

## CHROMIUM OXIDES AS CATHODES FOR LITHIUM CELLS

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### Summary

The performances of organic electrolyte lithium cells with the chromium oxides,  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_2$ ,  $\text{Cr}_5\text{O}_{12}$ ,  $\text{Cr}_2\text{O}_5$ ,  $\text{Cr}_6\text{O}_{15}$ , and  $\text{Cr}_3\text{O}_8$ , as cathodes, have been examined. The discharge behaviors of the couples  $\text{Li}/\text{Cr}_2\text{O}_5$ ,  $\text{Li}/\text{Cr}_6\text{O}_{15}$ , and  $\text{Li}/\text{Cr}_3\text{O}_8$ , gave satisfactory results, especially in terms of energy density. The highest calculated energy density, based on the weights of the chromium oxides and to a 2.0 V cutoff at  $0.5 \text{ mA}/\text{cm}^2$ , was  $1210 \text{ W h}/\text{kg}$  for the  $\text{Li}/\text{Cr}_3\text{O}_8$  couple. Further, the performance of a coin-type cell with a  $\text{Cr}_3\text{O}_8$  cathode was demonstrated, and it was found that the cell exhibited good rechargeability.

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### Introduction

Recently, a considerable amount of interest has been shown in the organic electrolyte lithium cell because of its high energy density and excellent reliability. Various metal oxides have been studied as cathodes for these cells. Among them, manganese dioxide is used in commercial cells. Recently, Besenhard *et al.* [1] found that chromium oxides such as  $\text{Cr}_3\text{O}_8$  and  $\text{Cr}_2\text{O}_5$  are very attractive cathode materials for lithium cells. The calculated theoretical energy density of the  $\text{Li}/\text{Cr}_3\text{O}_8$  couple was  $1080 \text{ W h}/\text{kg}$  based on the experimental value of utilization of  $\text{Cr}_3\text{O}_8$  and an average cell voltage of 3 V.

Besenhard *et al.* used a double-H-type test cell with glass diaphragms, and only proved the possibility of chromium oxides as cathode materials for organic electrolyte lithium cells. It is necessary to have more detailed characteristics of the cell if its full potential is to be realized. In this study, the discharge behavior of cells with various types of chromium oxides as cathode was examined and also the performance of coin-type cells is demonstrated.

## Experimental

The chromium oxides were prepared according to the literature [2].  $\text{CrO}_2$ ,  $\text{Cr}_2\text{O}_5$ , and  $\text{Cr}_3\text{O}_8$  were obtained by heating  $\text{CrO}_3$  for 24 h at 350 °C, at 340 °C, and at 270 °C, respectively, in an autoclave. The X-ray diffraction patterns of the reaction products were in good agreement with those reported previously.  $\text{Cr}_6\text{O}_{15}$  was obtained by heating  $\text{CrO}_3$  for 3 days at 220 °C in a pressure vessel of test-tube type [3] under an oxygen pressure of 110 MPa. The  $\text{Cr}_6\text{O}_{15}$  obtained contained small amounts of  $\text{Cr}_2\text{O}_5$  and  $\text{Cr}_3\text{O}_8$ .  $\text{Cr}_5\text{O}_{12}$  was prepared by heating a mixture of  $\text{CrO}_3$  and  $\text{CrO}_2$  (1:1 weight ratio) for 3 days at 220 °C under an oxygen pressure of 120 MPa. The X-ray diffraction patterns of the reaction products corresponded essentially with those of  $\text{Cr}_5\text{O}_{12}$  given by Wilhelmi [2].

The cells used for the electrochemical tests were constructed in a cylindrical configuration. The anode was a disk of lithium foil 15 mm in diameter, the separator was Teflon sheet, and the cathode consisted of a mixture of 0.1 g of chromium oxide, 0.15 g of graphite, and 0.04 g of Teflon powder, which was pressed into a tablet of 13 mm dia. under a pressure of about 9 MPa. The electrolyte was 1M  $\text{LiClO}_4$  in 1:1 by weight propylene carbonate–1,2-dimethoxyethane. The organic solvents and  $\text{LiClO}_4$  were dried in the usual manner. The coin-type cell had an external diameter of 12.5 mm and an external thickness of 2.5 mm; the cathode was a mixture of 0.085 g of  $\text{Cr}_3\text{O}_8$ , 0.01 g of graphite, and 0.010 g of Teflon powder, which was pressed into a tablet of 7.5 mm dia.; the separator was a microporous polypropylene sheet.

