

Formation of Polypyrrole Coatings onto Low Carbon Steel by Electrochemical Process

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ABSTRACT: Thin polypyrrole coatings ($\sim 10 \mu\text{m}$ thick) were formed on low carbon steel by an aqueous constant current electrochemical polymerization using oxalic acid as the electrolyte. The amount of polypyrrole coatings formed on steel increased with the applied current and monomer concentration. No significant change in the electropolymerization of pyrrole occurred as a result of increased electrolyte concentration. The induction time for electropolymerization decreased significantly with current density but was unaffected by the initial monomer and electrolyte concentration. The electropolymerization potential of pyrrole increased with increased current density (Cd), i.e., $E_p = 0.62 + 0.41 [Cd]$, and decreased exponentially with increased monomer and electrolyte concentration, $E_p = E_0 \exp^{-[M]}$. Scanning electron microscopy (SEM) showed that the microstructure of the polypyrrole coatings formed on steel was dependent on the current density to the extent that smoother and more uniform coatings are formed at low current density. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 417–424, 1997

INTRODUCTION

Electropolymerization is an effective technique for applying polymer coatings of varying thickness onto conductive substrates. It combines an electrochemical reaction with polymerization.¹ Electropolymerization of pyrrole has been traditionally performed by using inert metals as the working electrode (WE).^{2–10} Earlier attempts to electropolymerize pyrrole onto reactive metals was unsuccessful because of the preferred dissolution of the metals at a potential lower than the oxidation potential of pyrrole. The electropolymerization of pyrrole has been attempted on reactive metals such as steel, copper, and aluminum^{11,12} in different electrolyte–solvent systems. Electropolymerization of pyrrole in acetonitrile and tetrafluoroborate medium onto reactive met-

als such as aluminum (Al), indium (In), silver (Ag), and steel (Fe) was investigated by Prejza.¹¹ It was shown that the dissolution of these metals occurred in preference to the electropolymerization of pyrrole. Cheung et al. investigated the electropolymerization of pyrrole on a wide range of metals using propylene carbonate as the solvent and tetraethylammonium perchlorate and toluenesulfonate as the electrolytes.¹² They showed that polypyrrole–toluenesulfonate (PPy–TS) films could be formed on a wide range of metals. It was reported that the oxidation potential of pyrrole was increased while the current intensity decreased when titanium (Ti), steel (Fe), and Al were used as the working electrode. This behavior was attributed to the formation of a metal oxide layer which impeded electron transfer and electropolymerization. It was, however, noted that the presence of a metal oxide layer was necessary for the electropolymerization of pyrrole onto brass. The oxidation potential of PPy–TS films was also found to be dependent on the metal used as the

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working electrode. When platinum (Pt) was used as the working electrode, the electropolymerization of pyrrole appeared to be controlled by both diffusion and adsorption processes. In spite of these differences, the room-temperature electrical conductivity of fully oxidized free-standing PPy films ($\sim 20\text{--}50\text{ s cm}^{-1}$) was reported to be independent of the nature of the working electrode. Janssen and Beck performed the electropolymerization of pyrrole on steel in an aqueous medium containing partially neutralized polyacrylate.¹³ They reported that adherent PPy–polyacrylate composite film was formed at a low current density.

Schirmeisen and Beck performed galvanostatic electropolymerization of PPy from more than 20 nonaqueous and aqueous electrolytes containing different anions on Pt, gold (Au), copper (Cu), Ti, stainless steel (VA), and steel (Fe).¹⁴ They showed that electropolymerization proceeded effectively in many aqueous electrolytes, when passive metals such as Pt, Au, V2A, or Ti were the working electrode. However, electropolymerization failed to occur when reactive metals such as Cu or iron were used. In acidic conditions ($\text{pH} < 7$), these metals actively dissolve and electropolymerization could not occur. In basic conditions ($\text{pH} \geq 10$), the metals were passivated, but inorganic films were formed rather than polymer coatings. The only exception from this behavior was the electropolymerization of pyrrole onto steel using potassium nitrate as the electrolyte. Smooth, continuous, and adherent PPy coatings were formed on steel using electrolyte concentrations of $0.01\text{--}1\text{ M}$ and current densities of $0.5\text{--}10\text{ mA cm}^{-2}$. The degree of insertion of nitrate ions into the film was about 0.25.

