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Application of poly(*o*-phenylenediamine) in rechargeable cells

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Abstract

The electrochemical synthesis of poly(*o*-phenylenediamine) (PoPD) from an aqueous medium was suitably modified by controlling the switching potential to enhance the growth of the polymer. The charge–discharge data for the cell Zn/1 M $ZnSO_4$ (pH 4)/PoPD are presented. The polymer was modified by incorporating Pt microparticles into its matrix during electropolymerization. The PoPD-Pt composite electrode was also characterized as a cathode active material in aqueous cells.

1. Introduction

The increase in demand for high energy batteries necessitates work on a variety of electrode materials, especially on cathode materials. Among these, conducting organic polymer cathodes have the advantages of light weight, flexibility, ease of synthesis and absence of electrode deformation during charging and discharging over the conventional metal electrodes. A number of conducting polymers have been tested for battery applications [1–4]. Polyaniline is the most studied conducting polymer for this application. However, substituted polyanilines have been little studied. Recently, we have characterized poly(*N*-methylaniline) and its sulphonated analogue as cathode materials in rechargeable cells [5]. Other work has been reported on poly(*o*-methylaniline) [6].

There have been a number of reports on the synthesis, structural properties and applications of poly(*o*-phenylenediamine) (PoPD). The electropolymerization of *o*-phenylenediamine was reported by several authors [7–11]. The structure of the PoPD is essentially different from polyaniline and its derivatives in that PoPD is a ladder polymer with phenazine rings [8]. PoPD shows only one redox process at all pH values instead of two redox processes as in polyaniline [12, 13]. PoPD has been tested for applications in humidity sensors [14], biosensors [15], corrosion inhibition [16] and electrocatalysis [17–20]. A composite electrode of PoPD incorporated with Pt microparticles has been tested for the electrocatalytic reduction of hydrogen peroxide [19] and oxidation of methanol [20]. There has been no report on the application of PoPD as a cathode active material in rechargeable batteries. The ladder structure of poly(*o*-phenylenediamine) (PoPD) is expected to have a strong backbone that can tolerate over-oxidation of the polymer during charging better than polyaniline. Also electron transfer will be easier through its extended π-conjugation. This paper presents a modified electrochemical procedure for the synthesis of high quality PoPD film and its application in aqueous rechargeable cells. The result obtained on the use of Pt microparticle incorporated PoPD film as cathode in aqueous cells is discussed.

2. Experimental details

o-Phenylenediamine (s.d. fine) was used after recrystallization from hot water [21]. AR grade sodium sulphate (SRL), zinc sulphate (Ranbaxy), sulphuric acid (s.d. fine) and chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) (SRL) were used as received. Double-distilled water was used to prepare aqueous solutions.

A one-compartment cell with provision for three electrodes was used. The working electrode was either a Pt foil (geometric area = 0.5 cm^2) or a carbon rod (0.69 cm^2) or an indium-tin oxide (ITO) (1 cm^2) coated glass electrode. The reference electrode was either a saturated calomel electrode (SCE) or an amalgamated zinc plate and the counter electrode was a Pt foil.

The electrochemical experiments were performed with an EG&G, PAR Potentiostat/Galvanostat (model 263 A). IR spectrum of the polymer sample was recorded with a Jasco (model 410) FT-IR spectrophotometer. The surface topographies of thin films of polymers were recorded using Shimadzu, SPM 9500 atomic force microscope.