## Results and discussion

Typical constant current ( $0.5 \text{ mA/cm}^2$ ) discharge curves, at room temperature, for the cells with the various chromium oxide cathodes are shown in Fig. 1. The highest oxidation state chromium oxide,  $\text{CrO}_3$ , was not

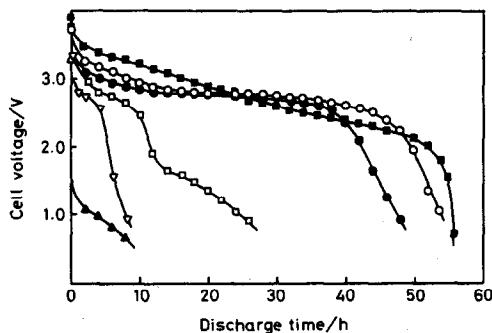


Fig. 1. Constant current ( $0.5 \text{ mA/cm}^2$ ) discharge curves of the Li/chromium oxide cells at room temperature. ■,  $\text{Cr}_3\text{O}_8$ ; ○,  $\text{Cr}_6\text{O}_{15}$ ; ●,  $\text{Cr}_2\text{O}_5$ ; □,  $\text{Cr}_5\text{O}_{12}$ ; ▽,  $\text{CrO}_2$ ; ▲,  $\text{Cr}_2\text{O}_3$ .

examined because it is somewhat soluble in organic donor solvents. As shown in the Figure, the cells with the higher oxidation state chromium oxides such as  $\text{Cr}_3\text{O}_8$ ,  $\text{Cr}_2\text{O}_5$ , and  $\text{Cr}_6\text{O}_{15}$  exhibit a good performance. The average oxidation numbers of these oxides are five or more. The highest calculated energy density of 1020 W h/kg, based on the weights of the chromium oxides and to a 2.0 V cutoff at  $0.5 \text{ mA/cm}^2$ , was found in the  $\text{Li/Cr}_3\text{O}_8$  couple, where the number of electrons transferred per Cr atom was 1.4. On the other hand, the energy densities of the cells with the lower oxidation state chromium oxides such as  $\text{Cr}_5\text{O}_{12}$ ,  $\text{CrO}_2$ , and  $\text{Cr}_2\text{O}_3$ , the average oxidation numbers of which are less than five, are considerably lower than those of the above three cells.

The significant difference in the discharge performances may be explained by structural considerations of chromium oxides.  $\text{Cr}_5\text{O}_{12}$ ,  $\text{CrO}_2$ , and  $\text{Cr}_2\text{O}_3$  have three-dimensional frameworks containing either  $\text{CrO}_4$  tetrahedra and  $\text{CrO}_6$  octahedra or octahedra only [4].  $\text{CrO}_3$  crystallizes in a chain type structure [4]. The structures of  $\text{Cr}_6\text{O}_{15}$ ,  $\text{Cr}_2\text{O}_5$ , and  $\text{Cr}_3\text{O}_8$  are unknown so far. These higher oxidation state chromium oxides are more likely to have layers or chains as structural elements, and their high utilization for the cathode reactions may be explained by the topotactic reaction of the chromium oxides with lithium [1].

