Synthesis and Characterization of $\text{Li}_x\text{fepo}_4/\text{C}$-Ppy Composite Cathode Material with Excess of Li$^+$ Doping

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Abstract: In-situ Polyppyrole (Ppy) coating was performed on the surface of Li$_x$FePO$_4$/C (x=0.95 to 1.20) particles using iron (III) tosylate as oxidizer. The composite material Li$_x$FePO$_4$/C (x=0.95 to 1.20) was synthesized by two step method. FePO$_4$/polyaniline particles were first synthesized by chemical precipitation and were further heat treated with lithium acetate and sucrose under reduced atmosphere. XRD pattern confirms that Li$^+$ addition to LiFePO$_4$ has increased interplaner spacing and of the unit cell size. Impurity phase appears with x=1.15 and 1.20 which further disappears after polymer coating. After polymerization process the XRD pattern shows Li$_x$FePO$_4$ and LiFePO$_4$/phases and both the phases have same electrochemical behavior. Morphology of the Li$_x$FePO$_4$/C and Li$_x$FePO$_4$/C-Ppy was studied by using FE-SEM and it was found that particles are spherical with size range below 200nm. Transmission Electron Microscope (TEM) also confirms that Li$_x$FePO$_4$/C isolated particles were well encapsulated within the polymer matrix.

Keywords: LiFePO$_4$/C composite, coating, polymer, in-situ polymerization

I. INTRODUCTION

The olivine structured LiFePO$_4$ has developed much interest as a promising cathode material for lithium ion battery due to its high theoretical capacity (170mAh/g), high structural stability excellent safety and low cost since it was first proposed by Goodenough [1, 2, 3]. However, the low electronic conductivity and slow 1-dimensional insertion/extraction of lithium ion through the structure have restricted the commercialization of this material [4, 5, 6]. The electrical conductivity of this material can be increased by metal doping in the structure and conductive surface coating.

[7, 8]. Further lithium ion diffusion can be increased by reducing the particle size [9, 10]. The conducting form of polyaniline (PANI) coated LiFePO$_4$ has increased the cyclability and rate capability [11]. Polyppyrole can be used as successful coating material to increase the cyclic stability of LiFePO$_4$/C cathode material [12]. Since the polyppyrole also have higher cyclability (500cycle), good theoretical capacity (70mAh/g) to store Li$^+$ and is electrochemically active so, it can increase the cyclability without much affecting the overall energy density of cathode [13].

During the processing such as synthesis and electrochemical activity of cathode material, the partial loss of Li$^+$ occurs. The first loss occurs during first charge of battery and was due to the formation of passivating solid electrolyte interphase (SEI) layer [12]. The second loss occurs due to long time charging/discharging process in the cathode material, this leads to the adherence of some Li-ion on surface of anode. And the final loss occurs if there is conductive surface coating of polymer, because during polymerization reaction loss of lithium occurs and polymer coated LiFePO$_4$/C material was observed as lithium deficient [13]. So, excess of lithium doping would be required in the structure of LiFePO$_4$/C material to improve the cyclability and capability of composite material.

Till now the properties of polyppyrole coated LiFePO$_4$/C with higher lithium doping has not studied. In the present work initially we have synthesized Li$_x$FePO$_4$/C (x = 0.95 to 1.20) particles in the nano-range to decrease the diffusion length and finally these particles were in-situ coated by polyppyrole to improved the cyclability and rate capability.

II. SYNTHESIS

A. Synthesis of Li$_x$FePO$_4$/C

The materials Li$_x$FePO$_4$/C(x=0.95 to 1.20) was synthesized in two step. In the first step FePO$_4$/PANI was synthesized by chemical precipitation method. To synthesize FePO$_4$/PANI, aqueous solution of 0.0278mol of (NH$_4$)$_2$HPO$_4$ and FeCl$_3$ was added with 0.5ml of aniline monomer units with continuous stirring for 8hrs at 65ºC. On addition of FeCl$_3$ to (NH$_4$)$_2$HPO$_4$ white precipitation of FePO$_4$ starts growing and turns dark green due to formation of Polyaniline after 3hr. The precipitate was filtered out and washed with di-ionized water and acetone.
In the second step different molar ratio of CH₃COOLi (0.95, 1.00, 1.05, 1.10 1.15 and 1.20) with respect to FePO₄ were homogeneously mixed using mortar-pestle for 1hr. The resulting mixture was further calcined at 700 °C under reduced atmosphere (Ar(90%)+H₂(10%)) for 15hrs and LiₓFePO₄/C material was obtained.

B. Synthesis of LiₓFePO₄/C-PPy

For the synthesis of LiₓFePO₄/C-PPy (x=0.95 to 1.20) composite material a known quantity of LiₓFePO₄ (1g) was added to 20 ml ethanol containing 20wt.% Iron(III)tosylate. The mixture was stirred in the temperature range of 1-5°C for 30min followed by addition of 252µl liquid pyrrole monomers. The suspension was kept stirred for another 30min in the temperature range of 2-5°C. The solution was filtered and washed with ethanol. The resulting composite LiₓFePO₄/C-PPy was kept in a vacuum oven for 5 hrs at 55°C.

