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Lithium-ion cell based on orthorhombic LiMnO_2

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Abstract

This paper will demonstrate that cathodes based on the high temperature form of orthorhombic LiMnO_2 , with the structure described by Hoppe, Brachtel and Jansen, have good capacity and cycle life. X-ray diffraction studies have revealed that cathodes prepared from orthorhombic LiMnO_2 undergo a structural change on being charged beyond a certain potential in which the original structure is converted to spinel $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$. Orthorhombic LiMnO_2 has been found to have long-term stability in ambient conditions and is easily prepared in a one-step reaction.

Keywords: Lithium-ion cells; Lithium; Manganese dioxide; Crystal structure

1. Introduction

LiMnO_2 is known to exist in several phases. Two phases, whose crystal structures have been well characterized, are a high temperature orthorhombic phase ($Pmnm$) and a tetragonal phase ($I4_1/amd$). Both structures involve cubic close packing but they differ in the arrangement of the ordering of the lithium and manganese cations. The tetragonal form, $\lambda\text{-Li}_2\text{Mn}_2\text{O}_4$, is prepared by electrochemically, or chemically, intercalating lithium into the LiMn_2O_4 spinel structure. It has an atacamite-type structure which is often referred to as being spinel related. Both LiMn_2O_4 and $\lambda\text{-Li}_2\text{Mn}_2\text{O}_4$ have been used as cathodes in lithium-ion cells [1,2]. The structure of the high temperature orthorhombic phase of LiMnO_2 was determined in detail by Hoppe et al. [3]. To our knowledge, the use of LiMnO_2 , having this structure, as the active material in the cathode of a reversible electrochemical cell has never, previously, been demonstrated.

Ohzuku et al. [4] have demonstrated the use of a low temperature form of orthorhombic LiMnO_2 , prepared by reacting an equimolar mixture of $\gamma\text{-MnOOH}$ and $\text{LiOH}\cdot\text{H}_2\text{O}$ at 450 °C, as the active cathode material in a reversible lithium-ion cell. More recently, Reimers et al. [5] developed improvements on Ohzuku's synthesis and found that low temperature LiMnO_2 can be prepared at very low temperature (100 °C) by ion exchange. However, they found that well-crystallized LiMnO_2

prepared at 450 °C had much poorer electrochemical behaviour than more disordered material prepared at 350 °C. Gummow et al. [6] studied LiMnO_2 prepared at moderate (600–620 °C) temperatures from $\gamma\text{-MnO}_2$ and LiOH in argon with carbon added as a reducing agent. Both Reimers and Gummow state, without giving direct evidence, that orthorhombic LiMnO_2 , which is conventionally synthesized at high temperatures, does not show good electrochemical activity.

2. Experimental

We have prepared orthorhombic LiMnO_2 by a classical high temperature solid-state reaction, verified Hoppe's structure by neutron diffraction, and have evaluated this material in cathodes of lithium-ion cells. High temperature orthorhombic LiMnO_2 was prepared by intimately mixing and pelletizing a 2:1 mole mixture of $\beta\text{-MnO}_2$ (Fisher Scientific Certified) and Li_2CO_3 (Aldrich 99.997% pure). The pellets were first calcined at 600 to 650 °C for several hours to remove the CO_2 , and then baked at 800 to 1000 °C for 1 to 3 days in a horizontal tube furnace under a flow of argon gas. Generally, one or two more grindings and firings were required to achieve a well-crystallized product. The progress of the reaction was followed by X-ray powder diffraction.

Neutron powder diffraction data of LiMnO_2 , prepared as described, were collected at the McMaster Nuclear Reactor using 1.3913 Å neutrons obtained from a [200]

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copper monochromator and a spectrometer described previously [7]. The raw data, collected with a position-sensitive detector, were corrected for the detector geometry according to the procedures of Ref. [8].

Lithium-ion cells were assembled in a 2325 coin cell format with pressed pellet cathodes containing orthorhombic LiMnO_2 mixed with 10 wt.% Super S carbon black (Chemetals Inc.) and 2 wt.% ethylene/propylene/diene monomer (EPDM) (Polysar), and pelletized anodes containing petroleum coke (premium needle coke) combined with 7.5 wt.% Super S carbon black and 2 wt.% EPDM binder. The cells were assembled, with polypropylene felt separators (Web Dynamics) and electrolyte containing 1 M $(\text{CF}_3\text{SO}_2)_2\text{N}^-\text{Li}^+$ (3M Company) in a 50/50 mixture by volume of propylene carbonate and dimethoxyethane, in a helium atmosphere glove box.

