Electrochemical characteristics of coated steel with poly(N-methyl pyrrole) synthesized in presence of ZnO nanoparticles

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Abstract
Poly(N-methyl pyrrole) (PMPy) coating was electrodeposited on steel substrates in mixed electrolytes of dodecyl benzene sulphonic acid with oxalic acid in the absence and the presence of ZnO nanoparticles (NPs). The morphology and compositions were characterized by Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy and Energy-dispersive X-ray spectroscopy. Electrode/coating/electrolyte system was studied by Electrochemical Impedance Spectroscopy. The comparison between the pore resistance (Rpo) of synthesized PMPy in the absence and presence of ZnO NPs indicated that the existence of ZnO increased the Rpo of the coating. The FESEM micrographs indicated that the size of micro-spherical grains in the morphology of PMPy is significantly reduced and the surface area of PMPy is increased with the presence of ZnO NPs. The increase of the ability to interact with the ions liberated during the corrosion reaction of steel and the increase of the rate probability for the occurrence of cathodic reduction of oxygen on the PMPy with the increase of the surface area can be considered as reasons for improvement of protective properties of synthesized PMPy in the presence of ZnO NPs.

1. Introduction

In recent years conducting polymers has attracted considerable interest for the development of advanced materials. They are readily formed in aqueous solutions on various substrates. These compounds are organic materials that generally possess an extended conjugated π-electron system along with a polymer backbone. Polypyrrole (PPy) and its derivatives such as poly(N-methyl pyrrole) (PMPy) are conducting polymers due to their high electrical conductivity, have been suggested to be used as protective coatings on oxidizable metals. Iroh and Su reported that PPy coatings significantly reduce the corrosion current and corrosion rate of steel while the corrosion performance of PMPy coatings is lower than PPy. It was explained that PMPy coatings have relatively low adhesion strength to the steel substrates. One of the principal reasons for PPy and PMPy which can function as anodic inhibitors is the existence of unsaturated bonds, –NH polar groups and some ions in the PPy and PMPy coatings.

Conducting polymer/inorganic oxide nanocomposites has recently attracted great attention due to their unique microstructure, physiochemical and electro-optical properties, and a wide range of their potential usage in battery cathodes and in the construction of nanoscopic assemblies in sensors and microelectronics. It is believed that with the development of material science, ZnO has found further applications in many fields. Other researchers reported that the presence of ZnO nanoparticles (NPs) can affect the electropolymerization process where ZnO acts as an incorporating agent. Since composites made from inorganic nanomaterials exhibit indispensable constancy, this design can be effectively employed for specific applications.

The addition of functionalized protonic acid, such as dodecyl benzene sulphonic acid (DBSA) to the polymer, leads to superior homogeneity of the polymer films and improves the process ability and solubility as well as the dispersion of conductive polymer particles in resins.

In this study the electrochemical synthesis of poly(N-methyl pyrrole) was performed on steel in the presence and absence of ZnO NPs in mixed electrolytes of DBSA with oxalic acid. The coating properties were analyzed by electrochemical impedance spectroscopy (EIS). Their corrosion protection properties have been established and compared together. The content of doped zinc in the polymer and the effect of ZnO NPs on the polymer morphology, were investigated.
2. Experimental details

2.1. Synthesis of ZnO NPs

The Zn(NO₃)₂·4H₂O and NaOH were used to synthesize ZnO NPs. The concentrations of Zn(NO₃)₂·4H₂O and NaOH were 0.45 M and 0.9 M respectively. The zinc nitrate solution was added drop wise (slowly for 40 min) in a beaker containing NaOH solution with high speed stirring at a temperature of about 55 °C. After 3 min, a white precipitate of ZnO was observed. The precipitated ZnO NPs were washed with deionized water and ethanol, and then dried in air atmosphere at about 60 °C [12]. The ZnO (NPs) powder was heat treated at 400 °C for 3 h.

