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A Novel Aluminium - Air Rechargeable Battery with Al_2O_3 as the Buffer to Suppress byproduct Accumulation Directly onto an Aluminium Anode and Air Cathode.

Ryohei Mori

An aluminium - air secondary battery was prepared with aluminium oxide placed adjacent to an aluminium anode and air cathode. Plain salt water was used as an electrolyte. The new structure of the aluminium-air battery exhibited a capacity that was almost constant when NaCl solution was refilled repeatedly, whereas the capacity of an aluminium - air battery with the general structure drastically deteriorates after the 1st cycle. It was found that aluminium oxide behaved as a buffer to suppress the accumulation of byproducts directly onto the electrodes. It was also suggested that aluminium ions conduct through the electrolytes which exist at the space between the aluminium oxide particles, and not through the bulk aluminium oxide.

Introduction

Due to fossil fuel depletion and the air pollution arising from its combustion, there is an urgent demand for renewable, clean fuel alternatives for our future energy supply.[1,2]Although rechargeable lithium-ion batteries are widely used in mobile phones, laptop computers, and similar electronic devices, their energy density is still insufficient to permit their use in electric vehicles. The most obscure energy storage technologies, due to the numerous challenges faced by researchers, are the metal–air batteries. Several metal–air batteries such as iron–air, aluminum–air and zinc–air batteries[3,4] have been investigated due to their promising energy densities; lithium–air batteries have been found to be the most promising for high-performance applications.[5,6] However, lithium is sensitive to ambient conditions such as humidity and oxygen, and is a scarce natural resource in some regions.

Aluminium, in contrast, is an abundant, attractive anode material for energy storage and conversion because of its high specific capacity, highly negative standard electrode potential [E° = -1.7 V vs. standard hydrogen electrode (SHE)], and environmentally benign characteristics. In addition, aluminium is the most recycled metal in the world and is inexpensive. When compared with zinc, lithium, and other metals, aluminium has unique advantages and disadvantages. Its relatively low atomic weight of 26.98 and trivalence confer it a gram-equivalent weight of 8.99 and an electrochemical equivalence of 2.98 Ah/g, compared with 3.86 Ah/g for lithium, 2.20 Ah/g for magnesium, and 0.82 Ah/g for zinc. Moreover, on a per-volume basis, aluminium yields 8.04 Ah/cm^3, compared with 2.06 Ah/cm^3 for lithium, 3.83 Ah/cm^3 for magnesium, and 5.85 Ah/cm^3 for zinc.[7]

A major barrier to commercialization is the high corrosion rate of aluminium in alkaline solutions, both under open-circuit conditions and during discharge. In order to reduce the self-corrosion of the aluminium anode, two methods are usually employed: creating an alloy of aluminium with other elements[8-10] or modifying the composition of the electrolyte.[11-17] However, these studies have been largely unsuccessful in the commercial production of aluminium-air batteries because by-products such as Al_2O_3 and $Al(OH)_3$ accumulate at both the anode and the cathode. Therefore, we propose covering the aluminium anode and the air cathode with ceramic aluminium ion conductors, preventing the corrosion of the anode that results from direct contact with the electrolyte, while retaining aluminium ion conduction.

