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Ion-Exchange-Mediated Pre-Association Gates Interfacial PCET

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Abstract

Interfacial proton-coupled electron transfer (I-PCET) is typically viewed as a single elementary reaction despite the accepted recognition that analogous solution-phase reactivity requires proton donor/acceptor pre-association. Herein, we examine the role of pre-association in I-PCET to a molecularly well-defined graphite-conjugated carboxylic acid (GC-COOH) surface site. We quantify electrolyte proton activity and I-PCET kinetics in acidic, acetate-buffered, and alkaline electrolytes as a function of NaClO₄ concentration ranging from 1 mole kg⁻¹ to 17 mole kg⁻¹. Measured I-PCET rates at GC-COOH are attenuated by a factor of 4.3 in acidic and 4.6 in acetate-buffered media relative to the rates expected based on the solution pH across this ionic strength range. In contrast, in alkaline electrolytes the apparent rate of I-PCET is far less diminished upon increasing NaClO₄ concentration. To account for these findings, we propose a multiple-step model for I-PCET in acidic and acetate-buffered media that invokes quasi-equilibrated exchange of interfacial Na⁺ for H₃O⁺ to form a hydrogen-bonded pre-association complex prior to rate-limiting concerted proton-electron transfer. In this model, a decrease in the ratio of interfacial vs bulk Na⁺ activity with added electrolyte inhibits H₃O⁺ pre-association, a phenomenon that is also captured in our molecular dynamics simulations. These studies emphasize the non-innocence of the supporting electrolyte species and exposes the key role pre-association equilibria play in I-PCET mechanisms. The work suggests that control over pre-association equilibria could be used as an effective handle for tailoring interfacial ion transfer reaction kinetics.

Introduction

Interfacial proton-coupled electron transfer (interfacial PCET or I-PCET) reactions play a central role in electrochemical catalysis and energy conversion technologies.¹⁻⁴ I-PCET reactions involve the reductive formation or oxidative scission of surface-hydrogen bonds and are thus key elementary reaction steps in hydrogen evolution and oxidation,^{5,6} oxygen evolution and reduction,^{7,8} carbon dioxide and nitrogen reduction,^{9,10} and fuel oxidation.^{8,11} Beyond electrocatalysis, I-PCET is operative in the stoichiometric reactions that occur in supercapacitors^{12,13} and sensors^{14,15} as well as non-Faradaic catalysis.¹⁶⁻¹⁹ In many instances, I-PCET is deleterious, including in corrosion,² parasitic hydrogen evolution,^{10,20,21} and electrolyte breakdown in both aqueous²² and aprotic electrolytes.²³⁻²⁵ Consequently,

a deep fundamental understanding of I-PCET reaction mechanisms is critical for the systematic development of sustainable catalysis and chemical energy conversion technologies.

Despite their ubiquity, I-PCET reactions remain poorly understood at a molecular level, particularly in comparison to the rich understanding of electrochemically-driven outer-sphere PCET (OS-PCET) reactions involving soluble molecules. This is in large part due to the distinct reaction mechanisms at play in interfacial as compared to outer-sphere PCET. For OS-PCET, electrons tunnel across the electrochemical double layer (EDL) to oxidize or reduce a soluble molecule and drive proton transfer. Since electrons can tunnel over length scales on par with or greater than the width of the EDL, the ionic composition and structure of the EDL plays a negligible role in OS-PCET kinetics. In contrast, for I-PCET, protons must transit the EDL to bind to specific surface sites and thus the ionic composition and structure of the EDL is expected to play a pronounced role in I-PCET.^{26–28}

The foregoing distinction is particularly germane because of the inherently concerted nature of I-PCET reactions. Electrochemical OS-PCET reactions can proceed via stepwise pathways with proton transfer either preceding (PT₁ET₂) or following (ET₁PT₂) a distinct electron transfer step or through a concerted proton-electron transfer (CPET) reaction pathway. In contrast, since electron re-distribution in a metal is nominally barrierless, I-PCET reactions proceed via concerted CPET pathways exclusively. Extensive studies of molecular PCET reactions in solution have shown that CPET pathways proceed through a three-step sequence, involving 1) quasi-equilibrated formation of a hydrogen-bonded pre-association complex between the redox active species and the proton acceptor, 2) rate-limiting CPET, and 3) subsequent dissociation of the successor complex (**Figure 1a**).^{29–31} Consequently, it has been shown that the overall rate of CPET is a function of the rate constant for the CPET step and the equilibrium constant for forming the pre-association complex.^{30,32,33} Indeed, it has been found that inhibited formation of the pre-association complex can substantially attenuate CPET rates.³⁴ Despite this rich appreciation of the multi-step nature of CPET reactions among molecules in solution, I-PCET reactions are generally described and modeled as single elementary reaction steps (**Figure 1b**) without explicit consideration of pre-association equilibria or their impact on reaction kinetics. Given the ubiquitous necessity for pre-association in molecular CPET, the obligate concerted nature of I-PCET, and the well-documented proton donor dependence of I-PCET processes,^{5,35–38} we hypothesized that similar pre-association equilibria may play a key, but overlooked, role in gating PCET at interfaces (**Figure 1c**). Unfortunately, the inherent complexity of most heterogeneous catalysts makes it difficult to isolate the impact of pre-association from other convoluting factors (e.g. surface restructuring, site blocking, etc.) that may also lead to promotion or inhibition of I-PCET.

Previously, we investigated the kinetics of aqueous I-PCET to well-defined reaction sites of graphite-conjugated carboxylic acid electrodes (GC-COOH).^{39–41} These materials, which are synthesized through a condensation reaction that links 3,4-diaminobenzoic acid to the native *ortho*-quinone moieties of glassy carbon, display well-resolved voltametric waves corresponding to I-PCET. The resultant pyrazine linkage connects the carboxylate through a continuous π -electron system to the electrode's band states, making it an authentic and molecularly defined host for I-PCET.^{39,41–43} Given the facile nature of electron redistribution in the graphitic carbon, the proton transfer coordinate is expected to define the majority of the barrier for I-PCET. Yet, we found that the maximal rate constants for I-PCET to GC-COOH in aqueous media of 20,000 s⁻¹ at pH 0 is far below the near diffusion limited rate (> 10⁹ s⁻¹) of proton exchange between oxo-acids in bulk water.^{44,45} This dramatic mismatch implies that the presence of the EDL serves to profoundly attenuate I-PCET rates. We hypothesized that this attenuation may arise in part due to the inhibited formation of the pre-association complex from which interfacial CPET occurs. Since the EDL is predominantly composed of the inert supporting electrolyte ions in the medium, we envision that changes to the supporting electrolyte strength could report on the dynamics within the EDL that effect I-PCET.

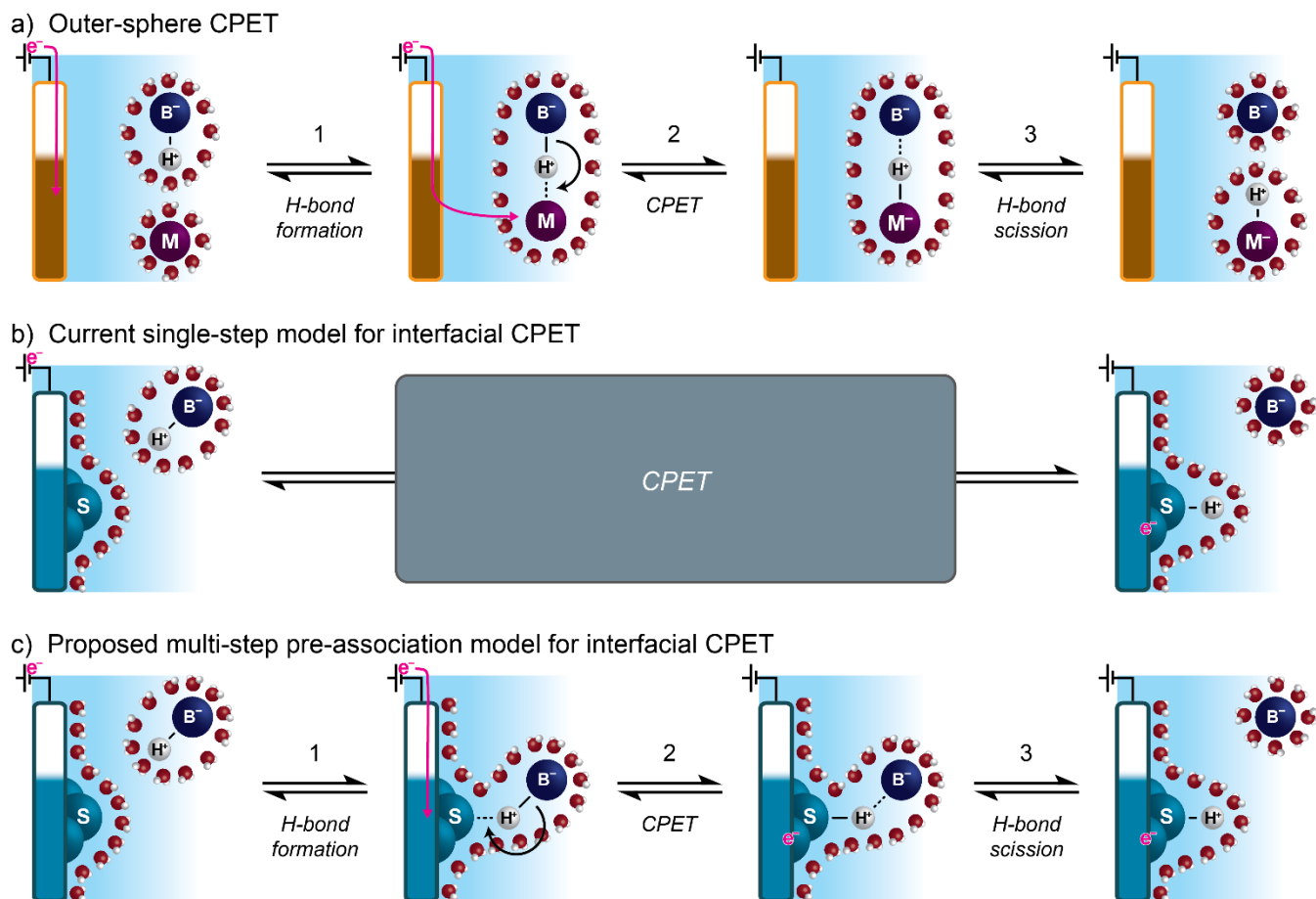


Figure 1 | Proposed pre-association mechanisms for outer-sphere and interfacial concerted proton-electron transfer (CPET): **a)** Outer-sphere CPET occurs in three steps: 1) association of a proton-donating acid “ B^+H ” and a PCET active molecule “ M ” into a co-solvated hydrogen-bonded pre-association complex in solution. 2) Proton transfer from “ B ” to “ M ” within the pre-association complex occurs at the same time as electron tunneling from the electrode to “ M ”, forming the PCET product “ M^+H ”. 3) Fragmentation of the successor complex into independently solvated base “ B ” and PCET product. **b)** Representation of the legacy model for I-PCET that invokes a single elementary step. **c)** Proposed pre-association mechanism for interfacial PCET occurs similarly with the following steps. 1) Formation of a co-solvated solution acid “ B^+H ” and surface active site “ S ” pre-association complex at the electrode/electrolyte interface. 2) Proton transfer from “ B ” to “ M ” within the pre-association complex coincident with electron transfer from the external circuit into the delocalized electrode band states, forming the PCET product “ S^+H ”. 3) Fragmentation of the successor complex into independently solvated base “ B ” and protonated surface site.

