

Electrochemical study of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as negative electrode for Li-ion polymer rechargeable batteries

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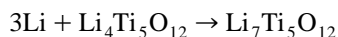
Abstract

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ a zero-strain insertion material was prepared by conventional method and by high energy ball milling (HEBM) of precursor to form nanocrystalline phases. The electrochemical performance of solid-state negative electrode was carried out using a solvent-free solid polymer electrolyte at 60°C and 80°C. A $\text{Li}_4\text{Ti}_5\text{O}_{12}$ vs. lithium cell discharged at C/12 delivered 155 mA h g⁻¹ for the conventional method and 157 mA h g⁻¹ for the method using high ball energy milling, corresponding respectively to 97% and 96% first-cycle coulombic efficiency. The chemical diffusion coefficient of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel-type compound is about 2×10^{-8} cm² s⁻¹. This is one order of magnitude higher than that of carbonaceous negative electrodes. $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which is a zero-strain insertion material, offers advantage for the SPE cell including safety, long life, and reliability. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a good reversibility and has no structural change (zero-strain insertion material) in the charge–discharge process. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was always demonstrated as a good candidate as negative electrode for solid state lithium ion batteries [1–4]. It offers a stable operating voltage of approximately 1.5 V vs. lithium. In principle, therefore, this material can be coupled with 4 V electrode as LiMn_2O_4 , LiNiO_2 or LiCoO_2 to provide a cell with an operating voltage of approximately 2.5 V which is twice that of nickel–cadmium or nickel–metal hydride cell. Lithium reacts with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ according to the reaction



because lithium insertion into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel displaces tetrahedrally coordinated lithium ion into octahedral

sites with the formation of a rock-salt-type $\text{Li}_7\text{Ti}_5\text{O}_{12}$ product. The safety remains a major issue for large scale-up Li-ion batteries, particularly when large amount of liquid electrolyte are used, because gas formation and electrolyte decomposition become very problematic. For this reason, it is essential that large scale Li-ion batteries use an anode (zero swelling) in combination with true solid-polymer electrolyte (SPE) with no added liquid solvent and no significant vapour pressure; the SPE also securely encapsulates both anode and cathode materials.

In this work, we report here the results of the DST and X-ray diffraction measurements for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ together with SEM observation, electrochemical discharge and charge, and slow cyclic voltammetry.

2. Experimental

The Li–Ti–O ternary phase was prepared by two methods. The first was the conventional method (method A) which is heating a mixture of TiO_2 anatase and Li_2CO_3 at 800° for 12 h in a nitrogen gas stream. The second method (method B) used was high energy ball milling (HEBM) of

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precursor to form nanocrystalline phases. These materials were then heat treated in order to obtain the desired phases. The samples were characterized by X-ray diffractometer, DST and scanning electron microscopy before intercalation. Differential scanning calorimetry (DSC) analysis was performed using the Perkin-Elmer DSC at a heating rate of 20 K min^{-1} under inert atmosphere. A Hitachi S-70 SEM was used to monitor particle size at each synthesis step. The discharge (intercalation) charge (deintercalation) cycling for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode was carried out using 4 cm^2 lab cell with a counter electrode of lithium metal (two electrodes). The initial cell chemistry for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode is based on Li metal (-)/SPE:copolymer based on POE and LiTFSI salt/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (+).

The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ working electrode was prepared by admixing 50 vol.% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to SPE and painting the mixture on copper foil with a doctorblade. The electrode was dried under vacuum at 85°C for 24 h before use. The discharge–charge cycle and slow cyclic voltammetry for this electrode were carried out using the galvanostatic,

potentiostatic methods (Macpile[®], Claix, France). All experiments were performed at 60 or 80°C . The measurement of chemical diffusion coefficient of Li-ion in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -PVDF was demonstrated with three electrode cells at 25°C using a liquid electrolyte of 1 M LiPF_6 in EC + DEC (1:1) and lithium metal as reference and counter electrodes.

