Short Communication

Gasometric corrosion-rate studies of magnesium alloy in magnesium batteries

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Abstract

The corrosion rate of AZ31 magnesium alloy during the discharge of anode-limited magnesium/silver chloride cells in different concentrations of sodium chloride is investigated by the gasometric technique. Corrosion rates are measured at different temperatures. From the data obtained, the cell capacity realised and the capacity loss due to local galvanic action of magnesium alloy are calculated. The variation of the rate of gas evolution and the total volume of gas collected at the end of discharge is explained on the basis of negative difference (i.e., increase of wasteful corrosion with increase in current density) and chunk effects (i.e., breakdown of hydroxide film along with magnesium particles at high current density).

Keywords: Magnesium batteries; Magnesium alloys; Corrosion; Gasometric studies

1. Introduction

By virtue of their high power and energy densities, long shelf life and reliability, magnesium silver chloride sea-water-activated batteries are proven candidates for many underwater applications. The latter applications include sonobuoys, torpedos, and air-drop underwater grenades [1,2]. The poor anode efficiency of pure magnesium in sea-water-activated batteries has led to the development of various magnesium alloys (with Al, Zn, Pb, etc.) that show increased anode efficiency [3]. In this paper, the anode efficiency of AZ31 magnesium alloy in sodium chloride solution is studied by gasometry, a technique that yields more reliable and reproducible results than the conventional weight-loss method. A continuous monitoring of the corrosion rate of metals is possible with this technique [4,5]. The effect of variation in both the concentration and the temperature of the battery electrolyte on cell capacity is also reported.

2. Experimental

2.1. Cell assembly

Magnesium/silver chloride cells were assembled using flat-type magnesium alloy plates (AZ31) and sintered silver chloride plates, each with an area of 2 cm × 2.5 cm and separated by thin polyvinyl chloride (PVC) wires. The outer faces of the magnesium plate and the edges in the vertical position of the cell were covered with PVC tape. The terminal lead wires were lacquered to avoid electrolyte contact.

The experimental assembly consisted of three parts, as shown in Fig. 1. The lower portion comprised a double-walled cylindrical glass unit in which the test cell (Mg/AgCl cell) was immersed in the electrolyte. The middle portion of the glass assembly contained two wires that provided connection to the test cell and an outlet for release of the gas pressure that was built up during the introduction of the test cell into the electrolyte. The top part of the assembly contained an outlet for gas collection that was made from a standard graduated burette surrounded by a glass jacket. The three parts of the glass assembly were fitted tightly together with glass joints. A constant temperature was maintained (within ± 1 °C) by circulating water through the double-walled jacket from a thermostatically controlled bath.

The gas released during the reaction was collected over 25% NaCl solution that was acidified with dilute H_2SO_4 so as to reduce the solubility of CO_2 and H_2. The accuracy of the measurements was improved further
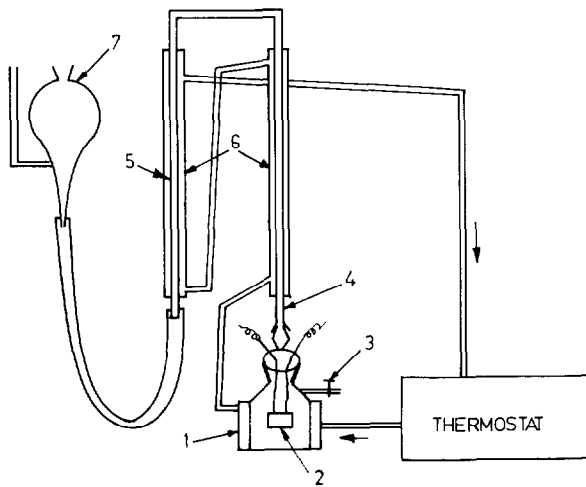
Fig. 1. Assembly for gasometric studies: (1) double-walled glass cell container; (2) cell; (3) stopcock for pressure release; (4) gas-carrying tube; (5) graduated burette; (6) outer jacket for water circulation, and (7) reservoir bulb.

by the addition of methyl orange to the above solution. This enhanced the visibility of the meniscus during measurements. The volume of gas was measured at atmospheric pressure using a pressure reservoir bulb. The reservoir was fitted with a narrow bore (2 mm) glass tube, one side of which was opened to the atmosphere to ensure that the pressure of the gas inside the tube was at atmospheric pressure. There was no need for aqueous tension correction as the liquid levels of the burette, both inside and outside, were kept the same throughout the experiment.

2.2. Experimental details

Since the efficiency of the magnesium/silver chloride cell is limited by the corrosion of the magnesium anode, anode-limited designs were used to arrive at a correlation between the realizable capacity of the cell and that lost due to wasteful corrosion. The cell was discharged at constant current to obtain capacity data. The rate of corrosion was monitored periodically at intervals of 30 min. The amount of wasteful corrosion was calculated from the total volume of hydrogen gas collected at normal temperature and pressure. For better comparison of the data obtained, the volume of hydrogen released was converted into the corresponding corrosion current density. The cell capacity and the corrosion current density were determined at current densities of 20, 40, 60 and 100 mA/cm^2 in 0.5, 0.25 and 0.125 M NaCl. The experiments were carried out at 25, 35 and 45 °C in a thermostatically-controlled water bath.

