EVALUATION OF A COMMERCIAL LIGNIN SAMPLE AS EXPANDER FOR LEAD- ACID BATTERY NEGATIVE PLATE BY CYCLIC VOLTAMMETRY STUDIES

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The effect of $BaSO_4$ and commercial lignin as additive, individually and in combination, on the performance of the negative plate of a lead acid battery was studied in sulfuric acid medium by cyclic voltammetry. The cyclic voltammograms were analysed to study the oxidation-reduction reaction of the negative plate. The results showed that the beneficial effect of $BaSO_4$ and the lignin sample on the discharge reaction of the lead electrode was as expected. The results indicate a dissolution-precipitation mechanism operating in the passivation of lead in sulfuric acid electrolyte. A concentration of 30 ppm of the lignin sample in sulfuric acid was found to be the optimum amount in terms of the negative plate performance.

Keywords: Lead acid battery, negative plate, expander and cyclic voltammetry.

INTRODUCTION

Generally three additives, namely, $BaSO_4$, carbon black and lignin are added to the negative plate mix of lead-acid battery to improve its performance. The overall effect of these expanders on the negative plate has been discussed in literature [1-15]. But the fundamental study regarding the mechanism of their action is very limited. In this work, the action of a commercial lignin sample as negative plate expander of lead acid battery has been studied by cyclic voltammetry, to gain some insight into its mechanism of action.

EXPERIMENTAL

Pure lead electrode of 99.99% purity supplied by Johnson Mathey, England was used as the working electrode. Lead piece of 1 cm length, 0.5 square cm of cross-section press-fitted into a teflon piece was used with its circular cross-section exposed to the electrolyte. The electrode was mechanically polished using 1/0, 2/0, 3/0 and 4/0 emery paper successively, degreased with trichloroethylene and was then treated with saturated solution of ammonium acetate to remove the surface oxide. The electrode was washed with double and triple distilled water successively before use.

A two-compartment all-glass cell was used for the experiments. The working electrode compartment was separated from the auxiliary electrode compartment by a porous glass diaphragm. A platinum electrode of size 4 cm x 4 cm served as the counter electrode. Potential measurements were made against a $Hg/Hg_2SO_4/H_2SO_4$ reference electrode. 4.5 M sulfuric acid (sp.gr. 1.26) was used as the electrolyte. Analar acid and triple distilled water were employed to prepare this electrolyte. Precipitated barium sulfate and sodium lignosulfonate (both commercial variety) were used as additives.

A voltage scanner (Wenking MVS 87) in conjunction with a potentiostat (LB 75 L) was used for the cyclic voltammetric studies (C.V.). The current potential response of the system was recorded using Rikadenky X-Y recorder (RW 201 T).

The potential range employed for the study was from -1400 mV to - 600 mV versus mercury/mercurous sulfate reference electrode. The working electrode was kept at -1400 mV for 15 minutes to remove the surface oxide prior to the potential sweep.

Experiments were conducted using five different compositions of the electrolyte: viz. 4.5 M sulfuric acid (I), 4.5 M sulfuric acid saturated with $BaSO_4$ (II), 4.5 M sulfuric acid saturated with $BaSO_4$ and containing 30 ppm lignin (III), 4.5 M sulfuric acid saturated with $BaSO_4$ and containing 60 ppm lignin (IV) and 4.5 M sulfuric acid saturated with $BaSO_4$ and containing 600 ppm lignin (V) at room
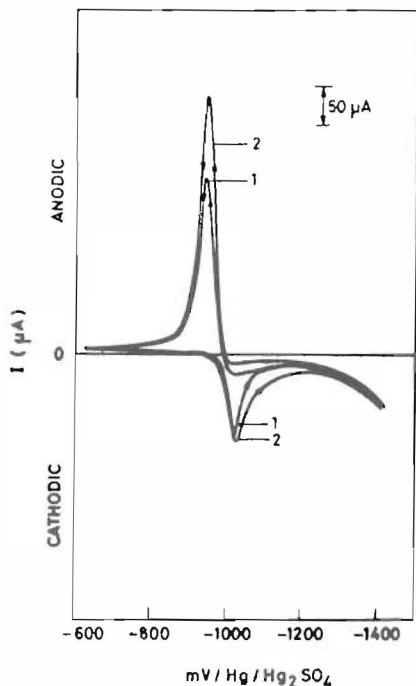
Fig. 1: Cyclic voltammogram of Pb electrode in
4.5 M sulfuric acid (v = 250 mV/sec)
(1) Initial   (2) After one hour

