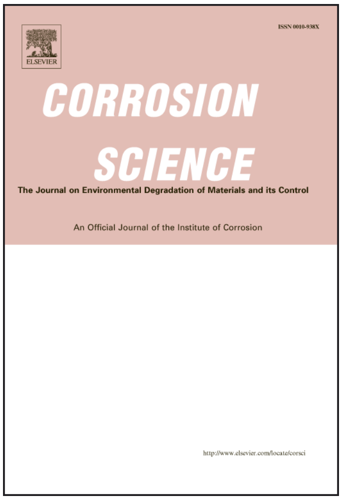

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PII: S0010-938X(14)00573-3
DOI: http://dx.doi.org/10.1016/j.corsci.2014.12.004
Reference: CS 6136

To appear in: *Corrosion Science*

Received Date: 1 October 2014
Accepted Date: 2 December 2014

Please cite this article as: A.D. Atrens, I. Gentle, A. Atrens, Possible dissolution pathways participating in the Mg corrosion reaction, *Corrosion Science* (2014), doi: http://dx.doi.org/10.1016/j.corsci.2014.12.004

Possible dissolution pathways participating in the Mg corrosion reaction

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Abstract

The Mg corrosion reaction sequence was considered in terms of possible elementary reaction steps, and their plausibility in relation to their thermodynamic status. The uni-positive Mg^+ reaction sequence is thermodynamically favoured, and can occur by a number of elementary steps. There are a number of possible dissolution reactions (which are defined are reactions which contribute no electrons to the corroding Mg electrode). It is impossible at this stage to conclusively determine the reaction mechanism without knowledge of the species present at the magnesium–water interface.

Keywords: A. magnesium; B. modelling studies

1. Introduction

1.1 Issues to be addressed

The uni-positive Mg^+ corrosion reaction sequence for Mg corrosion developed by Song, Atrens and co-workers [1-5] has the following two key aspects: (i) that the anodic and cathodic partial reactions occur preferentially at breaks in a partly protective film, and (ii) that the anodic partial reaction involves the uni-positive Mg^+ ion as a short-lived intermediate, which is extremely reactive, and can spontaneously react with water. This means that a fraction *k* of the available Mg^+ is oxidised by an anodic partial reaction to Mg^{2+}, by the reaction given in Eq. (2), and that the complement reacts with water by the dissolution reaction Eq. (3), which contributes no electrons to a corroding Mg electrode. Mg^+ as a reaction intermediate is consistent with the fact that transfer of two electrons in a single step is more unlikely than the transfer of one electron. That proposed reaction sequence is

$$Mg \rightarrow Mg^+ + e^- \tag{1}$$

$$kMg^+ \rightarrow kMg^{2+} + ke^- \tag{2}$$

$$(1-k)Mg^+ + (1-k)H_2O \rightarrow (1-k)Mg^{2+} + (1-k)OH^- + (0.5-0.5k)H_2 \tag{3}$$

$$(1+k)H_2O + (1+k)e^- \rightarrow (0.5+0.5k)H_2 + (1+k)OH^- \tag{4}$$

The sum of these reactions gives the expected overall reaction:

$$Mg + 2H_2O \rightarrow Mg^{2+} + 2OH^- + H_2 \tag{5}$$

Atrens et al [4,6] and Shi and Atrens [7,8] reviewed the available experimental evidence and concluded that this uni-positive Mg^+ reaction sequence was consistent with the available evidence regarding the details of Mg corrosion, in particular (i) that Mg corrodes with an apparent valence of less than 2.0 [9,10], and (ii) that the amount of evolved hydrogen increases with increasing anodic polarisation [4,7,8]. The fact that Mg corrodes with an apparent valence of less than 2.0 is explained by the fact that the corrosion is only partly electrochemical and that there is the dissolution reaction given by Eq. (3) that does not contribute any electrons to the corroding Mg electrode. The fact that the amount of evolved hydrogen increases with increasing anodic polarisation is also explained by Eq. (3). This uni-positive Mg^+ reaction sequence expects that the film-free area increases with anodic polarisation, so that the cathodic partial reaction also increases with anodic polarisation. Thus, the increase in hydrogen evolution with increasing potential has the following two causes: (i) increased cathodic hydrogen evolution because of an increased area on which the cathodic partial reaction occurs, Eq. (4), and (ii) increased hydrogen evolution by the dissolution reaction Eq. (3) because of the increasing amounts of Mg^+ on anodic polarisation, by Eq. (1).

The apparent valence for Mg during corrosion has been evaluated [9,10] using

$$V = \frac{2P_i}{P_H} \tag{6}$$

in which it is assumed that P_i is a good measure of the corrosion rate under electrochemical control as measured by Tafel extrapolation of a cathodic polarisation curve, and P_H is the corresponding (and measured essentially simultaneously) corrosion rate evaluated from the hydrogen evolution rate, and furthermore that P_H is a good measure of the total corrosion rate as measured by weight loss.

A perceived shortcoming of this uni-positive Mg^+ corrosion reaction sequence is the lack of observation of Mg^+ in solution. However, gas phase studies have shown that Mg^+ reacts spontaneously with water in micro-seconds [11-15]. Moreover, Mg^+ is involved in the production of Grignard reagents [16], and Mg^+ is also common in stars as MgH [17]. These studies show that Mg^+ exists, and indicate that Mg^+, produced by a reaction such as Eq. (1) at the Mg surface, reacts quickly with water. This indicates that Mg^+ does not exist in aqueous solutions, and the uni-positive corrosion reaction sequence does not require Mg^+ to exist in aqueous solution. The existence of Mg^+ on the Mg surface as suggested by Eq. (1) depends on the thermodynamics as presented subsequently in this paper.

Some recent papers [18-28] have suggested that Mg^+ is not required in the Mg corrosion reaction sequence. These papers are discussed in Section 1.2. Analysis of each of these papers indicates that there is no convincing experimental evidence to support their suggestion that Mg^+ is not required in the Mg corrosion mechanism. There is insufficient information available to determine the mechanism of Mg corrosion, under the formal definition of *mechanism* by the International Union of Pure and Applied Chemistry [29], and not enough to rule out any of the particular reaction sequences by which the corrosion process may progress.

