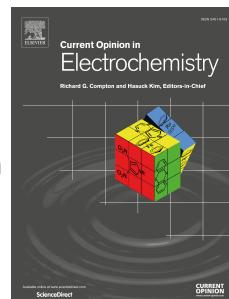


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PII: S2451-9103(23)00061-3

DOI: <https://doi.org/10.1016/j.coelec.2023.101268>

Reference: COELEC 101268

To appear in: *Current Opinion in Electrochemistry*

Received Date: 1 December 2022

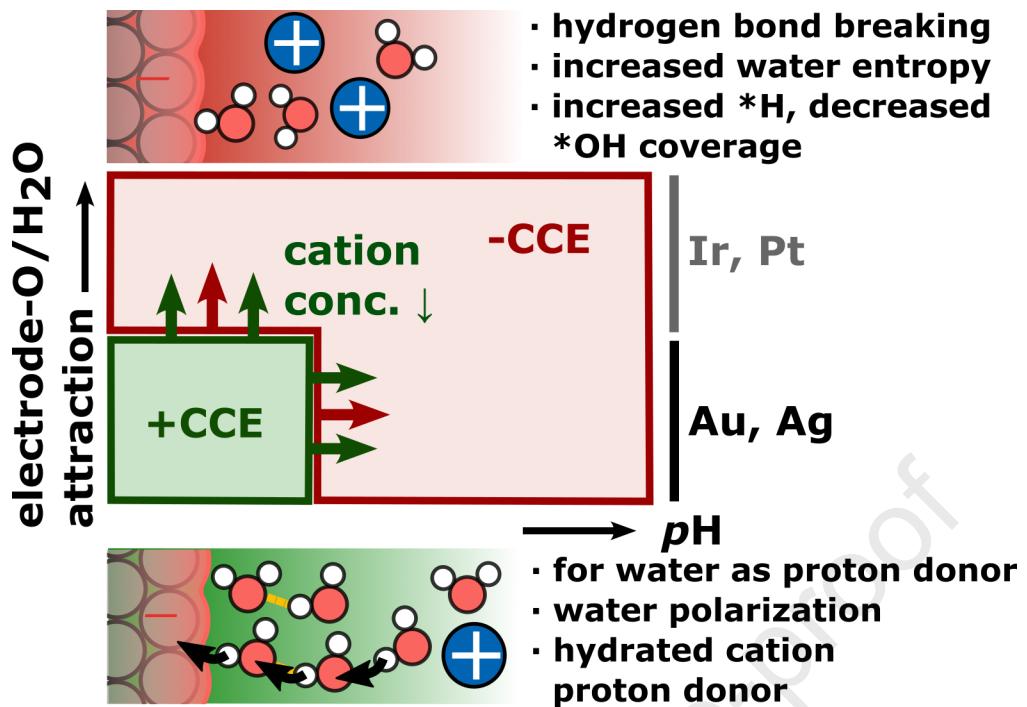
Revised Date: 1 March 2023

Accepted Date: 3 March 2023

Please cite this article as: Ringe S, Cation effects on electrocatalytic reduction processes at the example of the hydrogen evolution reaction, *Current Opinion in Electrochemistry*, <https://doi.org/10.1016/j.coelec.2023.101268>.

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Cation effects on electrocatalytic reduction processes at the example of the hydrogen evolution reaction

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Abstract

Cation effects provide invaluable insights about electrochemistry. In this review, I discuss them with a main focus on the hydrogen evolution reaction and a summary of recent *in situ* spectroscopic and electrochemical measurements as well as advanced computational simulation results conducted at varying cation identities, concentrations and pH. According to these works, the interfacial cation concentration is the main descriptor to explain cation and pH effects. The detailed mechanism (such as e.g. water polarization, water structure changes, field-stabilization of intermediates) depends strongly on potential, pH, oxophilicity of the electrode or the nature of the rate-limiting step and proton donor. With growing convergence in this field, cation effects remain a highly challenging as promising topic for research.

Introduction

Electrocatalysis happens at electrified solid-liquid interfaces. These interfaces have the electric double layer as a common characteristic whose composition and structure have been revealed over the last years to have an immense effect on the rate and selectivity of electrochemical processes.¹ In this review, we discuss these effects in the negative potential regime and at the example of the hydrogen evolution reaction (HER), where cations are the critical component for electrochemistry. Before starting, it is useful to list solid facts about electrified bare (no surface adsorbates) metal-liquid interfaces under reducing conditions, which have been confirmed by various independent studies:

- **The concentration of hydrated cations at the solid-liquid interface increases when moving to more negative potentials.**^{2,3} This is due to a more negative surface charge density σ . For an ideally polarizable electrode without specific adsorption and Helmholtz-like double layer nature, we have:⁴

$$\sigma = C_{\text{gap}} \cdot (U^{\text{SHE}} - U^{\text{SHE,PZC}}) \quad , \quad (1)$$

with the Helmholtz layer or gap capacitance⁵ C_{gap} , the applied potential U^{SHE} and the potential of zero charge (PZC) $U^{\text{SHE,PZC}}$, σ is roughly proportional to the interfacial electric field.⁴ Note that the potential reference scale does not change σ . The PZC is in this case a short-hand notation of the potential of zero free charge (PZFC) corresponding to a minimum in the double layer capacitance. It depicts the zero surface

charge point as if faradaic reactions would not contribute to it. Note, that the PZFC can change with electrolyte concentration or pH, if specific adsorption of electrolyte species falls into the zero-surface charge potential window.⁶

- **More acidic, i.e. larger cations (larger atomic radius and smaller hydrated radius) with a higher valence are more concentrated at the surface^{4,7-9}** The origin for this is yet to be confirmed, although continuum solvation models have indicated that hydrated cation-cation repulsion might be part of the reason for the cation size effects.⁴ Within this idea, it has been also shown that the higher interfacial cation concentration correlates with an increased double layer capacitance as well as surface charge density and thus interfacial electric field.^{4,7,8} It has to be stressed though that these conclusions are derived for dilute electrolytes and it is not clear how they would generalize for concentrated electrolytes in which ion pair formation or charge inversion have been observed.¹
- **Cations are partially solvated under the commonly applied negative potentials, with small cations (Na^+ , K^+) keeping most of their solvation shells resulting in a minor degree of specific adsorption^{3,10-18}** For larger cations such as Cs^+ at very negative potentials, the degree of specific adsorption might be enhanced.^{13,19}
- **At increasingly negative potentials, interfacial water starts to dielectrically saturate and orient with one or even two legs H-down towards the surface.^{2,3,8,20-24}**
- **The presence of cations affects the interfacial water structure.** Cations break the hydrogen bonds (HBs) of surface-bound water,²⁵ as well as the HB network of water in the outer Helmholtz plane (OHL) by reorienting and structuring water around the cations.^{3,20,22,23}

With this understanding in mind, I will present in the following a discussion about cation effects on the hydrogen evolution reaction (HER). As will become clear, cation and pH effects are highly entangled and can be often explained by the amount of accumulation of cations at the interface. The direction and mechanism of cation effects depends strongly on the

experimental parameters, such as pH, oxophilicity of the electrode or the applied electrode potential, but also the rate-limiting step and proton donor.

Cation and pH effects on hydrogen underpotential deposition

Unraveling the physical origin of cation and pH effects in electrocatalysis is an immense challenge due to the complexity of reactive electrified solid-liquid interfaces. We can reduce part of this difficulty by focusing on the thermodynamics of HER, i.e. the hydrogen adsorption step. The hydrogen underpotential deposition (H_{upd}) cyclic voltammetric (CV) peak position relates to the hydrogen binding energy (HBE) having contributions from both the direct binding of a single $^{\bullet}\text{H}$, as well as adsorbate-adsorbate interactions.^{26–28} Further, partial charge transfer during adsorption can result in a non-vanishing electrosorption valence and electric dipole moment which can interact with the electric double-layer field generated at non-vanishing surface charge density as given by Eq. 1.¹ While this can shift the CV peak position,²⁹ it has been found minor for hydrogen adsorption on metallic surfaces under vacuum environments.^{4,26,30–33} In the absence of partial charge transfer, the HBE becomes independent of pH on the reversible hydrogen electrode (RHE) scale U^{RHE} :

$$U^{\text{RHE}} = U^{\text{SHE}} + 0.0592 \cdot pH \quad , \quad (2)$$

i.e. the H_{upd} peak follows Nernstian behaviour. We note that when we talk in this review about pH effects, we will generally refer to a pH-independent potential reference scale (e.g. SHE) and mention explicitly if instead a dependence on pH at fixed RHE, i.e. a non-Nernstian effect, is meant. The Nernstian behaviour of the H_{upd} peak position has been observed for the adsorption to the Pt (111) under alkaline^{17,18} and acidic conditions³⁴ without any effect of the cation identity.³⁵

A pH dependence on RHE scale (i.e. non-Nernstian pH shifts), as well as cation identity and concentration effects, have been, however, observed during CVs of polycrystalline Pt (pc-Pt) electrodes (cf. Fig. 1a) which has triggered vivid scientific discussions.^{17,36} Experiments on (533) ((100) surface steps) and (554) ((110) surface steps) single crystalline electrodes could trace this behavior back to sharp surface step-induced voltammetric peaks (SIVPs) at the (100) or (110) step, respectively (cf. Fig. 1).^{34,37} When increasing the pH at a given RHE potential, the potential vs. pH-independent scale (SHE) keeps decreasing (Eq. 2), leading to an increase of the interfacial cation concentration. Under acidic conditions without the presence of cations, it was shown that the non-Nernstian behavior with pH vanishes (cf.

