH}^-$  ions. Since the 0.4 mm separator provides the best performance on the aluminum-air battery, the experiment will be conducted using two filter papers for the rest of the study. On the other hand, the cathode does not show degradation and can be reused for the rest of the test.

### **3.2 Effects of polypropylene pad thickness**

In this study, two different thicknesses of polypropylene pads were used, which is known as thin pad with thickness of 1.68 mm and thick pad with thickness of 4 mm. 3M of KOH was used as an anolyte, while the catholyte consists of 3M of  $\text{H}_2\text{SO}_4$ . Polarization test and constant discharge current test were performed to compare the effects of the polypropylene pad thickness on the performance of the battery.

In the polarization study shown in Figure 3(a), the maximum power density generated is greatly improved by reducing the thickness of the polypropylene pad. Thin polypropylene pad can provide higher power density which is about  $240 \text{ mW}\cdot\text{cm}^{-2}$  as compared to about  $80 \text{ mW}\cdot\text{cm}^{-2}$  achieved by thick polypropylene pad. The improvement is about three-fold for the thin polypropylene pad used as the medium to absorb the KOH electrolyte. This is because thin polypropylene pad has a better diffusion rate compared to thick polypropylene pad. The movement of ions is more favourable due to the short travel distance between anode and cathode which in turn, improves the power output of the battery as it can enhance the ions movement to facilitate better electrochemical reaction.

There is no distinguishable difference in the voltage reduction at a low discharge current for thin and thick polypropylene pads. At low discharge current, the voltage drop is dominated by the overpotential. Overpotential of the battery is usually affected by the effects of the catalytic surface. Since the cathode used in the experiments are the same, the results of

overpotential are not observed when comparing thin and thick polypropylene pads. The voltage tends to drop linearly due to ohmic loss as the discharge current increases. The charge transport of the reactant plays an important role in the ohmic loss. Comparison of thin and thick polypropylene pads, thick polypropylene pad suffers a more severe voltage drop than that of the thin polypropylene pad. This suggested that the movements of electrons in the thin polypropylene pad are freely and contribute to the higher voltage output. The sharp drop in voltage for thick polypropylene pad shows that the ohmic resistance in thick polypropylene pad is higher than the thin polypropylene pad. Since the ohmic resistance in thin polypropylene pad is the lowest, the power generated is also higher. Besides that, reducing the thickness of the polypropylene pad allows high discharge current. At high discharge current, the voltage drop is dominated by mass transport. In thin polypropylene pad, a discharge current of 155 mA is achieved as opposed to 95 mA for thick polypropylene pad. This is due to the reactants traveling in a shorter distance in thin polypropylene pad and enhancing the rate of electrochemical reaction.

The discharge performance of the battery for thin and thick polypropylene pad is illustrated in Figure 3(b). The discharge current used is 30 mA. In general, thin polypropylene pad outperform the thick polypropylene pad. Thin polypropylene pad can last 75 minutes of discharge while thick polypropylene pad can last only 53 minutes of constant discharge current at 30 mA. The discharge duration is improved by 40% for thin polypropylene pad. Moreover, the discharge voltage of the thin polypropylene pad is also higher than that of thick polypropylene pad. During the discharge cycle, thin polypropylene pad can provide voltage output ranging from 1.8 V to 1.2 V with gradual voltage reduction through the discharge period. On the other hand, thick polypropylene pad can only provide voltage output ranging from 1.5 V to 1.2 V. Since a thin polypropylene pad provides the optimum performance for the

aluminum-air battery, the experiment will be conducted using thin polypropylene pad for the next study.

### **3.3 Effect of anolyte concentration**

The concentration of the anolyte is also an important parameter that can affect the performance of the battery. The performance of the aluminum-air battery is investigated by varying the concentration of anolyte while the concentration of catholyte is kept constant. The polarization curves of the aluminum-air battery with different concentrations of anolyte and 3M of H<sub>2</sub>SO<sub>4</sub> catholyte are shown in Figure 4(a) and (b). In general, the performance of the battery is positively correlated to the concentration of anolyte. The OCV remains almost constant regardless of the concentration of anolyte at about 2.2 V. However, a sharp drop in voltage was observed when 1M of KOH was used. This is due to limited OH<sup>-</sup> ions available for the electrochemical process in 1M of KOH electrolyte. By using a higher concentration of KOH, more OH<sup>-</sup> ions are available for the electrochemical reaction and more power is generated. At 5M of KOH anolyte, the maximum peak power density is about 350 mW.cm<sup>-2</sup> and higher than that of the 1M of KOH anolyte used in the aluminum-air battery.

Furthermore, the performance of the aluminum-air battery is investigated with different discharge currents and different concentrations of anolyte while maintaining 3M of catholyte at constant. The discharge curves are plotted in Figure 4(c), (d) and (e). At discharge current of 10 mA, 1M of anolyte shows a quick drop in voltage from 1.9 V to 0 V within 70 minutes. No flat plateau voltage output is observed. Increasing the concentration of anolyte to 3M shows a better performance. It can provide the voltage output in the range of 1.6 V to 1.7 V by maintaining it for about 110 minutes before the energy is depleted. Further increasing the concentration of anolyte to 5M can extend the discharge duration to about 278 mins with the drawbacks of the lower voltage output of about 1.4 V. As the discharge current increases to 30 mA and 50 mA, there is a drop in voltage output and discharge duration. Taking 5M anolyte

as an example, the discharge duration is dropped to about 120 minutes and 50 minutes for discharge current of 30 mA and 50 mA, respectively. Moreover, the output voltage decreased sharply followed by the increase of the discharge current. This is because when discharge current is increased, more energy is drawn from the battery, and the electrochemical reaction rate is also increased. However, due to limited  $\text{OH}^-$  ions supply, the battery degraded rapidly at high discharge current. The amount of  $\text{OH}^-$  becomes the limiting factor that reduces the discharge duration of the aluminum-air battery. From the literature, the aluminum-air battery should show an improvement in performance with increasing of KOH concentration and the voltage output and discharge duration is positively correlated with the concentration of KOH electrolyte [20, 21]. Although the polarization curve is obeying the general observation in which a high concentration of KOH will result in a higher power and voltage as compared to a low concentration of KOH, the discharge curve does not show a similar trend. The discrepancy is due to dual electrolyte design of the battery. A linear relationship between the concentration of KOH with the performance of the aluminum-air battery only works in a single electrolyte system. In the dual-electrolyte aluminum-air battery, the performance is affected not only by the concentration of anolyte but also the concentration of catholyte. The difference in concentration for both the electrolytes will affect the ions cross over to initiate the electrochemical reaction.

