Microcomposite Electrochemical Capacitor: Electrocoating of Poly[N-(hydroxymethyl)carbazole] onto Carbon Fiber, Surface Morphology, Spectroscopic Surface Characterization, Electrochemical Impedance Spectroscopy

A. Sezai Sarac, Elif Altürk Parlak, Ersin Serhatlı, Tuba Çakır

Department of Chemistry, Polymer Science, and Technology, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

ABSTRACT: *N*-(Hydroxymethyl)carbazole (MeOHCz) was electrocoated on carbon fiber micro electrodes (diameter ∼ 7 μm) in different solvents by cyclovoltammetric method as thin film (0.17–2.73 μm). Surface characterization of electrocoated poly[*N*-(hydroxymethyl)carbazole] of carbon fiber microelectrode (CFME) was performed by reflectance FTIR spectroscopy, scanning electron microscopy, and cyclic voltammetry. Capacitor behavior of modified CFME was studied by electrochemical impedance spectrometry. The deposition rate of polymer growth affected the redox parameters of resulting coated CFME. The solvent effect on the redox and capacitor behavior of poly[*N*-(hydroxymethyl)carbazole] (PMeOHCz)-coated CFME was investigated, and electroactivity in acetonitrile (ACN) was the highest among the investigated solvents. On the other hand, the electrocoated polymer exhibited the faster charge/discharge process in propylene carbonate (PC). PMeOHCz thin film was very stable up to 1000 mV/s in ACN, PC, and dichloromethane (CH_2Cl_2). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 238–246, 2007

Key words: carbon fibers; microcomposite; electrochemical coating; surface characterization; reflectance FTIR

INTRODUCTION

Carbazole-based polymer systems have received attention because of their interesting thermal, electrical, and photo-physical properties.[1–4] Many heterocyclic nitrogen compounds, especially carbazole-based polymer systems, can be chemically polymerized to yield materials with interesting properties. Most studies examined the electrochemical oxidation of carbazole and its derivatives.[5–7] Polycarbazole (PCz) and its derivatives have been suggested for a number of applications such as redox catalyst, photoactive devices, sensors, and electrochromic displays,[8–16] showing fluorescence, photo activity, and conductivity properties.[17] However, capacitor behavior of PCz-coated carbon fiber microelectrode (CFME) was not reported in literature.

On the other hand, electropolymerization of conductive polymer onto carbon fiber offers the advantage of controlling the thickness and functionality of such a 'reactive' coating through selective processing parameters (i.e., the current density, monomer concentration, and solvent), and hence, uniform coatings may be achieved.[9,12–14] The inclusion of various functional groups into the electrografted polymers opens the possibility of using such modified fibers in the design and production of advanced reinforced polymeric materials, and microcomposite materials serving as electrochemical capacitors (EC).

Electrochemical capacitors, also called supercapacitors,[18–20] are unique devices exhibiting 20–200 times greater capacitance than conventional capacitors. The large capacitance exhibited by these systems has been demonstrated to arise from a combination of the double-layer capacitance and pseudocapacitance associated with the participation of adsorbed intermediates in the surface redox-type reactions. Electrochemical capacitors exhibit high cycle life and good stability, thus making them useful in applications such as lightweight electronic fuses, backup power sources for calculators, and surge-power delivery devices for electric vehicles. Commercially available ECs have been optimized for memory backup applications, which typically are 5 V loads requiring currents of 100 pA or less. ECs are maintenance-free substitutes for batteries in such applications.

Carbon as a material for the storage of energy in electrochemical capacitors seems to be extremely attractive, and these capacitors have been also exten-

sively developed because of the increasing demand for a new kind of accumulator of electrical energy with a high specific power of more than 10 kW/kg. The main advantage of this storage device is the ability of a high dynamic of charge propagation (short-term pulse) that can be useful in the hybrid power sources for electrical vehicles, digital telecommunication systems, UPS (uninterruptible power supply) for computers, and pulse laser technique. Higher energy densities can be achieved because charging occurs through the small volume of material. Taking into account the cost and compatibility of these two materials, the modification of carbon with very thin conducting polymer films is very interesting. Studies on nanocomposites and electrochemical nano- and micron-sized capacitors are very attractive because of their higher energy densities through the small volume of material.[21]

Capacitor behavior of CFME properties can be significantly enhanced by the formation of carbon/conducting polymers as nano and microcomposites by electropolymerization of a suitable monomer, i.e., carbazole derivatives, such system can represent a very well-defined region of pseudocapacitance properties because of the Faradaic redox reactions of their rich surface functionality.

In this article, we describe the electrochemical thin film coating of N-(hydroxymethyl)carbazole (PMeOHCz) onto CFME, and characterization of surface functionalities and surface morphology by FTIR reflectance, cyclic voltammetry, and scanning electron microscope (SEM). Evaluations of capacitor performance by different techniques, e.g., voltammetry, electrochemical impedance spectroscopy (EIS), charge/discharge characteristics are reported. Effect of solvent and scan rate on the redox properties and structure of thin polymeric film which was electrocoated onto CFME, was also investigated.

EXPERIMENTAL

Materials

N-(Hydroxymethyl)carbazole was synthesized according to the method described in literature.[21] Tetraethylammonium perchlorate (TEAP) was obtained from Fluka. CH$_2$Cl$_2$ and acetonitrile (ACN) were purchased from Riedel-Dehaen. Propylene carbonate (PC) was obtained from Sigma-aldrich. A high-strength (HS) carbon fiber C 320.000A (CA) (Sigri Carbon, Meitingen, Germany) containing 320,000 single filaments in a roving were used as working electrodes. All the electrodes were prepared by using CFME (diameter ~ 7 μm) attached to a copper wire with a Teflon tape. The electrode area keeps up constant (~ 0.5 cm^2) by adjusting the dipping length and covering the rest of the fibers with the Teflon tape in electrochemical cell.

