# Nano-particle $Li_4Ti_5O_{12}$ spinel as electrode for electrochemical generators

A. Guerfi[a], S. Sévigny[a], M. Lagacé[a], P. Hovington[a], K. Kinoshita[b], K. Zaghib[a,*]

[a]*Institut de Recherche d'Hydro-Québec, 1800 Boul., Lionel-Boulet, Varennes, Que., Canada J3X 1S1*
[b]*Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

## Abstract

$Li_4Ti_5O_{12}$ was obtained by solid-state reaction of a ternary precursor mixture, $TiO_2$, $Li_2CO_3$ and carbon. The influences of the reaction time, temperature and mixing method on the electrochemical performance of $Li_4Ti_5O_{12}$ were investigated. Electrochemical measurements and XRD diffraction characterization were used to determine the reversible capacity and $TiO_2$ residue in the final powder, respectively. Between 1.2 and 2.0 V versus Li, a reversible capacity as high as 165 mAh/g at 7.3 mA/g was obtained.
© 2003 Elsevier Science B.V. All rights reserved.

*Keywords:* Electrochemical generators; Solid-state reaction; Zero strain; Nano particles; $Li_4Ti_5O_{12}$

## 1. Introduction

Electrodes containing $Li_4Ti_5O_{12}$ have good Li-ion intercalation and de-intercalation reversibility and exhibit no structural change (zero-strain insertion material) during charge–discharge cycling. Thus, $Li_4Ti_5O_{12}$ is a interesting candidate in negative electrodes for solid-state [1–13] and liquid-type [1–6] lithium-ion batteries. This active material has a mid-discharge voltage close to 1.55 V versus $Li^+/Li$, which is very promising for electrodes in a large number of battery applications [4,5]. It can be used as an anode combined with: (a) high-voltage cathodes for Li-ion batteries and (b) carbon electrodes in hybrid supercapacitors suggested for the first time by Zaghib et al. [3,4]. In addition, $Li_4Ti_5O_{12}$ can be used as a cathode with lithium metal in primary rechargeable batteries (Fig. 1).

In this paper, we report on the results obtained with a zero-stain insertion material produced by a new synthesis process. This process is based on the use of a ternary precursor material [12,14]. The intent of the present paper is to extend these studies by providing a systematic analysis of a series of $Li_4Ti_5O_{12}$ samples obtained by several methods. The different parameters affecting the material performance, particle size and shape were investigated. The $Li_4Ti_5O_{12}$ powder was characterized by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) observations.

The electrochemical discharge and charge behavior was determined in a liquid electrolyte.

## 2. Experimental

The starting materials, $TiO_2$-anatase and $Li_2CO_3$, were commercially available with purities of 99 and 99.5%, respectively. A mixture of $TiO_2$ and $Li_2CO_3$ (molar ratio Ti/Li of 2.27) was prepared by two methods. In the conventional method, a binary mixture of $TiO_2$ and $Li_2CO_3$ was heated at 850 °C for 12 h in an air steam. In the second method, carbon was added to the starting materials ($TiO_2$, $Li_2CO_3$) to make a ternary mixture. Homogeneous mixed phases of the binary and ternary compositions were obtained by high-energy ball-milling.

After mixing, the powders were heat treated to form the desired phases. The samples were characterized by X-ray diffraction and scanning electron microscopy. The discharge (intercalation)–charge (de-intercalation) cycling of $Li_4Ti_5O_{12}$ was carried out in 4 $cm^2$ laboratory cells (two electrodes) with lithium metal as the counter electrode. The initial cell chemistry is based on the following configuration: Li metal(−)/electrolyte/$Li_4Ti_5O_{12}$(+) with a liquid electrolyte (EC/DMC + $LiClO_4$). The working electrode was prepared from a paste mixture of $Li_4Ti_5O_{12}$, carbon black for an electronic conductor additive and PVDF binder mixed in NMP. The paste was coated on aluminum Exmet. The electrode was dried under vacuum at 85 °C for 24 h before electrochemical evaluation. The discharge–charge cycling