temperature. The electrode was subjected to potential cycling at different scan rates from 1 mV/s to 250 mV/s in pure sulfuric acid (4.5 M) as well as in sulfuric acid (4.5 M)
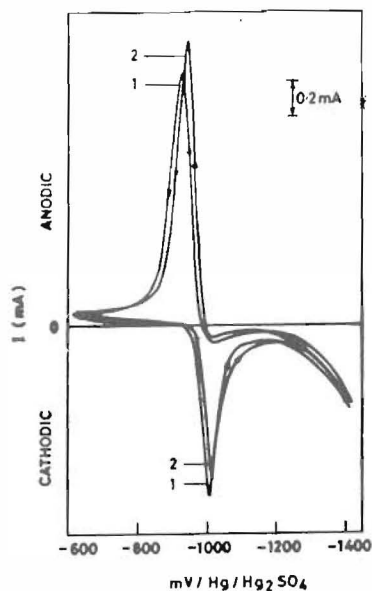
containing 30 ppm of lignin. Different parameters of the cyclic voltammogram, namely, peak current (i_p), peak potential (E_p) and peak charge (Q) were calculated and analysed.

RESULTS

The cyclic voltammogram taken initially and after one hour cycling in different electrolytes are given in Figs. 1-5. The parameters measured from those voltammograms are given in Table I.

The voltammograms have the same general characteristics in all the experiments conducted. When the potential is swept positive from -1400 mV, the current which is initially cathodic decreases and becomes anodic at the corrosion potential. The current, then increases to form an anodic peak (A_1). After the peak, current decreases to almost zero at more positive potential. On sweep reversal, a peak (C_1) is obtained at the cathodic side also. This behaviour is found to agree with the results reported earlier [16].

In 4.5 M sulfuric acid (I)

The CV (Fig. 1 and Table I) show that the initial anodic and cathodic currents (i_{pa} and i_{pc}) are 0.230 and 0.110 mA respectively. After one hour cycling, the values increase to 0.335 and 0.115 mA. For the initial CV the anodic and
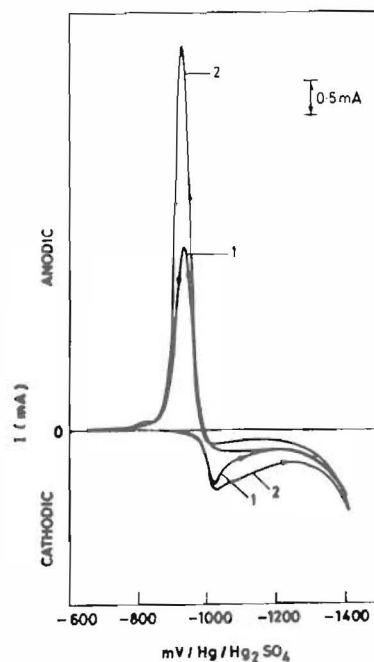

Fig. 2: Cyclic voltammogram of Pb electrode in 4.5 M sulfuric
acid solution saturated with barium sulfate (v = 250 mV/sec)
(1) Initial   (2) After one hour

Fig. 3: Cyclic voltammogram of Pb electrode in
4.5 M sulfuric acid solution containing lignin (30 ppm) and
saturated with barium sulfate (v = 250 mV/sec)
(1) Initial   (2) After one hour

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Fig. 4: Cyclic voltammograms of Pb electrode in 4.5 M sulfuric acid solution containing lignin (60 ppm) and saturated with barium sulfate (v = 250 mV/sec)
(1) Initial   (2) After one hour

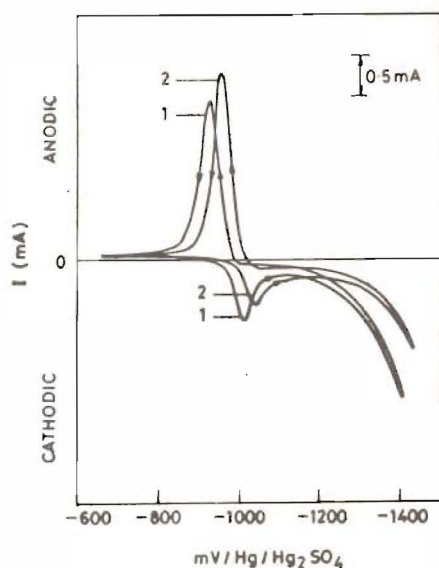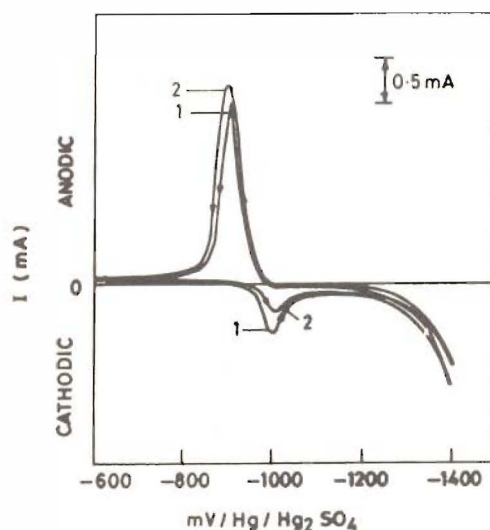*Fig. 5: Cyclic voltammogram of Pb electrode in 4.5 M sulfuric acid solution containing lignin (600 ppm) and saturated with barium sulfate (v = 250 mV/sec)*
(1) Initial   (2) After one hour

