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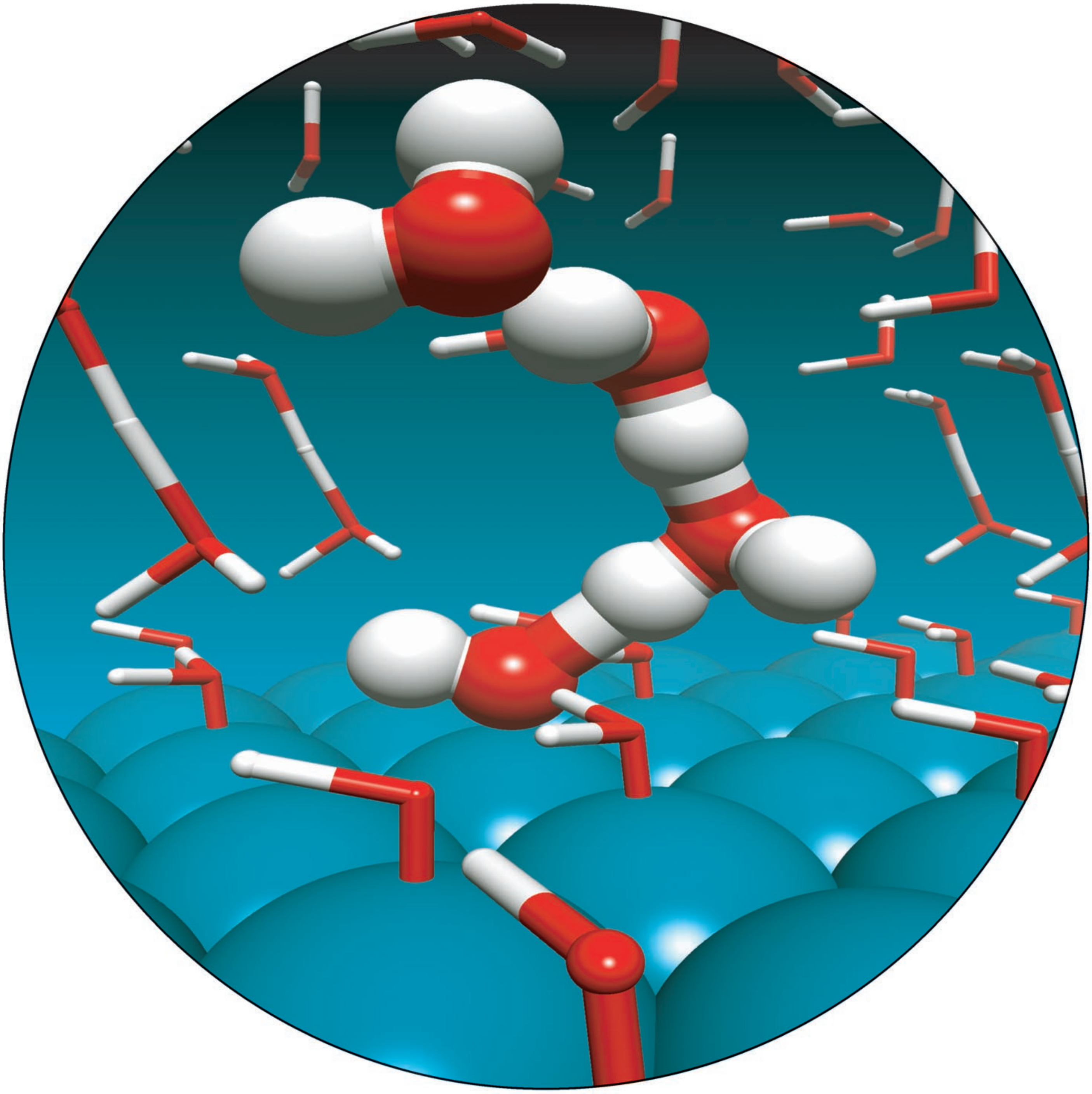

Ab-initio-Vorhersagen wurden verwendet, um die Veränderungen in Struktur und Reaktivität der Wasser-Metall-Grenzfläche als Funktion des angelegten Potentials zu verfolgen. Daraus resultierte ein elektrochemisches Phasendiagramm für Wasser über Pd(111). Weitere Details finden sich in der Zuschrift von M. Neurock und J.-S. Filhol auf den folgenden Seiten.

