

CORROSION RESISTANCE OF Nd-Fe-B MAGNETS COATED WITH POLYPYRROLE FILMS

M.C.E. Bandeira¹, F. D. Prochnow², I. Costa³, C.V. Franco²

¹ Universidade Federal do Mato Grosso do Sul - UFMS
Depto. de Química, Av. Filinto Müller, 1555, Campus Universitário
Cx Postal 549 - CEP: 79070-900 Campo Grande-MS, Brasil
e-mail: merlin@nin.ufms.br

² Universidade Federal de Santa Catarina UFSC-Campus Trindade, LEC,
Depto. de Química-CFM, 88040-900, Florianópolis-SC, Brasil

³ Instituto de Pesquisas Energeticas e Nucleares, IPEN/CNEN-SP
Caixa Postal 11049, CEP 05422-970, São Paulo-SP

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ABSTRACT

Nd-Fe-B magnets present outstanding magnetic properties. However, due to their low corrosion resistance, their applications are limited to non-corrosive environments. Nowadays, significant efforts are underway to increase the corrosion resistance of these materials, through the use of coatings. Herein are presented the results of a study on the corrosion resistance of Nd-Fe-B magnets coated with polypyrrole (PPY). The electrochemical behavior of coated and uncoated magnets has been studied by Electrochemical Impedance spectroscopy (EIS) in synthetic saliva. The results were compared to previous investigations, which were carried out under similar conditions, in Na₂SO₄ and NaCl solutions. In sulphate solution, the corrosion resistance of the PPY-coated magnet was 3 times larger (1600 Ω.cm²) than that of uncoated magnet (500 Ω.cm²). In NaCl solution, however, the corrosion resistance of coated and uncoated magnets were very similar (250 Ω.cm²). In synthetic saliva, both the uncoated and coated magnets presented good corrosion performance (1940 Ω.cm²). Such behavior can be attributed to the phosphate ions in saliva, which play a role as corrosion inhibitor, producing phosphating, at least partially, of the magnet surface. The PPY-coated magnets presented a strong diffusional control from moderate to low frequencies, caused by the polypyrrole film. The thicker PPY film increased the corrosion resistance of the magnet in synthetic saliva.

INTRODUCTION

The great interest in Nd-Fe-B alloys has encouraged many research groups around the world to investigate their properties and ways of increase these properties through compositional changes. The main aim of these studies has been to increase the Curie temperature (T_c) and corrosion resistance of these materials. The low corrosion resistance of these alloys has been attributed due to their complex microstructure composed of many phases where the main ferromagnetic phase present is the φ fase, Nd₂Fe₁₄B [1]. There is substantial evidence that the Nd-Fe-B magnets produced by powder metallurgy and sintered present intergranular corrosion, where the Nd rich phase located at the grain boundaries of the φ phase, corrodes preferentially, and eventually, detachment of the φ grains occurs [1,2]. Nowadays, the efforts are focused on improving the magnetic properties of these materials and also on increasing

the corrosion resistance by coatings [2-5]. In previous studies, the use polypyrrolic coating as a corrosion protection of Nd-Fe-B magnets surface has been evaluated and also the optimum deposition conditions for increased corrosion resistance were determined [6]. Other works investigated the corrosion protection provided by films of poly- $\{trans-[RuCl_2(vpy)_4]\}_n$ [7-9], and it was found that the Ruthenium centres in the film act as sacrifice anodes, temporarily protecting the magnets [10]. In a comparative study on the corrosion performance of Nd-Fe-B magnets coated with poly- $\{trans-[RuCl_2(vpy)_4]\}_n$ and PPY films [11] the magnets coated with this last type of film showed a corrosion resistance twice higher than that of the magnets coated with poly- $\{trans-[RuCl_2(vpy)_4]\}_n$. Other applications of Nd-Fe-B magnets are for orthodontic devices [12, 13] and dental prostheses [14]. However, due to their low corrosion resistance, there is a potential risk of toxic substances release to the human body, and also a decrease in the working performance of the device. Cytotoxicity tests carried out in a cell culture medium with the magnet showed that if properly encapsulated in a corrosion resistant casing, these magnets could be used as biomaterials for dental applications [14]. In this study, the corrosion resistance of Nd-Fe-B magnets, either coated with PPY film or uncoated, was investigated in synthetic saliva and Na_2SO_4 and $NaCl$ solutions. The influence of the PPY film on the corrosion resistance of the magnet was also investigated.

