

# Synthesis and characterization of metastable Li–Mn–O spinels from Mn(V)

W.P. Kilroy<sup>\*</sup>, S. Dallek, J. Zaykoski

Naval Surface Warfare Center, Carderock Division, 9500 MacArthur Blvd., West Bethesda, MD 20817, USA

Received 9 August 2001; accepted 2 October 2001

## Abstract

$\text{Li}_3\text{MnO}_4$  Mn(V) was synthesized from LiOH and  $\text{LiMnO}_4$ , and characterized by gravimetric, X-ray, and XPS analysis. This precursor was used to improve the calcination time required for the low temperature solid state synthesis of highly oxidized spinels,  $\text{Li}_2\text{Mn}_4\text{O}_{8+x}$ . TG calculations were used to show the effect of calcination conditions on phase purity. The effect of a second phase on cycling performance was evaluated. Published by Elsevier Science B.V.

**Keywords:** Lithium; Rechargeable battery; Manganese (V); Spinel; Thermogravimetry

## 1. Introduction

Lithium manganese oxides have been examined as a cathode material for rechargeable lithium batteries because they are inexpensive, environmentally benign, and provide good energy density. Preparation of the commercial  $\text{LiMn}_2\text{O}_4$  requires several days of calcination at temperatures  $>750^\circ\text{C}$ . Our work has focused on a new, faster, solid state approach of synthesizing defect spinels in a reproducible manner with the goal of eventually producing novel composite metal oxides.

The stoichiometric spinel,  $\text{LiMn}_2\text{O}_4$ , used as a cathode in commercial rechargeable batteries, exhibits capacity fading during cycling, especially in the 3 V range. This has been attributed to a Jahn–Teller distortion when lithium insertion induces a cubic to tetragonal phase transition associated with a decrease in the average oxidation state of Mn below +3.5. Recent studies have suggested that the capacity fade may not be attributable to Jahn–Teller distortion [1].

A variety of strategies have been evaluated to suppress the onset of the Jahn–Teller distortion associated with the  $\text{LiMn}_2\text{O}_4$  cathode. Small fluctuations in the stoichiometry of  $\text{LiMn}_2\text{O}_4$  via partial substitution of a metal such as Li for Mn in  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ , can increase the valence of Mn. Similarly an increase in the oxygen content of  $\text{LiMn}_2\text{O}_{4+x}$  would give rise to the meta-stable defect spinel  $\text{Li}_2\text{Mn}_4\text{O}_9$  when  $x = 0.5$ . It is impossible to synthesize an overly

oxidized  $\text{LiMn}_2\text{O}_4$ , i.e.  $\text{LiMn}_2\text{O}_{4+\delta}$  ( $\text{Li}_2\text{Mn}_4\text{O}_{8+x}$ ), and still maintain its original cation distribution. Upon oxidation, the average oxidation state of Mn will increase in proportion to the oxygen nonstoichiometry,  $x$ . Thus,  $x$ , and hence the valence of Mn, plays a significant role in determining both the electronic properties of the crystal structure and the electrochemical performance.

To our knowledge, there has been no attempt to combine both strategies, i.e. the low temperature preparation of a highly oxidized form of a substituted metal, M, composite Mn ( $>+3.5$ ) oxide such as  $\text{Li}_2\text{MMn}_3\text{O}_{8.0+x}$  where  $0 < x < 1$ . We undertook this effort by first investigating the formation of the fully oxidized form of  $\text{Li}_2\text{Mn}_4\text{O}_{8+x}$ , namely the cation defect structure  $\text{Li}_2\text{Mn}_4\text{O}_9$ , more correctly described as  $\text{Li}_{0.89}\square_{0.11}[\text{Mn}_{1.78}\square_{0.22}]\text{O}_4$ . Preparation of this material, synthesized by a solid-state reaction between lithium and manganese salts, is far from trivial and is time consuming. The fully oxidized material has never been realized. The required calcination temperature is also sufficient to partially decompose the  $\text{Li}_2\text{Mn}_4\text{O}_9$  into  $\text{LiMn}_2\text{O}_4$ . After careful re-examination of many solid state processes to prepare single-phase  $\text{Li}_2\text{Mn}_4\text{O}_9$ , either the selected precursors or the calcination time or temperature reported often gave rise to phase separation of  $\text{MnO}_2$  or  $\text{Mn}_2\text{O}_3$ . We previously reported the effect of using a precursor having a high oxidation state of Mn, i.e.  $\text{LiMnO}_4$ , to successfully prepare single-phase metastable spinel [2]. To evaluate the effect of oxidation state on the formation of  $\text{Li}_2\text{Mn}_4\text{O}_{8+x}$ , we investigated another highly oxidized precursor, namely  $\text{Li}_3\text{MnO}_4$ .

<sup>\*</sup> Corresponding author. Tel.: +1-301-227-1881; fax: +1-301-227-4580.  
E-mail address: kilroywp@nswccd.navy.mil (W.P. Kilroy).

