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Molecular-scale interactions in heterogeneous (photo)-electrocatalysis

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Current research into (photo)electrocatalysis is focused on increasing the reactivity of systems based on Earth-abundant elements, which requires kinetic models of their catalytic mechanisms. In transition metal oxides, adsorption and electron transfer steps typically involve changes in the metal's oxidation state and the colour of the electrode, which can be measured spectroscopically. In-situ spectro-electrochemical studies have exposed the unexpected role played by the density of active species and their cooperativity in dictating (photo)electrochemical performance. Here, we review how reaction pathways can be controlled by the presence, or not, of molecular-scale interactions between redox-active sites at the interface and discuss strategies to monitor them. We consider how the ability to probe and quantify such interactions opens new strategies to enhance catalytic performance and creates new opportunities for scientific discovery.

Scaling up (photo)electrocatalysis to meet global energy and industry demands requires robust catalysts based on earth-abundant elements.¹ Transition metal oxide (TMO) catalysts are currently the benchmark for many (photo)electrochemical reactions, but their stability and catalytic efficiency can suffer during operation, compromising performance.^{2,3} Boosting their activity requires understanding the steps of their catalytic mechanism to identify bottlenecks and strategies to fix them.

However, TMOs are often challenging to study compared to noble metal-based electrodes, as they are prone to multiple defects and exhibit complex surface chemistry. Moreover, they can also undergo structural reconstructions during operation that further complicate their characterisation.^{4–8} Despite these challenges, advances in optical and X-ray techniques offer access to the polarised TMO/ electrolyte interface under multiple, and increasingly operando, experimental conditions (pH, applied potentials, light intensities).^{9–12}

Mechanistically, heterogeneous (photo)electrocatalysis occurs via inner-sphere electron transfer processes that involve electronic and/or structural changes of the electrode's surface.

In TMOs, the applied bias and/or light irradiation driving (photo)electrochemical operation results in changes in the oxidation state of the metal and thus in the electronic occupation of d-orbitals, which often lead to colour changes.^{13,14} Optical spectro-(photo)-electrochemical methods can monitor, under catalytic conditions, the accumulation of redox equivalents and the build-up of reactive species before and during Faradaic processes.¹⁵ Using these methods recent studies have exposed the importance of reaching critical densities of active species at the surface and the role of interactions between these species in dictating catalytic mechanisms.

In this perspective, we discuss recent advances in optically probing and quantifying active species and their interactions in transition metal oxide-based (photo)electrocatalysts. We aim to emphasise strategies that leverage molecular-scale interactions to enhance activity and selectivity. We focus on and compare cases where (photo)electrocatalysts drive the 4-electron, Oxygen Evolution Reaction (OER). We highlight how, in TMOs, the sequential accumulation of redox equivalents and interactions between neighbouring active species may dictate the OER reaction pathways and, thus, the rate and potential-determining steps. Such interactions include both energetic interactions modulating the energetics of species and co-operative effects between neighbouring sites in the rate-determining step. Finally, we contrast TMOs and molecular (photo)-electrocatalysts to discuss further research directions and strategies to control cooperativity.

