Switching of Kinetically Relevant Reactants for the Aqueous Cathodic Process Determined by Mass-transport Coupled with Protolysis

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Electrocatalytic energy conversion driven by renewably generated electricity is a key technology to achieve a sustainable society in the future, namely, CO₂ reduction and hydrogen production. Despite increasing research efforts dedicated to these reactions, there is no consensus regarding the proton source directly participating in surface reactions under non-acidic pH conditions: Free proton (H⁺) versus proton-containing species (e.g., H₂O, H₂PO₄⁻, H₂CO₃⁻). We herein addressed this issue by rigorously quantifying the diffusion flux and protolysis rate during the aqueous hydrogen evolution reaction (HER). Our analysis revealed that there exists the linear free-energy relationship (LFER) between the pKₐ and the rate of protolysis (HA→H⁺+A⁻). Furthermore, the diffusion flux of the free proton as a consequence of the mass transport and protolysis failed to account for the typical current density of interest on the order of −10 mA cm⁻² at non-acidic pH levels when the pKₐ value and the molarity of the buffering species were low; e.g., < −0.1 mA cm⁻² was attainable at pH > 5 in 1.0 M KHCO₃ (pKₐ = 10.3). As a result, under such circumstance, the proton-containing species is suggested to directly react on the surface during the cathodic electrocatalytic reactions.

Introduction

Electrocatalytic processes possess the potential to achieve energy conversion in a sustainable manner when driven by the electricity generated from the renewable energy sources. The primary target in this regard is to catalytically convert the thermodynamically stable chemicals (H₂O, CO₂, and N₂)^[1–3] Often the aqueous phase is the reaction environment of choice in which the ubiquitous water functions as the proton source in the overall reaction. Therefore, in most cases, the overall reactions include the hydrogen evolution reaction (HER) as a half-reaction, either as the main or side reaction.

In spite of the significant research efforts dedicated to the HER in the last decades,[4–9] we still lack the fundamental understanding of its “true” kinetically relevant reactant participating in the surface reactions. The aqueous HER can be described in two ways in Equations (1) and (2):^[5]

(proton reduction) 2H⁺ + 2e⁻ → H₂, (1)
(water reduction) 2H₂O + 2e⁻ → H₂ + 2OH⁻ (2)

Historically, water electrolysis has been intensively investigated and even commercialized, which operates at highly acidic and alkaline pH levels.[10–12] In the acidic pH environment, the proton reduction reaction shown in Equation (1) is thought to represent the HER, given the large proton activity.[5,13] In contrast, the alkaline pH conditions are characterized by their small proton activity, and hence the HER therein can be dictated as the water reduction reaction presented in Equation (2).[5,13] One may, however, consider the “fast” protolysis of water [Eq. (3)]:

H₂O → H⁺ + OH⁻, (3)

in which the proton is produced that may function as the direct reactant even at alkaline pH levels.[14] As a whole, there has been no agreement as to the true kinetically relevant reactant of the HER at non-acidic pH levels.

Apart from the highly acidic or alkaline conditions, a mild reaction condition has recently emerged as an alternative choice of the reaction medium for water splitting. Being non-extreme pH conditions, the near-neutral pH electrolytes poten-
tially serve as a cost-effective reaction medium, which can also broaden the option for the electrocatalyst component. Notably, such a near-neutral pH condition is well compatible with the electrocatalytic CO₂ conversion, adding another motivation to the study.[19] We note in passing that the HER during CO₂ reduction is regarded as a side reaction, which needs to be suppressed to enhance the selectivity (or the Faradaic efficiency) toward the CO₂ reduction product.[16–18] Importantly, in the near-neutral pH medium, the electrocatalytic reaction rates can be greatly enhanced by adding the buffering species into the electrolyte solution,[19–21] whose presence significantly complicates the molecular level picture of the HER in comparison to the unbuffered extreme pH counterparts. From one perspective, the enhancement can be rationalized as simply originating from the buffering actions mitigating the local pH alteration, which is described by the Equations (4) and (5):

