Electrochemical behaviour of silica basic hybrid coatings deposited on stainless steel by dipping and EPD

Y. Castro a,*, A. Duran a, J.J. Damborenea b, A. Conde b

Article info

Article history:
Received 5 February 2008
Received in revised form 14 March 2008
Accepted 15 March 2008
Available online 26 March 2008

Keywords:
EPD coatings
Sol–gel
EPD
Electrochemical behaviour

Abstract

The aim of this work is the characterisation of the corrosion behaviour of stainless steel (AISI 304) substrates coated by dipping and electrophoretic deposition (EPD) from a sol–gel basic sol. Particulate silica sols (labelled NaSi) were prepared by basic catalysis from ethyltriethoxysilane (TEOS), methyltriethoxysilane (MTES) and sodium hydroxide. Coatings between 2 and 10 μm were prepared by using concentrated and diluted sols by dipping and EPD process and the corrosion behaviour of the coated substrates were studied through potentiodynamic and impedance spectroscopy measurements (EIS). Potentiodynamic studies of coatings produced by dipping reveal a strong dependence of the protective properties with the concentration of the sol. This behaviour was confirmed by EIS showing that only the coatings obtained from concentrated sol present enough protective properties. On the contrary, EPD coatings prepared from diluted NaSi sol showed an excellent corrosion resistance, maintaining a pure capacitive behaviour for long periods of immersion. EPD deposition is thus proposed as a good alternative method for obtaining thicker and denser coatings with good protective properties from dilute and stable sols.

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1. Introduction

Sol–gel process has demonstrated to be an effective route to prepare a great variety of materials and coatings at low cost and with very versatile applications in photocatalysis [1], sensors [2,3], self-cleaning coatings [4], antibacterial [5,6] and photovoltaic cell [7]. An increasing field of application of sol–gel coatings is the corrosion protection of metallic substrates [8–10]. The use of metals is restricted in applications where aggressive conditions can lead to corrosion, oxidation or wear, this including some applications in building, automotive, aircraft and home electrical appliances industries. Inorganic silica sol–gel coatings obtained by dipping provide good protection against oxidation [10], but the corrosion protection is not enough in aqueous solutions [11]. The presence of micro-cracks and pores is the major problem of this kind of systems. On the other hand, methyl containing-hybrid coatings have demonstrated to be a good barrier against electrolytic corrosion [12]. The presence of organic groups increases the ductility and the thickness of the coating both increasing the protective behaviour.

The best method to produce homogeneous sol–gel coatings is the dipping process but the maximum thickness attainable is quite low, below 400 nm for pure inorganic coatings and around 2–3 μm for hybrid ones. Highly concentrated sols and high withdrawal rates lead usually to non-homogeneous coatings with important border effects. The possibility of increasing thickness is important for enhancing the barrier properties for corrosion. An alternative method of deposition, widely applied for ceramic suspensions, is the electrophoretic deposition (EPD) that permits to obtain higher concentrations of oxides or sol–gel prepared colloidal particles [19] nor real applications from ceramic suspensions.

Some authors report the use of EPD from sol–gel suspensions [17,18]. However, they usually study the EPD from aqueous suspensions of oxides or sol–gel prepared colloidal particles [19] nor real sol–gel particulate sols. Hence, the sintering of the deposits needs temperatures higher than 1000 °C, thus impeding the use of most common metals as substrates.

The first paper reporting a silica coating produced by EPD using a sol–gel particulate sol appeared in 2000 [20]. The different parameters and conditions involved in the preparation of the sols (stability, atmospheric contact, water contact, pH, etc.) and the optimised deposition conditions (time, current density, potential, etc.) have been determined for these sols. On the other hand, the protective behaviour of dipping and EPD coatings was studied through potentiodynamic tests and important differences in...
the protective character were detected [21]. However, the mechanism implicated in the corrosion process has not been studied yet.

The aim of this work has been to compare the electrochemical behaviour using impedance spectroscopy measurements onto stainless steel AISI 304 of silica hybrid coatings produced from basic catalysed sols by dipping and EPD. The mechanism involved in the corrosion process and the effect of coatings density are studied to elucidate the differences observed for coatings prepared by both methods.

