

Electropolymerization of Pyrrole and *N*-Methylpyrrole on Mild Steel Surface

Ali Ashrafi¹, Mohammad Ali Golozar^{*1}, and Shadpour Mallakpour²

(1) Department of Materials Engineering, Isfahan University of Technology
Isfahan-84154, I.R. Iran

(2) Organic Polymer Chemistry Research Laboratory, College of Chemistry
Isfahan University of Technology, Isfahan-84156, I.R. Iran

Received 20 November 2002; accepted 16 July 2003

ABSTRACT

Electrochemical polymerization of various ratios of pyrrole and *N*-methylpyrrole monomers were performed in aqueous toluene-4-sulphonic acid sodium salt (T₄SNa) electrolyte, using galvanostatic method. The pH of electrolyte was adjusted by *p*-toluene sulphonic acid (PTSA). In order to prevent corrosion of mild steel substrates during coating deposition, all samples were pretreated in 0.5 M oxalic acid solution, employing galvanostatic method. This would passivate the steel substrate and facilitate the coating process as well. Corrosion resistance of coated substrates was investigated in 1 M NaCl solution using Tafel polarization technique. In addition, by using scanning electron microscopy (SEM), morphological characterization of coatings produced, was investigated. The ratio of 1 to 1 (pyrrole/*N*-methylpyrrole) could play an important role on corrosion properties of the resulting coated mild steel.

Key Words:

electropolymerization;
conductive polymers;
pyrrole;
pretreatment;
corrosion.

INTRODUCTION

Coatings on the surface of metals by polymeric materials have been widely used in industries for the protection of these materials against corrosion [1-5]. Electropolymerization is an effective technique for the surface coating of various conductive mate-

rials with wide variety of polymers with various thicknesses [6]. Electropolymerization of conductive polymers has been widely investigated [7-10]. Recently, electropolymerization of pyrrole on steel substrates has been investigated with the aim of

(*)To whom correspondence should be addressed.
E-mail: golozar@cc.iut.ac.ir

producing uniform and strongly adherent coatings [11-14]. It was found that only limited reactive systems (including electrolyte and dopants) could lead to the formation of polypyrrole coatings onto steel substrates. In order to obtain the polymerization potential, the electrolyte used for this purpose must be able to passivate the steel substrate during the first stage of electropolymerization. Other researchers have reported electropolymerization of pyrrole-co-(*N*-methylpyrrole) in oxalic acid solutions [15].

The aim of this research was to use passive steel substrates and investigate the possibility of electropolymerization of pyrrole and *N*-methylpyrrole on the surface of steel in order to prepare semiconductive and corrosion resistance steel. Thus, electrodeposition of polypyrrole, poly(*N*-methylpyrrole), and their copolymers were investigated in an aqueous solution such as toluene-4-sulphonic acid sodium salt (T_4SNa).

EXPERIMENTAL

Table 1 shows the chemicals which were used to prepare the electrolytes. The reagents were dissolved in deionized water. The working electrode as 0.35 cm² round substrate was made from mild steel sheet having the composition shown in Table 2. The counter electrode was a 10 × 3 × 0.1 cm stainless steel sheet. An Ag/AgCl electrode, manufactured by Perkins-Elmer, was used as the reference electrode. Prepassivation and electropolymerization were performed by an EG&G potentiostat/galvanostat system model 263A.

Samples were first degreased with carbon tetrachloride solution for 30 min. Prepassivation of substrates was carried out in 0.5 M oxalic acid solution using current density 0.1 mA/cm² for 2800 s. After prepassivation, the samples were rinsed with deionized water and then dried by warm air.

Electrochemical polymerization was carried out in

Table 1. Chemicals used to prepare the electrolytes.

Chemicals	Purity	Source
Pyrrole	>97%	Merck
<i>N</i> -Methylpyrrole	>99%	Merck
Toluene-4-sulphonic acid sodium salt	>99%	Merck
<i>p</i> -Toluene sulphonic acid	>99%	Merck
Oxalic acid	>98%	Merck

Table 2. Typical composition of mild steel substrate.

Element	Fe	C	Si	Mn
Weight (%)	98.5	0.7	0.3	0.5

Table 3. Chemical composition, pH and temperature of electrolytes.