* Corresponding author. Tel.: +1-450-652-8019; fax: +1-450-652-8424.
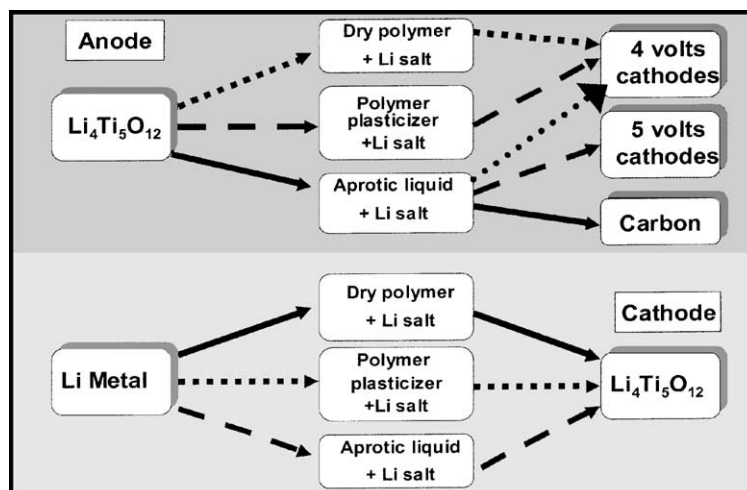*E-mail address:* karimz@ireq.ca (K. Zaghib).

Fig. 1. Electrochemical systems in combination with $Li_4Ti_5O_{12}$ electrodes.

and slow potential scan were performed using a constant current method (MacPile®, Claix, France).

## 3. Results and discussion

The colors of the $Li_4Ti_5O_{12}$ samples obtained from binary and ternary precursors were white and gray, indicating that the samples were electronic insulators and conductors, respectively. The initial open circuit voltage (OCV) between 2.5 and 3.0 V was independent of the synthesis process. During discharge the voltage drops quickly to below 2 V and decreases as the electrochemical reaction proceeds until the voltage reaches about 1.5 V [8].

### 3.1. Effect of reaction time

We have studied the effect of calcination (reaction) times of the ternary mixture ($TiO_2$, $Li_2CO_3$, carbon) at 850 °C. Fig. 2 shows the first and the second discharge–charge curves at C/24 rate. A small shoulder is observed on the charge curves of $Li_4Ti_5O_{12}$ obtained at shorter reaction time. This shoulder is attributed to incomplete solid-state reaction. The reversible capacity also depends on the reaction time. The $Li_4Ti_5O_{12}$ powders obtained after 3 and 7 h at 850 °C exhibit a reversible capacity of only 108 mAh/g. However, with a longer reaction time of 18 h and at $T = 850$ °C, the reversible capacity increased by 43% to 155 mAh/g.

### 3.2. Effect of reaction temperature

The mixed powders were heated from room temperature to different calcination temperatures: (a) 750 °C; (b) 800 °C; (c) 825 °C; (d) 850 °C for 18 h. Fig. 3B shows the discharge–charge curves for the first two cycles for the four samples. The cycles were obtained at the C/24 rate between 1.2 and 2 V. A shoulder in the potential profile is present in the

charge curves, but decreases with increasing reaction temperature. This result suggests that the solid-state reaction between $TiO_2$ and $Li_2CO_3$ is not complete when lower reaction temperatures are used. In Fig. 3C, we can see that a critical reaction temperature range between 800 and 825 °C is required for structural transformation. Cells containing $Li_4Ti_5O_{12}$ obtained at 750 °C exhibit only 103 mAh/g. The capacity increased with an increase in the reaction temperature. The $Li_4Ti_5O_{12}$ obtained at 850 °C yielded an intercalation plateau that increased to $x = 0.92$ (for the formula $Li_{(4/3+x)}Ti_{5/3}O_4$, corresponding to a reversible capacity of 161 mAh/g).

