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Supporting Information

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

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S1. Computational details

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S1.1 AIMD details. The interfaces are studied by constant temperature *ab initio* molecular dynamics (AIMD) simulations performed in VASP,^{1–4} where the temperature is kept at 350 K by a Nose thermostat.⁵ The motion of the atoms are treated classically and propagated with 1 fs timesteps. The mass of hydrogen atoms is set to 2 g/mol.

S1.2 Density functional theory details. The AIMD simulations utilize VASP¹⁻⁴ density functional theory (DFT) calculations with a 350 eV energy cutoff plane-wave basis, $2 \times 2 \times 1$ k-points, and spin-paired electron configuration (non spin polarized). Exchange-correlation effects are approximated by PBE⁶ and the D3¹⁷ van der Waals correction. The atomic regions are treated with the PAW formalism and one, three, six, nine and ten valence electrons are included for each H, Li, O, K, and Pt atom, respectively.

S1.3 Metadynamics details. Adsorption-solvation of Li⁺ or K⁺ at the water-Pt(111) interface is studied using the metadynamics formalism.^{8,9} The height of the ion above the surface is the only considered reaction coordinate and the bottom Pt layer is fixed in the bulk position such that the height is meaningful. The metadynamics approach adds a small repulsive Gaussian potential, at the location of the ion $\binom{j \cdot t_G}{Z_{LI/K}}$ every t_G time step in the AIMD simulation (eq S1). As the bias potential (W(z,t)) builds up, Li⁺ or K⁺ will move along the reaction coordinate, i.e. between the Pt(111) surface and the liquid water film.

$$W(z,t) = h \sum_{j=1}^{t/t_G} exp\left\{ \frac{(z_{Li/K}^{j+t_G} - z)^2}{2\omega^2} \right\} + c(t)$$
(S1)

We have used h = 0.001 eV, tG = 10 fs, and $\omega = 0.144$ Å and picked c(t) such that W(z,t) is zero at the height where Li⁺ or K⁺ is most stable at the water-Pt(111) interface. We set the energy to zero at the

interface, because we are interested in the energy cost of moving Li⁺/K⁺ to the liquid water film. Our Gaussian bias potential is applied faster than in ref¹⁰, but much slower than in ref¹¹ (The approach is more accurate when the bias potential is added slower). W(z,t) is the work required to move the ion along the reaction coordinate and, once the whole reaction path has been visited, -W(z,t) becomes in principle equal to the free energy change along the reaction path. However, in reality W(z,t) has some hysteresis and depends on the sampling time. We have therefore opted to calculate $\Delta G(z)$ as a time average of -W(z,t) (eq S2). The sampling of $\Delta G(z)$ is initiated after some initial time (t_i) allowing the ion to visit the whole reaction path.

$$\Delta G(z) = -\langle W(z,t) \rangle_{t > t_i} \tag{S2}$$

The standard deviation of $\Delta G(z)$ is a measure of hysteresis in W(z,t) and therefore a measure of the quality of the metadynamics simulation. Note that due to c(t), the minimum free energy at the water-Pt(111) interface is set to zero, and the standard deviation therefore vanishes for this minimum free energy.

S1.4 Calculating internal reaction energies. We also conducted normal AIMD simulations in order to calculate internal reaction energies. The internal energy $({}^{\langle E \rangle}_t)$ of a given system is calculated as the time average DFT energy (E_{DFT}) and time average kinetic energy (K) of the AIMD simulation (eq S3). The interface systems are sampled $(t-t_0)$ for at least 30 ps, after being equilibrated (t_0) for at least 1 ps. The equilibration time of each system is determined by monitoring when the internal energy stabilizes $(t_0 \text{ and } t-t_0 \text{ values are reported in Table S1, S2, S3, S4 and S5)}.$

$$\langle E \rangle_{t} = \frac{1}{t - t_{0}} \int_{t_{0}}^{t} E_{DFT}(t') + K(t')dt'$$
(S3)

The internal energies are used to calculate the energy cost (ΔE) of hydroxyl formation. The energy cost (ΔE) of forming n_{OH} hydroxyls at the interface is calculated as the internal energy of the interface with

 n_{OH} *OH species and (32- n_{OH}) H₂O molecules, plus the internal energy of $n_{\text{OH}}/2$ H₂ gas phase molecules, minus the internal energy of the K/Li + 32H₂O / Pt(111) reference system (eq S4). Similar to ref ¹², we add $3/2k_BT$ to the internal energy of gas-phase molecules, because their center-of-mass motions are not included in the MD simulations.

$$\Delta E = \left\langle E_{n_{OH} * OH + K/Li + (32 - n_{OH})H_2O/Pt(111)} \right\rangle_t + \frac{n_{OH}}{2} \left(\left\langle E_{H_2(g)} \right\rangle_t + \frac{3}{2} k_B T \right) - \left\langle E_{K/Li + 32H_2O/Pt(111)} \right\rangle_t$$
(S4)

Each interface system has been sampled by at least two independent AIMD simulations and the simulation with the most stable $\langle E \rangle_t$ is used to calculate reaction energies.

