

OPTIMIZATION OF LITHIUM IRON ORTHOSILICATE ELECTRODES SYNTHESIZED VIA VARIOUS METHODS

M.Kouthaman^a, R.Dhanalakshmi^{a,b}, R.Subadevi^a, M.Sivakumar^{a,*}

^a#120, Energy Materials Lab, Department of Physics, Alagappa University, Karaikudi-630 003, Tamil Nadu, India.

^bDepartment of Physics, Thiagarajar College, #139-140, KamarajarSalai, Madurai - 625 009, Tamil Nadu, India.

(* Corresponding Author: susiva73@yahoo.co.in (M.Sivakumar))

Abstract - Lithium iron orthosilicate ($\text{Li}_2\text{FeSiO}_4$) has attracted tremendous attention from the researchers due to its high theoretical capacity (166 mAhg^{-1} for one Li^+ and 332 mAhg^{-1} for two Li^+ per formula unit), excellent safety and environmental benignity. It is considered as a promising alternative cathode material for lithium-ion batteries [1]. Lithium iron orthosilicate cathode material was obtained by four different methods viz., solid state, polyol, sol-gel, and co-precipitation. The XRD pattern of the as-prepared cathode material by aforementioned methods has been observed. It can be seen that some of the peaks belonging to $\text{Li}_2\text{FeSiO}_4$ and some impurities have been detected. By using RAMAN analysis, the presence of D and G bands has been confirmed. The surface morphology of synthesized material has been studied by scanning electron microscopy. From these different routes, sample obtained via the Polyol route possess good crystallites with negligible impurity among other samples studied. However, Polyol route is a low temperature process, which is able to control some parameter of nucleation of nano particles such as size, shape and uniformity, etc. Therefore, it is resolved that polyol is the best method to synthesize lithium iron orthosilicate.

Key Words: solid state method; sol-gel method; lithium Iron orthosilicate; polyol method, cathode material.

1. INTRODUCTION

Lithium-ion batteries (LIBs) have been widely used in daily life such as mobile phones, laptops, etc. Cathode materials play a consistent role in improving electrochemical performance and for reducing the cost of the whole cell. For practical applications, new kinds of cathode materials with high capacity, large energy density, and low toxicity are required [2-3]. Lithium-ion batteries mostly rely on lithium transition metal oxide, such as LiCoO_2 , LiNiO_2 and LiMn_2O_4 . However, some issues including safety, toxicity and cost of these materials inhibit their further use in price sensitive and large-scale applications, such as hybrid electric vehicles. Therefore, many efforts have been made to find alternate cathode materials for lithium-ion batteries [4]. Regarding this, lithium transition metal orthosilicate (Li_2MSiO_4 , $\text{M} = \text{Fe}$,

Co , Mn , Ni , etc.) have been successfully synthesized and characterized as potential cathode materials for lithium ion batteries (LIBs). Different from lithium transition metal phosphate which has only one lithium ion per formula unit, Li_2MSiO_4 has two lithium ions per formula unit, suggesting a higher theoretical capacity than phosphates [5, 6]. However, as a polyanion cathode material, $\text{Li}_2\text{FeSiO}_4$ also suffers from the low intrinsic electronic conductivity and the slow diffusion of lithium ion. Therefore, tremendous efforts have been made to solve this problem, such as carbon incorporation, particle size reducing, and metal ion doping to improve electrochemical property of $\text{Li}_2\text{FeSiO}_4$ [7, 8]. In this paper, Lithium iron orthosilicate cathode material was obtained by four different methods like, solid state, polyol, sol-gel, and co-precipitation. The as prepared cathode materials were characterized by XRD, FTIR, RAMAN, and SEM.

2. EXPERIMENTAL

The cathode materials were synthesized by various methods; they are Solid state reaction, Sol-gel method, Polyol technique, and Co-Precipitation method.

