Molecular dynamics study of structure and reactions at the hydroxylated Mg(0001)/ bulk water interface

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ABSTRACT

A molecular level understanding of the aqueous Mg corrosion mechanism will be essential in developing improved alloys for battery electrodes, automobile parts, and biomedical implants. The structure and reactivity of the hydroxylated surface is expected to be key to the overall mechanism because (i) it is predicted to be the metastable surface state (rather than the bare surface) under a range of conditions and (ii) it provides a reasonable model for the outer corrosion film/water interface. We investigate the structure, interactions, and reactivity at the hydroxylated Mg(0001)/water interface using a combination of static Density Functional Theory calculations and second-generation Car–Parrinello *ab initio* molecular dynamics. We carry out detailed structural analyses into, among other properties, near-surface water orientations, favored adsorption sites, and near-surface hydrogen bonding behavior. Despite the short timescale (tens of ps) of our molecular dynamics run, we observe a cathodic water splitting event; the rapid timescale for this reaction is explained in terms of near-surface water structuring lowering the reaction barrier. Furthermore, we observe oxidation of an Mg surface atom to effectively generate a univalent Mg species (Mg⁺). Results are discussed in the context of understanding the Mg corrosion mechanism: For example, our results provide an explanation for the catalytic nature of the Mg corrosion film toward water splitting and a feasible mechanism for the generation of the univalent Mg species often proposed as a key intermediate.

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I. INTRODUCTION

Magnesium is a light, strong, nontoxic, and abundant element. As a result, magnesium alloys are promising materials for a wide range of applications, including as battery electrodes, automobile parts, and medical implants.^{1–7} Corrosion resistance is a key property of Mg alloys; for most applications, the corrosion rate should be as low as possible, though applications as medical implants require a corrosion rate tuned to the desired lifetime of the implant. Unfortunately, alloying Mg often leads to materials with very poor corrosion resistance, which limits the current use of Mg alloys.^{8–10} Despite its importance, the mechanism for aqueous corrosion of Mg remains unclear, which makes the design of corrosion resistant alloys challenging. A molecular level understanding of aqueous Mg corrosion will require knowledge of the structure and interactions at interfaces where key reactions take place. The presence of multiple relevant interfaces is shown by experiments focusing on the nature of the corrosion film formed when Mg is immersed in water.^{11–22} Immersing Mg in water leads to the formation of an MgO/Mg(OH)₂ corrosion film, with the Mg(OH)₂ being present at the outer film/water interface. Thus, the Mg(OH)₂/water interface is expected to be present throughout the aqueous corrosion process and knowledge of its structure is important. However, the cracked and porous nature of the corrosion film, combined with the localized nature of Mg corrosion, has been used to suggest it does not fully protect the underlying Mg substrate from interacting with water.²³ Indeed, the proposed corrosion mechanisms often assume that, at any given time, anodic reactions take place primarily at areas where water can interact directly with the underlying Mg substrate (i.e., effectively film-free areas).^{9,23} Thus, knowledge of the metastable metallic Mg/water interface is important for evaluating these mechanisms and understanding the Mg corrosion process.

The clean Mg(0001)/water interface is the obvious choice for a model system to represent metallic Mg at effectively filmfree regions, and it has indeed been the focus of many computational studies.^{24–33} However, we believe the fully hydroxylated Mg(0001)/water interface is also an important system as (i) it will likely be a metastable state at various conditions and (ii) it provides a reasonable model for the Mg(OH)₂/water interface; both these statements are justified below. Thus, study of the hydroxylated Mg(0001)/water interface should lead to insights into two of the important interfaces in Mg corrosion: the exposed metal/water interface and the outer corrosion film/water interface.

Results from a range of previous studies suggest that exposing the Mg(0001) surface to water will lead to (at minimum) islands of hydroxylated surface to form as a metastable state at a range of experimentally relevant conditions.^{25–28,30,33,34} For example, surface Pourbaix diagrams constructed by Williams et al. suggest that the hydroxylated surface will be more stable than the clean surface for a significant range of conditions.²⁵ More specifically, using lower and upper bounds for hydroxyl adsorption energies led to full hydroxylation being expected for potentials more positive than -2.4 V relative to the standard hydrogen electrode (SHE) for (i) pH above nine (lower bound adsorption energy) and (ii) pH above zero (upper bound adsorption energy). It is worth noting that the surface pH for a corroding Mg region is generally assumed to be above 11 at open circuit conditions due to the presence of $Mg(OH)_2$ on the outer surface.^{28,35} Furthermore, corrosion potentials for Mg tend to be approximately -1.5 V relative to the SHE (precise values vary between alloys and electrolytes).³⁴ Thus, construction of a surface Pourbaix diagram suggests the bare Mg/water interface will spontaneously transform into a hydroxylated Mg/water interface under common corrosion conditions.

A reasonable pathway to a hydroxylated surface involves water splitting followed by hydrogen either diffusing into the bulk metal or evolving as $H_{2(g)}$. The initial water splitting and hydrogen evolution barriers have been calculated as 0.7 and 0.3 eV, respectively.³³ Furthermore, calculations have previously shown that (i) water splitting becomes more exothermic as the surface becomes hydroxylated and (ii) the water splitting barrier is lowered by surface hydroxyl groups; this can be summarized as suggesting that surface hydroxylation is autocatalytic.^{26,27} Thus, based on barriers, Pourbaix diagrams and the autocatalytic nature of surface hydroxylation, we reasonably assume that (at minimum) islands of hydroxylated Mg will rapidly form at the bare metal/bulk water interface. Furthermore, ab initio molecular dynamics suggest that anodic polarization will significantly increase the rate of surface hydroxylation.³⁰ However, we currently do not know how this hydroxylated surface interacts with water: Thus, studying the hydroxylated Mg(0001)/bulk water interface is a natural step in investigating the aqueous corrosion mechanism.

A further reason to study the hydroxylated surface is to gain insight into the $Mg(OH)_2$ /bulk water interface, which we expect to be present as part of the corrosion film. Understanding water structuring at this interface is particularly key as the corrosion film has previously been shown to enhance cathodic hydrogen evolution (e.g., $H_2 O_{(aq)} + 2 e^- \rightarrow H_{2(g)} + 2 OH_{(aq)}^-$) for reasons that are not currently understood.^{17,36–38} The fully hydroxylated Mg(0001) surface is remarkably similar to the Mg(OH)₂ (0001) surface (explained below); thus, understanding structure at the hydroxylated Mg(0001)/bulk water interface should provide insight into the Mg(OH)₂/water interface and, subsequently, the catalytic nature of the corrosion film.

The similarity between the hydroxylated Mg(0001) and $Mg(OH)_2$ (0001) surfaces can first be seen from the primitive cell lattice parameters; the values for a and b are 3.23 Å for bulk Mg compared to 3.15 Å for Mg(OH)₂, meaning lattice mismatch is only about 2.5% between the two surfaces.^{25,39,40} The Mg(OH)₂ (0001) surface involves Mg atoms in a hexagonal lattice with hydroxyl groups in all hollow sites; half these hydroxyl groups point toward vacuum and are accessible to adsorbing water, while the other half of these hydroxyl groups point toward bulk and are hence inaccessible. For hydroxylated Mg(0001), previous studies have shown that hydroxyl preferentially adsorbs in either all fcc-hollow sites or all hcp-hollow sites.^{25,27} This pattern of adsorption leads to almost the same surface-area coverage of accessible hydroxyl groups for the (0001) surfaces of hydroxylated Mg (0.11 \AA^{-2}) and Mg(OH)₂ (0.12 Å⁻²); thus, the two surfaces are expected to lead to similar water structuring if water is not strongly influenced by the Mg atoms; we find that this assumption holds in the current work. Based on these similarities, we expect our investigation into the hydroxylated Mg(0001)/water interface to also provide important insights into the Mg(OH₂)/water interface and hence the behavior of the corrosion film.

