

Synthesis of highly dispersed FePO₄ cathode material for rechargeable lithium battery

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Abstract

Highly dispersed, porous and nano-sized FePO₄ have been synthesized by a facile aqueous and alcoholic medium for their application as cathode in rechargeable lithium batteries. Various dispersing templates in association with suitable solvents are used to introduce porosity and dispersive nature among the particles and to reduce the size of the particles. Characterization with FTIR, powder XRD and SEM suggests the formation of less crystalline, pure FePO₄ with high surface area and high porosity. Cyclic voltammetry has been employed to test the intercalation behaviour of lithium ions and confirms the reversible nature of the material. The role of the dispersing template for the material growth and the electrochemical performances of the synthesized FePO₄ as cathode in lithium battery have been discussed. It is found that poly(styrene-co-divinylbenzene) as the dispersing agent produces highly dispersed material with highest discharge capacity of 138 mAh.g⁻¹. Copyright © 2017 VBRI Press.

Keywords: Iron (III) phosphate, amorphous material, cyclic voltammetry, discharge capacity, lithium ion battery.

Introduction

LiFePO₄ has been regarded as the most promising and potential cathode material for the next generation (lithium-ion batteries) LIBs [1-7]. The causes of this popularity are to possess few advantageous properties such as, low cost starting materials, environment friendliness, high theoretical specific capacity (170 mAhg⁻¹), good operating voltage, flat charge-discharge potential and excellent cycling performances [8-15]. However, the synthetic methodologies of LiFePO₄ are associated with some cost intensive raw chemicals and also some harsh conditions such as, to maintain inert atmosphere and high temperature calcinations [16-21]. Otherwise, unexpected aerial oxidation produces undesirable Fe(III)-compounds. These difficulties make the procedure cost intensive. To prevail these drawbacks, it is intended to synthesize FePO₄ chemically rather LiFePO₄, followed by lithium ion insertion to form LiFePO₄ electrochemically during discharge process against Li anode in the LIBs [22-25]. In this way, the synthesis of LiFePO₄ using expensive raw materials such as iron(II) and lithium salts, and use of controllable inert gas reaction chamber can be avoided. However, in the general synthesis method crystalline FePO₄ is produced and use of such crystalline FePO₄ as cathode ends up with poor performance due to sluggish Li⁺-ion intercalation [26-28]. Therefore, to improve Li⁺-ion intercalation rate, highly dispersed FePO₄ with high surface area are demanded [24, 29-32]. In the present study, we have synthesized highly dispersed FePO₄ with

high surface area employing easier aqueous and alcoholic route varying different dispersing agent and their results are compared. These FePO₄ are used as cathode vs. Li anode and their electrochemical performances are investigated.

Experimental

Materials

Ethanol (Bengal Chemical, India, 98%), iron (III) nitrate nonahydrates (Merck, India, 98%), diammonium hydrogen phosphates (Merck, India, 99%), polyvinyl alcohol (Merck, Germany, 99%), citric acid (Merck, India, 99%), iron (III) chloride (Merck, India, 96%), ortho-phosphoric acid (Merck, India, 88%), oleylamine (Sigma-Aldrich, USA, 70%), styrene (Aldrich, USA, 99%), divinylbenzene (Aldrich, USA, 80%), ammonium peroxydisulfate (Merck, India, 98%), iron (III) nitrate nonahydrate (Alfa-aesar, 99.9%), carbon black (Alfa Aesar, USA, 99.9%), graphite powder (Alfa Aesar, USA, 99.99%), polyvinylidene fluoride (Aldrich, USA, 99.9%), N-methyl pyrrolidone, (Merck, USA, 99.5%), Li ribbon (Aldrich, USA, 99.9%), LiPF₆ (Alfa Aesar, 98%), ethylene carbonate (Aldrich, USA, 99.9%) and dimethyl carbonate (Aldrich, USA, 99.9%).

