ELSEVIER

Progress in Organic Coatings 53 (2005) 297–301

PROGRESS IN ORGANIC COATINGS

www.elsevier.com/locate/porgcoat

Corrosion protection of steel by polyaniline (PANI) pigmented paint coating

S. Sathiyanarayanan, S. Muthukrishnan, G. Venkatachari *, D.C. Trivedi

Central Electrochemical Research Institute, Karaikudi-630 006, India

Received 2 November 2004; received in revised form 16 February 2005; accepted 1 March 2005

Abstract

The corrosion performance of polyaniline (PANI) pigmented coating on steel has been studied by electrochemical impedance spectroscopy (EIS) in 3% NaCl and 0.1N HCl solutions. Initially, the impedance values were found to decrease due to the corrosion of steel in pin holes of the coating. However, on increased exposure time, the impedance values were found to increase due to the formation of passive film on the exposed steel in pin holes. These studies have shown that the polyaniline pigmented coatings are able to protect the steel both in acid and neutral media.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Corrosion; Steel; Polyaniline; Coatings; Impedance; Pin holes

1. Introduction

In recent years, corrosion protection of steel by conducting polymer coatings is reported. Both electropolymerised coatings and polymer pigmented paint coating have been found to offer corrosion protection. The advantage of protection by conducting polymer coating is that the coatings get more tolerance to pin holes due to their passivation ability. Several studies have been made on the use of electropolymerised polyaniline coating as corrosion protective coating on steel [1–7]. Mengoli et al. [8] have reported that polyaniline containing paints offer high corrosion resistant coatings.

Santos et al. [9] have studied the corrosion resistant property of steel coated with polyaniline by spraying a 2% solution of polyaniline in *N*-methyl pyrrolidine. They found that the steel coated with polyaniline gained nearly 100 mV in corrosion potential in 3% NaCl and a low corrosion rate was observed. This change in corrosion potential has been attributed to the formation of a passive layer. Further, these studies have shown that the PANI film loses water when kept out of the solution and returns to the original state after some time in contact with the solution without losing electrical and mechanical characteristics. This effect is probably due to the presence of air, which keeps PANI in the emaraldine oxidation state.

Wessling and Posdorfer [10] have studied the performance of polyaniline primer coatings on steel by salt spray test, electrochemical impedance spectroscopy and scanning Kelvin-Probe in 3% NaCl. The coating system with polyaniline primer has been found to be highly corrosion resistant.

The mechanistic investigation of corrosion protection of polyaniline coating on steel using scanning reference electrode technique has been made by Kinlen et al. [11]. They have found that polyaniline coatings passivate the pin hole defects in the coatings. Further, they have shown that phosphonic acid salts of polyaniline are more effective for corrosion protection than sulfonic acid salts. A model has been proposed for the protection of steel polyaniline coatings.

In all the above studies, it has been shown that the conducting polymer coating such as polyaniline stabilizes the potential of the metal in the passive region and maintains a protective oxide layer on the metal. Both SEM and XPS studies have revealed that an oxide layer has been formed between the PANI coating and the steel surface and is composed mainly of Fe_2O_3 above a very thin Fe_3O_4 layer [12–14].

* Corresponding author.
E-mail address: sathya_cecri@yahoo.co.in (G. Venkatachari).

