Electrodeposition of Poly(4-methyl carbazole-3-carboxylic acid) on Steel Surfaces and Corrosion Protection of Steel

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ABSTRACT: The electropolymerization of 4-methyl carbazole-3-carboxylic acid was successfully performed on a stainless steel (316L) surface with lithium perchlorate/acetonitrile as the supporting electrolyte. The corrosion resistance of the new coating, poly(4-methyl carbazole-3-carboxylic acid) (PCz), was investigated. To this end, potentiodynamic polarization curves, open circuit potentials, and electrochemical impedance spectroscopy were used to evaluate the capacity of the PCz coating to protect the steel surface. The corrosion tests indicated that PCz exhibited effective anodic protection in a corrosive test solution. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1496–1500, 2009

**Key words:** coatings; conducting polymers; synthesis

INTRODUCTION

Conducting polymers, including polypyrrole,[1–3] polyaniline,[4–7] polyindole,[8–11] and polycarbazole,[12–14] have been intensively investigated since the late 1970s. Among these polymers, polycarbazoles have been known for their good electroactivity and thermal, electrical, photophysical, and electrochromic properties. They have been suggested for a number of applications, such as electroluminescent devices, sensors, redox catalysts, and electrochromic displays.[15–18]

Protective conducting polymer coatings have been widely used for metal corrosion control. Since Deberry[19] reported in 1985 that polyaniline reduced the corrosion rate of stainless steel (SS) by anodic protection, polyaniline and its derivatives have been used as protective coatings. In 1996, Ahmad and MacDiarmid[20] found that electrochemically synthesized polyaniline was able to protect iron and steel. Camalet et al.[21] reported that polyaniline coatings electrochemically deposited from oxalic acid provided good protection to steel in acidic chloride solutions. Polypyrrole and its derivatives have also been investigated intensively for their ability to provide corrosion protection.[22–24] Lacaze et al.[25] showed that electrochemically synthesized polypyrrole coatings were effective for the corrosion protection of oxidizable metals such as iron, aluminum, and zinc.

SSs are of special interest for many applications because of their corrosion resistance. Although the formation of a thin oxide layer is effective for protecting SSs, the breakdown of this passive film leads to the initiation and propagation of localized corrosion.[26,27]

Carbazole-based polymer systems have structural similarities to polypyrrole and polyaniline; however, no attempts at using polycarbazole and its derivatives for corrosion control have been reported in the literature. In this article, we report for the first time the electrochemical polymerization of 4-methyl carbazole-3-carboxylic acid on an SS electrode and the corrosion behavior of this coating:
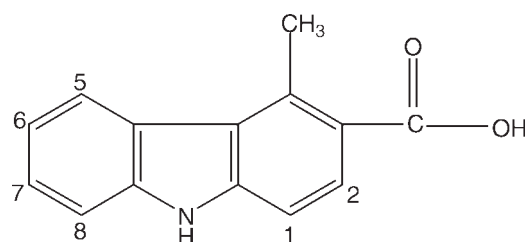
4-methyl carbazole-3-carboxcylic acid

The aims of this study were first to electrochemically synthesize poly(4-methyl carbazole-3-carboxylic acid) (PCz) on an SS electrode and second to investigate the corrosion resistance of the polymer-coated steel with potentiodynamic polarization, open circuit potential/time curves, and electrochemical impedance measurements in 3.5% NaCl.

EXPERIMENTAL

4-Methyl carbazole-3-carboxylic acid was synthesized chemically. The chemical synthesis of the monomer was previously described.[28] Acetonitrile (ACN) and lithium perchlorate ($LiClO_4$) were