3. Results and discussion

The volume of hydrogen evolved as a function of time in the various NaCl solutions at 25 °C and at

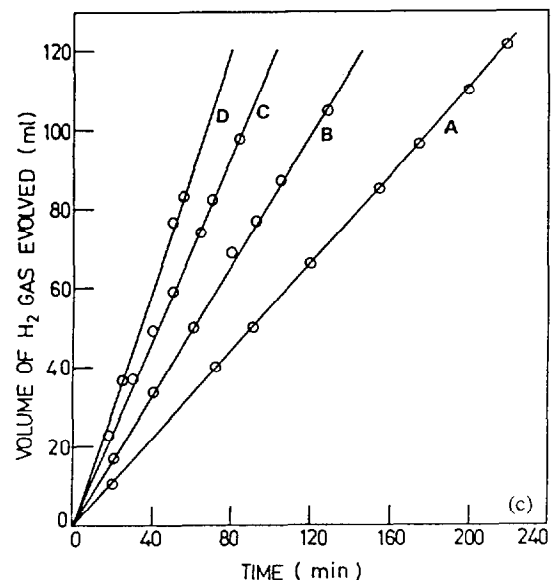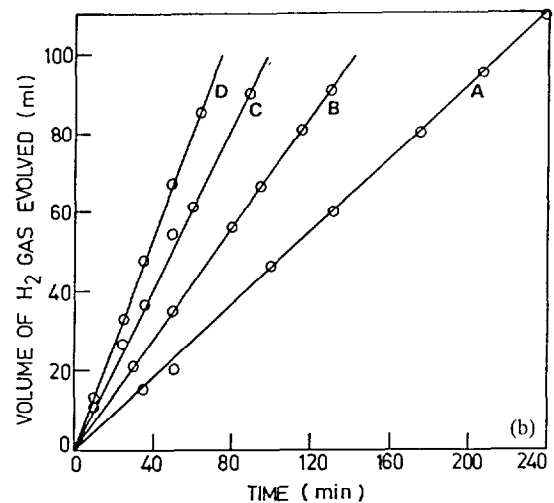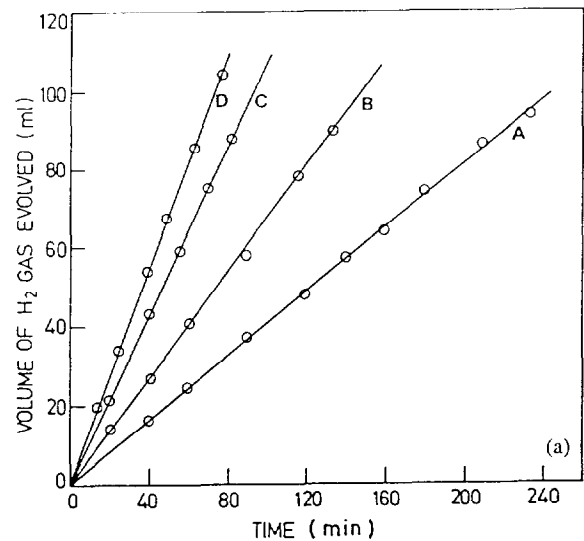Fig. 2. Volume of gas collected at 25 °C in: (a) 0.125 M, (b) 0.25 M, and (c) 0.5 M NaCl. Current density: (A) 20, (B) 40, (C) 60, and (D) 80 mA/cm^2.

different current densities is plotted in Fig. 2. The gas-evolution rates obtained from the slope of the curve for 0.5 M NaCl (Fig. 2(c)) are plotted against current density in Fig. 4. Similar behaviour is observed in 0.125 and 0.25 M NaCl, as is evident from the data listed in Table 1. The values of the slopes indicate that the rate of gas evolution increases at high current densities. Nevertheless, the total quantity of gas collected at the end of the experiment decreases with current density.

During cell discharge at high current densities, the oxide film on the magnesium surface breaks down, exposes the bare metal and, thereby, increases the gas-evolution rate. In spite of a high rate of gas evolution, the cell exhibits a high energy output due to the lower period of the discharge time.
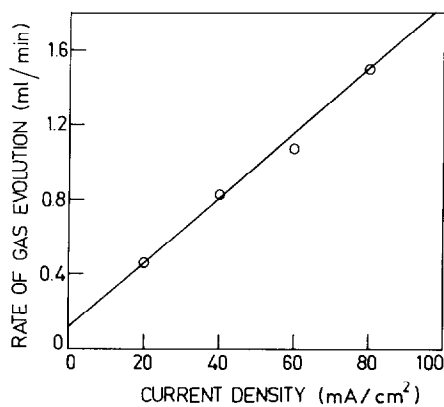

Fig. 3. Rate of gas evolution at different current densities at 25 °C in 0.5 M NaCl.

