Suppressing $Al(OH)_3$ Product Accumulation on Air Cathode of Al-Air Battery by Porous Silica Xerogel Composite Layer

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Abstract. In this study, the suitability of the porous silica xerogel composite as an insulating layer to suppress the $Al(OH)_3$ product accumulation on the air cathode of aluminum air battery (Al-air battery) has been investigated. The composite layers are composed of silica xerogel, graphite and black carbon. The coating process is done by spraying a composite solution on the cathode surface. In electrochemical experiments, an insulating layer has been successfully used to stabilize the output voltage in the battery with an insulating layer in the air cathode (BUL). It has been found that the cell voltage reaches stable values of about 0.7 V for 8 days for BUL while it drops for battery without an insulating layer (BWL). In BWL, the $Al(OH)_3$ is a primary agent in limiting the voltage stability and life time. For four unit cell of battery, the electric power is over 40 mW, which was enough to operate an LED by serial connection.

Keywords: porous silica xerogel, insulating layer, air cathode, Al air battery, life time

1 Introduction

Batteries are one of new energy storage divices that have received great attention because of the high-power density and longer life cycle. Variations in the types of the rechargeable batteries have been developed to meet the requirements in the electrical storage power. They have been penetrate the market of portable electronic divices such as cell phones, digital cameras and electric vehicles. One type of the rechargeable batteries is a metal air battery. Use of oxygen from the air for the metal air batteries is an advantage from an economic point of view because the air is free and abundant. Additional advantages are the theoretical specific capacity and energy density in the range from 377 to 1030 Ah/kg and from 934 to 2791 Wh/k [1], respectively Their values are about 2 – 10 folds higher than that of lithium ion batteries [2]. Among all the metal air batteries, the Al-air battery is the most promising candidates in terms of the discharge efficiency and capasity. The battery is composed of Al anode, electrolyte, separator dan the air cathode. The electrodes are very important component in the battery, because the reactions can take place during the electrochemical processes at the electrode surfaces [3]. In the air cathode, a reaction occurs:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad . \tag{1}$$

This is the reaction of oxygen from the air dan water in electrolytes this reaction produces OH^- at the cathode. Through electrolyte medium in the sample pores, OH^- migrates to the the aluminium anode, the discharge reaction occurs in form:

$$Al + 4OH^- \rightarrow Al(OH)_4^- + 3e^-. \tag{2}$$

Based on the two reactions above (1) and (2), the overall reaction of the aluminum air battery is

$$4Al + 3O_2 + 6H_2O + 4OH^- \rightarrow 4Al(OH)_4^-. \tag{3}$$

As a result, after discharge reaction:

$$4Al(OH)_4^- \rightarrow Al(OH)_3 + OH^-. \tag{4}$$

Aluminum hydroxide $Al(OH)_3$ is the reaction product participates which accumulate at the anode and air cathode sufaces. The products cover the surface on both of air cathode and anode in static cell, then cause cell degradation with low discharge capacity. To suppress the reaction product accumulation on the air cathode surface, it is necesarry to coat the air cathode surface using an insulating material. Beside covering the surface, the material must also provide a channel for the reaction of water in the electrolyte and oxygen, so that it can produce OH- ions on the cathode surface. Many studies have been carried out in order to investigate the use the insulating material to coat the air cathode of the Al-air batteries and their electrochemical characteristics. It has been reported that the BWL was tested using the aqueous NaCl electrolyte and operated at the applied current of 0.5 mA/cm2. At the begining, the cell voltage and 1 st discharge cycle capacity was about 0.7 V and 3.52 mAh/cm^2 [3]. When the actived carbon layer was used as an insulating layer on both the anode and air cathode, it inflicts positive changes in increasing battery capacity to 12.7 mAh/cm^2. However when alumina is used as an insulating material, the discharge capacity decreases to 4.7 mAh/cm^2 [4]. This is caused by the small pore size of the alumina layer compared to activated carbon. In the case, the pores is not easily inserted by electrolytes and it take places the incomplete reaction of the water and oxygen in the pore. Therefore, the smaller amount of OH- ions was produced during the electrochemical reaction. These investigations have reviled that the electrochemical characteristics depend strongly on the presence of insulating layer and pores in the air cathode. Therefore by controlling the type of porous insulating layer, it is possible to obtain an appropriate performance of the Al-air batteries.