Electrocatalysis

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Elucidation of the Electrochemical Activation of Water over Pd by First Principles**

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The water/metal interface is critical to the performance of a number of chemical, biological, and materials systems, including electrocatalysts for fuel cells, corrosion-resistant surfaces, electrochemically deposited electronic and magnetic films, and inorganic scaffolds for biomolecular adhesion. The reactivity and electrochemical behavior of the metal/solution interface is dictated by the explicit atomic and electronic structure that forms at the interface as a response to environmental conditions, such as an applied potential. Elucidating the structure and chemistry at this interface, however, is a considerable challenge because of the large number of molecular configurations that result from factors such as the various orientations of the water molecules in the hydrogen-bonded network, the presence and formation of different ions at various positions within the interface, and the range of reactions that can occur at different applied surface potentials. Spectroscopic resolution of the molecular-level transformations that occur at this interface as a function of the applied electrochemical conditions is difficult to obtain. Although theory has made important advances in elucidating gas-phase reactions on metal substrates, there have been very few ab initio studies of the metal/solution interface in the presence of an applied potential[1–3] These previous studies were pioneering, as they provided insights into the reactivity of the interface. Their treatment of the metal, the solution phase, and the polarizability of the interface with potential, however, was not quantitative enough to model the detailed surface chemistry accurately. Herein, we report the development and application of an ab initio quantum mechanical approach to simulate the specific changes in the atomic structure of the water/metal interface and its reactivity as a function of applied potential. The approach is used to derive what we believe is the first interfacial electrochemical phase diagram to be developed by ab initio calculations. More specifically, we examine the activation of aqueous water over Pd(111). The results demonstrate that the polarization of the interface is critical in correctly establishing the structure and the reactivity of the interface as a function of potential.

Generalized gradient corrected, periodic density functional theoretical calculations were carried out to determine the structures and the corresponding free energies for each of the phases that can form for water on the Pd(111) surface over a potential range of −0.5 to 2.5 V. The details of the calculations as well as the approach are reported in the Supporting Information. To simulate an applied potential, the metal slab is charged by selectively adding (or subtracting) a predetermined number of electrons (n_e) to (or from) the system. A compensating background charge (n_{bg}) was subsequently distributed homogeneously over the unit cell to maintain overall charge neutrality. Explicit water molecules were introduced into the vacuum region between the metal slabs to model the solution/metal interface. The density of water was optimized, which results in a value close to that of bulk water. The charged slab, along with the compensating background charge, polarizes the water region and thus simulates the electrochemical double layer (see Supporting Information for details of the calculations). The charged slab and compensating background charge interact with each other and thus influence the total energy of the system. To calculate an unbiased electronic energy, the DFT-calculated value E_{DFT} is corrected for the interaction between the electrons in the slab and the background charge by using the expression given in Equation (1).

$$E_{\mathrm{DFT}}(n_{\mathrm{e}},n_{\mathrm{bg}}) = E_{\mathrm{slab}}(n_{\mathrm{e}}) + E_{\mathrm{slab\text{-}bg}}(n_{\mathrm{e}},n_{\mathrm{bg}}) + E_{\mathrm{bg}}(n_{\mathrm{bg}}) \tag{1}$$

In Equation (1), E_{slab} is the energy of the slab without the background, E_{bg} is the energy of the background without the slab and $E_{\mathrm{bg\text{-}slab}}$ is the interaction energy between the slab and the background. The correction results in the total electron energy E_{elec} defined in Equation (2).

$$E_{\mathrm{elec}} = E_{\mathrm{DFT}} + \int_0^q \langle \overline{V_{\mathrm{tot}}}(Q) \rangle \mathrm{d}Q \tag{2}$$

$\overline{V_{\mathrm{tot}}}(Q)$ refers to the average electrostatic potential and Q refers to the excess charge of the unit cell. More details of this derivation are given in the Supporting Information. The total free energy of the system E_{free} must also include contributions for the excess electrons q at the Fermi potential φ_{vac}. This inclusion of these contributions results in Equation (3) for the potential-dependent free energy E_{free}.