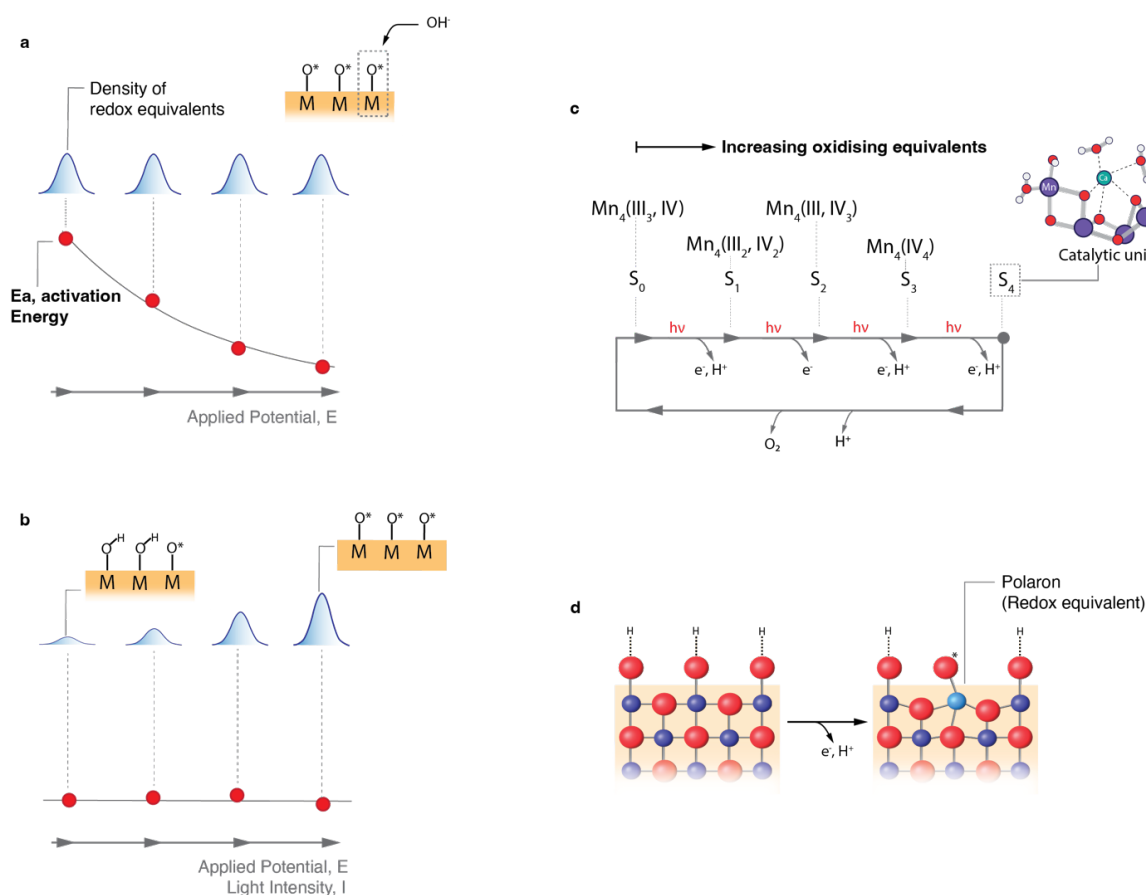


Figure 1. Extreme cases of single and multi-site catalysis (a) Some materials (such as noble metals) sustain reactions involving single sites that drives the catalytic cycle. In these systems the external driving force (e.g. applied potential) modulates primarily the energy of the active species at these sites, changing the activation energy and rendering the catalytic cycle more or less favourable. **(b)** Other materials such as some metal oxides sustain

reactions involving multiple sites that co-operate to yield the final product. In the extreme case for these systems the external driving force changes the density of active species or redox equivalents but the activation energy remains relatively constant. Intermediate scenarios also exist as discussed in the main text. **(c)** In the natural photosynthetic system, the oxygen evolution takes place in the Mn_4CaO_5 cluster which acts as a catalytic unit. Upon successive photo-excitations, the cluster accumulates oxidation equivalents, primarily changing the oxidation state of the Mn atoms. A total of 4 equivalents are needed to evolve O_2 . **(d)** The localisation of charge in transition metal oxides can lead to the formation of local structural distortions around the metal known as polarons. At the surface such localisation may be coupled to protonation/de-protonation, which can maintain charge balance and enable redox levelling, as also observed for the biological Mn_4CaO_5 cluster. These resulting 'surface polarons' or 'redox equivalents' can operate as the active species during chemical reactions.

Single-site vs multi-site reaction mechanisms

To a first approximation, most reaction mechanisms can be categorised as involving either single or multiple reaction sites.¹⁶ In the first case, the metal centre undergoes successive transformations during the catalytic cycle, such as protonation and nucleophilic/electrophilic attack, in an isolated manner until products are released. This model focuses on the changes in the oxygen binding energy between the different reaction intermediates and has been used to describe the activity of noble metals and many metal oxides. Its most powerful outcome is the Volcano plot — a correlation between the activity and a critical descriptor, like the binding energy-, and Sabatier's principle – the idea that the best-performing system will be the one that binds species not too strongly but not too weakly.¹⁷

In this mechanism, all equivalent intermediates have the same enthalpy and the reaction rate is controlled by the total surface energetics (**Figure 1a**). Consequently, the driving force (e.g. applied potential) acts by modulating the energy barrier for the transformation which is independent of the coverage of these intermediates.

