

# Deprotonation and Cation Adsorption on the NiOOH/Water Interface: A Grand-Canonical First-Principles Investigation

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## Abstract

Nickel-based oxides are highly active, cost effective materials for the oxygen evolution reaction in alkaline conditions. Recent experimental studies have revealed the importance of surface deprotonation and alkali metal cation adsorption on the activity of Ni oxide surfaces, in contact with aqueous alkaline electrolyte. As a first step to elucidate the role of the alkali adsorption for the activity, we performed first-principles electronic structure calculations to address the stable surface structures of  $\beta$ -NiOOH(0001) as a function of the operating conditions in an electrochemical environment. We present a grand-canonical approach to compute the surface Pourbaix diagram of the  $\beta$ -NiOOH/water interface for the processes of deprotonation and alkali metal cation adsorption. The results of this study emphasize the importance of double layer effects, including the adsorbate-induced change of surface dipole moments and the rearrangement of water molecules due to their strong interaction with the adsorbed species, for the most stable interface structure.

**Keywords:** Nickel (Oxy)hydroxides; Deprotonation; Pourbaix Diagram;

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## 1. Introduction

Green hydrogen will be essential as a fuel of a defossilized energy economy [1]. Compared with conventional fuels such as coal, natural gas and oil, hydrogen has the highest specific energy [2], and if used in fuel cells it constitutes a clean,  
5 efficient and sustainable technology [3].

An already well-developed and cost-effective green technology for hydrogen production is alkaline water electrolysis, in which hydrogen gas is produced from the water splitting reaction under alkaline conditions [4]. In alkaline electrolyzers the anode and the cathode are immersed in highly concentrated alkaline  
10 solutions (e.g., NaOH or KOH). These electrodes are separated by a porous and electrically insulating separator material, which is filled with a highly ionically conducting medium for hydroxide ions ( $\text{OH}^-$ ) transport from cathode to anode. The separator hinders  $\text{H}_2$  and  $\text{O}_2$  gases to crossover between the electrodes.

The electrochemical oxidation and reduction reactions take place at the anode and cathode surface, respectively. At the anode, the oxygen evolution reaction  
15 (OER:  $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4e^-$ ) produces oxygen gas,  $\text{O}_2$ , while at the cathode, hydrogen gas is produced via reduction of water in the hydrogen evolution reaction (HER:  $4\text{H}_2\text{O} + 4e^- \rightarrow 2\text{H}_2 + 4\text{OH}^-$ ) [4]. The standard equilibrium potential of the overall water splitting reaction is 1.23 V. However, the practical operating cell voltage for hydrogen evolution lies between 1.5-2.0 V. The  
20 additional voltage, also referred to as overvoltage or overpotential, must be applied to overcome the energy barriers of the OER. The overall system efficiency thus remains between 59-70 % for commercially available electrolyzers [5, 6]. Improvement of this efficiency and increasing the hydrogen production rate are  
25 pivotal practical goals to achieve for this technology.

Ni-based oxides are earth-abundant materials and recognized as promising electrocatalyst materials for alkaline electrolyzers. They offer a favourable combi-

nation of high electrochemical activity and stability [7, 8]. Many attempts have been made to improve the electrochemical activity of Ni materials via modification of the composition and structure of the catalyst material, e.g., using doping  
 30 it with iron [9, 10]; via novel synthetic design of nanoparticles and porous materials to increase the active surface area [11, 12, 13, 14]; or OER enhancement through modifications in pH or the type and concentration of ionic species in the electrolyte [15, 16].

Recent experimental studies by Diaz-Morales *et al.* and Garcia *et al.* have re-  
 35 vealed the importance of surface deprotonation as well as alkali metal cation adsorption on the OER activity of nickel oxyhydroxide (NiOOH) surfaces in contact with the alkaline electrolyte [15, 16]. The earlier study by Diaz-Morales *et al.* employed *in situ* Surface Enhanced Raman Spectroscopy (SERS) to investigate pH-dependent interfacial changes of NiOOH under OER conditions [15].  
 40 It was found that in highly alkaline pH, the degree of surface deprotonation increases, thereby producing negatively charged surface species ( $\text{NiOO}^-$ ) that lead to an enhanced OER activity [15].

Garcia *et al.* investigated the effect of electrolyte alkali metal cations ( $\text{A}^+$ ,  
 45 where A is Li, Na, K, Cs) on OER activity of NiOOH. The consistent activity trend of  $\text{Cs}^+ > \text{Na}^+ > \text{K}^+ > \text{Li}^+$  was found for both pure NiOOH as well as NiOOH containing iron impurities. Combining the deprotonation and alkali metal cation adsorption effects, one may speculate that the interaction of cations with negatively charged surface oxygen species ( $\text{NiOO-A}^+$ ) plays an important  
 50 role in stabilizing cations on the surface [16].

Even more recently, the mechanism of OER based on deprotonation was investigated on the (0001) facet of NiOOH using density functional theory (DFT), which provided further support for the role of deprotonation in OER activity [17]. These calculations suggested that the deprotonation step is the potential-  
 55 determining step with an overpotential of 0.44 V. It was discussed that this step also oxidizes  $\text{Ni}^{3+}$  to  $\text{Ni}^{4+}$ , while not changing the oxidation state of surface oxygen atoms [17].

