HIERARCHICAL URCHIN-LIKE LFP MESOCRYSTALS COATED WITH N-CONTAINING CARBON FOR LI-ION BATTERIES

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Introduction

Li-ion cells offer the largest energy density and output voltage of all known rechargeable battery technologies thus becoming a prime candidate to power next generation of Electric Vehicles and Hybrid Electric Vehicles. Since its identification by Padhi *et. al.* [1] in 1997, olivine LiFePO$_4$ (LFP) has been intensively studied as a potential electrode material for Li-ion batteries for various reasons such as high voltage (3.5 V vs. Li/Li$^+$), high theoretical capacity (170 mAhg^{-1}), ease of synthesis, low cost and good stability. However, the main drawback of LFP as electrode material lies in its low intrinsic electronic and ionic conductivity. In this context, extensive research has been done to address present problems including reduction of the particle size, coating with conductive agents and most recently synthesis of porous LFP monoliths [2, 3].

Mesocrystals as described by Cölfen *et al.* [4] are 3D ordered nanoparticle superstructures with new chemical and physical properties rising from their unique hierarchical mesostructure. These specific morphologies composed of nanoscaled hierarchically assembled units can be considered as possible future high rate capability electrodes due to porous internal framework that provides high accessibility for the electrolyte.

In this work, we report a facile synthesis route at low temperature for obtaining uniform and highly pure LFP/N-containing carbon mesocrystals with exciting urchin-like morphology.

Experimental

The preparation of LFP/N-containing carbon mesocrystals was carried out by solvothermal reaction in an Anton Paar autoclave reactor as described below. Initially, stochiometric amounts (3mmol) of LiOH, FeCl$_2$·4H$_2$0 and H$_3$PO$_4$ (85 wt % solution) were dissolved into 20 mL of absolute EtOH under vigorous magnetic stirring until homogeneous dark green solution was formed. N-acetylglucosamine (C$_5$H$_{15}$NO$_6$) was added as a carbon precursor. The precursor solution was placed in an autoclave which was then heated at 200 ℃ for 24 hours. The obtained black precipitate was centrifuged and repeatedly washed with DI water until the supernatant was colorless, then dried in a vacuum oven at 80 ℃ overnight. The LFP/N-containing carbon mesocrystals were further carbonized under a nitrogen flow at 700 ℃ for 6 hours in order to increase the conductivity of the carbon coating and thus the electrochemical performance.

The crystalline phases were identified with X-ray diffraction (XRD, Bruker D8 Advance) equipped with Cu-Kα radiation. Refinement of experimental data has been performed using Pseudo-Voigt profile matching (Fullprof, Windows version 2009). Carbon and nitrogen content of the prepared powders were determined by elemental analysis (PerkinElmer). The mesocrystal size and morphology was visualized using scanning electronic microscope (SEM) and high-resolution transmission electron microscope (HR-TEM, Topcon EM-002B).

Results and discussion

The comparison between the experimental and calculated XRD patterns as shown on Fig. 1 is in good agreement with the literature data [5], confirming the presence of olivine LiFePO$_4$ (space group: *Pnma*) as the only crystalline phase in the synthesized powder. The observed intensity data are shown by a dotted line, while the solid line corresponds to the calculated pattern of LiFePO$_4$. The bottom line represents the difference between the observed and calculated intensities. The vertical ticks correspond to the Bragg positions of LiFePO$_4$ (ICDD PDF No. 40-1499).
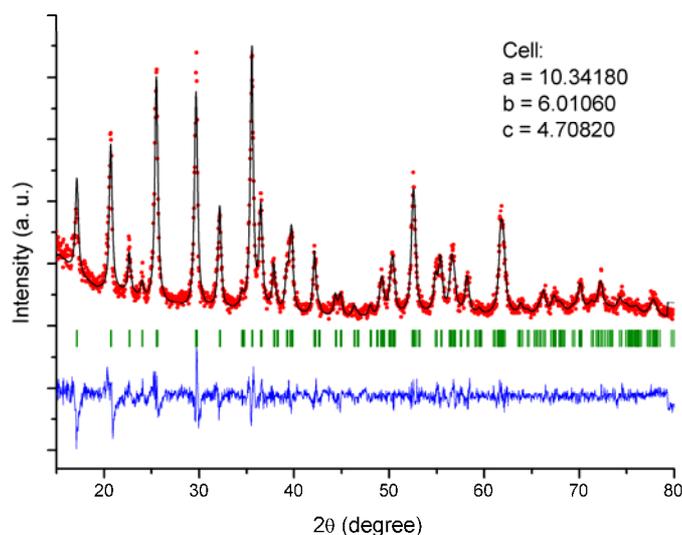

Fig. 1 XRD data matching using Fullprof software and Pseudo-Voigt profiles.

