PERFORMANCE OF POROUS PLASTIC SEPARATORS IN ZINC/BROMINE CELLS

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Summary

Bromine transport through a range of acetone-extracted, microporous plastic materials has been studied with reference to their use as separators in zinc/bromine cells. Each separator type was characterized in terms of an equivalent thickness, and values of the latter were determined by a variety of methods

Samples that were acetone-extracted and then either air-dried or hot-water-quenched exhibited equivalent thicknesses that were far less than would be expected from the porosity and tortuosity of the respective materials this was especially true in the presence of a polybromide phase The equivalent thickness could be increased to a value consistent with the physical properties by pretreatment with a surfactant solution, or by incorporating surfactant in the electrolyte

It is shown that the measured faradaic efficiencies of cells are in good agreement with those calculated from the bromine transport properties of the chosen separators

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Introduction

When a zinc/bromine cell is charged, the bromine formed at the positive electrode dissolves to some extent in the electrolyte Should this bromine-containing solution be freely transported to the zinc deposit formed on the negative electrode, then the direct chemical reaction between the two species would cause the cell to exhibit a very high rate of self-discharge. For a cell to be practical, it is therefore essential to include some type of separator to restrict access of bromine to the zinc deposit

Appropriate separator materials range from ion-exchange membranes to microporous plastics In systems where a zinc bromide electrolyte is used, without any complexing agent for the bromine being added, bromine concentrations of up to 2 M can occur, and an ion-exchange membrane is

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required to reduce the bromine diffusion to an acceptable level Separators of this type have been studied extensively [1], but are too expensive for use in practical battery systems

Another approach is to add a quaternary ammonium bromide to the electrolyte [2 - 4] This forms a liquid polybromide addition compound with the bromine generated during charging, and reduces the concentration of aqueous bromine to a sufficiently low level [5, 6] to allow the use of inexpensive microporous plastic separator material

Although both the above methods reduce the bromine flux to the negative electrode, a small amount of bromine is still able to reach and react with the zinc deposit, thus reducing the faradaic efficiency of the cell This will occur even if the zinc is cathodically protected during charging, as suggested by Mader and White [7], since in such a situation any transported bromine will be available for reaction immediately the charging process is terminated Thus, the rate at which bromine passes through the separator must be determined if faradaic and energy efficiencies are to be estimated with any certainty

A model for the rate of transport of bromine to the negative electrode in a cell using a porous separator has been developed by Lee and Selman [8]. These authors have shown that diffusion of bromine through the separator is the rate-controlling factor, and that the transport rate (N_{sep}) of bromine across the separator is given by

$$N_{sep} = \frac{D_{sep}(C_B - C_Z)}{x} \tag{1}$$

where D_{sep} is the effective diffusivity of bromine in the separator, C_B and C_Z are the bulk bromine concentrations in the positive and negative compartments, respectively, and x is the separator thickness Studies have shown that C_Z is small relative to C_B because the rate of reaction of zinc and bromine is rapid compared with the rate of transport of bromine through the separator Van Zee *et al* [9] have presented a simplified model of a zinc/bromine battery, and represent the passage of bromine to the negative by an expression similar to eqn (1)

Thus, the common assumption is that the rate of bromine transport is proportional to the difference in bromine concentrations between the positive and negative compartments Neither of the above mathematical models has considered the effect of a second phase, such as polybromide, on separator performance, it has been assumed that the bromine transport is controlled by the concentration of bromine in the aqueous phase. Nevertheless, polybromide is generated at the positive electrode throughout the charging process, and in at least one battery design [10], it is deliberately dispersed through the aqueous phase of the positive-side electrolyte during discharge in order to enhance the performance of the bromine electrode [11]

Preliminary work in these laboratories showed that, under some circumstances, the rate of bromine transport did not follow the relationship

given by eqn (1), but was nearly independent of aqueous-phase bromine concentration Further, the value of the bromine flux under these conditions was much higher than would be expected from separator properties, and was sometimes accompanied by anomalous ohmic losses in the separator Visual examination of separators removed from such cells showed them to be coated with a polybromide phase, suggesting that the abnormal behaviour might arise from preferential wetting of the separator by this phase Tests showed that cells exhibited a much improved performance when employing a separator that had been pretreated with a surfactant. It was therefore decided to investigate the addition of surfactants to the system in more detail The results of these studies are presented below

Investigations have demonstrated [12, 13] that the residual processing oil usually present in commercially-available separator material causes degradation in battery performance and eventual failure Stable cell operation thus requires extraction of any such oil Consequently, all the work presented in this paper is concerned with the performance of solvent-extracted separators

The effectiveness of the various separator materials in controlling the rate of transport of bromine is expressed in terms of an equivalent thickness, which can be regarded as the thickness of a stagnant layer of electrolyte allowing the same rate of transport of bromine as the separator A large value of the equivalent thickness will reduce the bromine transport but will increase the cell ohmic resistance, thus increasing faradaic efficiency and decreasing voltaic efficiency, respectively Clearly, there is an optimum value of equivalent thickness that gives the highest energy efficiency, this value might be expected to be a function of such factors as temperature, electrolyte composition, and load current

Experimental

Separator characteristics and pretreatment

Six separator materials were tested, all being microporous plastic/silica composites Three consisted of flat Daramic© sheet of different thicknesses (W R. Grace) one was a pillared Daramic of the type described by Exxon investigators [10], one was comprised of Evans Submicro® (Evanite Corp.), while the final example was an experimental proprietary material which we have designated Type C The pillared Daramic is fabricated with an array of short posts formed on the separator to act as an integral spacer The various flat Daramic samples are designated throughout by their nominal thickness Samples of each separator type were analysed by extracting the sample with acetone to constant weight, and then calcining the extracted residue at 600 °C in a platinum dish Silica was determined in the residue from calcination by the loss in weight following evaporation with hydrofluoric and sulphuric acids

Porosity and tortuosity were determined by the water uptake and the diffusion ingress methods, respectively, these are described in detail by Tye

and Vasanthakumar [14] The indirect method of thickness measurement described by these investigators was employed to estimate the average physical thickness, for comparison, thicknesses were also determined with a micrometer These methods are applicable only to flat materials; consequently the pillared material could not be tested for the above properties The surface structure of all the flat materials was examined under an optical microscope

All separators were extracted prior to testing by refluxing acetone over the sample for approximately 15 min. The extracted sample, immediately on removal from the refluxing equipment, was dried in a current of warm air, or plunged into warm (~ 70 °C) water, or immersed in 10 g l^{-1} surfactant solution (~ 70 °C) for at least 15 min Samples given these pretreatments are hereafter referred to as air-dried, water-quenched, and surfactant-treated, respectively

Reagents

Zinc bromide was prepared by reacting reagent-grade hydrobromic acid with zinc oxide, and evaporating the resulting solution to form a concentrated zinc bromide stock-solution of approximately 8.5 M The latter was analysed for both bromide and zinc to ensure that the Br Zn stoichiometry was $2\ 00 \pm 0\ 01$ Working electrolytes prepared from this stock solution normally had a pH of 3 to 4, when necessary, the pH was adjusted by small additions of concentrated hydrobromic acid or sodium hydroxide The two quaternary ammonium bromide (QBr) compounds, *N*-methyl-*N*-ethylmorpholinium bromide (EMMB) and *N*-methyl-*N*-ethylpyrrolidinium bromide (MEPB), were prepared as described in previous papers [6, 15]

