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SHORT COMMUNICATION

Capacitive behavior of polycarbazole- and poly (N-vinylcarbazole)-coated carbon fiber microelectrodes in various solutions

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Abstract The electrochemical behavior of polycarbazole (PCz) and poly(N-vinyl carbazole) P(NVCz) was investigated by means of electrochemical impedance spectroscopy (EIS). Supporting electrolytes made from various combinations of solvents (acetonitrile and propylene carbonate) and salts (sodium perchlorate, lithium perchlorate, and tetraethyl ammonium perchlorate) were employed in the investigation. Information on the double layer capacitance (C_{dl}) and specific capacitance (C_{sp}) of P(NVCz) was achieved by cyclic voltammetry (CV), chronoamperometry and chronopotentiometry. Carbon fiber microelectrodes (CFME) were electrocoated by cyclic voltammetry in a monomer-free solution and displayed film thicknesses in the range ~200 nm to ~4.8 μm. The capacitive behavior of the PCz- and P(NVCz)-coated carbon fiber microelectrodes was also investigated by CV. The effects of the type of electrolyte and solvent on the electrochemical impedance spectroscopic data were subsequently fitted with an ((R(C(R(Q(RW))))(CR))-equivalent circuit model to calculate the numerical values of the proposed components. The obtained experimental C_{sp} values for PCz/CFME and P(NVCz)/CFME, as measured in $LiClO_4$/ACN, were 280.5 mF g^{-1} and 294.1 mF g^{-1}, respectively.

Keywords Electrochemical impedance spectroscopy · Carbon fiber microelectrode · Electrocoating · Electrochemical properties · Equivalent circuit

1 Introduction

Conducting polymers are modern materials that have found remarkable applications in current technologies as a result of their conductivity and electroactivity. Moreover, they demonstrate significant potential for new applications. Their synthesis and properties have been extensively studied due to a growing interest in the polymerization mechanism and redox transformations between conductive and passive states [1]. Conductive polymers have been investigated since the late 1970s [2–4], and with the aim of finding technical applications, numerous studies have been dedicated to the synthesis and characterization of materials such as polycarbazole [5, 6], polyaniline [7], polypyrrole [8, 9], poly(N-vinyl carbazole) [10], poly(carbazole-co-p-Tolylsulfonyl pyrrole) [11], poly(N-methylpyrrole-co-carbazole) [12], poly(3,4-ethylenedioxythiophene) [13, 14] poly(N-methylpyrrole-co-N-methylcarbazole) [15] and poly(N-methylpyrrole-co-N-ethylcarbazole) [16]. These polymers are chemically stable in a variety of solutions (from strongly acidic to basic) and are able to perform well within a wide range of temperatures.

Recently, carbon-based materials have increased in popularity thanks to their electrochemical applications [17, 18]. As an electrode material, carbon has several advantages (e.g., good polarization of the electrode, a high surface area, a considerable process capacity, as well as thermal and chemical stability) as compared to other electrode materials [19]. Furthermore, the application of carbon electrode materials has received great interest

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because of their accessibility, ease in processability and relatively low cost. Already well established chemical and physical methods of activation render it possible to produce materials with a developed surface area and a controlled distribution of pores determining the electrode/electrolyte interface for electrochemical applications [20]. A further development of these techniques, e.g., to analyze such thin layers, is fundamental to understand the interfacial interaction between the carbon surface and its polymer coating [21]. Modified reinforcing fibers can potentially be employed as advanced reinforced polymeric composite materials, with possible applications in high-strength structural materials for aircrafts, suspension bridges [22] and biosensor applications [23]. The capacitor behavior of CFME can be significantly enhanced by the formation of carbon-conducting polymers in nano- and micro-composites by electropolymerization of a suitable monomer (e.g., carbazole derivatives). Electrochemical impedance spectroscopy has proved to be a powerful tool for studying polymer film electrodes [24–30]. Such systems can represent a well-defined region of pseudo-capacitance properties, given the Faradaic redox reactions of their rich surface functionality [31]. Porous carbon, the most frequently selected electrode material, offers a large surface area and a good polarization due to its porosity, which makes it a promising electrode material for supercapacitor applications [32–34].

