An electrochemical impedance study of thin polycarbazole films

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ABSTRACT

A voltammetric and electrochemical impedance study of glassy carbon electrodes galvanostatically coated with approximately 23 nm of polycarbazole (GC/PCZ) was conducted in various concentrations of aqueous H_2SO_4 and KNO_3 and their mixtures. Cyclic voltammetry showed strong dependencies on both the electrolyte type and concentration, while the impedance characteristics were influenced much less. This was shown to be due to strong ion transport effects in voltammetry which became insignificant in the small amplitude impedance experiments, which were dominated by electron transport though the polycarbazole layer. Thus combination of the two techniques provided a more complete description of the polycarbazole electrochemistry. Both techniques provided evidence of cation insertion which extended the range of electroactivity to lower potentials at high KNO_3 concentrations and when both KNO_3 and H_2SO_4 were present.

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1. Introduction

Polycarbazoles [1–4] have been attracting increasing attention for a variety of applications including electronic [5] and electrochromic [6] devices, solar cells [7], sensors [3,8–10] electrocatalysis [11,12], charge storage [13–16], and ion extraction [17]. However, the properties and electrochemistry of this class of polymers has received limited attention relative to other conducting polymers such as polypyrrole and polyaniline.

This work was prompted by reports that polycarbazole supports and coatings exhibit remarkable synergy with Pt for the electrochemical oxidation of formic acid [11,18,19]. While formic acid oxidation at pure Pt is known to proceed primarily through the indirect pathway with production of blocking intermediates (mainly adsorbed CO), addition of PCZ diverts the reaction towards complete oxidation of FA to CO_2 via a direct pathway. One major issue reported for PCZ is its intrinsic high resistance, which dramatically decreases the FA oxidation activity when thicker films are used [18]. The purpose of this work is to extend the preliminary impedance study reported in [18], in order to investigate the turn-on of the PCZ conductivity and the influence of the electrolyte.

The in situ conductivity and capacitive behavior of polycarbazole has been investigated by electrochemical impedance spectroscopy (EIS) in a number of previous studies [8,11,13,16,18,20,21]. Ates and Sarac [20] reported impedance data for polycarbazole-coated carbon fibers in propylene carbonate and acetonitrile with $LiClO_4$ and Et_4NClO_4 electrolytes. The results were analyzed by fitting to the circuit shown in Fig. 1, where R_u is the solution resistance, C_{dl} is the double layer capacitance, R_1 is "electrolyte resistance" (it is not clear to us how this is distinct from R_u), CPE is a constant phase element representing the capacitance at the film|electrolyte interface, R_2 is a charge transfer resistance, W is the Warburg impedance of the polymer, C_{CF} is the capacitance of the carbon fiber electrode, and R_{CF} is its resistance. It was found that the electrolyte/solvent combination used in the electrochemical deposition of the polymers, the deposition method, and the electrolyte/solvent combination used in the EIS all influenced the properties of the polycarbazole layers. This methodology was also applied to a range of polycarbazole derivatives [15].

Gupta et al. [21] found that amorphous polycarbazole films prepared in acetonitrile containing Bu_4NClO_4 exhibited faster ion exchange and high doping levels than more ordered films prepared with Bu_4NBF_4. "Near-Ohmic" impedance behaviour has been reported for polycarbazole films in KCl(aq), which is useful for bioelectric sensing [8].

Here we present voltammetric and EIS results obtained in various combinations of aqueous H_2SO_4 and KNO_3 for glassy carbon electrodes galvanostatically coated with polycarbazole. H_2SO_4 was used here because it was the electrolyte used for our electrocatalytic studies [18]. Comparing its effect with that of KNO_3 provides information on possible pH effects.

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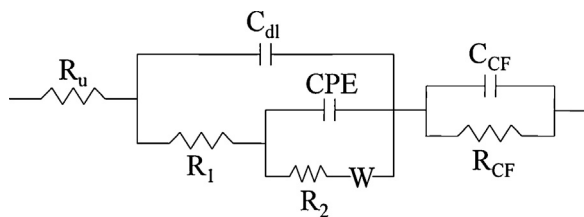E-mail address: ppickup@mun.ca (P.G. Pickup).

Fig. 1. Equivalent circuit used by Ates and Sarac [20] for modeling impedance results for electrocoated polycarbazole films on carbon fiber microelectrodes.

2. Experimental

2.1. Chemicals

Carbazole (AlfaAesar; 95%), sulfuric acid (Fisher Scientific), potassium nitrate (BDH), dichloromethane (Sigma Aldrich; ACS reagent, 99.9%), tetrabutylammonium hexafluorophosphate (Fluka; electrochemical grade, 99.0%), (Alfa Aesar; 95%) were used as received. All measurements were recorded at ambient temperature under a nitrogen atmosphere following purging for 15 min. Deionized water was used throughout the experiments.

