Short Communication

Corrosion of magnesium alloy in aqueous magnesium perchlorate battery electrolyte — a gasometry study

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Abstract

The corrosion aspects of magnesium AZ 31 alloy in magnesium perchlorate at different temperatures have been examined using the gasometry technique. The results are used to determine the optimum electrolyte concentration from the viewpoint of battery applications. The studies also reveal that increase in temperature brings about a gradual increase in the gas evolution rate. These results have been explained in terms of dissolution/film-formation mechanisms and the disintegration phenomenon.

Introduction

For application as a negative electrode in batteries, magnesium possesses several advantages such as high electrode potential (2.37 V), low electrochemical equivalent (0.45 g A^{-1} h^{-1}, greater stability towards corrosion (which results in a high shelf life of about five years), relative abundance from sea bitterns, and low toxicity [1]. This has encouraged the authors to examine magnesium as an anodic material in conjunction with certain novel N-halogen organic cathode depolarizers for the development of new magnesium battery technology [2–7]. Corrosion has been the greatest single deterrent in the exploitation of magnesium as a successful battery anode [8]. Thus, in order to achieve the required long-term operating characteristics of magnesium-based cells, it is imperative to obtain a more basic understanding of the electrode processes involved in their operation. To this end, the work reported has employed the gasometric technique to examine the corrosion behaviour of magnesium AZ 31 alloy in various concentrations of magnesium perchlorate (0.5 to 2.5 M) and at various temperatures ranging from 30 to 45 °C. The data have been correlated with results obtained from the conventional weight-loss method. Another recent study, based on impedance and rotating-disc electrode measurements of the magnesium/magnesium perchlorate system, has been reported elsewhere [9, 10].

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Experimental

In contrast to the traditional weight-loss method, the gasometric technique is a precise and accurate method for determining the kinetics of metal corrosion. The instrumental design of the set-up, fabricated in-house, is described elsewhere [11].

Magnesium AZ 31 alloy (composition: Al 2.5 to 3.5 wt.%; Zn 0.60 to 1.4 wt.%; Mn 0.15 to 0.70 wt.%) plates of $2 \times 2 \times 0.8$ cm were employed. The electrodes were cloth-buffed in the presence of pumice and then degreased with trichloroethylene. The net area of the electrode exposed to the electrolyte was 9.1372 cm^2 and the average weight was 1.01 to 1.02 g. The volume of the solution used in each experiment was 100 ml. The entire gasometric set-up was maintained at a constant temperature. The volume of gas evolved was measured at regular intervals over a period of 3 h. The magnesium alloy sheets were then removed from the cell and cleaned in a boiling solution of 20 wt.% H_2CrO_4 and 0.02 wt.% $AgNO_3$ for 2 min [12]. The experiments were conducted in 0.5, 1.0, 1.5, 2.0 and 2.5 M magnesium perchlorate solutions at 30, 35, 40 and 45 °C.

Results and discussion

When magnesium comes in contact with the electrolyte, a magnesium hydroxide film is formed on the metal surface. This is due to the dissolution of Mg^{2+} ions in the solution and subsequent precipitation with OH^- ions that are produced by the reduction of water according to the following mechanism:

$$Mg \longrightarrow Mg^{2+} + 2e^- \tag{1}$$

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2 \tag{2}$$

$$Mg^{2+} + 2OH^- \longrightarrow Mg(OH)_2 \tag{3}$$

In order to account for the nature of the anodic film, two hypotheses have been advanced, namely:

(i) the formation and dissolution of magnesium hydroxide [13];

(ii) a magnesium hydride film may exist as an intermediate species [14].

In the first hypothesis, thermodynamic calculation of the mixed-potential corresponding to the experimental value is not feasible, whereas, in view of the presence of reactive fresh magnesium at the electrode/electrolyte interface, the intermediate formation of magnesium hydride [15] could be envisaged, i.e.:

$$Mg + 2H_2O + 2e^- \longrightarrow MgH_2 + 2OH^- \tag{4}$$

$$MgH_2 + 2OH^- \longrightarrow Mg(OH)_2 + H_2 + 2e^- \tag{5}$$

When magnesium is immersed in an aqueous electrolyte, hydrogen is evolved in quantities corresponding to the metal dissolved. The mechanism of magnesium dissolution in acidic and neutral media differs from that in alkaline medium. In the formed media, the mechanism of magnesium dissolution is as follows:

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2 \tag{6}$$

In neutral salt solutions, the dissolution of magnesium is faster in the initial stages, i.e., prior to the formation of the $Mg(OH)_2$ film. Hence, the evolution of gas is greater in the initial stages. After the formation of the film, the gas evolution attains a limiting value. This is presumably due to protection of the surface from further corrosion.