cathodic charges (Q_a and Q_c) are found to be 49 and 16 millicoulombs. After one hour cycling, they increase to 68 and 29 millicoulombs.

In sulfuric acid (4.5 M) saturated with barium sulfate (II)

The CV (Fig. 2 and Table I) show that the initial anodic and cathodic peak currents (i_p) are 1.440 and 0.980 mA

respectively. After one hour cycling, their values change to 1.680 and 0.880 mA. For the initial CV, the anodic and cathodic charges (Q_a and Q_c) are found to be 388 and 154 millicoulombs respectively. After one hour cycling, they change to 426 and 118 millicoulombs. Thus there is a considerable increase in the peak current and charge (i_p and Q) values compared to the previous case.

TABLE I: Data from CV of lead electrode in different electrolytes at scan rate 250 mVs^{-1}

Electrolyte	Anodic peak potential (mV)		Cathodic peak potential (mV)		Anodic peak current (mA)		Cathodic peak current (mA)		Anodic charge (coulomb)		Cathodic charge (coulomb)	
	A	B	A	B	A	B	A	B	A	B	A	B
4.5 M H$_2$SO$_4$ (I)	-940	-945	-1015	-1025	0.230	0.335	0.110	0.115	0.049	0.068	0.016	0.029
4.5 M H$_2$SO$_4$ + BaSO$_4$ (II)	-930	-950	-1010	-1020	1.440	1.680	0.980	0.880	0.388	0.426	0.154	0.118
4.5 M H$_2$SO$_4$ + 30 ppm lignin + BaSO$_4$ (III)	-930	-925	-1020	-1030	2.600	5.500	0.800	0.850	0.520	0.890	0.144	0.252
4.5 M H$_2$SO$_4$ + 60 ppm lignin + BaSO$_4$ (IV)	-920	-950	-1010	-1040	1.950	2.300	0.750	0.550	0.460	0.474	0.164	0.108
4.5 M H$_2$SO$_4$ + 600 ppm lignin + BaSO$_4$ (V)	-910	-900	-1000	-1010	2.000	2.200	0.550	0.300	0.546	0.444	0.114	0.066

*** A = Initial,   B = After one hour cycling

In sulfuric acid (4.5 M) + 30 ppm lignin and saturated with barium sulfate (III)

The CV (Fig. 3 and Table I) show that the initial i_{pa} and i_{pc} of 2.600 and 0.800 mA change to 5.500 and 0.850 mA respectively after one hour cycling. For the initial CV, the anodic and cathodic charges are 520 and 144 millicoulombs respectively which increased to 890 and 252 millicoulombs after one hour cycling.

Thus there is a considerable increase in the peak current and charge values when compared with those in other compositions of electrolyte studied.

In sulfuric acid (4.5 M) + 60 ppm lignin and saturated with barium sulfate (IV)

The CV (Fig. 4 and Table I) show that one hour potential cycling changes i_{pa} and i_{pc} from 1.950 and 0.750 mA to 2.30 and 0.550 mA respectively. For the initial CV, the Q_a and Q_c are found to be 460 and 164 millicoulombs respectively. After one hour cycling the respective values are 474 and 108 millicoulombs. Thus, i_{pa} and Q_a values after one hour cycling are higher than those in electrolyte compositions I, II and V but less than those in composition III. But, the corresponding i_{pc} and Q_c values are less when compared with those in electrolyte compositions II and III.

In sulfuric acid (4.5 M) + 600 ppm lignin and saturated with barium sulfate (V)

The CV (Fig. 5 and Table I) show that the initial i_{pa} and i_{pc} values are 2.000 and 0.550 mA respectively. After one hour cycling, they change to 2.200 and 0.300 mA. The anodic and cathodic charges (Q_a and Q_c) which are 546 and 114 millicoulombs initially change to 444 and 66 millicoulombs respectively after one hour cycling. The above results show that the i_{pa} and Q_a values after one hour cycling are higher than in electrolyte compositions I and II but less than those in III and IV.

