JOURNAL OF APPLIED ELECTROCHEMISTRY 23 (1993) 1031–1038

Thin film polyaniline–polyaniline electrochemical cells

J. Y. LEE*, L. H. ONG*, G.K. CHUAH§

Department of Chemical Engineering and Department of Chemistry§ National University of Singapore, 10 Kent Ridge Crescent, Singapore 0511*

Received 17 August 1992; revised 18 December 1992

Electrodeposited polyaniline (PANi) in the emeraldine oxidation state was used as the electrodes of open rechargeable cells containing 1 M $HClO_4$ as the electrolyte. The cells could be charged at very high hourly rates to 85% of the redox charge in the leucoemeraldine–emeraldine transition of the polymer. Contrary to normal behaviour of rechargeable cells, the coulombic efficiency improved with increasing rates of charge injection and withdrawal. This is attributed to less charge being dissipated by self-discharge at high rates of discharge. The poor charge retention was caused by reactions between the charged electrodes and their environment. The decrease in cell voltage on standing may also be induced by internal redox reactions of PANi of different oxidation states present at the electrodes as a result of incomplete oxidation or reduction during cell operation. Ultraviolet (u.v.) spectroscopy of the charged electrodes identified mostly protonated leucoemeraldine at the negative electrode and pernigraniline at the positive electrode. The irreversibility in the oxidation from the emeraldine state to the pernigraniline state accounts mostly for the degeneration of cell performance after prolonged cycling.

1. Introduction

Among the various applications proposed for polyaniline (PANi), use of the polymer in rechargeable batteries has been most extensively researched [1–12] and has culminated in the introduction of a series of lithium–PANi button cells by Bridgestone/Seiko in the late eighties. Instead of coupling PANi to an active metal such as lithium or zinc, an all-polymeric configuration was suggested as a means to reduce production cost [11, 12]. Technical feasibility is assured as PANi in the commonly prepared state of emeraldine‡ can be easily oxidized or reduced electrochemically. The use of a common material for both electrodes enables *in situ* chemical or electrochemical formation of the electrode active materials, not unlike the practice adopted in acid–lead battery manufacture. Furthermore, the abandonment of active metal allows aqueous formulations to be used for a higher electroactivity of PANi. Such advantages were, nonetheless, undermined by the relatively low rate of utilization and high rate of self-discharge in the experimental cells [12]. The electrochemical origin of such operational difficulties is examined in the light of additional experimental findings in this work.

2. Experimental details

PANi was deposited on platinum foils of dimensions 2.5 cm × 1.25 cm from a solution of 0.5 M aniline in 1 M $HClO_4$. Deposition was carried out potentiostatically for about 300 s at 0.8 V against a Ag/AgCl reference electrode in a conventional three-electrode system using a large platinum gauze as the counter electrode. All chemicals used were of AR grade and aniline was further purified by distillation over zinc dust. The electrolyte was deaerated for 15 min prior to deposition. All experiments were carried out at room temperature.

The PANi deposit was characterized by cyclic voltammetry in 1 M $HClO_4$. The potential range of −0.2 to 0.6 V was scanned at rates from 20 to 500 mV s^{-1}. The charge in the cathodic half of the voltammogram was extrapolated to zero scan rate and the extrapolated value (Q_s) was used as the redox charge available from the polymer†. Chronoamperometry measurements by Genies and Tsintavis [13] indicated that the redox charge in the oxidation of emeraldine could be much lower than the reduction of emeraldine. Although the charge in the cathodic half of the voltammogram between −0.2 and 0.6 V consists mainly of the reduction of emeraldine, it was still used as a matter of convenience for the calculation of the hourly rates (CA-rates) in charging and discharging. The depth of charge was subsequently discounted from 100% (although not to the extent of 50% as suggested by Genies *et al.* [13]) to reflect the charge imbalance between the two redox processes. The doping level (x) was calculated from the values of Q_s and the anodic charge accumulated

‡For the sake of brevity, emeraldine, leucoemeraldine and pernigraniline are used synonymously with their polymers.

†An electrochemical system consisting of electroactive polymers can be considered as a hybrid between rechargeable batteries and supercapacitors [27]. When the electrochemical response of the systems arises mainly from the bulk of the material instead of from surface layers only, the use of the term 'rechargeable battery' is preferred [11]. In the present case, the variation of electrode charge with scan rate is a positive indication of the contributions from the bulk phase, even for films containing charges as little as 6 mC cm^{-2}.

0021-891X © 1993 Chapman & Hall

during deposition (Q_p) according to the equation [13]:

$$x = 2Q_s/(Q_p - Q_s) \quad (1)$$

x was found to be 0.4 which agreed well with the electrochemical preparations of PANi [14].

Most of the deposit attached only loosely to the electrode. The loose deposit was dislodged by washing with water and by ultrasonic dispersion. Only the thin and transparent layer of PANi that remained on Pt was used as the battery electrode. For films with deposition charge about 1C, a comparison of Q_s before and after the dislodgement procedure showed that about 75% of the available charge was lost.

