

Corrosion Characterization of Electrodeposited Organometallic Films on Nd-Fe-B Permanent Magnets

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Abstract: The coating of Nd-Fe-B magnets with electrodeposited films from monomers *trans*-[RuCl₂(vpy)₄] where vpy = 4-vinyl pyridine, in acetonitrile/diclorometane (4/1) solutions and the investigation of the corrosion resistance of magnets coated with these polymeric films have been the objectives of this study. Electrochemical impedance spectroscopy (EIS) in Na₂SO₄ and NaCl 0,5M solutions was carried out to compare the electrochemical properties of the coated and uncoated magnets. The results indicated that the polymeric film improved the corrosion resistance of permanent magnets in Na₂SO₄ solution. The complex impedance diagram showed two superimposed capacitive arcs. The capacitance value of the film was estimated to be nearly 10⁻⁴ F. Morphological characterization of the electrodeposited films was carried out by scanning electron microscopy.

INTRODUCTION

Nd-Fe-B permanent magnets were discovered in 1983 with outstanding magnetic properties. Since then, their properties have been considerably improved[1]. Due to their high energy product, applications of this material have increased in the last decade. The main applications include consumer electronics, computer peripherals, acoustics, office automation, and magnetic resonance imaging. Nevertheless, poor corrosion resistance and thermal stability are the main drawbacks for the use of Nd-Fe-B in some applications. A number of scientific and technological studies have been conducted to find alternative processes to overcome these limitations[2-4]. Alloy modifications were carried out to improve these properties but were at the expense of impairing others[5-6]. The aims of these studies were to improve the Curie temperature (T_c), and the corrosion resistance. The poor corrosion resistance of Nd-Fe-B magnets is due in part to the multiple phases present in the alloy. Intergranular corrosion probably occurs near the grain boundary regions in sintered Nd-Fe-B, causing the Nd-rich and B-rich intergranular regions to corrode preferentially, and lead to the loosening and fallout of ϕ particles (the most important ferromagnetic phase in this material)[7]. Nowadays, significant efforts are underway to increase the corrosion resistance of this material, through the use of coatings [4,8-9].

Electropolymerization from metallic complex monomers has been exhaustively studied [10-13]. Increasing interest in this technique is due to its availability and the broad range of applications at a small cost. Electrodeposition of films with incorporated redox centers constitutes an alternate method of application in electrocatalysis and corrosion protection, due to the low oxidation-state of immobilized transition metals in the polymeric matrix. Low oxidation-state metals immobilized in polymeric matrix can increase the corrosion resistance of the coated substrate acting as sacrificial anodes. Anodically electrodeposited organic coatings on steels have been reported[14]. The disadvantage of oxidative electrodeposition on active metals and alloys is the anodic dissolution of

the substrate at potentials similar to those required for the electropolymerization reactions[15-22]. To overcome this problem, researchers [23] have utilized preliminary passivation to successfully apply anodic potential during electropolymerization, without dissolution of the substrate. In our laboratory, reductive electropolymerization has been used as an alternate method of corrosion protection of active substrates such as Nd-Fe-B magnets. Our laboratory has synthesized and characterized a novel complex with a general formula *trans*-[RuCl₂(L)₄], where L = vpy = 4-vinyl pyridine, with reductive electropolymerized sites. In electroreductive processes, the films are generated on cathodic regions of the substrates, with increased stability during deposition. Recently we demonstrated the feasibility of reductive electropolymerization on inert electrodes of Pt and Pd, as well as on sintered substrates of Fe+5%Ni and Fe+10%Ni alloys and obtained good results with the L = 4-vinylpyridine ligant[9,10].

EXPERIMENTAL

Reagents and Synthesis: Commercially available reagents and analytical grade solvents were used in this investigation. RuCl₃.3H₂O (Jonhson-Matthey) and 4-vinylpyridine (Aldrich) were used without further purification. The synthesis of ruthenium blue solution and *trans*-[RuCl₂(vpy)₄] was carried out using a method described in the literature[12].

Preparation of samples: Nd-Fe-B magnets produced by Sumitomo were prepared for coating by polishing on 400 grit emery paper, followed by an ethanol wash. The exposed sample area for coating was 0.95 cm².