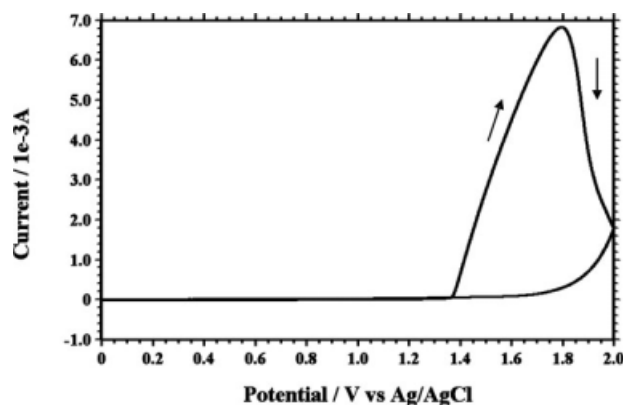*Correspondence to:* M. Düdükcü (mdudukcu@mersin.edu.tr).

Figure 1 Cyclic voltammogram of bare SS recorded in a monomer-free ACN/0.1M LiClO$_4$ solution (scan rate = 50 mV/s).

regent-grade and were used without any further purification process. The electrochemical polymerization of 0.05M 4-methylcarbazole-3-carboxylic acid was carried out in an ACN (Merck)/0.1M LiClO$_4$ (Fluka, Germany) solution on an SS electrode.

The electrochemical processes were performed in a conventional three-electrode cell with a computer-controlled electrochemical analyzer (Austin, TX; CHI 660A). A platinum sheet (area = 1 cm^2) and Ag/AgCl (saturated KCl) electrodes were used as the counter and reference electrodes, respectively. The SS electrode was a cylindrical rod 0.7 cm in diameter, and the exposed area was 1.54 cm^2, whereas the rest of the electrode was embedded in a thick polyester block. The SS that was used had the following composition: C, 0.025 wt %; Mn, 1.88 wt %; Si, 0.53 wt %; S, 0.01 wt %; P, 0.039 wt %; Ni, 10.4 wt %; Cr, 16.59 wt %; Mo, 2.1 wt %; and N, 0.04. The surface of the steel electrode was polished mechanically with emery paper of different grit sizes (600–1200 mesh) and was washed with distilled water and dried.

Electropolymerization was achieved potentiodynamically in the potential range of 0–1.5 V. Electrochemical corrosion tests were performed in 3.5% NaCl solutions at room temperature. Before the polarization measurements, the electrodes were immersed into a corrosive test solution, and the open circuit potential was monitored until a constant value was reached. The anodic polarization curves were started from the open circuit potential at the scan rate of 5 mV/s. Electrochemical impedance measurements were recorded after various immersion times at the open circuit potentials in the frequency range of 10^5 to 10^{-3} Hz with an amplitude of 10 mV.

RESULTS AND DISCUSSION

Electrochemical synthesis

The cyclic voltammogram of the bare SS was recorded in a monomer-free ACN/0.1 M LiClO$_4$

solution (Fig. 1). The electrode surface remained in a passive state in a potential region between 0 and 1.4 V versus Ag/AgCl. The current value started to increase beyond 1.4 V because of transpassive dissolution of the SS, and an irreversible anodic wave was seen. At potentials more positive than about 1.7 V, the current decreased because of the passive layer formation.

A cyclic voltammogram of 4-methylcarbazole-3-carboxylic acid monomer is shown in Figure 2. The electrochemical oxidation of the monomer was carried out in an ACN/0.1M LiClO$_4$ solution containing 0.05M 4-methyl carbazole-3-carboxylic acid. As shown in Figure 2, the monomer oxidation started at 1.2 V, and a certain oxidation wave can be seen at about 1.4 V, corresponding to the formation of a radical cation of carbazole.[16]

Figure 3 shows the electrochemical growth of the polymer film. Well-defined oxidation and reduction waves can be seen between 0.4 and 1.4 V, indicating the growth of the polymer on the electrode surface. The resultant PCz films were dark green and very adherent to the steel surface.

Corrosion protection by the polycarbazole film

The anodic polarization curves recorded after 2 h of exposure to a 3.5% NaCl solution for steel and polymer-coated steel electrodes are presented in Figure 4. At this time, the open circuit potentials of the SS and SS/PCz electrodes were +0.057 and +0.110 V, respectively. The anodic current for the coated electrode was lower than that for the steel in the potential region of 0.03–0.3 V.

