

## CHARACTERISTICS OF AMORPHOUS CHROMIUM OXIDE AS A CATHODE FOR LITHIUM ORGANIC SOLVENT CELLS

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### Summary

Amorphous chromium oxide ( $a\text{-CrO}_x$ ) was obtained by heat-treating mixtures of  $\text{Cr}_3\text{O}_8$  and water at various temperatures. The discharge performance of lithium organic solvent cells with  $a\text{-CrO}_x$  as cathode was examined as a function of the oxygen content and of the specific surface area of  $a\text{-CrO}_x$ . The crystal systems of  $\text{Cr}_3\text{O}_8$ ,  $\text{Cr}_2\text{O}_5$ , and  $a\text{-CrO}_x$  were also analysed by the electron diffraction technique.  $\text{Cr}_3\text{O}_8$  and  $\text{Cr}_2\text{O}_5$  crystallized with the orthorhombic structure, while  $a\text{-CrO}_x$  showed only diffuse electron diffraction spots.

### 1. Introduction

A wide variety of metal oxides has been studied as the cathode material for primary and secondary organic electrolyte lithium batteries. Among them, high oxidation state chromium oxides such as  $\text{Cr}_2\text{O}_5$  and  $\text{Cr}_3\text{O}_8$  have recently become of interest because of the high energy density, the high cell voltage and the reversible character of lithium incorporation [1 - 3]. The calculated theoretical energy density of the  $\text{Li}/\text{Cr}_3\text{O}_8$  couple is 1210 W h/kg (based on experimental utilizations of  $\text{Cr}_3\text{O}_8$ ), a value which is about double that of the  $\text{Li}/\text{TiS}_2$  couple.

In the course of our study on the  $\text{Li}/\text{chromium oxide}$  cells, a new amorphous phase of chromium oxide ( $a\text{-CrO}_x$ ) was obtained by heat-treating a mixture of  $\text{Cr}_3\text{O}_8$  and water. The lithium cell with  $a\text{-CrO}_x$  as the cathode showed a high energy density and good performance as a rechargeable system for the whole range of lithium concentration [4]. In this study,  $a\text{-CrO}_x$  having various oxygen contents and specific surface areas was prepared, and its discharge performance as a cathode for lithium cells was examined. In addition, the morphology and the crystal systems of  $\text{Cr}_3\text{O}_8$ ,  $\text{Cr}_2\text{O}_5$ , and  $a\text{-CrO}_x$  were examined using transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

## 2. Experimental

$\text{Cr}_2\text{O}_5$  and  $\text{Cr}_3\text{O}_8$  were obtained by heating 1.0 g of  $\text{CrO}_3$  in an autoclave (volume:  $4.7 \text{ cm}^3$ ) for 24 h at  $340^\circ\text{C}$  and at  $250 - 270^\circ\text{C}$ , respectively, according to the phase diagram of Wilhelmi [5]. Amorphous chromium oxides were prepared by heating a mixture of 0.7 g of  $\text{Cr}_3\text{O}_8$  and 30 ml of water at  $200 - 300^\circ\text{C}$  for 24 h.

The chromium–oxygen stoichiometry was determined by reducing the sample to  $\text{Cr}_2\text{O}_3$  using TGA (Rigaku Denki TG4) in air. TEM and SEM examinations were carried out using a Hitachi 100C system and a Horiba EMAX-800 system, respectively. The BET surface area was measured with a Quantasorb Sorption system.

The cells used for electrochemical tests were constructed in a cylindrical configuration. The anode was a disk of lithium foil 15 mm in diameter. The separator was a microporous polypropylene sheet. The cathode was 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 13 mm in diameter under a pressure of 9 MPa. The electrolyte was 1M  $\text{LiClO}_4$  in 1:1 propylene carbonate–1,2-dimethoxyethane by weight. The organic solvents were dried prior to use. Lithium perchlorate was dried under vacuum for 24 h at  $120^\circ\text{C}$  and then for 5 h at  $200^\circ\text{C}$ . All the electrochemical measurements were carried out after at least one overnight stand under zero current flow.

