

# Current understandings of the sluggish kinetics of the hydrogen evolution and oxidation reactions in base

Qingying Jia,<sup>\*,1</sup> Ershuai Liu,<sup>1</sup> Li Jiao,<sup>2</sup> Jingkun Li,<sup>1</sup> Sanjeev Mukerjee<sup>1</sup>

<sup>1</sup> Department of Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts, 02115, United States

<sup>2</sup> Department of Chemical Engineering, Northeastern University, Boston, Massachusetts, 02115, United States

\* To whom correspondence should be addressed. E-mail: [q.jia@neu.edu](mailto:q.jia@neu.edu).

## Highlights

- The HBE theory centers on the inherent properties of the surface.
- The bifunctional mechanism further considers the interactions between surface intermediate adsorbates ( $H_{ad}$  and  $OH_{ad}$ ).
- The pzfc theory further considers the interfacial double layer environment and the transportation of reaction intermediates ( $OH_{ad}$ ).
- The 2B theory further incorporates the cation effects into the picture of the interfacial double layer region in alkaline electrochemistry.

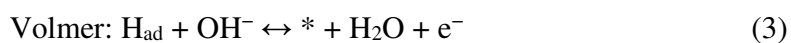
**Abstract.** The hydrogen evolution and oxidation reactions (HER/HOR) in alkaline media are the most fundamental electrochemical reactions in alkaline electrochemistry.

Surprisingly, their kinetics is still elusive and under extensive debates. Herein, a critical review of the four schools of thoughts of the alkaline HER/HOR kinetics is given, focusing on the key discrepancies in the underlying mechanisms and experimental supports within these thoughts.

The hydrogen evolution and oxidation reactions (HER/HOR) are the most fundamental electrochemical reactions involving the simplest molecule H<sub>2</sub>. Clear understandings of their kinetics lay the foundation of the mechanistic understandings of more complicated reactions involving more complex reactants. For example, the Butler-Volmer equation<sup>[1]</sup> and the Sabatier's principle<sup>[2]</sup> were initially demonstrated by studying the HER kinetics in low pH media, and later extended to many other reactions in acid. It is now the most fundamental principles in electrochemistry. On the other hand, the kinetics of the HER/HOR in alkaline media remains elusive. It is under extensive debate why the HER/HOR rates are sensitive to pH, and to the surface structure when in base. Correspondingly, the explanations of the promotion of the alkaline HER/HOR kinetics induced by some transition metals such as Ni, Ru, *etc.* also conflict sharply. The clouds over the alkaline HER/HOR kinetics leave the scientific foundation of alkaline electrochemistry in question. A coherent theory shall provide natural explanations of all aforementioned puzzles, and constitutes the underlying principles of alkaline electrochemistry.

There are currently four different opinions of the essence of the slow kinetics of the HER/HOR of Pt-based electrocatalysts in base, and the catalytic roles of the second metal in promoting the HER/HOR of Pt surfaces. In spite of the extensive debates within the thoughts, it is generally believed that the HER/HOR proceed via the Tafel-Heyrovsky-Volmer mechanism in base and the Volmer step is the rate determining step (rds):





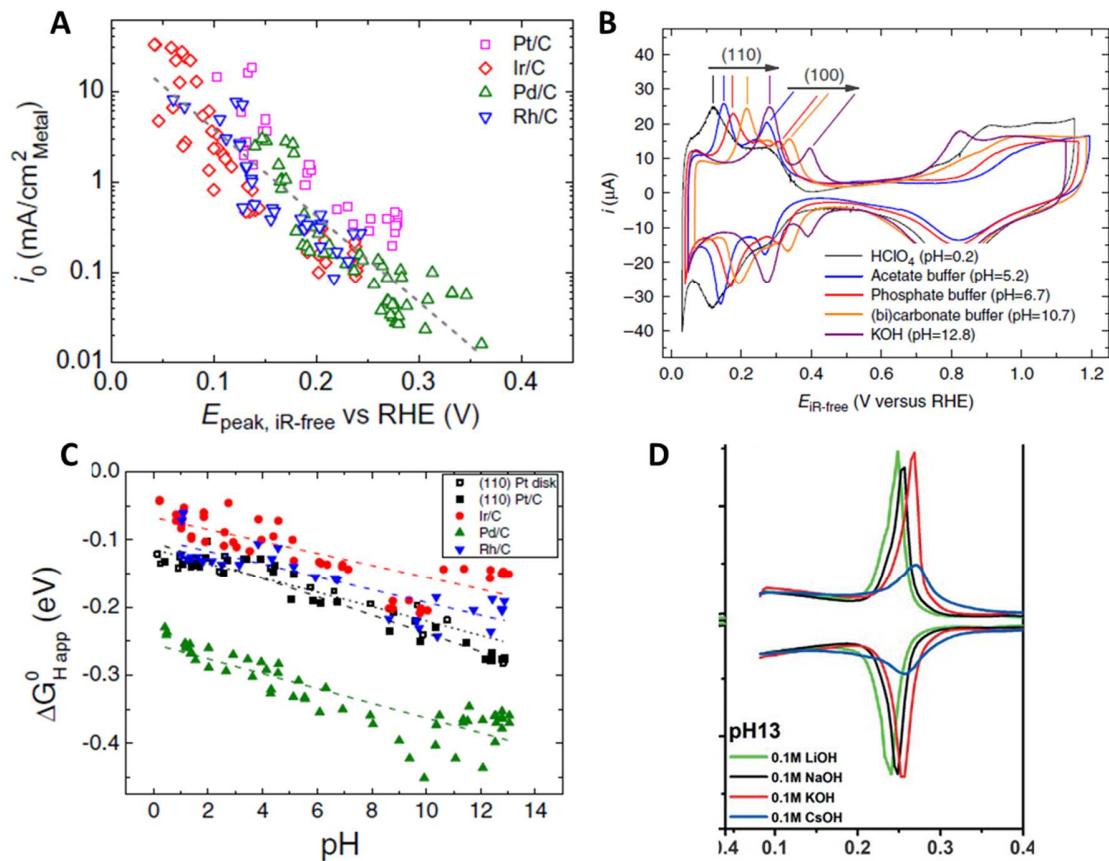
although the Heyrovsky as the rds was also proposed,<sup>[3]</sup> and cannot be distinguished from the Volmer being the rds by Tafel analysis as both cases can give a Tafel slope of 120 mV/dec.<sup>[4]</sup> Nevertheless, it is interesting to note that different thought focuses on different participants in the Volmer step. The hydrogen binding energy theory (HBE) centers on the surface binding to the  $\text{H}_{\text{ad}}$  and  $\text{H}_2\text{O}_{\text{ad}}$ .<sup>[5-8]</sup> The bifunctional mechanism centers on the  $\text{H}_2\text{O}_{\text{ad}}$  dissociation that produces  $\text{H}_{\text{ad}}$  for the HER and  $\text{OH}_{\text{ad}}$  as a possible reactant for the HOR interacting with the  $\text{H}_{\text{ad}}$ .<sup>[9, 10]</sup> The potential of zero free charge (pzfc) theory focuses on the transportation of  $\text{OH}^-$  throughout the double layer region via  $\text{H}_2\text{O}$ .<sup>[11]</sup> And the 2B theory relies on the profound catalytic roles of alkali metal cations ( $\text{AM}^+$ ) for the HER and HOR via interactions with the  $\text{OH}_{\text{ad}}$ .<sup>[12]</sup> The main arguments of each opinion in association with with the corresponding experimental supports, and the key discrepancies within the opinions are briefed below, with the hope to shed light on the alkaline HER/HOR kinetics.

