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Kinetic study of the aqueous electropolymerization of acrylamide, acrylonitrile and *N,N'*-methylene-bisacrylamide on an aluminium alloy cathode

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This study concerns the potassium persulphate electroinitiated polymerization of acrylamide, acrylonitrile and *N, N'*-methylene-bisacrylamide on a 5182 aluminium–magnesium alloy. Kinetic studies of the polymerization gave the polymerization as $-\mathrm{d}[M]/\mathrm{d}t = K(CD)^{0.99}[\text{Persulphate}]^{1.12}[M]^{2.33}$, where *CD* is current density (mA cm^{-2}), $[M]$ is monomer concentration (mol cm^{-3}), *K* is a constant and *t* is time (s). It is proposed that the thick swollen polymer coating restricted the diffusion of monomers and initiators to the electrode. The problem of mass transfer by diffusion in the present system was confirmed by measurements of the diffusion coefficient and by electron transfer fraction experiments carried out through the use of a cyclic voltammetry technique.

1. Introduction

Chromic acid anodization has been a conventional electrolytic process for coating aluminium alloys with an oxide which has decorative, protective or other properties. The aerospace industry has used this technique to protect aluminium alloys from corrosion and to provide a good surface for adhesive bonding. However, this process is not environmentally favourable because spent chromic acid, which contains very toxic hexavalent chromium (chromate Cr^{6+}) is left for disposal. This presents a large problem in many industries, especially the metal finishing industry.

Electropolymerization, an alternative process, provides polymeric coatings on aluminium alloys without involving toxic chemicals such as the chromate in chromic acid anodization. Several research groups have demonstrated formation of polymer coatings on metals through an efficient and economical electropolymerization process [1–9]. This coating technique can be directly used to prepare materials for potential applications in highly-demanding fields such as electronics, the aerospace industry and the automobile industry. One of the advantages of electropolymerization is that the chemical and physical properties of the polymer coating can be tailored by proper choice of monomer(s) and reaction conditions. In other words, the electropolymerization can be controlled if the kinetics of a specific monomer(s) system are known, Therefore, understanding of the kinetics is very important in designing an electropolymerization process.

In this work the electropolymerization of acrylamide (AM), acrylonitrile (AN) and *N*, *N'*-methylene-bisacrylamide (MBA) was done on an aluminium alloy, using an aqueous medium. The reasons for selecting AM and AN are that the former provides strong adhesion to the aluminium alloy substrate, while the latter also provides hardness to the coating and helps depress the swelling of the coating. The use of the cross-linking agent (MBA) is to prohibit the formed polymer coating from dissolving back into the aqueous solution, since polyacrylamide is very soluble in water. One important criterion for the monomers is that they must have reasonable water solubility since the process is carried out in aqueous medium. AN has good water solubility as compared with many other common vinyl monomers. Its water solubility is 7 g/100 ml water, which is sufficient for the electropolymerization process since only a small amount of monomer is consumed. AM and MBA, however, have high solubility in water.

The effects of the major reaction parameters (time, current density, monomer concentration, initiator concentration) on the polymer amount are reported herein. In addition, diffusion studies were used to interpret the experimental polymerization rates resulting from the kinetic experiments. The diffusion of the various species and the diffusion resistance of the polymer film were studied from intermittent cyclic voltammetry experiments in-situ during an electropolymerization run, with the use of potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$).

The diffusion coefficient of the $Fe(CN)_6^{3-}$ ions to the electrode was calculated from the following equation [10]

$$i_{\text{red}} = 2.69 \times 10^5 n^{3/2} A\,C\,D^{1/2} V^{1/2} \qquad (1)$$

where i_{red} is the reducing current in amperes, n is the number of electrons transferred, A is the surface area of the electrode in cm^2, C is the concentration of $Fe(CN)_6^{3-}$ ion in mol cm^{-3}, D is the diffusion coefficient in cm^2 s^{-1} and V is the scan rate in volt s^{-1}.

The diffusion coefficient was determined from a plot of i_{red} versus $V^{1/2}$, where the i_{red} is the peak height of the reduction scan.

