

Antimony in lead–acid cells. III. Transport measurements

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The mechanism of transport of Sb(V) in H₂SO₄ through 12 commercial separators was investigated. This was carried out by comparing the diffusion coefficient of Sb(V) with the electrical ionic conductivity which should be simply related if diffusion is the rate-controlling transport process. Rates increased as convective flow became dominant. Separators with pore diameters below 2 μm and above 20 μm showed transport rate control by diffusion and convective flow, respectively. Between 2 and 20 μm both processes contributed significantly.

1. Introduction

The dissolution of antimony from both positive and negative antimonial–lead grids is well documented [1, 2] and has been confirmed in Part II of this series [3]. However, the mechanisms of transport of this dissolved antimony and the influence of the separator are less well understood. In the present communication a wide range of commercial separators are examined with respect to their influence on the transport of antimony: an attempt is made to correlate behaviour with pore size. This is done by invoking the equation [4]:

$$D/\bar{D} = \kappa/\bar{\kappa} \quad (1)$$

where D is the diffusion coefficient of a species in free solution, \bar{D} is the measured diffusion coefficient of the same species through a separator, κ is the electrical ionic conductivity of the bulk electrolyte and $\bar{\kappa}$ is the measured conductivity of the separator flooded with the same electrolyte.

Equation 1 is based upon the principle that the modifying effect of the separator on the diffusion coefficient and conductivity is the same. It assumes the absence of a significant contribution from ion-exchange effects and hence is applicable to separators rather than membranes. The degree of saturation of the separator (fraction of filled volume) must be the same for the \bar{D} and $\bar{\kappa}$ determinations.

2. Experimental details

A Perspex transport cell was constructed (Fig. 1) in which the separator was interposed between two compartments each containing a stirrer. Separators were cut, using a punch, to fit tightly into the central region eliminating leakage around the edge.

Separator materials investigated are shown in Table 1. Before testing, ribs were carefully removed with a sharp blade and the separators, cut to size, were soaked in 3.4 M H₂SO₄ for at

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Table 1. Details of commercial separators

Trade name	Manufacturer/ Supplier	Description	Mean effective pore diameter (μm)
Daramic (Industrial)	Grace, Burlington, Massachusetts, USA	High density polyethylene with silica filler	0.03
Darak 2000	Grace, Hamburg, West Germany	Phenolic resin on support of polyester fibres	0.4–0.8
Darak 5000			1
Darak Armorib AR-60		Phenol–formaldehyde resin on a fibrous cellulose base.	20
Amer-Sil	Amerace, Butler, New Jersey, USA	PVC-based microporous	0.01–4 (peak at 0.04)
Ace-Sil		Rubber-based with silica filler	0.5–7
Jungfer	Lewis Industrial Products, Newport, Monmouthshire, UK	Sintered PVC	15–20
Evanite Submicro	Evans Products, Corvallis, Oregon, USA	Polyethylene microporous	< 0.1
Porvic 1	Electric Power Storage, Manchester, UK	PVC-microporous, leached filler	1–3
Porvic 2		Sintered PVC	10–25
Varley	Berec (Varley Batteries Ltd), London, UK	Rubber (latex) with kieselguhr	5
Vylam	Oldham, Manchester, UK	Phenol formaldehyde resin on cellulose base with sintered PVC	50–75

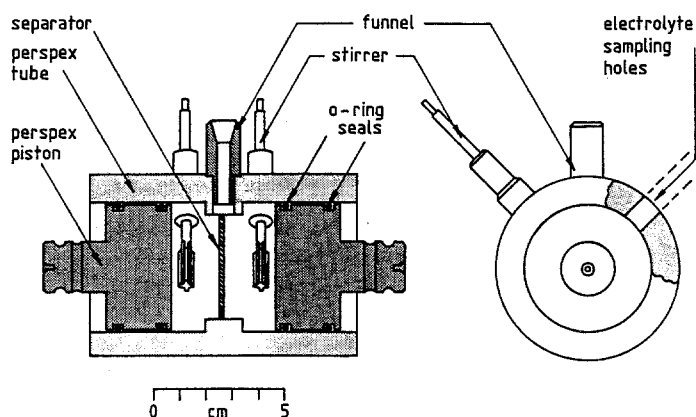


Fig. 1. Cell for transport measurements.

least 24 h prior to use. Pore sizes extracted from trade literature and other sources [4, 5] are also shown in Table 1.

When making a transport measurement, the cell (Fig. 1) was set up with 3.4 M H_2SO_4 throughout, care being taken to ensure that solution levels in the two end compartments were the same and aligned with a horizontal mark on the cell by moving the pistons appropriately. Volumes of solution on either side of the separator were 35 and 50 cm^3 . To begin a run, 25 ml of solution was removed from the larger volume and immediately replaced with the same quantity of solution but containing approximately 10 mg of antimony. Both compartments were stirred vigorously and sampling from both was carried out at intervals: 0.20 and 0.35 ml of solution were removed from the antimony-donating and antimony-receiving compartments, respectively, and replaced with equal volumes of antimony-free solution. The preparation and analysis of solutions were discussed in Part I [6].

Conductivity measurements were made using an apparatus allowing pre-soaked samples of separator to be held under light pressure between two parallel platinized platinum discs. Electrical conductivity of the material was determined using a Wayne Kerr bridge (B642) operating at 1592 Hz. Both transport and conductivity measurements were made in a constant temperature air box operated at 25°C. Thickness measurements were made with a Mercer thickness gauge applying a pressure of $\sim 24 g cm^{-2}$. The concentration of acid used in this work (3.4 M H_2SO_4) was chosen to approximate to the mean value present in a cell undergoing cycling between 0 and 100% states of charge [7].

3. Results and discussion

Diffusion data were interpreted using the relationship derived by Mysels and McBain [8]

$$\frac{\bar{D}A}{\ell} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) t = \ln \left(\frac{C_1 - C_2}{C_1' - C_2'} \right) \quad (2)$$

where A and ℓ are the diffusion area and length (i.e. separator thickness), V_1 and V_2 are the volumes of compartments with concentrations C initially and C' at time t where subscripts 1 and 2 refer to donating and receiving compartments,

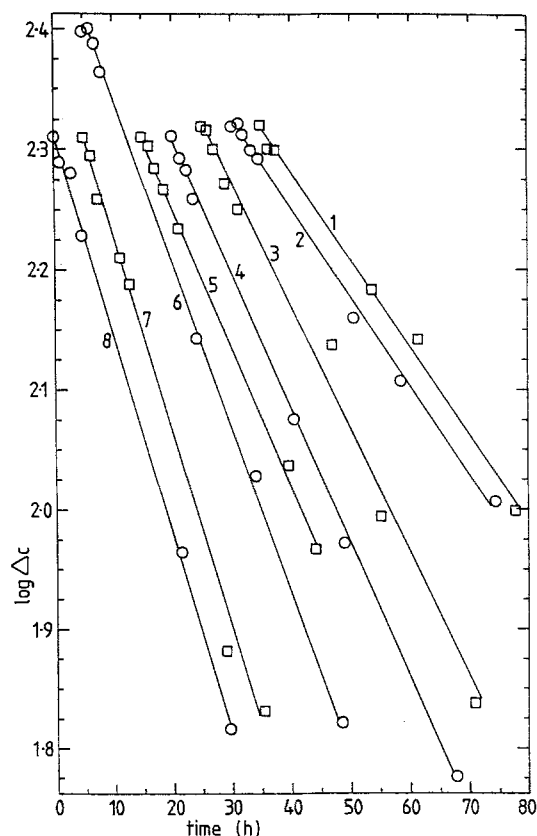


Fig. 2. Transport data plotted according to the equation of Mysels and McBain [8]. Electrolyte, 3.4 M H_2SO_4 ; temperature, 25°C; working area of separators, 9.7 cm^2 except for Evanite Submicro which was 7.0 cm^2 ; Units of ΔC , $\mu g cm^{-3}$. Zeros on time axis incremented at 5 h intervals for clarity. Separator: 1, Varley; 2, Daramic; 3, Porvic 1; 4, Amer-Sil; 5, Ace-Sil; 6, Evanite Submicro; 7, Darak 5000; 8, Darak 2000.

respectively. Equation 2 follows from Fick's first law with the constraint of conservation of mass. Thus a plot of $\log (C_1' - C_2')$ versus t should give a straight line of slope $-\bar{D}A(V_1^{-1} + V_2^{-1})/2.3\ell$ and intercept $\log (C_1 - C_2)$.

Ideally, application of Equation 2 requires that negligible amounts of diffusing substance are removed during the course of a run. In order to approach this in the present work, volumes removed were small (0.4% and 1% of the total volumes in the donating and receiving compartments, respectively, per sampling). Plots according to the above theory are shown in Figs 2-4. In all cases the data fitted the equation well and slopes of the best straight lines through the

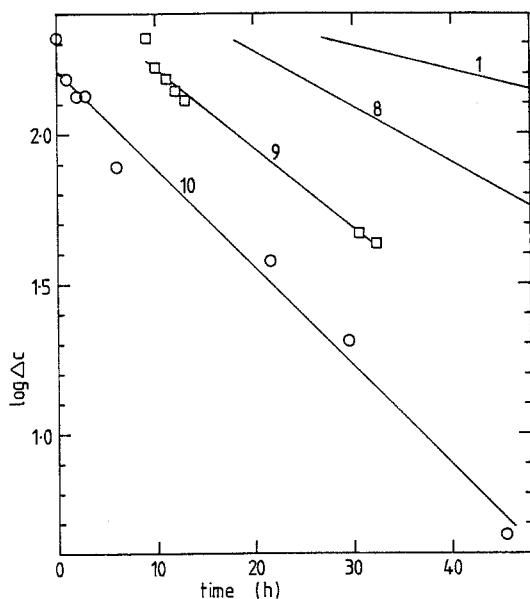


Fig. 3. Transport data for two sintered PVC materials. Details as for Fig. 2; zeros incremented at 9 h intervals. Separator: 9, Jungfer; 10, Porvic 2. Lines for separators 1 and 8 shown for comparison.

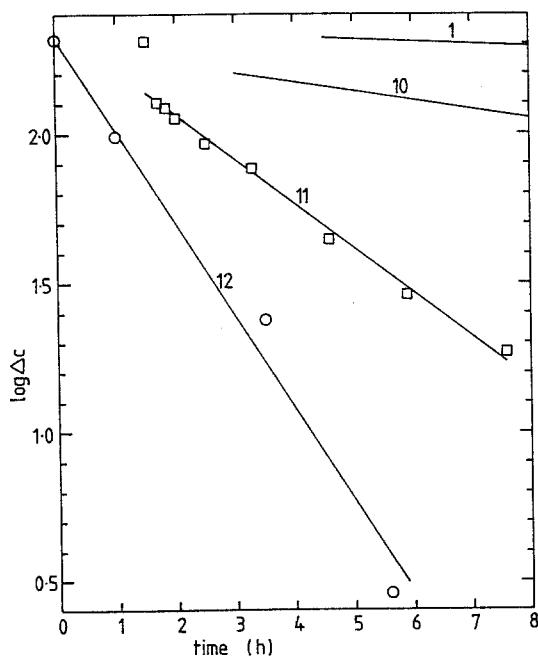


Fig. 4. Transport data for two materials incorporating phenol-formaldehyde resin on a cellulose base. Details as for Fig. 2; zeros incremented at 1.5 h intervals. Separator: 11, Vylam; 12, Darak Armorib AR-60. Lines for separators 1 and 10 shown for comparison.

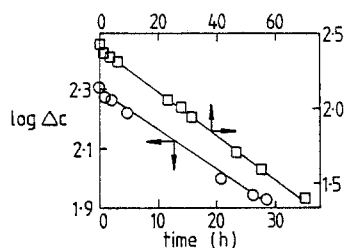


Fig. 5. Transfer of Sb(III) across two separators. □, Evanite Submicro; ○, Amer-Sil; Other details as for Fig. 2.

points were determined by a linear regression analysis.

One run was performed in which 20 layers of Evanite Submicro were interposed between the two compartments. Negligible amounts of antimony were found in the receiving compartment for run times up to 100 h. Use was made of this result in Part II [3]; clearly soluble antimony generated in the cell was transported to a negligible degree from one compartment to the other through the 20 layers of separator. In order to calculate D/\bar{D} values for each separator, a knowledge of D was required for Sb(V) in 3.4 M H_2SO_4 . Dawson *et al.* [9] obtained a value for Sb(III) but no value for Sb(V) could be found in the literature. Consequently a value was determined by invoking the equation

$$(D/\bar{D})_{Sb(III)} = (D/\bar{D})_{Sb(V)} \quad (3)$$

which should be applicable for a given separator. Values of \bar{D} were determined for the two separators, Amer-Sil and Evanite Submicro, which have small pores and for which a diffusive transport mechanism was anticipated: data are presented in Fig. 5 and Table 2 revealing an estimated value for the diffusion coefficient of Sb(V) in 3.4 M H_2SO_4 of $2.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

Ionic conductivity data are shown in Table 3 together with other parameters. A plot of $[(D/\bar{D})/(\kappa/\bar{\kappa})]$ versus pore size is shown in Fig. 6. Clearly for materials with large pores the ratio $[(D/\bar{D})/(\kappa/\bar{\kappa})]$ was small indicating that the major transport mechanism for separators with pores of diameter $> 20 \mu\text{m}$ was convective flow. The driving force for convection in this work resulted from the vigorous stirring induced on each side of the separator. Convective forces are present in a battery during cycling due to gassing and to variations of temperature and

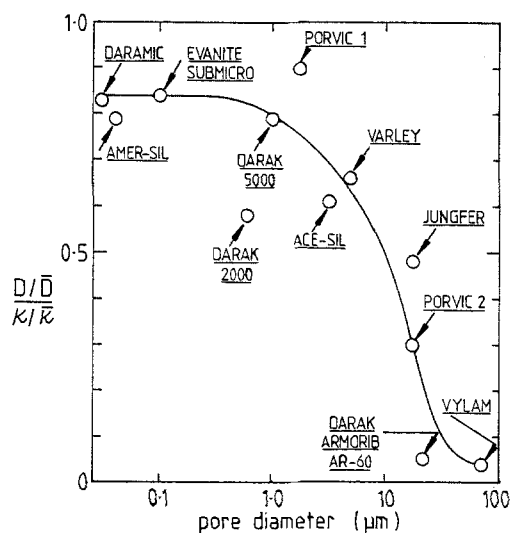
Table 2. Estimation of diffusion coefficient of Sb(V) in 3.4 M H₂SO₄ at 25° C

	Diffusion coefficient ($\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)
$(\bar{D})_{\text{Sb(V)}}$	1.20 ^a 0.77 ^b
$(\bar{D})_{\text{Sb(III)}}$	1.39 ^a 0.82 ^b
$D_{\text{Sb(III)}} [9]$	3.0
$D_{\text{Sb(V)}} \text{ (Equation 3)}$	2.6 ^a 2.8 ^b
$D_{\text{Sb(V)}} \text{ (average)}$	2.7

^a With Amer-Sil separator.^b With Evanite Submicro separator.

concentration of the acid. However, they may not be as great as in the present studies and this is presumably why batteries constructed with separators having large pores may deliver satisfactory performance. At the other end of the pore spectrum (diameters < 2 μm) the transport mechanism was principally diffusion. There was a transitional region (2–20 μm) where transport occurred via a combination of both mechanisms.

A totally diffusive mechanism would be expected to reveal a diffusion to conductivity ratio of unity. The data in Fig. 6 tend to a limiting value of 0.84 which suggests the presence of a systematic error: possibilities include the value of $D_{\text{Sb(V)}}$ deduced or the conductivity determination. Alternatively, the effective thick-

Fig. 6. Plot of $[(D/\bar{D})/(\kappa/\bar{\kappa})]$ versus pore size for determination of transport mechanism.

ness of any particular separator may be less for diffusion than for conductivity [11] particularly where stagnant layers are removed by vigorous stirring in the former case.

Considerably more antimony is released into the solution from the positive grid than from the negative grid [1–3]. Consequently, a separator which inhibits the transport of Sb(V) may be beneficial in slowing the rate of antimony poisoning of the negative active material. The present results would therefore favour the choice of a material with small pores in this particular respect. This prediction appears to be justified

Table 3. Measurements made on commercial separators in 3.4 M H₂SO₄ at 25° C

Separator	Wet thickness (mm)	D/̄D	$\kappa/\bar{\kappa}$	Code number in Figs 2–4
Daramic	0.85	3.2	3.8	2
Darak 2000	0.45	2.7	4.6	8
Darak 5000	0.55	2.2	2.8	7
Darak Armorib AR-60	0.64	0.10	2.1	12
Amer-Sil	0.78	2.3	2.9	4
Ace-Sil	0.86	1.9	3.2	5
Jungfer	0.19	3.8	7.9	9
Evanite Submicro	0.31	3.5	4.2	6
Porvic 1	0.56	3.4	3.8	3
Porvic 2	0.70	0.85	2.9	10
Varley	2.6	1.1	1.6	1
Vylam	0.95	0.13	3.0	11

$\kappa = 0.812 \Omega^{-1} \text{ cm}^{-1}$ [10]. $D = 2.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Table 2).

by results [12] in which the loss of charge after 7 days on open circuit stand at 38°C with various separators increased in the order microporous PVC < sintered PVC < resin-bonded paper. Such an advantage must be balanced against possible disadvantages such as slower wetting rates with smaller pores [5]. Also, antimony released from the negative grid would be less accessible to the positive active material where it could be adsorbed and immobilized [3]. Thus, a reasonable approach might be to eliminate antimony from the negative grid while incorporating an antimonial-lead positive grid.

Implications of this work and design considerations will be discussed more fully in Part IV of this series [13].

4. Conclusions

The mode of transport of Sb(V) through a separator is dependent upon pore size. Mass transfer rates are diffusion controlled for materials with pore diameters below 2 μm.

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