

Synthesis, Structural Characterization and Electrochemical Performance of In-situ Dual-Phase $\times \text{Li}_4\text{Ti}_5\text{O}_{12}/(1-x) \text{TiO}_2$ Nano-Composites for Li-ion Batteries

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Research Article

Received date: 07/12/2018

Accepted date: 18/12/2018

Published date: 25/12/2018

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Keywords: Electrochemical, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), Nano-Composites

ABSTRACT

In-situ dual phase $\times \text{Li}_4\text{Ti}_5\text{O}_{12}/(1-x)$ of LTO: TO due to varying heat treatments of the same dried gel with Li:Ti=4.5:6. Composites of LTO with TiO_2 showed reduced band gaps and predicted increased electronic conductivity of the samples for enhanced electrochemical performance as anodes of Li-ion batteries. XPS showed that in both LTO and LTO/TO nano-composites, Ti cations are in the oxidation state of 4+, indicating the charge neutrality and suitability for oxidation/reduction reactions during Li-ion intercalation/de-intercalation.

INTRODUCTION

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anodes are being proposed as alternative to widely used graphite-based anodes in commercial lithium-ion batteries for electric vehicles and energy storage systems as the latter ones suffer from dendritic growth of lithium on the anode surface at high current density because of their low lithium insertion potentials of 0.1V posing the risks of short circuits^[1-3]. In electrode materials, Lattice strains are the main reason for capacity fading over cycling. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ bears good cyclability as it maintains a stable structure (zero strain) during electrochemical cycling with a negligible change in the unit cell volume during Li intercalation and de-intercalation^[4,5]. LTO systems do not suffer from Solid Electrolyte Interface (SEI) formation owing to their high operating potential of 1.55 V as compared to reduction potentials of common electrolytes, which makes it suitable for high rate operations^[4,6,7] but still the rate performance is limited by their low electronic conductivity which hinders its commercialization^[8]. However, intensive research is being carried out to improve the conductivity by using suitable dopants 3 i.e Zn, Sr, V, Al, La etc.^[9-13], modifying the surface morphologies^[6,14,15], particle size reduction and making composites with metals or metal oxides like LTO-Au, LTO-Ag, LTO-CNTs, LTO-Cu, LiF/Ti, Fe/Li₃PO₄, LTO-Li₂TiO₃, LTO-Li₂Ti₃O₇. Composites of compounds i.e polycrystalline materials provide enhanced grain boundaries in the phase interfacial areas hence increasing the lithium storage as compared to the bulk LTO. Enriched grain boundaries in dual phase materials provide a large number of diffusion mediating defects which causes fast diffusivity hence increasing the rate performance. These dual phase materials introduce interfacial pseudo capacitive effects due to abundant phase interfaces. The pseudo capacitive effects provide fast lithium insertion extraction and additional electrochemical lithium storage at the interfacial sites hence improving the high rate capability and cycle stability. Various synthesis reports of LTO revealed that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ generally comprises of an extra phase of TiO_2 which can only be removed after long hours annealing at high temperatures. This causes aggregation of particles making large area inactive for electrochemical reactions. Various methods that have reported TiO_2 free $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Phase are not feasible for commercial scale production of the material. Interestingly, TiO_2 (Anatase) itself has a high electrochemical activity with a theoretical capacity of 330mAh which encourages the idea of optimization and utilization of dual phase of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ TiO_2 (Anatase or Rutile) instead of compromising on particle size in an attempt to remove it. Anatase- TiO_2 has been reported to have fast lithium diffusion owing to its large lattice space along c-direction (9.51 Å) as compared to Rutile- TiO_2 .

Currently, many groups have examined the effects of TiO₂ on the electrochemical behavior of LTO by synthesizing composites of LTO-Anatase TiO₂ and LTO-Rutile TiO₂. Besides, studies revealed that the second phase of TiO₂ also plays a role in preventing particle aggregation and grain growth, due to competitive crystallization between the two phases and the steric hindrance effect.

