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Synthesis, characterization and electrochemical performance of Yttrium metal ions doped Li₄Ti₅O₁₂nanoparticles for Lithium-ion batteries

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ABSTRACT

Spinel $Li_4Ti_5O_{12}(LTO)$ has been considered as a promising anode material in lithium-ion batteries (LIBs). But its disadvantage of low electronic conductivity limits its application to spread wide. This is overcome by dopingsome of the metal ions in the crystal lattice site of LTO. In this regardYttrium metal ions dopedLTO(Y_xLTO) nanoparticles were fabricated using solvothermal method from TiO₂, LiOH.H₂O and Y(NO₃)₃.6H₂O as reactants. The synthesized products were subjected to X-ray diffraction analysis (XRD) which showed no change in the crystal structure owing to the substitution of yttrium ions in the titanium site. Also the increased lattice constant, increases the rate of lithium ion diffusion in the electrode material. The morphological studies were performed from Field Emission Scanning Electron Microscopy (FESEM) and High Resolution Transmission Electron Microscopy (HRTEM) along with particle size analysis obtained for varying dopant concentrations. The vibrational groups present in LTO were also identified from Fourier Transform Infrared analysis (FT-IR). Moreover their lithiation–delithiation process were characterized by electrochemical measurement that showed Y_x LTOto exhibit good cyclic stability, enhanced cyclic behavior and performance in comparison to undoped Li₄Ti₅O₁₂ nanoparticles (NPs) that could serve as better anodes for LIBs.

Keywords: Lithium Titanate, nanoparticles, Anode material, Lithium-ion Batteries, Solvothermal method, Y-Doping, Electrochemical study.

INTRODUCTION

Lithium-ion batteries (LIBs) play a vital role in our daily life owing to its wide range of applications that include electrical, electronic, medical and other space requirements. Though various anode materials could effectively replace graphite, Lithium titanate ($Li_4Ti_5O_{12}$) proves to be a more suitable candidate due to the various advantages it offers in comparison to other electrode materials. $Li_4Ti_5O_{12}$ (LTO) possesses zero-strain insertion characteristics, which brings negligible volume change to the crystal structure. Further it has a flat operating voltage of 1.55 V vs. Li^+/Li and considered to be environmentally safe [1, 2]. Though it exhibits a theoretical capacity of 175 mAhg⁻¹, it still acts as a poor conductor in its de-lithiated form. Hence doping is one of the many possible ways available to improve its conductivity and thereby enhance its performance for LIBs application [3, 4].

The structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ belongs to a cubic system with space group $Fd\bar{3}m$, in which 75% of lithium ions are located on tetrahedral 8a sites, and 25% of lithium ions and Ti⁴⁺ions are randomly distributed at octahedral 16d sites.

All the oxygen ions occupy the 32e sites. Substitution of a small quantity of Ti^{4+} , Li^+ , or O^{2-} with other ions greatly improves the kinetics of the material in terms of capacity delivery, cycling life and rate capability [5]. It is already reported that doping Cr^{3+} , Co^{3+} , Ni^{2+} , La^{3+} , Y^{3+} , Zr^{4+} , Ru^{4+} , Mo^{4+} , Mn^{4+} , V^{5+} , Ta^{5+} , Nb^{5+} , or Sr^{2+} has resulted in improved rate capability mainly by enhancing the electronic conductivity [6, 7].

Very few research works are carried out by doping rare earth metal ions to LTO. In this paper, efforts are made to dope yttrium (Y^{3+}) ions into the lattice site of LTO through solvothermal method and its electrochemical and cyclic performances are studied. Further, the effect of doping on the structural, morphological and spectral behavior is also investigated in detail.

MATERIALS AND METHODS

2.1.Chemicals

LiOH.H₂O (99.995%) and Y (NO₃)₃.6H₂O (99.8%) were purchased from Sigma Aldrich. TiO₂ from Qualigens Fine chemicals Pvt. Ltd and Ethanol (99.9% AR) grade was purchased from Changshu Yangyuan Chemical Co., Ltd. They were used as received without further purification and all the reactions were performed using de-ionized water.

