J Appl Electrochem (2008) 38:1363–1368
DOI 10.1007/s10800-008-9572-9

ORIGINAL PAPER

# Application of electrochemical noise to evaluate outdoor atmospheric corrosion of copper after relatively short exposure periods

**E. García-Ochoa · J. González-Sánchez · F. Corvo · Z. Usagawa · L. Dzib-Pérez · A. Castañeda**

Received: 23 November 2007 / Revised: 28 March 2008 / Accepted: 16 April 2008 / Published online: 29 April 2008

**Abstract** This study focused on the application of electrochemical noise to assess the protection level of corrosion products formed on copper during relatively short exposure time in different outdoor atmospheres. Electrochemical noise, cathodic reduction measurements and gravimetric (mass loss) analysis were applied to copper samples exposed at urban and rural/industrial areas in Cuba for 4 months. Measurements of Electrochemical current noise indicated that the poorest protective corrosion products were formed on samples exposed to atmospheres with high concentration of $H_2S$ which agreed with the corrosion rate determined by mass loss and electrochemical chronopotentiometry (cathodic reduction). The electrochemical noise methodology proposed in this work showed acceptable and reproducible results by using an electrochemical cell in which the electrolyte was formed by a distilled-water wetted cloth in contact with the compounds present on a corroded metallic surface. This methodology indicated that the corrosion protection level of the corrosion products formed on copper is related to the corrosivity of the atmosphere.

**Keywords** Electrochemical noise · Atmospheric corrosion · Cathodic reduction · Corrosion products

## 1 Introduction

The atmospheric corrosion of copper has been studied extensively due to the vast use of this metal in many engineering applications including the electrical-electronic industry [1–4]. Copper corrosion products formed during field exposure have been analyzed using several techniques, including X-ray Photoelectron Spectroscopy (XPS), Infrared Reflection Absorption Spectroscopy (IRAS), Auger Electron Spectroscopy (AES) and X-ray Diffraction (XRD) [5–7]. However, these techniques are limited by their non-quantitative nature. It has been reported that during outdoor exposure copper develops patinas composed of cuprite $Cu_2O$, brochantite $Cu_4SO_4(OH)_6$, antlerite $Cu_3SO_4(OH)_4$, posnjakite $Cu_4SO_4(OH)_6 \cdot H_2O$, and atacamite $Cu_2Cl(OH)_3$ [4].

The majority of research carried out on the study of copper patinas has been focussed upon those formed by long atmospheric exposures over a number of years but little attention has been paid to the analysis of copper patinas formed during short exposure periods such as a 1–6 months. This is important in terms of understanding the initial stages of copper corrosion and patina formation and could also be useful for determining atmospheric corrosivity if evaluations are carried out at different sites. During atmospheric corrosion the formation of the surface

---

E. García-Ochoa · J. González-Sánchez (✉) · L. Dzib-Pérez
Centro de Investigación en Corrosión, Universidad Autónoma de Campeche, Av. A. Melgar s/n, Col. Buenavista, C.P. 24030 Campeche, Cam, Mexico
e-mail: jagonzal@uacam.mx

F. Corvo
Instituto de Ciencia y Tecnologia de Materiales (IMRE), Universidad de la Habana, Cuba, calle zapata esq a G, Vedado, Plaza, Ciudad de la Habana, Cuba

Z. Usagawa
Centro de Estudios Ambientales de Cienfuegos, Carretera Castillo Jagua-Juraguá, km 1½, Cienfuegos, Cuba

A. Castañeda
Grupo de Corrosión, Dirección de Química, Centro Nacional de Investigaciones Científicas, Ave. 25 y calle 158, Cubanacan, Playa, Ciudad de la Habana, Cuba

electrolyte takes place through the accumulation of contaminants deposited on the surface and the wetting effect of rain, humidity and other water deposition processes. Under these conditions, a layer of corrosion products is formed; the protective properties of this layer depend on its chemical composition, compactness, structure, porosity and on the type and quantity of contaminant deposition.

