Surface preparation of planar lead electrodes for electrochemical studies in sulphuric acid solutions

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Abstract

There are wide discrepancies in the reported current density values (i_p and $i_{o,\,her}$) obtained from potentiodynamic studies on lead in sulphuric acid solutions. Furthermore, it is well known that preparative procedures exert a marked influence on the data obtained for planar electrodes. The present investigation confirms a variation in current density values with different methods of polishing and the effect of subsequent cycling. From analysis of the results, a well-defined procedure is derived to produce an electrode with a constant-response-modified-surface (CRMS). This yields current densities that vary by only ±2%. Scanning electron micrographs of the treated electrodes provide additional evidence in support of a CRMS.

Introduction

Although the Pb/H$_2$SO$_4$ system has been the subject of many studies, there is a wide variation in the values reported for both the current density and the peak potentials [1–20]. In particular, a discrepancy appears in the number of peaks reported for the lead to lead sulphate reaction using cyclic and linear sweep voltammetric experiments. Although attempts have been made [1, 2] to obtain near-constant current densities, specific values for a given pretreatment (e.g., polishing) have not been reported. A summary of current-density data [2, 10] is given in Table 1. The present work suggests procedures to obtain near constant values under potentiodynamic conditions.

Experimental

Cast, machined, cylindrical lead rods (99.99%, supplied by BHAS) of dia. 0.2 cm^2, each shrouded in a Teflon sheath, were used in all experiments. The electrolyte consisted of AnalaR sulphuric acid diluted to 4.5 M with triply-distilled water. Experiments were performed with a computer-interfaced BAS-100-A Electrochemical Analyser. Data were recorded on a digital printer and plotter.

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TABLE 1

Variation in current density for Pb $\rightarrow$ PbSO$_4$ reaction in cyclic and linear sweep voltammetric studies

Experimental conditions				Sweep rate (mV s^{-1})	Current (mA cm^{-2})	Reference
Purity of Pb (%) and method of polishing[a]	Electrolyte (H$_2$SO$_4$) composition	Temp. (°C)	Potential range (mV)			
(99.999 +)	1.250 sp.gr.	—	−600 to −100 (SHE)	3.5 13.5 62.5	5.0 15.0 70.0	11
Pure, MP	30 wt.%	—	+1800 to −1800 (Hg/Hg$^+$)	1.2 3 12	2.23 8.0 8.9	12
Pure, MP and EP	0.5 M	25	−200 to −1000 (RHE)	50	84.0	13
(99.99)MP	5 M	25	−750 to −1000 (SCE)	10 90	28.0 68.0	14
(99.999)EP	5 M	—	−250 to −500 (SHE)	3 3	9.9 4.2	10
(99.98)EP Precycled for 150 cycles	0.5 M	20	−500 to −1500 (Hg/Hg$^+$)	5 20 40 80	6.0 14.3 20.7 23.6	16
Pure, MP	1.30 sp.gr.	—	−700 to −1200 (Hg/Hg$^+$)	10	16.0	17
(99.999)MP	5.25 M	23	−800 to −1050 (Hg/Hg$^+$)	5 10 20 30 60	0.165 0.26 0.37 0.44 0.72	18

(99.999)MP	5 M	25	-1200 to $+1600$ (Hg/Hg$^+$)	30	2	19
(99.997)CP	1.250 sp.gr.	—	-1300 to $+2000$ (SCE)	4.17	10.8	20
Pure, MP/Precycled/ H-evolved	de-oxygenated 0.5 M H$_2$SO$_4$	21	-500 to -1500 (Hg/Hg$^+$)	200 200 200 200	69.3 25.6 120.0 14.1	Fig. 1(b) [2] Fig. 6 [2] Fig. 5 [2] Fig. 5 [2]

^{a}MP - Mechanical polishing   EP - Electropolishing   CP - Chemical (etching) polishing

A three-electrode H-type cell was used with an $Hg/Hg_2SO_4/4.5$ M H_2SO_4 reference electrode and a pure-lead-sheet (5 cm^2) counter electrode. All experiments were carried out at 25 ± 1 °C. The stages employed in preparing the electrode surface were designated as follows.