We have synthesized in-situ XLi₄Ti₅O₁₂/(1-x) TiO₂ (with x=0,30,40,60,70) nano-composites and pristine Li₄Ti₅O₁₂ (LTO) by sol-gel method and thoroughly studied the structural and electrochemical performance of the prepared samples. Though sol-gel is a simple and commercial scale method that gives superior homogeneity owing to molecular scale mixing and good crystallinity, its limitation of yielding extra phases of TiO₂ in Li₄Ti₅O₁₂ systems particularly at low temperatures, proves helpful in the *in-situ* composite formation of Li₄Ti₅O₁₂/TiO₂ (LTO/TO). Literature reports that *in-situ* composites of compounds enhance the electrochemical reaction kinetics of the electrodes in Li-ion batteries, whereas, mechanical mixtures of LTO and TiO₂ create high internal resistance in the cell due to increased charge transfer resistance within the particles. This work is devoted to the comparative study of XLi₄Ti₅O₁₂/(1-x) TiO₂ nano-composites ie with varying weight% of both Li₄Ti₅O₁₂ and TiO₂.

EXPERIMENTAL

The calculated amount of titanium butoxide was added in the mixture of ethanol absolute and acetic acid (mixture volume ratio of 75:25%), followed by stirring for 2.5 hours. Here acetic acid is a chelating agent which forms a homogeneous gel that gives rise to narrow particle size distribution and good dispersion after heat treatment. A weighed quantity of lithium acetate was dissolved in distilled water, added to the above-prepared mixture and stirred for 2.5 hours. To control the particle size to nanometers scale and prevent aggregation of particles polyvinyl alcohol (PVA) solution was added as a surfactant. 0.25 g of PVA was added in 20 ml distilled water and stirred vigorously at 80°C to get a clear solution. This solution was added in the prepared gel and stirred. The resulting gel was dried at 120°C to evaporate the organic solvents and heated at 350°C in air atmosphere until PVA was decomposed and carbon content was burnt yielding white powder **Table 1**. The white powder with a molar ratio of Li:Ti=4.5:5 was calcined at 8000°C for 5h to yielded pure Li₄Ti₅O₁₂ powder. Powder with molar ratio Li:Ti=4.5:6 yielded 40% LTO/60%ATO on calcining at 600°C/5hrs, 30%LTO/70%ATO at 600°C/10hrs, 60%LTO/40%ATO at 700°C/5hrs and 70% LTO/30% RTO at 800°C/5 hrs. We can see that higher temperature synthesis (800°C) of LTO/TO composites gives rise to the rutile phase of TiO₂ instead of anatase.

Table 1. Molar ratios of Li: Ti, heating temperature/time and crystallite size of the samples.

Li:Ti molar ratio	Sample	Temperature	Time (hours)	Crystallite size (nm)
4.5:5	Pristine LTO	800°C	5h	53
4.5:6	40% Li ₄ Ti ₅ O ₁₂ /60% ATO	600°C	5h	29
4.5:6	30% LTO/70% ATO	600°C	10h	30
4.5:6	60% LTO/40% ATO	700°C	5h	48
4.5:6	70% LTO/30% RTO	800°C	5h	55

