

Kinetics and Efficiency of Aqueous Electropolymerization of Pyrrole onto Low-Carbon Steel

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ABSTRACT: The effect of process parameters on the conversion, P , and current efficiency, η , for the aqueous electropolymerization of pyrrole on low-carbon steel has been investigated. The amount of polypyrrole coatings formed on steel, W_p , increased with the charge passed, Q , and the initial pyrrole concentration $[M]$, but was unaffected by the electrolyte concentration. The conversion of pyrrole into polypyrrole, $P = W_p/W_M$, increased with electropolymerization time, and the applied current, and decreased with the initial monomer concentration. The oxalic acid concentration had no significant effect on conversion. The current efficiency for the electropolymerization of pyrrole performed by using high applied current, $I(I \geq 40 \text{ mA})$, and high pyrrole concentration, $[M] \geq 0.5M$, rose to its highest value at short polymerization times, $t < 300 \text{ sec}$. It then decreased and leveled off at longer times, $t \geq 1,000 \text{ sec}$. At low applied current, $I \leq 20 \text{ mA}$, and low pyrrole concentration, $[M] \leq 0.25M$, the current efficiency increased gradually with increased reaction parameters ($[M]$, I , and t) and reached a maximum value at $t = 1,000 \text{ sec}$. A retrogression of the current efficiency occurred at $t \geq 1,000 \text{ sec}$, for the reaction performed by using applied current of 10 mA. Overall, the current efficiency varied between 39 and 130%, with the higher values occurring at high pyrrole concentration and high applied current. The current efficiency was determined from the ratio of the experimental and theoretical electrochemical equivalents for polypyrrole. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 617–624, 1997

Key words: kinetics; efficiency; aqueous-electropolymerization; polypyrrole-on-steel

INTRODUCTION

Electrochemical polymerization has the ability to form uniform and continuous coatings on conductive substrates. It is fast and inexpensive and allows *in situ* analysis and monitoring of the coating process. In this study, constant current electropolymerization is used. The total charge passed during electropolymerization, Q , is determined as the product of the applied current, I , and the time, t , of application. In constant potential

coullometry, the total charge passed can be related to the concentration of the electroactive species in the cell (see reference 1).

Polypyrrole coatings are electrochemically formed on low-carbon steel with the intention to protect the substrate from corrosion. The process parameters, such as initial pyrrole concentration, oxalic acid concentration, applied current, and reaction time, are systematically varied. By determining the dependence of the coating process on the process parameters, we can control the coating formation process effectively and optimize the coating structure and properties. One area of the coating formation process of interest is the efficiency. The efficiency of electropolymerization

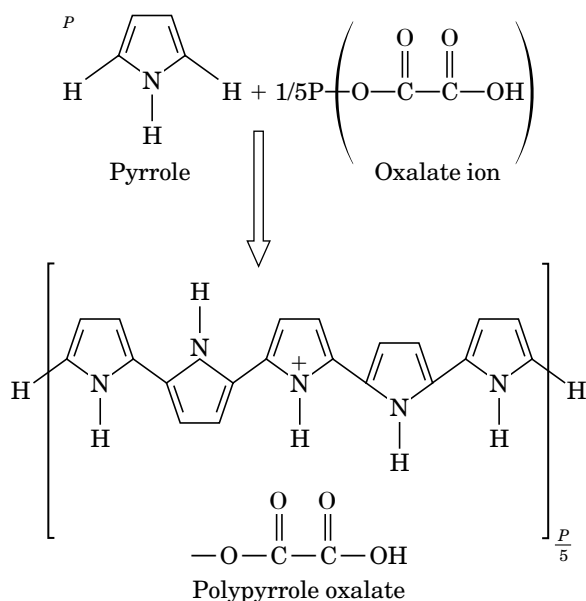
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refers to the amount of polymer formed with respect to the charge passed. The electrochemical formation of polypyrrole involves the conversion of pyrrole into polypyrrole by the transfer of electrons and the release of hydrogen ions.²⁻⁵ As a result, by determining the weight of polypyrrole formed and comparing it with the initial weight of pyrrole in the feed, one can estimate the extent of conversion.

The first step in the electrochemical polymerization (oxidation) of pyrrole is the formation of radical cations. Dimerization of the radical cations is accompanied by the loss of two hydrogen ions from the 2,5 position of the pyrrole ring. The dimer has a lower half-wave oxidation potential than the monomer; hence, further oxidation of the dimer occurs preferentially.² The electrochemically formed polypyrrole can undergo further oxidation, resulting in a partial positive charge on the pyrrole ring.⁶ As a result of this, the polymer associates with an anionic species (from the electrolyte salt) in order to maintain charge neutrality.⁷

The current efficiencies were determined in accordance with the method established by Schirmeisen and Beck.⁸ The schematic representation of the formation of polypyrrole is shown below (Scheme I):



Scheme 1 Formation of doped polypyrrole.