**Hydrogen binding energy (HBE) theory.** Currently the most prevailing theory for the alkaline HER/HOR kinetics is the HBE theory pioneered by Sheng, Gasteiger, and Yan.<sup>[6-8, 13, 14]</sup> This theory states that the binding energy between the metal and hydrogen ( $E_{\text{M-H}}$ ) solely determines the HER/HOR rate of the metal. Experimental supports for this theory include the nearly linear correlation between the HER/HOR rates of several transition metals including Pt, Ir, Pd, and Rh and the position of their underpotential deposited hydrogen  $\text{H}_{\text{UPD}}$  peaks ( $E_{\text{peak}}$ ) (Figure 1A) that is believed to be linearly related to  $E_{\text{M-H}}$  ( $E_{\text{M-H}} = -E_{\text{peak}}F$  where  $F$  is the Faraday constant) (Figure 1B).<sup>[13]</sup> Later Yan *et al.*<sup>[5]</sup> refined the HBE theory by inducing the apparent Gibbs free energy of hydrogen

adsorption  $\Delta G_{H,app}$  ( $\Delta G_{H,app} = \Delta G_H - \Delta G_{H_2O}$  wherein  $\Delta G_H$  and  $\Delta G_{H_2O}$  are the intrinsic Gibbs free energy and the Gibbs free energy of water adsorption, respectively), on the basis of the consideration of the desorption/adsorption of water together with hydrogen. They accordingly stated that it is the  $\Delta G_{H,app}$  rather than the  $\Delta G_H$  that is related to the  $H_{UPD}$  peak and the HER/HOR rates. In the refined HBE theory, the  $\Delta G_{H_2O}$  weakens with increasing pH whereas the  $\Delta G_H$  remains constant, resulting in increasing  $\Delta G_{H,app}$  with increasing pH, thereby matching the positive shift of the  $H_{UPD}$  peak and the decreasing HER/HOR rates with increasing pH (Figure 1C). The weakening of the Pt- $H_2O_{ad}$  bond is supported by the recent Quantum Mechanics Molecular Dynamics modeling by Goddard *et al.*<sup>[15]</sup> The refined HBE theory was further proposed to account for the  $AM^+$ -induced  $H_{UPD}$  peak shift (Figure 4D) given that the  $AM^+$  weakens the Pt- $H_2O_{ads}$  bond resulting in strengthened  $\Delta G_{H,app}$ ,<sup>[16, 17]</sup> as well as the trend of the HER/HOR rates in the order of  $LiOH > NaOH > KOH > CsOH$  since  $Cs^+$  weakens the Pt- $H_2O_{ads}$  the most and  $Li^+$  weakens the least.<sup>[16, 17]</sup>

However, the HBE theory does not comply with the recent findings<sup>[12]</sup> that increasing the  $AM^+$  concentration, which is supposed to weaken the Pt- $H_2O_{ads}$ <sup>[17]</sup> selectively increases the HER but not the HOR rate of the stepped Pt surfaces, but has no effect on the HER/HOR rates of the Pt(111) surface.<sup>[18]</sup> Another phenomenon the HBE theory finds difficult to account for is that while the HER/HOR rates of all Pt surfaces shift with pH in a similar way,<sup>[11]</sup> the  $E_{peak}$  of the stepped Pt surfaces is pH-dependent (*e.g.* irregular Nernstian shift with pH) whereas of the Pt(111) surface is pH-independent. These phenomena indicate that the correlation between the HER/HOR rates and the  $E_{peak}$  is not universal. Collectively speaking, the Pt(111) and stepped Pt surfaces behavior very

