

In Operando Characterization of Li Composite Battery Electrode by Ellipsometry and Raman Spectroscopy. The Case of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Based Anode.

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Lithium titanium oxide thin films are increasingly popular anode materials for applications in lithium-ion microbatteries and hybrid supercapacitors, due to their improved safety, cost and cycle lifetime. Nanoengineering of their stoichiometry and crystallinity can modify their lithium-site occupancy and stretch the materials specific capacity. So far, research efforts have mainly focused on the pure spinel phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and only a small fraction is dedicated to a broader spectrum of titanium-based metal oxide thin films. In this work, Pulsed Laser Deposition (PLD) is used by alternating LTO and Li_2O ablations to create a wide landscape in the composition of titania-based micro-anodes. Their structures are studied by Raman Spectroscopy (RS) and their performances by In Operando Spectroscopic Ellipsometry (SE).

Key words

microbatteries, lithium titanium oxide, pulsed laser deposition, spectroscopic ellipsometry, Raman spectroscopy



Introduction

The expected growth in the number of sensor nodes and other Internet-of-Things devices in the next decade imposes the development of sustainable micro-power

sources, whose manufacturing should preferably be compatible with Silicon processing methods for economic reasons. Titania-based electrodes are one among other alternative to metal Li matching these conditions, the most studied one being the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The insertion

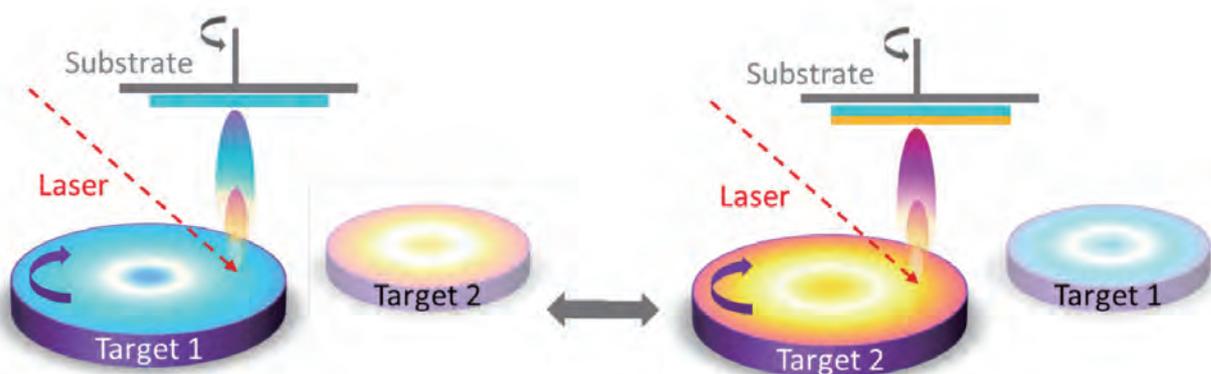


Figure 1 Multi-layer deposition in the PLD. A full cycle is completed after the ablation of each target with a fixed number of pulses. Two targets are alternated repeatedly in cycles until the desired film thickness are reached.

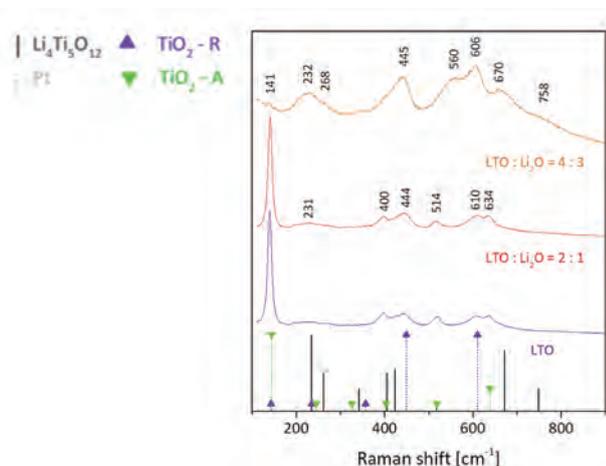


Figure 2 Raman spectra of LTO thin films with different amounts of additional Li_2O . Growth conditions are indicated with the deposition pulse ratio LTO : Li_2O . Raman references for TiO_2 Rutile and Anatase are from literature.^[1]