In terms of the specific discharge capacity of the battery, it is shown that higher concentration of KOH electrolytes will produce higher specific discharge capacity. At discharge current of 10 mA, 1M of KOH achieved a specific discharge capacity of 174.33  $\text{mAh}\cdot\text{g}^{-1}$  and it is improved to 690.30  $\text{mAh}\cdot\text{g}^{-1}$  for 5M of KOH while maintaining the concentration of catholyte at 5M. The improvement is caused by the increases in  $\text{OH}^-$  ions when higher concentration of KOH is used. This specific discharge capacity is still low and can be improved by increasing the discharge current. When the discharge current is increased

to 30 mA, the specific discharge capacity is greatly improved to about five folds for 1M of KOH to 873.64 mAh.g<sup>-1</sup> and about two folds for 5M of KOH to 1329.33 mAh.g<sup>-1</sup>. This is because as the discharge current increases, more OH<sup>-</sup> ions are utilized in electrochemical reactions and hence, produce better electrical performance and reduce the rate of parasitic reaction.

### 3.4 Effect of concentration of catholyte

In this section, the effect of different concentrations of H<sub>2</sub>SO<sub>4</sub> catholyte is evaluated using 30 mA of discharge current while maintaining same concentration of KOH anolyte. The polarization study of the different concentration of catholyte with 5M of anolyte is illustrated in Figure 5(a) and (b). The test result showed that high concentration of catholyte can boost the performance of the battery. When 1M of catholyte is used, the maximum current and power density achieved are about 190 mA.cm<sup>-2</sup> and 200 mW.cm<sup>-2</sup>, respectively. Increasing the concentration of the catholyte to 5M boosts the current and power density to about 450 mA.cm<sup>-2</sup> and 500 mW.cm<sup>-2</sup>, respectively. Based on a previous study, a solid-state aluminum-air battery usually has a low performance due to the impeded ionic diffusion in the electrolyte. A solid-state gel-electrolyte usually provides a few or tens of mW.cm<sup>-2</sup> [39-41]. In this study, the maximum power density is about 13.88 mW.cm<sup>-2</sup>, which is comparable to the solid-state aluminum-air battery. Although the polarization curve shows that increasing the concentration of catholyte improves the power density, the results in the discharge curves do not agree with the observation in the polarization curve. This is because the diffusion of the ions through the polypropylene pad and separator is a complicated process and affects the discharge performance of the battery.

When 1M of anolyte is used and the catholyte is varied from 1M to 5M, the initial discharge voltage remains relatively close to each other as shown in Figure 5(c) and (d). This suggested that the discharge voltage is not affected by the concentration of the catholyte when

1M of anolyte is used. The discharge voltage is limited by the anolyte concentration, and this is the limiting factor that affects the performance of the battery. Since the anolyte used is 1M, the performance is relatively low, and the discharge duration is short. The longest discharge duration is achieved by 1M of anolyte with 1M of catholyte is about 23 mins only. Hence, the low concentration of catholyte will lower the discharge duration and reduce the capacity of the battery. This is due to an increase of the half-cell reaction at the cathode side, which in turn involves the formation of water molecules at the cathode. As a result, more water molecules are formed and block the surface area and eventually, causing the battery to discharge rapidly due to the water clogging on the cathode used in the battery. This is also known as flooding of the electrode [11]. There is no improvement in half-cell reaction on the anode side due to the limited  $\text{OH}^-$  ions provided by the low concentration of KOH used at the anode. Although the half-cell reaction at the cathode side increases the formation of  $\text{H}^+$  ions for the anode to undergo an electrochemical reaction, it does not help to improve the performance of the battery. The performance is limited due to the low concentration of anolyte used at the aluminum anode and not sufficient fresh  $\text{OH}^-$  ions supplied to the cathode to complete the electrochemical reaction. Hence, a high concentration of catholyte is unfavourable for low concentration of anolyte as it cannot help to improve the discharge performance while reducing the discharge duration.

There is a significant improvement in the discharge duration when the concentration of the anolyte is increased to 5M. When 5M of KOH and 1M of  $\text{H}_2\text{SO}_4$  is used, the discharge duration is significantly improved to 125 mins. The improvement of discharge duration is due to the higher amount of  $\text{OH}^-$  ions available in 5M of KOH for the electrochemical reaction. However, the voltage is generally lower as compared to 1M of KOH and 1M of  $\text{H}_2\text{SO}_4$ . This is because, at a high concentration of anolyte and low concentration of catholyte, the diffusion of  $\text{OH}^-$  ions from the anode to the cathode is faster than that of the diffusion of  $\text{H}^+$  ions from the cathode to the anode. Therefore, the limiting factor now occurs at the cathode in which the

half-cell reaction at the cathode is not able to match with the anode. As a result, low voltage output is observed. On the other hand, when the concentration of catholyte is increased to 5M, the voltage output is greatly improved. More than 1.5 V is observed followed by a sharp decrease in voltage suggesting that the discharge duration is short. This is because a high reaction rate induces a large amount of water formation at the cathode which reduces the binding site for electrochemical reaction.

