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# The negative difference effect and unipositive Mg<sup>+</sup>

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## Abstract

This paper evaluates current understanding of the negative difference effect (NDE) in the corrosion of magnesium. Research from the 1950s is reviewed which provides strong support for the existence of the unipositive magnesium ion. Further evidence in support of the existence of Mg<sup>+</sup> is provided by the fact that the simplest possible reaction sequence is consistent with the experimental evidence. The unipositive Mg<sup>+</sup> ion NDE mechanism has been shown to be useful in providing a framework within which it is possible to evaluate the expected rate of production of Mg<sup>++</sup> and H<sub>2</sub>. However, the uncertainty concerning the existence of the unipositive Mg<sup>+</sup> ion means that there is scope for further research.

**Keywords:** Magnesium corrosion, Negative Difference Effect, NDE, Unipositive magnesium ion, Mg<sup>+</sup> ion

## 1. Introduction

There continues to be significant interest in the negative difference effect (NDE)<sup>[i]</sup> for magnesium corrosion. This interest is warranted by the fact that the NDE is of central importance to the corrosion of magnesium <sup>[ii, iii, iv, v]</sup>, including galvanic corrosion <sup>[vi, vii, viii, ix]</sup> and stress corrosion cracking <sup>[x, xi]</sup>. The NDE is also probably an issue for magnesium anodes used in cathodic protection, (see e.g. <sup>[xii, xiii]</sup>). Furthermore, as discussed herein, there are aspects of the NDE that still need to be resolved even though it is more than fifty years since the paper by Petty et al <sup>[xiv]</sup> in which strong evidence was presented for the existence of the unipositive magnesium ion, Mg<sup>+</sup>.

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The electrochemical corrosion of magnesium is in many respects a model system for research as it is relatively easy to measure all the quantities of importance, including (i) the magnesium metal mass loss, (ii) the amount of the stable ion  $Mg^{++}$  in solution and (iii) the amount / volume of hydrogen produced<sup>xv</sup>; (hydrogen is associated with the cathodic partial reaction). Furthermore, it is also worth stressing that magnesium corrosion is inherently complicated and includes <sup>[ii, iii]</sup> (i) a partially protective surface film in many aqueous solutions, (ii) the equilibrium ion is the  $Mg^{++}$  ion, (iii) localised corrosion is often the dominant form of corrosion in many solutions, (iv) microgalvanic corrosion<sup>[xvi]</sup> between microstructural features is important during the corrosion of magnesium alloys (v) magnesium has a very negative corrosion potential and (vi) there is the possibility of a partially protective surface hydride<sup>[xvii]</sup>.

There are currently<sup>[i, ii, iii]</sup> two mechanistic approaches to the magnesium NDE and these are designated herein as: (i) “the unipositive  $Mg^+$  ion NDE mechanism” and (ii) “the magnesium self-corrosion mechanism”.

“The unipositive  $Mg^+$  ion NDE mechanism” derives from the research work of Song et al <sup>[xviii, xix]</sup> which examined the then existing<sup>[xx]</sup> four theories for the magnesium NDE, the prior experimental results, the results of a targeted experimental program and, as a synthesis, formulated stepwise a new mechanism based on what are still considered<sup>[ii, iii]</sup> to be the two critical aspects of magnesium corrosion: (i) the surface of magnesium, in most aqueous solutions, is covered by a partially protective surface film, and (ii) the postulate that the unipositive  $Mg^+$  is involved as an early step in the electrochemical oxidation of magnesium and moreover that the unipositive  $Mg^+$  has a sufficient lifetime to react chemically with other available species. It is clear that, during the anodic oxidation of magnesium metal, the transfer simultaneously of two electrons to form  $Mg^{++}$  is much less probable than the transfer first of one electron to form  $Mg^+$ . However, a key issue is the lifetime of the  $Mg^+$  ion. Does the  $Mg^+$  ion “immediately” attract a second electron to form the equilibrium species  $Mg^{++}$ , or does the  $Mg^+$  ion exist for a sufficiently long time period so that it can react with other species in a chemical reaction? “The unipositive  $Mg^+$  ion NDE mechanism” postulates that there exists the unipositive  $Mg^+$  and moreover postulates that the lifetime of the unipositive  $Mg^+$  is sufficient for the unipositive  $Mg^+$  to react chemically with other available chemical species.