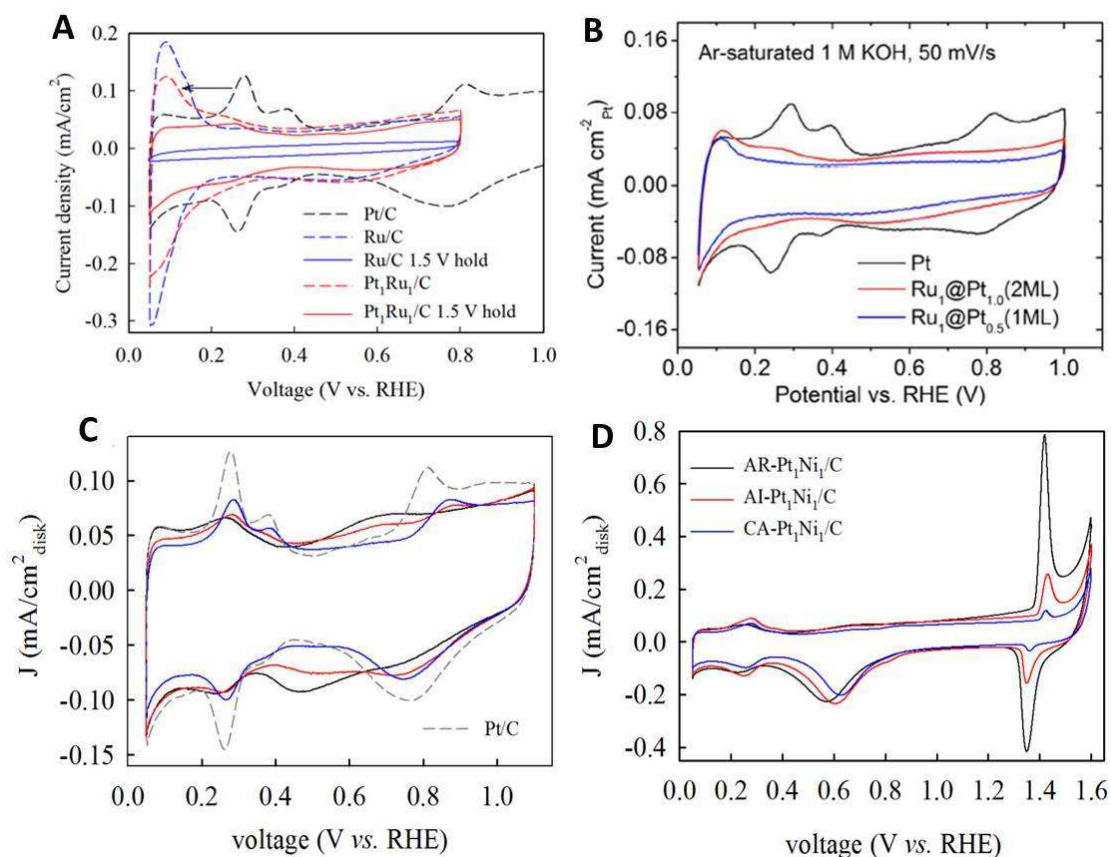
differently in terms of cation effects and the  $H_{UPD}$  shift with pH, but their HER/HOR rates shifts similarly with pH. This phenomenon hasn't been fully accounted for by the HBE theory that links the HBE with the  $H_{UPD}$  peak position.



**Figure 1.** (A) Exchange current densities of HOR/HER on Pt/C, Ir/C, Pd/C, and Rh/C as a function of the lowest  $H_{UPD}$  desorption peak potential from CVs. (B) Steady state CVs of Pt collected in selected Ar-saturated electrolytes at a sweep rate of 50mV/s. (C)  $\Delta G_{H,app}^0$  as a function of pH for (110) facet of Pt disk (hollow black square), (110) facet of Pt/C (solid black square), Ir/C (red solid sphere), Pd/C (green solid up-triangle) and Rh/C (blue solid down-triangle). (D) CVs of Pt(553) recorded at pH 13 in 0.1m MeOH, where Me is Li, Na, K, or Cs, as indicated. Part A is reproduced from reference [14]; part B is reproduced from [13]; part C is reproduced from reference [5]; part D is reproduced from reference [16].

Recently, it was reported that the Ru@Pt/C<sup>[6, 19]</sup> and Ni@Pt/C<sup>[20]</sup> core-shell nanoparticles (NPs) with pure Pt surfaces show superior HER and/or HOR activities to the counterpart Pt/C NPs because the strain and/or ligand effects induced by Ru or Ni weaken the Pt-H

binding energy. These results exclusively support the HBE theory as all other theories require the second metal to be present on the surface to promote the HER/HOR. However, Jia *et al.*<sup>[21]</sup> showed that even trace amount of Ru (0.5  $\mu\text{M}$ ) in the alkaline electrolyte can dramatically promotes the HER/HOR of Pt/C, and accordingly questioned whether the clean Pt surfaces at *ex situ* conditions are still free of Ru under *in situ* electrochemical conditions wherein Ru has strong tendency to migrate onto the Pt surfaces.<sup>[22]</sup> Since the surface Ru is associated with a prominent peak around 0.1  $\text{V}_{\text{RHE}}$  in the cyclic voltammogram (CV) in alkaline (Figure 2A),<sup>[19, 21]</sup> this peak may be used to judge the presence of surface Ru in alkaline *in situ*. For example, the CV of the Ru@Pt NPs shows a  $\text{H}_{\text{UPD}}$  peak at 0.1 V in alkaline (Figure 2B), suggesting the presence of surface Ru rather than a clean Pt surface proposed.<sup>[6]</sup> The CV of another case of Ru@Pt/C NPs in alkaline was not provided.<sup>[23]</sup> Similarly, Jia *et al.* recently suggested that the presence of Ni on Pt surfaces in alkaline can be examined by their characteristic features in the CVs in alkaline (Figure 2C and 2D). This *in situ* evidence, however, was not given to justify the claimed pure Pt surfaces in the Ni@Pt/C NPs subjected to the acidic immerse treatment.<sup>[20]</sup> In brief, if the HBE theory governs the alkaline HER/HOR kinetics, the  $\Delta G_{\text{H,app}}$  will be the sole activity descriptor of the HER/HOR activity, and potentially it is possible to boost the HER/HOR activity of a pure Pt surface by changing the subsurface metal. However, the key experimental evidence for the HBE theory, the link between the  $\text{H}_{\text{UPD}}$  peak position and the HER/HOR rate, as well as a clean Pt surface with optimized  $E_{\text{Pt-H}}$  with superior HER/HOR activity to the unmodified Pt-surface, is questionable.

