



# Three-dimensional and hierarchically porous bulk battery electrode



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## ARTICLE INFO

### Article history:

Received 9 October 2015

Received in revised form

19 May 2016

Accepted 21 May 2016

Available online 24 May 2016

### Keywords:

Battery

LiFePO<sub>4</sub>

Bulk electrode

Energy density

## ABSTRACT

Current-collector-, binder-free and three-dimensional (3D) bulk electrodes with hierarchically porous architecture have been prepared via using different-sized urea formaldehyde resin (UFR) as templates. The prepared 3D bulk electrodes, consisting of active material, rapid ion and electron transport pathways, have millimetric electrode thickness. Higher volumetric capacity and superior rate capability simultaneously are achieved. This work enlighten a way to obtain high power and energy density electrode.

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## 1. Introduction

Lithium-ion batteries (LIBs), a component of electrical energy storage with largest energy-density, are currently playing a key role in storing multiple clean energy such as wind, solar, nuclear and tide power, and powering the diverse devices from electric vehicles to microchips [1–4]. Since the first report by Pahdi et al. [5], the phospho-olivine LiFePO<sub>4</sub> have been widely investigated and commercially employed owing to its high theoretical/practical specific capacity (170 mAh/g), inherent low cost, environmental friendliness, and intrinsically excellent safety [5–8]. These innate advantages make it much attractive for developing advanced large-scale lithium-ion cells, subsequently integrated to battery pack for powering electric vehicles (EV), hybrid electric vehicles (HEV) and plug-in hybrid electric vehicles (PHEV) [9–12]. However, this material has intrinsically poor ionic and electronic conductivity. Fortunately, hierarchically porous LiFePO<sub>4</sub> materials coated with electro-conductive carbon could effectively overcome the both electronic and ionic transport limitations [13,14].

Conventional strategy that design calendared film electrodes to obtain adequate rate capability is being widely applied. However, insulating polymer binder has to be introduced to hold the active material together with current collector in the film electrodes manufacturing processes. The introduction of insulating binder

would negatively influence the electrical conductivity of prepared film electrode. Consequently, conductive additives with low density have to be introduced for balancing electron conduction in film electrodes for obtaining adequate rate capability. This make the film electrodes generally consisted ~30% by volume and ~10% by weight of inactive materials, which adversely affects volumetric energy density of the electrode. Moreover, Some active materials with particular architecture (e.g., core/shell-type, aggregate-type) are easy to be crushed up in calendared process.

In this work, 3D and hierarchically porous bulk battery electrode consisting of nano-sized LiFePO<sub>4</sub> particles were fabricated by template-sacrifice method. The low-cost UFR synthesized through facile soft chemistry route at room temperature were used as template [15]. Interconnected hierarchical 3D pore network and continuous electro-conductive carbon network formed inside bulk electrode offer highly conductive ion and electron transport pathways, enabling higher volumetric capacity and superior rate capability.

## 2. Experimental

### 2.1. Synthesis of spherical micrometric and submicrometric UFR

For spherical micrometric UFR, 14.0 g of urea was dissolved into 180 mL deionized water. Subsequently, 30.0 g formaldehyde (37 wt %) was added under magnetic stirring to obtain a solution. Then, 240 mL ethanol (99 wt%) and 6 mL formic acid (98 wt%) was added to the above solution and stirred in 30 min. The obtained solution

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was left to stand for 24 h without stirring.

For submicrometric UFR, 14.0 g of urea was dissolved into 600 mL deionized water. 30.0 g formaldehyde (37 wt%) was added under magnetic stirring to obtain a solution. After that, 6 mL commercial disperser (CN-6368 purchased from Weifang Dadong Chemical Co., LTD; solvent: water; solute: nanosized SiO<sub>2</sub> and polymer with specific structure) was added, following by an introduction of 6 mL formic acid as catalyzer (98 wt%) with a stir of 20 min. The obtained suspension was left to stand for 24 h without stirring.

Finally, the white precipitate was washed no less than 8 times with deionized water by suction filtration, and subsequently dried at room temperature.

## 2.2. Preparation of LiFePO<sub>4</sub> powders

Firstly of all, LiOH·H<sub>2</sub>O (6.69 g) was dissolved in 40 mL deionized water in a beaker under magnetic stirring. 4 mL H<sub>3</sub>PO<sub>4</sub> (85 wt%) was added in the beaker to obtain a white suspension. Subsequently, FeSO<sub>4</sub>·7H<sub>2</sub>O (14.6 g) and ascorbic acid (0.23 g) were added into the suspension, and stirred for 5 min. 20 mL of polyethylene-glycol(200) was poured into the beaker. The reagent was quickly placed into a 120 mL-capacity stainless steel autoclave and sealed. The sealed autoclave was heated at 200 °C for 1 h. After the autoclave was cooled down to room temperature, precipitate was filtered and washed no less than 8 times with deionized water, and finally dried at room temperature overnight.