2. Experimental

Silica sols (NaSi) were prepared by basic catalysis. Tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) were used as sources of silica and sodium hydroxide (NaOH) as catalyst. The synthesis process is described by Jonschker et al. [22]. All the process was performed under stirring, reflux and N2 flow, maintaining the sol under 5°C and preserved from atmosphere contact. The final concentration of silica was 267 g/l and the composition 94% SiO2–6% Na2O. The sol consists on a suspension of nanoparticles of size below 10 nm and presents a low stability with time, with viscosities rising from 16 to 100 mPa s in 1 h. Thus, the initial sol was diluted with absolute ethanol up to 188 g/l and stored in closed condition at 5°C and preserved from atmosphere contact. The sol under 5°C was diluted with absolute ethanol up to 188 g/l and stored in closed condition at 5°C and preserved from atmosphere contact. The sol under 5°C was diluted with absolute ethanol up to 188 g/l and stored in closed condition at 5°C and preserved from atmosphere contact. The sol under 5°C was diluted with absolute ethanol up to 188 g/l and stored in closed condition at 5°C and preserved from atmosphere contact.

Glass-slides and AISI 304 steel substrates were used to prepare dipping and EPD coatings. Glass substrates were cleaned in ultrasonic bath with ethanol. Steel substrates were cleaned with a commercial alkaline solution (P3Emalan5668: P3Emalan0469, Miele, Germany) for 5 min and subsequently washed with deionised water at 60 and 25°C.

Dip-coatings were prepared from NaSi sols with 267 and 188 g/l onto glass slides and stainless steel AISI 304 with withdrawal rates up 45 cm/min to obtain coatings with thicknesses between 5 and 2 μm, respectively. However, dip-coatings thicker than 3 μm presents border defects and lack of homogeneity, visible by optical inspection.

EPD coatings were deposited in galvanostatic conditions using the diluted sol, 188 g/l, and using the AISI 304 steel as working electrode and graphite as counter-electrode. A potentiostate–galvanostate AMEL 551 (Italy) was used as power sources. EPD tests were performed applying a constant current density of 0.6 mA/cm² and varying the deposition time from 10 to 45 min. This process was performed in closed condition under N2 reflux and maintaining the sol at 5°C.

The coatings produced by both methods were dried at room conditions and sintered at 500°C for 30 min in air.

The thickness of coatings was measured on glass substrates with a profilometer (Talystep, Taylor Hobson, UK), and by gravimetry for coatings onto stainless steel.

Direct current and alternating current electrochemical techniques have been used to evaluate the corrosion behaviour of the coatings, using a conventional three electrodes cell; with a saturated calomel electrode as reference, a rolled platinum wire as counter electrode, and 1 cm² of the material under study as working electrode. The three electrodes were connected to a Gamry CMS 105 potentiostatic card.

Two types of DC measurements were used. Firstly, the electrochemical potential reactivation test–EPR- was performed on the bare surface of the dip-coated specimens to determine the degree of sensitisation induced on the steel substrate by the sintering process. This test was performed in a solution of 0.5 M H2SO4 + 0.01 M KSCN according to the standard ASTM G108. Secondly, anodic polarisation curves were performed in 3.56 wt.% NaCl aqueous solution at a sweep rate of 0.16 mV/s, starting the curve at a potential at least 300 mV/SCE below the OCP.

Electrochemical impedance measurements (EIS) were performed using sine wave signals of 10 mV amplitude and a frequency sweep from 50 kHz to 10 mHz. The measurements were made at the corrosion potential and each value was the mean of five measurements in a logarithmic sweep of frequencies (10 points per logarithmic unit).

