ALKALI CATION SPECIFIC ADSORPTION ONTO LATE-TRANSITION METAL ELECTRODES

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A thesis submitted in partial fulfillment of the requirements for a baccalaureate degree in Chemical Engineering with honors in Chemical Engineering

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ABSTRACT

The presence of alkali cations in electrolyte solutions is known to impact the rate of electrocatalytic reactions, though the mechanism of such impact is not conclusively determined. We use density functional theory (DFT) to examine the specific adsorption of alkali cations to fcc(111) electrode surfaces, as specific adsorption may block catalyst sites or otherwise impact surface catalytic chemistry. Solvation of the cation-metal surface structure was investigated using explicit water models. Computed equilibrium potentials for alkali cation adsorption suggest that alkali and alkaline earth cations will specifically adsorb onto Pt(111) and Pd(111) surfaces in the potential range of hydrogen oxidation and hydrogen evolution catalysis in alkaline solutions. 

This results presented in this thesis are included within “J. N. Mills, I. T. McCrum, and M. J. Janik. “Alkali cation specific adsorption onto fcc (111) transition metal electrodes” Physical Chemistry Chemical Physics 16 (2014) 13699-13707.”
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Finally, I would like to thank my family for their continued support of my education and life ambitions over the years.
Chapter 1

Introduction

Fuel cells are an important part of emerging renewable energy sources. They have the capacity to produce electrical energy from stored chemical energy. Proton Exchange Membrane fuel cells have experienced limited industrial success, but as of yet fuel cells with alkaline electrolytes are not as efficient. Alkaline fuel cells are not as prominently used, partly due to slower electrode kinetics as compared to PEM fuel cells. If the cause for these lowered kinetics can be determined and improved upon, alkaline fuel cells may provide similar efficiency to PEM fuel cells with lowered cost through use of renewable electrode metals.

Specific interactions of the fuel cell’s electrolyte on the electrode surface affect the kinetics of the cell, and these are determined by the configuration and chemical properties of the cell. Under certain conditions, it may be favorable for ions from the electrolyte to adsorb to the electrode surface by transferring a partial charge onto the metal. This has been studied in the context of Proton Exchange Membrane fuel cell and the adsorption of anions such as sulfates, but less so with cation adsorption in alkaline fuel cells [1,2]. Experimentally, it has been observed that alkali/alkaline earth cations used with basic electrolytes can exhibit lower rates than acidic electrolytes for the oxygen reduction reaction (ORR) on Au and Pt [3] and to hydrogen oxidation reaction (HOR) on Pt [4], and that the hydrogen oxidation rate is orders of magnitude lower in alkaline environments as compared to acidic counterparts [5]. No definitive conclusions have been drawn to explain these results, but specific cation adsorption to the hydrogen oxidation electrode could play a role. Herein, Density Functional Theory is employed to determine the favorability of alkali metal cation
adsorption onto close packed transition metal surfaces at to the conditions where hydrogen adsorption would occur.

The consideration of cation specific adsorption in alkaline fuel cells is relevant to understanding the rates of surface reaction observed experimentally. However, it is difficult to study these interactions in the laboratory due to nature of the electrolyte-electrode interface and the simultaneous reaction that occur thereon. Quantum chemical methods like DFT are most useful in modeling specific interactions like those of interest here. DFT methods have been used previously to model anion adsorption onto electrode surfaces [2, 6-9], so reasonably the same practices could be applied to study alkali cation adsorption.

Halides [10], (bi)sulfate [1], and alkali metal cations [3, 4] have been shown to affect the rate of electrocatalytic reactions in aqueous solution. Specific adsorption could account for these observed effects, though the conclusive mechanistic cause in each case is undetermined. As seen on platinum electrodes, sulfate specific adsorption can be responsible for blocking adsorption sites necessary to the ORR [1]. Nonspecific interactions have been proposed to explain kinetic variations observed in systems involving alkali metal cations on the rates of the HOR and ORR in alkaline environments [4], including covalent interaction in the solution phase, where partially solvated cations impact hydroxide adsorption [3, 4]. In the same manner that anions have been shown to adsorb and affect the ORR, cations can adsorb to the electrode surface at low potentials. The result of this is site blockage or other disturbances to the catalytic, electronic or structural properties of the system.