Linear Sweep Voltammetry and cathodic reduction (Chronopotentiometry) are two electrochemical techniques that have been successfully used for the quantitative analysis of copper oxides formed during the corrosion of this metal [8, 9]. These are powerful techniques for determining corrosion product composition and have been utilized to assess the atmospheric corrosion rate of different metals [10–12]. Electrochemical noise (EN) measurements offer a new approach to study atmospheric corrosion as it is capable of assessing the protective properties of the corrosion products formed on metal surfaces. In the present case this technique involved the recording of current fluctuations taking place between two similar electrodes separated by a wetted cloth; one electrode is the surface under evaluation whilst the other is a clean non-corroded copper sample. The current or potential fluctuations measured are associated with the electrochemical behavior of the corroded electrode. It can be considered as a non-intrusive technique as the metal sample is not perturbed by an electrical signal. The EN methodology has been applied successfully for the study of atmospheric corrosion in artificial and natural atmospheres giving information on the severity and morphology of the attack as a function of time [13, 14].

In this study we focused on the application of EN measurements to assess the protection level offered by corrosion products formed on Cu in different outdoor atmospheres during a relatively short exposure period. Chronopotentiometric measurements (Cathodic reduction) were conducted to determine the presence of different copper compounds forming the patinas. The results from EN measurements in terms of the standard deviation of the current noise signal ($\sigma$I) were consistent with the corrosion rate obtained from mass loss measurements and cathodic reduction applied to copper samples after exposure in urban, rural/industrial and hot spring atmospheric conditions in Cuba.

## 2 Experimental

### 2.1 Exposure conditions

Copper plates of 150 × 100 mm and 1 mm thick were exposed outdoors at different sites. We selected five sites distributed in an area of 6 $km^2$ in which there are urban, rural/industrial and hot spring conditions. The samples were exposed for 4 months starting on February 2006 (winter) up to June 2006 (summer) at a small rural community located in the Cuban central province of Cienfuegos which is about 30 km from the southern shoreline. Thus the influence of airborne salinity is not important.

The most important economic activity of this town is the sugar processing industry, which together with every day transportation activities is the main source of air contaminants.

Samples were placed at 3 m from the ground and oriented toward the nearest pollution sources. Differences between relative humidity, rain and temperature are not considered due to the relatively small area. The main differences concern air pollution.

The five selected exposure points were numbered: as P2, P4, P5, P7 and P8, using this numbering code to identify the samples. Three copper samples were exposed in each site. Site P2 was located in a small urban area which is affected by small levels of contaminants produced by the sugar industry. This site is surrounded by cane plantations which are irrigated with treated wastewater coming from the sugar distillery and yeast production. P4 was an urban site located near a road, without direct influence of any pollutant source.

The site P5 was the most exposed to gaseous emissions produced by vehicles and trains transporting sugar cane to the sugar mill. It is located about 1 km to the southeast of the waste storage deposit, but not in the predominant wind direction.

P7 was located about 600 m from the waste storage deposit, near to the alcohol distillery.

Finally P8 was located about 100 m away in the southern direction from the alcohol distillery and about 300 m from the yeast factory. The highest gaseous emissions are expected for this site, in which $SO_2$, $NO_x$, CO, $H_2S$ and volatile organic compounds have been reported.

After 4 months of exposure, the atmospheric corrosion rate of the copper samples was determined. Two samples from each site were subjected to gravimetric analysis. The third sample was subject to electrochemical cathodic reduction and electrochemical noise measurements.