\[
\begin{align*}
\text{HA} & \rightarrow \text{H}^+ + \text{A}^-, \\
\text{HA} + \text{OH}^- & \rightarrow \text{A}^- + \text{H}_2\text{O},
\end{align*}
\]

where A denotes the buffering ions such as H₃PO₄⁻² or H₂CO₃⁻². In fact, in many studies, the proton released by the buffering action (or, the protolysis) is considered to directly participate in elementary steps of both the HER and CO₂ reduction.[19,20,22] Looking at the system from a different angle, one can consider that such buffering ions may directly interact with the catalytically active site, in which the direct reduction of the proton-containing species evidences the HER [Equation (6)]:[21,22–27]

\[
2\text{HA} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{A}^-.
\]

Putting all together, there are in total five possibilities as the representation of the HER in the aqueous system with the buffering species, as schematically summarized in Scheme 1.

In this study, we attempted to elucidate the kinetically relevant reactant of the HER in the aqueous phase that directly participates in the elementary steps. We focused on the diffusion flux of the proton and the proton-containing species, which is regarded as the maximum attainable reaction rates irrespective of the catalysts. Logically speaking, if the diffusion flux of species X (either the proton or the proton-containing species) is smaller than the target reaction rate (such as 10 mA cm⁻², corresponding to an approximate solar-to-hydrogen efficiency of 10% in solar water splitting[9]), this species X cannot be the predominant reactant that achieves this rate. Our study demonstrates that proton generation via protolysis can indeed enlarge the limiting diffusion current density of the direct proton reduction. Nevertheless, at non-acidic pH levels, because the protolysis rate of the protonated species and the activity of free proton in the bulk were too small to account for the appreciable current densities even under the influences of the protolysis, direct reduction of the proton-containing species HA or H₂O was indicated to proceed at such reaction rates. The results presented in this study highlight the significance of electrolyte engineering as a key aspect of electrocatalysis that determines the direct reactant and thereby impacts the transition states of the proton-coupled reactions.

**Results and Discussion**

We start with the analysis of the protolysis from a general view. The protolysis reaction shown in Equation 4 proceeds in both forward and backward directions at the following rates of \( r_f \) and \( r_b \), respectively [Eqs. (7) and (8)]:

\[
\begin{align*}
\text{r}_f & = k_i c_{\text{HA}}, \\
\text{r}_b & = k_b c_{\text{HA}}, \quad \text{c}_i,
\end{align*}
\]

in which \( k_i \) and \( k_b \) are the rate constants in the forward and backward directions, respectively, and \( c_i \) denotes the concentration of the species \( i \) that satisfies the Equation (9) with is activity \( a_i \).
where \( c_i \) denotes the concentration, \( c_i^0 \) is the standard concentration (usually 1 M), and \( \gamma_i \) is the mean activity coefficient.\(^{[15]}\) At equilibrium in which both rates are the same, the following relationship becomes apparent [Eq. (10)]:

\[
K_a = \lim_{[A] \to 0} \frac{a_{H^+} \cdot a_A}{a_{H^+} a_{A^+}} = \frac{k_f}{k_b},
\]

with \( K_a \) being the equilibrium constant. Of note, this \( K_a \) value for the protolysis (or the acid dissociation reaction) is used in practice to calculate the pK\(_a\) value using the Equation (11)

\[
pK_a = -\log(K_a).
\]

Protolysis is one of the most ubiquitous reactions that is involved in most chemical and biological processes, and as such, this reaction has long been the interest of a broad research community.\(^{[29,30]}\) In fact, some experimentally measured data are available concerning the forward and backward reaction rate constants for the acid-base reactions, including H\(_2\)O and HCO\(_3^-\), among others.\(^{[29]}\) The reported rate constants in the forward direction are summarized in Figure 1 with respect to the pK\(_a\) value. Apparently, the rate constant \( k_f \) on the logarithmic scale was found to increase with a decrease in the pK\(_a\) values in a linear fashion, indicating that a so-called linear free-energy relationship (LFER) exists for the protolysis.\(^{[29,31]}\)

