Characterization of Poly(Indole-5-Carboxylic Acid) in Aqueous Rechargeable Cells

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ABSTRACT: Self-doped poly(indole-5-carboxylic acid) (P5CO$_2$H) is electrodeposited from acetonitrile containing 0.1M LiClO$_4$ as electrolyte and characterized by UV–vis, IR, cyclic voltammetry, and scanning electron microscopy techniques. The polymer is evaluated as a cathode active material together with a Zn anode in rechargeable cells containing 1M ZnSO$_4$ at pH 5. The cell shows an open circuit voltage of 1.36 V and a specific capacity of 67 Ah kg^{-1}. The ac impedance study shows a predominant diffusion mechanism. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 917–922, 2005

Key words: conducting polymer batteries; conducting polymers; poly (indole-5-carboxylic acid); self-doped polymer

INTRODUCTION

The use of conducting polymers in plastic batteries is the most popular application.[1–3] Conducting polymer batteries are rechargeable. In comparison to ordinary batteries, they offer advantages such as light weight, high energy and power densities, and the absence of electrode dissolution. The energy storage in conducting polymer-based batteries is due to a simple electrochemical doping-dedoping redox process. In principle, there can be six possible types of batteries that use conducting polymers for either positive or negative electrodes or both, as shown below.[4,5]

Type I: p-conducting polymer/electrolyte/Li
Type II: p-conducting polymer/electrolyte/n-conducting polymer
Type III: p-(high-doped)-conducting polymer/electrolyte/p-(low-doped)-conducting polymer
Type IV: n-(low-doped)-conducting polymer/electrolyte/n-(high-doped)-conducting polymer
Type V: Metal oxide or sulfide/electrolyte/n-conducting polymer
Type VI: undoped conducting polymer/electrolyte/Li

Of the six types, Type I is the most commonly studied configuration. This is because a high open-circuit potential is expected for lithium-based batteries. Extensive studies have been made on the characterization of rechargeable cells based on polyaniline, polypyrrole, and polythiophene.[5–7] Recently, we evaluated the performance of cells using poly(N-methylaniline), its sulfonated analogue, polyisothianaphthene, and poly(o-phenylenediamine) as cathode active materials.[8–10]

Poly(indole-5-carboxylic acid) (P5CO$_2$H) is an interesting conducting polymer because, depending on the pH of the solution, it can be self-doped.[11] Poly-3-(2-ethanaesulfonate)thiophene and poly-3-(4-butanesulfonate)thiophene were the first self-doped polymers reported in literature.[12,13] Such self-doped polymers possess an anionic dopant ion (SO$_3^-$ or COO$^-$) covalently attached to the polymer backbone, forcing predominant cation movement during the doping/dedoping process. Self-doped polymers are endowed with several unique properties.[14,15] They can have fast redox kinetics due to the absence of the need for the diffusion of an external dopant into the polymer matrix. Although there have been some reports on the synthesis and characterization of P5CO$_2$H,[16–18] there are no studies on the applications of this polymer except in a micro pH sensor.[11]

The application of the self-doped P5CO$_2$H as an electrode material in rechargeable cells is expected to have certain definite advantages compared to the use of the conventional p-doped conducting polymers. It is possible to assemble a Type VI battery with P5CO$_2$H, whereas the conventional p-doped polymers are used in Type I cells. In Type VI, the charging and discharging processes involve mere transfer of ions from one electrode to the other and, as a result, the electrolyte volume actually required becomes negligibly small.[2–5] In fact, very thin ionically conducting membranes may be used to separate the electrodes and thus, in principle, higher specific energies and energy densities are attainable. Another important ad-

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vantage of P5CO$_2$H is that it remains quite electroactive at pH 5 and, hence, can be a better alternative to polyaniline in the construction of aqueous rechargeable cells. This study aims to characterize P5CO$_2$H as a cathode active material in aqueous rechargeable cells. The synthesis and also the spectral, electrochemical, and morphological characterization of the polymer are briefly described.

