

# Rechargeable thin film batteries of polypyrrole and polyaniline

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Thin films of polypyrrole (PPy) and polyaniline (PANi) were electrochemically deposited on stainless steel substrate under potentiostatic control. Secondary batteries were assembled using these polymers as active electrode materials and propylene carbonate (PC) solutions of tetraethyl ammonium perchlorate (TEAP) as the electrolyte. In repeated charge and discharge tests, the all PANi cells performed better than the PPy-PANi cells in voltage characteristics, recyclability, charge retention and coulombic efficiency. There appears to be an optimum charging current for the polymer cells and charging the cells at rates notably different from the optimum value reduced the cell performance substantially. It is suggested that the cells operate under kinetic control and charging at extreme rates either reduces the participation of polymer redox in the overall cell operation or produces mass transfer limitations.

## 1. Introduction

Among the conductive polymers, polypyrrole (PPy) and polyaniline (PANi) are most noted for their applications in atmospherically stable rechargeable batteries. In these batteries, the oxidized polymers are often used as cathodes with lithium or other metals as anodes to maximize the cell potential. The necessity of thorough removal of water in lithium batteries is difficult for polymers such as PANi where better films are deposited from the aqueous medium. In principle, all-polymer batteries will circumvent such difficulty with the added advantage of higher specific cell capacities resulting from the light weight of polymers. The fabrication of all polymer cells can also be much simpler (see experimental section below). Some early prototype cells of relevance here, however, did not deliver good performance [1, 2]. Low cell voltage, polymer overoxidation and poor charge retention were some of the major problems. Although low cell voltage can be improved through the use of layer cells, other problems require a better understanding of polymer properties which were lacking until recently. This work reports initial findings on rechargeable batteries of the types PPy/PANi and PANi/PANi with the intention of updating the information in this area. Contrary to expectation, the all polymer batteries did not have satisfactory cell characteristics, despite the fact that individual polymer electrodes, when connected up with their metallic counterparts, constituted quite respectable secondary cells. There were, however, positive indications that some of the existing problems could be overcome.

## 2. Experimental details

Thin films of PPy and PANi of approximate areas

1.2 cm × 3.5 cm were electrochemically deposited on 316 stainless steel strips in a conventional three-electrode setup with a platinum counter electrode and Ag/AgCl reference electrode. The stainless steel strips were carefully polished and cathodically etched to improve film adhesion. One side of the strip was masked so that deposition could only occur on the reverse side. The PANi was formed from an aqueous solution of 0.5 M aniline in 1 M HClO<sub>4</sub> at +0.8 V while a propylene carbonate (PC) solution containing 0.1 M pyrrole and 0.1 M tetraethyl ammonium perchlorate (TEAP) was used for the polymerization of pyrrole at +0.95 V. All chemicals used were of analytical reagent grade and pyrrole and aniline were further refined by distillation. The polymerization and subsequent electrochemical characterization of the polymers were carried out on an EG&G 273 potentiostat/galvanostat. The average doping levels in PPy and PANi were estimated to be 33% and 50%, respectively. The presence of the emeraldine oxidation state in the as-synthesized polyaniline samples was deduced from the presence of a strong quinoid absorption band at about 2 eV in the u.v. absorption spectra of dilute N-methylpyrrolidinone (NMP) solutions of the polymer base [3].

The polymer-coated stainless steel strips were thoroughly rinsed (HClO<sub>4</sub> for PANi and PC for PPy) and dried in dynamic vacuum for two to three days. For the assembly of thin film batteries, two of the strips were pressed together with a polypropylene separator between them. The separator was impregnated with about 0.5 ml of 0.1 M of TEAP in PC as the electrolyte. The assembly was then sealed in wax to prevent air entry. After the polarity of the cell was determined, the cell was subjected to an initial discharge to zero the cell potential. Subsequent charge