3. Results and discussion

The colour of the prepared samples for both methods was white, indicating that the samples were electronic insulators. The analysis of crystal structure of the samples by XRD (Fig. 1) shows that they have a defect spinel-framework structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and that all diffraction lines indexed in terms of (h,k,l) are assigned for a face-centered cubic lattice. The lattice parameter a was obtained to be $a = 8.36 \text{ \AA}$. The intensities well reflect the space group of $Fd3M$, where lithium ions are located at the tetrahedral 8 (a) sites, and tetravalent titanium ions ($3 d^\circ$) and lithium ions are randomly distributed at octahedral

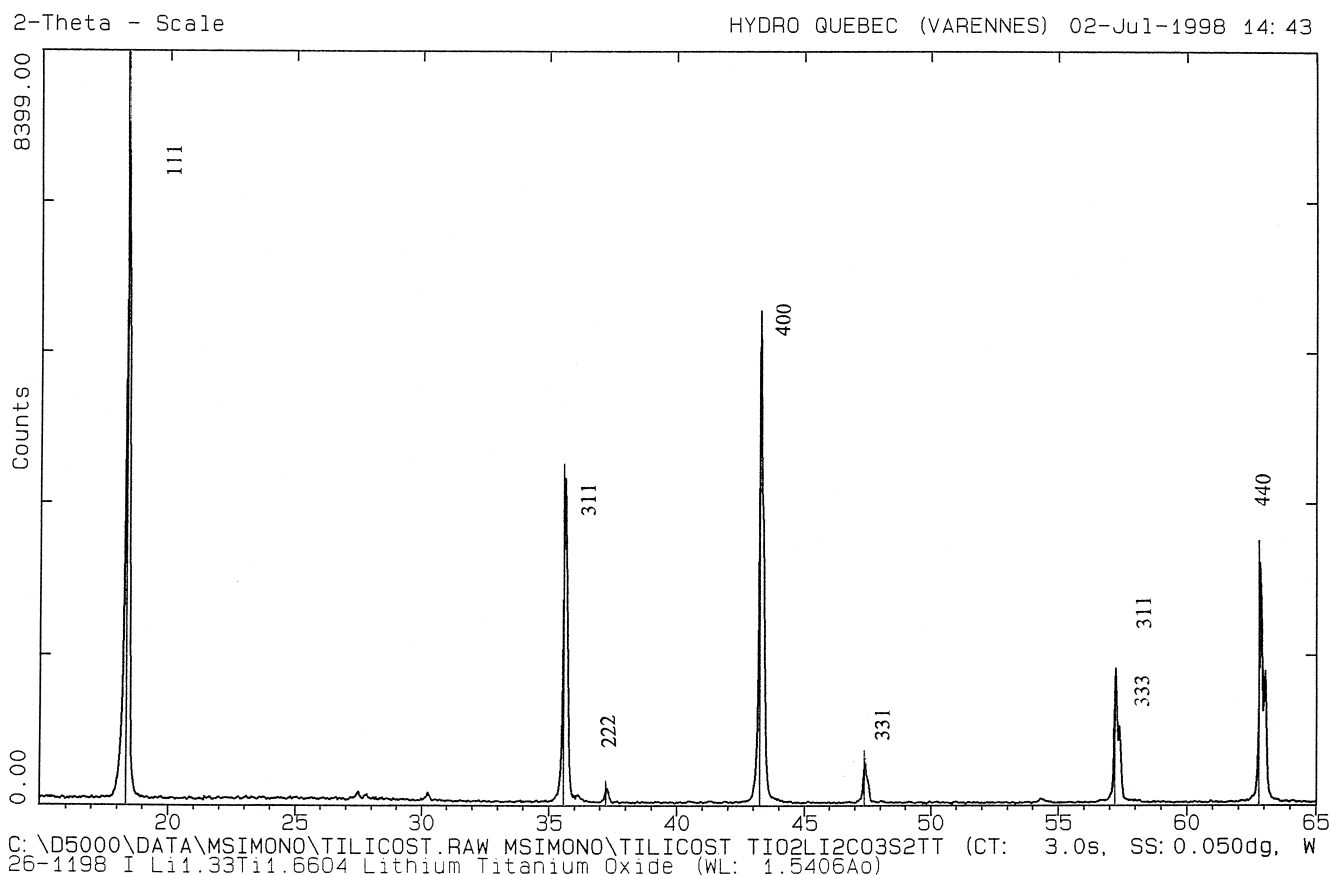


Fig. 1. X-ray diffraction patterns of white sample of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

16 (d) sites by the ratio of $\text{Li}/\text{Ti} = 1/5$, while oxygen ions are located at the 32 (e) sites.