0300-9440/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2005.03.007

It has been reported by Wrobleski et al. [15] that the doped electrically conducting form of polyaniline film (film of thickness 0.005 cm) on steel with epoxy top coat gave excellent performance in 3.5% NaCl and 0.1 M HCl even at scribed areas. The mechanism of protection of conducting polymer coating has been investigated by Jain et al. [16]. It has been stated that the doped conducting polymer will generate an electric field which will restrict the flow of electrons from the metal to an outside oxidizing species thus preventing the corrosion. Among the conducting and non-conducting polyaniline, it has been reported that the non-conducting polyaniline performed well as corrosion resistant coating [17]. However, the studies on the anticorrosive properties of undoped polyaniline casted on mild steel have shown that the performance of PANI coated system is not good due to the poor adhesion [18]. In the review by Mc Andrew [19], it has been stated that the future for the use of electrically conducting polymers as corrosion resistant coatings appears promising, especially as additives to improve the performance of the existing coating systems. Studies on the use of poly(phenylene oxide) [20] and poly(2,5-bis(*N*-methyl-*N*-hexylamine)-*p*-phenylene vinylene [21] as pigment in paint have shown that the paints containing these pigments are highly corrosion resistant.

In a recent study [22], it is reported that the lower polyaniline loaded paint has been found to be more corrosion resistant. In this paper, the corrosion resistant property of polyaniline pigmented coating on steel in acid and saline solutions is reported.

2. Experimental

2.1. Synthesis of polyaniline pigment

Reagent grade aniline was purified by distillation in the presence of small amount of zinc dust. The 0.1 M of the freshly distilled aniline dissolved in 0.1 M HCl was precooled. To this reaction mixture, freshly prepared solution of 0.1 M ammonium persulphate kept at a temperature of 5–10 °C was slowly added with constant stirring for 2 h. Finally polyaniline, a dark green coloured polymer was obtained and the efficiency of polymerization was about 50%. The polymer thus obtained was filtered and repeatedly washed with distilled water to remove the excess acid. The polyaniline was characterized by FTIR and UV–vis spectroscopy and molecular weight was determined by GPLC method (Shimadzu, Japan) and was found to be 16,260.

The UV–vis spectrum (Fig. 1) shows the absorption peak at 336 nm due to the π–π^* transition in the benzenoid ring and at 578 nm due to the donor–acceptor interaction of quinonoid ring. The well known cation radicals and localized polaran peaks were observed at 449 and 775 nm. The major IR absorption (Fig. 2) bands at 1555 and 1453 cm^{-1} are the characteristic bands due to the nitrogen–quinonoid ring structure and peaks for polyaniline are observed at 1632 cm^{-1}, for N–H bending, 1555 and 1494 cm^{-1} for nitrogen benzenoid–quinonoid ring structure, the other IR characteristics are observed at 1126, 1036 cm^{-1}.

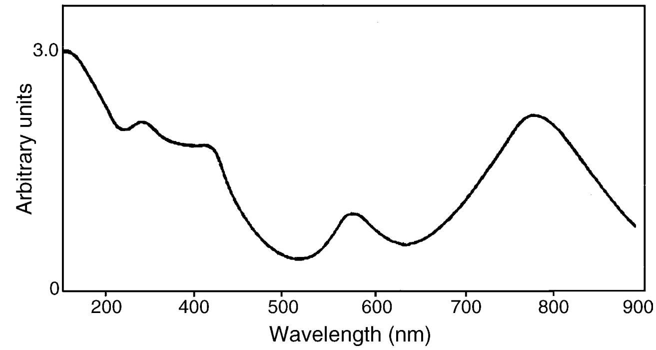


Fig. 1. UV-visible spectrum of polyaniline.

The polyaniline containing paint was prepared as per the procedure [23] using vinyl resin (molecular weight: 30,000) as binder and polyaniline as the only pigment. The characteristics of the paint and the coating are as given below:

Touch dry (h)	1.0
Complete dry (h)	2
Volume solids (%)	30–33
Thickness/coat (μm)	50 ± 5
PVC (%)	9–10

2.2. Methodology

Carbon steel specimen of size 5 cm × 1.5 cm × 0.2 cm were pickled and coated with PANI containing paint. A glass tube of 0.9 cm diameter of length 3 cm was fixed on the coated steel with adhesive (m-seal). The solution of 3% NaCl and 0.1N HCl was taken in the glass tube. A platinum foil and a saturated calomel electrode (SCE) were placed inside the glass tube. This assembly was connected to the Electrochemical Impedance Analyzer (Model 6310 EG&G). Impedance measurements were carried out for a frequency range of