Determining the favorable conditions for cation adsorption leads to the understanding of whether specific adsorption may be responsible for the lowered rates observed in alkaline electrokinetics. DFT is used to model systems involving H, Li, Na, K, Cs, and Ba on fcc (111) surfaces including Pt, Pd, Ni, Au and Ag. These metals are common electrode components in alkaline fuel cells, and these simple cations serve to model interactions undergone by the more
complex organic cations that would be employed in a polymer electrolyte. DFT calculations estimate the equilibrium adsorption potentials for these systems. The influence of the electric field from the electrode is accounted for with surface/dipole field interaction approximations. Solvation is approximated for our computational model by the explicit inclusion of static water molecules in the system. Potentials were compared to those where the HOR occurs in alkaline environment to determine if alkali metal cations can adsorb in that range and compete for adsorption sites and possibly lower the observed reaction kinetics.
Chapter 2

Methods

2.1 Density Functional Theory Methods

Electronic structure calculations were performed using the Vienna ab initio Simulation Package [11-13], with a plane wave basis set and the Perdew-Wang (PW91) exchange-correction [14] functional. The Projector Augmented Wave (PAW) approach was used to model core potentials [15]. A 5x5x1 Monkhorst-Pack mesh was used to sample k-space [16]. The cutoff energy for the plane-wave basis set was 450 eV and structural optimization was complete when forces on atoms were less than 0.02 eV Å⁻¹. Due to pseudo-slab interactions, dipole corrections were included in the surface normal direction (IDIPOL=3, LDIPOL=TRUE).

2.2 Lattice Modeling

Experimental metal lattice constants were used, as given in Table 1. A 3x3 surface cell modeled the electrode surface, leading to a $\frac{1}{9}$ monolayer adsorption of alkali metals. Surface slabs contained four layers of depth and the bottom two layers were frozen during optimization. Hollow sites were most favorable for adsorption for all cations on all of the surfaces considered, and the energy difference between hcp and fcc sites was negligible.
Table 2-1: Conventional cubic cell dimension used for fcc metals [17]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Lattice Constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(111)</td>
<td>4.09</td>
</tr>
<tr>
<td>Au(111)</td>
<td>4.08</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>3.52</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>3.89</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>3.92</td>
</tr>
</tbody>
</table>

### 2.3 Calculating Cation Adsorption Equilibrium Potential

Figure 2-1: Adsorption diagram of a solvated cation, $C^+$, binding to a transition metal surface. A solvation shell surrounds the free cation and also binds with the cation to the surface through adsorption.

The specific adsorption process for a cation onto a metal surface can be written as a reaction:

$\ast + C^+_{aq} + e^- \rightarrow C^*$ (1)

where $\ast$ represents the bare fcc(111) surface, $C^+_{aq}$ the aqueous solvated cation, and $C^*$ the adsorbed species. The Gibbs energy of adsorption as a function of electrode potential on an absolute potential scale, $U_{abs}$, can be written as:

$\Delta G_{ads}(U_{abs}) = G_{C^*} - G_{\ast} - G_{C^+_{aq}} + eU_{abs}$ (2)
where \( e \) represents the absolute value of the electron charge and \( G_x \) is the chemical potential of species \( x \). The free energy of the cation adsorbed to the surface \( G_{C^+} \) is calculated as:

\[
G_{C^+} = E_{C^+}^{DFT} + ZPVE - TS_{vib} \tag{3}
\]

where \( E_{C^+}^{DFT} \) is the DFT energy of the adsorbed cation system, \( ZPVE \) accounts for the zero point vibrational energy, and \( TS_{vib} \) is the vibrational entropy of the adsorbed species. The free energy of the bare surface \( G_* \) is approximated presuming adsorption does not alter the electrode entropy:

\[
G_* = E_*^{DFT} \tag{4}
\]

The cation free energy in aqueous alkaline solution is approximated by calculating the free energy of the cation in the gas phase and adding an experimentally measured solvation free energy for the cation in a 1 M solution (\( \Delta G_0^{solvation} \)):

\[
G_{C^+}^{(aq)} = G_{C^+}^{(g)} + \Delta G_0^{solvation} \tag{5}
\]

The cation free energy in the gas phase, \( G_{C^+}^{(g)} \), is calculated by adding a translational entropy correction (\( -TS_{trans} \)) at standard conditions to the DFT calculated energy:

\[
G_{C^+}^{(g)} = E_{C^+}^{DFT} - TS_{trans} \tag{6}
\]

Solvation free energies are taken at standard conditions and, therefore, adsorption free energies are determined relative to 1 M concentrations of the cations in aqueous solutions. Adsorption free energies at other concentrations could be calculated provided activity corrections to the non-standard state are available.