Solutions	Number						
	1	2	3	4	5	6	7
Pyrrole (mol/L)	0.25	0.20	0.15	0.125	0.10	0.05	0.00
<i>N</i> -Methylpyrrole (mol/L)	0.00	0.05	0.10	0.125	0.15	0.20	0.25
T_4SNa (mol/L)	0.06	0.06	0.06	0.06	0.06	0.06	0.06
pH	4.5	4.5	4.5	4.5	4.5	4.5	4.5

a one-compartment polypropylene cell. The working electrode (anode) was a prepassive sample, and the counter electrode (cathode) was stainless steel sheet. The galvanostatic technique using constant current density of 0.1 mA/cm² was employed. Electropolymerization aqueous solutions used in this work, contained 0.06 M T_4SNa (as auxiliary electrolyte), and various ratios of pyrrole and *N*-methylpyrrole (in each solution the sum of monomer concentration was 0.25 M). The pH of the solutions was adjusted to 4.5 using *p*-toluene sulphonic acid (PTSA). Table 3 shows the chemical composition, pH, and the temperature of electrolyte used. Total time of electrochemical polymerization was 5000 s.

Employing a Philips XL30 scanning electron microscope (SEM), morphology of coatings produced was investigated. The polarization (Tafel) test was conducted with a potentiostat/galvanostat system, model 263A. Bare (without coating or pretreatment), pretreated, and coated steel substrates were examined in 1 M NaCl solutions, within the range of -250 mV to 500 mV vs. open circuit potential (OCP). The scan rate used was 0.5 mV/s.

In each case, at least 5 experiments (such as pretreatment, electropolymerization, and polarization) were carried out and the similarity of results was investigated using statistical ANOVA test using Microsoft Excel XP 2002 software.

RESULTS AND DISCUSSION

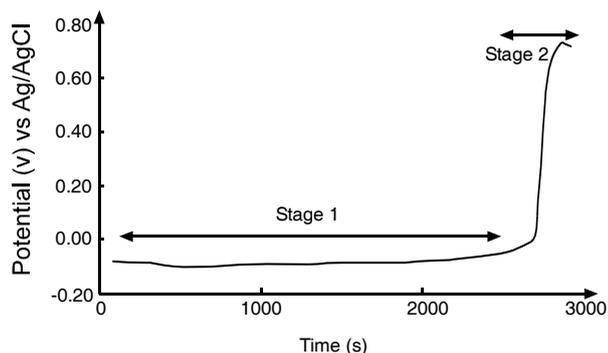
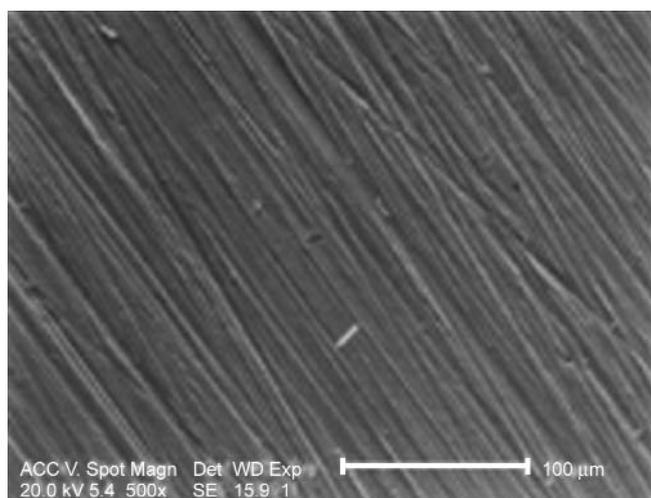
Figure 1 shows the potential-time curve for the prepas-

Table 4. Results obtained from ANOVA test of pretreatment process.

Source of variation	SS	df	MS	F	P-Value	F _{crit}
Between groups	41163.71	4	10290.93	0.303249	0.875543	2.419185

sivation of steel in oxalic acid solution.

In this curve, two distinct stages are characterized. The first stage (approximately 2600 s) is related to the formation of iron (II) oxalate on the steel surface. The second stage (immediately increases in the potential after approximately 2600 s) is related to decomposition of the previously formed layer. In this work, the pretreatment was carried out within the potential/time range of the first stage. So that, the entire substrate surface was covered by this layer. Table 4 shows the ANOVA test of pretreatment results. From these data it is clear that all of the results obtained could be reproduced quite well.

**Figure 1.** Potential- time curve for the prepassivation of steel in oxalic acid solution.**Figure 2.** SEM Micrograph of the sample before pretreatment.

Figures 2 and 3 show the SEM micrographs of the samples before and after pretreatment. The crystalline particles of iron (II) oxalate are clearly observed on pretreated samples.

