Modeling reaction pathways for hydrogen evolution and water dissociation on magnesium

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Abstract

There are several chemical and electrochemical reactions that occur on a solvated magnesium surface, many of which contribute to the localized corrosion of magnesium and its alloys. The hydrogen evolution reaction (HER) is of particular interest because corrosion rates for different Mg alloys can be estimated by *in situ* monitoring of HER from a corroding sample surface. Therefore, a detailed mechanism for the HER on magnesium is proposed that connects the initial water dissociation reaction with the Tafel reaction through a self-consistent pathway involving adsorbed species. First principles modeling using Density Functional Theory (DFT) is used to map this reaction pathway on Mg(0001) and to determine the thermodynamic variables and kinetic barriers for each reaction in the scheme. An alternative mechanism for HER is also modeled that involves subsurface hydrogen, but this mechanism is found to have a negligible Gibbs free energy. It is also found that water dissociation occurs over the Mg—Mg bridging site and has a large thermodynamic driving force. Reactions involving multiple water molecules and adsorbed species are modeled, as well, and it is found that the presence of H_{ads} and OH_{ads}

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provides a thermodynamic driving force for water dissociation while also increasing the activation barrier for the Tafel reaction. Hence, DFT calculations show that the presence of adsorbed species can have a large impact on the kinetics of chemical and electrochemical reactions that occur on the Mg surface.

Keywords

Magnesium, Hydrogen Evolution Reaction, Kinetics, Thermodynamics, Modeling

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1. Introduction

Aqueous corrosion of magnesium (Mg) and its alloys has been the topic of intense research recently as more industries search for lightweight alloys to replace structural components in automobiles, aerospace vehicles, and defense applications [1]. The corrosion properties of several commercial Mg alloys are known [2-4], but some researchers have also expanded into designing and characterizing custom alloys [4, 5], in an attempt to enhance the corrosion resistance of the base metal. Pure Mg corrodes so rapidly that careful experimental design is needed to properly characterize the chemical and electrochemical reactions happening on the metal surface [6-15]. Even more challenging is identifying adsorbed intermediate species and quantifying how surface coverage impacts the kinetic rates of competing reactions at the surface.

Although chemical reactions occurring during magnesium alloy dissolution can vary depending on alloy composition, magnesium corrosion proceeds primarily through the balance of the anodic reaction

and the corresponding cathodic reaction

One of the key products of the cathodic reaction in magnesium corrosion is H_2 , and *in situ* monitoring of H_2 evolution from a corroding Mg surface is often used to calculate corrosion rate. The hydrogen evolution reaction (HER) on metal surfaces follows the Volmer-Tafel mechanism, which involves diffusion and subsequent recombination of H_{ads} adatoms [16]. In the Tafel step, adsorbed hydrogen atoms diffuse across the surface and, once in close proximity, form a covalent bond and evolve in the form of H_2 gas. This reaction has the form

and is known as the Tafel reaction. Rewriting Equation (3) on the Mg surface gives

In the present work, Equation (4) was studied by mapping the minimum energy path (MEP) for H_{ads} adatom diffusion and recombination on the Mg(0001) surface. Different paths were explored in order to determine the most probable mechanism for HER on Mg(0001).

Equation (4) was developed under the assumption that the Tafel mechanism depends expressly on the presence of H_{ads} species. This is a generally accepted fact of HER on metal surfaces, although Equation (2) by itself does not directly imply that adsorption must occur. Given that it was previously shown that adsorption of both H_{ads} and OH_{ads} species is thermodynamically favorable on Mg(0001) [17], a new scheme for the cathodic reaction on Mg

is proposed that invokes the adsorption of *both* H_{ads} and OH_{ads} species. The proposed scheme for Mg is motivated by the recent work of Sharifi-Asl and Macdonald, in which the authors proposed a mechanism for the HER on copper that also depends on adsorbed species [16].

In the first proposed reaction, water dissociation on the Mg surface leads to co-adsorption of H_{ads} and OH_{ads} at adjacent surface sites:

This is the chemical analogue of the Volmer reaction. When Equation (5) involves multiple water molecules, the end result is formation of adsorbed $Mg(OH_{ads})_2$ units and hydrogen evolution:

It is proposed that this reaction occurs in three distinct steps:

Equation (9) is simply the Tafel reaction defined in Equation (4), but with co-adsorbed OH_{ads} species. Equation (6) is the balance of the anodic and cathodic reactions set forth in Equations (1) and (2)—with the key difference being the dependence of adsorbed species as reaction intermediates. Indeed, Equation (6) was already shown to be thermodynamically favorable [17], and the current work focused on defining its kinetic pathways according to the detailed scheme put forth in Equations (5)-(9). More specifically, the present modeling work focused on mapping the MEPs for Equations (7)-(9). Equations (5) and (8) define water dissociation on the Mg surface—both without and with adsorbed species, respectively. As stated previously, Equation (9) is simply the Tafel reaction and the final step in the HER scheme. Equations (7)-(9) involve

multiple water molecules and are presented as “concerted reactions” in subsection 3.3. Investigation of concerted reactions enabled the development of a full reaction pathway for the cathodic reaction on Mg, in which all thermodynamic variables and kinetic barriers were determined from first-principles calculations on model surfaces.

