

RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF LITHIUM TITANATE (LTO) NANOCOMPOSITES VIA SOLUTION GROWTH ROUTE FOR Li-ION BATTERIES

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ABSTRACT

The novel bimetal oxide composite of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was successfully synthesized by solution growth technique. The structural and microstructural properties of synthesized powders were characterized by powder X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray-spectroscopy (EDX). The electrochemical performance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode was investigated using galvanostatic charge-discharge techniques. The electrochemical property of the Lithium titanate anode was investigated. The good electrochemical performance is ascribed to the stable lithium storage host structure, decreased electrochemical resistance and enhanced lithium-ion diffusion coefficient. Therefore, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ may be a promising alternative anode material for Li-ion batteries.

Keywords: Lithium titanate (LTO) nanocomposites, Li-Ion batteries.

1. INTRODUCTION

There is a remarkable interest in developing alternative and sustainable energy storage systems to meet modern society needs due to fossil fuel depletion. Compared with other existing energy storage systems, batteries are promising and lots of efforts have been taken by researchers to develop efficient device with affordable price. The development of Lithium-ion batteries with enhanced safety and a long cycle life is vital for mainly energy storage devices used in specific some fields such as electric vehicles (EVs) or hybride electrical vehicles (HEVs), cameras, laptops and mobile phones. Recently, researchers are attempting to develop the advanced nanomaterials for energy storage devices especially for batteries. Among the Nanostructured materials such as lithium cobalt oxide (LiCoO_2) (1), lithium iron phosphate (LiFePO_4) (2,3), lithium manganese oxide (LiMn_2O_4) (4) or oxides of vanadium (V_2O_5) (5-7), manganese (MnO_2) (8,9) have been used as the cathode in Lithium ion batteries. Similarly, anode (TiO_2 and graphite) materials have been developed for Lithium ion batteries (10-15). Ti-based materials have been intensively investigated and observed as good potential negative electrode materials for lithium-ion batteries owing to their safety, excellent rate capability and superior cyclic stability. These materials have shown several advantages for example easy and swift charging within ten minutes. Spinel lithium titanate has a high lithium intercalation voltage of 1.55 V against a lithium electrode with a theoretical capacity of 170 mAhg^{-1}

and an actual discharge capacity of over 160 mAhg^{-1} . Now a day's new kind of anode materials being developed in order to reduce the cost as well as to make highly efficient devices. Among the new anode materials, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is one of the right choices for anode materials due to its superior performance (16-18). $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanomaterials have been prepared using several methods for instance hydrothermal methods (19), sol-gel process (20, 21), solid state reaction (22), spray pyrolysis, hydrothermal- microwave synthesis, gel-emulsion, and gel combustion (23-25). In this work, the preparation and characterization of nanostructured novel bimetal oxide $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by solution growth technique.

2. EXPERIMENTAL

2.1. Materials preparation

Lithium titanate was prepared by solution growth technique. In a typical experimental procedure, titanium oxysulfate (TiOSO_4) and lithium hydroxide ($\text{LiOH.H}_2\text{O}$) were dissolved in double distilled water under strong stirring and consequently a precipitate was obtained. The precipitate was dried at 80°C in hot air oven for 10 hr. Finally, colorless powder was obtained which was then heat treated at 850°C in a muffle furnace for 3 h. The structural property of synthesized powder was studied using various advanced characterization techniques.

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2.2. Materials Characterization

The X-ray diffraction (XRD) patterns of all the samples were measured on a (XPRT-PRO) diffractometer with monochromatic $\text{CuK}\alpha$ - radiation ($\lambda = 1.5406\text{\AA}$). FT-IR spectra of the samples were recorded on a (Thermo Nicolet 380, USA) spectrometer using a KBr pellet technique in the range of $4000\text{--}400\text{ cm}^{-1}$. The SEM - EDX were recorded on a (JEOL JSM-6360LV) using an accelerating voltage of 30.0 kV

2.3. Fabrication of electrodes

1.3504 g of lithium titanate and 0.9079 g of carboxymethylcellulose (CMC) were taken in the porcelain dish and mixed well by adding few drops of distilled water. Then, 0.0966 g of binder was also added into the above mixer and then the mixture was homogeneously mixed manually with the aid of spatula. The paste is coated on the electrode using the Dr. Blade method. Then the electrode was dried in oven at 75°C for 1 hour. Lithium was used as counter electrode and polypropylene was used as the separator. 1 M LiPF_6 was dissolved in ethylene carbonate (EC) / dimethyl carbonate (DMC) /1, 2-diethyl carbonate (DEC) and used as the electrolyte. The cell was assembled inside the glove box under the argon atmosphere. Galvanostatic charge/discharge cycle test was carried out for all the assembled cells at ambient temperature with constant current mode (0.1 mA) up to 1.5 V for charging and up to 2 V for discharging.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction Analysis

Fig. 1 depicts the XRD pattern of synthesized powder. For Lithium titanate the crystalline peaks appear at 18.34 , 35.60 and 43.28° and those peaks are assigned to (111), (311) and (400) crystalline planes of cubic phase ($\text{Li}_4\text{Ti}_5\text{O}_{12}$). The appeared peaks clearly indicate the formation of Lithium titanate. It should be indicated that the appearance of three more peaks at 21.98 , 22.21 and 22.63° . These peaks are assigned to the reduced form of titanium oxide. The formation of titanium oxide (JCPDS no. 76-1690) along with lithium titanate (JCPDS no. 49-0207) may be beneficial in terms of storage capacity when it is used as anode material in the lithium ion batteries. The average crystallite size of the prepared material was calculated from the Scherrer equation:

$$D = k\lambda / \beta \cos\theta$$

Where D is the average crystallite size, λ is the X-ray wavelength, β is the full width at half maximum, K is a constant related to crystallite shape, and β in 2θ axis of diffraction outline must be in

radians. The θ can be in degrees, since the $\cos\theta$ corresponds to the equal number.

