

Electropolymerization of *N*-Hydroxyethylcarbazole on Carbon Fiber Microelectrodes

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Received 7 August 2007; accepted 28 May 2008

DOI 10.1002/app.29556

Published online 16 March 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: *N*-Hydroxyethylcarbazole (EtOHCz) was electropolymerized on carbon fiber microelectrodes (CFMEs). The polyEtOHCz-modified CFME was characterized with FTIR-ATR, scanning electron microscopy, cyclic voltammetry, and electrochemical impedance spectroscopy. The polymer/CFME electrode exhibited the capacitive behavior and also good stability up to 2.0 V. The presence of hydroxylic group of the monomer seems to be an advantage on polymerization because of the unpaired

electrons of oxygen, which would make ease at first stage for the adsorption on carbon fiber. The estimated value of the low-frequency redox capacitance (C_{LF}) was found to increase with increasing dc potential. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 136–142, 2009

Key words: poly(*n*-hydroxyethylcarbazole); carbon fiber microelectrode; electrochemical impedance spectroscopy; electropolymerization

INTRODUCTION

Conducting polymers such as polyaniline, polythiophene, and polypyrrole have been extensively studied in the past two decades because of their potential application as active electrode material in energy conversion systems and also electrochemical supercapacitors.^{1–4} Carbon fibers combine high tensile strength and high tensile modulus with low weight. They are ideal reinforcing material for lightweight structures, e.g., in aerospace applications, capacitors,⁵ and also in biosensors.⁶ Carbon fibers consist of stacked hexagonal carbon layers, forming small coherent units (crystallites) of only a few micrometer size in the stacking direction.⁷ Electropolymerization on CFMEs can improve the interfacial properties between carbon fibers and the polymeric matrix.^{8–11} The disposable nature and low price of carbon microfibers are advantages for their use as electrodes. Electrocoating of copolymers with conductive and nonconductive contents onto carbon fibers have recently been studied.¹² However, the interfacial reactive groups need to be strongly bound to the carbon surface so that these polymer materials can survive

other subsequent treatments, i.e., treatment with thermoset thermoplastic resin systems. Because of their electrical and photoelectrochemical properties, carbazole (Cz)-based polymers have received much attention recently.^{13–15} As a sensor electrode, it has been known that PCz electrodes have a good response to dopamine, which is a biologically important substance.¹⁶ However, poor mechanical properties limit the use of this type of PCz electrode.

Electrochemical impedance spectroscopy (EIS) is a powerful technique to study charge transfer, diffusion, and capacitance of conducting polymer-modified electrodes. Theoretical models have been developed to explain the impedance characteristics of homogeneous films¹⁷ and porous membranes.¹⁸ For the uniform films, a model considering the diffusional transport of single type of charge carrier (electron or ion) across the film with a charge transfer process at metal–film interface was proposed.¹⁹ This model could explain the Randles circuit behavior, the Warburg contribution, and the capacitive responses at low frequencies.

In this article, we describe the electrochemical coating of poly(*N*-hydroxyethyl carbazole) (polyEtOHCz) onto carbon fiber microelectrodes (CFMEs), and their characterization by cyclic voltammetry (CV), scanning electron microscopy (SEM), and FTIR-ATR technique. EIS was used to investigate the capacitive behavior of the conducting polymer-modified CFMEs.

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EXPERIMENTAL

Materials

All chemicals were used as received from Sigma Aldrich (Munich, Germany) without further purification. High-strength (HS) carbon fibers C320.000A (CA) (Sigri Carbon, Meitingen, Germany) containing 320,000 single filaments in a roving were used as working electrodes. All of the electrodes were prepared by using a "brush" electrode consisting of carbon fibers (diameter of one fiber = 7 μm) attached to a copper wire with a Teflon tape. The electrode area was kept at constant ($\sim 0.5 \text{ cm}^2$) by adjusting the dipping length and covering the rest of the fibers with the Teflon tape. The area of carbon fiber electrode was calculated according to the following equation: $A = 2\pi rh$, where $r = 3.5 \mu\text{m}$ (radius of carbon fiber) and $h = 1.5 \text{ cm}$ (the height of fiber dipped into solution).