The relationship between the concentration of anolyte and catholyte is significant at high discharge current. Figure 6 shows a discharge curve at a discharge current of 100 mA for different concentrations of anolyte and catholyte. The battery equipped with 1M of KOH is not able to discharge using discharge current of 100 mA. Hence, experiments are conducted using 3M, 5M and 8M of KOH with different concentrations of catholyte. At 3M of KOH with different concentrations of catholyte, increasing the concentration of catholyte reduced the discharge duration and the voltage output. However, the combination 3M of KOH and 3M of H<sub>2</sub>SO<sub>4</sub> does not obey the phenomenon in which it has the highest discharge duration and voltage output. This behavior is similar to the combination 1M of KOH and 1M of H<sub>2</sub>SO<sub>4</sub> at discharge current of 30 mA. This suggested that maintaining the same concentration of anolyte and catholyte can provide the highest voltage output and discharge duration for the aluminum-air battery. Maintaining the same concentration is important to ensure a constant flux rate in exchanging H<sup>+</sup> and OH<sup>-</sup> ions which in turn maintains a better battery performance. Both the cathode and anode do not overtake each other and hence, ensure more stable performance. However, this behaviour is not observed for the combination of 5M of KOH and 5M of H<sub>2</sub>SO<sub>4</sub>. Although it maintains the highest voltage output as shown in Figure 5(d), the discharge duration is not the longest as compared with other concentrations of catholyte. As discussed before, a high concentration of catholyte will reduce the discharge duration due to the formation of water molecules in the half cell reaction. The same observation is recorded when the concentration

of anolyte is increased to 8M. Lower voltage output and lower discharge duration is associated with increasing the catholyte concentration.

The specific discharge capacity tends to reduce with increasing catholyte concentration. Under discharge current of 30 mA, the 5M of anolyte with 1M of catholyte achieved the highest specific discharge capacity of 1390.92 mAh.g<sup>-1</sup> in this study. It tends to reduce to only 714.06 mAh.g<sup>-1</sup> when the concentration of catholyte is increased to 5M. At high catholyte concentration, water flooding of electrolytes tends to limit the reaction at the cathode site. Hence, causing a reduction in ORR and performing poorly in the aluminum-air battery. The same phenomenon is observed for high discharge current as well. Hence, there is a close relationship between the concentration of anolyte and catholyte. At a constant concentration of anolyte, increasing the concentration of catholyte will decrease the discharge duration and voltage output. It is better to keep a low concentration of catholyte to get a better voltage output and longer discharge duration. However, this is not always true as maintaining the same concentration of anolyte and catholyte (for 1M and 3M) can ensure better voltage output and higher discharge duration except for a high concentration of catholyte at 5M. When 5M of KOH and 5M of H<sub>2</sub>SO<sub>4</sub> is used, it can increase the voltage output but not the discharge duration.

### **3.5 Comparison between single and dual electrolyte system**

Unlike a dual electrolyte system, a single electrolyte system is simple and only needs KOH anolyte for the battery. Besides, filter paper is also not needed and a polypropylene pad act as the separator to isolate the anode and air cathode. Since only KOH is involved in the electrochemical reaction, the electrochemical reaction is different from the dual electrolyte system. The electrochemical reactions for single electrolyte aluminum-air battery are indicated in Equation 1 to Equation 3. The theoretical voltage is generally lower for a single electrolyte system. A comparison study between the performance of a single electrolyte system and a dual electrolyte system is conducted using different concentrations of KOH electrolyte. The

comparison is based on the dual electrolyte system with cathode concentration fixed at 3M of  $\text{H}_2\text{SO}_4$  and 4 ml of KOH electrolyte is added to the polypropylene pad for both electrolyte systems.

As shown in polarization curves in Figure 7(a) and (b), the OCV for the single electrolyte system is lower than that of the dual electrolyte system. Single electrolyte system can achieve OCV of about 1.6 V which is about 30% lower than that of the dual electrolyte system with OCV of about 2.1 V. The improvement of OCV in the dual electrolyte system is due to the higher oxygen reduction reaction in the acidic medium of the cathode as indicated in Equation 4 and Equation 5. There are few benefits associated with the dual electrolyte system. Firstly, the voltage output for a dual electrolyte system is always higher than that of the single electrolyte system. Secondly, the voltage drops due to increasing the discharge current is generally lower for the dual electrolyte systems. Moreover, the dual electrolyte system shows improvement in the maximum capacity of the battery and power generated. For 1M of KOH, the maximum power density produced in the single electrolyte system is about  $33 \text{ mW}\cdot\text{cm}^{-2}$  and it is then improved to  $170 \text{ mW}\cdot\text{cm}^{-2}$  for the dual electrolyte system. This enhancement is also observed for 3M and 5M of KOH and the power density is increased by 3 folds and 3.5 folds respectively for the dual electrolyte system. This improvement is obvious, suggesting that dual electrolyte system possess a huge potential for the aluminum-air battery. The improvement in the cathodic reaction is the main factor leading to the high-power density produced in the dual-electrolyte system.

The discharge curve illustrated in Figure 7(c) shows the comparison of the aluminum-air battery for both electrolyte systems. The aluminum-air batteries are tested under discharge current of 30 mA. Two scenarios are observed from the experimental results, the discharge voltage for the dual electrolyte system is always higher than that of the single electrolyte system and the discharge duration for the dual electrolyte system is always lower than the single

electrolyte system. In 1M of KOH, a dual electrolyte system can produce voltage higher than 1.5 V and remain for about 39 mins. On the other hand, 1M of KOH single electrolyte system shows a constant voltage of only about 1 V for about 41 mins. The voltage is about 50% lower while maintaining almost similar discharge duration. The difference in discharge duration is more obvious for a higher concentration of KOH electrolyte. In 5M of KOH, the discharge duration for the dual electrolyte and single electrolyte systems are about 84 minutes and 113 minutes respectively. However, the voltage output for a dual electrolyte system range from 2 V to 1.5 V during the discharge cycle while it is only 1.2 V for a single electrolyte system. As discussed previously, the improvement in voltage is due to the improvement of ORR reaction. More  $\text{OH}^-$  ions will be consumed during the process and leads to higher water generation at the cathode side. Since a limited amount of KOH electrolyte is added in the polypropylene pad,  $\text{OH}^-$  ions are consumed at a higher rate for electrochemical reaction and the KOH electrolyte for the dual electrolyte system dried out at a rapid rate and the discharge duration is reduced.