The second approach (e.g. see <sup>[vi]</sup>) is designated herein “the Mg self-corrosion mechanism”. This approach postulates that magnesium evinces “self-corrosion” and

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moreover, this approach postulates that the magnesium “self-corrosion” continues even during laboratory experiments where the magnesium specimen is maintained by a potentiostat at a constant potential or if there is a constant current delivered to the magnesium specimen by a galvanostat. It is indeed worth stressing that the Mg self-corrosion approach postulates the existence of a significant self-corrosion rate even under these conditions of potentiostatic or galvanostatic control. It is postulated that there is an electrochemical rate of magnesium oxidation caused by the applied current or potential and in addition there is additional magnesium corrosion due to the magnesium self-corrosion.

The purpose of this paper is to assess the evidence for these two approaches, in particular to assess the evidence for the existence and the possible lifetime of  $Mg^+$  as an intermediate in the electrochemical oxidation sequence between metallic Mg and  $Mg^{2+}$ , the stable Mg ionic species in aqueous solutions.

### 2. Phenomenology of NDE

A simple way to describe the NDE is to consider a magnesium anode, which is in a de-aerated electrolyte, and which is subjected to an applied anodic galvanostatic current,  $I_{applied}$ . The applied anodic galvanostatic current is given by:

$$I_{applied} = I_a - I_c = n = l - q \quad (1)$$

where  $I_a$  is the rate of the anodic partial reaction,  $I_c$  is the rate of the cathodic partial reaction,  $n$  is the net total number of electrons,  $l$  is the number of electrons in the anodic partial current and  $q$  the number of electrons in the cathodic current. If the applied anodic current is sufficiently large compared with the cathodic partial current, the anodic current is much larger than the cathodic current, i.e.  $I_a \gg I_c$ , it is possible to neglect  $I_c$ , and the applied current is equal to the anodic current to a good approximation, i.e.  $I_{applied} = I_a$ . If the overall corrosion reaction of Mg is considered in terms of only the final reaction products, then the following are the partial reactions:



for which it is possible to formulate the following notional equations for the “measured” partial anodic and cathodic current:

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$$I_{Mg,m}^n = 2N_{Mg^{2+}} \quad (4)$$

$$I_{H,m}^n = 2N_{H_2} \quad (5)$$

where  $N_{Mg^{2+}}$  is the number of Mg<sup>2+</sup> ions measured entering the solution as a result of the applied current  $I_{applied}$ ,  $N_{H_2}$  is the corresponding number of H<sub>2</sub> molecules and the units are mol/(unit time). It has been found experimentally <sup>[xiv, xx]</sup> that the quantity of Mg dissolved is greater than can be explained coulometrically using the Faraday Law on the assumption that Mg is oxidized to the dipositive magnesium ion. The departure from 100% current efficiency has been expressed<sup>[xiv]</sup> by the mean valence number,  $V$ , defined by

$$V = I_{applied}/N_{Mg^{2+}} = 2(I_{applied}/I_{Mg,m}^n) \quad (6)$$

where  $I_{applied}$  needs to be expressed in units of (mol of electrons)/(unit time). The physical significance of  $V$  is discussed later. It is sufficient at this stage to point out that a value of  $V = 2$  is to be expected for 100% current efficiency. Values of  $V$  between 1.33 and 1.66 were measured<sup>[xiv]</sup> for magnesium in dilute aqueous inorganic-salt solutions. This means that a central experimental observation of the NDE for Mg is that there is a systematic error of up to 30% for the amount of Mg dissolved calculated from electrochemistry (from the Faraday Law and the assumption that Mg is oxidized to the dipositive magnesium ion). It is worth stressing that this systematic error applies to all electrochemical measurements relating to the corrosion rate of magnesium in aqueous solutions. That is, all electrochemical measurements are expected to have an associated systematic error.

The NDE has been defined <sup>[i, ii, iii, xviii, xix]</sup> in terms of the difference  $\Delta$ :

$$\Delta = I_s - I_{H,m}^n \quad (7)$$

where  $I_s$  is the spontaneous rate of the hydrogen evolution reaction (HER) on the Mg surface at the free corrosion potential and  $I_{H,m}^n$  corresponds to the measured HER rate for the applied galvanostatic current  $I_{applied}$ . For most metals like Fe and Zn, in an acid solution, when the potential is increased, the anodic dissolution rate increases and the cathodic hydrogen evolution rate decreases <sup>[xxi, xxii]</sup>. For these cases,  $\Delta$  is greater than zero because  $I_s$  is greater than  $I_{H,m}^n$ . However, on Mg, the hydrogen evolution behavior is different. For Mg, it is found experimentally that the hydrogen evolution rate increases rather than decreases with increasing potential. Thus  $\Delta$  is negative, i.e.  $\Delta$  is less than zero because  $I_{H,m}^n$  is greater than  $I_s$ !