Previous reports have been devoted to the effect of solvents and electrolytes on the redox properties and structures of electrochemically coated thin polymeric films of polycarbazole [35] on CFME. This article describes the use of EIS to evaluate the capacitor performance of CFMEs electrocoated by means of a cyclic voltammetric procedure with polycarbazole and poly(N-vinylcarbazole) obtained in various solutions.

2 Experimental

2.1 Materials

Carbazole (Cz, >99% purity) and electrolytes (sodium perchlorate ($NaClO_4$, >98%), lithium perchlorate ($LiClO_4$, >98%), tetraethyl ammonium perchlorate (TEAP)) were purchased from Merck. N-vinylcarbazole (NVCz, 98%) was bought from Aldrich. Acetonitrile (ACN), propylene carbonate (PC, >99%) and acetone (99.7%, Purex PA) were obtained from Carlo Erba.

A high strength (HS) C320000A (CA) carbon fiber (Sigri Carbon, Meitingen, Germany), containing 320000 single filaments in a roving, was used as a working electrode. All electrodes were prepared using CF (diameter ~7 μm). The exposed area of the working electrode was kept constant (~0.33 cm^2) by adjusting the dipping length and covering the rest of the fibers with Teflon tape.

2.2 Instrumentation

The electrochemical measurements were performed using a E.G&G Princeton Applied Research Model 2263-1 potentiostat/galvanostat controlled by a personal computer. The set-up included a Faraday cage and BAS Cell Stand C_3. The electrochemical experiments were carried out with a three-electrode glass cell. Carbon fiber, Pt wire and Ag|AgCl (3 M KCl) were used as the working, counter and reference electrodes, respectively. To avoid interference of contaminants, the working electrode was renewed before each experiment. The electrochemical depositions of PCz and P(NVCz) on the electrode surface were achieved in ACN and PC solvents. The concentration of both Cz and NVCz monomers was 1 mM. After the electrochemical polymerization, the electrodes were rinsed with the same solvents used for deposition. CV was carried out in the potential range from 0.0 to +1.4 V versus Ag|AgCl (3 M KCl). Electrochemical impedance spectroscopic (EIS) measurements were conducted by means of PARSTAT 2263-1 potentiostat/galvanostat/FRA, in a monomer free electrolyte (ACN and PC) with a perturbation amplitude of 10 mV over a frequency range 0.01 Hz–100 kHz.

3 Results and discussion

3.1 Electrochemical impedance spectroscopy study of polycarbazole and poly(N-vinyl carbazole)

Electrochemical impedance spectroscopic measurements were performed on PCz and P(NVCz)-coated CFMEs in various solution ($NaClO_4$/ACN for P(NVCz) and 0.1 M $LiClO_4$/PC and ACN, TEAP/ACN and PC for PCz) in which polymeric films were obtained [35]. The impedance is a complex quantity defined as $Z_{(\omega)} = v_{(\omega)}/I_{(\omega)}$, where $v_{(\omega)}$ is the transform of an alternating potential signal applied to the system and $I_{(\omega)}$ is the transform of the resulting alternating current signal. The impedance is a function of the signal frequency. It is generally represented as:

$$Z_{(w)} = |Z|e^{i\theta}.$$

Its magnitude or modulus is |Z|, and its phase angle is θ. Both |Z| and θ may also be functions of frequency. As the imaginary contribution increases, the phase angle increases. When the phase angle is 90° and the current is out of phase with the voltage, the impedance is purely imaginary representing capacitance [36]. Nyquist (complex plane impedance) plots were used to estimate the low-frequency

