

The preparation and electrochemical properties of chromium oxides CrO_x both in lithium and sodium aprotic electrolytes

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Abstract

Chromium oxides CrO_x were prepared under various conditions from CrO_3 . Their capacity and reversibility as cathodic materials both in LiClO_4 /propylene carbonate and NaClO_4 electrolytes were measured. The charge density in lithium electrolyte (750 C/g) was higher than that in sodium one (400–600 C/g). Coin cells were assembled with CrO_x cathode; their capacity was 0.1 A h for 2025 size, and the average voltage 3.0 V.

Introduction

The proposals of using chromium oxides CrO_x in lithium cells were introduced by Besenhardt and Schöllhorn [1], who used chromium oxide as a cathode in lithium cells. Much interest was paid to lower oxides of chromium by Takeda *et al.* [2, 3]. They prepared various crystalline as well as amorphous species and found rather high specific capacity and reversibility of them. Recently, lithium batteries with CrO_x as cathode material appeared on the market [4, 5].

A general formula CrO_x is used by convention for a series of hardly identified phases, which occur as intermediates in the thermal decomposition of chromium oxide CrO_3 . Substances of composition Cr_3O_8 , Cr_6O_{15} , Cr_2O_5 , Cr_5O_{12} , and CrO_2 were identified in the mixture of reaction products together with final oxide of trivalent chromium Cr_2O_3 . Preparation of any individual species is rather difficult. Under hydrothermal conditions, amorphous Cr_3O_8 is formed. Recently, a lot of interest has been paid to the properties of this material [6–9].

The aim of this paper is to present various phenomena connected with the preparation and electrochemical behaviour reactions of chromium oxides both in sodium and lithium aprotic electrolytes. Oxides and the products of their lithiation will be characterized and their cathodic capacity, reversibility and charge density will be given. A question arises, whether these substances are suitable as cathodes in aprotic electrolytes and the answer is the subject of this paper.

Experimental

Preparation of CrO_x oxides

Chromium oxide CrO_3 (pur.) was dried at 150 °C for 1 h. Essentially, two ways were used for its thermal decomposition: (i) heating in air to 250–380 °C for 2 or

20 h; (ii) heating under 2.0–2.4 MPa of pure oxygen in a stainless steel reactor.

The reaction product was grinded in a laboratory ball mill and kept in a desiccator. To remove the oxide, Cr_3O_8 product was leached in water for 1 h; the solid substance was washed and dried (in vacuum 1–10 Pa, 110 °C for 8 h).

Chemical lithiation

Instead of usual butyllithium procedure [10], the older ammonia method [11] was used for lithiation of chromium oxides.

Electrochemical lithiation

A simple preparative cell was used for electrochemical lithiation. The body of the cell was made from polytetrafluoroethylene (PTFE). The sample holder from stainless steel contained a cavity for 2 g of experimental material (chromium oxide mixed with carbon black and polyphenylene oxide as a binder). This cavity was covered with a nickel screen. The counter electrode was a piece of lithium. All manipulation with the preparative cell was done in a dry box in an argon atmosphere (<20 ppm of H_2O). The electrode was polarized cathodically with a current 2–5 mA until required charge passed. Then, the electrode was rinsed with dried propylene carbonate (PC) and the residual PC was removed by washing in benzene. Finally, the electrode was dried for 1 h in vacuum.

Electrodes and cells

The chromium oxide CrO_x was mixed with an equal quantity by weight of PTFE-impregnated carbon black (80 wt.% PTFE). The blend was spread on a platinum screen and fixed by pressing.

A three-electrode cell was used for investigations. Both reference and counter electrodes were made from metallic lithium or sodium. The screen covered with the CrO_x was mounted on a PTFE holder and fastened by means of glass screw joints.

1 M LiClO_4 and/or 1 M NaClO_4 solution in PC was used as the electrolyte. PC was dried with CaH_2 , and distilled in vacuum. Finally, the electrolyte was dried by refluxing in a stream of dry nitrogen.

Experimental coin cells

A mixture of 83 wt.% CrO_x , 15 wt.% graphite, and 2 wt.% polyphenylene oxide were mixed and a solvent containing 20% of light hydrocarbons (petrol) and 80% perchlorethylene was added. Cathodes of diameter 15 mm and height 0.9 mm were pressed by 200 MPa after most of the solvent had been removed by evaporation. The mass of the cathode was 0.33 g. Coin cells (size 2025, i.e. diameter: 20 mm, height: 2.5 mm) were assembled from the cathodes, lithium anodes, and 1 M LiClO_4 in a mixture of 1,2-dimethoxyethane (1,2-DME) and PC (1:1) as the electrolyte.

