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Review Article

Coupled cation and pH effects in the hydrogen evolution reaction: An electrostati perspective

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Cation effects on the hydrogen evolution reaction (HER) have been recognized for nearly a century yet their physical origins, particularly their strong coupling with pH, remain debated. Experiments show pronounced and often confusingly inverted trends in HER activity with cation identity and concentration, which vary with pH, electrode material, and applied potential. Despite extensive research, no unified framework has reconciled these observations. In this perspective, we revisit these trends from an electrostatic point of view. Using Butler−Volmer−Frumkin theory, we show that inverted cation trends between acidic and alkaline electrolytes arise naturally from the opposite roles of Frumkin corrections in proton- versus water-mediated Volmer steps. Multiple inversions observed under alkaline conditions further expose the limitations of single-factor, primarily atomistic, explanations, while a recent electrostatic framework accounting for local potential and electric field effects offers a coherent picture of many trends. These considerations highlight interfacial electrostatics as a critical factor and motivate integrated approaches bridging continuum and atomistic descriptions.

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Introduction

The hydrogen evolution reaction (HER) has long served as a central reaction in electrochemical kinetics, playing a pivotal role in establishing fundamental concepts such as exchange current density, Tafel relationships, and structure−activity correlations, owing to its relative simplicity and practical significance [1−6]. Occurring at electrode−electrolyte interfaces, HER performance is profoundly influenced by the local reaction environment, which is governed by the electrolyte composition [7−14]. Evidence of cation identity and concentration impacting the HER in acidic solutions was reported by Herasymenko and Slendyk as early as 1930 [7]. These experimental observations motivated Frumkin's seminal work in 1933, which laid the theoretical foundation for understanding electrolyte effects in electrochemical reactions [15,16].

While early HER studies focus primarily on acidic electrolytes, renewed interest in alkaline HER has emerged in recent years, driven both by the practical relevance of alkaline water electrolysis and by the recognition that alkaline environments expose fundamental limitations of conventional HER descriptors originally developed for acidic systems [8,10,17−20]. The pronounced pH dependence of HER kinetics can be related to vital roles of the interfacial water structure [18,21,22], hydrogen bond network [20,23], hydroxide interactions [19,24,25], and electric field [26−31]. The interplay of these phenomena renders alkaline HER an insightful probe of interfacial effects to advance the understanding of electrochemical reactions at solid−liquid interfaces.

Importantly, the pronounced pH dependence of HER kinetics is almost invariably accompanied by strong cation effects, indicating that pH and cation identity cannot be treated as independent variables [11−13,22]. Both effects are mediated through the structure of the electric double layer (EDL) and their manifestations depend sensitively on catalyst nature and applied potential. Although the effects of pH and cations have each been extensively studied, and a wide range of mechanistic interpretations have been proposed [32−34], a unified kinetic framework that consistently accounts for their coupled influence is still lacking. In particular, experimentally observed inversions of cation trends between acidic and alkaline conditions, as well as their strong dependence on potential and catalyst nature, remain difficult to rationalize consistently across different systems [13,27,35,36].

In this perspective, we revisit these coupled pH-cation effects from the standpoint of classical theories of electrode kinetics, for example, Butler–Volmer–Frumkin theory, emphasizing the role of the local electrostatic environment. By comparing typicalexperimental trends, we aim to clarify the physical origins of inverted cation effects and to assess the extent to which established theories can account for HER kinetics across different pH regimes.

