Simplification of Aluminum Air Battery by Gelation Electrolyte and Investigation of Material for Cathode Electrode

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This study devoted to developing water-activated aluminum air batteries, which could repeatedly generate electricity by adding water to the electrolyte. Two aluminum air batteries, using polymer gelation electrolyte and paper-absorbent electrolyte, have been investigated. In addition, we also considered two materials for the cathode electrode, which were carbon sheet and carbon nanotube-loaded carbon sheet. The aluminum air batteries used environmentally-friendly sodium chloride (NaCl) for the electrolyte. The developed batteries are portable and flexible, which can be used for low-power and on-demand electricity generation activated by water.

Keywords: aluminum air battery, gelation electrolyte, water absorbing polymer, carbon nanotube, carbon sheet.

(Received: 24 July 2018, Revised: 9 January 2019)

1. Introduction

Recently, renewable energy development has been extensively conducted all over the world. Energy production by consuming fossil fuel is not sustainable. Petroleum and coal are finite and cause global warming problem [1]. The lithium air battery, which is based on the combination of metallic lithium and gaseous oxygen, theoretically has the maximum energy density [2]. Currently, this battery is usually used for cars and mobile phones. However, lithium is expensive. Therefore, researchers are trying to find other low-cost materials to replace lithium [3].

Aluminum is the most abundant metal in the Earth's crust. Comparing with aluminum, only lithium has a slightly higher electrochemical equivalent (3.86 Ahg^{-1}) [4]. Furthermore, the theoretical specific volumetric capacity of aluminum is the highest among metallic fuels (8.04 Ahcm^3) [5]. These advantages along with its low price-per-energy unit have increased the interest in using it as an anode material in metal-air battery systems, specifically, in alkaline metal-air batteries. In the aluminum air battery, by-products such as Al_2O_3 and $\text{Al}(\text{OH})_3$ are produced. These by-products are insulators and therefore increasing the internal resistance of the battery. In recent years, ingenious measures have been taken to prevent the accumulation of these by-products [6].

The aluminum air batteries usually use aqueous electrolytes. In the simplest configuration, it has the shape as shown in Fig. 1 with the anode and cathode electrodes immersed in the aqueous electrolyte. This configuration has the disadvantage of electrolyte leakage.

There are various kinds of electrolyte in metal-air batteries [7]. In the aluminum air battery, strong alkaline such as sodium hydroxide or potassium hydroxide are often used. Sodium chloride aqueous solution is also used as a convenient and safe electrolyte. There is almost no harm caused by using sodium chloride. Since it is low cost and abundant, it is an optimum electrolyte for portable aluminum air batteries.

Solidification of the electrolyte is an essential step for obtaining all-solid-state aluminum air battery. Solidification of an electrolytic solution includes complete solidification or gelation. The advantages of solidified electrolytes include no internal shorting, leakage of electrolyte, and non-combustible reaction products at the electrode surface [8]. Various combinations of substances and electrolytes can be used for electrolyte solidification. In general, there are three methods to make polymer electrolytes [9]: (i) dry solid-state polymer, (ii) plasticized polymer electrolyte, and (iii) polymer composites. Polymer-based gelling agents are usually used to make gelation electrolytes. The water-absorbing polymer is one of the gelling agents. This water-absorbing polymer is low-cost and safe, which is usually used for making diapers.

The cathode electrodes of the aluminum air battery are basically made of conductive materials that can receive electrons and reduce oxygen. Since the carbon sheet has high conductivity and flexibility, it can be used for the cathode. In addition, carbon nanotube (CNT) has some unique characteristics such as high conductivity and large surface area thanks to its nanofiber structure [10]. Therefore, it is suitable for using as a cathode material. CNT is classified into single-walled and multiwalled structures. Single-walled CNT is superior in performance, but it is 10 times more expensive than multiwalled CNT [11]. Some studies about aluminum air batteries using gelation electrolytes have been reported [12], [13]. These batteries were based on wet gel electrolytes.

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Fig. 1 Reference diagram of an aluminum air battery.