2.1 Solid state reaction:

The stoichiometric amounts of Lithium carbonate, Iron oxalate, Silicon dioxide and Citric acid monohydrate were used as the starting materials. The starting materials were ground for 1 hour using mortar and pestle. Then the precursor was calcined at 800°C for 10 hour under Ar atmosphere. Finally we obtain the final product of the material.

2.2 Sol-gel method:

The $\text{Li}_2\text{FeSiO}_4$ was prepared by sol-gel method based on citric acid. Analytical reagents CH_3COOLi , $\text{Fe}(\text{NO}_3)_3$, tetraethyl orthosilicate, and citric acid in a molar ratio of 2:1:1:3 were used as starting materials. CH_3COOLi and $\text{Fe}(\text{NO}_3)_3$ were first dissolved in distilled water. A saturated

aqueous solution of citric acid was slowly added to the above solution under magnetic stirring. After the formation of homogeneous solution, it was transferred into a reflux system where an ethanol solution of tetraethyl orthosilicate was also added. Under magnetic stirring, the reflux was carried out at 80 °C for at least 12 h until a clear greenish solution was formed. The solution was taken out, and then it was kept at 75 °C under magnetic stirring to evaporate ethanol and water. The resulting wet gel was dried in a vacuum oven at 100 °C. The dry gel was ground and then calcined at 800 °C for 12 h in flowing argon.

2.3 Polyol method

Stoichiometric molar ratio of Lithium acetate, Iron acetate and Silicon acetate were dissolved in a polyol solvent of Diethylene glycol (DEG). The mixed solution was refluxed near to the boiling point of the polyol solvent (245 °C) for 16 h. After that, the reacted solution was washed several times with ethanol and acetone. The resulting particles were dried in a vacuum oven at 150 °C for 1 day. Finally $\text{Li}_2\text{FeSiO}_4$ sample obtained.

2.4 Co-precipitation method

The precursor of $\text{Li}_2\text{FeSiO}_4/\text{C}$ was synthesized according to co-precipitation method. First, a certain amount of PEG200 was dissolved in distilled water, and the precipitating reagent ammonia water ($\text{NH}_3 \cdot \text{H}_2\text{O}$) was added drop wise until the pH of the mixed solution reached about 10. Then ethanol and deionized water was mixed solution of stoichiometric $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and tetraethyl orthosilicate (TEOS) was dropped into the above PEG200 solution under vigorous stirring, immediately, umber precipitate was formed. Subsequently, stoichiometric $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ was dispersed in the above solution. After stirring for about 30 min, the resulting mixture was evaporated by a rotary evaporator under vacuum at 80 °C, the excess solvent was removed and the final wet precursor was obtained. The wet precursor was then calcined at 700 °C for 10 h in flowing argon gas to obtain $\text{Li}_2\text{FeSiO}_4/\text{C}$ powders.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

Typical XRD profile of as-synthesized samples by various synthetic routes (pre-mentioned) are shown in Figure 1. The intensity of the peaks in XRD patterns is giving clear information about the crystalline nature of the samples and pure phase information as well. From these patterns, one can observe that the sample prepared via Polyol method exhibits higher intensity, sharper and tinier shift when compared to the pure $\text{Li}_2\text{FeSiO}_4$ [JCPDS 14-1657] [9]. It is worth noting that no diffraction peaks ascribable to carbon

are detected, probably due to amorphous phase of the carbon. The carbon present in the precursor acts as a good reducing agent to prevent the oxidation state in Fe^{2+} . It paved a way to obtain the phase pure material. In XRD pattern Polyol sample (PM) resulting a good crystallinity because it is a low temperature and energy efficient method [10], some impurity is also present in this pattern such as Li_2SiO_3 , Fe_2O_3 and $\text{Li}_2\text{Fe}(\text{Si}_2\text{O}_6)$, which may be observed from the patterns. From the diffraction patterns of the samples prepared via all methods, it is observed that the Polyol and sol-gel methods have better relation with pure material than the other methods studied.