3. Results and discussion

3.1. *PoPD growth and characterization*

The electrodeposition of PoPD was carried out from an aqueous electrolyte solution containing 5×10^{-2} M of monomer and 0.5 M Na_2SO_4 at pH 1. Concentrated H_2SO_4 was used to adjust the solution pH to 1. The oxidation potential of the monomer at a Pt electrode was observed to be at 0.6 V vs SCE. Initially, a constant potential of 0.6 V was applied to deposit the polymer. However, no film was obtained at the working electrode as the current drastically dropped to a very small value and the colour of the electrolyte solution changed to reddish brown, suggesting dissolution of the products. Increasing the deposition potential from 0.6 V to a higher value, up to 1 V did not yield any deposit. In a similar way, the use of a galvanostatic method also resulted in a rapid increase in the potential with no effective film deposition. Cyclic voltammetry technique was invariably used for the electrodeposition of PoPD [12, 13, 22, 23]. Therefore, in the present study, the growth of PoPD at Pt was followed by cycling between −0.3 and 1.2 V vs SCE at 50 mV s^{-1} (Figure 1). In the first cycle (inset in Figure 1), an oxidation peak with large anodic current appeared at 0.6 V. With increase in number of cycles, the anodic current at 0.6 V decreased significantly due to the electrode coverage with the newly formed polymer film. The growth was defined by only one redox couple ($E_p^a = -0.16\,V$, $E_p^c = -0.25\,V$). Similar growth patterns were observed on ITO and carbon substrates.

The anodic growth current on Pt attained a maximum of about 2 mA cm^{-2}, after which the current decreased. This was inferred to be due to simultaneous degradation of the film at such high switching potential of 1.2 V. The following experiment confirmed this. The switching potential was kept at 1.2 V for the first 20 cycles and at 1 V for the next 30 cycles. After 50 cycles, the switching potential was maintained at 0.6 V. By this procedure, the growth of the polymer film was sustained to almost double the thickness as compared to the film obtained earlier using a constant switching potential of 1.2 V.

There are only very few reports on the growth of PoPD [23–25]. Yano [23] proposed a mechanism for the electropolymerization of *o*-phenylenediamine. But, his linear 1,4-substituted benzenoid–quinonoid structure differed from the phenazine ring-based ladder structure of PoPD proposed by Dai et al. [25]. The electropolymerization of *o*-phenylenediamine was suggested to take place through EC mechanism [26]. The monomer was initially oxidized anodically to give the monocation radical, which then underwent chemical coupling to produce a dimer that could be further oxidized. The dication of the dimer could undergo either polymerization to produce a linear chain polymer or become cyclized to yield a ladder structure through the polymerization of the oxidized products. The PoPD film formation was reported to be a non-autocatalytic process and the polymerization mainly took place during the cathodic potential scan [24].

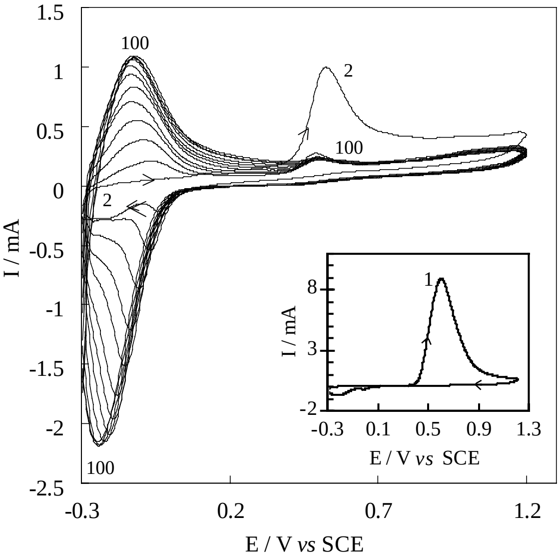
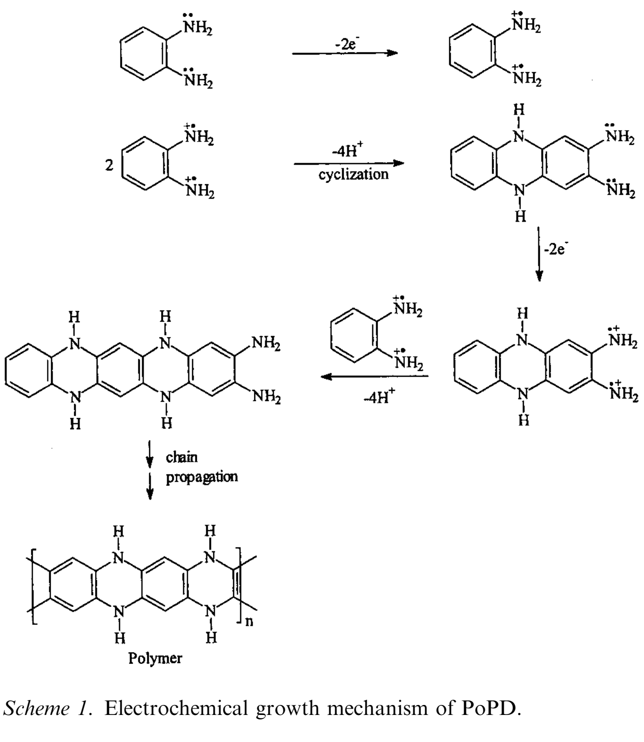


