Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electrochemical Behaviour of the AA2024 Aluminium Alloy Modified with Self-Assembled Monolayers/Polyaniline Double Films

Daiane Piva B. Silva [a], Rodrigo S. Neves [a] & Artur J. Motheo [a]
[a] Department of Physical Chemistry, Institute of Chemistry of São Carlos, University of São Paulo, São Carlos, SP - CEP, Brazil

Version of record first published: 28 May 2010

To cite this article: Daiane Piva B. Silva, Rodrigo S. Neves & Artur J. Motheo (2010): Electrochemical Behaviour of the AA2024 Aluminium Alloy Modified with Self-Assembled Monolayers/Polyaniline Double Films, Molecular Crystals and Liquid Crystals, 521:1, 179-186

To link to this article: http://dx.doi.org/10.1080/15421401003720124

Mol. Cryst. Liq. Cryst., Vol. 521: pp. 179–186, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421401003720124

Electrochemical Behaviour of the AA2024 Aluminium Alloy Modified with Self-Assembled Monolayers/Polyaniline Double Films

DAIANE PIVA B. SILVA, RODRIGO S. NEVES, AND ARTUR J. MOTHEO

Department of Physical Chemistry, Institute of Chemistry of São Carlos,
University of São Paulo, São Carlos, SP – CEP, Brazil

The electrochemical characteristics of the AA2024 aluminium alloy modified with octadecyltrimethoxysilane (ODTMS) + polyaniline (PANi) and propiltrimethoxysilane (PTMS) + (PANi) were studied in the present work. The results show that the different protective coatings shift the values of corrosion and pit potentials to more positive values making the system nobler and indicate that the double film ODTMS + PANi present the best protection against corrosion characteristics, that is probably due to the two contributions: anodic protection associated with the barrier effect.

Keywords AA2024; corrosion protection; double films; polyaniline; SAM

Introduction

The development of new corrosion protection methods for aluminium and its alloys is motivated by both economic and environmental reasons, since these materials are among the most used in several industry branches and the conventional corrosion protection methods are mainly based on chromium coatings baths. These chromate containing baths are aggressive to the environment and alternatives are necessary. Some of the potential alternative organic coatings for aluminium corrosion protection are those based on self-assembled monolayers (SAM) [1–9], conducting polymer films [10–21] and, in recent years, SAM/polymer double films [22].

Among the SAMs studied as coatings for aluminium surfaces are those of several kind of organosilanes molecules [23–27]. These kind of SAMs require hydroxylated surfaces, since the monolayer organization is based on the formation of a polysiloxane, linked to the surface by the formation of silanol groups [28]. This characteristic makes them a suitable choice to modify oxide surfaces, as is the case of the aluminium and its alloys surfaces, naturally covered by an oxide layer.

Address correspondence to Artur J. Motheo, Laboratory of interfacial Electrochemistry – Institute of Chemistry of São Carlos University of São Paulo, Av. Trabalhador São-Carlense 400 – C.P. 780, São Carlos, SP 13560-970, Brazil. Tel.: +55 (16) 3373 9932; Fax: +55 (16) 3373 9952; E-mail: artur@iqsc.usp.br

The SAMs capabilities for aluminium [5,9] and some aluminium alloys [1,2] corrosion protection have been studied with promising results. The way as a SAM acts on corrosion protection can be classified as direct or indirect. In the first case the monolayer blocks the corroding species access to the protected surface, while in the second case the SAM promotes the adhesion of a second coating layer [22,29]. When the SAM acts directly, the characteristics as the aliphatic chain length and the functional groups at the molecule tail can be optimised to block the corroding species access to the surface [6,7]. When acting as a primer, the SAM tail group could be optimised in order to present a strong interaction with the second coating, improving the adhesion of the protective layer. The nature of this interaction could be just physical [29] or it can involve chemical bonds, as in the case of polyaniline grafting polymerization over functionalised organosilanes SAMs [30,31]. Suitable combinations of substrates, SAMs and a second coating can be achieved to combine the direct and indirect mechanisms.

Conducting polymer films are also possible alternative corrosion protective coatings for aluminium based materials. Since De Berry's pioneer work on steel corrosion protection by PANi films [21], the performance of such kind of coatings has been tested over different materials. The most interesting feature involved in the PANi aluminium corrosion protection mechanism is the PANi capability to restore defects on the oxide layer that naturally covers the material, maintaining its integrity and natural corrosion protective character. Additionally, the polymeric film also acts as a barrier to the corroding species access to the material surface.