As a prerequisite for understanding the kinetic processes involved in the OER,

the relevant local reaction conditions at the interface need to be revealed. Any  
60 mechanistic study should be preceded by the identification of the stable adsorbate structures [18]. Herein, we employ a first-principles grand-canonical approach to explore the thermodynamic stability of NiOOH/water interfaces for the processes of deprotonation and alkali metal cation adsorption under varying electrochemical conditions with respect to pH and electrode potential. We will discuss the crucial importance of double-layer effects such as  
65 the adsorbate-induced surface dipole moment as well as the explicit presence of water molecules [19, 20, 21, 22] for the computed surface Pourbaix diagrams.

## 2. Computational Methods

*Model system.* The bulk structure of  $\beta$ -NiOOH used in our simulations is based  
70 on our previous study [23]. It is represented as a model system with a  $1 \times 2 \times 1$  unit cell, the stability of which compares well with the most stable bulk phases reported in the literature [24]. The material has the ABBCC oxygen stacking sequence [25], for which hydrogen atoms present in the inter-layer space create a saturated number of hydrogen bonds between the layers, in agreement  
75 with infrared spectroscopy measurements [26]. Surface structures were modelled as three-layer slabs of  $\beta$ -NiOOH(0001) with  $3 \times 4$  unit cells. Stoichiometric surface structures include 12 Ni atoms, 24 O atoms, as well as 12 H atoms per layer of the slab for  $\beta$ -NiOOH(0001). These unit cell configurations are commensurate with the addition of explicit water layers. A water coverage of 5/6  
80 ML at NiOOH(0001), initially equilibrated with *ab initio* molecular dynamics simulation at 140 K for 8 ps (1 fs time-step), was used [23]. The H-down configuration of water was found to be more stable on NiOOH(0001) due to formation of H-bonds between water and unsaturated surface O atoms.

The (0001) facet of NiOOH is terminated with 50% of O\* and 50% OH\*, as  
85 shown in Fig. 1 (a). Surface deprotonation was modelled by successive removal of surface H atoms from the surface, while keeping the unit cell electroneutral at any given degree of deprotonation. Thereafter, adsorption of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and

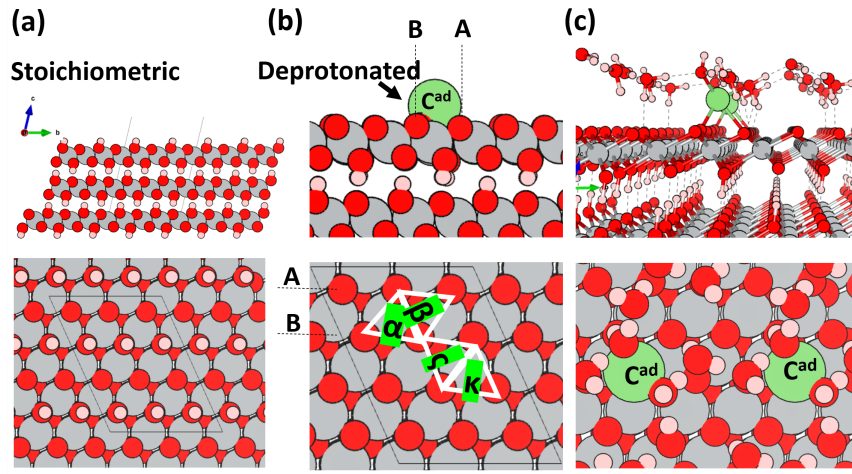


Figure 1: Side and top views of the stoichiometric NiOOH(0001) slab considered in this study. Gray, red and pink are Ni, O and H atoms, respectively. (a) Shows the stoichiometric system. (b) Side and top views of fully-deprotonated NiOOH(0001), indicating the four possible three-fold adsorption sites, among which site  $\alpha$  was found to be the most stable for alkali metal cations. The green atom represents an adsorbed cation. (c) Side and top views of the fully deprotonated cation adsorbed surface covered with explicit water molecules

$\text{Cs}^+$  ions on the fully deprotonated surface was considered, as shown in Fig. 1 (b). To find the most stable adsorption site for cations, all possible surface O  
 90 adsorption sites on the deprotonated surface - including all atop, bridge and the three-fold sites - were examined, from which the cations were found to be stabilized only on the four possible three-fold sites. Among these sites, site  $\alpha$ , as shown in Fig. 1 (b), was found to be the most stable site for all cations, which is on top of the surface Ni atom and involves two of the deprotonated O atoms,  
 95 as shown in Fig. 1 (b). The relative stability of these four sites is provided in Tab. 1.

*DFT+U calculations.* Spin-polarized DFT-based calculations were performed with the Vienna Ab initio Simulation Package (VASP) [27, 28]. The ionic  
 cores were represented by projector augmented waves (PAW) [29]. Kohn-Sham  
 100 one-electron wave functions were expanded in a plane wave basis set with an

Table 1: Relative stability of cation adsorption on various adsorption sites at deprotonated NiOOH(0001) (see Fig. 1)

Adsorption site	Li (meV)	Na (meV)	K (meV)	Cs (meV)
$\alpha$	0.0	0.0	0.0	0.0
$\beta$	61.3	63.9	62.5	56.2
$\kappa$	181.0	193.0	75.6	54.4
$\zeta$	158.0	174.0	51.8	46.9

energy cutoff of 500 eV. Electronic exchange and correlation effects were incorporated within the generalized gradient approximation (GGA), using the PBE exchange–correlation functional [30]. The DFT+U method has been employed to account for the strong correlations of *d*-electrons of Ni atoms. We used the  
105 approach by Dudarev *et al.* [31] with an effective Hubbard  $U_{\text{eff}}$  parameter (U–J) of 5.5 eV, which was calculated by Li and Selloni [32] using linear response theory [33]. A geometry relaxation for bulk NiOOH was performed with a  $12 \times 12 \times 8$  Monkhorst–Pack k-point mesh [34] and a force threshold of  $0.01 \text{ eV } \text{\AA}^{-1}$ . For geometry optimizations of the slab models, we used  $5 \times 5 \times 1$  k-points, and a  
110 force threshold of  $0.05 \text{ eV } \text{\AA}^{-1}$ .

