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Improvement of electrochemical performances of $LiFePO_4$ cathode materials by coating of polythiophene

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ABSTRACT

A series $LiFePO_4$/polythiophene ($LiFePO_4$/PTh) composites were synthesized by in situ polymerizing thiophene monomers on the surface of $LiFePO_4$ particles. Electrochemical impedance spectra (EIS) measurements show that the coating of polythiophene significantly decreases the charge transfer resistance of $LiFePO_4$ electrodes. Transmission electron microscopy (TEM) tests show that $LiFePO_4$ could be completely coated by addition of proper amount of polythiophene. The electrochemical performance of polythiophene and $LiFePO_4$/PTh for lithium insertion and extraction was examined by charge/discharge testing. The composites demonstrated an increased reversible capacity and better cycling ability compared to the bare $LiFePO_4$.

1. Introduction

Since $LiFePO_4$ was first reported as cathode materials for lithium ion battery in 1997 by Goodenough and coworkers [1], it has showed a great prospect for replacement of traditional cathode material $LiCoO_2$. Lithium iron phosphate with the olivine structure has received much attention due to its relatively large theoretical capacity (170 mAh g^{-1}), inexpensive, environmental friendly, and stability [1–3]. However, because of its ordered olivine-type struture, the main problem with this material is low electronic conductivity and slow kinetics of lithium ion diffusion through the $LiFePO_4$/$FePO_4$ interface [3,4]. Over the past decades, many efforts have been devoted to improving the electronic conductivity and electrochemical properties of $LiFePO_4$ through different approaches. Different new methodologies of materials preparation have been used to compensate for this apparent drawback, such as freeze-drying methods [5] and spray pyrolysis [6]. And many modifying works also been done [7–16], mainly included heterogeneous doping by metal ions, coating with an electron-conducting phase (mostly carbon) and particle size minimization. Among above choices, carbon coating was considered as an easy and effective way to get better electronic conductivity and electrochemical properties of $LiFePO_4$, but it remained to be solved that carbon-coated cathode materials led to a loss in energy density since carbon was electrochemically inactive.

Conducting polymers have been widely studied over the past decades due to their unique semi-conducting and optoelectronic properties [17–22]. Recently, the combination of $LiFePO_4$ and conductive polymers has attracted many attentions [23–27]. Conductive polymer additives can be used as both conductive agents and cathode materials. Wang et al. [23] and Park [24–26] reported ppy–$LiFePO_4$ compsites demonstrated the better cycling performance. Murugan et al. [27] fabricated $LiFePO_4$–PEDOT nano-hybrid offers discharge capacity (166 mAh g^{-1}) close to the theoretical value (170 mAh g^{-1}) with excellent capacity retention and rate capability. Since polythiophene is a conductive polymer and has storage capacity in lithium ion cells, a coating of polythiophene on the particles would increase the electronic conductivity of $LiFePO_4$.The polythiophene could also participate in lithiation and de-lithiation reactions, contributing to the specific capacity of the composites. In this study, we prepared a series of coated composites. The electrochemical properties of $LiFePO_4$/PTh composites as cathode materials were systematically investigated.

2. Experimental

2.1. Material preparation

$LiFePO_4$ was synthesized by solid-state reaction with a stoichiometric mixture of Li_2CO_3 (AR, Taishan Chemical Plant), $FeC_2O_4{\cdot}2H_2O$ (AR, Fluka), and $NH_4H_2PO_4$ (AR, Mingfeng Reagent Corporation) as previously described in [28] and it is briefly described here. The mixture was initially heated at 350 °C for 5 h, further treated at 650 °C for 18 h in high purity argon flow. The resultant powders were air-cooled to room temperature, and then the bare $LiFePO_4$ was prepared. The PTh and $LiFePO_4$/PTh were synthesized by in situ polymerization. The $LiFePO_4$ powder about 2 g was dispersed in $CHCl_3$ solution, forming $LiFePO_4$ and $CHCl_3$ suspension. The suspension was bubbled with argon gas for 30 min to remove O_2. While the suspen-

