

Study on the Electrolyte Containing AlBr_3 and KBr for Rechargeable Aluminum Batteries

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Abstract

The reversible redox reaction of Al^{3+}/Al or Al deposition/dissolution was investigated in ethylbenzene containing AlBr_3 and KBr as an electrolytic solution for rechargeable aluminum batteries. KBr as a supporting electrolyte was also necessary for the reversible Al deposition/dissolution. This reversible redox reaction was observed on both glassy carbon (GC) and Pt electrodes. However, the charge/discharge tests showed that the GC and Pt electrodes had different ratios of discharge capacity to charge capacity and current density for the Al deposition. A scanning electron micrograph of deposited metallic Al showed it had a rounded shape, suggesting that the growth of dangerous dendritic Al was efficiently inhibited in the present electrolyte solution.

Keywords: aluminum secondary battery, multivalent cation battery

1. Introduction

Lithium ion batteries (LIBs) are used for various mobile applications because of high voltage, light weight etc., leading to high specific energy and power density. The LIBs are also being applied to electric vehicles (EVs), but they are insufficient for a long drive without recharging. High specific energy density is an essential factor for EV applications, and can be realized by increasing voltage or/and capacity. Recently, new rechargeable batteries with high theoretical specific energy density like air-metal batteries (Kraytsberg & Ein-Eli, 2011; Kumar et al., 2010) and multivalent cation batteries (Mizrahi et al., 2008; Aurbach et al., 2007; Jayaprakash et al., 2011) have attracted attention. Both batteries have lower theoretical electromotive force than LIBs, but they have much higher theoretical specific capacity than LIBs, greatly improving specific energy density. Magnesium is being investigated as a promising negative electrode active material for multivalent cation batteries because it has larger specific capacity and is easy to handle and abundant on the earth (Mizrahi et al., 2008; Aurbach et al., 2007).

Aluminum has the highest theoretical volumetric capacity (8.04 Ah cm^{-3}), (Li & Bjerrum, 2002) which is about 4 times larger than lithium, and it is the most abundant metal in the earth's crust. Jayaprakash et al. assembled the rechargeable aluminum-ion battery with an ionic liquid, 1-ethyl-3-methylimidazolium chloride, containing AlCl_3 (Jayaprakash et al., 2011). Recently, some ionic liquids have been researched as electrolytes for batteries and plating baths etc (Jayaprakash et al., 2011; Jiang et al., 2006). However, ionic liquids for use in Al plating baths are too expensive to be used for commercial batteries. From 1970s, aromatic hydrocarbons dissolving AlBr_3 and KBr have been investigated for Al plating (Elam & Gileadi, 1979; Peled & Gileadi, 1976; Capuano & Davenport, 1971). The electrolyte solutions showed high conductivity, and shiny metallic Al was deposited on several metal and carbon substrates. However, to our knowledge, the anodic dissolution of Al in the electrolytes has hardly been investigated.

In this study, we investigated the effect of KBr concentration on electrical conductivity and the Al deposition/dissolution in several ethylbenzene solutions dissolving AlBr_3 and KBr . Also the Al deposition/dissolution at glassy carbon (GC) and Pt electrodes in these electrolyte solutions was characterized by cyclic voltammetry (CV) and charge/discharge tests. Transition metals like Pt, Au and Cu are often used as substrates for the Al plating (Elam & Gileadi, 1979; Peled & Gileadi, 1976; Capuano & Davenport, 1971), but they were narrower in potential window than GC. Elam and Gileadi found that the Al deposition/dissolution at the GC electrode reversibly proceeded in the ethylbenzene solutions containing AlBr_3 and KBr (Peled & Gileadi,

1976). We investigated the usefulness of GC and Pt electrodes as a substrate for the Al deposition/dissolution which was important for rechargeable Al battery applications.