Although H₂ dissociation on Mg(0001) has been modeled extensively [18-37], H₂ *desorption* from Mg(0001) was only studied by Pozzo and Alfè [19] and Vegge [20]. Moreover, none have modeled the reaction path for water dissociation on Mg(0001) or determined the transition state for HO—H bond breaking. Hence, the reported work is the first attempt to use first-principles surface modeling to study multiple steps in the cathodic reaction on Mg(0001), from initial water dissociation to final hydrogen evolution. Missing from the present model is true metal dissolution, as written in Equation (1). Although the Mg surface is oxidized locally through the adsorption of OH_{ads} species, there is no explicit removal of metal atoms from the surface, and the local electronic density on the Mg atoms (measured through partial charges) is not precisely +2. Nevertheless, this study puts forth a detailed kinetic mechanism for the cathodic reaction on Mg that is validated by thermodynamics and builds upon previous findings related to OH_{ads} and H_{ads} adsorption on Mg.

2. Theory

A surface model of magnesium was built from an optimized Mg hcp crystal by cleaving a 4×4×4 supercell along the [0001] direction. The model slab contained 64 Mg atoms (4 slab layers, each with 16 atoms) with a slab thickness of 7.7 Å and 10.5 Å of vacuum separation between periodic images. Atomic coordinates were optimized using periodic boundary conditions and delocalized internal coordinates [38]. During all surface optimizations, atomic

coordinates in the bottom two slab layers were held fixed in their bulk positions. Interatomic forces were converged to within 4.0×10^{-2} Hartree/nm and energies to within 2×10^{-5} Hartree. Only the Γ point was used for calculations on the large surface models, and a dipole correction was applied in the z direction [39, 40]. For some models, implicit solvation was included by embedding surfaces in a continuous dielectric medium of water represented by the Conductor-like Screening Model (COSMO) [41]. The dielectric constant of the medium was chosen to be that of bulk water at standard conditions, i.e. 78.54. Further details of the surface model development can be found in a previous work [17].

Reaction pathways for HER and water dissociation were studied by mapping the MEP for movement of adsorbed species (denoted X_{ads}) on the Mg(0001) surface. The MEP barrier is a true transition state if it corresponds to a first order saddle point on the potential energy surface.

According to transition state theory, the barrier height at the transition state is equal to the activation energy, $\Delta^\ddagger G$, and the reaction rate, $k(T)$ at temperature T is given by the equation [42]

$$k(T) = \frac{k_B T}{hc} e^{-\Delta^\ddagger G^0 / RT}, \quad (10)$$

where k_B is the Boltzmann constant, h is Planck's constant, c is the species concentration, $\Delta^\ddagger G^0$ is the standard Gibbs energy of activation, and R is the universal gas constant. Hence, the relative sizes of $\Delta^\ddagger G^0$ for different reactions can be compared in order to estimate the rate-limiting step along a reaction pathway. Again, this is predicated on verifying that the MEP barrier is a true transition state.

There are several computational techniques for transition state searching, to include combinations of the linear and quadratic synchronous transit methods (LST/QST) [43] and the

nudged elastic band (NEB) method [44]. These methods typically search for a transition state by taking the coordinates of reactant and product geometries and optimizing “images” along the potential energy surface. An alternative is to start from a suspected transition state and optimize along the direction of the negative gradient. A more robust method is using constrained geometry optimization to map the potential energy surface. This approach requires multiple input structures for intermediate steps in the MEP, and suspected stationary points have to be re-optimized. Despite this, constrained geometry optimization was used as the primary method in the current work because it provided more control over the position of adsorbed species in the model. It is also efficient for probing reaction paths that have combinations of different mechanisms. For example, the Tafel reaction consists of both H_{ads} diffusion and H—H bond formation; these processes happen at different rates, but both can be probed by constraining a single variable, the H—H interatomic separation. For some reactions, the results of constrained geometry optimization were compared with LST/QST and NEB.

