

## PERFORMANCE OF ZINC/BROMINE CELLS HAVING A PROPIONITRILE ELECTROLYTE

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### Summary

A study has been made of a small, zinc/bromine, circulated-electrolyte cell having a propionitrile-based electrolyte on the positive side and an aqueous electrolyte on the negative. It has been shown that the faradaic efficiency is approximately 50% when using a microporous plastic separator, but this increases to nearly 90% if the separator is changed to a filter paper/microporous plastic compound type. A small, further increase in faradaic efficiency can be obtained by incorporating a quaternary ammonium bromide into the propionitrile phase. In addition, some information is presented on cell resistance and the effect of temperature and discharge current density on cell performance.

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### Introduction

One of the main difficulties to be overcome in the realization of a zinc/bromine cell is control of the rate of bromine transport to the zinc electrode. Because of the rapid reaction of bromine with zinc, this rate must be restricted to a low value if a satisfactory faradaic efficiency is to be attained. If the bromine liberated during charging is allowed simply to dissolve in the electrolyte, then relatively high concentrations ( $\sim 2$  M) will result, and an ion-exchange membrane will be required to restrict the bromine transport to an acceptable value. Such cells have been described by Will [1]. Since suitable ion-exchange membranes are expensive, other methods of controlling the bromine transport have been sought.

A common approach has been to incorporate a quaternary ammonium bromide in the electrolyte. If correctly chosen, a liquid polybromide phase is formed which incorporates the major part of the bromine formed during charging, and the aqueous phase in contact with this polybromide has only a relatively low ( $\sim 0.1$  M) bromine concentration. Under these conditions, an inexpensive, porous, plastic separator is sufficient to restrict bromine trans-

port to an acceptable rate [2 - 5]. In this paper, such cells will be termed 'polybromide systems'.

An alternative procedure for obtaining an aqueous phase that is low in bromine has been described by Singh *et al.* [6, 7]. The method involves the use of propionitrile (PN) as a solvent for bromine. This nitrile is immiscible with water, inert towards bromine, and an excellent solvent for the  $\text{Br}_3^-$  ion. Also, since the partition coefficient for bromine between the PN and aqueous phases is of the order of 10 - 40 for a typical battery electrolyte [6], a zinc/bromine cell based on a PN/water two-phase solvent should show low rates of bromine transport to the zinc electrode and a low rate of self-discharge. Further, charge-transfer complexes are formed with bromine in PN [7, 8] that give solutions of good conductivity. This means that voltage losses due to ohmic effects may be acceptable.

Singh *et al.* [6] have outlined a cell design in which the PN phase is circulated over the positive electrode and the aqueous phase over the negative, the phases being prevented from mixing by a microporous plastic separator. However, although there are considerable data available on the physical chemistry and electrochemistry of this system [9], there is little information as to cell performance. In this work, measurement has been made of the performance of a small zinc/bromine cell of the configuration shown in Fig. 1; the results are compared with those reported previously for polybromide systems.

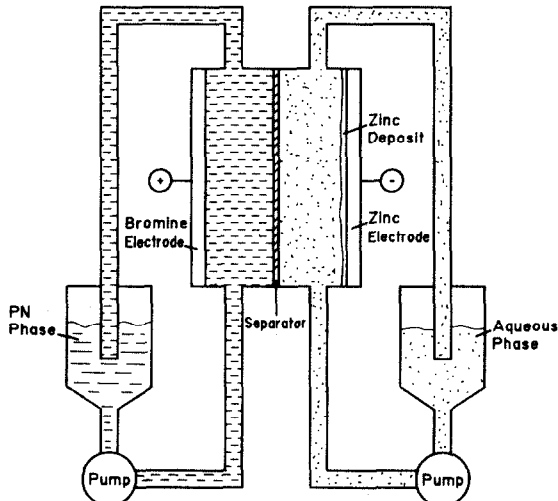


Fig. 1. Diagram of zinc/bromine cell with a propionitrile electrolyte.

## Experimental

### Cell design

The cell design has been described previously [10]. Briefly, the cell consisted of a two-section polypropylene body that allowed a microporous

plastic separator to be located between the electrodes, such that there was a nominal 0.7 mm gap between each electrode and the face of the separator. Electrolyte was circulated from external reservoirs of 35 cm<sup>3</sup> working volume by SPM-100, all-PTFE, nutating-disc pumps (Fluocarbon Inc., Anaheim, California); the connecting tubing and fittings were also of PTFE. The electrolyte flow rate was about 2 cm<sup>3</sup> s<sup>-1</sup>.

A titanium disc, 50 mm in diameter and 1 mm thick, was used as the negative (zinc) electrode. The positive electrode comprised either a similar disc having a platinum gauze of approximately 42 mm dia. spot-welded to it, or a two-layer, plastic-bonded-carbon (PBC) electrode formed on an expanded-metal support which was spot-welded to a 0.3 mm titanium sheet current collector [11]. Flat gaskets of silicone rubber were used to prevent leakage past the edges of the electrodes; these seals blanked off an annular ring at the periphery of each electrode, leaving an active area of approximately 16 cm<sup>2</sup>.

In most cases, the separator consisted of a 0.6 mm thick disc of flat, microporous plastic material (Daramic<sup>®</sup> from W.R. Grace (Aust) P/L); this material was previously extracted with acetone to remove processing oil [5]. For some tests, a compound separator was employed, consisting of the 0.6 mm Daramic<sup>®</sup> sheet interleaved between 50 mm dia. discs of Whatman No. 50 filter paper. Polyethylene spacer grids, fabricated in the author's laboratories, were used to support the separator and to maintain the desired electrode-to-separator clearance.

### *Reagents*

The preparation of zinc bromide and the various quaternary ammonium bromides has been described in a previous paper [10].

### *Test equipment*

The cell was subjected to charge/discharge cycling using a programmable galvanostat that was designed and constructed in the author's laboratories. This unit was controlled, and data recorded, by an AIM-65<sup>®</sup> micro-computer (Rockwell Corp., Anaheim, California). The cell resistance was measured continuously during charge and discharge by modulating the current at 1 kHz, and calculating the resistance from the amplitude ratio and phase difference of the 1 kHz components of the cell current and voltage.

The potential of the bromine electrode was monitored against a platinum wire immersed in the positive-side reservoir. Since the platinum takes up the open-circuit potential of the bromine electrode [11], this gives a direct measurement of the bromine electrode overpotential. Electrode ohmic resistance was evaluated by measurement of the 1 kHz component of this potential. Testing was conducted in a controlled-temperature cabinet. The electrolyte temperature was maintained at 25 ± 1 °C for most tests, but could be varied between about 5 and 50 °C when it was desired to study the effect of temperature on performance.

### *Electrolyte preparation*

The electrolyte composition was based on the results reported by Singh *et al.* [9], and was selected as being representative of a part-charged system. This was necessary since, with the electrode area and electrolyte volumes in use, it was not possible to utilize fully the capacity of the electrolyte.

The electrolyte was prepared by mixing equal volumes of a 1.25 M solution of bromine in PN and an aqueous solution containing 1.5 M zinc bromide and 3 M sodium chloride. The phases were allowed to separate, and equal volumes of each were taken for use in the cell. For some tests, a quaternary ammonium bromide was added to the PN phase to give an initial concentration of 1 M. Quaternary ammonium salts are not normally soluble in PN but are soluble in the presence of bromine, probably due to the formation of addition compounds of the polybromide type.

### *Test procedures*

The electrochemical activity of cells was assessed by charging at 25 mA cm<sup>-2</sup> for 1 h, followed by a discharge at the same current density. During charge, the current was interrupted for 1 s at 15 min intervals in order to measure the cell open-circuit voltage; in order to evaluate the cell performance at various states of discharge, current-voltage measurements were made at the beginning of discharge and at 15 min intervals thereafter. The current densities used for these measurements were varied from 0 to 62.5 mA cm<sup>-2</sup> in steps of 12.5 mA cm<sup>-2</sup>, and the cell voltage, current density, electrolyte temperature, cell resistance, and bromine potential were recorded at each current density. The test was terminated when the cell voltage had fallen to 1.0 V.

Cell performance during extended cycle testing was evaluated by a constant-current charge at 25 mA cm<sup>-2</sup>, usually for 2.5 h, followed by discharge at the desired current density (usually 25 mA cm<sup>-2</sup>) to a 1 V cut-off. The cell was then loaded with a 1  $\Omega$  resistor for 15 min with electrolyte circulation maintained, followed by a 15 min open-circuit period without circulation, before commencing the next cycle. The parameters listed above were logged at 10 s intervals, and these values were then used to calculate the number of ampere hours that were charged and discharged, the average cell voltage during charge and discharge, the average electrolyte temperature, and the faradaic, voltaic, and energy efficiencies.

While bromine transport through the separator could be calculated from the ampere hours charged and discharged and the cycle time, an independent assessment of this transport rate could be obtained from a zinc solution rate test [5]. This involved substituting a weighed zinc disc for the negative electrode and circulating the positive- and negative-side electrolytes as usual, for the desired time, with the cell on open circuit. The cell is then disassembled as quickly as possible, and the zinc sheet washed, dried, and weighed. The bromine transport rate was calculated from the loss in weight of the zinc.

### *Bromine distribution in various electrolytes*

The procedure for determining bromine distribution involved taking 25 cm<sup>3</sup> of an aqueous solution containing 1.5 M zinc bromide and 3 M sodium chloride in a separating funnel, and shaking this with 25 cm<sup>3</sup> of a PN solution, 1.25 M in bromine and 1 M in the desired quaternary ammonium bromide (QBr). The combined aqueous/PN phases were allowed to stand in a controlled-temperature cabinet for 1 - 2 h to ensure that they reached the desired temperature, were reshaken to equilibrate at temperature, and given 15 min to separate. Each phase was then run into separate 50 cm<sup>3</sup> stoppered cylinders, the volume was recorded, and the cylinders were held in a water bath maintained at the appropriate temperature until samples could be taken for bromine analysis.

Resistivity measurements were made on both the aqueous and PN phases by using a commercial dip-type conductivity cell and a General Radio type 1650A impedance bridge.

Since the dimethylethylpropylammonium bromide (2-MEP) compound was quite effective in reducing aqueous bromine concentration, and had been prepared in quantity, it was selected for use in subsequent tests.

## **Results**

### *Effect of QBr salts on bromine distribution*

Although the distribution of bromine between aqueous and PN phases has been studied extensively by Singh *et al.* [9], no results have been reported for systems containing QBr compounds, although these authors have stated that the use of such materials reduced the aqueous phase bromine concentration. A short series of tests was therefore made to evaluate the effect on bromine distribution of QBr additions to the PN phase.

The results obtained are presented in Table 1. It can be seen that the addition of QBr compounds reduces the amount of bromine entering the aqueous phase. In general, the unsymmetrical aliphatic compounds are more effective than the cyclic materials of similar molecular weight, while the effectiveness of the unsymmetrical aliphatics increases with increasing molecular weight. Increasing the temperature from 25 to 50 °C increases the amount of bromine in the aqueous phase by a factor of about 2.

The resistivity of the phases was not much affected by the presence of QBr compounds. Typical values for the aqueous and PN phases at 25 °C were 7.7 and 22 Ω cm, while corresponding values at 50 °C were 5.3 and 17 Ω cm.

### *Cell polarization resistance*

Current-voltage curves, taken during the cell polarization tests at about 30% dissolution of the zinc deposit [11], are shown in Fig. 2. The results presented are for a simple PN electrolyte (*i.e.*, no QBr) on the positive side, and for a platinum-mesh/titanium electrode pair. Clearly, the cell voltage

TABLE 1  
Bromine distribution in propionitrile systems

Quaternary ammonium bromide (QBr)	Molecular wt. of QBr	25 °C		50 °C		
		Bromine distribution (%)		Bromine distribution (%)		
		Aqueous [Br <sub>2</sub> ] (M)	PN	Aqueous [Br <sub>2</sub> ] (M)	PN	
None	—	0.038	2.8	0.072	5.1	94.9
<i>Aliphatic compounds</i>						
Tetraethylammonium bromide	210	0.013	1.0	0.026	2.0	98.0
Triethylmethylammonium bromide	196	0.014	1.1	0.031	2.5	97.5
Diethyldimethylammonium bromide	182	0.019	1.4	0.040	3.1	96.9
Ethyltrimethylammonium bromide	168	0.025	2.0	0.053	4.1	95.9
Tetramethylammonium bromide	154	0.032	2.5	0.063	5.1	94.9
Dimethylethylpropylammonium bromide	196	0.014	1.1	0.026	2.1	97.9
Triethylpropylammonium bromide	224	0.007	0.65	0.015	1.3	98.7
<i>Cyclic compounds</i>						
N-methyl-N-ethylmorpholinium bromide	210	0.031	2.4	0.060	5.0	95.0
N-methyl-N-ethylpyrrolidinium bromide	194	0.017	1.3	0.035	2.7	97.3

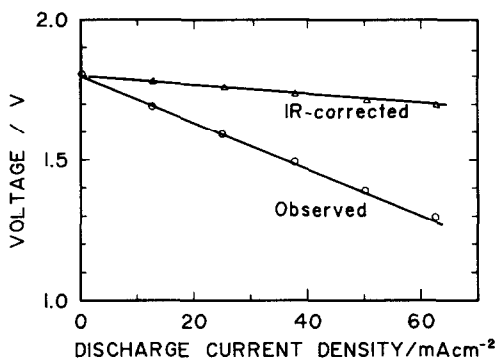


Fig. 2. Voltage as a function of discharge current density. Cell with compound separator and platinum-gauze/titanium electrode pair. Charge current  $25 \text{ mA cm}^{-2}$ , temperature  $25^\circ\text{C}$ .

shows a linear relation to current density, for both the as-measured voltage and for that obtained after *IR* correction. Since this latter relation is linear, the activation polarization can be expressed in the form of a resistance which is termed the 'polarization resistance'.

Cell polarization resistance values measured using platinum-mesh/titanium electrodes were  $1.5 \Omega \text{ cm}^2$  for a PN electrolyte and  $1.9 \Omega \text{ cm}^2$  when 1 mol of 2-MEP was present. With a two-layer PBC bromine electrode and the 2-MEP-containing electrolyte, the polarization resistance was  $1.7 \Omega \text{ cm}^2$ . All these values refer to an electrolyte temperature of  $25^\circ\text{C}$ .

Singh *et al.* [9] quote values of approximately  $1 \Omega \text{ cm}^2$  for the polarization resistance of both bromine and zinc electrodes, corresponding to a cell polarization resistance of  $2 \Omega \text{ cm}^2$ , which is in fair agreement with the values measured in this work. These values may be compared with the polarization resistances of polybromide cells, namely, about  $0.5 \Omega \text{ cm}^2$  when using platinum-mesh/titanium and  $0.3 \Omega \text{ cm}^2$  when the platinum mesh was replaced with a PBC bromine electrode.

### Cell efficiency

The initial test cell employed a platinum-mesh/titanium electrode pair and a 0.6 mm Daramic<sup>®</sup> separator. Typical results for the efficiency of this combination are shown in the first data row of Table 2. The faradaic efficiency is low at about 50%, giving an overall energy efficiency of only 38%. Also, addition of 2-MEP to the PN phase does not improve the faradaic efficiency (second data row, Table 2), although this might be expected from the reduction in aqueous-phase bromine concentration experienced when this compound is added. The Daramic<sup>®</sup> separator used in the above tests had been extracted with acetone and washed in hot water prior to use. Similar results were obtained, however, with as-received material. Assuming that the zinc deposit is fully dissolved during each cycle, the bromine transport rate through the separator can be calculated from the faradaic efficiency [5], and a value equivalent to a current density of about  $7 \text{ mA cm}^{-2}$

TABLE 2  
Cell performance with PN electrolyte

Electrolyte composition (PN phase prior to equilibration)		Separator type	Cell efficiency (%)		Bromine transport (mA cm <sup>-2</sup> )	Cell resistance ( $\Omega$ cm <sup>2</sup> )	
Bromine (M)	2-MEP (M)		Faradaic	Voltaic		Charge	Discharge
1.25	0	Flat Daramic®	51.8	72.4	6.9	10.3	7.8
1.25	1	Flat Daramic®	48.1	72.2	7.7	8.3	6.9
1.25	0	Compound	87.4	75.2	1.5	8.0	7.8
1.25	1	Compound	92.3	75.1	0.9	8.0	7.4



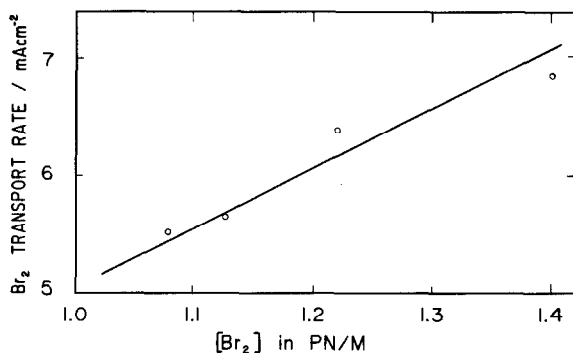


Fig. 3. Bromine transport through Daramic<sup>®</sup> separator material determined by zinc solution rate method.

was estimated for the above tests. The bromine transport rate (as measured independently using the zinc solution rate test [5]) is presented in Fig. 3 as a function of the bromine concentration in the PN phase. The average PN-phase bromine concentration over a 2.5 h cycle is calculated to be 1.35 M; from Fig. 3, the corresponding transport rate is  $6.8 \text{ mA cm}^{-2}$ . This is in good agreement with that estimated from the faradaic efficiency, and this gives support to the suggestion that the poor efficiency is caused by a high bromine transport rate, and not, for example, by penetration of the separator by a rough zinc deposit.

During these tests, it was observed that a fraction (estimated as 5 - 10% of the initial volume) of the PN phase was transferred to the negative side, where it formed a layer over the surface of the aqueous electrolyte. Thus, the high bromine transport may be caused by passage of the PN phase itself through the separator.

It has been observed previously [5] that a compound separator formed by interleaving flat Daramic<sup>®</sup> between two layers of Whatman No. 50 filter paper minimized wetting of the Daramic<sup>®</sup> by a polybromide phase, with consequent improvement in faradaic efficiency. Therefore, such a compound separator was tested in PN-electrolyte cells, with the results shown in Table 2. A large increase in faradaic efficiency was observed with this separator (to about 87%), without any penalty in the form of a reduced voltaic efficiency; it follows that the energy efficiency increases to about 66%. The addition of 1 M 2-MEP to the PN phase brings about a further increase in faradaic efficiency (~92%) in cells using the compound separator, with a corresponding improved energy efficiency of 69%.

The effect of change in the thickness of the separator was tested by replacing the 0.6 mm Daramic<sup>®</sup> with 0.25 mm material. The faradaic efficiency with a compound separator incorporating this thinner material was approximately 88% for a positive-side electrolyte without added 2-MEP. This is quite similar to the value obtained with the thicker Daramic<sup>®</sup> (see Table 2).

There was no visible amount of PN phase transferred to the negative compartment in any of the tests made with compound separators. Indeed, this observation held for much longer tests in which 50 consecutive charge/dicharge cycles were completed.

The compound separators employed in all the above tests were assembled with the Daramic<sup>®</sup> placed between the two layers of filter paper. Trials were made in which both layers of paper were located on the negative side of the Daramic<sup>®</sup>. Four cycles were run with such a separator, PBC and titanium electrodes, and a positive-side electrolyte containing 1 M 2-MEP. The faradaic efficiency fell from an initial 82% to 77% over four cycles. The cell was then reassembled with the Daramic<sup>®</sup> situated between the filter papers; the faradaic efficiency averaged 90.4% over nine cycles, increasing steadily from an initial value of 85%, to 93% by cycle 7. Following this, both papers were again placed on the negative side of the Daramic<sup>®</sup> and the cell re-tested. Faradaic efficiency was initially 90%, but fell to a value of 75% by the fifth cycle. Thus, placement of the filter paper in relation to the Daramic<sup>®</sup> appears to be quite important if maximum efficiency is to be obtained.

It has been shown [5] that pretreatment of Daramic<sup>®</sup> separators with a surfactant, or incorporation of a surfactant into the electrolyte, can lead to a useful improvement in faradaic efficiency when working with polybromide systems. Therefore, several cells having Daramic<sup>®</sup> (*i.e.*, not compound) separators were cycle-tested with electrolytes containing surfactants (sodium dodecylbenzene sulphonate, sodium dodecyl sulphate, phosphate ester and Triton X-100<sup>®</sup> were those selected). No lasting improvement in faradaic efficiency was found with any of these surfactants, and in most cases the faradaic efficiency ranged from 30 to 40%, that is, less than that achieved with an unmodified electrolyte under corresponding conditions.

It was considered possible that the PN phase could be excluded, in part, from the separator if a small amount of the aqueous phase was transferred to the positive side; this might lead to a higher proportion of aqueous phase being taken up by the separator, with possible improvement in efficiency. Such a possibility was examined using PBC/titanium electrodes and a PN phase containing 1 M 2-MEP. The results of adding 5 cm<sup>3</sup> of aqueous phase to the positive side are given in Table 3. It can be clearly seen that the use of the mixed positive-side electrolyte leads to improvements in faradaic and voltaic efficiencies by 3% and 4%, respectively. The actual voltaic efficiency is lower than that reported above (bottom data row, Table 2), due to the higher-than-normal resistance of the PBC electrode used.

The effect of change in initial bromine concentration was also studied in this test series, and the results presented in Table 3 show that increasing the bromine concentration reduces faradaic efficiency but increases voltaic efficiency. The latter effect is consistent with the findings of Singh *et al.* [9], who reported that increase in bromine concentration in the PN phase increased conductivity.

TABLE 3

Effects of aqueous phase addition and initial bromine concentration

Positive-side electrolyte <sup>†</sup>		Cycles	Cell efficiency <sup>††</sup> (%)			Bromine transport rate (mA cm <sup>-2</sup> )	Cell resistance (Ω cm <sup>2</sup> )	
[Br <sub>2</sub> ]* (M)	Aqueous** (cm <sup>3</sup> )		Faradaic	Voltaic	Energy		Charge	Discharge
1.25	nil	12	92.9	66.9	62.2	0.83	10.5	10.0
1.25	5	12	95.6	70.9	67.7	0.51	9.0	8.6
2.5	5	3	89.4	72.8	65.1	1.25	8.5	8.5
0.63	5	3	96.4	67.9	65.5	0.42	9.2	9.0

<sup>†</sup> Contains 2-MEP.

<sup>††</sup> Values averaged over number of cycles quoted.

\*Initial concentration in PN phase prior to equilibration with 1.5 M zinc bromide, 3 M sodium chloride.

\*\*Volume of aqueous phase added to positive compartment.

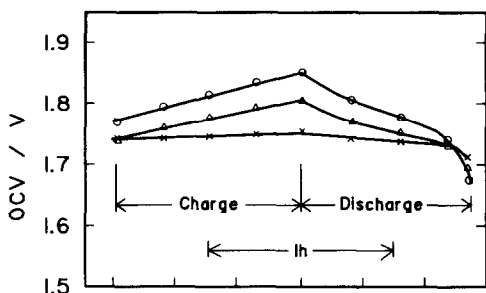


Fig. 4. Cell open-circuit voltage over one cycle:  $\circ$ , propionitrile electrolyte (compound separator);  $\Delta$ , propionitrile electrolyte containing 1 M 2-MEP (compound separator);  $\times$ , aqueous electrolyte (polybromide system). Conditions are 25 °C and 25 mA cm<sup>-2</sup> current density, with platinum gauze and titanium electrodes.

### Cell voltage

The open-circuit voltage (OCV) of cells having a PN electrolyte on the positive side was recorded at intervals during polarization tests. Figure 4 shows the variation in OCV over a full cycle for a simple PN electrolyte, a PN/1 M 2-MEP electrolyte, and an aqueous polybromide system. The average cell voltage is noticeably greater for the PN systems, perhaps due to the higher bromine concentration, but there is a relatively large increase in OCV which is less easy to explain. The zinc and bromine concentrations would change by about 0.2 M during the charge from initial values of 1.5 M and 1.2 M, respectively. These small changes should cause only millivolt changes in the cell voltage once the negative electrode has become covered with zinc, which takes only one or two minutes. In practice, the voltage change during charge for the PN electrolytes was 85 mV (PN alone) and 64 mV (PN/2-MEP), as compared with 8 mV for the polybromide system. This

implies that either there is some unexpected effect occurring during charge to change the activity of one of the reacting species, or that there is a potential developed across the PN/aqueous interface.

To study this point further, electrode potential measurements were made for a zinc electrode in the aqueous phase, and for a platinum electrode in the PN phase, of solutions prepared to have the composition of the initial electrolyte and of the electrolyte resulting from a 1 h charge at  $25 \text{ mA cm}^{-2}$ . Potentials were read against a saturated calomel electrode. The OCV values for a complete cell estimated from these potential readings were 1.752 V for the initial electrolyte and 1.765 V after 1 h of charging. This is an increase of 11 mV over the charge period as compared with the value of 85 mV observed when an actual cell was charged. The large difference between these values gives some support to the suggestion that the large increase in cell voltage observed during charge is due to a potential occurring at the PN/aqueous interface.

Data already presented allow a first-order estimate of the cell resistance. Consider a cell assembled from platinum gauze and titanium electrodes, a compound separator, and assume the PN/aqueous interface lies at the junction of the microporous plastic and the negative-side filter paper. For such a case, the length of the current path through the PN phase consists of the positive-side electrode-to-separator distance (0.7 mm nominal) and the equivalent thickness [5] of the PN-saturated filter paper plus Daramic<sup>®</sup>, while the aqueous path is the equivalent thickness of the negative side filter paper plus the separator-to-electrode distance (again 0.7 mm nominal). If the equivalent thickness of the 0.6 mm Daramic<sup>®</sup> is 2 mm [5] and that of each filter paper (as determined by a resistance technique [5]) is 0.7 mm, then, using the resistivity values for the electrolytes given earlier, the resistance of the electrolyte path is  $(0.34 \times 22.4) + (0.14 \times 7.7) = 8.7 \ \Omega \text{ cm}^2$ . The resistance of the metal electrodes is low; an estimate of  $0.3 \ \Omega \text{ cm}^2$  is probably conservative. Thus, the total ohmic resistance of this cell is estimated to be  $9.0 \ \Omega \text{ cm}^2$ . This value was calculated for the electrolyte compositions applying at the beginning of charge, but it is in fair agreement with the whole-cycle average value of  $8 \ \Omega \text{ cm}^2$  (Table 2). A more accurate evaluation of average cell resistance over the whole cycle would require knowledge of the composition and conductivity of the electrolytes at all stages of charging and discharging.

When using Daramic<sup>®</sup> as the sole separator material, the cell resistance showed an unusual pattern. At the start of charging, the normal value of about  $8 \ \Omega \text{ cm}^2$  would be observed, but as charging proceeded the cell resistance increased, reaching about  $16 \ \Omega \text{ cm}^2$  by the end-of-charge. Immediately discharge commenced, the cell resistance decreased abruptly to about  $8 \ \Omega \text{ cm}^2$ , and did not show any further anomalous behaviour before end-of-discharge. The effect was barely noticeable on the first cycle of a series, but it increased with successive cycles and was usually fully developed by the third or fourth cycle. It was also more noticeable with simple PN electrolytes than with those containing a quaternary ammonium bromide, and was

not seen when using compound separators. No explanation can be offered for this resistance change.

The value for the voltaic efficiency can be calculated using the above estimate of cell ohmic resistance, the polarization resistance reported earlier, and the average cell OCV during charge and discharge. Taking a polarization resistance of  $1.7 \Omega \text{ cm}^2$ , an average cell OCV of 1.8 V, and the current density for both charge and discharge as  $25 \text{ mA cm}^{-2}$ , a voltaic efficiency of 73% is calculated, which is close to the values reported in Table 2 for a metal electrode, compound separator, cell. A PBC bromine electrode has a higher resistance than the platinum gauze, and the voltaic efficiency with such an electrode would be reduced to about 70%.

#### *Effects of current density and electrolyte temperature*

All the cell performance data presented above were taken at an electrolyte temperature of  $25^\circ \text{C}$  and with a current density of  $25 \text{ mA cm}^{-2}$ . Since it is of interest to assess the effect of both discharge current density and electrolyte temperature on cell efficiency, cycle tests were carried out over the temperature range  $5 - 50^\circ \text{C}$ , with the charging current maintained at  $25 \text{ mA cm}^{-2}$  and the discharge varied between 5 and  $62.5 \text{ mA cm}^{-2}$ . Approximately 30 cycles were required to cover this range of temperatures and current densities; because of this, the charging time was kept at 1 h in order to minimise the period taken by a complete test sequence. Tests were conducted using both Daramic<sup>®</sup> and compound separators.

Figures 5 and 6 show the effect of current density on the faradaic, voltaic, and energy efficiencies of cells having Daramic<sup>®</sup> and compound separators, respectively. For both types of separator, the faradaic efficiency increases with increasing current density. This follows from the diffusion of bromine through the separator, which gives the effect of a constant self-discharge throughout the whole cycle. For constant-current charging and discharging without any interval between cycles, the relation would be:

$$E_t = \frac{I_D(I_C - I_B)}{I_C(I_D + I_B)} \times 100\% \quad (1)$$

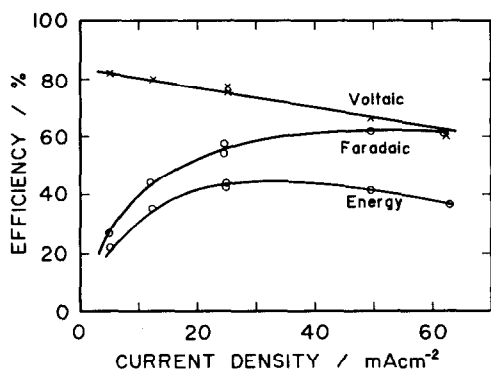


Fig. 5. Effect of current density on cell efficiency. Daramic<sup>®</sup> separator at  $25^\circ \text{C}$ .

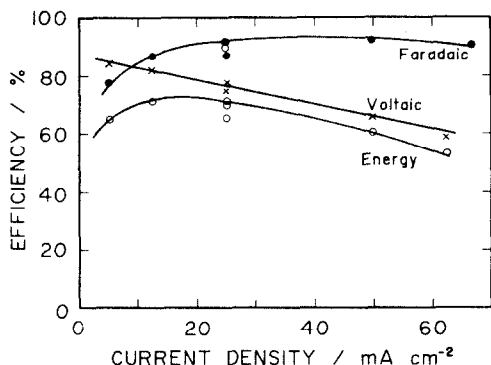


Fig. 6. Effect of current density on cell efficiency. Compound separator at 25 °C.

where  $E_f$  is the faradaic efficiency,  $I_C$  the charging current density,  $I_D$  the discharge current density, and  $I_B$  the bromine transport rate through the separator expressed as a current density. Thus, if  $I_C$  is held at a constant value and  $I_D$  increased from zero, the faradaic efficiency increases rapidly from zero and approaches the value  $(I_C - I_B)/I_C$  as  $I_D$  becomes large in comparison to  $I_B$ .

When using a 0.6 mm Daramic<sup>®</sup> separator and an electrolyte temperature of 25 °C,  $I_B$  was found to be about 7 mA cm<sup>-2</sup> by the zinc solution rate method (see above) so that  $E_f$  would have a maximum value of  $(25 - 7)/25$  or 72%, and the values shown in Fig. 5 can be compared with this. Since, in practice, there was a period of open-circuit operation between cycles, the maximum efficiency would be a little lower than that estimated from eqn. (1). Change in discharge current density would have the same effect, qualitatively, with a compound separator, but the maximum achievable efficiency would be ~94% because of the lower bromine transport through this type of separator.

The above calculation assumes that the deposited zinc is redissolved completely during discharge. This appears to be a valid assumption at current densities below 50 mA cm<sup>-2</sup>, but above this current density some zinc appears to remain undissolved when the cell voltage has fallen to the cut-off value, perhaps due to uneven current distribution. Under such circumstances, the faradaic efficiency is reduced below the value expected when only bromine transport through the separator is considered.

The voltaic efficiency decreases linearly with current density (Fig. 5), which is consistent with the voltage losses being due to internal cell resistance. The voltaic efficiency may be estimated from the relation:

$$E_v = \frac{V - I_D R}{V + I_D R} \quad (2)$$

where  $E_v$  is the voltaic efficiency,  $V$  the mean cell OCV (assumed to be the same during charge and discharge), and  $R$  the sum of the cell ohmic and polarization resistances.

Energy efficiency is the product of the faradaic and voltaic efficiencies; since these change in opposite directions with change in current density, it follows that energy efficiency is relatively constant over a range of current densities. In practice, a plot of energy efficiency against current density passes through a shallow maximum, the values of current density at the maximum being about  $15 \text{ mA cm}^{-2}$  and  $30 \text{ mA cm}^{-2}$  for the compound and Daramic<sup>®</sup> separators, respectively. The value at the maximum is about 73% for the compound separator cell; the corresponding value for a PN electrolyte containing 1 M QBr was about 76%, the slightly higher energy efficiency being due to the higher faradaic efficiency attained with QBr-containing electrolytes.

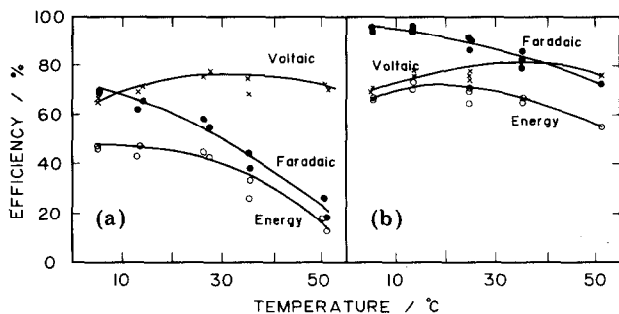


Fig. 7. Effect of electrolyte temperature on efficiency: (a) Daramic<sup>®</sup> separator, (b) compound separator; current density  $25 \text{ mA cm}^{-2}$ .

Figure 7(a) and (b) shows the relation between cell performance and electrolyte temperature for systems with a Daramic<sup>®</sup> and a compound separator, respectively. The data in both cases are for a current density (both charge and discharge) of  $25 \text{ mA cm}^{-2}$  and for a PN electrolyte without any added QBr.

It is to be anticipated that the faradaic efficiency should decrease with increasing temperature, as the diffusion coefficient of bromine would be expected to increase by approximately 2% per °C (a general value for most diffusion coefficients) and, as shown in Table 1, the equilibrium bromine concentration in the aqueous phase is doubled by a 25 °C increase in temperature. Thus, the bromine transport rate at 50 °C might be expected to be a factor  $2 \times 1.02^{(50-25)}$  ( $= 3.3$ ) greater than that measured at 25 °C, while at 5 °C the transport rate should be 40% of the 25 °C value. These estimates assume that the transport rate is proportional to both the diffusion coefficient of bromine and to the equilibrium concentration of bromine in the aqueous phase.

Actual bromine transport values are presented as a function of temperature in Fig. 8 and the 50/25° and 5/25° ratios can be calculated from these data. For a compound separator, these were calculated to be 3.1 and 0.4, respectively; that is, in good agreement with those estimated above. However, with the Daramic<sup>®</sup> separator the corresponding ratios were 2.1 and 0.6; that

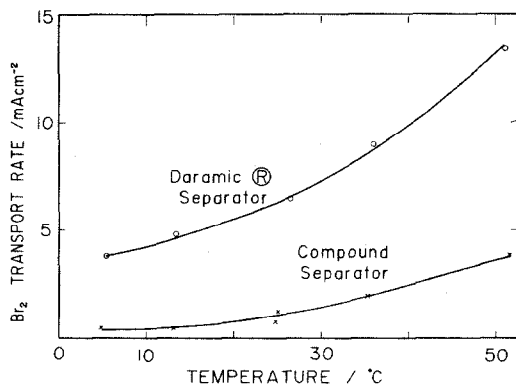


Fig. 8. Bromine transport through separator as a function of temperature. PN positive-side electrolyte; no QBr. O, Daramic® separator; X, compound separator.

is, somewhat lower than anticipated. This may be consistent with the observation that when using Daramic® some of the high-bromine-concentration PN phase moves directly through the separator into the aqueous phase, giving an additional factor affecting bromine transport which could well have a lower temperature coefficient than that used to calculate the estimated ratios.

Voltaic efficiency would be expected to increase with increasing temperature; the most important mechanism being the reduction in electrolyte resistivity with rising temperature. Such an increase in efficiency is observed up to about 30 °C; thereafter the effect reverses: cell resistance increases and voltaic efficiency decreases with further rise in temperature. This effect, observed with both compound and Daramic® separators, was traced to a gradual increase in separator resistance with time, especially noticeable at 50 °C. No mechanism can be suggested to explain the observation.

Since, at least below 30 °C, faradaic and voltaic efficiencies are affected in opposite sense by change in temperature, energy efficiency is relatively independent of temperature in the 5 - 30 °C range. Above about 30 °C, both the voltaic and the faradaic efficiency decrease with increasing temperature and, consequently, there is a marked decrease in energy efficiency above this temperature.

#### *Longer-term cell performance*

All the data presented above are the result of short-term testing, but the stability of cell performance over a larger number of cycles is of interest if this system is to be used in a practical battery. Consequently, several test series have been made in which cells have been subjected to 50 charge/discharge cycles. The cells have incorporated a PBC bromine electrode and a compound separator.



TABLE 4  
Stability of cell performance

Efficiency* (%)	PN electrolyte		PN-1 M 2-MEP electrolyte	
	cycles 1 - 10	cycles 41 - 50	cycles 1 - 10	cycles 41 - 50
Faradaic	84.8 ± 1.9	89.0 ± 1.1	92.0 ± 1.7	93.2 ± 0.5
Voltaic	72.3 ± 1.4	69.6 ± 2.1	72.4 ± 0.9	71.4 ± 0.5
Energy	61.3 ± 1.7	61.9 ± 1.3	66.6 ± 2.0	66.5 ± 0.8

\*Average values for cycles quoted.

The cell efficiencies, averaged over the first and last 10 cycles of the test series are shown in Table 4, for both a simple PN electrolyte and a PN phase containing 1 M of 2-MEP. These results reveal that there is no significant deterioration in cell performance over the test period.

## Discussion

The results presented above confirm that a zinc/bromine cell using a propionitrile-based, positive-side electrolyte can operate with acceptable efficiency. Such an efficiency cannot be achieved with commercially-available microporous plastic separator materials; the propionitrile phase leaks through these and results in low values for both the faradaic and the energy efficiencies. The only satisfactory results were attained by use of a compound filter paper/Daramic<sup>®</sup>/filter paper separator; the combination of such a separator with a propionitrile phase containing a quaternary ammonium bromide gave a faradaic efficiency of approximately 93%. The addition of a small amount of aqueous phase to the positive-side electrolyte appears to reduce even further the rate of bromine transport through the compound separator, a faradaic efficiency in excess of 96% being observed under such conditions. All these results are for an electrolyte temperature of 25 °C and a current density of 25 mA cm<sup>-2</sup>, and under these conditions voltaic efficiency is 70 - 75% depending on the bromine electrode used, giving energy efficiencies in the range 65 - 70%.

It is of interest to compare these results with those obtained for an all-aqueous electrolyte, aqueous bromine concentration being controlled by addition of a quaternary ammonium bromide to the electrolyte. The efficiency of cells corresponding to those employed for the PN studies, but used with polybromide systems, is given in ref. 10. Using a compound separator with a 2 M zinc bromide electrolyte containing 3 M potassium chloride and a 1:1 mixture of *N*-ethyl-*N*-methylpyrrolidinium bromide and dimethylethylpropylammonium bromide as the quaternary ammonium bromide, the resulting faradaic, voltaic, and energy efficiencies were 96%, 87% and 84%, respectively. The higher energy efficiency found is due mainly

to the higher voltaic efficiency, which, in turn, is a consequence of the lower cell resistance ( $3.5 \Omega \text{ cm}^2$  as compared with  $8 - 9 \Omega \text{ cm}^2$  for the PN system — see Table 2), and the absence of any of the phase-boundary potential believed to be generated in the PN cell. Moreover, the use of a compound separator is not essential with the polybromide system, as high faradaic efficiency can be obtained with a surfactant-treated, microporous plastic separator [5]. The efficiencies measured for a cell incorporating a separator of 0.6 mm Daramic<sup>®</sup> treated with sodium dodecylbenzene sulphonate, tested at  $25^\circ\text{C}$  and  $25 \text{ mA cm}^{-2}$  were, respectively, 96%, 91%, and 87% for the faradaic, voltaic, and energy components. The observed increase in voltaic and energy efficiencies demonstrates the advantage of using the simple separator, where this does not result in reduced faradaic efficiency.

Change in electrolyte temperature affects cell performance: faradaic efficiency decreases with increase in temperature due to increase in the bromine diffusion coefficient and the increased aqueous phase bromine concentration. However, voltaic efficiency increases with temperature, due to increased electrolyte conductivity up to about  $30^\circ\text{C}$ , above which value the cell resistance shows an anomalous increase with further rise in temperature. For cells using a compound separator, the overall effect on energy efficiency is to make it nearly independent of temperature in the range  $5 - 30^\circ\text{C}$ , passing through a shallow maximum at about  $20^\circ\text{C}$ .

Change in discharge current density causes faradaic efficiency to increase with increase in current density. This can be understood in terms of the bromine transport through the separator acting as a self-discharge rate independent of current density, which means that this self-discharge current would be a smaller proportion of a higher current density. Voltaic efficiency decreases with increasing current density due to the higher  $IR$  loss at higher currents. Again, at least for cells using a compound separator, the overall effect on energy efficiency is to make it relatively independent of discharge current density in the  $5 - 50 \text{ mA cm}^{-2}$  range, there being a shallow maximum at about  $15 \text{ mA cm}^{-2}$ .

The effect of temperature and discharge current density have also been studied for polybromide systems [12] and the results are qualitatively similar to those described above, although voltaic and energy efficiencies are greater.

In summary, by use of the appropriate separator, zinc/bromine cells using propionitrile as the positive-side solvent can be made to exhibit an acceptable faradaic efficiency. The propionitrile phase has, however, a much lower conductivity than the corresponding aqueous phase and, consequently, voltaic and, hence, energy efficiencies fall below those shown by polybromide system cells. Other disadvantages of the propionitrile system are the toxicity and flammability of the solvent. Further, although the compound filter paper/microporous plastic/filter paper separator is effective in laboratory scale cells, it may be difficult to apply to full-scale cells and batteries.

The propionitrile system does have some advantages. The positive-side electrolyte is of low viscosity, and is easily pumped around the system.

Also, it has a low freezing point, and is free from the possibility of solid formation which can cause difficulty with polybromide systems [5]. Further development of propionitrile systems of the type described will probably require development of an inexpensive separator material which is preferentially wetted by the aqueous phase.

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