



Atomistic simulation of initial stages of iron corrosion in pure water using reactive molecular dynamics

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ABSTRACT

Reactive Force Field Molecular Dynamics (ReaxFF-MD) was used to study the initial stages of iron corrosion in pure water. The simulations were performed on iron under various applied external electric fields and temperatures. Oxide film formation was accompanied by iron dissolution in water, indicating active corrosion and supporting the expected thermodynamic behavior of iron in pure water. Oxide film thickness and iron dissolution increased with increasing applied external electric field. Corrosion rates increased slightly with increasing temperature within the temperature range of this investigation (300–350 K). Critical stages of the iron corrosion process during the simulations were identified as dissociation of water to OH⁻ and H⁺, adsorption of OH⁻ on the iron surface, penetration of oxygen into iron to form iron oxides, and dissolution of iron into solution. Comparisons of the simulated charge distributions and pair distribution functions to those of reference oxides showed the formed oxide compositions were not pure phases, but rather a mixture of oxides.

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1. Introduction

Corrosion of steel reinforcement is one of the most prevalent deterioration mechanisms in reinforced concrete structures. The annual cost of corrosion in highway bridges alone is estimated to be above \$8 billion, but it is widely accepted that the costs have increased over the past decade [1,2]. Therefore, there is a critical need for the development of innovative, inexpensive, and ubiquitously effective corrosion mitigation strategies in the form of new corrosion-resistant steels and corrosion inhibitors. The development of these new materials has been hindered by the gaps in the fundamental understanding of the passivity of steels in concrete and lack of tools to intelligently design and test them. Trial-and-error procedures to produce new and affordable materials to resist steel corrosion in concrete have been, to a large degree, ineffective.

Passivity and chloride-induced depassivation of iron and carbon steel in highly alkaline environments, such as the ones provided by concrete (pH > 13), have been studied extensively using electrochemical [3–14] and nano-scale surface characterization techniques [15–21]. Electrochemical studies have provided macro-scale observations of the nature of the passive films and factors

affecting chloride-induced depassivation processes. Nano-scale surface characterization studies have revealed the molecular structure of passive films that form in highly alkaline environments. These studies are in agreement with theoretical passivity models that propose an inner barrier layer that forms directly on the metal substrate, and outer layer that precipitate through the hydrolysis of cations ejected from the inner layer [22,23]. However, there is still significant debate regarding how chlorides break down these films to initiate active corrosion [24–27].

The testing of the hypotheses on the passivity and chloride-induced depassivation processes of iron or carbon steel in highly alkaline environments is inherently challenging due to the limitations of the nanoscale analytical or spectroscopic techniques in observing kinetic processes. These techniques do not allow in-situ monitoring of the surfaces where processes such as film formation and dissolution take place. On the other hand, atomistic modeling has the potential to serve as a tool in developing fundamental understanding of passivity and depassivation behaviors of steels in concrete and for designing new corrosion-resistant steels and corrosion inhibitors. In recent years, Reactive Force Field Molecular Dynamics (ReaxFF-MD) has emerged as a simulation framework to conduct such studies [28–37].

For example, Jeon et al. [38] used ReaxFF-MD to study iron oxidation as it relates to surface reactivity in catalysis and energy applications. These simulations were performed on different

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surface orientations of pure iron surfaces under applied external electric fields in a non-aqueous (dry) environment containing oxygen. The effect of temperature (up to 900 K) on oxidation was investigated. It was shown that ReaxFF-MD was successful in simulating oxidation kinetics of such systems and providing complementary information to existing experimental data. Although several ReaxFF-MD investigations exist for the study of oxidation and corrosion processes in non-ferrous metals in aqueous environments [31–35], the investigation of iron in such environments is limited [29,39,40]. Pan and van Duin [39] and Pan [40] demonstrated the possibility of using ReaxFF-MD in simulating iron oxidation at the iron-water interface and its potential to study passivation and depassivation processes. These simulations identified three distinct stages of iron oxidation based on the chemical species generated and oxidation rate. In early stages, oxides were mixed and unstable; however, in later stages stable oxides were formed, followed by a significant reduction in oxidation rates. Pan [40] described the last stage of oxide formation as passivation of the iron surface, which is not expected in pure water (pH = 7)—iron experiences active corrosion in neutral environments [41].

The present study further investigates the feasibility of using ReaxFF-MD simulations to study iron oxidation in water, with the ultimate goal of simulating passivation and depassivation processes in highly alkaline environments. ReaxFF-MD simulations were performed on pure iron surfaces for different surface orientations (i.e., (111), (110) and (100)) under various applied external electric field. Since the results of the simulations of different iron surfaces were similar, only the results of the Fe(110)-water simulations are presented in this paper. The simulations of (111) and (100) orientations are provided as [supplementary material](#). The effect of temperature, in the typical range of exposure conditions of reinforced concrete structures (300 to 350 K), on oxidation was also investigated. The results of this study are compared with ReaxFF-MD simulations of nickel [34], which is known to passivate in neutral, or even more acidic, environments [42,43]. This comparison is intended to show the difference in oxidation behavior of these two metals, and provide support for the feasibility of using ReaxFF-MD simulations to study passivity of iron in highly alkaline environments in the future.

