

AMORPHOUS CHROMIUM OXIDE; A NEW LITHIUM BATTERY CATHODE

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Summary

The charge and discharge behaviour of lithium cells with amorphous chromium oxide as the cathode material has been examined. Amorphous chromium oxide, a-Cr₃O₈, with a high specific surface area was prepared by heat treating a mixture of Cr₃O₈, water, and (NH₄)₂SO₄ at 250 °C. The cells with a-Cr₃O₈ showed satisfactory discharge performance in terms of energy density. The energy density was 1800 W h kg⁻¹ at a current density of 1 mA cm⁻². Cells gave good rechargeability over a wide range of charge transfer.

Introduction

Recently, chromium oxides with high oxidation states have attracted attention as cathodes for lithium cells because of their high energy density and high cell voltage [1 - 4]. Among these, the couples Li/Cr₂O₅ and Li/Cr₃O₈ have given satisfactory discharge behaviour, especially in terms of energy density. The highest energy density, namely, 1210 W h kg⁻¹, has been calculated for the Li/Cr₃O₈ couple to a 2.0 V cut-off at 0.5 mA cm⁻² (based on weights of chromium oxides). This energy density is about twice that of the Li/TiS₂ couple [2].

In the course of our studies on Li/chromium oxide cells, a new amorphous phase of chromium oxide has been obtained by heat treating a mixture of Cr₃O₈ and water. This chromium oxide is amorphous to X-ray diffraction (XRD) and the composition is close to Cr₃O₈. The oxide is referred to here as a-Cr₃O₈.

A lithium cell with a-Cr₃O₈ exhibited a high energy density and a good charge/discharge performance for a wide charge transfer range [3]. The average oxidation state of chromium is +5.3 in a-Cr₃O₈. The maximum charge transferred is calculated to be 2.3 e/Cr, assuming the lowest chromium oxidation state to be Cr(III). If the charge in a-Cr₃O₈ is "used" completely, the couple Li/a-Cr₃O₈ could prove to be a lithium battery with a very high energy density. However, at a constant current density of 0.5 mA

cm^{-2} and a discharge to 2.0 V, the charge transferred was 1.4 e/Cr for the couple Li/cryst. Cr_3O_8 , and 1.5 e/Cr for Li/a- Cr_3O_8 . The specific surface area of a- Cr_3O_8 (BET method) was 3 - 5 $\text{m}^2 \text{g}^{-1}$, which is only twice that of crystalline Cr_3O_8 . This small difference in specific surface area is due to the aggregation of the small particles in a- Cr_3O_8 [4]. If a more dispersive state of a- Cr_3O_8 could be obtained, then the specific surface area would be increased and the performance of the Li/a- Cr_3O_8 cell would be further improved.

In this study, the dispersive state of a- Cr_3O_8 was modified by adding $(\text{NH}_4)_2\text{SO}_4$ to the mixture of Cr_3O_8 and water. The resulting material was examined as a cathode material for lithium cells.

Experimental

Crystalline Cr_3O_8 was obtained by heating CrO_3 in an autoclave for 24 h at 270 °C. Amorphous Cr_3O_8 , having various surface areas, was prepared by heating a mixture of 0.7 g of Cr_3O_8 , 30 ml of water, and a small amount of $(\text{NH}_4)_2\text{SO}_4$ for 24 h at 250 °C.

The cells used for the electrochemical tests were constructed with a cylindrical configuration. The anode was a disc of lithium foil (dia.: 14 mm; height: 0.5 mm) and the separator was a sheet of microporous polypropylene. The cathode consisted of a mixture of chromium oxide (50 mg), acetylene black (10 mg) and Teflon powder (1 mg), which was pressed into a pellet of diameter 13.5 mm. The electrolyte was 1 M LiClO_4 in a 1:1 mixture (by weight) of propylene carbonate and 1,2-dimethoxyethane.

X-ray photoelectron spectroscopy (XPS) spectra were collected (Cr 2 $P_{3/2}$) with a Shimadzu ESCA 750 spectrometer. The samples were protected against moisture during measurements. The lithium ion diffusivity was obtained by the method reported by Nagelberg and Worrell [5].