2. Method

2.1 Preparation of Electrolytes

Electrolyte solutions were prepared in an Ar-filled glove box. AlBr_3 , KBr and ethylbenzene were purchased from Wako Pure Chemical Industries, Ltd. and used as received. A brown flask was used to shade light. Three electrolytes were prepared by dissolving 1 M AlBr_3 and 0.125, 0.25 or 0.5 M KBr in ethylbenzene. A mixed solution of ethylene carbonate (EC) and diethylcarbonate (DEC) (1:1, by volume) containing 1 M LiPF_6 (Tomiyama Pure Chemical Industries, Ltd.) was used for comparison.

2.2 Electrochemical Measurements

An electrochemical glass cell was assembled with a GC rod ($\Phi = 5$ mm) as the working electrode and an Al plate as the reference and counter electrodes, and then covered with an Al foil for light interception. After that, the electrochemical cell was put in an Ar-filled desiccator. All the operations were carried out in the Ar-filled glove box. The GC electrode was polished with 3 μm alumina suspension, and then sonicated in an ultrapure water to remove the alumina. For electrical conductivity measurements, a pair of Pt black electrodes (surface area: 2 cm^2) were used.

Electrochemical measurements were performed with SI1287 potentiostat (Solartron), SI1260 impedance analyzer (Solartron) and HJ1001SM8 charging/discharging system (Hokuto Denko). To evaluate ionic conductivity of each electrolyte, electrochemical AC impedance spectroscopy was applied. The AC impedance measurements were carried out in the frequency range of 1 to 0.1 MHz with the perturbation of 10 mV. Charging was carried out at 1.0 mA cm^{-2} for 1 h and discharging was done at the same current to a cut-off potential of 1.0 V vs. Al/Al^{3+} .

2.3 Observation of Deposited Al Metal Configuration

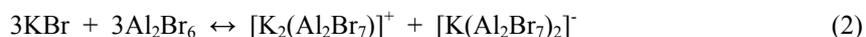
The morphology of metallic Al deposited on a Pt sheet (1 \times 1 cm^2) working electrode was observed by scanning electron microscopy (SEM). Deposited metallic Al was gently washed in methanol and dried at room temperature. SEM images were taken with VE-9800 (Keyence).

3. Results and Discussion

Figure 1 shows Arrhenius plots of electrical conductivity for ethylbenzene solutions containing 1 M AlBr_3 and 0.50, 0.25 or 0.125 M KBr as well as the (EC+DEC) (1:1) solution with 1 M LiPF_6 for reference. Activation energy for ionic conduction (E_a) was calculated by using the following equation.

$$\ln \kappa = \ln A - \left(\frac{E_a}{RT} \right) \quad (1)$$

Where κ is the electric conductivity, A is frequency factor, R is gas constant and T is temperature. The electrical conductivity ($\sim 10^{-3}$ S cm^{-1}) for the solutions containing 0.25 and 0.50 M KBr was higher than that ($\sim 10^{-4}$ S cm^{-1}) for the solution containing 0.125 M KBr, as reported previously (Reger et al., 1979, pp. 869-873). E_a was 16.4, 12.4 and 11.7 kJ mol^{-1} for the solution with 0.50, 0.25 and 0.125 M KBr, respectively. These electrolyte solutions showed lower electrical conductivity than the (EC+DEC) (1:1) solution containing 1 M LiPF_6 , as shown in Figure 1, while the former showed similar E_a value to the latter which was a conventional electrolyte for Li-ion battery. Reger et al. suggested the mechanism of ionic conduction containing hopping of ionic species from one ionic cluster to the next one (Reger et al., 1979, pp. 873-879). They also suggested that in ethylbenzene solutions containing AlBr_3 and KBr some kinds of ionic complexes were formed by the following reaction:



AlBr_3 exists as a dimer like Al_2Br_6 in each solution, and 0.5 M KBr is stoichiometrically enough for 1 M AlBr_3 . Decreasing the ratio of the concentration of KBr to AlBr_3 decreases the number of $[\text{K}_2(\text{Al}_2\text{Br}_7)]^+$ and $[\text{K}(\text{Al}_2\text{Br}_7)_2]^-$ ions formed at equilibrium (2), leading to the decrease in ionic conductivity. This can explain the results in Figure 1.

