

Coatings of Poly-*p*-Aminophenol at Carbon Electrodes: Electrochemical Behavior

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Summary: Polymer coated carbon electrodes were prepared by reductive electro-polymerization of *p*-aminophenol in 1.0 M nitric acid. Polymer films thus formed were then investigated by voltammetric and electrochemical impedance spectroscopy. Impedance studies in 1.0 M nitric acid revealed that these coatings showed mixed behavior both resistive and capacitive.

Introduction

Modification of solid electrodes by polymerization of monomers continues to be focus of current research. This work relates to the study of poly-*p*-aminophenol coated electrodes designed for the production of hydroxylamine [1]. There are only a few reports in literature on reductive polymerization of *p*-aminophenol, except for AFM and SEM images and use of poly-*p*-aminophenol films on ITO and HOPG surfaces obtained by electro-reduction of *p*-aminophenol through potential cycling method [2]. Conducting polymers contain (π -electron backbones responsible for their unusual electronic properties such as electrical conductivity, low energy optical transitions, low ionization potential and high electron affinity. The extended (π -conjugated) system of the conducting polymers has single and double bonds alternating along the polymer chain. The higher values of the electrical conductivity obtained in such organic polymers have led to the name 'synthetic metals'. Many applications of conducting polymers in analytical chemistry and in biosensing devices have been reviewed [3-7].

Conducting polymers have widened the possibility of modifying the surfaces of conventional electrodes thereby imparting new and interesting properties. They find applications in electrocatalysis, separations, chromatography, and as membranes. They have opened up new technological possibilities in the design of chemical and biochemical sensors [8]. Presently, a large number of monomers are known that form conducting polymers based on

chemical or electrochemical preparation techniques. Such strong systems include substituted derivatives of hydrocarbons. The massive effort put into the basic research and development of conducting polymers is naturally related to hopes of feasible technical applications. One of the most promising ways to obtain high performance proton-conducting polymer electrolyte membranes is the use of hydrocarbon polymers for the polymer backbone. The discovery that it is possible to control the electrical conductivity of polymers over the range from insulating to metallic has led to substantial efforts to prepare conducting polymers for technological applications. Conducting polymers have also presented a strong fundamental scientific challenge which has been taken up by a diverse community of chemists, physicists, materials scientists, and theoreticians both in academia and in industry [9]. Electro-polymerization in a substantially aqueous solution was used to form thick (*e.g.* greater than 2 microns or 30 weight %) and thermally stable coatings of thermoplastic materials onto electrically conductive filler materials (*e.g.* rods, plates, fibers) [10]. Chemically modified electrodes exhibit unique behavior that can greatly benefit electrochemical sensing [11]. An amperometric biosensor for glucose, based on a novel polymeric matrix was prepared by electrochemical polymerization of *p*-aminophenol in the presence of glucose oxidase on platinum substrates in a potassium chloride solution at a potential of 0.6 V versus silver / silver chloride [12]. The electrochemical oxidation of *o*-aminophenol was

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studied by cyclic voltammetry on platinum and glassy carbon electrodes. Films formed on platinum exhibited a voltammetric response that was dependent on the final potential applied during the electro polymerization. Although a less electro-active film was obtained on platinum electrodes cycled at higher potentials, modified glassy carbon electrodes showed a well-defined redox response independently of the potential range used [13]. There are different studies related to impedance of polymers. Conducting poly(*o*-aminophenol) films deposited on platinum electrodes were studied by quartz crystal impedance [14]. Impedance spectroscopy was also used to study the effect of solution pH on the electrochemical behavior of poly-*o*-aminophenol modified electrodes [15]. The impedance response of electrochemically synthesized poly-*o*-toluidine films was measured by Presa *et al.* [16]. Use of measurement models was suggested as an intermediate step in the analysis of impedance data by Orazem *et al.* [17]. This work presents an insight into the electrochemical behaviour and properties of electro-reductively prepared poly-*p*-aminophenol.

