Key role of chemistry versus bias in electrocatalytic oxygen evolution

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The electrocatalytic oxygen evolution reaction supplies the protons and electrons needed to convert renewable electricity into chemical fuels[1–3]. Electrocatalysts accelerate the reaction by facilitating the two fundamental processes involved, electron transfer[4] and chemical bond formation/rupture[5]. The result is complex electrochemical kinetics that challenge development of renewable energy conversion technologies. Yet at sufficient rates, the current depends exponentially on overpotential[1,2,6,7]. For outer-sphere redox reactions this behavior emerges because the bias acts on the reaction coordinate in line with Butler-Volmer theory[8], therefore Tafel analysis affords mechanistic details under quasi-equilibrium[9,10,11] or steady-state assumptions[12]. However, oxidative charges also participate in chemical bond formation/rupture[13–15], but the role on electrocatalytic rate is unknown since the unclear effect of bias on inner-sphere chemistry renders Tafel analysis phenomenological[8]. Here we show such chemical bond making/breaking mediates the electrocatalytic rate. The applied bias is found to affect current through charge accumulation rather than acting directly on the reaction coordinate. Activation free energy is shown to depend linearly on the amount of oxidative charge stored in the electrocatalyst. We demonstrate how this relationship underlies electrocatalytic performance, how it can be computed/measured, and anticipate these results will aid in the design of new electrocatalytic materials.

Influence of charge on OER activity

The effects of chemical bond making/breaking steps on the oxygen evolution reaction (OER) rate become evident when pulse voltammetry is used to compare potential, charge, and performance (for details see Supplementary Discussion and Supplementary Fig. 1). The charge (total with respect to cathodic bias, unless otherwise noted) stored in the catalyst at a given potential is quantified by integrating the current response to the

cathodic voltage pulses, as highlighted for an amorphous IrO_x electrocatalyst calcined at 250 °C in Fig. 1a. This approach gives access to the Tafel plot (Fig. 1b) as well as the relationships between stored charge and potential (*iR* corrected vs. RHE, unless otherwise noted) or log current shown in Figs. 1c, d, respectively. For other samples see Supplementary Figs. 2-7.

The Tafel plot (Fig. 1b) shows the expected behavior. Up to 1.54 V the Tafel slope is 39 mV/dec, in line with the 40 mV/dec observed for Ir electrocatalysts[15]. Anodic of 1.54 V the Tafel slope increases to ~64 mV/dec, ascribed to a change in the rate determining step (rds)[9]. Charge is also bi-linear in potential (Fig. 1c), with the slope change at 1.54 V indicating the capacitance drops from ~22.1 mF to ~15.9 mF. These values exceed the expected double layer capacitance (see Supplementary Tables 1 and 2), and areal capacitances are 1-2 of orders of magnitude greater than that of an ideal electrode (Supplementary Table 2), suggesting additional means of pseudocapacitive charge storage are active[16], as is known for Ir (and Ru) based materials[17].

This pseudocapacitive charge storage appears to be connected to OER kinetics. Unlike the Tafel plot, the charge vs. log current profile (Fig. 1d) is linear throughout the potential range. Other materials (Supplementary Figs. 2-7), and the transient current response (Supplementary Discussion and Supplementary Figs. 1-8), provide identical trends, suggesting the observed behavior is general and that the OER rate may respond directly to pseudocapacitive charge.