Materials synthesis procedure

Highly dispersed FePO₄ were synthesized applying aqueous and alcoholic (ethanol) medium using different starting chemicals and different dispersing agents. In case

of aqueous medium, iron (III) nitrate nonahydrates and diammonium hydrogen phosphates were used as iron and phosphate source, respectively; and polyvinyl alcohol (PVA), citric acid or mixture of them were used as dispersing agent. Additionally, poly(styrene-co-divinyl benzene) nano emulsion was used to synthesize highly dispersed FePO_4 .

On the other hand, in case of ethanolic medium, iron (III) chloride and ortho-phosphoric acid were used as iron and phosphate source, respectively; and oleylamine was used as template.

Method-I– In order to produce 3.0 g of FePO_4 , 8.2 g of iron (III) nitrate nonahydrate (Merck, India, 98%) and 2.653 g of diammonium hydrogen phosphates were dissolved separately in two beakers containing 50 ml of water. In the next step, 1.0 g of polyvinyl alcohol dissolved in 25 ml hot water was added to the iron (III) nitrate solution and the mixture was stirred for four hours to get homogeneous clear solution. Afterwards, the prepared diammonium hydrogen phosphate solution was added to the previous solution drop-by-drop with constant stirring and the stirring process was continued for the next four hours. The resulting mixture was allowed to settle, followed by two hours continuous heating at 80-90 °C. A yellow colloidal precipitate was appeared. The solvent water was evaporated to dryness and thus a yellow solid powder was obtained, which was first dried at 100 °C and then calcined at 450 °C for 4 hours in a tubular furnace in atmospheric condition. After cooling down to room temperature, the material was stored for further use.

In another two methods, the required chemicals and reaction methodology are same as *Method-I*, only change is in the dispersing agents, viz. citric acid (1.0 g) in *Method-II*; and mixture of polyvinyl alcohol (0.5 g) and citric acid (0.5 g) in *Method-III*.

Method-IV– 14 ml styrene and 1 ml divinylbenzene were added to a beaker containing 20 ml of ethanol. In another beaker, 1.0 g polyvinyl alcohol was dissolved in 64 ml water by heating and stirring. Then the first solution was poured into the second solution with constant stirring. 0.5 g Ammonium peroxodisulfate was added to the reaction mixture, followed by heating and stirring at 80°C, which was continued up to 5 hours. A white colloidal suspension of poly(styrene-co-divinylbenzene) was resulted [33-36]. 8.044 g Iron (III) nitrate nonahydrate (Alfa-aesar, 99.9%) was added slowly into the colloidal suspension followed by constant stirring. 2.653g di-ammonium hydrogen phosphate dissolved in 50 ml of water was added drop-wise from a burrate with constant stirring. An off-white gelatinous precipitate was appeared, which was filtered with suction and washed with water and then ethanol. The precipitate was heated at 450°C in a tubular furnace for 4 hours in air and then it was preserved for further use when cooled down to room temperature.

Method-V– 3.361 g Iron (III) chloride was dissolved in 100 ml of ethanol in a beaker. Then 30 ml of oleylamine was added to it and stirred for four hours. In the next step, 1.266 ml of ortho-phosphoric acid dissolved in 10 ml of ethanol was added drop-wise with constant stirring, which

was continued for next four hours. A reddish-brown precipitate was appeared. The ethanol in the mixture was evaporated to dryness. Then the resulting solid material was calcined at 450 °C in the tubular furnace for 4 hours in air. After cooling to room temperature the material was collected for characterization.

Characterization

The synthesized materials were characterized by FTIR (Prestige-21, Shimadzu, Japan), Powder XRD (Ultima III Rigaku, Japan; $\text{Cu K}\alpha$, $\lambda=1.5406 \text{ \AA}$) and SEM (JEOL, JSM-6360, UK). Powder XRD was recorded with the synthesized materials, which were calcined at 450 °C and 700 °C in the region of $2\theta=10-80^\circ$.