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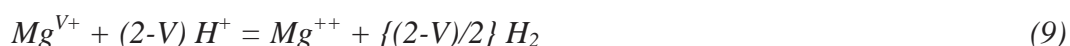
Nevertheless, it is worth stressing that Eq(7) may lead to inappropriate conceptualization; Eq(7) could lead to the expectation that  $I_{H,m}^n$  corresponds entirely to a cathodic current, whereas there is the possibility that  $I_{H,m}^n$  (and the hydrogen produced) partly corresponds to a chemical reaction (or alternatively corresponds partly to self-corrosion) and not only to an electrochemical reaction.

### 3. Existence of the Unipositive Magnesium Ion

Petty et al <sup>[xiv]</sup> studied the anodic oxidation of magnesium metal in a range of de-aerated aqueous inorganic-salt solutions. They found that, in every case, the quantity of Mg dissolved was greater than could be explained coulometrically on the assumption that Mg was oxidized to the dipositive magnesium ion. They expressed the departure from 100% current efficiency by the mean valence number,  $V$ , defined by Eq (6). Values of  $V$  for magnesium in the following dilute inorganic salt solutions were measured to be as follows:  $MgSO_4$ :  $V = 1.38$ ;  $Na_2SO_4$ :  $V = 1.41$ ;  $NaCl$ :  $V = 1.50$ ;  $KClO_3$ :  $V = 1.66$ ;  $KI$ :  $V = 1.54$ ;  $CaCl_2$ :  $V = 1.66$ . They were able to exclude the possibility that this phenomenon could be caused by partial disintegration of their magnesium electrode or to particles of magnesium metal detaching from the magnesium metal anode. They observed that vigorous hydrogen gas evolution continued at the anode for several minutes after current cessation, whereas the gas evolution at the cathode stopped at the same time as the applied current was stopped. Their interpretation was that the primary anode product was capable of reducing the solvent and they suggested the following reaction:



Furthermore, in most of their experiments, the amount of  $H_2$  gas generated was in reasonable agreement with the amount predicted from the applied current and the following equation:



The exception was the case of the experiments in the  $KClO_3$  solutions, in which the amount of  $H_2$  gas generated was less than expected; this was attributed to reduction of some of the chlorate to chloride by the unipositive  $Mg^+$  ions.

Petty et al <sup>[xiv]</sup> interpreted their experiments as showing that the first step in the anodic oxidation of Mg was the unipositive ion  $Mg^+$ , produced by means of

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and that this  $Mg^+$  ion could be further oxidized electrochemically to the stable species  $Mg^{++}$  by:



or alternatively the unipositive  $Mg^+$  ion could be chemically oxidized to  $Mg^{++}$  by chemically reducing other available species. The other available species could be the solvent water (which could be reduced to produce hydrogen gas) or the species could be an oxidant like  $KClO_3$  (which could be reduced to produce  $Cl^-$  ions) or there could be a combination of reduction reactions. The mean valence number reflected the probability (in a given solution) of the further oxidation of the unipositive  $Mg^+$  ion by means of the electrochemical reaction (11) compared with all the other possible chemical reactions (such as (9)). The physical significance of the minimum measured value of  $V$  (1.33) was attributed <sup>[xiv]</sup> to the electrochemical production of two unipositive magnesium ions to each dipositive magnesium ion, and the maximum measured value of  $V$  (1.66) was attributed to the ratio of one unipositive magnesium ion to two dipositive magnesium ions. This research by Petty et al <sup>[xiv]</sup> implied that during the anodic oxidation of Mg there existed the unipositive  $Mg^+$  ion, and that this unipositive  $Mg^+$  ion could reduce other species in solution. Furthermore, Petty et al <sup>[xiv]</sup> indicated, but did not provide any supporting evidence, that similar effects had also been observed for copper, aluminium, zinc and cadmium electrodes associated with their oxidation. Moreover, Drazic and Popic <sup>[xxiii]</sup> indicated that the anodic dissolution of Fe and Cr was also anomalous in that more material dissolved than would be expected from the Faraday Law with the use of the expected valance of the equilibrium ions.