Atomic coordinates of each geometry in the MEP were optimized by constraining a single interatomic distance in 0.1 Å steps. The MEPs for HER—consisting of diffusion of H_{ads} and chemical desorption of H_2 —were mapped by constraining the interatomic distance between H_{ads} species. Similarly, water dissociation reactions were mapped by constraining the HO—H bond length. After developing the full MEPs, selected points were re-optimized without constraints, and the Hessian matrices were calculated to determine if the structures were stationary points on the potential energy surface, i.e. local minima, transition states or higher order saddle points. Transition states were confirmed by the presence of exactly one unstable vibrational mode with an imaginary frequency. Frequency analysis was also used to generate the vibrational partition function and resulting thermochemical data, such as vibrational entropy and

Gibbs free energy, at $T = 298$ K. The zero-point energy, ZPE, and vibrational Gibbs free energy, G_{vib} , were then added to the electronic energies, E . For clarity, all energies that include thermal corrections are denoted as Gibbs free energies, G .

All calculations were performed with DMol3, as implemented in the Materials Studio suite of modeling programs [45-47]. Energies were calculated with Density Functional Theory (DFT) using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional to approximate exchange and correlation [48]. The orbitals were represented by a numerical, atom-centered basis—the DMol3 DNP basis set—which includes p orbital polarization on hydrogen atoms. The orbital cutoff was 4.4 Å. Mg atoms were represented with effective core pseudopotentials (ECPs), as provided in the DMol3 program [49]. Convergence of the self-consistent energies was aided by the use of fractional orbital occupations with a small thermal smearing parameter (0.005 Hartree) [50, 51]. Atomic coordinates and energies for all models can be provided upon request.

3. Results and Discussion

3.1. Hydrogen evolution reaction (HER)

The Tafel reaction in Equation (4) was studied by mapping the MEP for H_{ads} diffusion and recombination on the Mg(0001) surface. A plot of relative energy vs. $d_{\text{H-H}}$ is shown in Fig. 1. At the beginning of the MEP, two H_{ads} adatoms are adsorbed in adjacent fcc sites (previously shown to be the lowest energy sites [17]) with $d_{\text{H-H}} = 3.11$ Å. This structure is shown in Fig. 2(a). Relative electronic energies and thermodynamic variables for selected stationary points along the MEP are listed in Table 1.

Fig. 1

Fig. 2

Table 1

Interatomic distances, electronic energies and thermodynamic variables for selected stationary points along the MEP for H_{ads} adatom diffusion and recombination on Mg(0001). Structures shown in Fig. 2. E = electronic DFT energy; ZPE = zero-point energy; G_{vib} = vibrational Gibbs free energy; G^0 = standard Gibbs free energy (includes contributions from electronic, ZP, and vibrational energies). Calculations were done in vacuum, with no implicit or explicit solvation.

Step	$d[\text{H}—\text{H}]$ (Å)	ΔE (eV)	ZPE (eV)	G_{vib} (eV)	ΔG^0 (eV)
1	3.11	0.0	2.26	-3.07	0.0
9	2.34	0.17	2.26	-3.10	+0.14
22 ^a	1.07	1.17	2.18	-3.12	$\Delta^\ddagger G^0 = +1.04$
25	0.76	0.54	2.26	-3.26	+0.36

^aStep 22 is a true transition state possessing exactly one imaginary vibrational frequency (see Appendix). Thus, its relative free energy is the standard Gibbs energy of activation, $\Delta^\ddagger G^0$ for H_{ads} adatom recombination.

As the H—H interatomic distance is shortened, relative energies initially increase. As shown in Fig. 1, there is a small energetic barrier around $d_{\text{H-H}} \approx 2.4$ Å. At this point in the MEP, energy increases due to one H_{ads} adatom diffusing across the Mg—Mg bridging site. After diffusion, energy decreases slightly, and the two co-adsorbed H_{ads} atoms are now situated in adjacent hcp and fcc sites, separated by $d_{\text{H-H}} = 2.34$ Å. This structure is shown in Fig. 2(b) and is the same geometry found in previous modeling studies of H₂ dissociation [18]. The relative Gibbs free energy of this geometry is +0.14 eV, due to the fact that H_{ads} adsorption is slightly weaker at hcp sites [17].

When $d_{\text{H-H}}$ is shortened below 2.34 Å, the relative energy begins to rise sharply. This occurs because H_{ads} species approach one another above a bridging site. The MEP peaks at $d_{\text{H-H}} = 1.07$ Å, and the structure is shown in Fig. 2(c). Although many others have identified this structure as the barrier to H₂ dissociation, only Du *et al.* [33] and Vegge [20] have verified that it is a true transition state through vibrational analysis. The Hessian for this structure was computed, and it was verified that the geometry is a first-order saddle point possessing exactly one imaginary vibrational frequency. The unstable mode consists of symmetric H—H bond stretching, and displacement vectors of the mode are shown in the Appendix. The DFT-

