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Electrochemical Behaviour of Silica Deposited on Stainless Steel by Electrophoretic Deposition

Ni Made Intan Putri Suari*
Delyana Ratnasari
Sahara Tulaini
W. Widiyastuti
Heru Setyawan
Department of Chemical Engineering, Faculty of Industrial Technology and System Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia
**e-mail:* madeintan@chem-eng.its.ac.id

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Abstract. The purpose of this paper is to evaluate the characteristics of corrosion protection of stainless steel substrates coated with silica by electrophoresis with pulsed direct current (PDC) and constant direct current (CDC) with anodization. Electrophoresis was carried out using silica sol from sodium silicate solution as an electrolyte solution. Stainless steel functioned as an anode and carbon as a cathode with a constant electrode distance of 2 cm. The amplitude, duty cycle, and anodization effect on stainless steel corrosion protection characteristics were evaluated. The samples were characterized by linear polarization and electrochemical impedance spectroscopy (EIS) to see the characteristics of metal corrosion protection and scanning electron microscopy (SEM) analysis to see the morphology of the coating. This study showed that PDC electrophoresis and CDC accompanied by anodization could obtain silica film with good corrosion protection characteristics (high pore resistance and low admittance). Linear polarization results showed that metal corrosion protection behavior was increased by anodization. Similar results were obtained by EIS analysis which showed that pore resistance increased by anodization. The highest pore resistance obtained by the constant current with anodization is 543 ohms, and the lowest admittance is 0.0217. Corrosion protection characteristics are also influenced by the amplitude and duty cycle during electrophoresis. Silica film with a high pore resistance and a low admittance were obtained at a frequency, amplitude, and duty cycle of 80 Hz, 0.5 volts, and 60%, respectively. The silica film produced by pulsed electrophoresis resulted in better coating characteristics than by constant current with anodization, which is seen from the pore resistance value and its admittance.

Keywords: Anodization, Carbon, Corrosion, Electrophoresis, Silica

INTRODUCTION

Corrosion, a degradation of a material by a chemical or electrochemical reaction with its environment, is a hazardous and costly issue for most metal equipment such as pipelines, bridges, and oil drilling platforms. A lack of knowledge hinders the ability to prevent failures. Degradation of underground pipes, for example, is influenced by the

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compositions, microstructures, and designs of materials, as well as by a raft of environmental conditions such as soil oxygen level, humidity, salinity, pH, temperature, and biological organisms (Li et al., 2015). Therefore, efforts must be made to improve the corrosion resistance of metals.

One material used as an anticorrosive coating was chromate. It has been used since a few years ago. Though currently, its use is restricted because it has high toxicity. A great effort was made to overcome this problem by producing a new protective coating with anticorrosive properties and good adhesion strength as well (Dalbin et al., 2005).

One of the materials used as an alternative coating is silica because it is quite simple to synthesize and has good compatibility with most coating materials (Yin et al., 2022). Much work has been done to study the corrosion properties of silica as an organic coating. Lu et al. studied the effects of the size of nano silica as well as of silica content on the corrosion resistance of a fluoropolymer-silica coating. It showed that silica with a mean diameter of 150 nm has the good dispersive capacity and corrosion protection (Lu et al., 2019). A silane-functionalized polybenzoxazine coating added with silica nanoparticles could improve the coating's corrosion resistance. They increased the barrier properties and anodic inhibition induced by forming passive Fe-silicate compounds (Zhou et al., 2014).

One method of coating is chemical vapor deposition. This method could produce a good coating that is large in coating thickness, uniform in distribution, and good in combination with the matrix (Liu, 2017). However, these processes need high temperatures. Air plasma spray is also one of the coating methods. Previous research about alumina-titania-based plasma sprayed coating obtained from nanostructure precursors has been done. Results indicate that nanostructured coatings produced from these precursors could improve performance (Marra et al., 2016). But these processes need a high temperature, and the materials are typically deposited as powder.

The other methods are dip coating and electrophoresis deposition (EPD). Stainless steel was coated with silica using sol-gel produced from tetraethoxysilane (TEOS), methyltriethoxysilane (MTES), and sodium hydroxide by dip coating methods and electrophoresis deposition. It showed that in terms of corrosion resistance, coating with EPD can produce a thicker and denser coating with better protection properties than dip coating when using a dilute and stable sol (Castro et al., 2008). In addition, the other advantages of the EPD method are that the costs are cheaper, more environmentally friendly, and the deposition rate is faster. Pulse electrophoretic deposition could reduce the particle size distribution in a suspension and produce a uniform particle layer (Naim et al., 2010).

