

On the corrosion behaviour of magnesium and its alloys using electrochemical techniques

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Abstract

Measurements of Tafel slopes and impedance are used to examine the corrosion aspects of magnesium and its alloys AZ 31 (Mg–Al–Zn), AZ61 (Mg–Al–Zn) and AP 65 (Mg–Al–Pb) in aqueous magnesium perchlorate solution. Impedance studies show that the electrode/electrolyte interfacial mechanism is activation-controlled. The results are explained in terms of stability of the film on the metal surface and on the influence of the specific alloy constituents on the hydrogen overvoltage. Variation of anodic potential during impedance measurements on magnesium alloys indicates a stepwise decrease in the charge-transfer resistance with gradual increase in anodic potential.

Keywords: Corrosion; Nyquist plots; Tafel slope; Charge-transfer resistance; Double-layer capacitance; Magnesium passivation potential

1. Introduction

The employment of magnesium, as an anodic material in different types of batteries has been the subject of much attention in recent years. Magnesium offers several advantages as a negative electrode material [1,2], e.g. a high electrode potential (-2.37 V versus NHE), a low electrochemical equivalent (0.45 g per Ah), good stability towards corrosion, relative abundance from sea bitterns, low toxicity. This has prompted the authors to investigate magnesium in conjunction with certain novel N-halogen organic compounds for use in battery devices [3–7].

Corrosion has been considered as one of the prime deterrents to the exploitation of magnesium as a successful negative electrode. Thus, in order to achieve long-term performance of magnesium-based cells, it becomes imperative to obtain a thorough understanding of the associated electrochemical behaviour. Accordingly, the present study examines the corrosion aspects of magnesium and its alloys in various concentrations of magnesium perchlorate. Various battery parameters, i.e. Tafel slope, exchange-current density (i_0), charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}) are reported. A similar study using a rotating-disc electrode technique has been reported elsewhere [4].

2. Experimental

Magnesium metal of 99.8% purity (impurity contents: 0.18% Si, 0.005% Cu, 0.006% Fe, 0.0005% Ca, 0.005% Ni, 0.004% Zr) and magnesium alloy sheets as received from Magnesium Elektron, UK, were employed as electrodes. The compositions of the various magnesium alloys are given in Table 1.

Tafel studies (E -log i) were carried out using a BAS 100 A Electrochemical Analyzer (Bioanalytical System, USA). The electrochemical cell consisted of magnesium or its alloys as the working electrode (exposed area: 1 cm^2), an Ag/AgCl reference electrode, and a platinum-foil counter electrode. Before use, the working electrodes were cloth buffed in the presence of pumice and then degreased with trichloroethylene. The experiments were performed in various concentrations of magnesium perchlorate (E. Merck) at different scan rates, viz., 1, 5 and 10 mV s^{-1} , at a potential that ranged between the open-circuit value (OCP) and -1000 mV . The

Table 1
Composition (wt.%) of magnesium alloys

| Alloy | Al | Zn | Pb | Mn |
|-------|---------|----------|---------|-----------|
| AZ 31 | 2.5–3.5 | 0.60–1.4 | | 0.15–0.70 |
| AZ 61 | 5.8–7.2 | 0.15–1.5 | | 0.15–0.25 |
| AP 65 | 6.0–7.0 | 0.40–0.7 | 4.4–5.0 | 0.15–0.30 |

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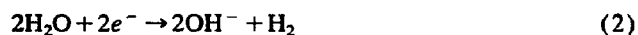
Tafel slope and exchange-current density (i_0) were calculated from the E -log i plots.

Impedance measurements of magnesium and its alloys were carried out using a Princeton Applied Research Corporation Model 368 AC impedance system. This system comprised an automated potentiostat/galvanostat coupled with a lock-in analyzer which were controlled by a PC. The real and imaginary parts of the electrochemical cell were obtained in various concentrations of magnesium perchlorate over the frequency range 10 mHz–1 kHz using a 10 mV peak-to-peak a.c. excitation. By varying the amplitude of this perturbation between 5 and 20 mV, almost no change in the frequency response of the electrode/electrolyte interface takes place. A dummy cell that consisted of a resistor/capacitor parallel combination (RC-R) was used to check the accuracy of the measurements. The experiments were also conducted on an AZ 31 alloy electrode in 2 M magnesium perchlorate at different anodic potentials.

