Long-term cycle stability at a high current for nanocrystalline LiFePO$_4$ coated with a conductive polymer

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Abstract
Highly uniform hierarchical-microstructured LiFePO$_4$ particles with dumbbell- and donut-shape and individual LiFePO$_4$ nanocrystals were prepared by a hydrothermal method utilizing citric acid or a triblock copolymer (Pluronic P123) as a surfactant. The cathode composed of the individual nanocrystalline LiFePO$_4$ particles exhibited higher specific capacity than the cathodes composed of the hierarchically assembled microparticles. Coating a conductive polymer, poly-3,4-ethylenedioxythiophene (PEDOT), on the surface of LiFePO$_4$ particles improved the battery performances such as large specific capacities, high rate capability and an improved cycle stability. The nanocrystalline LiFePO$_4$ particles coated with PEDOT (20 wt%) exhibited the highest discharge capacities of 175 and 136 mAh g$^{-1}$ for the first battery cycle and 163 and 128 mAh g$^{-1}$ after 500 battery cycles, with a degradation rate of 6–7%, at the rates of 1 and 10 C, respectively.

Keywords: Lithium-ion battery, nanocrystal, conductive polymer, cycle stability

Classification number: 4.03

1. Introduction
Lithium ion batteries are one of the great successes of electrochemical energy sources for not only modern portable electronic devices but also future electric vehicles including plug-in hybrid electric vehicles [1–3]. An olivine structure material, LiFePO$_4$, has emerged as one of the most promising cathode materials with good structural stability, lower toxicity and relatively low cost, which was first reported by Padhi et al [4]. LiFePO$_4$ has a theoretical capacity of 170 mAh g$^{-1}$ with a stable plateau voltage at 3.45 V versus Li/Li$^+$. However, the application of LiFePO$_4$ seems to be challenging to achieve [8–10]. It has been demonstrated that the improved performance was able to obtain by reducing the particle size to sub-micrometer and by enhancing the particle crystallinity, since electrode reaction occurs at the surface and requires the ions’ transport into the electrode lattices [5–15]. Nanodimensional materials provide large surface area and short diffusion length. Hydrothermal synthesis is an effective method to obtain well-crystallized materials with well-defined morphologies, since the hydrothermal process is carried out under high pressure [11–15]. The particle size and morphology can be controlled by a careful choice of surfactants, solvents and reaction parameters in hydrothermal synthesis [11–16].
Surfactant molecules can act as a template or be adsorbed onto the particle surfaces during particle growth, which determines the particle size and morphology of the product.

Considerable efforts have been made to improve the conductivity and the charge/discharge rate by surface coating with conductive materials [2, 8–16]. Since the interface characteristics is a key factor for the electrode performance, coating of the LiFePO₄ particles with conductive materials, such as carbon, conductive polymers, ceramics or metals, is expected to improve the electrode performance. Conductive polymers, such as poly-3,4-ethylenedioxythiophene (PEDOT), are attractive materials in covering inorganic crystallite surfaces in terms of improving not only electrical conductivity but also mechanical flexibility [8–10, 16]. Conductive polymer coated on the nanoparticles can accommodate small volume expansion/contraction during discharging/charging process, which will reduce cracking of the electrode with ageing. Another advantage of conductive polymers is that they can be coated under mild processing conditions compared to carbon coating. In addition to their electrical conductivity and mechanical flexibility, conductive polymers can also improve lithium ion accessibility and diffusion pathways within battery cathodes.

In this work individual LiFePO₄ nanoparticles and donut-and dumbbell-shaped LiFePO₄ microstructures hierarchically constructed with the nanoplates were synthesized by a hydrothermal method, using various surfactants to controllable size and shape of LiFePO₄ particles. Then, in order to increase the conductivity of the electrode surfaces, these particles were coated with PEDOT. The electrochemical performances of these conductive polymer-coated LiFePO₄ nanocrystalline particles and microstructures were examined in terms of specific capacity, cycle stability and rate capability as the cathodes of Li⁺ ion batteries.

2. Experimental

2.1. Materials and synthesis of LiFePO₄ and LiFePO₄–PEDOT coated cathode materials

All chemicals and materials were obtained from the Sigma-Aldrich corporation and used without further purification. All aqueous solutions were prepared with ultra-pure water deionized by a millipore milli-Q system (18 MW cm⁻¹). LiOH (99%), FeSO₄·7H₂O (99+%) and H₃PO₄ (85%) were used as starting materials. Citric acid, C₆H₈O₇ (99%), or a triblock copolymer (P123), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) was used as a surfactant to control the particle growth and surface morphology. LiFePO₄ crystalline particles were synthesized by a hydrothermal method from the stoichiometric mixture of LiOH, FeSO₄·7H₂O and H₃PO₄ (3 : 1 : 1 molar ratio). L-ascorbic acid (C₆H₈O₆, 99%) was added as a reducing agent to the stoichiometric mixture of the starting materials (Fe²⁺; C₆H₈O₆ = 4 : 1 molar ratio). Ethylene glycol was added into the aqueous solution to disperse the inorganic salts (1 : 1 volume ratio). The resulting gray solution was transferred into a 125 ml teflon-lined stainless steel autoclave and heated for 12 h at 160°C. After the hydrothermal reaction was completed, the precipitate was completely washed and dried at 80°C.

