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# Lithium ion cells using a new high capacity cathode

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## Abstract

The application of a new series of layered first row transition metal oxides as cathodes in lithium ion cells is demonstrated. The cathodes were made from a quaternary oxide of lithium, chromium, and manganese belonging to the compositional series  $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$  with  $x > 2.2$ ,  $0 < y < 2$  and  $z \geq 0$ . The layered structure is stabilized by the partial substitution of the manganese by chromium and lithium atoms and by the partial or complete oxidation of the manganese to the +4 oxidation state. Crown Copyright © 2001 Published by Elsevier Science B.V. All rights reserved.

**Keywords:**  $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$ ; Cathode; Lithium ion cell

## 1. Introduction

There is a continuing demand for new alternative intercalation compounds suitable for use as positive electrodes in lithium ion batteries. Such compounds must combine large charge storage capacity, good reversibility at high to moderate current densities, low cost, a high degree of safety, and absence of toxicity. An operating voltage near 3.5 V on a single plateau is usually desired. For cathodes based on first row transition metal oxides, this typically requires a layered oxide structure that remains intact during cycling. Recently, we have succeeded in preparing a series of new cathode materials displaying competitive capacities with reasonably good cycling stability at moderate current densities [1]. These materials appear to be possible alternatives to  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  for lithium ion cell cathodes. This paper discusses the electrochemical characterization of these new compounds in lithium-ion and lithium half-cells under a range of operating conditions.

## 2. Experimental

$\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$  samples for this study were prepared by a procedure described in a previous work [1]. These samples were cast into electrode sheets by a doctor blade technique and tested in coin cells. The cathodes were prepared from a

mixture of active material, Super S carbon black, graphite (Lonza KS4) and binder (Kynarflex 2801) in a weight ratio of 76:8:8:8. The mixture was formed into a slurry in a binder solution containing 4 wt.% of Kynar Flex 2801 in *n*-methyl pyrrolidinone (NMP) and cast as a film on aluminum foil by the doctor blade method. The cast was dried for 24 h in a convection oven at 60°C and then densified by pressing between two metal rollers. Electrode discs of 1.27 cm diameter were punched from the cast. The electrodes typically had a thickness of approximately 50 µm.

The anodes for the lithium ion cells were prepared from mesocarbon microbeads (MCMB 2800) slurried with a 4 wt.% solution of Kynarflex 2800 in NMP cast onto copper sheets by the doctor blade method. The proportions were adjusted to produce MCMB anodes containing 5 wt.% of binder. The MCMB anode casts were dried in the same way as the cathode casts but were not densified further. The anodes typically had thicknesses between 50 and 60 µm. Discs of 1.27 cm diameter were punched and weighed. The anode discs were matched to cathodes such that the ratio of active materials in the cathode and anode was between 1.1 and 1.2 by weight. For the half-cell studies, anodes of metallic lithium (Foote Mineral) were punched as discs of 1.65 cm diameter and 0.05 cm thickness.

An electrolyte containing 1M  $\text{LiPF}_6$  in 1:1 ethylene carbonate:dimethyl carbonate (Mitsubishi Chemical) was used in all the electrochemical testing. The electrochemical cycling was carried out in 2325 coin cells, each containing an internal spring and spacer to maintain an adequate pressure on the electrode stack. Two layers of microporous polypropylene (Celgard 3501) separated the electrodes.

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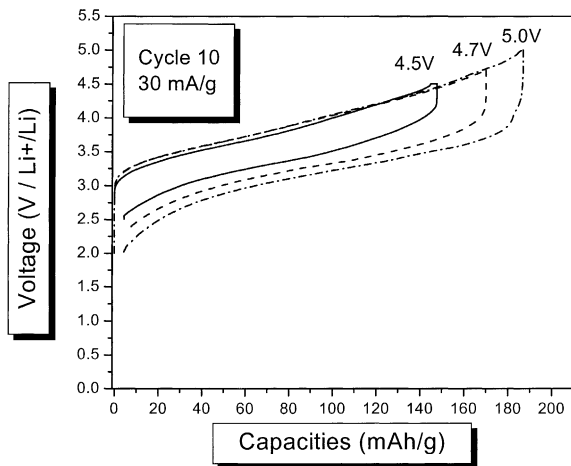


Fig. 1. Voltage profiles for the 10th cycle of  $\text{Li}/\text{Li}_3\text{CrMnO}_{4+z}$  cells cycled between voltage limits of 2.5–4.5, 2.3–4.7, and 2.0–5.0 V, respectively at 30 mA/g.

### 3. Discussion

As a first step, the material was evaluated in coin cells with metallic lithium anodes. The voltage profiles for the 10th cycle of  $\text{Li}/\text{Li}_3\text{CrMnO}_{4+z}$  cells cycled between voltage limits of 2.5–4.5, 2.3–4.7, and 2.0–5.0 V, respectively at 30 mA/g are shown in Fig. 1. The reversible capacity can be extended without a noticeable Coulombic inefficiency by increasing the voltage limits to 2.0–5.0 V. The capacity was retained almost unchanged for the first 30 cycles on cycling over a voltage window of 2–5 V, and then developed a noticeable fade.

