Supplementary Information

**Li$_3$NiO/Ni Heterostructure with Strong Basic Lattice Oxygen Enables Electrocatalytic Hydrogen Evolution with Pt-like Activity**

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Materials and Methods

Chemicals: Nickel(II) nitrate hexahydrate (99%, Sigma-Aldrich), potassium permanganate (>99%, Sigma-Aldrich), sulfuric acid (≥95%, VWR), phosphoric acid (≥85%, VWR), nitric acid (98%, Fisher Scientific), ammonium hydroxide (30 %, Sigma-Aldrich), graphite flake (>99.99%, Sigma-Aldrich), Li metal strips (99.9%, Alfa Aesar). All chemicals were used as-received.

Synthesis of NiO/graphene composite (NiO/G). Graphene oxide (GO) was prepared by the modified Hummers method and was used as aqueous dispersions with a concentration of 3.0 mg mL⁻¹. While under vigorous stirring, 20 mL solution containing 0.6 g Ni(NO₃)₂•6H₂O was slowly added to 60 ml GO solution. The pH of the mixed solution was adjusted to ~ 10 using ammonium hydroxide, which induced precipitation of Ni(OH)₂ on GO surface. The mixture was continuously stirred for 2 h to ensure completion of precipitation, and was then transferred to a Teflon-lined autoclave reactor. The reactor was heated at 180°C for 12 hours and then cooled to room temperature. The graphene composites were collected by vacuum filtration, washed with nanopure water and freeze-dried. The dried powders were calcined at 500°C for 2 hours under 30 sccm Ar, which produce NiO/G composite that contains ~ 60 wt% NiO. NiO/G composites with different NiO contents were synthesized by varying the amount of Ni(NO₃)₂•6H₂O while keeping the same GO content.

Synthesis of LiₓNiO/Ni catalysts. The as-synthesized NiO/G composites were vacuum dried at 70°C for 12 hours prior to use. They were transferred to an Ar-filled glovebox and mixed with metallic Li in a nickel crucible. The crucible was slowly heated to 250°C using a hotplate and kept at this temperature for 20 min to ensure completion of reaction. Afterwards the mixture was cooled naturally to room temperature and solidified. The mixture was then transferred out of glove box and immersed in ethanol for at least 24 hours to leach off unreacted Li metal and Li oxides. The catalyst powder was collected via vacuum filtration, washed repeated using water and vacuum dried.

Synthesis of Ni foam catalysts. The as-received Ni foam was first annealed in air at 600 °C for 1 h to introduce sufficient NiO layers. The annealed Ni foam was
transferred in the Ar-filled glove box and reacted with Li metal using the same method as detailed above. After reaction, the treated Ni foam was also washed with ethanol and water, and was tested directly as HER catalyst after drying.

Materials Characterization

Powder X-ray diffraction was performed using a Rigaku Miniflex diffractometer operating at 30 kV and 15 mA using Cu Kα radiation (λ= 1.5406 Å). SEM images were collected using a field-emission Hitachi S-4700-II microscope. TEM images were acquired from a FEI Tecnai F20ST electron microscope (for the high-resolution images) and a JEOL JEM-2100F microscope at 200 KV. The Ni concentration was quantified using a Shimadzu AA-6200 atomic absorption spectrophotometer. Raman spectra were collected using a Renishaw inVia Raman microscope with a 532 nm laser. The specific surface area and pore size distribution were analyzed using a Micromeritics Tristar 3000 analyzer. The XPS spectra were collected using a Thermal Escalab 250 X-ray photoelectron spectrometer. The binding energies were calibrated by assigning the C 1s peak at 284.5 eV. Near-edge X-ray absorption fine structure (NEXAFS) data were collected in a total electron yield (TEY) configuration on BL 11.0.1.2 at Lawrence Berkeley National Laboratory’s Advanced Light Source.² Electrical contact to the samples was made in order to collect the drain current used to measure the TEY signal as a function of x-ray energy. These TEY spectra were then normalized to the incident beam’s instantaneous flux and spectrum (across the same energy range and step sizes as the measurements on the actual samples) using a gold mesh upstream and the direct signal on a photodiode, respectively. Finally, the following standard x-ray absorption corrections were made using Athena software package: the background of each sample’s spectrum was removed by subtracting a linear fit to the pre-edge region and further normalized by dividing it by a quadratic fit to the post-edge region.

