



## Evaluation of Anticorrosion Behavior of Automotive Electrocoating Primers by the AC-DC-AC Accelerated Test Method

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### ABSTRACT

A protective coating was applied onto the phosphated panels using cathodic electrocoating in two different dry film thickness  $8\mu\text{m}$  and  $20\mu\text{m}$ . The corrosion resistance of cathodic electrocoatings was studied using AC/DC/AC method. Twelve cycles of AC/DC/AC tests were carried out for each sample; 6 cycles DC voltage of  $-4\text{ V Vs. Ag/AgCl}$  for 20 minutes and the other 6 cycles with  $-4\text{ V Vs Ag/AgCl}$  for 2 hours. During DC potential application, transient electrical current density through the coated substrates was monitored. After each cycle of AC/DC/AC test, bode plots of samples were investigated. The results showed that by decreasing the thickness of electrocoating, the barrier properties of the film were declined drastically. On the other hand, applying DC potential for a longer time (2 hours) prepared harsh condition for degradation of the coating. The sample with normal thickness ( $20\mu\text{m}$ ) failed after 6 cycles while the sample with lower thickness ( $8\mu\text{m}$ ) failed only after 3 cycles. Prog. Color Colorants Coat. 7(2014), 187-199. © Institute for Color Science and Technology.

### 1. Introduction

Protection against corrosion in car industry is of great importance which is provided using a cathodic electrocoating primer [1-4].

Corrosion test methods for painted metals can be divided nearly into two groups; electrochemical and non-electrochemical. Electrochemical tests can be run by D.C. or A.C. power supplies [5,6]. Electrochemical impedance spectroscopy (EIS) is used widely to

investigate the behavior of coated metals immersed in aggressive solutions. Electrochemical impedance over a large frequency range provides information about various processes involved in protective effects of the coatings. The application of EIS to coated metals provides a useful technique in the study of the corrosion performance of protective primers. Performing this test on a coated metal takes days, weeks and sometimes months to get relevant

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information [7-12].

So far, many studies have evaluated the performance of protective properties of different materials using electrochemical techniques like EIS method. EIS test method provides quantitative information about the mechanism of corrosion process and protective properties of tested coating like pore resistance ( $R_{po}$ ) and coating capacitance ( $C_c$ ). In this method, the protective properties of organic coatings under corrosive conditions can be linked with the equivalent circuit elements [13-15].

There is an explicit interest in rapid assessment methods for practical applications that provide a faster sign of corrosion processes in the coated metals. AC/DC/AC is a rapid method for testing the coated metals. It consists of a combination of DC and AC measurements [16-19]. The AC/DC/AC test uses EIS to observe the condition of the coating before and after an electrochemical disbonding step.

The test consists of three steps:

- (1) an EIS measurement is run to find out the initial condition of the coating;
- (2) a DC potential is applied to produce hydroxyl ions and hydrogen gas and stimulate delamination and;
- (3) an EIS measurement is run to assess the condition of the coating after DC polarization.

Steps 2 and 3 are repeated to apply more stress until the anticorrosion behavior of the sample fails.

Any changes in the impedance spectrum can be attributed to a coating deterioration (pore formation) and a delamination process in the metallic surface due to hydrogen gas and hydroxyl ion production (if a cathodic reaction takes place)[20-23]. For the first time, Hollaender et al. [21-23] in 1970 developed a rapid method for evaluating protective properties of coated metals used in food packaging. This combined method (AC/DC/AC test) consists of applying a direct current (DC) and the electrochemical method based on

alternating current (AC). Suay et al. [2, 3, 16-18] used the electrochemical AC/DC/AC test for investigating the protective behavior of powder coatings and electrocoatings applied over steel substrates. Bierwagen and colleagues [24,25] electrochemically evaluated the insitue corrosion at metal/coating interface using accelerated AC/DC/AC test and embedded electrodes. Allahar and coworkers [19,20] characterized the potential changes at relaxation step of modified AC/DC/AC test (the AC/DC/AC test coupled with wet and dry cycles) by a mathematical model for calculating the characteristic times.

The aim of this study was to investigate the effect of DC potential and its application time on the protective behavior of cathodic electrocoatings with different dry film thicknesses. In this research, two different dry film thicknesses were prepared by applying different CED voltages (280 & 180 V) at a constant time of 120 s.

