Supporting Information

Revealing the role of NH$_4$VO$_3$ treatment on Ni-rich cathode materials with improved electrochemical performance for rechargeable lithium-ion batteries

Congcong Zhang,$^a$ Siyang Liu,$^b$ Junming Su,$^a$ Chunguang Chen,$^b$ Mengmeng Liu,$^a$ Xiang Chen,$^a$

Jianhua Wu,$^c$ Tao Huang$^a$ and Aishui Yu$^{a,b}$

$^a$ Laboratory of Advanced Materials, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Collaborative Innovation Center of Chemistry for Energy Materials, Institute of New Energy, Fudan University, Shanghai 200438, China

$^b$ Department of Chemistry, Fudan University, Shanghai 200438, China

$^c$ Jiangmen KanHoo Industry Co. , Ltd., Jiangmen City, Guangdong 529040, China

E-mail: asyu@fudan.edu.cn; Phone: +86-21-51630320; Fax: +86-21-51630320;
Fig. S1 (a) XRD patterns of the pristine and 0.25, 0.5, 1.0 wt% NH₄VO₃ treated NCM622 materials at 450 ºC; Rietveld refinement of (b) 0.5 wt%–300 ºC, (c) 0.5 wt%–600 ºC and (d) 0.5 wt%–750 ºC.
Fig. S2 (a) the first charge-discharge curves at 0.2 C and (b) cycling performance of the pristine and 0.25, 0.5, 1.0 wt% NH$_4$VO$_3$ treated NCM622 sintered at 450 °C.

Table S1 Detailed values of discharge capacity and capacity retention for pristine and different amount of NH$_4$VO$_3$ treated NCM622 sintered at 450 °C

<table>
<thead>
<tr>
<th>Samples</th>
<th>Discharge capacity (mAh g$^{-1}$)</th>
<th>Capacity retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1$^{st}$</td>
<td>6$^{th}$</td>
</tr>
<tr>
<td>Pristine</td>
<td>174.7</td>
<td>166.1</td>
</tr>
<tr>
<td>0.2 wt%--450°C</td>
<td>175.2</td>
<td>166.4</td>
</tr>
<tr>
<td>0.5 wt%--450°C</td>
<td>172.5</td>
<td>166.4</td>
</tr>
<tr>
<td>1.0 wt%--450°C</td>
<td>173.5</td>
<td>166.3</td>
</tr>
</tbody>
</table>

The effect of NH$_4$VO$_3$ amount on electrochemical performance of NCM622 is investigated and shown in Figure S2 and Table S1. There are no difference in the shape of first charge-discharge curves for all samples and all samples have the similar initial discharge capacity (174.7, 175.2, 172.5, and 173.5 mAh g$^{-1}$ for the pristine, 0.25 wt%, 0.5 wt%, and 1.0 wt% NH$_4$VO$_3$ treated samples, respectively), indicating that NH$_4$VO$_3$. 
treatment has no harm to the inherent electrochemical capability of active materials. For the pristine NCM622, the discharge capacity decays to 154.1 mAh g\(^{-1}\), with a capacity retention of 92.8 %. In case of the NH\(_4\)VO\(_3\) treated samples, the discharge capacities at the 100th cycles are 158.3, 159.9, 158.9 mAh g\(^{-1}\) with capacity retentions of 95.1 %, 96.1 %, and 95.6 %, respectively. This result indicates that an appropriate amount of NH\(_4\)VO\(_3\) treatment (0.5 wt%) is most effective for improving the cycling performance of NCM622. Therefore, the 0.5 wt% NH\(_4\)VO\(_3\) treatment amount is subsequently used to study the effect of calcination temperature on electrochemical performance of NCM622.
Fig. S3 pH value changes as a function as time for the pristine and 0.5 wt%–450 °C samples.
**Fig. S4** XPS spectra of V 2p\(_{3/2}\) for the pristine and 0.5 wt% NH\(_4\)VO\(_3\) treated samples at different annealing temperature.
Table S2 Detailed values of discharge capacity and capacity retention for the pristine and 0.5 wt% NH$_4$VO$_3$ treated NCM622 sintered at different temperature

<table>
<thead>
<tr>
<th>Samples</th>
<th>Discharge capacity (mAh g$^{-1}$)</th>
<th>Capacity retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1$^{\text{st}}$</td>
<td>6$^{\text{th}}$</td>
</tr>
<tr>
<td>Pristine</td>
<td>174.7</td>
<td>166.1</td>
</tr>
<tr>
<td>0.5wt%–300ºC</td>
<td>174.3</td>
<td>165.7</td>
</tr>
<tr>
<td>0.5wt%–450ºC</td>
<td>172.5</td>
<td>166.4</td>
</tr>
<tr>
<td>0.5wt%–600ºC</td>
<td>173.1</td>
<td>162.9</td>
</tr>
<tr>
<td>0.5wt%–750ºC</td>
<td>168.1</td>
<td>160.3</td>
</tr>
</tbody>
</table>
Fig. S5 XPS spectra of O1s for the pristine and 0.5 wt% NH₄VO₃ treated NCM622 sintered at different temperature.
Table S3 The refined XPS binding energies and peak percent for the pristine and 0.5 wt%–450 °C samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pristine</th>
<th></th>
<th>0.5wt%–450°C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bind energy (eV)</td>
<td>Peak percent (%)</td>
<td>Bind energy (eV)</td>
<td>Peak percent (%)</td>
</tr>
<tr>
<td>C 1s</td>
<td>C-C</td>
<td>284.8</td>
<td>27.8</td>
<td>284.9</td>
</tr>
<tr>
<td></td>
<td>C-H</td>
<td>286.3</td>
<td>35.0</td>
<td>286.4</td>
</tr>
<tr>
<td></td>
<td>C-O</td>
<td>287.5</td>
<td>8.5</td>
<td>288.2</td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>289.1</td>
<td>3.7</td>
<td>289.4</td>
</tr>
<tr>
<td></td>
<td>C-F/CO₃</td>
<td>290.8</td>
<td>25.0</td>
<td>290.9</td>
</tr>
<tr>
<td>O 1s</td>
<td>M-O</td>
<td>530.1</td>
<td>5.0</td>
<td>530.2</td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>533.3</td>
<td>45.6</td>
<td>532.5</td>
</tr>
<tr>
<td></td>
<td>C-O</td>
<td>533.8</td>
<td>49.4</td>
<td>533.9</td>
</tr>
<tr>
<td>F 1s</td>
<td>LiF</td>
<td>684.5</td>
<td>40.5</td>
<td>685.0</td>
</tr>
<tr>
<td></td>
<td>LiₓPO₃Fₓ/LiₓPFₙ</td>
<td>685.1</td>
<td>32.0</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>C-F</td>
<td>687.6</td>
<td>27.5</td>
<td>687.9</td>
</tr>
</tbody>
</table>