$$E_{\mathrm{free}} = E_{\mathrm{DFT}} + \int_0^q \langle \overline{V_{\mathrm{tot}}}(Q) \rangle \mathrm{d}Q - q\,\varphi_{\mathrm{vac}} \tag{3}$$

The method described above was used to map out the phase diagram for the electrooxidation and electroreduction of water over Pd. Although a diverse range of structures at the water/metal interface is possible, we follow only the most thermodynamically stable structures. The free energies for the interfacial water, hydride, and hydroxide/metal interfaces and their reactive transitions are simulated as a function of potential to establish the electrochemical phase diagram for water on the Pd(111) substrate.

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Water adsorbs at the potential of zero charge on the Pd(111) surface in a form similar to that of the well-known hexagonal bilayer structure[4] in which water molecules assemble in a hexagonal ring structure on the surface, as seen in Figure 1 a (top metal/water interface) and 1 b (bottom metal/water interface). The water molecules closest to the surface are bound with the oxygen end oriented toward the surface because of the interaction of the filled $1b_1$ orbital of water and empty d states on the metal. As we sweep to more-negative potential, the water at the surface rotates to orient its positively charged hydrogen atoms toward the more negatively charged metal surface as is seen in the left-hand panel of Figure 1. This potential-dependent change in orientation is known as the water flip–flop mechanism and is well established in electrochemistry. Furthermore, the Pd–H bond distance decreases while the Pd···O distance increases, as shown in Figure 1. The distance between the oxygen atoms and the surface decreases as the potential is made more positive. The changes were found to be continuous over the range of potentials examined, thus reflecting the continuous polarization of the interface.

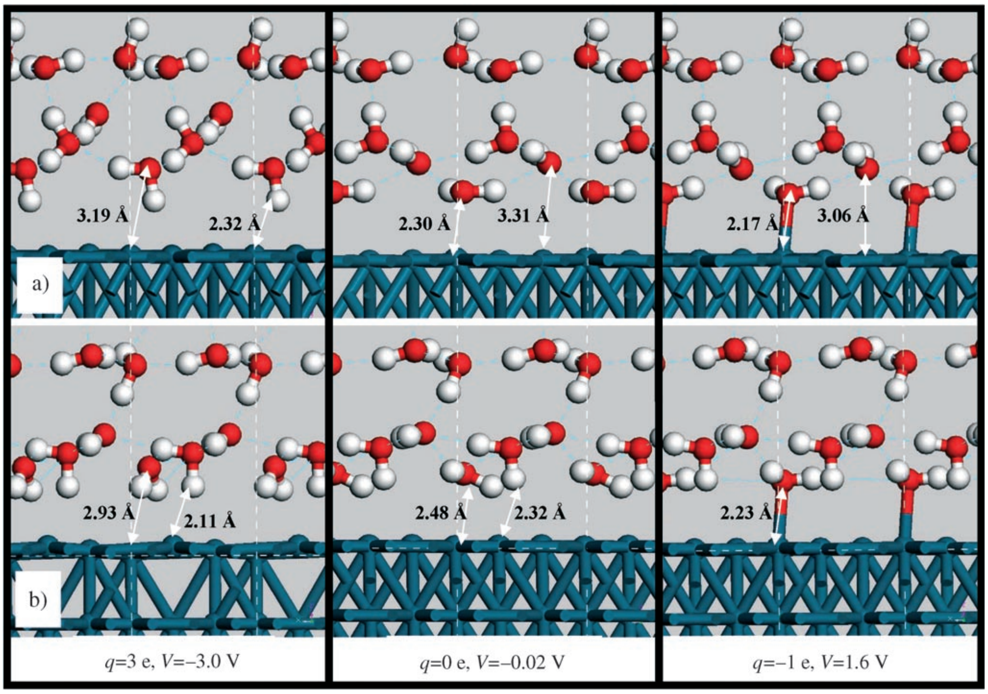

Figure 1. The optimized structure of the water/palladium interface at different applied potentials. The upper set of figures refers to the surface structure that forms at the top of the electrode (a). The lower set of figures refers to the surface structure that forms at the bottom of the electrode (b). The potential (referenced to the NHE) and the corresponding charge are given at the bottom of the Figure below each interface. The unit cell is outlined with white dashed lines. The blue dashed lines refer to the hydrogen bonds.

