

## MODIFIED CHROMIUM OXIDES FOR HIGH-RATE LITHIUM INTERCALATION CATHODES

J. O. BESENHARD\* and M. SCHWAKE

*Department of Inorganic Chemistry, University of Münster, Wilhelm-Klemm-Str. 8, D-4400 Münster (F.R.G.)*

N. MISAILIDIS

*Department of Physical Chemistry, Aristoteles University, 54006 Thessaloniki (Greece)*

### Summary

Normal pressure thermal decomposition of  $\text{CrO}_3$  containing *ca.* 2.5 wt.%  $\text{SO}_3$  yields a new chromium oxide phase  $\text{CrO}_x(\text{SO}_3)_x$ ,  $x$  being close to 2.5. This material is different from  $\text{Cr}_2\text{O}_5$  and is practically free from sulfur. Sulphur trioxide obviously acts as a catalyst for oxygen removal. Compared with  $\text{Cr}_3\text{O}_8$ ,  $\text{CrO}_x(\text{SO}_3)_x$  is characterized by better high rate discharge behaviour. Moreover,  $\text{CrO}_3$  contamination in  $\text{CrO}_x(\text{SO}_3)_x$  is much lower than in  $\text{Cr}_3\text{O}_8$  prepared at normal pressure; this is of importance for the long-term storage behaviour of Li/ $\text{CrO}_x$  batteries. The low-rate energy density of  $\text{CrO}_x(\text{SO}_3)_x$  is inferior to that of  $\text{Cr}_3\text{O}_8$ .

### Introduction

Chromium oxides of the approximate composition  $\text{Cr}_3\text{O}_8$  have been shown to be useful high-energy-density cathode materials for primary and secondary organic electrolyte Li batteries [1 - 3]. The discharge properties of chromium oxides,  $\text{CrO}_x$  ( $2 < x < 3$ ), depend very much on the conditions of preparation. At low rate, energy densities up to 2000 W h  $\text{kg}^{-1}$  have been attained with high surface area amorphous  $\text{Cr}_3\text{O}_8$  [4], but the preparation of this material needs much effort. Simple thermal decomposition of  $\text{CrO}_3$  at normal pressure yields a much poorer  $\text{CrO}_x$  material (energy density *ca.* 1100 W h  $\text{kg}^{-1}$ ).

A common problem with all  $\text{CrO}_x$  preparations is a sharp drop in the chemical diffusion coefficient of lithium ( $\tilde{D}_{\text{Li}^+}$ ) in  $\text{LiCrO}_x$  at Li/Cr ratios  $>ca.$  1.0 [4, 5], and therefore the high rate discharge behaviour is disappointing. Moreover, there is usually a fairly large amount of unreacted  $\text{CrO}_3$  remaining which is soluble in organic electrolytes. Prolonged decomposition at normal pressure decreases the  $\text{CrO}_3$  contamination at the expense of a

\*Author to whom correspondence should be addressed.

loss of oxygen (and hence energy density) from  $\text{CrO}_x$ . This problem can be overcome by the use of high oxygen pressures (of the order of kbar [6]).

We have tried to find alternative and practicable routes to the preparation of modified  $\text{CrO}_x$  in order to (i) improve their high rate discharge behaviour and (ii) to decrease their  $\text{CrO}_3$  contamination.

## Results and discussion

An interesting high rate discharge behaviour and also low  $\text{CrO}_3$  contamination were observed for  $\text{CrO}_x$  preparations obtained by heating mixtures of  $\text{CrO}_3$  plus 1 - 5 wt.%  $\text{SO}_3$  to *ca.* 270 °C in Pyrex tubes under atmospheric pressure. After some hours of tempering at 270 °C the preparations were practically free from sulfur (verified by X-ray fluorescence). The Cr/O ratios (determined by iodimetric titration) were always slightly higher than 3/8.