P is the degree of polymerization; the counter ion is hydrogen oxalate, which is inserted into the

coatings for charge compensation during electropolymerization; $\frac{1}{5}$ is the degree of insertion of the counter ion and was determined by elemental analysis. By use of the above model, the theoretical electrochemical equivalent, EE_{th} , for polypyrrole can be shown to be

$$EE_{theory} = M/(zF) = (M_M + yM_A)/[(2 + y)F] \quad (1)$$

where M_M is the molecular weight of the repeat unit ($M_M = 65$), M_A is the molecular weight of the oxalate ion, $y = \frac{1}{5}$, and F is Faraday's constant (96,500 coulombs per equivalent).

The experimental electrochemical equivalent can be determined from eq. (2):

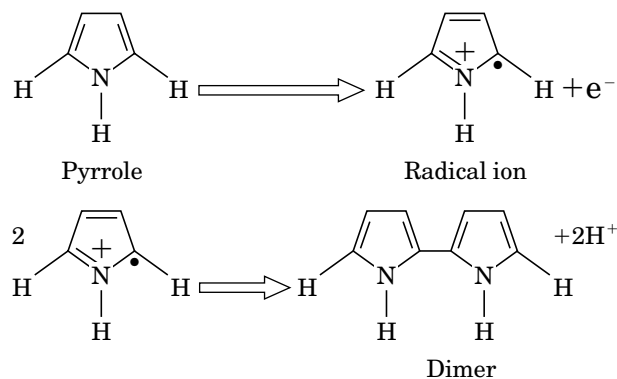
$$EE_{exp} = W_p/Q \quad (2)$$

where W_p is the weight of polypyrrole coatings, and Q is the charge passed. Since the constant current method was used, the charge passed was determined as the product of applied current, I , and the electropolymerization time, t , i.e., $Q = I \times t$.

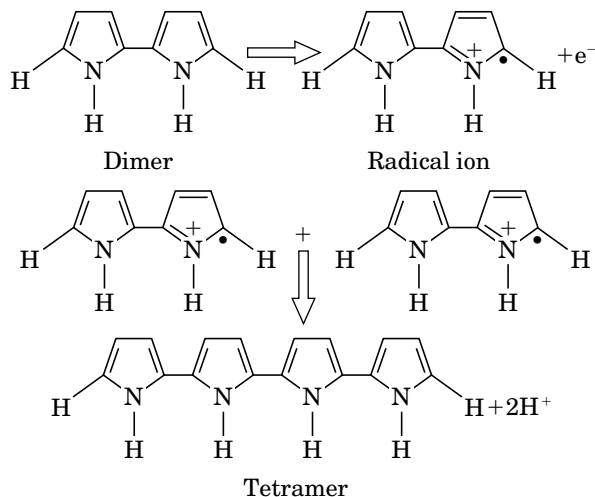
The current efficiency, η , is obtained from eq. (3):

$$\eta = EE_{exp}/EE_{theory} \quad (3)$$

The rate constant for the electropolymerization of pyrrole can be evaluated by recalling that the electropolymerization of pyrrole is preceded by the dimerization of the radical cation.



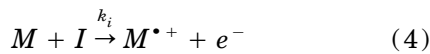
It was also reported that the dimer has a lower oxidation potential and should be oxidized in preference to the monomer.^{2,9,10} The oxidized dimers will couple with each other to form a tetramer.



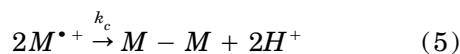
Further coupling could occur between the tetramer radical ion with itself or with a dimer. The possibility of a hexamer or octamer radical ion coupling with themselves or with a dimer or tetramer radical ion also exists. The coupling reaction will cease when the application of electric current is discontinued.

If the monomer is represented as M , then the reaction scheme can be written as follows¹¹⁻¹³:

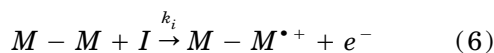
Initiation



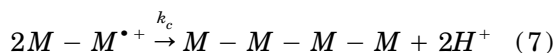
Coupling



Oxidation of dimer



Coupling of dimer radical cation



The electrochemical polymerization can be approximated to a series of oxidation (initiation) and coupling (propagation) steps. The formation of the monomer radical cation, $M^{\bullet+}$, is the slowest of the initiation reactions. Recall that it was shown that the oxidation potential of the dimer is lower than that for pyrrole.^{2,9,10} We can assume that the oxidation potential of the intermediate

species (dimer, tetramer, hexamer, octamer or prepolymer) and the rate constant for coupling, k_c , are irrespective of the size of the species.

