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A novel cathode $Li_2CoMn_3O_8$ for lithium ion batteries operating over 5 volts

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The spinel phase, $Li_2CoMn_3O_8$, can be used as a cathode in secondary lithium batteries, Li/$LiPF_6$,propylene carbonate/$Li_2CoMn_3O_8$, with a discharge capacity of *ca.* 40 mAh g^{-1} at 5.0 V increasing to *ca.* 130 mAh g^{-1} at 3.8 V. This appears to be the first single cell system to operate reversibly over 5 volts.

Lithium ion rechargeable batteries which employ lithium transition metal oxide cathodes and carbon anodes have applications ranging in size from portable electronic devices to zero emission vehicles (ZEV).[1] Recent developments include 4 V cathodes based on $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$,[2] low temperature synthesis of new cathodes such as $LiMnO_2$[3] and $Li_{1.5}Na_{0.5}MnO_{2.85}I_{0.12}$[4] working below *ca.* 4 V and improved electrolytes[5] which have made it possible to explore the potential range to 5 V *vs.* Li/Li^+. Tarascon *et al.*[6] observed two oxidation–reduction peaks near 4.5 V and 4.9 V for $LiMn_2O_4$. Cells with high operating voltage have been reported with cathodes based on spinel structure compounds, including 4.8 V for $LiNiVO_4$[7] and $LiCr_XMn_{2-X}O_4$[8] and 4.7 V for $LiNi_XMn_{2-X}O_4$.[9,10] For some electrochemists, especially aiming to commercialize high power ZEV, it has been a primary target to discover a cathode which works over 5 V, linked to high specific capacity and good cycling stability. We show here that a complex spinel $Li_2CoMn_3O_8$ possesses an operating voltage over 5 V, with excellent cycle performance and specific discharge capacity, up to the potential limit of 5.3 V, of *ca.* 40 mAh g^{-1}. To our knowledge, this is the first cathode working over 5 V.

An oxidizing atmosphere was used in the initial synthesis of the spinel phase $Li_2CoMn_3O_8$.[11] In the present study, $Li_2CoMn_3O_8$ was obtained more simply by conventional ceramic synthesis in air. Starting materials were Li_2CO_3, CoO and $MnCO_3$, all reagent grade. A stoichiometric mixture was ground intimately, fired in air, initially at 650 °C to drive off CO_2, then at 800 °C for 3 days with intermittent regrinding, to complete the reaction, and finally at 600 °C for 3 days, before quenching to room temperature. Oxygen loss from the as-prepared sample occurred above *ca.* 650 °C, involving possible structural changes, and thus the above synthesis procedure with the final annealing at 600 °C was chosen as the optimum conditions to obtain a pure phase. Further study on the phase(s) formed above *ca.* 650 °C are in progress.

The powder X-ray diffraction (XRD) pattern of $Li_2CoMn_3O_8$ (Stoe Stadi/P diffractometer, Cu-Kα_1 radiation) was indexed in the cubic space group $Fd3m$ with lattice parameter $a=8.1317(17)$ Å, Fig. 1. High fluorescence backgrounds, caused by an interaction between Co/Mn and Cu-Kα_1 radiation, allowed us to determine only a likely cation distribution by the Rietveld method, using the pattern fitting structure refinement (PFSR) program in the Stoe software package. Powder XRD patterns for various cation distributions on 8a and 16d sites were generated theoretically, using the atomic positions of the spinel phase $Li_4Mn_5O_{12}$, *i.e.*, $Li_{8a}[Li_{0.33}Mn_{1.67}]_{16d}O_4$,[12] with isotropic thermal parameters of 0.05 for all atomic positions, and compared with the observed pattern. Rietveld refinement was then carried out for models having likely cation distributions. The most probable model, with minimum R values,[13] was found to be $Li_{8a}[Co_{0.5}Mn_{1.5}]_{16d}O_4$: Li fully occupies tetrahedral 8a sites; Co and Mn are distributed in octahedral 16d sites with a molar ratio of 1:3. Cation ordering in octahedral 16d sites remains a possibility because, although there is no evidence of superstructure reflections in Fig. 1, Co and Mn have very similar atomic scattering factors.