III. CHARACTERIZATION

The morphology was observed with field emission scanning electron microscopy (FE-SEM, FEI, Quanta 200F) operating at 20kV. The X-ray diffraction pattern was obtained, on Bruker, D8 ADVANCE diffractometer with CuKα radiation. The phase and structure analysis was performed using XRD data on PANalytical’s X’Pert HighScore Plus software. Images of samples were observed using transmission electron microscopy (TEM, with FEI-TECHNAI-20) operating at 200kV.

IV. RESULT AND DISCUSSION

A. XRD Analysis

The fig. 1 shows the X-ray diffraction pattern of LiₓFePO₄/C(x=0.95 to 1.20). All the peaks of patterns for the samples having composition x = 0.95 to 1.10 represent pure single phase and can be indexed on the basis of olivine type orthorhombic structure with space group pnma of LiFePO₄ (with JCPDS file no. 98-005-9133). For x=1.15 and 1.20 compositions the impurity phase LiₓPO₄ appears along with LiFePO₄.

From the fig.1 it was observed that there is continuous shift of peak towards lower Bragg angle for LiₓFePO₄/C(x=0.95 to 1.15). The peak shift was due to the excess of lithium along 1-dimensional (010) direction [14]. Peak shift relative to LiFePO₄ can be easily observed from fig 2 and it was found that maximum peak shift occurs for the sample composition x = 1.15. But for the same material impurity phase LiₓPO₄ appears at 2θ=22.32º and 23.16º and grows for further addition of lithium (for x=1.20). The peak shift towards lower Bragg angle has increased the interplaner spacing, this results to generate uniform strain in the crystal lattice [14]. Due to this uniform strain the crystal structure becomes unrelaxed. From the diffraction pattern it was found that crystallites for x=1.10 have maximum strain, without LiₓPO₄ phase impurity. The LiₓPO₄ considered as impurity phase, because the phase does not have electrochemical properties [15, 16]. For x=1.20 peaks tends to come at their respective positions and there was a slight increase in the peak intensity of LiₓPO₄ impurity phase, showing that addition of more lithium goes to the crystallites of LiₓPO₄ instead to provide strain to crystallite of LiFePO₄. The absence of carbon peak in the diffraction pattern may be due to amorphous phase of carbon or/and low content.

The lattice parameter of LiFePO₄ was worked out using the Bragg law for the orthogonal system:

\[ d = \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2} \]

The calculations were performed using three maximum intensity peaks and obtained values of lattice parameters were listed in table1.

| Table 1. Variation of lattice parameter with Li⁺ doping. |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|
| LiₓFePO₄                        | a (Å)           | b (Å)           | c (Å)           | V (Å³)          |
| x = 0.95                       | 10.2994         | 5.9935          | 4.6263          | 285.58          |
| x = 1.00                       | 10.3154         | 5.9949          | 4.6707          | 288.84          |
| x = 1.05                       | 10.3212         | 6.0041          | 4.6794          | 289.99          |
| x = 1.10                       | 10.3219         | 5.9515          | 4.7268          | 290.38          |
| x = 1.15                       | 10.3561         | 6.0284          | 4.7236          | 294.90          |
| x = 1.20                       | 10.3421         | 5.9937          | 4.6902          | 290.97          |

So, excess lithium content has increased the crystallite volume from 285.58 to 294.90 Å³ for LiₓFePO₄/C and hence interplaner spacing, this originates the shift of peak intensity towards lower Bragg angle.

B. Explanation of XRD after PPy coating

Fig.3 shows the XRD pattern of LiₓFePO₄/C(x=0.95 to 1.20) coated with Polypyrrole composite material (LiₓFePO₄/C/PPy(x=0.95 to 1.20)). All the major peaks were matched with olivine type pnma structure (with JCPDS file no. 01-083-2092).

![Fig.1 XRD pattern of LiₓFePO₄/C(x=0.95 to 1.20) - Click to view](image)

![Fig. 2 Relative shift in 2θ values with respect to Li₁₀FePO₄ - Click to view](image)

![ICITEE logo](image)
From the diffraction pattern it was found that all the peaks have nearly same position and there was no significant shift in the peak positions, showing that LiFePO₄ crystallites were strain free. Diffraction pattern of composite material Liₓ₋₀.₀₅FePO₄₋ₓCPPy shows a weak intensity peak corresponding of Li₀.₀₅FePO₄₋₀.₀₅ (with JCPDS No. 98-10-8284) at 17.95°. Li₀.₀₅FePO₄ and LiFePO₄ both have same electrochemical behavior and lithium storage capacity [17]. Other peaks of Li₀.₀₅FePO₄ phase become significant gradually for higher lithium content (for x=0.95 to 1.10) and Li₁₋₀.₀₅FePO₄₋₀.₀₅CPPy composite material shows highest no/intensity of peaks for Li₀.₀₅FePO₄ phase. Peak intensity for this phase further decrease for x=1.15 and 1.20. The increase in the peak intensity of Li₀.₀₅FePO₄ phase for x=1.10 shows that this material donate maximum Li⁺ to PPy.

