Journal of Applied Electrochemistry (2005) 35:117–122
DOI 10.1007/s10800-004-3994-9

A low external temperature method for synthesis of active electrode materials for Li batteries – Part A: Synthesis of pure manganese spinel

S. UZUNOVA[1], B. BANOV[1], A. MOMCHILOV[1]*, S. VASSILEV[1], T. STANKULOV[1] and I. UZUNOV
[1]*Institute of Electrochemistry and Energy Systems (former CLEPS), Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 10, 1113 Sofia, Bulgaria*
[2]*Institute of General and Inorganic Chemistry Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
*(*author for correspondence, e-mail: aamomch@cleps.bas.bg)*

Received 22 June 2004; accepted in revised form 7 July 2004

Key words: fluidised bed, intercalation compounds, lithium batteries, low temperature synthesis

Abstract

A low external temperature method (LETM) of active electrode material synthesis for lithium ion batteries has been proposed. The method consists of a two-step process, which is comprised of drying fine droplets of a solution of the starting compound in a liquid drying agent at 200 °C, followed by calcination of the obtained precursor in a fluidised bed at a furnace temperature of 300 °C. The method prevents uncontrolled growth of particles during the initial thermal pre-treatment and the final firing process. Lithium manganese spinel has been selected for describing the proposed LETM of synthesis. The properties of the spinel obtained by LETM are compared with those of a spinel obtained by the classical immobilised solid state synthesis at 750 °C. On electrochemical cycling, the capacity loss after 100 cycles of the LETM spinel at 11% is significantly lower than that for the spinel prepared by solid state methods (21.5%). However, only 3% difference is seen in the total integral capacity over the 100 cycles between spinels prepared by the different methods.

1. Introduction

Recent years have seen increased application of rechargeable lithium batteries due to their excellent electrochemical parameters. Frequently used electrode materials include intercalation compounds of transition metals of groups 4, 5 and 6 [1–4]. The charge/discharge process includes reversible intercalation of lithium ions into the structure of the electrode material, which determines the rate of the electrochemical process.

The rate of the electrochemical reaction follows Fick's Law of diffusion and the factors determining intercalation time are:

– particle size, specific density of the intercalation compound, diffusion coefficient, concentration of lithium ions in the electrolyte, electrode potential, stoichiometric index of lithium in the intercalation compound and the coefficient of auto-diffusion. These factors can be generally divided into two groups: factors subject to control, and invariant factors. The particle size, and in particular its radius, is one of the most significant factors in determining the rate of reversible lithium ion intercalation and hence the charge/discharge rate of the battery. It is well known that rapid charge/discharge of these systems is associated with a considerable decrease in capacity. Hence thin electrodes with a large specific surface area are desirable. The active material powders with very small particle sizes, however, have low densities and therefore larger electrode volumes are required for the same active mass.

A suitable particle size can be achieved via two principal methods: mechanical, such as grinding or ultrasonic treatment; and chemical such as sol-gel or co-precipitation [5–7]. The grinding of pre-synthesised active electrode material is aimed at reducing particle size by crushing, thus increasing the specific surface area and reducing the current loading. This approach favourably affects the charge/discharge process by reducing the intercalation time of lithium ions. However the crushing of the particles creates internal structural stress in the electrode material. To eliminate this shortcoming, recent studies have been aimed at finding new chemical methods for synthesis of electrode materials for lithium batteries [5–13].

Some of these methods involve: emulsion drying, sputtering drying and sol-gel technologies [5–10]. The mixing process of the individual components used with these methods is carried out at the molecular level, thus ensuring good homogeneity and stoichiometry of the material. Generally, the initial precursor obtained by these methods at temperatures lower than 350 °C is fine-grained, but during subsequent sintering stages at higher temperatures uncontrolled particle growth occurs in accordance with Tamm's Law [5–10].

Here we present a new procedure for synthesis of active electrode materials through a low external synthesis temperature method that avoids the uncontrolled growth stage of other methods.

2. Experimental

The developed method comprised two stages:

Stage 1: Preparation of the precursor by drying droplets of the solution containing the respective components in a liquid drying agent (e.g. transformer oil – IEC60296/2003) heated up to 200 °C and immiscible with the solution.