Effect of sweep rate

The CVs obtained at different scan rates are given in Figs. 6 and 7. The parameters peak current (i_{pa} and i_{pc}) and the corresponding charge values (Q_a and Q_c) obtained at different sweep rates are given in Tables II and III.

It is found that i_{pa} and i_{pc} increase with increase in sweep rate while Q_a and Q_c decrease with sweep rate.

DISCUSSION

The current maximum obtained on the positive going sweep in sulfuric acid at a potential of -930 mV corresponds to the
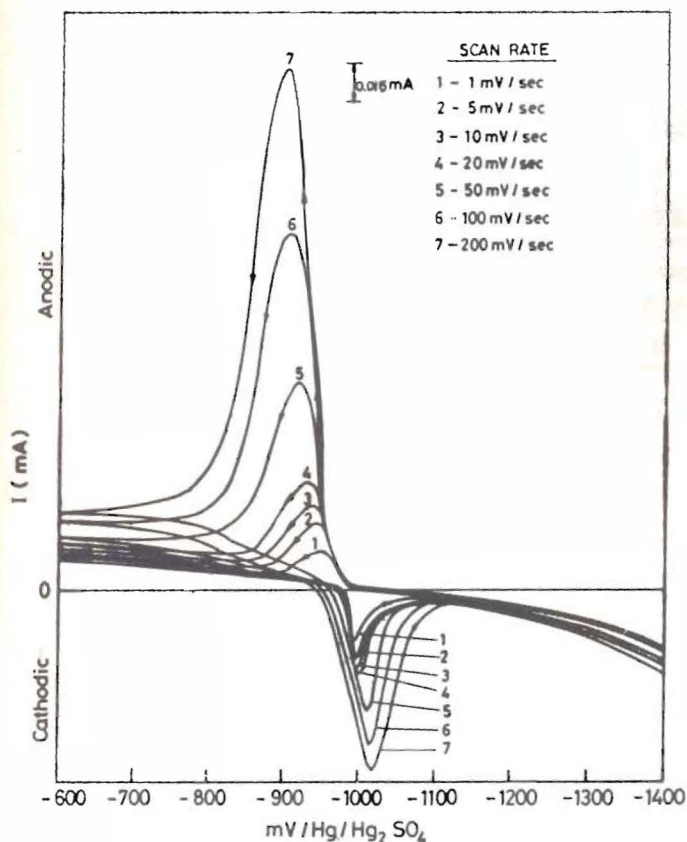

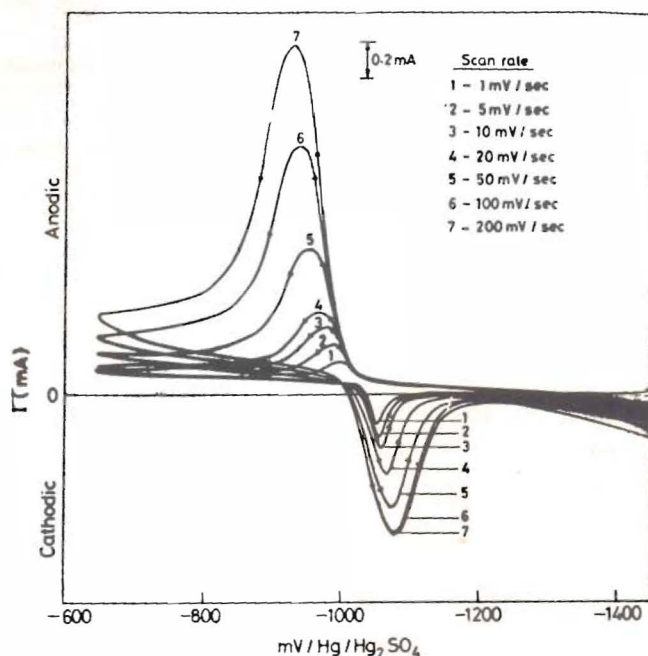*Fig. 6: Cyclic voltammograms of Pb electrode in 4.5 M sulfuric acid solution at different scan rates*

Fig. 7: Cyclic voltammogram of Pb electrode in 4.5 M sulfuric acid solution containing lignin (30 ppm) and saturated with barium sulfate at different scan rates

dissolution of lead forming lead sulfate. The process is equivalent to the discharge of the negative plate of a lead acid battery. The observation that the current decreases to very low value after the peak suggests the formation of a passivating layer of lead sulfate.