Comparison of the specific discharge capacity between single and dual electrolyte systems showed that, there is a great improvement especially for 1M and 3M of KOH electrolytes as indicated in Figure 7. The improvement is about three folds and two folds, respectively. However, the improvement is not obvious for 5M of KOH. Although the specific discharge capacity remained same for both systems, the dual electrolyte system still outperforms the single electrolyte system by producing a higher OCV. Hence, the introduction of a dual electrolyte system can enhance the ORR of the cathode which improves the electric performance of the aluminum-air battery. Therefore, a dual electrolyte system offers higher voltage and power output with reduced discharge duration as compared to a single electrolyte system. In the long-term operation, the battery performance can be enhanced by supplying fresh electrolyte into the anolyte and catholyte. When the volume of electrolyte is sufficient,

the battery can discharge for a longer time while maintaining a constant discharge voltage until the aluminum anode is fully consumed.

### **3.6 SEM and XRD analysis**

The aluminum anode tends to undergo self-corrosion and remains as a main issue in the aluminum-air batteries that cannot be eliminated. Most studies emphasized on introducing different additives to reduce the corrosion rate. High corrosion rate reduces the aluminum anode utilization efficiency and generates hydrogen gas as a by-product due to the parasitic reaction between  $\text{OH}^-$  ions and the aluminum anode. The corrosion is more severe in the aqueous aluminum-air battery using liquid alkaline electrolyte. This is due to direct contact of the aluminum anode with the aqueous alkaline electrolyte. In order to control the corrosion rate of the aluminum anode, a limited amount of KOH electrolyte was absorbed in polypropylene pad and the polypropylene pad acts as a barrier to prevent excess KOH electrolyte reacts with the aluminum anode and reduce the parasitic reaction. SEM and XRD analysis were conducted to examine the surface morphology of the aluminum anode after the reaction to gain understanding on the corrosion scenario at the aluminum anode.

Figure 8 shows the SEM image of the pristine aluminum anode and the aluminum anode after discharging using 10 mA with different concentrations of KOH electrolyte. It was found that when the concentration of the KOH electrolyte increases from 1M to 5M, the aluminum anode surface becomes rough as compared to the original aluminum anode before the discharging test. As the electrolyte concentration increases to 1M, the surface starts to become uneven, and some powdery structure starts to form on the aluminum anode surface. However, most of the aluminum anode surface is still flat suggesting that the corrosion is not severe. When the concentration of the KOH electrolyte is increased to 3M, a more powdery-like structure is found. The surface becomes very rough, pits and holes are observed. At this point, a very small amount of flat surface is still observable. Lastly, the corrosion is the severest for

5M of KOH. The surface is highly uneven, and a high percentage of the powdery-like structure is observed on the aluminum anode suggesting that many impurities are deposited on the surface. High concentration of alkaline electrolyte promotes the formation of impurities substances on the aluminum anode surface. There is no flat surface as observed from the SEM image. It can be deduced that corrosion is getting severe as the concentration of the KOH electrolyte used is increasing. In the macroscopic view shown in Figure 8, the aluminum anode shows a greater corrosion, and the surface of the aluminum anode becomes rougher for high concentration of KOH. Although the aluminum is severely corrosion under the discharge testing for 5M concentration, the aluminum anode can be reused in the aluminum-air battery after polishing the aluminum anode to remove the aluminum hydroxide on the surface. Fresh aluminum will be readily available again after the aluminum hydroxide is removed. In the long run, when the aluminum anode is fully consumed and converted to aluminum hydroxide, the aluminum hydroxide can be recycled back to aluminum which makes the aluminum-air battery a green energy storage system.

XRD test is then performed to investigate the components of the impurities formed on the aluminum anode. The powdery-like structure is removed from the aluminum plate and tested. By comparing the peak of the impurities with the database, it was found out that most of the impurities are aluminum hydroxide and aluminum as shown in Figure 8(e). Aluminum hydroxide is formed as a by-product during the electrochemical reaction in generating electricity after the discharge test, as predicted in the electrochemical reaction in Equation 3. Aluminum hydroxide will shorten the life cycle of the battery. Accumulation of the aluminum hydroxide on the aluminum anode will create a barrier that prevents the active site of the aluminum. Hence, the rate of the reaction will reduce and eventually stop as fresh aluminum is not readily available for the electrochemical reaction. At last, it causes a decrease in battery performance.

#### **4.0 Conclusion**

A novel polypropylene based dual-electrolyte aluminum-air battery with mixed pH electrolyte configurations for anode and cathode is developed and the performance of the battery is characterized. The thickness of the separator and polypropylene pad, concentration of anolyte and catholyte are important parameters affecting the performance of the dual-electrolyte aluminum-air battery. From the study, it was found that 0.4 mm of separator produced the optimum battery performance. Moreover, a thin polypropylene pad is more favored than the thick polypropylene pad for the dual-electrolyte aluminum-air battery. It is noted that the effects of the anolyte and catholyte concentration on the electrical performance of the aluminum-air battery are not positively correlated as the concentration of the anolyte and catholyte depends on each other in affecting the electrical performance of the battery. In general, high concentration of anolyte and catholyte will improve the power density and capacity of the battery. On the other hand, the discharge study showed that high concentration of catholyte will reduce the discharge duration of the battery. A higher corrosion rate is also associated with high concentration of the anolyte used at the anode. A comparison of single and dual electrolyte aluminum-air batteries was conducted, and it showed that dual electrolyte system can perform better than single electrolyte system. The open circuit voltage, discharge voltage, and specific discharge capacity are improved for the dual electrolyte system compared to the single electrolyte system. The optimum combination of the parameters is 5M of anolyte and 1M of catholyte in which it can generate a specific discharge capacity of 1390.92 mAh.g<sup>-1</sup>. The performance of the aluminum-air battery is limited by the separator material and the ORR at the cathode. Future study on separator and air cathode material can be conducted to increase the overall performance of the dual electrolyte aluminum-air battery.