CHARACTERIZATION

The crystal structure of the samples obtained was characterized using powder X-Ray Diffraction (XRD) using a PANalytical X'Pert Pro MPD diffraction instrument with Cu Ka1 radiation (λ=0.154056 nm) in the 2θ range of 10 to 90 with a scan rate of 0.02° per minute. X-ray Photoelectron Spectroscopy (XPS) measurements were carried out using a Kratos XSAM 800 instrument with Al Ka X-ray radiation during XPS analysis. Scanning Electron Microscopy (SEM) was performed using a Jeol JSM-5910LV to examine the morphology of the samples. The chemical composition and phase formation of the samples was determined by Thermogravimetric Analysis (TGA). Diffused Reflectance Spectroscopy (DRS) was studied to estimate the variation in the electronic structures of the LTO/TO composites in comparison with pristine LTO. The electrochemical performance of the synthesized powder was evaluated by galvanostatic charge-discharge testing against lithium as a counter electrode. The electrode was prepared by a slurry coating procedure. The slurry was prepared by grinding and sonicating 80 wt% Li₄Ti₅O₁₂, 10 wt % acetylene black and 10 wt% polyvinyl ideneflouride PVDF binder in N-methyl pyrrolidinone solvent. Binder was first dissolved in the solvent by magnetic stirring and heating at 80°C. Lithium titanate was dispersed in N-methyl pyrrolidinone by ultra sonication. Binder solution was added slowly and the mixture was further sonicated to get a uniform slurry. This slurry was uniformly coated on copper foil current collector by brush coating. Several coats were applied to get 3 mg/cm² loading. The electrodes were dried in vacuum oven at 100°C for 12 hours. 2025 type coin cell was fabricated in argon-filled glove box using polyethylene as sea parator and 1M LiPF6 in Ethylene carbonate/Dimethyl carbonate (1:1) as elthe ectrolyte. The electrochemical charge-discharge tests of the samples were performed in the voltage range of 1.0-2.5 V **Figure 1**.

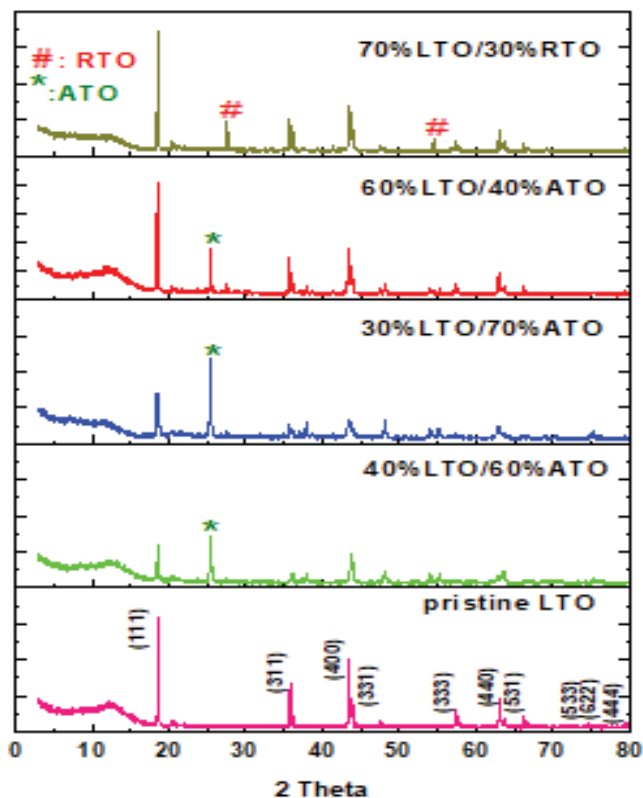


Figure 1. XRD patterns of (a) Pristine LTO, (b) 40% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /60% ATO (c) 30% LTO/70% ATO (d) 60% LTO/40% ATO (e) 70% LTO/30% RTO.

RESULTS AND DISCUSSION

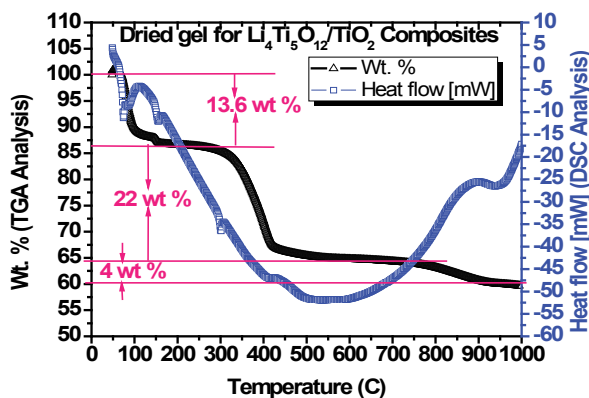


Figure 2(a). TGA/DSC curves of dried gel with Li:Ti molar ratio of 4.5:6 for LTO/TO composites.