Beck and Michaelis reported the formation of strongly adherent and smooth PPy coatings onto a steel working electrode by aqueous electropolymerization using oxalic acid as the electrolyte.¹⁵ They showed that the adherence strength of the coatings was as high as 11.5 N mm^{-2} for $1\text{ }\mu\text{m}$ films but decreased with increasing coating thickness. The surface roughness of the PPy–oxalate film was found to be relatively low in comparison to other polypyrrole salts. The polymer films were essentially nonporous. The porosity of the film increased only slightly on elongation of the coating in the direction parallel to the iron substrate by 1–2%.

Hülser and Beck investigated the electropolymerization of PPy on Al from different aqueous elec-

trolytes.^{16,17} They showed that electropolymerization of adherent and homogeneous PPy coatings on Al occurred in these electrolytes. The electrolytes that were successful at initiating aqueous electropolymerization of pyrrole on Al include nitric acid, sulfuric acid, and oxalic acid. The ability to form an adherent PPy coating increased from left to right. Pretreatment of the Al by polishing (PD) or by anodic (galvanostatic) activation (GA) was found to be essential for the formation of a coherent and adherent PPy coatings. The presence of pores in the Al_2O_3 layer played an important role in the electrochemical process. In all cases, the Al_2O_3 layer containing pores, usually filled with electrolytes, were converted into $\text{Al}_2\text{O}_3\text{--PPy}$ sandwich layers. The sandwich Al/ Al_2O_3 /PPy structure behaved as a condenser with electronically conducting Al and PPy plates. The Al_2O_3 /PPy sandwich layers showed an unusually high permittivity of about 10^3 . Ferreira et al. investigated the influence of solvent and electrolytes on the electropolymerization of pyrrole on steel.¹⁸ They observed that the rate of corrosion of steel in acidic medium increased in the absence of pyrrole. Electropolymerization of pyrrole was shown to depend on the acidity of the medium. Electropolymerization of pyrrole in acetonitrile produced a PPy–ferric oxide composite film. However, in basic solvents, the coatings are composed of only PPy. In this article, we report the dependence of aqueous electropolymerization of pyrrole onto low carbon steel in an oxalic acid electrolyte on the electrochemical process variables such as the applied current, initial monomer concentration, electrolyte concentration, and reaction time.

EXPERIMENTAL

Materials

Pyrrole (98%) and oxalic acid (98%) were purchased from Aldrich Chemical Co. Tetrachloroethylene and methanol were also purchased from Aldrich. The reagents were dissolved in deionized water prepared in our department.

The working electrode was an 0.5 mm -thick QD low carbon steel panel purchased from the Q-panel Co. The working electrode was degreased with tetrachloroethylene for about 1 h prior to electrochemical polymerization. The counterelectrodes were composed of two Ti alloy plates. A saturated Calomel electrode (SCE), manufac-

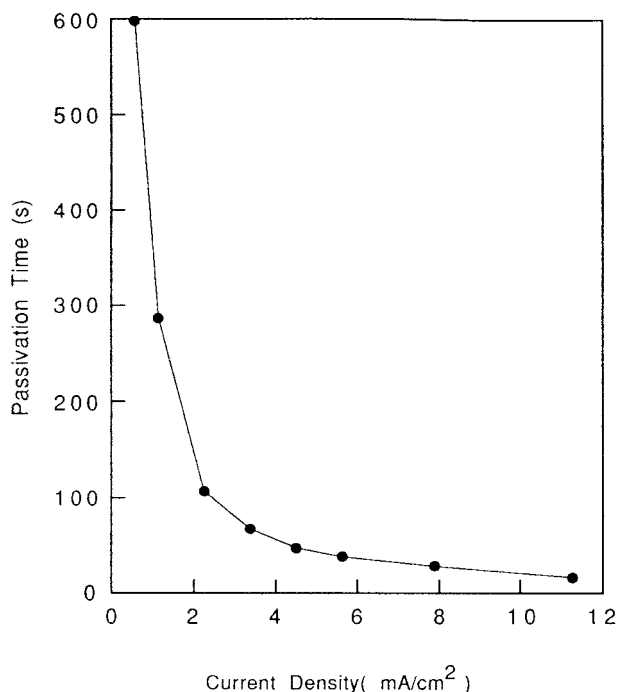


Figure 1 Dependence of induction time for electropolymerization of pyrrole onto steel (passivation time) on the applied current density.