2.2. Electrolyzerization of PMPy and PMPy/ZnO NPs

The elemental composition analysis of the steel plate substrate of 1 cm² was: (wt. %: 2.71% C, 0.49% Si and 94.79% Fe). The counter electrode was a platinum foil with 2 cm² surface area and a saturated calomel electrode was used as the reference; all the potential values were referred to this electrode. The steel working electrodes were degreased in ethanol and dried at 45 °C after being mechanically polished with fine emery paper of 320–1200 grades. The N-methyl pyrrole (MPy) (Aldrich, 99%) and DBSA (Aldrich, 70 wt.% solution in 2-propanol) used in the experiment were always stored in darkness.

The electropolymorization of MPy was done using a single compartment cell in mixed electrolytes of oxalic acid and DBSA in 50 cyclic voltammograms with a potential range from −0.4 to 1.2 V. The concentration of MPy was 0.03 M while the concentration of ZnO NPs. In the presence of ZnO NPs was prepared from baths containing MPy and ZnO NPs. In the preparation of this bath, 50 mg of ZnO NPs was added to 0.03 M solution of MPy monomer, 0.1 M DBSA and 0.1 M oxalic acid. The scan rate for the electropolymorization of PMPy in the presence and absence of ZnO NPs was 100 mV s⁻¹.

The thicknesses of the PMPy and also of the PMPy/ZnO NPs were approximatley 2.18 μm and 2.03 μm respectively.

The electropolymorized PPy in the presence and absence of ZnO NPs on steel surface was scraped off and Fourier Transform Infrared Spectroscopy (FT-IR) spectra of the polymer powders were taken using a Nicolet 380 FT-IR instrument. Scanning electron micrographs and Energy-dispersive X-ray spectroscopy (EDX) were taken with a Joel JSM-840A Field Emission Scanning Electron Microscopy (FESEM) with operating voltage 5 kV. The average crystalline size was found to be about 27.56 ± 0.06 nm for the sample prepared by this method. The values of the distance (d) between adjacent planes in the (hkl) are calculated from the Bragg equation λ = 2dsinθ; the lattice constants a, b, c, the interplanar angle, the angle ϕ between the plane (hkl), of spacing ds, and the cell volumes are calculated from the Lattice Geometry equation [17]. The (112) and (201) peaks of ZnO NPs were used to calculate the lattice parameters (Table 1).

2.1.2. FT-IR of ZnO NPs

Fig. 2 shows the FT-IR spectra for the ZnO NPs heat treated at 400 °C. The special peak at 448.89 cm⁻¹ represents the bonding between Zn—O [18,19]. The FT-IR spectra of ZnO NPs showed that the high purity of ZnO NPs was synthesized by this method.

2.1.3. TEM of ZnO NPs

To determine the size and shape of ZnO NPs, the powder sample calcined at 400 °C was dispersed in acetone under sonication for 1 h. Fig. 3 shows the TEM of ZnO NPs. As can be seen, the shape of nanoparticles is spherical and cubic at random. This is due to the fact that when the reaction time and temperature increase the nanoparticles become random in shape [20]. The size histograms of the ZnO NPs are shown below their respective TEM images. The histograms show that the main particle size of the ZnO NPs was about 41 ± 7 nm.

![Fig. 1. XRD patterns of the ZnO NPs heat-treated at 400 °C for 3 h.](image-url)
3.2. Cyclic voltammetry

The cyclic voltammogram of the steel electrode in monomer free oxalic acid solution in scan rate 100 mV.s$^{-1}$ is given in Fig. 4(a). In the first stage the peak potential value for characteristic oxidation–passivation and re-passivation processes for steel was determined about $-0.1$ and 0.1 V in oxalic acid environment. This behavior can be explained by the formation of a strong passivating ferrous oxalate layer on the steel surface. In the second stage, the DBSA peak was obtained by applying the same potential range and scan rate with the first stage in a mixed electrolyte of oxalic acid and DBSA. Fig. 4(b) shows that the peak of passivation became wider when the mixture of electrolytes was used.