The electron transfer fraction associated with the $Fe(CN)_6^{3-}$ ions was determined from the cyclic voltammetry experiments. This transfer fraction represents the ease of the electron transfer across the electrode-polymer interface in the electrochemical cell. A fall in the electron transfer fraction implies that the reduction becomes more difficult to achieve. At high scan rate, the value of E_{red} becomes dependent on the scan rate as the electrochemical reaction becomes more irreversible. The electron transfer fraction can be obtained from a plot of E_{red} versus log V according to the following equation [11]

$$E_{red} = E_{const} - 2.303\,RT(\log V)/fNF \quad (2)$$

where E_{red} is the reduction potential in volts, R is the gas constant, T is the temperature in K, V is the scan rate in volts s^{-1}, f is the electron transfer fraction, F is the Faraday constant and N is the number of electrons transferred.

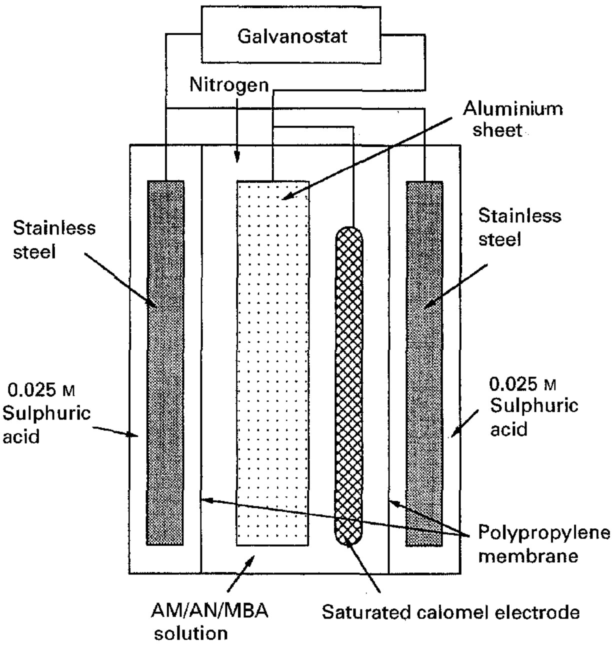
2. Experimental Procedure

2.1. Materials

Reagent grade acrylamide and reagent grade acrylonitrile were used for the research and the inhibitor was removed by passing it dropwise through an inhibitor-removal column (DHR-4). Reagent grade *N*, *N*′-methylene-bisacrylamide was used as purchased.

2.2. Electrochemical cell

A schematic description of the electrochemical cell is shown in Fig. 1a. The electrochemical cell used for the research was composed of a 21.5 × 14.5 × 6 cm^3 glass chromatographic tank into which a Delrin tank (10 × 9 × 4.5 cm^3 was placed. The Delrin tank's sides were drilled with holes and covered by polypropylene membranes (0.4 μm pore size, SEPA membrane) one on each tank side. The most important advantage of such a three-compartment cell is that the polymer coating can be applied evenly on both sides of the metal substrate. The metal substrate was placed inside the central cathode compartment, while the counter electrodes (anodes), stainless steel plates, were placed in the outside compartments. Constant direct current or voltage was supplied by a Princeton Applied Research potentiostat model no. 363.



(a)

Figure 1 (a) Schematic description of the three-compartment electrochemical cell.

2.3. Treatment of aluminium alloy before coating

The aluminium alloy 5182, provided by the ALCOA research center, had the following elemental composition in wt %

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Other	Al
0.20	0.35	0.15	0.20–0.50	4.0–5.0	0.10	0.25	0.10	0.15	Remainder

This aluminium alloy 5182 was pretreated according to a standard alkaline etching treatment [12]. The aluminium alloy was first treated in a 1.5 M sodium hydroxide solution at 65 °C for 5 min. This treated aluminium was then rinsed in tap water at room temperature thoroughly and de-smutted by dipping for 5 min in 10 vol % nitric acid at room temperature. After de-smutting, the sample was rinsed thoroughly in distilled water at room temperature and air-dried in the hood. The sample was used within 5 h after it was judged dry.

2.4. Electropolymerization procedure

The electropolymerization of AM/AN/MBA on to 5182 aluminium alloy was carried out in the three-compartment cell (Fig. 1a) described above. Appropriate amounts of the monomers, initiator and any possible inert electrolyte were dissolved in distilled water and the resulting solution, with a total volume of 200 ml, was deoxygenated with nitrogen gas for 30 min. The mixture was poured into the Delrin tank which comprised the central compartment of the three-compartment cell. The outside, anode compartment contained 160 ml of 0.025 M sulphuric acid. Nitrogen gas was then purged over the surface of the cathode solution for 15 min to form an inert blanket before the current was switched on. After electropolymerization, the aluminium electrode was carefully rinsed with copious distilled water to remove any trapped monomers and initiator present in the swollen, cross-linked copolymer. The coated aluminium was then air-dried at room temperature overnight. It was further vacuum-dried at 150 °C to constant weight. The weight of the coating was measured from the weight difference of the Al electrode before and after the electropolymerization.

