

ICONN 2015 [4th - 6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Time Dependent Preparation of Electrochemically Active Lithium Titanate Anode for Lithium Ion Batteries

Marie Rose Jesina Delavictoire¹, T. Manovah David¹, D. Muthu Gnana
Theresa Nathan¹, Mary George², D. Sangeetha³ and P. Sagayaraj^{1*}

¹Department of Physics, Loyola College (Autonomous), Chennai-600034, India

²Department of Chemistry, Stella Maris College (Autonomous), Chennai-600086, India

³Department of Mechanical Engineering, Anna University, Chennai- 600025, India

Abstract: Lithium titanate proves to be an important anode material for Li-ion batteries. Its unique characteristics make it a promising material for portable electronic devices, hybrid and non hybrid electric vehicles. An efficient and facile solvothermal method has been employed in this paper to prepare spinel structured lithium titanate nanostructures at different durations of time. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles were prepared from reaction between TiO_2 and $\text{LiOH}\cdot\text{H}_2\text{O}$ in water/ethanol mixture with subsequent heat treatment. As a lithium intercalation material, high crystallinity is important for $\text{Li}_4\text{Ti}_5\text{O}_{12}$. X-ray diffraction analysis (XRD) of the synthesized nanoparticles showed good crystallinity and phase purity which is important for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as a lithium ion intercalation anode material. The morphology and electrochemical performance is found to be strongly dependent on the experimental conditions. The morphology of the particles observed from field emission scanning electron microscope (FESEM) was found to be rod-like, cubical and spherical in shape subjected to different time durations. The transmission electron microscope (TEM) analysis supports the morphological structures observed from FESEM. Also the chemical composition of the material analyzed from energy dispersive X-ray analysis (EDX) confirms the presence of Ti and O with their respective ratios. The electrochemical test indicates good electrochemical performance of the lithium titanate nanoparticles which finds its application in energy storage systems.

Keywords: Time Dependent Preparation, Electrochemically Active Lithium Titanate Anode, Lithium Ion Batteries.

Introduction

Rechargeable batteries play an important role in storage and conversion of electrochemical energy. The lithium ion batteries (LIBs) prove to be a good candidate for energy storage applications like communication and consumer electronic devices, electric power tools, hybrid, plug-in and electric vehicles¹. However, considering the safety issues, LIBs are found to be slightly poor. Therefore, to overcome this set back certain electrode materials are favored. Among them, spinel structured lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) is being established to be a promising anode for LIBs through intercalation and deintercalation mechanism. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is considered

to be a material with zero-strain due to its structural stability during Li-insertion and extraction process². Moreover, the material possesses stable operating voltage of 1.55 V and excellent reversibility. In addition, the high lithium ion mobility of lithium titanate gives high rate performance compared to other anode materials³. Various morphologies of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 such as nanotubes⁴, nanosheets⁵ and nanowires⁶ synthesized by different methods have been previously studied for lithium-ion battery applications. In this article, we report the synthesis of nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ via a simple solvothermal route for different durations of time. The crystallinity and morphological changes corresponding to different experimental conditions are observed. The cyclic voltammetry behavior of the as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanostructures is also measured.

Experimental

The preparation of lithium titanate nanoparticles was prepared using TiO_2 and $\text{LiOH}\cdot\text{H}_2\text{O}$ in ethanol-water solvent mixture. 0.4 g of AR grade TiO_2 powder was added to LiOH solution under magnetic stirring. After 30 min of stirring, the suspension was transferred into a Teflon-lined stainless steel autoclave in which the reaction took place for different durations of time (12 h, 24 h and 36 h) corresponding to a temperature of 150 °C. The resultant powder was washed with distilled water and dried at 60 °C for 15 h and finally annealed at 500 °C for 3 h to obtain spinel structure. The samples were labeled as LTO-12, LTO-24 and LTO-36 corresponding to the reaction time 12 h, 24 h and 36 h, respectively.

