



# Electrodeposition of poly(*N*-methylpyrrole) on stainless steel in the presence of sodium dodecylsulfate and its corrosion performance



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## ABSTRACT

Poly(*N*-methylpyrrole)-dodecylsulfate (PNMPy-DS) coating was electro synthesized by potentiodynamic method on a stainless steel in oxalic acid solution containing sodium dodecylsulfate for the first time. The effects of electrochemical synthesis parameters, such as applied potential, scan rate and cycle number, on the protective behaviors of PNMPy-DS films were investigated and the optimum synthesis conditions were determined. The PNMPy-DS coating was characterized by the cyclic voltammetry, FT-IR spectroscopy and SEM methods. Corrosion protection behavior of this polymer-coated steel was investigated in 0.5 mol L<sup>-1</sup> HCl solution by potentiodynamic polarization and EIS methods. The results show that the PNMPy-DS coating provides effective protection for the stainless steel against to corrosion due to the fact that the large negatively charged dodecylsulfate dopant in the polymer structure electrostatically repels corrosive chloride ions and delays their access to metal surface.

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## 1. Introduction

Stainless steels are mainly Fe–Cr-based alloys including more than 12% Cr [1]. Stainless steels have been one of the most commonly used materials for applications in the fields of marine systems, nuclear, chemical, aircraft, food, construction industries and biomedical [2–5]. Their comprehensive usage is a result of a unique combination of perfect mechanical strength, biocompatibility, low cost, and high corrosion resistance, which originates from passive films formed on the surface. It is generally recognized that the passive films consist primarily of Cr oxide and/or hydroxides [6,7]. In aqueous conditions, the Cr enrichment in the passive film is due to selective dissolution of Fe from passive film into an electrolyte [8,9]. Thus, stainless steels might still be corroded in specific areas, such as environments containing chloride or sulfate ions [10].

In recent years, one of the methods used to reduce the rate of corrosion of metals is the coating of surfaces with a conducting polymer film. Conducting polymers such as polyaniline, polypyrrole, polythiophene, and their derivatives are the most commonly used as protective coatings [11–15]. Conducting polymer coatings generally increase the resistance of metals against different corrosive species. The corrosion of stainless steels is also

effectively inhibited by these coatings synthesized by the electrochemical methods [12,13,16–18]. The dopant anions incorporated into conducting polymers affect both the polymerization process and the properties of the resultant polymers [19,20]. The dopant ion employed during electro synthesis can have a marked effect on the anion-exchange selectivity series of conducting polymers [16,21]. In some cases, the incorporation of larger hydrophobic dopant ions, e.g. dodecylsulfate (DS<sup>-</sup>), results in the formation of a polymer capable of cation exchange with quite hydrophobic nature [22,23]. For example, the polypyrrole coating electro synthesized from solution containing the DS<sup>-</sup> dopant ion is permeable only to cations and thus, corrosive ions delay penetration on the electrode surface through polymer film [15,24,25]. Consequently, the use of this dopant during electropolymerization of monomer provides a significant reduction in the corrosion rate of metals.

Although there have been a number of studies on the protective properties of poly(*N*-methylpyrrole) (PNMPy) coatings electrochemically synthesized on low carbon steel [26,27], AISI 316 stainless steel (SS) [28], mild steel [29,30] and copper [31–34], there is no an investigation on the AISI 304 stainless steel. In this study, we have performed the electro synthesis of PNMPy-dodecylsulfate coating on AISI 304 SS surface by using the potentiodynamic technique in aqueous oxalic acid solution containing *N*-methylpyrrole monomer in the presence of DS<sup>-</sup> ion for the first time. The corrosion protection properties of the coating were investigated by the linear and cyclic potentiodynamic polarization, and EIS methods in 0.5 mol L<sup>-1</sup> HCl solution.

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## 2. Experimental

### 2.1. Materials and methods

Sodium dodecylsulfate (SDS,  $\geq 98.5\%$ , Sigma–Aldrich), sulfuric acid (95% Panreac), hydrochloric acid ( $\geq 37\%$ , Sigma–Aldrich) and oxalic acid dihydrate (Riedel-deHaen) chemical reagents were used without any further purification. *N*-Methylpyrrole (98%) was obtained from Aldrich and distilled before use. All solutions were prepared with double-distilled water.