MATERIALS AND METHODS

Samples: Nd-Fe-B magnets provided by Crucible–U.S.A were used in this study. The surfaces of the magnet samples were prepared by grinding with SiC paper from 200 to 1000 mesh. A glycerin/ethanol solution (1:1) was used as cooling fluid during grinding.

Electrochemical cell: Electropolymerization was carried out in an electrochemical cell using a three electrode arrangement composed of working electrode (magnet), counter-electrode (Pt wire) and reference electrode (saturated calomel electrode, SCE).

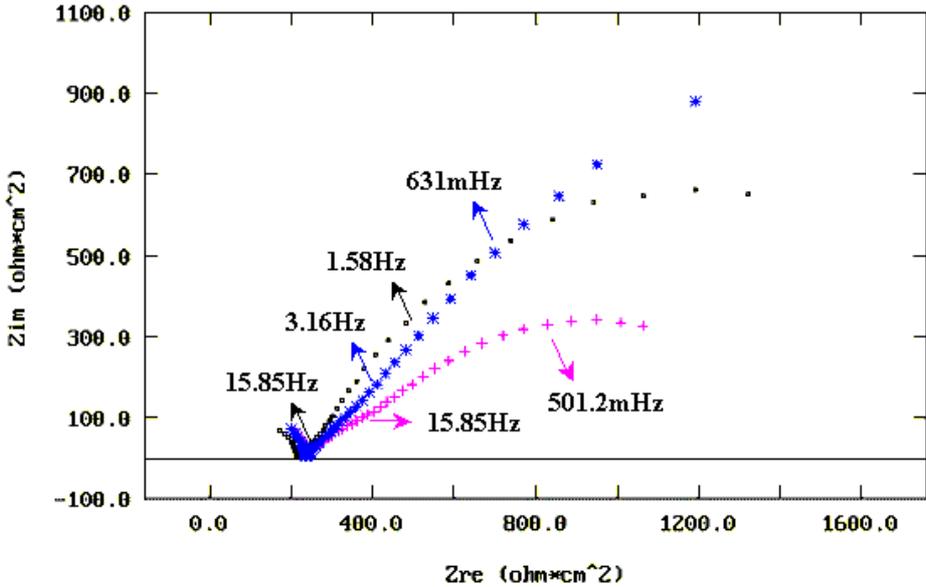
Electropolymerization: Chemicals and solvents of an analytical grade were used in the electrochemical studies. An aqueous solution of oxalic acid ($H_2C_2O_4$) $0.1\text{mol}\cdot\text{dm}^{-3}$, pH 2, was used as support electrolyte. The pH of the electrolyte was adjusted with concentrated NaOH. The pyrrole monomer was vacuum distilled and then stored at low temperature and in a dark container. The monomer concentration was $0.1\text{mol}\cdot\text{dm}^{-3}$ and the total volume used (electrolyte + monomer) was 40 mL. The polymeric films tested in this study were obtained via electrochemical polarization, by galvanostatic deposition ($t = 1800\text{s}$ and $i = 1.5\text{mA}/\text{cm}^2$ or $4.0\text{mA}/\text{cm}^2$), using a 273A PAR Potenciostat/Galvanostat.

Electrochemical Impedance Spectroscopy (EIS): EIS measurements were carried out with the Nd-Fe-B magnets, either coated with PPY film or uncoated, in $0.5\text{mol}\text{dm}^{-3}$ $NaCl$, $0.5\text{mol}\text{dm}^{-3}$ Na_2SO_4 and synthetic saliva solutions. The data were obtained under potentiostatic control at the corrosion potential using a SI 1255 Solartron Frequency Response Analyzer, coupled to a 273A PAR Potenciostat/Galvanostat.