Figure 4 shows a typical potential-time curve for the electropolymerization of prepassivated steel in various solutions.

In contrast with electropolymerization in oxalic acid solution showing three stages [5], in Figure 4, only two distinct stages are characterized. Using oxalic acid as polymerization electrolyte, three stages are observed in potential-time curves. But in this research work, the first stage is not observed (Figure 4). This could be due to prepassivation of steel before polymerization treatment. The first stage in this research (Figure 4) is related to dissolution of iron (II) oxalate and the second stage is related to the polymerization process. During the dissolution of iron (II) oxalate, the potential is increased. After the first stage, the potential is reduced about 0.05V, and then in the second stage becomes constant. The reduction of potential in the first of the second stage is related to nucleation of polymer on the surface. After nucleation the potential will be constant and equal to polymerization potential of pyrrole, *N*-methylpyrrole, or both of them. At this constant potential, the electropolymerization continues to proceed.

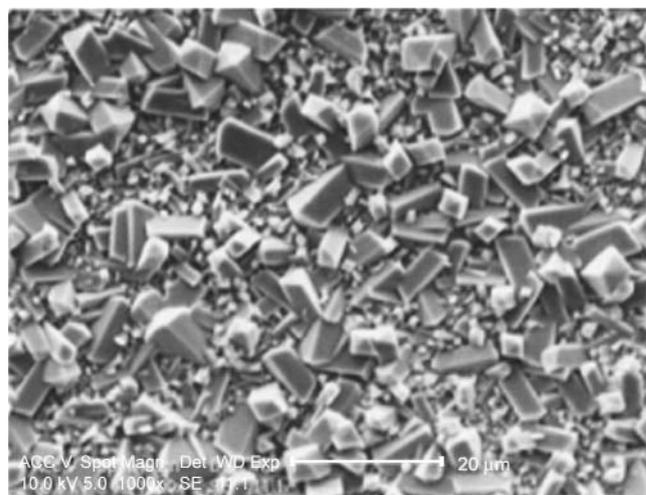
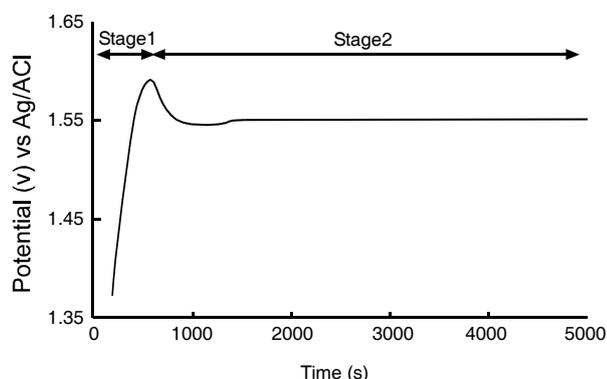
**Figure 3.** SEM Micrograph of the sample after pretreatment.

Table 5. Results obtained from ANOVA test of electropolymerization process.

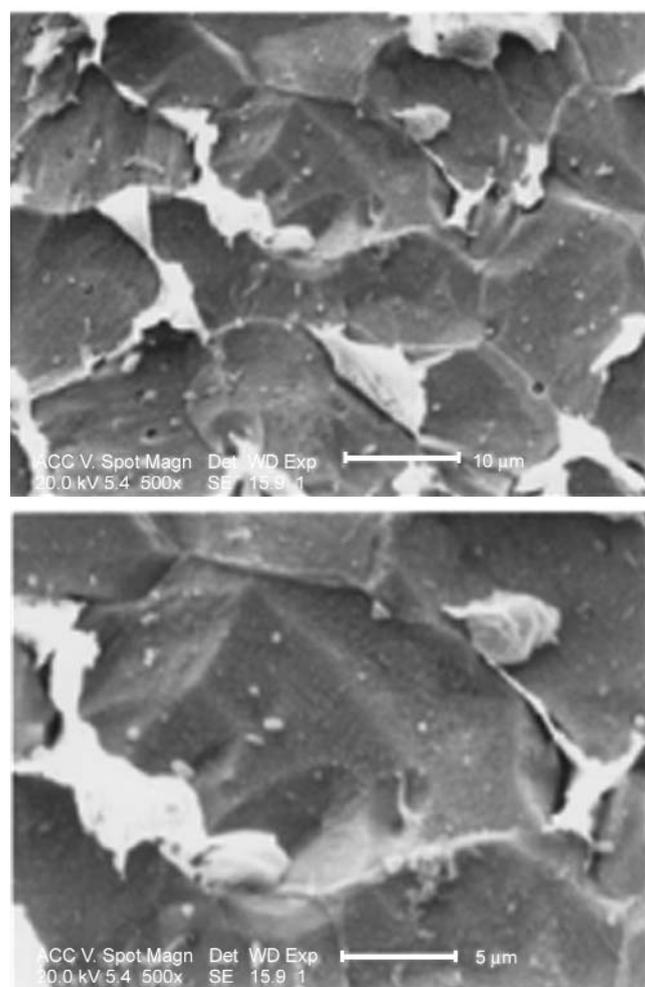
Source of Variation	SS	df	MS	F	P-Value	F crit
No.1	0.000353	4	0.000883	0.097599	0.983123	2.419185
No.2	0.00154	4	0.000385	0.248185	0.9105	2.419185
No.3	0.00154	4	0.000385	0.0248185	0.9105	2.419185
No.4	0.000862	4	0.000216	0.238195	0.916484	2.419185
No.5	0.000648	4	0.000162	0.178978	0.949051	2.419185
No.6	0.017326	4	0.004332	2.824872	0.261890	2.419185
No.7	0.000469	4	0.000117	0.129752	0.971423	2.419185