More recently, a natural consequence of these studies was the combination of SAMs and conducting polymer films as aluminium based materials corrosion protective coatings [22]. This approach basically aims to improve the polymer films adhesion to the aluminium surfaces, using the SAM as an adhesion promoter however the combination of both films improves the corrosion protection of the final coating.

Concerning to the substrate for studies on alternative corrosion protective coatings, the AA2024 alloy is a suitable choice for the study since it is extensively used in aircraft industry due to its mechanical performance and low density and, due to this fact, some attention has been dedicated to its corrosion protection study [1,10,32–37]. This alloy contains about 3.8–4.9 wt% of copper and 1.2–1.8 wt% of magnesium in its composition and the corrosion usually takes place at high concentration copper regions at the material surface, which acts as cathodic sites in galvanic couples with the aluminium alloy matrix. This mechanism favours the occurrence of localized corrosion processes (pit corrosion). Recently, the US Air Force has demonstrated interest in the development of aluminium alloys (mainly AA2024 and AA7075 alloys) corrosion protection coatings with 30 years lifetime before maintenance [38].

Based on these arguments this paper presents a study of the electrochemical behaviour of the AA2024 aluminium alloy modified with propyl-trimethoxy-silane (PTMS) and octadecyl-trimthoxy-silane (ODTMS) SAMs, PANi films and SAM/PANi double films. PTMS and ODTMS are suitable choices for this application due to its relatively simple monolayer deposition process and high stability [25].

Experimental

The electrochemical experiments were performed in a single compartment electrochemical cell, using a saturated calomel electrode (SCE) as reference electrode and a platinum sheet (2.5 cm^2 of geometric area) as counter electrode. The experiments were performed using NaCl (Synth PA) 0.6 mol dm^{-3} as working solution.

The reagents used in the coatings preparation were ODTMS (Fluka – 90%), PTMS (Fluka – 90%), anhydrous ethanol (Aldrich – PA), glacial acetic acid (Mallinckrodt – PA), aniline (Aldrich – PA), sulphuric acid (Synth – PA) and ammonium persulphate (Synth – PA). MilliQ-UV purified water was used in all the experimental procedures.

The aluminium samples (1.13 cm^2 of geometric area) were gradually polished using emery papers from P100 to P1200 grades, with constant rinse of MilliQ water, in order to obtain a surface with homogeneous distribution of slots. In this paper, these are called bare samples. After this procedure, the samples were immersed in a glacial acetic acid solution (pH = 3), in a sonic bath, during one hour and dried in air. This treatment results in surfaces equivalent to the finishing of aluminium for industrial applications. The samples submitted to this process are called pre-treated.

For the SAMs deposition the dipping solutions were prepared adding 0.75% of the organosilane (PTMS or ODTMS) in volume to a mixture of 1:9 water: ethanol, the pH of the solution was adjusted to 4 with glacial acetic acid, and then the solution was stirred for 10 minutes to ensure the total organosilanes hydrolysis. The samples were then immersed in the dipping solution for 10 minutes and dried with nitrogen. This procedure is known to result in homogeneous and stable SAMs over hydroxylated surfaces [25].

For the polymeric film deposition a saturated PANi solution was obtained by adding 7% of undoped PANi (chemically synthesized) in N-methyl-pyrrolidone (NMP) and submitting the solution to a sonic bath for 15 minutes. The pre-treated samples were then painted with the PANi solution and dried at 50°C under vacuum for 3 hours. The process was done three times in order to obtain homogeneous films.

The double films were obtained by submitting the SAM coated samples to the above described procedure.

The potentiodynamic polarization curves were obtained using a potentiostat/galvanostat EG&G PAR model 273A in a potential range of 1 V around the open circuit potential, with a sweep rate of 0.5 mV s^{-1}. All the electrochemical experiments were performed at 25 ± 1°C. Optical images were obtained using an optical microscope Leica model DFC 208 coupled to a system of image acquisition.