In this research, we proposed a different approach that was using dry gelation saline electrolyte and dry paper-absorbent saline electrolyte to develop two types of water-activated aluminum air battery. These batteries could be preserved for long time without electrode corrosion; and they could be activated by adding a little amount of water to the dry electrolytes to generate electricity until the electrolytes become dry again. The developed batteries could generate stable output for several water-adding cycles. To the best of our knowledge, this is the first study using this approach for the aluminum air battery. In addition, because we aimed at making low-cost, portable, and flexible batteries, we also investigated multiwalled CNT and carbon sheet used for the air cathode.

2. Method and materials

2.1. Gelation electrolyte-based battery (GEB)

The structure of a GEB is shown in Fig. 2. A flexible silicone sheet with the thickness of 3 mm was utilized to make the battery case. A 10 mm diameter circle hole was drilled in the silicone sheet for keeping the dry gelation electrolyte. The open area of this circle hole (0.785 cm^2), which is in direct contact with the electrodes, is the active surface area of this battery. The silicone case was then adhered to the anode made of aluminum plate by a bond (SuperX Clear, Cemedine Co., Japan). Aluminum plate thickness is 0.3 mm. After filling the hole with the dry gelation electrolyte, the other side of the hole was covered by the cathode. The dry gelation electrolyte was fabricated as described in Fig. 3. First, to achieve electrolytic gelation, we mixed water-absorbent polymer (0.75 g) with 10 ml of 10 wt% saline. The water-absorbent polymer (Super Absorbent Polymer, Newstone International Corporation, Japan) is nonconductive and usually used in diapers. The water-absorbent polymer transformed the saline to gel. Second, the wet gelation electrolyte was dried in an electric oven at 60°C for 10 hours. Finally, the dried gelation electrolyte was grinded in a mortar to obtain the dry powder of gelation electrolyte.

Fig. 2 The structure of a GEB.

Fig. 3 The fabrication process of the dry gelation electrolyte.

Fig. 4 Actual images of a GEB used for experiments.

Actual images of the water-activated GEB used for experiments are displayed in Fig. 4. The dry gelation electrolyte (0.1 g) was filled inside the battery case. Then, a cathode made of carbon sheet or CNT-loaded carbon sheet was put on the hole and a clip was used to hold the cathode to the battery case.

To activate the battery in our experiment, deionized water was injected into the electrolyte portion of the battery by a syringe needle.

Fig. 5 Diagram of activation method.

Fig. 6 The structure of a PB.

The battery can also be activated by tap water when practically used. As shown in Fig. 5, the injection needle was laterally inserted through the silicone case into the electrolyte. The dry gelation electrolyte absorbed injected water quickly and became wet gelation electrolyte. Therefore, the injected water could not leak out of the battery case. The amount of water initially injected was 50 μl . After discharging time, the battery can be reactivated by injecting water again.

2.2. Paper-based battery (PB)

The second type of aluminum air battery fabricated in this research is a flexible PB. In this type of battery, aluminum foil (aluminum wrapping paper) was used for the anode. This material is inexpensive and flexible. Aluminum foil thickness is 11 μm . Fig. 6 shows the structure diagram of the flexible PB. Paper filter was utilized to make a paper-based electrolyte-absorbent separator between the anode and the cathode. We used the paper filter (MF-Millipore, VSWP09025) with film thickness of 100 μm , pore size of 0.025 μm . To improve the hydrophilicity of the paper filter, we conducted ozone treatment using an UV-ozone cleaner (Filgen, UV253E) for 5 hours each side of the paper filter. The paper filter was dipped in a sodium chloride solution at a concentration of 10 wt% for 10 min. Then, it was dried at room temperature for 10 hours.

The active surface area of this battery was 1 cm^2 . To activate, 10 μl deionized water was injected to the paper filter layer with pre-loaded electrolyte.

2.3. Cathode materials

Two carbon-based materials, carbon sheet and CNT-loaded carbon sheet, were used as the cathode of the developed aluminum air batteries. The carbon sheet (C1-P2, Azumi, Japan) is composed of 50 % carbon fiber and 50 % pulp fiber binder. It has the thickness of 0.22

mm, dry weight of 54 gm^{-2} , and electric resistance of 20 Ω/square . The carbon sheet was used without undergoing any further processing.

