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**A comparative study on the corrosion protection of Nd-Fe-B magnetic alloys using polypyrrolic or poly {*trans*-[RuCl<sub>2</sub>(vpy)<sub>4</sub>] } coatings**

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**Abstract**

The present work reports a comparison between the corrosion behaviour of Nd-Fe-B magnets coated with polypyrrolic and poly {*trans*-[RuCl<sub>2</sub>(vpy)<sub>4</sub>] } films. These films were electro polymerised on the surface of magnet samples by Cyclic Voltammetry and Galvanostatic techniques. Electrochemical Impedance Spectroscopy (EIS) and Scanning Electron Microscopy (SEM) were carried out to characterise the modified surface. EIS results showed that Nd-Fe-B magnets coated with polypyrrolic films depicted charge transfer resistance twice that of those coated with poly {*trans*-[RuCl<sub>2</sub>(vpy)<sub>4</sub>] } films in Na<sub>2</sub>SO<sub>4</sub> aqueous solution. The influence of the electrochemical parameters on the corrosion properties of the films is also discussed.

**Introduction**

Nd-Fe-B magnets present superb properties compared to several other commercially available magnets. Nonetheless, due to their low thermal stability and corrosion resistance, the applications for those materials are limited to non-corrosive environments [1]. Several research centres both from universities and industries have tried to increase the Curie Temperature (T<sub>c</sub>) and to improve the corrosion resistance of Nd-Fe-B magnets [2,3]. Several approaches have been investigated to improve the corrosion resistance and reduce the cost of the material. As part of a long range project to protect materials against corrosion by electrochemically coating metallic surfaces, we initiated a research work coating Nd-Fe-B magnets with electroactive pyrrol or poly-{*trans*-[RuCl<sub>2</sub>(vpy)<sub>4</sub>] } films.

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Electrocoating using pyrrole has been the focus of different research works [4,5] whereas the use of poly- $\{trans-[RuCl_2(vpy)_4]\}$  began with the work of Franco and col. [6]. Further studies carried out by our research team confirmed the high performance of the  $trans-[RuCl_2(vpy)_4]$  complex monomer as a starting material for coating several alloys and steels [7]. In view of the promising success of the approach in preventing corrosion by electrocoating metal surfaces, we reported recent results on the electroreductive polymerisation and corrosion resistance of  $trans-[RuCl_2(vpy)_4]$  on Nd-Fe-B magnets in  $Na_2SO_4$  solution [8-9]. In order to test new monomers a new set of experiments was carried out to analyse the influence of the electrochemical parameters on the corrosion properties of polypyrrole films and the corresponding corrosion protection behaviour. A comparison using results from both coatings is also established herein, making it possible to rank the corrosive protection properties of both polypyrrole and  $trans-[RuCl_2(vpy)_4]$  films.

## Experimental procedure

*Solutions and chemicals:* The synthesis of  $\{trans-[RuCl_2(vpy)_4]\}$  has been described elsewhere [6]. Commercially available chemicals and solvents of an analytical grade were used in the synthesis of the monomer and for electrocoating. The main chemicals employed were 4-vinyl pyridine (Aldrich), trihydrated ruthenium chloride (Jonhson-Matthey) and solvents. Chromatographic grade solvents were employed in the electrochemical tests. The pyrrole monomer was previously distilled under vacuum.

*Samples:* Nd-Fe-B magnets produced by Crucible-USA were polished using 400-grit emery paper and rinsed in tetrachloroethylene.

*Electrocoating:* The magnets were Galvanostatically coated with polypyrrole films, applying a current density of  $1.5mA/cm^2$  during 1800 seconds in oxalic acid solution ( $H_2C_2O_4$ )  $0.1mol.dm^{-3}$  and pH 2. Poly $\{trans-[RuCl_2(vpy)_4]\}$  films were produced by cyclic voltammetric scanning at 30 cycles, between 0.2 and  $-2.75V$  vs. SCE at  $50mV.s^{-1}$ . The concentration of the monomer in a solution of acetonitrile / dichloromethane (4:1) was  $5mmol.dm^{-3}$ . A  $0.1mol.dm^{-3}$  tetrabutylammonium hexafluorophosphate solution was used as electrolyte [10].