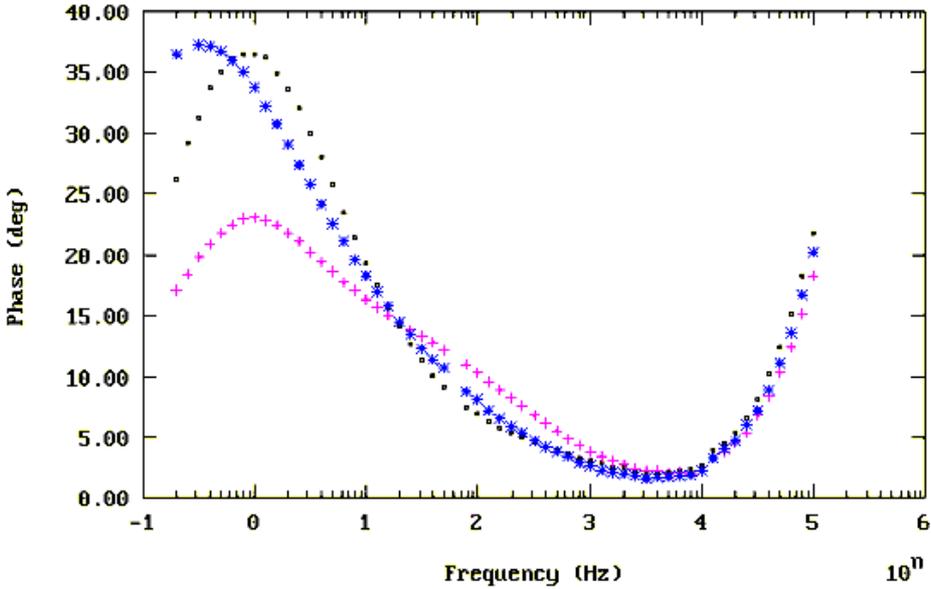
RESULTS AND DISCUSSION

Figure 1 shows the Nyquist and Bode diagrams for Nd-Fe-B magnets, either uncoated or coated with PPY films, in synthetic saliva. The PPY films were obtained by polymerization either under a current density of $1.5\text{mA}/\text{cm}^2$ or $4.0\text{mA}/\text{cm}^2$. Both films were electrochemically reduced after polymerization. The Nyquist diagram for the uncoated magnet shows an incomplete semicircle at high frequencies (HF), whereas at low (LF) and

medium frequencies (MF) a time constant is clearly seen on the Bode diagram, Fig. 1b. The time constant at LF to MF is likely related to a diffusion process, whereas at HF the EIS data are possibly due to charge transfer processes, mainly at the more reactive areas of the magnet tested, which are mostly the porosities of the magnet [15]. The semicircle diameter at HF (approximately $200 \Omega \cdot \text{cm}^2$) indicates a moderately high resistance for the processes related to this time constant. This result indicated that the test medium (synthetic saliva) is not highly corrosive to the magnet tested, and the phosphate layer, eventually formed in this environment, could hinder the charge transfer phenomena associated to it.



(a)



(b)

Figure 1: Nyquist (a) and Bode (b) diagrams for uncoated (\blacksquare), and PPY coated under 1.5 mA/cm^2 ($Q_t = 2.7 \text{ C/cm}^2$) and (+) PPY coated under 4.0 mA/cm^2 ($Q_t = 7.2 \text{ C/cm}^2$)(*) Nd-Fe-B magnets in synthetic saliva solution.

The second semicircle at lower frequencies, also incomplete in the frequency range tested, is probably due to faradic processes. The high values of this semicircle diameter (order of $10^3 \Omega \cdot \text{cm}^2$) also suggest a high resistance of the Nd-Fe-B magnet in synthetic saliva, despite of the usually low corrosion resistance of these types of magnets in mildly aggressive environments. It is most likely that the presence of phosphate ions in this medium lead to the formation of a phosphate layer on the magnet, increasing its corrosion resistance.