Equations 1 and 2 express specific adsorption as occurring with a single electron transferred to form the adsorbed species. For most adsorption configurations considered, the cation retains a partial positive charge and a dipole moment is established in the surface normal direction. The free energy change of adsorption is corrected to include the interaction of this dipole moment with an interfacial electric field:

\[
\Delta G_{ads}(U_{abs}) = G_* - G_{C^+} + eU_{abs} + \frac{\mu_{C^+} - \mu_*}{d} (U_{abs} - U_{pzc}) \tag{7}
\]
where $\mu_*$ is the dipole moment of the bare surface, $\mu_C*$ is the dipole moment of the surface-cation system, $U_{pzc}$ is the electrode potential at zero charge, and $d$ is the distance between the electrode surface and the solution phase countercharge within an approximate, classical Helmholtz model. We use a $d$ value of 3 Å, consistent with that used by others within a concentrated electrolyte [18]. This dipole correction effectively allows the adsorption to occur with partial electron transfer. Equation 8, the derivative of $\Delta G_{ads}$ with respect to $U$, gives the net electron transfer upon adsorption:

$$
\frac{d\Delta G_{ads}}{dU} = e^{-} + \frac{\mu_C* - \mu_*}{d}
$$

(8)

The equilibrium adsorption potential, $U^0_{abs}$, can be solved for by setting $\Delta G_{ads}$ to zero in equation 7:

$$
U^0_{abs} = -G_C + G_* + G_{C*} + U_{pzc} \left( \frac{\mu_C* - \mu_*}{d} \right)
$$

(9)

At potentials above $\Delta G^0_{ads}$, little cation specific adsorption would be expected. Potentials significantly below $U^0$ would be expected to attain at least the $\frac{1}{9}$ ML coverage used in the DFT model.

The adsorption equilibrium potential can be shifted to the scale of a normal hydrogen electrode by using the conversion:

$$
U_{NHE} = U_{abs} - 4.6 \text{ V}
$$

(10)

The value of 4.6 V [19] is consistent with that calculated by DFT methods and is in the experimental range of 4.4-4.8 V [19-24]. In this work, we take $U_{pzc}$ as zero on a NHE scale, consistent with the approach used by others when employing a similar model to examine surface adsorbate interactions [18]. Equations 9 and 10 may be combined to give the cation equilibrium adsorption potential on a NHE scale as

$$
U^0_{NHE} = -G_C* + G_* + G_{C*} + e*4.6V + \frac{\mu_C* - \mu_*}{d}
$$

(11)
This method for calculation of $U_{NHE}^0$ neglects the additional stabilization of the adsorbed cation due to solvation, though cation solvation in the bulk electrolyte phase is included in the $\Delta G_{solvation}^0$ value. The non-solvated $U_{NHE}^0$ value is, therefore, expected to provide a minimum adsorption equilibrium potential, with solvation stabilization pushing adsorption to higher potentials.

### 2.4 Surface Solvation

The stabilization effects due to a solvated surface were modeled by calculating the Gibbs free energy change of adsorption of $H^+$, $Na^+$, and $Ba^{2+}$ on Pt (111) when optimized with varying numbers of explicit water molecules. Platinum was used due to its relevance in fuel cell catalysis and because it is most likely to show greatest alkali competition for adsorption sites. Equation 1 can be amended to include this solvation as:

$$\text{(H}_2\text{O)}^n\text{C}^+ + e^- \rightarrow \text{C(H}_2\text{O)}^n$$

where $(\text{H}_2\text{O)}^n$ represents the surface with $n$ water molecules absorbed and $\text{C(H}_2\text{O)}^n$ represents the surface with these water molecules and the cation adsorbed.