Recently, Lebouil et al [27] studied Mg corrosion using atomic emission spectro-electrochemistry (AESEC). They found that the amount of dissolved Mg was significantly greater than expected from application of the Faraday law. They proposed that the corrosion occurred by the combination of the electrochemical reaction:

$$Mg \rightarrow Mg^{2+} + 2e^- \tag{7}$$

and the dissolution reaction:

$$\mathrm{Mg} + 2\mathrm{H_2O} \rightarrow x\mathrm{Mg}^{2+} + (1-x)\mathrm{Mg(OH)_2} + \mathrm{H_2} + 2x\mathrm{OH}^- \qquad (8)$$

It is possible to show that (i) the experimental data of Lebouil et al [27] are consistent with the uni-positive Mg^+ corrosion reaction sequence, and that (ii) the experimental data cannot distinguish between the uni-positive Mg^+ reaction sequence, and the reaction sequence described by the combination of Eqs. (7) and (8). The reason is that the two reaction sequences propose both (i) an electrochemical step, plus (ii) a dissolution step; and the products $Mg(OH)_2$, Mg^{2+}, and OH^- are in rapid equilibrium making the product species of Eqs. (5) and (8) indistinguishable.

The dissolution reaction, Eq. (8) involves the reaction of three species, which is considered an unlikely occurrence, and is consequently unlikely as a single step reaction. Nevertheless, it is possible that this dissolution reaction can occur by a number of simpler elementary reaction steps.

That consideration prompted this paper, which has the aim of examining the possible elementary reaction steps for Mg corrosion, with the aim of achieving a deeper understanding of the Mg corrosion process. This examination has been conducted on the basis that:

1. A thermodynamic analysis, on the basis of the assumption that kinetic factors are not controlling factors of the reaction sequence, can provide insights into the possible reaction mechanism;
2. An overall reaction, such as Eq. (5), can be understood as the net outcome of a reaction sequence: a series of elementary reactions each involving at most two reactant chemical species;
3. The rate of any individual elementary reaction can be understood as dependent on an activation energy, which is directly related to the standard Gibbs energy of formation of an unstable, short-lived transition state present during the elementary reaction process;

4. If the reaction sequence includes steps that are thermodynamically unfavourable (i.e. with a positive change in Gibbs energy), the mechanism can be interpreted to be less likely than the alternatives (subject to the first assumption);
5. Individual elementary reactions which involve only the transfer of charge are considered fast relative to other reactions; and
6. Reactions which produce more than two products are considered irreversible.

1.2 Recent literature on Mg^+

Samaniego, Hurley and Frankel [18] repeated those experiments of Petty et al [30], which had claimed that the Mg^+, produced during Mg corrosion, was stable for minutes, and could be transported to a different location where an oxidant could be reduced. Samaniego, Hurley and Frankel [18] found that there were other reducing species present in the experiment, which could reduce the oxidant, and concluded that the existence of Mg^+ could not be proven by this method. This finding by Samaniego, Hurley and Frankel [18] is entirely consistent with the gas phase studies that indicate that Mg^+ reacts spontaneously with water in microseconds [11-15]. This indicates that, whilst Mg^+ at the corroding Mg surface quickly reacts with water, Mg^+ does not exist in aqueous solutions.

Frankel et al. [19] suggested a Mg corrosion reaction sequence that is designated herein the increased exchange current density reaction sequence. This reaction sequence proposes that that Mg corrosion can be explained by the following assumptions: (i) the anodic partial reaction is simply Eq. (7) in one step, (ii) the cathodic partial reaction is simply the hydrogen evolution reaction on the corroding Mg surface, as given by:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (9)$$

(iii) there are no other reactions, (iv) there are no surface films, and (v) the rate of hydrogen evolution increases with anodic polarisation because of an extremely rapid increase of the exchange current density for the hydrogen evolution reaction. The assumption of no surface film was required for this reaction sequence to be different to the uni-positive Mg^+ in which a surface film is an integral part of the corrosion reaction sequence. The current density of the cathodic partial reaction, i_c, at a potential, E, can be expressed as follows.

$$i_c = i_{c0} \exp \{-(E - E_{ce})/\beta_{c0}\} \tag{10}$$

where i_{c0} is the exchange current density of the cathodic partial reaction, E_{ce} is the equilibrium potential for the cathodic partial reaction, and β_{c0} is the Tafel constant for the cathodic partial reaction. It is assumed that the rate of increase of the exchange current density, i_{c0}, is sufficiently rapid to offset the rapid exponential decrease of the cathodic partial reaction with anodic polarisation as given by the second term.

There has been no attempt to verify the increased exchange current density reaction sequence. There have been no measurements related to the exchange current density of the cathodic reaction.

Support for the increased exchange current density reaction sequence has, nevertheless, been expressed by [20-22] based on a measured increase in hydrogen evolution after anodic polarisation. These studies were all in the early stages of corrosion of Mg, where there was an acceleration of the corrosion rate accompanied by an observed increase in the area that was actively corroding attributable to the breakdown of the original surface film. These studies did not carry out any measurements of the exchange current density of the cathodic reaction. Thus the suggestion these studies support the increased exchange current density reaction sequence is based on speculation rather than experimental evidence. In so far as the increase in the hydrogen evolution rate was caused by the observed increase in corroding area, these studies equally support (i) the uni-positive Mg^+ reaction sequence, and (ii) a reaction sequence based on the enrichment during the early stages of corrosion of Fe-rich particles on the corroding surface.

The increased exchange current density reaction sequence assumes *inter alia* that: (i) the anodic partial reaction is simply Eq. (7) in one step, (ii) the cathodic partial reaction is simply the hydrogen evolution reaction on the corroding Mg surface, as given by Eq. (9), and (iii) there are no other reactions. A direct consequence of these assumptions is that the increased exchange current density reaction sequence predicts that the apparent valence of Mg during corrosion is always equal to 2.0. However, there is compelling evidence that the apparent valence of Mg is less than 2.0 [9,10,31-33].

King, Birbilis and Scully [34] asserted that the charge passed as measured by electrochemical impedance spectroscopy (EIS) during Mg corrosion in various chloride solutions was equal to that which they measured from mass loss. This is analogous to an apparent valence of Mg of 2.0. Analysis of their results indicates that the agreement was because of their particular choice of critical parameters, the values of the anodic Tafel slopes, β_{a0}, used in their data analysis. They did not use their experimental values, which were constant and are plausible. Instead they chose values that differed by a factor a five, and were up to 10 times larger than their experimental values. If their experimental values of β_{a0} are used to evaluate the corrosion rate associated with their EIS data, then the evaluated values of apparent valence of Mg in their experiments are significantly less than 2.0. In addition, it is also possible to evaluate the corrosion rate, P_i, from their measured, iR-corrected, polarisation curves [34] (which were measured soon after specimen immersion in the solution) and to evaluate the corrosion rate from their weight loss data [34], P_W, which provides an average value for the whole corrosion test. In this evaluation i is the measured current density and R is the resistance between the specimen and the reference electrode. Their values of P_i were one to two orders of magnitude lower than their values of P_W; and were consistent with Gandel et al [35], and Sudholz et al [36]. Furthermore, the data of King, Birbilis and Scully [34] indicated that the corrosion rate typically decreased during their corrosion tests, so that a corrosion rate measured in the early stages of the corrosion tests, such as P_i, should be greater than the average corrosion rate, as measured by the weight loss, P_W. Thus their measurements [34] of P_i one to two orders of magnitude smaller than P_W seems to indicate that their electrochemical measurements need to be considered carefully.

