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Electrochemical characterization of a new high capacity cathode

C. Storey^a, I. Kargina^a, Y. Grincourt^a, I.J. Davidson^{a,*}, Y.C. Yoo^b, D.Y. Seung^b^a*Institute for Process Chemistry and Environmental Technology, National Research Council, Ottawa, Canada K1A 0R6*^b*Samsung Advanced Institute of Technology, Suwon 440-600, South Korea*

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Abstract

This paper reports on the electrochemistry of a new series of layered manganese oxide cathodes for lithium-ion cells. 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. The series covers the range of compositions $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$ for which $2.2 < x < 4$, $0 < y < 2$ and $z \geq 0$. Crown Copyright © 2001 Published by Elsevier Science B.V. All rights reserved.

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

1. Introduction

Although, LiCoO_2 is extremely well-suited for use in cathodes of lithium-ion cells, the high cost of batteries based on LiCoO_2 precludes their use in large scale or modestly priced applications. Cathodes based on LiMn_2O_4 provide a lower cost alternative, but suffer from lesser capacity and difficulties with capacity retention at elevated temperatures. Cathodes made from LiNiO_2 alone, or as a solid solution with LiCoO_2 , have attractive capacities but concerns about their safety persist. Consequently, there is still a need for improved cathode materials. The ideal cathode material will combine low cost with the desirable performance characteristics of high capacity, good rate capabilities and long cycle life. Recently, we have developed a new series of compounds that show considerable promise at meeting at least the first of these requirements. These new materials are quaternary oxides of compositions $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$ for which $2.2 < x < 4$, $0 < y < 2$ and $z \geq 0$. Cathodes formed from these materials exhibit a high specific capacity with a sloping, single-plateau voltage curve.

Cathodes based on mixed oxides of lithium, chromium and manganese at various compositions have been studied by many groups. Pistoia et al. [1] and Wang et al. [2] were amongst the first to demonstrate the use of chromium substituted manganese spinel phases as cathodes in secondary lithium cells. Compounds of formula $\text{Li}_2\text{Cr}_x\text{Mn}_{2-x}\text{O}_4$ have been studied by Davidson et al. [3,4] and by Dahn et al.

[5]. The experimental data from the latter publication was incorporated into a US patent issued to Dahn and Zheng [6]. The patent describes a process for making materials of formula $\text{Li}_y\text{Cr}_x\text{Mn}_{2-x}\text{O}_{4+z}$ where $y \geq 2$, $0.25 < x < 2$ and $z \geq 0$. However, only two of the 37 samples described in the patent had a composition in which y was greater than 2 and for those samples y was only slightly increased to 2.2.

2. Experimental

Two different processes were employed to prepare samples of $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$ used for this study. The first involved preparing a mixed oxide of chromium and manganese by spray drying an aqueous solution of the metal salts and then thermally decomposing them. The second method was to form a mixed hydroxide of chromium and manganese by co-precipitation. The mixed oxides or hydroxides were mixed with LiOH and treated thermally to form various compositions of $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$.

For example, a solution containing (12.30 g, 0.05 mol) of manganese acetate tetrahydrate, $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (Aldrich), and (10.05 g, ~ 0.0167 mol) of chromium acetate hydroxide, $\text{Cr}_3(\text{OH})_2(\text{CH}_3\text{CO}_2)_7$ (Aldrich), dissolved in 500 ml of de-ionized water was dried in a commercial (Buchi 190) mini spray-drier. The dried metal acetate mixture was calcined in air at 400°C for 3 h. A mass of 2.8 g of this oxide was slurried with 13 ml of a 4 M solution of lithium hydroxide in de-ionized water and heated treated in an alumina crucible in a tube furnace under flowing air. The heating regime was controlled to heat the sample slowly,

* Corresponding author. Tel.: +1-613-990-0347; Fax: +1-613-991-2384.
E-mail address: isobel.davidson@nrc.ca (I.J. Davidson).

