

Review Article

Atomistic Modeling of Corrosion Events at the Interface between a Metal and Its Environment

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Atomistic simulation is a powerful tool for probing the structure and properties of materials and the nature of chemical reactions. Corrosion is a complex process that involves chemical reactions occurring at the interface between a material and its environment and is, therefore, highly suited to study by atomistic modeling techniques. In this paper, the complex nature of corrosion processes and mechanisms is briefly reviewed. Various atomistic methods for exploring corrosion mechanisms are then described, and recent applications in the literature surveyed. Several instances of the application of atomistic modeling to corrosion science are then reviewed in detail, including studies of the metal-water interface, the reaction of water on electrified metallic interfaces, the dissolution of metal atoms from metallic surfaces, and the role of competitive adsorption in controlling the chemical nature and structure of a metallic surface. Some perspectives are then given concerning the future of atomistic modeling in the field of corrosion science.

1. Introduction to Corrosion Mechanisms

The following statement was made by Pletnev in regards to the corrosion of iron by chlorides in acidic media.

It is a common point of view that the chemical nature and structure of the surface of a metal, which is in contact with an electrolyte, are decisive in the kinetics of electrochemical reactions that proceed on this surface [1].

This “common point of view” is manifested in the great body of work in corrosion science that proposes mechanisms that explain how corrosion reactions occur (see, for instance, the monograph edited by Marcus) [2]. Corrosion in aqueous environments proceeds via an electrochemical mechanism, in which the coupled anodic and cathodic reactions take place at unique sites within the material/environment interface. The reactions themselves involve transfer of electrons or ions—often both—across the electrochemical double layer [3]. For this reason, the mechanisms via which corrosion

proceeds can be strongly influenced by perturbations in the surface and interfacial environment.

In many cases, the chemical reactions that together constitute a proposed mechanism or reaction scheme should be considered as placeholders: representative entities that subsume a host of microkinetic processes such as mass transport, surface adsorption and desorption, and bond-making/bond-breaking chemical reactions. Pletnev’s “chemical nature and structure” of the materials/environment interface are, in fact, rather complex quantities. Figure 1 contains an illustration that presents, schematically, some of the important elements of this interface and the processes relevant to corrosion [4].

Important classes of variables that impact the process and nature of corrosion in a material include the temperature, local environment, and the stress on the material. Environmental factors may include flow rates, pH, and speciation [5, 6]. The nature of the electrolyte is also significant: different corrosion mechanisms may be favored when the electrolyte is changed [7]. The conductivity of the electrolyte also affects the Ohmic drop in potential between the cathodic

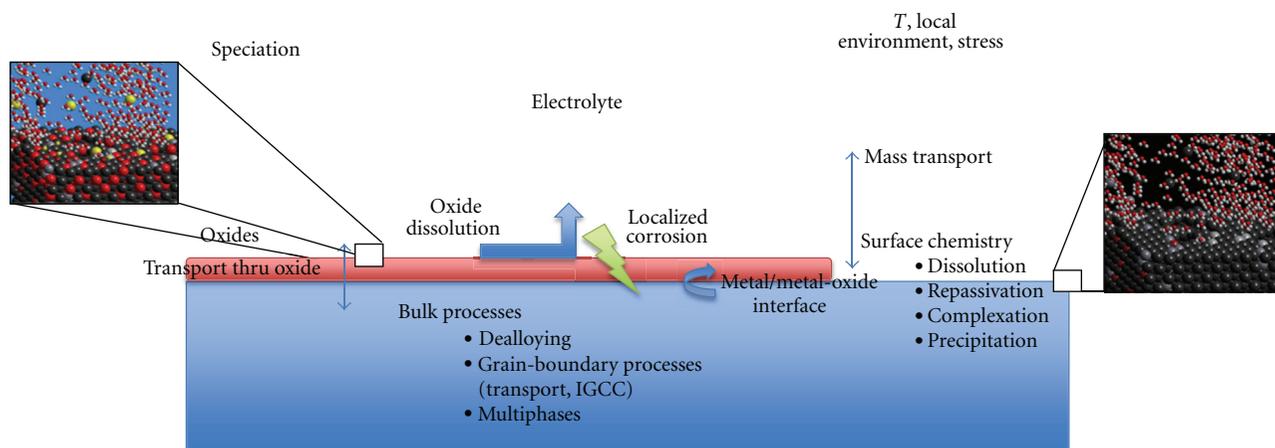


FIGURE 1: Schematic of the materials/environment interface. Features relevant to corrosion are labeled. Reproduced from [4].

and anodic reaction sites in situations such as crevice corrosion and pitting [8]. Mass transport processes at the interface often define the kinetics of corrosion reactions. These processes may occur across a hydrodynamic boundary layer, through an oxide film, or involve migration of species within the metallic component [9–13]. Each of these rates may be corrosion limiting. The microstructure of the metal itself can have important consequences for the process of corrosion. Corrosion may be intergranular, in which case corrosion occurs preferentially at the grain boundaries [14–17]. Crystallographic pitting has been observed in some cases, where the corrosion morphology reflects the crystallographic order of the material substrate [18, 19]. Galvanic coupling can occur between precipitates in the material and the bulk matrix [20], and stress-corrosion cracking pathways may be controlled by microstructural effects and phase distributions [21]. Grain boundary engineering has, in some cases, been employed to optimize corrosion resistance of certain materials [17, 22, 23].

While not comprehensive, the above list serves to illustrate that corrosion rate is a highly nonlinear function of multiple materials and environmental variables. This nonlinearity is, ultimately, the reason why, for some scientists and engineers, corrosion science presents such a rich and complex field of study.