Williams, McMurray and co-workers [23-25] used the elegant Scanning Vibrating Electrode Technique (SVET) to study the early stages of Mg aqueous corrosion, during which there was the breakdown of the surface film formed during specimen preparation. They found spatially separated anodes and cathodes, attributable to filiform corrosion, and to micro-galvanic corrosion due to Fe-rich phases in low purity Mg. They found that that the magnitude of the area-integrated anodic current was equal to the area integrated cathodic current, as required by electrical neutrality, giving confidence in their measurements. They assumed that there was no other important phenomena during corrosion, and stated that their measurements therefore indicated that there was no need for the Mg^+ ion in the Mg corrosion reaction sequence. That is true of their measurements, if there were no other phenomena, during Mg corrosion. They assumed that the anodic current was given by Eq. (7), but did not measure weight loss to check if the weight loss corresponded to that which would be expected if this was indeed the anodic reaction, rather than the combination of Eqs. (1) to (3). They did measure, in some cases, the amount of evolved hydrogen and found that the amount of evolved hydrogen was significantly higher than expected from the measured cathodic current. Thus their data indicated that there were other corrosion processes in their experiments in addition to their measured anodic and cathodic currents, and moreover, the additional evolved hydrogen measured in their experiments was as expected if the anodic reaction does indeed involve the uni-positive Mg^+ ion.

Swiatowska, Volovitch and Ogle [26] developed an elegant measurement technology: atomic emsision spectro-electrochemistry based on measuring the concentration of ions in solution. They concluded that Mg corroded directly to Mg^{2+} ions in a sulphate and chloride solution, and that the corrosion did not involve Mg^+. Eq.(5) does indeed indicate that it is in principle possible to measure the corrosion rate of Mg by a measurement of the quantity of corroded Mg^{2+} ions. However, in practice, the low solubility of $Mg(OH)_2$ means that the quantity of Mg^{2+} in solution significantly underestimates the quantity of Mg^{2+} ions that have been corroded from the Mg metal. The subsequent study of Lebouil et al [27] from the same laboratory, allowed a mass balance to be carried out, which indicated that only 60% of the Mg^{2+} ions were actually measured. It would be expected that the same would apply to the previous study by Swiatowska, Volovitch and Ogle [26], and also to the subsequent study by Rossrucker et al [28] who used a different apparatus to carry out essentially equivalent measurements. Thus the experimental basis is not valid for these studies [26,28]. It is worth stressing that Lebouil et [27] nevertheless found that the amount of Mg dissolved was much greater than expected from the Faraday Law, despite the fact that they measured only 60% of the corrosion. As discussed above, the data of Lebouil et al [27] are consistent with the uni-positive Mg^+ reaction sequence, and also with their proposed reaction sequence, which also involved a dissolution reaction, in their proposal, the dissolution reaction is Eq. (8). Similar conclusions are arrived at for the studies of Swiatowska, Volovitch and Ogle [26] and Rossrucker et al [28] if their measurements are corrected for the fact that their measurements significantly under-estimated the amount of Mg^{2+} ions that were actually corroded in their experiments.

1.3 Thermodynamic considerations

Table 1 presents values of the standard Gibbs energy of formation of species of interest, in the states specified in Table 1, except MgOH. Under conditions of constant temperature and pressure (as is the case in the relevant Mg corrosion experiments), the standard Gibbs energy of formation is identical to the standard chemical potential. In this work Gibbs energy of formation is used to refer to this quantity. The values reported in Table 1 use a reference state temperature of 298.15 K, a reference state pressure of 1 bar, and for aqueous species, a reference state molality of a hypothetical ideal solution of 1 mol kg^{-1}. The thermodynamic quantities are from [37,38] and Perrault for (Mg^+) [39] and are consistent with those of Song [1].

The value for the standard Gibbs energy of formation of Mg^+ reported by Perrault [39] was derived by Pobedinskii, Krestov, and Kuzmin [40]. This was calculated based on the assumption that the enthalpy and entropy of formation can be determined based on ion radius (from [41]), and correlations of entropy and enthalpy of hydration for monovalent alkali metal ions, and their respective radii. Independent evaluation of the values of standard Gibbs energy of formation is beyond the scope of this paper; nevertheless, this approach for the determination of the available value of the standard Gibbs energy of formation of Mg^+ appears to be reasonable. The implications of different values for the standard Gibbs energy of formation of Mg^+ are discussed later. However, the value for Mg^+ reported by Pobedinskii, Krestov, and Kuzmin [40] implies that Mg^+ is unstable in the presence of water, and so is consistent with other studies [11-15] of the Mg^+ species.

Perrault [39] realised that there was no available value of the standard Gibbs energy of formation of MgOH. He assumed an arbitrary value, and by considering the implications of this value, showed that the initial assumed value was much too large. Elementary reactions involving MgOH are discussed in this work; however the change in Gibbs energy for these reactions is considered indeterminate. MgH discussed in the context of the elementary reactions in this work can be considered equivalent to an adsorbed hydrogen atom, such as those referenced in Eqs. (3) and (4). As Mg and H form a stable gaseous compound, MgH(g), the standard Gibbs energy of formation of said compound is used for thermodynamic considerations as a best approximation of the standard Gibbs energy of formation of hydrogen adsorbed to the Mg surface. Note that the states of all molecular species with thermodynamic data are specified in Table 1.

For ease of comparison, the change in Gibbs energy ($\Delta G°$) is given for each reaction, even if the reaction is electrochemical. The equilibrium constant is given by: $K_{eq} = \exp(\Delta G°/RT)$ [42], where R is the universal gas constant, and T is the absolute temperature; the reference state for the equilibrium constant is consequently the same as for the standard Gibbs energy of formation data provided in Table 1.