*Grand-canonical approach.* Our goal is to explore the thermodynamic stability of the NiOOH(0001)/water system for the processes of deprotonation and cation adsorption under varying electrode potential and pH. This can be achieved by employing the combination of periodic DFT calculations and the grand-canonical approach based on the computational hydrogen electrode (CHE) [35, 36, 37, 38]. In this approach, the change in the Gibbs free energy due to the formation of interface structure, normalized by the unit area, is given by,

$$\Delta\gamma = \frac{1}{A} \left( \Delta G_{\text{ads}}^{\text{tot}} - \sum_i n_i \mu_i \right), \quad (1)$$

where,  $\Delta G_{\text{ads}}^{\text{tot}}$  is the change in the Gibbs free energy of adsorption,  $\mu_i$  is the electrochemical potential of ions in the electrolyte, and  $n_i$  is the number of

Table 2: Standard redox potentials and cohesive energies of alkali metals

Cation	half-cell reaction	$U^0$ (V vs. SHE)	$E_A^{cohesive}$ (eV)
$\text{Li}^+$	$\text{Li}^+(aq) + e^- \rightleftharpoons \text{Li}(s)$	$U^0 = -3.04$	-1.63
$\text{Na}^+$	$\text{Na}^+(aq) + e^- \rightleftharpoons \text{Na}(s)$	$U^0 = -2.714$	-1.113
$\text{K}^+$	$\text{K}^+(aq) + e^- \rightleftharpoons \text{K}(s)$	$U^0 = -2.925$	-0.934
$\text{Cs}^+$	$\text{Cs}^+(aq) + e^- \rightleftharpoons \text{Cs}(s)$	$U^0 = -3.03$	-0.804

adsorbed species  $i$  per unit cell surface area,  $A$ . In the CHE scheme, it is assumed that the electrode and the electrolyte are thermodynamic reservoirs for electrons and ions such as protons, respectively, whereas the reference system typically corresponds to the standard hydrogen electrode (SHE) [35, 39]. At standard conditions (T=298 K, and P= 1 atm, and pH = 0), molecular hydrogen in the gas phase is in equilibrium with the solvated proton and the electron ( $\frac{1}{2}\text{H}_2(g) \rightleftharpoons \text{H}^+(aq) + e^-$ ). Therefore, in thermodynamic equilibrium the corresponding chemical potential of hydrogen in the gas phase is equal to that of a proton-electron pair. Consequently, referring the potential to the SHE, we can avoid the calculation of the proton solvation energy in water and instead use the gas-phase energy of  $\text{H}_2$  which can easily be calculated based on DFT:

$$\tilde{\mu}_{\text{H}^+} + \tilde{\mu}_{e^-} = \frac{1}{2}\mu_{\text{H}_2} - eU_{\text{SHE}} - k_{\text{B}}T \ln(10) \text{pH}. \quad (2)$$

This way, the adsorption free energy is approximated by the total binding energy obtained using periodic DFT calculations, while the electrode potential  $U$  and pH enter this equilibrium expression to account for deviations from the standard conditions. The CHE is not only applicable to coupled proton-electron transfer processes but it can also be applied to any solvated ionic species [35, 40, 41]. For  
115 alkali metal cations  $\text{A}^+$ , this can be realized by the half-cell reaction,  $\text{A}^+(aq) + e^- \rightleftharpoons \text{A}(s)$  at  $U = U^0$  vs. SHE, where  $U^0$  corresponds to the standard redox potential, as listed in Tab. 2.

In thermodynamic equilibrium,

$$\tilde{\mu}_{A^+} + \tilde{\mu}_{e^-} = \mu_A - e(U_{\text{SHE}} - U^0) + k_B T \ln(a_{A^+}), \quad (3)$$

where  $a_{A^+}$  is the thermodynamic activity of the cation  $A^+$ . We assumed an activity of 0.1, which for an ideal solution correspond to a cation concentration of 0.1 M. The derivation of the Gibbs free energy of adsorption for the independent processes of deprotonation and cation adsorption is provided in the Supplementary Information (SI). For both processes of deprotonation and alkali metal cation adsorption at NiOOH(0001)/water, the total free energy is given by,

$$\Delta\gamma^{total} = \frac{1}{A} (\Delta E_{ads}^{tot} - n_H \Delta\tilde{\mu}_{OH^-} - n_C \Delta\tilde{\mu}_{A^+}), \quad (4)$$

where  $\Delta G_{ads}^{tot}$  can be approximated by  $\Delta E_{ads}^{tot}$ , which is obtained from DFT calculations, neglecting entropy and zero-point energy corrections,  $n_H$  is the number of hydrogen atoms removed from the surface and  $n_A$  is the number of adsorbed cations. Moreover, we have

$$\Delta E_{ads}^{tot} = E_{slab-ads|(water)} - E_{slab|(water)} + \frac{n_H}{2} E_{H_2} - n_A E_A^{cohesive}, \quad (5)$$

with

$$\Delta\tilde{\mu}_{OH^-} = eU_{\text{SHE}} + k_B T \ln(10) \text{ pH}, \quad (6)$$

and

$$\Delta\tilde{\mu}_{A^+} = -e(U_{\text{SHE}} - U^0) + k_B T \ln(a_{A^+}). \quad (7)$$

In Eq. 5,  $E_A^{cohesive}$  is the cohesive energy of alkali metals, the values of which are shown in Tab. 2.  $E_{slab-ads|(water)}$  and  $E_{slab|(water)}$  are the total energies of the optimized slab (including a water layer) with and without adsorbed species, calculated from DFT.