Fig. 1. Representative cyclic voltammograms for the growth of PoPD film from an electrolyte containing 5×10^{-2} M *o*-phenylenediamine and 0.5 M Na_2SO_4 (pH 1) at a Pt electrode (0.5 cm^2) (inset: first cycle). Scan rate: 50 mV s^{-1}. The numbers in the figure denote the cycle number.

In the present work, the FT-IR spectroscopic data were useful to identify whether, the PoPD was a linear or a ladder polymer. The IR data correlated very well with those reported in literature for PoPD by other authors [13, 27]. The important observation was the presence of a band at 840 cm^{-1}, which was assigned to 1,2,4,5-tetrasubstituted benzene ring [28]. In otherwords, PoPD is inferred to have a ladder structure made up of phenazine rings. The following mechanism is proposed for the electrochemical growth of PoPD (Scheme 1).



Scheme 1. Electrochemical growth mechanism of PoPD.

The two-probe conductivity of PoPD film coated on an ITO substrate was measured to be 1.2×10^{-4} S cm^{-1}. The band gap energy of the polymer was calculated to be 2 eV from the electronic spectral data. The PoPD polymer is neutral in both oxidized and reduced forms and protons are involved in the redox process [12, 17]. The insignificant participation of the dopant anion during oxidation [24] is responsible for the poor conductivity of the polymer. The redox peak currents decreased with increase in pH which was attributed to the decrease in the apparent rate of charge transport in the film [22]. In the present work, the cyclic voltammograms of the PoPD film deposited on both Pt and carbon substrates showed good redox characteristics up to pH 4 (Figure 2). The characteristics of the rechargeable cell with the polymer as cathode and zinc as anode have been studied in 1 M $ZnSO_4$ at pH 4.

3.2. *Charge–discharge behaviour*

PoPD was coated on a large area cylindrical carbon electrode (14.5 cm^2) as described earlier by cyclic voltammetry using the controlled switching potential method. A large area zinc sheet (15 cm^2), lightly amalgamated by dipping into 1 M $HgCl_2$ for 1 min, was used as the anode. The two electrodes were assembled in a cell containing aqueous electrolyte solution of 1 M $ZnSO_4$ at pH 4. The cell showed an instantaneous open circuit potential of 1.5 V, which sharply decreased to about 1.3 V in about 30 min of standing. Thereafter, it remained unchanged. The cell was discharged and then charged at three current ratings of 1, 0.6 and 0.3 mA. The charging potential was limited to 1.5 V and the discharging potential to 0.65 V. At each current rating, the charge–discharge curves were recorded atleast for 10 cycles. Figure 3 shows typical charge–discharge curves for the second cycle. Based on the weight of the discharged polymer (10 mg), the average specific capacity was calculated to be 48 Ah kg^{-1} at 1 mA, 69 Ah kg^{-1} at 0.6 mA and 123 Ah kg^{-1} at 0.3 mA. The specific capacity showed very little change with increasing number of discharge cycles (Figure 4). The cyclic voltammogram of the polymer recorded with zinc as the anode showed a 30% decrease in the redox capacity for about 500 cycles.

