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Charge–discharge characteristics of a lead oxide–zinc secondary battery system

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Performance characteristics of a rechargeable cell using PbO_2 and Zn electrodes and inorganic sulphate electrolytes were studied and compared to those of a conventional lead–acid test cell. The PbO_2–Zn battery exhibits only limited advantages over the lead–acid system.

1. Introduction

In recent years, a certain interest in secondary batteries, using lead oxide and zinc electrode pairs and sulphate or sulphuric acid electrolytes, has been documented in the literature, e.g. [1–4]. Although 'superior' performance with respect to conventional lead–acid batteries was claimed as far as the initial voltage and electrical capacity are concerned, corrosion of the zinc electrode remained a major problem in spite of the use of certain additives (such as quinoline derivatives) unless the zinc was amalgamated. The electrolyte in one patented battery [4] contains five inorganic sulphates and two organic components whose role is to improve the properties of Zn deposited during recharging and to minimize corrosion of Zn during storage etc. It appears, therefore, that this relatively complicated battery system would have to exhibit significantly better overall performance than the conventional lead–acid system if it were to become a serious commercial contender.

The purpose of this study was to compare, via a number of performance tests, the charging–recharging characteristics of a simplified lead oxide–zinc battery to those of a conventional lead–acid cell of the same size. To minimize internal resistance, the alternating, spaced anode and cathode plates were connected together in a parallel mode allowing relatively large current flows at potential drops corresponding to a cell with a single electrode pair. Since long-term storage properties were not an objective of the examination, no special additives were employed, nor was a mercury compound added to induce amalgamation of the zinc surface. The performance tests were intended to gain preliminary knowledge about the relative capability and limitations of the lead oxide–zinc system; a comprehensive study of long-term behaviour was beyond the scope of this project.

2. Apparatus and procedure

The cell assembly consisted of a 10 cm × 4.7 cm × 15 cm (inside dimensions) rectangular plexiglass container with three Pb and three Zn electrode plates placed into 2 mm wide slots at the cell bottom. Each electrode had dimensions of 10.2 cm × 10.3 cm and had a central protrusion (1.3 cm wide) used for soldering copper wires to it. The active face area per electrode was 101.69 cm^2, yielding an overall active electrode surface of 1220 cm^2. The electrode separation distance was 5 mm. The cell contained 450 cm^3 of electrolyte solution with an effective height of about 11.3 cm. The external current path was established by connecting the soldered copper wires to resistance loads in discharge experiments, and to a d.c. power source in charge experiments. Current and voltage drop across the cell were measured by conventional digital voltmeter devices.

Lead oxide electrodes were prepared by anodic

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oxidation of clean lead plates in a zinc sulphate solution under carefully controlled conditions. The open cell potential between the smooth uniform PbO_2 layer and the electrolyte solution in the charged battery was measured to be − 1.203 V against a 1.0 mol dm^{-3} KCl − calomel electrode. The zinc electrodes were made of commercially available Zn plates after degreasing and cleaning; their potential in the electrolyte solution of the charged battery was found to be 1.102 V using the same reference electrode (this value corresponds to 0.821 V on the conventional H_2-scale and is very close to the standard potential of the Zn/Zn^{++} reaction: 0.763 V).

A second, reference battery was also employed for the purpose of comparison. Using the same container, but replacing the Zn plates with Pb plates, and the electrolyte solution by a 35 wt % (sp. gr. ≃ 1.26) sulphuric acid solution; this system is a small facsimile of a Type N50 JASO car battery [5]. The uniform PbO_2 anode layer was obtained by closely controlled electrolysis. The anode and cathode plates were connected together in a parallel manner to achieve the highest possible current flow in the given system.

