## Supplementary Information

# Towards identifying the active sites on $RuO_2$ (110) in catalyzing oxygen evolution

Reshma R Rao,<sup>a</sup> Manuel J Kolb,<sup>b†</sup> Niels Bendtsen Halck,<sup>c</sup> Anders Filsøe Pedersen,<sup>d</sup> Apurva Mehta,<sup>e</sup> Hoydoo You,<sup>f</sup> Kelsey A Stoerzinger,<sup>g‡,</sup> Zhenxing Feng,<sup>h</sup> Heine A Hansen,<sup>c</sup> Hua Zhou,<sup>i</sup> Livia Giordano,<sup>aj</sup> Jan Rossmeisl,<sup>k</sup> Tejs Vegge,<sup>c</sup> Ib Chorkendorff,<sup>d</sup> Ifan E L Stephens<sup>d§</sup> and Yang Shao-Horn <sup>abg\*</sup>

<sup>a</sup>Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States <sup>b</sup>Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States <sup>c</sup>Department of Energy Conversion and Storage, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark <sup>d</sup>Section for Surface Physics and Catalysis, Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark eSLAC National Accelerator Laboratory, Menlo Park, CA 94025, United States <sup>f</sup>Argonne National Laboratory, Materials Science Division, Argonne, Illinois 6043, **United States** <sup>g</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States <sup>h</sup>School of Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, OR 97331, United States <sup>i</sup>X-ray Science Division, Argonne National Laboratory, Argonne, IL 60439, United States <sup>j</sup>Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Milano, Italy <sup>k</sup>Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100

Copenhagen, Denmark

<sup>†</sup>Current address: FYSIKUM, AlbaNova, Stockholm University, S-10691 Stockholm, Sweden and SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, 443 Via Ortega, Stanford, California 94305, United States

<sup>‡</sup>Current address: Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland Washington 99354, United States <sup>§</sup>Current address: Royal School of Mines, Imperial College London, South Kensington Campus, London, SW 2AZ, United Kingdom

## **Corresponding Author**

\*shaohorn@mit.edu

#### Cyclic Voltammetry



Figure S1: Cyclic voltammograms of a  $RuO_2$  (110) single crystal surface in Arsaturated 0.1 M HClO<sub>4</sub> solution (~pH 1.2) measured at a scan rate of 50 mV/s with different lower potential limits.

#### **Oxygen-sensitive rods measured in CTR**

The intensity of the diffracted beam measured at a given value of (h,k,l) is a function of the scattering factor of the atoms as well as their relative positions. Mathematically, the measured intensity for a particular reflection (h,k,l) is the square of the structure factor, which can be written as:

$$F_{(h,k,l)} = \sum_{i=1}^{atoms} f_{(i)} e^{2\pi(hu+hv+lw)}$$

where  $f_{(j)}$  is the scattering factor of atom j and x, y and z are the fractional coordinates of atom j. The repeating unit for RuO<sub>2</sub> (110) is shown in Figure S2.



Figure S2: Repeating unit for  $RuO_2(110)$  showing two distinct Ru atoms at (0,0,0) and (0.5, 0.5, 0). Grey and red spheres represent Ru and O atoms respectively.

Substituting the value of the fractional co-ordinates for the 2 independent Ru atoms, we obtain:

$$F_{(h,k,l)} = f_{(Ru)}e^{2\pi(0)} + f_{(Ru)}e^{2\pi(0.5h+0.5k)}$$
$$F_{(h,k,l)} = 1 + f_{(Ru)}e^{\pi(h+k)}$$

Thus, for h + k values that are odd,  $F_{(h,k,l)} = 0$  and the contribution from the Ru sublattices vanish. Since these rods derive their intensity predominantly from the position of oxygen atoms, they are known as 'Oxygen rods'.

#### Fitting model

Three possible surface terminations of RuO<sub>2</sub> (110) can be accessed<sup>1-4</sup>, as shown in Figure S3. The Ru-O termination would be accessed at very reducing conditions, where both the bridge and CUS oxygen are absent. The O1 termination is stoichiometric, where the bridge Ru site is filled with a bridging oxygen and the CUS Ru site is empty. The O2 termination is most oxidized, where both the bridge and CUS Ru sites are filled. For the purpose of this study, all structures are referenced with respect to the O1 stoichiometric termination.