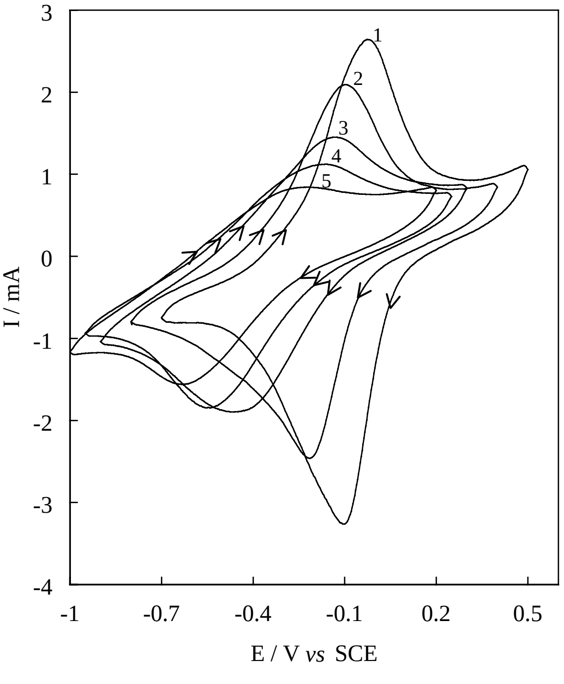


Fig. 2. Cyclic voltammograms of PoPD film deposited on carbon substrate in electrolyte containing H_2SO_4 + Na_2SO_4 (Total ionic strength is 1 M) at different pH. The numbers in the figure represent the value of pH. Scan rate: 50 mV s^{-1}.

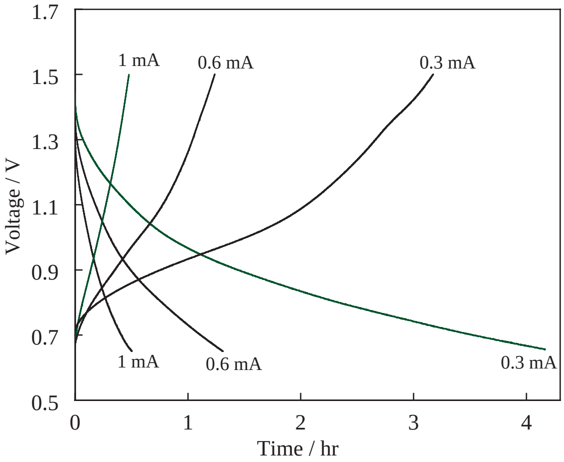


Fig. 3. Charge–discharge curves of the cell Zn/1 M $ZnSO_4$ (pH 4)/PoPD at various current ratings.

3.3. *Modification of PoPD for battery application*

The basic requirements for the use of a material as an electrode in rechargeable batteries are good conductivity, high electrochemical reversibility and stability in the electrochemical potential window available for the

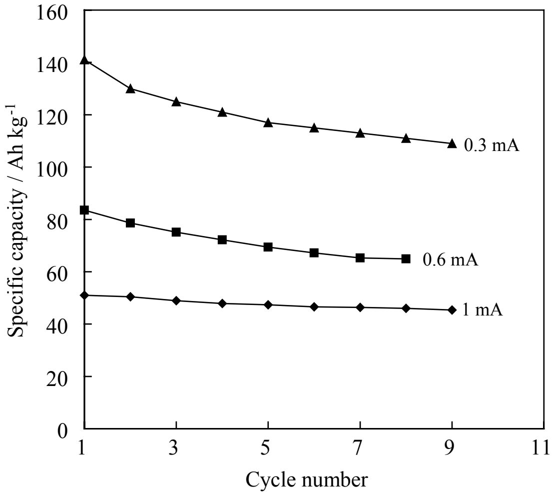


Fig. 4. Variation of specific capacity of the cell Zn/1 M $ZnSO_4$ (pH 4)/PoPD with cycle number at various current ratings.

charging and discharging of the cell. PoPD has good electrochemical stability and redox activity but its conductivity is rather poor (10^{-4} S cm^{-1}). Therefore, a fundamental improvement in the polymer film conductivity becomes essential to obtain better values of specific capacity. It has not been possible to improve the conductivity of PoPD by the usual changes in the concentrations of the monomer and electrolyte, synthesis method, temperature of polymerization and nature of dopant anion.