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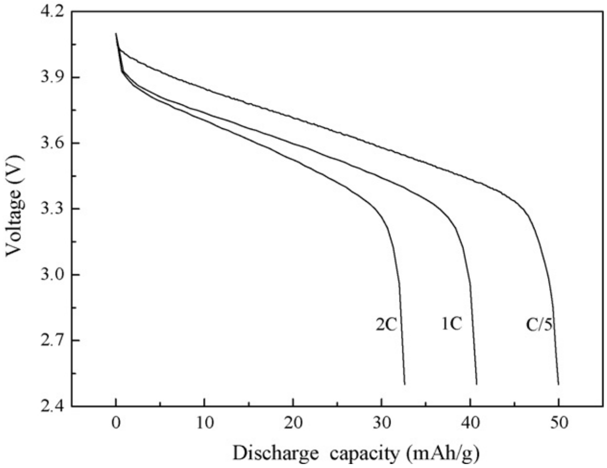

Fig. 1. The initial discharge curve of as-prepared PTh at various C-rates.

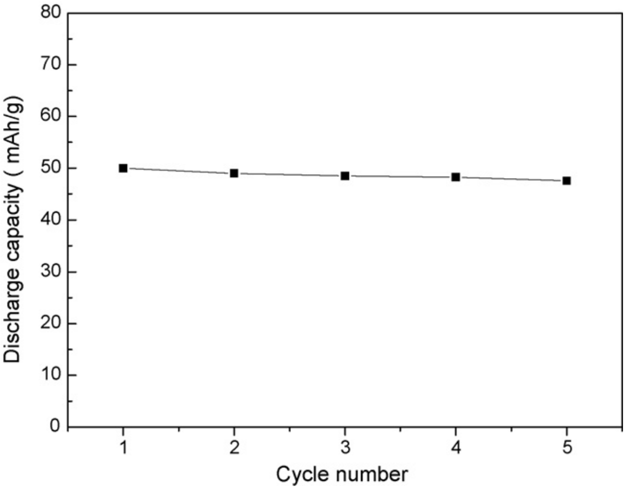

Fig. 2. The cycling capability of as-prepared PTh at C/5.

sion was magnetically agitated, the distilled thiophene with various contents was injected into the suspension, and then $FeCl_3$ and deionised water (1:3 by molar) were added to the suspension. The polymerization reaction was carried out for 12 h at 30 °C under a continuous argon flow. The resultant products were filtered, then thoroughly washed with deionised water and anhydrous ethanol several times and dried at 80 °C for 48 h under vacuum, thus a series $LiFePO_4$/PTh composites were produced.

2.2. Materials characterization

Thermogravimetric analysis (TGA) was performed to determine the actual amount of polythiophene in composites using a Synthetic Thermo gravimetric Analyser (STA449C, NETZSCH Corporation). The morphology of $LiFePO_4$/PTh composites was observed using a high resolution transmission electron microscopy (HRTEM) (JMS-3010, Japan). Conductivity measurement using four-probe testing instrument (SX1934, Jiangsu) was made on a disc-shaped pellet by four-point direct current method at room temperature. The disc-shaped pellet was pressured into 13 mm diameter and 2 mm thickness.

2.3. Electrochemical measurement

The cathode was a mixture of active material (bare $LiFePO_4$, PTh, $LiFePO_4$/PTh composites), conductive additive (acetylene black) and binder (polytetrafluorethylene, PTFE) with a weight ratio of 75:20:5. The mixture was rolled into a 100 μm thin sheet with uniform thickness from which 12 mm diameter pellets were cut. The pellet, with the approximate active material loading of 20 mg per square centimeters, was used as the cathode electrode. The electrolyte was 1 mol/L $LiClO_4$ in ethylene carbonate and dimethyl carbonate (1:1 by volume). Lithium foil was used as the counter and reference electrodes. The separator was Celgard 2400 microporous membrane. The cell was assembled in an argon glove box. The galvanostatical charge–discharge experiments were operated by Arbin instrument (BT-2000) between 2.5 V and 4.1 V versus Li/Li^+ at various rates. AC impedance measurements were carried out using CHI660C Electrochemical Working Station (Chenhua, Shanghai). The amplitude of the EIS signal was 5 mV over the frequency range between 100 kHz and 0.01 Hz. All the electrochemical measurements were performed at ambient temperature.