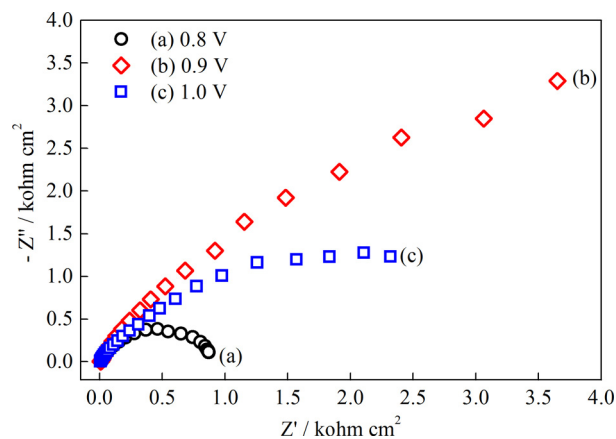
Electrochemical measurements were performed with a conventional three-electrode system comprising a bare or polymer-coated stainless steel (SS) disk electrode (4-mm in diameter) as working electrode, Ag/AgCl containing  $3 \text{ mol L}^{-1}$  NaCl solution (BAS MF-2052 RE-5B) as reference electrode, and platinum foil ( $1\text{-cm}^2$  in surface area) as counter electrode. The disk electrodes were prepared by embedding SS rod into a 1-cm diameter Teflon cylinder holder. The surface of the SS electrode was abraded by using wet emery paper of grit size 240, 600, 1200 and 2000, consecutively. This electrode was immersed in double-distilled water and then it was dried at room temperature. The polymer-coated electrodes were washed with double-distilled water to remove adsorbed electrolytes, monomers and the soluble oligomers formed during electrosynthesis of the coating before studies. Then, they were dried at room temperature. The linear potentiodynamic polarization measurements (Tafel tests) were carried out by anodic sweeping  $\pm 0.200 \text{ V}$  range of open circuit potential ( $E_{\text{OCP}}$ ) vs. Ag/AgCl at a  $1 \text{ mV s}^{-1}$  scan rate in  $0.5 \text{ mol L}^{-1}$  HCl solution. The linear potentiodynamic polarization curves were analyzed by using IviumSoft software (version 2.102) and the corrosion rate parameters were automatically calculated by using this software. EIS measurements were performed in the frequency range of  $100 \text{ kHz}$ – $0.1 \text{ Hz}$  with  $5 \text{ mV}$  perturbation at the  $E_{\text{OCP}}$  of substrates for different immersion times in  $0.5 \text{ mol L}^{-1}$  HCl solution. The analysis of impedance curves was done by fitting the experimental results to equivalent circuit models by using ZView 3.2c software (Scribner Associates Inc., UK). All measurements were repeated at least three times to ensure reproducibility.

All electrochemical studies were carried out by using the Ivium CompactStat electrochemical analyzer. Fourier Transform Infrared (FTIR) spectra of the polymer coatings were recorded directly with a Bruker Alpha spectrometer with ATR attachment (Bruker Corporation Ltd.) in the region from  $400 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$ . Spectral resolution was  $4 \text{ cm}^{-1}$ . Scanning electron microscopy (SEM) micrographs of the polymer coating were taken with a FEI Quanta 400F Field Emission Scanning Electron Microscopy (FESEM) (Fei Ltd., Japan).