Equation 4 can be expressed as an equation of two-dimensional planes for the different surface configurations and a specified cation activity as a function of electrode potential and pH. This is shown in Fig. 2 for the case of deprotonation



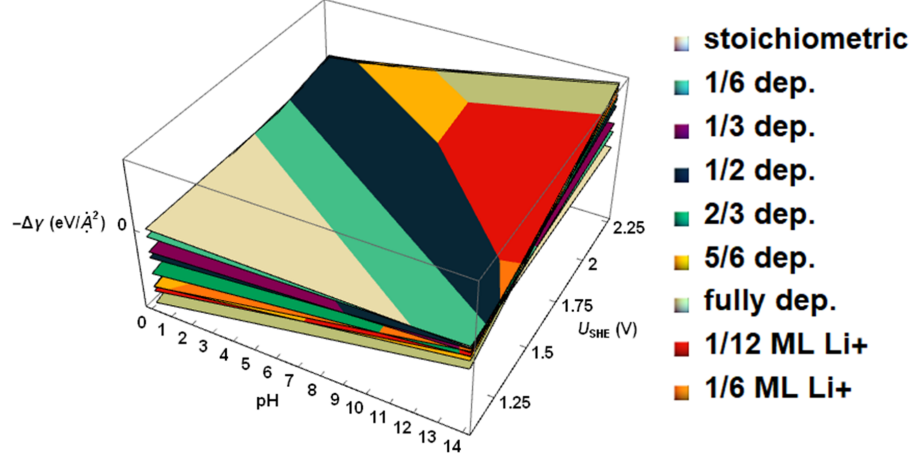


Figure 2: An example for phase diagram of deprotonation and cation adsorption at NiOOH(0001). Thermodynamic activity of 0.1 was assumed for  $\text{Li}^+$ .

and  $\text{Li}^+$  adsorption. In thermal equilibrium, the most stable deprotonated surface is determined from the lowest  $\Delta\gamma^{\text{deprotonation}}$  at a given potential and pH. As will be discussed, this way, the Pourbaix diagram for surface deprotonation can be constructed.

*Double-layer effects.* Cation adsorption/desorption on metallic or oxide surfaces induces a relatively large dipole moment at the interface [42, 43, 44], which interacts with the interfacial electric field caused by the electrode potential. Since the electrode potential is not explicitly accounted for in periodic DFT calculations, the Gibbs free energy needs to be corrected for this effect. Following the approach presented by Mills *et al.* for cation adsorption on fcc(111) electrode surfaces [45], Eq. 4 can be rewritten as,

$$\Delta\gamma^{\text{corrected}} = \Delta\gamma^{\text{total}} + \frac{p_{\text{slab-ads}(\text{water})}^{\text{dipole}} - p_{\text{slab}(\text{water})}^{\text{dipole}}}{d}(U_{\text{abs}} - U_{\text{PZC}}), \quad (8)$$

where  $p_{\text{slab-ads}(\text{water})}^{\text{dipole}}$  is the induced surface dipole at the deprotonated surface with cation adsorption, and  $p_{\text{slab}(\text{water})}^{\text{dipole}}$  is that for the stoichiometric NiOOH (0001) surface. In both cases, the slab forms an interface with a water layer.  $d$

is the width of the double layer, i.e., the distance between electrode surface and electrolyte which lies in the range of 2.5 and 3.5 Å; here, we apply the value of  
135  $d=3$  Å consistent with the previous study [45].

The absolute potential scale,  $U_{abs}$ , can be shifted to the SHE scale, using the conversion  $U_{abs} = U_{SHE} + 4.44$  eV, as recommended by Trasatti [46]. The potential at zero charge,  $U_{PZC}$ , is linearly correlated to the electrode work function in the absence of the electrolyte [47]. However, this correlation is empirical and it depends on the degree of orientation of surface water molecules as well as the electron density redistribution at the interface [48]. Mills *et al.* assumed  $U_{PZC}$  as zero in their similar investigation [45]. We consider  $U_{PZC} = \Phi^0 + const.$  as hyperparameter, with  $\Phi^0 = 5.3$  eV as the experimentally measured work function of NiOOH [49], and evaluate a range of values from (-4.5,-3.5) eV for the constant term. This covers a range of (0.8, 1.8) V vs. SHE for  $U_{PZC}$ , in which NiOOH was reported to be stable in a pH range of 2 to 14 [50]. A change in the surface dipole moment relative to the stoichiometric surface due to deprotonation and cation adsorption was obtained from the direct correlation with the corresponding work function shift [51],

$$\Delta p^{dipole} = -\frac{\varepsilon_0}{e} \Delta \Phi = -\frac{1}{180.95} \Delta \Phi, \quad (9)$$

where  $\varepsilon_0$  and  $e$  are vacuum permittivity and elementary charge. The work function is calculated from the difference between the Fermi energy and the value of the one-electron potential in the vacuum region.

