



Short communication

## Film-shaped sol–gel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode for lithium-ion microbatteries

J. Mosa\*, J.F. Vélez, I. Lorite, N. Arconada, M. Aparicio

Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, 28049 Madrid, Spain

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## ABSTRACT

Homogeneous and transparent film-shaped spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrodes on gold coated quartz were synthesized by sol–gel and a dipping procedure after thermal treatments at 700 °C. The influence of the lithium precursor content on the phase composition, structure and electrochemical behavior of this material was studied. Spectral ellipsometry measurements and SEM–EDX analysis indicate an average thickness between 385 and 560 nm. Rutile  $\text{TiO}_2$  is detected using grazing incidence X-ray analysis and Micro-Raman in compositions with a lower content of lithium. Good galvanostatic cycling and very flat discharge–charge profiles confirm the high purity of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrodes obtained with the higher lithium content composition.

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### 1. Introduction

Rechargeable thin film microbatteries have recently become the topic of widespread research for use in low power applications and energy storage systems for electronic devices [1–4]. The general requirements of the microbatteries for these applications are high specific energy, wide range of temperature stability, low self discharge rate and flexibility of cell design [5]. Thin film Li-ion batteries fabricated using only solid-state materials by a thin-film process is a promising method for synthesizing 3D electrodes for microbatteries [7–12]. This alternative approach allows the incorporation of porosity into nanometer sized material, thus maintaining good particle contacts and adequate particle size, while maximizing the rate capability benefits of shorter diffusion pathways [13,14].

Spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  has been considered as one of the most prospective anode materials for Li-ion batteries because of its excellent reversibility and long cycle life. It has an excellent Li-ion mobility and exhibits almost no structural change (zero-strain insertion material) during charge–discharge cycling [15–18]. This electrode can be deposited using several thin film deposition techniques, as sol–gel process [19]. Li-ion intercalation in  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  occurs via a two-phase coexistence process, resulting in a very stable (dis)charge voltage at around 1.55 V (vs.  $\text{Li}/\text{Li}^+$ ). During the (dis)charging process the lithium content can be varied for  $\text{Li}_x\text{Ti}_5\text{O}_{12}$  between  $4 < x < 7$ , resulting in a maximum theoretical gravimetric capacity of  $175 \text{ mAh g}^{-1}$ . The lattice parameter for a spinel unit cell ( $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ )<sub>8</sub> is 8.36 Å, which means that the maximum obtainable volumetric capacity is  $610 \text{ mAh cm}^{-3}$  [5,20]. The low electrical conductivity becomes a major drawback which is unfavorable to high rate capability [21,22], because the polarization of the electrode becomes serious when is charge/discharged at a higher current density. A great deal of effort has been made in order to improve the electronic conductivity and power performance of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . Reducing the particle size [23,24], doping with metal (Mg, Cr, Fe, Ni, V, Mn and Ag) [25–29] and modifying its particles with carbon [30,31] have been reported. Kavan and Grätzel reported on the Li-insertion activity of a nanosized spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  prepared via sol–gel route [23]. Various morphologies, such as nanoparticles [32], microspheres [33], hollow spheres [34], nanoflowers [35] and three-dimensional macroporous structures [14] and different thin-film approaches have been reported [13,36–39]. Since sol–gel route synthesis is a general and effective route for the preparation of micro/nanostructured materials

\* Corresponding author at: Instituto de Cerámica y Vidrio (CSIC), C/Kelsen 5, Campus de Cantoblanco, 28049 Madrid, Spain. Tel.: +34 91 735 58 40; fax: +34 91 735 58 43.

E-mail addresses: [jmosa@icv.csic.es](mailto:jmosa@icv.csic.es) (J. Mosa), [maparicio@icv.csic.es](mailto:maparicio@icv.csic.es) (M. Aparicio).

with well controlled morphology and structure, here we report on the sol–gel synthesis and coating preparation by dipping of spinel thin films  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . Synthesis parameters as Li/Ti molar ratio have been adjusted to examine their influence on the phase composition, structure and electrochemical behavior of the electrode.