EXPERIMENTAL

Indole-5-carboxylic acid (Acros), lithium perchlorate (Acros), and zinc sulfate (Ranbaxy) were used as received. Acetonitrile (Merck) was purified by ordinary distillation, and hot molecular sieves were added to remove the residual water. Aqueous solutions were prepared with double-distilled water. A conventional, single-compartment, three-electrode cell assembly was used to perform electrochemical experiments. For cyclic voltammetry measurements, the polymer was directly electrodeposited on a Pt plate (0.14 cm^2) in acetonitrile. The reference electrode was an Ag wire, and the counter electrode was a large Pt foil (2 cm^2). For the testing of assembled cells, the polymer was electrodeposited on a carbon substrate (5.2 cm^2), and an amalgamated Zn plate was used as the anode.

The electrochemical experiments were performed with an EG and G, PAR potentiostat/galvanostat (model 263 A). Impedance studies were carried out with an EG and G, PAR (Model 6310) electrochemical impedance analyzer. The UV–vis and IR spectral data were recorded with Jasco (model 7800 and model 410) spectrophotometers. Scanning electron micrographs (Hitachi model 450) were obtained for a thin film of the polymer electrodeposited on indium-tin-oxide (ITO) substrates.

RESULTS AND DISCUSSION

Synthesis and characterization

Indole-5-carboxylic acid was electropolymerized in acetonitrile containing 2×10^{-2} M of monomer and $0.1M$ LiClO$_4$. The potentiodynamic curve recorded for the oxidation of the monomer at a Pt electrode showed a peak at 1.4 V versus Ag wire. A constant potential of 1.0 V was necessary for the electropolymerization. The potentiostatic method was used to collect bulk samples of the polymer for further characterizations, like two-probe conductivity, IR, and SEM. For studying the redox properties of P5CO$_2$H, thin films were obtained by the cyclic voltammetry method (Fig. 1). A uniform film of green color was obtained after about 30 cycles in the potential range between -0.2 and 1.2 V.

The two-probe conductivity of the polymer was measured to be 3.16×10^{-3} S cm^{-1}. Figure 2a shows the IR spectrum of the polymer. The band at 1680
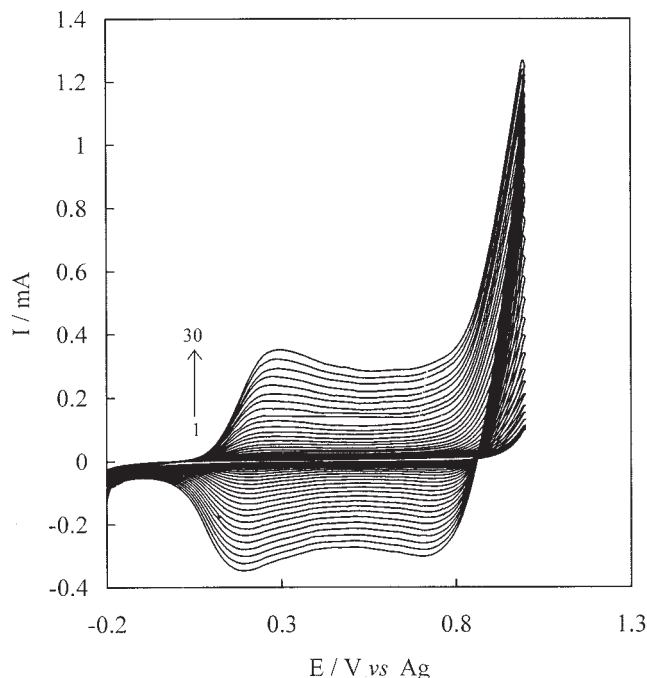

Figure 1 Cyclic voltammetric growth of P5CO$_2$H on a Pt electrode (0.14 cm^2) in acetonitrile containing 2×10^{-2} M monomer and $0.1M$ LiClO$_4$. The numbers in the figure represent the cycle number. Scan rate: 20 mV s^{-1}.

cm^{-1} is due to the C=O stretch of the carboxylic acid side group. The broad band at 3400 cm^{-1} due to –OH stretch of the carboxylic acid can also be seen. The important observation is the absence of the characteristic bands at 1080 cm^{-1} and 928 cm^{-1} for the perchlorate dopant. This shows that the oxidized polymer backbone is charge compensated by the covalently bound carboxylate anions, thus confirming the self-doping mechanism. The scanning electron micrograph of the electrochemically prepared P5CO$_2$H is shown in Figure 3. The polymer has an irregular morphology with grains of various sizes and shapes. The micrograph taken at a higher magnification shows a porous structure.