Fig. 2 presents the DSC trace obtained for the HEBM precursor sample, showing the transformation to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ starts around 450°C . As shown in Fig. 3, synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ obtained by HEBM (method B) presents a narrow primary particle size distribution centered around $0.6\ \mu\text{m}$.

Galvanostatic curve (Fig. 4) shows the initial discharge–charge capacities at rate $C/12$. The initial open circuit voltage (OCV) was $2.96\ \text{V}$. During the discharge the voltage drops quickly down to below $2\ \text{V}$ and decreases as the reaction proceeds until the voltage reaches about $1.5\ \text{V}$. The cell was cycled between 1.2 and $2\ \text{V}$. The first coulombic efficiency (1 CE) was 97% . The cell delivered $155\ \text{mA h g}^{-1}$ which may be compared to the theoretical capacity of about $175\ \text{mA h g}^{-1}$. The sample prepared by method B delivered $157\ \text{mA h g}^{-1}$ and the 1 CE was about 96% .

The sample prepared by method B is comparable to the method A. However, sample B is prepared at low temperature.

Fig. 5a shows the capacity vs. the cycle number, at 60°C the stability of this electrode can be attributed to the stability of the $[\text{Ti}_{1.67}\text{Li}_{0.33}]\text{O}_4$ framework and to the minimal dilation ($< 1\%$) of the cubic unit cell that occurs on lithium insertion. During discharge at different DOD values, the area specific impedance (ASI) was measured through current interruptions at 5 and $30\ \text{s}$.

The ASI at 1.6 and $1.5\ \text{V}$ are very stable with the cycle life. At 80°C , the cell has also good stability (Fig. 6). So $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is not dissolved at high temperature.

The cell has long life and very good cyclability. We believe that zero-strain insertion materials and a lithium ion conductive solid polymer are necessary for the implementation of long life, and safe solid state lithium ion polymer batteries.

The chemical diffusion coefficient of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel-type compound was found to be more than $2 \times 10^{-8}\ \text{cm}^2\ \text{s}^{-1}$ at 25°C . This value was obtained by the cyclic voltammetry data using same method as Nishizawa et al. [4]. This is one order of magnitude higher than for carbonaceous negative electrodes. This high diffusion coefficient may also allow the use, at high rapid charge–dis-