Ubbelohde viscosimeter was used for measuring of viscosity of solvents at 40°C.

Electrochemical polymerization and electrochemical impedance spectroscopic measurements

Polymerization reactions were performed electrochemically in CH$_2$Cl$_2$ solution containing 0.05M TEAP and monomer. Cyclic voltammogram (CV), of the polymers were obtained with Parstat 2263-1(software; powersuit) in a three-electrode setup employing CFME as working, and Ag/AgCl as reference electrode. Electropolymerization at constant potential electrolysis conditions was carried out using Wenking model LB 81 Potentiostat. Electrochemical impedance measurements were conducted in monomer free electrolyte solution with a perturbation amplitude 10 mV over a frequency range 0.01–100 kHz with Parstat 2263-1 (software; powersuit).

FTIR-ATR spectrometry

Electrografted CFMEs (with a single-grafted CF) were analyzed by FTIR reflectance spectrometry (Perkin–Elmer, Spectrum One B, with an ATR attachment Universal ATR-with ZnSe crystal).

Fiber surface morphology

All modified carbon fibers were analyzed by scanning electron microscopy (SEM) using a Hitachi S-2700 scanning electron microscope (Nissei Sangyo GmbH, Rathingen, Germany), which was connected to an energy dispersive X-ray microanalyzer (EDX) (Kevex type delta V, Foster City, CA). The excitation energy was 10 keV at a beam current of 0.5 nA.
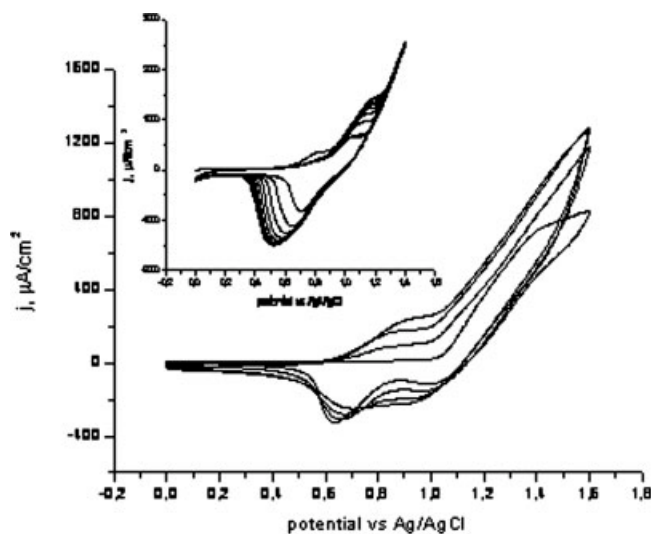
RESULTS AND DISCUSSION

Synthesis of monomer

N-(Hydroxymethyl)carbazole (N-MeOHCz) was prepared by Tawney method.[22] To a suspension of 10 g (0.06 mol) of carbazole in 25 mL of 37% formaldehyde, 2 mL of 5% sodium hydroxide was added at 30°C (Scheme 1). Within 10 min, all the carbazole had dissolved and a mildly exothermic reaction had
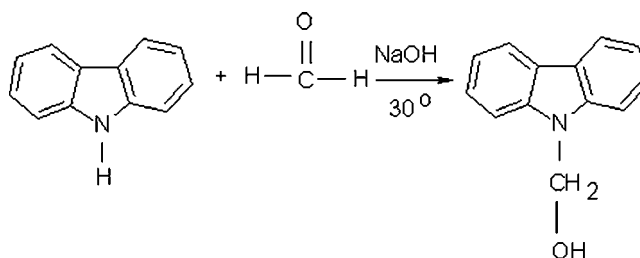

Scheme 1 The monomer(N-MeOHCz) synthesis.

Figure 1 Potentiodynamic growth of MeOHCz on CFME in 0.05M TEAP/CH$_2$Cl$_2$ (scan rate: 60 mV/s). Inset: Potentiodynamic growth of Cz on CFME in 0.05M TEAP/CH$_2$Cl$_2$(scan rate: 60 mV).

raised the temperature to 33°C. Separation of the product began promptly. After 2.5 h, at room temperature the solution was filtered, dried in vacuum. Several recrystallizations were made from n-hexane. The product have resulted a mp: 133°C, and yield obtained as 65%. ^{1}H-NMR, FTIR absorption frequencies data was as following: ^{1}H-NMR (DMSO-d_6), (ppm): 5.7–5.9 (d,2H),6.3–6.6 (t,1H), 7.2–8.2 (m,8H).