2.5. Diffusion studies

Potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$) was used to study diffusion phenomena associated with the initiator and monomers in the AM/AN/MBA electropolymerization system. The theoretical basis for these measurements was discussed in the introduction section. The procedure has been used extensively in studies of diffusion in electrode coatings [10]. The experiments were carried out using a cyclic voltammetry (CV) technique with a BAS-100 electrochemical analyser. The counter electrode was a pure platinum coil, while the working electrode was an alkaline pretreated aluminium sheet. Argon gas was bubbled into the solution throughout the experiment. A series of voltammograms were taken at scan rates of 4, 8, 10 and 12 $\mathrm{mV\,s^{-1}}$ to determine their corresponding i_{red} values. The electron transfer fraction experiments were carried out at high scan rates, 100, 150, 200 and 250 $\mathrm{mV\,s^{-1}}$.

3. Results and discussion

3.1. Effect of current density

Experiments were done for a variety of current densities and times of 10, 16, 23 and 30 min. Fig. 2 presents the coating amount as a function of time at different current densities. After an initial induction period, the coating amount increases linearly with time at constant current density. An increase in current density promotes a greater concentration of primary radicals, thus enhancing the rate of polymerization initiation. At the same time, high current density also increases the probability of radical termination. However, since this is a cross-linked system, this problem is not a major concern to network molecular weight.

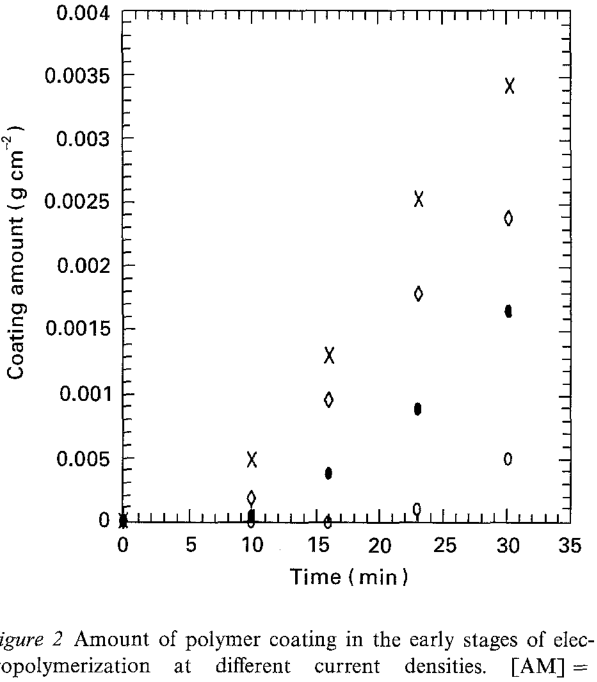


Figure 2 Amount of polymer coating in the early stages of electropolymerization at different current densities. [AM] = [AN] = 0.5 M, [MBA] = 0.05 M, [Persulphate] = 0.05 M. ○ 0.1 $\mathrm{mA\,cm^{-2}}$; ● 0.2 $\mathrm{mA\,cm^{-2}}$; ◇ 0.3 $\mathrm{mA\,cm^{-2}}$; × 0.4 $\mathrm{mA\,cm^{-2}}$.

A short induction period, about 5 min, was observed in the experiments. This is probably due in part to residual oxygen left in the solution during the transferring process. In addition, water reduction is a competitive reaction in the system; water reduction will lower the persulphate reduction efficiency, leading to a delay in the electropolymerization. More gas was liberated at the beginning of the process, but it became less vigorous as the thick coating was formed. This is because the polymer coating formed on the Al electrode has an inhibitory effect on water reduction. As reported by Otereo and Garcia [13], the presence of a thin polyacrylamide film could prohibit water reduction from interfering with the polymerization.