Results and discussion

In a previous study, a- Cr_3O_8 was prepared by heating a mixture of Cr_3O_8 and water. The samples thus obtained were amorphous to X-rays. In order to increase the dispersive state and the active surface of the a- Cr_3O_8 , various additives were introduced to the Cr_3O_8 - H_2O system. Ammonium sulfate proved to be an effective additive. It is known that the adsorbed SO_4^{2-} makes the oxide surface highly acidic and limits the grain growth of the particles [6]. In the present study 0.7 g of Cr_3O_8 , 30 ml of water, and 10 mg of $(\text{NH}_4)_2\text{SO}_4$ were mixed thoroughly and then heated for 24 h at 250 °C. The XRD patterns showed the resulting material to be amorphous. BET measurements demonstrated that the specific surface area had increased from 9 $\text{m}^2 \text{g}^{-1}$ to 17 $\text{m}^2 \text{g}^{-1}$; this was three-to-five times larger than that found in the previous study.

Figure 1 shows the open-circuit voltage (OCV) and the constant-current (1 mA cm^{-2}) discharge curves for cells with the highly dispersed a- Cr_3O_8 . The discharge curves for cells with crystalline Cr_3O_8 and the a- Cr_3O_8 prepared by previous methods are also given. The OCV is considered to be a "quasi-OCV", *i.e.*, the deviation is within 1 mV for 1 h after a constant current of 0.1 mA cm^{-2} has been passed for a given period. The OCV curve exhibited a gradual declining slope to 2.3 e/Cr. This observation suggests that the cathodic reaction proceeds with the formation of a single homogeneous phase, that is, an intercalation compound. The calculated energy density, based on the OCV curve, is around 2000 W h kg^{-1} . The constant discharge 1 mA cm^{-2} curves demonstrate that a- Cr_3O_8 treated with $(\text{NH}_4)_2\text{SO}_4$ exhibits high energy density. The discharge curve has a gentle slope and extends to 2.0 e/Cr; this corresponds to an energy density of 1800 W h kg^{-1} or 4550 W h l^{-1} (1.0 V cut-off). These findings are in marked contrast to those reported previously for crystalline and amorphous Cr_3O_8 , the discharge curves of which extended to 1.3 e/Cr and 1.5 e/Cr, respectively.

Figure 2 gives the discharge performance of cells with a- Cr_3O_8 prepared with $(\text{NH}_4)_2\text{SO}_4$ at various current densities. Even at current densities as high as 5 mA cm^{-2} , the discharge voltages remain at 1.8 V to 1.0 e/Cr. At a low current density of $20 \mu\text{A cm}^{-2}$, the discharge curve plateau extends to 2.2 e/Cr, which corresponds to an energy density of 2000 W h kg^{-1} (1.0 V cut off). Since chromium in a- Cr_3O_8 has an average oxidation state of +5.3, the maximum charge transferred is 2.3 e/Cr, assuming the lowest chromium oxidation state is Cr(III). At the lower current density, Cr^{6+} in a- Cr_3O_8 has been completely reduced to Cr^{3+} without any appreciable polarization.

A current-pulse technique [5] was used to assess the chemical diffusion coefficient of lithium ions (\tilde{D}_{Li}) in chromium oxides. A constant current of 0.5 mA cm^{-2} was applied for 30 s to cells using crystalline Cr_3O_8 and a- Cr_3O_8 . The variation of the transient voltage (ΔE) with time (t) was plotted against $t^{-1/2}$. \tilde{D}_{Li} was calculated from the slope of the linear region, where a

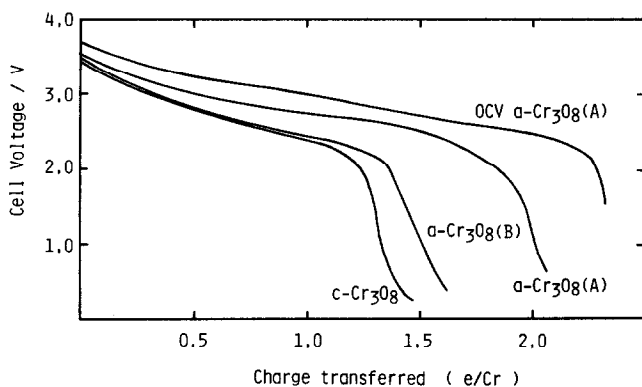


Fig. 1. Constant-current (1.0 mA cm^{-2}) discharge curves of Li/chromium oxide cells at room temperature. c- Cr_3O_8 , crystalline Cr_3O_8 ; a- Cr_3O_8 (A), prepared from Cr_3O_8 , H_2O , and $(\text{NH}_4)_2\text{SO}_4$; a- Cr_3O_8 (B), prepared from Cr_3O_8 and H_2O .