Open electrochemical cells were set up using two of the PANi electrodes. The hourly rates of charging and discharging were based on the available charge of the limiting electrode. An acidic medium of 1 M $HClO_4$ was used to maintain a high electroactivity of the PANi electrodes. The potential of the positive electrode was followed with respect to a Ag/AgCl reference electrode. As the cells had negligible solution resistance, the potential of the negative electrode could be obtained by subtracting the positive electrode potential from the overall cell voltage.

The cells were charged and discharged at the same rates to about 85% depth. Somewhat higher rates were used to shorten the duration of the experimental runs. The coulombic efficiency of each charge/discharge cycle was closely monitored and the experiment was interrupted once the efficiency fell below 30%.

PANi and Pt in the pristine, and in various charged and discharged states was completely dissolved in N-methyl pyrrolidone (NMP) and the solution was examined by u.v. spectroscopy for structural determination.

3. Results and discussions

3.1. *Performance of PANi electrodes*

A typical test cell would consist of two PANi electrodes with Q_s about 40 mC. The small open cell voltage (in tens of mV) was zeroed by shorting the cell terminals. The cell was then charged at 0.1 mA for 6 min followed immediately by a discharge at the same rate to zero cell voltage. The corresponding hourly charging rate and the depth of charge were approximately 8.5CA and 85%, respectively. The coulombic efficiency of the cell was therefore the ratio of time spent in discharge and charge. Charge/discharge was continued for 20 cycles or until the coulombic efficiency fell below 30%, whichever came first.

Figure 1(a) shows the first 20 cycles of the charge–discharge curve of the test cell. Conditioning runs, which served to stabilize the state of electrodes [15], were not necessary. The potential of the positive electrode (against the Ag/AgCl reference), which was followed during the course of the experiment, is plotted in Fig. 1(b). There was a noticeable increase in cell voltage from 0.64 V in the first cycle to 0.95 V in the 20th cycle. From the similarity between the envelopes of the potential transients in Fig. 1(a) and (b), the increase seems to derive mainly from the rapid escalation of the positive electrode potential. At potentials of 0.9 V and above, increased *IR* drop in the electrode also led to high cell voltage which began to level off only after the 15th cycle. Despite this, the coulombic efficiency of the cell was relatively constant during the 20 runs, dipping slightly from 58% in the first cycle to 50% in the 20th cycle (Fig. 2).

The low coulombic efficiency could be due to several factors such as irreversibility in the cell redox reactions, the occurrence of side reactions and poor charge retention of PANi electrodes. In principle, a charged PANi–PANi cell functions by reducing PANi from pernigraniline to emeraldine at the positive electrode, and by oxidizing PANi from leucoemeraldine to emeraldine at the negative electrode. The first reaction is known to have certain inherent irreversibilities [16]. Although such irreversibilities probably explain the gradual decrease in coulombic efficiency as the positive electrode deteriorates over time, it alone cannot account for the low coulombic efficiency prevalent in all the runs. On the other hand, it is difficult to assess directly the extent of side reactions, particularly in the first ten runs, in the absence of abrupt jumps in the charging curve. By comparison, poor charge retention, due to deactivation of PANi electrodes, seems to be a more obvious cause of low coulombic efficiency.

Poor charge retention caused the cell to dissipate all its charge in 150 min on standing. The self-discharge rate is somewhat exaggerated by the small capacity of the test cell. A comparison of the rates of potential decay between discharge at 0.1 mA and self-discharge shows that the latter may account for a substantial amount of lost charge, at least initially. As the cell voltage decreased more rapidly than the potential of the positive electrode (Fig. 3), the oxidation of the negative electrode was probably the main cause of self discharge. The difficulty of reduced PANi to retain stored charge over extended periods explains why the conductive polymer is often used as the positive electrode in lithium rechargeable batteries.

When the test cell was charged and discharged at the increased rate of 0.2 mA for 3 min, the coulombic efficiency improved to 83%. Conversely, a lower rate of 0.05 mA for 12 min decreased the coulombic efficiency to 42% (Fig. 4.) As the use of thin PANi films effectively removed rate limitation by ionic movement in the film [17], the normal cell behaviour of increasing coulombic efficiency with decreasing discharge rate was not observed. As self-discharge occurred surreptitiously at all times, the fraction of charge lost to self-discharge was minimised by the use of shorter discharge time at higher discharge rate, and the coulombic efficiency increased as a result. The argument is supported by independent experiments in which the test cell was discharged at twice the rate of charging. The coulombic efficiency improved again because of the reduction in the discharge time.