As an obvious follow-on series of experiments, Petty et al <sup>[xiv]</sup> performed experiments to determine if it was possible that other species could be reduced by the unipositive  $Mg^+$  ion some considerable distance away from the anodic oxidizing magnesium electrode and not in contact with the magnesium electrode. Petty et al <sup>[xiv]</sup> studied the reduction of (i) the aqueous permanganate ion to the solid substance manganese dioxide and (ii) the aqueous silver ion to the solid substance elementary silver. In their experiments, Petty et al <sup>[xiv]</sup> allowed a solution containing the aqueous permanganate ion (or alternatively the aqueous silver ion) to flow past the anodic oxidizing Mg electrode, to flow through a filtering medium of glass wool to remove any solid substance and finally to flow into a settling vessel, from which settling

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vessel solution any solid substance was filtered and analyzed. They found that manganese dioxide (or alternatively elementary silver) was produced in the settling vessel, so that the reduction of (i) the aqueous permanganate ion to the solid substance manganese dioxide and (ii) the aqueous silver ion to the solid substance elementary silver occurred under conditions that the reaction occurred remote from the anodic oxidizing magnesium anode, providing further evidence for the existence of the unipositive  $Mg^+$  ion, and furthermore further evidence that the unipositive  $Mg^+$  ion was stable in aqueous solutions for some minutes.

Subsequently, Rausch et al <sup>[xxiv, xxv, xxvi, xxvii]</sup> took this research to what was for them the next obvious step. They argued that the unipositive  $Mg^+$  ion should also be produced in appropriate non-aqueous solvents, and furthermore that the unipositive  $Mg^+$  ion could be used to reduce organic compounds in these solutions. They showed indeed that during the anodic oxidation of magnesium in a range of non-aqueous solutions, there was evidence of the existence of the unipositive  $Mg^+$  ions, due to the reduction of organic compounds, which reduction did not occur by the magnesium metal alone, nor by the solvent alone, but which reduction occurred in the presence of an anodic dissolution of the Mg, and was consistent with the production of the unipositive  $Mg^+$  ions as an intermediary.

However, Hull <sup>[xxviii]</sup> reported that it was not possible to detect the unipositive Mg ion,  $Mg^+$ , with a ring-disc electrode. Hull <sup>[xxviii]</sup> carried out experiments with a rotating ring-disc electrode in 1M NaBr and expected to be able to detect the unipositive Mg ion,  $Mg^+$ , assuming the ion had a lifetime in excess of several milliseconds and assuming that the ion could be detected in the presence of the dissolved hydrogen concurrently produced at the disc by the anodic dissolution of the magnesium electrode. Hull <sup>[xxviii]</sup> concluded that the long lived reducing capacity at an anodically dissolving anode most probably results from the presence of minute solid or colloidal magnesium particles, other possibilities could be the species  $Mg^{2+}Mg$  or  $H_{(aq)}$  (hydrogen dissolved in the aqueous electrolyte solution).

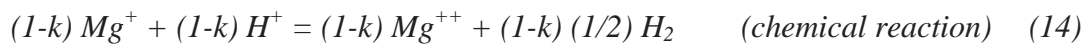
However, it is plausible that Petty et al <sup>[xiv]</sup> were able in their work to exclude as an explanation minute magnesium metal particles. On the other hand, if the long lived reducing capacity associated with an oxidizing magnesium electrode is in fact associated with the species  $H_{(aq)}$ , there is then nevertheless the issue of the production of this species. It would be conceivable that  $Mg^+$  could react chemically rather quickly to produce the  $H_{(aq)}$ . This means that a search for  $Mg^+$  has to take into account that the lifetime of  $Mg^+$  might be quite short.



#### 4. The Unipositive Mg<sup>+</sup> Ion NDE Mechanism

The unipositive Mg<sup>+</sup> ion NDE mechanism <sup>[ii, iii, xviii, xix, xxix]</sup> proposes that the key aspects for magnesium corrosion in an aqueous solution are (i) a partially protective surface film and (ii) the production of the unipositive Mg ion, Mg<sup>+</sup>. Song et al <sup>[xviii, xix]</sup> presented comprehensive treatments for the NDE including both effects and the simplest possible reaction sequence involving the unipositive Mg ion, Mg<sup>+</sup>. A somewhat different approach is adopted herein based on the expectation that the unipositive Mg ion, Mg<sup>+</sup>, can be converted to the equilibrium Mg<sup>++</sup> ion either electrochemically (e.g. Eq (11)) or chemically (e.g. Eq (8)). It is assumed for simplicity that no other chemical reduction reaction is possible. Moreover, the present treatment assumes that the influence of the partially protective film is constant (a simplifying assumption) so that it is possible to consider only the influence of the unipositive Mg ion, Mg<sup>+</sup>.

