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Co-adsorption of cations causes the apparent pH dependence of hydrogen adsorption on a stepped platinum single-crystal electrode

Xiaoting Chen^{[a],+}, Dr. Ian T. McCrum^{[b],+}, Dr. Kathleen A. Schwarz^[c], Prof. Dr. Michael J. Janik^[b], and Prof. Dr. Marc T.M. Koper^[a]

^[a]Leiden Institute of Chemistry, Leiden University PO Box 9502, 2300 RA, Leiden, The Netherlands ^[b]Department of Chemical Engineering, The Pennsylvania State University, 51 Greenberg Complex, University Park, Pennsylvania 16802, United States ^[c]National Institute of Standards and Technology, Material Measurement Laboratory, 100 Bureau Dr., Gaithersburg, Maryland 20899, United States

Abstract

The successful deployment of advanced energy-conversion systems depends critically on our understanding of the fundamental interactions of the key adsorbed intermediates (hydrogen *H and hydroxyl *OH) at electrified metal-aqueous electrolyte interfaces. Herein, the effect of alkali metal cations (Li⁺, Na⁺, K⁺ and Cs⁺) on the non-Nernstian pH shift of the step-related voltammetric peak of the Pt(553) electrode is investigated over a wide pH window (1 to 13) by means of experimental and computational methods. Our results show that the co-adsorbed alkali cations along the step weaken the OH adsorption at the step sites, causing a positive shift of the potential of the step-related peak on Pt(553). Density functional theory calculations explain our observations on the identity and concentration of alkali cations on the non-Nernstian pH shift, and demonstrate that cation-hydroxyl co-adsorption causes the apparent pH dependence of “hydrogen” adsorption in the step sites of platinum electrodes.

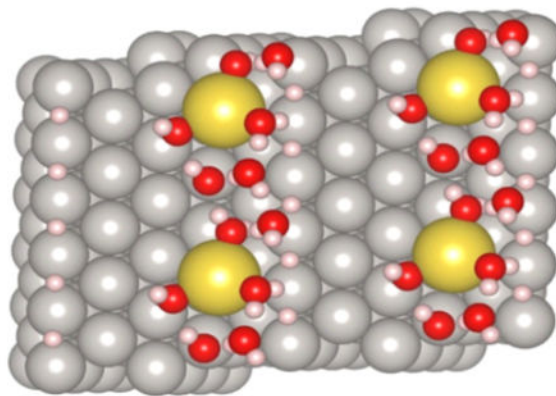
Graphical Abstract

Combination of experimental and computational work shows that the apparent pH dependence of hydrogen adsorption in step and defect sites of platinum electrodes is due to the co-adsorption of cations with hydroxyl. A model for this effect, of key importance for interpreting the electrocatalytic activity of platinum, is outlined.

Correspondence to: Marc T.M. Koper.

⁺These authors contributed equally

Supporting information for this article is given via a link at the end of the document.



Keywords

step-related hydrogen adsorption; stepped platinum single crystal; cation co-adsorption; pH dependence; Non-Nernstian potential shift

Platinum is the most frequently used catalyst material in electrocatalysis, especially for fuel cells and electrolyzers. Characterizing the adsorption of hydrogen (*H) and hydroxyl (*OH) on the platinum surface under electrochemical conditions is of key importance for understanding hydrogen evolution, hydrogen oxidation, oxygen reduction, and the oxidation of carbon monoxide and small organic molecules^[1–3]. An unsolved puzzle in the electrochemistry of platinum is the anomalous non-Nernstian shift with pH of the voltammetric peak associated with the adsorption of hydrogen on step and defect sites. The pH dependence of this peak has been interpreted as a pH-dependent binding energy of H to step sites, and has been correlated with the pH-dependent hydrogen evolution activity of platinum^[4]. However, in previous work, our groups have suggested that the step-related H adsorption/desorption voltammetric peak instead involves the replacement of *H by *OH^[5], and have interpreted its non-Nernstian pH dependence as due to either a residual non-integer charge on adsorbed water^[6] or to the co-adsorption of electrolyte cations with adsorbed OH in the step^[7]. In a desire to solve this important puzzle, we present a combined experimental and computational study showing how the step-related H adsorption peak of a Pt(553) electrode depends on pH, electrolyte cation, and electrolyte ionic strength. The Pt(553) is a model surface consisting of five-atom wide terraces of (111) orientation and steps of (110) orientation, and was chosen as representative of all surfaces with (110) step sites. Our results provide strong evidence for co-adsorption of cations and *OH at step sites of a platinum electrode, and allow for the formulation of a comprehensive model of the apparent non-Nernstian pH dependence of the step-related voltammetric peak over a wide pH window.

