Key role of chemistry versus bias in electrocatalytic oxygen evolution

https://doi.org/10.1038/s41586-020-2908-2

Received: 14 November 2019

Accepted: 16 September 2020

Published online: 18 November 2020

Check for updates

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The oxygen evolution reaction has an important role in many alternative-energy schemes because it supplies the protons and electrons required for converting renewable electricity into chemical fuels¹⁻³. Electrocatalysts accelerate the reaction by facilitating the required electron transfer⁴, as well as the formation and rupture of chemical bonds⁵. This involvement in fundamentally different processes results in complex electrochemical kinetics that can be challenging to understand and control, and that typically depends exponentially on overpotential^{1,2,6,7}. Such behaviour emerges when the applied bias drives the reaction in line with the phenomenological Butler-Volmer theory, which focuses on electron transfer⁸, enabling the use of Tafel analysis to gain mechanistic insight under quasi-equilibrium⁹⁻¹¹ or steady-state assumptions¹². However, the charging of catalyst surfaces under bias also affects bond formation and rupture¹³⁻¹⁵, the effect of which on the electrocatalytic rate is not accounted for by the phenomenological Tafel analysis⁸ and is often unknown. Here we report pulse voltammetry and operando X-ray absorption spectroscopy measurements on iridium oxide to show that the applied bias does not act directly on the reaction coordinate, but affects the electrocatalytically generated current through charge accumulation in the catalyst. We find that the activation free energy decreases linearly with the amount of oxidative charge stored, and show that this relationship underlies electrocatalytic performance and can be evaluated using measurement and computation. We anticipate that these findings and our methodology will help to better understand other electrocatalytic materials and design systems with improved performance.

We explore the effects of chemical bond making/breaking steps on the oxygen evolution reaction (OER) rate of iridium oxide electrocatalysts using pulse voltammetry to compare potential, charge and performance (for details, see Supplementary Discussion and Supplementary Fig. 1).

Influence of charge on OER activity

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 ($IrO_x/Ti-250$ °C) in Fig. 1a. This approach gives access to the Tafel plot (Fig. 1b), as well as to the relationships between stored charge and potential (Ohmic potential drop, *iR*, corrected versus RHE, unless otherwise noted; RHE,

reversible hydrogen electrode) or log(current), as shown in Fig. 1c and Fig. 1d, respectively. For other samples, see Supplementary Figs. 2–7.

The Tafel plot (Fig. 1b) shows the expected behaviour: up to 1.54 V the Tafel slope is 39 mV dec⁻¹, in line with the 40 mV dec⁻¹ observed for Ir electrocatalysts¹⁵; anodic of 1.54 V, the Tafel slope increases to about $64 \text{ mV} \text{ dec}^{-1}$, which is ascribed to a change in the rate-determining step (rds)⁹. Charge is also bilinear in potential (Fig. 1c), with the slope change at 1.54 V indicating that the capacitance drops from about 22.1 mF to about 15.9 mF. These values exceed the expected double-layer capacitance (see Supplementary Tables 1, 2), and areal capacitances are 1-2 orders of magnitude greater than that of an ideal electrode (Supplementary Table 2). These differences suggest that additional means of charge storage are active¹⁶, with such pseudocapacitance known for Ir- (and Ru-) based materials¹⁷. In addition, unlike the Tafel plot, the charge–log(current) profile (Fig. 1d) is linear throughout

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1.58

1.56

ຣ^{1.54}

Э Н Ц 1.52 S 1.50

1.46

1.44

45

4.0

3.5

3.0

2.5

2.0

1.5

10

-2.0

-2.0

ш 1.48

d

Fotal charge (mC)

IrO_/Ti-250 °C

-1.5

IrO,/Ti-250 °C

-1.5

-1.0 -0.5

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

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

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

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

-0.5

-1.0

0.0

log[OER current (mA)]

0.5

Fig. 1|Measured electrocatalytic response of IrO,/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 versus

log[OER current (mA)] log(current) in milliamperes) from pulse voltammetry. c, d, Charge versus potential (c) and versus log(current) (d) from pulse voltammetry. For other samples, see Supplementary Figs. 2-7.

0.5 1.0

0.0

 $R^2 = 0.999$

 $R^2 = 0.997$

1.5 2.0

 $R^2 = 0.999$

 $R^2 = 0.996$

1.5

2.0

1.0

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 that the observed behaviour is general and that the OER rate may respond directly to pseudocapacitive charge.