3. Results and discussion

3.1. Effect of sintering treatment on steel substrates

In order to evaluate potential damages induced to the substrate by the sintering process, EPR test was performed on specimens without any coating but undergoing the same heat treatment than the coated samples [24,25]. The heat treatment applied to sol–gel coatings for sintering might affect the structure of the metal substrates. This effect is quite obvious for many authors when working with coatings for aluminium alloys, but quite often, its influence is not taken into account when the substrate is a 304 stainless steel, forgetting that this steel might also experience a sensitization that is not taken into account when the substrate is a 304 stainless steel, forgetting that this steel might also experience a sensitization that is not taken into account when the substrate is a 304 stainless steel, forgetting that this steel might also experience a sensitization that is not taken into account when the substrate is a 304 stainless steel, forgetting that this steel might also experience a sensitization that is not taken into account when the substrate is a 304 stainless steel, forgetting that this steel might also experience a sensitization that is not taken into account when the substrate is a 304 stainless steel, forgetting that this steel might also experience a sensitization that is not taken into account when the substrate is a 304 stainless steel, forgetting that this steel might also experience a sensitization that is not taken into account when the substrate is a 304 stainless steel, forgetting that this steel might also experience a sensitization that is not taken into account when the substrate is a 304 stainless steel, forgetting that this steel might also experience a sensitization that is not taken into account when the substrate is a 304 stainless steel.
Figure 2. Potentiodynamic curves of NaSi coatings with different thickness obtained by dipping using the concentrated and diluted sols.

Figure 3. Potentiodynamic curves of uncoated AISI 304 with and without sintering process compared with a coating of 2 μm obtained by dipping using the diluted sols.

Figure 4. Impedance spectroscopy measurement of NaSi coating with 3 μm of thickness obtained by dipping using the concentrated sol.

to this heat-treatment. Coated areas were used to study the protective properties of the coatings while bare zones were tested to evaluate the degree of sensitisation induced by the sintering process. In Fig. 1a are gathered some of the EPR curves, obtained on different specimens. As observed, for most cases the ratio between the reactivation current density $I_r$ and the activation current density $I_a$ ranges about 0.001–0.006 revealing a low degree of sensitization of the substrate. Fig. 1b shows that the sintering process has only induced slight changes in corrosion properties with respect to the untreated AISI 304. There is a slight increase of the passive current density of about half order of magnitude and a decrease of the pitting potential around 80 mV.

3.2. Electrochemical characterisation of coating produced by dipping

Dip-coatings were prepared using the concentrated and diluted solutions onto glass substrates and stainless steel AISI 304 varying the withdrawal rate. Coatings obtained onto glass slide were used to determine the thickness by profilometry. Maximum thickness of 2 μm was obtained from 188 g/l and coatings of 2.1 and 3 μm were prepared from concentrated sol.

Potentiodynamic curves reveal some differences depending on the concentration of the sol used to deposit the protective coatings, Fig. 2. Polarisation curves corresponding to coatings prepared from the concentrated sol (267 g/l) with 2.1 and 3.0 μm show a long passive range of about 600 and 800 mV length with low passive current densities about $10^{-10}$ and $10^{-11}$ A/cm². Both cases represent an improvement of about 400 mV for the breakdown potential and a decrease of between two or three orders of magnitude in the passive current density respectively to AISI 340.

Conversely, the results for the coating deposited from the diluted sol show a much shorter passive stage and higher current density compared to the there of coatings prepared deposited from the concentrated sol. Regarding the steel substrate Fig. 3, this coating does not supply any improvement. It’s steady state potential has shifted towards cathodic values and the breakdown potential is now placed at $-150$ mV/SCE, 50 mV, below the corrosion potential of the steel, without a significant decreasing of the corrosion rate.

Although polarisation curves of coated specimens do not supply quantitative corrosion rate, qualitative information can be obtained from studying the curve shape. The curves reveal that sol–gel layers exert a barrier effect isolating the metal substrate from the steel, reducing the active area exposed to the electrolyte. The passive current density is the result of current flowing through the bare steel placed at the bottom of pores or defects, which area is much smaller than the exposed area of the coated sample, and the ion movement forced through the sol–gel film. In this sense, the lower the value, the lower is the corrosion degradation of the system.

On the other hand, the breakdown potential supplies information about the resistance of the coating to ion movements through the film. In principle, higher values of the breakdown potential suggest that higher polarization is required to allow ion movement (this is, corrosion process) to take place. In this sense, coated steel is able to withstand higher polarizations than uncoated steel without experienced any damage. Obviously, this does not mean that the polarisation imposed was not causing degradation of the coating.

