

Supporting Information

Influence of Strain on the Surface–Oxygen Interaction and the Oxygen Evolution Reaction of SrIrO₃

Ding-Yuan Kuo¹, C. John Eom¹, Jason K. Kawasaki^{2,3,#}, Guido Petretto⁴,

Jocienne N. Nelson², Geoffroy Hautier⁴, Ethan J. Crumlin⁵, Kyle M. Shen^{2,3},

Darrell G. Schlom^{1,3}, and Jin Suntivich^{1,3,*}

¹ *Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853, USA*

² *Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853, USA*

³ *Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, NY 14853, USA*

⁴ *Institute of Condensed Matter and Nanosciences (ICMN), Université catholique de Louvain, Louvain-la-Neuve 1348, Belgium*

⁵ *Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

[#]*Present Address: Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, WI 53706, USA*

* Correspondence: jsuntivich@cornell.edu

Content

DFT computation details	S2
Adsorption energy analysis	S3
APXPS result of SrIrO ₃ (001) on DSO and LSAT at 250 °C (Fig. S1)	S4
Surface charge density of SrIrO ₃ (001) on DSO and LSAT (Fig. S2)	S5
Integrated CVs of SrIrO ₃ (001) on DSO and LSAT (Fig. S3)	S6
Free energy of surface adsorbate states on SrIrO ₃ /DSO and SrIrO ₃ /LSAT (Fig. S4 & S5)	S7
Energy relation of OH _{ad} and O _{ad} of IrO ₂ (110) and SrIrO ₃ (001) (Fig. S6)	S8
Fit parameters for the O 1s peak analysis of SrIrO ₃ (001) (Table S1)	S8
Geometric models for the DFT calculations (Table S2-S4)	S9

DFT Computation Details. The Perdew-Burke-Ernzerhof (PBE) approximation for the exchange correlation functional and a plane wave cutoff energy of 520 eV have been used. Spin-orbit coupling has been included in all the calculations.

The adsorption energy for a generic adsorbate X_{ad} is defined as

$$E_{ad}(X) = E_{DFT}(SrIrO_3X_{ad}) - E_{DFT}(SrIrO_3) - E_{DFT}(X)$$

where E_{DFT} refers to the total DFT energy for the system with and without the adsorbate and to the energy of the adsorbate itself. For the adsorbates considered here, we used:

$$E_{DFT}(H) = E_{DFT}(H_2)/2$$

and

$$E_{DFT}(O) = E_{DFT}(H_2O) - E_{DFT}(H_2),$$

based on the DFT total energies of the H_2 and H_2O molecules.

The values of the Gibbs free energies for the OER intermediates have been calculated as

$$\Delta G(X) = E_{ad}(X) + ZPE_X - TS_X$$

where ZPE and TS represent the zero point energy and entropic corrections for the generic adsorbate X, respectively. The values for these corrections have been taken from Ref. (1).

It should be noted that, since the values of $E_{DFT}(O)$ and of the ZPE and TS corrections are strain independent, the evolution of the energy difference as a function of the strain shown in **Figure 2B** can be regarded as the difference between Gibbs free energies as well.

Figures S4 and S5 represent the variation of the DFT Gibbs free energy ΔG , with respect to the water covered surface, as a function of the applied potential V . The slope of the curves is determined by the charge of the system considering the contribution coming from the evolution of the two adsorption sites in the supercell. The lowest value of the energy identifies the stable configuration for each applied potential and determines the regions outlined in **Figure 4B**.

Adsorption Energy Analysis. We use the potential at the adsorption peak (V_{peak}) and the potential window at 90% peak current as an error bar to demonstrate the peak width difference between adsorbates. In the CV of $\text{SrIrO}_3(001)$, we observe three adsorption peaks in the potential window from 0.3 to 1.5 V vs. RHE, which we assign to peak 1 (~ 0.6 V vs. RHE), peak 2 (~ 1.0 V vs. RHE), and peak 3 (~ 1.4 V vs. RHE), respectively.