3. Results and discussion

3.1. Synthesis and electrochemical properties of polythiophene

Polythiophene was synthesized by chemical polymerization, during which the positive charged species of polarons or bipolarons were generated. The electronic conductivity of polythiophene was measured to be about 3.1 $S\,cm^{-1}$. The first discharge curve of as-prepared PTh at various C-rates in a lithium ion cell is shown in Fig. 1. It has a discharge plateau in the voltage range of 3.3–3.8 V versus a Li/Li^+ reference electrode. The as-prepared PTh demonstrated a discharge capacity 49.98 $mAh\,g^{-1}$, 40.76 $mAh\,g^{-1}$, and 32.61 $mAh\,g^{-1}$ at the current density of C/5, 1C and 2C, respectively. The plot of discharge capacity at C/5 of as-prepared PTh versus cycle number is shown in Fig. 2. Although its capacity declined with cycling, it remained stable after 5 cycles. The reaction mechanism of PTh electrode in the charge/discharge process is analyzed. When charging the PTh electrode, the PTh releases electrons, and a charge-compensating anion ($ClO_4{}^{2-}$) intercalates into the PTh chain to maintain charge neutrality. During discharging, the anion ($ClO_4{}^{2-}$) de-intercalates from the PTh and enters into the electrolyte. The reaction can be expressed as follow:

$$\text{Cathode}: \quad [PTh^0]-e + ClO_4{}^{2-} \rightarrow [PTh^+]ClO_4{}^{2-}$$

$$\text{Anode}: \quad Li^+ + e^- \rightarrow Li$$

3.2. The morphology of $LiFePO_4$/PTh composites

Three $LiFePO_4$/PTh composites samples were prepared with PTh contents of 5.86 wt.%, 10.56 wt.%, and 12.85 wt.%. In order to observe PTh coating on the surface of $LiFePO_4$ particles, HRTEM observation was carried out. Fig. 3 shows the TEM images of $LiFePO_4$/PTh composites. When the PTh is in a low levels (Fig. 3a), $LiFePO_4$ particle surface can only be observed in a very small amount into a granulated PTh, most of the surface largely bare. When the PTh content reached 10.56 wt.% (Fig. 3b), with the PTh content increasing, $LiFePO_4$ particle surface gradually coated by PTh coating uniformly and completely, which formed thin and relatively uniform layer of PTh-coated. When the PTh content continues to increase, which is up to 12.85 wt.% (Fig. 3c), the surface of PTh coating on $LiFePO_4$ particles surface gets thickening and $LiFePO_4$/PTh composites particles appear PTh particles. The PTh coating can reduce the contact resistance between $LiFePO_4$ particles, it may also plays an important role to enhance electronic conductivity of composites. From the above, we can see that a reasonable amount PTh could form an uniform and complete coating, and so small or too large amount PTh may cause uncoated or too thickness coating both an ineffective way.

3.3. Electrochemical impedance spectra properties of $LiFePO_4$/PTh composites

To understand the PTh coating effect in more detail, EIS measurements were performed on the bare $LiFePO_4$ and $LiFePO_4$/PTh composites cells. Prior to the EIS testing, the cells were cycled galvanostatically for three cycles to ensure the stable formation of the SEI layers on the surface of the electronic active particles.