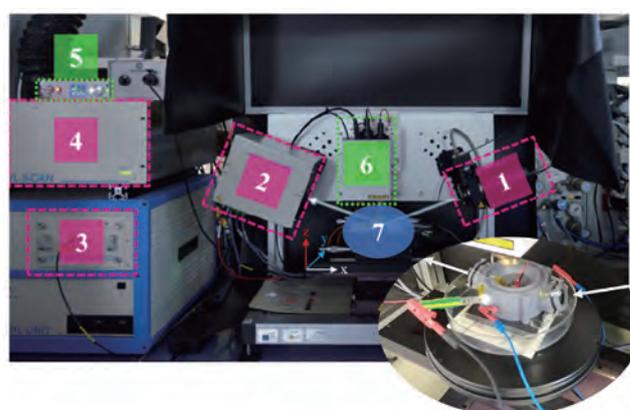


Figure 3 UVISEL (red) and Raman Superhead (green): 1: Polarizer, 2: Modulator, 3: Source, 4: Detector, 5: Laser, 6: Raman optics, 7 and insight: electrochemical cell for in operando studies.

of extra lithium into the LTO structure would have a large impact on the accessible capacity of the battery assuming every Ti^{4+} is reduced to Ti^{3+} . Typically, LTO is used in the 1.5-3 V range because discharging to 0 V was reported to be unfavorable for the Li-ion diffusion beyond $\text{Li}_7\text{Ti}_5\text{O}_{12}$. Deeper insight about the structural consequences of cycling such alloys to very low potentials is one target of this work.

Thin film fabrication

The concept of the multi-layer PLD deposition with two different alternating targets is schematically shown in Figure 1.

In this work, the targets were $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_2O . Depositions have been carried out on 1cm^2 Si wafer previously covered with Pt layer to provide electrical accessibility of the anode thin films.

Analyzing tools, HORIBA Raman SuperHead and UVISEL Spectroscopic Ellipsometer

Raman spectra were collected using a HORIBA Raman SuperHead, coupled to an iHR320 monochromator equipped with a Sincerity CCD detector and a laser at $\lambda = 532\text{ nm}$.

Figure 2 illustrates the Raman spectra of structural evolutions of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel phase upon a staggered lithium addition. It reveals the main presence of anatase and rutile phases and no evidence of spinel LTO for lower lithium contents. With increasing the Li_2O addition, the anatase signal vanishes and some vibrational modes of LTO become evident. Rutile appears to be present at any lithium concentration, which was confirmed by X-ray diffraction.

Literature has reported that nano-scaled TiO_2 shapes have increased the capabilities of lithium uptake for titania-based anodes and promoted their electrochemical

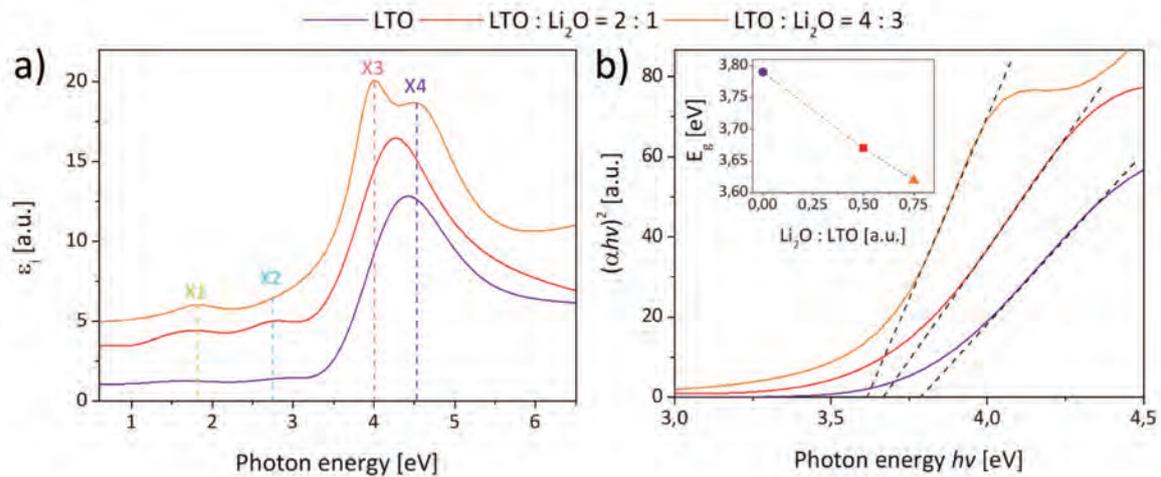


Figure 4 Imaginary part of the permittivity ε_2 for LTO thin films for different LTO : Li₂O ablation ratios in (a). Vertical dashed lines indicate significant changes in absorption bands upon lithium addition, marked and color-coded according to X1 – X4. In (b) the evolution of the band gap for different LTO : Li₂O pulse ratio (as inset) are shown.

activity and performance in batteries^[2-5]. While this report is being written, the scanning probe microscope for characterization of such nano objects in operando (HORIBA Electrochemical Tip Enhanced RS) is running first experiments at IREC.