## 2. Experimental

$\text{Li}_3\text{MnO}_4$  was prepared by slowly heating a 2:1 stoichiometric ratio of an intimately ground mixture of  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{LiMnO}_4\cdot 3\text{H}_2\text{O}$  in a tube furnace under flowing oxygen using intermittent grinding at about 125 °C. Heating was continued at 170 °C for several hours.

$\text{LiMnO}_4$  was prepared by passing an aqueous solution of  $\text{KMnO}_4$  through a Dowex lithiated cation exchange resin. The  $\text{LiMnO}_4$  was dried at ambient temperature in a dry room at 1% humidity.

The extent of hydration of both precursors was predetermined to be  $\text{LiOH}\cdot 0.984\text{H}_2\text{O}$  and  $\text{LiMnO}_4\cdot 2.91\text{H}_2\text{O}$  using a TA Instruments, Inc. 951 thermogravimetric analyzer.

The spinel was prepared in a tube furnace by calcination of an intimately ground mixture of a 1:5 stoichiometric ratio of  $\text{Li}_3\text{MnO}_4$  and  $\text{MnOOH}$  (Chemetals). The synthesis was studied over a temperature range from 400 to 550 °C under oxygen gas.

Powder X-ray diffraction was used to determine the purity of the precursors and the phase purity of the spinels. The extent of oxidation of the spinel was determined by TG weight loss measurements under helium.

The oxidation state of the  $\text{Li}_3\text{MnO}_4$  was determined by XPS measurements using a Physical Electronics 5400 spectrometer with a monochromatic aluminum X-ray source operating at 400 W and a photoelectron take-off angle of 45°. The samples were pressed in indium foil, spectra collected for the C 1s, Mn 2p, and O 1s regions, and the Mn 2p<sub>3/2</sub> binding energies were corrected versus the C 1s reference of 285.0 eV.

Cathodes, containing a slurry of 70% active material, 20% super P carbon, 10% PVDF binder in PC, were sprayed as a thin film onto a stainless steel current collector. The film was vacuum oven-dried at 220 °C. Lithium was pressed onto a Ni exmet grid and the electrodes, separated by two plies of 3401 celgard, were bound between glass plates. The electrolyte was 1 M  $\text{LiPF}_6$  in a 1:1 mixture of ethylene carbonate and ethylmethyl carbonate (EC:EMC). Finished cells were heat-sealed in laminated Al-mylar-polyethylene bag and cycled at a 0.05 mA/cm<sup>2</sup> discharge rate at ambient temperature.

## 3. Discussion

Binary metal oxides often show nonstoichiometry because transition metals such as Mn are stable in different oxidation states. This nonstoichiometry can greatly influence the electrochemical performance of spinel cathodes. The spinel phase is temperature dependent, i.e. a composition rich in  $\text{Mn}^{+4}$  forms preferentially at low temperatures. As the temperature is raised above about 400 °C, the percentage of  $\text{Mn}^{+3}$  increases, eventually forming the stoichiometric  $\text{LiMn}_2\text{O}_4$  with an average Mn valence of +3.5. The choice of starting materials is important to obtain pure highly oxidized lithium manganospinel at low temperature.

As previously reported, many precursor mixtures [3] give rise to second phases or require very long calcination times [4]. The calcination time and temperature are dependent on the precursors. We have found that spinels reported to be prepared in a few hours, generally contained a second phase. Others have reported poorly oxidized spinels, even after 3 days of calcination [5]. This is especially true with low oxidation state Mn precursors such as  $\text{MnCO}_3$ . Higher oxidation state Mn precursors, such as  $\text{LiMnO}_4$  and  $\text{Li}_3\text{MnO}_4$ , allow reactions to be completed in a shorter time.

## 4. Synthesis and characterization of $\text{Li}_3\text{MnO}_4$

### 4.1. Furnace synthesis

$\text{Li}_3\text{MnO}_4$  was prepared by intermittently grinding gram size mixtures of precursors in a tube furnace under flowing oxygen. At 125 °C, a gradual change in color from violet to deep blue to sky blue was observed. If heated overnight, without intermittent grinding, the sky blue product still contains unreacted  $\text{LiOH}$  (20.5 peak:32.5 shoulder),  $\text{LiMnO}_4$  (13:31.2; 35.0 peaks) and an unidentified lithiated Mn oxide peak at 21.0 as shown by the X-ray spectra in Fig. 1a. The weight loss was 90% of theoretical; confirming additional calcination was required. Weight loss was 100% of theoretical after calcining in the tube furnace at 160–170 °C for about 4 h with intermittent grindings, as illustrated by the X-ray spectra of the blue-green  $\text{Li}_3\text{MnO}_4$  in Fig. 1b.