## 2. Experimental

The precursor sols were synthesized employing titanium isopropoxide (ABCR, 97%) and lithium acetate (Aldrich, 99.99%). The solutions (atomic ratios Li/Ti = 4/5, 5/5 and 6/5) were prepared by mixing both precursors with absolute ethanol (Panreac) as solvent, acetic acid (Merck, 100%) as surfactant agent, water for hydrolysis and HCl as catalyzer. The final molar ratios of Li: Ti: ethanol: acetic acid: water: HCl were 4, 5 or 6: 5: 120: 10: 13: 0.1. Lithium acetate was first dissolved in alcohol and acetic acid, and subsequently titanium alkoxide and water were incorporated for starting the sol–gel hydrolysis and condensation reactions by stirring at room temperature for 2 h. Viscosity (Sine-waveVibroViscometer SV-1A) and pH measurements at room temperature were performed to analyze the homogeneity and stability of sols.

Four-layer coatings were prepared by dipping on different substrates using a withdrawal rate between 14 and 19  $\text{cm min}^{-1}$ . Quartz substrates were used to assess the homogeneity of the coating and thickness measurement; silicon substrates for X-ray measurements and gold coated (50 nm) quartz substrates, prepared by sputtering, for electrochemical characterization. Thermal treatments at 700 °C were performed to sinter the coatings and obtain the adequate crystalline structure.

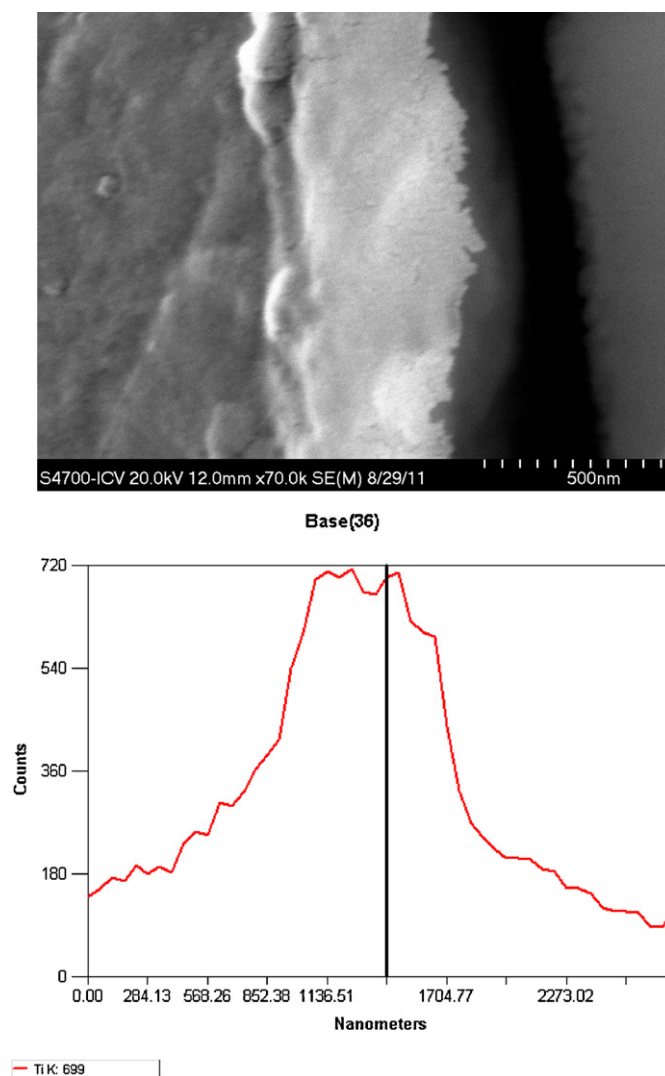
Spectral Ellipsometric measurements were performed using a Variable Angle Spectroscopic Ellipsometer (WVASE32, M-2000UTM, J.A. Co., Woollam) to characterize thickness ( $e$ ) and refractive index ( $n$ ) of films deposited onto gold coated quartz substrates. The spectra were taken in the visible region, between 250 and 900 nm at a variable incident angle of 65, 70 and 75°. The data were fitted using the WVASE32 software and taking into account a Cauchy model. Characterization of the coatings also includes analysis of a cross-section of coated samples performed by scanning electron microscopy (HITACHI S-4700 field emission) and elemental chemical analysis by Energy Dispersive X-ray Spectroscopy (EDX, NORAN system six) connected to the FE-SEM. Morphology of the samples were also analyzed using a transmission electron microscopy (TEM, H-7100 Hitachi, Japan) by scratching the coating.

The crystal structure of the obtained coated samples was characterized by Grazing incidence X-ray diffraction (step: 0.040° and angle: 0.5°) using a Siemens D-5000. Raman study was carried out using a Confocal Micro-Raman (Witec alpha-300R) with laser excitation of 532 nm.