UVISEL phase modulation ellipsometer by HORIBA Scientific was used for optical characterization of the samples. The setup, combined with Raman Superhead is illustrated on Figure 3.

While Raman informs on the structural properties, UV-Visible ellipsometry reveals thickness and optical properties of thin films, the latter correlated to their electrical properties. Figure 4 displays optical properties as imaginary part of dielectric function in a) and bandgap deduced from Tauc plot in b) for LTO with different Li concentrations.

Absorption bands (X1 – X4) occurring in Figure 4 (a) can be attributed to interactions between the electronic states of the Li_{2s} orbital and the hybridized molecule orbitals of O_{2p} and Ti_{3d} forming the TiO₆ octahedra^[6]. The evolution of these bands is highly correlated to Li diffusion modes through the film and can be controlled by in operando ellipsometry.

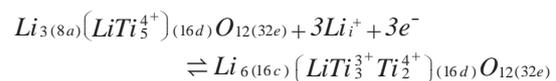
Let us first state that a detailed ex situ SE study of the optical properties of LTO:Li₂O composites preceded the operando analysis. It allowed composition analysis by means of usual ellipsometric modeling of effective medium. Then, optical properties for layer evolution during cycling was compared to Figure 4, depending on the Li₂O content and optical absorption bands could be assigned to specific Li ions energetic levels (and corresponding occupancy inside the spinel structure) according to literature. These results set a solid ground for further

SE analysis in a dynamic environment.

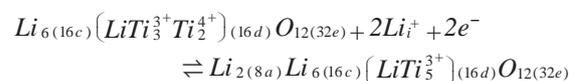
Electrochemical performance of the films, discharge to very low potential

The electrochemical experiments have been achieved in 1 M LiPF₆ electrolyte and lithium acting as counter and reference electrode in a classic three-electrode setup.

From theory and literature^[7,8], the standard reaction potential for the intercalation of three Li⁺ into spinel Li₄Ti₅O₁₂ is known to be 1.5 V vs. Li/Li⁺ and follows a mechanism expressed in the following equation:



Under continued discharge below 0.6 V vs. Li/Li⁺, two additional lithium ions can be intercalated at tetrahedral 8a sites in Li₇Ti₅O₁₂ by reducing two remaining Ti⁴⁺ as described in the different following equation:



Cyclic voltammograms (CV) and chronopotentiometry measurements have been collected at different current densities in the potential range of 0.3 – 3.5 V vs. Li/Li⁺ and are shown in Figure 5 for different LTO : Li₂O films. For the calculation of specific capacities, the thicknesses determined by SE have been implemented.

Constant current charge and discharge (chronopotentiometry) curves in Figure 5 (b, d, f) exhibit a steady increase in the specific capacities, strongly correlated to the addition of Li₂O during deposition. Excellent charge/discharge profiles are reached with well-defined plateaus for the