Fig. 5(a) shows the cyclic voltammograms in a mixture of MPy monomers, oxalic acid and DBSA which were obtained by applying the same potential range and scan rate in the absence of ZnO NPs. The monomer oxidation process was observed as the current increased at about 0.7 V, in the first forward scan. The oxidation current value decreased for the second and following cycles. This oxidation process leads to the formation of a stable film PMPy deposited on the surface. On the other hand, the thin PMPy film deposited during the forward scan of the first cycle was thought to be very adherent and compact, because the passivation peak of the steel electrode decreased after 10 cycles. With the successive voltammetric cycles applied for film growth, the oxidation–reduction process of PMPy was observed as anodic and cathodic waves between approximately 0.7 and 0.1 V, in the forward and reverse scans. Fig. 5(b) shows that after 34 cycles, the steel surface was completely covered with PMPy because of the disappearance of the passivation peak. In addition, the peak height of the monomer oxidation process decreased. The decrease of current density is an evidence of the decrease of polymer growth on the steel surface coated with PMPy. The decrease is because of the polymerization holdback due to side oxidation products (oxidative degradation) and/or increasing resistance of the PMPy coating during the polymerization process [21].

Fig. 6 shows the cyclic voltammograms of synthesized PMPy in the presence of ZnO NPs in a mixture of oxalic acid and DBSA by applying the same potential range and scan rate in the absence of ZnO NPs. Comparison between Figs. 6(a) and 5(a) shows that the passivation peak shape changes after the first cycle. The reason of this result can be explained from the interaction between ZnO and DBSA. The comparison between Figs. 6(b) and 5(b) shows that the decrease of current density of the monomer oxidation in the presence of ZnO NPs is much more than that in the absence of ZnO NPs after 34 cycles. The decrease of electrolyte conductivity due to the presence of ZnO NPs.

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\theta$</th>
<th>hkl</th>
<th>$d_{hkl}$ (nm)</th>
<th>Structure</th>
<th>Lattice parameter (nm)</th>
<th>$\cos \varphi$</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO NPs</td>
<td>67.9</td>
<td>(112)</td>
<td>0.1379</td>
<td>Hexagonal</td>
<td>$a=0.3211$, $c/a=1.6772$</td>
<td>0.8482</td>
<td>27.56±0.06</td>
</tr>
<tr>
<td>69.2</td>
<td>(201)</td>
<td>0.1356</td>
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<td></td>
</tr>
</tbody>
</table>

Fig. 2. FT-IR spectra of ZnO NPs heat treated at 400 °C for 3 h.

Fig. 3. Transmission electron microscopy (TEM) image and the size histograms of ZnO NPs heat treated at 400 °C for 3 h.

Fig. 4. Cyclic voltammograms obtained from (a): steel passivation in 0.1 M oxalic acid, (b): steel passivation in mixture of 0.1 M oxalic acid and 0.1 M DBSA.
and increasing resistance of the PMPy coating during the polymerization process are the reasons for this phenomenon. In addition, ZnO NPs might act as a barrier and reduce direct interaction between monomers and the steel surface as working electrode. Fig. 7 shows the role of DBSA in the polymerization of MPy monomers in the presence of ZnO NPs. It is generally admitted that the process begins with the adsorption of the DBSA molecules on the ZnO particle surface [23]. Interaction takes place through the hydrophilic head group of DBSA, the hydrophobic part being consequently directed toward the aqueous phase. A second layer of emulsifier molecules is then adsorbed on the first layer to provide an energetically stable arrangement. The net result is the formation of a DBSA bilayer which can solubilize the MPy monomers in the hydrophobic interlayer and promote polymerization at the interface of ZnO NPs and the working electrode surface. The absorption towards the steel surface is facilitated by the negative charge of the hydrophilic head in DBSA. The changing of the peak related to passivation in the electropolymerization of MPy monomers in the presence of ZnO NPs can confirm the interaction between DBSA and ZnO NPs.