Recently, SiO_2 ceramic in the form of silica xerogel has been prepared using a sago waste ash [5,6] as a starting powder. It has been shown that in an amorphous state up to a partial crystal structure at 800oC, silica xerogels have micro- to meso-pore sizes. Based on the pore size, it is possible to provide channels for transport of oxygen and electrolyte diffusion. The aim of this study was to produce high capacity batteries as a result of using silica xerogel composite layer in the air cathode. In this paper, we present the used experimental procedures, and discuss the influence of using silica xerogel composite layer on the performance of Al-air batteries.

2 Experimental Procedure

2.1 Preparing and sintering of silica xerogel

Amorphous silica xerogel was extracted from sago waste which was obtained from Sago processing plant in Kendari, Indonesia. The complete extraction for making silica xerogel follows the procedure carried out by [5]. With using the procedure, high purity of about 98.8% and average particle size from 100 – 180 nm for amorphous silica xerogel was obtained. Furthermore, for behavioring the thermal on silica xerogel powder, an electric furnace system was used to sinter the silica xerogel powder at 1000ºC. A controlled heating rate of 5ºC/min has been maintained up to the desired temperature and the temperature has been kept constant for 2 hours. The cooling was performed by natural convection after turning the furnace off and leaving the samples inside.

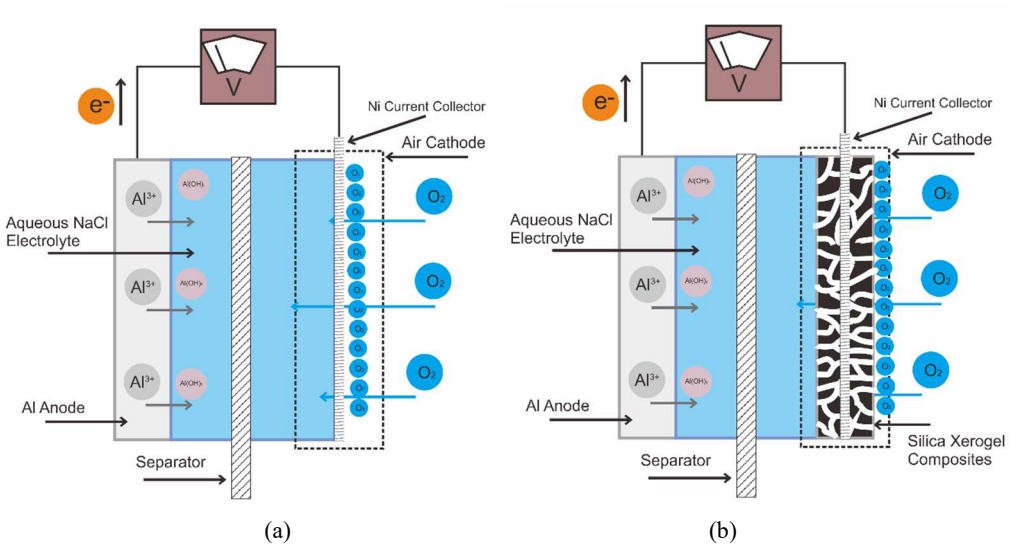


Figure 1. A schematic drawing for the aluminium air battery structure (a) without and (b) with silica xerogel composite as an insulating layer in the air cathode.

2.2 Preparing insulating material layer

The porous silica xerogel as prepared in 2.1 is used as an insulating layer composite in the air cathode. For preparing an insulating layer composite in the air cathode, it was prepared using the composition on a dry basis of 50 wt.% silica xerogel sintered at 1000ºC, 25 wt.% graphite, 20 wt.% carbon black, and 5 wt.% polyvinylidene fluoride (PVDF) as a binder. Then, it was mixed with 20 mL aceton and then stirred at room temperature for 30 minutes until all PVDF was completely dissolved. After that, the mixture was ultra-sonicated for at least 10 minutes to remove the air bubbles. The solution was coated onto the surface of a nickle 300

mesh substrate using a glass pipette. The coated substrate was dried at room temperature and then was stored in a desiccator for a further treatment.

