Supporting Information for

Accurate surface control of core-shell structured LiMn_{0.5}Fe_{0.5}PO_{4}@C for improved battery performance

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**Experimental Section**

**Chemicals**

Resorcinol was purchased from Beijing Yili Fine Chemicals Co., Ltd. Formaldehyde solution (37%) was purchased from Beijing Modern Oriental Fine Chemistry Co., Ltd. Ammonia solution (25%) was purchased from Beijing Chemical Works. Metal salts MnSO_{4}·H_{2}O and FeSO_{4}·7H_{2}O were purchased from Xilong chemical Co., Ltd. All chemicals were used as received without further purification.

**Synthesis of LMFP nanoparticles**

Pristine LiFe_{0.5}Mn_{0.5}PO_{4} nanoparticles were synthesized by the modified solvothermal method. \cite{10,32} H_{3}PO_{4} (10 ml, 3M) was mixed with tetraethylene glycol (TEG) (150 ml) in a
500 ml beaker. Then LiOH (2 M) aqueous solution was slowly added into the above mixture to adjust the pH to 8.6 under vigorous stirring, and a milk white suspension was formed through the neutralization reaction. Subsequently, 20ml aqueous solution containing MnSO$_4$ (15 mmol) and FeSO$_4$ (15mmol) was introduced into the mixture under stirring, resulting in a grey-green suspension. After stirring for about 20 min under room temperature, the mixture was transferred into an autoclave which was sealed and heated to 250 °C, and maintained at the same temperature for 12 h. Afterwards, the autoclave was cooled down to room temperature. The grey-green product was collected via centrifugation and washed with H$_2$O for two times and then ethanol once. The final product was dried at 80 °C for 6 h. The collected precipitates was characterized by inductively coupled plasma (ICP) analysis for chemical composition, from which the chemical composition is determined to be LiMn$_{0.5}$Fe$_{0.5}$PO$_4$. The collected powder was then used as the pristine LMFP sample with a very low carbon content of 0.13 %.

**Synthesis of thickness-controlled LMFP@C composites**

The thickness of the carbon coating layer on LFMP nanoparticles can be controlled by varying the initial concentrations of the starting materials LFMP and resorcinol monomer. In a typical synthesis procedure, a suspension of LMFP was prepared by dispersing LMFP nanoparticles (183.65 mM) in a mixed solvent of H$_2$O and ethanol (H$_2$O:EtOH=2:1, v/v) with the help of ultrasonication, followed by the addition of resorcinol monomer reach the concentration of 6.055 mM. Subsequently, a small amount of ammonia (NH$_3$·H$_2$O, 25% wt%) was added into the mixture to adjust the pH value in the range of 9-10. Finally, a certain amount of formaldehyde solution (37% wt% in H$_2$O) was added to make sure the mole ratio between resorcinol and formaldehyde fixed at 1:1.4. The mixture was stirred continuously for about 20 h under room temperature, and the color of the mixture gradually turned from grey-green to deep brown during the stirring period. The brown precipitates (denoted as LMFP@RF) were collected by centrifugation, washed three times with deionized water and once with alcohol, and then dried at 80 °C in an electric oven for 5 h. The resulting sample was heated in a quartz tube to 400 °C at a rate of 3 °C/min in Ar/H$_2$ (95/5 in volume%) atmosphere and kept at this temperature for 2 h, and then further heated to 700 °C with a
heating rate of 5 ºC/min, and kept at this temperature for 15 h. The obtained composite was denoted as LMFP@C1. The carbon content was determined to be 1.81 wt%.

LMFP@C2, LMFP@C3 and LMFP@C4 were obtained by changing the initial concentrations of the reactant as follows: 113.02 mM LMFP and 6.05 mM resorcinol for LMFP@C2, 70.63 mM LMFP and 10.09 mM resorcinol for LMFP@C3, and 84.76 mM LMFP and 40.36 mM resorcinol for LMFP@C4. The rest of the reaction conditions were the same as for sample LMFP@C1. The carbon contents for LMFP@C2, LMFP@C3 and LMFP@C4 are 2.52, 5.15 and 13.50 wt% respectively.

LMFP@C samples with the coating thickness of 2, 5, 8 and 10 nm were prepared by slightly changing the initial concentrations of reactants according to those used for LMFP@C1-C3 respectively. For LMFP@C sample with 2 nm nanoshell, the only change is that the concentration of LMFP was decreased from 183.65 mM for LMFP@C1 to 169.52 mM while the amount of resorcinol was kept unchanged. For 5 nm carbon-coated sample, it only needed to change the concentration of resorcinol from 10.09 mM for LMFP@C3 to 8.07 mM. For LMFP@C samples with the coating thickness 8 and 10 nm, the concentrations of the resorcinol used for them were increased from 10.09 mM for LMFP@C3 to 15.13 mM and 22.20 mM respectively. The other experiment conditions are exactly the same as those for synthesis of LMFP@C1-C3.

The LMPF@C samples with coating thickness of 2.5, 4, 7 and 12 nm were prepared by controlling the reaction time during the RF polymerization period in the synthesis of LMFP@C4. The reaction time was fixed to 1.5 h, 3 h, 6 h and 12 h respectively, then the produced LFMP@RF samples were subjected to the same graphitization procedure as for LMFP@C4, and the resulting LMFP@C with 2.5, 4, 7 and 12 nm coating layers were obtained.