Charge-storage mechanism

Cyclic voltammetry performed under acidic conditions on Ir oxide samples with little or no crystallinity shows redox processes occurring at 0.8 V-1.0 V and near the OER onset that are assigned to Ir^{III}/Ir^{IV} and Ir^{IV}/ Ir^v redox couples, respectively¹⁸ (Supplementary Fig. 9b). The capacitive behaviour originating from these broad redox features is smooth with potential-a behaviour manifest in the charge-storage mechanism. This is illustrated by the evolution of charge versus potential for IrO_y in a window of about 0.8-1.6 V shown in Supplementary Fig. 10a, with the total capacitance (about 20 mF) relatively independent of potential. For other catalyst samples the magnitude of the total capacitance varies (see Supplementary Table 1 and Supplementary Fig. 10), but the total capacitance of any particular catalyst remains fairly constant from 0.8 V to 1.6 V.

The capacitance values are put into context when using the Brunauer-Emmett-Teller (BET) surface areas of the catalyst samples (Supplementary Table 3) to estimate surface hole (h^+) coverages (θ_{h+}). For crystalline samples (Deacon-treated Alfa Aesar, AA-D) oxidized from 0.8 V to about 1.6 V, this gives a value of about 0.8 h⁺ per surface Ir or about 0.8 monolayers (ML), whereas amorphous Alfa Aesar (AA) IrO_x that is expected to undergo bulk charging reaches $\theta_{h+} \approx 8$ ML in the same potential window. These hole concentrations are quantifiable by operando X-ray absorption spectroscopy (XAS), making it ideal for uncovering the atomic details of the charge storage (for details, see Supplementary Information).

For the Ir L_{2.3} edges, the integral intensity of their white lines (IWL), measured as a function of applied potential, guantifies the number of empty 5d states and hence the oxidation state of Ir (refs. ^{7,19}; see Supplementary Fig. 11). The plot of the steady-state IWL of IrO_x (calcined at 250 °C) versus potential in Fig. 2a shows that the Ir oxidation state increases linearly with bias. Furthermore, the white-line intensity at 11,221.5 eV tracks the IWL, enabling potentiodynamic XAS¹⁸ at this energy (Supplementary Fig. 11) to show that the Ir oxidation state increases linearly with charge up to about 20 mC (Fig. 2b). Above about 20 mC, Ir oxidation cannot fully account for the stored charge, implying that 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-} (refs. ^{7,20}).

Two types of O with 2p hole character, μ_2 -O and μ_1 -O oxyl, can be distinguished in the OK-edge XAS, appearing at about 529 eV and around 528.3 eV, respectively^{20,21}. Figure 2c shows no evidence for the presence of either species 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 that oxidative charge is accumulated by surface deprotonation (coupled to electron transfer) over the entire potential range, 0.95-1.70 V (non-*iR* corrected). This relationship is general (Supplementary Fig. 13).

OER mechanism on Ir-based materials

With deprotonation identified as the dominant charge-storage mechanism, we study its influence on the OER rate by density functional theory (DFT) calculations. We first equilibrate IrO₂ (110) surfaces in water using ab initio molecular dynamics (MD) at the Perdew-Burke-Ernzerhof level while varying θ_{h+} (see Supplementary Discussion and



Fig. 2 | **Charge storage under steady-state and potentiodynamic conditions. a**, The L₃+L₂ IWL (left) and the normalized fluorescence yield (FY) signal at 11,221.5 eV (right) of steady-state operando Ir L-edge XAS of IrO_x/Ti-250 °C versus the potential, together with the dry sample and reference IrO₂; for details, see Supplementary Fig. 11. **b**, Correlation of the signal change of the IrL₃ edge at 11,221.5 eV versus total charge. Sample: IrO_x/Ti-250 °C. **c**, Steady-state operando O K-edge XAS of IrO_y/graphene-250 °C at (non-*iR*-corrected)

Supplementary Videos 1–5) and generate a phase diagram of θ_{h+} versus potential (Fig. 3) using MD snapshots. Equilibration in water introduces Frumkin behaviour^{8,22} (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 effects²³. Minimum-energy paths were computed in two ways: (i) with fixed electrochemical bias^{24,25} and (ii) with fixed number of electrons²⁶. 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}:

 $\begin{array}{l} (1)^* + H_2O \rightarrow OH_{ads} + H^+ + e^- \\ (2) OH_{ads} \rightarrow O_{ads} + H^+ + e^- \\ (3) O_{ads} + H_2O \rightarrow OOH_{ads} + H^+ + e^- \\ (4) OOH_{ads} \rightarrow OO_{ads} + H^+ + e^- \end{array}$

where * denotes an empty μ_1 site and e^- denotes the electron.

