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Charge–discharge characteristics of polyvinylpyridinium hydrobromide perbromide–carbon paste electrodes*

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The work mainly focuses on the electrode characteristics of poly(4-vinylpyridine)–carbon paste composites in aqueous Br^- electrolytes. The reversible driving of the Br^-/Br_3^- couple 'inside' the polymer is initially much faster in KBr than in $ZnBr_2$. However, after repeated cycling, the paste electrodes are also conditioned to $ZnBr_2$, so that charging/discharging of bromine can be carried out with $\sim 1\,A\,dm^{-2}$ applied without causing excessive polarization. The possible use in secondary Zn/Br_2 batteries of a poly(4-vinylpyridine) solid matrix, which both complexes the halogen and collects the current, is a distinct possibility. This view is supported by the low self-discharge tested for poly(4-vinylpyridinium hydrobromide perbromide) which compares favourably with the previous state-of-the-art.

1. Introduction

The behaviour of a metal redox couple on polyvinylpyridine coated electrodes has been extensively investigated [1, 2]: electrodes modified with this polymer, which is electronically non-conductive, become electrochemically responsive owing to their permeation and ion-exchange properties [3].

When a poly(4-vinylpyridine) film deposited onto an inert electrode substrate is loaded with Br_2 by anodic oxidation of aqueous HBr, it probably also produces some electronic conduction via a halogen–halide electron hopping mechanism [4]. Accordingly, we tested d.c. conductivities (10^{-6} to $10^{-7}\,\Omega^{-1}\,cm^{-1}$) for dried pellets of commercial poly(4-vinylpyridinium hydrobromide perbromide) [5].

In aqueous HBr or KBr, films of this complex exhibit interesting properties, both as regards the reversible 'internal' electrochemical driving of bromine and stability towards the unwanted side-reactions (brominations, degradative oxidations) which very often affect other polymeric systems [6, 7]. Conversely, in $ZnBr_2$ electrolyte, the response to the Br^-/Br_3^- couple slows down and the storage capacity of bromine apparently drops [4]: this fact is a serious handicap in view of the practical use of the polymer as cathode matrix in a Zn/Br_2 cell.

This paper has the objective of a possible application for aqueous Zn/X_2 (X = Br, I) batteries, but using a different experimental approach: poly(4-vinylpyridine) was dispersed in carbon powder to obviate the resistivity caused by Zn(II) and the charging–discharging characteristics of the composite investigated. These carbon paste [8] electrodes, notwithstanding their small size, can predict the cathode performance of a larger Zn/X_2 device.

2. Experimental details

2.1. *Materials*

Poly(4-vinylpyridinium hydrobromide perbromide), poly(4-vinylpyridine) crosslinked with 2% divinylbenzene were Fluka products used as supplied. Quaternized poly(4-vinylpyridinium bromide) was prepared from linear poly(4-vinylpyridine), $M_w = 50\,000$ (Polysciences) and *n*-octyl bromide (Fluka) according to [9]. The product, very soluble in methanol but insoluble in water, had the following elemental composition (calculated values in brackets): C = 54.9 (60.4), H = 7.5 (8.0), N = 5.4 (4.7), Br = 24.5 (26.8). Other chemicals were reagent grade, all commercially available, and used as supplied.

The carbon paste electrodes were assembled according to a standardized procedure: 40 mg of finely milled powdered vitreous carbon and polymer (from 0.0 to ~60% of the total amount) were made into a paste with 1 ml of the electrolytic solution and then put inside a glass tube (i.d. = 0.33 cm, h = 10 cm) sealed at the bottom by a G_0 glass frit (this was the side of the electrode dipping into the solution for ~0.5 cm). The paste was then pressed onto the glass frit from the opened end of the tube by a vitreous carbon rod (diameter, 0.3 cm) which constituted the current collector. Figure 1 illustrates a typical electrode.

The solutions were prepared with deionized and then distilled H_2O; 99.9% purity nitrogen was used for purging the electrolytic systems.

2.2. *Apparatus and procedure*

In the cells, the compartment of the working electrode (containing 30 ml of electrolyte) was separated from

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that of the counter electrode by a salt bridge, to minimize interdiffusion of the solutions; zinc or platinum sheets were the counter electrode, and a SCE was used as reference. Charging/discharging was carried out either potentiostatically or galvanostatically; in the former case oxidation was at 0.8 V and the corresponding reduction at 0.0 V. During galvanostatic runs (i applied from 0.2 to 1.0 mA), the potential of the working electrode was monitored w.r.t. SCE by a high impedance voltmeter (Keithley 175).

