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STRUCTURAL INVESTIGATION OF HEAT-TREATED Li_2FeSiO_4 CATHODE MATERIAL PREPARATION

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ABSTRACT- Li_2FeSiO_4 based materials have attracted a great deal of interest as cathodes for Lithium batteries for its excellent thermal stability and good cyclability. Li_2FeSiO_4 has been synthesized via sol-gel method using acetic acid as a catalyst. The sample was characterized by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy and Scanning Electron Microscopy (SEM).All the results were analyzed in detail.

Keywords- [Lithium batteries, Cathode, Li_2FeSiO_4]

1. INTRODUCTION

Rechargeable lithium-ion batteries have been widely used as energy storage devices due to their high energy density and design flexibility. One of the families of transition metal silicates (Li_2MSiO_4) has been attracted great interests owing to environmental benign, high specific capacity and stability [1]. Among the transition metal silicate materials, Li_2FeSiO_4, which is potentially low-cost and safe cathode material for large-scale Li-ion battery application, can deliver a good reversibility on cycling because the presence of strong Si-O bonds can promote the same lattice stabilization effect as that in $LiFePO_4$. Li_2FeSiO_4 may deliver a nominal capacity of 332mAh/g by possibly exchanging two lithium ions. Iron and silicon are the most abundant and lowest cost elements, and hence offer the prospect of preparing cheap and safe cathodes [2-4].

Lithium iron orthosilicate cathode material predominantly requires Fe, Li and SiO_4 composites. At this state all tetrahedral oxides in Li_2FeSiO_4 are forming the orthorhombic or monoclinic crystalline structures. Then, sol gel method paved a way to obtain composite orthorhombic crystalline cathode material. But the calcination temperature plays an important role in the material preparation because of the presence of oxide based material which was totally reflected at various oxidation states [5].

In this paper, here in we report about the synthesis of Li_2FeSiO_4cathode material. Various methods such as solid-state reaction, sol-gel, hydrothermal, spray technology, supercritical fluid, microwave-solvothermal, combustion methods have been adopted for the synthesis of Li_2FeSiO_4. Among the above said methods, sol-gel method is being

adopted as the precursors are high chemically active which is responsible for the formation of the gel [6].Therefore in this method,SiO_2 silicate source and acetic acid catalyst are used as the starting materials for the preparation. Then as prepared gel sample was subjected to heat treatment. And, hence an investigation on the structure and presence of impurities of the final calcined sample has been carried out.

2. EXPERIMENTAL

In this case, Li_2FeSiO_4 were synthesized by acetic acid-assisted sol-gel method. Stoichiometry amounts of analytical reagents, $CH_3COOLi.2H_2O$, $FeC_2O_4.2H_2O$, SiO_2 and were used as starting materials. $FeC_2O.2H_2O$ and 20ml de-ionized water mixer was taken.$CH_3COOLi.2H_2O$, SiO_2 and ethanol mixer was taken to slowly added iron oxide solution. A saturated aqueous solution of acetic acid was slowly added to maintain the pH 6-7. Under magnetic stirring the reflux was carried out at 80°C for 5h, until a clear yellowish solution was transferred into gel form, obtained gel was dried at 100°C for 12h. Then the precursor was heat-treated at 350°C for 2h followed by calcinations at 700°C for 10h under Ar flowing atmosphere to obtain the final product.