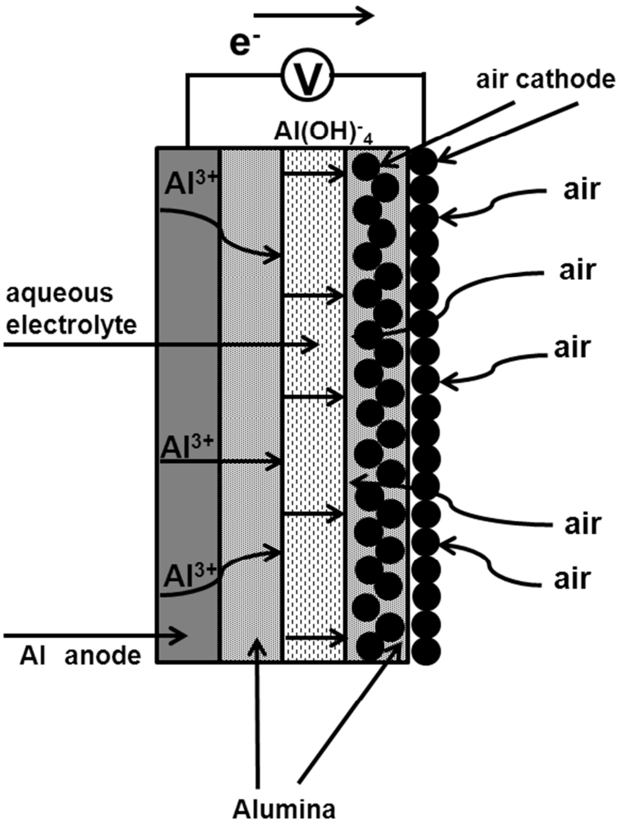

Fig. 1. A schematic figure of ALFA

In a previous study, $Al_2(WO_4)_3$ was used as an aluminium ion conductor on both the anode and air cathode, and we successfully created an aluminium-air battery with secondary battery properties that was stable for one month.[18,19] However, it should be noted that $Al_2(WO_3)_4$ has an intrinsic electrical conductivity of nearly 4 x 10^{-6} Scm^{-1} at 600°C.[20] From previous studies, we had learned that when $Al_2(WO_4)_3$ films and the lid consist of the bulk solid electrolyte, it was not possible to obtain a functional secondary battery because the conductivity of $Al_2(WO_4)_3$ is not high at room temperature. Therefore, it was suggested that liquid electrolyte was penetrating into the solid electrolyte region (the space between the ceramic particles) to reach the electrode. Hence, we suggested that even with insulating material to replace the solid electrolyte part, it should be able to function as a secondary battery. Additionally, tungsten which is present in the solid electrolyte, is not economically feasible for commercial use. It is a great advantage to use a general insulator oxide ceramic as the material covering the electrode. We chose aluminium oxide as the electrode covering material to challenge our assumption as it is known as a major by-product that is responsible for disrupting the functioning of aluminium – air batteries. In this study we use a trite aluminium oxide to cover the electrode when preparing an aluminium – air secondary battery.

Experimental

In this study, the aluminium-air cell is termed ALFA cell as an acronym of its major components: an air cathode, an Al_2O_3 lid (we refer to the material which covers the air cathode as the "lid"), an Al_2O_3 film, and an aluminium anode.

The air cathode was composed of conductive carbon and polyvinylidenedifluoride (PVDF) dissolved in N-methyl-pyrrolidone (in ratios of 2:1:7, respectively) on a nickel mesh current collector. To prepare the "lid", the powders were mixed in the proportion 8:1:1 (Al_2O_3 : carbon : PVDF) and pressed into disks. An aluminium board was used as the anode. The Al_2O_3 film was prepared by coating the aluminium anode with a printing slurry composed of Al_2O_3 powder, polyvinylidenedifluoride (PVDF) dissolved in N-methyl-pyrrolidone (2:1:7), and then annealed at 130°C. All chemicals were purchased from Wako Chemical Co. Ltd. (Osaka, Japan). A 10% NaCl aqueous solution was used as the electrolyte. The structure of the prepared cells can be summarized as | air cathode | Al_2O_3 + carbon | NaCl | Al_2O_3| Al metal | (ALFA cell, Fig. 1).