All the measurements in this study were taken after stabilization of the open-circuit potential, E_{OCP} , i.e. 10 min after immersion of the electrode in the electrolyte which was stirred during the entire experiment. Pure nitrogen gas was bubbled through the test solution for about 30 min in order to remove the oxygen before each experiment. The temperature was maintained at 30 ± 0.5 °C. The pH of the experimental solution was 7.02. The pH of the experimental solution was found to remain unchanged throughout the experiment. All potentials are reported with respect to an Ag/AgCl reference electrode ($E=0.210$ V versus NHE).

3. Results and discussion

Although the standard potential of the magnesium electrode is -2.43 V, the steady-state working potential is generally about -1.50 V. This deviation in potential is due to the formation of a magnesium hydroxide film on the metal surface. The latter results from the precipitation of Mg^{2+} ions in the solution wherein OH^- ions are produced by the reduction of water according to the following reaction mechanism:



3.1. Tafel studies

A typical Tafel plot for AZ 31 alloy in 2.0 M $Mg(ClO_4)_2$ solution at a sweep rate of 1 mV s^{-1} is shown in Fig. 1. The Tafel region -1450 to -1350 mV is selected to draw another E -log i plot in Fig. 2. This has a slope of 102 mV per decade and an exchange-current density of $1.31 \times 10^{-5} \text{ A cm}^{-2}$. The values of the slope are found to lie within a fairly narrow range (107 ± 7 mV per decade), both for each alloy and for all concentrations of magnesium perchlorate. The

slopes and the corresponding i_0 values are listed in Table 2. The i_0 values depend on the alloy composition, as well as the nature and concentration of the electrolyte. The decrease in i_0 values with respect to the working electrode material is: $Mg > AP 65 > AZ 61 > AZ 31$.

The high value of i_0 for alloy AP 65 is due to the presence of lead and is explained in terms of a shift in potential towards more negative regions because of the high hydrogen overvoltage of lead [8]. This suggests that the hydroxide film is less adherent in the case of AP65 alloy and can easily be dislodged from the surface so that the passivation effect is lowered. In fact, this film disruption is so extensive that the magnesium electrode begins to approach its theoretical potential and as it does so, it becomes more and more soluble and corrodible.

The presence of zinc in the AZ 31 and AZ 61 alloys causes a shift in the potential towards a more positive value. Thus, smaller values of i_0 are obtained. Hydrogen evolution is also considered as one of the factors that control the i_0 value. For example, the AZ 31 and AZ 61 alloys have alloying constituents with low hydrogen overvoltages that are responsible for low i_0 values when compared with alloy AP 65. The i_0 versus electrolyte concentration plot shows a maximum at 2.0 M beyond which the i_0 remains constant. This can be explained by a decrease in conductivity of the electrolyte beyond 2.0 M.

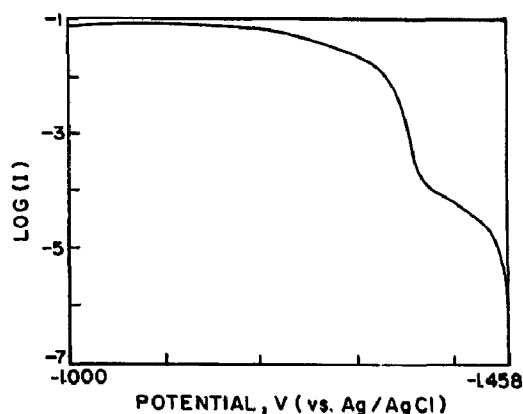


Fig. 1. Typical E -log i plot for AZ 31 alloy in 2.0 M magnesium perchlorate solution at a scan rate of 1.0 mV s^{-1} .

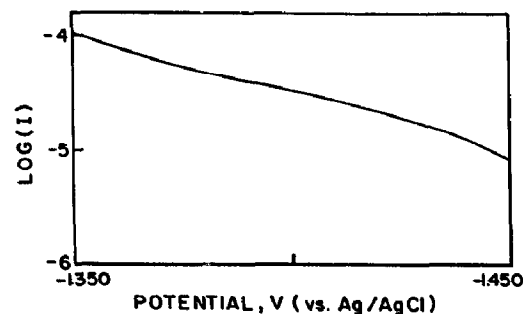


Fig. 2. Expanded Tafel region for AZ 31 alloy in 2.0 M magnesium perchlorate solution at a scan rate of 1.0 mV s^{-1} .

