

Studies on a lead–acid cell with electrodeposited lead and lead dioxide electrodes on carbon

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Abstract

Performance characteristics of a lead–acid cell with electrodeposited lead and lead dioxide electrodes on carbon are evaluated in aqueous sulfuric acid at concentrations ranging from 1 to 4 M. The discharge capacity is practically independent of the discharge rate within the current range studied (~ 1 to 15 mA cm^{-2}). The capacity increases with cycling, possibly due to slow attainment of a ‘spongy’ character for the negative electrode active mass. The capacity also increases with the amount of deposition, reaching a more or less limiting value beyond an optimum deposition. Steady-state discharge behavior, represented by a voltage plateau, shows a nearly Nernstian response, which indicates that the basic electron-transfer processes are quite fast. Experiments involving less than full charge–discharge cycles showed the charging efficiency to pass through a maximum with charging current. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

In an earlier communication [1] we explained the rationale behind the idea of developing a lead–acid cell with thin layers of active materials deposited on lightweight, electronically conducting substrates. Such an electrode configuration is expected to reduce the ‘dead weight’ of the lead–acid system and, thereby, to increase the effective specific energy. Moreover, if the thickness and morphology of the layers can be carefully controlled, then the most efficient utilization of the active materials can be achieved. This is due to the fact that insulating layers of PbSO_4 are formed at both the electrodes of a lead–acid cell on discharge that limits the penetration depth of the electrode reactions inside the active mass. As controlled deposition can be conveniently obtained via an electrochemical route, this technique has been used in the present study to prepare the thin-layer electrodes.

Another advantage of using thin layers of Pb and PbO_2 on suitable substrates is concerned with the polluting nature of lead and its compounds. Safe disposal of exhausted lead–acid batteries and recycling of the lead content are gradually creating more problems, both socially

and legally, with increasing environmental consciousness. Batteries with the electrode configuration proposed here have much lower lead content than conventional ones with either lead grids or spines, and thus render the former environmentally more acceptable. Here lies a major importance of the present work.

Czerwinski and Zelazowska [2,3] have recently reported that the electrochemical behaviour of Pb and PbO_2 electrodeposited on reticulated vitreous carbon is similar to that of Pb and PbO_2 generated on pure metallic lead. A number of conductive materials, including carbon, have also been suggested [4] as substitutes for the lead current-collectors in lead–acid cells. Accordingly, the performance of lead–acid cells with Pb and PbO_2 electrodeposited on carbon electrodes has been studied in the present work in different H_2SO_4 concentrations from the point of view of both total cell and individual electrode performance.

2. Experimental

Lead was electrodeposited galvanostatically from a fluoborate bath [5] on cylindrical carbon rods obtained from flashlight dry cells. Only the flat surface at one end with an area of 0.125 cm^2 was kept exposed by covering

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the remaining surfaces with Teflon tape. The efficiency of deposition was estimated by determining gravimetrically the amount of lead deposited. The PbO_2 electrodes were formed from the Pb electrodes during initial charging of the cell. It was found that a primary anodization in 0.05 M H_2SO_4 at 0.1 mA for 30 min was necessary for efficient initial charging in higher acid concentrations. The H_2SO_4 concentration was varied from 1 to 4 M.

The cells constructed for experimentation were of flooded-electrolyte type and did not use separators. For the study of individual electrode behaviour, a saturated calomel reference electrode was used. The charge–discharge behavior of prototype cells was studied with the help of a constant-current source (DB-300, DB Electronics Corporation, India), a digital multimeter (DM 6104B, Electronics, India), and an X-t recorder (Omnigraphic 2000, Houston Instruments, USA). All experiments were performed at room temperature.

3. Results and discussion

The amount of lead deposited during preparation of the electrodes is proportional to the deposition time, as expected, at a deposition current of 30 mA (see Fig. 1). The slope of the plot is less than the theoretical value, however, and shows that the deposition efficiency is around 80%. In subsequent experiments, a deposition current of 15 mA was used for preparation of the electrodes.