### 3. Results and Discussion

140 We first discuss the effect of accounting for explicit water layers as well as the induced dipole on the stable surface structure of NiOOH(0001), followed by the discussion on the origin of this effect. Fig. 3(a) shows the change in the surface Gibbs free energy of adsorption, calculated in the gas phase, as a function of potential for a varying degree of deprotonation (Eq. 4) at a constant pH value  
145 of 13. At a given potential, the lowest value of  $\Delta \gamma$  corresponds to the most

stable surface state. As the potential increases, deprotonation becomes more favourable at NiOOH(0001). Fig. 3(b) shows the results computed in the gas phase but by accounting for the interaction term of induced surface dipole by deprotonation with the electrode potential (Eq. 8). It is seen that the surface  
150 dipole can significantly facilitate the deprotonation by decreasing the free energy of adsorption. This effect will be discussed later by computing  $\Delta\Phi$  as a function of the degree of deprotonation.

Figure 3(c) shows the effect of explicit surficial water layers on the stable interface structure of NiOOH(0001)/water for varying degrees of deprotonation.  
155 Compared with the gas phase system in Fig. 3(a), surface water molecules tend to prevent deprotonation by increasing the change in the adsorption free energy. In fact, water molecules stabilize surface OH species by forming hydrogen bonds with them. This effect has been explained in more detail in our previous work on the structure of water at NiOOH(0001) [23]. Fig. 3(d) shows the computed phase diagram by accounting for the shift in work function due to both  
160 deprotonation and the presence of surface water molecules. As for the discussion on Fig. 3(b), the induced dipole decreases the change in the free energy of adsorption and thereby facilitates deprotonation at a given potential.

Table 3 reports the computed work function and the resulting shift in the surface  
165 dipole, both in gas phase and in the presence of explicit water molecules, for varying deprotonation states. Consistent with the recent DFT calculations in Ref. [17] it was found that deprotonation leads to electron transfer from surface Ni atoms to surface O atoms, which is evidenced by the change in the oxidation state of Ni from  $\text{Ni}^{3+}$  to  $\text{Ni}^{4+}$ . This leads to a significantly polarized surface as  
170 the deprotonation degree increases, and as a result the surface dipole, with a direction towards the surface, increases. It should also be noted that a favourable H-down orientation of water at the surface further increases  $\Delta p$  toward the surface, which is consistent with the previous study [52]. Moreover, our calculated work function of 5.33 eV in the presence of water for the stoichiometric NiOOH  
175 surface agrees well with the value reported in an experimental study [49]. In the case of cation adsorption, as reported in Table 3, the electron transfer is from

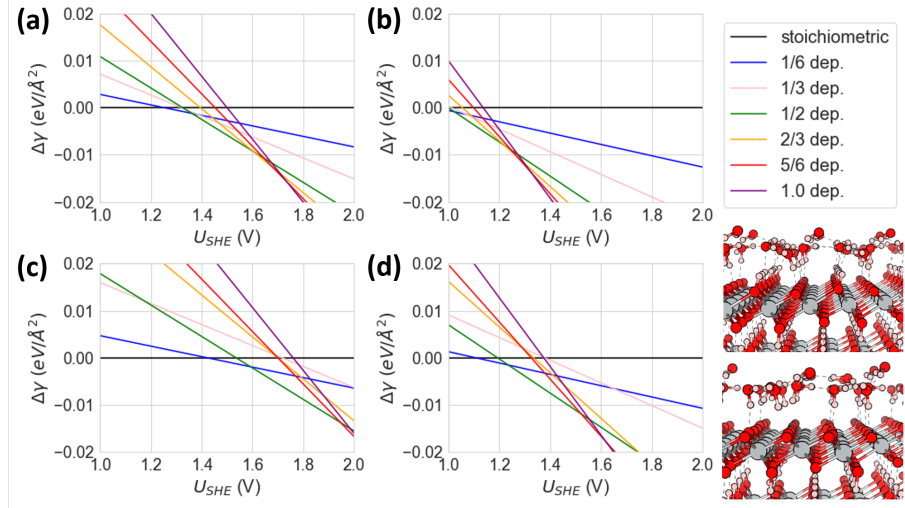


Figure 3: Phase diagram for deprotonation at pH=13. (a) in gas phase, (b) in gas phase with dipole correction, (c) with explicit water layer and (d) with explicit water layer and dipole correction

the adsorbed cation to the surface Ni, resulting in a change in the oxidation state from  $\text{Ni}^{4+}$  to  $\text{Ni}^{3+}$ .

Figure 4 shows the shift in work function with respect to the stoichiometric NiOOH(0001) surface as a function of deprotonation and alkali metal cation adsorption. In gas phase calculations, the work function of NiOOH(0001) increases by  $\approx 3$  eV in going from the stoichiometric to the fully deprotonated surface. On the other hand,  $\Delta\Phi$  decreases significantly upon cation adsorption in the gas phase, with a visible trend that the larger the cation the more significant the decrease. For the deprotonation process, H-down surface water molecules further contribute to the shift in  $\Delta\Phi$ , while for cation adsorption strong interactions between water molecules and the cation lead to directional water adsorption and modify the charge distribution at the interface. This results in a smaller drop in the work function for cation adsorption in the presence of water molecules, although the trend with respect to the cation size remains the same as in the gas phase.