In the current paper, we investigate the hydroxylated Mg(0001)/bulk water interface using a combination of static Density Functional Theory (DFT) calculations and *ab initio* molecular dynamics (AIMD). We first use static calculations to probe the surface plus water monomer system in order to gain insight into surface–water interactions without complications from water–water interactions. We subsequently analyze the results from our AIMD run, dividing the analysis into two parts: (i) analysis of the structuring up until the point the first reaction occurs (22 ps) and (ii) analysis of each reaction in turn using knowledge from step (i) to understand the driving forces behind them. Finally, we discuss our results in the context of furthering our understanding of the Mg corrosion mechanism.

II. METHODS

A. Computational details

All calculations in the current work were carried out using CP2K version 6.1, except those used to calculate the potential of zero charge (PZC).^{41,42} The optB88-vdW functional was used throughout, except for PZC calculations, due to its inclusion of dispersion effects and its previously demonstrated accuracy in describing bulk water.^{43–47} We used Goedecker–Teter–Hutter (GTH) pseudopotentials optimized for the PBE functional; core charges were +2, +6, +1 for magnesium, oxygen, and hydrogen respectively.^{48–50} For obtaining our MD trajectory, we used the standard (non-molopt) TZV2P basis sets for oxygen and hydrogen combined with our sspd+s-5gau basis set for Mg.^{24,41} For all other calculations, we

used the mTVZ2P basis sets for oxygen and hydrogen and our rc7pt5-sspd+s basis set for Mg.^{24,51} The mTZV2P and TZV2P basis sets have previously been shown to give a similar, accurate description of bulk water, while the accuracy of our Mg basis sets has previously been demonstrated by comparison to plane-wave calculations for a range of properties.^{24,52-54} CP2K uses multiple grids to carry out numerical integration, with absolute and relative cutoff energies used to control the accuracy of integration.⁴¹ In the current work, we used absolute/relative grid cutoffs of 8000/800 eV when water was present and 800/500 eV when only Mg was present; we have previously shown these values to be well converged.²⁴

For PZC calculations, we used the PBE functional due to previous studies showing that it leads to accurate work function and PZC values for a range of metals.^{48,49,55–58} We used a dipole correction in order to account for the asymmetric nature of our cells and to obtain a vacuum level for each interface (water/vacuum and metal/vacuum).⁵⁹ We used CP2K version 2022.1 for these calculations, as version 6.1 (used for other calculations) did not allow the position of the dipole correction to be set manually. We calculated the PZC from an MD run by taking snapshots of the trajectory and running single-point energy calculations. In these cases, we added an extra 8 Å of vacuum to the cell to ensure that sufficiently large regions of flat-vacuum potential could be identified.

B. Second-generation Car-Parrinello dynamics

We used second-generation Car–Parrinello (SGCP) dynamics in order to make our MD as efficient as possible. This involves (i) using wavefunction extrapolation, (ii) not converging the density self-consistent field (scf) loop as tightly as in Born–Oppenheimer dynamics, and (iii) correcting temperature drifts from loose-scf convergence by using a modified Langevin thermostat.^{60,61} For wavefunction extrapolation, we used the always stable predictor–corrector method with an extrapolation order of one.^{62,63} We set the scf convergence tolerance to 1×10^{-4} for our MD run, compared to 1×10^{-6} for other calculations. The modified Langevin thermostat we used leads to the equation of motion,

$$\frac{dv_{In}}{dt} = \frac{F_{In}^{(SGCP)}}{M_I} - \gamma_{\rm L} v_{In} + \eta(t, \gamma_{\rm L} + \bar{\gamma}_{\rm D}, T_{\rm t}), \qquad (1)$$

where *I* is an atom index, *n* is a direction index (*x*, *y* or *z*), v_{In} is the velocity of atom *I* in direction *n*, $F_{In}^{(SGCP)}$ is the force on atom *I* in direction *n* calculated with loose-scf convergence, M_I is the mass of atom *I*, γ_L is the Langevin friction coefficient, $\bar{\gamma}_D$ is an empirical parameter, *t* is time, T_t is the thermostat target temperature, and η is a random Gaussian distribution that effectively adds kinetic energy to the system. The $\bar{\gamma}_D$ term is a modification to the standard Langevin thermostat that effectively adds back the heat the loose-scf convergence dissipates from the system; the actual equilibrium temperature (T_{Eq}) will only match the target temperature if this empirical parameter is set correctly. We describe the process of determining $\bar{\gamma}_D$ values in detail in the supplementary material, but the general process is to run a short-simulation and estimate the error in $\bar{\gamma}_D$ values ($\Delta \bar{\gamma}_D$) using the following approximate equation:²⁴

$$\Delta \bar{\gamma}_{\rm D} = \frac{T_{\rm t} - T_{\rm Eq}}{T_{\rm Eq}} (\gamma_{\rm L} + \bar{\gamma}_{\rm D}). \tag{2}$$

C. Molecular dynamics details

Figure 1 shows the setup of our MD cell. The metal surface consists of six atomic layers of a $p(6 \times 6)$ hexagonal cell ($6 \times 36 = 216$ Mg atoms) with a monolayer of hydroxyl groups (36 OH, one per surface Mg) adsorbed in the fcc-hollow sites. We placed the hydroxyl groups in fcc-hollow sites as previous calculations have found these sites to be the most favorable.^{25,27,33} Our cell initially contained 144 water molecules above the hydroxylated surface, with a vacuum region separating water from the non-hydroxylated Mg surface. The lattice parameters were 19.26, 19.26, and 47.78 Å for *a*, *b*, and *c* respectively; note the *a* and *b* were determined from optimization of the bulk Mg cell (6×3.21 Å = 19.26 Å). These parameters led to a water thickness of ~12 and ~17 Å of vacuum; these values are estimated from plots of region thicknesses shown in the supplementary material.

We used an NVT ensemble with the modified Langevin thermostat described above. During the production calculations, the target temperature was set to 300 K, $\gamma_{\rm L}$ was set to 0.001 fs⁻¹, and the $\bar{\gamma}_{\rm D}$ values were set to 1.95×10^{-4} fs⁻¹ (Mg), 1.53×10^{-4} fs⁻¹ (hydroxyl oxygen atoms), 0.0 fs⁻¹ (water oxygen atoms), and 4.22 $\times 10^{-4}$ fs⁻¹ (hydrogen atoms). The accuracy of this parameterized thermostat is discussed in the supplementary material. We simulated ~32 ps, with the first 7 ps considered the equilibration time. Due to reactions occurring during the simulation, we use only the period 7–22 ps to analyze structural properties. Our integration time step was set to 0.5 fs due to the presence of hydrogen atoms. We used only the Gamma point for k-point sampling due to the large size of our cell.