At the free corrosion potential, the anodic partial reaction is assumed to occur in two steps (12) and (13). The first step is the same as (10) above. The second step assumes that some fraction (*k*) undergoes an electrochemical anodic oxidation to the equilibrium Mg<sup>++</sup> ion; {this reaction is the same reaction as (11) above}. The complement (*1-k*) fraction of the unipositive Mg<sup>+</sup> ion population reacts chemically by reaction (14) with water (or with H<sup>+</sup> ions as written here for convenience) to produce the stable Mg<sup>++</sup> ion and H<sub>2</sub>: {this reaction is equivalent to (8) above}. The two anodic partial reactions (12) and (13) are balanced by the cathodic partial reaction (15); {this reaction is the same as (3) above}.



Equations (12) to (15) can be summed to give the following overall reaction, which is the same as the sum of Eq(2) and (3):



When there is an applied current, and the applied current obeys Eq(1), then it is necessary to modify Eqs (12) to (15) as follows:



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$$pk Mg^+ = pk Mg^{++} + pk e \quad (13')$$

$$p(1-k) Mg^+ + p(1-k) H^+ = p(1-k) Mg^{++} + p(1-k) (1/2) H_2 \quad (14')$$

$$q H^+ + q e = q (1/2) H_2 \quad (15')$$

If it is assumed that the anodic and cathodic currents are given according to Eq(1), then it is possible to write the following equation balancing the factors  $q$ ,  $p$  and  $k$  from Eqs (12') to (15') as follows:

$$q = l - n = p(1+k) - n \quad (17)$$

The quantity of hydrogen produced can be evaluated from Eqs (14') and (15') as follows:

$$I_{H,m}^n = 2 N_{H_2} = q + p(1-k) \quad (18)$$

Substituting Eq (17) into Eq (18) gives

$$I_{H,m}^n = p + pk - n + p - pk = 2p - n = 2 N_{Mg^{2+}} - n = I_{Mg,m}^n - I_{applied} \quad (19)$$

On rearrangement this gives

$$I_{Mg,m}^n - I_{H,m}^n = I_{applied} \quad (20)$$

Or in other words, the unipositive  $Mg^+$  ion NDE mechanism predicts that

$$\{2(N_{Mg^{2+}} - N_{H_2})\} = I_{applied} \quad (21)$$

Equations (20) and (21) are formally the same. However, preference might be given to the use of Eq(21) as this equation deals with the quantities which can be measured directly  $\{N_{Mg^{2+}}$  and  $N_{H_2}\}$  or determined by the experimental arrangement {namely the applied anodic current,  $I_{applied}$ }. In contrast,  $I_{Mg,m}^n$  and  $I_{H,m}^n$  are “notional” quantities, and the use of Eq (20) could give the misleading impression that these quantities might necessarily correspond to only the anodic and cathodic partial currents, respectively. Clearly they do not correspond to the only anodic and cathodic partial currents, respectively, in the unipositive  $Mg^+$  ion NDE mechanism because of the appreciable amount of the chemical reaction Eq (14).

Pure Mg showed the NDE <sup>[xix]</sup> in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub>, as demonstrated in Fig. 1. In both acid solutions the rate of hydrogen evolution increased with increasing applied current density. As predicted by the unipositive  $Mg^+$  ion NDE mechanism, Eq(21) was valid<sup>[i]</sup>, as shown by Fig. 2: the measured value of  $\{2(N_{Mg^{2+}} - N_{H_2})\} = I_{Mg,m}^n - I_{H,m}^n$  [in units of  $\mu\text{mol}$ ]

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gave a straight line of unit slope when plotted against the applied current density,  $I_{applied}$  [in units of  $\mu\text{mol}$  of electrons]. Similarly, Song et al <sup>[xviii]</sup> showed that Eq(21) was valid for pure magnesium corroding in 1N NaCl. However, it is worth stating that the data could be better in both studies <sup>[xviii, xix]</sup>, so there is scope for more research in this area.