### 2.2 Gravimetric analysis

The gravimetric evaluation was carried out using traditional weight loss methodology. Previous to exposure, samples were degreased with acetone, cleaned by immersing for 1 min in 30% nitric acid to eliminate all possible corrosion products, rinsed with distilled water and dried. Before exposure, samples were weighed with an accuracy of 0.0001 g. After exposure, corrosion products were mechanically removed by scraping without affecting the metal surface and afterwards the samples were immersed in a 10% sulphuric acid to remove completely the corrosion products. The samples were then rinsed with water, dried and weighed to evaluate the mass loss. Mass loss is reported in g $m^{-2}$ which is the conventional unit used in atmospheric corrosion studies.

### 2.3 Electrochemical noise

The EN measurements were conducted using a two working electrode assembly as shown schematically in Fig. 1.

The working electrode one (WE1) was a small area of the corroded copper plate, and a 2 $cm^2$ copper plate acted as working electrode two (WE2), which was ground to a 600 grit finish, washed and dried with acetone. An absorbent cloth of 2.2 × 2.2 $cm^2$ and 1 mm thick was positioned between WE1 and WE2. The cloth was moistened with 2 mL of distilled water which subsequently formed an aqueous electrolyte along with soluble components of the corrosion product films formed on the surface of each copper plate. The small quantity of water allowed the formation of an electrolyte representative of the environment to which the samples were exposed. Current noise measurements were carried out 20 min after the electrochemical arrangement was setup. EN measurements were performed with a ACM Gill DC instrument recording 2048 points taking one data point every 0.5 s. The procedure was repeated three times on each sample at different areas of the corroded surface.

The protection characteristic of the corrosion products formed on the samples was determined through electrochemical current noise using the standard deviation of the current noise signal "$\sigma$I", and the localisation index "LI".

Statistical analysis of the electrochemical noise signal is considered an easy way of obtaining information on the electrochemical behaviour of corroding metals [15, 16]. One of the most important statistic parameters is the standard deviation of the current noise signal (the square root of the variance) $\sigma$I the value of which is expected to increase as the corrosion rate increases as well as when the corrosion tends to be highly localised [16]. The other combined statistical parameter also used in the present study is the localisation index "LI" which is determined according to:

$$\mathrm{LI} = \frac{\sigma_{\mathrm{I}}}{\mathrm{I}_{\mathrm{RMS}}} = \frac{\sigma_{\mathrm{I}}}{\sqrt{\sigma_{\mathrm{I}}^2 - <\mathrm{I}>^2}} \qquad (1)$$

This parameter takes values from 0 to 1. When the value of LI is between 0.001 and 0.01, it indicates uniform corrosion, values between 0.01 and 0.10 indicate a combination of uniform and localised corrosion. Finally, when LI has values between 0.1 and 1.0 it represents predominately localised corrosion processes [17].

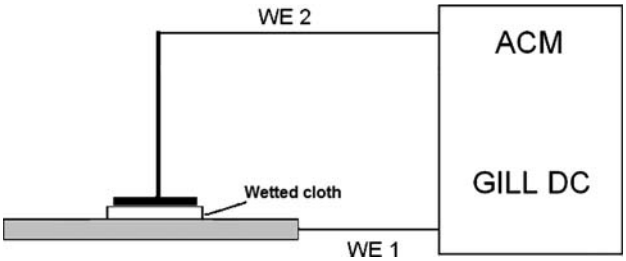

**Fig. 1** Set up for the electrochemical noise measurements

### 2.4 Cathodic reduction tests

After the electrochemical noise measurements the samples were subjected to cathodic polarisation (Chronopotentiometry). A conventional three-electrode electrochemical cell was utilised. The flat Cu samples acted as the working electrode. A platinum mesh of 1 $cm^2$ was used as the auxiliary electrode and a saturated calomel electrode (SCE) was used as reference, to which all potentials are referred. A surface area of 1 $cm^2$ of the copper specimens was delimited by a rubber seal over which a glass cell with an open base of 1 $cm^2$ was fixed. The cell was 12 cm high with an increasing square transverse area with an open end of 3 $cm^2$. The cathodic polarisation involved the application of a current density of 1.25 mA $cm^{-2}$ in a 0.1 M KCl solution purged with ultrapure nitrogen gas. The reagents used to prepare the electrolyte were of analytical grade. The tests were carried out three times at different areas on each sample using fresh deoxygenated KCl solution. Chronopotentiometry was conducted using a Potentiostat/Galvanostat (EG&G model Versastat) controlled by a personal computer.