S-1. The electrode was polished mechanically using various grades (0/0, 1/0, 2/0, 3/0 and 4/0) of silicon carbide paper with a 1:1 mixture of paraffin and kerosene as lubricant. It was then degreased with trichloroethylene.

S-2. The electrode was anodically polished in 10% $HClO_4$ [10] at a current density of 1 A cm^{-2} [13] for 5 s. It was then thoroughly cleaned with triply-distilled water and immediately introduced into the experimental cell (to avoid any oxide formation).

S-3. The electrode was subjected to 15 cycles (pre-cycling) between -1.40 and -0.40 V.

S-4. Hydrogen was evolved for 60 s at -2.20 V.

S-5. The reproducibility of the i_p and E_p values for the lead to lead sulphate reaction was determined by sweeping the electrode between -1.40 and -0.40 V at 30 mV s^{-1}.

S-6. Log i versus E plots were recorded after the electrodes had undergone treatments S-1 to S-5 and then been subjected to continuous potential sweeps between -2.20 and -1.20 V at 10 mV s^{-1} until a constant response was obtained. This ensured that the electrode was in equilibrium with hydrogen and gave good reproducibility.

Results and discussion

Although the hydrogen evolution reaction (her) on lead in sulphuric acid has been studied in detail, there remains considerable variation in the reported values for the Tafel slope and the exchange-current density, see Table 2. Hence, to ensure that near constant and reproducible results are obtained from potentiodynamic experiments, the electrode surface was prepared using the above detailed procedure.

Anodic process (Pb → PbSO_4)

Table 3 provides typical data from several experiments. Electrodes that have undergone various preparative steps are named hereafter 'modified' electrodes and designated the M-series (M-1–M-6). It is evident from the information given in Table 4 that mechanical polishing (Fig. 1(a)) gives $i_{pa,}$ values with a standard deviation of 6.71%. The latter rises to 15.91% for the same electrode upon cycling (Fig. 1(b)). This is contrary to expectation since, as discussed below, cycling should reduce the percentage deviation.

TABLE 2

b and i_o values for hydrogen evolution reaction on lead

Experimental conditions	Tafel slope, b (mV decade^{-1})	Exchange current-density, i_o (A cm^{-2})	Reference
H$_2$SO$_4$ electrolyte	–	10^{-12}	22, 29
293 K, 0.005–0.05 M H$_2$SO$_4$	118	–	23
0.5 M H$_2$SO$_4$	120	–	24–26
H$_2$SO$_4$ electrolyte	120	–	27
Pb, chemical polishing, 0.25 M H$_2$SO$_4$	125 ± 14	$47 \times 10^{-12} \pm 4 \times 10^{-12}$	28
Pb, chemical polishing, 0.5 M NaOH	129 ± 4	$3.4 \times 10^{-7} \pm 5.5 \times 10^{-1}$	28
aq. HClO$_4$ electrolyte	~100	–	30
Pb in various electrolytes, pretreated electrode, 294 K			
0.5 M H$_2$SO$_4$	~150	–	2
0.5 M (NH$_4$)$_2$SO$_4$, pH = 4.04	~140		
0.5 M Na$_2$SO$_4$, pH = 4.02	~150		
Pb, chemical etching, Potentiodynamic, 0.01–100 mV s^{-1}, 295 K	159–160	–	31
5 M H$_2$SO$_4$		5.66×10^{-7}	22
0.5 M H$_2$SO$_4$		3.38×10^{-8}	
0.1 M H$_2$SO$_4$	–	2.83×10^{-7}	
0.05 M H$_2$SO$_4$	–	1.26×10^{-8}	
0.01 M H$_2$SO$_4$	–	6.0×10^{-5}	
Chemical etching, 40 mV s^{-1}, linear sweep voltammetry in 0.1 M H$_2$SO$_4$	152	1×10^{-1}	33
H$_2$SO$_4$ electrolyte	118	–	34

TABLE 3

Parameters derived from cyclic voltammograms of Pb/4.5 M H_2SO_4 at 30 mV s^{-1}

Electrode designation	Method of polishing	Anodic		Cathodic		No. of check cycle*	Fig. no.
		$E_{p, a}$ (mV)	$i_{p, a}$ (mA cm^{-2})	$E_{p, c}$ (mV)	$i_{p, c}$ (mA cm^{-2})		
M-1	MP (S-1)	−911	7.8125	−1008	4.0975	1	1(a)
		−906	8.9360	−1009	2.4125	2	
		−915	7.8506	−1011	2.1510	3	
M-2	MP/Precycled	−910	10.4125	−1013	2.6945	1	1(b)
	(S-1 & S-3)	−921	7.5545	−1016	2.1840	2	
		−920	8.2070	−1016	2.0815	3	
M-3	MP/Precycled/	−891	25.9155	−1016	5.6650	1	2
	H-evolved	−883	35.8355	−1019	5.6180	2	
	(S-1, S-3 & S-4)	−885	34.7695	−1021	5.1205	3	
		−881	30.8685	−1023	4.9685	4	
M-4	MP/EP	−918	8.0105	−1002	5.6435	1	3(a)
	(S-1 & S-2)	−915	4.7700	−1002	2.7450	2	
		−918	4.3325	−1000	2.3315	3	
M-5	MP/EP/	−923	10.3895	−1014	3.2940	1	3(b)
	Precycled	−918	9.4210	−1014	2.6855	2	
	(S-1, S-2 & S-3)	−924	7.9695	−1020	2.5285	3	
M-6	MP/EP/	−888	48.3855	−1009	8.3430	1	
(CRMS)	Precycled/	−884	48.0520	−1012	8.3155	2	
	H-evolved (S-1,	−882	48.7435	−1013	8.0335	3	
	S-2, S-3 & S-4)	−881	48.9185	−1014	7.8215	4	
		−879	49.1745	−1015	7.7405	5	4(a)
		−879	49.2755	−1016	7.5560	6	
		−878	49.4005	−1016	7.6280	7	
		−878	49.5315	−1016	7.6675	8	
		−877	49.5910	−1016	7.6155	9	
		−877	49.6580	−1017	7.5590	10	4(b)

*Between any two check cycles, the electrode was cycled 4 times between −1400 and −400 mV at 200 mV s^{-1}, followed by hydrogen evolution at −2.20 V for 60 s.

A mechanically polished electrode (M-3) subjected to precycling and hydrogen evolution gives almost the same percentage deviation (with regard to M-2), Fig. 2. The current density, however, increases by a factor of 3–4 compared with an electrode that had not undergone hydrogen evolution. An electrode (M-4) subjected to electropolishing (EP) after mechanical polishing (MP), Fig. 3(a), gives a standard deviation of 30%. Nevertheless, if the same electrode experiences 15 precycles (M-5), the deviation in $i_{p,a}$ values is reduced to 13.18%, Fig. 3(b). Furthermore, the deviation is drastically reduced to 1.64% if the electrode is subjected to hydrogen evolution after MP, EP and precycling (M-5), Fig. 4(a), (b).

TABLE 4

Standard deviation (SD) of results obtained from cyclic voltammograms of Pb/4.5 M H_2SO_4 at 30 mV s^{-1}

Electrode designation	Anodic			Cathodic		
	$i_{p, a}$ (mA cm^{-2})	Standard deviation (%)	Compared with M-6 (%)	$i_{p, c}$ (mA cm^{-2})	Standard deviation (%)	Compared with M-6 (%)
M-1	8.3745	6.71	17.14	3.1295	30.79	39.36
M-2	8.9835	15.91	18.31	2.3880	12.84	30.03
M-3	30.8755	16.06	63.20	5.3170	6.55	66.87
M-4	6.1715	30.00	12.63	3.9825	42.53	50.09
M-5	9.1795	13.18	18.79	2.9115	13.00	36.62
M-6 (CRMS)	48.8550	1.64	100.00	7.9510	4.93	100.00
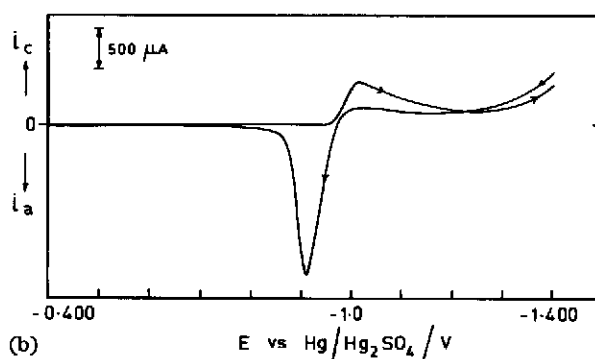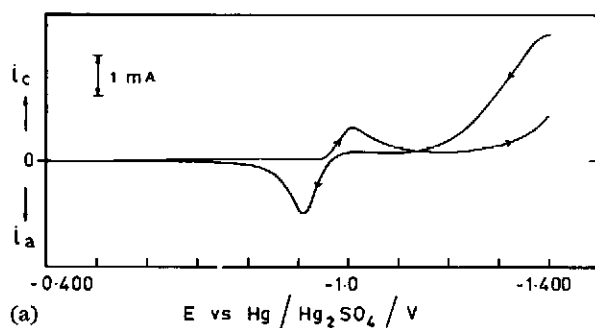
Fig. 1. Cyclic voltammogram for lead in 4.5 M H_2SO_4; scan rate 30 mV s^{-1} (1st check cycle). (a) Fresh electrode, M-1; (b) precycled electrode, M-2.

It is evident from the data given in Table 3 that the electrodes undergoing hydrogen evolution shift the $E_{p, a}$ to more anodic values [10]. Moreover, the current density value is increased by a factor of 3–4 and 6–7 in the cases of M-3 and of M-6 treatment, respectively.
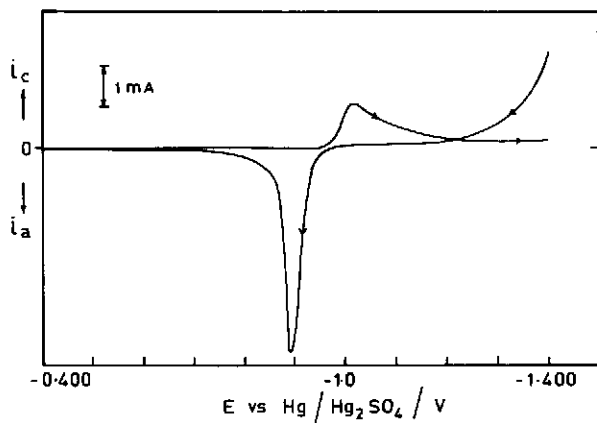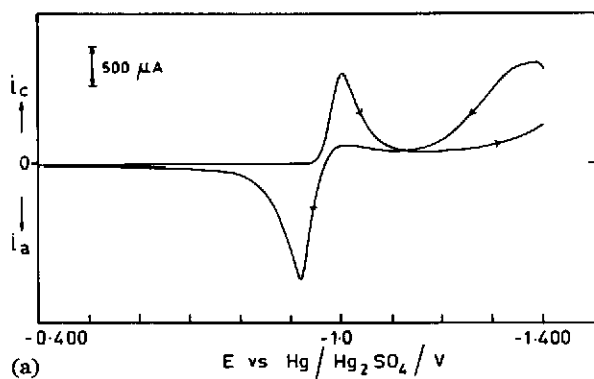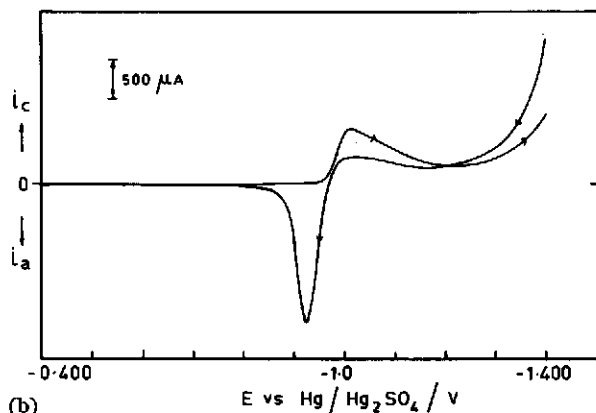
Fig. 2. Cyclic voltammogram for M-3 lead electrode in 4.5 M H$_2$SO$_4$; scan rate 30 mV s^{-1} (1st check cycle).

(a)

(b)

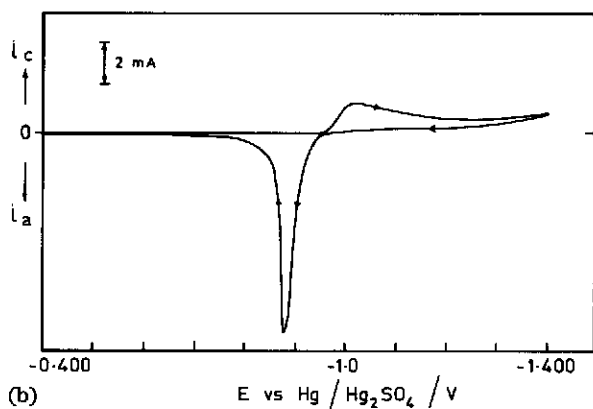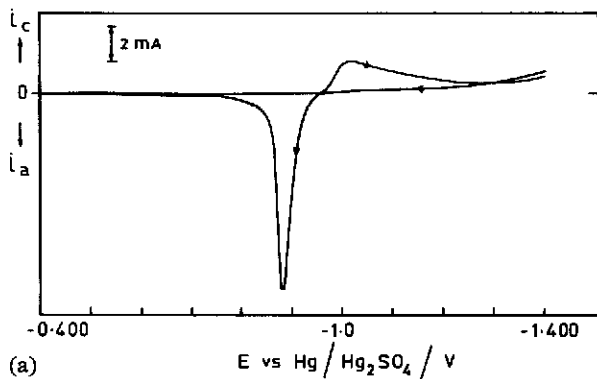Fig. 3. Cyclic voltammogram for lead in 4.5 M H$_2$SO$_4$; scan rate 30 mV s^{-1} (1st check cycle). (a) Fresh electrode, M-4; (b) precycled electrode, M-5.

Fig. 4. Cyclic voltammogram for M-6 lead electrode in 4.5 M H_2SO_4; scan rate 30 mV s^{-1}. (a) 5th check cycle; (b) 10th check cycle.

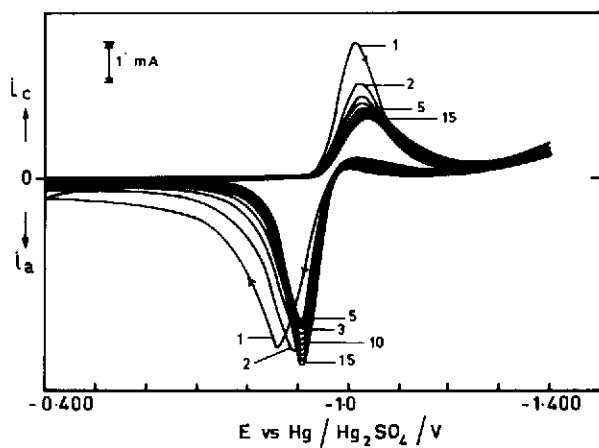

Fig. 5. Cyclic voltammograms for mechanically polished, electropolished, and precycled lead electrode (0.2 cm^2) in 4.5 M H_2SO_4; scan rate 200 mV s^{-1} for precycling.

The cyclic voltammograms shown in Fig. 5 are typical of those for pre-cycled electrodes, irrespective of whether the latter are subjected to MP or EP, or both. Such electrodes exhibit a change in the mechanism of $PbSO_4$ formation: from initial dissolution, precipitation, and growth to instantaneous nucleation and growth.

From the results given in Table 1, it can be seen that, for a given sweep rate (e.g., 3 mV s^{-1}), the current density for the lead to lead sulphate reaction is reported to exhibit values ranging from 5 to 10 mA cm^{-2}. Even in the same study [10], there is a two-fold increase in i_p values at the same sweep rate. It is also highly puzzling to note very low values, viz., 0.44 mA cm^{-2} at 30 mV s^{-1} [18]. Compared with this latter value, the value reported here (49 mA cm^{-2}) is more than 2 orders of magnitude larger. This is probably due to different methods employed in preparing the electrodes. In ref. 18, the electrode was simply mechanically polished, M-1, while in the present investigation a series of steps is employed to produce a constant-response-modified-surface (CRMS), M-6, which results in highly consistent values of the current density for the different electrochemical reactions. The significant increase in current density values after hydrogen evolution may be due either to pitting of the surface [1] or to cathodic disintegration of lead. Both would result in an increase in the surface area of the electrode [21].

Electrodes that have undergone M-1, M-2, M-4, and M-5 processes, i.e., without any hydrogen treatment, have $E_{p,a}$ values between -906 and -924 mV. By contrast, the values for electrodes subjected to hydrogen evolution are more positive, i.e., -877 and -891 mV. In the former processes, a solid-state precipitation (or instantaneous nucleation and growth — because of the presence of residual lead sulphate crystals) could possibly take place. Usually, this does not require much overpotential to proceed [10]. With the latter type of electrodes, i.e., for electrodes on which hydrogen was evolved, the mechanism of lead sulphate formation may involve liquid phase nucleation and growth (or dissolution–precipitation). This process requires a high overpotential to initiate nucleation and growth.

Cathodic process (PbSO$_4 \rightarrow$ Pb)

With reference to Table 4, it can be seen that the CRMS electrode (see Fig. 6(c), later) gives the minimum standard deviation, viz., 4.95%. For other electrodes, the deviation lies between 12 and 41.53%. In the case of M-3 treatment, the deviation is very close to that for M-6. It is inferred from Fig. 2 that the minimum deviation observed with M-3 treatment is due to precycling followed by hydrogen evolution.

Hydrogen evolution reaction (her)

Values for the Tafel slope and the exchange current for hydrogen evolution on lead determined by various authors [2, 23–34] are given in Table 2. In the present work, difficulties were encountered with regard to obtaining a Tafel slope of 120 mV decade^{-1}, as was also found by Fletcher and Matthews [1, 2]. Stirring the electrolyte at moderate rates, however, helped in sur-
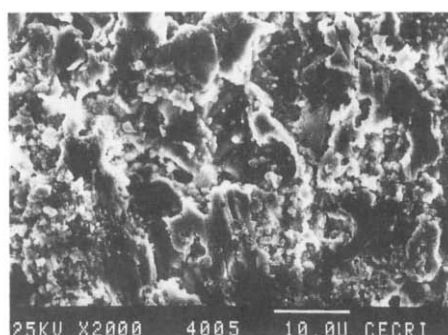
TABLE 5

Effect of potential range on cathodic Tafel slope and exchange current density for hydrogen evolution on (CRMS) lead in 4.5 M H_2SO_4
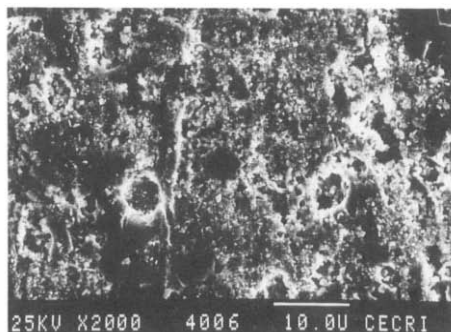Scan rate 10 mV s^{-1}.