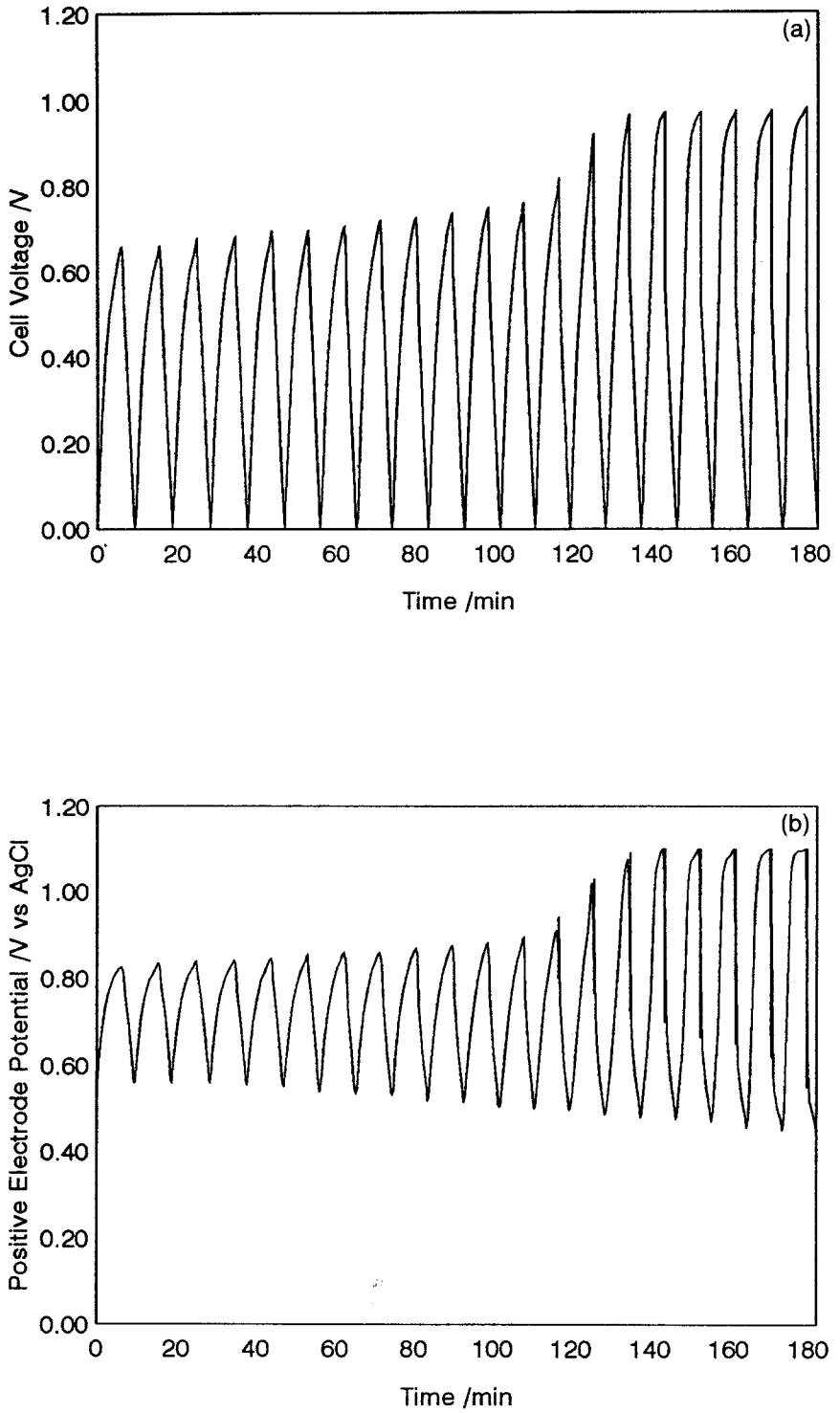

Fig. 1. (a) Charge–discharge curves of a PANi–PANi test cell of $Q_s = 42$ mC charging and discharging at 0.1 mA. (b) The corresponding variations in the cathode (positive electrode) potential (against Ag/AgCl reference).

Although self-discharge was brought about by the gradual deactivation of the charged electrodes, there was no indication of a permanent decrease in cell reversibility. A cell depleted of all its charge on standing could be restored in no different way from a fresh cell. Indeed, when the depleted electrodes were analysed by u.v. spectroscopy, only the emeraldine form of PANi was detected.

The open circuit potentials of the charged electrodes are determined by the reactions between the electrodes and the environment. In the case of the leucoemeraldine negative electrode, the increase in potential is due to the oxidation of leucoemeraldine, most notably by dissolved oxygen in the acidic electrolyte. The aerial oxidation of leucoemeraldine was recently reported to be accelerated under illumination by u.v./vis. light [18]. Better cell performance may therefore be expected from a sealed system whereby both oxygen and light access are restricted. The dissolved oxygen in the electrolyte can also be reduced through the addition of inorganic salts or oxygen scavengers.