Herein, we investigate the role of the EDL and pre-association on I-PCET mechanisms by quantifying the thermodynamics and kinetics of I-PCET at GC-COOH electrodes across a wide range of supporting electrolyte concentrations. Specifically, we measure i) proton activity, ii) I-PCET thermochemistry, and iii) I-PCET kinetics in highly acidic, highly alkaline, and buffered electrolytes, each containing 1 to 17 molal (moles kg^{-1} or “m”) $NaClO_4$. We find that proton activity and equilibrium potential for I-PCET to GC-COOH track together, with increasing ionic strength increasing the proton activity and I-PCET potential in acidic electrolyte and minimally altering either parameter in buffered and alkaline electrolytes. Relative to rates predicted based on the measured proton activity changes, we find that I-PCET rates are

substantially attenuated in acidic and buffered electrolytes (a decrease in ~ 0.04 log units per molal, spanning a factor of ~ 4.5 across the range studied). In alkaline electrolytes, the relatively minor attenuation in measured proton activity is mirrored by the lack of substantial change in I-PCET rate across ionic strength. Based on these findings, we develop a mechanistic model for I-PCET that invokes a pre-association step involving the exchange of a supporting electrolyte ion from the EDL with the proton donor/acceptor, prior to rate-limiting CPET, a phenomenon that is also captured in molecular dynamics simulations. These findings highlight that ostensibly inert supporting electrolytes play a critical role in modulating I-PCET kinetics and establishes a framework for understanding how electrolytes influence the kinetics of interfacial ion transfer reactions that underpin electrochemical energy conversion and catalysis.

Results and Discussion

Experimental conditions

The studies described below employed NaClO_4 -based aqueous electrolytes due both to sodium perchlorate's relative inertness and its technological relevance. Unlike other commonly used highly soluble electrolytes, degassed aqueous NaClO_4 is not expected to contribute to a solid electrolyte interface (SEI) that could potentially convolute kinetic analysis of I-PCET.^{46–52} Furthermore, highly concentrated NaClO_4 -based “water in salt” electrolytes (WiSE), which maintain a wide electrochemical window and high conductivity,^{13,53–57} are practically relevant to a number of catalytic⁵⁸ and energy storage technologies.^{13,53–57}

All data in this study were collected under three proton donor/acceptor conditions (unbuffered acidic, acetate buffered, and unbuffered alkaline) each for 1 m, 5 m, 9 m, 13 m, and 17 m NaClO_4 allowing for comparison between acidity conditions and across a wide range of ionic strength. We assessed I-PCET across this extreme range of solution concentrations to perturb reaction conditions significantly enough to probe the hypothesized ionic strength-dependence of I-PCET reactivity. All measurements were conducted in solutions with consistent proton donor and acceptor ratios that are unchanged over the course of the experiment. To do so, the requisite amount of HClO_4 , NaOH , or acetic acid/sodium acetate buffer was added such that in the absence of dry NaClO_4 the electrolytes would contain a consistent relative mole fraction equivalent to 0.1 M HClO_4 for the acidic media, 0.1 M NaOH for the basic media, and 0.05 M acetic acid (AcOH) plus 0.05 M sodium acetate (NaOAc) for the buffered media. These donor/acceptor concentrations were chosen to minimize pH changes during and between experiments while minimal altering the overall concentration of dissolved species.

Effect of ionic strength on proton activity probed by a reversible hydrogen electrode

Before assessing the effect of electrolyte concentration on I-PCET thermodynamics and kinetics at GC-COOH it was first essential to quantify how ionic strength affects the activity of I-PCET reactants in concentrated aqueous media. Given that highly concentrated solutions are observed to be more acidic,⁵⁹ it is essential to differentiate if kinetic changes in I-PCET reactivity are simply due to a shift in proton activity and donor/acceptor equilibria or to additional concentration-dependent processes. As such, it is imperative to understand how the relative proton donor and proton acceptor *activities* are affected by a change in ionic strength for a fixed ratio of proton donor and acceptor molar *concentrations*.

To determine the electrochemical proton activity of each electrolyte, we measured the potential of a reversible hydrogen electrode (RHE) comprised of a platinum on PTFE gas diffusion electrode (Pt-GDE) under 1 atm H_2 . This method was necessary given the limitations of using a standard pH meter in concentrated media.^{3,59} Critically, the RHE potential (E_{RHE}) encompasses the ionic strength-dependent contributions of *all* species involved in the hydrogen evolution reaction (HER) and reverse hydrogen

oxidation reaction (HOR) equilibrium that together define solution proton activity. (See **Supplementary Note 2.1** for an extended discussion of E_{RHE} relevant to this work.)

For electrolytes of three different well-defined proton donor/acceptor concentrations we observed markedly different effects on E_{RHE} as a function of electrolyte ionic strength. **Figure 2** displays the E_{RHE} of a Pt-GDE in contact with solutions of 1 m to 17 m NaClO_4 with added 0.1 M HClO_4 , 0.1 M acetate buffer, and 0.1 M NaOH . In the presence of 1 m NaClO_4 , E_{RHE} equals -0.055 V (all potentials are reported vs the standard hydrogen electrode, SHE, unless otherwise stated) for the acidic electrolyte, -0.254 V for the buffered electrolyte, and -0.742 V for the alkaline electrolyte. These measured E_{RHE} values relay proton activities equivalent to pH values of 0.9, 4.3, and 12.6, respectively. Using a pH probe, the respective pH values of these 1 m NaClO_4 solutions were found to be 1.0, 4.3, and 12.6, indicating close agreement of these two methods at this relatively dilute concentration. Moving to higher concentrations, distinct trends were observed for the acidic, buffered, and alkaline media. From 1 m to 17 m, E_{RHE} for the acidic electrolytes shifts positively to $+0.056$ V (red). Over the same range, E_{RHE} for the buffered electrolyte and alkaline electrolytes shifts negatively to -0.271 V (green) and -0.767 V (blue), respectively. Linear regression analysis (gray dotted lines) of the E_{RHE} values from 1 m to 17 m returns slopes of $+6.9 \pm 0.6 \text{ mV m}^{-1}$, $-1.1 \text{ mV m}^{-1} \pm 0.5 \text{ mV m}^{-1}$, and $-1.7 \text{ mV m}^{-1} \pm 0.4 \text{ mV m}^{-1}$ for the acidic, buffered, and basic electrolytes, respectively ($\pm$ error equals 2σ). While a measured change in E_{RHE} might in principle be convoluted by artifacts of liquid junction potentials,⁵⁹ we estimate that these contributions are small (see **Supplementary Note 2.2**) and the measured change thus arises predominantly from changes in species activities. The increase of E_{RHE} in the HClO_4 electrolytes indicates an increase in the activity of the proton donor, H_3O^+ , versus the proton acceptor, H_2O . This pH change is equivalent to a 1.9 unit drop in pH_{eff} . Conversely, a negative shift of E_{RHE} in the buffered and alkaline electrolytes relay a slight *increase* in pH_{eff} of about 0.27 and 0.41 units for the buffered and alkaline electrolytes, respectively. As a function of molality, a negative E_{RHE} shift corresponds to an increase in proton acceptor activity relative to proton donor activity, i.e. acetate versus acetic acid and hydroxide versus water. These data demonstrate that in the presence of a common electrolyte (NaClO_4), the ionic strength-dependent proton activity of the three donor/acceptor conditions at constant molar ratio varies widely depending on the identity of the donors and acceptors involved.

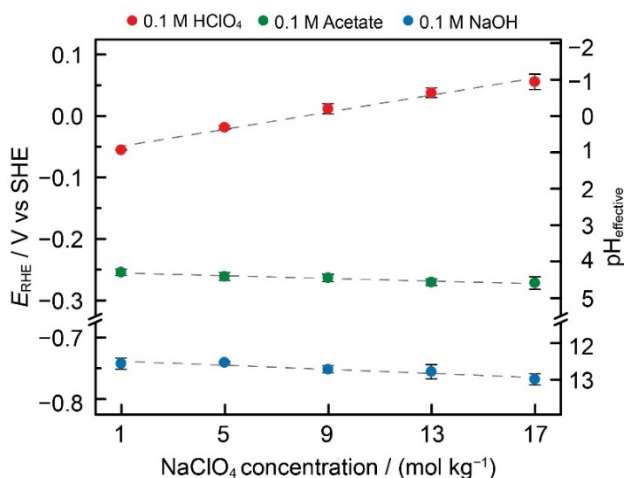
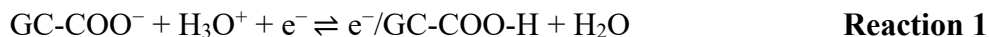


Figure 2 | E_{RHE} as a function of molality. Potentials of a Pt-GDE in contact with 0.1 M HClO_4 (red), acetate buffer (green), and NaOH (blue) under 1 atm H_2 as a function of NaClO_4 concentration. Data points are the mean of three measurements, error bars represent 2σ , and dotted gray lines represent linear fits to each data set. The right vertical axis denotes the effective pH, calculated by dividing the E_{RHE} values of the left axis by 0.059 V pH^{-1} .

The dissimilar proton activity dependence on supporting electrolyte concentration for the acidic, buffered, and alkaline electrolytes studied can be understood through differential interaction between dissolved protic (H_3O^+ , OH^-) and proton-innocent (Na^+ , ClO_4^-) ions. Changes in water activity alone, which span only a factor of two between 1 m and 17 m,^{58,60} are insufficient to account for the observed changes in E_{RHE} (**Equation 1**). The large positive shift in E_{RHE} of the HClO_4 electrolytes evinces a differential increase in the activity of H_3O^+ relative to water as NaClO_4 concentration increases. This increase in activity can be rationalized in terms of an increasing competition between H_3O^+ and Na^+ for solvent molecules, resulting in the destabilization of H_3O^+ relative to water. On the other hand, competition for solvent molecules is less perturbative in alkaline media as OH^- is more weakly solvated than H_3O^+ , a general property of anions,^{48,49,57,61} resulting in the small observed change in E_{RHE} . Likewise, in acetate buffered solution, the solution pH is set by the activities of AcOH and AcO^- which, as neutral and anionic species are also weakly solvated compared to H_3O^+ , resulting in retention of the species' buffering ability and little change in E_{RHE} across the studied ionic strength range.

Effect of ionic-strength on I-PCET thermodynamics at GC-COOH

With an understanding of the bulk activities of proton donors and acceptors in hand, we employed GC-COOH electrodes to study the effects of electrolyte concentration on the thermodynamics of interfacial electrochemical reactions. As in previous studies,^{1,39,41} GC-COOH electrodes were prepared by heating glassy carbon plates in an ethanolic solution of 3,4-diaminobenzoic acid (**Figure 3a**). Upon application of a negative potential GC-COOH carboxylate active sites bind protons, enforcing single electron addition from the external circuit to maintain the electrode potential, constituting an interfacial proton-coupled electron transfer reaction. As these sites are well-defined and consistent, the surface-proton bonds formed are uniform and have a defined bond strength. **Figure 3b** depicts the I-PCET reaction at GC-COOH's carboxylate site for an unspecified proton donor. The overall reaction at GC-COOH when the bulk proton activity is set by the $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ couple is:



When set by the AcOH/AcO^- couple, it is:



And when set by the $\text{H}_2\text{O}/\text{OH}^-$ couple, it is:



where GC-COO^- represents the deprotonated carboxylic acid site with an accompanying hole and $\text{e}^-/\text{GC-COO-H}$ represents the protonated site with an accompanying electron in the electrodes band states. Comparing **Reaction 1** through **Reaction 3** to HER^{Error! Reference source not found.} and HOR (**Reaction S1** and **Reaction S2** in **Supplementary Note 2.1**)^{Error! Reference source not found.} highlights that proton binding at GC-COOH and the HER/HOR are both I-PCET reactions with identical proton/electron stoichiometry and terminal proton donor/acceptor dependencies. As detailed previously,^{39–41} the molecularly defined structure and position within the EDL of GC-COOH active sites make these electrodes particularly well suited to investigating on-electrode ion-transfer reactions.