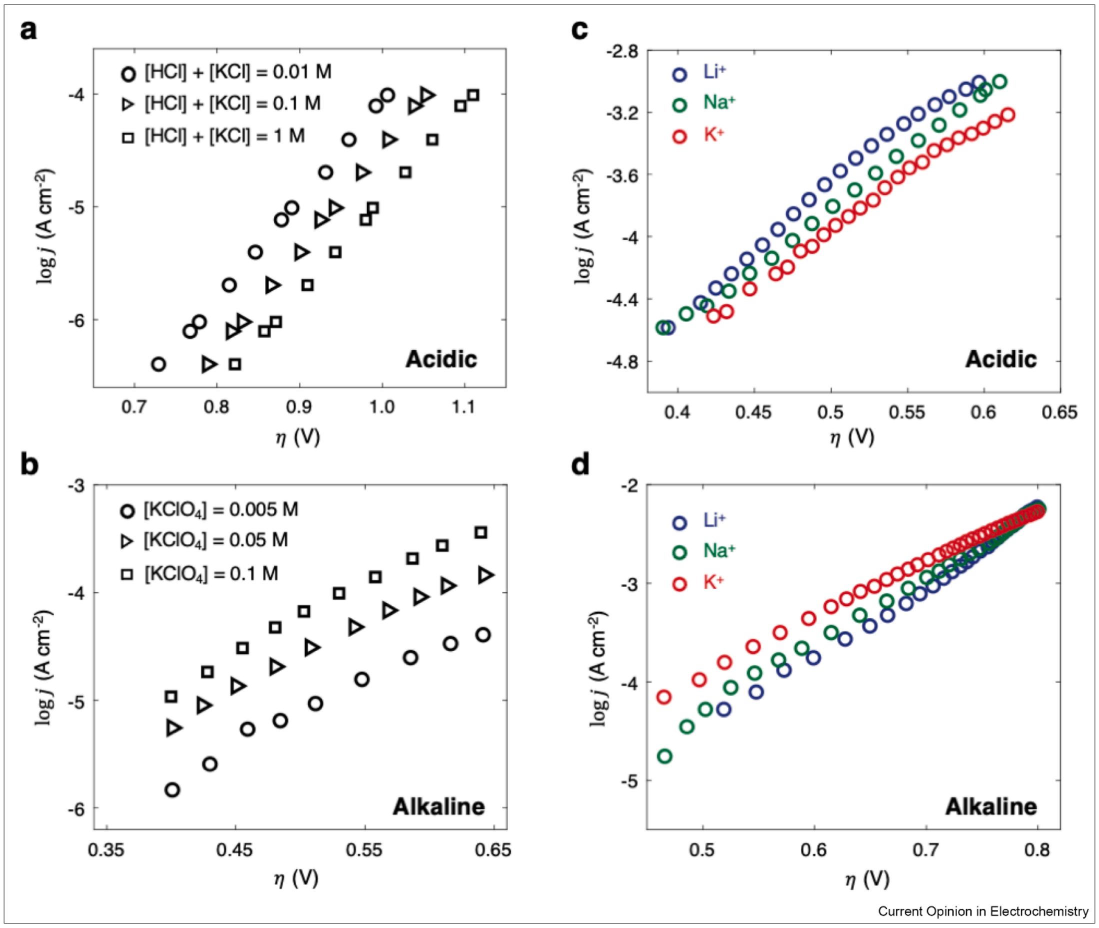
Inverted cation trends under acidic and alkaline conditions

Figure 1 summarizes the effects of supporting cation concentration and cation identity on HER activity under acidic and alkaline conditions. Here, the term "supporting cation concentration" refers to variations in electrolyte concentration at fixed pH (*i.e.*, ionic strength). We focus on experimental data for Hg, Au, and Ag, for which the reaction mechanisms are well established. On these catalysts, the Volmer step is widely regarded as the rate-determining step (RDS) due to their weak hydrogen binding [1,3,37–39].

As shown in Figure 1a, increasing the supporting cation concentration decreases HER activity in acidic media. By contrast, the activity increases with supporting cation concentration under alkaline conditions (Figure 1b). For cation-identity effects, the HER activity on Ag and Au follows the trend $Li^+ > Na^+ > K^+$ in acidic solutions [39], as shown in Figure 1c. The same trend has also been reported on Hg [40], supporting the generality of this trend across metals with weak hydrogen binding. However, this trend reverses to $Li^+ < Na^+ < K^+$ in alkaline media at moderate overpotentials on Au and Ag [11,13], as shown in Figure 1d.