## 2. Experimental

An anticorrosive epoxy coating (supplied by BASF Co. with commercial reference cathoguard 500) was cathodically deposited on phosphated normal steel substrates. Coatings were deposited for two minutes at the deposition voltages of 280V and 180V to obtain 20 and 8 $\mu$ m dry film thickness, respectively. Anodes (stainless steel panels) were placed parallel to the working electrode (phosphated normal steel panels-supplied by Posco Co. with commercial reference KD36) at the distance of 19.0 cm. There was an anode/cathode area ratio of 1:3. The composition of the electrophoretic bath was 20wt% of non volatile content and the PBr (the ratio of pigment to binder content) of electrodeposition bath was 0.2. The electrocoated samples were cured at 165 $^{\circ}$ C for 20 minutes as shown in Table1. Dry film thickness of the electrocoatings was measured by thickness gauge (Elcometer-456) and the average thickness of five points was reported for each sample.

**Table1:** Identification of samples.

Sample code	Dry film thickness ( $\mu$ ) $\pm 2$
E08	8
E20	20

**Table2:** Specification of DC step of AC/DC/AC cycles.

Cycle number	D.C. voltage (volts)	Time of D.C. voltage application (min)
1	-4	20
2	-4	20
3	-4	20
4	-4	20
5	-4	20
6	-4	20
7	-4	120
8	-4	120
9	-4	120
10	-4	120
11	-4	120
12	-4	120

Electrochemical impedance spectroscopy (EIS) test was carried out on coated samples exposed to 3.5% (w/w) NaCl in deionised water with IVIUM comp AC stat instrument. The exposed surface area was 1 cm<sup>2</sup>. A carbon sheet acted as the counter electrode and an Ag/AgCl electrode was used as the reference electrode (concentration of KCl solution was 3.5 M).

The impedance tests were carried out over a frequency range of 100 kHz down to 10 mHz using an amplitude voltage of 10 mV inside a faraday cage to minimise external interferences on the system. The impedance spectrum was analysed using Z-view software.

The first EIS measurement shows the initial state of the coated test panel. After that, the test sample was treated for a certain time with a constant cathodic voltage. At relaxation step, the potential profile of the sample was investigated to reach a steady state. The relaxation time is defined as the time to achieve a stable open circuit potential. EIS measurements are performed after relaxation step of each cycle.

Twelve cycles of AC/DC/AC test were carried out on coated samples. Specification of each cycle is shown in Table2.

### 3. Results and discussion

The variation of electrical current density during the DC potential application at twelve AC/DC/AC cycles for E08 and E20 samples is shown in Figure (1).

The variation of open circuit potential at  $t=3$  hours during the twelve AC/DC/AC cycles for E08 and E20 samples is shown in Figure (2).

EIS results of first six AC/DC/AC cycles is shown in Figures (3) and (4) for E08 and E20 samples, respectively.

EIS results of the second six AC/DC/AC cycles is shown in Figure (5).

The equivalent circuit models, shown in Figure 6, were employed to analyse the EIS spectra. The first circuit consisted of electrolyte resistance ( $R_s$ ), pore resistance ( $R_{po}$ ) and coating capacitance ( $C_c$ ) and the second circuit consisted of polarization resistance ( $R_p$ ) or charge transfer resistance ( $R_{ct}$ ) and double layer capacitance ( $C_{dl}$ ) too. The chi-squared parameter of the fit was usually below 0.1.

For the E20 sample at first six cycles of AC/DC/AC test, one time constant was observed, so the Randle model was employed for fitting EIS test data. On the other hand, for E20 sample at second six cycles and E08 sample at all of the carried cycles, two time constants were observed, so the Mansfeld model was employed for fitting EIS test data.

Fitting results of first AC/DC/AC cycle are shown in Figure (7) for E20 sample.

Fitting results of seventh AC/DC/AC cycle are shown in Figure (8) for E20 sample.

Figures (9) to (12) show the fitted elements of EIS measurements.