Once charged to a given level, each carbon paste sample was withdrawn from the cell and temporarily stored in a sealed flask with 30 ml of fresh electrolyte, thus delaying the discharging process for the programmed time. The maximum charge storable in the crosslinked poly(4-vinylpyridine) (PVP) was considered that bound to the Br_3^- content of the commercial poly(4-vinylpyridinium hydrobromide perbromide), i.e. $1.45\,C\,mg^{-1}$, corresponding to about 0.8 Br_3^- ions for each pyridine moiety in the polymer. A similar assumption, made on the basis of one Br_3^- for each nitrogen (resulting from elemental analysis), gave a maximum charge content of $0.577\,C\,mg^{-1}$ for the quaternized poly(4-vinyl-*n*-octylpyridinium bromide (PVNOP bromide).

The electrochemical apparatus consisted of a Mod. 551 potentiostat, a Mod. 567 wave form generator and a Mod. 731 integrator (all by Amel, Milan). Current/time and potential/time plots were recorded on a Mod. 50000 Gould–Brians *x–y* recorder.

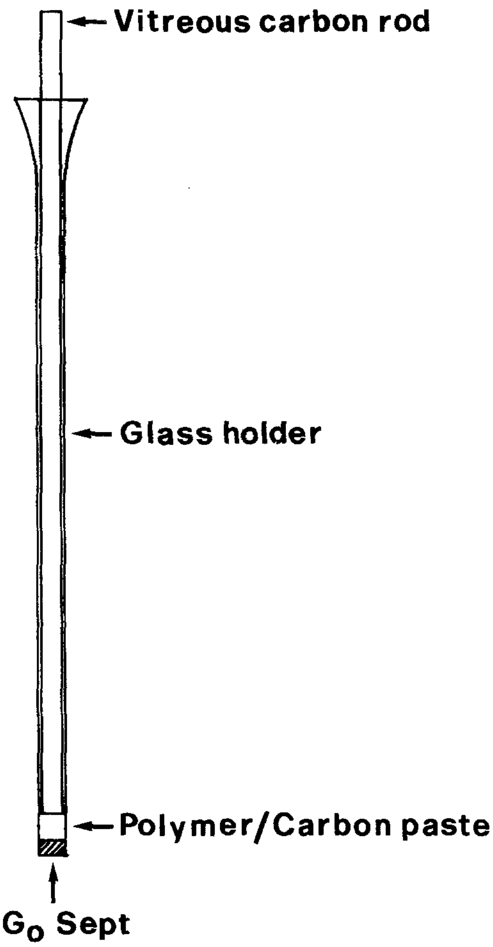

Fig. 1. Assembly of polymer/carbon paste electrodes.

Table 1. Blank experiments

$I_{applied}$ (*mA*)	$E_{initial}$ (*V, SCE*)	E_{final} (*V, SCE*)	*Electrode*	*Run* (*No.*)	*Charging* (*C*)	*Delay* (*h*)	*Discharging* (*C*)	*Yield* (*%*)
(*a*) *Potentiostatic electrolyses; electrolyte* 1 *M* Br^- (*KBr* + *HBr, pH* ≃ 1)								
			A	6	1.27	15	0.51	40
			A	7	3.50	15	1.37	39
			B	5	2.10	16	0.58	28
			B	1	3.50	40	0.14	4
			A	4	2.20	42	0.35	16
			A	3	1.66	65	0.16	10
			A	5	1.60	113	0.13	8
			B	2	3.60	134	0.14	4
			B	3	5.00	307	0.18	4
(*b*) *Galvanostatic electrolyses; electrolyte* 1*M* Br^- (*KBr* + *HBr, pH* ≃ 1)								
1.000	0.37	1.58	A	12	5.00	17	1.66	33
1.000	0.47	1.27	A	13	5.00	95	0.25	5
(*c*) *Galvanostatic electrolyses; electrolyte* 2 *M* Br^- ($ZnBr_2$ + *HBr, pH* ≃ 1)								
0.200	0.52	0.90	B	6	5.00	17	1.16	23
0.400	0.61	0.93	B	8	5.00	17	1.66	33
1.000	0.73	1.06	B	9	5.00	17	1.78	36
0.200	0.60	0.89	B	7	5.00	113	0.09	2
1.000	0.73	1.08	B	10	5.00	113	0.10	2
(*d*) *Galvanostatic electrolyses; electrolyte* 2*M* I^- (ZnI_2 + *HI, pH* ≃ 1)								
1.000	0.00	0.55	C	1	5.00	17	0.41	8
1.000	0.27	0.53	C	2	5.00	17	0.98	20
1.000	0.27	0.54	C	3	5.00	17	1.25	25
1.000	0.28	0.54	C	4	5.00	65	0.40	8
1.000	0.27	0.56	C	5	5.00	89	0.33	7

3. Results and discussion

3.1. *Blank experiments*

Table 1 summarizes charging/discharging data from a set of blank experiments. Three different electrodes (A, B, C) containing only carbon powder mixed with the electrolyte were used; each run shown in Table 1 was labelled with the number of the *n*th charging/discharging cycle of the electrode.

