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Electrolyte and solvent effects of electrocoated polycarbazole thin films on carbon fiber microelectrodes

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Abstract

Carbazole was electrochemically synthesized on carbon fiber microelectrodes (CFMEs) in different electrolyte and solvent media. The characterization of polycarbazole thin films formed on micron sized carbon fiber electrodes was performed by electrochemical methods (i.e., cyclic voltammetric measurements, solid state conductivity measurements (four point probe), spectrophotometric methods (ultraviolet/visible spectroscopy (UV–vis), *ex situ* spectroelectrochemistry, fourier transform infrared reflectance spectroscopy (FTIR-ATR)) and scanning electron microscopy (SEM). The best electrolyte and solvent in regards to yield, conductivity and charge for the electrografting was sodium perchlorate in acetonitrile, whose conductivity was 3.60 mS cm^{-1}, had a yield of 89% and had a charge of 5.50C. The effects of scan rate, feed ratio, supporting electrolyte and solvent type on the electropolymerization are discussed.

1. Introduction

There have been many studies concerned with the synthesis, characterization and application of conductive polymers, such as polypyrrole, polyaniline, polythiophene, and poly(*N*-vinyl carbazole) [1–5], due to their technical applications. Polycarbazole (PCz) is one of many relatively new conducting polymer groups with good electrochemical characteristics, and its conductive form can easily be obtained by the electrochemical method [6]. Investigations related to chemical modification or copolymerization of carbazole with other monomers have led to the use of PCz and its derivatives as redox catalysts, photoactive devices, sensors, electrochromic display, electroluminescent devices and biosensors [7–9]. Random copolymerization of *N*-methylpyrrole (*N*-MePy) with carbazole (Cz) has been chemically and electrochemically performed in previous studies [10]. Conducting polymers have strong intermolecular interactions resulting in infusible and insoluble polymers [11]. Due to poor processibility of conducting polymers, there have been many attempts to improve electrically conducting polymers.

For more than 10 years, many research teams have synthesized and studied the properties of soluble conjugated polymers. It was teams observed that the presence of various substituent groups on the monomer unit increases the solubility, but often decreases the conductivity [12]. As a consequence, regioregular conjugated polymers have been synthesized in order to alleviate this problem [13]. There are few studies describing the synthesis by oxidation of heteroatomic copolymers containing carbazole units [14]. One of the reasons for the lack of interest in this technique is that it is difficult to obtain polycarbazoles with high molecular weight through an oxidative route. Although in a strongly acidic medium the anodic route can lead to the formation of oligomers of carbazole [15], the oxidation of a carbazole derivative in organic medium principally leads to the formation of a dimer [16], which is generally soluble in the medium. Nevertheless, the presence of carbazole groups as repetitive chain units is interesting for many reasons.

First, they possess intense ultraviolet absorption spectra and can be used in electroluminescent devices [17–18]. Secondly, carbazole derivatives are good electron donors [19], which means they can be used in studies of photo-induced energy transfer and electron transfer to electron acceptors. The last property makes carbazole-containing polymers attractive in regards to many electronic applications and photo electronic applications [20–22].

Electrochemical oxidation of milimolar carbazole in acetonitrile containing [0.1 M tetra-*n*-butylammonium perchlorate (TBAPC) at +1.3 V (vs SCE)] yields an amorphous conducting film which adheres to the platinum (Pt) electrode. For polymer formation, subsequent reoxidation of the dimer is essential. The 9,9′-dimer does not meet this requirement due to its high oxidation potential. Therefore, it would not further polymerize from this positions. Consequently, "polycarbazole" might be derived from the 3,3′-dimer and might essentially have a poly(3,6-carbazolediyl) structure. Chronoamperometric and chronopotentiometric oxidation studies have shown that transfer of electrons (*n*) for carbazole oxidation fall in the range 2.5–2.8. For authentic 3,3′-dicarbazyl the *n* value is 1.92. Most likely, the oxidation of the 3,3′-dimer yields the same type of conducting polymers as obtained from carbazole. This would further substantiate the poly(3,6-carbazolediyl) structure [23].

The elemental analysis data ($(C_{12}H_{13}N)$) $(ClO_4)_{0.45}$ reveal that these films are very rich in hydrogen and contain a high level of perchlorate anions. The films are most likely a mixture of low-molecular-weight oligomers, unlike the crystalline radical cation salts obtained by Chiang et al. in a very pure THF solvent [24]. In order to examine the effect of the polydispersity on some electrochemical properties, Chevrot et al. studied the electrochemical behavior of poly(*N*-alkylcarbazole) dissolved in dichloromethane [25]. Only a few studies are devoted to the electrochemical behavior of conjugated polymers in solution [26–28].

The carbazole system, though yielding a very poor polymer or only oligomers, is of interest from a reaction-mechanistic point of view. The reaction medium affects the isomer distribution drastically. In the presence of sulfuric acid using dichromate as the oxidant only the 3,3′-dicarbazyl is formed; whereas in the absence of sulfuric acid the 9,9′-dicarbazyl is also formed.

Electropolymerization of carbazole, pyrrole, thiophene, and their copolymers onto CFME has been investigated as a novel method for tailor-making CFME-polymer interphases to promote fiber-matrix adhesion [29]. Electro-grafting of copolymers with conductive and nonconductive contents onto carbon fibers has also recently been studied [30–35].

In this study, Cz is electro-grafted on CFME in different electrolyte and solvent media. This article highlights the essential details of the procedures and the results of characterization of PCz by electrochemical methods (CV), solid state conductivity measurements (four point probe conductometer), spectrophotometric methods (UV–vis, *ex situ* spectroelectrochemistry, FTIR-ATR) and surface morphology (SEM images).

2. Experimental

2.1. *Materials*

Carbazole (Cz, >99%), sodium perchlorate ($NaClO_4$, >98%), lithium perchlorate ($LiClO_4$, >98%), tetraethylammonium perchlorate (TEAP), tetraethylammonium tetrafluoraborate ($TEABF_4$), propylene carbonate (PC, >99%), and acetone (99.7%, Purex PA) were obtained from Merck. Potassium perchlorate ($KClO_4$, >99.5%) was from Fluka. Acetonitrile (ACN) was from Carlo Erba. High Strength (HS) carbon fibers C320000A (CA) (Sigri Carbon, Meitingen, Germany) containing 320,000 single filaments were used as working electrodes. Indium tin oxide (ITO) coated glass slides (0.7 cm × 5 cm, $R \leq 10$ ohm cm^{-2}) were used for the *in situ* spectroelectrochemical studies. All chemicals were high grade reagents and were used as received.