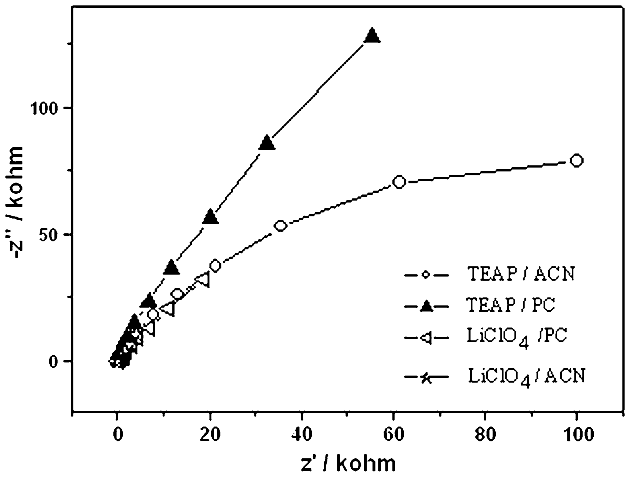

Fig. 1 Nyquist plot of PCz in 0.1 M TEAP/ACN, TEAP/PC, $LiClO_4$/PC and $LiClO_4$/ACN

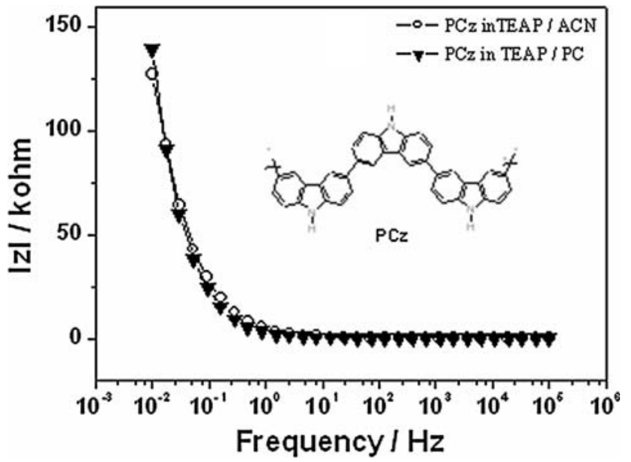

Fig. 2 Bode-magnitude plots of PCz; in 0.1 M TEAP/ACN and TEAP/PC, *Inset* Structure of PCz

redox capacitance of the polymer-modified CFMEs. Low frequency redox capacitance values were obtained from the slope of a plot of the imaginary component (Z_{im}) of the impedance at low frequencies versus inverse of the reciprocal frequency (f) using the following equation [37]: $C_{LF} = (2\pi f Z_{im})^{-1.}$

Nyquist plot of PCz/CFME in various solutions indicates that specific capacitance (C_{sp}) of TEAP/ACN (29.7 mF g^{-1}) is higher than that of TEAP/PC (23.1 mF g^{-1}) (Fig. 1). The difference between ACN and PC is not significant for the C_{sp} values (Fig. 1).

When $LiClO_4$ was used as a supporting electrolyte, both C_{sp} (280.5 mF g^{-1}) and C_{dl} (660 mF g^{-1}) were higher for electrodes made in ACN, compared those made in PC (C_{sp} = 91.6 mF g^{-1} and C_{dl} = 144.8 mF g^{-1}). The result indicates the importance of choosing an appropriate solvent and electrolyte. It is crucial to make the right choice especially when there is a need for increasing the capacitance of the electrocoated thin polymer film on CFMEs. In the previous study [35], the maximum current density, 6.5 μA cm^{-2} (9th scan was taken), was obtained for $LiClO_4$/ACN. However, minimum current densities, 0.5 and 0.4 μA cm^{-2} (9th scan was taken), were obtained for $NaClO_4$/PC and $LiClO_4$/PC, respectively. It can be concluded that the capacitive behavior of coated PCz and P(NVCz) depends on thin film formation conditions and electrodeposition process. Thicker films were obtained in $LiClO_4$/ACN.

A value of double layer capacitance, C_{dl}, can be calculated from a Bode-Magnitude plot, by extrapolating the linear section to value $\omega = 1$ (log w = 0), employing the relationship $|Z| = 1/C_{dl}$ [38]. A C_{dl} value obtained in TEAP/PC (56.5 mF g^{-1}) is higher than in TEAP/ACN (47.8 mF g^{-1}) as shown in Fig. 2.