The experiments consisted of two major types: medium-drain and high-drain tests, depending on the overall circuit resistance and the discharge time period. During the charge period a constant d.c. voltage drop of 2.7 V was imposed on the batteries and electrolysis was carried out at least until stabilization of the current, observed about 1 h after the outset of charging. The stabilized current was about 320–340 mA in the lead–acid system and 200–210 mA in the PbO_2/Zn system with the saturated $Na_2SO_4/ZnSO_4$ electrolyte. Charging was extended to 3 h in selected experiments.

The PbO_2/Zn system was investigated using three different electrolytes: (A) a mixture of saturated Na_2SO_4 and $ZnSO_4$; (B) saturated $ZnSO_4$ and (C) saturated Na_2SO_4 in a 1 g dm^{-3} H_2SO_4 solution; the small amount of acid was added to avoid the formation of $Zn(OH)_2$ as a gelatinous colloid. Crystal formation was eliminated by preparing the solution at about 15° C, then applying 5–10 charging–discharging cycles. During this preparation process the temperature rises to 24° C and the pH decreases from 4.64 to 2.36. Because of its relatively better performance, the first system (denoted henceforth as the PbO_2/Zn–(A) system) was given major attention: its open cell electromotive force is 2.305 V.

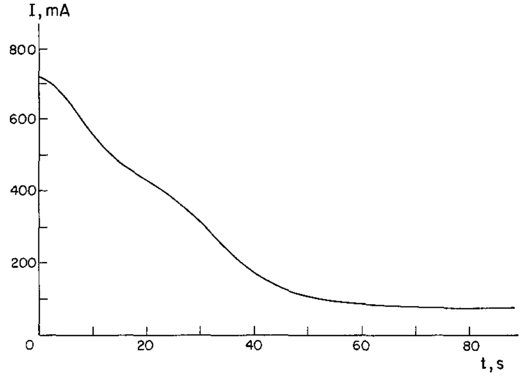

Fig. 1. High-drain discharge curve obtained in the PbO_2/Zn–(A) system.

3. Experimental results and discussion

The discharge behaviour across a relatively low resistance was studied by means of a 7.5 cm long BWG #18 Chromel-A (80–20 Nickel–Chromium) resistance wire whose fractional increase in resistivity is about 6.85% at 850–900 K, which corresponds to the red-glow state of the resistor during the early stage of discharge. Hence, the resistance changes from 0.107 ohm (red-glow) to about 0.1 ohm (room temperature) during the discharge process shown in Figs. 1 and 2. In the PbO_2/Zn system the current drops rather gradually and reaches a relatively constant low level of about

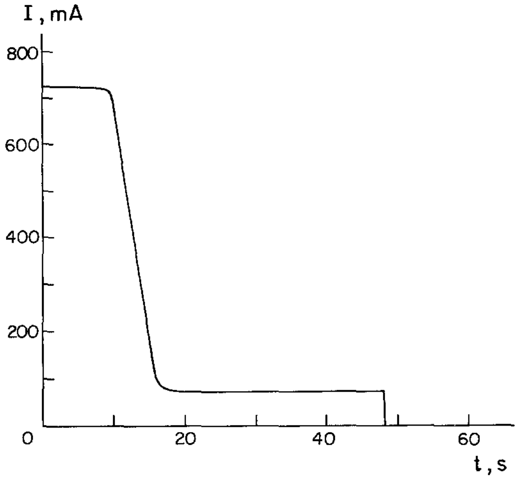

Fig. 2. High-drain discharge curve obtained in the lead–acid system.

