Performance characteristics of a pilot sea-water activated battery with $Pb/PbCl_2$ cathodes, prepared by cyclic voltammetry

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Abstract

Cyclic voltammetry was utilized in preparation of $PbCl_2$-active material on the surfaces of lead electrodes in 1.0 M HCl solutions. X-ray diffraction analysis proved that only $PbCl_2$ was formed and no other products could be detected. The morphology of the $Pb/PbCl_2$ surface layer, as revealed by scanning electron microscopy, showed a primitive dependence on the employed voltammetric conditions. The $Pb/PbCl_2$ electrodes prepared by cyclic voltammetry were employed as cathodes in a pilot sea-water activated cell using Mg–alloy anodes. The voltage-time and current-time discharge curves of the pilot cell were examined as a function of the Mg% in the anode material, magnitude of the load resistance and salinity of the electrolyte. The discharge characteristics of a pilot 5-cell battery were also tested. Under the optimum conditions, the voltage of a unit cell attained 1.2 V which agrees well with the voltage of the corresponding conventional cells. In addition to the easy method of preparation, the present cathodes are characterized by many advantages over those prepared by the traditional techniques.

Introduction

The $Pb/PbCl_2$ electrode is used as an economical substitute for the Ag/AgCl electrode in sea-water activated batteries which employ a Mg–alloy anode [1–3]. In practice, the substitute electrode is prepared by various means such as fusion casting [1], hot pressing [4] and cold pressing [5] techniques. Nevertheless, the performance characteristics of this electrode are inferior to those of the Ag/AgCl electrode. This may partially be ascribed to the specific properties of $PbCl_2$ and partially to the method of preparation of the $Pb/PbCl_2$ electrode.

Previous galvanostatic, potentiostatic and cyclic voltammetric studies of the Pb electrode in aqueous HCl and NaCl solutions revealed that the overall anodic reaction leads to the formation of a thin layer of $PbCl_2$ on the surface of the lead anode [6–10]. Accordingly, the present work is devoted to utilize a recently established cyclic voltammetry technique [11] to prepare a relatively thick $PbCl_2$ surface layer on Pb electrodes. It would be expected that the characteristics of the $PbCl_2$-active material prepared by this electrochemical mean exceed those of $PbCl_2$ prepared by the previous conventional techniques. Therefore, the study is extended to examine the performance characteristics of a pilot sea-water activated battery including the electrochemically prepared $Pb/PbCl_2$ electrode as cathode.

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Experimental

$PbCl_2$-active material

Cyclic voltammetry technique was used for preparation of the $PbCl_2$-active material on the surface of a Pb sheet which served as the working electrode. A platinum wire, 99.9% BDH, was used as the counter electrode. The reference electrode was a saturated calomel electrode (SCE) prepared from AR grade BDH chemicals. The employed electrolytic cell consisted of a tall beaker containing 1.0 M HCl solution. The counter electrode was fitted into a compartment separated from the main electrolyte by means of a G_4 sintered-glass disc to affect separation of the anodic and cathodic reaction products. The potentials were measured relative to the SCE via a salt bridge which was filled with 1.0 M HCl solution and placed with its tip almost touching the working electrode. All experiments were carried out at 25 ± 2 °C using for each experiment a fresh solution and a new set of electrodes.

The cyclic voltammetry experiments were performed by using a Wenking potentioscan model POS 73 and recorded automatically by means of an Ominographic *X-Y* recorder model 2000. The morphology of the as-formed spongy lead $PbCl_2$ surface layer was examined with a scanning electron microscope (JEOL model JSM 35). In addition, X-ray diffraction analysis of the formed layer was carried out using a Philips X-ray diffractometer PW 1390, with a nickel filter and copper radiation.

Sea-water activated batteries

The pilot sea-water activated single cell consisted of some form of encasement including an anode, a cathode and an electrolyte. Similarly, a battery consisted of a multiplicity of cells connected in series.

The encasement was a rectangular Perspex trough of the inside dimensions 10.0 cm length, 3.0 cm width and 2.0 cm height. The trough was provided with vertical grooves on its side walls to fix the electrodes at a constant anodic-cathodic distance (0.3 cm) throughout all the measurements. In each cell, two holes of 0.2 cm diameter were drilled through the walls of the trough, one at the bottom of one side (inlet) and the other at the top of the opposite side (outlet). The electrolyte was forced to flow through these holes, in and out the cell, with a constant rate (0.5 l h^{-1}) by means of a simple pump.

