



# Lithium iron phosphate spheres as cathode materials for high power lithium ion batteries



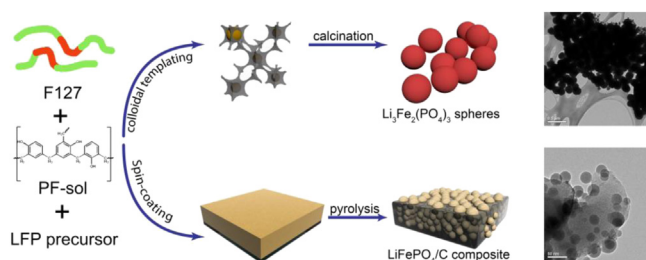
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## HIGHLIGHTS

- $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$  nanospheres were fabricated by templating and calcination.
- Spherical  $\text{LiFePO}_4$  particles embedded in carbon films were formed by spin casting.
- Both types of lithium iron phosphate spheres were tested as  $\text{Li}^+$ -battery cathodes.
- The spherical  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$  particles had a capacity of  $100 \text{ mA h g}^{-1}$  at 2.5 C rate.
- $\text{LiFePO}_4/\text{C}$  composites had capacities of 130 and  $50 \text{ mA h g}^{-1}$  at C/2 and 16 C rates.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Electrode materials composed of micrometer- and sub-micrometer-sized spherical particles are of interest for lithium ion batteries (LIBs) because spheres can be packed with higher efficiency than randomly shaped particles and achieve higher volumetric energy densities. Here we describe the synthesis of lithium iron phosphate (LFP) phases as cathode materials with spherical morphologies. Spherical  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$  particles and  $\text{LiFePO}_4$  spheres embedded in a carbon matrix are prepared through phase separation of precursor components in confinement. Precursors containing Li, Fe, and P sources, pre-polymerized phenol–formaldehyde (carbon source), and amphiphilic surfactant (F127) are confined in 3-dimensional (colloidal crystal template) or 2-dimensional (thin film) spaces, and form spherical LFP particles upon heat treatment. Spherical  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$  particles are fabricated by calcining  $\text{LiFePO}_4/\text{C}$  composites in air at different temperatures.  $\text{LiFePO}_4$  spheres embedded in a carbon matrix are prepared by spin-coating the LFP/carbon precursor onto quartz substrates and then applying a series of heat treatments. The spherical  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$  cathode materials exhibit a capacity of  $100 \text{ mA h g}^{-1}$  (83% of theoretical) at 2.5 C rate.  $\text{LiFePO}_4$  spheres embedded in a carbon matrix have specific capacities of 130, 100, 83, and  $50 \text{ mA h g}^{-1}$  at C/2, 2 C, 4 C, and 16 C rates, respectively (PF\_600\_2), revealing excellent high-rate performance.

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## 1. Introduction

Due to its low cost, environmental compatibility, and intrinsic thermal safety, lithium iron phosphate ( $\text{LiFePO}_4$  or LFP) ranks among the most promising cathode materials for LIBs that target

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the hybrid electric vehicle (HEV) and electric vehicle (EV) markets [1–4]. However, the low electronic and ionic conductivities of bulk LFP particles have restricted their rate performance, which is critical for HEV and EV power sources [5–8]. The electronic conductivity of LFP can be improved by coating it with carbon or metallic conductive layers [9–13]. The ionic conductivity can be boosted by doping with isovalent ions, and rate capabilities are improved by employing LFP nanoparticles [14]. The rate performance of LFP electrodes can be also improved by using nanoporous electrodes, because the interfacial area between a nanoporous electrode and the electrolyte is greatly increased [15–19]. Combinations of nanostructuring and conductive coatings increase the electronic and ionic conductivities simultaneously. 3DOM/m LiFePO<sub>4</sub>/C composites with high surface areas, well-ordered structure, and good electronic conductivity have shown excellent rate performance (84 mA h g<sup>-1</sup> at 5 C rate) [20]. Hierarchically porous LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C composites have also been reported to exhibit very high rate performance [21–23]. The biggest disadvantage of using porous electrode materials is their low volumetric energy density, a point that will be addressed by the work described in this article.

The volumetric energy density of a battery is an important factor for electronic devices in which the available space for the power source is limited, such as portable devices. Electrodes composed of nanoparticles generally have good electrochemical performance (i.e., higher specific capacity and higher rate performance than electrodes composed of micron-sized particles) but low volumetric energy density as the nanoparticles are poorly packed. The volumetric energy density of an electrode depends strongly on its tap density, which is a macroscopic property that is affected by the morphology and the size of the bulk particles. In most cases, micrometer-sized particles have higher tap densities but worse electrochemical performance than particles with nanometer dimensions. For particles of similar size, the shape of the particles has a strong effect on tap density. Electrodes made of spherical particles normally have higher tap densities than those composed of irregular particles, as the spherical particles can be packed with higher efficiency [24–27]. One way to overcome the dilemma between electrochemical performance and tap density is to fabricate micron-sized spherical particles with nanometer-sized features, which are accessible to the electrolyte. Hollow LiFePO<sub>4</sub> spheres and porous LiFePO<sub>4</sub> microspheres have been fabricated for LIBs, and showed both high rate performance and high volumetric energy densities [28–30].