The rate of the electropolymerization calculated from the slope of the linear zone of the plot is presented in Fig. 3. The dependence of the rate on current density was determined from the slope of the graph shown in Fig. 4. It was found that the rate of polymerization at constant monomer and initiator concentrations was directly proportional to the current density raised to a 0.99 power.

3.2. Effect of persulphate concentration

The amount of the polymer coating formed on the Al electrode was studied at four different persulphate concentrations: 0.02 M, 0.035 M, 0.050 M and 0.065 M. The results are plotted as a function of reaction time, as shown in Fig. 5. At constant persulphate concentration, the amount of the coating increases linearly with time. Increasing persulphate concentration also increases the amount of coating formed per unit time. The 5-min induction period was again observed, and the reasons are believed to be the same as described for current density above. The rate of the polymerization was measured as the initial slope of the linear

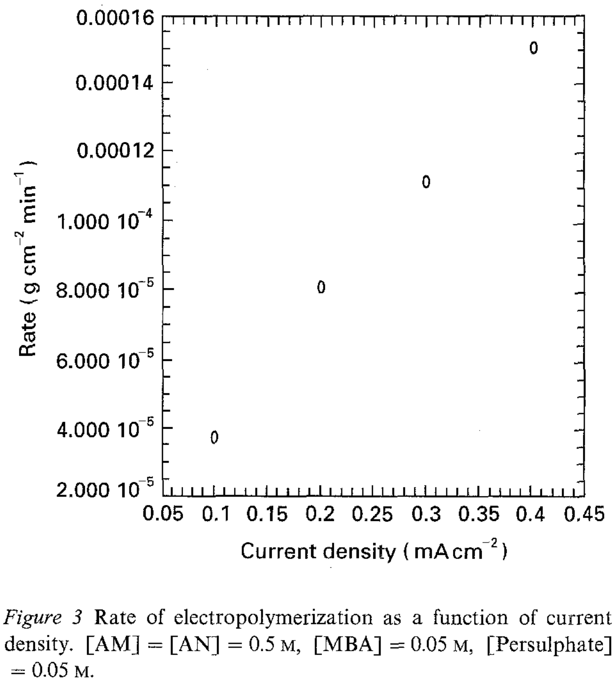


Figure 3 Rate of electropolymerization as a function of current density. [AM] = [AN] = 0.5 M, [MBA] = 0.05 M, [Persulphate] = 0.05 M.

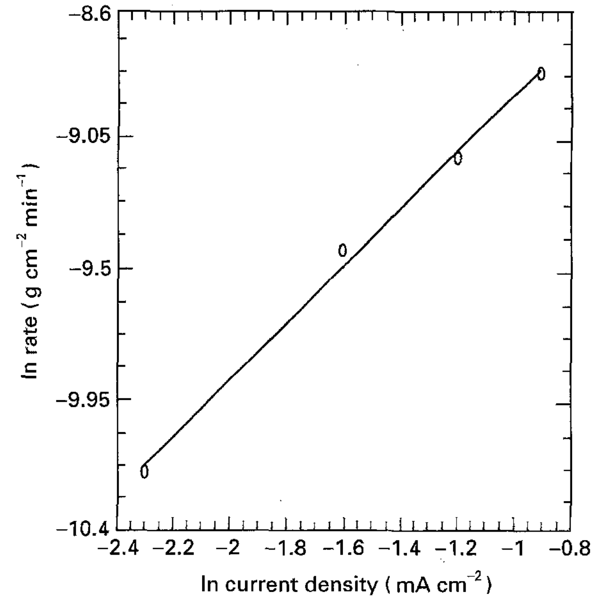


Figure 4 Current density exponent determination. [AM] = [AN] = 0.5 M, [MBA] = 0.05 M, [Persulphate] = 0.05 M. $y = -7.8781 + 0.994x$.