Bode-phase plots of PCz in (TEAP/ACN and PC, $LiClO_4$/ACN and PC) and P(NVCz) in ($NaClO_4$/ACN) are presented in Fig. 3. The plots of PCz and P(NVCz)/CFME in TEAP/PC, $LiClO_4$/ACN are presented low phase angle at higher frequencies, >100 Hz, because of the prevailing influence of the electrolyte resistance. The result indicates that system behaves like an ideal resistor, characterized by a very low Bode-phase angle value. In the frequency range 1–100 Hz, the film shows transition from a resistive to a capacitive behavior [28]. At frequencies <1 Hz, the Bode-phase angle approaches a plateau, and the electric signal reaches maximum penetration in the pores of the PCz and P(NVCz) electrode (Fig. 3). The maximum phase angle (80°) can be observed for P(NVCz) in $NaClO_4$/ACN at a frequency of 10 Hz, which is comparable to PCz in TEAP/ACN and PC and $LiClO_4$/ACN and PC. At lower frequencies, PCz coating yields a phase angle of ~70° in TEAP/PC, which is higher than P(NVCz) in $NaClO_4$/ACN.

The double layer capacitance (C_{dl}) is attributed to charge accumulation at a polymer solution interface. The highest value (660 mF g^{-1}) was obtained for PCz in $LiClO_4$/ACN. The R_p values can be associated with redox processes within the polymeric film as shown in Table 1. R_p values were higher in propylene carbonate than in acetonitrile. However, the lowest R_p values were obtained for PCz in $LiClO_4$/ACN (3.91 kΩ). ACN has lower dielectric constant (36.64 ε) and viscosity (0.31 mm^2 s^{-1}) than PC (dielectric constant: 66.14 ε, and viscosity: 1.38 mm^2 s^{-1}).

A comparison of electrochemical impedance parameters of P(NVCz) films formed by either CV, chronoamperometry or chronopotentiometry was made in electrolytes with different inert salts ($NaClO_4$ and $LiClO_4$) and ACN as solvent (Table 2). The highest double layer capacitance was obtained for films by CV in 0.1 M $LiClO_4$/ACN (C_{dl} = 290 mF g^{-1}). A specific capacitance value (C_{sp} = 294.1 mF g^{-1}) was obtained in the same solution for a film

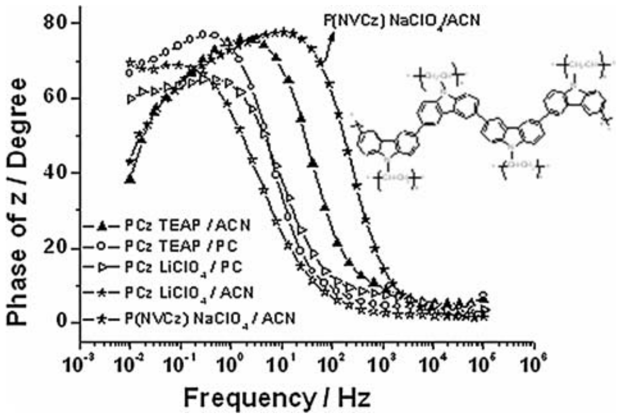

Fig. 3 Bode-phase plots of PCz in 0.1 M TEAP/ACN, TEAP/PC, $LiClO_4$/PC, $LiClO_4$/ACN, and P(NVCz) in 0.1 M $NaClO_4$/ACN. Scan rate of 100 mV s^{-1} by applying 8 scans between 0.0 and 1.4 V versus Ag|AgCl (3 M KCl). $[Cz]_0 = 1$ mM, $[NVCz]_0 = 1$ mM

Table 1 Electrical parameters of PCz in various solution

PCz in	Rs/kΩ	Rp/kΩ	C_{sp}/ mF g^{-1}	C_{dl}/ mF g^{-1}	Phase angle/ degree
TEAP/ACN	0.2	99.6	29.7	47.8	75.3
TEAP/PC	0.3	54.9	23.1	56.5	76.9
$LiClO_4$/PC	0.2	18.7	91.6	144.8	64.9
$LiClO_4$/ACN	0.05	3.9	280.5	660.0	68.7

