

## Short Communication

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### Charge–discharge behaviour of lead/mercury cell in aqueous sulphuric acid

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#### Abstract

The charging voltage of an electrochemical cell consisting of Pb/PbSO<sub>4</sub> and Hg/Hg<sub>2</sub>SO<sub>4</sub> electrodes in aqueous H<sub>2</sub>SO<sub>4</sub> increased rapidly from a low to a high plateau region. The time required for this transition to occur increases with decreasing acid concentration. This has been attributed to the complete passivation of the mercury anode by an Hg<sub>2</sub>SO<sub>4</sub> layer and the subsequent replacement of the existing process (Hg → Hg<sub>2</sub>SO<sub>4</sub>) by another one (Hg → Hg<sup>2+</sup>) under this layer. Though the discharge efficiency of anodically grown Hg<sub>2</sub>SO<sub>4</sub> is found to increase with acid concentration, the discharge capacity of the mercury electrode decreases due to its lower charge acceptance characteristics at higher acid concentration. Nevertheless, the overall discharge efficiency of the total cell is found to pass through a maximum when the acid concentration is varied. On cycling the cell at any particular current density, both the discharge efficiency and the capacity are found to increase over the first few charge–discharge cycles before assuming fairly steady values.

#### Introduction

Recently, an acidic lead/mercury battery was proposed [1] as a modification of the well-known lead/acid battery, in which an Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode replaces the Pb/PbO<sub>2</sub> electrode. The rationale behind the proposal is that, from theoretical considerations, this system should be resistant to water electrolysis during charging and should have unchanged electrolyte composition during discharging. These properties are expected to impart both maintainance-free characteristics and miniaturization possibilities. To realise these expectations in practice, a detailed study is required of the charge–discharge behaviour, as well as of the fundamental electrochemistry. The present paper aims at these objectives and is a continuation of earlier work [1, 2].

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## Experimental

The cell under study consisted of a cast-lead rod (99.99% pure) and a mercury pool electrode, each having an exposed surface area of  $\sim 2 \text{ cm}^2$ . The charge-discharge behaviour was studied using a constant-current source (DB - 300, D.B. Electronics, India) and a digital multimeter (DM 6104 B, Electronics Corporation, India). Other electrochemical experiments were carried out using a hanging mercury drop electrode (model 303 A, Princeton Applied Research (PAR), U.S.A.) of  $0.0105 \text{ cm}^2$  surface area, a potentiostat (Model 173, PAR), a universal programmer (Model 175, PAR), a digital coulometer (Model 179, PAR), and an X-Y recorder (Model 2000, Houston Instruments, U.S.A.). AnalaR grade  $\text{H}_2\text{SO}_4$  (BDH) and triple-distilled water were used to prepare the solutions. All measurements were taken at room temperature ( $30 \pm 2 \text{ }^\circ\text{C}$ ).

## Results and discussion

On charging the cell under study at 1 mA, two voltage plateau regions were obtained (Fig. 1); this is a general feature of this system [1]. The lower plateau region can be considered to represent the following overall reaction:



with a minimum voltage requirement of 0.97 V [1]. The observed rapid increase of the charging voltage after a certain time can be explained as follows. The anodic reaction is the growth of a passivating layer of  $\text{Hg}_2\text{SO}_4$  on mercury. After complete blockage of the mercury surface, a new anodic process must begin, presumably under the  $\text{Hg}_2\text{SO}_4$  layer, that results in a voltage jump. The data in Fig. 1 show that this transition from the lower to the higher plateau region at a constant charging current requires longer times in lower concentrations of  $\text{H}_2\text{SO}_4$ . It has been shown earlier [2] that anodically grown  $\text{Hg}_2\text{SO}_4$  becomes more porous with decreasing acid concentration. The observed dependence of the transition time on acid concentration can, therefore, be attributed to increased porosity of the  $\text{Hg}_2\text{SO}_4$  layer.