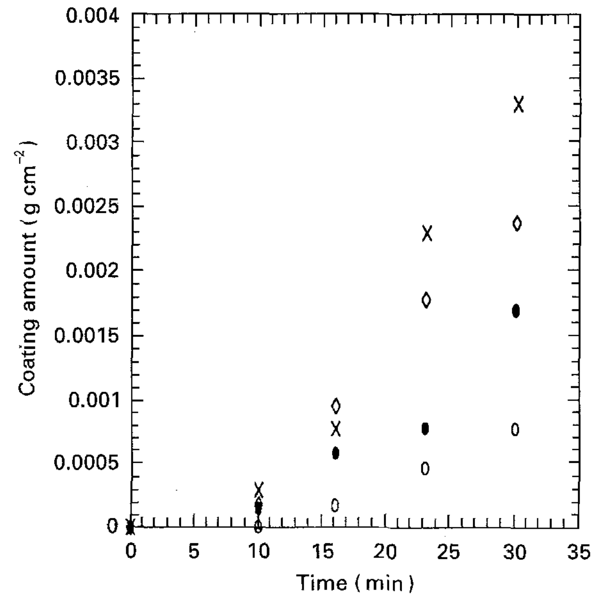


Figure 5 Amount of polymer coating in the early stages of electropolymerization for different persulphate concentrations. [AM] = [AN] = 0.5 M, [MBA] = 0.05 M, [Persulphate] = 0.05 M. Current density = 0.3 mA cm^{-2}. ○ 0.02 M; ● 0.035 M; ◇ 0.05 M; × 0.065 M.

zone of the plot, which is given in Fig. 6. A 1.12 power of the persulphate concentration on the polymerization rate, R_p, at constant current density and monomer concentration was obtained (Fig. 7).

3.3. Effect of initial monomer concentration

The study of the coating amount as a function of reaction time at different initial monomer concentrations: 0.35, 0.50, 0.65 and 0.75 M is presented in Fig. 8. The coating amount increases with initial monomer concentration and time. There was an induction period of about 5 min as in previous experiments. The polymerization rate, which was calculated from the initial slope of the linear region of the coating amount versus time graph, was plotted as a function of the initial monomer concentration in Fig. 9. A linear graph was obtained in the ln rate versus ln monomer concentration (Fig. 10), and the dependence of the polymerization rate on the monomer concentration at constant density and persulphate concentration was determined to be 2.33.

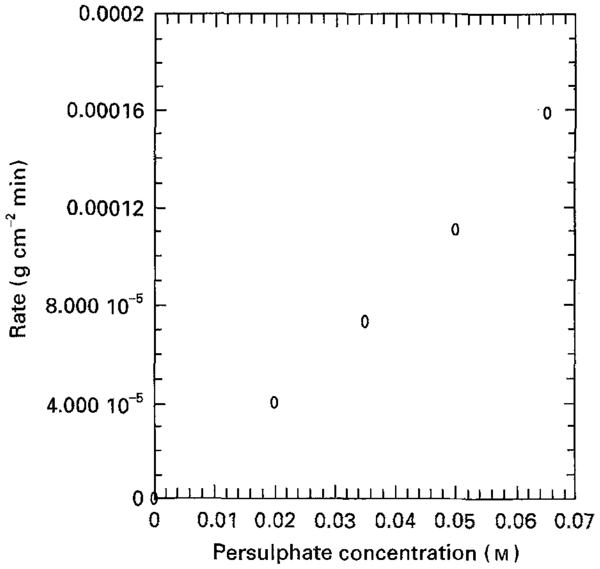


Figure 6 Rate of polymerization as a function of persulphate concentration. [AM] = [AN] = 0.5 M, [MBA] = 0.05 M, [Persulphate] = 0.05 M. Current density = 0.3 mA cm^{-2}.

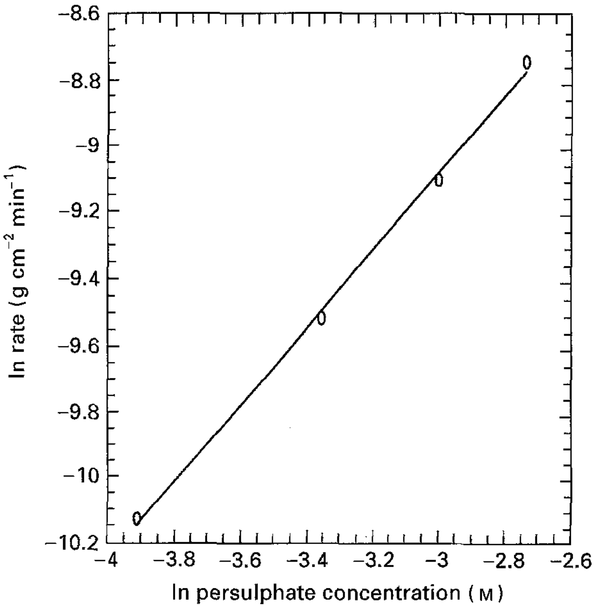


Figure 7 Persulphate concentration exponent determination. [AM] = [AN] = 0.5 M, [MBA] = 0.05 M, [Persulphate] = 0.05 M. Current density = 0.3 mA cm^{-2}. $y = -5.5905 + 1.11634x$.