2.2. Working electrode preparation

Glassy carbon electrodes (GC; CH Instruments; 0.071 cm^2) were polished with 0.05 μm alumina and rinsed well with water before use. Polycarbazole films were galvanostatically (0.28 mA cm^{-2}) deposited from dichloromethane containing 0.1 M tetrabutyl-ammonium hexafluorophosphate and 0.01 M carbazole using a polymerization charge density of 28.2 mC cm^{-2}. These polycarbazole electrodes are designated as GC/PCZ. The mass of the PCZ film (m_{PCZ}) can be estimated by assuming 100% polymerization efficiency and using eq. 1 [11].

$$m_{PCZ} = \frac{Q_{Polym} \cdot M_{PCZ}}{F.Z} \tag{1}$$

Where Q_{Polym}, M_{PCZ}, F, and Z are polymerization charge, the molar mass of carbazole (167.2 g mol^{-1}), the Faraday constant (96485 C mol^{-1}), and number of electrons associated with polymerization of one monomer (2.3) [11], respectively. The calculated mass of PCZ was 212 ng, which correspondes to a film thickness of ca. 23 nm based on an assumed density of ca. 1.3 g cm^{-3}. A new film was prepared for each electrolyte employed.

2.3. Instrumentation and impedance fitting

An EG&G Model 273A Potentiostat/Galvanostat run by a PC through M270 commercial software was used for voltammetric measurements. A saturated calomel electrode (SCE) and a platinum wire formed the reference and counter electrode, respectively. For impedance measurements an EG&G Model 5210 Lock-in Amplifier was also used and the system was run through Power-Suite commercial software. Electrochemical impedance measurements were performed over the range of 10 kHz to 0.1 Hz using an ac amplitude of 10 mV. Before any impedance measurement, the electrode was held for 2 min at the dc offset potential to reach electrochemical equilibrium. Data analysis and equivalent circuit fitting was performed with ZView2 software (Scribner Associates Inc.). All cyclic voltammograms shown are for the 2nd cycle, with the scan stopped at +0.1 V between the 1st and 2nd cycles. The CVs for the two cycles were very similar in all cases.
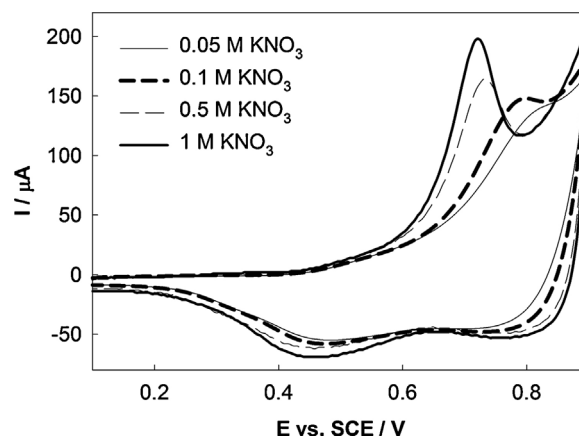

Fig. 2. Cyclic voltammograms at 100 mV s^{-1} for GC/PCZ electrodes in various concentrations of KNO$_3$.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 2 shows cyclic voltammograms of GC/PCZ electrodes in various concentrations of KNO$_3$(aq). Although the general form of the voltammograms did not change greatly as the electrolyte concentration was decreased, there were clear changes in the anodic peak position and height that can be attributed to increased resistance. In addition, the speed of the current response to scan reversal at the upper potential limit reveals an increase in time constant that must be due to resistance effects. In contrast, the cathodic peak at ca. 0.47 V actually shifted to more positive potentials as the KNO$_3$ concentration was decreased. This is opposite to the effect that increased resistance would produce, indicating that some other factor dominated changes in the position of this peak. The resistance effect can be attributed largely to changes in the solution resistance (see section 3.4; Table 1). The positions of both the anodic and cathodic peaks would also be influenced by changes in the Donnan potential [22], which would increase with decreasing KNO$_3$ concentration, resulting in ca. 77 mV positive shifts for both peaks over the 1 M to 0.05 M range. The combined effects of the solution resistance and Donnan potential can therefore adequately explain the changes with KNO$_3$ concentration seen in Fig. 2.

Fig. 3 compares voltammograms of GC/PCZ films in solutions of KNO$_3$, H$_2$SO$_4$ and mixtures of these two electrolytes. Addition of
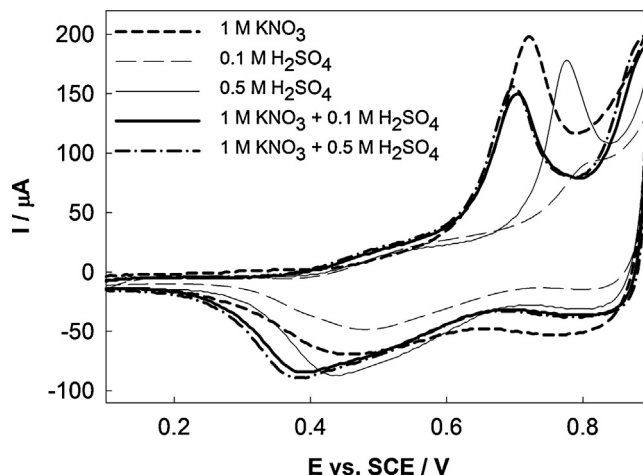

Fig. 3. Cyclic voltammograms at 100 mV s^{-1} for GC/PCZ electrodes in various concentrations of KNO$_3$ and H$_2$SO$_4$ and some of their combinations.