2.2. *Preparation of the CFMEs*

The electrodes were prepared by using a 3 cm length of the CFME (diameter ~7 μm) attached to a copper wire with Teflon tape. Only 1.0 cm of the carbon fiber was dipped into the solution to keep the electrode area constant (~0.0022 cm^2). Cyclic voltammetric results were also compared by using a platinum button ($A = 0.159$ cm^2) as the working electrode.

2.3. *Instruments*

Cyclic voltammetry (CV) of the polymers was performed with Parstat 2263-1 (software, powersuit and Faraday cage, BAS Cell Stand C_3) in a three-electrode system setup employing CFME as a working electrode, platinum wire as a counter electrode, and a silver wire pseudo-reference electrode in a solution of 0.1 M $TEABF_4$, $NaClO_4$, $LiClO_4$ in ACN or $LiClO_4$, $KClO_4$, $NaClO_4$, TEAP in PC, and TEAP in CH_2Cl_2. For example, the pseudo-reference electrode (silver wire) was externally calibrated using a 5 mM solution of ferrocene (Fc/Fc^+) in 0.1 M $LiClO_4$/PC. The $E_{1/2}(Fc/Fc^+)$ value of ferrrocene was obtained at +0.57 V for each measurement.

A Coulometer (Metrohm E 211) was used as a current source for galvanostatic depositions. Polymerization reactions were electrochemically performed galvanostatically in PC and ACN solution containing 0.1 M $LiClO_4$ and $NaClO_4$.

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

UV–Visible spectra were obtained both for electrochemically coated indium tin oxide (ITO) glass and oligomers formed in solution using a Shimadzu 160 A recording spectrophotometer.

Electrochemical syntheses of films were performed galvanostatically on a Pt plate electrode with a surface area of 1.68 cm^2. Solid state electrical conductivity measurements were carried out for films removed from the electrode surface. A Keithley 617 electrometer was connected to a four point probe head with gold tips.

Electrical conductivity was calculated from the following equation:

$$\sigma = V^{-1}/(\ln 2/\pi . d_n) \qquad (8)$$

where d_n is thickness in cm, V is applied potential in V and I is current in A.

The chosen electro-grafted carbon fibers were analyzed by scanning electron microscopy (SEM) using a Leo 1530-Gemini machine (Oberkochen, Germany).

3. Results and discussion

3.1. *Electropolymerization of carbazole on CFMEs by cyclic voltammetry*

Cyclic voltammograms of PCz thin films electrochemically deposited on an CFME recorded in 0.1 M TEABF$_4$, LiClO$_4$, TEAP, NaClO$_4$ and KClO$_4$ as supporting electrolytes in ACN, PC and CH$_2$Cl$_2$ are shown in Figure 1. The onset potentials of carbazole with