Potentiodynamic curves of the sol–gel coatings reveal a strong dependence of the protective properties on the concentration of the sol. Maximum thickness of 2 μm obtained by dipping from diluted sol is not enough for enhancing corrosion protection. On the other hand, the coatings obtained from the concentrated sol...
Fig. 5. NaSi coating, 3 μm thickness, deposited by dipping from the concentrated sol. (a) Equivalent circuit used to fit the spectrum. Experimental and fitted impedance spectrum, (b) 4 h, (c) 13 days of immersion.

Table 1
Experimental and fitted data for the NaSi coating, 3 μm thickness, deposited by dipping from the denser sol

<table>
<thead>
<tr>
<th></th>
<th>4 h</th>
<th>2 days</th>
<th>13 days</th>
<th>31 days</th>
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<td>Exp</td>
<td>Sim</td>
<td>Exp</td>
<td>Sim</td>
<td>Exp</td>
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<tr>
<td>$C_{\text{real}}$ (F cm$^{-2}$)</td>
<td>$4.9 \times 10^{-10}$</td>
<td>$8.1 \times 10^{-10}$</td>
<td>$5.2 \times 10^{-10}$</td>
<td>$2.6 \times 10^{-9}$</td>
<td>$5.8 \times 10^{-10}$</td>
</tr>
<tr>
<td>$R_{\text{po}}$ (Ω cm$^2$)</td>
<td>$2 \times 10^5$</td>
<td>$2.63 \times 10^5$</td>
<td>$1 \times 10^5$</td>
<td>$1.63 \times 10^5$</td>
<td>$2.9 \times 10^4$</td>
</tr>
<tr>
<td>$Q_{\text{dl}}$ (F cm$^{-2}$)</td>
<td>$5.5 \times 10^{-9}$</td>
<td>$1.2 \times 10^{-8}$</td>
<td>$1.45 \times 10^{-8}$</td>
<td>$1.1 \times 10^{-8}$</td>
<td>$3.9 \times 10^{-8}$</td>
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show an important dependence in the passivation current density but not in the breakdown potential for different thickness.

Impedance measurements performed during long immersion times reveal also differences on the behaviour of the specimens. These differences and the ability of the coatings to sustain long-term immersions will condition the corrosion resistance of the samples.

Coatings of two different thicknesses deposited from the concentrated sol show a response comprised by two time constants from the beginning of immersion, Fig. 4. Specimens coated with 3 μm describe a first time constant at high frequency range (10^2 to 10^5 Hz). The experimental value for the capacitance estimated from the slope of the impedance modulus is 4 × 10^{-10} F cm^{-2}. Such low value corresponds to the capacitance of a non-conductive coating and therefore it is related to its dielectric properties. At intermediate frequency range (10^{-1} to 10^2 Hz), a second time constant appears. In this frequency range the maximum of the phase angle has decreased and also the slope of the |Z| deviates slightly from
NaSi 188 g/l
H₂O/alcoxie = 1,18

Fig. 8. Evolution of the weight/area vs. time for NaSi 188 g/l at 0.6 mA/cm².

−1, (−0.76), therefore the experimental capacitance of this second time constant is about 5.5 × 10⁻⁹ F cm⁻². Despite being too low for a double layer capacitance it is within the range of possible values for an electrochemical double layer corresponding to the response of the substrate through the pores or defects existing in the sol–gel layer [26,27]. Their small size make the pore resistance still quite high (about 10⁻⁴ Ω cm² after 3 days of immersion) and the active exposed area is very small leading to a high impedance.

However, both time constants evolve rapidly at longer immersion times. After 13 days the high frequency time constant tends to vanish, shifting toward even higher frequencies placing the maximum of the phase angle out of the range of the equipment. As results the maximum plotted at medium frequencies domains the spectrum. It moves towards higher frequencies and becomes wider, covering a broader frequency range (10⁻² to 10¹ Hz). The value of the capacitance also increases from 10⁻⁹ to 1.45 × 10⁻⁸ F cm⁻² after three days in solution, and to 6.15 × 10⁻⁸ F cm⁻² after 30 days. This progressive increase is the result of a decrease of the pore resistance and also an increase of the area of the substrate exposed [28].