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4 calculated $\Delta^\ddagger G^0$ for this reaction is +1.04 eV, relative to step 1 (+0.90 eV, relative to step 9).
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6 This value agrees with the ZPE-corrected barrier for H₂ desorption of +1.05 eV calculated by
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8 Vegge using the harmonic approximation to transition state rate theory [20]. In comparison, the
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10 barrier computed without ZPE corrections is 1.17 eV; hence thermal corrections to the activation
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12 energy of H₂ on Mg(0001) are small, which was also the case in Vegge's calculation [20]. The
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14 present DFT results are also consistent with the experimental estimate of ~1.0 eV activation
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16 energy for H₂ desorption from Mg [52].
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21 As the H_{ads} adatoms are brought closer together, the H₂ molecule is formed and “evolves”
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23 from the surface. Fig. 2(d) shows the product of HER on Mg(0001), which is represented by a
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25 single H₂ molecule physisorbed 3.8 Å above the surface. The optimized H—H interatomic
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27 distance is 0.76 Å, and the relative Gibbs free energy is +0.36 eV. This indicates that the Tafel
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29 reaction on Mg(0001) is endothermic.
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33 The relative energy values listed in Table 1 were calculated in vacuum. However, the
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35 impact of solvation on HER was also modeled with an explicit water molecule oriented both
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37 parallel and perpendicular to the surface. The results are plotted in Fig. 1. The relative energies
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39 calculated for HER in the presence of explicit water (plus signs and squares) were very similar to
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41 those calculated in vacuum (x's), regardless of the orientation of the additional adsorbed water
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43 molecule (both parallel and perpendicular structures shown in Appendix). This indicates that the
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45 presence of water near the Mg/H interface should have little effect on the Tafel reaction. Hence,
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47 no additional implicit solvation (e.g. COSMO) was used to study H_{ads} diffusion and
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49 recombination on Mg(0001).
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55 Table 2 compares activation barriers, E_a , and relative electronic energies, ΔE_{elec} , for HER
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57 on Mg(0001) determined with different methods. Given that most previous studies of H₂
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dissociation on Mg(0001) have employed NEB in VASP [53], it was quickly verified that both constrained geometry optimization (with subsequent re-optimization) and LST/QST in DMol3 find the same transition state structures as NEB. However, differences in the computed energies are expected because VASP calculations use a different basis set than DMol3.

Table 2

Comparison of activation barriers, E_a and relative electronic energies, ΔE for H_{ads} adatom recombination on Mg(0001) obtained with different transition state searching methods and simulation environments. LST/QST = linear synchronous transit/quadratic synchronous transit method implemented in DMol3. NEB = nudged elastic band method implemented in VASP.

Method	Environment	E_a (eV)	ΔE (eV)
Constrained geom. opt	vacuum	1.17	+0.54
	explicit water (parallel)	1.14	+0.52
	explicit water (perpendicular)	1.18	+0.52
LST/QST	vacuum	1.06	+0.36
NEB	vacuum	0.96	+0.27

Each of the different computational methods listed in Table 2 identified the structure in Fig. 2(c) as the transition state for H_{ads} adatom recombination. In addition to this, two additional paths were explored with the constrained geometry optimization method. The first involved H_{ads} adatom recombination directly over a Mg atom (as opposed to over a bridging site). This path has a much higher activation energy of ~ 1.9 eV. Hence, H_{ads} adatom recombination over the Mg—Mg bridging site should occur more rapidly than over a Mg atom. The second path involved the diffusion of a subsurface H atom, which then recombines with an adsorbed species to generate H_2 gas. The MEP of this mechanism is plotted in Fig. 3, and relative energies of selected points are listed in Table 3.

At the beginning of the MEP, $d_{H-H} = 2.30$ Å. One H atom is adsorbed in a surface fcc site, while the other is situated directly below the surface, in an octahedral interstitial site between the top two layers of Mg. The structure is shown in Fig. 4(a). This structure is energetically

favorable, and the computed binding energy is -0.20 eV, relative to H₂. This is consistent with other theoretical studies that have computed favorable binding energies for atomic H absorbed at subsurface sites [54-56]. Moreover, it is reasonable for an arrangement like that shown in Fig. 4(a) to occur in the topmost layers of the Mg surface because it is known that hydrogen can penetrate into and diffuse through Mg and its alloys [29, 57].

Just as in Fig. 1, shortening the H—H interatomic distance below 2.30 Å causes energy to increase. At the peak of the MEP, $d_{\text{H-H}} = 1.01$ Å and $E_a = 1.33$ eV. At this point, the two H atoms are in close proximity but are still embedded in the Mg surface (see Fig. 4(b)). The final step of the MEP has H₂ physisorbed 3.8 Å above the Mg surface. The structure of the product, shown in Fig. 4(c), is identical to that in Fig. 2(c), and re-optimization found $d_{\text{H-H}} = 0.76$ Å. This subsurface HER mechanism has $\Delta G^0 = +0.038$, indicating no strong thermodynamic driving force. Moreover, its activation energy is much higher: $E_a = 1.33$ eV for subsurface recombination versus ~1.0 eV for Tafel recombination. Hence, the Tafel reaction should be faster, given equal concentrations of surface and subsurface H species.