### 3.3. Influence of carbon additive

In this work, we studied a new approach to synthesize $Li_4Ti_5O_{12}$ by adding carbon in the starting powder mixture. To produce $Li_4Ti_5O_{12}$, one of the critical issues is how to mix the starting materials to produce a homogeneous powder. Because we are using a dry process to produce the titanate oxide, adding carbon in the precursor has a positive effect on the homogeneity of the mixed powder. The carbon plays an important role to facilitate intimate mixing of the precursor materials in the dry process. Two curves that show the first cycle for $Li_4Ti_5O_{12}$ obtained with and without carbon are presented in Fig. 4. The binary composite (without carbon) exhibits 153 mAh/g of reversible capacity with a coulombic efficiency of 96.8%. However, with the ternary compound (carbon additive), the solid-state reaction is improved by about 10% because of the carbon in the powder. The carbon can have two roles: (i) as reducing agent, improves the reaction in the bulk powders and increases lithium diffusion in the particles to enhance complete transformation; (ii) the carbon additive helps to reduce the particle size and produce an agglomerate of small particles in a chain-like structure; (iii) to increase the inter-particle contact and disturb the undesirable particle growth. The reversible capacity for the
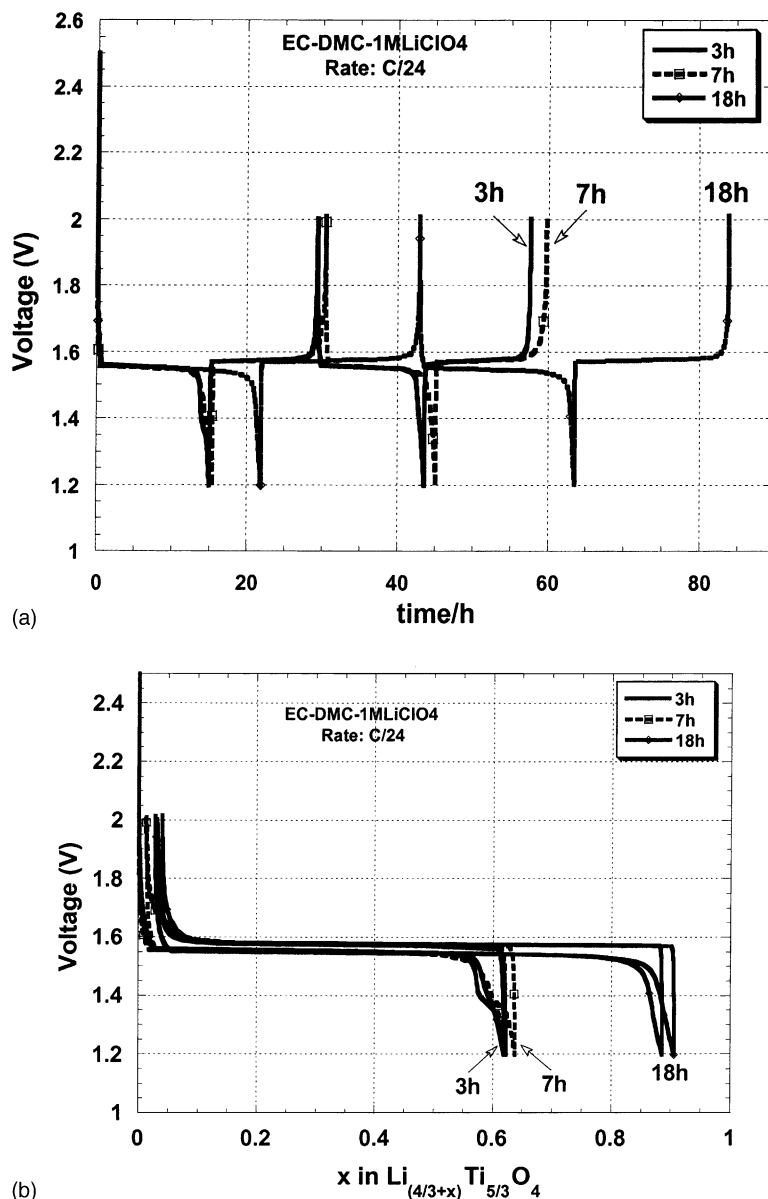
Fig. 2. Relationship between reaction time and electrochemical performance: (a) discharge curves as function of time; and (b) discharge curves as a function of intercalated lithium ($x$) in $Li_{(4/3+x)}Ti_{5/3}O_4$.