According to Figure (1), the magnitude of electrical current density of E20 sample is 6 orders less than E08 sample at the first six cycles. It manifests better protective properties of E20 sample because of its thicker electrocoating dry film and better resistance against applied electrical stress and diffusion of water and corrosive ions during the AC/DC/AC test. At the second

6 cycles of AC/DC/AC test, by application of DC potential for 2 hours, the protective properties of E20 sample were dropped and the transient electrical current density through the E20 and E08 samples are the same. Less protective electrocoating layer in E08 sample causes protective properties failure at the first cycle of AC/DC/AC test.

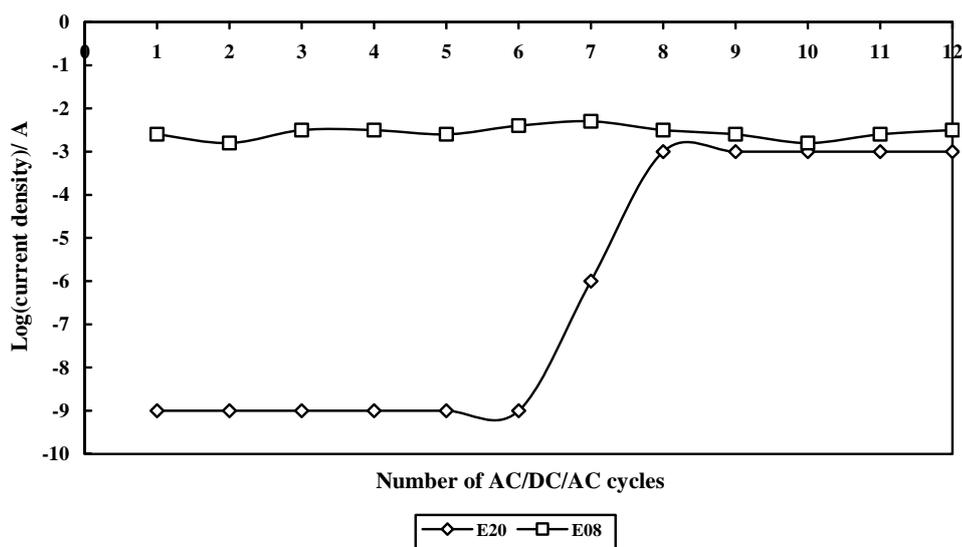


Figure 1: Variation of electrical current density during the DC potential application.

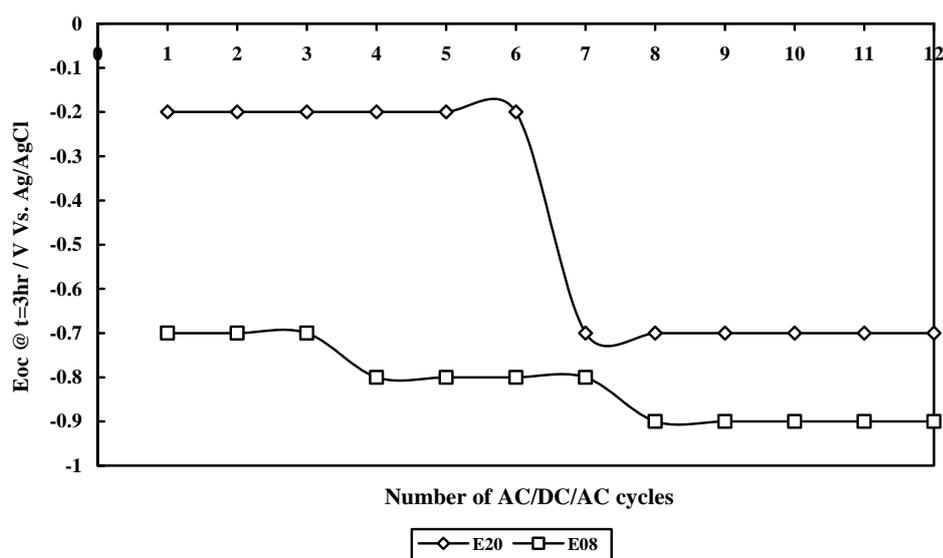


Figure 2: Variation of open circuit potential after 3 hours of applying DC potential during AC/DC/AC test.

As shown in Figure (3), the monitored open circuit potential of E20 sample is 0.45 V more than E08 sample after three cycles. These results confirm better

protective properties of E20 sample. The electrocoating layer as an insulating layer leads to a more open circuit potential at relaxation step of AC/DC/AC test.