Discharge of a cell consisting of the electrodeposited electrodes in aqueous H_2SO_4 showed the usual voltage plateau behavior. The discharge time, corresponding to the rapid fall of cell voltage, was more conveniently determined by noting the time at which the cell voltage attained a cut-off value of 1.8 V. Discharge times were found to be practically inversely proportional to the discharge currents, as indicated by the slopes of the corresponding logarithmic plots (Table 1). The discharge capacities were, therefore, independent of the discharge currents within the range studied.

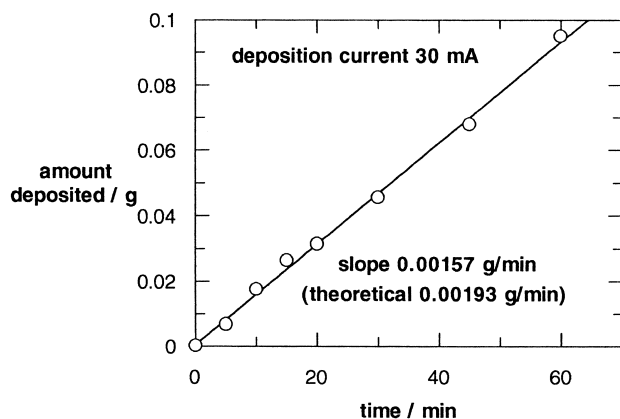


Fig. 1. Variation of amount of lead deposited with deposition time.

Table 1

Slopes of logarithmic plots of discharge time vs. discharge current for different amounts of deposition at different cycles

Deposition mode	Cycle 5	Cycle 10	Cycle 15	Cycle 20	Cycle 25
5 min × 15 mA	-0.97	-0.96	-0.95	-0.95	
10 min × 15 mA	-1.17	-1.12	-1.12	-1.14	-1.13
20 min × 15 mA	-1.18	-1.09	-1.11	-1.09	
30 min × 15 mA	-1.12	-1.07	-1.04	-1.04	
40 min × 15 mA	-1.10	-1.00	-1.03	-1.02	-1.08
60 min × 15 mA	-1.07	-1.08	-1.06	-1.06	-1.06

Discharge capacities, however, increased significantly with number of successive cycles, as shown in Fig. 2. The capacities obtained at a discharge current of 1 mA are presented in this figure. The increase in capacity with cycling is due to the increase in the effective surface area of the deposited Pb and PbO_2 layers, which is a common feature of lead–acid cells with all types of electrodes, at least during the initial cycles. The capacity (Q) can be fitted to an empirical relationship with the number of cycles (N) given by

$$Q = AN / (1 + BN) \quad (1)$$

Plots of Q^{-1} vs. N^{-1} were found to be reasonably good straight lines, from which A and B were calculated (Table 2) for cells with electrodes having different amounts of deposition. At sufficiently high cycle numbers, Eq. (1) predicts a limiting value of capacity (Q_α) given by the quantity A/B . These limiting capacities (Fig. 3) and the capacities at different cycles (Fig. 2) were found to increase with the amount of deposition, quite steeply at first and then gradually, leading to practically constant values beyond a deposition for 30–40 min at 15 mA. This amount of deposition thus appeared to be the optimum required in preparing electrodeposited electrodes. The extent of discharge of a lead–acid cell is determined by complete passivation of both the electrodes by PbSO_4 layers. There-

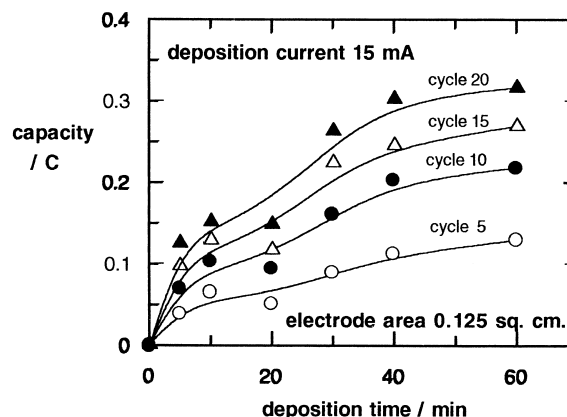


Fig. 2. Variation of capacity at 1 mA discharge current with deposition time used for preparing electrodes, at different cycles.