To understand the cation size effect on the electronic charge distribution, we

Table 3: Calculated work function and induced surface dipole for various surface adsorption states along with the oxidation state of surface Ni atoms.

adsorption state	Work Function (eV)	Surface Dipole (D)	Oxidation State
stoichiometric   gas (water)	4.96 (5.33*)	0.0 (-0.00987)	12 Ni <sup>3+</sup>
1/6 deprotonated   gas (water)	5.43 (5.93)	-0.01254 (-0.0258)	1 Ni <sup>4+</sup> , 11 Ni <sup>3+</sup>
1/3 deprotonated   gas (water)	5.91 (6.44)	-0.02523 (-0.03934)	2 Ni <sup>4+</sup> , 10 Ni <sup>3+</sup>
1/2 deprotonated   gas (water)	6.47 (6.91)	-0.04009 (-0.05181)	3 Ni <sup>4+</sup> , 9 Ni <sup>3+</sup>
2/3 deprotonated   gas (water)	7.03 (7.52)	-0.05501 (-0.068)	4 Ni <sup>4+</sup> , 8 Ni <sup>3+</sup>
5/6 deprotonated   gas (water)	7.63 (7.80)	-0.07081 (-0.07544)	5 Ni <sup>4+</sup> , 7 Ni <sup>3+</sup>
1.0 deprotonated   gas (water)	8.21 (8.10)	-0.08632 (-0.0834)	6 Ni <sup>4+</sup> , 6 Ni <sup>3+</sup>
1.0 dep. - 1/12 Li*   gas (water)	6.80 (7.49)	-0.04891 (-0.06709)	5 Ni <sup>4+</sup> , 7 Ni <sup>3+</sup>
1.0 dep. - 1/12 Na*   gas (water)	6.03 (7.36)	-0.02845 (-0.06379)	5 Ni <sup>4+</sup> , 7 Ni <sup>3+</sup>
1.0 dep. - 1/12 K*   gas (water)	5.17 (7.10)	-0.00571 (-0.05693)	5 Ni <sup>4+</sup> , 7 Ni <sup>3+</sup>
1.0 dep. - 1/12 Cs*   gas (water)	4.98 (6.95)	-0.00067 (-0.05287)	5 Ni <sup>4+</sup> , 7 Ni <sup>3+</sup>

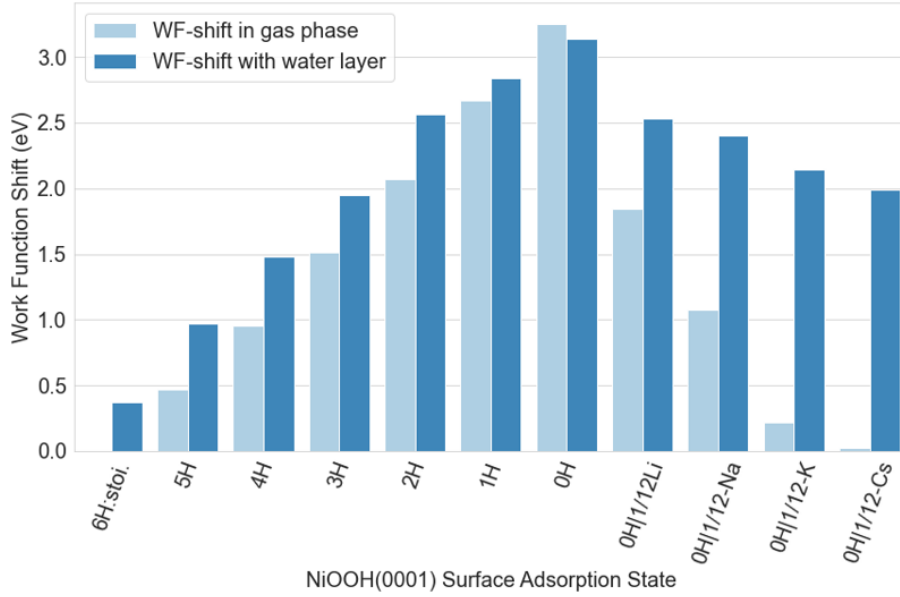


Figure 4: Shift in the work function relative to the stoichiometric NiOOH(0001) surface in the gas phase for varying deprotonation degree and adsorption of alkaline metal cations, in the absence and presence of explicit surface water molecules.

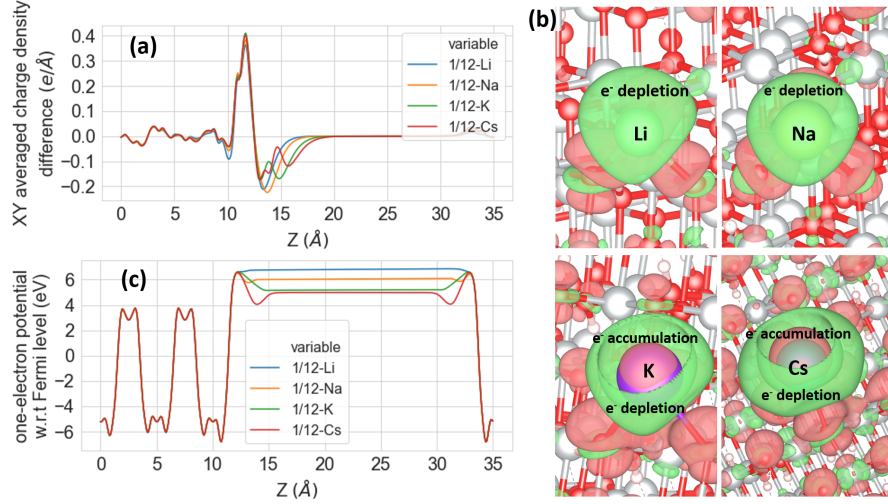


Figure 5: (a) In plane (XY) averaged charge density difference, (b) 3D charge density difference. Green shows electron depletion zone, purple shows electron accumulation zones. (c) XY averaged one-electron potential along the surface normal for various alkali metal cation adsorption at NiOOH(0001)