## 3. Results and discussion

The X-ray diffraction patterns of  $\text{Cr}_2\text{O}_5$  and  $\text{Cr}_3\text{O}_8$  obtained in this experiment were in good agreement with those previously reported [5, 6]. An amorphous phase was obtained by heating a mixture of 0.7 g of  $\text{Cr}_3\text{O}_8$  and 30 ml of water. Broad X-ray diffraction lines of  $\text{Cr}_3\text{O}_8$  were observed for samples obtained by heat-treating a mixture of 0.7 g of  $\text{Cr}_3\text{O}_8$  and 20 ml of water or less, as was also the case for a mixture of 0.7 g of  $\text{Cr}_3\text{O}_8$  and 50 ml of water. No amorphous phase was obtained on heat-treating a mixture of  $\text{Cr}_2\text{O}_5$  and water. Therefore the following discussion is concerned with amorphous samples prepared by heating the 0.7 g of  $\text{Cr}_3\text{O}_8$ –30 ml of water mixture.

Table 1 shows the characteristics of the amorphous chromium oxides obtained by heat-treating this mixture at various temperatures ( $\text{Cr}_3\text{O}_8$  prepared at various temperatures was used as the starting material). In this Table, column 1 represents the preparation temperature and the characteristics of the  $\text{Cr}_3\text{O}_8$  starting material. The energy density reported in column 2 was calculated from the constant current ( $500 \mu\text{A}/\text{cm}^2$ ) discharge curves to a 2.0 V out-off and the weight of the chromium oxides. The oxygen content in  $\text{a-CrO}_x$  decreases slightly with increase in the heat-treatment temperature. The specific surface area obtained by the BET method is  $3 - 5 \text{ m}^2/\text{g}$ , which is almost twice that of  $\text{Cr}_3\text{O}_8$ . The small difference in the specific surface area

TABLE 1

Characteristics of a-CrO<sub>x</sub>

Sample no.	1			2			
	Temperature (°C) (CrO <sub>3</sub> → Cr <sub>3</sub> O <sub>8</sub> )	BET surface (m <sup>2</sup> /g)	O/Cr (CrO <sub>x</sub> )	Temperature (°C) (Cr <sub>3</sub> O <sub>8</sub> → a-CrO <sub>x</sub> )	BET surface (m <sup>2</sup> /g)	O/Cr (CrO <sub>x</sub> )	Energy density (W h/kg)
1	260	2.4	2.6 <sub>0</sub>	200	2.9	2.6 <sub>0</sub>	1240
2				230	2.8	2.5 <sub>4</sub>	1250
3				250	2.9	2.4 <sub>8</sub>	1010
4				270	4.7	2.4 <sub>9</sub>	1110
5	265	2.2	2.6 <sub>1</sub>	200	3.4	2.5 <sub>5</sub>	1170
6				230	4.3	2.5 <sub>1</sub>	1250
7				250	3.7	2.5 <sub>0</sub>	1190
8				270	4.4	2.4 <sub>8</sub>	1110
9	270	2.0	2.6 <sub>2</sub>	200	2.5	2.5 <sub>3</sub>	1260
10				230	2.9	2.5 <sub>3</sub>	1230
11				250	3.4	2.4 <sub>7</sub>	1220
12				270	2.6	2.4 <sub>9</sub>	1100
13	275	2.0	2.5 <sub>5</sub>	200	2.9	2.6 <sub>2</sub>	1290
14				230	4.4	2.6 <sub>0</sub>	1290
15				250	3.5	2.5 <sub>2</sub>	1070
16				270	4.0	2.4 <sub>9</sub>	1150

between crystalline Cr<sub>3</sub>O<sub>8</sub> and amorphous CrO<sub>x</sub> may be due to the aggregation of the small particles in a-CrO<sub>x</sub>, as shown by the TEM and SEM microphotographs reproduced in Figs. 1 and 2.

The discharge performance of a-CrO<sub>x</sub> is not markedly affected by the preparation temperature when this is between 200 and 270 °C. Cells using a-CrO<sub>x</sub> prepared at 300 °C, however, showed a poor discharge performance. In fact, the amorphous Cr<sub>3</sub>O<sub>8</sub> obtained at 300 °C included a small amount of Cr<sub>2</sub>O<sub>5</sub> phase.

In another paper [4], the cycling characteristics of Li cells with Cr<sub>2</sub>O<sub>5</sub>, Cr<sub>3</sub>O<sub>8</sub> and a-CrO<sub>x</sub>, respectively, were presented for various ranges of charge transfer (e<sup>-</sup>/Cr), such as 0.1 - 0.3, 0.4 - 0.6 and 0.7 - 0.9 e<sup>-</sup>/Cr. The Li/Cr<sub>2</sub>O<sub>5</sub> cells showed a poor cycling performance over the whole range, whilst the Li/Cr<sub>3</sub>O<sub>8</sub> cell showed a good rechargeability in the deep charge transferred region. In fact, in the e<sup>-</sup>/Cr range between 0.7 and 0.9, no significant degradation was observed up to the 200th cycle. On the other hand, if the cycling regime was maintained between 0.1 and 0.3 e<sup>-</sup>/Cr, the charging efficiency rapidly failed upon cycling. By contrast, the Li cell with a-CrO<sub>x</sub> as cathode had a good cycling performance over the whole range of charge transferred. Such cycling behavior of the Li/Cr<sub>3</sub>O<sub>8</sub> and Li/a-CrO<sub>x</sub> cells is shown in Fig. 3. The improved rechargeability may be due to the large effective surface area of a-CrO<sub>x</sub>. As shown in Table 1, the surface area of