2.2.Synthesis

Yttrium was doped in LTO in the presence of mixed solvents of ethanol and water taken in equal volumes. 1.049 g of LiOH.H₂O was first dissolved in the solvent mixture. The Yttrium precursor was prepared with varying concentrations of 0.5 M, 1.5 M and 2.5 M % of Y (NO₃)₃.6H₂O dissolved in de-ionized water. To the dissolved LiOH aqueous solution, the above prepared yttrium solution was added and stirred. Further a certain amount of TiO₂ was added finally and stirred for about an hour. The resultant white precipitate was transferred to a Teflon-lined stainless steel autoclave of 200 ml capacity. The hydrothermal synthesis was carried out at 200 °C for 12 h. After naturally cooling the autoclave to room temperature, the precipitate was separated by centrifugation. The obtained product was washed with DI water and ethanol several times, followed by drying and calcination at 800 °C for 5 h. The Y doped LTO products were denoted as Y_{0.5}LTO, Y_{1.5}LTO and Y_{2.5}LTO corresponding to the doping percentages of yttrium. The same procedure was followed without the addition of Yttrium precursor to obtain pure LTO NPs.

2.3.Electrochemical measurement

The electrochemical performance of $Y_xLTO(x=0.5, 1.5 \text{ and } 2.5 \text{ M }\%)$ was tested in CR2032 coin-type cells. Typically, Y_xLTO , carbon black, and polyvinylidenefuoride (PVDF) with a weight ratio of 8: 1 : 1 were mixed in n-methyl pyrrolidinone (NMP) to form a uniform slurry, which was then coated onto a Cu foil substrate and dried in a vacuum oven at 120 °C for 12 h. Half-cells were assembled in a glovebox using Li foil as counter electrode, Celgardmicroporous polypropylene membrane 2300 was used as separator, and a mixture of 1 M LiPF₆ in ethylene carbonate and dimethyl carbonate (1 : 1 by volume) was employed as electrolyte. The electrochemical behavior was analyzed by making coin type half-cell in an Argon filled glove box. The performance of the cells was evaluated galvanostatically in the voltage range of 1– 2.5 V at a current rate of 0.1 C on a multi-channel battery cycler.

2.4 Characterization techniques

The as-synthesized Y_xLTO products are characterized to analyze their structural, morphological, spectral and electrochemical behavior. The crystal structure, phase and crystallinity of the material were confirmed from powder X-ray diffraction (XRD) analysis which was recorded by GE XRD 3003 TTX-ray diffractometer using monochromatic Nickel filtered Cu K_α ($\lambda = 1.5416$ Å) radiation in the 2 θ range of 10° to 70°. The morphology, average size and elemental composition of the as-prepared nanoparticles were determined from the CARL ZEISS SUPRA 55 Field Emission Scanning Electron Microscopy (FE-SEM) that has the attachment of an Energy Dispersive X-ray Analyzer (EDX). This was further confirmed from High Resolution Transmission Electron Microscopy (HR-TEM) analysis done using the JEOL JEM 2100 and the selected area diffraction pattern (SAED) was also recorded to examine the crystallinity and phase formation of the as-synthesized nanoparticles. The FT-IR spectral analysis was also obtained from the Perkin Elmer Spectrum RX 1.Their electrochemical performance was studied from coin cell fabrication.

RESULTS AND DISCUSSION

3.1. Powder X-ray diffraction analysis

Fig. 1(a-d) shows the powder X-Ray diffraction patterns of pure and as-obtained yttrium doped $Li_4Ti_5O_{12}$ nanoparticles for different doping concentrations (x= 0.5 M, 1.5 M and 2.5 M%). The Y_xLTOXRD patterns are compared with pure LTO and seen to be quite similar. The Bragg peaks are compared with standard JCPDS data (26-1198) and indexed to cubic spinel structure with space group $Fd\bar{3}m$. However, there appears two impurity peaks corresponding to Li_2TiO_3 and $LiTiO_2$ in the XRD pattern for the Y doping concentration of x= 0.5 M %. From Fig. 1, the major peaks of spinel structure are found to be (111), (311), (400), (511) and (440), respectively apart from which no other impurity peaks can be deducted, indicating that yttrium has doped into the lattice sites of LTO.