analyzed the charge density difference caused by electron transfer between the various adsorbed cations and the NiOOH(0001) surface in the gas phase. Figure (a) shows the XY averaged charge density difference along the surface normal from which the internal charge polarization can be observed by the adsorption of larger cations, i.e.,  $K^+$  and  $Cs^+$ . This effect can be better illustrated by showing the 3D charge density difference, as presented in Fig. (b). Unlike  $Li^+$  and  $Na^+$ , electronic charge  $e^-$  is accumulated on  $K^+$  and  $Cs^+$ . As shown in Fig. (c), the internal charge polarization for larger cations leads to a significant potential drop along the surface normal and thereby a larger decrease in  $\Delta\Phi$ . With the consideration of explicit water molecules, this effect is suppressed due to the strong interaction of water with adsorbed cations and the resulting charge redistribution. Interestingly enough, such a strong reduction of the work function due to a stronger polarization of larger adsorbed ions has also been observed for anionic halide adsorption on metal surfaces [51, 53].

The effect of alkali metal cation adsorption on the electronic structure of metals

and oxides has been a lasting subject of interest [42, 43, 44]. Lindgren and Wallden reported the work function change of Cu(111) upon varying the coverage of  $\text{Na}^+$  and  $\text{Cs}^+$  [54]. Similar trends were observed for both cations including  
 210 (1) a coverage-dependent change in the work function, (2) a significant drop of around 2-4 eV at lower coverage, (3) a minimum in the curve at lower coverage. Moreover, the decrease was found to be larger for  $\text{Cs}^+$  than  $\text{Na}^+$ . In addition, the same trend was reported for  $\text{K}^+/\text{Rh}(111)$  [55],  $\text{Cs}^+/\text{W}(100)$  [56], and  
 215 for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$  adsorption on  $\text{TiO}_2(100)$  [57]. A more recent experimental study reported that the local work function around an adsorbed  $\text{K}^+$  decreases by  $1.5 \pm 0.3$  eV on CuO thin films. Realizing this local effect is particularly important for oxide surfaces where adsorbed alkali metals invoke more localized charge transfer as compared with the metal surfaces [58].

Figure 6 shows the computed Pourbaix diagrams of  $\text{NiOOH}(0001)$  considering different degrees of deprotonation and also  $\text{Li}^+$  adsorption. In the absence of explicit surface water molecules, as depicted in Figure 6(a), deprotonation becomes more favourable as the pH and potential increase; however, in this case  $\text{Li}^+$  adsorption is less favorable than deprotonation, thus its corresponding surface state does not appear in the diagram. This is mainly due to the large  
 225 negative standard redox potential of alkali metals, which shifts  $\Delta\gamma$  of the corresponding surface state to more positive values (see Eq. 4, Eq. 7, Table 2 and Figure 2). To balance this effect, one needs to further stabilize the cations on the surface. Figure 6(b) shows the Pourbaix diagram generated from gas phase  
 230 calculations but accounting for the dipole interaction term in the surface free energy of adsorption (Eq. 8). As previously discussed, the interaction of the induced dipole moment, that is caused by deprotonation, with the electrode potential further facilitates the deprotonation at lower potentials and lower pH values; however, still with this correction  $\text{Li}^+$  adsorbed state is less favorable  
 235 than deprotonation states which is in contradiction with experiment [16].

Given the relatively large experimental  $\text{Li}^+$  solvation free energy of -4.985 eV [45, 59], it is crucial to include solvation effects for the adsorbed cations. As shown in Fig. 6(c) for the system at 5/6 ML water coverage, the strong interaction

between water molecules and  $\text{Li}^+$ , as well the hydrogen bond formation between  
 240 water and the surface, lead to further stabilization of the interface structure  
 and appearance of  $\text{Li}^+$  adsorption in the high potential and pH region of the  
 Pourbaix diagram. Thus, there is a competitive adsorption between  $\text{Li}^+$  and  
 protons, similar to the competitive adsorption between chloride and protons on  
 Pt(111) [60, 61, 62].

245 As shown in Fig. 6(d), including the dipole effects caused by both surface water  
 and deprotonation significantly modified the computed Pourbaix diagram and  
 shifted the stable regions to lower potential and pH values. In other words, the  
 interaction of induced dipole with electrode potential facilitates both deprotona-  
 tion and Li desorption from the surface. Figure S1 illustrates the sensitivity of  
 250 the generated Pourbaix diagrams to the hyperparameters of the model, namely,  
 the potential of zero charge and the width of the double layer.