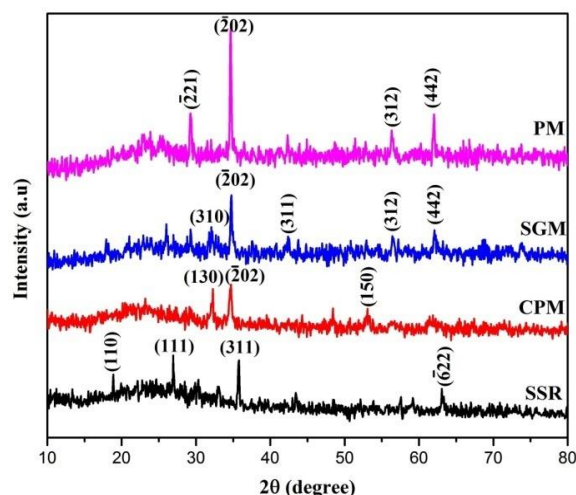


Figure 1. XRD Pattern of as-prepared $\text{Li}_2\text{FeSiO}_4$

3.2 FTIR Analysis

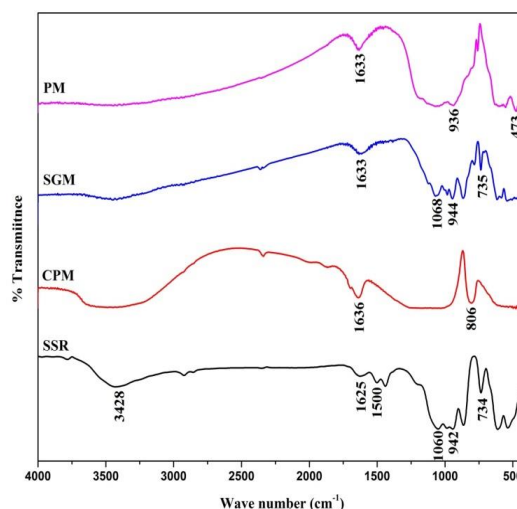


Figure 2-FTIR analysis of as-prepared $\text{Li}_2\text{FeSiO}_4$

Fourier Transform Infrared Spectroscopy (FTIR) can show additional structure information of as-prepared materials. Figure 2 shows the FTIR spectra of the $\text{Li}_2\text{FeSiO}_4$

samples prepared by Solid State Reaction (SSR), Co-precipitation (CPM), Sol-gel (SGM) and Polyol method (PM). FT-IR was performed to investigate the strong vibration of Si-O-Si in $\text{Li}_2\text{FeSiO}_4$ existed, depending on the different characteristic peaks of Si-O (735 and 936) in Li_2SiO_3 and $\text{Li}_2\text{FeSiO}_4$. The infrared bands at 735, 1060 and 1068 cm^{-1} attributed to the asymmetric vibration of Si-O-Si in SiO_4 tetrahedra. The peak at 1500 cm^{-1} represents the C-O vibrations in Li_2CO_3 owing to the exposure in air [11]. The bands at 944 and 936 cm^{-1} correspond to the stretching vibration of Si-O bonds in SiO_4 tetrahedra. The O-H stretching is appeared in the region at $3500 - 3100\text{ cm}^{-1}$.

3.3 Raman Analysis

Raman Spectroscopy is a useful tool to characterize sp^2 bonded carbon covering on the surface of the material. Figure 3 shows the Raman spectra of the prepared sample $\text{Li}_2\text{FeSiO}_4$. As shown in Figure (3) two broad peak (about 1300 and 1600 cm^{-1}), which are assigned to the disordered (D) and graphene (G) bands of carbon. This can be observed in both Sol-gel and Polyol processes. The ratio of D and G bands describe ordering of carbon on the lithium iron orthosilicate, ratio is smaller and ordering is high. The ratio was found to be 0.84 for Polyol and 0.80 for Sol-gel, which indicates that carbon in the material is evenly ordered, that make Polyol method based sample has good electronic conductivity as compared to Sol-gel. At the same time small intensity peak at 900 cm^{-1} , assigned to internal binding and stretching vibration of SiO_4 tetrahedra.

