Biotemplating of Phosphate Hierarchical Microstructures: Rechargeable $LiFePO_4$/C Spirulina

Yang Xia[1], Wenkui Zhang[1]*, Hui Huang[1], Yongping Gan[1], Zhen Xiao[2], Lingchao Qian[1] and Xinyong Tao[1]*

[1]*College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou, 310014, P. R. China.*
[2]*Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P.R. China.*

Experimental Section

The $LiFePO_4$ samples were synthesized as follows: 6 mmol of $LiOH{\cdot}H_2O$ and 2 mmol of $FeSO_4{\cdot}7H_2O$ were dissolved in 20 mL H_3PO_4 solution (0.1 M) and 20 mL D-glucose solution (0.1 M), respectively. After that, the $LiOH/H_3PO_4$ suspension was added into the $FeSO_4$/D-glucose solution with slightly stirring. Since the basic pH condition could be preferable to maintain the original shape of spirulina, the pH value of the precursor suspension was adjusted to 8 by adding ammonia solution. Subsequently, 5 mL of spirulina solution was dropped into the precursor suspension under magnetic stirring. As the spirulinas dispersed, the resulting precursor suspension was transferred into a 50 mL Teflon-lined autoclave. The autoclave was sealed in a stainless steel tank and heated at 180 ^oC for 20 h. After being cooled to room temperature, the reactor was centrifuged, washed with de-ionized water, and dried at 80 ^oC. Finally, in order to remove the adsorbed water, the samples was heated at 650 ^oC for 4 h under a mixed flowing atmosphere (200 mL/min, 10 vol.% H_2 and 90 vol.% N_2).

Powder X-ray diffraction (XRD) was carried out with an X' Pert Pro diffractometer using Cu Kα radiation (λ = 0.15418 nm) in the 2θ range from 10 - 80^o. The morphology of the product was

* Corresponding author. E-mail: msechem@zjut.edu.cn; tao@zjut.edu.cn

characterized by optical microscope (Olympus SZX16), scanning electron microscope (SEM, Hitachi S-4800, S-4700) equipped with an energy dispersive X-ray spectroscopy (EDS) system, transmission electron microscope (TEM, FEI Tecnai G2 F30) and high resolution TEM (HRTEM). The thermal analysis was determined by SDT Q600 (TA Instruments, U.S.A) in oxygen at a heating rate of 10 ^{o}C min^{-1} from room temperature to 700 ^{o}C. The Raman spectrum was obtained from DXR SmartRaman Spectrometer (Themo Fisher, U.S.A). Nitrogen adsorption-desorption isotherms for surface area and pore analysis were measured with an ASAP 2010 (Micromeritics Instruments). The analysis of element content was measured by X-ray fluorescence spectrometry (XRF, ARL ADVANT' X IntelliPowerTM 4200, Themo Fisher, U.S.A).

The performance of the $LiFePO_4$ as positive electrode was evaluated using a coin-type cell (size 2025), which was assembled in an argon-filled glove box. A composite electrode was prepared by mixing the $LiFePO_4$, acetylene black and polyvinylidene fluoride binder in the weight ratio of 80:10:10. The blended slurries were pasted onto an aluminum current collector, dried at 120 ^{o}C for 12 h in vacuum. Lithium metal was used as the anode and a 1 M solution of $LiPF_6$ in ethylene carbonate and dimethyl carbonate (1:1, by volume) was used as the electrolyte with a Celgard membrane as the separator.

The charge-discharge tests were performed on a Neware battery test system in the voltage range of 2.5 - 4.2 V at room temperature. A CHI 650b work-station was applied for cyclic Voltammograms (CV) and electrochemical impedance spectroscopy (EIS) tests. CV tests were carried out in the voltage range of 2.5 - 4.2 V at a scan rate of 0.1 mVs^{-1}, and EIS tests were carried out in the frequency range of 0.1 - 10^6 Hz.