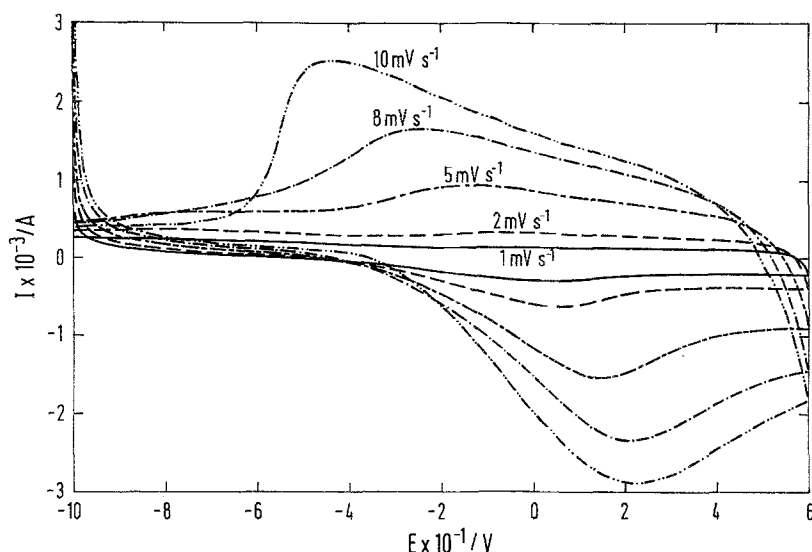


Fig. 1. Cyclic voltammograms of polypyrrole in 0.1 M TEAP in PC.

and discharge tests were then commenced with the cell under constant current conditions. Overnight self discharge tests were also conducted to assess the stability of the batteries. A Hokuto Denko HA 301 potentiostat was used for the controlled charging and discharging of the cells.

All measurements were made at room temperature.

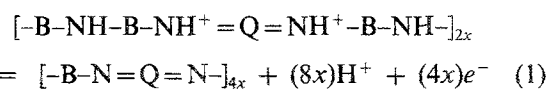
### 3. Results and discussions

The electrochemical activity of the polymers was characterized by cyclic voltammetry (CV). For PPy on stainless steel, the electrolyte used was 0.1 M TEAP in PC and the scan was conducted between  $-1$  V to  $+0.6$  V (with respect to AgCl) at the rate of 1 to  $10 \text{ mV s}^{-1}$ . For PANi on stainless steel, an aqueous electrolyte of 1 M  $\text{HClO}_4$  was used in addition to 0.1 M TEAP in PC. The scan limits were  $-0.4$  V to  $+1$  V at the rate of 1–20  $\text{mV s}^{-1}$ . Representative voltammograms are shown in Figs 1 and 2. As they are not significantly different from the many others reported in the literature, the interpretation of the voltammograms will not be elaborated here.

#### 3.1. PPy–PANi batteries

The open-circuit potential of the cell as assembled was about 18 mV with PANi being the positive electrode. A comparison of the estimated capacities of each electrode indicated that the PPy electrode was limiting. Without loss of generality, the redox reactions occurring on the individual electrodes during charging under the prevailing experimental conditions can be summarized as follows (while the reverse reactions prevail for discharging):

##### Positive electrode



where B and Q denote  $\text{C}_6\text{H}_4$  groups in the benzenoid and quinoid configurations, respectively.