In multi-site reactions, the metal centres undergo successive oxidation (or reduction) during the catalytic cycle until they eventually cooperate to generate the final product. In its simplest form, this model focuses on the accumulation of redox states within a specific catalytic unit.¹⁸ This framework has been successfully used to describe the reactivity of molecular complexes and most notably the Mn_4CaO_5 cluster that drives photosynthetic oxygen evolution.¹⁹

During the Kock cycle in PSII, the Mn_4CaO_5 cluster undergoes successive oxidations, coupled with deprotonations that keep charge balance, which leads to the generation of meta-stable states that store oxidation equivalents (**Figure 1c**).^{20,21} Four equivalents must accumulate in the cluster for oxygen evolution to take place.¹⁹ In this mechanism, the reaction rate is controlled primarily by the rate of generation of oxidising equivalents. Thus, in the case of (photo)electrocatalysts, the driving force acts primarily by modulating the number of redox equivalents (**Figure 1b**).

Notably, the distinction between single and multi-site pathways is not straightforward or categorisable by catalyst type. For example, for the same catalyst, the mechanism can depend on the reaction conditions. Similarly, in some molecular electrocatalysts, while the reaction mechanism has been successfully described using single-site models, empirically, it is observed that dimer catalysts often outperform their monomer counterparts.^{22,23} For instance,

the benchmark ruthenium 2,2'-bipyridine-6,6'-dicarboxylate (Ru-bda) complex has been observed to oxidise water through different mechanisms depending on the coordinating environment.²⁴ Ligands hindering interaction between Ru active centres favour monometallic mechanisms (known as water nucleophilic attack, WNA). In contrast, ligands that facilitate connectivity, such as pi-pi stacking interactions, favour a multi-metallic pathway by interaction of two metallic sites (known as I2M). Importantly, multi-site mechanisms can be faster, suggesting that co-operativity, when energetically and sterically possible, might provide some advantages.^{25–27}

Transition metals can sustain many valence states, therefore favouring successive oxidation/reductions. At the surface of TMOs, these redox processes are often coupled with proton release/uptake to maintain charge balance similar to that occurring in the Mn_4CaO_5 cluster in PSII. Moreover, these surface redox equivalents can be associated with structural changes leading to the formation of polaronic states – analogous to the distortions formed in the bulk upon charge injection (electrochemically or via light excitation).^{28–31} ¹⁴ These surface polarons or localised redox equivalents operate as the active species driving catalysis (**Figure 1d**).

Recent studies have suggested that the catalytic mechanisms of some TMO (photo)-electrocatalysts are determined by two key performance descriptors: the density of localised redox equivalents, and the inter-site interactions between them. This need to accumulate interacting redox equivalents parallels with the mechanisms typically proposed for molecular complexes, and is often not captured with simple theoretical models of reactivity on model surfaces for heterogeneous (photo)electrocatalysts.

Rate-determining steps with weakly interacting active species

Key evidence on the role of the local density of active species has been inferred from metal oxide photo-anodes. Several mechanistic studies of the OER on Fe_2O_3 have shown a direct correlation between the current density and the concentration of oxidation equivalents, typically associated with $\text{Fe}=\text{O}$ species (corresponding to surface valence band holes).^{32–36} Specifically, third-order reaction kinetics were observed, suggesting the need to accumulate three neighbouring oxidised states to drive the rate-determining step (RDS).

Density functional theory (DFT) simulations and micro kinetic studies further corroborate that in Fe_2O_3 photoanodes, surface holes are stored at different metal-oxo sites via a series of proton-coupled electron transfer steps. This accumulation was calculated to be energetically favourable with little interaction between neighbouring holes up to 30% surface coverage.³⁷ Such ability to easily store redox equivalents at the surface mimics the redox levelling that takes place in the Mn_4CaO_5 cluster in plants and has important implications for the RDS.

Notably, in the multi-site regime of Fe_2O_3 , the activation energy of the OER was found to be only weakly dependent on the density of active species (i.e. the surface hole coverage), with calculations confirming a higher activation barrier for single-site pathways (**Figure 2a**).^{37,38} Importantly, for the modelled surface, DFT suggested that the low barrier was due to the involvement of OH^- in the RDS, which is made possible thanks to the availability of 3 neighbouring holes. While further theoretical and experimental work is required to account for the full electronic and structural complexity, taken together, these experimental and computational results suggest that Fe_2O_3 can operate in a regime in which any repulsive or

attractive interactions are less important than the total density of surface oxo species. Kinetically, this leads to the measured rate-law behaviour.

Analogous rate-law mechanisms have also been inferred in other metal oxide photoanodes such as BiVO_4 and TiO_2 both for OER and other reactions like methanol and ethanol oxidation.^{39–43} Critically, in these systems, the Turn-Over Frequency (TOF) was observed to be independent of the externally applied voltage but dependent on valence band energetics (**Figure 2b**), with a more oxidising valence band leading to higher TOF.³⁸ These observations suggest that in these oxides, the reaction mechanism and rate are fixed by the total density of weakly interacting oxidised equivalents or surface polarons.