These changes are also well resolved at impedance modulus Bode plot. The slope decreases rapidly from −0.93 to −0.83 within the first three days of immersion and reaches a value of −0.78 at the end of the impedance test (38 days).

All these changes in Bode plots (phase angle and |Z| plots) show that, the contribution of the substrate to the total impedance of the system becomes more important and evident with time, when the aggressive media is able to reach the substrate through the porosity existing in the coating. However, either the corresponding values obtained for the medium-frequencies time constant (10⁻⁸ F cm⁻²) and decline in the slope of |Z| shows the existence of a depression in the impedance diagram, which response could be associated either with diffusive behaviour of the coating or capacitive behaviour at the bottom of the defects.

The literature relative to degradation of polymer-coated metals assess that the impedance of these systems could be simulated by means of diverse equivalent circuits which represent the aging process of the coating [28,29]. The most common one is that one comprised by two Randles circuits. However, in some systems an arc (or fragment of it) is described at low frequencies. Thus, the low frequency arc does not cross the Z_real axe. This would mean that either the charge transfer resistance is too high or the presence of a diffusion phenomenon.

As it was described elsewhere [30], the impedance diffusion of the charge carriers can be also be fitted by a CPE with n deviated from 0.5 connected in parallel to a diffusion resistance, R_diff, which represents the finiteness of the length of the diffusion path. Depending on the type of coating it is not always possible to measure the resistance for low frequencies and then, the R_diff becomes very large (infinite) showing that diffusion path is very long compared to the diffusion rate/coefficient of the charged species, which can be interpreted as an increasing density of the medium in which the diffusion takes place. In this case, the resulting equivalent circuit is the one described in Fig. 5. By using this equivalent circuit a good agreement between experimental and modelled data is achieved with very low relative errors assigned to each parameter (<2%), Table 1.

In the same figure, it is shown that the most common equivalent circuit used to fit the response of damage coatings leads to a just slightly worst fitting-curve modelled 1, but the relative error corresponding to the R_diff is as high as 35%. This result suggests that the second time constant placed at medium-low frequencies is rather due to a diffusional response than a resistive one.

The specimens coated with a thinner layer, 2.1 μm (Fig. 6) show from the beginning of the immersion a time constant at high-intermediate frequencies (10 to 10⁵ Hz) which capacitance, estimated from the experimental values, increases from 10⁻¹⁰ F cm⁻² obtained during the first week of immersion to 10⁻⁹ F cm⁻² for the rest of the test (36 days).

As in the previous case, this value corresponds to the dielectric properties of the sol–gel coatings. However, in contrast to the specimen of 3 μm thickness, in this case the second time constant...
does not plot a capacitive arc but in the $|Z|$ of impedance versus the frequency, the diagram shows a linear stage with a slope of $-\frac{1}{2}$. This slope remains practically constant for 7 days, showing a diffusive response. At longer immersion times, the slope continues decreasing, ending with a value about $-0.32$ for 36 days of test. This slope decrease indicates that the response changes from diffusive to resistive.

Basically both coatings have the same behaviour. For both, the response of the substrate domain the spectra when immersion time increases. The differences in the shape of the Bode plots at intermediate-low frequencies are a consequence of the different morphology of the pores or defects existing in the coating [31,32]. While for the thicker coating (3 $\mu$m), the diffusive reveals as an arc, in the thinner film the $|Z|$ Bode plot shows at low frequency a linear stage with a slope of $-0.5$, characteristic of diffusion process at infinite layer.

The coating deposited from the NaSi sol (188 g/l) with thickness of 2 $\mu$m revealed the same type of behaviour but highlighted with respect to the denser sol. As observed in Fig. 7 after 15 min of immersion the Nyquist plot already describes a linear stage with a slope of 1, which corresponds to a diffusion tail. Bode plots corroborates this response by means of the characteristic value of 45° in the phase angle and the slope of 0.5 at the $|Z|$ vs. frequency plot. Thus, from the beginning of the test, the main contribution comes from the substrate, leaving the high frequency time constant corresponding to the coating out of the diagram. This means that signal flows through the less resistive paths behaving as a porous electrode. However, as the movement of the species through these paths is still hindered slowing the rate of the cathodic reaction down, the response is plotted like a diffusion tail rather than a capacitive arc related to the double layer capacitance of the bare substrate at the bottom of the defects.