The cyclic voltammograms at various sweep rates were recorded in acetonitrile containing $0.1M$ LiClO$_4$ (Fig. 4). The appearance of two redox couples is similar to that reported in literature by various authors.[16,19,20] Mackintosh and Mount[16] assigned the first redox process observed in acetonitrile containing LiClO$_4$ to a one-electron transfer involving the trimer of indole and the second redox process to the polymer. Evidence for the indole trimer was presented from the mass and NMR spectroscopic studies. Zotti and coworkers[19] and Talbi and colleagues[20] made independent studies in acidic aqueous solutions at various pH values. They assigned the first pH independent redox process to a one-electron transfer involving the doping of the polymer. The pH dependent second process was attributed to oxidation and deprotonation to give the fully oxidized polymer.
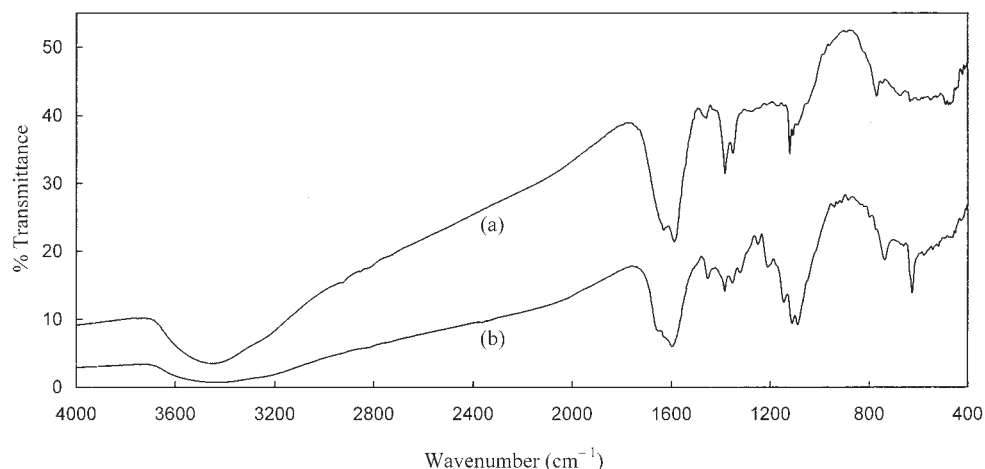
Figure 2 FT-IR spectrum of electrochemically prepared (a) P5CO$_2$H and (b) polyindole.