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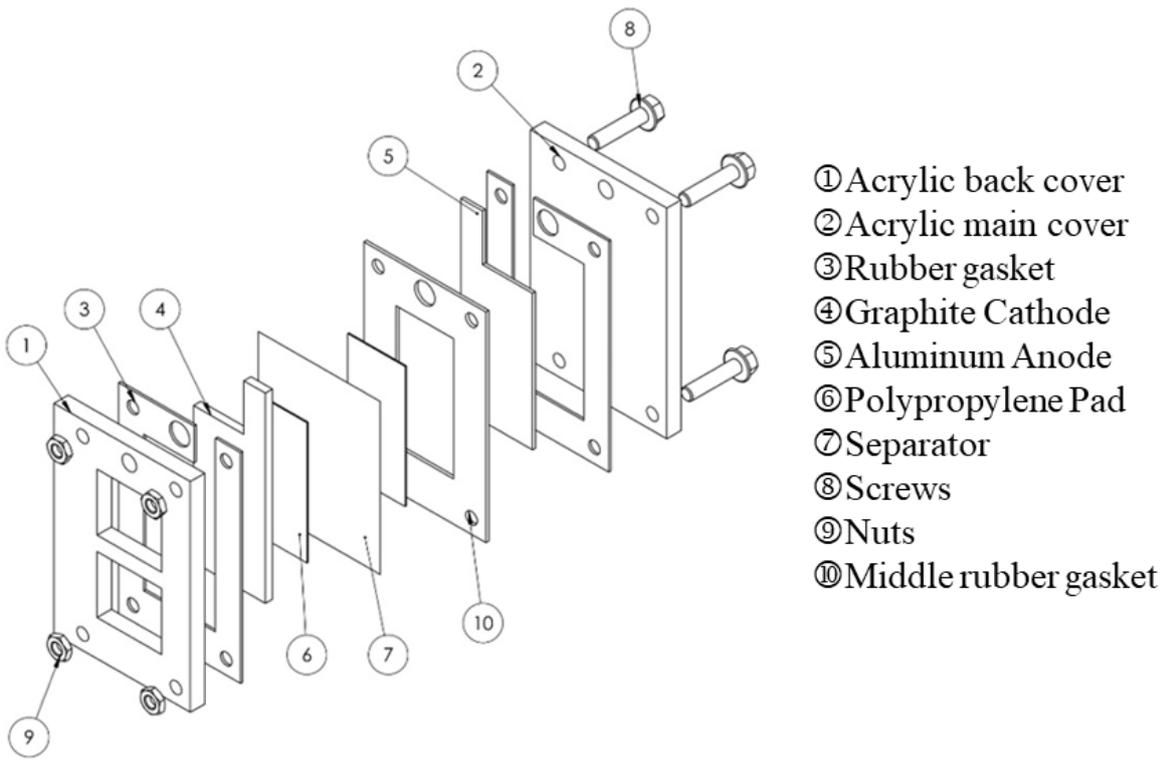


Figure 1. Schematic diagram of the polypropylene dual electrolyte aluminum-air battery.

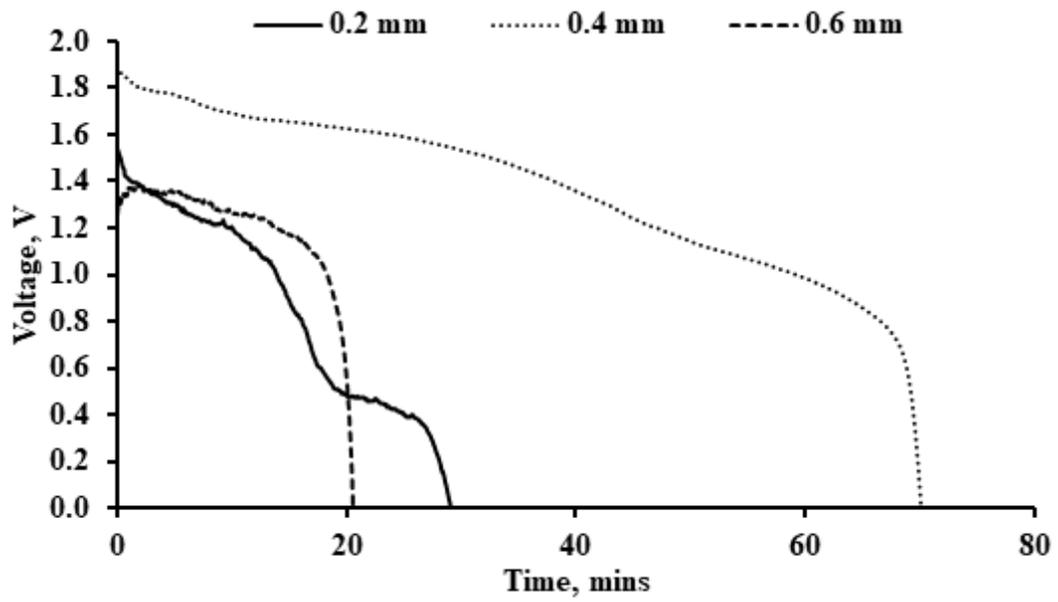


Figure 2. Discharge curve of different thickness of separator in the dual electrolyte aluminum-air battery.

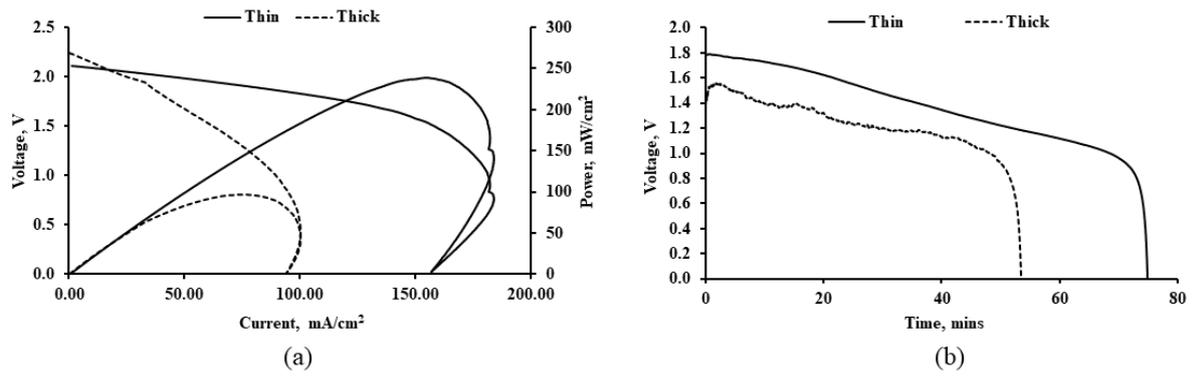


Figure 3. (a) Polarization curve and (b) discharge curve of the thin vs thick polypropylene pad in the dual electrolyte aluminum-air battery.