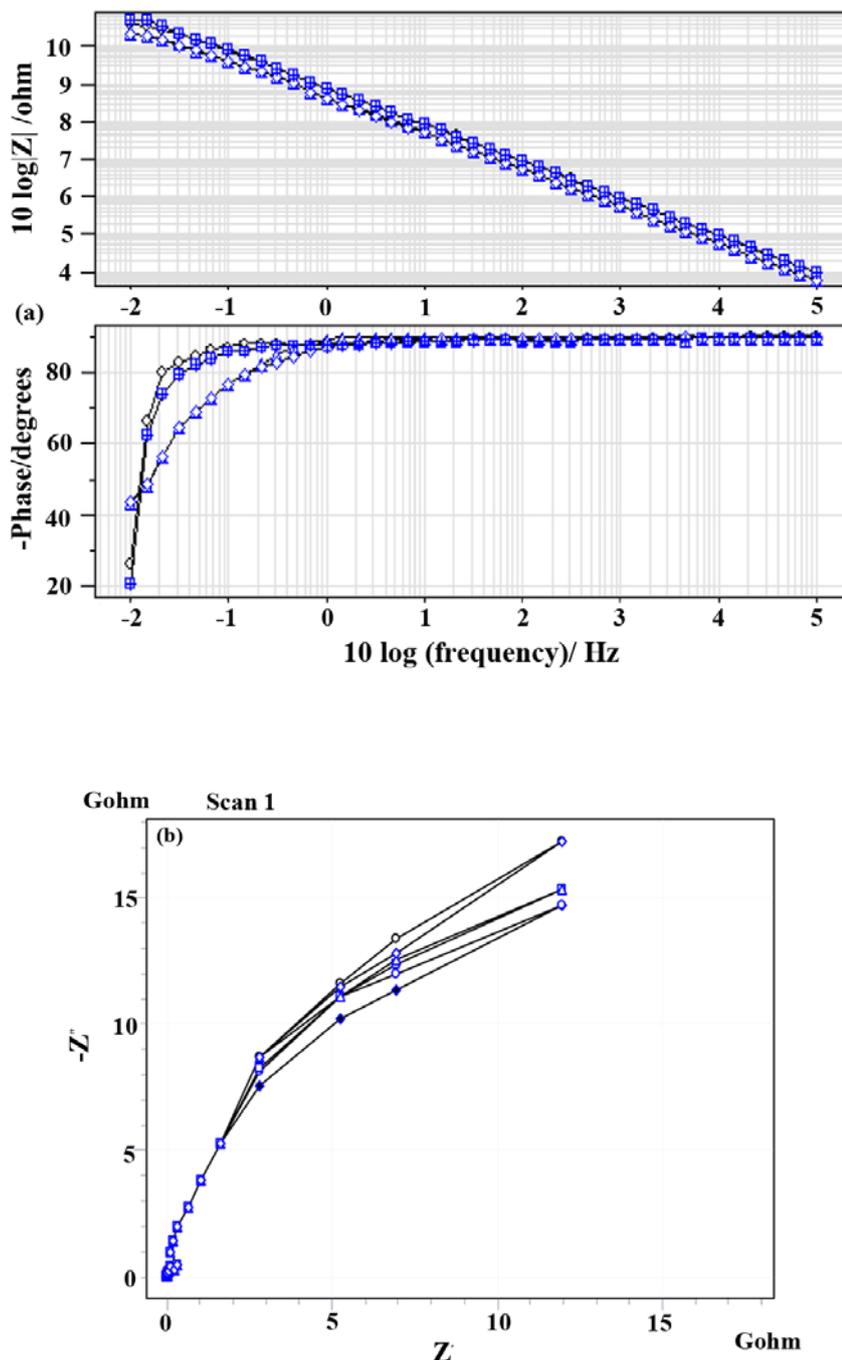
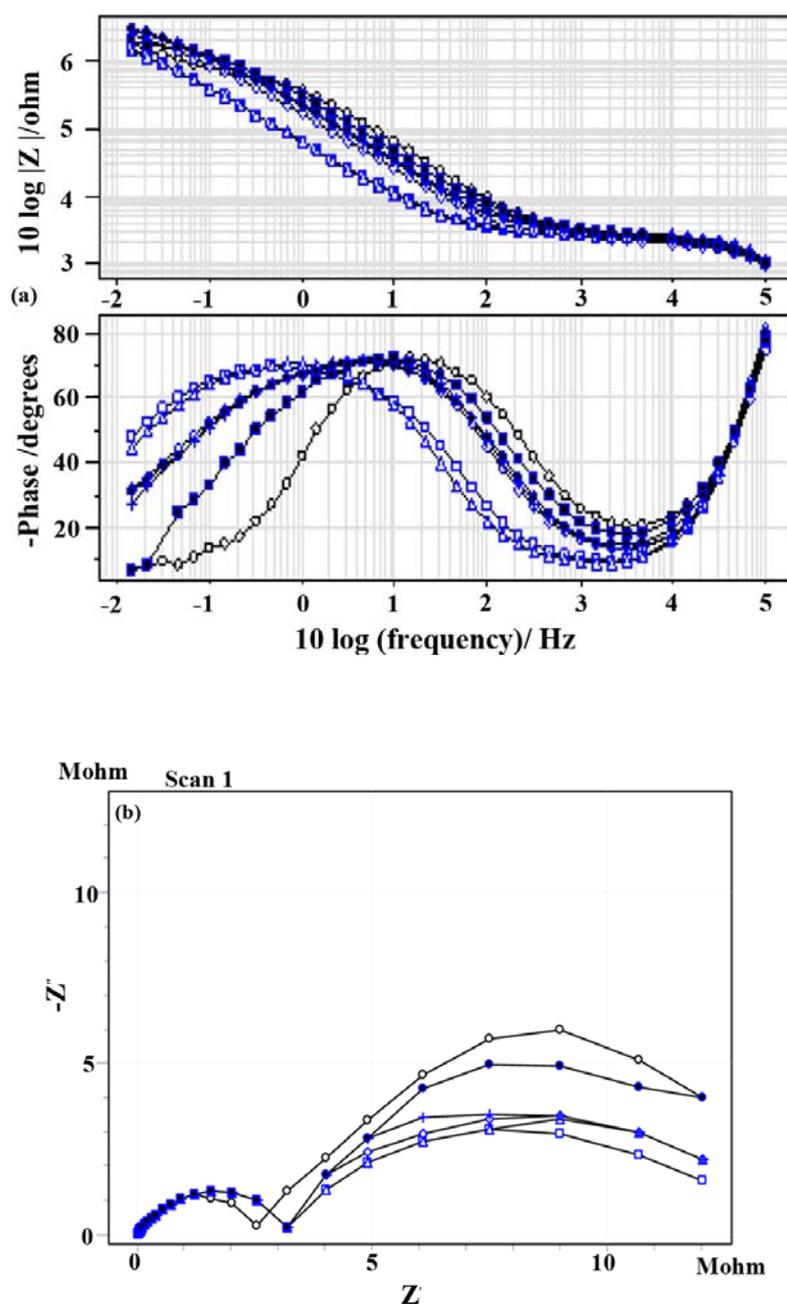