Electrochemical characterization was performed by cyclic voltametry (CV) and galvanostatic charge discharge studies. The measurements were carried out preparing laboratory model cells by a galvanostat/potentiostat (VersaStat TMII, Princeton Applied Research, USA). The cathode mixture was obtained by mixing the synthesized material with carbon black, graphite powder and Polyvinylidene fluoride (PVDF) in the ration of 80:8:8:4 in presence of N-methyl pyrrolidone (NMP) as solvent [17, 37-39]. The carbon black, graphite powder and the PVDF serve as conducting support and binder, respectively. The slurry, as obtained, was then spread over aluminium foil and the coated foil was heated at 60 °C under vacuum to remove the solvent, NMP. The coated foil was then pressed using a hydraulic press at 8 Tcm^{-2} to achieve a better contact between the active material and the current collector. The coated foil was finally heated at 80 °C under vacuum for 12 hour to remove NMP completely and thus the positive electrode was ready for cell fabrication [18, 40, 41].

The cell was assembled inside a glove bag by purging dry argon gas. Li ribbon was pasted on a nickel foil to be used as an anode. LiPF_6 , equivalent to one molar, was dissolved in 1:1 ethylene carbonate (EC) and dimethyl carbonate (DMC) mixture and used as the electrolyte and a porous polypropylene (PP) film soaked with the electrolyte was used as separator [42-44]. The CVs were recorded with the differently synthesized FePO_4 as working electrode, Li^+/Li as reference electrode and 1 M LiPF_6 in EC+DMC (1:1) as electrolyte, at the scan rate of 0.1 mVs^{-1} . The charge-discharge studies were carried out with the laboratory model cells within the potential range of 2.0 to 4.2 Volts at 0.1 C rates [30, 45-49].

Results and Discussion

FTIR spectroscopy

Fig. 1 demonstrates FTIR spectra of FePO_4 synthesized in *Method I*. There are two types of bands observed in the FTIR spectrum of FePO_4 in the region of $400-1200 \text{ cm}^{-1}$.

The bands in the region of $850-1150 \text{ cm}^{-1}$ are arisen due to the intramolecular stretching vibration (ν_3 and ν_1) of P-O bond of phosphate group and the bands in the region of $400-700 \text{ cm}^{-1}$ are arisen due to the intramolecular bending (ν_4 and ν_2) vibrational mode of phosphate group.

The bands located at 1060 cm^{-1} (ν_3) and 943 cm^{-1} (ν_1) are assigned to the stretching mode of vibration of P-O bond in PO_4^{3-} anion. Whereas, the bands located at 470, 565 and 642 cm^{-1} are assigned to the bending (ν_4 and ν_2) vibration of PO_4^{3-} anion [50-52].

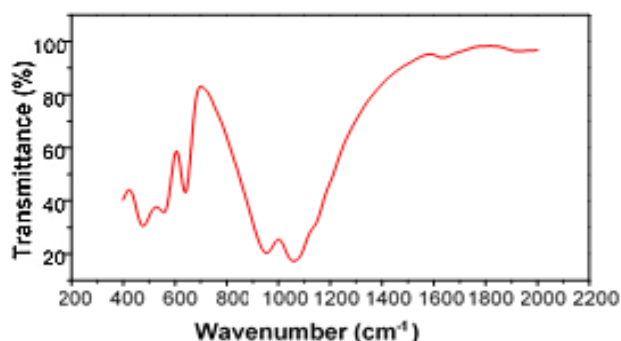


Fig. 1. FTIR spectrum of FePO_4 produced in *Method-I*.