### 4.2. TG synthesis

We attempted to study the reaction mechanism by heating the reactants slowly under oxygen in a TG instrument. The reaction initially proceeds through dehydration of the precursors as shown in Fig. 2. The weight loss is in excellent agreement with the expected loss of water of hydration from the pre-analyzed mixture of  $\text{LiMnO}_4\cdot 2.91\text{H}_2\text{O}$  and  $2\text{LiOH}\cdot 0.984\text{H}_2\text{O}$ , (66.21% measured versus 66.40% calculated). This was followed by the highly exothermic decomposition of the  $\text{LiMnO}_4$  that occurs near 150 °C. After isothermal heating at 170 °C, the observed weight loss was only 58.8% compared to the theoretical 53.4 wt%. loss expected. This disparity illustrates the notable difference between heating a 5 g mixture in a furnace and heating 5 mg in a TG instrument. The dehydration process and very exothermic reaction disrupts the compactness of the small mg-size mixture, creating an inhomogeneous mixture that is not completely reacted in the TG instrument. Mixture homogeneity is achieved in the furnace through intermittent grinding.

### 4.3. $\text{Li}_3\text{MnO}_4$ characterization

The thermal decomposition behavior of the  $\text{Li}_3\text{MnO}_4$  is shown in Fig. 3. The  $\text{Li}_3\text{MnO}_4$ , heated at 20 °C/min under nitrogen, begins to slowly decompose beyond 200 °C, and

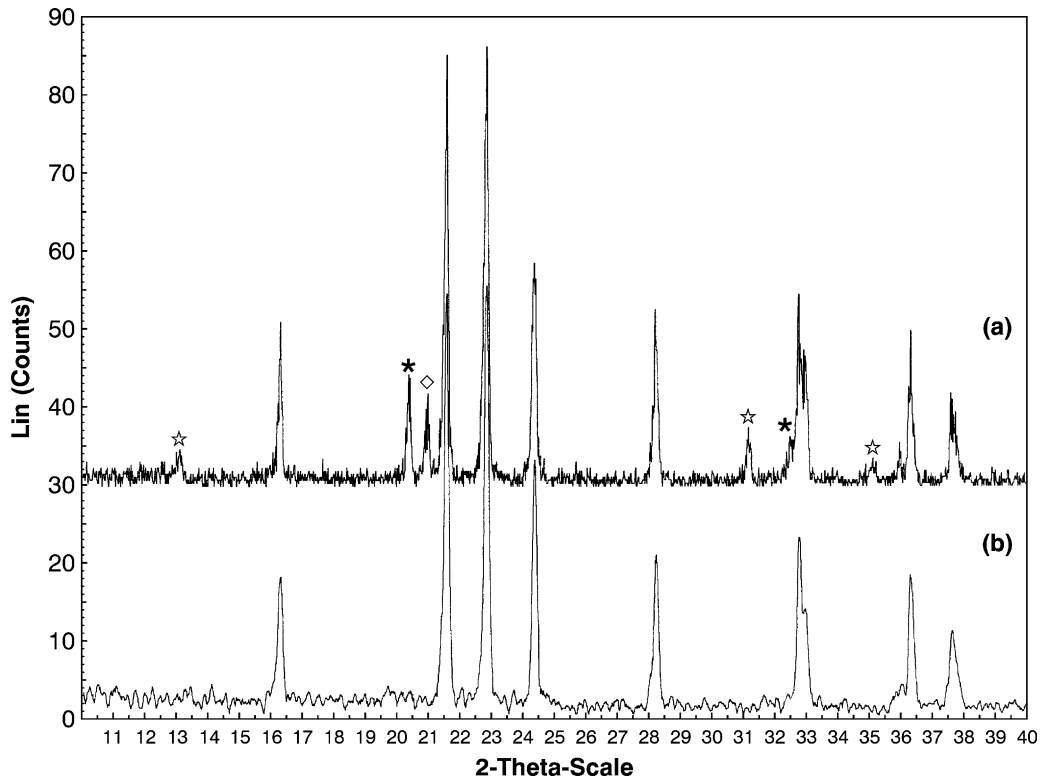


Fig. 1. X-ray spectra of  $\text{Li}_3\text{MnO}_4$  prepared at 125 °C (curve a) and at 170 °C (curve b).  $\text{LiOH}$ ★;  $\text{LiMnO}_4$ ◇.

accelerates near 400 °C. X-ray analysis of a sample heated briefly at 350 °C in a furnace, even under  $\text{O}_2$ , confirms formation of some  $\text{Li}_2\text{MnO}_3$ . Similarly when  $\text{Li}_3\text{MnO}_4$  is washed with methyl alcohol, X-ray analysis shows partial

decomposition into  $\text{Li}_2\text{MnO}_3$  with corresponding DTG data showing a larger peak at 363 °C. X-ray analysis of the product heated as high as 800 °C confirms the final product is  $\text{Li}_2\text{MnO}_3$ . The observed residual weight of 94.30% is in