D. Water orientations

We define a given orientation of water using three angles: roll, tilt, and azimuthal. The meanings of these angles are illustrated in Fig. 2, while the method to obtain them is described in the supplementary material. For convenience, we will also briefly outline their meaning here. Tilt angles are our main focus as they describe the direction of the water dipole relative to the surface. A negative tilt angle involves the water dipole pointing toward the surface, while a positive tilt angle involves the water dipole pointing away from the surface; note that we are defining the dipole direction



FIG. 1. Snapshot of our MD trajectory for the hydroxylated Mg(0001)/bulk water interface. This image was generated using ovito 64



FIG. 2. Illustration of our water orientation coordinate system. A given orientation is represented by roll, tilt, and azimuthal angles; rotations are applied in this order to map from a reference orientation to a given orientation. With the labeling in the figure, the axes of rotation are a, -b, and c for roll, tilt, and azimuthal rotations, respectively (these also correspond to the x, -y, and z axes). Note that in our MD simulation, the surface normal points along the c vector. Also note that at least two of the roll/lilt/azimuthal angles are equal to zero degrees for every water orientation shown above. Images were created in part using the VESTA software.⁶⁶

to point from negative charge density toward positive charge density. A larger magnitude roll angle suggests a larger z-displacement between the hydrogen atoms of water, though for a given roll angle the z-displacement will approach zero as the magnitude of the tilt angle approaches 90° . The azimuthal angle effectively determines the direction of the water dipole component in the surface plane (the direction of the xy-component of the dipole).

III. RESULTS

A. Hydroxylated surface + water monomer

We carried out optimizations for a single water monomer adsorbed onto a $p(3 \times 3)$ hydroxylated Mg(0001) surface to investigate the surface-water interaction without interference from water-water interactions. We used the hydroxylated surface with hydroxyls adsorbed in the fcc-hollow sites since these have previously been calculated as being the most stable hydroxyl adsorption sites.^{25,27,33} Idealized adsorption sites and orientations are illustrated in Fig. 3 while the stable minima found are shown in Fig. 4. Note that our conformer naming scheme involves appending a rough description of the water orientation to the name of the occupied adsorption site (e.g., atop-OH-Perp involves water sitting directly above a hydroxyl group with the water dipole pointing toward vacuum). More precise information on the water position and orientation for each structure can be found in the supplementary material.

We were able to find minima with water adsorbed in four distinct adsorption sites: bridge-Mg-Mg, bridge-Mg-OH,



FIG. 3. Illustration of the adsorption site positions and water orientations explored in the current work. A verbal description of each site position is also given in a table in the supplementary material. Note that the idealized Hup orientation displayed has tilt and roll angles of 45° and 88°, respectively. The large gold spheres are Mg atoms, with those in the uppermost plane being linked by bonds to the red oxygen atoms, and the remainder being one layer below. The hydrogen atoms are represented by small white spheres.

bridge-OH-OH, and atop-OH. However, we could not find stable minima at either the hollow or atop-Mg sites; this suggests that water will not directly interact with the metal atoms on the surface. Adsorption energies span a narrow range of -0.35 to -0.41 eV, with 6 of the 7 sites spanning an even smaller range of -0.39 to -0.41 eV. This contrasts markedly with bare metal plus water adsorption energies, where the atop site is generally significantly more favorable than other adsorption sites; for example, for the unhydroxylated Mg(0001) surface–water adsorption at the atop site led to E_{Ads} that was 0.2 eV more negative than the next most favorable site.²⁴ In terms of surface–water interaction strength, an adsorption energy of approximately -0.4 eV contrasts with our calculated water dimer association energy of -0.21 eV.

Our surface plus water monomer calculations suggest: (i) direct metal-water interactions are unimportant, (ii) the surface has only a weak directing effect on water (shown by the small range of adsorption energies), and (iii) water interacts more strongly with the surface than with other individual water molecules. Point (ii) in particular differs from the unhydroxylated metal surface and suggests that a higher concentration of water should be able to adsorb at the hydroxylated surface since the greater number of sites with highly negative adsorption energies should lead to a greater effective concentration of adsorption sites (i.e., both atop and bridge sites being energetically accessible leads to more available sites than if only atop sites were energetically accessible); this is indeed observed in our MD run (discussed below).

B. Metastable structure from molecular dynamics

Knowledge of structure at the hydroxylated Mg(0001)/bulk water interface is a prerequisite to understanding driving forces for its reactivity. Therefore, in this section, we analyze the metastable structuring observed in our MD run before water splitting occurred. Thus, we use the period of 7–22 ps in this section; this is where the structure has had time to equilibrate to a metastable state but before any reaction has occurred.



FIG. 4. Optimized geometries and adsorption energies for the $p(3 \times 3)$ Mg(0001) hydroxylated surface plus one water monomer. Images were created, in part, using VESTA.⁶⁵

1. Effects of water on the surface

Addition of water to the hydroxylated Mg(0001) surface leads to a large fraction of the surface hydroxyl (~80%) donating a hydrogen bond to water. Note, we define a hydrogen bond as being present if $r(O_A O_D) < 3.5$ Å and $< O_D O_A H_D < 35^\circ$, where H_D and O_D are hydrogen and oxygen atoms on the donor water, while OA is the oxygen atom on the acceptor water. This high degree of surface-water hydrogen bonding may be expected to significantly perturb the surface structure, but it appears to have had a minimal effect. For example, we calculated the average z-positions of the top layer of Mg atoms and hydroxyl oxygen atoms and compared them to what we would expect to find in vacuum (see the supplementary material for the relevant figure). To compare to vacuum, we look at the z-spacing between these atoms (top-layer Mg and hydroxyl oxygen) and the third layer of Mg atoms. In our MD simulations, the interlayer z-spacing increases by only ~0.1 Å, meaning the top-layer Mg and hydroxyl groups are displaced only slightly toward the bulk water. We also examined the angle between the surface normal vector (pointing toward bulk water) and the hydroxyl O-H bond vector (pointing from oxygen to hydrogen) for both hydrogen bonded and non-hydrogen bonded hydroxyl groups. The distribution of angles was found to be essentially identical (the figures are shown in the supplementary material) for both types of hydroxyl group (hydrogen bonded and non-hydrogen bonded), indicating that the interaction

with water is not strongly affecting the orientation of the adsorbed hydroxyl groups. In summary, the structure of the hydroxylated Mg(0001) surface does not appear to be significantly altered in spite of strong surface-water interactions.

2. Water planar distribution

Figure 5(a) shows the planar distribution of water oxygen atoms from the Mg surface, with the zero defined as the average position of the top-layer Mg atoms. We observe an intense (high probability density) peak between 3 and 4 Å from the surface. This peak has a small tail at ~4.5 Å followed by a region of depletion and a second peak at 7 Å. This shape suggests that there are multiple types of water near the hydroxylated surface. We defined four types of water in an attempt to understand the shape of the planar distribution; they are introduced in the text below and also in Table I.

The first peak in the planar distribution (at ~4 Å) is too far from the surface to result from direct interaction with Mg. It is reasonable to assume this peak arises due to water interacting with the surface hydroxyl groups, the hydrogens of which sit ~2 Å from the surface. Thus, we defined a solAds group as any water molecule that forms at least one hydrogen bond with a surface hydroxyl group. We find this definition leads to a sharp, symmetrical peak in the planar distribution with a mean planar distance of 3.8 Å.



FIG. 5. (a) Distribution of planar distances of water oxygen atoms from the Mg surface including breakdowns into different water classifications and (b) breakdown of the "solCon2" planar distribution based on hydrogen bonding behavior. Note that the zero planar distance is defined by the average planar (z) position of top-layer Mg atoms.