The crystallinity of " $\text{CrO}_x(\text{SO}_3)$ " preparations depends greatly on the temperature program during melting/thermal decomposition of the  $\text{CrO}_3$ - $\text{SO}_3$  mixture. Samples prepared by slowly heating (4 °C  $\text{min}^{-1}$ )  $\text{CrO}_3$  plus 2.5 wt.%  $\text{SO}_3$  up to 270 °C, followed by 20 h tempering at the final temperature, were poorly crystalline [7]. Apart from weak reflections (some of them due to small amounts of  $\text{Cr}_2\text{O}_3$ ) there was only one dominant peak, corresponding to a *d*-value of *ca.* 291 pm.

The crystallinity of  $\text{CrO}_x(\text{SO}_3)$  is improved considerably by increasing the time interval of direct contact between  $\text{SO}_3$  and  $\text{CrO}_3$ . Temperatures around 200 °C proved to be most suitable because the volatility of  $\text{SO}_3$  dissolved in  $\text{CrO}_3$  melt is not too high in this temperature range. A diffractogram of fairly crystalline  $\text{CrO}_x(\text{SO}_3)$  is shown in Fig. 1.

As  $\text{CrO}_x(\text{SO}_3)$  is practically free from sulfur it must be regarded as a new chromium oxide, prepared by  $\text{SO}_3$ -catalyzed thermal decomposition of  $\text{CrO}_3$ . The presence of  $\text{SO}_3$  obviously lowers the temperature of  $\text{CrO}_3$  decomposition;  $\text{SO}_3$  may also have a kind of "baking powder effect", creating some porosity during evaporation. Typical  $\text{CrO}_3$ -contents of  $\text{CrO}_x(\text{SO}_3)$  are of the order of 0.3 - 0.5% (depending on the duration of tempering).

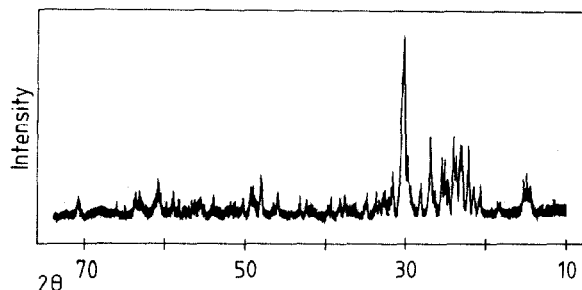


Fig. 1. X-ray diffraction pattern of  $\text{CrO}_x(\text{SO}_3)$  (Cu  $K\alpha$ -radiation). Temperature programme: 50 °C (30 min), 200 °C (1 h), 270 °C (6 h); starting composition:  $\text{CrO}_3$  + 2.5 wt.%  $\text{SO}_3$ .

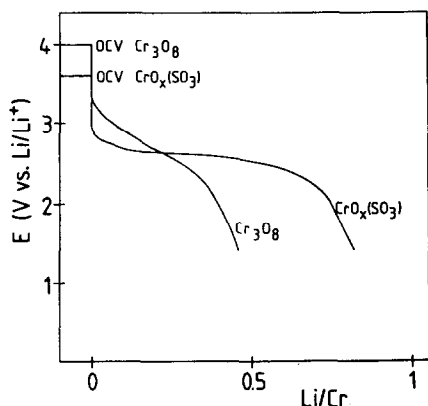
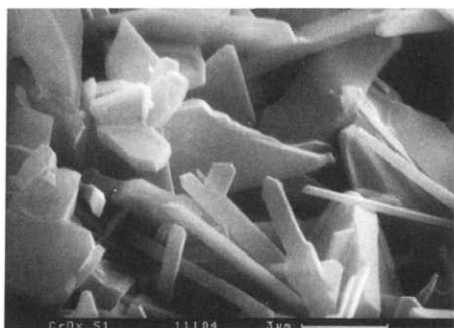


Fig. 2. Discharge characteristics of  $\text{Cr}_3\text{O}_8$  and  $\text{CrO}_x(\text{SO}_3)$  in 1 M  $\text{LiClO}_4/\text{PC-DME}$  (50-50) at  $5 \text{ mA cm}^{-2}$ .

