Analysis of the Kinetics and Current Efficiency of Pyrrole Galvanostatic Electropolymerization

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ABSTRACT: We propose a modified kinetic equation for the galvanostatic electropolymerization of pyrrole based on equal rates of monomer disappearance and its galvanostatic electropolymerization associated with applied current (I). The equation is distinguished by a zero-order kinetic plot and takes into account the effects of the pyrrole initial concentration ($[M]_0$) and current efficiency (η). We propose a mechanism for obtaining a η of less than 100% and increasing η with increasing $[M]_0$ and I on the basis of the diffusion of radical cations ($M^{\bullet+}$) from the anode surface to the bulk solution after the electroreduction of $M^{\bullet+}$ to monomer molecules at the cathode. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1167–1169, 2005

Key words: pyrolle; anodic polymerization; kinetic equation

INTRODUCTION

The important advantages of pyrrole polymeric coatings obtained by anodic galvanostatic electropolymerization on low-carbon steel in oxalic acid aqueous solution (these coatings are pinhole-free, adherent, tough, and corrosion resistant and have good conductivity) have widened interest in these coatings.[1–5] However, theoretical approaches to the kinetics and current efficiency (η) of the pyrrole galvanostatic electropolymerization have not been sufficiently investigated. This study was dedicated to further development of these issues.

KINETIC EQUATIONS FOR THE STAGE OF THE CHARGE TRANSFER

Considering that the rate-determining stage of pyrrole electropolymerization is the anodic formation of the radical cations ($M^{\bullet+}$) from monomer molecules (M)[4,6]

$$M - e^- \xrightarrow{k} M^{\bullet+} \tag{1}$$

and neglecting the diffusion limitation due to the relatively high monomer concentration and low current density, one can see that the kinetics of stage 1 is described by the general kinetic equation of charge transfer:[7]

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$$-V\frac{d[M]}{dt} = kS[M] \tag{2}$$

where V is the volume of the electrolyte solution (cm^3), $[M]$ is the pyrrole concentration (mol/L), t is the time (s), S is the area of the anode surface, and k is the heterogeneous rate constant of the anodic reaction [eq. (1); cm/s]:

$$k = k_0 \exp\left[\frac{(1-\alpha)F}{RT}(E - E^0)\right] \tag{3}$$

where k_0 is the heterogeneous standard rate constant (cm/s), α is the charge-transfer coefficient, E is the anode potential, E^o is the standard potential, and R is the gas constant, T is the absolute temperature, and F is the Faraday constant.

Su and Iroh[4] used eq. (2) to describe the kinetics of the galvanostatic process corresponding to the applied constant current (I; A). Including in eq. (2) the I/F value (mol/s), Su and Iroh[4] obtained the following equation:

$$-V\frac{d[M]}{dt} = \frac{k_1[M]I}{F} \tag{4}$$

where k_1 is a constant expressed by eq. (5) for keeping the same dimensions in the left and right sides of eq. (4) (this was not noted in ref. 4).

$$k_1 = kS\frac{F}{I} \tag{5}$$

Integrating eq. (4), where I is constant, one can see that[4]

$$-\ln(1 - P) = \frac{k_1 Q}{FV} \qquad (6)$$

where P is the conversion and $Q = It$ is the charge passed (C).

The linear dependence $\ln(1 - P)$ versus Q at different I values corresponding to eq. (6) is confirmed by Figure 10 in ref. 4 (the other figures mentioned herein are also from ref. 4). Our addition [eq. (5)] explains the insignificant change in the plot slope (Fig. 10, ref. 4) with changing I values. This change is caused by changes in E and I and, hence, k [eq. (3)] in the same direction, which causes an insignificant change in k_1 [eq. (5)].

At the same time, eqs. (5) and (6) have the following drawbacks: they do not reflect the effects of the pyrrole initial concentration ($[M]_0$) and η on the kinetics. Our kinetic analysis, shown later, eliminates these drawbacks.