The derivation of Eq(21) assumed that  $k$  was a constant, that is, there was the assumption that a constant fraction  $k$  of the unipositive Mg ion underwent further electrochemical oxidation to  $Mg^{++}$ . There is no particular reason that this assumption should be valid, so it is somewhat fortuitous that magnesium corrosion was consistent with Eq(21) for corrosion in 1N HCl and 1N  $H_2SO_4$  as shown by Fig. 2 and in 1N NaCl as shown by Song et al <sup>[xviii]</sup>. The work of Tunold et al <sup>[xx]</sup> indicated that  $k$  does not need to be a constant, whereas the research of Petty et al <sup>[xiv]</sup> was consistent with a constant value of  $k$ .

### 5. The Mg Self-corrosion Mechanism

The concept of self-corrosion is a useful means of rationalizing experimental results. For example, in the evaluation <sup>[vi, vii]</sup> of galvanic corrosion of magnesium caused by an idealized steel fastener, it was useful to employ the concept of magnesium self-corrosion and moreover, the rate of magnesium-self corrosion was evaluated to be quite high, 230 mm/y. However, it is not particularly useful as a scientific theory because there is no testable prediction.

### 6. Evaluation of Evidence for Unipositive Magnesium

The research of Petty et al <sup>[xiv]</sup> and Rausch et al <sup>[xxiv, xxv, xxvi, xxvii]</sup> provides strong support for the existence of the unipositive magnesium ion,  $Mg^+$ , in the anodic oxidation of magnesium in a range of aqueous and non-aqueous solutions. Evidence of the existence of the unipositive  $Mg^+$  ions has been advanced by the observation of the reduction of various species, which reduction did not occur by the magnesium metal alone, nor by the solvent alone, but which reduction occurred in the presence of an anodic dissolution of the Mg, and is consistent with the production of the unipositive  $Mg^+$  ions as an intermediary with an appreciable lifetime.

Further support is provided by the fact that magnesium corrosion was consistent with Eq(21) for corrosion in 1N HCl and 1N  $H_2SO_4$  as shown by Fig. 2 and in 1N NaCl as shown by Song et al <sup>[xviii]</sup>. That is, the mass balance of the amount of applied current, the amount of magnesium corroded, the amount of  $Mg^{++}$  produced, and the amount of hydrogen produced is

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consistent with the existence of the unipositive  $Mg^+$  ion. Evidence in support of the existence of  $Mg^+$  is further provided by the fact that the simplest possible reaction sequence, {essentially reactions (12) to (15)}, is consistent with all the experimental evidence, including the electrochemical impedance spectroscopy <sup>[xix]</sup>. It is also supported by the observations of Song and co-workers <sup>[xxx, xxxi, xxxii]</sup> that the Mg corrosion mechanism involves “anodic H evolution” which is different to “cathodic H evolution”.

### 7. Concluding Remarks

It is clear that there is uncertainty concerning the existence of the unipositive Mg ion,  $Mg^+$ . This topic does not appear to have received any serious application of modern techniques of analytical chemistry or electrochemistry, and this offers considerable scope for increasing our understanding of a fundamental aspect of magnesium corrosion. Nevertheless, the unipositive  $Mg^+$  ion NDE mechanism has been useful in providing a framework within which it is possible to evaluate the expected rate of production of  $Mg^{++}$  and  $H_2$ .

The most convincing evidence for the existence of the unipositive Mg ion,  $Mg^+$  stems from research work <sup>[xiv]</sup> carried out in the 1950s that showed that (i) there is a long lived reduction capacity associated with an anodically oxidizing magnesium electrode consistent with the existence of the unipositive Mg ion,  $Mg^+$ , and (ii) the postulated  $Mg^+$  provides a credible framework by which to carry out a mass balance, i.e. to calculate the amount of  $H_2$  produced from the applied current and the amount of  $Mg^{++}$  produced (via e.g. Eq(21)). There could be other explanations for the long lived reducing capacity at an anodically dissolving magnesium anode, but these other explanations nevertheless do not provide a convincing case against the existence of the unipositive magnesium ion,  $Mg^+$ . However, there is support by subsequent research <sup>[xviii, xix]</sup> for (ii).

The following are some suggestions for research that flow from this evaluation of the current understanding of the magnesium NDE.

- It would be good to have a serious application of modern techniques of analytical chemistry and electrochemistry to the study of the unipositive magnesium ion,  $Mg^+$ . Does it exist? If the unipositive magnesium ion,  $Mg^+$ , does exist, what are its chemical and physical properties?