Despite the obvious symmetry of these inverted trends, recent studies have primarily focused on cation-identity

Figure 1



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Effect of supporting cation concentration on HER activity **(a)** on Hg in 0.001 M HCl with added KCl [1] and **(b)** on Au in 0.001 M KOH + 0.005/0.05/0.1 M $KClO_4$ solutions [13]. **(c)** Effect of cation identity on HER activity on Ag(111) in 0.09 M $XClO_4$+ 0.01 M $HClO_4$ solutions, where X = Li^+, Na^+, or K^+ [39]. **(d)** Effect of cation identity on HER activity on Au in 0.1 M LiOH/NaOH/KOH solutions [13]. HER, hydrogen evolution reaction.

effects in alkaline electrolytes, whereas the inversion of cation trends between acidic and alkaline electrolytes has rarely been studied [27]. In the following section, we show that the inverted trends in Figure 1 can be qualitatively rationalized within Butler–Volmer–Frumkin theory by considering only the local electrostatic effects.

Interplay of cation and pH effects from the view of Frumkin corrections

The Volmer step corresponds to proton discharge in acidic media

$$H^+ + e^- \rightarrow H_{ads},$$

and water molecule discharge in alkaline media [2].

$$H_2O + e^- \rightarrow H_{ads} + OH^-.$$

The Frumkin corrections highlight the importance of the local electrostatic potential at the reaction plane (RP), which influences both the thermodynamic driving force and the local concentrations of reactive species [15]. As illustrated in Figure 2, the potential at the RP, ϕ_{RP}, modifies the electrostatic free energies of H^+ and OH^- and thereby alters the activation barriers of the Volmer step. In both acidic and alkaline cases, the activation barriers shift with ϕ_{RP} by $-\alpha e_0 \phi_{RP}$, where α is the transfer coefficient and e_0 is the elementary charge.

Although ϕ_{RP} exerts a common effect on the activation barrier, its influence on reactant availability differs between acidic and alkaline conditions. Under the RDS approximation, the backward reaction of the Volmer step is neglected. In acidic media, H^+ is the proton donor and its concentration at the RP is determined by the Boltzmann distribution,

$$[H^+]_{RP} = [H^+]_b \exp\left(-\frac{F\phi_{RP}}{RT}\right), \tag{1}$$

where $[H^+]_{RP}$ and $[H^+]_b$ denote the proton concentration at the RP and in the bulk solution, respectively, R is the gas constant, T the temperature, and F the Faraday constant. In contrast, in alkaline media, the proton donor is the water molecule, whose concentration is assumed to be independent of ϕ_{RP}.

On this basis, the Butler Volmer Frumkin theory yields the following corrected Tafel relations for acidic solutions [1]

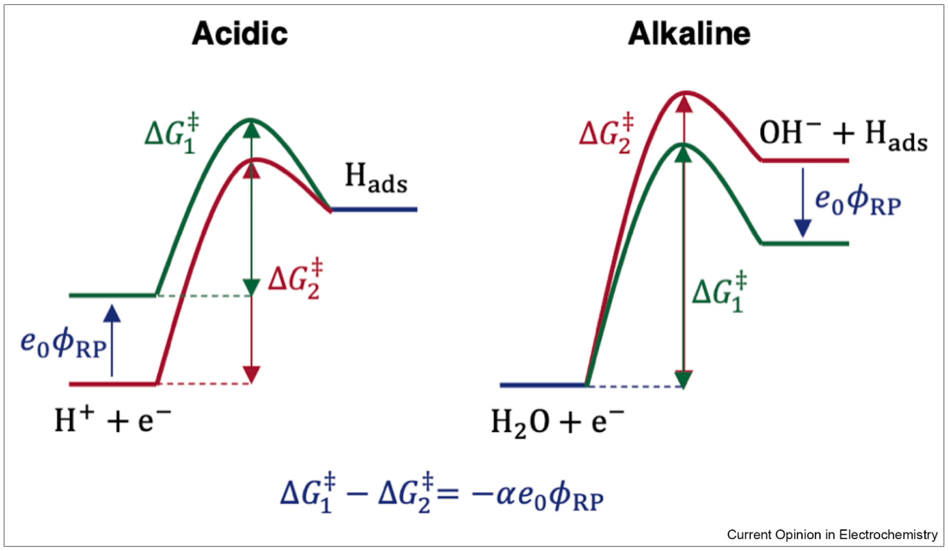
$$\log|j| = \frac{\alpha F}{RT\ln 10}\eta - \frac{(1-\alpha)F}{RT\ln 10}\phi_{RP} + (1-\alpha)\log\,[H^+]_b + \text{const}, \tag{2}$$