Results and Discussion

The potentiodynamic polarisation curves for the AA2024 alloy surface submitted to the different treatments based on the ODTMS SAM and the double film ODTMS-PANi, in contact with the corroding medium, are shown in Figure 1. Since the same basic behaviour is observed for the PTMS basic modifications, its polarisation curves are not shown. The main electrochemical parameters for all the studied samples are presented in Table 1.

The bare aluminium alloys are covered by a thin oxide layer that begins to dissolve at potentials above the corrosion potential ($E_{corr} = -0.678$ V). When the sample is in contact with the aggressive corroding solution, increasing the potential results in pitting corrosion. The pitting potential ($E_{pit} = -0.608$ V) is characterized by a drastic increase of the current, related to a break of the oxide protective layer. The values of E_{corr} and E_{pit} are very close, showing that, for this alloy, the process of pitting corrosion occurs almost simultaneously with the process of uniform corrosion.

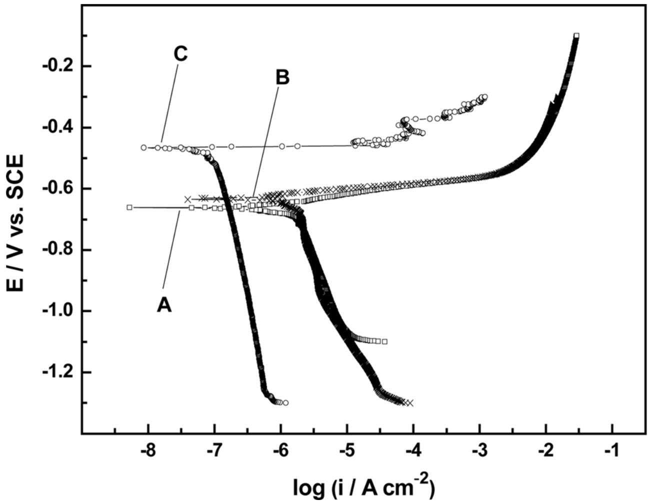

Figure 1. Potentiodynamic polarization curves for the AA2024, submitted to different surface modification methods, in contact with a 0.6 mol dm^{-3} NaCl solution. (a) Pre-treated, (b) ODTMS, and (c) ODTMS + PANi.

For the samples pre-treated in acetic acid, a thicker and more homogeneous oxide passive layer is formed and the E_{corr} and E_{pit} are slightly shifted to more positive values (−0.647 V and −0.584 V, respectively), as well as the corrosion current density (i_{corr}) slightly decreases. The results show that the pre-treatment changes the oxide layer properties, but does not result in significant changes in protection against corrosion.

The effect of the different electrochemical characteristics of both the bare and pre-treated samples on the surface aspect, before and after the polarisation curves, can be observed in Figures 2 and 3a. Before the polarisation curve (Fig. 2a), the bare alloy surface has a homogeneous distribution of scratches, due to the polishing process and no visible pit, while after the polarization curve (Fig. 2b), it is noted the occurrence of many pits, that appear to be deep, resulting from the anodic processes that took place during the polarization. Meanwhile, for the pre-treated sample after the polarisation curve (Fig. 3a), it is possible to

Table 1. Main electrochemical parameters obtained from potentiodynamic polarization curves

Sample	E_{corr}/V	i_{corr}/A cm^{-2}	E_{pit}/V	CR/mpy
Bare	−0.678	1.79×10^{-6}	−0.608	1.93×10^{-2}
Pre-treated	−0.647	1.69×10^{-6}	−0.584	1.82×10^{-2}
PTMS	−0.646	1.26×10^{-6}	−0.590	1.36×10^{-2}
ODTMS	−0.636	1.19×10^{-6}	−0.585	1.28×10^{-2}
PANi	−0.590	1.23×10^{-6}	−0.548	1.33×10^{-2}
PTMS + PANi	−0.447	5.93×10^{-7}	−0.390	6.38×10^{-3}
ODTMS + PANi	−0.476	1.12×10^{-7}	−0.426	1.21×10^{-2}

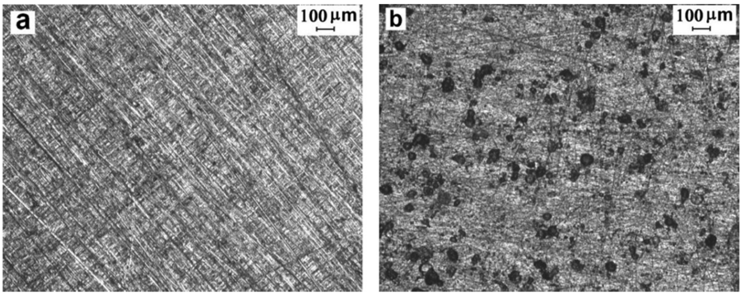

Figure 2. Images obtained by optical microscopy for the bare AA2024 aluminium alloy (5x magnification). (a) before and (b) after corrosion testing.