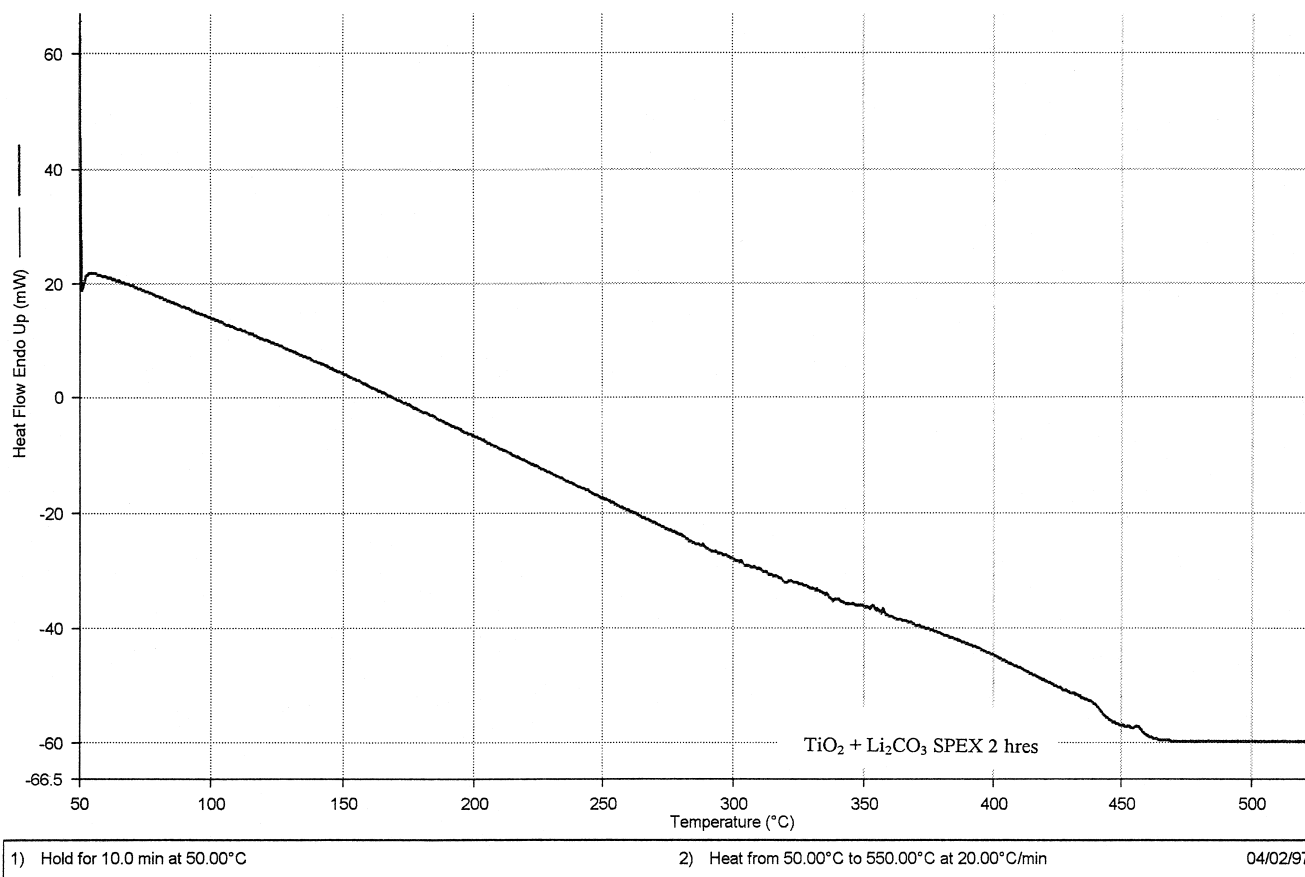


Fig. 2. DSC of sample $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared by method B.

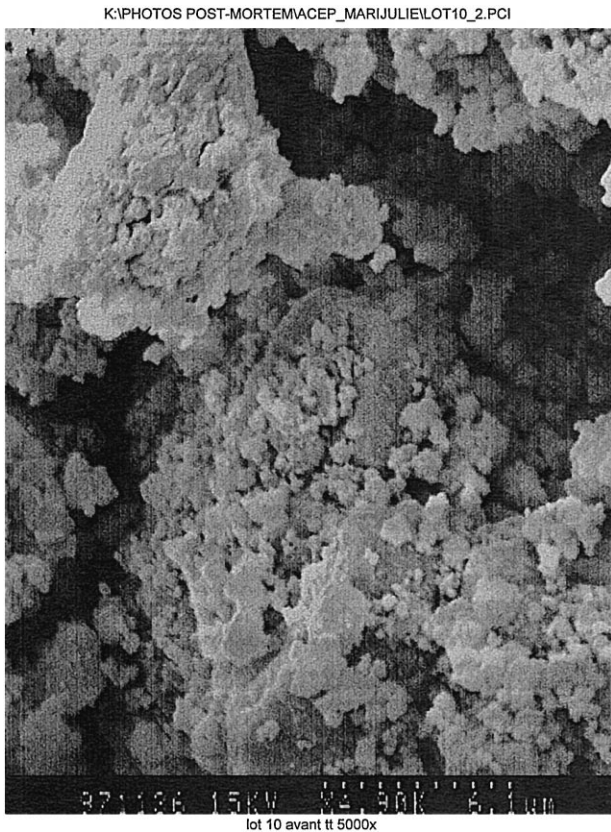


Fig. 3. SEM image of sample $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

