A kinetic descriptor for the electrolyte effect on the oxygen reduction kinetics on Pt(111)

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Proton-exchange membrane fuel cells demand efficient electrode–electrolyte interfaces to catalyse the oxygen reduction reaction (ORR), the kinetics of which depend on the energetics of surface adsorption and on the electrolyte environment. Here we show an unanticipated effect of non-specifically adsorbed anions on the ORR kinetics on a Pt(111) electrode; these trends do not follow the usual ORR descriptor, that is *OH binding energy. We propose a voltammetry-accessible descriptor, namely reversibility of the *O ↔ *OH transition. This descriptor tracks the dependence of ORR rates on electrolyte, including the concentration/identity of anions in acidic media, cations in alkaline media and the effect of ionomers. We propose a model that relates the ORR rate on Pt(111) to the rate of the *O to *OH transition, in addition to the thermodynamic *OH binding energy descriptor. Our model also rationalizes different trends for the ORR rate on stepped Pt surfaces in acidic versus alkaline media.

The operating energy efficiency of proton-exchange membrane fuel cells (PEMFCs), an appealing power source for transportation, remains well below the thermodynamic value of 83%, primarily because of the high overpotential of the cathodic oxygen reduction reaction (ORR) toward a more complete understanding of the various factors that determine ORR kinetics. Part of this progress was guided by a descriptor-based approach, in which the activity of the catalyst is related to the binding energy of the key adsorbed intermediates. A widely adopted ORR activity descriptor is the oxygen or hydroxyl adsorption energy. Using such a descriptor as the key catalyst property, catalyst-dependent ORR activities are arranged in a so-called volcano plot, with the best catalyst possessing the most optimal oxygen binding energy located at the top of the volcano. However, the ORR has multiple oxygen-containing intermediates, and they cannot all be optimized independently because their binding energies exhibit a scaling relation: if one binding energy changes, the others change as well, often in a very predictable way. Such scaling relations eliminate the possibility of independent tuning of each intermediate, and yield a minimum thermodynamic overpotential that cannot be overcome by solely engineering the solid surface for optimum adsorption. Thus, a formidable challenge is to break the scaling relation, with limited experimental success achieved to date.

One important (often tacit) assumption in the volcano approach is that a catalytic reaction has a single descriptor. However, it is well known that (electro)catalytic reactions may have multiple descriptors; hydrogen evolution/oxidation in alkaline media is a good example, the multiple descriptors of which are currently much discussed in the literature. For the ORR, it appears that oxygen-containing species on Pt(111), which is relevant to the oxygen reduction kinetics on Pt(111) to the rate of the *O to *OH transition, in addition to the thermodynamic *OH binding energy descriptor. Our model also rationalizes different trends for the ORR rate on stepped Pt surfaces in acidic versus alkaline media.

Results

CVs and ORR activities of Pt(111) in 0.1 and 0.02 M HClO₄. We first investigated how NSA anions affect the chemisorption of oxygen-containing species on Pt(111), which is relevant to the electrocatalytic performance for ORR. Figure 1a compares the blank cyclic voltammograms (CVs) of Pt(111) in HClO₄ for two concentrations, that is, the customary 0.1 M and a more diluted 0.02 M solution, both showing the typical voltammetric characteristics of a Pt(111) surface. Negligible differences in the hydrogen underpotential desorption (Hupd, between 0.07 and 0.35 V) or double-layer charging (DL, between 0.35 and 0.55 V) regions were observed between the two electrolytes, indicating the absence of surface reconstruction or specific adsorption. On the other hand, a small but significant difference in the reversible OH adsorption
(OH$_{ad}$, between 0.55 and 0.85 V) region is observed, with an overall higher charge of OH$_{ad}$ in 0.02 M compared with 0.1 M HClO$_4$ (Fig. 1b). The similar OH$_{ad}$ profiles between 0.1 M HClO$_4$ and a control electrolyte (0.02 M HClO$_4$ + 0.08 M KClO$_4$) suggest that OH$_{ad}$ formation is more sensitive to the anion concentration than to the electrolyte pH (see the corresponding curve in Fig. 1b). This indicates that the saturation coverage of OH$_{ad}$ is electrolyte dependent (as it is known that perchlorate interacts with OH$_{ad}$ (refs. 24,25), it presumably interferes with the lateral interactions between adsorbed OH).

