

## *On the use of pyrrole black in zinc-halogen batteries*

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The storage of  $\text{Br}_2/\text{Br}^-$  and  $\text{I}_2/\text{I}^-$  couples in a conducting polymer matrix, polypyrrole coated on a reticulated vitreous carbon disc, is described and the application of these positive electrodes in zinc-halogen model batteries is discussed. The cell based on the polypyrrole bromine adduct shows the higher open circuit voltage which, however, depends on the state of charge. Such cells self discharge thus limiting their usefulness. In the case of the iodine cell the self discharge is due to loss of iodine from the polymer to the bulk solution, but with the bromine cell the cause is oxidative bromination and depolymerization of the polypyrrole.

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### 1. Introduction

The anodic synthesis of pyrrole black in several aqueous acids and the voltammetric behaviour of these materials have recently been described [1]. Whereas in sulphuric acid and hydrochloric acid a carbon electrode covered by a pyrrole black film does not maintain a stable open circuit potential, in HBr and HI it behaves during steady state and cyclic voltammetric experiments as a solid conductive matrix for the reversible  $\text{Br}_2/\text{Br}^-$  and  $\text{I}_2/\text{I}^-$  couples and hence for the storage of charge. Thus the use of pyrrole black as a positive electrode for secondary cells was suggested. Polymers combining in their structure redox properties and conduction appear promising for light-weight battery applications [2-15]. The present work assesses, through longer term tests, whether the described pyrrole black  $\text{X}_2/\text{X}^-$  systems have any application as positive electrodes in zinc-bromine or zinc-iodine batteries.

### 2. Experimental details

The cyclic voltammetry was carried out with

standard three-compartment cells using a vitreous carbon disc (area  $0.075 \text{ cm}^2$ ) as the working electrode and a SCE reference electrode. During larger scale electrochemical tests the pyrrole black  $\text{X}_2/\text{X}^-$  electrode (positive) was coupled to a zinc electrode (negative) in a model battery assembled as follows. A reticulated vitreous carbon (RVC) disc (radius 2.5 cm, height 0.5 cm) attached with conducting epoxide glue to a graphite disc as current collector [16] constituted the support for the active polymer. The RVC (manufactured by Fluorocarbon Co., Anaheim-California) had a porosity grade of 100 pores  $\text{inch}^{-2}$ . A cellulose membrane separated the RVC from a zinc disc (radius 2.5 cm) which also provided the second electrical contact. The system was mounted inside a polyethylene cylindrical cell. Before battery experiments the RVC was coated with the active polymer by *in situ* electropolymerization of the monomer. To this end the RVC was used as anode (0.8 V vs SCE) for the required time in a separated cell containing  $0.07 \text{ mol dm}^{-3}$  pyrrole and aqueous  $0.5 \text{ mol dm}^{-3}$  HBr. The weight of the deposit could be predetermined by controlling the coulombs transferred during these

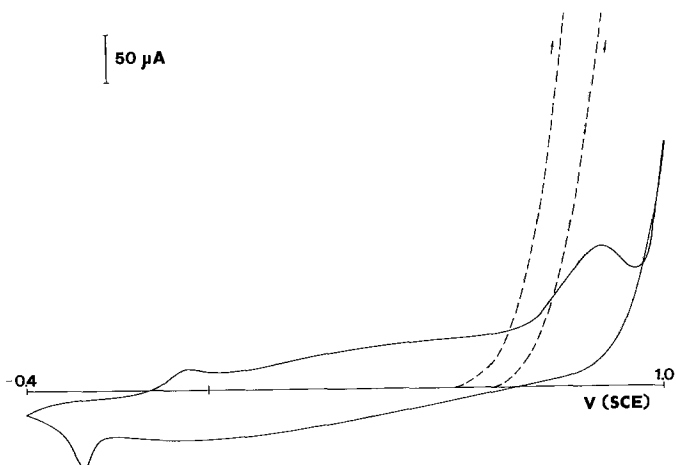


Fig. 1. Solid curve, voltammetric pattern achieved after repeated cycling of a vitreous carbon disc in a  $0.07 \text{ mol dm}^{-3}$  pyrrole solution in  $0.5 \text{ mol dm}^{-3}$  TEAP/ $\text{CH}_3\text{CN}$ ; dotted curve, as above but with TEABr electrolyte. Scan rate  $40 \text{ mV s}^{-1}$ .

electrolyses. The polypyrrole electrode, once mounted in the cell, was filled with electrolyte solution which also embedded the cellulose membrane.

Charge-discharge curves were obtained by recording the total potential of the cell as a function of time under controlled current (in the range  $1\text{--}10 \text{ mA cm}^{-2}$ ). Product analyses were carried out by elemental microanalysis and mass spectrometry: in the latter case a VG ZAB 2F spectrometer was used according to procedures described below.

The chemicals used in this work were all commercially available and were used as supplied.

### 3. Results and discussion

#### 3.1. Voltammetry

Fig. 1 (solid curve) shows a cyclic voltammogram for a polypyrrole film prepared according to Diaz *et al.* [17] by oxidation of pyrrole in a

$\text{CH}_3\text{CN}$  solution containing  $0.07 \text{ mol dm}^{-3}$  pyrrole and  $0.5 \text{ mol dm}^{-3}$  tetraethylammonium perchlorate (TEAP). The curve was recorded after repetitive cycling of the film in the medium used for the preparation. When, in the same solvent, tetraethylammonium bromide (TEABr) is the background electrolyte, neither potentiostatic oxidation ( $+1.0 \text{ V}$ ) nor continuous cyclic scans (dotted curve of Fig. 1) allow the formation of the polymer as  $\text{Br}^-$  oxidation appears to prevent oxidation of pyrrole.

In contrast, the behaviour in aqueous solution is different. Fig. 2 shows cyclic voltammetry for the carbon disc in  $0.07 \text{ mol dm}^{-3}$  pyrrole and  $0.5 \text{ mol dm}^{-3}$  HBr. During the first positive going scan (curve 1) only a single broad oxidation peak is observed: the (low) cathodic current then present on the reverse scan indicates the formation of the polypyrrole film in its oxidized form. Therefore  $\text{Br}^-$  oxidation, which thermodynamically is (probably) easier than that of pyrrole in this medium, seems to be initially

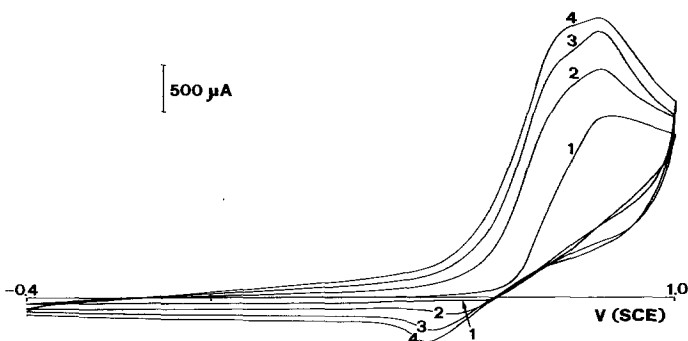


Fig. 2. Successive cyclic voltammograms for a vitreous carbon disc in  $0.07 \text{ mol dm}^{-3}$  pyrrole in aqueous  $0.5 \text{ mol dm}^{-3}$  HBr. Scan rate  $50 \text{ mV s}^{-1}$ .

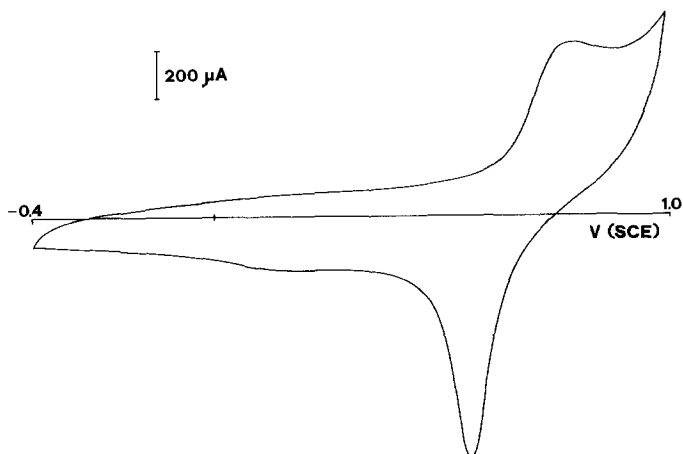


Fig. 3. Cyclic voltammetry of a polypyrrole electrode in aqueous  $0.5 \text{ mol dm}^{-3}$  HBr. Scan rate  $10 \text{ mV s}^{-1}$ .

inhibited by the presence of pyrrole in solution. Bromide ion oxidation, however, takes place during the following cycles (curves 2–4): the overall anodic current increases and two peaks are clearly seen. Moreover, a cathodic peak due to the reduction of the bromine (perhaps complexed by bromide as tribromide ion) is present. During further cycles the polymer film thickens and the current due to the  $\text{Br}_2/\text{Br}^-$  couple increases.

If this polypyrrole electrode is then transferred to a solution containing only  $0.5 \text{ mol dm}^{-3}$  HBr, the couple  $\text{Br}_2/\text{Br}^-$  inside the film gives well formed peaks, as shown by Fig. 3.

A polypyrrole electrode prepared according to Diaz *et al.* [17] then cycled in  $0.5 \text{ mol dm}^{-3}$  HBr substantially reproduces the cyclic voltammetric pattern of Fig. 3. However, the charge associated with the peaks decreases to about 50% in 5–6 cycles and then continuously although much more slowly, whereas the electrode prepared in aqueous HBr appears stable for more than 30 cycles if the anodic limit is restricted to  $0.8 \text{ V}$  [1].

When polypyrrole electrodes prepared in either  $\text{CH}_3\text{CN}/\text{TEAP}$  or  $\text{H}_2\text{O}/\text{HBr}$  are transferred to  $\text{CH}_3\text{CN}$  solution containing TEABr as electrolyte,  $\text{Br}^-$  oxidation appears to occur only very irreversibly and after oxidation neither electrode maintains a stable open circuit potential near to that of the  $\text{Br}_2/\text{Br}^-$  couple.

Therefore two points which are relevant for setting up a model battery are underlined by these voltammetric results:

1. It is necessary to operate in aqueous acid electrolyte. Indeed, only here can the polymer store the halogen. It is not clear whether the halogen is present as  $\text{Br}_2$  absorbed into the film or as  $\text{Br}_3^-$  electrostatically bound to the positively charged polymer. In any case the inability to cycle bromine in acetonitrile demonstrates that the structure of the polymer varies with the medium and that protonated N atoms linking  $\text{Br}_3^-$  moieties may significantly contribute to the strong complexation of  $\text{Br}_2$  inside the film when an acid aqueous electrolyte is used.

2. No substantial difference exists, at least with regard to bromine complexation, between the pyrrole black prepared in aqueous solution and the polypyrrole synthesized according to Diaz *et al.* [17]. The higher stability of the former on cycling results from a resistance to anodic bromination (see later) probably accounted for by some preconditioning of the material.

### 3.2. Battery experiments

#### 3.2.1. Electrode preparation.

As mentioned above, the active polymer was synthesized *in situ* by anodizing (at  $0.80 \text{ V}$ ) the RVC in  $0.5 \text{ mol dm}^{-3}$  HBr containing  $0.07 \text{ mol dm}^{-3}$  pyrrole. Since the throwing power of the polymer is low due to its conductivity, fresh electrolyte solution was continuously flowed through the RVC anode during the electrolyses to aid complete coverage. The most homogeneous deposits were obtained by passing  $800\text{--}1000 \text{ C}$  ( $160\text{--}200 \text{ C cm}^{-2}$ ) during the electrolysis and this roughly

corresponds to the synthesis of 300–370 mg of active polymer (based on a  $0.37 \text{ mg C}^{-1}$  stoichiometry) [1].

If all the halogen contained in such material (43–44%, by elemental analysis) is free and may be driven between  $\text{Br}_3^-$  and  $3\text{Br}^-$  by the exchange of  $2\text{F}$  (assuming that no bromination of the polymer has occurred during the oxidation process) an electric capacity of  $350 \text{ C g}^{-1}$  (referred to active material) may be deduced, which under the assumption of the same electropolymerization stoichiometry leads to a ratio of 0.13 between charge capacity of the electrode and the charge spent for its preparation. Such capacity clearly refers to the  $\text{Br}_2/\text{Br}^-$  couple only; in fact the intrinsic redox centres of polypyrrole may also store charge but their contribution, although not quantified here, is low compared to  $\text{Br}_2/\text{Br}^-$ , at least in terms of power.

A model cell based on  $\text{I}_2/\text{I}^-$  was subsequently investigated, but polymer synthesis was carried out in bromide electrolyte. Direct electropolymerization of pyrrole in HI is, in fact, very difficult [1].

The electrodes prepared as described were washed with deionized water and then filled with the electrolyte, aqueous  $0.05 \text{ mol dm}^{-3} \text{HX}$  and  $0.5\text{--}2.0 \text{ mol dm}^{-3} \text{ZnX}_2$ . When the  $\text{I}_2/\text{I}^-$  system was investigated, the polypyrrole bromine electrode was initially submitted to 5–6 cycles of charge–discharge ( $1\text{--}2 \text{ mA cm}^{-2}$  for 5–10 min) in iodide medium to convert the bromine adduct into the iodine analogue. A similar preconditioning procedure (but using bromide electrolyte) was generally also adopted for polypyrrole bromine electrodes to achieve more reproducible results during full charge–discharge cycles of the battery.

**3.2.2. Charge–discharge cycling.** Charge–discharge cycles obtained both at uncoated RVC electrodes and at pyrrole black covered electrodes are plotted in Figs 4 and 5 for bromine and iodine cells. These curves were obtained according to the following procedure: A controlled positive (for charge) or negative (for discharge) current ( $6 \text{ mA cm}^{-2}$ ) was applied for 120 s and the voltage thus obtained was reported as the *a* plot. The current was then switched off

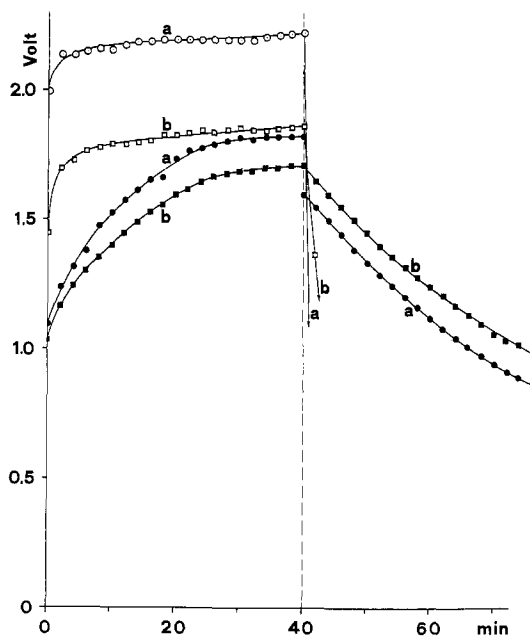


Fig. 4. Charge (left side) and discharge (right side) curves of the Zn/ZnBr/polypyrrole- $\text{Br}_2$  cell. Potentials on load:  $\circ$ , uncoated electrodes;  $\bullet$  polymer coated electrodes. Potentials on open circuit:  $\square$ , uncoated electrode;  $\blacksquare$  polymer coated electrode.

for 10 s and the new value of the potential was reported as the *b* plot. This time was long enough to achieve rather stable potential values. With film covered electrodes the cell voltages show a constant decay with discharge (especially with the bromine cells). This unusual behaviour, already described for poly(2,5-thienylene) iodide

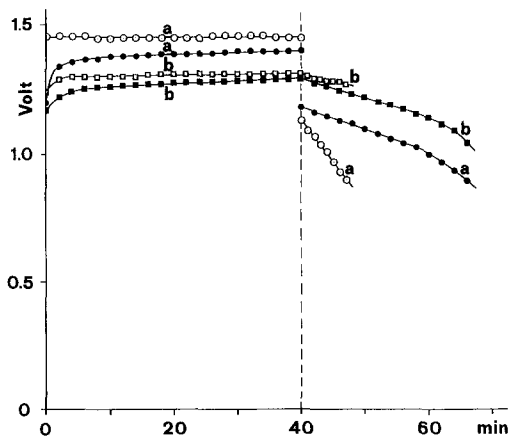


Fig. 5. Charge–discharge curves of the Zn/Zn $\text{I}_2$ /polypyrrole- $\text{I}_2$  cell. (For key to symbols see Fig. 4.)

adducts [18] makes the identification of the state of full discharge rather problematic. We chose to consider that full discharge of both iodine and bromine cells had occurred when the open circuit voltage had dropped to 1.0 V (with  $6 \text{ mA cm}^{-2}$  applied current the discharged cell has a voltage of 0.9 V). This choice was based on the experimental observation that both cells undergo self discharge (see below) on standing at open circuit and their voltages tend asymptotically to 1.0 V (in practice after  $\sim 30$  h of rest time). Other features may be deduced from Figs 4 and 5.

(a) In the absence of polymer the overpotential (the difference between *a* and *b* plots) is higher for the bromine than for the iodine cell. Such overpotentials decrease strongly in the presence of the polymer.

(b) In the absence of the polymer the self discharge of the cell is always very fast, especially for the bromine cell which practically has no discharge curve; in other words RVC/halide intercalates are not produced and the halogens diffuse into solution.

(c) The potentials attained in the presence of pyrrole black are considerably lower (particularly for the bromine cell) than those expected for the free  $\text{X}_2/\text{X}^-$  couples.

(d) Current yields ( $Q_{\text{disch}}/Q_{\text{ch}}$ ) are higher for pyrrole black/bromine (85%) than for pyrrole black/iodine cells (65%).

(e) The polymer affects the characteristics of the bromine much more than those of the iodine cell.

Whereas for uncoated RVC electrodes overpotential and self discharge are easily explained by the reactivity and mobility of the halogens, the behaviour of filmed electrodes is basically accounted for by complexation of the halogens by the polymer.

Different strengths of complexation of the halide inside the polymer might also account for the dependence of the voltage on the state of charge (which is unusual for classical devices, and may be peculiar to the halide adducts with conductive polymers [18]). On the other hand, the shape of the curves (convexity in the charge, concavity in the discharge) is, in our opinion, due, at least in part, to the intrinsic redox centres

of polypyrrole. Owing to their lower potential these have some 'buffering' effect. This effect is clearly more evident for the bromine complex which has a higher potential than the iodine analogue.

*3.2.3. Life of the battery.* The electrodes of Figs 4 and 5, prepared with 1000 C should contain  $\sim 370$  mg of active polymeric adduct, corresponding for the polypyrrole bromine electrode to a maximum capacity of 130 C (due to bromine only). In fact, this value was not achieved because it was necessary to avoid overoxidation and irreversible damage of the polymer, which here occurred when the cell voltage exceeded 1.9 V. Therefore charging cycles at  $6 \text{ mA cm}^{-2}$  for 40 min (Figs 4, 5) involved 55% of the theoretical capacity. For the  $\text{Br}_2$  cell 20 cycles to this state of charge and 30 of higher and lower depth were carried out without observing a significant drop of performance when these cycles were carried out sequentially (as in Figs 4 and 5) and the positive electrodes were not charged above 50% of the theoretical maximum capacity. In these conditions the ratio  $Q_{\text{disch}}/Q_{\text{ch}}$  was above 90% for the bromine and 80% for the iodine devices.

*3.2.4. Self discharge.* Fig. 6 shows the self discharge of model batteries based respectively on polypyrrole bromine (curve 1) and polypyrrole iodine (curve 2) positive electrodes. The experiments were carried out by charging the cells to the same state of charge (about 50% of the maximum) and then discharging them either immediately or after increasing rest times. The residual charge ( $Q_{\text{disch}}/Q_{\text{ch}}$ ) were then plotted as a function of the rest times.

It can be seen that both cells are affected by very significant self discharge and that it is higher for the iodine system. Self discharge of this device is not surprising: iodine is not very strongly complexed by the polymer and during charge-discharge cycles or on standing some iodine is seen in solution. Self discharge of the bromine complex is, however, more puzzling since negligible bromine concentrations were found in solution in equilibrium with the charged polymer electrodes. For this reason an investigation on the interaction of bromine with pyrrole black in the electrolyte environment was carried out.

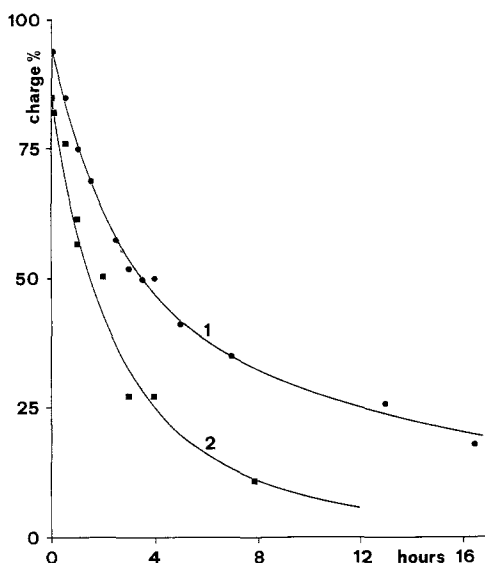


Fig. 6. Curve 1, self discharge data for the Zn/ZnBr<sub>2</sub>/polypyrrole-Br<sub>2</sub> cell; curve 2, self discharge data for the iodine analogue. Initial state of charge 50%.

### 3.3. Bromination study

Hydrogen peroxide (0.15 mol) was added to pyrrole (0.1 mol) in 0.1 mol dm<sup>-3</sup> HBr. After stirring for 1 h at room temperature, the precipitated pyrrole black was recovered, washed by diluted HBr and H<sub>2</sub>O and dried under vacuum to constant weight (4.5 g). The elemental analysis of the polymer (sample A) is reported in Table 1; the resistivity of a pellet (pressed under 10 tons inch<sup>-2</sup>) was 75 Ω cm.

Two samples of this material (400 mg each) were dispersed in separated flasks containing 30 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> HBr and 30 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> HBr + 0.4 mol dm<sup>-3</sup> Br<sub>2</sub> + NaBr (to dissolve the bromine) respectively. After 3 days the polymers were recovered, washed by dilute HBr and dried in a vacuum overnight. After this treatment a resistance increase of 2–3 times for the

first sample and more than a factor of 10 for the second was observed. The sample which had interacted with bromine was analysed by mass spectrometry to determine its content of HBr and Br<sub>2</sub> according to a procedure already adopted for the analysis of halogen doped polyacetylene [19]. Thus the sample material was introduced to the ion source under electron impact conditions (70 eV, 200 μA, temperature = 200°C) and having focused the analyser on the selected ion species (HBr: m/z = 80; Br<sub>2</sub>: m/z = 158) the variation of the absolute abundance of each ion was monitored as a function of time. The resulting peak of HBr was 7 s wide. The peak of Br<sub>2</sub> was much wider (× 118) and its area was 11 times higher. Now, HBr might have been formed by pyrolysis of brominated units, but the Br<sub>2</sub> peak and its shape probably indicate the presence of unbound, strongly complexed bromine.

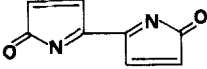
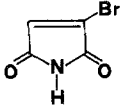
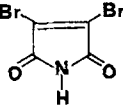
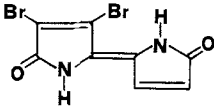
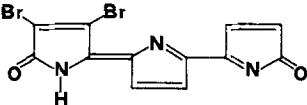
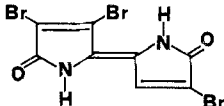
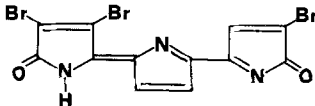
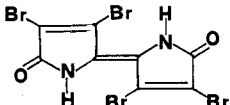
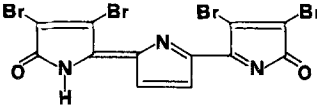
The reaction of the pyrrole black with bromine was repeated by sealing 1 g of polymer, 4 g (0.025 mol) of bromine and 250 cm<sup>3</sup> of 0.5 mol dm<sup>-3</sup> HBr in a flask. The solution was not previously degassed and light was not excluded. After a week the solid was separated from the solution and each phase was analysed. The bromine content of the filtered solution was less than 1% of the initial amount: mass spectrometry, moreover, revealed the presence of brominated oligomers (see below). The solid was stirred in a large amount of 0.5 mol dm<sup>-3</sup> KBr + 0.05 mol dm<sup>-3</sup> HBr and then washed on a filter by a similar solution to extract any possible bromine from the polymer. After drying under vacuum 0.970 g were recovered. In this case the analysis of the product by mass spectrometry revealed a negligible presence of Br<sub>2</sub>, but the elemental analysis (Table 1, sample B) showed that extensive bromination had occurred: the resistance of a pressed pellet had now dramatically increased to 5.5 × 10<sup>8</sup> Ω cm. Other properties of the product had also

Table 1. Elemental analysis data of polypyrrole-Br<sub>2</sub> adducts obtained in the bromination study

Sample	Experimental composition				Formula*
	C	H	N	Br	
A	45.02	3.29	13.01	25.91	C <sub>4</sub> H <sub>3.51</sub> N <sub>0.99</sub> Br <sub>0.35</sub> O <sub>0.85</sub>
B	26.03	1.02	7.18	58.44	C <sub>4</sub> H <sub>1.88</sub> N <sub>0.95</sub> Br <sub>1.30</sub> O <sub>0.85</sub>
C	28.85	1.23	7.91	54.90	C <sub>4</sub> H <sub>2.04</sub> N <sub>0.94</sub> Br <sub>1.14</sub> O <sub>0.74</sub>

\*Normalized with respect to C<sub>4</sub>.

Table 2. Mass spectrum of the acetone soluble fraction of the interaction products of pyrrole black with bromine\*

Peak	<i>m/z</i>	Formula	Suggested structure
a	79-81	Br	-
b	80-82	HBr	-
c	131-133	C <sub>3</sub> BrO	g - Br
d	160	C <sub>8</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>	
e	175-177	C <sub>4</sub> H <sub>2</sub> BrNO <sub>2</sub>	
f	182-184-186	C <sub>2</sub> Br <sub>2</sub>	-
g	210-212-214	C <sub>3</sub> Br <sub>2</sub> O	h - CONH
h	253-255-257	C <sub>4</sub> HBr <sub>2</sub> N <sub>2</sub> O <sub>2</sub> <sup>†</sup>	
i	318-320-322	C <sub>8</sub> H <sub>4</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	
l	352-354-356-358	C <sub>7</sub> HBr <sub>3</sub> NO	p - Br
m	380-382-384	C <sub>12</sub> H <sub>4</sub> Br <sub>2</sub> N <sub>3</sub> O <sub>2</sub>	r - Br
n	381-383-385	C <sub>12</sub> H <sub>3</sub> Br <sub>2</sub> N <sub>3</sub> O <sub>2</sub>	
o	396-398-400-402	C <sub>8</sub> H <sub>3</sub> Br <sub>3</sub> N <sub>2</sub> O <sub>2</sub>	
p	431-433-435-437-439	C <sub>7</sub> HBr <sub>4</sub> NO	s - CONH
q	458-460-462-464	C <sub>12</sub> H <sub>3</sub> Br <sub>3</sub> N <sub>3</sub> O <sub>2</sub>	t - Br
r	459-461-463-465	C <sub>12</sub> H <sub>4</sub> Br <sub>3</sub> N <sub>3</sub> O <sub>2</sub>	
s	474-476-478-480-482	C <sub>8</sub> H <sub>2</sub> Br <sub>4</sub> N <sub>2</sub> O <sub>2</sub>	
t	537-539-541-543-545	C <sub>12</sub> H <sub>3</sub> Br <sub>4</sub> N <sub>3</sub> O <sub>2</sub>	

\* Spectra were recorded with the DER ionization mode, 70 eV, temperature of the ion source = 150–200°C.

<sup>†</sup> Confirmed by exact mass measurement, (most intense peak of the spectrum).

changed, thus about 50% could be dissolved in acetone. The insoluble phase had the elemental composition reported in Table 1 (sample C).

The solution was analysed by mass spectrometry and the data are collected in Table 2. Several molecular ions of oxidized and bromin-

ated oligomers (possibly modified by pyrolysis in the ion source) and their fragmentation peaks are detected. The same mixture of compounds is basically observed in the acid filtered solution mentioned above.

So pyrrole black interaction with bromine

seems to cause extensive degradation of the polymer on a long timescale.

#### 4. Conclusion

The attractive concept of using a conducting polymer as substrate for the reversible storage of halogen/halide couples in secondary cells has been realized, to some extent, in this work. However, cells based on pyrrole black seem to be far from any possible applicability because of self discharge.

The self discharge of the iodine electrode arises because the halogen is only weakly held in the polymer lattice and is lost to the electrolyte. With the  $\text{Br}_2/\text{Br}^-$  couple chemical reaction of the bromine with the polymer is probably the cause. This point requires some further discussion in the light of the following facts:

(a) The interaction of bromine vapour with polypyrrole synthesized by air oxidation in  $\text{H}_2\text{SO}_4$  was found to affect favourably the electrical properties of the polymer which was transformed from insulator to conductor [20].

(b) The interaction of bromine with cyclopentadiene in aprotic medium was found to involve deprotonation and bromination steps, but the polymer showed improved thermostability, conjugation and electrical conductivity [21].

Here the reaction of bromine with pyrrole black seems to occur similarly and deprotonated and brominated chains probably retain the ability to store  $\text{Br}_2$  and the adducts keep good conductivity at least in the wet state. Indeed, although any reaction of  $\text{Br}_2$  with polypyrrole involves battery self discharge, this process does not lead to any apparent degradation in the electrical performance. However, a steady state condition is unlikely to be attained with time as bromine in the electrolyte also appears to cause the depolymerization of pyrrole black: this leads to dissolution and loss of the solid matrix capable of storing  $\text{Br}_2$ . The study of the chemical bromination suggests such changes in a battery, even if only on a longer timescale. It is also true, however, that the polymer chemically synthesized in acid medium may be richer in

oligomers [22] but degradation probably occurs with any polypyrrole sample.

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