Electropolymerization

Electrochemical coatings of N-(hydroxymethyl)carbazole (initial monomer concentration of 1 mM) on
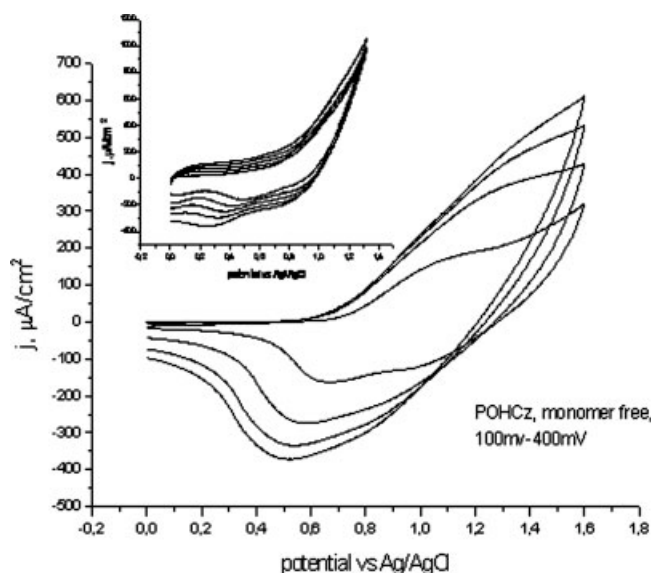
Figure 2 Scan rate dependence of PMeOHCz on CFME in 0.05M TEAP/CH$_2$Cl$_2$.(scan rate: 100–400 mV/s). Inset: Scan rate dependence of PCz on CFME in 0.05M TEAP/CH$_2$Cl$_2$.

CFME working electrode was carried out in 0.05M TEAP/CH$_2$Cl$_2$ by cyclovoltammetric method (Figure 1), and electrochemical behavior and the redox properties of thin film coating of the PMeOHCz/CFME were followed by CV during the electrogrowth process. For comparison, the electropolymerization of carbazole (Cz) was also carried out in the similar conditions (Inset of Fig. 1).

Cyclic voltammograms corresponding to the potentiodynamic electrochemical coating (and electrooxidation of film electrocoated onto CFME) of N-(hydroxymethyl)carbazole (MeOHCz) on carbon fiber microelectrode(CFME) were given in Figure 1. Application of potential between 0 and 1.6 V versus Ag/AgCl reference electrode induces the development of a redox system corresponding to the doping/undoping process of the growing film. A redox system grows rapidly at about 0.87 V versus Ag/AgCl with a slower electrodeposition rate than PCz
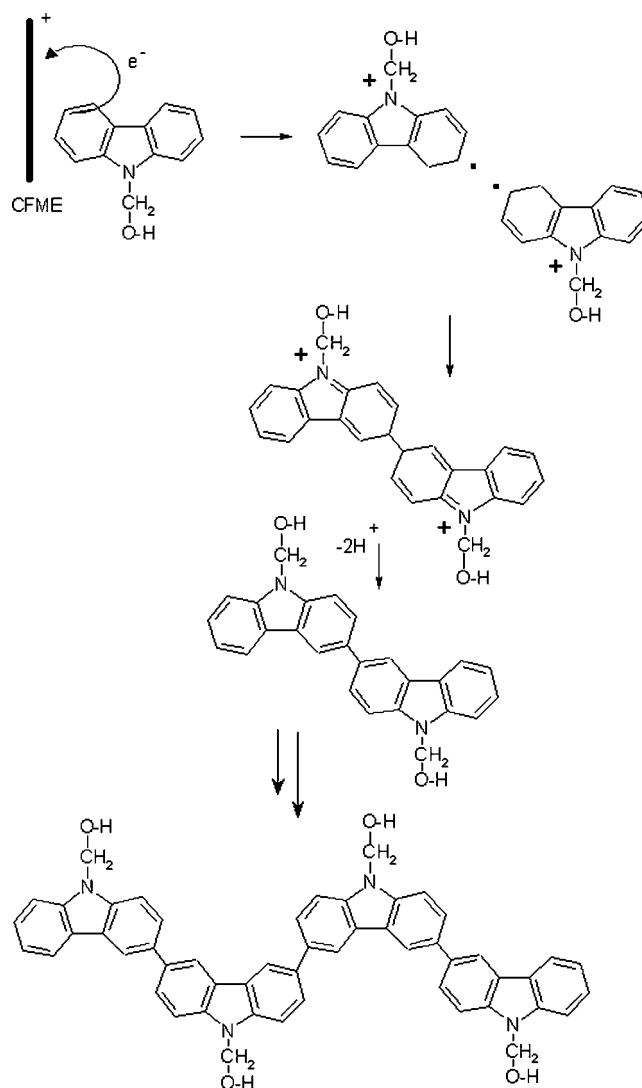
Scheme 2 The electrochemical oxidation and growth mechanism of MeOHCz on CFME.
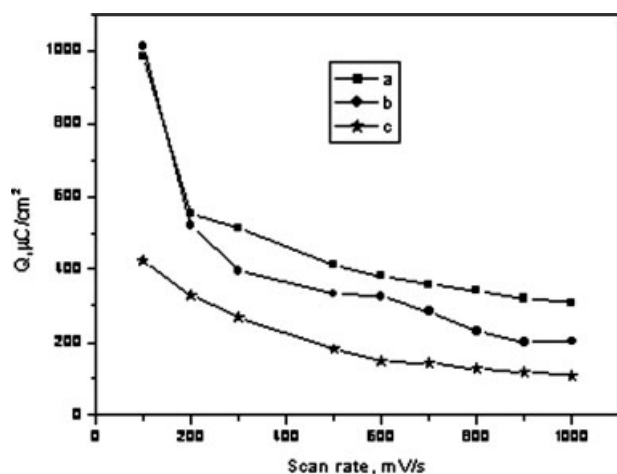
Figure 3 Charge versus scan rate plot of poly[*N*-(hydroxymethyl)carbazole] in 0.05M TEAP. (a) ACN, (b) PC, (c) CH$_2$Cl$_2$.