The specific capacity was found to be very dependent on current density and temperature. The capacity retention for a  $\text{Li}/\text{Li}_3\text{CrMnO}_{4+z}$  cell cycled between 2.5 and 4.5 V at 10 mA/g is plotted in Fig. 2. At 10 mA/g the specific

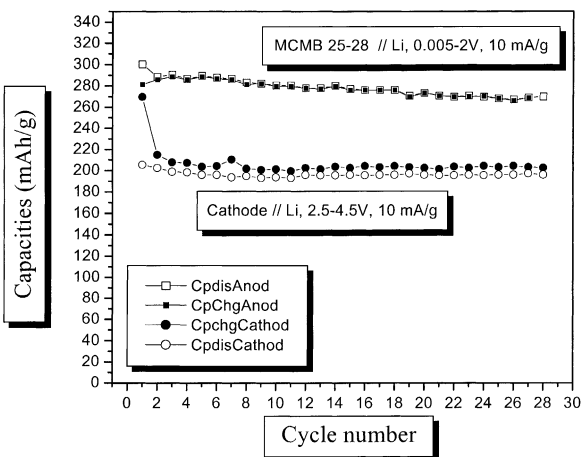


Fig. 2. Plot of specific capacities vs. cycle number for  $\text{Li}/\text{Li}_3\text{CrMnO}_{4+z}$  and  $\text{Li}/\text{MCMB}$  half-cells at 10 mA/g.

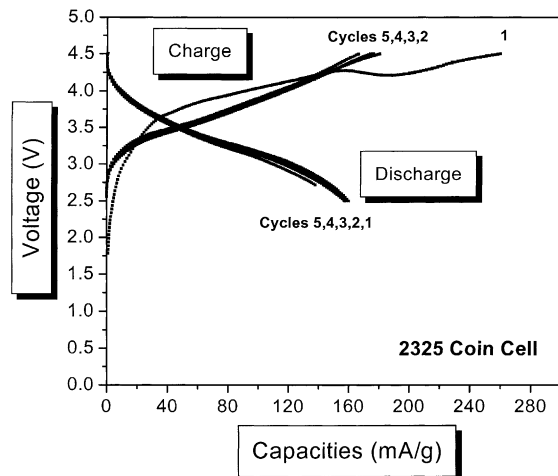


Fig. 3. Voltage profiles of the first five cycles of a  $\text{MCMB}/\text{Li}_3\text{CrMnO}_{4+z}$  lithium ion cell cycled at a current density of 10 mA/g of active cathode material.

capacity is near 200 mAh/g, but it decreases with increasing current density such that, it is about 140 mAh/g at 30 mA/g. The capacity was found to increase with temperature such that, at 40°C, capacities near 200 mAh/g were achieved at 30 mA/g current density. A plot of capacity retention at the elevated temperature had about the same slope as that at ambient temperature. Fig. 2 also shows the specific capacity of a MCMB electrode cycled in a half-cell with a metallic lithium anode. The cell was cycled between voltage limits of 0.005–2 V at 10 mA/g to characterize the electrodes for use in lithium ion cells with  $\text{Li}_3\text{CrMnO}_{4+z}$  cathodes. Both, the MCMB, and the  $\text{Li}_3\text{CrMnO}_{4+z}$  electrodes are cycled at stable capacities in lithium half-cells.

Fig. 3 is a plot of the voltage profiles of the first five cycles of a  $\text{MCMB}/\text{Li}_3\text{CrMnO}_{4+z}$  lithium ion cell cycled at a current density of 10 mA/g of active cathode material. The capacity of the lithium ion cell was about 20% less than cells with metallic lithium anodes evaluated under similar conditions. The authors expect that the capacity can be increased to near that of a half-cell by improving the cell assembly and capacity balance between the cathode and the MCMB anodes.

### 4. Conclusions

The use of a new type of chemically stabilized layered manganese oxide in lithium half-cells and lithium ion cells with MCMB anodes was explored. The material shows only mild fade in capacities when cycled over voltage windows as broad as 2–5 V and on cycling at moderately elevated temperatures. Under more typical cycling conditions the capacity retention was exceptionally good. For the material to be truly useful as a cathode for lithium ion cells, the electrochemical kinetics must be improved. The initial evaluation of the material in a lithium ion cell with a

MCMB anode showed a significant reduction in capacity in comparison to that of a lithium half-cell, but can probably be improved on with better cell balancing and electrode fabrication.

## **References**

- [1] C. Storey, I. Kargina, Y. Grincourt, I.J. Davidson, Y.C. Yoo, D.Y. Seung, J. Power Sources 97–98 (2001) 541–544.