*Electrochemical Impedance Spectroscopy (EIS):* EIS was carried out in a model SI 1255 Solartron equipment and a model 273 A Potentiostat/Galvanostat controlled by a model 398 electrochemical impedance program. EIS measurements were carried out at an open circuit potential (OCP) at room temperature, in  $0.5mol.dm^{-3}Na_2SO_4$  and  $0.5mol.dm^{-3}NaCl$  solutions using a "flat cell". The analysed frequency ranged from 100KHz to 10mHz.

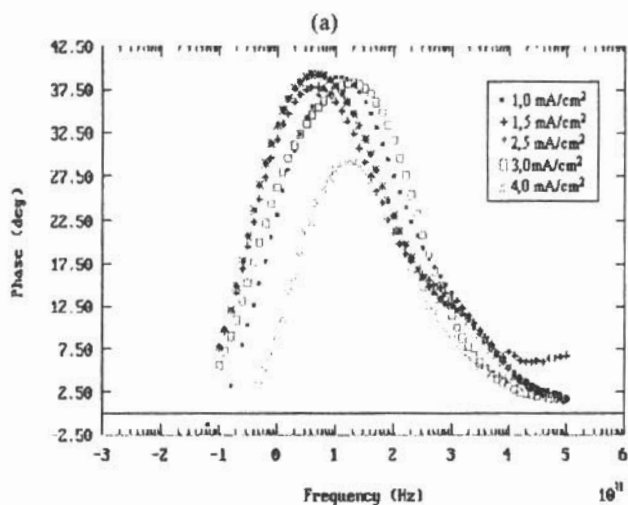
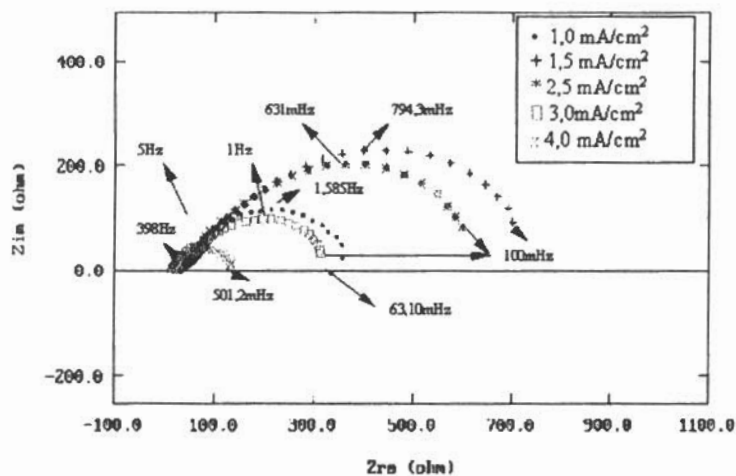
Studies on the electropolymerisation of pyrrole at several electrochemical parameters were performed in an oxalic acid solution  $0.5M$  at pH 2 during 1800s, varying the current density from 1 to  $4mA/cm^2$ . The formed coatings were analysed in a  $0.5MNa_2SO_4$  solution by EIS, LPR (Linear Resistance Polarisation) and SEM.

## Results and Discussion

Electrocoating with polypyrrol: a considerable amount of oxalate was formed on the metallic surfaces upon electropolymerisation with polypyrrole in oxalic acid solution. The corrosion protection resulted from a combined action of the polypyrrol film and oxalate [5]. Morphological studies have shown that no substantial changes occur as the current density changes during the electrocoating process. On the other hand, as one can see from Figure 1 and Table 1, the electropolymerisation current density considerably affects the corrosion resistance of the magnets. The optimum value for the current density during the electropolymerisation of polypyrrole was determined to be  $1.5 \text{ mA/cm}^2$ .

*EIS as a function of immersion time:* Optimum parameters were established and used to test the behaviour of polypyrrole coatings in  $\text{Na}_2\text{SO}_4$  solution as a function of time using EIS. Data were fitted to an equivalent circuit shown in Figure 2(a), yielding an excellent match. After 4 hours immersed, a third time constant appeared and could be associated to a corrosion process. The equivalent circuit fit and corresponding figures are shown in Figure 2(b) and Table 2. The EIS results also indicated that the properties of polypyrrole films remained unchanged during the entire immersion period taken for the present study. However, the circuit element associated to the oxalate layer depicted considerable changes especially regarding its capacitive component. The corrosion process observed after 4 hours of immersion was probably due to the evolution of pores in the oxalate layer. Linear Polarisation Resistance estimates are listed in Table 3. The coatings formed using an electropolymerisation current density of  $1.5 \text{ mA/cm}^2$  improved the protection offered to the magnet surface by a factor of 4 as compared to non-coated magnet surfaces.