Fig. 3

Fig. 4

Table 3

Electronic energies and thermodynamic variables for selected stationary points along the MEP for subsurface H* diffusion and recombination on Mg(0001). Structures shown in Fig. 4.

step	$d[\text{H—H}]$ (Å)	ΔE (eV)	ZPE (eV)	G_{vib} (eV)	ΔG^0 (eV)
1	2.30	0.0	2.20	-3.14	0.0
14 ^a	1.01	1.33			
17	0.76	0.016	2.26	-3.19	+0.038

^aStep 14 is unstable against geometry optimization. Hence, no thermodynamic variables were calculated for this point in the MEP.

3.2 Water dissociation reaction

Just as with the Tafel reaction for HER, the reaction pathway for water dissociation (as written in Equation [5]) was studied with constrained geometry optimization. The MEP for HO—H bond breaking on the Mg(0001) surface was mapped by constraining the distance between H_{ads} and OH_{ads} species in 0.1 Å steps and referencing energies to the optimized starting structure. A plot of relative energy vs. d_{HO-H} is shown in Fig. 5. At the beginning of the MEP, a single H_2O molecule is chemisorbed on the Mg(0001) surface, with the oxygen atom situated 2.26 Å directly above a Mg atom. This structure is shown in Fig. 6(a). As before, selected stationary points on the MEP were re-optimized, and the Hessian matrices were calculated. Relative electronic energies and thermodynamic variables for selected steps are listed in Table 4.

Fig. 5

Fig. 6

Table 4

Electronic energies and thermodynamic variables for selected stationary points along the MEP for H_2O dissociation on Mg(0001). Structures shown in Fig. 6.

step	$d[H-OH]$ (Å)	ΔE (eV)	ZPE (eV)	G_{vib} (eV)	ΔG^0 (eV)
1	0.99	0.0	2.60	-3.23	0.0
4 ^a	1.27	0.87	2.83	-3.02	$\Delta^\ddagger G^0 = +1.31$
23	3.17	-1.78	2.48	-3.12	-1.78

^aStep 4 is a true transition state possessing exactly one imaginary vibrational frequency (see Appendix). Thus, its relative free energy is the standard Gibbs energy of activation, $\Delta^\ddagger G^0$ for H—OH bond dissociation.

As the HO—H interatomic distance increases, relative energies initially increase. This occurs because the H_2O molecule rotates from a parallel orientation to a perpendicular orientation, while simultaneously shifting from the atop site to the Mg—Mg bridging site. As shown in Fig. 5, the MEP peaks at $d_{HO-H} = 1.27$ Å. This is the transition state for water dissociation, in which HO—H bond breaking occurs over the bridging site. The structure is

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4 shown in Fig. 6(b). This geometry was verified to be a true transition state, and the unstable
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6 vibrational mode consists of O—H bond “rocking.” (Displacement vectors of unstable mode
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8 shown in the Appendix). This proves that the O—H bond becomes unstable when situated over
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10 the Mg—Mg bridging site. The DFT-calculated $\Delta^\ddagger G^0$ for this reaction is +1.31 eV, which is
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12 much higher than the barrier of 0.87 eV computed without ZPE corrections. Thus, in contrast to
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14 HER, thermal corrections to the barrier for water dissociation are quite large and cannot be
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16 neglected.
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21 As the $d_{\text{HO-H}}$ increases further, H_{ads} and OH_{ads} species diffuse across the surface and
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23 occupy nearest neighbor fcc sites. The “product” geometry is shown in Fig. 6(c), where $d_{\text{HO-H}} =$
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25 3.17 Å; this was previously shown to be the lowest-energy adsorption configuration [17]. The
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27 relative Gibbs free energy for Equation (5) is -1.78 eV. This indicates that water dissociation on
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29 Mg(0001) is exothermic, which is consistent with a previous first principles thermodynamic
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31 study [17].
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36 The relative energy values listed in Table 4 were calculated in vacuum. However, the
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38 impact of solvation on H_2O dissociation was also modeled with both explicit water molecules
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40 and the COSMO implicit solvent medium, and the results are plotted in Fig. 5. The relative
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42 energies calculated for H_2O dissociation in the presence of explicit water (squares) and COSMO
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44 (plus signs) were very similar to each other and were only slightly higher than those calculated in
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46 vacuum (x's). The primary difference was the shift in the transition state position when using
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48 COSMO. This resulted from the fact that molecular chemisorption was different when COSMO
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50 was applied to simulation cell. More specifically, COSMO caused the chemisorbed water in Fig.
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52 6(a) to orient perpendicular to the Mg(0001) surface, with the two hydrogen atoms closest to the
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Table 5 compares E_a and ΔE values for water dissociation on Mg(0001) determined with different methods. COSMO slightly underestimates ΔE (compared to vacuum), but the E_a values are similar (see barrier heights in Fig. 5). Despite the chosen method, the activation barrier for water dissociation is generally higher in models with multiple water molecules compared to that for a single molecule. This is because hydrogen bonding interactions between adjacent molecules increase stability in the double layer, thereby increasing the barrier required for any single molecule to dissociate. This could be studied further by incorporating an extended network of water molecules that better mimics the structure of the double layer or by using *ab initio* molecular dynamics to optimize the hydrogen bonded network. However, this is beyond the scope of the reported work.

