Use of Sodium Bicarbonate as a Chloride-Free Aqueous Electrolyte to Explore Film Formation and the Negative Difference Effect on Pure Magnesium

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Hydrogen evolution rates upon magnesium were explored in 0.1 M sodium bicarbonate (NaHCO₃) solution, with pH 8.4. Although the negative difference effect (NDE) was observed on Mg in 0.1 M NaHCO₃, the hydrogen evolution rates showed a peculiar behavior in this electrolyte, where the hydrogen evolution rates first increased in the proximity of the open circuit potential and then decreased, with increasing anodic potential. This transition of the slope of hydrogen evolution rates versus applied anodic potential varying from positive to negative was revealed for the first time on Mg. In NaHCO₃, hydrogen evolution rates decreased with time, even in the NDE region where hydrogen evolution rates increased with anodic potential. It is posited that dissolution of the air-formed surface film and evolution of a hydroxide-free magnesium carbonate film on Mg were responsible for the observed hydrogen phenomena. These findings have significant implications in clarifying the source of superfluous hydrogen upon anodically polarized Mg.

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In the context of engineering alloys, a phenomenon of magnesium (Mg) that has been long considered unusual, is that the hydrogen evolution reaction (HER) kinetics upon Mg increase when an anodic polarising signal is applied. This phenomenon was first reported by Beetz as early as 1886, while electrolysis of sulfate and chloride solutions using Mg as electrodes. Since the difference between the rate of hydrogen evolution at the corrosion potential (Ecorr) and an anodic potential has been found to be negative, this phenomenon has been termed as the negative difference effect (NDE). It has been revealed that this phenomenon is not unique to magnesium per se, and is a characteristic of numerous reactive metals, however, reactive metals other than Mg are rarely studied (or utilized) in aqueous electrolytes. In aqueous environments, Mg (E⁰H₂O⁺OH⁻ = −2.37 V) dissolves to form Mg²⁺ ions (the anodic reaction) as shown in Equation 1, whilst hydrogen evolution (E⁰H₂O = −0.83 V) is the accompanying cathodic reaction, Equation 2, at such potentials:

\[ \text{Mg}(s) = \text{Mg}^{2+} + 2e^- \]  

[1]

\[ 2\text{H}_2\text{O} + 2e^- = \text{H}_2 \uparrow + 2\text{OH}^- \]  

[2]

The physical origins of the NDE have long been a point of scientific curiosity. Recent works by Williams and co-workers show that this phenomenon is not unique to magnesium per se, and is a characteristic of numerous reactive metals, however, reactive metals other than Mg are rarely studied (or utilized) in aqueous electrolytes. In aqueous environments, Mg dissolves to form Mg²⁺ ions (the anodic reaction) as shown in Equation 1, whilst hydrogen evolution is the accompanying cathodic reaction. The reason for the transition of the slope of hydrogen evolution rates versus applied anodic potential is not yet clear.

Regarding the effectiveness of impurity enrichment on the NDE, experiments in recent years allow the following statements to be made. Firstly, the enrichment efficiency of cathodic impurities (the reversible potentials of which are well above the Ecorr of Mg and its alloys and below the hydrogen-water equilibrium) has been reported to be very low (<1%) in Mg. Secondly, as demonstrated by cathodic current measurements via SVET and through extrapolation of cathodic kinetics, the high hydrogen evolution kinetics observed on anodically polarized Mg cannot be ascribed solely to the enrichment of the impurities on the surface of pure Mg. A bi-layered (often dark) corrosion film that predominantly is comprised of Mg(OH)₂ as the outer layer and MgO as the inner layer, is formed on Mg in electrolytes such as NaCl, NaOH, and pure water. This dark corrosion film has been suggested to catalyse the water reduction reaction.

The rate of hydrogen evolution on this dark film has been found to be non-uniform, with the freshly formed regions showing higher dissolution rates. The overall hydrogen evolution occurring on Mg cannot fully be accounted for by the H₂ evolved on the detected cathodic sites. It is posited that dissolution of the air-formed surface film and evolution of a hydroxide-free magnesium carbonate film on Mg were responsible for the observed hydrogen phenomena. These findings have significant implications in clarifying the source of superfluous hydrogen upon anodically polarized Mg.

The high hydrogen evolution kinetics observed on anodically polarized Mg cannot be ascribed solely to the enrichment of the impurities on the surface of pure Mg. A bi-layered (often dark) corrosion film that predominantly is comprised of Mg(OH)₂ as the outer layer and MgO as the inner layer, is formed on Mg in electrolytes such as NaCl, NaOH, and pure water. This dark corrosion film has been suggested to catalyse the water reduction reaction.

The rate of hydrogen evolution on this dark film has been found to be non-uniform, with the freshly formed regions showing higher rates of hydrogen evolution. The enrichment of the hydrogen evolution occurring on Mg cannot fully be accounted for by the H₂ evolved on the detected cathodic sites. It is posited that dissolution of the air-formed surface film and evolution of a hydroxide-free magnesium carbonate film on Mg were responsible for the observed hydrogen phenomena. These findings have significant implications in clarifying the source of superfluous hydrogen upon anodically polarized Mg.