Conductive polymer, PEDOT, was prepared by polymerizing 3,4-ethylene dioxythiophene monomer and a dopant, para-toluene sulfonic acid (p-TSA), at a 2 : 1 mole ratio by using anhydrous FeCl₃ as an oxidizing catalyst [16, 17]. The PEDOT was dissolved in DMSO or cresol. PEDOT was coated on the LiFePO₄ particles by simply dispersing the LiFePO₄ powder in the conductive polymer solution at room temperature and evaporating the solvent in a vacuum oven at 60°C.

2.2. Characterization

Powder x-ray diffraction profiles were recorded on a Philips PW1050 diffractometer using graphite-monochromated CuKα radiation (λ = 1.54056 Å). Data were collected over the 2θ range from 10° to 100° for 4 s in each 0.02° step at ambient temperature. The structural parameters were refined by using the Rietveld program FULLPROF [18]. Scanning electron microscopes (FESEM JSM-6700F and SEM JSM-6380, JEOL, Japan) were used to examine the particle morphology. The electrochemical measurements were carried out using coin cells (CR 2032 type) assembled in a dry room. The cathodes were prepared by compressing and drying after spreading a mixture slurry of the active material (LiFePO₄/PEDOT coated), acetylene black (AB) and polyvinylidene fluoride (PVDF) in NMP. The electrolyte was 1 M LiPF₆ in a 1 : 1 mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) and the separator was a porous polyethylene film (Celgard 2300 µm). The cells were cycled with a constant current mode (galvanostatically) in a potential range of 2.0–4.3 V using a multichannel battery test system (Maccor Series 4000, USA).

3. Results and discussion

3.1. Structure and morphologies

The observed, calculated and difference XRD patterns from the Rietveld refinement for the as-synthesized nanocrystalline LiFePO₄ are shown in figure 1. All diffractions for the nanocrystalline LiFePO₄ in the powder XRD patterns were indexed by an orthorhombic structure with the Pnma space group.
Table 1. The final atomic coordinates, isotropic temperature factors and agreement factors from the structural model for LiFePO₄.

| Atom | Site | g   | x   | y   | z   | B (Å²) |
|------|------|-----|-----|-----|-----|--------|
| Li   | 4a   | 0.5 | 0.0 | 0.0 | 0.0 | 0.60   |
| Fe   | 4c   | 0.5 | 0.282| 0.250| 0.974| 0.70   |
| P    | 4c   | 0.5 | 0.096| 0.250| 0.420| 0.66   |
| O1   | 4c   | 0.5 | 0.095| 0.250| 0.743| 0.45   |
| O2   | 4c   | 0.5 | 0.457| 0.250| 0.215| 0.45   |
| O3   | 8d   | 0.5 | 0.170| 0.049| 0.283| 0.45   |

Space group: Pnma \(a = 10.318\,\text{Å}, b = 5.995\,\text{Å}, c = 4.697\,\text{Å}\)

\[R_p = 8.17\%, \quad R_{wp} = 10.70\%, \quad R_{exp} = 14.67\%, \quad \chi^2 = 0.53\]

Figure 2. SEM images of (a) individual nanocrystalline LiFePO₄ powders, (b) dumbbell-shaped microstructure LiFePO₄ assembled with nanoplates and (c) donut-shaped microstructure LiFePO₄ assembled with nanoplates.

**Figure 2.** SEM images of (a) individual nanocrystalline LiFePO₄ powders, (b) dumbbell-shaped microstructure LiFePO₄ assembled with nanoplates and (c) donut-shaped microstructure LiFePO₄ assembled with nanoplates.

