



Challenges in synthesizing carbon-coated LiFePO₄ nanoparticles from hydrous FePO₄ and their electrochemical properties

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ABSTRACT

Carbon-coated LiFePO₄ nanoparticles are obtained from a polymer-coated hydrous FePO₄ which is synthesized via the in situ polymerization of aniline. The difficulty in synthesizing a pure LiFePO₄ phase comes from achieving the exact stoichiometry between the added Li source and hydrous polyaniline-coated FePO₄. It is important to consider the amount of residual H₂O and polyaniline in FePO₄ to achieve the exact stoichiometry of Li vs. Fe. The phase impurities induced by inappropriate amount of Li severely deteriorate the electrochemical performance of C-coated LiFePO₄. On the other hand, the carbon-encapsulated LiFePO₄ nanoparticles with the exact amount of Li show a capacity of ~145 mAh g⁻¹ at 5 C, and exhibit a capacity of 170 mAh g⁻¹ for 250 cycles at 0.1 C which is nearly theoretical value.

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1. Introduction

Since LiFePO₄ was first reported as a potential cathode material in Li-ion batteries [1], it has given rise to a great deal of excitement, as well as controversy, in the research community. The most interesting fact is that LiFePO₄ has the obvious advantage of being composed of safe and inexpensive materials [2–5]. This LiFePO₄ belongs to the group of materials so called an olivine structure in which phosphorous ions occupy the tetrahedral sites with Fe²⁺ and Li⁺ in two distinct octahedral sites in a hexagonal array of oxygen ions [1].

It is obvious that the low electronic conductivity of LiFePO₄ (<10⁻⁹ S cm⁻¹ at ambient temperature) [6] may limit its application, so intensive work has been done to develop nanostructures in which its electronic conduction can be enhanced either by the presence of an electronic conductor or the doping of foreign atoms [7–13]. The method of incorporating carbon includes mixing the active LiFePO₄ materials with carbon, or adding polymer additives which are subsequently carbonized by calcination [14–19]. Carbon-coated LiFePO₄ with polymer additives has the extra advantage of having a reduced particle size because the polymers or carbon near the LiFePO₄ prevent particle growth during the crystallization of LiFePO₄. Smaller particle size of active material enables a rapid diffusion of Li⁺, and diffusivity of Li⁺ has also been a subject of extensive study [20]. Merely mixing the polymer

additives with the active materials, however, does not insure the proper encapsulation of carbon for electronic percolation. The resulting morphology may become a composite material with carbon, as opposed to completely encapsulated LiFePO₄. In this respect, Wang et al. [21] reported that completely C-coated LiFePO₄ can be achieved from Fe³⁺ salts via the in situ polymerization of aniline [22].

When adding an Li source to FePO₄, however, there is some difficulty in achieving the exact stoichiometry of Li to Fe (1:1 molar ratio), because FePO₄ undergoes a hydrothermal synthesis with aniline, and the resulting FePO₄ is a hydrated form of iron phosphate (FePO₄·2H₂O) [23]. Herein, we explain the challenges involved, along with experimental details, and show that C-coated LiFePO₄ with the exact amount of Li exhibits excellent electrochemical performances. The effect of excessive Li which may be caused by the uncertain stoichiometry of Li to Fe is also discussed in this report.

2. Experimental procedure

The in situ polymerization method was adopted to synthesize polyaniline-coated FePO₄ nanoparticles using FeCl₃, NH₄H₂PO₄, and aniline (C₆H₅NH₂) in D. I. water as reported elsewhere [21,22]. The resulting water solution contained polyaniline-coated FePO₄. A vacuum filter with a ~50 nm-pore membrane was used to collect the precipitates. After filtering, the obtained greenish powder was dried under vacuum overnight. Li acetate (CH₃COOLi) was added to the obtained FePO₄, and following the two-step heat treatment was carried out for synthesis of LiFePO₄ under a reductive

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atmosphere (Ar/H₂). Transmission electron microscopy (TEM, JEM-300F; JEOL) was performed at an accelerating voltage of 300 kV. For the TEM analysis, a small amount of C-coated LiFePO₄ was dispersed in ethanol via sonication. The resulting solutions were dropped on an amorphous-carbon-coated copper grid, and dried in an oven before the analysis. The amount of residual water and polyaniline in the polyaniline-coated FePO₄ were investigated by thermo gravimetric analysis (TGA; Q-5000 IR, TA instruments) under a dry air flow from RT to 750 °C.