To estimate the free energy of formation of OH_{ad} and O_{ad} on SrIrO_3 , we examine the potential of the OH_{ad} (alkaline: $\text{H}_2\text{O}_{\text{ad}} + \text{OH}^- \rightarrow \text{OH}_{\text{ad}} + \text{H}_2\text{O} + \text{e}^-$) and O_{ad} (alkaline: $\text{OH}_{\text{ad}} + \text{OH}^- \rightarrow \text{O}_{\text{ad}} + \text{H}_2\text{O} + \text{e}^-$). The electrochemical potential of OH_{ad} ($\Delta G_{\text{OH}} = V_{\text{OH peak}}$) and O_{ad} ($\Delta G_{\text{O}} = V_{\text{OH peak}} + V_{\text{O peak}}$) correspond to the free energies of $\text{H}_2\text{O}_{\text{ad}} \rightarrow \text{OH}_{\text{ad}} + \frac{1}{2}\text{H}_2$ and $\text{H}_2\text{O}_{\text{ad}} \rightarrow \text{O}_{\text{ad}} + \text{H}_2$, respectively. There are three possible scenarios as followed: (1) peak 1 shows the OH adsorption; peak 2 shows the O adsorption, (2) peak 1 shows the OH adsorption; peak 3 shows the O adsorption, and (3) peak 2 shows the OH adsorption; peak 3 shows the O adsorption. The adsorption energy relation of SrIrO_3 in these scenarios are shown in **Figure S6**.

We observe the adsorption energy relation of SrIrO_3 in scenario (1) deviates from the adsorption energy relation of IrO_2 implying that the assumptions in this case may be incorrect.

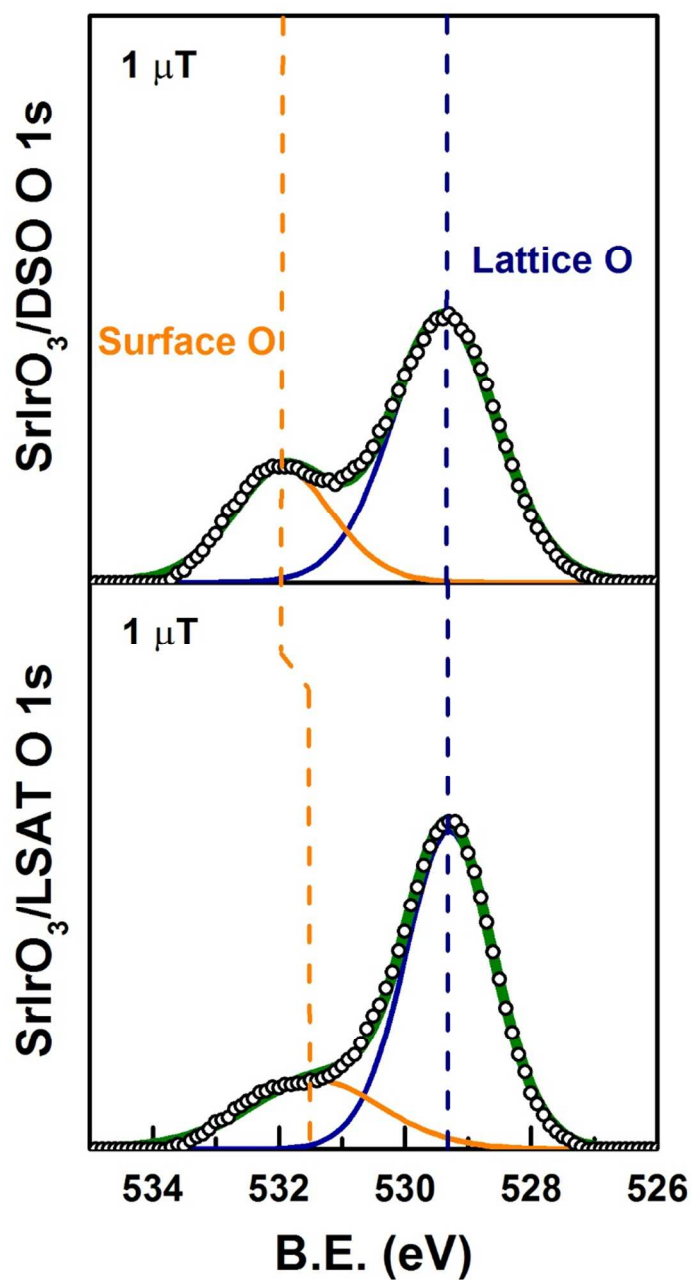


Figure S1. APXPS for O 1s of a SrIrO₃ film on DSO (top) and LSAT (bottom) under 1 μTorr oxygen pressure at 250 °C. Black circles: experiment data; navy line: lattice O; orange line: surface O; green line: the sum of the fit; y-axis: normalized intensity; x-axis: binding energy.

