Output Current Characteristics of Different Density Graphite Cathodes for an Al-Cl₂ Cell in an 1-ethyl-3-methylimidazolium Chloride-aluminum Chloride Mixture Ionic Liquid

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ABSTRACT

To enhance three phase interfaces on graphite cathodes in an Al-Cl₂ cell, graphite cathodes with different densities (1.27, 1.32, 1.40, 1.57, and 2.00 g cm⁻³) were evaluated in an 1-ethyl-3-methylimidazolium chloride -AlCl₃ mixture ionic liquid electrolyte at 313 K. The relation between current and cell voltage or power and current of the cathodes investigated here. Surface profiles of the graphite by mercury intrusion porosimetry suggested that there are effective pore diameters for penetration of the electrolyte, lower density graphite has more pores on the surface than graphite with higher densities.

Keywords : Ionic Liquid, Al-Cl₂ Cell, Graphite Electrode

1. Introduction

We have proposed an aluminum scrap recovery process by an electrochemical technique.¹ This process is schematically illustrated in a paper by the present authors.² In that process, chlorination of the aluminum scrap by a chlorination cell reaction is the most important process because input energy can be reduced in the electrowinning process. An ionic liquid as the electrolyte for the cell is attractive because the electrode reactions of the active metals progress at lower temperatures in the liquid, and a lower operation temperature contributes to avoid evaporation of the AlCl₃ which is produced by the cell reactions in the liquid acid. In previous papers, we reported basic data of a aluminum-chlorine fuel cell in a 1-ethyl-3-methylimidazolium chloride (EMIC) -AlCl₃ ionic liquid.³,⁴

The cell characteristics were evaluated by using cylindrical and circular cone type cathodes and a pure aluminum anode. The results showed that remaining chlorine gas bubbles on the cathode decreases the cell performance. The circular cone type cathode is superior to the cylindrical type cathode as it prevents chlorine gas bubbles remaining on the cathode. In these papers, it was found that a larger number of three phase interfaces of chlorine gas, electrolyte, and graphite are advantageous for good cell performance. When using sponge-like carbon which allows the electrolyte to permeate more easily, penetration of the electrolyte could be confirmed but the electric resistance of the carbon was large, and as a result only a small output current was obtained. From this result, sintered graphite was considered a possible candidate for the cathode electrode material assuming that the electric resistance of sintered graphite was low. In this paper, three phase interfaces on the graphite cathode made from different density graphite cathodes were used to evaluate cell performance.

2. Experiment

The electrochemical cell (ϕ = 50 × 120 mm) used here is made of Pyrex glass, and the anode of the cell was pure aluminum plate (Kojundokagaku, 99.999%), 70 × 30 mm. The graphite cathodes were supplied by Nippon Steel & Sumikin Chemical Co., Ltd. Graphite cathodes with five different densities (1.27–2.0 g cm⁻³) were cut into cylindrical shapes of φ = 21 mm diameter and 20 mm height. External views of these electrodes are shown in Fig. 1, and chlorine gas was introduced to the graphite cathodes through a glass tube. A PTFE plate was placed near the chlorine gas outlet to avoid direct contact between the aluminum anode and the chlorine gas. The minimum distance of the bottom face of the graphite and the front edge of the aluminum anode was 45 mm. The electrolyte was a mixture of 1-ethyl-3-methylimidazolium chloride (EMIC: Merck, 99%) and aluminum chloride (AlCl₃: Fluka, 99.0%) with 180 cm³ of this mixture prepared in a two to one molar ratio in a glass vessel equipped with a cooling system. Chlorine gas (Showa Denko, 99.99%) was introduced into the electrolyte; excess chlorine gas after the cell reaction was absorbed by 1 M NaOH solution.

The electrodes were connected to a potentiostat (Hokuto Denko, HZ-5000), and the current-voltage relation was measured at a voltage range from the open circuit voltage to 0.5 V with a scan rate of 1.0 × 10⁻² Vs⁻¹ in the ionic liquid. All experiments were performed at 313 K, with the temperature controlled by a water cooling and heating apparatus located outside of the cell. The graphite surfaces were observed by a scanning electron microscope (SEM, JEOL 6010PLUS), and the porosity of the graphite electrodes were measured by a mercury intrusion porosimeter (Shimadzu Autopore-9420).