The equilibrium thermodynamics of I-PCET at GC-COOH were quantified at each solution condition using slow scan-rate cyclic voltammetry. **Figure 3c** shows a cyclic voltammogram (CV) of GC-COOH in

an electrolyte containing 1 m NaClO₄ plus 0.1 M NaOH, with a pH of 12.6, as measured by both a pH probe and E_{RHE} . Starting from 0 V vs SHE the GC-COOH active sites are entirely deprotonated. Upon application of a negative potential, the electrochemical proton affinity of the surface sites increases, causing the carboxylic acid to bind a proton at -0.45 V.^{39,41} To maintain the electrostatic potential of the electrode, as the proton crosses the EDL to bind to the surface a compensatory electron must flow from the external circuit to maintain the potential of the electrode. This electron flow is evidenced in the CV by the reductive wave at this potential. Polarizing to more negative potentials causes the two slightly Brønsted basic pyrazine nitrogen atoms to each bind a proton as well. The peaks near -0.65 V corresponding to the pyrazine I-PCET are twice as large as the carboxylate peak, given the two-to-one ratio of pyrazine nitrogen atom to carboxylic acid sites. Sweeping from negative to positive potentials raises the sites' effective pK_a values, first deprotonating the pyrazines at -0.65 V and the carboxylic acid moiety at -0.45 V. The mean of the peak cathodic and anodic peak potentials corresponding to the I-PCET at the surface carboxylate was taken as the reaction's equilibrium potential.

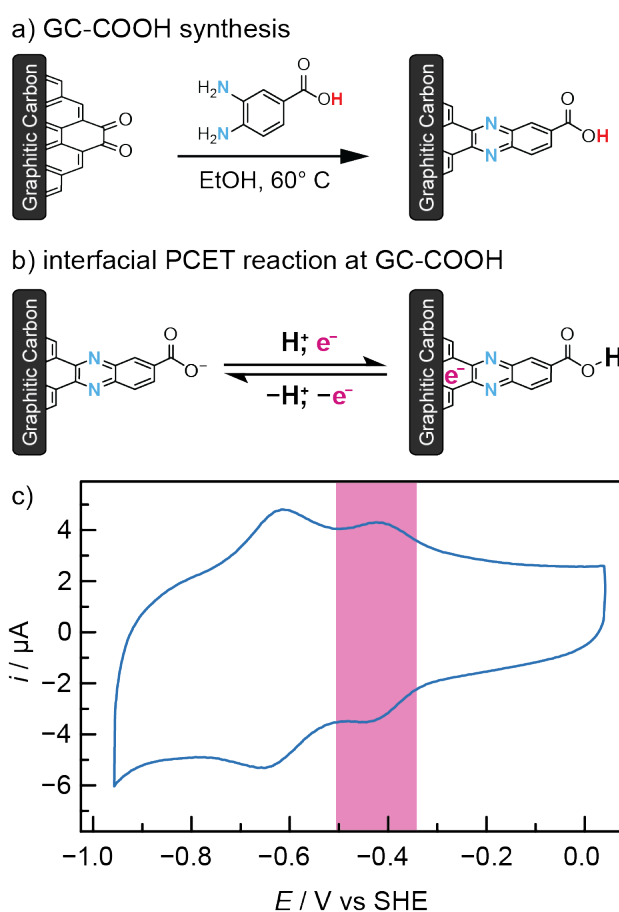


Figure 3 | GC-COOH preparation, I-PCET reactivity, and a cyclic voltammogram (CV). a) Illustration of the condensation of 3,4-diaminobenzoic acid to an *ortho*-quinone surface moiety on glassy carbon to produce a GC-COOH site. b) I-PCET at a GC-COOH site, comprising proton binding to the GC-COO⁻ site with compensatory electron flow into the electrode band states, represented by “e⁻”. c) CV of the reaction in 1 m NaClO₄ plus 0.1 M NaOH electrolyte showing pyrazine I-PCET peaks at -0.65 V and carboxylate I-PCET at -0.4 V, shaded pink.

The supporting-electrolyte-concentration dependence of I-PCET thermochemistry was assessed by measuring equilibrium potentials (E^{eq}) of I-PCET at GC-COOH at the same proton donor and electrolyte conditions of the above E_{RHE} measurements. **Figure 4** displays carboxylate I-PCET E^{eq} values as a

function of NaClO_4 concentration for the same acidic, buffered, and basic proton donor conditions as in the above E_{RHE} studies (See **Supplementary Data 3.1** for representative cyclic voltammograms from each condition.) **Figure 4a** shows E^{eq} for I-PCET referenced to the pH independent SHE scale. In the presence of 1 m NaClO_4 , E^{eq} occurs at 0.34 V for the acidic electrolyte, 0.12 V for the buffered electrolyte, and -0.42 V for the alkaline electrolyte. These E^{eq} values at ~ 1.1 M total ionic strength are within a few millivolts of the expected E^{eq} vs E_{RHE} measured previously for a 1 M solution.³⁹ As ionic strength increases from 1 m to 17 m NaClO_4 , E^{eq} for the acidic electrolytes increases significantly to 0.49 V, whereas E^{eq} for the buffered and alkaline electrolytes decreases only slightly to -0.09 V and -0.46 V, respectively. These changes are similar but not exactly equal to the E_{RHE} shifts observed in **Figure 2**.

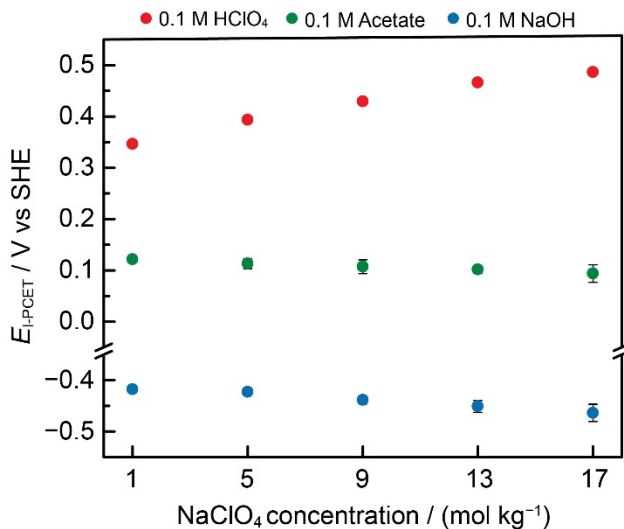


Figure 4 | Potential of I-PCET at GC-COOH as a function of NaClO_4 concentration referenced to SHE E^{eq} in solutions range from 1 m to 17 m NaClO_4 with solution proton activity set by 0.1 M HClO_4 (red), acetate buffer (green), and NaOH (blue). Data points are the mean of three measurements, error bars represent 2σ , dotted gray lines represent linear regressions, and shaded regions represent a 95% confidence band for each data set.

Effect of ionic strength on I-PCET kinetics

With an understanding of I-PCET thermodynamics at GC-COOH electrodes, we sought to investigate the mechanism of I-PCET. This was achieved by measuring I-PCET kinetics as a function of ionic strength and ionic-strength-dependent proton activity using the method of Laviron, also known as trumpet plot analysis.^{30,39,62} In the method of Laviron, for a surface-confined electron transfer reaction, CVs such as in **Figure 3** are collected across several orders of magnitude in scan rate. As the scan rate increases to a point where the surface reaction is out of equilibrium, the CV's anodic and cathodic peak potentials (E_{peak}) begin to separate.²⁹ Plotting the equilibrium-potential-normalized peak potentials ($E_{\text{peak}} - E^{\text{eq}}$) as a function of scan rate results in a characteristic trumpet shape (**Figure 5, top**). The experimental $E_{\text{peak}} - E^{\text{eq}}$ data in the trumpet plots can then be fit to the $E_{\text{peak}} - E^{\text{eq}}$ points of simulated CVs (**Figure 5 top, purple arc**) to extract site normalized apparent rate constants (k_{app} in s^{-1}) describing the equilibrium (zero overpotential) exchange rate of I-PCET. Our previous report presents a detailed explanation of this method and its application to I-PCET at GC-COOH.³⁹

Across solutions of constant ionic strength, we previously showed that the kinetics of I-PCET at GC-COOH are highly dependent on solution pH, with I-PCET being fastest at pH extremes and slowest at intermediate pH. Derived from simple linear-free-energy rate-potential dependencies, our mechanistic model faithfully captures the observed dependence over three orders of magnitude in the apparent rate

constant and fourteen orders of magnitude in the proton activity. In our model, dubbed the “caldera model” given the rate dependency’s inverted-volcano shape, the overall apparent rate constant, k_{app} , is simply the sum of the individual pH-dependent apparent rate constants for I-PCET proceeding through two separate proton donor/acceptor couples (**Figure 5** bottom, green). One couple consists of H_3O^+ as the proton donor for I-PCET and water as the conjugate acceptor (the “acid” reaction, equivalent to **Reaction 1**), while the other consists of water as the proton donor and OH^- as the conjugate acceptor (the “base” reaction, equivalent to **Reaction 3**). In acidic conditions where the activity of H_3O^+ far outweighs OH^- , the acid reaction prevails and its component pH-dependent apparent rate constant, $k_{app,acid}(pH)$ (**Figure 5** bottom, red) far exceeds that of the H_2O/OH^- couple, $k_{app,base}(pH)$ (**Figure 5** bottom, blue). Alternatively, in alkaline conditions, OH^- activity far exceeds H_3O^+ activity and $k_{app,base}$ is larger. While other buffering species may be present in solution, we showed that at GC-COOH, acetic acid and acetate serve only to set solution pH and are not competent proton donors or acceptors in the EDL. Therefore **Reaction 2** governs the overall thermochemistry but does not control the rate of I-PCET. As derived in our previous study, the two pH-dependent component apparent rate constants are each a function of only two parameters, the rate constant at standard state (k_{acid}^0 at pH 0 for acid, and k_{base}^0 at pH 14 for base) and a linear-free-energy scaling constant for each reaction (α_{acid} for the acid reaction and α_{base} for the base reaction). The overall caldera-shaped pH dependence can be written as:

$$k_{app}(pH) = k_{app,acid}(pH) + k_{app,base}(pH) \quad \text{Equation 1}$$

$$k_{app,acid}(pH) = k_{acid}^0 10^{-(1-\alpha_{acid})pH} \quad \text{Equation 2}$$

$$k_{app,base}(pH) = k_{base}^0 10^{\alpha_{base}(pH-pK_w)} \quad \text{Equation 3}$$

$$k_{app}(pH) = k_{acid}^0 10^{-(1-\alpha_{acid})pH} + k_{base}^0 10^{\alpha_{base}(pH-pK_w)} \quad \text{Equation 4}$$

In our previous study, the four governing parameters were determined to be $k_a^0 = 21,000 \text{ s}^{-1}$, $k_b^0 = 5,000 \text{ s}^{-1}$, $\alpha_a = 0.66$, and $\alpha_b = 0.70$ for I-PCET at GC-COOH at 1 m ionic strength. While the caldera model successfully captures the kinetic pH dependence of moderately dilute solutions, it was not developed to predict how electrolyte concentration controls I-PCET rates.