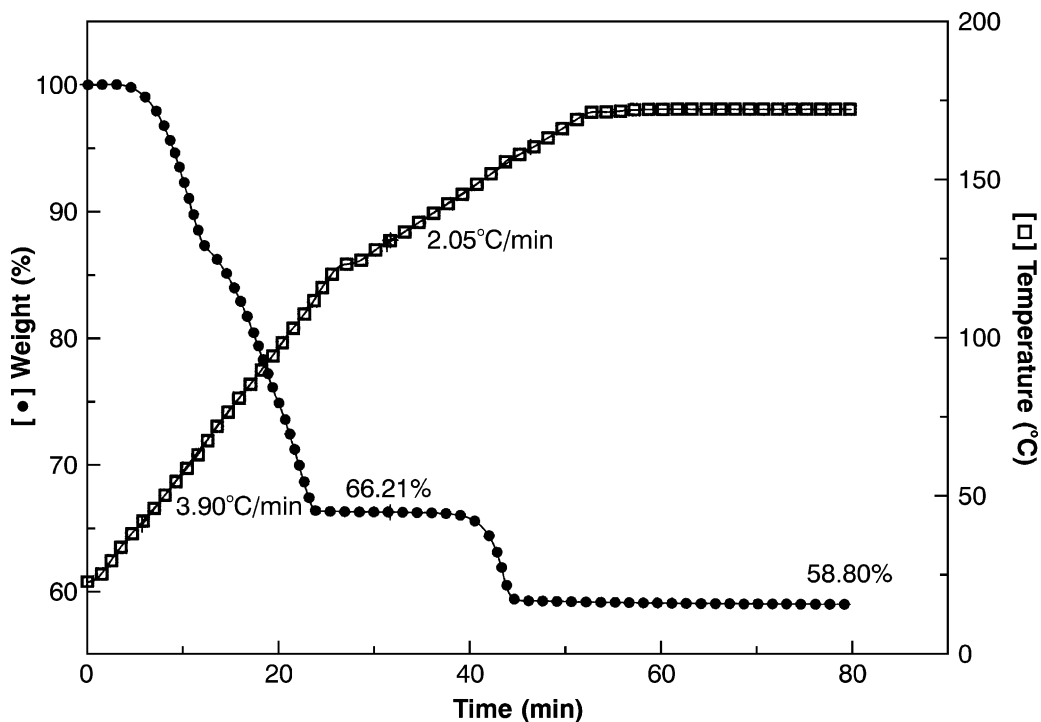


Fig. 2. Weight loss vs. calcination time for the reaction of  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{LiMnO}_4\cdot 3\text{H}_2\text{O}$  under oxygen gas at 2 °C/min in a TG instrument.

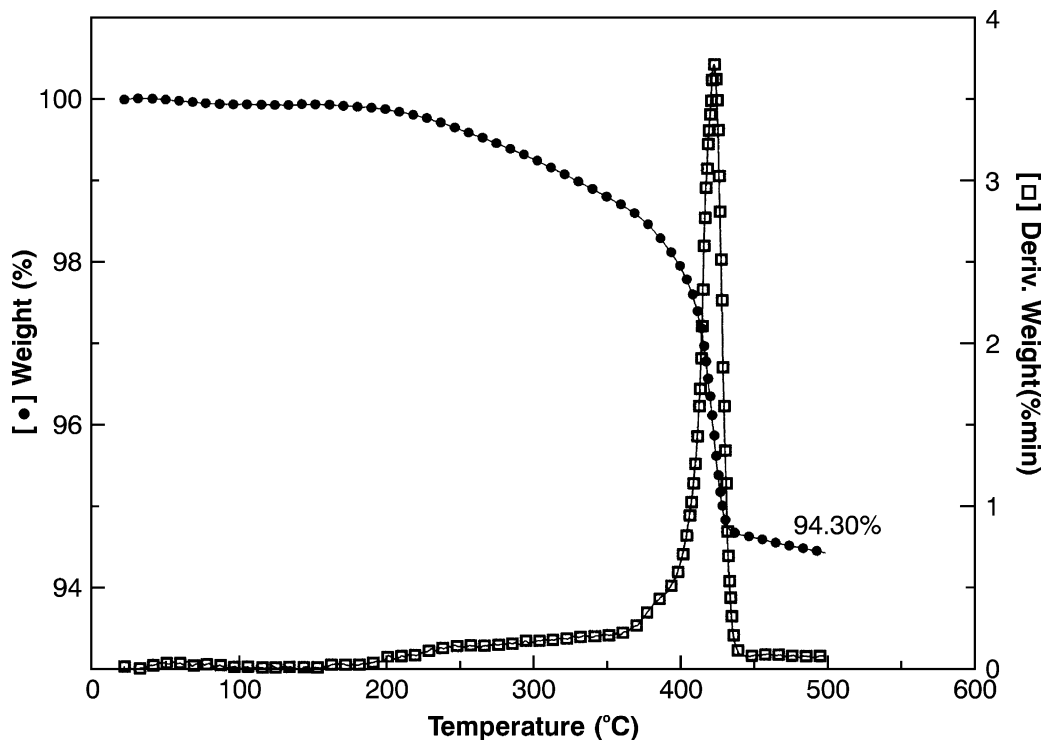


Fig. 3. TG curve for the thermal decomposition of  $\text{Li}_3\text{MnO}_4$  heated at  $20^\circ\text{C}/\text{min}$  under nitrogen gas.