Electropolymerization, CV, and EIS

Polymerization reactions were performed electrochemically by scanning the potential between 0 and 1.4 V (scan rate = 50 mV/s) in dichloromethane (CH_2Cl_2) solution containing 0.05M tetraethylammonium perchlorate (TEAP) and 10 mM monomer. CV of the polymers was performed with a PARSTAT 2263-1 (software: powersuit) in a three-electrode setup employing CFMEs as working electrode. Also, Pt button was used as the working electrode, $A = (0.002 \text{ cm}^2)$ with a diameter of 0.5 mm. The reference electrode was Ag|AgCl (3M NaCl aq). Counter electrode was Pt wire.

Electrochemical impedance measurements were conducted in monomer-free electrolyte solution with a perturbation amplitude of 10 mV over a frequency range 0.01Hz–100 kHz with PARSTAT 2263-1 (software: powersuit).

ATR-FTIR-ATR measurements

Thin polymeric films electrocoated onto the carbon fiber surface were analyzed by using an Perkin Elmer FTIR-ATR spectrometer with an ATR attachment.

Scanning electron microscopy

The chosen electrocoated fibers were analyzed by SEM using JEOL (Japan Electron Optics Laboratory, JSM S410 scanning electron microscope, which was connected EDS microanalyzer) Noran Voyager II Quantitative microanalysis with a Freedom detector, Noran Instruments, Japan. The excitation energy was 5 keV at a beam current of 60 μA .

AFM

The AFM images reported in this study were obtained using an ExplorerTM, Scanning Probe Microscope (TopoMetrix-ThermoMicroscope-VEECO). In this analysis the non-contact mode was used. The tips used were high resonance frequency silicon tips (frequency range 354–409 kHz), with a 120 μm long cantilever, a tip of 3–6 μm base, 10–20 μm long and a 20 nm tip radius. The raw data collected were processed by the TopoMetrix SPMLab NT Version 5.0 using left shadowing. In order to perform AFM analysis, the carbon fibres were attached to a piece of silicon wafer using a thin layer of Tempfix adhesive (Neubauer Chemikalien, Germany).

RESULTS AND DISCUSSION

Electropolymerization

The polymerization reaction was performed electrochemically at a constant potential or potentiodynamically in 0.05M TEAP- CH_2Cl_2 and 10 mM EtOHCz monomer. Application of potential between 0 and 1.4 V versus Ag/AgCl induces the development of a redox system corresponding to the doping/undoping process of the growing film. The cyclic voltammograms obtained during polymer film growth on both CFMEs and Pt electrodes are presented in Figure 1(a,b). Figure 1(a,b) also shows the nucleation loop indicating the start of the polymerization. During successive scans, small increase in the current was observed, and it corresponds to the deposition of an electroactive film onto the electrode surface. The cyclic voltammograms indicated that the redox process takes place at 0.82 V on CFME and 0.91 V on Pt disk electrode (area = 0.002 cm^2). The measured parameters of interest on cyclic voltammograms are the ratio of anodic peak currents and cathodic peak currents ($i_{\text{pa}}/i_{\text{pc}}$), and $E_{\text{pa}} - E_{\text{pc}}(\Delta E)$, the separation of peak potentials. For a Nernstian wave, the ratio $i_{\text{pa}}/i_{\text{pc}} = 1$, regardless of the scan rate. The separation of peak potentials (ΔE) is also a useful test for reversible behavior for the reaction. At steady state, $\Delta E = 59/n \text{ mV}$ at 25°C for reversibility. From the CVs in Figure 2, the couple is irreversible as the separation of peak potentials (ΔE) are 230 and 300 mV, and the $i_{\text{pa}}/i_{\text{pc}}$ of the CVs are 0.15 and 0.19 on CFME and Pt, respectively. We also observed that the cathodic charge Q_c is higher than the anodic one (Q_a). This effect has also been reported in the literature.²⁰