Phases in the "lid" and "film" were investigated by X-ray diffraction (XRD) using a diffractometer (RAD-RU, Rigaku Corp. Tokyo, Japan) with Cu Kα radiation of 40 kV-200 mA. "Lid" and "film" structures were examined using a field-emission type scanning electron microscope (SEM) (Sirion, FEI company, USA) with an acceleration voltage of 5 or 10 kV. Electrochemical performance was evaluated galvanostatically (SP-150, Bio Logics, France). Electrochemical impedance spectroscopy (EIS) was conducted from 1 MHz to 100 mHz with a 10 mV amplitude. Cyclic voltammetry was carried out at the scan rate of $5mVS^{-1}$. All electrochemical measurements were carried out under ambient

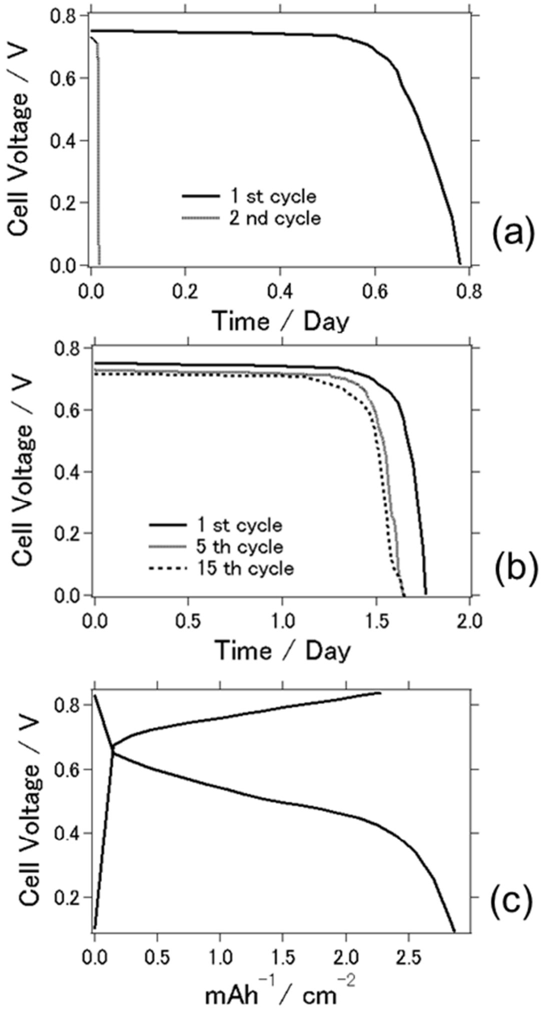

Fig. 2. Discharge curves of ALFA cell. (a) Normal type Aluminium air battery (b) ALFA cell (c) 1 st charge-discharge curve of ALFA cell.

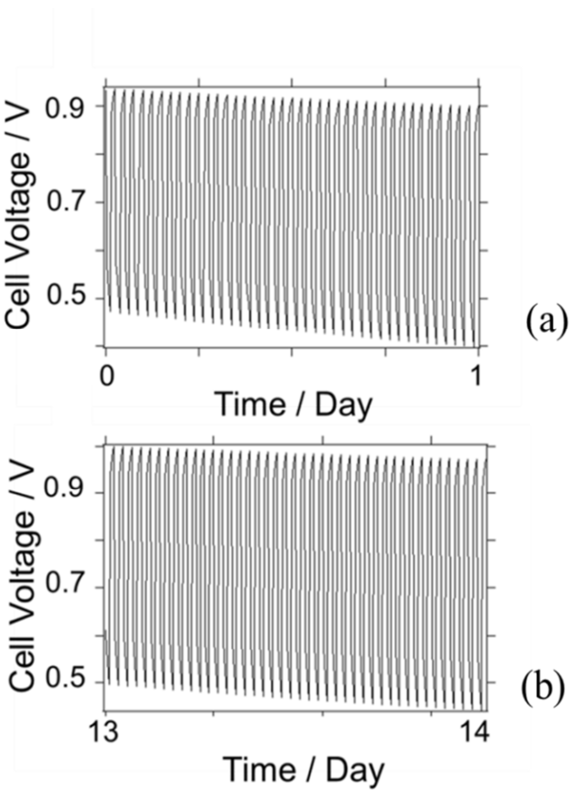

Fig. 3. Charge-discharge curves of ALFA cell. (a) 1st 24 hours (b) last 24 hours.

atmosphere conditions.