3. Results and discussion

Fig. 1 is the X-ray diffraction trace of a typical product of this reaction, with stick diagrams of the diffraction patterns of orthorhombic LiMnO_2 , spinel LiMn_2O_4 and spinel-related $\lambda\text{-Li}_2\text{Mn}_2\text{O}_4$ from the powder diffraction file of the International Centre for Diffraction Data plotted below for comparison. This particular sample was calcined at 600 °C followed by two intervals of three days each at 800 °C. The diffraction pattern shown was taken after eleven months of storage under ambient conditions, and serves to demonstrate that, unlike $\lambda\text{-Li}_2\text{Mn}_2\text{O}_4$, the orthorhombic form of LiMnO_2 is air stable.

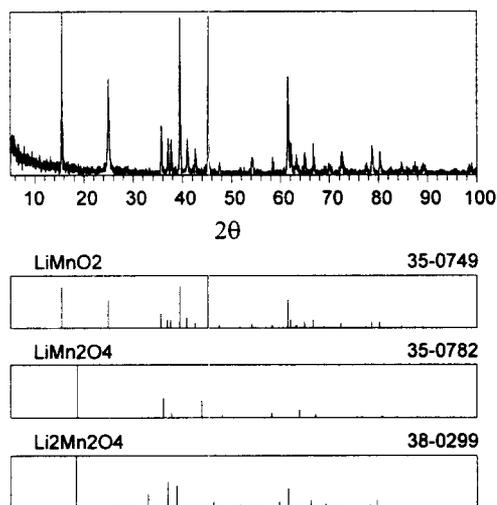


Fig. 1. Diffraction pattern of orthorhombic LiMnO_2 , after eleven months' storage in air, with stick diagrams of the diffraction patterns of orthorhombic LiMnO_2 , spinel LiMn_2O_4 and spinel-related $\lambda\text{-Li}_2\text{Mn}_2\text{O}_4$ from the powder diffraction file of the International Centre for Diffraction Data plotted below for comparison.

The LiMnO_2 structure was refined from the neutron powder diffraction pattern with a Rietveld profile refinement program, 'Rietan' [9]. The refinement was initiated with the atomic positions of Hoppe et al. [3]. Twenty parameters were allowed to refine: three lattice parameters, four atomic z-coordinates, four isotropic thermal parameters, a scale factor, a detector zero-point offset, six background parameters and the half-width parameter, w . The observed (symbols) and calculated (line) neutron diffraction patterns are plotted in Fig. 2. The difference is plotted below on the same scale. The refined structure, tabulated in Table 1, agrees well with Hoppe's refinement from single crystal X-ray diffraction data.

Lithium-ion cells with orthorhombic LiMnO_2 cathodes were evaluated by constant current cycling. Fig. 3 shows the first five cycles for a cell cycled at 1.37 mA/g of LiMnO_2 between voltage limits of 1.5 and 4.0 V. The anomalies in the first discharge and in the third charge are due to brief, accidental, power interruptions. The low rate is necessary for the rather thick (≈ 1 mm) electrodes used in this experiment. Except for the lower upper voltage limit, the voltage curves are very similar to those shown in Fig. 6 of Ref. [2] for cells containing $\lambda\text{-Li}_2\text{Mn}_2\text{O}_4$ cathodes. Reimers et al. [5] and Gummow et al. [6] have found that LiMnO_2 prepared at lower temperatures undergoes an irreversible conversion to a spinel-type form on cycling. X-ray diffraction studies on materials recovered from cycled cells also reveal that the orthorhombic LiMnO_2 prepared at high temperature converts to $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ on being charged to greater than about 50% of its theoretical capacity (285 mAh/g).

Another coke/ LiMnO_2 cell was cycled between 1.5 V and a progressively increasing upper voltage limit. The first two cycles, to voltage limits of 3.0 and 3.5 V, respectively, showed very high irreversible capacities.

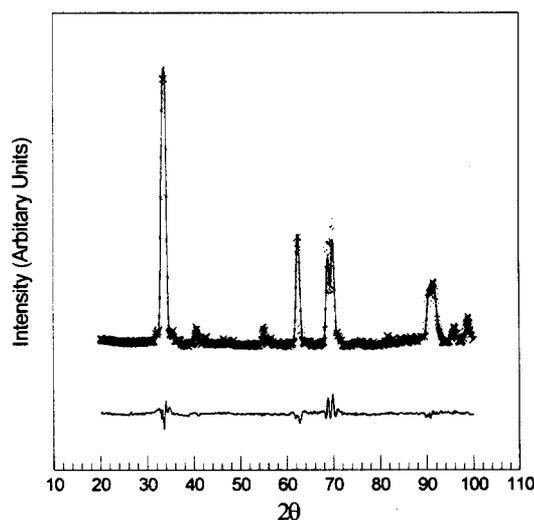


Fig. 2. Observed (symbols) and calculated (line) neutron powder diffraction patterns for orthorhombic LiMnO_2 . The difference in the patterns is plotted below on the same scale.