Results and Discussion

Polarization Behavior of Coatings

Different electrodes modified with slow scan linear sweep voltammetry (at 0.5 mV/s and 6.5 mM *p*-aminophenol in 1.0 M nitric acid) and cyclic voltammetry (30 cycles) were used to compare their polarization behavior in nitric acid with that from bare carbon as shown in Fig. 1. While using different techniques for deposition, slow scan linear sweep voltammetry was found to give better deposition of *p*-aminophenol on carbon. Coatings deposited on carbon at various scan rates were compared by running polarization curves in nitric acid. A comparison of coatings obtained by linear sweep voltammetry was performed by cathodic reduction of nitric acid. Hydrogen evolution shifted toward more cathodic potentials at polymer coatings electrodeposited at slow scan rate (*e.g.* at 0.1 mV/s) than at higher scan rates like 0.5 and 10 mV/s, as evident from Fig. 2, indicating that polymerizing at very slow scan rates gives better coatings.

Impedance Spectroscopy and Simulation Results

Electrochemical impedance spectroscopy was used for investigating the electrochemical

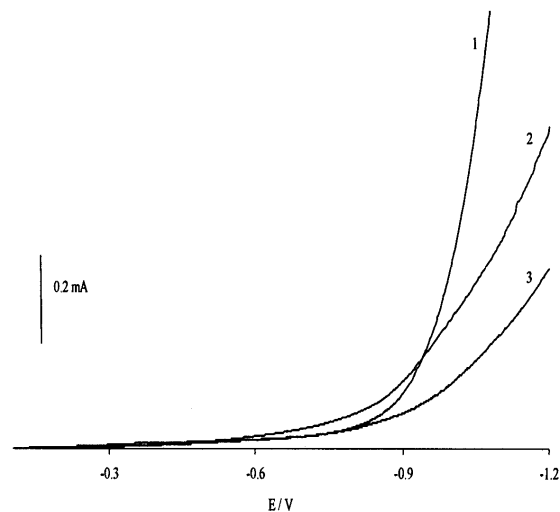


Fig. 1: Linear sweep voltammetric response in 1.0 M HNO₃ at [1] bare carbon, and at films of poly-*p*-aminophenol electrodeposited on carbon by [2] thirty successive cyclic voltammetric scans, and by [3] slow scan rate linear sweep voltammetry

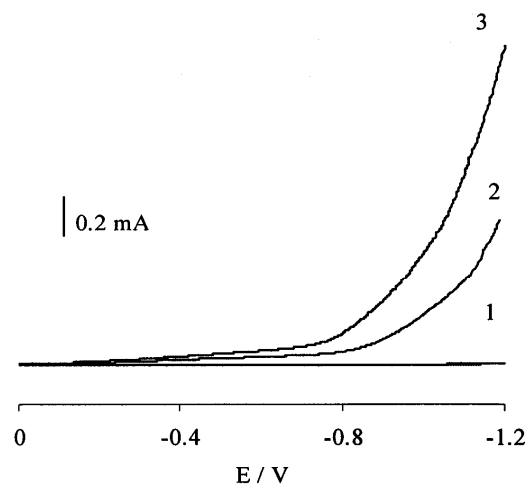


Fig. 2: Linear sweep voltammetric response in 1.0 M HNO₃ from coatings of poly-*p*-aminophenol electrodeposited by linear sweep voltammetry with scan rates: [1] 10, [2] 0.5 and [3] 0.1 mV/s

properties of poly-*p*-aminophenol coatings obtained by electro-polymerization of *p*-aminophenol, using constant potential electrolysis. Bode plot of impedance is given in Fig. 3; representing high