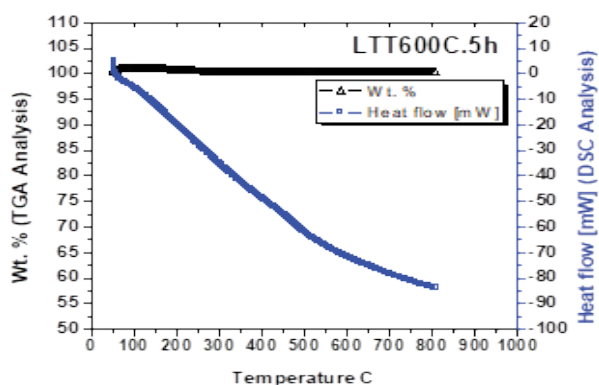


Figure 2(b). TGA/DSC curves of LTO/TO composite prepared at the minimum temperature/time of 600°C/5h.

TGA of dried gel with Li:Ti molar ratio of 4.5:6 for LTO/TO composites and LTO/TO composite prepared at the minimum

temperature/time of 600°C /5h are shown in **Figure 2a and 2b** respectively. Initial weight loss of 13 wt% from 25°C to 350°C is due to evaporation of water and organic solvents used in the sol-gel synthesis. 22 wt% loss from 350°C to 500°C is attributed to burning of carbon content of decomposed PVA added for limiting the particle size. No significant weight loss appears on heating above 500°C as stable phases of TiO_2 and $Li_4Ti_5O_{12}$ are formed indicating straightening of TGA curve. However, small weight loss of 4% gradually happened as heated to 850°C resulting from the decomposition of Li_2CO_3 . DSC curve shows exothermic peaks around 100-150°C, 180°C, and 300°C owing to evaporation of water/ethanol, acetic acid and a carbon content from the gel. A wide endothermic peak appeared around 500°-800°C which indicated the formation of *in-situ* LTO/TO phases **Figure 3**.

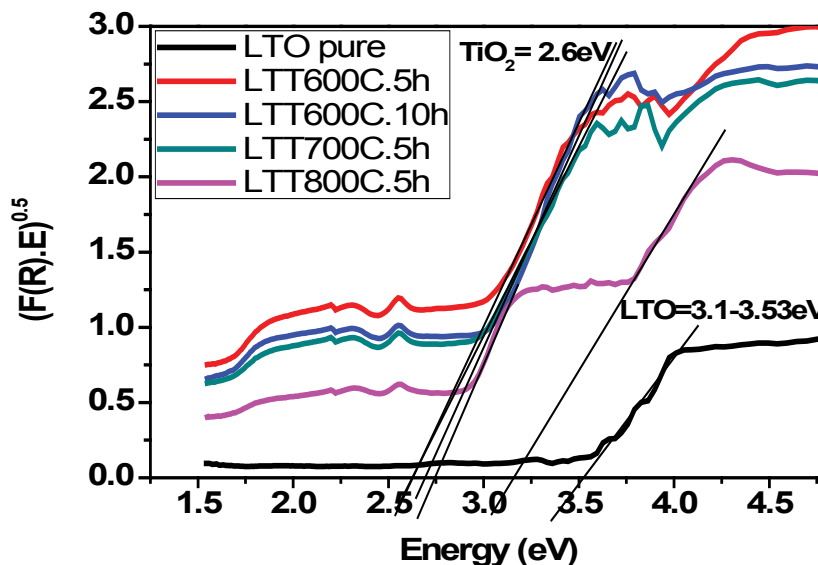


Figure 3. Band gaps of pristine LTO and LTO/TO composites.

DRS of all the samples were studied and band gaps were calculated using Kubelka Munk function to estimate the variations in the electronic structures with the varying LTO/TO compositions. Both LTO and TO have a direct band gap. Band gap of pure LTO was found to be 3.5 eV showing an insulator like behavior (predicting poor electronic conductivity). All LTO/TO composites showed band gaps of both phases ie LTO at 3.1eV (insulator like) and TiO_2 at 2.6 eV (conductor like behavior). Bandgap measurements predict that making composites of LTOs with TiO_2 increases the electronic conductivity of LTOs which will enhance the electrochemical performance of anodes.

