



Enhanced cathode performance of nano-sized lithium iron phosphate composite using polytetrafluoroethylene as carbon precursor



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HIGHLIGHTS

- Pyrolysis of PTFE promotes cathode performance.
- Fluorine-free carbon layer on LiFePO_4 particles are formed.
- PTFE restricts the LiFePO_4 particle growth.
- PTFE shifts the particle size distribution to the nanometer region.

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ABSTRACT

Herein we report a facile and efficient solid state synthesis of carbon coated lithium iron phosphate (LiFePO_4/C) cathode material achieved through the pyrolysis of polytetrafluoroethylene (PTFE). The current investigation is comparatively analyzed with the results of the composites of LiFePO_4/C (LFP/C) synthesized using polystyrene-block-polybutadiene (PS-*b*-PBD), polyethylene (PE) and sucrose as carbon precursors. The optimized LFP/ C_{PTFE} composite is synthesized at 700 °C using 10 wt.% PTFE. The composite exhibits remarkable improvement in capacity, cyclability and rate capability compared to those of LFP/C synthesized using (PS-*b*-PBD), PE and sucrose. The specific discharge capacities as high as 166 mA h g^{-1} (theoretical capacity: 170 mA h g^{-1}) at 0.2 C and 114 mA h g^{-1} at 10 C rates were achieved with LFP/ C_{PTFE} . In addition, the composite exhibits a long-term cycling stability with the capacity loss of only 11.4% after 1000 cycles. PTFE shifts the size distribution of the composite to nanometer scale (approximately 120 nm), however the addition of sucrose and other polymers do not have such an effect. According to TEM and XPS analysis, LFP/ C_{PTFE} particles are mostly coated with a few nanometers thick carbon layer forming a core–shell structure. Residual carbon does not contain fluorine.

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1. Introduction

Lithium ion battery technology has been applied in many portable electronic devices, electric/hybrid vehicles and stationary energy storage systems for storing solar and wind power as the most promising sustainable energy storage solution [1,2]. Among several cathode materials olivine-type LiFePO_4 (LFP) is one of the most widely studied and generally considered to be a promising battery materials used in Plug-in Hybrid Electric Vehicle/Electric Vehicle (PHEV/EV) [1,3,4]. Besides the advantages of this material, such as low cost, high thermal and cycling stability, low toxicity and

relatively high theoretical capacity (170 mA h g^{-1}), unfortunately, low electronic conductivity and slow diffusion of lithium ions across the two-phase boundary of LFP seriously limit its rate capability [5,6]. To overcome these problems, several strategies have been implemented including particle size minimization [7,8], doping with supervalent cations [9], carbon nanocoating [10–13] or carbothermal formation of the surface conducting phase [5,6,8,14,15]. To date, carbon coating (LFP/C) has been one of the most commonly used method to improve the specific capacity, rate capacity and cycling performance of LFP [5,6,8]. Depending on the pyrolysis behavior of carbon precursor, suppressing of the particle growth leading to both particle size minimization and intimate carbon contact can occur as an enhancement factor for the performance of LFP [8,16]. However, it is quite difficult to obtain a homogeneously coated carbon shell on LFP particles during the

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heat treatment. In case of partial formation of carbon shell, an insufficient electronically conducting network would lead to decrease in the rate capability of the material.

There are mainly two methods for carbon coating of LFP particles. One is direct mixing of various particulate carbon materials, such as carbon nanomaterials (graphene, carbon nanotube, etc.) by mechanical means [6,17], but mostly leading non-uniform carbon coating. The other method is *in situ* deposition by using the pyrolysis of a carbon precursor, which usually results in more uniform coating compared to the previous method [6]. Previous studies for *in situ* carbon coating have mostly focused on the synthesis of LFP/C composite materials by using low weight organic precursors [18], such as sucrose, glucose or citric acid as the carbon source. Although the polymer pyrolysis method is a relatively simple and effective way to form carbon-coated materials, it has been rarely applied for coating the LFP particles [8,12,16]. In such a process, choosing a proper polymer precursor is an important step to obtain reduced size of LFP/C particles coated uniformly with a few nanometers thick carbon layers [8,16].

In this regard, recently, it was reported that an efficient solid state synthesis of carbon and nitrogen coated high performance $\text{LiFePO}_4/\text{CN}$ was achieved via polymer pyrolysis method at 700°C [8]. It was claimed that PANI was leading to restrict the LFP particle growth by crosslinking of the polymer during the pyrolysis. The specific discharge capacities as high as 164 mA h g^{-1} at 0.1 C and 100 mA h g^{-1} at 10 C rates were achieved with $\text{LiFePO}_4/\text{CN}$ particles, which are mostly coated with a few nanometers thick C–N layer. In another report, Nien and Chen [19] prepared LFP/C samples formed by calcinating amorphous LFP in the presence of various polymers such as polystyrene, polyethylene oxide, polybutadiene at 600°C . They reported that polystyrene (5 wt.%) derivative with functionalized aromatic groups exhibited an improved performance. They achieved a capacity of 147 mA h g^{-1} and 90 mA h g^{-1} at 0.1 C and 3 C rates, respectively. Additionally, Yu and Fang [20] announced that LFP/C composite prepared using polystyrene nano-spheres (7 wt.%) sintered at 800°C displayed a discharge capacity of 167 mA h g^{-1} and 150 mA h g^{-1} at 0.1 C and 1 C, respectively.