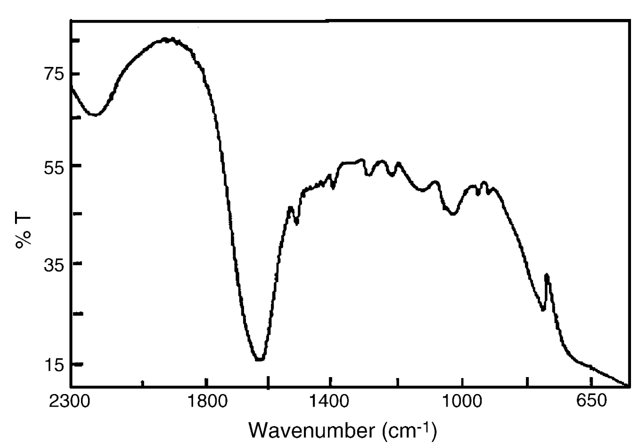


Fig. 2. FTIR spectrum of polyaniline.

100 KHz to 0.1 Hz with an ac amplitude of 20 mV. From the Nyquist plots the resistance (R_c) and capacitance (C_c) of the coating and the charge transfer resistance (R_{ct}), and the interfacial double layer capacitance (C_{dl}) values were obtained using Zview software.

3. Results and discussion

The corrosion behaviour of the polyaniline pigmented coating on steel has been determined by measuring the open circuit potential and impedance characteristics in 3% NaCl and 0.1N HCl solutions for different time intervals. Fig. 3 shows the variation of the open circuit potential with time for coated steel in 3% NaCl. It can be seen that the OCP has decreased from 298 to 51 mV versus SCE initially and has started to shift in the noble direction after the 5th day of immersion. Afterwards the OCP reached a steady value of 280–290 mV versus SCE. The initial decrease of OCP may be due to the initiation of corrosion in the pin holes. The presence of polyaniline in the coating favours oxidation of the ferrous ions to stable passive iron oxide film at the pin hole region. Due to this reaction, the OCP has been shifted to noble values after 5 days of immersion. The high positive values of OCP indicate the formation of a protective passive film on iron. The presence of a Fe_2O_3 layer between PANI coating and steel surface has been confirmed by SEM and ESCA studies [12–14,24].

The Nyquist plots of PANI pigmented coated steel samples at different immersion time in 3% NaCl are shown in Fig. 4. The diagrams show two capacitance loops, one at high frequency range followed by a larger one at low frequencies. The first capacitance loop is attributed to the coating characteris-

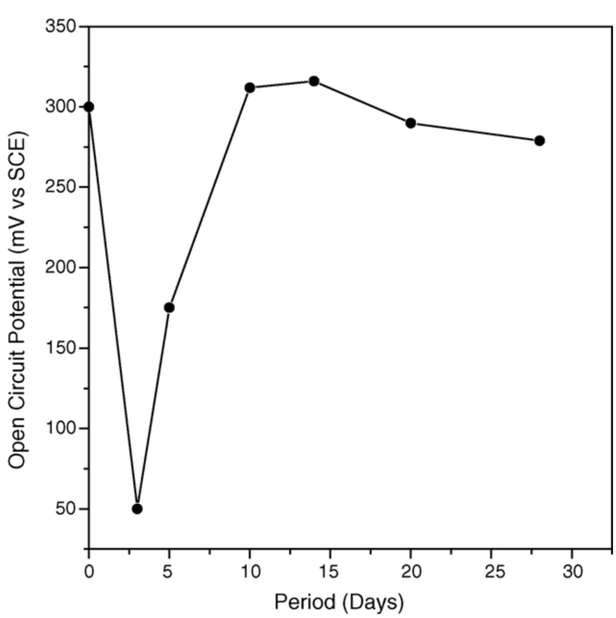


Fig. 3. Variation of open circuit potential of PANI pigmented paint coating on steel in 3% NaCl.