### 3.3. FESEM and EDX of coatings

Fig. 8(a) and (b) shows a high magnification FESEM image of PMPy in the presence and the absence of ZnO NPs respectively, in a mixture of DBSA and oxalic acid. Other researchers reported that the morphology of PPy and its derivative films present a cauliflower-like structure constituted by micro-spherical grains. It has been reported that this cauliflower structure is related to the dopant intercalation difficulty in the disordered polymeric chain [24].
and (b) shows that the morphology of the PMPy and PMPy/ZnO NPs is similar but the size of the cauliflower structure is smaller for the PMPy/ZnO NPs. Fig. 9 shows the EDX of PMPy and PMPy/ZnO NPs. These results show the existence of zinc element in the electropolymerized PMPy in the presence of ZnO NPs. In addition these results show that the existence of ZnO NPs leads to an increase in the amount of doped sulfur in polymer (Table 2). On the other hand, the low weight percentage of Fe in PMPy/ZnO NPs indicates that the porosity and the amount of dissolved Fe$^{2+}$ during electropolymerization of PMPy in the presence of ZnO NPs are lower than the electropolymerized PMPy in the absence of ZnO NPs.

3.4. FT-IR spectroscopy

The FT-IR spectrum of the polymers coatings are shown in Fig. 10. The peak at 449.76 cm$^{-1}$ in the spectrum of PMPy/ZnO NPs is related to Zn–O [15] in Fig. 10b. A large descending baseline appears in the spectral region of 1700 to 2500 cm$^{-1}$ in the spectrum indicating the free-electron conduction in conducting polymers [21]. In the FT-IR spectrum of synthesized PMPy and PMPy/ZnO, peaks at 3422.15 cm$^{-1}$ and 3380.09 cm$^{-1}$ can be attributed to N–H bond. The FT-IR spectrum of synthesized MPPy in mixed oxalic acid and DBSA (Fig. 10a) indicates the characteristic bands for DBSA at 1124.47 cm$^{-1}$–1188.76 cm$^{-1}$ (for SO$_3$), 676.92 cm$^{-1}$ and 1048.66 cm$^{-1}$ (both S O stretch) [25,26]. The FT-IR spectrum of synthesized PMPy/ZnO NPs in mixed oxalic acid and DBSA shows that the special peaks that belong to S O stretches are located at 670.16 cm$^{-1}$ and 1050.85 cm$^{-1}$ and the corresponding peaks for SO$_3$ are located at 1118.88 cm$^{-1}$ and 1180.41 cm$^{-1}$ in Fig. 10b. The slight shift in the wavenumbers for the SO$_3$ and S O stretches in the FT-IR spectrum of PMPy/ZnO NPs compared to the PMPy spectrum, can account for the interaction between the DBSA and the ZnO in the PMPy/ZnO NPs. In Fig. 10, peaks at 1658.74 cm$^{-1}$ (Fig. 10a) and 1654.79 cm$^{-1}$ (Fig. 10b) are related to C–NC bond in the spectrum of PMPy and PMPy/ZnO NPs respectively. The strong band at 2851.54 cm$^{-1}$ (Fig. 10a) and 2854.03 cm$^{-1}$ (Fig. 10b) can be associated with aliphatic C–H in spectra of PMPy and PMPy/ZnO NPs respectively.