tured by Corning Co., was used as the reference electrode. Galvanostat electropolymerization of pyrrole was performed by an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273A.

Electropolymerization

Electropolymerization of pyrrole was carried out in a one-compartment PPy cell. The current densities used in this study ranged from 0.22 to 11.26 mA/cm². The initial concentration of oxalic acid was varied from 0.05 to 0.4M, while the initial monomer concentration was varied from 0.1 to 0.8M.

The coated steel was rinsed with methanol and dried at 65°C in a vacuum oven to constant weight. The weight of the coatings was determined as the difference between the coated and noncoated steel (control).

Characterization

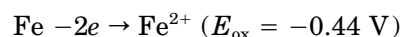
Elemental analysis of the coatings extracted from coated steel was performed by Galbraith Laboratories. The morphology of the coated and noncoated substrate was examined by scanning elec-

tron microscopy (SEM). The samples were shadowed with carbon to enhance their conductivity.

RESULTS AND DISCUSSION

Effect of Current Density

The concentration of pyrrole and oxalic acid were kept constant at 0.25 and 0.1M, respectively. The induction time for polymerization decreased with increased current density (Fig. 1). The decrease in the induction for electropolymerization was proportionate to the increment in the current density. Increasing the current density from 0.56 to 3.38 mA/cm² (500% increase) resulted in a sharp reduction in induction time from 598 to 67 s (90% reduction). A subsequent increase in the current density from 4.50 to 11.26 mA/cm² (150% increase) resulted in a more gradual decrease in the induction time from 47 to 16 s (66% reduction) (Table I). The induction time is the time expended during the dissolution of steel and ends at the onset of formation of iron oxalate (passivation time) (Fig. 2). At low current density ($C_d \leq 0.22$ mA/cm²), the potential of the reaction remained constant and negative ($E_p = -0.4$ V vs. SCE), resulting in the dissolution of the steel (Fig. 2):



The total charge passed during the passivation of steel remained nearly unchanged between 335 mC/cm² at 0.56 mA/cm² and 180 mC/cm² at 11.26 mA/cm² (Table II). An about 2000% change in the current density (0.56–11.26) caused only a 50% change in the passivation charge. The passivation of steel is accomplished by the formation of an iron oxalate (FeC₂O₄) interlayer (electropolymerization potential [E_p] ≥ 0.5 V)^{14,15}:

Table I Dependence of Electropolymerization Potential and Induction Time for Polymerization on the Current Density

Current Density (mA/cm ²)	Induction Time (s)	Peak Potential (V vs. SCE)	Reaction Potential (V vs. SCE)
1.13	287	0.84	0.66
2.25	109	0.88	0.71
4.50	47	1.04	0.80
7.88	28	1.34	0.95