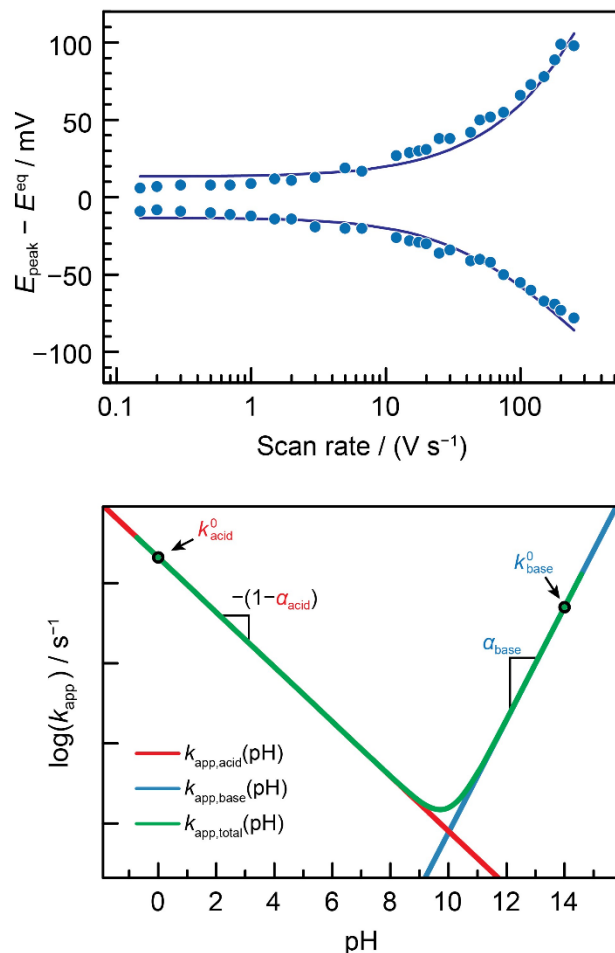


Figure 5 | Representative trumpet plot (top) and idealized k_{app} vs pH dependence expected from the caldera model at constant ionic strength (bottom). Top) A trumpet plot depicting the separation of peak potentials from the equilibrium potential ($E_{\text{peak}} - E_{\text{eq}}$) as a function of scan rate for I-PCET at GC-COOH in 1 m NaClO_4 plus 0.1 NaOH. (pH 12.6). Blue dots represent measured potentials and purple arcs represent simulated best fit peak positions for CVs with $k_{\text{app}} = 770 \text{ s}^{-1}$ for this particular data set. **Bottom)** Representation of caldera model for I-PCET at GC-COOH across pH values at 1 molar total ionic strength.²² The “V” shape of the total observed rate constant $k_{\text{app,total}}(\text{pH})$ is the sum of those for the acid and base reactions. The acid component $k_{\text{app,acid}}(\text{pH})$ is shown in red, anchored at pH 0 by k_{acid}^0 with a pH dependence log-linear with $-(1-\alpha_{\text{acid}})$ and the base component $k_{\text{app,acid}}(\text{pH})$ is shown in blue, anchored at pH 14 by k_{base}^0 with a pH dependence log-linear with α_{base} .

To assess the role of supporting electrolyte ions on I-PCET kinetics, trumpet plots were collected from 1 m to 17 m NaClO_4 in the same acidic, buffered, and alkaline electrolytes as above. I-PCET **Figure 6a** shows k_{app} values extracted from trumpet plots for the three proton donor/acceptor conditions from 1 m to 17 m NaClO_4 . (See **Supplementary Data 3.2** for a representative trumpet plot from each condition.) Starting from the 1 m NaClO_4 condition, k_{app} values extracted equal $9200 \pm 1700 \text{ s}^{-1}$ for the acidic condition, $1300 \pm 460 \text{ s}^{-1}$ for the buffered condition, and $920 \pm 240 \text{ s}^{-1}$ for the basic condition. These values are very close to those expected from the caldera model for a ~ 1 m solution. Traversing this range in electrolyte concentrations, the values of k_{app} as a function of concentration are best understood on a logarithmic scale. For acidic conditions, k_{app} is unchanged at $10^{4.0} \text{ s}^{-1}$ for all ionic strengths studied. This contrasts with the observation for acetate buffered electrolytes where k_{app} decreases from $10^{3.1} \text{ s}^{-1}$ at 1 m to $10^{2.4} \text{ s}^{-1}$ at 17 m, a factor of ~ 5.5 . Lastly, k_{app} values obtained for alkaline media increases only slightly

from $10^{3.0}$ at 1 m to $10^{3.1}$ at 17 m, within experimental error of each other and of the value measured at pH 13 in the caldera model study.³⁹ Upon cursory examination, the kinetics of I-PCET seem to be independent of ionic strength in unbuffered acidic and alkaline media whereas in buffered media I-PCET slows with increasing ionic strength. However, when these *insignificant changes in k_{app}* based on ionic strength for acidic electrolytes are viewed in context of the associated *significant changes in pH_{eff}* (**Figure 2**, red) and, similarly, the *significant changes in k_{app}* for the acetate buffered electrolytes are viewed in the context of *insignificant changes in pH_{eff}* , (**Figure 2**, green) it becomes apparent that an ionic-strength-dependent factor beyond proton activity must control I-PCET rates in concentrated media.

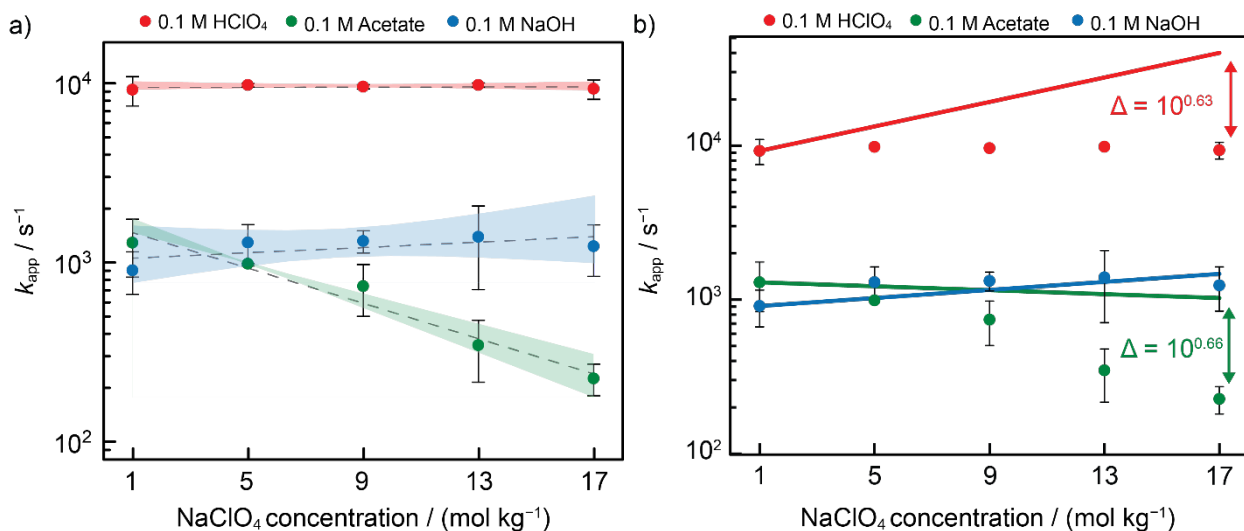


Figure 6 | Apparent rate constant (k_{app}) for I-PCET at GC-COOH as a function of electrolyte concentration.

a) Values of k_{app} extracted from trumpet plots for each of three proton donor/acceptor conditions are plotted as a function of molality. Data points are the mean of three measurements; error bars represent 2σ , dotted gray lines represent linear regressions, and shaded regions represent 95% confidence bands for each data set. **b)** Values of k_{app} from panel a (circles) and predicted ionic strength dependence of k_{app} based on changes in pH_{eff} (lines) calculated by adjusting the measured 1 m value using the estimated change in pH_{eff} from **Figure 2** regressions and appropriate scaling coefficients, α_{acid} and α_{base} , from **Figure 5**.

Careful examination of the trends in E_{RHE} shown in **Figure 2** and I-PCET rate constants shown in **Figure 6a** reveals an unexpected symmetry between the increase of E_{RHE} for acidic solutions and the decrease in k_{app} for buffered solutions. For acidic electrolytes, a linear regression of E_{RHE} against concentration predicts an increase in E_{RHE} equivalent to a 1.9 unit decrease in pH_{eff} as the concentration is increased from 1 m NaClO₄ to 17 m NaClO₄. According to **Equation 2** and assuming $\alpha_a = 0.66$, this pH decrease should correspond to an increase k_{app} of 0.64 log units, in sharp contrast to the measured increase of 0.01 log units (**Figure 6b**, red). On the other hand, an analogous linear regression for the buffered system of E_{RHE} against concentration predicts a small decrease in E_{RHE} equivalent to a 0.3 unit increase in pH_{eff} as the concentration is increased from 1 m NaClO₄ to 17 m NaClO₄. In contrast to the relatively small k_{app} decrease of 0.10 log units predicted by **Equation 6** ($\alpha_a = 0.66$) for such a small pH change, the observed change in k_{app} is a decrease of 0.76 log units, resulting in a very similar *relative* k_{app} decrease of 0.66 log units (**Figure 6b**, green). Thus, it can be observed that in both the acidic and buffered cases, the observed rate is lower than would be predicted based on pH_{eff} alone, whether this manifests as a decrease in the observed k_{app} (as in buffered solutions) or as the absence of the expected increase in k_{app} (as in acidic

solutions). Moreover, the relative rate decrease is similar in both cases, corresponding to an effective pH increase of ~ 2 units. These observations evince that the measured kinetic changes cannot be rationalized exclusively by applying our pre-existing kinetic model to ionic-strength-dependent changes in E_{RHE} . Furthermore, it is apparent that the striking similarity between the relative rate decreases as a function of ionic strength in acidic and buffered media suggests that a common effect governs the deviations from expected behavior in both systems. Contrastingly, in alkaline electrolytes, changes in ionic strength do not impart a substantial change in proton activity (**Figure 2**, blue) or apparent rate (**Figure 6a**, blue). Consequently, any ion strength contributions to rate attenuation are muted in unbuffered alkaline media (**Figure 6b**, blue).

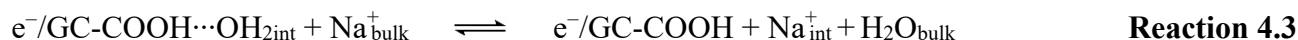
Model

To explain the decrease in I-PCET rate constants relative to those predicted by the caldera model, we introduce a complementary mechanistic framework for I-PCET that explicitly accounts for the need to form a pre-association complex prior to rate-limiting CPET and explicitly recognizes the role of supporting electrolyte ions on pre-association equilibria. As outlined earlier, the key aspect of I-PCET kinetics that the caldera model fails to capture is a relative decrease in the reaction rate in acidic and buffered solutions as supporting electrolyte concentration increases. To reconcile this discrepancy, we invoke that quasi-equilibrated exchange of electrolyte ions with proton donors/acceptors is necessary to form the hydrogen bonded pre-association complex required for I-PCET. To preserve the local electrostatic potential at the EDL, this ion exchange must involve pairs of like-charged electrolyte ions, that is Na^+ for H_3O^+ and ClO_4^- for OH^- . For a more detailed discussion concerning the presence of charge-matched co-ions at the interface, see **Supplementary Note 2.4**. We posit that this ion-exchange step becomes increasingly unfavorable upon increasing the concentration of electrolyte ions, leading to the observed inhibition of the overall reaction in acidic and buffered media. Notably, we anticipate that the displacement of ClO_4^- is less hindered at high concentrations relative to the displacement of Na^+ due to the weaker interaction of anions with water and/or surface moieties. This difference in behavior between ions is in line with the observed rate attenuations in acidic and buffered electrolytes where Na^+ displacement precedes CPET being much more pronounced than those in basic electrolytes where ClO_4^- displacement precedes CPET. Indeed, as both solution acidification and I-PCET rate attenuation are proposed to arise from competition between Na^+ and H_3O^+ , the proposed model also rationalizes the seeming insensitivity of the measured rate in acidic electrolytes to ionic strength (**Figure 6a**, red). The competitive effects are equal and opposite, and the measured rates in acidic and buffered solutions are attenuated relative to pH_{eff} to a nearly identical degree (**Figure 6b**, green and red), as the relative rate attenuation arises from a similar origin in both cases. This model is further discussed, justified, and formalized below.

The decrease in I-PCET rates relative to molality-dependent proton activity, pH_{eff} , in acidic and buffered concentrated NaClO_4 electrolytes reflects a negative reaction order in supporting electrolyte ion concentration. Activity changes associated with the terminal reactive species in the thermodynamics of each I-PCET reaction, as shown in **Reaction 1** through **Reaction 3**, cannot account for the observed trend, as the effect of the proton donor/acceptor activity changes have already been accounted for in adjusting for pH_{eff} . Notably the method of Laviron requires quantification of reaction kinetics at equilibrium,⁶² where the surface activities of protonated (GC-COOH) and deprotonated (GC-COO⁻) sites are equal to each other.³⁹ As mentioned above, these equilibrium potentials change minimally across the NaClO_4 concentration range relative to E_{RHE} (**Figure 4**). Consequently, though not explicitly apparent in **Reaction 1** through **Reaction 3**, we invoke the increase in the Na^+ and ClO_4^- ion activities themselves are the principal origin of the observed attenuation in I-PCET kinetics.