## 3. Results and discussion

### 3.1. Potentiodynamic synthesis of poly(*N*-methylpyrrole)-dodecylsulfate on SS

The electropolymerization of NMPy monomer was performed by using the potentiodynamic technique on the surfaces of the passivated SS electrode. The passivation process was carried out by using the linear sweep voltammetry technique in the range from  $-0.5 \text{ V}$  to  $0.3 \text{ V}$  vs. Ag/AgCl at a  $4 \text{ mV s}^{-1}$  scan rate in  $0.3 \text{ mol L}^{-1}$  oxalic acid solution. After passivation, the electropolymerization of monomer was initiated with NMPy monomer and SDS additions to the polymerization solution. The poly(*N*-methylpyrrole)-dodecylsulfate synthesized in the presence of SDS was denoted as PNMPy-DS. The electrosynthesis conditions as applied potential, scan rate, and cycle number effecting the formation of PNMPy-DS coatings were investigated and the optimum



**Fig. 1.** Nyquist plots in  $0.5 \text{ mol L}^{-1}$  HCl solution for PNMPy-DS coatings prepared between  $-0.4 \text{ V}$  and the upper potentials of (a) 0.8, (b) 0.9, and (c) 1.0 V (vs. Ag/AgCl) at a  $50 \text{ mV s}^{-1}$  scan rate with 10 cycles.

conditions were determined to obtain the best corrosion protection performance.

Electrochemical impedance spectroscopy (EIS) allows the quantitative determination of coating properties without affecting the coating and its performance. Hence, EIS was employed to determine the optimum synthesis conditions. Firstly, PNMPy-DS coatings were prepared between  $-0.4 \text{ V}$  and various upper potentials (0.8, 0.9, and 1.0 V vs. Ag/AgCl) at a  $50 \text{ mV s}^{-1}$  scan rate with 10 cycles. Electrochemical impedance spectra of the electrodes prepared were recorded after a 30 min immersion period at  $E_{\text{OCP}}$  in  $0.5 \text{ mol L}^{-1}$  HCl solution and shown in Fig. 1. The largest semicircle is observed at 0.9 V (vs. Ag/AgCl) potential and its diameter may be accepted equal to charge transfer resistance ( $R_{\text{ct}}$ ) value. Table S1 shows the  $R_{\text{ct}}$  values obtained from the EIS curves for parameters effecting the formation of PNMPy-DS coatings. As shown in Table S1, the PNMPy-DS coating synthesized at +0.9 V upper potential provides the best protection properties of SS against to corrosion. Therefore, the potential range is determined to be between  $-0.4$  and  $+0.9 \text{ V}$  (vs. Ag/AgCl) for the electrosynthesis of PNMPy-DS. When the upper potential applied for the electrosynthesis of polymer film is higher than  $+0.9 \text{ V}$  (vs. Ag/AgCl), the polymer film can be overoxidized that result in the reduction of electroactivity. Its permeability increases due to the overoxidation of polymer coating. Therefore, the protective properties of the coating reduce [31,35,36].

Secondly, the effect of the scan rate (10, 25, 50, and  $100 \text{ mV s}^{-1}$ ) on the electrosynthesis of PNMPy-DS is investigated by keeping other parameters constant. The optimum scan rate is determined by considering the Nyquist plots recorded in  $0.5 \text{ mol L}^{-1}$  HCl solution for prepared coatings. As seen in Fig. 2 and in Table S1, the PNMPy-DS coating synthesized at  $50 \text{ mV s}^{-1}$  scan rate shows the best corrosion resistance, and the optimum scan rate is chosen as  $50 \text{ mV s}^{-1}$ . It may be suggested that the polymer film is overoxidized at lower scan rates and it does not deposit sufficiently on the substrate at higher scan rates.

Thirdly, the different cycle numbers (5, 10, 20, and 40) were applied to synthesize PNMPy-DS films in the potential range between  $-0.4$  and  $+0.9 \text{ V}$  (vs. Ag/AgCl) at  $50 \text{ mV s}^{-1}$  and the Nyquist curves of PNMPy-DS coated SS electrodes in  $0.5 \text{ mol L}^{-1}$  HCl solution is presented in Fig. 3. When compared the  $R_{\text{ct}}$  values given in Table S1, the PNMPy-DS coating synthesized at 10 cycle numbers has the best corrosion protection performance, so that the optimum cycle number is selected as 10.

Fig. 4 shows cyclic voltammograms (CVs) recorded during electrosynthesis of PNMPy-DS on passivated SS electrode in  $0.3 \text{ mol L}^{-1}$  oxalic acid solution containing  $0.1 \text{ mol L}^{-1}$  NMPy and  $0.05 \text{ mol L}^{-1}$

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