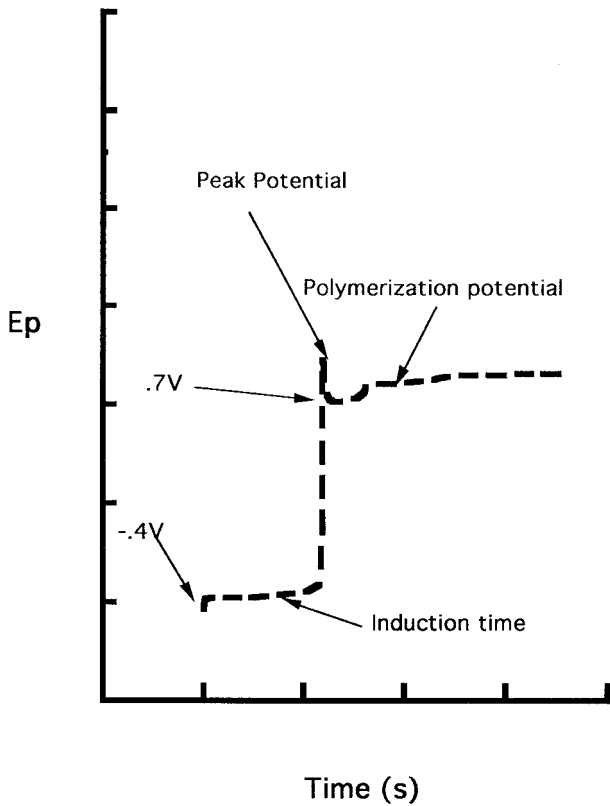
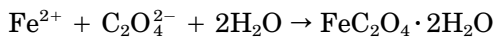


Figure 2 Induction time for electropolymerization of pyrrole onto steel using oxalic acid as the electrolyte.



The electropolymerization of pyrrole is believed to commence at the end of the induction period at a positive potential value ($E_p \geq 0.5$ V vs. SCE) (Fig. 2). The electropolymerization potential of

Table II Relationship Between Induction Time and Total Charges Passed During Induction Period

Current Density (mA/cm ²)	Induction Time (s)	Passivation Charge (mC/cm ²)
0.56	598	335
1.13	287	324
2.25	109	245
3.38	67	226
4.50	47	211
5.63	38	214
7.88	28	220
11.26	16	180

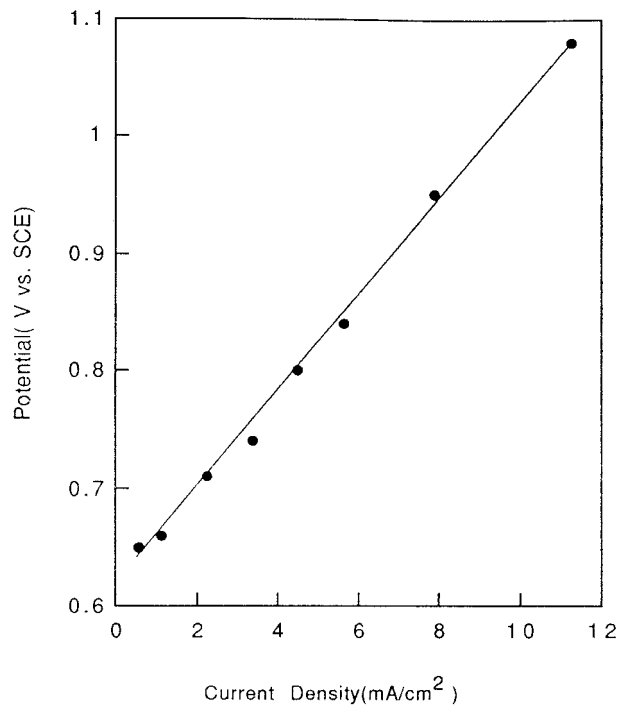


Figure 3 Dependence of polymerization potential on the current density.

pyrrole increased linearly with current density (Cd) (Fig. 3) and followed the relationship