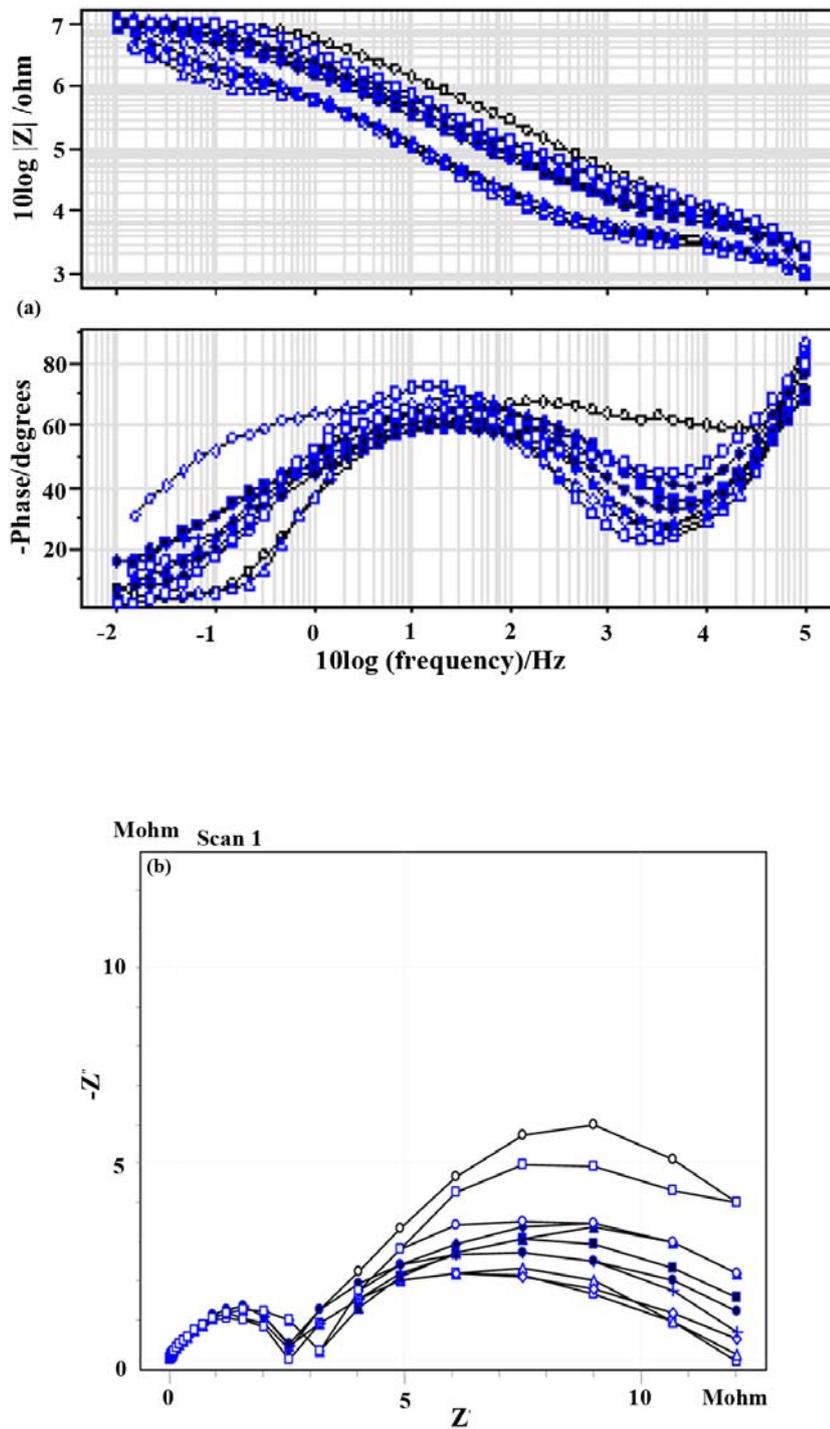
Figure 3: (a) Bode plots of AC/DC/AC test for E20 sample, (b) Nyquist diagrams of AC/DC/AC test for E20 sample (O:cycle#1, ◇:cycle#2, ▲:cycle#3, □:cycle#4, ■: cycle#5, △:cycle#6).