Results and Discussion

Powder X-ray diffraction pattern of the as-obtained $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are shown in Fig.1. The diffraction peaks were compared and indexed to cubic spinel structure with standard data (JCPDS no. 49-0207)⁷. As seen from figure, due to high annealing temperature, well sharpened peaks are observed indicating good crystallinity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanostructures⁸. This accounts for the ordering of local structure and release of lattice strain. However, there is also a small amount of anatase TiO_2 in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ⁹. In Fig. 1(a), when the reaction proceeds for a duration of 12 h, we observed well resolved peaks corresponding to ($2\theta = 18.63^\circ$, $2\theta = 37.1^\circ$, $2\theta = 43.7^\circ$ and $2\theta = 63.3^\circ$) among which the predominant growth along (400) plane can be ascribed to the one dimensional growth of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanostructure. Also diffused scattering is observed for some values of scattering angles which are attributed to an amorphous phase. Fig. 1(b, c) show the diffraction pattern of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ formed after 24 h and 36 h of reaction time. Here, besides the peaks already obtained for a reaction duration of 12 h, an additional peak corresponding to ($2\theta = 62.5^\circ$) is obtained showing increased growth along the different planes which leads to the formation of different $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanostructures. There is a relative change in the intensities of diffraction peaks with corresponding changes in the reaction time. The mean size of nanocrystallites found using Debye-Scherrer formula for all three nanostructures is 50 nm, 35 nm and 25 nm

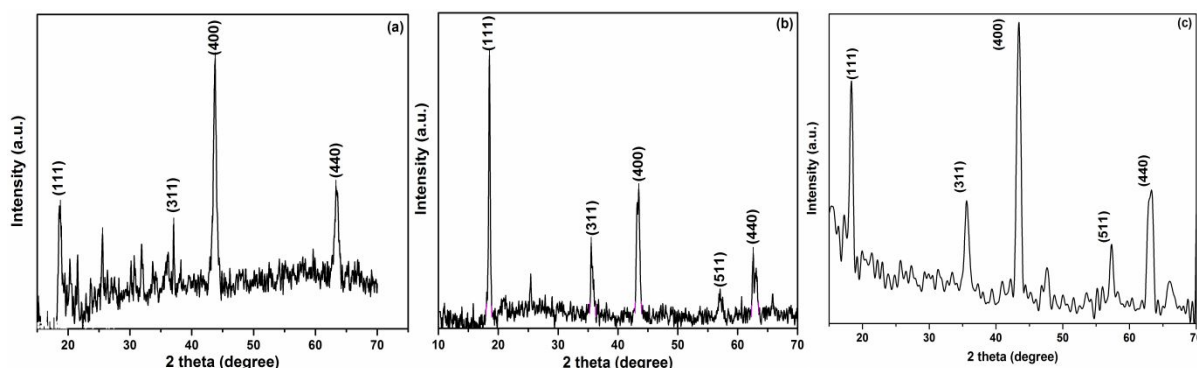


Fig.1 XRD patterns of LTO-12, LTO-24 and LTO-36

Fig. 2 shows the morphologies of the various samples analyzed from FESEM. The morphology of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles is observed to change with increase in reaction time. As the reaction proceeds to 12 h (a), 24 h (b) and 36 h (c), three different nanostructures of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were observed. They were found to be rod-like, cubical and spherical in shape respectively. The surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles possessing a rod-like morphology are seen to be rough with randomly attached nanoparticles¹⁰. The rods look oriented in different directions. The average size of nanorod was found to be 250 nm. As seen in Fig. 2b, well defined cube shaped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles are formed with their size about 105 nm. There also seems to be some agglomerations¹¹. The increase in reaction time to 36 h has led to the formation of nanospheres which are monodispersed having uniform size around 40 nm with rather smooth surface¹².