The CNT-loaded carbon sheet was fabricated as follows: CNT coating liquid (N7006L, KJ Specialty Paper, Japan), which contains 6.1 wt% multiwalled CNT with average diameter of 9.5 nm and length of 1.5 μm [14], was treated with an ultrasonic washer for 30 min and an ultrasonic homogenizer for 1 min to improve CNT dispersion; consequently, the carbon sheet was immersed in the prepared CNT liquid for 1 min followed by drying at 60 $^{\circ}\text{C}$ for about 2 hours in an electric oven. Since it was curved and distorted after drying, it was pressed on a flat glass by a heavy book (2.4 kg) for 24 hours to make it as flat as possible.

The surfaces of the two cathode materials were observed by a scanning electron microscopy (SEM) (Hitachi S4300) as shown in Fig. 7. After coating the carbon sheet by the CNT liquid, there was a thin layer of CNT covered on the surface of the carbon sheet (Fig. 7 (b) compared with Fig. 7 (a)).

Fig. 7 SEM images of the carbon sheet (a) and CNT-loaded carbon sheet (b).

Fig. 8 Equipment schematic of the measurement setup.

2.4. Measurement setup

A data acquisition system (DAQ, National Instruments NI USB-6210) connected to a customized LabVIEW interface on a computer (PC) was used to monitor the voltage generated by the developed aluminum air battery (AAB) discharged by an external resistor (R) (Fig. 8). We used a 1 k Ω resistor (if not stated otherwise) as the external resistor to discharge the battery.

3. Results and discussion

3.1. Gelation electrolyte-based battery (GEB)

First, we investigated the influence of salt concentration in the gelation electrolyte on the output of the GEB using the carbon sheet cathode. Seven saline concentrations of 0.5, 3, 10, 12, 14, 16, and 20 wt% have been checked. The salt concentration of 0.5 wt% was experimented as it is equivalent to human sweat. The salt concentration of 3 wt% was experimented as it is corresponding to seawater. The experimental results are shown in Fig. 9. This figure shows the maximum discharging voltage of the GEBs as a function of the saline concentration. Obviously, the discharging voltage increased as the concentration increased. However, there was little difference in the discharging voltage when the concentration increased from 10 to 20 wt%. Therefore, we decided to use 10 wt% concentration for all batteries.

Fig. 9 Maximum discharging voltage output of the GEBs using the carbon sheet cathodes as a function of the saline concentration in the gelation electrolyte.

Fig. 10 Discharging voltage of the GEBs with the cathodes made of carbon sheet (dashed line) and CNT-loaded carbon sheet (solid line).

Second, the cathode materials were investigated. After adding water to the dry gelation electrolyte, the voltage across the load was measured. The results are shown in Fig. 10. When using the carbon sheet for the cathode, there was a tendency that the voltage value gradually decreased from the maximum value of 270 mV.

The discharging voltage gradually decreased to 20 mV after about 120 hours. This result shows deterioration of the battery. Since water was not injected continuously, the gelation electrolyte became dry after long-time usage.

The shrinkage of the gelation electrolyte when drying created gaps between the electrodes and the electrolyte, which prevented electrons to pass through. This was considered the main reason for the deterioration. In addition, the by-products of Al_2O_3 and $\text{Al}(\text{OH})_3$ were produced in the electrolyte and they accumulated on the anode and cathode surfaces. The accumulation of these by-products led to the increase of the internal resistance of the battery, as a result, degrading its performance.

On the other hand, the battery using the CNT-loaded carbon sheet for the cathode generated about 170 mV higher voltage than that of the battery using the carbon sheet cathode. Based on this data, we can confirm that the battery performance has been improved significantly by coating CNT to the carbon sheet-based cathode. This improvement may be attributed to high conductivity and high electron mobility of CNT [15].

Third, we investigated the recyclability of the developed battery. A discharging cycle is defined as a period from adding water until the discharging voltage drops to 20 mV. In this experiment, after each discharging cycle, the same amount of water (50 μl) was added to the electrolyte to start the next cycle. Fig. 11 shows the output data of the first and the ninth discharging cycles of the water-activated GEBs with the cathodes made of the carbon sheet (Fig. 11 (a)) and the CNT-loaded carbon sheet (Fig. 11 (b)), respectively. The data showed stable voltage output after 9 cycles for both batteries. After about 30 cycles, the output decreased

about a half of the first cycle. The deterioration of the batteries is believed to be due to the degradation of the electrolyte (lower the concentration of salt in the gelation electrolyte) and the generation of the insulative by-products of Al_2O_3 and $\text{Al}(\text{OH})_3$. We are now studying how to improve the stability and increase the number of reuse cycles. Finally, the power density and maximum discharging voltage of the batteries have been measured. The results are shown in Fig. 12. Fig. 12 (a) shows the GEB using the carbon sheet for the cathode and Fig. 12 (b) shows the GEB using the CNT-loaded carbon sheet for the cathode. The data was measured by discharging these batteries by various resistors with the resistance values of 10 Ω , 30 Ω , 50 Ω , 100 Ω , 300 Ω , 510 Ω , 1 k Ω , 5 k Ω , and 10 k Ω , respectively.