These changes in the positions of water molecules can be attributed to the presence of the strong electric field that results at the surface from the charging of the metal slab. The large dipole moment of the water molecule (1.85 D) aligns with the local electric field at the interface. This leads to the specific orientation of the water molecules. At more-positive potentials the water molecules are aligned with their oxygen end directed toward the surface, whereas at more-negative potentials the hydrogen atoms point toward the surface. The resulting force on the water molecules at the metal surface is balanced by the direct bonding between the water and the surface, hydrogen bonding between coadsorbed water molecules, and hydrogen bonding with water molecules in the solution layer. The dipole moments tend to migrate toward the zone where the electric field is maximized (namely, close to the surface). This situation helps to explain why the second layer of water tends to move closer to the surface.

Above 1100 mV, the free energy of the hydroxide phase becomes lower than that of the water phase, thus resulting in a phase change. The water molecules bound through their oxygen atoms are initially activated. The reaction involves the formation of a proton along with a surface hydroxyl intermediate, both of which are stabilized by hydrogen bonding with neighboring water molecules in solution and on the surface. The proton that forms rapidly transfers to water molecules in the solution layer above the surface by means of proton shuttling (Figure 2 a). Proton transfer is enhanced in this way by the repulsive interaction between the solvated proton and the positively charged surface. Diffusion is thus the result of electromigration.

In addition to the direct water-activation path, the hydroxide ion that forms at the surface can subsequently assist in water activation by abstracting a proton from a water molecule in the second layer. This situation leads to the activation of water molecules in the second solvent layer. The change of structure from the water phase to the hydroxide phase is reversible with potential. Nevertheless, the potential associated with this change is discontinuous between these two routes. This discontinuity is related to the changes in the structure described above that occur between the two routes. Water dissociates to form a surface hydroxide ion and a hydrated proton. The structural reorganization that takes place upon dissociation ultimately leads to the resulting discontinuity. The structure that forms is shown in Figure 2 c.

At more negative potentials, the dissociation of water is activated by the interaction between the metal and the hydrogen atoms on water to form a surface hydride and a hydroxide anion that moves into the solution phase. The phase change between the water and the hydride route is calculated to occur at 0.5 V. The atomic hydrogen that forms is situated at the threefold-symmetric face-centered-cubic sites, whereas the hydroxide ion migrates away from the