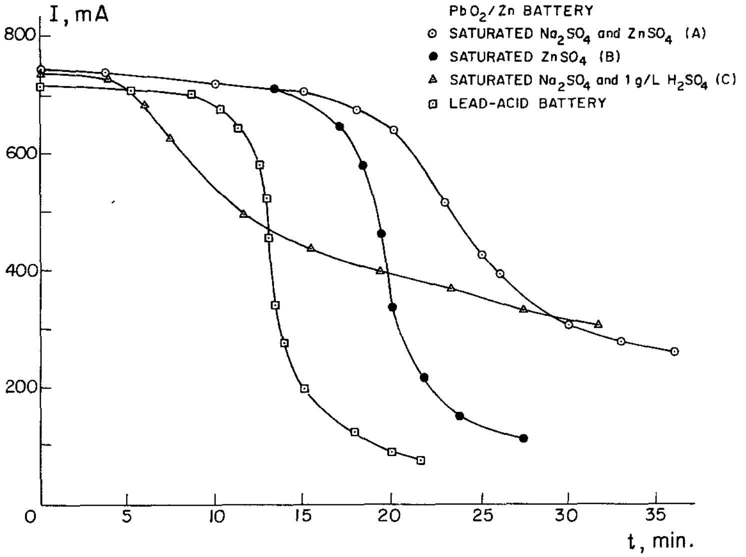

Fig. 3. Variations of current with time during medium-drain discharge.

92 mA after about 1 min of discharge. The lead–acid battery maintains the original high current (about 720 mA) for about 12 s, but the current drops very quickly to about 90 mA and then essentially to zero at about 48 s. Similar observations pertain to the accompanying voltage drop across the batteries; the PbO_2/Zn system reaches a steady value of 0.7 V after about 1 min, whereas the lead–acid system has a CVD of 0.33 V after 40 s of discharge, falling gradually to a relatively stable 60 mV at about 80 s. Taking an 80 s period of discharge, the PbO_2/Zn cell delivers 22.24 C electricity and 22.74 J electrical energy, whereas the lead–acid system delivers 12.30 C and 14.48 J.

Discharge characteristics observed in the instance of medium resistance loading are shown in Figs. 3 and 4. In this configuration the initial total resistance (load and internal), 2.4 Ω, increases to about 7 Ω after 20 min of discharge. The PbO_2/Zn system with electrolyte A and B retains the essentially initial current up to about 15 min and the subsequent decrease is gradual, although more pronounced in the case of electrolyte B. Electrolyte C causes a more monotonic decrease in current, whereas the lead–acid battery undergoes a severe current drop at about 12 min of discharge time. Taking 20 min as reference, the PbO_2/Zn–(A) system delivers 862.70 C electricity and about 1.13 kJ d.c. energy whereas the lead–acid system delivers 592.6 C and 0.925 kJ during the same period.

A clear-cut interpretation of the discharge

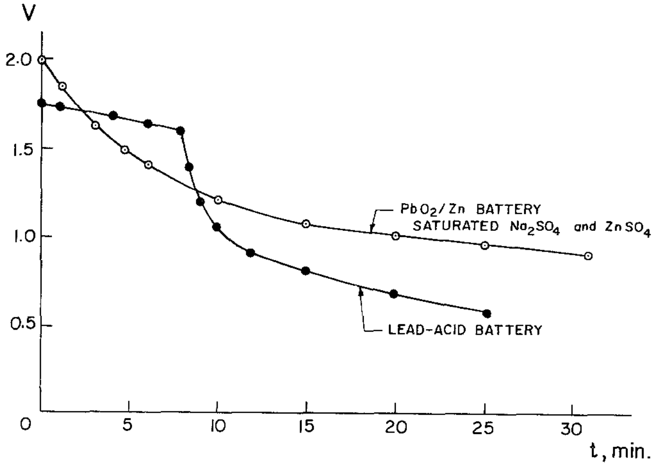

Fig. 4. Variations of voltage drop with time during medium-drain discharge.