The more porosity of voids in the electrocuting layer causes the more open circuit potential shift towards negative values. At seventh cycle of AC/DC/AC test, the magnitude of open circuit potential was dropped at about 0.4 V, indicating the

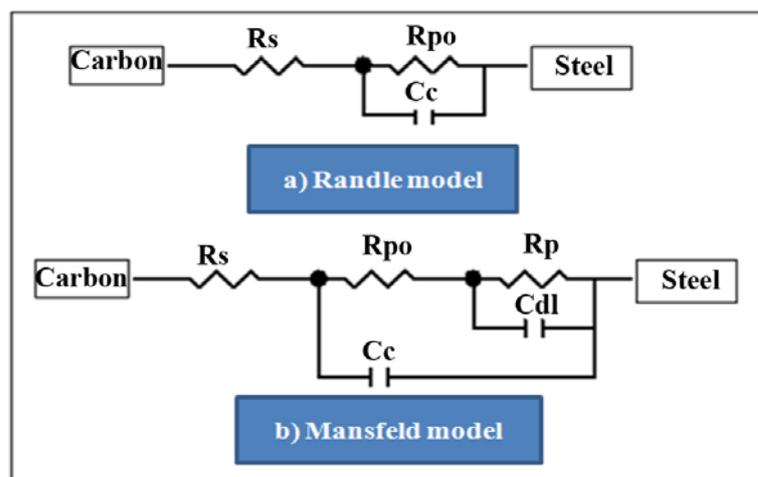
loss of protective properties of E20 sample. On the other hand, for the E08 sample, the magnitude of open circuit potential was dropped about 0.1 V after three cycles, showing degradation of the E08 sample after three cycles of AC/DC/AC test.



