Preparation of LiFePO₄ added PPy as cathode materials for li-ion battery

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Abstract. LiFePO₄ is an alternative cathode material for lithium-based battery cells. LiFePO₄ demonstrates many advantages such as non-toxicity, low cost, and stable structure. One of the main problems of LiFePO₄ is its low electronic conductivity, which results in its poor rate capability due to the poor kinetics of lithium intercalation/deintercalation process. The objective of this study is to increase the electrical conductivity of LiFePO₄. An in-situ carbon source such as polypyrrole PPy was applied to prepare LiFePO₄/C composites by heat treatment. The nature of polypyrrole in the system can be considered not only as carbon source, but also as a structure director. The LiFePO₄/C composites were prepared with the addition of PPy which were varied between 2.5, 5, 7.5, 10 and 15 % weight, and graphite also added in the amount of four times the PPy content. The crystal structure, surface morphology, elemental analysis, and conductivity of LiFePO₄/C composites were characterized by X-ray diffraction and scanning electron microscopy combined with energy dispersive spectrometry and use of LCR meter, respectively. The XRD patterns of LiFePO₄/C composites showed that the LiFePO₄/C particles belong to a pure orthorhombic system of olivine-type structure (Pnma, JCPDS: 40-1499). Carbon phase was not found apparently from the XRD pattern, which indicated that it may be present in amorphous form. The particles morphology were composed of primary particles approximately 400 nm in diameter, with homogeneous pores and were agglomerated, while carbon deposition was observed on the surface. The addition of PPy increased the conductivity of materials. The highest conductivity of LiFePO₄/C composite was 9.74 × 10⁻² S cm⁻¹ reached by the addition of 15% PPy.

1. Introduction

This research is part of Advanced Materials Science and Technology Centre, National Nuclear Energy Agency’s program in new and renewable energy research for sustainable energy sources. LiCoO₂ and LiMnO₂ cathode materials preparation has been done [1, 2]. In this research, lithium ferophosphate (LiFePO₄) will be developed as an alternative to cathode materials for lithium-based battery cells. The lithium battery is expected to be a solution to energy issues related to environmental issues. The use of lithium battery cathodes materials in phosphate form will be readily paired with solid lithium electrolyte, glass, or polymer. Since the pioneering work of Padhi [3], orthophosphate LiFePO₄ has been intensively studied as cathode material for Li-ion batteries. As one of the most promising cathode materials, LiFePO₄ has been intensively investigated for large lithium ion batteries in electrical vehicles (EVs and HEVs). LiFePO₄ demonstrates many advantages such as non-toxicity, low cost, and stable structure that...
makes it is safe to use as a large lithium battery cathode material in electric and hybrid vehicles with a high theoretical capacity (170 mAh/g). However, LiFePO₄ has an inherently low electrical conductivity, which results in its poor rate capability due to the poor kinetics of lithium intercalation/deintercalation process [4]. Also reported the LiFePO₄ phase did not have a high capacity was due to some lithium or iron disorder with around 7 % iron on the lithium sites [5-7]. The electronic conductivity of LiFePO₄ at room temperature is about 10⁻⁶ S/cm [8], and electrochemical capacity of materials is 85 mAh/g [4]. Such low conductivity makes it difficult to attain the theoretical capacity of LiFePO₄ as the Li-ion battery cathode. Nowadays many approaches have been successfully adopted to improve its electrical conductivity, such as the control of particle size, and metal cation doping such as carbonaceous materials and some metals enhance the charge/discharge performance [9-12]. These factors (particle size and conductive coating) are largely affected by the method of preparation. Therefore, to produce commercially available LiFePO₄ a proper preparative method is an urgent research target [13]. The cathode conductivity is primarily determined by iron content. The choice of phosphate salts is due to the molecular size that allows the lithium ion to move from and to the electrolyte in the process of charged/discharged. The lithium content in the cathode can be expected as an ion source of a lithium redox energy of the metal cations and allows for faster ion transfer. In addition, the bonds between oxygen atoms in phosphate are stronger than cobalt, so some LiFePO₄ cells have heat resistance properties in their use [4, 14].