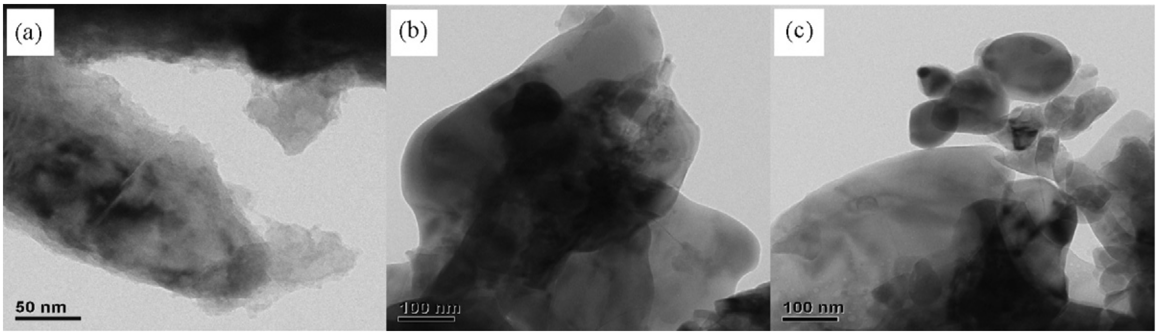

Fig. 3. The TEM images of $LiFePO_4$/PTh composite: (a) 5.86 wt.% PTh, (b) 10.56 wt.% PTh, and (c) 12.85 wt.% PTh.

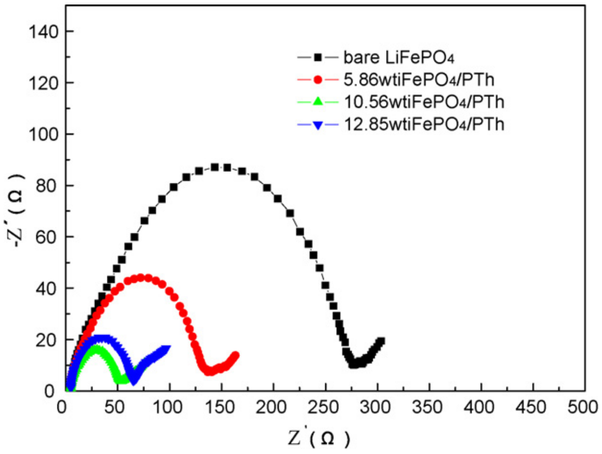

Fig. 4. EIS (Nyquist plots) of the bare $LiFePO_4$ and $LiFePO_4$/PTh composite after three cycles.

Table 1
Electrode kinetic parameters of bare $LiFePO_4$ and $LiFePO_4$/PTh composite obtained from equivalent circuit fitting of experimental data.

Sample	R_s (Ω)	R_{ct} (Ω)	i_o (mA)
Bare $LiFePO_4$	3.29	280.20	0.0902
5.86 wt.% $LiFePO_4$/PTh	4.54	84.76	0.298
10.56 wt.% $LiFePO_4$/PTh	4.06	50.92	0.496
12.85 wt.% $LiFePO_4$/PTh	3.97	64.12	0.394

i_o, exchange current density of the electrode; $i_o = RT/nFR_{ct}$.

The EIS test was then measured in the fully discharged (lithiation) state. Fig. 4 shows typical Nyquist plots of the bare $LiFePO_4$ and $LiFePO_4$/PTh composites cells. The high frequency region of the semicircle represents the migration of the Li^+ ions at the electrode/electrolyte interface through the SEI layer, whereas, the middle frequency range of the semicircle corresponds to the charge transfer process. The low frequency region of the straight line is attributed to the diffusion of the lithium ions into the bulk of the electrode material or so-called Warburg diffusion. A simplified equivalent circuit models was constructed to analyze the impedance spectra in Fig. 4. The EIS were fitted using an equivalent circuit, which is shown in Fig. 5. A constant phase element CPE was placed to represent the double layer capacitance and passivation film capacitance. The fit between the experimental data and equivalent circuit is very well. Table 1 shows the parameters of the equivalent circuit for the bare $LiFePO_4$ and $LiFePO_4$/PTh composites obtained from computer simulations using the Zview2.0 software. The resistance of the R_s is similar to bare $LiFePO_4$ and $LiFePO_4$/PTh composites. It is because the cells were prepared by adding the same conductive carbon black agent and reaction in the same electrolyte.