It appears from the above discussion that the higher voltage plateau region is entirely due to the mercury electrode. To understand such behaviour in more detail, linear potential sweep experiments were conducted on a hanging mercury drop electrode (HMDE). The resulting voltammograms show an anodic current loop in the reverse (negative going) scan when the forward scan is taken to a sufficiently positive potential (Fig. 2). The position of the observed anodic peak in the current loop region passes through a minimum around 1.4 V (versus SHE) in  $\sim 4.5 \text{ M H}_2\text{SO}_4$  (Table 1). Thus, this peak may be tentatively attributed to water oxidation for which the  $E^\circ$  value is 1.23 V. Now, if it is assumed that during growth the anodically formed  $\text{Hg}_2\text{SO}_4$  layer becomes progressively impermeable to  $\text{Hg}_2^{2+}$  or  $\text{SO}_4^{2-}$  ions

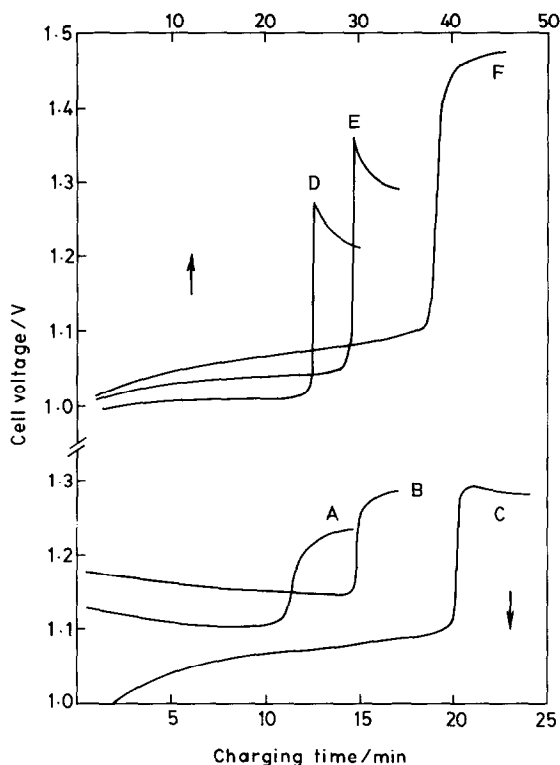
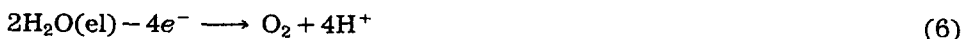
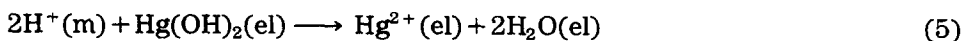
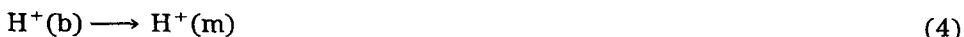
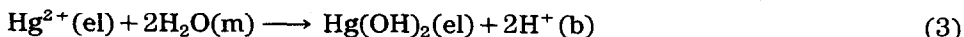


Fig. 1. Charging curves at 1 mA of lead/mercury cell with different  $\text{H}_2\text{SO}_4$  concentrations: A, 3.84 M; B, 3.07 M; C, 2.23 M; D, 1.92 M; E, 1.54 M; F, 0.77 M.

while always remaining permeable to  $\text{H}_2\text{O}$  molecules, then the mercury surface is expected to become completely blocked after some time. On continuation of the charging process further  $\text{Hg}^{2+}$  ions will be generated on the underlying Hg surface, which will, in turn, ionize  $\text{H}_2\text{O}$  in the pores of the  $\text{Hg}_2\text{SO}_4$  layer and drive away  $\text{H}^+$  ions. Reversal of the direction of the potential scan will result in re-entrance of  $\text{H}^+$  ions into the passivating layer and consequent liberation of  $\text{H}_2\text{O}$  at the underlying Hg surface. This process is controlled by the diffusion of  $\text{H}^+$  ions through the  $\text{Hg}_2\text{SO}_4$  layer. Thus, the oxidation of  $\text{H}_2\text{O}$  released at the mercury surface under the passivating  $\text{Hg}_2\text{SO}_4$  layer appears to be the only reasonable explanation of the appearance of the above mentioned anodic peak.