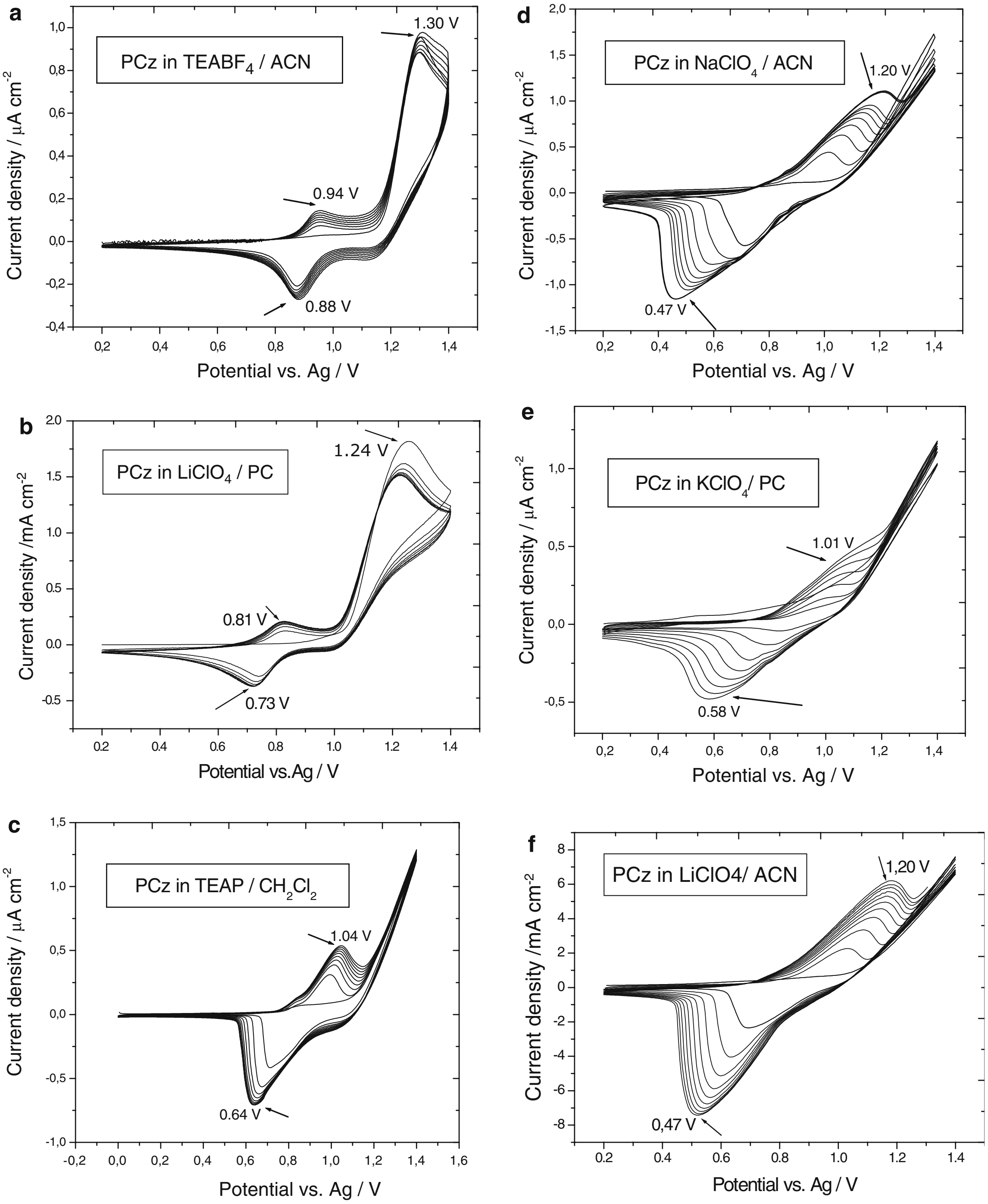


Fig. 1. Multisweep voltammogram of PCz in 0.1 M (a) TEATFB/ACN, (b) LiClO$_4$/PC, (c) TEAP/CH$_2$Cl$_2$, (d) NaClO$_4$/ACN, (e) KClO$_4$/PC and (f) LiClO$_4$/ACN on CFME. Scan rate was 100 mV s^{-1}. About 8 cycles between 0.0 and 1.4 V. [Cz]$_0$ = 10^{-3} M.

$TEABF_4$/ACN and $LiClO_4$/PC were obtained at 1.10 and 1.00 V as shown in Figure 1(a) and (b), respectively. The redox process of PCz appeared at 0.94 and 0.81 V in $TEABF_4$/ACN and $LiClO_4$/PC, respectively [36]. Both PCz and Cz monomer oxidation potential decreased in $LiClO_4$/PC. The decrease may be due to the higher dielectric constant of PC than ACN, resulting in an electroactive polymer film. After the first cycle, the peak intensity at +0.94 V increased and potentials shifted toward higher values. Upon repeated scans, new redox processes appeared at lower potentials, indicating the formation of an electro-active polymer film. The i_a/i_c ratio is 0.75 on CFME which is higher than an Platinum (0.47) in TEAP/CH_2Cl_2. Therefore, PCz coated on CFME is more reversible than on Platinum. The anodic and cathodic peak potentials of PCz were also observed in TEAP/CH_2Cl_2, $NaClO_4$/ACN, $KClO_4$/PC and $LiClO_4$/ACN (Figure 1(c)–(f)). The cyclic voltammogram of carbazole in TEAP/CH_2Cl_2 exhibited weak oxidation. Gradual increases in the intensity of the cathodic wave with repeated scans indicates that the reaction product is gradually deposited on the surface of the CFME (Figure 1(c)). The anodic peak of PCz was broad in the case of $KClO_4$/PC as shown in Figure 1(e). In $LiClO_4$/ACN solution, the anodic peaks of PCz shift to higher potentials from 1.0 to 1.16 V. The reduction peaks decrease from 0.69 to 0.53 V (Figure 1(f)).

Cyclic voltammograms of PCz were also studied in different solutions ($NaClO_4$ and $LiClO_4$in ACN or PC) for comparison. The maximum current density was obtained for $LiClO_4$/ACN at 6.5 μA cm^{-2} (9th cycle was taken) but minimum current densities were obtained in $NaClO_4$/PC and $LiClO_4$/PC, which were 0.5 and 0.4 μA cm^{-2} (9th cycle was taken), respectively (Figure 2).

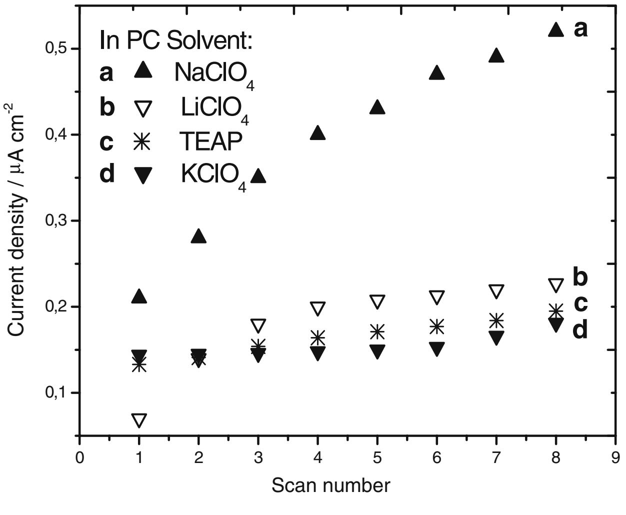


Fig. 2. PCz was electro-coated in different supporting electrolytes in PC using multiple 8 cycles and taken 4th cycle. (Scan rate: 100 mV s^{-1}, $[Cz]_0 = 10^{-2}$ M.

The maximum charges of PCz on anodic peak current densities were obtained in $LiClO_4$/ACN during the electrogrowth of polymer film in two different electrolytes, $NaClO_4$ and $LiClO_4$ (100 mV s^{-1}). By comparison, the copolymerization of methylpyrrole with ethylcarbazole was also electrochemically studied on CFME as previously reported. The maximum charges were obtained in $LiClO_4$/PC on anodic peak current densities of P[MPy-co-ECz] during the electrogrowth of polymer film at 100 mV s^{-1} [37].

Electrochemical behavior of the film was also studied in $LiClO_4$ as a supporting electrolyte in ACN, PC, 50% ACN-H_2O and 50% PC-H_2O medium. The aim was to determine the influence of water in ACN and PC solvents. Results are summarized in Table 1. The anodic peak potential of PCz is 0.80 V in 50% ACN-H_2O. This value is smaller than the anodic peak potential of PCz which is 1.1 V in 50% PC-H_2O mixture. There has been much speculation about the "water effect." It has been suggested that water might reduce the solubility of oligomers [38] and thus lead to faster deposition on the electrode. Some authors have proposed that water, owing to its higher dielectric constant (80 compared to 37 of acetonitrile), reduces the Coulombic repulsion between the radical cations [39–43] facilitating radical-radical coupling. Obviously, this opinion cannot offer a convincing explanation for other monomer-solvent systems, e.g., pyrrole in propylene carbonate (PC) [44], in which water has a detrimental effect. Zotti et al. [45] proposed that the reaction-released protons should protonate pyrrole and its oligomers and that such protonated species in front of the electrode should prevent further electrooxidation. Water then scavenges protons because of its stronger basicity when compared to carbazole.