Fig. 1c).^{34,38} Although not completely free of controversy,¹⁷ this is strong evidence that the observed non-Nernstian pH shift might be simply related to the changing interfacial cation concentration. On the contrary, anion effects were excluded as a possible factor which could in principle influence the PZFC. These insights are important, since the PZFC of Pt facets under alkaline conditions falls into the potential region where even *H and *OH adsorption can more significantly contribute and lead to a pH-dependent PZFC⁶ resulting in a more complex relation of surface charge density and pH as well. In contrast, smaller cations like Na⁺ or K⁺ are commonly not expected to be specifically adsorbed as detailed in the introduction and the PZFC should thus not shift with their concentration. Thus, a cation concentration effect is conceptually easier to understand than a pH effect and possible explanations on how it can affect the SIVPP are summarized in Fig. 1b and discussed in the following. Cation concentration can be locally increased, either by going to more negative potentials, increasing the bulk cation concentration, or moving to larger cations, resulting in a shift of the SIVP position (SIVPP) to more positive potentials.

Ab initio molecular dynamics (AIMD) simulations have shown that the presence of a higher *H coverage detaches chemisorbed water³⁹ and forces it into a hydrogen-bonded, structured state.^{40–42} The necessary displacement of strongly-bound water makes the HBE intrinsically dependent on the water adsorption energy as well. Chemisorption of water, however, involves partial charge transfer.⁴³ Due to this, the HBE becomes non-Nernstian which might explain the SIVPP shifts.^{43,44} Since without the presence of cations, the pH effect is minimal, this suggests cation accumulation to be the more decisive factor though in changing water binding (rather than for example pH-driven changes in the PZFC) and thus the apparent HBE. We also add that water adsorption is weaker on the (111) compared to the (100) and (110) facets,⁴⁵ thus water binding and cation effects on the SIVPP may be less important for the (111) facet in agreement with the experimental observations.

The non-Nernstian HBE leads naturally also to a non-Nernstian *H coverage. The higher *H coverage at higher pH (at fixed RHE) leads to a weakening of the Pt-H bond due to adsorbate-adsorbate repulsion.⁴⁶ This has been confirmed by a decreased Pt-H frequency from various *in situ* vibrational spectroscopic techniques.^{47–51} Additionally Raman spectroscopy has revealed that an increased pH (local cation concentration) at fixed RHE converts H-down water to tetrahedrally hydrogen-bonded water.⁵² This stands in contrast to a bare metallic electrode for which a more negative potential at SHE scale would lead to more

H-down bonded water. Thus, it seems likely that the increased *H coverage which was also observed by the same study is the key and reduces the Pt-water interaction bringing the water into a more strongly hydrogen-bonded structure in line with the AIMD simulations of the Groß group.^{40,41}

Koper and co-workers have instead argued in a different direction and claimed that the SIVP relates to a replacement of surface step-bound *OH instead of H_2O by *H .^{34,37,57,58} The *OH adsorption CV peak on terraces is usually observed at 0.6–0.85 V vs. RHE,⁵⁸ at more negative potentials the *OH coverage is zero (cf. Fig. 1a).⁵⁹ However, vacuum adsorption data both from experimental^{60–63} and computational^{26,64} side have indicated a stronger HBE on the (100) and (110) facets relative to the (111) terrace. This trend, in particular the higher stability of (110) than (111) does not match the CV peak positions of the H_{upd} onset shown in Fig. 1a.³⁶ This suggests that the SIVP might have contributions from another species, such as *OH . In favor of this idea are also the *OH adsorption trends. The onset of *OH adsorption at ≈ 0.6 V vs. RHE is at lower potentials on the (111) compared to the (533) surface. This is again inverse to a series of computational^{36,65–68} and experimental^{69–73} studies suggesting *OH adsorption to be stronger to under-coordinated surface sites like surface steps or defects rather than e.g. the (111) terrace. Moreover, evidence for *OH being stable on stepped facets, but not on (111), under reducing H_{upd} conditions has been collected from infrared adsorption spectroscopy (IRAS),⁷⁴ as well as carbon monoxide displacement studies.⁷⁵ These studies thus suggest that *OH adsorption on steps might indeed fall into the H_{upd} region and contribute to the SIVP.³⁶ On the other hand, CO stripping studies have also indicated an increase of *OH adsorption with increasing pH (at fixed RHE) which is not in line with the observed SIVPP shifts.⁷⁶