In this case, the external field generated by the applied voltage acts to modulate the rate of light-driven generation of surface redox equivalents and therefore their surface density, thereby increasing their free energy, as opposed to controlling the reaction's activation energy (**Figure 1b**). This behaviour has important design considerations. Notably, structural modifications, such as band and defect engineering, are the primary routes for reaction control as they can enhance the rate of generation or energy of the surface redox equivalents.

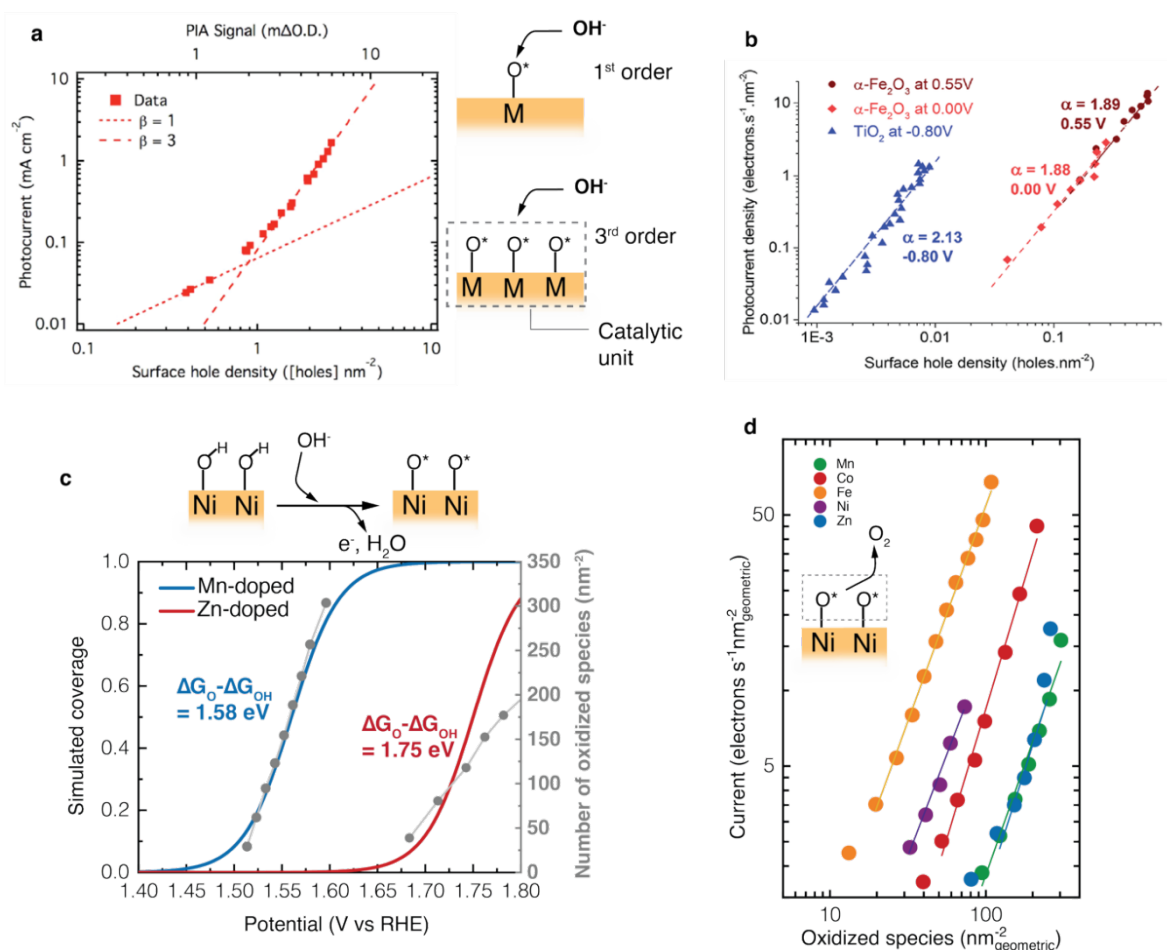


Figure 2 Reaction kinetics in weakly interacting oxides. (a) Fe_2O_3 photoanodes exhibit rate-law kinetics. A first order on the density of surface holes was observed at low coverages while at high coverages a third order dominates indicating the need to accumulate three oxidised equivalents to drive the oxygen evolution. (b) In Fe_2O_3 and TiO_2 photoanodes the

reaction order (α) of the rate determining step was found to be independent of the applied voltage but the reaction speed depends strongly on electronic structure. **(c)** In NiO electrocatalyst the application of potentials greater than 1.4V vs RHE leads to the accumulation of oxo (*O) species. The binding energy for *O species is higher in Mn-doped than Zn-doped oxides but **(d)** the order of the rate-determining step of the reaction is found to be independent of doping (2nd order). *(a) adapted from³²; (b) adapted from⁴⁰; (c) and (d) adapted from⁴⁴.*