Electrochemical methods

Chronopotentiometric measurements were performed by a simple device with automatic current reversal at potential levels 3.9 and 1.3 V (for LiClO_4/PC) respectively 3.6 and 1.0 V (for NaClO_4) with constant current.

Triangular single-shot voltammetry was performed using scanning rate $v=0.0064$ V/s after the electrode had been polarized anodically (3.35 V or 3.1 V in lithium and sodium electrolytes, respectively) for various time intervals t_a between the successive voltammetric runs. Chromium oxide prepared by decomposition of CrO_3 under pressure 2.2 MPa of oxygen at 320 °C was used for this purpose. The

electrode was polarized anodically to the starting potential of 3.35 V in lithium electrolyte and 3.1 V in the case of sodium electrolyte for various time interval t_α between two successive voltammetric runs.

Electrode admittances were measured by means of a potentiostat, a.c. millivoltmeter and an analog phasemeter; the latter two were replaced by an X-Y recorder at ultra-low frequencies (to 0.0005 Hz) and by the evaluation of Lissajous ellipses.

The testing of coin cells is described together with experimental data.

Electric conductivity

The pellets were prepared from the mixtures of CrO_x with PTFE-impregnated carbon black, and were fastened between two electrodes. These electrodes were mounted by constant moment into a modified micrometer screw gauge, and the electric conductivities were measured by multimeter M1T 291.

Other methods

X-ray diffraction patterns were recorded on a diffractogram DRON-2 (made in Russia). Unstable products of lithiation were filled in a special sample holder and covered with Mylar (transparent polyester) foil in a dry box.

Scanning electron microscope TESLA BS 350 was used for observation of particles morphology.

Results

Identification of reaction products

Thirty samples of chromium oxides were prepared under various conditions. All products were identified by RTG powder analysis and diffractograms were compared with results published by Wilhelmi [12]. The preparation of samples can be divided into four groups:

(i) Samples prepared by heating for 2 days for temperatures 250, 270, 290, 300, 330, 360, 380, 400 and 430 °C. Their composition varied from almost pure Cr_3O_8 at 250 °C to a mixture of CrO_2 and Cr_2O_3 at the highest temperature; in the intermediate temperature range, the reaction mixture was more complex.

(ii) Samples prepared by heating for 2 days followed by leaching in water. These samples did not contain Cr_3O_8 in detectable amount. The particles are slightly damaged by the action of water, as it is apparent from the diffuse character of the diffraction lines.

(iii) Samples prepared by heating for 2 h (Fig. 1): at lowest temperatures, the sample contains CrO_3 only. Even at 280 °C, there is some residual chromium oxide together with Cr_3O_8 . Generally, the temperature limits for other oxides are shifted towards higher temperatures, as it should be expected.

(iv) Samples prepared by heating for 2 h at high oxygen pressure (2–2.4 MPa), and at temperatures 320 and 400 °C: CrO_2 was the main product at 400 °C (Fig. 2).

Chemical lithiation

The sample prepared at high pressure and temperature 320 °C was used for the experiment.

The amount of lithium used for chemical lithiation corresponded to ratio 0.5 Li/1 Cr. The composition of lithiated product was 27.63% Cr, 4.91% Li, 0.47% ammonia, and the rest (66.99% by weight) was oxygen.

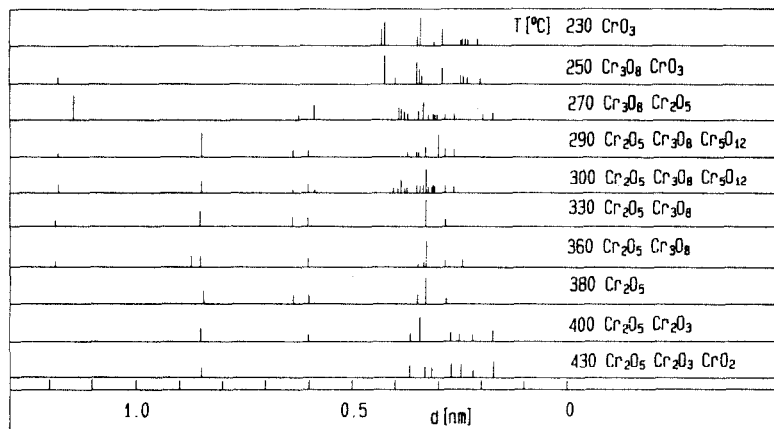


Fig. 1. X-ray diffraction patterns of samples prepared by 2 h heating.