Anodization, a process of metal oxide formation carried out with the help of electric currents, could produce pores in metal that can improve the performance of the material. Hexagonally ordered domain structures can be formed in anodic alumina films by repeated anodization and stripping of the porous oxide. The pore's density is initially high but decreases with anodizing time as dominant pores deepen. Very small pores exist in native oxide in air or nucleate after electropolishing. Pore growth may start when the electric field increases at the pore bottoms and acid dissolve the oxide locally (Li et al., 1998).

The previous study reported electrophoresis deposition of silica by the constant current on metal as the object. The silica film obtained could increase the corrosion resistance of the metal, but this method showed a deficiency: the lack of silica film density on the metal surface, and the film is less homogeneous (Suari & Manulang, 2011). However, it needs advanced research to improve the film homogeneity and the coating's strength, which affect the corrosion resistance of metals. Therefore, in this study, coating silica on stainless steel surface by pulsed currents electrophoresis deposition and providing anodization before constant current electrophoresis was carried out.

MATERIALS AND METHODS

The silica sol was made from a sodium silicate solution. Sodium silicate 28%wt was mixed with 1000 mL of demineralized water until a final concentration of 2.5%wt. Then the solution was mixed with cation resin and formed silicic acid with pH 2. The size of silica particles in sol was controlled by adding the silicic acid to the KOH solution at a constant rate and at a temperature of 60 °C. (Tsai, 2004). Furthermore, the silica sol was mixed with isopropanol and SiO_2 with a mole ratio of CH_3COOH: isopropanol: SiO_2 of 0.1938: 0.5048: 0.0028 (Plsko et al., 2014).

Anodization was carried out with oxalic acid as an electrolyte solution. Stainless steel plate (1.5 cm × 5 cm × 0.2 cm) was placed as the anode and a carbon plate as a cathode with a constant electrode distance of 2 cm. The two electrodes were connected to a DC power supply. The concentration of the electrolyte solution and the time of anodization were varied.

Electrophoresis was then carried out with DC current on the anodized stainless steel. The same steps were done for electrophoresis by pulsed currents by varying the amplitude and duty cycle of 0.1 volt - 0.6 volt and 30% - 80%, respectively, and without anodizing treatment.

Before anodizing and electrophorizing, stainless steel plates were cleaned from rust and dirt with an H_2SO_4 solution.

The corrosion protection characteristics of the formed silica films were analyzed by linear polarization and EIS. In this test, three electrodes were used. Stainless steel, which has been electrophoresed used as a working electrode, Ag/AgCl is used as the reference electrode, and platinum is used as the counter electrode. These three electrodes were dipped in 3.5% NaCl solution. In addition, SEM analysis was carried out on the anodized and electrophorized stainless steel.

RESULTS AND DISCUSSION

Before being used for electrophoresis, particle size distribution (PSA) analysis of sol silica was carried out to determine the particle size distribution of silica contained in the silica sol and its zeta potential value. From the PSA test performed, the particle size distribution was obtained at 144.5 nm with a zeta potential of -1.26 mV. Because the zeta potential was negative, it can be determined that stainless steel in the electrophoresis process is connected to the positive electrode (anode) and carbon as the opposite electrode (counter electrode) connected to the negative electrode (cathode).

The Physical Appearance and Norphology of Metal after Anodization

Anodization produced a thin white layer on the surface of stainless steel. Then electrophoresis was carried out on the anodized stainless steel. A transparent thin film was obtained on the electrophorized stainless steel surface. So physically, it appeared that stainless steel, which has been anodized, has the same color as the electrophorized stainless steel. Physically the appearance and the color of layers formed by variations of oxalic acid concentration were similar. The same results can also be seen in anodized stainless steel with the variation of time of anodization. The higher the anodizing time, the thicker layer could form (seen from the layer's color, which was increasingly visible with the increase of anodizing time), as shown in Figure 1. For electrophorized stainless steel without anodization, it appeared that the physical appearance was almost the same as stainless steel, which has not been treated because the color of the coating was transparent.