Another theory is that the hydrogen evolution occurs at bare Mg surface (anodic dissolution front) which is believed to be created due to the local breakdown of the film. Therefore, the stability of the film or otherwise, is expected to affect the NDE. It has been shown that no-NDE on Mg is observed in the absence of a thick hydroxide film in Tris(hydroxymethyl)aminomethane hydrochloride.
electrolyte (buffered at 7.5), although the rates of hydrogen evolution are significantly high. In contrast, Fajardo, et al. show that NDE is present on Mg in pH 3 citric acid buffer although no apparent film was noticed on Mg. However, no ‘cathodic activation’ is observed on Mg measured by potentiodynamically polarising the Mg specimen post anodic dissolution in both the cases. Thus, the role of surface film- the air-formed film and the corrosion product film on the hydrogen evolution kinetics during anodic polarization of Mg still remains ambiguous, needing further studies.

The foregoing introduction, raises the following logical questions:

(a) How does the NDE affect by having a non-hydroxide corrosion (or dissolution) product on Mg? (b) How is the NDE affected by the absence of the air-formed film on Mg? (c) What occurs when the corrosion (or dissolution) product precipitates on the surface with a delay? The present study was designed to address these questions, for which 0.1 M NaHCO₃ was assessed as being a suitable electrolyte for the following reasons. Bicarbonate ions buffer the electrolyte at a pH of approximately 8.4, as per the reactions presented in E4 and 5.

\[
\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}, \quad \text{pK}_a = 10.32 \quad [4]
\]

\[
\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}, \quad \text{pK}_a = 14 \quad [5]
\]

In addition, at a buffered pH of 8.4, Mg ions can form MgCO₃ in the bicarbonate solution, according to Equation 6.

\[
\text{Mg}^{2+} + \text{CO}_3^{2-} \rightarrow \text{MgCO}_3(s), \quad \log K_{sp} = -7.8 \quad [6]
\]

Since MgCO₃ is sparingly soluble in comparison to Mg(OH)₂ (precipitation of MgCO₃ and Mg(OH)₂ will occur when Mg²⁺ ion concentration reaches nearly 13.2 μM and 135 μM, respectively), it will form a film more readily (than Mg(OH)₂), especially when the ionic concentration exceeds the solubility product. Finally, the air-formed film is known to be attacked by bicarbonate ions more aggressively than by chloride ions. Therefore, the bare Mg surface is likely to be exposed before any corrosion product film (likely to be MgCO₃) can form on the Mg surface in the bicarbonate solution.

Therefore, it is possible to empirically study the hydrogen evolution behavior both in the absence and the presence of a corrosion product film (likely to be MgCO₃) on Mg anodic potentials by using 0.1 M NaHCO₃, with such anticipated characteristics well suited to understanding the role of the air-formed film and the corrosion product (MgCO₃) ion the NDE on Mg.

**Materials and Methods**

**Materials.**—High-purity Mg was utilized in the present work, with the impurity levels determined via inductively coupled atomic emission spectroscopy (ICP-AES), and found to be (in wt. %), Al: 0.011, Zn: 0.008, Cu: 0.001, Si: 0.018, Fe: < 0.001, Ca: 0.009, Mn: 0.025 and Ni: <0.001. Rectangular specimens with an area of 1 cm² were mounted in epoxy resin after making an electrical connection at their rear using insulated copper wire, served as working electrodes. These specimens were successively ground to a 2000 grit SiC finish and subsequently cleaned ultrasonically in ethanol for electrochemical tests. The initial pH of the 0.1 M NaCl and 0.1 M NaHCO₃ solutions used herein were 5.6 – 6.0 and 8.4, respectively.

**Electrochemical tests.**—A three electrode arrangement was used for electrochemical experiments. Prior to any electrochemical polarization, specimens were stabilized for 10 min in open circuit conditions. Pure Mg was potentiodynamically polarized at a scan rate of 0.5 mV s⁻¹ in 0.1 M NaHCO₃, and parallel testing was also conducted (for comparison) in 0.1 M NaCl.

Both in potentiostatic and the galvanostatic mode, a 30 C cm⁻² net anodic charge was passed to determine the corresponding hydrogen that evolved over the surface of the Mg in both electrolytes. The volume of the hydrogen that evolved was collected using an inverted funnel and burette over the specimen being polarized. Following hydrogen-collection experiments, the same specimens were then subjected to potentiodynamic polarization at a scan rate of 0.5 mV s⁻¹ to examine changes in their anodic and cathodic kinetics due to anodic polarization. The potentials reported herein have not been corrected for IR drop.

All the tests were repeated at least three times to check for reproducibility.

**Mass loss tests.**—Mass loss measurements were carried out in combination with volumetric hydrogen collection by using an inverted funnel and burette over the specimen for 24 hours in 0.1 M NaHCO₃, and four days in 0.1 M NaCl. The specimens were then removed from the electrolyte and cleaned as per the ASTM G1 standard. A chromic acid solution (200 g L⁻¹ CrO₃) was used to clean the specimens and for removal of corrosion products. In order to determine corrosion rates, an analytical balance of ±0.01 Mg accuracy was used to measure the mass of the samples before and after the mass loss tests.

**Characterization of corrosion products.**—Corrosion products that formed on Mg in the two electrolytes were studied for their morphology by using a stereomicroscope (Leica S8APO equipped with the image-processing software, LAS V4.5) and an environmental scanning electron microscope (ESEM) (FEI Quanta 200) operating in low-voltage mode. The ESEM was equipped with energy dispersive spectrometry (EDS), used to identify the constituent elements of the corrosion product. Crystalline phases of the corrosion film, which formed in the two electrolytes, were determined by using X-ray diffraction in a Rigaku Smart Lab X-ray diffractometer with Cu Ka1(1.54059 A) irradiation. X-ray photoelectron spectroscopy was also used to analyze the corrosion product formed on the Mg specimens that were anodically polarized at different applied potentials in 0.1 M NaHCO₃. XPS of these specimens was carried out in a Kratos AXIS Supra (Kratos Analytical, UK) instrument with an analysis chamber pressure of <2 × 10⁻⁸ torr and a monochromatic Al Kα (1486.6 eV) X-ray source. A take-off angle of 90° was used, while the internal reference was the adventitious carbon peak at 284.7 eV. The XPS data were analyzed by using the software, ESCApe.