The environmental reasons for the deactivation of the positive pernigraniline electrode in self-discharge

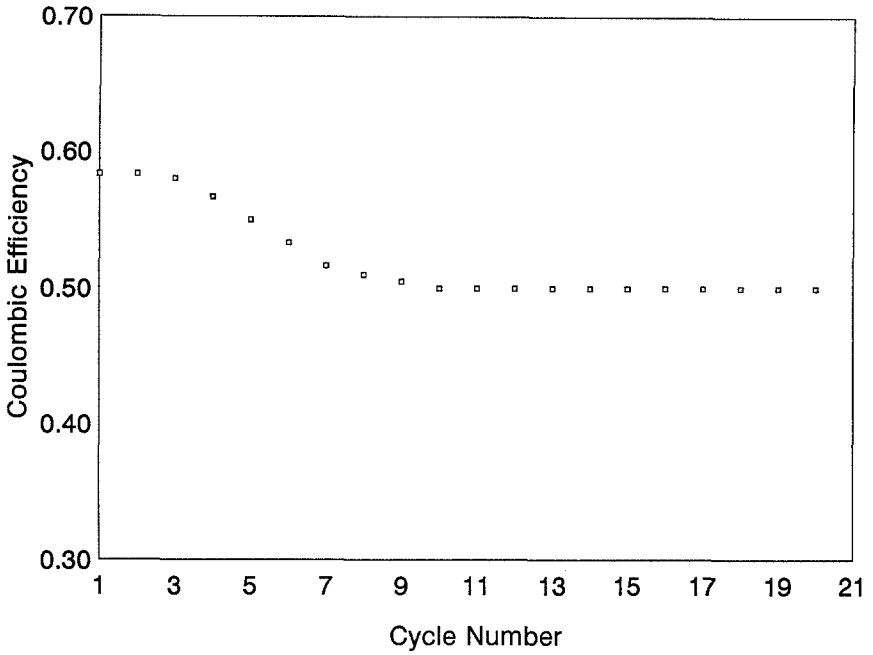

Fig. 2. Coulombic efficiency of the first twenty cycles ($Q_s = 42\,\mathrm{mC}$).

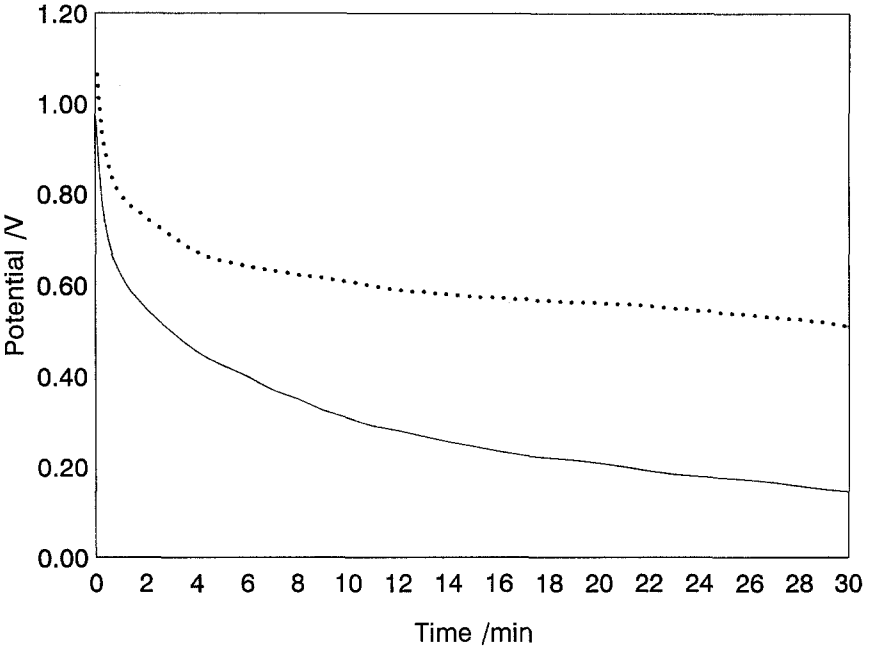

Fig. 3. Self-discharge (solid curve) and the corresponding decay in the positive electrode potential (dotted curve).

is less clear. According to Shinozaki *et al.* [19]. the self discharge in conductive polymer electrodes is caused by the decomposition of the electrolyte followed by polymer undoping. The decomposition of ClO_4^- was unlikely in the present case in view of the small open circuit potential of the negative electrode. On the other hand, pernigraniline is known to be reducible by water under acidic conditions, leading to the degradation of PANi. The reaction consumes PANi and the electrode capacity decreases. As a self-discharged cell may be easily restored to its full capacity, the irrevocable loss of active materials at the positive electrode due to degradative hydrolysis of PANi was probably limited. Likewise other mechanisms that necessarily impart permanent losses of PANi, such as partial dissolution of the polymer and/or the redox reactions between polymer electrodes and polymer degradation products, can also be dismissed on the same basis.

The internal redox reactions of PANi at the electrodes may constitute a notable source of the potential shifts in the electrodes and the reduction of cell voltage on standing. The reactions consequent upon incomplete oxidation or reduction of PANi during cell operation, result in a mixture of PANi of discrete oxidation states being formed at the electrodes. The suggestion that discrete, rather than continuous oxidation states should prevail at least on the molecular level has been expounded [20]. Redox reactions between PANi in different oxidation states can be anticipated, and may constitute an important mechanism in self discharge in the presence of only a trace amount of electrolyte.

