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OPTIMIZATION OF LITHIUM CONCENTRATION IN LITHIUM IRON ORTHOSILICATE VIA POLYOL ROUTE

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Abstract - *In recent decade, silicate based cathode materials have received a great attention due to its specific capacity (~330 mAh/g)(Ni et al. 2017). Hence, it is used as a Lithium intercalated electrode in LIBS. In this study, Lithium iron orthosilicate cathode materials were prepared by polyol method and studied the effect of concentration of Lithium in $Li_{(2+x)}FeSiO_4$/C composites (0 less than or equal x less than or equal 0.5) toward its physical property of Lithium iron orthosilicate. The as-prepared material was characterized by X-ray diffraction, FTIR, Raman and TEM. Structural determination was carried out with the help of powder XRD. Carbon coated on the as- synthesized materials was evident through D and G bands of Raman analysis. FTIR provides the valuable information on the stretching and bending vibrations of Si-O and Fe-O. Finally, the morphology of the as prepared sample shows nano sized crystallites. From the investigation, x=0.5 mol concentration of lithium has been optimized in terms of the structural aspect.*

Key Words: cathode, Lithium ion batteries, orthosilicate, polyol method, physical property.

1. INTRODUCTION

Development and promotion of Lithium Ion Batteries (LIB) have widely dominated in commercial application for store and utilize energy in terms of electric, on account of its peculiar properties, LFSted as high energy conversion efficiency, low self discharge, better cycle life and light weight[1,2]. Choice of the cathode materials is very essential factor in LIBs to fix the price, control level of toxicity, improve safety problems and predict the capacity of battery. Apart from small scale usage, LIBs are frequently used in large scale applications such as hybrid electric vehicles, renewable power plant to store the intermediate energy[3]. More commercialized cathode materials for LIBs are layered, spinel and olivine structure. The presence of polyanionic compound in the cathode materials provides good thermal stability to the LIB, because of strong covalent bond interaction between Si-O. At the same time, Lithium transition metal orthosilicate (Li_2FeSiO_4) was considered a potential cathode material on account of its environmental benignancy, abundant source materials, inexpensive, structural stability and high theoretical capacity [(330 mAh g^{-1}) than $LiFePO_4$ (170 mAh g^{-1}) due to the probability which takes place multielectron reaction]. Significantly, practical electrochemical performance of Li_2FeSiO_4 was not considerably too good due to its low intrinsic electronic conductivity and slow lithium ion diffusion which inhibits its future applications in electric vehicles and plugin electric vehicles[4]–[7]. The improvement in the electronic conductivity was a major problem identified by many researchers. In order to achieve better electronic conductivity and lithium mobility three strategies can be suggested, conductive carbon coating on the active materials, particle size reduction and isovalent cation doping. Individually and merging all the strategies, these methods have been used to improve the electrochemical performance of Lithium iron orthosilicate. From their reports carbon coating and particle size reduction can effectively improve the electrochemical performance of LFS. Nishimura et al. [8] was intensively investigated the valid structure of LFS by combined the results of HR-XRD and TEM approaches. S. Zhang et al.[9] the LFS powder have nano distribution of crystallites about 80 nm, this attributes that nano size crystallites can be yielded molecular level mixing of starting materials. Decreasing the particle size of polyanion materials can shorten the diffusion path of Lithium ion. From the report of S. Zhang [10], comparative study between $Li_2Fe_{0.97}Mg_{0.03}SiO_4$ and Li_2FeSiO_4 was carried to understand the electrochemical performance and structural properties of the cathode material. Particularly, the role of dopant can enhance the structural stability, lithium ion diffusion capacity and reduces the electrochemical impedance of the material. V. Aravindan et al.[11] demonstrated that the composite electrode comprising of 42 wt% of carbon improve the electronic conduction of electrode. In this paper, an attempt was made to prepare nanosized Lithium iron orthosilicate/C by increase the concentration of Lithium (0.5) via polyol route, TTEG as a solvent. The structural and morphological properties of the prepared samples were investigated with the aid of XRD, FTIR, Raman Spectra and TEM.