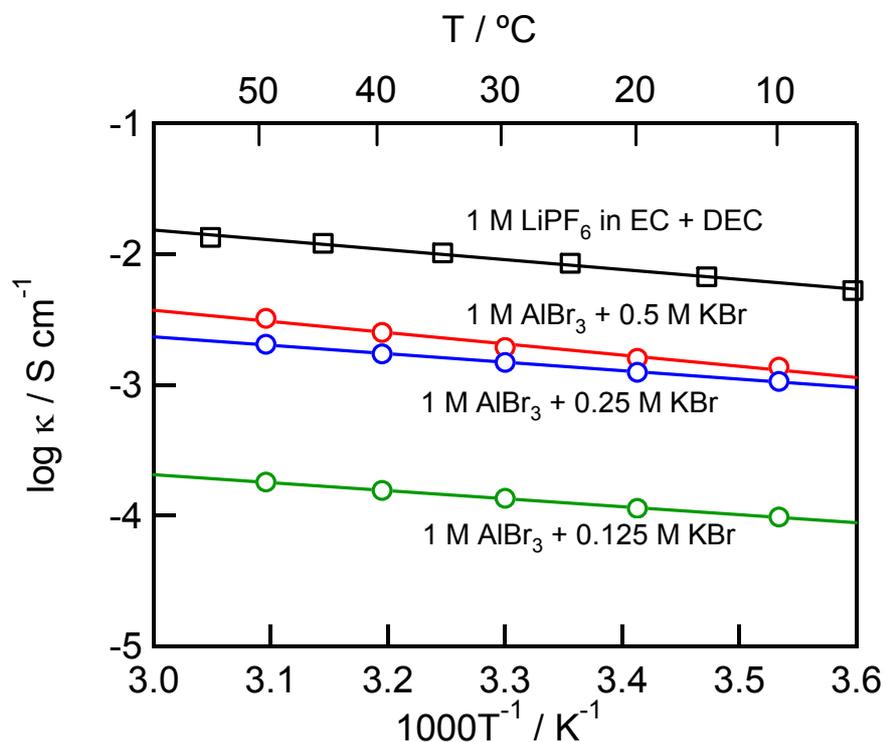


Figure 1. Arrhenius plots of electrical conductivity for ethylbenzene solutions containing 1 M AlBr₃ and 0.5, 0.25 or 0.125 M KBr and an (EC + DEC) solution containing 1 M LiPF₆

Figure 2 shows the cyclic voltammograms (CVs) of a GC electrode in the ethylbenzene solutions containing 1 M AlBr₃ and 0.50, 0.25 or 0.125 M KBr. Figure 2 exhibits the oxidation peak current due to Al dissolution depends on the concentration of KBr, while the reduction current due to Al deposition starts at more negative potentials than 0 V vs. Al/Al³⁺, irrespective of KBr concentration, suggesting that large overpotentials are required for the Al deposition, and the onset potential does not depend on the KBr concentration. Moreover the reduction current depended on the KBr concentration, suggesting that the rate for Al deposition was influenced by the KBr concentration. Gileadi et al. also have obtained the similar CVs in a potential range between -0.1 and 1.4 V vs. Al/Al³⁺ with ethylbenzene solutions containing AlBr₃ and different concentrations of KBr, and suggested that adding KBr into the AlBr₃ solution triggered the formation of Al₂Br₇⁻ which accelerated electrodeposition of Al (Elam & Gileadi, 1979; Peled & Gileadi, 1976).