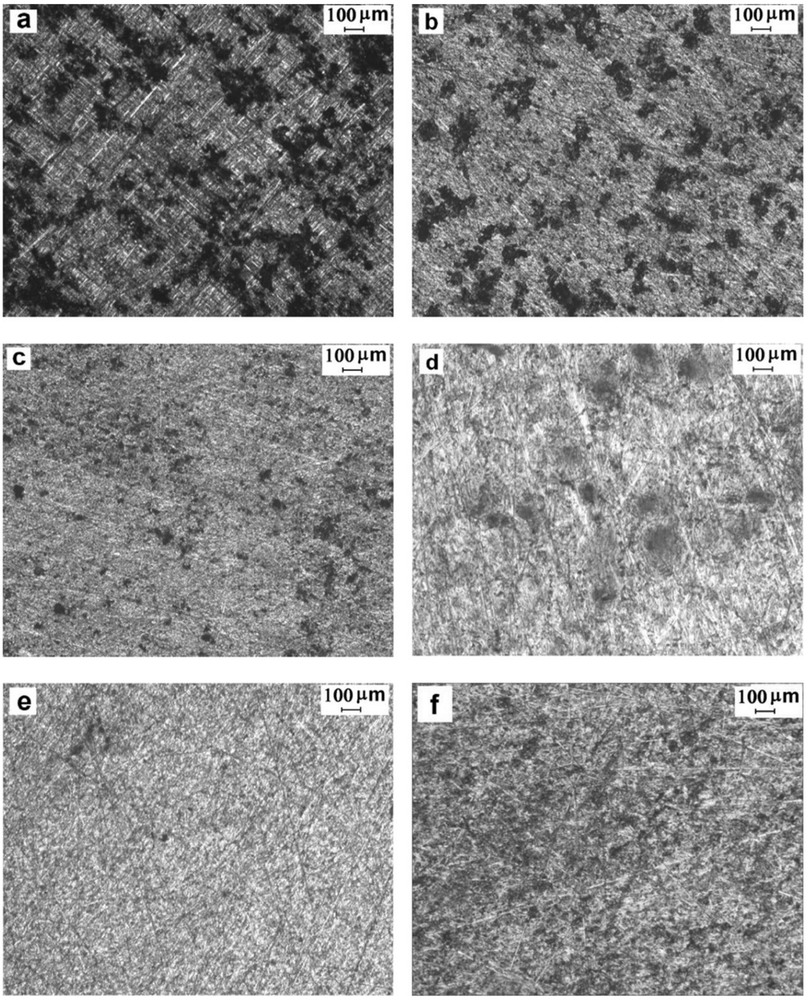

Figure 3. Images obtained by optical microscopy for the AA2024 aluminium alloy with different coatings after the corrosion tests. The coatings were removed in order to verify the surface aspect. (a) pre-treated, (b) PTMS, (c) ODTMS, (d) PANi, (e) PTMS+PANi, and (f) ODTMS+PANi.

observe that the pre-treated sample shows a uniform distribution of corrosion points over the entire surface, that seem to be more superficial than those observed in the bare sample.

In the case of the SAM coated samples, for both the PTMS and ODTMS coatings, the E_{corr} is not significantly affected when compared to the pre-treated sample. It shifts about +10 mV for the ODTMS and remains almost the same for the PTMS. The E_{pit} is kept almost at the same value. The corrosion current and corrosion rate are also kept in the same magnitude (approximately the same values as the pre-treated).

The surface treatment with both SAMs lead to a similar behaviour around the E_{corr}, however, the two coatings exhibit different behaviours related to the pit corrosion, that occurs at high anodic over potentials, as observed in Figure 3. While the pre-treated sample (Fig. 3a) shows homogeneous distribution of pits over the entire surface, the sample covered with PTMS (Fig. 3b) presents fewer corrosion points, which are further suppressed when using ODTMS (Fig. 3c). Comparing the results obtained, it can be concluded that the ODTMS film appears to be more stable in areas of high potential, presenting fewer defects, which may be due to the greater body length of the aliphatic chain of the surfactant.