**Results**

**Electrochemical kinetics of Mg in 0.1 M NaCl and 0.1 M NaHCO₃.**—Typical potentiodynamic polarization curves for pure Mg in 0.1 M NaHCO₃ and 0.1 M NaCl are shown in Figure 1. The
Table I. Corrosion rates of pure magnesium and hydrogen that evolved during mass loss test and the corrosion current densities measured by using Tafel extrapolation in 0.1 M NaCl and 0.1 M NaHCO₃.

| Electrolyte     | Corrosion rate (mg cm⁻² day⁻¹) | H₂ evolved (ml cm⁻² day⁻¹) | i_corr (mA cm⁻²) |
|-----------------|---------------------------------|----------------------------|-----------------|
| 0.1 M NaCl      | 0.37 ± 0.05                     | 0.12 ± 0.06*               | 0.011 ± 0.004*  |
| 0.1 M NaHCO₃    | 11.02 ± 4.65                    | 11.34 ± 4.48*              | 0.481 ± 0.109*  |

*Corresponds to Mg corrosion rates obtained from conversion of the hydrogen evolution rates at open circuit potential and corrosion current densities.

anodic kinetics of Mg is nearly an order of magnitude higher in the former in comparison to that in the latter. Nevertheless, the cathodic kinetics seems unaffected by the nature of the anionic species of the electrolyte. As a result, the E_corr of Mg was found to be ≈200 mV lower in 0.1 M NaHCO₃ than that in 0.1 M NaCl. It is useful to mention the fact that at the end of the potentiodynamic polarization test, the pH of the 0.1 M NaCl was found to be close to 9, while that of the 0.1 M NaHCO₃ solution was 8.4, which means that the pH of the latter remained constant, while that of the former changed significantly. The i_corr values along with the corrosion rates that were obtained through mass loss tests are summarized in Table I. The volume of the hydrogen that evolved during the mass loss tests is also shown in the Table I. Both the potentiodynamic polarization test as well as the mass loss test show that pure Mg corrodes 30–45 times more in 0.1 M NaHCO₃ than in 0.1 M NaCl. The hydrogen evolution behavior in the two solutions is discussed below.

Hydrogen evolution behavior in 0.1 M NaCl and 0.1 M NaHCO₃.—The comparison between the hydrogen evolution volume versus the time plots for Mg specimens that were exposed to 0.1 M NaCl and 0.1 M NaHCO₃ during the mass loss test (that is, under freely corroding condition) is shown in Figure 2. In the early stages of the experiment, as determined from the slope of the curves, the hydrogen evolution rate in 0.1 M NaHCO₃ was found to be 90 times higher than that in 0.1 M NaCl. However, beyond a particular time, the rate of hydrogen evolution on the Mg specimen became extremely feeble in 0.1 M NaHCO₃, while in 0.1 M NaCl, it seemed to remain constant even after four days of immersion. Notably, a significant scatter in hydrogen evolution rates was observed in the bicarbonate solution, which is not the case in the chloride solution. In-situ examination of the Mg surface that was exposed for 10 min in 0.1 M NaHCO₃ in freely corroding conditions revealed the presence of locally attacked regions and deep etching (Figure 3). Visual observation revealed copious evolution of hydrogen at these locally attacked regions. Since these areas were found to have been covered with corrosion products on the removal of the specimen from the solution and exposure to air, not much could be said about the nature of the surface that caused the copious hydrogen evolution.

Plots of the volume of hydrogen that evolved versus time on Mg at applied anodic potentials of −1.8, −1.5 and −1.2 V SCE as well as at applied anodic current densities of 2, 3.5 and 5 mA cm⁻² in 0.1 M NaHCO₃ are shown in Figures 4a and 4b, respectively. It is evident from the curves that the rate of hydrogen evolution on Mg (as calculated from the linear region of the plots) decreased with increasing anodic potentials in 0.1 M NaHCO₃. Thus, it can be suggested that although the NDE on Mg in 0.1 M NaHCO₃ exists above −1.8 V SCE, the anodic potential of −1.2 V SCE or the applied anodic current density of 2 mA cm⁻² the hydrogen evolution rates decrease on anodic polarization.

Similarly, the hydrogen evolution rates on Mg were also determined in 0.1 M NaCl, except at −1.8 V SCE because it is below the E_corr (−1.725 V SCE) of Mg in 0.1 M sodium chloride solution. In addition, hydrogen evolution measurements on Mg in the two electrolytes were also made at their respective E_corr. The pH of the chloride solution rose to approximately 10.5 – 11, while that of the bicarbonate solution remained at 8.4, at the end of all the potentiostatic and galvanostatic experiments. The mean values of the hydrogen evolution rates at different applied anodic current densities and potentials in 0.1 M NaCl and 0.1 M NaHCO₃ are compared in Figure 5.