To account for the observed kinetic dependence on NaClO₄ concentration, we propose an I-PCET reaction mechanism in which the rate-limiting elementary CPET occurs from a hydrogen-bonded pre-association complex (**Figure 7**). We invoke CPET from the pre-association complex as rate-limiting because of the observed dependence of the rate on electrode potential³⁹ which implies a rate-limiting step that involves the transit of charge across the EDL. In contrast, formation of a hydrogen-bonded pre-association complex does not formally require charge to transit the EDL and thus a mechanism in which pre-association is rate-limiting would not be expected to give rise to a strong dependence of I-PCET kinetics on the applied potential. In acid (**Reaction 1**), the putative pre-association complex for the forward reaction consists of an H₃O⁺ ion hydrogen bonded to GC-COO⁻ and the corresponding pre-association complex for the reverse reaction consists of a water molecule hydrogen bonded to GC-COOH. Supporting electrolyte ions are not explicitly involved in I-PCET in net, and thus it would be unexpected for the rate of elementary CPET to depend strongly on their concentration. However, the formation of pre-association complexes in both directions does require the displacement of Na⁺ from the EDL to the bulk medium. As such, the observed dependence of I-PCET rate on supporting electrolyte concentration is more likely to arise from the formation of an I-PCET pre-association complex, a supporting-electrolyte-ion dependent step, than from supporting-electrolyte-ion independent CPET. In particular, the equilibrium constant for forming these pre-association complexes is expected to depend on the ratio of interfacial vs bulk Na⁺ activity as a function of NaClO₄ concentration. Notably, studies of the cation dependence of double layer capacitance have indicated that electrolyte concentrations within the thin layer of solution where a solid electrode and liquid electrolyte meet can exceed bulk solution concentrations by several orders of magnitude across a variety of metal surfaces, in some cases exceeding the bulk solubility of the electrolyte. Indeed, bulk electrolyte concentrations of just 50mM were found to support interfacial concentrations of 4M – a concentration ratio of roughly 80.^{63,64,65} Based on these findings, we postulated that the interfacial and bulk Na⁺ activities are unlikely to track in a 1:1 fashion with added NaClO₄ as maintaining such a large concentration ratio in a concentrated bulk electrolyte would imply an impossibly high interfacial Na⁺ concentration. Thus, we hypothesized that increasing the NaClO₄ concentration serves to increase bulk Na⁺ activity more so than interfacial Na⁺ activity, thereby inhibiting formation of I-PCET pre-association complexes.

To include pre-rate limiting interfacial co-ion exchange in I-PCET involving a hydronium-donor, as occurs in both the HClO₄ and acetate buffered electrolytes, **Reaction 1** can be expanded to three steps:



Where the subscript “int” indicates an interfacial species. **Error! Reference source not found.**, shown pictorially in **Figure 7**, includes: **Reaction 4.1**, a Na⁺ ion leaving the interface to accommodate a H₃O⁺ donor that hydrogen bonds to the surface carboxylate to form the pre-association complex (hydrogen bonding is represented by triple bullets, “...”); **Reaction 4.2**, the CPET reaction step; and **Reaction 4.3**, a Na⁺ ion returning to the interface following the PCET step. In **Reaction 4.1** and **Reaction 4.3**, Na^{int} represents the ensemble average of all configurations of Na⁺ at the interface in the vicinity of the graphite-conjugated acid site, including contributions from fully solvated Na⁺⁺, Na⁺ in the EDL non-specifically

adsorbed to the electrode surface, and any Na^+ coordinated specifically to surface $\text{COO}(\text{H})$ moiety. **Error! Reference source not found.** requires Na^+ to return to the EDL following I-PCET because the neutralization of the cationic H_3O^+ during I-PCET creates a charge imbalance near the interface. As $\text{Na}_{\text{int}}^+ \rightleftharpoons \text{Na}_{\text{bulk}}^+$ precedes the rate limiting step, the forward reaction slows as the activity of $\text{Na}_{\text{bulk}}^+$ increases relative to Na_{int}^+ . Conversely, the concluding step $\text{Na}_{\text{bulk}}^+ \rightleftharpoons \text{Na}_{\text{int}}^+$ should become more favorable with increased $\text{Na}_{\text{bulk}}^+$, but this equilibrium follows the rate limiting CPET and therefore does not affect the forward rate of **Error! Reference source not found.** Likewise, in the reverse direction, the microscopic reverse of step **Reaction 4.3**, $\text{Na}_{\text{int}}^+ + \text{H}_2\text{O}_{\text{bulk}} \rightleftharpoons \text{H}_2\text{O}_{\text{int}} + \text{Na}_{\text{bulk}}^+$, precedes the rate-limiting CPET step, imposing the same inhibitory effect on the reverse I-PCET pathway. This common inhibitory effect on the forward and reverse I-PCET manifests in the observed lowering of the exchange rate for I-PCET involving a hydronium-donor upon increasing ionic strength.

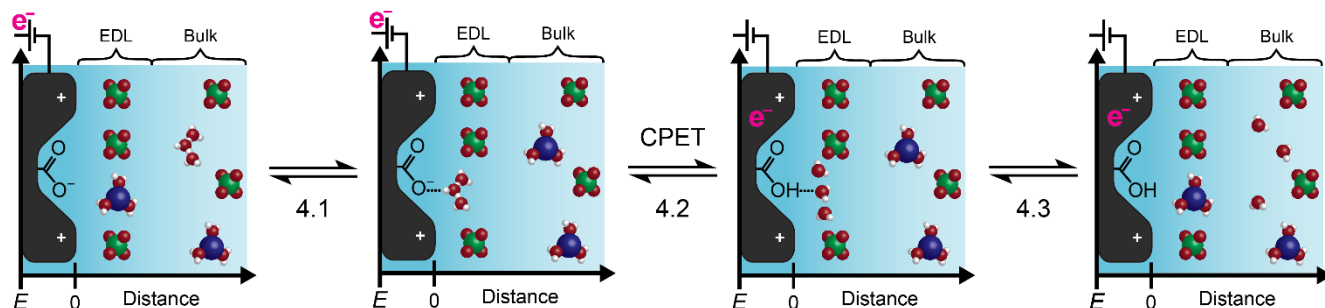
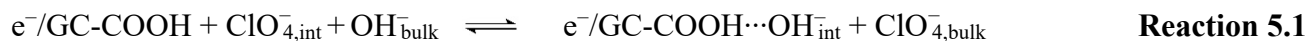


Figure 7 | Putative three-step mechanism for I-PCET when H_3O^+ acts as the proton donor. (Reaction numbers reflect text assignments.) 4.1: Na^+ liberation from the EDL accompanies H_3O^+ (shown as H_7O_3^+) binding to the carboxylate surface site to form the I-PCET pre-association complex. 4.2: Concerted proton electron transfer from the pre-association complex to form the hydrogen-bonded successor complex. Electron flow from the external circuit compensates interfacial proton transfer. 4.3: The successor complex fragments, liberating the produced water from the EDL. Na^+ returns to the EDL to reestablish the charge state present before I-PCET. In the electrode surfaces the “+” symbols reflect the surface potential versus E_{PZFC} (the electrode-solution iso-potential) at the relevant E_{PCET} for each pH_{eff} condition.

In alkaline media where OH^- acts as a proton acceptor, **Reaction 3** can be expanded to include anion movement just as **Reaction 1** is expanded to include cation movement in **Error! Reference source not found.** In this case it is helpful to write out the I-PCET in the reverse direction with OH^- accepting a proton from the surface.



Error! Reference source not found. involves the displacement of interfacial ClO_4^- by OH^- from the bulk (**Reaction 5.1**) preceding the rate limiting CPET step (**Reaction 5.2**) as well as a subsequent return of anionic ClO_4^- to the EDL (**Reaction 5.3**). Just as in **Error! Reference source not found.**, the post-rate-limiting return of ClO_4^- to the EDL is needed to reestablish interfacial charge neutrality and ensure that

the microscopic reverse of **Error! Reference source not found.** also involves pre-rate-limiting interfacial ion displacement.

To probe the atomistic details of the pre-association step in acidic electrolytes, we performed molecular dynamics simulations of GC-COO⁻ active sites bound to a graphite surface in an electrolyte consisting of aqueous 0.05 M HClO₄ and NaClO₄ at 1 m, 3 m, and 5 m (Simulation details can be found in **Supporting Information Section 1.8**). To assess the role of the supporting electrolyte in hydronium coordination to GC-COO⁻, we calculated the free energy of the H₃O⁺ as a function of its distance, r , from the carboxylate as the concentration of NaClO₄ was increased (**Figure 8**, right). The difference in the free energy, $\Delta\mathcal{F}$, between H₃O⁺ in the bulk ($r = 25$ Å) vs H₃O⁺ hydrogen bonded to the GC-COO⁻ ($r = 2.7$ Å, the bottom of the $\Delta\mathcal{F}$ well near the surface) increases from -13 ± 3 meV to 16 ± 1 meV as the NaClO₄ concentration increases from 1 m to 5 m. This change indicates that H₃O⁺ binding to GC-COO⁻ is destabilized by 29 ± 3.5 meV over this molality range, supporting the notion that inhibited pre-association is a key contributor to the observed attenuation in I-PCET kinetics with added electrolyte.

To further understand the role of Na⁺ ion interactions with GC-COO⁻ in affecting H₃O⁺ pre-association, we decomposed the total free energy difference for H₃O⁺ pre-association into contributions from varying degrees of Na⁺ coordination to GC-COO⁻ within the first coordination shell (See **Supplementary Data 3.3** for more details). For 1 m NaClO₄, 65% of the simulation displayed no Na⁺ coordination to GC-COO⁻ whereas in 31% a single Na⁺ ion was coordinated to the GC-COO⁻. Relative to the full simulation average binding energy, H₃O⁺ binding is stabilized by 4 ± 5 meV in the absence of Na⁺ coordination and destabilized by 7 ± 5 meV in the presence of a single Na⁺ ion coordinating. For 5 m NaClO₄, the simulations show GC-COO⁻ coordination with either 0, 1, or 2 Na⁺ ions for 29%, 46%, and 24% of the simulation, respectively. This amounts to an increase in the average coordination number from 0.40 to 0.97 Na⁺ ions upon a fivefold increase in bulk NaClO₄ concentration. Relative to the average over the full simulation at 5 m, H₃O⁺ binding energies differ by -11 ± 3 , -0 ± 3 , and $+33 \pm 7$ meV, for 0, 1, or 2 coordinated Na⁺, respectively. Notably, comparing the subset of simulations with no Na⁺ coordination in the first coordination shell, H₃O⁺ binding is still disfavored by 22 ± 3 meV as the molality increases from 1 m to 5 m, indicating that while coordination of Na⁺ in the first coordination shell of the GC-COO⁻ plays a substantial role, a significant fraction of the observed trends persist even in the absence of these interactions. Additionally, the simulations highlight that there are many possible modes of Na⁺ association to the surface, the ensemble average of which is reflected in the Na_{int}⁺ parameter in the above expressions. The molecular dynamics simulations thus capture the putative inhibition of H₃O⁺ pre-association with increased electrolyte strength.