Constant performances were achieved in a few runs; on delaying the discharge less than one day from the charge, significant amounts of bromine were still found in the electrode. However, after 48 h, about 90% of the initial charge was generally lost.

The ability to retain halogen may be ascribed to: (i) the peculiar shape of the electrodes (a separator, although very soft, exists between carbon and solution); (ii) adsorption of Br_3^- at carbon particles.

Intercalation phenomena, which may be predicted for lamellar graphite [8], seem less likely for vitreous carbon.

In conclusion, owing to the temporary storage of bromine inside the blanks, no difference between their redox response in Br^- electrolyte and that of polymer-containing electrodes can be expected by a sweep technique, even at low (0.1 mV s^{-1}) scan rates. This fact was confirmed by our experiments. Furthermore, in potentiostatic runs, at least two days must be taken into account for self-discharge of the carbon.

3.2. *PVP–C paste electrodes in Br^- electrolytes*

Unlike the blanks, the polymer-containing sample electrodes (PVP crosslinked with DVB) require some charging/discharging cycles in order to be conditioned for reproducible bromine storage, even in Br^- electrolytes not containing Zn^{2+} ions. The plain curve of Fig. 2, obtained at the 8th cycle, represents the current–time characteristics of both potentiostatic oxidation (charging) and the corresponding reduction (discharging) of a PVP–C paste electrode in KBr/HBr (Br^- = 1 M) at pH ~ 1. This sample contained 5 mg of polymer (12.5% of the paste). The charge supplied was 7 C (96% of the maximum); that recovered 223 h later was 4.88 C, corresponding to a coulombic yield of 70%.

When a similar experiment was performed *ab initio* in $ZnBr_2$ electrolyte, the potentiostatic currents were many times lower than those shown in Fig. 2, even after many charging/discharging cycles. In $ZnBr_2$ also the PVP–C paste system consequently shows a partially inhibited electrochemical driving of Br_3^-/Br^-, as happens on the analogous PVP film electrodes [4].

However, if a sample previously cycled in KBr until full activation is then transferred to $ZnBr_2$ electrolyte, oxidation/reduction of the bromine couple takes place at acceptable rates (dotted curves in Fig. 2). The electrode was the same as that used in the experiments in KBr (9 cycles) and the current–potential characteristics in Fig. 2 refer to the third cycle in $ZnBr_2$; 5.12 C

