Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

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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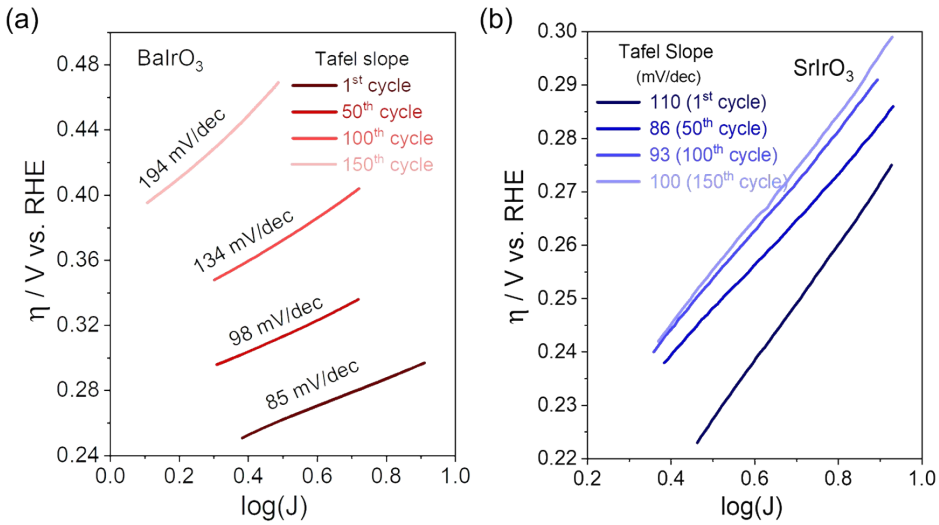

Figure S1 Evolution of Tafel curves of $BaIrO_3$ (a) and $SrIrO_3$ (b) after certain number of electrochemical cycling.

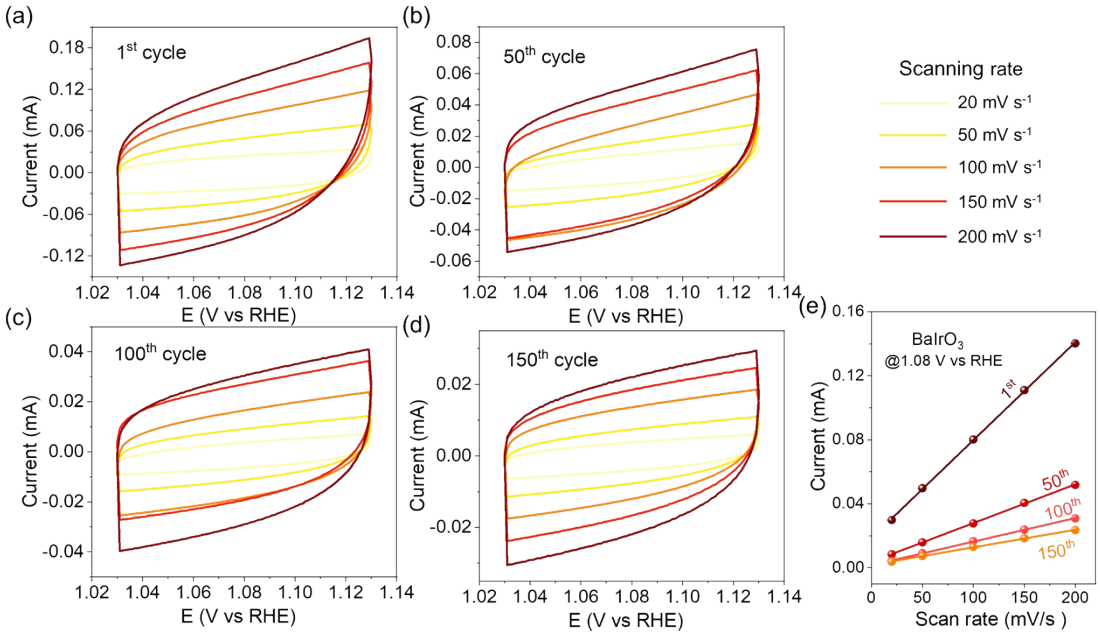

Figure S2 Cyclic voltammograms and charging currents for DL capacitance measurements in $BaIrO_3$. The electric double-layer capacitance was calculated by fitting the curve of charging current (at 1.08 V vs RHE) and scan rate.