The rates of initiation, R_i , and propagation, R_p , can be written as follows:

Rate of initiation, R_i

$$R_i = \frac{d[M^{\bullet+}]}{dt} = \frac{k_i[M]I}{FV} \quad \text{for constant process} \quad (8)$$

Rate of coupling, $R_c = R_p$

$$R_c = -\frac{d[M^{\bullet+}]}{dt} = k_c[M^{\bullet+}]^2 \quad (9)$$

At steady state, $R_i + R_c = 0$

$$\text{i.e., } \frac{d[M^{\bullet+}]}{dt} = \frac{k_i[M]I}{FV} - k_c[M^{\bullet+}]^2 = 0 \quad (10)$$

$$[M^{\bullet+}] = \left(\frac{k_i I [M]}{V F k_c} \right)^{1/2} \quad (11)$$

$$R_p = k_c[M^{\bullet+}]^2 = \frac{k_i[M]I}{FV} = -\frac{d[M]}{dt} \quad (12)$$

where k_i is the rate constant for initiation, k_c is the rate constant for coupling (propagation), I is the applied current, F is the Faraday's constant (96,500 coulombs/mol), V is the volume of the monomer-electrolyte solution, $[M]$ is the monomer concentration, and $[M^{\bullet+}]$ is the concentration of the radical cation.

By solving eq. (12) and substituting $(1 - P)M_0$ for $[M]$, we obtain eq. (13):

$$-\ln(1 - P) = \frac{k_i I t}{FV} \quad (13)$$

By substituting $I \times t = Q$, we obtain an expression that relates the conversion to the charge passed per unit volume

$$-\ln(1 - P) = \frac{k_i Q}{FV} \quad (14)$$

k_i can be determined from the slope of $\ln(1 - P)$ versus t or $\ln(1 - P)$ versus Q plot.

The conversion, P , is taken as the ratio of the

weight of the polymer coatings, W_P , to the initial weight of pyrrole, W_M , in the feed:

$$P = \frac{W_P}{W_M} \quad (15)$$

In this article, the effect of applied current, initial pyrrole concentration, electrolyte concentration, and reaction time on the current efficiency and conversion is presented. The dependence of the weight of the polypyrrole coatings formed on low-carbon steel on the charge passed and the process parameters, respectively, was also determined. It is hoped that by manipulating the electrochemical process parameters, optimal coating microstructure and coating properties will be established. Pyrrole was chosen for this study because the starting material is soluble in water and allows for controllable film formation in aqueous medium. The aqueous electrochemical polymerization of pyrrole is easy to control, cost effective, and environmentally safe. Polypyrrole is also one of the class of conducting polymers that have corrosion-resistant capability. The electropolymerization of pyrrole onto reactive metals such as steel and aluminum is believed to be an effective replacement for the hazardous chromate rinse process used to prime steel. The structure and properties of polypyrrole coatings are, however, dependent on the electrochemical process variables. Judicious control of the reaction variables is necessary in order to form pinhole-free, adherent, tough, and corrosion-resistant polypyrrole coatings.

EXPERIMENTAL

Materials

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

The working electrode is a 0.5-mm-thick QD low-carbon steel panel purchased from the Q-panel Company. The working electrode was degreased with tetrachloroethylene for about an hour prior to electrochemical polymerization. The counter electrodes were composed of two titanium alloy plates. A saturated calomel electrode (SCE),

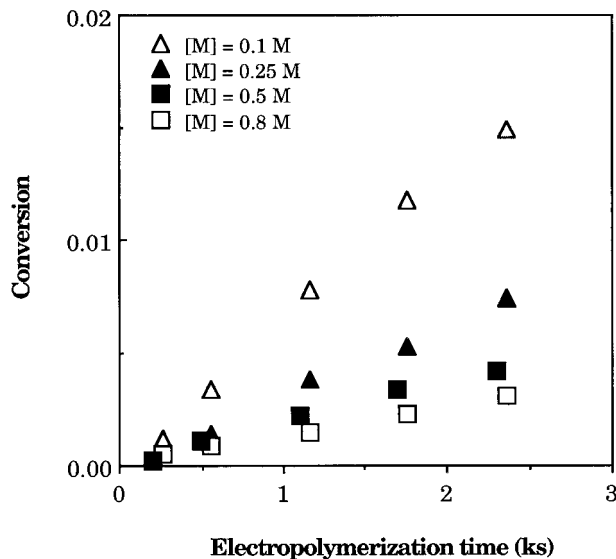


Figure 1 Dependence of conversion on initial pyrrole concentration and time.

manufactured by Corning Company, was used as the reference electrode. Constant-current electropolymerization of pyrrole was performed with an EG & G Princeton Applied Research Potentiostat/Galvanostat, Model 273A.