With time this response is even better resolved since the pore resistance decrease from $10^4$ to $10^3 \Omega \cdot cm^2$. Besides, the slope increases from $-0.5$ to $-0.69$. This increase might suggest a change from a diffusive behaviour process in an infinite layer at 15 min to another taking place in a finite layer after 2 days of immersion.

**Fig. 11.** Fitted impedance spectrum of the NaSi coating of 4.3 $\mu$m deposited by EPD deposition: (a) 4 days; (b) 28 days.
Fig. 12. Impedance measurement of the coating with 7 μm of thickness obtained by EPD: (a) Bode plots; (b) Nyquist plot; (c) a close up of the squared area of the Nyquist plot.

Therefore, for the layer obtained from the diluted sol impedance diagrams show a response typical for porous electrodes. Although initially the corrosion rate might be slow because the corrosion reactions are limited by the access of the oxygen to the cathodic areas placed at the bottom of the defects, the damage is taking place and with time it grows and progresses either through the coating/substrate interface or into deeper areas of the substrate.

The results show that the dip-coatings obtained from the concentrated solution have a better behaviour than those from the diluted one. The dilution of the sol likely increases the coating porosity and the number of the defects.

3.3. Electrochemical characterisation of EPD coating

Although the corrosion behaviour of coatings prepared from concentrated sol is better than performance of diluted sol coatings, the stability of concentrated sol (NaSi 267 g/l) is low and evolves quickly with time and atmospheric contact. This ageing process is very difficult to stop even maintaining the sol under controlled conditions. The dilution of the sol with ethanol up to 188 g/l retards the gelling process and the viscosity keeps constant around 4 mPa s for ∼96 h approximately at 5 °C.

Therefore EPD process was considered to obtain more compact coatings from diluted sol. This process is a well-known method for preparing coatings and self-supported layers in ceramics field but it had not been used on the particulate sol–gel suspension [20]. The deposition is the result of the impact of these nanoparticles against the electrode of opposite sign when an electric field is applied to the suspension between two electrodes. This effect produces denser coatings by packing the particles onto the steel surface.

EPD tests were performed for 188 g/l sol at a current density of 0.6 mA/cm² and varying deposition time from 10 to 45 min (Fig. 8). The deposited mass slowly increases up to deposition time of 20 min, but there is an important increase from t > 20 min.

EPD-coatings with thickness of 4.3, 4.8 and 7.2 μm, indicated with a red circles in the plot, were selected to be studied of corrosion protective layers.

Potentiodynamic curves performed in sodium chloride solution revealed a passive behaviour characterised by a nearly vertical anodic branch with a passive current density ranging from 1 × 10^{-11} to 1 × 10^{-10} A/cm², Fig. 9. However, it also reveals that the length of the passive stage depends on the coating thickness. In general, the specimens with a thickness about 4 μm depict longer passive stages than those with 7 μm of thickness. This behaviour observed in the thicker coatings can be related with the appearing of defects.

These differences in potentiodynamic curves are confirmed by the impedance measurements, since at longer immersion time all the specimens evolve differently.

Fig. 13. Polarisation curves of two coatings obtained by dipping and EPD process with 3 and 4.3 μm of thickness, respectively.
Electrochemical impedance spectra of the specimens with lower thickness, 4.3 μm, describe just a time constant for four days, Fig. 10. The high value of $|Z|$ reached at low frequencies together with the value of the slope close to $-1$, suggest a pure capacitive behaviour typical for a dielectric coating behaving as a barrier. The capacitance estimated from the Bode plots is about $10^{-9}$ F cm$^{-2}$.

Despite the general shape of the $|Z|$ Bode plots were not changing significantly for 7 days, the magnitude of the impedance slightly decreases as the capacitance becomes slightly larger. These hardly appreciable changes are consequence of the small size of the porosity of the coatings, which resistance is still very high being invisible for the perturbation signal.

