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Polypyrrole-coated α -LiFeO₂ nanocomposite with enhanced electrochemical properties for lithium-ion batteries

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Keywords

ion, lithium, properties, electrochemical, batteries, coated, enhanced, polypyrrole, nanocomposite, α -LiFeO₂

Disciplines

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Abstract

A conducting α -LiFeO₂-polypyrrole (α -LiFeO₂-PPy) nanocomposite material was prepared by the chemical polymerization method as a cathode material for lithium-ion batteries. The porous α -LiFeO₂ was prepared via the microwave hydrothermal method and a post-annealing. The X-ray diffraction, Fourier transmission infrared spectroscopy, and field emission scanning electron microscopy measurements showed that the α -LiFeO₂ nanoparticles were coated with PPy. The polypyrrole coating improves the reversible capacity and cycling stability (104 mAh g⁻¹ at 0.1 C after 100 cycles) for lithium-ion batteries. Even at the high rate of 10 C, the electrode showed more than 40% of the capacity at low rate (0.1 C).

Key words: α -LiFeO₂-PPy nanocomposite; microwave hydrothermal; lithium-ion batteries; cathode.

1. Introduction

Lithium ferrite (LiFeO_2), a layered cathode material, has attracted much attention because it is non-toxic, environmentally friendly, and low-cost [1, 2]. As is well known, α - NaFeO_2 -type LiCoO_2 cathode materials are in widespread use in commercial lithium-ion batteries. Layered LiCoO_2 has a rock salt structure, where alternate layers of Li and Co occupy the octahedral sites of a cubic close packed oxygen array [3]. LiCoO_2 is more toxic and more expensive than oxides of other transition metals (Mn, Ni, Fe, etc.) [4-6]. LiFeO_2 has different forms, including the α -, β -, γ -forms, etc. α - LiFeO_2 has a disordered-cation cubic rock-salt structure with space group $Fm\bar{3}m$. β - LiFeO_2 with space group of $C2/c$ is formed an intermediate phase during the ordering process. γ - LiFeO_2 with space group $I4_1/amd$ is obtained by reducing the symmetry from cubic to tetragonal by ordering the Li^+ and Fe^{3+} ions at octahedral sites [1-3, 6].

α - LiFeO_2 has many advantages as a cathode material for the lithium-ion battery as a substitute for LiCoO_2 in terms of lower price and environmental friendliness. The charging reaction can be written as:

with $x = 1$, this reaction provides a theoretical capacity of 282 mAh g^{-1} . However, Kanno [3] reported a maximum value of $x = 0.1$ for the α - NaFeO_2 -type structure. The charged electrodes should contain iron in a mixed oxidation state (III and IV). The first charge voltage plateau is above 4 V, corresponding to the $\text{Fe}^{+3}/\text{Fe}^{+4}$ couple reaction, however, large voltage hysteresis is observed during the discharge step. Sakurai et al. reported that unusual Fe^{+4} ions generated during charging may play an important role in the occurrence of voltage hysteresis [7]. Kanno et al. also pointed out that the conversion proceeds from the corrugated layer structure LiFeO_2 to an amorphous phase during the first charge, and the charge-discharge

process after the second cycle proceeds in the amorphous phase [3]. According to the structural change in α -LiFeO₂ in the charge/discharge process by X-ray diffraction (XRD) and X-ray diffraction near-edge structure (XANES) spectroscopy, Morales et al. confirmed that Fe²⁺ may exist after the first discharge, and the strong exothermic peak close to 398 K in the differential scanning calorimetry (DSC) curve may result from the reaction of Fe⁴⁺ with electrolyte [8].

The electrical conductivity is extremely low, however, because the iron ions on lithium sites block the lithium diffusion pathways. There are mainly two ways to increase the electrical conductivity: one way is to fabricate nanosized α -LiFeO₂. Nanosized materials have short pathway lengths for lithium ion transport and a large contact area between the electrode and electrolyte for improving the reaction rate at the interface [9]. The other way is to coat a conductive material on the surface of the α -LiFeO₂ [8]. Using the hydrothermal method, nanosized FeOOH can be prepared in different crystal phases and morphologies [10-14]. Later, FeOOH can be converted into α -LiFeO₂ via a solid-state reaction. Polypyrrole (PPy) is a popular conducting polymer due to its ability to store electric charge and act as a binder [15-17]. Our group has successfully used PPy to improve the performance of cathode and anode materials in lithium-ion batteries, in such composites as S-PPy, SnO₂-PPy, and LiV₃O₈-PPy [18-20]. However, the synthesis of polypyrrole-coated α -LiFeO₂ composite for use in lithium-ion batteries has not been explored yet.