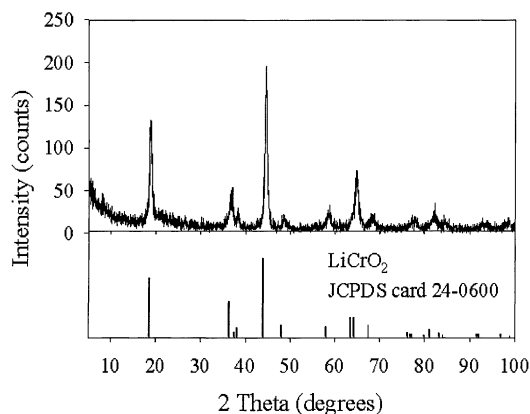


Fig. 1. X-ray diffraction pattern for $\text{Li}_3\text{CrMnO}_{4+z}$ with comparison to ICDD diffraction pattern for LiCrO_2 with $R\bar{3}m$ structure as a stick diagram below.

over 5.5 h, to 450°C , hold at 450°C for 2 h and then allow the sample to cool slowly in the furnace to room temperature.

The sample was reground and then fired in a tube furnace at 700°C for 3 h under in a flow of argon gas. Fig. 1 is a X-ray diffraction pattern of the sample after heat-treatment. Chemical analysis of the sample by atomic absorption found the composition to be $\text{Li}_{(3.30\pm 0.25)}\text{Mn}_{(1.06\pm 0.08)}\text{Cr}_{(0.94\pm 0.05)}\text{O}_{(5.54\pm 0.28)}$, with the oxygen content estimated by difference.

A second sample was prepared by spray drying a 1.0 l solution containing 24.677 g of manganese acetate (Aldrich) and 22.075 g of chromium acetate hydroxide (Aldrich). The metal salts were calcined at 475°C for 4 h in air. A quantity of the calcination product, 4.014 g, was combined with 20.85 ml of a 4 M aqueous solution of LiOH (Anachemia) as a slurry. The mixture was slowly heated to 450°C in air and held at that temperature for 2 h. After cooling, the sample was ground by hand with a mortar and pestle and then transferred to an alumina boat for a final heat treatment in flowing argon at 700°C for 4 h. A chemical analysis by atomic absorption determined a composition of $\text{Li}_{(2.95\pm 0.22)}\text{Mn}_{(0.91\pm 0.07)}\text{Cr}_{(1.09\pm 0.06)}\text{O}_{(4.11\pm 0.20)}$ for this sample.

Similarly, a range of compositions of $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$ were prepared from solutions of $\text{Mn}(\text{CH}_3\text{CO}_2)_2$ and $\text{Cr}_3(\text{OH})_2(\text{CH}_3\text{CO}_2)_7$, spray dried and then thermally decomposed at 450°C . The dried oxides were mixed with a 4 M solution of LiOH in a ratio of 1 g of oxide to 5.2 ml of LiOH solution. The target and chemically analyzed compositions are listed in Tables 1 and 2 for the chromium-rich and manganese-rich samples, respectively. The chemical analysis was done by atomic absorption and the oxygen compositions are calculated by difference.

The electrochemical cycling of the materials prepared by the spray drying procedure were carried out in 2325 coin cells each containing an internal spring and spacer to

Table 1

Chemical compositions and discharge capacities of Cr-rich $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$

Sample	Target (Cr/Mn)	Composition analysis (atomic absorption)	Discharge capacity (cycle: 1, 10, 20) (mAh/g)
A	1.05/0.95	$\text{Li}_{2.9}\text{Mn}_{0.99}\text{Cr}_{1.01}\text{O}_{5.4}$	152, 158, 165
B	1.10/0.90	$\text{Li}_{3.1}\text{Mn}_{0.95}\text{Cr}_{1.05}\text{O}_{5.4}$	179, 186, 191
C	1.15/0.85	$\text{Li}_{3.1}\text{Mn}_{0.90}\text{Cr}_{1.10}\text{O}_{5.1}$	171, 178, 182
D	1.20/0.80	$\text{Li}_{3.4}\text{Mn}_{0.85}\text{Cr}_{1.15}\text{O}_{5.7}$	189, 153, 133
E	1.25/0.75	$\text{Li}_{3.3}\text{Mn}_{0.80}\text{Cr}_{1.20}\text{O}_{4.9}$	215, 180, 180
F	1.30/0.70	$\text{Li}_{3.1}\text{Mn}_{0.75}\text{Cr}_{1.25}\text{O}_{5.4}$	188, 132, 113
G	1.35/0.65	$\text{Li}_{3.2}\text{Mn}_{0.69}\text{Cr}_{1.31}\text{O}_{5.1}$	193, 135, 113
H	1.40/0.60	$\text{Li}_{3.3}\text{Mn}_{0.66}\text{Cr}_{1.34}\text{O}_{5.9}$	197, 143, 150
I	1.45/0.55	$\text{Li}_{3.1}\text{Mn}_{0.59}\text{Cr}_{1.41}\text{O}_{5.0}$	180, 125, 120
J	1.50/0.50	$\text{Li}_{2.8}\text{Mn}_{0.54}\text{Cr}_{1.46}\text{O}_{5.2}$	221, 162, 171