3.5. Corrosion study

3.5.1. Open circuit potential studies

The electrode potential can be manipulated in order to get anodic protection through galvanic contact with a charged conducting polymer [27]. The variation of open circuit potentials (OCP) with time for the uncoated steel and steel coated with PMPy and PMPy/ZnO NPs in 3.5% NaCl is shown in Fig. 11. The coating containing PMPy/ZnO NPs is able to maintain more noble potential values in comparison to PMPy and uncoated steel. It is well known that corrosion protection of conducting polymers is essentially a form of anodic protection. Recent investigations have shown that a substrate metal coated with a charged conducting polymer will poise the electrode potential in the passive range in the absence of any redox reaction. However, the discharge of the conducting polymer film can be seen in the presence of a redox reaction, which is predictable even in the passive regime. Thus, the potential will change to negative values. The length of time during which the potential is maintained in passive regime depends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt%</th>
<th>C</th>
<th>O</th>
<th>Fe</th>
<th>S</th>
<th>Zn</th>
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</thead>
<tbody>
<tr>
<td>Poly(N-methyl pyrrole)/ZnO NPs</td>
<td>81.7</td>
<td>14.3</td>
<td>0.5</td>
<td>3.2</td>
<td>0.3</td>
<td></td>
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<tr>
<td>Poly(N-methyl pyrrole)</td>
<td>80.6</td>
<td>14.8</td>
<td>1.6</td>
<td>3.0</td>
<td>–</td>
<td></td>
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</tbody>
</table>
solution was used to analyze the Electrode/PMPy/ZnO NPs/electrolyte.

3.5.3. EIS study

The EIS study was conducted to investigate the electrochemical behavior of the steel and coated steel with PMPy and PMPy/ZnO NPs samples in 3.5% NaCl solution. The EIS results showed that the corrosion of PMPy in the presence of ZnO NPs can increase the surface area of the polymer, therefore increasing the rate of corrosion. The FESEM results showed that the synthesis of PMPy/ZnO NPs can increase the surface area of the carbon steel.[29,30]. The FESEM results showed that the synthesis of PMPy/ZnO NPs can increase the surface area of the carbon steel.[29,30]. The FESEM results showed that the synthesis of PMPy/ZnO NPs can increase the surface area of the carbon steel.[29,30].

3.5.2. Potentiodynamic polarization

The potentiodynamic polarization curves obtained for uncoated steel and coated steel with PMPy and PMPy/ZnO NPs in 3.5% NaCl can support this hypothesis. The performance of an organic coating as corrosion protection can be described by several factors; barrier effects which prevent oxygen and moisture from reaching the metal substrate, reaction with the corrosive ions and formation of a passivation layer.[33,34]. A better estimate of the coating deterioration evolution can be obtained by taking into account the rate of corrosion.

The potentiodynamic polarization curves obtained for uncoated steel and coated steel with PMPy and PMPy/ZnO NPs in 3.5% NaCl solution are shown in Fig. 12. The corresponding corrosion potentials (Ecorr), corrosion currents (icorr) and corrosion rate (CR) are listed in Table 3. The shift of the corrosion potential of coated steel with PMPy/ZnO NPs to more positive in comparison with uncoated steel shows an inhibition of the corrosion process by the PMPy/ZnO NPs coating. In contrast, the corrosion current decreased from 0.5638 (uncoated steel) to 0.0936 mA cm$^{-2}$ (steel coated with PMPy/ZnO NPs). In addition these results show that the corrosion rate of coated steel with PMPy/ZnO NPs decreases in comparison with PMPy.

3.5.3. EIS study

Electrochemical impedance spectroscopy (EIS) in 3.5% NaCl solution was used to analyze the Electrode/PMPy/ZnO NPs/electrolyte and the Electrode/PMPy/electrolyte system of the steel coated by synthesized polymer in a mixture of oxalic acid and DBSA. The electrochemical parameters of the PMPy/ZnO NPs/electrolyte and PMPy/electrolyte systems were evaluated by employing the ZSimWin software. We observed an excellent agreement between experimental results and the parameters obtained from the R (C [R(Q)]) (RC) equivalent circuit model for PMPy/ZnO NPs (Fig. 13) and PMPy (Fig. 14) where the chi-squared ($\chi^2$) is minimized to $10^{−3}$ value. The $R_s(C_s [R_p (R_Q)]) (R_{CEF}C_{CE})$ equivalent circuit model was used in the simulation of the impedance behavior of the films with the experimentally obtained impedance data. The model was built using series components; the first is the bulk solution resistance of the polymer and electrolyte, $R_s$. The second is the parallel combination of the capacitance of the polymer coating, $C_s$ and $R_Q$, where $R_Q$ is the pore resistance which is due to the formation of ionically conducting paths through the coatings.

