Supplemental Information

Understanding the Stabilization Effect of the Hydrous IrO$_x$ Layer formed on Iridium Oxide Surface during the Oxygen Evolution Reaction in Acid

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Figure S1 Evolution of Tafel curves of BaIrO$_3$ (a) and SrIrO$_3$ (b) after certain number of electrochemical cycling.
Figure S2 Cyclic voltammograms and charging currents for DL capacitance measurements in BaIrO$_3$. The electric double-layer capacitance was calculated by fitting the curve of charging current (at 1.08 V vs RHE) and scan rate.
The electric double-layer capacitance ($C_{dl}$) was calculated from the scan-rate dependent CVs in non-Faradaic potential region with various scan rates.\(^1\) The $C_{dl}$ was calculated according to the equation $i_c = vC_{dl}$, where $C_{dl}$ is the double-layer capacitance (mF), $v$ is the scan rate (mV s\(^{-1}\)), $i_c$ is charging current (mA). Thus, a plot of $i_c$ as a function of $v$ yields a straight line with a slope equal to $C_{dl}$. 

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Figure S3. Cyclic voltammograms and charging currents for DL capacitance measurements in SrIrO\(_3\). The electric double-layer capacitance was calculated by fitting the curve of charging current (at 0.95V vs RHE) and scan rate.
Figure S4. CV profiles of 1st, 50th, 100th, 150th cycle for BaIrO$_3$ and SrIrO$_3$ with currents normalized by the ECSA.
Figure S5. Comparison of the Ir L_{III}-edge EXAFS curves for the pristine and reacted BaIrO$_3$ (a) and SrIrO$_3$ (b) with a $k$ range of $3 \leq k \leq 10$ Å$^{-1}$. These data are $k^2$-weighted and not phase-corrected.
Figure S6. TEM images of reacted BaIrO$_3$. (a) A typical oxide particle after electrochemical cycling, (b) high-resolution TEM image showing the crystalline structure at the exposed region.
Figure S7. (a) Reaction setup of BaIrO$_3$ catalyst after holding at 1.6 V vs. RHE for 12 hours, (b) corresponding UV-Vis spectrum of the reacted H$_2$SO$_4$ electrolyte.
Figure S8. The optical photos of the initial (a) and reacted BaIrO$_3$ (b) after holding at 1.7 V vs RHE taken from the operando Raman experiments. Insets are the corresponding Raman spectra.
Figure S9. The Raman spectra of pristine and reacted IrO\textsubscript{2} after holding at 1.6 V vs RHE for 12h.
Figure S10. Cyclic voltammograms of BaIrO$_3$ and SrIrO$_3$ at different scan rates in 0.5 M H$_2$SO$_4$. 
Figure S11 Evolution of XRD patterns of pristine BaIrO$_3$ and reacted BaIrO$_3$ after holding at 1.3 and 1.4 V vs. RHE in 0.5 M H$_2$SO$_4$ solution for 12 hours.
Figure S12. PDOS of BaIrO$_3$ as calculated by DFT in which the Fermi level is 0 eV.
Table 1. The parameters from the Rietveld refinement of BaIrO$_3$ and SrIrO$_3$.

<table>
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<th>Compound</th>
<th>Space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α(°)</th>
<th>β(°)</th>
<th>γ(°)</th>
<th>V$_{\text{unit-cell}}$ (Å$^3$)</th>
<th>R$_p$</th>
<th>R$_{wp}$</th>
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<tr>
<td>BaIrO$_3$</td>
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<td>90</td>
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<td>90</td>
<td>850.15</td>
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Reference