It should be noted that the above studies have not taken into account the self-doping nature of the polymer. P5CO$_2$H was reported to be a self-doped polymer.[11] Pickup[21] has demonstrated the self-doping in poly-(3-methylpyrrole-4-carboxylic acid) (poly-MPC) by electrostatically binding the cationic complexes, such as methyl viologen (MV^{2+}) and Co(bpy)$_3^{2+}$, to the carboxylic group of the polymer. When poly-MPC was immersed in 2×10^{-4} M Co(bpy)$_3$ (ClO$_4$)$_2$ solution for 5 min and subsequently transferred to 0.01M NaClO$_4$ solution, the cyclic voltammogram of the polymer showed the redox process corresponding to the Co(bpy)$_3^{2+}$ cationic complex in addition to the usual poly-MPC redox process.
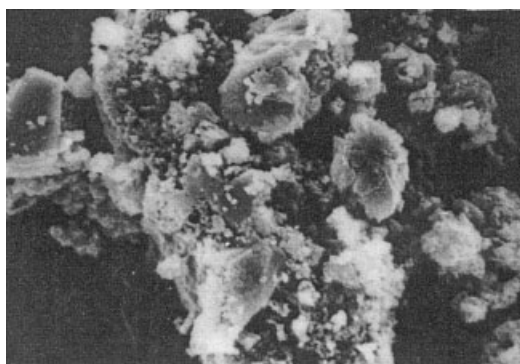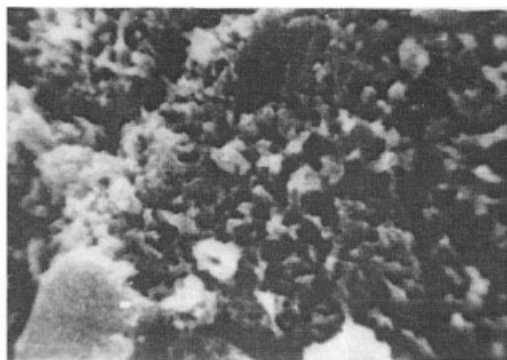
Figure 3 Scanning electron micrographs of P5CO$_2$H film electrodeposited on ITO substrate at different magnifications.
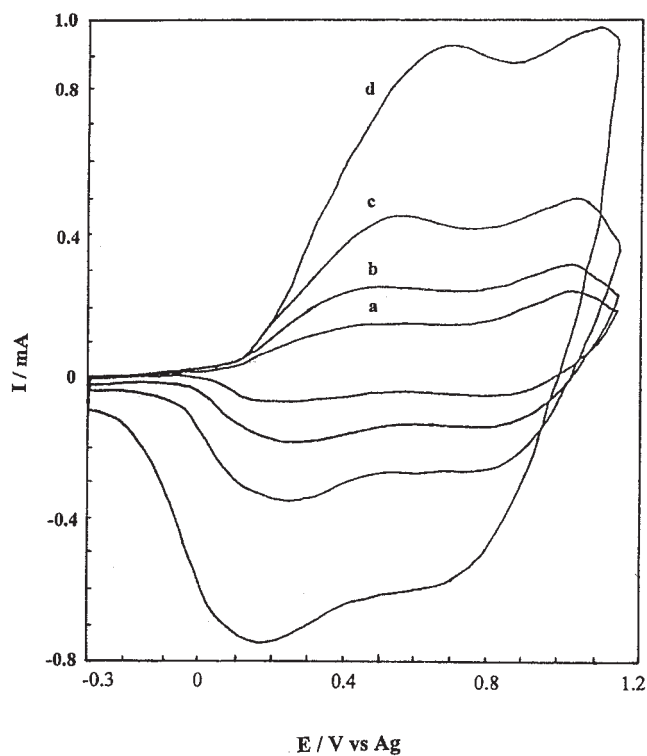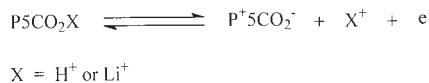

Figure 4 Cyclic voltammograms of P5CO$_2$H in acetonitrile containing 0.1M LiClO$_4$. Scan rate: (a) 5 mV s^{-1}, (b) 10 mV s^{-1}, (c) 20 mV s^{-1}, and (d) 50 mV s^{-1}.

$$P5CO_2X \rightleftarrows P^+5CO_2^- + X^+ + e$$

$$X = H^+ \text{ or } Li^+$$

Scheme 1 Redox reaction in $P5CO_2H$.

The IR data in the present study clearly demonstrate the self-doping mechanism in $P5CO_2H$. There are no bands observed at 1080 cm^{-1} and 928 cm^{-1} for perchlorate dopant in the oxidized $P5CO_2H$. The perchlorate bands are clearly observed in the case of polyindole, where the self-doping mechanism cannot be operative (Fig. 2b). The redox mechanisms suggested by both Zotti and colleagues[19] and Talbi and coworkers[20] were evolved in acidic solutions at pH < 3. The present data obtained in acetonitrile are not sufficient to prove the formation of the trimer species (first redox process). Considering the self-doping nature of $P5CO_2H$, the second redox process is inferred to involve the exchange of the cation between the oxidized and reduced forms of the polymer, as shown in Scheme 1. The charge-discharge characteristics of $P5CO_2H$ are evaluated only in the potential range of the second redox process.