We next define solCon ("Con" for connected) as water that forms at least one hydrogen bond with solAds but no hydrogen bonds with the surface hydroxyl (making solCon and solAds mutually exclusive). However, this classification leads to a broad, asymmetric peak in the planar distribution (it is not shown explicitly, but it would be the sum of solCon1 and solCon2). Therefore, we further broke solCon down into two groups: (i) solCon2 is water that forms at least two hydrogen bonds with solAds, and (ii) sol-Con1 is water that forms one hydrogen bond with solAds. Finally, we define solOther as water that does not fit into any of the other classifications. With this definition, solCon1 leads to a reasonably symmetric peak in the planar distribution with a mean planar distance of 6.1 Å. However, solCon2 still leads to a broad feature that appears to be bimodal with peaks near 4.5 and 5.5 Å. The shape of the solCon2 peak is a reflection of the range of hydrogen bonding arrangements present, as shown in Fig. 5(b). The first solCon2 peak at ~4.5 Å results from molecules forming at most one hydrogen bond with solCon2 and solOther, while the second peak results from sol-Con2 water that forms at least two hydrogen bonds with solCon2 and solOther.

With our water types defined, we can count the average number of each over the course of the simulation. We found an average of 26.4 solAds water for our surface with 36 hydroxyl groups, which corresponds to 0.73 monolayers (ML) of adsorbed water. For context, the standard ice bilayer structure would lead to a 0.33 ML coverage (12 water adsorbed) or arguably a 0.66 ML coverage if the upper half of the bilayer was considered as adsorbed (it would be labeled solCon using our criteria). Thus, water is densely packed near the hydroxylated surface, which can be seen visually by the sharpness and intensity of the solAds peak in Fig. 5(a). We find an average of just 20.3 solCon molecules, 8.7 of which are sol-Con2 and 11.6 of which are solCon1, despite these water types being spread over a much larger volume than solAds. The relatively smaller number of solCon water, compared to solAds, is due to the large degree of solAds–solAds hydrogen bonding (discussed below).

3. Where does water adsorb?

We wish to know which water adsorption sites are preferred for the hydroxylated Mg(0001)/bulk water interface. While it is difficult to separate the various types of bridge sites with geometric parameters, we can separate the atop-OH and bridge sites using the concept of xy-distances. These are calculated the same way as distances, except the z-components of position are ignored (note our surface normal points along the z-axis). For the ideal atop-OH

TABLE I. Description and definition of classifications of water molecules used in our analysis. Note that to fall into a given classification, a water molecule must comply with all parts of the definition, the semicolons in the definitions are effectively AND operators. The shorthand $n_H(OH)$ refers to the number of hydrogen bonds formed with surface hydroxyl groups, while $n_H(solAds)$ refers to the number formed with solAds water.

Classification	Description	Definition	
solAds	Water strongly adsorbed on the surface	$n_{\rm H}({\rm OH}) \ge 1$	
solCon	Non-adsorbed water that forms hydrogen bonds with solAds	$n_{\rm H}({\rm OH}) < 1; n_{\rm H}({\rm solAds}) \ge 1$	
solCon2	Non-adsorbed water that forms at least two hydrogen bonds with solAds	$n_{\rm H}({\rm OH}) < 1; n_{\rm H}({\rm solAds}) \ge 2$	
solCon1	Non-adsorbed water that forms exactly one hydrogen bond with solAds	$n_{\rm H}({\rm OH}) < 1; n_{\rm H}({\rm solAds}) = 1$	
solOther	Any other water (non-adsorbed and no hydrogen bonds to solAds)	$n_{\rm H}({\rm OH}) < 1; n_{\rm H}({\rm solAds}) < 1$	

site, the xy-distance from oxygen in a water molecule to the nearest hydroxyl oxygen is zero compared to 1.6 Å (half the lattice spacing) for the bridge-OH-OH site. We gain insights into the adsorption behavior by looking at two functions of the xy-distance from water oxygen to hydroxyl oxygen: (i) the xy radial distribution function (rdf) gives information on which sites are energetically most favorable and (ii) the probability density for the xy-distance from oxygen on water to the nearest hydroxyl oxygen atom gives information on where water will actually sit (this distribution effectively reflects free energy differences between adsorption sites).

Figure 6(a) shows the xy-rdf between oxygen atoms of water and surface hydroxyl groups. We find that the solOther group leads to an essentially flat distribution with an rdf value of 1. This shows that, as expected, the xy-distance distribution of solOther to surface atoms is effectively random, which results from the large distances between solOther water and the surface. SolAds water are found to have a preference to be as close to the ideal atop-OH site as possible, with a single maximum at 0 Å. This is slightly different to what might be expected from the surface + monomer calculations, where atop and bridge adsorption sites led to similar adsorption energies. We can rationalize the greater preference of the atop site under bulk conditions by comparing the atop-OH-Flat and bridge-OH-OH-Hup structures (Fig. 4). For the atop-OH-Flat conformer, the water accepts a single hydrogen bond, while in the bridge-OH-OH-Hup structure, it is effectively accepting two hydrogen bonds. Thus, the addition of other hydrogen bond donors (e.g., other water molecules) would be expected to stabilize the atop-OH-Flat structure more than the bridge-OH-OH-Hup structure, as is consistent with the xy-rdf. Turning to the solCon groups, we find the xy-rdf of both solCon2 and solCon1 to differ slightly from that of solOther. SolCon2 has a slight preference to sit at large xy-distances from hydroxyl groups; this reflects a small preference to sit horizontally (xy) displaced from the nearby solAds water, which likely makes it easier to form hydrogen bonds with two separate solAds. Conversely, solCon1 has a slight preference for the atop-OH site, reflecting a preference to sit directly above a solAds water.

Figure 6(b) shows the probability distribution for the xydistance from oxygens on water molecules to the nearest surface hydroxyl groups. The plot for solOther effectively represents the

entropic limit, where water has no preference for any site. In this case, we find an average xy-distance of 1.1 Å from the nearest hydroxyl. In contrast, solAds leads to a broad distribution with a mean value of 0.8 Å. Thus, while the atop-OH seems to be the most energetically favorable, solAds sits at significant distances from the idealized site and has a large degree of horizontal freedom. For context, similar calculations for the bare metal/bulk water interface led to a mean xy-distance of 0.5 Å with very low probabilities beyond xydistances of 0.8 Å.²⁴ Thus, the hydroxylated surface is only weakly directing compared to the bare metal surface. This is consistent with the surface plus monomer calculations where we found only small differences in energy between a range of structures, while bare Mg plus monomer calculations were previously found to have a strong preference for the atop site.²⁴ This weak directing effect may partly explain the high solAds coverage for the hydroxylated surface; the large degree of horizontal freedom for adsorbed water allows a large number to fit on the surface (compared to the bare metal surface, for example).

4. Water orientations

We can obtain a more detailed picture of the near-surface water structure by looking at the water orientations. We focus on the dipole direction in the main paper as this can contribute significantly to the energy required to remove an electron from the surface; discussion of roll angles is deferred to the supplementary material. The dipole direction is described by the tilt angle; if we define the dipole as pointing from the oxygen atom to the water bisector, then a positive (negative) tilt angle means the dipole points away from (toward) the surface.

Figure 7 shows the tilt angle distributions for the three nearsurface water types. All near-surface water types show a preference for positive tilt angles, with mean values of $+35^{\circ}$, $+25^{\circ}$, and $+16^{\circ}$ for solAds, solCon2, and solCon1, respectively. Thus, the near-surface water layer can be thought of electrostatically as a dipole pointing with the negative end toward the surface. We can understand this preference, and the shapes of each distribution, by breaking down each tilt distribution in terms of hydrogen bonding behavior. For example, the strong preference for solAds to have positive tilt angles results from most solAds donating at least one hydrogen



FIG. 6. (a) The xy radial distribution function (z coordinates are ignored) for xy-distance from water oxygen atoms to surface hydroxyl oxygen atoms. (b) Probability distribution for xy-distance from water oxygen atoms to the nearest surface hydroxyl oxygen atoms. The xy-distance is the distance calculated if z-components of positions are ignored. Figure (a) can be interpreted similarly to a standard radial distribution function; values above 1 are favorable distances, while those below 1 are unfavorable.



