

# Molybdate Doped Polypyrrole: Preparation, Properties and Application

Ha Manh Hung<sup>1,2</sup>, Le Minh Duc<sup>3</sup>, Tran Vinh Dieu<sup>4</sup> and Vu Quoc Trung<sup>1</sup>

1. Faculty of Chemistry, Hanoi National University of Education, Cau Giay District, Hanoi, Vietnam

2. Faculty of General Education, Hanoi University of Mining and Geology, Dong Ngac, Tu Liem, Hanoi, Vietnam

3. Faculty of Chemical Engineering, Danang University of Technology, Lien Chieu District, Danang, Vietnam

4. Centre of Polymer Research, Hanoi University of Science and Technology, Hai Ba Trung District, Hanoi, Vietnam

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**Abstract:** Molybdate doped-polypyrrole (PPy) was electropolymerised on the mild steel surface. The morphology of polymer film was studied with scanning electron microscopy (SEM). The chemical structure of polymer was characterized with Raman spectroscopy. The presence of molybdate doped inside polypyrrole was identified by EDX spectra. The thermal analysis (TGA) showed that polypyrrole was stable up to 500 °C. The corrosion protection of the polymer film was investigated by electrochemical methods showing that the polymer film acted as a barrier layer and molybdate as an inhibitor for corrosion protection of metal. Molybdate dopant was the key component of "self-healing" polypyrrole film.

**Key words:** Polypyrrole, corrosion protection, electrochemical impedance spectroscopy, molybdate.

## 1. Introduction

Since polyacetylene was investigated [1], various applications of conducting polymer have been reported [2, 3]. They have promised in antistatic materials [4] and they have been incorporated into commercial displays [5] and batteries [6]. It is suggested they are also promising in organic solar cells [7], printing electronic circuits [8], organic light-emitting diodes [9], actuators [10], electrochromism [11], supercapacitors [12], chemical sensors [13] and biosensors [14], electromagnetic shielding [15]. Due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process, conducting polymer still has some limitations in using. Utilization of the conducting polymer for corrosion protection coating is one of these applications, and many papers have been presented in the last decade.

Preparation of polyacetylene was made by oxidation in gaseous phase; however, at present, the conducting polymers such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh) for the corrosion protection have been prepared by electrochemical oxidation in liquid phase.

Polyaniline was firstly reported in 1985 for application in corrosion protection of metal [16]. Then Wessling pointed out that the conducting polymer coating of polyaniline and polypyrrole possibly possessed self-healing properties [17]. The passive oxide layer in the interface of metal substrate-conducting polymer could be spontaneously reformed at a flawed site by oxidative capability of the conducting polymer [18-21].

After polymerisation, the conducting polymer could be conductive and got redox properties. Conducting polymer can oxidize steel substrate and shift the electrode potential towards to the positive potential, in which the steels are protected by the passive oxide formed beneath the conducting polymer. The

**Corresponding author:** Vu Quoc Trung, Ph.D., professor, research fields: nanocomposites, conducting polymers and thin films. E-mail: vuquoctrung@nctnam.vn.

application of the conducting polymer coating to the corrosion protection of steels was reviewed by Tallman et al. [18]. The role of dopant anions was paid much more attention in improving the corrosion behaviour of conducting polymer film on metal. Due to toxicity, chromium as known as excellent corrosion inhibitor is replaced by another one that more environmental friendly. Molybdate is one of the alternatives choosing [22]. Besides, the electropolymerisation of conducting polymer on active substrate has some problem. The dissolving of substrate is so fast that the polymerisation is prevented to take place on the surface.

In this paper, the molybdate doped PPy films were studied to electrosynthesised on mild steel. The corrosion protection ability was also investigated. The role of molybdate dopants in corrosion protection were shown.

## 2. Experiments

### 2.1 Chemicals

Pyrrrole (Py) monomer (Merck) was distilled under nitrogen before using,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{H}_2\text{C}_2\text{O}_4$  were purchased from Merck and used without any further purifying.