A fitting procedure of the experimental data to some equivalent circuits was carried out and the equivalent circuit that produced the best adjustment is one composed by a resistor in series with a diffusional component, both in series with a resistor (R2), and this last component in parallel with a capacitor (C1), associated to a second time constant. The diffusional component at HF, with Warburg behavior (W_{s1}), typical of porous materials, is due to the porosities of the magnet used in this investigation [16].

The EIS results for porous materials depend on the ac signal penetration. When the signal penetrates through the whole pore, the pore behaves as a flat electrode and the phase angle approaches -90 degrees. On the other hand, when the signal does not penetrate the fully length of the pore, the ac signal detects only partially the pore and the phase angle approximates those typical of porous material, i.e., -45 degrees. Beside, a mixed behavior typical of porous and planar electrodes might also occur. This last type of behavior was found by Aoki et al [17] for Aluminium electrodes exposed to citric acid solution and it was caused by the nature of the Aluminium oxide that is in fact a double layer oxide composed by an inner barrier layer and an external and porous layer.

The semicircle diameter at LF for the magnet in synthetic saliva was approximately $1940 \Omega \cdot \text{cm}^2$, showing that in this medium the magnet is significantly more resistant comparatively to the other test solutions used, such as NaCl ($250 \Omega \cdot \text{cm}^2$) and Na_2SO_4 ($500 \Omega \cdot \text{cm}^2$) [11]. As mentioned previously it is most likely due to the corrosion inhibiting character of the synthetic saliva, that can promote phosphating of the magnet and increase its corrosion resistance [18].

For the PPY coated magnet using a current density of 1.5 mA/cm^2 , the semicircle at LF shows a lower diameter and bends towards the real axis. The presence of an incipient and incomplete semicircle at MF is also indicated. This interaction of the process associated to this time constant with that at lower frequencies is the probable reason for this result. This process is indicated by a shoulder in the Bode diagram at frequencies around 100 Hz. The phase angle peak at LF is lower than that obtained for the uncoated magnet, probably due to the conducting character of the polymeric film used (PPY), leading to the decrease in the semicircle diameter at LF. For thin films, the conducting character of the film must prevail over its barrier character. It is also possible that an oxalate layer has been formed together with the PPY film during polymerization [18-20]. However, it was not possible to separate the EIS results of those two layers, the oxalate and the PPY film. The results presented in this work are in conformity with those proposed by H. Nguyen Thi Le et al [20] for a PPY film deposited on iron sample and tested by EIS in a 3% (wt%) NaCl solution.

The Nyquist diagram for the PPY coated magnet using a current density of 4.0 mA/cm^2 shows the increase of impedance. The equivalent Bode diagram shows the displacement of the phase angle peak to lower frequencies and the increase in the phase angle suggesting an increase in the capacitive behavior, likely due to hindered faradic processes. This is caused mainly by the differences in thickness and morphology of the PPY films formed at the two current densities tested. The charge involved in the polymerization of the film formed with a current density of 4.0 mA/cm^2 was 2.5 times higher than that for film formed at 1.5 mA/cm^2 , and consequently, the first ones have increased thickness. The film thicknesses were estimated based on the total charge of polymerization [19, 20], and values of 2.5 and 12 μm were obtained for films grown at 1.5 and 4.0 mA/cm^2 , respectively.

In order to evaluate the corrosion resistance of the PPY coated magnets, it was assumed that in these magnets the corrosion resistance was provided by the PPY film and it was dependent on the film thickness and morphology. The film obtained at $4.0\text{mA}/\text{cm}^2$ was thicker and more compact than that obtained at $1.5\text{mA}/\text{cm}^2$. Accordingly, the electrolyte diffusion through this last film is more difficult and, consequently, the corrosion protection afforded by this film is better.

The morphologies of the PPY films obtained by electropolymerization using the current densities of $1.5\text{mA}/\text{cm}^2$ and $4.0\text{mA}/\text{cm}^2$ were evaluated by Scanning Electron Microscopy (SEM) and these are shown in Figure 2. The SEM micrographies of the PPY films indicate similar morphologies for both films and small changes in their porosities. The SEM micrograph of the PPY film obtained at $4.0\text{mA}/\text{cm}^2$ after immersion test in syntethic saliva shows a more compact film than that obtained at $1.5\text{mA}/\text{cm}^2$, as Figure 2 exemplifies.