2. Atomistic Models

Scientists working in the fields of surface science and solid-state physics have made it possible, in recent years, to directly simulate interfacial reactions with atomistic resolution using electronic structure methods or interatomic potentials, finding particular applications in the design and modeling of heterogeneous catalysts [24–26]. Whereas heterogeneous catalysis might be described as the deployment of a material to manipulate its environment, corrosion is the inverse process: the modification and depletion of a material by its environment. The deterioration of a solid-state material as a consequence of its interactions with a fluid phase, however, involves processes that are typically slower and involve

higher-energy transition states than the catalysis of a molecular transformation by a substrate [27]. Although it is not, at the present time, possible to include all of the elements contained within Figure 1 within some massively parallel computational simulation of corrosion (although for some particular mechanisms and materials this has been attempted) [28, 29], it is possible to deconstruct certain elements deemed to be critical within a given application. For instance, in cases of localized corrosion or corrosion cracking, one may focus on the chemistry occurring at a bare-metal/solution interface [30–32]. In cases where oxide growth is relevant, one can focus on ensembles that consist of defect states in the oxide material [33, 34]. It is also possible to look at dissolution processes from oxide surfaces or to interrogate questions regarding bulk or surface thermodynamic stability [4, 35, 36]. The field of computational materials science is currently growing such that, by coupling continuum kinetic or fracture mechanics models with atomistic scale codes or phase-field theory, it may soon be possible to realistically simulate increasingly comprehensive portions of Figure 1 [28, 29, 37]. The list of examples and references provided in this section should by no means be considered comprehensive, but it is an attempt to capture recent efforts, as well as historical modeling studies that are relevant to scientific studies of corrosion phenomena conducted in the present research group.

Atomistic modeling techniques can, at present, be grouped into four main categories: molecular modeling, static band-structure calculations, molecular dynamics, and Monte Carlo methods [38–40]. Molecular modeling encompasses the field of (generally) small-molecule calculations [40]. Molecular orbital theory is used to solve the electronic structure problem, which in turn allows access to molecular properties, such as HOMO-LUMO (highest occupied and lowest unoccupied molecular orbitals, resp.) gap, bond lengths and bond angles, and energetics of reactant, intermediate, transition, and product states. Extensions of molecular orbital theory allow, for example, the modeling of cationic states of metals when dissolved in solution phase [41, 42], the study of metallic nanoparticles [43], investigations of

bonding of water and oxygen to metal atoms and clusters [44, 45], and the evaluation of molecular properties of chemical inhibitors [46, 47].

Static band-structure calculations are drawn more from the fields of density functional theory and solid-state physics [48]. These calculations were originally developed to evaluate the properties of solids, in a similar way to how molecular orbital theory calculations are used to evaluate the properties of molecules. From a reaction point of view, the electronic and atomistic properties of reactant, product, intermediate, and transition states can also be evaluated using these methods, allowing insights to be gained regarding rate-limiting steps, for example, in mass-transport processes such as solid-state diffusion [49–51] or phase transformations [52]. These techniques can be extended to look at surfaces as well, as has been applied heavily in the field of heterogeneous catalysis [24] and electrocatalysis [25], and, more recently, to problems in corrosion [35, 53–57]. This technique, as well as molecular modeling, is limited primarily by the computational cost of performing such calculations. Ensembles containing small numbers of atoms, either isolated as a cluster in space or in cells with periodic boundary conditions, must therefore be carefully constructed to imitate the system one is trying to model, and the appropriate caveats should be given regarding artifacts that may be induced by these idealized conditions. Furthermore, the inability to readily incorporate dynamic effects means that reactions which require significant thermal reorganization—such as the formation of solvation shells around ions during a dissolution event—may be difficult to capture reliably. Overall, however, these methods can be powerfully applied to interrogate detailed, atomistically resolved reaction mechanisms and mass transport processes relevant to corrosion. Their dependence upon electronic structure evaluation makes them the most flexible and reliable, in terms of fundamental, deterministic physics but, at the same time, makes them exceedingly expensive in terms of computational cost and user time.

Molecular dynamics simulations can be used to simulate reaction events, particularly those involving high energy or thermally stimulated processes. While simulations using electronic structure techniques to evaluate the forces on atoms and their thermal trajectories can be performed, the cost of such methods is usually far too high to enable useful time scales to be reached within the scope of the simulation. Therefore, modelers employing molecular dynamics will typically apply interatomic potential techniques. These techniques employ simple algorithms for evaluating forces on atoms as a function of their relative positions in space, for example, the embedded atom method [58–60]. Based on this technique, one can simulate the evolution of corrosion morphologies, diffusion processes in materials, the behavior of defects in materials, such as grain boundaries, and the rates at which oxidation or other processes occur. Examples include the oxidation of aluminum and zirconium metals [28, 34], the structure of the metal/water interface [61–69], and the evolution of radiation damage effects in nanolayered materials [70].

Kinetic Monte Carlo simulations go beyond dynamic effects but utilize atomistically determined information for the rate constants of fundamental atomistic and molecular transformations to perform stochastic updates to the state of a system, which, in this context, may be considered its atomistic configuration [71, 72]. This method, therefore, is not limited to dynamic time scales but, instead, depends on the accuracy of the rate information passed to the model from lower length scale models. These models have been applied to look at atomic and molecular arrangements of adsorbates on metal surfaces [73] and growth of molecular films [74], as well as to bimetallic dissolution problems [75–77]. Monte Carlo models can also be applied to search for equilibrium structures, such as crystallographic pitting morphologies or defect clusters in materials such as metals and oxides [78, 79].

In the following, several applications of atomistic modeling to understand the details of various corrosion reactions are reviewed, drawing primarily upon studies performed within our research group. The paper concludes with a perspective on the state of contemporary modeling in corrosion research and some statements concerning our expectations for the future of this field.