In this study, the switching potentials were kept constant (1.4 V) to compare the current densities (μA cm^{-2}) in ACN, PC, and by adding 50% water. Current densities of ACN and 50% ACN-H_2O were obtained as 0.22 and 0.52 μA cm^{-2}, respectively. However, current densities of PC and 50% PC-H_2O were obtained as 0.08 and 0.29 μA cm^{-2}, respectively. Thus, ACN exhibits a higher current density than PC. An additional 50% water in ACN and PC inreases the current densities.

Electrochemical coating of PCz on CFMEs were analyzed in the presence of the different alkali cations (Li^+, Na^+, K^+) and other organic cations (Tetraethyl ammonium) in PC (Figure 3). In each case, additional amounts of cation produced a positive shift of the anodic peak potential and a decrease in electroactivity. The highest current density vs. scan number was found in $NaClO_4$/PC (0.5 μA cm^{-2}), and the lower current density was found in $LiClO_4$/PC (0.2 μA cm^{-2}) (Figure 3). For all cations, the anodic peak current densities decrease linearly from 0.5 to 0.2 μA cm^{-2} in $NaClO_4$/PC. The involvement and the size of the cation might have an influence on the polymer conductivity. It is shown that the larger the cation, the lower the conductivity of the polymer.

Table 1. Redox parameters of PCz were electro-coated in $LiClO_4$ (as supporting electrolytes) in different solvents on CFME

PCz ($LiClO_4$in)	*Ep_a^a/V	*ΔEp^a/V	*Ep_a^b/V
ACN	1.02	0.63	1.16
50 % ACN-H_2O	0.83	0.09	1.39
PC	0.81	0.08	1.24
50 % PC-H_2O	1.08	0.13	1.39

Using multiple 8 cycles and taken 4th cycle. (Scan rate: 100 mV s^{-1}, $[Cz]_0 = 10^{-2}$ M).
*Potentials were measured in V and deviation ±0.003 V.
[a]Anodic peak potential of polymer, V.
[b]Anodic peak potential of monomer, V.

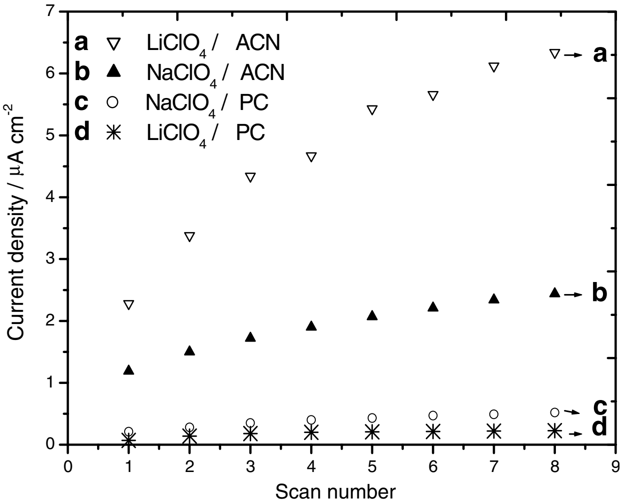


Fig. 3. Current density vs. scan number graph of PCz in different supporting electrolytes ($NaClO_4$ and $LiClO_4$) in different solvents (ACN and PC) on CFMEs at 100 mV s^{-1} $[Cz]_0 = 10^{-3}$ M.

3.2. *Effect of scan rate*

3.2.1. *Effect of scan rate on electrogrowth of carbazole*

Changing the scan rate at which the polymers were grown appears to have an effect on the electrogrowth mechanism, as described in Scheme 1. According to this mechanism, carbazole is first oxidized at the anode giving 3,3′-dicarbazyl cation, and electrogrowth of the oligomers (dimer, trimer, tetramer) formed during electropolymerization. The cyclic voltammogram of PCz formed indicates that during the first few cycles oligomeric species or small polymer chains dissolve during oxidation and reduction cycles. This process leaves longer polymer chains which remain adhered to the CFME surface. Hence, the charge stabilizes after a few cycles.

3.2.2. *Effect of scan rate in monomer-free solution*

The coated film was washed with monomer-free electrolyte solution and its redox behavior was studied. Oxidation and reduction peaks were observed by increasing the applied potential (Figure 4). These anodic processes are associated with two cathodic waves occurring at 0.70 and 0.95 V, respectively, by reverse scans. Such behavior may correspond to the formation of the radical cations of carbazolic units during the first oxidation step followed by their oxidation into dications through the second step as described for poly(*N*-alkylcarbazole) [46].

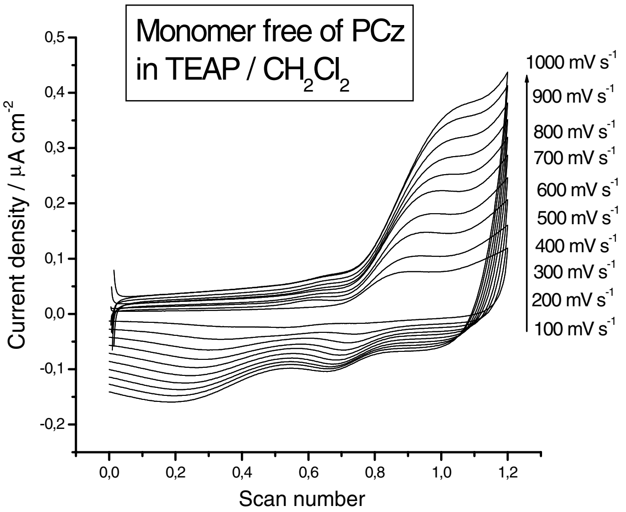


Fig. 4. CV of PCz in monomer free formed by 10 cycles in different scan rates (From 100 mV s^{-1} to 1000 mV s^{-1} by increasing of 100 mV s^{-1} on CFME in 0.1 M TEAP/CH_2Cl_2. $[Cz]_0 = 10^{-3}$ M.

