Polymer Modified Graphite: Voltammetric Reduction of Selected Organics

Inam-ul-Haque

Department of Chemistry, University of Engineering and Technology, Lahore, Pakistan

Email address
namihaque@yahoo.com

Citation

Abstract
Polymer coated graphite electrodes were obtained by reductive electropolymerization of para-aminophenol in 1.0 M nitric acid. Linear sweep voltammetry was employed to investigate electrolytic reduction of selected organics at these electrodes. Results pertaining to poly-para-phenylenediamine modified graphite electrodes are also reported. Suitability of these electrodes for the analytical determination of several environmentally relevant substrates is demonstrated.

1. Introduction
Nitrobenzene and related molecules continue to be of interest from the perspective of their detection and determination in the environmental milieu. Preliminary work to this end is described.

Modification [1] of solid electrodes by polymerization of monomers continues to be an interesting subject. For instance, poly-para-aminophenol coated electrodes [2] have been used for production of hydroxylamine [3-4]. Electropolymerization in a substantially aqueous solution was used to form thicker (greater than 2 microns or 30 weight %) and thermally stable coatings of thermoplastic materials onto electrically conductive filler materials (rods, plates, fibers) [5]. Chemically modified electrodes exhibit unique behavior that can greatly benefit electrochemical sensing [6]. An amperometric biosensor for glucose, based on a novel polymeric matrix was prepared by electrochemical polymerization of para-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 [7]. The electrochemical oxidation of ortho-aminophenol was 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 electropolymerization. Although a less electroactive 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 [8]. There are different studies related to impedance of polymers. Conducting poly-ortho-aminophenol films deposited on platinum electrodes were studied by quartz crystal impedance [9]. Impedance spectroscopy was also used to study the effect of solution pH on the electrochemical behavior of poly-ortho-aminophenol modified electrodes [10]. The impedance response of electrochemically synthesized poly-ortho-toluidine films were measured by Presa et al. [11]. Use of measurement models was suggested as an intermediate step in the analysis of impedance data by Orazem et al. [12]. References [13-19] summarize related studies.
2. Experimental

2.1. Material and Methods

2.1.1. Electrodes
All cyclic, linear sweep and differential pulse voltammetric experiments were performed in a three-electrode cell containing graphite (0.1256 cm²) as the working electrode, a platinum short-wire auxiliary electrode and a silver/silver chloride, chloride reference electrode.

2.1.2. Instrumentation
Potentiostat EG&G Princeton Applied Research Corp Versastat II was used for conducting voltammetric experiments. Data was acquired using M 270 Electrochemistry research software on a dedicated PII microprocessor coupled to the potentiostat.

2.1.3. Chemicals and Solutions
Para-aminophenol and para-phenylenediamine were purchased from Fluka and used after recrystallization from ethanol. Nitric acid BDH was used and 1.0 M solution was prepared with de-ionized water. Nitrobenzene, acetone and para-nitroaniline from Merck were all analytical grade.

Solutions were prepared using doubly distilled water purified with a Millipore ion exchange unit. All experiments were made at room temperature (∼25°C).

2.1.4. Electrode Preparation
After cleaning, graphite working electrodes were subjected to chemical pre-treatment. Graphite electrodes were first dipped in 20% sodium hydroxide for thirty minutes then thoroughly rinsed with water. Afterward electrodes were dipped in 50% nitric acid for thirty minutes, followed by thorough rinsing with water. Different techniques were used for the deposition of poly-para-aminophenol and poly-para-phenylenediamine.

2.2. Electropolymerization

2.2.1. Cyclic Voltammetry
Graphite disk electrodes were coated with poly-para-aminophenol by reduction of 6.5 mM para-aminophenol solution in 1.0 M nitric acid using the cyclic voltammetric technique. Potential cycling was done between -0.1 to -1.2 V at the scan rate 100 mV/s. For each coating, a fresh graphite disk was used.

2.2.2. Constant Potential Electrolysis
Poly-para-aminophenol coatings were obtained by constant potential electrolysis of 6.5 mM and 13.0 mM para-aminophenol solution in 1.0 M HNO₃. Similarly, Poly-para-phenylenediamine [13] coatings were obtained using two-electrode system and the potential was controlled with a homemade power supply.

2.2.3. Linear Sweep Voltammetry
Slow scan linear sweep voltammetry was also used for the deposition of poly-para-aminophenol at graphite disk electrodes.

After deposition electrodes were first rinsed with dilute nitric acid until all of the excess para-aminophenol got washed away and afterward with distilled water.