$P5CO_2H$ is electrochromic in that the film becomes green in the oxidized state and yellow in the reduced state and the color change is stable and reversible for several cycles. Figure 5 shows the *in situ* optical absorption spectra recorded for the polymer coated on ITO electrode in the background electrolyte solution of acetonitrile containing $0.1M$ $LiClO_4$. The increase in
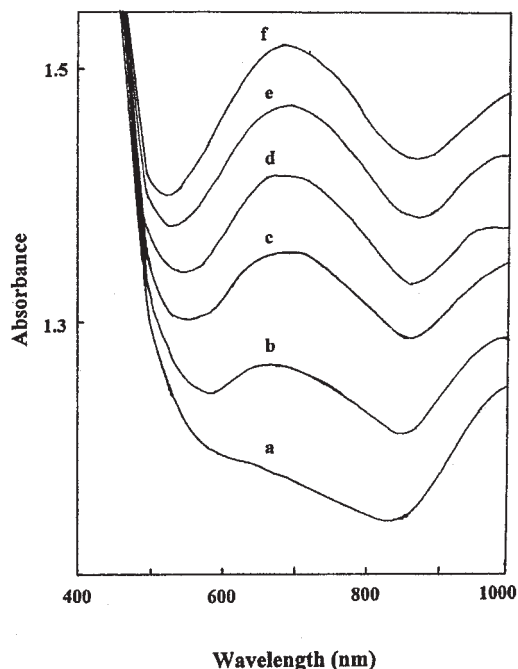

Figure 6 Optical absorption spectrum of electrochemically deposited $P5CO_2H$ film on ITO glass electrode. Inset: showing the band gap of the $P5CO_2H$ film. a = 2.303 A/d, where A = absorbance, d = film thickness.

the intensity of the peak at 670 nm with increase in potential from 0.4 V to 0.8 V clearly demonstrates the change in the state of the color of the film. The band gap energy of the polymer was calculated from the electronic spectral data obtained for the dry film coated on the ITO substrate. The substrate absorption, if any, was corrected by introducing an uncoated substrate of the same size as the reference. The absorption coefficient α was estimated by using the relation $\alpha = (2.303 A) / d$ where A is the absorbance and d is the thickness of the polymer coating. The relationship between α and the energy gap is given by[22] $\alpha = (h\nu - E_g)^{1/2}$ where E_g is the energy gap and $h\nu$ is the radiation energy. A plot of α^2 versus $h\nu$ gives an intercept on the energy axis, which corresponds to the energy band gap. In the present work, the E_g value is estimated to be 2.4 eV (Fig. 6).

Application of $P5CO_2H$ in rechargeable batteries

The following describes the results obtained on the charge-discharge of an assembled aqueous cell with $P5CO_2H$ as cathode, Zn as anode, and $1M$ $ZnSO_4$ as electrolyte at pH 5. The polymer was deposited on a carbon substrate (5.2 cm^2) from acetonitrile containing 2×10^{-2} M of monomer and $0.1M$ $LiClO_4$ by applying