Self-discharge mechanisms due to the shuttle of soluble redox species between the two electrodes was

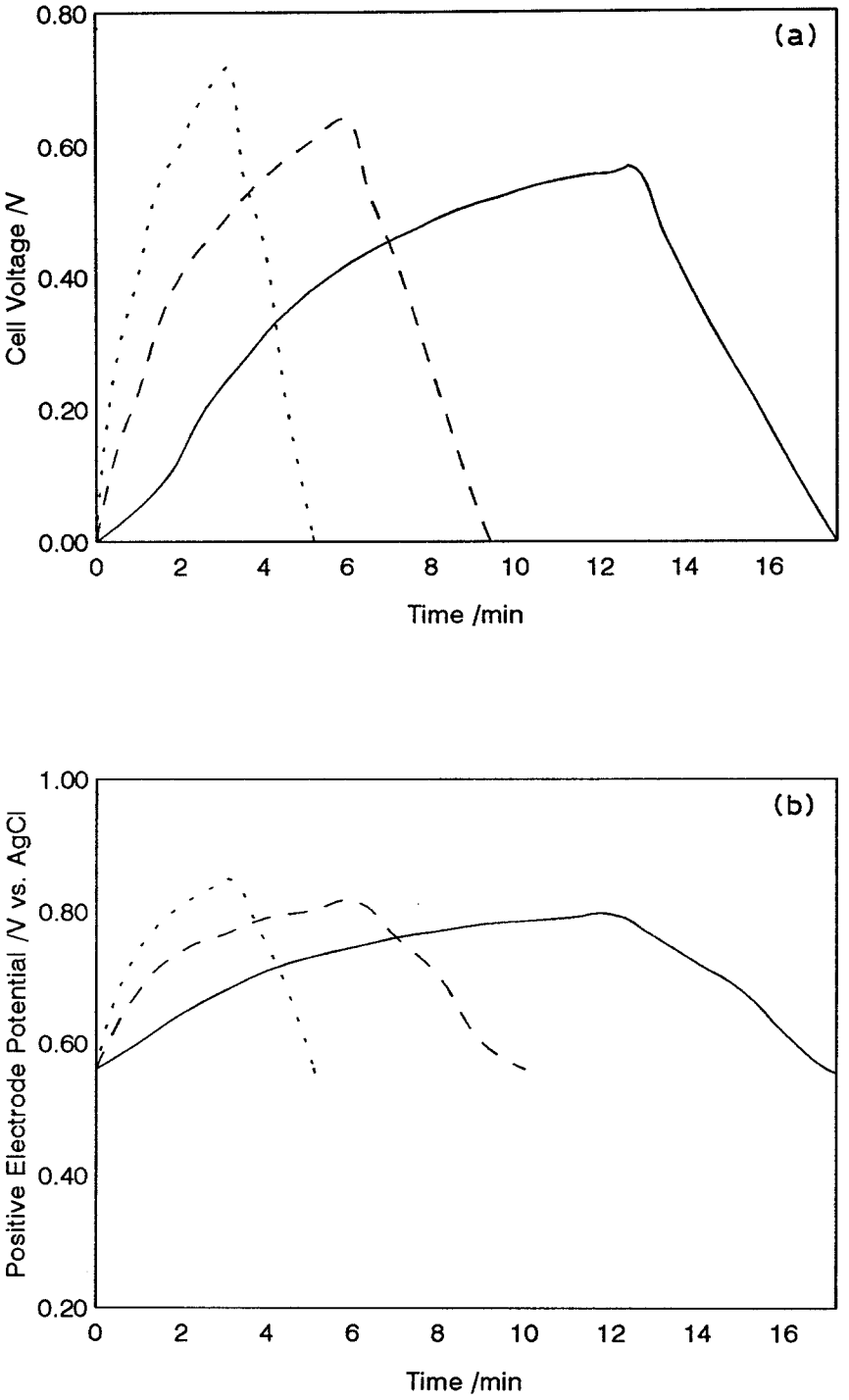

Fig. 4. (a) Charge–discharge curves for the same test cell charging and discharging at (—) 0.05 mA, (- - - -) 0.1 mA and (····) 0.2 mA. (b) The corresponding variations in the positive electrode potential (against Ag/AgCl reference).

less likely to be of concern here because of the use of high purity organic reagents that were relatively free from metal impurities such as Fe, Ni and Cr.

3.2. *U.v. spectroscopy of charged electrodes*

U.v. spectroscopy was used to determine the structure of PANi electrodes in the pristine and in the various charged states. No attempt was made to deprotonate PANi in NH_4OH before its dissolution in NMP. The u.v. spectrum of the pristine, as deposited, PANi electrode in Fig. 5 is dominated by two peaks at 330 nm and 640 nm, respectively. The 330 nm peak is present in almost all forms of PANi and is generally attributed to the π–π^* transition of the polymer [21]. The peak at 640 nm is characteristic of the benzenoid–quinoid transition in the emeraldine base. The absence of a rising baseline in the 700–900 nm region indicates complete deprotonation of the as-synthesized PANi in NMP. A colour change from green to blue as protonated emeraldine solubilised in NMP is also evidence of the conversion into the base form.