A static H$_2$O structure was used due to the computational requirements of DFT. The structure of $\text{C(H}_2\text{O)}^n$ was determined by first optimizing the surface with one water molecule, then adding another molecule to this optimized structure and recalculating to find the lowest energy conformation, continuing up to $n$ H$_2$O molecules (herein up to $n=10$). Adding this method modeling solvation to equation 7 yields

$$\Delta G_{ads}(U_{abs}) = G_{\text{C(H}_2\text{O)}^n} - G_{(\text{H}_2\text{O})^n} - G_{C^+} + eU_{abs} + \frac{\mu_{C^+} - \mu_*}{d} (U_{abs} - U_{pzc})$$

where $G_{\text{C(H}_2\text{O)}^n}$ is the free energy of the cation adsorbed on the Pt(111) surface with $n$ H$_2$O molecules and $G_{(\text{H}_2\text{O})^n}$ is the free energy of $n$ H$_2$O molecules adsorbed on the Pt(111) surface prior to cation addition. Dipole moments are updated to include the effects of solvation on the cation and
(H₂O)_n systems. These values are calculated similarly as before, but include harmonic vibrational degrees of freedom of adsorbed molecules in ZPVE and entropy corrections. During optimization of the adsorbed species, the water molecules were in a ‘relaxed’ initial state, representing the minimum energy structure of n static water molecules on the Pt (111) surface. Upon cation optimization, the cation was removed from the structure and the H₂O molecules near the surface were relaxed to yield the initial solvated surface energy from the structure with the optimum positioning of water molecules for each cation.
Chapter 3

Results and Discussion

Figure 3-1 illustrates the structure of an adsorbed cation species on an un-solvated surface. The cation is adsorbed in the energetically preferential hollow site. A single lattice cell is shown to focus on the surface chemistry, but can be imagined to repeat in the x and y directions.

![Figure 3-1 An example of the structure of an adsorbed cation-surface species (Na⁺ on Pt(111)).](image)

Table 3-1: Cation adsorption equilibrium potentials (eV) to fcc (111) electrode surfaces, U₀ [V-NHE] calculated using DFT methods and equation 11.

<table>
<thead>
<tr>
<th></th>
<th>H⁺</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Cs⁺</th>
<th>Ba²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>-0.07</td>
<td>-1.30</td>
<td>-0.90</td>
<td>-0.98</td>
<td>-0.80</td>
<td>-1.31</td>
</tr>
<tr>
<td>Pd</td>
<td>0.09</td>
<td>-1.63</td>
<td>-1.19</td>
<td>-1.35</td>
<td>-1.09</td>
<td>-1.43</td>
</tr>
<tr>
<td>Ni</td>
<td>0.05</td>
<td>-2.06</td>
<td>-1.61</td>
<td>-1.85</td>
<td>-1.68</td>
<td>-1.86</td>
</tr>
<tr>
<td>Au</td>
<td>-1.29</td>
<td>-2.76</td>
<td>-2.40</td>
<td>-2.74</td>
<td>-2.64</td>
<td>-2.46</td>
</tr>
<tr>
<td>Ag</td>
<td>-0.65</td>
<td>-2.63</td>
<td>-2.11</td>
<td>-2.52</td>
<td>-2.44</td>
<td>-2.62</td>
</tr>
</tbody>
</table>
Table 3-2: VASP energies (eV) for bare fcc (111) surfaces and single atom adsorption.

<table>
<thead>
<tr>
<th>Cation</th>
<th>(E_{\text{DFT}}^c)</th>
<th>(E_{\ast})</th>
<th>(\Delta G_{\text{TS}})</th>
<th>(\Delta G_{\text{TRANS}})</th>
<th>(\Delta G_{\text{SOLV}})</th>
<th>(G_{\text{C+,aq}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>12.53</td>
<td>-11.41</td>
<td>0.20</td>
<td>-11.41</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>Li(^+)</td>
<td>5.34</td>
<td>-4.99</td>
<td>0.41</td>
<td>-3.99</td>
<td>0.90</td>
<td>0.01</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>5.18</td>
<td>-3.89</td>
<td>0.46</td>
<td>-2.89</td>
<td>0.79</td>
<td>0.78</td>
</tr>
<tr>
<td>K(^+)</td>
<td>4.35</td>
<td>-1.55</td>
<td>0.48</td>
<td>-1.55</td>
<td>0.78</td>
<td>0.74</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>3.87</td>
<td>-2.67</td>
<td>0.53</td>
<td>-2.14</td>
<td>0.74</td>
<td>0.74</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>15.39</td>
<td>-13.04</td>
<td>0.53</td>
<td>-12.51</td>
<td>1.88</td>
<td></td>
</tr>
</tbody>
</table>

Table 3-3 shows the cation properties for the corrections for ZPVE, entropy and aqueous cation solvation, using the experimental free energies of solvation for each cation at standard state which can be found in Appendix A [25]. These values range from -2.67 eV for Cs\(^+\) to -13.0 eV for Ba\(^{2+}\), clearly confirming that cation solvation must be considered. Table 3-3 also lists the entropy corrections for gas phase ions which range from 0.197 to 0.529 eV.