$Li_4Ti_5O_{12}$ obtained from the ternary mixture is 165.4 mAh/g, and the columbic efficiency is 98.8% in the first cycle.

### 3.4. Effect of mixing method

The mixing process is a key step to improve the reversible capacity and reduce the content of $TiO_2$ impurities. In this study, we have evaluated the performance of $Li_4Ti_5O_{12}$ produced from different mixing methods: (i) standard mixer (Blinder, model Osterizer, Sunbeam); (ii) jar-milling; and (iii) high-energy ball-milling. The precursors for these tests were based on ternary mixtures. With the standard mixer, we obtained powders that showed local phase separation with areas of white and black colors clearly visible. This result is contrary to others mixing techniques which produce

homogenous gray powders. Table 1 summarizes the results for $Li_4Ti_5O_{12}$ obtained by different methods, their reversible capacity and coulombic efficiency.

The electrochemical behavior of $Li_4Ti_5O_{12}$ prepared by the three methods is shown in Fig. 5. The presence of a shoulder in the potential profile in the charge curves depends on the mixing method. This shoulder is more pronounced with $Li_4Ti_5O_{12}$ obtained with the conventional mixer (Fig. 5a). A very small shoulder is still present in $Li_4Ti_5O_{12}$ produced by jar-milling. It appears that an incomplete solid-state reaction is responsible for the shoulder observed in the potential profile in the charge curves. High-energy ball-milling seems to be a more efficient method to produce very homogenous powders. The $Li_4Ti_5O_{12}$ produced by this method had a charge curve that did not show any shoulder in

(A)

(B)

