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STRUCTURAL STUDIES OF $NaFePO_4$ NANOCOMPOSITE FOR SODIUM ION BATTERIES

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Abstract *Sodium ion batteries have a tremendous attraction recently as the best alternative to lithium ion batteries for potential application in large scale electrical energy storage devices. Among the various classes of iron phosphate cathodes used in sodium ion batteries, $NaFePO_4$ is one of the most attractive host materials for advanced sodium ion batteries owing to its structural stability. A new polyanionic $NaFePO_4$nanocomposite has been synthesized via sol–gel route. The structural evolution of the material was characterized by powder X-ray diffraction.The intensity of the peaks of $NaFePO_4$ is much stronger, which implies that the structure of the material is more orderly. The presence of certain functional groups was identified using Fourier transform infra–red spectroscopy. The FT-IR spectrum of sodium ion phosphate mainly consists of vibrational peaks of PO_4^{3-} groups. The local structure of $NaFePO_4$ was investigated by laser Raman spectroscopy. The Raman shift appeared in the range of 400–700cm^{-1}that belongs to Fe-O vibrations. The surface morphology of the sample was analyzed using scanning electron microscope with various magnifications. The particle size was found to be in the range 100–200nm. These results explored that the as-prepared $NaFePO_4$nanocomposites may be a promising candidate as cathode material for sodium ion batteries.*

Keywords: *Sodium ion batteries, $NaFePO_4$, Phosphates, cathode material.*

Introduction

Lithium ion batteries are widely used as power sources for advanced portable electronics because of their high energy density. However, the relative scarcity of lithium has impeded the application of lithium ion batteries for future large scale energy storage. [1] Therefore, there is a broad interest in the development of alternative sodium ion batteries due to wider availability and low cost of Na, which is two hundred times more abundant than lithium in nature[2]. To make sodium ion batteries aggressive, a critical component is cathode material. Polyanionictransistion metal phosphates with open framework structures play an important role for the growing scientific field as electrode materials for sodium ion batteries. It is mainly due to the incredible structural and thermal stabilities of this class of materials. In particular, iron based phosphate compounds such as $NaFePO_4$, $[Na_{1-x}Li_x]MnFe_2(PO_4)_3$, $Na_3Fe_3(PO_4)_4$, $FePO_4$, $Na_2Fe(P_2O_7)$ have been intensively studied as positive electrode materials for sodium ion batteries[3]. Recently, it has been reported that new iron based phosphates $Na_2M_2Fe(PO_4)_3$ (M=Co and Ni) as dual anode/cathode material for sodium ion batteries[4]. These materials have been prepared by solid state reaction, revealed the promising electrochemical properties.Electrochemical insertion of sodium ion phosphates $Na_3Fe_2(PO_4)_3$ has shown that sodium ions can be accommodated into this host[5]. Similar to $LiFePO_4$, $NaFePO_4$ might be a good candidate as electrode materials in electrochemical cells. They are known for their excellent redox abilities and thermal stability, also transition metal phosphates have been studied in detail.

In this work, we have synthesized $NaFePO_4$ materials using sol-gel route. The structural characterization of sodium based electrode material includes X-ray diffraction(XRD), Fourier transform spectroscopy(FT-IR), Raman Spectroscopy and scanning electron microscopy(SEM).

ChemicalsUtilized

Chemicals like Sodium Acetate, Iron(II) sulphate, Ammonium dihydrogen phosphate, citric acid, acetone and ethanol were used for the preparation of sodium ion phosphate.

Material Synthesis

The nanocomposite $NaFePO_4$ was synthesized via sol-gel route. Initially sodium acetate and citric acid was dissolved in 20ml of de-ionized water under magnetic stirring at 80°C. Then a stoichiometric amount of Iron(II) sulphate and Ammoniumdihydrogen phosphate was 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 h under vacuum. Finally, the gel was finely ground and then calcined at 800°C for 10 h under Argon atmosphere.

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 CuKα 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 sample were observed using a scanning electron microscope (FEG quanta 250).

Result and Discussion

XRD Analysis

The crystal structure of the as prepared sodium iron phosphate was examined by X-ray diffraction analysis and has been illustrated in theFig.1. The nature of the peaks depends on the method of synthesis. The peak position, intensity and the sharpness of the peak for the sample prepared by sol-gel method indicates the pure crystalline nature of the material. The XRD patterns explicitly show that the as-synthesized material has predominant peaks at 2θ = 32.01, 33.07, and 35.35° corresponds to the miller indices (220),(121) and (002) respectively. This pattern is in good agreement with the JCPDS:89 - 0816, for orthorhombic structure with Pnma space group. The peaks may be raised due to the presence of olivine type material having orthorhombic system with primitive lattice.The calculated lattice parameter for the obtained sample was found as a = 8.4553Å, b = 5.5934Å, c = 5.0666Å. The unit cell volume was determined as 239.619 m^3[6]. Therefore, from the patterns it is observed that the sample prepared by sol-gel method exhibits good crystallinity with sharp peaks.