Table 2
 i_0 and Tafel slope values for magnesium and its alloys at various potential scan rates and for various concentrations of $\text{Mg}(\text{ClO}_4)_2$ solution ^a

| Concentration (M) | 1 mV s ⁻¹ | | 5 mV s ⁻¹ | | 10 mV s ⁻¹ | |
|-----------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|
| | Slope (mV dec ⁻¹) | i_0 (A cm ⁻²) | Slope (mV dec ⁻¹) | i_0 (A cm ⁻²) | Slope (mV dec ⁻¹) | i_0 (A cm ⁻²) |
| a) AZ 31 alloy | | | | | | |
| 0.1 | 104 | 1.00×10^{-5} | 104 | 9.96×10^{-6} | 106 | 9.80×10^{-6} |
| 0.3 | 104 | 1.04×10^{-5} | 105 | 2.02×10^{-5} | 106 | 9.88×10^{-6} |
| 0.5 | 103 | 1.03×10^{-5} | 104 | 1.04×10^{-5} | 105 | 1.00×10^{-6} |
| 1.0 | 103 | 1.10×10^{-5} | 105 | 1.07×10^{-5} | 104 | 1.06×10^{-5} |
| 1.5 | 102 | 1.14×10^{-5} | 104 | 1.14×10^{-5} | 105 | 1.20×10^{-5} |
| 2.0 | 103 | 1.31×10^{-5} | 105 | 1.30×10^{-5} | 104 | 1.28×10^{-5} |
| b) AZ 61 alloy | | | | | | |
| 0.5 | 106 | 1.20×10^{-5} | 107 | 1.16×10^{-5} | 107 | 1.11×10^{-5} |
| 1.0 | 106 | 1.56×10^{-5} | 109 | 1.29×10^{-5} | 108 | 1.20×10^{-5} |
| 1.5 | 105 | 1.91×10^{-5} | 107 | 1.74×10^{-5} | 108 | 1.55×10^{-5} |
| 2.0 | 105 | 2.54×10^{-5} | 106 | 1.98×10^{-5} | 107 | 1.50×10^{-5} |
| c) AP 65 alloy | | | | | | |
| 0.5 | 108 | 2.26×10^{-3} | 109 | 2.18×10^{-3} | 112 | 2.02×10^{-3} |
| 1.0 | 111 | 2.56×10^{-3} | 110 | 2.48×10^{-3} | 111 | 2.34×10^{-3} |
| 1.5 | 110 | 2.86×10^{-3} | 111 | 2.74×10^{-3} | 112 | 2.68×10^{-3} |
| 2.0 | 110 | 3.12×10^{-3} | 112 | 2.94×10^{-3} | 111 | 2.76×10^{-3} |
| d) Magnesium | | | | | | |
| 0.5 | 113 | 3.98×10^{-2} | 113 | 3.76×10^{-2} | 115 | 3.42×10^{-2} |
| 1.0 | 114 | 4.12×10^{-2} | 114 | 4.02×10^{-2} | 115 | 3.96×10^{-2} |
| 1.5 | 113 | 4.24×10^{-2} | 112 | 4.16×10^{-2} | 114 | 4.03×10^{-2} |
| 2.0 | 112 | 4.46×10^{-2} | 113 | 4.28×10^{-2} | 115 | 4.15×10^{-2} |

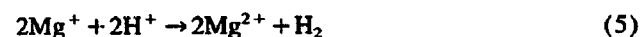
^a dec⁻¹ = per decade of log i_0 .

3.2. Corrosion reactions

Magnesium is oxidized to oxide, hydroxide or the divalent ion in the presence of magnesium perchlorate solution. There are two possibilities. First, the fine particles of metal may become separated from the electrode surface [9]



Second, the monovalent ion is oxidized by a H^+ ion



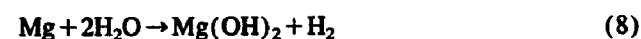
or, when in contact with water, the following conversion takes place



This results in the formation of the stable valency of magnesium and the evolution of hydrogen. Other side reactions are also possible, such as disproportionation of Mg^+ ions into magnesium metal and Mg^{2+} ions



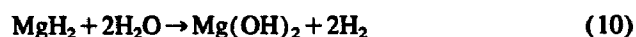
The magnesium atoms thus formed can be reduced in an aqueous magnesium perchlorate solution as follows



The properties of the magnesium electrode are related to the existence of an intermediary compound, magnesium hydride



that may be oxidized by water in the presence of magnesium perchlorate solution as follows



The relative rates of the above reactions determine the corrosion rate of a magnesium alloy.