Figure 5 *In situ* optical absorption spectra of $P5CO_2H$ coated on ITO substrate at various applied potentials of (a) 0.3 V, (b) 0.4 V, (c) 0.5 V, (d) 0.6 V, (e) 0.7 V, and (f) 0.8 V versus Ag.
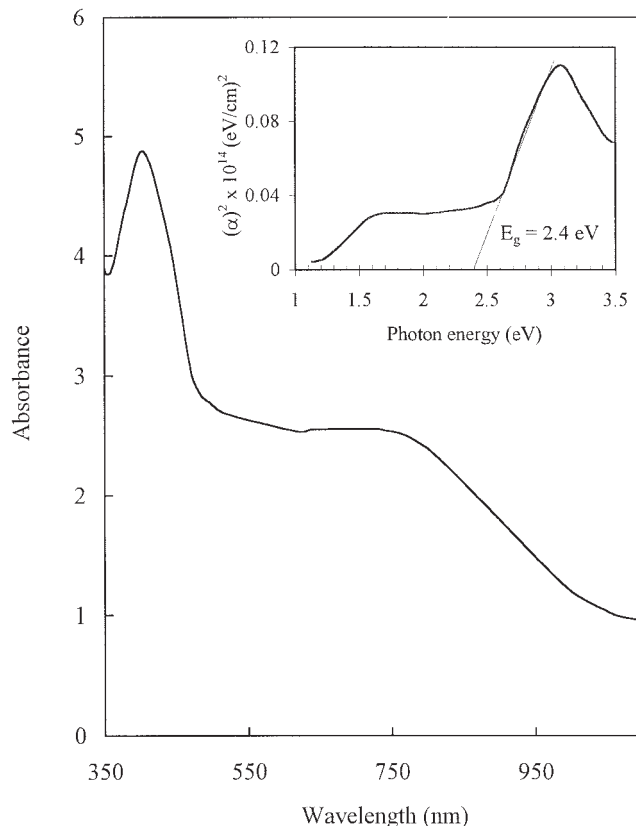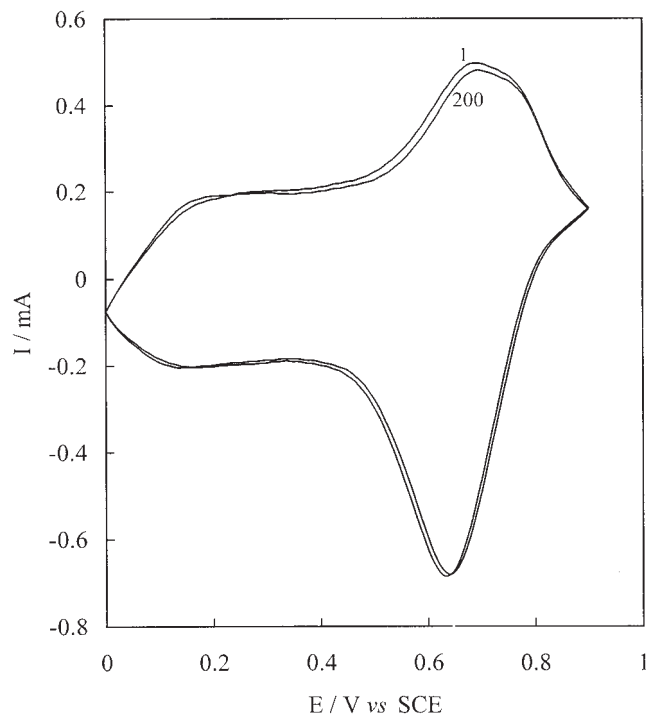
Figure 7 Redox stability of P5CO$_2$H film (Pt = 0.14 cm^2) in aqueous electrolyte of 1M ZnSO$_4$ at pH 5. The numbers in the figure denote the cycle number. Scan rate: 20 mV s^{-1}.

Figure 9 Charge-discharge curves of the cell Zn/1M ZnSO$_4$ (pH 5) / P5CO$_2$H at various current ratings.

a constant potential of 1 V versus Ag wire for a period of 50 min. The deposit was then transferred to 1M ZnSO$_4$ at pH 5 to fix the redox range. Stable redox
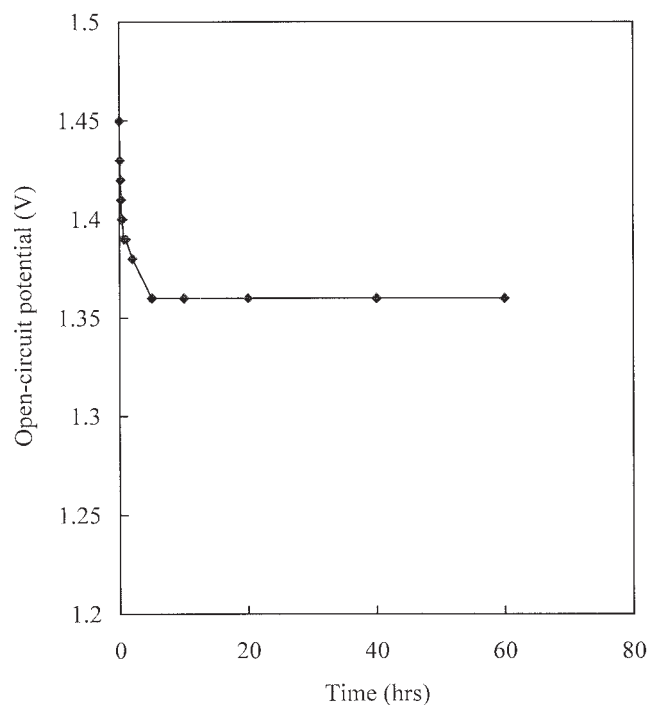
behavior was observed for over 200 cycles (Fig. 7). The cell Zn/1M ZnSO$_4$ (pH 5) / P5CO$_2$H was charged to 1.5 V, and the self-discharging was monitored. The cell potential gradually decreased to about 1.36 V in about 5 h of standing, and thereafter it remained unchanged (Fig. 8). The charge-discharge experiments were carried out in the potential range between 0.7 V and 1.5 V versus Zn (second redox process) at three different current ratings of 1, 1.5, and 2 mA and the typical curves are shown in Figure 9. At each current rating,