Tafel analysis suggests that step 2 is rate-limiting¹⁰; step 3 has also been suggested as the rds (refs. ^{26,27}), whereas the remaining proton-coupled electron transfers are probably barrierless²⁶. We found that water nucleophilic attack on a surface oxyl (step 3) is rate-limiting and we focus on it (see Supplementary Information).

External bias and rate

We consider the activation energy (E_a) for oxyl-water coupling with fixed bias, beginning with the potential of zero charge for the $\theta_{h+} = 3/4$ ML surface (Supplementary Fig. 15d). We find that O–O



potentials applied 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 versus 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. a.u., arbitrary units.



Fig. 3 | **Computed surface pH-potential phase diagram.** The potential is versus a normal hydrogen electrode (NHE). The phase diagram is constructed for a rutile-type IrO_2 (110) surface with total hole coverage with respect to the fully protonated surface indicated (see Supplementary Discussion and Supplementary Figs. 14, 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) forms an O–O bond with μ_1 -O at the transition state (middle)–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) 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 potential of zero charge for surfaces with $\theta_{h+} = 1/2$ ML, 3/4 ML and 1 ML (in order of increasing exothermicity) under constant-potential conditions. For $\theta_{h+} = 1/2$ ML, 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 $\theta_{h+} = 3/4$ ML (1/2 ML) surface; the small arrows indicate that E_a marginally drops with capacitive charging. The arrow labelled Q_T shows the effect of the corresponding total charge for the $\theta_{h+} = 3/4$ ML surface where an additional 0.5 V bias oxidizes the surface to $\theta_{h+} = 1$ ML. Q'_T shows the effect of reducing $\theta_{h+} = 3/4$ ML to $\theta_{h+} = 1/2$ ML. Red squares show E_a as a function of ΔH_{rxn} under constant-charge conditions. The empty red squares show surfaces with adsorbed Cl, which was used to investigate a non-reducible ligand (see Supplementary Information). Blue diamonds show solvent free energies. **c**, E_a for O–O coupling as a function of θ_{h+} .

coupling occurs with concerted transfer of H to a μ_2 -O site (Fig. 4a). Similar to previous observations²⁶, E_a is 0.63 eV with a heat of reaction (ΔH_{rxn}) near zero, as denoted by the corresponding green triangle in Fig. 4b. The two additional green triangles at $\Delta H_{rxn} \approx 0$ eV in Fig. 4b show that 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 labelled Q_c .

If the surface oxidation state is not constrained when increasing the 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, $Q_{\rm T}$, is indicated by a dashed arrow in Fig. 4b. Oxidative charging reduces $\Delta H_{\rm rxn}$ to about $-0.2 \, {\rm eV}$; moreover, oxidation lowers $E_{\rm a}$ (from about 0.60 eV to 0.23 eV). Similarly, Fig. 4b shows that reducing $\theta_{\rm h+}$ from 3/4 ML to 1/2 ML (Supplementary Fig. 15c) increases $E_{\rm a}$ to 0.78 eV, and the change induced by this total charge, $Q'_{\rm T}$, is not compensated by pure capacitive charging $(Q'_{\rm c})$.

These results demonstrate that E_a for O–O coupling obeys the Brønsted–Evans–Polanyi (BEP) relationship, which is familiar from traditional catalysis, with E_a depending linearly on ΔH_{rxn} , which in turn is controlled by oxidative (rather than capacitive) charge. According to classical electrochemical theory, such behaviour is consistent with inner-sphere reactions, in which the reacting species adsorbed on the electrode surface are insensitive to any double layer, and inconsistent with outer-sphere reactions involving weakly interacting species far from the electrode surface that obey Butler–Volmer kinetics⁸.

Oxidative charge and rate

Whereas the previous examples suggest that the E_a value of the rds is dominated by bond formation/rupture chemistry⁵, 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: $E_a = \zeta \theta_{h+} + \kappa$, where the constants ζ and κ are the analogues of the BEP slope (α) and intercept (E_0), respectively, allowing the electrocatalytic response of IrO₂ to be computed through an Eyring-like equation:

$$i = k_0 \theta_{\mu 1} \exp\left(-\frac{\zeta \theta_{h+} + \kappa}{k_B T}\right), \tag{1}$$

where the prefactor k_0 is independent of θ_{h+} (see Supplementary equation (13)), $\theta_{\mu 1}$ is the μ_1 -O coverage, k_B is the Boltzmann constant and *T* is the temperature.