##### Negative electrode

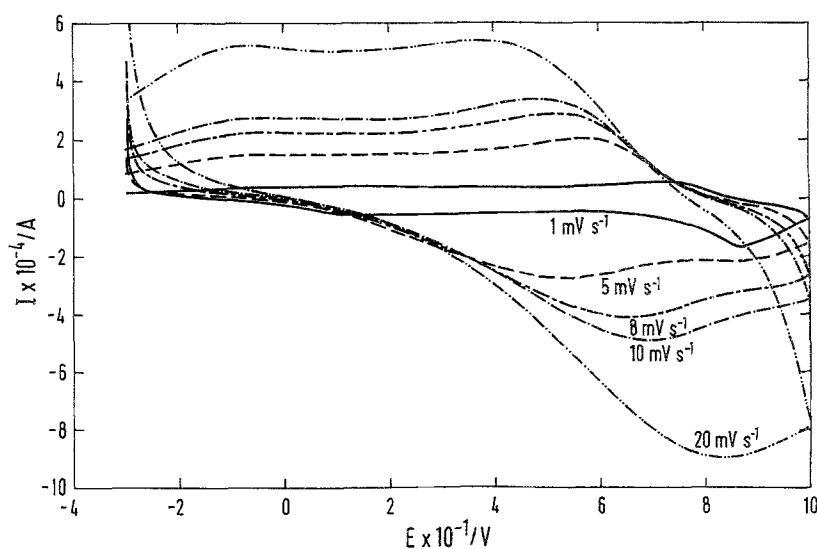
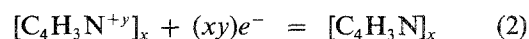


Fig. 2. Cyclic voltammograms of polyaniline in 0.1 M TEAP in PC.

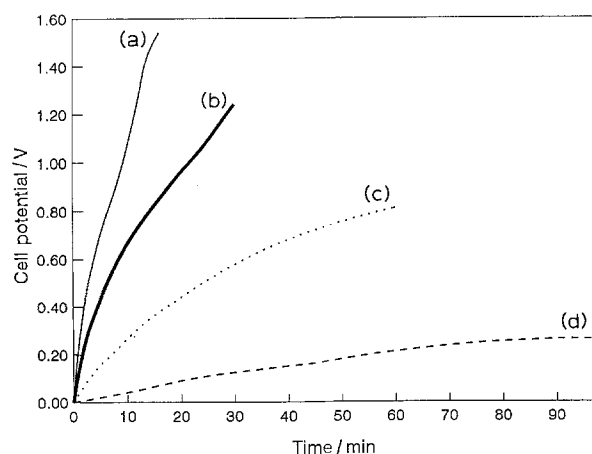
Table 1. Coulombic efficiencies of PPy-PANi cells at 25°C

Estimated capacity/mC	Charging rate/ $\mu\text{A cm}^{-2}$	Discharging rate/ $\mu\text{A cm}^{-2}$	Coulombic efficiency/%
500	25	25	35
		12.5	28
		5	18
		2.5	12
500	2.5	2.5	20
		1.25	15
		0.5	10
		0.25	7
430	45	45	47
		22.5	48
		9	39
		4.5	26
620	130	130	60
		65	53
		26	29
		13	18

Although the reaction at the negative PPy electrode can be generally described as the reduction of oxidized PPy to the neutral state with the concomitant expulsion of the  $\text{ClO}_4^-$  dopant anion, the oxidation at the positive PANi electrode is less certain in view of the ambiguity associated with oxidation of PANi beyond the emeraldine state [4]. The reaction according to Equation 1 is representative only of the extreme oxidation to the pernigraniline state [5]. Elemental analysis of the oxidized polyemeraldine sample revealed about 50% loss of dopant anions which is consistent with the reaction stoichiometry. (Incomplete undoping is expected because of non-exhaustive discharge of the electrode and/or the presence of expelled protons and dopants as sorbed electrolyte within the polymer [6].) The oxidation of polyemeraldine is generally considered to be less reversible than the well known emeraldine-leucoemeraldine transition; the oxidation products are easily hydrolysed in acidified aqueous medium leading to the progressive degradation of the polymer [7-9, 15]. The degradation of PANi, however, can be lessened in aprotic solvents [10], amidst some loss in the rate of redox reactions [11].