Charge storage mechanism

Cyclic voltammetry (CV) performed under acidic conditions using Ir oxides with little or no crystallinity shows redox processes at 0.8 V to 1.0 V and near the OER onset, which are assigned to Ir^{III}/Ir^{IV} and Ir^{IV}/Ir^{V} redox couples, respectively[18] (Supplementary Fig. 9b). The capacitive behavior originating from these broad redox features is smooth with potential, behavior manifest in the charge storage mechanism. Consider, for instance, the evolution of charge vs. potential for IrO_x in a window of ~(0.8 to 1.6) V, Supplementary Fig. 10a. The total capacitance (~20 mF) is relatively independent of potential, and while its magnitude is sample dependent (see Supplementary Table 1 and Supplementary Fig. 10), the total capacitance of any particular catalyst remains similar over 0.8 V to 1.6 V. The magnitude of these numbers becomes apparent when BET area (Supplementary Table 3) is used to derive surface hole coverages (θ_{h+}). For crystalline (AA-D) at ~1.6 V the surface hole coverage is ~0.8 h^+ per surface Ir, or ~0.8 monolayer (ML). Amorphous Alpha-Aesar IrO_x, where bulk charging is expected, reaches θ_{h+} ~8 ML at the same potential. These hole concentrations are quantifiable by *operando* X-ray absorption spectroscopy (XAS), making it ideal for uncovering the atomic mechanism of charge storage (for details see Supplementary Text).

For the Ir $L_{2,3}$-edges, the integral intensity of their white lines (IWL) quantifies the number of empty 5d states on Ir, hence Ir oxidation state[7,19], as a function of potential (see Supplementary Fig. 11). The steady-state IWL of IrO_x (calcined at 250 °C) vs. potential, Fig. 2a, reveals the Ir oxidation state increases linearly with bias. Furthermore, the WL intensity at 11,221.5 eV tracks the IWL, enabling potentiodynamic XAS[18] at this energy.

With potentiodynamic XAS (Supplementary Fig. 11) we find the Ir oxidation state increases linearly with charge up to ~20 mC, Fig. 2b. Above ~20 mC Ir oxidation cannot

fully account for the stored charge, implying additional means are active. This finding is consistent with Ir oxides entering a negative charge transfer regime for oxidation states beyond Ir^{IV}, resulting in the formation of O^{I-} [7,20].

Two types of O with 2p hole character, μ_2-O and μ_1-O oxyl, can be distinguish in the O K-edge XAS, appearing at ~529 eV and ~528.3 eV, respectively[20,21]. Fig. 2c shows no evidence for either at 0.40 V, but increasing the bias to 1.67 V populates μ_2-O. Subsequent reduction to 0.77 V results in μ_2-O loss, which is reversed upon increasing the potential to 1.27 V, above which μ_2-O coverage continuously increases. Thus, μ_2-O formation is reversible and continues into the OER, where μ_1-O begins to coexist with μ_1-OH (Supplementary Fig. 12b).

Potentiodynamic XAS at 529 eV further reveals a linear correlation between charge and μ_2-O coverage, Fig. 2d, suggesting oxidative charge is accumulated by deprotonation of O (coupled to electron transfer) over the entire potential range, 0.95 V to 1.70 V (non-*iR* corrected). This relationship is general (Supplementary Fig. 13).

OER mechanism on Ir-based materials

Identifying deprotonation as the dominant charge storage mechanism allows its influence on OER rate to be studied by density functional theory (DFT) calculations. We began by equilibrating IrO_2 (110) surfaces in water using *ab initio* molecular dynamics (MD) at the PBE level while varying θ_{h+} (see Supplementary Discussion and Supplementary Videos 1-5). A θ_{h+} vs. potential phase diagram, Fig. 3, was generated using MD snapshots. Equilibration in water introduces Frumkin behavior[22,8] (Supplementary Fig. 14) and broadens the surface deprotonation window in agreement with experiment.

Knowing the phase diagram, we can turn to OER kinetics beginning with $\theta_{h+} = 3/4$ ML (Supplementary Fig. 15d) by taking the initial structure from an MD snapshot while retaining two water bilayers to recover surface solvation effects[23]. Minimum energy paths were computed in two ways: i) with fixed electrochemical bias[24,25] and ii) with fixed number of electrons[26]. The former is the experimental condition; the latter is a constraint to probe the degree to which an elementary step is chemical.