3. Results and Discussion

The relation between cell voltage and current in the Al-Cl₂ cell using the graphite cathodes with different densities are shown in Fig. 2. From the figure, the relation is almost linear from 2.1 V and the gradient of the cathode E (2.0 g cm⁻³) curve is steeper than that of the other (A-D) cathodes decreasing with decreasing graphite cathode density. The current with graphite cathode A, 1.27 g cm⁻³, at 0.5 V showed the best performance with about 92 mA, an about 53% improvement over that of cathode E. The relation between the density of the graphite cathode and the average current at 0.5 V is shown in Fig. 3. At the average current of 0.5 V, electrode E shows little variation while electrodes A, B, and C show large current variations. In the range of densities from 1.6 to 2.0 g cm⁻³, the current value gradually increased when the density...
decreased and there was a sharp current increase when the carbon density decreased from 1.6 to 1.27 g cm\(^{-3}\).

The output power in the graphite cathodes with the five different densities was calculated from the results of Fig. 2 and the results are plotted in Fig. 4. The maximum powers of the electrodes from A to E are 64, 52, 47, 43 and 39 mW, respectively. The maximum current and power of electrode A are 1.7 and 1.5 times that of the electrode E, respectively.

From these results, electrode A with the lower density demonstrated the best performance among these carbon electrodes with five different densities. To investigate the reasons for this further, surface observations by SEM and measurements of the pore distributions by a mercury intrusion porosimeter were carried out for all the electrodes.

Figure 5 shows SEM images of the surfaces of the A, D, and E electrodes. The SEM image of electrode A shows many pores on the electrode surface, and it can be seen that there are pores that coalesce to result in larger area pores. In these larger pores, the depth of the pores is also deeper than the smaller pores. In electrode D, there are somewhat smaller pores observed in the electrode surface. In electrode E, it was not possible to confirm pores at this magnification. The observations confirmed that the surface area increases as the density of the graphite in the electrode became lower.

The results of the mercury intrusion porosimetry is shown in Fig. 6. Figure 6 does not show electrode E as the reproducibility was poor in the measurement conditions here. The increment pore volume shows the changes in the pore volume with changes in pore diameter. Therefore a higher value of pore volume indicates that more pores of that diameter are present. Figure 6 shows the occupancy ratio of about 40 µm diameter pores to be the most common in electrodes A and B, about 12 and 24 µm diameters in electrode C, and about 5 µm diameters in electrode D. Overall, as the graphite density decreases, the ratio of larger diameter pores increases.

According to Fannin et al., the viscosity of the EMIC-AlCl\(_3\) mixture ionic liquid (2:1 mol) is calculated to be 83 cp at 313 K a temperature\(^6\) where pure water has the value of 0.65 cp,\(^7,8\) the value of the ionic liquid viscosity is more than two orders of magnitude larger than that of water, and even with an electrolyte such as an aqueous solution that can penetrate small pores, it may be impossible for the ionic liquid electrolyte to penetrate to the electrode surface.

From the above results, and considering that the reaction takes place on the graphite cathode surface, a schematic representation of the situation of the pores is shown in Fig. 7. In the Al-Cl\(_2\) cell, Cl\(_2\) gas is introduced from the bottom part of the cell and then Cl\(_2\) bubbles dissolve into the ionic liquid electrolyte and become smaller. In the low density graphite cathodes, it may be considered that an increase in the current does not simply express an increase of electrode surface area, as only the parts which have effective pore

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**Figure 1.** External views of the graphite electrodes used in this experiment.

**Figure 2.** Relation between current and cell voltage in Al-Cl\(_2\) cell.

**Figure 3.** Relation between density of graphite cathode and current at 0.5 V in Al-Cl\(_2\) cell.

**Figure 4.** Relation between current and power in Al-Cl\(_2\) cell.
sizes would contribute to the electrode reaction. Also, even if a pore with a very small diameter is present on the surface of the electrode, the actual surface area increases but the effective electrode area does not increase as the electrolyte cannot penetrate the pore.

The variations in the current values of the graphite with low density in Fig. 3 may be due to change in the penetration of the electrolyte to a surface having many pores of relatively large diameters.

Further improvements to the Al-Cl₂ cell performance is expected to be possible by developing an electrode with many pores having effective diameters for improved penetration of the electrolyte.

4. Conclusions

The output characteristics of an aluminum-chlorine cell with different densities of the graphite cathode was investigated in an EMIC-AlCl₃ ionic liquid at 313 K. The results of the experiments may be summarized as follows.

1. The output current in the lowest density cathode (1.27 gcm⁻³) is higher than with the higher density cathodes.
2. The lowest density cathode showed the maximum power output, 1.5 times that of the highest density cathode (2.0 gcm⁻³).
3. In the graphite electrodes of 1.27 and 1.32 gcm⁻³ densities, a pore diameter of 40 µm was the main pore size at the electrode surface. A higher graphite density was characterized by smaller pore diameters.

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