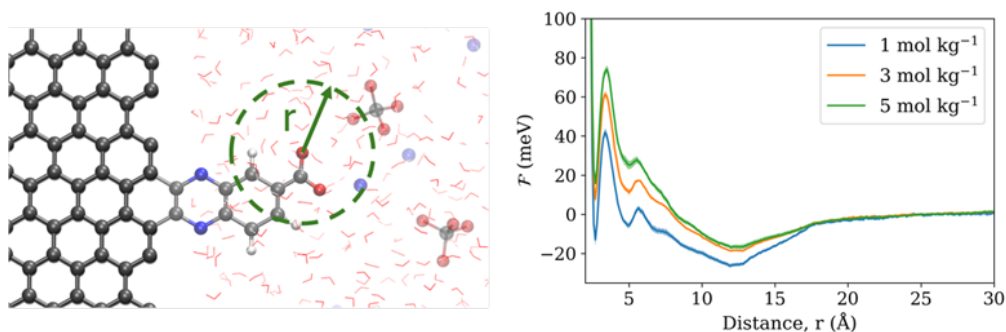


Figure 8 | Molecular dynamics simulation snapshot and free energy as a function of the distance from the GC-COO⁻ group as the concentration of NaClO₄ is varied. **Left:** a configuration from the molecular dynamics simulation of a GC-COO⁻ site with an aqueous solution of 0.05 M HClO₄ and 1 m NaClO₄. The dashed line denotes the distances from the carboxylate oxygen atoms used to compute the relative free energy. **Right:** Relative Helmholtz free energies ($\mathcal{F}$) of H₃O⁺ as a function of r , the distance from one of the carboxylate oxygen atoms, as a function of NaClO₄ concentration. Free energies are aligned to the bulk value at 25 Å. From this one observes that as the concentration of NaClO₄ supporting electrolyte is increased from 1 m to 5 m, the hydronium is destabilized in the carboxylate-coordinated position ($r = 2.7$ Å) relative to the bulk ($r = 25$ Å) by 29 meV. The shaded region around each line denotes the 1 σ statistical error in the mean obtained from the simulations.

To account for the impact of the co-ion exchange pre-equilibria on I-PCET rates, we introduce complementary ionic-strength-dependent rate equations to those of **Equation 2** and **Equation 3** that define the constant ionic-strength caldera model. Incorporating an inverse dependence of I-PCET's apparent rate constant on the ratio of bulk to interfacial NaClO₄ activity results in the following equations:

$$k_{\text{app,acid}}(\text{pH}_{\text{eff}}, m) = k_{\text{acid}}^0 \times \frac{a_{\text{Na}^+}^{\text{int}}(m)}{a_{\text{Na}^+}^{\text{bulk}}(m)} a_{\text{H}_2\text{O}}^{\text{bulk}}(m) \times 10^{-(1-\alpha_{\text{acid}})\text{pH}_{\text{eff}}} \quad \text{Equation 5}$$

$$k_{\text{app,base}}(\text{pH}_{\text{eff}}, m) = k_{\text{base}}^0 \times \frac{a_{\text{ClO}_4^-}^{\text{int}}(m)}{a_{\text{ClO}_4^-}^{\text{bulk}}(m)} a_{\text{H}_2\text{O}}^{\text{bulk}}(m) \times 10^{\alpha_{\text{base}}(\text{pH}_{\text{eff}} - \text{p}K_{\text{w}})} \quad \text{Equation 6}$$

The “ a ” terms refer to the activity of the subscripted species in either the superscripted bulk or interfacial phase. These interfacial activities reflect the aggregate contributions from all Na⁺ and ClO₄⁻ ions interacting with the electrode surface. Each *activity* term and apparent rate constant, k_{app} , term is noted as a function of the bulk supporting electrolyte molality “ m ,” with each term separately dependent on the bulk ion *concentration*. A full derivation of **Equation 5** and **Equation 6**, including the explicit dependence on water activity appear in the **Supplementary Note 2.3** and **Supplementary Note 2.4**. Defining the bulk ion activities and the bulk activity of water to be unity at 1 mol kg⁻¹ ionic strength and referencing the unknown interfacial ion activities as unity as well, **Equation 5** and **Equation 6** collapse into **Equation 2** and **Equation 3** at the 1 m reference state. The proposed interfacial ion transfer reactions, though potentially operative at these lower concentrations, only exert apparent rate control when I-PCET rates are measured over a large range of ionic strength conditions. As written, it is clear that an increase in bulk ion activity relative to the interfacial ion and bulk water activities leads to an overall rate decrease as ionic strength increases at a fixed pH_{eff}.

Differing dependencies between bulk vs. interfacial activities for ClO₄⁻ ions and bulk vs. interfacial activity for Na⁺ ions as a function of bulk NaClO₄ concentration give rise to the more muted scaling of observed I-PCET rates versus pH_{eff} in the basic electrolytes. As mentioned above, at 17 m in both electrolytes where H₃O⁺ acts as the proton donor, the apparent rate constant for I-PCET is about 4.5-times less than would be expected from **Equation 2** based on the measured proton activity (**Figure 6b**, red & green). The complementary factors included in **Equation 5**, but not **Equation 2**, that is $\frac{a_{\text{Na}^+}^{\text{int}}(m)}{a_{\text{Na}^+}^{\text{bulk}}(m)} \times a_{\text{H}_2\text{O}}^{\text{bulk}}(m)$, must account for this change. According to this model, in light of the 2-fold decrease in $a_{\text{H}_2\text{O}}^{\text{bulk}}(m)$ from 1 m to 17 m NaClO₄,⁶⁰ a ~2.25-fold increase of $a_{\text{Na}^+}^{\text{bulk}}(m)$ compared to $a_{\text{Na}^+}^{\text{int}}(m)$ over the same range must be additionally hindering ion transfer, thereby slowing I-PCET at high ionic strength. Notably, this scaling in bulk and interfacial Na⁺ activity differs only minutely between the acetate buffered electrolytes that occur

near 0 V vs the potential of zero free charge (E_{PZFC} , the electrode potential that equals the bulk solution potential) and the HClO_4 electrolytes at least 0.25 V positive of E_{PZFC} , two cases where the EDL structure and ion excess are expected to differ significantly. In basic media, k_{app} displays no significant dependence on ionic strength, implying that the two-fold increase in k_{app} predicted by pH_{eff} measurements and **Equation 3** are wholly negated by the effect of the decrease in water activity in **Equation 6**, suggesting that changes $\frac{a_{\text{ClO}_4^-}^{\text{int}}(m)}{a_{\text{ClO}_4^-}^{\text{bulk}}(m)}$ are comparatively minor (**Figure 6b**, blue).

The stark difference in interfacial versus bulk activity scaling for the Na^+ and ClO_4^- ions likely stems from different solvation thermodynamics between the more charge-dense cation and diffusely charged anion.^{48,57} Competition for solvation increases the chemical activity of bulk Na^+ ions versus Na^+ ions in the EDL and promotes coordination to the active site, thereby inhibiting the exchange of Na^+ for H_3O^+ (**Figure 9**, left). Conversely, the more diffusely charged ClO_4^- is less destabilized by the paucity of solvent, minimally effecting its bulk vs EDL activity, and is expected to more weakly interact with the active site. Consequently, increasing ClO_4^- activity imparts minimal change in the pre-association reaction quotient when OH^- acts a proton acceptor (**Reaction 5.1**) and thus, leads to no substantial deviation in I-PCET rates relative to those expected from the caldera model (**Figure 9**, right). Indeed, though impossible to verify experimentally,⁵⁹ computational models suggest Na^+ and ClO_4^- could have asymmetric individual ion activity coefficients in the bulk.^{66–68}

Both **Equation 5** and **Equation 6** relay two activity-based ionic-strength-dependent effects on I-PCET apparent rate. One of these relates to the change in proton donor/acceptor activities (pH_{eff}), classically considered in I-PCET, and one relates to the product of the activities of species not historically thought to effect I-PCET, that is supporting electrolyte ions and bulk water, that is $(\frac{a_{\text{ion}}^{\text{int}}(m)}{a_{\text{ion}}^{\text{bulk}}(m)} \times a_{\text{H}_2\text{O}}^{\text{bulk}})$. These effects are only distinguishable when I-PCET thermochemistry and equilibrium kinetics can be measured independently as developed herein. Within both unbuffered acidic and alkaline media, each system's effective rate increase due to pH_{eff} and decrease due to $\frac{a_{\text{ion}}^{\text{int}}(m)}{a_{\text{ion}}^{\text{bulk}}(m)} \times a_{\text{H}_2\text{O}}^{\text{bulk}}$ are equal in magnitude and thus cancel out to no net change in k_{app} (**Figure 6**). The ionic strength dependence of electrolyte proton activity and I-PCET kinetics on reactions involving two very different supporting electrolyte and donor/acceptor ions suggests that this compensation of ion-dependent bulk proton donor/acceptor activity and pre-rate-limiting interfacial co-ion exchange equilibria may be general to cations and anions, and that the relative strength of these effects can be qualitatively predicted based on the ions' solvation thermodynamics and coordinating ability.

In contrast to the ionic-strength independence of k_{app} observed in unbuffered acidic and basic solutions, k_{app} for I-PCET decreases markedly in acetate buffered electrolytes with increasing ionic strength. This observed decrease arises from the fact that the acceptor/donor couple responsible for setting the bulk proton activity (acetic acid and acetate) are not the kinetically relevant species involved in I-PCET. Thus, unlike in unbuffered acidic solution, the inhibited displacement of Na^+ from the EDL at high ionic strength is not compensated by an increase in bulk proton activity. Indeed, pH_{eff} remains constant across the concentration range (**Figure 2**, green), suggesting that interactions between the acetate acid/acetate buffer and the supporting electrolyte are minimal (**Figure 9**, middle). In these buffered conditions, below pH 10 H_3O^+ remains the kinetically relevant proton donor, and still must displace Na^+ ion from the EDL prior to CPET just as in the strong acid case. Thus, upon accounting for the differential pH variations across the two conditions, both the buffered and strongly acidic media display very similar rate attenuations of ~ 0.7 log units with increasing ionic strength. This common scaling indicates Na^+ transfer between the interface

and electrolyte gates I-PCET as long as H_3O^+ is the kinetically relevant I-PCET proton donor and kinetically incompetent buffers play an orthogonal role in setting the proton activity in the bulk medium.

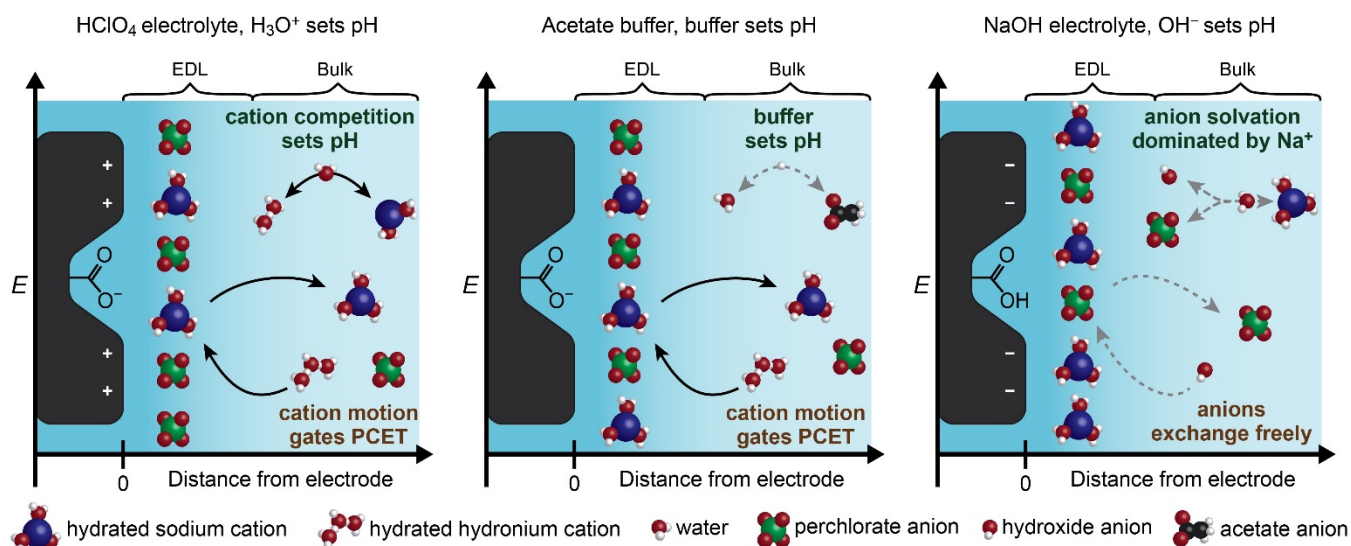


Figure 9 | Ion interactions under acidic, buffered, and alkaline conditions. **Left)** For acidic electrolytes, competition for solvation/coordination and ion repulsion increases H_3O^+ activity and inhibits $\text{Na}^+/\text{H}_3\text{O}^+$ exchange. These effects are equal and opposite, resulting in apparent I-PCET rates that are ionic strength independent. **Center)** For acetate buffered electrolytes, proton activity is kept constant by the buffer but $\text{Na}^+/\text{H}_3\text{O}^+$ exchange is still inhibited as ionic strength increases, slowing apparent I-PCET rates. **Right)** For alkaline electrolytes, competition and repulsion between OH^- and ClO_4^- is weaker, resulting in minimal changes in OH^- activity and $\text{ClO}_4^-/\text{OH}^-$ exchange equilibria, yielding no substantial change in apparent I-PCET rates with ionic strength. In the left and right panels “+” and “-” reflect the surface potential versus E_{PZFC} (the electrode-solution iso-potential) at the relevant E_{PCET} for each pH_{eff} condition.