3. Electrochemistry of Water on Metallic Surfaces

The structure of water molecules on metallic surfaces has been studied by various experimental and theoretical methods [80, 81]. One detail that has emerged from these studies is that liquid water tends to be more structured at the interface, due to the necessity for water molecules to arrange in such a way to preserve hydrogen bonding characteristics, despite the discontinuity presented by the interface [63, 81–83]. Additionally, metal-water interactions may impose their own preferences/constraints on the interfacial structure of water [84, 85]. A common model that has been adopted by modelers and experimentalists alike is the “bilayer” [86]. In this structure, water molecules adsorb at atop sites on the metal surface via donation of electron density from the lone pair on oxygen to the frontier orbitals or “dangling bonds” of the surface metal atoms. A second layer of water molecules arranges on the surface in such a way as to form hexagonal overlayer hydrogen bonded to the water molecules directly bound to the surface. Molecular dynamics simulations have suggested that such networks are rather stable on many metallic surfaces, and this general picture has been supported by neutron diffraction experiments [63, 82, 83].

In a work we recently performed to examine the role of ordering of water molecules in crack tips, motivated by the observation of fast transport of ions to the crack tip during stress-corrosion cracking [87], we utilized the *ab initio* molecular dynamics technique to examine the emergence of water structure on the Ni(001) surface [88]. A short molecular dynamics simulation was performed using density functional theory and the Hellman-Feynman theorem to determine forces on the atoms [38]. The code VASP was used to perform these simulations [89–93]. The simulation was

short in the sense that only a few picoseconds of time could be simulated, whereas estimates of 100 ps for water equilibration in supercell molecular dynamics simulations have been given in the literature [94]. The simulations are performed using three-dimensionally periodic supercells. This geometry allows the band structure of the exposed Ni(100) surface to be modeled realistically, as well as for bulk water to be imitated in the periodic ensemble. The periodicity in the direction normal to the slab means that the simulation is actually considering an array of nickel slabs, spaced about 2 nm apart. Similar choices are often made when simulating surface chemistry, as the slabs are usually spaced far enough apart to avoid direct interactions. However, in the case where the environment may possess some ordering, we may expect that the interaction between slabs could become more significant. In this way, the simulation we are performing is somewhat imitative of the situation in which there is a tight 2 nm width crack front.

Over the course of the molecular dynamics simulation, the position of the oxygen atoms was monitored to look for evidence of structure, as opposed to homogenization, across the entire volume of the fracture space. The probability distribution for oxygen atoms obtained from the molecular dynamics simulation is reproduced here in Figure 2. Similarly to the previous findings cited above, water molecules show some ordering in the region close to the metal. This ordering can be discerned by the presence of pronounced peaks in the distribution function of oxygen close to the interface. Since the slab spacing is small in this simulation (2 nm, or enough for 5 water layers), the ordering appears to persist throughout the entire region of the simulation cell. This result implies that a 2 nm crack is sufficiently narrow to confine the water molecules in such a way as to enforce certain “packings” of the water molecules. From a surface point of view, the results suggest that some ordering of water molecules may be expected to occur for a distance of up to 1 nm from the metallic surface. This ordering of water molecules will have implications for the diffusion of ions and molecules along surfaces, such as the newly formed surfaces that grow during a cracking event, or penetration along internal cracks in a substance.

In addition to organizing into “ice-like” configurations, water molecules have the opportunity to react on metal surfaces to form hydrided surfaces, oxidized surfaces, or hydroxylated surfaces [95]. The nature of this reaction is strongly dependent on the identity of the metal, as well as the electrochemical potential. For instance, as the electrochemical potential is made cathodic, the Fermi level of the metal is raised, which makes electron transfer to the protons in water to become more favorable, leading to the formation of atomic hydrogen via the mechanism:



On the other hand, making the surface more anodic depletes electrons from the metal, lowering the Fermi level

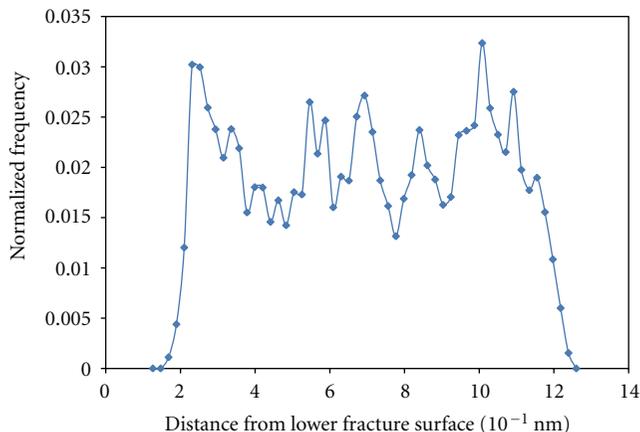
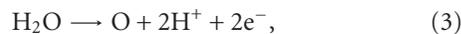
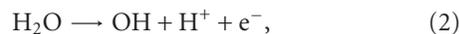


FIGURE 2: The ordering of water molecules during molecular dynamics simulation of the region in between the two Ni(100) fracture surfaces exposed to water. The normalized frequency refers to the frequency with which oxygen may be found at a given distance from the electrode surface, normalized such that the integrated frequency goes to unity.

and thus making the metal a good electron acceptor. Hence, such reactions as



become energetically favorable.