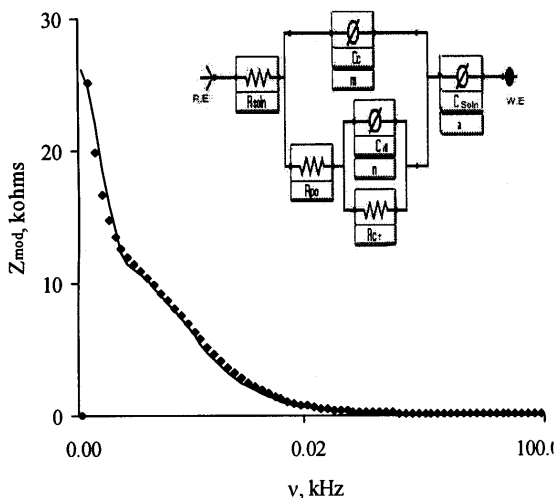


Fig. 3 Fit of impedance data in 1.0 M HNO₃ to equivalent model for poly-*p*-aminophenol films on carbon cathodes. Experimental (diamonds), equivalent model fit (line). Films were prepared by electro-deposition from 13.0 mM *p*-aminophenol solution in 1.0 M HNO₃

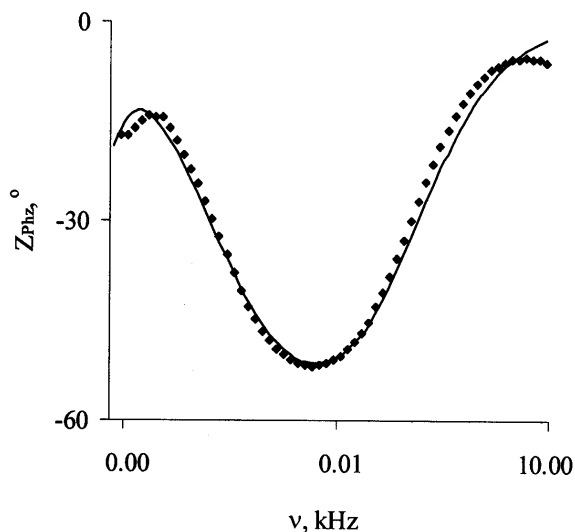


Fig. 4 Fit of phase angle data in 1.0 M HNO₃ to equivalent model for poly-*p*-aminophenol films on carbon cathodes. Experimental (diamonds), equivalent model fit (line). Films were prepared by electro-deposition from 13.0 mM *p*-aminophenol solution in 1.0 M HNO₃

impedance values (10-25 kohms) at lower frequencies, and impedance equal to zero at higher frequency of 100 kHz. Bode highest phase angle was observed to be 53° in Fig. 4 showing that coatings were not truly capacitive in nature, but exhibited both the conductive and capacitive behavior.

Simulation of impedance data was carried out to gain insight into electrochemical properties of polymer coatings by model given as inset in Fig. 3. Equivalent model gave the best visual fitting of the impedance, phase angle and Nyquist plot as given in Figs. 3, 4 and 5. R_{sol} represents the solution resistance having a value of 139.8 Ω, and R_{ct} and R_p can be ascribed to the charge transfer and polarization resistance of the polymer films, with values of 1.598 Ω, and 3.69 KΩ, respectively. Whereas the capacitance of porous coating can be described in terms of coating capacitance $110 \times 10^{-6} \text{ S*s}^a$, double layer capacitance $55.72 \times 10^{-6} \text{ S*s}^a$ and capacitance of double layer formed by seeping of electrolyte in pores of electrode $-50.72 \times 10^{-3} \text{ S*s}^a$, whilst exponents n , m , and a , are indicative of the degree of non-ideality in the impedance behavior. Solution capacitance in pores of coating was found to be negative presumably because it is modeled in series