Conclusion

In this study we used graphite-conjugated carboxylate active sites to quantify how supporting electrolyte concentration controls the thermodynamics and kinetics of interfacial proton coupled electron transfer over a range of NaClO_4 concentrations and solution proton activities. We find that electrolyte concentration has a twofold effect on I-PCET kinetics. Firstly, in unbuffered acidic media competition for solvation between Na^+ and H_3O^+ decreases the effective bulk solution pH, which would be expected to accelerate I-PCET. However, increased Na^+ activity in the bulk medium inhibits $\text{Na}^+/\text{H}_3\text{O}^+$ exchange in the EDL, required for formation of the PCET pre-association complex. This latter effect serves to inhibit I-PCET in acidic and acetate-buffered solutions relative to the rate predicted from changes to solution pH alone. These two effects, bulk pH decrease and inhibited donor pre-association are equal and opposite in unbuffered acidic media resulting in no net change in observed I-PCET kinetics as a function ionic-strength. In contrast, in acetate-buffered NaClO_4 solutions, the pH is set by the buffer, not the hydronium proton donor, thus, I-PCET apparent rates decrease with increasing ionic strength because the inhibition of donor pre-association is no longer offset by a decrease in solution pH. In alkaline electrolytes a minor change in proton activity and relatively weak interaction between OH^- and ClO_4^- similarly result in no substantial change in I-PCET rates as a function of ionic strength. These kinetic data support a multistep mechanism for I-PCET in which an interfacial ion exchange reaction gates the formation of a surface

PCET pre-association complex. Molecular dynamics simulations further support the hypothesis that inhibited pre-association complex formation attenuates I-PCET rates in acidic electrolytes.

The mechanistic model presented above illustrates that supporting electrolyte ions play a critical role in interfacial proton-coupled electron transfer reactivity by modulating solution proton activity and interfacial ion exchange equilibria despite being formally spectators to the overall reaction. Our findings highlight that I-PCET is best viewed as the series of at least the three steps shown in **Figure 7** rather than as a single elementary step. Consequently, refined models of I-PCET should including the influence of supporting electrolyte and the exchange of reactivity and spectator ions required to form pre-association complexes within the EDL. Though the observed effects of ionic strength may only become apparent at high bulk ionic strength, interfacial supporting electrolyte ions are always present in the EDL and therefore must move to accommodate the pre-association of reactive species at the electrode interface.

The foregoing findings on the role of concentrated spectator electrolytes on I-PCET kinetics offers mechanistic insights into key observations in electrocatalysis and battery science. For instance, saturated NaClO₄ electrolytes, often termed water-in-salt electrolytes (WiSE), are employed in aqueous batteries to suppress hydrogen evolution. While it is unclear, in most cases, what species is setting the proton activity in WiSE systems (particularly upon repeated battery cycling), if a weak acid (e.g. adventitious bicarbonate) is setting the proton activity, our data would suggest that the hydrogen suppression in WiSE systems may arise from inhibited pre-association of hydronium, just as we observe for acetate buffered media. In the context of electrocatalysis, our finding that supporting electrolytes inhibits H₃O⁺ pre-association, could partly explain why concentrated electrolytes promote selectivity for proton-independent CO₂ adsorption^{21,69} and CO-CO coupling⁹ steps in CO₂ reduction catalysis⁵⁸ relative to competing hydrogen evolution. As these examples highlight, electrolytes provide a rich parameter space for tuning pre-association equilibria to tailor interfacial electrochemical reactivity.

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Competing Interest Statement

The authors declare they have no competing financial interests.

Author Contribution Statement

N.B.L. and Y.S. conceived the research and developed experiments. N.B.L. conducted all experiments. N.B.L. performed data analysis with assistance from J.G.G., J.E.K. and T.E.M. conducted molecular dynamics calculations. N.B.L., N.K.R., and Y.S. developed the initial I-PCET kinetic model with continued contributions from all authors. N.B.L., J.G.G., S.A., J.E.K., T.E.M., and Y.S. wrote the manuscript with input from all authors.

References

- (1) Warburton, R. E.; Soudackov, A. V.; Hammes-Schiffer, S. Theoretical Modeling of Electrochemical Proton-Coupled Electron Transfer. *Chem. Rev.* **2022**, *122* (12), 10599–10650.
- (2) Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*; National Assoc. of Corrosion Engineers: Houston, TX, 1974.
- (3) Bard, A. J.; Faulkner, Larry R. *Electrochemical Methods: Fundamentals and Applications, Second Edition*; John Wiley & Sons, Inc., Hoboken, NJ, 2001.
- (4) Mayer, J. M. Bonds over Electrons: Proton Coupled Electron Transfer at Solid–Solution Interfaces. *J. Am. Chem. Soc.* **2023**, *145* (13), 7050–7064.
- (5) Jung, O.; Jackson, M. N.; Bisbey, R. P.; Kogan, N. E.; Surendranath, Y. Innocent Buffers Reveal the Intrinsic pH- and Coverage-Dependent Kinetics of the Hydrogen Evolution Reaction on Noble Metals. *Joule* **2022**, *6* (2), 476–493.
- (6) Dubouis, N.; Grimaud, A. The Hydrogen Evolution Reaction: From Material to Interfacial Descriptors. *Chem. Sci.* **2019**, *10* (40), 9165–9181.
- (7) Reier, T.; Nong, H. N.; Teschner, D.; Schlögl, R.; Strasser, P. Electrocatalytic Oxygen Evolution Reaction in Acidic Environments – Reaction Mechanisms and Catalysts. *Adv. Energy Mater.* **2017**, *7* (1), 1601275.
- (8) Koper, M. T. M. Theory of Multiple Proton–Electron Transfer Reactions and Its Implications for Electrocatalysis. *Chem. Sci.* **2013**, *4* (7), 2710–2723.
- (9) Schreier, M.; Yoon, Y.; Jackson, M. N.; Surendranath, Y. Competition between H and CO for Active Sites Governs Copper-Mediated Electrosynthesis of Hydrocarbon Fuels. *Angew. Chem., Int. Ed.* **2018**, *57* (32), 10221–10225.
- (10) Marcandalli, G.; Monteiro, M. C. O.; Goyal, A.; Koper, M. T. M. Electrolyte Effects on CO₂ Electrochemical Reduction to CO. *Acc. Chem. Res.* **2022**, *55* (14), 1900–1911.
- (11) Joo, J.; Uchida, T.; Cuesta, A.; Koper, M. T. M.; Osawa, M. Importance of Acid–Base Equilibrium in Electrocatalytic Oxidation of Formic Acid on Platinum. *J. Am. Chem. Soc.* **2013**, *135* (27), 9991–9994.
- (12) Singh, C.; Paul, A. Physisorbed Hydroquinone on Activated Charcoal as a Supercapacitor: An Application of Proton-Coupled Electron Transfer. *J. Phys. Chem. C* **2015**, *119* (21), 11382–11390.
- (13) Bu, X.; Su, L.; Dou, Q.; Lei, S.; Yan, X. A Low-Cost “Water-in-Salt” Electrolyte for a 2.3 V High-Rate Carbon-Based Supercapacitor. *J. Mater. Chem. A* **2019**, *7* (13), 7541–7547.
- (14) Cobb, S. J.; Ayres, Z. J.; Newton, M. E.; Macpherson, J. V. Deconvoluting Surface-Bound Quinone Proton Coupled Electron Transfer in Unbuffered Solutions: Toward a Universal Voltammetric pH Electrode. *J. Am. Chem. Soc.* **2019**, *141* (2), 1035–1044.
- (15) Ryu, J.; Wuttig, A.; Surendranath, Y. Quantification of Interfacial pH Variation at Molecular Length Scales Using a Concurrent Non-Faradaic Reaction. *Angew. Chem., Int. Ed.* **2018**, *57* (30), 9300–9304.
- (16) Wesley, T. S.; Román-Leshkov, Y.; Surendranath, Y. Spontaneous Electric Fields Play a Key Role in Thermochemical Catalysis at Metal–Liquid Interfaces. *ACS Cent. Sci.* **2021**, *7* (6), 1045–1055.
- (17) Howland, W. C.; Gerken, J. B.; Stahl, S. S.; Surendranath, Y. Thermal Hydroquinone Oxidation on Co/N-Doped Carbon Proceeds by a Band-Mediated Electrochemical Mechanism. *J. Am. Chem. Soc.* **2022**, *144* (25), 11253–11262.
- (18) Lodaya, K. M.; Tang, B. Y.; Bisbey, R. P.; Weng, S.; Westendorff, K. S.; Toh, W. L.; Ryu, J.; Román-Leshkov, Y.; Surendranath, Y. An Electrochemical Approach for Designing Thermochemical Bimetallic Nitrate Hydrogenation Catalysts. *Nat. Catal.* **2024**, *7* (3), 262–272.

- (19) Westendorff, K. S.; Hülsey, M. J.; Wesley, T. S.; Román-Leshkov, Y.; Surendranath, Y. Electrically Driven Proton Transfer Promotes Brønsted Acid Catalysis by Orders of Magnitude. *Science* **2024**.
- (20) Weng, S.; Toh, W. L.; Surendranath, Y. Weakly Coordinating Organic Cations Are Intrinsically Capable of Supporting CO₂ Reduction Catalysis. *J. Am. Chem. Soc.* **2023**, *145* (30), 16787–16795.
- (21) Wuttig, A.; Yaguchi, M.; Motobayashi, K.; Osawa, M.; Surendranath, Y. Inhibited Proton Transfer Enhances Au-Catalyzed CO₂-to-Fuels Selectivity. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113* (32), E4585–E4593.
- (22) Suo, L.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X.; Luo, C.; Wang, C.; Xu, K. “Water-in-Salt” Electrolyte Enables High-Voltage Aqueous Lithium-Ion Chemistries. *Science* **2015**, *350* (6263), 938–943.
- (23) Qin, X.; Balbuena, P. B.; Shao, M. First-Principles Study on the Initial Oxidative Decompositions of Ethylene Carbonate on Layered Cathode Surfaces of Lithium-Ion Batteries. *J. Phys. Chem. C* **2019**, *123* (23), 14449–14458.
- (24) Choi, D.; Kang, J.; Park, J.; Han, B. First-Principles Study on Thermodynamic Stability of the Hybrid Interfacial Structure of LiMn₂O₄ Cathode and Carbonate Electrolyte in Li-Ion Batteries. *Phys. Chem. Chem. Phys.* **2018**, *20* (17), 11592–11597.
- (25) Lundström, R.; Gogoi, N.; Melin, T.; Berg, E. J. Unveiling Reaction Pathways of Ethylene Carbonate and Vinylene Carbonate in Li-Ion Batteries. *J. Phys. Chem. C* **2024**.
- (26) Bard, A. J. Inner-Sphere Heterogeneous Electrode Reactions. Electrocatalysis and Photocatalysis: The Challenge. *J. Am. Chem. Soc.* **2010**, *132* (22), 7559–7567.
- (27) Schmickler, W.; Santos, E. *Interfacial Electrochemistry*; Springer Science & Business Media, 2010.
- (28) Sarabia, F.; Gomez Rodellar, C.; Roldan Cuenya, B.; Oener, S. Z. Exploring Dynamic Solvation Kinetics at Electrocatalyst Surfaces. *Nat. Commun.* **2024**, *15* (1), 8204.
- (29) Savéant, J. M.; Costentin, C. *Elements of Molecular and Biomolecular Electrochemistry: An Electrochemical Approach to Electron Transfer Chemistry*, Second edition.; Wiley: Hoboken, NJ, 2019.
- (30) Costentin, C.; Robert, M.; Savéant, J.-M.; Teillout, A.-L. Concerted Proton-Coupled Electron Transfers in Aquo/Hydroxo/Oxo Metal Complexes: Electrochemistry of [Os^{II}(Bpy)₂py(OH₂)]²⁺ in Water. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106* (29), 11829–11836.
- (31) Weinberg, D. R.; Gagliardi, C. J.; Hull, J. F.; Murphy, C. F.; Kent, C. A.; Westlake, B. C.; Paul, A.; Ess, D. H.; McCafferty, D. G.; Meyer, T. J. Proton-Coupled Electron Transfer. *Chem. Rev.* **2012**, *112* (7), 4016–4093.
- (32) Costentin, C.; Robert, M.; Savéant, J.-M.; Teillout, A.-L. Concerted and Stepwise Proton-Coupled Electron Transfers in Aquo/Hydroxo Complex Couples in Water: Oxidative Electrochemistry of [Os^{II}(Bpy)₂(Py)(OH₂)]²⁺. *ChemPhysChem* **2009**, *10* (1), 191–198.
- (33) Hammes-Schiffer, S.; Soudackov, A. V. Proton-Coupled Electron Transfer in Solution, Proteins, and Electrochemistry. *J. Phys. Chem. B* **2008**, *112* (45), 14108–14123.
- (34) Mayer, J. M. Proton-Coupled Electron Transfer: A Reaction Chemist's View. *Annu. Rev. Phys. Chem.* **2004**, *55* (1), 363–390.
- (35) Su, L.; Chen, J.; Yang, F.; Li, P.; Jin, Y.; Luo, W.; Chen, S. Electric-Double-Layer Origin of the Kinetic pH Effect of Hydrogen Electrocatalysis Revealed by a Universal Hydroxide Adsorption-Dependent Inflection-Point Behavior. *J. Am. Chem. Soc.* **2023**, *145* (22), 12051–12058.
- (36) Jackson, M. N.; Surendranath, Y. Donor-Dependent Kinetics of Interfacial Proton-Coupled Electron Transfer. *J. Am. Chem. Soc.* **2016**, *138* (9), 3228–3234.