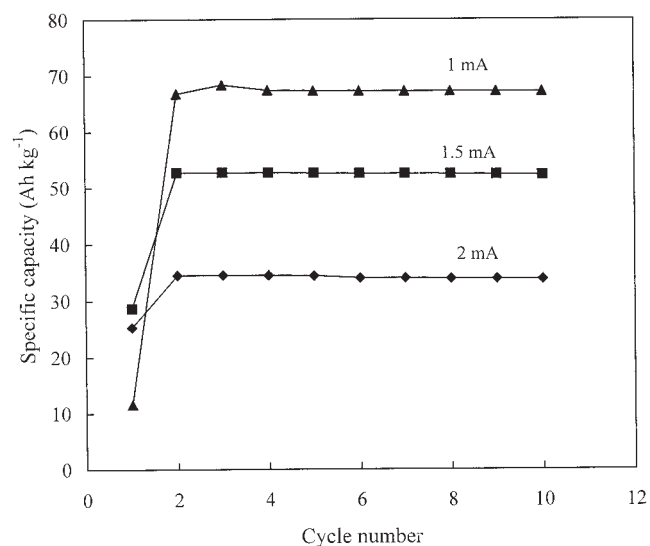**Figure 8** Variation of open-circuit potential of the cell Zn/1M ZnSO$_4$ (pH 5) / P5CO$_2$H against time.

Figure 10 Variation of specific capacity of the cell Zn/1M ZnSO$_4$ (pH 5) / P5CO$_2$H with repeated charge-discharge cycling at various current ratings.
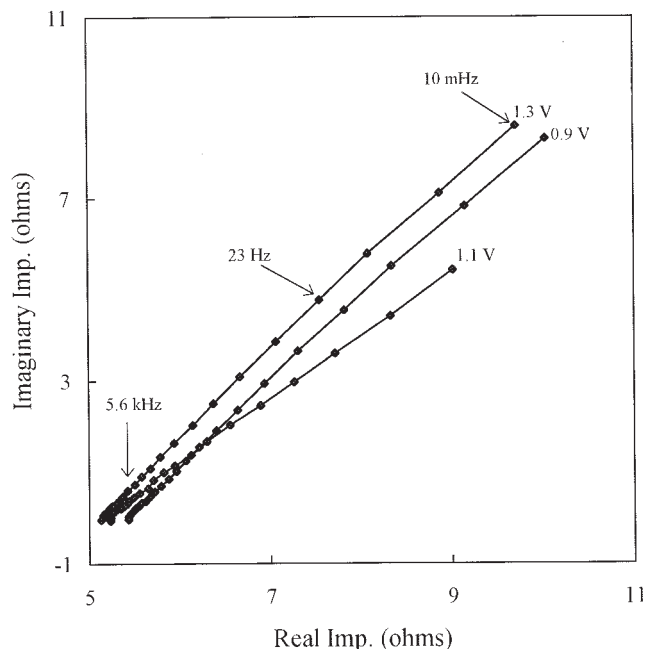
Figure 11 Impedance spectra of the cell $Zn/1M$ $ZnSO_4$ (pH 5) / $P5CO_2H$ at various applied dc potentials in the frequency range of 10 mHz to 100 kHz.

the cell was charged and discharged for at least ten cycles to check the recyclability and stability. Based on the weight of the charged polymer (22 mg), the average specific capacity was calculated to be 34 Ah kg^{-1} at 2 mA, 52 Ah kg^{-1} at 1.5 mA, and 67 Ah kg^{-1} at 1 mA. The specific capacity showed very little change with increasing the number of discharge cycles except for the first cycle (Fig. 10).