*Polypyrrole vs. poly-{trans-[RuCl<sub>2</sub>(vpy)<sub>4</sub>]} coatings:* Recent results on electrocoating Nd-Fe-B with poly-{trans-[RuCl<sub>2</sub>(vpy)<sub>4</sub>]} were described in recent literature reports [8-9]. However, the coatings were not efficient enough to compete with the ones commercially available. In view of this fact, polypyrrole films have been chosen as an alternative [11-12]. Figure 3 illustrates the morphology of poly-{trans-[RuCl<sub>2</sub>(vpy)<sub>4</sub>]} (figure 3a) and polypyrrole (figure 3b) coatings, both electropolymerised onto the surface of Nd-Fe-B magnets. From figure 3 one can easily observe the roughness of the surface of poly-{trans-[RuCl<sub>2</sub>(vpy)<sub>4</sub>]} (figure 3a). Figure 4 compares the EIS results of magnets coated with polypyrrole and poly-{trans-[RuCl<sub>2</sub>(vpy)<sub>4</sub>]} in  $\text{Na}_2\text{SO}_4$  solution.



(b)

Figure 1: EIS (a) Nyquist and (b) Phase diagram of Nd-Fe-B magnets coated with polypyrrole applying different polymerisation current densities. Frequency range: 100KHz to 10mHz at  $E_{eq}$  in  $0.5 \text{ mol.dm}^{-3} \text{ Na}_2\text{SO}_4$  solution.

Table 1: Values determined from EIS data for the elements of equivalent circuits corresponding to polypyrrole films from different polymerisation current densities.

J(mA. cm <sup>-2</sup> )	C <sub>PPY</sub> (μF.cm <sup>-2</sup> )	R <sub>PPY</sub> (Ω.cm <sup>2</sup> )	C <sub>OX</sub> (μF.cm <sup>-2</sup> )	R <sub>OX</sub> (Ω.cm <sup>2</sup> )	C <sub>DL</sub> (μF.cm <sup>-2</sup> )	R <sub>CT</sub> (Ω.cm <sup>2</sup> )
1.0	520	40.8	78	231.5	160	121.0
1.5	193	46.0	309	729.5	-	-
2.5	120	23.6	460	625.0	160	70.41
3.0	112	1.66	420	201.7	790	112.7
4.0	130	6.35	230	43.15	380	69.36

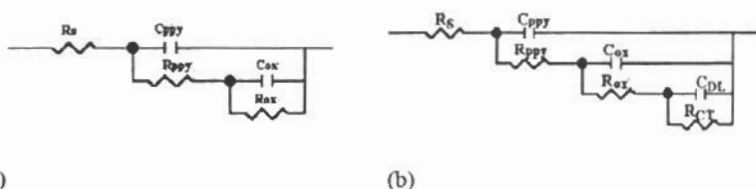


Figure 2: Equivalent circuit proposed for the EIS data obtained from different immersion periods: (a) Up to 3h, and (b) after 3h immersed in Na<sub>2</sub>SO<sub>4</sub>.

Table 2: Values obtained from EIS data for the elements of equivalent circuits corresponding to polypyrrole films electropolymerised under 1.5mA.cm<sup>-2</sup>

Immersion time (hours)	C <sub>PPY</sub> (μF)	R <sub>PPY</sub> (Ω)	C <sub>OX</sub> (μF)	R <sub>OX</sub> (Ω)	C <sub>DL</sub> (mF)	R <sub>CT</sub> (Ω)
1.5	60	35	620	1600	--	--
3.0	36	37	707	1540	--	--
4.0	45	33	780	1060	36	95
5.0	64	33	870	1037	20	50

The phase diagram shown in figure 4b clearly shows the presence of two time constants for films coated with polypyrrole whereas only one time constant was observed for poly- $\{trans\text{-}[\text{RuCl}_2(\text{vpy})_4]\}$ . The high-frequency time constant was associated to the polypyrrole film itself whereas the low frequency one was associated to the magnetic-corrosive solution resistance interface (Charge Transfer Resistance).