Bader charges^{13–15} and work functions have been calculated with increased vacuum (~29 Å instead of ~15 Å) and 450 eV energy cutoff. The reported values are averages of the Bader charges and work functions for atomic configurations taken at 0.5 ps intervals along the MD trajectories.

S2. Results and discussion

S2.1 Metadynamics reaction path sampling. Each metadynamics simulation is conducted as one continuous AIMD trajectory. Figure S1 and Figure S2 show the height of the Li⁺ ion and the K⁺ ion as a function of simulation time (both without and with adsorbed *OH). The sampling of $\Delta G(z)$ (eq S2) is initiated at the time (t_i) when the ion reaches the interface region for the second time.



Figure S1: Li⁺ reaction path sampling (height of Li⁺ above the Pt(111) surface versus time) (a) without *OH and (b) with *OH.



Figure S2: K⁺ reaction path sampling (height of K⁺ above the Pt(111) surface versus time) (a) without *OH and (b) with *OH. The trial period used h = 0.0015 eV.

S2.2 Reaction energies. For all conducted AIMD simulations we have tabulated energy cost (ΔE),

average Bader charge in the Pt(111) slab ($\langle Q[Pt_{48}] \rangle_t$), average Bader charge of the cation ($\langle Q[Li^+/K^+] \rangle_t$), , average work function ($\langle WF \rangle_t$), average number of hydrogen bonds ($\langle HB \rangle_t$), surface bound H₂O* coverage (θ_{H2O*}), the chosen thermalisation time (t_0), and the sampling time (t- t_0). The average Bader charges and $\langle WF \rangle_t$ are calculated from atomic configurations taken at 0.5 ps intervals along the AIMD trajectories. The number of hydrogen bonds at a given time is calculated by counting how many of the H atoms are situated between 1.25 Å to 2.40 Å from one of the O atoms.

For the different situations studied (Li⁺(int) + e^- , Li⁺(aq) + e^- , K⁺(int) + e^- , and K⁺(aq) + e^-), we have plotted the energy of the AIMD simulations with $n_{OH} = 0$ and the energy cost of *OH formation (eq S4) from the AIMD simulations with $n_{OH} = 1$. The plotted energies are cumulative averages and are more accurate at larger *t*-*t*₀. The most stable energy for $n_{OH} = 0$ after the full sampling time is used as the reference $({E_{K/Li} + 32H_2O/Pt(111)})$ and therefore set to 0 eV.

S2.2.1 *OH formation without alkali.

n _{OH}	ΔΕ	$\langle Q[Pt_{48}] \rangle_t$	-	$\langle WF \rangle_t$	$\langle HB \rangle_t$	$ heta_{ m H2O^*}$	t ₀	<i>t-t</i> ₀
0	0 eV	-0.16 e	-	4.3 eV	56.0	0.16 ML	22 ps	35 ps
1	0.87 eV	+0.26 e	-	4.5 eV	54.9	0.19 ML	20 ps	33 ps

Table S1: AIMD simulations with n_{OH} *OH at the pure water / Pt(111) interface (No alkali).¹⁶

S2.2.2 *OH formation with Li⁺ at the water-Pt(111) interface, i.e Li⁺(int) + e⁻.

n _{OH}	ΔΕ	$\langle Q[Pt_{48}] \rangle_t$	$\langle Q[Li^+]\rangle_t$	$\langle WF \rangle_t$	$\langle HB \rangle_t$	$ heta_{ m H2O^*}$	t ₀	<i>t-t</i> ₀
0 0	0 eV	-0.65 e	+0.90 <i>e</i>	4.3 eV	52.4	0.01 ML	1 ps	34 ps
	0.11 eV	-0.64 e	+0.90 <i>e</i>	4.7 eV	51.7	0.01 ML	27 ps	23 ps
1 1	0.40 eV	-0.26 <i>e</i>	+0.90 e	3.9 eV	53.3	0.08 ML	2 ps	35 ps
	0.41 eV	-0.24 <i>e</i>	+0.90 e	3.7 eV	53.4	0.08 ML	22 ps	34 ps

Table S2: AIMD simulations with n_{OH} *OH at the Li(int) + water / Pt(111) interface.