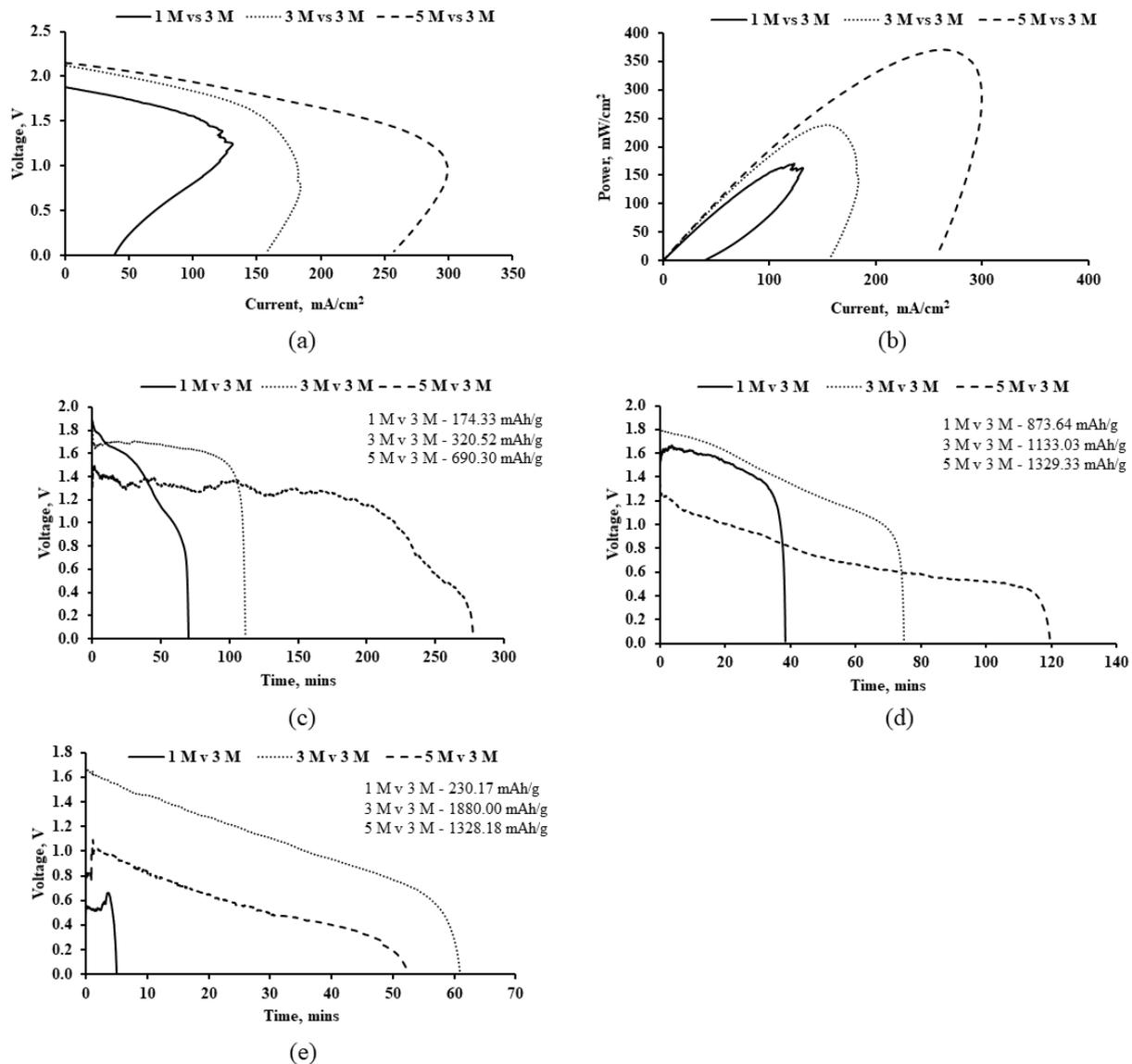


Figure 4. Polarization characteristics of the aluminum-air battery (a) Voltage vs current density, and (b) Power density vs current density and the discharge curve for various current densities (c) 10 mA, (d) 30 mA and (e) 50 mA using different concentrations of electrolyte.