Various types of Mg–alloy anodes of the chemical composition given in Table 1 were examined. All the anodes were cut from 0.1 cm thick sheet of dimensions 3 cm$\times$2 cm which filled the entire cross section of the encasement and fitted with an arm (0.5 cm$\times$1.0 cm) for connection. The Mg–alloy powder was used either compressed (200 t cm^{-2}) in presence of 5% carbon black as a binder or in cloth bags.

The cathodes were cut from 0.1 cm thick sheet of Pb (99.999% Johnson Matthey and Co. Ltd.) and had the same geometrical shape and dimensions as the anodes. The $PbCl_2$ active mass was formed on the surface of the Pb sheet by cyclic voltammetry in 1.0 M HCl solution. The employed voltammetric conditions were: starting potential (E_s) -800 mV, switching potential (E_λ) 400 mV and potential sweep rate (ν) 1000 mV min^{-1}. Under these conditions, the Pb electrode was subjected to five complete cycles followed by five anodic half-cycles. This is a brand new method for preparation of the $Pb/PbCl_2$ electrode.

The employed electrolytes were simulated sea-water of various strength of salinity, namely 1.5–3.6% aqueous NaCl solutions.

TABLE 1

Chemical composition of the employed Mg–alloy anodes

Anode	Metal (%)						
	Mg	Al	Zn	Mn	Si	Fe	Cu
Al[a]	0.03	99.50	0.10	0.05		0.04	0.05
Al–Mg 3%[a]	3.00	96.10	0.20	0.01	0.50	0.04	0.05
Mg 50%[b]	50.00	49.20	0.20	0.01	0.05	0.04	0.05
Mg–6565[c]	41.50	58.40	0.01	0.01	0.04	0.01	
Mg–84/1[c]	49.60	50.20	0.01	0.01	0.05	0.02	
Mg–AZ 91[c]	90.30	8.64	0.78	0.15	0.06	0.01	0.01

[a]Samples were obtained from Company of Nonferrous Industries, Helwan, Egypt.
[b]Sample Metal Pullver A 5111 was obtained in powder form from St. Georgen BEI, Salzburg, Austria.
[c]Samples provided by Norsk Hydro, Magnesium Gesellschaft GmbH, Essen, Germany.

The discharge experiments of a cell or a battery were carried out through a selected resistance. Voltage-time (V-t) and current-time (j-t) curves were measured, under various conditions, by means of conventional digital avometer devices. The discharge characteristics were examined as a function of the Mg% of the anode, the load resistance and the salinity of the electrolyte.

Results and discussion

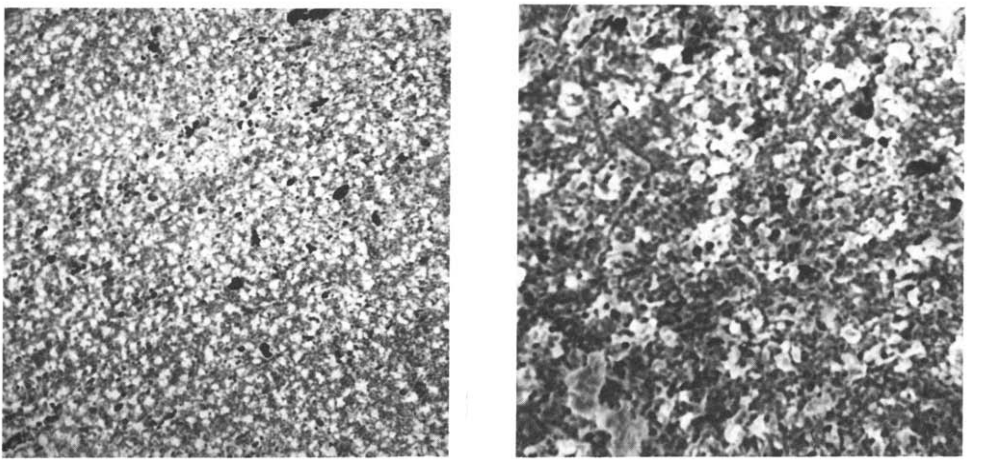
Surface morphology and X-ray diffractometry

A one complete cycle of potential sweep between E_s and E_λ produces a relatively thin and fine-grained spongy lead surface layer, that contains many large holes. On subjecting the electrode to a succession of five complete cycles, it was possible to form a relatively thick and more dense spongy lead surface layer (Fig. 1(a)). The formation of such a spongy lead layer is necessary for building up of a thicker and more compact $PbCl_2$ surface layer (Fig. 1(b)) by a definite number (five) of consecutive only anodic half-cycles. This technique has been discussed in further details for the building up of a relatively thick $PbCl_2$ layer on the surface of the Pb electrode in aqueous NaCl solution [11].