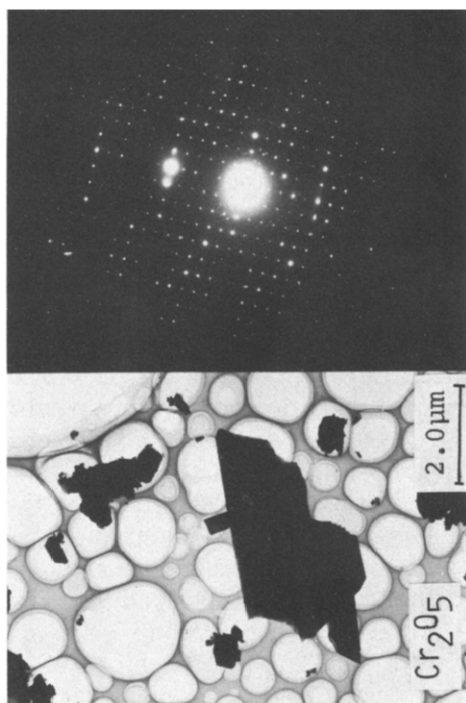
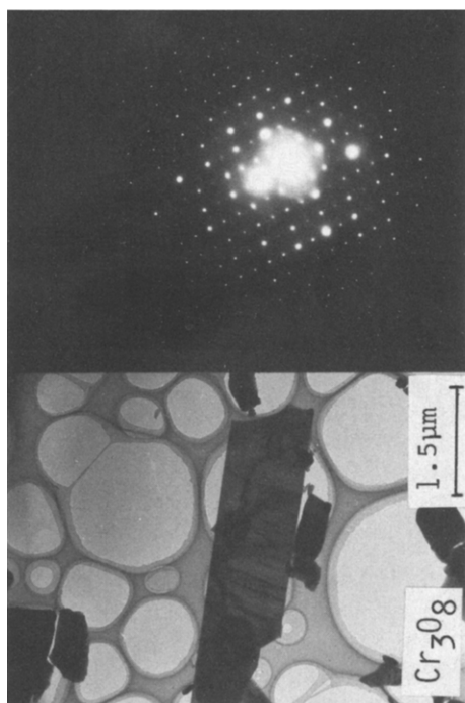
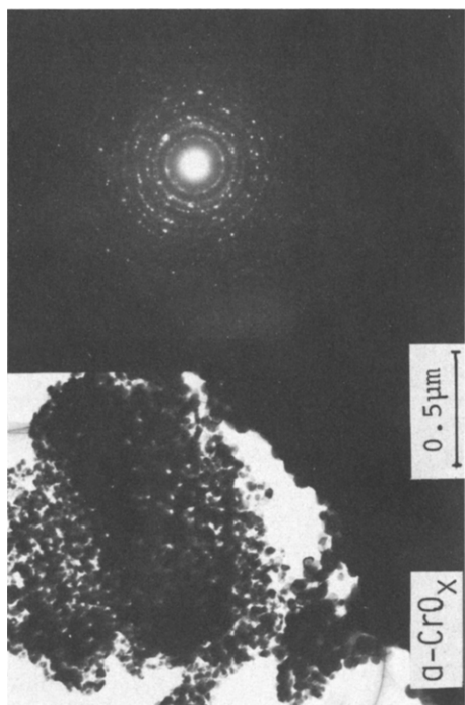


Fig. 1. Transmission electron micrographs of Cr<sub>3</sub>O<sub>8</sub> (prepared at 265 °C), a-CrO<sub>x</sub> (sample No. 9) and Cr<sub>2</sub>O<sub>5</sub> (prepared at 340 °C).