(8 scans, by CV) R_p Polarization resistance, R_s solution resistance

Table 2 Electrical parameters of P(NVCz) (electrodeposited in 1 mM monomer solution in various solution, $NaClO_4$/ACN and $LiClO_4$/ACN) by the methods of CV, chronoamperometry and chronopotentiometry

P(NVCz) methods/	R_s/kΩ	R_p/ kohms	C_{sp}/ mF g^{-1}	C_{dl}/ mF g^{-1}	Phase angle/ degree
$NaClO_4$/ACN					
CV	0.3	196.3	15.3	2.5	81.2
Chronoamper.	0.1	28.2	21.0	13.2	75.0
Chronopoten.	0.2	9.6	280.5	53.2	47.0
$LiClO_4$/ACN					
CV	0.2	11.8	107.2	290.0	68.1
Chronoamper.	0.08	7.9	294.1	139.0	41.2
Chronopoten.	0.1	23.0	129.1	39.7	41.2

R_p Polarization resistance, R_s solution resistance

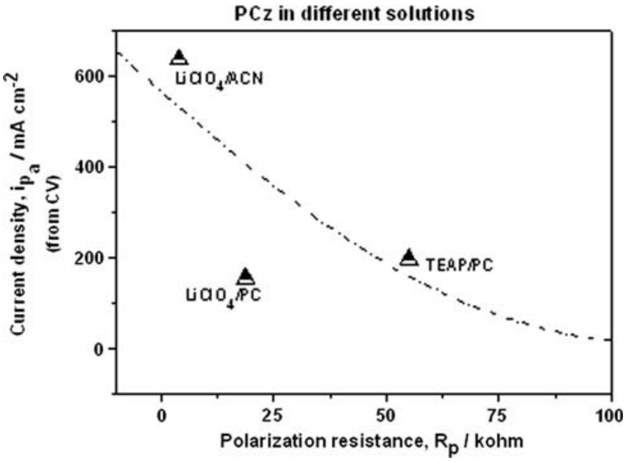

Fig. 4 Current density versus polarization resistance (R_p) relationship of PCz. $[Cz]_0 = 1$ mM

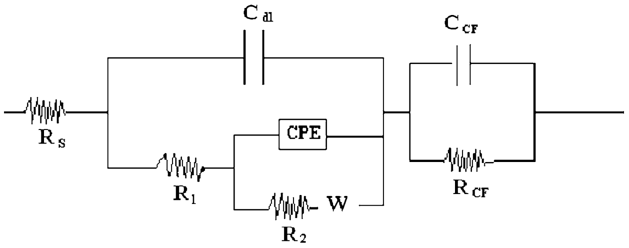

Fig. 5 Electrical equivalent circuit model ((R(C(R(Q(RW))))(CR)) used via simulation program

formed by means of chronoamperometry. The lowest polymerization resistance value ($R_p = 7.9$ kΩ) was measured for a film produced chronoamperometrically in $LiClO_4$/ACN.

PCz coated by chronoamperometrically in $LiClO_4$/ACN has higher C_{sp} and C_{dl} values compared to $NaClO_4$/ACN. Capacitance of the electrode increases with the electrode surface due to the polymerization charge. An inverse relationship between current density and polymerization resistance (R_p) was obtained from a Nyquist plot (Fig. 4).

3.2 Electrical equivalent circuits

Electrochemical parameters of the CFME/PCz and P(NVCz)/Electrolyte systems were evaluated by employing the ZSimpWin (version 3.10) software from Princeton Applied Research. We observed an excellent agreement between experimental and simulated data. The corresponding chi-square (χ^2) was ca. 10^{-4}. χ^2 is the function defined as the sum of the squares of the residuals. An electrical equivalent circuit model, (((R(C(R(Q(RW))))(CR))) was used in simulation of the impedance behavior of the thin film i.e., to fit the experimentally obtained impedance data. The model (Fig. 5) was built previously [7, 17, 18, 32] using series of components; the first one is the bulk solution resistance of the polymer and the electrolyte, R_s, the second one is the parallel combination of the double layer capacitance, C_{dl}, and electrolyte resistance, R_1. A series connection to R_1 made up from using constant phase element (CPE) in parallel with R_2 and W,