Beyond photo-irradiated systems, multi-site rate-law catalytic behaviour has also been observed when TMOs are employed as dark electrocatalysts. For example, comparative studies of the OER on BiVO₄ and Fe₂O₃ have revealed the same reaction mechanism in the dark and upon illumination.^{33,45}

For doped Ni oxides, optical spectroscopy revealed the accumulation of oxidised nickel species at applied potentials beyond 1.40 V_{RHE} (**Figure. 2c**)⁴⁴ – attributed to metal-oxo intermediates (*O). Their accumulation was found to depend on the type of dopant with Mn-doped samples forming oxo species at ~200 mV lower overpotential than the Zn-doped counterpart. Such quantitative observations suggest a stronger binding of *O on the Mn-doped sample. Critically, despite these energy differences, the rate of water oxidation exhibited a second-order dependence on the density of oxidised equivalents for both samples (**Figure. 2d**). Such behaviour is consistent with a rate-determining step involving the chemical combination of the two oxo species.

These results highlight that water oxidation on doped NiO electrocatalysts involves an interplay between the potential-determining step – the formation of *O species – and the rate-determining step – the combination of adjacent *O. Interestingly, different kinetics and apparent reaction orders are observed depending on the nickel oxide/oxyhydroxide, both with different fabrication routes and thus morphology, as well as *operando* external inputs, such as magnetic fields. However, the origins of these mechanistic differences remain mostly unexplored.^{46–48}

Collectively, the experimental results suggest that achieving optimal catalysis requires a system that binds *O species just right so as not to be limited by their formation (like in Zn-doped NiO) or their ability to react (Mn-doped). More fundamentally, the similar rate-law behaviour observed in some photo- and electrocatalysts points towards the general role of localised redox equivalents in these oxides. They suggest strong parallelism in active species formation irrespective of whether the charge is electronically injected or photo-generated. This opens the door to knowledge transfer between fields, which could help understand both the dynamics of charge localisation and accumulation or what dictates the strength of polaron-polaron interactions, which is of known importance in other functional solids.^{31,49}

Rate-determining steps with more strongly interacting active species

Similar to nickel-based oxides, spectro-electrochemical studies of IrO_x catalysts have identified the fingerprints of surface species as a function of applied potential.⁵⁰ These species were associated with water adsorption and successive deprotonation which in turn, modulated the Ir d-orbital occupancy, thus causing a measurable change in the colouration of the electrode.⁵¹

Kinetic analyses suggest that the current density scales exponentially with the increase in surface coverage. Such behaviour contrasts with similar measurements on nickel oxide electrodes and transition metal oxide photoanodes discussed in the previous section and suggests that in IrO₂ the applied potential has a double role: controlling the density of active species and modulating the activation barrier of the reaction. From an experimental viewpoint, this conclusion could be reached by analysing the adsorption isotherms measured spectro-electrochemically. These were found to deviate from the Langmuir model and to be better described as Frumkin isotherms (**Figure 3a**), in which the enthalpy of the active species changes with the applied potential.

Such behaviour could be rationalised by taking into account the role of interactions between neighbouring active species. Specifically, it was observed that, while the total density of active states is important, repulsive interactions between them can have a dominant effect. At higher densities, such interactions destabilise the surface and render it more reactive. This behaviour is consistent with other studies, based on DFT analyses, reporting a reduction of the activation energy with increasing surface coverage and which explain the dependence of the reaction rate on the surface coverage (**Figure 3b**).⁵² Similar coverage-dependent binding energies and adsorbate interactions have been observed in other systems such as amorphous cobalt phosphate, CoOOH and RuO₂.^{53–55}

One plausible reason for the contrasting behaviour between IrO₂ and other oxides like Fe₂O₃ could be the difference in the oxidation character of the active states. The surface-active species in Fe₂O₃ are highly oxidising, with an energy dictated by its valence band maxima,³⁸ and thus can sustain fast catalysis even at relatively low surface coverages (typically < 0.3 of monolayer under one sun irradiation). In contrast, the less oxidising Ir-states in IrO₂ require additional repulsive interaction to accelerate the reaction and thus operate more efficiently at higher surface coverages. In this case, modulating the strength of the interaction becomes key to designing catalysts that operate at low overpotentials. But further work is needed to understand this behaviour in detail.

