Ab Initio Modeling of the Aqueous Electrochemistry of Nickel

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Interim Report for:
Contract M004040001 AG

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**Introduction**

As described in the statement of work (SOW), the purpose of this research is to elucidate the atomic-scale interface structures, mechanisms, and electrochemical processes that can influence the stress corrosion cracking behavior of nickel-base alloys exposed to high purity, high temperature, deaerated water. Specifically, the research focuses on understanding the atomic scale structure, dynamics, and reactivity of the metal/water interface. Additionally, the research will elucidate regions of phase stability and quantify the energetics of the electrochemical reactions that occur.

These studies represent some of the first *ab initio* calculations of metallic surfaces polarized in aqueous solution. In this first phase of work on nickel alloys, advantage was taken of our previous work on copper.

The tasks from the SOW are as follows:

1. Construct a model of alternating layers of Ni(111) surfaces and water. The model shall be of sufficient size to ensure the calculations are appropriately accurate.
2. Investigate the effects of increasing potential on nickel/water reactions. Interfacial potential shall be increased via removing electrons from the model. A range of potentials shall be explored to investigate both water adsorption/reorientation and the initial stages of metal oxidation.
3. Similar to Task 2, investigate the effects of decreasing potential on nickel/water reactions. Interfacial potential shall be increased via adding electrons to the model. A range of potentials shall be explored to investigate water adsorption/reorientation, water reduction and hydrogen evolution.
4. Where possible, compare the results of this study to previous atomistic modeling studies and to experimental data. The final report should include a discussion of significant findings, similarities and discrepancies between model and experimental results, and suggest future work to more accurately model the electrochemical reactions that occur during the stress corrosion cracking of nickel-base alloys exposed to high purity, high temperature deaerated water.
**Work to Date**

During the first six months of this project, progress has been made on Tasks 1-3. The Ni(111) model has been constructed and validated against literature data for lattice spacing, magnetic moment, and work function. The computational approach is described briefly below, followed by descriptions of the results of studies on (a) the energetics of water bilayers on Ni(111), including the effects of the orientation of the water dipole relative to the surface, (b) the effects of adsorbed and absorbed atomic hydrogen on those energetics, including the effects of lattice position of the hydrogen, (c) the effects of polarizing the Ni(111)-H surface in both the anodic and cathodic direction on the interfacial energetics, including the effects of the crystallographic location of the hydrogen. The future work planned is also described.

**Computational Details**

The Ni(111)-H$_2$O interface was modeled using the periodic gradient-corrected plane-wave density functional theory as implemented in the VASP$^1$ code by Kresse and Hafner. The metal water interface was examined by carrying out calculations using a periodic slab architecture where the metal surface is defined by 3-4 layers of metal atoms and the solution phase placed between the metal slab with a density close to that of liquid water. Ionic and core interactions were modeled via relativistic Vanderbilt ultra-soft pseudopotentials$^2$, and energy cut-offs of 396 eV were used. A super-cell was constructed containing 27 Ni atoms (three Ni(111) planes containing nine atoms in each plane) and 24 water molecules (8 monolayers). Calculations performed using the RPBE functional$^3$ and a 3x3x1 Monkhorst-Pack k-point mesh$^4$ closely reproduced the magnetic moment of Ni ($0.64\mu_B$ versus $0.61\mu_B$ for bulk Ni$^5$), and gave a work-function that was 0.50 eV lower than experiment$^6$. There is some deviation though in the reported work function measurements. Work-function changes measured in this study have been corrected to reflect this problem in the otherwise high-performance RPBE functional.