The pores on the surface of stainless steel after anodization with variations of oxalic acid concentration can be seen in Figure 2. From the figure, it appeared that the higher the concentration of oxalic acid, the more pores were formed. This is because the higher the concentration of the solution, the reaction that occurs at the interface of metal/solution becomes faster. The faster the reaction, the more pores form on the metal surface, and the metal surface looks rougher. Because the electrolyte solution used is an acid solution, the reaction that occurs is more directed to the formation of pores than the formation of an oxide layer on the stainless steel surface.

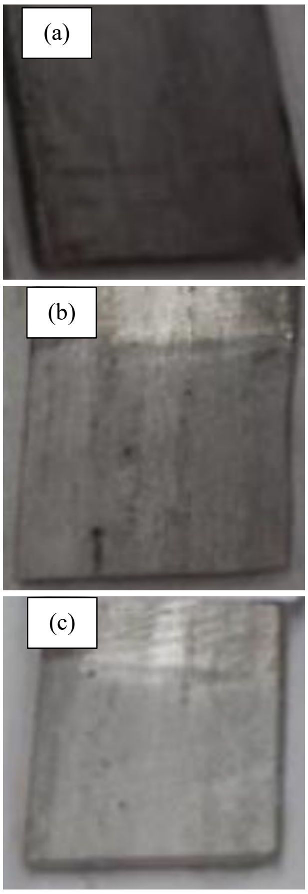

Fig. 1: Physical appearance of anodized stainless steel with variation of anodization time (a) bare steel; (b) 10 min; (c) 30 min

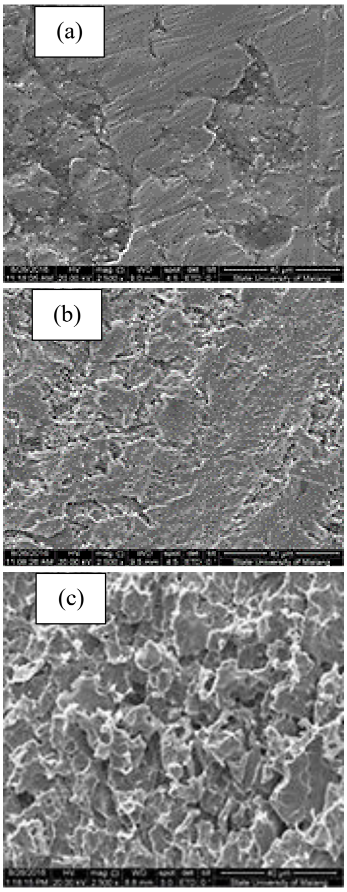

Fig. 2: SEM image of anodized stainless steel with the variation of oxalic acid concentration (a) bare steel; (b) 0.1 molar; (c) 0.5 molar

The Properties of Corrosion Protection and Characteristics of Silica Coating on Anodized Stainless Steel

A linear polarization analysis was carried out to determine the corrosion resistance of stainless steel coated with silica. From the polarization curve (Tafel plot) could be obtained the corrosion potential (E_{corr}) and corrosion current (I_{corr}) of each sample and bare steel. The obtained Tafel plot in Fig. 3 showed that the potential corrosion of coated stainless steel was shifted compared with bare steel. It can be seen that the higher the oxalic acid concentration, the more corrosion potential tends to be more positive (shifting to the right). The highest corrosion potential was obtained for samples that were anodized by the oxalic acid concentration of 0.5 molar. By increasing the oxalic acid concentration, the pores formed on the surface of stainless steel increased and became dense because reaction rate at the interface of metal/solution became faster. So, when it electrophorized, a more uniform and firmly silica layer was formed on the surface of stainless steel, and it obtained a higher resistance. The higher the resistance, the potentials needed for corrosion (E_{corr}) were increased, and the currents were decreased. The transferred currents become decrease because of a barrier from the silica film. The decrease of currents indicates that the reaction rate decreased, in this case, the corrosion rate, so the corrosion resistance was increased. Thus, it can be said that the higher the oxalic acid concentration during anodization, the higher corrosion resistance will be obtained.

EIS analysis was performed to evaluate the characteristics of the silica film. From EIS analysis, could be obtained impedance spectra for each sample. The impedance spectra were then fitted to obtain the electrical equivalent circuit model. The values of each parameter could be obtained from the equivalent circuit model. From the parameter values, the characteristics of the silica layer could be seen.