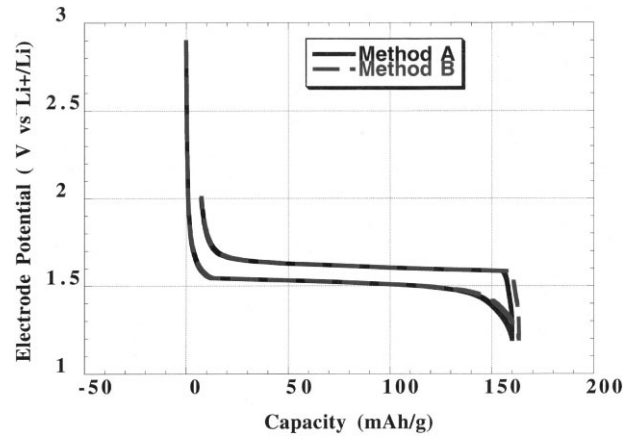


Fig. 4. Discharge and charge curves of two $\text{Li}/\text{SPE}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells at C/12. (a) Prepared by method A; (b) prepared by method B.

charge for pulse applications, of such GSM or PNGV applications.

4. Conclusions

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ gives 155 and 157 mA h g^{-1} , respectively with the method A and method B. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be prepared at lower temperature by using HEBM method.