The corrosion rate ($\text{mg cm}^{-2} \text{min}^{-1}$) for bare magnesium, AZ 31, AZ 61 and AP 65 alloy in 2.0 M magnesium perchlorate solution is 0.0888, 0.0029, 0.0044 and 0.0493, respectively [2].

3.3. Impedance measurements

Since a simple electrochemical system consists of a double-layer capacitance, a solution resistance and a charge-transfer resistance, the use of an a.c. signal can provide more information than that obtained from a d.c. polarization technique. The impedance locus diagram is obtained by applying a 10 mV rms sinusoidal potential between the working and reference electrodes through a potentiostatic circuit; the potential-current function gives the impedance value. The magnitude (Z)/phase (θ) relation of the impedance is given by $Z' = Z \cos \theta$ for the real part and $Z'' = Z \sin \theta$ for the imaginary part. Typical Nyquist plots for magnesium and its alloys in 2.0 M magnesium perchlorate solution are shown in Figs. 3 and 4. The diameter of the semicircle gives the

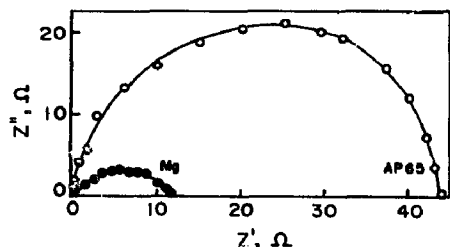


Fig. 3. Nyquist plots for magnesium and AP 65 alloy in 2.0 M magnesium perchlorate solution.

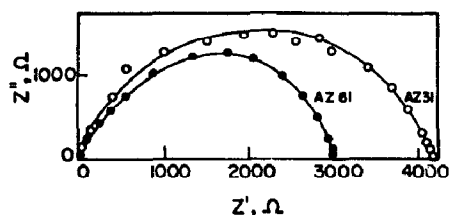


Fig. 4. Nyquist plots for magnesium alloys in 2.0 M magnesium perchlorate solution.

charge-transfer resistance (R_{ct}) at the electrode/electrolyte interface. From R_{ct} values, the exchange-current density (i_0) and double-layer capacitance (C_{dl}) have been calculated using the following expressions:

$$i_0 = [RT/nF] 1/R_{ct} \quad (11)$$

$$C_{dl} = 1/2\pi f_{max} i_0 \quad (12)$$

The intercept on the x-axis at the higher frequencies gives the solution resistance (R_s). The latter is the uncompensated resistance between the working and the reference electrodes. The nature of the curves indicates whether the system is activation-controlled (a semicircle), diffusion-controlled (a 45° straight line), or a combination of both. In each case, semicircles have been obtained and this indicates that the electrode/electrolyte interface in this study is controlled predominantly by activation-controlled processes. It is also evident that in the case of the Mg/Mg(ClO₄)₂ system, the resistance is negligibly small and, hence, can be ignored. The resulting parameters such as R_{ct} , i_0 and C_{dl} are shown in Table 3.

The results reveal that R_{ct} decreases gradually with increase in Mg(ClO₄)₂ concentration up to 2.0 M; beyond this concentration, the trend is reversed. The value of R_{ct} is minimum in the 2.0 M electrolyte. The i_0 values are in good agreement with those obtained above from Tafel measurements. The order of the i_0 values with respect to magnesium and its alloys is: Mg > AP 65 > AZ 61 > AZ 31. The same trend has been observed for Tafel measurements. This is because an increase in i_0 should correspond to an increase in the corrosion rate. Thus, the dissolution rate is the greatest for the magnesium metal. Elements with a low hydrogen overvoltage and a low electrode potential with respect to magnesium will experience less dissolution of the surrounding matrix [10]. This explains why the i_0 values for the AZ 31 alloy are lower than those for the AP 65 alloy and bare magnesium.

The C_{dl} values for magnesium, AP 65, AZ 61 and AZ 31 electrodes in 2.0 M Mg(ClO₄)₂ solution are 363.50, 144.10, 6.29 and 5.24 μF, respectively. The low value of C_{dl} for the AZ 31 alloy implies the formation of a relatively thick and compact protective film on the metal surface.

