

Short Communication

# Discharge behaviour of electro-deposited lead and lead dioxide electrodes on carbon in aqueous sulfuric acid

Kaushik Das, Aparesh Mondal

*Department of Chemistry, Jadavpur University, Calcutta-700032, India*

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## Abstract

Lead and lead dioxide electrodes on carbon are prepared by electro-deposition and subsequent electro-oxidation. Their behaviour as lead/acid battery electrodes is studied. It is found that while the oxidation of lead to lead sulfate is diffusion controlled, the reduction of lead dioxide to lead sulfate is a surface process. The efficiencies of both the reactions vary with sulfuric acid concentration, and each passes through a maximum. Unlike the lead dioxide electrode, the discharge capacity of the lead electrode is found to depend heavily on the discharge rate. The current–voltage characteristics of a prototype cell that consists of two electro-deposited electrodes improve with an increase in the acid concentration.

*Keywords:* Electrodes; Lead; Lead dioxide; Carbon; Discharge; Lead/acid batteries

## 1. Introduction

The lead/acid battery still remains one of the most versatile and reliable secondary power sources, even after 130 years since its discovery. Though the technology has been upgraded continuously over the years, two inherent weaknesses of the system are difficult to overcome completely. One of these has been recognized relatively recently, that is the polluting nature of lead and its compounds, for which only protective measures can be taken both at the manufacturer's and at the user's ends. The other is the low energy density (by weight) of the active materials lead and lead dioxide and, consequently, of the whole system.

The low energy density of a practical lead/acid battery mainly results from two factors that can be tackled technologically. These are: (i) the use of lead as both the grid material and the internal connectors, and (ii) the poor utilization of the active materials. The availability of new, light-weight, electronically conducting materials based on carbon and other polymers may be helpful with respect to the first factor. The requirement of mechanical and chemical stability makes the carbon-based conductors to be first-choice materials. Second, as the operation of a lead/acid battery results in the formation of insulating lead sulfate layers on both the

electrodes, the electrode reactions cannot penetrate very deep inside the active material. A thin layer of active material would, therefore, be sufficient. This layer can be deposited electrochemically, and is expected to yield an improved efficiency of utilization. Moreover, the electro-deposition route would enable the direct use of Pb(II) salts, rather than a conversion first to Pb(O) and then a reoxidation to Pb(II), as is usual in present-day, pasted-plate technology. The development of light-weight electrodes with high efficiency will undoubtedly sharpen the competitive edge of the lead/acid system, particularly with respect to its possible use in the electric vehicles of the future.

In this paper, a study is reported of the discharge of lead and lead dioxide electrodes deposited on carbon in different concentrations of aqueous sulfuric acid. The lead electrode was electro-deposited directly on to the substrate and the lead dioxide electrode was prepared by electro-oxidation of the former. The two electrodes were studied separately, as well as in combination, i.e., in the form of an actual cell.

## 2. Experimental

Lead was electro-deposited galvanostatically on a cylindrical carbon rod with an exposed surface area of

0.2 cm<sup>2</sup> from a solution of 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub> and 1 M NaNO<sub>3</sub>. The deposition efficiency was determined by re-dissolving the deposit electro-chemically in a known volume of 0.1 M HNO<sub>3</sub> solution and measuring the cathodic current peak on a platinum electrode by linear potential sweep voltammetry. For this purpose, a calibration curve was earlier prepared from a series of Pb(NO<sub>3</sub>)<sub>2</sub> solutions of known concentration in 0.1 M HNO<sub>3</sub> using the same technique.

The equipment used in the present work was as follows. For potentiodynamic studies on lead and lead dioxide electrodes a potentiostat/galvanostat (Model 173), a universal programmer (Model 175) and a digital coulometer (Model 179), all from Princeton Applied Research, USA, were used. The discharge behaviour of a prototype cell was studied with the help of a constant-current source (DB-300, DB Electronics, India) and a digital multimeter (DM 6104B, Electronics Corporation, India). All the experiments were carried out at room temperature.

### 3. Results and discussion

Fig. 1 shows that the efficiency of cathodic electro-deposition of lead from a Pb(NO<sub>3</sub>)<sub>2</sub> solution on a carbon electrode decreases with increasing deposition current. Therefore, it seems that the contribution of a competing cathodic process, in this case clearly hydrogen evolution, becomes greater at higher deposition currents. The limiting efficiency has been found to be around 80%, as obtained by extrapolating to very low currents. Efficiency also decreases with the time of deposition at

a fixed deposition current (Fig. 1), which is difficult to rationalize simply on the basis of the existence of a competing cathodic process. Such loss in efficiency may be ascribed to the poorly adherent nature of the deposit, particularly at long times of deposition (as noted visually). This is possibly due to the accompanying gas evolution.