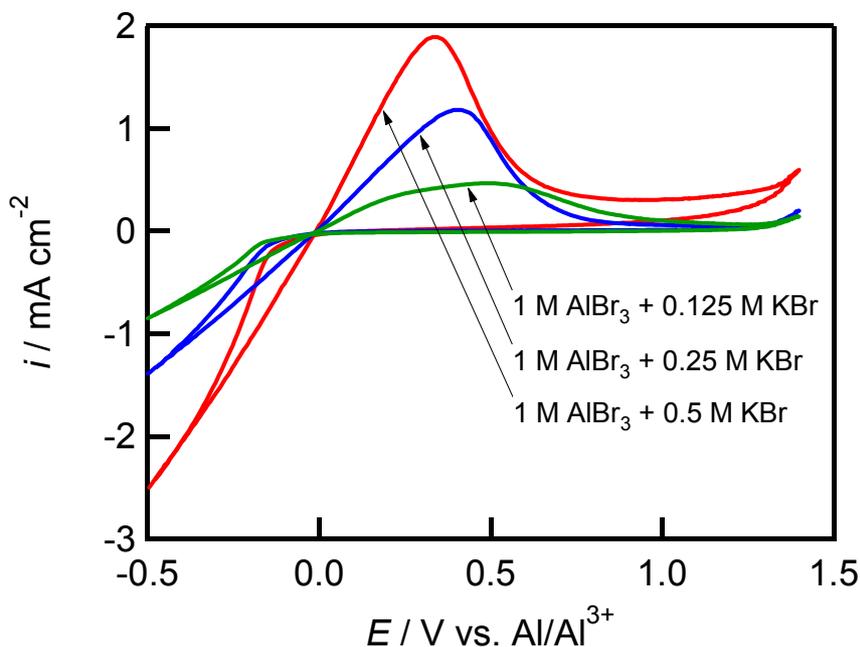


Figure 2. Cyclic voltammograms of a GC electrode in ethylbenzene solutions containing 1 M AlBr_3 and 0.5, 0.25 or 0.125 M KBr. Sweep rate: 50 mV s^{-1}

Figure 3 shows CVs of GC and Pt electrodes in an ethylbenzene solution containing 1 M AlBr_3 and 0.5 M KBr at scan rates of 10 and 50 mV s^{-1} . In both cases, the Al deposition and dissolution were clearly observed. Over-all reaction was indicated as Equation (3) (Peled & Gileadi, 1976).



The reduction current density for the GC electrode is twice as high as that for the Pt electrode. On the other hand, the ratio of oxidation charge to reduction charge (C_o/C_r) was 77.7% for the GC electrode and 93.5% for the Pt electrode although the reduction and oxidation current density due to Al deposition/dissolution on the GC electrode was higher than that on the Pt electrode. During the CV measurement, the metallic Al deposited on the GC electrode fell off, which was responsible for smaller C_o/C_r value for the GC electrode. On the CV of the Pt electrode, a small oxidation peak was observed at 1.0 V. According to Elam and Gileadi (1979) this peak is due to the faradaic Br adsorption reaction on the Pt surface as follows;



For the GC and Pt electrodes, both reduction and oxidation currents were not influenced by scan rate, suggesting that in the Al deposition and dissolution the charge transfer process was rate-determining.