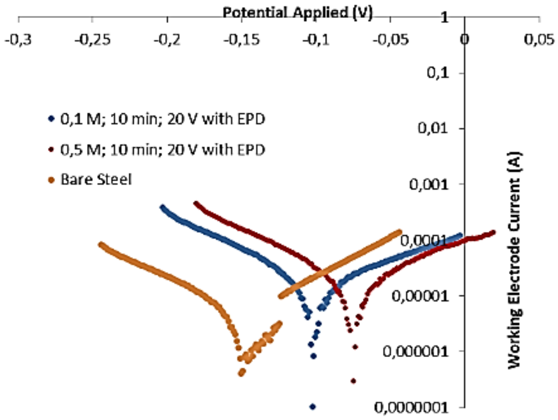

Fig. 3: Polarization curves of anodized stainless steel with electrolyte concentration variation

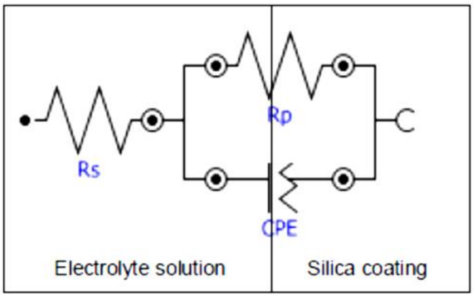

Fig. 4: Electrical equivalent circuit

The circuit model in Figure 4 is an equivalent circuit model suitable for fitting the data from the impedance spectra obtained in this study. Where R_s is resistance in the electrolyte solution, R_{pore} is used to determine the damaged area in the coating. *CPE* is a constant phase element containing element *Y0*, and *N*. *Y0* is an admittance showing the easiness of current flowing through the coating because of the pores, and *N* is a constant indicating whether the coating is a resistor or capacitor (Bonora et al., 1996). This equivalent circuit model shows that the coating acts as a barrier layer with a high coating resistance paralleled with a small coating capacitance. This showed that the formed silica coating has small pores, so the exposed area was small. This makes it difficult for water and oxygen molecules to penetrate into the silica coating and reach the metal surface. So the possibility of electrochemical reactions on metal surfaces was low. Quantitatively several parameters obtained by fitting the equivalent circuit model are shown in Table 1.

Table 1. Electrical equivalent circuit parameter for a constant time (10 minutes) and voltage (20 volts) of anodization by varying the oxalic acid concentration

Element	Bare steel	0.1 molar	0.2 molar	0.3 molar	0.4 molar	0.5 molar
R_{pore}	16	51	46.3	192	121	543
Y_0	0.0018	0.017	0.014	0.014	0.016	0.022

Table 1 showed that for all samples with varying concentrations, the value of R_{pore} was higher than the bare steel and tended to increase with the increase of oxalic acid concentrations. The highest R_{pore} was obtained at an oxalic acid concentration of 0.5 molar. This showed that a silica coating with a small pore was obtained at this concentration, and the electron transfer resistance was high, so only a few electrolytes penetrated through the pore (Pepe et al., 2006). Because corrosion is an electrochemical process involving the transfer of electrons, this showed that this coating has good corrosion protection characteristics. Similar results were obtained by polarization analysis, which at a concentration of 0.5 molar, a silica coating with the highest ability to inhibit corrosion was obtained.

Besides concentration, the anodization time also affected the corrosion protection characteristics of the silica coating shown in Table 2.

Table 2. Parameter value of polarization curve for a constant molarity (0.5 molar) and voltage of anodization (20 volt) by varying the anodization time

Parameter	Bare steel	10 min	15 min	20 min	25 min	30 min
Corrosion rate (mm/year)	0.27	0.22	0.19	0.22	0.077	0.32
E_{corr} (V)	-0.15	-0.76	-0.09	-0.08	0.097	-0.14
I_{corr} (A)	2.3×10^{-5}	1.9×10^{-5}	1.7×10^{-5}	1.9×10^{-5}	6.6×10^{-6}	2.8×10^{-5}
Polarization resistance(ohm)	1,200	1,479	1,579	1,737	3,094	1,589

