Supporting Information for:

Atomic Structure of Pt₃Ni Nanoframe Electrocatalysts by in Situ X-ray Absorption Spectroscopy

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Figure S1. Front and side views of in situ electrochemical XAS cell. The bottom has a port for a Ag/AgCl reference electrode and the top has a port for a Pt wire counter electrode. Gas or liquid flow can be carried out through the side ports.
Figure S2. TEM images of (a) Pt$_3$Ni(1.0) and (b) Pt$_3$Ni(1.5). Scale bars = 25 nm.

Figure S3. X-ray diffraction patterns of Pt$_3$Ni(1.0) and Pt$_3$Ni(1.5) as-prepared after annealing on carbon support.
Figure S4. EXAFS fitting of first coordination shell for Ni K-edge and Pt $L_3$-edge data of the as-prepared nanoframe catalyst (after annealing and before electrochemistry). For Ni K-edge EXAFS, $\Delta k = 2-13$ Å$^{-1}$ and $\Delta R = 1.2-3$ Å. For Pt $L_3$-edge EXAFS, $\Delta k = 2-14$ Å$^{-1}$ and $\Delta R = 1.8-3.1$ Å.

Table S1. Fitting parameters from EXAFS fitting of as-prepared nanoframe catalysts

<table>
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<tr>
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<th>$N_{PtNi}$</th>
<th>$N_{NiPt}$</th>
<th>$N_{PtPt}$</th>
<th>$N_{NiNi}$</th>
<th>$N_{Pt}$</th>
<th>$N_{Ni}$</th>
<th>$R_{PtNi}$</th>
<th>$R_{NiPt}$</th>
<th>$R_{NiNi}$</th>
<th>$N_{NiO}$</th>
<th>$R_{NiO}$</th>
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<td>Pt$_3$Ni(1.0)</td>
<td>4.4 (1.7)</td>
<td>7.9 (1.5)</td>
<td>4.7 (1.5)</td>
<td>0.7 (0.4)</td>
<td>9.1 (3.2)</td>
<td>8.6 (1.9)</td>
<td>2.661 (0.023)</td>
<td>2.710 (0.010)</td>
<td>2.637 (0.015)</td>
<td>4.8 (0.5)</td>
<td>2.050 (0.008)</td>
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<td>Pt$_3$Ni(1.5)</td>
<td>3.1 (1.3)</td>
<td>7.9 (1.4)</td>
<td>5.0 (1.3)</td>
<td>1.0 (0.6)</td>
<td>8.1 (2.6)</td>
<td>8.9 (2.0)</td>
<td>2.664 (0.019)</td>
<td>2.720 (0.010)</td>
<td>2.646 (0.015)</td>
<td>3.4 (0.5)</td>
<td>2.051 (0.010)</td>
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Figure S5. EXAFS fitting of first coordination shell for Ni K-edge and Pt L₃-edge data of the nanoframe catalyst after electrochemistry (rinsed with DI water and dried under N₂). For Ni K-edge EXAFS, ∆k = 2-12 Å⁻¹ and ∆R = 1.5-3.1 Å. For Pt L₃-edge EXAFS, ∆k = 2-13.5 Å⁻¹ and ∆R = 1.8-3.1 Å.

Table S2. Fitting parameters from EXAFS fitting of nanoframe catalyst after electrochemistry

<table>
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<tr>
<th></th>
<th>N_{PINi}</th>
<th>N_{NiPi}</th>
<th>N_{PiPi}</th>
<th>N_{NiNi}</th>
<th>N_{Pi}</th>
<th>R_{PINi}</th>
<th>R_{PiPi}</th>
<th>R_{NiNi}</th>
<th>J_{Pi} (%)</th>
<th>J_{Ni} (%)</th>
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<tr>
<td>Pt₃Ni(1.0)</td>
<td>2.1 (0.7)</td>
<td>5.7 (1.0)</td>
<td>5.6 (1.0)</td>
<td>4.1 (1.0)</td>
<td>7.7 (1.7)</td>
<td>9.8 (2.0)</td>
<td>2.660 (0.008)</td>
<td>2.715 (0.008)</td>
<td>2.651 (0.009)</td>
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<tr>
<td>Pt₃Ni(1.5)</td>
<td>1.6 (0.7)</td>
<td>5.5 (1.3)</td>
<td>6.3 (1.2)</td>
<td>4.4 (1.2)</td>
<td>7.9 (1.9)</td>
<td>9.9 (2.5)</td>
<td>2.671 (0.007)</td>
<td>2.725 (0.010)</td>
<td>2.659 (0.010)</td>
<td>79</td>
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</table>
Figure S6. Raw $k^3$-weighted $\chi(k)$ EXAFS spectra for Pt L$_3$-edge of Pt$_3$Ni(1.0) in three conditions; before, during, and after the oxygen reduction reaction.
Figure S7. Raw $k^3$-weighted $\chi(k)$ EXAFS spectra for Pt L$_3$-edge of Pt$_3$Ni(1.5) in three conditions; before, during, and after the oxygen reduction reaction.