After calculating the current based on the resistance value and the measured voltage, the current density was calculated by dividing the calculated current value to the active surface area between the electrolyte and the electrodes (0.785 cm^2). The power density was calculated based on the current density and the measured voltage. From Fig. 12, the power density was at the maximum when 100 Ω resistor was used for discharging the GEB with the CNT-loaded carbon sheet cathode and 300 Ω resistor was used for discharging the GEB with the carbon sheet cathode.

Fig. 11 Recycle experiment: discharging voltage of the GEBs recorded at the first and the ninth water-activated cycles. The GEBs with cathode made of the carbon sheet (a) and the CNT-loaded carbon sheet (b).

Fig. 12 The power density and maximum discharging voltage of the GEBs made with the carbon sheet cathode (a) and the CNT-loaded carbon sheet cathode (b).

In other words, the internal resistance of the GEB with the CNT-loaded carbon sheet cathode was estimated around 100 Ω and that of the GEB with the carbon sheet cathode was estimated around 300 Ω . This result also confirms the better conductivity of the CNT-loaded carbon sheet compared with that of the carbon sheet. In addition, it should be noted that nonconductive polymer was used for the electrolyte. It can be expected that the internal resistance will be lower than the above values if conductive polymer is used. Comparing Fig. 12 (a) with Fig. 12 (b), the power density of the GEB using the CNT-loaded carbon sheet cathode was about an order of magnitude higher than that of the GEB using the carbon sheet cathode. It proved the effectiveness of adding CNT to the cathode of the developed battery.

3.2. Paper-based battery (PB)

The PB is aimed at flexible and portable applications, so it was deliberately designed with thin shape and light weight. Therefore, this battery type could keep much less amount of electrolyte compared to the GEB type. Accordingly, the power generation time became much shorter. However, power generation was possible with tiny amount of water injection. Water injection volume used for the designed PB was 10 μL . Water was added to the paper filter layer with pre-loaded electrolyte.

Fig. 13 Three-cycle discharging voltage of the PBs using the carbon sheet cathode (a) and the CNT-loaded carbon sheet cathode (b).

We repeated 3 cycles of adding water when the discharging voltage dropped to about 20 mV to check the recyclability of this battery as shown in Fig. 13. The graphs showed that the output time of the battery was around 80 minutes.

Fig. 14 Power density and maximum discharging voltage of the PBs made with the carbon sheet cathode (a) and the CNT-loaded carbon sheet cathode (b).

When water was added again, the discharging voltage immediately recovered. Even after one-month storage the battery showed the same characteristics.

The deterioration of the battery after some cycles were also due to the lower concentration of the electrolyte and by-products generation as described in the previous section.

The power density and the maximum discharging voltage of these PBs were also measured as shown in Fig. 14. Fig. 14 (a) shows the PB using the carbon sheet cathode and Fig. 14 (b) shows the PB using the CNT-loaded carbon sheet cathode. The resistance values used for this measurement were 10 Ω , 30 Ω , 50 Ω , 100 Ω , 322 Ω , 510 Ω , 1 k Ω , 5 k Ω , and 10 k Ω .

The calculation method was the same as described in the previous section. The active surface area of this battery was 1 cm². Similar to the GEB, the power density of the PB using the CNT-loaded carbon sheet cathode was about an order of magnitude higher than that of the PB using the carbon sheet cathode. When using the carbon sheet cathode, the highest power density of 0.0746 mW/cm² was obtained at 510 Ω . While, when using the CNT-loaded carbon sheet cathode, the highest power density of 0.754 mW/cm² was obtained at 100 Ω . These resistance values were the estimated internal resistances of the two batteries.

