Scientific Journal of Impact Factor (SJIF): 4.72

e-ISSN : 2348-4470
p-ISSN : 2348-6406

International Journal of Advance Engineering and Research Development

National Conference On Nanomaterials, (NCN-2017)

Volume 4, Special Issue 6, Dec.-2017 (UGC Approved)

THE PREPARATION OF Fe-TRANSITION-METAL OXIDE HOST SILICATE AS A POSITIVE ELECTRODE CANDIDATE FOR LI-ION SECONDARY BATTERIES

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ABSTRACT: *Lithium ironorthosilicate is one of the most promising positive electrode materials for next generation lithium-ion batteries. Among the current cathodes, Li_2FeSiO_4 has great attention due to good thermal stability, non-toxicity and environmental benignity. Iron orthosilicate offers good structural stability lithium intercalations in Li-ion batteries. Iron and silicon are the most abundant and lowest cost elements [1]. It provides a nominal capacity of 332mAh/g by exchanging lithium ions during cycling [2].In this work, an attempt has been made to synthesize lithium ironorthosilicate via sol-gel method using TEOS (Tetraethylorthosilicate) as a silicate source. The structural property was studied by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Raman and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The XRD analysis shows the prepared sample has an orthorhombic structure with the space group of Pmn_{21}.FTIR analysis progresses the vibration of SiO_4 and LiO_4 tetrahedra (525 and 422 cm^{-1}).The Raman shift was identified in the range of 400~700 cm^{-1} belongs to Fe-O vibrations.*

Key words: *Lithium ironorthosilicate, TEOS, XRD, FTIR, RAMAN, and SEM*

INTRODUCTION

Up to date, LIBplaysa vital role inhybrid electric vehicles and portable electronics[3]. An energetic candidate of positive electrode determinesenergy density, safety and life cycle of LIBs. Therefore, the development of cathode is still being a demand like eco-friendly, low cost and especially high-energy density and high safety [4]. Now a days, following typical cathodestructures are available based on inorganic compounds, which islayered, spinel and poly-anion structure [5]. According to the bonding nature of transition metals with oxygen, these bondinghas been classified into the full octahedronsuch as layered $LiMO_2$ (M=Ni, Co and Mn) [6], octahedron/tetrahedron hybrid such as spinel $LiMn_2O_4$and full tetrahedron structures[7].The full tetrahedron structure(Li_2MSiO_4, M=Fe, Co and Mn) provideshigh theoretical capacity (332mAh/g)due to more lithium atom embedded into the structure[8]. More recently, full tetrahedron orthosilicate (Li_2FeSiO_4)was proposed as a promising cathodefor LIBs. The Li_2FeSiO_4 has much higher theoretical capacity than that of $LiFePO_4$ and high thermal stability appropriate to strong Si-O bonding. [1,9,10]. Li_2FeSiO_4suffers from poor ionic mobility, low electronic conductivity and poor rate capability owing to full tetrahedron nature[8]. Various techniques are available to overcome these drawbacks such as conductive material coating, metallic ion doping in Si sites and particle size reduction. Among these techniques, particle size reduction has been remarkable techniqueto enhance the peak properties of LIB cathode[11-13]. Still date, various successful methods are available for thesynthesis of lithium ironorthosilicate such as solid state, hydrothermal, sol-gel methods. Above methods, sol-gel method is effective method for crystalline material preparation [14-15]. In this work, Li_2FeSiO_4 was synthesizedvia sol-gel method using TEOS as a silicate source. The structural property of prepared sample wasinvestigated using XRD, FT-IR, RAMAN and SEM analysis. In focus, FT-IR and Raman analysis explores the status for the tetrahedral bonding of prepared sample.

EXPERIMENTAL:

The lithium ironorthosilicateprepared viasol-gel method using acetic acid as a catalyst.Lithium acetate dehydrates, iron oxalatedehydrates and TEOS(tetraethylorthosilicate) were taken in 4:1:1 ratio. Considerable amount of $CH_3COOLi.2H_2O$ and $FeC_2O_4.2H_2O$ was dissolved in 20ml of ethanol. TEOS and 1.5 ml acetic acid were stirred with de-ionized water. After minutes, TEOS precursor was slovenly added to ethanol mixer and followed continuous vigorous stirring. TEOS will react to form silicate source.The solution was evaporated at 80ºC with continuous stirring to form the transparent gel. The obtained gel was dried at 150ºC for 12 h. The dried powder was carried out and milled by ball milling process, and calcined at 800ºC for 10 h under Ar atmosphere and to obtain final composite. This sol-gel-sol growth developed a tetrahedral network due to the formation of an oxide network through polycondensation reactions of a molecular precursor and to theproper calcinedprocess.