Table 2

Fitting parameters for the equation $Q = AN/(1 + BN)$

Deposition mode	A	B	Q_{α} / C
5 min × 15 mA	0.0085	0.0214	0.400
10 min × 15 mA	0.0172	0.0621	0.278
20 min × 15 mA	0.0116	0.0291	0.400
30 min × 15 mA	0.0200	0.0260	0.769
40 min × 15 mA	0.0270	0.0392	0.690
60 min × 15 mA	0.0328	0.0541	0.606

fore, for electrodeposited electrodes, the optimum deposition should correspond to such a thickness of the deposited active material layer that matched the penetration depth of the electrode reaction until complete passivation occurred.

The effect of H_2SO_4 concentration on the discharge behaviour of the cell was studied within the range 1 to 4 M H_2SO_4 . The cycling characteristics of the positive $PbO_2/PbSO_4$ electrode are poor in 4 M H_2SO_4 as the electrical contact between the carbon substrate and the active mass failed repeatedly after a few cycles. At lower acid concentrations, however, there is no such problem regarding loss of adhesion of the active mass with the substrate on cycling. As expected, the plateau voltage during discharge was found to be dependent on the acid concentration. Fig. 4 shows the variation of plateau voltage obtained at 0.5 mA discharge with $\log (H_2SO_4 \text{ activity}/H_2O \text{ activity})$ to examine the applicability of the Nernst equation under steady-state discharge represented by the plateau region. The activities were obtained from the literature [6–8]. Although linear behaviour is observed, the slope of the straight line is lower than the Nernstian slope. On the other hand, if these plateau voltages are measured at different discharge currents and plotted, as in Fig. 5, for different acid concentrations, straight lines are obtained. Such observations suggest that the slopes of these lines give the internal resistance of the cell with different H_2SO_4 concentrations. The internal resistance is found to be lower in 2.5 M H_2SO_4 than in either 1 or 4 M

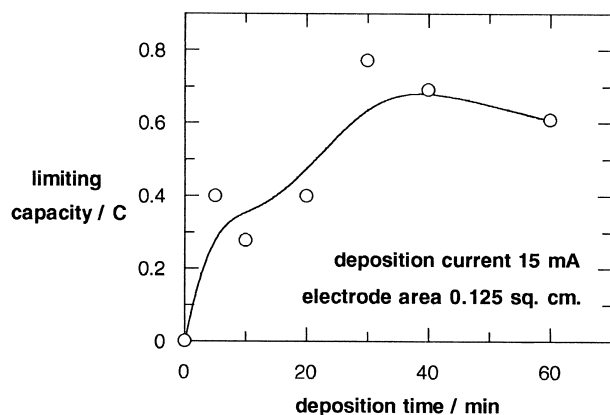


Fig. 3. Variation of limiting capacity (Q_{α} ; see text) at 1 mA discharge current with deposition time used for preparing electrodes.

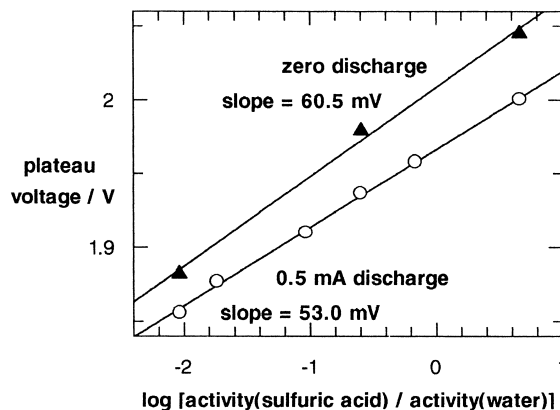


Fig. 4. Test of applicability of Nernst equation during steady-state discharge.

H_2SO_4 . The compactness, and hence the resistance, of the insulating $PbSO_4$ layer formed at both the electrodes during discharge is expected to increase with H_2SO_4 concentration, while the resistance of the electrolyte decreases. The observed minimum internal resistance in 2.5 M H_2SO_4 thus appears to be due to a combined effect of these two opposing tendencies. It is interesting to note that if these lines are extrapolated to zero discharge current and the plateau voltages obtained as intercepts are plotted against $\log (H_2SO_4 \text{ activity}/H_2O \text{ activity})$ as before, Nernstian behavior is obtained with a correct slope (Fig. 4). In fact, zero discharge current can be considered to be equivalent to an equilibrium situation.

