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COMMUNICATION

Energy-entropy competition in cation-hydroxyl interactions at the liquid water-Pt(111) interface

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Electrochemical reaction rates are sensitive to interactions between electrolyte cations and adsorbed reaction intermediates, e.g., cation-*OH interactions in the oxygen reduction reaction on platinum. Here, we calculate the free energy interaction between adsorbed *OH and K⁺/Li⁺ situated at the liquid water-Pt(111) interface using ab initio molecular dynamics (AIMD) and metadynamics. Li⁺ stabilizes *OH by 0.1±0.1 eV and K⁺ destabilizes *OH by 0.1±0.1 eV, in qualitative agreement with experimental cyclic voltammogram (CV) measurements. In contrast, the internal energy of *OH is stabilized by 0.3 eV and 0.4 eV for Li⁺ and K⁺, respectively. This demonstrates, that entropy significantly destabilizes cation-*OH interactions and is vital in order to understand even the relative influence of cations at interfaces.

The presence of cations in the electrolyte can have significant impact on electrochemical reaction rates, if the cations interact with reaction intermediates on the electrode surfaces.^[1–3] Cations with large charge densities such as Li⁺ and Ba²⁺ stabilize *OH groups on Pt(111) compared to K⁺ and increase the over-potential for the oxygen reduction reaction.^{4,5} Under alkaline conditions, the *OH stabilization is visible in the CV as a modification of the current envelope associated with *OH formation (see reference 5–7 for details). In 0.1 M LiOH, the current from *OH formation reaches a maximum value at an electrostatic potential of ~0.1 V lower than in KOH and CsOH. The shift to lower electrostatic potential indicates a free energy stabilization of adsorbed *OH species by Li⁺ ions.^{8–11}

We obtain the free energy stabilization of adsorbed *OH due to Li⁺ or K⁺ situated at the liquid water-Pt(111) interface by modeling a liquid water film on Pt(111). The *OH

stabilization is taken as the difference in the free energy cost of moving the Li⁺/K⁺ cation from the liquid water-Pt(111) interface into the liquid water film with and without one *OH species on the surface. The free energy cost of moving Li⁺ into the water film is increased by 0.1±0.1 eV when *OH is present on the surface, i.e. Li⁺ stabilizes *OH by 0.1±0.1 eV. In contrast, K⁺ destabilizes *OH by 0.1±0.1 eV. We also conduct regular AIMD simulations and find that having K⁺/Li⁺ at the interface rather than in the water film stabilizes the *OH internal energy by 0.3 eV for Li⁺ and 0.4 eV for K⁺. The discrepancy between changes in free energy and changes in internal energy points to significant entropy losses when *OH interacts with K⁺/Li⁺ situated at the interface.

The water-Pt(111) interfaces are set up in the ASE program¹² and modeled as (32-*n*_{OH})H₂O molecules on top of a 3 × 4 orthogonal Pt(111) surface with a thickness of four atomic layers (*n*_{OH} is the number of adsorbed *OH, i.e 0 or 1). The interfaces are studied by constant temperature AIMD simulations performed in VASP,^{13–16} where a Nose thermostat¹⁷ keeps the temperature around 350 K. The AIMD simulations utilize density functional theory (DFT) calculations with 350 eV plane-wave energy cut-off and PBE¹⁸ with the D3¹⁹ van der Waals correction to approximate exchange-correlation effects (computational details are identical to those used in ref ¹¹). Furthermore, metadynamics^{20–23} is used in combination with AIMD to obtain Li⁺/K⁺ adsorption-solvation free energy profiles and the interactions between Li⁺/K⁺ and adsorbed *OH. The height (*z*) of Li⁺/K⁺ above the surface is the only reaction coordinate included in the metadynamics and the bottom Pt layer is fixed in bulk positions, so the height is well-defined. Additional computational details for AIMD, DFT, and metadynamics are included in ESI. For clarity, we note that the stabilization (or destabilization) of the system due to cation-*OH interactions can be interpreted both as the cation stabilizing the *OH species and as the *OH species stabilizing the cation, but that these interpretations are physically equivalent.

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A Li atom is inserted at the water-Pt(111) interface (without *OH), where it ionizes to Li^+ and an electron in the Pt slab.^{24,25} The Bader charge of Li^+ is +0.90 e . The metadynamics adsorption-solvation free energy profile ($\Delta G(z)$, Fig. 1a) shows that Li^+ prefers a position 4.2 Å above the surface. Fig. 1b shows a snapshot from the AIMD simulation with Li^+ situated at 4.2 Å. The Li^+ ion is less stable at distances closer to the surface and in the region between 5 and 8 Å (Fig. 1a). However, the Li^+ stability at 8.7 Å is equal to the stability at 4.2 Å, so there is no free energy cost of moving Li^+ from the water-Pt(111) interface to the liquid water film.