Figure 4 Current density versus charge-transfer resistance, R_{ct} relationship. PMeOHCz electrodeposited on CFME potantiostatically in TEAP/CH$_2$Cl$_2$. The current density values is obtained from CV of PMeOHCz in TEAP electrolyte in three different solvents; ACN (the smallest R_{ct}), PC, CH$_2$Cl$_2$ (the biggest R_{ct}).
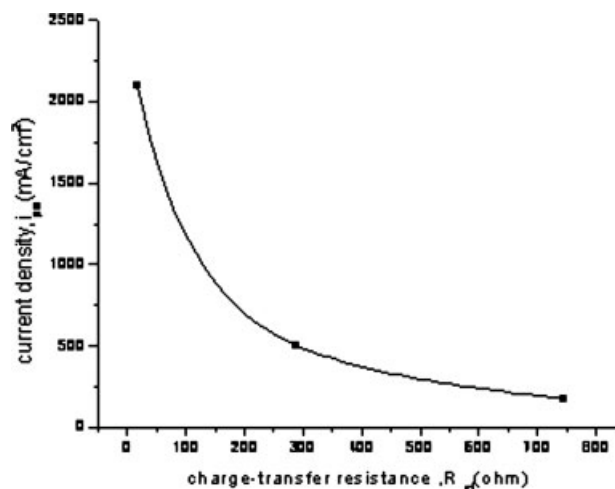
(Fig. 1 inset). A regular growth was observed for both polymers as a linear increase in current with subsequent cycles indicating the polymer electrodeposition on CFME.

The effect of scan rate on electropolymerization was shown in Figure 2. Scanning in monomer free solution (only in 0.05M TEAP/CH$_2$Cl$_2$ electrolytic solution) was performed to understand the diffusion properties and the effect of electrolyte on electrodeposited polymer film from 1 mM MeOHCz in 0.05M TEAP/CH$_2$Cl$_2$. The peak currents in the cyclic voltammogram appeared to increase linearly with the increase of scan rate suggesting that electroactive layer is deposited on the electrode and the oxidation and reduction processes are not limited by diffusion. The half-wave potential ($E_{1/2}$) of the PMeOHCz is about 0.85 V versus Ag/AgCl higher than PCz ($E_{1/2}$ = 0.45 V) indicating that PMeOHCz electrode is more stable.

Scheme 2 represents the electrochemical oxidation and growth mechanism of MeOHCz on CFME, in which initial formation of radical cation is followed by coupling and deprotonation results in dimer (and oligomer, polymer) formations. The electrocoated polymer shows a relatively high electroactivity in ACN (Fig. 3). The order of the current densities in different solvents (Fig. 4) indicates the ease of coupling reaction of radical cation species in ACN than in PC and CH$_2$Cl$_2$, where the charge-transfer resistance in double layer is the lowest among these solvents (Scheme 2).

Effect of scan rate and solvent on the electropolymerization of *N*-(hydroxymethyl) carbazole

The effect of scan rate was also investigated for the electropolymerization process of *N*-(hydroxymethyl)-

carbazole (Table I). The change of the scan rate affected the redox parameters of electrogrowth. The peak separation between anodic and cathodic peak potentials (ΔE) during polymer growth was the smallest with 20 mV/s of scan rate, indicating the better reversibility of polymer growth, and the increase of ΔE with scan rate is of due to ohmic resistance of the modified electrode which effects the electrochemical reversibility (Table I).

In addition to the cyclovoltammetric coatings, electropolymerization of MeOHCz was also performed at a constant potential 1.4 V for 1 h. After electropolymerization, poly(MeOHCz)-coated CFME electrode was washed with monomer free electrolyte and solvent, and then the effect of electrolyte on the redox behavior of these electrodes was studied (Fig. 3). Polymer electrode was stable up to 1000 mV/s in all solvents, however, the anodic currents determined at 0.69 V for 1000 mV/s scan rate was the highest in ACN. The order of the current densities in different solvents are as following: ACN (2099 mA/cm^2) > PC (502 mA/cm^2) > CH$_2$Cl$_2$ (175 mA/cm^2). As shown in Figure 3, the polymer shows a relatively highest electroactivity in ACN.

TABLE I
The Effect of Scan Rate on Redox Parameters of Polymer Growth[a] (MeOHCz) : 1 mM

Scan rate	E_a (V)	E_c (V)	ΔE (V)	i_a/i_c
20	0.739	0.668	0.071	0.619
40	0.811	0.609	0.202	0.264
60	0.839	0.636	0.203	0.233
80	0.837	0.687	0.150	0.293

[a] Redox parameters are determined from 2nd cycle.

Solvent	Dielectric constant	Kinematic viscosity (10^4 m^2/s)	R_s (Ω)	R_{ct} (Ω)	C_{dl} (μF/cm^2)
ACN	36.64	0.31	38	18	5650
PC	66.14	1.38	3.4	289	513
CH$_2$Cl$_2$	8.90	0.44	837	745	794

The separation between anodic and cathodic peaks is associated with ion transport resistance involved in these redox reactions.[23–26] Thus, the difference between the anodic and cathodic peak potentials (ΔE) can serve as indication for the resistance of ion migration in the electrode. The variation of ΔE with the solvent of poly(MeOHCz)/CFME indicated that CH$_2$Cl$_2$ ($\Delta E_{CH_2Cl_2} = 0.28$) has highest resistance of ion migration. This fact was also proved by charge-transfer resistance (R_{ct}) values obtained in different solvents by EIS, i.e., the highest R_{ct} was obtained for CH$_2$Cl$_2$ and the smallest R_{ct} was obtained for ACN (Table II). Poly(MeOHCz)/CFME in ACN ($\Delta E_{ACN} = 0.05$) revealing to a lower resistance electrolyte penetration. The electroactivity of poly(MeOHCz)/CFME is also higher in ACN than that in PC and

CH$_2$Cl$_2$ (and the rate of charge transport is higher too). High viscosity of PC causes a decrease of heterogeneous electron-transfer rate,[27] the polymer obtained in PC has lower double-layer capacitance (C_{dl}) and highest R_{ct} in ACN, and low viscosity of ACN might be an advantage for obtaining better final electrical properties. The results can be attributed to the difference in the environment of diffusion of the solvents/electrolyte, and to combination of dielectric and viscosity effect of solvents (Table II).[28]

Additionally, inverse relationship between the current density and R_{ct} was obtained, and decrease in conjugation (decrease in current density of peak in electrocoated polymer film) results an increase in R_{ct} (Fig. 4).