LiFePO₄ has a discharge voltage of about 3.4 V versus lithium. It shows no obvious fading even after several hundred cycles, and shows power capabilities comparable to that of the mixed layer oxides [15]. Typical compositions of cathode films are metal substrates LiFePO₄ 72 wt. %, acetylene black 8 wt. %, and 20 wt. % polyethylene oxides as binder. Acetylene black ensures electrical conductivity throughout the film [16], and the binder makes the film intact during processing. These materials are dissolved on a metal substrate using acetonitrile.

In the previous works, we have studied the addition of polyacrylic acid, (PAA) [17] and polyacrylic acid (PLA) to LiFePO₄ [18], and the addition of organic matters as reducing agents as well as a carbon sources [19, 20]. In this paper we will report the preparation of LiFePO₄/C composites by addition of PPy as carbon source to to increase the electrical conductivity of LiFePO₄. The characterization focused on exploring the relationship of structure and properties of materials.

2. Experimental

2.1 Materials
The experiment was carried out by using materials of lithium ferrophosphate, LiFePO₄ (MTI China, purity = 99%), polypyrrole, PPy (Aldrich, purity = 99 %), and graphite, C (Aldrich, purity = 99%).

2.2 Methodology
The starting materials were LiFePO₄, PPy, and C. They were mixed in the mortar. The LiFePO₄ was purchased from MTI China as obtained without further treatment. The weight ratio of the PPy in the mixture to LiFePO₄ were varied as 0, 2.5, 5, 7.5, 10 and 15 %, with samples code in a row is K0, K1, K2, K3, K4 and K5 respectively. The graphite added were 4 times of PPy content. The mixture then heated in furnace at 300 °C for 1 h. The products then ready for characterizations.

2.3 Characterizations
To determine the crystal phase composition of the LiFePO₄/C composites, XRD analysis was carried out at room temperature using a Pananalytical-Empyrean diffractometer (Japan) with Cu Kα radiation (λ = 0.15406 nm), over the 2θ collection range of 5°-80°. The accelerating voltage of 40 kV, emission current of 300 mA and the scanning speed of 4°/min were used. The particles size and elemental analysis
were measured using SEM combined with EDS (JEOL JSM 6510 LA, Japan) working on a 20 kV voltage. Electrical conductivity measurements were performed using LCR meter HIOKI 3532-50, China.

3. Results
The morphologies of the LiFePO$_4$/C composites were investigated using SEM. The surface of LiFePO$_4$ coated with a carbon layer can inhibit the particle growth and help obtain a smaller particle [21]. While surface coatings and nanosized syntheses have proved to improve the power density, they are usually associated with lower tap density for the cathode-anode material as the particle size decreases [22].

![Figure 1](image_url)

**Figure 1.** The morphologies of the LiFePO$_4$/C composites for LFP/PPy 0, 2.5, 5, 7.5, 10 and 15 % as sample code of K0, K1, K2, K3, K4 and K5 respectively. Investigated using SEM with a magnification of 5000X.
Figure 1 (K0) shows the arrangement of LiFePO\(_4\) particles without the addition of PPy. The arrangement of these particles is agglomerated which its distance between the particles is a wide vacancy. Figure 1 shows the panoramic morphologies for LFP/PPy 2.5 % (K1); this image informs LiFePO\(_4\)/C particles with a size distribution (1-5 \(\mu\)m). Detailed investigations of the particles showed that they were composed of primary particles approximately 400 nm in diameter, and homogeneous pores with carbon deposition were observed on the surface. Figure 1 (K2, K3, K4 and 5) shows the spherical morphology for the LFP/PPy 5, 7.5, 10 and 15 % respectively. Similar to LFP/PPy 2.5 %, all the LiFePO\(_4\)/C particles comprised 200 nm-diameters, and homogenous pores were formed in these samples. The particles are less agglomerated and tend decreased in size with increasing PPy content compared those in K1 sample.