Figure S3: Energy cost of *OH formation (eq S4) at the Li(int) + water / Pt(111) interface, as a function of elapsed sampling time (t- t_0).

S2.2.3 *OH formation with Li⁺ situated 8.9 Å from the surface, i.e Li⁺(aq) + e^- .

n _{OH}	ΔΕ	$\langle Q[Pt_{48}] \rangle_t$	$\langle Q[Li^+]\rangle_t$	$\langle WF \rangle_t$	$\langle HB \rangle_t$	$ heta_{ m H2O^{*}}$	t ₀	<i>t-t</i> ₀
0	0 eV	-0.65 e	+0.91 <i>e</i>	4.2 eV	52.8	0.01 ML	9 ps	45 ps
	0.08 eV	-0.66 e	+0.90 <i>e</i>	4.2 eV	52.0	0.02 ML	9 ps	35 ps
1	0.68 eV	-0.26 e	+0.90 <i>e</i>	4.2 eV	52.6	0.07 ML	39 ps	44 ps
	0.69 eV	-0.26 e	+0.91 <i>e</i>	4.0 eV	52.8	0.08 ML	35 ps	43 ps

Table S3: AIMD simulations with n_{OH} *OH at the Li_{8.9Å}(aq) + water / Pt(111) interface.



Figure S4: Energy cost of *OH formation (eq S4) at the $Li_{8.9Å}(aq)$ + water / Pt(111) interface, as a function of elapsed sampling time (*t*-*t*₀).

S2.2.4 *OH formation with K⁺ at the water-Pt(111) interface, i.e K⁺(int) + e^- .

n _{он}	ΔΕ	$\langle Q[Pt_{48}] \rangle_t$	$\langle Q[K^+]\rangle_t$	$\langle WF \rangle_t$	$\langle HB \rangle_t$	$ heta_{ m H2O^*}$	t ₀	<i>t-t</i> ₀
0	0 eV	-0.65 e	+0.90 e	4.2 eV	52.1	0.01 ML	18 ps	34 ps
0	0.11 eV	-0.66 e	+0.89 e	3.8 eV	52.6	0.01 ML	10 ps	33 ps
0	0.57 eV ^a	-0.25 e	+0.88 e	3.6 eV	52.6	0.05 ML	14 ps	34 ps
1	0.29 eV	-0.29 <i>e</i>	+0.88 e	4.0 eV	54.9	0.08 ML	2 ps	33 ps
1	1.17 eV	-0.24 <i>e</i>	+0.89 e	4.1 eV	51.9	0.04 ML	8 ps	33 ps

Table S4: AIMD simulation with n_{OH} *OH at the K(int) + water / Pt(111) interface.

^{*a*} One water molecule is dissociated (by hand) into *OH and H*.



Figure S5: Energy cost of *OH formation (eq S4) at the K(int) + water / Pt(111) interface, as a function of elapsed sampling time (t- t_0).

S2.2.5 *OH formation with K⁺ situated 8.9 Å from the surface, i.e K⁺(aq) + e^- .

n _{он}	ΔΕ	$\langle Q[Pt_{48}] \rangle_t$	$\langle Q[K^+]\rangle_t$	$\langle WF \rangle_t$	$\langle HB \rangle_t$	$ heta_{ m H2O^{\star}}$	t ₀	<i>t-t</i> ₀
0	0 eV	-0.66 e	+0.90 <i>e</i>	3.9 eV	52.1	0.01 ML	17 ps	44 ps
0	0.30 eV	-0.64 e	+0.90 <i>e</i>	4.2 eV	51.3	0.01 ML	38 ps	36 ps
1	0.65 eV	-0.25 e	+0.90 e	3.5 eV	53.1	0.07 ML	70 ps	64 ps
	0.94 eV	-0.22 e	+0.90 e	4.0 eV	53.0	0.02 ML	6 ps	36 ps

Table S5: AIMD simulation with n_{OH} *OH at the K_{8.9Å}(aq) + water / Pt(111) interface.



Figure S6: Energy cost of *OH formation (eq S4) at the $K_{8.9Å}(aq)$ + water / Pt(111) interface, as a function of elapsed sampling time (*t*-*t*₀).

S2.2.6 Accuracy of the reaction energies. We were able to perform two independent AIMD simulations for each interface with Li that deviate by ≤ 0.11 eV in average internal energy at the end of the simulation (See Table S2, Table S3, Figure S3, and Figure S4). We therefore consider the stated internal reaction energies for "Li⁺(aq) + *e*-" and "Li⁺(int) + *e*-" in Table 1 of the main text as reasonably accurate (i.e. within ± 0.1 eV).