3. RESULTS AND DISCUSSION

A. XRD analysis

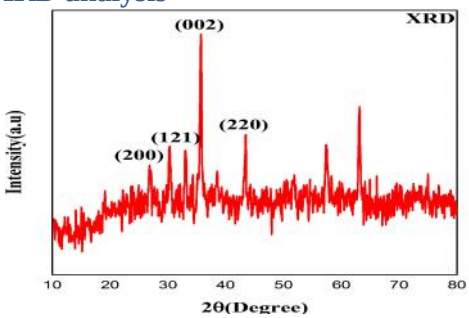

Figure 1 - XRD pattern of Li_2FeSiO_4 prepared sample

X-ray diffraction (XRD) analysis was performed to investigate the crystallographic information using a powder x-ray diffractometer with non-mono chromates CuKα X-ray source. Figure.1**.** shows XRD patterns of theLi_2FeSiO_4sample prepared by sol-gel method in between the angle 2θ=10 to 80°C. The average crystalline size can be calculated from Scherrer equation D=kλ/βcosθ. Where, D=Crystalline size, k=Constant parameter (0.94), λ=Wavelength of X-ray, β=Full width half maximum and θ=Bragg position of peak. The average crystalline size of the sample calculated from Scherrer equation is 34.02 nm. The lattice parameter of the sample is calculated as a=6.6077Å, b=5.3824Å, c=5.0262Å [7]. The unit cell volume of the prepared sample is 178.75$Å^3$. Figure.2. shows the FT-IR spectra of the Li_2FeSiO_4 sample prepared by sol-gel method. The functional group vibrations of the sample have been studied using FT-IR in the region 4000-400 cm^{-1}. FT-IR was performed to investigate the strong vibration of Si-O-Si in the Li_2FeSiO_4 existed, depending on the different characteristics peaks of Si-O in Li_2SiO_3 and Li2FeSiO4. The infrared bands at 943 and 863 cm^{-1} can be contributed to the stretching modes of Si-O bonds in SiO_4tetrahedral [5]. The bands at 735 and 1062cm^{-1} attributed to the asymmetric vibration of Si-O-Si and stretching vibration of O=Si-O. The peaks at 1505 and 1442cm^{-1} are corresponding to the C-O vibration in Li_2CO_3 owing to exposure in air. The bands at 525 and 422cm^{-1} can be attributed to the bending vibration of Si-O and O-Li-O for SiO_4 and LiO_4 tetrahedral [8]. The O-H stretching is appeared in the region 3500-3100cm^{-1}.

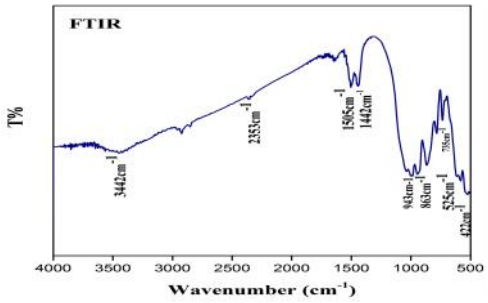

Figure 2- FTIR spectra of Li_2FeSiO_4 prepared sample

Figure.3. shows the Raman spectra of the prepared samples. The Raman shift appeared in the range of 400~700cm^{-1} belonging to Fe-O vibrations of SiO_4. The band alignment has been projected based upon findings of available literature on silicate ($FeSiO_4$) as reported by F. Ruusheng et al. [8], the bands at 146 and 346 cm^{-1} can be consigned to SiO_4 translational and vibrational modes. The bands at 482 and 698cm^{-1} are oriented to Fe translational mode, O-Si-O symmetric and asymmetric bending.

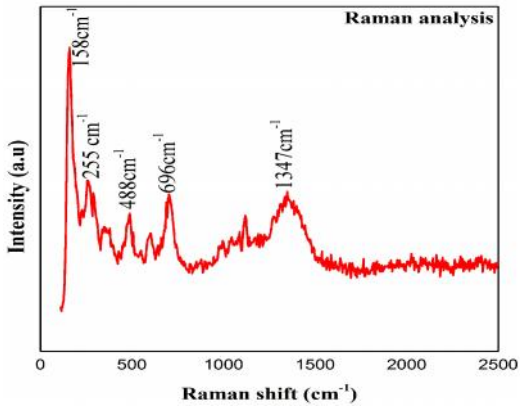

Figure 3- Raman analysis of Li_2FeSiO_4 prepared sample

The surface morphology of prepared samples was observed using scanning electron microscopy with various magnifications. The SEM images with various magnifications are shown in figure.4. From the images, it is observed that there is no homogeneous nature and the particles are agglomerated bit throughout the surface.

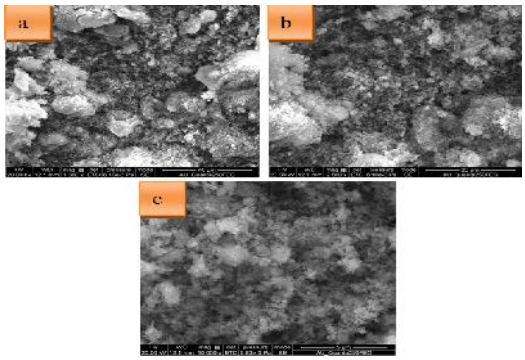

Figure 4-SEM images of prepared sample with various magnifications (1.3K, 2.6K, 5k)

CONCLUSION

The Li_2FeSiO_4 was synthesized by means of acetic acid assisted sol-gel method based on acid catalyst and used the SiO_2 silicate source. The sample possesses the crystalline orthorhombic phase with P_{mn21} symmetry which is analyzed by XRD. And the synthesized sample exhibits crystallites of 30-35 nm in size. FTIR, Raman spectroscopy and SEM images were concluded as the impurities are presented on sample owing to the exposure in air. The calcination temperature makes a main role on complex oxidation states. So the sample may have some impurities. From this one can conclude that the material prepared using sol-gel is needed for few refinements in Li_2FeSiO_4material preparation.

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