The open circuit potentials for SS and SS/PCz plotted against the exposure time in 3.5% NaCl are shown in Figure 5. The initial open circuit potentials of the SS and coated SS electrodes were measured to
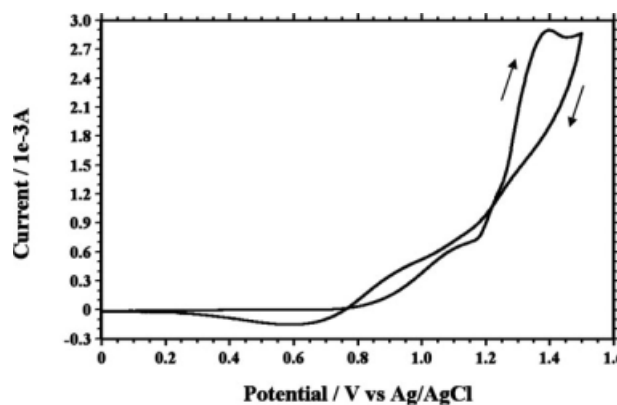

Figure 2 Cyclic voltammogram taken during the oxidation of 4-methyl carbazol-3-carboxylic acid in an ACN/0.1M LiClO$_4$ solution containing 0.05M monomer (scan rate = 50 mV/s).
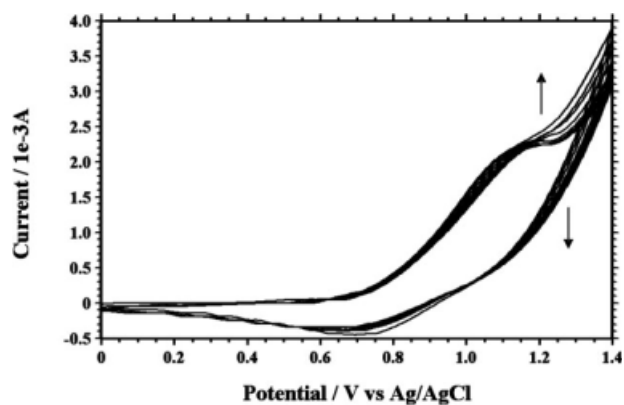
Figure 3 Cyclic voltammogram recorded during polymer film growth on an SS electrode in an ACN/$0.1M$ LiClO$_4$ solution containing $0.05M$ 4-methyl carbazol-3-carboxylic acid (scan rate = 50 mV/s).

be -0.209 and $+0.161$ V, respectively. SS/PCz had more noble open circuit potential values with respect to the bare SS electrode after 336 h of exposure to a corrosive solution. This can be explained as follows: the polymer coating limited the diffusion of corrosive species to the metal surface and behaved like a barrier. At this time, the open circuit potential of the SS/PCz electrode was measured to be -0.150 V. The reduction of the open circuit potential of the SS/PCz electrode with time can be explained by electrochemical degradation of the polymer film by aggressive chloride ions.