Electropolymerization

The electropolymerization of pyrrole was carried out in a one-compartment polypropylene 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. Electropolymerization was performed for 300–2,400 sec.

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, Inc. The ratio of pyrrole to hydrogen oxalate ion was determined to be 5 : 1.

RESULTS AND DISCUSSION

Figures 1–3 show the variation of conversion $\{P = (W_P/W_M)\}$ with the initial pyrrole concentra-

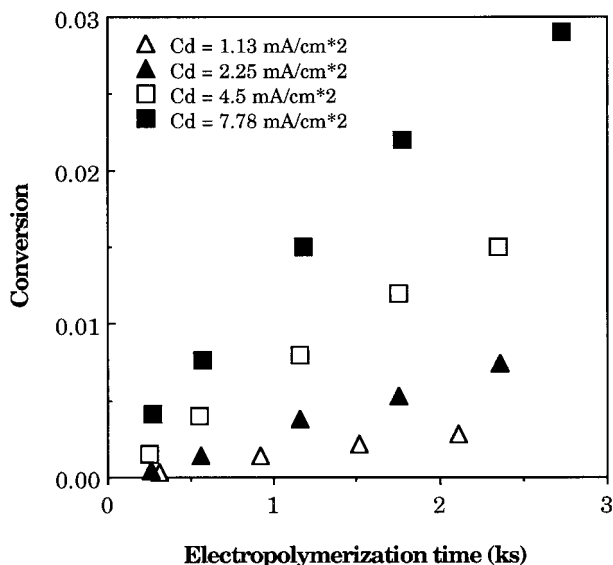


Figure 2 Dependence of conversion (C_d) on the applied current (working electrode area = 8.89 cm^2).

tion, the oxalic acid concentration and the applied current, respectively, as a function of electropolymerization time. The initial pyrrole concentration was varied between 0.1 and $0.8M$, while the electrolyte concentration and applied current were varied between 0.05 and $0.4M$ and 10 to 70 mA, respectively. Electropolymerization time was varied between 200 and 3,000 sec. The conversion of polypyrrole varied inversely with initial pyrrole

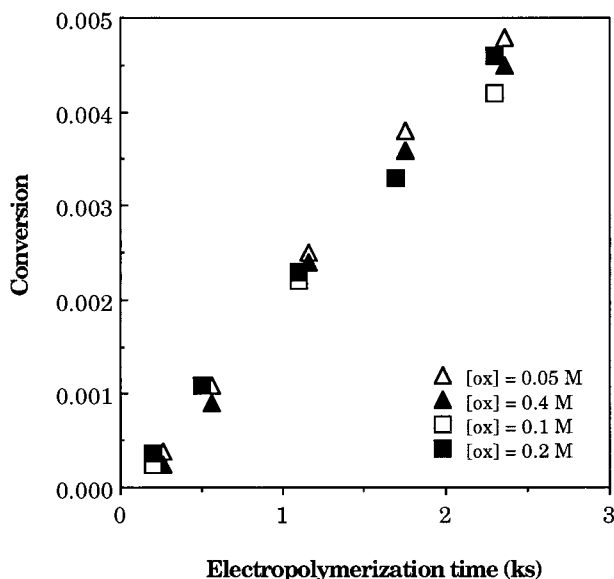


Figure 3 Dependence of conversion on oxalic acid concentration ($[ox]$).