$$E_p = 0.62 + 0.041 [\text{Cd}]$$

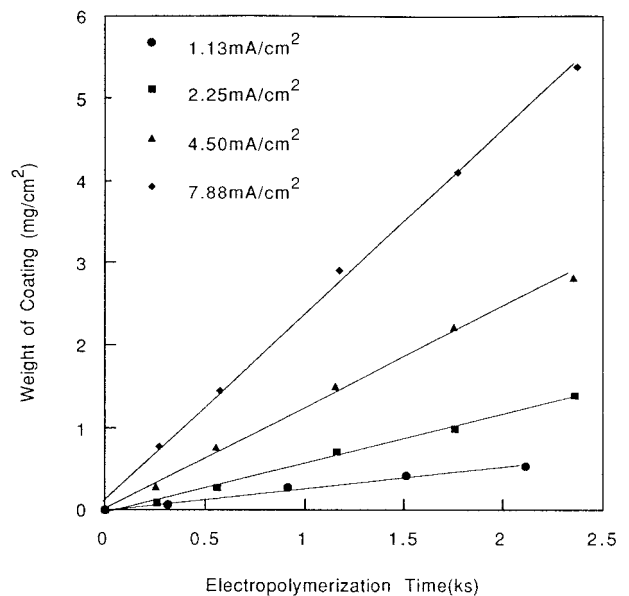


Figure 4 Dependence of PPy coating formation on current density. $[M] = 0.25M$; $[\text{Ox}] = 0.1M$; WE = low carbon steel.

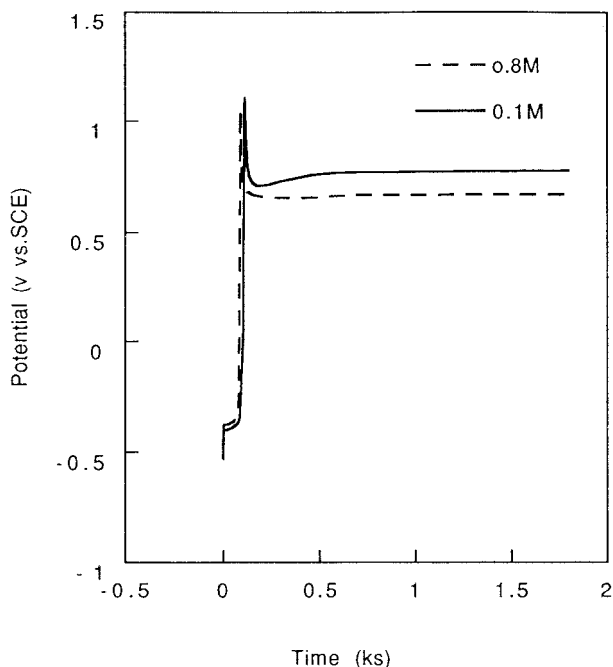


Figure 5 Dependence of induction time and electropolymerization potential on pyrrole concentration.

The amount of PPy coatings formed on steel increased with an increased electropolymerization potential in agreement with our earlier findings.¹⁹ The weight of PPy coatings formed onto steel increased proportionately with current density and electropolymerization time (Fig. 4). The weight of the electrode before and at the end of induction time (passivation time) was determined and no significant change occurred. The passivation time was taken as the starting time for the electropolymerization of pyrrole.

Effect of Initial Monomer Concentration

The concentration of oxalic acid was kept constant at 0.1M and the current density was kept constant at 2.25 mA/cm², while pyrrole concentration was varied from 0.1 to 0.8M. The concentrations of pyrrole did not have any noticeable effect on the passivation time (Fig. 5). This suggests that pyrrole was not involved in the passivation of steel. The polymerization potential was found to decrease exponentially with increased pyrrole concentration:

$$E_p = E_{ox} \exp^{-[M]}$$

About a 14% decrease in the polymerization po-

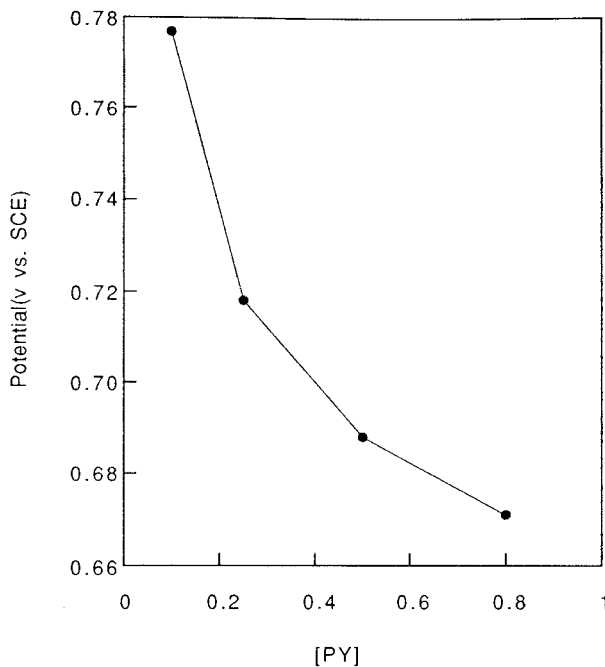


Figure 6 Dependence of polymerization potential on initial pyrrole concentration.