Figure S3: Three distinct surface terminations of rutile  $RuO_2$  (110), namely (A) the reduced Ru-O termination, (B) the O1 termination with only bridging oxygen present and (C) the O2 termination with both bridging and CUS oxygen atoms present. Pink and red spheres represent Ru and O atoms respectively.

A model of the (110) surface was created in GenX, which is shown in Figure S4. Four distinct layers were modeled, namely: the 'adsorbed' layer, the 'surface' layer, the 'sub-surface' layer and the 'bulk' structure. Atoms in the first three layers are assigned numbers to uniquely identify them. Only the lattice parameter in the z direction in the bulk structure is allowed to relax, and thus atoms in the bulk structure have not been named. Subsequent tables listing the fitting parameters and fitting results use the same naming scheme as Figure S4.



Figure S4: The model created in GenX for fitting the crystal truncation rod data. The atoms in the adsorbed oxygen, surface and sub-surface layer are labeled with the element type and a number in parenthesis. Pink and red spheres represent Ru and O atoms respectively.

Table S1: The parameters allowed to vary for the fitting process. The minimum and maximum columns indicate the upper and lower bound set for the parameter respectively. The parameter nomenclature is based on the description in Figure S4.

Parameter	Min	Max	
Intensity	1.00E-06	1.00E+06	
BULK			
c lattice parameter	9.50E-01	1.05E+00	
SUB-SURFACE LAYER			
c lattice parameter	9.50E-01	1.05E+00	
0 (1) Δz	-3.00E-02	3.00E-02	
0 (2) Δz	-3.00E-02	3.00E-02	
0 (3) Δz	-3.00E-02	3.00E-02	
0 (4) Δz	-3.00E-02	3.00E-02	
0 (5) Δz	-3.00E-02	3.00E-02	
0 (6) Δz	-3.00E-02	3.00E-02	
0 (7) Δz	-3.00E-02	3.00E-02	
0 (8) Δz	-3.00E-02	3.00E-02	
Ru (1) Δz	-3.00E-02	3.00E-02	
Ru (2) Δz	-3.00E-02	3.00E-02	
Ru (3) Δz	-3.00E-02	3.00E-02	
Ru (4) Δz	-3.00E-02	3.00E-02	
SURFACE LAYER			
0 (1) Δz	-3.00E-02	3.00E-02	
0 (2) Δz	-3.00E-02	3.00E-02	
Ru (1) Δz	-3.00E-02	3.00E-02	
Ru (2) Δz	-3.00E-02	3.00E-02	
ADSORBED			
0 (3) Δz	-2.00E-02	2.00E-02	
0 (3) occupancy	7.50E-01	1.05E+00	
0 (4) Δz	-1.50E-02	2.50E-02	
0 (4) occupancy	7.50E-01	1.05E+00	
0 (5) $\Delta z$ (*only for 1.5 V structure)	-1.50E-02	3.50E-02	
0 (5) occupancy (*only for 1.5 V	7.50E-01	1.05E+00	
structure)			
$0 (5) \Delta y$ (*only for 1.5 V structure)	-1.00E-01	2.00E-02	

# **Fitting results**

Table S2: Final atomic positions obtained for the structure at 0.5 V<sub>RHE</sub>. Additional parameters that were fitted and are not included in the table are: c lattice parameter for the bulk structure = 1.010(1), c lattice parameter for the sub-surface layer = 1.020(2), occupancy for O(3) = 0.95(1) and occupancy for O(4) = 1.01(2). The parameter nomenclature is based on the description in Figure S4. The figure of merit obtained for this structure was 0.089.

Parameter	x	У	Z
SUB-SURFACE LAYER			
Ru(1)	0	0	-0.007(4)
Ru (2)	1.555	3.175	-0.004(2)
Ru (3)	1.555	0	3.162(2)
Ru (4)	0	3.175	3.163(3)
0 (1)	0	3.175	5.00(4)
0 (2)	0	0	4.56(2)
0 (3)	1.555	4.445	3.11(1)
0 (4)	1.555	1.905	3.22(2)
0 (5)	0	0	2.13(4)
0 (6)	0	3.175	1.311(4)
0 (7)	1.555	1.27	-0.15(2)
0 (8)	1.555	5.08	0.10(2)
SURFACE LAYER			
Ru (1)	0	0	6.275(6)
Ru (2)	1.555	3.175	6.362(7)
0 (1)	1.555	1.27	6.29(4)
0 (2)	1.555	5.08	6.54(2)
ADSORBED			
0 (3)	0	3.175	7.91(4)
0 (4)	0	0	8.96(2)
Direction vectors			
VEC1	3.11	0	0.000
VEC2	0	6.35	0.000
VEC3	0	0	6.350

Table S3: Final atomic positions obtained for the structure at 1.0 V<sub>RHE</sub>. Additional parameters that were fitted and are not included in the table are: c lattice parameter for the bulk structure = 0.99(1), c lattice parameter for the sub-surface layer = 0.98(3), occupancy for O(3) = 1.02(5) and occupancy for O(4) = 0.82(9). The parameter nomenclature is based on the description in Figure S4. The figure of merit obtained for this structure was 0.092.

Parameter	X	У	Z
SUB-SURFACE LAYER			
Ru (1)	0	0	-0.018(4)
Ru (2)	1.555	3.175	0.019(5)
Ru (3)	1.555	0	3.197(5)
Ru (4)	0	3.175	3.154(6)
0(1)	0	3.175	4.92(3)
0 (2)	0	0	4.240(1)
0 (3)	1.555	4.445	3.07(1)
0 (4)	1.555	1.905	3.08(2)
0 (5)	0	0	1.81(5)
0 (6)	0	3.175	1.213(5)
0 (7)	1.555	1.27	-0.02(4)
0 (8)	1.555	5.08	-0.16(2)
SURFACE LAYER			
Ru (1)	0	0	6.288(9)
Ru (2)	1.555	3.175	6.406(7)
0 (1)	1.555	1.27	6.18(3)
0 (2)	1.555	5.08	6.199(4)
ADSORBED			
0 (3)	0	3.175	7.59(1)
0 (4)	0	0	8.48(1)
Direction vectors			
VEC1	3.11	0	0.000
VEC2	0	6.35	0.000
VEC3	0	0	6.350

Table S4: Final atomic positions obtained for the structure at 1.3 V<sub>RHE</sub>. Additional parameters that were fitted and are not included in the table are: c lattice parameter for the bulk structure = 1.02(1), c lattice parameter for the sub-surface layer = 0.99(3), occupancy for O(3) = 0.90(6) and occupancy for O(4) = 0.80(8). The parameter nomenclature is based on the description in Figure S4. The figure of merit obtained for this structure was 0.071

Parameter	X	У	Z
SUB-SURFACE LAYER			
Ru (1)	0	0	0.009(7)
Ru (2)	1.555	3.175	0.022(8)
Ru (3)	1.555	0	3.22(1)
Ru (4)	0	3.175	3.16(2)
0 (1)	0	3.175	4.95(7)
0 (2)	0	0	4.39(9)
0 (3)	1.555	4.445	3.05(9)
0 (4)	1.555	1.905	3.09(6)
0 (5)	0	0	1.93(3)
0 (6)	0	3.175	1.23(4)
0 (7)	1.555	1.27	0.03(7)
0 (8)	1.555	5.08	0.03(5)
SURFACE LAYER			
Ru (1)	0	0	6.32(2)
Ru (2)	1.555	3.175	6.41(3)
0(1)	1.555	1.27	6.22(6)
0 (2)	1.555	5.08	6.54(8)
ADSORBED			
0 (3)	0	3.175	7.50(3)
0 (4)	0	0	8.39(4)
Direction vectors			
VEC1	3.11	0	0
VEC2	0	6.35	0
VEC3	0	0	6.35

Table S5: Final atomic positions obtained for the structure at 1.5 V<sub>RHE</sub>. Additional parameters that were fitted and are not included in the table are: c lattice parameter for the bulk structure = 0.98(1), c lattice parameter for the sub-surface layer = 1.01(1), occupancy for O(3) = 0.95(6), occupancy for O(4) = 0.97(2) and occupancy for O(5) = 0.94(5). The parameter nomenclature is based on the description in Figure S4. The figure of merit obtained for this structure was 0.081

Parameter	х	У	Z
SUB-SURFACE LAYER			
Ru (1)	0	0	0.004(1)
Ru (2)	1.555	3.175	0.014(1)
Ru (3)	1.555	0	3.194(2)
Ru (4)	0	3.175	3.177(3)
0 (1)	0	3.175	5.23(2)
0 (2)	0	0	4.34(2)
0 (3)	1.555	4.445	3.21(1)
0 (4)	1.555	1.905	3.24(6)
0 (5)	0	0	1.902(4)
0 (6)	0	3.175	1.20(1)
0 (7)	1.555	1.27	0.03(1)
0 (8)	1.555	5.08	0.027(9)
SURFACE LAYER			
Ru (1)	0	0	6.348(5)
Ru (2)	1.555	3.175	6.375(2)
0 (1)	1.555	1.27	6.51(2)
0 (2)	1.555	5.08	6.576(1)
ADSORBED			
0 (3)	0	3.175	7.529(1)
0 (4)	0	0	8.57(2)
0 (5)	0	0.579(5)	9.67(4)
Direction vectors			
VEC1	3.11	0	0
VEC2	0	6.35	0
VEC3	0	0	6.35

Parameter	0.5 V	1.0 V	1.3 V	1.5 V
SUB-SURFACE LAYER				
Ru (1)	-0.007(4)	-0.018(4)	0.009(7)	0.004(1)
Ru (2)	-0.004(2)	0.019(5)	0.022(8)	0.014(1)
Ru (3)	3.162(2)	3.197(5)	3.22(1)	3.194(2)
Ru (4)	3.163(3)	3.154(6)	3.16(2)	3.177(3)
0 (1)	5.00(4)	4.92(3)	4.95(7)	5.23(2)
0 (2)	4.56(2)	4.240(1)	4.39(9)	4.34(2)
0 (3)	3.11(1)	3.07(1)	3.05(9)	3.21(1)
0 (4)	3.22(2)	3.08(2)	3.09(6)	3.24(6)
0 (5)	2.13(4)	1.81(5)	1.93(3)	1.902(4)
0 (6)	1.311(4)	1.213(5)	1.23(4)	1.20(1)
0 (7)	-0.15(2)	-0.02(4)	0.03(7)	0.03(1)
0 (8)	0.10(2)	-0.16(2)	0.03(5)	0.027(9)
SURFACE LAYER				
Ru (1)	6.275(6)	6.288(9)	6.32(2)	6.348(5)
Ru (2)	6.362(7)	6.406(7)	6.41(3)	6.375(2)
0 (1)	6.29(4)	6.18(3)	6.22(6)	6.51(2)
0 (2)	6.54(2)	6.199(4)	6.54(8)	6.576(1)
ADSORBED				
0 (3)	7.91(4)	7.59(1)	7.50(3)	7.529(1)
0 (4)	8.96(2)	8.48(1)	8.39(4)	8.57(2)
0 (5)	N/A	N/A	N/A	9.67(4)

Table S6: Summary of z component of final atomic positions obtained for the structures at 0.5  $V_{RHE}$ , 1.0  $V_{RHE}$ , 1.3  $V_{RHE}$  and 1.5  $V_{RHE}$ .



Figure S5: (A) (02L) (B) (20L) and (C) (11L) rods measured at the four different potentials, 0.5  $V_{RHE}$ , 1.0  $V_{RHE}$ , 1.3  $V_{RHE}$  and 1.5  $V_{RHE}$  as indicated. The experimentally measured intensities are shown in open points and the best-fit results from the fitting process are shown in solid lines of the corresponding color.

#### Sensitivity of fit analysis

In order to validate that the fitted CTR data are sensitive to the position of the oxygen atop the  $Ru_{CUS}$  site as well as the oxygen bound to the  $Ru_{BRI}$  site, a detailed sensitivity of fit analysis was performed. A single bond distance (for instance, the  $Ru_{CUS}$ -O distance) was constrained to a value higher or lower than the best-fit solution, while all other parameters were allowed to vary as described in the original model (Table S1).



Figure S6: Sensitivity of fit analysis for the CTR data obtained at 0.5  $V_{RHE}$ . For each panel, the parameter that is constrained is noted and the bond distance obtained for the unconstrained adsorbates is shown. The experimentally measured intensities are shown in open points and the fitting results are shown in solid lines of the corresponding color. Grey arrows are used to indicate the region where the fitted intensities are noticeably different from the best-fit solution.



Figure S7: Sensitivity of fit analysis for the CTR data obtained at 1.0  $V_{RHE}$ . For each panel, the parameter that is constrained is noted and the bond distance obtained for the unconstrained adsorbates is shown. The experimentally measured intensities are shown in open points and the fitting results are shown in solid lines of the corresponding color. Grey arrows are used to indicate the region where the fitted intensities are noticeably different from the best-fit solution.

In order to capture the hydrogen bonding between adsorbed CUS oxygen and bridging oxygen observed by DFT (Figure 2H and 2I), the oxygen atoms in the CTR model (obtained with a y-value constrained to that of the bulk) were moved to the DFT predicted y values. Figure S8A and S9A show the resultant oxygen rods, (01L) and (10L) with the DFT-obtained y position. In addition, if the resulting structure was allowed to relax, the resulting fitted structure obtained is shown in Figure S8B and S9B. The quality of the resulting fit and overall bond length are relatively insensitive to the y displacement of the adsorbed oxygen atoms predicted by DFT.

A.  $\Delta y_{\text{CUS OXYGEN}}$  = 0.52 Å and  $\Delta y_{\text{BRIDGE OXYGEN}}$  = 0.158 Å

 $Ru_{CUS}-O = 2.72 \text{ Å}, Ru_{BRI}-O = 2.23 \text{ Å}$ 

B. Best-fit solution, with  $\Delta y_{\text{CUS OXYGEN}}$  = 0.52 Å and  $\Delta y_{\text{BRIDGE OXYGEN}}$  = 0.158 Å





Figure S8: Sensitivity of fit analysis for the CTR data obtained at 0.5  $V_{RHE}$ . (A) The best-fit solution with the y position for the adsorbed oxygen moved to the DFT predicted value. (B) The best-fit solution with the y position of the adsorbed oxygen moved to the DFT predicted value and the other parameters allowed to relax.



Figure S9: Sensitivity of fit analysis for the CTR data obtained at 1.0  $V_{RHE}$ . (A) The best-fit solution with the y position for the adsorbed oxygen moved to the DFT predicted value. (B) The best-fit solution with the y position of the adsorbed oxygen moved to the DFT predicted value and the other parameters allowed to relax.



Figure S10: Sensitivity of fit analysis for the CTR data obtained at 1.3  $V_{RHE}$ . For each panel, the parameter that is constrained is noted and the bond distance obtained for the unconstrained adsorbates is shown. The experimentally measured intensities are shown in open points and the fitting results are shown in solid lines of the corresponding color. Grey arrows are used to indicate the region where the fitted intensities are noticeably different from the best-fit solution.



Figure S11: Sensitivity of fit analysis for the CTR data obtained at 1.5  $V_{RHE}$ . For each panel, the parameter that is constrained is noted and the bond distance(s) obtained for the unconstrained adsorbates is shown. The experimentally measured intensities are shown in open points and the fitting results are shown in solid lines of the corresponding color. Grey arrows are used to indicate the region where the fitted intensities are noticeably different from the best-fit solution.



Figure S12: Ball and stick models for the best-fit structures obtained for the (A)  $0.5 V_{RHE}$  (B)  $1.0 V_{RHE}$  (C)  $1.3 V_{RHE}$  and (D)  $1.5 V_{RHE}$  from the crystal truncation rod data. The number in parenthesis denotes the value of uncertainty in the bond length in the last digit. Pink and red spheres represent Ru and O atoms respectively.

#### **Evaluating the relative Gibbs adsorption energies as a function of potential**

DFT-generated diagrams showing the relative Gibbs adsorption energies of the different adsorbate configurations as a function of applied electrochemical potential can be constructed based on the computation hydrogen electrode approach proposed by Nørskov *et al*<sup>5</sup>. We base our calculations relative to the RuO<sub>2</sub> (110) stoichiometric surface. The stoichiometric surface consists of –O present on the Ru bridge site with the CUS site empty or filled with an adsorbed water.

The stability of a surface as a function of potential depends on how many protons are lost or gained relative to the stoichiometric surface. For example, consider the first water dissociation on the CUS site:

 $H_2O + * \Leftrightarrow -OH + H^+ + e^-$ 

The Gibbs free energy change can be expressed as:

$$G(-OH) - G(*) = G(H_2O) - G(H^+ + e^-)$$

where  $G(H^+ + e^-) = -eV - kTln(a_{H^+})$ Therefore,

$$G(-OH) - G(*) = G(H_2O) + eV + kTln(a_{H^+})$$

For a proton activity of 1, the difference in Gibbs free energy is directly proportional to the potential, with the proportionality constant being the number of electrons (or protons) reduced relative to the stoichiometric surface.

# **Structures considered and their energetics**

Table S7: Absolute values of the adsorption energy, ZPE and TS and Gibbs Free Energy for different adsorbate configurations on the Ru bridge and CUS sites on the RuO<sub>2</sub> (110) surface

Species on bridge site	Species on CUS site	Adsorption energy (eV)	Zero point energy	TS@298K	Gibbs Free Energy of adsorption (eV)
X	X	-0.257	0.000	0.000	-0.213
H <sub>2</sub> O	H₂O	-1.496	2.658	0.444	-0.166
0	X	0.000	0.135	0.101	0.017
0	H₂O	-1.168	1.497	0.259	-0.459
ОН	X	-1.001	0.753	0.126	-0.620
ОН	H₂O	-2.083	2.141	0.301	-1.006
ОН	OH/H₂O	-1.815	1.844	0.252	-0.895
0	OH/H₂O	-0.577	1.204	0.262	-0.049
0	ОН	0.239	0.888	0.240	0.586
О/ОН	H <sub>2</sub> O/OH	-1.247	1.455	0.214	-0.536
ОН	ОН	-1.170	1.500	0.260	-0.460
О/ОН	H₂O/O	-0.388	1.218	0.250	0.153
О/ОН	ОН/ОН	-0.277	1.152	0.283	0.215
О/ОН	O/H₂O	-0.430	1.220	0.245	0.114
0	0	1.816	0.285	0.231	1.800
0	00	4.532	0.391	0.410	4.436
ОН	00	3.090	1.053	0.341	3.426

ОН	ООН	2.167	1.674	0.359	2.871
0	ООН	3.546	1.042	0.359	3.867
ОН	OOH_O	189.751	1.587	0.299	190.429
ОН	OOH_OH	0.307	1.587	0.302	1.017
OH_O	ОН_ОО	1.756	0.960	0.364	2.055
OH/O	OH/OOH	0.873	1.264	0.289	1.395
ОН	00/0	1.787	0.974	0.304	2.123
OH/O	OOH/O	1.872	0.993	0.325	2.207
OH/O	OOH/OH	0.914	1.261	0.295	1.432
OH/O	00H/00	3.205	1.048	0.329	3.544
OH/O	ООН	2.722	1.370	0.381	3.230
OH/O	0/00	2.463	0.672	0.268	2.633
OH/O	00/0	2.396	0.679	0.291	2.558
OH/O	0/00Н	1.932	0.982	0.354	2.247
OH/O	OO/OH	1.687	0.965	0.301	2.020
OH/O	00/00	3.768	0.742	0.319	3.926
OH/O	00/00H	3.215	1.032	0.360	3.530
0	OOH/OH	1.857	0.968	0.315	2.185
0	OOH/O	2.667	0.668	0.338	2.801

#### Comparison between experimental and DFT bond lengths



Figure S13: Comparison between the experimental and average theoretical Ru-O bond length for the (A) CUS and (B) bridge site. The same trends are observed both experimentally and theoretically and we find that the differences in values of the bond lengths are within 20%.

#### Additional DFT considerations

Computationally, it was found that a structure with alternating -00 and -0 on the CUS site and a fully oxidized bridge site is found to be  $\sim 0.1$  eV more stable than state VI (observed in the CTR data) at the OER potential, but we ascribe this to the calculational uncertainty associated with the specific choice of (PBE-GGA) exchange correlation functional to study OER intermediates<sup>6</sup> and the lack of explicit water in the calculations. Figure S14 shows a diagram evaluating the stability of adsorbate structures as a function of potential, with the inclusion of this structure.



Figure S14: DFT-generated diagram showing the relative Gibbs adsorption energies of the most stable facets for increasing applied electrochemical potential. The structure realized at a specific potential is the one with the lowest free energy at that potential, and the transition from one stable structure to another (depicted by the intersection point of two lines) corresponds to an experimentally observed redox transition. The x-axis shows the applied potential of the cyclic voltammogram trace (black) and the calculated DFT potential vs RHE. The most stable facets at each voltage are shown in thick lines, with the adsorbate configuration corresponding to the filled lines noted above them. The navy blue line at high potentials corresponds to the structure with alternating –OO and –O on the CUS site and a fully oxidized bridge site.

Calculations were also performed using GPAW! with the RPBE functional<sup>7,8</sup>. The kpoint sampling was performed with a Monkhurst-Pack grid of 4x4x1 and a grid spacing of 0.18 Å. The atoms were simulated using the new setups for Ru and O (gpaw-setups 0.9.11271). The super cells are identical to the ones discussed in the main text and were set up using the ASE<sup>9</sup>.



Figure S15: DFT-generated diagram showing the relative Gibbs adsorption energies of the most stable facets for increasing applied electrochemical potential using the RPBE functional. The structure realized at a specific potential is the one with the lowest free energy at that potential, and the transition from one stable structure to another (depicted by the intersection point of two lines) corresponds to an experimentally observed redox transition. The x-axis shows the applied potential of the cyclic voltammogram and the calculated DFT potential *vs* RHE. The most stable facets at each voltage are shown in thick lines, with the adsorbate configuration corresponding to the filled lines noted above them.



Free energy diagrams for the proposed OER mechanism

Figure S16: Free energy diagram at 0  $V_{DFT-RHE}$  for the OER mechanism based on DFT calculations showing the six possible intermediates. The dashed line indicates an unstable and an –OOH precursor state, which is needed for –OO formation.



Figure S17: Free energy diagram at 1.23  $V_{DFT-RHE}$  for the OER mechanism based on DFT calculations showing the six possible intermediates. The dashed line indicates an unstable and an –OOH precursor state, which is needed for –OO formation.

### References

<sup>1</sup> YD Kim, AP Seitsonen, S Wendt, J Wang, C Fan, K Jacobi, H Over, G Ertl, *The Journal of Physical Chemistry B*, 2001, 105(18), 3752-3758

<sup>2</sup> K Reuter, M Scheffler, *Physical Review B*, 2001, 65(3), 035406

<sup>3</sup> K Reuter, M Scheffler, *Surface Science*, 2001, 490(1), 20-28

<sup>4</sup> YS Chu, TE Lister, WG Cullen, H You, Z Nagy, *Physical Review Letters*, 2001, 86(15), 3364-3367

<sup>5</sup> JK Nørskov, J Rossmeisl, A Logadottir, L Lindqvist, JR Kitchin, T Bligaard, H Jónsson, *The Journal of Physical Chemistry B*, 2004, **108**(46), 17886-17892

<sup>6</sup> R Christensen, HA Hansen, CF Dickens, JK Nørskov, T Vegge, *The Journal of Physical Chemistry C*, 2016, **120**(43), 24910-24916.

<sup>7</sup> JJ Mortensen, LB Hansen, KW Jacobsen, *Physical Review B*, 2005, **71**(3), 035109.

<sup>8</sup> J Enkovaara, C Rostgaard, JJ Mortensen, J Chen, M Dułak, L Ferrighi, J Gavnholt, C Glinsvad, V Haikola, HA Hansen, *Journal of Physics: Condensed Matter*, 2010, **22**(25), 253202.

<sup>9</sup> A Larsen, J Mortensen, J Blomqvist, I Castelli, R Christensen, M Dulak, J Friis, M Groves, B Hammer, C Hargus, et al., *Journal of Physics: Condensed Matter*, 2017, **29**(27), 273002.