The OH$_{ad}$ adsorption energy of a Pt surface has been widely used to predict the corresponding ORR activity, on the basis of two proposed mechanisms. The first mechanism suggests that OH$_{ad}$ serves as a non-reactive spectator and blocks surface active sites for the adsorption of molecular O$_2$ (refs. 26,27). As a result, a lower OH$_{ad}$ coverage ($\Theta_{OH}$) at the potential of interest (ORR activity is customarily evaluated at 0.9 V versus Reversible Hydrogen Electrode (RHE)) results in a higher ORR activity because of a higher pre-exponential factor ($1-\Theta_{OH}$) in the rate expression. Here, it is important to note the distinction between N$\equiv$S$\equiv$A$\equiv$ (for example, ClO$_2^-$ and methanesulfonate) and specifically adsorbed anions (for example, HSO$_4^-$ and Br$^-$); the latter (located in the inner Helmholtz plane) directly impact the ORR rate by contributing to the ($1-\Theta_{OH}$) term (where $\Theta_{OH}$ includes both OH and specifically adsorbed anions) of the rate expression given by Marković et al. (28,29). The second mechanism is based on the notion that OH$_{ad}$, as an intermediate, binds too strongly on Pt(111), and needs to be weakened by ~0.1 eV to reach the top of the volcano (30). It has been proposed that an experimental measure of the OH$_{ad}$ adsorption strength can be indicated by the electrode potential required for a $\Theta_{OH}$ of 1/6 monolayer, that is, 40μC cm$^{-2}$ for Pt(111) (dashed line in Fig. 1b)”29. A more negative (positive) potential then means stronger (weaker) OH$_{ad}$ adsorption strength. Both mechanisms predict a lower ORR activity for Pt(111) in 0.02 M HClO$_4$ compared with 0.1 M HClO$_4$ because of a higher $\Theta_{OH}$ and a more negative potential for 1/6 of $\Theta_{OH}$.

Strikingly, we find the opposite trend experimentally. Figure 1c compares the ORR polarization curves of Pt(111) in different electrolytes (see Methods and Supplementary Fig. 1 for ORR test and data processing), all of which show three distinguishable regions: a mixed kinetic-diffusion control region (0.8 $<$ E $<$ 1.0 V), followed by a well-defined diffusion-limiting current region (0.3 $<$ E $<$ 0.7 V) and a region where Hupd interferes with ORR (0.1 $<$ E $<$ 0.3 V). The half-wave potential ($E_{1/2}$, the potential at half of the diffusion-limiting current density) of Pt(111) in 0.1 M HClO$_4$ is around 0.86 V, in agreement with the literature (31). Pt(111) in 0.02 M HClO$_4$ shows higher ORR activity than in 0.1 M HClO$_4$ as evidenced by a positive shift of $E_{1/2}$ by 25 mV. The mixed-region curve (where the ORR kinetic parameters were derived and compared) of Pt(111) in the control 0.02 M HClO$_4$ + 0.08 M KClO$_4$ electrolyte overlaps with that in 0.1 M HClO$_4$ showing that the ORR activity depends on anion concentration but not on electrolyte pH (see the corresponding curve in Fig. 1c). We find that the Tafel slope increases slightly with the HClO$_4$ concentration, but is close to 60 mV dec$^{-1}$ in all cases (Fig. 1d and Supplementary Table 1), which agrees well with the literature and suggests that the ORR mechanism is independent of electrolyte (32). We note here that, for ORR on Pt surfaces, derivation of the rate-determining step (RDS) from the measured Tafel slope is not straightforward and remains disputed (33). At a constant overpotential of 0.3 V, a lower activation energy of 20.5 kJ mol$^{-1}$ was obtained in 0.02 M HClO$_4$, than in 0.1 HClO$_4$ (31.1 kJ mol$^{-1}$, see Methods for testing and processing details for activation energy and
Supplementary Fig. 2 for corresponding Arrhenius plots), underscoring the negative impact of ClO$_4^-$ on the ORR kinetics.