Stage 2: Firing of the initial precursor in a gas phase fluidised bed. The firing process was carried out in a furnace at a temperature of 300 °C (the so-called low external temperature).

The synthesis conditions of the two stages ensure the elimination of uncontrolled particle growth of both the initial precursor and the final product.

During Stage 1 the liquid drying agent hinders the coalescence of sprayed droplets and uncontrolled increase in their volume, i.e. of the precursor particle size. The particle size of the initial precursor can be controlled by varying the solution concentration and the volume of the droplets. This includes water evaporation and most probably some initial decomposition of the starting compounds. The evaporated gases form pores on the surface of the particles. The transformer oil then covers the particle surface and fills the particle pores. To remove the transformer oil the starting precursor was rinsed with petroleum ether until colourless eluent was obtained. Nevertheless, a residual amount of oil remains trapped in the particles' pores.

During Stage 2 the precursor is calcined in a fluidised bed at 300 °C. The transformer oil ignites when the temperature rises up to 250–300 °C with a corresponding thermal energy change of about 48 MJ kg^{-1}. This thermal effect facilitates the synthesis reaction of the active material powder, which takes place at a relatively low external temperature in the furnace.

The advantages of the fluidised bed in comparison to the synthesis in an immobile layer are the following:

- prevention of growth of the precursor particles due to their isolation from each other via the gaseous phase;
- a shifting of the reaction equilibrium towards the products due to the rapid removal of reduction gases generated during the synthesis reaction and high oxygen concentration in the supplied air.

To illustrate the proposed method, a LETM manganese spinel was synthesised and its physicochemical and electrochemical characteristics were compared with those of an analogous spinel obtained by classical immobilised solid-state methods from Li_2CO_3 and MnO_2 for 24 hours at 750 °C [14, 15].

The manganese spinel is an interesting target for detailed investigation since it has been well studied and the factors affecting its specific capacity and cycling performance such as stoichiometry, crystal lattice parameter, synthesis temperature and cooling rate are well known [14, 15].

The reagents used for the LETM synthesis were manganese acetate, $Mn(CH_3COO)_2{\cdot}4H_2O$ and lithium acetate, $Li(CH_3COO)_2{\cdot}H_2O$. A homogeneous mixture of aqueous solutions of these salts in a 2:1 molar ratio was dried in droplet form with a determined volume following the above-described stages. The time treatment for the second stage was 4 h.

A schematic summary of the method is shown in Figure 1. A homogeneous mixture of solutions (1) and (2) prepared from components in mixer (3) is dried in the form of droplets in a non-mixing drying agent in reactor (4). The obtained precursor is rinsed (5), dried again in reactor (6) and fired in a fluidised bed kiln (7).

X-ray analysis was carried out using a Philips ADP 15 diffractometer with Cu K_α radiation in order to identify the crystalline phase of the synthesised powders. The specific surface area was evaluated by the B.E.T method on a FlowSorb II 2300 apparatus at a standard pressure of 760 mm Hg, a standard temperature of 273.15 K and an N_2/He ratio of 1:1 in the gas mixture. The electron micrographs were obtained using a JEOL- Superprobe 733. The FTIR spectrum of the synthesised material was recorded as a KBr pellet in the 400–2000 cm^{-1} region with a Nicolet 320 spectrometer. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed in a Pt crucible in air at a heating rate of 10 °C min^{-1} in order to determine the thermal properties of the precursor with a DERIVATOGRAPH-1500 combined thermal analyser. The electrochemical behaviour of $LiMn_2O_4$ was investigated in a three-electrode cell over the voltage range 3.0–4.5 V using a charge–discharge C/3 current rate in a laboratory cycling system with computer control. The electrolyte was 1 M $LiClO_4$ in EC:DMC (1:1). The tested electrodes were prepared by mixing the active material (15 mg) with teflonised acetylene black in a 1:1 ratio. The obtained mass was pressed onto an aluminum foil with a diameter of 15 mm at a pressure of 10 t cm^{-2}.