## 3 Results and discussion

### 3.1 Weight loss measurements

The corrosion rates of copper samples were calculated by considering the total exposed area and 4 months testing. The corrosion rates obtained were: 2.5, 6.0, 10.4, 16.2 and 26.0 g $m^{-2}$ for samples P4, P5, P2, P8 and P7 respectively. g $m^{-2}$ is the commonly used unit in atmospheric corrosion studies which normally indicate the mass loss in 1 year; in the present case the time was 4 months.

### 3.2 Electrichemical noise

Current time series obtained from electrochemical noise measurements conducted on samples exposed at sites P7, P2 and P4 are presented in Fig. 2. On these samples the corrosion rate determined by mass loss could be classified as high, medium and low respectively. The current time series clearly indicate that the signal amplitude dramatically changes depending on the protection offered by the corrosion products formed. The current time series from sample P7 which presented the highest corrosion rate showed the highest signal amplitude and, conversely, signals with the lowest amplitude corresponded to sample P4 which presented the lowest corrosion rate [18, 19].

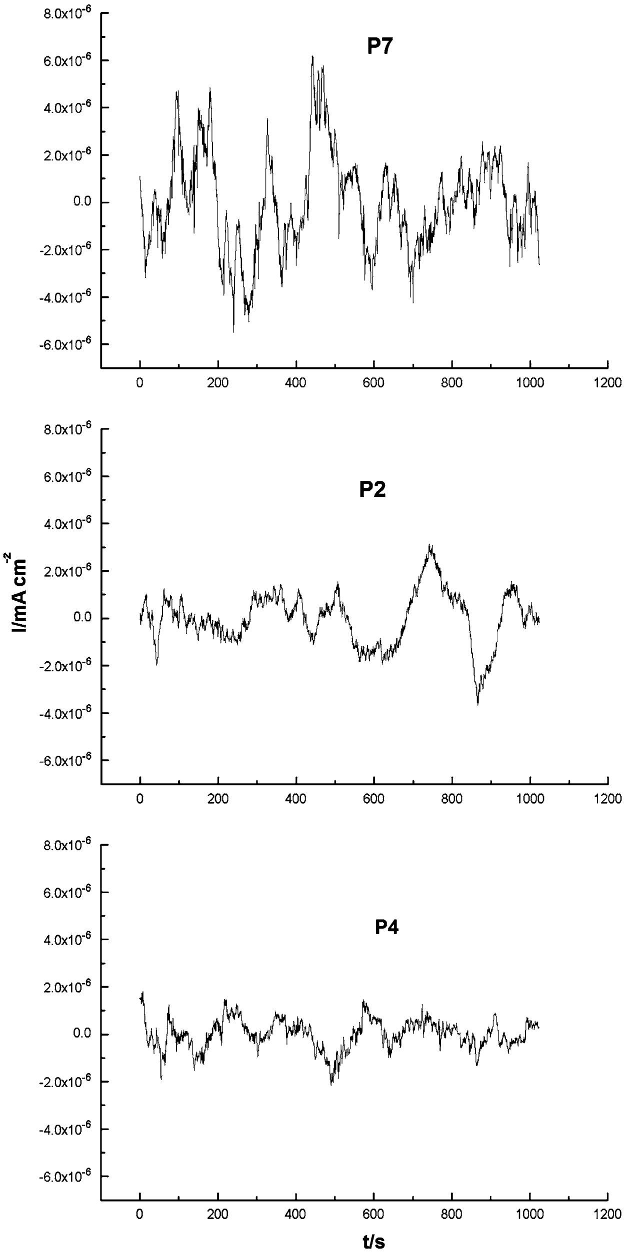

**Fig. 2** Current time series from samples exposed at: (**a**) P7, (**b**) P2 and (**c**) P4

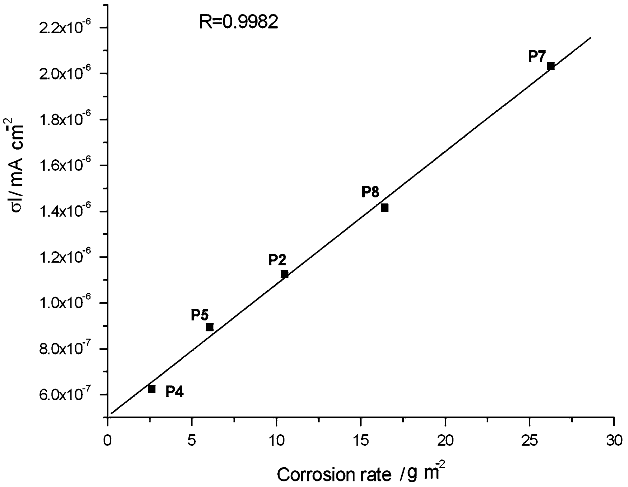

**Fig. 3** Standard deviation in current σI versus corrosion rate (g m$^{-2}$) determined by mass loss

This result is supported by the fact that current noise signals contain information about faradaic phenomena taking place during the corrosion process [20].

