Structure And Electrodchemical Performance Of Bare And Ti Doped Li_2FeSiO_4/C Nanocomposite Cathode Material For Lithium Ion Batteries

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Abstract:

The bare and Ti-doped Li_2FeSiO_4/C samples have been prepared by sol-gel method. The samples have been characterized using XRD, SEM-EDAX and FTIR techniques to investigate the effect of Ti doping on Li_2FeSiO_4/C. Rietveld refinement of the XRD data has been carried out on pure and Ti-doped LFS/C samples, which confirms the formation of an orthorhombic structure with $Pmn2_1$ space group. The conductivity of the sample has been characterised by AC impedance analysis. The $Li_2Fe_{0.8}Ti_{0.2}SiO_4$/C sample exhibits an excellent conductivity of $1.012x10^{-4}$ Scm^{-1}, which is two orders of magnitude higher than that of bare Li_2FeSiO_4/C. The electrochemical Li ion intercalation properties of pure and Ti- doped LFS/C in aqueous electrolytes have been carried out by cyclic voltammetry (CV) studies. The Ti-doped material exhibited an excellent electrochemical performance in the aqueous electrolyte including good oxidation/reduction reversibility and cyclability. The diffusion coefficients of Li-ions through the interface across the liquid electrolyte to solid bare and Ti-doped LFS/C are $3.23 x10^{-15}$and $2.43 x10^{-12}$ cm^2/s, respectively. The improved electrochemical performance is attributed to the enhanced electronic conductivity, better structural stability and higher Li-ion diffusion coefficient of the sample which reveals a good ionic mobility inside the Ti-doped LFS/C orthorhombiccage.

Keywords: Composite cathode, Doping, electrochemical properties, aqueous electrolyte, Lithium ion batteries.

1. Introduction

The need for large-scale batteries impels the development of high-performance materials for lithium ion batteries. The Conventional cathode materials such as $LiCoO_2$, $LiNiO_2$, as $LiMn_2O_4$, $LiMnO_2$, etc, [1] have been rated as potentially viable cathodes for commercial applications. However, these materials bear limitations such as higher cost, toxicity and inherent chemical and thermal instability towards its application potential. Several researchers extensively explored by developing suitable polyanion cathodes such as phosphates ($LiMPO_4$, M=Fe, Mn, Co), fluorophosphate (Li_2MPO_4F), silicates (Li_2MSiO_4, M= Fe, Mn, Co), etc.,[2]. Recently lithium transition metal orthosilicate Li_2FeSiO_4has been considered as a promising new generation cathode material. The Li_2FeSiO_4 (LFS) has been explored as one of the most attractive candidates due to its low cost, high safety, environmentally benign and high theoretical capacity (332 $mAhg^{-1}$) [3]. Furthermore, compared with existing cathodes, LFS possesses a lower band gap and a stronger Si-O bond, which is expected to improve the electrochemical performance.

Despite advantages, LFS/C suffers from poor cyclability due to its lower electronic/ ionicconductivityandslowlithiumiondiffusionrate,whichlimits its largescale application in lithium-ion batteries. Numerous approaches have been attempted to enhance the electrochemical performance of LFS such as carbon coating, particle downsizing and doping of metal transition ions [4]. Among these strategies, the aliovalent substitution is the more effective technique which creates defects in the lattice to enhance the conductivity. In the present work, the bare and Ti doped Li_2FeSiO_4/C composite cathode has been prepared by the sol-gel method with out any impurity phases.The impact of aliovalent Tidoping on the structural and electrochemical performance of Li_2FeSiO_4 has been explored in the present attempt.

2. Experimental

2.l sol-gelpreparation

The Lithium Acetate (Sigma Aldrich, regent grade 99.55%), Iron nitrate nano hydrate(Sigma Aldrich, 99.9%), TEOS(Sigma Aldrich 99.995), tetra butyl titanate (Sigma Aldrich, 99%) and citric acid were used as raw material for the preparation of the bare and Ti doped Li_2FeSiO_4/C samples. The highly crystalline Li_2FeSiO_4/C and $Li_2Fe_{0.8}Ti_{0.2}SiO_4$/C nanopowders were prepared by the sol-gel method reported elsewhere[1].