Powder XRD pattern

Powder XRD patterns of differently synthesized FePO_4 calcined at $450\text{ }^\circ\text{C}$ and $700\text{ }^\circ\text{C}$ is shown in **Fig. 2a**, whereas **Fig. 2b** shows the XRD pattern of FePO_4 , calcined at $700\text{ }^\circ\text{C}$. **Fig. 2a** shows that there are two major peaks at $2\theta=20.352^\circ$ and $2\theta=25.841^\circ$ for the materials obtained after calcinations at 450°C [27,53,54]; and the same materials, when calcined at $700\text{ }^\circ\text{C}$ show different peak patterns (**Fig. 2b**). The XRD peak patterns displayed in **Fig. 2b** were compared with JCPDS file no. 290715 for FePO_4 and complete peak position matching was observed. However, only two major peaks are observed when the materials were calcined at 450°C . This indicates that the crystalline particle growth occurs above $450\text{ }^\circ\text{C}$.

It is known to us that synthesis of material at higher temperature produces more crystalline product. This is due to the increase of compactness between the particles at higher temperature and thus porosity among the particles decrease. Herein, the materials which we obtained after calcinations at 450°C are less crystalline and highly dispersed. Since, increases of crystallinity results in decrease of porosity among the particles, the materials were sintered at an optimum temperature of 450°C to facilitate dispersive nature of the particles with little crystallinity. Crystallinity as well as porosity is an important factor essential for a good electrode material to accelerate the lithium-ion intercalation and de intercalation processes.

Scanning electron microscopy

SEM images are taken to investigate the particle morphology of the materials. **Fig. 3** has illustrated the five SEM images of FePO_4 compounds obtained from five different methods.

The SEM images reveal that the materials comprise of different grain size with dissimilar porosity. *Method-I* exhibits a smaller size particle with higher porosity in comparison with *Method-II* and an average result was found in *Method-III*. The particles are nano to micrometer in size in *Method-I*.

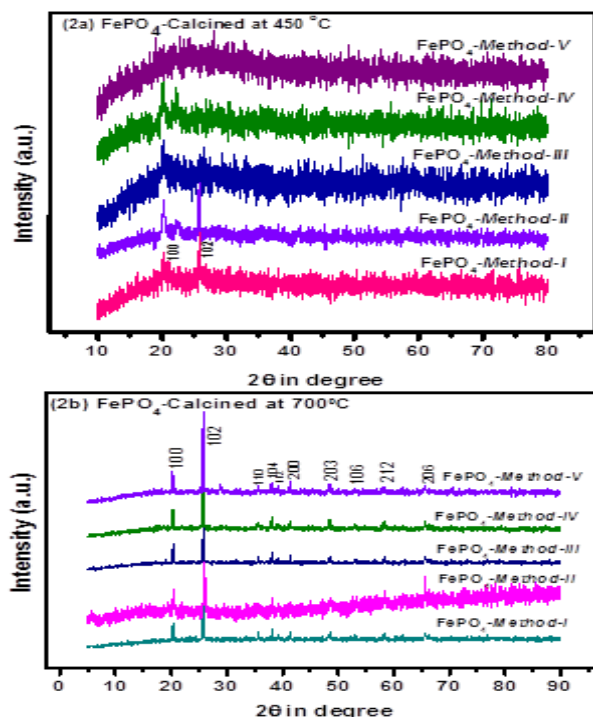


Fig. 2. Powder XRD patterns of differently synthesized FePO_4 calcined at (a) $450\text{ }^\circ\text{C}$ and (b) $700\text{ }^\circ\text{C}$.