Table 5

Comparison of activation barriers, E_a and relative electronic energies, ΔE for water dissociation on Mg(0001) obtained with different MEP searching methods and simulation environments. LST/QST = linear synchronous transit/quadratic synchronous transit method implemented in DMol3.

Method	Environment	E_a (eV)	ΔE (eV)
Constrained geom opt			
	vacuum	0.87	-1.78
	explicit water	1.06	-1.54
	COSMO	1.00	-1.48
	vacuum	1.64	-1.76
LST/QST	explicit water	1.76	-2.18

3.3 Concerted reactions

A major objective of this investigation was to generate a self-consistent, detailed kinetic mechanism for the cathodic reaction on Mg. This involved modeling all intermediate reactions between water dissociation and H_2 evolution on the Mg(0001) surface. It was proposed that the

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4 cathodic reaction on Mg(0001) proceeds through three steps (Equations [7-9]). Assuming that
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6 these three reactions happen sequentially, the transition states that were identified for the Tafel
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8 reaction (Fig. 1) and HO—H bond breaking (Fig. 5) were used as a framework to study
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10 concerted reaction mechanisms involving multiple molecules and adsorbed species.
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14 The culmination of studying these three independent reactions was the development of a
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16 concerted reaction path for Equation (6); the concerted reaction scheme is plotted in Fig. 7, with
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18 corresponding structures shown in Fig. 8. As shown in Fig. 7, the concerted pathway involves
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20 three distinct reaction steps, each possessing its own activation energy and relative energy. These
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22 will now be discussed in detail.
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26 The first step corresponds to Equation (7). The “reactant” structure, shown in the top left
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28 of Fig. 8, consists of two water molecules adsorbed on the Mg(0001) surface. One molecule
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30 adsorbs with its oxygen atom at the atop site, while the second molecule orients with its
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32 hydrogen atoms down. This arrangement maximizes hydrogen bonding between adjacent water
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34 molecules. When one molecule dissociates, it passes through the transition state for HO—H
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36 bond breaking, labeled TS1 in Figs. 7-8. The dissociating molecule sits in the Mg—Mg bridging
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38 site, just as in Fig. 6(b), while the second water molecule remains hydrogen bonded to the OH
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40 group. After HO—H bond dissociation, OH_{ads} and H_{ads} occupy nearest neighbor fcc sites, while
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42 the second water molecule remains adsorbed over a neighboring Mg atom. This reaction has $E_a =$
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44 $+1.06$ eV and $\Delta E = -1.54$ eV. These values can be compared to those for a single water molecule,
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46 namely, $E_a = +0.87$ eV and $\Delta E = -1.78$ eV. In comparison to the case with a single water
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48 molecule, the reaction path for water dissociation with multiple molecules has a slightly higher
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50 activation energy and smaller free energy, which can be attributed to hydrogen bonding
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52 interactions between adjacent water molecules. Despite this, however, water dissociation still has
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4 a strong thermodynamic driving force and should not be hindered by hydrogen bonding
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6 interactions in the double layer.
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9 **Fig. 7**