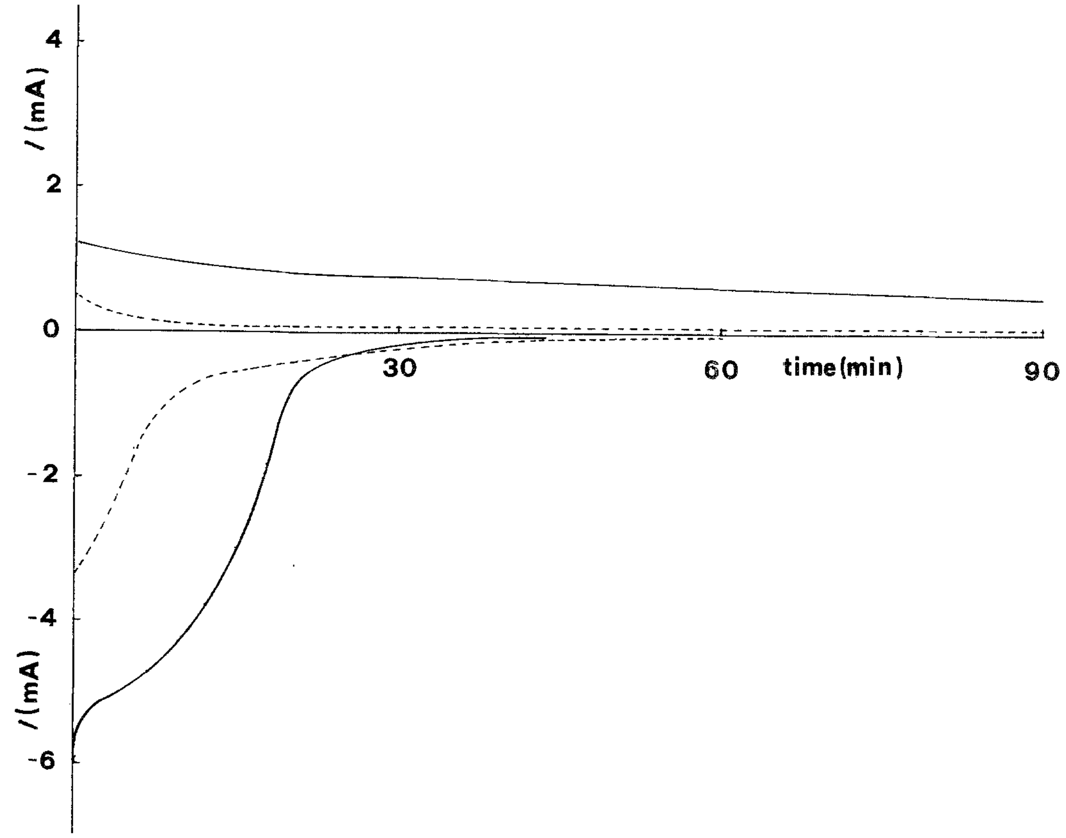

Fig. 2. Potentiostatic charging (0.8 V)/discharging (0.0 V) of a 12.5% PVP/C electrode. Plain curves: Br^- = 1 M (KBr + HBr, pH ~ 1, electrolyte). Dotted curves: Br^- = 2 M ($ZnBr_2$ + HBr, pH ~ 1, electrolyte). Delay times at between charging/discharging > 200 h.

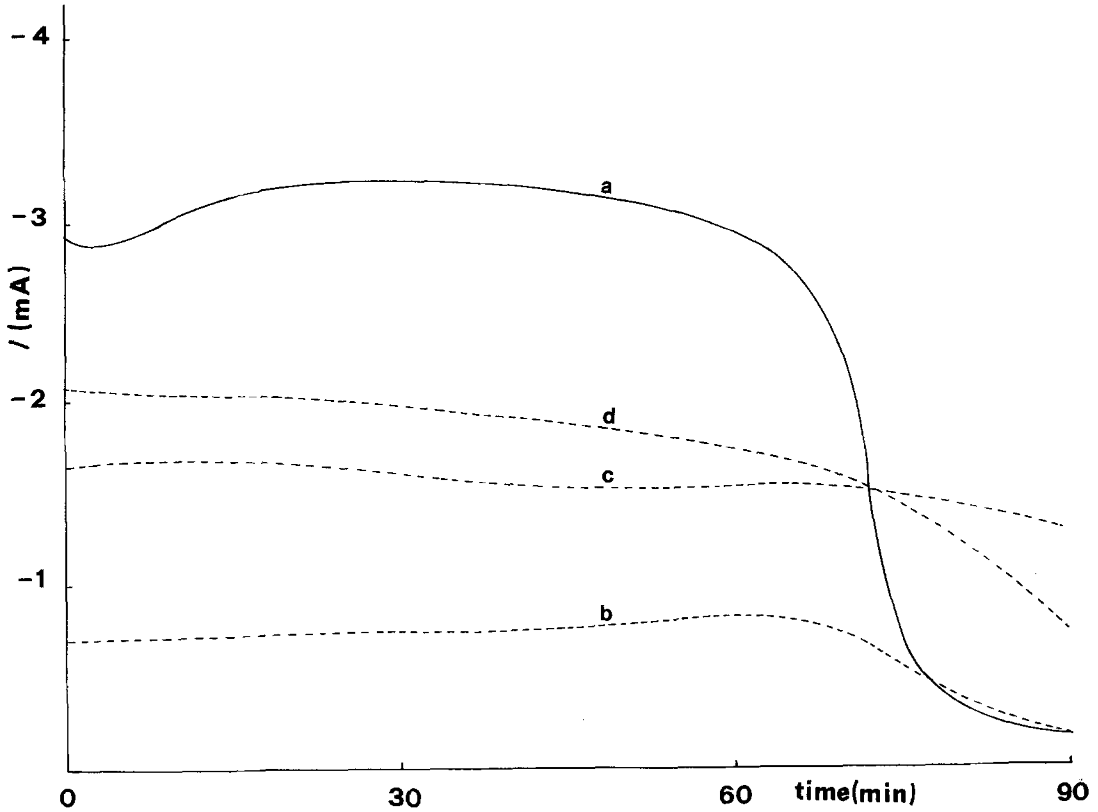

Fig. 3. Potentiostatic discharging (0.0 V) of a 37.5% PVP/C electrode. Plain curve (a): Br^- = 1 M (KBr + HBr, pH ~ 1, electrolyte). Dotted curves (b, c, d): Br^- = 2 M ($ZnBr_2$ + HBr, pH ~ 1, electrolyte). Delay time (yields): a = 590 h (89%); b = 16 h (92%); c = 256 h (77%); d = 112 h (83%).

were transferred by oxidation and 2.20 C (43% yield) were recovered 235 h later by reduction.

Figure 3 shows the discharges of a paste electrode containing 15 mg of PVP (37.5%). Here, the plain curve represents the current/time plot during the potentiostatic reduction in KBr of the electrode charged with 15.55 C (69% of the maximum). Although the maximum current density is 20 to 30% lower than that observed in Fig. 2, its shape is flat for almost the entire discharging process, which was delayed 590 h from charging; 13.80 C, corresponding to a yield of 89%, were eventually recovered.