From Table 2, it can be seen that the corrosion rate of anodized and electrophoresed stainless steel was lower than bare steel. The value tends to be smaller with the longer anodization time. Similarly, the corrosion current (I_{corr}) value tends to be smaller by increasing the anodization duration. In comparison, the corrosion potential (E_{corr}) and the polarization resistance tend to be higher by increasing the anodization time. This shows that a longer anodization time could produce a silica coating with good corrosion protection characteristics. It is because the pore formed on the metal surface were denser, so more silica could be attached to the metal. The highest corrosion potential and polarization resistance, with the lowest corrosion rate and corrosion current, were obtained at an anodization time of 25 minutes. This showed that 25 minutes was the optimum anodization time in the anodizing process with an electrolyte concentration of 0.5 molar and an anodization voltage of 20 volts. By increasing the anodization time (30 minutes), more could be formed more pore and more irregular pore, so it damages the metal surface. This causes uneven silica coating on the metal surface, which affects the corrosion protection characteristics of the coating.

The Corrosion Protection Properties and Characteristics of Silica Coating on Electrophorized Stainless Steel by Pulsed Current

Silica coating was evaluated using EIS method. It resulted that the amplitude and duty cycle of the pulsed current affected the characteristics of the coating. Figure 5 shows the impedance spectra and the results of fittings for electrophoresis with amplitude variations of 0.1 volts to 0.6 volts. The electrical equivalent circuit model suitable for an amplitude of 0.1 volts is shown in Figure 4. It showed that the silica coating acts as a barrier layer paralleled with a small capacitance value, so water and oxygen molecules make it difficult to reach the metal surface.

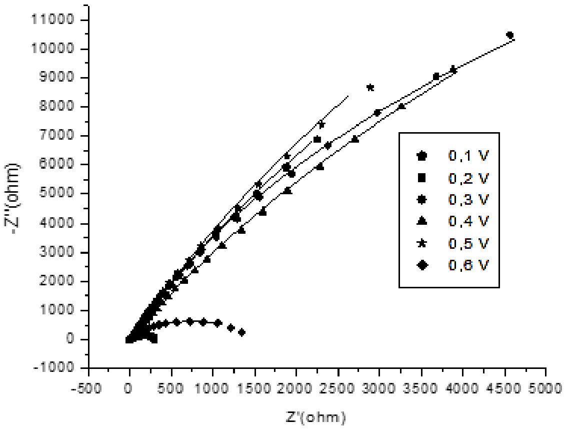

Fig. 5: EIS plot and fitting results of electrophorized stainless steel with a constant duty cycle and frequency of 50% and 80 Hz by varying the amplitude.

By increasing the amplitude of 0.2 volts, the silica coating resistance decreased, water and oxygen molecules could reach the metal surface, and the electrochemical reactions occurred on the interface of metal/silica coating. The equivalent circuit model for fitting the impedance spectra is shown in Figure 6a. By increasing the amplitude of 0.3 volts to 0.5 volts, the equivalent circuit in Figure 4 is constantly suitable for fitting the impedance spectra. This showed that the silica coating could act as a barrier layer with a high resistance at a high amplitude. However, by increasing the amplitude of 0.6 volts, the suitable equivalent circuit model was shown in Figure 6b, which showed that the resistance of the coating was decreased, and water and oxygen molecules could reach the metal surface. It is because the higher the amplitude during electrophoresis, the deposition rate of silica to the metal surface becomes higher, so an uneven coating was obtained. While the lower amplitude, the deposition rate becomes very low, so it takes a long time to form a coating on the metal surface. It affects the homogeneity of the coating and also affects the corrosion protection characteristics of the silica coating.