In previous work, we developed a methodology for simulating the electrochemical double layer in density functional theory models of interfaces [96]. Using this method we were able to predict the potentials at which hydrogen, water, hydroxide, and oxygen are stable species on metallic surfaces, such as Ni(111) [30, 31]. These predictions are represented in Figure 3, which plots the free energy for each of the possible surface phases (OH, O, H, and H₂O) that may be produced when water reacts with a metallic surface. The free energies are obtained by computing the energy of slab models for the surface that consist of several layers of Ni(111) planes, exposed to a supercell of water molecules, in addition to the adsorbed surface phase. The energies are corrected for the electrochemical potential using the method cited above [96]. The results correlated well with experimental determinations for the onset of oxidation of the metallic surfaces [97].

We also used the same technique to directly evaluate the nature of bonding between copper and hydroxide [98]. We found that, even when significant changes in the electrochemical potential were made, the overall binding energy did not change significantly, and this was attributed to the fact that, when the Fermi energy of the metal was raised or lowered in response to changes in the applied potential, the orbitals of the bonding hydroxide species tended to follow. The adsorption geometry, on the other hand, did change significantly, with rotation of the OH dipole moving in such a way as to counteract the electric field across the double layer. The binding of water, on the other hand, does

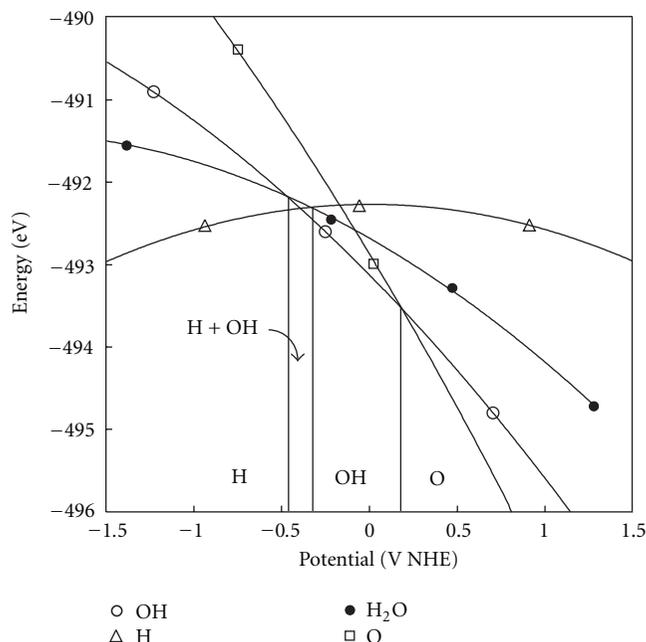


FIGURE 3: Phase diagram for surface hydride, molecular water, hydroxy and oxy species on Ni(111) at pH 0. Reproduced with permission from [30].

change more significantly, because the orbitals on water molecules are engaged much more weakly with the frontier orbitals on the metal surface; the metal-oxygen bond in the chemisorption of water is such that the highest occupied molecular orbitals on the water molecule are beyond the range of the electrochemical double layer. This relationship between the electronic structure of the metal (FERMI and D in Figure 4) and the hydroxyl molecular orbitals (S1 and P11, P12, P13 bands in Figure 4) and the water molecular orbitals (S2, P21–P24 in Figure 4) is shown as a function of the applied surface charge in Figure 4. It can be seen that the energy levels of the hydroxyl, which is bonded to the surface, closely track the Fermi level of the metal, whereas the energy levels associated with the water molecule are only weakly correlated.

In the same study we tracked the change in the OH geometry as the potential was made more anodic. During this process, the proton of the adsorbed OH begins to transfer to the second layer of H₂O close to the interface, tending towards the formation of H₃O⁺ and an adsorbed O species (an important step in surface oxidation by H₂O). One consequence of this OH-H₂O adduct formation is an increase in the capacitance of the system due to the delocalization of positive charge across the first “inner-layer” of the solution environment. These simulations represent prepassive chemistry: events that will occur prior to, or during, the formation of passive oxide layers on nickel and copper metal.

In a related study, a series of geometry optimizations was performed for a model Cu(111)-H₂O interface, with the potentials made successively more anodic at each step [99].

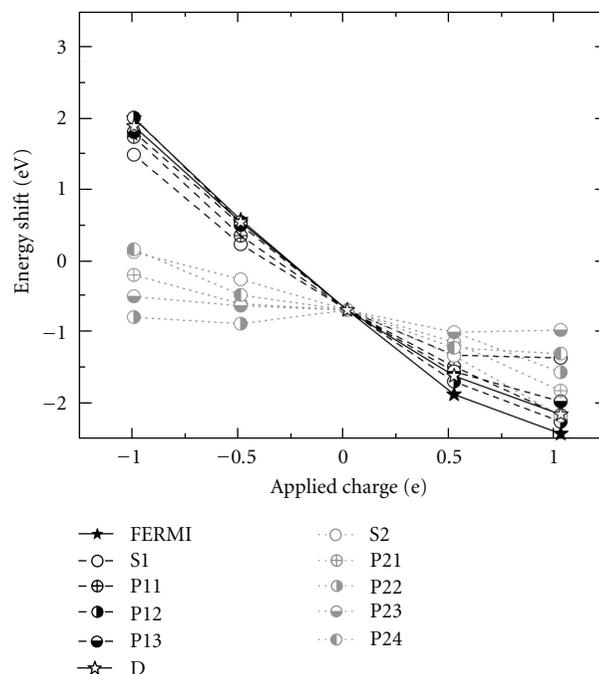


FIGURE 4: The shifts in energy of the Fermi level, copper d-band center (D), s and p bands of the oxygen of adsorbed OH (black symbols, dashed lines, S1, P11, P12, P13), and s and p bands of the oxygen of first-layer water molecules (gray symbols, dotted lines, S2, P21, P22, P23, P24) relative to the zero-charge values. Reproduced with permission from [98].