Table 2. Potentiostatic charging/discharging of PVP in Br^- electrolytes

Electrode	*PVP* (%)	*Run* (*No.*)	*Charging* (*C*)	*Delay* (*h*)	*Discharging* (*C*)	*Yield* (%)
(*a*) $Br^- = 1\,M$ (*KBr + HBr, pH* $\simeq 1$)						
D	12.5	5	4.00	213	3.12	78
D	12.5	8	7.00	223	4.88	70
D	12.5	9	7.00	456	4.13	59
E	12.5	2	3.50	136	3.08	88
E	12.5	3	4.00	359	3.43	86
E	12.5	4	6.00	453	4.70	78
F	37.5	7	11.90	88	11.40	96
F	37.5	8	14.80	282	12.74	86
F	37.5	9	15.55	590	13.80	89
G	62.5	4	12.50	596	12.48	100
G	62.5	5	19.30	900	14.29	74
G	62.5	6	20.40	1080	14.69	72
(*b*) $Br^- = 2\,M$ ($ZnBr_2$ *+ HBr, pH* $\simeq 1$)						
D	12.5	13	5.00	148	2.91	58
D	12.5	12	5.12	235	2.20	43
F	37.5	19	14.00	67	11.33	81
F	37.5	17	14.25	112	11.83	83
F	37.5	12	12.00	139	9.94	83
F	37.5	13	13.75	256	10.62	77
F	37.5	15	14.00	376	9.65	69
F	37.5	16	14.15	618	6.70	47

The dotted curves plotted in Fig. 3 represent discharging characteristics obtained when the sample electrode was transferred to $ZnBr_2/HBr$ ($Br^- = 2\,M$, pH ~1). The rate of Br_3^-/Br^- driving improved during repeated cycles. Thus, the average discharging current, which at the 2nd cycle (nine preceding runs had been performed in KBr) was 25% of that achieved in KBr, is seen to treble at the 8th cycle.

For electrodes containing 25 mg of PVP (62.5%) charge capacity increases and bromine appears even more closely complexed inside the material. However, the potentiostatic charging/discharging currents in KBr were more than halved with respect to those obtained with the 12.5% PVP sample. Once transferred to $ZnBr_2$, these electrodes always show exceedingly slow responses and their performance was no longer investigated.

It may be concluded that, with increasing PVP/C ratio, two opposite factors influence the behaviour of the electrodes: an increase in charge capacity (bound to Br_3^- complexation), and a decrease in conductivity of the composite. Optimum conditions seem to be almost realized with samples containing 30 to 40% of PVP. Table 2 accounts quantitatively for the data so far discussed. Comparison with Table 1 emphasizes the low self-discharge rate of PVP electrodes: the somewhat higher rate in $ZnBr_2$ than in KBr is probably due to the higher (2 : 1) Br^- used in the former electrolyte.

Figure 4 shows the potential/time characteristics of a 37.5% PVP sample electrode obtained during galvanostatic oxidation/reduction (1 mA applied, $ZnBr_2$/HBr, pH ~1), which are closer to the actual operations of a practical battery. The voltage shows an acceptably flat shape for both charge and discharge: the latter was delayed 113 h after the former and the coulombic yield was 65%. Relatively high anodic and cathodic overvoltages were observed with respect to the reversible bromine electrode; in these conditions coulombic yields are generally lower than in the corresponding potentiostatic runs. Since this second fact cannot be explained as an increase in self-discharge rate, it is probably due to forced polarization during oxidation, in which some bromine is produced which then diffuses into the solution without being complexed by PVP. Clearly, better power balancing and coulombic yields were obtained for lower *i* applied.

3.3. *PVNOP bromide–C paste electrodes in $ZnBr_2$ electrolyte*

Carbon paste electrodes containing 17.7, 35.5 and 55.0% of the quaternized bromide were assembled, with theoretical charge capacities of respectively 4.1, 8.2 and 12.7 C. Their behaviour during potentiostatic charging/discharging differs from that of PVP analogues in that relatively fast Br_3^-/Br^- driving is possible *ab initio*. In other words, neither preconditioning in KBr, nor many activation cycles are necessary to reach at least the currents shown in Figs 2 and 3. Table 3 summarizes the results achieved with these electrodes which, with increasing polymer content, exhibit the same performance trend shown by the PVP–C composites. In fact, optimum charge storage ability and lowest self-discharge rates were obtained with the 35.5% sample; furthermore, probably because