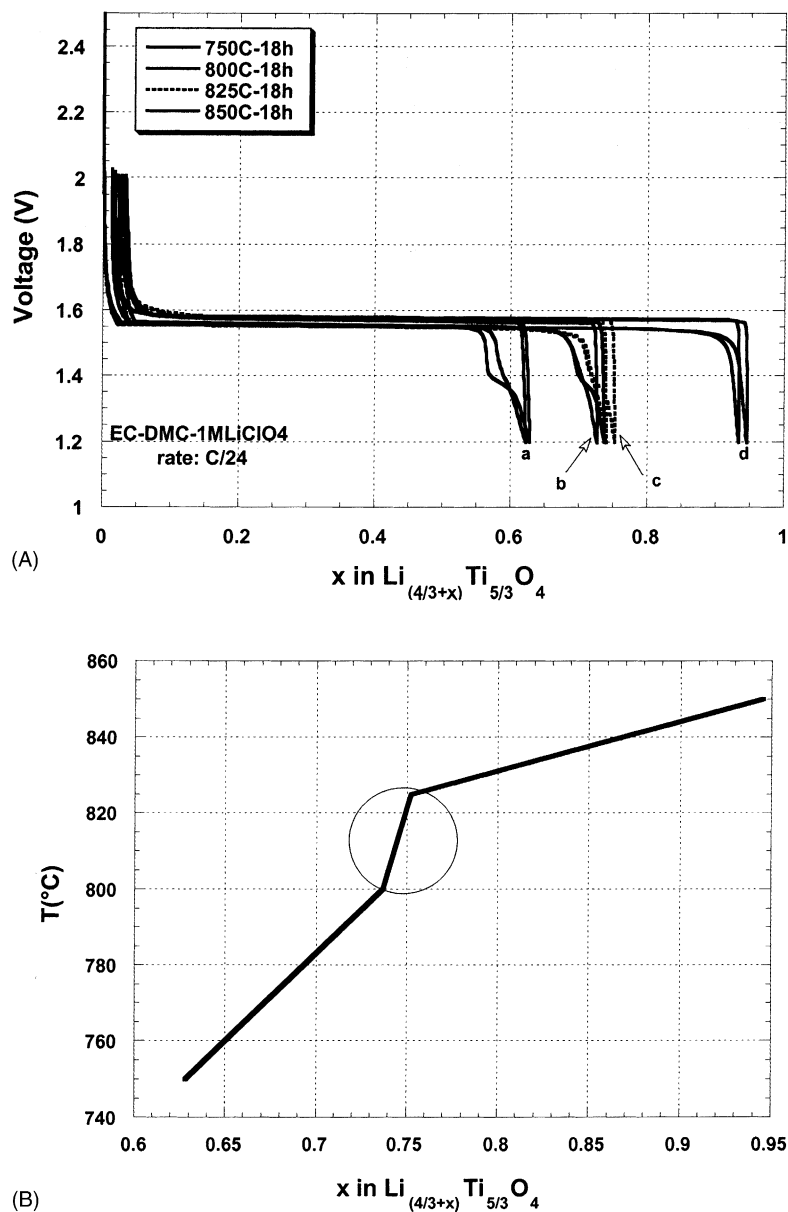Fig. 3. Discharge–charge curves obtained with $Li_{(4/3+x)}Ti_{5/3}O_4$ produced at different reaction temperatures: (a) 750 °C; (b) 800 °C; (c) 825 °C; and (d) 850 °C.

Table 1
Preparation conditions, lithium intercalation capacity ($x$), the first coulombic efficiency (1CE) of $Li_4Ti_5O_{12}$

| Sample number | Carbon additive | Mixing method | Reaction temperature (°C) | Reaction time (h) | $x$ in $Li_{(4/3+x)}Ti_{(5/3)}O_4$ | First cycle coulombic efficiency |
|---|---|---|---|---|---|---|
| 1 | C | Conventional | 850 | 18 | 0.613 | 95.00 |
| 2 | C | Ball-milling | 850 | 3 | 0.622 | 97.94 |
| 3 | C | Ball-milling | 850 | 7 | 0.637 | 95.60 |
| 4 | C | Ball-milling | 750 | 18 | 0.627 | 95.11 |
| 5 | C | Ball-milling | 800 | 18 | 0.737 | 97.04 |
| 6 | C | Ball-milling | 825 | 18 | 0.752 | 96.80 |
| 7 | C | Ball-milling | 850 | 18 | 0.945 | 98.80 |
| 8 | – | Ball-milling | 850 | 18 | 0.905 | 96.80 |
| 9 | C | Jar-milling | 850 | 18 | 0.881 | 97.73 |