Morphology

The morphologies of the polymers obtained with different scan numbers were investigated comparatively by scanning electron microscopy (SEM) (Fig. 5). Poly[N-(hydroxymethyl)carbazole] on CFME were grown potentiodynamically (by cyclovoltammetry) with scan rate of 50 mV/s from solution of 1 mM MeOHCz in 0.05M TEAP/CH$_2$Cl$_2$.

Because the aromatic and heterocyclic structure of MeOHCz is same to Cz except the N-(hydroxymethyl) substituent on carbazole nitrogen, poly
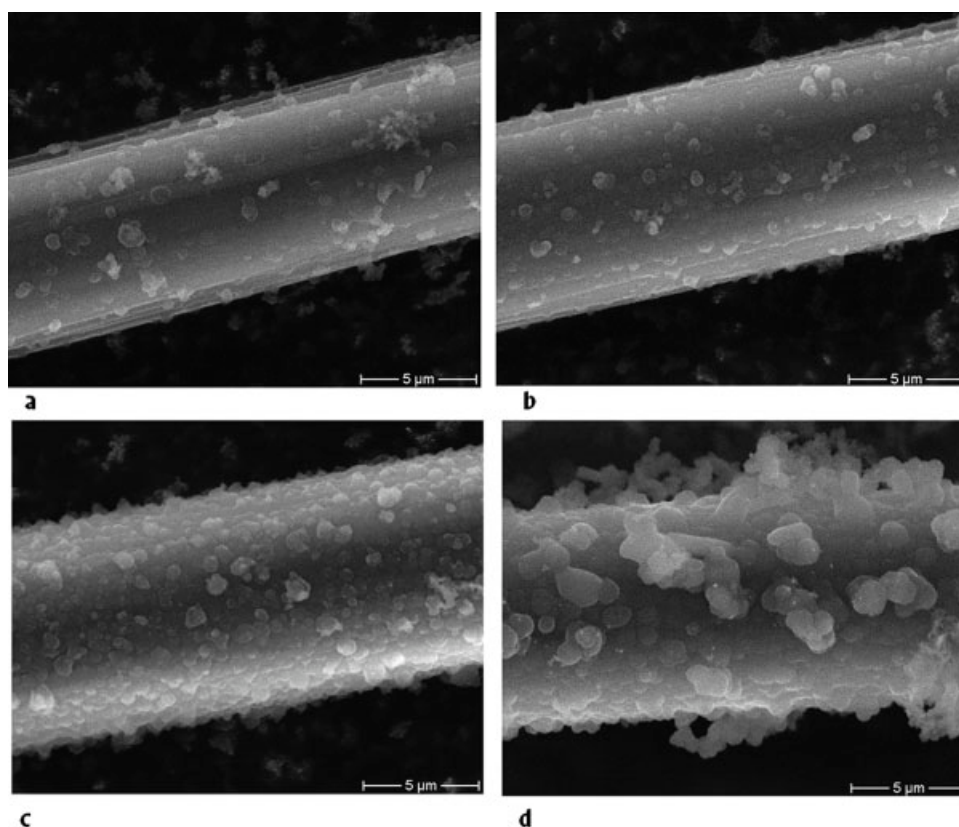

Figure 5 SEM photographs of poly[N-(hydroxymethyl)carbazole] (a) 3 cycle, (b) 5 cycle, (c) 10 cycle, (d) 15 cycle.
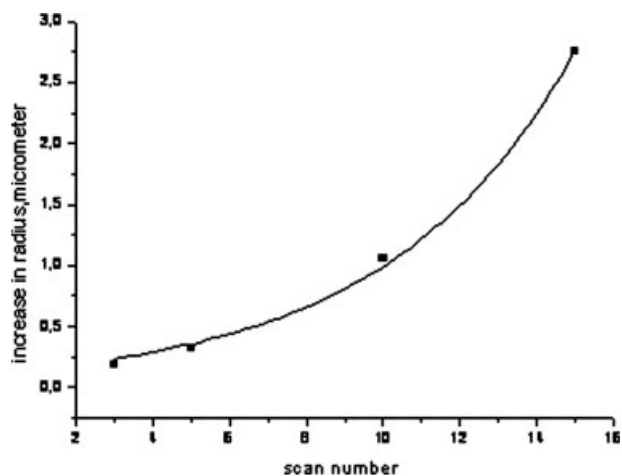
Figure 6 Avarage increase in radius of polymer film (obtained from SEM photographs) versus cyclovoltametric scan number.