FT-IR Analysis

The FT-IR spectrum was observed for the investigation of the structure of the sample. The analysis was carried out in the area of PO_4 group oscillations[7]. The Fig.2 represents the FT-IR spectrum of the sample prepared by sol-gel method. The broad band arising around 1054cm^{-1} is assigned to the absorbed peak resulted by PO_4^{3-} asymmetric stretching. The weak peaks arising around 630cm^{-1} corresponds to the symmetric stretching vibrations of PO_4^{3-}. The bands corresponding to the asymmetric deformation of PO_4^{3-} are located in the region 540-580cm^{-1}[8]. It can also be observed that P-O stretching modes appears in the range of 1000-850cm^{-1}, as well as P-O bending modes was observed below 700cm^{-1}.The bands arising around 3400 and 1610cm^{-1} assigns to O-H stretching mode. It is well known that FT-IR spectrum of phosphates mainly consist of inner vibrated peaks of PO_4^{3-} groups and some other groups. Thus from the FT-IR spectrum of the samples, it can be confirmed that this material is in phosphate type [9].

Raman Spectroscopy

The local structure of $NaFePO_4$ was investigated by optical spectroscopy (Fig.3). The occurrence of tetrahedral PO_4^{3-} groups with four internal modes is noted. The Raman shift appeared in the range of 400-700cm^{-1} belongs to Fe-O vibrations. The peaks at 950, 590 and 420cm^{-1} are assigned to v_1,v_4 *and* $v_2$modes respectively. The asymmetric stretch $v_3$mode is splitted into two different signals at 1090 and 1120 cm^{-1} because of the distortion of PO_4^{3-} groups[10].

SEM Analysis

The surface morphology of the sample was analyzed using scanning electron microscope for the as-prepared samples with various magnifications are shown in Fig.4. In sol-gel method, the particle size was found to be in the range of 100–200nm. The formation of small particles in sol-gel methodcan attribute to the dehydration reaction caused by the direct condensation polymerization of phosphate groups. In addition to it, an agglomeration phenomenon appears in the particles leading to small amount of secondary particles of larger size ranging from 100–150nm.

Conclusion

Depending on the method of synthesis, crystalline sodium ion phosphate was obtained. Crystalline nature and diffraction patterns were observed using XRD analysis. Raman and FT-IR spectroscopy have analyzed the functional group vibrations of the prepared sample. Scanning electron microscope was employed towards studying their surface morphology. Therefore, proceeding towards this direction will be possible to further improve the performance of the material in order to achieve a sodium ion battery with a cost/ performance ratio competitive with lithium battery systems.

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FIGURE CAPTIONS

Figure1. XRD pattern of as-prepared $NaFePO_4$
Figure 2.FT-IR spectra of as-prepared$NaFePO_4$
Figure 3. Raman spectra of as-prepared$NaFePO_4$
Figure 4.SEM images of the prepared sample at various magnifications (10, 50 and 100k)