Electrochemical Studies

All electrochemical tests were performed using a Pine Bipotentiostat Electrochemical Workstation (Pine Instruments, USA) and a standard three-electrode configuration, with a saturated calomel reference electrode (SCE) and a graphite rod counter.
electrode. The behavior of Pt/C was studied separately in a dedicated setup to avoid Pt contamination. The SCE electrode was calibrated in hydrogen saturated 0.5M H₂SO₄ electrolyte using two Pt wires as the working and counter electrodes. The catalyst ink was prepared by mixing 10 mg catalysts with 950 μL water/isopropanol (1:3 v/v) and 50 μL 5 wt% Nafion solution, and was sonicated for at least 30 min to ensure uniform dispersion prior to use. To prepare the working electrode, 2–16 μL of the catalyst ink was drop-casted onto a 5 mm glassy carbon disk electrode. The mass loadings for LiₓNiO/Ni and Pt/C electrocatalysts were optimized as 0.6 and 0.3 mg cm⁻², respectively. The electrolytes used in this work were 0.5 M H₂SO₄ (pH=0.3), 1.0 M potassium phosphate buffer (KPi, pH=7.0), and 1.0 M KOH (pH=13.8). The catalysts were activated by ~ 100 cyclic voltammetry cycles (0 ~ 0.5V vs RHE, 10 mV/s) prior to collecting HER polarization curves. The linear sweep voltammograms (LSVs) were collected at 5 mV s⁻¹. All LSV curves were iR corrected using the standard equation of \( E_{\text{corrected}} = E_{\text{measured}} - iR_s \), where \( E_{\text{corrected}} \), \( E_{\text{measured}} \) and \( i \) refers to the iR-corrected potential, measured potential and recorded current, respectively. \( R_s \) is the equivalent resistance measured by electrochemical impedance spectroscopy (EIS) employing the same electrode configuration. The onset potential for the HER was defined as the potential that first reached the current density of 0.2 mA/cm², which is approximately 10 times the background current of 0.02 mA/cm². The electrochemically active surface area (ECSA) of was estimated using the equation of ECSA = \( C_{\text{dl}} / C_s \), where the \( C_{\text{dl}} \) and \( C_s \) refer to the double layer capacitance and a specific capacitance value of 22 \( \mu \) F cm⁻², respectively.
Figure S1: TEM images of NiO/graphene composite used in this work. The size of NiO was 50 ~ 100 nm and its weight concentration was 60%.

Figure S2: a) nitrogen absorption-desorption isotherms and b) pore-size distributions of pristine NiO/G and Li\textsubscript{x}NiO/Ni catalysts.
Figure S3: Additional high-resolution TEM images of the Li$_x$NiO/Ni heterostructures. The inverse fast Fourier transition images and line intensity profiles are also shown to highlight Ni-deficient NiO nanoclusters.
Figure S4: XPS survey spectra of Li$_x$NiO/Ni catalyst before and after annealing. The quantified atomic concentrations are also included.
Figure S5: XRD of Li$_x$NiO/Ni (a) and Ni/G (b) after dispersed in water for 3 days.

Figure S6: Deuteroro chloroform (CDCl$_3$) FT-IR spectroscopy analysis of Li$_x$NiO/Ni catalyst and NiO reference powders. Each material was treated at 80°C under flow of Ar before introducing CDCl$_3$ and the spectra were acquired after 3 min of dosing CDCl$_3$. 
Figure S7: Structural and electrochemical characterization of the Pt/C catalyst used in this work: a) TEM image; b) XRD pattern and c) cyclic voltammograms in 0.1M HClO₄ at 50 mV/s.

Figure S8: Polarization curves for a) LiₓNiO/Ni catalyst and b) Pt/C catalyst under increasing areal loadings in 1.0M KPi. These curves were used to determine optimal mass loading for catalyst evaluation.
Figure S9: Comparison of HER polarization curves for catalysts prepared from NiO/G composites with different NiO content as noted. These results were acquired at 5.0 mV/s in 1.0M KPi, and the catalysts loadings were all 0.6 mg/cm².

Figure S10: Comparison of electrochemical active surface area (ESCA) of LiₓNiO/Ni in different electrolytes. The ESCA was estimated using double layer capacitance from current-scan rate relationships at 0.05 V (vs. RHE).
Figure S11: Additional high-resolution TEM images and analysis of the Li$_x$NiO/Ni catalyst after 50 hours of operation at 20 mA cm$^{-2}$ in (a,b) pH = 0.3 and (c,d) pH = 7.0.