The negative and the positive electrode discharge processes of a lead/acid battery have been studied on the electro-deposited lead electrode in different concentrations of aqueous sulfuric acid by linear potential sweep voltammetry. The experiments involving the anodic process, i.e., Pb → PbSO<sub>4</sub>, can be performed directly on the deposited electrode, while those pertaining to the cathodic process i.e., PbO<sub>2</sub> → PbSO<sub>4</sub>, are conducted after holding it at a sufficiently positive potential (1.8 V versus saturated calomel electrode) for 15 to 20 min to convert the deposited lead into lead dioxide completely. For both the processes, current peaks are obtained and the results are given in Table 1.

The anodic peak currents ( $i_p^a$ ) are found to vary linearly with the square root of the potential scan rate ( $\nu$ ). This is similar to the observations noted earlier [1–3] with pure lead electrode and indicates diffusion control. The latter is thought to be due to the diffusion of the Pb<sup>2+</sup> ions through the initially formed lead sulfate layer which acts as a semi-permeable membrane. The slopes of the  $i_p^a$  versus  $\nu^{1/2}$  lines can, therefore, be related to the diffusion coefficient of Pb<sup>2+</sup> through this membrane which, in turn, depends on its porosity. These slopes are found to vary with acid concentration and pass through a maximum at around 3 M H<sub>2</sub>SO<sub>4</sub> (Fig. 2), similar to that observed earlier for pure lead

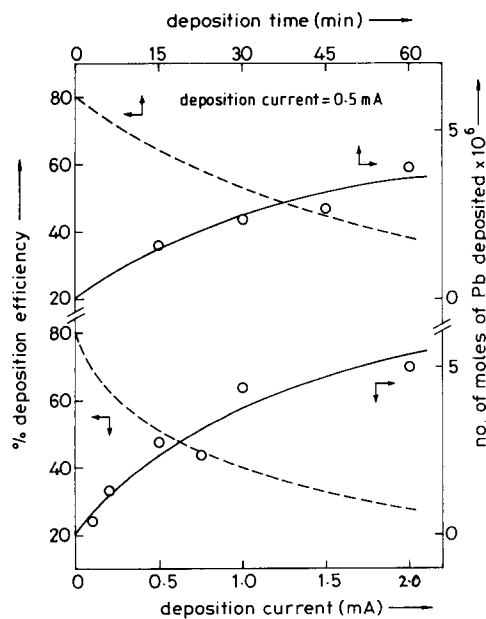


Fig. 1. (—) Variation of amount of lead deposited on a carbon substrate and (---) % deposition efficiency with deposition current and time from 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub> + 1 M NaNO<sub>3</sub> electrolyte.

Table 1

Variation of anodic ( $i_p^a$ ) and cathodic ( $i_p^c$ ) peak currents (mA) for an electro-deposited lead electrode (deposition at 1 mA for 30 min) at different potential scan rate ( $\nu$ ) and in different concentrations of aqueous sulfuric acid

H <sub>2</sub> SO <sub>4</sub> (M)		$\nu$ (V s <sup>-1</sup> )				
		0.005	0.01	0.02	0.05	0.10
0.50	$i_p^a$	6.0	9.0	13.0	20.0	
	$i_p^c$		2.5	6.25	13.0	20.0
1.00	$i_p^a$	9.0	14.0	19.5		
	$i_p^c$		6.5	14.5	27.0	
2.00	$i_p^a$	12.5	19.0	27.5		
	$i_p^c$		4.0	11.75	27.0	52.5
2.50	$i_p^a$	10.75	15.75	22.50		
	$i_p^c$		5.0	9.5	20.5	39.5
3.00	$i_p^a$	12.0	17.5	27.0	45.0	
	$i_p^c$			3.5	13.0	27.5
4.00	$i_p^a$	9.0	14.5	21.0	38.0	
	$i_p^c$			1.0	6.0	12.0
5.00	$i_p^a$	6.0	10.0	18.5	31.5	47.0
	$i_p^c$					

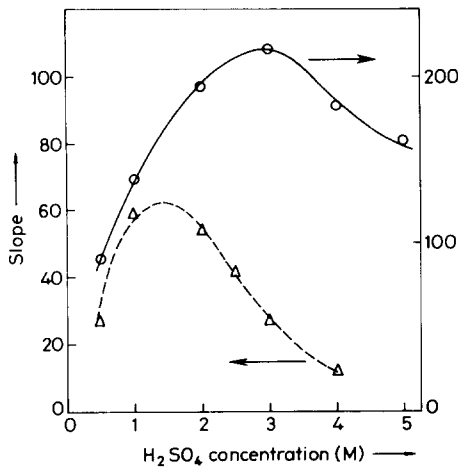


Fig. 2. (—○—) Variation of slopes of *i*<sub>p</sub><sup>c</sup> vs.  $\nu^{1/2}$  lines and (---△---) *i*<sub>p</sub><sup>a</sup> vs.  $\nu$  lines with H<sub>2</sub>SO<sub>4</sub> concentration for an electrode prepared with a deposition current of 1 mA for 30 min.