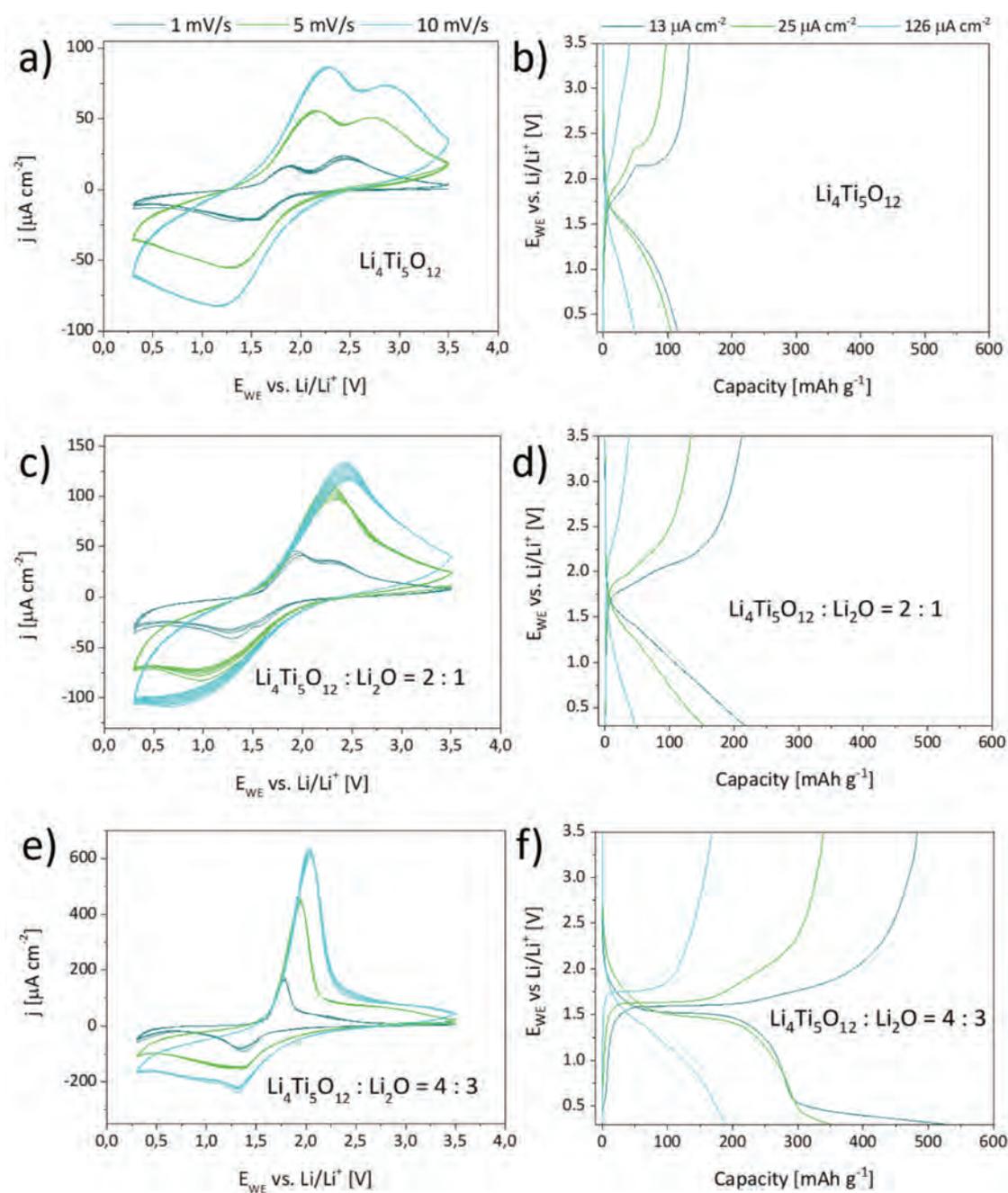


Figure 5 Cyclic voltammograms (left) and constant current charge/discharge curves (right) of LTO layers without additional Li_2O in (a,b) and with additional Li_2O in a pulse ratio of 2:1 (c,d) and 4:3 (e,f) for LTO : Li_2O , respectively. The electrochemical window ranges between 0.3 – 3.5 V vs. Li/Li^+ . The applied current densities are $13 \mu\text{A cm}^{-2}$, $25 \mu\text{A cm}^{-2}$ and $126 \mu\text{A cm}^{-2}$.

$\text{Ti}^{3+/4+}$ transition (Figure 5 (f)) under further Li_2O addition, resulting in the extraordinary high specific discharge capacity of 298 mAh g^{-1} at 0.5 V vs. Li/Li^+ for the 4:3 ablation ratio. An additional plateau appears to begin below 0.5 V vs. Li/Li^+ , which may be attributed to the extra lithium uptake described earlier by Yi et al.^[9] under the occupation of octahedral 16c and tetrahedral 8a sites.^[10]

To obtain further insights about phenomena taking place at these very low potentials, we performed operando SE during the first cycle on a pristine film with high Li-content (LTO: Li_2O ratio of 4:3).