For conductivity measurements, a pellet (8 mm diameter; 2–3 mm thickness) was cold-pressed uniaxially at 150 MPa, sintered at 950 °C for a few hours in order to increase the mechanical strength, slowly cooled to 600 °C and maintained at 600 °C for 3 days before quenching to room temperature. In/Ga paste electrodes were coated on opposite sides of the sintered pellet. Impedance measurements were carried out over the frequency range 30 mHz–1 MHz, using combined Solartron 1250/1286 and Hewlett-Packard 4192 instrumentation. The data were analyzed in the complex impedance (Z^*), admittance (Y^*) and modulus (M^*) formalisms,[14] using in-house software.

Impedance data at −23 °C are shown in Fig. 2. Three arcs are seen. The high frequency well resolved arc has an associated capacitance of 4.7×10^{-12} F, typical of a bulk response. The middle frequency arc, with an associated capacitance of 4.5×10^{-10} F, corresponds to a grain boundary resistance. The low frequency arc has capacitance *ca.* 2.3×10^{-7} F, and may be indicative of Schottky barrier phenomena[15] at the sample–electrode interface. No spikes attributable to a blocking electrode response were seen in the measured temperature and frequency ranges. The main current carriers thus appear to be electrons. Bulk conductivity data are shown as a function of temperature in Arrhenius format in Fig. 3. Activation energy for conduction is estimated to be *ca.* 0.31 eV. The conductivity is *ca.* 6.8×10^{-4} S cm^{-1} at 30 °C. High electronic conductivity in oxides is most frequently observed in mixed valency semiconductors.[16] In the case of $Li_2CoMn_3O_8$, if some of the Mn^{4+} are reduced to Mn^{3+}, charge balance is preserved by oxidation of Co^{2+} to Co^{3+}. Thus, from a combination of the Rietveld refinement and impedance results, $Li_2CoMn_3O_8$ is most likely written as $Li_{8a}[Co^{2+}{}_{0.5-Y}Co^{3+}{}_{Y}Mn^{3+}{}_{Y}Mn^{4+}{}_{1.5-Y}]_{16d}O_4$, $0<Y\leqslant0.5$ (exact value not known).

Electrochemical measurements were made in a glass test cell containing a $Li_2CoMn_3O_8$ composite as the positive electrode, Li metal foil as the negative electrode, Li metal as a reference and 1 M $LiPF_6$ dissolved in propylene carbonate as the electrolyte. The $Li_2CoMn_3O_8$ composite electrode was prepared by blending 5 wt.% acetylene black as an active material and 5 wt.% mixture of polyvinylidene fluoride and *N*-methyl-2-pyrrolidone as a binder. Cycle tests were carried out galvanostatically at a current density of 0.5 mA cm^{-2}.