We will first describe the key experimental findings. Figure 1a shows cyclic voltammograms for the Pt(553) electrode in 0.1 M HClO₄ (pH=1), 0.01 M HClO₄ (pH=2) and 0.001 M HClO₄ (pH=3) electrolytes. The voltammogram of the Pt(553) electrode in HClO₄ shows three main features: a broad H adsorption-desorption feature on the (111) terrace ($0.05 < E < 0.35 \text{ V}_{\text{RHE}}$), a step-related voltammetric peak involving the replacement of H by OH ($E=0.13 \text{ V}_{\text{RHE}}$) and an adsorption-desorption peak for OH adsorbed on (111) terraces

($0.60 < E < 0.85 V_{\text{RHE}}$). Strikingly, there is no pH or ionic strength effect on the step-related voltammetric peak. An ionic strength effect would be expected if the adsorbates on the step carry a residual charge^[6]. There is either a slight pH or an anion (ClO_4^-) effect on the OH adsorption-desorption feature on terraces, which may be due to the interaction of perchlorate with the OH adlayer^[8]. Figure 1b shows the voltammetric profiles of the Pt(553) electrode recorded in 0.1 M HClO_4 (pH=1) electrolytes containing 0.01 M Li^+ , Na^+ , K^+ and 0.001 M Cs^+ , respectively. The step-related voltammetric peak is unaffected by the nature of the cation at this pH. Note that in Figure 1a we cannot change pH without changing also the ionic strength if we do not want to add other cations. Still, based on the combined results in Figures 1a and b we can state with good certainty that between pH 1 and 3 there is no effect of pH and ionic strength, and that at pH=1, there is no cation effect (given that there is no effect of ionic strength). Voltammograms and peak potentials are typically reproducible and reversible. In the absence of cations, the error is less than 1 mV. In the presence of cations, we estimate the error in the peak potentials as approximately 2 to 3 mV, based on three independent measurements. Values for the peak potentials are given in Table S1 in the Supporting Information.

Figure 2 shows that the effect of the four cations on the step-related voltammetric peak of the Pt(553) electrode becomes apparent when voltammograms are recorded in pH=3, 0.001 M HClO_4 , with different amounts of alkali perchlorate salts. For clarity, we show only the step-related voltammetric peak in Figure 2; the voltammograms of the Pt(553) electrode in the whole potential window ($0.0 V_{\text{RHE}}$ to $1.0 V_{\text{RHE}}$) are shown in Figure S1. Figure 2 shows that with increasing concentration of alkali metal cation, the step-related voltammetric peak is shifted to more positive potential in comparison with the peak potential in HClO_4 ($0.130 V_{\text{RHE}}$). The shift is more pronounced for larger cations: for 0.01 M Li^+ (Fig. 2a), Na^+ (Fig. 2b), K^+ (Fig. 2c) and 0.01 M Cs^+ (Fig. 2d) containing electrolytes, the step-related voltammetric peak is shifted to $0.147 V_{\text{RHE}}$, $0.151 V_{\text{RHE}}$, $0.154 V_{\text{RHE}}$ and $0.168 V_{\text{RHE}}$, respectively (see also Fig. 3). All values in Fig. 3. were derived from the step-related voltammetric peak potentials during the forward scan and are summarized in Table S1.