good agreement with the calculated value of 94.28% according to the reaction

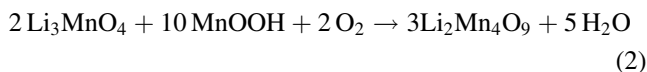


The oxidation state of the green-blue material heated extensively at  $130^\circ\text{C}$  and the blue-green material calcined 4 h at  $170^\circ\text{C}$  was determined to be +5 from XPS studies. This implies that the  $\text{Li}_3\text{MnO}_4$  prepared at  $130^\circ\text{C}$  may approach that of a single-phase material with sufficient calcining and grinding. Fig. 4 compares the binding energy of  $\text{Li}_3\text{MnO}_4$  with  $\text{MnO}_2$  and  $\text{KMnO}_4$  standards and previously reported XPS reference data.

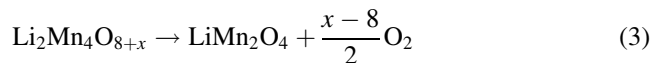
## 5. Synthesis and analysis of the spinel

We examined the effects of calcination time and temperature on the reaction of  $\text{Li}_3\text{MnO}_4$  with a variety of Mn precursors. If the temperature is too low, a high degree of oxidation may not be achieved, even after days of heating, because of slow reaction kinetics. At higher temperatures, the reverse (decomposition) reaction will compete with formation of the spinel. This critical temperature dependence was investigated by TG analysis.

“ $\text{Li}_2\text{Mn}_4\text{O}_9$ ” was prepared by reaction of  $\text{Li}_3\text{MnO}_4$  with  $\text{MnOOH}$  under oxygen in a tube furnace, according to the reaction



The extent of the oxidation of the “ $\text{Li}_2\text{Mn}_4\text{O}_9$ ” spinel, i.e. the resulting  $\text{Li}_2\text{Mn}_4\text{O}_{8+x}$  was analyzed by X-ray and TG analysis. The  $\text{Li}_2\text{Mn}_4\text{O}_{8+x}$  undergoes a two-step thermal decomposition with loss of oxygen when heated under inert gas near  $400^\circ\text{C}$  according to the reaction



At higher temperatures, further reaction occurs according to the reaction



The oxygen content of the spinel was determined by comparing the ratio of successive TG weight plateaus with the theoretical TG weight plateaus. This is illustrated by the TG curve of a commercial  $\text{LiMn}_2\text{O}_4$  sample shown in Fig. 5a. The weight plateau ratio (94.10/100) for the  $\text{LiMn}_2\text{O}_4$  sample is in exact agreement with the theoretical value of 0.9410 calculated from the gravimetric factors of the ratio of the molecular weights of the solid phases as shown in Eq. (4).

The TG curve of an oxidized spinel,  $\text{Li}_2\text{Mn}_4\text{O}_{8+x}$ , prepared by calcination at  $460^\circ\text{C}$  for 6 h, is shown in Fig. 5b. The first weight loss, from room temperature to about  $100^\circ\text{C}$ , is due to the evolution of adsorbed and combined water. The second weight loss, beginning near  $400^\circ\text{C}$ , is attributed to the decomposition of  $\text{Li}_2\text{Mn}_4\text{O}_{8+x}$  into  $\text{LiMn}_2\text{O}_4$ . The third weight loss, from 600 to  $800^\circ\text{C}$ , is decomposition of  $\text{LiMn}_2\text{O}_4$ . This final weight loss was used as a corroborative measurement for the TG method. The