and for alkaline solutions [9,41],

$$\log|j| = \frac{\alpha F}{RT\ln 10}\eta + \frac{\alpha F}{RT\ln 10}\phi_{RP} + \alpha\log\,[OH^-]_b + \text{const}, \tag{3}$$

with η being the overpotential (defined as $-E_{RHE}$, where E_{RHE} is the applied potential versus the reversible hydrogen electrode), j the current density, and $[OH^-]_b$ the bulk OH^- concentration.

Figure 2



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Schematic illustration of local electrostatic effects on the free energy diagrams of the Vomer step under acidic and alkaline conditions. An increase in ϕ_{RP} raises the electrostatic free energy of H^+ by $e_0\phi_{RP}$ and lowers that of OH^- by the same amount. As a result, the activation barriers in both cases shift by $-\alpha e_0 \phi_{RP}$.

Eqs. (2) and (3) exhibit an inverse Frumkin effect in acidic versus alkaline media, that is, shifting ϕ_{RP} to more positive values suppresses the HER in acidic solution but enhances it in alkaline solution. This occurs because, although a more positive ϕ_{RP} increases the thermodynamic driving force under both conditions, it reduces the surface proton concentration through electrostatic interactions in acidic media, with a larger coefficient governing the latter effect. In alkaline media, the electrostatic contribution enters only through the barrier term.

Within this framework, the role of cations in the supporting electrolyte arises from their influence on the spatial potential distribution across the EDL. Specifically, variations in supporting cation concentration and identity modulate the EDL structure and, thereby, alter ϕ_{RP}, ultimately impacting HER kinetics.

Following classical double layer theories, the effect of supporting cation concentration can be evaluated using the Gouy—Chapman—Stern (GCS) theory and modern variants thereof [42,43]. The EDL model is constructed by describing the potential drop from the metal surface to the bulk solution. For monovalent electrolytes, we have

$$E_{\mathrm{M}} - E_{\mathrm{pzc}} = \sigma_{\mathrm{free}}\left(\frac{\delta_1}{\epsilon_1} + \frac{\delta_2}{\epsilon_2}\right) + \frac{2RT}{F}\operatorname{arsinh}\left(\frac{F\lambda_{\mathrm{D}}\sigma_{\mathrm{free}}}{2RT\epsilon_{\mathrm{S}}}\right), \tag{4}$$

where E_{M} and E_{pzc} are the electrode potential and potential of zero charge versus a reference electrode, respectively; σ_{free} is the free surface charge density; δ_1 and δ_2, and ϵ_1 and ϵ_2 are the thicknesses and dielectric permittivities of the inner and outer Helmholtz layers. The first term on the right-hand side represents the potential drop across the compact Helmholtz layers, while the second term corresponds to the potential drop across the diffuse layer, that is, the potential at the outer Helmholtz plane. Here, ϵ_{S} is the electrolyte permittivity and $\lambda_{\mathrm{D}} = \sqrt{\frac{RT\epsilon_{\mathrm{S}}}{2F^2 c_{\mathrm{b}}}}$ is the Debye length, with c_{b} being the bulk cation concentration.

In the case of $E_{\mathrm{M}} - E_{\mathrm{pzc}} < 0$, ϕ_{RP} is negative. As the supporting cation concentration increases, ϕ_{RP} is shifted toward more positive values (Figure 3a). According to Eqs. (2) and (3), this shift suppresses the HER kinetics in acidic media while improving it in alkaline media. Consequently, the inverted activity trends for acidic and alkaline conditions in Figures 3b and 3c naturally reproduce the experimental behaviors in Figure 1.