MODIFIED KINETIC EQUATION

We propose a new kinetic equation based on the equal rates of the monomer disappearance and its galvanostatic electropolymerization:

$$-10^{-3} V \frac{d[M]}{dt} = \frac{\eta I}{100 q} \qquad (7)$$

where η is the current efficiency (%) and q is the charge necessary for converting 1 mol of pyrrole into polypyrrole (C). The dimensions of the left and the right sides of eq. (7) are the same (mol/s). As shown by Su and Iroh[4]

$$q = 2.2F \qquad (8)$$

With eqs. (7) and (8) and also the equation for P:

$$P = \frac{[M]_0 - [M]}{[M]_0} \qquad (9)$$

where $[M]_0$ is the pyrrole initial concentration (mol/L) after the integration of eq. (7) for η and I is constant, we obtain a modified kinetic equation:

$$P = \frac{10 \eta Q}{2.2 FV [M]_0} \qquad (10)$$

Considering that the kinetics in the form of the dependence $\ln(1 - P)$ versus Q has been described (Figs. 10–12, ref. 4) and expanding $-\ln(1 - P)$ in a series for

TABLE I
Confirmation of Eq. (11) for a range of η, $[M]_0$, P, and Q values

$[M]_0$ (mol L^{-1})	η (%)[a]	$-\dfrac{\ln(1-P)}{Q}$ (C^{-1})[b]	$-\dfrac{[M]_0 \ln(1-P)}{Q\eta}$ (mol L^{-1} C^{-1})
0.1	54.4	3.3×10^{-4}	6.1×10^{-7}
0.25	64.3	1.5×10^{-4}	5.8×10^{-7}
0.5	81.9	9.1×10^{-5}	5.6×10^{-7}
0.8	87.5	6.3×10^{-5}	5.8×10^{-7}

[a] Values were taken from Figure 8 of ref. 4.
[b] Values were taken from Figure 11 of ref. 4.

P small values (≤ 0.03), we find $-\ln(1 - P) = P$. Hence eq. (10) can be transformed into eq. (11):

$$-\ln(1 - P) = \frac{10 \eta Q}{2.2 FV [M]_0} \qquad (11)$$

The integration of eq. (7) under the conditions, where η is constant, is carried out approximately at $t \geq 0.5$–1 ks (details are given later). These η values, given in Figure 8 of ref. 4 (Table I; $t \geq 1$ ks) as average in time values, were used to confirm the validity of eq. (11). Indeed, as shown in the fourth column of Table I, the obtained values were in a close range of 5.6–6.1 $\times 10^{-7}$, for a wide range of η (54, 4–87.5), $[M]_0$ (0.1–0.8), and $-\ln(1 - P)/Q$ values. Thus, the slope of the $\ln(1 - P)$ versus Q plots for different $[M]_0$ values (Fig. 11, ref. 4) fit the theoretical values. The change in the slope of $\ln(1 - P)$ versus Q plots for different I values was also in agreement with eq. (11): the maximum ratio of the slopes was 1.1 (Fig. 10, ref. 4) at a maximum ratio of the η values equal to 1.2 at $t \geq 0.5$ ks (Fig. 7, ref. 4).

Equation (7) follows zero-order kinetics. However, at small P values, eq. (11) gives first-order kinetics. Analogously, the first order corresponds to eq. (6), independent of the P value, unlike the second-order kinetics accepted[4] for this equation.

CURRENT EFFICIENCY

The η values considered previously at $t \geq 1$ ks were less than 100%. This effect and also the influence of I on η (Fig. 7, ref. 4) and $[M]_0$ (Fig. 8, ref. 4) are not explained in ref. 4.

To explain these effects, we accepted the existence of a partial diffusion of one or more intermediate products of electropolymerization from the reaction layer at the anode surface to the bulk solution. Because P can be determined equally by two methods[4] (by weighing the polymer coating deposits and by the decrease in the monomer concentration in solution), the products of the partial diffusion from the anode
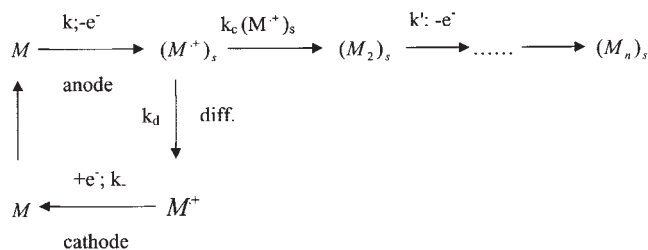
Scheme 1 Reduction of cathodic products (k_c = rate constant of coupling; k' = rate constant of the $M \cdot {}_2^+$ formation; k_d = rate constant of $M^{\bullet+}$ diffusion, depending on the diffusion coefficient of $M^{\bullet+}$ and hydrodynamic parameters; k_- = rate constant of the $M^{\bullet+}$ electroreduction).