Electrocoating: Nd-Fe-B magnets were coated with poly-{*trans*-[RuCl₂(vpy)₄] } films, electrodeposited by cyclic voltametric scanning at 30 cycles, between 0.2 and 2.8V vs. SCE at a scan rate of 50 mV.s⁻¹. The monomer concentration was 5mM in CH₃CN/CH₂Cl₂ (4/1) and the electrolyte used was 0.1M TBAFp (tetrabutylammonium hexafluorophosphate) [24]. Electrodeposition was carried out in an electrochemical cell with one compartment at room temperature and connected to a 273A Princeton Applied Research Potentiostat/Galvanostat, interfaced with a DOS-compatible computer through a National Instrument GPIB.

Impedance Spectroscopy (EIS): EIS were carried out in a Solartron Model SI 1255 and a model 273A Potentiostat/Galvanostat controlled by an electrochemical impedance software model 398. EIS measurements were carried out at room temperature in a flat cell, in NaCl and in 0.5M Na₂SO₄ solutions at the open circuit potential (OCP). Nd-Fe-B magnets with and without the poly-{*trans*-[RuCl₂(vpy)₄] } film were studied to compare their performance. The Boukamp program EQVCRT was used to analyze the EIS results.

RESULTS

Electrochemical Impedance Spectroscopy. EIS was used to investigate the electrochemical response of Nd-Fe-B magnets coated with poly-{*trans*-[RuCl₂(vpy)₄] }, as a function of immersion time in both, 0.5 mol dm⁻³ Na₂SO₄ and 0.5 mol dm⁻³ NaCl solutions. The thickness of the film was approximately 1 μm.

Figures 1 and 2 present the Nyquist plots corresponding to tests in sulphate and chloride solutions, respectively. They show a capacitive arc at high to moderate frequencies in both electrolytes. The arc is slightly flattened, as the kinetic- and diffusion-controlled regions superimpose each other. This can be attributed to two main factors: the reduced thickness of the film and lack of homogeneity in the polymer layers [16]. At high frequencies, the processes associated with the capacitive arc are related to magnet sample/polymeric film interface. These lead to the semicircle, from which the values of film resistance (R_F), film capacitance (C_F) and solution resistance (R_S) can be estimated. Nevertheless, the interaction of the two processes, the kinetically and the

diffusion controlled ones, can introduce significant errors in the estimated values of the equivalent circuit elements proposed to describe this phenomenon.

The equivalent circuit models obtained from the fit of these EIS plots were quite complex, and the best fit included two CPEs. At high frequencies, the CPE can be associated to R_S connected in series with a parallel combination of a capacitance C_F and a resistance R_F , where the last two elements reflect the properties of the polymer, as described by Lyons [25]. At moderate and low frequencies (lower limit 0.01 Hz), the CPE may express the polymeric film/solution interface, from which the main circuit element is related to the corrosion process described by the charge transfer resistance (R_{CT}), connected in parallel with a double layer capacitance (C_{DL}). In order to fit the impedance, the following equivalent circuit was performed: (RQ) (RQ) R, where Q=CPE.

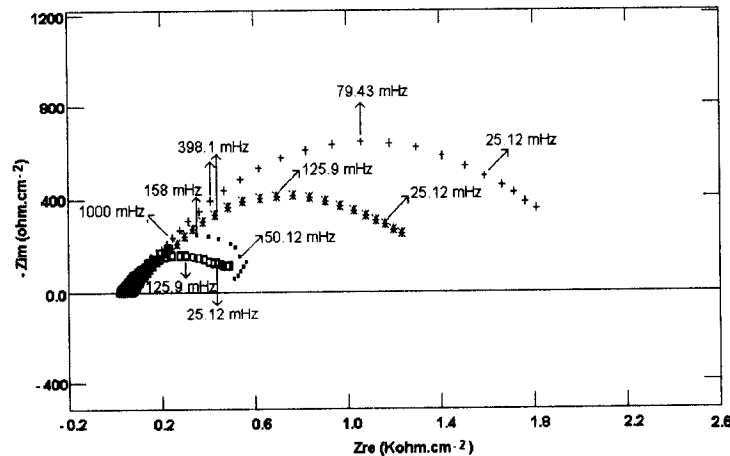


Figure 1 : Nyquist diagrams of poly- $\{trans-[RuCl_2(vpy)_4]\}$ coated Nd-Fe-B magnets _ 10min (after OCP stabilization); + 2h; * 4h of immersion in 0.5M Na_2SO_4 solution at OCP. □ uncoated Nd-Fe-B magnets. Frequency range: 100kHz-10mHz.