To explain the cation-dependent SIVPPs with *OH replacement, specifically adsorbed cations have been considered.^{34,36,37,77} However, specific adsorption at least of small alkali cations such as Na^+ or K^+ is rather minor at the considered potentials (cf. introduction). From more realistic full-electrolyte AIMD simulations, the presence of cations was found to destabilize *OH ,¹⁰ which could be related to a disruption of the HB network which is known to stabilize *OH .^{6,78} Together, this suggests that an increased interfacial cation concentration could break the HB network and destabilize *OH , in line with the observed SIVP shifts. Another possible explanation is that the stronger electric field with higher cation concentration destabilizes *OH via dipole-field interactions,^{79,80} similar to what we

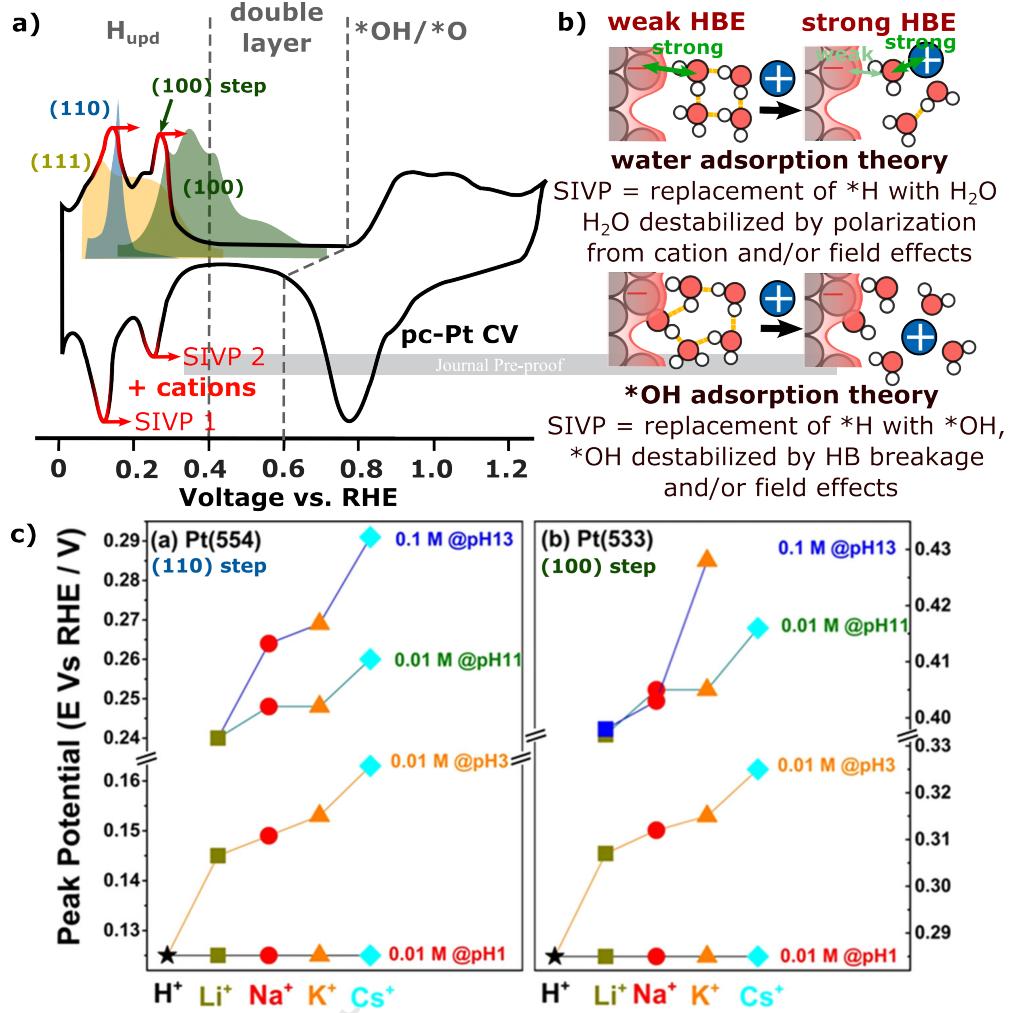


FIG. 1. Cation effects on the cyclic voltammogram of polycrystalline Pt (pc-Pt). a) Assignment of CV peaks of pc-Pt⁵³ by comparison to the (111),⁵⁴ (100)⁵⁵ and (110)⁵⁶ single crystal Pt CVs (shaded regions, arbitrary scaling of current). The common assignments³⁶ about the H_{upd} , double layer region and $*OH$ adsorption region have been further indicated. The two distinct peaks in the H_{upd} region have been assigned to surface (100) and (110) step-induced voltammetric peaks (SIVP). These peaks shift as a function of pH (at fixed RHE), cation concentration and identity. b) Common theoretical models to explain the shift in the SIVP position, changes in the water or $*OH$ binding to the surface with cation concentration. c) Shifts of the SIVP position as experimentally measured on Pt(554) and Pt(533) single crystalline electrodes.³⁷ The results stress the vanishing pH-effect in the absence of cations.

