STRUCTURAL AND MORPHOLOGICAL OPTIMIZATIONS OF Li_2FeSiO_4 CATHODE MATERIAL FOR NEXT GENERATION LIBs

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Abstract - *The optimization of Li_2FeSiO_4 cathode materials were synthesized by combination of solid state method and calcinations at high temperature, using TEOS and SiO_2 as a various silicate sources. The poly anionic silicate material reveals high security, high theoretical capacity, environmental benignity with low cost, therefore is considered as one of the most capable candidate in LIBs. Li_2FeSiO_4 suffers from poor ionic mobility, low electronic conductivity and poor rate capability [1]. In this work, an attempt has been made to reduce the particle size of prepared samples in order to tailor its properties. The final materials have been characterized by XRD, FTIR, RAMAN, SEM and EDX analyses. The SEM analysis showed very tiny particles less than 100nm that are clubbed together on the surface of the huge particles. From the above investigations, the prepared materials can be used as one of the cathode materials for next generation LIBs.*

Key words: TEOS, SiO_2, solid state method, Li_2FeSiO_4, EDX.

1. INTRODUCTION

In modern year, the demands for energy storage devices along with high power and energy density of lithium ion battery are considerable. Hence, the need of developments for cathode material is important in next generation lithium ion battery. High theoretical capacity, high safety, environmental acceptability and cost are also the key factors for the improving cathode materials [1-3]. Recently, polyanionic cathode materials obtained wide attention due to their high safety and cost efficiency when compared with traditional metal oxide cathodes such as $LiMn_2O_4$, $LiCoO_2$ and $LiMO_2$ (Ni,Fe) [4].$LiFePO_4$ is one of the polyanionic cathode materials and it has 170mAhg^{-1} theoretical capacity whereas it provides poor thermal stability [5].

Among these polyanionic cathode materials creates considerable attention, as such as (Li_2MSiO_4, M=Mn, Fe and Co) orthosilicate group. Especially Li_2FeSiO_4 has provides high theoretical capacity ~333 mAhg^{-1} due to the extraction of more than one Li ion per formula unit and it also shows that better electrochemical properties [6]. As well as, Li_2FeSiO_4 has high thermal stability owing to the formation of strong Si-O bonding and is easy to synthesis. In addition to that an attempt has made to provide the tremendous benefits of silicate chemistry while explore the strong lattice stability compare to $LiFePO_4$, due to the strong Si-O bonds in Li-Fe-Si-O [7]. However, these shows the lowering electronegativity in Si vs P will effect in a lowering of the Fe^{II} – Fe^{III} couple. Above result suggests that these materials should have a lower band gap and therefore have a higher conductivity [1].

Inappropriately, Li_2FeSiO_4 suggest low electronic conductivity (1.0×10^{-4} s cm^{-1}) and poor rate capability (1.0×10^{-17} cm^{2}s^{-1}) due to the phenomenon of diffusion of Lithium is poor in electrochemical performance [8]. Several strategies, together with cation doping [9], carbon coating [10] and nano- architecting [11] have been adopted to overcome these difficulties. Out of these, Nano-architecture is an effective way to enhance the diffusion kinetics in lithiation-delithiation processing [12]. However, such nano-architecture process can promote diffusion capability and electronic conductivity, through the particle size reduction on the material surface [10]. Various methods are available for synthesis Lithium iron orthosilicate such as solid state[13], sol-gel[11], hydrothermal [14], co-precipitation[15] also. In the group of, solid state method is one of the low cost and simplest method.

In this work, an attempt has been made by solid state method through various silicate sources like SiO_2 and TEOS (Tetraethyl orthosilicate) with ball milling techniques. Finally, obtained samples were characterized by XRD, FT-IR, RAMAN, SEM with EDX analyses to understand the structural, morphological and compositional detail. Meanwhile, the effects of the solid

state process on the surface of the composite were investigated.

2. EXPERIMENTAL

2.1 Method 1(P_1):

The Li_2FeSiO_2 was prepared by a solid state reaction process using amorphous nano size SiO_2. Stoichiometric amounts of $CH_3COOLi.2H_2O$, $FeC_2O_4.2H_2O$ and SiO_2 were dispersed in ethanol. The mixture was stirred at 50°C until the ethanol as evaporated. Then the ball milling was carried out for 30 mins with 200 rpm. The mixture was heat treated in a horizontal quartz tube from ambient temperature to 750°C at the heating rate 3°C/min and kept at that temperature for 10 h in Ar atmosphere. The final sample was label in P_1.

2.2 Method 2(P_2):

The Li_2FeSiO_2 composite was prepared by solid state reaction method using tetraethyl orthosilicate (TEOS). The starting materials were $CH_3COOLi.2H_2O$, $FeC_2O_4.2H_2O$ and TEOS taken in the appropriate molar ratio. The raw materials were dispersed in ethanol, and then the mixture was stirred at 80°C for 24 h. the resulting precursor was decomposed at 350°C for 5 h and then followed by calcined at 650°C for 10 h. The final sample P_2 was labeled.