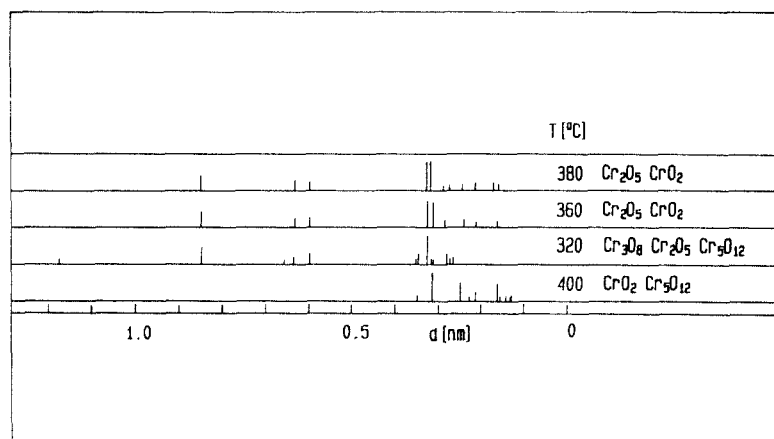


Fig. 2. X-ray diffraction patterns of samples prepared at elevated pressure.

The distances d in starting oxide and in the product of lithiation are included in Table 1. Stronger lines are less marked and weakest lines almost disappeared. Moreover, a slight shift towards smaller interlayer distances is visible there. Finally, some new and weak lines appeared in the diffractogram.

The morphology of particles was observed in scanning electron microscope. Apparently, the size and shape of particles is not considerably changed by lithiation. The edges of particles seem not to be so sharp and marked as they are on starting material.

Electrochemical lithiation

The same sample as in previous paragraph was used for electrochemical lithiation. The electrode was prepared in form of a pellet (diameter 30 mm) from a mixture of 76% of oxide, 19% of graphite and 4.8% of polyphenylene oxide as a binder. Several experiments were performed, using different electric charges corresponding to the ratio Li:Cr from 0.15 to 1.5. The result of investigations by X-ray diffraction is shown in

TABLE 1

Lattice parameters of starting and lithiated CrO_x

Starting oxide		Lithiated oxide		Δ (%)
d (nm)	intensity	d (nm)	intensity	
0.8456	s	0.8355	w	-1.2
0.6314	w			
0.5986	w	0.5918	w	-1.1
		0.3458	w	
0.3277	s	0.3267	s	-0.3
		0.3152	m	
0.3133	m	0.3142	m	+0.2
0.2814	w			
0.2763	w			
0.2739	w			
		0.2483	w	
0.2437	w	0.2442	w	+0.2
0.2138				

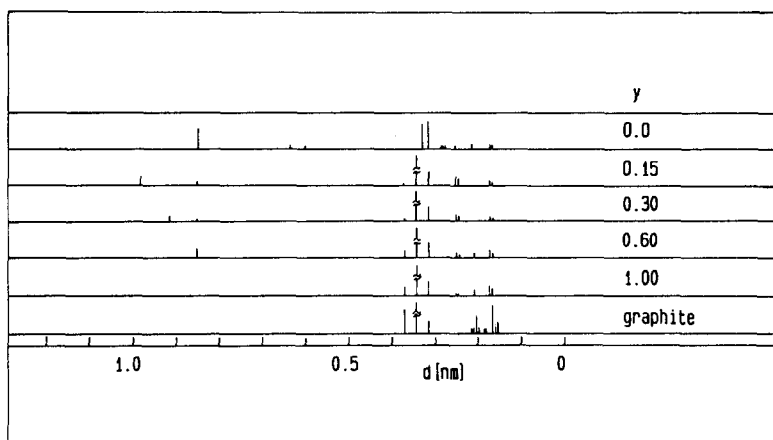


Fig. 3. X-ray diffraction patterns of samples prepared by electrochemical lithiation.