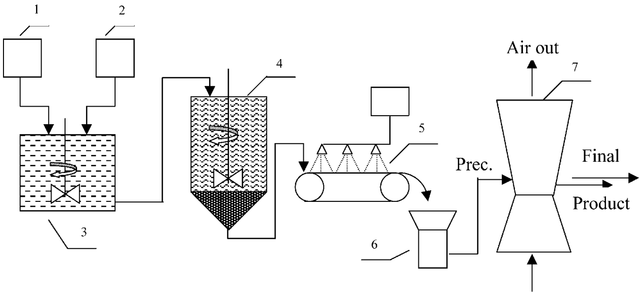

Fig. 1. Technological scheme of the synthesis by LETM: 1, 2 – containers, 3 – mixer, 4 – reactor, 5 – washing process, 6 – drying process, 7 – furnace.

3. Results and discussion

3.1. *DTA/TGA*

Figure 2 presents the DTA/TGA data. The TG data show a loss in sample mass of 56.2% over the temperature range 250–300 °C. The loss is about 13% less than the calculated value of 69.43%, which correspond to the loss of CO_2 and H_2O from the precursors. This loss difference is the reason for the assertion above that some initial decomposition of the starting compounds occurs during Stage 1. The DTA data show a maximum exothermic effect at around 300 °C. This sharp peak corresponds to the combustion of small residual quantities of transformer oil in the precursor, which act as a combustible fuel for the synthesis. The high dispersity of the obtained precursor and the presence of a combustible agent are the key to rapid synthesis at a relatively low furnace temperature (300 °C).

3.2. *IR spectra*

The IR spectra of spinels synthesised by LETM and classical methods are presented in Figure 3a, b. In both spectra two distinct absorption peaks are observed. These peaks are centred around 518 and 617 cm^{-1} for the spinel synthesised by LETM and around 511 and 606 cm^{-1} for the classically synthesised sample. These bands are attributed to the Mn–O vibration mode due to the MnO_6 octahedra, whereas the Li-O vibration mode, due to the LiO_4 tetrahedra, lies within the region 200–400 cm^{-1} [16, 17]. The slightly higher wave numbers of the LETM spinel absorption peaks could be attributed to a shorter Mn–O band. This assertion is supported by the smaller lattice parameter a calculated from the XRD data for the LETM spinel (see 3.4). The observed small broadening of the LETM spinel absorption peaks, synthesized in non-equilibrium conditions, is an indication of the microcrystallinity of the obtained compound.

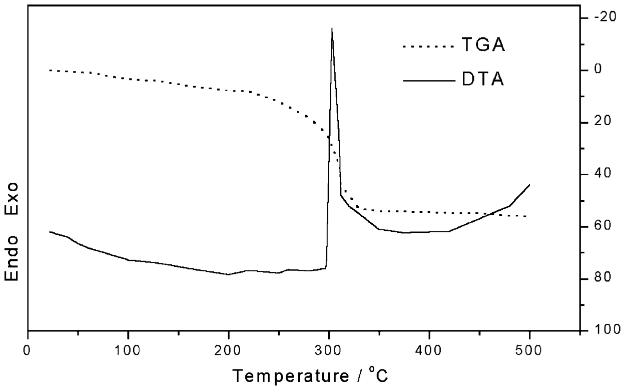

Fig. 2. The DTG/DTA curves of the precursor obtained at 200 °C.