The above discussion can be summarised by the following scheme:



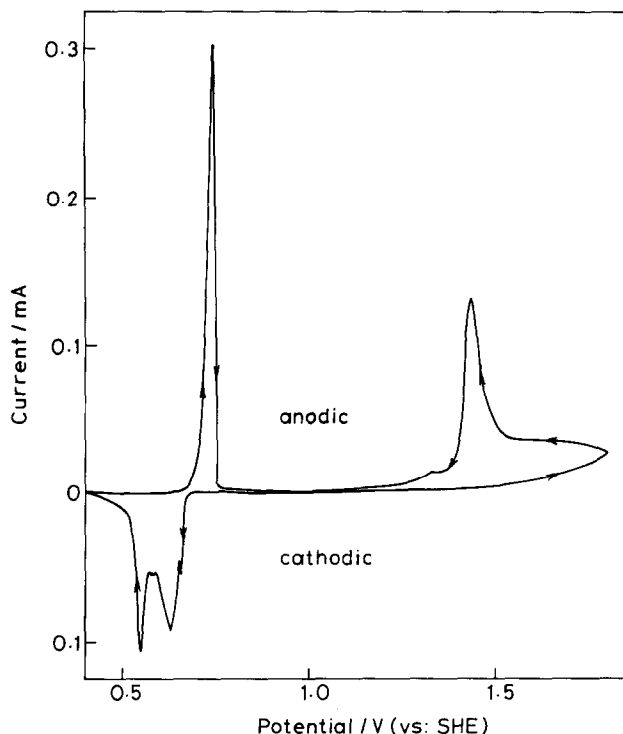


Fig. 2. Cyclic voltammogram for a hanging mercury drop electrode in 3.57 M  $\text{H}_2\text{SO}_4$  at  $0.02 \text{ V s}^{-1}$ .

TABLE 1

Variation of anodic peak potential ( $E_p$ ) in current loop with  $\text{H}_2\text{SO}_4$  concentration ( $c$ )

$c$ (M)	2.17	2.53	2.89	3.61	4.33	5.05	5.41	5.77
$E_p$ (V) vs. SHE	1.79	1.68	1.58	1.47	1.40	1.44	1.63	1.74

Here el, m, and b signify underlying mercury surface,  $\text{Hg}_2\text{SO}_4$  layer, and bulk electrolyte, respectively. Steps (2) and (3) occur during the forward (positive going) scan and steps (4)–(6) during the reverse scan. Therefore, the primary electrochemical process in the higher voltage plateau region is  $\text{Hg} \rightarrow \text{Hg}^{2+}$  in place of  $\text{Hg} \rightarrow \text{Hg}_2\text{SO}_4$ .

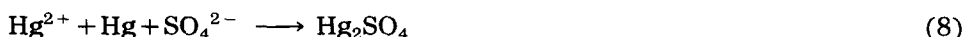
It is interesting to discover whether overcharging beyond the formation of the  $\text{Hg}_2\text{SO}_4$  layer can effectively contribute to the discharge capacity of the mercury electrode. For this purpose, the total anodic charge ( $Q_a^t$ ) given to an HMDE and the cathodic charge ( $Q_c$ ) recovered were measured, as well as the component of the anodic charge ( $Q_a$ ) corresponding to the conversion of mercury into  $\text{Hg}_2\text{SO}_4$  (the charge under the first anodic peak of Fig. 2).

The data can be fitted into an equation of the type:

$$Q_c = aQ_a + b(Q_a^t - Q_a) \quad (7)$$

The results, given in Table 2, show that if the charging is confined to the production of  $\text{Hg}_2\text{SO}_4$  alone, the charge acceptance ( $Q_a$  values) of the mercury electrode rapidly decreases with increasing  $\text{H}_2\text{SO}_4$  concentration. This is in qualitative agreement with data obtained from charging the total cell. Thus, though the discharge efficiencies ( $a$  values) increase considerably with increasing acid concentration, the actual discharge capacities ( $aQ_a$  values) show a reverse trend. On the other hand, if the charging is continued beyond complete blocking of the mercury surface by the passivating layer, most of the excess charge given is wasted through the side reactions as explained above (low  $b$  values). The situation becomes progressively worse as the  $\text{H}_2\text{SO}_4$  concentration increases.