Metal microparticles electrodeposited into polymer-modified electrodes have recently received considerable attention for application in electrocatalysis. The main purpose for incorporating metallic particles into a polymer matrix is to increase the surface area of these materials and, thus, promote the catalytic efficiency. Pt dispersed conducting polymers have been found to activate various electrochemical reactions namely, reduction of protons [29–31], oxygen reduction [32–36], hydrogen oxidation [34, 37–39] and oxidation of small organic molecules such as methanol [30, 40–45]. Polyaniline films with dispersed Pt particles exhibited enhanced electrocatalytic activity towards such reactions as oxidation of ethylene glycol [46, 47] and formic acid [48, 49]. Pd incorporated poly(*N*,*N*-dimethyl aniline) showed good catalytic activity for the oxidation of formic acid [50]. The electrocatalytic reduction of H_2O_2 and oxidation of methanol on Pt microparticle dispersed PoPD film have been reported [19, 20]. However, very little attention (if any) has been paid to other than electrocatalytic properties of such metal dispersed polymer modified electrodes. In this study, platinum microparticles were incorporated into PoPD matrix during electropolymerization and the Pt dispersed PoPD film was characterized as a cathode active material in aqueous cells.

The PoPD-Pt composite electrode was prepared as follows. The electrolyte for the simultaneous deposition of polymer and Pt particles was an aqueous 0.5 M Na_2SO_4 solution containing 5×10^{-2} M of *o*-phenylenediamine and 2.4×10^{-3} M of chloroplatinicacid. The pH of the solution was adjusted to 1 by addition of H_2SO_4. Figure 5a shows the cyclic voltammograms recorded during the electrodeposition of PoPD on a carbon substrate. From this, the potential range for co-deposition of the polymer and Pt at a carbon substrate was fixed between –0.8 and 1.2 V vs SCE. The reduction of Pt^{4+} to Pt can be accomplished in the potential range between −0.2 and +0.2 V [51]. Figure 5b shows the cyclic voltammograms recorded during the co-deposition of PoPD and Pt at a carbon substrate. For the same number of cycles, the growth current for the composite film was about three times higher than that observed for the PoPD alone. The large cathodic current at −0.8 V

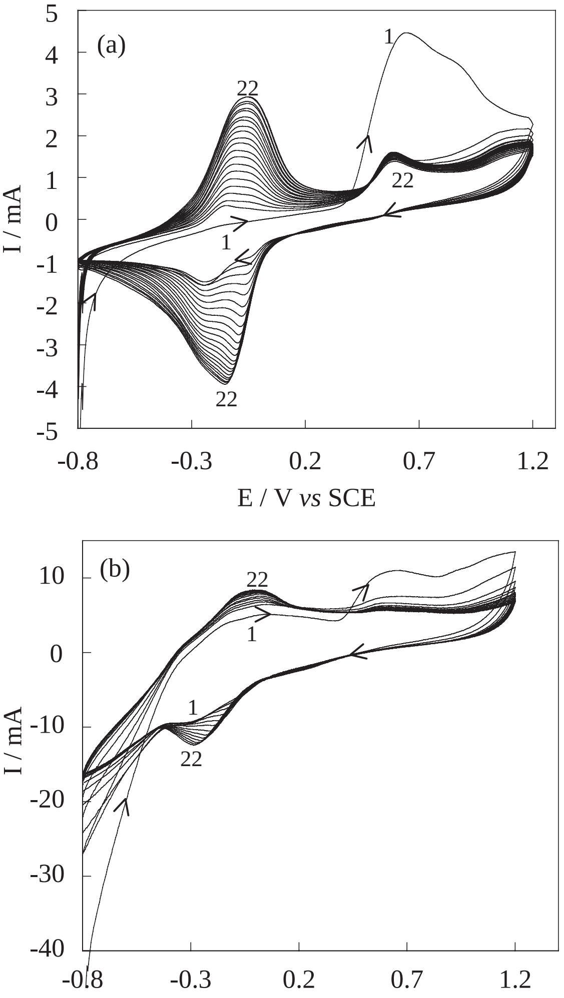


Fig. 5. Representative cyclic voltammograms for the growth of PoPD at a carbon electrode from an electrolyte containing (a) 5×10^{-2} M *o*-phenylenediamine and 0.5 M Na_2SO_4 (pH 1) and (b) 5×10^{-2} M *o*-phenylenediamine, 0.5 M Na_2SO_4 and 2.4×10^{-3} M $H_2PtCl_6{\cdot}6H_2O$ Scan rate: 50 mV s^{-1}.