In order to confirm that this peak shift is caused by the alkali cation and not related to the anion, similar experiments were performed in 0.0005 M H_2SO_4 (pH=3). Figure S2 in the Supporting Information shows that the step-related voltammetric peak in the SO_4^{2-} containing electrolytes follows the identical trend as in the presence of ClO_4^- , confirming that the shift of the step-related voltammetric peak at $0.130 V_{\text{RHE}}$ is a result of the presence of co-adsorbed cations. The step-related voltammetric peak involves the replacement of H by OH and this adsorbate replacement reaction is driven to more positive potentials by the presence of alkali cations, implying that alkali cations destabilize the formation of OH at the steps^[7b].

Figure 4 illustrates the cation dependence of the step-related voltammetric peak in alkaline electrolytes of pH=11 (Fig. 4a–c) and 13 (Fig. 4d). In alkaline electrolytes, the peak potential moves to more positive potential (on the RHE scale) than in acidic media^[5] (see also Fig. 3). Figure 4a–c were obtained by adding different amounts of Li^+ , K^+ and Cs^+ perchlorate to 0.001 M NaOH. Fig. 4a shows that in the presence of Li^+ the step-related voltammetric peak is shifted negatively to $0.245 V_{\text{RHE}}$ compared to pure NaOH (0.255

V_{RHE}). The effects of Na^+ and K^+ on the step-related voltammetric peak are quite similar and therefore adding K^+ to NaOH does not lead to a significant shift. Figure 4c shows that in the presence of Cs^+ the step-related voltammetric peak is shifted positively (to $0.268 V_{\text{RHE}}$) compared to 0.001 M NaOH .

Figure 4d compares the voltammograms of the Pt(553) electrode observed in different alkali electrolytes at pH 13. The corresponding values for the step-related voltammetric peak potential obtained in 0.1 M solutions of LiOH , NaOH , KOH and CsOH are $0.249 V_{\text{RHE}}$, $0.255 V_{\text{RHE}}$, $0.267 V_{\text{RHE}}$ and $0.272 V_{\text{RHE}}$, respectively (see Fig. 3). The trend with the size of the cation is the same as in acidic media, the presence of Li^+ having a less destabilizing effect on the formation of OH in the step than Cs^+ . Given the problematic cleanliness of CsOH at 0.1 M , the shape of the step-related H peak may indicate contributions from contamination. The voltammograms of the Pt(553) electrode in the whole potential window ($0.0 V_{\text{RHE}}$ to $1.0 V_{\text{RHE}}$) are available in Figure S3.

To better understand the apparent pH effect, the co-adsorption of the alkali metal cations with hydrogen (*H) and hydroxyl (*OH) along the step of Pt(553) was evaluated using density functional theory (DFT). The DFT calculations followed the methodology outlined previously^[7b], with further details given in the Supporting Information. The environment near the step edge was simulated using both a low adsorbed cation coverage ($1/6$ monolayer, ML), which is favorable at a low electrolyte pH, and a high cation coverage ($1/3$ ML), favorable at a high electrolyte pH. For the same potential on an RHE scale, alkali cation adsorption becomes more favorable with increasing pH. This is because alkali cation adsorption thermodynamics, when considered independently, are not pH dependent, whereas the hydrogen electrode potential shifts to more negative values on the NHE scale at high pH.

Figure 5 gives the DFT calculated step-related voltammetric peak potential plotted against the experimentally measured potential from the voltammograms measured at low pH (pH = 3, 0.01 M cations) and at high pH (pH = 13, 0.1 M cations). This calculated peak potential represents the potential to desorb (adsorb) hydrogen at 1 monolayer (ML, defined per step atom) and adsorb (desorb) hydroxide. Both the hydrogen and hydroxide covered step are solvated with explicit water molecules (structures shown in Figures S4 and S5), and the potential is calculated in both the presence and absence of a co-adsorbed Li, Na, K, or Cs cation along the step. Figure S6 more clearly highlights the effect of cation coverage on the step associated peak potential. Figure S7 shows the adsorption potential of Na^* as a function of coverage along the step of Pt(553).