The choice of elementary steps was made by first considering the OER under acidic conditions as four proton-coupled electron transfers[26,27]:

1) $\quad * + H_2O \rightarrow OH_{ads} + H^+ + e^-$

2) $\quad OH_{ads} \rightarrow O_{ads} + H^+ + e^-$

3) $\quad O_{ads} + H_2O \rightarrow OOH_{ads} + H^+ + e^-$

4) $\quad OOH_{ads} \rightarrow OO_{ads} + H^+ + e^-$,

where * denotes an empty μ_1 site.

Tafel analysis suggests the second step is rate-limiting[10]; step 3 has also been suggested as the rds[26,27]. The remaining proton-coupled electron transfers are likely barrierless[26]. We found water nucleophilic attack (step 3) is rate-limiting and focus on it (see Supplementary Text).

External bias and rate

Consider the activation energy (E_a) for oxyl–water coupling with fixed bias, beginning with the potential of zero charge (pzc) for the $\theta_{h+} = 3/4$ ML surface (Supplementary Fig. 15d). We find O-O coupling occurs with concerted transfer of H to a μ_2-O site, Fig. 4a.

Similar to previous observations[26], E_a is 0.63 eV with a heat of reaction (ΔH_{rxn}) near zero, as denoted by a green triangle in Fig. 4b. The two additional green triangles at $\Delta H_{rxn} \sim 0$ eV in Fig. 4b show increasing the bias by 0.1 V and 0.5 V to capacitively charge the surface while constraining $\theta_{h+} = 3/4$ ML has little impact on E_a; the change is indicated by an arrow labeled Q_C.

If the surface oxidation state is not constrained when increasing bias by 0.5 V, however, the fully oxidized limit is reached (Supplementary Fig. 15e). The effect of including this additional oxidative charge to yield the total charge, Q_T, is indicated by a dashed arrow in Fig. 4b. Oxidative charging reduces ΔH_{rxn} to ~-0.2 eV; moreover, oxidation lowers E_a (from ~0.60 eV to 0.23 eV). Similarly, Fig. 4b shows reducing θ_{h+} from 3/4 to 1/2 ML (Supplementary Fig. 15c) increases E_a to 0.78 eV, and the change induced by this total charge, Q_T', is not compensated by pure capacitive charging (Q_C').

These results demonstrate E_a for O-O coupling obeys the Brønsted–Evans–Polanyi (BEP) relationship familiar from traditional catalysis. That is, E_a depends linearly on ΔH_{rxn}. Changes in ΔH_{rxn} are dominated by oxidative rather than capacitive charge, behavior expected from classical electrochemical theory as the kinetics of inner-sphere reactions should be insensitive to building a double-layer[8].

Oxidative charge and rate

While the previous examples suggest E_a of the rds is dominated by bond formation/rupture chemistry[5], they contain the electrode potential. The degree to which θ_{h+} alone mediates the relationship between E_a and ΔH_{rxn} is found by computing E_a while fixing the number of electrons to decouple the rds from the electrode. Doing so does not change the mechanism or break the linear relationship between E_a and ΔH_{rxn}, red squares in Fig. 4b. That is, $E_a = E_0 + \alpha \Delta H_{rxn}$ in the absence of electron transfer. Furthermore, the BEP slope (α) is insensitive to the chemical nature of the ligands introducing oxidative charge (see Supplementary Fig. 16 for Bader charges). The open red squares in Fig. 4b, for example, show the same trend when spectator O(H) is replaced by Cl (see Supplementary Discussion for details). Thus, as the surface becomes more reduced or oxidized, E_a increases or decreases, respectively. This dependence on θ_{h+} is consistent with inner-sphere chemistry; removing the solvation layers results only in a small change to the BEP relationship (Fig. 4b), in line with the expected minor role of the double layer on inner-sphere reaction kinetics.

The linear dependence of log current on θ_{h+} can now be seen to emerge because oxidation controls ΔH_{rxn}. The BEP relationship can then be recast as in Fig. 4c: $E_a = \zeta \theta_{h+} + \kappa$, allowing the electrocatalytic response of IrO$_2$ to be computed though an Eyring-like equation:

$$i = k_0 \theta_{\mu1} \exp\left(-\frac{\zeta\theta_{h+} + \kappa}{k_B T}\right) \quad \text{(Eq. 1)},$$

where the prefactor k_0 is independent of θ_{h+} (see Supplementary Eq. 13).