U.v. spectra of the charged electrodes (Figs 6 and 7) show significantly different features. The spectrum of the charged negative electrode (light yellowish–green) exhibits two peaks at 330 nm and 450 nm (Fig. 6) and

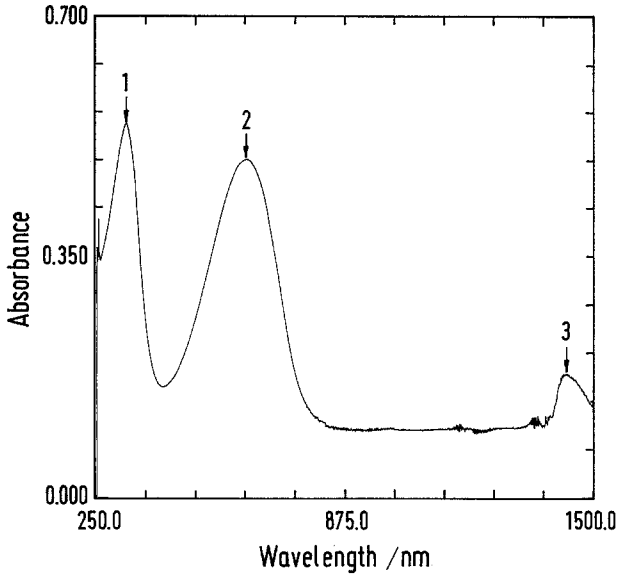

Fig. 5. U.v. spectrum of a NMP solution of pristine, as-synthesized PANi in the emeraldine oxidation state. Peaks 1 and 2 are located at 330 and 640 nm, repectively.

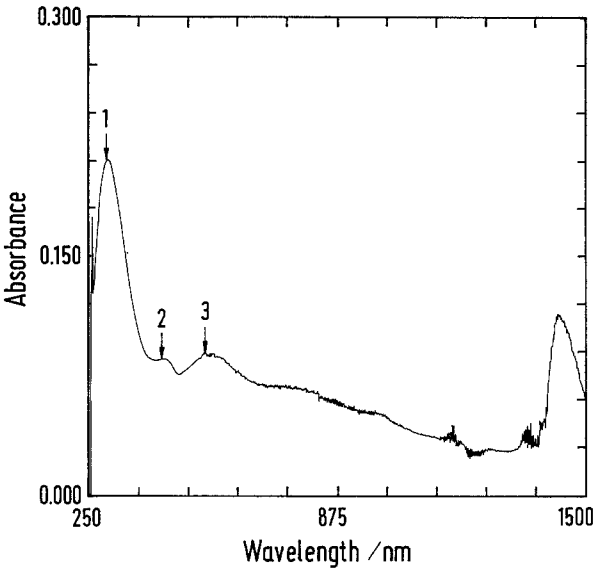

Fig. 7. U.v. spectrum of a NMP solution of the charged positive electrode. Peaks 1, 2 and 3 are located at 296, 433 and 542 nm, respectively.

a rising baseline spanning from 500 to 1500 nm. The peak at 450 nm, together with the rising baseline, which often indicates conductivity, is taken to imply the presence of leucoemeraldine in the protonated form. The assignment of absorption peaks in the spectrum of the charged positive electrode (Fig. 7) is based on a comparison with the spectrum of pernigraniline. MacDiarmid [22] recently reported the chemical synthesis and isolation of pernigraniline base in the solid state. Prior to his work the presence of pernigraniline was mostly inferred from the solution spectra of emeraldine in concentrated H_2SO_4 [23]. Although pernigraniline, as the most oxidized form of PANi, has been involved frequently in the interpretation of the cyclic voltammograms of PANi, its electrochemical synthesis to an isolable solid form was only briefly mentioned in an early XPS report of Snauwart *et al.* [24], and has not been presented since then. In general all peaks in pernigraniline spectrum

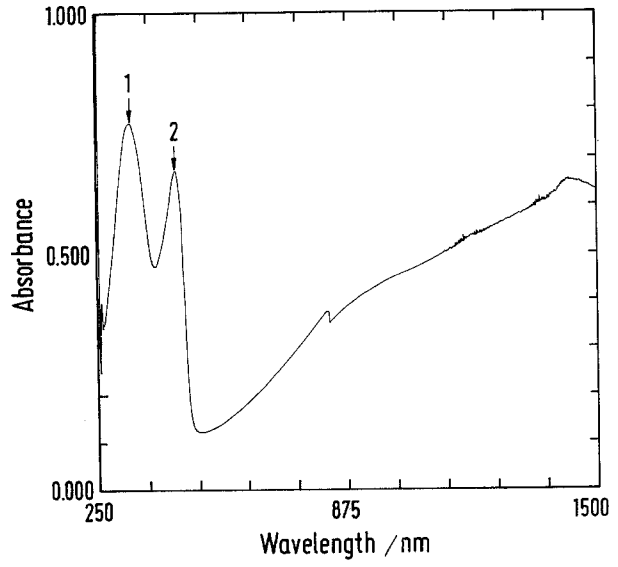

Fig. 6. U.v. spectrum of a NMP solution of the charged negative electrode. Peaks 1 and 2 are located at 330 and 450 nm, respectively.