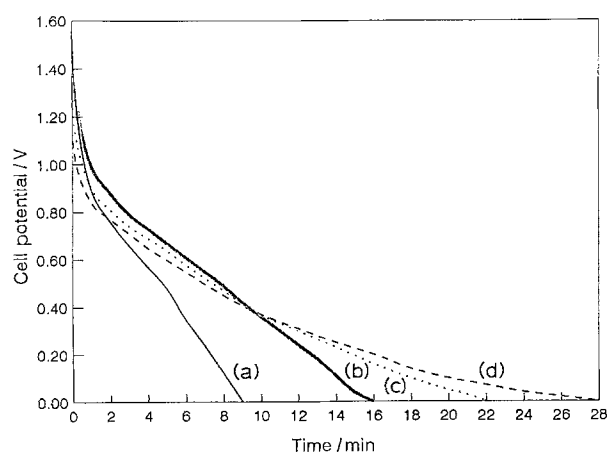
Except for the cell charged at a very low current density of  $2.5 \mu\text{A cm}^{-2}$ , each cell was charged to about 75% of its capacity (based on the limiting PPy electrode) using constant current at various rates (Table 1). Subsequent discharge to near zero cell potential was carried out sequentially according to the rates in Table 1, with the cell always restored to its full capacity after each discharge. The same table also shows the coulombic efficiencies of the cells as summarized from the individual charge-discharge curves such as Fig. 3 and Fig. 4.

There is no clear plateau in the chronopotential curves except for the case corresponding to the very low charging rate of  $2.5 \mu\text{A cm}^{-2}$  (approximately a  $C/55$  rate). Despite this, most charging was stopped at 75% of the estimated capacity to prevent any irreversible damage to the polymers. The final cell potentials

Fig. 3. Charging curves of PPy-PANi cells. Current density: (a) 130, (b) 45, (c) 25 and (d)  $2.5 \mu\text{A cm}^{-2}$ .

were found to be strongly dependent on the charging rates. As the difference between the open-circuit potential and the closed-circuit potential upon current interruption was not in proportion to the current, it could not have been caused by IR losses in the cell alone. Although it is tempting to attribute the near linear decrease of cell potential as a manifestation of the capacitive charges [12, 13], we believe that the phenomenon was more closely associated with the chemistry of the redox reactions and should also be examined in the light of other apparent cell anomalies.

As shown in the entries in Table 1, in contrast to normal battery performance, the coulombic efficiency and the recyclability of the cell are improved by an increasing charging rate. A significant decrease in all aspects of cell performance was, however, observed when the current density exceeded the  $4C$  rate. An average of 50-60% of the charges could be recovered from a freshly prepared cell at moderate charging rates. On prolonged charge and discharge tests, the cell with  $45 \mu\text{A cm}^{-2}$  rate showed the most satisfactory recyclability. No sign of cell deterioration was observed after 10 cycles of operation, whereas deterioration was imminent after 5 cycles for the cell charged at  $130 \mu\text{A cm}^{-2}$ . In self discharge tests, the former also fared better in comparison with the rest.

Fig. 4. Discharge curves of PPy-PANi cell ( $Q_s = 620 \text{ mC}$ ,  $i_{\text{chg}} = 130 \mu\text{A cm}^{-2}$ ). Current density: (a) 135, (b) 65, (c) 26 and (d)  $13 \mu\text{A cm}^{-2}$ .

The apparent cell anomalies can be rationalized in terms of slower polymer redox electrode kinetics relative to the redox reactions in commercial batteries. At very low rates of charging, some background reactions with relatively low redox potentials (possibly the oxidation of substrate) might by themselves be sufficient to deliver most of the current demand and the reversible redox of the polymer is not significant in the cell operation. As the rate of charging increases, there comes a point when the background reactions have reached their limiting current densities, after which the contribution from polymer redox must necessarily increase to compensate for the increasing shortfall in total current demand. In such case the cell potential rises rapidly in response to a kinetically controlled process. The more reversible process of polymer redox subsequently imparts improved cell performance, such as in the areas of coulombic efficiency, recyclability and charge retention. As the charging rate continues to increase, normal battery performance returns once the polymer redox begins to be rate-limited by mass transfer processes.