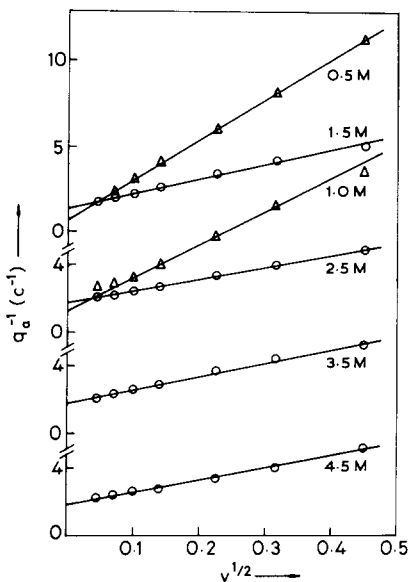


Fig. 3. Plots of *q*<sub>a</sub><sup>-1</sup> vs.  $\nu^{1/2}$  in different concentrations (M) of aqueous H<sub>2</sub>SO<sub>4</sub>.

electrode. Diffusion of the Pb<sup>2+</sup> ions through the membrane becomes slower as the lead sulfate layer is expected to be more compact, i.e., less porous, with increasing H<sub>2</sub>SO<sub>4</sub> concentration in the electrolyte. At the same time, during electro-oxidation of lead to lead sulfate, the metal side of the membrane becomes alkaline as the electrogenerated Pb<sup>2+</sup> ions tend to drive away the H<sup>+</sup> ions towards the solution side, which is confirmed by the formation of basic lead sulfates under the overlying PbSO<sub>4</sub> layer [4-6]. This effect should be more significant at lower acid concentrations, thereby making the actual diffusing species a complex of Pb<sup>2+</sup> and OH<sup>-</sup> ions which is much larger in size than Pb<sup>2+</sup> ions. Thus, the diffusion again becomes slower at low acid concentration in spite of the greater porosity of the lead sulfate layer, and hence the slope of the *i*<sub>p</sub><sup>c</sup> versus

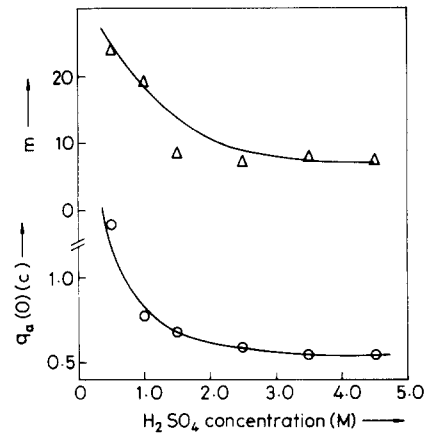


Fig. 4. Parameters of Eq. (1) in different concentrations of aqueous H<sub>2</sub>SO<sub>4</sub>: (○) *q*<sub>a</sub>(0), and (△) *m*.

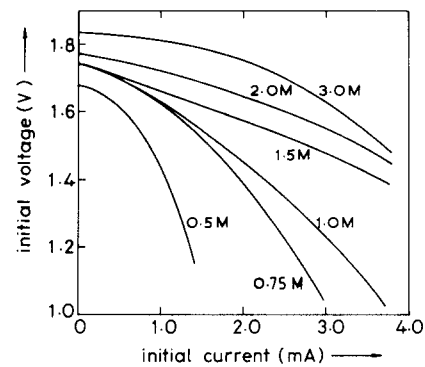


Fig. 5. Plots of initial voltage vs. initial current for cell based on two electro-deposited (deposition current 3 mA for 30 min) lead electrodes in different concentrations of aqueous H<sub>2</sub>SO<sub>4</sub>.

$\nu^{1/2}$  line decreases with decreasing acid concentration beyond a critical value. The appearance of the maximum can be rationalized in this way.

By contrast, the cathodic process shows a linear dependence of peak current (*i*<sub>p</sub><sup>c</sup>) on the first power of  $\nu$ , which indicates the involvement of a surface species [7]. Again, the slopes of the *i*<sub>p</sub><sup>c</sup> versus  $\nu$  plots pass through a maximum at around 1.5 M H<sub>2</sub>SO<sub>4</sub> (Fig. 2). This may be considered to arise out of the simultaneous existence of two opposing factors. With increase in acid concentration, the electrode surface passivates more readily due to the presence of greater amounts of the precipitating anion that effectively blocks some potentially active surface sites. At lower acid concentrations, the cathodic process can penetrate deeper inside the lead dioxide phase by opening up new surface sites while going from one layer to the next, before complete passivation. On the other hand, the cathodic process involves the participation of H<sup>+</sup> ions that are definitely less available at lower acid concentrations. Jointly, these two effects give rise to the observed maximum.