FIG. 7. Probability distributions for water tilt angles for (a) solAds, (b) solCon2, and (c) solCon1 water. In each case, the distribution is broken down by the hydrogen bonding behavior of water. For example, the label " ⇒ SolCon; SolAds" means water that donates a hydrogen bond to both solCon and solAds (the "," is acting as an AND operator). Similarly, the label "1 ⇒ con1/other" means water that donates exactly one hydrogen bond to a water molecule in either group solCon1 or solOther (the forward slash is effectively an OR operator).

bond to solCon; since the oxygen in solCon is generally further from the surface than in solAds, a positive tilt angle is needed to donate these hydrogen bonds. A similar explanation applies to solCon2; the majority of solCon2 donate hydrogen bonds to solCon1 or solOther, which favors positive tilt angles in either case. As we move to further distances from the surface, there is a greater balance between hydrogen bonds being donated to groups below (closer to the surface) and above (further from the surface) and thus the average tilt angle approaches zero (the value for bulk water).

5. Hydrogen bonding

Hydrogen bonding is an important driving force for the structuring of bulk water; thus, knowledge of hydrogen bonding interactions is expected to be key to understanding the structure and reactivity of near-surface water. Table II shows the average number of hydrogen bonds donated and accepted for near-surface water, excluding hydrogen bonds formed with the adsorbed hydroxyl (i.e., we only count water–water hydrogen bonds). It is first worth noting that the number of hydrogen bonds donated is similar (~1.7) for all types of water. This suggests that the formation of ~1.7 hydrogen bonds per water is a driving force for the structuring observed. In contrast, the number of hydrogen bonds accepted varies significantly between different types of water, ranging from 1.16 for solAds to 2.17 for solCon2. The low acceptor number for solAds is due to

TABLE II. Average number of water–water hydrogen bonds formed for different water groups. n_{Donr} , n_{Acc} , n_{H} refer to the average number of hydrogen bonds donated, accepted, and donated plus accepted per water molecule. The value $n_{\text{Acc}} - n_{\text{Donr}}$ is referred to as the acceptor surplus in the text. N is the average number of water molecules for each classification. Note that numbers in this table do not include hydrogen bonds between water and hydroxyl.

Classification	n _{Donr}	n _{Acc}	$n_{\rm H}$	$n_{\rm Acc} - n_{\rm Donr}$	Ν
solAds	1.67	1.16	2.84	-0.51	26.4
solCon2	1.71	2.17	3.99	0.46	8.7
solCon1	1.71	1.90	3.61	0.19	11.6
solOther	1.74	1.82	3.56	0.08	97.5

it accepting at least one hydrogen bond from the surface hydroxyls, meaning each solAds accepts closer to 2.2 hydrogen bonds in total. Since the solAds group donates 1.67 hydrogen bonds to water, each solAds donates 0.51 more hydrogen bonds to water molecules than it accepts; we describe this as each solAds having an acceptor surplus of -0.51 (number accepted minus number donated is the acceptor surplus). If we multiply this surplus by the average number of solAds, this leads to -13.46, which means the remaining water must accept 13.46 more hydrogen bonds than they donate. A negative acceptor surplus has also been found for water adsorbed at the bare metal/water interface for various systems; in this case, it is effectively canceled out by groups of near-surface water that only donate a single hydrogen bond while the other hydrogen interacts with the However, a hydrogen-surface interaction is likely less surface.⁴ favorable for the hydroxylated surface. As a result, the solAds negative acceptor surplus is balanced by other water accepting more than 1.7 hydrogen bonds each.

Figure 8 shows how hydrogen bonding behavior varies with distance from the surface. Focusing on the acceptor surplus values, we find a maximum at ~5 Å from the surface. This acceptor surplus appears to decay slowly with distance, reaching zero at ~12 Å from the surface, which suggests that the presence of solAds has at least a minor effect on water at distances far from the surface due to the large number of solAds combined with the negative acceptor surplus. We believe that this positive acceptor surplus for near-surface water is a key driving force for the water splitting reaction, which we discuss below; a hydroxyl ion is expected to have an acceptor surplus of 3 (accepting 4 hydrogen bonds and donating 1) and its generation can reduce the need for near-surface water with positive acceptor surpluses.⁶⁷

6. Potential of zero charge

Directly linking our simulation with experimental conditions requires us to calculate the PZC, which corresponds to the electrode potential our simulation is carried out under. For a given snapshot from our cell setup, this involves calculating the difference between the Fermi energy of our system and the potential energy of an electron in the vacuum region adjacent to the water region. Similarly,



FIG. 8. (a) Average number of water-water hydrogen bonds donated and accepted at varying distances from the surface. (b) The difference between acceptor and donor values (acceptor minus donor) at varying planar distances from the surface; we refer to this value as the acceptor surplus.

we can calculate the work function at each MD step from the difference between the Fermi energy and the potential energy of an electron in the vacuum region adjacent to the unhydroxylated metal surface. The difference between work function and PZC values calculated in this way (PZC minus work function) will be referred to as $\Delta \Phi_{total}$, and it corresponds to the combined effect of the hydroxyl and water layers on the metal work function. While we could average the instantaneously calculated PZC values to calculate the potential of our system, our previous study suggests it will be more accurate to do the following: (i) obtain a work function from experimental or plane-wave calculations and (ii) calculate the PZC as the sum of this work function and the calculated $\Delta \Phi_{total}$ value.²⁴ This approach should reduce basis set errors, and it is what we use to calculate our final PZC value.

Figure 9(a) shows an example of the planar-averaged potential data used to calculate instantaneous $\Delta \Phi_{total}$ values. The geometry has been shifted such that the unhydroxylated surface sits at 0 Å; consequently, the vacuum levels are at ~45 Å (unhydroxylated surface/vacuum) and 35 Å (water/vacuum). Furthermore, the y-axis has been shifted such that the Fermi potential (Fermi energy divided by elementary charge) is at 0 eV per electron. The instantaneous $\Delta \Phi_{total}$ value is then the difference between the two vacuum levels. Figure 9(b) shows these instantaneous $\Delta \Phi_{total}$ values over our MD trajectory as well as their moving average. From this process we find an average $\Delta \Phi_{total}$ value of -1.66 eV. We can combine this with a previously calculated Mg work function value of 3.60 eV, to get an estimated absolute PZC value of 1.94 V for the current system.²⁴ This PZC is relative to the vacuum level; a more useful value is obtained



FIG. 9. (a) Averaged Hartree potential along the cell z-direction (the surface normal direction) for one snapshot, and (b) calculated work function and PZC values at various timesteps. For (a), values are relative to the Fermi potential (V_f), which we define as the Fermi energy divided by the elementary charge. The flat region at 35 Å is the vacuum level for the water/vacuum interface, while the region at 45 Å corresponds to the vacuum level for the unhydroxylated metal/water interface. Plotted this way, the potential at the water/vacuum level corresponds to the PZC value, while the potential energy at the metal/vacuum level corresponds to the work function. For (b), solid lines indicate the moving average, while markers represent instantaneous values. Note, we refer to the "PZC-work function" values as $\Delta \Phi_{total}$ in the main text.

by using the estimated absolute potential of the standard hydrogen electrode ($4.4V \pm 0.2 V$) to get a PZC estimate of $-2.46 V.^{68}$ For context, Mg corrosion potentials are commonly between -1.4 and -1.5 V relative to the standard hydrogen electrode, which suggests our simulation effectively represents a cathodically polarized system.³⁴ However, it is worth noting that the general lack of direct metal–water interactions suggests that the structuring is unlikely to be strongly dependent on the applied potential. Furthermore, the majority of reactions we observed (water adsorption being the exception) would not be expected to have a strong potential dependence since they do not involve electrons being transferred to/from the metal surface.