It was found that the charge transfer resistance (R_{ct}) of the $LiFePO_4$/PTh composites was smaller than the bare $LiFePO_4$. This indicated that the coating layer obtained from PTh enhanced the electronic contacts between $LiFePO_4$ particles. Among the three samples, 10.56 wt.% $LiFePO_4$/PTh showed the lowest resistance and largest exchange current density (i_o), suggesting that the PTh coating on the $LiFePO_4$ particles surface greatly improved the performance of the Li-battery.

Fig. 6 shows the initial discharge curves of bare $LiFePO_4$ and $LiFePO_4$/PTh composites under constant current density of C/12 rate. The specific capacity was calculated based on the total weight of electroactive materials (PTh + $LiFePO_4$). The bare $LiFePO_4$ delivered an initial discharge capacity 127.44 mAh g^{-1}. Due to the poor electronic conductivity (ca. 10^{-9}–10^{-10} S cm^{-1}) of bare $LiFePO_4$, the initial capacity achieved here is quite low. The polythiophene has a practical capacity 49.98 mAh g^{-1} at the C/5 rate as described in Fig. 1, which is much lower than that of $LiFePO_4$ with a theoretical capacity 170 mAh g^{-1}. So, an increase in PTh content in the composites would reduce the specific capacity of the composites electrode. However, an increase in PTh would improve the electronic conductivity of the composites and increase the utilisation of $LiFePO_4$, inducing an enhanced specific capacity. Therefore, the spe-

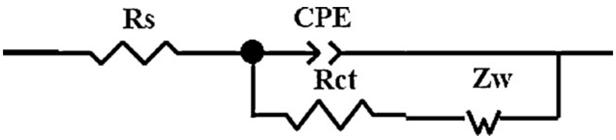

Fig. 5. Equivalent circuit used for fitting the EIS experimental data.

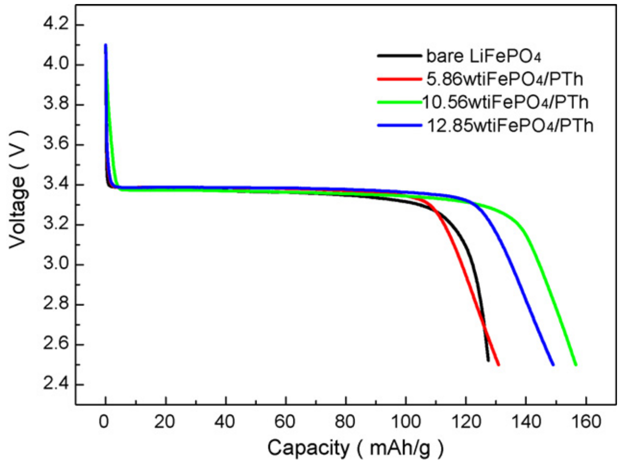

Fig. 6. The initial discharge curves of bare $LiFePO_4$ and $LiFePO_4$/PTh composite under constant current density of C/12 rate.

Table 2
The electronic conductivity of $LiFePO_4$ and $LiFePO_4$/PTh composites.

Sample	Electronic conductivity ($S\,cm^{-1}$)
Bare $LiFePO_4$	10^{-9}–10^{-10}
5.86 wt.% $LiFePO_4$/PTh	6.76×10^{-5}
10.56 wt.% $LiFePO_4$/PTh	2.31×10^{-2}
12.85 wt.% $LiFePO_4$/PTh	2.89×10^{-2}