3.4. Kinetic study of the electropolymerization

From the above experimental results, the rate of polymerization, R_p, follows the empirical rate expression.

$$R_p = K(CD)^{0.99}\,[\text{Persulphate}]^{1.12}\,[M]^{2.33} \quad (3)$$

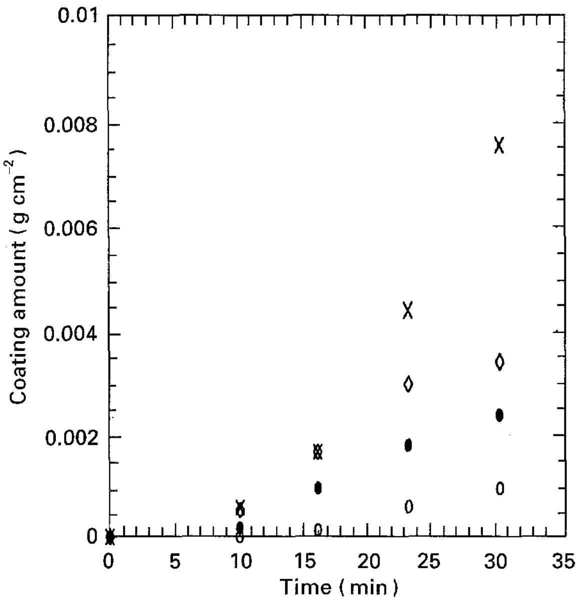


Figure 8 Amount of polymer coating in the early stages of electropolymerization for different monomer concentrations. [AM] = [AN] = monomer concentration, [MBA] = 0.1[AM], [Persulphate] = 0.05 M, current density = 0.3 mA cm^{-2}. ○ 0.35 M; ● 0.5 M; ◇ 0.65 M; × 0.75 M.

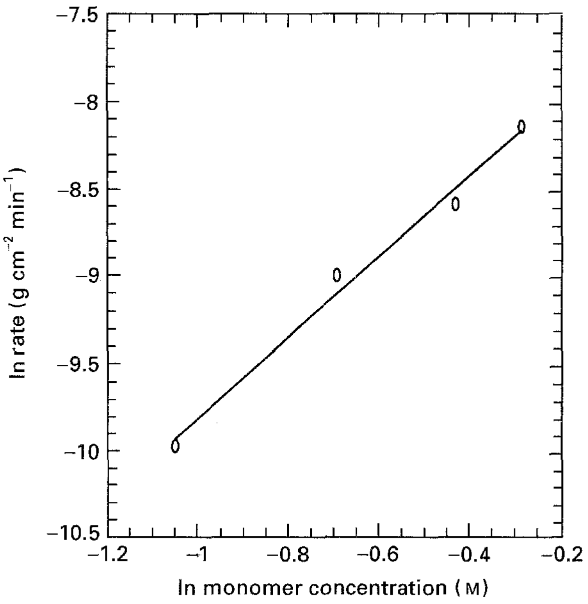


Figure 10 Monomer concentration exponent determination. [AM] = [AN] = monomer concentration, [MBA] = 0.1[AM], [Persulphate] = 0.05 M, current density = 0.3 mA cm^{-2}. $y = -7.4847 + 2.3259x$.