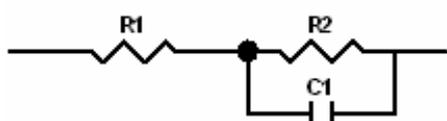
**Figure 4:** (a) Bode plots of AC/DC/AC test for E08 sample, (b) Nyquist diagrams of AC/DC/AC test for E08 sample (O:cycle#1, +:cycle#2, ◆:cycle#3, □:cycle#4, ■: cycle#5, △:cycle#6).



**Figure 5:** (a) Bode plots of AC/DC/AC test for electrocoated samples, (b) Nyquist diagrams of AC/DC/AC test for electrocoated samples (O:cycle#7(E20), +:cycle#8(E20), ◆:cycle#9(E20); ●:cycle#10(E20), ■: cycle#11(E20), ●:cycle#12(E20), ◇: cycle#7(E08), ●: cycle#8(E08),◆: cycle#9(E08); △: cycle#10(E08), ▲: cycle#11(E08), □: cycle#12(E08)).



**Figure 6:** Equivalent circuit models used to fit the EIS results a) for one time constant (1-6 cycles for E20), b) for two time constants samples (1-12 cycles for E08, 6-12 cycles for E20).

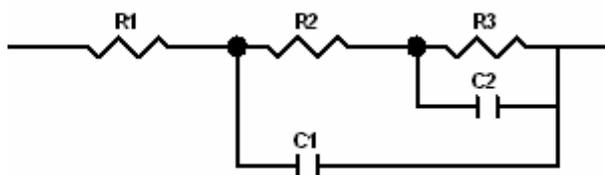


Element	Freedom	Value	Error	Error %
R1	Fixed(X)	1000	N/A	N/A
R2	Free(+)	3.9142E10	2.9744E09	7.599
C1	Free(+)	3.5635E-10	4.868E-12	1.3661
Chi-Squared:		0.059597		
Weighted Sum of Squares:		1.4303		

**Figure 7:** Fitting results of EIS data for E20 sample at first cycle of AC/DC/AC test.

DC potential was applied to E20 and E08 samples at all cycles of AC/DC/AC test; the mechanical stresses caused by  $H_2$  bubbles in the electrocoating film of E08 sample are greater than E20 sample. According to the results of Figure (11), decreasing trend can be seen for

charge transfer resistance of E08 sample during the AC/DC/AC test. Due to the observation of two time constants in EIS test results from the seventh cycle,  $R_{ct}$  parameter was fitted from the seventh cycle for E20 sample.



Element	Freedom	Value	Error	Error %
R1	Fixed(X)	1000	N/A	N/A
R2	Free(+)	2.2707E05	16528	7.2788
R3	Free(+)	8.5443E05	1.117E05	13.073
C2	Free(+)	3.6173E-07	6.4902E-08	17.942
C1	Free(+)	2.295E-10	2.4022E-11	10.467

Chi-Squared: 0.20742

Weighted Sum of Squares: 4.9782

Figure 8: Fitting results of EIS data for E20 sample at seventh cycle of AC/DC/AC test.