The Tafel plot and charge vs. log current profile computed using Eq. 1 are in agreement with experiment, Fig. 5. A Tafel slope of 39 mV/dec is found up to 1.58 V before increasing to 77 mV/dec; crystalline IrO$_2$ has Tafel slopes of 43-47 mV/dec and 71-76 mV/dec over the same potential windows (Supplementary Figs. 2 and 3). From the calculations the bend in the Tafel slope can now, however, be ascribed to a change in the response of θ_{h+} to potential, Fig. 5b, rather than the qualitative change in mechanism

suggested by Tafel analysis[9]. The computed log current vs. θ_{h+} profile is linear, Fig. 5c, consistent with experiment.

We anticipate this linear dependence of log current on charge is common. This is because bond rupture/formation is slow compared to electron transfer and BEP behavior is expected when bond making/breaking is the principal contributor to the reaction coordinate[5]. In support of this assertion, we find all the Ir-based catalysts show linear log current vs. charge profiles, Supplementary Figs. 2-8. Moreover, so do NiFe layered double hydroxides in alkaline electrolyte, Supplementary Fig. 17. While such behavior can emerge trivially on an electrode with constant capacitance, we argue it is rooted in OER catalysis, as shown for Ir based materials.

Activation free energies

An important consequence of these findings is that the linear activation free energy relationships underlying the electrocatalytic OER can be probed experimentally. In these cases the rds is decoupled from the potential, giving the θ_{h+} vs. log current profile a slope of $-k_{B}T \ln(10)/\zeta$. Assuming surface deprotonation charging and using BET areas from Supplementary Table 3, we find $\zeta \sim$ -1.2 and -1.3 eV/ML for the AA-D and AA-450°C catalysts, respectively. These values compare favorably with the computed $\zeta \sim$ -1.3 eV/ML, Fig. 4c. For κ we find 1.4 eV to 1.7 eV experimentally and ~1.6 eV from DFT.

Conclusions and Outlook

Demonstrating inner-sphere chemistry controls electrocatalytic OER rates establishes a fundamental link between thermal- and electrocatalysis. This enables tools and concepts developed to describe traditional catalysts to be applied to their electrochemical counterparts. Principal among these are the linear activation free energy relationships mediating catalytic rates, which we have shown can be measured and computed to offer new means of understanding and improving electrocatalysis.

References

1. Gür, T. M. Review of electrical energy storage technologies, materials and systems: challenges and prospects for large-scale grid storage. *Energy Environ. Sci.* 11, 2696–2767 (2018).
2. Seh, Z. W. *et al.* Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* 355, eaad4998 (2017).
3. Hu, C., Zhang, L. & Gong, J. Recent progress made in the mechanism comprehension and design of electrocatalysts for alkaline water splitting. *Energy Environ. Sci.* 12, 2620–2645 (2019).
4. Marcus, R. A. Electron transfer reactions in chemistry. Theory and experiment. *Rev. Mod. Phys.* 65, 599–610 (1993).
5. Marcus, R. A. Theoretical relations among rate constants, barriers, and Broensted slopes of chemical reactions. *J. Phys. Chem.* 72, 891–899 (1968).
6. Seitz, L. C. *et al.* A highly active and stable IrOx/SrIrO3 catalyst for the oxygen evolution reaction. *Science* 353, 1011–1014 (2016).
7. Nong, H. N. *et al.* A unique oxygen ligand environment facilitates water oxidation in hole-doped $IrNiO_x$ core–shell electrocatalysts. *Nat. Catal.* 1, 841–851 (2018).

8. Schmickler, W. & Santos, E. *Interfacial Electrochemistry*. (Springer, 2010). doi:10.1007/978-3-642-04937-8

9. Shinagawa, T., Garcia-Esparza, A. T. & Takanabe, K. Insight on Tafel slopes from a microkinetic analysis of aqueous electrocatalysis for energy conversion. *Sci. Rep.* 5, 13801 (2015).