In this article, we introduce the polymers of polytetrafluoroethylene (PTFE), polyethylene (PE), polystyrene-block-polybutadiene (PS-*b*-PBD) and sucrose as carbon precursors for the solid state synthesis of LFP/C composites. Among the cathode materials synthesized at 700°C using 10 wt.% carbon precursors, LFP/C_{PTFE} composite exhibits an outstanding electrochemical performance compared to others. PTFE restricts the size of LFP/C particles, however using PE, PS-*b*-PBD and sucrose as carbon precursors does not significantly influence it. Although fluorine doping [21,22] in the LFP/C_{PTFE} was expected for the possible factor of high performance, no fluorine footprint was observed by XPS measurements. A mixture of nanometer and micrometer size LFP/C_{PTFE} particles is formed as a result of the pyrolysis of PTFE. This composite seems to meet the need of excellent capacity retention and high performance in the power system for electric vehicles and stationary-storage applications.

2. Experimental

2.1. Synthesis of LiFePO_4/C composites

As the starting materials for the solid-state synthesis, stoichiometric amounts of analytical grade 2.24 g of Li_2CO_3 (Alfa-Aesar), 10.99 g of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Aldrich), 6.98 g of $(\text{NH}_4)_2\text{HPO}_4$ (Carlo-Erba) as well as 2.25 g of polystyrene-block-polybutadiene (PS-*b*-PBD, Aldrich), polyethylene (PE, Alfa-Aesar), polytetrafluoroethylene (PTFE, Alfa-Aesar) or sucrose (Carlo-Erba) as carbon source precursors were thoroughly planetary milled in mortar for 2 h

(300 rpm) in the mixture of different solvents. For all LFP/C samples, 10 wt.% of carbon precursors were used. Depending on the precursor used the following solvent mixtures (50 ml) were prepared; ethanol and toluene (1:1 v/v) mixture to dissolve PE and PS-*b*-PBD was heated at 120°C for 1 h, ethanol and N-methylpyrrolidine (NMP, Merck) (1:1 v/v) mixture for PTFE and ethanol for sucrose. The resulting gel was dried at 100°C in a furnace and then heated to 350°C for 6 h in Ar atmosphere. The decomposed mixture was pressed into pellets and sintered under Ar flow at 700°C for 12 h in order to obtain the crystalline phase composites. The cathode materials prepared using PS-*b*-PBD, PE, PTFE and sucrose were denoted as LFP/C_{PS-*b*-PBD}, LFP/C_{PE}, LFP/C_{PTFE} and LFP/C_{Sucrose}, respectively as shown in Table 1.

2.2. Characterization of cathode materials

The crystallographic structural characterization was performed by X-ray powder diffraction. XRD of the LFP/C composites was carried out on a Rigaku Miniflex 600 diffractometer equipped with Cu-K α radiation of $\lambda = 0.15405\text{ nm}$ in the range of $0^\circ < 2\theta < 80^\circ$. The micromorphology of the LFP/C powders was observed using a JEOL JSM6510-LV scanning electron microscope (SEM). Transmission electron microscopy (TEM) measurements were performed using JEOL JEM 2100 HRTEM operating at 200 kV (LaB₆ filament) with energy dispersive spectroscopy (EDS) systems. The carbon content was estimated using thermogravimetric analysis method (Mettler-Toledo TGA-851). Particle size analysis (PSA) of the composites was investigated by dispersing the materials in water using Malvern Mastersizer-2000. X-ray photoelectron spectroscopy (XPS) measurements were obtained using SPECS GmbH PHOIBOS-150 X-ray photoelectron spectrometer with monochromatic Al K α (1486.6 eV).

2.3. Cell fabrication and electrochemical measurements

The crystalline cathode active materials of LFP/C were mixed and grounded with Super P (12 wt.%, Timcal Co.) and polyvinylidene fluoride (PVdF, 8 wt.%) as a binder dissolving in NMP for 30 min. The resulting mixture was casted uniformly onto an aluminum foil and dried at 100°C . Electrodes were punched in the form of a disc having $5\text{--}7\text{ mg cm}^{-2}$ of active material, pressed and dried at 100°C for 4 h. The coin cells (CR2032) were assembled in an argon-filled glove-box (Vigor) with a Li metal disc as anode and Whatman GF/D glass-fiber as separator and 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in vol. ratio) as the electrolyte. Cyclic voltammograms (CV) (between 2.0 and 4.3 V) and galvanostatic charge/discharge measurements were carried out (between 2.2 and 4.2 V) with PAR VersaSTAT Multi channel potentiostat/galvanostat.

3. Results and discussion

3.1. Material characterization

The crystal structures of LFP/C powders prepared using the carbon precursors of PS-*b*-PBD, PE, PTFE and sucrose were confirmed by X-ray diffraction (XRD) (Fig. 1). All peaks on each curve can be indexed as a single phase with an ordered orthorhombic olivine structure with a space group *Pmnb* (ICDD (PDF-2/Release 2011 RDB) DB card number: 01-074-9597) indicating the successful synthesis of phase-pure LiFePO_4 (lattice parameters: $a = 10.323\text{ \AA}$, $b = 6.007\text{ \AA}$, $c = 4.689\text{ \AA}$, $\pm 0.003\text{ \AA}$ depending on the materials). There were no obvious diffraction peaks corresponding to other impurity peaks such as Li_3PO_4 , Fe_2P . This reveals that the carbon coating did not result in any change in crystal structure of

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