Table 5 shows the ANOVA test of electropolymerization results. Again it is observed that, all of the data obtained are reproducible, i.e. ANOVA No~1. Figures 5, 6 and 7 show the SEM micrographs of the coatings produced in various solutions (solutions No.1, 4 and 7). Coatings of polypyrrole, poly(*N*-methylpyrrole), and coating with the ratio of 1 to 1 (py/mpy) have a uniform morphology with no microcracks or porosity. Figure 8 shows the microcracks in the coatings produced in solutions No.2 and 5. These microcracks in the process of coatings from solutions No. 3 and No. 6 were also observed.

Table 6 shows the Tafel polarization results obtained from bare, pretreated, and coated steels in various solutions. As the results show, coatings in all instances increase the corrosion potential and decrease the corrosion current density of steel substrates. It is very important to note that in the case of coating with polypyrrole and coating with the solution of 1:1 (py/mpy) we have observed higher decrease in the corrosion current density. This could be due to the absence of microcracks and porosity in these coatings.

**Figure 4.** Typical potential-time curve of the electropolymerization of prepassivated steel.

Based on our observations (Table 6), pretreatment of steel samples would increase the corrosion current density. Therefore, we concluded that prepassivation of the steel substrates, not only does not prevent the surface of the steel from corrosion, but also it increases the rate of corrosion.

**Figure 5.** SEM Micrographs of the coating obtained in solution No.1 (0.25 pyrrole + 0.06 T₄SNa (mol/L))

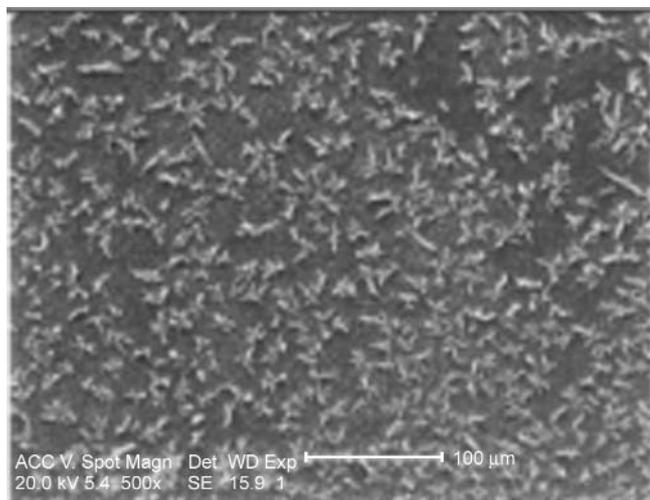


Figure 6. SEM Micrograph of the coating obtained in solution No.4 (0.125 pyrrole, 0.125 *N*-methylpyrrole, 0.06 T₄SNa (mol/L)).