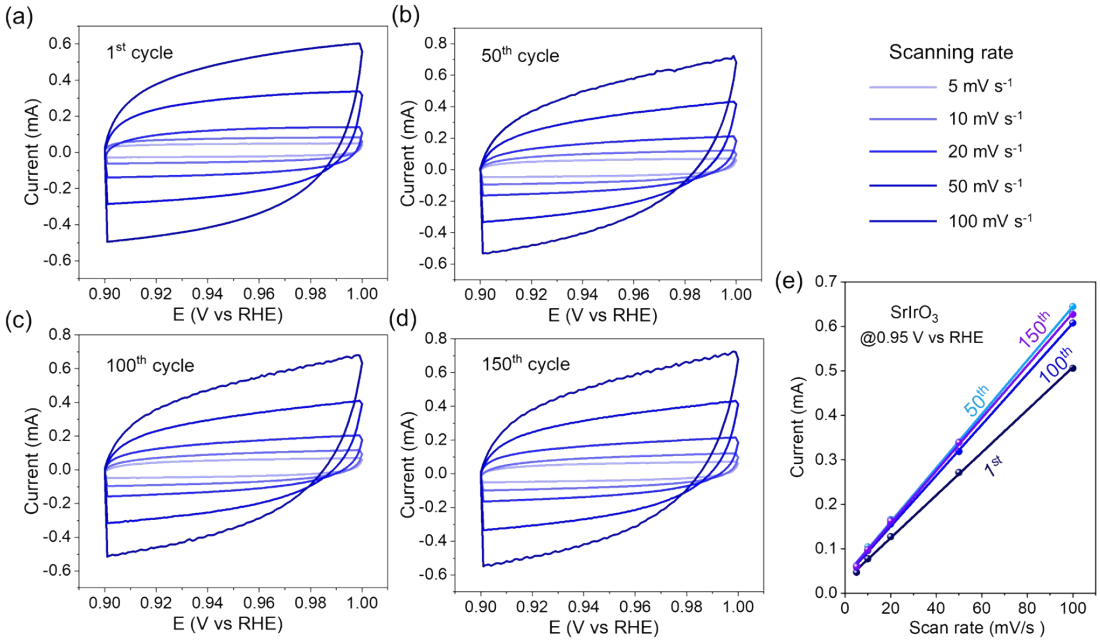

Figure S3. Cyclic voltammograms and charging currents for DL capacitance measurements in $SrIrO_3$. The electric double-layer capacitance was calculated by fitting the curve of charging current (at 0.95V vs RHE) and scan rate.

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}.