Below −1.2 V SCE and above E_corr, the hydrogen evolution rates on Mg (Figure 5) are found to be significantly higher in 0.1 M NaHCO₃ in comparison to that in 0.1 M NaCl, although the cathodic kinetics of Mg (Figure 1) in the two electrolytes were similar. It has been revealed

![Figure 2](http://example.com/fig2.png)  
*Figure 2. Hydrogen evolution during mass loss testing in 0.1 M NaCl and 0.1 M NaHCO₃, showing two typical curves for each electrolyte.*

![Figure 3](http://example.com/fig3.png)  
*Figure 3. Photographic image of the surface of pure Mg following 10 minutes of exposure in 0.1 M NaHCO₃, showing localized corrosion.*
that the NDE exists with increasing rates of hydrogen evolution with anodic polarization over a narrow range of potentials above $E_{corr}$ in 0.1 M NaHCO₃, while in 0.1 M NaCl, the NDE exists with increasing hydrogen evolution rates with anodic polarization at all the potentials (examined in this work) on Mg (Figure 5). For further credence to the existence of a small region of the NDE with increasing hydrogen evolution rates with polarization, the hydrogen evolution rate on Mg was also determined at a further lower potential, namely, −1.9 V SCE in 0.1 M NaHCO₃ (Figure 5a). Since the hydrogen evolution rate at −1.9 V SCE lies between the hydrogen evolution rates obtained at $E_{corr}$ and −1.8 V SCE; it is suggested that Mg exhibits the NDE with a positive slope for hydrogen evolution rates versus anodic polarization in the 0.1 M NaHCO₃ solution, albeit in the narrow potential range. This crossover from a positive slope to negative slope of hydrogen evolution rate versus anodic potential is a unique feature observed on Mg in 0.1 M NaHCO₃, which is being reported for the first time to the best of the knowledge of the authors. On the contrary, few authors have reported a transition from decreasing hydrogen evolution rates to increasing hydrogen evolution rates when there is an increase in the anodic polarization of Mg in HCl, H₂SO₄, and buffers of 0.1 M citric acid (pH 3) and 0.1 M boric acid (pH 7).

The hydrogen evolution behavior on Mg in 0.1 M NaCl and 0.1 M NaHCO₃ markedly differs on one more count, that is, the drop in the hydrogen evolution rate on Mg in 0.1 M NaHCO₃ with time, as noted from Figures 2 and 4. This drop in the hydrogen evolution rate occurs concurrently with the formation of the corrosion product and, so, it can be attributed to the formation of visible corrosion products on the surface. On the contrary, in NaCl, the hydrogen evolution volume on Mg versus the time showed a nearly constant rate even after the corrosion products covered the entire surface during the mass loss test (Figure 2), as well as during potentiostatic, and galvanostatic tests (related data are not shown here to reduce the size of the paper.)

The corrosion product that was formed on the surface of the Mg in 0.1 M NaHCO₃ was black-brown, whereas a dark grey-black film (dark corrosion film) was formed on Mg in 0.1 M NaCl (Figure 6). The EDS mapping of the black-brown spiky flower-like corrosion product formed on Mg in 0.1 M NaHCO₃ showed it to be rich in carbon (Figure 7). The rough areas that surround these spiky flower-like corrosion products also show the presence of carbon apart from Mg and O. However, the smooth surrounding regions display the presence of only Mg and O.

Typical XRD profiles of Mg that were dissolved (to pass 30 C cm⁻² net anodic charge) in 0.1 M NaHCO₃ at −1.8 V SCE and
Figure 6. Stereo microscopic image of Mg after potentiostatic polarization to pass a net charge of 30 C cm\(^{-2}\) (a) in 0.1 M NaCl at \(-1.2\) V\(_{SCE}\) showing dark-grey-black corrosion product; and in 0.1 M NaHCO\(_3\) at (b) \(-1.2\) V\(_{SCE}\) (c) \(-1.5\) V\(_{SCE}\) (d) \(-1.8\) V\(_{SCE}\) showing black-brown spiky flower-like corrosion product.

Figure 7. SEM images of Mg after potentiostatic polarization at (a) \(-1.8\) V\(_{SCE}\) (b) \(-1.5\) V\(_{SCE}\) and (c) \(-1.2\) V\(_{SCE}\) in order to pass an applied charge of 30 C cm\(^{-2}\) in 0.1 M NaHCO\(_3\). (Inset: EDS mapping of the corrosion product that was formed, and the composition of locations marked using EDS).

Table: Composition in at %

| Location | Mg  | O   | C  |
|----------|-----|-----|----|
| 1        | 33.8| 66.2| -  |
| 2        | 8.4 | 40.0| 51.6|
| 3        | 69.8| 30.2| -  |
| 4        | 23.3| 23.7| 53.0|

Figure 8. X-ray diffraction spectra of Mg corrosion products following dissolution in 0.1 M NaHCO\(_3\) at \(-1.8\) V\(_{SCE}\) and 0.1 M NaCl at \(-1.2\) V\(_{SCE}\). Peaks are revealed showing Mg (*) MgO (+), Mg(OH)\(_2\) ($) and Nesquehonite (MgCO\(_3\) \cdot 3H\(_2\)O) (#).

(nesquehonite mineral), while MgO and Mg(OH)\(_2\) were present on the Mg that was dissolved in 0.1 M NaCl (Figure 8).

XPS, a technique sensitive to surface with the ability to resolve the chemical state of the constituent elements, was also used to
The chemical composition of the corrosion product that was obtained via XPS is shown in Table III. The surface of the Mg dissolved at −1.2 and −1.5 VSCE contained predominantly MgO and Mg(OH)₂, along with MgCO₃. It should, however, be noted that the formation of MgO and Mg(OH)₂ due to the cleaning of the specimen in distilled water and the subsequent exposure of the specimen to the atmosphere before it was taken for XPS analysis could not be ruled out. The specimen that dissolved at −1.8 VSCE revealed extensive coverage of the surface by a black-brown spiky corrosion product and a very low fraction of the shiny surface. In XPS studies, this specimen showed an extensive presence of MgCO₃ (Table III).