From the experimental results, there seems to exist an optimum charging current for the PPy-PANi cells. Polymer cells that are charged at rates very different from the optimum value tend to deteriorate faster either by interference of irreversible secondary reactions or by diffusion limitations on polymer redox common to normal battery operation.

The PPy-PANi cells were dismantled at the end of the tests. While PPy remained contained in its own phase, some PANi was found to have diffused into the separator. There was also partial detachment of the PANi film from the electrode. This was probably due to swelling of aqueous-grown PANi in nonaqueous electrolyte. The penetration of PANi into the separator could also be partly responsible for the less than ideal performance of the polymer cells.

### 3.2. All PANi batteries

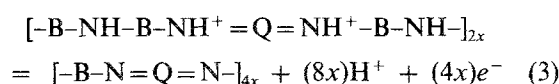
The early 'all PANi' cell of Jozefowicz [1] using PANi electrodes in the forms of polyemeraldine and poly-leucoemeraldine was able to deliver a cell potential of only 0.4 V. In order to increase the cell potential, the polyemeraldine electrode could, in principle be further oxidized while keeping the degradative overoxidation under control. In the present work, nonaqueous cells were formulated with two identical PANi electrodes initially in the emeraldine oxidation state. The use of nonaqueous electrolyte was deliberate to reduce the hydrolysis of oxidized polyemeraldine that led to polymer degradation. As only one type of electrode material needed to be prepared, the cell assembly was greatly simplified. An *in situ* electrode forming process not unlike that used for lead-acid batteries [14] ensued to form the PANi electrodes in different oxidation states. During the first charging of the cells, polyemeraldine at the anode was oxidized while that at the cathode was reduced. The redox reactions for

Table 2. Coulombic efficiencies of all-PANi cells at 25°C

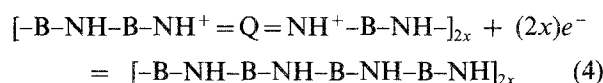
Estimated capacity/mC	Charging rate/ $\mu\text{A cm}^{-2}$	Discharging rate/ $\mu\text{A cm}^{-2}$	Coulombic efficiency/%
460	28	28	60
		14	55
		5.6	42
		2.8	30
790	5	5	15
		2.5	13
		1	11
		0.5	8

charging (forward reactions) and discharging (reverse reactions) can be summarized as follows:

#### Positive electrode



#### Negative electrode



According to the model proposed by MacDiarmid and coworkers [15], oxidation of PANi should be viewed as a continuous process with the fraction of oxidation sites (imine units) varying from 0 to 1. Hence the Reactions (3) and (4) are used only to represent categorically the stoichiometry involved in polymer oxidation and reduction. The work here does not address the actual oxidation states of PANi, but rather uses the many oxidation and reduction reactions that are possible with PANi to explain the battery operation.

The all PANi cells were subjected to the same performance tests as conducted for the PPy-PANi cells. In order to prevent degradation in the oxidized emeraldine state, the cells were only charged to 50% of their capacities using current densities at 1C and 0.1C rates. The results are summarized in Table 2.

The all PANi cells have generally improved voltage characteristics (Figs 5 and 6) and coulombic efficiencies.

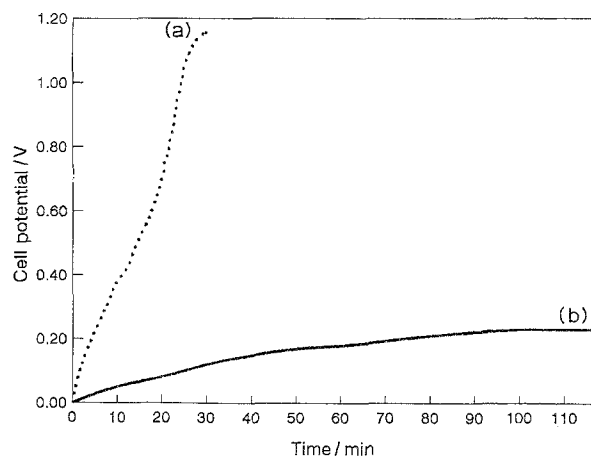


Fig. 5. Charging curves of all-PANi cells. Current density: (a) 28 and (b)  $5 \mu\text{A cm}^{-2}$ .