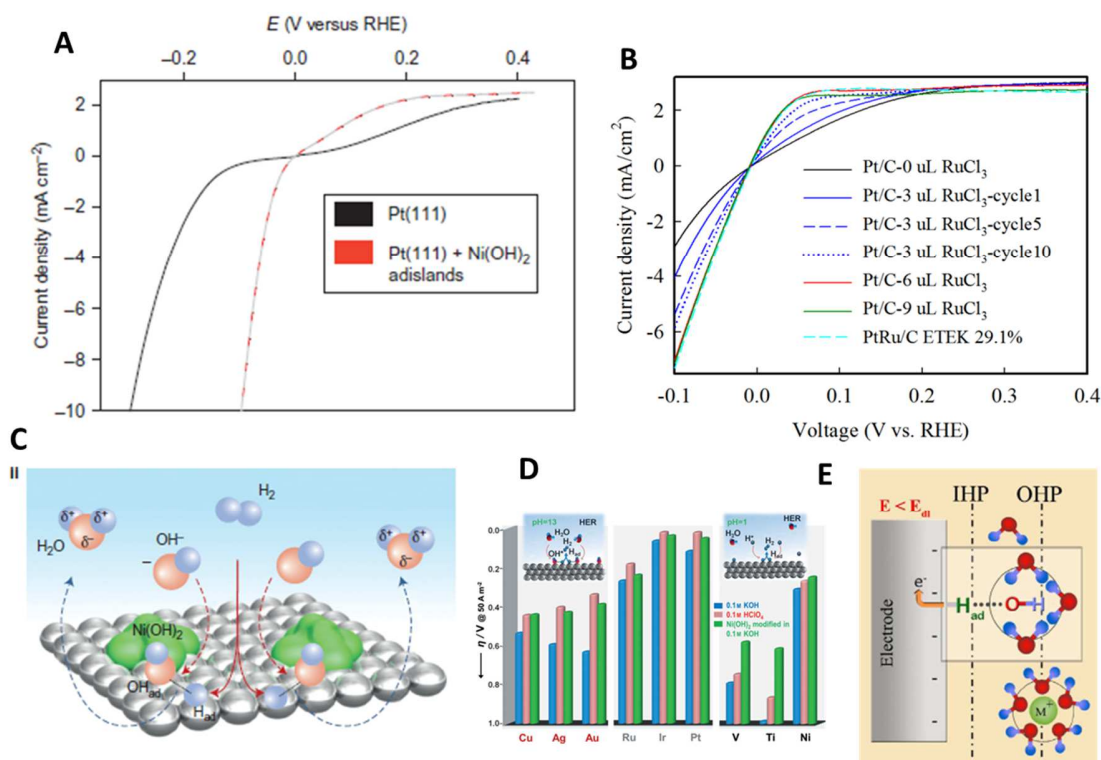


**Figure 2.** (A) CV plots of Pt/C, Ru/C, and Pt<sub>1</sub>Ru<sub>1</sub>/C; and of the latter two after holding the potential at 1.5 V for 5 minutes collected in an Ar-saturated 0.1m KOH electrolyte at a scan rate of 20 mV/s at room temperature. (B) Pt surface area-normalized voltammetry curves. The CVs of as-received (AR)-Pt<sub>1</sub>Ni<sub>1</sub>/C, acid immersed (AI)-Pt<sub>1</sub>Ni<sub>1</sub>/C, and CV-activated (CA)-Pt<sub>1</sub>Ni<sub>1</sub>/C collected in an Ar-saturated 0.1 M KOH electrolyte at 20 mVs<sup>-1</sup> with the upper potential limit of 1.0 V<sub>RHE</sub> (C) and 1.6 V<sub>RHE</sub> (D). Part A is reproduced from reference <sup>[21]</sup>; Part B is reproduced from reference <sup>[6]</sup>; Part C and D is reproduced from reference <sup>[12]</sup>.

**Bifunctional mechanism.** While it is uncertain whether Ni or Ru in the core can boost the alkaline HER/HOR of Pt surfaces, Markovic's<sup>[9, 10]</sup> and Jia's<sup>[12, 21]</sup> groups demonstrated that the surface Ni or Ru can improve the alkaline HER/HOR rates of Pt surfaces (including Pt(111), Pt polycrystalline, and Pt/C NPs) by using the surface deposition methods (Figure 3A and 3B). Accordingly, Markovic *et al.*<sup>[9, 10]</sup> proposed the bifunctional mechanism wherein the Ni or Ru promotes the water dissociation easing the generation of H<sub>ad</sub> as the reactant of the H<sub>2</sub> recombination on adjacent Pt sites for the HER,