In general, in 0.1 M NaHCO₃, it has been seen that the lower the applied potentials (≥ −1.8 VSCE), the more are the corrosion products that are precipitated on the surface of the Mg for the passage of the same applied net anodic charge, as illustrated in Figures 6 and 7. The rate of hydrogen evolution and therefore the coupled (excess) Mg dissolution follows the order −1.2 VSCE < −1.5 VSCE < −1.8 VSCE, although the Mg dissolved as per anodic current densities measured at the potentiostat is lowest for −1.8 VSCE. The total Mg ion concentration in the solution versus time estimated based on the average current densities at the potentiostat and the volume of hydrogen evolved (converted to Mg dissolution), indicated that the Mg specimens being polarized at −1.2 VSCE would cause the solution to reach the critical 13 μM Mg²⁺ ion concentration (required for MgCO₃ precipitation) later than those being polarized at −1.5 VSCE and −1.8 VSCE. Also, for the same net anodic charge the total Mg dissolution will be lower for −1.2 VSCE.

Therefore, the surface coverage of Mg with carbonate film starts earlier on Mg being polarized at −1.8 VSCE and −1.5 VSCE than that on Mg specimen being polarized at −1.2 VSCE, and greater coverage of surface with carbonate film is observed for the same net anodic charge at lower applied anodic potentials (Figures 6 and 7). However, it should be pointed out that on a few occasions, the Mg specimen held at −1.5 VSCE has been found to possess a higher amount of corrosion product than that which dissolves at −1.8 VSCE for the same net anodic charge passed.

Furthermore, it was observed that higher the MgCO₃ coverage on the Mg surface (Figures 6 and 7), the greater was the reduction in the hydrogen evolution rates (Figure 4) on Mg in 0.1 M NaHCO₃. At the end of the potentiostatic or galvanostatic polarization to pass net anodic charge of 30 C cm⁻², lower surface coverage by MgCO₃ and higher hydrogen evolution rates were observed on Mg polarized at −1.2 VSCE when compared to that at −1.8 VSCE.

Post-dissolution kinetics of Mg in 0.1 M NaHCO₃ and 0.1 M NaCl.—A comparison of the potentiodynamic polarization of Mg samples that were galvanostatically polarized at 5 mA cm⁻² in 0.1 M NaCl and 0.1 M NaHCO₃ along with those Mg samples that were in the as-ground condition, is shown in Figure 10. In the NaCl solution, the cathodic kinetics of Mg increased due to prior anodic polarization in comparison to the kinetics of Mg in the as-ground condition, thus exhibiting ‘cathodic activation’. In contrast, after anodic dissolution in 0.1 M NaHCO₃, no cathodic activation was observed, and the cathodic kinetics lowered marginally. The anodic kinetics of the Mg specimens that were subjected to prior anodic dissolution decreased in comparison to the specimen in the as-ground condition in both the solutions (Figure 10).

Table II. Measured binding energies (eV) of Mg 2p, O 1s and C 1s in Mg, MgO, Mg(OH)₂ and MgCO₃.

|        | Mg 2p  | O 1s  | C 1s  |
|--------|--------|-------|-------|
| Mg (metallic) | 48.5 ± 0.2 | -     | -     |
| MgO     | 49.5 ± 0.2 | 530.4 ± 0.2 | -     |
| Mg(OH)₂ | 49.5 ± 0.2 | 531.2 ± 0.2 | -     |
| Mg(CO)₃ | 50.6 ± 0.2 | 531.9 ± 0.2 | 289.2 ± 0.2 |
| C-C (adsorbed C) | -     | -     | 284.7 |

Figure 9. Typical X-ray photoelectron spectra of Mg 2p, O 1s and C 1s peaks for Mg specimen that is dissolved at −1.2 VSCE in 0.1 M NaHCO₃.
In order to examine the effect of applied anodic potentials, Mg specimens dissolved at $-1.2$, $-1.5$ and $-1.8$ Vsce (to pass a net charge of 30 C cm$^{-2}$) in 0.1 M NaHCO$_3$ were subjected to potentiodynamic polarization (Figure 11). It appears that the prior anodic polarization affects the anodic and cathodic kinetics of as-ground Mg. However, it is shown later that the anodic and cathodic kinetics of Mg do not merely depend on the potential. The decline in cathodic kinetics (due to prior anodic polarization) was marginal. All the Mg specimens that were dissolved at different anodic potentials in 0.1 M NaHCO$_3$ showed a substantial decline in the anodic kinetics in comparison to the Mg specimen that was in the as-ground condition (Figure 11).

The extent of the corrosion product (MgCO$_3$) that was formed on specimens after potentiostatic dissolution is shown in photographic images that were captured in situ under the solution (Figure 11). The specimen that dissolved at $-1.2$ Vsce showed a significant fraction of the shiny surface when compared to the other two. The drop in the anodic kinetics of Mg specimen dissolved at $-1.2$ Vsce was much lower when compared to Mg specimens dissolved at $-1.8$ and $-1.5$ Vsce. Furthermore, at $-1.5$ Vsce where possibly the largest surface coverage of Mg by MgCO$_3$ occurred (although it is not very clear from images, as they were captured under the solution, visual observation revealed this), anodic (and cathodic) kinetics reduced to the lowest level. It is likely that the corrosion product that is formed (MgCO$_3$) hinders the diffusion of the Mg ion to lower the anodic kinetics.

