Supplementary Information

Fabricating three-dimensional mesoporous carbon network-coated LiFePO4/Fe nanospheres using thermal conversion of alginate-biomass

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References

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S1. Synthesis of 3DMCN-LFP/Fe-NSs

The selection of main reagents include Fe(NO$_3$)$_3$•9H$_2$O (98.5%, Tianjin Kermel Chemical Reagent Co., Ltd.), Sodium alginate (SA, Tianjin Kermel Chemical Reagent Co., Ltd.), (NH$_4$)$_2$HPO$_4$ (99%, Tianjin Bodi Chemical Co. Ltd.), CH$_3$COONa•3H$_2$O (NaAc, 99%, Tianjin Bodi Chemical Co. Ltd.), glucosum anhydricum(99.8%, Tianjin Damao Chemical Co., Ltd.), and LiOH•H$_2$O (90%, Tianjin Damao Chemical Co., Ltd.). Distilled water and absolute ethyl alcohol major uses are as a solvent.

The 3DMCN-LFP/Fe-NSs composite was prepared via a green route with alginate as biotemplate (Figure S1). For synthesis specific described below. Firstly, 1 g SA powder soluble in 50 ml distilled water, and stirring for 36 h to make it fully swelling, and thus the alginate biotemplate hydrosol were obtained. Then the 2% (w/v)
ALG-hydrosol was stored in 90 °C water for 60 min to reduce viscosity and improve the activity of polymer chain. Subsequently, 0.01 mol Fe(NO₃)₃•9H₂O was dissolved in 20 ml deionized water at 90 °C and added, dropwise, to the ALG-hydrosol with vigorous stirring at 90 °C, immediately formed a yellow hydrogel while stirring for 60 min. Then, 0.01 mol (NH₄)₂HPO₄ and 0.01 mol NaAc aqueous solution were slowly added to the ALG-Fe hydrogel with stirring to form a beige precipitation in the system at room temperature with pH balance of 4. After stirring for 12h, the resultant mixed sediments was centrifuged two times by washing with distilled water to remove the impurity ions. In order to protect the porous structure of carbon aerogel, replacement of water by ethanol, and the deposit was dried in oven at 60 °C. Finally, the dry FePO₄/ALG mixtures were mixed with LiOH•H₂O and glucosum anhydricum in a molar ratio of 6:1. To provide a better reduction atmosphere, more than the theoretical value (equation S1 and S2) for the amount of carbon. The precursor powder were annealed at 300 °C for 3h, and then calcination treatment at 700 °C in flowing nitrogen for 8h. For comparison, the samples were denoted as 3DMCN-LFP/Fe-NSs (with alginate biotemplate incubated at 90 °C), LFP/Fe (with alginate biotemplate incubated at ambient temperature), LFP/C (common carbon-coated under the same conditions). LFP sample come from Peking University leading science and technology industry co., LTD

\[
C₆H₁₂O₆ \rightarrow 6H₂O + 6C \quad \text{(S1)}
\]

\[
2FePO₄ + 2LiOH + C \rightarrow 2LiFePO₄ + CO₂ + H₂O \quad \text{(S2)}
\]
S2. Structure characterizations and analyses

Figure S2 FT-IR spectrum studies. (a) FTIR spectra of the different samples. (b) The fingerprint infrared spectra of the different samples.

To analyze the functional groups of biocarbon, the FT-IR spectrum of pure ALG is shown in Figure S2aA. The broad band at 3500 cm$^{-1}$ is ascribed to the O-Hstretching vibration of water and another characteristic absorption band of O-H, at 3150 cm$^{-1}$, is considered to be a functional group connection on the residual carbon. The dominant bands near 1696 and 1460 and 1400 cm$^{-1}$ are respectively derived from the O-H and CH$_2$ and CH$_3$ asymmetry stretching vibration of biocarbon. The broad band from 500 to 700 cm$^{-1}$ is inferred that it was caused by the unsaturated bond.$^1$
The infrared active of LiFePO$_4$ is mainly caused by PO$_4^{3-}$ group. In Figure S2aB, we know the infrared spectral bands of LiFePO$_4$ are mainly distributed over two wavenumber ranges from 400 to 650 cm$^{-1}$ and 850 to 1225 cm$^{-1}$. The dominant bands from 850 to 1225 cm$^{-1}$ belong to the stronger absorbing frequency bands of PO$_4^{3-}$, including PO$_2$ stretching vibration, P-O stretching vibration ($\nu_3$ and $\nu_1$). The bands observed at 400 to 650 cm$^{-1}$, correspond to PO$_2$ bending vibration and Fe-O symmetrical stretching vibrations.