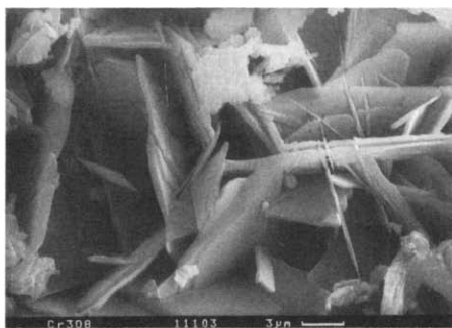
The high rate discharge behaviour of  $\text{CrO}_x(\text{SO}_3)$  (temperature programme and starting composition, see Fig. 1) compared with that of  $\text{Cr}_3\text{O}_8$  (20 h at  $270^\circ\text{C}$ , normal pressure) is shown in Fig. 2. For easier reproducibility, compact electrodes were made by a standardized procedure: addition of 15 wt.% of graphite powder and pressing onto a stainless steel grid at  $10\,000 \text{ kg cm}^{-2}$  for 1 min. The porosity of the electrode was not optimized for high rate discharge.

Apart from the "harder" discharge characteristics and better high rate utilization,  $\text{CrO}_x(\text{SO}_3)$  differs from  $\text{Cr}_3\text{O}_8$  by its lower OCV prior to discharge. In the early stages of discharge,  $\text{CrO}_x(\text{SO}_3)$  cathodes also show significantly lower cell voltages than  $\text{Cr}_3\text{O}_8$  cathodes. This is true even for very low discharge rates, and verifies that the different discharge behaviour of  $\text{CrO}_x(\text{SO}_3)$  is not simply due to particle size/porosity effects. The discharge behaviour of less crystalline  $\text{CrO}_x(\text{SO}_3)$  is slightly poorer [7].

Electron micrographs of  $\text{CrO}_x(\text{SO}_3)$  (temperature programme and starting composition, see Fig. 1) show a surprisingly crystalline material (Fig. 3(a)); its particle size is comparable with that of  $\text{Cr}_3\text{O}_8$  (Fig. 3(b)).



(a)



(b)

Fig. 3. Electron micrographs of chromium oxide samples; for preparation procedure see text. (a)  $\text{CrO}_x(\text{SO}_3)$ ; (b)  $\text{Cr}_3\text{O}_8$ .

TABLE 1

BET surface area determinations of chromium oxides

Sample	Specific surface area (BET method) ( $\text{m}^2 \text{g}^{-1}$ )	
	Particle size <i>ca.</i> 0.5 - 2 mm	Particle size <i>ca.</i> 1 - 10 $\mu\text{m}$
$\text{Cr}_3\text{O}_8$	1.48	2.6
$\text{CrO}_x(\text{SO}_3)$	0.56	3.7

$\text{CrO}_x(\text{SO}_3)$  samples prepared by simply heating the  $\text{CrO}_3$ - $\text{SO}_3$  mixture are much less crystalline [7].

In agreement with the electron micrographs, BET surface area determinations ( $\text{N}_2$  adsorption) show relatively small surface areas for both chromium oxides,  $\text{Cr}_3\text{O}_8$  and  $\text{CrO}_x(\text{SO}_3)$  (Table 1). Grinding has a greater effect on the surface area of  $\text{CrO}_x(\text{SO}_3)$  than on  $\text{Cr}_3\text{O}_8$ .

Low rate discharge curves of  $\text{CrO}_x(\text{SO}_3)$  show a significant "Spannungs-sack" at a Li/Cr ratio of *ca.* 0.45 (Fig. 4). Beyond this point the discharge and charge of  $\text{CrO}_x(\text{SO}_3)$  is related to phase transformations. Therefore, no meaningful chemical diffusion coefficients,  $\tilde{D}_{\text{Li}^+}$ , can be measured by electrochemical techniques — they appear to be of the order of  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$ , in spite of the high rate capabilities of  $\text{CrO}_x(\text{SO}_3)$ .

The OCV of Li/ $\text{CrO}_x(\text{SO}_3)$  cells prior to discharge is *ca.* 3.6 V; this is about 300 mV less than the undesired high value of Li/ $\text{Cr}_3\text{O}_8$  cells.