Table 1. Elemental analysis of the LiFePO\(_4\)/C composites samples.

| Name of sample/PPy content (wt. %) | Elemental analysis (mass %) |
|----------------------------------|-----------------------------|
|                                  | C    | O    | P    | Fe    |
| K1/2.5                          | 24.20| 31.57| 15.96| 28.27 |
| K2/5                            | 24.43| 40.48| 13.71| 21.38 |
| K3/7.5                          | 26.60| 32.66| 13.91| 26.83 |
| K4/10                           | 30.11| 33.50| 13.86| 22.54 |
| K5/15                           | 36.24| 34.75| 11.55| 17.46 |

The XRD patterns of samples for K1, K2, K3, K4 and K5 can be seen in Figure 2. There are insignificant difference patterns for these samples. The majority of diffraction lines can be indexed as a single phase belongs to an ordered olivine structure with the orthorhombic Pnmb space group. The main diffraction peaks of LiFePO\(_4\) occurs at angles \(2\theta\) = 17.04°, 20.7°, 24°, 29.6°, 30.98°, 35.5°, and 42.2° correspond to the crystal planes [020], [011], [101], [200], [210], [201], and [112] mark as bar in Figure 2. The phases of LiFePO\(_4\) are in the sharp diffraction peaks illustrate the highly crystalline. The nature of polypyrrole in the system can be considered not only as structure director, but also as a carbon source.
Carbon phase was apparently not found from the XRD pattern, which indicates it may be present in amorphous form. These results correspond to the literature [23].

Analysis of the complex permittivity is measured and usually done with the technique of curve-fitting based on normally, one of the following models: Debye model, Cole-Cole, Cole-Davidson, a model of Havriliak-Negami and KWW. An analysis of curve-fitting is usually used to find the relaxation time. In addition, Cole-Cole plot of dielectric constants have also been used to analyse parameters of the dielectric [24]. As shown in the Figure 3, Cole-Cole plot for composite material LiFePO$_4$/C straight line at low frequency range in the initial state and a half circle in the middle and high frequency range. It was found that a linear line appears at low frequencies, reveals that the passivation film stable.

**Figure 3.** Cole-Cole plot from the results of measurements of electrical conductivity of LiFePO$_4$/C for a sample of K5.

**Figure 4.** The electrical conductivity graph of LiFePO$_4$/C composites for sample of K1, K2, K3, K4 and K5 as a function of frequency.
The radius of a half circle appears in the medium to high frequency range with the voltage increasing, revealed that happens a decrease in resistance transfer. Conductivity measurement is carried out using High Precision LCR-meter which is connected to a computer for data acquisition. The addition of PPy is increasing the conductivity of materials. In addition of PPy 5% and 7.5% i.e. a sample of K2 and K3, the conductivity tends to decrease compared to samples of K1. This may be caused by the limited mobility of the charge carriers and the establishment of a neutral ion pairs and ion aggregates. On the larger content of PPy i.e. 10 and 15% the particle distribution may be spread more evenly, forming a network of LiFePO$_4$/C in an amount more so the conductivity then increases. The highest conductivity of LiFePO$_4$/C composite was 9.74 × 10$^{-2}$ S cm$^{-1}$ reached by addition of 15% PPy. The LiFePO$_4$ conductivity before added of PPy is 4 × 10$^{-4}$ S cm$^{-1}$ [25] increase to 9.74 × 10$^{-2}$ S cm$^{-1}$ by addition of 15% PPy, or an increase in 243.5 time.

4. Conclusion
There is insignificant difference for diffraction pattern of samples K1, K2, K3, K4 and K5 using XRD. Diffraction patterns showed that LiFePO$_4$ dominate the main peaks are marked by 3 strongest diffraction peaks at angles 2θ = 20.73°, 24°, 33°, and 33.7°. The nature of polyprrole in the system can be considered not only as a director of the structure, but also as a source of carbon. But the peak corresponding to the carbon is not visible, due to the amorphous structure.

Morphology of LiFePO$_4$/C composite surface was observed using SEM showed particles of LiFePO$_4$/C with a varied size distribution (1-5 µm). A detailed investigation of the particle consists of primary particles with a diameter less than 5 µm, the homogeneous pore and carbon deposition observed on the surface.

The addition of PPy is not immediately increase the conductivity of materials acquired. In addition of PPy 5% and 7.5% i.e. a sample of K2 and K3, the conductivity tends to decrease compared to samples of K1. This may be caused by the limited mobility of the charge carriers and the establishment of a neutral ion pairs and ion aggregates. On the much more content of PPy i.e. 10 and 15%, the particle distribution may be spread more evenly, forming a network of LiFePO$_4$/C in an amount more so the conductivity then increases.

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