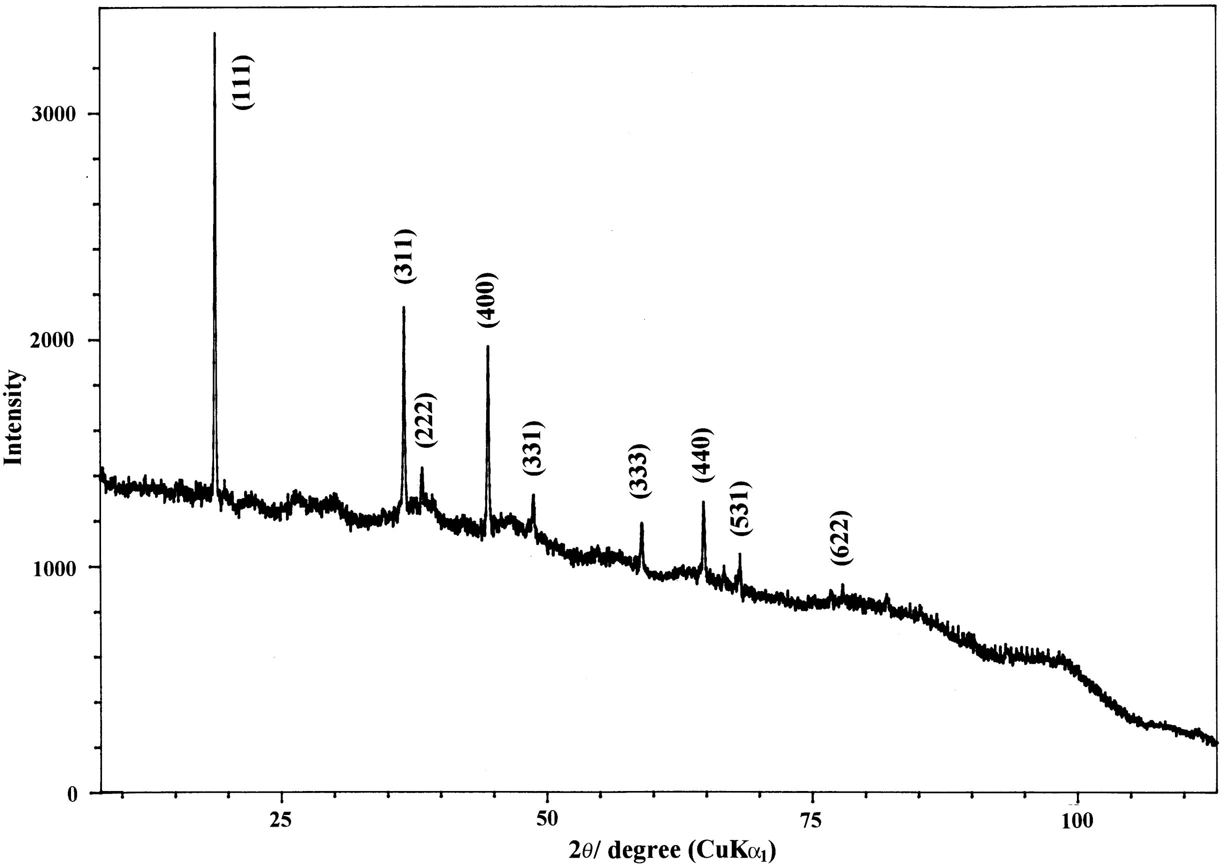

Fig. 1 Powder XRD profile for $Li_2CoMn_3O_8$

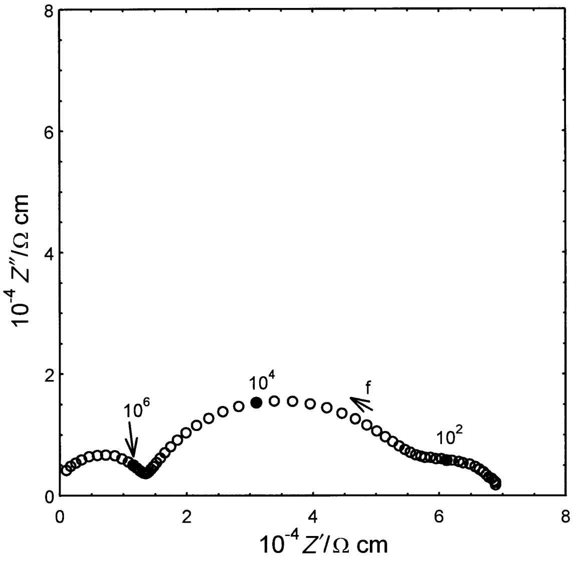

Fig. 2 Impedance data for $Li_2CoMn_3O_8$ at −23 °C

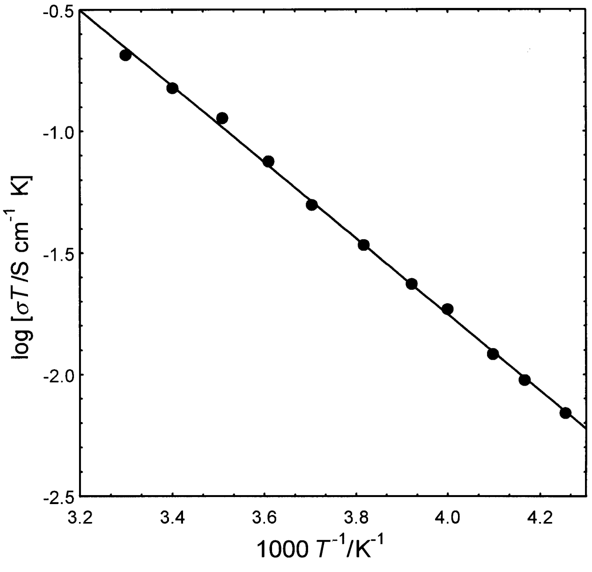

Fig. 3 Conductivity Arrhenius plot for $Li_2CoMn_3O_8$

The cell was cycled four times between 3.0 V and 5.1 V, before charging to 5.3 V. Fig. 4 shows a potential profile for the first 5.3 V cutoff measurement. Two plateaux are seen in both charge and discharge curves and correspond to two-step extraction/reinsertion of lithium from/into the cathode material. On charge, the plateau centered on 4.0 V has the capacity, estimated at the sharp transition point between the two plateaux, of 61.8 mAh g^{-1}. On converting the capacity to X in $Li_{2-X}CoMn_3O_8$, X reaches 0.84 at the transition point. The potential scan was limited to 5.3 V owing to possible electrolyte decomposition at higher potentials. Up to 5.3 V, the plateau centered on 5.2 V possesses the capacity of 76.5 mAh g^{-1}, which corresponds to a change in X of 1.04. The