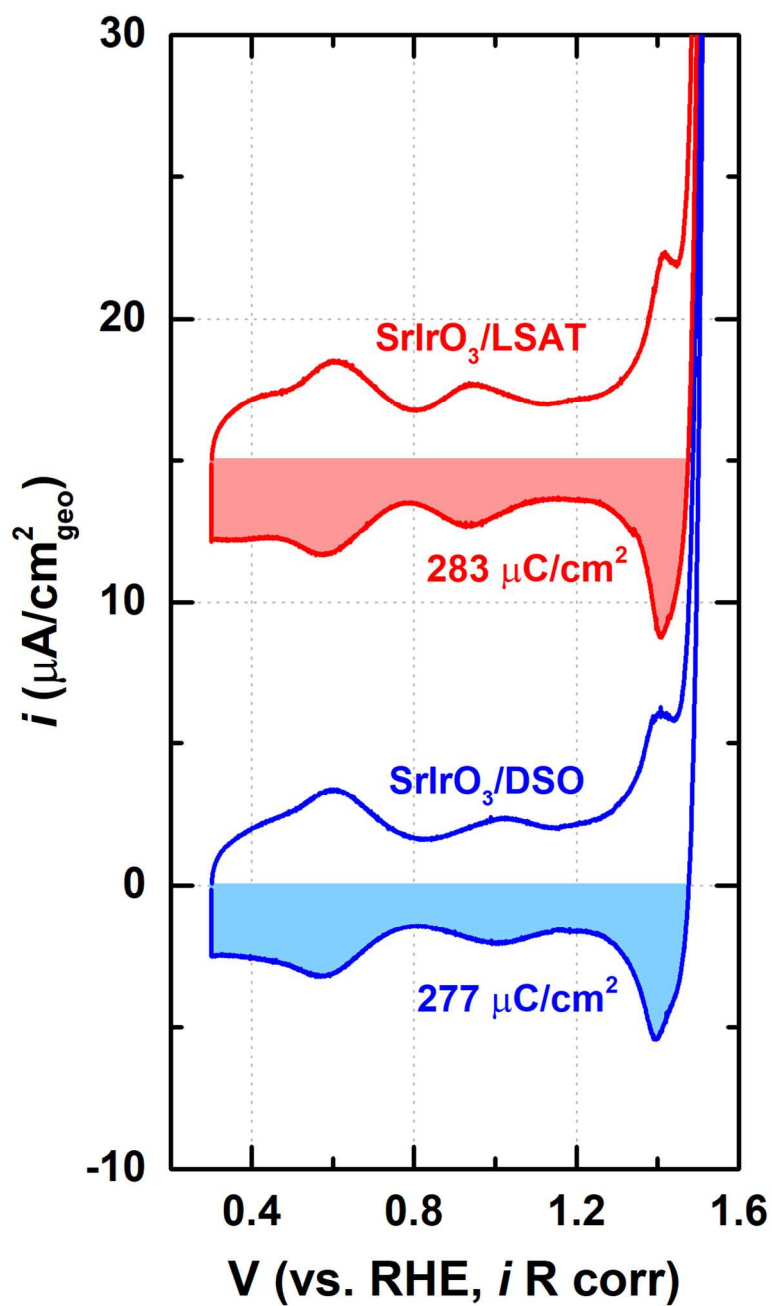


Figure S2. CV of $\text{SrIrO}_3(001)$ films in an Ar-saturated 0.1 M KOH electrolyte at a 10 mV/s scan rate. The surface charge density obtained by integrating the colored area is 277 and $283 \mu\text{C}/\text{cm}^2$ for $\text{SrIrO}_3/\text{DSO}$ and $\text{SrIrO}_3/\text{LSAT}$, respectively.

