



## ROLE OF CATIONIC SURFACTANT CTAB ON LITHIUM IRON ORTHOSILICATE

<sup>1</sup>K. Diwakar, <sup>1</sup>P. Rajkumar, <sup>2</sup>R. Dhanalakshmi, <sup>1</sup>R. Subadevi, <sup>1</sup>M. Sivakumar,  
<sup>1</sup>School of Physics, <sup>2</sup>Department of Physics,  
<sup>1</sup>Alagappa University, Karaikudi-630 004. Tamil Nadu, India.  
<sup>2</sup>Thiagarajar College, #139-140, Kamarajar Salai, MADURAI - 625009, India.

**ABSTRACT-** Lithium iron orthosilicate is a promising cathode material for hybrid electric vehicles owing to its excellent properties such as low toxicity, high thermal stability, abundance in nature, relatively high theoretical capacity etc., In this work, an attempt has been made to synthesize cathode material  $\text{Li}_2\text{FeSiO}_4$  with CTAB (cetyltrimethylammonium bromide) as a surfactant via modified co-precipitation route. Structural and morphological analyses of as-synthesized sample have been investigated by X-ray diffraction, Fourier transform IR spectra, Raman studies and SEM. During the synthesis route, influences of CTAB surfactant on Lithium iron orthosilicate was correlated and discussed.

**Keywords-** [Lithium ion battery; cathode; surfactant]

### 1. INTRODUCTION

Lithium ion batteries are a type of rechargeable battery which is widely used for portable electronic devices. Due to its highest energy density and its life cycle can be sustained for more than 10 Kilo cycles depending on their working conditions [1]-[3]. Development of LIB is quite diverse because of steady increasing demand on high energy storage devices. Among the cathode materials, lithium based metal oxide poses poor intrinsic safety which causes fire owing to the release of oxygen into the electrolyte. In order to control the oxygen release, polyanion type materials like phosphate, silicate, sulfate and borate preferably offer more safety and stability as compared to Metal oxide based cathode materials since oxygen is covalently bonded. Besides these by considering some

aspects such as excellent electrochemical behavior form on the feasibility and economic viability, abundance of raw materials, eco-benign nature are concerned to make promising cathode material[4],[5].

Particularly orthosilicate material  $\text{Li}_2\text{FeSiO}_4$  gaining more attention due to it offers two lithium ions per unit formula in both extraction and insertion process with theoretical capacity of  $\sim 330 \text{ mAh g}^{-1}$ . However, it is difficult to synthesize the pure phase of  $\text{Li}_2\text{FeSiO}_4$ ; hence very few only studied the electrochemical properties of orthosilicate. These cathode also posses the lower electronic conductivity, which is three times less than  $\text{LiFePO}_4$ . The low intrinsic electronic conductivity was evaded by a few ways, such as reducing crystallite size, by adding dopant, surface modification/ coating

with conductive carbon or metal nanoparticles [6]. Surfactant plays a vital role to control the particle size in nano scale. Thus, this work aims to obtain the well crystallite  $\text{Li}_2\text{FeSiO}_4$  material by CTAB as a surfactant via modified co-precipitation method [7], [8].

## 2. EXPERIMENTAL

Analytical grades of the Lithium acetate-Li ( $\text{CH}_3\text{COO}_2$ ), Iron (II) acetate-Fe ( $\text{CH}_3\text{COO}_2$ ), Tetraethyl orthosilicate- $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\text{NH}_3$ , cetyltrimethylammonium bromide (CTAB) were employed as a starting materials to prepare the  $\text{Li}_2\text{FeSiO}_4$  by co-precipitation process. Preparation starts with 20 wt% CTAB was dissolving in the de-ionized water to form two different solutions. Consequently, Ammonium was added into the solution drop wise to maintain the pH of about 10. Then the stoichiometric amounts of Iron and silicate sources separately mixed with de-ionized water and ethanol, that can be added drop wise into the dispersoid solution under vigorous stirring. After the formation of amber precipitate, Lithium acetate is dispersed into the solution for 1 hour stirring. Subsequently, the resultant mixture is dried in vacuum oven at  $80^\circ\text{C}$  to remove the excess solvent. Then obtained precursor was calcined at  $700^\circ\text{C}$  for 12 hours, resulting  $\text{Li}_2\text{FeSiO}_4$  particles.