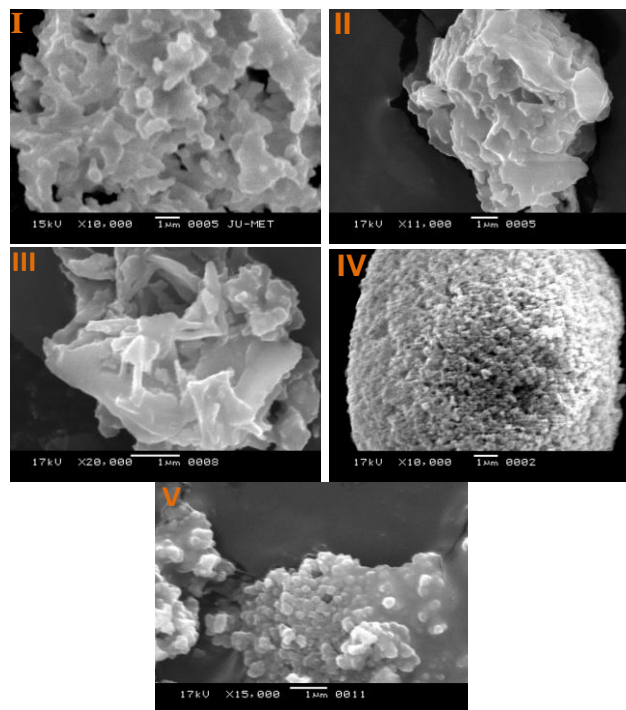


Fig. 3. SEM images of differently synthesized FePO_4 .

In *Method-V* where ethanol was utilized as solvent, the particles are smaller than *Method-I*. Besides, the particles are found to be spherical in shape, which increases their surface area. This is to be mention here that the small size and large surface area of the materials enhances the Li^+ ion diffusion into the cathode.

Best result is obtained in *Method-IV*, where, the particles are seen to be nanometer in size, well ordered and highly dispersed.

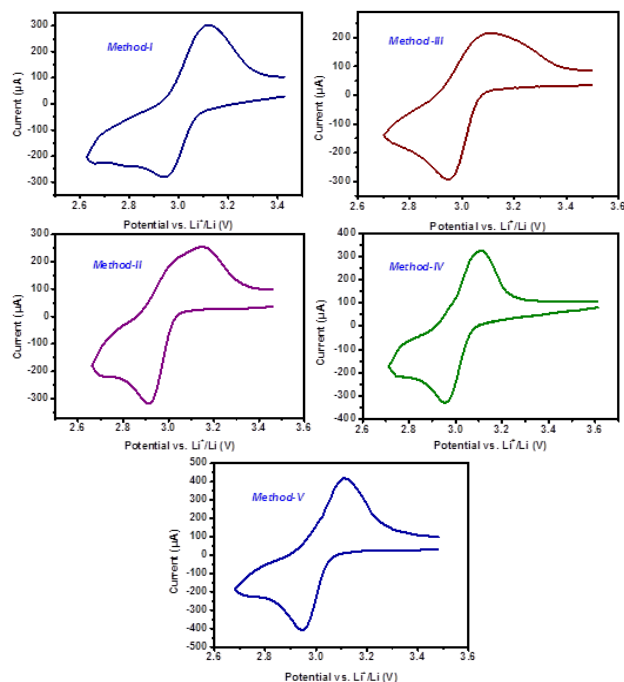


Fig. 4. Cyclic voltammograms of differently synthesized FePO_4 vs. Li^+/Li in 1 M LiPF_6 in EC+DMC (1:1) at the scan rate of 0.1 mVs^{-1} .

Electrochemical characterization

Cyclic voltammograms of differently synthesized FePO_4 are displayed in Fig. 4. CVs were performed to find out the redox position and the electrochemical reversibility of the materials. The oxidation and reduction peak potential of different FePO_4 is tabulated in Table 1.

Table 1. Oxidation and reduction peak potential vs. Li^+/Li of differently synthesized FePO_4 .