Further, in order to understand the effect of corrosion product (MgCO$_3$) film on the cathodic kinetics, an Mg specimen was exposed to 0.1 M NaHCO$_3$ for 52 h in a free corrosion condition. After 52 h, the Mg electrode surface was entirely covered by the corrosion product (MgCO$_3$), and hydrogen evolution seemed to stop. The cathodic kinetics of this Mg specimen after exposure was nearly two orders of magnitude lower than that which was observed before exposure in 0.1 M NaHCO$_3$ (Figure 12). Therefore, it appears that the coverage of the bare Mg surface by the MgCO$_3$ film lowers its anodic and cathodic kinetics and, that the greater the amount of the corrosion product, the greater is the drop in the kinetics.

Further studies, inclusive of in-situ characterization of the corrosion product that is formed upon Mg specimens in the environments tested herein, are required to quantify a correlation between the extent of MgCO$_3$ surface coverage with the extent of decreased cathodic kinetics.

### Discussion

It is evident from the present study that the rate of hydrogen evolution on the surface of Mg is much higher in 0.1 M NaHCO$_3$ than that in 0.1 M NaCl in the potential range below $-1.2$ Vsce. Magnesium shows NDE at all the anodic potentials in 0.1 M NaCl with a positive slope for hydrogen evolution rates with anodic polarization, on the contrary, Mg shows NDE with a positive slope only over a narrow range of potentials just above E$_{corr}$ in 0.1 M NaHCO$_3$. Another discernible difference the Mg shows between the two solutions is that the hydrogen evolution rate in 0.1 M NaHCO$_3$ decreases after a specific period of exposure, unlike the constant rate of hydrogen evolution noticed in the NaCl solution. Furthermore, Mg does not show 'cathodic activation', due to prior anodic dissolution in the 0.1 M NaHCO$_3$ solution in contrast to its behavior in the 0.1 M solution of NaCl. These observations are discussed below.

Since 0.1 M NaHCO$_3$ solution maintains a pH of 8.4 unlike 0.1 M NaCl solution where the pH reaches 10.5–11 in the steady state condition, it is necessary to examine the role of pH on the factors mentioned above. Figure 13 compares the rates of hydrogen evolution that were measured over Mg in 0.1 M NaHCO$_3$ (based on the linear region of hydrogen evolution volume versus time plot) in the present work with that reported in different buffers (0.1 M citric acid with pH 3, 0.1 M boric acid with pH 7 and borate buffer with pH 10.5) by Rossrucker et al.$^{38}$ Notably, the rate of hydrogen evolution at different applied anodic current densities is significantly higher in the case of 0.1 M NaHCO$_3$ when compared to that in the pH 7 buffer$^{38}$ despite the fact that the pH of 0.1 M NaHCO$_3$ is higher at 8.4. This suggests the fact that the lower pH of the bicarbonate solution in relation to 0.1 M NaCl (where the pH drifts to 10.5) cannot be the sole cause of high hydrogen evolution rates in the 0.1 M NaHCO$_3$ solution. This proposition that pH alone is not responsible for the observed high hydrogen evolution rates in 0.1 M NaHCO$_3$ is supported by the fact that the authors have observed significantly lower hydrogen evolution rate on Mg during anodic polarization in 1 mM InCl$_3$ + 0.1 M NaCl despite this solution having a pH of 4.$^{34}$

However, it is necessary to address the effect of the possible rise in surface pH in this solution (0.1 M NaHCO$_3$) due to overwhelming of the buffer capacity on the hydrogen evolution rates with respect to potential and/or time. During dissolution, the Mg$^{2+}$ ions are introduced into the electrolyte (0.1 M NaHCO$_3$) according to Equation 1.

### Table III. Area Ratios of Mg, MgO, Mg(OH)$_2$ and MgCO$_3$ contributions to the elemental peaks obtained from deconvolution of the XPS spectra for Mg specimen that was dissolved at different applied anodic potentials in 0.1 M NaHCO$_3$.

| Area Fraction | Mg dissolved at $-1.2$ Vsce | Mg dissolved at $-1.5$ Vsce | Mg dissolved at $-1.8$ Vsce |
|--------------|-----------------------------|-----------------------------|-----------------------------|
|              | O1s | Mg 2p | C 1s | O1s | Mg 2p | C 1s | O1s | Mg 2p | C 1s |
| Mg           | -   | 0.01  | -   | -   | -     | -   | -   | -     | -   |
| MgO          | 0.23 | -     | -   | 0.21 | -     | -   | 0.2 | -     | -   |
| Mg(OH)$_2$   | 0.16 | -     | -   | -   | -     | -   | -   | -     | -   |
| MgO + Mg(OH)$_2$ | 0.61 | 0.34  | 0.47 | 0.79 | 0.62  | 0.45 | 0.98| 0.98  | 0.78 |
| C-C          | -  | 0.53  | -   | -   | -     | -   | -   | -     | -   |

![Figure 10. Potentiodynamic polarization of pure Mg at a scan rate of 0.5 mV s$^{-1}$ in the as-ground condition and when pre-polarized at 5 mA cm$^{-2}$ galvanostatically to pass 30 C cm$^{-2}$ in 0.1 M NaHCO$_3$ and 0.1 M NaCl.](https://example.com/figure10.png)
Figure 11. (a) Potentiodynamic polarization of pure Mg at a scan rate of 0.5 mV s\(^{-1}\) in the as-ground condition and after polarising at different applied potentials in 0.1 M NaHCO\(_3\). In situ photographic images of the Mg specimen (under the 0.1 M NaHCO\(_3\) solution) immediately after potentiostatic polarization at (b) \(-1.8\) V\(_{SCE}\), (c) \(-1.5\) V\(_{SCE}\), and (d) \(-1.2\) V\(_{SCE}\) to pass 30 C cm\(^{-2}\) before commencement of potentiodynamic polarization of these anodically dissolved specimens. MgCO\(_3\) covered the surface to different extents although 30 C cm\(^{-2}\) was passed in all the cases during potentiostatic polarization.