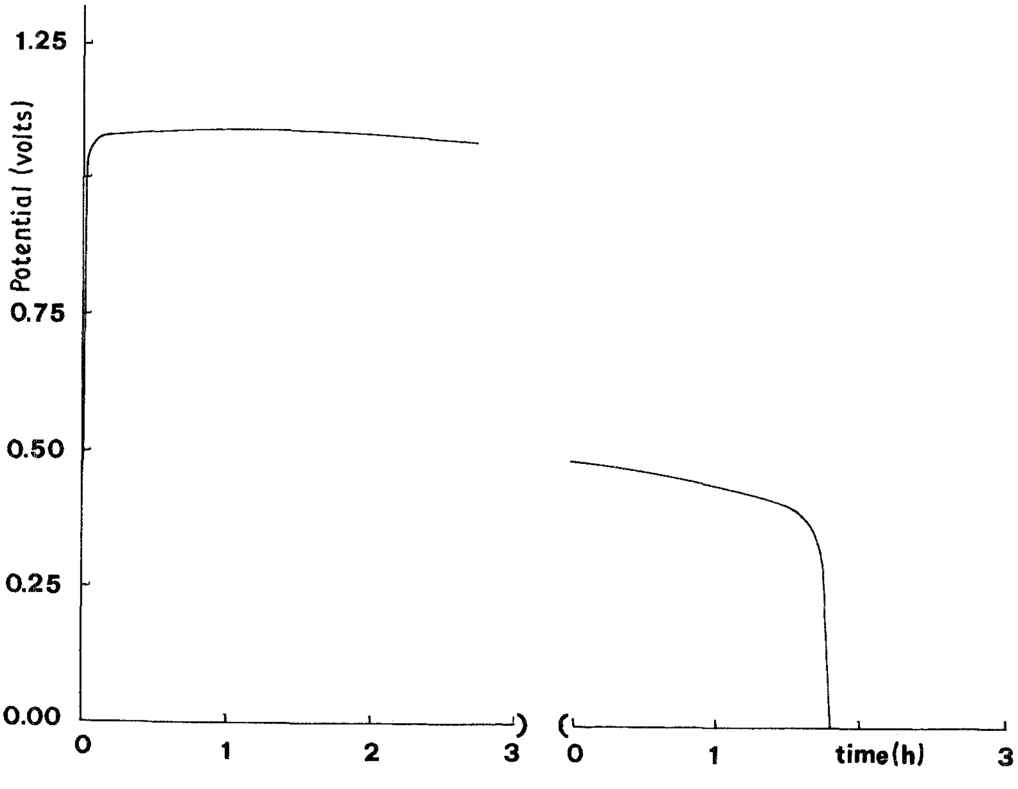

Fig. 4. Galvanostatic charging/discharging (1.000 mA) of a 37.5% PVP/C electrode in 2 M Br^- electrolyte ($ZnBr_2$ + HBr, pH ~1). Delay time = 113 h.

Table 3. Charging/discharging of PVNOP bromide in 2 M Br^- electrolyte ($ZnBr_2$ + HBr, pH $\simeq$ 1)

$I_{applied}$ (mA)	$E_{initial}$ (V, SCE)	E_{final} (V, SCE)	Electrode	PVNOP bromide (%)	Run (No.)	Charging (C)	Delay (h)	Discharging (C)	Yield (%)
(a) Potentiostatic experiments									
			H	17.7	5	3.70	112	1.97	53
			H	17.7	6	3.70	140	1.71	46
			H	17.7	4	3.70	520	0.68	18
			I	35.5	1	7.40	64	5.64	76
			I	35.5	4	6.90	86	5.27	76
			I	35.5	2	7.40	113	5.20	70
			I	35.5	6	7.40	140	4.66	63
			I	35.5	5	7.40	480	2.89	39
(b) Galvanostatic experiments									
0.200	0.76	0.89	H	17.7	9	4.10	113	1.88	46
0.200	0.79	0.89	H	17.7	10	4.10	210	1.81	44
1.000	0.77	1.17	H	17.7	13	4.10	113	2.24	55
0.200	0.75	0.86	I	35.5	8	5.00	113	3.75	75
0.200	0.75	0.86	I	35.5	9	5.00	210	3.38	68
1.000	0.76	1.14	I	35.5	12	5.00	113	3.79	76
1.000	0.48	1.42	L	55.0	1	10.00	113	0.76	8

of the faster electrode response achieved by this polymer/carbon composition, better coulombic yields than those of the PVP analogue were found in the galvanostatic runs. The *E*/*t* characteristics thus obtained for various *i* applied are shown in Fig. 5. After a standard 113 h delay between oxidation and reduction, the coulombic yields were steadily 75 to 80%. The plots are relatively flat for any *i* applied, but clearly the better power balancing between charging/discharging processes is obtained for the lowest (0.200 mA) current.