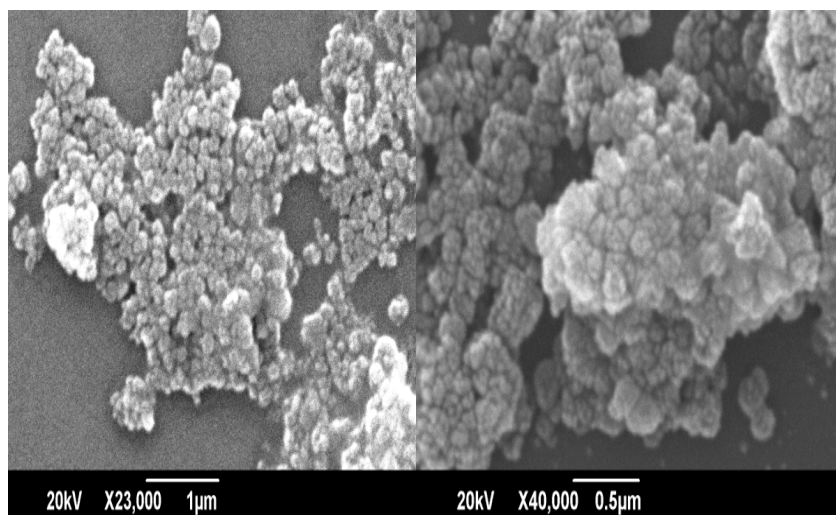


Figure 4. Scanning electron Micrographs of (a) pristine LTO (calcined at 800°C/5h) and (b) LTO/TO composite (calcined at 600°C/5h).

Scanning electron micrographs **Figure 4** shows average particle size less than 100 nm for pristine LTO (calcined at 800°C/5h) and less 50 nm for LTO/TO composite (calcined at 600°C/5h). This is consistent with the average crystallite sizes of the samples calculated from Scherrer’s formula, which suggests that PVA surfactant helped in preventing aggregation of particles and restricted the particle growth to less than 100 nm even at 800°C.