Table 3 PCz and P(NVCz) were electrocoated by CV, chronoamperometric and chronopotentiometric methods, depends on the parameters calculated from the equivalent circuit of (R(C(R(Q(RW))))(CR) (electrodeposited in 1 mM monomer solution, in 0.1 M $NaClO_4$/ACN, at a scan rate of 100 mV s^{-1}, and 8th scan)

(R(C(R(Q(RW))))(CR)	PCz	P(NVCz) performed by different techniques		
Components	CV	CV	Chronoamp.	Chronopot.
R_s/kΩ	0.073	0.24	0.089	0.19
C_{dl}/mFg^{-1}	2.55	0.14	0.52	0.021
R_1/kΩ	0.0044	0.65	0.26	0.092
Q/Y_o/Sμs^{-n}	1610	1.03	10.1	56.70
n	0.69	0.76	0.61	0.64
R_2/kΩ	3.17	194	27.9	9.19
W/Y_oSμs^{-n}	3420	4.61	90.5	471
C_{CF}/μFg^{-1}	3×10^{-5}	0.034	0.72	2.46×10^{-4}
R_{CF}/kΩ	13.2	0.063	0.019	29.8
Chi-squared (χ^2)	3.9×10^{-4}	5.9×10^{-4}	2.4×10^{-4}	1.0×10^{-4}

R_2 is the charge transfer, and W is the Warburg impedance of the polymer. CPE describes the capacitor at the film | electrolyte interface considering the irregular geometry of the surface of the polymer network and the counter-ions binding to sites of different energies [39, 40]. This may be considered as an inhomogeneous model because the properties of the first layer differ from those of the bulk film [41]. This approach is justified by the observation that the film density decreases from the CFME surface in the direction to the film electrolyte boundary, especially in the case of electrochemically deposited polymer layers. The CPE elements have been used to describe both the double layer capacitance and the low frequency pseudocapacitance, their frequency dependent nature being attributed to the non-uniformity of the electric field at rough electrode surfaces [42–45]. A capacitor element (C_{CF}) is introduced in parallel with a charge transfer resistor (R_{CF}) corresponding to electrocoated carbon fiber microelectrode. It was observed that at low frequencies, the impedance behavior becomes that of a pure capacitor [20]. Simulation results are given in Table 3. This electrical equivalent circuit was successfully applied to fit experimental data to explain the interface between the carbon fiber microelectrode, the polymer film and electrolyte in this potential range.

The experimental results of C_{dl} were compared with theoretical results obtained from equivalent circuits. The approximately 90 circuit models were tested. Simulation results showed that the ((R(C(R(Q(RW))))(CR)) electrical equivalent circuit model [46, 47], presented in Fig. 5, can be successfully applied to fit the experimental data to explain the interface between the polymer film and electrolyte in this potential region (Table 3).

4 Conclusion

The thin conductive PCz films, electrocoated by the CV method ($C_{sp} = 280.5$ mF g^{-1}) and P(NVCz) films, electrocoated by the chronoamperometric method ($C_{sp} = 294.1$ mF g^{-1}) showed better charge/discharge process in $LiClO_4$/ACN. Capacitive behavior in various solutions indicates the importance of choosing an appropriate solvent for forming the polymeric thin film/CFME system. Thus, electrochemically modified CFMEs can be used for energy storage in electrochemical capacitors (micro-capacitors). In this article, it was shown that nano- to micron-size electrocoating of PCz and P(NVCz) on micron-sized carbon fibers enables micro-scale energy storage. The results were also successfully evaluated by the ((R(C(R(Q(RW))))(CR)) equivalent circuit model. In general, simulation results confirmed that the proposed electrical equivalent circuit was a powerful tool to explain the experimental data and the interaction between the carbon fiber microelectrode, the polymer film and the electrolyte interface.

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