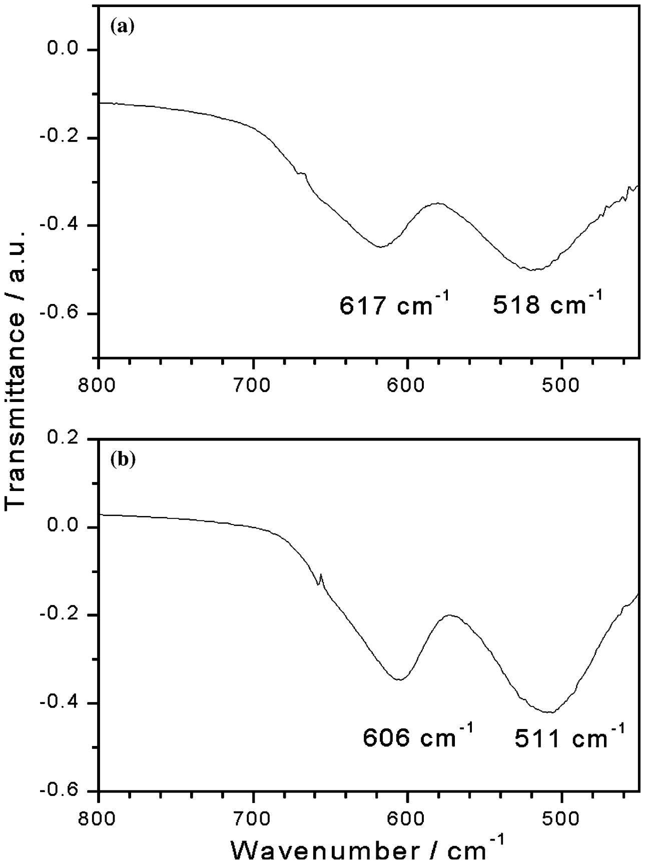

Fig. 3. IR spectrum of the LETM synthesised manganese spinel compared with the same compound obtained at 750 °C.

3.3. *Chemical analysis*

The chemical analysis of the precursor (prepared at 200 °C) shows that the assumed initial stoichiometry is not altered during the stage 1. This can be explained by the lack of solubility of the initial components in the drying agent.

The final product synthesised at 300 °C was also subjected to analysis and the results indicate that it is not necessary to use excess amounts of the lithium salt in order to ensure the proposed stoichiometry as is in the case of the classical synthesis. Our previous investigations [9, 10] show that an excess of 1–5 mol% of lithium ensures near perfect stoichiometry of the final product ($Li_{1.03}Mn_2O_4$). However, in the present case the solid state synthesis of the spinel was carried out at temperatures of 700–800 °C for 24 h. The volatility of lithium salts at temperatures above 500 °C is well known and the excess amount completely compensates the losses.

3.4. *XRD analysis*

The structure of the LETM spinel was determined by X-ray powder diffraction measurements. The sample was identified as a single-phase spinel in the *Fd*3*m* space group. The X-ray pattern of the final product is shown in Figure 4a. For comparison, Figure 4b shows the X-ray pattern of the manganese spinel prepared by

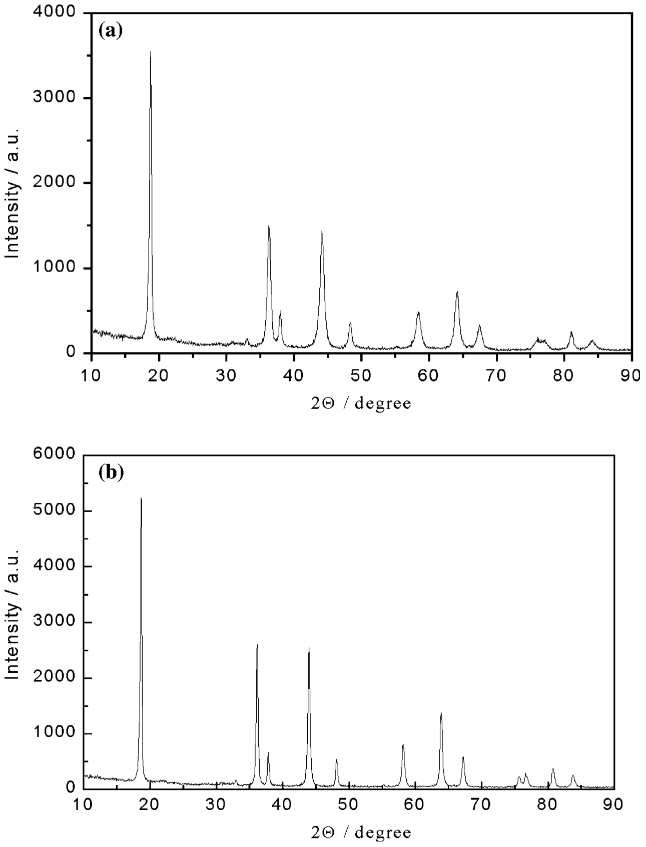

Fig. 4. X-ray patterns of $LiMn_2O_4$ (a) synthesised by LETM and (b) the classical method.