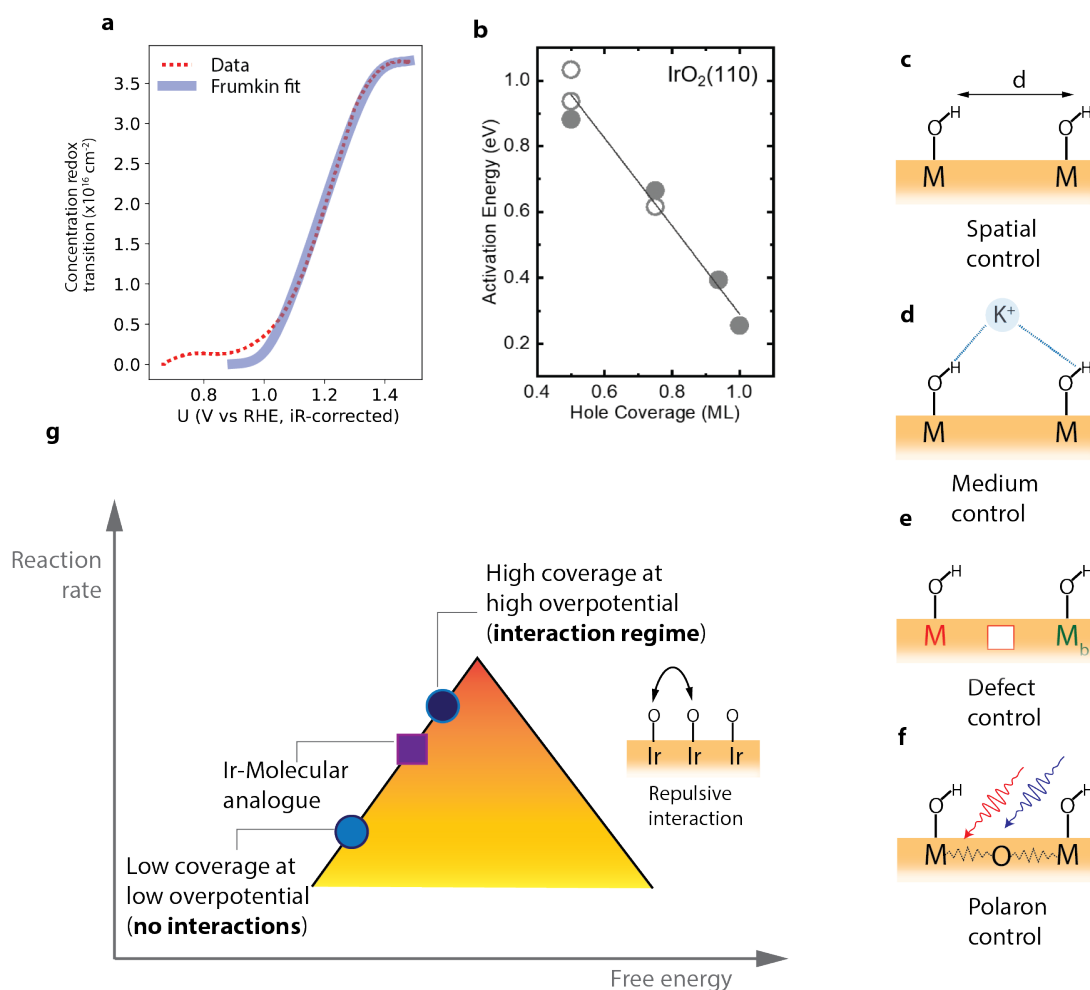


Figure 3 Kinetics in stronger-interacting oxides and strategies to control molecular-scale interactions. (a) Optically measured electroadsorption isotherm in IrO_x for a transition associated with the deprotonation of a bridge oxygen, preceding the formation of the oxygenated active species. The isotherm exhibits a Frumkin response reflecting repulsive interactions between active species. (b) Computed activation energy of the rate determining step on IrO_2 as a function of hole coverage. The interaction between surface localised redox equivalents may be tuned by (c) controlling the spatial separation between active species, (d) modulating the characteristics of the reaction media (e.g. supporting ions), (e) controlling the density of defects, (f) applying polaron-control strategies. (g) Schematic volcano plot comparing a solid and a molecular Ir based-catalyst. At low applied voltages the molecular catalyst performs better. However, at high overpotentials strong interactions between active species render the solid more reactive. Catalyst optimisation requires strategies that yield electrodes which either sustain optimally oxidising active species (sufficient but not too much that they poison the surface) or incorporate interactions which render them more reactive. (a) adapted from⁵⁰; (b) adapted from⁵⁶ with data from⁵².