- (37) Jackson, M. N.; Jung, O.; Lamotte, H. C.; Surendranath, Y. Donor-Dependent Promotion of Interfacial Proton-Coupled Electron Transfer in Aqueous Electrocatalysis. *ACS Catal.* **2019**, *9* (4), 3737–3743.
- (38) Kuo, D.-Y.; Lu, X.; Hu, B.; Abruña, H. D.; Suntivich, J. Rate and Mechanism of Electrochemical Formation of Surface-Bound Hydrogen on Pt(111) Single Crystals. *J. Phys. Chem. Lett.* **2022**, *13* (27), 6383–6390.
- (39) Lewis, N. B.; Bisbey, R. P.; Westendorff, K. S.; Soudackov, A. V.; Surendranath, Y. A Molecular-Level Mechanistic Framework for Interfacial Proton-Coupled Electron Transfer Kinetics. *Nat. Chem.* **2024**, *16* (3), 343–352.
- (40) Warburton, R. E.; Hutchison, P.; Jackson, M. N.; Pegis, M. L.; Surendranath, Y.; Hammes-Schiffer, S. Interfacial Field-Driven Proton-Coupled Electron Transfer at Graphite-Conjugated Organic Acids. *J. Am. Chem. Soc.* **2020**, *142* (49), 20855–20864.
- (41) Jackson, M. N.; Pegis, M. L.; Surendranath, Y. Graphite-Conjugated Acids Reveal a Molecular Framework for Proton-Coupled Electron Transfer at Electrode Surfaces. *ACS Cent. Sci.* **2019**, *5* (5), 831–841.
- (42) Jackson, M. N.; Surendranath, Y. Molecular Control of Heterogeneous Electrocatalysis through Graphite Conjugation. *Acc. Chem. Res.* **2019**, *52* (12), 3432–3441.
- (43) Jackson, M. N.; Oh, S.; Kaminsky, C. J.; Chu, S. B.; Zhang, G.; Miller, J. T.; Surendranath, Y. Strong Electronic Coupling of Molecular Sites to Graphitic Electrodes via Pyrazine Conjugation. *J. Am. Chem. Soc.* **2018**, *140* (3), 1004–1010.
- (44) Eigen, M. Proton Transfer, Acid-Base Catalysis, and Enzymatic Hydrolysis. Part I: Elementary Processes. *Angew. Chem., Int. Ed.* **1964**, *3* (1), 1–19.
- (45) Eigen, M. Kinetics of Proton Transfer Processes. *Discuss. Faraday Soc.* **1965**, *39*, 7.
- (46) Reber, D.; Grissa, R.; Becker, M.; Kühnel, R.-S.; Battaglia, C. Anion Selection Criteria for Water-in-Salt Electrolytes. *Adv. Energy Mater.* **2021**, *11* (5), 2002913.
- (47) Zhao, Y.; Hu, X.; Stucky, G. D.; Boettcher, S. W. Thermodynamic, Kinetic, and Transport Contributions to Hydrogen Evolution Activity and Electrolyte-Stability Windows for Water-in-Salt Electrolytes. *J. Am. Chem. Soc.* **2024**.
- (48) Borodin, O.; Self, J.; Persson, K. A.; Wang, C.; Xu, K. Uncharted Waters: Super-Concentrated Electrolytes. *Joule* **2020**, *4* (1), 69–100.
- (49) McEldrew, M.; Goodwin, Z. A. H.; Kornyshev, A. A.; Bazant, M. Z. Theory of the Double Layer in Water-in-Salt Electrolytes. *J. Phys. Chem. Lett.* **2018**, *9* (19), 5840–5846.
- (50) Suo, L.; Borodin, O.; Sun, W.; Fan, X.; Yang, C.; Wang, F.; Gao, T.; Ma, Z.; Schroeder, M.; von Cresce, A.; Russell, S. M.; Armand, M.; Angell, A.; Xu, K.; Wang, C. Advanced High-Voltage Aqueous Lithium-Ion Battery Enabled by “Water-in-Bisalt” Electrolyte. *Angew. Chem., Int. Ed.* **2016**, *55* (25), 7136–7141.
- (51) Suo, L.; Oh, D.; Lin, Y.; Zhuo, Z.; Borodin, O.; Gao, T.; Wang, F.; Kushima, A.; Wang, Z.; Kim, H.-C.; Qi, Y.; Yang, W.; Pan, F.; Li, J.; Xu, K.; Wang, C. How Solid-Electrolyte Interphase Forms in Aqueous Electrolytes. *J. Am. Chem. Soc.* **2017**, *139* (51), 18670–18680.
- (52) Han, J.; Mariani, A.; Passerini, S.; Varzi, A. A Perspective on the Role of Anions in Highly Concentrated Aqueous Electrolytes. *Energy Environ. Sci.* **2023**, *16* (4), 1480–1501.
- (53) Liang, T.; Hou, R.; Dou, Q.; Zhang, H.; Yan, X. The Applications of Water-in-Salt Electrolytes in Electrochemical Energy Storage Devices. *Adv. Funct. Mater.* **2021**, *31* (3), 2006749.
- (54) Dong, C.; Xu, F.; Chen, L.; Chen, Z.; Cao, Y. Design Strategies for High-Voltage Aqueous Batteries. *Small Structures* **2021**, *2* (7), 2100001.

- (55) Lee, M. H.; Kim, S. J.; Chang, D.; Kim, J.; Moon, S.; Oh, K.; Park, K.-Y.; Seong, W. M.; Park, H.; Kwon, G.; Lee, B.; Kang, K. Toward a Low-Cost High-Voltage Sodium Aqueous Rechargeable Battery. *Mater. Today* **2019**, *29*, 26–36.
- (56) Tomiyasu, H.; Shikata, H.; Takao, K.; Asanuma, N.; Taruta, S.; Park, Y.-Y. An Aqueous Electrolyte of the Widest Potential Window and Its Superior Capability for Capacitors. *Sci. Rep.* **2017**, *7* (1), 45048.
- (57) Sakamoto, R.; Yamashita, M.; Nakamoto, K.; Zhou, Y.; Yoshimoto, N.; Fujii, K.; Yamaguchi, T.; Kitajou, A.; Okada, S. Local Structure of a Highly Concentrated NaClO₄ Aqueous Solution-Type Electrolyte for Sodium Ion Batteries. *Phys. Chem. Chem. Phys.* **2020**, *22* (45), 26452–26458.
- (58) Zhang, H.; Gao, J.; Raciti, D.; Hall, A. S. Promoting Cu-Catalysed CO₂ Electroreduction to Multicarbon Products by Tuning the Activity of H₂O. *Nat. Catal.* **2023**, *6* (9), 807–817.
- (59) Degouange, D.; Dubouis, N.; Grimaud, A. Toward the Understanding of Water-in-Salt Electrolytes: Individual Ion Activities and Liquid Junction Potentials in Highly Concentrated Aqueous Solutions. *J. Chem. Phys.* **2021**, *155* (6), 064701.
- (60) Toner, J. D.; Catling, D. C. Water Activities of NaClO₄, Ca(ClO₄)₂, and Mg(ClO₄)₂ Brines from Experimental Heat Capacities: Water Activity >0.6 below 200K. *Geochim. Cosmochim. Acta* **2016**, *181*, 164–174.
- (61) Marcus, Y. The Thermodynamics of Solvation of Ions. Part 2.—The Enthalpy of Hydration at 298.15 K. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83* (2), 339.
- (62) Laviron, E. General Expression of the Linear Potential Sweep Voltammogram in the Case of Diffusionless Electrochemical Systems. *J. Electroanal. Chem.* **1979**, *101* (1), 19–28.
- (63) Garlyyev, B.; Xue, S.; Watzele, S.; Scieszka, D.; Bandarenka, A. S. Influence of the Nature of the Alkali Metal Cations on the Electrical Double-Layer Capacitance of Model Pt(111) and Au(111) Electrodes. *J. Phys. Chem. Lett.* **2018**, *9* (8), 1927–1930.
- (64) Xue, S.; Garlyyev, B.; Auer, A.; Kunze-Liebhäuser, J.; Bandarenka, A. S. How the Nature of the Alkali Metal Cations Influences the Double-Layer Capacitance of Cu, Au, and Pt Single-Crystal Electrodes. *J. Phys. Chem. C* **2020**, *124* (23), 12442–12447.
- (65) Morales, J. W.; Galleguillos, H. R.; Hernández-Luis, F.; Rodríguez-Raposo, R. Activity Coefficients of NaClO₄ in Aqueous Solution. *J. Chem. Eng. Data* **2011**, *56* (8), 3449–3453.
- (66) Sun, L.; Liang, X.; Solms, N. von; Kontogeorgis, G. M. Analysis of Some Electrolyte Models Including Their Ability to Predict the Activity Coefficients of Individual Ions. *Ind. Eng. Chem. Res.* **2020**, *59* (25), 11790–11809.
- (67) Saravi, S. H.; Panagiotopoulos, A. Z. Individual Ion Activity Coefficients in Aqueous Electrolytes from Explicit-Water Molecular Dynamics Simulations. *J. Phys. Chem. B* **2021**, *125* (30), 8511–8521.
- (68) Valiskó, M.; Boda, D. Unraveling the Behavior of the Individual Ionic Activity Coefficients on the Basis of the Balance of Ion–Ion and Ion–Water Interactions. *J. Phys. Chem. B* **2015**, *119* (4), 1546–1557.
- (69) Wuttig, A.; Yoon, Y.; Ryu, J.; Surendranath, Y. Bicarbonate Is Not a General Acid in Au-Catalyzed CO₂ Electroreduction. *J. Am. Chem. Soc.* **2017**, *139* (47), 17109–17113.