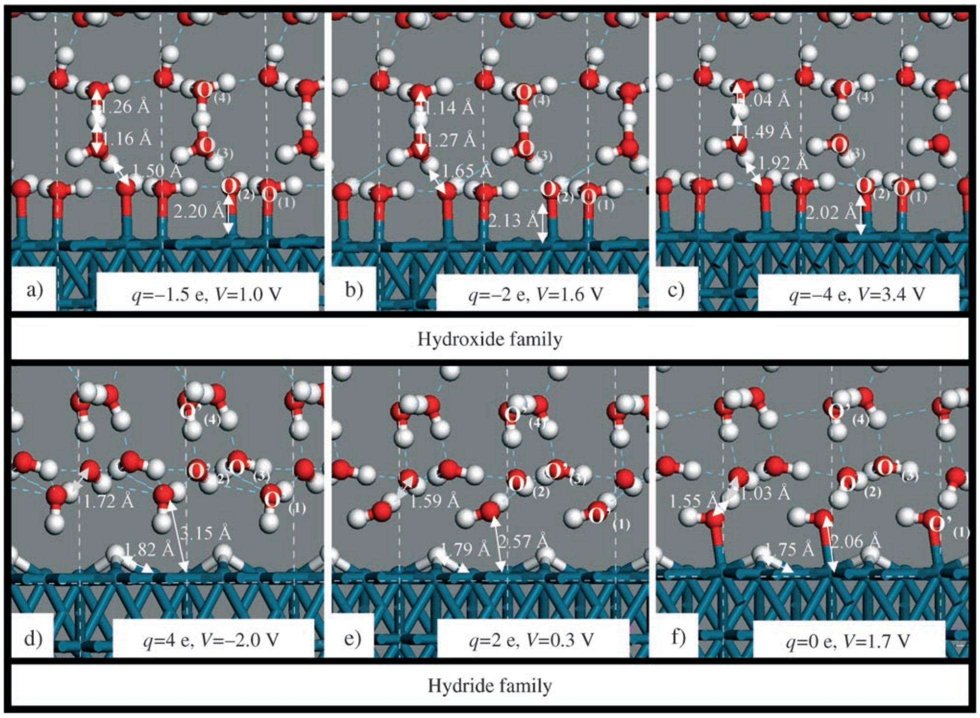

Figure 2. Evolution of the structure of the palladium/hydroxide interface (top of electrode) as a function of applied potential (a–c). The evolution of the palladium-hydride interface (bottom of electrode) as a function of potential (d–f). The associated metal potential (referenced to the NHE) and charge of the slab are presented in each case. The unit cell is outlined with a white dashed line. The blue dashed line shows hydrogen bonds.

surface through a sequence of rapid proton-transfer steps, and subsequently forms three hydrogen bonds with neighboring water molecules. At even lower potentials, the OH^- intermediate diffuses further away from the surface by means of proton shuttling along a chain of water molecules. Figure 2 d–f shows the transfer of the proton from $(O'_{(1)}H)^-\cdots(H_2O'_{(2)})$ to $(O'_{(1)}H\text{-}H\text{-}O'_{(2)}H)^-$ and then onto $(O'_{(1)}H_2)\cdots(O'_{(2)}H)^-$.

The discontinuity of the potential between the water and hydroxide routes at 0.5 V can be attributed to the transfer of an electron from the surface when one of the adsorbed water molecules dissociates to form the charged OH^- species and the surface hydride. This process allows for the reduction of the surface charge and an increase in the potential. When the potential of the cell is decreased further, the strong electrostatic repulsion between the surface and the OH^- ions leads to field-induced diffusion of the OH^- ions, even at 0 K.

The free energies for the water, hydride, and hydroxide phases can be followed as a function of potential and thus used to construct the phase diagram for the electrochemical activation of water shown in Figure 3 a. The most stable surface structure at potentials below 0.5 V is that of the hydride, which is accompanied by the formation of OH^- ions in solution. The most stable surface structure between 0.5 and 1.1 V corresponds to water adsorbed on Pd. The hydroxide surface is the most favorable at potentials greater than 1.1 V; in this case, the protons that form are stabilized as H_3O^+- or $H_5O_2^+$-type intermediates in solution. At any given potential, the energy difference between the water, hydride, and hydroxide curves constitutes the overall free-energy differences for the reactions that connect these phases. An important point to note is that the free-energy differences (reaction energies) change as the potential is changed. This is a result of the polarization of the interface. The lines drawn at 0.5 and 1.1 V in Figure 3 denote the phase transitions, where two different surface phases coexist. The surface phase can be transformed at constant potential by changing the number of electrons passed.

The evolution of the charge with the change in applied potential for the most stable states is presented in Figure 3 b. The variation of the charge with potential is nearly linear and displays capacitor-like behavior in which step changes occur as a result of the phase transitions. The slopes of the three lines are different from each other, which suggests that there are changes in the unit-cell capacitance that are linked to the strong change in the charge repartition. This is the polarization of the interface that leads to changes in the properties of the metal, such as adsorption and surface reactivity, as the potential is changed. Nevertheless, at 0.5 and 1.1 V, there are discontinuities in the charge. These discontinuities arise as a result of the phase transition between the two redox species at constant potential. This first-order phase transition is linked to the coexistence of two different species on the electrode surface that are interconverted on changing the charge [Eq. (4) and Eq. (5)].

$$\mathrm{Pd{-}H_2O} + 1\,\mathrm{e}^- \rightarrow \mathrm{Pd{-}H} + \mathrm{OH}^- \quad (\text{at } 0.5\ \mathrm{V}) \tag{4}$$

$$\mathrm{Pd{-}OH} + \mathrm{H}^+ + 1\,\mathrm{e}^- \rightarrow \mathrm{Pd{-}H_2O} \quad (\text{at } 1.1\ \mathrm{V}) \tag{5}$$

The electrochemical activation of water over Pd has been examined experimentally, thus allowing for a comparison with the theoretical results.[5,6] The electroadsorption of hydrogen