Taking into account the I_a/I_c ratio, which is close to unity and independent of the peak potential between 100 and 1000 mV s^{-1}, the first electronic transfer is fast and the redox process follows a quasi-reversible mechanism. On the other hand, the second redox process is not reversible according to the Ip_a/Ip_c ratio. Dications would be more reactive than cation radicals in this medium. The scan rate dependence of the electroactive film peak current was investigated only on the first reversible system. The peak current (i_p) for a reversible voltammogram at 25 °C is given by the following equation: $i_p = (2.69\times 10^5).A.D^{1/2}.C_0.\nu^{1/2}$ where ν is the scan rate, A is electrode area, D is the diffusion coefficient of electro-active species and C_0 is the concentration of electro-active species in the solution. Peak current is proportional to $\nu^{1/2}$ in the range of scan rates where diffusion control applies [47]. Between 100 and 1000 mV s^{-1}, the peak current of the first system evolves linearly with the square root of the scan rate, which indicates a diffusion limited redox process.

3.3. *Effect of monomer concentration on the yield, conductivity and charge*

Both the solid state conductivity and yield vs. initial monomer concentration for PCz are given in Figure 5. An increase in carbazole concentration leads to an increase in the solid state conductivity of the resulting thin polymer film. While the concentration of monomer increases 10 times from 5×10^{-3} M to 5×10^{-2} M, the conductivity of PCz rises from (0.08 ± 0.05) mS cm^{-1} to (6.36 ± 0.05) mS cm^{-1}. The solid state conductivity of polycarbazole with respect to initial carbazole concen-

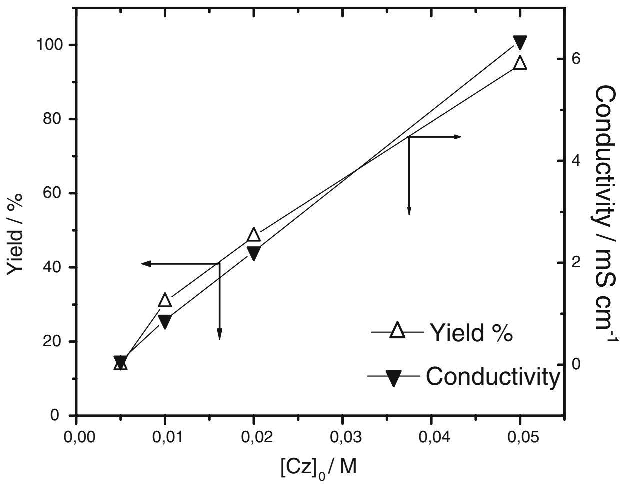


Fig. 5. Effect of initial monomer concentration ([Cz]$_0$) on PCz, solid state conductivity and % yield.

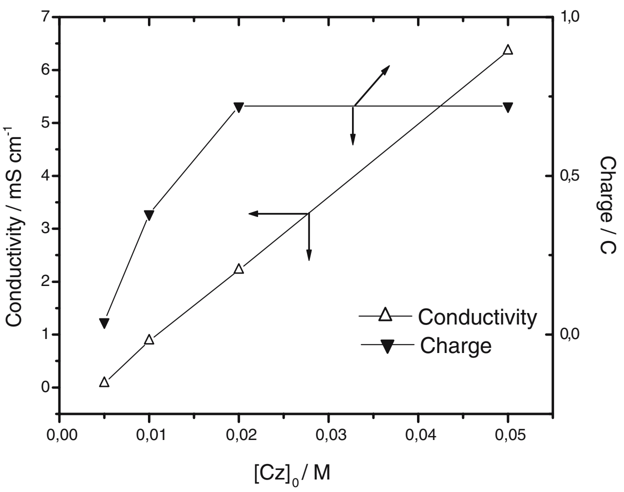


Fig. 6. Solid state conductivity and charge on CFMEs in 0.1 M NaClO$_4$/ACN.

tration was linearly proportional to conductivity. i.e., an increasing monomer concentration leads to an increase in the amount of radical cations. This increases the conjugation length of the polymer and also increases the conductivity of the polymer (Figure 6).

3.4. *Effects of dielectric constant, dipole moment, viscosity, anodic and cathodic current density ratios (I_a/I_c) and thickness values on PCz in different solvents*

Dielectric constant, dipole moment, and viscosity of the solvent affected the electropolymerization of Cz (Fig1(a)–(f)) and the redox properties, and thickness of the PCz film (Table 2). This is because the solvent-polymer interaction on the polymer chain is dependent on the dielectric constant [48] and dipole moment [49] of the solvent chosen for electropolymerization.

Viscosity of solvents were measured (Ubbelohde viscosimeter) by the flow time of solution through a simple glass capillary. The lowest viscosity was obtained in ACN (0.31 mm^2 cm^{-1}) compared to PC (1.38 mm^2 cm^{-1}), DMF (0.74 mm^2 cm^{-1}) and CH$_2$Cl$_2$ (0.44 mm^2 cm^{-1}). Anodic and cathodic current density ratios (I_a/I_c) of NaClO$_4$/ACN solution was the highest one (0.93, reversible). The thickness of the coated PCz film in NaClO$_4$/ACN (4.83 μm, with higher dielectric constant 36.64 ε) was higher than the PC (1.85 μm) and the CH$_2$Cl$_2$ (0.25 μm) as shown in Table 2.

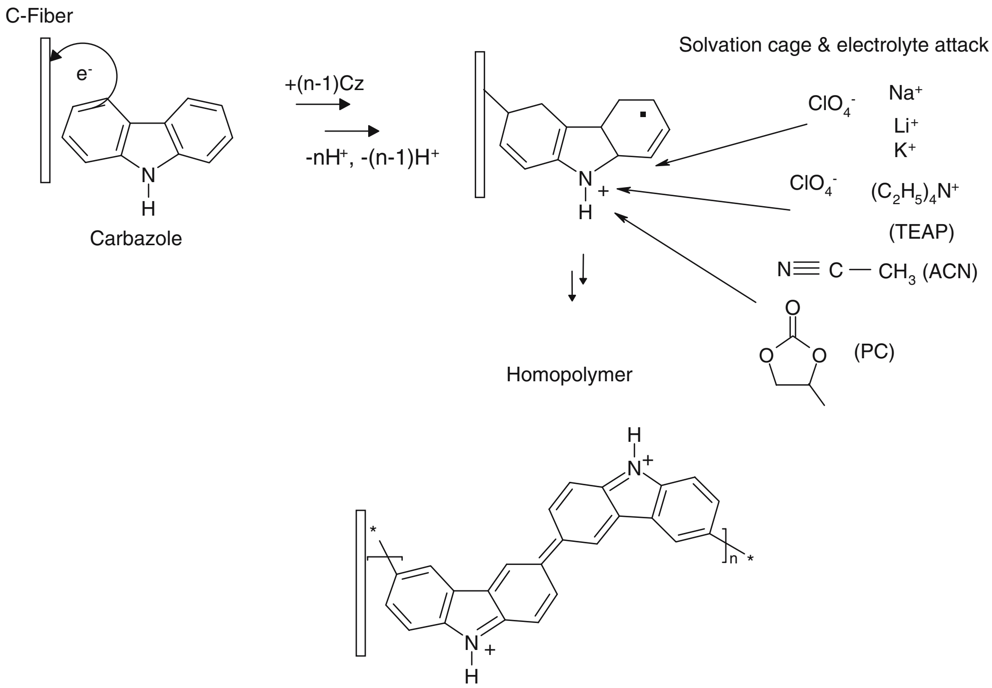
3.5. *FTIR reflectance spectrum of electrocoated of polycarbazole on CFME*