2.3 Method for assemblying and characterizing Al-air battery

Fig. 1 shows a schematic drawing of the aluminium air battery structure without and with insulating layer composite in the air cathode for the electrochemical experiment. For BWL, the cell was composed of two rectangular electrodes, namely the anode and cathode with a size of 5 x 6 cm2 and they are separated by a porous tissue truwipes separator membrane inserted between them. The anode is the 1100 aluminium sheet and the air cathode is the nickle 300 mesh substrate. A 10% NaCl was used as electrolyte and injected on the surface of separator. The battery was clamped between Acrylic sheets, not shown in the figure. Two-terminals from the copper and nickle mesh as the current collector were used to measure the cell voltage of the battery. The constant current discharging tests were performed by using a battery testing system (BTS-MPTS, China) at a discharge density of 0.2 mA. For the battery with insulating composite layer in the air cathode (BUL), it was prepared following the same procedure and structure but its air cathode is insulating composite layer attached onto nickle 300 mesh substrate.

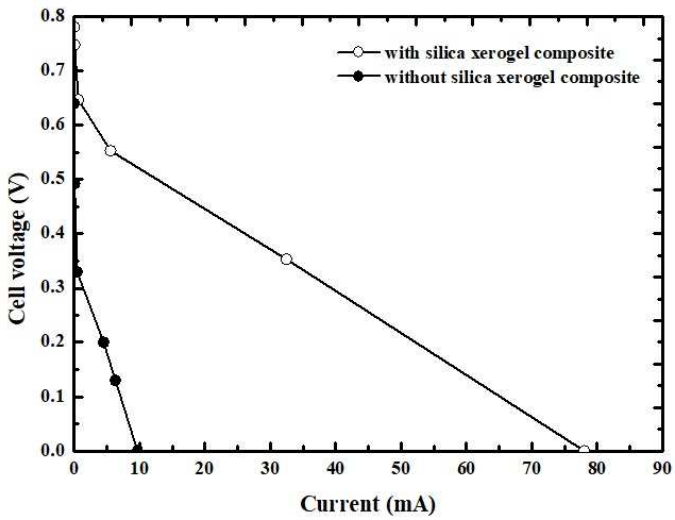


Figure 2. The voltage-current profiles for external loads of Al-air battery cell assembled with and without silica xerogel composite as an insulating layer in air cathode.

2 Results and Discussion

Fig. 2 shows the voltage-current profiles for external loads of of 0, 10, 100, 1 K, 10 K, and 100 KΩ. It can be seen that the open circuit voltage is 0.67 – 0.7 V and 0.53 – 0,62 V, while the current in the short-circuit is 2.65 mA and 0.97 mA. As a insulating layer is absent on the surface of the electrode, the current decreases due to the reduced surface area of the electrode, as a result of covering the surface by the insoluble reaction products of $Al(OH)_3$. For the BUL, the maximum power is 4.72 mW at 100 Ω. Fig. 3 shows discharge profiles for BUL and BWL. For