(MeOHCz) structure resembles to PCz (cauliflower-like).[29] Increasing scan number (corresponds to increase in applied charge) during electrodeposition, results in an increase in diameter of CFME. The thickness versus scan number graph was plotted according to the average thickness as measured from SEM of samples. Carbon fiber working electrode has diameter dimensions in micrometer, and the coated film (poly MeOHCz) has a radius of about 3 μm. This system can be considered as a microcomposite electrode system. The data obtained under these conditions, which can be used as calibration curve for different scan numbers, and CV results can be used to determine the thickness of the film (Fig. 6).
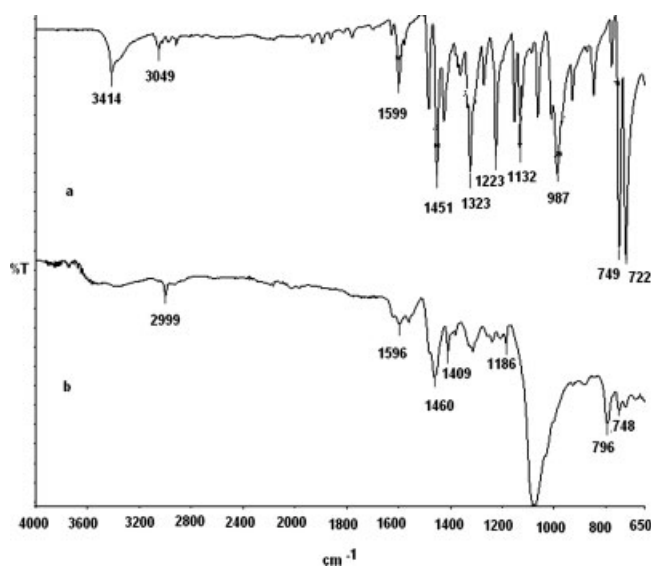

Figure 7 FTIR-ATR spectra of (a) monomer, (b) polymer obtained in TEAP/CH$_2$Cl$_2$ with the scan rate of 50 mV/s.

## Reflectance FTIR surface spectra of poly(MeOHCz) coated CFME

The FTIR-reflectance spectra of electrografted poly [N-(hydroxymethyl)carbazole] prepared at constant potential electrolysis condition was taken (30 min electrolysis at 1.4 V). The monomer has characteristics peaks at 3414, 1626, 1599, 1451, 1323, 1223, 987, 749, 722 cm^{-1} [Fig. 7(a)]. The FTIR-ATR spectrum of N-(hydroxymethyl)carbazole indicated that the peak at 3414 cm^{-1} attributed to alcohol band stretching, and 2916 cm^{-1} can be attributed to methyl (CH$_2$) groups of N-(hydroxymethyl)carbazole, 1539 cm^{-1} is due to aromatic ring of carbazole (Cz), and 1223 cm^{-1} (carbazole C—N stretching), at 745 cm^{-1} are evidence for the out of plane bending of aromatic C—H deformation [Fig. 7(a)]. In the FTIR-ATR spectrum of PMeOHCz-coated CFME surface, some shifts and some new peaks appearances are observed when it is compared with the monomer spectrum. Figure 7(b) represents the reflectance FTIR spectra of poly(-MeOHCz) coated on CFME, the peak at 796 cm^{-1} attributed to C—H deformation of out of plane of trisubstituted 1,2,4 carbazole cycle and 748 cm^{-1} C—H deformation out of plane-adjacent 4H 1,2,3,4 at the end of chains of disubstituted carbazole cycle[30] the band located at 1313 cm^{-1} is confirmed by the valence vibration of C—N bond of carbazole cycle.[31] Moreover, the peaks at 1090 cm^{-1}, which is attributed to doping of ClO$_4^-$ anion because of the doping of the electrolytes of TEAP/CH$_2$Cl$_2$.[32] The peak at 1596–1460 cm^{-1} is also evidence for aromatic stretching of double bond C=C.[33]

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) allows to study the charge transfer, ion diffusion, and capacitance of conducting polymer-modified electrodes. The typical Nyquist plots of poly[N-(hydroxymethyl)carbazole]-coated CFME in different solvents
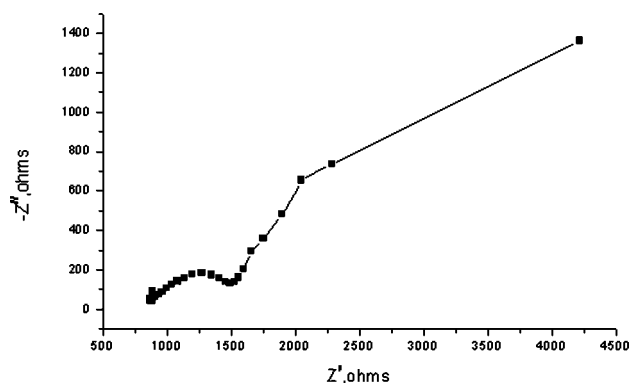
Figure 8 Nyquist plot of PMeOHCz in TEAP/CH$_2$Cl$_2$.
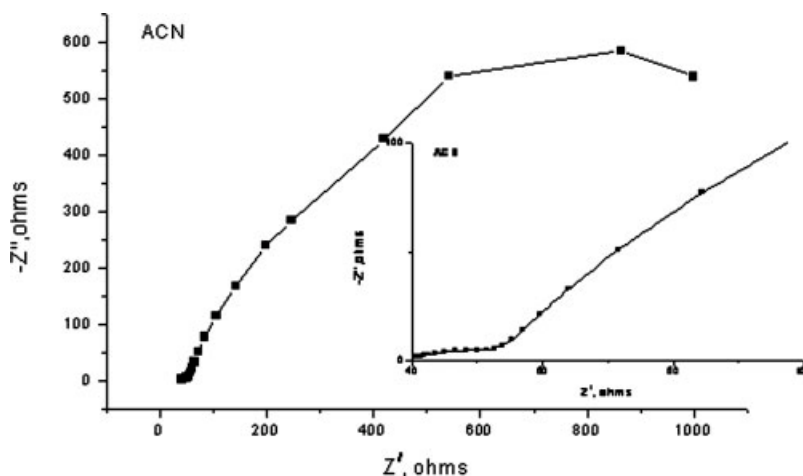
Figure 9 Nyquist plot of PMeOHCz in TEAP/ACN. Inset: Nyquist plot of PMeOHCz in TEAP/ACN. (High frequency region was expanded).