Pore-size distribution analysis

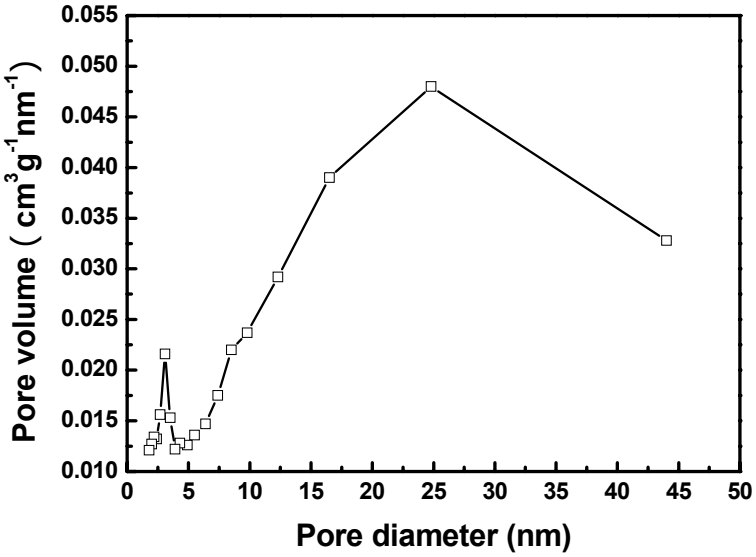

Fig. S1 The pore-size distribution of the spirulina templated $LiFePO_4$/C sample.

Thermal analysis

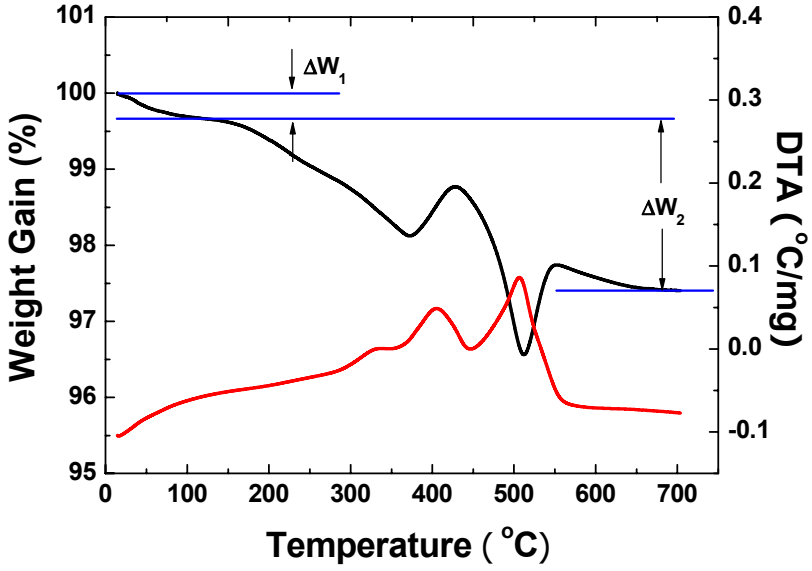

Fig. S2 TG/DTA curves of the spirulina-templated $LiFePO_4$/C sample.

XRF analysis

Table S1 XRF analysis of $LiFePO_4$/C samples

Elements	Commercial materials #1		Commercial materials #2		This work	
	Weight %	**StdErr**	**Weight %**	**StdErr**	**Weight %**	**StdErr**
Fe	36.00	0.17	36.30	0.17	36.54	0.17
P	19.12	0.11	19.58	0.11	19.39	0.11
Mg	0.678	0.032	0.272	0.014	0.562	0.028
K	0.005	0.0006	0.005	0.0006	0.007	0.0007
Ca	0.0113	0.0006	0.0355	0.0018	0.0522	0.0026
Fe/P molar ratio	0.650 (Fe) / 0.632 (P) = 1.028		0.644 (Fe) / 0.617 (P) = 1.044		0.654 (Fe) / 0.626 (P) = 1.045	

Note: Here, we only have chose the main Elements of $LiFePO_4$ products and listed in the table.