3.4. *PVP–C paste electrodes in ZnI_2 electrolyte*

The solid-state lithium–iodine cell, exploiting halogen complexation inside a poly(2-vinylpyridine) matrix, is used as a reliable primary cell for low current applications (e.g. pacemakers) [10, 11]. Conversely, no data (to our knowledge) are available on the electrode behaviour of poly(2-vinylpyridine) or poly(4-vinylpyridine) iodine complexes in aqueous acid electrolytes. Although the energetics of an aqueous Zn/I_2 battery are less advantageous than those of the Zn/Br_2 system,

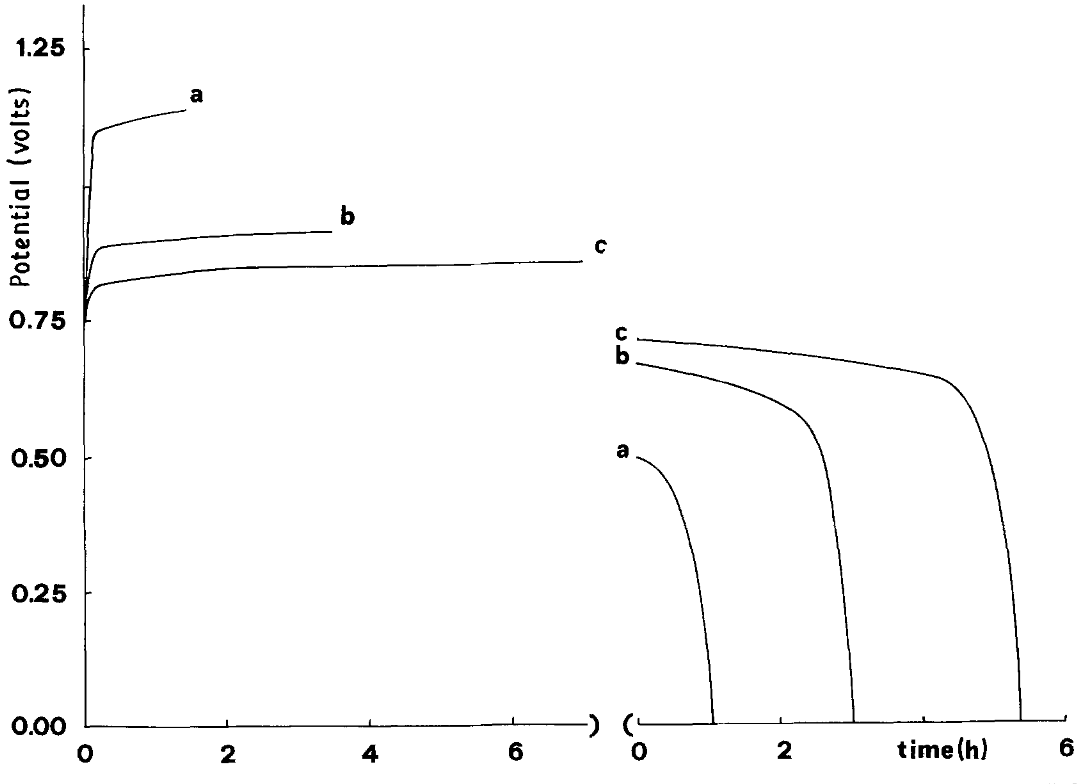

Fig. 5. Galvanostatic charging/discharging of a 35.5% PVNOP/C electrode in 2 M Br^- electrolyte ($ZnBr_2$ + HBr, pH ~ 1) for various $i_{applied}$: a = 1.000 mA, b = 0.400 mA, c = 0.200 mA. Delay times = 113 h.

Table 4. Galvanostatic charging/discharging of PVP in 2 M I^- electrolyte (ZnI_2 + HI, pH $\simeq$ 1)

Run (*N*)	E_{initial} (*V, SCE*)	E_{final} (*V, SCE*)	*Charging* (*C*)	*Delay* (*h*)	*Discharging* (*C*)	*Yield* (%)
3	0.25	0.62	10.00	21	9.81	98
5	0.24	0.56	10.00	113	9.49	95
7	0.25	0.59	10.00	720	8.10	81

Electrode F (37.5% PVP).
I_{applied} = 1.000 mA.
E_{initial}, E_{final} are the potentials at the beginning and at the end of charging, respectively.

some experiments comparable with the data presented here were also performed in this direction. A 37.5% PVP carbon paste electrode, previously activated in KBr, was transferred into 2 M I^- (ZnI_2/HI pH ~ 1) and amperostatic charging/discharging cycles were then carried out with careful exclusion of O_2 from the electrolyte (especially during storage), since O_2 may easily fake data by oxidizing I^- to I_3^-.