Fig. 3, where the diffractogram of graphite is given for comparison. It was not necessary to consider the diffraction pattern of polyphenylene oxide due to its great diffusivity and rather low content of the binder in the electrode.

Similarly as in previous paragraph, new diffraction lines appear in the course of lithiation. Most apparent is a line at $d = 0.09$ nm. If the degree of lithiation is increased, this line is shifted towards lower values and it disappears at $\text{Li}:\text{Cr} > 1.0$. Similar is the behaviour of a new line at 0.2 nm. Unfortunately, the lines at 0.3 nm are superimposed by a strong line of graphite and are not elucidated.

Voltammetry

Two processes are apparent on voltammetric curves measured in lithium electrolyte. The starting potential E_1 of the first one is 3.35 V, i.e., just at the starting point of

TABLE 2

Voltammetry of CrO_x electrode

Run no.	E_1^a U_{CrO_x} (mV)	I_{max}^b (μA)	E_{max}^b (mV)	E_2^a $U_{\text{carb.bl.}}$ (mV)	Reoxidation (h)
1	3350	220	2050	750	0
2	3350	160	1900	820	16
3	3350	138	1900	900	5
4	3350	122	2000	950	3
5	3350	134	1900	1000	60

^a E_1, E_2 : initial potential of voltammetric wave (of CrO_x or carbon black).

^b $E_{\text{max}}, I_{\text{max}}$: maximum of peak.

the voltammetric curve. Maximum of the first process E_{max} is in limits 1.9–2.05 V (Table 2), and corresponding peak current is I_{max} . As we see from Table 2, the peak current decreases slowly from the first to the fourth curve (on the same electrode) and it is slightly higher if the time of the anodic polarization (t_α) is sufficiently long.

The second process is the electrochemical reaction of the lithium from electrolyte with carbon black. The potential E_2 is the potential at which the mentioned process becomes apparent. It increased from run nos. 1 to 5. However, this increase is perhaps only virtual due to decrease of the first process, thus decreasing the background for the second one.

The same electrode material (by the same scanning rate and starting potential 3.1 V) in sodium electrolyte was tested. Apparently, there are two voltammetric processes. The first one starts at 3.1 V and its maximum is moved from 2.05 V (1st run) to 1.4–1.6 V (2nd–6th run). The decrease of the peak current is perhaps slower than in the case of lithium. However, general properties including slow reaction are rather similar both for lithium and sodium systems.

Cyclic chronopotentiometry

The cyclic chronopotentiometry at constant current load 10 mA/g (of mixture CrO_x -carbon black-PTFE) was studied on all sorts of CrO_x .

The open-circuit voltage of fresh CrO_x electrodes is generally within the limits of 3.6–3.8 V with the exception of oxide treated with water, the open-circuit voltage of which was 3.5–3.6 V. The electrode potential of an electrode under current load is lower, of course, and the point of smallest slope of the discharge curve was at 2.5–2.7 V. Sometimes there was some margin evidence of multistep nature of the discharge process.

A typical example of results is given in Fig. 4, where the specific capacities (in C/g) are plotted for cathodic cycles nos. 1, 2, 10 and 50 for material prepared at various temperatures, and for 2 h decomposition time. As it follows from Fig. 4, the best specific capacity (750 C/g, i.e., 1.43 electrons per 1 atom Cr) was obtained if the sample was prepared at decomposition temperature 320 °C.

Similar measurements were performed for all other preparation ways. The results are summarized in Table 3. According to them, samples prepared by 2 h decomposition should be recommended for the cathodes of lithium primary cells.

The influence of current load on the specific capacity is shown in Fig. 5 in logarithmic scales. The curve plotted there was obtained on a sample prepared under

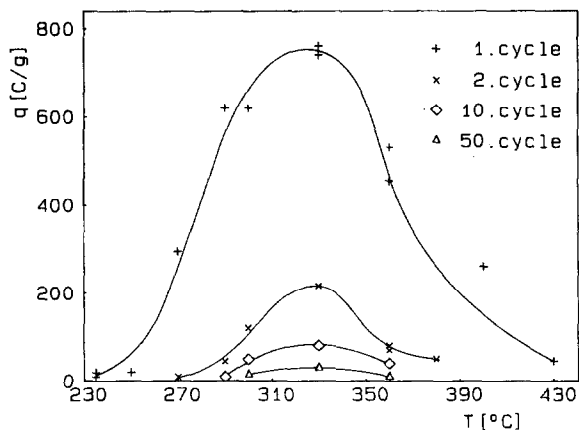


Fig. 4. Specific charge (to potential 1.3 V) of samples prepared by heating for 2 h; electrolyte: 1 M LiClO_4 /propylene carbonate.