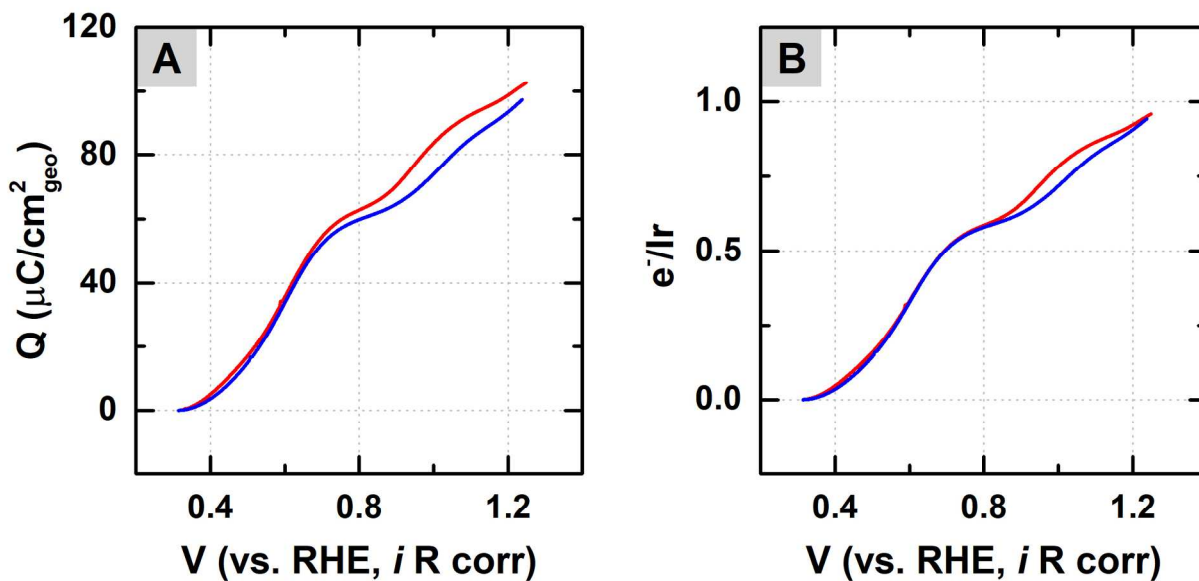


Figure S3. (A) Surface anodic charge density and (B) the number of electron transferred per Ir on the surface *versus* potential for SrIrO₃ on DSO (blue) and SrIrO₃ on LSAT (red) obtained from integration of CV.

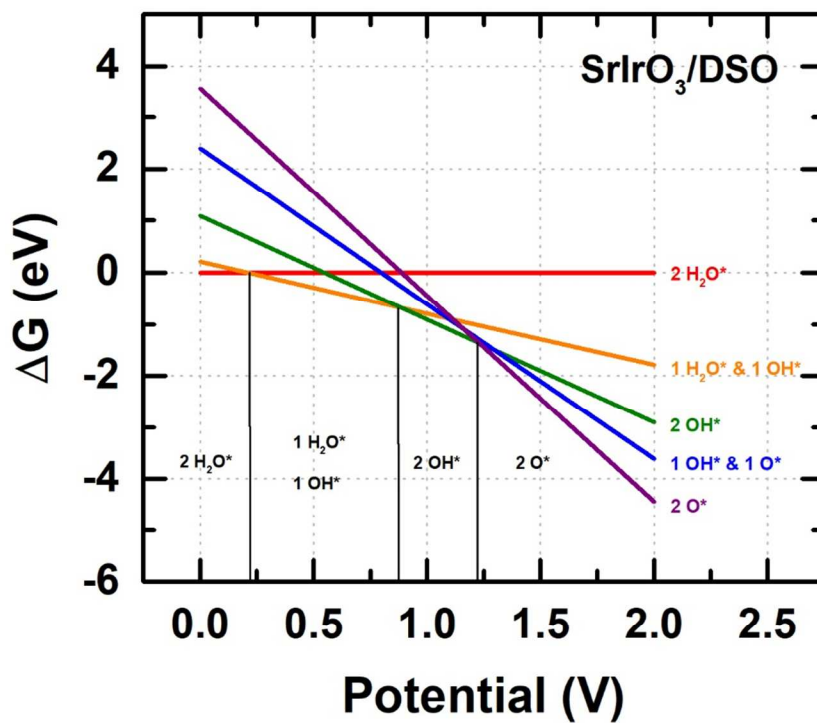


Figure S4. The potential-dependent free energy of surface adsorbate states on $\text{SrIrO}_3/\text{DSO}$.