are given in Figures 8–10. The results indicated the semicircle behavior at high frequency and capacitive behavior at low frequency. That semicircle can be attributed to the process occurs at the polymer-electrolyte interface at high frequencies, which is expected to be the double-layer capacitance (C_{dl}) in parallel with the charge-transfer resistance (R_{ct}) because of the charge exchange and compensation at the polymer-solution interface.[34]

Bode magnitude plot gives extrapolating the linear section to the log Z axis at $w = 1$ (log $w = 0$) yields the value of C_{dl}[33] from the relationship:

$$|Z| = 1/C_{dl}$$

The C_{dl} is attributed to charge accumulation at polymer-solution interface that was highest (5650 µF/cm^2) for ACN. The R_{ct} values can be associated with

redox processes within the polymeric film. As can be seen in Table II, R_{ct} values are higher in CH_2Cl_2 and PC than in ACN, however, the lowest R_{ct} values were obtained in ACN that this solvent has the medium dielectric constant and lowest viscosity among the solvents used.

The results indicated that the choice of solvent is important for the value of capacitance of the polymer coated CFME.

From the frequency (f_0) corresponding to the maximum of the imaginary component (Z'') of the semicircle, the time constant Γ of every electrode can be calculated using the relationship:

$$\Gamma = 1/2\pi f_0 \tag{1}$$

The values of Γ obtained from the Nyquist plots are 3.8 ms (CH_2Cl_2), 0.24 ms (ACN), and 0.13 ms (PC) for PMeOHCZ/CFME in different solvents. The lower
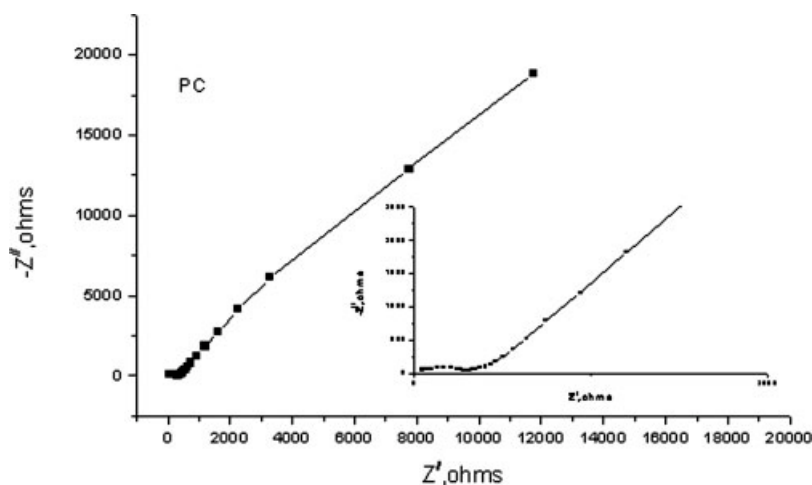
Figure 10 Nyquist plot of PMeOHCz in TEAP/PC. Inset: Nyquist plot of PMeOHCz in TEAP/PC. (High frequency region was expanded).
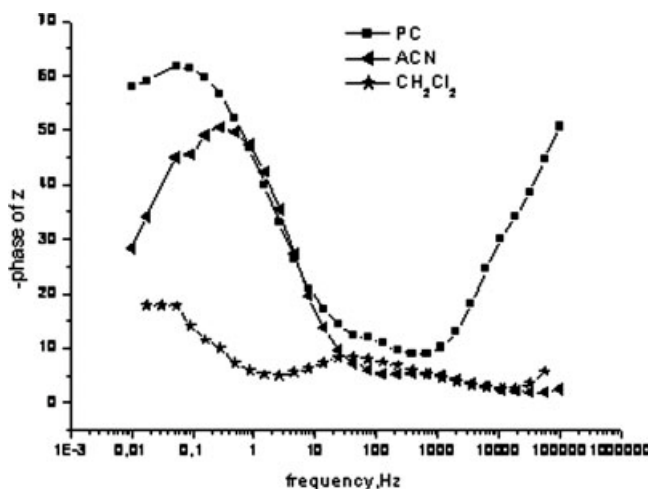
Figure 11 Bode plot of PMeOHCz (a) PC, (b) ACN, (c) CH$_2$Cl$_2$.

Γ value is preferred for electrochemical capacitor for fast charge/discharge processes.[31] PMeOHCz/CFME show faster charge/discharge process in PC.

In the bode phase plot of PMeOHCz in TEAP/PC, the bode phase angle approaches a plateau (61°), in the frequency region of 49–89 mHz which film indicates capacitor behavior, In the frequencies, 0.16–41 Hz, phase transition from capacitor to resistor behavior was observed. In the frequencies, 41–698 Hz film showed resistor behavior, in the frequency region of 698–100 kHz transition from resistor to capacitor behavior was observed (Fig. 11).

The bode phase plot of PMeOHCz/CFME in TEAP/ACN is indicated that at higher frequency >100 Hz, because of the prevailing influence of the electrolyte resistance, it behaves like ideal resistor by having a very low bode phase angle. In the frequencies 1–100 Hz, the film shows transition from resistor to capacitor. At frequencies <1 Hz, the bode phase angle approaches to a plateau, and in this time scale, the electrical signal reaches maximum penetration in the pores of the PMeOHCz electrode (Fig. 11).