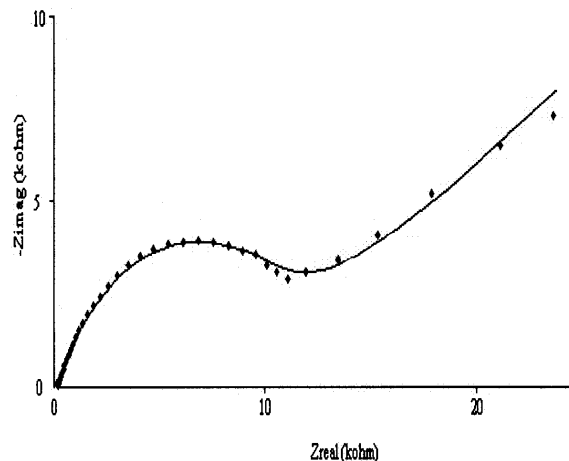


Fig. 5: Graphic output for fitting of equivalent model, for the Nyquist plot of electrochemical impedance spectroscopy carried out for poly-*p*-aminophenol coating at carbon electrode in 1.0 M HNO₃, experimental (dotted), equivalent model fit (smooth line), coating was obtained by electrolysis of 13.0 mM *p*-aminophenol solution in 1.0 M HNO₃

(Table-1). Possible explanation for the negative capacitive behavior of solution in pores of coating arises from very low frequency when there was a high resistance and impedance was measured at DC voltage 0 V, the impedance tends towards zero. There are instances in literature of negative capacitances [18].

Table-1: Parameters obtained from Equivalent Model Fitting.

Parameters	Value
Rsoln	139.8 ohm
Rct	1.598 kohm
Rpo	3.69 kohm
Cc	$110.0 \times 10^{-6} \text{ S*s}^a$
N	35.85×10^{-3}
Cdl	$5.572 \times 10^{-3} \text{ S*s}^a$
M	686.6×10^{-3}
Csoln	$-50.66 \times 10^{-3} \text{ S*s}^a$
A	2.334

(Rsoln) Solution resistance, (Rct) Charge transfer resistance, (Rpo) polarization resistance, (Cc) Coating capacitance, (Cdl) double layer capacitance, (Csoln) Solution capacitance in pores of coating. n, m, and a, are constants

Figs. 6 and 7 demonstrated that with the change in the deposition condition from constant potential electrolysis to cyclic voltammetry, value of resistance and diameter of the Nyquist semi-circle changed as it is dependent on the deposition conditions, in comparison to bare carbon, where no semi circle was observed in Nyquist plot as shown in Fig. 8. Very high resistance in Nyquist plot (Fig. 7) as compared to the corresponding values in case of coatings obtained by constant potential electrolysis (Fig. 6) implies that more resistive coatings were

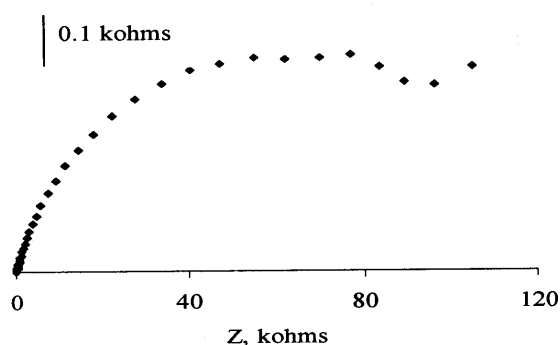


Fig. 6: Nyquist plot for coating obtained by two-electrode electrolysis of 13.0 mM *p*-aminophenol for 3.0 hrs in 1.0 M nitric acid, coatings obtained at -1.1 V

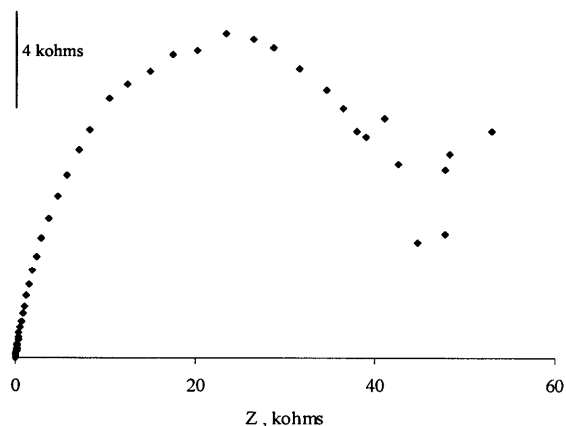


Fig. 7: Nyquist plot for coating obtained by running 30 cycles of CV in 6.5 mM *p*-aminophenol solution in 1.0 M nitric acid at 100 mV/s