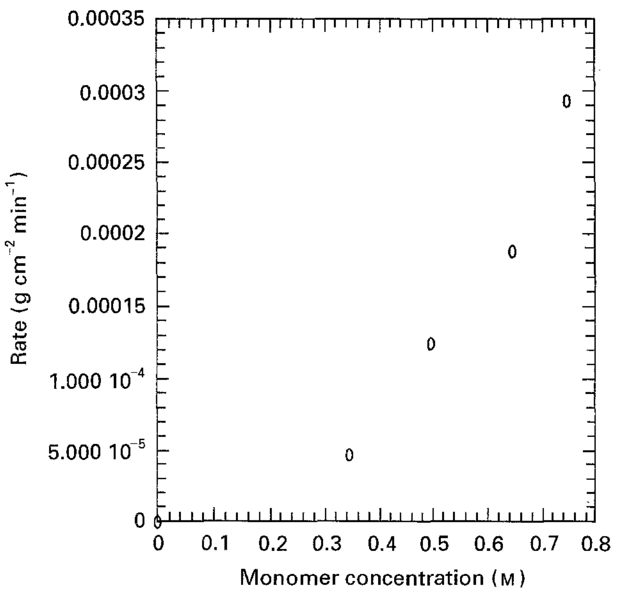


Figure 9 Rate of electropolymerization as a function of monomer concentration. [AM] = [AN] = monomer concentration, [MBA] = 0.1[AM], [Persulphate] = 0.05 M, current density = 0.3 mA cm^{-2}.

where K is a constant, CD is the current density and M is the monomer concentration.

A CD exponent of about 0.5 has been reported for the electropolymerization of acrylamide [14] and N,N' dimethylacrylamide [15]. However, a higher CD exponent, 0.99, was found in our AM/AN/MBA electropolymerization system. No polymerization occurred in the present system in the absence of current. The polymerization induced in the present system is due to the electrochemical formation of active species.

Normally, the effect of initiator on R_p is not critical as long as there is sufficient initiator present in the system. The rate is typically controlled by the current density and monomer concentration. However, in this particular system, the mobility of the large size persulphate ion is greatly affected by the presence of the thick swollen coating formed on the electrode. The diffusion of the large size persulphate ion becomes difficult. This certainly imposes a large effect upon the R_p dependence on persulphate concentration.

The thick swollen coating formed on the electrode inhibits a diffusion of the monomers and initiators; therefore, the low diffusion rate of the monomers and initiators to the electrode caused the initiation to be the rate-determining step [16], resulting in an increased dependence of R_p on $[M]$. A high dependence of R_p upon $[M]$ has been mentioned in previous free radical polymerization studies [17–21].

3.5. Diffusion studies

Cyclic voltammograms using a coated glassy carbon electrode are shown in Fig. 11. At low scan rates, the reduction potentials are constant. The reduction peak (above the horizontal axis) is due to the conversion of hexacyanoferrate (III) to hexacyanoferrate (IV), and the oxidation peak (below the line) is the reverse reaction. The diffusion coefficient values, calculated from Equation 1 in the introduction section, for the uncoated and coated glassy carbon electrodes are summarized in Table I.

Very little polymer was generated on the glassy carbon electrode for a reaction time less than 10 min. The D value obtained on the glassy carbon electrode electropolymerized for 10 min reaction time is about 70% of the D value on the uncoated electrode. A thin swollen film is formed in the early stage of the electropolymerization process which increasingly hinders the diffusion of ions and monomer to the electrode. As process time increases, the coating becomes thicker.

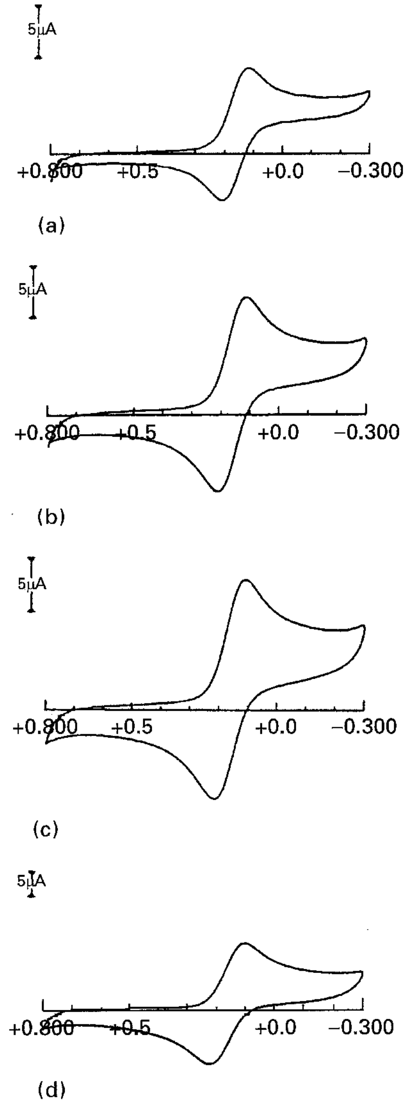


Figure 11 Cyclic voltammograms of $Fe(CN)_6^{3-}$ on a AM/AN/MBA polymer coated glassy carbon electrode at (a) 4 mV s^{-1}; (b) 8 mV s^{-1}; (c) 10 mV s^{-1}; (d) 12 mV s^{-1}.