and the  $\text{OH}_{\text{ad}}$  hosted on these oxophilic sites facilitates removing  $\text{H}_{\text{ad}}$  on adjacent Pt sites for the HOR (Figure 3C). By showing that adding  $\text{Ni}(\text{OH})_2$  onto a wide variety of metal surfaces including Ni leads to a universal 3-5 fold enhancement in the HER rate (Figure 3D),<sup>[24]</sup> Markovic *et al.* proposed that the needs to break the water to generate  $\text{H}_{\text{ad}}$  is the major reason for the slower HER kinetics in alkaline compared to in acid. In the reverse direction (Eq. 3), the slower HOR kinetics in alkaline was ascribed to the extra energy required to bring the negatively charged  $\text{OH}^-$  close to the negatively charged surface to remove  $\text{H}_{\text{ad}}$  (Figure 3E); whereas in acid the neutral  $\text{H}_2\text{O}$  can easily remove  $\text{H}_{\text{ad}}$  forming  $\text{H}_3\text{O}^+$ .<sup>[25]</sup> However, these key arguments of the bifunctional mechanism were strongly questioned by Gasteiger *et al.*<sup>[7]</sup> They pointed out that  $\text{H}_2\text{O}$  is a very fast  $\text{H}_{\text{ad}}$  donor with a low energy barrier on Pt surfaces, and also the two different sources of  $\text{H}_{\text{ad}}$  in acid vs alkaline shall result in a drastic change of the HER/HOR rates with pH rather than the gradual changes observed. In addition, water is always the dominant species in the solution within the pH value ranging from 1-13, and shall be available to remove  $\text{H}_{\text{ad}}$  for the HOR even in alkaline. While this issue may be partly addressed by the recent finding by Koper *et al.*<sup>[11]</sup> that the reorientation energy of water increases with increasing pH as a result of the positive shift of the pzfc, it seems to be unnatural that the HER/HOR rates of Pt surfaces slow down simultaneously with increasing pH, but they have different causes.