Table 1
Rietveld refinement of room temperature neutron diffraction data for LiMnO_2

Atom	Site	x	y	z	Occupancy	B (\AA^2)
Mn	2a	0.25	0.25	0.632(5)	1.0	0.5(4)
Li	2a	0.25	0.25	0.100(9)	1.0	0.2(7)
O	2b	0.25	0.75	0.142(4)	1.0	0.5(3)
O	2b	0.25	0.75	0.602(4)	1.0	0.5(3)

Space group: $Pm\bar{m}n$ (D_{2d}^{13}).

Wavelength: 1.391 \AA .

Lattice parameters: $a = 2.8048(3)$ \AA ; $b = 4.5755(6)$ \AA ; $c = 5.7494(7)$ \AA .

Halfwidth parameters: $U = 1.50$; $V = -1.20$; $W = 0.779(8)$.

Scattering lengths: Li (-0.190); Mn (-0.373); O (0.5803).

Weighted profile $R = 7.40$; Profile $R = 5.61$; Bragg $R = 4.47$; Expected $R = 3.42$.

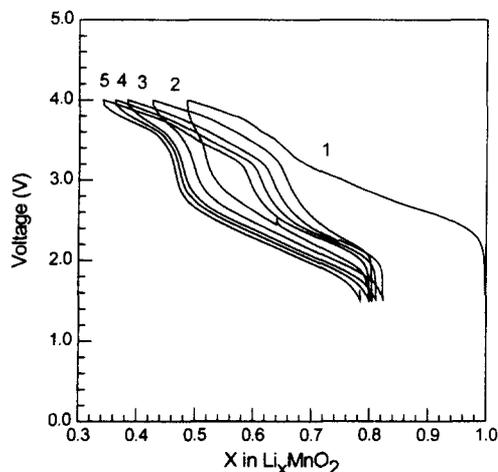


Fig. 3. First five charge/discharge cycles of a coke/ LiMnO_2 cell between voltage limits of 4.0 and 1.5 V. The anomalies in the first discharge and in the third charge are due to brief, accidental, power interruptions.

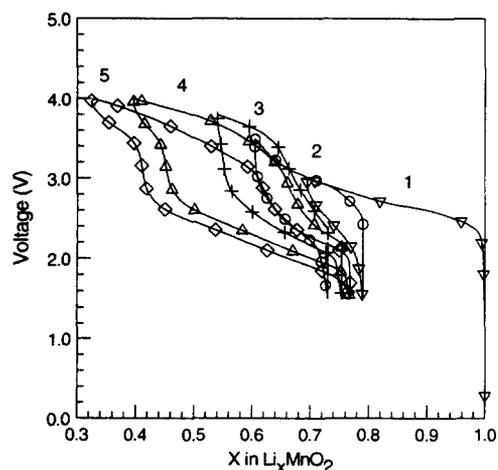


Fig. 4. First five cycles of a coke/ LiMnO_2 cell cycled to progressively higher voltage limits: (∇) first cycle to 3.0 V; (\circ) second cycle to 3.5 V; (+) third cycle to 3.8 V, and (Δ) fourth and (\diamond) fifth cycles to 4.0 V.

As shown in Fig. 4, the second charge pushed the cathode to 40% of its theoretical capacity. The third charge to a voltage limit of 3.8 V, indicated by the plus symbols in Fig. 4, took the cathode to 46% of its nominal capacity. The subsequent discharge, however, provided 12% more capacity than the charge had consumed. The fourth and fifth cycles to 4.0 V provided further small gains in discharge capacity relative to the prior charge. The first two discharges show no evidence of the higher voltage plateau (above 3.6 V) associated with lithium occupation of tetrahedral sites. Although it is difficult to see in Fig. 4, the third discharge shows a small amount of the high voltage plateau indicating that the conversion to spinel $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ began on the third charge. The coincidence of the phase conversion with increased reversible capacity suggests that it is critical to the functioning of LiMnO_2 -based cathodes, and may explain previous negative reports regarding the electrochemical activity of high temperature LiMnO_2 .