Discharge capacities of both the electrodes are measured separately using the potentiodynamic technique (Table 2). As both the positive and the negative electrode

Table 2

Anodic ( $q_a$ ) and cathodic ( $q_c$ ) discharge capacities (coulombs) of an electro-deposited electrode (deposition at 0.5 mA for 30 min) at different potential scan rates ( $\nu$ ) and in different concentrations of aqueous sulfuric acid

$\nu$ (V s <sup>-1</sup> )		H <sub>2</sub> SO <sub>4</sub> (M)					
		0.50	1.00	1.50	2.50	3.50	4.50
0.200	$q_a$	0.09	0.10	0.20	0.20	0.19	0.19
	$q_c$	0.10	0.11	0.15	0.15	0.10	0.09
0.100	$q_a$	0.12	0.13	0.24	0.24	0.22	0.24
	$q_c$	0.13	0.12	0.16	0.16	0.12	0.12
0.05	$q_a$	0.16	0.17	0.29	0.29	0.27	0.29
	$q_c$	0.15	0.13	0.16	0.17	0.15	0.15
0.02	$q_a$	0.24	0.25	0.37	0.37	0.35	0.36
	$q_c$	0.17	0.14	0.16	0.19	0.18	0.19
0.01	$q_a$	0.32	0.30	0.43	0.42	0.39	0.38
	$q_c$	0.16	0.14	0.16	0.18	0.21	0.21
0.005	$q_a$	0.42	0.34	0.49	0.45	0.42	0.42
	$q_c$	0.16	0.13	0.16	0.18	0.22	0.22
0.002	$q_a$	0.54	0.37	0.56	0.48	0.47	0.45
	$q_c$	0.12	0.12	0.16	0.18	0.23	0.22

processes of a lead/acid battery lead to passivation of the electrodes, this technique yields the maximum available capacity at a particular rate of discharge which is directly related to the potential scan rate ( $\nu$ ). The capacities corresponding to the anodic process  $\text{Pb} \rightarrow \text{PbSO}_4$  ( $q_a$ ) are found to obey the following empirical equation (Fig. 3):

$$q_a^{-1} = m\nu^{1/2} + [q_a(0)]^{-1} \quad (1)$$

where  $q_a(0)$  is the limiting value of the capacity as  $\nu$  approaches zero, i.e., at an infinitely slow rate of discharge. Fig. 4 shows the variation of  $q_a(0)$ , as well as  $m$ , with acid concentration. Though the capacity is found to be greater at lower acid concentrations (< 2 M), so also is  $m$ . This implies a strong dependence of the capacity on the rate of discharge. Therefore,

for the negative electrode, the practically useful acid concentrations are greater than about 2 M. Moreover, an inspection of the capacities (Table 2) available from the cathodic process  $\text{PbO}_2 \rightarrow \text{PbSO}_4$  ( $q_c$ ) reveals that, in general, these are smaller than the corresponding  $q_a$  values and also do not change much with either discharge rate or acid concentration. Thus, the capacity available from the total cell is found to be determined mainly by the positive electrode.

A serious shortcoming of the cell constructed from two electro-deposited lead electrodes is that it tends to self-discharge rapidly. It is possible that this difficulty can be overcome by controlling the deposition in such a way that eliminates any exposed carbon surface, which prevents local cell formation. In spite of the self-discharge, however, the fundamental current–voltage characteristics of the cell consisting of electro-deposited electrodes can be obtained by discharging it through a series of resistances and extrapolating to zero time of discharge. Fig. 5 shows plots of initial voltage versus initial current for a constant-load discharge in aqueous sulfuric acid. It is found that the voltage decreases more rapidly with current at lower acid concentrations (< 1 M). From this and the earlier results it may, therefore, be concluded that the proposed cell will be optimally useful at around 2.5 M H<sub>2</sub>SO<sub>4</sub>.

## References

- [1] K. Das and K. Bose, *Bull. Electrochem.*, 2 (1986) 387.
- [2] R.D. Armstrong and K.L. Bladen, *J. Appl. Electrochem.*, 7 (1977) 345.
- [3] J.P. Carr, N.A. Hampson and R. Taylor, *J. Electroanal. Chem.*, 33 (1971) 109.
- [4] P. Ruetschi, *J. Electrochem. Soc.*, 120 (1973) 331.
- [5] D. Pavlov and R. Papova, *Electrochim. Acta*, 15 (1970) 1483.
- [6] D. Pavlov, *Electrochim. Acta*, 13 (1968) 2051.
- [7] A.J. Bard and L.R. Faulkner, *Electrochemical Methods*, Wiley, Chichester, 1980, Ch. 12.