Figure 3 shows a plot of σI versus corrosion rate (g m$^{-2}$) determined by mass loss measurements. The good correlation presented by these two parameters indicates that samples located at site P7 have the highest corrosion rate in terms of mass loss and the highest σI, whereas samples located at site P4 have the lowest values.

Samples with the highest corrosion rate also had corrosion product layers with the poorest protective properties as indicated by the values of σI. This result agrees with the fact that these samples were located at sites P8 and P7 with high atmosphere aggressiveness due to the presence of $H_2S$. Excellent agreement exists among literature reports concerning short time exposure of copper to $H_2S$ containing atmospheres [21, 22]. It has been demonstrated that sulphidation of copper mainly leads to the formation of $Cu_2S$, and that sulphidation is very sensitive to changes in relative humidity.

The corrosion protection capacity of the corrosion product layers formed on metals exposed to outdoor conditions depend upon the characteristics of the atmosphere. Tran et al. [21] found that the tarnish layers formed on copper exposed to moist air containing $H_2S$ at concentrations close to the real outdoor or indoor conditions are a mixture of copper oxides and copper sulphides.

Figure 4 presents the values of LI plotted versus values of corrosion rate determined by the gravimetric method. All values of LI were lower than 0.01 which indicates that the corrosion was uniform.

The value of LI was higher for plates located at sites P8 and P7 in which the Cu samples have higher corrosion rates. The LI values indicate that the corrosion product layer