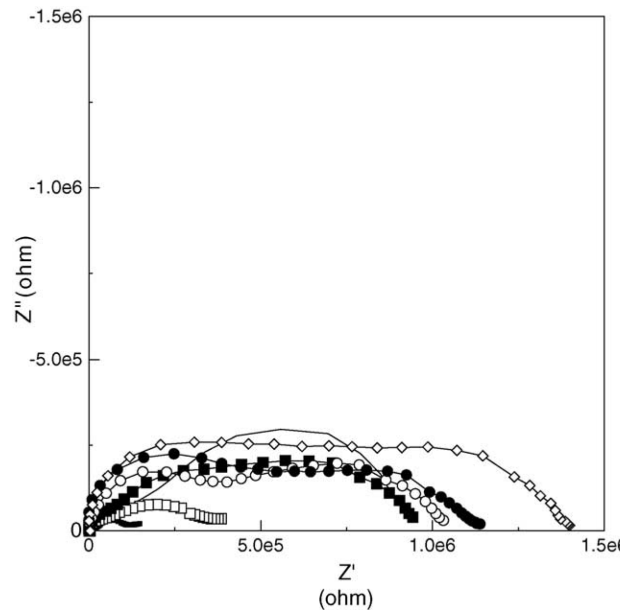
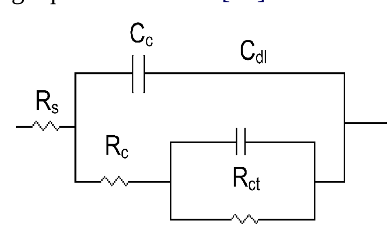


Fig. 4. Impedance behaviour of PANI pigmented paint coating on steel in 3% NaCl. (—) Initial; (■) 3 days; (□) 5 days; (■) 10 days; (○) 15 days; (●) 20 days; (◊) 25 days.

tics and the second one to the processes occurring underneath the film [25]. This type of behaviour is usually analysed with the following equivalent circuit [26]:



In the above equivalent circuit, R_s is the solution resistance, C_c the capacitance of the coating, R_c the resistance of the coating, C_{dl} the capacitance of the interfacial double layer and R_{ct} is the charge transfer resistance. The impedance parameters for the above equivalent circuit have been obtained with Zview software. Table 1 gives the impedance parameters for polyaniline pigmented coating on steel in 3% NaCl.

It can be seen that the resistance value of the coating (R_c) is decreased initially from 520 to 220 kΩ cm^2 after 3 days of immersion and then increased gradually to 690 kΩ cm^2 after 28 days of immersion. This shows the increased protective property of the coating. The capacitance values of the coating (C_c) are decreased from 1.7 to 0.22 nF/cm^2 indicating the protective property of the coating. However, in conventional paint coating, due to ingress of chloride ions and water, the resistance of the paint film will decrease and the capacitance of the film will increase with time. The charge transfer resistance (R_{ct}) value is decreased from 830 to 110 kΩ cm^2 and then increased to 960 kΩ cm^2 after 28 days of immersion. The initial decrease of R_{ct} may be due to small amount of dissolution of iron but the subsequent formation of passive

Table 1
Impedance parameters of polyaniline pigmented paint coating on steel in 3% NaCl