2. Computational methodology

The molecular dynamics simulations were based on the Reactive Force Field (ReaxFF) interatomic potentials developed by van Duin et al. [37,44] and performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) framework [45] on the Extreme Science and Engineering Discovery Environment (XSEDE) [46]. Details of ReaxFF are provided by van Duin et al. [44,47–49]; therefore, only a summary background of ReaxFF theory is presented here.

Unlike the atomic force field models that are used in non-reactive molecular dynamics (MD) simulations of non-reactive processes [50–53], ReaxFF allows modeling of chemical reactions that include breaking and forming of bonds, where bond order is determined empirically from the interatomic distances. Unlike computationally expensive quantum mechanical (QM) calculations, ReaxFF treats chemical bonding implicitly, which yields significant computational efficiency. In other words, ReaxFF bridges the gap between the non-reactive MD and the computational quantum-chemistry [34]; therefore, ReaxFF-MD approach is well suited to study complex systems such as metal-electrolyte interfaces.

The system energy, E_{system} , is calculated using various partial energy contributions as per:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{tor}} + E_{\text{lp}} + E_{\text{H-bond}} + E_{\text{vdWaaals}} + E_{\text{Coulomb}} \quad (1)$$

where E_{bond} is the energy associated with forming atomic bonds; E_{over} and E_{under} are, respectively, the over-coordination and under-coordination penalty energies; E_{tor} is the energy associated with torsion angle terms; and E_{lp} and $E_{\text{H-bond}}$ are lone-pair energies and hydrogen-bond energies, respectively. E_{vdWaaals} and E_{Coulomb} are the terms to handle nonbonded interactions, namely, van der Waals and Coulomb interactions. The last two energy terms, E_{vdWaaals} and E_{Coulomb} , are computed for all atom pairs, while all other energy terms are calculated for the bond order between particles i and j . In ReaxFF theory, atomic charges are calculated using a geometry-dependent charge distribution that is determined using charge equalization (QEq) methods [54–56].

In this study, oxidation is studied under applied external electric field, E_{el} , using the method proposed by Chen and Martinez [57], and implemented by Assowe et al. [34], which includes the modification of the electrostatic energy, by the perturbation of the potential produced by the electric field, and recalculation of the new charge distribution. Electrostatic forces associated with the external electric field are calculated for each charged particle as the product of the charge and the external electric field [57].

In this paper, force field parameters for simulating iron/water interface were obtained from Aryanpour et al. [29], which included all parameters for determining bond order, bond energy, valence angle energy, torsional angle energy, and van der Waals energy (provided as [supplementary material](#)). Since Aryanpour et al. [29] used these parameters to model an iron-oxyhydroxide system, we used Density Functional Theory (DFT) calculations to determine the surface formation energy and water adsorption energy on the Fe(110) surface and compared these to values obtained from MD simulations using the force-field parameters from Aryanpour et al. [29]. We found good agreement between the two methods; details of this comparison are provided in [supplementary material](#).

Iron-water interface were investigated for Fe(110) at 300 K and 1 atm pressure. Periodic boundary conditions were applied along x and y directions and a fixed boundary condition was imposed along the z direction. A reflecting wall was applied at the end of the simulation cell to confine the water molecules. The initial configuration for the Fe(110) system is shown in [Fig. 1](#). The initial inter-molecule distance between water molecules and the dimension of the vacuum slab along the z direction were determined based on the density of water which is 0.99 g/cm³ at 300 K and 1 atm. The simulation cell had 480 water molecules and 2016 iron atoms. Nose-Hoover thermostat [58,59] is employed in all simulations to maintain the prescribed system temperature for canonical (NVT) ensemble. Maxwell-Boltzman distribution was chosen to set the initial velocities for different temperatures. The equations of motion were integrated with a time step of 0.1 fs in all cases for both short-range and long-range forces. The simulations were carried out at three external electric fields: 20 MeV/cm, 25 MeV/cm and 30 MeV/cm. To study the influence of the external electric field on the oxidation of iron, the electric field was applied 3 Å from the surface of the iron. It should be mentioned here that iron oxidation reactions with external electric field intensity of 15 MeV/cm are extremely slow or not activated at this timescale, and oxidation has not started after 150 ps. The effect of temperature is investigated (under 25 MeV/cm external electric field) to cover a practical range that represents the exposure conditions for concrete structures (300–350 K).

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