tential occurred when the monomer concentration was increased by 75% (Fig. 6). The lowering of the electropolymerization potential with in-

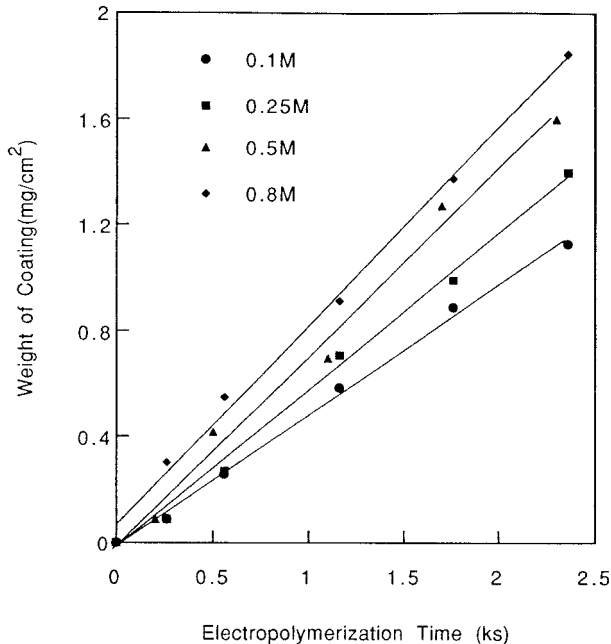


Figure 7 Dependence of coating formation on initial pyrrole concentration. Cd = 8.89 mA/cm²; [Ox] = 0.1M; WE = low carbon steel.

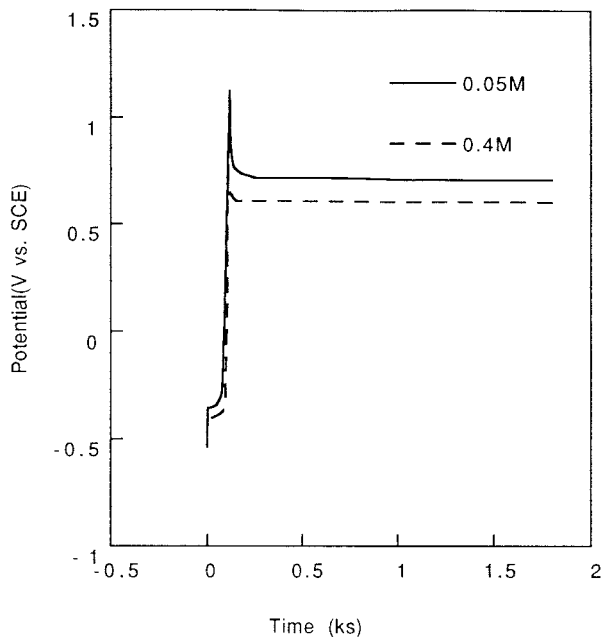


Figure 8 Dependence of polymerization potential on electrolyte concentration and electropolymerization time.

creased monomer concentration may be due to improved conductivity of the PPy-coated steel surface. It was reported that the FeC_2O_4 layer is more insulating than is the $FeC_2O_4-(PPy-(C_2O_4)_{.225})$