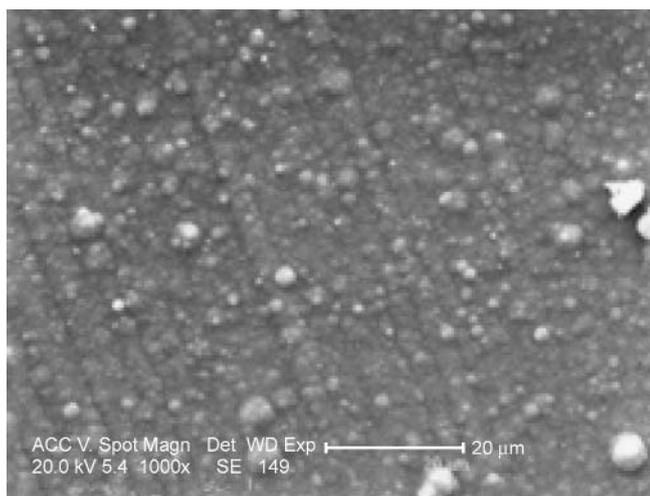


Figure 7. SEM Micrograph of the coating obtained in solution No.7 (0.52 *N*-methylpyrrole, 0.06 T₄SNa (mol/L)).

Table 6. Corrosion potential and current density of bare steel, pretreated steel and various coated steels.

Sample	E _{cor} (mV) vs. Ag/AgCl	I _{corr} (A/cm ²)
Bare steel	-530	2.1×10 ⁻⁵
Pretreated steel	-260	3.0×10 ⁻⁵
Steel coated in solution No.1	-201	2.0×10 ⁻⁶
Steel coated in solution No.2	-314	4.8×10 ⁻⁶
Steel coated in solution No.3	-273	5.0×10 ⁻⁶
Steel coated in solution No.4	-201	2.0×10 ⁻⁶
Steel coated in solution No.5	-187	5.5×10 ⁻⁶
Steel coated in solution No.6	-165	4.0×10 ⁻⁶
Steel coated in solution No.7	-140	3.1×10 ⁻⁶

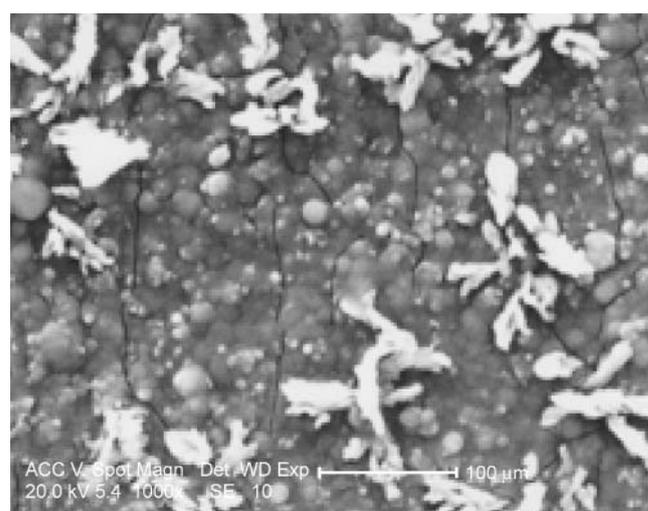
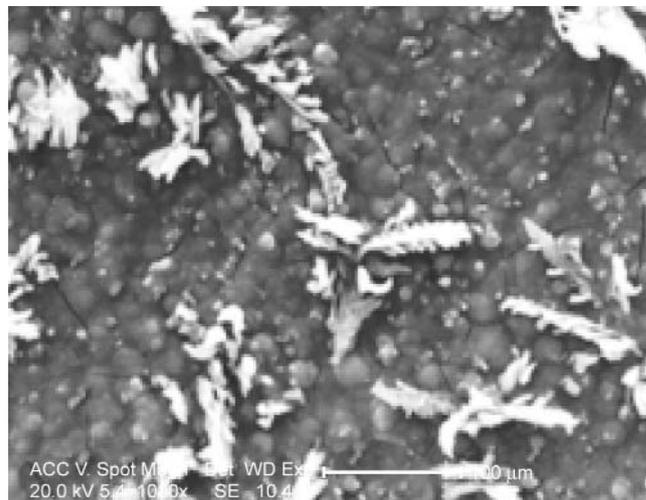


Figure 8. SEM Micrographs of the microcracks in the coatings obtained from solutions No. 2 (0.2 pyrrole, 0.05 *N*-methylpyrrole, 0.06 T₄SNa (mol/L)) and No. 5 (0.1 pyrrole, 0.15 *N*-methylpyrrole, 0.06 T₄SNa (mol/L)).

CONCLUSION

From the results obtained in this research, we can reach to the following conclusions:

1- Pyrrole and *N*-methylpyrrole monomers can be successfully polymerized via electropolymerization technique on the surface of mild steel. In this process it is important to note that if the auxiliary electrolyte cannot passivate the steel in the first stage of polymerization, we can use pretreated steel.