The above proposed circuit seemed most adequate to fit the data produced in all the situations, that is, coated and uncoated Nd-Fe-B magnets, in NaCl and Na_2SO_4 electrolytes. The poly- $\{trans-[RuCl_2(vpy)_4]\}$ coated Nd-Fe-B magnet tested in Na_2SO_4 solution produced a maximum value of R_{CT} (ca. $2.5\text{ k}\Omega\cdot\text{cm}^2$) after 2 hours of immersion. After 4 hours, R_{CT} decreased to ca. $1.4\text{ k}\Omega\cdot\text{cm}^2$, and after 6 hours, corrosion products were visible on the surface. The maximum value of R_{CT} may have been due to the formation of a passive oxide layer [18], which reduces the rate of charge transfer between the metal and the polymer film. This oxide layer fails quickly, due to its low stability, as the Nd-Fe-B magnet is very active.

Figure 1 also shows the impedance diagram corresponding to the uncoated Nd-Fe-B magnet. The R_{CT} of the coated magnet after 2 hours in the sulfate solution (ca. $2.5\text{ k}\Omega\cdot\text{cm}^2$) was approximately 4 times higher than that of the uncoated magnet (ca. $0.6\text{ k}\Omega\cdot\text{cm}^2$) in the same solution. The double layer capacitance corresponding to the coated (2 hours of immersion) and the uncoated magnet, were around 930 and $2200\text{ }\mu\text{F}\cdot\text{cm}^2$, respectively. These results show that the electrodeposited film provides temporary protection to the substrate. The protective characteristics of the film however decreased with immersion time, which could be attributed to the permeation of the thin film by the aggressive species in the electrolyte.

The solution resistance (R_S) was ca. $15\text{ }\Omega\cdot\text{cm}^2$ in Na_2SO_4 and NaCl solutions, in the electrochemical impedance test of uncoated Nd-Fe-B magnets. The R_S was higher in both solutions, NaCl (18

$\Omega.\text{cm}^2$) and Na_2SO_4 ($44 \Omega.\text{cm}^2$), when the magnet was tested after coating. This behavior can be rationalized in terms of the electronic resistance of the film (electron transport between the redox centers $\text{Ru}^{2+/3+}$) which is in series with R_s , producing the ohmic drop.

Similar EIS immersion experiments were carried out in 0.5 mol dm^{-3} NaCl solution (Fig. 2). No significant differences were found in the values of the circuit elements for the coated and the uncoated magnets in this solution. This result indicates that the polymer film formed on the magnet did not protect the substrate in this aggressive solution. The R_{CT} of the coated magnet reached a maximum value after 2 hours ($R_{CT} = 0.5 \text{ k}\Omega.\text{cm}^2$), but after 3 hours of immersion, corrosion products were visible on the surface. The corrosion products formed were more abundant on the magnets exposed to NaCl solution than on those immersed in Na_2SO_4 solution.

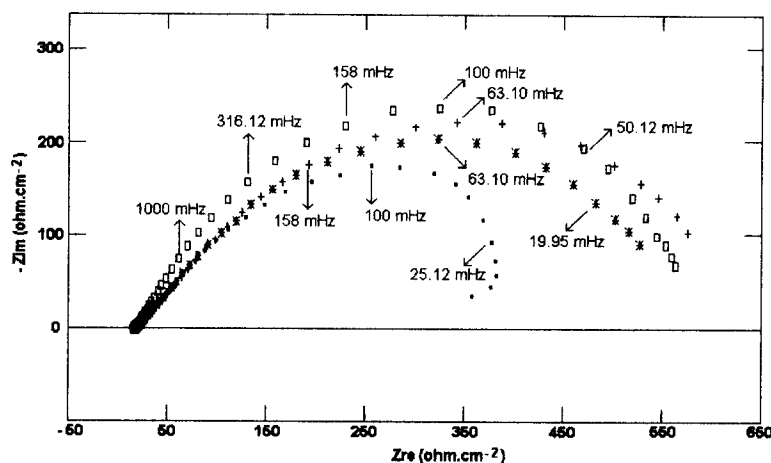


Figure 2: Nyquist diagrams of poly- $\{trans\text{-}[\text{RuCl}_2(\text{vpy})_4]\}$ coated Nd-Fe-B magnets
 _ 10min(after OCP stabilization); + 2h; * 4h of immersion in NaCl 0.5M solution at OCP.
 □ uncoated Nd-Fe-B magnets. Frequency range: 100kHz to 10mHz.