Gas volume versus time measurements

The volume of gas evolved from magnesium AZ 31 alloy in various concentrations of magnesium perchlorate electrolyte (0.5 to 2.5 M) and at various temperatures (30 to 45 °C) is plotted as a function of time in Figs. 1 and 2, respectively. Clearly, the gas evolution increases with both electrolyte concentration and temperature up to a certain limit. For each concentration, the gas evolution is greater initially and then reaches a limiting value. From these observations, it is concluded that the mechanism of the corrosion in the initial stages of the reaction involves the combined effects of magnesium dissolution and magnesium hydroxide film formation. The latter is responsible for the reduction in the gas-evolution rate [4, 16, 17]. Gas evolution is maximum in 2.0 M solution, and decreases appreciably in both higher and lower electrolyte concentrations. This behaviour is due either to a lowering of the conductivity of the electrolyte or to the formation of a passive film on the electrode surface. As noted above, the gas evolution also increases with temperature (Fig. 2) and probably results from an enhancement in the solubility of $Mg(OH)_2$ [18, 19].

Evaluation of corrosion rates

The corrosion rate ($g\ m^{-2}\ h^{-1}$) has been calculated from the measurements of the total volume of gas evolved and the results are compared with those obtained from weight-loss measurements in Table 1. Corrosion rate versus concentration plots are given in Fig. 3. At each temperature, the corrosion rate increases with concentration up to 2 M and then declines. The latter arises from the formation of a stable film on the electrode surface that has a lower conductivity than the bare metal itself [19]. The relationship between corrosion rate and temperature is displayed in Fig. 4. It can be seen that increase in temperature brings about a corresponding rise in the corrosion rate.
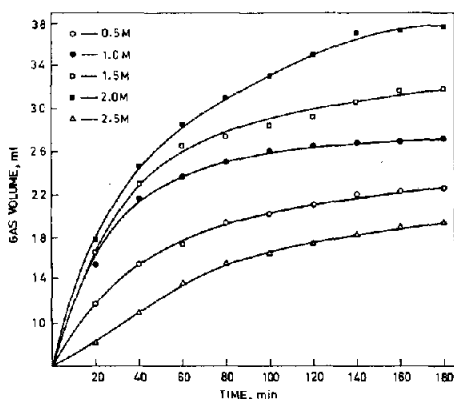

Fig. 1. Gas volume vs. time curves for magnesium AZ 31 alloy in different $Mg(ClO_4)_2$ concentrations at 45 °C.
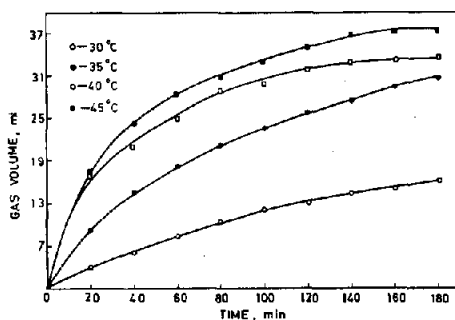
Fig. 2. Gas volume vs. time curves for magnesium AZ 31 alloy at various temperatures in 2.0 M $Mg(ClO_4)_2$.

TABLE 1

Influence of temperature and $Mg(ClO_4)_2$ concentration on corrosion parameters of magnesium AZ 31 alloy

| Temperature (°C)	Concentration (M)	Total volume gas evolved (ml)	Weight loss[a] (g)	Weight loss[b] (g)	Corrosion rate[a] (g m^{-2} h^{-1})
30	0.5	13.4	0.0131	0.0123	5.3051
	1.0	17.0	0.0166	0.0163	6.7303
	1.5	23.5	0.0230	0.0224	9.3037
	2.0	27.5	0.0269	0.0260	10.8873
	2.5	8.5	0.0083	0.0081	3.3652
35	0.5	18.0	0.0173	0.0170	7.1262
	1.0	21.4	0.0206	0.0200	8.4723
	1.5	28.4	0.0269	0.0260	11.0852
	2.0	30.7	0.0295	0.0289	12.1541
	2.5	14.0	0.0135	0.0131	5.5426
40	0.5	19.8	0.0187	0.0182	7.8388
	1.0	25.4	0.0240	0.0239	10.0559
	1.5	29.2	0.0276	0.0271	11.5603
	2.0	33.8	0.0319	0.0300	13.3814
	2.5	16.7	0.0157	0.0154	6.6115
45	0.5	22.6	0.0211	0.0208	8.9467
	1.0	27.2	0.0253	0.0250	10.7685
	1.5	31.8	0.0296	0.0289	12.5896
	2.0	37.6	0.0350	0.0352	14.8858
	2.5	19.4	0.0181	0.0178	7.6805