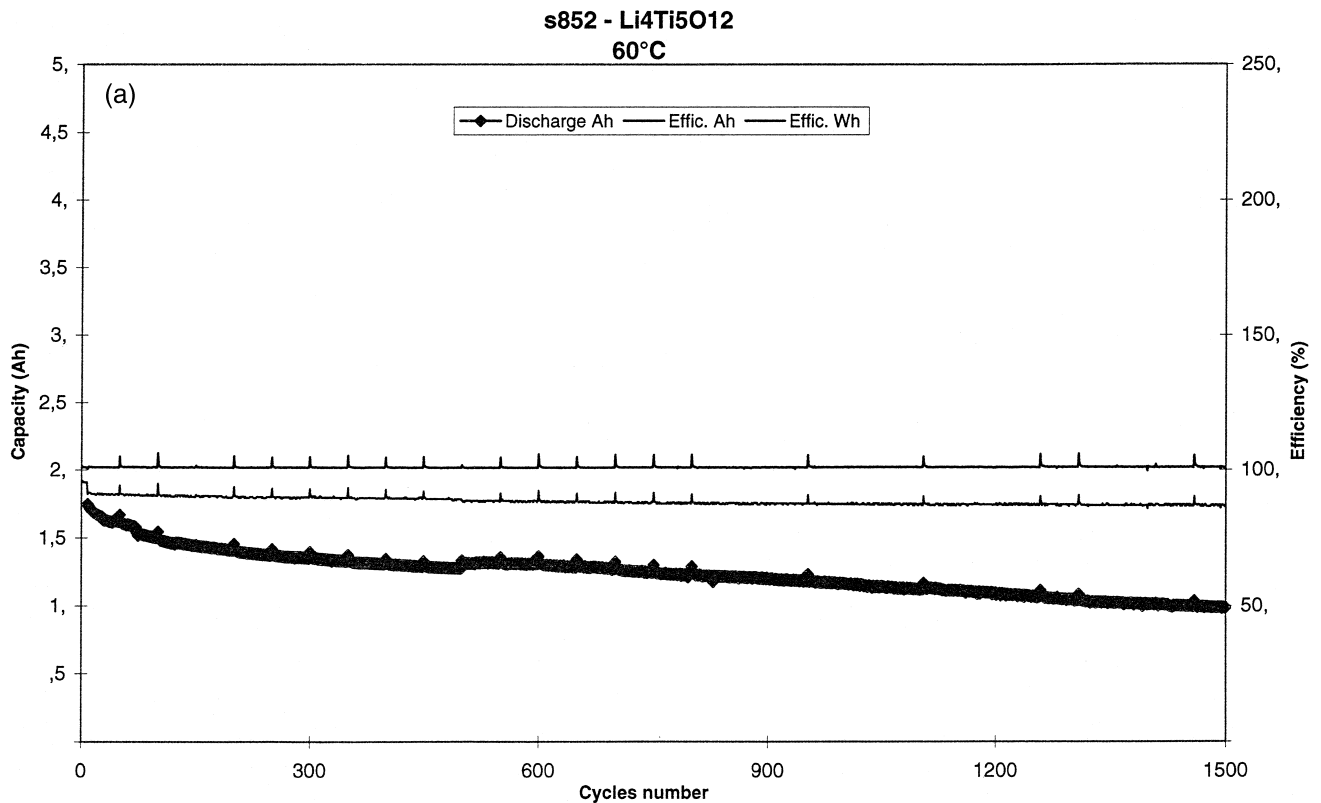


Fig. 5. (a) Capacity vs. cycle life of the cell $\text{Li}/\text{SPE}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ at 60°C ; (b) ASI vs. cycle life of the cell $\text{Li}/\text{SPE}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ at 60°C .