Cycling tests were performed using coin-type half cells (2016 type) with a Li counter electrode. The working electrode consisted of the active material, super P carbon black, and a polyvinylidene fluoride binder at a weight ratio of 8:1:1. One mole of LiPF₆ in ethylene carbonate/diethylene carbonate (1/1 vol.%) (Cheil Industries Inc.) was used as the electrolyte. The cells were cycled between 2.0 V and 4.3 V after the first discharge from the initial open-circuit voltage. The pure LiFePO₄ phase was tested from 0.1 C to 5 C (1 C = 170 mA g⁻¹, based on the theoretical capacity of LiFePO₄).

3. Results and discussion

Fig. 1 shows the TGA analysis of the polyaniline-coated FePO₄ nanoparticles under air. The weight loss is due to the residual water and oxidation of polyaniline. The weight loss of ~19 wt.% before 200 °C indicates that the FePO₄ nanoparticles are in the hydrated form (2H₂O/FePO₄·2H₂O = 19.27 wt.%) [23]. It cannot be excluded, however, that some residual water is also present with the nanoparticles, and the amount of polyaniline is approximately 3 wt.% [21]. Therefore, these considerations should be taken into account when attempting to add a stoichiometric amount of Li source. Since the synthesis of polyaniline-coated FePO₄ involves hydrothermal conditions, the presence of some residual water is inevitable, even after drying, and this will affect the phase purity of the resulting C-coated LiFePO₄.

The X-ray diffraction patterns of the C-coated FePO₄ nanoparticles prepared with different amounts of Li source are presented in Fig. 2. The diffraction peaks are indexed to olivine-type LiFePO₄ with the space group, *Pnma* (62) (JCPDS #40-1499) for Li/Fe = 1.00, but several impurity phases are detected with increasing amount of excess Li. The average grain size of LiFePO₄ with a stoichiometric amount of Li was estimated by the Scherrer equation [24–26], and calculated to be ~40 nm, which is consistent with the TEM data

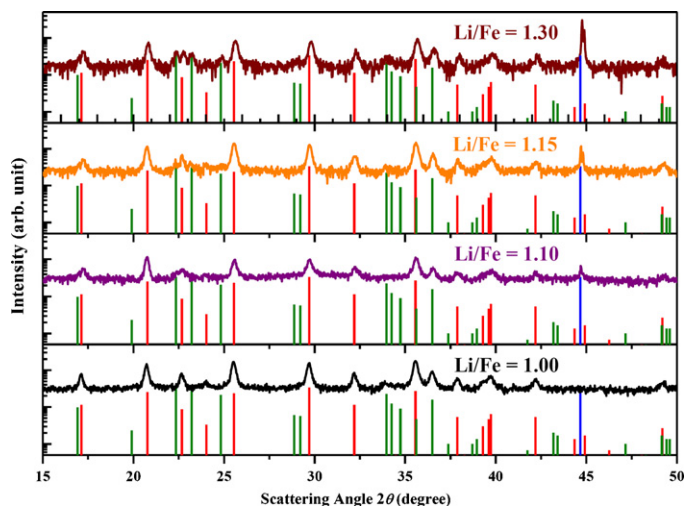


Fig. 2. X-ray diffraction patterns of the C-coated LiFePO₄ nanoparticles with different molar ratio of Li to Fe. The ideal peak positions and intensities for LiFePO₄ (red), Li₃PO₄ (green), and Fe (blue) are marked at the bottom, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