The overall magnesium (Mg) corrosion reaction consumes Mg and water; produces magnesium hydroxide, and hydrogen; and is given by:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \qquad \Delta G° = -359{,}337 \text{ J mol}^{-1},\ K_{eq} = 9.05 \times 10^{+62} \tag{11}$$

Magnesium hydroxide is thermodynamically favoured so it is expected to be the dominant product of reaction between stoichiometric quantities of water and magnesium. Where water is in substantial excess, magnesium hydroxide is in equilibrium with dissolved Mg ions and hydroxide ions according to:

$$Mg(OH)_2 \rightleftharpoons Mg(OH)^+ + OH^- \qquad \Delta G° = +49{,}706 \text{ J mol}^{-1},\ K_{eq} = 1.96 \times 10^{-9} \tag{12}$$

$$Mg(OH)^+ \rightleftharpoons Mg^{2+} + OH^- \qquad \Delta G° = +14{,}717 \text{ J mol}^{-1},\ K_{eq} = 2.64 \times 10^{-3} \tag{13}$$

Both dissociation reactions are thermodynamically unfavourable, and Mg is only sparingly soluble as Mg^{2+} and $Mg(OH)^+$. For instance, in a solution of pH 10.35, the pH value expected at a corroding Mg surface [4], the activity of the ions are as follows: $[OH^-] = \sim 2.24 \times 10^{-4}$ mol L^{-1}, $[MgOH^+] = \sim 8.75 \times 10^{-6}$ mol L^{-1}, and $[Mg^{2+}] = \sim 1.03 \times 10^{-4}$ mol L^{-1}.

The series of individual or elementary reaction steps for the Mg corrosion reaction, Eq. (11), has not been conclusively determined. Mg corrosion is known to be electrochemically mediated, with Mg relinquishing electrons to form ions at the anode (measurable as Mg^{2+} in solution), and H_2O (or H^+) accepting electrons to evolve H_2 gas at the cathode. However, measurements of current between anode and cathode do not balance with the mass of reaction products evolved as per Eq. (11) [1-4,9]. This implies that the reaction proceeds by a combination of both dissolution and electrochemical processes.

1.4 Aims

The aim of this paper is to elucidate which reaction sequences are likely contributors to the Mg corrosion reaction by (i) considering the possible electrochemical, dissolution, and mixed reactions, and (ii) considering these possible reactions in terms of the possible intermediate species. The various possible dissolution and electrochemical reactions are explored to evaluate the plausibility of particular component reactions. Reaction sequences are less likely if they contain elementary reaction steps with a large positive change in Gibbs energy of reaction. The more plausible reaction sequences are those with each individual step leading to a reduction in Gibbs energy.

2. Analysis

2.1 Electrochemical reactions

2.1 Anode

The electrochemical mechanism involves ionisation of Mg at the anode, ultimately to the sparingly soluble $Mg(OH)_2$ (brucite), and $Mg(OH)^+$ and Mg^{2+} by the reactions of Eqs. (14) and (15). Solid $Mg(OH)_2$ may precipitate within the surface film, or in the bulk liquid, and similarly $MgOH^+$ ions may form within the surface film, or in the bulk liquid. The overall anodic partial reaction is:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 + 2e^- \qquad \Delta G° = -359{,}337 \text{ J mol}^{-1},\ K_{eq} = 9.05 \times 10^{+62} \quad (14)$$

or under basic conditions, the overall anodic partial reaction is:

$$Mg + 2OH^- \rightarrow Mg(OH)_2 + 2e^-, \qquad \Delta G° = -519{,}221 \text{ J mol}^{-1},\ K_{eq} = 9.30 \times 10^{+90} \quad (15)$$

The magnesium hydroxide product forms a permeable layer on the surface of corroding Mg.

The overall anodic partial reaction can be comprised of the possible elementary reactions given as Eqs. (16) to (21), with a final conversion to magnesium hydroxide given by the reverse of reaction (12). The thermodynamically favoured reaction sequence cannot be determined by thermodynamic potentials as none of the individual reactions is thermodynamically unfavourable.

$$\mathrm{Mg} + \mathrm{OH}^- \rightleftharpoons \mathrm{Mg(OH)}^+ + 2\mathrm{e}^- \qquad \Delta G° = -496{,}515\ \mathrm{J\ mol}^{-1} \tag{16}$$
$$\mathrm{Mg} \rightleftharpoons \mathrm{Mg}^+ + \mathrm{e}^- \qquad \Delta G° = -256{,}563\ \mathrm{J\ mol}^{-1} \tag{17}$$
$$\mathrm{Mg} \rightleftharpoons \mathrm{Mg}^{2+} + 2\mathrm{e}^- \qquad \Delta G° = -454{,}798\ \mathrm{J\ mol}^{-1} \tag{18}$$
$$\mathrm{Mg}^+ \rightleftharpoons \mathrm{Mg}^{2+} + \mathrm{e}^- \qquad \Delta G° = -198{,}235\ \mathrm{J\ mol}^{-1} \tag{19}$$
$$\mathrm{Mg}^+ + \mathrm{OH}^- \rightleftharpoons \mathrm{Mg(OH)}^+ + \mathrm{e}^- \qquad \Delta G° = -212{,}290\ \mathrm{J\ mol}^{-1} \tag{20}$$
$$\mathrm{Mg}^{2+} + \mathrm{OH}^- \rightleftharpoons \mathrm{Mg(OH)}^+ \qquad \Delta G° = -14{,}717\ \mathrm{J\ mol}^{-1} \tag{21}$$

An intermediate MgOH with an Mg valence state of +1 has been proposed previously. It seems apparent that this is not stable as it has not been isolated, however it is possible that it is present as a short–lived intermediate. The possible electrochemical elementary reactions involving MgOH are as follows.

$$\mathrm{Mg} + \mathrm{OH}^- \rightleftharpoons \mathrm{MgOH} + \mathrm{e}^- \qquad \Delta G° = \text{indeterminate} \tag{22}$$
$$\mathrm{MgOH} \rightleftharpoons \mathrm{Mg(OH)}^+ + \mathrm{e}^- \qquad \Delta G° = \text{presumably –ve} \tag{23}$$

Surface charge on the corroding Mg surface is expected to be shared between Mg atoms as presented in Eq. (24), unless the reported standard Gibbs energy of formation of –256,563 J mol^{-1} (or –61.32 kcal mol^{-1}) for Mg$^+$, from Pobedinskii, Krestov, and Kuzmin [40], is incorrect.

$$\mathrm{Mg}^{2+} + \mathrm{Mg} \rightleftharpoons 2\mathrm{Mg}^+ \qquad \Delta G° = -58{,}328\ \mathrm{J\ mol}^{-1} \tag{24}$$

This reaction is anticipated to have rapid kinetics as it involves only a transfer of charge between different magnesium species, which are in constant close contact. This would mean the dominant charged species of the Mg metal surface could be expected to be Mg$^+$.