Table 2

Chemical compositions and discharge capacities of Mn-rich $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$

Sample	Target (Mn/Cr)	Composition analysis (atomic absorption)	Discharge capacity (cycle: 1, 10, 20) (mAh/g)
A	1.05/0.95	$\text{Li}_{2.8}\text{Mn}_{1.10}\text{Cr}_{0.90}\text{O}_{4.5}$	147, 141, 145
B	1.10/0.90	$\text{Li}_{3.1}\text{Mn}_{1.07}\text{Cr}_{0.93}\text{O}_{6.6}$	148, 169, 175
C	1.15/0.85	$\text{Li}_{3.1}\text{Mn}_{1.15}\text{Cr}_{0.85}\text{O}_{4.7}$	141, 144, 150
D	1.20/0.80	$\text{Li}_{3.2}\text{Mn}_{1.17}\text{Cr}_{0.83}\text{O}_{4.5}$	100, 117, 126
E	1.25/0.75	$\text{Li}_{3.3}\text{Mn}_{1.22}\text{Cr}_{0.78}\text{O}_{4.6}$	89, 96, 101
F	1.30/0.70	$\text{Li}_{2.8}\text{Mn}_{1.30}\text{Cr}_{0.70}\text{O}_{4.9}$	89, 115, 118
G	1.35/0.65	$\text{Li}_{2.9}\text{Mn}_{1.36}\text{Cr}_{0.64}\text{O}_{4.9}$	122, 130, 132
H	1.40/0.60	$\text{Li}_{3.0}\text{Mn}_{1.40}\text{Cr}_{0.60}\text{O}_{5.3}$	87, 102, 108
I	1.45/0.55	$\text{Li}_{3.0}\text{Mn}_{1.46}\text{Cr}_{0.54}\text{O}_{5.4}$	87, 121, 108
J	1.50/0.50	$\text{Li}_{2.9}\text{Mn}_{1.51}\text{Cr}_{0.49}\text{O}_{5.0}$	128, 122, 120

maintain an adequate pressure on the electrode stack. The anodes were lithium (Foote Mineral) discs of 1.65 cm diameter and 0.05 cm thickness while the electrolyte was 1 M LiPF_6 in 1:1 ethylene carbonate:dimethyl carbonate (Mitsubishi Chemical).

The materials were cast into electrode sheets and tested in coin cells. Cathodes were prepared from a mixture of 0.456 g of active material, 0.047 g of super S carbon black, and 0.049 g of graphite (Lonza KS4). The mixture was formed into a slurry with 1.206 g of a binder solution containing 3 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 in air at low heat on a hot plate and then at 110°C for 20 min in a convection oven. Electrode discs of 1.27 cm diameter were punched from the cast and densified by pressing each disc with a force of 500 lb on a hydraulic press. The electrodes typically had a thickness between 0.008 and 0.013 cm after pressing. The discharge capacities of cells cycled between 2.5 and 4.5 V at a current density of 7.2 mA/g are listed in Tables 1 and 2 for the 1st, 10th and 20th cycles for the range of compositions of $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$ indicated.

In the second synthesis procedure, a Cr–Mn hydroxide was prepared by co-precipitation. An aqueous solution of 2 M concentration in chromium nitrate was prepared by adding a specified quantity (according to the targeted Cr/Mn ratio) of manganese nitrate to the solution with the final composition adjusted using water. Slowly pouring caustic alkali aqueous solution containing 6 M sodium hydroxide into the concentrated transition metal nitrate solution caused the co-precipitation of Cr hydroxide and Mn hydroxide. The precipitation was finished when the pH of the mixed solution reached a value of 10. The Cr–Mn double hydroxide was obtained by filtering the deposits and the rinsing with water. The water rinsing was repeated while continuously measuring the pH value until the pH reached 6–7. The resulting double hydroxide was dried at 100°C in air.