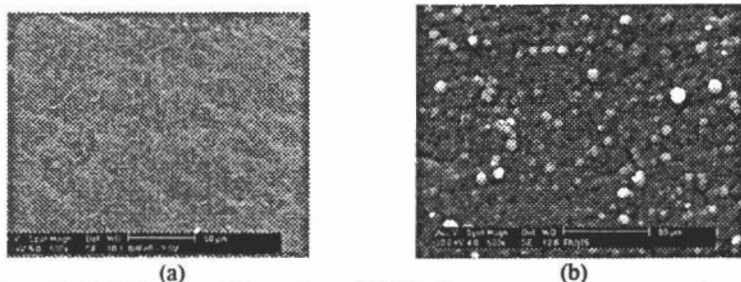


Figure 3: SEM image of the surface of Nd-Fe-B magnets electrocoated with (a) poly- $\{trans-[RuCl_2(vpy)_4]\}$ [9]; and (b) polypyrrole [present study]. Magnification 500 X; Acceleration voltage:20K V.

The results showed that the resistance associated to the relaxation process at low frequencies was about twice as great for magnets coated with polypyrrole (1600 ohms) as compared to those coated with poly- $\{trans-[RuCl_2(vpy)_4]\}$  (850 ohms). An equivalent circuit (Figure 5) could be proposed using the computational program ZPlot/ZView based on the EIS data shown in Figure 4. The values corresponding to the equivalent circuit components are summarised in table 3. EIS experiments performed in NaCl solution (figure 4) revealed that identical processes occurred for both polypyrrole and poly- $\{trans-[RuCl_2(vpy)_4]\}$  films with the presence of only one time constant at low-frequencies due to the corrosive process. Contrary to what was expected for the behaviour of films immersed in sulphate ion solution, the polypyrrole film offered less permeation resistance to chloride ions and consequently a time constant was not observed at high-frequencies for the polypyrrole film.

Table 3: Values obtained for the different elements of equivalent circuit from EIS data.

Corrosive medium	Coating	$C_{film}(\mu F.cm^{-2})$	$R_{film}(\Omega.cm^2)$	$C_{DL}(\mu F.cm^{-2})$	$R_{CT}(\Omega.cm^2)$
Na <sub>2</sub> SO <sub>4</sub>	PPY	58.2	34.5	642.8	1595
	VPY	--	--	888.0	868
NaCl.	PPY	--	--	771	275
	VPY	--	--	5525	254

The charge transfer resistance of samples coated with poly- $\{trans-[RuCl_2(vpy)_4]\}$  was about 30% lower than the that obtained in the presence of sulphate ions. For samples coated with polypyrrole, the charge transfer resistance in NaCl medium was about 6 times lower than that observed in Na<sub>2</sub>SO<sub>4</sub>.