The differences between the anodic and cathodic peaks in the electropolymerization obtained by CV might indicate that most of the primary products of the monomer (or oligomer) oxidation is transformed

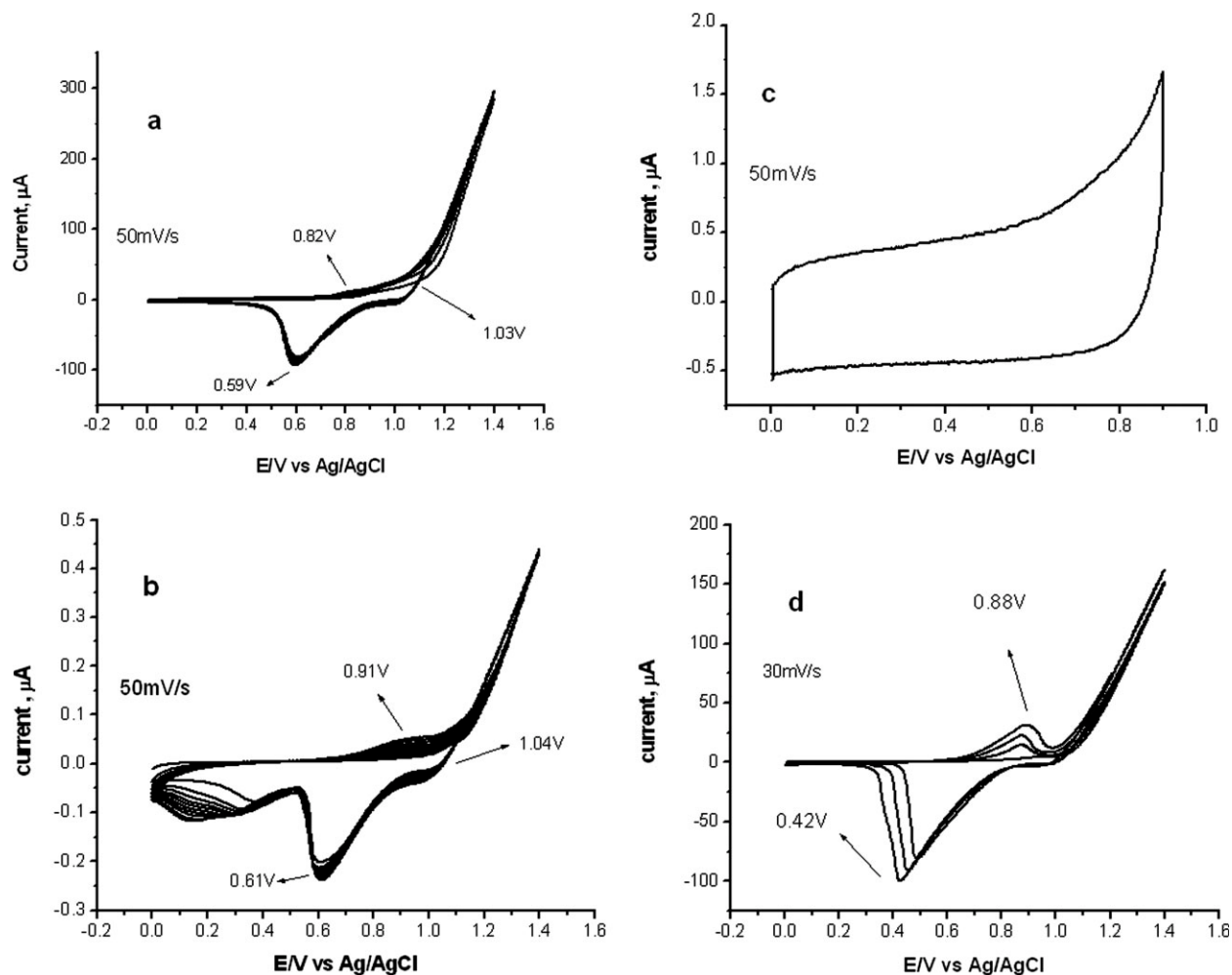


Figure 1 Potentiodynamic growth of EtOHCz in 0.05M TEAP-CH₂Cl₂ on (a) CFMEs (scan rate: 50mV/s) and (b) Pt disk electrode (scan rate: 50 mV/s); (c) potentiodynamic growth of polyEtOHCz in 0.05M TEAP-CH₂Cl₂ in the range of (0–0.9 V) on CFME (scan rate: 50 mV/s) and (d) polyEtOHCz in 0.05M TEAP-CH₂Cl₂ with scan rate: 30 mV/s on CFME.

neutral monomer (or oligomer) during the cathodic scan. Such behavior can be attributed to the interaction of radical cation oligomers (formed during the successive oxidations by CV) with solvent molecules, which eases the cathodic reduction of such species.

To get more information about this point, the CVs for the uncoated(bare) electrodes cycled without entering the oxidation interval of the monomer, i.e., up to 0.9 V (without allowing monomer oxidation properly). This cathodic peak was not observed at 0.9 V and low current density was obtained [Fig. 1(c)]. A weak intensity of the growing cathodic and anodic waves [when compared with Fig. 1(a,b)] can be related to a low polymerization yield. Figure 1(d) shows that when scan rate was lowered to 30 mV/s, more favorable polymerization efficiency was achieved.

The films were then washed with monomer-free electrolyte solution and their redox behavior was studied. The oxidation potentials of PolyEtOHCz are 0.99 V and 0.96 V on CFME and Pt, respectively. The nature of CFME leads to an increase in the oxi-

dation potential of EtOHCz; our previous studies also support this finding¹¹ [Fig. 3(a)]. $E_{1/2}$ value of polyEtOHCz on CFMEs (0.91 V) is 0.05 V greater than that of Pt electrode (0.86 V).

Between 20 and 200 mV/s, the peak current of the redox systems evolves linearly with the square root of scan rate, which indicates a diffusion-limited redox process.²¹ Interestingly, as shown in Figure 2(a), the larger current density were observed for both polymer growth and polymer film on CFMEs when compared with that of Pt [Fig. 2(b)], for anodic and cathodic peak currents because of higher surface area of CFMEs in the same volume of solution as electropolymerization is faster and more polymer electrodeposited on CFMEs.²²

FTIR-ATR spectrum of electrocoated polymer film on CFMEs

The FTIR-ATR-Reflectance spectra was recorded for electrografted polyEtOHCz that was prepared at a