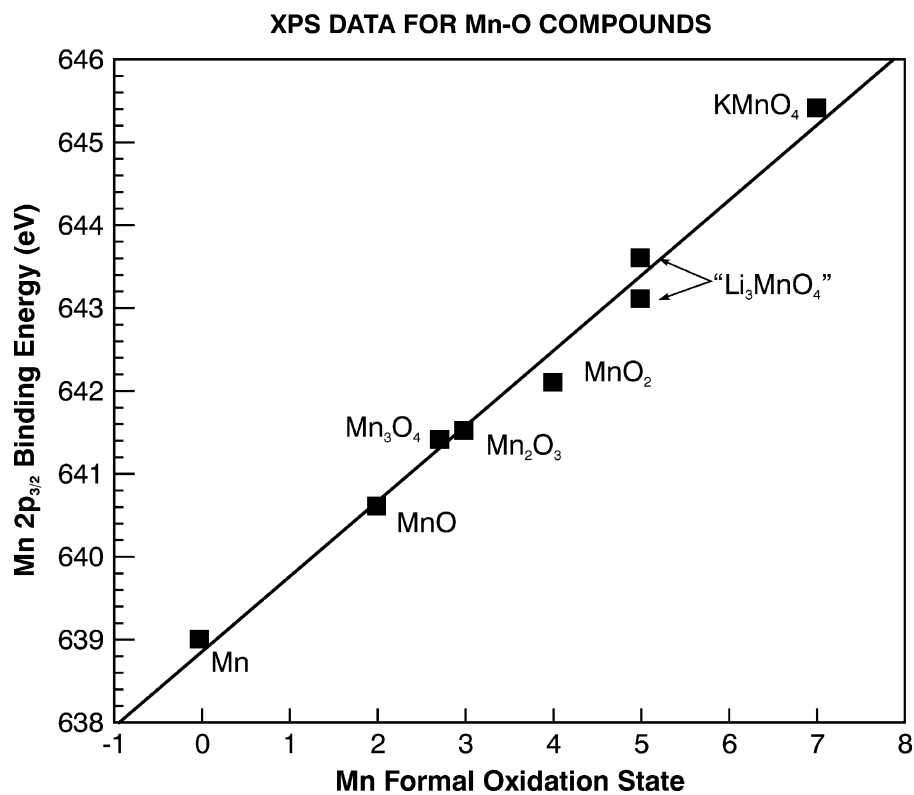


Fig. 4. X-ray photoelectron spectra of binding energy for  $\text{Li}_3\text{MnO}_4$  measured vs.  $\text{MnO}_2$  and  $\text{KMnO}_4$  standards and relative to literature reference materials.

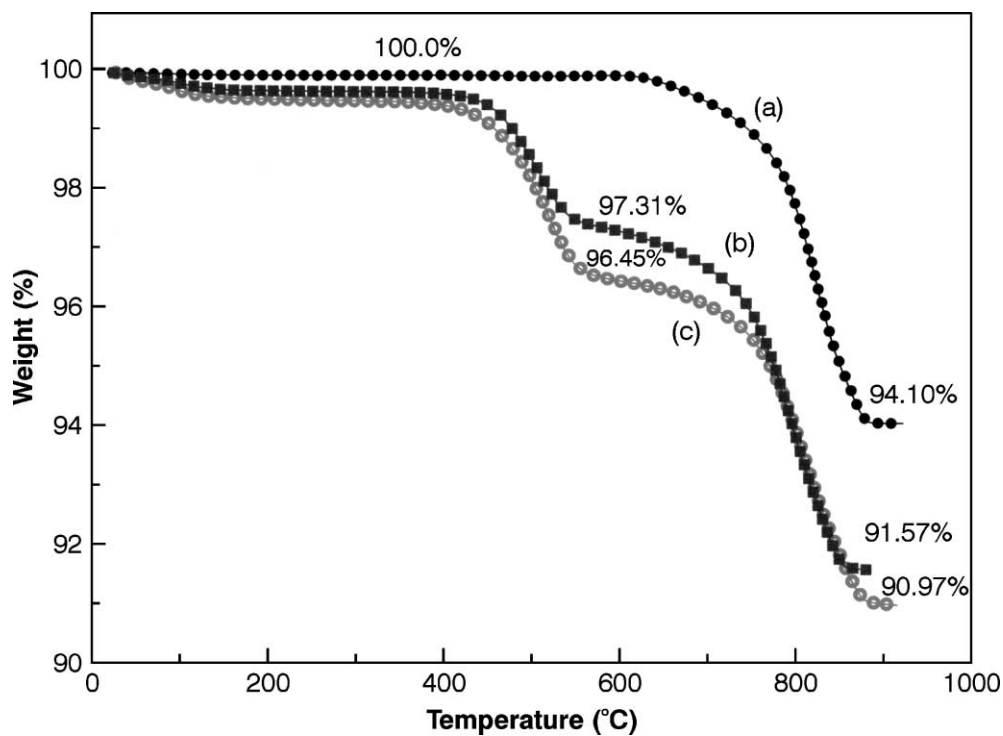


Fig. 5. TG study of spinels heated at  $20^\circ\text{C}/\text{min}$  under nitrogen gas. (a) Commercial  $\text{LiMn}_2\text{O}_4$ ; weight loss ratio = 0.9410; (b) Oxidized single phase spinel,  $\text{Li}_2\text{Mn}_4\text{O}_{8.55}$ ; weight loss ratio = 0.9410; (c) Two-phase material; spinel weight loss ratio = 0.9432.

(91.57/97.31) experimental ratio of 0.9410 is in exact agreement with the theoretical (510.445/542.444) product/reactant ratio of the molecular weights of the solid phases in Eq. (4). This agreement is indicative of a pure spinel of composition  $\text{Li}_2\text{Mn}_4\text{O}_{8.55}$  that has decomposed on the first plateau into pure  $\text{LiMn}_2\text{O}_4$ . Any deviation of TG plateau values from the theoretical value of 0.9410 can be attributed to a second phase, because a pure spinel of composition  $\text{Li}_2\text{Mn}_4\text{O}_{8+x}$ , should decompose according to Eqs. (3) and (4).