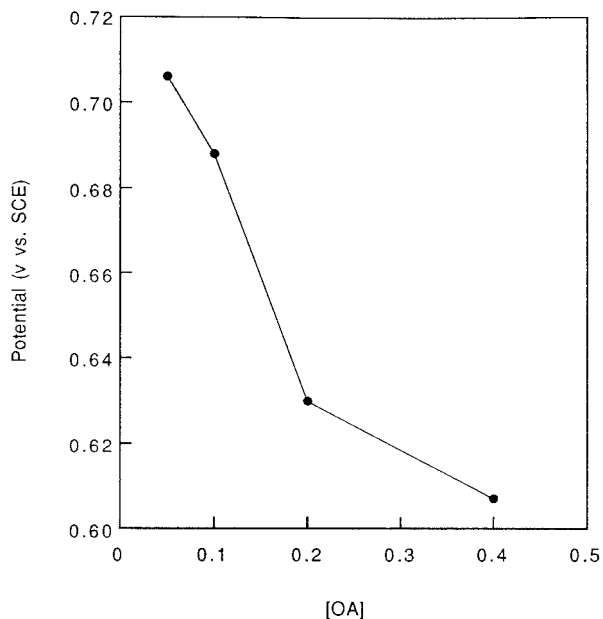


Figure 9 Dependence of polymerization potential on electrolyte concentration.

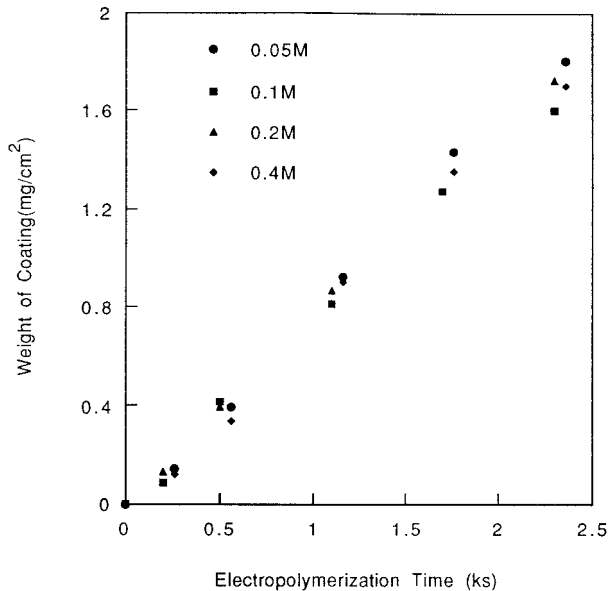


Figure 10 Dependence of polymerization of pyrrole on electrolyte concentration. $Cd = 2.25 \text{ mA/cm}^2$; $[M] = 0.5M$; WE = low carbon steel.

composite interlayer.¹⁵ The formation of PPy increased with pyrrole concentration and electropolymerization time (Fig. 7). The increment in the amount of PPy formed due to increased pyrrole concentration was, however, significantly lower than that obtained with an equivalent increase in the current density. For instance, doubling the current density from 2.25 to 4.5 mA/cm^2 resulted in the doubling of the amount of PPy formed from 12.4 to 25 mg (about a 102% increase) after 39 min of electropolymerization; however, doubling the monomer concentration from 0.1 to 0.2M resulted in only a slight increase in the amount of PPy formed from 14.2 to 15.3 mg (~ 7.8% increase) after 38 min of electropolymerization.

Effect of Electrolyte Concentration

The concentration of pyrrole was kept constant at 0.5M and the current density was maintained at

Table III Elemental Composition of PPy-Oxalate Coatings Formed on Low Carbon Steel