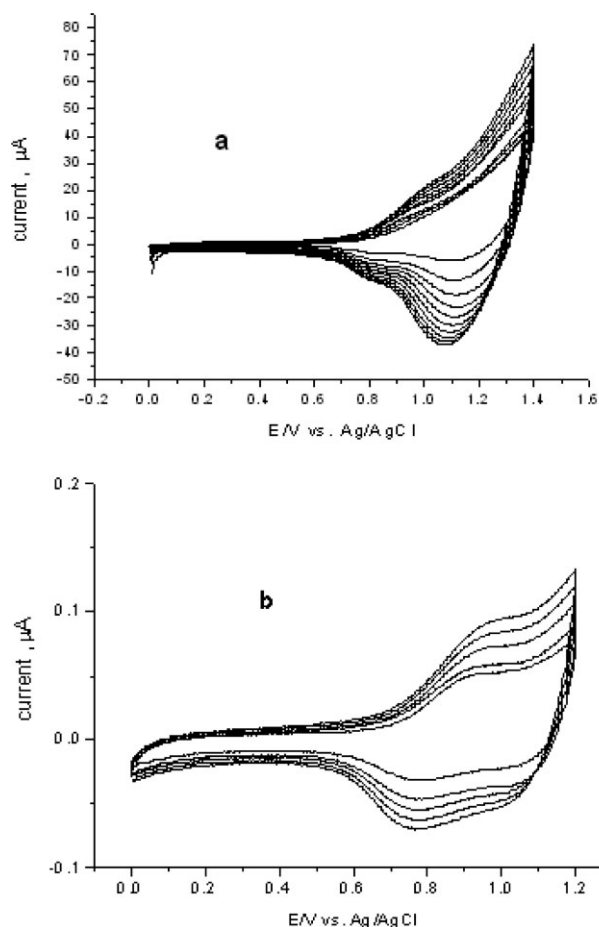


Figure 2 Scan rate dependence of polyEtOHCz on (a) CFMEs and (b) Pt disk electrode in 0.05M TEAP-CH₂Cl₂.

constant potential (1.4 V versus Ag/AgCl) for 1.5 h. The EtOHCz monomer shows bands at 3195, 1624, 1458, 1244, 996, 748–750 cm⁻¹ [Fig. 4(a)]. In the FTIR-ATR spectrum of polyEtOHCz, there are some shifts in the wave numbers of the bands, and some

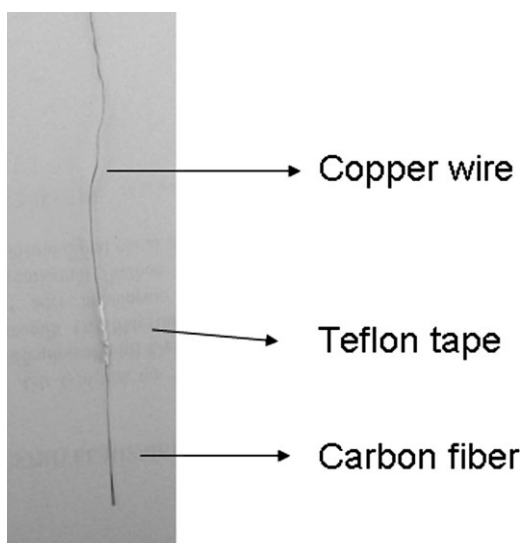


Figure 3 The photograph of carbon fiber brush electrode.

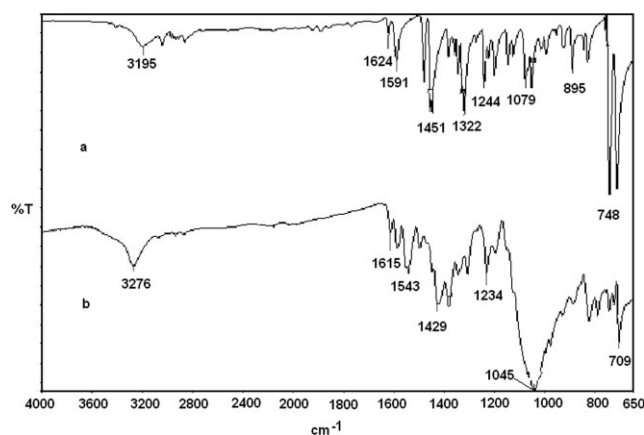


Figure 4 FTIR-ATR spectra of (a) EtOHCz and (b) poly EtOHCz obtained on CFMEs in TEAP-CH₂Cl₂.

new peaks appeared when compared with the monomer spectrum.

Figure 4(b) represents the FTIR-ATR spectra of polyEtOHCz obtained by electropolymerization on CFMEs. The peaks at 827–794 cm⁻¹ can be attributed to C–H deformation of out-of-plane of trisubstituted 1,2,4-carbazole cycle and 749 cm⁻¹ (C–H deformation out of plane-adjacent 4H 1,2,3,4- at the end of chains of disubstituted carbazole cycle).²³ The band located at 1234 cm⁻¹ is confirmed by the valence vibration of C–N bond of carbazole cycle.²⁴ Moreover, the peaks at 1045 cm⁻¹ are attributed to doping with ClO₄⁻ anions coming from the electrolytes in TEAP-CH₂Cl₂.²⁵ Finally, this spectrum shows that the bands of this polymer at 1615–1499 cm⁻¹ show evidence for aromatic stretching of double bond C=C.²⁶