Results and discussion

Figure 2 (a) shows the 1st and 2nd discharge curves of the aluminium-air cell without the "lid" and "film". The cell capacity of the 1st cycle was 15.91 mAhcm^{-2}. However, when we tried to discharge the cell a second time, the cell voltage fell steeply and cell capacity was 0.11 mAhcm^{-2}. This behavior is typical of a basic aluminium air cell. After being discharged, an aluminium - air cell cannot be used again, since it is a primary battery.[8-16] In contrast, figure 2 (b) shows the discharge curves of a prepared ALFA cell. The capacity was initially 21.2 mAhcm^{-2}, and 19.7 mAhcm^{-2}, 20.1 mAhcm^{-2} at the 5th and 15th cycles, respectively. It is clearly demonstrated that the capacity was almost constant at every cycle. However, it should be noted here that due to evaporation of the electrolyte, the NaCl solution was refilled before every measurement cycle in order to obtain sufficient electrical contact. In addition, the applied current was 0.5 mA/(cm^{-2}) for both figure 2(a) and (b). Figure 2(c) indicates the 1st charge-discharge curve of ALFA cell with an applied current of ±3.0 mA/(cm^{-2}). Initial capacity was 2.86 mAhcm^{-2}. It should be noted that when applied current is strong and reaches cut-off voltage in a short time, we could obtain charge-discharge curve as indicated in Fig.2(c). However, we could not obtain repeatable charge-discharge curve when applied current is weak as shown in Fig. 2(b).

Figure 3 displays charge-discharge curves collected over a 2 week period at an applied current of ±3.0 mA/(cm^{-2}). Each figure displays the charge-discharge curves of the first and last 24 hours of the measurement period. The data shows that the ALFA cell is stable for two weeks. It is remarkable that by covering electrodes with an aluminium oxide insulator it was possible to achieve almost constant capacity at every discharge cycle, and keep the cell functioning for 2 weeks.

Figure 4 presents the X-ray diffraction pattern of an ALFA cell. Fig. 4 (a) shows the Al_2O_3 powder used in this study. It is clear that the powder is composed of the Al_2O_3 phase. After the charge-discharge reaction, the "lid" shows the additional NaCl phase, which originates from the electrolyte (Fig.4 (b)). On the other hand, the "film" has an additional $Al(OH)_3$ phase. An Al metal phase has emerged from the Al metal anode which lies under Al_2O_3 film (fig.4 (c)). Compared to previous studies, no other aluminium, tungsten or sodium related complex phases were detected at either the "lid" or "film". Just Al_2O_3 and $Al(OH)_3$ phases were detected which is said to be the major byproducts that stop the aluminium air cell electrochemical reaction.

Nyquist plots of the ALFA cell are shown in Fig. 5. The measurements were carried out after 30 seconds, 3 minutes, and up to 7 days after the charge-discharge reaction was initiated. It was observed that cell impedance gradually increases as the charge-discharge reaction proceeds further. This can be inferred due to the