The reaction energies for "K⁺(aq) + e" and "K⁺(int) + e" could be considered less accurate based on the deviation in the average energy between the independent AIMD simulations for each interface (Table S4, Table S5, Figure S5, and Figure S6). However, we are confident in our conclusions based on the following reasons. The two simulations with K at the interface and without *OH differ by only 0.11 eV, so we believe that this interface is well described. The two simulations with K at the interface in the presence of *OH have energy cost of 0.29 eV and 1.17 eV, respectively. However, a closer inspection of the high energy simulation shows that K has left the interface and is situated 7.5 Å above the surface in the end of the simulation. According to our findings in Figure 2, the movement of K⁺ from the interface to 7.5 Å has a relatively low free energy cost, but a high internal energy cost explaining in part the high internal energy of this simulation. It is also our experience that it is relative easy to set up a system in an unfavorable configuration, but seldom possible to set up the system in a too stable configuration that also persists over time. We therefore have confidence in the 0.29 eV value.

For "K⁺(aq) + e^{-n} " the two independent simulations differ by 0.3 eV both in the case with *OH and in the case without *OH. Based on these deviations there is a large uncertainty. However, we do get an internal reaction energy for *OH formation, which is very similar to the "Li⁺(aq) + e^{-n} " case. We do expect that *OH formation has the same energy cost in "K⁺(aq) + e^{-n} " and in "Li⁺(aq) + e^{-n} ", because the cation is too far away from the *OH species for direct interactions.

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S2.3 Structure details. Here we present structural details for the AIMD simulations behind the numbers presented in Table 1 of the main text, i.e. the most stable $n_{OH} = 0$ and $n_{OH} = 1$ AIMD simulations for each of the studied situations (Li⁺(int) + e^- , Li⁺(aq) + e^- , K⁺(int) + e^- , and K⁺(aq) + e^-). The figures show (i) average atomic density as a function of height above the Pt(111) surface, (ii) radial distribution function between the cation and H, O, Pt, and O_{OH} atoms (O_{OH} is the O atom in the *OH species), (iii) and x,y motion (parallel to the surface) of the cation in the time intervals $t-t_0 = [0ps, 10ps], [10ps, 20ps]$ etc.

The main observations are:

- The atomic densities (both with and without *OH) for Li⁺ at the interface (Figure S7) and K⁺ at the interface (Figure S9) are largest at the heights where the metadynamics free energy profiles are most stable. This confirms that Li⁺ and K⁺ are most stable at these heights.
- The atomic densities for Li⁺ (Figure S8) and K⁺ (Figure S10) fixed at a height of 8.9 Å show that at 8.9 Å the cations are situated in the middle of the region with bulk liquid water density. The cations also have ~3 Å of liquid water both above and below them. We therefore believe that cations at this height in the liquid water film approximate well cations in bulk liquid water.
- There is no well-defined bond between the cation and the *OH species, as seen from the lack of a distinct peak between Li/K and O_{OH} in the radial distribution functions for *OH + Li + 31H₂O / Pt(111) (Figure S7) and *OH + K + 31H₂O / Pt(111) (Figure S9).
- The x,y motion of Li/K is heavily restricted when both the cation and *OH species are present at the interface. The restriction of the cation motion is clear from the plot of the x,y cation motion for $*OH + Li + 31H_2O / Pt(111)$ and $*OH + K + 31H_2O / Pt(111)$ compared to the x,y cation motion in any of the other simulations.

We have defined the radial distribution functions (g(r)) such that the number of B neighbors (n_{A-B}) that each A species has within some distance, r_{max} , is given by eq S5. ρ_{tot} is the atomic density in the computational cell (total number of atoms divided by total volume).

$$n_{A-B}(r < r_{max}) = \int_{0}^{r_{max}} 4\pi r^2 g_{A-B} \rho_{tot} dr$$
(S5)



Figure S7: For L1 (int) + e^{t} without *OH (top row) and with *OH (bottom row); we show atomic densities as a function of height above the Pt(111) surface, radial distribution functions between Li and H, O, Pt, and O_{OH}, and the x,y motion of the cation in different time intervals for *t*-*t*₀.



densities as a function of height above the Pt(111) surface, radial distribution functions between Li and H, O, Pt, and O_{OH} , and the x,y motion of the cation in different time intervals for *t*-*t*₀.



densities as a function of height above the Pt(111) surface, radial distribution functions between K and H, O, Pt, and O_{OH} , and the x,y motion of the cation in different time intervals for *t*-*t*₀.



densities as a function of height above the Pt(111) surface, radial distribution functions between K and H, O, Pt, and O_{OH} , and the x,y motion of the cation in different time intervals for *t*-*t*₀.

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