The corrosion performance of polycarbazole films on SS was investigated with electrochemical impedance spectroscopy in 3.5% NaCl. Figure 6 shows Nyquist and corresponding phase angle/log frequency plots representative of the polymer-coated SS as a function of the exposure time. The first measurement was obtained 2 h after immersion. The Nyquist plot obtained at this time showed a depressed semicircle in the frequency range of 10^5 to 10^{-2} Hz. The resistance corresponding to the
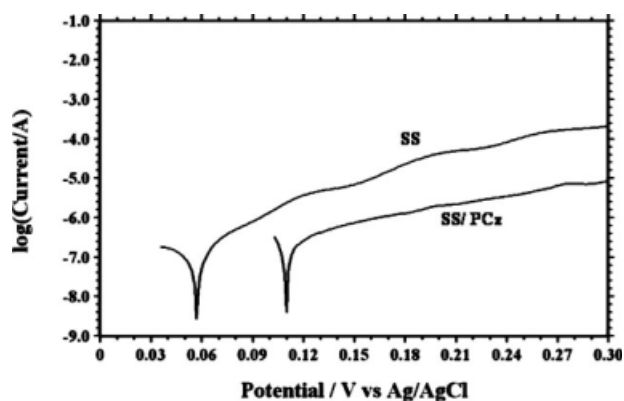
Figure 4 Anodic polarization curves recorded for SS and SS/PCz electrodes after 2 h of exposure in a 3.5% NaCl solution.
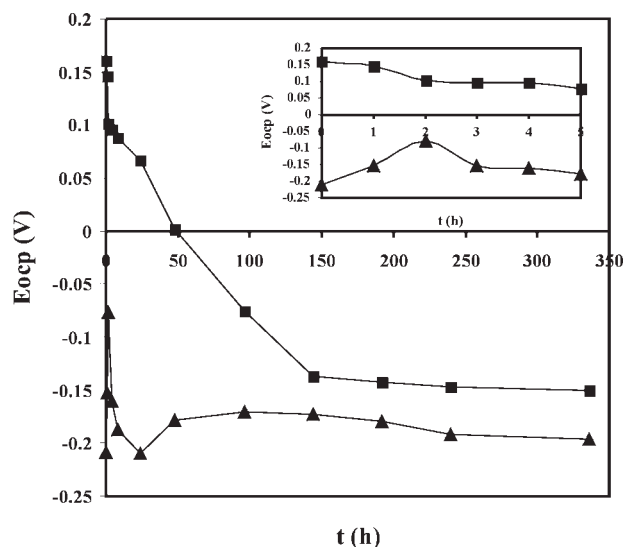
Figure 5 Open circuit potential (E_{ocp})/time (t) curves for (▲) SS and (■) SS/PCz electrodes in a 3.5% NaCl solution.

depressed semicircle was attributable to the charge-transfer resistance.[29] The semicircle at the high frequencies represents the capacitance–resistance couples for the polymer and polarization at the metal–polymer interface. The charge-transfer
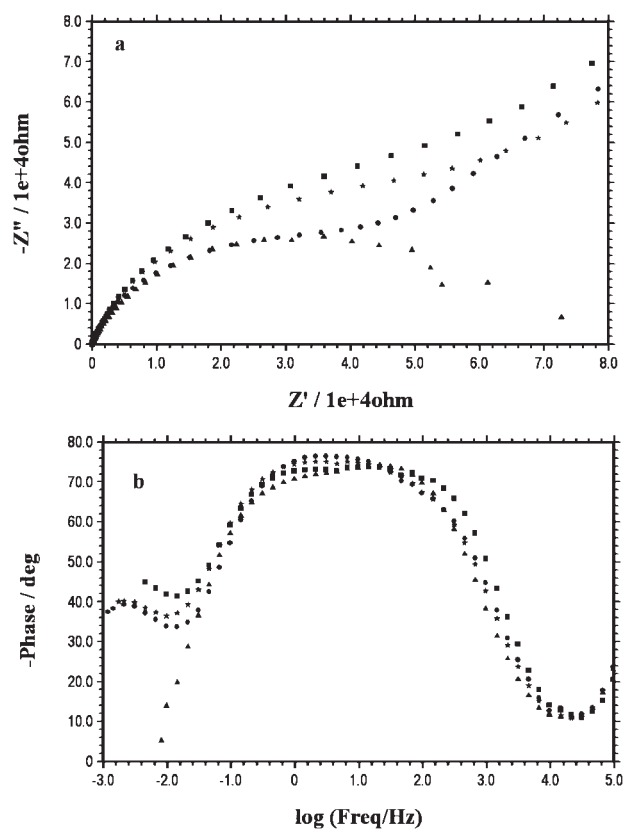
Figure 6 (a) Nyquist (imaginary impedance Z'' vs real impedance Z') and (b) phase angle/log frequency plots recorded for an SS/PCz electrode in a 3.5% NaCl solution for various exposure times: (▲) 2, (■) 24, (∗) 92, and (●) 336 h (frequency = 10^5 to 10^{-3} Hz).