In addition to the total cell, the behaviour of the individual electrodes on discharge were also studied in different H_2SO_4 concentrations. Plots of plateau potential vs. \log discharge current were found to be linear (Fig. 6) showing Tafel-like behavior. The slopes of these lines were found to have more or less the same value in different H_2SO_4 concentrations for both the electrodes. This observation possibly indicates that the overpotential generated during the discharge of both the electrodes is

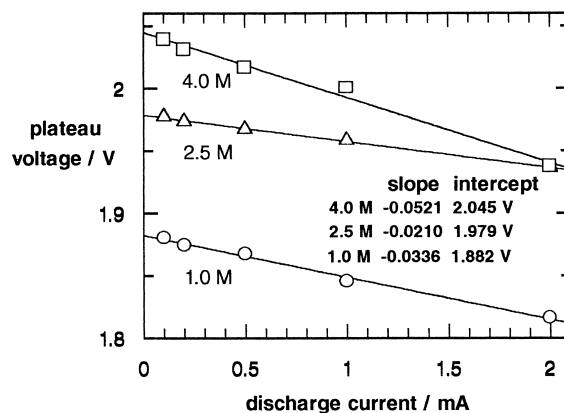


Fig. 5. Variation of discharge plateau voltage with discharge current at different H_2SO_4 concentrations.

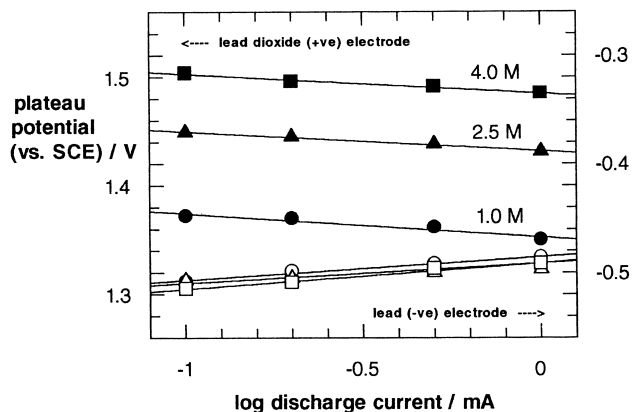


Fig. 6. Variation of discharge plateau potential with log discharge current for $\text{PbO}_2/\text{PbSO}_4$ and Pb/PbSO_4 electrodes at different H_2SO_4 concentrations.

due mainly to the growth of the passivating PbSO_4 layer, and not to the electron-transfer processes as such, within the current range studied. It was earlier [9–11] postulated that the PbSO_4 formed on discharge acts like a perm-selective membrane, which restricts the movement of SO_4^{2-} ions through it, so that this layer can grow only by outward diffusion of electrogenerated Pb^{2+} ions through it. As the plateau region represents steady-state discharge, the rate of diffusion of Pb^{2+} ions through the PbSO_4 membrane under this condition should match the rate of generation of these ions, i.e., the discharge current. Therefore, the concentration of Pb^{2+} ions under the membrane should be a function of the discharge current. This concentration determines the plateau potential according to the Nernst equation as the electron transfer is considered to be sufficiently fast. For a two-electron process, the Nernstian slope is around 30 mV. In the present case, the observed slope of around 20 mV for the linear plots of plateau potential vs. log discharge current thus indicates that the concentration of Pb^{2+} ion accumulated under the PbSO_4 layer is proportional to $[\text{discharge current}]^{2/3}$ during steady-state discharge.

The abovementioned perm-selectivity of the PbSO_4 layer is clearly demonstrated by another feature of Fig. 6. That the same line was obtained for the discharge of Pb/PbSO_4 electrode in different concentrations of H_2SO_4

Table 3
Discharge capacities (C) of electrodes in different H_2SO_4 concentrations with different discharge currents

Electrode	H_2SO_4 concentration (M)	Discharge current (mA)	
		0.5	0.2
Pb/PbSO_4	1.0	0.238	0.251
	2.5	0.053	0.084
	4.0	0.041	0.060
$\text{PbO}_2/\text{PbSO}_4$	1.0	0.572	0.613
	2.5	0.196	0.162
	4.0	0.072	0.057