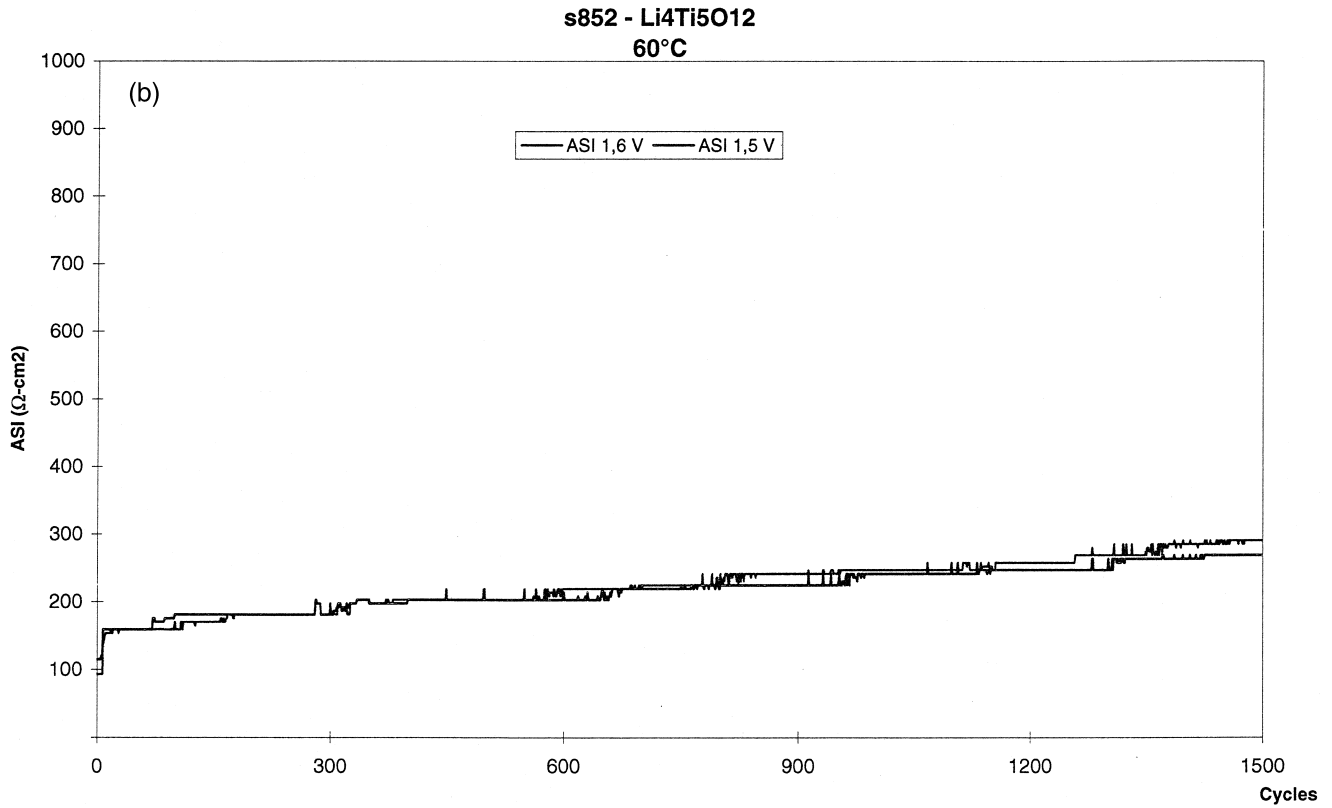
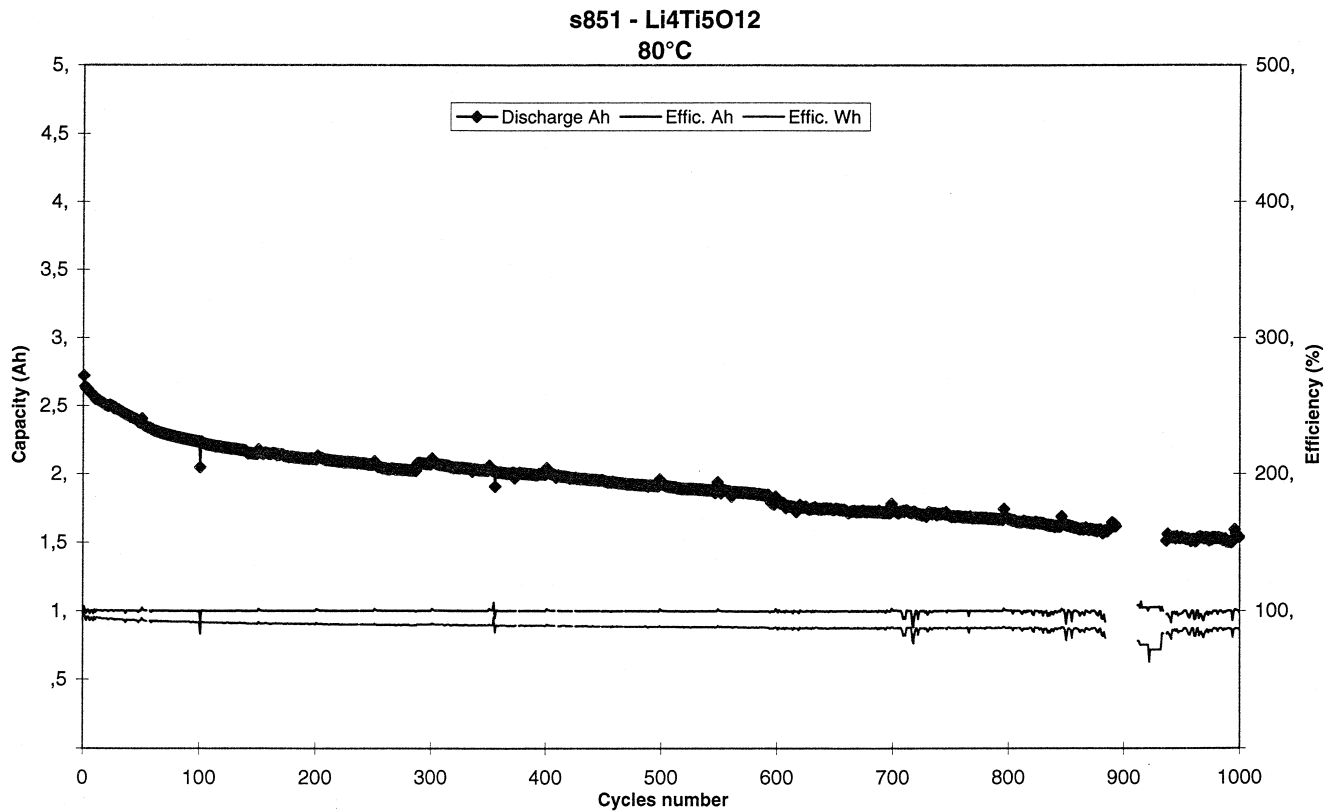


Fig. 5 (continued).

Fig. 6. Capacity vs. cycle life of the cell Li/SPE/Li₄Ti₅O₁₂ at 80°C.

The exceptional stability of this electrode was demonstrated at 60°C and 80°C.

The chemical diffusion coefficient of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is about $2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ over the composition range. This is more than one order of magnitude higher than that of carbonaceous negative electrodes.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$, a zero-strain insertion material, is advantageous for SPE batteries with safety, long life, and reliability.

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