TABLE I
Parameters of the Equivalent Circuits for the SS/PCz Electrode for Different Immersion Times

Immersion time (h)	R_1 (Ω)	CPE$_1$ (mF/cm^2)	n_1	R_2 (Ω)	T_{ILW} (s)	R_{ILW} (Ωcm^2)	Equivalent circuit
2	8.89 (1.07)	5.57×10^{-5} (1.01)	0.79 (0.22)	38,961 (5.38)	—	—	
24	9.49 (1.08)	3.78×10^{-5} (1.18)	0.84 (0.26)	106,080 (4.73)	181.8 (17.68)	365,480 (12.39)	
92	11 (1.33)	4.56×10^{-5} (1.47)	0.84 (0.33)	89,280 (5.41)	205.8 (15.28)	196,350 (12.04)	
336	8.89 (1.47)	5.04×10^{-5} (1.64)	0.85 (0.36)	61,026 (5.06)	199.1 (14.50)	137,980 (11.47)	

The data in parentheses are the estimated errors.

resistance is described for a kinetically controlled electrochemical reaction such as electron transfer between a metal and a polymer film.[30]

The Nyquist plots obtained for 24, 92, and 336 h exhibit a partially formed semicircle at high frequencies and a linear part at low frequencies [Fig. 6(a)]. The linear portion in the low-frequency region represents the presence of a diffusion-limited process. In corresponding phase angle/log frequency curves [Fig. 6(b)], a large change occurs between 2 and 24 h in the low-frequency region. After 2 h of exposure, the phase angle passes through a maximum and then falls. After 24 h, the phase angle becomes greater than 45° beyond 10^{-2} Hz. With increasing time, the phase angle decreases to about 40° at the low frequencies (see Table I).

The software program Zview was used to fit the experimental data to the appropriate models and to determine the characteristic parameters as a function of the exposure time.

In Table I, R_1 is the electrolyte resistance, CPE$_1$ is the constant phase element of the capacitance of the polymer coating, and R_2 represents the charge-transfer process. T_{ILW} and R_{ILW} describe the Warburg coefficients and resistances, respectively. The impedance of the metal–polymer coating interface does not behave like a capacitor. A constant phase element (CPE) was used for the double-layer capacitance to describe the nonhomogeneities in the system; the impedance of constant phase element (Z_{CPE}) can be described as follows:

$$Z_{CPE} = 1/C(iw)^n, \quad i = (-1)^{1/2}$$

where C represents the real capacitance and $w = 2\pi f$ is the angular frequency, where f is frequency.[31] The n values are the correlation coefficients for the CPE lying between 0.5 and 1. As shown in Table I, the R_1 values were in a narrow range (8.89–11 Ω). An increase in the R_2 values was observed from 38,961 to 106,080 Ω between 2 and 24 h. The increase was related to the stabilization of the passivation at the metal–polymer interface. The barrier property of the PCz coating was very good at that time. After 336 h of immersion, R_2 decreased to 61,026 Ω. The reduction of the R_2 values with increasing immersion time can be interpreted as a result of the water uptake process. The double-layer capacitance values of the polymer coating were in the range of 3.78–5.57 $\times$ 10^{-5} mF/cm^2. The T_{ILW} and R_{ILW} values were obtained for polymer-coated steel after 2 h of exposure. R_{ILW} changed from 365,480 to 137,980 Ω cm^2 after 336 h of immersion.

CONCLUSIONS

PCz was successfully electropolymerized onto an SS electrode in aprotic media. An electroactive and

strongly adherent polymer film was obtained. The results of corrosion tests indicated that the metal–PCz interface remained stable after a long exposure time, such as approximately 340 h, in 3.5% NaCl. PCz acted as a barrier coating and delayed the corrosion of steel in highly corrosive media.

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