The Cr–Mn double hydroxide obtained through the co-precipitation method described above was mixed with lithium hydroxide, and the mixture was placed in an alumina crucible and fired in a horizontal tube furnace under flowing argon. The sample was fired for 24 h at 650–700°C. After the firing, the product was gradually cooled to room temperature and milled to a powder to be used as the cathode active material.

After preparing several active materials of various Li/Cr/Mn ratios, each sample was examined by an X-ray diffraction method. The cathodes were prepared by casting and drying a slurry made from 85 wt.% active material with 10 wt.% acetylene black and 5 wt.% polyvinylidene fluoride (PVDF) in NMP. The substrate was Al foil and the diameter of punched cathodes was 10 mm. The anodes were prepared by punching lithium metal film, having the thickness of 0.8 mm and the diameter of 12 mm. The diameters of the electrodes were chosen to fit a commercial coin cell case of the type 2016. These coin cells have a diameter of 20 mm

and a height of 1.6 mm. The cell stack consisted of a three-layer sandwich of the cathode, cell separator, and lithium anode wetted with electrolyte solution. The separator was a microporous polypropylene film and the electrolyte contained 1 M LiPF_6 in a 50/50 mixture by volume of ethylene carbonate and dimethyl carbonate. The cells were assembled and crimped in a glove box with a helium atmosphere. The coin cells were charged and discharged at a current density of 3.6 mA/g over a voltage range of 4.3–2.5 V.

3. Discussion

The X-ray diffraction pattern shown in Fig. 1 is consistent with the compound being a layered oxide in which layers of lithium atoms alternate with layers containing mixtures of manganese, chromium and lithium atoms. The diffraction pattern can be compared to that of LiCrO_2 as indicated by the bar diagram under the diffraction pattern. The diffraction pattern of the $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$ sample is similar to that of LiCrO_2 but there are differences in the relative intensities of the peaks and the peaks of $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$ are shifted to higher angle relative to those of LiCrO_2 .

A Rietveld refinement of the X-ray diffraction pattern of the sample of composition $\text{Li}_{2.95}\text{Mn}_{0.9}\text{Cr}_{1.09}\text{O}_{4.11}$ was calculated with an $R\bar{3}m$ structural model using the program Rietan [7]. The refinement found the crystallographic unit cell dimensions to be 2.876 Å for the *a* and *b* directions and 14.25 Å for the *c*. The volume of the crystallographic unit cell is calculated to be 102.1 Å³, significantly lower than that of LiCrO_2 at 104.9 Å³.

A plot of the evolution of the voltage versus capacity profiles for the first 45 cycles of a cell with a cathode of composition $\text{Li}_{2.95}\text{Mn}_{0.9}\text{Cr}_{1.09}\text{O}_{4.11}$ is provided in Fig. 2. The cell was cycled at 30 mA/g between voltage limits of 2.5–4.5 V. The sloping single-plateau voltage profile is

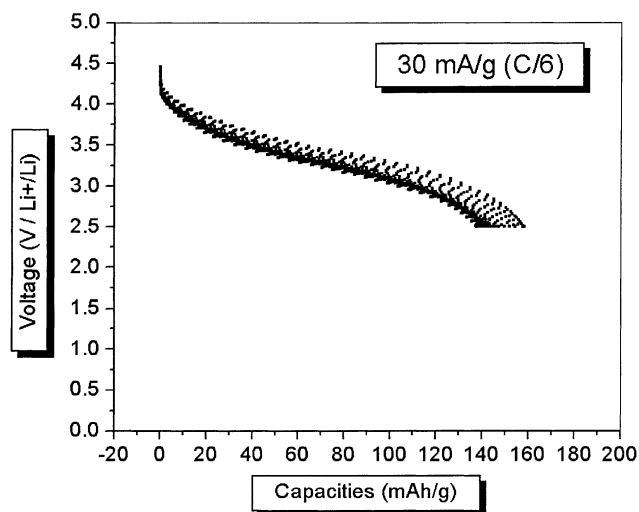


Fig. 2. Discharge voltage profiles for the first 45 cycles of a Li/ $\text{Li}_3\text{CrMnO}_{4+z}$ cell cycled between 2.5 and 4.5 V at 30 mA/g.

