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Oxidative electropolymerization of pyrrole from neat monomer solution

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Abstract

Oxidative electrochemical polymerization of pyrrole at gold, indium doped tin oxide on glass, and stainless steel type 304 was accomplished from neat monomer solution containing only supporting electrolyte (0.05–0.3 M *n*-tetrabutyl ammonium perchlorate, *n*-tetrabutyl ammonium hexafluorophosphate, or *n*-tetrabutyl ammonium tetrafluoroborate) by multiple scan cyclic voltammetry. The results presented demonstrate that thick (>1–14 μm), stable, highly conductive (up to 0.6 S/cm) polypyrrole films can be readily prepared on a wide range of electrode substrates using this simple electrochemical method.

Keywords: Electrochemistry; Conducting polymer; Polypyrrole; Cyclic voltammetry

1. Introduction

Due to their light weight, high conductivity, good stability and redox state-dependent physico-chemical properties such as color and volume, intrinsically conducting polymers (ICPs) such as polypyrrole (PPy), polyaniline, and polythiophene continue to be actively investigated [1,2]. Synthesis of conducting polymers can be accomplished chemically or electrochemically usually from dilute aqueous or nonaqueous solutions of the relevant monomer. Polypyrrole is one of the most frequently investigated ICPs [3]. PPy is easy to synthesize both chemically and electrochemically, exhibits good electrical conductivity, and is relatively stability under ambient conditions.

Several years ago, White and coworkers investigated the electrochemistry of neat redox liquids in the absence of any added inert solvent [4–7]. Electrochemistry in neat redox liquids was shown to have several advantages, including a wide voltage window when compared to water and other commonly used electrochemical solvents and unique transport layer fluid properties. Subsequently, Murray and coworkers [8] demonstrated that electropolymerization of aniline and pyrrole could be accomplished from neat solutions. However, the authors did not characterize the resulting products that they believed to be oligomers. In view of the growing importance of ICPs, we wish to report the results of preliminary studies demonstrating that thick, conductive, stable films of intrinsically conducting polymers, here, specifically, polypyrrole, can be readily synthesized electrochemically from neat monomer in the absence of an inert diluting solvent.

2. Experimental

2.1. Reagents

Sodium perchlorate (Aldrich), *n*-tetrabutyl ammonium perchlorate ($TBAClO_4$; 99+%, Alfa Aesar), *n*-tetrabutyl ammonium hexafluorophosphate ($TBAPF_6$, >99%, Sigma), and *n*-tetrabutyl ammonium tetrafluoroborate ($TBABF_4$; Alfa Aesar) were purchased as A.C.S. analytical grade or better and were used as received. Pyrrole (98%, Sigma) was distilled

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and stored in the dark under nitrogen at 5 °C until use. Gold foil (0.002 in thick, 99.95%, Alfa Aesar), stainless steel foil (type 304, 0.001 in thick, Alfa Aesar) and indium tin oxide on glass (R_s, 4–8 Ω, Delta Technologies) were used to construct the homemade working electrodes used in this study.

2.2. Electrodes

ITO/glass electrodes were prepared by wrapping a piece of copper wire around the top of one side of a 5 mm × 5 mm square of ITO/glass and then applying silver epoxy to establish good electrical contact between the surface of the ITO and the copper wire touching it. The exposed copper wire and silver epoxy were then coated with insulating epoxy to ensure that only the exposed ITO surface would serve as the electrode.

The Au and stainless steel type 304 (ss-304) working electrodes were cleaned by gentle abrasion with alumina and diamond polish. These electrodes were then rinsed with distilled water, sonicated in a dilute solution of Alconox®, rinsed again with distilled water, and then briefly air-dried. ITO/glass working electrodes were first rinsed with analytical grade methanol and acetone then sonicated in Alconox®, rinsed with distilled water and finally briefly air-dried. All Au and ITO/glass working electrodes were characterized by cyclic voltammetry (CV) at 100 mV/s using 2 mM potassium ferricyanide in 1.0 M KNO_3 prior to use. ΔE_p was typically <105 mV.

2.3. Electrochemical Instrumentation

Cyclic voltammetry experiments were conducted using a Bioanalytical Systems (BAS) 100B electrochemical workstation.

2.4. Electrochemical synthesis

Polypyrrole (PPy) films were electrochemically synthesized by multiple scan cyclic voltammetry using 2 mL aliquots of freshly distilled pyrrole containing the desired electrolyte, either *n*-tetrabutyl ammonium perchlorate, *n*-tetrabutyl ammonium hexafluorophosphate, or *n*-tetrabutyl ammonium tetrafluoroborate. Three electrolyte concentrations were investigated: 0.05, 0.15, or 0.30 M. A 10 mL beaker served as the single compartment electrochemical cell. Working electrodes were homemade from 5 mm × 5 mm squares of gold foil, ITO/glass, or stainless steel foil, type 304. An Ag/AgCl (3 M NaCl; Bioanalytical Systems) electrode served as the reference electrode and a homemade Pt gauze flag (1 cm × 1 cm; 100 mesh, 99.9%, Aldrich) was used as the counter electrode. The working electrodes were typically cycled for 40–120 cycles between 1000 and −1000 mV versus Ag/AgCl (3 M NaCl; BAS) at 100 mV/s in order to affect electropolymerization. All experiments were performed at room temperature.

2.5. Electrochemical characterization

Once polymerization was accomplished the polypyrrole-coated working electrode was removed from the electrochemical cell, rinsed generously with acetone, methanol, and deionized water. The electrode was then characterized by CV in the potential range from +1000 to −1000 mV versus Ag/AgCl (3 M NaCl) at a scan rate of 100 mV/s in aqueous, monomer-free 1.0 M potassium nitrate solution.

2.6. Electrical conductivity

The electrical conductivity of polypyrrole films prepared using the above protocol was evaluated using the van der Pauw method [9]. 5 mm × 5 mm squares of polypyrrole films were lifted from the working electrode using Scotch® heavy duty mounting tape. Colloidal silver liquid (Ted Pella) was used to facilitate good electrical contact between four 0.005 in. diameter (99.99%, Alfa Aesar) gold wires and the four corners of the polymer film. The gold wires were soldered using indium metal (low melting) to four pins of a 14-pin low profile IC socket (Jameco Electronics). A constant current of 8 μA was applied to two of the four pins and the voltage across the remaining two pins was measured following the National Institute of Standards and Technology protocol [9].

The average film thickness used in the calculation of the electrical conductivity of the polypyrrole films was obtained from the average of a minimum of three scans made at different positions on the polymer film (scan length: 2000 μm, profile: hills, scan speed: medium, resolution: high, stylus force: 10–30 mg) using a Dektak ^{3}ST profilometer equipped with a 12.5 μm diameter stylus. The average variation in any three thickness measurements for any one polymer film was less than 22%.

2.7. Atomic force microscopy (AFM)

PPy film morphology was investigated ex situ using a Quesant Q-scope 350 atomic force microscope operating in tapping mode. Noncontact NSC-16 silicon cantilever tips were used. Micrographs were minimally processed using streak removal when appropriate. Images were obtained by scanning 22 μm × 22 μm regions at a scan rate of 1.5 Hz. Three separate regions of each polymer film were characterized in order to verify that the AFM images were representative of that sample. All AFM images are shown in the 3D height mode. Bright colors indicate higher regions on the sample while darker colors indicate lower regions on the sample.

3. Results and discussion

Oxidative electrochemical polymerization of pyrrole at gold, ITO/glass, and stainless steel type 304 (ss-304) has been accomplished from neat monomer solution containing