X-ray diffraction patterns of the $PbCl_2$ surface layer, formed under selected voltammetric conditions, was determined and the results are given in Table 2. The obtained data reveal that the layer is formed of $PbCl_2$ in the crystalline orthorhombic structure, no other species appear to be present. Moreover, the observed lattice parameters are consistent with the standard values.

Performance characteristics

The $Pb/PbCl_2$ electrodes prepared by cyclic voltammetry, under the above mentioned constant conditions, were used as cathodes in a pilot sea-water battery. These electrodes are characterized by the following advantages over the others prepared by hot-pressing [4], cold-pressing [5] and fusion casting [1] techniques. Namely, the presented electrodes do not need neither carbon to impart conductivity, a binder for cohesion of the active material, a metal grid as current collector nor a base for the cathode to facilitate



(a) (b)

Fig. 1. Electron micrographs of (a) spongy lead and (b) $PbCl_2$ surface layers. Magnification 2000×.

TABLE 2

Characteristics of X-ray diffraction patterns of the $PbCl_2$ formed in 1.0 M HCl solution by cyclic voltammetry

Observed		(*h k l*)	Observed lattice parameters (Å)[a]		
d (Å)	I/I_0		*a*	*b*	*c*
4.502	18	(002)	4.512	7.812	9.005
4.034	100	(101)			
3.004	30	(120; 022)			
2.449	26	(103)			
2.434	26	(031)			

[a]The standard lattice parameters are: $a = 4.52$ Å, $b = 7.60$ Å, and $c = 9.03$ Å.

intercell connections. Moreover, the design of the present cell encasement removes the need for nonconductive separators, which were required in the previous cells, to form a space for free ingress of the electrolyte and egress of the corrosion products.

Voltage-time curves

Discharge curves of the developed $Pb/PbCl_2$–Mg cells were examined as a function of the Mg% in the anode material and the results are illustrated in Fig. 2. Each cell was discharged continuously through 5 Ω load, which represents a moderate rate of drain, and 3% NaCl solution was employed as an electrolyte. In general, it could be observed that the discharge voltage is relatively high within the few initial minutes. This could be correlated to the inherent advantage that the original Pb-substrate, which is not far from the surface, is used as a current collector and thus allows instantaneous activation of the cell. Thereafter, the voltage decreased to a steady value and the rest of the discharge curves are almost flat. The shape of the discharge curve