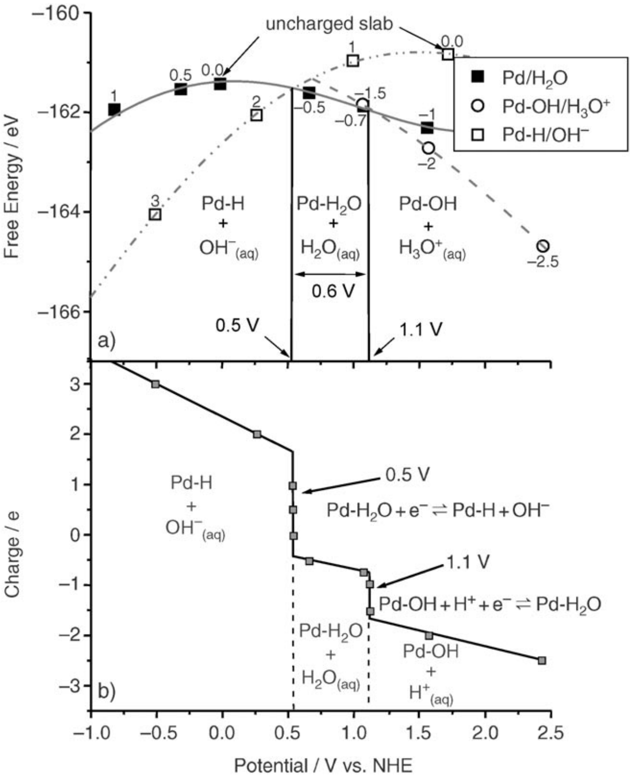

Figure 3. a) The evolution of the palladium/water interfacial free energy as a function of the biased potential referenced to the NHE. The number close to each calculated point is the slab charge. The most stable surface structure is the one that has the lowest free energy. b) The evolution of the slab charge with potential for the corresponding stable structures. The three different stable structures are presented. The associated electrochemical reactions associated with the transition from one stable structure to another one are given.

over Pd(111) takes place through the surface reaction Pd–$H_2O + 1e^- \rightarrow$Pd–H + OH^-, which proceeds experimentally at 0.4 V versus the normal hydrogen electrode (NHE).[6] This reaction was found to be irreversible. This experimental irreversibility is consistent with the large hysteresis found in our simulations in which hydrogen does not electrodesorb from the surface back into H^+ ions, even at much higher potentials (at 0 K). These observations suggest that hydrogen electrodesorption is a slow and activated process. The reversible formation of a hydroxide layer from adsorbed water was found by experiment[5] to occur at a potential of 0.7–0.9 V in acidic solution. The reversibility of this reaction is consistent with our results in which the switch from the water to the hydroxide route occurs directly. The experimental results show that the transitions from the surface-hydride to the surface-water phase and the surface-water to the surface-hydroxide phase occur at 0.4 V and 0.7–0.9 V, respectively. This is in good accordance with our results, which show transitions at 0.5 and 1.1 V, respectively.

The ab initio method developed herein enabled us to simulate the molecular changes in surface structure at the metal/solution interface during the electrocatalytic oxidation and reduction of water on Pd(111). The ability to simulate the polarizability of the water/metal interface was found to be important in predicting the appropriate response of the interface to changes in potential. The electrooxidation of water was predicted to occur at 1.1 V in an acidic solution. The electroreduction of water occurs at 0.5 V in a basic solution. Although the results may be improved by employing larger models of the surface and carrying out finite-temperature calculations, they still show reasonably good agreement with the experimental results. Adsorbed water is activated by the uptake of an electron from the metal to form an adsorbed hydride and an aqueous hydroxide ion. This reaction occurs through a similar proton-transfer path. The synergistic cooperation between the metal and the solution is required to activate water in both electrooxidation and electroreduction processes. The simulations tend to correctly capture other important physicochemical processes, such as the potential-dependent water orientation, the reductive and oxidative activation of water, and the electromigration of ions in solution. The method developed is general and should be applicable for following potential-dependent behavior of the interfacial transformations for many other electrochemical systems.

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Keywords: ab initio calculations · electrochemistry · phase diagrams · water chemistry

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