classical solid state methods. It is important to note that the LETM spinel pattern exhibits striking similarity and a good crystallinity compared to the classically prepared sample. Thus, the pattern of the spinel obtained by LETM suggests that the real synthesis temperature is higher than the externally supplied temperature of 300 °C. The calculated lattice parameter (8.2108(9) Å) of LETM prepared spinel is lower than that of the spinel prepared by the classical method at a final temperature of 750 °C (8.2352(10) Å). This small difference in lattice parameter may be associated with the observed small excess of lithium in the classically prepared sample. The line profile analysis was used for calculating the mean coherent domain size. The latter was found to be about 10 nm in the case of the LETM prepared sample and 25 nm in the classically prepared sample.

3.5. *SEM analysis*

The morphology of the precursor and the LETM spinel was studied by SEM (Figure 5a;b). Micrographs of a pure manganese oxide spinel prepared by the classical synthesis method at two different temperatures: 450 °C at the beginning of the synthesis (Figure 5c) and 750 °C at the end of the process (Figure 5d) are shown for comparison [18]. The last two micrographs show the growth of particles during synthesis, which vary in size from 0.2 to 0.3 μm at 450 °C to about 1 μm at 750 °C, in accordance with Tamm's rule. Since, the main particle growth occurs at high temperatures, retention at this temperature should be minimal for small particle sizes. On the other hand, the final synthesis temperature is of major importance for high ordering of the crystal lattice. The precursor synthesised by the LETM (Figure 5a) shows well-shaped spherical particles of about 300–500 nm. The particle shape can be attributed to the droplets used in the initial drying in a non-miscible liquid agent at a temperature around 200 °C. It is easy to assess that by changing the two parameters (droplet volume and/or concentration of the initial solution) precursor particles with different sizes can be prepared. The final product also possesses spherical particles of about 100–200 nm without visible particle growth. This can be explained by the firing of the precursor in a fluidised bed, since under these conditions the particles are well isolated from each other by the gaseous phase. Thus, the particles of low temperature spinel are assumed to be agglomerate of 10–20 coherent domains, while about 40 coherent domains are assumed to form a particle of the classical spinel.

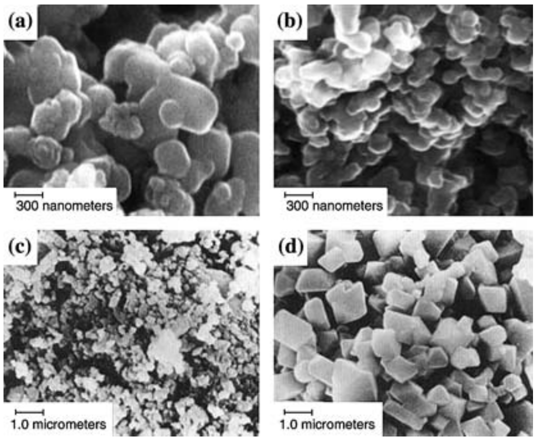

Fig. 5. SEM pictures of $LiMn_2O_4$ synthesised by LETM at (a) 200 °C, and (b) 300 °C, compared with a sample prepared by the classical method at (c) 450 °C, and (d) 750 °C.

The B.E.T specific surface area of the LETM prepared spinel is about 8.7 $m^2\ g^{-1}$ corresponding to a mean particle size of 150 nm, while the spinel prepared by the classical method has a specific surface area of 1.5 $m^2\ g^{-1}$, with a corresponding particle size of about 1 μm (Table 1).

3.6. *Electrochemical testing*

The charge/discharge curve of the LETM synthesised spinel is shown in Figure 6a. The charge/discharge curve of the spinel, synthesised by the classical method (Figure 6b), is displayed again for comparison. Both curves exhibit two plateaus at about 4.0–4.1 and 3.9–4.0 V. The appearance of such plateaus in the charge/discharge curves is associated with a two-stage mechanism of electrochemical lithium intercalation [19]. These plateaus become more expressed with increasing the

Table 1. Comparative characteristic of LETM spinel and spinel prepared by classical method

