Note

Cathodic Performance of CuO Electrode in Propylene Carbonate*

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Many materials have been recently proposed for high energy batteries with nonaqueous organic electrolytes. In the course of these investigations, some oxides,¹⁾⁻⁷⁾ AgO, PbO₂, CrO₃, Bi₂O₃, CuO, MoO₃,^{5), 8)} Ag₂CrO₄,^{5), 9)} MnO₂,¹⁰⁾⁻¹²⁾ have been reported as the cathode materials. Among several cathode materials¹³⁾⁻¹⁶⁾ which have been investigated so far by the authors, it was found that the rest potential of a CuO electrode in propylene carbonate containing 1 M LiClO₄ was *ca.* +0.3 V against S.C.E., and, moreover, the electrochemical equivalent of CuO was rather small. If lithium was employed as an anode, the Li/CuO battery would produce a high theoretical value of the energy density of *ca.* 2000 Whr/kg. In this note, the deterioration of the active material, CuO, was studied with regard to the cathodic performance.

Experimental Technique

Propylene carbonate was dehydrated by the treatments shown in the previous report¹⁷⁾ and the final content of H₂O was below 70 ppm. Commercial LiClO₄ (guaranteed reagent of the Ishizu Seiyaku Ltd.) and fine CuO powder (extra pure reagent of the same Co.) were dried at 150°C under vacuum for 8-10 hr and 3 hr, respectively. The CuO tablet cathode (geometry of the upper surface area: 1.33 cm²) was prepared by pressing the mixture of CuO, graphite and polyethylene powder at 3 t/cm². This electrode was fixed on the edge of a glass tube with epoxy resin adhesive, and the electrical contact was kept by a graphite rod and its powder.

The glass beaker containing 100 ml electrolyte was used as an electrolytic cell. The counter electrode was a platinum plate of 2×3 cm² and the reference electrode was S.C.E. with a Luggin capillary. Prior to the electrochemical measurements, dry nitrogen gas was bubbled into the electrolyte.

Results and Discussion

The effect of the graphite content on the cathodic polarization curves is shown in Fig. 1. The polarization characteristics were much improved with the increase of the graphite content, but they declined with the increase of the content of polyethylene powder owing to the low electric conductivity.

The continuous discharge curves at a constant current of 0.75 mA/cm² were shown in Fig. 2. The cathode potential decreased during the discharge, and the current efficiency of CuO calculated on the assumption of the two electron discharge process was to be *ca.* 20%.

Fig. 1 Potential-current density curves at the CuO electrode at 30°C

Graphite content: -○- 5%, -●- 15%, -△- 30%, -▲- 50%. Polyethylene content: 5%.

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Fig. 2 Potential variation and coulometric efficiency during continuous discharge at a constant current at 30°C

CuO: ●— 200 mg, ○— 400 mg. Current density: 0.75 mA/cm².

The results of X-ray analysis of the active material during the discharge are shown in Fig. 3. These X-ray patterns showed that the peaks of CuO were gradually decreased, and the peak of Cu₂O at 42° 34' was observed on the all patterns. On the other hand, the peak at 49° 12' was disappeared on the pattern after 16% of CuO in the cathode had discharged at a constant current. The peaks due to Cu appeared on the patterns after a discharge at a constant potential of -1.0 V vs. S.C.E., and, also, after the constant current discharge. These results show that CuO would be reduced stepwise: CuO → Cu₂O → Cu, though the detailed mechanisms have not been clarified.

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Fig. 3 X-ray diffraction patterns of CuO electrodes

CoK α , A: Before discharge, B: After discharge at a constant potential of -0.5V vs. S.C.E. (consumed CuO: 2.5%), C: After discharge at a constant potential of -1.0V vs. S.C.E. (consumed CuO: 9.7%), D: After discharge at a constant current (0.75 mA/cm², consumed CuO: 16.0%)