## 3. RESULT AND DISCUSSION

### A. XRD analysis

Figure 1 shows XRD pattern of  $\text{Li}_2\text{FeSiO}_4$  synthesized by using CTAB as a surfactant. Reflection peaks of all starting materials are suppressed in the XRD result. At the same time, the desired material is not formed due to the complex formation the solution which comprises of so many elements in it. From this result, it is clear that there is an amorphous nature of desired material. However this material can be characterized by other investigation to bring the strong evidence to claim whether the surfactant is

good or not for the material synthesis. As conclude XRD, the pure phase of  $\text{Li}_2\text{FeSiO}_4$  is not obtained which is clearly manifested.

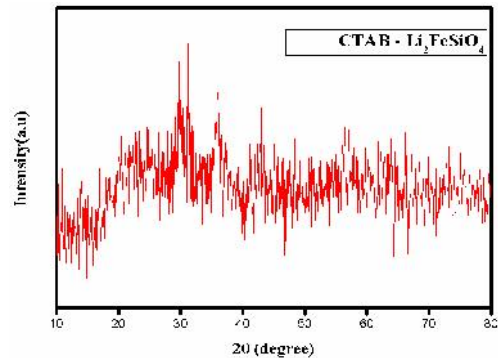


Figure 1- XRD patterns of prepared  $\text{Li}_2\text{FeSiO}_4$  sample

### B. FTIR and Raman studies

Moreover, impurities was easily appeared during the preparation of the material by co-precipitation process. Therefore, FTIR is a basic tool to investigate the existence of different phase of the sample. From here, the vibrational absorption band around  $866\text{ cm}^{-1}$  can be attributed to the stretching vibrations of  $\text{SiO}_4$ . Similarly, band about  $750\text{ cm}^{-1}$  and  $440\text{ cm}^{-1}$  are observed owing to the finger region of  $\text{Li}_2\text{SiO}_3$  and Li-O respectively. Carbon is not coated on the prepared material which can be confirmed by the raman because starting material is involved to form the carbon coating on the sample[9].

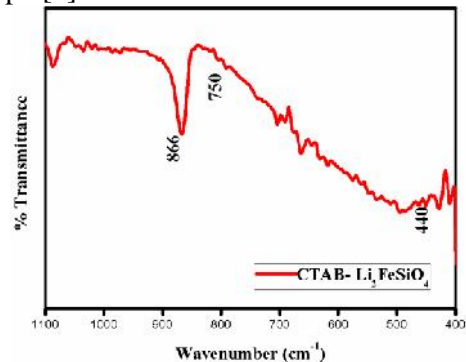


Figure 2- FTIR analysis of prepared  $\text{Li}_2\text{FeSiO}_4$  sample

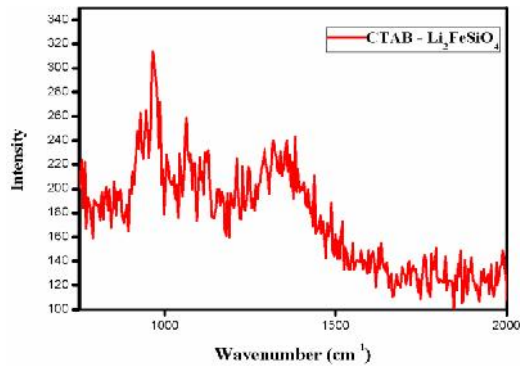


Figure 3- sample Raman analysis of prepared  $\text{Li}_2\text{FeSiO}_4$

### C. SEM

Morphology of the sample is also investigated by Scanning Electron microscope, this figure depicts that there is a non uniform structure of the desired material. Hence it is clear that the sample is not initiated during the reaction process.

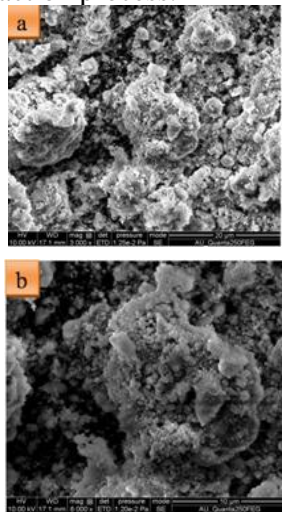


Figure 4- SEM images of prepared  $\text{Li}_2\text{FeSiO}_4$  sample

### CONCLUSION

In the case of metal oxide preparation, the surfactant CTAB acts as the nucleation centre and controls the morphology of the material. Thus, there is a trail to make the material  $\text{Li}_2\text{FeSiO}_4$  by using surfactant CTAB

via co-precipitation methods. The material couldn't obtain its pure phase as some difficulties is being arised due to the reaction rate.