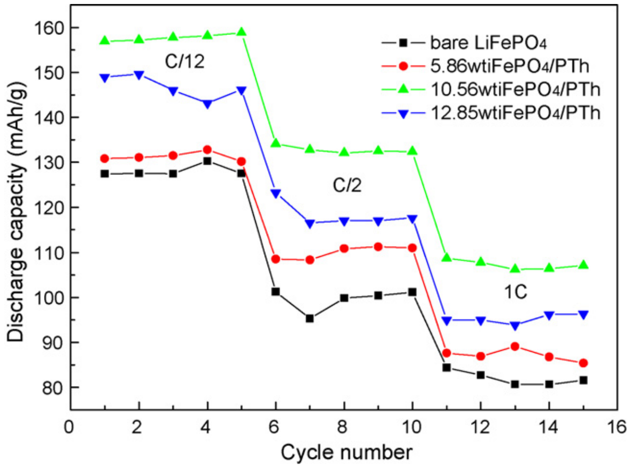

Fig. 7. The rate and cycling capability of bare $LiFePO_4$ and $LiFePO_4$/PTh composite at various C-rates.

cific capacity of $LiFePO_4$/PTh is compromised by the polythiophene content. From Table 2, as we can see the 5.86 wt.% $LiFePO_4$/PTh sample has a electronic conductivity of $6.76 \times 10^{-5}\,S\,cm^{-1}$, which is five orders abruptly increased to bare $LiFePO_4$, which indicate that the PTh coating is very effective in enhancing the electronic conductivity of $LiFePO_4$.When the content of PTh up to 10.56 wt.% and 12.85 wt.%, they showed almost the same $\sim 10^{-2}\,S\,cm^{-1}$, so we can concluded that there is an proper amount of addition to improve the electronic conductivity. From Fig. 6, we can also see that 12.85 wt.% $LiFePO_4$/PTh sample has little effect on increase the specific capacity although with a higher electronic conductivity. So 10.56 wt.% polythiophene addition may be a reasonable choice. The 10.56 wt.% $LiFePO_4$/PTh sample has a discharge 156.53 $mAh\,g^{-1}$ at the C/10 rate, it is very close to the theoretical capacity.

The rate and cycle ability of the bare $LiFePO_4$ and $LiFePO_4$/PTh composites were examined by galvanostatic cycling tests and the results are shown in Fig. 7. To evaluate the rate capability of samples, various current densities corresponding to C/12, C/2 and 1C were applied during five cycles. The figure indicated that the 10.56 wt.% $LiFePO_4$/PTh sample demonstrated the best rate capability and cycling performance with initial discharge capacities 156.93 $mAh\,g^{-1}$ at C/12, 134.12 $mAh\,g^{-1}$ at C/2, and108.17 $mAh\,g^{-1}$ at 1C, respectively. The lower discharge capacity at high current density was attributed to the slow diffusion of Li-ion in the $LiFePO_4$ particle. The bare $LiFePO_4$ has the lowest capacity. This is because the poor electronic conductivity of the bare $LiFePO_4$, inducing poor utilisation of $LiFePO_4$ active materials. In particular, the 10.56 wt.% $LiFePO_4$/PTh sample showed superior initial discharge capacity, capacity retention, and rate capability to bare $LiFePO_4$. This was related to the high electronic conductivity of the $LiFePO_4$ particles coated with 10.56 wt.% PTh as shown in Table 2 and small charge transfer resistance as shown in Table 1. By coating the conductive polythiophene on the surface of the $LiFePO_4$ particles, the electronic conductivity can be significantly improved, which facilitates the charge transfer reaction, leading to better utilisation of the active materials. The active materials with better electronic conductivity should have better capacity retention on cycling. The cycling results show that the $LiFePO_4$/PTh composites have better cycle ability than that of the bare $LiFePO_4$.

4. Conclusions

Effect of the polythiophene coating on the electrochemical properties of the $LiFePO_4$, which was synthesized by in situ polymerization was investigated. The PTh coating can improve electronic conductivity of $LiFePO_4$, and therefore facilitate the charge transfer reaction, which has been confirmed by EIS measurements. TEM images revealed that 10.56 wt.% PTh can form an uniform and complete coating. The 10.56 wt.% $LiFePO_4$/PTh possesses the highest initial specific capacity 156.86 $mAh\,g^{-1}$ at C/12 rate, better cycle ability, and good rate capability. Compared to bare $LiFePO_4$, the $LiFePO_4$/PTh composites containing 10.56 wt.% PTh is a promising cathode material for lithium ion batteries.

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