3. Results andDiscussion

3.l Structural and opticalanalysis

The XRD pattern of bare and Ti doped LFS/C are shown in Fig.1A. The XRD pattern of Ti-doped LFS/C composite is similar to the pristine LFS/C sample, which can be well indexed to the orthorhombic structure of LFS with a space group $Pmn2_1$[5]. The peak shifts or an emergence of newpeaks in the XRD patterns are not observed which substituting agents occupy in the crystal structure perfectly. A full Rietveld refinement was carried out on bare and Ti doped samples, the lattice parameters are obtained as a=6.21A, b=5.23A and c=4.98A for LFS/C, a=6.28 A, b=5.33A and c=4.92A for $Li_2Fe_{0.8}Ti_{0.2}SiO_4$/C. The reliability factor are, s =1.23 and Rw=9.56% for bare LFS/C sample, s=1.17 and Rw=8.89% for $Li_2Fe_{0.8}Ti_{0.2}SiO_4$/C composite. The refined results reveal that the unit cell volume of the Ti incorporated LFS/C expands thus facilitating the migration of lithium ions to improve the electrochemical kineticreactions.

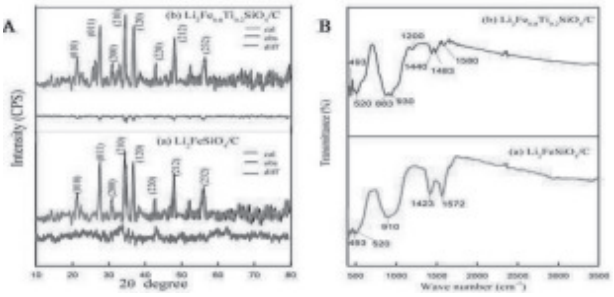


Figure1: A) The XRD pattern and B) FTIR spectra of bareand Tid oped LFS/C nanocomposite cathode.

The FTIR spectrum of the bare and Ti doped LFS/C samples are shown in Fig. 1B. The small peak noticed at 493 $cm^{-1}$is due to the stretching vibrations of Li-O in LiO_4 tetrahedra. The band observed at 520 cm^{-1} can be assigned to the bending vibration of(SiO_4^{4-}) [6]. The absorption peak at 910 cm^{-1} can be attributed to the stretching vibration of $(SiO_4)^{4-}$ group [7]. The characteristic bands of the carboxylic group are observed at 1423 and 1572 cm^{-1}. The bands due to the carboxylic group are distorted when Ti is incorporated into the LFS/C sample. The FTIR results reveal that the Ti incorporation does not distort the tetrahedron orientation of LiO_4, FeO_4 and SiO_4 of theLFS/C.

3.2 MorphologicalAnalysis

TheFE-SEMmicrographsofthebareLFS/ CareshowninFig.2a,whichexhibitsthe larger group of particles that consist of aggregated small particles that have fused together during calcination. Figure. 2b shows that the rearemany fine particles are agglomeratedin the sample.

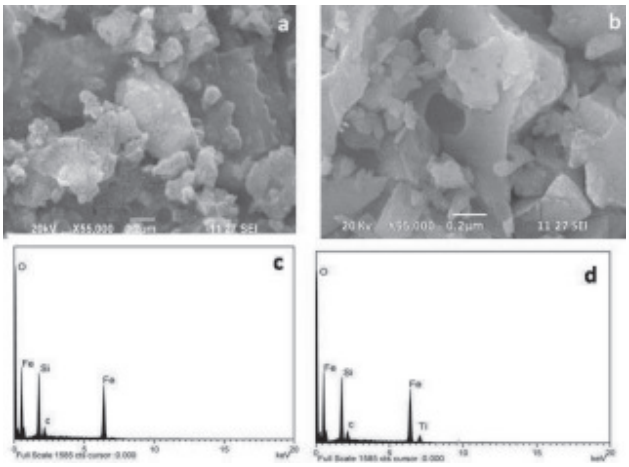


Figure2:a&b)FE-SEM micrographs; c&d) EDAX spectra of bare and Tidoped LFS/C nanocomposite cathode.

The small particles on the surface grow up and tend to form an assembly of particles with more or less uniform morphology. The Ti-incorporation intotheLFS/Chostsignificantly improves the surface uniformity which is beneficial for increasing the lithium ions and electronic conduction. The presence of the Ti in the $Li_2Fe_{0.8}Ti_{0.2}SiO_4$/C sample is confirmed by EDAX analysis, shown in Fig.2 c&d.