S. no.	Time (days)	R_c ($\Omega\,cm^2$)	C_c ($F\,cm^{-2}$)	R_{ct} ($\Omega\,cm^2$)	C_{dl} ($F\,cm^{-2}$)
1	Initial	5.2×10^5	1.7×10^{-9}	8.3×10^5	2.8×10^{-9}
2	3	2.2×10^5	2.7×10^{-9}	1.1×10^5	3.9×10^{-9}
3	5	2.7×10^5	5.6×10^{-10}	3.8×10^5	3.9×10^{-9}
4	10	3.1×10^5	1.5×10^{-10}	1.1×10^6	1.5×10^{-9}
5	14	3.8×10^5	1.1×10^{-10}	1.2×10^6	3.5×10^{-9}
6	20	4.6×10^5	1.6×10^{-10}	8.3×10^5	2.0×10^{-9}
7	28	6.9×10^5	2.2×10^{-10}	9.6×10^5	2.9×10^{-9}

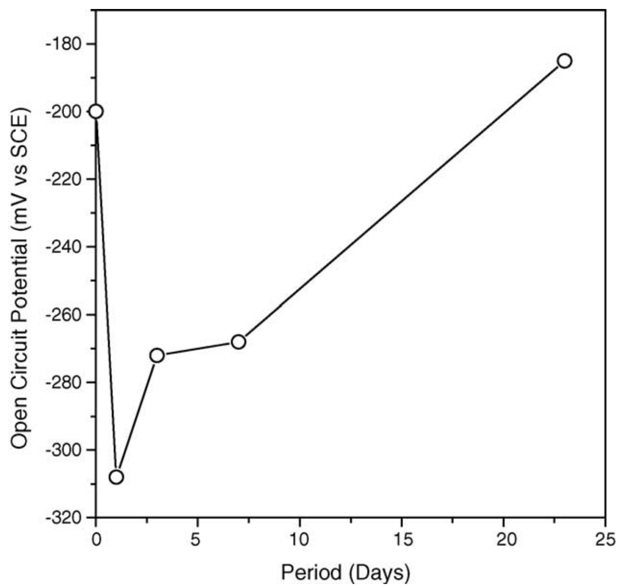


Fig. 5. Variation of open circuit potential of PANI pigmented paint coating on steel in 0.1N HCl.

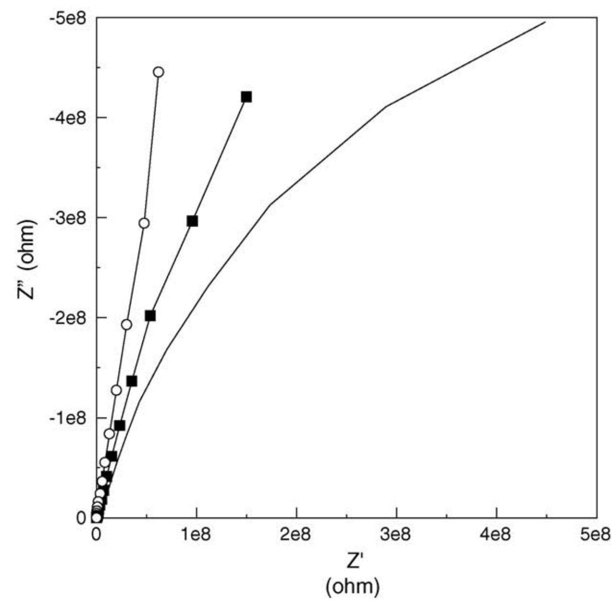
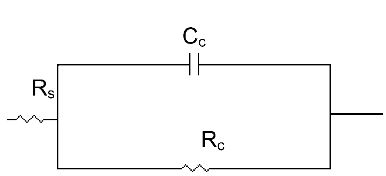


Fig. 6. Impedance behaviour of PANI pigmented paint coating on steel in 0.1N HCl. (—) Initial; (■) 7 days; (○) 24 days.

film, which resulted in the increased of R_{ct} value. The high R_{ct} value even after 28 days of immersion indicates the negligible dissolution of iron under the film.