Cation-identity effects can be explained within the same electrostatic framework by considering differences in effective solvation size. When the finite size of cations are incorporated into the GCS description via the Bikerman model [44], the potential drop across the EDL is given by,

$$E_{\mathrm{M}} - E_{\mathrm{pzc}} = \sigma_{\mathrm{free}}\left(\frac{\delta_1}{\epsilon_1} + \frac{\delta_2}{\epsilon_2}\right) + \operatorname{sign}(\sigma_{\mathrm{free}})\frac{2RT}{F}\operatorname{arsinh}\left(\sqrt{\frac{1}{2\gamma}\left(\exp\left(\frac{\gamma}{2}\left(\frac{F\lambda_{\mathrm{D}}\sigma_{\mathrm{free}}}{RT\epsilon_{\mathrm{S}}}\right)^2\right) - 1\right)}\right), \tag{5}$$

where $\gamma = 2c_{\mathrm{b}}d_i^3$ accounts for finite ion size effects, with d_i being the effective ion diameter.

Larger solvated cations exhibit a reduced propensity to accumulate in the EDL, resulting in a more negative ϕ_{RP}. For alkali cations, the effective size follows $d_{\mathrm{Li^+}} > d_{\mathrm{Na^+}} > d_{\mathrm{K^+}}$, reflecting their decreasing solvation strength [45,46]. This trend induces ϕ_{RP} that follows $\mathrm{Li^+} < \mathrm{Na^+} < \mathrm{K^+}$. The results obtained using representative values of $d_{\mathrm{Li^+}} = 8\,\mathrm{Å}$, $d_{\mathrm{Na^+}} = 7\,\mathrm{Å}$, and $d_{\mathrm{K^+}} = 6\,\mathrm{Å}$ are shown in Figure 3d. As a result, the HER activity follows $\mathrm{Li^+} > \mathrm{Na^+} > \mathrm{K^+}$ in acidic solutions and the inverse order in alkaline solutions (Figures 3e and 3f), reproducing experimentally observed trends in Figure 1.

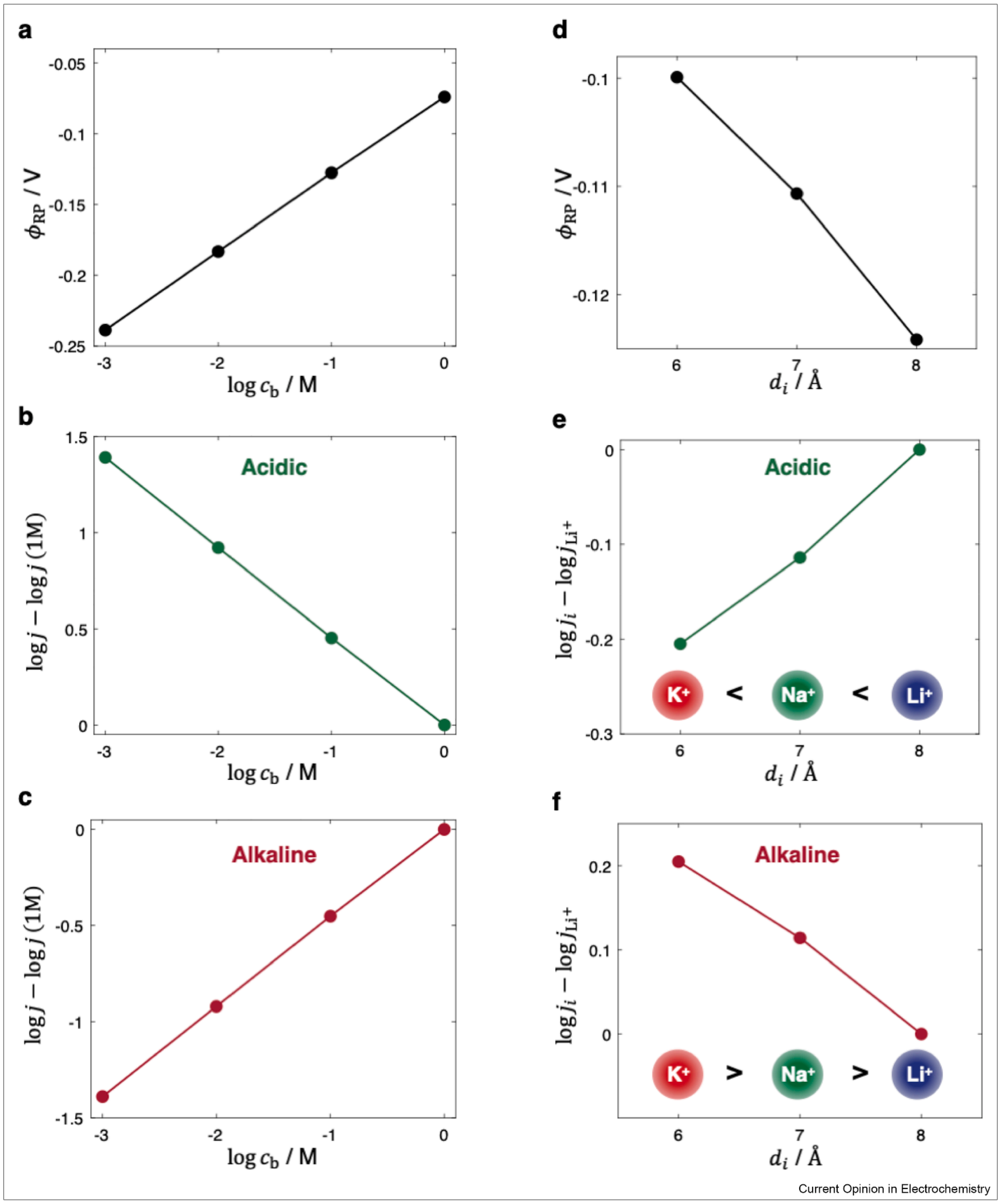
Multiple inversions of cation trends under alkaline conditions

