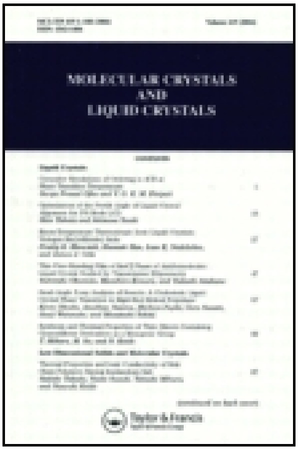

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electrochemical study of the lithium insertion mechanism into $Li_4Ti_5O_{12}$

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Version of record first published: 04 Oct 2006

To cite this article: Sylvere Sarciaux, Annie Le Gal La Salle, Dominique Guyomard & Yves Piffard (1998): Electrochemical study of the lithium insertion mechanism into $Li_4Ti_5O_{12}$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 311:1, 63-68

To link to this article: http://dx.doi.org/10.1080/10587259808042367

Mol. Cryst. Liq. Cryst., 1998, Vol. 311, pp. 63–68
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Printed in India.

Electrochemical study of the lithium insertion mechanism into $Li_4Ti_5O_{12}$

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OCV measurements, cyclic voltammetry and chrono-amperometric measurements have been performed to provide information on the type of mechanism of Li insertion into $Li_4Ti_5O_{12}$ spinel material. Step-wise potentiodynamic electrochemical techniques allow us to distinguish between a single-phase versus two-phase reaction and to conclude on the type of growing mechanism (nucleation-and-growth or homogeneous growth) and the evolution upon cycling.

Keywords: $Li_4Ti_5O_{12}$; Li insertion; insertion mechanism; chrono-amperometry.

INTRODUCTION

$Li_4Ti_5O_{12}$ spinel material, known to intercalate reversibly 3Li per formula unit (175Ah/kg) at 1.55V vs Li, can be used as the negative electrode of 2V lithium-ion batteries [1, 2]. Continuous galvanostatic Li cycling data of $Li_4Ti_5O_{12}$ show a very weak hysteresis between charge and discharge curves, together with an excellent capacity retention upon cycling [3], which is uncommon for a two-phase insertion reaction in a 3-D framework structure [3]. XRD results indicate that the insertion reaction occurs without a noticeable change in the lattice dimension (so-called zero-strain reaction) [3], which could explain the constant capacity upon cycling, but does not help in determining the reaction mechanism (single-phase or two-phase). Then, neither electrochemical nor XRD results provide information on the Li insertion mechanism.

With the purpose of bringing a more comprehensive understanding of the Li insertion mechanism into $Li_4Ti_5O_{12}$, this work presents an electrochemical investigation through OCV measurements, cyclic voltammetry and chrono-amperometric measurements.

EXPERIMENTAL

$Li_4Ti_5O_{12}$ was prepared by solid state reaction between TiO_2 and $LiOH.H_2O$ at 800°C during 12 hours. The XRD pattern revealed the presence of Rutile TiO_2 and Li_2TiO_3 as impurities at very low concentrations. The electrochemical studies were performed on Swagelok™ Li / EC+DMC+$LiPF_6$ / ($Li_4Ti_5O_{12}$+ carbon black+ PVDF) cells [4] monitored by a Mac-Pile system in potentiodynamic and galvanostatic modes. Intermittent galvanostastic experiments, using relaxation periods until a voltage variation of 1 mV/h was attained, allowed us to measure the OCV (Open Circuit Voltage) evolution versus Li composition (with a resolution of 1mV). Scan rates ranging from 0.5mV/h to 10mV/h (obtained from 5mV steps, i.e. 1 step/10h to 2 steps/h) were used for potentiodynamic measurements. All voltages given in the text are reported versus the reference system Li^+/Li.

RESULTS

Equilibrium voltage

GITT (Galvanostatic Intermittent Titration Technique) was used in order to follow the variation of OCV and CCV (Close Circuit Voltage) with Li content. Results, given in **Figure 1** show that charge and discharge OCV's are perfectly flat in the whole composition range, characteristic of a first order (two-phase) transformation [5], with an equilibrium voltage (defined as the mean value) of 1.562V. The extremely small polarization (defined as $|OCV-CCV|$), less than 8mV, together with the rapid relaxation (less than 4hrs) to a voltage very close to the equilibrium (less than 2mV), are signatures of fast kinetics.