The presence of the alkali metal cation adsorbed near the step weakens low coverage hydroxide adsorption, shifting the step associated peak to more positive potentials, as we have shown previously^[7b]. Figure 5 illustrates that density functional theory can be used to additionally capture the differences in the shift of the step associated peak with cation identity and with increasing electrolyte pH. Additionally, the co-adsorbed alkali cation shows a smaller weakening effect on high coverage ($1/3$ ML) hydroxide adsorption (Figure S6), such that in a high pH electrolyte, hydroxide adsorption at $1/3$ ML is more favorable than at $1/6$ ML. In our prior work^[7b], the weakening effect of co-adsorbed Na^* on low coverage hydroxide adsorption was explained by the adsorbed cation retaining some positive

charge and disrupting the strong hydrogen bonding between adsorbed hydroxide and adsorbed water and lengthening the bond between adsorbed water and the Pt surface. We find the trend in the effect of the cation identity on hydroxide adsorption is correlated with the retained charge on the adsorbed cation (which is proportional to the surface-normal dipole moment generated on cation adsorption), where Li retains the least positive charge, and weakens hydroxide adsorption the least, and Cs retains the most positive charge, and weakens hydroxide adsorption the most.

While the absolute magnitude of the step-associated peak potential calculated by density functional theory is dependent on the explicit water solvation structure, the effect of the cation and trend between the cations is relatively independent of water structure (Figure S8). Further, the effect of the adsorbed cation in weakening hydroxide adsorption remains the same when implicit solvation is considered (Figure S9), though the magnitude of the effect is reduced.

These combined experimental and computational results support that the apparent effect of pH is an effect of the presence of an alkali metal cation co-adsorbed along the step, weakening hydroxide adsorption. The approximate potential of zero (free) charge of a stepped Pt surface at pH=1 suggests that alkali metal cations would not be specifically adsorbed in the H/OH adsorption region at low pH. The PZC of the stepped surface is estimated to be 0.2 to 0.3 V more negative than the 0.3 V_{RHE} value of Pt(111) at a pH=1^[9], i.e. at ca. 0.0 to 0.1 V_{RHE} . As a result, there are no apparent pH or cation effects at this pH (Figure 1). As the electrolyte pH is increased, hydrogen and hydroxide adsorption shift to lower absolute potentials (or equivalently the potential of zero charge shifts to more positive potentials on the RHE scale) into the region where alkali metal cation specific adsorption along the Pt step is favorable. The step associated peak now exhibits a non-Nernstian shift, illustrating an apparent pH effect as well as an effect of alkali cation identity and concentration (Figure 2). These effects are due to the adsorption of the alkali metal cation along the step at low coverage, and its weakening of hydroxyl adsorption. As the pH is further increased, the peak shifts further into the region where cation adsorption is more favorable, leading to an increased coverage of alkali metal cation adsorbed along the step. This causes a greater weakening of hydroxide adsorption, yielding a greater shift in the step-associated peak (Figure 3). Additionally, increasing the cation concentration at low pH, which makes higher coverage alkali metal cation adsorption more favorable, causes a greater shift in the step associated peak (Figure 2).

The results presented above are independent of step orientation and step density, as we will elaborate in a separate publication. While the involvement of cation adsorption in what is traditionally known as the “hydrogen region” of platinum electrodes has been inferred before from experimental results^[10] and DFT^[7], our combined results here provide the clearest evidence to date that cation-hydroxyl co-adsorption in the step sites is responsible for the apparent pH dependence of the step-related “hydrogen peaks”. This implies that the “hydrogen region” identified for the pristine Pt(111) surface^[11] is rather a “hydrogen-hydroxyl-cation” region for a polycrystalline platinum electrode.