TABLE 3

Specific capacities q for 1th, 2th and 10th chronopotentiometric cycle at current load 10 mA/g_{ox}

Sample	1st cycle		2nd cycle		10th cycle	
	q_1 (C/g _{ox})	q_2 (C/g _{ox})	q_2/q_1	q_{10} (C/g _{ox})	q_{10}/q_1	
2 h decomposition	750	210	0.280	80	0.107	
2 days decomposition	720	215	0.299	45	0.063	
2 days decomposition washed	570	255	0.447	60	0.105	
high pressure decomposition (2 h, 320 °C)	645	398	0.617	137	0.212	

elevated oxygen pressure and it has two branches with a knee at 6 mA/g approximately. At lower current loads, the specific capacity is almost constant. The discharge of the electrode is slow enough so that the whole electroactive substance undergoes the reaction. At higher current load, the specific capacity is inversely proportional to current load (i.e., the slope of the right branch in Fig. 5 equals to -1), as it should be for a diffusion-controlled process in a planar electrode.

The cyclic chronopotentiometry at the same current load for all samples of CrO_x in sodium electrolyte was also studied. As in the case of lithium, the best performance was reached on the samples prepared by the decomposition of CrO_3 at normal pressure. However, the optimal temperature seems to be slightly shifted (340 °C in comparison to 330 °C).

Specific conductivity

The specific conductivities of various CrO_x samples mixed 1:1 with PTFE-impregnated carbon black at room temperature were measured and compared to the composition of prevailing phases. Generally, the highest conductivity (of the order

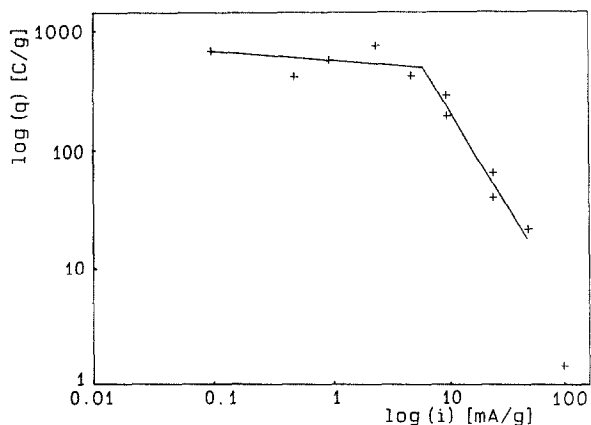


Fig. 5. Influence of current load on specific charge in 1 M LiClO₄/propylene carbonate.

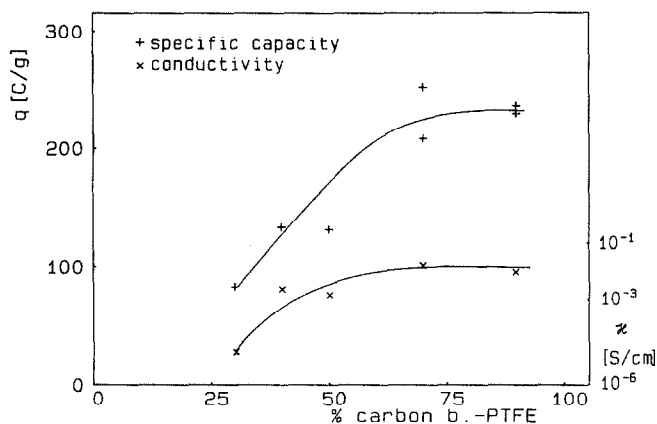


Fig. 6. Specific capacity and conductivity of sample prepared under high oxygen pressure in dependence of content carbon black-PTFE mixture.

S/cm) was found if the prevailing phase in CrO_x was CrO₂. If the prevailing phase was Cr₂O₅, then the conductivity decreased to 10⁻¹ S/cm and it was of the order 10⁻² S/m for samples containing Cr₃O₈ mainly.

The influence of the ratio CrO_x:carbon black at current load 10 mA/g on the specific conductivity and on the specific capacity is given in Fig. 6.

