Short Communication

Electrochemical Phase-formation Processes at a Mercury Electrode in Sulphuric Acid

KAUSHIK DAS

Physical Chemistry Section, Jadavpur University, Calcutta - 700 032 (India)

Summary

The oxidation of mercury and the reduction of Hg_2SO_4 at a mercury drop electrode have been studied in different concentrations of H_2SO_4. Linear potential-sweep experiments indicate that the oxidation process occurs mainly at the electrode surface at low sweep rates, while the reaction penetrates more deeply into the metallic phase at higher sweep rates. The porosity of the resulting Hg_2SO_4 layer increases with decreasing H_2SO_4 concentration. Tafel plots suggest that the process is a two-electron mechanism with a transfer coefficient of unity. Exchange-current densities increase with increasing H_2SO_4 concentration and reach limiting values. The reduction of Hg_2SO_4 shows diffusion-controlled behaviour and the slope of the i_p *versus* $v^{1/2}$ plot passes through a maximum with varying H_2SO_4 concentration.

Introduction

A modified version of the well-known lead/acid battery has been proposed recently by the present author [1] in which the positive PbO_2-PbSO_4 electrode has been replaced by an $Hg-Hg_2SO_4$ electrode. The purpose of this modification is to eliminate two major inherent drawbacks of the conventional lead/acid battery, namely, the increase of internal resistance with discharge and the loss of water during recharge. The former problem sets a lower limit on the electrolyte volume required for a given capacity, thus making miniaturisation of the system quite difficult, while the latter problem necessitates continuous maintenance of the battery in the form of frequent "topping up". The combination of $Pb-PbSO_4$ and $Hg-Hg_2SO_4$ electrodes is expected to be free from these limitations as the overall process leaves the conductivity of the electrolyte unchanged, and water electrolysis is unlikely to be appreciable [1].

It is evident that the actual performance of the proposed acidic lead/mercury system is determined by the kinetics and mechanism of the respective electrode reactions. The $Pb-PbSO_4$ electrode has been extensively

studied from this point of view, but little attention has been paid to the Hg–Hg$_2$SO$_4$ electrode [2], despite its wide use as a reference electrode. The object of the present work is to study the formation of Hg$_2$SO$_4$ on mercury, as well as its reduction in sulphuric acid of varying concentration.

Experimental

Experiments were performed on a hanging mercury drop of constant surface area (0.0105 cm^2) provided by appropriate equipment (model 303 A, Princeton Applied Research). Voltammograms were obtained using a potentiostat (model 173, Princeton Applied Research), a voltage scan generator (model VSG 72, Bank Elektronik) and an X–Y recorder (model 2000, Houston Instruments). AnalaR grade H$_2$SO$_4$ (B.D.H.) and triply-distilled water were used to prepare solutions of different concentrations. The measurements were carried out at 25 ± 2 °C. All the potentials in this paper are reported with regard to the standard hydrogen electrode (SHE).

Results and discussion

A linear potential sweep in the positive direction on a hanging mercury drop in aqueous H$_2$SO$_4$ yields an anodic current peak. This must be due to the formation of a passivating layer of Hg$_2$SO$_4$. Figure 1 shows the plots of $i_p^a \nu^{-1/2}$ *versus* $\nu^{1/2}$ for different H$_2$SO$_4$ concentrations ($C_{H_2SO_4}$), where i_p^a is the anodic peak current and ν is the potential sweep rate. At low sweep rates, these plots have a tendency to become linear and to pass through the origin. At high sweep rates, however, $i_p^a \nu^{-1/2}$ gradually approaches a limiting value. These observations suggest that i_p^a bears a functional relationship to ν of the following form:

$$i_p^a = A\nu[1 + B\nu^{1/2}]^{-1} \tag{1}$$

Therefore, at very low sweep rates $i_p^a \alpha \nu$, which is characteristic of the electrochemical reaction of a surface-attached species [3]. This indicates that the oxidation of mercury, and the subsequent formation of a passive Hg$_2$SO$_4$ layer, occurs mainly at the electrode surface under this condition. As the sweep rate increases, however, i_p^a progressively exhibits diffusion-controlled behaviour, *i.e.* $i_p^a \alpha \nu^{1/2}$, indicating that the growth of the Hg$_2$SO$_4$ layer takes place via diffusion of Hg(I) ions (generated at the electrode surface) through the pores of the passivating layer. Thus, it is clear from eqn. (1) that the parameter A can be considered as a relative measure of the number of nucleation sites on the mercury surface, and A/B as the porosity of the Hg$_2$SO$_4$ layer so formed. Values for these parameters are given in Table 1. The A values are found to increase with decreasing $C_{H_2SO_4}$ and, therefore, it seems reasonable to conclude that those surface mercury atoms not directly covered by ions of the electrolyte actually act as nucleation centres, and that the overall process is of the dissolution–precipitation type. An examination of the A/B values indicates that the Hg$_2$SO$_4$ layer becomes more porous in less-concentrated H$_2$SO$_4$ solutions.
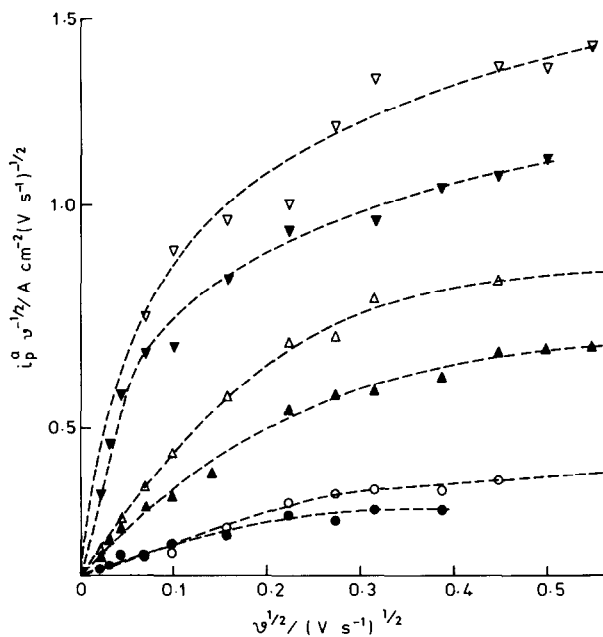
Fig. 1. Plots of $i_p^a \nu^{-1/2}$ vs. $\nu^{1/2}$ for different H_2SO_4 concentrations ($\triangledown$, 1.5 N; $\blacktriangledown$, 3.75 N; $\triangle$, 5.6 N; $\blacktriangle$, 7.5 N; $\circ$, 11.2 N; $\bullet$, 14.95 N).

TABLE 1

Eqn. (1) parameters

$C_{H_2SO_4}$ (N)	1.5	3.75	5.6	7.5	11.2	14.95
A (A cm^{-2}(V s^{-1})$^{-1}$)	16.1	9.80	4.35	3.46	1.72	0.91
B ((V s^{-1})$^{-1/2}$)	9.84	6.47	3.00	3.60	4.35	2.74
(A/B) (A cm^{-2} (V s^{-1})$^{-1/2}$)	1.64	1.52	1.45	0.96	0.40	0.33