Figure 12. Cathodic polarization of pure Mg at a scan rate of 0.5 mV s\(^{-1}\) in 0.1 M NaHCO\(_3\) before and after exposure to 0.1 M NaHCO\(_3\) for 52 h in the free corrosion (open circuit) condition.

The pH close to the Mg electrode can increase due to an increase in the surface concentration of the \(\text{OH}^-\) ions as a result of the hydrogen evolution reaction (Equation 2). Countering this pH change, as per Equation 4, is the \(\text{HCO}_3^-\) dissociation into \(\text{CO}_3^{2-}\) ions and \(\text{H}^+\) ions.

Figure 13. Hydrogen evolution rates on Mg versus applied anodic current density in different buffers and in 0.1 M NaHCO\(_3\).

It is also necessary to take into account the precipitation of MgCO\(_3\) (as per Equations 6) on the Mg surface as this will upset both the hydrogen evolution and Mg corrosion kinetics.

Aqion software was used to calculate the possible pH change when Mg is allowed to corrode in pure water due to Reactions 1 and 2.
In 0.1 M NaHCO₃ solution due to reactions in Equations 1–6 at various Mg²⁺ ion concentrations. The solubility product of MgCO₃ in 0.1 M NaHCO₃ was determined to be 13 µM. It turns out that in the case of pure water the solution pH will rise to 9.4 for 13 µM of Mg²⁺ ion concentration and reach to a maximum of 10.4 at the solubility limit of Mg(OH)₂, that is, 135 µM Mg²⁺ ion concentration. On the other hand, 0.1 M NaHCO₃ solution will reach a maximum pH of 8.4 for 13 µM of Mg²⁺ ion in the solution (the limit of solubility of MgCO₃ in water) as beyond this concentration MgCO₃ is expected to precipitate, irrespective of the pH of the solution. That is, MgCO₃ is expected to form a film on Mg surface before any appreciable change in surface pH could occur. Our hydrogen evolution versus time plots indeed show much higher dissolution of Mg in the solution, before a notable decline in hydrogen evolution rates is noticed. According to the Equation 2, a large upset in solution pH causing a significant decline is anticipated, which however didn’t occur. In fact, such vigorous hydrogen evolution can increase convection and bring down the possible effect of pH overwhelming. Our proposition that the hydrogen evolution rates on Mg surface are dominated more by the film coverage or its absence than pH is further discussed below.

In the bicarbonate solution, Mg surface showed locally attacked regions in the freely exposed conditions with intense hydrogen evolution (Figure 3). It is likely that these regions are ‘bare’ and are created by the dissolution of the air-formed film due to bicarbonate ions. A corollary of this suggestion is that the high hydrogen evolution rates in the bicarbonate solution arises from the high exchange current density for hydrogen equilibrium at the bare surface, which is hard to measure. This is indicated by the observed high corrosivity of bicarbonate ions, which has also been reported in the literature.13,28,43,44 Thus it can be suggested that HCO₃⁻ ions have higher efficiency in creating bare Mg sites.

It is useful to examine the reason for the existence of the NDE which shows a transition from positive slope in a narrow anodic potential range that is close to Ecorr to negative slope beyond −1.8 V SCE in the plots of hydrogen evolution rates versus anodic potential on Mg in 0.1 M NaHCO₃, as opposed to NDE with only increasing hydrogen evolution rates with anodic polarization at all anodic potentials which exists on Mg in 0.1 M NaCl. The rise in the anodic potential is expected to accelerate not only the anodic dissolution of Mg but also reprecipitation, especially when the surface ionic concentrations of Mg²⁺ and CO₃²⁻ exceed the solubility limit of MgCO₃. However, until such time (for a constant potential) and/or potential (for a constant time) in which the ionic concentration will exceed the solubility of magnesium carbonate, two competing processes, namely, (1) the creation of bare surfaces and (2) the lowering of hydrogen evolution (cathodic) kinetics due to the lowering of overvoltage are expected to occur. The extent of hydrogen evolution depends on which of these two processes dominates. This could be the reason why Mg shows NDE region having a positive slope of hydrogen evolution rates with anodic polarization in 0.1 M NaHCO₃ in a narrow range while in 0.1 M NaCl this NDE region is seen at all anodic potentials (depend on the ability of the anions to dissolve the air-formed film on the surface). It is possible that the Mg specimen had the highest bare surface, free of the air-formed film, only at −1.8 V SCE in the 0.1 M NaHCO₃ solution. Although visual observations, which reveal a surface that is ‘devoid of the film’, support this assumption, experimental evidence is required to confirm it.

This proposition of the two competing forces that lead to the observed H2 evolution rates on Mg in 0.1 M NaHCO₃ is further supported by the fact that, even at a given potential, within the NDE regime with positive slope for hydrogen evolution rates with anodic polarization, Mg shows a decline in the hydrogen evolution rates with time. It is expected that more carbonates will precipitate on the surface as the dissolution of Mg proceeds with time (when the concentration of the Mg ion exceeds the solubility product ≈13.2 µM). This precipitation causes the drop in the hydrogen evolution rates and cathodic kinetics, which has been observed in the present study.