Obviously, the FT-IR spectrum of 3DMCN-LFP/Fe-NSs is like the vibration superposition of pure ALG and pure LiFePO$_4$. The change of the peaks indicate that OH$^-$, -COO$^-$ and -CH$_2$ groups in the ALG biomolecules play the important role in the chemical interaction between the ALG and the iron and lithium ions. By comparing the FT-IR spectrum of 3DMCN-LFP/Fe-NSs and pure LFP sample from Figure S2b, for the 3DMCN-LFP/Fe-NSs sample all the PO$_4^{3-}$ bands shows the blue shift and the vibration transmittance weakened from those of pure LFP sample. These changes indicate that there are in situ nanocomposit linkages between the LiFePO$_4$ nanoparticles and the mesoporous biocarbon coating network.
The TG curve of 3DMCN-LFP/Fe-NSs (Figure S3a) has a weight swings stage in the temperature range of 350–530 °C, which is mainly attributed to carbon thermal decomposition and Fe$^{2+}$ oxidation. And then in the temperature range of 530–600 °C, the 3DMCN-LFP/Fe-NSs sample gains weight due to the oxidation courses of Fe metal and residual Fe$^{2+}$.

Calculation of carbon and Fe metal content by TG analysis (Figure S3a): The LFP blank sample was sintered under flowing oxygen to completely oxidize the Fe$^{2+}$ ions in a temperature range from 45 to 800 °C. About 2.5% weight gain was observed during the temperature sweep from 350 to 550 °C in the TG curve of LFP sample. Relatively, for the 3DMCN-LFP/Fe-NSs sample, the weight loss was 9.8%, and about
2% weight loss of absorbed water. In the TG curve of the Fe metal sample (Figure S3b), illustrate the oxidation course of Fe metal higher than 530 °C in air. This result corresponds to the weight increase stage of the 3DMCN-LFP/Fe-NSs sample in Figure S3a. The carbon content in the 3DMCN-LFP/Fe-NSs composite was roughly calculated to be 12.5% (equation S3). The Fe metal content in the 3DMCN-LFP/Fe-NSs composite was roughly calculated to be 1.23% (equation S4).

\[
C_{WT} = \frac{9.8\% + 2.5\%}{1 - 2\%} = 12.5\% \quad \text{(S3)}
\]

\[
Fe_{WT} = \frac{1.4\% - 0.2\%}{1 - 2\%} = 1.23\% \quad \text{(S4)}
\]
Figure S4 (a) Raman spectrum of 3DMCN-LFP/Fe-NSs. (b) The red curve shows multiple Lorentzian fits, and the blue curves show the individual Lorentzian components at ~1318, 1561 cm\(^{-1}\) with a full-width at half maximum value. (c) The inset is the corresponding nitrogen adsorption-desorption isotherm loop for different samples. (d) Pore size distribution for different samples.

Since the distribution and structure of 3DMCN in the sample has strong influence on the electrochemical properties of LiFePO\(_4\),\(^7\) Raman spectroscopy and pore analysis were applied. Raman experiments can detect the molecular structure in the surface region.\(^8\) The Raman spectrum of 3DMCN-LFP/Fe-NSs sample in Figure S4a presented two prominent broad bands of carbon around 1320 (D-band) and 1590 cm\(^{-1}\) (G-band), suggesting that the biocarbon has been coated on the surface. Usually, the peak area and intensities of D and G bands affected by growth and size of
different carbon phases. The peak intensity ratio between D and G bands ($I_D/I_G$) has become one of the important signals to estimate the degree of graphitization. The D-band is attributed to the presence of defects, i.e. the ratio is proportional to the content of disordered carbon. The $I_D/I_G$ ratio is 1.31, indicating that the coated carbon might be amorphous phase. The result is consistent with the XRD and HRTEM test, less carbon micro-crystal may have a very dispersed state and small size. Disordered carbon possesses vast defects and weak the anisotropy of the surface properties can provide additional active sites for lithium-ion storage and electron conduction, can also relax strain stress for volume change in the charge/discharge and crystal growth process. To differentiate the overlapping peak, the spectrum was simply fitted using two Lorentzian peaks at 1318, 1561 cm$^{-1}$ (Figure S4b) with a full-width at half maximum (FWHM) of 96,96 cm$^{-1}$ respectively, and the peak area ratio ($A_D/A_G$) is 1.46. The calculation results are further confirmed with the previous testing results.