TABLE I The diffusion coefficient and electron transfer fraction of 0.005 M hexacyanoferrate (III) ion through uncoated and AM/AN/MBA polymer coated glassy carbon electrode

Polymerization time[a] (min)	Diffusion coefficient $\times 10^{-6}$ (cm^2 s^{-1})	Electron transfer fraction
0 (uncoated)	2.30	0.336
10	1.69	0.258
16	0.73	0.125
30	0.42	0.103

[a] Polymerization was carried out in a 0.5 M AM/0.5 M AN/0.05 M MBA monomer system with 0.05 M persulphate as the initiator, at − 1.60 V versus saturated calomel electrode.

A dramatic drop in *D* value was observed after electropolymerization for 16 min; an even lower *D* value was obtained after 30 min reaction time. These suggest that the ions and monomer have more difficulty diffusing through the thicker polymer coating, Therefore, diffusion has become significant at a coating thickness of 20–30 μm.

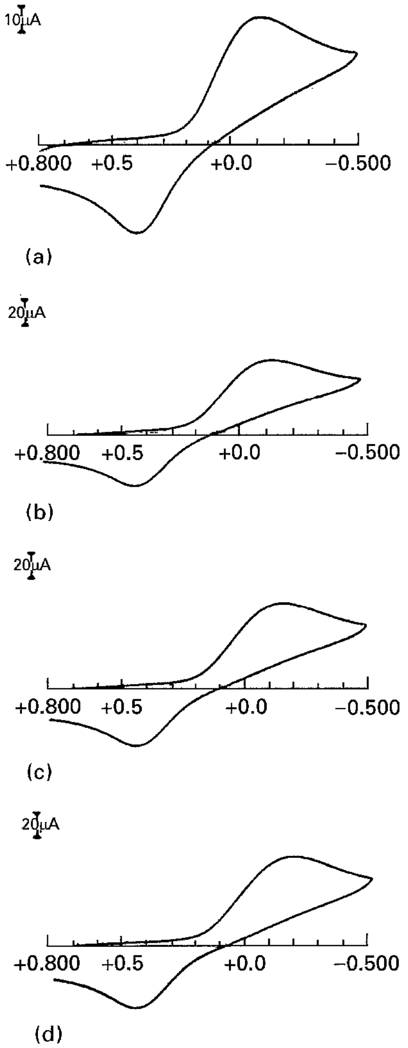


Figure 12 Cyclic voltammograms of $Fe(CN)_6^{3-}$ on a AM/AN/MBA polymer coated glassy carbon electrode at (a) 100 mV s^{-1}; (b) 150 mV s^{-1}; (c) 200 mV s^{-1}; (d) 250 mV s^{-1}.

A change of an electrode surface has a tremendous effect on the electrode transfer ability in an electrochemical system. At high scan rates, the reduction potential is not a constant. Fig. 12 shows cyclic voltammograms carried out at high scan rates, and the resulting *f* values are tabulated in Table I.

A relatively smaller *f* value was obtained on the glassy carbon electrode electropolymerized for 10 min compared with the *f* value obtained on the uncoated electrode, indicating that the electron transfer and thus the initiation reaction is somewhat more difficult. The induction reaction was much more difficult in the 16 min polymer-coated glassy carbon electrode, as shown by the large drop in *f* value. A slightly smaller *f* value was found in the glassy carbon electrode electropolymerized for 30 min. The results indicate that the polymer formed early in the electropolymerization process reduces the electron transfer ability in the system, and the effect becomes more severe as a thicker coating is formed on the electrode.

4. Conclusions

A polymer coating based on acrylamide and acrylonitrile monomer, crosslinked by *N*,*N*′-methylene-bis-acrylamide, was synthesized on an aluminium alloy by means of aqueous electropolymerization, using potassium persulphate as an initiator. The polymerization rate was found to be $R_p = K(CD)^{0.99}$ [Persulphate]$^{1.12}$ $[M]^{2.33}$. The unusually high exponents in comparison with earlier work result from diffusion limitations in the relatively thick swollen polymer coatings formed on the aluminium electrode. The results of the diffusion studies confirmed the mass transfer problem in the present system.

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