### 2.2 Preparation of Polypyrrole Films

Mild steel CT3 (TISCO company, Thai Nguyen, Vietnam) was used as substrate (C: 0.16%; Mn: 0.62%; Si: 0.15%; P: 0.010% and S: 0.042%, according to GOST 001-2001-TCVN 1656-75 standard). The mild steel electrode mechanically polished with abrasive paper (1000-grade) and rinsed in water firstly and then in ethanol before each experiment, constituted the working electrode. A Pt sheet was used as an auxiliary electrode. All potentials were measured versus silver/silver chloride reference electrode (AgCl/Ag).

The PPy film (N1) was synthesized in solution containing 0.1 M  $\text{H}_2\text{C}_2\text{O}_4$  and 0.1 M pyrrole at room temperature using the three-electrode cell. Sample N2 was synthesized in the condition above with addition

of 0.01 M  $\text{Na}_2\text{MoO}_4$ . The mild steel CT3 sheet ( $1 \text{ cm}^2$ ) used as working electrode was cleaned in an ultrasonic bath with ethanol. Electropolymerization of pyrrole was carried out using galvanostatic mode and carried out with a Zahner Workstation (Zenium).

### 2.3 Characterization of the Polypyrrole Films

Thermal gravimetric analysis (TGA) was done by Ghimashu-50 H with scan rate of  $10^\circ\text{C}/\text{min}$  in atmospheric condition. The chemical structure of the nanocomposites was characterized by Raman spectroscopy. Raman spectra were recorded by Laser Raman Spectrophotometer (Ramalog 91, USA). EDX spectra and SEM images were obtained with SEM-HITACHI-4800 under energy of 10 keV.

### 2.4 Corrosion Protection Test

The open circuit potential (OCP), Tafel curves and electrochemical impedance spectroscopy were obtained in 3% NaCl solution with Zahner (Zenium) Workstation.

## 3. Results and discussion

### 3.1 Film Preparation

PPy doped with molybdate was electrosynthesised in solution containing 0.1 M  $\text{H}_2\text{C}_2\text{O}_4$  and 0.1 M pyrrole at room temperature. During polymerisation at constant potential (0.9 V v.s Ag/AgCl), the current was increased and get stable which was high enough for PPy forming (curve N1). At the beginning of polymerisation, the high current could be due to the dissolution of mild steel substrate very strong. Thank to  $\text{C}_2\text{O}_4^{2-}$  anion, steel surface was passivated and pyrrole could be polymerised.

In the presence of molybdate and oxalate dopants at the same time in the electrolyte, the result current (curve N2) was also increased but smaller than that of the above condition. It maybe due to the formation of passive film with molybdate was easier than that of oxalate anion. So that the dissolution of steel substrate could not inhibit the polymerisation of pyrrole monomer.