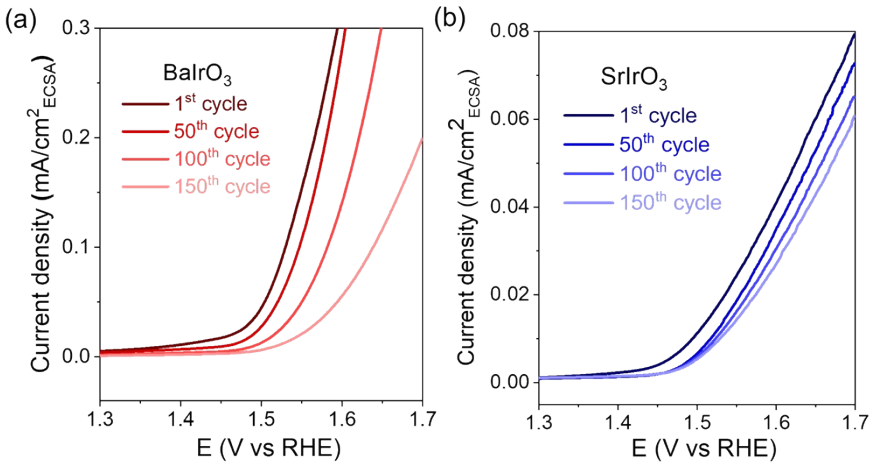

Figure S4. CV profiles of 1st, 50th, 100th, 150th cycle for $BaIrO_3$ and $SrIrO_3$ with currents normalized by the ECSA.

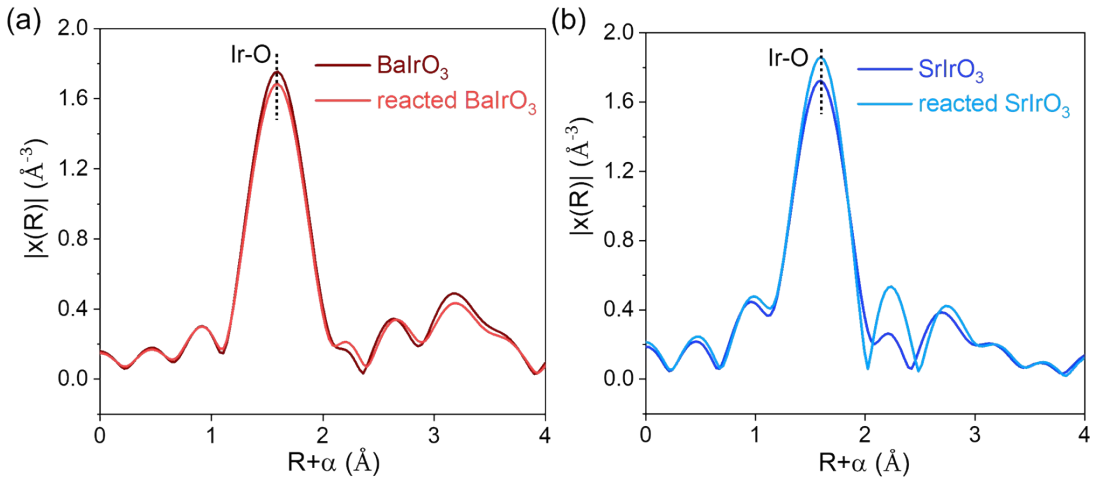

Figure S5. Comparison of the Ir L_{III}-edge EXAFS curves for the pristine and reacted $BaIrO_3$ (a) and $SrIrO_3$ (b) with a k range of $3 \leq k \leq 10$ Å^{-1}. These data are k^2-weighted and not phase-corrected.

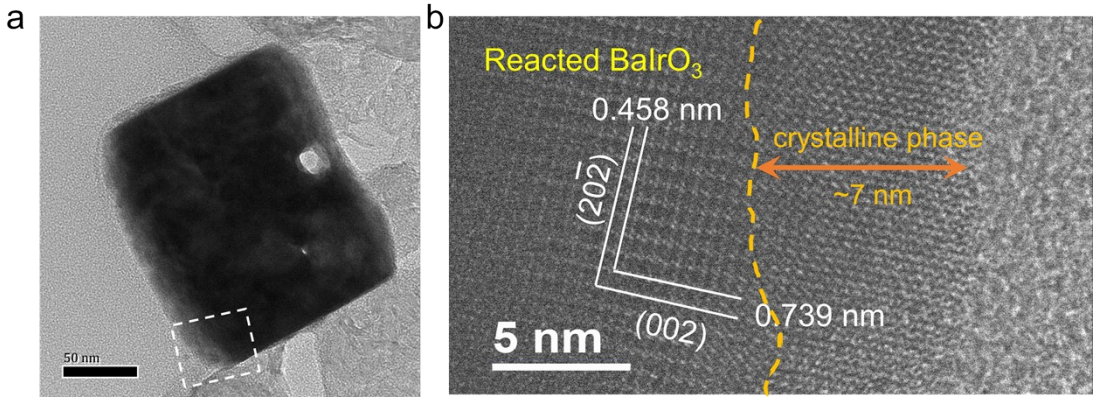

Figure S6. TEM images of reacted $BaIrO_3$. (a) A typical oxide particle after electrochemical cycling, (b) high-resolution TEM image showing the crystalline structure at the exposed region.