The FTIR-reflectance spectra of electro-grafted polycarbazole prepared under the defined experimental conditions are given in Figure 7. A significant band at 1093 cm^{-1} has been attributed to perchlorate ion, which is due to the electrolytes in NaClO$_4$/PC. Characteristic peaks observed at 3559, 1626, 1233, and 681–728 cm^{-1}, corresponding to –CH$_3$ (sp^3 CH stretching), –C–N (stretching of aromatic C–N bonds or vibration of disubstituted benzene ring), and –C–H (out-of-plane deformation of C–H bond in benzene ring) [50], also provide evidence of polymer formation on the CFME. For the polymer, the band at 1626 cm^{-1} can be assigned to the anti-symmetric and symmetric C–C stretching deformation. In the region above 2000 cm^{-1}, the absorption typical of organic conductors obtained at 3559 cm^{-1} band (N–H stretching) which is observed very sharp around 3000 cm^{-1}. Peak intensities around 1100 cm^{-1} were examined as shown in Figure 8. The characteristic peaks at 1062, 1071, 1093, 1094, and 1095 cm^{-1}, are due to the perchlorate ion obtained in KClO$_4$/PC, LiClO$_4$/ACN, NaClO$_4$/PC, TEAP/PC, and NaClO$_4$/ACN. The peak at 1094 cm^{-1} is lower than the perchlorate anion in TEAP/PC. Peak shifts are obtained for KClO$_4$/PC (at 1062 cm^{-1}) to NaClO$_4$/ACN (at 1095 cm^{-1}) (Figure 8).

Table 2. Dielectric constant (permittivity) and dipole moments at 20 °C [48, 49], viscosity, anodic and cathodic current density ratios (I_a/I_c) and thickness value on PCz in various organic solvents

Solvents	Dielectric constant/ε	Dipole moment/D	η/mm^2 s^{-1}	I_a/I_c	Thickness/μm
PC	66.14	4.90	1.38	0.83	1.85
ACN	36.64	3.92	0.31	0.93	4.83
DMF	38.25	3.82	0.74	0.75	(n.d)*
CH$_2$Cl$_2$	9.14	1.60	0.44	0.79	0.25

*(n.d):not determined.



Scheme 1. Mechanism of electrografting of PCz on Carbon fiber microelectrodes (Radical cation and dication formation).

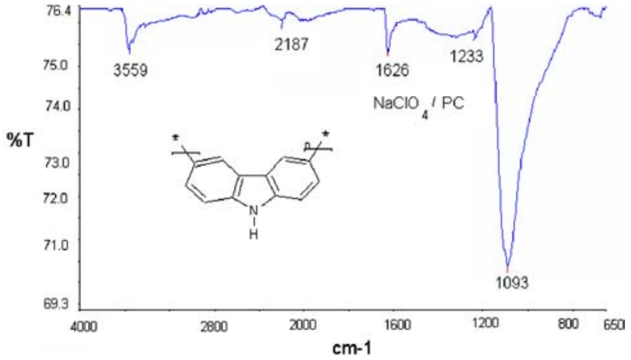


Fig. 7. FTIR-Reflectance of grafted PCz on CFME (in 0.1 м $NaClO_4$/PC), $[Cz]_0 = 10^{-2}$ м. Inset: Carbazole structure.

Increases in the electronegativities of cations from K^+, Li^+ and Na^+, peaks (at 1062 cm^{-1}, 1071 cm^{-1}, 1095 cm^{-1}) shift to higher wave numbers (Figure 9).

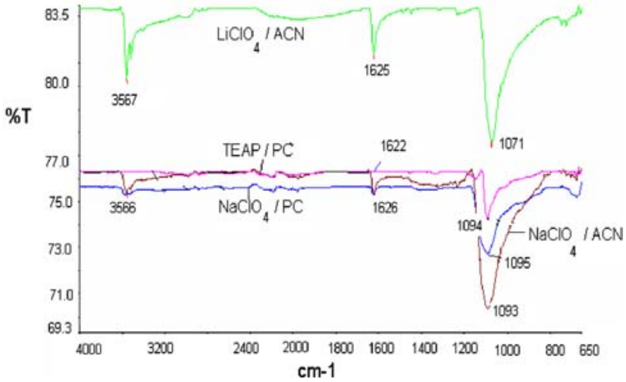


Fig. 8. FTIR-Reflectance of grafted PCz on CFME, (in 0.1 м $LiClO_4$/ACN, TEAP/PC, $NaClO_4$/ACN, and $NaClO_4$/PC), $[Cz]_0 = 10^{-2}$ м.

Cyclic voltammogram results also showed that the maximum current density was obtained in $NaClO_4$/ACN (potentiodynamically) which is similar to the above finding.