Physicochemical and Electrochemical parameters	Low temperature spinel	Spinel prepared by the classical method
B.E.T., /[m^2 g^{-1}]	8.7	1.5
Coherent domain size, /[nm]	10	25
Particle size, /[nm]	100–200	1000
Parameter of the crystal lattice, /[Å]	8.2108(9)	8.2352(10)
Peak position, /[cm^{-1}]	518; 617	511; 606
Discharge capacity at the 5th cycle, /[mAh g^{-1}]	120	130
Discharge capacity at the 100th cycle, /[mAh g^{-1}]	109	106
Capacity loss at the 100th cycle, /[%]	11.4	21.5

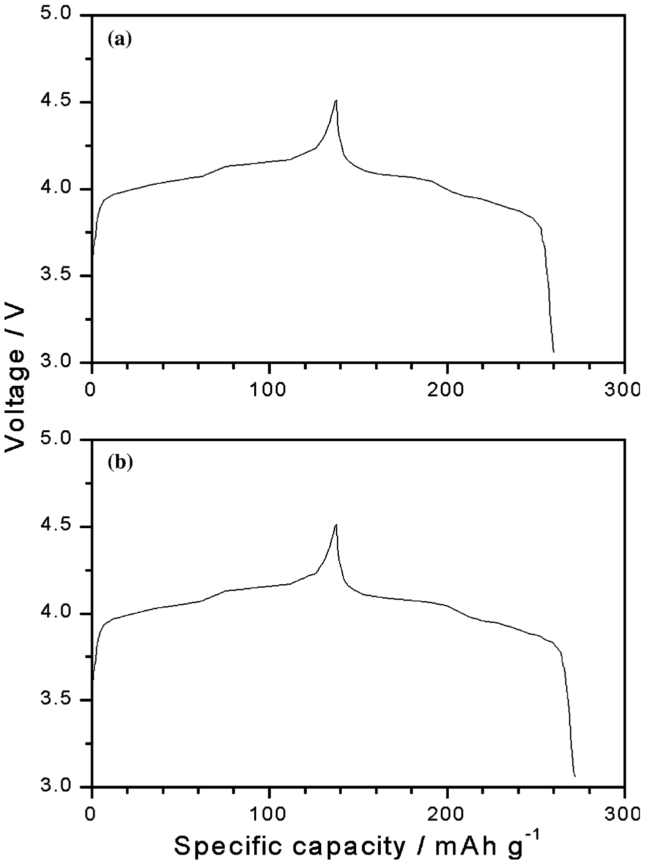

Fig. 6. Initial charge–discharge curves of cathodes with LETM (a) and classical (b) $LiMn_2O_4$.

heating temperature during the classical synthesis [15] which is usually attributed to the improvement of the crystallinity of the sample. Thus, the similarity of the curves is consistent with the assumption that the real internal temperature of the LETM synthesis is higher than that externally supplied.

The LETM prepared spinel displays a reversible capacity of 120 mAh g^{-1} on the 5th cycle and 109 mAh g^{-1} after 100 cycles, while in the case of the classically prepared sample, the capacity on the 5th cycle is 130 mAh g^{-1} decreasing to 106 mAh g^{-1} after 100 cycles. The cycling behaviour of both materials is represent in Figure 7. Two different slopes are observed in both of the cycling data curves. The curve for the classically prepared spinel shows a change in slope around cycle 30, whereas in the LETM prepared spinel this change occurs at cycle 20. The cycling decline for both of the materials is summarized in Table 2.

It is well known that the crystal structure, oxygen content and surface area are factors that significantly affect capacity. The lower lattice constant of the LETM prepared sample might be reflected in the lower initial capacity (123 mAh g^{-1}, i.e. 81% of the theoretical value) of this sample, compared to that of the classically prepared spinel (135 mAh g^{-1}). Irrespective of this, the total capacity loss after 100 cycles is 11.4% (0.14 mAh g^{-1} at cycle) compared with 21.5% (0.29 mAh g^{-1} at cycle) for the classical method.

Nevertheless, the total integral capacity after 100 cycles for both materials does not differ by more than 3%.

4. Conclusions

- It is demonstrated that it is possible to synthesise active electrode materials for lithium batteries by a low external temperature method.