The expanded XRD plot for (111) peak in the range 2Θ = 15° to 20° is illustrated in Fig. 2 (a-d). A shift towards the lower angles is observed with increase in doping concentrations, indicating the increase in lattice constant due to the ionic radius of Y³⁺ (0.9Å) being larger than that of Li⁺ (0.76 Å) and Ti⁴⁺ (0.605 Å). The lattice constants are calculated to be 8.33 Å, 8,356 Å, 8,345 Å, 8.3876 Å corresponding to x= 0 M, 0.5 M, 1.5 M, 2.5 M%. Thus the increase in lattice constant by the substitution of a larger ion could broaden the pathway for Li⁺ ion diffusion. Also the difference in the ionic radius between Y³⁺ and Ti⁴⁺ creates lattice distortion leading to defects in LTO [8].



Fig.1 XRD pattern of Y_xLTO for x=0 (a), x=0.5 (b), x=1.5 (c) and x=2.5 (d)



Fig.2 Diffraction peak expanded for $2\Theta = 15^{\circ}$ to 20°

3.2.FESEM analysis

The morphological study of Y doped LTO NPs was done using Field Emission Scanning Electron Microscopy (FESEM) and shown in Fig. 3 (a-d). It is observed that doping does not change the morphological aspect of the doped LTO NPS when compared with pure LTO and hence the same cubic morphology is maintained in the case of Y doped LTO also. The samples are well crystallized. The size of nanoparticles covers a wide range from about 80 - 150 nm for all the three cases.



Fig. 3 FESEM images of $Y_xLTOfor \ x=0$ (a), x=0.5 (b), x=1.5 (c) and x=2.5 (d)

However in the case of high doping levels of Yttrium (1.5 and 2.5 M %), there are particles whose size seems to appear larger in comparison to Y=0.5 M % and undoped LTO NPS. This is attributed to the increase of calcination temperature from 500 °C for pure LTO to 800 °C in the case of doped samples that has resulted in the growth of bigger particles [9]. Also for high doping concentration of x= 2.5 M, the morphology seems to be slightly distorted [8]. The nanoparticles are free from clustered formations or agglomerations.

3.3 EDX analysis

The elemental composition of the Y_xLTO NPs was confirmed from EDX analysis. Fig. 4 (a-c) shows the presence of titanium and oxygen in the Y doped LTO samples. The presence of Yttrium was identified for higher doping concentrations of x= 1.5 and 2.5, but very feeble yttrium presence could be detected for x= 0.5 due to lower level of doping. This shows that Y^{3+} ions have entered into the lattice site of $Li_4Ti_5O_{12}$ and substituted for Ti^{4+} resulting in the formation of Y doped LTO. Moreover, Lithium being a light metal produces low energy characteristic radiations and hence could not be detected from EDX analysis as observed in the case of pure LTO nanoparticles. Hence requires other techniques like XPS or Li NMR to identify the presence of lithium[10].





Fig. 4 EDX spectra of Y_xLTO corresponding to x=0.5 (a), x=1.5 (b) and x=2.5 (c)

3.4.HRTEM analysis

The structural features of Y doped samples are analyzed from HRTEM imaging. Fig. 5 (a-d) depicts the HRTEM images corresponding to different doping values of LTO NPs. It is evident that there is no change in the morphology between the pure and doped samples of LTO as observed from FESEM analysis. Further, owing to the increased doping value, the morphology appears to be slightly distorted and the particles appear bigger in comparison to pure LTO NPs. In addition, the lattice fringe images were also examined to view the microstructural information of the as-prepared products. As seen from Fig.5, the lattice fringes are clearly visible along with some lattice distortions. This is probably due to the substitution of an ion with greater ionic radius of $(Y^{3+}= 0.9\text{Å})$ than the host ion $(Ti^{4+}= 0.605 \text{ Å})$ in the crystal lattice site [8]. The typical selected area electron diffraction (SAED) patterns indicate that the nanoparticles are crystalline in nature. The d-spacing values were calculated from SAED data and compared with their corresponding XRD results and the major reflections are indexed to their respective diffraction planes. The d-spacing calculated from SAED data for $Y_{1.5}LTO$ and $Y_{2.5}LTO$ samples matches well with the major reflections namely; (111), (311), (400), (511) and (440) of XRD results but whereas for $Y_{0.5}LTO$, the major reflections are observed from (111), (311), (400) and (440) planes. Thus all the three doped samples confirm the cubic spinel structural formation of the nanocrystals.