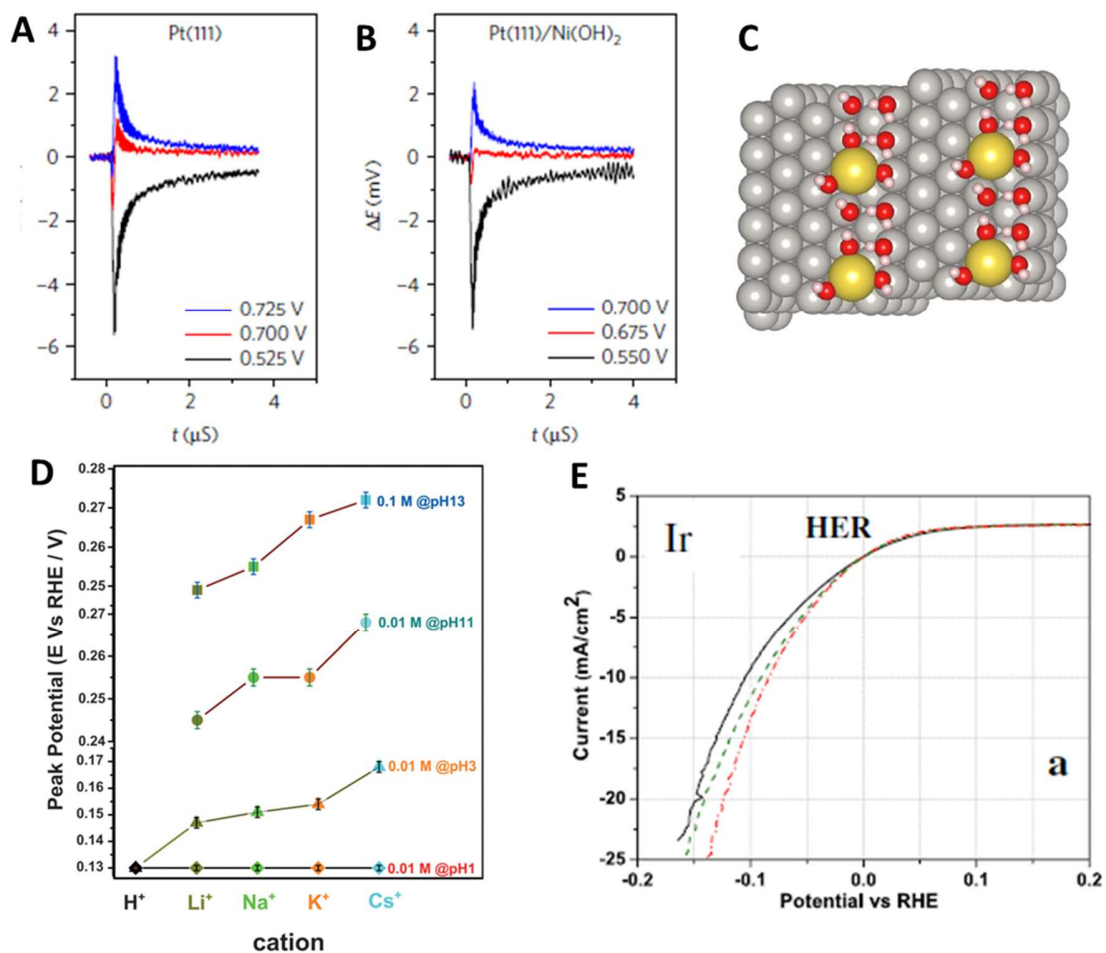


**Figure 3.** (A) HOR/HER polarization curves for Pt(111) (black) and Pt(111) modified with Ni(OH)<sub>2</sub>-coverage ~20% (dashed red and grey). (B) HOR polarization curves of Pt/C with 0, 3, 6, and 9 mL doped 5 mM RuCl<sub>3</sub> and Pt<sub>1</sub>Ru<sub>1</sub>/C collected in a H<sub>2</sub>-saturated 0.1M KOH electrolyte at a scan rate of 10 mV/s and a rotation rate of 2500 rpm at room temperature. (C). Schematic representation of the HOR on Ni(OH)<sub>2</sub>/Pt(111); Ni(OH)<sub>2</sub> provides the active sites for adsorption of reactive OH<sub>ad</sub>, and Pt provides the active sites for dissociative adsorption of H<sub>2</sub> and production of H<sub>ad</sub>, which then react with reactive OH<sub>ad</sub>. (D) Comparison between activities for the HER, expressed as overpotential required for a 5 mA/cm<sup>2</sup> current density, in 0.1M HClO<sub>4</sub> and 0.1M KOH for both bare metal surfaces and Ni(OH)<sub>2</sub>-modified surfaces. (E) Schematic illustration showing the hydrated OH<sup>-</sup> approaches the surface H<sub>ad</sub>. Part A and C are reproduced from reference [19]; Part A is reproduced from reference [21]; Part D is reproduced from reference [24], Part A is reproduced from reference [25].

Another issue of the bifunctional mechanism for the HOR is the lack of experimental evidence for the presence of OH<sub>ad</sub> within the HER/HOR potential region. This was recently addressed by the experimental finding that the surface Ru can host OH<sub>ad</sub> within the HER/HOR potential region.<sup>[21]</sup> Despite so, the catalytic roles of the Ru-hosted OH<sub>ad</sub> are not clear as pointed out by Gasteiger *et al.*<sup>[19]</sup> Alternatively, Yan *et al.*<sup>[26]</sup> stated that the surface Ru or Ni induced HER/HOR improvement may also be accounted for by the HBE theory since these oxophilic metals bind water more strongly than Pt, resulting in

weakened  $E_{M-H}$ . Unlike the bifunctional mechanism, the HBE theory requires only one cause for the sluggish HER/HOR kinetics in base.

**Pzfc theory.** Another theory that requires only one cause for the sluggish HER/HOR kinetics in alkaline is the pzfc theory recently proposed by Koper *et al.*<sup>[11]</sup> It states that the pzfc shifts positively with increasing pH. As a result, the HER/HOR potential is more negative to the pzfc, resulting in higher reorganization energy of water to transport  $\text{OH}^-$  throughout the interfacial double layer region, corresponding to a higher energetic barrier of the Volmer step (Eq. 3). On the basis of the pzfc theory, Koper *et al.*<sup>[11]</sup> ascribed the improved HER kinetics of the Pt(111) surface via  $\text{Ni}(\text{OH})_2$  deposition to the negative shift of the pzfc that is observed by the laser-induced temperature-jump experiment (Figure 4A).



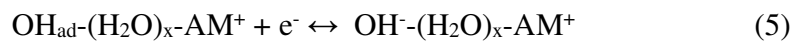
**Figure 4.** Laser-induced coulостatic potential transients collected for the Pt(111) electrode (A), and for the Pt(111) electrode decorated with Ni(OH)<sub>2</sub> (B). (C) Representative structure of the hydroxide and water covered step of Pt(553), in the presence of Na<sup>+</sup> (in a 3x1 unit cell). (D) Cation dependence of the (110)-step related voltammetric peak at various pH. 0.01M@pH3 means 0.01M cation concentration at pH 3. (E) Polarization curves for the HER on Ir in 0.1 M KOH and 0.1 M KOH containing 10<sup>-2</sup> M Li<sup>+</sup> and 10<sup>-4</sup> M Ba<sup>2+</sup>. Part A and B are reproduced from reference <sup>[11]</sup>; Part C and D are reproduced from reference <sup>[16]</sup>; Part E is reproduced from reference <sup>[27]</sup>.

Another merit of the pzfc theory is that it provides a natural explanation why the HER/HOR rates of Pt(111) and stepped Pt surfaces shift similarly with pH while their H<sub>UPD</sub> peaks shift differently. Unlike the HBE theory that ascribes the sharp H<sub>UPD</sub> peak of stepped Pt surfaces solely to the oxidative removal of H<sub>ad</sub>, Koper and Janik *et al.*<sup>[16, 17]</sup> argued that it originates from the replacement of H<sub>ad</sub> by OH<sub>ad</sub>. As a result, the peak

position is not only related to the binding energy to  $H_{ad}$ , but also to the  $OH_{ad}$ . They further found that the  $AM^+$  can adsorb onto the stepped Pt surface and weaken the Pt- $OH_{ad}$  bond, resulting in a positive shift of the  $H_{UPD}$  peak. As the pzfc shifts positively with increasing pH, the Pt surface is more negatively charged, which promotes the adsorption of the positively charged  $AM^+$ . Consequently, the concentration of adsorbed  $AM^+$  increases with increasing pH, hereby positively shifting the  $H_{UPD}$  peak.<sup>[16, 17]</sup> This cation effect on the  $H_{UPD}$  peak position is absent for the Pt(111) surface since it does not bind  $AM^+$  within the HER/HOR potential region. Therefore, the irregular Nernstian shift of the  $H_{UPD}$  peak of stepped Pt surfaces is caused by the adsorption of  $AM^+$ , whereas the regular Nernstian shift of the  $H_{UPD}$  peak of the Pt(111) surface is due to the absence of adsorbed  $AM^+$  cations. Koper *et al.*<sup>[16, 28]</sup> noticed that the  $H_{UPD}$  peak of both Pt(111) and stepped Pt surfaces shifts with pH the same way as the pzfc, which appears to suggest that the adsorbed  $AM^+$  shifts not only the  $H_{UPD}$  peak position, but also the pzfc like the surface  $Ni(OH)_2$ .<sup>[11]</sup> This implicates that the adsorbed  $AM^+$  cations also have profound effects on the HER/HOR rates of Pt surfaces via affecting pzfc. However, although the pzfc theory provides plausible explanations of the pH-dependent HER/HOR rates and the  $AM^+$  cation effects on the  $H_{UPD}$  peaks for both Pt(111) and stepped Pt surfaces, it appears to be insufficient when considering the  $AM^+$  cation effects on the HER/HOR kinetics of stepped Pt surfaces. Markovic *et al.*<sup>[27, 29]</sup> found that adding  $AM^+$  cations into the alkaline electrolyte improves the HER rates of the stepped Pt, Ir, and Ru surfaces, but not the HOR. This  $AM^+$ -induced selective HER enhancement cannot be explained by the  $AM^+$ -induced shift of the pzfc that affects the HER/HOR simultaneously. Most recently, the so-called 2B theory that combines the hard-soft acid-base (HSAB) theory<sup>[30]</sup> and the

