



A novel low-cost and simple colloidal route for preparing high-performance carbon-coated LiFePO₄ for lithium batteries

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ABSTRACT

Nanosized carbon-coated lithium iron phosphate (LiFePO₄/C) particles were synthesized using a novel low-cost colloidal process with LiH₂PO₄, FeCl₂ and anhydrous *N*-methylimidazole (NMI) as starting materials, following by a short annealing step at 600 °C. The ~3–5 nm thick carbon coating comes from the carbonization of molten salt NMIH⁺Cl⁻ derived from NMI; the resulting carbon contents of the LiFePO₄/C powder is 2.53 wt.%. The materials were characterized by thermogravimetric and differential thermal analysis, differential scanning calorimetry, powder X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy, atomic absorption spectroscopy, Raman spectroscopy, four-point probe method, cyclic voltammetry and galvanostatic cycling experiments in coin cells. The LiFePO₄ phase reveals agglomeration of semi-spherically particles with an average individual size of 35 ± 4 nm. Carbon-coated LiFePO₄ possesses electronic conductivity of 1.4 × 10⁻³ S cm⁻¹ at room temperature causing a markable increase in rate capability. Cycling the cells between 2.2 and 4.2 V vs. Li⁺/Li resulted in a discharge capacity of 164 mAh g⁻¹ at the first cycle of C/20 and 162 mA hg⁻¹ after 35 cycles, which corresponds to over 95% of the theoretical capacity of olivine LiFePO₄.

1. Introduction

Lithium iron phosphate (LiFePO₄) is considered as a promising alternative to replace the existing cathode materials for lithium-ion batteries. This is due to many factors including its low cost, non-toxicity, thermal stability in the fully charged state, flat voltage plateau (3.45 V vs Li⁺/Li) and long operation life. It exhibits a high theoretical specific capacity of 170 mAh g⁻¹. In spite of these advantages, LiFePO₄ has a poor Li⁺ diffusion coefficient (1.8 × 10⁻¹⁸ m² s⁻¹) and an intrinsic low electronic conductivity (ca. 10⁻⁹–10⁻¹⁰ S cm⁻¹) at room temperature [1–3]. To overcome these disadvantages, various attempts have been made, mainly by reducing of the grain size of the cathode particles to shorten its electron and Li⁺ path within the particles, and also by increasing its electron conductivity through coating of the LiFePO₄ particles with carbon. This was usually performed by pyrolyzing organic compounds during the synthesis [2] or by adding a conductive organic compound such as carbon [4], graphene [5] or polymers [6].

The reason behind the use of carbon coating is mainly to improve the surface electronic conductivity of LiFePO₄ particles in order to fully utilize the active material at high current rates. Carbon coating can also reduce the particle size of LiFePO₄ by blocking particle growth

agglomeration during sintering [7–10]. Reduction of particle size has been employed as an effective method to improve the high-rate capacity and cycling stability of LiFePO₄ materials [8,11–13]. Reports have shown that annealing temperature control and particle size are crucial conditions for the improvement of the high-rate capacity and cycling stability of LiFePO₄ materials [3,7,8]. In general, a decrease in particle size to a nanometer scale enhances the ionic diffusion rate and increases lithium ion transport number [14,15]. Carbon coatings, though, have drawbacks, some of which are high processing cost and reduced tap density (bulk density of a powder after compaction process) which may lead to low energy density of the battery cells [16,17].