The impedance of the cell was measured at various dc applied potentials in the frequency range between 10 mHz and 100 KHz. The impedance plots are shown in Figure 11. The results obtained in the potential range between 0 and 0.7 V versus Zn are highly scattered (plots not given). This region corresponds to the first redox reaction and is not relevant to the study. In the potential range between 0.9 and 1.3 V corresponding to the polymer redox reaction, the plots of imaginary impedance versus real impedance show good correlation. The straight lines inclining at an angle of $45°$ obtained in this potential range are inferred to be due to the diffusion of cations away from the polymer electrode. The absence of a semicircle at the high frequency region indicates that the charge transfer reaction is so fast that the diffusion of the cation is playing a predominant role.

CONCLUSIONS

The electropolymerization of indole-5-carboxylic acid resulted in a self-doped polymer with a conductivity of 3.1×10^{-3} S cm^{-1}. The polymer was characterized for its structure, morphology, and redox stability. The energy gap was calculated to be 2.4 eV. The cell $Zn/1M$ $ZnSO_4$ / $P5CO_2H$ showed an open-circuit potential of 1.36 V and a specific capacity of 67 Ah kg^{-1} at 1 mA. The impendence data suggested diffusion of the cation as the rate-limiting process.

References

1. Nigrey, P. J. Jr.; MacInnes, D.; Nairns, D. P.; Macdiarmid, A. G. J Electrochem Soc 1981, 128, 1651.
2. Scrosati, B, Ed. Applications of Electroactive Polymers; Chapman & Hall: London, 1993.
3. Chilton, J. A.; Goosey, M. T., Eds. Special Polymers for Electronics and Optoelectronics; Chapman & Hall: New York, 1995.
4. MacInnes, D. Jr.; Druy, M. A.; Nigrey, P. J. J Chem Soc Chem Commun 1981, 317.
5. Novak, P.; Muller, K.; Santhanam, K. S. V.; Haas, O. Chem Rev 1997, 97, 207.
6. Morishita, M.; Abe, S.; Nojiri, A.; Shinozaki, K. Electrical Engineering in Japan 1987, 107, 177.
7. Santhanam, K. S. V.; Gupta, N. Trends Polym Sci 1993, 1, 107.
8. Sivakumar, R.; Saraswathi, R. J Power Sources 2002, 104, 226.
9. Sivakkumar, S. R.; Saraswathi, R. J Power Sources 2004, 137, 322.
10. Sivakkumar, S. R.; Saraswathi, R. J Appl Electrochem 2004, 34, 1147.
11. Bartlett, P. N.; Farrington, J. Bull Electrochem 1992, 8, 208.
12. Jen, K. Y.; Obodi, R.; Elsenbaumer, R. L. Polym Mater Sci Eng 1985, 53, 79.
13. Patil, A. O.; Ikenoue, Y.; Besescu, N.; Calaneri, N.; Chen, J.; Wudl, F.; Heeger, A. J Synth Met 1987, 20, 151.
14. Ferraris, J. P.; Guerrero, D. J. In Handbook of Conducting Polymers; Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; Chapter 10.
15. Shinozaki, K.; Tomizuka, Y.; Nojiri, A. Jpn J Appl Phys 1984, 23, L892.
16. Mackintosh, J. G.; Mount, A. R. J Chem Soc Faraday Trans 1994, 90, 1121.
17. Mackintosh, J. G.; Redpath, C. R.; Jones, A. C.; Smith, P. R. R. L; Mount, A. R. J Electroanal Chem 1995, 388, 179.
18. Mackintosh, J. G.; Redpath, C. R.; Jones, A. C.; Smith, P. R. R. L.; Reed, D.; Mount, A. R. J Electroanal Chem 1994, 375, 163.
19. Zotti, G.; Zecchin, S.; Schiavon, G. Chem Mater 1994, 6, 1742.
20. Talbi, H.; Billaud, D.; Louarn, G.; Pron, A. Spectrochim Acta Part A 2001, 57, 423.
21. Pickup, P. G. J Electroanal Chem 1987, 225, 273.
22. Santhanam, K. S. V.; Sharon, M. Photoelectrochemical Solar Cells; Elsevier: New York, 1998; p 174.