Electrochemical characterization (Multichannel Potentiostat VMP3 from Biologic) was carried out by galvanostatic cycling in a three-electrode cell using the coated sample as working electrode, and lithium foils as reference and counter electrodes. 1  $\text{mol L}^{-1}$   $\text{LiPF}_6$  solution in a 1:1 (w:w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) from Merck was used as electrolyte. Tests cell was assembled in an argon-filled glove box with water content around 5 ppm, measured with a dew-point hygrometer (“Easidew Online”, Michell Instruments). The cell was discharged and charged between 2.0 and 1.2 V (vs.  $\text{Li/Li}^+$ ) under a current density of 17  $\mu\text{A cm}^{-2}$ .

## 3. Results and discussion

The sols are transparent without the presence of phase separation or precipitates. The pH values of the three sols are about 6.0 due to the presence of HCl and acetic acid that lower the higher pH

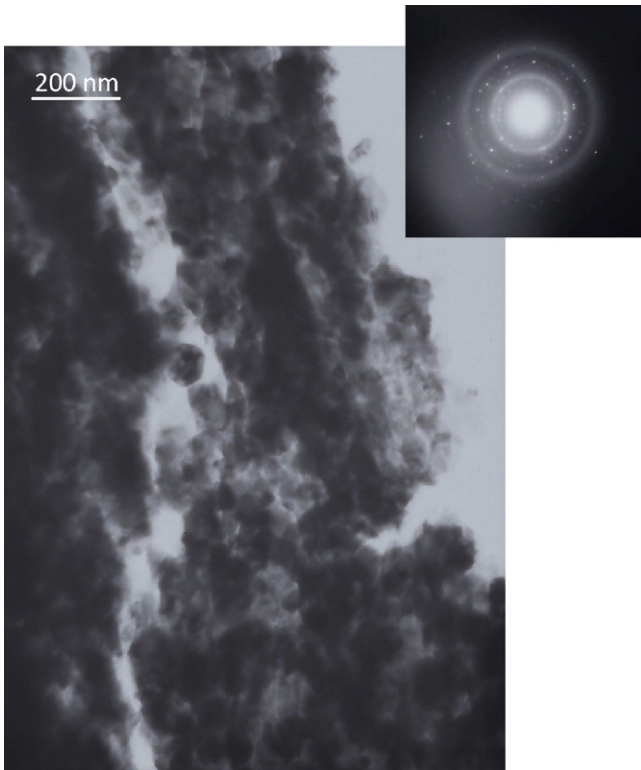


**Fig. 1.** (a) Cross-section SEM micrograph of a coated sample prepared with the Li/Ti = 6/5 sol and (b) EDX results performed along a line from the left side (quartz substrate) to the right area (resin).

obtained from the dissolution of the lithium salt. The viscosity values at room temperature just after the sol synthesis were 2.3, 2.7 and 2.1  $\text{mPa s}$  for Li/Ti = 4/5, 5/5 and 6/5 compositions, respectively. The measurement in the following 90 h showed similar values, evidencing the absence of an accelerated aging of the solutions, and indicating that they are suitable for the preparation of coatings by dipping.

Optimized solutions allowed obtaining homogeneous and transparent coatings on different substrates. Spectral ellipsometry measurements indicate a thickness between 50 and 55 nm for the gold layer. Thickness of the coatings was 450, 560 and 385 nm for Li/Ti = 4/5, 5/5 and 6/5 compositions, respectively, based on the variations of sols viscosity and specific withdrawal rates.

Fig. 1a shows the cross-section SEM micrograph of a coated sample prepared with the Li/Ti = 6/5 sol. The image presents a homogeneous and well-bonded layer, despite the polishing process. The thickness of the coating is between 350 and 400 nm, in accordance with the ellipsometry results. This value can be also confirmed by EDX analysis. Fig. 1b displays the EDX results performed along a line from the left side of Fig. 1 (quartz substrate) to the right area (resin used in the preparation of the sample for microscopic observation). The plot clearly shows the presence of lithium

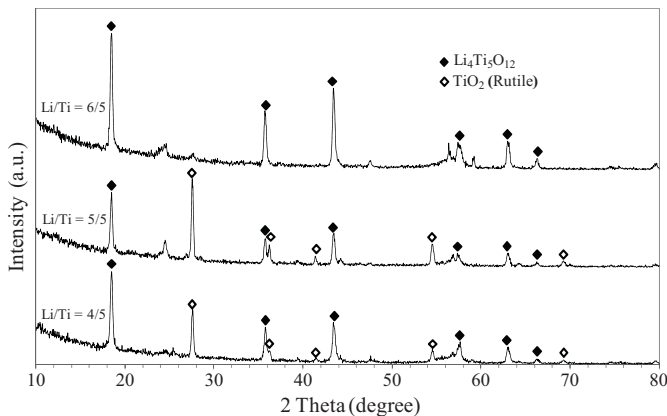


**Fig. 2.** TEM image of powder scratched from a coated sample prepared with the Li/Ti = 6/5 sol. Inset shows the corresponding FFT of the image.