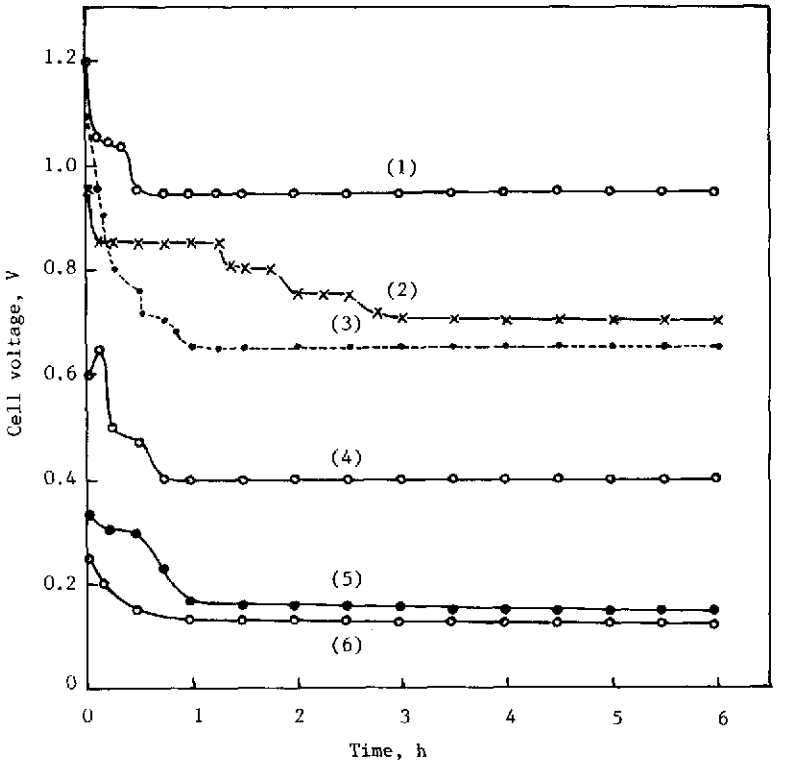


Fig. 2. Influence of the Mg% in the anode material on the voltage-time discharges: (1) Mg–AZ 91, (2) Mg–84/1; (3) Mg–50 (pressed powder); (4) Mg–50 (powder bag); (5) Al–Mg 3%, and (6) pure Al anode.

and the magnitude of the output voltage compare favourably with those of similar batteries in service at present [1]. Inspection of Fig. 2 reveals that the cell voltage ranges between 0.2 V in presence of the pure Al anode and approaches 1.2 V in case of the Mg–AZ 91 anode. The least voltage observed in conjunction with the Al-anode may be referred to the presence of an insulating oxide film on the metal surface [12, 13]. Moreover, a direct proportionality between the cell voltage and the Mg% in the anode material could easily be observed. These results are in good agreement with the fact that the voltage of a cell depends primarily upon the types of anode and cathode employed or the electrochemical system involved [14]. Accordingly, it could be concluded that the Mg–AZ 91 is the most suitable anode in correspondence to the highest voltage delivered.

Typical discharge curves are shown in Fig. 3 for the $Pb/PbCl_2$–Mg 6565 cell discharged through various resistances (2–20 Ω) in aqueous 3% NaCl solution. The discharge curve of the cell including Mg–AZ 91 anode through 20 Ω resistance is enclosed for comparison. In this configuration, the system retains the initial voltage up to a certain period of time depending on the loaded resistance. Thereafter, the voltage drops in a sharp step with a spread of approximately 0.15 V and then steadily persists for a longer period of time reaches 17 h. These data point to the feasibility of a promising long-life power source suitable for moderate drains.

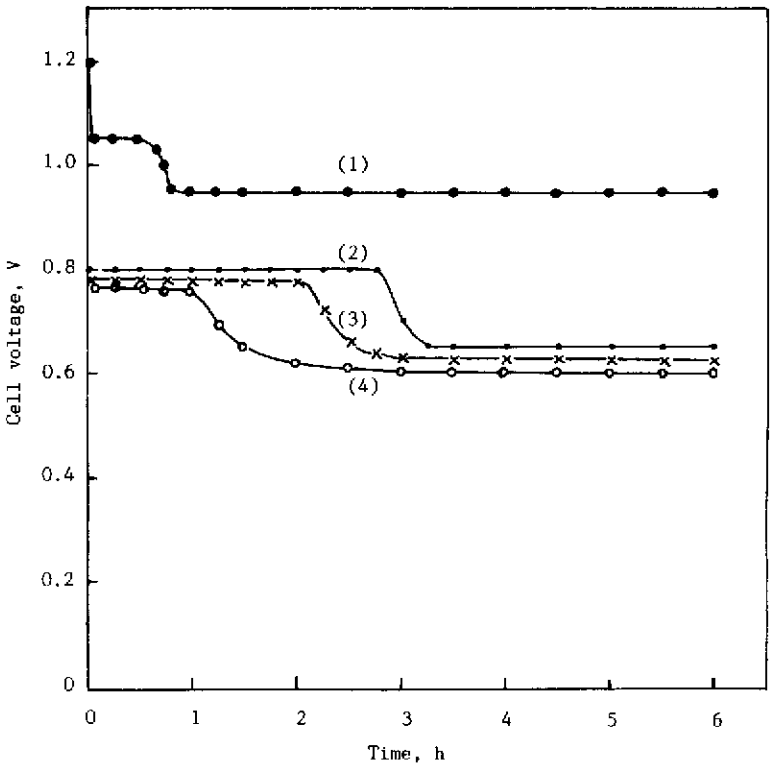


Fig. 3. Influence of the load resistance on the voltage-time discharges: (1) 20.0 Ω, Mg–AZ 91 anode; (2) 20.0 Ω, Mg–6565; (3) 5.0 Ω, Mg–6565, and (4) 2.2 Ω, Mg–6565 anode.

