

SYNTHESIS AND STRUCTURAL ANALYSIS OF NaFePO₄ NANOCOMPOSITE FOR SODIUM ION BATTERIES

V. Priyanka¹, R.Subadevi², M.Sivakumar^{3*}

^{1,2,3} #120, Energy Materials Lab, Department of Physics, Alagappa University, Karaikudi-630 003, Tamil Nadu, India.

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

Abstract - Sodium-ion batteries (SIBs) have attracted attention as a competitive alternative to LIBs because of their low cost and the wide availability of sodium resources. Polyanionic Transition-metal phosphates with open-framework structures have been subject to growing scientific interest as electrode materials for sodium-ion batteries. This is mainly due to the remarkable structural and thermal stabilities of this class of materials. In particular, iron-based phosphate compounds such as NaFePO₄ have been intensively studied as positive electrode materials for sodium ion batteries. The material is synthesized via sol-gel and solid state methods and its structural studies have been analyzed. The crystalline nature of the material was analyzed using X-ray diffraction for both the methods. The intensity of the peaks of NaFePO₄ prepared by sol-gel method seems to be higher than solid state method. The presence of functional groups and vibrational peaks of PO₄³⁻ groups were identified using Fourier transform infra - red spectroscopy. The raman shift for Fe-O vibrations was investigated by laser raman spectroscopy. The morphology and the microstructure of the sample were studied using scanning electron microscopy. The particle size was found to be between 100-150nm. The results revealed that as prepared NaFePO₄ nano composite prepared by sol-gel method serves as promising cathode material for sodium ion batteries.

Key Words: Sodium ion batteries, NaFePO₄, Cathode material, Structural studies, Sol-gel method.

1. INTRODUCTION

Vehicle electrification is one of the most significant solutions that address the challenges of fossil fuels depletion, global warming, CO₂ pollution and so on. Sodium is the fourth most abundant element in the earth's crust and United States alone has huge reserves of 23 billion tons of soda ash. Therefore, sodium-ion chemistry is an attractive and alternative energy storage technology to replace LIB because of its abundance (uniformly distributed everywhere across the world) and inexpensive raw material cost for preparing sodium-based electrode materials [1, 2]. Sodium

has a redox potential of E_{Na⁺/Na} = -2.71 V versus standard hydrogen electrode; it is only 0.3 V above that of lithium indicates that rechargeable cells based on sodium chemistry are one of the promising energy storage technologies. Besides these advantages, so many sodium-based energy storage technologies are available, such as, sodium-sulfur cells, sodium-air cells, ZEBRA cells and sodium ion cells [3]. As compared with other sodium-based storage technologies, sodium ion cells possess advantages such as high voltage (approximately 3.6 V), operating well even at room temperature, inexpensive electrode and electrolyte-active materials and, more significantly, easy portability[4]. In view of safety and cost concerns, polyanion-based compounds have been explored for LIBs during the last two decades. These include olivine phosphates [LiMPO₄ (M=Fe, Mn, Ni, etc.)], favorite fluorophosphates and fluorosulfates[5].

2. EXPERIMENTAL

2.1 Method 1(S₁): In solid state method all the raw materials such as sodium acetate, Iron(II) sulphate and Ammonium dihydrogen phosphate are taken in the stoichiometric ratio. It is ball milled for 4 hours and dried at 150°C for 12 hours. After ball milling the raw materials are calcined at 350°C for 4 hours. Again it is calcined at 600°C for 6 hours by passing argon gas.

2.2 Method 2(S₂): In sol gel method, Initially sodium acetate and citric acid were dissolved in 20ml of de-ionized water under magnetic stirring at 80°C. Then a stoichiometric amount of Iron(II) sulphate and Ammonium dihydrogen phosphate were added to the above solution and stirred until a gel was formed. Once the formation of gel occurs it is transferred into a petridish and dried at 120°C for 10 hours under vacuum to form xerogel. Finally, the xerogel was finely ground and then calcined at 800°C for 10 hours under argon atmosphere.

2.3 Characterization: To find out the crystalline phase structure of the as-prepared materials, powder X-ray

diffraction analysis (model : PANalytical X-pert Pro diffractometer) was carried out by CuK α radiation (wavelength = 0.154nm). The functional group vibration was analyzed using a Thermo Nicolet 380 FT-IR spectrophotometer using KBr pellets in the range 4000 – 400cm⁻¹ and through laser raman spectrometer, (STR 500, LASER RAMAN SPECTROMETER ,SEKI, JAPAN). The surface and particle morphology of the samples were observed using a scanning electron microscope (FEG quanta 250).

3. RESULTS AND DISCUSSION

3.1 Structural characterizations:

A) XRD analysis:

The XRD patterns of the as prepared samples NaFePO₄ by solid state and sol-gel method denoted as S₁ and S₂ respectively is shown in the figure(1). The vertical bars at the bottom of the graph corresponds to the expected positions of the bragg reflections. The positions of all the diffraction peaks allow us to identify the material as NaFePO₄ with olivine structure. The sample obtained by sol-gel method was found to be more crystalline than solid state reaction. This may be due to low temperature that allows for the fine control of the product's chemical composition.