The computed Pourbaix diagrams for the adsorption of other alkali metal cations  
 are shown in Figure S2. Whereas we also find a stability pocket for  $\text{Na}^+$  adsorp-  
 tion, no stable  $\text{K}^+$  and  $\text{Cs}^+$  adsorbate phases appear in the calculated Pourbaix  
 255 diagrams. This is due to the fact that the larger the cations, the more positive  
 the shift in their Gibbs free energy of adsorption.  $\text{K}^+$  and  $\text{Cs}^+$  might still ad-  
 sorb on  $\text{NiOOH}(0001)$ , but at lower concentrations which are associated with  
 a smaller mutual dipole-dipole repulsion upon adsorption. Unfortunately, such  
 low concentrations are below the scope of the present study because of the sig-  
 260 nificantly increased computational effort for larger surface unit cell required to  
 model lower concentrations. Another possibility would be that  $\text{K}^+$  and  $\text{Cs}^+$  are  
 present as non-specifically adsorbed cations.

The substantial difference between the Pourbaix diagrams in Fig. 6(a) and Fig-  
 ure 6(d) indicates the importance of accounting explicitly for the surficial water  
 265 layer and dipole interaction effects to obtain an accurate prediction of the stable  
 interface structure for these systems. In this respect, oxide and hydroxide elec-  
 trodes also behave differently compared to close-packed metal electrodes. For  
 example, in the grand-canonical evaluation of the Pourbaix diagrams of Pt(111)  
 in contact with halide-containing aqueous electrolytes the explicit and also im-



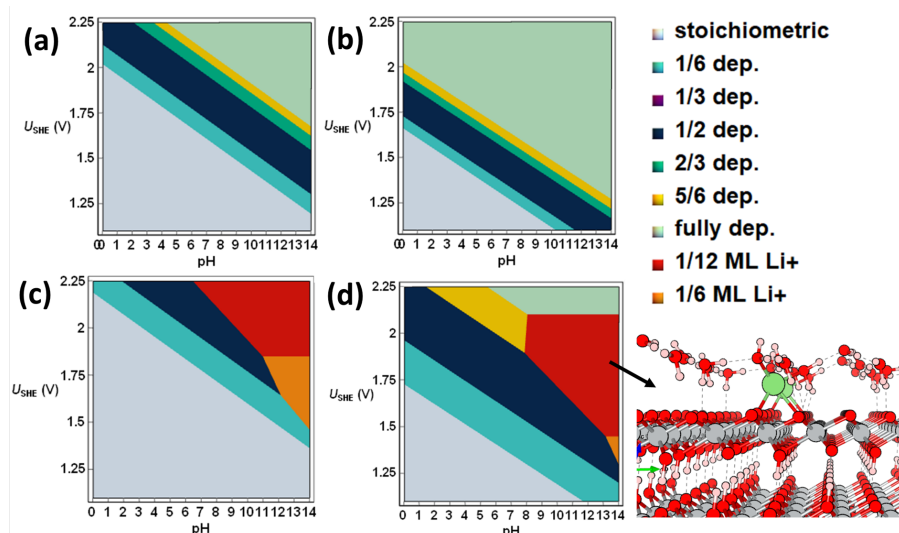


Figure 6: Computed Pourbaix diagram for deprotonation and Li adsorption at NiOOH(0001) in (a) gas phase, (b) gas phase with dipole correction (c) with explicit water layer, (d) with explicit water layer and accounting for dipole correction. A thermodynamic activity of 0.1 was assumed for  $\text{Li}^+$ .

270 plicit presence of water can be safely neglected, still a semi-quantitative agree-  
 ment with the experiment can be obtained [62]. This is due to the relatively  
 weak and rather non-directional interaction of liquid water with close-packed  
 metal electrodes [63]. In contrast, the interaction of water with hydroxide and  
 oxide surfaces has a much stronger covalent character leading to a much more  
 275 directional bonding of the water molecules, which then becomes significantly  
 modified in the presence of adsorbed cations.

This study represents the first important step towards a better understanding  
 of the enhancement in the OER activity due to surface deprotonation and alkali  
 metal cation adsorption on NiOOH. We speculate that this enhancement is  
 280 linked with the stronger polarizability of the cations that increases with their  
 size and thereby also leads to larger decrease in the work function upon specific  
 adsorption. Experimental strategies have been proposed to enhance the OER  
 activity of NiOOH-based materials by manipulating the work function through  
 electron injection [64], which would support our speculation. However, we did

285 not find stable specific adsorbate phases for the two largest cations  $K^+$  and  $Cs^+$   
under operating conditions. Hence this change of the work function might also  
be caused by non-specifically adsorbed cations. Furthermore, it remains to be  
seen whether the direct interaction of the adsorbed alkali metal cations with  
the reaction intermediates of the OER also contributes to the enhancement.  
290 Further DFT-based computations are required to understand this effect.

#### 4. Conclusions

In order to elucidate the role of the presence of alkali ions for the activity of  
the oxygen evolution reaction, we applied a grand-canonical scheme based on  
the computational hydrogen electrode to determine the most stable interface  
295 structures of  $\beta$ -NiOOH/water under varying pH and electrode potential for the  
deprotonation and alkali metal cation adsorption processes. We discussed the  
crucial importance of double-layer effects due to induced surface dipole moment  
and the explicit treatment of surficial water molecules. We found that the sur-  
face electronic properties change more significantly with the size of the adsorbed  
300 cations due to their stronger polarizability. Accounting for these effects provided  
an explanation on the experimentally observed alkali metal cation adsorption  
on the deprotonated NiOOH surfaces under OER conditions. Still, open ques-  
tions remain with respect to the particular form of the cation adsorption phases  
which will be the focus of ongoing research efforts.

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