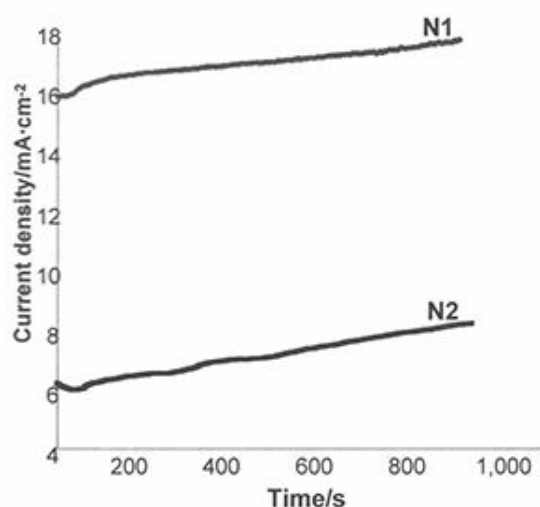
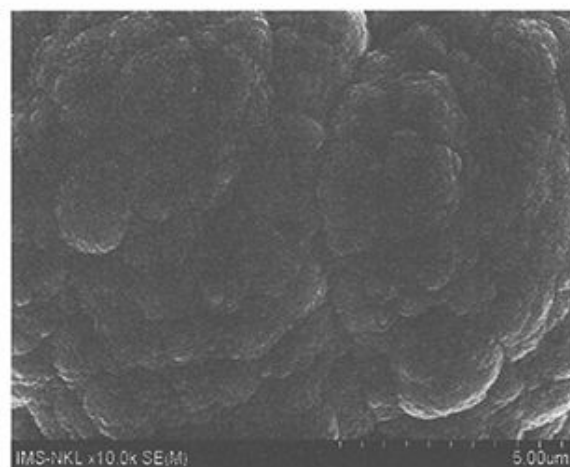
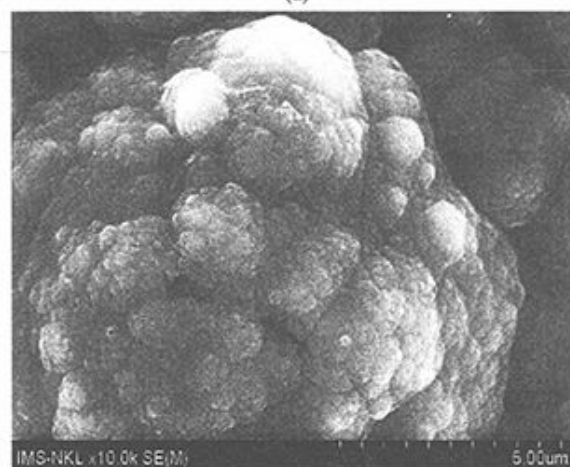


Fig. 1 Polymerization of PPy at constant potential 0.9 V.



(a)



(b)

Fig. 2 SEM images of (a) N1 and (b) N2.

### 3.2 Morphology and Characterization of the PPy Film

#### 3.2.1 SEM Images

SEM image of samples N1, N2 were presented in Fig. 2. The films were homogenous and the typical cauliflower structure could be seen on both surface.

The presence of molybdate dopants did not affect the surface morphology of the PPy films.

#### 3.2.2. Raman Spectra

Chemical structure of PPy films were characterized with Raman scattering spectroscopy (Fig. 3). Table 1 gives the assignments of some Raman bands of samples N1 and N2. Various vibration modes collected on the PPy/Ag spectra, as well as theoretically calculated by Faulques et al. [19] were used to compare. The wavenumber  $1,593 \text{ cm}^{-1}$  was assigned for the C=C double bond of PPy in the oxidised state.

#### 3.2.3 Thermal Analyses and EDX Spectra

Thermal analysis of N1 and N2 were presented in Fig. 4. There are three temperature ranges showed on the curves: from 0-100 °C, 100-400 °C and 400-600 °C. Under 100 °C, the weight loss originated from the release of water inside samples. This proves that in the composition of the PPy films made up of redundant water. In the temperature range of 100-400 °C, the mass decrease is mainly due to the decomposition of monomer residues and oligomers. For the temperature of 400-600 °C, the decrease is due to the decomposition of PPy.

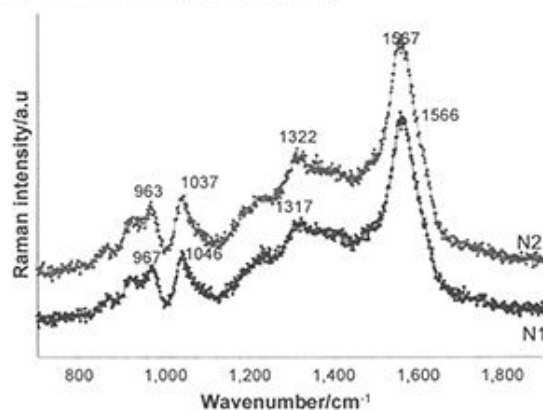


Fig. 3 Raman spectra of N1 and N2.