Cation effects in alkaline electrolyte exhibit a level of complexity that goes beyond trends summarized in Figure 1. Not only cation-identity and concentration but also the applied overpotential, solution pH, and catalyst material jointly determine the observed activity trends.

For instance, on Au electrodes, the HER activity follows $\mathrm{Li^+} < \mathrm{Na^+} < \mathrm{K^+}$ at moderate overpotential but reverses to $\mathrm{Li^+} > \mathrm{Na^+} > \mathrm{K^+}$ at a very high overpotential (Figure 1d). In contrast, on Pt, the activity consistently follows $\mathrm{Li^+} > \mathrm{Na^+} > \mathrm{K^+}$ over a wide potential range [11,13]. Supporting cation concentration effects likewise display strong pH and catalyst dependencies. Increasing the $\mathrm{K^+}$ concentration promotes the activity on Au at pH 11 (Figure 1c) but slows it down at pH 13, whereas increasing the $\mathrm{Li^+}$ concentration enhances the activity at both pH 11 and 13. On Pt, supporting cation concentration effects also exhibit multiple inversions depending on pH [12,13].

Despite extensive efforts, most proposed mechanisms rationalize only a subset of these cation trends. Considerations based on hydrogen binding energy [11,17], solvent reorganization energy [18,22], hydrogen bond network connectivity [20,47], or hydroxide transport [36,48,49] often provide internally consistent explanations yet struggle to reconcile trends across different catalysts, pH values, and potential ranges [27].