The film-free surface hypothesis that is proposed here to explain the observance of the NDE region, where the hydrogen evolution rates increase with anodic polarization, close to the corrosion potential also derives its strength from the previous work on Mg in NaCl by Fajardo and Frankel.45 In their work Fajardo and Frankel explain the localized hydrogen evolution through partial coverage of active sites.45 According to the model by Fajardo and Frankel,45 the current that is associated with hydrogen evolution during anodic polarization can be illustrated by the following equation:

$$i_{HER} = K_{HER} e^{\left(\frac{zF}{RT} \left(\alpha_{Mg} - \alpha_{HER} \right) (E - E_{rev,Mg}) + \sigma_{HER}\right)}$$

where $\alpha_{Mg}$, $\alpha_{HER}$ are charge transfer coefficients, $z = 2$, for both anodic and cathodic reactions; $\sigma$ is defined as $\sigma = E_{rev,H} - E_{rev,Mg}$; and the pre-exponential term is given by

$$K_{HER} = i_{0,H,H,Me} \lambda_{Mg} \left(\frac{1}{xF^{2}MgN_{T}}\right)$$

where $i_{0,H}$ and $i_{0,H,H,Me}$ are the exchange current densities for the Mg oxidation and HER, respectively; $N_{T}$ is the total number of atoms on the surface; and the parameter $\lambda_{Mg}$ is associated with deactivation of active Mg sites.

This model suggests that the hydrogen evolution rate with anodic polarization can increase if the charge transfer coefficient of the Mg oxidation reaction is higher than that for HER,45 a condition which is assumed to be valid at any anodic potential (or anodic current density). This model assumes that the rate of production of active Mg sites and their deactivation is equal, that is, a steady state exists. However, a scrutiny of our results suggests that ‘carbonate’ film formation leads to an unsteady state condition, as is indicated by the drop in the hydrogen evolution with time. Thus, the model is valid only if the anodic polarization does not cause a ‘carbonate’ like film formation. Further, the model cannot predict the decrease in the hydrogen evolution rates with anodic polarization that is observed beyond the applied anodic potential of −1.8 V SCE or applied anodic current density of 2 mA cm⁻² on Mg in 0.1 M NaHCO₃. This could be because the model assumes that the deactivation parameter ($\lambda_{Mg}$) is independent of the potential which may not apply to the case of 0.1 M NaHCO₃.

The importance of the dissolution of the air-formed film and the corrosion product in the manifestation of the NDE and hydrogen evolution rates is further indicated through a comparison of hydrogen evolution rates on Mg in 0.1 M NaHCO₃ and in different buffers in Figure 13. The buffers with pH 3 and 7 show a transition from decreasing hydrogen evolution rates to increasing hydrogen evolution rates with increasing anodic potential when their buffering capacity is weakened and Mg(OH)₂ film formation is likely. While the buffer with pH 10.5 (borate buffer), where Mg(OH)₂ will always be present on the surface of Mg, shows the NDE with increasing rates of hydrogen evolution with anodic polarization throughout the anodic potentials.38 In contrast, the dissolution of air-formed film and delayed precipitation of carbonate in 0.1 M NaHCO₃ results in a transition from a positive to negative slope of hydrogen evolution rates versus the anodic potentials and eventual decrease in hydrogen evolution rates when carbonate precipitates. In the 0.1 M NaCl, the composition of the flaky dark corrosion film formed is similar to that of the air-formed film on Mg.32,46-50 Hence, it is possible to suggest that this in-situ-formed dark film breaks down at approximately the same rate as that of the air-formed film in NaCl, which results in the constant renewal of the anodic dissolution front (bare surface). The schematic diagrams in Figures 14a and 14b show the contrast between the progression of dissolution and hydrogen evolution rates on Mg in 0.1 M NaCl and 0.1 M NaHCO₃ with time.

An examination of the kinetics of the Mg in 0.1 M NaHCO₃ by using techniques such as SVET and the gravimetric method to measure the evolved hydrogen and model using DFT calculations is needed to provide further insights into the mechanism(s) of the kinetics. Further, it is essential to examine the effect of the concentration of bicarbonate ions on the potential at which the NDE region with positive slopes of hydrogen evolution rates versus the anodic potential transitions to a
negative slope, in order to improve the understanding of the causes of the NDE.

In light of the present investigation, we would like to suggest that the breakdown of the air-formed film on Mg to create ‘bare Mg sites’ is a necessary condition for superfluous hydrogen evolution at anodic potentials, which can cause the NDE. The occurrence of the NDE is controlled by (i) the interaction of the electrolyte and the air-formed film (ii) the precipitation of the corrosion product and (iii) the physical nature of the corrosion product that is formed. These factors are, in turn, dependant on the pH and the chemistry of the solution.

Conclusions

1. Vigorous hydrogen evolution occurred on Mg immersion in 0.1 M NaHCO₃ despite the solution being weakly alkaline having a pH of 8.4.
2. A transition from increasing hydrogen evolution rates with anodic polarization to decreasing one was observed on Mg in 0.1 M NaHCO₃.
3. The observed atypical trend of hydrogen evolution rates on Mg during anodic polarization in 0.1 M NaHCO₃ is a consequence of the competing processes of creation of ‘bare Mg’ sites and the lowering of hydrogen evolution (cathodic) rates due to the lowering of the overpotential with anodic polarization (as per the Butler-Volmer equation).
4. No anodically induced ‘cathodic activation’ was observed on anodically dissolved Mg in 0.1 M NaHCO₃ as measured by cathodic potentiodynamic polarization.
5. Formation of MgCO₃ corrosion product film on Mg surface reduces the rate of hydrogen evolution on it.

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