Utilization diagrams show, as expected, that the advantage of  $\text{CrO}_x(\text{SO}_3)$  over  $\text{Cr}_3\text{O}_8$  increases with discharge rate. This is demonstrated by Fig. 5, showing utilizations of  $\text{Cr}_3\text{O}_8$  and  $\text{CrO}_x(\text{SO}_3)$  in dependence of current density.

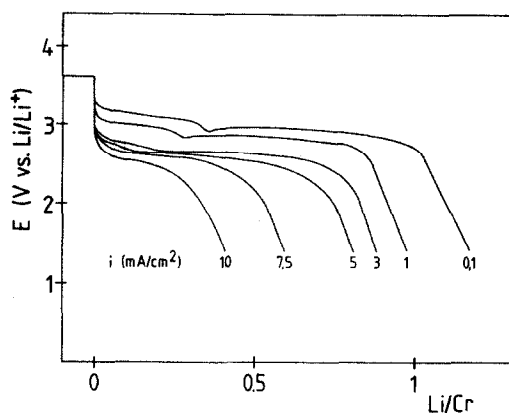


Fig. 4. Discharge characteristics of  $\text{CrO}_x(\text{SO}_3)$  + 15 wt.% graphite pressed powder electrodes in 1 M  $\text{LiClO}_4/\text{PC-DME}$  (50-50).

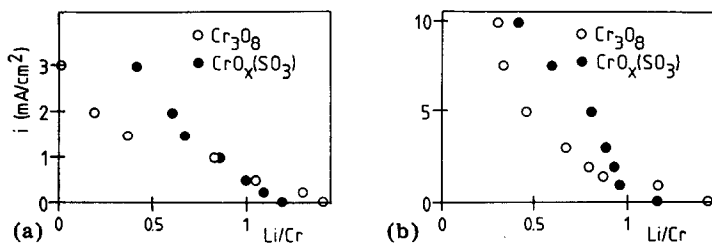


Fig. 5. Utilization of chromium oxide electrodes in dependence of discharge rate, cut-off voltage 1.5 V vs.  $\text{Li/Li}^+$ . (a) 1 M  $\text{LiClO}_4/\text{PC}$ ; (b) 1 M  $\text{LiClO}_4/\text{PC-DME (50-50)}$

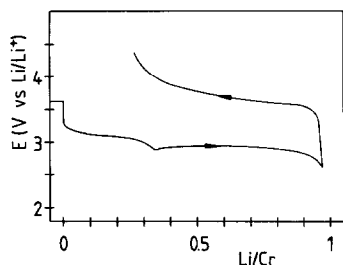


Fig. 6. Charge/discharge of  $\text{CrO}_x(\text{SO}_3)$  + 15 wt.% graphite pressed powder electrode on Pt grid in 1 M  $\text{LiClO}_4/\text{PC-DME (50-50)}$ ,  $i = 100 \mu\text{A cm}^{-2}$ .

The relatively high utilization of  $\text{Cr}_3\text{O}_8$  at *ca.*  $10 \text{ mA cm}^{-2}$  in  $\text{LiClO}_4/\text{PC-DME}$  may be misleading. Despite the very "slopy" discharge characteristic of  $\text{Cr}_3\text{O}_8$ , the utilization figure is quite high because of the low cut-off voltage. At *ca.*  $1 \text{ mA cm}^{-2}$  there is a cross-over of the utilization/current density characteristics shown in Fig. 5(a) and (b), *i.e.*, at low current densities the higher energy density of  $\text{Cr}_3\text{O}_8$  is becoming dominant. In preliminary cycling experiments the behaviour of  $\text{CrO}_x(\text{SO}_3)$  was very similar to that of  $\text{Cr}_3\text{O}_8$  (Fig. 6).

## Conclusion

Thermal decomposition of  $\text{CrO}_3$  in the presence of  $\text{SO}_3$  yields a new chromium oxide phase with interesting high rate discharge behaviour in organic electrolytes. A further advantage of this material is its very low content of  $\text{CrO}_3$  contamination. This is of importance not only for pollution control but also for long-term storage of  $\text{Li/CrO}_x$  batteries.

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