The adsorption-solvation free energy profile for Li^+ with one adsorbed *OH species is shown in Fig. 1c. Li^+ is now most stable at 4.4 Å above the surface (Fig. 1d). The free energy cost of moving Li^+ away from the *OH species and into the liquid water film is 0.1 eV, i.e. 0.1 eV more than without adsorbed *OH, which indicates that Li^+ stabilizes the free energy of *OH by 0.1 eV. Fig. 1 also includes free energy uncertainties. We estimate the uncertainty as $\sigma_{\Delta G(z)}/\sqrt{n}$, where $\sigma_{\Delta G(z)}$ is the standard deviation and n the number of times Li^+ moves between the interface and the liquid water film, which we take to represent the number of uncorrelated “measurements” of the free energy profile. With uncertainties, the Li^+ -*OH interaction stabilizes the free energy by 0.1 ± 0.1 eV.

In Fig. 1e, we have plotted the average DFT energy from the metadynamics trajectories with and without adsorbed *OH as a function of the Li^+ distance above the surface (height). This provides an approximation for the internal energy with Li^+ at different heights (although the metadynamics bias potential can introduce errors to the internal energy plots). The two resulting plots have minimum internal energies at ~ 4 Å. For Li^+ without adsorbed *OH, the internal energy profile resembles the free energy profile, but Li^+ is slightly more stable at the water-Pt(111) interface compared to what is observed in the free energy profile. For Li^+ with *OH, the internal energy of Li^+ at the water-Pt(111) interface is even more favorable compared to what is observed in the free energy profile. Finally, when comparing the difference in the two internal energy plots at 5 to 9 Å, one might expect a larger Li^+ -*OH free energy stabilization than 0.1 eV. The discrepancy is due to entropy, which mainly disfavor Li^+ close to *OH.

Fig. 1. Without adsorbed *OH; (a) Li^+ adsorption-solvation free energy profile as a function of height above the Pt(111) surface and (b) snapshot of Li^+ situated at 4.2 Å above the surface. The dashed line shows the maximum distance from the surface probed by metadynamics, i.e. Li^+ is prohibited from moving further from the surface (forbidden region). With adsorbed *OH; (c) Li^+ adsorption-solvation free energy profile and (d) snapshot of Li^+ situated at 4.4 Å. (e) Average DFT energy as a function of Li^+ height both with and without adsorbed *OH. (f) Species designation. The minimum free energy and internal energy is set to zero in all plots.

The adsorption-solvation free energy profile for K^+ (without *OH) is shown in Fig. 2a and has a broad free energy minimum around 5.6 Å above the surface. Fig. 2b shows a snapshot with K^+ situated at 5.6 Å. The K^+ ion can move to within 3.3 Å of the surface with a free energy cost of 0.1 eV, before a strong repulsion is observed (Fig. 2a). Meanwhile, the free energy cost of moving K^+ to a distance of 9.2 Å above the surface is 0.2 eV. The K^+ ion adsorbed at the interface is therefore stabilized by at least 0.2 eV compared to being solvated in the liquid water film. Note that K^+ (Fig. 2a) differs from Li^+ (Fig. 1a) in terms of the preferred height (5.6 Å vs. 4.2 Å) and free energy cost of moving to the liquid water film (0.2 eV vs. 0.0 ± 0.1 eV).

When *OH is adsorbed on the surface, the K^+ adsorption-solvation free energy profile changes substantially (Fig. 2c). The most stable height of K^+ is now much closer to the surface (3.5 Å, Fig. 2d), whereas the free energy cost of moving K^+ away from the water-Pt(111) interface is reduced to 0.1 ± 0.1 eV. In other words, K^+ destabilizes *OH by 0.1 ± 0.1 eV.

In Fig. 2e, the internal energy profiles are approximated by the average DFT energy as a function of K^+ height above the surface. The internal energy profiles indicate that the presence of K^+ stabilizes the internal energy of *OH substantially, as the energy cost of moving K^+ away from the interface is at least 0.2 eV larger with adsorbed *OH than without *OH. However, no

part of this stabilization is present in the free energy (Fig. 2c) and the K^+ -*OH interaction must therefore include a large entropy cost.

Fig. 2. Without adsorbed *OH; (a) K^+ adsorption-solvation free energy profile as a function of the height above the Pt(111) surface and (b) snapshot of K^+ situated at 5.6 Å above the surface. The dashed line shows the maximum distance from the surface probed by metadynamics, i.e. K^+ is prohibited from moving further from the surface (forbidden region). With adsorbed *OH; (c) K^+ adsorption-solvation free energy profile and (d) snapshot of K^+ situated at 3.5 Å. (e) Average DFT energy as a function of K^+ height both with and without adsorbed *OH. (f) Species designation. The minimum free energy and internal energy is set to zero in all plots.

The obtained *OH free energy stabilization in the presence of Li^+ compared to K^+ agrees qualitatively with the Li^+ -*OH stabilization in CV experiments.^{4–7} This is the case even though the modeled OH coverages, temperature, and cation concentrations deviate from experiments and the calculated free energy differences are not obtained at constant electrostatic potential.