The SEM images shown in Fig. 2 reveal the 3D highly uniform mesocrystal-like morphology of LFP/N-containing carbon composites, easily achievable by solvothermal synthesis. The lower magnification image (Fig. 2b) shows single spherical urchin-like mesocrystal (d~20μm) formed from rods as primary mesocrystal units. As seen from the Fig. 2c, the rods are centrally aligned in earth-magnet-like manner.

Higher magnification SEM micrograph (Fig. 2d) shows that the length of the primary rods is not uniform (range between 400nm-1µm in length and about 200nm in width).
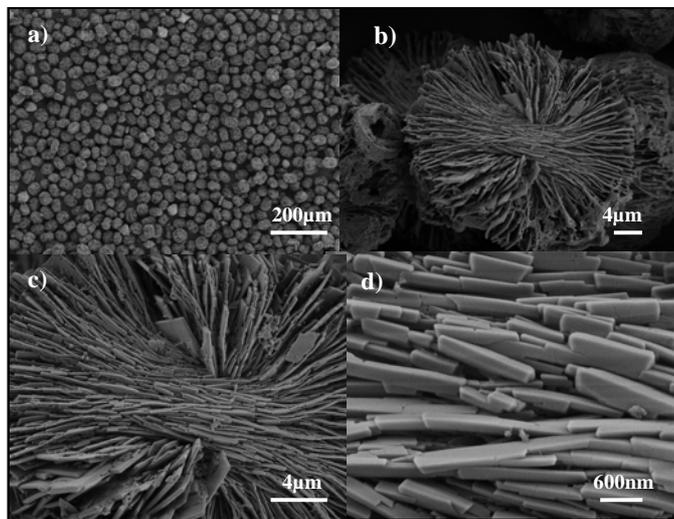

Fig. 2 SEM images of the LFP/N-containing C mesocrystals at four different magnifications.

Fig. 3a shows TEM image of one primary rod. The HR-TEM in Fig. 3b shows the edge of the previously shown primary rod forming the urchin-like mesocrystal. Here, we can clearly see the lattice fringes with *d* spacing of 2.5Å indicating single crystallinity of the rods corresponding to (020) planes of orthorhombic $LiFePO_4$ phase. In addition, in Fig. 3b it can be also seen that an amorphous N-containing carbon layer with a thickness of 2-3 nm covered the surface of the crystal.
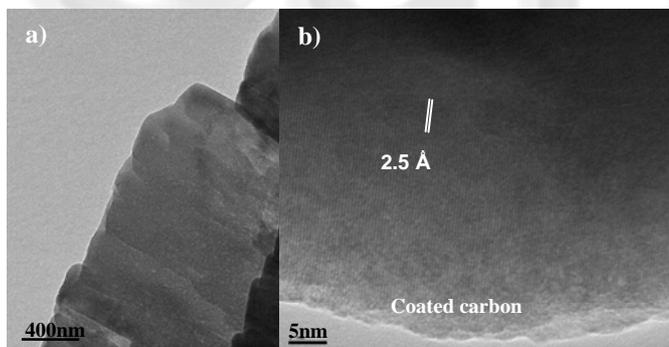

Fig. 3 HR-TEM images of an individual primary LFP/N-containing C rod.

Elemental analysis revealed that the final composite material contains 12 wt % of such amorphous carbon coating and 1.5 wt % of nitrogen doped within the carbon. N-doping in carbon materials is known to dramatically increase the conductivity due to its electron excess [6].

We are currently studying the electrochemical performance of the presented materials when used as cathodes in Li-ion battery system. Preliminary conductivity measurements confirm that indeed the materials coated with N-doped carbon exhibit a substantial increase in their electronic conductivity.

Conclusions

Urchin-like mesocrystals of LFP coated with a thin N-containing carbon layer were prepared via a simple in-situ solvothermal route. The obtained materials showed a hierarchical assembly, crystallinity and high purity.

References
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