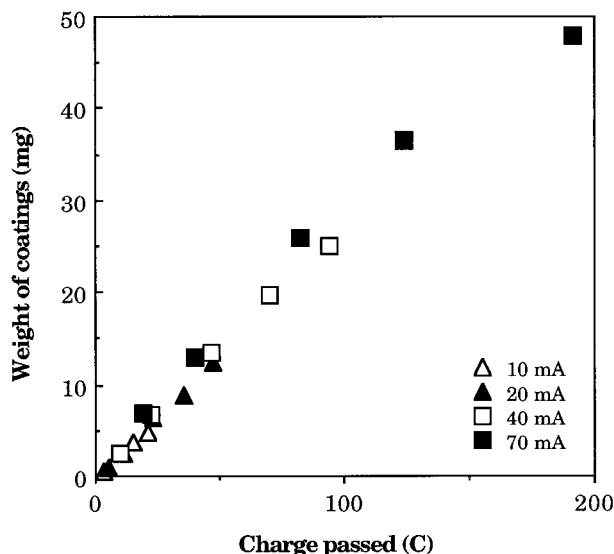


Figure 4 Dependence of the weight of polypyrrole coatings formed on steel on the charge passed and the applied current.

concentration (Fig. 1) and proportionately with applied current (Fig. 2) and reaction time (Figs. 1–3). Increasing the initial pyrrole concentration from 0.1 to $0.8M$ (700% increase) resulted in a decrease in the conversion from 1.5 to 0.31% ($\sim 80\%$ decrease) for $t = 40 \text{ min}$, $[OA] = 0.1M$, $I = 20 \text{ mA}$, and working electrode area of 8.89 cm^2 . The inverse relationship between pyrrole concentration and conversion was also confirmed at short reaction times. For example, increasing the pyrrole concentration from 0.1 to $0.8M$ (700% increase) resulted in a decrease in conversion from 1.2 to 0.05% (96% decrease) for $t = 2.5 \text{ min}$ (all other reaction conditions were maintained constant). The effect of applied current on conversion is shown on Figure 2. Increasing the applied current from 10 to 70 mA (600% increase) resulted in an increase in conversion from 0.36 to 2.9% (700% increase) (Figure 2) ($t = 46 \text{ min}$, $[M] = 0.25M$, $[OA] = 0.1M$). Conversion was not dependent on the electrolyte concentration (Fig. 3). Increasing oxalic acid concentration from 0.05 to $0.4M$ (700% increase) resulted in only a slight change in conversion from 0.48 to 0.45% (6% change) at $t \sim 40 \text{ min}$ ($[M] = 0.5M$, $I = 20 \text{ mA}$).

The dependence of the weight of polypyrrole coatings formed on steel on the charge passed as a function of the reaction parameters (I , $[M]$ and $[OA]$) is shown on Figures 4–6. The weight of polypyrrole coatings increased with the charge passed and was unaffected by the magnitude of

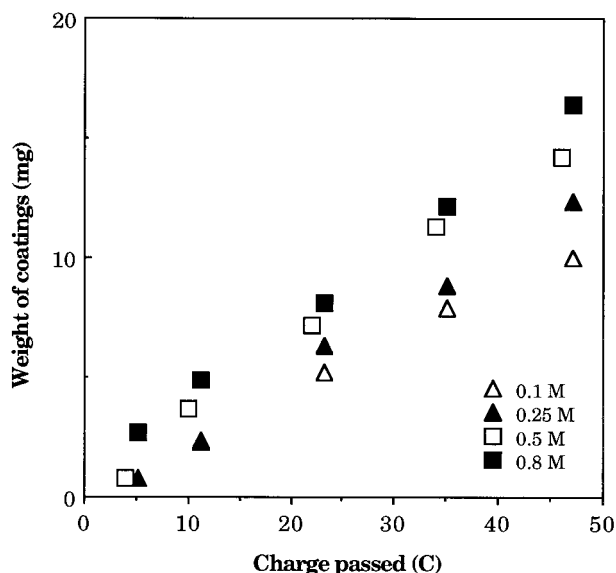


Figure 5 Dependence of the weight of polypyrrole coatings formed on steel on the charge passed and the initial pyrrole concentration.

the applied current, as was expected (Fig. 4). The weight of polypyrrole coatings increased with pyrrole concentration per unit charge (Fig. 5). The weight of polypyrrole coatings increased from 0.8 to 2.7 mg as the pyrrole concentration was increased from 0.1 to 0.8M, for 23 coulombs of charge passed (Fig. 5). However, the weight of

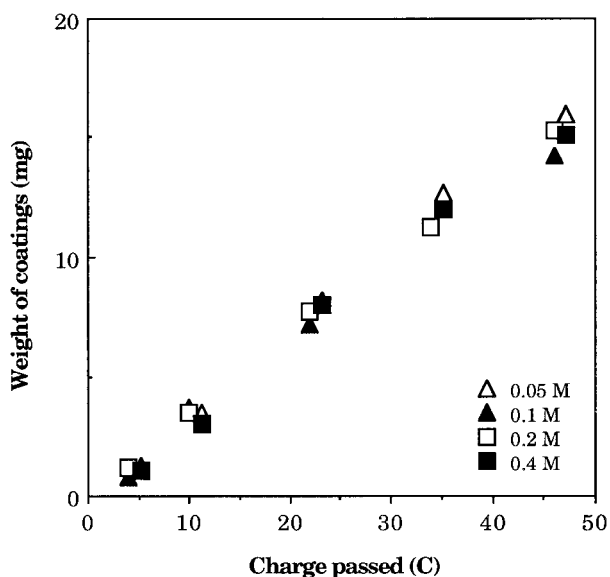


Figure 6 Dependence of the weight of polypyrrole coatings formed on steel on the charge passed and oxalic acid concentration.