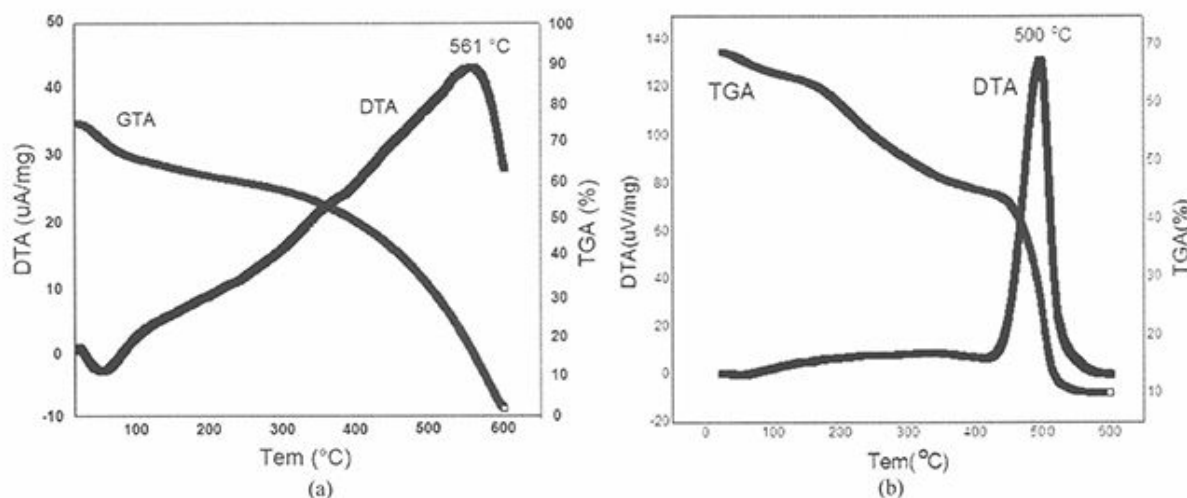
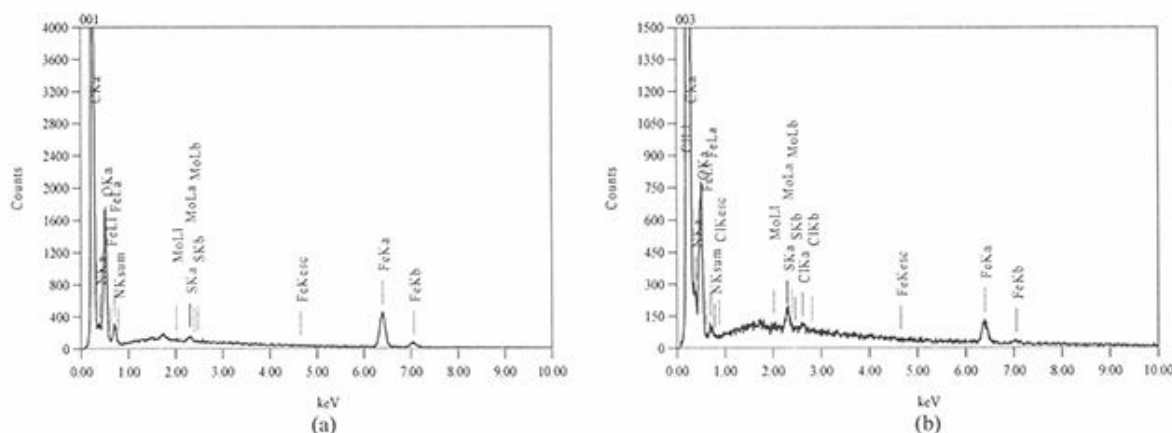
**Table 1** Wavenumbers and assignments of the Raman bands of N1 and N2.