The $\Delta \Phi_{\text{total}}$ value calculated in the current work is significantly more negative than that for the unhydroxylated Mg(0001)/water interface, where a value of -1.06 eV was found when using CP2K.²⁴ To gain some insight into this, the contributions to $\Delta \Phi_{\text{total}}$ can be approximately separated into those from the water and those from the adsorbed hydroxyl groups. The contribution from the adsorbed hydroxyl groups was found to be -2.23 eV; this value was obtained by carrying out a single-point energy calculation on the optimized hydroxylated Mg(0001) surface with no water present. The large negative contribution from the adsorbed hydroxyl groups is somewhat expected due to their high (monolayer) coverage and close Mg-O interactions; adsorbates generally cause negative contributions to $\Delta \Phi_{total}$ due to the "pillow effect," where surface electron density tails are essentially pushed back into the metal due to Pauli repulsion.^{69–71} We therefore estimate the water to contribute +0.57 eV to $\Delta \Phi_{\text{total}}$. This positive contribution is the opposite to what would be expected based on the direction of water dipoles, which oppose the surface dipole (the negative end for water points toward the surface, for a pure metal the negative end points toward vacuum). Thus, the positive contribution from water likely arises from an electronic effect, resulting from the high concentration of surface to water hydrogen bonds.

C. Reactions

Table III shows a summary of the main reaction events that occurred during our MD run. The overall combination of reactions can be summarized as

$$Mg^* + 2 H_2 O_{(aq)} \longrightarrow Mg - (OH)_{ads} + OH_{(aq)} + H_{2(aq)},$$
 (3)

where Mg^{*} is a top-layer surface Mg atom and we have avoided assigning charges at this point. We extracted short trajectories for each reaction event, which we have included in a data repository; below, we analyze the reactions in more detail by looking at geometric information and calculated charges along these reaction trajectories. Furthermore, we look at the behavior of the products of the water splitting reaction in order to characterize their charge states (mainly whether the free hydrogen should be thought of as a proton or hydride).

Note, that while these reactions occurred on short timescales during our simulation, we make no claims about their typical timescales. The goal of reporting and analyzing these pathways is to: (i) provide plausible reaction pathways for the evolution of this interface and (ii) provide an understanding as to how the structuring of this interface may affect general reactivity. For example, one conclusion from analyzing these pathways is that reactions resulting in a net increase in hydrogen bond acceptors should be enhanced due to the positive acceptor surplus near the surface. While calculating barriers and expected rates would be highly beneficial, this would require technically challenging and expensive calculations beyond the scope of the current work.

1. Water splitting

Figure 10 shows geometric information and charges along the trajectory (see Fig. 11) for the water splitting reaction that occurred ~23.3 ps into our simulation. The reaction coordinate is effectively shown by Fig. 12(a), which displays the O-H distance for the dissociating bond over the reaction trajectory. This suggests the dissociation starts ~40 fs into the plotted reaction trajectory. This is consistent with the atomic charges plotted in Fig. 10(b), which start changing at ~40 fs into the reaction trajectory. The calculated charges suggest that the splitting water molecule becomes more negatively charged as it dissociates (from -0.19 e at the start of the reaction trajectory to -0.66 e at the end). The majority of this negative charge appears to be transferred to the hydrogen in the dissociating O-H bond, while the generated OH atoms carry a slightly more negative charge than before the splitting event. Regardless, the charge analysis suggests that both reaction products should be thought of as negatively charged. For example, at the end of the reaction trajectory, the free hydrogen is assigned a charge of -0.39 and -0.40 e from iterative Hirshfeld and Mulliken methods, respectively. However, the surface charge (the sum of Mg and adsorbed hydroxyl

TABLE III. Summary of the key reactions that occurred during our MD run on the hydroxylated Mg(0001)/bulk water interface. Note we have avoided assigning any charge here; the charges on each species are discussed in the text. Also note that the notation Mg^{*} refers to a top-layer surface Mg atom (i.e., one with hydroxyls adsorbed in adjacent hollow sites).

Equation	Time (ps)	
$H_2O_{(aq)} \rightarrow H_{(aq)} + OH_{(aq)}$	23.3	
$Mg^* + H_2O_{(aq)} \rightarrow Mg - (H_2O)_{ads}$	28.1	
$Mg - (H_2 O)_{ads} + OH_{(aq)} \rightarrow Mg - (OH)_{ads} + H_2 O_{(aq)}$ $H_2 O_{(aq)} + H_{(aq)} \rightarrow H_{2(aq)} + OH_{(aq)}$	28.9 29.5	
	Equation $\begin{array}{c} H_2O_{(aq)} \rightarrow H_{(aq)} + OH_{(aq)} \\ Mg^* + H_2O_{(aq)} \rightarrow Mg - (H_2O)_{ads} \end{array}$ $\begin{array}{c} Mg - (H_2O)_{ads} + OH_{(aq)} \rightarrow Mg - (OH)_{ads} + H_2O_{(aq)} \\ H_2O_{(aq)} + H_{(aq)} \rightarrow H_{2(aq)} + OH_{(aq)} \end{array}$	



FIG. 10. Changes in geometries and charges during the water splitting event. (a) Length of the dissociating O–H bond, (b) select charges calculated using the iterative Hirshfeld method,⁷² (c) the number of hydrogen bonds accepted and donated for the dissociating water, and (d) planar positions of the oxygen and hydrogen for the dissociating O–H bond.

charges) remains constant over the reaction trajectory, which means the extra negative charge on the splitting water does not come from the surface and, therefore, must come from the other water molecules.

We probed the coordination environments of the OH and H generated by the water splitting reaction by calculating radial distribution functions, shown in Fig. 12. For the free hydrogen atom [Fig. 12(a)], we find that it is coordinated more closely by other hydrogen atoms rather than oxygen atoms. Since the hydrogen in water carries a positive charge, this supports the assignment of negative charge to the free hydrogen atom and suggests it is best thought of as a free hydride. We can also use these rdf values to calculate coordination numbers for both the free hydride and OH groups. We find first shell coordination numbers of 3.9 for the free hydride using a distance cutoff of 0-2 Å and 4.1 for the OH oxygen using a distance cutoff of between 1.2 and 2.2 Å. This coordination number for the OH group is consistent with its assignment as a hydroxyl ion; hydroxyl ions are expected to accept four hydrogen bonds in an aqueous environment.⁶⁷

The assignment of the free hydrogen atom as an effective free hydride may appear surprising, but it is supported by three clear pieces of evidence: (i) Both iterative Hirshfeld and Mulliken charge schemes (which are conceptually very different algorithms) assign near identical negative charges to the species, (ii) the free hydrogen is coordinated by exclusively the water H atoms, which themselves carry positive charge, and (iii) the hydrogen evolution reaction is simple to understand if the free hydride is negatively charged but would be difficult to conceive of otherwise.