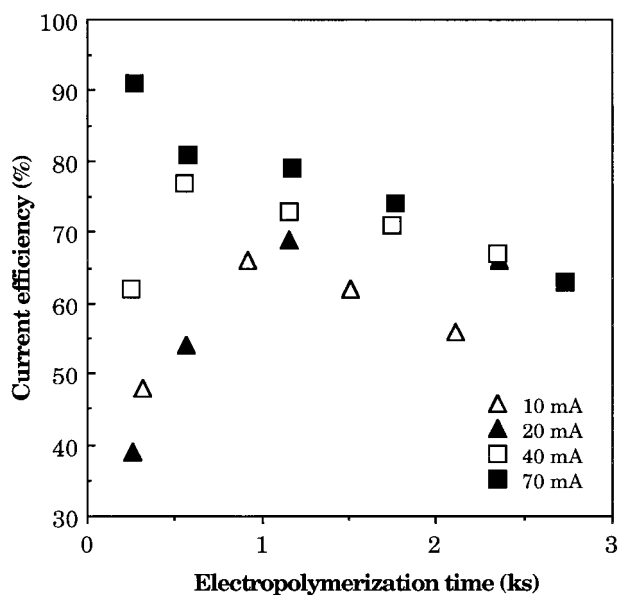


Figure 7 Dependence of current efficiency on the applied current and reaction time.

polypyrrole coatings per mole of pyrrole (monomer efficiency) decreased with increased pyrrole concentration. The weight of coatings per mole of pyrrole decreased from 8 to 3 mg/mol as the pyrrole concentration was increased from 0.1 to 0.8M. Increasing electrolyte concentration decreased the efficiency per mole of electrolyte (electrolyte efficiency). The weight of polypyrrole coatings was unaffected by the electrolyte concentration (Fig. 6), indicating that the electrolyte was not involved in the coupling reaction. The weight of polypyrrole coatings formed on steel increased with the charge passed and pyrrole concentration but was unaffected by the applied current or the oxalic acid concentration.

The dependence of the current efficiency on the reaction parameters is shown on Figures 7–9. Generally, the current efficiency rose to a maximum value at low reaction time, followed by a gradual decrease before attaining a constant value that is invariant with time (Figs. 7–9). The effect of applied current and initial pyrrole concentration is shown on Figures 7 and 8, respectively. For the electropolymerization of pyrrole performed by using high applied current ($I \geq 40$ mA) and high pyrrole concentration ($[M] \geq 0.5M$), the current efficiency rose to its highest value at short reaction times, $t < 300$ sec. It then decreased and leveled off at longer times, $t \geq 1,000$ sec. At low applied current ≤ 20 mA and low pyr-

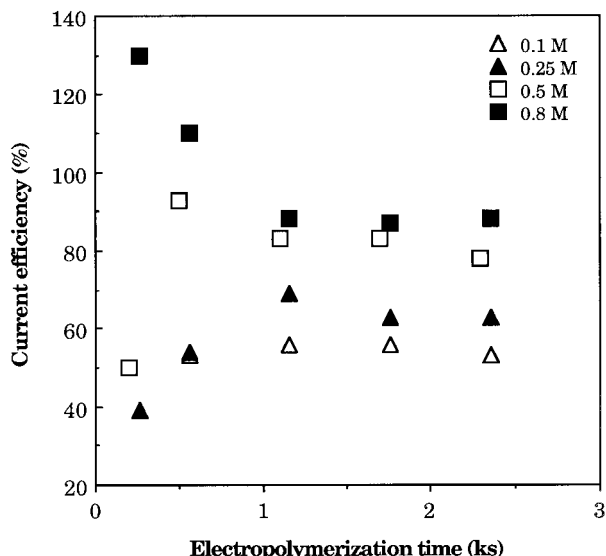


Figure 8 Dependence of current efficiency on initial pyrrole concentration.