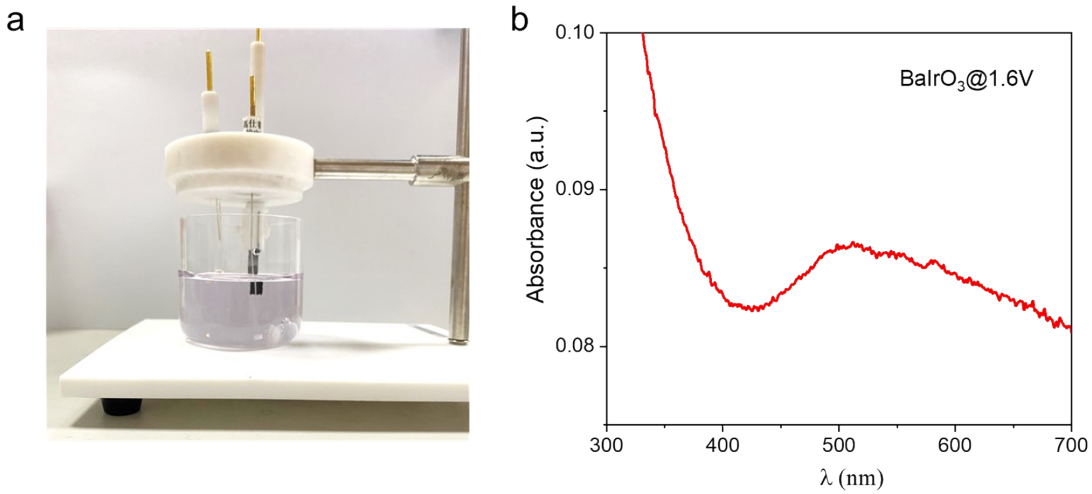

Figure S7. (a) Reaction setup of $BaIrO_3$ catalyst after holding at 1.6 V vs. RHE for 12 hours, (b) corresponding UV-Vis spectrum of the reacted H_2SO_4 electrolyte.

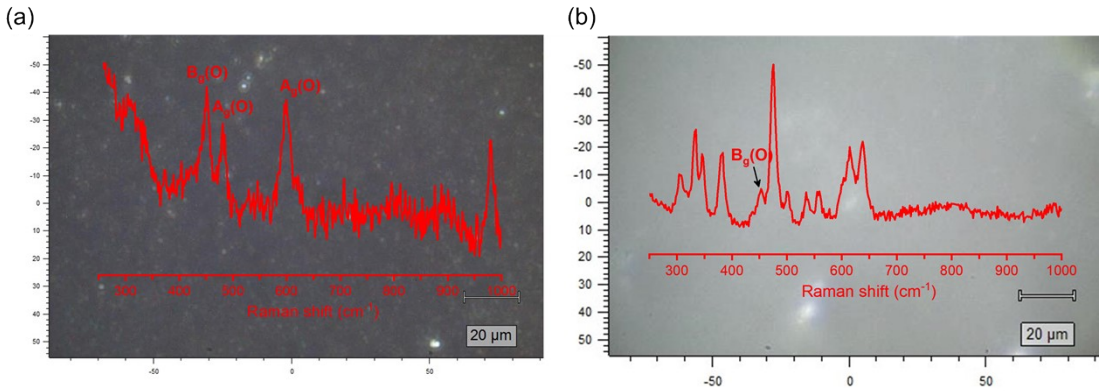

Figure S8. The optical photos of the initial (a) and reacted $BaIrO_3$ (b) after holding at 1.7 V vs RHE taken from the *operando* Raman experiments. Insets are the corresponding Raman spectra.