2. Material and Method

LFS nanocrystallites were synthesized by polyol route using TTEG as a solvent[12]. Here, stoichiometric amounts of

iron (II) acetate, tetra ethoxysilane ($C_8H_{29}O_4Si$) (TEOS), Lithium acetate, tetraethylene glycol were taken as the starting materials. All the starting materials were dissolved in the ethanol+water (30+30 ml) solution separately in a beaker. Afterwards, it poured into the polyol solvent TTEG and stirred vigorously at 100°C. Consequently, the solution was transferred to round bottom flask with condensation unit. After 16 hours, the solution was centrifuged to obtain the sample. Then, the obtained Mn doped LFS powder was dried in vacuum oven for removing residual solvent. With the help of mortar and pestle the powder materials were grounded and characterized.

3. Result and discussion

3.1 XRD

A typical XRD pattern of $Li_{2x}FeSiO_4$ (x=0.5) Lithium iron orthosilicate is shown in figure1. XRD pattern of $Li_{2.5}FeSiO_4$ can be indexed to orthorhombic structure with space group of Pmn_{21}[11]. Increasing the stoichiometric amount of Li in LFS ($Li_{2.5}FeSiO_4$), indicates that diffraction peaks are well matched with LFS pattern, have no appearance of extra reflections. This pinpoints that Lithium enters the structures of LFS rather than forming any lattice change. The insoluble starting material is not good for homogeneous mixing, however, the starting materials in polyol method are well dispersed in the fluid medium, reduces the diffraction peaks of starting materials[9]. This addition may be expected of the increment of lithium diffusion.