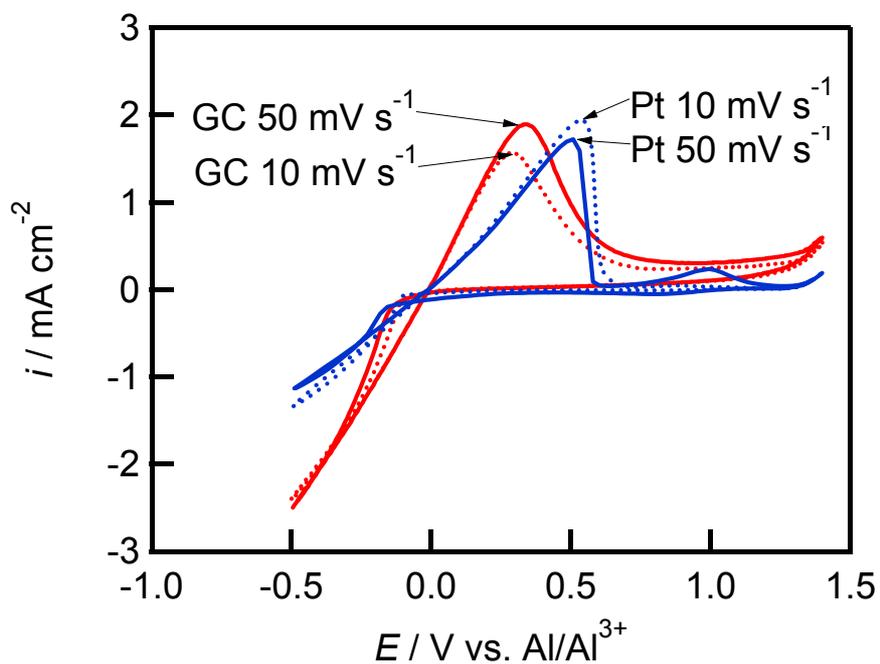


Figure 3. Cyclic voltammograms of GC and Pt electrodes in an ethylbenzene solution containing 1 M AlBr_3 and 0.5 M KBr . Scan rate: (solid) 50 mV s^{-1} and (dotted) 10 mV s^{-1}

Figure 4 shows change in charge and discharge capacities with cycle number for electrochemical cells with a GC or Pt electrode as the negative electrode and an Al plate as the positive electrode. Metallic Al was deposited on the GC or Pt electrode during each charge process and dissolved during each discharge process. For the GC electrode, the ratio of discharge capacity to charge capacity ($C_{\text{dis}}/C_{\text{ch}}$) was around 60%, which was consistent with the $C_{\text{o}}/C_{\text{r}}$ value evaluated from CV measurements. In contrast, the $C_{\text{dis}}/C_{\text{ch}}$ value for the Pt electrode was 80% at the first cycle and gradually increased with charge/discharge cycle up to around 100%. These also suggest the metallic Al deposited on the GC electrode easily fell off, and that on the Pt electrode strongly attached.