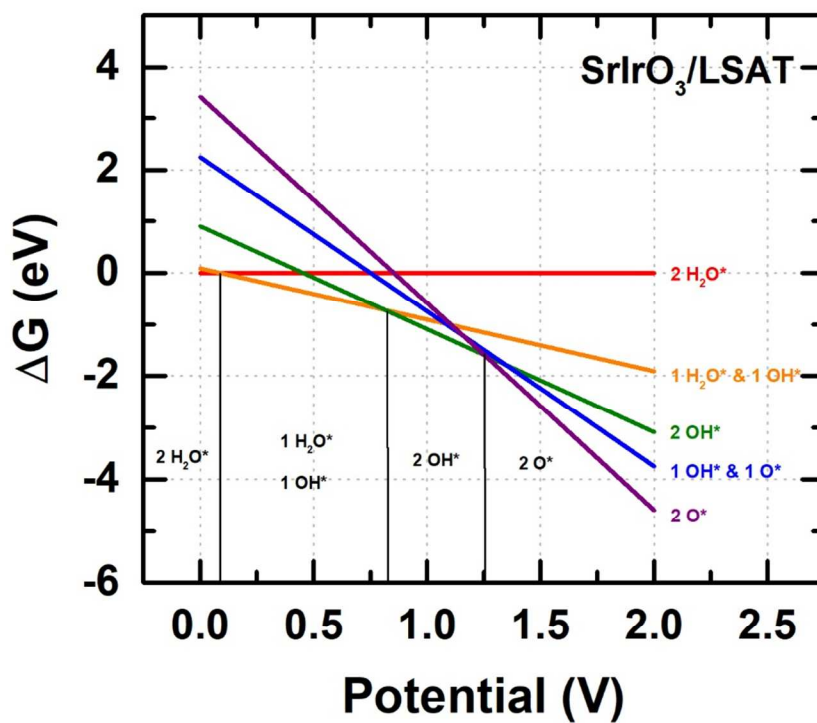


Figure S5. The potential-dependent free energy of surface adsorbate states on $\text{SrIrO}_3/\text{LSAT}$.

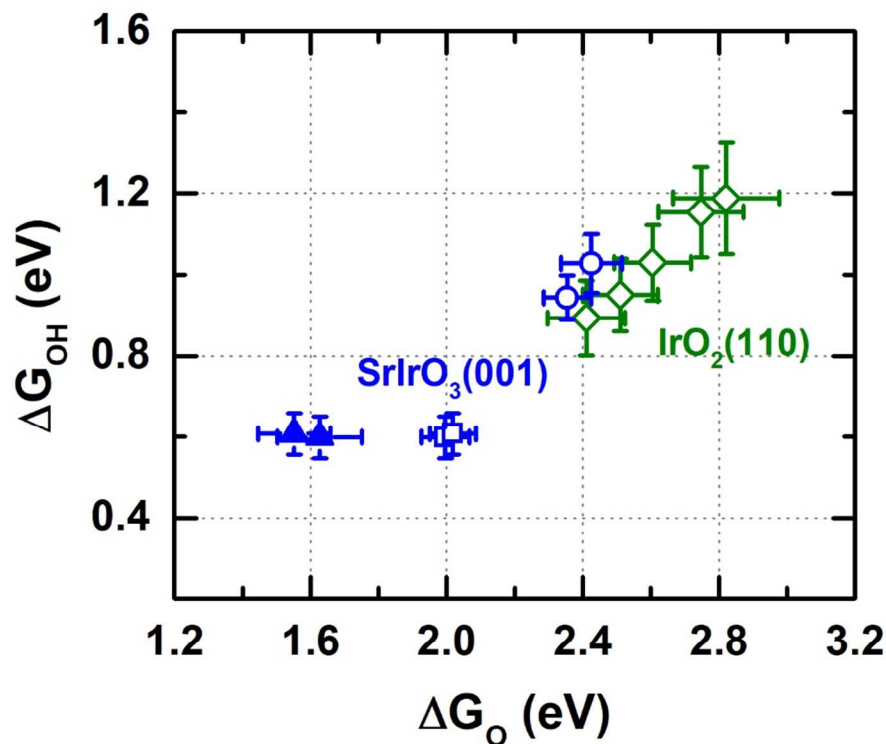


Figure S6. The energy relation between OH_{ad} and O_{ad} on $\text{IrO}_2(110)$ and $\text{SrIrO}_3(001)$. Green hollow diamonds: IrO_2 reproduced from Ref. (2); Blue hollow squares: SrIrO_3 using first peak as OH adsorption and third peak as O adsorption; Blue hollow circles: SrIrO_3 using second peak as OH adsorption and third peak as O adsorption; Blue solid triangles: SrIrO_3 using first peak as OH adsorption and second peak as O adsorption.

T (°C)	$p\text{O}_2$ (μTorr)	Substrate	Lattice O 1s			Surface O 1s		
			Position (eV)	FWHM (eV)	Area (%)	Position (eV)	FWHM (eV)	Area (%)
25	1	DSO	529.4	1.8	52.39	531.5	2.0	47.61
		LSAT	529.3	1.6	50.77	531.1	2.3	49.23
	10^5	DSO	529.4	1.9	48.29	531.4	1.9	51.71
		LSAT	529.3	1.6	52.07	531.1	2.3	47.93
250	1	DSO	529.4	2.0	70.79	532.0	1.9	29.21
		LSAT	529.3	1.6	75.08	531.4	2.5	24.92

Table S1. Fit parameters for the O 1s peak analysis of $\text{SrIrO}_3(001)$.