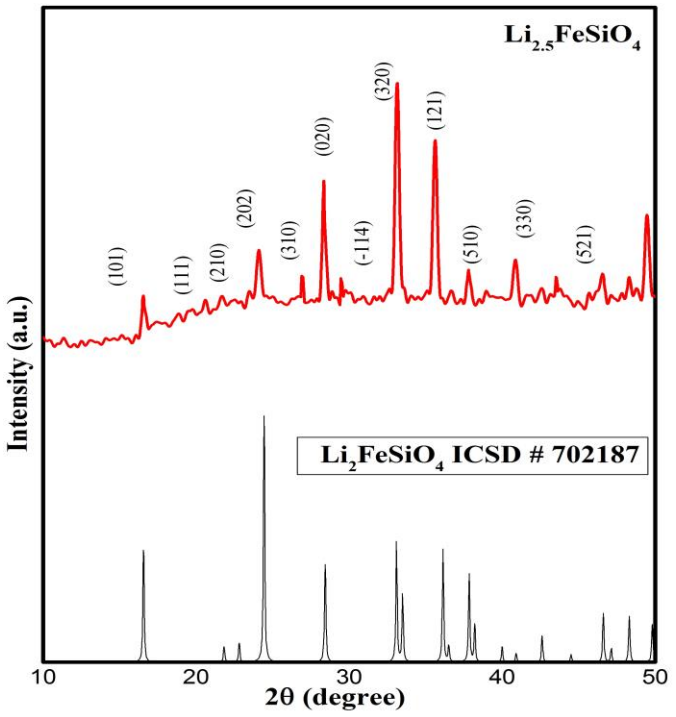

Fig-1: XRD Pattern of as-prepared $Li_{2.5}FeSiO_4$

3.2 FTIR AND RAMAN

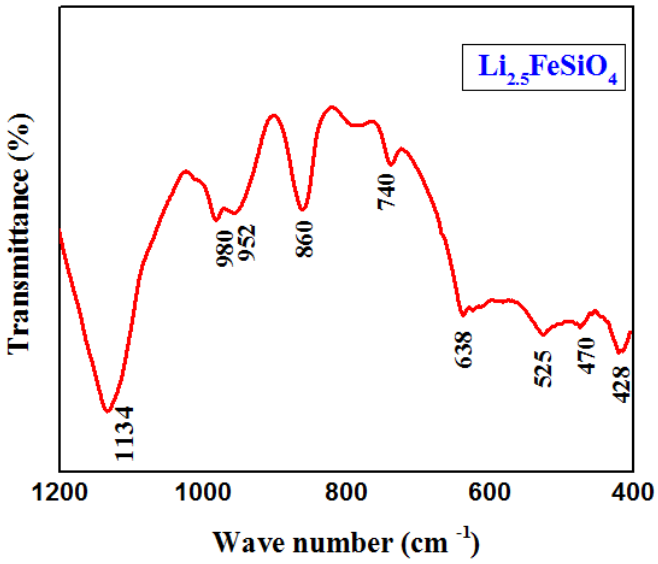

Fig-2: FTIR spectra of as-prepared $Li_{2.5}FeSiO_4$

Form the FTIR analysis, the vibration of peaks of Fe-O and Si-O was observed for $Li_{2.5}FeSiO_4$ shown in Fig.2. The peaks around the 528 cm^{-1} can attribute the bending vibration of $[SiO]^{4-}$ which occurs due to the displacement of oxygen atoms of the tetrahedral form. The vibration for O-Si-O in $Li_{2.5}FeSiO_4$ has strong absorption at 979 cm^{-1}. The Si-O-Si from Li_2SiO_3 peak observed at 740cm^{-1} in the fingerprint region, indicates the presence of impurity[13]–[15]. Hence whenever increase in the concentration of Lithium above stoichiometry, would lead to the formation of impurities. The carbon content on $Li_{2.5}FeSiO_4$ was depicted in Fig. 3. The presence of D and G band confirms the carbon formation [16].

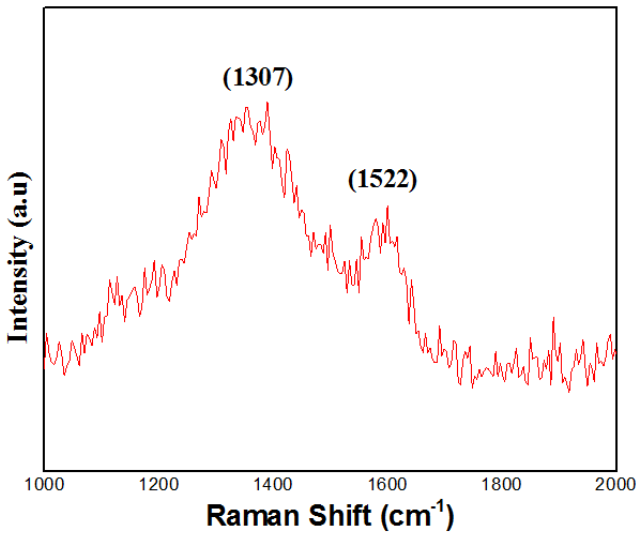

Fig- 3: Raman spectra of as-prepared $Li_{2.5}FeSiO_4$

3.2 TEM

Fig. 4 shows the TEM image of $Li_{2.5}FeSiO_4$ of cathode materials. The uniformly distributed spherical particles were chained with carbon. The nano crystallite of $Li_{2.5}FeSiO_4$ can be observed through TEM and particles have good morphology with average particle size of ~70 nm. This would be enhancing the Lithium ion diffusion process.

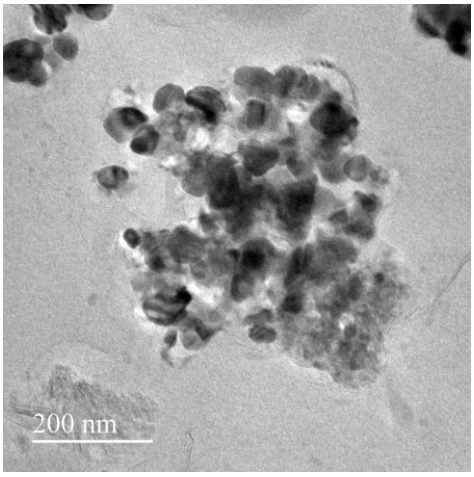

Fig- 4: TEM image of as-prepared $Li_{2.5}FeSiO_4$

4. CONCLUSIONS

$Li_{2.5}FeSiO_4$ was prepared via Polyol method using TTEG as solvent. The samples can be indexed on the basis of orthorhombic unit cell with space group Pmn_{21}. Nano-particles can be observed through TEM analysis. D and G bands were observed at 1350 and 1575 cm^{-1} respectively. While increasing Li-ion concentration from 2 to 2.5, that would be increase the impurities Li_2SiO_3, which might be confirmed by FTIR Peak at 740 cm^{-1}.

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