In this study, α -LiFeO₂-PPy nanocomposite was synthesized using a chemical polymerization method. The structural characterization and electrochemical performance of the α -LiFeO₂-PPy composite are discussed and compared with the performance of bare α -LiFeO₂ cathode material.

2. Experimental

2.1 Preparation of β -FeOOH

The β -FeOOH was prepared by using a microwave autoclave method. 3.244 g of FeCl_3 (Sigma-Aldrich) was dissolved in 200 ml distilled water to obtain a final concentration of 0.1 M in a beaker. Then, the solution was sonicated to dissolve the FeCl_3 particles to achieve a homogeneous system. The solution was transferred into sealed Teflon vessels and reacted for 5 min at 120 °C using a Milestone Microsynth Microwave Labstation (Germany) [21]. After cooling down naturally and washing 3 times with distilled water, the brown product, β -FeOOH, was dried at 60 °C in a vacuum oven for 12 h. The collected powder was used for further characterization and as the precursor to prepare α -LiFeO₂.

2.2 Preparation of α -LiFeO₂

The α -LiFeO₂ was prepared by heating appropriate molar ratios of β -FeOOH and LiOH·H₂O (Sigma-Aldrich). A stoichiometric amount of each material was ground and heated at 400 °C for 3 h in air atmosphere in a tube furnace. The brown product was washed 3 times with distilled water and dried at 60 °C in a vacuum oven for 12 h. The synthesis procedure was repeated in order to obtain single α -LiFeO₂ phase.

2.3 Preparation of α -LiFeO₂-polypyrrole composite

The α -LiFeO₂-polypyrrole composite was prepared by the chemical polymerization method with sodium *p*-toluenesulfonate (pTNa) as the dopant and FeCl_3 as the oxidant. The molar ratio of monomer pyrrole to dopant was 3:1, and the molar ratio of monomer pyrrole to oxidant was 1:3 [20]. Firstly, α -LiFeO₂ was dispersed into a solution (50 ml) of pTNa (0.01 M) and pyrrole (0.03 M). Secondly, the mixture was magnetically stirred while the oxidant agent, FeCl_3 solution, was slowly added to the aqueous solution. The gradual change of colour from brown to black indicated the formation of PPy. Stirring of the reaction mixture

was maintained for 20 h. Finally, the black mass was washed 3 times with distilled water and dried at 60 °C in a vacuum oven for 12 h. In order to calculate the PPy content, pure PPy powder was also prepared using the same chemicals as mentioned above.

2.4 Materials characterization

The products, β -FeOOH, α -LiFeO₂, and α -LiFeO₂-polypyrrole composite, were analysed by X-ray diffraction (XRD; GBC MMA) with Cu K α radiation, as well as by field emission scanning electron microscopy (FESEM; JEOL 7500, equipped for energy dispersive X-ray (EDX) spectroscopy). For PPy analysis, Fourier transform infrared (FTIR) spectrographs were collected using a Nicolet Avatar 360 FTIR Fourier transform infrared spectrometer. Thermogravimetric analysis (TGA) was performed by using a SETARAM Thermogravimetric Analyzer (France) in air to determine the changes in sample weight with increasing temperature and to estimate the amount of polypyrrole in the sample.

2.5 Electrochemical measurements

The electrodes were prepared by mixing 80 wt.% α -LiFeO₂ or α -LiFeO₂-polypyrrole composite with 15 wt.% carbon black and 5 wt.% carboxymethyl cellulose (CMC) binder. The slurry was spread onto aluminium foil substrates. The coated electrodes were dried at 60 °C in a vacuum oven for 24 h to remove water molecules. The electrode was then pressed using a disc with a diameter of 14 mm to enhance the contact between the aluminium foil, active materials, and conductive carbon. Subsequently, the electrodes were cut to a 1×1 cm² size. The average active materials loading rate is around 5 mg cm⁻². CR 2032 coin-type cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) using lithium metal foil as the counter electrode. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK KGaA, Germany). The cells were galvanostatically charged and discharged in the range of 4.5–1.5 V

at different current densities using a computer-controlled charger system manufactured by Land Battery Testers. A Biologic VMP-3 electrochemical workstation was used to perform electrochemical impedance spectroscopy (EIS; ac amplitude 5 mV, frequency range 100 kHz-0.01 Hz).