The evolution of the open circuit potential value of steel coated with PANI pigmented paint in 0.1N HCl with time is shown in Fig. 5. It can be seen that the open circuit potential value decreased from −0.200 to −0.300 V initially and then increased to the initial value. The impedance diagrams for steel coated with PANI pigmented paint in 0.1N HCl for different immersion time are shown in Fig. 6. In this case, only one semi circle is observed which may be due to the resistance and capacitance of the coating. Besides the impedance behaviour of coating is capacitive nature and the tendency for capacitive nature increases with immersion time. The equivalent circuit for such behaviour can be represented as



Using the above equivalent circuit, the resistance and capacitance values of the coating have been obtained with Zview software. Table 2 gives the impedance parameters for coated steel in 0.1N HCl. The resistance values of the coating are in the range of 1.8×10^9 to 2.9×10^{10} $\Omega\,cm^2$ and the capacitance values are in the range of 0.5–0.14 nF/cm^2. The high resistance values and low capacitance values indicate the highly protective nature of PANI pigmented paint coating. Using salt fog test, it has been reported that PANI containing alkyd and vinyl-based coatings are able to protect more than 500 h of exposure [27]. On comparing the impedance values

Table 2
Impedance parameters of polyaniline pigmented paint coating on steel in 0.1N HCl

S. no.	Time (days)	R_c ($\Omega\,cm^2$)	C_c ($F\,cm^{-2}$)
1	Initial	1.79×10^9	5.04×10^{-10}
2	1	1.45×10^9	6.67×10^{-10}
3	3	4.54×10^9	6.14×10^{-10}
4	7	1.83×10^{10}	3.38×10^{-10}
5	24	2.93×10^{10}	1.38×10^{-10}

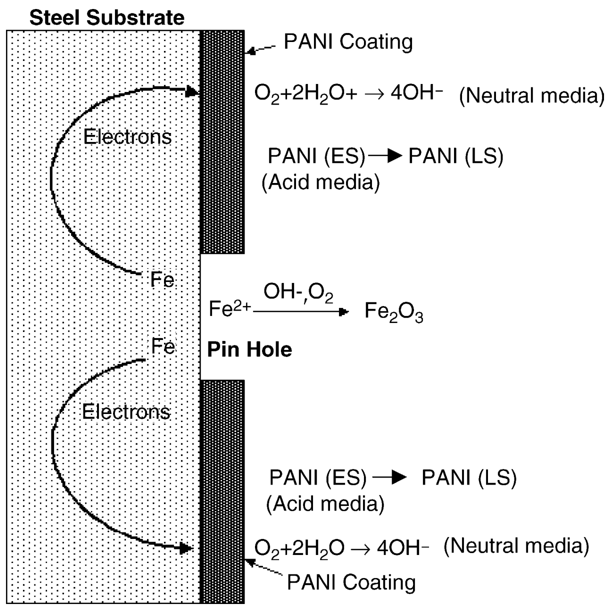


Fig. 7. Schematic diagram of mechanism of iron passivation by PANI pigmented paint coating on steel.

for 0.1N HCl with those obtained in 3% NaCl, the impedance values are high in 0.1N HCl medium.

The mechanism of passivation of steel by PANI coating is schematically shown in Fig. 7. Due to conducting nature of the coating, the oxygen reduction reaction takes place on the coating, while the oxidation of ferrous ions to iron oxides takes place on the exposed iron surface at pin hole areas and under the film in neutral media. However, in acid media the passivation of pin holes takes place by the cathodic complementary reaction of

$$\text{PANI (ES)} \rightarrow \text{PANI (LS)}$$

Due to the conversion of LS in acid media, the coating is changed from conducting to non-conducting stage, which is reflected from the increased capacitive behaviour of coating with immersion time.

4. Conclusions

The corrosion performance of polyaniline pigmented paint coating on steel has been studied in 3% NaCl and 0.1N HCl solutions by electrochemical impedance spectroscopy (EIS). Studies have shown that polyaniline pigmented coating on steel is highly corrosion resistant in both neutral and acidic media. This coating is found to be highly protective in acidic media than neutral media. It also passivates the iron surface and enhances its protective property.