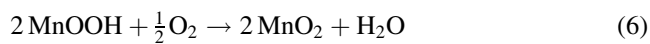
When a  $\text{MnOOH}$  and  $\text{Li}_3\text{MnO}_4$  precursor mixture is calcined in the furnace for only 3 h at  $435^\circ\text{C}$  under oxygen, X-ray data show the product is  $\text{Li}_2\text{Mn}_4\text{O}_{8+x}$  and a small amount of a second phase,  $\text{MnO}_2$ . The gravimetric factor of 0.9432, calculated from the TG decomposition curve, Fig. 5c, is not the 0.9410 value expected for a single-phase material. This leads to an incorrect value of the oxygen stoichiometry,  $x$ , in  $\text{Li}_2\text{Mn}_4\text{O}_x$ , calculated to be 8.72, from the solid phase ratio of Eq. (3) as follows

$$\frac{2 \text{LiMn}_2\text{O}_4}{\text{Li}_2\text{Mn}_4\text{O}_x} = \frac{2(180.81)}{2(6.941) + 4(54.938) + 15.999x} = \frac{96.45\%}{99.54\%} \quad (5)$$

The introduction of a second phase may occur because several Mn compounds decompose at temperatures near that of the oxidized spinel.  $\text{Li}_2\text{Mn}_4\text{O}_{8+x} \cdot \text{MnOOH}$  presents a different problem. Both  $\text{Li}_3\text{MnO}_4$  and  $\text{MnOOH}$  are oxidized by  $\text{O}_2$ , and a competitive oxidation process occurs.

Oxidation of  $\text{MnOOH}$  can occur when  $\text{MnOOH}$  is calcined under  $\text{O}_2$  for several hours at  $390^\circ\text{C}$ , as indicated by

the following equation:



This is demonstrated by the TG data shown in Fig. 6. Initially there is uptake of some  $\text{O}_2$  by  $\text{MnOOH}$  producing a small weight gain. The first weight loss corresponds to the loss of water from the oxidation reaction. The gravimetric factor,  $98.76/100.1$ , or 0.987, is in agreement with the 0.988 value calculated from the  $(2 \text{MnOOH}/2 \text{MnO}_2)$  molecular weight ratio of the solid phases. Oxidation continues, until a second weight loss occurs, corresponding to the decomposition of  $\text{MnO}_2$ .

The appearance of a second phase is not only a function of the kinetics of competing reactions, as in the above case, but it is also a function of the subsequent reactivity of the  $\text{MnO}_2$  produced. As the calcination temperature, and time increases from  $435^\circ\text{C}$  for 3 h to  $460^\circ\text{C}$  for 6 h, as demonstrated by the TG behavior of Fig. 5b and c, the  $\text{MnO}_2$  concentration diminishes.

## 6. Electrochemistry

Capacity fading in the 4 V region, with good capacity retention over the 3 V range, has been attributed to a change in the surface particles in the 4 V range and oxidation of the  $\text{Mn}_2\text{O}_4$  framework, when  $\text{LiMn}_2\text{O}_4$  was cycled over the entire voltage range [1]. Capacity fading in the 4 V region was not observed when our two-phase material (Fig. 5c), comprised of the oxidized spinel and a small amount of

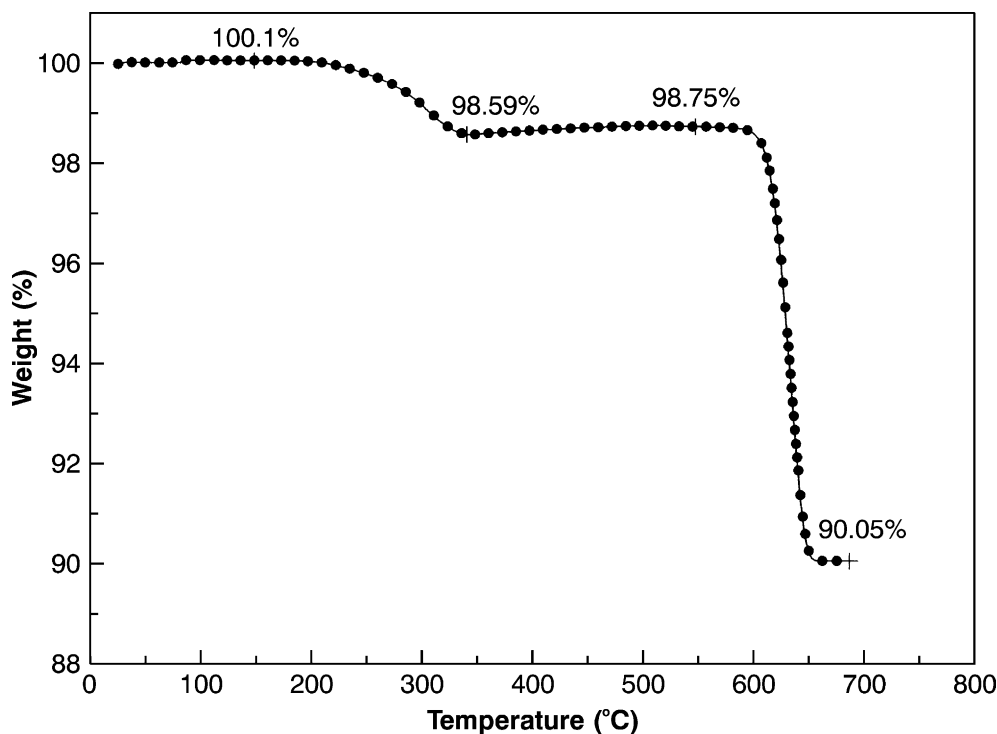


Fig. 6. TG behavior of  $\text{MnOOH}$ , when calcined at  $20^\circ\text{C}/\text{min}$  in the presence of the purge gas, oxygen, illustrating the competitive oxidation that can occur when reacted with  $\text{Li}_3\text{MnO}_4$  under oxygen.