BWL, as shown in Fig. 5, initially, the cell voltage value sharply decreases with an increasing of the discharge time up to 0.4 days. Further from 0.4 to 6 days, however, leads to a slower change of this value. Therefore, the cell voltage of the battery does not experience the stability for discharging. All these facts can be attributed to presence of $Al(OH)_3$ accumulation on the surface of both the anode and air cathode. The surfaces of aluminium anode and nickle mess cathode have direct contact with the electrolyte. Therefore, in the case of a rapid rate in decreasing the cell voltage, the surfaces of both the anode and cathode are blocked by $Al(OH)_3$ formed at the beginning of discharge through the reduction of oxygen. The $Al(OH)_3$ precipitates result in the appearance of corrosion on the surfaces and the surface area of those electrode will not be accessed by either air or electrolyte, making them unavailable for the electrochemical reaction. Furthermore, a decrease in the rate for the cell voltage after 0.4 days is attributed to a small change for surface area on both the anode and cathode to contact with the electrolyte. Therefore, $Al(OH)_3$ is a primary limiting agent in terms of capacity and cycleability. Such observations are in agreement with the findings of the study of Stadie *et.al.*, and Fotouhi *et.al.*, [7,8]. It is hypothesized that the decrease in the discharge voltage correlates well with the decrease of the air and electrolyte accessibility to the electrode surface area.

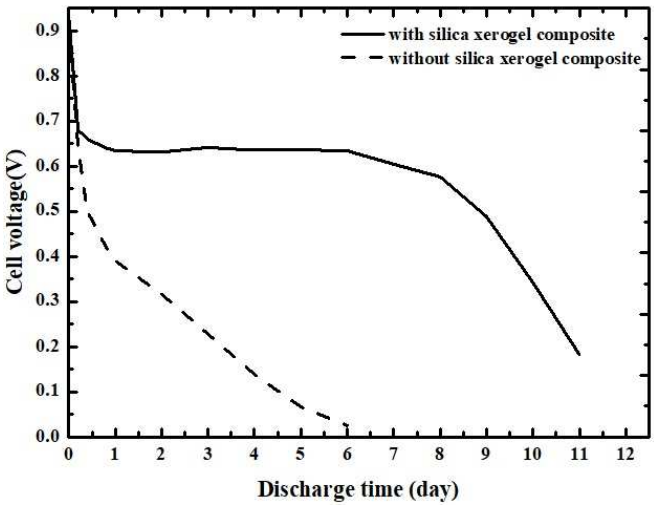
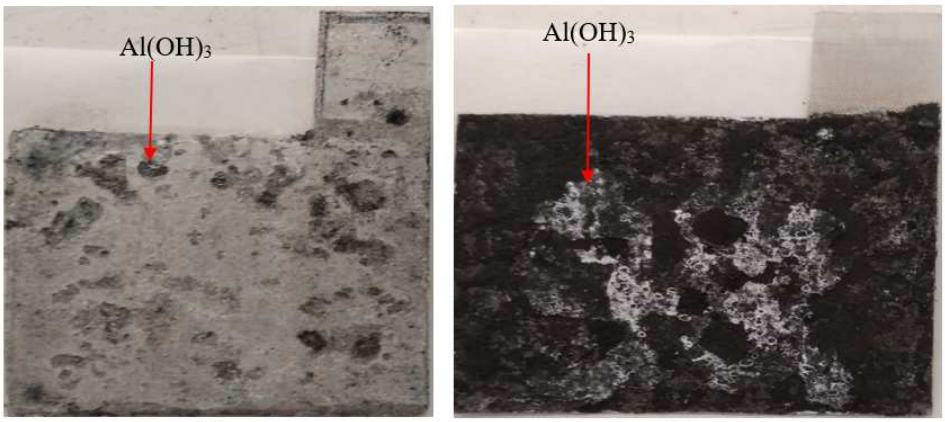


Figure 3. Discharge profiles of Al-air battery cell assembled with and without silica xerogel composite as an insulating layer in air cathode. The current was 0.2 mA.

For BUL, it can be seen that initially, the cell voltage value sharply decreases with an increasing of the discharge time up to 0.2 days, and then it reaches stable values of about 0.7 V, which is a characteristic of the cell voltage for basic aluminium air cell [4,8]. In the begining, a rapid decrease of the cell voltage with time is because of the reduction of the surface area of aluminum anode and the pore sizes blocked by the reaction product of $Al(OH)_3$ as shown in Fig. 4. It appears that the reaction product is white and grey. At a stable condition from 0.2 days to 8 days, the cell voltage value of about 0.7 V is greater than the value obtained at the BWL. It can be attributed to the presence of corrosion on the electrode surfaces, electrolyte diffusion and oxygen transport in the pores of composites. The insulating material composites is composed of silica xerogel, graphite, and carbon black. The surface of Ni current collector in air cathode is coated by an insulating material of the composites, so that $Al(OH)_3$ accumulates on the surface