3. Results and Discussion

3.1. Polarization Behavior of Coatings

Different electrodes modified with slow scan linear sweep voltammetry (0.5 mV/s from 6.5 mM para-aminophenol in 1.0 M nitric acid) and cyclic voltammetry (30 cycles) were used to compare polarization behavior of nitric acid with that from bare graphite. While using different techniques for deposition, slow scan linear sweep voltammetry was found to yield better deposition of poly-para-aminophenol on graphite. Coatings deposited on graphite 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. Reduction of nitric acid becomes more cathodic at polymer coating at slow scan rate (0.1 mV/s) than at higher scan rates like 0.5 and 10 mV/s.
3.2. Electroreduction of Nitrobenzene

Figure 1 shows reduction of a saturated solution of nitrobenzene in 1.0 M nitric acid. Nitrobenzene was reduced in the region -0.2 to -0.4 V. Scan rate dependence and concentration dependence of nitrobenzene was performed. Linear sweep voltammetric peak current of nitrobenzene with square root scan rate is given in Figure 2. Concentration variation of nitrobenzene is given in Figure 3 with \( y = 0.1439x - 0.0173, R^2 = 0.9825 \)

3.3. Electroreduction of Para-Nitroaniline

Figure 4 shows reduction of a saturated solution of para-nitroaniline in 1.0 M nitric acid. Para-nitroaniline was reduced in the region -0.2 to -0.4 V. Variation of linear sweep voltammetric currents with concentration of para-nitroaniline is shown in Figure 5 with \( \frac{\partial \ln i}{\partial \ln C} = 1.0 \) and \( y = 0.0692x + 0.061, R^2 = 0.9291 \).

3.4. Electroreduction of Acetone

Reduction of acetone was also observed at about -0.5 V, Figure 6. When concentration of acetone was varied from 0 to 2.5 mM, \( \frac{\partial \ln i}{\partial \ln C} = 0.92 \) was obtained from Figure 7, \( y = 0.1721x + 0.0177, R^2 = 0.9773 \).

Figure 3. Linear sweep voltammetric current vs concentration of nitrobenzene in 1.0 M HNO\(_3\) at poly-para-aminophenol modified graphite electrodes. Modified electrode obtained after 1 h electrolysis of 6.5 mM p-aminophenol in 1.0 M HNO\(_3\), scan rate 100 mV/s. \( y = 0.1439x - 0.0173, R^2 = 0.9825 \).

Figure 4. Linear scan current potential curves in (1) 1.0 M HNO\(_3\) and (2) 2.0 mM para-nitroaniline in 1.0 M HNO\(_3\) at poly-para-aminophenol modified graphite electrodes. Modified electrode was obtained after 30 scans between -0.1 and -1.2 V in 6.5 mM para-aminophenol + 1.0 M HNO\(_3\), scan rate 100 mV/s.

Figure 5. Linear sweep voltammetric current vs concentration of para-nitroaniline in 1.0 M HNO\(_3\) at poly-para-aminophenol modified graphite electrodes. Electrodes modified using 30 scans between -0.1 and -1.2 V in 6.5 mM para-aminophenol + 1.0 M HNO\(_3\), scan rate 100 mV/s.

Figure 6. Linear scan current potential curves (1) 1.0 M HNO\(_3\) and (2) 1.26 mM acetone in 1.0 M HNO\(_3\) at poly-para-aminophenol modified graphite electrodes. Electrodes were modified using 30 scans between -0.1 and -1.2 V in 6.5 mM para-aminophenol + 1.0 M HNO\(_3\), scan rate 100 mV/s.

Figure 7. Linear sweep voltammetric current vs concentration of acetone in 1.0 M HNO\(_3\) at poly-para-aminophenol modified graphite electrodes. Modified electrode prepared by 30 scans between -0.1 and -1.2 V using 6.5 mM para-aminophenol in 1.0 M HNO\(_3\), scan rate 100 mV/s.
3.5. Electroreduction of Benzodiazepines

Electrochemical behaviour of diazepam (Figure 8) and temazepam were studied on poly-para-aminophenol coated graphite electrodes. Figure 9 indicates linear relationship between current and concentration of temazepam. Linear relationship of current and concentration plots for the reduction of diazepam was also studied using two techniques, i.e. linear sweep voltammetry Figure 10 and differential pulse voltammetry Figure 11.

4. Conclusions

Polymer coated graphite electrodes were used to investigate electrolytic reduction of nitrobenzene, para-nitroaniline, acetone and benzodiazepines. Modified electrodes were found active for analytical determination of these organic compounds.

All the organics show an electrochemical reaction order \( (\partial \ln i / \partial \ln C) \) equal to unity respectively at the polymer modified graphite electrodes.

References


