Supporting information for

Highly ordered staging structural interface between LiFePO$_4$ and FePO$_4$

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Figure S1 XRD patterns of (a) the pristine Nb-doped LiFePO$_4$ and (b) chemical delithiation (10 atom %) LiFePO$_4$ sample (nominal).
Figure S2 Rietveld patterns of Nb-doped LiFePO$_4$ sample. Observed (red circles) and calculated (black solid line), Bragg reflection peaks (brown solid ticks) and the difference curve (below) are shown. The structural parameters are $a = 4.6943$ Å, $b = 10.3270$ Å and $c = 6.0048$ Å, $R_p$: 8.17, $R_wp$: 10.7, $R_{exp}$: 3.16 (not corrected for background).

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>Biso.</th>
<th>Occ.</th>
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<td>0.00000</td>
<td>0.00000</td>
<td>5.02627</td>
<td>0.47858</td>
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<tr>
<td>Nb</td>
<td>0.01719</td>
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<tr>
<td>Fe</td>
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<td>0.28238</td>
<td>0.25000</td>
<td>0.10024</td>
<td>0.46296</td>
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<tr>
<td>P1</td>
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<td>0.09310</td>
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<td>0.64297</td>
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<tr>
<td>O1</td>
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Figure S3. TEM image of the pristine Nb-doped LiFePO$_4$

Figure S4. Charge and discharge curves of the as-prepared Nb-doped LiFePO$_4$ sample
**Figure S5** (a) The unmarked ABF-STEM image (Figure 1a) at [010] zone axis and (b) schematic views of the mismatch of two phases (LiFePO$_4$, FePO$_4$).
Figure S6 The unmarked ABF-STEM image (Figure 2a) at [010] zone axis.
**Figure S7** Filtered STEM images of Nb-doped LiFePO₄. (a) ABF mode, (b) HADDF mode with Nb occupied in lithium site) and (c) HADDF mode with no Nb occupied in lithium site at [010] zone axis.
Table S1 Standard ICP elemental analysis of the pristine Nb-doped LiFePO$_4$ and chemical delithiation (10 atom % Lithium ion) of Nb-doped LiFePO$_4$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic ratio of elements</th>
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<tr>
<td></td>
<td>Li</td>
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<tr>
<td>The initial design</td>
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<td>2% Nb-doped LiFePO$_4$</td>
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<td>Chemical delithiated 10%</td>
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