Morphology

To understand the surface appearance of the polymer electrode on CFMEs, SEM was used. The SEM micrographs of electrografted polyEtOHCz prepared at constant potential (1.4 V vs. Ag/AgCl) for 1.5 h is

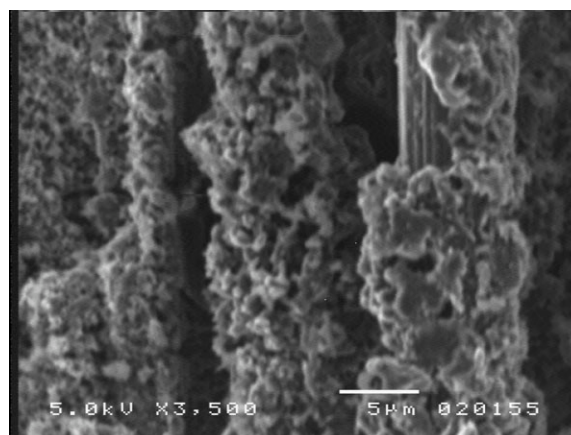


Figure 5 Scanning electron micrographs of polyEtOHCz at 3500 times magnification.

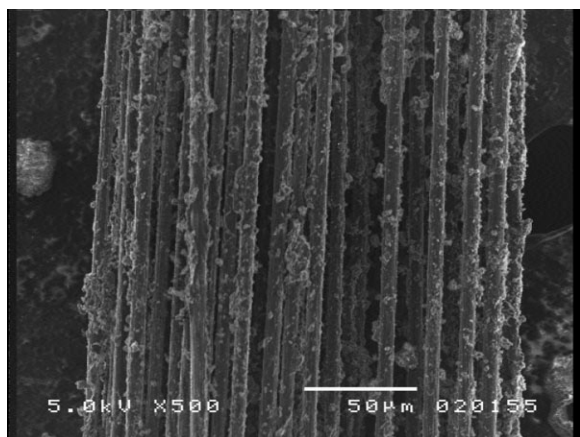


Figure 6 Scanning electron micrographs of polyEtOHCz at 500 times magnification.

shown in Figures 5 and 6. Polycarbazole is known to show a cauliflower-like structure.²⁷ The SEM micrographs (Figs. 5 and 6) of electrochemically prepared polyEtOHCz resembles PCz morphology.²¹

Figures 5–7 show SEM and AFM images of a carbon fiber electrocoated by electropolymerization of EtOHCz. The carbon surface is partially covered by the polymer (Figs. 5 and 6) as bulky grains. In Figure 7 (AFM), the initial stage and grain formation of the coating, when compared with SEM (Figs. 5 and 6), can be seen. The coated area has a small grain structure that proceeds through the sites of striations of the carbon fiber in an ordered fashion. The grains organize themselves linearly on the striations. The nucleation points on the striations of the carbon fiber surface are distributed rather homogeneously. The fractal structure is formed by the coalescence of grains in close proximity. The SEM pictures in Figures 5 and 6 indicate the latter stages of such coating, which is characterized by bulky growth and a rough surface with areas of different coating thickness (Fig. 6).

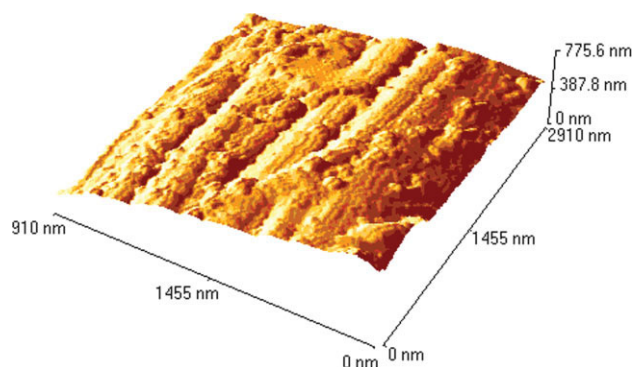


Figure 7 AFM images of polyEtOHCz obtained potentiostatically for 10 min at 1.4 V. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