Method	Oxidation peak potential (V)	Reduction peak potential (V)
I	3.12	2.94
II	3.15	2.91
III	3.11	2.95
IV	3.11	2.95
V	3.11	2.94

All the materials exhibit reversibility in CV curves, however the extent of reversibility may differ from each other as infer from the curve. The oxidation and reduction peaks were observed at an average voltage of 3.11 and 2.94 volts, respectively [23, 54]. The electrochemical performances of the materials were investigated by the charge-discharge studies with the fabricated laboratory model cells made of different FePO_4 . The cells were discharged first and then charged. During discharge, Fe(III)PO_4 is reduced by Li and LiFe(II)PO_4 is formed. Whereas, on charging, reverse process occurs; LiFe(II)PO_4 is oxidised and thus, Fe(III)PO_4 and Li are produced. The charge-discharge were carried out galvanostatically at 0.1 C rate, exhibits different capacities for different materials. The charge-discharge profile for each material in the first cycle is illustrated in Fig. 5 [23, 26, 27, 30, 54].

The discharged capacities, obtained from the charge-discharge profile, are 120, 110, 122, 138, 132 mAhg^{-1} in

Method I, II, III, IV, and V, respectively. The capacity is different because the feature of the material is different, which is arisen during synthesis. Few factors such as, porosity, dispersiveness, particle sizes etc. principally control the specific capacity and finally performance of the material in the cell. The performance of the material, synthesized in Method IV, was found to be most excellent, where the dispersion template was poly(styrene-co-divinylbenzene) nano emulsion. On the other hand, the material synthesized in alcoholic medium (Method-V), performed satisfactorily, where oleylamine was used as the template.

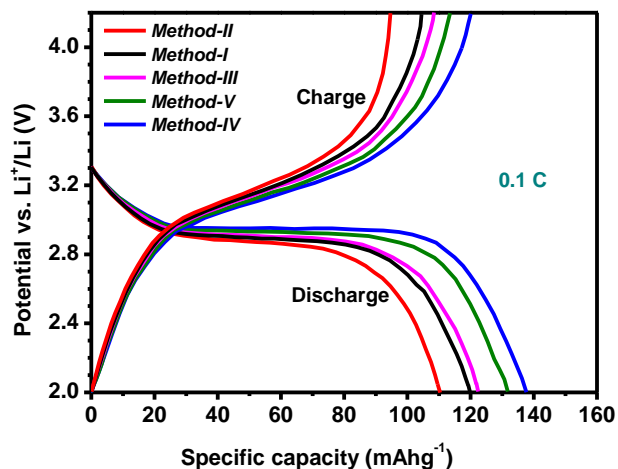


Fig. 5. Charge-discharge curves of differently synthesized FePO_4 .

Conclusion

Highly dispersed FePO_4 has been synthesized employing facile aqueous and alcoholic routes. Different dispersing template such as, polyvinyl alcohol, citric acid, poly(styrene-co-divinylbenzene) and oleylamine have been used to increase the porosity, dispersiveness and decrease the particle size of FePO_4 . Powder XRD and SEM reveal that all the materials are porous, dispersed and nano to micrometer in size. However, results are to some extent different from each other because the activity of different template are different, which ultimately reflects on their battery performances. Polyvinyl alcohol is acting as better template than citric acid in aqueous medium. In ethanol medium, performance of oleylamine is satisfactory. However, the excellent result comes from the material, where poly(styrene-co-divinylbenzene) nano emulsion was used as the template. Herein, the material is highly dispersed, mesoporous, orderly oriented and nanometer in size.

The feature of material effects on its cell performance. The FePO_4 , where the dispersion template was poly(styrene-co-divinylbenzene) nano emulsion shows the most excellent performance among the other materials synthesized in aqueous method. The discharge capacity was found 138 mAhg^{-1} at 0.1 C rate. On the other hand, the material synthesized in alcoholic medium, where oleylamine was used as the template performs satisfactorily. In this case, the discharge capacity was found 132 mAhg^{-1} at 0.1 C rate.

Author's contributions

Conceived the plan: BM, IBM, SG. Performed the experiments: BM. Data analysis: BM, IBM, SG. Wrote the paper: BMD, IBM, SG. Authors have no competing financial interests.

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