Supercell models of $\text{SrIrO}_3(001)$ on DSO (unstrained):

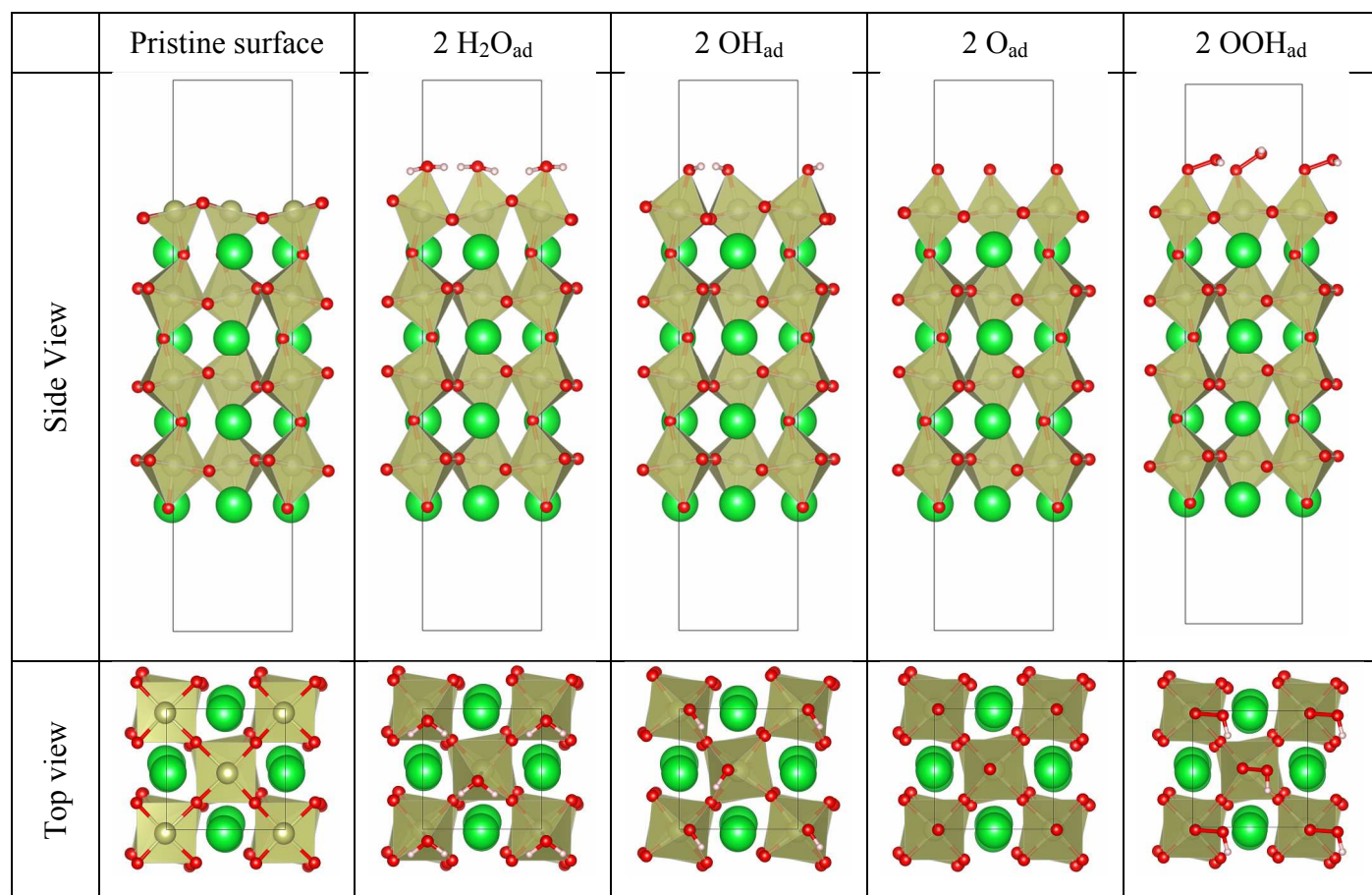


Table S2. Supercell models for the pristine surface, $\text{H}_2\text{O}_{\text{ad}}$, OH_{ad} , O_{ad} , and OOH_{ad} of $\text{SrIrO}_3(001)$

on DSO. Yellow, red, green, and white spheres represent Ir, O, Sr, and H atoms, respectively.