*Table 1. Numerical value of the empirical constants in the equation of diffusional rate control**

K	*n*	*Remarks*	*References*
0.42 (neg. plate) 0.35 (pos. plate)	1.39	$-22 - 50^\circ$ C 6.81 mol dm^{-3} H_2SO_4 0.014 – 550 mA cm^{-2}	[12]
0.014	1.40	6.0 mol dm^3 H_2SO_4 50° C	[13]
6.8×10^{-3}	1.42	4.37 mol dm^{-3} H_2SO_4 25° C	[13]
2.3×10^{-3}	1.41	10.20 mol dm^{-3} H_2SO_4 25° C	[13]
0.17	0.87	$i < 30$ mA cm^{-2}	[14]
0.04	1.62	$i > 30$ mA cm^{-2}	
0.37	0.95	–	[15]
–	1.30	–	[11]
9.44	0.31	Lead–acid system medium-resistance discharge; $S_t = 0.03$	This work
0.165	0.24	Low-resistance discharge; $S_t = 0.02$	This work
13.37	0.73	PbO_2/Zn–A system; medium-resistance discharge; $S_t = 0.03$	This work
0.111	1.00	Low-resistance discharge; $S_t = 0.07$	This work

* t: min; I: amp; S_t: standard error of estimate, i.e. the root mean square of the log (t)-deviations about the linearized form of Equation 1 (no statistical information available in the quoted literature).

characteristics in terms of reaction mechanisms is not possible at the present time, but instructive comparisons with previous studies may nevertheless be made. At the onset of discharge of a lead–acid cell, the voltage drop is due primarily to charge transfer resistance in the double layer [6] and the main rate-limiting step is the formation of microdendritic lead sulphate crystals [7]. Lead oxide may react with sulphate ions or sulphuric acid in various reaction steps [8]; at low-current densities (< 1 mA cm^{-2}) PbO_2 covered lead tends to dissolve anodically at about 1.6 V/RHE and an increase in the number of active sites is believed to be responsible for electrode activity [9]. At high current densities the distribution of lead sulphate across the electrode plates becomes nonuniform and conversion to sulphate is stronger at or near the surface. This transition to unevenness occurs around 30 mA cm^{-2} on the negative plate, but on the positive plate it may occur at as low a current density as 6 mA cm^{-2} [10]. In view of the magnitude of the experimental current densities (about 1–7 mA cm^{-2}), no simple explanation via the mechanisms discussed in the literature may be offered for the relatively high activity during the initial discharge period, although the major reason may well be the fast kinetics of the various parallel $Pb \rightarrow PbSO_4$ paths. On the other hand, the decrease in current flow with time after the initially active period can be correlated with high statistical accuracy by the relationship

$$t = \frac{K}{I^n} \tag{1}$$

where K and n are empirical constants. Equation 1 represents [11–13] diffusional rate control due to transport of sulphate ions from the bulk towards the electrode surface. As shown in Table 1, the numerical value of K varies considerably, whereas the numerical value of n remains within the same order of magnitude. One may conclude that the falling-current region of the discharge curves is governed in all likelihood by the rate of diffusive transport of the sulphate ions in both battery systems.

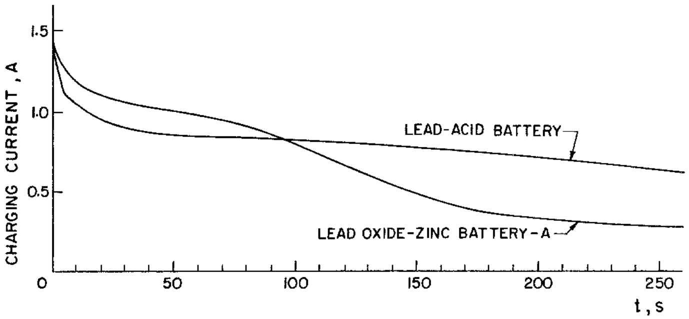

Fig. 5. Variation of charging current with time.