Mg^{2+} cannot split water as indicated in Eq. (25); this reaction is thermodynamically unfavourable. In contrast, Mg$^+$ can split water as indicated in Eqs. (26). This means that the basic postulation is sound for the uni-positive Mg$^+$ reaction sequence, in particular Eq. (3). It is instructive to also consider the splitting of water by Mg, as presented in Eq. (27), which is also thermodynamically favoured.

$$Mg^{2+} + H_2O \rightleftharpoons Mg(OH)^+ + H^+ \qquad \Delta G^\circ = +65{,}225\ \mathrm{J\ mol^{-1}} \qquad (25)$$

$$Mg^+ + H_2O \rightleftharpoons Mg(OH)^+ + H^+ + e^- \qquad \Delta G^\circ = -133{,}010\ \mathrm{J\ mol^{-1}} \qquad (26)$$

$$Mg + H_2O \rightleftharpoons Mg(OH)^+ + H^+ + 2e^- \qquad \Delta G^\circ = -389{,}573\ \mathrm{J\ mol^{-1}} \qquad (27)$$

Assuming similar orders of magnitude of activation energies for the elementary reactions, the anodic chemical reaction mechanism most likely consists of contributions from Eqs. (16) to (20), (24), and (26). Direct solubilisation of Mg^{2+} from the surface seems unlikely due to its propensity to share charge with other Mg species, which are obviously in high concentration at the metal surface. This conclusion relies on the value for standard Gibbs energy of formation of Mg^+, and is addressed further in the discussion.

2.2 Cathode

The overall cathodic partial reaction in acidic solutions is:

$$2H^+ + 2e^- \rightarrow H_2 \qquad \Delta G^\circ = 0\ \mathrm{J\ mol^{-1}} \qquad (28)$$

Under basic conditions the overall cathodic partial reaction is:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \Delta G^\circ = +159{,}884\ \mathrm{J\ mol^{-1}} \qquad (29)$$

Reactions Eqs. (28) and (29) occur at the water-metal interface. The cathodic reaction is not favoured, but when balanced with the potential from the anodic reaction, the overall reaction is viable. That is, the overall corrosion reaction given by Eq. (11) has a negative change in Gibbs energy. The possible elementary cathodic reactions are given by Eqs. (30) to (35). The intermediate species MgH is relatively less stable, and preferentially reacts with other MgH, H^+ ions, and water molecules, to form Mg and H_2 species. MgH represents an H atom on the Mg surface.

$$Mg + H^+ + e^- \rightleftharpoons MgH \qquad \Delta G^\circ = +140{,}670\ \mathrm{J\ mol^{-1}} \qquad (30)$$

$$\mathrm{Mg + H_3O^+ + 2e^-} \rightarrow \mathrm{Mg + OH^- + H_2} \qquad \Delta G^\circ = +79{,}942\ \mathrm{J\ mol^{-1}} \tag{31}$$
$$\mathrm{H_2O + Mg + e^-} \rightleftharpoons \mathrm{MgH + OH^-} \qquad \Delta G^\circ = +220{,}612\ \mathrm{J\ mol^{-1}} \tag{32}$$
$$\mathrm{2MgH} \rightarrow \mathrm{2Mg + H_2} \qquad \Delta G^\circ = -281{,}340\ \mathrm{J\ mol^{-1}} \tag{33}$$
$$\mathrm{MgH + H^+ + e^-} \rightleftharpoons \mathrm{Mg + H_2} \qquad \Delta G^\circ = -140{,}670\ \mathrm{J\ mol^{-1}} \tag{34}$$
$$\mathrm{MgH + H_2O + e^-} \rightarrow \mathrm{Mg + OH^- + H_2} \qquad \Delta G^\circ = -60{,}728\ \mathrm{J\ mol^{-1}} \tag{35}$$

It is plausible (and thermodynamically favourable) to form magnesium hydride, MgH_2, in place of Mg + H_2 (g), in any of these elementary reactions. The equilibrium between Mg, MgH_2, and H_2 can be trivially calculated from the standard Gibbs energy of formation included in Table 1, but is of little practical interest to determining the reaction sequences of interest.

2.2. Dissolution reactions

Possible direct dissolution reactions equivalent to Eq. (11) are: (i) direct hydration as given in Eqs. (36) to (41), (ii) oxide-mediated as given in Eqs. (42) to (44), and (iii) hydronium-mediated as given in Eq. (45).

Direct hydration is the process by which magnesium directly splits water molecules without electron transfer through the metal. For this overall reaction to progress by elementary steps, two alternative mechanisms can be postulated. In the first step, water adsorbs to the surface of the magnesium as an Mg-H_2O complex, represented here as Mg●H_2O which then reacts:

$$\mathrm{Mg + H_2O} \rightleftharpoons \mathrm{Mg{\bullet}H_2O} \qquad \Delta G^\circ = \text{indeterminate} \tag{36}$$
$$\mathrm{Mg{\bullet}H_2O + H_2O} \rightleftharpoons \mathrm{Mg(OH)_2 + H_2} \qquad \Delta G^\circ = \text{indeterminate} \tag{37}$$
$$\mathrm{2Mg{\bullet}H_2O} \rightarrow \mathrm{Mg + Mg(OH)_2 + H_2} \qquad \Delta G^\circ = \text{indeterminate} \tag{38}$$

In the second step, the reaction progresses through splitting of water molecules between two Mg atoms, which then adsorb the H^+ and OH^- species:

$$\mathrm{Mg + H_2O} \rightleftharpoons \mathrm{Mg{\bullet}H_2O} \qquad \Delta G^\circ = \text{indeterminate} \tag{39}$$
$$\mathrm{Mg{\bullet}H_2O + Mg} \rightleftharpoons \mathrm{MgOH + MgH} \qquad \Delta G^\circ = \text{indeterminate} \tag{40}$$
$$\mathrm{2MgOH} \rightleftharpoons \mathrm{Mg(OH)_2 + Mg} \qquad \Delta G^\circ = \text{indeterminate} \tag{41}$$

None of the elementary reactions in Eqs. (36)-(41) have a determinable change in Gibbs energy of reaction as it does not appear that Mg is stable in the presence of adsorbed water, as per Eq. (27), and the hydroxyl ion is not expected to adsorb, but react electrochemically, as per Eq. (16), unless a particular combination of Eqs. (22) and (30) is possible. Considering that Eq. (30) is not thermodynamically favourable, and Eq. (22) is also indeterminate, this seems unlikely. This mechanism can probably be dismissed from the observation that Mg dissociates H_2O at room temperature, which is supported by XPS measurements [43].