**Water Bilayers on Ni(111)**

There are two uniform bilayer structures of water possible on the Ni(111) surface (Figures 1a&b, also reference 7). These were simulated under zero charge conditions,
and the energies and geometric parameters are given in Table 1. The results for ‘double’ bilayers are also given (Figures 1c&d). The H-up configuration is the most stable for both single and double bilayers, allowing more favorable metal-water interactions (as characterized by the more negative $\Delta E$) and hydrogen-bonding (higher $E_{\text{H-bond}}$). The internal strain is also lower than that in the H-down configuration, as demonstrated by the larger vertical O-O separation of approximately 1Å, as opposed to 0.3Å or lower in the H-down layers. While the H-up configuration is favored under equilibrium 0 K conditions, experimental measurements of low temperature ice configurations on H$_2$O indicate that protons are in fact disordered in the matrix. This may be attributed to a combination of thermal, entropic and non-equilibrium conditions which have not been considered in the calculations.
Figure 1. Bilayer and double bilayer structures on Ni(111)

It is significant to note that the work function ($\Delta \Phi$, relative to bare nickel) is decreased by 3.40eV when the bilayer is in the H-up configuration, and increased by 0.10eV when H-down. This effect is a combination of the surface charge redistribution due to adsorption, and the crossing of the water dipole. The addition of a second H-up bilayer increases the work function by 0.30eV, whereas the addition of a second H-down bilayer increases the work function by 1.23eV. Similar effects have been observed on Cu(111) and a rationale for this has yet to be constructed$^9$. 
Table 1. Results from DFT calculations on the structure and energetics of water bilayers on Ni(111), including absolute energies (E) relative to the single and double H-up bilayers respectively; average hydrogen bond energies (E_{H-bond}), adsorption energy (ΔE), change in work-function (ΔΦ) relative to bare nickel, nickel-oxygen bond distances (d(Ni-O)), and bilayer-width (d(O-O)), for the bilayer configurations shown in Figure 1.

<table>
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<tr>
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<th>H-up</th>
<th>H-down</th>
<th>Double H-up</th>
<th>Double H-down</th>
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<tbody>
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<td>E (eV)</td>
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<td>0.000</td>
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<td>-3.10</td>
<td>+1.33</td>
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<tr>
<td>d(Ni-O) (Å)</td>
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<tr>
<td>d(O-O) (Å)</td>
<td>1.03</td>
<td>0.303</td>
<td>0.92</td>
<td>0.105</td>
</tr>
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</table>

Hydrogen Beneath Water Bilayers on Ni(111)

In order to probe the energetic of hydrogen diffusion into Ni we start by examining the stability of atomically adsorbed hydrogen at different position on and within Ni. Hydrogen atoms were placed at various crystallographic sites beneath a H-up water bilayer on Ni(111) (Figure 2) and the total energies calculated at the potential of zero charge. Table 2 details the results of these calculations. Energies are given relative to the HCP phase, and changes in work function from bare Ni(111). The OCT and TET are sub-surface absorption phases between the first and second layer of Ni(111). The coverage of hydride is 1/9 ML.
As might be expected, there is only a small preference for the HCP over the FCC sites. The change in work function (a contribution from the water bilayer and the hydride) is essentially the same as that from the water bilayer alone, and so we may expect that hydride beneath the H-up interface does not significantly affect the electrochemistry of the interface under zero charge conditions. Studies of H at the reducing H-down surface in bulk conditions (not bilayer) are presented below, and
suggest that the effect on the work function (and therefore, the electrochemistry) is much more significant. Calculations of H below the H-down bilayer are in progress.

We find that the absorption process for hydrogen into nickel is endothermic by at least 0.635 eV (FCC to OCT) at the potential of zero charge. Transition states and kinetic parameters for adsorption are currently being determined, as well as the energetics of hydrogen absorption at more negative potentials.

**Electrochemical Dependence of the Ni(111) – Bulk Water Interface, Ni(111)-H2O(s)**

The Ni(111) – bulk water interface (designated Ni(111)-H2O(s)), was modeled using a 3x3 Ni(111) super-cell with twenty four water molecules separating the periodic slabs (Figure 3). The more complex structure of the bulk water component was derived from ab initio molecular dynamics simulations. The potential of zero charge was determined from the work function of the system, and the energy at other potentials was calculated by performing simulations with varying numbers of electrons\textsuperscript{10}. The periodic slab contains two surfaces, one in the H-up configuration, and one in the H-down configuration. The measured potential is therefore an average between the two ordering structures. The resulting ‘phase-diagram’ is presented below (Figure 4).
Figure 3. Ni(111)-H$_2$O$_{(s)}$ periodic slab super-cell. Note the asymmetry between the two slab faces that arises from the ordering of protons in the equilibrium structure.
Figure 4. Phase diagram for water on Ni(111). Filled circles are DFT data points, and the dashed curve is a quadratic fit to the data. Open circles are taken from a quadratic parameterization derived solely from the given PZC and capacitance of the interface. Energies have not been corrected for zero-point contributions.