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Figure 1

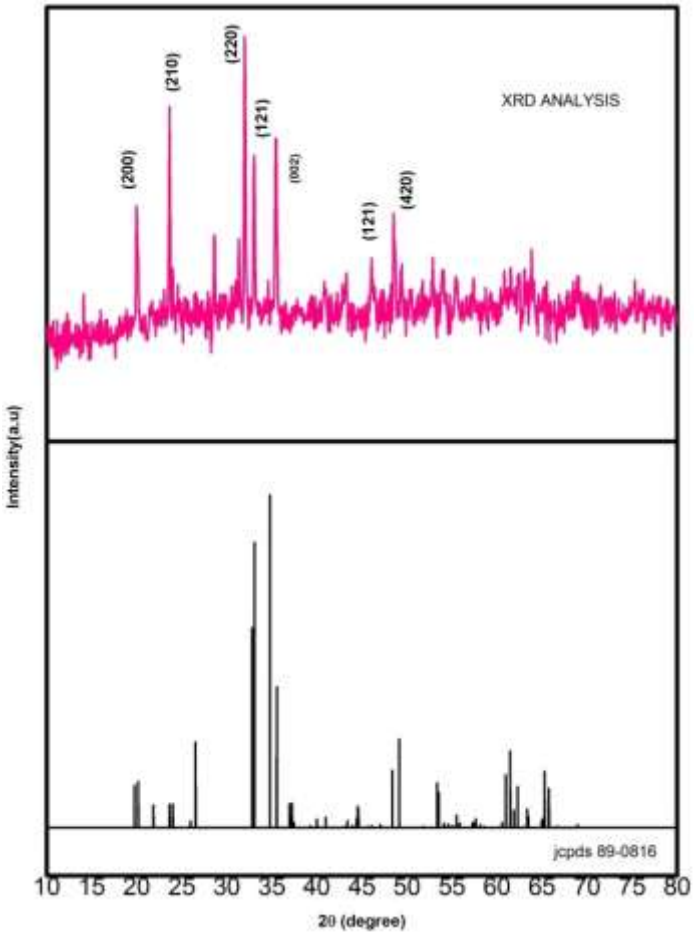

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Figure 2

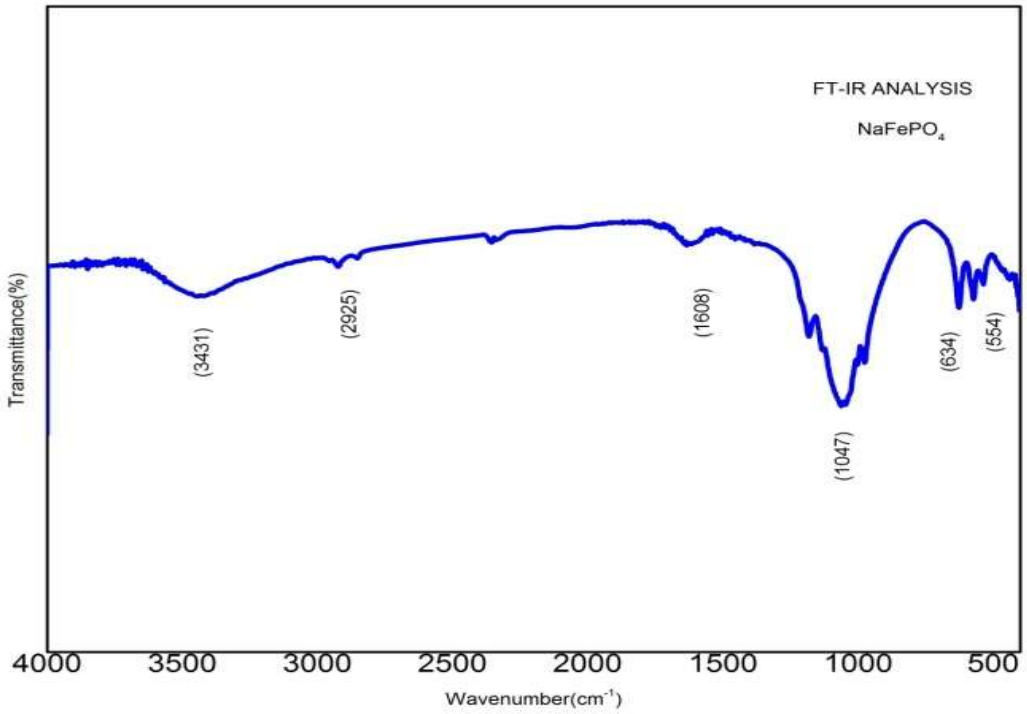

