JOURNAL OF APPLIED ELECTROCHEMISTRY 17 (1987) 515–524

Studies of Zn|ZnX$_2$|polyaniline batteries. I. X = Cl and Br

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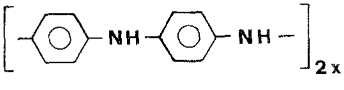
Received 24 March 1986; revised 12 May 1986

The cycling behaviour of polyaniline in chloride and bromide media is discussed. In both media some charge, equivalent to a charge storage capacity of $100\,\mathrm{A\,h\,kg^{-1}}$, may be stored in the first oxidation step of polyaniline. Further evidence is presented that the oxidation product is emeraldine rather than the fully oxidized imine. In chloride media, attempts to store more charge led to rapid irreversible changes in the polymer and degradation in battery characteristics. In bromide media, further charge may be stored via the Br^-/Br_3^- couple and, although the Br_2 attacks the polymer slowly, the polymer retains the ability to cycle charge efficiently and gives a stable open-circuit voltage. The nature of the changes caused by Br_2 attack on the polyaniline is discussed. It is concluded that bromide is the better electrolyte, but self discharge by slow exchange of Br_3^- in the polymer with Br^- in the surrounding electrolyte remains an unsolved problem.

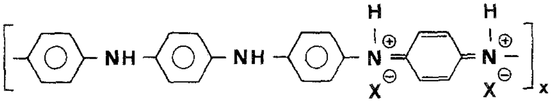
1. Introduction

The last few years have seen intense activity towards the development of a 'polymer battery' [1] where the electroactive materials are conducting polymers. A favoured polymer has been polyacetylene [2] because it may be both p-doped by the intercalation of anions and n-doped by the intercalation of alkali metal cations. Both doping reactions are highly reversible and the combination of p- and n-doped materials leads to a rechargeable battery with a large voltage and high energy density. Unfortunately, however, the characteristics of the cell are limited by the poor chemical stability of polyacetylene particularly when positively charged [3, 4]. Hence the charge storage characteristics of other organic conductors are receiving attention.

Polyaniline was first prepared in the 19th century [5]; Moreover, its high conductivity and the possibility for utilizing its redox properties for electrical energy storage have been recognized for some time [6, 7]. Recent studies have concentrated on understanding the multistep oxidation processes of the neutral polymer [8–11]. Reversible charge–discharge cycling is likely to be limited to the first oxidation step; in acid solution it has recently been concluded by two different groups that the first oxidation product is the emeraldine salt, II [12] or the imine salt, III [9–11]



neutral polyaniline, I



emeraldine salt, II

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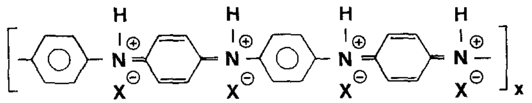

imine salt, III

In both cases it can be seen that the doping process involves both protons and electrons and it was concluded by both groups that further oxidation leads to irreversible changes to the polymer. Whether the couple is in fact I/II or I/III, the potential for the redox change in the polymer is 0.2–0.3 V versus SCE, rather low for a battery electrode, but the absence of degradation processes and the ability of polyaniline to store considerable charge through this redox process have led to proposals for both aqueous [13] and non-aqueous batteries [14].

In the present study the charge–discharge characteristics of Zn–polyaniline batteries with both $ZnCl_2$ and $ZnBr_2$ electrolytes have been examined. Particularly with the $ZnBr_2$ cell, attention has been paid to the behaviour of the polyaniline when oxidized beyond the first oxidation step. The aim of the study was to assess whether the charge-storage capability of the polymer could be increased by oxidation of the Br^- in the polymer to Br_3^- and to investigate the structural changes resulting from attack by bromine. In an earlier paper it was shown that the Br^-/Br_3^- couple could be cycled within polypyrrole, but the stability of the oxidized polymer was insufficient for battery application [15].

2. Experimental details

The polyaniline electrodes were prepared and the model battery assembled by the following procedure. The support for the polyaniline was a high-porosity, reticulated vitreous carbon (RVC) disc (radius, 2.5 cm; height, 0.5 cm) fixed to a graphite disc as a current collector. This structure was mounted inside a cylindrical, polyethylene cell and was separated from the zinc disc electrode by a cellulose membrane. A hole in the zinc electrode allowed the introduction of a probe to control the potential of the RVC electrode versus SCE. The polyaniline film was applied electrochemically; the cell was filled with a solution of 1.5% aniline in 0.5 mol dm^{-3} H_2SO_4 and the potential of the RVC was held at 0.8 V versus SCE. To enhance the uniformity of deposition, the solution was pumped through the cell. The weight of the deposit was determined from the charge using a calibration graph. After this preparation the polyaniline was conditioned to the chosen electrolyte by repeated soaking of the cell with new aliquots of this electrolyte for 24 h.

Charge–discharge cycles were obtained at constant current, and the voltage between the zinc and polyaniline electrodes was monitored as a function of time.

Some experiments used a 0.06 cm^2 polished, vitreous carbon disc electrode as the support for the polyaniline. In these cases the film was formed by cycling the potential between −0.3 V and +0.8 V versus SCE in a solution of 1.5% aniline in 0.5 mol dm^{-3} H_2SO_4 and then conditioned with the medium of choice. Experiments with these electrodes employed a standard, three-electrode cell.

The compositions of both the chemically and electrochemically prepared samples of polyaniline were determined by elemental analysis. The composition of films after exposure to Br_2 was also investigated by mass spectroscopy (Hitachi–Perkin Elmer RMV spectrometer). Conductivities were measured on pressed (3 tons cm^{-2}) polyaniline discs; a Kulike and Soffa four-probe head (linearly arranged) was used in conjunction with a digital voltmeter and ammeter (Keithley).

All chemicals were commercially available grades and were used as supplied. The RVC was from Fluorocarbon Co. and had a porosity of 100 pores per inch.

3. Results and discussion

3.1. *Chemical composition of the polyaniline samples*

Before constructing the model battery, some tests were performed to determine the yield of polyaniline (mg C^{-1}) and its chemical composition. The polymer was deposited from a solution of 1.5% aniline in 0.5 mol dm^{-3} H_2SO_4 onto platinum and gold anodes (each of area 10 cm^2) and used a potential of +0.8 V. Ten experiments were carried out and charges between 1 and 10 C cm^{-2} were used in the polymerizations. After each deposition the electrode was carefully rinsed with the aqueous acid, then water and then vacuum-dried overnight before being weighed to determine the polymer yield; the weight of polymer increased linearly with charge. The polymer was then subjected to elemental analysis. The data are reported in Table 1.

A similar set of experiments were carried out with 0.5 mol dm^{-3} HBr as the electrolyte. In addition, polyaniline was prepared by chemical oxidation with H_2O_2 in both H_2SO_4 and HBr. H_2O_2 rather than $S_2O_8^{2-}$ was selected as the oxidizing agent since with HBr the latter leads to free bromine and the polyaniline would contain sulphate as well as bromide ions. Table 1 also reports data for these polyaniline samples.

Clearly, when prepared at +0.8 V versus SCE or chemically with H_2O_2, the polyaniline should be in its oxidized state and it should retain an anion during washing and drying. On the other hand, some exchange of Br_3^- for Br^- would be expected during the procedure for the sample prepared electrochemically in HBr. Clearly the chemical composition of the chemically and electrochemically prepared samples are similar, and the chemically prepared samples have a good conductivity. Moreover, calculations that assume the anions present in the polymer are Br^- and HSO_4^- suggest similar oxidation states for all samples of polyaniline. Certainly there is no evidence that the sample prepared electrochemically in HBr has suffered extensive bromination at +0.8 V.

3.2. *Charge–discharge cycling*

A model battery (A) was assembled with a polyaniline electrode prepared by passing 500 C and then conditioned with the electrolyte 2 mol dm^{-3} $ZnCl_2$ + 0.5 mol dm^{-3} NH_4Cl (pH ≃ 4) [13]. After preparation at +0.8 V, the polyaniline would be expected to be *ab initio* charged and, indeed, the open circuit potential of the battery was 1.3 V. When the battery was discharged at 30 mA the voltage dropped slowly until the passage of 85 C, but thereafter the voltage decreased rapidly from 0.4 V towards zero. Subsequent charge–discharge cycling showed the maximum charge in the polymer to be 80–90 C, and charging at 30 mA to higher charges caused the voltage of the cell to exceed 1.6 V where over-oxidation of the polymer is likely.

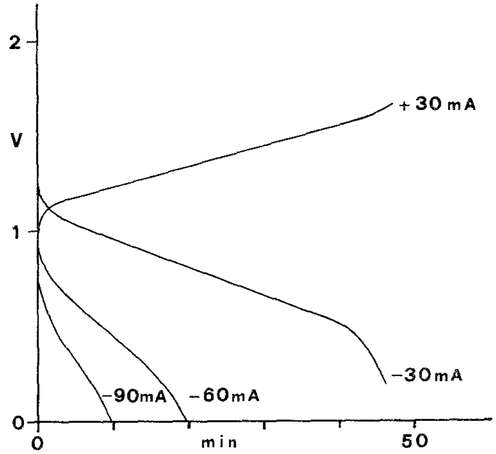

Fig. 1. Charge–discharge characteristics of a Zn–2 mol dm^{-3} $ZnCl_2$ + 0.5 mol dm^{-3} HN_4Cl–polyaniline (synthesis 500 C) cell.

Fig. 1 shows a typical charging curve (at 30 mA) and three discharge curves for currents of 30, 60 and 90 mA. With the discharge current of 30 mA, and considering the cut voltage to be +0.4 V (where d*E*/d*t* changes rapidly), the coulombic efficiency for the cycle is almost

Table 1. Polymer yield and/or compositions of polyaniline samples prepared electrochemically (E) and chemically (C) with H_2O_2

Preparation	*Electrolyte*	*Elemental analysis (%)*						*Polymer yield ($mg\ C^{-1}$)*	*Resistance ($\Omega\ cm$)*
		C	*H*	*N*	*S*	*Br*	*Total*[a]		
E	H_2SO_4	48.02	4.13	9.31	8.91	–	88.17	0.53 ± 10%	–
E	HBr	43.89	3.58	8.31	–	36.50	92.28	0.42 ± 15%	–
C	H_2SO_4	47.09	4.18	9.00	9.07	–	87.48	–	70
C	HBr	41.59	3.93	7.88	–	32.99	86.39	–	100

[a] The total was calculated by assuming that all S was present as sulphate and by adding the corresponding O percentage.

Table 2. Performance data for two polyaniline–zinc cells. The electrolytes were (A) 2 mol dm^{-3} $ZnCl_2$ + 0.5 mol dm^{-3} NH_4Cl; (B) 2 mol dm^{-3} $ZnBr_2$ + 1.0 mol dm^{-3} NH_4Br

Cell	*Charge (C)*	*Rest time (h)*	*Open circuit voltage (V)*	$I_{discharge}$ *(mA)*	*Charge returned (C)*	*Coulombic efficiency (%)*
A	83	–	1.41	30	82	99
	97	–	1.50	30	86	89
	80	–	1.36	60	60	75
	80	–	1.32	90	36	45
	80	3	1.30	30	73	92
	86	20	1.20	30	68	79
	85	65	1.20	30	58	68
	78	89	1.20	30	57	73
B	Synthesis	–	1.43	30	133	–
	135	–	1.52	30	133	99
	135	–	1.52	60	115	85
	132	–	1.55	90	97	73
	128	30	1.32	30	117	91
	145	70	1.24	30	106	73
	130	162	1.12	30	78	60
	135	331	1.00	30	55	40

Estimated short circuit currents: cell A, 190 mA; cell B 220 mA.

100% (see also Table 2). On the other hand, the charge and discharge curves in Fig. 1 show that the energy efficiency is only about 60%. As expected these performance characteristics degrade increasing discharge current.

Table 2 summarizes some characteristics of cell A and particularly addresses the rate of self discharge. It can be seen that self discharge is slow, but the coulombic efficiency for a charge–discharge cycle decreases from > 90% to about 70% with rest periods of up to 90 h.

A second model battery (B) was assembled with a polyaniline electrode, deposition charge 750 C, and an electrolyte 2 mol cm^{-2} $ZnBr_2$ + 1 mol dm^{-3} NH_4Br. Fig. 2 shows charge and discharge curves for this cell, while Table 2 also summarizes the behaviour on discharge with three different current densities and after various rest times on open circuit. Cell B shows a higher open-circuit voltage and short current than cell A, but the rate of self discharge seems very similar.

Since polyaniline in its oxidized form is very stable to air, self discharge could be ascribed to shorting by zinc dendrites or, more likely, degradation of the polyaniline (mechanical detachment or chemical modification). Certainly extensive degradation is not occurring since the change in coulombic efficiency is not fast and the rate of self discharge is quite similar for the

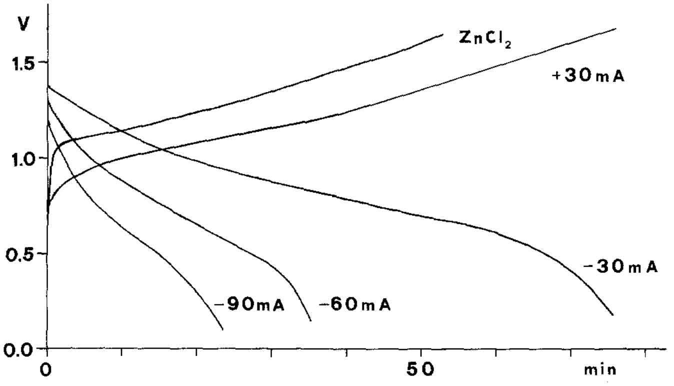

Fig. 2. Charge–discharge characteristics of a Zn/2 mol dm^{-3} $ZnBr_2$ + 1 mol dm^{-3} NH_4Br/polyaniline (synthesis 750 C) cell.

polymer with Cl^- and Br^- electrolytes. On the other hand, after 20–30 cycles in either electrolyte, there is increased polarization during both charge and discharge.

The capacity of the polyaniline electrodes reported in Table 2 allows a discussion of the oxidized state of polyaniline. Using the known polymer yields (Table 1), the N content of the films in cells A and B are 1.75×10^{-3} and 2.63×10^{-3} g atoms, respectively. Hence, if the oxidation of polyaniline occurs via the couple I/III, the expected capacities of the two electrodes would be 170 and 255 C respectively. In fact, the maximum capacity corresponds to only 50% of these figures and hence it appears that the oxidation occurs only to emeraldine salt, i.e. couple I/II. This is consistent with the conclusions of a recent paper [12]. In any case the charge density for the polyaniline appears to be 90–95 A h kg^{-1}, a reasonably high value but well below that previously claimed [14]. If the maximum conductivity is observed with the emeraldine salt (II) as recently claimed [16], the further oxidation may be inhibited because of the resulting loss of conjugation, possibly involving solitons. In a battery, such inhibition will lead to decreases in energy efficiency and, anyway, the polyimine structure seems more susceptible to hydrolysis and thus irreversible over-oxidation.

3.3. *Cyclic voltammetry*

The over-oxidation of polyaniline has been studied by cyclic voltammetry using thin films of the polymer (0.6–0.8 C cm^{-2}) electrodeposited onto

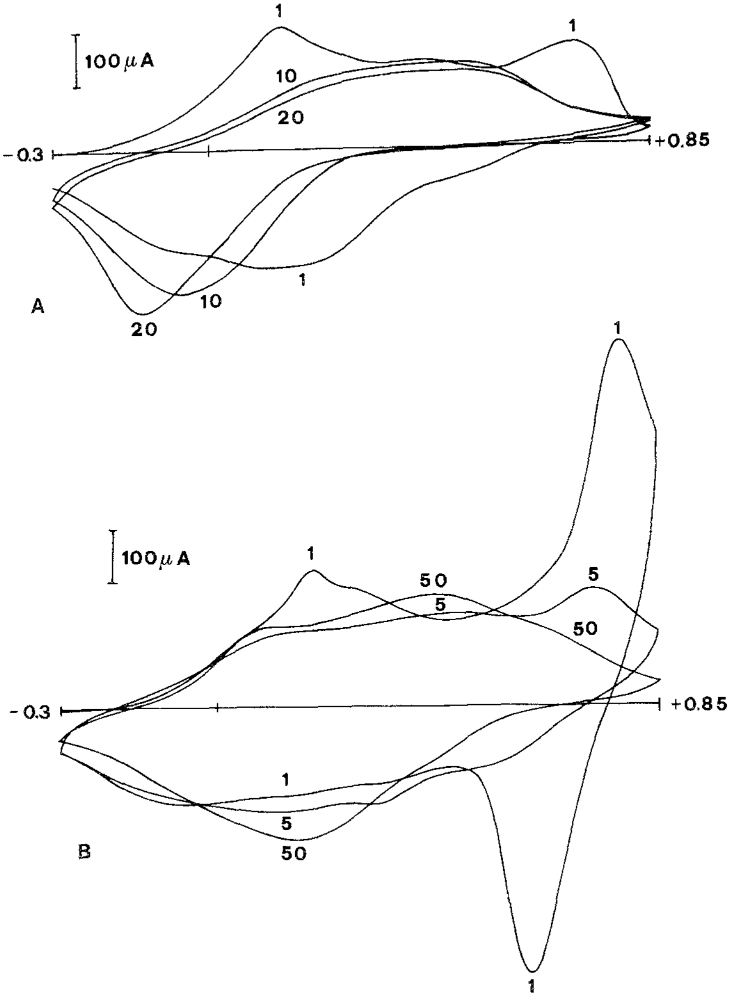

Fig. 3. Cyclic voltammograms (10 mV s^{-1}) of polyaniline films. Electrolyte composition: (A) 2 mol dm^{-3} $ZnCl_2$ + 0.5 mol dm^{-3} NH_4Cl; (B) 2 mol dm^{-3} $ZnBr_2$ + 1 mol dm^{-3} NH_4Br; (C) 2 mol dm^{-3} $ZnBr_2$ + 0.1 mol dm^{-3} HBr (see next page). The number of the cycle is reported for each curve.

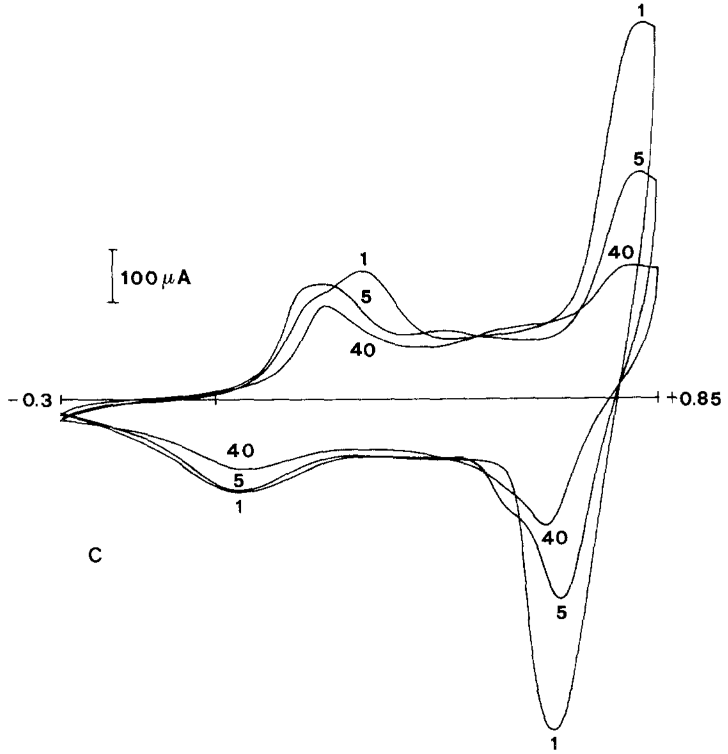

Fig. 3. Continued.

a vitreous carbon disc electrode. The potential scan rate was $10\,\mathrm{mV\,s^{-1}}$ and the range −0.30 to +0.85 V versus SCE. It is well known that in this potential range, polyaniline shows three redox couples [9–11]. The most negative is probably due to the I/II couple (some authors would suggest the I/III couple), while the most positive (0.7–0.8 V) might be due to the II/III couple or, as has been concluded in the literature, to the oxidation of imine moieties to radical cations. Such species would not be stable in aqueous solutions and would probably degrade to quinones [9–11] which could then be responsible for the intermediate redox process around 0.5 V.

Fig. 3A shows the way in which the cyclic voltammetric response of polyaniline in 2.0 mol $\mathrm{dm^{-3}}$ $ZnCl_2$ + 0.5 mol $\mathrm{dm^{-3}}$ NH_4Cl develops with time. Clear changes are seen: on the first scan two well-developed anodic peaks are seen, while by the tenth cycle most of the oxidation charge is associated with a broad peak at intermediate potentials. At the same time the main cathodic peak shifts to more negative potentials. Certainly, totally irreversible changes result from cycling the peak beyond +0.3 V. After 40 cycles the response reaches almost a steady state and although significant charge is still cycled it is about 40% lower than in the first cycle.

Fig. 3B shows a similar experiment with polyaniline in 2 mol $\mathrm{dm^{-3}}$ $ZnBr_2$ + 1 mol $\mathrm{dm^{-3}}$ NH_4Br. The major difference is on the first sweep where a large anodic peak and coupled reduction peak is observed towards the positive limit. These peaks are due to the Br^-/Br_3^- couple within the polymer. During subsequent cycles these peaks fade and by 50 cycles the response is similar to chloride media with predominantly broad oxidation–reduction peaks. Again, it is clear that irreversible changes occur which reduce the ability of the polymer to interact with anions; such behaviour would be expected if a quinone–hydroquinone couple became responsible for the cycled charge.

Fig. 3C shows the cycling behaviour in 2 mol $\mathrm{dm^{-3}}$ $ZnBr_2$ + 0.1 mol $\mathrm{dm^{-3}}$ HBr (pH 0.7). The pattern is quite different; the changes over 40 cycles are much less marked and the peaks for the Br^-/Br_3^- couple are still clearly seen, even if diminished in height. In contrast, with Cl^- media pH 0.7, the degradation of the polymer is even more rapid than that demonstrated by Fig. 3a.

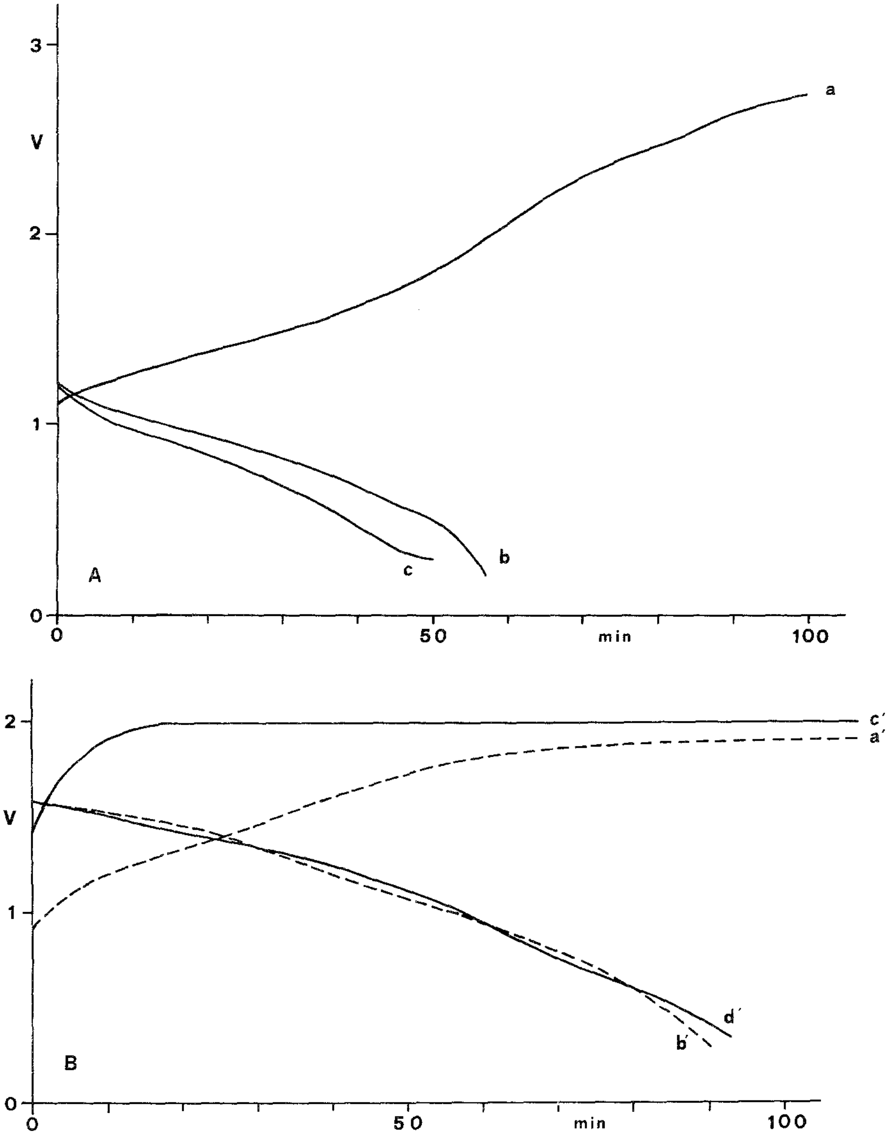

Fig. 4. (A) High-depth charge–discharge behaviour of the cell of Fig. 1. Curve a, first charge; curve b, first discharge; curve c, fourth discharge. (B) High-depth charge–discharge behaviour of a Zn/2 mol dm^{-3} $ZnBr_2$ + 1 mol dm^{-3} NH_4Br/polyaniline (synthesis 490 C) cell. Curve a′, 5th charge; curve b′, 5th discharge; curve c′, 19th charge; curve d′, 19th discharge.

3.4. *High-depth charge–discharge behaviour*

Fig. 4A (curve a) shows the voltage–time relationship during the charging of cell A (chloride electrolyte, pH 4, with polyaniline electrode formed with 500 C); the cell was charged to 200 C with a current of 30 mA. It can be seen that after the first oxidation step of polyaniline ($\simeq$ 80 C) the cell voltage rises more rapidly until a second plateau is reached around 2.6 V. This demonstrates a second oxidation stage associated with the polyaniline electrode since the zinc electrode is effectively unpolarized. The high voltage indicates the involvement of the Cl^-/Cl_2 couple; the open circuit voltage was 1.95 V immediately after charging was terminated, but this rapidly decreased, reaching 1.55 V in 5 min. When the cell was immediately discharged (30 mA) without any rest time, only 98 C could be obtained (curve b). Three further such high-depth charge–

discharge cycles led to a further drop in coulombic efficiency – curve c only shows the discharge of 79 C. Thus these experiments with cell A confirm the conclusions from cyclic voltammetry. Beyond the first oxidation stage, probably due to the couple I/II, further oxidation is totally irreversible but leads to some degradation in performance.

To study the over-oxidation with a 2 mol dm^{-3} $ZnBr_2$ + 1 mol dm^{-3} NH_4Br electrolyte, cell C was constructed with a polyaniline electrode prepared with 490 C to make it comparable to cell A. The charge–discharge behaviour is recorded in Fig. 4B. Curve a′ is the fifth charge to 200 C following four charge–discharge cycles. It can be seen that after 140 C the cell voltage reaches a steady-state value of +1.9 V. This high value suggests the potential of the polyaniline electrode is determined by the Br_3^-/Br^- couple. After the charge was ended, the open circuit voltage was 1.76 V and this remained steady. On discharge, 160 C were recovered, a coulombic yield of 80%. By the 19th cycle the *V–t* changed slightly. The constant potential on charge was reached very quickly (apparently the I/II couple no longer contributed substantially to the charge) and the system behaved very much like a $Br_3^-Br^-$ electrode. The discharge curve was almost unchanged and the coulombic efficiency remained at 80%.

These data look very promising but, in fact, the situation is not as simple as the curves suggest. This is shown by the data in Table 3. The top line reports the charge stored *ab initio* in the device as a result of the preparation. During cycles 1, 2, 5, 7 and 11 the recoverable charge increases steadily, reaching a limiting coulombic efficiency of 80%. Cycles 3, 6, 12 and 20 show the effect of storing the cell on open circuit before discharge. In cycle 3, after 87 h on open circuit, only 75 C were recovered; this is approximately the charge stored by the couple I/II (see section 3.2). After 15 h on open circuit (cycle 6), 120 C were recovered and approximately 33% of the charge could be ascribed to the Br_3^-/Br^- couple. The loss of charge on open circuit does not, however, lead to irreversible damage to the polymer as shown by subsequent cycles without open circuit stand. On the other hand, the ability to hold charge seems to improve with cycling up to cycle 12 but later deteriorates (cycle 20), so changes must be occurring to the polymer.

The bromine formed during the early charges reacts with the most active portions of the polyaniline (oligomers? outer surfaces?) leaving most of the polymer unaffected (note the charge for the I/II couple remains almost constant), and thereafter attack by Br_2 slows down and the charge for the Br_3^-/Br^- couple is stored more reversibly. Very long store times allow the bromine to react with less active or less accessible sites and thereafter charge loss is more due to Br_3^- exchange with Br^- in the electrolyte. It should be stressed that the brominated polymer still allows charge stored as Br_3^- to be cycled. Exchange between anions in the polymer and the electrolyte was confirmed by inserting a

Table 3. Characteristics of cell C (high depth charge–discharge cycling), with charge and discharge currents of ± 30 mA; short circuit current of 270 mA

Cycle	*Charge (C)*	*Rest time (h)*	*Open circuit voltage (V)*	*Charge returned (C)*	*Coulombic efficiency (%)*
0	–	–	1.37	84	–
1	200	–	1.74	133	66.5
2	200	–	1.74	146	73.0
3	200	87	1.30	75	37.5
5	200	–	1.75	161	80.5
6	215	15	1.56	120	55.8
7	200	–	1.74	175	87.5
11	200	–	1.78	182	91.0
12	215	30	1.72	155	72.0
19	200	–	1.81	175	87.5
20	215	55	1.60	25	10

Table 4. Elemental analysis and resistivity for brominated samples of polyaniline

Sample	*Bromination*	*Residual* Br_2 *(g)*	*Recovered polymer (g)*	*Elemental analysis (%)*					*Resistivity* (Ω *cm)*
				C	*H*	*N*	*Br*	*S*	
E(HBr)[a]	Battery	–	–	14.63	1.16	2.53	53.60	–	2×10^2
C(HBr)[b]	$ZnBr_2$, 2 mol dm^{-2} (pH = 2)	1.75	3.58	21.44	0.57	2.67	66.56	–	1.8×10^5
C(HBr)	$ZnBr_2$, 2 mol dm^{-3} NH_4Br, 1 mol dm^{-3}	1.66	3.67	20.58	0.59	2.36	66.97	–	1.25×10^5
$C(H_2SO_4)$	ZnBr, 2 mol dm^{-3} NH_4Br, 1 mol dm^{-3}	1.99	3.65	21.57	0.60	2.47	66.27	1.18	1.2×10^5
$C(H_2SO_4)$[c]	Br_2	–	+0.9	15.31	1.02	2.94	62.06	2.98	$\sim 10^3$

[a] Recovered after 6×10^3 C oxidation.

[b] The bromination was carried out by reacting 2 g polyaniline with 8 g Br_2 for 1 month.

[c] The reaction was carried out with 0.5 g polymer made to interact with Br_2 gas for 1 week and then kept under dynamic vacuum for a week.

Nafion cation exchange membrane when self discharge was slowed substantially, although other characteristics degraded substantially.

A fourth cell, D, was constructed with a 2 mol dm^{-3} $ZnBr_2$ + 0.05 mol dm^{-3} HBr electrolyte, but its performance was no different from cell C. This was disappointing in view of the cyclic voltammetric results (see section 3.3). A final cell, E, was prepared, again with 2 mol dm^{-3} $ZnBr_2$ + 1 mol dm^{-3} NH_4Br, but with polyaniline (800 C) deposited from HBr in the hope that the polymer would be formed in a fully brominated condition; however, the performance of this cell was again similar to that of cell C.

Cell E was finally subjected to a series of high-depth charges, about 6000 C. The polyaniline was recovered and then washed, dried and analysed. Table 4 shows that the bromine content is increased (cf. Table 1) but the conductivity is retained.

3.5. *Bromination studies*

Three samples of polyaniline, prepared by H_2O_2 oxidation in different electrolytes, were left to react with Br_2 in the dark for 1 month and the resulting polymer was recovered and studied. Relevant data are reported in Table 4. The following should be noted: (a) over 90% of the polymer is recovered, as estimated from the weights and carbon contents before and after bromination; (b) extensive bromination has occurred, equivalent to 2.5–3 Br per aromatic ring; this may be seen from both bromine content and the H/C ratios; (c) the product is still a semiconductor, but the measured resistivity is much higher than the unbrominated polyaniline. Table 4 also reports data for a sample brominated with bromine vapour.

A polyaniline brominated in cell E was subjected to mass spectroscopic analysis at 120° C using an electron impact source (70 eV). The major fragments are reported in Table 5. These suggest that most of the bromine is bound to carbon and that some oxygen is contained in the sample. In contrast, the sample brominated with bromine vapour gave a mass spectrum demonstrating that most of the bromine was present as Br_2 or HBr. This is consistent with the high H/C ratio in the elemental analysis.

4. Conclusions

Polyaniline when used as a positive electrode in a zinc–polyaniline battery has a charge storage capacity of about 100 A h kg^{-1}. This figure, referred to dry polymer, was computed by assuming that polyaniline (I) is converted to protonated emeraldine (II) with bromide counter ion. Overoxidation in Cl^- media leads to irreversible changes in chemical composition and strong degradation in battery performance. In Br^- media, over-oxidation is possible. Changes in the polymer do occur due to bromination, but additional charge may be stored as Br_3^-. The performance is not completely stable on cycling,

Table 5. Mass spectroscopic data for brominated polyaniline. The relative abundances were calculated referring to ^{79}Br isotope

m/e	*Relative abundance*	*Ionic species*
79	27	Br
80	100	HBr
104	12	C_2HBr
131	55	C_4H_4Br
157	23	C_6H_6Br
158	8	Br_2
168	12	C_6H_3NBr
171	11	$CHBr_2$
182	4	C_2Br_2
185	23	$C_6H_6N_2Br$, C_6H_4NOBr, $C_6H_2O_2Br$
221	2	$C_5H_3Br_2$
235	8	$C_6H_5Br_2$
263	45	$C_6H_5N_2Br_2$, $C_6H_3ONBr_2$, $C_6HO_2Br_2$
273	3	C_3Br_3
313	4	$C_6H_4Br_3$
327	21	$C_6H_4NBr_3$, $C_6H_2OBr_3$
341	15	$C_6H_4N_2Br_3$, $C_6H_2NOBr_3$, $C_6O_2Br_3$
342	20	$C_6H_5N_2Br_3$, $C_6H_3NOBr_3$, $C_6HO_2Br_3$
407	4	$C_6H_5NBr_4$, $C_6H_3OBr_4$
419	14	$C_6H_3N_2Br_4$, C_6HNOBr_4

and self discharge would prevent prolonged storage in the charged state. Other interesting observations were

(a) Efficient aniline electropolymerization occurs in HBr.

(b) Polyaniline has a low reactivity to Br_2 vapour although it is absorbed.

(c) In the solution phase, the aromatic rings of polyaniline are attacked and some oxygen is found in the polymer. Indeed the data suggests that the hydrolysis of over-oxidized polyaniline to quinone may precede bromination.

(d) Even so, the brominated polymer stores charge and gives a stable, high potential as well as cycling efficiency.

Acknowledgement

The financial support by NATO (grant no. RG 83/0815) is gratefully acknowledged. The authors thank Mrs A. Randi of the CNR for experimental assistance.

References

[1] G. K. Chandler and D. Pletcher, Specialist Periodical Reports – Electrochemistry (The Chemical Society, Oxford) **10** (1985) 115.

[2] P. J. Nigrey, A. G. MacDiarmid and A. J. Heeger, *J. Chem. Soc. Chem. Comm.* (1979) 594.

[3] G. C. Farrington, B. Scrosati, D. Frydrych and J. DeNuzzio, *J. Electrochem. Soc.* **131**, (1984) 7.

[4] R. Bittihn, D. Naegele, G. Kohler and R. Denig, *Mol. Cryst. Liq. Cryst.* **121** (1985) 221.

[5] R. F. Nelson in 'Techniques of Electroorganic Synthesis' Part I (edited by N. L. Weinberg) John Wiley and Sons, New York (1974) p. 621.

[6] M. Jozefowicz, L. T. Yu, G. Belorgey and R. Buvet, *J. Polymer Sci. Part C***16** (1967) 2943.

[7] R. De Sourville, M. Jozefowicz, L. T. Yu, J. Perichon and R. Buvet, *Electrochim. Acta* **13** (1968) 1451.

[8] A. F. Diaz and J. A. Logan, *J. Electroanal. Chem.* **111** (1980) 111.

[9] T. Kobayashi, H. Honeyama and H. Tamura, *ibid.* **161** (1984) 419.

[10] *Idem, ibid.* **177** (1984) 281.

[11] *Idem, ibid.* **177** (1984) 293.

[12] J. C. Chiang and A. G. MacDiarmid, *Synt. Met.* **13** (1986) 193.

[13] N. L. D. Somasiri and W. Wanqun, *Mol. Cryst. Liq. Cryst.* **121** (1985) 187.

[14] E. M. Genies, A. A. Syed and C. Tsintavis, *Mol. Cryst. Liq. Cryst.* **121** (1985) 181.

[15] G. Mengoli, M. M. Musiani, R. Tomat, S. Valcher and D. Pletcher, *J. Appl. Electrochem.* **15** (1985) 697.

[16] E. W. Paul, A. J. Ricco and M. S. Wrighten *J. Phys. Chem.* **89** (1985) 1441.