In the bode phase plot of PMeOHCz in CH$_2$Cl$_2$, two plateaus were observed between 45 Hz and 10 mHz, however, the bode phase angle was 18° meaning that the PMeOHCz/CFME in CH$_2$Cl$_2$ indicates lower capacitive behavior than in PC and ACN.

Figure 11 also indicates the effect of solvent on the polymer capacitor behavior, and capacitance increases by following order, PC > ACN > CH$_2$Cl$_2$.

CONCLUSIONS

Electrodeposition and surface characterization of thin film of poly(MeOHCz) (with a thickness increase of 170–2730 nm) electrodeposited onto CFME, clearly

indicates that the electrodeposition conditions has an important effect on the electropolymerization of MeOHCz (e.g., scan rate). PMeOHCz-coated CFME exhibited very high electrochemical stability up to scan rate of 1000 mV/s. The thin conductive polymeric film showed better charge/discharge process in PC (dielectric constant is the highest), different redox properties, and capacitive behaviors in different solvents, indicating the crucial effect of solvents on polymeric thin film properties on carbon surface. These results indicate that electrochemically modified carbon fiber microelectrodes (by conductive thin polymer film coating) can be used for the storage of energy in electrochemical capacitors (super micro-capacitors). In this article, it was proven that, nano to micron size coatings of conductive polymers on micron-sized carbon fibers allows micro-scale energy storage applications with success.

References

1. Morisihima, Y. Prog Polym Sci 1990, 25, 949.
2. Novakowska, M.; White, B.; Guillet, J. E. Macromolecules 1989, 22, 3903.
3. McCormick, C. L.; Hoyle, C. E.; Clark, M. D. Macromolecules 1990, 23, 3124.
4. Madhavan, S.; Santhanam, K. S. V. Mol Cryst Liq Cryst 1988, 160, 111.
5. Ambrose, J. F.; Nelson, R. F. J Electrochem Soc 1968, 115, 1159.
6. Ambrose, J. F.; Carpenter, L. L.; Nelson, R. F. J Electrochem Soc 1975, 122, 876.
7. Sundaresan, N. S.; Santhanam, K. S. V. Indian J Technol 1986, 24, 417.
8. Sarac, A. S.; Bardavit, Y. Prog Org Coat 2004, 4, 85.
9. Jamal, M.; Sarac, A. S.; Magner, E. Sens Actuators B Chem 2004, 97, 59.
10. Yavuz, O.; Sarac, A. S. Abstr Paper Am Chem Soc 1999, 218, U405.
11. Sezer, E.; Ustamehmetoğlu, B.; Sarac, A. S. Int J Polym Anal Char 1999, 5, 157.
12. Sarac, A. S.; Serantoni, M.; Tofail, S. A. M.; Cunnane, V. J. J Nanosci Nanotechnol 2005, 5, 1677.
13. Sarac, A. S.; Serantoni, M.; Tofail, S. A. M.; Cunnane, V. J. McMonagle, J. B. Appl Surf Sci 2005, 243, 183.
14. Sarac, A. S.; Tofail, S. A. M.; Serantoni, M.; Cunnane, V. J. J Mater Sci 2004, 39, 2945.
15. Sarac, A. S.; Sezer, E.; Ustamehmetoglu, B. Polym Adv Technol 1997, 8, 556.
16. Sarac, A. S.; Sezer, E.; Ustamehmetoglu, B.; Mannschreck, A.; Stephan, B. Polym Adv Technol 1997, 8, 563.
17. Taoudi, H.; Bernede, J. C.; Bonnet, A.; Morser, M.; Godoy, A. Thin Solid Films 1997, 304, 48.
18. Kötz, R.; Carlen, M. Electrochim Acta 2000, 45, 2483.
19. Deyang, Q.; Shi, H. Electrochim Acta 1998, 74, 99.
20. Zheng, J. P.; Jow, T. R. J Power Sources 1996, 62, 155.
21. Nishino, A. J Power Sources 1996, 60, 137.
22. Tawney, P. O.; Synder, R. H.; Bryan, C. E.; Conger, R. P.; Dovell, F. S.; Kelly, R. J.; Stiteler, C. H. J Org Chem 1960, 25, 56.
23. Kakiuchi, T. Electrochim Acta 1998, 44, 171.

24. Abd El-Rahman, H. A. Thin Solid Films 1997, 310, 208.
25. Csahok, E.; Vieil, E.; Inzelt, G. J Electroanal Chem 2000, 482, 168.
26. Robberg, K.; Paasch, G.; Dunsh, L.; Ludwig, S. J Electroanal Chem 1998, 443, 49.
27. Zang, X.; Leddy, J.; Bard, A. J. J Am Chem Soc 1985, 107, 3719.
28. Conway, B. E. Electrochemical Supercapacitors: Scientific, Fundemantals, and Technological Applications; Plenum Publishing: New York, 1999; p 366.

29. Inzelt, G. Electrochim Acta 1983, 34, 83.
30. Wellinghoff, S. T.; Schwab, S. T.; Herrera, C. D.; Jenekhe, S. A.; Racchini, J. R. Synth Met 1988, 22, 273.
31. Kham, K.; Sadki, S.; Chevrot, C. Synth Met 2004, 145, 135.
32. Papez, V.; Inganas, O.; Cimrova, V.; Nespurek, S. J Electroanal Chem 1991, 282, 123.
33. Sezer, E.; Ustamehmetoglu, B.; Sarac, A. S. Synth Met 1997, 107, 7.
34. Burke, A. J Power Sources 2000, 91, 37.