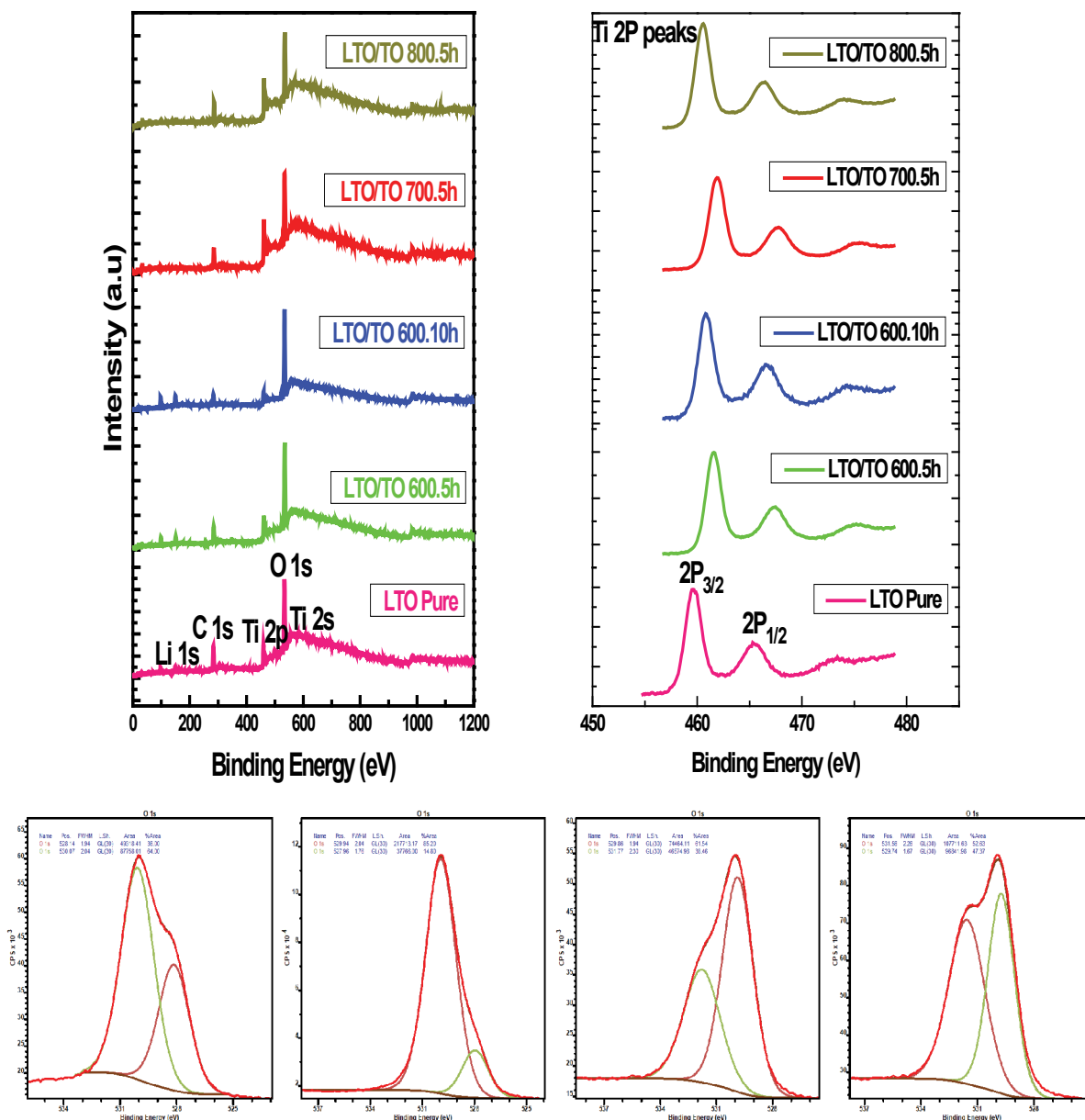


Figure 5. (a) Survey scan XPS spectra, (b) high-resolution spectra of Ti2p and (c) high-resolution spectra of O1s of pristine LTO and LTO/TO composites.

XPS was carried out to obtain information about the surface structure of LTO and LTO/TO samples, and their high-resolution Ti2p and O1s binding energy regions are shown in **Figure 2**. Survey scans of pristine LTO and all the LTO/TO composites were recorded to detect all the elements present. The binding energies were calibrated based on the graphite C1s peak at 284.5 eV. Peaks at 464.4eV and 458.7eV were attributed to Ti2p1/2 and Ti 2p3/2 and indicated that oxidation states of the Ti were 4+ in both LTO and LTO/TO composites **Figure 5**. This result is in good agreement with the value of the valence of titanium in both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 . The CASA XPS program with a

Gaussian-Lorentzian mix function and Shirley background subtraction were employed to de-convolute the O1s spectra of the samples. O1s peaks at 530.2 eV were attributed to O_2 associated with Ti-O bond in the synthesized materials. O1s peaks at 531.8 eV are linked to the O_2 and H_2O adsorbed on the surface of the materials.

CONCLUSION

In-situ dual phase $\text{xLi}_4\text{Ti}_5\text{O}_{12}/(1-x)\text{TiO}_2$ (with $x=0,30,40,60,70$) nano-composites and pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were synthesized by sol-gel. TGA/DSC studies of dried uncalcined gel showed the formation of LTO/TO phases around 600°C to 800°C. Calcined powder at 600°C/5h showed the structural stability of the LTO/TO phase at heat treatment of up to 800°C. XRDs confirmed well crystalline phases of all the samples with varying wt%. of LTO:TO due to varying heat treatments of the same dried gel with Li:Ti=4.5:6. Composites of LTO with TiO_2 showed reduced band gaps and predicted increased electronic conductivity of the samples for enhanced electrochemical performance as anodes of Li-ion batteries. XPS showed that in both LTO and LTO/TO nanocomposites,

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