The degree of reversibility of the battery systems was studied in a series of repetitive charge–discharge experiments. Using the 0.1 Ω Chromel A load resistance, the batteries were discharged for a 20 s period and then charged-up for about 710 s. Typical charging curves, obtained at a constant d.c. voltage drop of 2.7 V, are shown in Fig. 5. The charging current for the lead–acid battery continues to drop slowly after 250 s; at 300 s its value is 0.55 A, at 400 s it is 0.44 A, at 500 s it is 0.4 A, at 700 s it is 0.37 A. The PbO_2/Zn system, on the other hand reaches 0.26 A at 300 s, and at 700 s its value is 0.23 A. Thus, over a 710 s period the lead–acid battery acquires an electric charge of 294.3 C and a nominal d.c. energy content of 1.04 kJ, whereas the PbO_2/Zn battery acquires 281.8 C and a nominal d.c. energy content of 742 J. Consequently, during the 20 s discharge period the PbO_2/Zn battery renders about 3%, whereas the lead–acid battery renders only 1.5% of its acquired charge. If the 80 s discharge period is considered, the appropriate figures are 7.9% and 3.1%, respectively, and the ratio of d.c. energy output to the d.c. energy input is 3.1% and 1.4%, respectively.

The behaviour of batteries over an extended charging period was studied by charging at an imposed voltage drop of 2.7 V, for up to 3 h. Under such circumstances the PbO_2/Zn system acquires 1.33 kC charge and a 3.6 kJ nominal energy content in contrast with the 1.90 kC charge acquisition and 5.1 kJ nominal energy content of the lead–acid battery.

The variation of open-cell voltage with time of the charged batteries also offers an instructive comparison. While the lead–acid system has an initial open-cell voltage of 2.23 V, the PbO_2/Zn-(A) battery has 2.57 V; the lead–acid cell drops its open-cell voltage to 2 V after about 1.5 h and this value remains unchanged over at least a 12 h period (length of test). The lead oxide–zinc cell drops its open-cell voltage to about 2.3 V after 1 h,

Table 2. Comparison of certain characteristics of the lead–acid and PbO_2/Zn–(A) battery system

	Lead–acid cell	*PbO_2/Zn–(A) cell*
Electrolyte mass (kg)	0.567	0.540
Cumulative mass of electrodes (kg)	1.430	1.215
Mass of plexiglass container (kg)	0.293	0.293
Total mass of battery (kg)	2.290	2.048
Relative mass of battery	1.000	0.907
Energy density (mWh kg^{-1}) associated with		
–charging for 3 h	548	423
–charging for 710 s	110.8	87.2
–medium drain discharge; 20 min	98.6	132.5
–high drain discharge; 80 s	1.543	2.670
Initial open-cell voltage (V)	2.23	2.57
Open-cell voltage 2 h after charging (V)	2.00	2.20
Open-cell voltage 12 h after charging (V)	2.00	2.00

to 2.2 V after 2 h, then the value drops in a linear fashion to 2.1 V after 6 h and finally to 2.0 V in 12 h. The initial rate of voltage drop was found to be 0.28 V h^{-1} for the lead–acid cell and 0.57 V h^{-1} for the PbO_2/Zn–(A) cell. It appears that self-discharge processes, involving various chemical reactions between PbO_2 and the electrolyte, have faster kinetic characteristics in the latter cell than in the former [5].

A comparison of energy densities leads to further interesting results. Although the PbO_2/Zn–(A) system is about 10% lighter (see Table 2), the energy density is essentially a function of the direction of current flow: the lead–acid battery absorbs roughly 30% more energy per unit mass, whereas in discharge the lead oxide–zinc system delivers 34–73% more energy per unit mass (at least under the experimental conditions of this study).

The experimental results show certain advantages of the lead dioxide–zinc cell; it is lighter than the lead–acid cell, its current flow and voltage drop decreases more gradually during discharge, it has a higher open-cell voltage and, although its stored electric density is lower than that of the lead–acid cell, its specific energy delivery during discharge is higher. On the other hand, the figures in Table 2, which are within the same order of magnitude, do not indicate clear-cut superiority in either sense. The PbO_2/Zn–(A) system does compare favourably with the lead–acid system in the performance tests performed and it may eventually offer a viable alternative as a battery, at least in certain applications. Much more study will be required before optimal design can be effected.

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