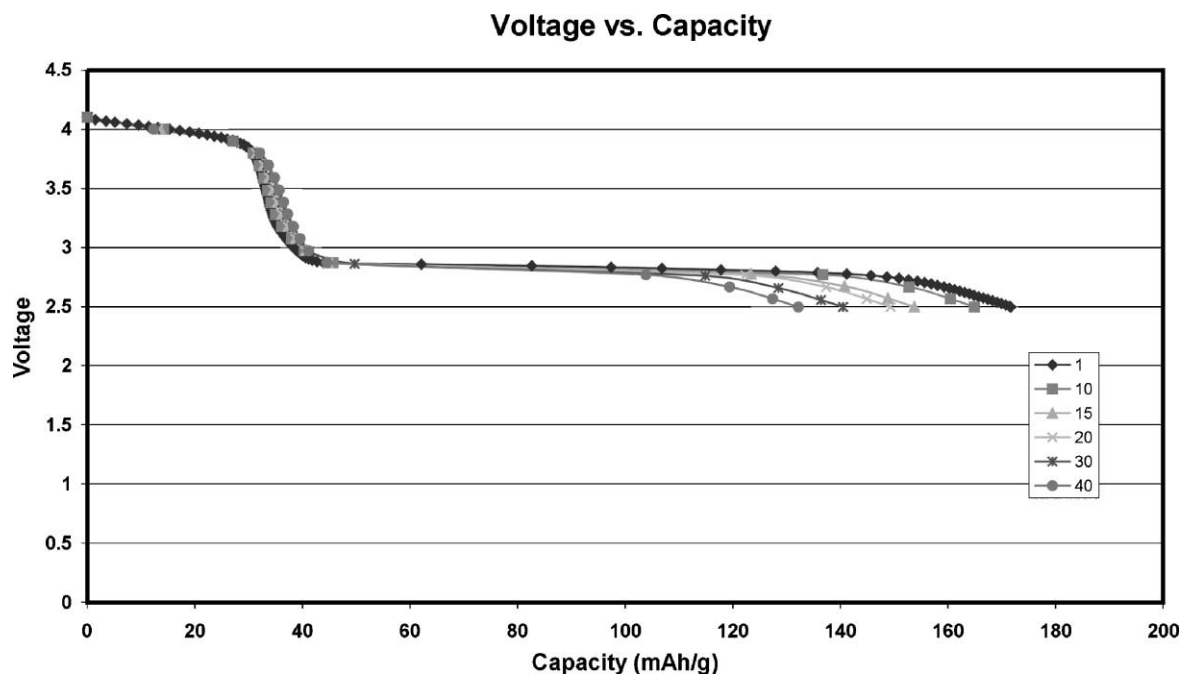


Fig. 7. Discharge profiles of the two-phase material (Fig. 5c) cycled in a bag cell at a discharge rate of  $0.05 \text{ mA/cm}^2$  and a charging rate of  $0.025 \text{ mA/cm}^2$ .

$\text{MnO}_2$ , was cycled, as shown in Fig. 7. The initial capacity of  $171 \text{ mAh/g}$  is less than the  $>220 \text{ mAh/g}$  capacity obtained with the single-phase spinel [2]. A small increase in the  $4 \text{ V}$  capacity was observed after 40 cycles. The cell was stored for 2 days without cycling after the 10th cycle and for 1 day after the 20th and 30th cycle. There is a disproportionate drop-off in capacity between the 10th and 20th when compared with that of the 1st and 10th cycle. This loss of capacity after storage appears to be more attributable to dissolution of  $\text{Mn}^{+3}$  than to Jahn–Teller distortion.

#### Acknowledgements

The authors greatly appreciate the XPS study provided by Dr. Pat Hagans. The NSW In-house Laboratory

Independent Research (ILIR) Program provided funding support for this study.

#### References

- [1] S. Kang, J.B. Goodenough, *J. Electrochem. Soc.* 147 (10) (2000) 3621.
- [2] W.P. Kilroy, W.A. Ferrando, S. Dallek, *J. Power Sources* 97/98 (2001) 336.
- [3] C. Masquelier, M. Tabuci, K. Ado, R. Kanno, Y. Kobayashi, Y. Maki, O. Nakamura, J. Goodenough, *J. Solid State Chem.* 123 (1996) 255.
- [4] M. Thackeray, M. Rossouw, A. de Kock, A. de la Harpe, R. Gummow, K. Pearce, D. Liles, *J. Power Sources* 43 (1993) 289.
- [5] S. Choi, A. Manthiram, *J. Electrochem. Soc.* 147 (2000) 1623.