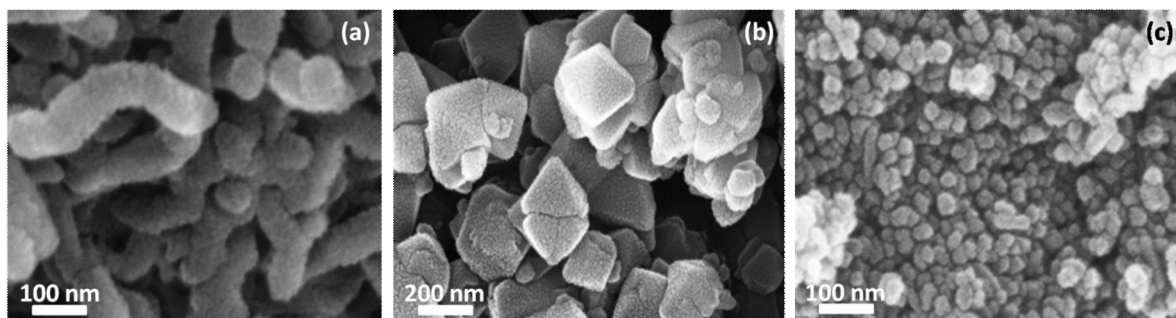


Fig. 2 FESEM images of LTO-12, LTO-24 and LTO-36

The transmission electron microscopy was used to further investigate the microstructure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanostructures. The structure and size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanostructures as seen in Fig. 3 are in good agreement with those seen from FESEM analyses. The nanorods and nanocubical structure are well observed and confirmed. The smooth surface of nanosphere is clearly seen and seems to be densely packed structure¹². In addition, the EDX analyses the purity of materials and stoichiometric ratios of elements present. Fig.4 shows the EDX spectra of all three $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanostructures. The atomic % and presence of Ti and O are observed from which their respective ratios are known that are consistent with the experimental precisions. As lithium is not in the EDX detection range, the content of lithium cannot be determined using EDX¹³.

