Supporting Information

A Hollow Sphere Secondary Structure of LiFePO₄ Nanoparticles

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Experimental

Preparation. Hollow-sphere-secondary-structured LiFePO₄ was prepared by precipitating Li₃PO₄ and Fe₃(PO₄)₂ sequentially with CTAB (cetyltrimethylammonium bromide) and heating the mixture at 120 °C for 5 hours hydrothermally and then at 700 °C for 6 hours in an inert atmosphere (Scheme S1). The first intermediate precipitate (Li₃PO₄) was prepared by adding phosphoric acid to an aqueous solution of LiOH. An aqueous mixture of FeSO₄ and CTAB (cetyltrimethylammonium bromide) was added to the first solution containing the Li₃PO₄ precipitate. The measured pH of each solution was indicated in Scheme S1 (pH was not adjusted). The resultant concentration is 1.2 M LiOH, 0.4 M FeSO₄, 0.4M H₃PO₄ and of 0.16 M CTAB.

Cell Test. The 2016R-type coin half cell configuration were used with 1.15M LiPF₆ in 3:7 v/v ethylene carbonate/dimethyl carbonate (EC/DMC) as electrolyte for charge and discharge tests. Lithium foil was used as anode. Cathode was constructed by mixing active materials, polyvinylidene fluoride (PVdF) as a binder and Super P carbon black as a conduction enhancer at a weight ratio of 8:1:1 in a NMP solvent. The mixed slurry was cast onto Al foil by a doctor blade coater (loading density of active material = 3 mg cm⁻²); heated at 130 °C for 20 minutes to evaporate its solvent; and then pressed by using a roll press. Two different LiFePO₄ were used as active materials: the hollow-sphere-secondary-structured LiFePO₄ prepared from the sequential precipitation mentioned above as well as the commercially available one (non-hollow, ~ 200 nm) made by solid state reaction as a
reference for comparison. Carbon content was estimated at ~ 2 wt. % for both LiFePO₄ by elemental analysis based on combustion method.

**Scheme S1** Preparation of olivine phase LiFePO₄ via sequential precipitation in presence of a carbon precursor (CTAB). 1.2 M LiOH, 0.4 M FeSO₄ and 0.4M H₃PO₄ were used in the presence of 0.16 M CTAB (Cetyltrimethylammonium bromide, CH₃(CH₂)₁₅N(Br)(CH₃)₃). The measured (not adjusted) value of pH of each solution was indicated.
Fig. S1 Scanning electron microscopic images of cross-section of hollow LiFePO$_4$. The cross-sectioned samples were prepared by focused ion beam (FIB). The sample was partly melt due to the high energy of FIB during the sample preparation. It was difficult to obtain clear images of one layer hollow sphere that is dominantly populated (a and b) because whole volume of thin shell was melt down. A rare population of secondary particles has a structure of multi-layer hollow sphere (c and d).
Scheme S2 Formation of a hollow sphere secondary structure of Li$_3$PO$_4$ particles. The second precipitate Li$_3$PO$_4$ is formed on the first precipitate Li$_2$HPO$_4$, sacrificing the first one in presence of Li$^+$.  

Fig. S2 Electron microscopic photos of non-hollow Li$_3$PO$_4$ obtained from high pH synthesis adjusted by NH$_4$OH. Only primary particles with ~50 nm dimension are observed without a secondary structure of defined geometry.
Fig. S3 X-ray diffraction (XRD) patterns of the intermediate precipitates (a and b) and the thermally treated ones (c and d) obtained through the each step of the sequential precipitation. The olivine phase LiFePO₄ was obtained after calcination. Also, XRD patterns of the reference (e) and non-hollow control (f) are shown for comparison.
Fig. S4 (a and b) Potential profiles of half coin cells of hollow-sphere-secondary-structured (a) and non-hollow reference (b) LiFePO$_4$. This figure is exactly the same one as Figure 3a and 3b except of abscissa. Energy density is used in these plots instead of capacity (Q). From 10C, the hollow-sphere-secondary-structured LiFePO$_4$ passed the non-hollow reference LiFePO$_4$ ahead in terms of energy density. (c) Ragone plot. Only the mass of active cathode materials was considered for calculation of power and energy densities.