3. Results and Discussion

The precursor of β -FeOOH was prepared by using a microwave autoclave method. The X-Ray diffraction (XRD) pattern of β -FeOOH is presented in Fig. 1(a). The β -FeOOH sample diffraction peaks are consistent with reported values (JCPDS 34-1266). Fig. 1(b) shows a field emission scanning electron microscope (FESEM) image of β -FeOOH. The obtained β -FeOOH has rod-like nanoparticle morphology, with a nanorod diameter of about 50 nm and length of 100 nm.

Fig. 2 shows the XRD patterns of α -LiFeO₂ and α -LiFeO₂-PPy. In the preparation of α -LiFeO₂, the sintering temperature and the excess lithium content in the starting mixture were critical parameters for obtaining pure-phase α -LiFeO₂ nanoparticles. The pure-phase α -LiFeO₂ was obtained under the conditions of Li/Fe = 3, 400 °C, and 3 h. The main peaks were indexed in the cubic system with lattice parameter $a = 4.158\text{\AA}$, which is quite consistent with the reported value (JCPDS 17-938) (Fig. 2). Fig. 2 also reveals that the XRD pattern of the α -LiFeO₂-PPy composite is similar to that of α -LiFeO₂ in terms of peak position. The main peaks in the pattern of the PPy-coated composite are broader than the uncoated material. This may be due to the reaction between LiFeO₂ and pyrrole to form the coating on the surface, which could reduce the crystal size of the pristine LiFeO₂. No obvious diffraction peaks of any impurity phases were observed. In order to confirm that the PPy was coated on the α -LiFeO₂ particles, Fourier transform infrared (FTIR) analysis was conducted. The Fourier transform infrared (FTIR) spectra obtained for the PPy, α -LiFeO₂, and α -LiFeO₂-PPy are

shown in Fig. 3. The α -LiFeO₂-PPy has the typical absorption peaks of PPy as shown in Fig. 3. The band at 1546 cm⁻¹ is due to aromatic C=C in PPy. C=N and C-N show peaks around 1190 cm⁻¹ and 1300 cm⁻¹, respectively. The aromatic C-H in PPy is responsible for the peak at 1041 cm⁻¹ [22-25]. The results demonstrate that the PPy was successfully coated on the surface of the α -LiFeO₂ particles.

To quantify the amount of PPy in the α -LiFeO₂-PPy composite, TGA analysis was carried out in air. Fig. 4 shows the TGA curve of the α -LiFeO₂-PPy composite along with those of bare α -LiFeO₂ and PPy powder when heated from 40 to 800 °C at a rate of 10 °C min⁻¹ in air. Bare PPy powder burns off at 520 °C and there are around 6.0 wt.% dopant or oxidant remaining. While the bare α -LiFeO₂ powder maintains a constant weight throughout the temperature range used for this experiment. The α -LiFeO₂-PPy composite shows a single-step weight loss at a temperature of around 450 °C, which corresponds to the burning of PPy. There is no further weight loss after the initial decomposition of PPy. Therefore, the change in weight before and after the burning of PPy directly translates into the amount of PPy in the α -LiFeO₂-PPy. Using this method, it can be calculated that the weight percentage of PPy in this composite is 16.6 wt.%.

FESEM images of the bare α -LiFeO₂ and the α -LiFeO₂-PPy composite are shown in Fig. 5(a, b). The particle size of the bare α -LiFeO₂ ranges from 10 nm to 100 nm. After introducing the PPy, cauliflower-like nanoparticles of PPy were coated on the surfaces of the α -LiFeO₂ particles. The PPy matrix reduces the particle-to-particle contact resistance, thus significantly enhancing the electrical conductivity of the composite. In order to further confirm the presence of PPy, energy dispersive X-ray (EDX) mapping was used to observe the distribution of PPy (Fig. 5(c-f)). The coloured points correspond to the presence of the elements Fe, C, and N, respectively. The N and C are elements of PPy. The results show that

N and C are distributed uniformly throughout the whole area, which indicates that the PPy particles had uniformly coated the surfaces of the α -LiFeO₂ nanoparticles.