As mentioned in the Introduction, the hydrogen evolution/hydrogen oxidation reaction (HER/HOR) rate has also been observed to depend on pH, in a way that has been correlated with the pH dependence of the step peak^[4]. However, HER/HOR shows the same pH dependence on a step-free Pt(111) electrode, so that there cannot be a chemical relation between these two observations, at least not for Pt(111)^[12]. Still, the cation may block or inhibit active sites^[13], alter the structure of near-surface water, or adsorbed hydroxyl (*OH) may be involved in the hydrogen oxidation/evolution and other electrocatalytic reaction mechanisms as the cation alters its structure and stability. The alkali metal cation identity has also been shown to effect the activity of CO oxidation on Pt electrodes^[10a]; while understanding the mechanism of this effect requires further study, we find here that the trend in hydroxide adsorption strength matches the trend in CO oxidation activity, with stronger adsorption giving higher activity. Our results will help in the interpretation of further studies on cation effects on electrocatalytic reactions on platinum.

Experimental and Computational Methods

Cyclic voltammetry measurements in this study were performed following the procedures as outlined previously^[10a]. The density functional theory simulations and calculation of adsorption potentials were performed following the procedures outlined previously^[7]. Further detailed information on experimental and computational procedures can be found in the Supporting Information.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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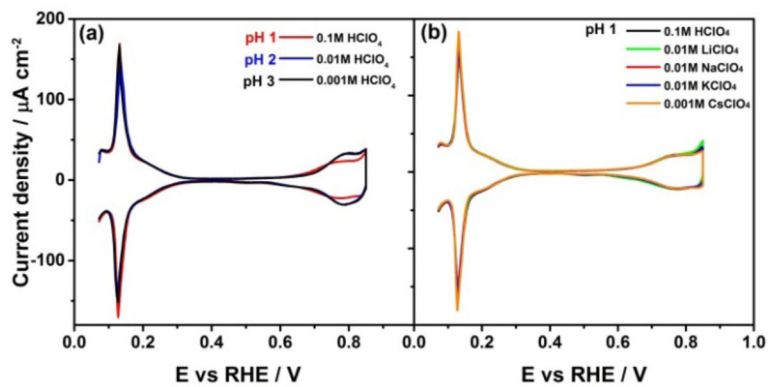


Figure 1. Cyclic voltammogram of Pt(553) recorded in (a) 0.1 M¹ HClO₄ (pH=1), 0.01 M HClO₄ (pH=2) and 0.001 M HClO₄ (pH=3) solutions and (b) 0.1 M HClO₄ (pH=1) solution without and with MeClO₄, where Me is Li, Na, K, or Cs, as indicated. Scan rate: 50 mV s⁻¹.

¹M has been used to represent the SI unit mol/L to conform with the requirements of the journal