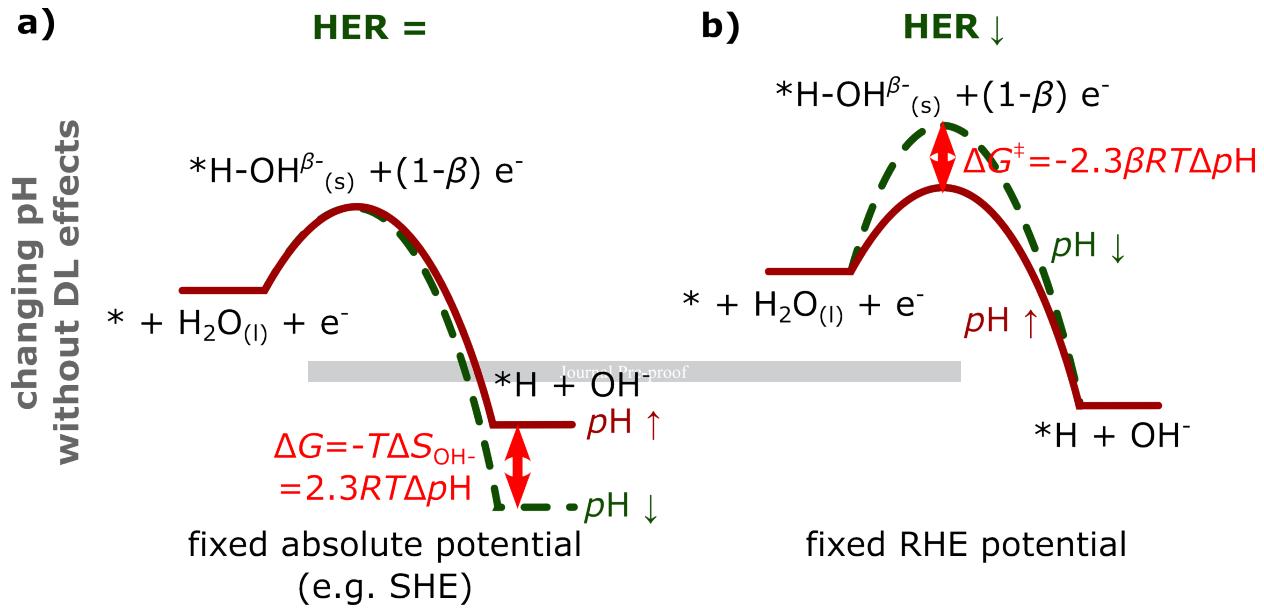


FIG. 2. **pH effects on the free energy diagram of alkaline HER.** pH effects on the Volmer step under absence of electric double layer effects and under assumption of water as the proton donor on SHE (a) and RHE (b) potential scale. ΔG refers to the change in the Volmer step reaction energy, and ΔG^\ddagger to the change in the activation energy due to changes in the pH.

discussed for ${}^*\text{H}_2\text{O}$ as well. Again, however, it might be difficult to explain the absence of the SIVP shift when no cations are present, since the PZFC and thus also the surface charge density shift significantly with the pH as described above.

In sum, two convincing explanations have been provided for the SIVPP shifts with pH/interfacial cation concentration. It is generally difficult to decide for one or the other hypothesis, since water and ${}^*\text{OH}$ adsorption are highly correlated via the HB network and oxophilicity of the electrode⁶⁷ as we will further discuss below.

Cation and pH effects on hydrogen evolution

For HER under alkaline conditions, the Volmer step is considered to be rate-limiting and water the proton donor.^{38,81–84} For this case, we expect the HER rate to be independent of pH on a pH-independent potential reference (SHE) scale,^{85,86} as illustrated in Fig. 2a, and proven by alkaline experimental HER results on Au, Pt, and Ir.^{81,82} Due to this, the HER rate is expected to depend on pH on an RHE scale, as shown in Fig. 2b, making the SHE scale more useful for comparing experiments at different pH. The RHE scale, can be, however, still needed, to discuss coverage effects, as these follow roughly an RHE-dependence.