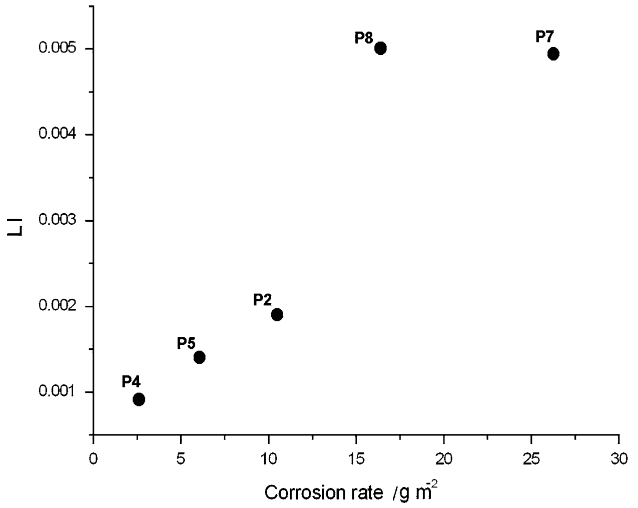

**Fig. 4** Localisation index IL versus corrosion rate (g m$^{-2}$) determined by mass loss

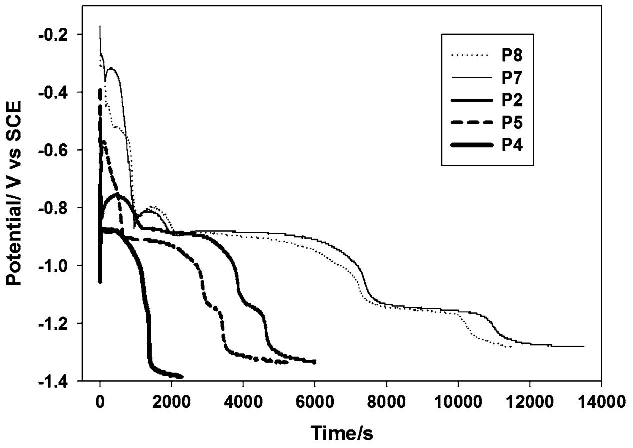

**Fig. 5** Potential–time curves recorded by Chronopotentiometries for Cu samples in 0.1 M KCl. Current density: −1.25 mA cm$^{-2}$

formed is less protective inducing a corrosion process that is more localised than uniform. It has been reported that high relative humidity enhances the rate of growth of both $Cu_2S$ and $Cu_2O$, but the growth rate of copper oxides is more sensitive to humidity than that of copper sulphides, leading to corrosion products enriched in copper oxides at relative humidity around 80% [21]. In Cuba the average relative humidity during the exposure period was around 80%.

An important aspect of the electrochemical noise measurements was that consistent results were obtained with the use of a non-conventional electrochemical cell. Although this technique gives no information on the chemical composition of the corrosion products it gives valuable information on the protective characteristic of the corrosion product layers.

### 3.3 Cathodic reduction measurements

The results of cathodic reduction tests on copper samples in 0.1 M KCl are presented in Fig. 5 as Chronopotentiometry plots for samples exposed for 4 months at the different sites.

The corrosion rates obtained from the cathodic reduction tests were 4.6, 11.7, 16.3, 28.12 and 30.3 g m$^{-2}$ for samples P4, P5, P2, P8 and P7, respectively, showing the same tendency as that obtained from mass loss measurements; the highest corrosion rate corresponded to P7 and the lowest to sample P4.

Considering that the reduction of both CuO and $Cu_2O$ occur almost simultaneously in neutral 0.1 M KCl solution as reported by Nakayama et al. [8, 9] at a potential around −860 mV versus SCE, a corrosion rate was determined and expressed in units of g m$^{-2}$.

As shown in Fig. 5, a single plateau associated with the reduction of corrosion products is observed at around −860 mV in the curve of sample P4. The reduction plateau seen after the single plateau was due to hydrogen evolution [23].

In curves for samples P5 and P2, the delay in potential decay after the plateau of around −860 mV becomes increasingly greater and the appearance of another plateau around −1,145 mV is more evident. Finally in the curves for samples P8 and P7 a plateau at around −1,146 mV is clearly observed. This plateau has been well defined and is associated with $Cu_2S$, which is a crystalline compound that has a more negative reduction potential than the copper oxides [7, 23]. The cathodic reduction results indicated a major presence of sulphur compounds in samples P8 and P7 compared to samples P2 and P5 with an incipient presence in sample P4. This coincides with the description of the characteristics of these sites.

One reason for this behaviour of the corrosion products is that the formation of $Cu_2O$ is a pure electrochemical process which needs a critical amount of surface water, whereas the formation of $Cu_2S$ is a mixed electrochemical and purely chemical process. The presence of $H_2S$ and changes in relative humidity must involve the formation of non-uniform corrosion product layers thus changing their protective properties.