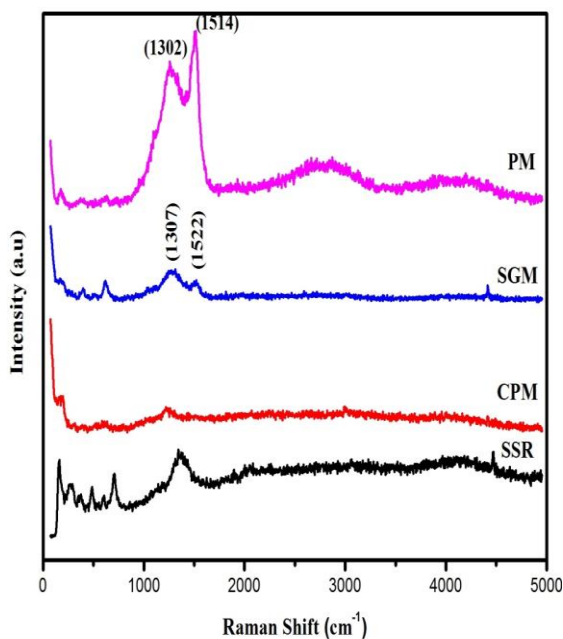


Figure 3-Raman analysis of as-prepared $\text{Li}_2\text{FeSiO}_4$

3.4 SEM Analysis

Figure 4 (a), (b), (c) and (d) shows the morphological studies of the $\text{Li}_2\text{FeSiO}_4$ are illustrated in figure by various synthesis processes like Co-precipitation, Polyol process, Sol-gel and Solid State reaction, with the various magnifications. Generally, particles are micron sized with irregular shape, which may attribute to interconnection from the carbon frameworks formed during the heat treatments. Compare to all these methods, uniform particles has been observed in the Sol-gel and Polyol method samples.

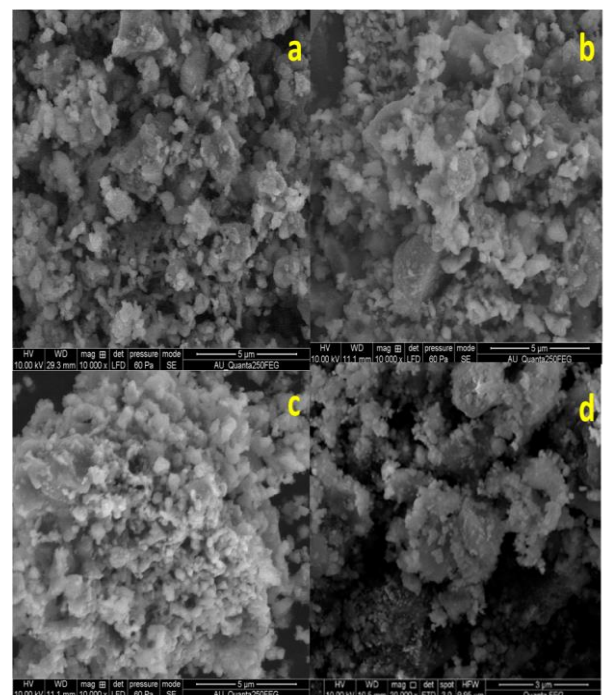


Figure 4-Sem images of as-prepared $\text{Li}_2\text{FeSiO}_4$

4. CONCLUSION

The Lithium iron orthosilicate has been synthesized with different route such as solid state, Sol-gel, and Co-precipitation method. Among these routes, polyol is the best method to synthesize the nano sized Lithium iron orthosilicate cathode material. These could be confirmed by Structural and morphological analysis like XRD, FTIR, RAMAN and SEM. The crystalline nature of the samples was investigated through XRD with different diffracted angle. From the XRD result, Polyol aided route possess clear diffracted angle with good intensity. Likewise, stretching and asymmetric vibration of Si-O and Si-O-Si explained by FTIR. By using RAMAN analysis the presence of D and G bands has been confirmed. The surface morphology of synthesized material has been studied by scanning electron microscopy.