decreasing the η values can are most likely $M^{\bullet+}$, which are further reduced to M on the cathode, including participation in the reduction of cathodic products (Scheme 1).

To explain the influence of I (Fig. 7, ref. 4) and $[M]_0$ (Fig. 8, ref. 4) on η for steady-state processes, that is, the stationarity of the chemical reactions and diffusion, where $[M^{\bullet+}]_s \gg [M^{\bullet+}]$, we used the following equations:

$$k_c V_r [M^{\bullet+}]_s^2 = \frac{10\eta I}{2.2F} \quad (12)$$

$$kS[M] = k_c V_r [M^{\bullet+}]_s^2 + k_d [M^{\bullet+}]_s \quad (13)$$

where s indicates the concentration in the reaction layer and V_r is the volume of the reaction layer at the anode. The dimensions are k_c (L mol^{-1} s^{-1}), V_r (cm^3), $[M^{\bullet+}]$ (mol/L), and k_d (cm^3/s); for other dimensionalities, see eq. (2).

k is a function of E [see eq. (3)]; however, after the electropolymerization begins, the potential remains practically constant at times.[5] Because the P value is small (Figs. 10–12, ref. 4), $[M] \cong [M]_0$, and eq. (13) can be written as:

$$kS[M]_0 = k_c V_r [M^{\bullet+}]_s^2 + k_d [M^{\bullet+}]_s \quad (14)$$

Eqs. (12)–(14) allowed us to carry out the analysis of the influence of I and $[M]_0$ on η.

From eq. (14,) we find $[M^{\bullet+}]_s$:

$$[M^{\bullet+}] = -\frac{k_d}{2k_c V_r} + \sqrt{\left(\frac{k_d}{2k_c V_r}\right)^2 + \left(\frac{kS}{k_c V_r}\right)[M]_0} \quad (15)$$

From eq. (15), it follows that $[M^{\bullet+}]_s$ is a function of $[M]_0$ and I. The latter is caused by the dependence of I on E and the influence of E on k [eq. (3)].

At a given I (when k is constant) and with the different $[M]_0$ values from eqs. (12),(14), and (15), η increased with increasing $[M]_0$, which was confirmed by results reported in Figure 8 of ref. 4.

At a given $[M]_0$ and with different I values, $[M^{\bullet+}]_s$ changed because of the change in k [eq. (15)]. For increasing I values, an increase in the E was necessary, and consequently, k also increased [eq. (16)]. Equation (12) in the form

$$\eta = \frac{k_c V_r 2.2 [M^{\bullet+}]_s^2}{10I} \quad (16)$$

allowed us to assume that with increasing I, because $[M^{\bullet+}]_s$ increases, the ratio $[M^{\bullet+}]_s^2 / I$ increased, and η increased also. This was in accordance with Figure 7 of ref. 4. As it follows from Figures 7 and 8 of ref. 4, at an electropolymerization time $t \geq 0.5$–1 ks, the η value was close to constant, which was caused by the steady state process (Scheme 1) and the sufficient passivation of the anode. The absence of the steady state at $t \geq 0.5$–1 ks corresponded to a smaller $[M^{\bullet+}]_s$ and, hence, an increase in η (Figs. 7 and 8, ref. 4). The absence of the full passivation of the anode probably dominated at low I and $[M]^o$, and hence, the η values decreased (Figs. 7 and 8, ref. 4).

In conclusion, new theoretical approaches for analysis of the kinetics and η of pyrrole galvanostatic electropolymerization were developed in this study and were confirmed by most detailed experimental data in this field, as obtained by Su and Iroh;[4] these approaches can be used in the future for other electropolymerization systems.

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