Supporting Information

Deciphering cycling voltage dependent failures of O3-layered cathode for sodium ion battery

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Figure S1. SEM images of the NFM sample. (a, b) low and (c, d) high magnification SEM images of the NFM.
**Figure S2.** dQ/dV profiles of the NFM cathode upon (a) 2.0-4.0 V and (b) 2.0-4.3 V cycling.
Figure S3. (a-c) STEM-HAADF images of NFM sample before and after cycling. (d-e) Normalized grain size distribution of the primary particles before and after cycling. (a, d) Pristine NFM, (b, e) after 200 cycles in the voltage ranges of 2.0-4.0 V, (c, f) after 200 cycles in the voltage ranges of 2.0-4.3 V.
Figure S4. XRD Rietveld refinement results of the NFM cathode. (a) pristine, (b) after 200 cycles in the voltage range of 2.0-4.0 V, (c) after 200 cycles in the voltage range of 2.0-4.3 V.
Figure S5. STEM-HAADF images of the NFM cathode after 200 cycles at different cutoff voltages. (a) 4.0 V, (b) 4.3 V. The red arrows indicate surface cracks, and the yellow arrows represent intragranular cracks.
Figure S6. STEM-HAADF images showing surface crack evolution with increasing cycling numbers at 2.0-4.0 V. (a) 10 cycles, (b) 50 cycles, (c) 200 cycles.
Figure S7. (a) High-magnification STEM-HAADF image of surface crack after 200 cycles in the voltage range of 2.0-4.0 V. (b) Lattice structure in the surface crack region.
Figure S8. STEM-HAADF images of the NFM sample after cycling. (a) 50 cycles, (c) 200 cycles. (b, d) High resolution lattice images from the grain bulk showing the inner bulk lattice remains layered structure after cycling.
Figure S9. STEM-HAADF images, EDS elemental mappings of Na, Ni, Fe, Mn, and corresponding spectra of sample A (a) and sample B (b), showing grain interior with uniform elemental distribution after 200 cycles in the voltage range of 2.0-4.0 V.
Figure S10. STEM-HAADF images showing surface crack evolution with increasing cycling numbers at 2.0-4.3 V. (a) 10 cycles, (b) 50 cycles, (c) 200 cycles.
Figure S11. (a) High-magnification STEM-HAADF image of surface crack after 200 cycles in the voltage range of 2.0-4.3 V. (b) Lattice structure from the crack surface region.
Figure S12. (a) Low-magnification STEM-HAADF image of the sample after 200 cycles in the voltage range of 2.0-4.3 V. (b-d) High resolution lattice images from the grain bulk showing the planar defects and the nano-void. (b-c) intragranular cracks, (d) nano-void).
Figure S13. STEM-HAADF images, EDS elemental mappings of Na, Ni, Fe, Mn and corresponding spectra from the grain interior of sample A (a) and sample B (b), after 200 cycles in the voltage range of 2.0-4.3 V.
Figure S14. (a) The capacity retentions after 50 cycles in the voltage ranges of 2.0-4.0 V, 2.0-4.15 V and 2.0-4.3 V. (b-c) STEM-HAADF images of the NFM sample after 50 cycles in the voltage range of 2.0-4.3 V.
Figure S15. (a) Low-magnification STEM-HAADF image of the sample after 10 cycles at 2.0-4.3 V. (b) High resolution lattice image from the grain bulk. White arrows indicate the bulk defects. (c) High resolution lattice image from grain bulk. (d-e) Atomic-resolution STEM-HAADF image and its corresponding line profile, showing cation interlayer mixing feature.
Figure S16. (a) Low-magnification STEM-HAADF image of the sample after 50 cycles at 2.0-4.3 V. (b) High resolution lattice image from grain bulk. (c-d) Atomic-resolution STEM-HAADF image and its corresponding line profile, showing cation interlayer mixing feature.
Figure S17. (a) Low-magnification STEM-HAADF image of the sample after 200 cycles at 2.0-4.3 V. (b) High resolution lattice image from the grain bulk. (c-d) Atomic-resolution STEM-HAADF images and their corresponding line profile, showing heavy interlayer mixing feature.
Table S1. Summary of electrochemical performance of O3-NFM in the literatures.