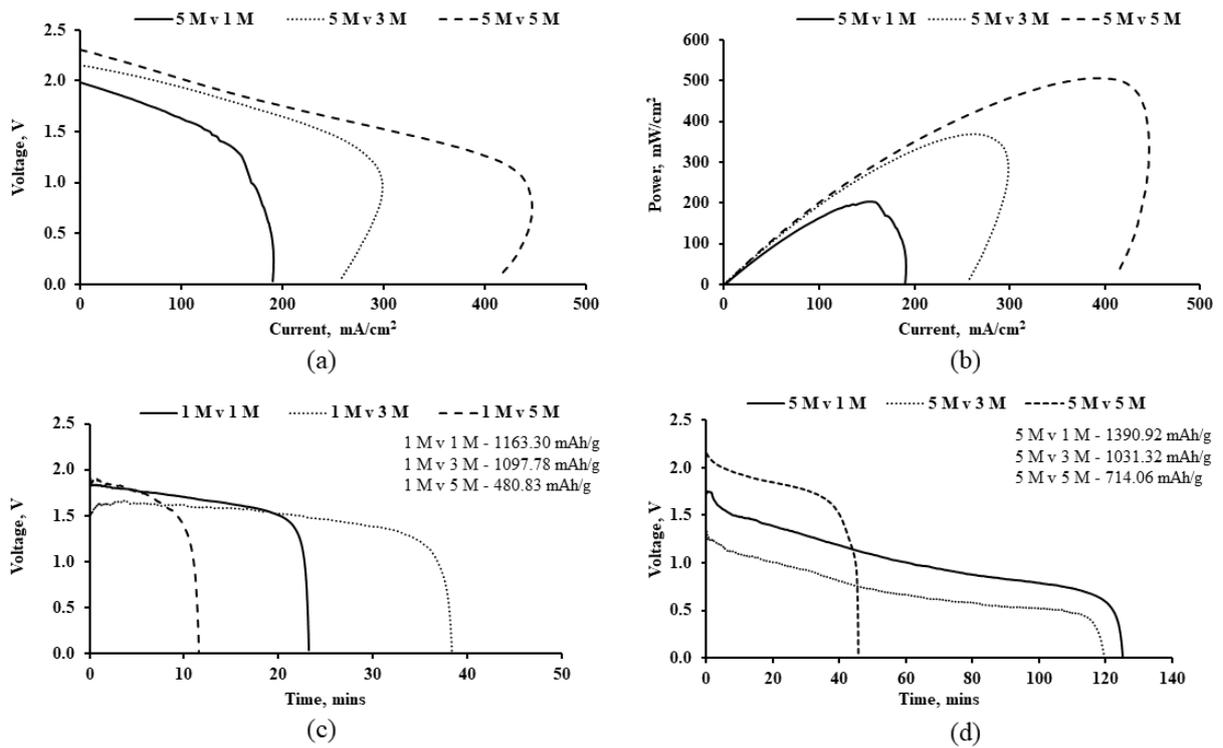


Figure 5. Polarization characteristics of the aluminum-air battery (a) Voltage vs current density, and (b) Power density vs current density and the discharge curve at 30 mA for (c) 1M KOH and (d) 5M KOH in comparing the effects of catholyte concentration.

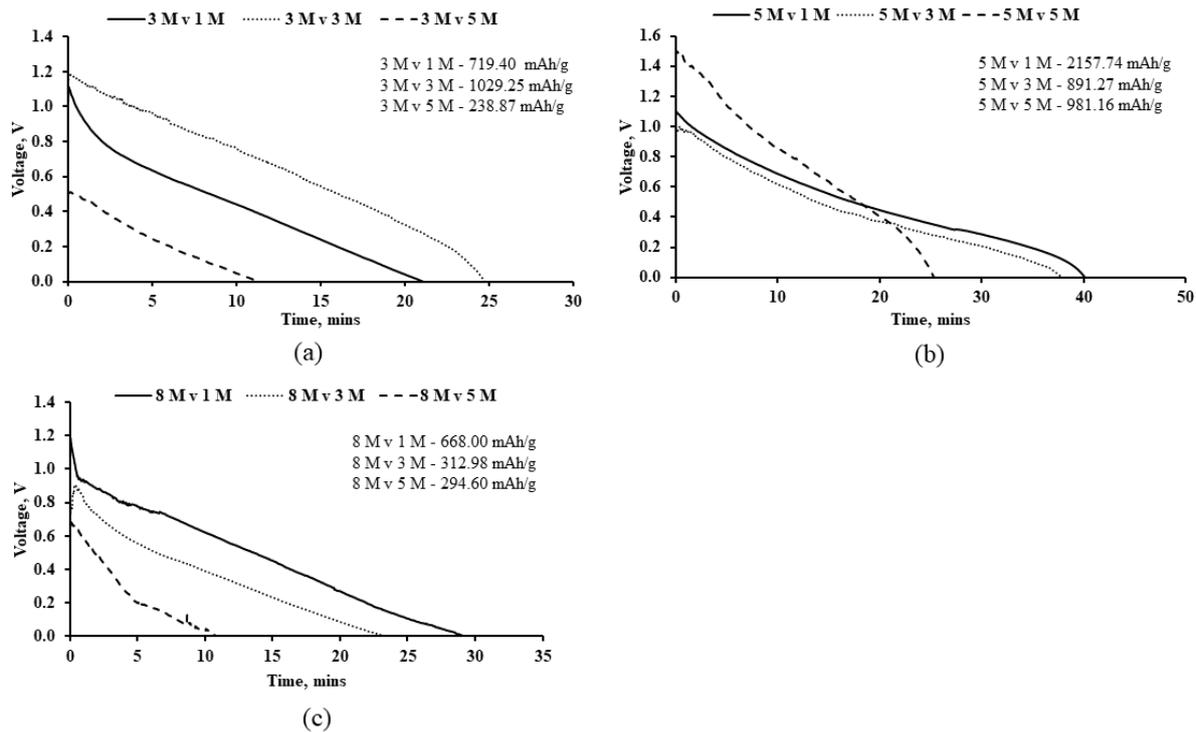


Figure 6. Discharge curve for (a) 3M of KOH, (b) 5M of KOH and (c) 8M of KOH in comparing the effects of catholyte concentration using discharge current of 100 mA.