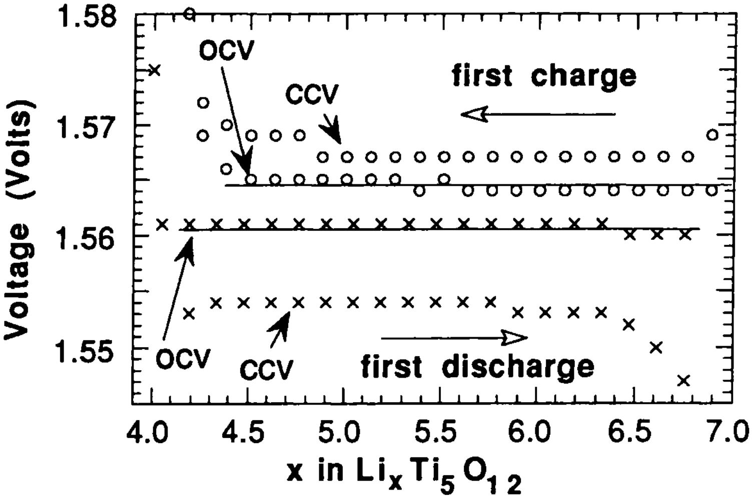

Figure 1: Variation of OCV and CCV with Li content at first cycle.

Cyclic voltammetry

Typical current-voltage curves obtained from cyclic voltammetry experiments are reported in **Figure 2**. Insertion and deinsertion voltage ranges do not overlap, but begin at approximately the same onset voltage V_{on}, a typical behavior of a two-phase insertion reaction [6]. This onset voltage (1.561V) is characteristic of the $Li_4Ti_5O_{12}$ / $Li_7Ti_5O_{12}$ biphasic reaction and corresponds exactly to the equilibrium voltage determined from GITT.

The shape and position of I-V curves vary with the cycle number, but the total capacity remains constant. When increasing the cycle number, the discharge and charge peak voltages vary over the few first cycles and then remain approximately constant. Concomitantly, the shape of these I-V peaks evolves and a shoulder appears at larger polarization (the polarization is defined as $|V-V_{on}|$). This evolution occurs in a smaller number of cycles at lower scan rates.

The theoretical shape of I-V curves in a biphasic Li insertion reaction is triangular with an ascending linear $|I|$ versus V variation [6], where the slope $[I / (V-V_{on})]$ is proportional to the displacement rate of the interphase zone, i.e.

corresponds to the kinetics of the reaction. The evolution of the voltammogram towards larger polarization could then be interpreted in terms of a slower insertion kinetics. According to this reasoning, the first discharge could correspond to an initially slow insertion process, which could be due to a kind of initial adaptation ("mise en forme") of the material.

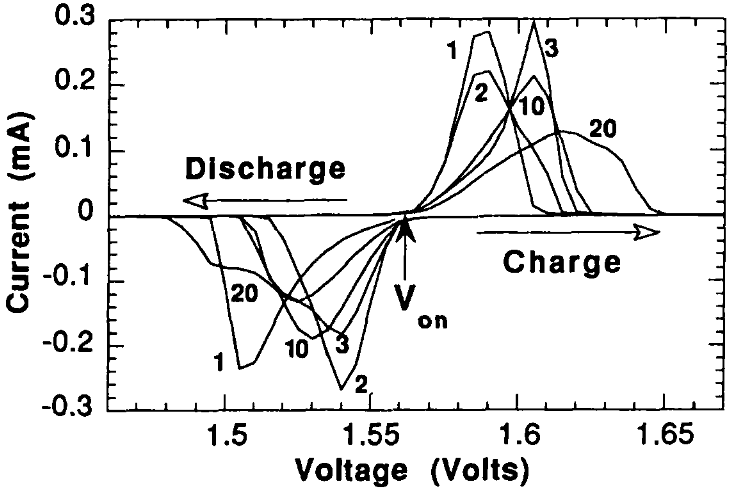

Figure 2: Evolution of the current-voltage curves with the cycle number. The scan rate was 5mV/0.581hr.