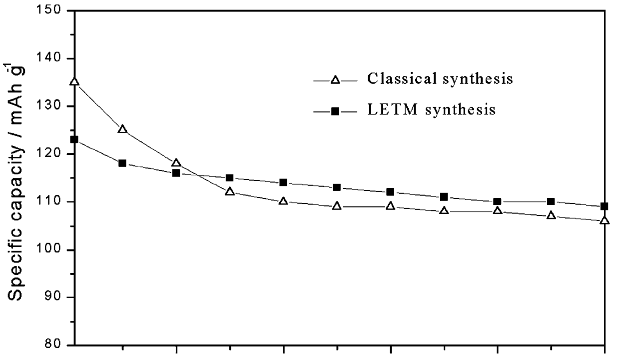

Fig. 7. Long term cycling behaviour of LETM and classically prepared manganese spinels.

Table 2. Capacity decline for both materials after 100 cycles

Type of spinel			
Classical synthesis			
Cycles	1–30	31–100	1–100
Capacity loss per cycle	0.77 mAh g^{-1}	0.086 mAh g^{-1}	0.29 mAh g^{-1}
LETM synthesis			
Cycles	1–20	21–100	1–100
Capacity loss per cycle	0.35 mAh g^{-1}	0.0875 mAh g^{-1}	0.14 mAh g^{-1}

- Lithium manganese spinel prepared by LETM possesses very similar physicochemical properties and electrochemical behaviour to the samples obtained by classical solid-state synthesis at 750 °C.
- The integral capacity over 100 cycles of lithium manganese spinel obtained by the low external temperature method is equivalent to that of the spinel prepared by the classical solid state procedure at 750 °C, due to the enhanced reversibility of the LETM spinel.

References

1. T. Ohzuku, M. Kitagawa and T. Hirai, *J. Electrochem. Soc.* **137** (1990) 769.
2. J.N. Rimers, J.R. Dahn and U. Sacken, *J. Electrochem. Soc.* **140** (1993) 2972.
3. T. Ohzuku and A. Ueda, *J. Electrochem. Soc.* **141** (1994) 2752, and references there in.
4. T. Ohzuku, A. Ueda and M. Nagayama, *J. Electrochem. Soc.* **140** (1993) 1862.
5. K.T. Hwang, W.S. Um, H.S. Lee, J.K. Song and K.W. Chung, *J. Power Sources* **74** (1998) 169.
6. T. Tsumura, A. Shimizu and M. Inagaki, *J. Mat. Chem.* **14** (1993) 995.
7. Y. Li, C.Wan, Y. Wu, C. Jiang and Y. Zhu, *J. Power Sources* **85** (2000) 294.
8. P. Bardoux, J.M. Tarascon and F.K. Shokoochi, *J. Solid State Chem.* **94** (1991) 185.
9. S.T. Myung, N. Kumagai and S. Komaba, *ITE Letters on Batteries, New Technology & Medicine,* 1(2000)B18(38).
10. W.S. Yoon and K.B. Kim, *J. Power Sources* **81–82** (1999) 517.
11. M. Yoshio, S. Inoue, M. Hyakutake, G. Piao and H. Nakamura, *J. Power Sources*, **34** (1991) 147.
12. Y. Hia, H. Takeshige, H. Noguchi and M. Yoshio, *J. Power Sources* **56** (1993) 61.
13. W. Liu, K. Kowal and G.C. Farrington, *J. Electrochem. Soc.* **143** (1996)3590.
14. V. Manev, B. Banov, A. Momchilov and A. Nasalevska, *J. Power Sources* **57** (1995) 99.
15. V. Manev, A. Momchilov and A. Kozawa, *Progress in Battery & Battery Materials,* **14** (1995) 105.
16. T.J. Richardson, S.J. Wen, K.A. Striebel, P.N. Ross Jr. and E.J. Cairns, *Meter. Res. Bull.* **32** (1997) 609.
17. C. Julien and M. Massot, *Mater. Sci. Eng.* **97** (2003) 217.
18 A. Momchilov, V. Manev, A. Nassalevska and A. Kozawa, *J. Power Sources* **41** (1993) 305.
19. W. Liu, K. Kowal and G. Farrington, J. Electrochem. Soc. **145** (1998) 459.