Table 3-3: Cation Properties at 300 K and 1M, Calculated with equations 5-6

<table>
<thead>
<tr>
<th>Cation</th>
<th>(E_{\text{DFT}})</th>
<th>(TS_{\text{TRANS}})</th>
<th>(\Delta G_{\text{SOLV}})</th>
<th>(G_{\text{C+,aq}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>12.53</td>
<td>0.20</td>
<td>-11.41</td>
<td>1.38</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>5.34</td>
<td>0.41</td>
<td>-4.99</td>
<td>0.90</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>5.18</td>
<td>0.46</td>
<td>-3.89</td>
<td>0.78</td>
</tr>
<tr>
<td>K(^+)</td>
<td>4.35</td>
<td>0.48</td>
<td>-1.55</td>
<td>0.74</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>3.87</td>
<td>0.53</td>
<td>-2.67</td>
<td>1.88</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>15.39</td>
<td>0.53</td>
<td>-13.04</td>
<td></td>
</tr>
</tbody>
</table>

The impact of the dipole corrections was analyzed before determining conclusions from the adsorption potentials. Figure 3-1 shows the change in adsorption free energy as a function of potential for three of the cations, \(H^+, K^+,\) and \(Ba^{2+}\) on the Pt(111) surface, both with (equation 7)
and without (equation 2) the dipole correction. The adsorbed $H^+$ retains no net charge, as evidenced by the lack of change in the surface dipole moment after adsorption, and therefore the adsorption free energies with and without dipole corrections are identical. Other cations retain a positive net charge, contributing to a slope of $\Delta G_{ads}$ versus $U$ which is less than 1. This slope is equal to the net electron transfer upon adsorption, and these values are given in Table 3-5. Net electron transfers around 1 for $H^+$ indicate full electron transfer. As no positive charge remains, the solvation interaction with the $H^+$ surface is not expected to differ significantly from that of the bare surface. The adsorption potential for $H^+$ on Pt of -0.07 V is within the experimentally measured hydrogen adsorption region on Pt(111) [26]. This value is slightly lower than that typically reported using the computational hydrogen electrode approach [27], suggesting some variability introduced by the use of the $H^+$ cation free energy and experimental solvation energy as compared to the use of a gas-phase $H_2$ free energy.

For other ions, the surface dipole moment upon adsorption is significant, generally increasing with ion size. The dipole correction does not vary significantly across metals, though Pt and Au consistently show the largest dipole moments while Ni and Ag have the smallest. Examining the $\frac{\Delta G_{ads}}{\Delta U}$ values, $Li^+$ generally transfers close to 0.8 e$^-$ while $Cs^+$ transfers closer to $\frac{2}{3}$ e$^-$. Partial electron transfer may be interpreted as signifying full electron transfer with adsorption, followed by a non-Faradic current required to maintain constant electrode potential arising from the need to counteract the established surface dipole. The established dipole moment is significant enough to suggest that the adsorbed alkali cations will be stabilized further by solvation. Dipole moments are listed in Table A-2 in Appendix A.
Figure 3-2: Free energy of adsorption for H+, K+, and Ba+2 onto a Pt(111) electrode as a function of electrode potential. Adsorption free energies are reported with (equation 7) and without (equation 2) dipole corrections. Without dipole correction: red- K+, green- Ba+2; with dipole correction: light blue- K+, orange- Ba+2; purple- H+ with and without dipole correction.

Table 3-4: Values of $\Delta G_{\text{ads}}$ for cation adsorption to fcc(111) metal surfaces. These values represent net electron transfer upon adsorption, calculated via equation 8.

<table>
<thead>
<tr>
<th></th>
<th>H+</th>
<th>Li+</th>
<th>Na+</th>
<th>K+</th>
<th>Cs+</th>
<th>Ba+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>1.00</td>
<td>0.81</td>
<td>0.72</td>
<td>0.64</td>
<td>0.63</td>
<td>1.60</td>
</tr>
<tr>
<td>Pd</td>
<td>1.00</td>
<td>0.82</td>
<td>0.75</td>
<td>0.67</td>
<td>0.67</td>
<td>1.67</td>
</tr>
<tr>
<td>Ni</td>
<td>1.00</td>
<td>0.84</td>
<td>0.78</td>
<td>0.70</td>
<td>0.69</td>
<td>1.71</td>
</tr>
<tr>
<td>Au</td>
<td>1.00</td>
<td>0.81</td>
<td>0.74</td>
<td>0.65</td>
<td>0.61</td>
<td>1.60</td>
</tr>
<tr>
<td>Ag</td>
<td>1.01</td>
<td>0.84</td>
<td>0.78</td>
<td>0.69</td>
<td>0.66</td>
<td>1.68</td>
</tr>
</tbody>
</table>