Fig. 5 HRTEM images, lattice fringes and SAED pattern of Y_xLTO corresponding to x=0 (a), x=0.5 (b), x=1.5 (c) and x=2.5 (d)

3.5. FT-IR Analysis

The FT-IR spectra of the Y doped LTO samples are shown in Fig. 6 (a-c). The spectra of all the three Y_xLTO nanoparticles do not show much change with variation in the doping concentrations. The peak at around 3800 cm⁻¹ indicate the presence of hydrogen-bonded O-H stretching which is absent in the LTO structure. The –CH₃ stretching vibrations are assigned to bands formed at about 1600 cm⁻¹, which in the case of $Y_{0.5}LTO$ and $Y_{2.5}LTO$ appears at 1591.73 cm⁻¹ and 1594 cm⁻¹ and is absent for $Y_{1.5}LTO$. All the three YLTO samples show the C=O bands which lie almost closer in value at 1437 cm⁻¹, 1439 cm⁻¹ and 1411 cm⁻¹ respectively [9]. The bands found at 1044.10 cm⁻¹, 1053.47 cm⁻¹, 1046.94 cm⁻¹ for x= 0.5 M, 1.5 M and 2.5 M are confined to the presence of C-O vibrations. The Ti-O vibrations are confirmed from the peaks observed in the range 2200 - 2400 cm⁻¹[11]. These vibrations though weak yet observed at 2918.14 cm⁻¹, 2399.59 cm⁻¹ and 2917.77 cm⁻¹. Moreover, the bands lying below 600 cm⁻¹ are due to the vibrations of the metal-organic groups, such as Li-O-R or Ti-O-R and Y-O, thus validating the presence of yttrium in the lattice sites of LTO [12].



Fig. 6 FTIR spectra of Y_x LTO corresponding to x=0.5 (a), x=1.5 (b) and x=2.5 (c)

3.8. Electrochemical Characterization

The electrochemical performance of the electrode materials are well studied from their cyclic behavior. Fig.7 (a-c) shows the charging and discharging curve of Y doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles prepared from ethanol/water solvents, obtained between 0 and 2.5 V (vs. Li/Li^+) at a C-rate of 0.1 C measured for 50 cycles with a half-cell system. The lithiation and de-lithiation mechanism of $Y_{0.5}\text{LTO}$, $Y_{2.5}\text{LTO}$ can be well understood from the cyclic behavior of the samples. During discharging, the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibits a lithiation behavior for 3.0 Li per formula to be $\text{Li}_7\text{Ti}_5\text{O}_{12}$ with rock salt structure. As seen from Fig.7, the flat working potential platform (charge process, 1.64 V and discharge process, 1.52 V) indicates the two-phase evolution between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ [13].

The initial discharge capacities for both Y_{0.5}LTO (216.95 mAh g⁻¹) and Y_{2.5}LTO (220.39 mAh g⁻¹) are found to exceed the theoretical capacity of LTO (175 mAh g⁻¹). This extra capacity is contributed from the electrolyte decomposition that forms a surface film on the sample [14, 15]. Also the first discharge capacity is known to be affected by several factors, such as specific surface area, morphology, crystallization, lattice defect and impurity phases within the electrode materials which could also lead to the increase capacity obtained at the first cycle [16]. Though the discharge capacities of Y doped LTO decreases from its initial value after the 1st cycle, they show better discharge capacities even at the end of 50th cycle when compared to undoped LTO. Moreover, their reversible reaction mechanism continues for the complete 50 cycles unlike pure LTO where the electrochemical behavior ends within a few cycles. The final discharge capacities for $Y_{0.5}LTO$ and $Y_{2.5}LTO$ are 117.7 mAh g⁻¹ and 121 mAh g⁻¹, while that of undoped LTO is 94.7 mAh g⁻¹ indicating that high electronic conductivity contributes to higher discharge capacity. These features suggest that the entry of Y³⁺ ions into LTO increases the stability of LTO during the intercalation/de-intercalation of Li ions by acting as a bridge between the particles thereby, improving the contact area between the electrode and the electrolyte for enhanced surface electrochemical reactivity, and shortening the diffusion distance of electrons and Li ions [17, 8]. Further both $Y_{2.5}LTO$ and $Y_{0.5}LTO$ show better electrochemical performance when compared to pure LTO and the doping content of Y=2.5 M gives a slightly higher capacity value than the other. Hence it can be authenticated that doping yttrium has enhanced the cyclic behavior of Li₄Ti₅O₁₂NPs.