To further understand the energy and entropy contributions to (alkali) cation-*OH interactions we performed regular AIMD simulations and obtained internal reaction energies for $H_2O(l) \rightarrow$

*OH + $\frac{1}{2}H_2(g)$ with Li^+/K^+ at the liquid water-Pt(111) interface and with Li^+/K^+ fixed at a height of 8.9 Å above the Pt(111) surface (Table 1) (calculational details in ESI). The *OH formation energy is affected by both the cation and the negative charge added to the Pt(111) surface when Li/K is introduced to the system. With $Li^+(aq)$ ($K^+(aq)$) situated in the liquid water film 8.9 Å above the surface, the internal energy cost of *OH formation is reduced from 0.87 eV without any cations¹¹ to 0.7 eV (0.7 eV). We assign this stabilization to the shift in surface charges, where *OH formation changes the Bader charge in the Pt(111) slab from $-0.16 e$ to $+0.26 e$ without alkali and from $\sim -0.65 e$ to $\sim -0.26 e$ with alkali. When Li^+ (K^+) is moved to the water-Pt(111) interface the energy cost is further reduced to 0.4 eV (0.3 eV). We assign this additional internal energy stabilization to the cation-*OH interactions. Despite the cation-*OH internal energy stabilization, there is no well-defined bond formation between the cation and *OH (see radial distribution functions in ESI). However, the Li^+/K^+ motion is strongly confined when situated at the interface together with adsorbed *OH, which likely explains the observed entropy cost (see cation x,y motion in ESI).

Table 1. Internal reaction energies (ΔE) for $H_2O(l) \rightarrow$ *OH + $\frac{1}{2}H_2(g)$ with (alkali) cations at the interface (int), cations in the liquid water film (aq) and without cations taken from ref¹¹ ('No alkali'). All atoms are free to move in the AIMD simulations for $Li^+(int) + e^-$, $K^+(int) + e^-$, and 'No alkali', whereas the bottom Pt layer is frozen and the cation is fixed at a height of 8.9 Å above the surface in $Li^+(aq) + e^-$ and $K^+(aq) + e^-$.

	$Li^+(aq) + e^-$	$Li^+(int) + e^-$	$K^+(aq) + e^-$	$K^+(int) + e^-$	No alkali ¹¹
ΔE	0.7 eV	0.4 eV	0.7 eV	0.3 eV	0.87 eV

The *OH free energy is stabilized by ~ 0.1 eV having Li^+ at the water-Pt(111) interface (Fig. 1), whereas the internal *OH formation energy differs by ~ 0.3 eV between $Li^+(aq)$ and $Li^+(int)$ (Table 1). We therefore deduce a ~ 0.2 eV entropy penalty ($-T\Delta S$ at $T = 350$ K) associated with the Li^+ -*OH interaction. Similarly, K^+ destabilizes the *OH free energy by ~ 0.1 eV (Fig. 2), while moving K^+ from the liquid water film to the water-Pt(111) interface stabilizes the *OH internal energy by ~ 0.4 eV (Table 1). Therefore, the entropy cost in the K^+ -*OH interaction is ~ 0.5 eV.

Our results indicate that the reason why Li^+ stabilizes the free energy of *OH, whereas K^+ does not, is because the Li^+ -*OH interaction has lower entropy penalty than the K^+ -*OH interaction. The entropy of aqueous K^+ is much larger than the entropy of aqueous Li^+ ($-TS^0 \sim -0.37$ eV and -0.05 eV at $T = 350$ K for $K^+(aq)$ and $Li^+(aq)$, respectively).²⁶ Assuming the entropy of the two ions are more similar when they are situated near the adsorbed *OH would explain the net stabilization from Li^+ compared to K^+ . A cation-*OH entropy cost also fits with experimental observations of Pt(111) CVs in 0.1 M $HClO_4$ and in 0.1 M $NaOH$ at different temperatures.²⁷ In $HClO_4$, the current envelope related to *OH formation shifts to lower electrostatic potential at higher temperatures, indicating that the reaction $H_2O(l) \rightarrow$ *OH + $H^+(aq) + e^-$ increases entropy (i.e. $-T\Delta S$

stabilizes the reaction free energy at higher temperatures). Oppositely, in 0.1 M NaOH, higher temperatures shift the current envelope maximum to higher electrostatic potentials, indicating that the presence of Na⁺ cations decreases the entropy associated with *OH formation.

Our results highlight the challenges and the complexity needed to model cation effects. Previous DFT calculations with static water found that the presence of potassium destabilizes the internal energy of adsorbed *OH.²⁸ Similarly, it has been found that the electric field from cations destabilize *OH species on Pt(111).^{1,29,30} These interactions change dramatically when the model explicitly includes both liquid water and cations such that the internal energy of *OH species is now stabilized by K⁺ and Li⁺. Furthermore, entropy changes negate this stabilization and free energy calculations are needed to fully describe the effect of Li⁺ and K⁺ ions on adsorbed *OH species.

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Conflicts of interest

There are no conflicts to declare.

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