role concentration, $[M] \leq 0.25M$, the current efficiency increased gradually with increased reaction parameter (I , $[M]$, and t) and leveled off after 1,000 sec of electropolymerization. A retrogressive decrease in the current efficiency occurred at $t \geq 1,000$ sec for the reactions performed by using an applied current of 10 mA. Overall, the current efficiency varied between 39 and 130%, with the higher values occurring at high pyrrole concentra-

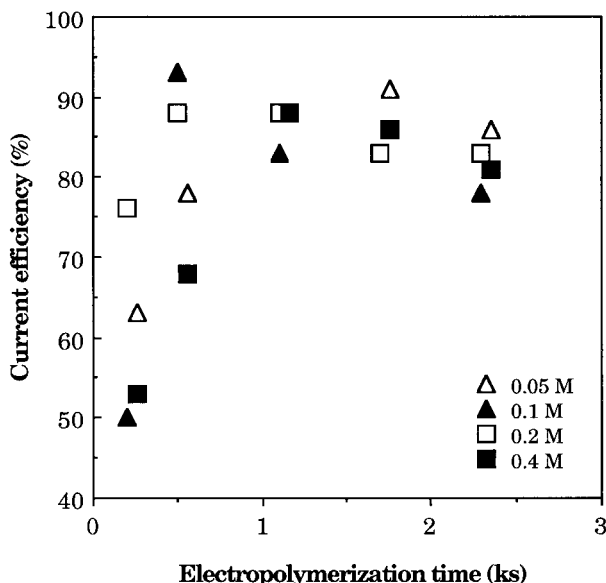


Figure 9 Dependence of current efficiency on oxalic acid concentration.

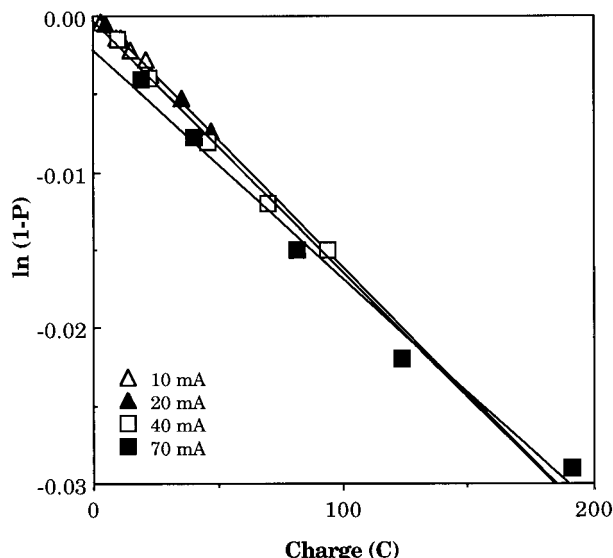


Figure 10 Variation of the rate constant for polymerization with applied current.

tion and high applied current. Figure 9 shows the dependence of the current efficiency on the electrolyte concentration and time. At low reaction times, $t < 600$ sec, the current efficiency increased with electropolymerization time, $t \leq 600$ sec, and leveled off at $t \geq 1,000$ sec. A subsequent increase in the reaction time above 1,000 sec resulted in no significant changes in the current efficiency (Fig. 9).

Figures 10–12 show a second-order kinetic

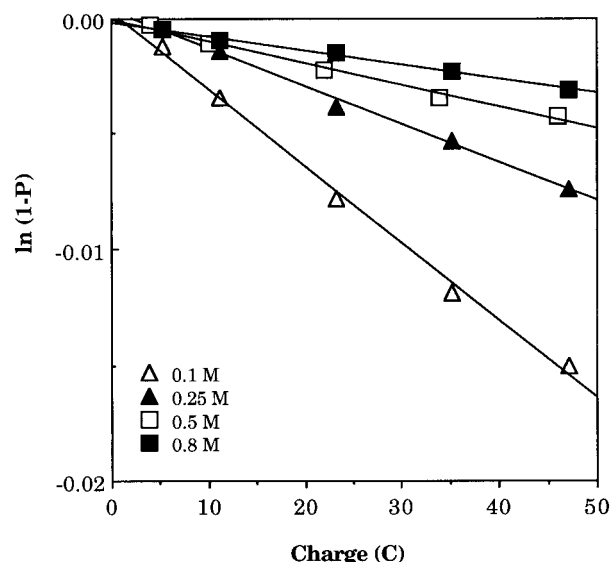


Figure 11 Variation of the rate constant for polymerization with initial pyrrole concentration.