Controlling inter-site interactions

A direct materials consideration from these observations is that highly active catalysis requires electrodes which either sustain optimally oxidising active species or incorporate interactions which can render them more reactive at high surface coverages. Modifying the intrinsic oxidising character of transition metal oxides involves defect and band engineering strategies. In this sense, it is necessary to strike a balance as excessively oxidising species could lead to a high coverage of surface oxo species, unreactive for subsequent O-O bond formation. Routes for controlling active-species cooperativity might entail control of their spatial

distribution and modulation of the connecting medium between them – the electrolyte or the lattice (**Figure 3c-f**).

From a spatial viewpoint, studies comparing molecular Ir dimers with IrO_x have shown that in the molecular case, the coordination environment can be used to control the interaction between the metal centres.⁵⁷ Steric effects induced by bulky ligands were observed to hinder co-operativity leading to single-molecule reactivity. As a consequence, while at low overpotentials, the dimer outperformed the oxide, at high applied voltages and large surface coverage, repulsive interactions rendered IrO_x more reactive (**Figure 3g**).

Similar behaviour was observed when comparing CoOOH and Co-Fe Prussian blue analogues electrocatalysts.⁵⁵ The Co-Fe system exhibited weaker interactions but was able to react at lower overpotentials /coverages compared to CoOOH, which requires cooperativity to become active. However, at high coverages, in the interaction regime, the oxyhydroxide outperformed (**Figure 3g**).

The synthetic flexibility attainable in molecules and molecular solids offers the prospect of designing catalysts that take the best of both worlds: highly-oxidising metal centres capable of reacting at low overpotentials, but that also sustain interactions that magnify their response at higher coverages. There is already encouraging evidence pointing towards a transfer of design strategies between homogeneous and heterogeneous catalysis. For example, in molecular catalysts, the presence of dangling free carboxylic acids in the coordination sphere was observed to aid proton-coupled electron transfer steps and improve reaction kinetics,⁵⁸ and currently, similar coordination-control strategies are being translated to materials design.^{59–61}

Modulating the electrolyte offers an alternative route to control interactions. In the liquid phase, this might involve exploiting the energetic and steric effects induced by supporting ions (**Figure 3d**). Optical, X-ray and IR studies on IrO_x have shown that cations in the electrolyte and the structure of water at the interface act as modulators of interactions between active species.⁶² Similarly, in Ni or NiFe oxyhydroxides, it has been observed that cations can significantly influence the OER catalytic activity via noncovalent interactions. Despite increasing evidence, a detailed mechanistic understanding of the role played by parameters such as the pH and the supporting ions is still missing.^{63–65}

In the solid phase, interactions might be controlled via nano-structuring, which can modulate the spatial separation between metal centres, and via targeted defect distributions (**Figure 3e**), which can offer extra states for charges to localise.⁶⁶ Moreover, it may be important to account for the polaronic nature of the active species in which charge and structure are strongly coupled (**Figure 3f**).^{67,68}

Future directions on probing and exploiting interactions

From a mechanistic viewpoint, while recent works in some oxides suggest that the density of localised redox equivalents and their interactions play a key role in reactivity, further studies are needed to assess the universality of these observations. Some areas might require special attention.

First, it will be important to account for structural and energetic disorder in the electrode and measure the specific location where reactivity occurs. This has implications for mechanistic proposals because while redox equivalents might localise across the whole surface, it is often unclear if catalysis occurs through the surface or if it happens exclusively at steps and edges.

Second, finding ways to systematically measure the impact of disorder in the energetics and interaction of redox equivalents will also be important. To date, there has been little quantitative analysis of the implications of such energetic disorder on the catalysis kinetics. For this, assessing the impact of surface structural reconstructions and developing tools to manage them will be crucial.