The cation adsorption free energies provide indication as to whether cation specific adsorption will occur in potential ranges of interest for HOR/HER catalysis in alkali containing electrolytes. The $H^+$ adsorption potential is significantly more positive than all other cations on all metals, prior to any consideration of any adsorbed cation solvation. Provided both $H^+$ and alkali cations are present at concentrations of 1M, the $\Delta G_{\text{ads}}$ will be significantly more negative for $H^+$
at any potential and alkali cations are not likely to compete for adsorption sites. At a pH of 14, the $H^+$ adsorption potential would shift negatively by 0.826 V-NHE. At this low $H^+$ concentration, the free energies of adsorption of $Na^+$ and $Cs^+$ become more favourable than $H^+$ adsorption on Pt(111), with $K^+$ becoming close as well. The $Na^+$, $K^+$, and $Cs^+$ free energies on Pd (111) also near that of $H^+$ at pH 14. As solvation of $H^+$ is not likely to alter the adsorption free energies, these initial non-solvated values are a reasonable estimate for $H^*$ formation. Specifically adsorbed alkali cations are expected to be stabilized by solvation interactions, pushing their equilibrium adsorption potentials further positive and suggesting greater competition with hydrogen for adsorption sites during HOR/ORR in base.

Surface solvation was approximated by adding $n=1$-$10$ static water molecules during $H^+$, $Na^+$, and $Ba^{2+}$ optimization. Equilibrium potentials are calculated via equation 13 and plotted as a function of water molecules solvating the surface during proton adsorption in Figure 3-b. Solvation does not significantly alter the proton adsorption potential, as evidenced by a near constant equilibrium potential even with increased surface solvation. The solvation effects are greater on $Na^+$ and $Ba^{2+}$ adsorption, as seen in Figures 3-4 and 3-5, respectively.

![Figure 3-3: Equilibrium adsorption potential for $H^+$ adsorption onto the Pt(111) surface calculated including the effects of explicit surface solvation (equation 13), given for a varying number of water molecules included in the solvation model. Data points are included a relaxed-water method for the energy of the surface-water system before cation addition.](image-url)
Figure 3-4: Equilibrium adsorption potential for Na\(^+\) adsorption onto the Pt(111) surface calculated including the effects of explicit surface solvation (equation 13), given for a varying number of water molecules included in the solvation model. Data points are included using relaxed water reference for the energy of the surface-water system before cation addition.

Figure 3-5: Equilibrium adsorption potential for Ba\(^{2+}\) adsorption onto the Pt(111) surface calculated including the effects of explicit surface solvation (equation 13), given for a varying number of water molecules included in the solvation model. Data points are included using relaxed water reference for the energy of the surface-water system before cation addition.
Figure 3-6 illustrates the optimal structures for $n=6$ H$_2$O molecules (Other values of $n$ available in Appendix B). Comparing Figures 3-6.1 and 3-6.2 suggests adsorbed H$^+$ only slightly perturbs the water structure, and only 1 of the 6 water molecules appears to interact directly with the adsorbed H$^+$. From Figure 3-6.3 and 3-6.4, Na$^+$ and Ba$^{2+}$ have 4 H$_2$O molecules closest to them, with direct interactions forming a partial 1$^{st}$ solvation shell at the electrode surface. Relative to the un-solvated surfaces, Na$^+$ and Ba$^{2+}$ atoms move slightly further from the Pt(111) surface when solvated, though no insertion of water molecules between the cations and the surface was observed. Attempts to locate such non-specifically adsorbed states lead either to specific adsorption or a less stable structure.