Electrode admittance

The admittance of an electrode-contained sample obtained under high oxygen pressure was measured in lithium electrolyte in the potential range from 3.8 to 1.8 V (in 0.2 V steps) and finally at 3.8 V again. An example of admittance diagram in complex plane (at 3.4 V) is shown in Fig. 7. As admittances increase with frequency, the high-frequency part of the spectrum up to 2000 Hz is most apparent there. The loop is not symmetrical and approaches to an almost pure R-C (resistance and

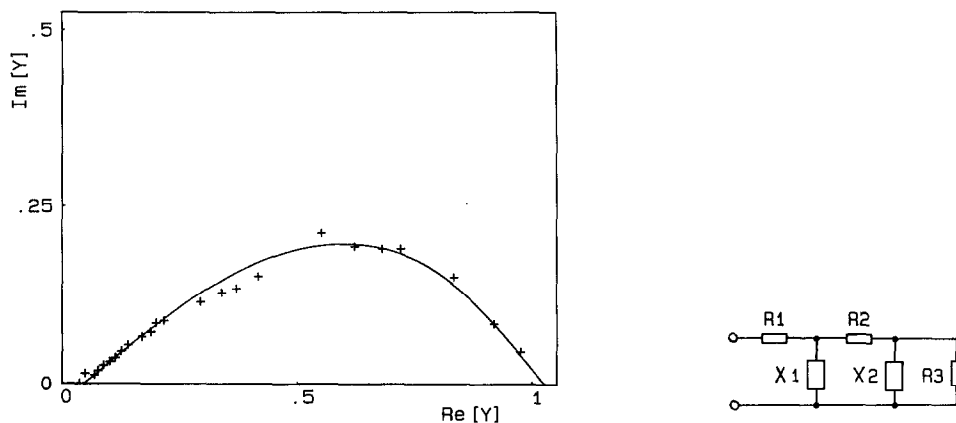


Fig. 7. Admittance diagram for an electrode at 3.4 V in $\text{LiClO}_4/\text{propylene carbonate}$ electrolyte. The farthest right point corresponds to 2000 Hz.

Fig. 8. Diagram of equivalent-electrode circuit (R in Ω , W in $\text{S Hz}^{1/2}$).

TABLE 4

Components of equivalent circuit in 1 M $\text{LiClO}_4/\text{propylene carbonate}$ electrolyte

E (mV)	R_1 (Ω)	X_1 ($\text{mS Hz}^{1/2}$)	R_2 (Ω)	X_2		R_3 (Ω)
				W ($\text{mS Hz}^{1/2}$)	C (mF)	
3800	44.4	0.346	524		8.77	9940
3600	31.9	0.284	363	2.40		3225
3400	39.7	0.248	499	7.05		1001
3200	37.6	0.269	510	70.50		
3000		0.145	668	66.90		
2800	44.3	0.269	562	1.63		415
2600		0.166	235		6.58	3016
2400	26.2	0.171	868		5.10	8755
2200		0.222	945		4.73	10600
2000	38.5	0.135	1061		3.91	21700
1800	39.3	0.0935	2320			1600
3800	48.1	0.344	1760		52.4	2300

capacitance in series) behaviour at high frequencies, while the diffusional behaviour is more apparent at low frequency part.

Equivalent-circuit corresponding with admittance diagram is indicated in Fig. 8. The components of the equivalence circuit were estimated by means of a simple programme, which works in an interactive way and resolves one component after another starting with high-frequency resistor R_1 (see Fig. 8). The results are presented in Table 4, the components X_1 and X_2 are assumed as a capacity (C_i) or a Warburg type admittance at $\omega=1$ ($|W_i|$).

The Warburg admittance measured in sodium electrolyte passes through a maximum at 2.5–2.7 V (3.2 V in lithium system), i.e., somewhat more negative if the difference

TABLE 5

Comparison of reversibility $\text{CrO}_x\text{-Na}$ and $\text{CrO}_x\text{-Li}$ systems

System	Voltammetry $I_{2\text{max}}/I_{1\text{max}}$	Chronopotentiometry Q_2/Q_1
$\text{CrO}_x\text{-Na}$	0.782	0.406
$\text{CrO}_x\text{-Li}$	0.728	0.280

of the standard potentials $\Delta E_{\text{Li-Na}} = -0.331$ V is considered. Moreover, the maximum value ($3.04 \text{ mS Hz}^{1/2}$ at $\omega = 1$) is in a ratio 1:23 lower. Some estimations on diffusion coefficient can be drawn. If the component W_2 is a true diffusion admittance, than this ratio yields in the ratio of the diffusion coefficient $D_{\text{Li}}:D_{\text{Na}} = 23^2 \approx 500$ provided that the concentration profile of alkali metal insertion into Me_yCrO_x has equal slope $\partial y/\partial E$.