Fig. 6(a, b) shows typical charge-discharge curves for different cycles of α -LiFeO₂ and α -LiFeO₂-PPy electrodes in coin test cells using lithium as the counter and reference electrode between 1.5 and 4.5 V (vs. Li⁺/Li). Although all the samples showed some irreversible capacity losses, but the amount of irreversible capacity loss of α -LiFeO₂-PPy composite is much lower than that of the bare α -LiFeO₂. The cycling stabilities of bare α -LiFeO₂; α -LiFeO₂-PPy composite and PPy electrodes at 0.1 C (C=282 mA g⁻¹) are shown in Fig. 6(c). It can be seen that the discharge capacity of bare α -LiFeO₂ continuously decreases in the first 10 cycles and reaches 78.4 mAh g⁻¹ after 100 cycles, which is only 36.6% of its initial capacity (214.2 mAh g⁻¹), indicating poor cycle life. In comparison, the α -LiFeO₂-PPy composite electrode shows great enhancement of the capacity retention. The α -LiFeO₂-PPy composite electrode shows an initial discharge capacity of 198.8 mAh g⁻¹, and after 10 cycles, it reaches to a fairly stable capacity of 115.3 mAh g⁻¹. The capacity retention after 100 cycles is around 90%, referring to the 10th cycle. The pure PPy electrode shows a low capacity of about 50 mAh g⁻¹ at 0.1 C.

To further investigate the electrochemical performance of the bare α -LiFeO₂ and the α -LiFeO₂-PPy composite electrodes, the rate capability was tested, as shown in Fig. 6(d). The α -LiFeO₂ and α -LiFeO₂-PPy composite electrodes were measured at different rate from 0.1 C to 10 C, followed by a return to 0.1 C. The specific capacity of α -LiFeO₂ was very low when the rate capability was more than 1 C. The α -LiFeO₂-PPy composite electrode, however, showed the highest specific capacity of 45.9 mAh g⁻¹ at a current density of 10 C. There is less than a 15% capacity loss for the α -LiFeO₂-PPy composite electrode after changing the current density from 0.1 C to 10 C and back to 0.1 C over 40 cycles, showing the relatively good cycling stability.

In order to verify that the conductive PPy coating is responsible for the good performance of the cell with the α -LiFeO₂-PPy electrode, electrochemical impedance spectroscopy (EIS) measurements were performed on the bare α -LiFeO₂ and α -LiFeO₂-PPy composite electrodes. Fig. 7(a) shows the Nyquist plots of the electrodes at a discharge potential of 2.0 V vs. Li/Li⁺ at 25 °C after cycling over 10 cycles. All the impedance curves show two compressed semicircles in the high to medium frequency region, which could be assigned to the film resistance (R_f) of solid electrolyte interphase (SEI) and charge transfer resistance (R_{ct}), respectively. A line inclined at approximately 45° reflects the Warburg impedance (W) which is associated with the lithium-ion diffusion in the bulk of the active material. While the high-frequency intercept of the semicircle refers to the uncompensated resistance (R_l) which included the particle-particle contact resistance, electrolyte resistance, and the resistance between the electrode and the current collector [26, 27]. The R_f , R_{ct} and R_l for the α -LiFeO₂ and α -LiFeO₂-PPy electrodes were obtained using the equivalent circuit shown in the inset of Fig. 7(a) (calculating by Zview). By comparing the diameters of the semicircles, the R_f of the cell with α -LiFeO₂-PPy electrode is much smaller than for the cell made from bare α -LiFeO₂ electrode, due to the conductivity PPy layer which prevented the SEI forming ($9.5 \times 10^{-9} \Omega$ and 7.5Ω , respectively). The R_{ct} of the cell with α -LiFeO₂-PPy electrode is also lower than for the cell made from bare α -LiFeO₂ electrode due to the enhancement in electronic conductivity (231.7Ω and 386.9Ω). Under the same cell condition, the R_l of the cell with α -LiFeO₂-PPy and α -LiFeO₂ electrode are similar (8.9Ω and 10.1Ω).