Differently from the observed for the SAM coatings, the direct application of PANi on the pre-treated samples changes the surface electrochemical behaviour, shifting the E_{corr} about 60 mV to more positive values and the E_{pit} is about 40 mV in the same direction. This behaviour comes from the undoped PANi film ability to absorb charges from charged species present in solution, avoiding that the redox reactions to occur on the metal surface [19].

After the polarization curve, the polymer film was removed and the surface aspect was verified via optical microscopy (Fig. 3d). It is observed the occurrence of fewer defects, which appear to be more superficial when compared to the samples pre-treated and coated with SAMs.

When the aluminium samples are coated by the SAM-PANi double films, the E_{corr} is remarkably shifted to more positive values, about 200 mV for PTMS-PANi and 170 mV for ODTMS-PANi coating, when compared with the pre-treated samples. The pitting potential is also shifted to more positive values, about 190 mV for PTMS-PANi and 160 mV for ODTMS-PANi. The displacement on both the E_{corr} and E_{pit} demonstrates the strong anodic protection character provided by the double films coatings when compared to the SAM and PANi single coatings.

The SAMs application prior to the PANi coating also decreases the i_{corr} about 2 times in the case of PTMS and about 11 times for ODTMS, when compared with the PANi single coating. This behaviour reflects the reduction of the cathodic and anodic reactions rate, which slows down the alloy corrosion process.

After the polarisation curves, the double films were removed from the samples and the surface aspect was verified by using optical microscopy (PTMS-SAM in Fig. 3e and ODTMS-PANi in Fig. 3f). The images show that the corrosion points are almost eliminated in the samples covered by the double films and that their aspect is very similar to that observed for the uncovered samples not submitted to polarisation (Fig. 2a). The images prove the efficient corrosion protective behaviour for both of the SAM-PANi double films.

Conclusions

The presented results show that all the different protective coatings shift the values of E_{corr} and E_{pit} potentials to more positive values and resulting in some degree of corrosion protection, however, the results indicate that the SAM-PANi double films corrosion protection properties are remarkably more effective when compared to the SAM and PANi single coatings. In this aspect, the values of both potentials present the following trend: PTMS < ODTMS < PANi < PTMS + PANi < ODTMS + PANi.

Additionally, the SAM-PANi double-films decrease the values of i_{corr}, indicating that the cathodic and anodic processes rates decrease, especially in the ODTMS-PANi case.

The optical micrographs corroborate all the electrochemical results, reinforcing the superior corrosion protective behaviour of the SAM-PANi double films when compared to the SAM and PANi single coatings.

Acknowledgments

The authors thank the financial support from Brazilian funding agencies CNPQ and FAPESP.