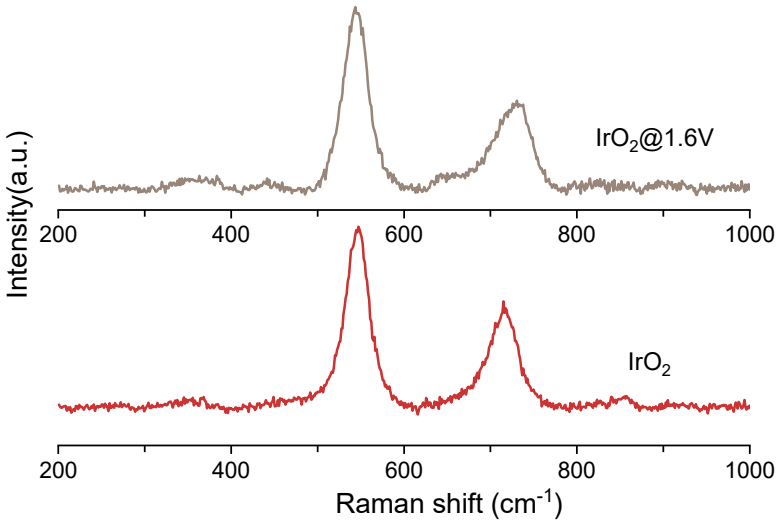

Figure S9. The Raman spectra of pristine and reacted IrO_2 after holding at 1.6 V vs RHE for 12h.

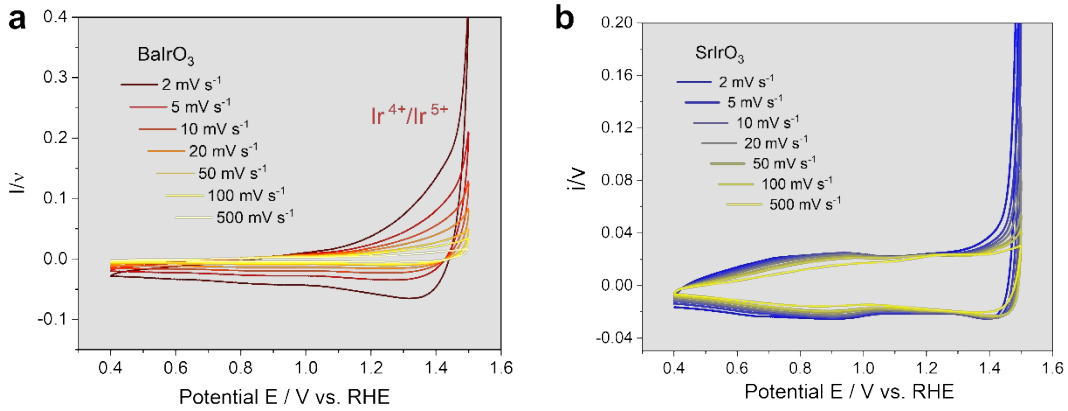

Figure S10. Cyclic voltammograms of $BaIrO_3$ and $SrIrO_3$ at different scan rates in 0.5 M H_2SO_4.