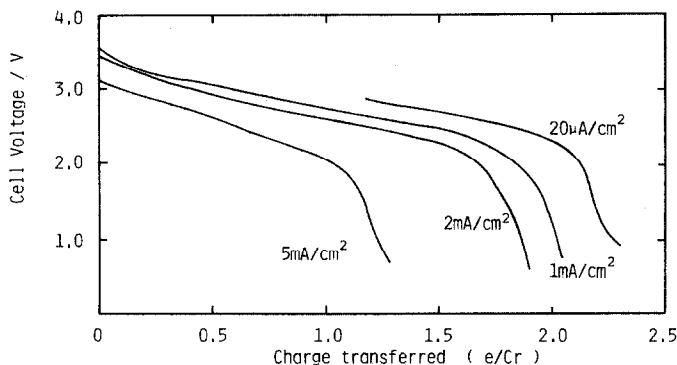


Fig. 2. Discharge curves at various current densities for Li/a-Cr₃O₈ cell.

molar volume of a-Cr₃O₈ of 112 cm³ was used. Values of \tilde{D}_{Li} are given in Fig. 3 in the charge transfer range of 0 - 1.2 e/Cr. In both cases, \tilde{D}_{Li} is around 10⁻⁸ cm² s⁻¹ and decreases with increase in the depth of discharge. No apparent difference is observed in \tilde{D}_{Li} values obtained for crystalline Cr₃O₈ and a-Cr₃O₈. This suggests that the high energy density of a-Cr₃O₈ under high current density is not due to the high diffusivity of Li ions in the bulk of a-Cr₃O₈, but to the large surface area and the high reactivity of the surface.

The XPS spectra of crystalline Cr₃O₈ and a-Cr₃O₈ are shown in Fig. 4 as a function of the charge transfer in Cr₃O₈. By computer fitting, the spectra can be resolved into two peaks, near 576.4 and 579.0 eV; these correspond to the chemical shifts of Cr³⁺ 2P_{3/2} in Cr₂O₃ (576.5 eV) and Cr⁶⁺ 2P_{3/2} in CaCrO₄ (578.8 eV), respectively. The intermediate oxidation states, Cr⁵⁺ and Cr⁴⁺, were not observed. That is, the chromium oxides at various amounts of charge transfer consist of a mixture of Cr⁶⁺ and Cr³⁺ oxidation states. The Cr⁶⁺ state in crystalline Cr₃O₈ or a-Cr₃O₈ is directly reduced to the Cr³⁺ state by reaction with the lithium. For crystalline Cr₃O₈, the peak of the Cr⁶⁺ state disappears at 1.5 e/Cr, where the cell voltage of the discharge curve falls to zero. At around 1.5 e/Cr, the diffusion of lithium ions in Cr₃O₈ is slow so that all the surface of the chromium oxide becomes covered with Cr³⁺ ions.

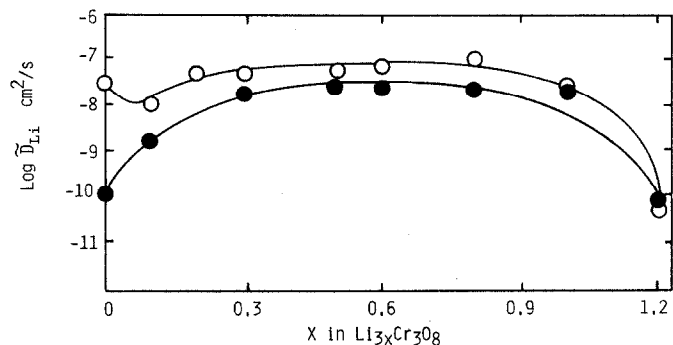


Fig. 3. Chemical diffusion coefficient (\tilde{D}_{Li}) in Li_{3x}Cr₃O₈. ●, a-Cr₃O₈; ○, crystalline Cr₃O₈.