Experimental observations have shown that an increase in passivation potential gradually decreases the radius of the semicircle. The charge-transfer resistance values are found to be 338, 238 and 150 Ω for applied potentials of 10, 30 and 50 mV, respectively (Fig. 5). This polarization behaviour can be interpreted via the concept of anion adsorption on the surface oxide layer whereby a field-assisted transport of ions through the passive layer is introduced to account for the ion-current density upon raising the oxidation potential. On applying this concept, it follows that anions are adsorbed at the electrode/electrolyte interface to a concentration that

Table 3

Impedance parameters of magnesium and its alloys in various concentrations of Mg(ClO₄)₂ solution at open-circuit potential

| Concentration (M) | R_{ct} (Ω) | i_0 (A cm ⁻²) | C_{dl} (μF) |
|-------------------|--------------|-----------------------------|---------------|
| a) AZ 31 alloy | | | |
| 0.5 | 6776.00 | 3.78×10^{-6} | 7.11 |
| 1.0 | 5793.00 | 4.42×10^{-6} | 5.84 |
| 1.5 | 4537.00 | 5.64×10^{-6} | 5.56 |
| 2.0 | 4154.00 | 6.16×10^{-6} | 5.24 |
| b) AZ 61 alloy | | | |
| 0.5 | 4280.00 | 5.98×10^{-6} | 9.20 |
| 1.0 | 3390.00 | 6.58×10^{-6} | 8.70 |
| 1.5 | 3422.00 | 7.48×10^{-6} | 6.61 |
| 2.0 | 3045.00 | 8.41×10^{-6} | 6.29 |
| c) AP 65 alloy | | | |
| 0.5 | 101.00 | 2.55×10^{-4} | 190.00 |
| 1.0 | 82.00 | 3.12×10^{-4} | 171.18 |
| 1.5 | 64.75 | 3.95×10^{-4} | 155.00 |
| 2.0 | 43.75 | 5.85×10^{-4} | 144.10 |
| d) Magnesium | | | |
| 0.5 | 20.50 | 1.25×10^{-3} | 670.00 |
| 1.0 | 17.00 | 1.51×10^{-3} | 592.50 |
| 1.5 | 15.25 | 1.68×10^{-3} | 422.70 |
| 2.0 | 11.25 | 2.28×10^{-3} | 363.50 |

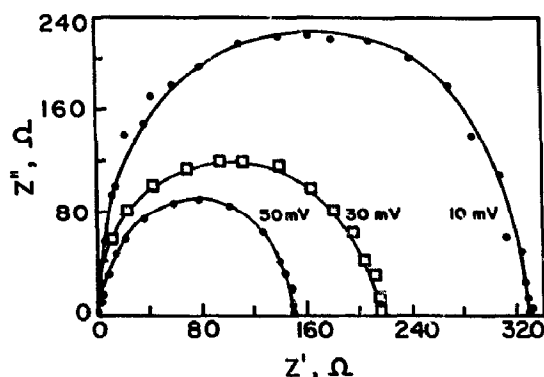


Fig. 5. Nyquist plots for AZ 31 alloy in 2.0 M magnesium perchlorate solution at different anodic potentials.

depends on the applied anodic potential. The higher the anodic potential, the more the number of ions present at the interface. These will be incorporated in the outermost layer of the passive film by occupying anion vacancies in the film and, thereby, will lead to the film-breakdown process that is responsible for the decrease of the semicircle radius.

Simulation calculations have been performed [11] in order to explain the variations in the Nyquist plots obtained in this study. This involves the assumption of fractal geometry for the interfacial region. These calculations have revealed that, during passivation, morphological changes in the electrode take place and cause the charge flux to diffuse. This, in turn, explains the anomalous trend in the decrease in the charge-transfer resistance values.

4. Conclusions

From the results of these investigations, the following conclusions may be drawn:

(i) Impedance studies on magnesium and its alloys in magnesium perchlorate electrolyte reveal that the electrode/electrolyte interfacial process is determined by an activation-controlled reaction.

(ii) The dissociation is greatest in the case of the AP 65 (Mg–Al–Pb) alloy and hence the charge-transfer resistance, R_{ct} , is lower than that for either the AZ 31 (Mg–Al–Zn) or the AZ 61 (Mg–Al–Zn) alloy.

(iii) The values of i_0 and C_{dl} follow the following sequence (with respect to the chosen electrode): Mg > AP 65 > AZ 61 > AZ 31.

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