After 11 days in solution two time constants are already visible in the Bode plot, and get resolved even better with longer immersion times. These two time constants appear clearly separated at the phase angle Bode plot. A maximum related to the contribution of the coating locates at higher frequencies, which shifts to even higher frequencies with time up to 28 days. Similarly, in the $|Z|$ plot the linear stage related to the capacitive behaviour (slope close to $-1$) get shorter. Additionally, a second time constant appears in the range from $10^{-2}$ to $10^{2}$ Hz as a second maximum at the phase angle plot and a second linear stage which slope deviates from $-1$ with time, reaching a value of $-0.6$ at the end of the test. This contribution corresponds to the response of the substrate through the pores, showing a diffusive response for the substrate. A similar behaviour is obtained for the coating with 4.8 μm (not shown).

Fig. 11 gathers the fitted data obtained by the same equivalent circuit described for the dipping coatings. As observed, there is a good correlation between the experimental and modelled data, as well as a good agreement for each parameter.
Conversely, the impedance response for thicker coatings hardly changes during the whole period of immersion, Fig. 12. From the very beginning the phase angle value is rather low for the whole range of frequencies and it is not possible to resolve the time constant related to the dielectric properties of the coating. Because the response of the system is mainly governed by the contribution of the substrate and coating capacitance is not measurable anymore at frequencies below 1 MHz.

For EPD thicker coatings the response of the system is neither capacitive nor resistive, but diffusive. From the beginning of the immersion the phase angle plots a value close to 45° characteristic of diffusion processes control. This is more clearly observed at the Nyquist diagram by means of a linear stage called diffusion tail. This response suggests that the corrosion process is occurring at the coating metal interface and the adhesion at the interface will decrease progressively because water soluble species might accumulate within the disbonding volume. The small size of the pores of the coatings allows the retention of the hydrostatic pressure which will result in coating deformation of rupture with time. Then, the pore resistance will become significantly smaller and the diffusion control is not longer observed in the Bode plots.

3.4. Electrochemical behaviour of coatings for EPD and dipping

Fig. 13 shows the polarisation curves of two coatings with similar thickness obtained (3/4 μm) by dipping and EPD process from concentrated and diluted sol, respectively. The passivity current density is very low in both cases, 10−11 A/cm², although the passive stage is longer for the EPD coating than for the coating obtained by dipping process, indicated a more dense coating and therefore a smaller density of defects. This behaviour was confirmed at long immersion time using the impedance spectroscopy (Fig. 14). For the beginning of the immersion time a pure capacitive behaviour was observed for the EPD coating respect to the dipping coating that present two-time constant. After 4 days of immersion, the EPD coating maintains the capacitive response. However for the dipping coating, the high frequency time constant has shifted even to higher frequencies, indicating an increase of the area of the substrate exposed or a major contribution of the substrate to the total impedance of the system. Finally, after 15 days of immersion, both coatings present two time constants, representing a similar porous resistance.

This study permit to confirm that the electrophoretic deposition is a good alternative method to perform thicker and denser coatings, as good protective properties, using more diluted solution, without problem of aging and stability.

4. Conclusion

Electrochemical characterisation of coatings above 2 μm prepared from NaSi concentrated sol reveals a very good anticorrosive behaviour confirmed by DC and EIS measurements. However, dip-coating obtained from dilution NaSi sol does not supply improvements respecting to bare substrate.

EPD coatings produced from diluted and stable NaSi sol reveal an excellent behaviour with acceptability response up to long periods of immersion in electrolyte 3.56 wt.% NaCl aqueous solution.

EPD is a good alternative process to produce thicker and denser coatings from dilute sols with good protective properties. EIS measurements performed for long exposure time show that the two time constants takes longer to appear for EPD coatings. And once they are clearly resolved either the response of the coating or the substrate contributes to the total impedance of the system until the end of the immersion tests, suggesting a denser structure and smaller size of the defects.

Acknowledgments

This work has been partially financed by EU BRITE Project No. BE-97-5111 and CICYT (MAT2006-04375).

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