3.6. *UV–Vis spectrophotometric results*

3.6.1. *Ex situ spectroelectrochemistry for soluble species* Carbazole was electrocoated on CFME in $LiClO_4$ and $NaClO_4$ as supporting electrolytes in ACN and PC solvents. After completing the electropolymerization processs, an *ex situ* UV–visible spectrum of solution was taken between 300 and 750 nm. This indicates

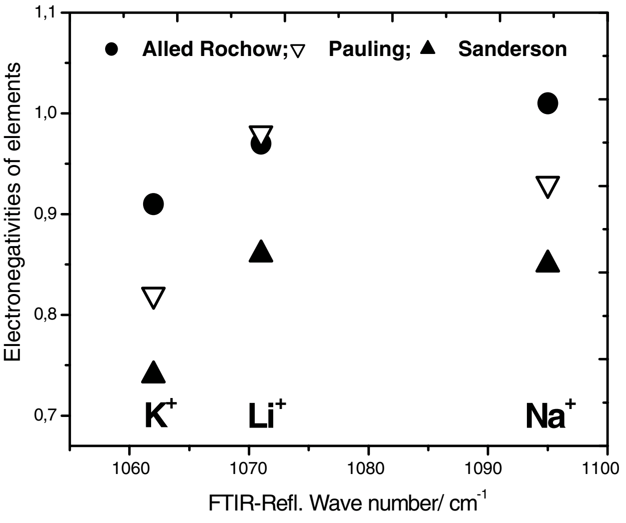


Fig. 9. Relationship with FTIR-Reflectance shifts in (using K^+, Li^+ and Na^+ cations) peaks and electronegativities (a: Alled-Rochow, b: Pauling, c: Sanderson).

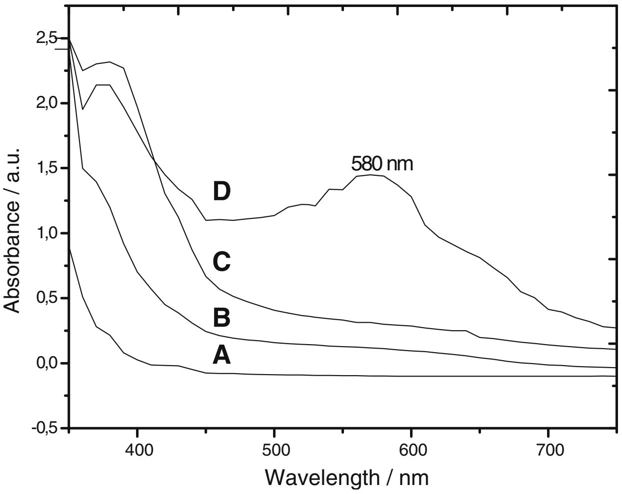


Fig. 10. Ex situ UV–vis spectra of oligomeric species of electrolyte solution, 0.1 M (A) $LiClO_4$/ACN, (B) $NaClO_4$/ACN, (C) $NaClO_4$/PC and (D) $LiClO_4$/PC. $[Cz]_0 = 10^{-2}$ M.

that the highest oligomer or soluble polymer content was obtained in $LiClO_4$/PC as shown in Figure 10. (Absorbance peak at 580 nm). The maximum absorbance for oligomers was obtained in $LiClO_4$/PC. However, the minimum absorbance for oligomers was obtained in $LiClO_4$/ACN (at 500 nm). This may be due to the higher conjugation in PC.

3.6.2. Ex situ *spectroelectrochemistry for coated polymer on ITO*

Spectroelectrochemical methods were also employed to study the changes in band position of polymers during oxidation (p-doping). Polymer films for spectroelectrochemical analysis were electro-polymerized on ITO glass and subsequently washed with ACN. They were then placed in a quartz cuvette with a counter and reference electrodes. Fast switching times (10 seconds) were obtained between −1.2 V to +1.2 V, and large optical changes were attained in $NaClO_4$ /ACN (Fig. 11). The film optical band gap was obtained at 3.05 eV. The electronic band gap (Eg), defined as the onset for the π–π^* interband transition is close to 3.2 eV [51], in agreement with literature. When a potential higher than 0.55 V was applied, two absorption bands appear at 395 nm and around 800 nm which have been attributed to the radical cation and dication of carbazole, respectively [52].

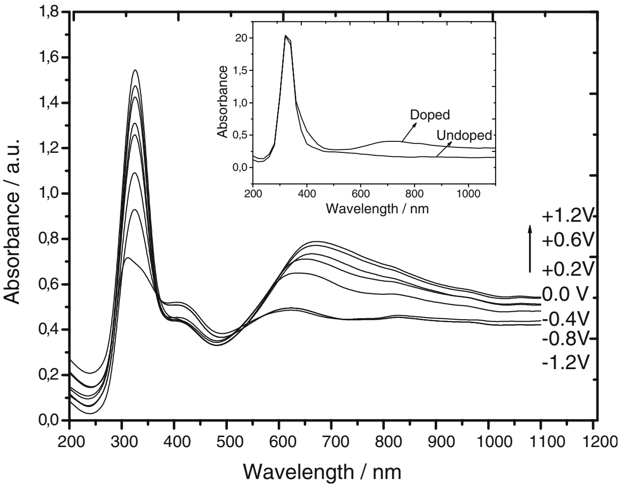


Fig. 11. In situ absorption spectra of PCz film during the doping process in 0.1 M $NaClO_4$ /ACN. Potential sweep was measured from −1.2 to +1.2 V. The film was prepared by potantiostatic method at 1.2 V. Reference spectrum measured at 0.0 V. $[Cz]_0 = 10^{-2}$ M. Inset: UV–visible absorption spectra of oxidized (1) and neutral that was obtained by reduction −1.0 V for 30 s. (2) PCz film on ITO.

The coated film was reduced to an undoped state by applying a negative voltage at −1.2 V. At −1.2 V the polymer is colourless (fully reduced form), but the color gradually changes to green by application of 0.2 V. At a higher potential it turns deep green. This type of multicolor behavior is important for the preparation of electrochromic materials.

UV–visible spectra were taken for the doped and undoped forms of PCz films, which were galvanostatically deposited on ITO substrates (0.2 mA cm^{-2}) (Figure 11 inset). Re-oxidation of the film shows that a decrease in the absorption peak occurs at 320 nm with the appearance of a new broad peak beyond 700 nm, which is attributed to the formation of delocalized cationic charge carriers. These measurements indicate that the oligomeric species are also formed in the solution when they react with the other oligomers. This leads to random homopolymer formation.