A control experiment was performed in order to compare the influence of coated-carbon and mixed-carbon on the performance of testing materials. A certain amount of resorcinol monomer and formaldehyde was added to a mixed solvent of H₂O and ethanol (H₂O:EtOH=2:1, v/v) with the pH value adjusted by ammonia to 9-10, and the mixture was
kept stirring for 24 h. The obtained red RF polymeric resin precipitates were collected and rinsed with water by centrifugation, and then dried at 80 °C. Afterwards, 0.03g of the obtained RF precipitates was mixed with 0.5g (70.63 mM) LMFP totally under the same reaction conditions and heat treatments as for LMFP@C1, 2, 3, and 4. This resulting sample was denoted as LMFP-C, and the carbon content is 2.91 wt%.

**Transition metal dissolution**

The metal dissolution measurement was carried out according to a modified method. Typically, 200 mg of the olivine compound was stored in a closed vial containing 2 mL electrolyte solution under Ar atmosphere, and then the mixtures were moisture-contaminated by 100 ppm H$_2$O. The solution was removed after 14 days of storage at 55 °C, and then was put on a heating plate to evaporate the organic electrolyte. A small amount of HNO$_3$ was added to the residue to dissolve the metal ion. Then the mixture was filtrated to remove the insolubles, diluted to a certain volume by distilled water, and finally analyzed by ICP (Model: ICPE-9000, Shimadzu Corporation) for the presence of metal.

**Characterization**

The size and morphology of the LFMP and LFMP@C samples were characterized using a JEOL 6701F scanning electron microscope (SEM) operated at 10 kV. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were carried out with a JEOL-2100F transmission electron microscope. X-ray diffraction (XRD) data were collected with a Shimadzu XRD-7000s diffractometer equipped with a Cu K\(\alpha\) radiation (\(\lambda = 1.54056\ \text{Å}\)) in the range (10~80°). Raman spectra were obtained with an NTegra spectra system (NT-MDT). Fourier-Transfer Infrared (FT-IR) spectra were recorded in the range 4000-400 cm$^{-1}$ with Nicolet iN10 IR microscope (Thermo Fisher Scientifc). Differential scanning calorimetry (DSC) analysis was performed on a Mettler-Toledo DSC1 STAR$^e$ system. The conductivity tests were performed on a Four-Point Probe test equipment (Model: RST-8, Guangzhou 4-Probe tech Co., Ltd.). The chemical composition of the synthesized LiMn$_{0.5}$Fe$_{0.5}$PO$_4$ active materials was determined using inductively coupled
plasma (Model: ICPE-9000, Shimadzu Corporation) analysis and the amount of carbon contents in the final products was determined by an LECO CS-344 carbon/sulfur analyzer.

**Electrochemical evaluation**

Electrochemical measurements were performed using CR2032 coin cells assembled in an argon-filled glove box with lithium metal as the counter and reference electrodes. Charge and discharge measurements for the cells were carried out on a Land CT2001A battery test system. For LMFP@C cathode materials, all cells were cycled in a constant current mode at a 1/10C-rate to 4.5 V, and discharged to 2.5 V at a specific rate (1C=170 mAh/g). The cathodes were prepared by mixing the active materials, super-P (SP), and poly (vinyl difluoride) (PVDF, Aldrich) at a weight ratio of 80:10:10, pasting on a pure Al foil (99.6%, Goodfellow) and cutting into circular electrodes of 0.64 cm² area. Celgard polypropylene membrane was used as a separator. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in wt %) obtained from Guotai-Huarong New Chemical Materials Co., Ltd. Electrochemical impedance spectra (EIS) were performed on an electrochemistry workstation (Princeton PARSTAT 2273).
Figure S1. TEM images of LMFP@C samples with controlled thickness of 2, 5, 8 and 10 nm.

Figure S2. LMFP@C samples with coating thickness of 2.5, 4, 7 and 12 nm, prepared by controlling the reaction time for 1.5 h, 3 h, 6 h and 12 h respectively in the synthesis of LMFP@C4.
Figure S3. SEM images of the hydrothermally synthesized LMFP (a), LMFP@RF (b) and LMFP@C (c).
Figure S4. TEM images of samples before calcination: (a) LMFP@RF1, (b)LMFP@RF2, (c) LMFP@RF3, and (d) LMFP@RF4. The surface RF layers are around 2.4 nm, 4.2 nm, 8.3 nm, and 20 nm in thickness, respectively.

Figure S5. TEM image of LMFP@C3 after battery cycling. No shedding of carbon layer is detectable and the thickness remains around 6 nm for LFMP@C3, indicating the core-shell structured samples are pretty stable during cycling.
Figure S6. Color contrast between the electrolytes removed from pristine LMFP and LMFP@C2 after a period of high-temperature storage. The color of pristine LMFP (labeled as number 1) is much deeper than that of LMFP@C2 (labeled as number 2), indicating that the amount of Fe dissolution is more than that of pristine LMFP.
Table S1 Chemical composition of the synthesized LMFP, LMFP@RF2 and LMFP@C2 determined by inductively coupled plasma (ICP) analysis on Mn and Fe, showing the composition of Mn and Fe is not changed during RF coating process and the high temperature treatment.

<table>
<thead>
<tr>
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<th>Pristine LMFP</th>
<th>LMFP@RF2</th>
<th>LMFP@C2</th>
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<tbody>
<tr>
<td>Fe (ppm)</td>
<td>8.87</td>
<td>6.49</td>
<td>8.68</td>
</tr>
<tr>
<td>Mn (ppm)</td>
<td>8.80</td>
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<tr>
<td>Mn:Fe</td>
<td>1.009:1</td>
<td>1.036:1</td>
<td>1.011:1</td>
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Table S2 Conductivity test of LMFP and LMFP@C2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrical conductivity (S/cm)</th>
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<tbody>
<tr>
<td>Pristine LMFP</td>
<td>N/A</td>
</tr>
<tr>
<td>LMFP@C2</td>
<td>6.54×10⁻²</td>
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