As Table 4 shows, attention was focused on coulombic yields and self-discharge results, both of which compare favourably with those obtained from bromine systems and which are probably due to stronger iodine complexation in the polymer and lower solubility of this halogen in the electrolyte. Figure 6 shows the *E*/*t* plots recorded during a typical experiment. Also in this case, 1 mA applied caused the overpotentials seen from the bromine analogue, showing that the material has a relatively high internal resistance. In aqueous acid electrolyte, in which pyridine nitrogen undergoes extensive protonation, the complex appears to be electrostatic in nature, differing from the more conductive charge transfer analogue of solid state devices. The former situation must clearly be assumed for bromine PVP complexes.

4. Conclusions

The resistance of PVP films to driving by the Br^-/Br_3^- couple in Zn(II) containing electroytes was ascribed to crosslinking of pyridine nitrogens by the strongly complexed cations [4]. Data on polymer–C paste electrodes confirm this view, as similar problems are faced *ab initio* with PVP, whereas no internal resistance increase is observed with the quaternized PVNOP bromide when substituting $ZnBr_2$ for KBr electrolytes. However, unlike film electrodes, PVP carbon paste samples may be conditioned to $ZnBr_2$: PVP chains in the composite undoubtedly have degrees of freedom which are inhibited in a homogeneous film. Consequently, PVP should not be underestimated as a possible matrix for bromine storage in a practical aqueous battery with a zinc anode.

Previous work shows that, using either tetraalkylammonium salts as the complexing agent of bromine

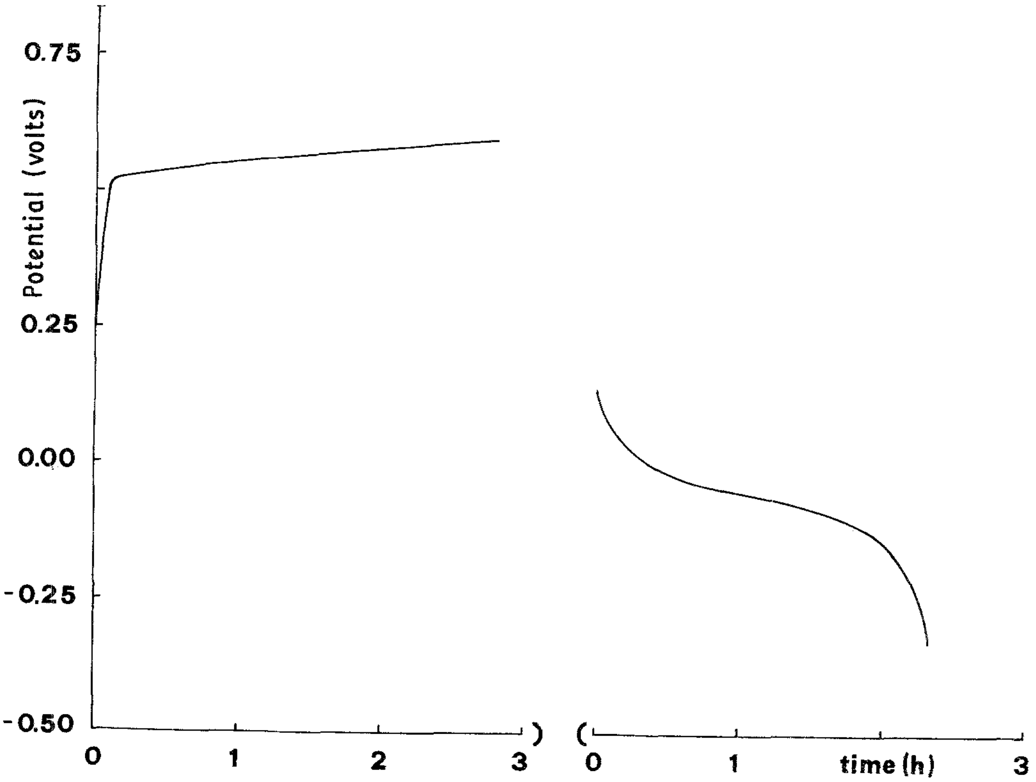

Fig. 6. Galvanostatic charging/discharging of a 37.5% PVP electrode in 2 M I^- electrolyte (ZnI_2 + HI, pH ~ 1). i_{applied} = 1.000 mA. Delay time = 720 h.

[12] or microporous separators and gelled electrolytes to reduce bromine diffusion, self-discharge remains at about 50% loss of capacity in 2 days [13]. Half-discharge time may be extended to 400 h with very effective sulphonated polytetrafluoroethylene membrane separators, but it does result in increased internal resistance [13]. Restricting our considerations to the 37.5% PVP sample:

(i) self-discharge data compare favourably with the previous state-of-the-art;

(ii) the capacity of the composite (not considering the weight of the halogen) is about $150\,\mathrm{A\,h\,kg^{-1}}$;

(iii) polarization is still acceptable at a drain current of $\sim 1\,\mathrm{A\,dm^{-2}}$.

This performance is at present not attained by most conducting polymers claiming to be potential cathodes for batteries.

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