One Day International Seminar on Materials Science & Technology (ISMST 2017)**4th August 2017****Organized by****Department of Physics, Mother Teresa Women's University, Kodaikanal, Tamilnadu, India****REFERENCE**

1. Z. Zhang, X. Liu, L. Wang, Y. Wu, H. Zhao, B. Chen, W. Xiong, *Electrochimica Acta*168 (2015) 8-15.
2. H. Qiu, H. Yue, T. Zhang, Y. Ju, Y. Zhang, Z. Guo, C. Wang, G. Chen, Y. Wei, D. Zhang. *Electrochimica Acta*188 (2016) 636–644.
3. H.Qiu, K. Zhu, H. Li, T. Li, L. Zhang, H. Yue, Y. Wei, F. Du, W. Chunzhong, G. Chen, D. Zhang. <http://dx.doi.org/10.1016/j.carbon.2015.02.056>.
4. C. Deng, S. Zhang, B.L. Fu, S.Y. Yang, L. Ma, *Materials Chemistry and Physics*120 (2010) 14–17
5. M.K. Devaraju, T. Tomai, I. Honma, *Electrochimica Acta*109 (2013) 75–81.
6. K. Gao, J. Zhang, S. Li, *Materials Chemistry and Physics*139 (2013) 550–556.
7. L. Zhang, S. Duan, X. Yang, G. Liang, Y. Huang, X. Can, J. Yang, M. Li, M. Croft, C. Lewis, *Journal of power sources* 274 (2013) 194-202
8. Y. Xu, W. Shen, C. Wang, A. Zhang, Q. Xu, H. Liu, Y. Wang, Y. Xia. *Electrochimica Acta*167 (2015) 340–347.
9. J-J. Lee, H-C. Dinh, S-I. Mho, I-H. Yeo, W. Cho, D.W. Kim. *Materials Letters*, <http://dx.doi.org/10.1016/j.matlet.2015.08.045>.
10. R. Muruganatham, M. Sivakumar, R. Subadevi. *Journal of power sources* 300 (2015) 496-506.
11. X. Du, H. Zhao, Y. Lu, C. Gao, Q. Xia, <http://dx.doi.org/10.1016/j.electacta.2015.12.039>



Subadevi Rengapillai received his Ph.D. in Alagappa University, and currently she is working Assistant professor in Alagappa University, Karaikudi. Her research interests focus on rechargeable Batteries, Super capacitors, Nano materials and Bio-diesel. She has published more than 39 papers in international journals.



Sivakumar Marimuthu received his Ph.D. in Alagappa University, and then Post-Doctoral Fellow in National Taiwan University, Taipei. Currently, he is now an Assistant professor in Alagappa University, Karaikudi. His research interests are in the areas of Batteries (Li-ion, Li-S and Na-ion), Super capacitors, Bio-fuels and Nano materials. He has published more than 41 papers in international journals.

BIOGRAPHIES

Kouthaman Mathiyalagan is presently a Ph.D. candidate in Department of Physics, Alagappa University at Karaikudi. His research interests focus on rechargeable batteries, like Li-ion, and Na-ion batteries.



Dhanalakshmi Renganathan is presently part time Ph.D. candidate in Department of Physics, at Alagappa University, and currently she is working Assistant professor in Department of Physics, Thiagarajar College at Madurai. Her research interests focus on energy materials devices, such as electrode materials for Li-ion, batteries.