tend to shift to shorter wavelengths. The 542 nm peak is indicative of PANi oxidation beyond the emeraldine state and compares fairly well with the 530 nm peak in MacDiarmid's work. The origin of the 433 nm peak cannot be ascertained but seems to derive from the remnants of protonated emeraldine. The flat baseline extending from 600 to 1250 nm probably arises from the insulating nature of pernigraniline. The positions of the peaks do vary with the extent of oxidation. In test cells which were driven until the coulombic efficiency fell below 30%, the positive electrode was more representative of pure pernigraniline: The 433 nm peak disappeared totally and the peak at 296 nm was split into two peaks at 278 and 324 nm, respectively. The colour of the 'depleted' positive electrode was blue with a lustrous purple tint.

The cell reactions for charging may be presented by the following equations in accordance with the determined structures of PANi in the charged states:

Positive electrode

$$[-\mathrm{B-NH-B-NH^+=Q=NH^+-B-NH-}]_{2x}$$
$$= [-\mathrm{B-N=Q=N-}]_{4x} + (8x)\mathrm{H^+} + (4x)\mathrm{e^-} \quad (2)$$

Negative electrode

$$[-\mathrm{B-NH-B-NH^+=Q=NH^+-B-NH-}]_{2x}$$
$$+(4x)\mathrm{e^-} + (2x)\mathrm{H^+}$$
$$= [-\mathrm{B-NH_2^+-B-NH-B-NH-B-NH-}]_{2x} \quad (3)$$

where B and Q denote C_6H_4 groups in the benzenoid and quinoid configurations, respectively.

Reaction 3 suggests a reduction of emeraldine to leucoemeraldine with the concomitant ejection of some dopant anions. The mechanism predominates mostly in very acidic medium (pH < 0), and has been verified by the early work of MacDiarmid [25].

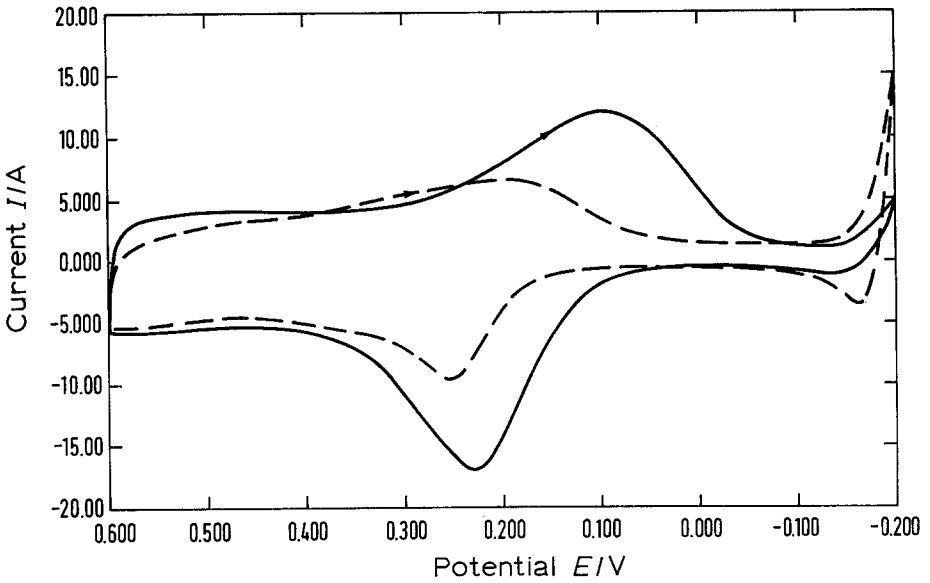

Fig. 8. Cyclic voltammograms of a PANi electrode in the uncharged state of emeraldine (solid curve) and of the same electrode oxidised at 1.0 V for 30 min (dashed curve). Cyclic voltammetry was carried out in 1 M $HClO_4$ at 100 mV s^{-1}.

Reaction 2 accounts for the deterioration of cell performance over extended periods. In an independent experiment, a positive electrode was purposely and severely oxidized in a neutral electrolyte; the presence of pernigraniline was confirmed by u.v. spectroscopy. Electrode deactivation was demonstrated by cyclic voltammetry, which showed a near 75% reduction of the initial capacity (Fig. 8). Interestingly, part of the reversibility was restored by repeated cycling in 1 M $HClO_4$. Probably some of the entrapped oxidized PANi species was reduced by the cathodic scan in cyclic voltammetry, and also by ending the scan at the relatively negative potential of −0.2 V [26].