The data presented in Fig. 2 reveal that the anodic peak current increases with decreasing $C_{H_2SO_4}$ at different potential sweep rates. With reduction in the concentration of the precipitating anion SO_4^{2-}, a greater proportion of the Hg(I) ions generated at the electrode surface can remain in the solution before being precipitated as Hg_2SO_4, thereby passivating the electrode. Indeed, a finite time-lag has been observed between the mixing of an Hg_2^{2+} solution with an SO_4^{2-} solution and the appearance of the precipitate of Hg_2SO_4, which naturally decreases with increasing concentration of the ions concerned [2]. Thus, with decreasing $C_{H_2SO_4}$, the electrode reaction can penetrate deeper into the metallic phase due to a slower passivation rate, as well as the resulting Hg_2SO_4 layer becoming more porous. These effects jointly lead to the relationships given in Fig. 2.
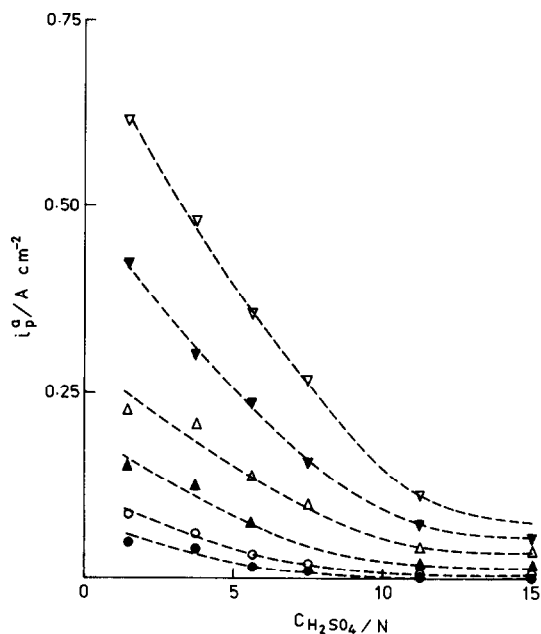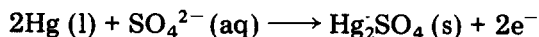
Fig. 2. Plots of $i_p{}^a$ vs. $C_{H_2SO_4}$ at different sweep rates ($\bullet$, 0.005 V s^{-1}; $\circ$, 0.01 V s^{-1}; $\blacktriangle$, 0.025 V s^{-1}; $\triangle$, 0.05 V s^{-1}; $\blacktriangledown$, 0.1 V s^{-1}; $\triangledown$, 0.2 V s^{-1}).

The Tafel parameters for the anodic process

$$2Hg\,(l) + SO_4{}^{2-}\,(aq) \longrightarrow Hg_2SO_4\,(s) + 2e^-$$

have been determined from steady-state polarization measurements. It has been found that, despite the formation of a solid passivating layer of Hg_2SO_4 on the electrode surface, a steady current can be obtained for a few minutes up to moderately high anodising overpotentials, and that the Tafel region extends over at least two decades of current density. The results obtained from current–potential measurements are given in Table 2 for different H_2SO_4 concentrations. The reversible potentials of an Hg–Hg_2SO_4 electrode (E_{rev}) have been calculated by using $a_{SO_4{}^{2-}}$ values reported earlier [4]. The average Tafel slope is 28.8 mV decade^{-1} which indicates a two-electron process with a transfer coefficient of unity. The exchange current densities

TABLE 2

Tafel equation parameters ($E = a + b \log i$ with i in 10^{-6} A cm^{-2})

$C_{H_2SO_4}$ (N)	0.7_1	1.4_3	2.8_5	4.2_8	5.7	7.1_3
E_{rev} (V)	0.68_0	0.67_9	0.67_9	0.67_7	0.67_5	0.67_2
a (V)	0.68_4	0.66_0	0.64_3	0.63_4	0.63_3	0.62_7
b(mV decade^{-1})	29.4	29.6	28.6	28.2	28.4	28.4
$\log i_o$	-0.14	0.64	1.26	1.52	1.48	1.58

(i_o) increase with $C_{H_2SO_4}$, reaching a limiting value around 4 N. This trend is in contradiction to that observed for $i_p{}^a$. It should be borne in mind, however, that i_o measures the characteristics of the electrode reaction at the reversible potential (E_{rev}), while $i_p{}^a$ corresponds to that at the peak potential $(E_p{}^a)$. The latter is found to shift appreciably towards more positive values with decrease in $C_{H_2SO_4}$ (Table 3), but the former remains practically constant (Table 2).