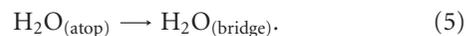
The model was, therefore, set up in an equivalent way to a cyclic voltammetry experiment, although kinetic processes were not explicitly taken into account. When the resulting geometries were plotted, it could be seen that, given a threshold surface charge density, phase transitions on the surface could be expected to emerge. These began with the simple water dissociation reactions, described above, but ultimately led to destabilization of the metallic copper surface and place exchange between the electron-rich oxygen species and the electron-depleted copper atoms. This series of phase transformations is plotted in Figure 5.

The stepwise charging of the model system and subsequent relaxation of the atomic structure prompted the following structural changes (Figure 5).

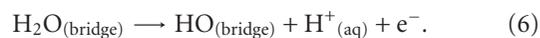
- (a) Chemisorption of H₂O to the atop site of a Cu atom:



- (b) Migration of H₂O from the atop site to a bridge site:



- (c) Deprotonation of the bridging H₂O to form OH_{ads} + H⁺_{aq} + e⁻:



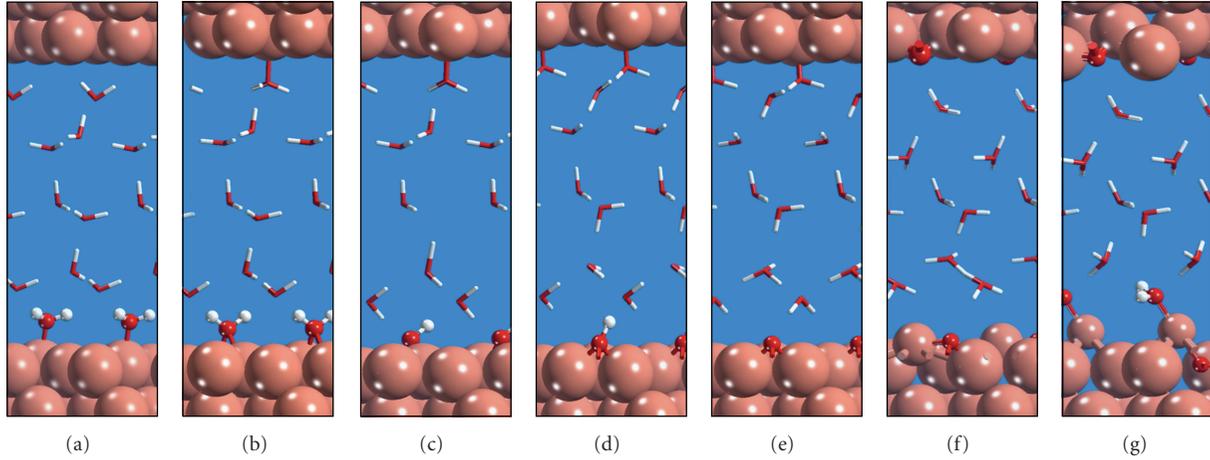
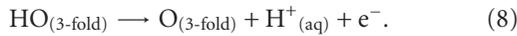


FIGURE 5: Charge-induced reaction sequence for the activation and migration of H_2O (a)–(c), OH (c)–(e) and O (e)–(g) on $\text{Cu}(111)$, followed by oxidation of Cu (f)–(g) effected by adsorbed oxygen [99].

- (d) Migration of the bridging OH to the threefold hollow site, consistent with the emergence of a second type of OH resonance in the surface enhanced resonance spectrum recorded by Niaura [100]:



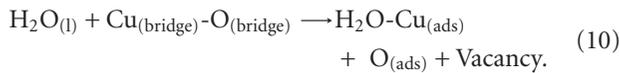
- (e) Deprotonation of OH_{ads} to form $\text{O}_{\text{ads}} + \text{H}^+_{\text{aq}} + \text{e}^-$:



- (f) Surface reconstruction by eruption of a Cu adatom from the surface layer. Adsorbed oxygen acts as a tether:



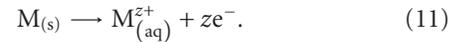
- (g) Complete displacement of the copper adatom by oxygen, resulting in a Cu_2O -like adlayer, in which O is adsorbed at the vacancy site left by the Cu atom, and this partially adsorbed Cu atom is now coordinated to H_2O , according to the reaction:



We have since generalized this work to a larger range of transition metals using a simplified version of the technique that does not require polarization of the interfacial cells but simply shifts the free energy of electrochemical reactions by an energy term $nF\Delta U$ [32]. This method works most simply when the transfers of an electron and proton occur simultaneously, as in the reaction schemes presented above, as these energies can be related to the energy of H_2 for a reference potential of the standard hydrogen electrode. The utility of this method to capture the leading terms for the free energy changes of electrochemical reactions was demonstrated in a joint paper between our research group and that of Rossmeisl and Nørskov [101].

4. Dissolution of Metal Atoms

Having demonstrated the capability to model the electrochemical reactions involving water on bare metal surfaces, we moved on to consider what is perhaps the quintessential reaction in any aqueous corrosion scheme—the dissolution event itself. This reaction is typically expressed by the chemical equation:



The above chemical equation highlights a tension between the forces of metal-metal bonding and the formation of bonds with species present in the aqueous solution. An analysis of the complexity contained within this tension was recently made through a series of papers published by Gileadi [27, 102, 103]. To understand how theoretically challenging this concept is, consider that molecular water is bound to transition and noble-metal close-packed surfaces by energies no more than a few tenths of an eV [104], whereas the surface cohesive energies are an order of magnitude greater [105]. The reason that such dissolution events do occur, on a regular and (from a corrosion mitigation perspective) inconveniently frequent basis, is that electric fields at the interface (of order $0.1 \text{ V}/\text{\AA}$) provide a gradient sufficiently strong enough to stabilize the formation and extraction of that metal atom in its ionic form [102].