3.2. Electrochemical performance of the LiFePO₄ coated with PEDOT

Nanocrystals have the benefit of enlarging the specific surface area with the decreased diffusion length for Li⁺.
ions. In this work, these particles were coated with a conductive polymer, PEDOT, in order to increase the charge transport kinetics. Figure 3 shows a typical cyclic voltammogram of a Li cell with the cathode composed of nanocrystalline LiFePO₄ coated with PEDOT (10 wt%). The pair of the Fe²⁺/Fe³⁺ redox couple with an oxidation peak at 3.55 V and a reduction peak at 3.33 V corresponds to the charge/discharge reaction of the battery. The peak shape is almost symmetric and the potential separation between the two peaks is small. The first charge/discharge curves of the lithium batteries assembled with the LiFePO₄–PEDOT (10 wt%) coated cathodes of three different morphologies are shown in figure 4(A). All the curves show reversible lithium extraction/insertion during the charging/discharging processes with varying specific capacities. The charge and discharge profile shown in figure 4(A) demonstrates that the individual LiFePO₄ nanoparticle cathode shows the highest specific capacity of 170 mAh g⁻¹. The dumbbell- and donut-shaped microstructure LiFePO₄ cathodes show capacity values of about 120 mAh g⁻¹. The increase in the specific capacity certainly reflects the increase in the specific surface area. In addition, the smaller the particle is, the more densely the particles can be packed with smaller interstitial volumes in the cathode. The tap density of the positive electrode composed of the nanocrystalline LiFePO₄ powder can be improved with better packing with smaller void volumes. High tap density leads to a high volumetric specific capacity. The tap densities of the positive electrode composed of individual LiFePO₄ nanocrystals, dumbbell- and donut-shaped hierarchical microstructures are 1.56, 1.20 and 1.06 g cm⁻³, respectively. As the nanocrystalline LiFePO₄ possesses the highest tap density among the various morphologies, a high volumetric specific capacity (260.5 mAh cm⁻³) was achieved. The cycle performances of the individual nanocrystalline particles, dumbbell-shaped and donut-shaped hierarchical microstructures of LiFePO₄ coated with PEDOT (10 wt%) were tested. The discharge specific capacities for 100 battery cycles are shown in figure 4(B). Specific capacities of 153, 107 and 102 mAh g⁻¹ after 100 charge-discharge cycles at a rate of 1 C, with degradation rated of approximately 11, 15% respectively, for the individual nanocrystals, dumbbell-shaped and donut-shaped hierarchical microstructures of LiFePO₄ coated with PEDOT (10 wt%).

Optimization of the amount of PEDOT coated on the LiFePO₄ nanoparticles was required to achieve the long cycle life and the high capacity. Figure 5 shows the battery performances of LiFePO₄ nanocrystals coated with 10, 20 and 30 wt% of PEDOT at a rate of 1 C for the consecutive 100 charge-discharge cycles. As shown in figure 5, the nanocrystals LiFePO₄ coated with PEDOT 20 and 30 wt% exhibited higher specific capacities than the theoretical capacity of LiFePO₄ only; the first discharge capacity of around 190 mAh g⁻¹ for 30 wt% PEDOT coated LiFePO₄ cathode and 175 mAh g⁻¹ for 20 wt% PEDOT coated LiFePO₄ cathode. The capacity loss for the LiFePO₄ coated with 30 wt% of PEDOT, 15% for 100 cycles, was the largest among the three cathodes, especially during the first five cycles. The cycle performance of LiFePO₄ coated with 20 wt% of PEDOT was superior to the cathodes of
30 or 10 wt% PEDOT coating. The capacity remained fairly constant with high capacity values for 100 battery cycles.

Long-term cycle stability at the standard 1 C rate and at a higher discharge current rate of 10 C for the individual nanocrystalline LiFePO$_4$ coated with PEDOT (20 wt%) was investigated and is shown in figure 6. The specific capacity at a rate of 10 C was 136 mAh g$^{-1}$ for the first battery cycle and 128 mAh g$^{-1}$ for the 500th cycle, with a degradation rate of approximately 6%. The specific capacity was 163 mAh g$^{-1}$ after 500 battery cycles at the rate of 1 C, with a degradation rate of 7%. The nanocrystalline LiFePO$_4$ particles coated with PEDOT (20 wt%) exhibited the high discharge capacities and the long-term cycleability. We believe the mechanical flexibility of the conductive polymer can give room for structural expansion and contraction modification caused by Li insertion and extraction, which results in the long-term cycle stability for the nanocrystalline LiFePO$_4$ coated with PEDOT cathode.

4. Conclusions

Nanocrystalline LiFePO$_4$ olivine crystals were prepared by a hydrothermal process. Uniform individual LiFePO$_4$ nanoparticles and the LiFePO$_4$ microstructures hierarchically assembled with the nanoparticles were synthesized by using P123 block copolymer and molecular surfactants, respectively. The well-dispersed individual LiFePO$_4$ nanoparticles coated with a conductive polymer, PEDOT, exhibit excellent battery performances in terms of a high rate capability and an improved cycle stability. The nanocrystalline LiFePO$_4$ coated with PEDOT (20 wt%) exhibited the best cycle performance with the largest specific capacity among the cathodes studied in this work. The specific capacity at a rate of 10 C was 136 mAh g$^{-1}$ for the first battery cycle and 128 mAh g$^{-1}$ for the 500th cycle, with a degradation rate of only about 6%.

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