C indicates carbon was added.
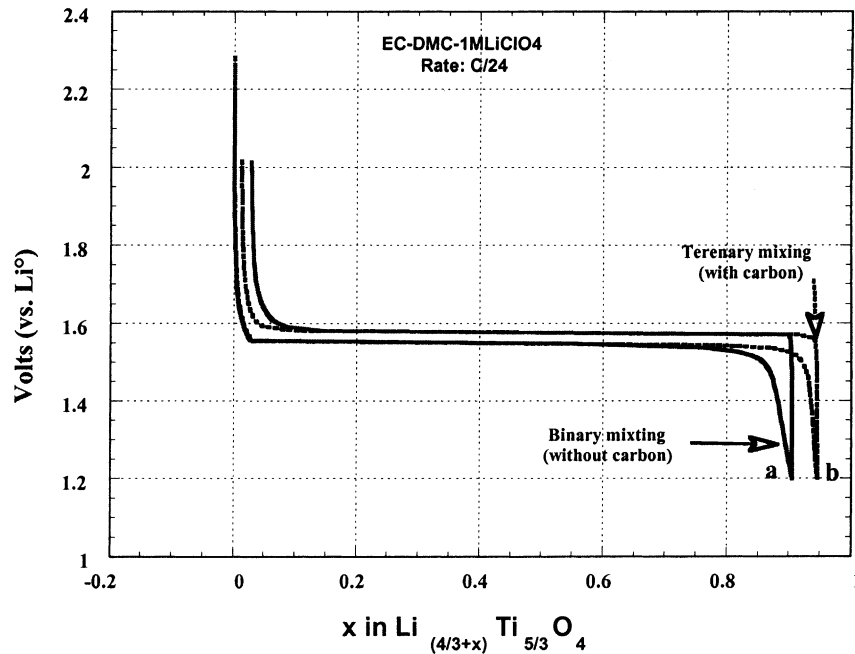
Fig. 4. Discharge–charge curves of $Li_{(4/3+x)}Ti_{5/3}O_4$ synthesized at 850 °C with and without carbon present in the mixture: (a) binary mixture; and (b) ternary mixture with carbon additive.

the potential profile, and complete reaction occurred. This phenomenon appears to be strongly dependent on the mixing method. The reversible capacity of $Li_4Ti_5O_{12}$ prepared by the conventional method was 86 mAh/g. However, higher capacities of 150 and 161 mAh/g were obtained with $Li_4Ti_5O_{12}$ prepared by jar-milling and ball-milling, respectively.

### 3.5. X-ray diffraction and SEM measurements

XRD analyses indicated that the main phase of the reaction product is $Li_4Ti_5O_{12}$ with the spinel structure. In general, the absence of the principal peak characteristic of $TiO_2$ localized at $2\theta = 25–24°$ in the product indicates the complete conversion of $TiO_2$ in the solid-state reaction.
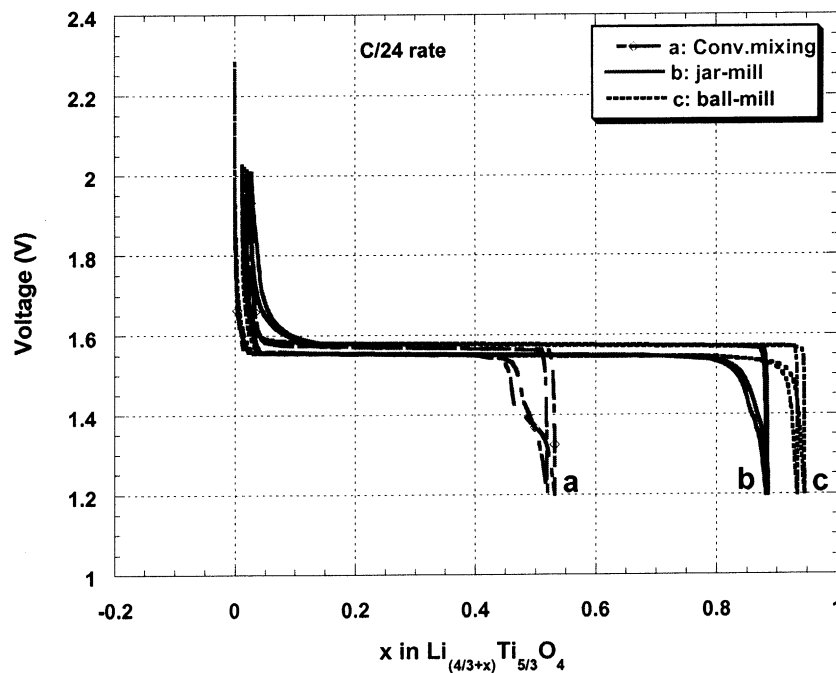