Fitting the data (10 data points in total, including H\(_2\)O, D\(_2\)O, HF, NH\(_3\), HSO\(_4^-\), H\(_2\)CO\(_3\), HCO\(_3^-\), C\(_6\)H\(_5\)COOH, C\(_2\)N\(_2\)H\(_5\), and CH\(_3\)COOH; some of them are omitted in Figure 1 for simplicity) yields the Equation (12):

\[
\log(k_f) = A \cdot \log(K_a) + B,
\]

with \( A = 0.99 \) and \( B = 11 \) (R\(^2\) = 0.999). Of note, this linear correlation implies that the backward reaction rate constant \( k_b \) is insensitive to \( K_a \) being approximately on the order of \( 10^{11} \) M\(^{-1}\)s\(^{-1}\) irrespective of the pK\(_a\) value (which is apparent when combining Equations (10) and (12)).

We then turned to capturing the trend in the rate of proton release via protolysis (Eq. 4) with respect to the pH and pK\(_a\) values. At a given \( K_a \) value, the rate constant in the forward direction could be determined using Equation 12. The relative fraction in the activity of species HA and A\(^-\) could be estimated using Equation 10 with the pH value being the sole valuable, with which the ac\(^-\) of those species is quantifiable once the total activity is known (tentatively set to unity here). With these rate constants and ac\(^-\) at a variety of pH and pK\(_a\) values, we quantified the rate in the forward direction (\( r_f \)) using Equation 7, which was then compiled against pH and pK\(_a\) values in a contour plot shown in Figure 2. The key quantitative observation here was that the \( r_f \) became smaller at a larger pK\(_a\) (corresponding to a smaller equilibrium constant) and a larger pH value in the bulk. This result suggests that, if the proton-containing species were the direct reactant participating in the surface reaction rather than the proton generated via protolysis, its contribution to the overall reaction rate would be more pronounced at larger pK\(_a\) values. Quantitatively determining the extent of such a contribution requires a more sophisticated treatment of the system, calling for further investigations.

In what follows, we show a more refined model to quantitatively assess the contribution of the mass transport coupled with the protolysis to the overall reaction rate. To this end, we considered a model composed of H\(^+\), OH\(^-\), A\(^-\), HA, and H\(_2\)O in which protolysis, diffusion, convection, and surface reactions are all at play. The model did not include the direct H\(_2\)O reduction (Panel 5 in Scheme 1), in which the solvent H\(_2\)O

![Figure 1. LFER for protolysis. For the deprotonation reactions (HA→H\(^+\)+A\(^-\)), the forward rate constants are plotted as a function of pK\(_a\) Data in closed symbol are adopted from reference,\(^{[29-31]}\) while the open symbols are calculated with the results obtained for LFER in this study.](image1)

![Figure 2. The generalized rate of proton release from proton-containing species (HA→H\(^+\)+A\(^-\)). The contour plot visualizes the rate of the proton production (\( r_f \)) via protolysis at various pH and pK\(_a\) values, which was calculated using the activity values of HA, A\(^-\), and H\(^+\) in the bulk. The total activity of HA and A\(^-\) was set to be unity.](image2)
itself behaves as the reactant, thereby masking the changes induced by the protolysis. Ultimately, in addition to the free proton involved in the reaction (Panel 1 in Scheme 1), there are two possible scenarios:

(1) The HA species is electrocatalytically inactive (Panels 2 and 3 in Scheme 1). This condition indicates that the HA at the proximity of the electrocatalyst surface does not participate in the surface reactions. In turn, the proton-containing species HA indirectly contributes to the overall reaction by releasing its proton, which participates in the reactions on the electrode surface.