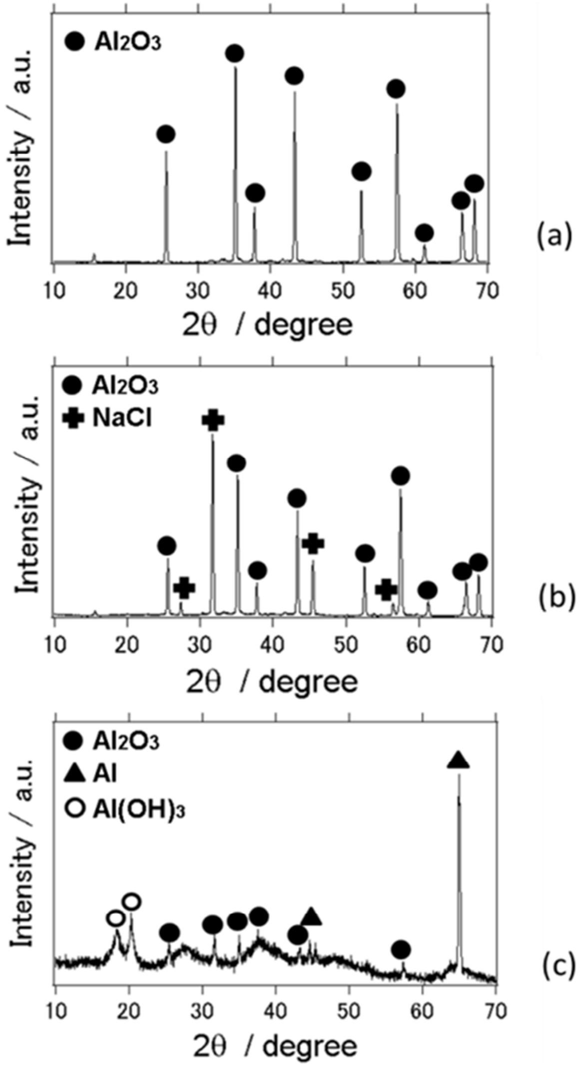

Fig. 4. X-ray diffraction pattern of (a) Al_2O_3 powder (b) Lid (c) Film For lid and film, XRD measurement was carried out after 5 days of charge-discharge experiments.

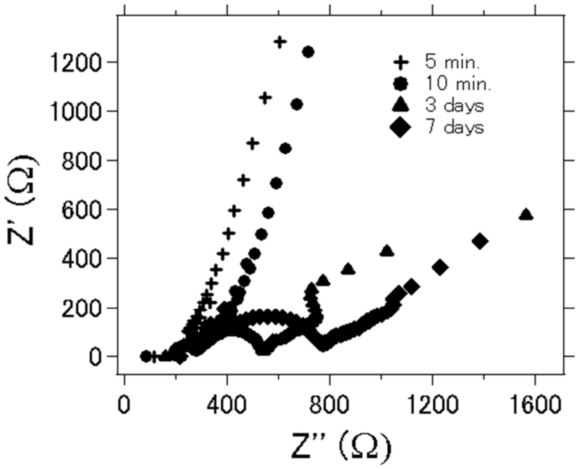

Fig. 5. Nyquist Plot of ALFA cell

accumulation of $Al(OH)_3$ on the film as we confirmed with the X-ray diffraction measurements On the other hand, the intrinsic conductivity of Al_2O_3 is 1 x 10^{14} Ω cm at room temperature.[21] If the "lid" and "film" are composed of bulk Al_2O_3, it is not possible to obtain a similar result for impedance. In this case, impedance will be much larger. Therefore, from impedance measurement experiments, it can be suggested that the "lid" and "film" are composed of porous structures and the impedance results reflect the resistance of the ALFA cell and the NaCl electrolyte itself, and not the resistance of Al_2O_3. This trend is similar to a previous study when by-products started to accumulate in the ALFA cell after a certain period of the charge-discharge reaction[18,19]. It is also deducted that the result reflects not only the ohmic resistance increase, but also the polarization resistance enhancement with increasing the number of the charge-discharge processes. A possible explanation for this phenomenon is the deterioration of the cathode, where carbon is burned by active oxygen species during the charge process[22].

To confirm the structure of the material in this study, we have performed SEM observations of the "lid" and "film". As shown in figure 6 (a), the "lid" is composed of a rugged Al_2O_3 porous structure, making it possible for the NaCl aqueous solution to penetrate into this structure. In addition, the surface of the "film" is not as rugged as the "lid" structure, although it is clear that the film is porous on the inside, where the NaCl aqueous solution can penetrate into the structure, as shown in (Figure 6(b)). Therefore, it can be inferred that the NaCl liquid electrolyte can penetrate into both the anode and cathode. In this study, the "lid" and "film" were prepared by simply dispersing Al_2O_3 particles followed by the pressing and coating procedures. The relationship between Al_2O_3 particle size, electrode preparation method and ALFC cell efficiency needs to be studied further.