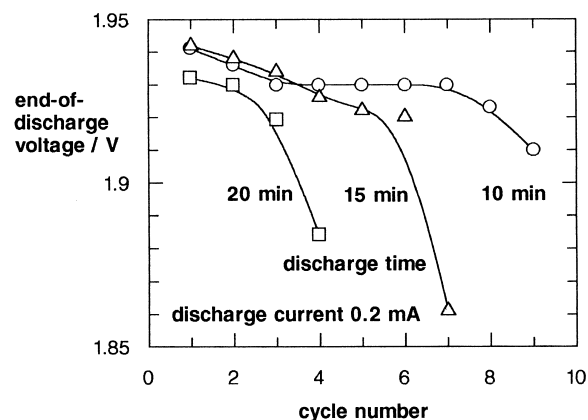


Fig. 7. Variation of end-of-discharge voltage with cycle number at different depths-of-discharge, followed by twice the charge input at 2 mA, for a cell capable of ~ 30 min discharge at 0.2 mA.

shows that the SO_4^{2-} concentration in the electrolyte does not determine the plateau potential. On the other hand, these potentials for the $\text{PbO}_2/\text{PbSO}_4$ electrode are found to be heavily dependent on the acid concentration, as this electrode reaction requires participation of H^+ ions whose movement is not restricted by the membrane.

The discharge capacities of the positive and the negative electrodes differ significantly. This can be seen from the data in Table 3, which show that the capacity obtained from the $\text{PbO}_2/\text{PbSO}_4$ electrode is greater than that from the Pb/PbSO_4 electrode. This is quite surprising in view of the fact that the capacity of the lead–acid battery is usually limited by the positive electrode. This may be either a strong point of the electrodeposited positive electrode or a consequence of the slow attainment of the ‘spongy’ character of the negative active mass, which is reflected by the gradual increase in the total cell capacity with cycling, as reported earlier. For both the electrodes, however, the capacity increases appreciably with dilution of the electrolyte, particularly at 1 M H_2SO_4 . This must be

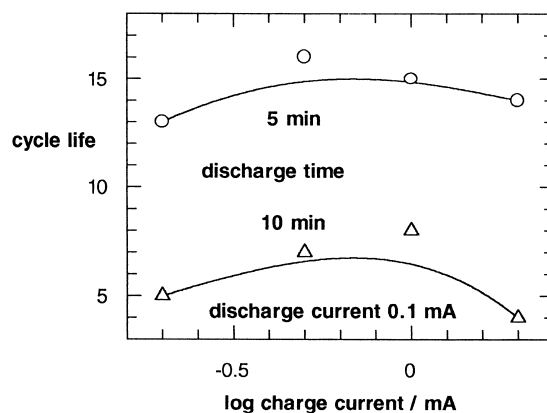


Fig. 8. Dependence of cycle-life on charge current at different depths-of-discharge, followed by twice the charge input, for a cell capable of ~ 30 min discharge at 0.1 mA.

due to the expected increased porosity of the PbSO_4 layer with decreasing acid concentration, which enables the layer to grow to a greater extent before complete passivation occurs. A marginal increase in capacity is also observed on decreasing the discharge current from 0.5 to 0.2 mA, particularly in case of the Pb/PbSO₄ electrode.

So far, the discussion has been based on the results obtained from experiments which involve complete discharge followed by full recharge at 1 mA for 20 to 30 min. For less than 100% depth-of-discharge, the input charge must be at least 4–5 times that of the charge removed to keep the cycling behaviour almost unchanged. At lower factors of charge replenishment, the cycle-life rapidly decreases. It is more convenient, however to study the effect of charge current on the efficiency of charging under this condition. Fig. 7 shows the variation of the end-of-discharge voltages at different depths-of-discharge with cycle number when charge inputs amounting to twice the charge removed are given during recharge at 2 mA. Expectedly, the cycle-life decreases with greater depths of discharge. When these experiments are repeated for different charge currents, the cycle-life passes through a maximum, as shown in Fig. 8. This indicates that the charge current

corresponding to the maximum is the most efficient. Though the optimum charge current thus obtained should be relevant only to the particular mode of charge–discharge cycle followed, it can be concluded that lower rates of charging might not always be beneficial from the point of view of charging efficiency for a lead–acid cell with electrodeposited electrodes.

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