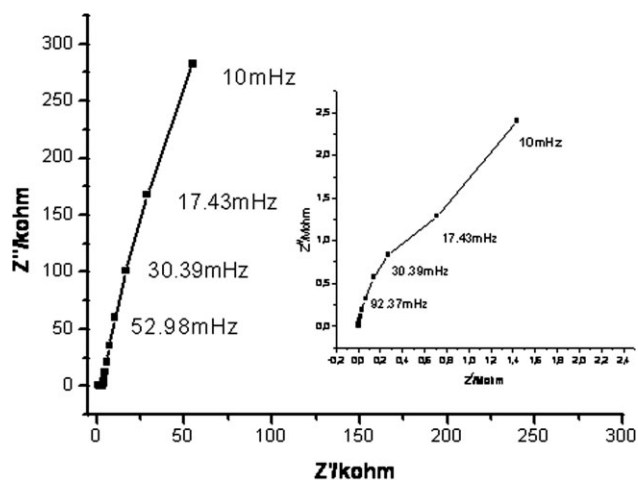


Figure 8 Complex impedance plot of polyEtOHCz, five cycles, on CFMEs in 0.05M TEAP-CH₂Cl₂, Q: 11.27 mC. Inset: complex impedance plot of PCz, five cycles, on CFMEs in 0.05M TEAP-CH₂Cl₂, Q: 1.514 mC. E_{dc} = open-circuit potential (0.48 V).

Electrochemical impedance characteristics of the polymer films

PCz and PolyEtOHCz were potentiodynamically coated on CFMEs, and then EIS measurements were performed. The complex plane impedance plots for polyEtOHCz and PCz were used to estimate the

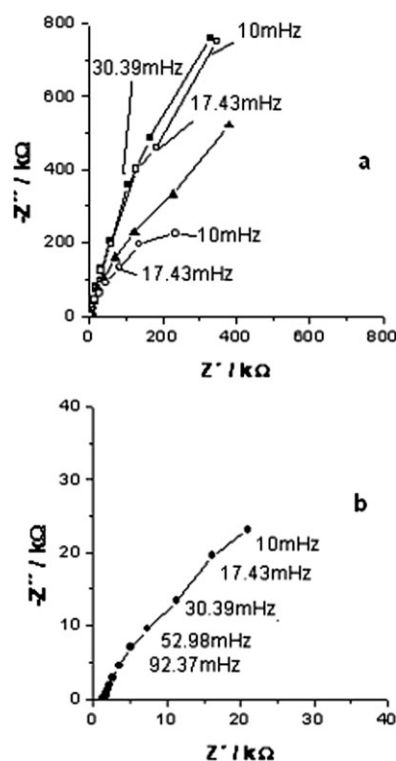


Figure 9 Complex impedance plots of (a) polyEtOHCz, five cycles, on CFMEs in 0.05M TEAP-CH₂Cl₂, Q: 11.27 mC, E_{dc} = +0.1 V (■), +0.3 V (□), +0.5 V (▲), +0.7 V (○); (b) polyEtOHCz, five cycles, on CFME in 0.05M TEAP-CH₂Cl₂, Q: 11.27 mC, E_{dc} = +1.2 V.