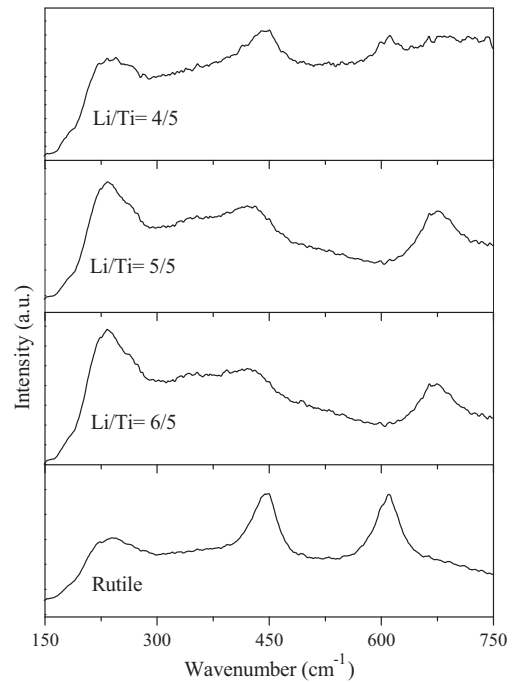
titanate coating and its thickness, close to the value established by ellipsometry and electron microscopy.

A TEM image of the material scratched from Li/Ti = 6/5 coating is presented in Fig. 2. Crystalline particles of very small size and high homogeneity can be observed, although obviously they are agglomerated. The corresponding Fast Fourier Transform (FFT) (inset in Fig. 2) indicates the crystalline nature of the film.

The X-ray analysis is crucial to determine the presence of crystalline structures and purity. Fig. 3 shows the grazing incidence X-ray results of coatings obtained with the three compositions, including the 43–44° interval of Li/Ti = 6/5 spectra in an expanded view. Both the stoichiometric composition (Li/Ti = 4/5) as slightly enriched in lithium (Li/Ti = 5/5) show a mixture of two crystalline phases: the face-centered cubic spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (JCPDS # 49-0207) and rutile  $\text{TiO}_2$  (JCPDS # 21-1276). This is the result of the low temperature thermal treatment used. Because the main objective of



**Fig. 3.** Grazing incidence X-ray of Li/Ti = 4/5, 5/5 and 6/5 coatings, including the 43–44° interval of Li/Ti = 6/5 spectra in an expanded view.

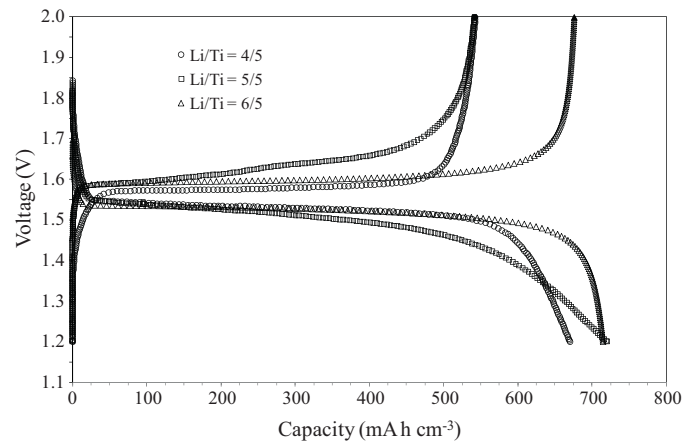


**Fig. 4.** Raman spectra of Li/Ti = 4/5, 5/5 and 6/5 coatings, including  $\text{TiO}_2$  for comparison.

this work was to obtain pure  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase without using temperatures above 700 °C, the third composition studied (Li/Ti = 6/5) had an even higher lithium content, which spectra presents a pure spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase. The lattice parameter  $a$  is 8.354, 8.356 and 8.360 Å for Li/Ti = 4/5, 5/5 and 6/5, respectively, which is in good agreement with the theoretical value of 8.358 Å. This result confirms that pure  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase is successfully synthesized [21].