3.3 Conductivitystudies

The Nyquist plot of the bare LFS/C is shown in Fig.3a. It has shown two

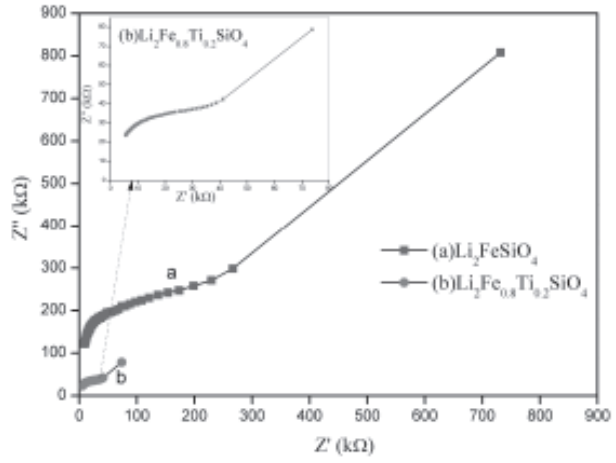


Figure 3: Nyquist plots of bare and Ti doped LFS/C nanocomposite cathode.

high-frequency semicircles and a low-frequency spike which is distinguished by fitting the Ny**q**uist plot using the Z-View software. The total conductivity of the LFS/C is calculated as 2.354 $x10^{-6}$ Scm^{-1} The Li_2Fe 0.8 Ti0.2 SiO_4/C shows a high-frequency semi circle with spike shown in Fig.3b. The total conductivity of the $Li_2Fe_{0.8}Ti_{0.2}SiO_4$/C calculated as 1.026 $x10^{-4}$ Scm^{-1}. The Ti doped LFS/C sample exhibits excellent conductivity which is two orders of magnitude higher than that of bare LFS/C sample which leads to better electrochemical properties.

3.4 Electrochemicalperformance

Figure.4a indicates the CV curve of bare Li_2FeSiO_4/C in a 5M $LiNO_3$ aqueous electrolyteat ascanrateof100mVfor50cyclesrampedbetween-0.5Vto1VverseSCE. A pair ofred oxpeakob served with peak separation potential of 0.2V. It should be not edthata small potential difference between oxidation and reduction peak is observed in the bare LFS/Csample, however, the shape of CVcurves found to change within creasing the number cycles which may cause the capacity fading. It is noteworthy that the Ti doped LFS/C exhibits similar CV curves (Fig.4(b)) after 50^{th} cycle with out exhibiting any difference in the value of oxidation or reduction peak potential. The Ti-doped material exhibited an excellent electrochemical performance in the aqueous electrolyte showing better electrochemical properties without much change in the peakposition.

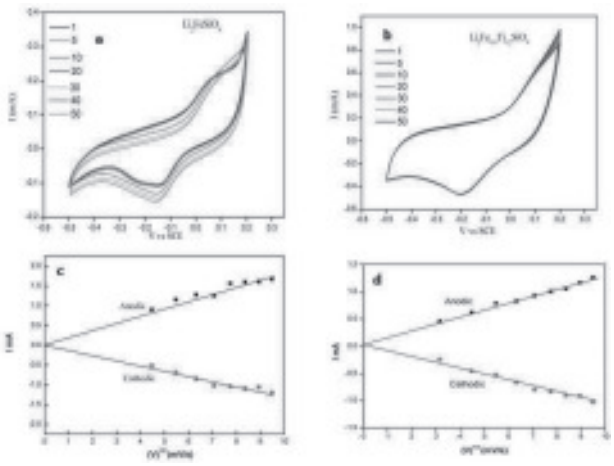


Figure 4: a&b) CV curves; c&d) Ip vs $v^{1/2}$ plots of bare and Ti doped LFS/C nanocomposite cathode.

The linear plots of Ip vs $V^{1/2}$ provide the evidence for chemically reverse redox process which is shown in Fig.4(c&d). The Lithium ion diffusion coefficient is calculated using Randles-Sevcik equation which

correlates the peak current and diffusion coefficient [8]. The diffusion coefficients of Li-ions through the interface across the liquid electrolyte to solid bare and Ti-doped LFS are 1.23 $x10^{-15}$ and 2.14 $x10^{-12}$ cm^2/s, respectively. The improved electrochemical performance is attributed to its enhanced electronic conductivity, better structural stability and higher Li-ion diffusion coefficient due to the proper amount of Ti embedded in the Fesites.

4. Conclusions

The impact of Ti doping on the structural and electrochemical performance of the Li_2FeSiO_4/C cathode material has been explored in the present attempt. The structure, morphology, electrochemical properties of the Li_2FeSiO_4/C were investigated by XRD, FE- SEM, FTIR, AC impedance and CV measurements. The conductivity ofthe Li_2FeSiO_4/C sample was enhanced by the incorporation of aliovalent Ti in the Fe site. The bare and Ti doped LFS/C samples possessed the orthorhombic structure with $Pmn2_1$ space group. The Ti substituted LFS/C composite exhibits excellent electrochemical reversibility and higher value of Li ion diffusion coefficient, which makes them an important candidate as a cathode counterpart for Lithium ionbatteries.

5. References

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