2- Coating of steel with pyrrole, *N*-methylpyrrole and poly(pyrrole-*co*-*N*-methylpyrrole) increase the corrosion potential and decrease the corrosion current density of steel and thus decrease the corrosion of steel.

3- Steel coated with polypyrrole, and steel coated in solution with the ratio of 1 to 1 (py/*N*-mpy) had minimum of corrosion current density.

4- Morphology of the coatings produced (with different ratios of pyrrole to *N*-methylpyrrole monomers in the solutions) was characterized using scanning electron microscope (SEM). In addition, corrosion resistances of coated steel substrates were investigated as well.

ACKNOWLEDGEMENTS

We wish to express our gratitude to the Research Affairs Division of Isfahan University of Technology (IUT), for partial financial support. We also would like to express our great appreciation to the laboratory's staff of Materials Engineering Department, Isfahan University of Technology, Iran.

REFERENCES

1. Jones D.A., *Principles and Prevention of Corrosion*, Macmillan Publishing, Chap. 1, New York (1992).
2. Camalet J.L., Lacroix J.C., Dung Nguyen T., Aeiyaeh S., Pham M.F., Petitjean J., and Lacaze P.C. Aniline electropolymerization on platinum and mild steel from neutral aqueous media, *J. Electroanal. Chem.*, **485**, 13-20 (2000).
3. Lacroix J.C., Camalet J.L., Aeiyaeh S., Chane-Ching K.I., Petitjean J., Chauveau E., and Lacaze P.C., Aniline electropolymerization on mild steel and zinc in a two-step process, *J. Electroanal. Chem.*, **481**, 76-81 (2000).
4. Zaid B., Aeiyaeh S., Lacaze P.C., and Takenouti H., A two step electropolymerization of pyrrole on Zn in aqueous media, *Electrochem. Acta.*, **43**, 2331-2339 (1998).
5. Marsh J., Scantlebury J., and Lion S., Poly (2-allyl) phenylene oxide electropolymer films as an adhesion-enhancing treatment for steel, *J. Appl. Polym. Sci.*, **59**, 897-903 (1996).
6. Diaz A.F., Martinez A., Kanazawa K.K., and Salmon M., Electrochemistry of some substituted pyrroles, *J. Electroanal. Chem.*, **130**, 181-187 (1981).
7. Entezami A. and Rahmatpour A., Electropolymerization of dissymmetric diheteroaryl ethylenes containing *N*-methylpyrrole, pyrrole and thiophene, *Eur. Polym. J.*, **34**, 871-878 (1998).
8. Massoumi B. and Entezami A., Electrochemically stimulated 2-ethylhexyl phosphate (EHP) release through redox switching of conducting polypyrrole film and polypyrrole/poly(*N*-methylpyrrole) or self-doped polyaniline bilayers, *Polym. Int.*, **51**, 555-560 (2002).
9. Massoumi B. and Entezami A., Controlled release of sulfosalicylic acid during electrochemical switching of conducting polymer bilayers, *Eur. Polym. J.*, **37**, 1015-1020 (2001).
10. Hosseini S.H., Gorgani F.A., and Entezami A., Poly(3-methoxyethoxythiophene) and its copolymers with aniline, thiophene, and pyrrole: Chemical and electrochemical synthesis, *Iran. Polym. J.*, **9**, 255-261 (2000).
11. Su W. and Iroh J.O., Kinetics and efficiency of aqueous electropolymerization of pyrrole onto low carbon steels, *J. Appl. Polym. Sci.*, **60**, 617-624 (1997).
12. Osadah Y. and Derossi D.E., *Polymer Sensors and Actuators*, Springer-Verlag, Germany (2000).
13. Yoon C.O., Sung H.K., Kim J.H., Barsoukov E., Kim J.H., and Lee H., The effect of low-temperature conditions on the electropolymerization of polypyrrole films with high density, high electrical conductivity, and high stability, *Synth. Met.*, **99**, 201-212 (1999).
14. Li Y. and Ouyang j., Effect of nonionic surfactant additives on the electropolymerization of pyrrole in aqueous solutions, *Synth. Met.*, **113**, 23-28 (2000).
15. Su W. and Iroh J.O., Electrodeposition mechanism, adhesion and corrosion performance of polypyrrole and poly (*N*-methylpyrrole) coating on steel substrates, *Synth. Met.*, **114**, 225-234 (2000).