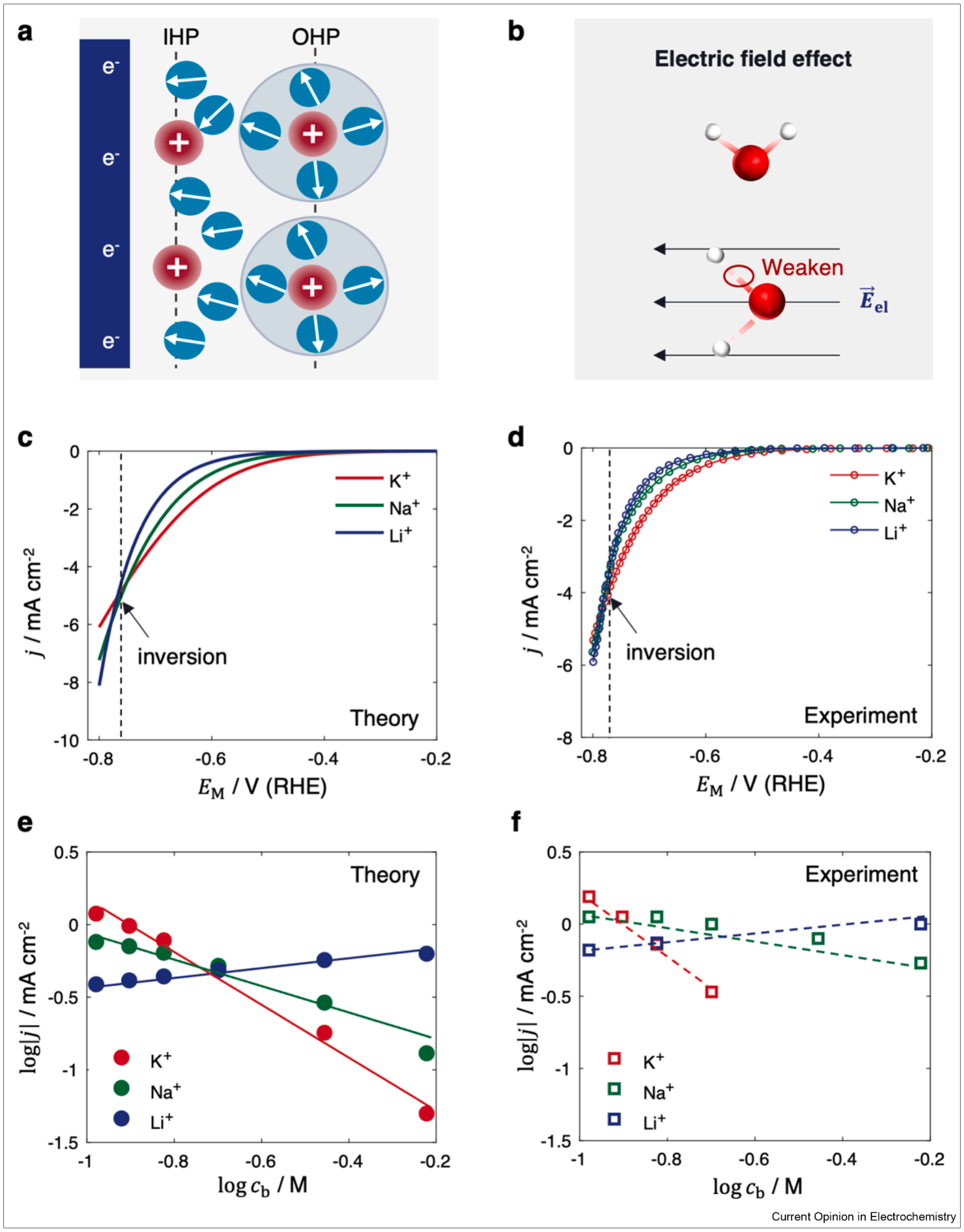
Figure 3



(a) Dependence of ϕ_{RP} (assumed $\phi_{RP} = \phi_{OHP}$) on supporting cation concentration, simulated using Eq. (4). Relative HER current density as a function of supporting cation concentration in (b) acidic media and (c) alkaline media, with $c_b = 1$ M taken as the reference. (d) Dependence of ϕ_{RP} on effective cation size, simulated using Eq. (5) at $c_b = 0.1$ M. Corresponding relative HER current density as function of effective cation size in (e) acidic media and (f) alkaline media, with Li^+ taken as the reference case. The parameters used in simulations are as follows: $\delta_1 = 2$ Å and $\delta_2 = 3$ Å in (a) $\delta_2 = d_i/2$ in (d), $\epsilon_1 = 8\epsilon_0$, $\epsilon_2 = 30\epsilon_0$, $\epsilon_s = 78\epsilon_0$, with ϵ_0 being the vacuum permittivity, $E_M - E_{pzc} = -1.0$ V, and $\alpha = 0.5$. HER, hydrogen evolution reaction; OHP, outer Helmholtz plane.