Table 3

Chemical composition, specific capacities and crystallographic cell dimensions of typical samples from co-precipitation method of synthesizing $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$

No.	Li mole (x)	Cr mole (y)	Mn mole (2 - y)	O mole (z)	1st charge/discharge (mAh/g)	5th discharge (mAh/g)	Crystal structure (a, c, unit cell volume)
1	2.65	1.25	0.75	1.86	240.12/201.94	204.01	Hexagonal (a = 2.885, c = 14.250, V = 102.77)
2	2.25	1.23	0.77	0.37	229.76/194.69	177.92	Hexagonal (a = 2.891, c = 14.288, V = 103.42)
3	3.44	1.22	0.78	1.55	278.17/204.93	191.65	Hexagonal (a = 2.875, c = 14.211, V = 101.78)
4	3.09	1.34	0.66	1.79	283.81/229.69	202.19	Hexagonal, (a = 2.891, c = 14.216, V = 102.92)
5	2.74	0.98	1.02	1.06	230.25/188.28	182.98	Hexagonal (a = 2.893, c = 14.223, V = 103.16)

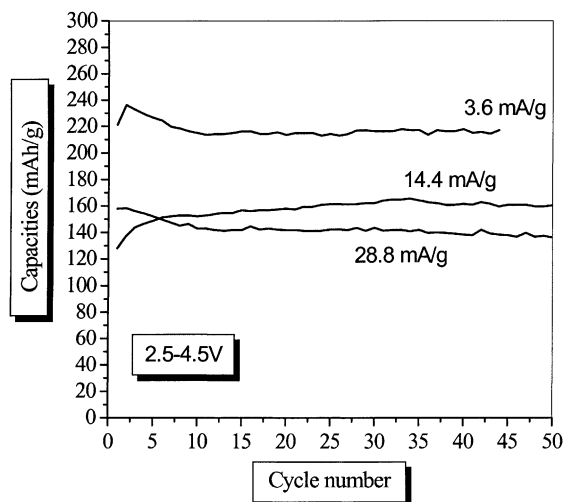


Fig. 3. Plot of specific capacities vs. cycle number for $\text{Li}/\text{Li}_3\text{CrMnO}_{4+z}$ cells cycled between 2.5 and 4.5 V at indicated current densities.

maintained on cycling. Fig. 3 shows the capacity retention at various current densities for other cells with the same material cycled between 2.5 and 4.5 V.

The discharge capacities at cycles 1, 10 and 20 for cells containing a range of compositions of $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$ are listed in Tables 1 and 2. These cells were cycled at 7.2 mA/g between voltage limits of 2.5 to 4.5 V. On cycling the phases with a higher concentration of Cr (designated as chromium-rich) first discharge capacities of up to 221 mAh/g were observed. The cell with a cathode of composition, $\text{Li}_{3.1}\text{Cr}_{1.05}\text{Mn}_{0.95}\text{O}_{5.4}$, demonstrated a stable capacity near 180 mAh/g over 50 cycles at 7.2 mA/g. Cells with cathodes of compositions $\text{Li}_{3.1}\text{Cr}_{1.10}\text{Mn}_{0.90}\text{O}_{5.1}$, $\text{Li}_{3.3}\text{Cr}_{1.20}\text{Mn}_{0.80}\text{O}_{4.9}$ and $\text{Li}_{2.8}\text{Cr}_{1.46}\text{Mn}_{0.54}\text{O}_{5.2}$ also showed very stable capacities of 180 and 170 mAh/g at 7.2 mA/g current density.

Table 3 lists the charge and discharge capacities of several samples of different formulas made by the co-precipitation procedure. The atomic ratios of Li, Cr, and Mn were determined by atomic absorption analysis. Oxygen contents

were estimated by difference. The lattice parameters: *a*, *b* and *c* are in (Å) units and the unit cell volumes are in units of (Å³).

4. Conclusions

The recently discovered quaternary oxides of lithium, chromium and manganese represent a new series of chemically stabilized layered manganese oxides. Unlike many other layered manganese oxides made by soft chemistry [8,9] or stabilized by partial chemical substitution of the manganese [3,10–12], these materials maintain a sloping single-plateau voltage profile over repeated electrochemical cycling. As cathodes for lithium-ion cells, these compounds offer high specific capacity but require further improvements in their electrochemical kinetics.

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