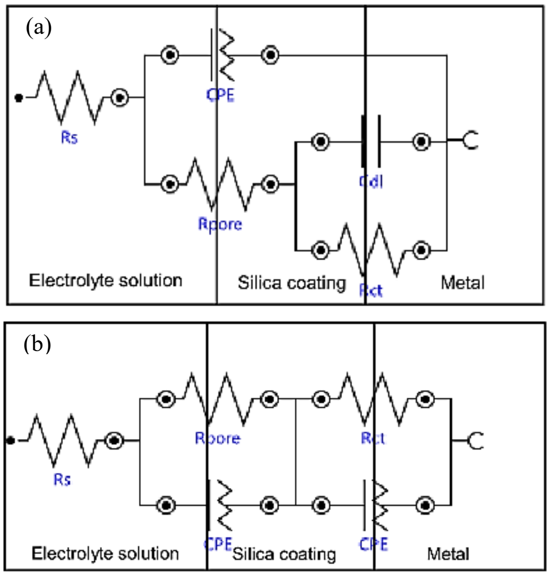

Fig. 6: Electrical equivalent circuit

Besides amplitude, the duty cycle also affects the characteristics of silica coating. Quantitatively, the values of equivalent circuit parameters by varying the duty cycle with a constant frequency and amplitude of 80 Hz and 0.5 volts, respectively, are shown in Table 3. It showed that the value of pore resistance increases with the duty cycle increase. But by increasing the duty cycle by 70% and 80%, the pore resistance value became lower. This is because, at a high-duty cycle (large T_{on} and small T_{off}), the silica particle deposition rate to the substrate was higher than the nucleation rate of the silica particles. So, more silica could be deposited on the metal surface. This affects the characteristics of the silica coating (seen from the value of pore resistance and admittance). But by increasing the duty cycle by more than 60%, more silica particles could be deposited and affect the homogeneity of silica coating. This causes a duty cycle of 70% and 80%; the pore resistance decreases, and the admittance increases. The highest pore resistance and the lowest admittance were obtained at a duty cycle of 60%. This showed that the duty cycle of 60% was the optimum duty cycle to produce a silica coating with good corrosion protection characteristics. Because this duty cycle could produce a coating with less pores and high electron transfer resistance, only a few electrolytes penetrate through the pores.

The mechanism for depositing silica particles on the stainless steel surface is as follows. When connected with a pulse current, stainless steel connected to a positive electrode was a function as an anode, and carbon connected to the negative electrode was a function as a cathode. This causes the negatively charged silica to move towards the positively charged stainless steel. In pulse current, there is an on-off mode. In the first mode, the silica particles, both primary particles and agglomerates, were moved toward the anode, and some particles were deposited on the stainless steel surface. In the off mode, the silica particles that had previously moved towards the anode were no longer moving and were positioned around the anode so that the area around the anode became denser. In addition, because of the sudden off mode, the agglomerate particles which initially move towards the anode could become deagglomerate (into primary particles). In the second mode, the silica particles moved again towards the anode, but because the area around the anode was denser than before, only primary particles easier to move toward the anode and deposited on the anode surface (stainless steel). And so on. So that this causes the layers formed on the stainless steel surface to be more homogeneous (in terms of size) and also affects the morphology of the layer, making it look more evenly. (Naim et al., 2010).

Table 3. Electrical equivalent circuit parameter

Parameter	30%	40%	50%	60%	70%	80%
R_s	174	8.18	11.91	4.85	5.62	2.79
Y_0	1.3x10^{-3}	1.6x10^{-3}	1.2x10^{-3}	6.9x10^{-4}	8.8x10^{-4}	2.4x10^{-3}
N	0.85	0.87	0.858	0.853	0.864	0.705
R_{pore}	57,077	54,400	107,540	788,290	511,440	175.92
Y_0	-	-	-	-	-	8.5x10^{-4}
N	-	-	-	-	-	0.99
R_{ct}	-	-	-	-	-	3,313

Comparing stainless steel electrophoresed with constant current accompanied by anodizing treatment and stainless steel electrophoresed with pulsed currents, the optimum conditions (high pore resistance and low admittance) for corrosion protection characteristics of the layer were obtained when the metal electrophoresed with pulsed currents. This can be seen from the value of the pore resistance and the admittance. The higher pore resistance values and the lower admission values were obtained when stainless steel was electrophoresed with pulsed currents than constant currents with anodization. This is because electrophoreses with pulse currents could form a more even and denser silica layer compared to electrophoresis with a constant current. Anodization treatment before electrophoresis with constant current causes the silica to be firmly attached to the stainless steel surface, but the silica layer formed was still not evenly distributed.

CONCLUSIONS

A good barrier property for corrosion protection of silica film was successfully deposited on stainless steel substrate by pulsed direct current electrophoresis method and constant current electrophoresis accompanied with anodization. The characteristics of the silica coating were influenced by the amplitude and duty cycle of the pulsed current as well as electrolyte concentration and anodization time. The corrosion protection characteristics of silica coating obtained by pulsed currents have better protection characteristics than those electrophoresed with a constant current accompanied by anodization because it has a lower admittance value and a higher value of pore resistance.

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