<table>
<thead>
<tr>
<th>Cycle voltage</th>
<th>Initial capacity</th>
<th>Cycle number</th>
<th>Capacity retention</th>
<th>Reference</th>
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<tr>
<td>2.0-4.0 V</td>
<td>136 mAh g⁻¹ (0.1 C)</td>
<td>100</td>
<td>80.5% (1 C)</td>
<td>1¹</td>
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<tr>
<td></td>
<td>123 mAh g⁻¹ (1 C)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2.0-4.0 V</td>
<td>128.0 mAh g⁻¹ (0.1 C)</td>
<td>100</td>
<td>83% (1 C)</td>
<td>2²</td>
</tr>
<tr>
<td>2.0-4.0 V</td>
<td>130.2 mAh g⁻¹ (0.1 C)</td>
<td>200</td>
<td>67% (1 C)</td>
<td>3³</td>
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<tr>
<td></td>
<td>122.0 mAh g⁻¹ (1 C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0-4.0 V</td>
<td>133.2 mAh g⁻¹ (0.1 C)</td>
<td>200</td>
<td>35.4% (1 C)</td>
<td>4⁴</td>
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<tr>
<td>2.0-4.0 V</td>
<td>132.0 mAh g⁻¹ (0.1 C)</td>
<td>15</td>
<td>92.4% (0.1 C)</td>
<td>5⁵</td>
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<tr>
<td>2.0-4.0 V</td>
<td>125.4 mAh g⁻¹ (0.1 C)</td>
<td>200</td>
<td>66.7% (1 C)</td>
<td>6⁶</td>
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<td></td>
<td>107.5 mAh g⁻¹ (1 C)</td>
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<tr>
<td>2.0-4.0 V</td>
<td>139.4 mAh g⁻¹ (0.1 C)</td>
<td>200</td>
<td>53.1% (1 C)</td>
<td>7⁷</td>
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<tr>
<td></td>
<td>128.0 mAh g⁻¹ (1 C)</td>
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<tr>
<td>2.0-4.1 V</td>
<td>135.1 mAh g⁻¹ (0.1 C)</td>
<td>150</td>
<td>46.9% (1 C)</td>
<td>8⁸</td>
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<td>2.0-4.3 V</td>
<td>157.6 mAh g⁻¹ (0.1 C)</td>
<td>15</td>
<td>64.4% (0.1 C)</td>
<td>5⁵</td>
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<td>1.5-4.2 V</td>
<td>159.6 mAh g⁻¹ (0.1 C)</td>
<td>100</td>
<td>58% (1 C)</td>
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<tr>
<td>2.0-4.0 V</td>
<td>131.2 mAh g⁻¹ (0.1 C)</td>
<td>200</td>
<td>68.8% (0.1 C)</td>
<td>this work</td>
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<tr>
<td></td>
<td>127.4 mAh g⁻¹ (0.1 C)</td>
<td>200</td>
<td>75.6% (1 C)</td>
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<tr>
<td>2.0-4.3 V</td>
<td>171.5 mAh g⁻¹ (0.1 C)</td>
<td>200</td>
<td>49.1% (0.1 C)</td>
<td>this work</td>
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Table S2. Crystallographic parameters of the NFM samples before and after 200 cycles refined by Rietveld method.

<table>
<thead>
<tr>
<th>NFM</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
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<tr>
<td>Pristine</td>
<td>2.97159</td>
<td>16.00726</td>
<td>122.413</td>
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<tr>
<td>2.0-4.0 V</td>
<td>2.96626</td>
<td>15.99753</td>
<td>121.899</td>
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<td>2.0-4.3 V</td>
<td>2.98153</td>
<td>16.15747</td>
<td>124.389</td>
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References:


