ANTIMONY IN LEAD–ACID CELLS
II. GENERATION AND UPTAKE OF SOLUBLE ANTIMONY

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Summary

The dissolution of antimony from antimonial-lead grids was examined by overcharging either cathodically or anodically with a pure lead grid as counter-electrode. Antimony was released as Sb(V) only, from grids operated in either mode; in neither case was Sb(III) detected. Immersion of a charged negative electrode in 3 4 M H_2SO_4 containing Sb(V) resulted in a slow uptake of Sb leading to contamination of the negative active material. The previously reported strong adsorption of soluble Sb by PbO_2 was confirmed in the present work The Sb-adsorbing ability of a number of other inorganic oxides was tested. γ-MnO_2, β-MnO_2, SnO_2 and TiO_2 all adsorbed more Sb than did PbO_2 on a weight-for-weight basis. Of these, the MnO_2 materials showed significant solubility in the 3.4 M H_2SO_4. The remaining two, SnO_2 and TiO_2, show promise for incorporation into cells to reduce the rate of poisoning of negatives.

Introduction

The transfer of Sb from grids to solution and active material has been investigated by Herrmann and Propstl [1] and by Dawson *et al.* [2]. They found that on cycling a lead–acid cell with antimonial grids, Sb was released from the grids of both polarities with the majority originating from the positive. Some of this soluble Sb was adsorbed by the charged positive active material with partial release on discharge; some was also taken up by the negative active material.

It is the purpose of the present paper to re-examine and extend these studies with the benefit of analytical techniques, allowing separation of Sb

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(III) and Sb(V) (discussed in Part I [3]) This will then lead on to measurements of the transport of soluble Sb between positive and negative electrode compartments in Part III [4].

Experimental

Preparation of pasted electrodes

Antimony-free lead grids were cleaned for at least 30 min in dilute HNO_3 prior to coating with commercial positive or negative pastes. They were then cured and the negative ones were dried; the positives were formed by anodic electrolysis in H_2SO_4 then washed and dried prior to use. Both pastes and grids were individually analysed [3] to ensure the absence of Sb.

Dissolution of Sb from grids

A cell with three compartments, separated by sintered glass frits, was used with grids contained in the end compartments. In each run only one grid, operated at 15 mA cm^{-2}, contained Sb, the other being Sb free. A facility for bubbling O_2-free N_2 through either anolyte or catholyte was included. In one run the central compartment contained 20 layers of a polyethylene separator (Evanite from Evans Products, Corvallis, Oregon) presoaked overnight in 3 4 M H_2SO_4 to restrict mass transport between the end compartments.

Adsorption of Sb by charged electrodes and compounds

Antimony-free negative and positive electrodes were fully charged in the three compartment cells in 3.4 M H_2SO_4 using Sb-free grids as secondary electrodes. Samples of the charged electrodes were shaken with aliquots of 3.4 M H_2SO_4 containing Sb(III) or Sb(V) in stoppered flasks These were stored at 25 °C with occasional shaking followed by analysis of the supernatant solutions for Sb [3].

The above procedure was repeated to examine adsorption onto the following: β-PbO_2, WO_3 (BDH Laboratory Reagents); $PbSO_4$ (Hopkin and Williams GPR); electrodeposited γ-MnO_2 (R2); nsutite ore—ρ-MnO_2 (R1), pyrolusite—β-MnO_2 (R30); SnO_2—cassiterite; ZrO_2; TiO_2—rutile, Ta_2O_5 (Hopkin and Williams Laboratory Reagents), RuO_2 (Aldrich); MoO_3 (Fisons Analytical Reagent), kieselguhr. Supernatant solutions from these compounds showing appreciable adsorption were analysed by atomic absorption spectroscopy (AAS) using the following lines Mn, 279.5 nm; Sn, 224.6 nm; Ti, 364.3 nm

Analytical techniques

The methods used were those presented in Part I [3].

Results and discussion

Dissolution of Sb from grids

Three runs were performed and the results are shown in Table 1. In run 1 Sb(V) was released from the anodically operated antimonial-lead grid as found by Dawson *et al.* [2]. In runs 2 and 3, using fresh grids and electrolyte in each case, the cathodically operated antimonial-lead grid surprisingly also released only Sb(V). In the latter run oxidation of dissolved Sb by contact with the anode was prevented by the incorporation of the 20 layers of separator; oxygen was also purged from the catholyte by bubbling N_2. The release of Sb(III) had been anticipated from the work of Dawson *et al* [2], but no trace of this valency state was detected. The possibility that, in previous studies, Sb(V) had been reduced by cathodically generated H_2 was also investigated. Hydrogen was bubbled for 90 min through H_2SO_4 solutions containing Sb(V) in the presence or absence of some charged negative active material or platinised Pt. In no case, however, was any Sb(III) detected.

The results in Table 1 confirm the finding of Herrmann and Propstl [1] that the majority of Sb released into the electrolyte originates from the positive (anodically polarised) grid.
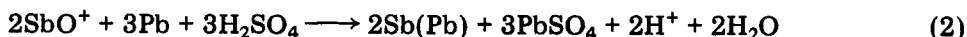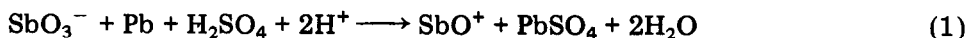
TABLE 1

Dissolution of Sb from antimonial-lead grids on overcharge

	Run 1	Run 2	Run 3
Grid containing Sb initially	Anode	Cathode	Cathode
Electrolysis time (h)	9	23	4
Percentage of original Sb found finally in electrolyte	0 55	0 04	0 05
Oxidation state of Sb in electrolyte	(V)	(V)	(V)

Approximately 0 17 g Sb initially in each run, electrolyte initially Sb free, runs 1 and 2, no separator, run 3, 20 layers of Evanite separator and N_2 continuously bubbled through catholyte

Uptake of Sb by charged negative electrodes

The uptake of Sb(III) or Sb(V) by charged negative electrodes is shown in Fig. 1. For up to 7 h there was negligible uptake of Sb(V) but a rapid uptake of Sb(III), as was found by Dawson *et al* [2]. It was found, however, that Sb(V) was incorporated when left in contact with the charged negative for longer times. It has not previously been recognised that this happens on open-circuit and suggests that the lead electrode reduces Sb(V) slowly to Sb(III) prior to its more rapid reduction to Sb
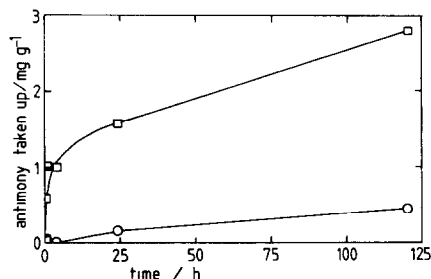
$$SbO_3^- + Pb + H_2SO_4 + 2H^+ \longrightarrow SbO^+ + PbSO_4 + 2H_2O \qquad (1)$$

$$2SbO^+ + 3Pb + 3H_2SO_4 \longrightarrow 2Sb(Pb) + 3PbSO_4 + 2H^+ + 2H_2O \qquad (2)$$

Fig 1 Progressive uptake of Sb by charged negative electrodes □, Sb(III), ○, Sb(V) Solution 3 4 M H_2SO_4, temperature 25 °C

This is an important result as it was shown earlier that Sb is released into the electrolyte from antimonial-lead grids only as Sb(V).

Charged negatives showed comparable uptakes of Sb when in contact with solutions containing either Sb(III) or Sb(V) for 16 days

Adsorption of Sb by positive electrodes

Charged and discharged positive electrodes were immersed in 3.4 M H_2SO_4 containing Sb(V). The analytical data in Table 2 show a large adsorption by charged electrodes (containing principally PbO_2) and a much reduced adsorption by discharged electrodes (with considerable transformation of PbO_2 to $PbSO_4$). These results are in general agreement with previous studies [1, 2, 5] which indicate that Sb is adsorbed and released by positive electrodes on charge and discharge respectively

TABLE 2

Adsorption of Sb(V) by positive electrodes

Positive electrode	Initial wt of Sb (mg) per g of sample	Equilibrium conc of Sb in soln (μg cm^{-3})	Wt of Sb adsorbed (mg) per g of sample	Sb adsorbed (%)
Unpasted pure lead grid	4 87	421	Not detected	—
	2 04	416	0 01	0 5
Fully charged pasted electrode	3 47	4 3	3 44	99
	6 02	19 7	5 74	95
Discharged pasted electrode	6 76	280	2 23	35
	2 87	124	2 02	70

Initial solution 420 μg cm^{-3} Sb(V) in 3 4 M H_2SO_4, temperature 25 °C, equilibration time 26 days

Adsorption of Sb by PbO_2 and $PbSO_4$

Adsorption isotherms of Sb(III) and Sb(V) onto powdered PbO_2 are shown in Fig. 2. As Dawson and co-workers found [2], PbO_2 has a greater

affinity for Sb(III) than for Sb(V), these workers suggested that the adsorption proceeds via a slow chemisorption which modifies the surface onto which physical adsorption takes place. Gorokhova [6] showed that adsorption of various ions onto PbO_2 involved chemisorption and that there was strongly-bound surface complex formation. Further, Kokarev et al [7] showed that PbO_2 adsorbed cations or anions from solutions above or below pH 6 respectively This suggests that, for the strongly acidic Sb-containing solutions in the present work, adsorption involves the $[SbO_3]^-$ anion or its trimer for Sb(V) uptake and $[SbOSO_4]^-$ or $[Sb(SO_4)_2]^-$ anions for Sb(III) uptake.

It was found that of the various common adsorption isotherms (e.g. Langmuir, Temkin, etc.) only the Freundlich isotherm fitted the data in Fig 2 over the whole range. Freundlich adsorption can be represented by the equation

$$x/m = kC^n \qquad (3)$$

x is the amount of solute adsorbed per weight m of adsorbent when present at equilibrium concentration C in solution: k and n are constants related to the surface area of the solid and the adsorption potential respectively. Equation (3) may be expressed in the form

$$\log(x/m) = n \log C + \log k \qquad (4)$$

A plot of $\log(x/m)$ versus $\log C$ is shown in Fig. 3. The similarity of the n and k values suggests the possibility that Sb(III) and Sb(V) species are converted to the same form: because of the oxidising nature of PbO_2 this form is most likely to involve Sb(V). Evidence in support of this suggestion was sought by steeping PbO_2, onto which Sb had been adsorbed, in pure H_2SO_4 for one week. Analytical data for supernatant solutions showed that 10% of the Sb was released into the solution always in the (V) valency state, even though adsorption had originally taken place from either Sb(III) or Sb(V) solutions.

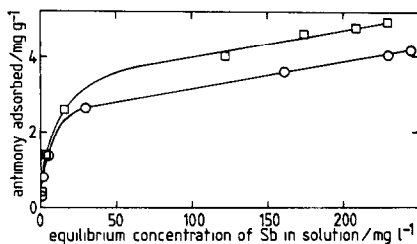There was no detectable adsorption of either Sb(III) or Sb(V) by $PbSO_4$

Fig 2 Adsorption isotherms of Sb onto PbO_2 Equilibration time 26 days, other details as for Fig 1
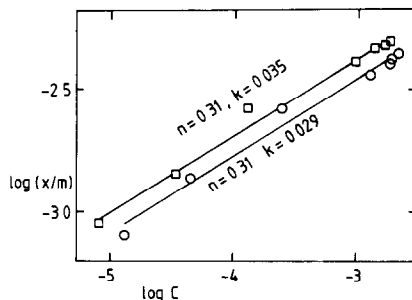
Fig 3 Adsorption isotherms of Sb onto PbO_2 confirming the Freundlich equation Units of C, molarity, other details as for Fig 2

Adsorption of Sb by various inorganic compounds

Since it has been shown that PbO_2 adsorbs Sb readily from solution, other adsorbates were also tested but, as Sb was released from grids only in the (V) state, adsorption of Sb(V) only was studied. In most cases, as for β-PbO_2, the data were best fitted by Freundlich isotherms; these are shown for SnO_2 and TiO_2 in Fig. 4. A given weight of SnO_2 adsorbed approximately twice as much Sb(V) as did the same weight of PbO_2 (Fig. 3) for a given final solution concentration. A comparison of values of n for SnO_2, TiO_2 and PbO_2 indicates that adsorption potentials were similar while k values, on the other hand, indicate higher surface areas for SnO_2 and TiO_2 compared with PbO_2.

A comparison of the adsorption of Sb(V) by different crystalline forms of manganese dioxide is shown in Fig. 5. The degree of adsorption was in the order γ-$MnO_2 > \beta$-$MnO_2 > \rho$-MnO_2 for any equilibrium concentration of Sb in solution. the k values, as expected, were in the same order as the surface areas (γ-MnO_2, 38 $m^2\,g^{-1}$; β-MnO_2, 15 $m^2\,g^{-1}$, ρ-MnO_2 8 $m^2\,g^{-1}$) [8].

Isotherms for materials showing low values of adsorption are shown in Fig 6 The degree of adsorption at a given equilibrium Sb(V) concentration of the substances tested was in the order γ-$MnO_2 > SnO_2 > \beta$-$MnO_2 > TiO_2 > PbO_2 > \rho$-$MnO_2 > WO_3 > RuO_2 > Ta_2O_5 >$ kieselguhr $> MoO_3$, ZrO_2. The last two adsorbed negligible amounts of Sb(V) from solution. The above list includes four oxides with adsorption levels above that of PbO_2. Interestingly,
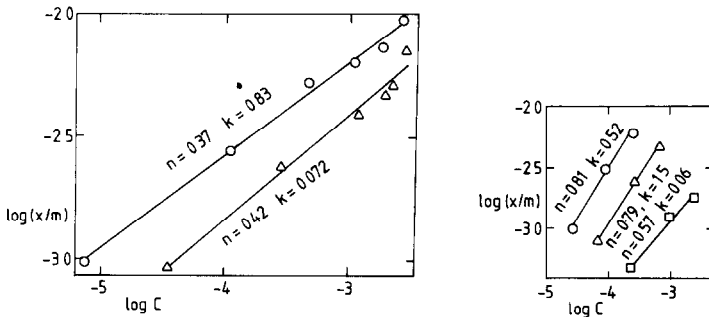

Fig 4 Freundlich plots of adsorption of Sb(V) onto SnO_2—cassiterite and TiO_2—rutile, ○, SnO_2, △, TiO_2 Other details as for Fig 3

Fig 5 Freundlich plots for adsorption of Sb(V) onto MnO_2 ○, γ-MnO_2, △, β-MnO_2, □, ρ-MnO_2 Other details as for Fig 3
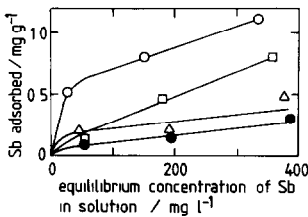

Fig 6 General adsorption isotherms ○, WO_3, □, RuO_2, △, Ta_2O_5, ●, kieselguhr Other details as for Fig. 3

SnO_2—cassiterite, β-MnO, TiO_2—rutile and β-PbO_2 all have the rutile structure; of the other compounds in the list only RuO_2 has this structure. This suggests that, in general, adsorption of Sb(V) is favoured onto oxides with the rutile structure.

The average concentrations of the adsorbent cations in the supernatant solutions were measured after equilibration with 3.4 M H_2SO_4 for 26 days and are shown in Table 3. Materials which might be used in cells as adsorbents for Sb would ideally have low solubilities Table 3 shows TiO_2 and SnO_2 to be preferable to MnO_2 in this respect.

TABLE 3

Dissolution of oxides in 3 4 M H_2SO_4

Oxide	Cation conc (mM)
TiO_2	1.1
SnO_2	0 10
β-MnO_2	10
γ-MnO_2	20

Equilibration time 26 days, temperature 25 °C

Conclusions

In general, the results were in agreement with previous work. Exceptions were (i) that Sb(V) was released from cathodically operated antimonial-lead grids on overcharge and (ii) that Sb(V) was taken up by charged negatives when sufficient time was allowed for reduction to Sb(III) to occur. The two oxides SnO_2 and TiO_2 adsorbed Sb(V) strongly and may prove to be useful additives to the cell to reduce concentrations of Sb in the electrolyte

Acknowledgements

References

1 W Herrmann and G Propstl, *Z Elektrochem*, *61* (1957) 1154
2 J L Dawson, M I Gillibrand and J Wilkinson, in D H Collins (ed), *Power Sources 3*, Oriel Press, Newcastle upon Tyne, 1970, p 1.
3 A A Jenkins and W C Maskell, *Analyst (London)*, *110* (1985) 1431
4 A. A Jenkins, W C Maskell and F L. Tye, *J Appl. Electrochem.*, accepted for publication

5 F Zehender, W Herrmann and H Leibssle, *Electrochim Acta*, **9** (1964) 55
6 N T Gorokhova, *Dvoinoi Sloi Adsorbts Tverd Elektrodakh*, **5** (1978) 29
7 G A Kokarev, M Y Fioshin, V E Kazarinov, N T Gorokhova and V A Kolesnikov, *Dvoinoi Sloi Adsorbts Tverd Elektrodakh*, **5** (1978) 93
8 C St Claire-Smith, J A Lee and F L Tye, *Manganese Dioxide Symp*, Vol 1, Electrochem Soc, Pennington, NJ, 1975, p 132