		Wavenumber (cm <sup>-1</sup> )			Assignment
PPy <sup>a</sup> [21]	PPy <sup>b</sup> on Zn [23]	PPy <sup>c</sup> on Al <sub>2</sub> O <sub>3</sub> [15]	N1	N2	
1676	1,584	1,593	1,566	1,567	C=C ring stretching
1524.4	1,414	1,500	1,367	1,388	C-C, C-N stretching
1307	1,327	1,373	1,317	1,322	
-	1,258	1,242	1,232	1,227	
1049.4	1,046	1,057; 1,092	1,048	1,037	C-H in plane deformation
955.8	989	973	967	963	C-H stretching
-	938	943	928	942	

(a) Theoretical calculation for oxidised PPy; (b) oxidised PPy prepared by electropolymerization; and (c) oxidised PPy prepared by chemical polymerization.

**Table 2** Decomposition range of N1 and N2.

Temperature range		0-100 °C	100-400 °C	400-600 °C	> 600 °C
Mass change	N1	13.17	30.40	56.43	0.00
%Δm	N2	5.78	29.16	55.06	10.00

**Fig. 4** TGA curves of (a) N1 and (b) N2.**Fig. 5** EDX analysis of (a) N1 and (b) N2.

The differences of the curves N1 and N2 could be seen. It was seen that sample N1 was completely decomposed at 600 °C, while sample N2 still remained. The composition of N2 remained above 600 °C could be inorganic compound made from iron and molybdate during electrochemical polymerization. The thermal decomposition of N1 and N2 were showed in Table 2.

It could be seen the molybdate spectra on the EDX results (Fig. 5) showing that molybdate was incorporated in the film during polymerisation of pyrrole. The amounts of elements in these samples are shown in Table 3. The presence of Mo help the PPy file more stable above 600 °C. Peak of iron cation could be observed on the spectra. Steel substract was dissolved during electrochemical polymerisation, so that they were detected.

### 3.3 Electrochemical Corrosion Test

#### 3.2.1 Change of Open Circuit Potential

OCP-time curves of PPy film in  $H_2SO_4$  0.05M were recorded. They are shown in Fig. 6.

As presented on the curve N0 (Fig. 6), the OCP was -0.476 V when dipping the bare steel CT3 in  $H_2SO_4$  0.05 M acid solution. It is clear the sample was corroded immediately. The sample N1 could remain the passive potential of steel for 7.5 h. Oxalate dopants of the PPy film could played an important role in protecting steel from corrosion. The release mechanism of oxalate dopants maybe used to explain this possitive affect. The PPy film doped with molybdate (N2) really presented the better affect in corrosion protection of steel. Pasive potential of steel could be remained in longer time, 13 h in acid medium. The release of molybdate due to the reduction of PPy film during corrosion protection of steel could help to form the inorganic compound that could inhibite the corrosion. Molybdate anion was mobile enough to release from PPy film and played as corrosion inhibitor [8, 9].

The good effect of  $MoO_4^{2-}$  in improving corrosion protection of PPy film could be seen in the Tafel plots (Fig. 8).

Table 3 Chemical composition of N1 and N2.

Element	N1 (% by weight)	N2 (% by weight)
C	27.54	28.14
N	33.79	28.88
O	31.13	30.12
S	-	-
Fe	4.06	4.10
Mo	-	4.41

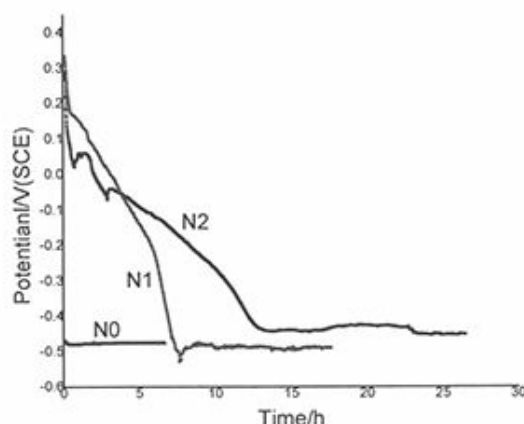


Fig. 6 OCP-time curve of sample N1, N2 and steel CT3 (N0) in solution  $H_2SO_4$  0.05 M.