The Nyquist plots of the two coatings. It can be seen that the Nyquist plots is a “depressed semi-circle” with the center of the circle below the x-axis.[31]. Instead of pure capacitors, constant phase elements (CPE) were introduced in the fitting procedure to obtain good agreement between the simulated and experimental data. The impedance of CPE is defined as $Z_{CPE} = Q^{-1} (j\omega)^{-n}$, where $Q$ is the combination of properties related to both the surface and the electroactive species independent of frequency; “n” is related to the slope of the log Z vs. log $\omega$ in the Bode plot; $\omega$ is the angular frequency. It should be noted that instead of $\Omega^{-1}$, $S$ can be also used and Q values are given in units of Siemens in Figs. 13 and 14 [32]. The CPE can be represented by the parameter $Q$ and the exponent “n”; it should be stressed that for simplicity Q is often considered as a capacitance. The constant phase element (CPE) which is $Q_1$ is parallel with $R_p$. The $R_p$ is the charge transfer resistance of the area of the polymer/electrolyte interface at which the corrosion occurs. The last component, a capacitance $C_{CE}$ is parallel with a charge transfer resistor ($R_{CEF}$) which is due to the pore in the surface of oxide layer. Simulation results for PMPy/ZnO NPs and PMPy show that this electrical equivalent circuit accurately fits to the experimental data to explain the interface between the electrode/PMPy/ZnO NPs or PMPy film and electrolyte (Table 4).

The performance of an organic coating as corrosion protection can be described by several factors; barrier effects which prevent oxygen and moisture from reaching the metal substrate, reaction with the corrosive ions and formation of a passivation layer.[33,34]. A better estimate of the coating deterioration evolution can be obtained by taking into account the rate of corrosion.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>t(h)</th>
<th>$E_{corr}$ (V)</th>
<th>$b_1$ (V/dec)</th>
<th>$b_2$ (V/dec)</th>
<th>$i_{corr}$ (mA cm$^{-2}$)</th>
<th>Corrosion rate (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>24</td>
<td>-1.21</td>
<td>0.193</td>
<td>0.254</td>
<td>0.5638</td>
<td>6.545</td>
</tr>
<tr>
<td>Steel/PMPy</td>
<td>24</td>
<td>-1.14</td>
<td>0.252</td>
<td>0.419</td>
<td>0.1713</td>
<td>1.989</td>
</tr>
<tr>
<td>Steel/PMPy/ZnO NPs</td>
<td>24</td>
<td>-1.02</td>
<td>0.526</td>
<td>0.458</td>
<td>0.0936</td>
<td>1.087</td>
</tr>
</tbody>
</table>

Fig. 10. FT-IR spectra of coated steel with (a); synthesized PMPy films from a mixture of 0.1 M oxalic acid and 0.1 M DBSA electrolyte. (b); synthesized PMPy/ZnO NPs films from a mixture of 0.1 M oxalic acid, 0.1 M DBSA and 50 mg of ZnO (NPs) electrolyte.

Fig. 11. Plots of open circuit potential against time (h) in 3.5% NaCl solution of (a) PMPy/ZnO NPs coated steel electrode, (b) PMPy coated steel electrode and (c) uncoated steel electrode.