Figure 7 shows the voltage profiles of the ALFA cell as a function of time. The cell was discharged galvanostatically at different rates ranging from 0.2 mA/cm^{-2} to 2.0 mA/cm^{-2}. At discharge rates between 0.2 – 1.0 mA/cm^{-2}, the voltage profiles were kept almost constant. With increasing discharge rates, a progressive decline of discharge voltage was observed. When the discharge current was 0.2 mAcm^{-2}, the capacity was 7.3 mAh cm^{-2}. As the discharge current increased to 0.5, and 1.0 mAh cm^{-2}, the capacity reached 17.1 and 32.8 mAh cm^{-2}, respectively. However, at 2.0 mA/cm^{-2}, the discharge curve became a slope instead of a plateau, and the discharge capacity decreased to 15.4 mAh cm^{-2}. This trend is similar to a previous study which implies the electrochemical reaction is proceeding irrespective of the material covering the electrode.[18,19]

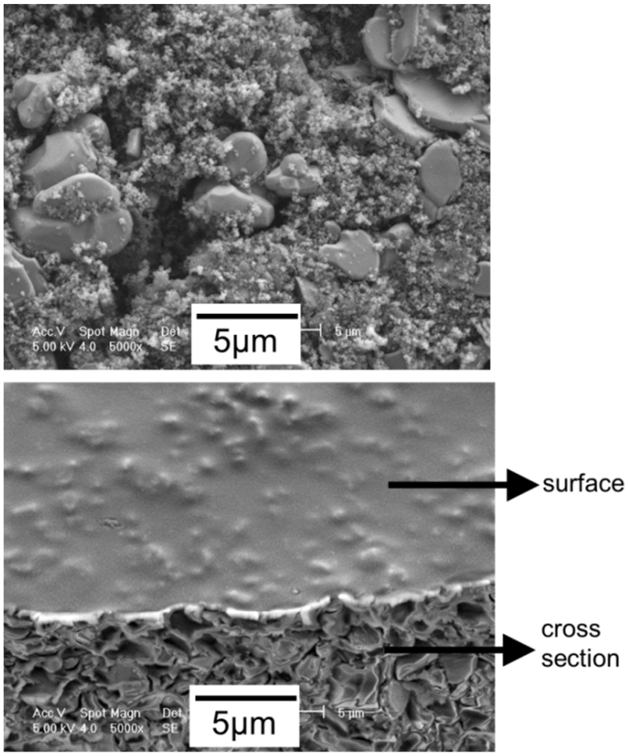

Fig. 6. SEM observation of (a) film (b) lid

Figure 8 displays the voltage versus time plot of the ALFA cell when the charge and discharge rate was ±4.0 mA/cm^{-2}. The potential of the Al^{3+} insertion/extraction plateau was not observed. When the cell was discharged, the voltage reached 0 V which was the cut off potential. In contrast, when the ALFA cell was charged, voltage saturation was not observed.

Figure 9 shows the cyclic voltammograms of the ALFA cell of the 1st, 3rd, 5th, 10th and 20th cycles measured between 0 and 2.0 V to characterize the redox reactions. A large cathodic current was observed in the first five cycles although it decreased as cycle numbers increased. The reduction peak positions for the 1st - 5th

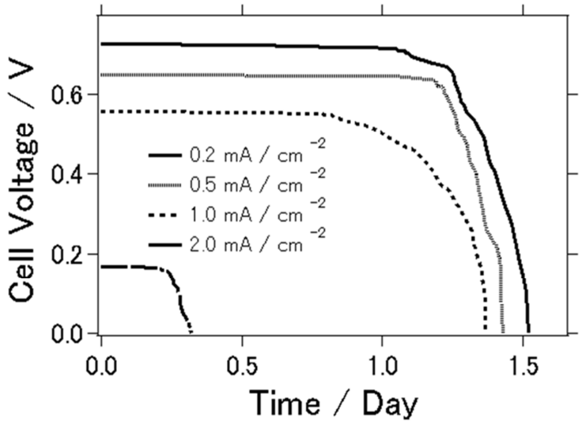

Fig.7. Rate performance of ALFA cell.

