Supporting Information

Multiple covalent interactions and open-void co-involved

\( \text{Mn}_3\text{O}_4/\text{nitrogen-doped porous carbon fiber hybrids as flexible anodes for lithium-ion batteries} \)

Zhen Li*  
College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai 201620, PR China  
*Corresponding author: lizhendiyi@163.com

1. Fabrication of LiMn\(_2\)O\(_4\) cathode

Nanophase LiMn\(_2\)O\(_4\) was prepared by a two-step method. Firstly, 100 ml of ethanol solutions containing manganese acetate (Mn(Ac)\(_2\)·4H\(_2\)O, 20 mmol) and lithium acetate (LiAc·2H\(_2\)O, 11 mmol) were evaporated under magnetic stirring at 90 °C to obtain a gray powder mixture. The resultant powders were further calcined at 750 °C in air for 6 h.

The LiMn\(_2\)O\(_4\) cathodes were prepared by compressing a mixture of the LiMn\(_2\)O\(_4\) powder, conductive material (Super P), and binder (polyvinylidene fluoride, PVDF) in weight ratios of 8:1:1 onto a round Al foil (1.1 cm\(^2\)). The density of the active material is about 2.7 mg cm\(^{-2}\).
2. Supporting dates

Fig. S1 XRD pattern of the as-prepared ZIF-8.

Fig. S2 Digital photographs of CFs mats before and after bending.
Fig. S3 (a) XPS survey spectra of NPCFs-0; (b) High-resolution XPS spectra of deconvoluted Mn 2p peak for the Mn$_3$O$_7$/NPCFs-1.4 product.

Fig. S4 Nitrogen adsorption–desorption isotherms of the as-synthesized products (a-c) and their corresponding pore size distribution curves (d-f) calculated from the adsorption branch by the BJH model.
Fig. S5 SEM images of NPCFs-0 (a and b) and Mn₃O₄ compounds (c and d) at different magnifications.

Fig. S6 FE-SEM images of CFs at different magnifications.
Fig. S7 Cycling test of CFs at a current density of 100 mA g\textsuperscript{-1}.

Fig. S8 (a and b) FE-SEM images of the Mn\textsubscript{3}O\textsubscript{4}/NPCFs-1.4 electrode after 100 cycles at different magnifications. (c-f) Elemental mapping images of C, N, O and Mn, respectively.
Table S1 The average discharge capacities during the rate test of Mn$_3$O$_4$, NPCFs-0 and Mn$_3$O$_4$/NPCFs hybrids. The discharge capacities for these three Mn$_3$O$_4$/NPCFs hybrids were calculated based on the weight of the whole composites.

<table>
<thead>
<tr>
<th>Current density (A g$^{-1}$)</th>
<th>0.05</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.5</th>
<th>0.8</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>0.05</th>
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</thead>
<tbody>
<tr>
<td>Mn$_3$O$_4$/NPCFs-2 (mAh g$^{-1}$)</td>
<td>641.3</td>
<td>525.5</td>
<td>390.1</td>
<td>258.9</td>
<td>150.9</td>
<td>51.6</td>
<td>2.9</td>
<td>2.4</td>
<td>2.3</td>
<td>1.9</td>
<td>535.8</td>
</tr>
<tr>
<td>Mn$_3$O$_4$ (mAh g$^{-1}$)</td>
<td>561.0</td>
<td>187.0</td>
<td>40.6</td>
<td>9.6</td>
<td>4.6</td>
<td>3.6</td>
<td>1.5</td>
<td>1.4</td>
<td>1.2</td>
<td>1.1</td>
<td>74.18</td>
</tr>
<tr>
<td>Mn$_3$O$_4$/NPCFs-1.4 (mAh g$^{-1}$)</td>
<td>1058.3</td>
<td>1006.0</td>
<td>892.1</td>
<td>775.6</td>
<td>666.0</td>
<td>586.5</td>
<td>552.9</td>
<td>482.9</td>
<td>408.8</td>
<td>320.7</td>
<td>1008.4</td>
</tr>
<tr>
<td>NPCFs-0 (mAh g$^{-1}$)</td>
<td>592.7</td>
<td>487.6</td>
<td>398.3</td>
<td>335.9</td>
<td>246.2</td>
<td>211.2</td>
<td>185.9</td>
<td>170.7</td>
<td>160.6</td>
<td>152.533</td>
<td>484.7</td>
</tr>
<tr>
<td>Mn$_3$O$_4$/NPCFs-1 (mAh g$^{-1}$)</td>
<td>895.8</td>
<td>793.8</td>
<td>707.4</td>
<td>659.4</td>
<td>585.9</td>
<td>516.9</td>
<td>470.5</td>
<td>418.5</td>
<td>336.2</td>
<td>247.1</td>
<td>878.9</td>
</tr>
</tbody>
</table>

To further understand the electrochemical results and lithiation activity of Mn$_3$O$_4$, the normalized capacity of Mn$_3$O$_4$ in Mn$_3$O$_4$/NPCFs hybrids was calculated according to the following equation:

$$C_{Mi} = \frac{C_{ti} - C_{Ci} \times (1 - W_M)}{W_M}$$

Where $C_{Mi}$ (mAh g$^{-1}$) is the normalized capacity of Mn$_3$O$_4$ in Mn$_3$O$_4$/NPCFs hybrids at a current density of “i”; $C_{ti}$ (mAh g$^{-1}$) is the average discharge capacity of the Mn$_3$O$_4$/NPCFs hybrids at a current density of “i”, which is calculated based on the total weight of the whole composites; $C_{Ci}$ (mAh g$^{-1}$) is the average discharge capacity of NPCFs-0 at a current density of “i”; $W_M$ (wt%) is the mass loading of Mn$_3$O$_4$ in Mn$_3$O$_4$/NPCFs hybrids, which is analyzed by TGA.

Taking Mn$_3$O$_4$/NPCFs-1.4 as an example, the $C_{ti}$ and $C_{Ci}$ at 50 mA g$^{-1}$ is calculated to be 1058 and 593 mAh g$^{-1}$, respectively. The $W_M$ of Mn$_3$O$_4$/NPCFs-1.4 is 63.1 wt%. Therefore, the $C_M$ at 50 mA g$^{-1}$ is estimated to be 1330 mAh g$^{-1}$.

It should be mentioned that when the current density increased to 800 mA g$^{-1}$ and higher, the discharge capacity of Mn$_3$O$_4$/NPCFs-2 is much smaller than that of NPCFs-0 (as shown in Table S1). Such an obvious capacity loss can be mainly attributed to the poor conductivity of Mn$_3$O$_4$ and the disappearance of open voids in Mn$_3$O$_4$/NPCFs-2 composites. The normalized capacities of Mn$_3$O$_4$ in Mn$_3$O$_4$/NPCFs-2 at 800 mA g$^{-1}$ and higher current densities were denoted as 0 mAh g$^{-1}$. 
Fig. S9 (a) XRD pattern of the as-prepared LiMn$_2$O$_4$; (b) Charge/discharge profiles of LiMn$_2$O$_4$ cathode within a voltage range of 3.3-4.4 V; (c) Cycling performance of LiMn$_2$O$_4$ electrode at a current density of 100 mA g$^{-1}$; (d) FE-SEM imagine of LiMn$_2$O$_4$ nanoparticles.