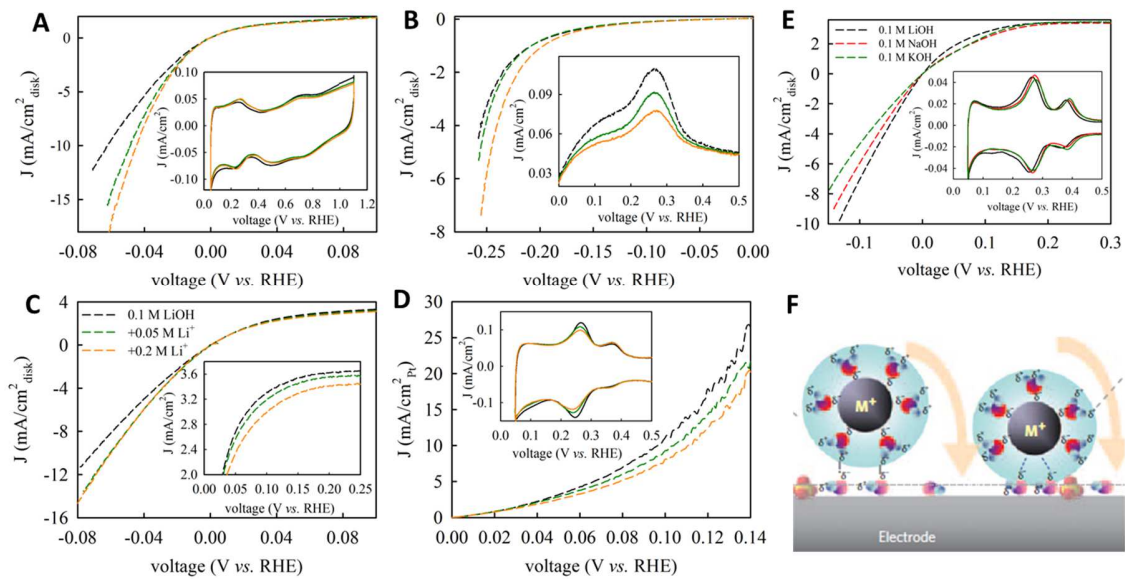
bifunctional mechanism was proposed by Jia *et al.*<sup>[12]</sup> to account for the AM<sup>+</sup> cation effects on the HER/HOR rates of Pt surfaces.

**2B Theory.** Jia *et al.*<sup>[12]</sup> found that increasing the concentration of AM<sup>+</sup> cations selectively promotes the HER of PtNi/C, Pt/C and Ni/C (Figure 5A-D), whereas changing the AM<sup>+</sup> identity affects both HER and HOR of Pt surfaces (Figure 5E). In addition, increasing the AM<sup>+</sup> concentration lowers the HOR limiting current of Pt (Figure 5C, insets) and reduces the sharp H<sub>UPD</sub> peak intensity of stepped Pt surfaces (Figure 5C, insets). These observations were explained as the AM<sup>+</sup> is anchored by the OH<sub>ad</sub> forming the OH<sub>ad</sub>-(H<sub>2</sub>O)<sub>x</sub>-AM<sup>+</sup> adduct as originally proposed by Markovic's group (Figure 5F),<sup>[18]</sup> rather than directly adsorbed onto the stepped Pt surfaces (Figure 4C). This argument is deduced from the reasoning that it is the OH<sub>ad</sub> rather than stepped Pt surfaces that triggers the catalytic roles of AM<sup>+</sup>, on the basis of the previous observations that the cation effects are absent on the HER/HOR kinetics of the Pt(111) surface at low potential region, but effective at elevated potentials when the surface is covered by OH<sub>ad</sub>,<sup>[31]</sup> or on the HER/HOR of Ni(OH)<sub>2</sub>/Pt(111) with Ni-induced OH<sub>ad</sub> on surfaces,<sup>[10, 29]</sup> By incorporating the concept of OH<sub>ad</sub>-(H<sub>2</sub>O)<sub>x</sub>-AM<sup>+</sup>, the Volmer step is rewritten as:



According to the HSAB theory, the AM<sup>+</sup> is a Lewis hard acid and binds strongly with the Lewis hard base OH<sup>-</sup>, whereas it binds weakly with the Lewis soft base OH<sub>ad</sub> as it is nearly neutral. The unbalanced binding energy on the two sides of Eq. 5 drives the OH<sub>ad</sub> desorption into the bulk electrolyte forming OH<sup>-</sup>, thereby boosting the Volmer step in one

direction only. Therefore, the  $\text{OH}_{\text{ad}}\text{-(H}_2\text{O)}_x\text{-AM}^+$  improves the HER but not the HOR, matching the  $\text{AM}^+$ -induced selective HER enhancement of Pt/C and  $\text{Pt}_1\text{Ni}_1/\text{C}$ . The HSAB theory can also account for the HER trend with changing  $\text{AM}^+$  identity (Figure 5E). As the Lewis acid hardness decreases in the sequence of  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ , the interaction energy between  $\text{OH}_{\text{ad}}$  and  $(\text{H}_2\text{O)}_x\text{AM}^+$  increases, whereas the interaction energy between  $\text{OH}^-$  and  $(\text{H}_2\text{O)}_x\text{AM}^+$  decrease, resulting in the reduced energy difference between  $\text{OH}^-$ - $(\text{H}_2\text{O)}_x\text{-AM}^+$  and  $\text{OH}_{\text{ad}}\text{-(H}_2\text{O)}_x\text{-AM}^+$  in the order of  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ . Thus, the driving force for the  $\text{OH}_{\text{ad}}$  desorption weakens in the order of  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ , matching the HER trend of  $\text{LiOH} > \text{NaOH} > \text{KOH}$ .



**Figure 5.** The HER/HOR polarization curves of (A)  $\text{Pt}_1\text{Ni}_1/\text{C}$ , (B)  $\text{Ni}/\text{C}$ , and (C)  $\text{Pt}/\text{C}$  collected in  $\text{H}_2$ -saturated 0.1 M LiOH with varying concentration of  $\text{LiClO}_4$ . (D) The HOR kinetic currents normalized by the  $\text{H}_{\text{UPD}}$  area of  $\text{Pt}/\text{C}$ . The insets in (A, B, and D) present the CV curves of  $\text{Pt}_1\text{Ni}_1/\text{C}$ ,  $\text{Ni}/\text{C}$ , and  $\text{Pt}/\text{C}$ , respectively, and in (C) presents the limiting currents of the HOR of  $\text{Pt}/\text{C}$ . (E) The HER/HOR polarization curves of the Pt polycrystalline electrode in  $\text{H}_2$ -saturated 0.1 M LiOH, NaOH, and KOH. The inset presents the CV curves. (F) Models for non-covalent interactions between hydrated alkali metal cations and adsorbed OH:  $(\text{H}_2\text{O})_{x-1}\text{M}^+\dots\text{H}_2\text{O}\dots\text{OH}_{\text{ad}}$  clusters, which correspond to hydrogen bonding between hydrated water and two  $\text{OH}_{\text{ad}}$  species; or  $\text{OH}_{\text{ad}}\dots\text{M}^+(\text{H}_2\text{O})_x$  clusters, which correspond to direct ion-dipole interactions between the cation and two  $\text{OH}_{\text{ad}}$  species. Part A-E are reproduced from reference [12]; Part F are reproduced from reference [18].

The promotional role of the  $\text{OH}_{\text{ad}}\text{-(H}_2\text{O)}_x\text{-AM}^+$  towards the HER in base implicates that the HER can be improved by enriching the abundance of  $\text{OH}_{\text{ad}}\text{-(H}_2\text{O)}_x\text{-AM}^+$ , which can be achieved by increasing the concentration of  $\text{AM}^+$ , as well as the abundance of  $\text{OH}_{\text{ad}}$ . This provides a plausible explanation of the well-known phenomenon that the HER of Pt can be significantly improved by enriching the interfacial sites between the Pt and oxides.<sup>[32]</sup>

Meanwhile, the cation effects on the alkaline HOR kinetics can be explained by the bifunctional mechanism based on the argument that the  $\text{AM}^+$  in the  $\text{OH}_{\text{ad}}\text{-(H}_2\text{O)}_x\text{-AM}^+$  adduct weakens the Pt- $\text{OH}_{\text{ad}}$  bond, in coordination with the pzfc theory. Increasing the  $\text{AM}^+$  concentration reduces the HOR kinetics of Pt surfaces, but not on surfaces with high oxophilicity such as Ni, Ru, and Ir<sup>[27]</sup> binding  $\text{OH}_{\text{ad}}$  overly strong. In addition, the slower HOR kinetics in NaOH/KOH compared to in LiOH (Figure 5E) can be related to the weaker Pt- $\text{OH}_{\text{ad}}$  bond. This argument can be further supported by the results of the CO oxidation that is also governed by the bifunctional mechanism.

If combining the 2B theory and the bifunctional mechanism, the cation effects appear to play key roles on the kinetics of alkaline HER/HOR by affecting the  $\text{OH}^-$  transportation throughout the double layer region. The presence of  $\text{AM}^+$  negative shifts the pzfc so as to cause the pH-dependence of the HER/HOR rates. In the meanwhile, it helps to remove  $\text{OH}_{\text{ad}}$  thus promotes the HER, whereas the weakened  $\text{OH}_{\text{ad}}$  bond may slow down the HOR.

### **Concluding remarks**

It seems like each of the four thoughts focuses on specific parts of the big picture of the alkaline HER/HOR electrochemistry. The HBE theory centers solely on the inherent properties of the catalytic surfaces. The bifunctional mechanism further considers the interactions between the intermediate adsorbates ( $H_{ad}$  and  $OH_{ad}$ ) on surfaces. The pzfc theory additionally considers the interfacial double layer environment and the transportation of reaction intermediates ( $OH_{ad}$ ). The 2B theory incorporates the profound cation effects into the picture of the interfacial double layer environment. The HBE theory is valid predicting the volcano trend of the HER/HOR activity of the elements grouped into three regions: those bind H and O too weak such as Au; those bind H and O too strong such as Ni, and those have nearly optimized binding energy toward H and O such as Pt. As for the latest case, the transportation of  $OH_{ad}$  throughout the double layer region appears to be the limiting factor for the HER/HOR in base.

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### **Conflict of Interest**

The authors declare no conflict of interest.

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Papers of particular interest, published within the period of review, have been highlighted as:

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