2.3 Characterization:

The structural and morphological characterizations of prepared samples were compared and done by using following studies. X-ray powder diffraction patterns were taken on PANalyticalX'pertpro powder diffraction with CuKα radiation. Fourier Transform Infrared and Raman spectra were performed on a Thermo Nicolet 380 FTIR spectrophotometer and SEKI focal. Scanning electron microscope with Energy-dispersive X-ray spectroscopy carried out on FEG Quanta 250.

3. RESULTS AND DISCUSSION

3.1 Structural characterizations:

A) XRD analysis:
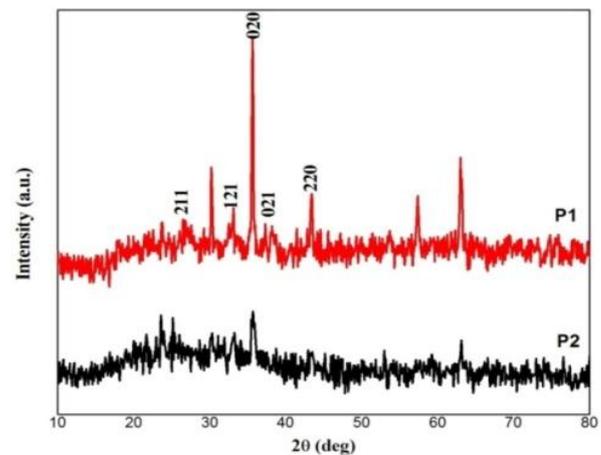
Fig-1: shows the XRD analysis of as prepared sample P_1 and P_2.

X-Ray diffraction pattern of prepared materials are compared in Fig.1. The sample P_1 provides good crystalline peaks compared with another sample. P_1 has made lattice arrangements with Li-Fe-O atoms when using amorphous nano SiO_2 in material synthesis, but P_2 did not make a well lattice arrangements, it was confirmed by these XRD patterns.

To obtain Li_2FeSiO_4 with good crystallinity, it was necessary to manage the synthesis condition precisely, such as the ratio of the raw materials and high calcinations temperature. From Fig.1.P_1, it can be seen that some impurities like Li_2SiO_3 and Fe_3O_4 were detected by solid state process using amorphous nano sized SiO_2. The prepared P_1 sample has orthorhombic structure with space group of Pmn_{21} [13]. The crystalline size can be calculated from Scherrer equation, $d = k\lambda/\beta cos\theta$. Where, d is the mean crystallite size, k is the constant parameter of shape factor (0.94), λ is the wavelength of source, β is the full width half maximum. Based on this, the average crystalline size of the prepared sample is 33.75nm. The lattice constants have been calculated to be a=6.4866Å, b=5.0392Å and c=6.8912Å. The unit cell volume of the prepared sample can be calculated as 225.25Å^3. From the diffraction patterns, one can optimize based on the literature (JCPDS 14 - 1657) that the sample P_1 has better matching and also the intensity than P_2.

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B) FTIR analysis:

The fundamental vibrational group of the Li_2FeSiO_4 was confirmed by FT-IR. Fig-2 shows the FT-IR spectra of the prepared samples P_1 and P_2 respectively. P_1 has strong finger print region compare to P_2 sample. The O-H stretching appears in the region 3500-3100 cm^{-1}.
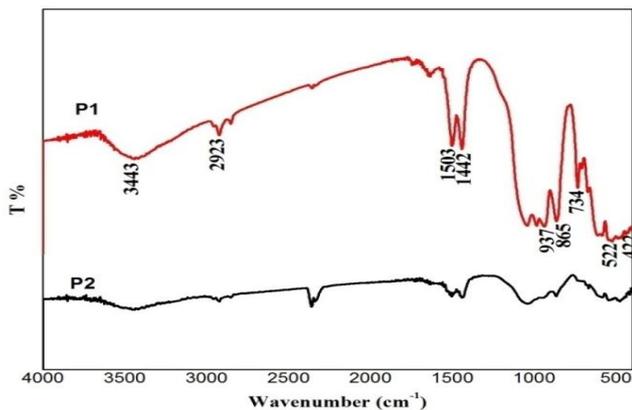
Fig-2: shows the FT-IR spectra of as prepared sample P_1 and P_2.

The vibrational spectra of Li_2FeSiO_4 were dominated by the fundamental vibrations of the LiO_4 and SiO_4 tetrahedra, where the LiO_4 vibration at (890 cm^{-1}), SiO_4 stretching and bending modes were identified in Fig .2.In infrared region of the internal mode vibrations of the silicate anion (1000–800 cm^{-1}region), one can recognize the asymmetric stretching (υ_1) mode at 847 $cm^{-1}$and the triplet (υ_3) modes at 865, 885 and 937 cm^{-1} [16]. The peaks at 1503 and 1442 cm^{-1} attributes that the C-O vibrations in Li_2CO_3. The band at 734 and 522 cm^{-1} corresponds to the bending vibration of Si-O-Si and Si-O bonds in SiO_4 tetrahedrons.

C) Raman analysis:
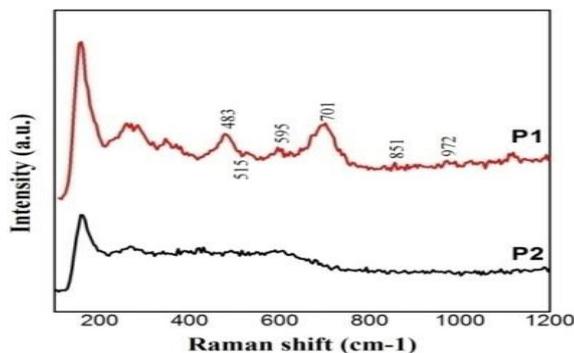
Fig-3: shows the Raman spectra of as prepared sample P_1 and P_2.

Fig-3 shows the Raman spectra of the prepared samples. As the structure of orthosilicate is built from LiO_4 and FeO_4 tetrahedra linked to $(SiO_4)^{4-}$ polyanions. The internal (SiO_4) vibrations of Li_2FeSiO_4 can be derived from the fundamental $(SiO_4)^{4-}$ modes υ_1 - υ_4 and the stretching and bending mode vibrations were well separated from each other. The Raman spectrum displays the mutual activity of the weak bands appeared at 851, 883, 972 and 990 cm^{-1} owing to the symmetric stretching of O-Si-O bridging bonds in Raman active modes. The peak at 851 and 883 cm^{-1} is the totally symmetric $(A_1 + B_1)$ mode and the peaks at 483,515,595 and 701 cm^{-1} are originates from the degenerate bending υ_4 modes. The Raman bands appeared in the range of 400 – 700 cm^{-1} belonged to Fe – O vibrations.

3.2 Morphological and elemental analysis:

D) SEM with EDX analysis:

The morphological study has been done by SEM analysis. Fig-(4-5) shows that the SEM images of the samples P_1 and P_2 with the various magnifications. It is observed that from Fig.4, there is relatively no much agglomeration has been presented in the P_1 sample prepared by the solid state reaction using amorphous nano SiO_2, than P_2 prepared by solid state reaction using TEOS. In sample P_1 have been observed, very tiny particles less than 100nm that are clubbed together and formed on the surface of the huge particles.

An EDX spectrum of as prepared samples P_1 and P_2 shows that the atomic ratio of Fe/Si/O is approximately (09.48/26.66/63.22) and (11.86/14.88/59.34).Besides, some impurity atoms are presented in the sample P_2 due to synthesis condition when using TEOS.
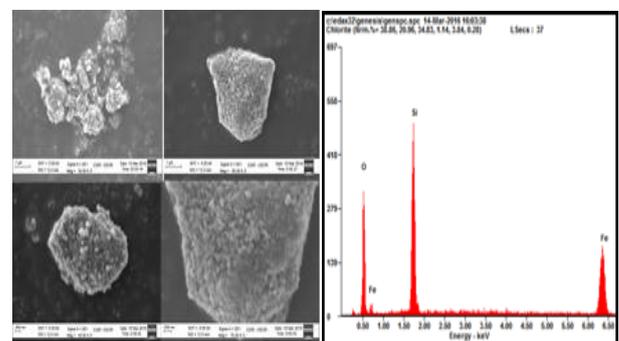
Fig -4: shows the SEM images of as prepared sample P_1 with EDX spectrum respectively.
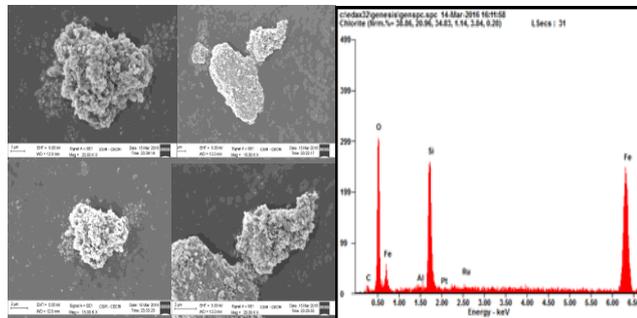
Fig -5: shows the SEM images of as prepared sample P_2 with EDX spectrum respectively.

4. CONCLUSIONS

An attempt has been made to prepare the lithium ion orthosilicate via solid state reaction using SiO_2 (P_1) and TEOS (P_2) as the silicate source. The infrared spectra of the internal mode vibrations of the silicate anion (1000–800 cm^{-1}region), one can recognize the asymmetric stretching (υ_1) mode at 847 $cm^{-1}$and the triplet (υ_3) modes at 865, 885 and 937 cm^{-1}.The Raman band appeared in the range of 400 – 700 cm^{-1} belonged to Fe – O vibrations. Surface morphology has been studied from the SEM with EDX analyses. From above investigations, the structure confirms that the sample prepared using SiO_2 as a silicate source has orthorhombic *Pmn21* space group with some impurities like Fe_3O_4 and Li_2SiO_3. Therefore, the amorphous nano size SiO_2 would suggest the good raw ingredient for the preparation of lithium ion orthosilicate. The tactic of developing a Li_2FeSiO_4 cathode by incorporating the raw material of amorphous nano SiO_2 has great advantages for next generation LIBs.

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