Acknowledgements

The authors express their sincere thanks to the Director, Central Electrochemical Research Institute, Karaikudi-630 006 for his keen interest and encouragement for pursuing the present investigation.

References

[1] I. Sekine, K. Kohara, T. Sugiyama, M. Yuasa, J. Electrochem. Soc. 139 (1992) 3090.
[2] W.K. Lu, L.R. Elsenbaumer, B. Wessling, Synth. Met. 71 (1995) 2163.
[3] V. Sauerland, R. Schindeler, Synth. Met. 82 (1996) 193.
[4] D. Sazou, C. Georgolios, J. Electroanal. Chem. 429 (1997) 81.
[5] M.C. Bernard, A. Hugot, S. Le Goff, S. Joiret, N.N. Dinh, N.N. Toan, J. Electrochem. Soc. 148 (2001) 12.
[6] A. Meneguszzi, M.C. Pharm, J.C. Lacroix, B. Piro, A. Ademier, C.A. Ferreira, P.C. Laceze, J. Electrochem. Soc. 148 (2001) B121.
[7] S. Sathiyanarayanan, S. Muralidharan, G. Venkatachari, M. Raghavan, Corros. Rev. 22 (2004) 157.
[8] G. Mengoli, M. Munari, P. Bianco, M. Musiani, J. Appl. Polymer Sci. 26 (1982) 4247.
[9] J.R. Santos Jr., L.H.C. Mattoso, A.J. Motheo, Electrochim. Acta 43 (1998) 309.
[10] B. Wessling, J. Posdorfer, Electrochim. Acta 44 (1999) 2139.
[11] P.J. Kinlen, V. Menon, Y. Ding, J. Electrochem. Soc. 146 (1999) 3690.
[12] B. Wessling, Adv. Mater. 6 (1994) 226.
[13] A. Talo, P. Passiniemi, O. Forsen, S. Ylassari, Synth. Met. 85 (1997) 1333.
[14] B. Wessling, Synth. Met. 85 (1997) 1313.
[15] D.A. Wrobleski, B.C. Benicewicz, K.G. Thompson, C.J. Bryan, Poly. Chem. 35 (1994) 265.
[16] F.C. Jain, J.J. Rosato, K.S. Kalonia, V.S. Agarwala, Corrosion 42 (1986) 700.
[17] T.P. Mc Andrew, A.G. Gilicinski, L.M. Robson, US Patent 5,441,772 (1995).
[18] W.S. Araujo, I.C.P. Margarit, M. Ferreira, O.R. Mattos, P. Lima Neto, Electrochim. Acta 46 (2001) 1307.
[19] T.P. Mc Andrew, TRIP 5 (1997) 7.
[20] P. Spellane, A. Yahkind, O. Abu-shanab, Metal corrosion protection with wash coat of polyphenylene oxide, US Patent 6,004,628 (1999).
[21] R. Fesser, W. Erning, Paper Presented at European Coating Conference, 16 June 2000.
[22] A.B. Samli, A.S. Pantekar, J. Rengarajan, P.C. Deb, Prog. Org. Coatings 47 (2003) 1.
[23] S. Sathiyanarayanan, S. Muthukrishnan, G. Venkatachari, D.C. Trivedi, Improvements in or relating to the development of polyaniline (pani) containing paint for corrosion prevention of steel, Indian Patent 042/NF (2004).
[24] B. Wessling, W.K. Lu, R.L. Elsenbaumer, Proc. Synth. Met. 71 (1995) 2163.
[25] A.A.O. Magalhaer, I.C.P. Margarit, O.R. Mattos, Electrochim. Acta 44 (1997) 4281.
[26] F. Mansfeld, Analysis and interpretation of EIS data for metals and alloys, Technical Report 26, Schlumberger, Tech., UK, 1993.
[27] G. Miller et al., European Patent 0,623,159 B1 (1999).