One way to interrogate this process via atomistic simulation is to begin by simply considering the role of metal-metal bonding in controlling corrosion morphologies. This issue has been addressed previously to some extent via kinetic Monte Carlo simulations of the dealloying of binary alloy systems and of crystallographic pitting [75, 76, 106]. We recently published work on Fe-Tc systems, showing how the degree of local coordination and local composition affect metal atom cohesive energies [4]. It was shown in that work that the number of nearest neighbors alone was insufficient, however, to capture the strength of these interactions, but that the organization of these neighbors was of great

significance. We performed a similar study on nanoparticles, close-packed and stepped surfaces of copper, and showed that generally surface cohesive energies correlated linearly with the number of nearest neighbors, but significant noise existed in this correlation such that individual topological features must indeed be taken into account [105].

Because it is fundamentally challenging to directly model the interplay between metal-metal cohesion and metal-solvent attraction using typical materials dynamics simulation techniques (such as embedded atom potentials) [107–110], we decided to build a model system that could explore aspects of the dissolution reaction using highly controlled, density functional theory calculations [111]. The model we built to study this system consisted of a Cu nanoparticle, with a single Cu adatom adsorbed on the surface in contact with a hemispherical “nanodroplet” close to a dozen water molecules (see Figure 6(a)). The metal particle was designed to be large enough to provide a fair representation of metal-metal bonding and electronic band structure, and the solution model is sufficient to model one to two layers of an emerging ion’s solvation sheath. The configuration of the solvent molecules was obtained by performing a quantum mechanical molecular dynamics simulation at 300 K and then cooling the system to an annealed configuration, which was governed by the hydrogen bonding between water molecules and their interactions with the metal particle. We then performed a series of geometry optimizations, similar to what had been performed for water molecules on Cu(111) surfaces in the study mentioned above, but rather than varying the system charge state, we varied the height of the metal atom above the particle surface stepwise.

To understand some of the mechanistic details of the study we performed the simulation under three separate sets of conditions (no water, water, and water plus an applied electric field, thus simulating a double layer). We plotted the charge states of the adatom as a function of the height above the surface (or, equivalently, as a function of the dissolution process), as well as the associated energies (Figures 6(b) and 6(c), resp.).

In the absence of solvent, the energy of the adatom appears to rise in a quasi-harmonic way, which will at some point vary from harmonicity and tend asymptotically to the value for the surface-binding energy of the adatom. There is some weak charging of the surface adatom. When the solvent molecules are present, the charge on the adsorbed copper atom is significantly more cationic. The Bader method yields a charge of +0.36 for the copper adatom in the solvent phase, even before dissolution occurs. Thus water molecules appear to “pre-charge” adsorbed metal atoms on the surface, as they form a partial solvation shell around the adatom. As the bond is broken (due to raising of the surface metal atom), the energy increases, as does the charge. Furthermore, the copper atom begins to form more and more bonds with the surrounding water molecules, eventually obtaining a rudimentary solvation shell.

The early part of the energy-distance curve, for distances less than 1 Å, is not so different from the case of the vacuum or “no solvent.” It appears that *the energy in the early stages of dissolution is mostly concerned with the strong effect of*

breaking bonds with the metal surface. In the latter part of the curve, for distances greater than 1 Å, the formation of bonds with the solvent environment alleviates the high energies incurred when the metal-surface bond is broken, in agreement with the “make-before-break” argument as posed in the manuscript by Gileadi [102]. The development of what appears to be a +1 charge on the Cu ion may be an indicator that the +1 state develops first, and then transition to +2 takes place as an outer-layer, electron-transfer event. The application of the electric field further lowers the energy trajectory of the dissolving ion.

5. Surface Chemistry Control of Corrosion Processes

Although water chemistry and bare-metal dissolution remain important focus areas for the development of our understanding of corrosion mechanisms, in many cases corrosion takes place in more complex media. For instance, in the oil and gas industry, it is known that numerous corrosion processes take place simultaneously, and, depending on the local conditions, one or other of these processes will be dominant at a given location [112]. Documented corrosion mechanisms that occur during crude oil refining operations include ammonium-chloride corrosion, ammonium bisulfide corrosion, high-temperature sulfide corrosion, cyanide accelerated corrosion, or stress corrosion cracking that may be brought on by hydrogen, chloride, sulfide, or carbonate [112].

Recently, we embarked upon a study of ammonium chloride corrosion mechanisms, focusing on the surface adsorption processes associated with this reaction scheme [113]. Ammonium chloride corrosion occurs when conditions in the process stream are such that the ammonia and hydrogen chloride in the vapor phase crystallize as hygroscopic NH_4Cl particulates and interact with condensed water vapor to form highly saturated chloride solutions attended by aggressive corrosion behavior [112, 114, 115]. It was demonstrated by Shimbarevich and Tseitlin that increasing the chloride content for a given NH_3 concentration can cause enhanced corrosion, and it was suggested that this occurs due to adsorption of chloride ions on the surface and the subsequent enhancement of anodic dissolution process [116]. At the same time it was shown that increasing the NH_3 concentration made the solution more basic, thus favoring OH adsorption on the surface, as opposed to Cl adsorption and hence hastening passivation [117].