This is in rough accordance with the results of the chronopotentiometry and with results obtained in LiClO_4 electrolyte.

Experimental coin cell

Two experimental coin cells of size 2025 were discharged into a resistor 10 k Ω . The initial open-circuit voltage was 3.8 and 3.79 V, respectively. The average cell voltage was 2.98 and 3.08 V, the capacity was 362 and 389 mC (i.e., 0.101 and 0.108 A h) for the discharge up to 2.0 V. These values correspond to energy density 987 and 1083 W h/kg of oxide CrO_x .

Cycling of Li-CrO_x and Na-CrO_x systems

The reversibility is apparent from Table 5, in which the behaviour of $\text{CrO}_x\text{-Na}$ system is compared with that of the system $\text{CrO}_x\text{-Li}$. The charge (or the peak current) for the second cycle is given in relation to the first cycle for chronopotentiometric and voltammetric measurements. In average, the performance of the second cycle is slightly better in the case of sodium as compared with lithium systems under equal conditions.

An explanation should be looked for in very low ionic radius of lithium ion. Therefore, lithium ions approach the oxygen anions much closer than sodium does. Therefore greater polarization of the lattice is generated owing to this and the decomposition of the host structure is enhanced. On the other hand, the lower capacity for sodium is also clear from the geometric factor.

Discussion

Chromium oxides CrO_x are hardly chemical individuals. Even if one of them was removed by leaching in water (Cr_3O_8), a mixture of others remained. Chemical analysis on chromium content cannot offer any reliable composition of samples due to rather small difference between various species (starting from Cr_3O_8 to Cr_5O_{12} , it increases from 54.9% to 57.5%). Also the average degree of oxidation is not easy analytically to find due to difficult dissolution of the samples.

The interlayer distances in chromium oxides undergo some changes in the course of lithiation, mostly towards smaller values. This is a quite general behaviour of lithium

intercalation and insertion compounds. For example, it was observed on Li_xWO_3 and Li_xCoO_2 nonstoichiometric systems. Most likely, it originates in very small ionic radius of lithium ion and, consequently, in the lattice distortion resulting from high intensity of electric field.

Methods of preparation and specific capacity

Generally, the best performance of chromium oxides was achieved if the temperature range 320–350 °C was chosen for decomposition of CrO_3 . Further, materials prepared by shorter decomposition were more suitable for cathodes of primary lithium cells. Under these conditions, the Cr_2O_5 oxide is the predominant composition. If the Cr_3O_8 oxide was removed by leaching in water, the capacity decreased substantially.

Preparation at elevated pressure yielded samples with increased content of CrO_2 . Their specific capacity was lower, but its cycling-induced decrease was slower.

On the contrary to the conclusion made by Takeda *et al.* [2, 3], the intercalation reversibility of CrO_x is not very good and decreases in the series $\text{CrO}_2 > \text{Cr}_2\text{O}_5 > \text{Cr}_3\text{O}_8$.

Low reversibility was also confirmed by voltammetry (see Table 2). The ratio Li:Cr (1.38) is in a good agreement with ref. 6.

Potential of CrO_x electrodes

From published values of Gibbs energy [9], the standard potentials of the reaction:



were estimated. The results are given in Table 6. As we see, they do not differ by more than 130 mV. Having in mind the width of cathodic discharge curves, all species present in so-called CrO_x can undergo cathodic reaction almost simultaneously.

Electrode admittance

The admittance spectrum of the electrode CrO_x was explained by an equivalence circuit containing five components. They were elucidated by an approximation programme and an attempt was made to explain their physical meaning.

(i) The series resistance R_1 is almost independent of potential and equals to $39 \pm 6 \Omega$. Most likely, it is a sum of two components, i.e., the resistance of electrode itself and the resistance of thin electrolyte layer between the Luggin capillary and the working surface of the electrode. Moreover, the electrolyte in the pores of the electrode and the internal resistance of electrode-active mass cannot be separated by the used means.