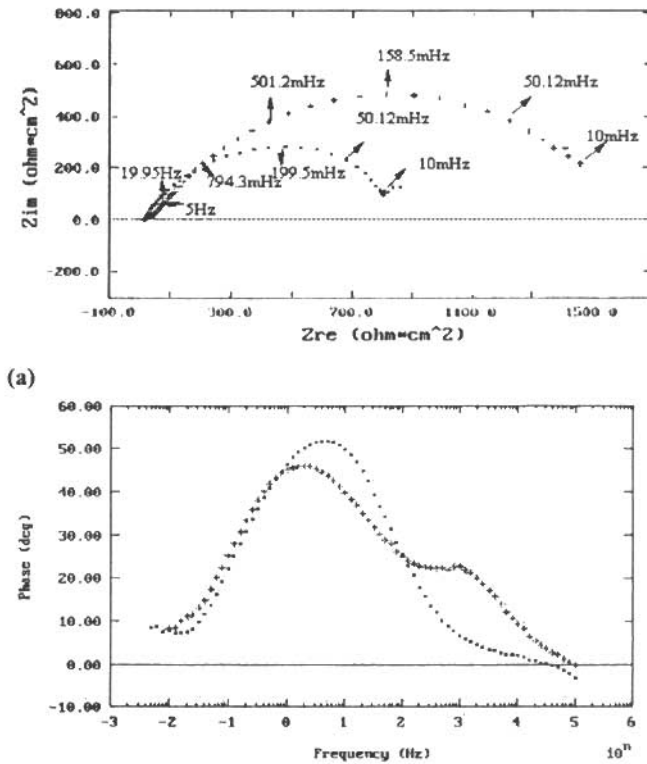


Figure 4: EIS (a) Nyquist and (b) Phase diagram of Nd-Fe-B magnets coated with polypyrrole (++) and (b) poly- $\{trans-[RuCl_2(vpy)_4]\}$  (□ □). Frequency range: 100kHz to 10mHz at  $E_{eq}$  in  $0.5 \text{ mol.dm}^{-3} \text{ Na}_2\text{SO}_4$  solution.

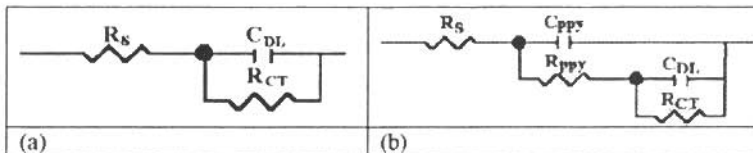


Figure 5: Proposed Equivalent Circuits for magnet coated with (a) poly- $\{trans-[RuCl_2(vpy)_4]\}$  and (b) polypyrrole.

This peculiar behaviour was probably related to the relative size of the ions. Since  $Cl^-$  ions are smaller than  $SO_4^{2-}$ , they diffuse easily through the film. As one

can observe from table 3, in NaCl medium both coatings failed to protect the magnet. Values of  $R_{CT}$  in the presence of chloride ions were about  $250 \Omega \cdot \text{cm}^2$  [8-9].

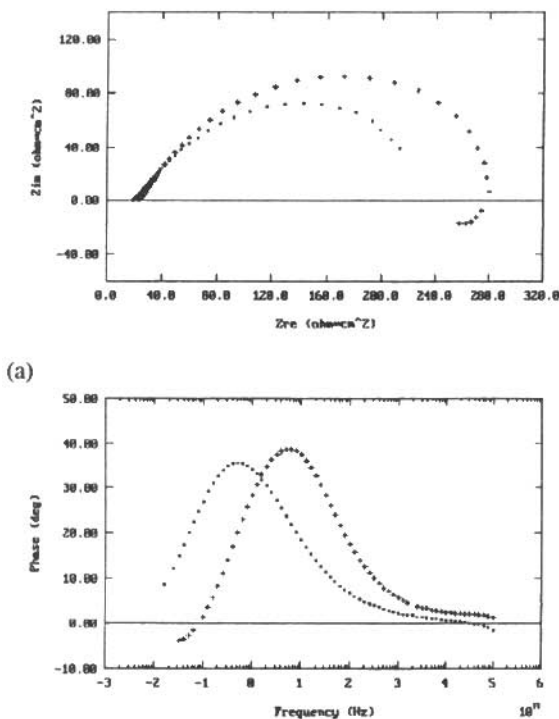


Figure 4: EIS (a) Nyquist and (b) Phase diagram of Nd-Fe-B magnets coated with polypyrrole (++) and poly- $\{trans-[RuCl_2(vpy)_4]\}$  (□ □). Frequency range: 100KHz to 10mHz at  $E_{eq}$  in  $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ Na}_2\text{SO}_4$  solution.

## Conclusions

Polypyrrole films are highly effective corrosion barriers to Nd-Fe-B magnets improving the corrosion protection by a factor of 4 as compared to poly- $\{trans-[RuCl_2(vpy)_4]\}$  coatings. A barrier was formed by a combined action of an oxalate layer and polypyrrole at the optimum electropolymerisation current density of  $1.5 \text{ mA/cm}^2$ . In sulphate solution, polypyrrole films protected the surface of the magnetic alloy twice as better as the other coating tested. In the presence of chloride, both coatings showed identical corrosion protection



behaviours offering fairly good results. EIS proved to be a good technique to evaluate the performance of coated surfaces immersed in corrosive solutions.

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