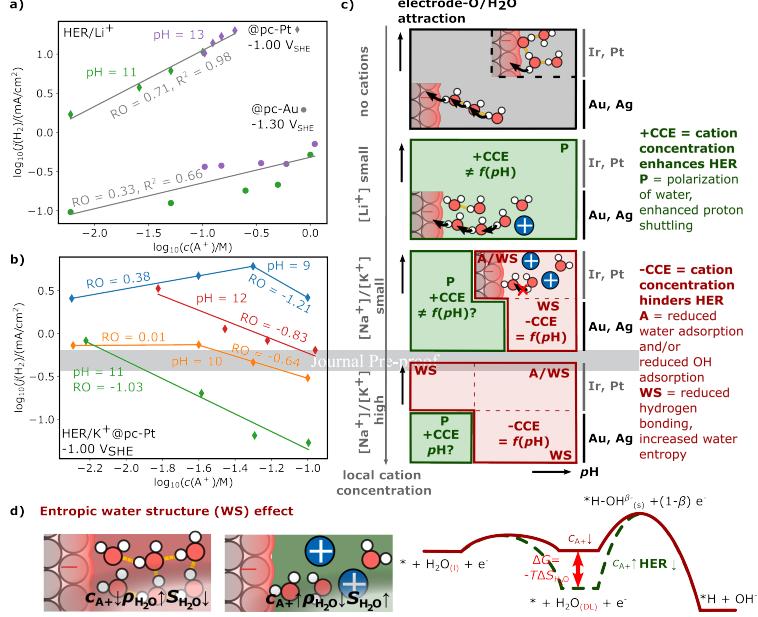


FIG. 3. Cation and pH effects on the alkaline hydrogen evolution reaction (HER). a) and b) Experimentally measured⁸⁷ HER current density vs. cation concentration (log-log plot) for different pH values and polycrystalline Au and Pt which is reploted here at fixed potential vs. SHE. The figure illustrates how for small cations like Li⁺ (a), the current becomes roughly pH-independent, increasing consistently for higher cation concentrations while for larger cations (b), there is a transition region for the cation reaction order which depends on pH. c) Schematic illustration of the current understanding of cation and pH effects on HER. +CCE: Normal cation concentration effect (with more cations increasing the HER rate). -CCE: Inverse CCE (with more cations decreasing the HER rate). An explanation for the +CCE might be the polarization (P) of water increasing the hydrogen transfer rate via proton shuttling. Explanations for the -CCE might be destruction of the hydrogen bond network and water structure (WS) and thus reduced proton shuttling rate, reduced adsorption of *OH, increased *H coverage due to weakened water adsorption (A), or increased water entropy due to reduced water concentration (WS, illustrated in d). Note, that the *OH adsorption energy increases also with the oxophilicity of the electrode⁶⁷ (the y-axis). $= f(pH)$: The HER current depends on pH at fixed potential vs. pH-independent reference (SHE), $\neq f(pH)$: The HER current is roughly pH-independent at fixed potential (pH-independent reference, SHE)

Following this thinking, Fig. 3a and b show the alkaline HER results from the work of the Koper group⁸⁷ re-plotted at a fixed SHE potential. For a small concentration of Li⁺ in Fig. 3a, the HER rate on pc-Pt shows a positive cation reaction order of ≈ 0.7 , for pc-Au of ≈ 0.3 . We will refer to this positive reaction order with regard to cation concentration as a

positive cation concentration effect (+CCE), while a negative reaction order will be referred to as negative CCE (-CCE). Due to larger cations being more concentrated at the interface, a +CCE often correlates with a cation identity effect (CIE) for which larger cations give a higher current, we thus abbreviate this with +CIE, and the inverse with -CIE. While in the case of pc-Pt, a single concentration dependent current is observed independent of the pH, the data is less clear in the case of pc-Au. Independence of the pH suggests that changes in the coverage of intermediates like ${}^*\text{H}$ or ${}^*\text{OH}$ might be of minor importance for the observed trend, as these are highly sensitive to the pH. Instead, the constant reaction order suggests that cations might participate in the reaction directly (cf. Fig. 3c), e.g. by polarizing water, thus increasing the proton donor strength of hydrated cations close to the interface^{9,88–91} making them a likely proton donor.^{9,90,92} This is in line with recent results showing a correlation of the HER rate with the acidity of multi-valent cations.⁹ It is also notable that there is a dependence of the reaction order on the oxophilicity of the electrode which provides an interesting topic for further research.

For K^+ as the electrolyte-containing cation (Fig. 3b), the +CCE holds instead only in the limit of less alkaline conditions and for small cation concentration. In agreement with this, previous experimental results have observed a +CIE for 0.1 M solutions on Ag under neutral conditions.⁸⁹ At less alkaline conditions, with increasing cation concentration, a turning point is, however, reached after which +CCE switches to -CCE (cf. Fig. 3b) as pointed out by others studies as well⁹³. This turning point seems to be reached at lower cation concentration, the higher the pH. After the turning point, the HER activity shows a strong pH effect. Before the turning point, the limited experimental data makes conclusions difficult, although it seems as if the pH dependence might be reduced to a level similar to Li^+ , as also indicated by the data of ref. 50 for Na^+ (Supplementary Fig. S1). The pH dependence indicates that the coverage of surface intermediates like ${}^*\text{H}$ and ${}^*\text{OH}$ could play a more significant role. It is important to mention though, that all conclusions that were made here on the ion concentration and pH-dependent changes of the reaction order are based on only a single experimental data set, often a single or two data points. Thus, future studies should be performed to verify conclusions drawn in this paragraph.