The above observations suggest that ORR rate on a Pt surface cannot be solely described by the thermodynamic binding energy descriptor, and imply the existence of another factor that accounts for the above-observed electrolyte effect. To pursue the origin of this effect, we revisit the ORR mechanism on Pt surfaces, which can be simplified as follows:

\[
\begin{align*}
O_2 + H^+ + e^- &\rightarrow \star OOH & (1) \\
\star OOH + H^+ + e^- &\rightarrow \star O + H_2O & (2) \\
\star O + H^+ + e^- &\rightarrow \star OH & (3) \\
\star OH + H^+ + e^- &\rightarrow H_2O & (4)
\end{align*}
\]

where * represents an adsorption site on the surface. This mechanism involves three adsorbed reaction intermediates, that is, \(\star OOH\), \(\star O\) and \(\star OH\). Probing these intermediates under reaction dynamics remains a huge challenge. However, existing experimental evidence from both ex situ and in situ ambient-pressure X-ray photoelectron spectroscopy (XPS) suggests that, within the mixed kinetic-diffusion potential region, the dominant surface species gradually change from \(\star O\) to \(\star OH\) with increasing ORR overpotential.

This highlights the role of \(\star O\) as a key surface adsorbate for ORR proceeding at the potential of interest, that is 0.9 V, and thus motivates us to investigate the voltammetry of \(\star O\) and to further probe its functional link with the ORR kinetics on Pt surfaces.

A descriptor for electrolyte effect on ORR. To study the kinetics of the \(\star O\) to \(\star OH\) transition, we recorded CVs of Pt(111) in an extended potential window (between 0.07 and 1.15 V) in HClO$_4$ of four concentrations (Fig. 2a). The upper potential limit of 1.15 V was chosen to avoid irreversible surface reconstruction of Pt(111). Following the traditional interpretation, we assigned the anodic peak located between 0.95 and 1.1 V as the oxidation of \(\star OH\) to \(\star O\). A typical characteristic of high-quality Pt(111) surface is the plateau between 0.85 and 1 V, which was previously interpreted as a high kinetic barrier to oxidize Pt(111) with a 1/3 monolayer of \(\Theta_{\star OH}\), based on density functional theory (DFT) calculations and electrochemical impedance spectroscopy (EIS) studies. The most pronounced trend from Fig. 2a is that the \(\star O\) peak shifts positively with the HClO$_4$ concentration, which suggests that \(\star OH\) to \(\star O\) conversion is easier in an electrolyte with a lower ClO$_4^-$ concentration. The reverse reduction of \(\star O\) to \(\star OH\) (step 3 of ORR) is then expected to show the same electrolyte dependence. However, the kinetically slow \(\star OH\) reduction peak overlaps with the fast \(\star OH\) desorption peak, giving rise to a broad reduction peak between 0.55 and 1 V in the CV (Fig. 2a), comprising both processes. Such a convolution poses experimental difficulties to probe the electrolyte-dependent kinetics of \(\star O\) to \(\star OH\) transition on Pt(111). To deconvolute these two processes, we performed experiments at different scan rates and different temperatures.
Leveraging the kinetic difference of *O to *OH transition and *OH desorption on Pt(111), we can manipulate their respective positions by recording CVs at different scan rates from 200 to 10 mV s⁻¹ (Fig. 2b). The two reductive processes were gradually deconvoluted with decreasing scan rate, and became fully separated at 10 mV s⁻¹. The forward and backward peaks corresponding to the *O ↔ *OH redox have a smaller peak-to-peak potential difference at a slower scan rate, proving that there is a kinetic barrier associated with this reaction. Another way to deconvolute the peak is to accelerate the sluggish *O ↔ *OH rate by increasing temperature. Recording CVs of Pt(111) as a function of temperature, we observe a gradual separation of the reduction peaks with increasing temperature (Supplementary Fig. 3). Notably, both scan-rate- and temperature-controlled experiments suggest an electrolyte dependence of the *O ↔ *OH kinetics, namely that it proceeds faster in more diluted HClO₄.

In another typical NSA electrolyte, that is methanesulfonic acid (MSA), we observed the same concentration dependence of the ORR activity on Pt(111), suggesting generality of the suppression effect of NSA anions towards ORR (Fig. 2c). Figure 2c plots the specific activity of ORR on Pt(111), denoted by the kinetic current density at 0.9 V (iₖ, see Methods for calculation details), which decreases with HClO₄ and MSA concentration (Fig. 2c), or more specifically, with lower perchlorate and methanesulfonate concentration. The measured iₖ of Pt(111) in 0.1 M HClO₄ is 1.93 mA cm⁻² in good agreement with the literature. The effect of the methanesulfonate concentration on the kinetics of the *O ↔ *OH process is also identical to the effect of the perchlorate concentration (Supplementary Fig. 4).

The observation that the rate of both *O ↔ *OH and ORR depend on the concentration of NSA anions in the same way, suggests that they are related; or more specifically, the rate of the *O ↔ *OH process may act as a descriptor of the ORR rate. To provide quantitative support for this relation, we plot the kinetic current at 0.9 V of ORR versus peak-to-peak separation (ΔEₚᵣₑₓ) of the *O ↔ *OH process in Fig. 3a,b. Increasing from 0.02 to 0.1 M HClO₄, the anodic and cathodic peak shifts positively and negatively, respectively, by ~25 mV, very close to the Eᵢₖ change of ORR (Fig. 1c). The smaller the ΔEₚᵣₑₓ, the more reversible the *O ↔ *OH process, and the faster the ORR rate. We will discuss possible interpretations of this relation in the Discussion section.

Effects of alkaline cations and ionomers. Having introduced a kinetic descriptor for the electrolyte effect on Pt(111) in acid solution, we now show its applicability in alkaline media, in which hydrated cations are the main electrolyte players. We recorded CVs of Pt(111) in 0.1 M and 0.02 M NaOH using a slow scan rate of 10 mV s⁻¹, to deconvolute the two cathodic processes (Supplementary Fig. 5a). At a lower NaOH concentration of 0.02 M, the peaks related to *O ↔ *OH redox are more reversible. According to the proposed descriptor, Pt(111) would show a higher ORR activity in 0.02 M than in 0.1 M NaOH, which was verified experimentally by a positive shift of Eᵢₖ by 12 mV (Supplementary Fig. 5b).

The kinetic descriptor also tracks the ORR dependence of monovalent cation identity in alkaline electrolytes. On Pt(111), the reversibility of *O ↔ *OH redox and ORR activity follow the same trend of LiOH < NaOH < KOH < CsOH (refs. 23,40). Our kinetic descriptor is also valid for the effect of bivalent cations, such as Ba²⁺, on the ORR kinetics of Pt(111) in alkaline solutions.

In real fuel cells, Pt catalysts are generally surrounded with hydrated PFA-based ionomer instead of anions or cations. We investigated the effect of ionomers on CVs and ORR activities of Pt(111) by depositing a thin layer of the widely adopted Nafion ionomer (see Methods for details). The orientation of Pt(111) was well preserved after the deposition, as evidenced from the negligible change in H₃ol profile (Fig. 4a). We observed a higher peak potential for the *OH to *O transition, and a lower ORR activity on Nafion-covered Pt(111) relative to the unmodified Pt(111), validating our kinetic descriptor (Fig. 4b). Further experimental support can be found in the work from Kodama et al., who showed that the ORR activity decreases as bare Pt(111) > perfluorosulfonimide-coated Pt(111) > Nafion-coated Pt(111), while the peak potential for the *OH to *O transition follows the opposite trend, in agreement with our kinetic descriptor. Our finding offers a plausible explanation for the counterintuitive observation that the addition of ionomers negatively impacts the electrochemical surface area of nanoparticulate Pt catalyst, yet deteriorates its intrinsic activity. This provides an important insight into the challenge of the performance transfer of advanced nanocatalysts from half-cell measurements to membrane electrode assembly (MEA) systems.

Electrolyte effect on stepped surfaces and an enhanced model. Finally, we want to show how our kinetic descriptor can be used to offer an explanation for an unsolved puzzle in understanding ORR activity trends on stepped Pt surfaces in acidic and alkaline media. To show the relation between our kinetic descriptor and ORR activity on stepped Pt, we employed a series of Pt(111) vicinal surfaces with (110) steps, denoted as [n(111)x(110)], including Pt(151514) [30(111)x(110)], Pt(554) [10(111)x(110)] and
Pt(553) [5(111)x(110)]. We verified the absence of surface facetting on our stepped Pt electrodes by integrating the charge densities of step-related $H_{upd}$ peaks and comparing them with those predicted from a hard-sphere model. By comparing their CV profiles with that of Pt(111), we assigned the oxidation peak between 1 and 1.15 V to the formation of *O on (111) terrace (*O_{terrace}), the intensity of which decreases with increasing step density (Supplementary Fig. 6). The *O_{terrace} peak of all stepped Pt surfaces shifts positively with the HClO₄ concentration (Supplementary Fig. 7), in line with the trend of Pt(111). From 0.02 to 0.2 M, the peak potential of *O_{terrace} on Pt(111) increased by 30 mV, followed by Pt(151514) of 25 mV, Pt(554) of 19 mV and Pt(553) of 14 mV (Fig. 5a). Following the voltammetry results and the kinetic descriptor, ORR activities on all Pt surfaces are expected to decrease with the HClO₄ concentration, in line with the sequence of Pt(111) > Pt(151514) > Pt(554) > Pt(553). This was experimentally verified by normalizing $j_0$ of other concentrations to that of 0.1 M HClO₄, as displayed in Fig. 5b, which suggests that a single-crystal Pt surface with a higher step density is less sensitive to the electrolyte effect. We therefore deduce that the electro-cate activity effect mainly applies to the (111) terraces of Pt surfaces, but also that terraces still make a significant contribution to the overall ORR activity of stepped Pt surfaces.

Stepped Pt surfaces are known to show higher ORR activities than Pt(111) in 0.1 M HClO₄. Previous studies have explained this phenomenon based on the oxygen binding energy descriptor. Two types of active sites, categorized by the so-called generalized coordination number, were proposed on stepped surfaces. One type of active site is adjacent to the steps, and the other type is in the terrace of the step. Site A (terrace atoms adjacent to steps) has a higher generalized coordination number than site B (basically equal to the terrace atom of Pt(111) electrode). This endows stepped Pt surfaces with lower oxygen binding energy and thus higher ORR activity on Pt(111) compared with stepped surfaces, in agreement with the experimental trend.

With this model, we can understand the longstanding puzzle of the different structure sensitivity of ORR on Pt surfaces in acid versus alkaline media—compared with stepped surfaces, the ORR rate of Pt(111) is lower in acid, but higher in alkaline media. In acid, site A serves as the dominant reactive site according to the thermodynamic descriptor, which explains the higher ORR rate of stepped surfaces. In alkaline media, previous studies found that alkali metal cations are preferentially located at the step sites. This results in a blockage of site A and as a result site B provides the main contribution to the ORR activity on stepped Pt surfaces.

**Discussion**

The ORR is a complex multi-proton multi-electron transfer reaction. In the traditional approach for modelling the ORR activities of various electrocatalysts, this complexity is mapped onto a single thermodynamic descriptor, namely the binding energy of *OH or *O on the catalyst. This descriptor has a proven ability to predict and/or reproduce many experimental trends, but there remain experimental observations for which this descriptor has no explanatory or predictive power. In this paper, we have shown that one such experimental observation is the effect of the electrolyte composition on the ORR rate. Specifically, in acidic media the concentration of non-specifically adsorbed anions (such as perchlorate and methanesulfonate), and in alkaline media the concentration of non-specifically adsorbed cations (such as the alkali cations), have a significant effect on the ORR rate on Pt(111), which does not follow the traditional thermodynamic descriptor. To this end, we have introduced a kinetic descriptor, namely the kinetic rate of the *O to *OH transition, which can be estimated from the reversibility of the *O $\leftrightarrow$ *OH transition on the (111) terrace. This kinetic descriptor tracks well the observed changes in the ORR rate with the concentration/identity of anions, cations and ionomers on Pt(111) surfaces (Supplementary Fig. 8). We also measured a higher ORR activity on polycrystalline Pt electrodes in a lower concentration of HClO₄ (Supplementary Fig. 9), showing that the effect also transfers to more practical surfaces.

This observation requires a discussion of the molecular basis for this kinetic descriptor. In the classical mechanism of ORR on Pt surfaces, equations 1–4, the transition from *O to *OH is the penultimate reaction step. In the prevalent thermodynamic model, the parameter that determines the rate of ORR is the thermodynamics
of the last step, namely the conversion of *OH to water, that is the binding energy of *OH. The weaker this binding, the more free Pt sites will be available for the ORR reaction at a given potential. As mentioned, this descriptor works well when changes in the electronic structure, for instance by alloying, lead to changes in the potential of the *OH ↔ H_2O transition. However, it is important to note that the onset of ORR, say 0.95 V_RHE, is in the potential window where the Pt(111) surface is still almost completely covered with the *O adsorbate. One may wonder what exactly this free site is on which ORR should take place, when this *O adsorbate just starts to be reduced to *OH. Also, as the onset of ORR is in the potential window where *O covers the surface, it becomes logical to expect that the rate at which this adsorbate is converted to *OH co-determines the ORR rate. Indeed, DFT calculations by Sakong et al. suggest that there is a competition between step 3 and step 4 for the RDS of ORR, and the energetics of step 3 is sensitive to electrochemical environment. One could argue that although the final step may be the (main) potential-determining step of the overall reaction, the preceding step can still be partially rate-determining. In general, it is unlikely that only one step in a mechanism fully controls the overall rate. If we accept that the rate of this step co-determines the overall rate, then it is reasonable that it is related to the rate of the *OH → *OH transition observed in the blank voltammetry, in the absence of oxygen. An important assumption here is that the *O ↔ *OH transition observed in the blank voltammetry is the same as the reaction in equation 3 in the ORR mechanism, or at least that these reactions have similar kinetic pathways. It is to be expected that under ORR conditions, the actual *O coverage is higher than in the absence of oxygen in solution, and it may therefore be that the *O intermediate formed during ORR is not exactly the same as the *O formed during the blank voltammetry.

A second important question is why this *O ↔ *OH transition is slow or kinetically irreversible, and why this rate is influenced by the concentration of non-specifically adsorbed anions or cations? First of all, it is important to nuance the term non-specifically adsorbed. We generally consider anions such as perchlorate and methanesulfonate as non-specifically adsorbed because they do not chemically interact with the platinum metal surface. However, there are several reports that have shown that once an *OH adlayer is formed on Pt(111), this induces a weak but distinguishable interaction with perchlorate. A similar statement holds for the effect of cations and their interaction with the *OH layer. Marković et al. have termed this latter interaction non-covalent. In recent DFT calculations, we have shown that *OH and near-surface cations compete for water...
solvation, and hence exhibit an indirect (non-covalent) interaction mediated through the interfacial water. From the results shown in Figs. 2a and 3a, we must conclude that a stronger interaction of the anions or cations with the OH layer leads to a slower kinetics of the $O \leftrightarrow \cdot OH$ transition. The exact reason for this influence of the anions or cations is not yet clear. Gómez-Marín et al. have performed some limited kinetic measurements of the $OH \rightarrow O$ reaction and provided evidence for nucleation-and-growth type kinetics. Drnec et al. have provided X-ray-based evidence that the peak at 1.05–1.1 V, that we associate with the formation of $O$, involves buckling of the surface to the extent that it may correspond to the onset of (reversible) place exchange, which would then suggest that the $O$ species may actually be a subsurface species. Their result implies that subsurface $O$ ($O_{subsurface}$) might be involved in the ORR mechanism, at least close to the onset potential. In this scenario, step 3 of the ORR mechanism becomes $O_{subsurface} \rightarrow \cdot OH$, which presumably involves a place exchange process ($O_{subsurface} \rightarrow O_{surface}$) followed by a surface reduction reaction ($O_{surface} \rightarrow \cdot OH$). If this step becomes (partially) rate-limiting, the rate of ORR can be also indicated by our descriptor. Potentiodynamic impedance spectroscopy results by Bondarenko et al. showed that the structures of the Pt(111)/electrolyte interface in the $O$ potential region in the absence and presence of ORR, are very similar. This hypothesis of the involvement of subsurface $O_{subsurface}$ in the ORR mechanism, at least at the onset potential, of course requires more direct experimental evidence, in relation to the exact reason for the slow kinetics of the $O_{surface} \rightarrow \cdot OH$ transition, including the role of anions. Anions are known to change the interfacial water configuration. Computational work by Eikerling et al. with an explicit water model has shown a strong impact of interfacial water on the energetics of adsorbed oxygen species on Pt(111) surface. Clearly a more detailed study of the kinetics of the $O \leftrightarrow \cdot OH$ transition will be needed to further elucidate the true nature of its slow kinetics. For the purpose of this paper, it suffices to reiterate our key assumption that its kinetics reflects the rate of equation 3 in the ORR mechanism, and this step is at least partially rate-determining in the overall ORR rate. Further microscopic understanding of ORR on Pt is limited by the lack of knowledge on the exact structure of $O$ reactant in step 3. DFT studies found there co-exists three different $O$ species on Pt(111) at the on-set potential. It, however, remains unknown which of these O species is (directly or indirectly) involved in the ORR. Future experimental and computational clarification of this aspect would permit more realistic modelling for this reaction. Finally, our results on the stepped Pt surfaces show that the ORR rates on these surfaces can be understood as the sum or combination of the ORR rates on two different sites: A-type step-related sites and B-type terrace-related (111) sites. The ORR rate on the A sites is dominated by the traditional thermodynamic descriptor, and under acidic conditions, these sites are more active than B sites, and hence the thermodynamic descriptor works well in explaining the activity trends in acid. However, in alkaline solution, cations block the A sites, and render them less active than the B sites. The ORR rate on the B-type (111) sites are dictated by the kinetic descriptor as introduced here. As a result, in alkaline media, Pt(111) is more active than stepped Pt surfaces. This simple model of two different descriptors for the A and B sites solves the paradox of the different ORR activity trends on stepped Pt electrodes in acidic and alkaline conditions.