References

[1] Hintze, P. E. & Calle, L. M. (2006). *Electrochim. Acta*, *51*, 1761.
[2] Reis, F. M., de Melo, H. G., & Costa, I. (2006). *Electrochim. Acta*, *51*, 1780.
[3] Sinapi, F., Julien, S., Auguste, D., Hevesi, L., Delhalle, J., & Mekhalif, Z. (2008). *Electrochim. Acta*, *53*, 4228.
[4] Aramaki, K. & Shimura, T. (2006). *Corr. Sci.*, *48*, 209.
[5] Jouet, R. J., Warren, A. D., Rosenberg, D. M., Bellinto, V. J., Park, K., & Zachariah, M. R. (2005). *Chem. Mater.*, *17*, 2987.
[6] Zamborini, F. P. & Crooks, R. M. (1998). *Langmuir*, *14*, 3279.
[7] Jennings, G. K., Munro, J. C., Young, T.-H., & Laibinis, P. E. (1998). *Langmuir*, *14*, 6130.
[8] Nozawa, K., Nishihara, H., & Aramaki, K. (1997). *Corr. Sci.*, *39*, 1625.
[9] Liakos, I. L., Newman, R. C., McAlpine, E., & Alexander, M. R. (2007). *Langmuir*, *23*, 995.
[10] Huerta-Vilca, D., Moraes, S. R., & Motheo, A. J. (2003). *J. Braz. Chem. Soc.*, *14*, 52.
[11] Breslin, C. B., Fenelon, A. M., & Conroy, K. G. (2005). *Mater. Des.*, *26*, 233.
[12] Huerta-Vilca, D., Moraes, S. R., & Motheo, A. J. (2003). *J. Appl. Electrochem.*, *33*, 355.
[13] Huerta-Vilca, D., Moraes, S. R., & Motheo, A. J. (2003). *J. Appl. Pol. Sci.*, *90*, 819.
[14] Moraes, S. R. & Motheo, A. J. (2006). *Mol. Crys. Liq. Crys.*, *448*, 261.
[15] Huerta, D. V., Moraes, S. R., & Motheo, A. J. (2004). *Synth. Met.*, *140*, 23.
[16] Conroy, K. G. & Breslin, C. B. (2003). *Electrochim. Acta*, *48*, 721.
[17] Wessling, B. & Posdorfer, J. (1999). *Electrochim. Acta*, *44*, 2139.
[18] Epstein, A. J., Smallfield, J. A. O., Guan, H., & Fahlman, M. (1999). *Synth. Met.*, *102*, 1374.
[19] Schauer, T., Joos, A., Dulog, L., & Eisenbach, C. D. (1998). *Prog. Org. Coat.*, *33*, 20.
[20] Santos, J. R. Jr., Mattoso, L. H. C., & Motheo, A. J. (1998). *Electrochim. Acta*, *43*, 309.
[21] DeBerry, D. W. (1985). *J. Electrochem. Soc.*, *132*, 1022.
[22] Cecchetto, L., Denoyelle, A., Delabouglise, D., & Petit, J.-P. (2008). *Appl. Surf. Sci.*, *254*, 1736.
[23] Abel, M.-L., Digby, R. P., Fletcher, I. W., & Watts, J. F. (2000). *Surf. Interface Anal.*, *29*, 115.

[24] Devaprakasam, D., Sampath, S., & Biswas, S. K. (2004). *Langmuir*, *20*, 1329.

[25] Thomsen, L., Watts, B., Cotton, D. V., Quinton, J. S., & Dastoor, P. C. (2005). *Surf. Interface Anal.*, *37*, 472.

[26] Yasseri, A. A., Kobayashi, N. P., & Kamins, T. I. (2006). *Appl. Phys. A*, *84*, 1.

[27] Kim, J., Wong, P. C., Wong, K. C., Sodhi, R. N. S., & Mitchell, K. A. R. (2007). *Appl. Surf. Sci.*, *253*, 3133.

[28] Ulman, A. (1996). *Chem. Rev.*, *96*, 1533.

[29] Maege, I., Jaehne, E., Adler, H.-J. P., Bram, C., Jung, C., & Stratmann, M. (1998). *Prog. Org. Coat.*, *34*, 1.

[30] Li, Z. F. & Ruckenstein, E. (2002). *J. Colloid Interface Sci.*, *251*, 343.

[31] Ruckenstein, E. & Li, Z. F. (2005). *Adv. Colloid Interface Sci.*, *113*, 43.

[32] Liu, Y., Sun, D., You, H., & Chung, J. S. (2005). *Appl. Surf. Sci.*, *246*, 82.

[33] Levine, K. L., Tallman, D. E., & Bierwagen, G. P. (2008). *J. Mater. Proc. Technol.*, *199*, 321.

[34] Lamaka, S. V., Zheludkevich, M. L., Yasakau, K. A., Montemor, M. F., & Ferreira, M. G. S. (2007). *Electrochim. Acta*, *52*, 7231.

[35] Hu, J.-M., Liu, L., Zhang, J.-Q., & Cao, C.-N. (2007). *Prog. Org. Coat.*, *58*, 265.

[36] Zheludkevich, M. L., Yasakau, K. A., Poznyak, S. K., & Ferreira, M. G. S. (2005). *Corr. Sci.*, *47*, 3368.

[37] Zheludkevich, M. L., Serra, R., Montemor, M. F., Yasakau, K. A., Salvado, I. M. M., & Ferreira, M. G. S. (2005). *Electrochim. Acta*, *51*, 208.

[38] Bierwagen, G. P. (2001). *J. Coat. Technol.*, *73*, 45.