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- It would be useful to carry out a series of measurements to study the anodic corrosion of pure magnesium in a range of aqueous solutions, in each of which a full mass balance was carried out, i.e. in each case it would be good to measure (i) the magnesium weight loss, (ii) the quantity of  $Mg^{++}$  in solution at end of experiment and (iii) the amount of  $H_2$  liberated. This suggestion is to extend the prior research of Petty et al <sup>[xiv]</sup> and Song et al <sup>[xviii, xix]</sup>. Solutions that should be included in such a study might include (i) neutral nor reacting solutions like  $MgSO_4$ ,  $K_2SO_4$ ,  $NaCl$ ,  $CaCl_2$ ,  $NaI$ ,  $AlBr_3$  .. at pH ~10.5 (saturated with  $Mg(OH)_2$ ); (ii) acid solutions such as 1N  $H_2SO_4$ ,  $HCl$ ,  $HI$  ..... and (iii) oxidizing solutions such as chlorate, permanganate etc.. It is suggested to carry out these experiments at constant applied current, using several values of current in each case, (alternatively, if a constant applied potential were to be used, it would be necessary to measure the current throughout the experiment).
- It would also be useful to extend this study of magnesium corrosion to organic liquids to build on the prior research of Rausch et al <sup>[xxiv, xxv, xxvi, xxvii]</sup>, and to extend the research to ionic liquids.
- Is it worthwhile to explore the possibility that there are similar effects in the anodic oxidation of copper, aluminium, zinc and cadmium as suggested by Petty et al <sup>[xiv]</sup>, and to explore if there are any anomalous effects in the anodic dissolution of Fe and Cr as suggested by Drazic and Popic <sup>[xxiii]</sup>?

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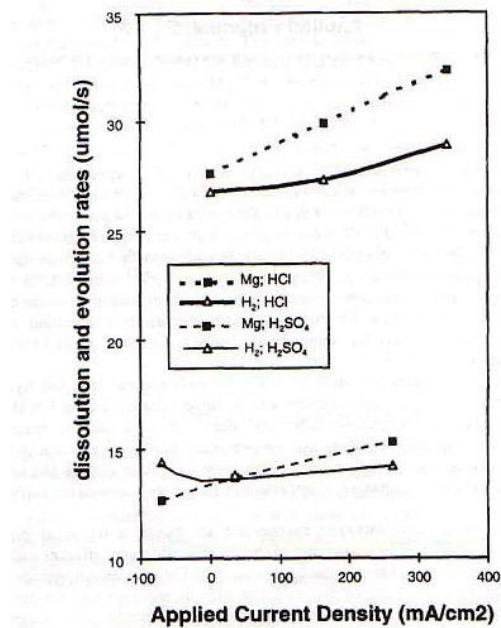


Fig. 1 Anodic magnesium dissolution rate and hydrogen evolution rate in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub>. Song et al <sup>[xix]</sup>.

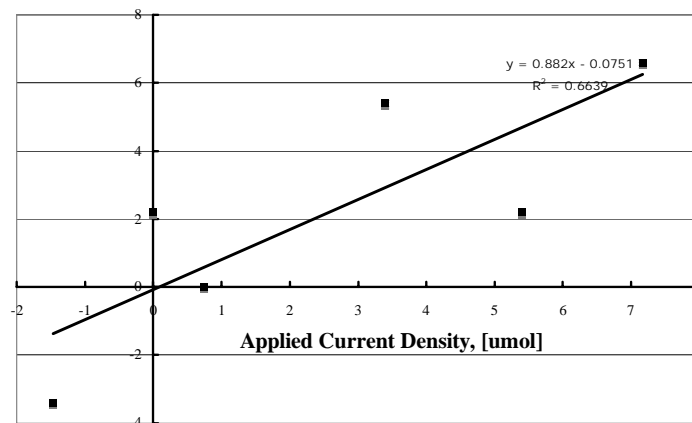


Fig. 2 Equation (21) was valid for the data of Figure 1: the value of  $\{2(N_{Mg^{2+}} - N_{H_2})\}$  [in units of  $\mu\text{mol}$ ] gave a straight line when plotted against the applied current density,  $I_{applied}$  [in units of  $\mu\text{mol}$  of electrons]. Song and Atrens <sup>[i]</sup> and Song et al <sup>[xix]</sup>.

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