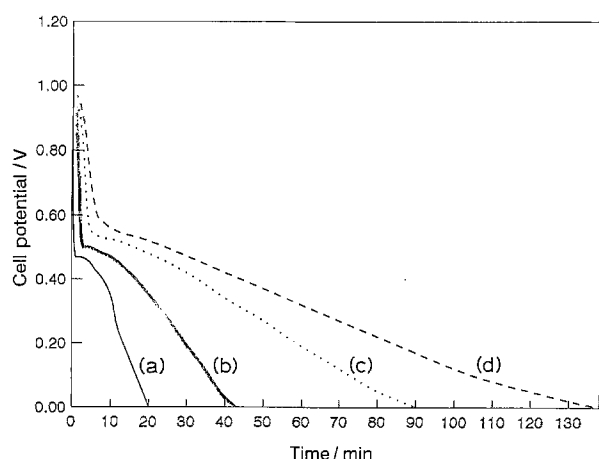


Fig. 6. Discharge curves of all-PANi cell ( $Q_s = 460 \text{ mC}$ ,  $i_{\text{chg.}} = 28 \mu\text{A cm}^{-2}$ ). Current density: (a) 28, (b) 14, (c) 5.6 and (d)  $2.8 \mu\text{A cm}^{-2}$ .

The capacity efficiency was higher than PPy-PANi cells, and up to 60% recovery could be achieved at the charging rate of 1C. There were also indications of approaching a cell potential plateau of 1.20 V (or 0.6 V after discounting the IR losses) at this charging rate. Similar to the PPy-PANi cells, a higher charging rate provides a better coulombic efficiency before the onset of mass transfer control. Ageing of the cells as demonstrated by the recyclability of the cells in repetitive charge and discharge tests was also reduced. The cells still suffered from poor charge retention in self-discharge tests. However, 24 h were needed to deplete the cells completely compared to only 16–18 h in the case of PPy-PANi cells.

The improved performance of all PANi cells in comparison with PPy-PANi cells could be attributed in part to the faster switching rate of PANi between its various oxidation states [16]. The use of nonaqueous electrolyte helps to stabilize PANi against oxidative degradation during switching [10, 11]. In order to examine whether the relatively poor performance of polymer cells was due to the quality of polymers being made, the PANi electrodes were paired up with amalgamated zinc electrodes in a  $\text{ZnCl}_2$  cell according to the method of MacDiarmid [17]. Very respectable cell characteristics were obtained. Related experimental evidence from this laboratory suggests that the poor performance of polymer cells may be traced to the use of polyemeraldine as anodes. Despite this, some of the cell irreversibilities can be reduced through the use of PANi electrodes prefabricated in more definite oxidation states (such as polyleucoemeraldine) and the use of electrolyte that reduces the detachment of PANi from the electrode surface [18]. The convenience of forming two electrodes of the PANi cell *in situ* will have to be abandoned for an improved cell performance. The present *in situ* practice may have produced PANi electrodes in mixed oxidation states whereby internal redox occurs in the

absence of electric field to induce the self-discharge problem. More work has been planned out to study the problem in depth.

#### 4. Conclusions

The findings from PPy-PANi and all PANi cells clearly demonstrate the viability of using these conductive polymers as active electrode materials. In general, the all PANi cells performed better than the PPy-PANi cells in voltage characteristics, recyclability, coulombic efficiency and stability. The operation of the prototype cells was under kinetic control and subsequently an optimum charging current was found for each cell. Charging at rates very different from the optimum value either reduced the participation of polymer redox in the overall cell operation, or rendered the cell under mass transfer control (normal cell behaviour). The cell performance at present is still not satisfactory. However, there are positive indications that some of the problems can be overcome through cell formulation and design.

#### Acknowledgement

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