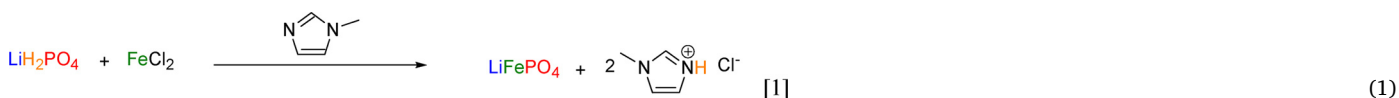
Doping the LiFePO₄ structure with supervalent cations (less than 1% in molar content) such as Mg⁺², Al⁺³, Ti⁺⁴, Nb⁺⁵, Zn⁺⁴, Mo⁺⁶, Cr⁺³, V⁺⁵, Co⁺² and Cu⁺², has been reported to increase the electronic conductivity of the material by two to eight times [18–22]. However, studies have shown that doping LiFePO₄ with Zr, Nb and Cr, for example, may block the lithium diffusion channels [23], thus hindering Li diffusion. Furthermore, doping may reduce the specific capacity of the sample when compared with the carbon-coated sample, not to mention also the cost of raw materials used in doping [24].

A variety of synthesis techniques have been reported to improve the battery performances of LiFePO₄/C cathode material, among which

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solid-state and solution-based methods are involved. Despite its production of highly crystalline and hydroxyl free LiFePO_4 , the solid-state method suffers several drawbacks including high energy consumption (partially because of the high temperature sintering), large particle size requirement and time consuming multi-step synthesis (10–24 h) [3]. Among the various techniques involved in solution-based methods, there is spray pyrolysis [25,26], co-precipitation [27], sol-gel [28,29], hydrothermal [30,31] and emulsion drying [32]. It is important to mention that most of these methods use relatively expensive divalent iron compounds as iron sources also require a complex synthesis process or a long heating process including long reaction times (6–24 h)



and production of large chemical and aqueous wastes. As a result, LiFePO_4/C becomes expensive and has not been widely commercialized.

Applications on industrial scale, usually, require that the processing cost be low, and that the preparation procedure be simple. Commercial production of LiFePO_4/C powders have been prepared by two processes: mechanochemical activation (MA) and carbothermal reduction (CTR). MA process requires crushing and mixing of the precursors in a high energy ball mill, thus its processing cycle is long (normally 24 h) and consumes high energy, therefore, costly [1]. The optimum sintering conditions are reported to be 600–700 °C for 4–24 h [1,33–36]. Reports showed that the high sintering temperatures might result in formation of some impurity phases, such as Fe_2P and Fe_3P [1], causing a decrease in the specific capacity and the cyclic stability of LiFePO_4 . On the other hand, the CTR process that uses reduction by carbon of Fe^{+3} species found in appropriate precursors requires further optimization in order to reduce the processing time as well as energy consumption, while performance is maintained by controlling the particle size and impurity content [1].

In this work, we report a novel and mild condition colloidal route to prepare carbon-coated LiFePO_4 particles, starting from LiH_2PO_4 and FeCl_2 with *N*-methylimidazole (NMI) as anhydrous organic solvent and excellent carbon source. The thermal, structural, chemical, electrical and electrochemical properties of the LiFePO_4 samples were investigated by thermogravimetric analysis (TGA/DTG), differential scanning calorimetry (DSC), Raman spectroscopy, field-emission scanning electron microscopy/transmission electron microscopy (SEM/TEM), powder X-ray diffraction (XRD), four-point probe method, cyclic voltammetry (CV) atomic absorption spectroscopy (AAS), and galvanostatic cycling experiments in coin cells.

2. Experimental

2.1. Materials

All chemicals used for the synthesis of LiFePO_4 were purchased from Aldrich and used without further purification. Lithium dihydrogen phosphate was purchased in 99.99% purity, anhydrous ferrous chloride was 98% pure and anhydrous *N*-methylimidazole (NMI) was 99.9% pure. The electrochemical coin cells were assembled using a lithium foil anode (Alfa Aesar, 99.9%), acetylene black (100% pure), polyvinylidene fluoride binder, PVdF (Kynar KF Polymer, W#1100, 600 000 g/mol), anhydrous *N*-methyl-2-pyrrolidone, NMP (Aldrich, 99.5%) and carbon-coated Al foil (Exopack #2651). The electrolyte was LiPF_6 dissolved in a 1:1 (wt.%) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (BASF); a porous polypropylene film (Celgard 2500) was used as a separator.