The existence of free water in the chromium oxides is the most serious problem in their practical application as cathodes in lithium cells. The crude  $\text{Cr}_3\text{O}_8$  showed a weight loss of about 0.6% on heating at  $200^\circ\text{C}$ . The characteristics of  $\text{Cr}_3\text{O}_8$  heat-treated for 24 h at various temperatures in open air, and the calculated energy density at  $25^\circ\text{C}$  on the basis of a 2.0 V cutoff at a current density of  $0.5 \text{ mA/cm}^2$  are shown in Table 1. The  $\text{Cr}_3\text{O}_8$  heated at  $250^\circ\text{C}$  and  $300^\circ\text{C}$  has the same oxygen content, within the limits of experimental error, as that of the crude  $\text{Cr}_3\text{O}_8$ , as determined by thermogravimetric analysis. The X-ray diffraction patterns of these samples corresponded to those of  $\text{Cr}_3\text{O}_8$ . The discharge performance of the cell is slightly improved by the use of the  $\text{Cr}_3\text{O}_8$  heated at  $250^\circ\text{C}$ , as shown in Table 1. On the other hand,  $\text{Cr}_3\text{O}_8$  was converted to the lower oxidation state chromium oxides such as  $\text{Cr}_2\text{O}_5$  by heating at  $350^\circ\text{C}$ . The cell with the  $\text{Cr}_3\text{O}_8$  heat-treated at  $350^\circ\text{C}$  showed a poor discharge performance.

TABLE 1

Characteristics of  $\text{Cr}_3\text{O}_8$  heat-treated at various temperatures

Heating temperature ( $^\circ\text{C}$ )	X in $\text{CrO}_x$	Observed phase	Energy density ( $\text{W h kg}^{-1}$ )
Crude $\text{Cr}_3\text{O}_8$	2.66	$\text{Cr}_3\text{O}_8$	1210
250	2.65	$\text{Cr}_3\text{O}_8$	1240
300	2.67	$\text{Cr}_3\text{O}_8$	1100
325	2.36	$\text{Cr}_2\text{O}_5$	850
350	1.52	$\text{Cr}_2\text{O}_3$	5

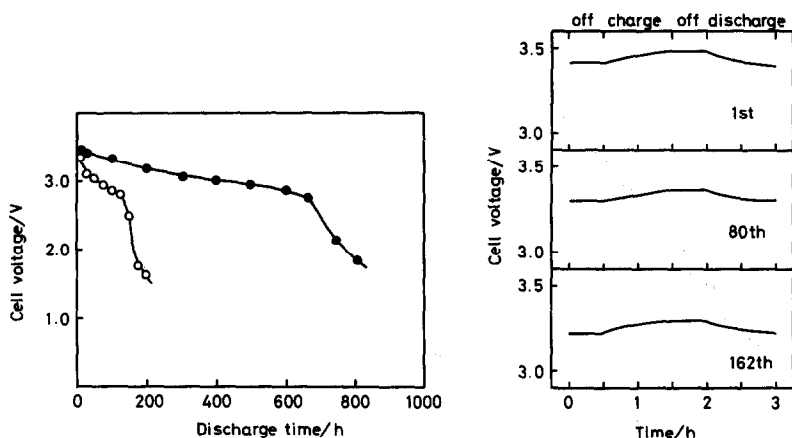


Fig. 2. Constant load discharge curves of the Li/Cr<sub>3</sub>O<sub>8</sub> coin-type cells at 20 °C. ●, 68 kΩ; ○, 15 kΩ.

Fig. 3. Charge–discharge cycles at 200 μA of the coin-type cell at room temperature.

The characteristics of coin-type cells with Cr<sub>3</sub>O<sub>8</sub> heat-treated at 250 °C were examined. In Fig. 2, the constant load discharge curves at 20 °C are shown. The discharge capacity is 33.3 mA h at a 68 kΩ load. The capacity corresponds to the transport of 1.5 electrons per Cr atom and the energy density is 308 W h l<sup>-1</sup>. The electrons transferred per Cr atom is in good agreement with results obtained in the cylindrical test cells. Generally, cells with the topotactic cathode process show a good rechargeability [5]. The charge–discharge curves of the coin-type cell at 200 μA are shown in Fig. 3, where the depth of discharge is 0.8%. As shown in this Figure, no significant change in the charge–discharge curves is observed during 160 or more test cycles. The rechargeable miniature cells could be used in an electronic wrist watch in combination with a solar cell.

Consequently, the high oxidation chromium oxides, especially Cr<sub>3</sub>O<sub>8</sub>, are promising cathode materials for organic electrolyte lithium cells in terms of energy density and rechargeability.

## References

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