Fig. 4 shows the Raman spectra of the three coatings, and the spectra of rutile  $\text{TiO}_2$  for comparison [40]. The three samples present the characteristic peaks of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase [41], while Li/Ti = 4/5 sample clearly shows a significant content of rutile, in particular observing the peak close to 600  $\text{cm}^{-1}$ . A depth profile scanning (not shown for simplicity) in steps of 50 nm were performed for the three samples. The results indicate that the composition is preserved along the thickness in each composition.

Fig. 5 displays the second discharge–charge profiles of coated samples prepared with the three compositions cycled at 17  $\mu\text{A cm}^{-2}$ . The discharge and charge curves obtained with



**Fig. 5.** Second discharge–charge profiles of Li/Ti = 4/5, 5/5 and 6/5 coatings cycled at 17  $\mu\text{A cm}^{-2}$ .

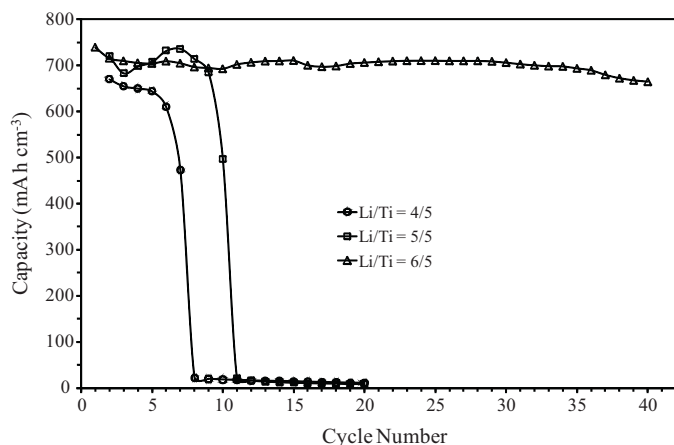


Fig. 6. Galvanostatic cycling at  $17 \mu\text{A cm}^{-2}$  of Li/Ti=4/5, 5/5 and 6/5 coatings.

Li/Ti = 6/5 composition shows a flatter plateau at a potential around 1.55 V (vs.  $\text{Li/Li}^+$ ), the reversible redox potential of spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , and a higher discharge and charge capacities compared with the other two compositions. This behavior can be due to the slower kinetics diffusion of lithium ions in samples with a higher content of impurities, rutile in this case. However, the discharge capacity values obtained for all the compositions are similar to the theoretical volumetric values,  $610 \text{ mAh cm}^{-3}$ , taking into account the low thickness of these electrodes [5]. The cycle performances of the three compositions (Fig. 6) confirm the previous results. The Li/Ti=6/5 sample presents an excellent behavior with almost no capacity decay after 40 cycles, corresponding to a homogeneous coating with a pure spinel phase. The other two compositions show initial good discharge capacities, but the presence of titania probably limit the lithium diffusion. Some authors [42–44] claimed the formation of a solid electrolyte interface (SEI) on the surface of Rutile titania electrode at the beginning of charge–discharge process. It is possible that this SEI layer seals the insertion positions after a few cycles.

#### 4. Conclusions

Film-shaped spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrodes on gold coated quartz substrates were synthesized by sol–gel using titanium isopropoxide and lithium acetate as precursors. Spectral ellipsometry measurements indicate average thickness of 450, 560 and 385 nm for Li/Ti = 4/5, 5/5 and 6/5 compositions, respectively. Both the stoichiometric composition (Li/Ti = 4/5) as well as the slightly enriched in lithium (Li/Ti = 5/5) show a mixture of two crystalline phases: the face-centered cubic spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and rutile  $\text{TiO}_2$ , while the third composition studied (Li/Ti = 6/5) only presents the spinel phase. Discharge–charge profiles of Li/Ti=6/5 composition cycled at  $17 \mu\text{A cm}^{-2}$  show a flatter plateau at 1.55 V (vs.  $\text{Li/Li}^+$ ) and a higher discharge capacity (close to the theoretical volumetric value,  $610 \text{ mAh cm}^{-3}$ ) compared with the other two compositions. Galvanostatic cycling confirms the previous results, and the Li/Ti = 6/5 sample presents an excellent performance with almost no capacity decay after 40 cycles.

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