Potentiodynamic studies show that the reduction of the anodically-formed Hg_2SO_4 layer is diffusion-controlled. Plots of cathodic peak current $(i_p{}^c)$ versus $\nu^{1/2}$ are presented in Fig. 3 for different H_2SO_4 concentrations. The slopes of these linear plots pass through a maximum around 3 N H_2SO_4 (Fig. 4). The peak current obtained from a linear potential-sweep experiment under diffusion control depends on the concentration (C) and the diffusion coefficient (D) of the electroactive species according to the relation $i_p\nu^{-1/2} = kCD^{1/2}$, where the constant k is determined by the extent of reversibility of

TABLE 3

Anodic $(E_p{}^a)$ and cathodic $(E_p{}^c)$ peak potentials of the Hg–Hg_2SO_4 electrode process

Sweep rate (V s^{-1})	$C_{H_2SO_4}$ (N)	1.5	3.7$_5$	5.6	7.5	11.2	14.9$_5$
0.01	$E_p{}^a$	0.78	0.75	0.72	0.72	0.66$_5$	0.63
	$E_p{}^c$	0.68	0.66	0.65	0.62$_5$	0.59	0.54
0.10	$E_p{}^a$	0.90	0.83$_5$	0.78$_5$	0.74$_5$	0.70	0.65
	$E_p{}^c$	0.64$_5$	0.63$_5$	0.62$_5$	0.60$_5$	0.56$_5$	0.50$_5$
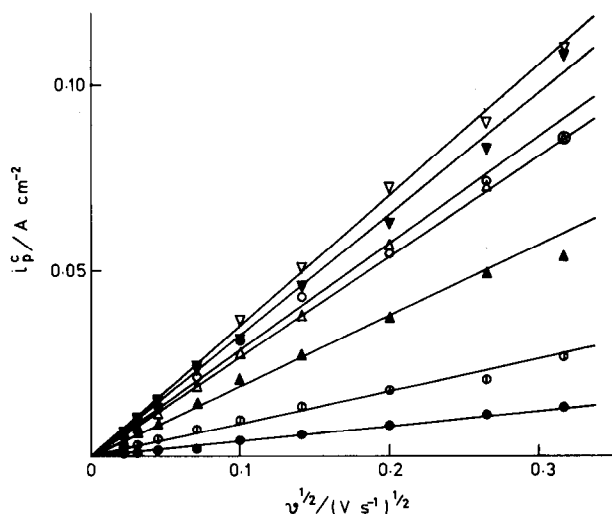
Fig. 3. Plots of $i_p{}^c$ vs. $\nu^{1/2}$ for different H_2SO_4 concentrations (○, 0.75 N; ▼, 1.5 N; ▽, 3.75 N; △, 5.6 N; ▲, 7.5 N; Φ, 11.2 N; ●, 14.95 N).
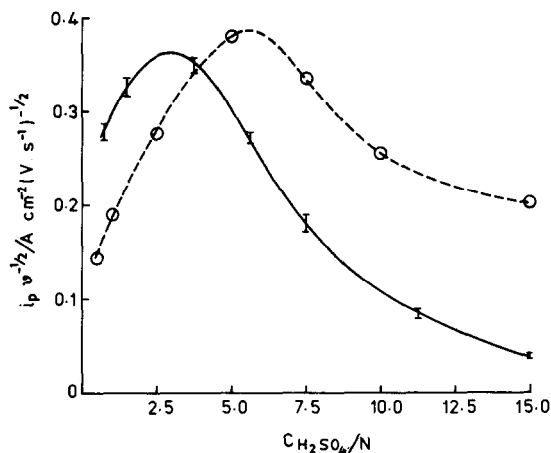
Fig. 4. Variation with $C_{H_2SO_4}$ of the slopes of i_p vs. $\nu^{1/2}$ plots for the processes $Hg_2SO_4 \rightarrow Hg$ (———) and $Pb \rightarrow PbSO_4$ (— — —).

the process [5]. As the Hg_2SO_4 layer becomes more porous with decreasing $C_{H_2SO_4}$, the diffusion coefficient of any species through this layer can be expected to increase as the effective concentration of Hg_2SO_4 decreases. Thus $CD^{1/2}$ and, accordingly, $i_p\nu^{-1/2}$, pass through a maximum. Interestingly, a similar observation has been noted earlier [6] in the case of the passivation of lead by a $PbSO_4$ layer, with a maximum $i_p\nu^{-1/2}$ value appearing around 5.5 N H_2SO_4 (Fig. 4). Therefore, it appears that the optimum concentration of H_2SO_4 in an acidic lead/mercury battery should be between 3 and 5.5 N for efficient discharge.

References

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