A further interesting observation is that pc-Au showed a +CCE over the whole concentration range for both Li^+ (Fig. 3a) and K^+ (Supplementary Fig. S2).^{50,87} Other studies agree that more oxophilic metals like Ir and Pt have a stronger tendency to show an -CIE^{18,94}

while less oxophilic metals like Ag and Au are more prone to show a +CIE.⁹⁵ Finally, it is noticeable that the CCE slope on pc-Au decreases with increasingly negative potential (potential-independent reference, SHE), and thus higher interfacial cation concentration, leading to a continuous transition from +CCE to -CCE (Supplementary Fig. S1).^{50,87} These results suggest that the +CCE/+CIE to -CCE/-CIE inversion is enforced by a high interfacial cation concentration (induced by a higher bulk concentration or more negative potential vs. PZFC), by a more oxophilic metal and by more alkaline conditions as summarized in Fig. 3c.

To come up with an explanation for the switch to -CCE/-CIE, let us follow first the idea of cations changing the coverage of *OH. A coverage of *OH or *H might remain even under highly reducing HER conditions.¹⁰ Stabilization of *OH e.g. by a second strongly *OH binding metal has been considered in the bi-functional mechanism to facilitate the Volmer step as long as it is not bound too strongly,⁹⁶ resulting in a volcano-like relation with the *OH adsorption energy.^{58,97} *OH has been also considered as a proton donor and acceptor to nearby water molecules to facilitate HER.¹⁰ For higher pH values (and thus more positive potential vs. RHE, Eq. 2) and more oxophilic metals we expect a higher *OH coverage which coincides qualitatively with the red -CCE region depicted in Fig. 3b. The shrinking of this -CCE region and transition to +CCE for smaller cations like Li⁺ can be explained by the smaller surface concentration of the cations which stabilizes a higher *OH coverage in line with the discussion of the last section.

Other authors performed detailed kinetic modeling on experimental data and suggested that *OH does not enhance HER, but instead slows it down due to site blocking, while water reorganization and water structure are instead the critical parameters.^{35,98} Without the presence of *OH, water structure depends on three physical parameters of the solid-liquid interface. First, the oxophilicity of the metallic electrode which increases the water coverage.⁶⁷ Second, the local concentration of cations which increases when moving to more negative potentials. Third, the coverage of *H which is increasing at a lower pH and higher interfacial cation concentration (see last section). Along this line, Koper and co-workers explained the beneficial effect of Ni(OH)₂ on the HER rate on Pt, not by the presence of *OH, but instead the negative shift of the PZFC which decreases the interfacial cation concentration following Eq. 1, loosening the water structure to results in faster proton transfer.³⁸ Employing *in situ* Raman spectroscopy other authors found that water points increasingly

H-down with increasing amount of Ni reducing the amount of tetrahedrally hydrogen bonded water and it was claimed that this water structure change leads to enhanced HER.⁵² Accordingly, some studies have suggested that the trends in HER for bimetallic Pt-catalysts with *OH adsorption energy could instead be explained by changes in the PZFC and water structure.^{38,79}

Keeping the electrode composition and potential (vs. pH-independent reference, SHE) fixed, the local cation concentration is the key parameter to control water structure and *H coverage. An increased interfacial concentration of cations leads to strong polarization⁹⁹ and constraining of water structure. This increases the reorganization during the Volmer step suppressing the HER rate.⁹⁹ At the same time, as illustrated in Fig. 3d structure-breaking cations such as Cs⁺ (or increased concentration of cations) break the water HB network^{20,99} and reduce the water concentration¹⁸, thus increasing the entropy of interfacial water⁹⁹ similar to what has been suggested for protons as proton-donors, too.¹⁰⁰ More cations would thus increase the entropic barrier for the Volmer step as illustrated in Fig. 3d.⁹⁹ These effects might only be relevant under sufficiently high interfacial cation concentration, meaning high bulk concentration and large cations, explaining the CCE switch summarized in Fig. 3c. Additionally, less oxophilic metals have a lower water coverage,⁶⁷ and more randomized water orientations visible also by the surface dipole being almost independent of the water coverage.⁶⁷ This suggests that the water network might more flexibly accommodate cations, without significant disturbance of the HB network. Finally, the *H coverage increases with cation concentration, as discussed above. This could explain the pH-dependence of the HER rate which arises at higher interfacial cation concentrations (by higher bulk concentration and moving from Li⁺ to K⁺ as cation, Fig. 3b). When increasing the pH, the *H coverage drops while +CCE switches to -CCE, suggesting that *H coverage might be efficient in blocking cation effects.