(2) The HA species is electrocatalytically active (Panel 4 in Scheme 1, in addition to Panels 2 and 3). Both the HA and H⁺ species directly interact with the surface of the electrode. In addition, the protolysis across the electrolyte among H⁺, OH⁻, A⁻, HA, and H₂O must be considered in a manner similar to the previous case.

For both cases, the diffusion flux is quantifiable using Fick’s law [Eq. (13)]:

\[ J_i = -D_i \frac{\partial c_i}{\partial x}, \]

in which \( J_i \) and \( D_i \) are the diffusion flux and the diffusion coefficient of species \( i \), respectively. The change in the concentration within the diffusion layer induced by the diffusion, the convection, and the protolysis are obtainable by considering the mass-balance among those phenomena under the considered boundary conditions (see the Experimental Section for the full description). With these comprehensive models, we computed the limiting diffusion current densities of the proton for case (1) and those of the proton and HA for case (2). More precisely, we consider “HA reduction” that dictates the limiting diffusion current densities originating from the diffusion flux of HA (Panel 4 in Scheme 1), while that for the H⁺ reduction is given by the diffusion of H⁺. For the latter current density, there are three possibilities as the source of the proton: (1) the free proton (Panel 1 in Scheme 1); (2) the proton generated by the protolysis of HA (Panel 2 in Scheme 1); and (3) the proton generated by the protolysis of H₂O (Panel 3 in Scheme 1). The limiting diffusion current density for the direct reduction of the free proton is readily obtainable using the Levich equation with the proton concentration in the bulk [Eq. (14)]:

\[ j_i = 0.62nFD_i^{1/3} \omega^{1/2} \nu^{-1/2} c_i, \]

in which \( n \) is the number of the electron involved (2 for the HER), \( F \) is the Faraday constant, \( \omega \) is the disk-rotation speed in the rotating disk-electrode (RDE) configuration, and \( \nu \) is the kinematic viscosity. We used \( \gamma c \) (or \( ac \); see Eq. 9) instead of \( c \) for the determination of the diffusion flux of Equations 13 and 14. This treatment was introduced to reflect the deviation from the ideal condition due to the phenomena inherent to the solutions denser than 0.1 M, where mean activity coefficient becomes considerably smaller than unity.[22,23]

The resulting limiting diffusion current densities are shown in Figure 3 for cases with the bicarbonate electrolyte (see also Supporting information Figures S1–S5 for other cases). We chose bicarbonate as the representative proton-containing species, because its \( pK_a \) value is relatively large (10.3; see the discussion concerning Figure 2) and it is also the common choice of the electrolyte for the electrocatalytic CO₂ reduction.[15–18] The pH values of the 0.5 and 1.0 M solutions were set to be 7.5 and 7.8, respectively, which corresponded to the ones saturated with CO₂, while that of 0.1 M was intentionally set to be 8.5, which was the same as the experimentally “as-prepared” 0.1 M solution (vide infra). Of note, the solubility of NaHCO₃ is 9.32 wt% (~1.2 M) in H₂O.[13]

Our calculations unambiguously propose the kinetically relevant reactant for the proton-coupled cathodic catalytic reactions in the aqueous phase by looking into the limiting conditions. In the absence of the protolysis, the Levich equation predicts the limiting diffusion current densities for the direct proton reduction to be on the order of \(-100 \text{nA cm}^{-2} \) ("H⁺ reduction without protolysis" in the figure). When the protolysis was taken into account, the attainable limiting diffusion current densities for the proton reduction were indeed enlarged to the values on order of \(-1 \text{μA cm}^{-2} \) ("H⁺ reduction with HA protolysis"); and the protolysis of HA (in this case, HCO₃⁻) increased further the limiting diffusion current densities of the proton reduction to the order of \(-100 \text{μA cm}^{-2} \) ("H⁺ reduction with HA protolysis"). Nevertheless, these quantitative analyses revealed that the limiting diffusion current densities for the

**Figure 3.** Reactant switching based on the analysis of limiting diffusion current densities in bicarbonate electrolytes at 3600 rpm. The calculated attainable total limiting diffusion current densities are shown for the 0.1, 0.5, and 1.0 M sodium bicarbonate (NaHCO₃) solutions at pH 8.5, 7.5, and 7.8, respectively.
proton reduction even under the influences of such protolysis reactions could not reach current densities on the order of 1 mA cm$^{-2}$. Since the limiting diffusion current densities are the maximum current densities attainable irrespective of the catalyst, this observation indicates that the proton reduction cannot account for the current densities of ca. 1 mA cm$^{-2}$ or more negative under those conditions.

Let us turn to the direct reduction of the proton-containing species as the origin of the appreciable current densities for the HER under the near-neutral pH conditions. In Figure 3, the limiting diffusion current densities computed for the direct reduction of the proton-containing species (HCO$_3^-$ in the current model case) are also presented and labeled as "HA reduction". The figure shows that the attainable limiting diffusion current density by the direct reduction of the proton-containing species was on the order of 10 mA cm$^{-2}$, being quantitatively three orders of magnitude greater than that of the proton reduction. Strikingly, therefore, such appreciable current densities are suggested to originate from the direct reduction of the proton-containing species.

In order to apply this finding to the experimental observations, we performed electrocatalytic HER testing. Firstly, cyclic voltammograms (CVs) were recorded using a Pt RDE as a model electrode in 0.5 M Na$_2$SO$_4$ electrolytes at pH 8. We note that under these conditions the sulfate ion SO$_4^{2-}$ is the predominant ion species, which does not contain the proton and therefore cannot chemically contribute to the cathodic reactions via forward protolysis (see the distribution of ions in Figure S6 in the Supporting information). As shown in Figure 4, only negligible current densities were observed in this potential range (down to −0.1 V versus reversible hydrogen electrode (RHE)), while the larger magnitude of current densities (e.g., −10 mA cm$^{-2}$) was apparent once more negative potentials were applied (see Figure S7 in the Supporting information), consistent with previous studies.$^{[13,34]}$ In other words, the measured current densities exceeded the limiting diffusion current densities via direct proton reduction (see Figure 3), indicating that the direct reduction of H$_2$O does proceed in these conditions. Of note, the fact that a larger overpotential was required for direct H$_2$O reduction than was required for proton reduction in the acidic media ($\approx$0 mV for Pt) suggests the kinetically slow nature of the H$_2$O reduction, which requires the catalytic dissociation of O$\cdots$H bonding.$^{[34–36]}$ Interestingly, such a picture holds true even in the presence of bicarbonate species. When the bicarbonate ion was present at a similar pH value of 8.5, current densities larger than those in the sodium sulfate electrolytes were experimentally observed. Furthermore, with the increase in the bicarbonate concentration, the current density was further enlarged at a given overpotential. Since the proton production via the protolysis of the bicarbonate is theoretically not capable of catching up such cathodic rates here (see our discussion concerning Figure 3), this observation strongly indicates that the direct reduction of the bicarbonate ions takes place to account for the observed current densities, rather than proton reduction. This finding is of critical importance for the community of the electrocatalytic CO$_2$ reductions, in which the proton H$^+$, rather than the bicarbonate HCO$_3^-$, is in most cases the considered direct proton source.

We close with a more general view that rationalizes the kinetically relevant proton source in the presence of buffering species. Figure 5 visualizes the limiting diffusion current densities toward the proton reduction (the sum of Panels 1 to 3 in Scheme 1) summarized with respect to the pK$_a$ and pH levels. For computing this figure, we considered a model system in which both HA and H$_2$O were present as the proton-containing species, and the ac$^+$ value of the species HA and A$^-$ at given pH and pK$_a$ values were determined with Equation 10 while the reaction rate constants were calculated with the LFER. The simulation results revealed significant variations in the attainable proton diffusion flux with pH and pK$_a$ values. As shown in the figures, the limiting diffusion current densities by the direct proton reduction became smaller with increasing pH and pK$_a$ values. Strikingly, when the pK$_a$ value was above 8 (including HCO$_3^-$ and HPO$_4^{2-}$ with pK$_a$ values of 10.3 and 12.7, respectively) at near-neutral pH levels, the limiting diffusion current density was below 10 mA cm$^{-2}$, indicating that the proton-containing species (HA and H$_2$O) need to be considered as the direct reactants participating in the surface reactions at such appreciable current density levels. In a more detailed example, in the carbonate electrolyte (pK$_a$ 10.3 for HCO$_3^-$/CO$_2^-$) that has been the common choice of the electrolyte for the CO$_2$ reduction reaction,$^{[15–18]}$ the limiting diffusion current densities by the proton reduction was significantly more positive than −0.1 mA cm$^{-2}$, while current densities on the order of tens of −1 mA cm$^{-2}$ have been repeatedly reported in the literature. Of note, although the computational simulation in this study was performed for the RDE configuration at 3600 rpm, the observation can be extended to other cases; the other typical conditions (such as a static electrochemical cell) yields a 0.5 mm-thick diffusion layer$^{[37]}$ that is 15-times thicker than the considered condition, leading to at most an approximately 15-times decrease in the limiting diffusion current densities. Because the smaller diffusion flux reaches the limiting conditions at the lower current density level, a similar picture holds.

![Image](image_url)

**Figure 4.** Experimentally obtained j–E relation for the HER. The cathodic polarization curves are shown in the figure, obtained using the Pt RDE in 0.5 M sodium sulfate (Na$_2$SO$_4$) (pH 8), 0.1 M sodium bicarbonate (NaHCO$_3$), 0.5 M NaHCO$_3$, and 1.0 M NaHCO$_3$, (pH 8.5). Conditions: 3600 rpm, 50 mV s$^{-1}$, H$_2$ atmosphere, 298 K.
true for the static system with limiting current densities being smaller than the value shown in Figure 5. Taken together, these observations clearly demonstrated that the bicarbonate ions HCO$_3^-$ rather than the proton itself was the kinetically relevant proton source for the electrocatalytic CO$_2$ reduction reaction. At appreciable current densities of practical interest, the electrolyte properties, regardless of the identity of electrodes, determine the participating reactant on the electrode surface for cathodic reactions such as HER and CO$_2$ reduction. Therefore, this study gives a clear guidance for the true proton-source participating in the surface reactions, which directly alters a molecular picture of transition states and in turn influences reaction kinetics and mechanism (Tafel analysis). While in most cases very little attention has been paid to the electrolyte conditions, the present study indicates electrolyte engineering as a critical concept impacting the electrocatalytic processes.

Conclusions

We rigorously analyzed the maximum attainable diffusion flux of the proton and the proton-containing species, which quantitatively describe reactant switching for the aqueous proton-coupled cathodic reaction depending on the current densities. We first compared the diffusion flux of the proton with and without the influences of the dissociation of the proton-containing species such as H$_2$O and buffering species (protolysis). Based on the mass-balance of the proton within the diffusion layer in which diffusion, convection, and protolysis concurrently occur, the diffusion flux of the proton became larger when protolysis was taken into account. However, the theoretically determined limiting diffusion current density for the proton reduction was found to be still significantly smaller than the experimentally observable appreciable current densities under the typical conditions of buffered near-neutral to alkaline pH levels (e.g., 0.1–1.0 M KHCO$_3$ at pH 8–9). Consequently, the direct reduction of the proton-containing species was suggested to be responsible for the proton-coupled cathodic reaction in a potential range where high current densities are attainable. Based on the finding described in this study, we emphasize the constraints by mass transport that drastically impact electrocatalytic process performances, demonstrating the significance of electrolyte engineering.