In conclusion, we have reported here the role of non-specifically adsorbing anions in suppressing the kinetics of ORR on Pt surfaces in acid. This anion effect is rationalized by the proposed descriptor – the reversibility of the $O \leftrightarrow OH$ transition on the (111) terrace, which is accessible from voltammetry. This descriptor tracks the ORR activity dependences on the concentration/identity of anions, cations and ionomers on Pt surfaces. We have proposed an enhanced model for ORR on the basis of the traditional thermodynamic descriptor and a kinetic descriptor, which rationalizes the different structure sensitivity of ORR activity on Pt surfaces in acid versus alkaline media. Our findings provide a more comprehensive model for ORR on Pt catalysts, which could potentially aid closure of the performance gap between half-cell and MEA measurements by considering the electrolyte effect and improvement of ORR activity using the upgraded ORR model.

**Methods**

**Electrochemical cells and electrolytes.** Electrochemical measurements were performed in a glass cell (for all acidic electrolytes) and a fluorinated ethylene propylene electrochemical cell (for all alkaline electrolytes). Prior to each measurement, all cell parts were cleaned by first immersing in a mix solution of H$_2$SO$_4$ (Sigma-Aldrich, 95.0–97.0%) and KMnO$_4$ (Sigma-Aldrich, ≥ 99.9%) overnight, then storing in a mixed solution of H$_2$SO$_4$ and H$_2$O$_2$. Millers KGaA, 35% for at least 2 hours, and finally boiling in ultra-high purity water (Merck Milli-Q) at 7000, 18.2 MΩ-cm at 298 K) at least five times. Electrolytes were prepared with ultra-high purity water and concentrated perchloric acid (traceSELECT, Fluka), concentrated methanesulfonic acid (Merck KGaA) or concentrated sodium hydroxide (Suprapur, Merck). Either disk- or bead-type platinum single-crystal electrodes were used as working electrodes in the hanging meniscus configuration. A flame-annaled platinum wire and a reversible hydrogen electrode were used as counter and reference electrode, respectively.

**Single-crystal electrodes.** Single-crystal Pt(111) and stepped electrodes, including Pt(151514), Pt(554) and Pt(553) were prepared by first flame-annaling with butane torches for 2 minutes, then quickly transferring to a cooling cell in an Ar/H$_2$ atmosphere of 3/1 (for Pt(111)) and 1/1 (for stepped Pt surfaces). After cooling to room temperature, the electrodes were dipped and covered with a droplet of ultra-high pure water for protection, before being transferred into the electrochemical cell for measurements. The Nafion coating solution was prepared by diluting commercial Nafion solution (Sigma-Aldrich, 5%) by 1,000 times. The coating solution (10 μl) was then added to the protective water droplet of Pt(111), and subsequently dried in a flow of Ar gas before electrochemistry tests.

**Electrochemical measurements.** Electrochemical tests were performed on a Biologic VSP-300 potentiostat using a three-electrode system. All potentials are reported against the RHE. The CVs were recorded in Ar-saturated electrolytes between 0.07 V and 0.9 V or between 0.07 V and 1.15 V (for extended CVs) at various scan rates, and reported after iR correction. A minimum scan rate of 10 mV s$^{-1}$ was chosen to avoid interference from trace amounts of contaminants. A blank CV of Pt(111) was always pre-recorded to assure the cleanliness and reproducibility of testing set-ups. We plotted the charge profile of $OH$ peak by integrating blank CVs, after double-layer correction. Specifically, we subtracted the drop of a ultra-high purity water for protection, before being transferred into the electrochemical cell for measurements. The Nafion coating solution was prepared by diluting commercial Nafion solution (Sigma-Aldrich, 5%) by 1,000 times. The coating solution (10 μl) was then added to the protective water droplet of Pt(111), and subsequently dried in a flow of Ar gas before electrochemistry tests.

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**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
M.L. and M.T.M.K. designed the experimental plan. M.L. carried out the experiments and data analysis. M.L. and M.T.M.K. wrote the manuscript.

Competing interests
The authors declare no competing interests.

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