INTRODUCTION

Li$_4$Ti$_5$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. Li$_4$Ti$_5$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 [1,6,7] 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 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/Li$_3$PO$_4$, LTO-Li$_2$TiO$_3$, LTO-Li$_2$Ti$_3$O$_7$. Composites of compounds ie 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 Li$_4$Ti$_5$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 Li$_4$Ti$_5$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 Li$_4$Ti$_5$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$_2$.

ABSTRACT

In-situ dual phase X Li$_4$Ti$_5$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.
Currently, many groups have examined the effects of TiO$_2$ on the electrochemical behavior of LTO by synthesizing composites of LTO-Anatase TiO$_2$ and LTO-Rutile TiO$_2$. Besides, studies revealed that the second phase of TiO$_2$ 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 XLi$_4$Ti$_5$O$_{12}$(1-x) TiO$_2$ (with x=0,30,40,60,70) nano-composites and pristine Li$_4$Ti$_5$O$_{12}$ (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 TiO$_2$ in Li$_4$Ti$_5$O$_{12}$ systems particularly at low temperatures, proves helpful in the in-situ composite formation of Li$_4$Ti$_5$O$_{12}$/TiO$_2$ (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 TiO$_2$ 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 XLi$_4$Ti$_5$O$_{12}$(1-x) TiO$_2$ nano-composites ie with varying weight% of both Li$_4$Ti$_5$O$_{12}$ and TiO$_2$.

**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 800°C for 5h to yielded pure Li$_4$Ti$_5$O$_{12}$ 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 TiO$_2$ instead of anatase.

<table>
<thead>
<tr>
<th>Li:Ti molar ratio</th>
<th>Sample</th>
<th>Temperature</th>
<th>Time (hours)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5:5</td>
<td>Pristine LTO</td>
<td>800°C</td>
<td>5h</td>
<td>53</td>
</tr>
<tr>
<td>4.5:6</td>
<td>40% Li$_4$Ti$<em>5$O$</em>{12}$/60% ATO</td>
<td>600°C</td>
<td>5h</td>
<td>29</td>
</tr>
<tr>
<td>4.5:6</td>
<td>30% LTO/70% ATO</td>
<td>600°C</td>
<td>10h</td>
<td>30</td>
</tr>
<tr>
<td>4.5:6</td>
<td>60% LTO/40% ATO</td>
<td>700°C</td>
<td>5h</td>
<td>48</td>
</tr>
<tr>
<td>4.5:6</td>
<td>70% LTO/30% RTO</td>
<td>800°C</td>
<td>5h</td>
<td>55</td>
</tr>
</tbody>
</table>

**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 (l=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% Li$_4$Ti$_5$O$_{12}$, 10 wt % acetylene black and 10 wt% polyvinylidene fluoride 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/cm$^2$ 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 electe electrolyte. 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% Li$_4$Ti$_5$O$_{12}$/60% ATO (c) 30% LTO/70% ATO (d) 60% LTO/40% ATO (e) 70% LTO/30% RTO.

RESULTS AND DISCUSSION

![Graph showing TGA and DSC analysis](image)

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$_4$Ti$_5$O$_{12}$ 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$_2$CO$_3$. 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 500ºC-800ºC which indicated the formation of in-situ LTO/TO phases Figure 3.

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.

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.
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 Li4Ti5O12 and TiO2. 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 O2 associated with Ti-O bond in the synthesized materials. O1s peaks at 531.8 eV are linked to the O2 and H2O absorbed on the surface of the materials.

CONCLUSION

In-situ dual phase XLi4Ti5O12/(1-x) TiO2 (with x=0,0.30,40,60,70) nano-composites and pristine Li4Ti5O12 were synthesized by sol-gel. TGA/DSC studies of dried uncalcined gel showed the formation of LTO/TO phases around 600ºC to 800ºC. Calcined powder at 600ºC/5h showed the structural stability of the LTO/TO phase at heat treatment of up to 800ºC. 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 TiO2 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,
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.

REFERENCES