For example, invoking a solvent reorganization energy that increases in the order $Li^+ < Na^+ < K^+$ accounts for the HER activity trend $Li^+ > Na^+ > K^+$ on Pt within Marcus theory [22] but offers no explanation for the inverted trend observed on Au. This inversion has been rationalized by a combined mechanism proposing that the RDS on Au is water dissociation, which is assisted by cations in the order $Li^+ < Na^+ < K^+$, whereas on Pt, the

Figure 4



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Schematic of the two-state EDL model, in which cations are either specifically adsorbed at the inner Helmholtz plane (IHP) or remain electrostatically attracted at the OHP. **(b)** Schematic of the electric field effect on water dissociation, wherein the electric field weakens the H−OH bond strength. **(c,d)** Comparison between the simulated **(c)** and experimental **(d)** polarization curves for HER on Au in 0.1 M KOH, NaOH, and LiOH. **(e,f)** Comparison between the simulated (e) and experimental (f) HER activity on Au with respect to supporting cation concentration. The figures are adapted from Ref. [27]. EDL, electric double layer; HER, hydrogen evolution reaction; OHP, outer Helmholtz plane.

RDS is the transport of hydroxide leaving the surface, which is inhibited by cations with strength $Li^+ < Na^+ < K^+$ [36,49]. While this mechanism reproduces the opposite cation-identity orders on Pt and Au, it conflicts with the trends that increasing supporting cation concentration can enhance HER activity, a condition that would be expected to exacerbate, rather than mitigate, the hydroxide transport inhibition.

Importantly, the proposed mechanisms focus primarily on the role of the cation identity, while the role of the supporting cation concentration remains much less understood. A major reason is the inherent difficulty of incorporating the concentration factor into first-principles calculations.

Recently, we proposed a theoretical framework that provides an intuitive explanation for many of these inverted cation trends [27]. A key concept is the distinction among different cation states, defined by their solvation structure and position within the EDL (Figure 4a). This framework highlights the central role of the local electrostatic environment, encompassing not only local potential effects but also local electric field effects, the latter of which influences water dissociation kinetics via the second Wien effect (Figure 4b). Cations in different states modulate the local electrostatic environment in distinct ways, thereby either promoting or inhibiting the HER activity. The relative populations of these cation states depend on cation identity, electrode potential, solution pH, and catalyst material, resulting in the observed inversions of cation trends. These are illustrated in Figures 4c and 4d for cation-identity effects and Figures 4e and 4f for supporting cation concentration effects.

These electrostatic considerations provide a simple yet physically consistent explanation for observed inversions of cation trends in acidic and alkaline environments, underscoring their generality and importance [50]. Rather than competing with atomistic interpretations, they point to the need for an integrated framework that holistically accounts for local electrostatics and atomistic features [35].

Outlook

Revisiting the coupled pH and cation effects in the HER underscores the critical role of the local electrostatic environment in governing interfacial electrochemical kinetics. While the discussion in this perspective focuses primarily on well-defined planar metal electrodes, the underlying electrostatic principles are expected to extend to more complex catalytic systems, such as transition metal phosphides and single-atom catalysts (*e.g.*, M–N–C materials). In these systems, additional complexity arises from the explicit heterogeneity of active sites, inducing a stronger coupling between local structure and electronic properties. Growing evidence suggests that the interplay between local electrostatics and site-specific electronic structure plays an important role [31].

Looking ahead, progress will require an integrated framework that bridges continuum electrostatics and atomistic-level descriptions, treating local potential, electric field, interfacial water structure, and ion solvation on an equal footing. A central methodological challenge is to consistently relate continuum-level descriptors, such as the reaction-plane potential and local electric field, to atomistic reaction coordinates and interfacial structures. In practice, interfacial properties are spatially heterogeneous and they exhibit pronounced spatiotemporal fluctuations [51,52]. Their rigorous definition and description under constant-potential conditions remains nontrivial. Additional complexity arises from the coupled evolution of ion distributions, solvent reorganization, and specific adsorption, which can simultaneously reshape the EDL and the reaction energetics. Developing predictive multiscale models will therefore require closer integration between continuum electrostatics, constant-potential atomistic simulations, and operando characterization of interfacial structure and fields. Such approaches will be essential not only for resolving longstanding questions surrounding the HER but also for developing a general understanding of electrolyte effects in electrochemical reactions.

On the experimental side, achieving consistent and quantitative validation of cation effects remains challenging as measured trends can be sensitive to trace impurities [53,54]. Distinguishing such extrinsic effects from intrinsic cation-dependent activity remains an important direction for future studies.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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