The Cl^- ion containing solution was clearly more aggressive than that having SO_4^- ions. The degree of aggressivity of a medium depends on the nature of the species present. Cl^- ions are well known as aggressive species in terms of corrosion. It is possible that they are adsorbed at the film surface, probably in competition with H_2O or OH^- species in the solution, and reach the substrate/film interface by migration across the film, under the influence of the electric field. The incorporation of Cl^- in the film, even limited to its extreme outer surface, is liable to completely modify its properties. The presence of Cl^- ions tend to promote the destruction of the polymeric film and also of the oxide layer formed on the metal. This modifies the balance of the metal /film/electrolyte thermodynamic system and possibly leads to local or general breakdown of the film.

The higher values of R_{CT} in Na_2SO_4 solution can be explained on the basis of the size of the anions. The SO_4^- are bigger than Cl^- , therefore the percolation rate of SO_4^- is lower than that of Cl^- . Besides this, chlorides form soluble compounds which hinder the formation of oxidized compounds of the metal that normally ensure passivation.

SEM and EDS analysis: The morphological characterization of poly- $\{trans\text{-}[\text{RuCl}_2(\text{vpy})_4]\}$ coated Nd-Fe-B magnets (Fig. 3a) was performed by scanning electron microscopy (SEM). The qualitative elemental analysis was carried out by energy dispersive spectroscopy (EDS), and this revealed the presence of immobilized Ru incorporated in the film (fig. 3b). The morphology of this film is similar to that observed in the poly- $\{trans\text{-}[\text{RuCl}_2(\text{pmp})_4]\}$ films on Pt electrode, reported earlier by

Franco et al. [11]. The roughness of the film probably enhanced the charge transfer at preferential sites, initiating thus, the corrosion attack of the substrate. This effect is particularly significant in Cl⁻ rich solutions in which this polymer film has low charge transfer resistance and consequently, higher capacitance values compared to those found on the same film in SO₄⁻ solutions.

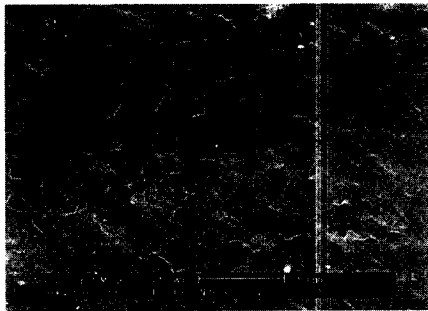


Figure 3a: SEM micrograph of poly- $\{trans-[RuCl_2(vpy)_4]\}$ coated Nd-Fe-B magnets. Magnification 500X.

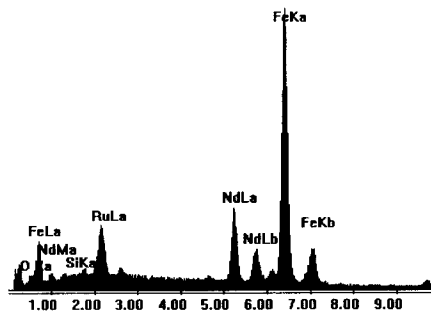


Figure 3b: EDS spectrum of poly- $\{trans-[RuCl_2(vpy)_4]\}$ coated Nd-Fe-B magnets. Energy: 20 kev.

CONCLUSIONS

The Cl⁻ and SO₄⁻ ions have different rates of charge percolation across both interfaces: solution/polymer film and polymer film/magnet sample. Notice that R_{CT} values are influenced by both, the electrolyte and the modified surface sample.

The poly- $\{trans-[RuCl_2(vpy)_4]\}$ coated Nd-Fe-B magnets showed R_{CT} values almost 4 times higher than those obtained for uncoated magnets in Na₂SO₄. In NaCl however, the circuit values were almost the same for the coated and uncoated samples.

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