—Communication—

Porous and Electrically Conducting Clay-Carbon Composite as Positive Electrodes of Lithium Secondary Cells

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In recent years many research groups have been concerned in lithium secondary cells, especially in cathode materials of the cells. Carbon materials (graphite, activated carbon and carbon black, etc.) have gained their interest as cathode materials of the Li secondary cells(1-3), and charge-discharge of the carbon cathode are believed to proceed through intercalation of ions into graphite-like crystallites. We have reported preparation and utilization of porous, mechanically strong, and electrically conducting clay-carbon composites, which are useful as electrodes of Zn-I₂ and Zn-O₂ cells(4-6). They are also useful as double layer type capacitors in aqueous media due to their high surface area and hydrophilic and lyophilic property of clay minerals. In order to clarify the applicability of the clay-carbon composite as the cathode material of Li secondary cells, we have examined the charge-discharge behavior of the Li cell using the clay-carbon composite as the cathode.

The clay-carbon composite ($\phi = 10$ mm, thickness = 2.5 mm) was prepared by firing mixtures of clay minerals (Kibushi clay) and porous carbon powder (Ketjen black ECDJ600) at composition of 85 / 15 in the same way as reported in our previous paper(4). Solvents were distilled and electrolytic salts were dried under vacuum. The charge-discharge tests were carried out using a beaker-type cell with a lithium counter electrode (1 cm x 1 cm) at a constant electric current (0.2 mA cm⁻²). The construction of the cell and electrochemical measurement were carried out under an argon atmosphere at room temperature.

Figure 1 shows charge-discharge curves of a Li|LiClO₄ in propylene carbonate|clay-carbon cell. From Fig. 1, maximum discharge capacity and energy density based on volume of the cathode are estimated to be about 110 mAh cm⁻³ and 0.18 Wh cm⁻³, respectively. During charging, two potential plateaus were observed at about 3.3 and 4.3 V. On the other hand, the discharging curve also shows two potential plateaus, one small plateau at about 2.8 V and a larger one at about 1.5 V. Figure 2 shows cyclic voltammograms of the clay-carbon composite cathode.

Fig. 1 Charge-discharge curves of the Li | LiClO₄ (1 M in propylene carbonate) | clay-carbon cell at current density of 0.2 mA cm⁻². Cut off potential : 4.5 V on charge and 1.0 V on discharge. (n) : number of cycle.

Fig. 2 Cyclic voltammograms of clay-carbon composite electrode in propylene carbonate solution of LiClO₄ (1 M) at various sweep regions. Sweep rate : 0.5 mV s⁻¹.

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In the case of short sweep range, we obtained voltammograms based on the electric double layer (Figs. 2(a) and (d)). On the other hand, at a wider sweep range broad anodic and cathodic peak currents were observed (Figs. 2(b), (c) and (f)). Repeated scanning gave the same voltammograms. Potential of the peaks do not closely agree with that of charge-discharge curves. However, these results support that the two electrochemically reversible reactions take place on the clay-carbon composite electrode in the potential regions. Although several researchers reported similar voltammograms for an activated carbon fiber cathode(2), a structural change of graphite-like crystallites limited the rechargeability. The present cathode showed better rechargeability presumably due to high surface area, low crystallinity of the present carbon powder and excellent mechanical strength of the composite. Recently, Watanabe and his coworkers investigated usefulness of carbon black-polyethylene glycol films as cathode materials of rechargeable Li cells(3) and reported that the charge-discharge process involved doping-undoping of ions into the polyaromatic structure of carbon black. We now assume occurrence of similar doping-undoping process of Li⁺ ion and ClO₄⁻ ion into the carbon powder,

where n and n' represent a charge stage of carbon, and these reactions expressed by Eqs. (1) and (2) correspond to the lower and higher potential plateaus regions in Fig. 1, respectively. The sum of n and n' values in Eqs. (1) and (2) are roughly estimated as 0.3-0.4 from the capacity of the cell. The large $n + n'$ value indicates that carbon surface in the composite fully participates in the electrochemical reactions due to the hydrophilic and lyophilic property of clay minerals.

Figure 3 shows the charge-discharge behavior of similar Li cells using propylene carbonate solution of LiBF₄ and LiPF₆. The charge-discharge curves for these cells show similar two potential plateaus observed in Fig. 1. However, the potential plateau at about 4.3 V in charging is smaller than that of the LiClO₄ system, and the rechargeability of the cells were worse than the cell using ClO₄⁻. We obtained similar charge-discharge curves by using a γ -butyrolactone solution, in which potential plateau at about 4.3 V in charging was also smaller than that observed in propylene carbonate solution. Among the electrolytic solutions tested, the propylene carbonate solution of LiClO₄ was the best. In this study, the energy density of the clay-carbon composite cathode is not so high compared to other cathode materials, but due to the easy preparation and handling, this composite cathode may be suitable for use in microelectronic devices such as a power source for memory back up.

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Fig. 3 Charge-discharge curves of the Li-clay-carbon cells at current density of 0.2 mA cm⁻². (a) : in 1.0 M of LiBF₄. (b) : in 1.0 M of LiPF₆.