After several cycles, the evolution of the voltammogram corresponds to the appearance of a second biphasic electrochemical process with a lower kinetics. Both biphasic processes seem to be strongly related because they show the same onset voltage and the sum of their capacities is constant. It looks like a second Li reservoir that fills and empties at a slower rate. Structural investigations are in progress in order to verify this hypothesis.

Chrono-amperometric study

The current versus time variations at each voltage step of a step-wise potentiodynamic experiment, so-called chrono-amperometric curves, provide information on the mechanism and kinetics of the electrochemical process. Examples of such curves are given in **Figure 3**.

The shape of chrono-amperometric curves is very different in the ascending and in the descending part of the |I|-V peak, a behavior characteristic of a biphasic Li insertion reaction [6].

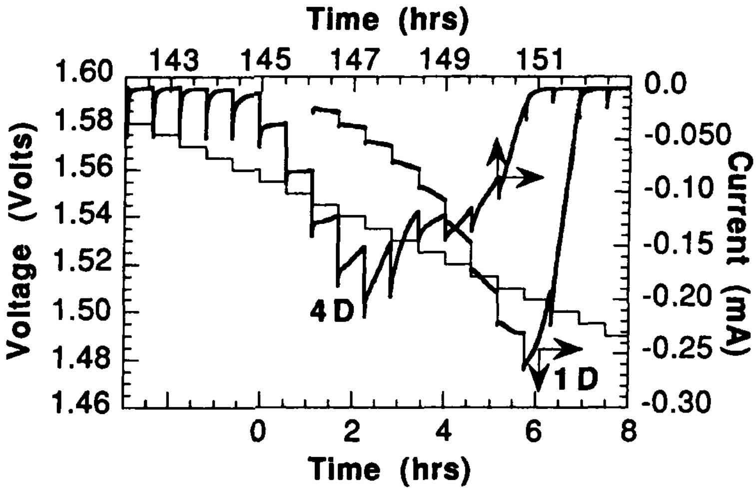

Figure 3: Chrono-amperometric curves at first (1D) and 4th discharge (4D), measured with a voltage scan of 5mV/0.581hr.

During the first cycle, the current increases versus time in the ascending part of the |I|-V curve, while it remains constant or decreases after several cycles. A current increase at constant voltage means an increase of the overall reaction rate that can be interpreted as an increase of the area of the phase interface (assuming a constant current per surface unit because of a constant ($V-V_{on}$) driving force) [7], i.e. a nucleation-and-growth mechanism. Therefore, a nucleation-and-growth Li insertion mechanism is observed during the first discharge, while a homogeneous growth of the $Li_7Ti_5O_{12}$ phase occurs during further cycles.

The successive chrono-amperograms of the 4th discharge clearly show the occurrence of two electrochemical processes with different mechanisms and kinetics, while those of the first discharge indicate a single process, in agreement with conclusions drawn from the I-V curves.

CONCLUSION

Both quasi-equilibrium voltage measurements, cyclic voltammetry and chrono-amperometry show undoubtedly the signature of a two-phase Li insertion reaction with fast kinetics. Cyclic voltammetry and coupled chrono-amperometry lead to additional information :

- first Li insertion proceeds via a slow nucleation-and-growth mechanism corresponding to a kind of processing of the material,
- a homogeneous growth occurs during further insertions with faster overall kinetics,
- a more complex insertion mechanism involving two biphasic systems with different kinetics is detected after several cycles.

This work shows the strength of electrochemistry and more specifically it demonstrates the power of step-wise potentiodynamic experiments as a sensitive probe to precisely characterize solid state insertion reactions. However, further work is needed in order to relate these electrochemical results to structural information; ^{7}Li NMR experiments are planned.

Acknowledgments
The authors are grateful to Yves Chabre for enlightening discussions on chrono-amperometric measurements.

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