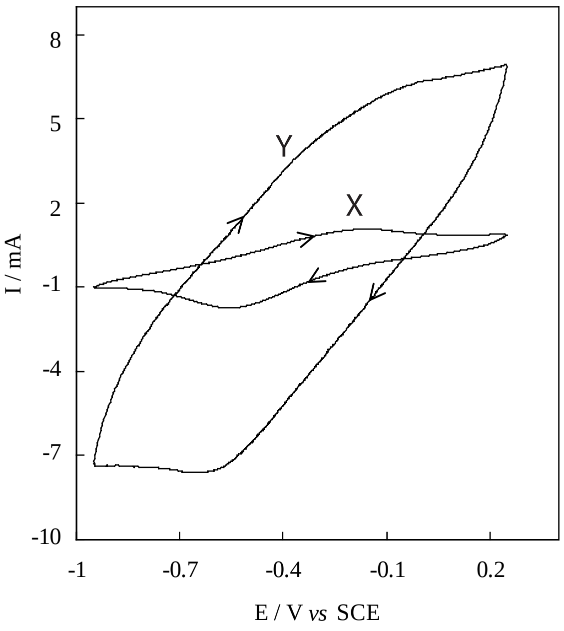


Fig. 6. Cyclic voltammograms at PoPD (*x*) and PoPD-Pt composite (*y*) in aqueous electrolyte containing H_2SO_4 + Na_2SO_4 (Total ionic strength is 1 M) at pH 4. Scan rate: 50 mV s^{-1}.

was due to the reduction of H^+ ions. The evolution of H_2 gas bubbles at the working electrode during the cathodic sweep to −0.8 V was visually observed. In Figure 6, the background cyclic voltammograms of the composite electrode are compared with those of the bare PoPD electrode at pH 4. The redox currents of the composite film were about four times higher than those of the PoPD film. The peak potentials were nearly the same for both the electrodes. The conductivity of the PoPD-Pt composite was measured to be 2.7×10^{-2} S cm^{-1}, which was about two orders of magnitude higher than PoPD itself (1.2×10^{-4} S cm^{-1}). In order to confirm the incorporation of the Pt particles into the PoPD matrix, the surface topography of the composite film was compared with that of the bare PoPD film (Figure 7). The surface of the PoPD was very smooth, whereas, Pt particles of size ranging between 100 and 500 nm were uniformly distributed in the PoPD-Pt composite film.

The performance of the cell assembled with PoPD-Pt composite electrode as cathode and Zn as anode was studied in 1 M $ZnSO_4$ at pH 4. The open circuit potential of the cell was stable at 1.24 V. Typical charge–discharge curves at three different current ratings were presented in Figure 8. The coulombic efficiency was nearly 100% at 1 mA. For about five cycles of testing, the specific capacity of the cell remained constant (Figure 9). The specific capacity was calculated to be 127 Ah kg^{-1} at 1 mA on the basis of the mass of the PoPD alone (10 mg) in the composite, since only PoPD was involved in the charge storage. A twofold increase in the specific capacity can be obtained by the use of Pt microparticles-dispersed PoPD cathode.