Taking into account that the exposure period was short, the formation of a highly protective patina was not possible.

## 4 Conclusions

The electrochemical noise technique was able to evaluate the protection level of corrosion products formed on copper samples during a relatively short exposure period to different outdoor atmospheres in terms of $\sigma$I and LI. These parameters showed a proportional relationship with the aggressiveness of the atmosphere.

The application of electrochemical noise using two electrodes offers the possibility of determining the sites where corrosion is more intense, the higher the amplitude of the signal, the higher the corrosion rate. This methodology permits evaluation using the natural surface electrolyte formed during atmospheric corrosion.

The three different methods used to evaluate the atmospheric corrosion of copper: gravimetric analysis, electrochemical noise ($\sigma$I and LI), and chronopotentiometry indicate the same pattern as a function of the exposure site.

Cathodic reduction measurements indicated that specimen P7 presented the highest corrosion rate followed by samples P8, P2, P5 and finally sample P4.

Using cathodic reduction it was possible to determine the presence of copper sulphide in the copper corrosion products, indicating the significant influence of $H_2S$ in the atmospheric corrosion of copper.

**Acknowledgements** The authors appreciate the contribution of C. Valdes and Y. Martin, E. Gonzalez and J. Perez (National Center for Scientific Research (CNIC), Havana City, Cuba). The authors thank Dr. David Greenfield (Sheffield Hallam University) for the revision and comments made to the manuscript.

## References

1. Lobnig R, Frankenthal R, Siconolfi D et al (1994) J Electrochem Soc 141:2935
2. Aastrup T, Wadsak M, Leygraf C et al (2000) J Electrochem Soc 147:2543
3. Morcillo M, Almeida E, Marrocos M, Rosales B (2001) Corrosion 57:967
4. Nassau K, Gallagher KP, Miller EA, Graedel TE (1987) Corros Sci 27:669
5. Strehblow H, Titze B (1980) Electrochim Acta 25:839
6. Persson D, Leygraf C (1990) J Electrochem Soc 137:3163
7. Itoh J, Sasaki T, Ohtsuka T (2000) Corros Sci 42:1539
8. Nakayama S, Kaji T, Shibata M, Notoya T, Osakai T (2007) J Electrochem Soc 154:C1
9. Nakayama S, Kimura A, Shibata M, Kiwabata S, Osakai T (2001) J Electrochem Soc 148:B467
10. Wall FD, Martinez M, Missert N, Copeland R, Kilgo A (2005) Corros Sci 47:17
11. Gamal A, Madhy EI (2005) Corros Sci 47:1370
12. Cox A, Lyon S (1994) Corros Sci 36:1167
13. García-Ochoa EM, Ramírez R, Torres V, Rodríguez FJ, Genescá J (2002) Corrosion 58:756
14. Torres V, Rodríguez FJ, García-Ochoa EM, Genescá J (2006) Anticorros Meth Mater 53:348
15. Eden DA, Rothwell AN (1992) Electrochemical noise data: analysis, interpretation and presentation. Corrosion/92; NACE International, Houston, TX, Paper No. 292
16. Cottis R, Turgoose S (1999) Electrochemical impedance and noise. NACE, Houston
17. Reichert DL (1996) In: Kearns JR, Scully JR, Roberge PR, Dawson JL et al (eds) Electrochemical noise measurements for corrosion applications. ASTM, Philadelphia
18. Uruchurtu J, Dawson JL (1987) Corrosion 43:19
19. Tan YJ, Bailey S, Kinsella B (1996) Corros Sci 38:1681
20. Garcia-Ochoa EM, Genescá J (2004) Surf Coat Tech 184:322
21. Tran TM, Fiaud C, Sutter EM (2005) Corros Sci 47:1724
22. Tran TM, Fiaud C, Sutter EM, Villanova A (2003) Corros Sci 45:2787
23. Watanabe M, Tomita M, Ichin T (2001) J Electrochem Soc 148:B522