The oxide-mediated reaction sequence is thermodynamically favoured, as presented by Eqs. (42) and (43). Eq. (43) indicates that there is not much energy released by the conversion of MgO to $Mg(OH)_2$, suggesting that the conversion kinetics may be slow.

$$Mg + H_2O \rightleftharpoons MgO + H_2 \qquad \Delta G^\circ = -332{,}039 \text{ J mol}^{-1} \tag{42}$$
$$MgO + H_2O \rightleftharpoons Mg(OH)_2 \qquad \Delta G^\circ = -27{,}298 \text{ J mol}^{-1} \tag{43}$$
$$MgO + H^+ \rightleftharpoons Mg(OH)^+ \qquad \Delta G^\circ = -57{,}534 \text{ J mol}^{-1} \tag{44}$$

The kinetics of magnesia hydration have been explored in the literature [44], and were found to proceed by Eq. (43), followed by dissolution as per Eqs. (12) and (13), followed by precipitation of $Mg(OH)_2$ at the interface between water layers chemically and physically adsorbed to the MgO surface (i.e. not directly on the MgO surface).

In addition, a side-reaction of MgO is also thermodynamically favoured, as presented by Eq. (44). The rate of this reaction sequence would depend on the relative rates of Eqs. (42) and (43), which would determine the surface coverage of MgO relative to Mg. The literature regarding magnesia dissolution indicates that both $Mg(OH)_2$ and MgO are not impermeable to water.

In the hydronium-mediated reaction sequence, the Mg metal can react with protons and water (effectively with hydronium complexes H_3O^+) to form $Mg(OH)^+$ and H_2 directly, as presented in Eq. (45). This reaction is limited by the presence of native Mg at the interface and the availability of H^+ ions.

$$Mg + H^+ + H_2O \rightleftharpoons Mg(OH)^+ + H_2 \qquad \Delta G^\circ = -389{,}573 \text{ J mol}^{-1} \tag{45}$$

2.3. Mixed reactions

Also plausible are reactions involving the intermediate ionisation species of the electrochemical pathway, i.e. Mg^+, Mg^{2+}, and $MgOH^+$. In particular, generation of $MgOH^+$ is possible through a single ionisation step by Mg-assisted auto-ionization of water, as given by Eq. (46). This effectively results in a change of valence state of the Mg from 0 to +2, with one electron being donated directly to the MgH complex and the other being freed to the metal matrix (and consequently to the cathode).

$$2Mg + H_2O \rightleftharpoons Mg(OH)^+ + MgH + e^- \qquad \Delta G^\circ = -248{,}903 \text{ J mol}^{-1} \qquad (46)$$

This sequence has a similar energy potential to any of the single ionization processes involved in the electrochemical reaction. It requires free surface sites of two Mg atoms, however, and is not strictly an elementary reaction: it has the same requirements of intermediate stability as Eqs. (36) to (41). The reaction may also proceed by the intermediate compound MgOH with a Mg valence state of +1 as given by Eqs. (47) and (48); as previously discussed, the plausibility of such a process is unknown. As the MgOH species has not been isolated, such an intermediate can be expected to be thermodynamically unfavourable.

$$2Mg + H_2O \rightleftharpoons MgOH + MgH \qquad \Delta G^\circ = \textit{indeterminate} \qquad (47)$$
$$MgOH \rightleftharpoons Mg(OH)^+ + e^- \qquad \Delta G^\circ = \text{presumably –ve} \qquad (48)$$

Finally, local charge on the metal surface (from a single ionisation step) may undergo charge transfer with surface water molecules, as given by Eqs. (49) and (50). These reactions are also not strictly elementary, but the combination of Mg and Mg^+ could potentially be abstracted as a positive charge shared between Mg atoms.

$$Mg + Mg^+ + H_2O \rightarrow Mg^{2+} + OH^- + MgH \qquad \Delta G^\circ = +22{,}377 \text{ J mol}^{-1} \qquad (49)$$
$$Mg + Mg^+ + H_2O \rightleftharpoons MgOH^+ + MgH \qquad \Delta G^\circ = +7{,}660 \text{ J mol}^{-1} \qquad (50)$$

Whilst the change in Gibbs energy of these reactions are positive, the values are small, indicating that there may be non-trivial quantities of these variants. The K_{eq} value for Eq. (50) is 4.12×10^{-2}, and so it cannot be entirely ruled out: for a surface dominated by charged Mg species, the reaction could occur non-trivially. This reaction sequence could also be interpreted as Eqs (20) and (30) occurring at the same location on the metal surface, making the electron transfer unmeasurable with conventional means.

Any of these single ionisation step processes result in $MgOH^+$ ions, which are soluble and can precipitate as magnesium hydroxide in the surface film upon exposure to OH^- ions, by the reverse of Eq. (12).

3. Discussion

3.1 Limitations of thermodynamics

The electrochemical reactions associated with Mg corrosion are thermodynamically favoured as was already known. In addition, a number of dissolution sequences are identified. It is impossible at this stage to conclusively determine the mechanisms of this reaction without knowledge of the species present at the magnesium–water interface. These would provide insight into the relative kinetics of the elementary reactions, which are currently uncertain. Until these are known, all that is possible to determine is the likely reaction sequences, which are accomplished by considering the thermodynamically favourable intermediates.

An elementary reaction step proceeds from reactants, through an unstable transition state to the reaction products. Transition state theory [45] holds that observed reaction rate constants of an elementary reaction step are directly related to the Gibbs energy of the transition state:

$$k = \kappa \frac{k_B T}{h} \exp\left(\frac{\Delta G^{\ddagger}}{RT}\right) \tag{51}$$

where $\Delta G^{\ddagger}$ indicates the change in Gibbs energy to progress from an initial state to the transition state [29] and closely related to an Arrhenius activation energy, k_B is the Boltzmann constant, h is the Planck constant, T is the absolute temperature, R is the ideal gas constant, and κ is the a transition constant (usually taken as 0.5 or unity). However, as transition states are unstable, their thermodynamic properties are often difficult to determine directly; if undetermined they can only be evaluated from kinetic data. In this case however, kinetic data is limited. Nonetheless, the theory can provide some residual insight into plausible reaction sequences, as is discussed below.

A reaction sequence is composed of multiple elementary reaction steps. Product species of all but the final step that are sufficiently stable for their thermodynamic properties to be measured are termed intermediates [29]. These are the majority of the species tabulated in Table 1 (excluding, obviously, the reactants and products of the overall reaction described in Eq. (5)).