Having analyzed the water splitting trajectory and the environment of the generated H/OH, we can suggest a driving force for the reaction. Before the O-H bond dissociates, the splitting water molecule accepts four hydrogen bonds and donates zero [Fig. 10(c)]. This hydrogen bonding environment is more typical of a hydroxyl group than a neutral water molecule, which likely lowers the energy of the hydroxyl product (and hence the water splitting barrier). The planar position of the splitting water (~6 Å from the surface) corresponds to a point where the acceptor surplus is near its maximum value [Fig. 8(b)], i.e., where water tends to accept more hydrogen bonds than it donates. This is relevant for two reasons: (i) It makes it more likely for a water with 4 acceptors and 0 donors to form and (ii) it means that species with positive acceptor surpluses will be more favorable than in a normal bulk water environment. Both the generated OH and H species effectively accept four hydrogen bonds each; thus, water splitting into these species is expected to be more favorable in areas with positive acceptor surpluses. The acceptor surplus is in turn caused by interactions between surface hydroxyl groups and near-surface water; thus, the surface hydroxyl groups are effectively driving the water splitting.

2. Surface adsorption/hydroxylation

Within 5 ps of the water splitting event, a top-layer Mg atom moved significantly toward the water region and gained a water adsorbate (the reaction event labeled "water adsorption"; see Fig. 13). Approximately 0.8 ps later, a hydrogen on the adsorbed water transferred to a nearby free (i.e., not adsorbed to the surface) hydroxyl group, this is labeled "hydroxyl adsorp-



40 fs







55 fs

80 fs



FIG. 11. Select snapshots for (a) the water splitting reaction trajectory and (b) the hydrogen evolution reaction trajectory. Times are relative to the start of the extracted reaction trajectory and correspond to the ∆Time values in the figures below. The dotted lines in (a) denote (i) hydrogen bonds for the water/hydroxyl and (ii) hydrogen atoms within 2 Å of the free hydrogen atom. Atoms of particular interest have been highlighted by changing their colors to purple (for oxygen) and yellow (for hydrogen). For all other atoms, the default Jmol colors are used: red for oxygen, white for hydrogen, and green for magnesium. Images were generated using Jmol.



FIG. 12. Radial distribution function (rdf) values for products of the water splitting reaction to other oxygen and hydrogen atoms. (a) rdf for free hydrogen to hydrogen and oxygen atoms, (b) rdf for hydroxyl oxygen to hydrogen and oxygen atoms. The identity of the hydroxyl oxygen changes over time; we define hydroxyl oxygen as an oxygen that initially formed part of a water molecule and has exactly one hydrogen atom within 1.3 Å. For (a), the red line marks the maximum position we use to calculate the hydrogen coordination number (the minimum is at zero and hence not shown), while for (b) the region between red lines is that used to calculate the hydrogen coordination number.



0 fs

b)

100 fs



FIG. 13. Select snapshots for (a) the water adsorption reaction trajectory and (b) the hydroxyl adsorption by substitution reaction trajectory. Times are relative to the start of the extracted reaction trajectory and correspond to the Δ Time values in the figures below. Atoms of particular interest have been highlighted by changing their colors to purple for oxygen, yellow for hydrogen, and blue for magnesium. For all other atoms, the default Jmol colors are used: red for oxygen, white for hydrogen, and green for magnesium. Images were generated using Jmol.

tion by substitution." These two events together correspond to hydroxylation of a surface Mg atom, an overall process that could be written as $Mg^* + OH_{(aq)} \rightarrow Mg - (OH)_{ads}$. We discuss both the water adsorption and hydroxyl substitution events

together due to their close relationship in both time and space. Figure 14 shows information for the initial water adsorption event, while Fig. 15 shows information for the hydroxyl substitution event.



FIG. 14. Changes in geometries and charges during the water adsorption (onto the metallic Mg) reaction event. (a) Distances from the Mg adsorption site to various other atoms, (b) planar position of the adsorbing oxygen and the Mg adsorption site, and (c) iterative Hirshfeld charges for various species. For (a), the Ow and OHy labels refer to oxygen on the adsorbing water and free hydroxyl group, respectively, while H_{Hy} refers to hydrogen on the free hydroxyl group.

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FIG. 15. Changes in geometries and charges during the "hydroxyl adsorption by substitution" reaction event. (a) Changes to the dissociating O–H bond length for the initially adsorbed water, (b) iterative Hirshfeld charges for various species.

Figure 14(a) shows distances from the Mg adsorption site (i.e., a top-layer Mg atom) to both the adsorbing water oxygen and the nearby hydroxyl ion generated from the initial water splitting event. The water adsorption event is effectively over by ~100 fs into the reaction trajectory when the Mg-O distance reaches ~2 Å; note that this distance is similar to the Mg-O distance for water adsorption on the bare Mg(0001) surface.²⁴ It is worth noting that the Mg atom also becomes closer to the hydroxyl oxygen atom during the adsorption event; this suggests the presence of a nearby hydroxyl group may be lowering the barrier for adsorption. Figure 14(b) shows the planar positions of the adsorbing oxygen and the Mg adsorption site. It is clear from this plot that the magnesium atom moves toward the water oxygen during the adsorption event, while the water oxygen stays in a similar planar position. Turning to calculated charges, Fig. 14(c) shows that the Mg adsorption site becomes significantly positively charged during the adsorption event, while the total surface charge (the sum of charges for all atoms originally part of the surface) remains constant; the iterative Hirshfeld charge on the Mg adsorption site atom changes from +0.53 e at the start of the trajectory to +1.12 e at the end of the reaction trajectory.

Thus, water adsorption occurs due to one Mg atom effectively transferring negative charge to the rest of the surface. Note that this can be thought of as an oxidation reaction despite the surface maintaining a constant charge. This is because one Mg atom (the adsorption site) effectively loses an electron, which is then delocalized over the rest of the surface sites. The main difference between this and standard anodic/oxidation equations for univalent metals ($M_{(s)} \rightarrow M^+_{(aq)} + e^-$) is that in this case, the oxidized atom remains at the surface; however, the rate of this reaction is still expected to show the potential-dependence characteristic of a metal anodic/oxidation reaction.

Figure 15 shows the dissociating O–H distance during the "hydroxyl adsorption by substitution" event. The hydrogen oscillates between the initial water and hydroxyl oxygen atoms, which can be observed in the fluctuations of the dissociating O–H bond length in Fig. 15(a) or by directly visualizing the reaction trajectory (which we include in the relevant data repository). Calculated Hirshfeld charges



FIG. 16. Changes in geometries and charges for the hydrogen evolution reaction event. (a) Bond length for the forming H₂ over the reaction trajectory, (b) iterative Hirshfeld charges. For (b), "H-free" refers to the free hydride (generated from water splitting) while "H-split" refers to the hydrogen that begins the reaction trajectory as part of a water molecule.

suggest that none of the relevant species change charge state. However, the transfer of a δ + hydrogen from an adsorbed water means that a neutral-charged adsorbate has effectively been exchanged for a negatively charged adsorbate.

In terms of driving forces for the water adsorption, the free hydroxyl ion is likely key based on (i) the lack of water adsorption directly to the metal before a free hydroxyl was present and (ii) the presence of the free hydroxyl close to the adsorption site. The hydroxyl was likely near the surface due to the overall positive charge of the surface atoms. This hydroxyl group will then create a δ - region of charge near the surface. This region would then be expected to lower the energy required for a nearby Mg atom to become δ + charged and move out of the surface plane as occurs in the water adsorption step. The subsequent hydroxyl adsorption step suggests that the Mg-hydroxyl interaction is stronger than the Mg-water interaction; this is expected due to the positive charge on the Mg, which will interact more strongly with a negative hydroxyl than a neutral water.