While this relaxed water reference method provides a reasonable approach to approximating solvation with static water molecules, it neglects the longer range solvation effects-
a dynamic molecular model would better fully capture the thermodynamics of a solvated bulk solution. However, the absorbance potential does converge with increasing number of water molecules, suggesting that there is little quantitative impact of long range effects. There would also be an entropy loss associated with strong water-cation interactions. Herein, the non-solvated adsorption equilibrium potentials are taken as a minimum value, and the maximum is capped at the potential from the relaxed water solution reference method due to the omission of this entropy loss. These values are for the single 1/9 ML coverage, and the significant retention of charge for the specifically adsorbed alkali cations suggests that adsorption will be strongly coverage dependent, becoming less favourable at higher coverages due to cation-cation repulsion.

The effects of solvation on the favourability of Na$^+$ and Ba$^{2+}$ cation adsorption are significant, greater than 1 eV for adsorption onto the Pt(111) surface. Solvation of the metal-cation bond screens and stabilizes the charge that remains on the cations when they adsorb to the surface, making the adsorption process more favourable. Solvation has a much smaller effect on the adsorption of a hydrogen cation, as shown in Figure 3-3, which is expected given its almost neutral charge on the surface and very small surface-hydrogen dipole moment. Given the large stabilizing effect of solvation on the cation adsorption process, it is likely that all cations considered could compete with hydrogen on Pt(111) for adsorption sites during HOR in alkaline solutions. If the maximum range of solvation corrections on Pt(111) are presumed transferable to the other (111) surfaces, competitive cation adsorption during HOR could be relevant on all of these metals—further modeling would be required to study solvation effects on other metals.

These results suggest the possible presence of cations on electrode surfaces in the HOR range in alkali hydroxide electrolytes, at least at 1/9 ML coverage and on Pt(111) and Pd(111) surfaces. The >1V range between the non-solvated and solvated values, together with the inability to definitively quantify the solvation effect on specific adsorption, limit the conclusiveness of DFT calculations in determining the extent of specific adsorption as a function of electrode potential,
but do support theory that it occurs. More advanced approaches to estimating free energies of solvation that allow for consideration of extended electrode surfaces would help further clarify this phenomena, though these are complicated by difficulties in modeling the impact of the surface and electrification on solvation dynamics.
Chapter 4

Summary and Conclusion

Density functional theory calculations were used to examine the specific adsorption of alkali cations to fcc (111) electrode surfaces. The adsorption equilibrium potential for cations, below which adsorption may occur to a significant degree, was estimated both with and without consideration of solvation of the adsorbed cations. Results suggest alkali and alkali-earth cations can specifically adsorb at low coverage in alkaline solutions around potentials where hydrogen oxidation or evolution catalysis may occur. Competitive cation adsorption is most favourable on Pt(111) but may occur to a lesser degree on other metals as well. Specific adsorption free energies are most favourable on electrode surfaces in the order of Pt(111) > Pd(111) > Ni(111) > Ag(111), Au(111). On all metals, alkali cations will transfer a partial electron upon adsorption, and the surface dipole moment thereby created will reduce the potential dependence of the adsorption free energy and motivate direct solvation by surface water molecule.

Surface solvation can be estimated using a relaxed water reference method of \(n=6\) static H\(_2\)O molecules surrounding the adsorbed cation. The unknown error stemming from the use of a single structure of static water molecules which does not consider the impact of cation interaction on solvation entropy limits the conclusiveness of the calculated adsorption free energies. Solvation of cations is more significant than that of proton adsorption, and the surface dipole moment provides a reasonable screening value for determining whether solvation is likely to impact the stability of adsorbed single-atom species.
Appendix A
Supplementary Tables

Table A-1: Experimental cation solvation free energies, eV, at 300 K and 1M [47].

<table>
<thead>
<tr>
<th>Cation</th>
<th>$\Delta G_{\text{SOLV}}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>-11.411</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>-4.985</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>-3.887</td>
</tr>
<tr>
<td>K$^+$</td>
<td>-3.151</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>-2.674</td>
</tr>
<tr>
<td>Ba$^+$</td>
<td>-13.04</td>
</tr>
</tbody>
</table>

Table A-2: Dipole moments (e Å) for bare fcc(111) surfaces (\(\mu_s\)) and surfaces with adsorbed atoms (\(\mu_C\)).