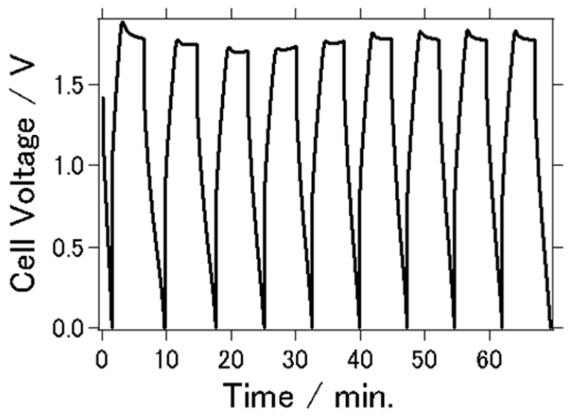

Fig.8. Rate performance of ALFA

cycles were located around 1.5 - 1.6 V whereas they shifted to around 1.2 - 1.3 V as the cycles proceeded. In addition, one can observe weak oxidation peaks around 1.3 - 1.4 V. This demonstrated that the redox pairs contribute to the gain and loss of electrons in the ALFA cell during the charge-discharge reaction. The reason for high intensities first five cycles is unknown; however this indicates a higher electrochemical reactivity during these cycles. For aluminium air battery, $Al(OH)_3$ is said to be the charge carrier[8-10, 11-17]. At ALFA cell, we also suggest that $Al(OH)_3$ is the main charge carrier. However, as we discussed in our previous study, when NaCl is used as an electrolyte, $Al(OH)_3$ and transitory compounds such as $Al(OH)_2Cl$, $Al(OH)Cl_2$, and $AlCl_3$ could also be the charge carriers. In addition, we have also speculated from our X-ray analysis study that even Na ion species may have possibility that participating the electrochemical reaction. Therefore, reduction peak at 1.5-1.6 V, can be attributed to charge career $Al(OH)_3$, or some another ion species. As far as we know, one has not seen detail study of charge career even for general type of aluminium – air battery, especially based on cyclic voltammetry. To investigate what ion species are exactly participating in ALFA cell electrochemical reaction, is our next main topic and we are preparing to research further. At the air cathode, the water in the electrolyte reacts with oxygen from the air and OH^- is produced at the cathode via following reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

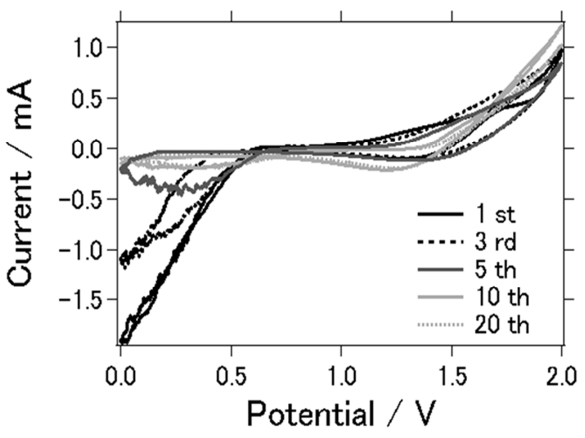

Fig. 9 Cyclic voltamogram of ALFA cell.