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Crystal structure of the prepared composite was analyzed by powder X-ray diffraction (PANanytical XPERT-PRO with Cu Kα radiation), analysis in the range of 2θ=10-80º. The functional group vibrations were identified by FT-IR spectroscopy (Thermo Nicolet 380 Instrument Corporation using KBr pellets) and Raman spectroscopy (SEKI, Japan). The surface morphology was studied by SEM analysis(FEG Quanta 250).

RESULT AND DISCUSSION

XRD ANALYSIS:

XRD analysis used to identify the phases of crystalline material and to calculate the unit cell dimension. XRD pattern of prepared composite isshown in Fig (i)thefinal composite has an orthorhombic structure with the space group of Pmn_{21} and there corresponding hkl values are marked. The average crystallite size is 26 nmcalculated from the scherrer equation. The unit cell volume of the as prepared sample is 167.90$Å^3$.Some crystallite impurity peaks were detected like Li_2SiO_3 and Fe_2O_3. Dislocation density was described as the length of dislocation lines per unit volume for impure phase crystal structure[16].The dislocation density calculated by,

$$\delta = \frac{1}{d^2}$$

The dislocation density of the sample can be calculated as δ=0.18. A small dislocation density is identified and it describesthe crystallization natureand defects of prepared sample[17].

FTIR ANALYSIS

The functional group vibration of the prepared sample was identified by FT-IR analysis. Fig (ii) shows the vibrational modes of prepared crystallize composite.From the table (i)SiO_4 and LiO_4 tetrahedrons were identified in prepared sample[18]. The bands around 735 and 1062 cm^{-1}indicates asymmetric vibration of Si-O-Si and stretching vibration of O=Si-O in Li_2SiO_3. The peaks at 1505 and 1443 cm^{-1}assign the C-O vibrations in Li_2CO_3 owing to exposure in air.

RAMAN ANALYSIS

Raman spectroscopy analysis used to aggregate vibrational, rotational and other low frequency modes of prepared sample. Raman spectra of prepared composite was shown the Fig (iii) the Raman shifts of lithium ironorthosilicate peaks are appeared at 167, 269, 473 and 692 cm^{-1} respectively detailed from the table (ii)[19].

SEM ANALYSIS

The surface morphology of the sample with various magnifications was shown the Fig.(iv). From the images, it is observed that there is no homogenous natures along with particles are agglomerated bit throughout the surface cause to surface owing to the air and the dislocation density of crystal.

CONCLUSION

In this work, lithium ironorthosilicate was synthesized by sol-gel method. The powder XRD pattern of prepared sample exhibited orthorhombic structure with Pmn_{21} space group. The calculated dislocation density 0.18indicates the presenceof impurity phases of crystal.LiO_4 and SiO_4 tetrahedronswere identified by spectroscopy analysis excluding FeO_4 tetrahedral site due to the formation of Fe_2O_3. Subsequently the prepared cathode material provides quasi tetrahedral structure, which also benefits the enhancement of the ionic mobility, electronic conductivity and rate capability respectively. The strategy of developing aquasi tetrahedral structure hassome advantages for LIBs.