Supercell models of $\text{SrIrO}_3(001)$ on LSAT (strained):

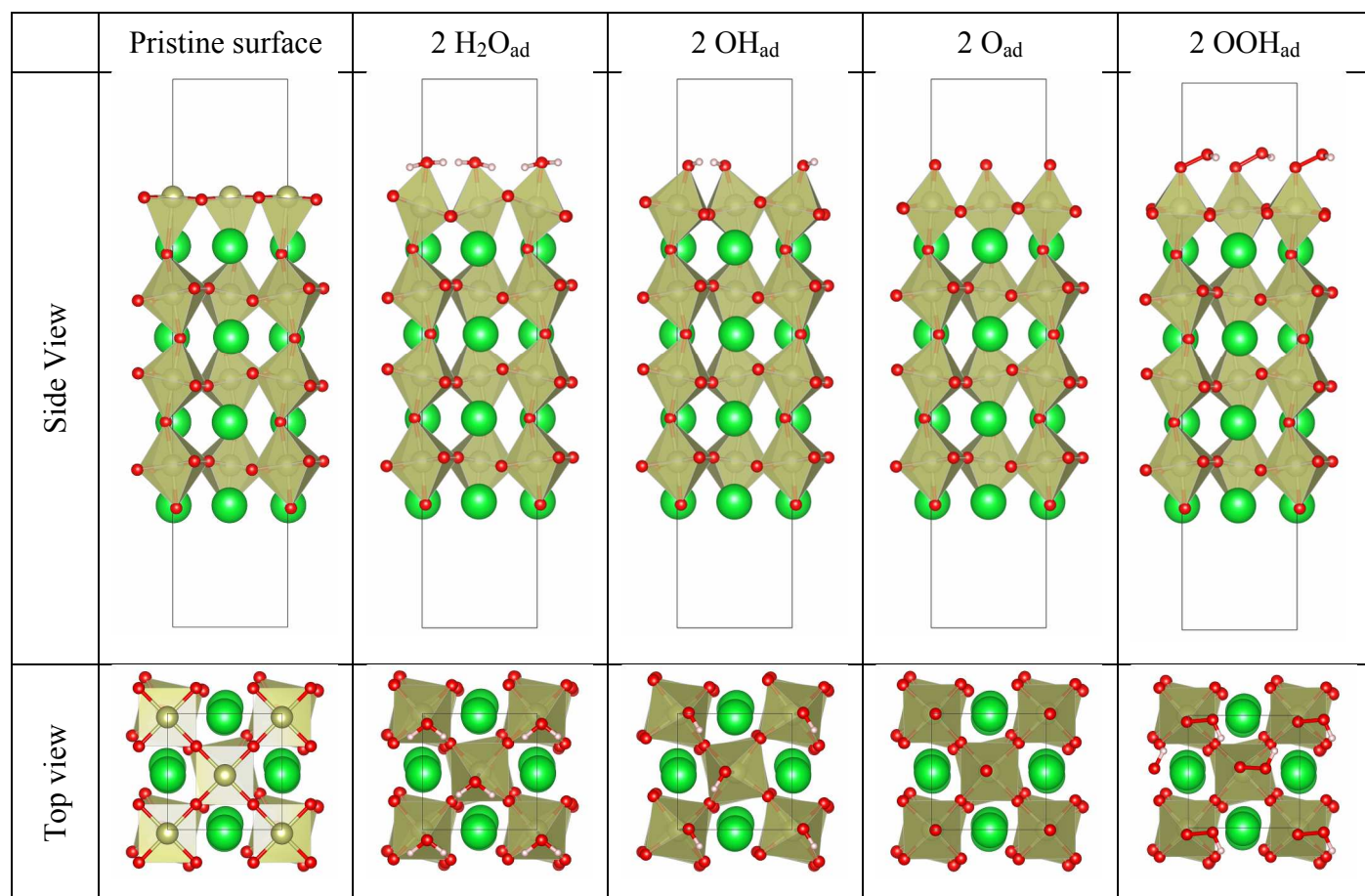


Table S3. Supercell models for the pristine surface, $\text{H}_2\text{O}_{\text{ad}}$, OH_{ad} , O_{ad} , and OOH_{ad} of $\text{SrIrO}_3(001)$ on LSAT. Yellow, red, green, and white spheres represent Ir, O, Sr, and H atoms, respectively.