The PPY coated magnets did not show corrosion during the period of tests in syntethic saliva (approximately 2h of immersion). According to the equivalent circuit proposed to represent the interfacial phenomena, no corrosion process was identified during the corrosion test period.

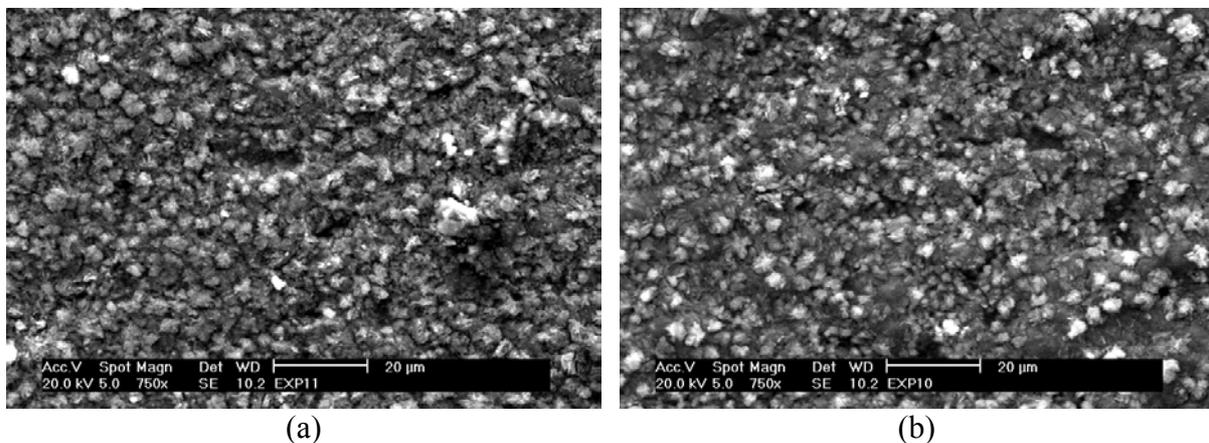


Figure 2: SEM micrographies of polypyrrole (PPY) film on Nd-Fe-B magnet (a) PPY obtained at $1.5\text{mA}/\text{cm}^2$ (total charge = $2.7\text{ C}/\text{cm}^2$) and (b) PPY obtained at $4.0\text{mA}/\text{cm}^2$ (total charge= $7.2\text{ C}/\text{cm}^2$).

The EIS results for PPY coated magnets ($Q_t = 2.7\text{ C}/\text{cm}^2$) in Na_2SO_4 solution showed a different behavior than in syntethic saliva. In the presence of SO_4^- ions the estimated resistance of the magnets was approximately $1600\Omega\cdot\text{cm}^2$ [11], whereas in the chloride solution the PPY film had no significant effect on the corrosion resistance of the magnet and it was nearly $250\Omega\cdot\text{cm}^2$, that is, of the same order of the uncoated magnet [11]. The syntethic saliva is a much less aggressive solution than $0.5\text{M Na}_2\text{SO}_4$ and 0.5M NaCl to Nd-Fe-B magnets. It contains a low concentration of chloride ions (0.02M) and phosphate ions, these latter acting as corrosion inhibitors.

CONCLUSIONS

The polypyrrole film was effective for corrosion protection of Nd-Fe-B magnets in syntethic saliva. This film also offered fairly good corrosion protection to this type of magnet in sodium sulphate solution, but had no effect in sodium chloride medium

The uncoated Nd-Fe-B magnet showed good corrosion resistance in syntethic saliva due to the corrosion inhibiting character of this solution, leading to the formation of a phosphate layer on its surface.

The polypyrrole film with thickness of 12 μm increased the impedance of the magnet in syntethic saliva, increasing its corrosion resistance in this medium.

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