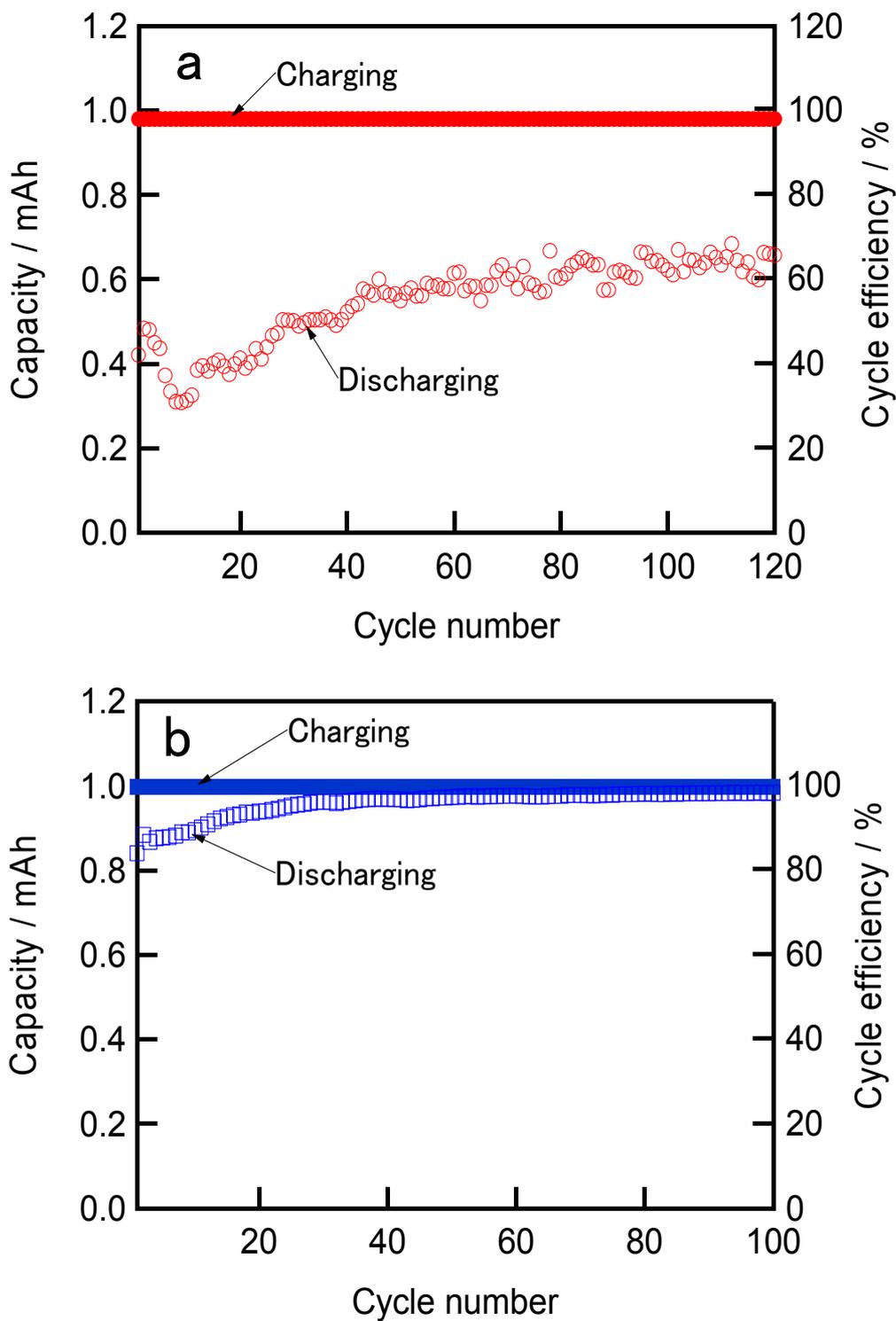


Figure 4. Charge and discharge capacities for (a) GC and (b) Pt electrodes in an ethylbenzene solution containing 1 M AlBr_3 and 0.5 M KBr . Charge and discharge current density: 1 mA cm^{-2} . Charge capacity: 1.0 mAh cm^{-2}

Figure 5 shows an SEM image of the Pt electrode surface after Al deposition at reduction current density of 2.5 mA cm^{-2} for 10 min in an ethylbenzene solution containing 1 M AlBr_3 and 0.5 M KBr. Al was also deposited on the GC electrode, but the Al deposits easily fell off while washing. In contrast the Al deposits on the Pt electrode had a spherical shape and dendrites were not formed, suggesting that the present electrolyte solution was favorable for rechargeable aluminum battery applications. In the case of electrochemical deposition of metallic Li and Mg with a current density of 2.0 mA cm^{-2} , whisker-like deposits of Li and round-shaped grains of Mg were observed (Ling et al., 2012). The non-dendritic morphology of Mg was associated with strong bonding between Mg atoms, and the weak Li-Li bond strength led to the dendrite growth (Ling et al., 2012). In the case of metallic Al deposition, the Al-Al bond will be stronger than the Li-Li bond, leading to the formation of the non-dendritic morphology. The reduction current of Al on GC electrode showed linear voltammograms, suggesting that the Al reduction reaction is under charge transfer controlled (Figure 3). Under the diffusion controlled condition with increased overvoltage, deposited Al may become dendritic structure (Diggle et al., 1969).