3. Hydrogen evolution

The final reaction we observed was the generation of a H₂ molecule at ~29.5 ps (the "hydrogen evolution" reaction event). Figure 16(a) shows the H–H distance over the reaction trajectory; this effectively represents the main reaction coordinate with H₂ being produced ~100 fs into the reaction trajectory. Calculated Hirshfeld charges [Fig. 16(b)] suggest that this reaction should be viewed as a δ – hydride combining with a δ + hydrogen atom from a water molecule in order to form neutral H₂. The reaction can thus be written as H₂ O(aq) + H⁻_(aq) \rightarrow H₂(g) + OH⁻_(aq). The driving force for this reaction is likely the inherent instability of free hydride ions.

IV. DISCUSSION

A. Catalytic nature of the corrosion film

Experiments on Mg corrosion have shown (i) the presence of an Mg(OH)₂-like species at the outer corrosion film and (ii) increased cathodic hydrogen evolution ($H_2 O_{(aq)} + 2 e^- \rightarrow H_{2(g)} + 2 OH^-_{(aq)}$) from this film.^{17,36–38} Results from our MD run can be used to provide an explanation for the catalytic nature of this film toward cathodic hydrogen evolution.

In our MD run, we observed a water splitting reaction that can be thought of as cathodic from the perspective of the splitting water molecule (in that it effectively gained electrons). Analysis of the water structuring suggested that this water splitting reaction was driven by water oversaturated with acceptor hydrogen bonds (accepting >2) near the hydroxylated surface. Note that this driving force is not expected to be present at the bare metal surface, in which case previous MD studies for multiple metals (including Mg) suggest that near-surface water does not accept >2 hydrogen bonds.^{24,66} This driving force leads us to expect water splitting to be more facile at the hydroxylated surface relative to the pristine surface. This same driving force is expected to be present at the Mg(OH)₂(0001) surface as the oversaturation of hydrogen bond acceptors is a result of water–hydroxyl interactions, which we expect to be similar for both Mg(OH)₂(0001) and hydroxylated Mg(0001) surfaces. To summarize, our calculations suggest that water near either the $Mg(OH)_2(0001)$ or hydroxylated Mg(0001) surface will be more prone to cathodic splitting due to the number of water molecules accepting >2 hydrogen bonds; this is consistent with, and provides an explanation for, the catalytic nature of the Mg corrosion film toward cathodic hydrogen evolution.

B. Reactivity of the hydroxylated metal

While previous calculations have suggested that a monolayer of hydroxyl will form on the Mg(0001) surface upon exposure to water, discussed in detail in the Introduction, the properties of this surface have remained unexplored. However, calculations in the current paper allow us to gain insight into both the reactivity and expected evolution of the hydroxylated Mg(0001) surface.

Monolayer hydroxylation of the Mg(0001) surface may be expected to restrict further adsorption directly onto the underlying Mg atoms both for steric and energetic reasons; indeed, calculations by Yuwono *et al.* suggest further surface hydroxylation becomes unfavorable between 1 and 1.2 ML.³¹ Consequently, previous kinetic models have limited each surface Mg to coordinate a maximum of one hydroxyl group, meaning 1 ML is the maximum possible coverage.^{28,31} However, our MD simulation illustrated that an effectively anodic adsorption event could take place even for the fully hydroxylated (1 ML) surface,

$$Mg^* + H_2 O_{(aq)} \longrightarrow [Mg - (H_2 O)_{ads}]^+ + e^-, \qquad (4)$$

where Mg^{*} corresponds to a top-layer Mg (i.e., one already coordinated to hydroxyl) and the charge is balanced by oxidation of this adsorption site. This oxidative adsorption reaction, combined with the "hydroxyl adsorption by substitution" reaction, suggests that coverage of hydroxyl in excess of 1 ML may occur and that it may be a metastable state. The degree of hydroxylation will depend on the relative rates of at least two reactions: (i) anodic Mg dissolution (Mg⁺ \rightarrow Mg²⁺ + e⁻) and (ii) oxidative adsorption (Reaction (4)]. Further work is therefore required to estimate these relative rates and the subsequent expected coverage. While our MD trajectory, which has been deposited into the relevant data repository, provides a useful starting point for this, it is beyond the scope of the current paper.

Reaction (4) is similar to the anodic adsorption of OH⁻ proposed by Taylor ($Mg^* + OH^-_{(aq)} \rightarrow Mg - (OH)_{ads} + e^-$).²⁸ This anodic adsorption has also been suggested as the initial oxidation event in the "univalent Mg" hypothesis for Mg corrosion, whereby a reactive univalent Mg is generated ($Mg \rightarrow Mg^+ + e^-$) followed by either a second anodic reaction ($Mg^+ \rightarrow Mg^{2+} + e^-$) or a chemical reaction to form hydrogen gas ($Mg^+ + H_2O \rightarrow Mg^{2+} + OH^- + 0.5H_2$).²³ Despite similar reactions being proposed previously, our simulations are to the best of our knowledge the first to show a single-electron anodic oxidation of Mg metal leading to a univalent Mg species. Further exploration of the properties of this species may therefore be instructive in assessing the feasibility of various aspects of the "univalent Mg" hypothesis.

V. CONCLUSIONS

We have used simulations to provide a detailed picture of structuring at the hydroxylated Mg(0001)/water interface with key

features including, but not limited to, (i) a high degree of adsorbed water coverage, (ii) adsorbed water being spread over multiple adsorption sites (i.e., the surface is only weakly directing), and (iii) near-surface water being oversaturated with acceptor hydrogen bonds (in excess of 2 per water). The reactivity of this interface was probed by analysis of both structural information and pathways for reactions observed in the MD run. Water splitting was observed despite the short timescale of our simulation, which was understood to result from interactions between water and adsorbed hydroxyl groups causing a deficiency in near-surface hydrogen bond acceptors and consequently favoring generation of species that accept more hydrogen bonds than they donate (such as hydroxyl ions). This driving force is also expected to be present at the Mg(OH)₂/water interface and thus provides an explanation for the experimentally observed catalytic nature of the corrosion film toward cathodic water splitting.

We observed a single-electron oxidative adsorption event (Reaction 4) in our simulation, effectively generating an Mg⁺ species on the surface of the metal. While similar reactions have been proposed by others, we believe this is the first instance of a detailed reaction pathway being identified. Depending on the rate of this reaction, and the reactivity of the product, it may have a significant impact on the structuring at the Mg/water interface (e.g., by allowing a greater than 1 ML hydroxylated surface). Furthermore, this oxidative adsorption reaction resembles a key step (Mg \rightarrow Mg⁺ + e⁻) in the univalent Mg hypothesis for corrosion; thus, further investigation into this species may allow the feasibility of the univalent Mg hypothesis to be demonstrated.

SUPPLEMENTARY MATERIAL

The supplementary material provides the technical details about the molecular dynamics simulations; details of how the tilt, roll, and azimuthal angles for water molecules are computed from the atomic coordinates; details of how the geometries of the relaxed surface with a monomer are found; graphs showing the effect of water on the surface atoms; and graphs of water roll angle distributions for water molecules near the surface.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

R. M. Fogarty: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **A. P. Horsfield**: Conceptualization (supporting); Funding acquisition (lead); Supervision (lead); Writing – original draft (supporting); Writing – review & editing (supporting).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request and openly available in zenodo at https://doi.org/10.5281/zenodo.6641864.

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