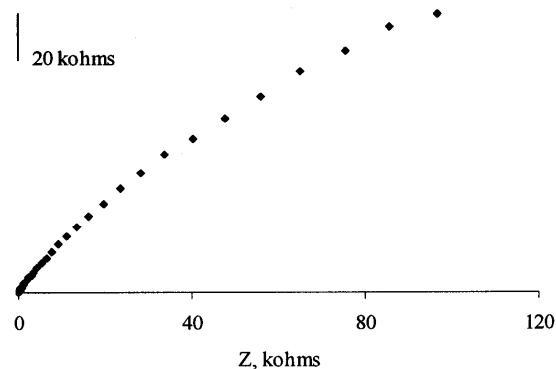


Fig. 8: Nyquist plot of bare carbon cathode in 1.0 M nitric acid

produced by cyclic voltammetric deposition. The above observation appears to be in line with impedance graphs where impedance of the two coatings was compared with that of bare carbon in Fig. 9.

FTIR Spectroscopic Results

The FTIR spectra of poly-*p*-aminophenol were obtained from the coatings detached from carbon surface. Absorption bands of each spectrum are shown in Fig. 10. The absorption bands associated with aromatic rings occurred near around $1500-1600 \text{ cm}^{-1}$, which may be considered to arise predominantly from double bonds, peaks in the range of $2200-2300 \text{ cm}^{-1}$ may be attributed to the presence

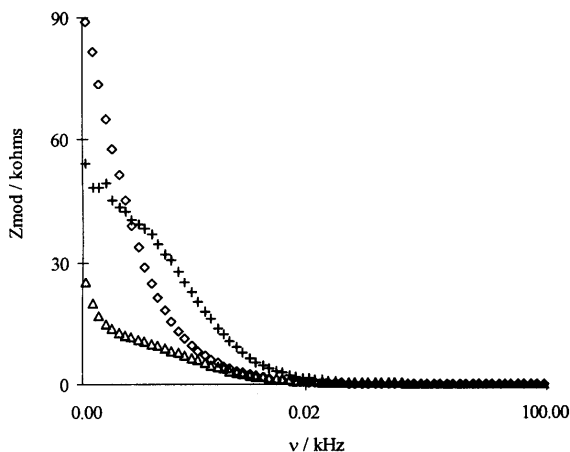


Fig. 9: Impedance graphs for coatings obtained by different electrochemical methods from 6.5 mM *p*-aminophenol in 1.0 M nitric acid: (\diamond) bare carbon, (Δ) carbon coated by constant potential electrolysis at -1.3 V, and (+) carbon coated by 30 cycles of CV

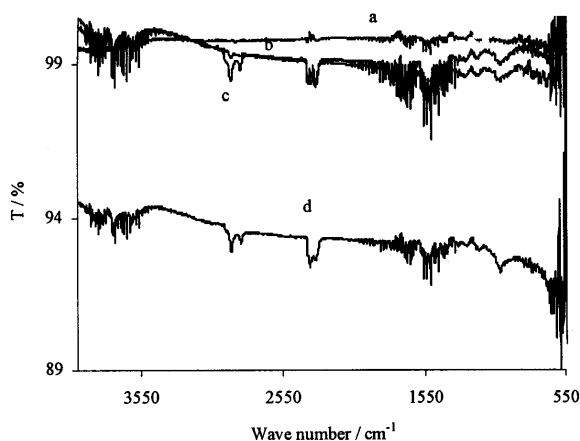


Fig. 10: FTIR scans of (a) bare carbon, (b) polymer coating obtained by constant potential electrolysis (run at -1.3 V for 24 hrs), (c) coating obtained by running 61 cycles of cyclic voltammetry, (d) coating obtained by running 81 cycles of cyclic voltammetry at 100 mV/s using 13.0 mM *p*-aminophenol solution in 1.0 M nitric acid

of nitrile group formed during process of polymerization of *p*-aminophenol. Broad aromatic OH stretch was observed at 3600 cm^{-1}

Experimental

Electrodes: All cyclic and linear sweep, voltammetric experiments were performed in a three electrode cell containing carbon (0.1256 cm^2) as working electrode, a platinum short-wire auxiliary electrode and a silver/silver chloride, chloride reference electrode.