Voltage-time discharges were also carried out to examine the performance characteristics of the model $Pb/PbCl_2$–Mg 6565 cell as a function of salinity of the electrolyte. Accordingly, the NaCl% in the electrolyte was varied within the range (1.5–3.6%) found in sea-waters and the discharge experiments were performed through 5 Ω load. For the sake of comparison, a run was carried out using a Mg–AZ 91 anode and 3.6% NaCl solution. The obtained results, in both cases, are represented in Fig. 4 which depicts that the cell voltage is slightly dominated by salinity of the electrolyte, whereas it is markedly affected by the quality or more accurately by the Mg% in the anode material. Furthermore, for the same Mg–6565 anode, as the NaCl% in the electrolyte increases, the relatively higher initial cell voltage becomes extant for a longer period of time before it drops to a somewhat lower value.

Performance tests were extended to investigate the discharge characteristics of 5-cell, series connected, batteries. These were constructed of $Pb/PbCl_2$ cathodes and Mg–AZ 91 or Mg–50 (compressed powder) anodes. Each battery was discharged in 3% NaCl solution on load of 25 Ω, equivalent to 5 Ω for each single cell. As can be seen in Fig. 5, the discharge curves show an initial gradual decrease of the battery voltage within the first hour, then the voltage attains a steady value which remains almost constant for about 24 h. The observed decrease in voltage approaches 50% for the battery containing the Mg–50 anodes whereas it reaches only 10% for that

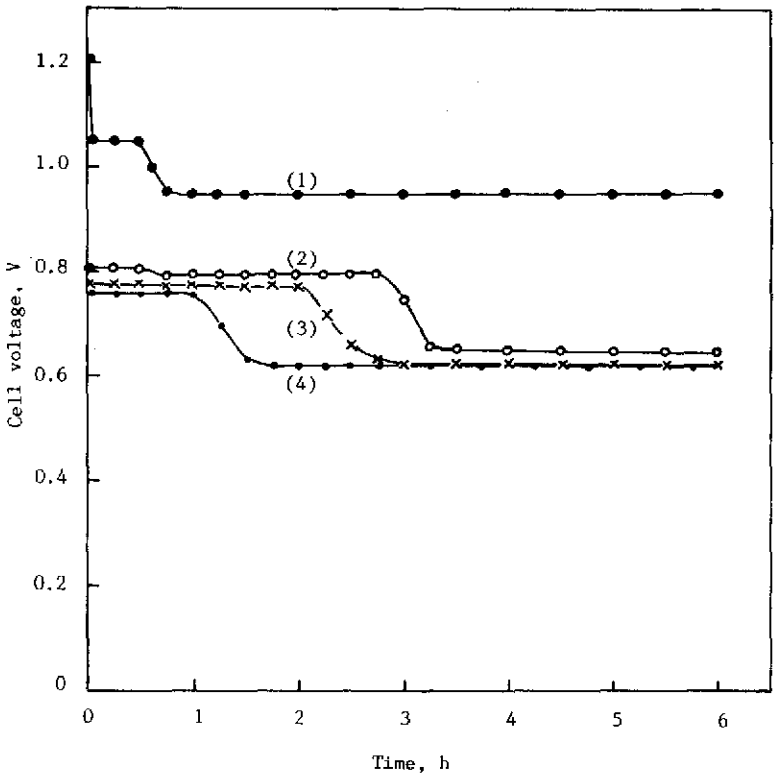


Fig. 4. Influence of the salinity of the electrolyte on the voltage-time discharges: (1) 3.6% NaCl, Mg–AZ 91 anode; (2) 3.6% NaCl, Mg–6565; (3) 3% NaCl, Mg–6565, and (4) 1.5% NaCl, Mg–6565 anode.