The OH^- is transported through the electrolyte and through the electrolyte in the “lid” and “film” to reach the Al anode, followed by the discharge reaction at the aluminium anode [23]:

$$Al + 4OH^- \rightarrow Al(OH)_4^- + 3e^-$$

Hence, the overall aluminium-air cell reaction is:

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

Eventually, aluminium hydroxide precipitates on the Al anode:

$$Al(OH)_4^- \rightarrow Al(OH)_3 + OH^-$$

In this study, accumulation on the Al_2O_3 film was confirmed by the X-ray diffraction pattern. In our previous study, $Al(OH)_3$ and Al_2O_3 were also observed on the “lid” and the “film” when $Al_2(WO_3)_4$ was used as the electrode covering material.[18, 19] When NaOH was used as an electrolyte, $Al(OH)_3$ is the charge carrying ion species. On the other hand, when NaCl is used as an electrolyte, the chemistry is a little more complex. Pletcher et al have reported that the speciation of the Al (III) is unclear and may depend on kinetics as well as thermodynamics. In addition, it is likely to change with either the Al (III) concentration and/or the pH, i.e. the extent of cell discharge. Possible Al (III) species include Al^{3+}, an aluminum hydroxide, alumina in various states of hydration and/or chloro complexes[24]. Furthermore, Gaber et al have shown that $Al(OH)_3$ and transitory compounds such as $Al(OH)_2Cl$, $Al(OH)Cl_2$, and $AlCl_3$ are the charge carriers[25].

In this study, we designed the cell so that that the Al ion was conducted through the NaCl electrolyte. If the Al ion is the charge carrier of the ALFA cell, it dissolves into the NaCl electrolyte when the cell is discharged, and the Al metal is deposited back either upon the Al anode or the Al_2O_3 film during cell charge. However, refining Al metal from Al_2O_3 necessitates such a large amount of electricity in a modern aluminium manufacturing industry that it may not be feasible. In this study, we have not confirmed if the Al ion or Al based species are the charge carriers of the ALFA cell. Note that when $Al_2(WO_3)_4$ was used as the electrode covering material in the previous study, one of the deposited phases was $Na_2(WO_4)(H_2O)_2$ after the charge-discharge reaction[18]. This proves that the sodium ion may also participate in the electrochemical reaction and replace it with an Al site in $Al_2(WO_3)_4$. Therefore, we cannot eliminate the possibility of an electrochemical reaction with other ion species such as Na^+ in this case. Furthermore, the influence of hydrogen formation during cell discharge needs to be discussed in a later study. In addition, we also suggest that the electrolyte evaporation was attributed to macro- and micro-pores formed in the lid because of the simplicity of the lid preparation technique. This issue needs to be further investigated. To prevent the evaporation of electrolyte, bulk aluminium oxide will have to be prepared to keep the NaCl aqueous solution from passing through the space between aluminium oxide particles, resulting in the blockage of aluminium ion conduction on the cell. An optimization point needs to be developed to suppress electrolyte evaporation to some extent while retaining ion conductivity in ALFA cells. One could also utilize heavy hydrophilic solvents such as glycerin to suppress electrolyte evaporation.

Nevertheless, for practical use, refilling NaCl is a simple step in maintaining secondary cell function. A detailed study of the mechanism should be carried out in the future in order to clarify the ALFA cell mechanism.

Most importantly, one can consider using aluminium as a secondary battery material, as it is more abundant, safer, and easier to handle than other metals such as lithium, zinc, magnesium and sodium.

Conclusions

An aluminium-air secondary battery was successfully assembled with, aluminium, aluminium oxide, and plain salt water. Aluminium is an abundantly available material making the ALFA cell a safe and cheap alternative. We believe the ALFA cell is very feasible and practical to use. The ALFA cell exhibits almost constant capacity when the NaCl solution is repeatedly refilled. It was found that aluminium oxide behaves as a buffer to suppress accumulation of byproducts directly onto the electrodes. It was also found that aluminium ion transfer occurs through the NaCl aqueous solution which exists in aluminium oxide particle spaces, and not through the bulk aluminium oxide.

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Notes and references

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