The Tafel plot and charge–log(current) profile computed using equation (1) are in agreement with experimental results (Fig. 5). A Tafel slope of 39 mV dec⁻¹ is found up to 1.58 V, before increasing to 77 mV dec⁻¹;



Fig. 5 | **Computed electrocatalytic response of IrO**₂, **a**, Tafel plot computed with DFT data from the $IrO_2(110)$ surface using equation (1). **b**, Computed θ_{h+} versus potential corresponding to **a**. **c**, Computed θ_{h+} versus log(current) corresponding to **a**.

crystalline IrO₂ has Tafel slopes of 43–47 mV dec⁻¹ and 71–76 mV dec⁻¹ over the same potential windows (Supplementary Figs. 2, 3). However, from the calculations, the bend in the Tafel slope can now be ascribed to a change in the response of θ_{h+} to the potential (Fig. 5b) rather than to the qualitative change in mechanism suggested by Tafel analysis⁹. The computed log(current) versus θ_{h+} profile is linear (Fig. 5c), consistent with experimental results.

We anticipate that this linear dependence of log(current) on charge is common. This is because bond rupture/formation is slow compared to electron transfer, and BEP behaviour is expected when bond making/breaking is the principal contributor to the reaction coordinate⁵. In support of this assertion, we find that all the Ir-based catalysts show linear log(current)-charge profiles (Supplementary Figs. 2–8), and so do NiFe layered double hydroxides in alkaline electrolyte (Supplementary Fig. 17). Whereas such behaviour can emerge trivially on an electrode with constant capacitance, we argue that 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+} -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 $\zeta \approx -1.2$ and -1.3 eV ML⁻¹ for the AA-D and AA 450 °C (AA calcined at 450 °C) catalysts, respectively. These values compare favourably with the computed $\zeta \approx -1.3$ eV ML⁻¹ (Fig. 4c). For κ , we find 1.4–1.7 eV experimentally and about 1.6 eV from DFT.

Conclusions and outlook

Demonstrating how inner-sphere chemistry controls electrocatalytic OER rates establishes a fundamental link between thermal catalysis and

electrocatalysis that enables tools and concepts of traditional catalysis to be applied to electrocatalysis. Principal among these are the linear activation free-energy relationships mediating catalytic rates, which we have shown can be measured and computed for understanding and improving electrocatalysis.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41586-020-2908-2.

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Data availability

All data are available in the main text or the supplementary materials and from the Open Research Data Repository of the Max Planck Society, https://doi.org/10.17617/3.48. Source data are provided with this paper.

Acknowledgements We thank HZB for synchrotron radiation beamtime and the High-Performance Computing Center Stuttgart (HLRS) for access to the HazelHen and Hawk supercomputers as part of the ECHO project. Part of this work was carried out at Petra III (beamline P64) and we thank V. Murzin, A. Tayal and W. Caliebe for assistance and acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for access. We thank M. Hashagen, J. Allan and F. Girgsdies for BET and X-ray diffraction measurements and A. Müller-Kauke for inductively coupled plasma-optical emission spectrometry measurements. Financial support from the German Research Foundation (DFG) under Priority Program 1613 and Grant STR 596/11-1 is acknowledged. P.S. acknowledges partial funding by the DFG under Germany's Excellence Strategy – EXC 2008/1 – 390540038 (zum Teil gefördert durch die Deutsche Forschungsgemeinschaft (DFG) im Rahmen der Exzellenzstrategie des Bundes und der Länder – EXC 2008/ 1 – 390540038).

Author contributions T.E.J. and D.T. designed the study, analysed data and wrote the manuscript. H.N.N. carried out electrochemical measurements with the help of M.K., H.P.T. and C.S.; H.N.N., L.J.F., C.S. and D.T. performed soft-X-ray measurements. H.N.N., A.B., J.T. and D.T. performed hard-X-ray measurements. T.E.J. performed DFT calculations with the help of S.P.; G.Z. prepared Cl-treated samples under the supervision of J.P.-R.; H.N.N. prepared the IrO_x-250 °C, IrO_x-450 °C and IrNi samples. J.P.-R., B.R.C., R.S. and P.S. offered guidance for the project. All authors commented on the manuscript.

Competing interests The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at https://doi.org/10.1038/s41586-020-2908-2.

Correspondence and requests for materials should be addressed to D.T. or T.E.J. **Peer review information** *Nature* thanks Shannon Boettcher and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

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