4. Conclusion

By using the water-absorbing polymer, it was possible to make gelation electrolyte. We also confirmed that the power generation can be recycled by a simple process of adding water. Since the water-absorbing polymer can hold water, the possibility of leakage of the electrolytic solution was neglected. Voltage recovery was confirmed even when the amount of water added was little, which could facilitate in the event of disaster or emergency. The developed batteries are safe because they are based on saline electrolyte. Long-term preservation of the batteries is possible because of the use of dry electrolytes. The results showed that the power density of the developed batteries could be improved up to an order of magnitude by using the CNT-loaded carbon sheet for the cathode instead of using the carbon sheet for the cathode. The fabricated batteries were portable and on-demand electricity generation, which can be applied for various applications requiring low-power and on-demand properties.

Acknowledgment

A part of this research was supported by AZUMI FILTERPAPER CO., Ltd.

Reference

- [1] N. L. Panwar, S. C. Kaushik, and S. Kothari, "Role of renewable energy sources in environmental protection: A

- review,” *Renew. Sustain. Energy Rev.*, Vol. 15, No. 3, pp. 1513–1524, 2011.
- [2] Y. Takeda, N. Imanishi, and O. Yamamoto, “Present status and issues for lithium/air battery using aqueous electrolyte,” *GS Yuasa Tech. Rep. (in Japanese)*, Vol. 7, No. 1, pp. 1–7, 2010.
- [3] F. Cheng and J. Chen, “Metal-air batteries: From oxygen reduction electrochemistry to cathode catalysts,” *Chem. Soc. Rev.*, Vol. 41, No. 6, pp. 2172–2192, 2012.
- [4] N. Nitta, F. Wu, J. T. Lee, and G. Yushin, “Li-ion battery materials: Present and future,” *Mater. Today*, Vol. 18, No. 5, pp. 252–264, 2015.
- [5] S. Choi, D. Lee, G. Kim, Y. Y. Lee, B. Kim, J. Moon, and W. Shim, “Shape-Reconfigurable Aluminum–Air Batteries,” *Adv. Funct. Mater.*, Vol. 27, No. 25, pp. 1–9, 2017.
- [6] Q. Li and N. J. Bjerrum, “Aluminum as anode for energy storage and conversion: A review,” *J. Power Sources*, Vol. 110, No. 1, pp. 1–10, 2002.
- [7] M. H. Braga, N. S. Grundish, A. J. Murchison, and J. B. Goodenough, “Alternative strategy for a safe rechargeable battery,” *Energy Environ. Sci.*, Vol. 10, No. 1, pp. 331–336, 2017.
- [8] R. C. Agrawal and G. P. Pandey, “Solid polymer electrolytes: Materials designing and all-solid-state battery applications: An overview,” *J. Phys. D. Appl. Phys.*, Vol. 41, No. 22, pp. 223–231, 2008.
- [9] D. T. Hallinan and N. P. Balsara, “Polymer electrolytes,” *Annu. Rev. Mater. Res.*, Vol. 43, pp. 503–525, 2013.
- [10] A. Nomura, K. Ito, and Y. Kubo, “CNT sheet air electrode for the development of ultra-high cell capacity in lithium-air batteries,” *Sci. Rep.*, Vol. 7, pp. 1–8, 2017.
- [11] M. S. Dresselhaus, G. Dresselhaus, A. Jorio, A. G. Souza Filho, and R. Saito, “Raman spectroscopy on isolated single wall carbon nanotubes,” *Carbon N. Y.*, Vol. 40, No. 12, pp. 2043–2061, 2002.
- [12] Z. Zhang, C. Zuo, Z. Liu, Y. Yu, Y. Zuo, and Y. Song, “All-solid-state Al-air batteries with polymer alkaline gel electrolyte,” *J. Power Sources*, Vol. 251, pp. 470–475, 2014.
- [13] A. A. Mohamad, “Electrochemical properties of aluminum anodes in gel electrolyte-based aluminum-air batteries,” *Corros. Sci.*, Vol. 50, No. 12, pp. 3475–3479, 2008.
- [14] L. KJ specialty paper Co., “KJ carbon nano liquid,” 2018. [Online]. Available: https://www.kjsp.co.jp/english/development/pdf/KJ_nano_liquid_e_20180214.pdf.
- [15] P. Avouris and J. Chen, “Nanotube electronics and optoelectronics,” *Mater. Today*, Vol. 9, No. 10, pp. 46–54, 2006.