The EIS can also be used to calculate the lithium diffusion coefficient using the following equation [28-30]

$$D = R^2 T^2 / 2 A^2 n^4 F^4 C^2 \sigma^2 \quad (2)$$

where R is the gas constant, T is the absolute temperature, A is the surface area of cathode (1 cm^2), n is the number of electrons transferred in the half-reaction for redox couple, which is

equal to 1, F is the Faraday constant, C is the concentration of Li ion in solid (2.01×10^{-3} mol cm^{-3}), D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), and σ can be obtained from the slope of the lines in Fig. 7(b).

$$Z_{re} = R_D + R_L + \sigma \omega^{1/2} \quad (3)$$

The lithium diffusion coefficients are calculated to be $2.0 \times 10^{-15} \text{ cm}^2 \text{s}^{-1}$ and $3.5 \times 10^{-14} \text{ cm}^2 \text{s}^{-1}$ for bare $\alpha\text{-LiFeO}_2$ and $\alpha\text{-LiFeO}_2\text{-PPy}$ nanocomposite, respectively, at 25 °C. This indicates that the Ppy coating layer on the $\alpha\text{-LiFeO}_2$ particles can improve the electrochemical kinetics.

A morphological study of the electrodes before cycling and after 100 cycles was also conducted. The electrodes before cycling show a similar smooth surface (Fig. 8(a,b)), while after cycling, the electrode morphology shows big differences. Fig. 8(c) is a FESEM image showing the surface of the $\alpha\text{-LiFeO}_2$ after 100 cycles. Big cracks can be clearly observed on the surface of the electrode. The $\alpha\text{-LiFeO}_2\text{-PPy}$ composite electrode surface is much smoother in Fig. 8(d). There are no clear cracks that can be observed on the surface, suggesting good structural stability of the composite electrode. This excellent stability of the electrode should be attributed to the presence of the well-dispersed PPy coating on the $\alpha\text{-LiFeO}_2$ powders. The PPy coating could work as a protecting layer to reduce the contact between the LiFeO_2 and the electrolyte, and thus to form a better solid electrolyte interphase (SEI) layer [31, 32]. Moreover, PPy could prevent cracking and pulverization of the $\alpha\text{-LiFeO}_2$ electrode [33].

4. Conclusions

Nanosized $\alpha\text{-LiFeO}_2$ has been synthesized at low temperature using a solid-state reaction method with $\beta\text{-FeOOH}$ as the precursor. A novel $\alpha\text{-LiFeO}_2\text{-PPy}$ composite was then prepared

by chemical polymerization. The α -LiFeO₂-PPy composite shows better capacity retention and higher rate capability than the bare α -LiFeO₂. The R_f and R_{ct} for the α -LiFeO₂-PPy nanocomposite electrode is much lower than that of the bare α -LiFeO₂ electrode, indicating enhanced electron transfer due to the good conductivity of coating PPy layer. The PPy can prevent the formation of cracks in electrodes during the charge/discharge process. The conductive PPy serves as both a conducting matrix and a protective coating.

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Artworks

Figure 1. X-ray diffraction pattern (a) and FESEM image (b) of β -FeOOH.

Figure 2. X-Ray diffraction patterns of α -LiFeO₂, and α -LiFeO₂-PPy composite.

Figure 3. FTIR spectrum of PPy, α -LiFeO₂, and α -LiFeO₂-PPy composite.

Figure 4. TGA curves of PPy, α -LiFeO₂, and α -LiFeO₂-PPy composite.

Figure 5. FESEM images of α -LiFeO₂ (a), α -LiFeO₂-PPy composite (b), and corresponding EDX mapping for the α -LiFeO₂-PPy composite image (c) as follows: Fe (d), C (e), and N (f).

Figure 6. Charge-discharge curves for selected cycles for electrodes of (a) bare α -LiFeO₂, and (b) α -LiFeO₂-PPy composite; (c) cycling behaviour of bare α -LiFeO₂; α -LiFeO₂-PPy composite and PPy electrodes; (d) rate capability for bare α -LiFeO₂ and α -LiFeO₂-PPy composite electrodes (C=282 mA g⁻¹).

Figure 7. (a) Impedance plots of the cathodes containing α -LiFeO₂ and α -LiFeO₂-PPy composite after cycling over 10 cycles at a discharge potential of 2.0 V vs. Li/Li⁺ at 25 °C at frequencies from 100 kHz to 10 mHz. The equivalent circuit is shown in the inset; (b) Real parts of the complex impedance versus $\omega^{-1/2}$ at 25 °C at an anodic potential of 2.0 V vs. Li/Li⁺.

Figure 8. FESEM images of the electrode surface of α -LiFeO₂ (a, c) and α -LiFeO₂-PPy composite (b, d) before (a, b) and after (c, d) 100 cycles.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8