Elements	Content (%)
C	58.67
H	3.70
N	16.85
O	17.47

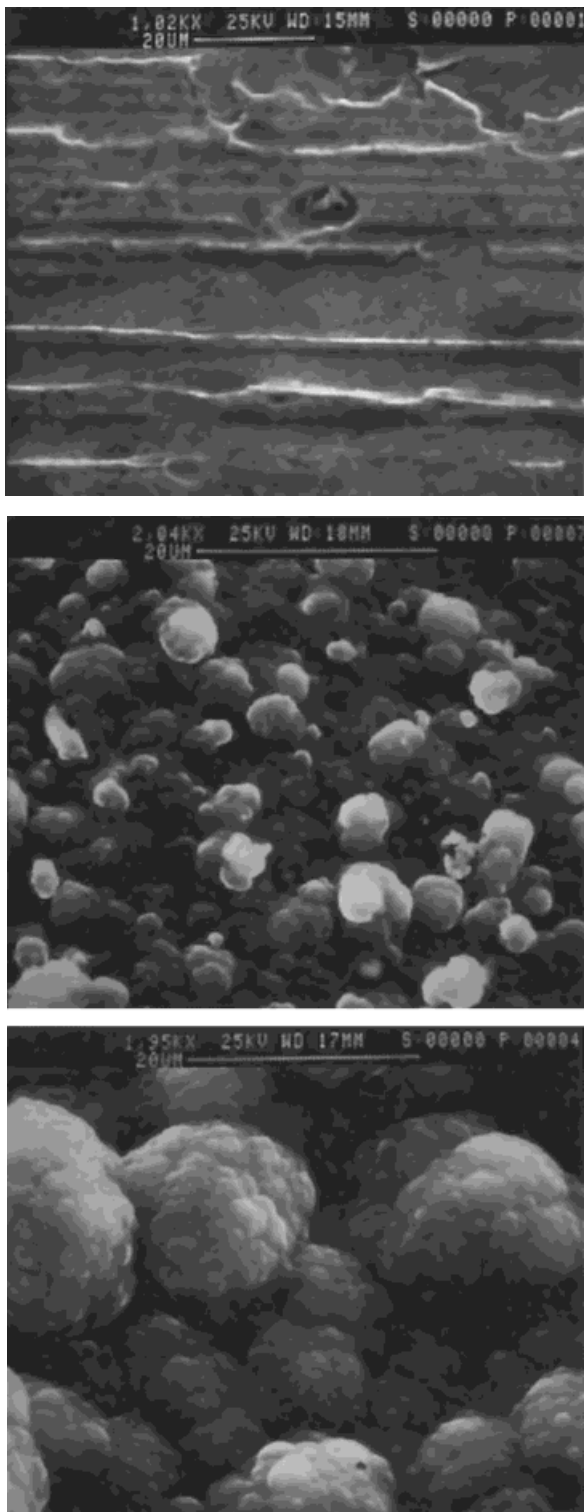


Figure 11 (Top) SEM micrograph of noncoated low carbon steel. SEM micrograph for low carbon steel coated with PPy formed by using (middle) low current density and (bottom) high current density.

2.25 mA/cm^2 while the concentration of oxalic acid was varied from 0.05 to 0.4 M . The induction time for polymerization was unaffected by electrolyte concentration (Fig. 8), confirming that the electrolyte was not involved in the passivation of steel. The electropolymerization potentials of pyrrole decreased gradually with electrolyte concentration (Fig. 9). Subsequent addition of oxalic acid ($2\text{H}^+ + \text{C}_2\text{O}_4^{2-}$)_{aq} after the passivation of steel (formation of FeC_2O_4 interlayer) lowers the resistance of the steel–oxalate interlayer, resulting in a decreased electrode potential.¹⁵ The amount of PPy formed onto the steel surface was independent of the electrolyte concentration (Fig. 10). Increasing the electrolyte concentration from 0.04 to 0.4 M resulted in no significant change in the amount of PPy formed, irrespective of the electropolymerization time. The role of oxalic acid is to passivate steel, initiate electropolymerization, and dope the PPy coatings.

Composition and Morphology of the Coatings

The elemental composition of the PPy oxalate coatings formed on steel is shown in Table III. Elemental analysis confirms the presence of oxygen in the coatings and indicates that oxalic acid is incorporated into PPy. Using the oxalate monoanion as the counterion, a mol ratio of pyrrole to the oxalate monoanion of $4.41 : 1$ was obtained.

The SEM pictures for low carbon steel and PPy-coated low carbon steel are shown in Figure 11. Overall, the surface of the PPy coatings is very smooth. The coatings formed by passing a lower current density for 30 min was smoother with fine microspheroidal grains. The PPy coatings formed at a higher current density ($\text{Cd} = 7.88 \text{ mA/cm}^2$) had a larger microspheroidal grain size than that formed at a lower current density ($\text{Cd} = 1.13 \text{ mA/cm}^2$). It is expected that the dependence of the morphology of the coatings on the current density would be reflected in the properties of the coatings.

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