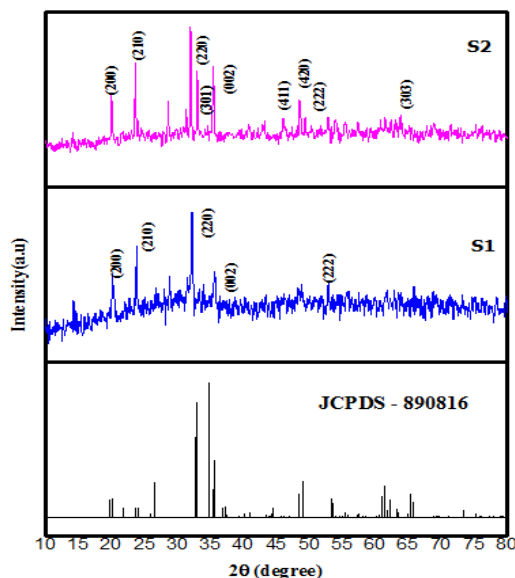


Fig-1: shows the XRD analysis of as prepared samples S1 and S2.

All the diffracted peaks are indexed to ordered orthorhombic structure with a space group of Pnma. The lattice parameter of the sample was found to be a = 8.4553Å,

b = 5.5934Å, c = 5.0666Å. The unit cell volume was calculated as 239.619m³[6]. Therefore, among the two methods sol-gel method reveals good result for the as prepared sample with good crystallinity.

B) FTIR analysis:

The FT-IR spectrums were analyzed for the presence of functional groups. The analysis was carried out in the area of PO₄³⁻ group oscillations [7]. The broad band arising around 1054cm⁻¹ is assigned to absorbed peak resulted by PO₄³⁻ asymmetric stretching. The weak peaks arising around 630cm⁻¹ corresponds to symmetric stretching vibrations. The bands corresponding to the asymmetric deformation of PO₄³⁻ are located in the region 540 - 580cm⁻¹. It can also be observed that P-O stretching modes appear in the range of 1000 – 850cm⁻¹ as well as a P-O bending mode was observed below 700cm⁻¹. The bands arising 3400 and 1600 cm⁻¹ assigns to O-H stretching mode [8,9].

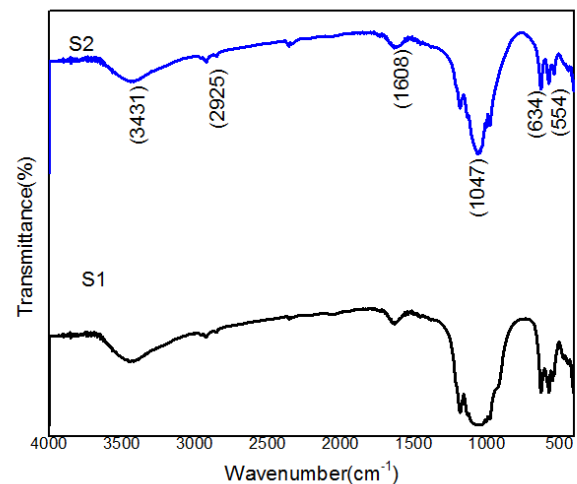


Fig-2: shows the FT-IR spectra of as prepared samples S1 and S2.

C) Raman analysis:

Fig 3 shows the Raman spectra of the prepared samples. The local structure of NaFePO₄ was analyzed by laser Raman spectroscopy. The Raman shift appeared in the range of 400 – 700cm⁻¹ belonging to Fe-O vibrations. The existences of tetrahedral PO₄³⁻ with internal modes have been observed. The peaks at 940, 580,420cm⁻¹ are assigned to various vibrational modes. The asymmetric stretch mode is split into two different signals at 1030 and 990cm⁻¹ because of distortion of PO₄³⁻[10].

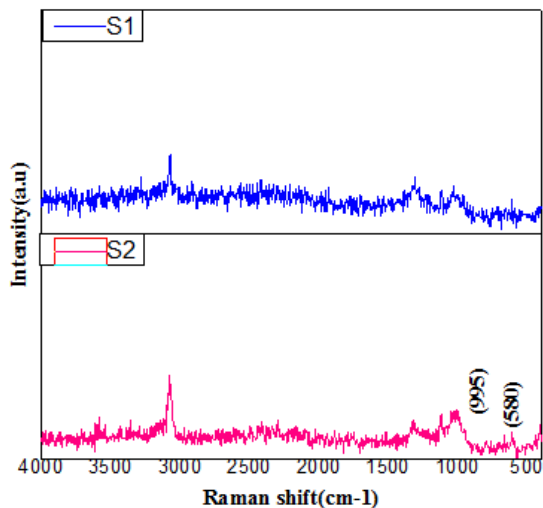


Fig-3: shows the Raman spectra of as prepared samples S1 and S2.

3.2 Morphological and elemental analysis:

D) SEM Analysis:

The surface morphology of the samples prepared by solid state and sol-gel method were analyzed using scanning electron microscope with various magnifications. The particle size of the sample S1 is in the range of 30 – 80nm. In sol-gel method the particle size was found to be in the range of 100 – 200nm. The sample synthesized by solid state method appears to be in cluster form. The formation of spherical particles in sol-gel method can be attributed to the dehydration reaction caused by the direct condensation polymerization of phosphate groups.

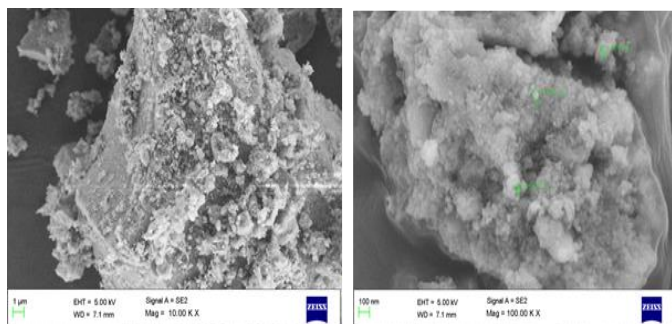


Fig -4: shows the SEM images of as prepared sample S1.

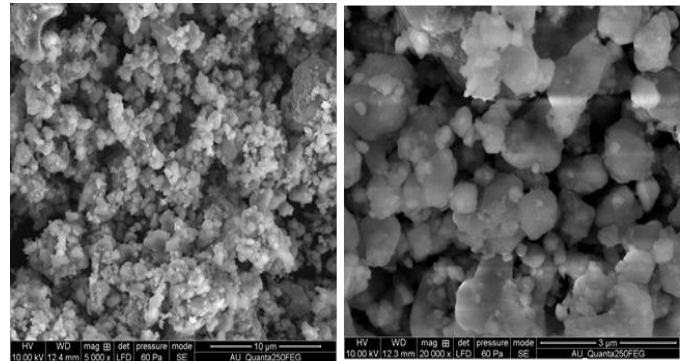


Fig -5: shows the SEM images of as prepared sample S2.

4. CONCLUSION:

Overall, NIBs are considered to be a promising alternative to LIBs due to the abundance of sodium and low cost; however, still it lags behind in performance as compared to LIBs. This is attributed to the size of Na⁺ ion which makes intercalation/deintercalation a difficult phenomenon and results in poor cycle life and low capacity which in turn affects the volumetric energy and power density. The NFP samples were synthesized by means of solid state and sol-gel method. The method of synthesis plays an important role for the material preparation. Crystalline nature and diffraction patterns were observed using XRD analysis. Raman and FTIR spectroscopy have analyzed functional group vibrations of the prepared sample. Scanning electron microscope was employed towards studying their surface morphology.

5. REFERENCES:

1. Ellis Bl, Nazar LF. Sodium and sodium energy storage batteries. *Curr Opin solid state Mater sci* 2012, 16:168-177.
2. Goodenough .JB, Rechargeable batteries: challenges old and new. *J Solid State Electrochem* 2012, 16:2019–2029.
3. Bullis K. Sodium-ion cells for cheap energy storage. *Technology review*, Published by MIT, Wednesday December 2, 2009.
4. Pan H, Hu YS, Chen L. Room-temperature stationary sodium-ion batteries for large-scale electric energy storage. *Energy Environ Sci* 2013, 6:2338–2360.
5. Recham N, Chotard JN, Dupont L, Delacourt C, Walker W, Armand M, Tarascon JM. A 3.6 V lithium-

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**

based fluorosulphate insertion positive electrode for lithium-ion batteries. Nat Mater 2010,9:68-74.

6. C.Li, X. Miao, W. Chu, P. Wu, D. G. Tong. J. Mater. Chem. 1-6 (2015).
7. X. Lin, Y. Zhao, Y. Dong, Q. Kuang, Z. Liang, D. Yan, X. Liu. Materials Science and Engineering B 197 (2015) 58-66.
8. L. ZhiMing, W. Xianyou, W. Ying, T. Anping, Y. Shun yi, H. LiangFu, Trans. Nonferrous Met. Soc. China 18(2008)346-350.
9. H. Zhuo, X. Wang, A. Tang, Z. Liu, S. Gamboa, P. J. Sebastian, J. Power Sources 160 (2006) 698-703.
10. Y. Kawabe, N. Yabuuchi, M. Kajiyama, N. Fukuhara, T. Inamasu, R. Okuyama, I. Nakai, S. Komaba, E. Chem. Communications 13 (2011) 1225-1228.