Furthermore, detailed structural and energetic characterisation of the redox equivalents may be important to rationalise why systems such as Fe_2O_3 and IrO_2 appear to operate via similar multi-hole mechanisms but at different surface coverages. Moreover, it may open the door to strategies to control redox equivalents and the mechanism, on demand, either via changes in the atomic composition and geometrical distortions or through polaron-control methods.^{4,31}

Finally, it is also essential to probe the electrostatics of the (photo)electrode/electrolyte interface. In particular, a better understanding of the impact of the electrolyte in controlling interactions as well as the role of proton uptake and release during the accumulation of redox equivalents is still needed. Protonation steps are central to the operation of the Mn_4CaO_5 cluster in PSII and, in electrochemistry, can impact the potential drop across the Helmholtz layer and the kinetics of the electron transfer and product formation.^{69,70}

From a materials development viewpoint, it will be important to explore new strategies to modulate the energetics of redox equivalents and their connectivity. Many important advances have already been made using MOFs,⁷¹ hybrid nanomaterials,⁷² single atoms⁷³ or heterogenised molecular catalysts⁷⁴. The similarities between homogeneous and heterogeneous transition metal catalysts also here suggest a possible knowledge transfer between disciplines.

The lessons learned in molecular electro-photocatalysis may prove useful to elucidate and tune reaction mechanisms in solids. For example, the synthesis of molecular catalysts with ligands that favour connectivity might inspire the design of TMOs with tailored atomic environments, both at the electrode itself and at the interface. Moreover, comparing the response of TMO electrodes with molecular analogues that exhibit similar motifs could facilitate computational experiments, accelerate the characterisation of active sites and inform on the parallels between molecular, solid-state and enzymatic catalysis.

Going beyond optical spectro-electrochemistry

Herein we have primarily highlighted studies in which redox equivalents and their interactions were probed using UV-Vis spectro-electrochemistry. Despite its technical simplicity, which facilitates the systematic comparison of different experimental conditions, the technique has some limitations. First, most studies to date were performed in transmission mode and required semi-transparent samples. This excludes many interesting materials (e.g. metals) or electrode characteristics closer to those used in applications (e.g. thick and scattering samples or oxides deposited on membranes).⁷⁵

Moreover, the transmitted beam probes both the bulk and the surface which may lead to overestimations of the density of redox equivalents, especially in very thick samples. Spectro-electrochemical methods that operate in reflectivity mode or direct ellipsometry measurements recording both the refractive index and absorption coefficient at different applied potentials could help circumvent these issues.^{76–80} Detailed analyses of absorption and refractive indices, deduced from ellipsometry and reflectivity signals, may also help understand the role of surface reconstructions and phase changes in the catalytic layers.⁸¹

Secondly, despite the experimental versatility of UV-Vis spectro-electrochemistry, this method lacks chemical sensitivity and the power to resolve the local structure and the electronic properties of the active sites. Given the critical role of charge accumulation in TMOs, quantitative assessments of the oxidation state and element sensitivity are needed to identify the active sites and build robust catalytic models.

Synchrotron techniques such as X-ray absorption (emission) spectroscopy can provide these data.^{10,82} However, the reduced experimental time limits the number of data points measurable. Developments in techniques such as energy-dispersive X-ray absorption fine structure (XAFS), capable of acquiring a whole energy spectrum in a single shot may help overcome these constraints.^{83–85} Similarly, more extensive implementation of fixed-energy scanning methods, such as X-ray absorption spectroscopy with cyclic voltammetry (XAS-CV), could complement the electro-absorption isotherms obtained via UV-Vis spectro-electrochemistry.⁸⁶

Moreover, high electronic and structural sensitivity will be useful to understand the role of the electrolyte in the accumulation of redox equivalents and their interactions. Surface-sensitive microscopy and vibrational techniques as well as methods to probe the interfacial electric fields, can inform about the structure of the electrolyte and its impact on the electrochemical interface.^{9,33,64,87}

Finally, time-resolved (Tr) methods, such as Tr-vibrational and electronic spectroscopy and Tr-XAS, may provide insightful data on the dynamics of the (dep)-protonation steps and the importance of redox-levelling in oxides. The ongoing development of time-resolved electron and X-ray sources and the increasing complementarity between techniques present opportunities to study molecular-scale reactivity at the surface of transition metal oxide surfaces.^{9,88,89}

Author Contribution

E.P. and J.R.D. conceived the idea. R.R., C.A.M and L.F. contributed substantially to articulating the key concepts. E.P and A.G wrote the manuscript with inputs from R.R., C.A.M., N.K., L.F. and J.R.D.

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Competing interests

The authors declare no competing interests.

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