The crystallite size of 50 nm was achieved for synthesized materials.

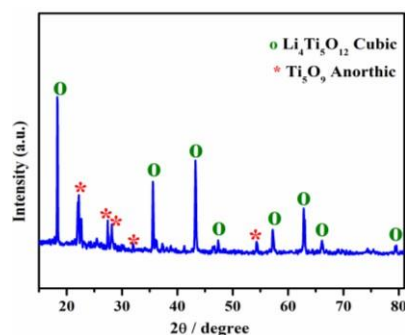


Fig.1 XRD patterns of Lithium titanate

3.2. SEM and EDX Analysis

Fig. 2 shows the SEM image of lithium titanate. The SEM image clearly reveals that the formation of homogeneous cubic morphological features. EDX spectrum of mixture of lithium titanate and titanium oxide nanopowders was measured (Fig. 3). It was found from the EDX spectrum that the presence of appropriate percentage of Ti and O in the synthesized sample. It should be indicated that the Li does not present in EDX spectrum because the Li is light weight element.

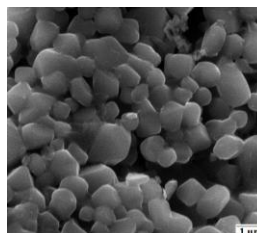


Fig.2 SEM image of Lithium titanate

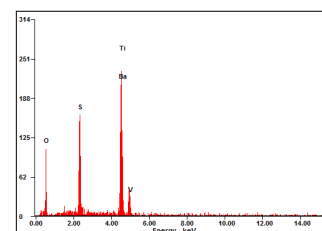


Fig.3 EDX spectrum of Lithium titanate

3.3. FT-IR Studies

Fig. 4 shows the FTIR spectrum of the synthesized sample i.e. a mixture of lithium titanate and titanium oxide nanopowder. The peaks were observed at 481 and 637 cm^{-1} due to the asymmetric stretching vibration of Ti-O-Ti. The peaks positioned in the range of $400\text{--}900\text{ cm}^{-1}$ reveals the symmetric stretching vibration of octahedron groups (26, 27).

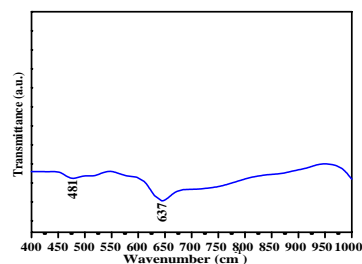


Fig.4 FT-IR spectrum of Lithium titanate

3.4. Raman studies

Raman spectroscopy is an effective technique to characterize the functional groups present in the synthesized samples. Fig. 5 shows the Raman spectrum of the synthesized sample i.e a mixture of lithium titanate and titanium oxide nanopowder. Recently, Xue Li and Wei Liu *et al.* reported that the peaks observed at 671, 227 and 427 cm^{-1} due to the A_{1g} , A_{1g} and E_g mode, respectively. (28-30). The peaks are observed at 670, 229 and 427 cm^{-1} are due to the ($2A_{1g}$) modes and E_g mode which are attributed to the vibrations of Ti-O bonds (TiO_6), O-Ti-O and stretching vibrations of Li-O in LiO_4 . This is one of the evidence for the formation of mixture of lithium titanate and titanium oxide nanopowder.

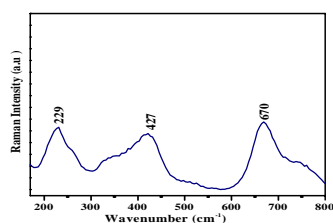


Fig.5 Raman spectrum of Lithium taitanate

3.5. Electrochemical Analysis

The investigations on the electrochemical property of the prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials were also carried out. The charge/discharge curve of lithium titanate anode is shown in Fig. 6. The lithium titanate anode shows discharge capacity of 83mAhg^{-1} at first cycle. The better lithium ion storage performance of the synthesized Lithium titanate anode may be due to the good electronic conductivity.

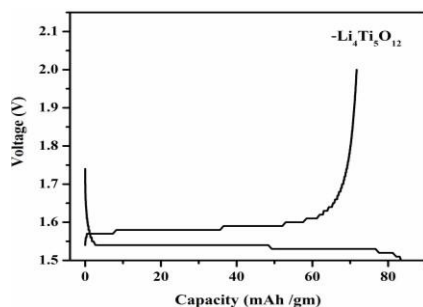


Fig.6 Charge/discharge performance of Lithium titanate

4. CONCLUSIONS

Lithium titanate has been successfully synthesized by simple solution growth from aqueous precursor solution of titanium. The XRD studies reveal the formation of lithium titanate. SEM observation demonstrated the formation of homogeneous cubic morphology.

The storage capacity of 83mAhg^{-1} was achieved for mixture of lithium titanate and titanium oxide nanopowder. Further studies are underway to improve the storage capacity of the synthesized material.

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