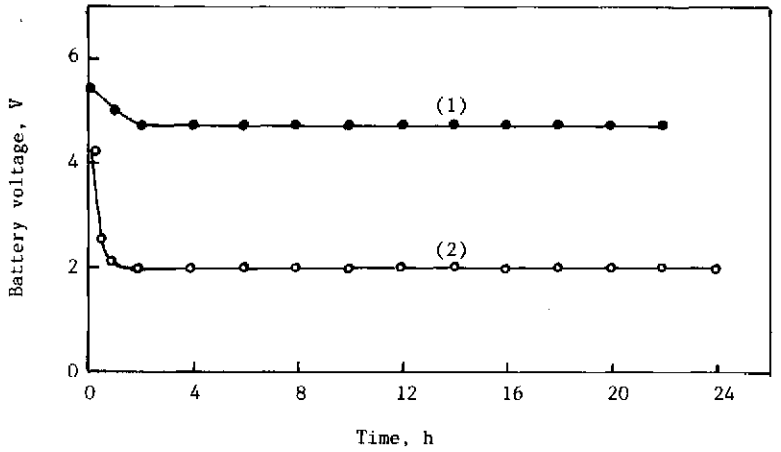


Fig. 5. Influence of the Mg% in the anode material on the voltage-time discharges of 5-cell batteries: (1) Mg–AZ 91 anodes and (2) Mg–50 (pressed powder) anodes.

including the Mg–AZ 91 anodes. These results lead to a conclusion similar to that reported for the unit cells; namely, the higher the Mg% in the anode material the higher is the voltage of the battery. In addition, the obtained data reveal that the latter system is intended to meet medium drain, long life, requirement for about 24 h discharge in the range 4.5–5.0 V. In comparison, a corresponding battery with $Pb/PbCl_2$ cathodes prepared by fusion casting [1] attains the end-point voltage after 4 h only.

Current density-time curves

The discharge behaviour of the $Pb/PbCl_2$–Mg cell across a resistance of 5 Ω was examined using various anode materials in 3% NaCl solution. Figure 6 shows in a general way that the initial current density out-put increases with increase of the Mg%

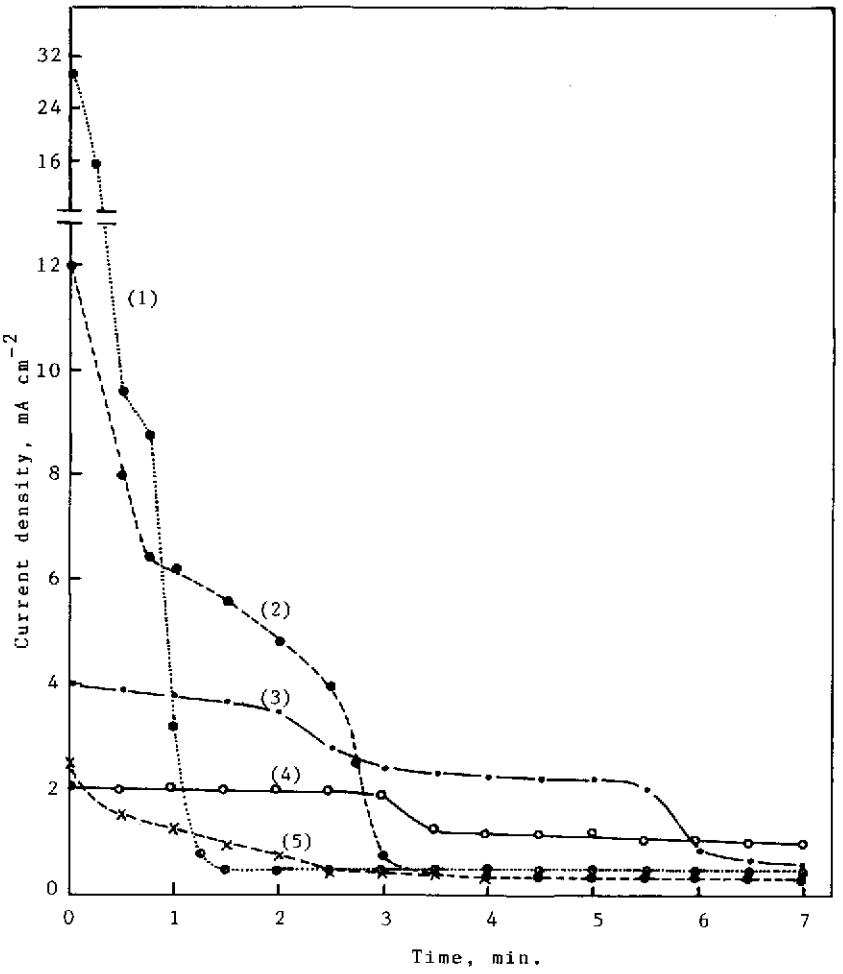


Fig. 6. Influence of the Mg% in the anode material on the current density-time discharges: (1) Mg–AZ 91; (2) Mg–50 (pressed powder); (3) Mg–84/1; (4) Al–Mg 3%, and (5) pure Al anode.