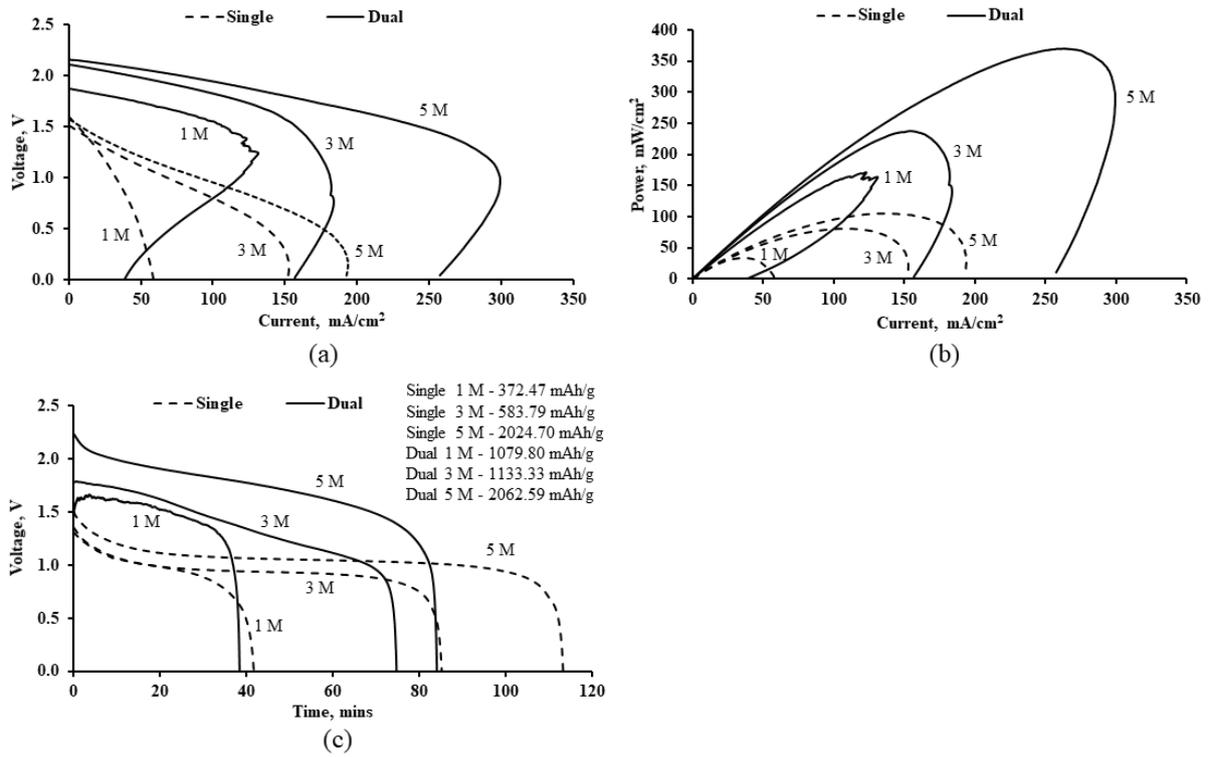


Figure 7. Polarization characteristics of the aluminum-air battery (a) Voltage vs current density, (b) Power density vs current density and (c) discharge curve at discharge current of 30 mA for single electrolyte and dual electrolyte system.

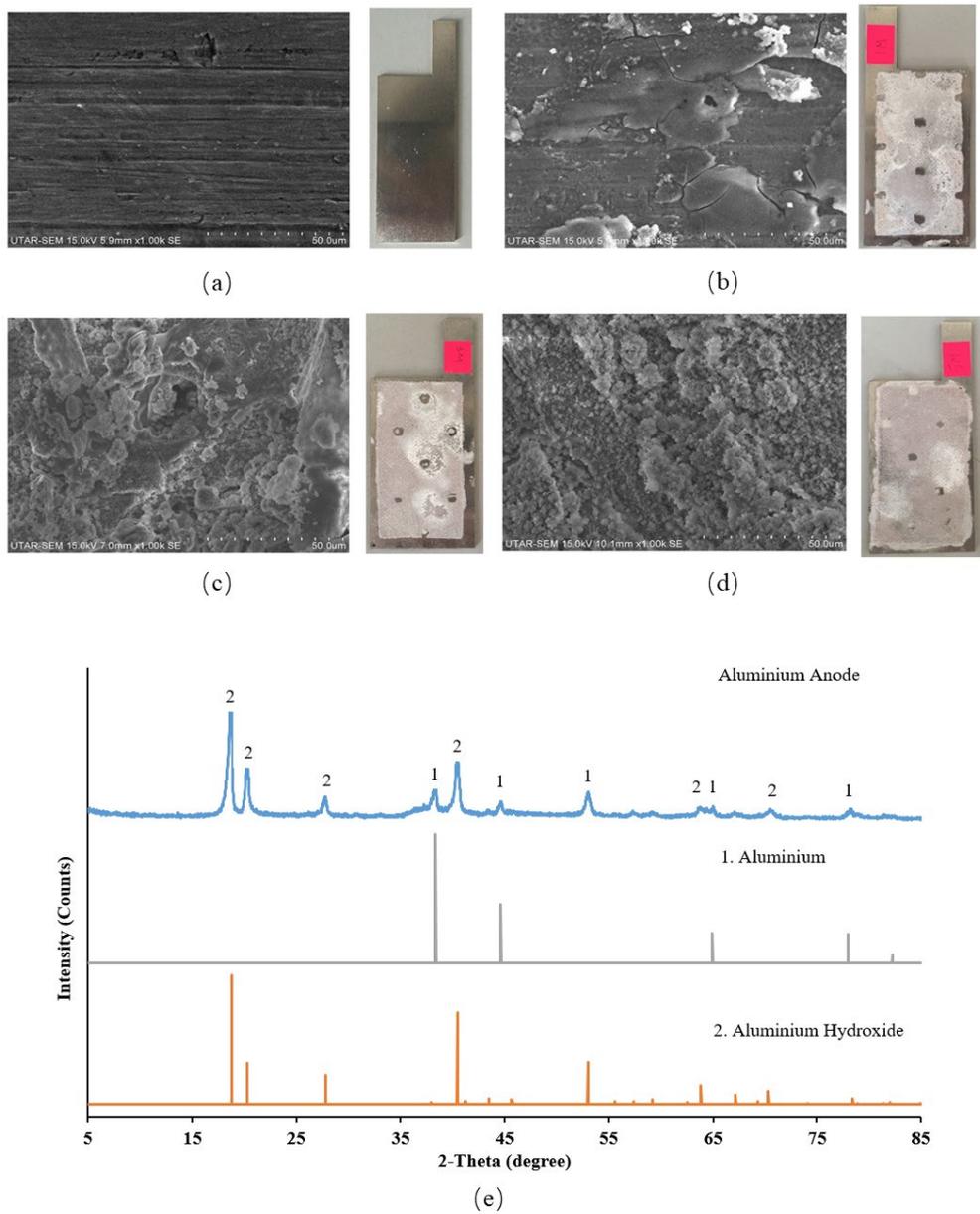


Figure 8. SEM images of 1000x magnification and macroscopic view of (a) pristine aluminum anode and after discharging using (b) 1M of KOH, (c) 3M of KOH, (d) 5M of KOH together with (e) XRD results of the aluminum anode after discharge test.