Figure S9: XPS and Raman characterization of the Li$_x$NiO/Ni catalysts before and after 50 hours operation at 20 mA cm$^{-2}$ in 0.5 M H$_2$SO$_4$: a) Ni 2p; b) O 1s XPS spectra and c) Raman spectra.
Figure S13: Synthesis of catalysts by electrochemical lithiation-delithiation of NiO/G. A battery setup was used, and was assembled using NiO/G cathode, Li metal anode and 1.0M LiPF₆ in EC/DEC electrolyte. The battery was cycled with the voltage window of 0.05 ~ 3V and ended in lithiation state. The battery was then dissembled and the cathode was isolated and washed for catalysis studies.

Figure S14: Photograph showing the preparation of LiₓNiO/Ni/Ni foam catalyst.
Figure S15: Fabrication of HER catalysts on Ni foam using the method detailed above: a) XRD patterns of Ni foam after different treatments; b) stability of the Ni foam based catalysts in different electrolytes.

**Table S1**: Summary of the electrochemical properties of the Pt/C electrocatalysts under different pH conditions.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>η (mV) @ 10 mA cm⁻²</th>
<th>η (mV) @ 100 mA cm⁻²</th>
<th>Tafel slope (@10 mA) (mV dec⁻¹)</th>
<th>Tafel slope (50–100 mA) (mV dec⁻¹)</th>
<th>η_geom (mA cm⁻²)</th>
<th>C_d</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH=0.3</td>
<td>17 mV</td>
<td>83 mV</td>
<td>26 mV/dec</td>
<td>115 mV/dec</td>
<td>1.1</td>
<td>1.6 mF/cm²</td>
</tr>
<tr>
<td>pH=7.0</td>
<td>53 mV</td>
<td>205 mV</td>
<td>65 mV/dec</td>
<td>320 mV/dec</td>
<td>0.70</td>
<td>1.1 mF/cm²</td>
</tr>
<tr>
<td>pH=13.8</td>
<td>33 mV</td>
<td>114 mV</td>
<td>49 mV/dec</td>
<td>121 mV/dec</td>
<td>0.83</td>
<td>1.3 mF/cm²</td>
</tr>
</tbody>
</table>

**Table S2**: Comparison of LiₓNiO/Ni with representative HER electrocatalysts in alkaline (pH ~ 14) electrolyte.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>η (mV) @ 10 mA cm⁻²</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>durability</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiₓNiO/Ni</td>
<td>36</td>
<td>50</td>
<td>50 h</td>
<td>This work</td>
</tr>
<tr>
<td>Mo-NiO/Ni</td>
<td>50</td>
<td>86</td>
<td>12 h</td>
<td>6</td>
</tr>
<tr>
<td>NiFeOₓ/CFP</td>
<td>100</td>
<td>N/A</td>
<td>100 h</td>
<td>7</td>
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<tr>
<td>Ni-N0.19</td>
<td>150</td>
<td>125</td>
<td>20 h</td>
<td>8</td>
</tr>
<tr>
<td>Ni/NiO/MoOₓ</td>
<td>11</td>
<td>34</td>
<td>25 h</td>
<td>9</td>
</tr>
<tr>
<td>Catalysts</td>
<td>η (mV) @ 10 mA cm⁻²</td>
<td>Tafel slope (mV/dec)</td>
<td>Durability</td>
<td>Refs.</td>
</tr>
<tr>
<td>----------------------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>------------</td>
<td>----------</td>
</tr>
<tr>
<td>NiCu@C composite</td>
<td>74</td>
<td>94.5</td>
<td>10 h</td>
<td>10</td>
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<tr>
<td>Ni/NiO</td>
<td>146</td>
<td>72</td>
<td>20 h</td>
<td>11</td>
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<tr>
<td>NiO/Ni-CNT</td>
<td>95</td>
<td>51</td>
<td>N/A</td>
<td>12</td>
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<tr>
<td>NiSₓ/NF</td>
<td>60</td>
<td>99</td>
<td>10 h</td>
<td>13</td>
</tr>
<tr>
<td>CFP/NiPₓ</td>
<td>117</td>
<td>58.7</td>
<td>~100 h</td>
<td>14</td>
</tr>
</tbody>
</table>

**Table S3:** Comparison of LiₓNiO/Ni with representative HER electrocatalysts in neutral (pH ~ 7) electrolyte.

**Reference:**