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FIGURE CAPTIONS
Fig (i) XRD analysis for prepared sample
Fig (ii) FT-IR analysis for prepared sample
Fig (iii) Raman analysis for prepared sample
Fig (iv) SEM analysis of prepared sample with various magnifications (40 K, 60 K and 160 k)
TABLE CAPTIONS
Table (i) Table for vibrational modes of prepared sample
Table (ii) Table for Raman shifts of prepared sample

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Figure (i)

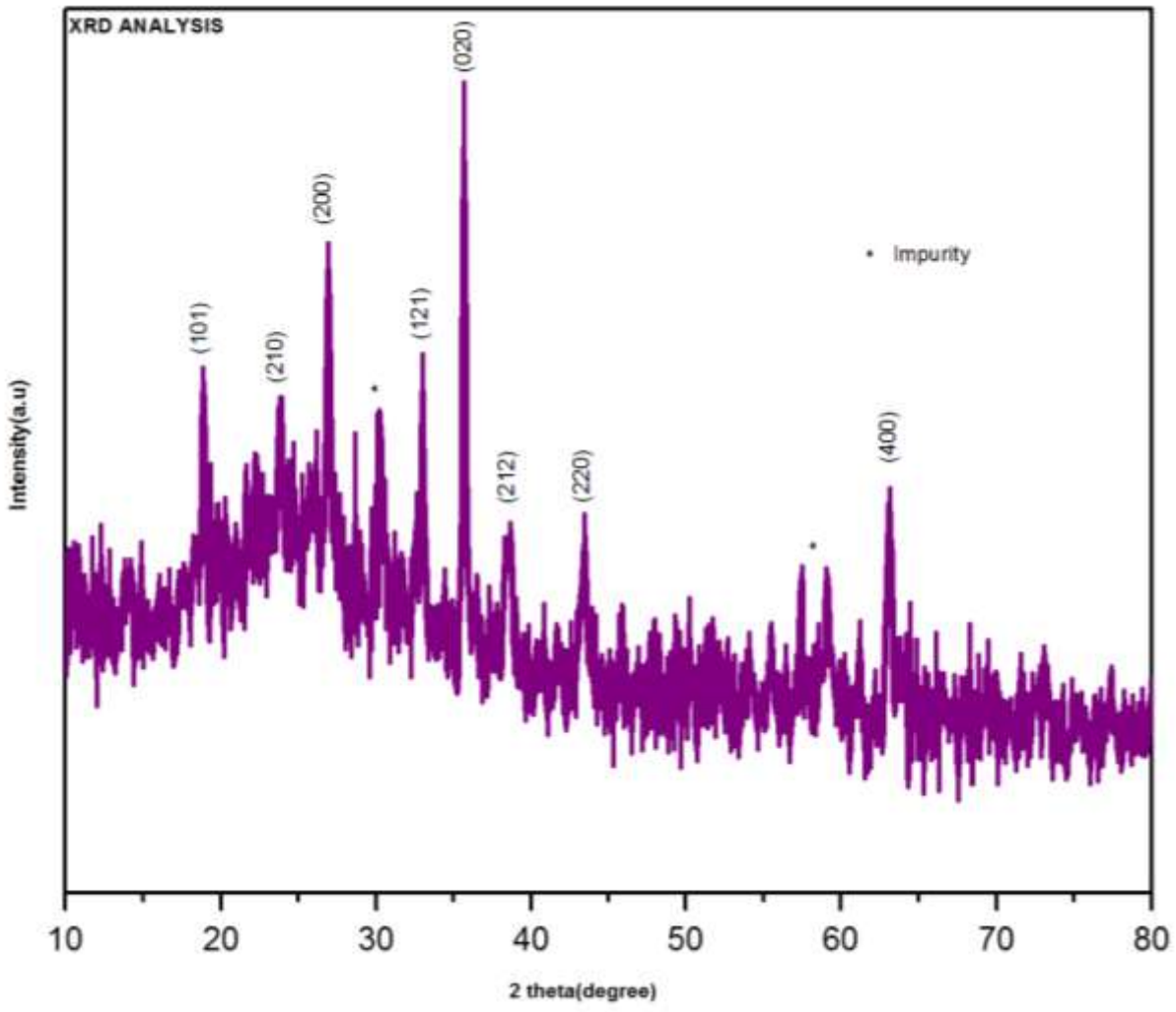

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Figure (ii)