in the anode material. Furthermore, the initial current density decreases at first gradually, over a short period of time, then drops sharply and finally reaches a relatively low level after 3 min of discharge.

The influence of the load resistance on the current density-time discharge characteristics of the $Pb/PbCl_2$–Mg 50 (pressed powder) cells in 3% NaCl solution was investigated. The data of Fig. 7 indicate that as the load resistance increases, the initial current density out-put decreases and retains its value for a longer time interval. In general, this is followed by a consequent gradual decrease of the current density and in particular the lowest resistance employed causes a severe current drop. Accordingly, by choice of various loading resistances, the $Pb/PbCl_2$–Mg cell could be able to fit a drain range adjusted at will.

A detailed explanation of the observed cell performance, in light of the previously reported reaction mechanisms, is not available at the present time. Nevertheless, it seems reasonable that the observed relatively high activity during the initial discharge period may be due to the fast kinetics of the reaction:

$$Mg + 2Cl^- \longrightarrow MgCl_2 + 2e^- \quad (1)$$

In addition, the consequent decay of the current with time may be correlated with a relationship of the type [15, 16]:

$$j^a = k/t \quad (2)$$

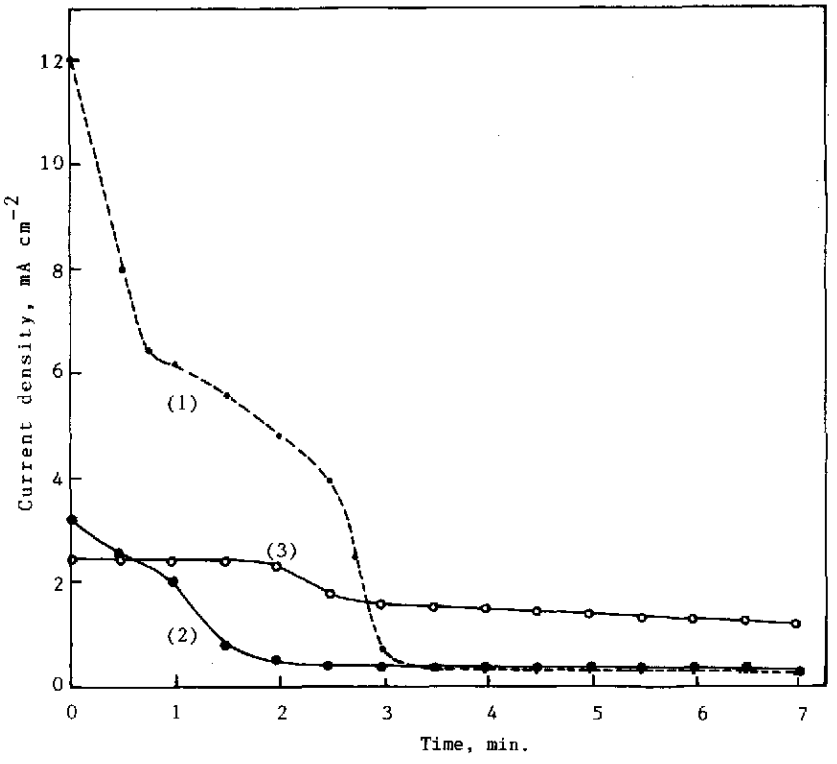


Fig. 7. Influence of the load resistance on the current density-time discharges: (1) 5 Ω; (2) 10 Ω, and (3) 20 Ω.

where k and a are empirical constants. Equation (2) implies that the electrode eqn. (1) is controlled by diffusion of Cl^- ions from the bulk of solution towards the electrode surface. However, previous investigators [17] had used eqn. (2) in a similar interpretation of the discharge characteristics of a lead/acid cell and calculated the corresponding values of the constants k and a.

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