If a reaction sequence is kinetically-controlled, that indicates that the rate of the overall reaction sequence is limited by particularly large Gibbs energies of a transition state. If it is thermodynamically-controlled, the difference in Gibbs energy between the transition state and the various stable species – reactants, intermediates, and products – is small. Under the latter circumstances, the Gibbs energy of the intermediates plays the governing role in the rate of the overall reaction sequence. At the extreme limit – of entirely negligible activation energies of transition states – a thermodynamically unfavoured intermediate plays a kinetically equivalent role to a transition state. If a reaction sequence includes intermediates that are highly unfavoured, the speed of progression through that particular pathway will – even under the most favourable kinetic circumstances (e.g. with negligible Gibbs energy of transition states) – be limited by the thermodynamically unfavoured intermediates. On the other hand, this does not necessarily imply that a pathway consisting of intermediates that are all thermodynamically favoured will have fast reaction rates – there may be large energy barriers in the form of unquantified transition states that fundamentally limit the reaction progression through that sequence.

Consequently, this analysis is constrained. It is not able to identify which reaction sequence is fastest, and consequently cannot provide the basis for determining the reaction mechanism. It can identify, however, if a particular reaction sequence must be slow due to thermodynamic limitations. That is, it can rule out particular reaction sequences, but not rule any in. It consequently can provide only an indication of the balance of probability as to which reaction sequences may be more or less likely.

The standard Gibbs energy of formation of the different reactants provides some additional information in a measure of their relative stability. The most thermodynamically favoured intermediate species of the different reaction sequences presented here, if identified at the corroding surface, would provide some corroborating evidence in support of the individual reaction sequence to which they contribute.

3.2 The electrochemical reaction sequence

The electrochemical reaction sequence seems most likely to progress by Eqs. (16), (17), (20), (26), and (27). This is concluded on the basis that Mg^{2+} would be expected to be unstable on contact with Mg, readily sharing charge to form Mg^{+} as given by Eq. (24). This is dependent on the current understanding of the standard Gibbs energy of formation of Mg^+. Using the values of standard Gibbs energy of formation given in Table 1, taking species surface activities $\alpha_{Mg} + \alpha_{Mg+} + \alpha_{Mg2+} = 1$, and average surface charge number as being the sum of $\alpha_{Mg+} + 2\alpha_{Mg2+}$, the proportion of the surface species as a function of average surface charge number can be determined, as shown in Fig. 1.

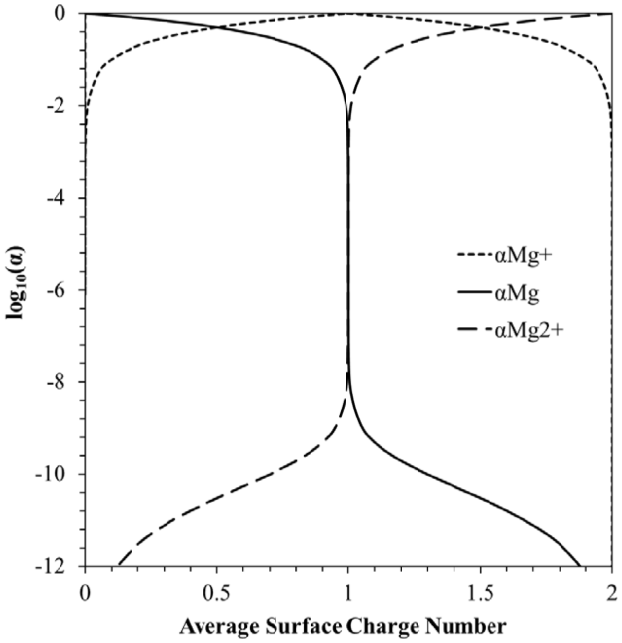

Figure 1: Magnesium species as a function of average surface charge number.

The behaviour shown in Fig. 1 is because the standard Gibbs energy of formation of Mg^+, $\Delta G_f^\circ{}_{Mg+}$, is more negative than half the standard Gibbs energy of formation of Mg^{2+}, i.e. $2\Delta G_f^\circ{}_{Mg+} < \Delta G_f^\circ{}_{Mg2+}$. If the current value for $\Delta G_f^\circ{}_{Mg+}$ is not correct, the surface behaviour may be substantially different. For example, if $\Delta G_f^\circ{}_{Mg+} = -198{,}234$ J mol^{-1}, the charged Mg species would follow the behaviour shown in Fig. 2. Under these circumstances, Eqs. (16), (18), (19), and (21) would instead provide the dominant elementary reactions within an electrochemical reaction sequence.

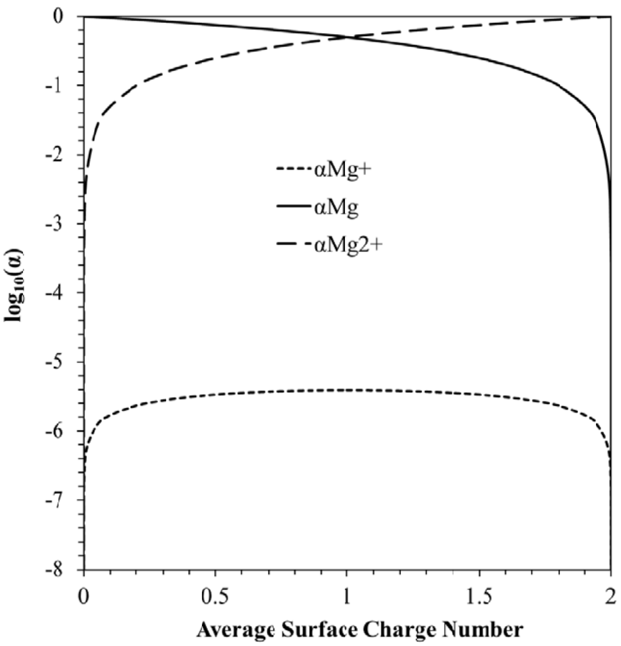

Figure 2: Magnesium species as a function of average surface charge number if the standard Gibbs energy of formation of Mg^+ has a much smaller value than indicated in the literature [40].

It can be concluded that the electrochemical reaction sequence at the anode is likely to take one of the pathways described above, dependent on the standard Gibbs energy of formation of Mg^+. Measurements of the surface species, or a better delineation of the Mg^+ standard Gibbs energy of formation, may clarify which of the above pathways is preferred, but given current data, the reaction sequence appears to progress by Mg^+.

The cathodic pathway is not of particular interest, except to note that in alkaline solutions Eqs. (32) and (35) are the more plausible reaction sequences due to the limited presence of H^+.

3.3 The dissolution reaction sequence

A dissolution reaction sequence in addition to the above electrochemical reaction sequence is necessary to explain discrepancies between measured Mg dissolution and the Faraday law [1,4,9]. Of the direct dissolution reactions, it appears that the direct hydration reaction sequence can be disregarded unless water or hydroxyl species can form temporarily stable adsorbed species at the surface. The hydronium-mediated reaction sequence depends on the presence of H^+ species, which will be of limited presence under alkaline conditions. The oxide-mediated reaction sequence appears plausible. That particular reaction sequence could be confirmed by measurement of MgO at the surface, or potentially by further kinetic studies making use of kinetic data of the hydration of MgO and possibly by extrapolation of the decomposition kinetics of $Mg(OH)_2$ to MgO at high temperatures.