of the layer and they have no contact with the surface of Ni current collector. In the case, we assume that the corrosion is absent on the Ni surface in the air cathode (Fig. 3b). This means that the surface in the air cathode is protected from corrosion, so that it can be continuously accessed by either air or electrolyte, making them available for the electrochemical reaction. This behavior is consistent with the results using alumina [4] and activated carbon [3] as an insulating layer in the air cathode. It was known that the specific surface area (SSA) dan average diameter of pore for the silica xerogel sintered at 1000oC, graphite, and carbon black were about 43 m^2/g and 2 nm [6], 126 m^2/g and 6 nm [7], 145 m^2/g and 0.96 nm [8], respectively. While the oxygen and Na+ and Cl- ions in the electrolyte have the diameter sizes of about 0.36 nm, 0.72 nm and 0.66 nm, respectively It seems that a relative range of the ions sizes is smaller than pore sizes of silica xerogel composites. In this case, the more electrolyte ions can easily diffuse through the pores and the reactions of oxygen and water can take place repeatedly to produce the higher amount of OH- ions at the cathode. As a result, it gets a higher discharge capacity for the air cathode with a insulating composite layer. However, the capacity is still limited by the presence of corrosion on the surface of aluminum anode.



(a) (b)

Figure 4. The reaction product of $Al(OH)_3$ attaches on the surface of (a) aluminum anode and (b) air cathode after discharge reaction during 10 days.

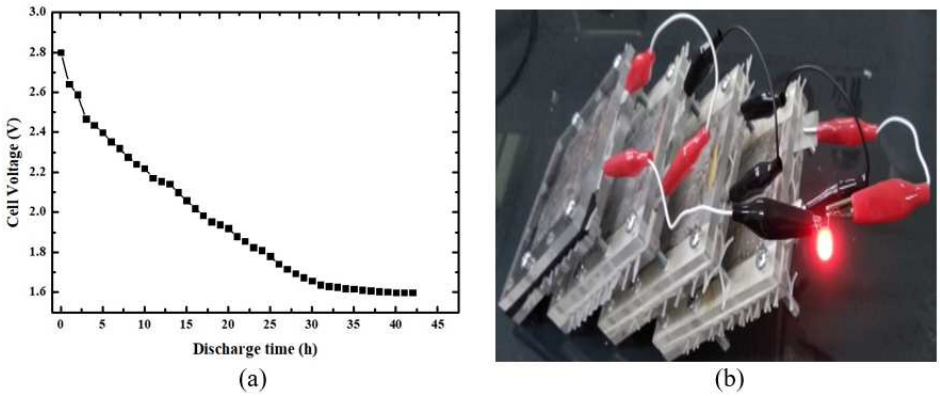


Figure 5. (a) Discharge profiles for four unit cells of the BUL, and (b) photograph of the test setup for four batteries connected in series using a small LED.

Fig. 5 shows discharge profiles for four unit cells of battery tested using a small LED. By stacking four cells in series, the cell voltage reaches 2.8 Volt with the power of about 40 mW, which is sufficient to illuminate a small LED with a forward voltage 2.5 – 3.5 V. Total discharge time reaches 48 h (two days), which was about one fifth that of the unit cell.

3 Conclusion

In this paper, the suitability of the porous silica xerogel composite as an insulating layer in the air cathode of Al-air battery has been demonstrated. In the electrochemical experiments, an insulating layer has been successfully enhance the stability of voltage and life time. It has been found that the the cell voltage for BUL reaches stable values of about 0.7 V for 8 days while it drops for BWL. A decrease in the cell voltage and stability for BWL is attributed to an insoluble reaction product of $Al(OH)_3$. The electric power is over 40 mW for the BUL. It is enough to operate an LED by serial connection of four unit cell of battery.

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