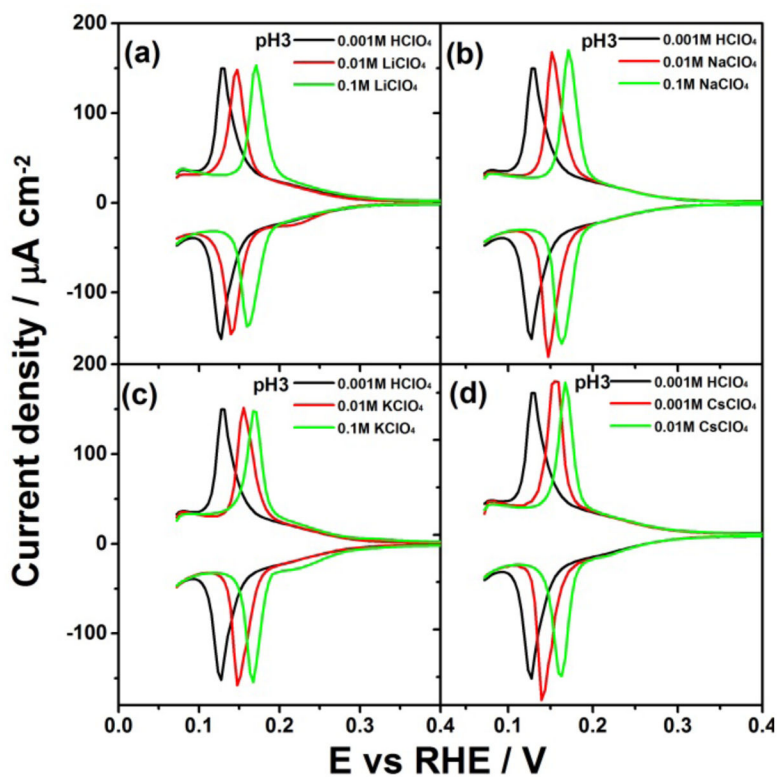


Figure 2.

Cyclic voltammograms of Pt(553) recorded in 0.001 M HClO₄ (pH=3) with (a) 0.01 M and 0.1 M LiClO₄, (b) 0.01 M and 0.1 M NaClO₄, (c) 0.01 M and 0.1 M KClO₄ and (d) 0.001 M and 0.01 M CsClO₄. The blank voltammogram for the Pt(553) recorded in 0.001 M HClO₄ (black line) is shown for comparison. Scan rate: 50 mV s⁻¹.

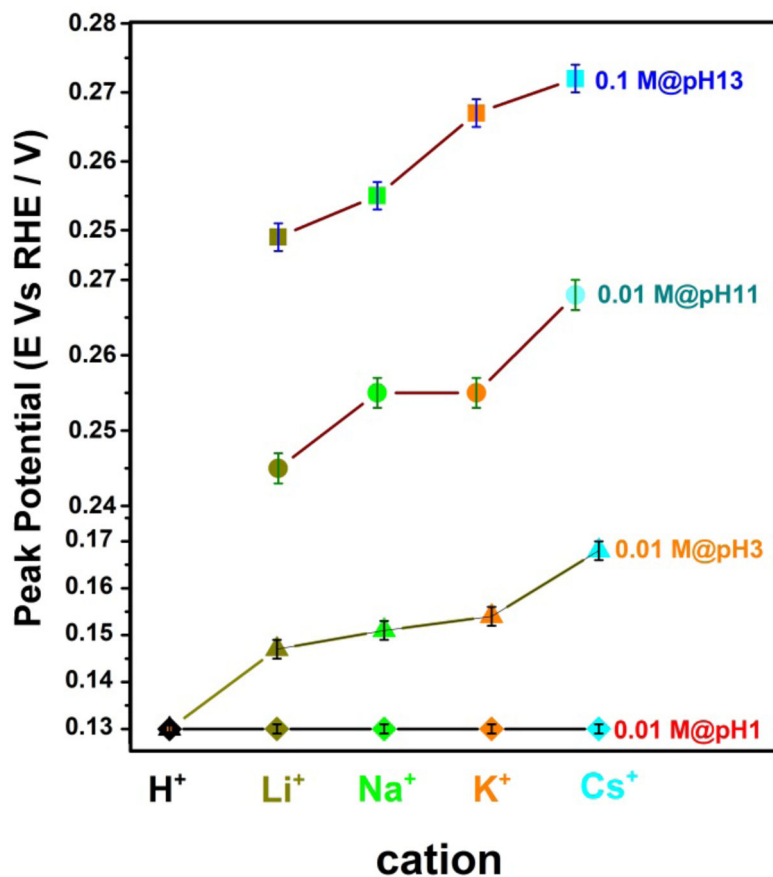


Figure 3. Cation dependence of the (110)-step related voltammetric peak at various pH. 0.01M@pH3 means 0.01 M cation concentration at pH=3. Peak potential determined in the positive-going scan. Error bars determined as discussed in the Supporting Information.