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Figure 3

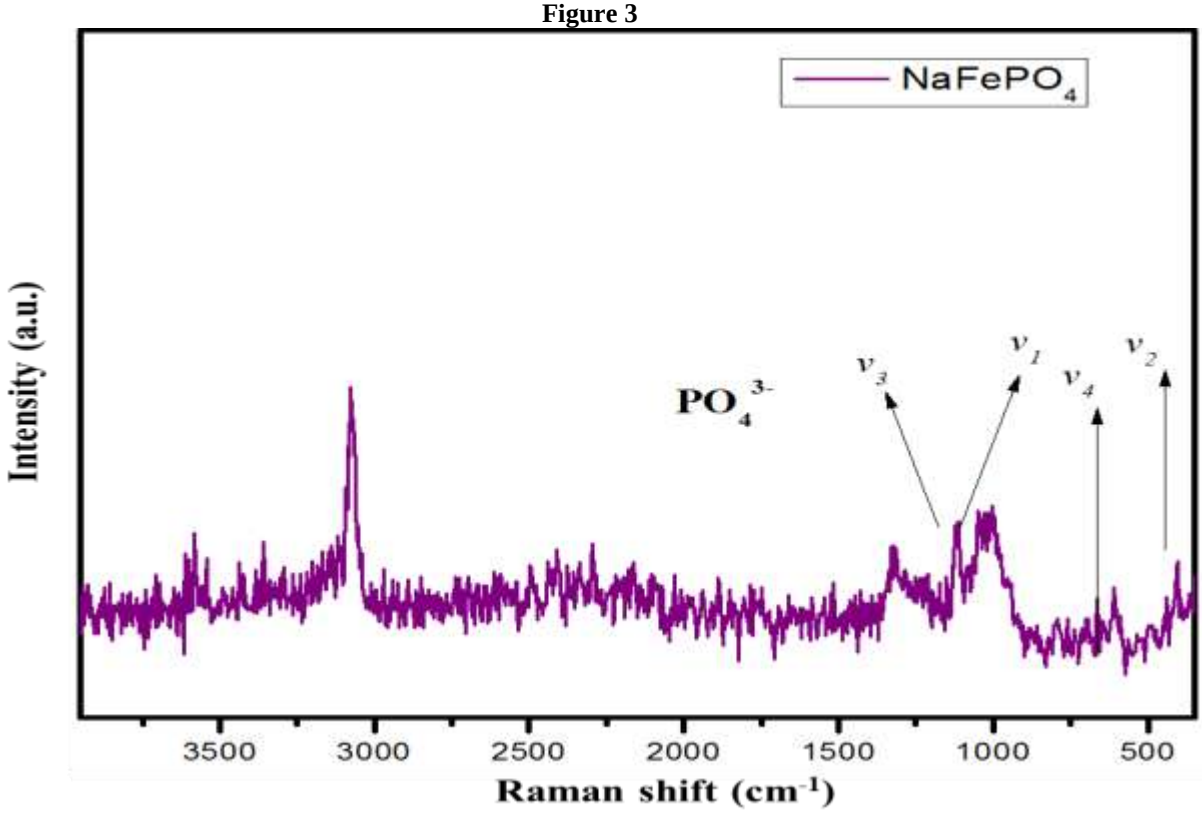

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Figure 4

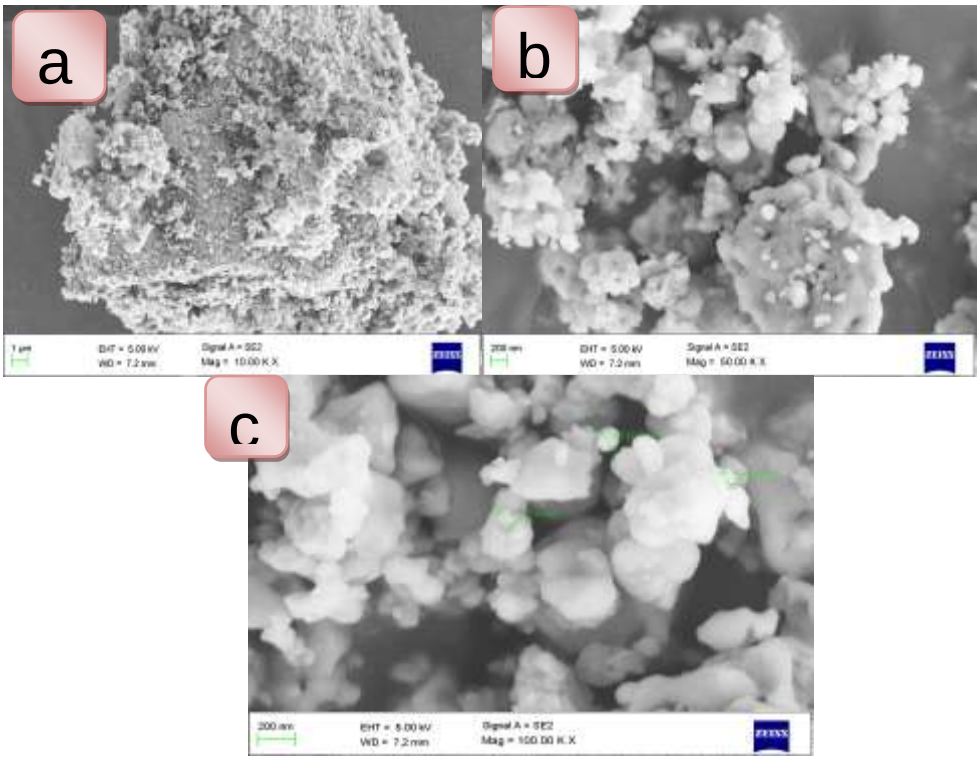

Figure (iv)