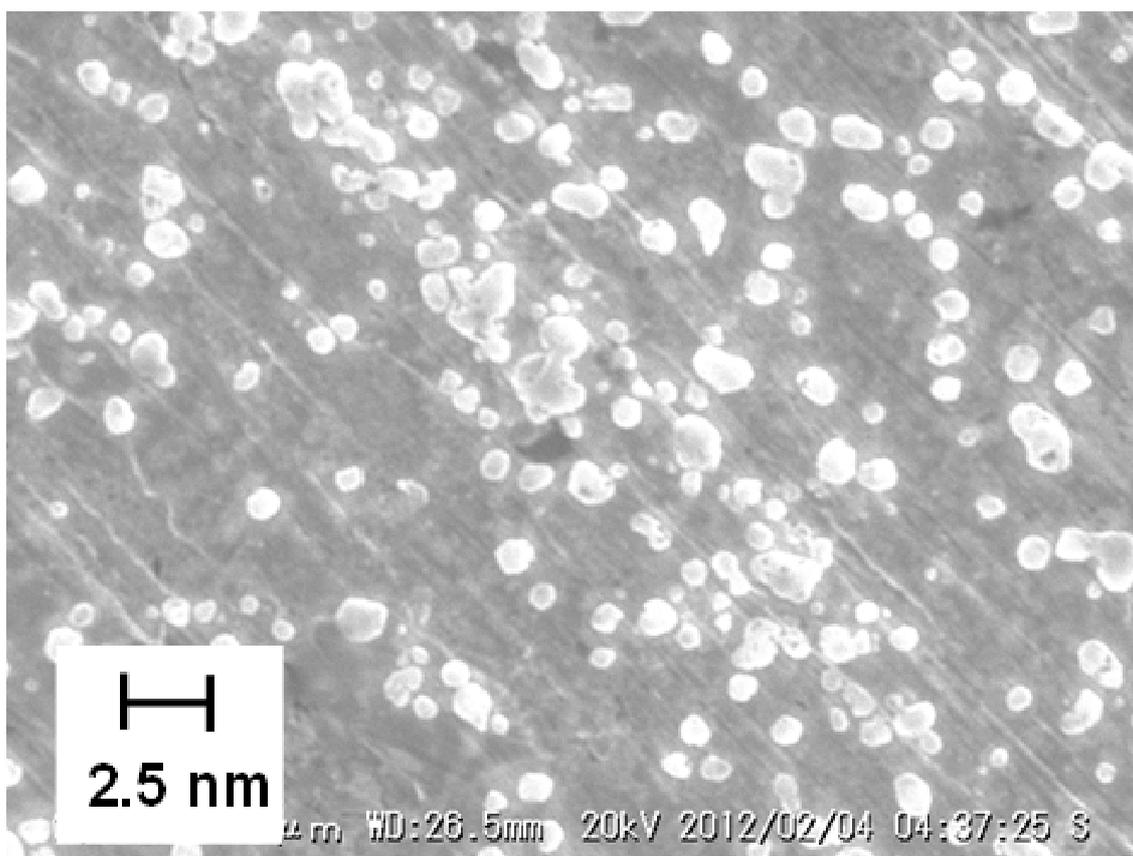


Figure 5. An SEM image of electrochemically deposited Al metal on a Pt electrode at reduction current density of 2.5 mA cm^{-2} for 10 min in an ethylbenzene solution containing 1 M AlBr_3 and 0.5 M KBr

4. Conclusion

The Al deposition/dissolution was investigated in ethylbenzene solutions containing AlBr_3 and KBr as electrolyte solutions for rechargeable aluminum batteries. In terms of ionic conductivity and current density for Al deposition/dissolution, the present electrolyte solutions were available for the battery application. The KBr concentration significantly influenced the rate for Al deposition/dissolution. In charge/discharge tests, the $C_{\text{dis}}/C_{\text{ch}}$ value for the Pt electrode was almost 100% while that for the GC electrode was 60% because Al deposited on the latter easily fell off. Deposited Al showed a rounded shape, suggesting that the dendritic growth was not observed.

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