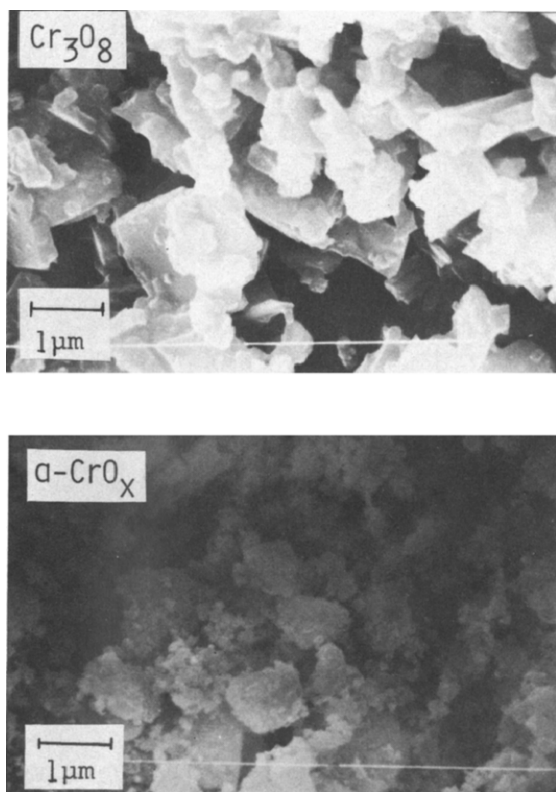


Fig. 2. Scanning electron micrographs of  $\text{Cr}_3\text{O}_8$  (prepared at  $265\ ^\circ\text{C}$ ) and  $\alpha\text{-CrO}_x$  (sample No. 9).

$\alpha\text{-CrO}_x$  is only about double that of  $\text{Cr}_3\text{O}_8$  because of the aggregation of primary particles to secondary particles. If a more dispersive state of  $\alpha\text{-CrO}_x$  could be obtained, the performance of the  $\text{Li}/\alpha\text{-CrO}_x$  cell would probably be improved even more: an attempt to prepare such a material is in progress in our laboratory.

In Fig. 1, TEM photographs and the electron diffraction patterns of  $\alpha\text{-CrO}_x$  (sample No. 9) are shown along with those of  $\text{Cr}_2\text{O}_5$  (prepared at  $340\ ^\circ\text{C}$ ) and  $\text{Cr}_3\text{O}_8$  (prepared at  $265\ ^\circ\text{C}$ ). The meshes supporting the chromium oxide particles were carbon micro grid.  $\text{Cr}_2\text{O}_5$  and  $\text{Cr}_3\text{O}_8$  show clear diffraction spots and each particle is a single crystal with a size of  $1 - 5\ \mu\text{m}$ . Diffuse electron diffraction spots, whose patterns do not agree with those of either  $\text{Cr}_3\text{O}_8$  or  $\text{Cr}_2\text{O}_5$ , have been obtained for  $\alpha\text{-CrO}_x$ . The oxygen/chromium ratio in  $\alpha\text{-CrO}_x$  was slightly lower than that in  $\text{Cr}_3\text{O}_8$  and higher than that in  $\text{Cr}_2\text{O}_5$ . Therefore, the amorphous chromium oxide is considered to be a small particle, new compound, the stoichiometry of which is between  $\text{Cr}_3\text{O}_8$  and  $\text{Cr}_2\text{O}_5$ . Figure 2 shows SEM photographs of  $\text{Cr}_3\text{O}_8$  and  $\alpha\text{-CrO}_x$ . The morphology of  $\alpha\text{-CrO}_x$  particles is not clear but it may possibly be described as an aggregation of small particles.