composition at 5.3 V is then estimated to be $Li_{0.12}CoMn_3O_8$, indicating that at least 6% Li still remains inside the positive electrode. It is thus likely that the plateau centered on 5.2 V continues over 5.3 V, finally yielding a plausible end composition $Co^{4+}Mn^{4+}{}_3O_8$. Improvement in electrolyte stability is needed to measure electrochemical properties at higher potentials. Discharge capacity is estimated roughly to be *ca.* 60 mAh g^{-1} at the plateau centered on 5.1 V and *ca.* 70 mAh g^{-1} at the plateau centered on 3.9 V, Fig. 4. The two plateaux appear to originate in the redox reactions (1) $Co^{2+}{}_{16d}\leftrightarrow Co^{3+}{}_{16d}$, (2) $Co^{3+}{}_{16d}\leftrightarrow Co^{4+}{}_{16d}$, (3)

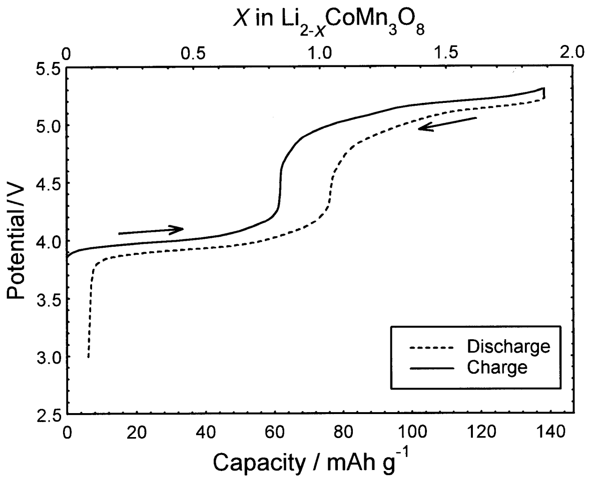

Fig. 4 Potential profile for $Li_2CoMn_3O_8$

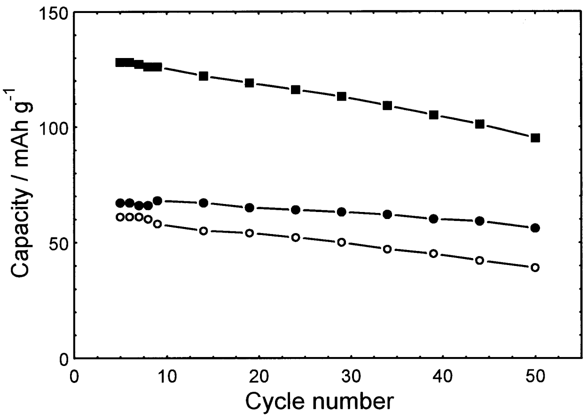

Fig. 5 Variation in discharge capacity of the plateau centered on 3.9 V (●) and the plateau centered on 5.1 V (○) upon cycling for $Li_2CoMn_3O_8$ (■ denotes the total discharge capacity; ■ = ● + ○)