VersaStat II (EG & G, Princeton Applied Research Corp) was used for linear sweep voltammetric experiments. Data were acquired using M270 Electrochemistry research software on a dedicated PII micro-processor coupled to the potentiostat.

Gamry potentiostat coupled with electrochemistry research software, Echem Analyst, was used for electrochemical impedance spectroscopy.

Chemicals and Solutions

p-Aminophenol purchased from Fluka was used after recrystallization from ethanol. Nitric acid (BDH) was used and its 1.0 M solution was prepared with de-ionized water.

Solutions were prepared using doubly distilled water purified with a Millipore ion exchange unit. All experiments were made at room temperature ($\approx 25\text{ }^\circ\text{C}$).

Electrode Preparation

After cleaning, carbon working electrodes were subjected to chemical pre-treatment. Carbon electrodes were first dipped in 20% sodium hydroxide for thirty minutes followed by thorough rinsing with water. Then the electrodes were dipped in 50% nitric acid for thirty minutes, followed by thorough rinsing with water. Different techniques were used for the deposition of *p*-aminophenol.

Cyclic Voltammetry

Carbon disk electrodes were coated with poly-*p*-aminophenol by reduction of 6.5 mM *p*-aminophenol solution in 1.0 M nitric acid using cyclic voltammetric technique. Potential cycling was done between -0.1 to -1.2 V at the scan rate 100 mV/s.

Constant Potential Electrolysis

Poly-*p*-aminophenol coatings were obtained by constant potential electrolysis of 6.5 mM and 13.0 mM *p*-aminophenol solution in 1.0 M HNO₃ at -1.1 to -1.3 V. The potential was controlled with a home made power supply.

Linear Sweep Voltammetry

Linear sweep voltammetry was used for the deposition of *p*-aminophenol at carbon disk electrode. Electro-deposition from 6.5 mM *p*-aminophenol solution in 1.0 M HNO₃ was carried out at slow scan rate (0.5 mV/s) in the potential range of -0.1 to -1.2 V in 1.0 M HNO₃.

After deposition, electrodes were first rinsed with dilute nitric acid until all of the excess *p*-aminophenol is washed away; later final washing was done by thorough rinsing with distilled water.

Polarization Curves

Polymer coatings obtained using above mentioned methods were polarized in nitric acid. Polarization curves of these polymeric films were run at the scan rate of 100 mV/s in the presence of 1.0 M nitric acid using VersaStat II.

Electrochemical Impedance Spectroscopy (EIS)

Impedance experiments were performed in 1.0 M nitric acid with a Gamry potentiostat within the frequency range 1.0 MHz - 0.01 Hz, amplitude 10 mV rms and DC voltage 0 V vs. Ag/AgCl, Cl⁻ electrode. Poly-*p*-aminophenol modified carbon electrodes of area 0.1256 cm² were used for electrochemical impedance measurements.

Simulation of EIS Data

Fitting of experimental data was done with EIS 300 software models.

FTIR Spectroscopy

IR scans were run at resolution of 4.0 cm⁻¹ between 4000-400 cm⁻¹ range using IR-prestige-21 (Fourier Transform Infra Red Spectrophotometer; Shimadzu). Polymer coatings obtained by constant potential electrolysis (run at -1.3 V for 24 h) and by

running cyclic voltammetric cycles (61 CVs and 81 CVs at 100 mV/s) were detached by scratching from carbon substrate and their IR-spectrum was obtained.

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