(a)



CONCLUSION

In summary, Yttrium doped $Li_4Ti_5O_{12}$ was synthesized from hydrothermal method. The effect of doping on the crystal structure and morphology was investigated. It could be concluded that Y^{3+} ions do not change the cubic spinel nature of the LTO and also no morphological changes except for slight distortions owing to the increase in

doping concentrations were observed from HRTEM analysis. Moreover, it is evident from the electrochemical studies carried out that doping greatly influences the cyclic behavior and thereby improves the performance of the electrode material. The charging/ discharging cyclic curves of $Y_{0.5}LTO$ and $Y_{2.5}LTO$ were obtained, compared and their discharge capacities show that $Y_{2.5}LTO$ exhibits better electrochemical performance than $Y_{0.5}LTO$. However both $Y_{0.5}LTO$ and $Y_{2.5}LTO$ seem to be stable and possess higher electronic conductivity than pure LTO. Thus the substitution of Y^{3+} ions has created better cyclic performance necessary for materials to be used for Li-ion battery applications.

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REFERENCES

[1] G.N. Zhu, Y.G. Wang, Y.Y. Xia, Energy Environ. Sci., 2012, 5, 6652–6667.

[2] Z.J. Ding, L. Zhao, L.M. Suo, Y. Jiao, S. Meng, Y.S. Hu, Z.X. Wang, L.Q. Chen, *Phys. Chem. Chem. Phys.*, **2011**, 13, 15127–15133

[3] C. P. Sandhya, Bibin John, C. Gouri, *Ionics*, **2014**, 20, 601–620

[4] K. Du, Z.D. Peng, G.R. Hu, Y.A. Yang, L. Qi, J. Alloys Compd., 2009, 476, 329–334.

[5] Yan Jing Hao, Qiong Yu Lai, JiZheng Lu, Xiao Yang Ji, *Ionics*, **2007**, 13, 369–373.

[6] Qianyu Zhang, Xi Li, Int. J. Electrochem. Sci., 2013, 8,6449 - 6456

[7] Ting Feng Yi, Li JuanJiang, J.Shu, CaiBoYue, RongSun Zhu, Hong BinQiao, *Journal of Physics and Chemistry of Solids*, **2010**, 71, 1236–1242

[8] Yu Jun Bai, Chen Gong, Ning Luna, Yong Xin Qi, J. Mater. Chem. A, 2013, 1, 89-96

[9] Jun Lu, Caiyun Nan, Qing Peng, Yadong Li, J. Power Sources, 2012, 202, 246-252

[10] Li Hong Yang, Vheng Dong, Juan Guo, J. Power Sources, 2008, 175, 575-580.

[11] Yue Li, Hailei Zhao, Zhihong Tian, WeihuaQiu and Xue Li, J. Alloys and compd., 2008, 455, 471-474.

[12] Chunming Zhang, Yaoyao Zhang, Jin Wang, Dan Wang, Dannong He, Yongyao Xia, *J. Power Sources*, **2013**, 236, 118-125.

[13] Na Li, Tao Mei, Yongchun Zhu, Linlin Wang, Jianwen Liang, Xing Zhang, Yitai Qian, Kaibin Tang, CrystEngComm., 2012, 14, 6435-6440.

[14] Jie Shu, Miao Shui, Dan Xu, Shan Gao, Tingfeng Yi, DongJie Wang, Xing Li, Yuanlong Ren, *Ionics*, **2011**, 17, 503–509

[15] ZijiaYua, Xianfa Zhang, Guiling Yang, Jing Liu, Jiawei Wang, Rongshun Wang, Jingping Zhang, *Electrochimica Acta.*, **2011**, 56, 8611–8617

[16] YugingSha,Bote Zhao, Ran Ran, Run Cai, Zongping Shao, J. Mater. Chem. A, 2013, 1, 13233-13243

[17] Byunghyun Choi, Dae-jin Lee, Mijungji, Young jin Kwon, Sung-Tae Park, *Journal of Korean Ceramic society*, **2010**, 47, 638-642.