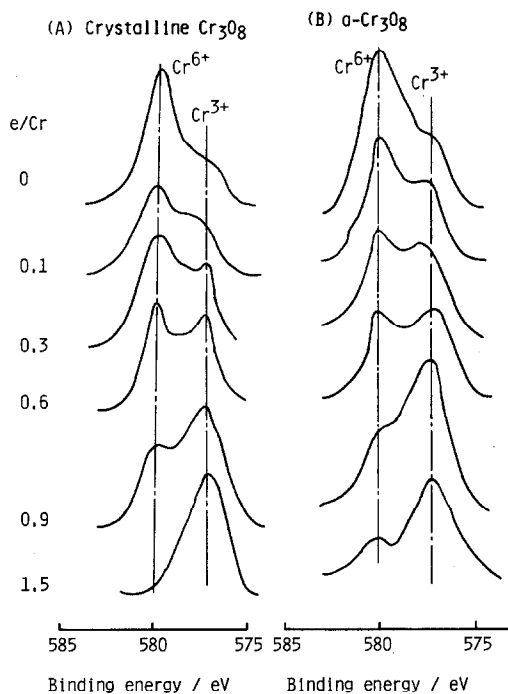


Fig. 4. XPS spectra of Cr $2P_{3/2}$ region for crystalline Cr_3O_8 (A) and a- Cr_3O_8 (B) as a function of charge transfer.

Therefore any further reaction is suppressed. For amorphous chromium oxides, on the other hand, the presence of a Cr^{6+} state on the surface is observed to the extent of about 25% at 1.5 e/Cr. The larger surface area of a- Cr_3O_8 is responsible for its superior discharge properties, although \bar{D}_{Li} in a- Cr_3O_8 is of the same order as in crystalline Cr_3O_8 .

In a previous paper [3], we reported the cycling characteristics of cells with chromium oxides. The cycling performances were examined for various ranges of charge transfer, such as 0.1 - 0.3, 0.4 - 0.6 and 0.7 - 0.9 e/Cr. The rechargeability of Li/crystalline Cr_3O_8 cells was good in the range 0.4 - 0.6 and 0.7 - 0.9 e/Cr, but poor in the range 0.1 - 0.3 e/Cr. Cells with a- Cr_3O_8 (which was prepared by heat treating mixtures of Cr_3O_8 and water) performed well as rechargeable systems over the whole range of charge transfer. However, the polarization on charging was significantly large in the range 0 - 1.0 e/Cr.

In this study, the rechargeability of the cell with the "new" a- Cr_3O_8 has been examined for wide charge transfer ranges. In Figs. 5 and 6, the charge/discharge curves for the Li/a- Cr_3O_8 cell are shown for the 0.5 - 1.1 and 0.2 - 1.2 e/Cr charge ranges. The cells were cycled at 1.0 mA cm^{-2} . The charging efficiency is almost 100% and the charge/discharge profiles show no significant degradation. This cell shows good rechargeability for a wide range of charge transfers.

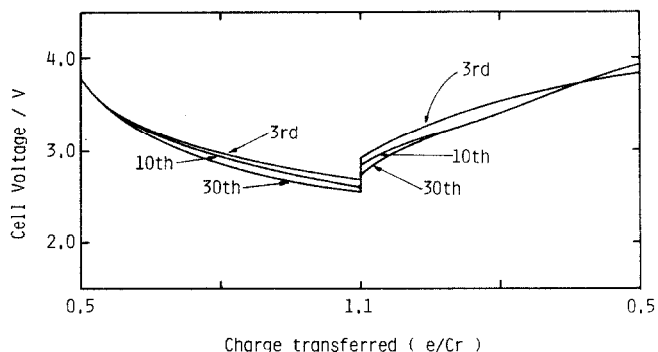


Fig. 5. Cycling behavior of Li/a-Cr₃O₈ cell at 1 mA cm⁻². Charge/discharge range: 0.5 - 1.1 e/Cr.

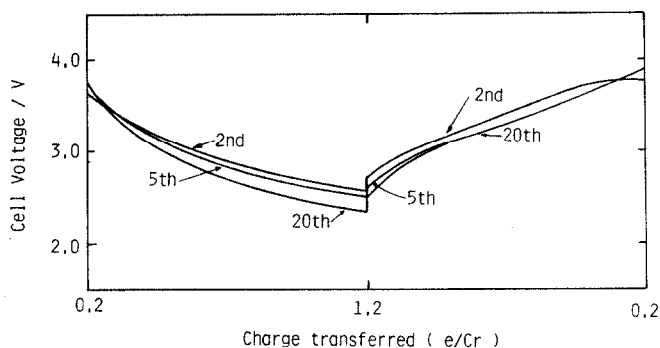


Fig. 6. Cycling behavior of Li/a-Cr₃O₈ cell at 1 mA cm⁻². Charge/discharge range: 0.2 - 1.2 e/Cr.

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