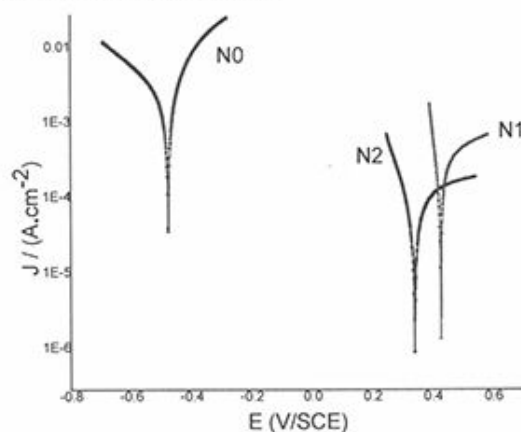


Fig. 7 Polarization curves of steel CT3 N0, N1 and N2.

In Fig. 7, both N1 and N2 samples have more positive corrosion potential 0.43 V and 0.33 V, respectively, than that of the bare steel CT3 in 0.05 M  $H_2SO_4$  solution (-0.476 V). It is suggested that the coatings doped PPy with the inhibite dopant has a significant effect of the protection for steel CT3. The corrosion current density of N1, N2 is  $9.05 \times 10^{-5} A/cm^2$  and  $2.96 \times 10^{-5} A/cm^2$ , respectively. Therefore, the



corrosion protection of N2 is better than N1.

Fig. 8 shows the electrochemical impedance spectra (EIS) of N0, N1 and N2 in  $H_2SO_4$  solution 0.05 M measured at rest potential. The obtained impedance spectra of the polymer film can be divided in three regions:

- Region 1 (high frequency > 1 kHz) characterizes the behavior of the electrolyte. Phase angle is nearly zero. The resistance of the electrolyte is about  $20 \Omega$ .
- Region 2 (middle frequency) shows the properties of the polymer film. The PPy film behaves as dielectricum with a capacitive impedance.

- Region 3 (low frequency) represents the interface polymer/substrate. There are the capacitance of double layer and the charge transfer resistance of the interface.

The EIS shows that N2 have higher impedance than that of N1. It could be explained by the presence of inorganic compound formed in the first step of polymerization on the surface of steel.

Fig. 9 shows EIS of N1 and N2 at  $-0.476$  V (after measurement of OCP). Obviously, the impedance of PPy films was higher than those values before measurement of OCP. This increase is due to when the

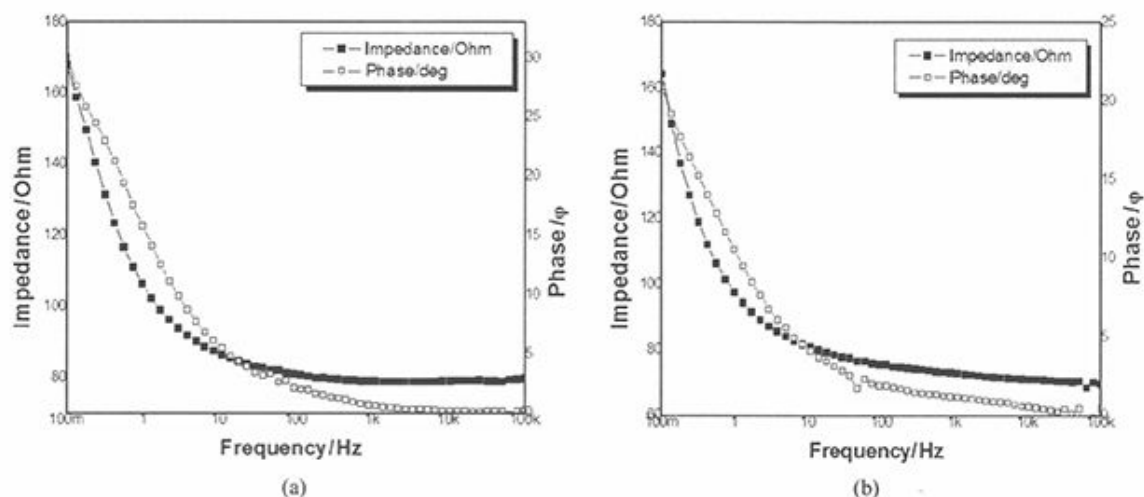


Fig. 8 EIS spectra of (a) N1 and (b) N2 in solution of  $H_2SO_4$  0.05 M at 0.43 V and 0.33 V, respectively.