$Co^{2+}{}_{16d} \leftrightarrow Co^{4+}{}_{16d}$ and/or (4) $Mn^{3+}{}_{16d} \leftrightarrow Mn^{4+}{}_{16d}$. Further work is needed to elucidate which reactions are responsible for the electrochemical performance. Fig. 5 shows the variation in discharge capacity with cycle number. Both plateaux centered on 5.1 V and 3.9 V exhibit excellent cycling stability, maintaining their discharge capacity to well over 50 cycles.

To date, $LiCoO_2$ is the only cathode used in commercial lithium ion batteries.[17] $LiMnO_2$[3] and $Li_{1.5}Na_{0.5}MnO_{2.85}I_{0.12}$[4] are possible candidates for substituting for the expensive and toxic $LiCoO_2$, subject to improved cycle performance in the former and working voltage in the latter. Possible applications are, however, limited to portable electronic devices, owing to operating voltages below *ca.* 4 V. The new $Li_2CoMn_3O_8$ cathode reported here possesses a very high working voltage, over 5 V for part of the charge–discharge cycle, with excellent cycling stability. Easy preparation procedure reduces the costs for synthesis. Although the specific capacity at the plateau centered on 5.1 V needs to be improved, $Li_2CoMn_3O_8$ and its possible solid solutions are promising candidates for cathodes in high voltage (>5.0 V) lithium ion cells, which could be used in high power, emission-free vehicles, with improved oxidation–resistant electrolytes.

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References

1 See, for example, K. Brandt, *Solid State Ionics*, 1994, **69**, 173.
2 See, for example, R. Koksbang, J. Barker, H. Shi and M. Y. Saidi, *Solid State Ionics*, 1996, **84**, 1.
3 A. R. Armstrong and P. G. Bruce, *Nature*, 1996, **381**, 499.
4 J. Kim and A. Manthiram, *Nature*, 1997, **390**, 265.
5 J. M. Tarascon and D. Guyomard, *Solid State Ionics*, 1994, **69**, 293.
6 J. M. Tarascon, W. R. McKinnon, F. Coowar, T. N. Bowmer, G. Amatucci and D. Guyomard, *J. Electrochem. Soc.*, 1994, **141**, 1421.
7 G. T-K. Fey, W. Li and J. R. Dahn, *J. Electrochem. Soc.*, 1994, **141**, 2279.
8 C. Sigala, D. Guyomard, A. Verbaere, Y. Piffard and M. Tournoux, *Solid State Ionics*, 1995, **81**, 167.
9 K. Amine, H. Tukamoto, H. Yasuda and Y. Fujita, *J. Electrochem. Soc.*, 1996, **143**, 1607.
10 Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao and J. R. Dahn, *J. Electrochem. Soc.*, 1997, **144**, 205.
11 G. Blasse, *J. Inorg. Nucl. Chem.*, 1964, **26**, 1473.
12 T. Takada, H. Hayakawa and E. Akiba, *J. Solid State Chem.*, 1995, **115**, 420.
13 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.
14 I. M. Hodge, M. D. Ingram and A. R. West, *J. Electroanal. Chem.*, 1976, **74**, 125.
15 See, for example, H. H. Sumathipala, M. A. K. L. Dissanayake and A. R. West, *J. Electrochem. Soc.*, 1995, **142**, 2138.
16 E. J. W. Verwey, P. B. Braun, E. W. Gorter, F. C. Romeijn and J. H. van Santen, *Z. Phys. Chem.*, 1951, **198**, 6.
17 T. Nagaura and K. Tozawa, *Prog. Batteries Sol. Cells*, 1990, **9**, 209.

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