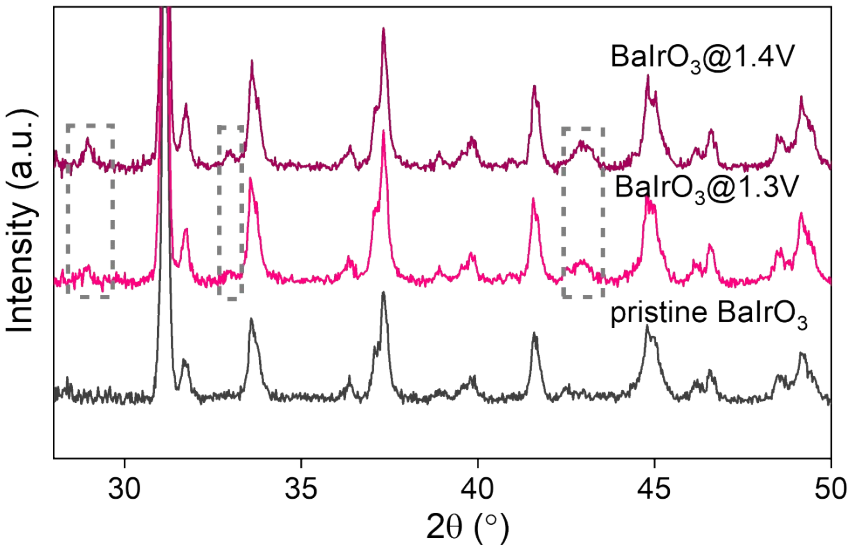

Figure S11 Evolution of XRD patterns of pristine $BaIrO_3$ and reacted $BaIrO_3$ after holding at 1.3 and 1.4 V vs. RHE in 0.5 M H_2SO_4 solution for 12 hours.

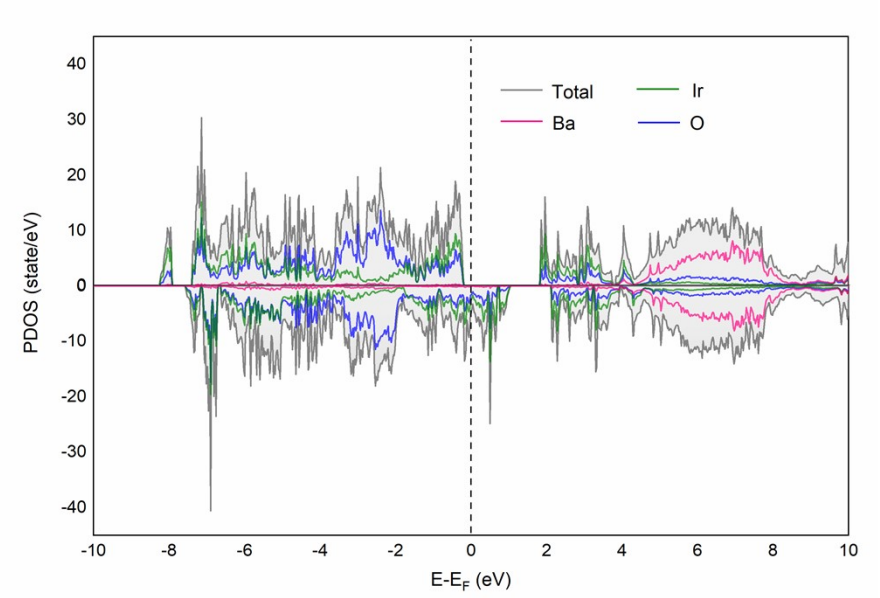

Figure S12. PDOS of $BaIrO_3$ as calculated by DFT in which the Fermi level is 0 eV.

Table 1. The parameters from the Rietveld refinement of $BaIrO_3$ and $SrIrO_3$.

Compound	**Space group**	**a (Å)**	**b (Å)**	**c (Å)**	α(°)	β(°)	γ(°)	$\mathbf{V_{unit\text{-}cell}}$ **(Å^{-3})**	R_p	R_{wp}
$BaIrO_3$	C 1 2/m 1	10.011	5.763	15.135	90	103.18	90	850.15	7.9	10.1
$SrIrO_3$	C 1 2/c 1	5.620	9.620	14.169	90	93.21	90	762.73	6.2	8.0

Reference

[1] McCrory, C. C.; Jung, S.; Peters, J. C.; Jaramillo, T. F., Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction. *J Am Chem Soc* **2013,** *135* (45), 16977-16987.