LiFePO₄/C in the pyrole composite is still same. From the constant particle size and EDS it is confirmed that there was no dilution of LiFePO₄ particle during polymerization of pyrole. This confirms that LiFePO₄ particles were chemically stable during polymerization; the fact was already confirmed by XRD analysis of LiFePO₄/C-PPy.

Fig. 3 XRD pattern of LiₓFePO₄₋ₓ/C-PPy (x=0.95 to 1.20)

The highest strain for x=1.10 pure phase structure results maximum Li₀.₀₅FePO₄ phase. It may happen because, due to strain, the crystallites donate more Li⁺ to polymers to come in relax stage. After coating no peaks were observed in the XRD patterns of LiₓFePO₄₋ₓ/C-PPy (for x=0.95 to 1.20) for LiFePO₄ impurity phase. It is concluded that this phase dilute during polymerization reactions and lithium of the phase may go to the polymer chains as polymer chains also have the ability to store Li⁺ [18]. For LiₓFePO₄₋ₓ/C-PPy (for x=1.15 and 1.20) composites both the phases LiₓPO₄ and LiFePO₄ contributes to the saturation of polymer chains for Li⁺. For LiₓFePO₄₋ₓ/C-PPy(for x=1.15 to 1.20) composite materials the observed intensity peak for Li₀.₀₅FePO₄ is reduced because, conversion of LiFePO₄ to Li₀.₀₅FePO₄ is suppressed due to presence of LiₓPO₄ phase.

C. Powder morphology

The morphology of as synthesized LiₓFePO₄/C and LiₓFePO₄₋ₓ/C-PPy powders is as shown in fig. 4(a, c) and (b) respectively. The SEM image of LiₓFePO₄/C shows spherical particles are agglomerated through carbon shell having size nearly 200nm this was further confirmed by Dynamic light scattering (DLS) studies. The carbon coating on LiₓFePO₄/C was confirmed by Energy Dispersive Spectroscopy (EDS). The EDS also confirms the ratio of Fe:P:O is 1:1:4. Fig.4(b) shows the SEM image of LiₓFePO₄₋ₓ/C-PPy. The two phases LiₓFePO₄/C and PPy are clearly distinguishable. The EDS shows that the ratio of Fe:P:O is 1:1:4 for LiFePO₄ (for x=1) is still maintained which clearly shows that stoictometry of elements is same in the PPy matrix showing LiₓFePO₄/C is attached to PPy by physical bonding. The particle size of

Fig. 4 FE-SEM micrograph of (a) Li₁₋₀.₀₅FePO₄₋₀.₀₅/C and (b) Li₁₋₀.₁₅FePO₄₋₀.₁₅/C-PPy and (c) Li₁₋₀.₁₅FePO₄₋₀.₁₅/C (d) EDS spectra of Li₁₋₀.₁₅FePO₄₋₀.₁₅/C-PPy

D. TEM Analysis

The typical TEM image of LiₓFePO₄/C-PPy is shown in fig 5. For the LiₓFePO₄/C-PPy composite, TEM image confirms that particles are embedded in the continuous polypyrrole matrix. The TEM image also confirms that particles are mono-dispersed and does not stick together due to their magnetic behavior as it can be seen in case of LiFePO₄/C from fig 5. The polypyrrole matrix behaves as fast conducting bridge and for such a system of mono disperse particles diffusion length of Li⁺ completely depends upon particles size[22].

Fig. 5 TEM image of LiₓFePO₄/C-PPy
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V. CONCLUSION

Polypyrrole coated Li$_4$FePO$_4$/C (x=0.95 to 1.20) composite was successfully synthesized. XRD pattern of Li$_4$FePO$_4$/C (x=0.95 to 1.20) confirms that Li$^+$ addition to LiFePO$_4$ has increased the cell volume and d-spacing due to which a uniform stress induced in the crystal. Impurity phase Li$_3$PO$_4$ has appeared for x=1.15 and 1.20. During polymerization the impurity phase diluted and was not appeared in XRD pattern. FE-SEM confirms the spherical morphology of Li$_4$FePO$_4$/C and Li$_4$FePO$_4$/C-Ppy particles having size 200 nm. The carbon shell and polymer coating on the particles were clearly visible in FE-SEM micrograph. TEM has further confirmed the Li$_4$FePO$_4$/C particles are encapsulated in the polypyrrole matrix.

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Published By: Blue Eyes Intelligence Engineering & Sciences Publication

Retrieval Number: B8010129219/2019@BEIESP
DOI: 10.35940/ijitee.B8010129219