Surfactants used included Fluka "purum" grade sodium dodecyl sulphate (SDS), the sodium salts of pentane, octane, and decane sulphonic acids, and technical grade dodecylbenzene sulphonic acid, sodium salt (SDBS) Other surfactants were commercially-available proprietary materials

Equivalent thickness from faradaic efficiency

Small zinc/bromine cells (16 cm^2 electrode area) were charge/discharge cycled, and the bromine transport across the separator estimated from the measured values of the charge and the discharge capacity. The cell design has been described previously [6], and, in brief, consisted of a two-section polypropylene unit that allowed a porous plastic separator to be located between the electrodes, such that a nominal gap of 0 7 mm was maintained between each electrode and the face of the separator Electrolyte was circulated from external reservoirs by means of small nutating-disc pumps; a flow rate of about 2 cm^3 s^{-1} was sufficient to disperse any polybromide throughout the aqueous phase. If a polybromide phase was present, both reservoirs were of 35 cm^3 working volume, but when zinc bromide alone was used, the volume of the positive-side reservoir was increased to 325 cm^3 This increase in volume allowed the use of low bromine concentrations while maintaining an acceptably small variation in bromine concentration throughout the cycle

Zinc/bromine systems often employ an electrolyte in which the zinc bromide concentration varies between 3 M and 1 M as the system is taken from the discharged state to full charge Consequently, the mid-range zinc bromide concentration of 2 M was chosen for this study

For some tests, a QBr compound was incorporated into the electrolyte in order to form a polybromide phase, and one of the two compounds mentioned above (EMMB and MEPB) was employed when such an addition was required When either of these compounds was added, the positive-side electrolyte was prepared by reacting 35 cm^3 of a 2 M zinc bromide, 1 M QBr solution with 0 035 mole of bromine, this simulated the composition that would be obtained in a cell with an electrolyte initially 3 M in zinc bromide and 1 M in QBr when half-charged. The negative electrolyte consisted of 35 cm^3 of 2 M zinc bromide with sufficient QBr added to simulate that present in the aqueous phase of the positive-side electrolyte, the values used were 0 33 M for EMMB [15] and 0 15 M for MEPB

For solutions without any QBr, the positive-side electrolyte was made 0 05 - 0.08 M in bromine, while the negative electrolyte was a simple 2 M zinc bromide solution For all electrolytes used in cycle tests, 7×10^{-5} M lead was added, in the form of chloride, to improve the quality of the zinc deposit [16]

Studies were carried out using a titanium sheet negative and a plastic-bonded-carbon positive electrode [11] For tests using flat separator material, plastic spacer grids were incorporated in the cell to maintain the desired separation between the electrodes and the separator

The test program was· charge at 25 mA cm^{-2} for 2 5 h, discharge at the same current density to a 1.0 V cut-off The cell was then shorted through a 1 ohm resistor for 15 min with the electrolyte circulating (in order to remove any residual zinc), followed by a further 15 min on open circuit without electrolyte circulation When starting with a freshly-prepared electrolyte, it took some time for the bromine concentration in the negative compartment to reach an equilibrium value, so the results of the first cycle were discarded and those of the next three were used to calculate the bromine transport

If it is assumed that (i) the only significant side reaction is the direct reaction of the deposited zinc with bromine that has passed through the separator; (ii) the zinc deposit is completely stripped at the end of each cycle so that there is no accumulation of zinc in the system, and (iii) the zinc deposit is sufficiently smooth not to enter the separator, then it can be shown [17] that

$$I_d = \frac{(Q_C - Q_D)}{t_C A} \tag{2}$$

where I_d is the rate of bromine transport through the separator (expressed as a current density); Q_C and Q_D are the ampere-hours of charge and discharge, respectively, t_C is the total cycle time, and A is the separator area

The equivalent thickness (defined more fully below) can then be calculated from·

$$d = \frac{nFD(C_B - C_Z)}{I_d} \qquad (3)$$

where n is the number of equivalents/mole for the reaction concerned, F is the Faraday constant, D is the diffusion coefficient of bromine in the electrolyte, and the other terms are as defined previously. The necessary D values have been measured by the rotating disc method and have been reported elsewhere [15], namely, $1\,06 \times 10^{-9}$ m^2 s^{-1} for 2 M zinc bromide, $0\,98 \times 10^{-9}$ m^2 s^{-1} for the zinc bromide/MEPB electrolyte, and $0\,79 \times 10^{-9}$ m^2 s^{-1} for zinc bromide/EMMB

The C_B values were the mean of the aqueous-phase bromine concentrations at the beginning and end of charge For the QBr-containing systems, the C_B values were estimated from measured equilibrium data. For the zinc bromide solutions, the C_B value for the discharged condition was determined by analysis of the electrolyte, while that for the charged state was estimated from the known amount of charge passed and the solution volume Since C_Z was small in comparison with C_B (typically 1% - 3%), it was usually set equal to zero for these calculations

All tests were made with the electrolyte temperature controlled to 25 ± 0.3 ℃.

Equivalent thickness from zinc corrosion

If a sheet of zinc foil is substituted for the negative electrode and electrolyte circulated with the cell on open circuit, then the amount of bromine transported to the negative can be estimated by the loss in weight of the zinc. This procedure avoids those uncertainties (inherent in cycle testing) associated with complete stripping of the zinc, and separator penetration by the zinc deposit.

A replica of a negative electrode was prepared from 0.4 mm zinc foil This was weighed, assembled into a cell, and electrolyte circulated under open-circuit conditions for a measured time On completion of the run, the circulation was stopped, the electrolyte drained, and the cell dismantled as quickly as possible, allowing the zinc sheet to be removed, washed in water and acetone, dried, and weighed. Reservoir volumes, electrolyte preparation and spacers were the same as for the cycle test procedures described above

Bromine concentration in the negative reservoir was determined at the end of each test by volumetric analysis The concentration in the positive-side solution was determined in a similar manner at both the beginning and end of each run when zinc bromide solution was used, but this was not possible in the presence of polybromide phase When polybromide was present, the electrolyte was drained into a stoppered cylinder, kept at 25 ℃ until the polybromide phase had settled out, and a sample of the aqueous phase was taken for analysis

The equivalent thickness can be calculated from the relation

$$d = \frac{DA(C_B - C_Z)t_D M_Z}{w} \tag{4}$$

where t_D is the test period, M_Z is the molecular weight of zinc; w is the weight of zinc dissolved, and the other symbols have their previously assigned meanings Note that w must be corrected for any change in the bromine concentration in the negative-side reservoir during the test

In order to test reproducibility, five replicate experiments were made on nominally 0 64 mm thick, flat Daramic that had been surfactant-treated in SDBS solution. The average equivalent thickness was 2 06 ± 0 094 mm, a relative standard deviation of 4.6%

Again, all tests were conducted at a solution temperature of 25 ± 0 3 °C

Equivalent thickness from diffusion cell tests

In the above methods for the direct measurement of equivalent thickness, the bromine transport through the separator was estimated indirectly, either from its effect on faradaic efficiency, or by reaction with zinc foil A more direct approach was to allow the bromine to accumulate in an initially bromine-free compartment and then to calculate the separator equivalent thickness from a knowledge both of the initial and the final bromine concentrations on each side of the separator and of the test period Such tests were carried out using a diffusion cell (Fig 1). This cell took the form of two, flanged, glass half-cells, of 47 mm i d , so that separators from the 16 cm² test cells could be tested intact The volume of each half-cell was approximately 63 cm³ Each of the cell sections was fitted with a B19 cone for filling and sampling, while a PVC flange was cemented onto the glass to allow the two sections to be bolted together The flange was mounted
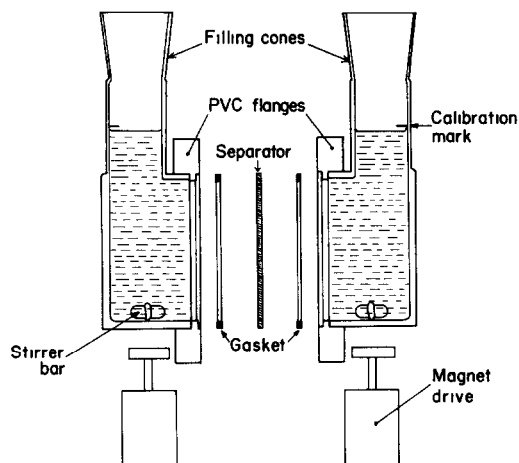

Fig 1 Schematic of diffusion cell

slightly beyond the edge of the glass in order to provide a well for a 0.8 mm flat gasket The solution in each compartment was agitated by a small PTFE-coated magnetic stirrer bar

The test procedure was to assemble the cell with the separator in place Each half-cell was then filled to a calibration mark with 1 M zinc bromide solution which had been equilibrated at the operating temperature The calibration mark on each neck was so located that there was no nett liquid head between the two sides The cell was then placed in the holder in a controlled-temperature cabinet held at 30 ± 0.2 °C, 3 cm^3 of 1 M zinc bromide was added to the low bromine concentration (receiving) side, and 3 cm^3 of approximately 1 M bromine in 1 M zinc bromide to the high bromine concentration (source) side, and the timer started. The cell was then stoppered, a very small gap being left to ensure each side was at atmospheric pressure, and the stirrers started. The test was then continued for the desired time, usually about 3 h On completion of each test, the solutions were transferred simultaneously to 250 cm^3 flasks, the elapsed time noted, the flasks stoppered, and the solutions analysed for bromine content

The equivalent thickness of the separator can be calculated from the relation

$$d = \frac{DAt_D}{\ln\dfrac{\Delta C_1}{\Delta C_2}} \left(\frac{1}{V_1} + \frac{1}{V_2}\right) \tag{5}$$

which is derived from the equations given by Tuwiner [18]. In eqn. (5)· ΔC_1 and ΔC_2 are the initial and final bromine-concentration differences between the two compartments, respectively; V_1 and V_2 are the two half-cell volumes; t_D is the test period; and the other symbols are as defined above

To calculate ΔC_1 , the initial bromine concentration in the source compartment must be known. This was estimated from a bromine balance using the final measured bromine concentrations and the known compartment volumes, a small correction being applied to allow for bromine losses during the test This correction was determined from the results of a series of blank runs performed with a titanium disc replacing the porous separator. To get some indication of reproducibility, four replicate tests were made using the nominally 0.64 mm Daramic material. These showed an equivalent thickness of 1 68 ± 0 031 mm, a relative standard deviation of 1.8%

The diffusion cell method offers the advantages of a self-contained piece of equipment· none of the pumps, fittings, or controls used with the earlier methods, is required However, the method is not well suited for use with solutions having a separate polybromide phase

Equivalent thickness from resistance measurement

All the direct methods of measuring equivalent thickness described above require a knowledge of the diffusion coefficient of bromine in the

solution concerned Although some values for such diffusion coefficients are available [15], there is some uncertainty in the data There is also uncertainty in the value of the aqueous bromine concentration, especially in the presence of a polybromide phase. The combined effects of these two uncertainties is to reduce the accuracy of the derived equivalent thickness. Resistance measurement provides a method for determining the equivalent thickness that does not require a knowledge of either the diffusion coefficient or the aqueous bromine concentration

Since only a fraction of the volume of the separator material is occupied by pores, both the conductivity of the separator and the diffusivity through it will be less than the corresponding values for the same thickness of electrolyte. It is convenient to designate the conductivity and diffusivity of an electrolyte-filled separator by the terms "apparent conductivity" and "apparent diffusivity". Tye [19] has shown that the apparent conductivity (k_{sep}) is related to the solution conductivity (k) by a relationship similar to that which holds between the apparent diffusivity (D_{sep}) and the diffusivity (D) in the bulk solution, namely.

$$\frac{k_{sep}}{k} = \frac{D_{sep}}{D} \tag{6}$$

It will be shown later that equivalent thickness is equal to $(D/D_{sep})x$ which is, expressing the result in terms of resistivity, $(r_{sep}/r)x$, where r_{sep} and r are the apparent and the solution resistivities, respectively Mader and White [7] report Van Zee as having developed a similar relation, the r_{sep}/r ratio is designated the MacMullin number.

The experimental procedure employed the same type of cell design as was used for the cycle and zinc-solution-rate tests The electrodes were made from platinum gauze spot-welded on to titanium backing sheets. The electrolyte was 0.1 M potassium chloride and was circulated through the cell by a twin-head peristaltic pump. Cell resistances were measured with a General Radio 1650A impedance bridge operated at 1 kHz A dilute electrolyte was chosen partly to bring cell resistance values into a convenient range for bridge measurements, and partly to avoid errors that arise when audio frequency measurements are made with concentrated electrolytes and plain (as opposed to platinized) platinum electrodes [20]

The resistance was first measured for a cell without a separator present, and then a second measurement was taken with a separator in place, the interelectrode distance being held constant — that is, the electrolyte path is shorter in the second instance by the physical thickness of the separator Several readings were taken for each individual sample using the parallel impedance (C_p) bridge range, and the equivalent cell series resistance extracted from these data by means of the equations given in the manufacturer's handbook The equivalent thickness was then calculated using the relation

$$d = \frac{A\Delta R}{\rho} + x \tag{7}$$

where ΔR is the difference in the resistance of a cell with and without a separator, ρ is the resistivity of the electrolyte, and the other symbols have their previously assigned meanings Measurements were taken at room temperature, the electrolyte temperature being recorded in order that the appropriate value of ρ was put in eqn (7) To test reproducibility, five determinations were made of the equivalent thickness of the nominally 0 64 mm flat Daramic over a five-month period. The average value was $1\ 70 \pm 0.047$ mm, a relative standard deviation of 2 8%

This method has the advantage of not requiring any analyses, or any knowledge of diffusion coefficients. It is not appropriate, however, for systems containing a separate polybromide phase

Results

Definition of equivalent thickness

The transport of a species is reduced through a separator because diffusion can proceed only through the pores that constitute a fraction of the total volume of the separator. The reduced transport rate will be determined both by the total porosity and by the average tortuosity of the separator material. The effect can be accommodated by using an apparent diffusivity which is less than that in the bulk solution, or by taking the separator material to have an effective (or equivalent) thickness greater than its physical thickness We have chosen to characterize separators in terms of such an equivalent thickness, which may be regarded as the thickness of stagnant electrolyte that will allow the same rate of bromine transport as does the separator Such an equivalent thickness can be defined by the relation

$$Dx = D_{sep}d \tag{8}$$

Note that eqn (8) is based on the assumption that there are no concentration gradients for the species of interest at the interfaces between the separator and either electrolyte. This is postulated since transport through the separator is by molecular diffusion, which is a much slower transport mechanism than the convective transport that prevails throughout the bulk electrolyte in all the cells used in this study [8]

Tye [19] has developed equations relating the apparent diffusivity D_{sep} to the porosity (P) and tortuosity (θ) of the separator material, i e ,

$$\frac{D_{sep}}{D} = \sum_n \frac{P_n}{\theta_n{}^2} \tag{9}$$

where θ_n is the tortuosity factor of an individual pore, and P_n is the volume fraction of pores of tortuosity θ_n More conveniently

$$\frac{D_{sep}}{D} = \frac{P}{\theta_a{}^2} \tag{10}$$

where θ_a is an average porosity defined by

$$\frac{1}{\theta_a{}^2} = \frac{1}{P} \sum_n \frac{P_n}{\theta_n{}^2} \tag{11}$$

For the special case where all pores have the same tortuosity, θ

$$\frac{D_{\text{sep}}}{D} = \frac{P}{\theta^2} \tag{12}$$

The equations relating apparent conductivity to separator characteristics are of the same form as eqns (9) - (12)

Combining eqns. (8) and (10) one obtains

$$d = \frac{\theta_a{}^2}{P} x \tag{13}$$

so that if P, θ_a, and x can be measured (as, for example, in ref 14) then d can be calculated.

Separator characteristics

The results of the measurements of separator characteristics are presented in Table 1 It can be seen that most of the samples contain approximately 15 wt.% of oil prior to extraction, even the pillared Daramic, which has already been extracted [12, 13], still contains 1 - 2% Examination by proton-NMR showed the extracted materials to be of the paraffin type, except for that from the Type C sample, which was an aliphatic phthalate, probably dioctyl phthalate In all the materials, the silica support is relatively pure; the residue after hydrofluoric acid volatilization being only about 1 4 wt % of the initial sample We were not able to characterize the plastic component

The values measured for porosity were, in general, somewhat above the 50% given in the individual manufacturer's data This may be a consequence of the extraction The thickness when measured by a micrometer was greater than that determined by the water absorption method This observation is in agreement with the findings of Tye and Vasanthakumar [14], and is expected for rough surfaces because the micrometer method yields the maximum value of thickness, that is, the thickness as measured across the roughness peaks Since transport rate through the separator is most likely a function of the average thickness, the water absorption method should give a more relevant value Optical examination confirmed that the separator surfaces were relatively rough

Equivalent thickness effect of surfactants

The equivalent thicknesses of separator samples that had been acetone-extracted and then either air-dried or water-quenched are given in Table 2 for electrolytes having a separate polybromide phase The data were obtained using the zinc-solution-rate procedure. It can be seen that there are considerable differences in the equivalent thickness values obtained for

TABLE 1

Separator characteristics

| Separator | Analysis (wt %) | | | Physical properties | | | |
	Acetone extractable	Silica	Non-silica solids	Porosity (%)	Tortuosity factor	Thickness (mm) Micrometer	Water absorption
0 25 mm Daramic	15 2	52 6	1 2	36 4	1 39	0 243	0 15
0 35 mm Daramic	16 1	50 9	1 4	67 7	1 64	0 338	0 27
0 64 mm Daramic	18 9	49 4	1 5	64 7	1 48	0 594	0 54
Pillared Daramic	1 4	59 6	1 5	†	†	0 626*	†
Submicro	12 2	57 2	1 6	69 4	1 52	0 673	0 66
Type C	12 6	40 7	1 0	52 4	1 57	0 590	0 52

*Web thickness
†Technique for porosity and tortuosity measurement applicable only to flat material

TABLE 2

Effect of pretreatment on separator equivalent thickness

Separator	Physical thickness* (mm)	Equivalent thickness (mm)			
		EMMB electrolyte		MEPB electrolyte	
		Dried	Water quenched	Dried	Water quenched
0 25 mm Daramic	0 15	0 21	0 32	0 11	0 18
0 35 mm Daramic	0 27	0 35	0 47	0 21	0 21
0 64 mm Daramic	0 54	0 76	0 95	0 45	0 63
Pillared Daramic	†	0 83	0 96	0 41	0 49
Submicro	0 66	1 14	1 49	0 86	0 91
Type C	0 52	1 95	1 80	1 33	1 30

*Water absorption data from Table 1
†See note, Table 1

EMMB- and MEPB-containing electrolytes From substitution of the measured porosity and tortuosity (Table 1) in eqn (13) the ratio of equivalent to physical thickness should be approximately 4 Only the Type C material approaches this ratio, and then only for the EMMB-containing electrolyte. In most cases, the water-quenched material shows a greater equivalent thickness than the air-dried counterpart

The calculated rate of bromine transport through each type of separator in either an EMMB or MEPB system is presented in Table 3. The data show that the rate is generally about the same in both electrolytes This finding is unexpected since the aqueous-phase bromine concentrations were 0 080 M (EMMB) and 0.036 M (MEPB), and after correction for the difference in diffusion coefficient between the two systems, the bromine

TABLE 3

Effect of separator pretreatment on bromine transport rate results for systems having a polybromide phase

Separator	Bromine transport (10^{-8} mole cm^{-2} s^{-1})			
	Air-dried		Water-quenched	
	EMMB system	MEPB system	EMMB system	MEPB system
0 25 mm Daramic	2 91	2 50	1 73	1 70
0 35 mm Daramic	1 69	1 50	1 18	1 40
0 64 mm Daramic	0 86	0 74	0 64	0 52
Pillared Daramic	0 85	0 80	0 59	0 66
Submicro	0 63	0 41	0 44	0 34
Type C	0 38	0 28	0 36	0 24

transport rate should be 1 8 times greater in the EMMB-containing electro-lyte It was observed that these separators, after use in the cell, were coated with a near-continuous film of polybromide phase on the positive-facing side, and were impregnated with a yellow material, presumably adsorbed polybromide The bromine concentration in the polybromide phase was similar for both electrolytes, being 5 25 M and 5.5 M for the MEPB- and EMMB-containing electrolytes, respectively

The apparent independence of the rate of bromine transport on the difference in aqueous bromine concentration across the separator was further tested using a 2 M zinc bromide solution (i e , no polybromide phase) with 0 64 mm Daramic separator material, in both the air-dried and water-quenched states, the bromine concentration in the positive compart-ment was varied between 0 02 and 0 1 M Bromine transport rates (measured by the zinc-solution-rate method) are presented in Fig 2 as a function of bromine concentration The results show that for these polybromide-free solutions the transport rate is directly proportional to bromine concentra-tion, and also that the water-quenched material exhibits a significantly lower transport rate (i.e , has a greater equivalent thickness) than the air-dried material The values for equivalent thickness, which are independent of the bromine concentration, are 0 77 mm for the air-dried and 1.45 mm for the water-quenched samples
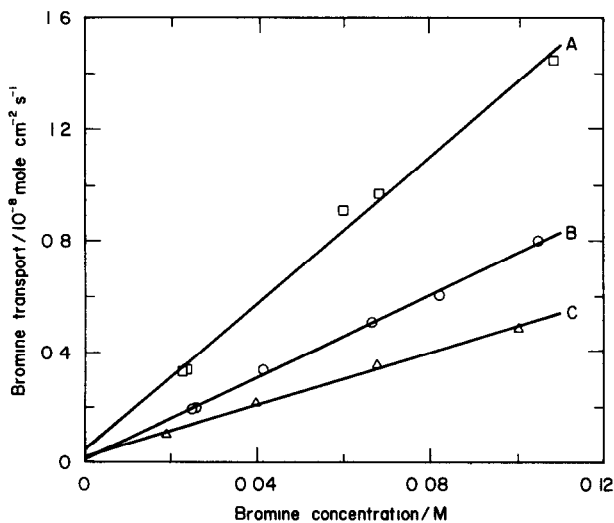

Fig 2 Rate of bromine transport through 0 64 mm Daramic in 2 M zinc bromide solu-tion A, air-dried separator, B, water-quenched separator, C, surfactant-treated separator

The presence of the film of polybromide on the separator surface, and the apparent adsorption of polybromide within the separator, suggested that the low equivalent thicknesses might be due to preferential wetting of the separator material by the polybromide phase To test this hypothesis, samples of the 0 35 mm Daramic were acetone-extracted, immersed for

about 15 mm in a 10 g l^{-1} solution of a given surfactant held at 70 $^{\circ}$C, rinsed, and cycle-tested using an EMMB-containing electrolyte. The equivalent thickness values estimated from the charge/discharge data are listed in Table 4 The results clearly show that treatment with the long-chain sulphonate and organic sulphate compounds (i e , SDBS and SDS) causes a considerable increase in equivalent thickness, as does the use of phosphate ester and Triton X-100® (octyl phenoxy polyethoxy ethanol) Pretreatment with SDBS was selected for more detailed study

TABLE 4

Separator equivalent thickness following pretreatment with various surfactants

Surfactant			Equivalent thickness (mm)[†]
Type	Chemical identity	Class	
No surfactant*	—	—	0 28
—	Pentane sulphonic acid, sodium salt	Anionic	0 33
—	Octane sulphonic acid, sodium salt	Anionic	0 33
—	Decane sulphonic acid, sodium salt	Anionic	0 49
—	Dodecylbenzene sulphonic acid, sodium salt (SDBS)	Anionic	0 88
—	Sodium dodecylsulphate (SDS)	Anionic	0 75
Gafac® RA-600	Phosphate ester	Anionic	0 95
Miranol® C2M	Fatty imidazoline derivative	Amphoteric	0 64
Triton® X-100	Octyl phenoxy polyethoxy ethanol	Nonionic	0 85

*Water-quenched separator
[†]For 2 M $ZnBr_2$/EMMB electrolyte

Table 5 presents the results of equivalent thickness determinations using the zinc-solution-rate procedure on a range of separator materials that had been pretreated by acetone extraction and treatment with SDBS The data cover systems with and without a separate polybromide phase present Aqueous-phase, positive-side bromine concentrations were 0 057 M, 0 080 M and 0 036 M for the 2 M zinc bromide, the EMMB-containing, and the MEPB-containing electrolyte, respectively By comparison with data presented in Table 2, it is confirmed that pretreatment with surfactant causes a considerable increase in separator equivalent thickness Further, the equivalent thickness is now independent of the bromine concentration difference across the separator, irrespective of whether a separate polybromide phase is present, or a simple zinc bromide solution is used (see curve C, Fig 2) It was noticeable also that the separators were quite clean when the test cell was disassembled, with only a few isolated drops of adhering polybromide that drained from the surface quite readily. There was no sign of the absorbed yellow compound seen with the air-dried or the water-quenched pretreatments

TABLE 5

Effect of pretreatment with SDBS on separator equivalent thickness

Separator	Equivalent thickness (mm)		
	2 M ZnBr$_2$ (no polybromide)	Polybromide (EMMB)	Polybromide (MEPB)
0 25 mm Daramic	0 73	0 69	0 75
0 35 mm Daramic	1 04	0 97	1 01
0 64 mm Daramic	2 06	2 02	1 92
Pillared Daramic	1 98	2 10	2 22
Submicro	2 14	2 36	2 40
Type C	2 54	2 67	2 89

Addition of surfactant to electrolyte

In the work described above, the separator was modified by pretreatment with a surfactant An alternative and possibly effective procedure would be to add surfactant to the electrolyte For example, Bellows *et al* [21] in their description of a 30 kW h electric-vehicle battery mention the use of an unstated additive which improved faradaic efficiency from 60% to 90% It was therefore decided to examine the possibility of direct addition of surfactant to the electrolyte

Preliminary tests were made using 0 35 mm Daramic with a 2 M zinc bromide/EMMB electrolyte incorporating 1 g l^{-1} of the desired surfactant The equivalent thickness was estimated from cycling tests Since many surfactants precipitate when added to this electrolyte, testing was confined to three compounds The results are shown in Table 6 As SDS proved to be the most effective additive, this surfactant was studied in more detail

The equivalent thickness of a range of separator materials was evaluated, using the zinc-solution-rate method, for the same range of electrolytes as was employed with the surfactant-pretreated samples. In the present instance, however, all separator samples were water-quenched before testing,

TABLE 6

Separator equivalent thickness with various surfactants as electrolyte additives

Name	Surfactant		Equivalent thickness (mm)[†]
	Chemical identity	Class	
No surfactant*	—	—	0 28
—	Decane sulphonic acid, sodium salt	Anionic	0 42
—	Sodium dodecylsulphate (SDS)	Anionic	0 99
Miranol® C2M	Fatty imidazoline derivative	Amphoteric	0 38

*Water-quenched separator
[†] 2 M ZnBr$_2$/EMMB electrolyte

TABLE 7

Separator equivalent thickness with surfactant in electrolyte

Separator	Equivalent thickness (mm)		
	2 M ZnBr$_2$ (no polybromide)	Polybromide (EMMB)	Polybromide (MEPB)
0 25 mm Daramic	0 69	0 72	0 72
0 35 mm Daramic	0 99	1 01	1 00
0 64 mm Daramic	1 85	1 84	1 95
Pillared Daramic	1 92	1 81	1 83
Submicro	2 32	2 20	2 20
Type C	2 64	2 25	2 52

and the electrolyte contained 1 g l^{-1} of SDS The resulting equivalent thickness values are presented in Table 7 As found for the surfactant-pretreated separators (Table 5), the equivalent thickness data for the various electrolytes are independent of bromine concentration (0.068 M for 2 M zinc bromide, 0 087 M and 0 036 M for EMMB- and MEPB-containing electrolytes, respectively), and are much greater than the values for corresponding air-dried and water-quenched samples (see Table 2) The absolute thicknesses are quite close to those measured with separator material pretreated with surfactant (Table 5)

Compound separators

A possible approach to preventing the formation of a film of polybromide phase over the bromine-side surface of the separator is to cover it with a thin layer of some other porous substance that is not wetted by polybromide. Qualitative contact-angle tests on readily available materials revealed that filter paper, pre-wetted with water or electrolyte, fulfils this requirement Consequently, a compound separator was prepared by interleaving water-quenched 0 64 mm Daramic between two Whatman No 50 papers, each cut to the same diameter as the Daramic and each pre-wetted with water

When the Daramic alone was tested for equivalent thickness by the zinc-solution-rate procedure, values of 0.61 mm (MEPB-containing electrolyte) and 1 08 mm (EMMB-containing electrolyte) were obtained, in fair agreement with those measured previously (Table 2) As before, the separator was coated with a film of polybromide on the positive-facing side, and stained yellow with adsorbed material If a compound separator was substituted for the Daramic, the equivalent thickness increased to 1 4 mm (MEPB) and 1 5 mm (EMMB), that is, the equivalent thickness is now essentially independent of bromine concentration. Examination of the compound separator on disassembly of the cell confirmed that there was no film of polybromide coating the positive-facing side, although the Daramic section was still noticeably stained with adsorbed polybromide

These results support the explanation that a layer of polybromide phase covering the positive-facing side of air-dried and water-quenched separators is the cause of the equivalent thickness appearing to be a function of electrolyte composition

Estimation of equivalent thickness by different procedures

Most of the values of equivalent thickness quoted in Tables 2 - 7 were measured by the zinc-solution-rate method It is desirable that these results be confirmed by using alternative methods of thickness measurement, it is especially relevant to compare them with corresponding values from charge/discharge cycle testing, as this procedure corresponds most closely to actual battery operation

The values obtained from three of the procedures described earlier, together with the value calculated using eqn (13) and the data of Table 1, are shown in Table 8 for each of the six types of separator material tested Samples used for the zinc-solution-rate and the diffusion-cell methods, and to obtain the data required for the calculated results, were treated in a warm 10 g l^{-1} solution of surfactant Triton X-100 prior to testing The resistance measurement samples were plunged into 70 °C water immediately after acetone extraction, surplus water was removed with tissue, and then the samples were alternately evacuated and repressurized while immersed in a 0 1 M potassium chloride solution containing approximately 1 g l^{-1} of Triton X-100, prior to being tested Agreement between the four sets of equivalent thicknesses is satisfactory, considering the very different experimental procedures used

TABLE 8

Separator equivalent thicknesses comparison of four procedures

Separator	Equivalent thickness (mm)			
	Zinc corrosion[†]	Diffusion cell	Separator resistance	Calculated*
0 25 mm Daramic	0 71	0 73	0 66	0 74
0 35 mm Daramic	1 00	1 02	1 00	1 07
0 64 mm Daramic	1 84	1 68	1 70	1 83
Pillared Daramic	1 87	1 65	1 68	—
Submicro	2 23	1 88	1 87	2 18
Type C	2 57	2 43	2 21	2 43

[†]Electrolyte 2 M $ZnBr_2$, neither QBr nor polybromide present
*Using eqn (13) — see text

A second set of comparisons was made, all tests being performed sequentially on the same set of test pieces For this series, equivalent thickness was evaluated, using cycle-test data, by the zinc-solution-rate method, and from diffusion cell results. The samples for this set were surfactant-

TABLE 9

Separator equivalent thickness comparison of three procedures

Separator	Equivalent thickness (mm)		
	Zinc solution rate*	Cycle testing*	Diffusion cell
0 25 mm Daramic	0 73	0 73	0 99
0 35 mm Daramic	1 04	0 96	1 33
0 64 mm Daramic	2 06	1 86	2 17
Pillared Daramic	1 98	1 88	2 30
Submicro	2 14	2 07	2 59
Type C	2 54	2 10	2 69

*Electrolyte 2 M $ZnBr_2$, neither QBr nor polybromide present Zinc-solution-rate data from Table 5

treated in 10 g l^{-1} SDBS at 70 °C The results are presented in Table 9 It can be seen that the values obtained from cycle testing and by the zinc-solution-rate method are in good agreement, and are quite comparable with the corresponding results of Table 8 However, the values from the diffusion-cell tests were greater than those of either of the other methods, the difference ranges from 12 to 39% as based on the corresponding zinc-solution-rate values, and averages 25% Repeating both the zinc-solution-rate and the diffusion-cell tests confirmed the original values for both procedures.

A further comparison of equivalent thickness evaluations from zinc-solution-rate and cycle-testing procedures was made for electrolytes containing 1 g l^{-1} SDS. These are shown in Table 10, and again there is fair agreement between the two procedures. Overall, for the results presented in Tables 9 and 10, the average ratio of values measured by the cycle test to the corresponding values measured by zinc solution rate is 0 99 with a

TABLE 10

Separator equivalent thickness comparison of zinc-solution-rate and cycle-test procedures

Separator	Equivalent thickness (mm)			
	EMMB electrolyte		MEPB electrolyte	
	Zinc solution rate*	Cycle test	Zinc solution rate*	Cycle test
0 25 mm Daramic	0 72	0 74	0 72	0 79
0 35 mm Daramic	1 01	1 09	1 00	1 09
0 64 mm Daramic	1 84	1 90	1 95	1 98
Pillared Daramic	1 81	1 80	1 83	2 11
Submicro	2 20	2 02	2 20	2 02
Type C	2 25	2 25	2 52	2 12

*Values from Table 7

standard deviation of 0 088, that is, there is no significant difference in the equivalent thicknesses obtained by the two methods

All the above comparisons were made using material that was either pretreated with surfactant or tested using electrolyte which contained surfactant. Since the behaviour of air-dried and water-quenched samples is quite different from that observed in the presence of surfactants, a comparison was made of the results for equivalent thicknesses derived from zinc-solution-rate (Table 2) and cycle-test (Table 11) data It can be seen that, unlike the results for surfactant-treated material, the cycle-test thickness values are much less than (in many cases only about 50%) those estimated by the zinc-solution-rate method If the equivalent thickness of air-dried separator is determined for a 2 M zinc bromide electrolyte ($i e$, no polybromide phase) by both the zinc-solution-rate and cycle-test procedures, the results are as shown in Table 12 It can be seen that the two sets of values are quite similar, which suggests that the difference in equivalent thickness described above is due to the presence of the polybromide phase, presumably through its tendency to wet the separator in the absence of surfactant

TABLE 11

Separator equivalent thicknesses from cycle test data polybromide-containing electrolytes

Separator	Equivalent thickness (mm)		
	MEPB system		EMMB system
	Air-dried	Water-quenched	air-dried
0 25 mm Daramic	0 092	0 099	—
0 35 mm Daramic	0 12	0 13	—
0 64 mm Daramic	0 32	0 40	0 50
Pillared Daramic	0 33	0 27	—
Submicro	0 38	0 58	0 64
Type C	0 86	0 84	0 95

TABLE 12

Equivalent thickness of air-dried separator 2 M zinc bromide electrolyte

Separator	Equivalent thickness (mm)	
	Zinc solution rate	Cycle test*
0 25 mm Daramic	0 29	0 28
0 35 mm Daramic	0 41	0 45
0 64 mm Daramic	0 76	0 72
Pillared Daramic	0 93	0 93
Submicro	1 11	1 00
Type C	2 22	1 84

*Corrected for C_z

In more detail, if the equivalent thickness of a separator is assessed by the zinc-solution-rate method, the sample cycle tested (4 cycles), and the equivalent thickness again evaluated from the zinc solution rate, the second value is very much lower than the first. For example, for 0.64 mm Daramic water-quenched and used with MEPB-containing electrolyte, the initial equivalent thickness was 0 63 mm while the value derived from cycle test data was 0 40 mm, and the subsequent zinc-solution-rate test (carried out immediately on completion of the cycle test) gave a value of 0.29 mm If the separator was then acetone-extracted, water-quenched, and again tested by the zinc-solution-rate procedure, the equivalent thickness was 0.71 mm, in fair agreement with the initial value The marked decrease of equivalent thickness seen after cycling, and its restoration to the initial value following extraction of adsorbed polybromide, suggest that increased penetration of the separator material by the polybromide phase during charge/discharge operation is the cause of the changes seen in equivalent thickness

Effect of separator pretreatment on faradaic efficiency

All the estimates of separator performance have been given in the form of equivalent thicknesses As this may not convey an immediate impression of the consequent faradaic efficiency, Fig 3 shows the calculated faradaic efficiency as a function of equivalent thickness, while Table 13 presents empirical results for one separator material (0.64 mm Daramic) after a range of pretreatments. Results in both cases are for polybromide-containing electrolytes using the test profile and electrolyte compositions described in the experimental section It can be seen, especially from the data of Table 13, that practically useful increases in faradaic efficiency follow both from
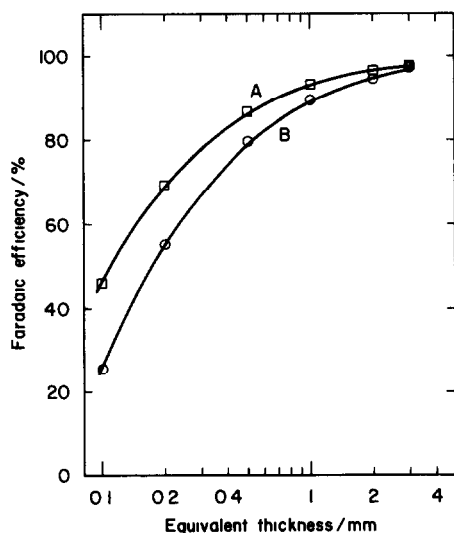

Fig 3 Faradaic efficiency as a function of equivalent thickness Calculated for 2 5 h, 25 mA cm^{-2} charge, discharge at same current density to 1 0 V, 0 5 h between cycles, 25 °C A, MEPB-containing electrolyte, B, EMMB-containing electrolyte

TABLE 13

Effect of separator pretreatment on faradaic efficiency 0 64 mm Daramic

Separator pretreatment	Faradaic efficiency (%)	
	MEPB	EMMB
Air-dried	79 5 ± 0 5	79 3 ± 0 4
Water-quenched	83 3 ± 0 3	83 7 ± 0 3
SDBS-pretreated	96 1 ± 0 2	94 5 ± 0 2
Water-quenched, SDS in electrolyte	96 4 ± 0 1	93 4 ± 0 8

pretreatment with surfactant, and from inclusion of surfactant in the electrolyte.

Stability of surfactant-treated separators

All the equivalent thicknesses reported above resulted from short-term tests, that is, from the one to three hours of a zinc-solution-rate test to the twenty hours required for four charge/discharge cycles. To assess the longer-term stability, the faradaic efficiency of typical cells was monitored over a much longer period of cycling, the constancy of this efficiency being taken as a measure of separator stability

A pillared Daramic separator, pretreated with SDBS, was tested using a 2 M zinc bromide/3 M potassium chloride/MEPB electrolyte The faradaic efficiency averaged 96.5% over 100 cycles, being 96.9% over the first ten and 95.5% over the last ten cycles For the direct addition of surfactant (SDS) to the electrolyte, a sample of water-quenched pillared Daramic was selected Unfortunately, this surfactant precipitates in the presence of 3 M potassium chloride, so it was necessary to substitute ammonium chloride for the potassium salt This reduces precipitation of the surfactant, but the average aqueous-phase bromine concentration over the whole cycle is increased to about 0 075 M from about 0.04 M, and the faradaic efficiency is, in consequence, lower than that with the potassium chloride electrolyte. Over a 50 cycle test, the average efficiency was 93 6%, the first ten cycles averaging 93 9% and the last ten 93 3%.

The above results indicate a promising level of stability for the separators In a practical battery, however, it would be necessary to maintain performance for at least 500 - 1000 cycles, so that longer-term testing is necessary

Untreated separators

A short test series was made using separator material in the as-received condition The equivalent thickness was measured, for an EMMB-containing electrolyte, by the zinc solution rate method, and also estimated from cycle-test data The results are shown in Table 14. It can be seen that the equivalent thicknesses are much greater than those for air-dried or water-quenched

TABLE 14

Performance of untreated separators

| Separator | Equivalent thickness (mm) | | |
| | Zinc solution rate | | Cycle testing |
	EMMB system	MEPB system	EMMB system
0 25 mm Daramic	0 74	0 32	0 70
0 35 mm Daramic	1 15	0 71	1 02
0 64 mm Daramic	2 34	1 51	1 66
Pillared Daramic	0 99	0 77	0 59
Submicro	2 26	1 26	₁ 69
Type C	3 03	2 26	1 90

samples (Table 2), and approximate to the values exhibited by surfactant-treated material (Table 5) The only exception to this is the pillared Daramic, this finding is consistent with previous results since it was in the extracted condition when received

Cell resistance was noticeably higher with the as-received samples For the six separator types examined, the increase in resistance averaged $1\ 8 \pm 0\ 8$ ohm cm^2 At a current density of 25 mA cm^{-2}, this would correspond to an increase in charging voltage of 0.045 V, and a corresponding decrease in cell voltage on discharge, $i e$, a loss of about 5% in voltaic efficiency

A film of polybromide phase covered the positive-facing side of the untreated separators, similar to that observed with the air-dried and water-quenched samples. Consistent with this, equivalent thicknesses measured when using MEPB-containing electrolytes were much lower than those for the corresponding EMMB-containing systems (Table 14).

In view of the tendency of polybromide phase to wet the untreated separator material, the relatively large equivalent thickness values are difficult to explain The presence of residual processing oil would reduce porosity, but the value quoted for porosity in the manufacturer's manual, namely, 50% - 55%, is only slightly less than that measured for most of the extracted material, and could not account for the magnitude of the increase in equivalent thickness If the suggestion is correct that the additional path for bromine transport in air-dried separator is via bromine adsorbed on the separator material, it may be that the processing oil is sufficiently strongly held to prevent adsorption of bromine, which would eliminate this hypothesized transport mechanism

Zinc dissolution during charging

In the mathematical model for the zinc/bromine cell on charge derived by Mader and White [7], it is assumed that the zinc becomes passive when the cell is charging, that is, there is no reaction with any bromine diffusing

through the separator from the positive compartment However, in a study of zinc corrosion in the zinc/bromine cell, Lee and Selman [8] assume that the zinc deposit reacts rapidly with bromine, regardless of the state-of-charge. Knowledge of the actual behaviour of the zinc is necessary if the equivalent thickness is to be calculated from cycle-test data, as the total quantity of bromine which diffuses through the separator will be decreased if the zinc becomes passive during the charging part of the cycle

Observation of the negative electrolyte reservoir has shown that the bromine concentration reaches a low and steady value soon after the commencement of charging. Since a continuous increase in bromine concentration would be expected if the zinc were passive, this suggests that the zinc deposit does indeed react with the bromine reaching the negative compartment To test this further, a cell was charged at 25 mA cm^{-2} for 4 h, and at the end-of-charge was drained, disassembled, and the zinc deposit weighed The weight of deposit was compared with that calculated from the amount of charge passed less the charge equivalent of the bromine diffusing through the separator (as calculated from the measured initial and final bromine concentrations, the diffusion coefficient of bromine, and the equivalent thickness of the separator). The result, expressed as the faradaic efficiency of zinc deposition, was 97.9% for the direct determination from the deposit weight, and 97.3% for the calculation from the amount of charge and the estimated bromine diffusion, these two values are in fair agreement.

An alternative procedure is to compare the actual bromine concentration in the end-of-charge electrolyte with that which should be present if no reaction with zinc took place; this latter value can be estimated from the measured positive-side bromine concentrations, the diffusion coefficient, and an estimate of the equivalent thickness ([18], eqns (13) and (14)). In the above test, the actual end-of-charge negative-side bromine concentration was 6.6×10^{-4} M, while the expected value for no reaction was $4 25 \times 10^{-2}$ M, a factor of 64 greater than that measured.

The above results indicate that bromine diffusing through the separator during charging reacts relatively rapidly with the zinc deposit.

Discussion and conclusions

The faradaic efficiency of a zinc/bromine cell is controlled by the rate at which bromine can pass through the separator material. It is therefore important to determine the rate, and this has been done for a range of commercially-available products. These have been specified in terms of equivalent thickness, which may be regarded as the thickness of a layer of stationary electrolyte that would have the same bromine transport rate as the separator.

All the separators examined in this study were composed of microporous polyolefin having finely-divided silica incorporated as a support. Six different separators were used: three different thicknesses of flat Daramic; a "pillared" Daramic; and two other flat materials, Submicro and

Type C All except for the pillared Daramic contained considerable pro-
cessing oil (Table 1): the pillared Daramic had been solvent extracted to
remove the bulk of this oil [12, 13] All separator materials were charac-
terized for porosity and tortuosity factor [14]. Since it has been shown that
it is desirable to remove processing oil to prevent degradation in electrode
performance [12, 13], most samples tested in the present work were acetone
extracted before measurements of equivalent thickness were made

With a 2 M zinc bromide solution, it was found that the equivalent
thickness was least for material that had been air-dried after extraction,
while hot water treatment of the extracted separator (termed water-
quenching) substantially increased the thickness, and treatment with a
surfactant gave a further increase. In all cases, the bromine transport rate
was proportional to bromine concentration difference across the separator
(Fig 2), that is, the equivalent thickness was independent of bromine
concentration If the electrolyte contained a quaternary ammonium bro-
mide, so that a separate polybromide phase appeared in the positive-side
compartment, results were quite different In this situation, the equivalent
thickness for the air-dried and water-quenched samples was again relatively
low, there being little difference between the two values, and appeared to
become dependent upon the aqueous-phase bromine concentration differ-
ence If the separators were pretreated with surfactant, there was a marked
increase in equivalent thickness which then became independent of bromine
concentration The absolute values of thickness for the surfactant-treated
samples were similar for both the zinc bromide solutions and those having
a polybromide phase present. Further, the thickness values were the same
for water-quenched samples when 1 g l^{-1} of surfactant was added to the
electrolyte Air-dried and water-quenched samples tested in the presence of
polybromide were consistently found to be covered on the positive-facing
side with an adherent layer of polybromide phase, and appeared also to show
a considerable adsorption of the polybromide phase throughout the separa-
tor. These effects were not seen with surfactant-treated separators. The varia-
tions in equivalent thickness described were obtained with all the different
separator samples tested. However, the difference in performance between
the air-dried and surfactant-treated cases was most marked for the Daramic
material and least apparent with the Type C separator.

Most of the above-described observations were obtained from zinc-
solution-rate tests. In order to confirm that this procedure gave an accurate
measure of equivalent thickness, the latter was determined by two indepen-
dent methods, namely, by using a diffusion cell and by resistance measu-
rement, and these results were further compared with those calculated from
measured values of porosity and tortuosity (Table 1). Agreement is generally
satisfactory: compared with zinc-solution-rate results, the diffusion cell,
the resistance, and the calculated thickness methods show ratios of 1 06 ±
0 16, 0.91 ± 0 06, and 1 01 ± 0.05, respectively. Further, thickness values
were compared with those estimated from cycle test data, and it was found
that for surfactant-treated separators the ratio to zinc-solution-rate results

averaged 0.99 ± 0.09 However, with the air-dried and water-quenched material the thicknesses found in the presence of polybromide were much smaller than those found by the zinc-solution-rate procedure (Tables 2 and 11). This does not appear to be due to errors in the measurement of thickness, but to a real difference in separator behaviour under cycle-test conditions, since independent measurements of thickness made before and during testing show a decrease in the equivalent thickness This change cannot be attributed to degradation of the material because if the separator is removed from the cell, re-extracted and dried (or water quenched), then the original equivalent thickness (as determined, say, by the zinc-solution-rate procedure) is restored

These findings have been unexpected. Models for zinc/bromine performance derived in the literature [7 - 10] assume that the bromine transport rate through the separator is directly proportional to the bromine concentration difference across the separator, and ignore any effects of pretreatment or of the presence of a polybromide phase. The results presented above show that these factors must be taken into consideration

There is little indication as to the mechanism that causes the increased bromine transport shown by the air-dried or water-quenched material over that which has been surfactant-treated As it seems unlikely that the various pretreatments would change the porosity or tortuosity of the separators, the equivalent thickness should not change with pretreatment. However, quite large changes were observed, and thus some additional, parallel path must be present for bromine transport across the separator. It is possible that some air could be retained in the air-dried separators when these were exposed to electrolyte, but this would tend to decrease the porosity and, hence, increase the equivalent thickness The only other suggestion which can, tentatively, be put forward is that there is adsorption of bromine within the separator, followed by surface migration. It thus appears that the adsorption of surfactant blocks that of bromine Whatever the mechanism, an additional effect must occur in the presence of polybromide, since the bromine transport rate then becomes independent of the positive-side aqueous-phase bromine concentration This seems to be related to the formation of an adherent film of polybromide phase on the positive-side face of the separator The polybromide has approximately the same bromine concentration whichever quaternary ammonium bromide is used, and the concentration in this adhering film presumably controls the bromine transport through the separator. We can put forward no hypothesis as to the transport mechanism under this condition

Since there is a large difference in bromine transport through air-dried and surfactant-pretreated separators — a factor of about 7 for the most strongly affected material — there is a marked increase in faradaic efficiency between cells using these materials, typically from 83% for the dried to 96% for the surfactant-treated. Thus, the use of surfactants is essential if satisfactory cell efficiency is to be attained when using separator material that has been extracted to remove processing oil

The surfactant effect can be achieved either by pretreatment of the separator in surfactant solution, or by addition of the surfactant to the electrolyte. Similar values of equivalent thickness and, hence, faradaic efficiency, result from each of these procedures, but the direct addition method places limitations both on the range of surfactants that can be used, and on the electrolyte composition, if precipitation of the surfactant is to be avoided. Therefore, pretreatment is probably the preferred approach, providing that separators so treated maintain their equivalent thickness for an acceptable period of service.

It is interesting to note that untreated separator material exhibits equivalent thickness values comparable with those displayed by surfactant-pretreated samples Cell resistance is higher, however, with the untreated material, and extraction plus surfactant-pretreatment could be desirable from the aspect of increased overall efficiency, quite apart from the requirement for extraction to prevent deterioration in electrode performance

Finally, only a small range of surfactants has been examined in this study. Of these, four were effective in increasing the equivalent thickness to a satisfactory value: three of them anionic and the other non-ionic It is quite possible that other surfactants would be effective also, and work to find such compounds would seem desirable, *e g* , to find compounds which can be added directly to the electrolyte without requiring any changes in its composition

Acknowledgements

List of symbols

A	Separator cross-sectional area
C_B	Bromine concentration in aqueous phase, bromine (positive) compartment
C_Z	Bromine concentration, zinc (negative) compartment
d	Equivalent thickness of separator material
D	Diffusion coefficient for bromine in bulk electrolyte
D_{sep}	Apparent diffusion coefficient for bromine in the electrolyte-filled separator material
F	Faraday constant
I_d	Bromine transport rate through the separator, expressed as a current density

k	Specific conductivity of bulk electrolyte
k_{sep}	Apparent specific conductivity of electrolyte-filled separator material
M_Z	Atomic weight of zinc
n	Equivalents per mole
P	Volume fraction of pores in separator
P_n	Volume fraction of pores of tortuosity θ_n
Q_C	Charge capacity
Q_D	Discharge capacity
r	Solution resistivity
r_{sep}	Apparent solution resistivity of electrolyte-filled separator material
ΔR	Difference in cell resistance with and without separator present
ρ	Resistivity of 0.1 M potassium chloride solution
x	Physical thickness of separator
t_C	Total cycle time
t_D	Test period, zinc-solution-rate and diffusion-cell tests
w	Weight of zinc dissolved, zinc-solution-rate procedure
θ_a	Average tortuosity factor for all pores
θ_n	Tortuosity factor for an individual pore

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