The potential of zero charge and the differential capacitance derived from this curve are –3.80V NHE and 9.4µF/cm² respectively. The experimental PZC is -0.02V NHE¹¹. This difference is most likely due to the occurrence of a phase transition, whereby the interface being measured is not in fact solely H₂O on Ni(111). A phase transition from unactivated water to its dissociation products is typically accompanied by a discontinuity in the surface charge, and thus experimental PZC measurements in fact capture a change in surface chemistry at which the charge discontinuously moves from negative to positive, rather than the PZC for a homogeneous surface phase. Such a rationale has been suggested for Cu(111)⁹, where the measured PZC corresponds closely with the transition from H₂O_{ads} to OH_{ads}. The results below suggest that the presence of hydride on the more reducing surface shifts the PZC to -0.2V NHE, closer to the experimental value¹¹.
Electrochemical Dependence of Ni(111)-H$^{\text{ATOP \_ (aq)}}$ and Ni(111)-H$^{\text{OCT (aq)}}$

The Ni(111)-H$_{(\text{aq})}$ interface was modeled similarly to Ni(111)-H$_2$O$_{(s)}$, and in two separate configurations. In the first configuration (or phase), H was placed at the atop site on the reducing side of the slab (where the proton ordering is such that the nearest water monolayer is H-down, Figure 5a.). Previous studies on Cu(111), indicate that adsorption of H occurs from a H-down structure$^9$. Thus, as the potential is moved negatively from the pzc, the water dipole inverts. This so-called water “flip-flop” behavior has been experimentally measured on several metal/solution systems. A second configuration was generated with H at the octahedral absorption site (Figure 5b). Phase diagrams for these two phases are superposed in Figure 6. Energies have not yet been corrected for zero-point vibrational contributions. It can be seen that the atop phase is most stable about zero-charge conditions, but for potentials negative of -1.3 V and positive of +1.0 V, the octahedral site is preferred. At these latter anodic potentials, however, we expect oxides to be formed on Ni(111). The addition of further phases, such as fcc, hcp and other possible water dissociation products (such as OH) is currently in progress and will complete the picture of surface chemistry of Ni(111).
Figure 5. Periodic slab super-cells of the (a) atop and (b) octahedral phases of Ni(111)-H$_{(aq)}$. 
Figure 6. Potential versus free energy curves for octahedral (solid) and atop (open, dashed) hydride phases on Ni(111). The atop phase is more stable than the octahedral between -1.3 and +1.0 V NHE. ZPE corrections have not been made.

Future Work

Extensions of the current work include the calculation of transition states intermediate to hydrogen absorption at the octahedral and tetrahedral sites, and the calculation of oxide states on Ni(111), both beneath bilayers and at the oxidizing face of the Ni(111)-H$_2$O$_{ls}$ slab. Models calculating the effect of sequential bilayers on the work function (and thus electrochemical behavior) of the Ni(111)-H$_2$O$_{ls}$ interface is also underway.

Further development of the method is also being pursued to move towards the modeling of a truly liquid phase water environment via the coupling of ab initio molecular dynamics simulations with the Filhol and Neurock methodology for extracting electrochemical potentials from DFT simulations$^{10}$.

Summary
Water and hydride phases have been modeled on Ni(111). At the potential of zero charge, water in the H-up configuration is preferred for water bilayers (Table 1), and the hcp site is preferred for hydrogen below this bilayer (Table 2). Adsorption of H beneath a H-up bilayer has little effect on the work function, whereas adsorption of H beneath a reducing H-down bulk water environment results in a shift in the potential of zero-charge by +3.60V. Superposition of potential versus free-energy curves for atop and octahedral hydride shows that the absorption phase is preferred at potentials away from the PZC (outside the -1.3 -> +1.0 V NHE range), although the energy preference for atop H₂O within this range is small (<0.2eV). Studies are underway to consider the activation energy for the absorption process, as well as oxidative chemistry on Ni(111).

References