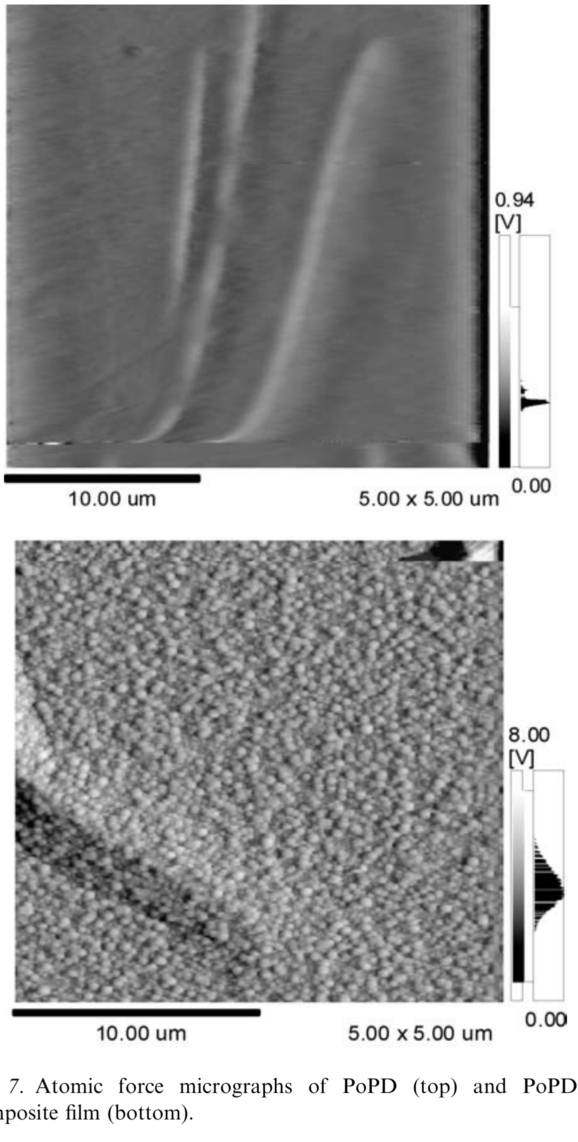


Fig. 7. Atomic force micrographs of PoPD (top) and PoPD-Pt composite film (bottom).

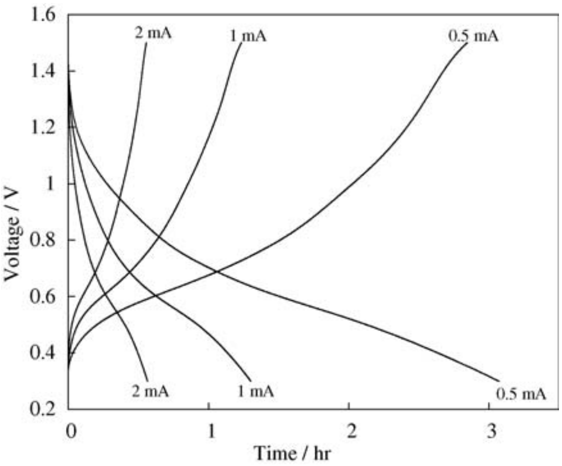


Fig. 8. Charge–discharge curves of the cell Zn/1 M $ZnSO_4$ (pH 4)/PoPD-Pt composite at various current ratings.

4. Conclusion

PoPD was grown electrochemically to a maximum growth current density of 4 mA cm^{-2} by controlling the switching potential during the cyclic voltammetric growth. The conductivity of the polymer film was 1.2×10^{-4} S cm^{-1} and the polymer band gap energy

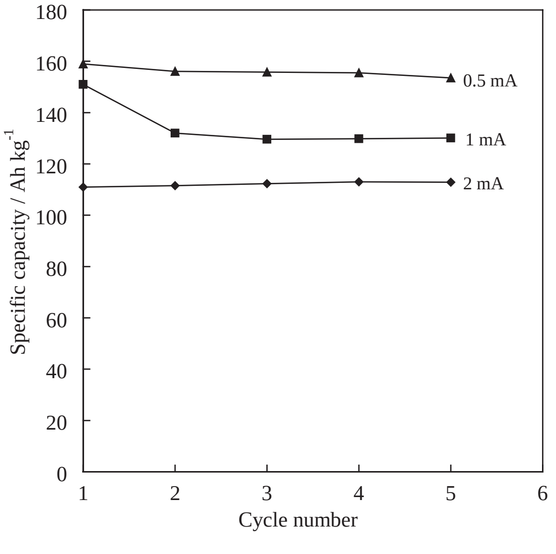


Fig. 9. Variation of specific capacity with the charge–discharge cycling of the cell Zn/1 M $ZnSO_4$ (pH 4)/PoPD-Pt composite at various current ratings.

was 2 eV. Modification of the polymer by incorporation of Pt microparticles enhanced the conductivity by about two orders of magnitude. The two cells assembled with PoPD and PoPD-Pt composite as cathode had specific capacity of 48 and 127 Ah kg^{-1} at a current rating of 1 mA respectively.

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