Fig. 5. Discharge–charge curves of $Li_{(4/3+x)}Ti_{5/3}O_4$ synthesized at 850 °C from ternary mixtures produced by: (a) conventional mixing; (b) jar-milling; and (c) ball-milling.
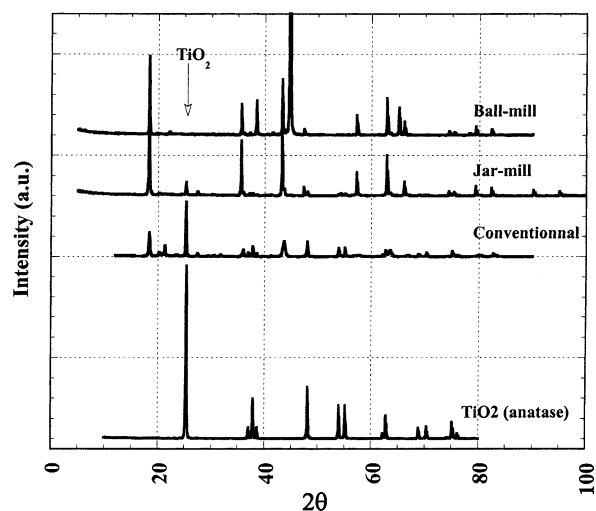
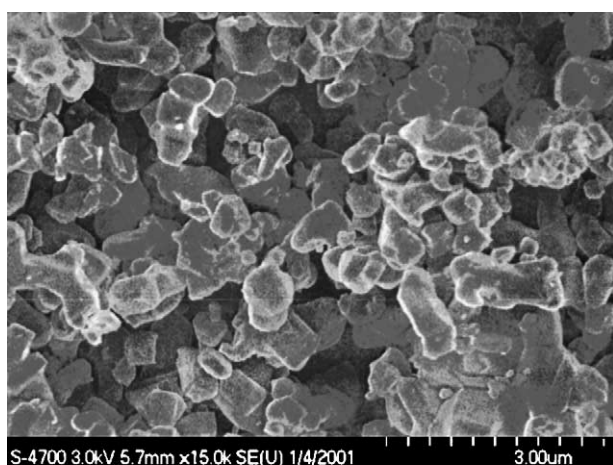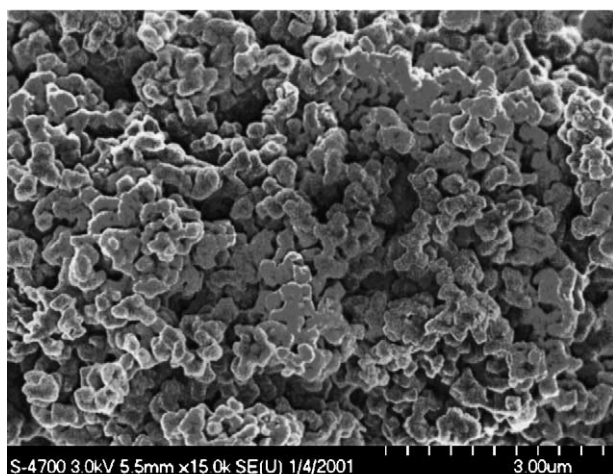Fig. 6. XRD patterns of pure $TiO_2$ (anatase) and $Li_{(4/3+x)}Ti_{5/3}O_4$ synthesized at 850 °C from ternary mixtures obtained after: (a) ball-milling; and (b) jar-milling.



(a)



(b)

Fig. 7. SEM micrographs of $Li_4Ti_5O_{12}$ obtained after (a) jar-milling; and (b) ball-milling.