3.7. *SEM images of electrocoated polymers on carbon fiber microelectrodes*

The surface morphology of the coated and uncoated single fibers were studied using scanning electron microscopy (SEM). The thickness of electrografted fiber (from SEM images) and different electrolytes and solvents indicated that the maximum thickness value of the electrografted sample of PCz was obtained in ACN (4.83 μm) (Figure 12(d)). The uncoated PAN-based CFME is given in Figure 12(a). However, the coated PCz was clearly observed in the $NaClO_4$/ACN medium at a magnification of 200 nm (Figure 12(c)). The SEM micrographs reveal that PCz electrocoated potentiodynamically on CFME in the $NaClO_4$/ACN medium. The micrographs of electrocoated polycarbazole on CFME also show a cauliflower-like structure (prepared at 0.1 M $NaClO_4$/ACN) [53]. The thickness of coated PCz in $TEAP/CH_2Cl_2$ was 0.25 μm (Figure 12(b)). The thickness of PCz in $KClO_4$/PC was 1.85 μm (Figure 12(f)).

4. Conclusion

The electropolymerization of carbazole was studied in different anhydrous organic solvents and supporting electrolytes on CFMEs. The UV–vis spectrum of the oxidized thin film in $NaClO_4$/ACN medium, and the

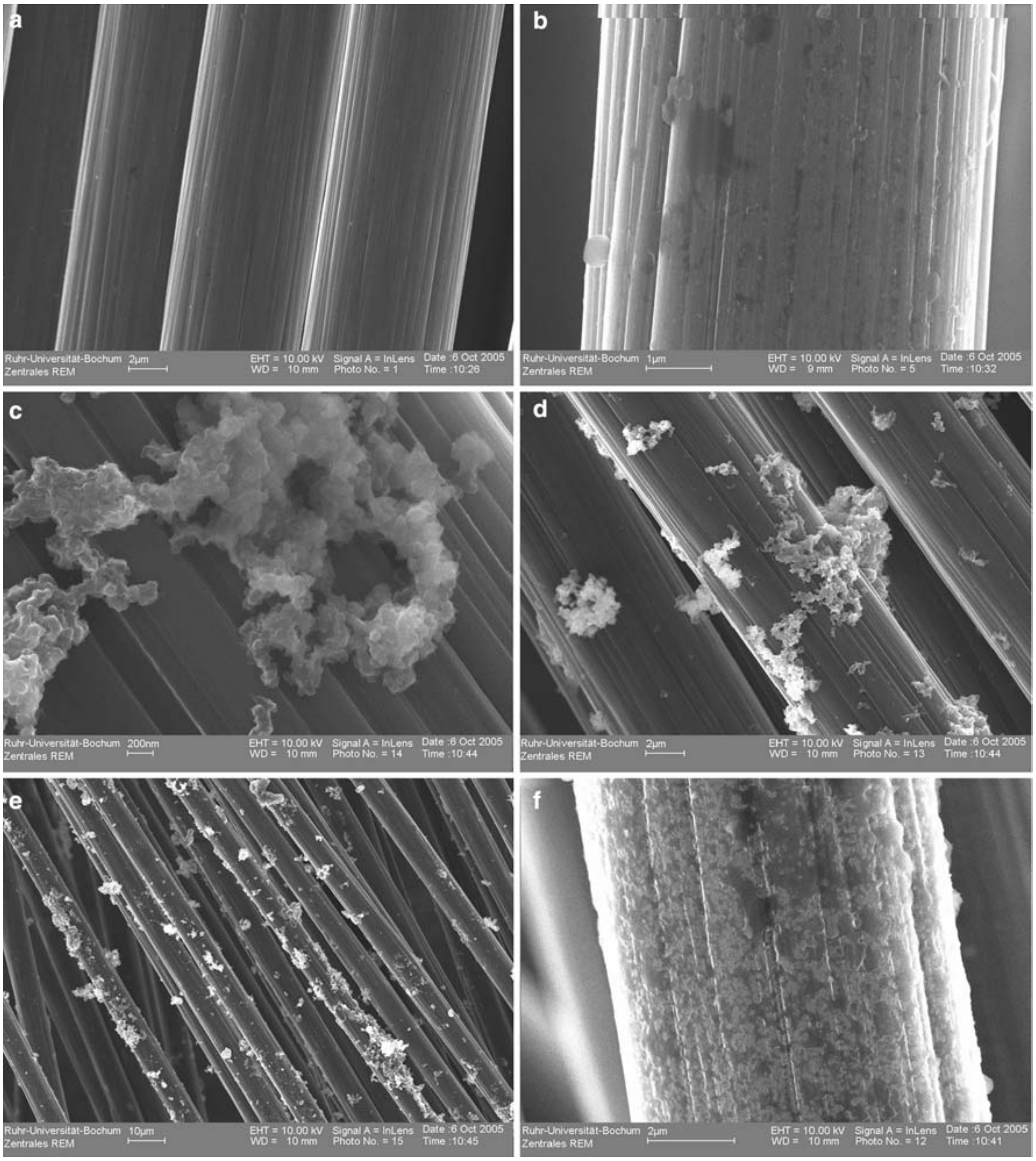


Fig. 12. SEM images of PCz on CFME; (a) Uncoated CFME CA 320,000; (b) PCz in TEAP/CH_2Cl_2 at magnification of 1 μm; (c) PCz in $NaClO_4$/ACN medium at magnification of 200 nm; (d) PCz in $NaClO_4$/ACN at magnification of 2 μm; (e) PCz in $NaClO_4$/ACN at magnification of, 10 μm; (f) PCz in $KClO_4$/PC at magnification of 2 μm.

optical band gap obtained at 3.05 ± 0.05 eV, was closer to previous findings (3.25 eV) [51, 54]. Due to a unique combination of stability, moderate aromatic character and structural versatility, carbazole-π-conjugated systems still represent the most widely investigated basic structure for the synthesis of molecular or polymeric materials with a narrow band gap [55]. Spectroelectrochemical studies confirm the electrochromic properties of the films, which turn from colorless to deep green during oxidation. The anodic current density in $NaClO_4$ was observed to be higher than the anodic current densities in $LiClO_4$, TEAP and $KClO_4$ in PC. The effects of solvent, supporting electrolyte type, and solid state conductivity results were examined. Mechanisms of electropolymerization of Cz were discussed. SEM images of electrocoated samples of PCz were taken in different solutions to compare thickness values. The maximum thickness was obtained in $NaClO_4$/ACN (4.83 μm), and polymer coating was achieved with 30 cycle at 100 mV s^{-1}.

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