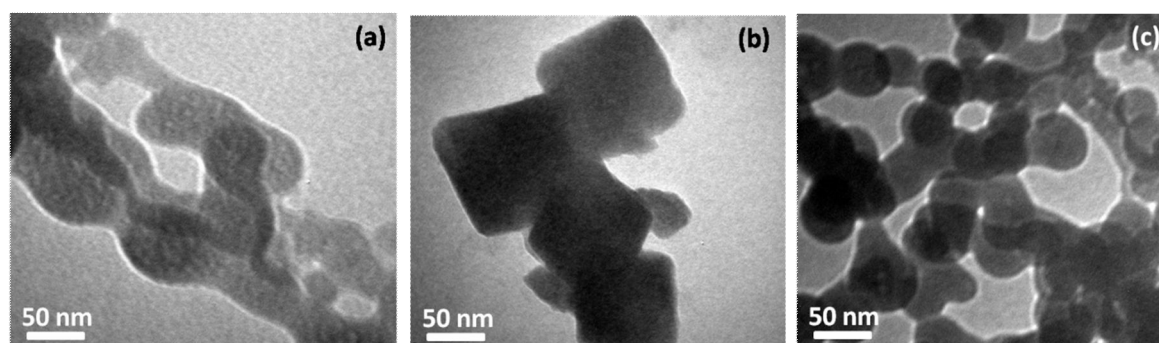


Fig.3 TEM images of LTO-12, LTO-24 and LTO-36

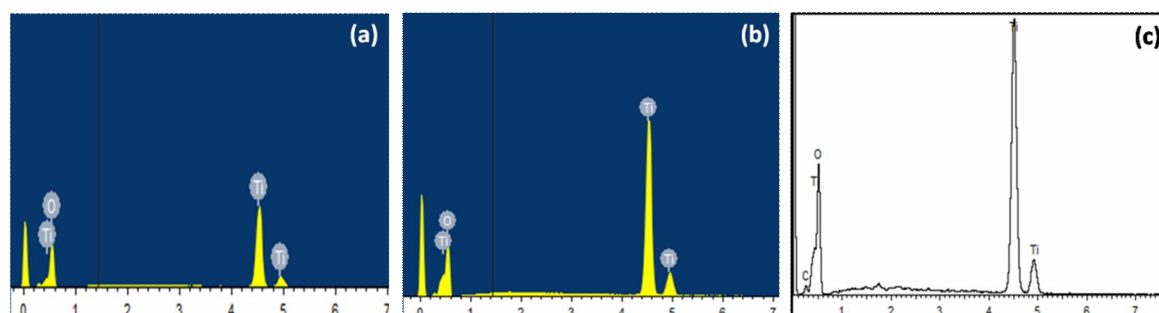


Fig.4 EDX pattern of LTO-12, LTO-24 and LTO-36

The electrochemical behavior of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is characterized by cyclic voltammograms (Fig.5). A three electrode system using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as working electrode, Ag/AgCl as reference electrode and platinum wire as counter electrode with H_2SO_4 as the electrolyte was used. The cyclic voltammetry curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was scanned from -0.1 V to 1.5 V at a scan rate of 20 mV/s. Fig.5 shows the cyclic voltammetry measurements for different cycles at a constant scan rate. A pair of redox peaks is seen corresponding to oxidation and reduction process that takes place in $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The cathodic peak occurs at about 0.3 V and anodic peak at about 0.4 V for all the three nanostructures. Due to the increased scan rate the cathodic peaks are overlapped while the anodic peaks are well retained indicating good kinetic process¹⁴. There is a difference between the oxidation peak and reduction peak which may be caused by the deposition time or electrochemical polarization. This also indicates some irreversible capacity loss in the electrode reaction process¹⁵. The broad peaks indicate high degree of crystallinity giving rise to a more reversible system and improved kinetic performance of the

electrode¹⁶. As the relation between peak currents and scan rates can be associated with the electrochemical reaction characteristics, the broadening of CV curves are attributed to the increased scan rate¹⁷.

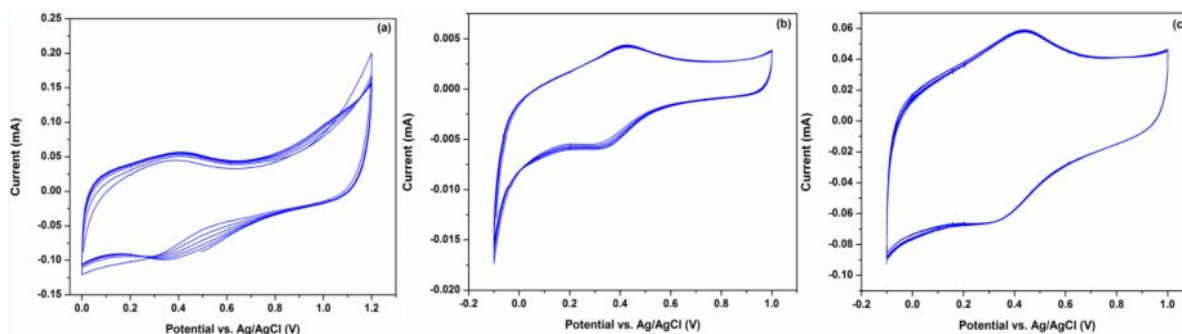


Fig. 5 Cyclic voltammograms of LTO-12, LTO-24 and LTO-36 at a scan rate of 20 mV/s for the initial 7 cycles

Conclusion

In summary, the phase composition, morphological changes and electrochemical property of different $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanostructures have been successfully synthesized and studied. The experimental condition of time duration plays a vital role in the formation of nanorods, nanocubes and nanospheres. The high annealing temperature leads to better crystallinity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Cyclic voltammograms measurements indicate that the electrochemical reaction of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was a reversible redox reaction with good reversibility and cyclic performance, reducing the overall reaction resistance and hence makes it a promising material for energy storage applications.

Acknowledgments

The authors acknowledge DST- SERB (SR/S2/LOP-29/2013) for providing experimental facilities at Department of Physics, Loyola College, Chennai.