Table 1
Slope value (cm³/min) in different concentrations of NaCl electrolyte

Current density mA/cm²	NaCl concentration (M)		
	0.5	0.25	0.125
20	0.46	0.42	0.39
40	0.83	0.70	0.69
60	1.08	1.00	1.08
80	1.50	1.33	1.31

The increase in the rate of gas evolution with increase in current density in different concentrations of sodium chloride is due to the negative difference effect of magnesium. This effect is defined as the difference between the hydrogen-evolution rate, ν_1, from an electrode without current flowing and the hydrogen evolution rate, ν_2, from the same electrode with an applied current. Usually, the two rates are not equal; a positive or a negative value depends on the electrolyte concentration and current density applied. When cells with magnesium alloy anodes are discharged at high current density, rate ν_2 (i.e., wasteful chemical dissolution) is greater than rate ν_1 and this leads to a 'negative difference effect' that increases with increase in current density.

From the discharge data and the volume of hydrogen released due to corrosion, the capacity of the cell and the capacity loss due to wasteful corrosion can be calculated. The values are presented in Tables 2 to 4. It is evident from the data for 0.5 M NaCl that as the current density is increased from 20 to 80 mA/cm² the capacity of the cell increases from 25 to 27 A min, whereas the wasteful corrosion decreases from 14.5 to 11.2 A min. This pattern is observed at all the concentrations and temperatures. This suggests that the capacity of the cell and the loss in capacity due to wasteful corrosion are complementary in nature and, thereby, keep the total output $(a+b)$ nearly constant. (Note: a is the capacity of the cell realized in A min, and b is the capacity loss of the cell due to local galvanic cell, gas evolution in A min.)

The output value $(a+b)$ approaches the input value (Q = weight of magnesium taken for the experiment, i.e., 0.316 g or 41.82 A min) at higher temperature. This is due to a concomitant increase in the b value, e.g., from 14.5 to 17.97 at 20 mA/cm² in 0.5 M NaCl. This shows that as the temperature is increased, the total amount of gas evolved also increases and, thereby, decreases the anode efficiency.

The output value $(a+b)$ does not approach the input value (Q) at lower temperatures, however. This difference between Q and $(a+b)$ can be attributed to the prevalence of chunk effects. The latter relate to the

Table 2
Capacity data for 0.5 M NaCl

Current density mA/cm²	25 °C			35 °C			45 °C		
	a [a]	b [b]	$(a+b)$	a	b	$(a+b)$	a	b	$(a+b)$
20	25.00	14.50	39.50	23.50	15.91	39.41	23.00	17.97	40.97
40	26.00	13.33	39.33	25.80	14.87	40.67	24.00	16.25	40.25
60	26.50	12.90	39.40	26.00	14.00	40.00	24.30	15.73	40.03
80	27.00	11.20	38.20	26.50	13.64	40.14	25.60	15.11	40.71

[a] a = capacity realized (A min).
[b] b = capacity loss due to local galvanic cell (gas evolution in A min).

Table 3
Capacity data for 0.25 M NaCl

Current density mA/cm^2	25 °C			35 °C			45 °C		
	a [a]	b [b]	$(a+b)$	a	b	$(a+b)$	a	b	$(a+b)$
20	24.80	14.20	39.00	24.30	15.43	39.73	24.00	17.53	41.53
40	25.40	12.66	38.06	24.80	14.74	39.54	24.00	16.08	40.08
60	26.20	12.00	38.20	25.80	13.40	39.20	25.20	15.56	40.76
80	26.60	10.80	37.40	24.80	13.40	38.20	24.00	14.87	38.87

[a] a = capacity realized (A min).
[b] b = capacity loss due to local galvanic cell (gas evolution in A min).

Table 4
Capacity data for 0.125 M NaCl

Current density mA/cm^2	25 °C			35 °C			45 °C		
	a [a]	b [b]	$(a+b)$	a	b	$(a+b)$	a	b	$(a+b)$
20	23.40	12.30	35.70	23.70	15.02	38.72	23.90	16.74	40.64
40	24.10	12.20	36.30	24.70	14.05	38.75	25.00	15.56	40.56
60	25.20	11.50	36.70	25.80	12.93	38.73	26.40	15.36	41.76
80	26.40	9.90	36.30	25.60	12.93	38.53	26.80	14.43	41.23

[a] a = capacity realized (A min).
[b] b = capacity loss due to local galvanic cell (gas evolution in A min).

separation of discrete magnesium particles on the surface of the magnesium, anode under load conditions and these account for the rise in wasteful corrosion with increasing current density. At the high current densities employed here, dark flakes containing aggregates of magnesium metal embedded in the hydroxide layer separated and left bare metal with an increased surface area. This effect, in turn, gave rise to the increase in current density.

4. Summary

The realizable capacity and the capacity loss of anode-limited magnesium/silver chloride cells have been determined from discharge data and gasometric measurements, respectively. The increase in corrosion rate with increase in current density has been explained on the basis of a negative difference effect. Further, the difference between the theoretical capacity and the

capacity output of the cell has been explained from the point of view of chunk effects.

Acknowledgement

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