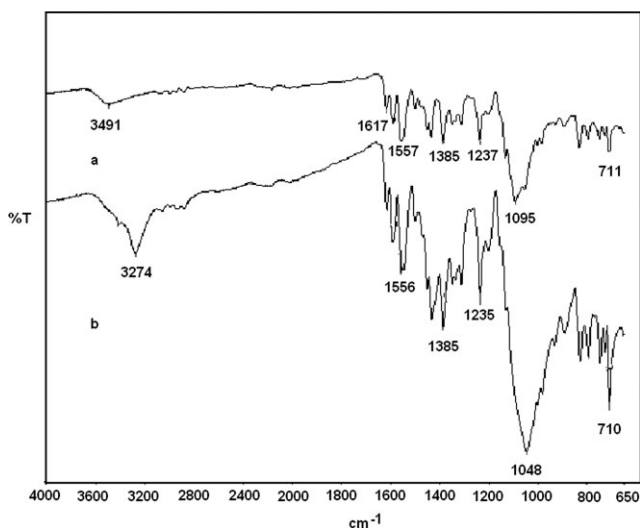


Figure 10 FTIR-ATR spectra of polyEtOHCz on CFMEs: (a) after application of 2.0 V potential and (b) before application of 2.0 V.

low-frequency redox capacitance of the polymer-modified CFMEs. At low frequency, the imaginary part of the impedance sharply increases, and the impedance plots tend to a vertical line; although trend "of a close to vertical line" will not only provide a strong conclusions regarding the capacitance changes, which might denote that the material is more reactive. Thus, the further calculations and equivalent circuit modeling are necessary (Fig. 8). The low-frequency redox capacitance (C_{LF}) was estimated from the value of the imaginary impedance ($-Z''$) at the lowest frequency used ($f = 0.01$ Hz) ($C_{LF} = -1/2\pi fZ''$). The impedance data shown in Figure 8 gives $C_{LF} = 56.4$ μ F for polyEtOHCz and $C_{LF} = 6.6$ mF for PCz, which is in agreement with the charge passed during electropolymerization (Q in Fig. 9). However, it should be mentioned that both PCz and polyEtOHCz were polymerized under identical experimental conditions (five cycles in the potential range 0–1.4 V at a scan rate of 50 mV/s). Therefore, it can be concluded that EtOHCz is more readily electropolymerized on CFMEs when compared with carbazole.

The impedance plots in Figure 8 were obtained at the open-circuit potential ($E_{dc} = 0.48$ V). Impedance plots of polyEtOHCz at different dc potentials are shown in Figure 9. The estimated value of the low-frequency redox capacitance (C_{LF}) was found to increase with increasing dc potential as follows: E_{dc} : 0.1, 0.3, 0.5, 0.7, and 1.2 V vs. C_{LF} : 21.0, 21.2, 30.4, 70.6, and 687.0 μ F, respectively.

These EIS results show that there is a dramatic increase in the redox capacitance between +0.7 and +1.2 V, which is in agreement with the cyclic voltammograms shown in Figure 3.

Polymer stability

PolyEtOHCz was prepared at constant potential (1.4 V vs. Ag/AgCl) for 1.5 h. Then, the obtained polymer was exposed to 2.0 V potential for 2 min, and the FTIR-ATR spectrum was taken (Fig. 10). A shift at the band at 1095 to 1048 cm^{-1} in the FTIR-ATR spectrum exposed 2 V potential and increase in percent transmission were observed. Since PEtOHCz film exposed to applied high potential for 2 min, because of the oxidation of polymer film, more dopant ion (ClO_4^-) incorporates into the polymer structure by leading to shift of the peak.²⁷ The FTIR-ATR spectrum of polyEtOHCz (after exposure to 2.0 V) indicates that the structure of polyEtOHCz changes very little when compared with the FTIR-ATR spectrum of the polymer before application of 2.0 V. These results indicated that the polymer is stable up to 2.0 V. This is not so common for conducting polymers.

CONCLUSION

N-Hydroxyethylcarbazole was electropolymerized more readily than carbazole on CFMEs. The hydroxylic group of the monomer seems to be a bonding between carbon fiber and polymer, the unpaired electrons of oxygen would make ease at first stage for the adsorption on carbon fiber. SEM micrographs indicated that polyEtOHCz shows a cauliflower-like structure. The polymer electrode showed capacitive behavior and also good stability up to 2.0 V. The estimated value of the low-frequency redox capacitance (C_{LF}) was found to increase with the increasing dc potential.

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