References

1. Gao X.P. and Yang H.X., Multi-electron reaction materials for high energy density batteries, *Energy Environ. Sci.*, 2010, 3, 174-189.
2. Cheng F., Tao Z., Liang J. and Chen J., Template-directed materials for rechargeable lithium-ion batteries, *Chem. Mater.*, 2008, 20, 667-681.
3. Tang F., Yang L., Fang S. and Qiu Z., $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Hollow microspheres assembled by nanosheets as an anode material for high-rate lithium ion batteries, *Electrochim. Acta*, 2009, 54, 6244-6249.
4. Chen J., Yang L. and Tang Y., Electrochemical lithium storage of TiO_2 hollow microspheres assembled by nanotubes, *J. Power Sources*, 2010, 195, 6893-6897.
5. Wang Y.Q., Gu L., Guo Y.G., He X.Q., Tsukimoto S., Ikuhara Y. and Wan L.J., Rutile- TiO_2 nanocoating for a high rate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode of a lithium-ion battery, *J. Am. Chem. Soc.*, 2012, 134, 7874-7879.
6. Han B.H., Lee Y.W., Kim S.J., Hwang B.M., Kim S.B., Kim W.S. and Park K.W., Enhanced electrochemical properties of size controlled TiO_2 nanowire electrodes for lithium-ion batteries, *Int. J. Electrochem Sci.*, 2013, 8, 8264-8271.
7. Li J., Li X., Yang J., Geng D., Li Y., Wang D., Li R., Sun X., Cai M. and Verbrugge M.W., Microwave-assisted hydrothermal synthesis of nanostructured spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode materials for lithium-ion batteries, *Electrochim. Acta*, 2012, 63, 100-104.
8. Shen L., Yuan C., Luo H., Zhang X. and Xia Y., Facile synthesis of hierarchically porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microspheres for high rate lithium-ion batteries, *J. Mater. Chem.*, 2010, 20, 6998-7004.
9. Sheng Lin Y., Gong Duh J., Chiao Tsai M. and Young Lee C., Self-assembled synthesis of monodispersed mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ beads and their applications in secondary lithium-ion batteries, *Electrochim. Acta*, 2012, 83, 47-52.
10. Li Y., Pan G.L., Liu J.W. and Gao X.P., Preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanorods as anode materials for lithium-ion batteries, *J. Electrochem. Soc.*, 2009, 156, A495- A499.

11. Fattakhova D., Petrykin V., Brus J., Kostlanova T., Dedecek J. and Krtil P., Solvothermal synthesis and electrochemical behavior of nanocrystalline cubic Li-Ti-O oxides with cationic disorder, Solid State Ionics, 2005, 176, 1877-1885.
12. Cheng Chao Li, Qiu Hong Li, Li Bao Chen and Hong Wang T., A facile titanium glycolate precursor route to mesoporous Au/Li₄Ti₅O₁₂ spheres for high-rate lithium-ion batteries, Appl. Mater. Interfaces, 2012, 4, 1233-1238.
13. Li Hong Yang, Dong C. and Guo J., Hybrid microwave synthesis and characterization of the compounds in the Li-Ti-O system, J. Power Sources, 2008, 175, 575-580.
14. Lai C., Cao X.L., Yuan X.C., Wang Y.L. and Ye S.H., Enhanced reversible capacity of Li₄Ti₅O₁₂ coated TiO₂ nanocomposites as lithium- ion battery anodes, Solid state Ionics, 2013, 249-250, 151-157.
15. Cheng-min Shen, Xiao-gang Zhang, Ying- Ke Zhou and Hu-lin Li, Preparation and characterization of Li₄Ti₅O₁₂ by sol-gel method, Mater. Chem. Phys., 2002, 78, 437-441.
16. Yan-jing Hao, Qiong-yu Lai, Dong-qiang Liu, Zhi-ui Xi and Xiao-yang Ji, Synthesis by citric acid sol-gel method and electrochemical properties of Li₄Ti₅O₁₂ as anode material for lithium-ion battery, Mater. Chem. Phys, 2005, 94, 382-387.
17. Jeng-Yu Lin, Chao-Chia Hsu, Hsin-Ping Ho, She-huang Wu, Sol-gel synthesis of aluminum doped lithium titanate anode material for lithium ion batteries, Electrochim. Acta, 2013, 87, 126-132.