2.2. Synthesis of lithium iron phosphate (LiFePO_4)

Lithium dihydrogen phosphate (LiH_2PO_4) (10 mmol, 1.030 g, 1.0 equiv) and anhydrous FeCl_2 (10 mmol, 1.267 g, 1.0 equiv) were dissolved in 120 mL of anhydrous *N*-methylimidazole, in an argon-filled glove box (VAC, argon, Praxair, 4.8 PP). The mixture was stirred at 45 °C for 24 h and the yellow precipitate was first filtered and dried overnight under vacuum. The dry product was heated in a tubular furnace (Lindberg/Blue M, model TF55035A-1) at 600 °C for one hour under vacuum to give a black powder of LiFePO_4/C . Formation of LiFePO_4/C is shown in Eq. (1):

2.3. Thermal, structural, chemical and electrical characterization

Thermal analyses (TGA and DSC) of as-synthesized powders of LiFePO_4 were carried out under nitrogen atmosphere in order to assess the thermal processes occurring during the annealing step (performed under vacuum). The samples were examined using a thermogravimetric analyzer (Seiko Instrument Inc., TG/TDA 6200) and a modulated differential scanning calorimeter, m-DSC (Mettler Toledo DSC1).

X-ray diffraction (XRD, Siemens D-5000 coupled to a silicon detector and equipped with a $\text{Co-K}\alpha_1$ X-ray source ($\lambda = 1.7890 \text{ \AA}$)) was used to determine the crystalline properties of the annealed samples. The data were collected in the 2θ range of 10–75 ($^\circ 2\theta$), at a step-scan between 0.1 and 0.3 s per 0.01° at 25 °C. An integrated Raman microscope system (RENISHAW inVia Raman Microscope), with an excitation wavelength supplied by an internal Ar^+ (514 nm) 5 mW laser, was used to determine the carbon structure of the carbon-coated LiFePO_4 particles. Field-emission scanning electron microscopy (FE-SEM, Hitachi S-4300 Se/N) was used to examine the nanostructure of the LiFePO_4 powder, whereas the thickness of the carbon layer surrounding the LiFePO_4 particles was observed with a high-resolution transmission electron microscope, HR-TEM (JEOL JEM-2100F TEM) operating at 200 kV.

Energy dispersive X-ray (EDX) analysis with 20 kV accelerating voltage was used to determine the chemical composition of the samples (except for lithium); the EDAX detector, model Sapphire, is integrated into the Hitachi scanning electron microscope. The Li and Fe contents of the synthesized samples were confirmed by atomic absorption/emission spectrophotometry (AAS/AES, Varian, SpectraAA 220 FS). For that purpose, 30 mg of LiFePO_4 powder were dissolved in a 1% (v/v) aqueous solution of the concentrated acids $\text{HNO}_3\text{:HCl}$ (1:1 v/v). Elemental analysis (EAS1108 model, Fisons instruments S.P.A.) was used to measure the carbon content of the carbon-coated sample.

The electronic conductivity of the carbon-coated sample was measured on a disc-shaped pellet (12 mm diameter and 1.25 mm thick) using the four-point probe van der Pauw method. A home-built measuring station (Keithley instruments inc.: 7001 switch system, 6220 precision current source and 2000 multimeter) was employed.

2.4. Electrochemical measurements

The electrochemical properties of lithium iron phosphate samples were measured as follows. In an argon-filled glove box (H_2O and $\text{O}_2 < 1 \text{ ppm}$), electrochemical coin cells were assembled using a lithium foil anode (1.54 cm^2) and 85% (wt.%) LiFePO_4/C powder mixed with 10% acetylene black and 5% PVdF dissolved in NMP as the cathode. The resulting cathode films were casted onto a carbon-coated Al foil, dried at 100 °C for 24 h under vacuum and cut into a circle shape

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