Natural biomass tend to form porous structure. To further validate the porous nature of the samples, evaluation of the porosity and specific surface area by the static volumetric method. According to International Union of pure and Applied chemistry (IUPAC) classification, Figure S4c exhibits type-IV $N_2$-adsorption isotherms of 3DMCN-LFP/Fe-NSs sample with $H_3$-type hysteresis in $P/P_0$ of 0.4−0.99, that indicates mesoporous characteristics with nonuniform and open wormlike pores. The BJH pore-size-distribution in Figure S4d shows that the 3DMCN-LFP/Fe-NSs sample has a hierarchical pore structure, which centers at 3-101 nm. The BET surface area and BJH desorption average pore width of the synthesized samples are summarized in Table S1gh, the large specific surface area mainly caused by the 3DMCN structure and sphere-like morphology (Figure 1j and Figure 3a). Such an 3DMCN structure can significantly increase the permeability of the electrolyte and
thus facilitate lithium-ion diffusion.

<table>
<thead>
<tr>
<th>samples</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>V [Å³]</th>
<th>C [wt%]</th>
<th>Df [g cm⁻³]</th>
<th>S BET [m² g⁻¹]</th>
<th>Dpore [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP</td>
<td>10.332</td>
<td>6.01</td>
<td>4.692</td>
<td>291.35</td>
<td>1.8</td>
<td>0.905</td>
<td>12.60</td>
<td>8.95</td>
</tr>
<tr>
<td>LFP/C</td>
<td>10.328</td>
<td>6.008</td>
<td>4.691</td>
<td>291.10</td>
<td>5.6</td>
<td>1.024</td>
<td>11.93</td>
<td>11.94</td>
</tr>
<tr>
<td>3DMCN-LFP/Fe-NSs</td>
<td>10.331</td>
<td>6.003</td>
<td>4.695</td>
<td>291.17</td>
<td>13.7</td>
<td>1.005</td>
<td>73.32</td>
<td>10.70</td>
</tr>
<tr>
<td>LFP/Fe</td>
<td>10.322</td>
<td>6.002</td>
<td>4.694</td>
<td>290.83</td>
<td>11.0</td>
<td>1.008</td>
<td>50.11</td>
<td>11.72</td>
</tr>
</tbody>
</table>

[a] a, [b] b, [c] c, [d] V: lattice volume of LiFePO₄ in the samples calculated by using Jade 6 XRD pattern-processing software. [e] C: carbon content determined of different samples. [f] Df: tap density calculated by a FT-100B Powder Tap Density Meter (About vibration 3000 times). The Brunauer-Emmett-Teller (BET) surface area [g] and BJH desorption average pore width [h] of different samples.
S3. Electrochemical properties

Figure S5 (a) First charge-discharge curves of 3DMCN-LFP/Fe-NSs cathode in different water-bath temperature (30, 50, 70, 90, 100 °C) and (b) time (30, 60, 120 min).
Figure S6 (a) A typical Nyquist plots of 3DMCN-LFP/Fe-NSs. (b) Lithium-ion diffusion and Charge-transfer process between the cathode particle.

Figure S6a shows the typical Nyquist plots of 3DMCN-LFP/Fe-NSs. The Z’ value of the starting point in high frequency is mainly caused by the physical resistances of the electrolyte and electrode, which corresponds to the ohmic series resistance (R_e). The intercept of the semicircle at high frequency region on the Z’ axis corresponds to the charge-transfer impedance (R_{ct}) caused by lithium-ion charge transfer between the interface of electrode and electrolyte. The slope of inclined line in low frequency represents the Warburg impedance (Z_W), which is directly related to the lithium-ion diffusion process in LiFePO_4 cathode (Figure S6b). The calculation of Lithium-ion diffusion coefficient (D_{Li}, cm^2 s^{-1}) references the equation from X. Y. Du et al.:}

\[ D = 2^{-1} R^2 T^2 A^2 n^4 F^4 C^2 \sigma^{-2} \]  
\[ Z' = R_e + R_{ct} + \sigma \omega^{-1/2} \]  

Where R, T, A, n, F, C, σ, and ω correspond to the gas constant, the absolute temperature, the surface area of the cathode (1.76 cm^2), the Faraday constant, the
concentration of lithium-ion, the Warburg factor, and angle frequency, respectively.

References

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