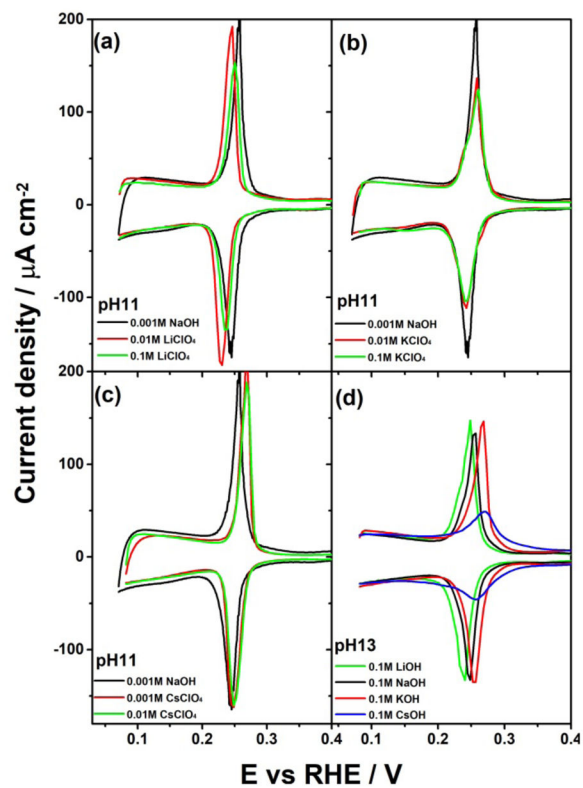


Figure 4.

Cyclic voltammograms of Pt(553) recorded at pH 11 (0.001 M NaOH) with (a) 0.01 M and 0.1 M LiClO₄, (b) 0.01 M and 0.1 M KClO₄, (c) 0.001 M and 0.01 M CsClO₄ and (d) at pH 13 in 0.1 M MeOH, where Me is Li, Na, K, or Cs, as indicated. Scan rate: 50 mV s⁻¹.

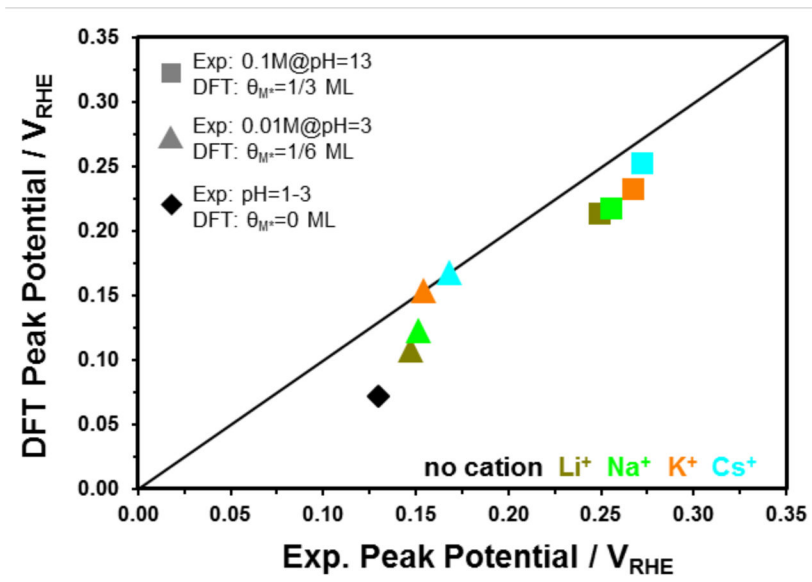


Figure 5. DFT calculated step-associated peak potential plotted against the experimentally measured peak potential. The triangular points correspond to potentials measured in a pH = 3 electrolyte with a cation concentration of 0.01 M and a simulated cation coverage of 1/6 ML. Square points correspond to potentials measured in a pH = 13 electrolyte with a cation concentration of 0.1 M and a simulated cation coverage of 1/3 ML. The black diamond represents the peak potential measured in acid (free from alkali metal cation). The black line gives $y=x$. A linear regression of the data gives a slope of 1.00, intercept of -0.03 , and an R^2 of 0.91.