10. De Faria, L. A., Boodts, J. F. C. & Trasatti, S. Electrocatalytic properties of ternary oxide mixtures of composition $Ru_{0.3}Ti_{(0.7-x)}Ce_xO_2$: oxygen evolution from acidic solution. *J. Appl. Electrochem.* 26, 1195–1199 (1996).

11. Lyons, M. E. G. & Brandon, M. P. A comparative study of the oxygen evolution reaction on oxidised nickel, cobalt and iron electrodes in base. *J. Electroanal. Chem.* 641, 119–130 (2010).

12. Mefford, J. T., Zhao, Z., Bajdich, M. & Chueh, W. C. Interpreting Tafel behavior of consecutive electrochemical reactions through combined thermodynamic and steady state microkinetic approaches. *Energy Environ. Sci.* 13, 622–634 (2020).

13. Corrigan, D. A. The catalysis of the oxygen evolution reaction by iron impurities in thin film nickel oxide electrodes. *J. Electrochem. Soc.* 134, 377 (1987).

14. Pearce, P. E. *et al.* Revealing the reactivity of the iridium trioxide intermediate for the oxygen evolution reaction in acidic media. *Chem. Mater.* 31, 5845–5855 (2019).

15. Grimaud, A. *et al.* Activation of surface oxygen sites on an iridium-based model catalyst for the oxygen evolution reaction. *Nat. Energy* 2, 16189 (2016).

16. Augustyn, V., Simon, P. & Dunn, B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy Environ. Sci.* 7, 1597–1614 (2014).

17. Conway, B. E. Electrochemical capacitors based on pseudocapacitance. in *Electrochemical supercapacitors: scientific fundamentals and technological applications* (ed. Conway, B. E.) 221–257 (Springer US, 1999). doi:10.1007/978-1-4757-3058-6_10

18. Kuo, D. Y. *et al.* Influence of surface adsorption on the oxygen evolution reaction on $IrO_2(110)$. *J. Am. Chem. Soc.* 139, 3473–3479 (2017).

19. Clancy, J. P. *et al.* Spin-orbit coupling in iridium-based 5d compounds probed by x-ray absorption spectroscopy. *Phys. Rev. B* 86, 195131 (2012).

20. Pfeifer, V. *et al.* In situ observation of reactive oxygen species forming on oxygen-evolving iridium surfaces. *Chem. Sci.* 8, 2143–2149 (2017).

21. Frevel, L. J. *et al.* In situ X-ray spectroscopy of the electrochemical development of iridium nanoparticles in confined electrolyte. *J. Phys. Chem. C* 123, 9146–9152 (2019).

22. Bard, A. J. & Faulkner, L. R. *Electrochemical methods - fundamentals and applications*. (John Wiley & Sons, Inc., 2000).

23. Gauthier, J. A., Dickens, C. F., Chen, L. D., Doyle, A. D. & Nørskov, J. K. Solvation effects for oxygen evolution reaction catalysis on $IrO_2(110)$. *J. Phys. Chem. C* 121, 11455–11463 (2017).

24. Otani, M. & Sugino, O. First-principles calculations of charged surfaces and interfaces: A plane-wave nonrepeated slab approach. *Phys. Rev. B* 73, 115407

(2006).

25. Bonnet, N., Morishita, T., Sugino, O. & Otani, M. First-principles molecular dynamics at a constant electrode potential. *Phys. Rev. Lett.* 109, 266101 (2012).

26. Ping, Y., Nielsen, R. J. & Goddard, W. A. The reaction mechanism with free energy barriers at constant potentials for the oxygen evolution reaction at the IrO_2(110) surface. *J. Am. Chem. Soc.* 139, 149–155 (2017).

27. Rossmeisl, J., Qu, Z.-W., Zhu, H., Kroes, G.-J. & Nørskov, J. K. Electrolysis of water on oxide surfaces. *J. Electroanal. Chem.* 607, 83–89 (2007).