On the reverse potential sweep, a current maximum is observed at a potential of -1010 mV representing the electroreduction of the anodic product, namely, lead sulfate to metallic lead. This corresponds to the charge process of the negative plate of the lead acid battery. The general nature of the voltammogram obtained confirms to that reported in literature [16].

The cathodic peak current (i_{pc}) is less than the anodic peak current (i_{pa}). Similarly the cathodic peak charge (Q_c) is less than the anodic peak charge (Q_a). These results indicate that the whole of the anodic product is not available for reduction during the cathodic scan. So, it can be inferred that the anodic process involves dissolution of the Pb to Pb^{++} ions which then gets converted to $PbSO_4$. This suggests of a dissolution-precipitation mechanism operating in the anodic passivation of the Pb in sulfuric acid. Part of the lead which dissolves during the anodic scan diffuses away from the electrode vicinity and thus is not available for reduction during the cathodic scan. Dissolution- precipitation mechanism of passivation has also been reported in literature for lead in sulfuric acid [17-20].

The cathodic peak (C_1) is not very sharp and is extended and significant current flows even after the cathodic peak. This suggests a possible diffusion control of the reduction process represented by the cathodic peak (C_1) through the semipermeable $PbSO_4$ layer. This is also suggestive of a porous layer of lead sulfate. The shift in the anodic peak to more negative potentials on cycling suggests that the lead formed during cathodic process is more active. So it can be inferred that a dissolution-precipitation mechanism operates in the reduction reaction also.

In the presence of barium sulfate, the i_{pa}, i_{pc}, Q_a and Q_c values are found to increase considerably compared to the corresponding values in sulfuric acid. This shows that more charge is required for the passivation and reduction steps. Thus, the addition of barium sulfate to the negative plate of lead acid battery can improve its discharge (capacity) and the charging process which is observed practically.

In presence of lignin, the i_{pa}, i_{pc} and the charge (Q) values are higher showing an improvement in the charge and discharge efficiency of the negative plate of lead acid battery. Interestingly the cathodic charge is less than that in the case of sulfuric acid containing barium sulfate.

In presence of barium sulfate and lignin, it is observed that the i_{pa}, i_{pc} and the (Q) values are still higher compared to those in sulphuric acid. This shows the possible beneficial effect lignin can have in presence of barium sulfate on the performance of the negative plate of lead acid battery. But hereagain the cathodic charge is considerably less compared to that in the case of sulfuric acid in presence of barium sulfate but is higher than in the case of pure sulfuric acid. In all the three electrolytes Q_c is found to be less than Q_a.

Among the three different compositions of lignin studied, namely, 30, 60 and 600 ppm (Table I), it is found that the Q_a and Q_c values are more in the case of 30 ppm. With increase in lignin concentration, the i_{pa} and i_{pc} values decrease. It may be concluded that a low concentration of the sample lignin (30 ppm) is suited for the optimum performance of negative plate of lead acid battery.

The cathodic peak is extended and more flat and diffused to greater extent in presence of 30 ppm lignin suggesting the formation of a more porous lead sulfate layer. From this it may be inferred that lignin increases the porosity and surface area of the negative plate. This may be the result of an adsorption mechanism by which lignin acts on the negative plate. The decrease in cathodic charge also is suggestive of such a mechanism.

TABLE II: Data from CV of lead electrode in 4.5 M sulfuric acid at different scan rates

Scan rate (mV/s)	Anodic current i_{pa} (mA)	Cathodic current i_{pc} (mA)	Anodic charge Q_a (coulomb)	Cathodic charge Q_c (coulomb)
1	0.015	0.018	0.625	0.620
5	0.027	0.023	0.375	0.360
10	0.033	0.029	0.355	0.313
20	0.042	0.032	0.258	0.260
50	0.081	0.047	0.201	0.159
100	0.138	0.060	0.152	0.101
200	0.203	0.069	0.101	0.070

TABLE III: Data from CV of lead electrode in 4.5 M sulfuric acid + 30 ppm lignin and saturated with $BaSO_4$ at different scan rates

Scan rate (mV/s)	Anodic current i_{pa} (mA)	Cathodic current i_{pc} (mA)	Anodic charge Q_a (coulomb)	Cathodic charge Q_c (coulomb)
1	0.200	0.180	2.600	1.250
5	0.300	0.240	0.780	0.600
10	0.400	0.320	0.720	0.425
20	0.480	0.460	0.713	0.407
50	0.840	0.660	0.635	0.308
100	1.460	0.800	0.600	0.288
200	2.000	0.820	0.545	0.245