Fig. 12. Polarization curves in 3.5% NaCl solution of (a) uncoated steel electrode, (b) PMPy coated steel electrode and (c) PMPy/ZnO NPs coated steel electrode.
considering the variation of $R_{po}$ and $C_C$ as a function of immersion time. Fig. 15(a), shows the variation of $R_{po}$ with immersion time. The decrease of $R_{po}$ with rising immersion time, indicates an increase in ionic conductivity of the coating and lower protective properties as a result of electrolyte penetration. The decrease and minimum of $R_{po}$ values have been associated with the formation and rupture of blisters and the subsequent increase and maximum to the deposition of corrosion products in the blister [35,36]. As can be seen, $R_{po}$ of the PMPy coating synthesized in the absence of ZnO NPs after 2 h immersion time decreases. The result shows that $R_{po}$ of the PMPy coating synthesized in the presence of ZnO NPs is more compared to the absence of the ZnO NPs (Fig. 15a). The variation of $C_C$ was another way to understand the behavior of the polymer (Fig. 15b). As the coating degrades, the polymer film resistance decreases and the coating capacitance increases. The increase of the capacitance values is an indication of the increase of water uptake (electrolyte) [37]. Comparatively, there is an agreement with the results of $R_{po}$ and $C_C$. The higher value of the resistance against the flow of ions of the electrolyte through the membrane is in accordance with the lower capacitance value. Other authors reported the effect of the nano-size additives to improve the barrier properties of polymers for diffusion of solvent/gasses [38]. The increase of PMPy surface area in the reaction medium is one of the advantages of the polymerization of PMPy in the presence of nanoparticles. One of the special properties of electro-active polymers is their ability to interact with the ions liberated during the corrosion reaction of steel in the presence of NaCl [38–41]. So their performance increases with the increase of surface area. The

FESEM micrographs suggest that the incorporation of ZnO NPs affects the morphology of the film significantly and can increase the surface area of the synthesized PMPy in the presence of ZnO NPs. Moreover, Iroh and Su [7] reported that, although PMPy acts similar to PPy coatings to reduce the corrosion rate and corrosion current of steel,

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Exposure time (hour)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>With ZnO NPs</td>
<td>$C_{\text{p}}$/μF.cm$^{-2}$</td>
<td>0.552</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{pp}}$/Ω.cm$^2$</td>
<td>13.2</td>
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<td>$R_{\text{e}}$/Ω.cm$^2$</td>
<td>6.309</td>
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<tr>
<td></td>
<td>$Q_{\text{f}}$/Y$_{oo}$/μS.cm$^{-2}$</td>
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<tr>
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<td>$N$</td>
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<tr>
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<td>$n$</td>
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<td>$R_{\text{pp}}$/Ω.cm$^2$</td>
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<td></td>
<td>$C_{\text{CF}}$/nF.cm$^{-2}$</td>
<td>67.40</td>
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</table>

Table 4 Electrochemical parameters obtained by simulation of the EIS results of the steel covered with PMPy films and PMPy/ZnO NPs, exposed to a 3.5% NaCl aqueous solution.
but the number of defects found on the coatings was more compared to the PPy coating. The EIS result shows the $R_{po}$ of synthesized PMPy coating synthesized in the presence of ZnO NPs is higher compared to its absence. Perhaps the existence of ZnO NPs within the coating can plug some pores and defects which can increase the $R_{po}$.

4. Conclusions

Poly(N-methyl pyrrole) was electrodeposited on steel substrates in the presence and absence of ZnO NPs. The EDX result indicated that the weight percentage of doped zinc in PMPy matrix was 0.3%. The FESEM micrographs showed that the incorporation of ZnO NPs affects the morphology of the film significantly and can increase the surface area of the synthesized PMPy in the presence of ZnO NPs. The results showed that $R_{po}$ and $C_p$ values as a function of immersion time for the PMPy coating synthesized in the presence of ZnO NPs is higher and lower respectively compared to the absence of ZnO NPs. The increase of the surface area can increase the ability of the PPy/ZnO NPs to interact with the ions liberated during corrosion reaction of steel in NaCl solution and/or it causes an increase in the rate probability for the occurrence of cathodic reduction of oxygen on the PMPy. In addition, the existence of ZnO NPs within the coating perhaps can plug some pores and defects, thus the $R_{po}$ increases.

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