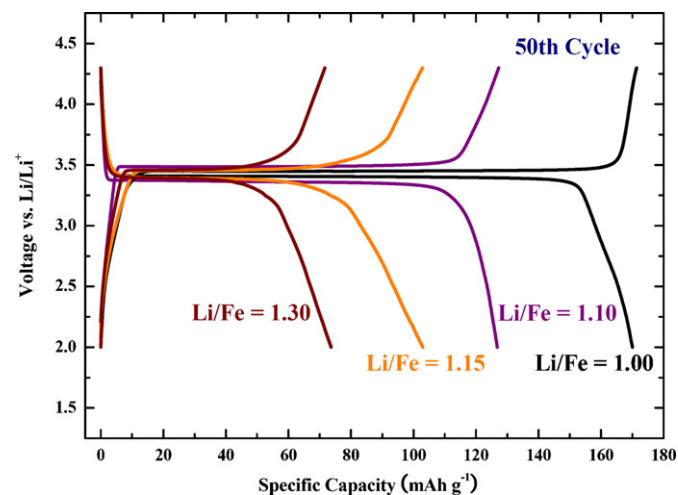


Fig. 3. Voltage profiles for the C-coated LiFePO₄ nanoparticles at the 50th cycle with different molar ratio of Li to Fe. All of the cells were cycled between 2.0 V and 4.3 V at 0.1 C rate.

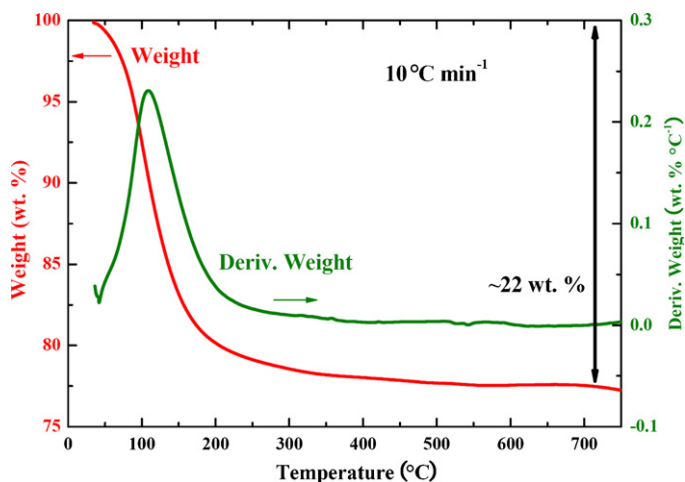


Fig. 1. Thermo-gravimetric analysis of the polyaniline-coated FePO₄ nanoparticles under air. The weight loss of ~22 wt.% is due to the residual water and oxidation of polyaniline.

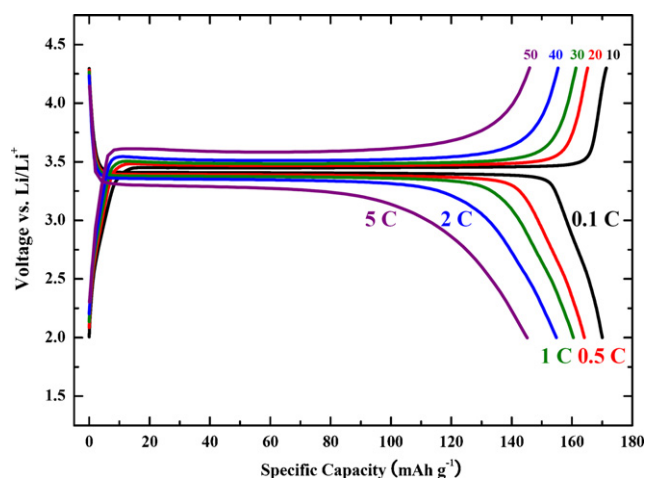


Fig. 4. Voltage profiles for the C-coated LiFePO₄ nanoparticles (Li/Fe = 1.00) at different current densities. All of the cells were cycled between 2.0 V and 4.3 V from 0.1 C to 5 C rate for 10 cycles each.

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