Experimental Section

Simulations. The simulation study was performed by solving the ordinary differential equations using MATLAB. We consider the limiting conditions in which the concentration of the reactive species (the proton and/or the proton-containing species) near the surface of the electrode were zero, while those in the bulk of the electrode follows the thermodynamic value (i.e., the bulk value determined by the equilibrium at given pH and pK$_a$ values). The diffusion flux was then determined by the Fick’s law (Equation 13 in the Results and Discussion section), while the diffusion fluxes of the species other than the reactive species were considered to be zero. More precisely, we set the following boundary conditions for case (1) “the HA species is electrocatalytically inactive” in the main text (Eqs. (15) to (19)):

\[ c_H^+ = 0, \]
\[ D_{HA} \frac{\partial c_{HA}}{\partial x} = 0, \]
\[ D_A \frac{\partial c_A}{\partial x} = 0, \]
\[ D_{OH} \frac{\partial c_{OH}}{\partial x} = 0, \]
\[ j_{lim,H^+} = -nF D_{H^+} \frac{\partial c_{H^+}}{\partial x}, \]  

while the equations below were considered for the case (2) “the HA species is electrocatalytically active” in addition to Equation 15 (Eqs. (20) to (23)):
The mean activity coefficient $\gamma$ was adopted from the available data-book\textsuperscript{[37]} and was used for the determination of the activity.

Importantly, we considered the change in proton concentration within the diffusion layer via protolysis with the relationship (Eq. (24)):

$$\frac{\partial c_H}{\partial x} = D_H \frac{\partial^2 c_H}{\partial x^2} - v(x, \omega) \frac{\partial c_H}{\partial x} + R_i = 0,$$

in which the first, second, and the third terms on the right side represent the change in the proton activity originating from diffusion, convection, and protolysis-deprotolysis rate, respectively\textsuperscript{[38,39]}. The velocity of the fluid in the above-equation is attainable with the Equation (25):

$$v(x, \omega) = (\omega \nu)^{0.5} \left[ -0.510 \left( \frac{\nu}{\nu_s} \right)^2 \chi^2 + 0.333 \left( \frac{\nu}{\nu_s} \right)^{1.5} \chi - 0.103 \left( \frac{\nu}{\nu_s} \right)^2 \chi^2 \right],$$

in which $\chi$ denotes the distance from the electrode surface.\textsuperscript{[40]} For simulations, the disk-rotation speed was set to be 3600 rpm.

Experiments. The RDE configuration was employed in this study with the polycrystalline Pt RDE purchased from BAS, Inc. Prior to each testing, the Pt RDE was first polished with a 1 μm diamond and then with a 0.05 μm alumina slurry (both purchased from BAS, Inc.). All measurements were conducted in the three-electrode configuration, with a Pt wire and Ag/AgCl (saturated with KCl) as counter and reference electrodes, respectively. The electrolytes were prepared with the following chemicals: Na$_2$SO$_4$ (> 99.99%), sodium hydroxide (NaOH; 99.99%), and NaHCO$_3$ (> 99.95%), purchased from Sigma-Aldrich. Before and during the measurements, hydrogen was supplied to the electrochemical cell at a flow rate > 20 ml min$^{-1}$ in order to insure a hydrogen-saturated atmosphere. The CVs were recorded at a scan rate of 50 mV s$^{-1}$ using a 16-channel, research-grade potentiostat system (VMP3) purchased from BioLogic Science Instruments. All current densities described in this report are expressed in terms of the geometric electrode surface area (0.071 cm$^2$), and all current–potential relationships were $iR$-corrected using measured impedance values (100 kHz, amplitude 10 mV, and 298 K) unless otherwise specified. The disk-rotation speed during the experiments was set to be 3600 rpm.

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Conflict of Interest

The authors declare no conflict of interest.

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