Potential range (mV vs. Hg/Hg$_2$SO$_4$)	$v = 10$ mV s^{-1}	
	Tafel slope, b (mV decade^{-1})	Exchange current density, i_o ($\times 10^{-10}$ A cm^{-2})
-1500 to -1700	125	8.4506
-1550 to -1700	125	8.4506
-1600 to -1800	128	11.4928
-1650 to -1850	125	8.4506
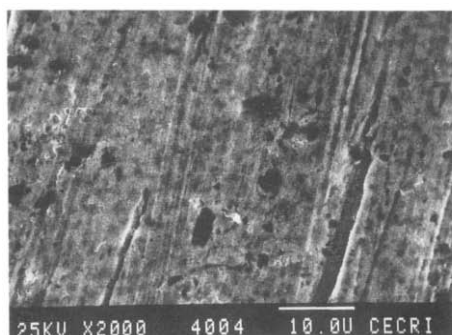
(a)

(b)

(c)

Fig. 6. Electron micrographs ($\times 2000$) of a lead electrode subjected to: (a) mechanical polishing; (b) mechanical- and electro-polishing followed by precycling; (c) CRMS treatment.

mounting this difficulty and values close to the 'classical' 120 mV [28] were obtained. The agitation prevented the accumulation of hydrogen bubbles on the electrode surface. Nevertheless, elaborate and time-consuming purification procedures of the type reported in ref. 28 are not necessary if a CRMS type

of electrode is used. Indeed, values of 125 mV per decade have been consistently obtained in the potential range -1500 to -1850 mV (Table 5). Likewise, $i_{o,\,her}$ values of $(9.9717 \pm 1.52) \times 10^{-10}$ A cm^{-2} have been obtained in different potential ranges, see Table 5.

Surface examination

Examination of an electrode subjected to MP (M-1) only, using scanning electron microscopy (SEM), shows that it is very difficult to avoid the inclusion of SiC particles (Fig. 6(a)). The same electrode after EP and precycling (M-5) reveals the presence of PbSO$_4$ crystals on a highly pitted surface (Fig. 6(b)). With further pretreatment involving hydrogen evolution, it is evident that the surface becomes smoother through the pits becoming less deep (Fig. 6(c)). This might originate from the development of similar and uniform lead crystallites from the lead sulphate.

The procedure reported here that renders the electrode surface different from that produced in other investigations is a combination of anodic polishing, precycling, and hydrogen evolution. The anodic polishing gives a surface that is modified by precycling and, upon hydrogen evolution, gives a constant-response-modified-surface (CRMS). Between any two experiments, hydrogen evolution for a specific period maintains the electrode surface area at a near constant value. This surface is able to give reproducible data for E_p, i_p, b_{her} and $i_{o,\,her}$.

Conclusions

It is possible to obtain highly reproducible results from potentiodynamic studies on the Pb/H$_2$SO$_4$ system by following a mechanical polishing, electropolishing, precycling, and hydrogen evolution reaction (designated CRMS or M-6 electrode). The error (standard deviation) is less than $\pm 2\%$. Using this modified electrode, a Tafel slope of 125 mV per decade and an i_o value of $(9.9717 \pm 1.52) \times 10^{-10}$ A cm^{-2} are obtained for the hydrogen evolution reaction on lead in sulphuric acid solutions.

Acknowledgement

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