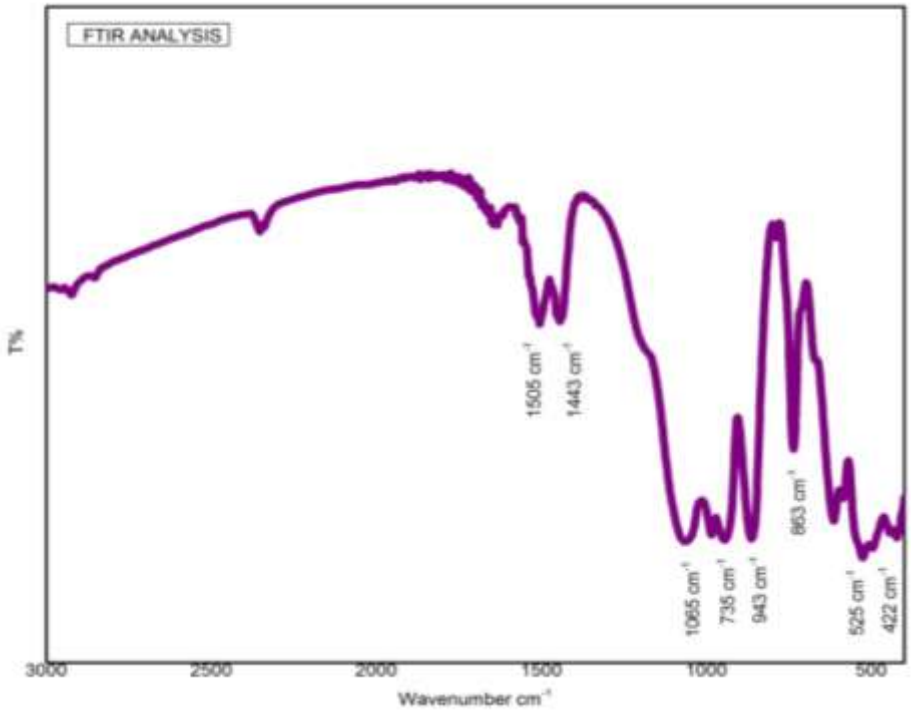

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Figure (iii)

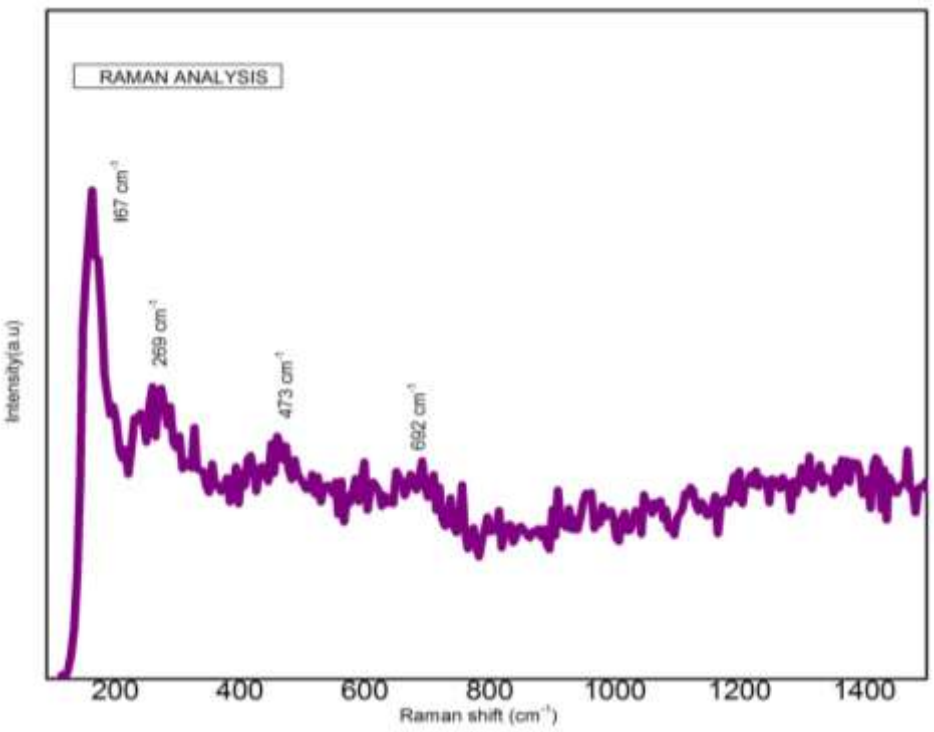

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Figure (iv)