To examine the effect of mixing method on the structure of $Li_4Ti_5O_{12}$, XRD analyses were conducted on materials produced after ball-milling, jar-milling and conventional mixing (Fig. 6). The samples obtained after ball-milling did not show the $TiO_2$ characteristic peak, while the samples prepared after jar-milling showed evidence for a small peak characteristic of $TiO_2$. Samples obtained after conventional mixing showed a large XRD peak attributed to $TiO_2$, and other less intense peaks for $Li_4Ti_5O_{12}$. This result suggests that mixtures obtained by ball-milling produces a more pure material.

Fig. 7 shows scanning electron micrographs of $Li_4Ti_5O_{12}$ obtained after jar-milling and ball-milling. The micrographs reveal that the morphology and particle size were affected by the preparation method. The particle size of the sample obtained by ball-milling (Fig. 7b) was 1.5 times smaller than that obtained by jar-milling (Fig. 7a). This difference can be related to the ability of the small carbon particles to penetrate between the particles of the reacting precursors to produce an intimate mixing. The ball-mill method gives a more homogenous powder, and the carbon particles are evenly distributed between the particles of the precursor particles.

## 4. Conclusion

The addition of carbon to the starting materials, $TiO_2$ and $Li_2CO_3$, was found to improve the structural and electrochemical performance of $Li_4Ti_5O_{12}$. The mixing method is a critical step to obtain pure $Li_4Ti_5O_{12}$ that is suitable for electrodes in Li batteries. More work is needed to control the particle shape and size to produce nano-particle material.

## References

[1] T. Ohzuku, Y. Iwakoshi, K. Sawai, J. Electrochem. Soc. 140 (1993) 2490.
[2] T. Ohzuku, A. Ueda, N. Yamamoto, J. Electrochem. Soc. 142 (1995) 1431.
[3] K. Zaghib, M. Armand, M. Gauthier, Proceedings of the 190th Electrochemical Society Meeting, San Antonio, 1996 (Abstract No. 93).
[4] K. Zaghib, M. Armand, M. Gauthier, in: J. Broadhead, B. Scrosati (Eds.), Proceeding of the Symposium on Lithium Polymer Batteries, The Electrochemical Society, Pennington, NJ, 1997, pp. 250–264.
[5] K. Zaghib, M. Armand, M. Gauthier, J. Electrochem. Soc. 145 (1998) 3135.
[6] S. Sarciaux, L.S. Sylvere, A. La Salle, D. Guyomard, Mol. Cryst. Liq. Cryst. 311 (1998) 63.
[7] S.I. Pyun, S.W. Kim, H.C. Shin, J. Power Sources 81–82 (1999) 248.
[8] A.N. Jansen, A.J. Kahaian, K.D. Kepler, P.A. Nelson, K. Amine, D.W. Dees, D.R. Vissers, M.M. Thackeray, J. Power Sources 81–82 (1999) 902.
[9] K. Zaghib, M. Simoneau, M. Armand, M. Gauthier, J. Power Sources 81–82 (1999) 300.
[10] S. Bach, J.P. Pereira-Ramos, N. Baffier, J. Power Sources 81–82 (1999) 273.

[11] H. Huang, E. Kelder, D. Simon, J. Schoonman, Proceedings of the 198th Meeting of the Electrochemical Society, Phoenix, The Electrochemical Society Inc., Pennington, NJ, October 2000 (Extended Abstract Nos. 91, 92, 98).

[12] K. Zaghib, M. Gauthier, F. Brochu, A. Guerfi, M. Massé, M. Armand, Canadian Patent #CA 2327370 (December 2000).

[13] P.P. Prosini, R. Mancini, L. Petrucci, V. Contini, P. Villano, Solid State Ionics 144 (2001) 185.

[14] A. Guerfi, S. Sévigny, K. Zaghib, Proceedings of the 100th Meeting of the Electrochemical Society, Philadelphia, The Electrochemical Society Inc., Pennington, NJ, May 2002 (Extended Abstract No. 823).