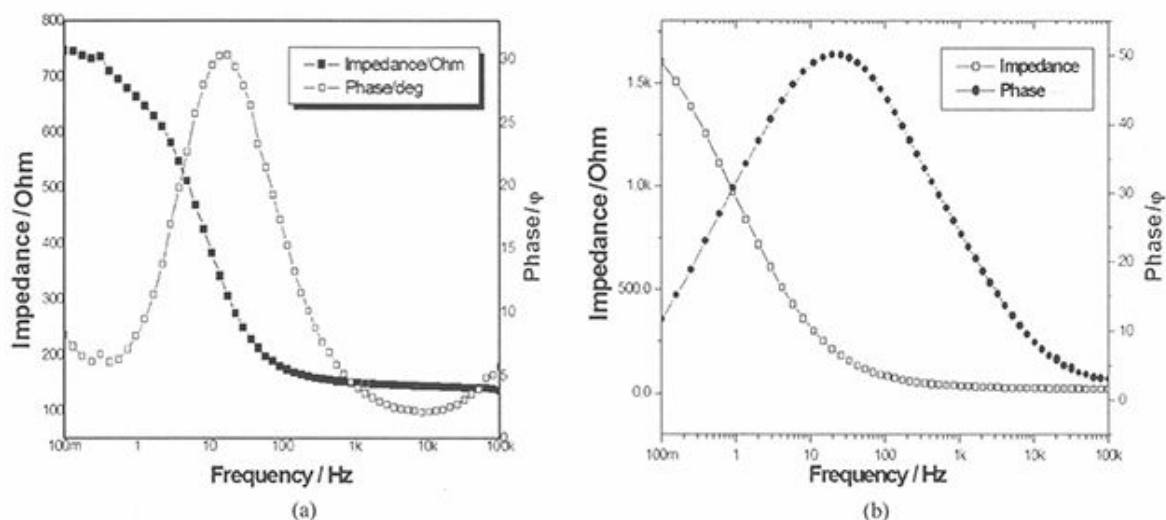


Fig. 9 EIS spectra of (a) N1 and (b) N2 in solution of  $H_2SO_4$  0.05 M at  $-0.476$  V.

OCP decreased from positive value to negative value, the anions doped in PPy released and PPy changed from the oxidized state to the reduced state and the impedance increased. Additionally, when oxalate anion or molybdate anion released from PPy, they reacted with iron cations to form insoluble compound on the steel surface. The impedance of N1 increased from 130  $\Omega$  (before measurement of OCP, at 0.43V) to 500  $\Omega$  (after measurement of OCP, at -0.476V). The impedance of N2 increased from 200  $\Omega$  (before measurement of OCP, at 0.33V) to 1.7 k $\Omega$  (after measurement of OCP, at -0.476V).

The results of EIS measurements show that N2 could prevent steel CT3 from corrosion better than N1. In other words, the presence of molybdate in the PPy film was the key of "self-healing" polypyrrole film.

#### 4. Conclusions

Molybdate doped-polypyrrole (PPy) was prepared by electrochemical polymerization successfully on steel CT3. The cauliflower structure could be seen on the polymer film by scanning electron microscopy (SEM). The chemical structure of polymer was characterized by Raman spectra. During electropolymerisation, molybdate anion should be doped in polypyrrole, although the positive polarisation was applied on the iron electrode. The thermal analysis (TGA) showed that polypyrrole was stable up to 500 °C. The polymer film acted as a barrier layer and molybdate played an important role of corrosion protection of metal. Molybdate dopant in the polymer film was the key element of "self-healing" action.

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