In actual charging of the cell under study, where current reversal is not applied, the accumulation of  $\text{Hg}^{2+}$  ions under the  $\text{Hg}_2\text{SO}_4$  layer during overcharge may result in the formation of cracks. Thus,  $\text{SO}_4^{2-}$  ions can again get access to the mercury surface and produce  $\text{Hg}_2\text{SO}_4$  according to the following chemical reaction



In this way, the loss of input charge may be prevented to some extent. This is indicated by an observed increase of discharge capacity with increased charging time, even beyond the transition in the voltage plateau.

The cell was discharged at different currents ( $i$ ) over the range 0.5–7.5 mA, after charging at 1 mA for a specified time  $t_c$ . The discharge voltage plateau varied between 0.97 and 0.92 V, followed by a rapid decrease. The discharge times ( $t_d$ ) obtained in different  $\text{H}_2\text{SO}_4$  concentrations can be fitted to a Peukert-type equation [3]

$$i = K(t_d/t_c)^n \quad (9)$$

The parameters of eqn. (9) are presented in Table 3. The  $K$  values can be considered to be the relative measures of discharge efficiencies under similar rates of discharge in different  $\text{H}_2\text{SO}_4$  concentrations. These are found to pass through a maximum around 1.5 M  $\text{H}_2\text{SO}_4$ , which agrees quite well with the speculation made earlier on the basis of potentiodynamic studies on mercury and lead in aqueous  $\text{H}_2\text{SO}_4$  [2]. Accordingly, the cycling characteristics of

TABLE 2

Parameters of eqn. (7) (see text) for different  $\text{H}_2\text{SO}_4$  concentrations (c)

$c$ (M)	1.44	2.17	2.89	3.61	4.33	5.05	5.77
$a$	0.343	0.379	0.574	0.614	0.667	0.788	0.829
$b$	0.186	0.140	0.136	0.118	0.103	0.074	0.053
$Q_a$ (C cm <sup>-2</sup> )	0.304	0.267	0.132	0.100	0.064	0.039	0.033
$aQ_a$ (C cm <sup>-2</sup> )	0.104	0.101	0.076	0.061	0.042	0.030	0.027

TABLE 3

Parameters of eqn. (9) (see text) for different  $\text{H}_2\text{SO}_4$  concentrations ( $c$ )

$c(\text{M})$	0.77	1.54	1.92	2.23	3.07	3.84
$n$	-0.84	-0.82	-0.94	-0.82	-0.87	-0.96
$K$	0.78	0.80	0.63	0.52	0.55	0.44

TABLE 4

Steady values of discharge efficiency ( $\eta$ ) and discharge capacity ( $Q_d$ ) after cycling in 1.5 M  $\text{H}_2\text{SO}_4$  at different currents ( $i$ )

$i$ (mA)	1.00	1.52	1.85	2.77	3.62	4.55
$\eta$	0.87	0.88	0.89	0.91	0.93	0.93
$Q_d$ (C)	0.78	0.61	0.98	0.87	0.68	0.72

the cell were studied in 1.5 M  $\text{H}_2\text{SO}_4$  with the same charging and discharging currents. This current was varied between 1 and 5 mA, while the cut-off voltages were set at 1.2 V for charging and 0.9 V for discharging. In all cases, the efficiency ( $\eta$ ) and the capacity ( $Q_d$ ) of discharge were found to increase over the first few ( $\sim 5$ ) charge-discharge cycles before reaching fairly steady values. These are presented in Table 4 and show that, while the discharge efficiencies increase slightly with the current employed, the discharge capacities appear to pass through a maximum around 2 mA, i.e., a current density of  $1 \text{ mA cm}^{-2}$ . The high value of the discharge efficiency ( $\sim 90\%$ ) obtained during cycling is evidently one of the strong points in favour of the proposed system.

## References

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- 2K. Das, *J. Power Sources*, 32 (1990) 401.
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