Supercell models of $\text{SrIrO}_3(001)$ considering half-coverage:

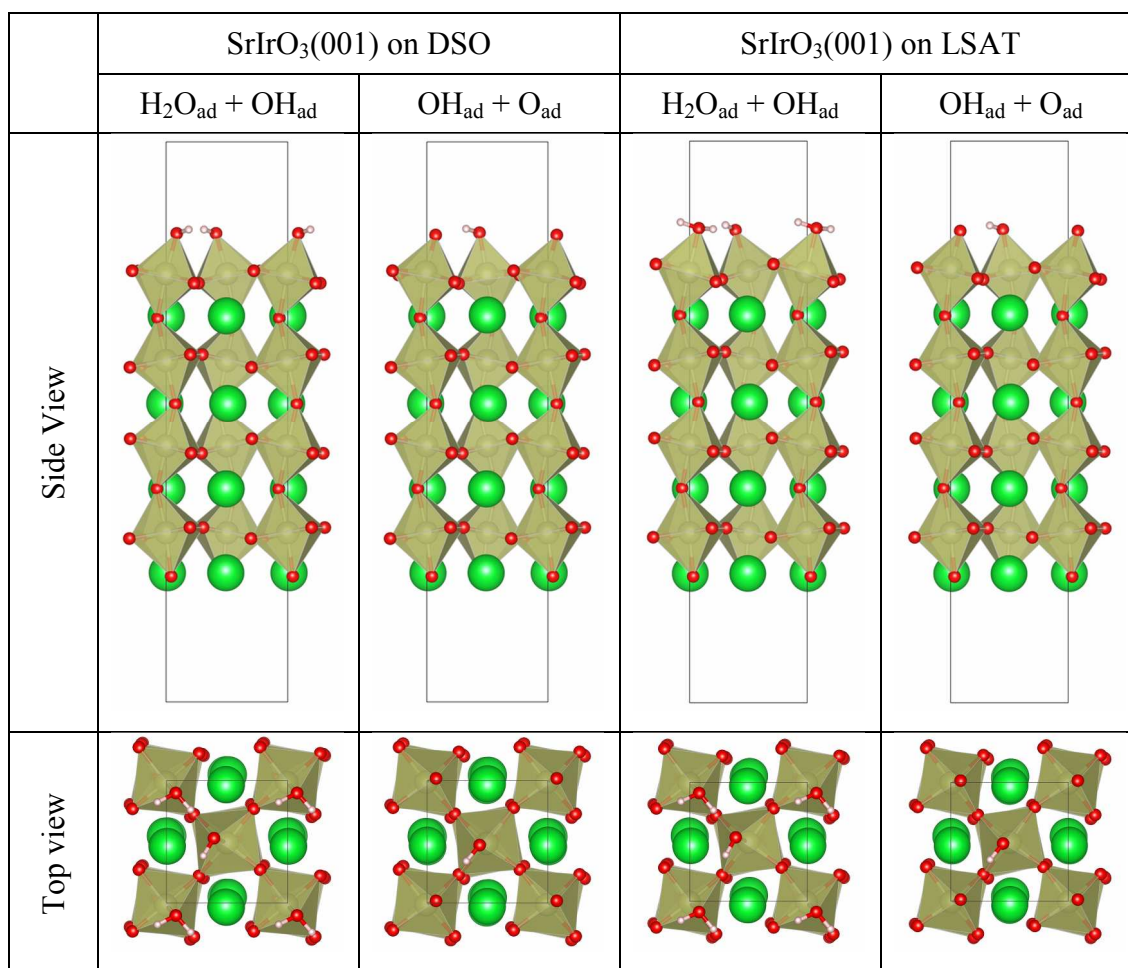


Table S4. Supercell models of $\text{SrIrO}_3(001)$ considering half-coverage. Yellow, red, green, and white spheres represent Ir, O, Sr, and H atoms, respectively.

References

- (1) Man, I. C.; Su, H.-Y.; Calle-Vallejo, F.; Hansen, H. A.; Martínez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J. Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces. *ChemCatChem* **2011**, 3 (7), 1159–1165.
- (2) Kuo, D.-Y.; Kawasaki, J. K.; Nelson, J. N.; Kloppenburg, J.; Hautier, G.; Shen, K. M.; Schlom, D. G.; Suntivich, J. Influence of Surface Adsorption on the Oxygen Evolution Reaction on IrO₂ (110). *J. Am. Chem. Soc.* **2017**, 139 (9), 3473–3479.