(ii) The admittance W_1 is only apparent at frequencies higher than 100 Hz. From 0.0935 mS $\text{Hz}^{1/2}$ at 1.8 V it increases slowly to 0.345 mS $\text{Hz}^{1/2}$ at 3.8 V. We ascribe

TABLE 6

Equilibrium potentials of various oxides estimated from thermodynamic data

Species	E^0 (mV)
CrO_3	2996
Cr_8O_{21}	2951
Cr_5O_{12}	2915
CrO_2	2869

it to the Xendzhek–Stender admittance of a semiinfinite porous electrode. Such an electrode acts as an infinite transmission line its admittance is:

$$\omega_1 = \sqrt{C/\rho} \quad (2)$$

where C is capacity of a layer of 1 cm thick and ρ is its resistivity. The value $\rho = 195 \Omega \text{ cm}$ was assumed, and capacity $C = 2.4 \cdot 10^{-5} \text{ F/cm}$ was evaluated from $W_1 = 0.35 \text{ mS Hz}^{1/2}$.

(iii) The series resistance R_2 is small in the potential range of electrochemical reaction (400–600 Ω) and it increases beyond this limits. The electric resistivity of CrO_x itself is fairly high and it should decrease markedly in the process of cathodic discharge. Therefore we suppose that it is responsible for the component R_2 .

(iv) The fourth component strongly depends on potential not only in value, but even in nature. In the range of electrochemical reaction, it has a nature of a Warburg admittance W_2 and it should be explained as the diffusion-controlled process. It is apparent in the range 2.8 to 3.6 V and it reaches a maximum (0.07 S $\text{Hz}^{1/2}$) at 3.2 V. Out of mentioned potential range, a capacity C_2 (4–6 mF) was observed. We suppose, that this component originates in surface capacity of polarized grains of CrO_x or carbon.

(v) It is difficult to draw any conclusion from the residual component R_3 . It is rather low at potential higher than 2.6 V, and it is perhaps connected with the discharge mechanism of some oxide species presented in so-called CrO_x .

Finally, admittance measurements have shown clearly the incomplete reversibility of CrO_x electrode. Both R_2 and C_1 increased considerably if potential returned back to 3.8 V after the whole series of measurement. If the explanation in points (iv) and (v) are correct, then the process of discharge would increase the physical surface of electroactive components in CrO_x (indicated by increase of double-layer capacity); it would also result in lowering particle size, mutual contacts, and perhaps electric conductivity, current load, electric resistance, and specific capacity.

The influence of current load on specific capacity is shown in Fig. 5. As it was mentioned above, up to current 6 mA/g approximately, the capacity was constant and close to 700 C/g, i.e. for time of discharge longer than $1.2 \cdot 10^5 \text{ s}$. Therefore, such behaviour should not appear in admittance experiments, because the lowest frequency used there was 0.0005 Hz. At higher current load and shorter discharge time, the capacity obeys an approximative formula:

$$Ci = \text{constant} \quad (3)$$

which is equivalent to:

$$i^2\tau = \text{constant} \quad (4)$$

(here, i is current load and τ is discharge time). This is in good agreement with the results of admittance measurements and it should be explained in the same manner.

Experimental coin cells

The energy density (close to 1 kW h/kg of oxide) was achieved in accordance with the general properties of the system $\text{CrO}_x\text{-Li}$. Such an energy density together with high cell voltage (over 3 V) suggest the main use of Li-CrO_x cells for application of microelectronics.

Conclusions

The electrochemical properties of chromium oxides CrO_x was studied. The results are suitable for optimalization of preparation procedure. On the contrary to work of

Takeda *et al.* [2], the investigated materials did not show good reversibility; this was also indicated by the analysis of chemically- and electrochemically-lithiated CrO_x .

However, the material is quite suitable for lithium primary cells, thanks to its high-energy density.

Capacity of Na-CrO_x galvanic primary cells is slightly (by 10–40%) lower than the capacity for lithium. The evidence was given that the apparent diffusion coefficient D_{Na} is at least by 1 or 2 orders of magnitude lower than D_{Li} . However, there is no essential difference in properties of both systems. Apparently, one of the most significant steps in the discharge/charge processes is irreversible chemical reaction of CrO_x itself, rather than the topochemical insertion of alkali metal ions.

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