[a]by gasometry method.
[b]by weight-loss method.
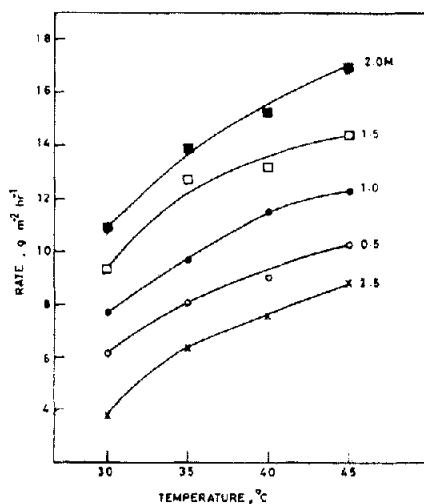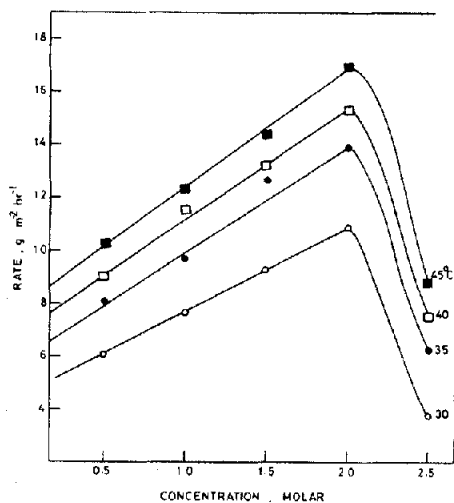
Fig. 3. Variation of corrosion rate with $Mg(ClO_4)_2$ concentration at different temperatures.

Fig. 4. Variation of corrosion rate with temperature for different $Mg(ClO_4)_2$ concentrations.

Reaction mechanisms of magnesium in magnesium perchlorate solution

Magnesium is oxidized to the monovalent ion in the presence of magnesium perchlorate solution [20], i.e.:

$$Mg \longrightarrow Mg^+ + e^- \tag{7}$$

and this is followed by further oxidation in presence of H^+ ions:

$$2Mg^+ + 2H^+ \longrightarrow 2Mg^{2+} + H_2 \tag{8}$$

or, in contact with water, the conversion takes place:

$$2Mg^+ + 2H_2O \longrightarrow 2Mg^{2+} + 2OH^- + H_2 \tag{9}$$

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

$$2Mg^+ \longrightarrow Mg + Mg^{2+} \tag{10}$$

This reaction may occur, provided fine particles of metal are present on the surface of the electrode. It is further possible that these two products (viz., Mg and Mg^{2+}) may associate and form an adduct [21], i.e.:

$$2Mg^{2+} \longrightarrow Mg \cdot Mg^{2+} \tag{11}$$

The magnesium atom thus formed can thereby be reduced in an aqueous medium as follows:

$$Mg \cdot Mg^{2+} + 2H_2O \longrightarrow Mg(OH)_2 + Mg^{2+} + H_2 \tag{12}$$
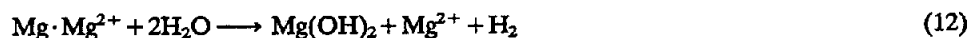
The properties of the magnesium electrode are related to the existence of magnesium hydride:

$$Mg + 2H^+ + 2e^- \longrightarrow MgH_2 \tag{13}$$

which may be oxidized by water in the presence of $Mg(ClO_4)_2$ solution as follows:

$$MgH_2 + 2H_2O \longrightarrow Mg(OH)_2 + H_2 \tag{14}$$

The relative rates of the above-cited reactions determine the corrosion rate of magnesium alloy. During the gasometry experiments, the formation of a black layer commenced on the electrode surface after 2 h. It is thought that this layer could comprise a mixture of $Mg(OH)_2$ film and very fine particles of the metal itself [22]. The hydroxide, thus formed, is not soluble and, thereby, could lead to a saturation state after 2 h. Thereafter the gas volume does not rise, as is evident from the gasometry experiments. The gas evolution rate has been found to increase with temperature. This behaviour could result from continuous damage to the film and from the separation of fine particles of the metal from the electrode by intergranular corrosion. The latter phenomenon is known as the disintegration effect [22, 23] and results in an increase in the active surface area of the electrode.

Conclusions

1. The dissolution of magnesium in a neutral electrolyte such as magnesium perchlorate is faster in the initial stages and hence gas evolution is found to be maximum during this period.

2. The overall reaction rate of magnesium corrosion is controlled by the rate of either proton or magnesium ion transfer through film and hence the mechanism of magnesium dissolution is governed primarily by dissolution, followed by film formation on the electrode surface.

3. The corrosion rate increases with increase in electrolyte concentration and falls beyond a critical concentration of 2.0 M.

4. It is suggested that increase in the gas evolution rate with temperature is caused by intergranular corrosion, a phenomenon known as the disintegration effect.

Acknowledgements

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