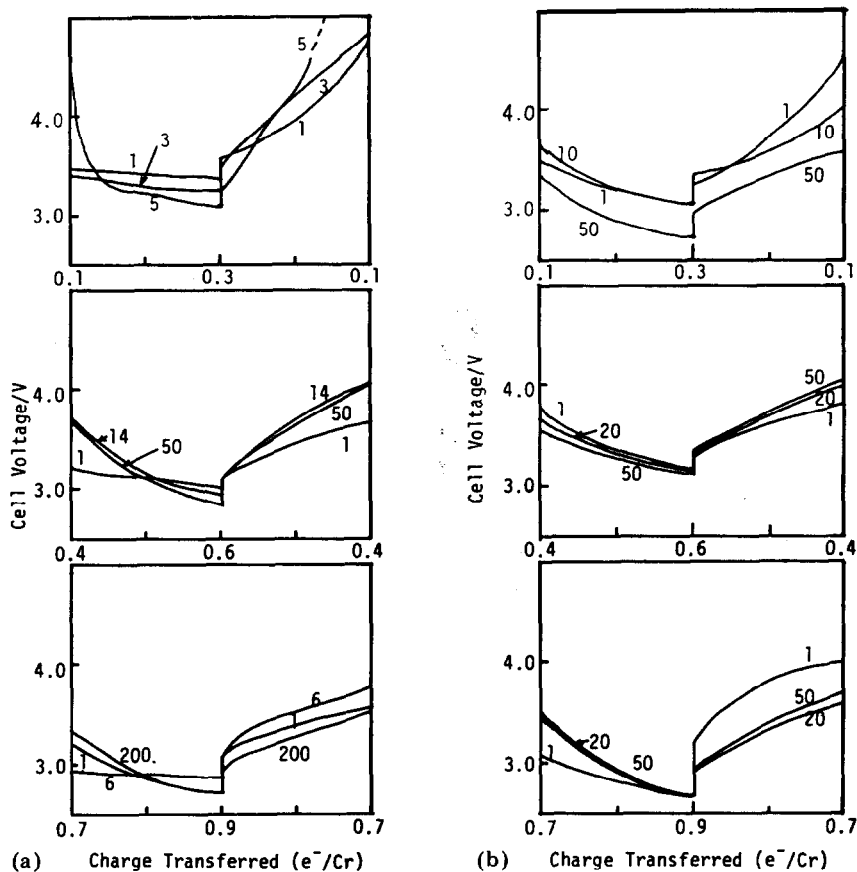


Fig. 3. Cycling behavior of the cells with: (a)  $\text{Cr}_3\text{O}_8$  (prepared at  $270^\circ\text{C}$ ), (b)  $\text{a-CrO}_x$  (sample No. 11).

The existence of the  $\text{Cr}_3\text{O}_8$  and  $\text{Cr}_2\text{O}_5$  phases was reported by Kubota [7], Roy and White [8], and Whilhelmi [9]. To date, no crystallographic data for these compounds have been given. The electron diffraction patterns of  $\text{Cr}_3\text{O}_8$  and  $\text{Cr}_2\text{O}_5$  obtained in this work could be indexed by an orthorhombic unit cell. The unit cell dimensions were determined to be  $a = 11.69 \text{ \AA}$ ,  $b = 6.17 \text{ \AA}$  and  $c = 16.42 \text{ \AA}$  for  $\text{Cr}_3\text{O}_8$ , and to be  $a = 8.42 \text{ \AA}$ ,  $b = 6.28 \text{ \AA}$  and  $c = 18.91 \text{ \AA}$  for  $\text{Cr}_2\text{O}_5$  from the powder X-ray diffraction patterns. The observed and calculated  $d$  values and relative intensities are presented in Table 2.

### Acknowledgements

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TABLE 2

X-ray data for  $\text{Cr}_3\text{O}_8$  and  $\text{Cr}_2\text{O}_5$ 

$\text{Cr}_3\text{O}_8$				$\text{Cr}_2\text{O}_5$			
$a = 11.69 \text{ \AA}, b = 6.17 \text{ \AA}, c = 16.42 \text{ \AA}$				$a = 8.42 \text{ \AA}, b = 6.28 \text{ \AA}, c = 18.91 \text{ \AA}$			
$hkl$	$d_{\text{obs}}$	$d_{\text{cal}}$	$I_{\text{obs}}$	$hkl$	$d_{\text{obs}}$	$d_{\text{cal}}$	$I_{\text{obs}}$
100	11.7	11.7	VS	100	8.5	8.4	S
010	6.2	6.2	W	010	6.3	6.3	M
200	5.85	5.85	M	102	6.3	6.3	M
103	4.98	4.96	W	011	5.97	5.96	M
202	4.77	4.76	VW	104	4.11	4.12	W
210	4.21	2.42	VW	201	3.70	4.11	W
203	4.02	4.00	VW		3.61		W
300	3.89	3.90	M				W
113	3.85	3.86	M	203	3.51	3.50	M
212	3.77	3.77	W	210	3.51	3.50	M
	3.71		W	105	3.46	3.45	M
014	3.41	3.42	W	212	3.28	3.28	VS
213	3.34	3.35	M	204	3.14	3.14	M
311	3.21	3.23	W	106	2.954	2.952	W
020	3.10	3.09	W	205		2.813	
312	3.07	3.06	W	213	2.811	2.811	M
021	3.05	3.03	VW	023		2.811	
121	2.959	2.951	W	116	2.675	2.671	W
214	2.880	2.877	VW				
304	2.818	2.814	W				
106	2.667	2.665	W				
215		2.597	W				
411	2.603	2.608					

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