In order to begin to understand the significance of surface processes to the corrosion mechanism occurring when mild steel is exposed to ammonium chloride and to attempt to evaluate these mechanisms that are driven by consideration of surface processes, we applied the techniques we had developed for water-metal interfaces to a more complex mixture of reactive species. In particular, we modeled the competitive adsorption of NH_x , OH_x , H, and Cl species on an exposed Fe(110) facet as a function of the local electrochemical potential. The relevant phase diagram, computed

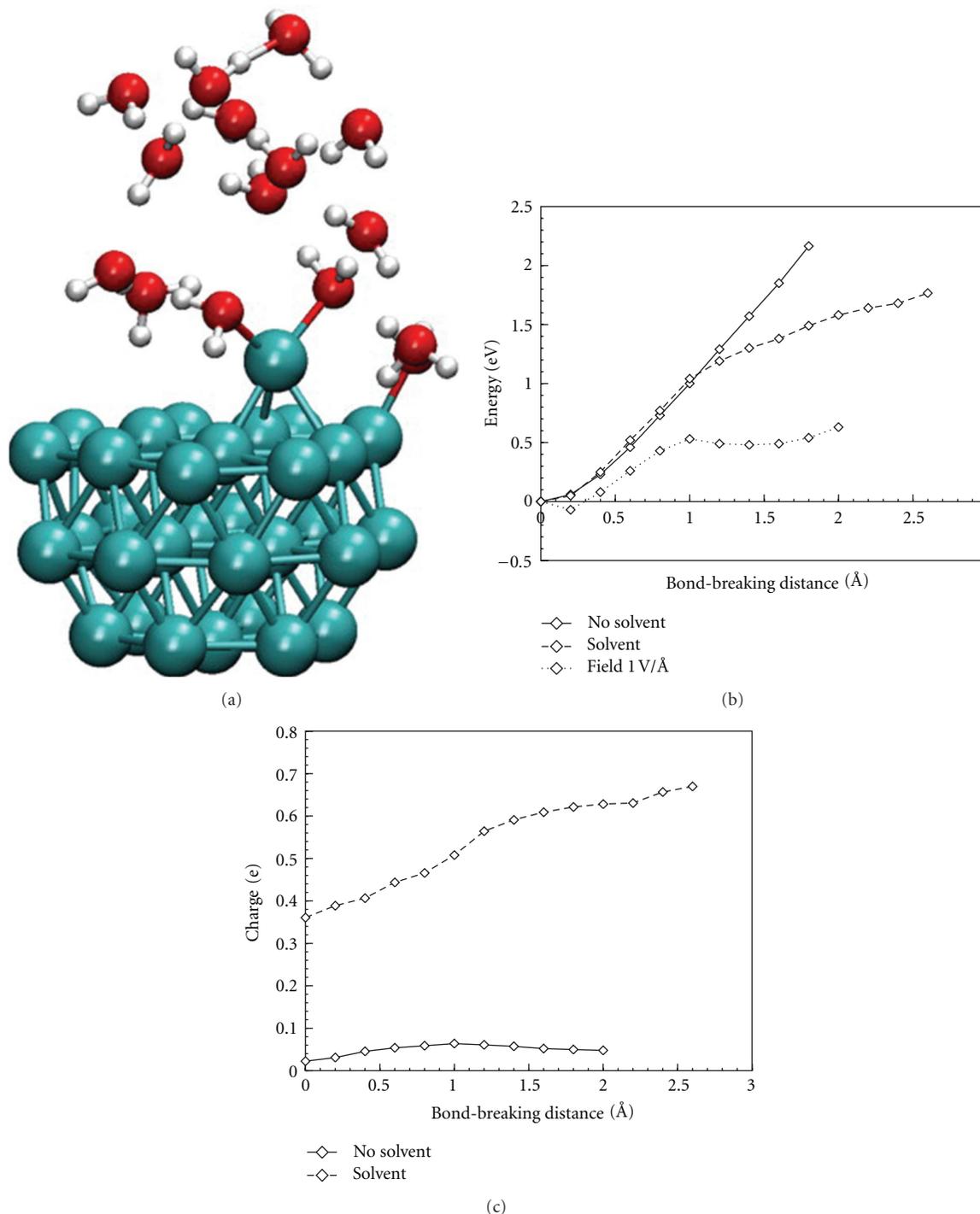


FIGURE 6: (a) Initial solvent-metal particle configuration, (b) electronic structure energies for dissolution/bond-breaking of a copper atom in proximity to a (111) copper surface, and (c) charges determined by the method of Bader for the copper adatom being “dragged” away from the (111) copper surface. Reproduced with permission from [111].

using our density functional theory slab calculations, is presented in Figure 7.

Figure 7 was calculated using a particular set of boundary conditions that apply to a saturated NH_4Cl solution, mimicking the case when a hygroscopic NH_4Cl salt film precipitates on the surface of a mild steel component.

Similarly to the case of water of transition metal surfaces, there is a range of H, OH, and O stabilities. Chloride in the solution phase, introduced by the equilibration of NH_4Cl salt film with condensed water, can also be adsorbed on to the surface between the electrochemical potentials of -450 and -420 mV SHE. In this window, which corresponds to

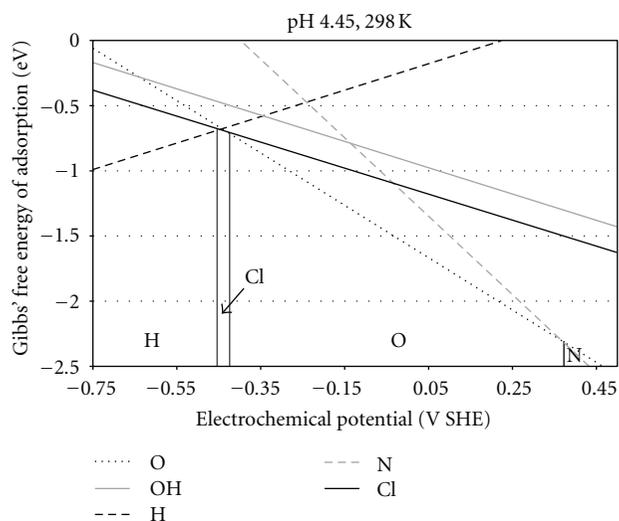


FIGURE 7: Free energy diagrams for surface coverage of the Fe(110) surface when exposed to a saturated NH_4Cl solution at pH 4.45 and 25°C (298 K). Reproduced with permission from [113].