While HER under alkaline conditions shows strong cation effects, these vanish under acidic conditions.^{9,91,99,101} The smaller overpotential under acidic conditions and thus reduced surface charge density (Eq. 1)³⁸ results in fewer interfacial cations, making surface accumulation competition with protons^{2,102} or water structure changes²⁰ and thus -CCE unlikely. In addition, protons are in excess and much better proton donors than cation-polarized water, removing the physical origin of the +CCE as noted above. Finally, the *H coverage is significantly decreased under acidic conditions, both due to the earlier HER

onset on an RHE scale and the decreased interfacial cation concentration. It is important to note, that running HER at high overpotentials, proton transport can become limited, leading to a switch to water as a proton donor.^{81,82} As a consequence of the much higher overpotential and water as proton donor, the regular polarization-induced +CIE effect on the HER rate has been observed.⁹

The direct correlation of *OH and water coverage and structure (by HBs to *OH^{20,40,103}),^{67,104} has made it difficult ~~to ultimately decide on the correct physical origin of cation effects.~~ An additional complication in this regard is that HER is often dominated by minority active sites such as stepped sites^{105–109} which may be present even on epitaxially grown surfaces.^{31,110} It will require future studies with controlled electrolyte concentration, pH and defined single crystalline electrodes in combination with *in situ* spectroscopic techniques to resolve coverage changes to ultimately resolve these effects.

Connection to other electrochemical reactions

Cation effects are not limited to HER, but have been a topic of intense debate for example in the electrochemical CO₂ reduction literature.^{4,7,30,89,111–117} It is interesting to note also in this case, the interfacial cation concentration has been found to control the activity and selectivity of the electrochemical reaction, with a higher cation concentration facilitating in an +CCE- and +CIE-like way the selectivity of specific product pathways.^{4,7,30,117} These pathways are limited by the formation of reaction intermediates with significant electric dipole that can be stabilized by interaction with the surrounding electric double-layer field or chemical coordination. It is important to mention that the current discussion of cation effects on CO₂ reduction rarely gives an appropriate account for the fact that the main competing reaction, the HER, is also strongly cation-dependent as elaborated on in this review. Indeed, it has been shown that under alkaline conditions, the HER rate is so significant, that the HER cation dependence directly affects the trends observed for the CO₂ reduction pathways as well, so that their cation dependence diverges from the conventional physical understanding.⁹

Varying the interfacial cation concentration can be used to engineer highly selective and active electrocatalyzers, as e.g. demonstrated by using crown ethers to suppress electrochemical CO₂ reduction in favor of HER,³ or in accumulating it on Nafion-coated electrodes^{7,101,118–123} to boost the CO₂ to C₂ reduction selectivity.

Conclusion

Cation effects have been of central interest to electrocatalysis for a long time. Since cations participate in the reaction mechanism, understanding them can give a detailed picture of electrochemical reaction kinetics and the electrified solid-liquid interface. From analyzing literature on hydrogen underpotential deposition and the hydrogen evolution reaction (HER), it was noticed here that cation identity, concentration and pH effects have often a common origin, the ~~change of the interfacial concentration of cations~~. Increasing the interfacial cation concentration affects the rate of HER by:

- 1. Polarizing water and increasing the proton transfer/shuffling rate to the surface.** This mechanism is expected to be important if the rate-limiting step is a proton-coupled electron transfer (PCET) with the proton coming from water, such as the Volmer step in alkaline HER. Further, it is only relevant in the limit of small interfacial cation concentration, low pH (high *H coverage), and weak water binding to the electrode.
- 2. Decreasing the *OH coverage and/or breaking the structure of interfacial water.** Cations break the hydrogen bond structure of interfacial water and generate an electric field, both of which reduce the coverage of *OH which might be slowing down HER. On the other hand, the depletion of interfacial water and the broken hydrogen bonds due to cation accumulation can increase the entropic barrier for proton transfer from water as well as the reorganization energy. This mechanism is also expected to be important for a PCET as rate-limiting step without limitations to the proton donor, but requires high interfacial cation concentrations (which are commonly not present under acidic conditions due to reduced overpotential), high pH (low *H or high *OH coverage), and electrodes with strong water bonding.

Although much knowledge and understanding have been gathered about cation effects in the last few years, they remain a highly challenging topic with a lot of room for future research.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT, Republic of Korea (NRF-2021R1C1C1008776).

Competing interests

The author declares no competing interests.

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** This study is to my knowledge the first which investigates the electrified solid-liquid interface with a fully quantum description of the electrode and full sampled electrolytic degrees of freedom. As such, it provides important insights about the charging of the electric double layer, its composition and structure.).

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Declaration of interests

- 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.
- The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: