Studies of $Zn/ZnX_2/polyaniline$ batteries. II. $X = I$

GIULIANO MENGOLI, MARCO M. MUSIANI

Istituto di Polarografia ed Elettrochimica Preparativa del CNR, Corso Stati Uniti, 4-35100 Padova, Italy

DEREK PLETCHER

Department of Chemistry, The University, Southampton SO9 5NH, UK

SERGIO VALCHER

Istituto Chimico G. Ciamician, Universitá di Bologna, via Selmi, 2-40100 Bologna, Italy

The characteristics of a $Zn/ZnI_2/polyaniline$ battery have been examined. It is demonstrated that the polymer has a charge storage capacity of $143\,A\,h\,kg^{-1}$ and an energy efficiency above 70%. The battery has an open circuit voltage of $1.2\,V$ and polarization during charges and discharges at $30–120\,mA$ were low. Self discharge is low compared to the chloride and bromide electrolyte batteries and charge recovery was 60% after 12 days stored on open circuit. It is shown that these promising characteristics may be interpreted in terms of a system where the polyaniline largely acts as a current collector and the I_3^-/I^- couple is rapid within the film. The kinetics of the system are determined by a.c. impedance.

1. Introduction

In Part I [1] the charge–discharge characteristics of $Zn/ZnX_2/polyaniline$ cells, where $X = Br$ or Cl, were investigated. It was shown that it is better to use a bromide electrolyte since degradation of the polymer during overcharge is less of a problem. Moreover, the aim of improving the performance of polyaniline batteries by making use of the Br_3^-/Br^- couple in addition to the redox couple of the polymer, could partially be fulfilled. Although during early cycles the bromine reacts slowly with the oxidized polyaniline, the resulting change in composition does not lead to any degradation of the storage properties of the polymer. Hence the power and charge storage density can be improved using a bromide electrolyte, and a good energy efficiency could be obtained during at least 20 charge–discharge cycles. However, the shelf life of charged batteries is poor because on open circuit Br_3^- in the polymer exchanges for Br^- in the surrounding electrolyte.

This paper explores the advantages of iodide electrolytes. The potential of the I_3^-/I^- couple overlaps that of the first oxidation step of polyaniline, believed to be the oxidation of polyaniline to emeraldine. Hence, the voltage–time curve on charge or discharge should show a single plateau, but the charge density should be greatly enhanced compared to a Cl^- electrolyte.

2. Experimental details

The construction of the model batteries was described in Part I [1]. A typical polyaniline electrode was prepared by anodic oxidation at $+0.8\,V$ of a solution of 1.5% aniline in $0.5\,mol\,dm^{-3}\,H_2SO_4$ at a reticulated vitreous carbon disc. After the passage of $500\,C$, the polyaniline was equilibrated in the battery electrolyte, $1.5\,mol\,dm^{-3}\,ZnI_2 + 1\,mol\,dm^{-3}\,NH_4I$ (pH 4).

Cyclic voltammetry and the impedance study used a polished vitreous carbon disc, area $0.06\,cm^2$, or occasionally a gold disc, area $0.28\,cm^2$, as the substrate for the polyaniline. The impedance measurements were made using a Solartron

1250 Frequency Response Analyser and 1186 Electrochemical Interface. The data were obtained at the rest potential of the electrode using an a.c. modulation, amplitude 5 mV and frequencies between 63 kHz and 100 mHz. Complex plane analysis was carried out with a Hewlett–Packard HP 1000/F computer.

3. Results and discussion

3.1. *Cyclic voltammetry*

The dotted curve in Fig. 1 is a cyclic voltammogram run at $10 \, mV \, s^{-1}$ for a solution of $1.5 \, mol \, dm^{-3} \, ZnI_2 + 1 \, mol \, dm^{-3} \, NH_4I$ at a bare vitreous carbon disc electrode. The anodic current positive to $+0.25 \, V$ is for the oxidation of I^-, and on the reverse sweep there is little cathodic charge because the product I_3^- has diffused into the solution. When the vitreous carbon was covered by polyaniline (formation charge, $0.49 \, C \, cm^{-2}$), the cyclic voltammogram changed to that shown as the full line in Fig. 1. Now the anodic current is due to two reactions, the first oxidation step of polyaniline believed to be the
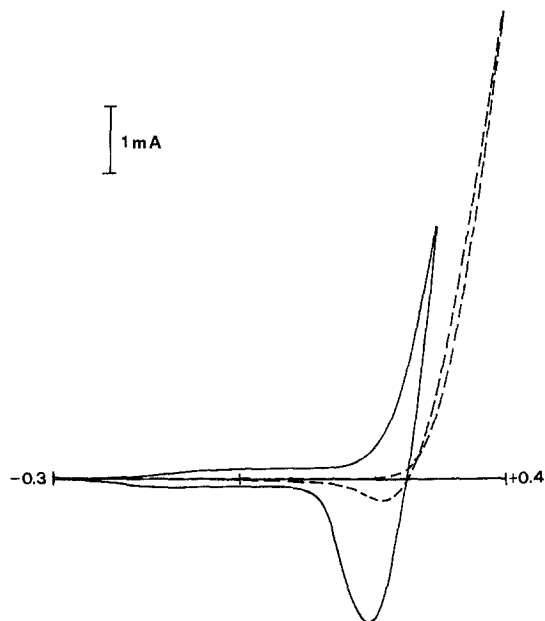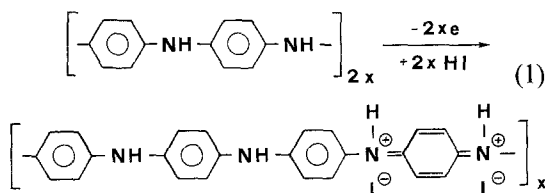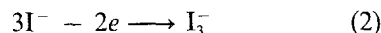

Fig. 1. Cyclic voltammograms, $(10 \, mV \, s^{-1})$ recorded at bare (dotted curve) and polyaniline-coated (synthesis 49 mC; solid curve) vitreous carbon in $1.5 \, mol \, dm^{-3} \, ZnI_2 + 1 \, mol \, dm^{-3} \, NH_4I$.

formation of emeraldine:

$$\left[-\left\langle O \right\rangle - NH - \left\langle O \right\rangle - NH - \right]_{2x} \xrightarrow[+2 \times HI]{-2 \times e} \quad (1)$$

$$\left[-\left\langle O \right\rangle - NH - \left\langle O \right\rangle - NH - \left\langle O \right\rangle - \overset{H}{\underset{\ominus}{N}} = \left\langle = \right\rangle = \overset{H}{\underset{\ominus}{N}} - \right]_x$$

and the oxidation of iodide:

$$3I^- - 2e \longrightarrow I_3^- \quad (2)$$

Reaction 1 leads to the small, broad peak around 0.0 V versus SCE while Reaction 2 gives the large current commencing at $+0.2 \, V$. It can be seen from the areas under the curve that there is a good charge balance for the reduction and oxidation processes with both couples. In the case of Reaction 2 this can only happen if it occurs within the film. The 50–100 mV negative shift of the current for the I^-/I_3^- oxidation when polymer covers the electrode is evidence that the polymer complexes the product and therefore that the product is held within the polyaniline. It should be noted that the I–E response for Reaction 1 is very similar to that for the corresponding process in Cl^- or Br^- media.

In the cyclic voltammogram shown in Fig. 1, the charge associated with Reaction 2 is $0.6 \, mC \, cm^{-2}$, almost 80% of that used in the synthesis of the film. Similar extents of charging were possible with several films prepared with charges in the range 0.24–$2.4 \, C \, cm^{-2}$. If the positive limit for the cyclic voltammogram was extended the anodic current for the I^-/I_3^- process increased further, but there was no longer a charge balance between the cathodic and anodic processes, suggesting that product was then leaving the film and that the 80% extent of charging is the maximum possible.

The storage of 0.8 C of charge by the couple I_3^-/I^- within the film per coulomb of charge used in the preparation of the film represents a very high concentration of the oxidized species within the film. Indeed, since the oxidation of aniline to emeraldine corresponds to 2.5 electrons per N atom (and the polymer yields and N analysis reported in Part I confirmed this to have a high current efficiency), it must be concluded that there is one triiodide ion associated with every
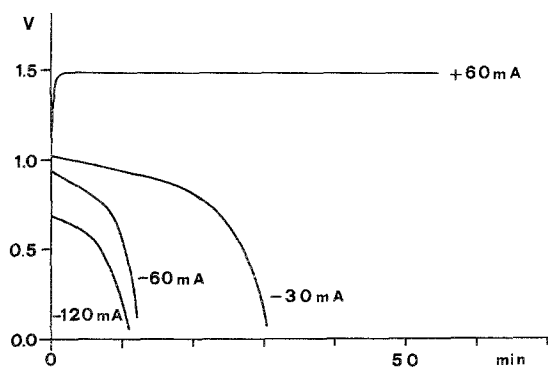
Fig. 2. Charge–discharge behaviour of the Zn/1.5 mol dm^{-3} ZnI$_2$ + 1 mol dm^{-3} NH$_4$I/carbon cell.

3.2. Charge–discharge cycling behaviour

The behaviour of a cell where the reticulated vitreous carbon (RVC) electrode was not covered by polyaniline was briefly studied. On charge at 60 mA, the cell voltages rapidly rose to +1.5 V and then remained steady. After 200 C the open circuit voltage was 1.26 V and on discharge at 30 mA (until the voltage dropped to 0.4 V), only 51 C were recovered (see Fig. 2). At higher discharge rates the coulombic efficiency was similar but the energy efficiency got even worse. The short circuit current for the charged cell was 260 mA (see Fig. 4). Finally, on open circuit stand self discharge was rapid and the coulombic efficiency of the charge–discharge cycle dropped to < 10% with a stand of 4 h.

Fig. 3 shows the greatly improved behaviour when the RVC is filmed with polyaniline (500 C used in its synthesis). The charge and discharge curves show quite flat curves throughout most of the processes and with currents in the range 30–120 mA, the coulombic efficiency was greater than 90%. Also it can be seen that the overpotentials for both charge and discharge are small especially since the model battery will have a significant iR drop between the electrodes. In those experiments the cell was charged only with 200 C. On the basis of the cyclic voltammetry, this represents only 50% of the possible charge and, indeed, cells charged to 300 C still performed
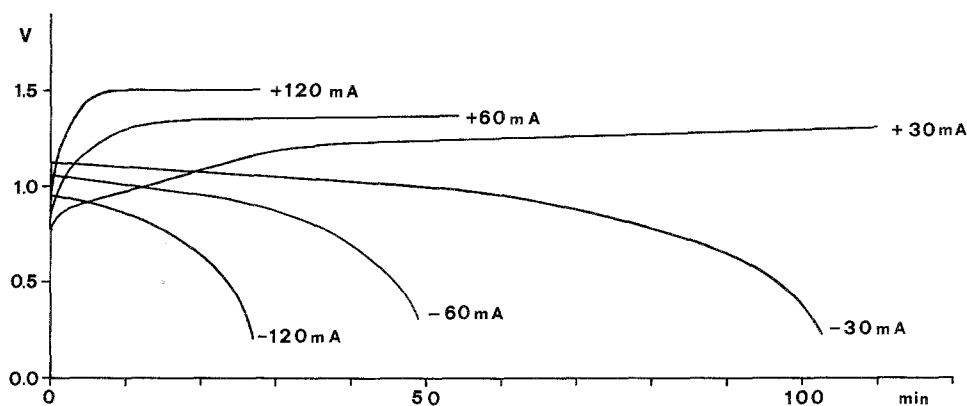
nitrogen atom in the film (the oxidation of I$^-$ to I$_3^-$ is a two-electron process). This in turn requires all amine and imine centres in the emeraldine to be protonated. It has been suggested that such extensive protonation would hinder the conjugation with a consequent drop in the conductivity [2]. However, it is possible that heavy loading by iodine may compensate for this loss of conjugation since it is known that some charged, unconjugated polymers, e.g. polyvinylpyridine [3–5], become semi-conductors when heavily doped by halogens. Alternatively, it could be assumed that the iodine exists in the film as I$_5^-$ as this reduces the number of positively charged N atoms required.

Fig. 3. Charge–discharge behaviour of the Zn/1.5 mol dm^{-3} ZnI$_2$ + 1 mol dm^{-3} NH$_4$I/polyaniline cell.

Table 1. *Charge–discharge behaviour of the* $Zn/ZnI_2 + NH_4I/polyaniline$ *cell. Each charge was 200 C. The first experiment refers to the initial discharge of the assembled cell, which is* 'ab initio' *charged*

Charging current (mA)	Rest time (h)	Open circuit voltage (V)	Discharging current (mA)	Charge returned (C)	Coulombic efficiency (%)
–	–	1.15	30	88	–
30	–	1.20	30	190	95.0
60	–	1.21	60	177	88.5
90	–	1.25	90	185	92.0
120	–	1.23	120	183	91.5
60	14	1.21	30	176	88.0
60	22	1.21	30	184	92.0
60	90	1.16	30	140	70.0
60	284	1.18	30	122	61.0

well giving a coulombic efficiency greater than 80%. As noted above, the polarization of the electrode is small and at 30 mA it is only about 100 mV throughout most of the charge and 200 mV at 50% discharge. As a result the energy efficiency is 70%. This result is particularly encouraging since the charge and discharge of the cell at 30 mA were separated by 23 h on open circuit. Table I shows the performance of the cell more clearly and even after 12 days on open circuit the coulombic efficiency exceeds 60%, so it must be concluded that the polyaniline in its oxidized state interacts strongly with the iodine. Certainly, self discharge is much less a problem than with the Cl^- and Br^- electrolyte cells.

Fig. 4 presents cell voltage versus cell current plots for three cells, i.e. the present cell under investigation together with, for comparison, a Zn/chloride/polyaniline cell and an iodide cell but with the RVC uncovered by polyaniline. The extrapolated short circuit current with the $Zn/ZnI_2/$polyaniline cell is 540 mA, a current density more than $0.1 \, A \, cm^{-2}$ based on the geometric area of the zinc electrode.

Overall the performance of the iodide cell is very promising.

3.3. *The a.c. impedance of the positive electrode*

The impedance of bare vitreous carbon and gold disc electrodes at their rest potential in a solution of $1.5 \, mol \, dm^{-3} ZnI_2 + 1 \, mol \, dm^{-3} NH_4I + 10^{-3} \, mol \, dm^{-3} I_2$ in water were measured. Typical plots of the imaginary component of the impedance, Z'', versus the real component, Z', are

shown in Fig. 5. Both curves may be accounted for by a Randles equivalent circuit and the computed values of the circuit components are reported in Table 2. (Since the centre of the high-frequency loop lies below the real axis the values of the double layer capacitance (C), obtained according to the formula $C = 1/2\pi f_{max} R_{CT}$, are only approximate. R_{CT} = charge transfer capacitance; f_{max} = frequency at top of the semicircle of Z'' versus Z' plot.)

While all the circuit components seem to have reasonable values, it is the charge transfer resist-
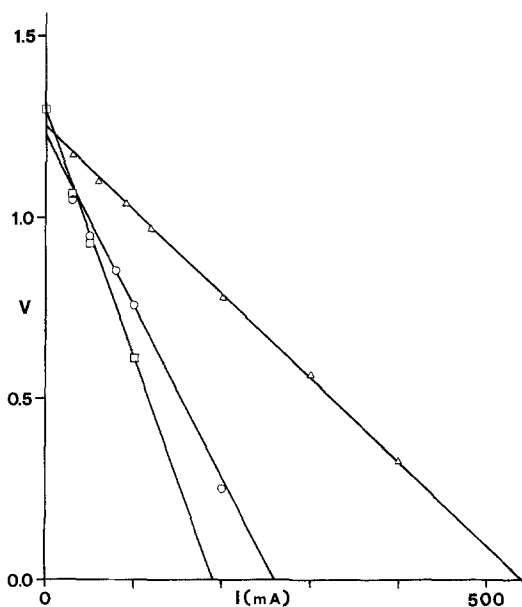

Fig. 4. Cell voltage versus cell current plots for charged cells. □, Zn/chloride/polyaniline cell; ○, Zn/iodide/carbon cell; △, Zn/iodide/polyaniline cell.
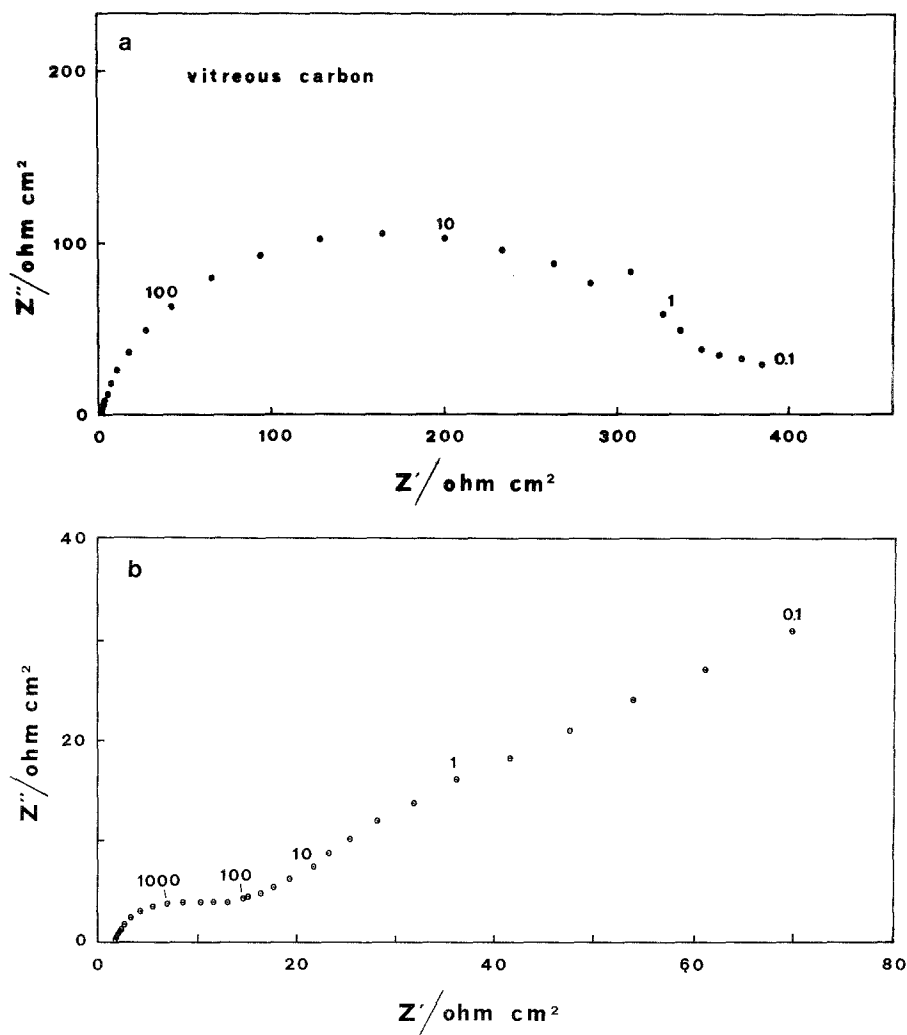
Fig. 5. Complex plane impedance plots recorded at vitreous carbon (a) and gold electrodes (b) in $1.5\,\text{mol}\,\text{dm}^{-3}\text{ZnI}_2$ + $1\,\text{mol}\,\text{dm}^{-3}\text{NH}_4\text{I}$ + $0.001\,\text{mol}\,\text{dm}^{-3}\text{I}_2$ (frequency in Hz).

ances which are important to the discussion of the battery behaviour. It is interesting to note that R_{CT} is much lower at gold than at carbon, suggesting that a gold surface can catalyse the I^-/I_3^- couple.

Fig. 6 shows the impedance plots for a polyaniline film deposited onto the polished vitreous carbon disc ($0.7\,\text{C}\,\text{cm}^{-2}$). Curve a is for the film in the battery electrolyte, $1.5\,\text{mol}\,\text{dm}^{-3}$ ZnI_2 + $1\,\text{mol}\,\text{dm}^{-3}\,\text{NH}_4\text{I}$ (but without added I_2), while curve b is for the film after it has been charged with iodine. Both may be described quite well by the Randles equivalent circuit, but the values for the circuit components are quite different,

(see Table 2). When discharged, the rest potential is $-0.035\,\text{V}$, the impedance high and the behaviour mainly capacitive. When charged with iodine, the equilibrium potential is $+0.178\,\text{V}$ and R_{CT} is very low; indeed, it is a factor of 100 less than that at gold and 2000 below that at uncovered vitreous carbon.

For curve c in Fig. 6, the charged polyaniline electrode was placed in the battery electrolyte with some added I_2, which leads to a further reduction in R_{CT}. Also, when an initially discharged polyaniline film was placed in a solution containing I_2, the equilibrium potential shifted positive and the R_{CT} was again low, confirming
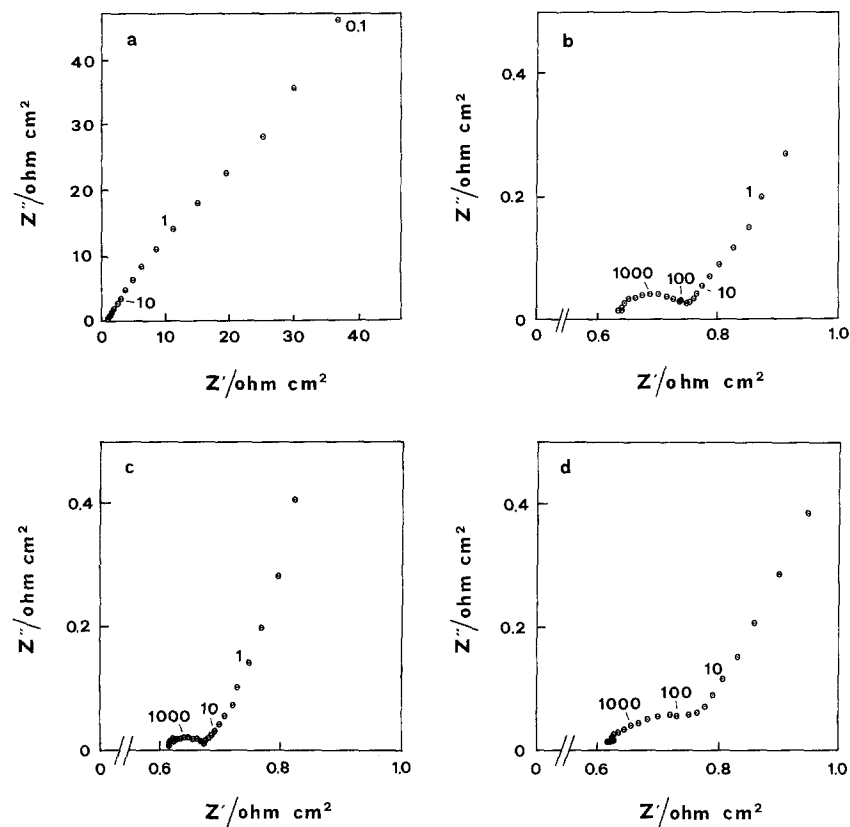
Fig. 6. Complex plane impedance plots for a polyaniline film (synthesis $42\,mC$) in $1.5\,mol\,dm^{-3}\,ZnI_2\,+\,1\,mol\,dm^{-3}\,NH_4I$ in the absence (a, b) and in the presence (c, d) of $0.001\,mol\,dm^{-3}\,I_2$. Plots a and c, discharged films; plots b and d, charged films.

Table 2. *Impedance data for the I_3^-/I^- couple at carbon and gold electrodes, both bare and covered by polyaniline*

Electrode	Charge for synthesis of polymer $(C\,cm^{-2})$	State of charge	I_2 in solution $(10^{-3}\,mol\,dm^{-3})$	Equilibrium potential (V)	R_{CT} $(ohm\,cm^2)$	f_{max} (Hz)	C $(\mu F\,cm^{-2})$
Carbon	–	–	Yes	0.17	350	15	30
	0.68	discharged	Yes	0.17	0.20	250	3200
	0.68	charged	Yes	0.18	0.07	1000	2300
	2.3	discharged	Yes	0.16	0.20	250	3200
	2.3	charged	Yes	0.18	0.08	1000	2000
	0.67	discharged	No	−0.04	Very high	–	–
	0.67	charged	No	0.18	0.13	1000	1200
	0.25	charged	No	0.17	0.60	250	1060
	0.25	charged	Yes	0.18	0.55	400	720
Gold	–	–	Yes	0.14	15	630	17
	0.15	charged	Yes	0.18	1.4	160	710
	0.54	discharged	Yes	0.17	0.25	400	1600
	0.12	discharged	Yes	0.17	1.2	200	660
	0.12	charged	Yes	0.17	1.0	250	640
	0.15	charged	No	0.16	2.5	65	980

the strong liking of the film for I$_2$. Reaction 2 can apparently take place both inside and on the outer surface of the film.

The values of the double layer capacitance also offer evidence that the I$_3^-$/I$^-$ takes place throughout the film and not at the metal–polymer interface. The capacitances are large and increase as R$_{CT}$ decreases. On the other hand the double layer capacitances determined in this work are lower than other values reported for polyaniline in the literature [6]. The pseudo capacitances increase with potential to +0.4 V, reflecting the charged nature of the polymer.

Table 2 also reports data for polyaniline films of various thicknesses (formation charges, 0.25–2.5 C cm^{-2}) and for both gold and carbon substrates. They confirm the low charge transfer resistance, i.e. high exchange current density, for the I$_3^-$/I$^-$ couple in polyaniline films.

4. Conclusions

The Zn/ZnI$_2$/polyaniline battery shows considerable promise and in all respects its performance is superior ·to cells with chloride or bromide electrolytes.

(a) The charge storage capacity may be estimated to be 143 A h kg^{-1}. This figure, referred to dry polymer, is computed by assuming, on the basis of the data of section 3.1, that one I$_3^-$ is stored for each N atom of emeraldine.

(b) Reasonable currents may be drawn and even with the model battery, flat discharge curves are obtained and polarization is low. As a result the energy efficiency on charge–discharge cycling is good.

(c) While some self discharge occurs, 60% of the charge could still be recovered after 12 days stored on open circuit. The iodide is more strongly held than bromine in the polyaniline and there is little evidence for chemical attack of the iodine on the polymer.

The impedance study confirms the rapid kinetics of the I$^-$/I$_3^-$ couple with polyaniline and is consistent with the interpretation that the battery performance depends on this couple and not the redox behaviour of the film itself. Thus the iodide electrolyte clearly represents a new approach to polyaniline batteries where the polymer is largely a current collector and a matrix to hold the I$_3^-$.

Acknowledgements

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