

## PREPARATION AND PERFORMANCE OF PLASTIC-BONDED-CARBON BROMINE ELECTRODES

K. J. CATHRO\*, K. CEDZYNSKA and D. C. CONSTABLE

*CSIRO, Institute of Energy and Earth Resources, Division of Mineral Chemistry,  
P. O. Box 124, Port Melbourne, Vic. 3207 (Australia)*

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### Summary

A range of carbon blacks has been used in conjunction with a polypropylene binder to form electrodes for zinc/bromine cells.

The resistivity of each of these carbon/plastic materials has been measured on hot-pressed pellets. The respective electrochemical activity has been determined from polarization tests using 2 cm<sup>2</sup> electrodes. These tests have shown that a two-layer electrode structure, with a surface layer containing a high fraction of carbon black, is necessary to obtain satisfactory activity. Best results have been achieved when this surface layer has been composed of blacks with a low bulk density and a high surface area.

The best of the carbon/plastic compositions has been used to prepare 16 cm<sup>2</sup> bromine electrodes for testing in zinc/bromine cells. It has been possible to make electrodes with an initial polarization resistance of 0.3 ohm cm<sup>2</sup> and an initial ohmic resistance of 0.8 ohm cm<sup>2</sup>. These values increase when the electrodes are left in contact with bromine-containing solutions, regardless of whether the electrodes have been charge/discharge cycled or not.

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### Introduction

Interest in the zinc/bromine couple as the basis for a rechargeable battery system has generated a need for bromine electrodes that are inexpensive, of high performance, and durable. Moreover, such electrodes should be compatible with the circulated electrolyte bipolar battery designs that have won acceptance as being the most practical for this system [1 - 5].

Titanium, coated with a catalyst on the bromine side, was used as electrode material [1, 3] in some early systems, but this material is expensive and subject to severe corrosion under conditions of cell reversal. Porous, vitreous carbon, bonded to a graphite substrate, gave an electrode of

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\*Author to whom correspondence should be addressed.

sufficient activity [4], but it is brittle, difficult to bond to plastic cell frames, and is also expensive. Thus, the material of choice for electrode fabrication in the zinc/bromine system has converged on plastic-bonded-carbon [2, 5, 6].

Plastic-bonded-carbon (PBC) is prepared as a conductive sheet from a mixture of powdered carbon (*e.g.*, a furnace black) and a suitable thermo-plastic binder (*e.g.*, polypropylene) by hot pressing, injection moulding, or extrusion. Tsien [7] has described the large-scale production of PBC electrodes by an extrusion process, while the Meidensha Company has described the preparation of bromine electrodes both by hot pressing carbon fibre sheets onto a PBC substrate [8, 9] and by extrusion methods [10, 11]. However, there is little published information on the performance of these electrodes.

This work covers the preparation of small PBC electrodes by a hot pressing technique, together with an assessment of their performance in a variety of electrolytes relevant to zinc/bromine cell operation. Initially, the resistivity of a range of carbon-plastic mixtures was studied using pressed pellets. This was followed by examination of the performance of the more conductive of these mixtures using a single-electrode test method. Finally, the most promising of these mixtures were formed into electrodes suitable for use in a small zinc/bromine cell. While PBC electrodes can function both as zinc and bromine electrodes, only the preparation and performance of bromine electrodes is discussed here.

## Experimental

### *Resistivity of PBC compacts*

Cylindrical PBC samples were prepared by pressing mixes in a heated steel die. The samples were 8.4 mm in diameter and usually about 10 mm high, although the height was varied from 5 to 18 mm in one series of tests. In making each sample, a lightly compressed mixture of carbon and polypropylene was brought to the working temperature over a period of 20 min, and then subjected to the desired pressure for 10 min. The sample was then allowed to cool under pressure, and finally ejected from the die.

The most serious difficulty in measuring the resistance of carbon-plastic compacts proved to be making a satisfactory contact between the measuring plates and the test piece, the contact resistance between the brass contact plate and the PBC being quite high. Attempts to cement contacts with silver-epoxy adhesive proved unsuccessful, and the only technique that gave consistently satisfactory results was to metallize the surfaces by either vacuum evaporation or electroless plating. The latter method was the more convenient; electroless nickel deposits proved satisfactory and were formed using the method described by Feldstein [12]. The curved surface of each sample was masked with paraffin wax so that only the flat ends were metallized. Electrical contact was made with each plated surface either by cementing a metal contact plate with silver-epoxy (E-Solder 3021, Acme

Chemical & Insulation Co.), or by clamping the test piece between stiff contact plates under a controlled load in an hydraulic press. The second method proved to be more rapid, and was used in most tests.

The electrical resistance was measured by a 4-terminal method. Measurements were taken with an applied force on the sample of 1.1 or 1.6 kN, except for some high carbon samples of low crushing strength when 0.8 kN was used. Within this range, loading had little effect on the value of resistivity obtained.

The carbons used comprised a range of furnace blacks, namely: ACARB SAF, 150P, FEF and 3H from Australian Carbon Black; Black Pearls 2000 and XC-72 from Cabot Corp.; and Ketjen black from Noury Chemical Corp. In addition, some tests were made with compacts prepared from Fluka powdered graphite (99.9%, with approx. 0.05% ash). Table 1 gives manufacturers' data for the carbons used. The polypropylene powder was Hostalen PPT 1070 from Hoechst Australia.

TABLE 1  
Properties of carbon blacks

Type	ASTM D1765 classification	Surface area ( $\text{m}^2 \text{g}^{-1}$ )	Average particle size (nm)	Pour* density ( $\text{kg m}^{-3}$ )
Acarb SAF	N110	143	11 - 19	357
Acarb 150P	N294	180	20 - 25	346
Acarb FEF	N550	43	40 - 48	358
Acarb 3H	N347	90	26 - 30	344
Black Pearl	—	1050	—	152
XC-72	—	254	30	253
Ketjen black	—	1000	30	150

\*ASTM D1513.

#### *Preparation and testing of small-scale PBC electrodes*

Having established the influence of the carbon/plastic ratio on the resistivity of PBC compacts, those with the lowest values were formed into rectangular electrodes. These were prepared by hot pressing a mixture of carbon black and polypropylene onto the lower 20 mm of a 60 mm long by 10 mm wide strip of 5 Cb 10 4/0 niobium expanded metal (Exmet Corp.); the upper, uncoated mesh served as the electrical lead. The compact was sandwiched between layers of aluminium foil and pressed directly between the press platens, without use of a die. After cooling under pressure the foil was removed and any excess plastic-carbon mix trimmed from the expanded metal support.

The performance of each electrode was evaluated by taking current-overpotential curves in a dilute solution of bromine in 6 M sodium bromide. Polarization curves were run using either a Utah Electronics model 0152 potentiostat, or, more usually, a galvanostat constructed in these laboratories.

The cell used in these tests consisted of a simple cylindrical vessel with a close-fitting cover. The counter electrode was of platinum gauze ( $\sim 2 \text{ cm}^2$ ), while the reference electrode — a short platinum wire sealed into a glass sheath — was positioned close to the test electrode. The use of such a platinum wire as reference is permissible since the bromine/bromide reaction is highly reversible on platinum, *e.g.*, ref. 13, and this arrangement allows direct reading of the working electrode overpotential. In nearly all cases, the test electrodes showed an open-circuit potential within  $\pm 0.002 \text{ V}$  of the platinum reference.

Except for one test series in which bromine concentration was varied, the experimental procedure was to pipette  $20 \text{ cm}^3$  of 6 M sodium bromide into the cell, de-aerate the solution with oxygen-free nitrogen, and then add  $1 \text{ cm}^3$  of 0.6 M bromine in 6 M sodium bromide, giving a bromine concentration of 0.029 M. The electrolyte was stirred with a PTFE-coated, magnetically-driven stirring bar, the rotational speed of which was adjusted such that further increase caused no change in the indicated overpotential. The polarization curve was then recorded using the equipment described above. Tests were conducted at room temperature, namely,  $22 \pm 3 \text{ }^\circ\text{C}$ .

#### *Preparation and testing of PBC electrodes for Zn/Br<sub>2</sub> cells*

Bromine electrodes for use in a zinc/bromine cell were prepared by hot pressing a 150P carbon black (30 wt.%), polypropylene (65 wt.%), carbon fibre (5 wt.%) mix onto a 51 mm dia. 5 Cb 10 4/0 niobium expanded metal grid which was, in turn, spot welded to a 0.3 mm thick titanium backing plate. The carbon fibre was added to improve the toughness of the pressed mix. The PBC layer was formed using 12 MPa pressure for 10 min at  $190 \text{ }^\circ\text{C}$ . After preparation of this substrate layer the electrode was cooled to room temperature, and (typically) 0.5 g of the desired top layer mix (usually of Black Pearls 2000 (60 wt.%) and polypropylene (40 wt.%) was spread over the substrate layer, the plunger inserted into the die, and the die plus electrode heated to the required press temperature, without application of pressure. The electrode was then formed at the desired pressure/time combination (typically  $190 \text{ }^\circ\text{C}$ , 12 MPa and 30 s), and immediately upon expiration of the nominated time, the heater was turned off and the die cooled as rapidly as possible by means of an air blast, pressure being maintained during the cooling period.

The cell design has been described in detail previously [14]. Briefly, the cell consists of a two-section polypropylene body that allows a porous plastic separator to be located between the electrodes, so that there is a nominal 0.7 mm gap between each electrode and the face of the separator. Part of each electrode is blanked off by the sealing gaskets used, giving an active area of approximately  $16 \text{ cm}^2$ . Electrolyte is circulated from external reservoirs of  $35 \text{ cm}^3$  volume by means of small nutating-disc pumps, the flow rate being about  $2 \text{ cm}^3 \text{ s}^{-1}$ . This flow rate is sufficient to disperse any polybromide present throughout the electrolyte. The separator was 0.6 mm Daramic® (W. R. Grace). The zinc electrode was usually a 1 mm thick titanium

disc, but for some of the longer term cycle tests a PBC zinc electrode was used.

The cell was subjected to charge/discharge cycling using a programmable galvanostat constructed in these laboratories. This was controlled, and the data recorded, by an AIM-65 microcomputer (Rockwell Corp.) used with interface circuitry constructed in these laboratories. The cell resistance was measured continuously during charge and discharge by modulating the current at 1 kHz, and calculating the cell resistance from the amplitude ratio and phase difference of the 1 kHz components of cell current and voltage.

In most cases, testing was conducted at  $25 \pm 0.3$  °C using a test profile consisting of a  $25 \text{ mA cm}^{-2}$  charge for 1 h, followed by a discharge at the same current density. To assess 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 between 0 and  $62.5 \text{ mA cm}^{-2}$ , in steps of  $12.5 \text{ mA cm}^{-2}$ . The cell voltage, current density, electrolyte temperature, cell resistance, and bromine potential were monitored at each current density. The test was terminated when the cell voltage fell below 1.0 V.

Electrode durability was evaluated using constant-current ( $25 \text{ mA cm}^{-2}$ ) charge/discharge cycles; the charge period was 2.5 h while the discharge was continued to a 1.0 V cut-off. A PBC zinc electrode was used during these tests as there was thought to be some attack on the titanium electrode during extended cycling. The bromine electrode was tested at intervals by dismantling the cell and making a polarization test against a titanium negative, as described above. Temperature was not controlled during these durability tests, and ranged from 15 to 35 °C.

## Results

### *Resistivity of PBC compacts*

The plastic-bonded-carbon used for the electrodes must have adequate electrical conductivity. When used in a bipolar cell design the required level of conductivity is not very high. For example, if an ohmic loss through a 1 mm thick sheet of 10 mV can be tolerated, then at a current density of  $40 \text{ mA cm}^{-2}$  the allowable resistance would be  $0.25 \text{ ohm cm}^2$ , equivalent to a resistivity of  $2.5 \text{ ohm cm}$ . It will be shown that such resistivity values can be attained quite readily.

To obtain a measure of the precision of the method, five replicates were prepared from a mix of FEF carbon black (40 wt.%) and polypropylene (60 wt.%) that was pressed at 182 °C and 24 MPa to form an 11.3 mm high cylinder. The resistivity was measured as  $0.42 \pm 0.047 \text{ ohm cm}$ , a relative standard deviation of 11%. Following these tests, the influence of formation pressure was examined over the range 12 - 47 MPa, at temperatures of 170, 187 and 218 °C. No significant effect of pressure was found. Further, resistivity values were found to be independent of sample size, as measured

by the height of the cylinder produced. Finally, the effect of using five different carbon blacks and graphite, at several carbon/polypropylene ratios, was studied. From the data given in Table 2, it can be seen that Ketjen black generally shows the lowest resistivities, while FEF is among the higher resistivity blacks. The resistivity of these two samples are shown as a function of their carbon content in Fig. 1. The relation between  $\log(\text{resistivity})$  and  $\log(\text{percent. carbon})$  is linear, with a slope of  $-2.7$ , over a wide range of composition. Thus it is possible to obtain a sufficiently low electrode resistance from a low conductivity, high density carbon (such as FEF) by making a relatively small increase in the weight fraction of the carbon in the mix. For example, if a resistivity of 1 ohm cm is considered adequate, then either 19% of Ketjen black or 31% of FEF could be used, and it may be more economical to use the less expensive FEF, if this does not bring about any problems in fabrication. It can be seen from the data shown in Table 2 that there is no advantage in employing graphite as the conductive component, as the resistivity of graphite/plastic pellets is higher than that of the carbon black mixes at all but the highest percentage of graphite.

TABLE 2

Specific resistance values for carbon blacks

Type	Resistivity, ohm cm*					
	10% (C)	20% (C)	30% (C)	40% (C)	60% (C)	80% (C)
FEF	155	3.3	1.1	0.42	0.16	0.13
3H	446	5.8	0.89	0.52	0.12	0.18
XC-72	28	4.0	0.56	0.45	0.09	—
Ketjen	5.4	1.0	0.25	0.13	—	—
Black Pearls 2000	15.1	1.8	0.34	0.30	—	—
Graphite	1670	—	18	2.0	0.27	0.04

\*Samples prepared at 24 MPa and 195 °C.

### *Performance of small-scale PBC electrodes*

Originally, it was intended to determine polarization curves using a rotating disc electrode, the rotation speed being high enough to suppress concentration polarization, and characterize the electrochemical activity of the carbon by estimation of the exchange current. This proved impractical because: (i) the overpotential-log current density plot was non-linear (see Fig. 2); and (ii) preparation of disc electrodes was both difficult and time-consuming. Consequently, the rapid test method described in the Experimental section was adopted.

Because with this technique the electrodes were prepared by hot pressing, a number of operating variables had to be examined. The most

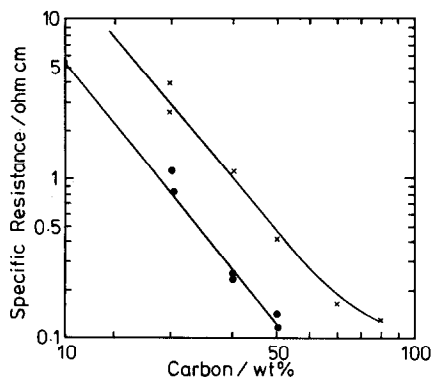


Fig. 1. Effect of fraction of carbon on resistivity. x, FEF; ●, Ketjen black.

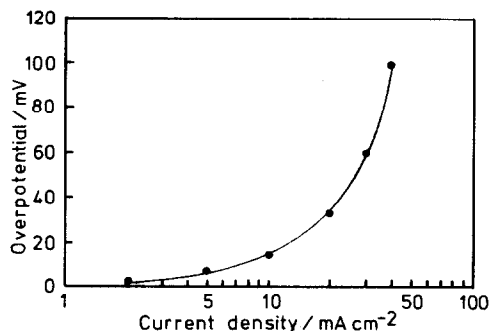


Fig. 2. Polarization curve for dilute bromine solution. Electrode is 60% Black Pearls 2000 over 40% FEF. Prepared at 80 MPa, 160 °C, 15 s. 0.029 M Br<sub>2</sub> at approx. 20 °C.

important of these were the composition of the compact and the temperature and pressure of formation. Electrode activity was taken as the current density at 100 mV overpotential.

Initial tests were made by pressing mixtures containing 40% carbon at 160 MPa for 30 min at 240 °C. Examination was made of FEF, 3H, Ketjen black, and Black Pearls 2000 carbons. Activity was poor, especially for the relatively-high-density FEF and 3H blacks ( $<0.1 \text{ mA cm}^{-2}$ ), while the high-area, low-density blacks (Ketjen black, Black Pearls 2000) showed activities of about  $3 \text{ mA cm}^{-2}$  at best. The reason for this poor activity was thought to be a high degree of encapsulation of the carbon by the plastic. To test this, a second (*i.e.*, top) layer of carbon black, without any admixed polypropylene, was pressed onto the electrode surface using the same formation conditions described for substrate formation. Electrode activity improved to  $7 \text{ mA cm}^{-2}$  for FEF,  $15 \text{ mA cm}^{-2}$  for Ketjen and  $19 \text{ mA cm}^{-2}$  for Black Pearls 2000. Because of the marked beneficial effect of using a high carbon top layer, subsequent studies were conducted on two-layer electrodes.

Although good electrode activity could be obtained by forming the top layer from high-area carbon black alone, the layer so formed was mechanically weak. If small amounts of polypropylene were added as a binder then the encapsulation effect reappeared, with resulting poor activity ( $0.2 - 2 \text{ mA cm}^{-2}$ ). The use of lower temperatures and pressures, combined with shorter pressing times, seemed desirable for the preparation of a top layer that contained polypropylene as a bonding material, since such conditions would be more likely to give an open, sintered structure, accessible to the electrolyte.

Several electrodes were so prepared with Black Pearls 2000 and polypropylene as the top layer mixture. Carbon loadings were held to approximately  $3 \text{ mg cm}^{-2}$ . This figure was not critical, since electrode performance was found to be only a weak function of carbon loading. The

substrate consisted of a 40 wt.% FEF-60 wt.% polypropylene mix pressed at 120 MPa for 10 min.

The performance of electrodes containing from 40 to 100 wt.% of Black Pearls 2000 in the top layer, and pressed at 40 MPa and 180 °C for 15 s was evaluated. The substrate was as described above. In addition to measurement of activity, the abrasion resistance of the top layer was assessed by inspection, and graded. The results are presented in Table 3. Carbon contents of 60 - 80 wt.% gave the best performance.

TABLE 3  
Effect of top-layer composition on performance

% Black Pearls 2000 (wt.%)	100	90	80	60	40
Activity ( $\text{mA cm}^{-2}$ )	33	35	40	42	28
Abrasion resistance*	p	p	g	vg	m

\*vg = very good; g = good; m = medium; p = poor.

The effect of pressing temperature was studied using electrodes prepared from either 60 wt.% or 80 wt.% Black Pearls 2000, and operating pressures of either 40 MPa or 80 MPa. The results are shown in Table 4. Although there is some scatter in these results, it appears that the activity is higher at 40 MPa rather than at 80 MPa, and that slightly better activity may be obtained by use of 80% carbon. Overall, however, differences are small and conditions for the preparation of a suitably active electrode do not seem critical. An attempt was made to prepare electrodes at 140 and 150 °C, of these only that pressed at 120 MPa and 150 °C could be tested, the others disintegrating on immersion in the electrolyte. The combined effect of pressure and press time at 180 °C was examined, using both 60 wt.% and 80 wt.% carbon. Results (Table 5) showed neither parameter had any marked effect within the ranges used, although electrodes prepared at 40 MPa appear to be slightly more active than those formed at higher or lower pressures.

TABLE 4  
Effect of pressing temperature on the performance of two-layered electrodes

Temperature (°C)	Activity ( $\text{mA cm}^{-2}$ )				
	60 wt.% carbon			80 wt.% carbon	
	40 MPa	80 MPa	120 MPa	40 MPa	80 MPa
150	—	—	55 (m)	—	—
160	41 (g)*	37 (vg)	—	51 (p)	50 (g)
180	42 (vg)	25 (vg)	—	48 (g)	38 (m)
195	40 (m)	39 (g)	—	32 (m)	9 (g)

\*Letters in brackets indicate abrasion resistance — see Table 3.



TABLE 5

Effect of pressure and pressing time on the performance of two-layer electrodes (Pressing temperature = 180 °C.)

Carbon (%)	Time (s)	Activity (mA cm <sup>-2</sup> )			
		20 MPa	40 MPa	80 MPa	120 MPa
60	5	—	42 (m)*	31 (g)	—
	15	20 (g)	42 (vg)	25 (vg)	32 (vg)
	30	—	32 (g)	34 (g)	—
80	5	—	50 (g)	40 (g)	—
	15	48 (m)	48 (g)	36 (m)	21 (m)
	30	—	36 (m)	41 (m)	—

\*Letters in brackets indicate abrasion resistance — see Table 3.

TABLE 6

Performance data for two-layered electrodes prepared from various carbon blacks

Carbon Type	Area (m <sup>2</sup> g <sup>-1</sup> )	Activity (mA cm <sup>-2</sup> )	
		60 wt.% carbon	80 wt.% carbon
FEF	43	3 (vg)*	8 (vg)
3H	90	9 (vg)	9 (vg)
SAF	143	3 (vg)	7 (vg)
Ketjen black	1000	20 (vg)	14 (g)
Black Pearls 2000	1050	21 (m)	35 (g)

\*Letters in brackets indicate abrasion resistance — see Table 3. Electrodes prepared at 80 MPa, 180 °C, and 15 s.

Parallel series of activity tests were conducted on electrodes produced from four other carbon blacks. The findings clearly show (Table 6) that the low packing density, high surface area blacks give the best performance.

The results reported in Tables 3 - 6 were obtained using a bromine concentration of 0.029 M. This value was increased to 0.12 M in a further series. The electrode activity was found to vary as (bromine concentration)<sup>0.5</sup>.

It is of interest that the magnitude of the limiting current, as shown for example in Fig. 2, is not changed by increasing agitation. This implies that the value of the limiting current is not controlled by the rate of transport of bromine to the electrode. Possible causes could be concentration polarization in the pores of the electrode, or slow adsorption or current transfer steps, but the available information is not sufficient to select between these possibilities.

Whatever the reaction mechanism, the results show that Black Pearls 2000 is the best carbon black for the top layer. The carbon/polypropylene mix should contain 60 - 80 wt.% of the carbon, and be pressed at 40 MPa

for 15 s at 160 - 180 °C, although the pressing conditions can be varied widely with only a small effect on electrode performance.

#### *Cells using PBC electrodes and polybromide electrolyte*

Most state-of-the-art zinc/bromine battery systems employ an electrolyte containing a quaternary ammonium bromide, which, if chosen correctly, forms a liquid-phase addition compound (polybromide) with the bromine liberated during charge. The aqueous-phase bromine concentration in equilibrium with this polybromide can be quite low, often 0.1 M or less, while the bromine concentration in the polybromide is typically between 5 and 9 M [2, 3, 5, 6]. During cell operation, the zinc concentration varies from 3 M in the discharged condition to 1 M at full charge.

In this work, the electrolyte was, unless otherwise stated, made up to approximate a half-charge composition at the beginning of a test run. To do this, 35 cm<sup>3</sup> of a 2 M zinc bromide/1 M *N*-methyl *N*-ethylmorpholinium bromide (EMMB) solution was reacted with 1.9 cm<sup>3</sup> of bromine (equivalent to 1.06 mole of bromine per litre of aqueous phase) to form the positive electrolyte, while the negative electrolyte was 2 M zinc bromide/0.33 M EMMB, this EMMB concentration being that in equilibrium with the polybromide phase formed as described [14]. Electrolyte pH was approximately 4. In long-term cycling tests lead was added to give a concentration of  $5 \times 10^{-5}$  M; this is necessary to obtain consistently smooth zinc deposits [15].

Note that the 70 cm<sup>3</sup> of electrolyte — the total volume in both reservoirs — has a capacity of 3.75 A h for a 1 M zinc concentration change, but that only 0.4 A h is used in the polarization test; thus there is little change in electrolyte composition during this relatively short cycle. Further, all cycles are zinc-limited on discharge due to the presence of a large excess of bromine.

Polarization tests made using this electrolyte and a cell having a PBC bromine electrode of average performance, yielded the results shown in Fig. 3. Closely similar results are obtained if a platinum gauze welded to a titanium backing sheet is substituted for the PBC electrode. It can be seen that cell voltage is linear with current density, and that there is only a slight change in performance between the freshly charged and the nearly discharged conditions. If the measured cell voltage is corrected for ohmic loss, the resultant curves are also quite linear and therefore it is clear that the non-ohmic losses can be expressed as an equivalent resistance, termed the "polarization resistance". Comparison of the as-measured and the *IR*-corrected curves show that the major voltage losses under load are due to the ohmic resistance of the cell.

The change in cell polarization resistance as a function of the fraction of the zinc deposit dissolved during discharge is shown in Fig. 4 for a cell using a platinum gauze positive. It can be seen that initially there is little change in polarization resistance, followed by a steady increase in this parameter after about 60% of the zinc has been removed. Measurement of the zinc and bromine electrode potentials shows this increase to occur wholly

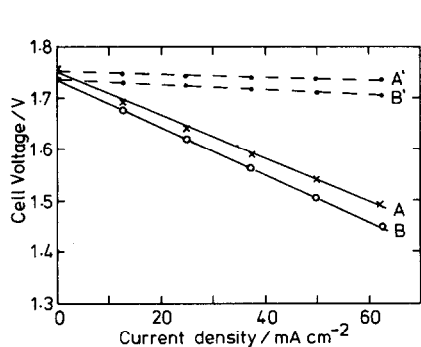


Fig. 3. Polarization curves for zinc/bromine cell. PBC positive and titanium negative electrodes. A, measured cell voltage at start of discharge; B, measured cell voltage when 93% of zinc deposit dissolved; A', cell voltage, *IR*-corrected, at start of discharge; B', cell voltage, *IR*-corrected, when 93% of zinc deposit dissolved.

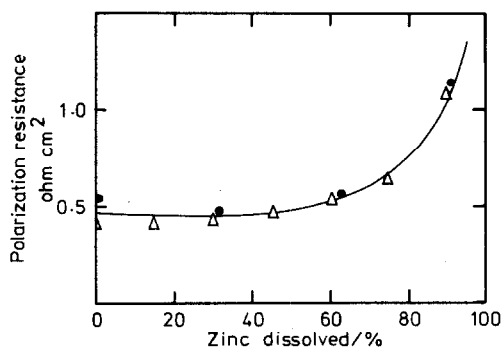


Fig. 4. Effect of fraction of zinc dissolved on cell polarization resistance. ●, 1 h charge, 15 min polarization interval; Δ, 4 h charge, 30 min polarization interval.

at the zinc electrode. Since the polarization resistance is constant over the first two-thirds of the discharge, values of this parameter quoted below are those measured when approximately 30% of the zinc has been dissolved.

The average cell polarization resistance at 25 °C measured for a PBC bromine/titanium zinc combination was  $0.279 \pm 0.079$  ohm cm<sup>2</sup> (26 samples). This may be compared to an average of  $0.46 \pm 0.09$  ohm cm<sup>2</sup> for the polarization resistance when the platinum gauze positive was substituted for the PBC electrode, and with the cell ohmic resistance of approximately 4 ohm cm<sup>2</sup>. It is also of interest to compare these values with the polarization resistance of a bromine electrode consisting of the substrate layer only, namely, 6.2 ohm cm<sup>2</sup>.

The polarization resistance values given above are for the whole cell, and incorporate that of both the zinc and bromine electrodes. Measurements of zinc electrode polarization against a reference electrode consisting of a strip of zinc metal immersed in the negative-side reservoir have given a value of  $0.07 \pm 0.02$  ohm cm<sup>2</sup>. Although this result is probably not of high accuracy due to poor placement of the reference electrode and a large ohmic correction, it suggests that the polarization of the bromine electrode is 0.21 ohm cm<sup>2</sup> for PBC material and 0.39 ohm cm<sup>2</sup> for platinum gauze.

The above data are for one temperature and one electrolyte composition, and it is of interest to study the effect of changes in both these parameters on the polarization resistance. The influence of electrolyte temperature was evaluated over the range 8 - 52 °C using the zinc bromide/EMMB electrolyte described above. From the results given in Fig. 5 it can be seen that although the cell polarization resistance decreases with increasing temperature, as might be anticipated, the change is relatively small.

Since EMMB has been found to cause some operational problems in zinc/bromine cells due to the formation of solid phases below about 15 °C

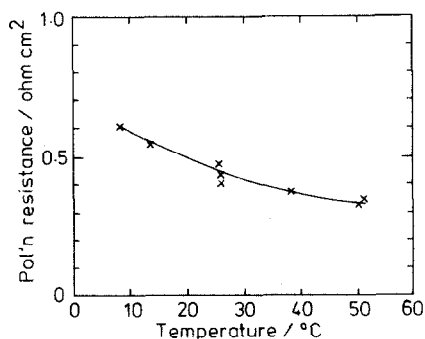


Fig. 5. Effect of electrolyte temperature on cell polarization resistance.

[14], the use of other quaternary ammonium bromides has been studied. Cell polarization resistance values have been determined for some of the more promising quaternary ammonium bromides found in earlier work, namely, *N*-methyl *N*-ethylpyrrolidinium bromide (MEPB), dimethylethylpropyl ammonium bromide (2MEP), and methyldiethylpropyl ammonium bromide (2EMP). Also, since potassium chloride is often added to the basic zinc bromide electrolyte to increase conductivity, one test was made to assess the effect of this addition. As with the changes in temperature, the effect of change in electrolyte composition on cell polarization resistance was found to be relatively small (Table 7).

TABLE 7

Effect of electrolyte composition on cell polarization resistance at  $26.1 \pm 0.3$  °C

Quaternary ammonium bromide*	[KCl] (M)	Polarization resistance (ohm cm <sup>2</sup> )
EMMB	—	0.37
MEPB	—	0.30
2MEP	—	0.35
2EMP	—	0.34
MEPB	3	0.38

\*All solutions 2 M in zinc bromide.

The maximum current density used in all the above tests was  $63 \text{ mA cm}^{-2}$ , and in all cases the cell voltage was a linear function of the current density. In one series of tests, the procedure was modified to examine cell performance at higher current densities. Measurements revealed (Fig. 6) that the linear relation between cell voltage and current density is maintained at least to a current density of  $270 \text{ mA cm}^{-2}$ , while the *IR*-corrected cell EMF shows only a slight deviation from the linear relation for current densities above  $175 \text{ mA cm}^{-2}$ . These findings were obtained using a zinc bromide/EMMB electrolyte. A closely similar result was observed with

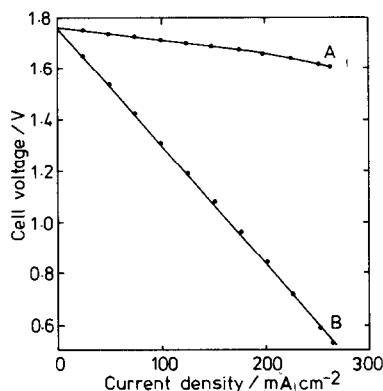


Fig. 6. Cell performance at high current density. Results are at 22 °C and for approx. 10% zinc dissolution. A, *IR*-corrected cell voltage; B, as-measured cell voltage.

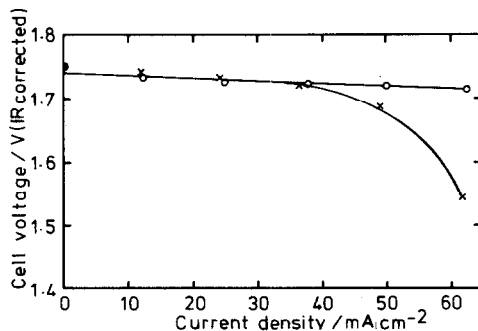


Fig. 7. Cell voltage with and without polybromide. x, No polybromide present —  $\text{ZnBr}_2/\text{Br}_2$  solution; O, polybromide phase formed from EMMB present.

zinc bromide/MEPB, even though the aqueous bromine concentration in this system is only approximately half that of the EMMB system.

#### *Performance of cells using electrolytes without polybromide*

No sign of any limiting current was seen in the presence of polybromide phase, despite the fact that the aqueous bromine concentration is approximately 0.08 M — a value which would be expected to give a limiting current of the order of 10 mA cm<sup>-2</sup> if the rate of reaction at the electrode was controlled by diffusion in the aqueous phase [16]. To examine this point, further tests were made using an electrolyte containing no quaternary ammonium bromide and, hence, no polybromide phase.

Tests without polybromide were made using an electrolyte containing zinc bromide without any additions other than that of bromine to the positive side. In order to keep the experimental conditions similar to those for tests with electrolytes containing quaternary ammonium bromides, the bromine concentration was held in the range 0.02 - 0.10 M. To prevent excessive changes in bromine concentration during charge and discharge, the positive-side volume was increased to 325 cm<sup>3</sup>.

The results of a polarization test are presented in Fig. 7, where the *IR*-corrected cell EMF for the simple zinc bromide electrolyte is compared with that obtained using a polybromide system, the positive electrode being a platinum gauze. It can be seen that, for a current density greater than about 25 mA cm<sup>-2</sup>, there is considerably more non-ohmic polarization for the simple electrolyte, with the apparent onset of a limiting current at about 60 mA cm<sup>-2</sup>. Measurement of the positive electrode potential confirmed that this increase occurred at the bromine electrode.

To study the onset of these limiting currents further, tests were made over a range of electrolyte flow rates and bromine concentrations using both

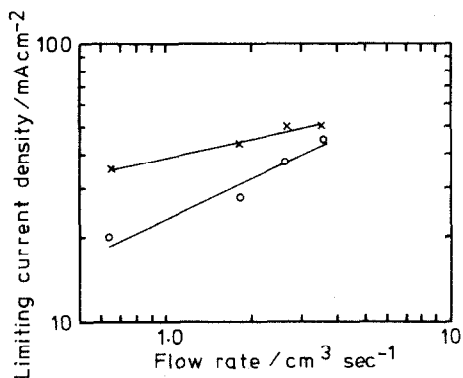


Fig. 8. Effect of electrolyte flow rate on limiting current density. Bromine concentration 0.037 M. 25 °C. ○, Platinum gauze bromine electrode; x, PBC bromine electrode.

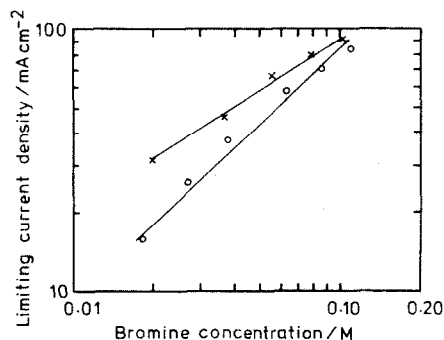


Fig. 9. Effect of bromine concentration on limiting current density. Electrolyte flow rate 160 cm<sup>3</sup> min<sup>-1</sup>. 25 °C. ○, Platinum gauze bromine electrode; x, PBC bromine electrode.

platinum gauze and PBC positive electrodes. In all cases, the negative was a 0.4 mm zinc sheet; this meant that charging could be avoided, and a single polarization run completed in 1 min, during which time the change in the bromine concentration was negligible. The current density was increased until a limiting current (caused by polarization of the bromine electrode) was obtained. These limiting current densities are shown as a function of flow rate in Fig. 8, and of bromine concentration in Fig. 9.

For the platinum gauze positive, the limiting current is proportional to (flow rate)<sup>0.50</sup> and (bromine concentration)<sup>0.93</sup>. These exponents are close to the values of 0.50 and 1.0 expected for diffusion control of the limiting current with developed laminar flow in a parallel plate electrolyser [16]. The calculated value of the limiting current for a bromine concentration of 0.04 M and a flowrate of 1 cm<sup>3</sup> s<sup>-1</sup> is 8 mA cm<sup>-2</sup>, well below the 25 mA cm<sup>-2</sup> measured. This may be because the equation is developed for plane electrodes and an unobstructed flow channel, whereas the cell used had a gauze electrode and spacing elements in the flow channel, both of which would tend to increase mass-transport rates.

With a PBC positive, the flow-rate exponent fell to 0.22, while that for bromine concentration was 0.63. These exponents are well below those expected for diffusion control in the aqueous phase, and it seems likely that some other process sets the value of the limiting current.

The most important result is that the limiting current for the simple zinc bromide electrolyte was always less than 80 mA cm<sup>-2</sup> for bromine concentrations similar to those found in equilibrium with polybromide phases. With dispersed polybromide, no limiting current is seen, even at a current density of 270 mA cm<sup>-2</sup>. In this respect, it is of interest to note that in one battery system where the polybromide phase is equilibrated with the aqueous phase external to the battery stack, and only the aqueous phase

circulated through the cells, it has been necessary to use porous flow-through bromine electrodes to avoid concentration polarization [6].

#### *Durability of PBC bromine electrodes*

All the above work was performed with freshly prepared PBC electrodes. In a practical battery, however, electrode performance must be maintained at a useful level for some hundreds of cycles. It is therefore desirable to obtain some information on the degree of performance degradation experienced by these PBC electrodes during cell operation.

To assess the degree of such degradation a cell was run for some 501 cycles using the test profile described in the Experimental section. The electrode performance was determined at suitable intervals by the polarization test method. The bromine electrode resistance increased from an initial value of  $0.32 \text{ ohm cm}^2$  to  $0.59$  at the end of the test, an increase of  $0.27 \text{ ohm cm}^2$ . However, the total apparent cell resistance (*i.e.*, the slope of the  $I$ - $V$  line) increased from  $4.3$  to  $6.9 \text{ ohm cm}^2$ , an increase of  $2.6 \text{ ohm cm}^2$ .

In order to resolve this difference between the increases in bromine electrode polarization and total cell resistance, a second electrode was run for some 500 cycles, but in this case the bromine electrode ohmic resistance was estimated from the amplitude ratio and phase angle between the  $1 \text{ kHz}$  components of the current and the bromine electrode potential. For this cell the bromine electrode polarization resistance increased by  $0.7 \text{ ohm cm}^2$  over the 500 cycles, while the electrode ohmic resistance increased by  $1.9 \text{ ohm cm}^2$ . This is a total increase of  $2.6 \text{ ohm cm}^2$ , which is equal to the increase in apparent cell resistance reported above. It therefore seems that most of the degradation in cell performance observed is due to deterioration in the bromine electrode, and that the major part of this deterioration is due to increase in its ohmic resistance. The electrodes discussed here were the best of those tested. In some other cases there was a change in the nature of the polarization curve after some 250 - 300 cycles, in that the polarization resistance was no longer independent of the current density, but increased with increasing current density.

It is not clear from the above tests whether the changes observed in the bromine electrode are caused by the cycling process, or whether contact with bromine-containing electrolyte alone is sufficient. To clarify this point, a PBC bromine electrode was immersed in  $2 \text{ M}$  zinc bromide/ $1 \text{ M}$  bromine solution at room temperature ( $\sim 25^\circ\text{C}$ ) for  $4230 \text{ h}$ ; the electrode was withdrawn periodically and its performance estimated via the polarization test. Initially, the polarization resistance was  $0.38 \text{ ohm cm}^2$  while the electrode ohmic resistance was  $1.28 \text{ ohm cm}^2$ . After  $2610 \text{ h}$  (approximately equivalent to 500 cycles) these values had risen to  $1.39$  and  $3.31 \text{ ohm cm}^2$ , respectively, increases of  $1.01$  and  $2.03$ . The increases are similar to those obtained in the cycle tests, which suggests that the deterioration observed is due to contact with a bromine-containing electrolyte rather than to physico-chemical changes to the electrode consequent upon cycling.

It is of interest to note that with further immersion in the bromine solution the polarization resistance continued to increase, reaching 2.15 ohm cm<sup>2</sup> after 4320 h (*i.e.*, approximately equivalent to 800 cycles), while the electrode ohmic resistance remained essentially constant. Drying this electrode at 110 °C overnight caused the polarization and ohmic resistances to fall to 0.59 and 1.8 ohm cm<sup>2</sup>, respectively. When the electrode was exposed to electrolyte again, however, both the ohmic and polarization resistances returned fairly rapidly (in less than 60 h) to the higher values found at the end of the immersion test.

The effect of exposure to zinc bromide/bromine solution on the carbon black alone was investigated by agitating Black Pearls 2000, previously heated to 250 °C to simulate approximately the conditions of electrode fabrication, with 2 M zinc bromide/1 M bromine for 1000 h at room temperature. The carbon black was then filtered, washed, dried, and the surface area determined by the BET method. This area, together with those for both untreated and preheated (250 °C) Black Pearls 2000 is given in Table 8. The results show that there is a marked decrease in surface area both after heating and after exposure to the bromine-containing solution. A bromine electrode was prepared using the carbon which had been leached in the zinc bromide/bromine solution: polarization and electrode ohmic resistances of 0.54 and 2.2 ohm cm<sup>2</sup> were obtained. These values are only marginally lower than those measured after 1000 h in the immersion test described above, namely, 0.76 and 2.6 ohm cm<sup>2</sup>.

TABLE 8  
Surface area of Black Pearls 2000

Sample	BET surface area (m <sup>2</sup> g <sup>-1</sup> )
As received	1360
Heated to 250 °C	1180
Heated to 250 °C, 1000 h in ZnBr <sub>2</sub> /Br <sub>2</sub>	812

#### *Performance of zinc/bromine cells — Discussion*

There are significant differences in electrode polarization between the use of an electrolyte containing dispersed polybromide as opposed to a zinc bromide solution having a bromine concentration similar to that existing in the aqueous phase of polybromide systems. In particular, a limiting current is not observed in the presence of polybromide (Fig. 7), but is found when using zinc bromide solutions containing no quaternary ammonium bromide. In the latter case, the effects found for electrolyte flow rate and bromine concentration, for a cell with a PBC bromine electrode, (Figs. 8, 9) are not consistent with the reaction rate being controlled by the rate of diffusion of bromine to the electrode. Limiting currents are also observed with a



platinum gauze electrode, but here the effects of bromine concentration and electrolyte flow rate are consistent with the limiting current being controlled by aqueous phase concentration polarization.

Kinoshita *et al.* [17] studied the electrolytic reduction of bromine in a two-phase electrolyte containing a polybromide phase and found that the reduction current was increased if drops of polybromide were allowed to contact the electrode. This is consistent with our finding that the limiting current value at a bromine electrode is greatly increased in the presence of a dispersed polybromide phase. Further, Po-Yen Lu and Alkire [18], in an examination of mass transfer in parallel-plate electrolyzers having a two-phase electrolyte showed that, for a sparingly soluble reactant, a large increase in mass transfer rate could be achieved by extraction of the reactant from a dispersed second phase. This mechanism could be relevant for cases where the value of the limiting current is due to concentration polarization in the aqueous phase.

With use, electrodes exhibit a noticeable decrease in electrode performance: both polarization and ohmic resistances increase with time, irrespective of whether the electrode is cycled or merely allowed to remain in contact with a zinc bromide/bromine solution. The mechanism of this performance degradation is not known, but possible explanations include:

(i) Loss of carbon black from the surface of the electrode: there is, in fact, some visible evidence of this when a new electrode is put into service. Surface area estimation made via bromine adsorption measurements [19], however, show relatively small changes over the life of the electrode. This suggests that any loss of carbon is not severe, and is not the main cause of the performance loss observed.

(ii) Absorption and reaction of bromine with polypropylene: this has been reported [20], and might result in structure changes within the electrode leading to loss of inter-particle contact. The temporary recovery in performance observed on drying used electrodes seems to give some support to this suggestion.

(iii) Slow oxidation of the catalytically active sites on the carbon by bromine: this could lead to a persistent loss in activity. A permanent increase in polarization resistance is observed, but this is usually smaller than the increase in ohmic resistance. Thus, this mechanism is unlikely to be the major reason for the loss in electrode performance.

(iv) Poisoning of carbon black by strong absorption of foreign materials (*e.g.*, plasticizers): those tests in which the polarization resistance was a function of current density may be an instance of this type of electrode degradation.

## Conclusions

Investigation of the conductivity of PBC compacts has shown that mixtures sufficiently conductive for use in bipolar electrodes can be obtained

using a wide variety of carbon blacks. Generally, the most conductive mixes are prepared from the low bulk density, high conductivity blacks such as Ketjen black and Black Pearls 2000. Compacts prepared from these latter materials are comparable to, or lower in, resistance than those prepared with powdered graphite. Conductivity of these mixes, while sufficiently high for bipolar electrodes, is inadequate if current must be drawn from one edge of an electrode, or from a localized area on the rear surface, as is the case for the end electrode of a bipolar stack. For such conditions it is necessary to form the PBC on a mesh and use this metal support as the current takeoff.

PBC material of adequate conductivity can be prepared from a wide range of carbon blacks if a relatively small adjustment is made in the fraction of carbon used in the mix. For example, the conductivity characteristic of a 20 wt.% Ketjen black/80 wt.% polypropylene mix can be duplicated with the FEF by increasing the carbon to 30 wt.%. The feasibility of such a substitution will depend on other requisite properties; for example, mix fluidity is of importance when injection moulding is the preferred method of fabrication.

The work was extended to the preparation of small ( $2 \text{ cm}^2$ ) electrodes for use in single electrode studies using an electrolyte comprising a dilute solution of bromine in 6 M sodium bromide. It was found that a two-layer structure was necessary to obtain a sufficiently active electrode. The substrate of this combination is relatively high in plastic and, hence, tough and non-porous: carbon fibre is usually added to increase the strength even further. The top layer (*i.e.*, that in contact with the bromine-side electrolyte) is high in carbon, and in consequence more friable and porous — the most active electrodes are obtained when blacks such as Ketjen or Black Pearls 2000 are used in this layer.

When the electrolyte is a dilute solution of bromine in concentrated bromide the electrode activity is satisfactory, but limiting currents are observed which are not affected by increase in agitation level. This suggests that the magnitude of these currents is not controlled by transport of bromine to the electrode surface. The mechanism controlling the magnitude current has not been defined, however.

One of the more active carbons — Black Pearls 2000 — has been used to prepare bromine electrodes for use in a small ( $16 \text{ cm}^2$ ) zinc/bromine cell. In early stages of cycling, the polarization and ohmic resistances of these electrodes have been found to be of the order of 0.3 and 0.8 ohm  $\text{cm}^2$ , respectively; these values give cells of satisfactory performance. When used with an electrolyte carrying a dispersed polybromide phase, no limiting current is observed up to a maximum current density of  $270 \text{ mA cm}^{-2}$ . Limiting currents are found, however, when an electrolyte consisting of a dilute ( $<0.1 \text{ M}$ ) solution of bromine in 2 M zinc bromide replaces the polybromide system. These limiting currents are similar in magnitude to those found with the  $2 \text{ cm}^2$  electrodes.

After 500 cycles, each of approximately 5 h total duration, some loss in bromine electrode performance is observed, the polarization and ohmic

resistances increasing to about 1 and 2.5 ohm cm<sup>2</sup>, respectively, for the best performed electrodes. Similar deterioration is observed if the electrode is simply immersed in a bromine-containing solution, without being charge/discharge cycled. This suggests that the degradation is brought about by reaction of some electrode component with bromine. The mechanism of this deterioration is not clear, but there is some evidence, by no means conclusive, that degradation of the plastic binder is one important factor.

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