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11 **Fig. 8**

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14 The second step in Fig. 7 corresponds to Equation (8). In this reaction, the second water
15 molecule dissociates, with the HO—H bond breaking again over the Mg—Mg bridging site
16 (labeled TS2). This reaction results in four adsorbed species on the Mg(0001) surface: two OH_{ads}
17 and two H_{ads} situated in four nearest neighbor fcc sites. This reaction has $E_a = +1.06$ eV and ΔE
18 = -2.16 eV. The activation energy is identical to that of the first step because the HO—H bond
19 breaks over a site with similar symmetry. The relative free energy, however, is much lower,
20 indicating that the thermodynamic driving force for water dissociation becomes stronger when
21 adsorbed species are already present on the surface. This agrees with previous findings about the
22 self-dissociation of water on Mg [13, 17].
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36 The final step in Fig. 7 is the Tafel reaction written in Equation (9). As modeled, the H_{ads}
37 species diffuse toward one another and react to form H₂ gas, while the two OH_{ads} remain on the
38 surface. H—H bond formation occurs over the Mg—Mg bridging site, just as in Fig. 2(c). This
39 reaction has $E_a = +1.40$ eV and $\Delta E = +0.61$ eV. When compared to the Tafel reaction without
40 adsorbed species—for which, $E_a = +1.17$ eV and $\Delta E = +0.54$ eV—the presence of OH_{ads}
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51 Despite the fact that the Tafel recombination step is calculated to be endothermic on
52 Mg(0001), the overall cathodic reaction, as written in Equation (6), is highly exothermic. This is
53 because the two intermediate steps for water dissociation (Equations [7-8]) have large negative
54 values of ΔE . This is also evidenced in Fig. 7, where the first two reaction steps drive the free
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energy into the negative region of the plot. The impact of alloying elements on the magnitude of ΔE will be the subject of future work.

4. Conclusions

A reaction scheme was developed that defines possible intermediate steps of the cathodic reaction in Mg corrosion; the scheme consists of a series of chemical and electrochemical reactions that are formulated with the presence of adsorbed OH_{ads} and H_{ads} species. The cathodic reaction was studied with periodic Density Functional Theory by mapping the minimum energy paths (MEPs) for water dissociation, H_{ads} adatom diffusion, and H_2 evolution on the Mg(0001) surface. These three different processes were first modeled independently to understand the precise mechanisms for bond breaking and formation on the metal surface. Concerted reaction mechanisms involving multiple water molecules and adsorbed species were also studied in order to develop a detailed reaction pathway for the cathodic reaction on Mg(0001). MEPs were constructed using constrained geometry optimization, and suspected stationary points were re-optimized. Hessian matrices were also calculated in order to perform vibrational analyses and compute thermodynamic variables for selected steps along each MEP.

To study the Tafel reaction on Mg(0001), the interatomic spacing between two H_{ads} species was constrained in 0.1 Å steps, and the energies were compared to the optimized starting geometry. Chemical desorption of H_2 was found to involve two steps: H_{ads} adatom diffusion and H—H bond formation at the Mg—Mg bridging site. H_{ads} adatom diffusion between adjacent fcc and hcp sites was found to have a very small kinetic barrier of +0.14 eV. In contrast, H—H bond formation occurs over the Mg—Mg bridging site, and has $\Delta^\ddagger G^0 = +1.04$ eV. Therefore, the diffusion of H_{ads} species will occur much more rapidly than the Tafel reaction at room temperature. Furthermore, the Tafel reaction was predicted to be endothermic on Mg(0001), with

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4 $\Delta G^0 = +0.36$ eV. Future investigations will study how the Tafel reaction varies on other cleavage
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7 planes, surfaces with defects, and Mg alloy intermetallic phases.
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9 An alternative mechanism for HER was modeled that involved the diffusion of
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11 subsurface hydrogen, which then recombines with an adsorbed species to generate H₂ gas. This
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13 subsurface mechanism was found to have a higher activation barrier and negligible Gibbs free
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15 energy, indicating that there is no strong thermodynamic driving force for subsurface hydrogen
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17 to diffuse to the surface and contribute to Mg HER.
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21 Water dissociation, which initiates the cathodic reaction on Mg, was also modeled using
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23 constrained geometry optimization, and the minimum energy path was mapped as a function of
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25 distance between nearest neighbor OH_{ads} and H_{ads} species. The MEP barrier occurred over the
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27 Mg—Mg bridging site, and frequency analysis verified that the geometry was a true transition
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29 state. Visualization of the unstable mode at the transition state revealed “rocking” of the O—H
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31 bond, a motion which ultimately drives the bond to break and enables dissociated species to
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33 adsorb to the Mg surface. Water dissociation to form OH_{ads} and H_{ads} species has $\Delta^\ddagger G^0 = +1.31$
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35 eV and $\Delta G^0 = -1.78$ eV, indicating that the reaction is highly favorable. This is consistent with
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37 previous DFT modeling studies that focused on the thermodynamics of water dissociation,
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39 without considering the explicit kinetic pathways [17].
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45 Lastly, a complete reaction pathway for the cathodic reaction on Mg(0001) was
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47 developed by modeling concerted reactions involving multiple water molecules. Results show
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49 that the overall cathodic reaction on Mg(0001) is highly exothermic, even though the final step—
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51 the Tafel reaction—is slightly endothermic. Furthermore, hydrogen bonding interactions
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53 between adjacent water molecules have a negligible effect on the kinetic barriers and
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55 thermodynamic variables that drive water dissociation. The presence of co-adsorbed species,
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4 however, does impact the energetics. Specifically, the presence of OH_{ads} promotes further water
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6 dissociation by driving the reaction path toward more negative values. It also raises the
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8 activation energy of the Tafel reaction, likely because of local charge transfer due to OH_{ads}
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10 chemisorption. From these findings, it is postulated that the kinetics of intermediate steps in the
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12 cathodic reaction on Mg will be dependent on the surface coverage of adsorbed species.
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41 42 **Appendix**