Fig. 1 | Measured electrocatalytic response of IrO$_x$/Ti-250°C. a, Section of the pulse voltammetry protocol (black) showing an oxidative and reductive pulse with the current response (red). **b**, Tafel plot (potential vs. log current in mA) from pulse voltammetry. **c**, Charge vs. potential and **d**, charge vs. log current from pulse voltammetry. For other samples see Supplementary Figs. 2-7.

Fig. 2 | Charge storage under steady-state and potentiodynamic conditions. a, The L$_2$ + L$_3$ IWL (left) and the normalized fluorescence yield signal at 11,221.5 eV (right) of steady-state *operando* Ir L-edge XAS of IrO$_x$/Ti-250°C vs. potential together with the dry sample and reference IrO$_2$, for details see Supplementary Fig. 11. **b**, Correlation of the signal change of the Ir L$_3$-edge at 11,221.5 eV vs. total charge. Sample: IrO$_x$/Ti-250°C **c**, Steady-state operando O K-edge XAS of IrO$_x$/Graphene-250°C at (non-*iR* corrected) potentials in the order indicated. Dashed lines show the peak position of μ$_2$-O (528.9 eV) and μ$_1$-OH (529.7 eV). **d**, Signal change at 529 eV vs. the total charge; reduced catalyst loading results in a smaller magnitude of charge than in **b**, see Supplementary Fig. 12a. Sample: IrO$_x$/Graphene-250°C; two experiments with different cathodic potentials are shown. For another sample see Supplementary Fig. 13.

Fig. 3 | Computed surface pH vs. potential (normal hydrogen electrode, NHE) phase diagram. Constructed for rutile-type IrO$_2$ (110) surface with total hole coverage with respect to fully protonated surface indicated. (See Supplementary Discussion, Supplementary Fig. 14, and Supplementary Fig. 15).

Fig. 4 | Computed mechanism and energetics of water-oxyl coupling. a, Mechanism on the (110) surface of IrO$_2$. In the initial state, a water molecule near the oxyl (left panel) forms an O-O bond with μ$_1$-O at the transition state (middle panel)—for clarity only waters directly involved are shown—with the simultaneous transfer of hydrogen to a surface μ$_2$-O through the formation of Zundel-like species. In the final state (right panel) a μ$_1$-OOH is present. **b**, E_a computed for O-O coupling plotted as a function of ΔH_{rxn}; ΔH_{rxn} becomes more negative as θ_{h+} increases. Green triangles show E_a at the pzc for surfaces with θ_{h+} = 1/2 ML, 3/4 ML, and 1 ML (in order of increasing exothermicity) under constant potential conditions. For θ_{h+} of 1/2 ML and 3/4 ML green triangles include results with capacitive charging from 0.1 V to 0.5 V, denoted by Q_C (Q_C') for the θ_{h+} = 3/4 ML (1/2 ML) surface; the small arrows indicate E_a marginally drops with capacitive charging. The arrow labeled Q_T shows the effect of the corresponding total charge for the θ_{h+} = 3/4 ML surface with an additional 0.5 V bias. Q_T' shows the effect of reducing θ_{h+} = 3/4 ML to θ_{h+} = 1/2 ML. Red squares show E_a as a function of ΔH_{rxn} under constant charge conditions. The unfilled red squares show surfaces with adsorbed Cl, which was used to investigate a non-reducible ligand (see Supplementary Text). Blue diamonds show solvent free energies. **c**, E_a for O-O coupling as a function of θ_{h+}.

Fig. 5 | Computed electrocatalytic response of IrO$_2$. a, Tafel plot computed with DFT data from the IrO$_2$ (110) surface using Eq. 1. **b**, Computed θ_{h+} vs. potential corresponding to **a**. **c**, Computed θ_{h+} vs. log current corresponding to **a**. OER current in **a** and **c** is in mA.

Competing interests Authors declare no competing interests.