In addition to the oxide-mediated dissolution reaction sequence, two distinct mixed reaction sequences were presented, outlined in Eqs. (46) to (48), and Eqs. (49) and (50). Both of these are limited by their reliance on reaction processes that were not strictly elementary. The latter, the Mg^+ mixed reaction sequence, is thermodynamically unfavourable, but not to a sufficient extent to disregard it as a potential contributor to the overall reaction.

Consequently, it seems most plausible that the disparity between measured dissolved Mg and the Faraday law is best explained by a combination of the electrochemical reaction sequence discussed above, and the oxide-mediated dissolution reaction sequence. This particular explanation appears to be supported by reports of an MgO layer underlying the magnesium hydroxide film on Mg corrosion interfaces [46,47]. This would at first glance to appear to be at odds with a conventional electrochemical reaction sequence. However, it must be considered that the MgO may be permeable to water and ion species, a feature that has been reported in the literature regarding MgO hydration kinetics. Alternatively, a surface film of MgO may localise positive charge to regions of virgin Mg surface, rendering those areas more favourable to the electrochemical reaction processes than the dissolution oxidation process.

Additionally it is nominally plausible for local sites on the surface to be acting individually as anodes or cathodes. However the presence of any positively charged species will lead to greater instability of MgH species, which are the intermediates in the cathodic reaction.

A surface dominated by hydrogenated species has not been considered. Such a condition is considered broadly unlikely if hydrogen is allowed to diffuse away from the interface, and as the hydrogenated species of Mg are in general of relatively lower stability, particularly under basic interface and bulk conditions.

3.4 Uni-positive Mg^+ reaction sequence

Previously a uni-positive Mg^+ reaction sequence outlined in Eqs. (1) to (4) was considered [1-5]. This is compatible with the reaction sequences discussed here; it can be matched by the electrochemical reaction sequence as provided by Eqs. (17), (20), (26), and the mixed reaction sequence involving Mg^+ outlined in Eqs. (49) and (50). Most elementary steps are thermodynamically favoured, so the reaction sequence is considered acceptable. The non-electrochemical component – the mixed reaction sequence – is not thermodynamically favoured, but is only slightly disfavoured and so cannot be rules out on that basis. It may be that this fits with the relatively low dissolution reaction rate versus the electrochemical reaction rate. Overall, however, it seems that the oxide-mediated reaction sequence provides a better explanation of the dissolution component of the reaction.

The existing value of the Gibbs energy for Mg^+ is plausible [40] but may not be correct. It is possible that the Gibbs energy is such that Mg^+ cannot exist in the presence of Mg or H_2O. In that case, the dissolution of Mg via the MgO intermediate is the expected reaction sequence.

3.5 Reaction pathways

The apparent valence of Mg during corrosion could provide, in principle, a measure of how much of the total corrosion is by an electrochemical pathway [9,10]. If the apparent valence is evaluated using Eq. (6), it is assumed that (i) the corrosion rate, P_i, evaluated using an electrochemical technique, is a good measure of the corrosion under electrochemical control, and (ii) that the corrosion rate evaluated from the evolved hydrogen, P_H, is a good measure of the total corrosion. If the apparent valence of Mg during corrosion were equal to 2.0, all of the corrosion would be totally by an electrochemical reaction sequence. For cases when the apparent valence of Mg during corrosion is less than 2.0, the simplest assumption is that there is some Mg dissolution, which does not contribute electrons to the electrochemical measurement system.

In practice, however, it is not clear that P_i is always a good measure of the amount electrochemical corrosion. Shi and Atrens [10] showed experimentally that some electrochemical corrosion could be isolated from the electrochemical measurement system.

Subsequently, Atrens and coworkers [4,6,31] have suggested that the evolving hydrogen bubbles could isolate some of the electrochemical corrosion from the electrochemical measurement system, because hydrogen is an insulator.

Thus, the apparent valence of Mg during corrosion provides an estimate of how much corrosion occurs by an electrochemical pathway only if there is no isolation of any electrochemical corrosion from the electrochemical measurement system, by e.g. shielding of corrosion by hydrogen bubbles.

4. Conclusions

The Mg corrosion reaction was considered in terms of possible elementary reaction steps and their plausibility in relation to their thermodynamic status.

1. The uni-positive Mg^+ electrochemical reaction sequence is thermodynamically favoured and can occur by a number of elementary steps.
2. There are a number of possible additional dissolution reaction sequences, of which the oxide-mediated reaction sequence seems most plausible.
3. It is impossible at this stage to conclusively determine the mechanisms of this reaction without knowledge of the species present at the magnesium–water interface.

Acknowledgements

This research was supported by the Australian Research Council Centre of Excellence Design of Light Alloys, CE0561574. Professor Evgueni Jak is thanked for useful discussions about the thermodynamics of Mg^+ and about ref [40].

Table 1 Values of the standard Gibbs energy of formation of species of interest. References [37] and [38] describe how the FACTSAGE thermochemical database determines the standard Gibbs energy of formation as given in Table 1; these values are consistent with the electrochemical potential values given in [1] when converted to standard Gibbs energy of formation, $\Delta G_f°$, via the relation $E° = –\Delta G_f°/zF$, where F is the Faraday, and z is the charge transferred by the reaction.

Species	Oxidation state of Mg	Standard Gibbs energy of formation (J mol^{-1})	Data source
Mg(s)	0	0	[1,37,38]
Mg^+ (aq)	+1	–256,563	[39,40]
Mg^{2+} (aq)	+2	–454,798	[1,37,38]
$MgOH^+$ (aq)	+2	–626,763	[1,37,38]
$Mg(OH)_2$(s)	+2	⁻833,717	[1,37,38]
MgO(s)	+2	–569,229	[1,37,38]
MgH_2(s)	–2	–36,748	[1,37,38]
MgH(g)	+1	140,670	[1,37,38]
H_2O (l)		–237,190	[1,37,38]
H^+ (aq)		0	[1,37,38]
OH^- (aq)		–157,248	[1,37,38]
H_2(g)		0	[1,37,38]

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Highlights

The Mg corrosion reaction was considered in terms of possible elementary reaction steps

The uni-positive Mg^+ electrochemical reaction sequence is thermodynamically favoured

There are a number of possible additional dissolution pathways

It is impossible to determine the reaction mechanism conclusively