Carbon coatings are known to boost the electronic conductivity of LFP particles and also to limit the growth of LFP particles at high temperatures [21,31–36]. In the synthesis of 3DOM/m LiFePO<sub>4</sub>/C

composites mentioned above, the precursor was confined in the octahedral and tetrahedral sites of a face-centered cubic (fcc) colloidal crystal template (CCT) composed of close-packed, 400-nm PMMA spheres. As illustrated in Fig. 1, this resulted in the formation of a network of spherical LiFePO<sub>4</sub> particles that were connected through a carbon matrix [20]. If such nanospheres would be separated from the carbon matrix, they could be used as a cathode material with higher volumetric energy density while preserving the high rate performance of the original composite. Since in the CCT synthesis, the special interactions between LiFePO<sub>4</sub> precursor, phenol–formaldehyde (PF) sol, and surfactant inside the confining space of the template resulted in the formation of nano-spherical LiFePO<sub>4</sub> particles [20], we wondered if this would also be true for different types of confinement where growth is limited to two dimensions, such as in thin films. Here we describe syntheses of nano-spherical Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and LiFePO<sub>4</sub>/C composites whose morphologies were influenced through the interplay between LFP precursor, PF sol, and amphiphilic surfactant inside confinement. Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was synthesized by calcining 3DOM/m LiFePO<sub>4</sub> composites in air to remove the carbon phase. Spherical LiFePO<sub>4</sub> particles embedded in a carbon matrix were synthesized by first spin-coating the precursor containing LFP-precursor, PF sol, and F127 in ethanol onto a quartz substrate and then pyrolyzing the aged composites under nitrogen. These syntheses are outlined in Fig. 1. Both approaches produced cathode materials that maintained high specific capacities (compared to the theoretical capacities) at high cycle rates with little loss over multiple cycles.

## 2. Experimental

### 2.1. Materials

The chemicals used in this study were obtained from the following sources: methyl methacrylate (MMA) monomer (99%), 2,2'-azobis(2-methyl propionamide) dihydrochloride (AMPD) initiator (97%), concentrated aqueous H<sub>3</sub>PO<sub>4</sub> solution (85 wt%), N-methyl-2-pyrrolidone (NMP) battery quality electrolyte (99.5%), polyvinylidene fluoride (PVDF), and lithium foil from Aldrich; Ketjenblack from AkzoNobel; lithium perchlorate (99.0%), ethylene carbonate (>99.0%), dimethyl carbonate (>99.0%) from Fluka; FeCl<sub>2</sub>·4H<sub>2</sub>O (98%), LiCl (99.5%), phenol (ACS reagent) and formaldehyde solution (37% aqueous solution) from Fisher Scientific; Pluronic F127 from BASF; hydrochloric acid (37%) from Malinckrodt Chemicals; and sodium carbonate (anhydrous, 99.7%) from J.T. Baker; 1 M LiPF<sub>6</sub> in ethylene carbonate–dimethyl carbonate–diethyl carbonate (EC–DMC–DEC, 4:3:3 vol. fractions, <50 ppm

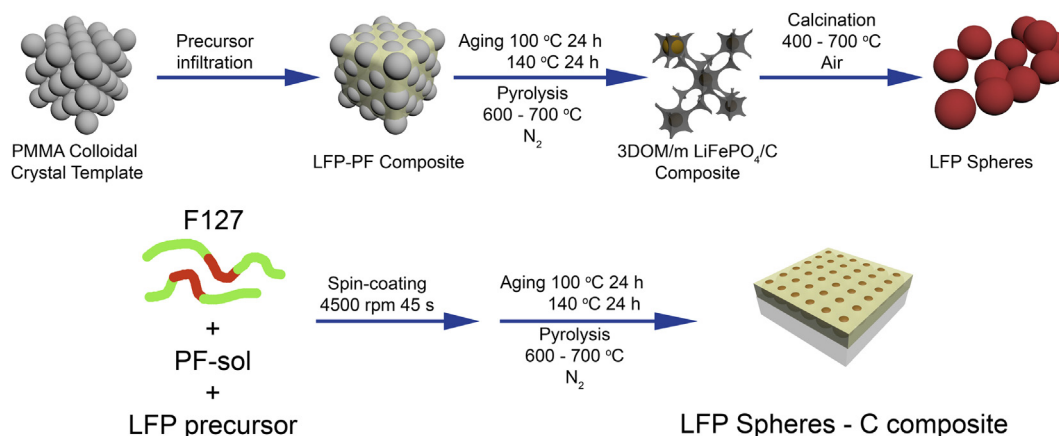


Fig. 1. Synthesis schemes to prepare LFP spheres and LFP sphere/C composites.

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