the important prepassive state, chloride may be active in accelerating the corrosion of the mild steel [1]. Chloride may also inhibit passivation by displacing oxygen from the surface [116, 118]. The high concentrations of ammonia present also lead to the prediction of a nitrogenated surface beyond 370 mV SHE (although at this potential a bare iron surface is unlikely, unless cracking of the oxide film occurs, or the film is destabilized by some other chemical reaction). Similar diagrams can be constructed for other systems, in which the pH may be buffered to a more alkaline value or at different temperatures. The surface analysis generally supports the overall mechanisms proposed by Pletnev et al., Shimbarevich and Tseitlin, and Alvarez and Galvele [1, 116–118], although a more detailed model coupling surface thermodynamics, kinetics, and mass transport processes would be required to provide a more comprehensive understanding of the problem.

6. Perspectives

In this paper we have highlighted three specific cases where atomistic modeling has provided additional insight into the pathways via which important corrosion processes, including prepassivation and water chemistry, metal dissolution, and competitive adsorption, may occur. In particular, computational modeling of atomistic processes allows the scientist to directly assess the applicability of various corrosion mechanisms to a particular materials/environment combination and to characterize the nature of the interface at nanometer-subnanometer resolution.

At the same time, there is still some way to go for the computational science community to be able to represent the kinds of length and time scales associated with the

macro- and mesoscopic corrosion processes. Some of these challenges include:

- (1) capturing adequate dynamic time scales for the rearrangement of solvent particles around atoms undergoing dissolution,
- (2) capturing not only details of the metal/environment interface but also the metal/oxide and oxide/environment interfaces,
- (3) Incorporating the very important effects of alloying components in both the metallic and oxide states in both solid solution and as particle inclusions,
- (4) Including the role of defect states, such as step edges, terraces, roughened surfaces, grain boundaries, and dislocations as potentially the most active sites at which corrosion events are going to occur.

The development of such advanced toolkits, using either state of the art potentials, such as the reactive force field [119], or multiscale modeling projects [28, 29, 37], is an active focus in our current portfolio of research projects.

That is not to say that the present toolkit does not allow the determination of meaningful insights into corrosion science. Using the kinds of density functional theory calculations, we have described above it is possible to do the following.

- (1) Predict thermodynamic and kinetic parameters for fundamental processes on metal and metal-oxide surfaces, such as water dissociation and adsorption of molecular and atomic species (such as NH_3 and Cl).
- (2) Understand the role local binding and morphology have on the thermodynamic cohesive energies of metal atoms exposed to the environment.
- (3) Explore dissolution trajectories and the influence of environmental species in raising or lowering the activation barriers to such processes. Consider, for example, the metal atom dissolution described in Section 3, but replacing a water molecule with a different ligand, such as chloride or nitrate, for example.
- (4) Adsorption and absorption of solution phase species, including hydrogen, for hydrogen embrittlement scenarios.
- (5) Computation of fundamental atomistic parameters for utilization in higher-level kinetic Monte Carlo simulations or phase field models.

The above five examples are just a subset of the kinds of simulations currently being performed for corrosion-related problems in the materials science literature. We anticipate many new applications developing that go beyond the specifications outlined here, as more groups adopt atomistic modeling within their research toolkit, and new algorithms and synergies with continuum or mesoscale techniques are developed.

A final point should be made regarding experimental validation. First-principles modeling techniques are subject

to variation depending upon the granularity and accuracy of the physics approximations used in their construction. For this reason, it is not uncommon to find variations, for example, in binding energies of molecules and materials calculated using different methods of 30–50 kJ/mol. Similarly, structural features, such as bond lengths and lattice parameters, can also be subject to variation depending upon the physics model selected. For these reasons, it is imperative that an equal, if not greater, effort continues to be applied in the characterization of interfacial phenomena using high-resolution, surface-specific probes (scanning tunneling microscopy and surface-enhanced Raman spectroscopy, e.g.). Improving resolution in both time and length scales is critical to provide the guidance needed for the improvement of the physics models that underlie the kinds of simulations described in this paper. As is the case in most research areas, advances in the understanding of corrosion processes can occur when a synergy is applied between the theoretical and experimental sciences.

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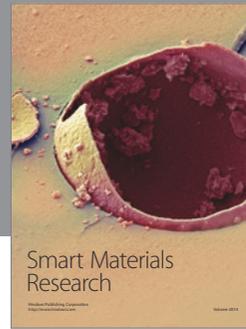
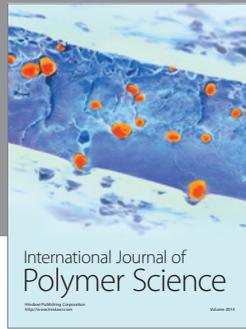
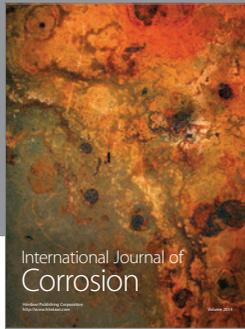
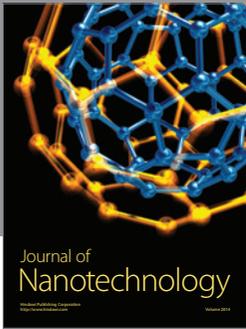
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