Cells built with high temperature orthorhombic LiMnO_2 cathodes have been cycled to more than 50 cycles without serious reduction in their reversible capacity. Fig. 5 is a plot of capacity, in mAh/g of LiMnO_2 , versus cycle number for a typical coin cell with relatively thick electrodes (~ 1 mm). This cell was cycled at 1.26 mA/g for the first eight cycles and then at 2.53 mA/g to the 55th cycle. The cell was cycled at constant current to 4.0 V. On the 35th discharge the lower voltage limit was reduced from 1.5 to 1.0 V, resulting in a modest increase in capacity. The large reduction in capacity on increasing the rate from 1.26 to 2.53 mA/g reflects the fact that the coin cell format uses rather thick electrodes, approximately 1 mm. The first cycle had an irreversible capacity loss of 79 mAh/g, which is believed to be due to lithium being consumed in the formation of a passivation film on the coke anode. At 1.26 mA/g, the cycleable capacity of this coin cell is about 132 mAh/g of LiMnO_2 , which when summed with the irreversible capacity loss on the first cycle, 211 mAh/g, is still much less than the theoretical

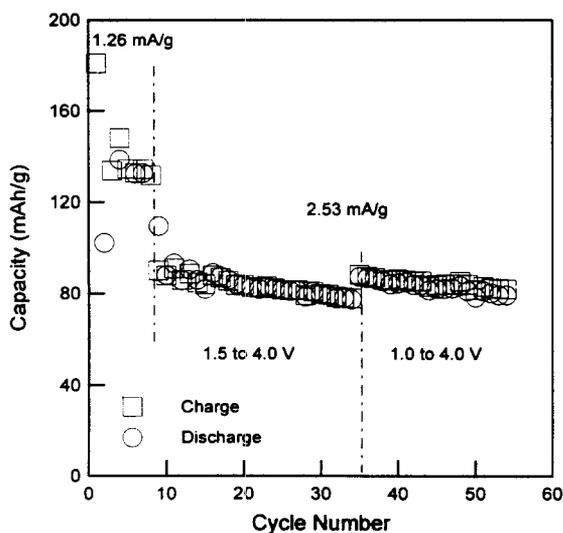


Fig. 5. Charge and discharge capacities as a function of cycle number for a thick electrode coin cell with an orthorhombic LiMnO_2 cathode and a petroleum coke anode.

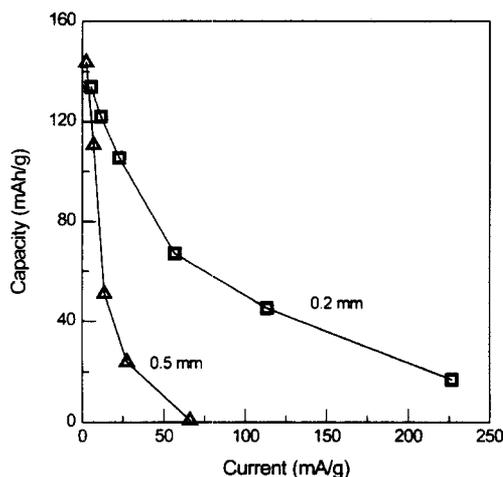


Fig. 6. Discharge capacities as a function of cycling rate for lithium-ion cells with LiMnO_2 cathodes of 0.5 and 0.2 mm thickness and petroleum coke anodes 66% thicker than the cathodes.

capacity of LiMnO_2 , 285 mAh/g, but comparable with the capacity to 4.0 V in a lithium-ion cell with a $\lambda\text{-Li}_2\text{Mn}_2\text{O}_4$ cathode and a coke anode [2]. The upper voltage limit, of 4.0 V, is required to prevent decomposition of the electrolyte. Presumably, more capacity would be attainable with orthorhombic LiMnO_2 cathodes if the electrolyte had a greater stability range.

Fig. 6 illustrates the variation in discharge capacity between 4.0 and 1.5 V as a function of cycling rate, charge and discharge, for coin cells with cathodes of 0.5 and 0.2 mm thickness, respectively. To achieve a

proper cell balance, the anodes in these cells were 66% thicker than the cathodes, and the excess volumes of the 2325 coin cells were filled with stainless-steel discs inserted between the anodes and the cell cases. At low rates, the capacity does not change much with electrode thickness, however, at high rates, the use of thinner electrodes dramatically improves the cycleable capacity of cells with high temperature orthorhombic LiMnO_2 cathodes.

4. Summary

We have demonstrated that cathodes based on the high temperature orthorhombic form of LiMnO_2 have good capacity and cycle life. X-ray diffraction and electrochemical studies have revealed that cathodes prepared from orthorhombic LiMnO_2 undergo a structural change on being charged beyond a certain potential in which the original structure is converted to spinel $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$. High temperature orthorhombic LiMnO_2 has long-term stability in ambient conditions, is easily prepared in a one-step reaction, and consequently, proves to be a practical and convenient precursor to $\lambda\text{-Li}_2\text{Mn}_2\text{O}_4$ in lithium-ion cells.

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