Supporting Information

Improved Electrochemical Performance and Capacity Fading Mechanism of Nano-sized LiMn$_{0.9}$Fe$_{0.1}$PO$_4$ Cathode Modified by Polyacene Coating

Liguang Wang$^a$, Pengjian Zuo$^{*a}$, Yulin Ma$^a$, Xinqun Cheng$^a$, Chunyu Du$^a$, Geping Yin$^a$ and Yunzhi Gao$^a$

$^a$School of Chemical Engineering and Technology, Harbin Institute of Technology, No.92 West-Da Zhi Street, Harbin 150001, China

*Corresponding Author: E-mail: zuopj@hit.edu.cn, zuopjhit@gmail.com (P. Zuo)

Tel./fax: +86-451-86403216
Figure S1. Nitrogen sorption isotherm with pore size distribution (inset) and LiMn$_{1-x}$Fe$_x$PO$_4$-PAS.

The porous structure and the BET surface area of LiMn$_{1-x}$Fe$_x$PO$_4$-PAS ($x = 0$ and 0.1) composite were investigated by N$_2$ adsorption-desorption experiments at 77K (Figure S1). The BET surface area measured is 65.6 and 71.5 m$^2$·g$^{-1}$ for LiMnPO$_4$-PAS and LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS, respectively. The average pore diameter is 3.49 and 3.59 nm for LiMnPO$_4$-PAS and LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS, respectively, which is calculated using the Barrett-Joyner-Halenda (BJH) method. The high surface area and the small average pore will facilitate the diffusion of Li$^+$ in the olivine-type LiMnPO$_4$ class of materials.
Figure S2. TG curves of (a) LiMnPO$_4$-PAS and (b) LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS.

Figure S3. LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS samples recorded with a heating rate of 10°C·min$^{-1}$ in an oxygen atmosphere with different amount of PAS: (a) 3 wt%, (b) 11 wt%, (c) 15 wt% and (d) 20 wt%.

The PAS contents in LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS powders were estimated by thermogravimetric (TG) measurement of the PAS coated LiMn$_{0.9}$Fe$_{0.1}$PO$_4$ products in oxygen atmosphere (Figure S3). The weight loss below 200°C is due to the evaporation of adsorbed moisture. It can be seen
that the maximum weight loss of the samples locates at 300-500°C, which is contributed to the PAS of the composite. By neglecting the tiny deviation, the PAS contents of LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS powders were estimated 3 wt%, 5.6 wt%, 11 wt%, 15 wt% and 20 wt%, respectively.

Figure S4. SEM images of LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS powders with different amount of PAS: (a) 3 wt%, (b) 11 wt%, (c) 15 wt% and (d) 20 wt%.

The PAS content of LiMnPO$_4$-PAS and LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS was 5.5 wt% and 5.6 wt%, respectively (Figure S2). From Figure S3 and S4, it can be seen that the increasing PAS content made agglomeration exacerbated, which reduced the conductivity of the materials (Table S1). While the 3wt% PAS in the composite cannot supply the integrated conducting layer on the surface of nanoplates and the conductive network among the particles, resulting in the low conductivity of
the composite. Therefore, the LiMn_{0.9}Fe_{0.1}PO_4-PAS composite with 5.6 wt% PAS exhibited the largest electrical conductivity.

**Table S1.** Conductivity of LiMn_{0.9}Fe_{0.1}PO_4-PAS powders with different amount of PAS.

<table>
<thead>
<tr>
<th>Samples</th>
<th>3 wt% (S·cm(^{-1}))</th>
<th>5.6 wt% (S·cm(^{-1}))</th>
<th>11 wt% (S·cm(^{-1}))</th>
<th>15 wt% (S·cm(^{-1}))</th>
<th>20 wt% (S·cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity</td>
<td>1.2×10^{-2}</td>
<td>1.5×10^{-1}</td>
<td>6.8×10^{-2}</td>
<td>5.4×10^{-2}</td>
<td>3.8×10^{-2}</td>
</tr>
</tbody>
</table>

**Figure S5.** The formation process of PAS. During the process, phenolic resin was dehydrated and dehydrocyclized as temperature increases and the final product was PAS.\(^1\)
**Figure S6.** Initial charge/discharge curves of LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS with different amount of PAS: (a) 3%, (b) 11%, (c) 15% and (d) 20%.

**Figure S7.** Cycling stability of Li/LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS cells with different amounts of PAS at 5 C rate: (a) 3%, (b) 5.6%, (c) 11%, (d) 15% and (e) 20%.
To determine the optimal carbon content of the composites, the LiMn$_{0.9}$Fe$_{0.1}$PO$_4$ cells with various amounts of PAS (3 wt% to 20 wt%) were prepared. Figure S6 shows the initial charge/discharge curves of the samples. The discharge capacities of the LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS manifestly increase with increasing PAS content up to 11 wt%, which is 48 mAh·g$^{-1}$ at 3 wt%, 160.7 mAh·g$^{-1}$ at 5.6 wt% and 157 mAh·g$^{-1}$ at 11 wt% at 0.1 C. For the samples with 15 wt% PAS and 20 wt% PAS, the discharge capacities drop to 146 and 143.5 mAh·g$^{-1}$, respectively. The decreased discharge capacity can be attributed to the growth in the charge-transfer resistance caused by the excessive presence of electrochemically inactive PAS and the agglomeration during pyrolysis (evident in Figure S4).

Figure S7 illustrates cycling stability of Li/LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS cells with different amounts of PAS at 5 C rate discharge. The highest specific capacity at the 5 C rate is obtained from the LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS composite with 5.6 wt % of PAS. After 50 cycles, this composite retains 111 mAh·g$^{-1}$, corresponding to 96.5% of its first discharge capacity, which is much higher than others. The electrochemical cycling data in Figure S6 are consistent with the microstructure and EIS results (Figure S8). From the Figure S8, we can see that the LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS composite with 5.6 wt % PAS has the smallest $R_{ct}$ and the largest $D$, which is agree well with the electrochemical performance. The strong adhesion conducting PAS layer on the surface of LiMn$_{0.9}$Fe$_{0.1}$PO$_4$ nanoplates and the well-distributed conducting wrinkled PAS nanoplates surrounding the LiMn$_{0.9}$Fe$_{0.1}$PO$_4$ particles form a network of electrically conducting paths for electrons. Meanwhile, the smaller LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS particles shorten the diffusion length for the Li$^+$ ions. Therefore, the electrode with 5.6 wt% PAS is expected to deliver the best electrochemical performance.
**Figure S8.** Nyquist plots of Li/ LiMn$_{0.9}$Fe$_{0.1}$PO$_4$-PAS cells with different amounts of PAS (a); the relationship plot of $Z'$ vs. $\omega^{-1/2}$ at low-frequency region (b).

**Table S2** The diffusion coefficient of the LMFP-PAS with different amounts of PAS.

<table>
<thead>
<tr>
<th>Samples</th>
<th>3 wt%</th>
<th>5.6 wt%</th>
<th>11 wt%</th>
<th>15 wt%</th>
<th>20 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(cm$^2$/s)</td>
<td>$6.34\times10^{-15}$</td>
<td>$2.34\times10^{-14}$</td>
<td>$1.67\times10^{-14}$</td>
<td>$1.50\times10^{-14}$</td>
<td>$6.34\times10^{-15}$</td>
</tr>
</tbody>
</table>

**REFERENCES**