## 2.3. Preparation of the bulk electrode

Due to the low hydrothermal synthesis temperature, The hydrothermally prepared LiFePO<sub>4</sub> have a nice sintering activity. Therefore, 0.5 g of hydrothermally-synthesized LiFePO<sub>4</sub> was homogenously mixed with 0.2 g spherical micrometric UFR and 0.3 g of submicrometric UFR to prepare bulk precursors. The mixture was then pressed into rounded pellets under ~20 MPa. The pellets were placed into a quartz tube furnace and heated under vacuum heat treatment from room temperature to 350 °C, and maintained for 1 h. At that temperature, an atmosphere (98 vol% Ar, 2 vol% H<sub>2</sub>) was flowed into the tube furnace. The pellets were subsequently heated up to 750 °C at a rate of 10 °C/min and keep that temperature for 20 min at a flow rate of 80 sccm in a horizontal tube furnace. For carbon deposition, high-purity C<sub>2</sub>H<sub>2</sub> gas was then introduced at a flow rate of 10 sccm at 750 °C for 30 min. The resultant pellets were cooled down to room temperature. After weighing the pellets, the 1 mm-thick electrodes were directly assembled to Li cells for electrochemical testing.

## 2.4. Characterization of material

Morphological studies of electrodes were conducted by scanning electron microscopy (SEM; Sigma-02-33) equipped with EDXS (Oxford, X-MAX-20). The phase of the electrode materials was characterized by X-ray diffraction (XRD; X'Pert PRO) using Cu K $\alpha$  radiation. Adsorption-desorption isotherms were recorded by using an ASAP 2020 surface area and porosity analyzer (Micromeritics Inc.) with nitrogen as the adsorption gas at 77 K. Mercury porosimetry analysis was conducted on AutoPore IV 9500 mercury porosimeter (Micromeritics Inc.). TG was carried out at a heating rate of 5 °C min<sup>-1</sup> under airflow to determine the quantity of active material.

## 2.5. Electrochemical testing

Electrochemical cells consisting of LiFePO<sub>4</sub>-based bulk cathode,

Li foil counter electrode, two layers of Celgard 2400 separator, liquid electrolyte (1 M LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate solution (1:1:1 v/v)), were constructed and handled in an argon-filled glovebox. After that, the bulk electrodes were assembled to 2430-type coin cell using Li metal as counter electrode in a glove box under high-pure Ar atmosphere, respectively. Electrochemical measurement of assembled half cell was performed on a LAND CT2001A tester (Wuhan Kingnuo Electronic Co.) in the voltage range 2.0–4.2 V at room temperature.

## 3. Results and discussion

Fig. 1 shows a scanning electron microscopy (SEM) image of porous spherical micrometric UFR. The resulting image reveal that the UFR samples consisted of microspheres with diameter ranging from 1 to 15  $\mu$ m, as determined by diameter distribution histograms (see Fig. 2). Most particles were single spheres and agglomerations were invisible. These monodisperse micrometric microspheres could provide a structurally robust scaffold into which the hydrothermally synthesized LiFePO<sub>4</sub> particles could extrude.

To further create more pores from 50 nm to 1  $\mu$ m for easing electrolyte transport and touch with surface of active materials, we fabricated submicrometric UFR. The SEM image in Fig. 3 indicates that the as-synthesized UFR are shapeless but with well-defined edges.

Fig. 4 shows the XRD patterns of obtained bulk electrode. As the result shown, the main phase of the sample can be identified as LiFePO<sub>4</sub> with an ordered olivine structure indexed to orthorhombic *Pnma* (JCPDScardnumber:83-2092). No impurities are detected in the XRD patterns.

Fig. 5 show SEM image of cross-sectional bulk electrode with different magnification. It is shown that the introduction of UFR with wider diameter distribution make the as-prepared bulk electrode have hierarchically, well-ordered and interconnected pore structure. Macropores created by monodisperse micrometric microspheres could act as reservoirs, which can rapidly provide electrolyte. At same time, submicrometric UFR created open pore structure having capillarity into the scaffold. It thereby makes bulk electrodes having an interconnected electrolyte-filled pore network that enables rapid Li-ion transport. The hierarchically macroporous bulk electrode with different sized pore structure could be obtained through controlling the amount and ratio of two

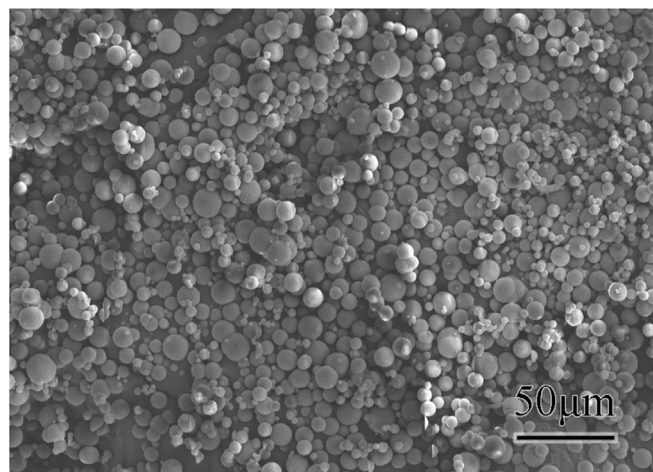


Fig. 1. SEM images of micrometric spherical UFR.

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