The first output of our SE analysis is the thickness evolution of the lithiated layer with time for the three different regimes (open symbols in Figure 6a referred to the right y-axis). Remarkably, the thickness evolution of the entire film follows quite accurately the shape of the charge injection for the 3 regimes, which indicates a change in volume upon lithiation/de-lithiation. In the imaginary part of the dielectric function, two distinctive features evolving with time are present in all cases, namely, a lower band at $\sim 1.5 \text{ eV}$, and a higher band at $\sim 4 \text{ eV}$ (Figure 6b).

For regime I, our data are in excellent agreement with

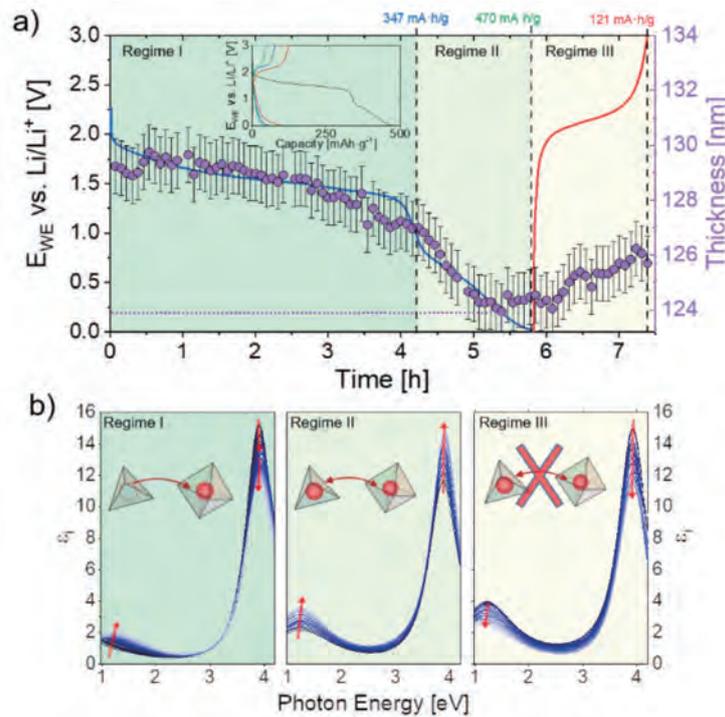


Figure 6 (a) Constant current charge and discharge curves collected under a current density of $3.6 \mu\text{A cm}^{-2}$ (0.17 C-rate) monitored by operando SE. The inset shows the charge-discharge profiles of the operando experiment as a function of capacity. Right-axis (purple) shows the thickness evolution of the entire film with time. (b) Optical absorption as a function of the photon energy corresponding to the three different regimes described in the main text (arrows indicate the evolution with time along the experiment). Insets represent the lithium occupancy in the LTO lattice.

previous experimental results and first principle calculations predicting that during lithiation from $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to $\text{Li}_7\text{Ti}_5\text{O}_{12}$, the intensity of the high energy band should decrease while the low energy band should increase^[11,12].

Beyond $\text{Li}_7\text{Ti}_5\text{O}_{12}$, i.e., regime II, the lithiation process is far less explored and, to the best of our knowledge, there is no experimental data to compare with. The increase in intensity of Dielectric function can be related to the role of oxygen in this regime upon further lithium insertions^[13-18]

Finally, during the charging process (regime III), both energy modes decrease their intensity. In terms of Li occupation, these observations indicate that only the Li inserted in regime II (at the 8a tetrahedral sites) was extracted upon charging, while the Li inserted in regime I (at 16c positions) could not leave the structure.

Overall, our results back up the relevant idea that the cycling range of LTO-based systems can be safely extended until the limit of ~ 0.2 V, which is beyond the typical value of 1V reported in the literature.

Conclusion

In this work, Pulsed Laser Deposition (PLD) was used by alternating LTO and Li_2O ablations to create a widelandscape in the composition of titania-based

micro-anodes.

The alternating ablation of LTO and Li_2O targets in the PLD provides a good strategy to fabricate highly performing anodes. Stable cycling was achieved down to potentials of 0.2 V. The structural consequences of cycling in the low potential region during the first discharge were studied using in operando SE. These results provide guidelines to extend the useful cycling range of LTO-based anodes to increase their competitiveness versus Li-metal anodes.

Note

This HORIBA readout contribution is a summarized version of the original paper “Safe extended-range cycling of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based anodes for ultra-high capacity thin film batteries” published in *Materials Today Energy* 25 (2022) 10 0979.

* Editorial note: This content is based on HORIBA’s investigation at the year of issue unless otherwise stated.

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