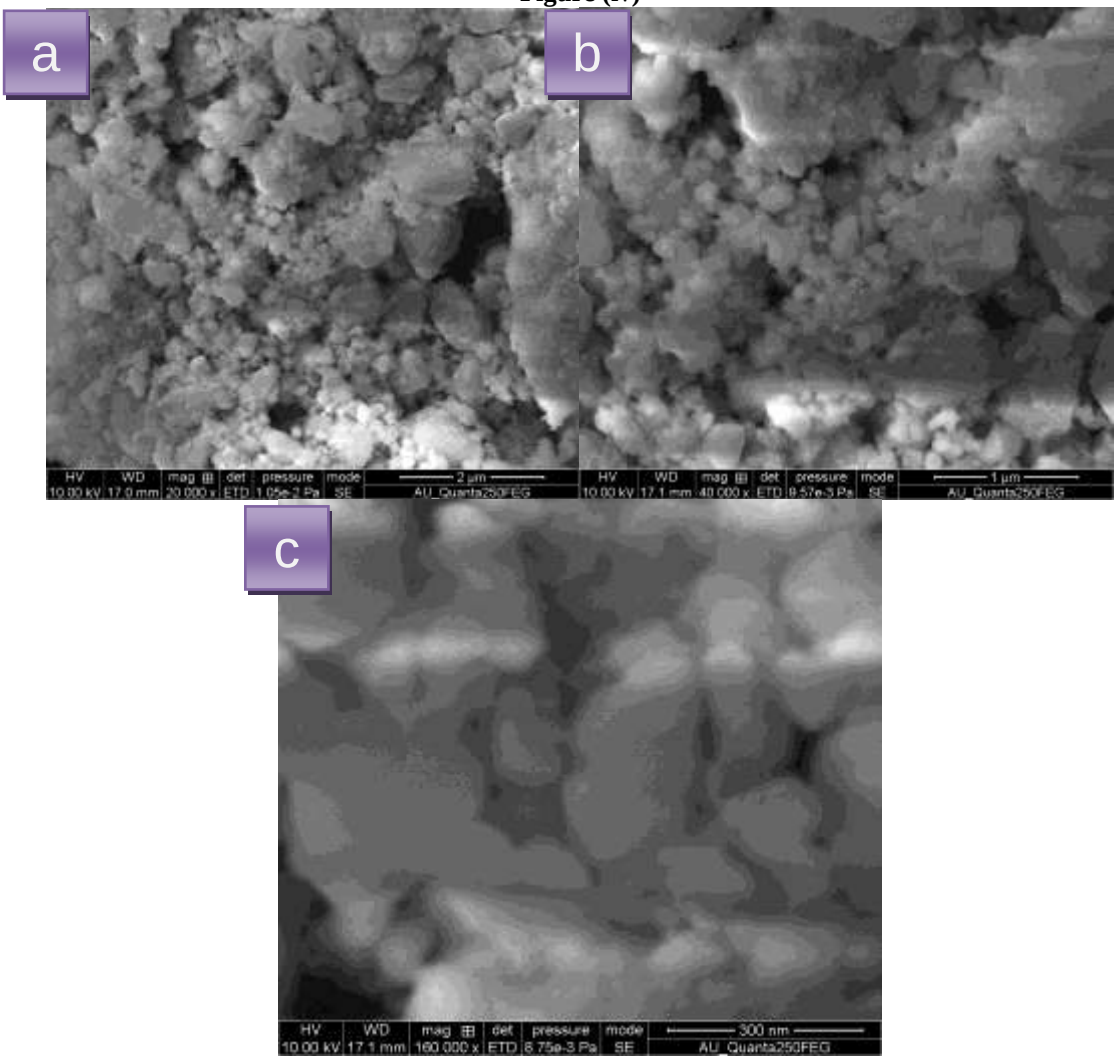

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Table (i)

Wave number (cm^{-1})	**Vibrational Modes**	**Presented structure**
422	Bending mode of Si-O	SiO_4
525	Bending mode of Li-O	LiO_4
863	Stretching modes of Si-O	SiO_4
943		

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Table (ii)

Raman shift (cm^{-1})	**Modes and bending**
167	SiO_4 translational mode
269	Fe translational mode
473	Si cation symmetric bending
692	O-Si-O asymmetric bending

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