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44 **Fig. A.1**

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46 **Fig. A.2**

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51 52 53 54 **References**

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Fig. 1. Minimum energy path (MEP) for H_{ads} adatom diffusion and recombination on Mg(0001) obtained by constrained geometry optimization. Reaction path was sampled by constraining the interatomic distance between H_{ads} species. Data are included for a model in vacuum (x's), a model with one explicit water molecule adsorbed parallel to the surface (plus signs), and a model with one explicit water molecule adsorbed perpendicular to the surface (squares).

Fig. 2. Optimized geometries at selected stationary points along the MEP for H_{ads} adatom diffusion and recombination on Mg(0001). (a) At the beginning of the MEP (step 1), two H_{ads} adatoms are adsorbed at adjacent fcc sites, separated by 3.11 Å. (b) After diffusion of one H_{ads} adatom to an hcp site (step 9 along the MEP). (c) Transition state for H_{ads} adatom recombination over the Mg-Mg bridging site (step 22 along the MEP). (d) Final point on the MEP (step 25), in which a single H_2 molecule is situated over the Mg(0001) surface.

Fig. 3. Minimum energy path (MEP) for subsurface H* diffusion and recombination on Mg(0001) obtained by constrained geometry optimization. Reaction path was sampled by constraining the H—H interatomic distance.

Fig. 4. Optimized geometries at selected stationary points along the MEP for subsurface H* diffusion and recombination on Mg(0001). (a) At the beginning of the MEP (step 1), one H_{ads} adatom is adsorbed at the fcc site, with a second H* atom situated at an octahedral subsurface site between the first and second Mg layers. (b) Pseudo transition state for subsurface H* recombination (step 14 along the MEP). (c) Final point on the MEP (step 17), in which a single H_2 molecule is situated over the Mg(0001) surface.

Fig. 5. Minimum energy path (MEP) for water dissociation on Mg(0001) obtained by constrained geometry optimization. Reaction path was sampled by constraining length of the H—OH bond.

Fig. 6. Optimized geometries at selected stationary points along the MEP for H_2O dissociation on Mg(0001). (a) At the beginning of the MEP (step 1), a single H_2O molecule is adsorbed parallel to the surface with the oxygen atom situated above an atop site. (b) Transition state for H_2O dissociation; H—OH bond scission occurs over the Mg-Mg bridging site (step 4 along the MEP). (c) Final point on the MEP (step 23), at which OH_{ads} and H_{ads} species are co-adsorbed at adjacent fcc sites.

Fig. 7. Concerted reaction pathway for H_2O dissociation and subsequent H_2 evolution on $\text{Mg}(0001)$. Intermediate steps in the reaction pathway are labeled with their respective chemistries, while transition states are labeled TS_x .

Fig. 8. Optimized geometries at stationary points along the concerted reaction pathway for H_2O dissociation and subsequent H_2 evolution on $\text{Mg}(0001)$. Relative energies for each structure are shown in Figure 7.

Fig. A.1. Same structures as shown in Figure 2, but with one explicit water molecule added to the model. The additional water is adsorbed at an adjacent Mg atop site, and the plane of the molecule is oriented parallel to the surface.

Fig. A.2. Same structures as shown in Figure 2, but with one explicit water molecule added to the model. The additional water is adsorbed above a Mg—Mg bridging site, and the plane of the molecule is oriented perpendicular to the surface.

Fig. A.3. Displacement vectors for the unstable vibrational mode corresponding to the transition state of H_{ads} adatom recombination on Mg(0001). This mode has an imaginary frequency of 1176.2 cm^{-1} . (a) Vertical projection of the mode, with a black line indicating the bridging site between nearest-neighbor Mg atoms. (b) Projection along the [110] vector. Atom sizes were reduced for easier visualization of the vectors.

Fig. A.4. Displacement vector for the unstable vibrational mode corresponding to the transition state of water dissociation on Mg(0001). This mode has an imaginary frequency of 406.1 cm^{-1} . (a) Vertical projection of the mode, with a black line indicating the bridging site between nearest-neighbor Mg atoms. (b) Projection along the $[-110]$ vector. Atom sizes were reduced for easier visualization of the vector.