<table>
<thead>
<tr>
<th>Bare Surface</th>
<th>H$^+$</th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Cs$^+$</th>
<th>Ba$^{\text{12}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>0.0166</td>
<td>0.000832</td>
<td>-0.567</td>
<td>-0.813</td>
<td>-1.06</td>
<td>-1.11</td>
</tr>
<tr>
<td>Pd</td>
<td>0.00834</td>
<td>0.0172</td>
<td>-0.520</td>
<td>-0.733</td>
<td>-0.971</td>
<td>-0.997</td>
</tr>
<tr>
<td>Ni</td>
<td>-0.0131</td>
<td>-0.0211</td>
<td>-0.506</td>
<td>-0.689</td>
<td>-0.906</td>
<td>-0.941</td>
</tr>
<tr>
<td>Au</td>
<td>0.0279</td>
<td>0.0205</td>
<td>-0.549</td>
<td>-0.764</td>
<td>-1.03</td>
<td>-1.13</td>
</tr>
<tr>
<td>Ag</td>
<td>0.0124</td>
<td>0.0295</td>
<td>-0.471</td>
<td>-0.635</td>
<td>-0.913</td>
<td>-1.02</td>
</tr>
</tbody>
</table>

Table A-3: Gas phase water properties at 300K (eV).

<table>
<thead>
<tr>
<th>$E_{\text{DFT}}$</th>
<th>ZPVE</th>
<th>$T_{\text{SIB+ROT+TRANS}}$</th>
<th>$U+PV$</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>-14.272</td>
<td>0.5645</td>
<td>0.6733</td>
<td>0.1035</td>
<td>-14.278</td>
</tr>
</tbody>
</table>
Appendix B
Supplementary Solvation Structure

Figure B 1: Relaxed solvated Pt(111) surface. a) 1 H$_2$O b) 2 H$_2$O c) 3 H$_2$O d) 4 H$_2$O e) 5 H$_2$O f) 6 H$_2$O g) 7 H$_2$O h) 8 H$_2$O i) 9 H$_2$O j) 10 H$_2$O
Figure B-2: Relaxed solvated Pt(111)+H surface. a) 1 H$_2$O b) 2 H$_2$O c) 3 H$_2$O d) 4 H$_2$O e) 5 H$_2$O f) 6 H$_2$O g) 7 H$_2$O h) 8 H$_2$O i) 9 H$_2$O j) 10 H$_2$O
Figure B-3: Relaxed solvated Pt(111)+Na surface. a) 1 H$_2$O b) 2 H$_2$O c) 3 H$_2$O d) 4 H$_2$O e) 5 H$_2$O f) 6 H$_2$O g) 7 H$_2$O h) 8 H$_2$O i) 9 H$_2$O j) 10 H$_2$O
Figure B-4: Relaxed solvated Pt(111)+Ba surface. a) 1 H₂O  b) 2 H₂O  c) 3 H₂O  d) 4 H₂O  e) 5 H₂O  f) 6 H₂O  g) 7 H₂O  h) 8 H₂O  i) 9 H₂O  j) 10 H₂O
ACADEMIC VITA

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EDUCATION: The Pennsylvania State University, University Park, PA | May 2015
Major: Chemical Engineering | Minor: Nanotechnology
Schreyer Honors Scholar

INTERNSHIPS:
Mondelēz International, East Hanover, NJ | May - August, 2014
RD&Q Intern for Lipids Ingredient Technology Team, Global Biscuit Category
  • Studied Oreo crème rheology to predict process flow behavior
  • Determined processing temperatures for crème based on fat system
  • Investigated the value of new in-line instruments to study crème aeration
  • Developed and conducted pilot plant trials

Schindler Elevator Corporation, Gettysburg, PA | May - August, 2013
Engineering Intern in Process Control, Adhesive Application
  • Studied adhesive bonding on laminate for cab panels
  • Hypothesized various possible causes and contributing factors
  • Implemented changes to work instructions to ensure quality of product

RESEARCH:
Penn State Chemical Energy Storage and Conversion Lab | 2012-2014
  • Studied competing and specific cation adsorption in alkaline fuel cells
  • Used computational quantum mechanics to optimize chemical structures
  • Calculated adsorption potentials of various cations on metal surfaces
  • Participated in 2012 Penn State Chemical Engineering REU Program
  • Computational skills in Materials Studio, VASP, Gaussian


LEADERSHIP:
Hospitality Director, Penn State Dance Marathon | April 2014 – April 2015
  • Served on the Executive Committee of the largest student-run philanthropy in the world
  • Oversaw the 260-person Hospitality Committee with 20 direct reports
  • Facilitated the procurement and service of all food and beverage donations
  • Past THON Involvement: Hospitality Captain, Development (2014)
    Donor and Alumni Relations Captain, Administrative Assistant (2013)
    Special Events Committee Member, Inspiration Chair (2012)