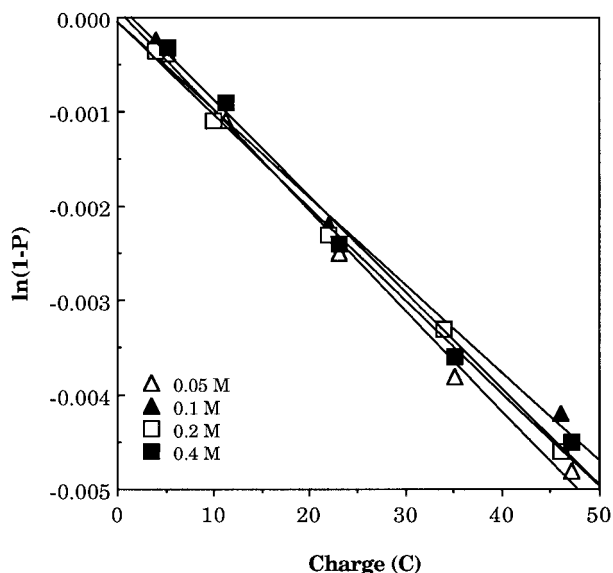


Figure 12 Variation of the rate constant for electro-polymerization of pyrrole on oxalic acid concentration.

plot, $\ln(1 - P)$ versus Q , for the aqueous electro-polymerization of pyrrole on low-carbon steel. The rate constant for electro-polymerization can be estimated from the slope of Figures 10–12. The slope of $\ln(1 - P)$ versus Q plot was unaffected by the value of the applied current, as was expected. Increasing the applied current from 10 to 70 mA resulted in no significant change in the slope from 1.35×10^{-4} to 1.47×10^{-4} (Fig. 10). Increasing the initial pyrrole concentration, however, resulted in a decrease in the slope of $\ln(1 - P)$ versus Q (Fig. 11). Varying the pyrrole concentration from 0.1 to 0.8M resulted in a decrease in the rate constant from 3.30×10^{-3} to 6.1×10^{-5} . The electrolyte concentration has no significant effect on the rate constant. Changing the electrolyte concentration from 0.05 to 0.4M resulted in no change in the slope (Fig. 12).

CONCLUSION

The effect of electro-polymerization reaction parameters on the conversion of polypyrrole and the efficiency of aqueous electro-polymerization on steel has been investigated. The conversion of polypyrrole increased with the applied current and decreased with initial pyrrole concentration.

There was no dependence of conversion on the electrolyte concentration. The amount of coatings formed on steel increased with the total charge passed but was unaffected by the applied current or the electrolyte concentration. It, however, increased with initial pyrrole concentration. The current efficiency was high at short reaction times. It declined gradually and remained unchanged after about 1,000 sec of electro-polymerization. Very high current efficiency was obtained at high monomer concentration and high applied current at short reaction times $t < 1,000$ sec.

ACKNOWLEDGMENT

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REFERENCES

1. EG&G Princeton Applied Research, Model 270/250 Research Electrochemistry Software User's Guide, 1992, EG&G Princeton Applied Research, Princeton, NJ.
2. E. M. Genies, G. Bidan, and A. F. Diaz, *J. Electroanal. Chem.*, **149**, 101 (1983).
3. H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, Eds., *Encyclopedia of Polymer Science and Engineering*, 2nd Ed., Vol. 13, Wiley, New York, 1988.
4. C. S. C. Bose, S. Basak, and K. Rajeshwar, *J. Phys. Chem.*, **96**, 9899 (1992).
5. B. Qian, Y. Li, B. Yan, and H. Zhang, *Synthetic Metals*, **28**, 51 (1989).
6. A. F. Diaz, J. I. Castillo, J. A. Logan, and W-Y. Lee, *J. Electroanal. Chem.*, **129**, 115 (1981).
7. A. Diaz, *Chemica Scripta*, **17**, 145 (1981).
8. M. Schirmeisen and F. Beck, *J. Appl. Electrochem.*, **19**, 401 (1989).
9. G. A. Wood, MS Thesis, University of Cincinnati, 1995.
10. G. A. Wood and J. O. Iroh, *Synthetic Metals* (1996).
11. J. H. Epsin, *Chemical Kinetics and Reaction Mechanisms*, McGraw-Hill Series in Advanced Chemistry, McGraw-Hill Book Company, New York, 1981, 30–34.
12. G. Odian, *Principles of Polymerization*, 2nd Ed., Wiley Interscience Publication, Wiley, New York, 1981, 46–72.
13. M. P. Stevens, *Polymer Chemistry*, 2nd Ed., Oxford University Press, Oxford, 1990, 332–334.