4. Conclusions

Open PANi–PANi rechargeable cells were assembled from electrodeposited PANi in the emeraldine state and 1 M $HClO_4$. The use of an acidic electrolyte enabled the cells to be charged rapidly, even at the high hourly rate of 8.5CA. During charging, emeraldine was reduced to leucoemeraldine at the negative electrode and oxidized to pernigraniline at the positive electrode. The last reaction is less reversible and accounts for the cell deterioration by loss of charge after multiple charging and discharging cycles. The cells could be charged to 85% of the redox charge in emeraldine–leucoemeraldine transition with a coulombic efficiency around 50% that depended on the rate of discharge. The low coulombic efficiency is attributed mostly to the self discharge of the cell which occurred concurrently during the discharge, with interference from irreversible side reactions playing a relatively minor role. The self-discharge is believed to be caused by the reactions between PANi and its environment. Particularly severe is the rapid oxidation of leucoemeraldine to emeraldine at the negative electrode. The internal redox reactions of PANi of different oxidation states in the electrodes as a result of incomplete redox of PANi during cell operation may also produce potential shifts that reduce the overall cell voltage. The major advantage of PANi–PANi cells, namely the ease of cell assembly by means of *in situ* electrode formation, is mostly offset by the self discharge problem of the PANi electrodes.

References

[1] A. G. MacDiarmid, S.-L. Mu, N. L. D. Somasiri and W. Wu, *Mol. Cryst. Liq. Cryst.* **121** (1985) 187.
[2] A. Kitani, M. Kaya and K. Sasaki, *J. Electrochemical Soc.* **133** (1986) 1069.
[3] A. G. MacDiarmid, L. S. Yang, W. S. Huang and B. D. Humphrey, *Synth. Met.* **18** (1987) 393.
[4] K. Okabayashi, F. Goto, K. Abe and T. Yoshida, *ibid* **18** (1987) 365.
[5] F. Goto, K. Abe, K. Okabayashi, T. Yoshida and H. Morimoto, *J. Power Sources* **20** (1987) 273.
[6] T. Nakajima and T. Kawagoe, *Synth. Met.* **28** (1989) C629.
[7] M. Mizumoto, N. Namba, S. Nishimura, H. Miyadera, M. Koseki and Y. Kobayashi, *ibid* **28** (1989) C639.
[8] E. Genies, P. Hany and Ch. Santier, *ibid* **28** (1989) C647.
[9] T. Osaka, S. Ogano, K. Naoi and N. Oyama, *J. Electrochemical Soc* **136** (1989) 306.
[10] T. Matsunaga, H. Daifuku, T. Nakajima and T. Kawagoe, *Polymers for Advanced Technologies* **1** (1990) 33.
[11] N. Li, J. Y. Lee and L. H. Ong, *J. Appl. Electrochem.* **22** (1992) 512.
[12] J. Y. Lee, L. H. Ong and G. K. Chuah, *ibid* **22** (1992) 738.
[13] E. M. Genies and C. Tsintavis, *J. Electroanal. Chem.* **200** (1986) 127.
[14] J. P. Travers, F. Genoud, C. Menardo and M. Nechtschein, *Synth. Met.* **35** (1990) 159.
[15] L. -S. Yang, Z. -Q. Shan and Y. -D. Liu, *J. Power Sources* **34** (1991) 141.
[16] E. M. Genies, A. Boyle, M. Lapkowski and C. Tsintavis, *Synth. Met.* **36** (1990) 139.
[17] J. -C. LaCrox and A. F. Diaz, *J. Electrochemical Soc.* **135** (1988) 1457.
[18] L. Wang, X. Jing and F. Wang, *Synth. Met* **41–43** (1991) 685.
[19] K. Shinozaki, A. Kabumoto, H. Sato, K. Watanabe, H. Umemura and S. Tanemura, *Synth. Met.* **38** (1990) 135.
[20] J. G. Masters, Y. Sun, A. G. MacDiarmid and A. J. Epstein, *ibid* **41–43** (1991) 715.
[21] R. P. McCall, J. M. Ginder, J. M. Leng, H. Y. Ye, S. K. Manohar, J. G. Masters, G. E. Asturias, A. G. MacDiarmid and A. J. Epsteins, *Phys. Rev. B* **41** (1990) 5202.

[22] A. G. MacDiarmid, S. K. Manohar, J. G. Masters, Y. Sun, H. Weiss and A. J. Epstein, *Synth. Met.* **41–43** (1991) 621.
[23] Y. Cao, *ibid* **35** (1990) 319.
[24] P. Snauwaert, R. Lazzaroni, J. Riga, J. J. Verbist and D. Gonbeau, *J. Chem. Phys.* **92** (1990) 2187.
[25] W. S. Huang, B. D. Humphrey and A. G. MacDiarmid, *J. Chem. Soc. Faraday Trans. I* **82** (1986) 2385.
[26] C. Q. Cui, L. H. Ong, T. C. Tan and J. Y. Lee, *J. Electroanal. Chem.*, **346** (1993) 477.
[27] B. E. Conway, *J. electrochemical Soc.* **138** (1991) 1539.