### REFERENCES

- [1]. S. Esaki, M. Nishijima, and T. Yao, "Cycle Performance Improvement of  $\text{LiMn}_2\text{O}_4$  Cathode for Lithium Ion Battery by 'Nano Inclusion' Formation," ECS Electrochemistry Letters, vol. 2, no. 10, pp. A93–A97, 2013.
- [2]. P. I. Svens, L. Johan, B. Mårten, and L. Göran, "HEV Lithium-Ion Battery Testing and Driving Cycle Analysis in a Heavy-Duty Truck Field Study," 2012.
- [3]. S. Renault, R. Stéven, B. Daniel, and E. Kristina, "Environmentally-Friendly Lithium Recycling From a Spent Organic Li-Ion Battery," ChemSusChem, vol. 7, no. 10, pp. 2859–2867, 2014.
- [4]. J. Warner and W. John, "Lithium-Ion Battery Applications," in The Handbook of Lithium-Ion Battery Pack Design, 2015, pp. 177–209.
- [5]. H. Awano and A. Hidekazu, "Development of  $\text{LiCoO}_2$  Used for Rechargeable Lithium-Ion Battery," in Lithium-Ion Batteries, 2008, pp. 1–15.
- [6]. X. B. Wu, X. H. Wu, J. H. Guo, S. D. Li, R. Liu, M. J. McDonald, and Y. Yang, "Polyanion Compounds as Cathode Materials for Li-Ion Batteries," in Green Energy and Technology, 2015, pp. 93–134.
- [7]. Z. Gong, G. Zhengliang, and Y. Yong, "Recent advances in the research of polyanion-type cathode materials for Li-ion batteries," Energy Environ. Sci., vol. 4, no. 9, p. 3223, 2011.
- [8]. L. Yu, Y. Linghui, L. Qiaosheng, and W. Haihui, "Synthesis of  $\text{LiFePO}_4\text{-C}$  cathode materials using a green and low-cost method," Ionics, vol. 15, no. 6, pp. 689–692, 2009.
- [9]. W. Honggowiranto, H. Wagiyo, and K. Evvy, "Characterization of  $\text{LiFePO}_4$  cathode

by addition of graphene for lithium ion batteries,” 2016.

[10]. S. Sarkar and S. Mitra, “Carbon Coated Submicron sized-LiFePO<sub>4</sub>: Improved High Rate Performance Lithium Battery Cathode,” *Energy Procedia*, vol. 54, pp. 718–724, 2014.

[11]. K. Li, L. I. Keyan, S. Junjie, and X. Dongfeng, “SITE SELECTIVITY IN DOPED POLYANION CATHODE MATERIALS FOR Li-ION BATTERIES,” *Functional Materials Letters*, vol. 06, no. 04, p. 1350043, 2013.

[12]. C. X. Gong, O. E. Bankole, and L. X. Lei, “The Effect of CTAB Additive on Performance of Layered Cathode Material Li<sub>0.96</sub>Na<sub>0.04</sub>Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>,” *Adv. Mat. Res.*, vol. 800, pp. 501–504, 2013.

[13]. G. Cai and C. Guoqiang, “Process development in synthesis and recycle of lithium ion battery cathode material.” .

[14]. P. Larsson, L. P, A. R, N. A, and T. J, “An ab initio study of the Li-ion battery cathode material Li<sub>2</sub>FeSiO<sub>4</sub>,” *Electrochem. commun.*, vol. 8, no. 5, pp. 797–800, 2006.

[15]. H. Gao, G. Haili, W. Lizhen, Z. Yong, and S. Yanhua, “Effects of solvent composition on the electrochemical performance of Li<sub>2</sub>FeSiO<sub>4</sub>/C cathode materials synthesized via tartaric-acid-assisted sol-gel method,” *Ionics* , vol. 20, no. 6, pp. 817–823, 2013.

[16]. Z. Zhang and S. S. Zhang, *Rechargeable Batteries: Materials, Technologies and New Trends*. Springer, 2015.

[17]. K. I. Ozoemena and S. Chen, *Nanomaterials in Advanced Batteries and Supercapacitors*. Springer, 2016.

[18]. R. Tan, T. Rui, Y. Jinlong, Z. Jiabin, W. Kai, L. Lingpiao, J. Shunping, L. Jun, and P. Feng, “Fast rechargeable all-solid-state lithium ion batteries with high capacity based on nano-sized Li<sub>2</sub>FeSiO<sub>4</sub> cathode by tuning temperature,” *Nano Energy*, vol. 16, pp. 112–121, 2015.

[19]. D. Ye and Y. Delai, “Development of high capacity Li-rich layered cathode materials for lithium ion batteries”.