Data availability All data is available in the main text or the supplementary materials and from the Open Research Data Repository of the Max Planck Society, https://dx.doi.org/10.17617/3.48. Source data for **Figs. 1-5** are provided with the paper.

Author contributions
TEJ and DT designed the study, analyzed data and wrote the manuscript. HNN carried out electrochemical measurements with the help of MK, HPT, and CS. HNN, LF, CS, and DT, performed soft X-ray measurements. HNN, AB, JT, and DT performed hard X-ray measurements. TEJ performed DFT calculations with the help of SP. GZ prepared Cl treated samples under the supervision of JPR. HNN prepared IrOx-250, IrOx-450 and IrNi samples. JPR, BRC, RS, and PS offered guidance for the project. All authors commented on the manuscript.

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Supplementary information contains Supplementary Methods, Supplementary Discussion, Supplementary Figures 1-22, Supplementary Tables 1-7, and References.

a

Non-*iR* corrected potential (V) / Current (mA)
Time (s)

Non-*iR* corrected potential
Current

b IrO$_x$/Ti-250 °C

$E = 0.039\log(i) + 1.501$
$E = 0.064\log(i) + 1.478$

$R^2 = 0.999$
$R^2 = 0.997$

E vs. RHE (V)
log OER current

c IrO$_x$/Ti-250 °C

$Q = 22.146E - 30.239$
$Q = 15.870E - 20.565$

$R^2 = 0.999$
$R^2 = 0.989$

Total charge (mC)
E vs. RHE (V)

d IrO$_x$/Ti-250 °C

$Q = 0.884\log(i) + 2.994$
$Q = 1.022\log(i) + 2.881$

$R^2 = 0.999$
$R^2 = 0.996$

Total charge (mC)
log OER current

a

dry sample

IrO$_2$ reference

$L_3 \cdot L_2$ white line area

Norm. FY signal at 11221.5 eV

E vs RHE (V)

b

IrO$_x$/Ti-250 °C

- - - Linear Fit
—— Linear Fit

Signal change at 11,221.5 eV

Total charge (mC)

- - - R^2 = 0.982
—— R^2 = 1

c

IrO$_x$/Ti-250 °C

1. potential 0.4 V
2. 1.67 V
3. 0.77 V
4. 1.27 V
5. 1.47 V
6. 1.57 V

Intensity (a.u.)

Photon energy (eV)

d

IrO$_x$/Ti-250 °C

■ E_i: 0.75 V
● E_i: 1.1 V
—— Linear fit

Signal change at 529 eV (a.u.)

Total charge (μC)

R^2 = 0.986

a

b

E_a (eV)

- ■ □ Fixed charge with solvent
- ▲ Fixed bias with solvent
- ◆ Fixed charge no solvent

Q_C Q_T' Q_C'

Q_T

—— Fit: All data with solvent
$E_a = 0.83\ H_{rxn} + 0.48\ (R^2 = 0.88)$

—— Fit: All data no solvent
$E_a = 0.70\ H_{rxn} + 0.36\ (R^2 = 0.89)$

Δ Heat of reaction (eV)

c

E_a (eV)

—— $R^2 = 0.963$

- ■ No Cl
- □ With Cl
- —— Linear Fit (All data points)
  $E_a = -1.33\theta_{h+} + 1.62$

Hole coverage (ML)

a

DFT

$E = 0.039\log(i) + 1.58$
$E = 0.077\log(i) + 1.58$

$R^2 = 0.998$
$R^2 = 0.998$

E vs. RHE (V)

log OER current

b

DFT

$\theta_{h+} = 1.16E - 1.17$
$\theta_{h+} = 0.57E - 0.24$

$R^2 = 0.999$
$R^2 = 0.998$

Hole coverage (ML)

E vs. RHE (V)

c

DFT

$\theta_{h+} = 0.045\log(i) + 0.66$
$\theta_{h+} = 0.044\log(i) + 0.66$

$R^2 = 1$
$R^2 = 1$

Hole coverage (ML)

log OER current