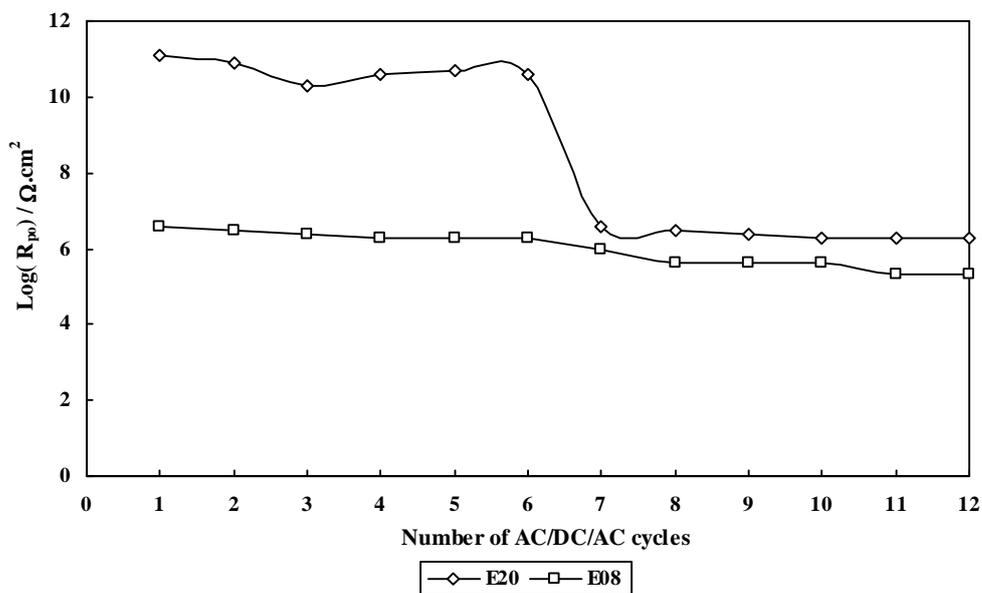


Figure 9: Pore resistance of the coating after different DC exposure cycles.

The results of  $R_{ct}$  variations for E08 sample show corrosion reactions at the metal/coating interface at the beginning of AC/DC/AC test. By increasing the cycle number and applying DC potential at longer times, the protective properties are reached to a greater extent. On

the other hand, the E20 sample has better resistance against corrosive conditions of the first six cycles. From the seventh cycle, corrosion reactions take place at metal/coating interface and the loss of protective properties would be significant.

According to the results of Figure (12), the variation of the double layer capacitance of the studied electrocoatings was not significant and the charge

transfer parameter was more influenced by corrosion reactions at metal/coating interface.

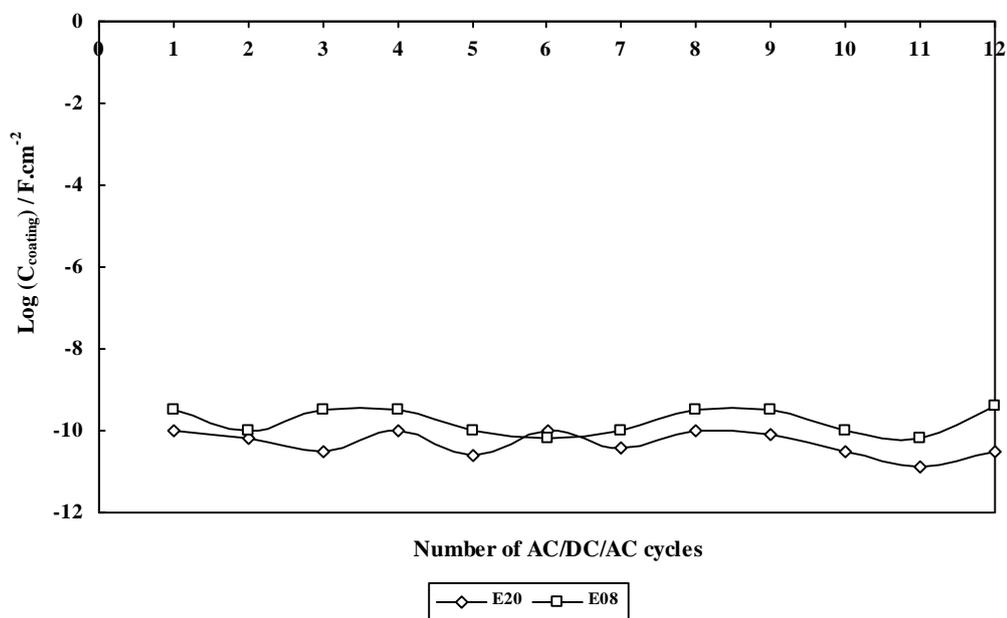


Figure 10: Coating capacitance of the coating after different DC exposure cycles.

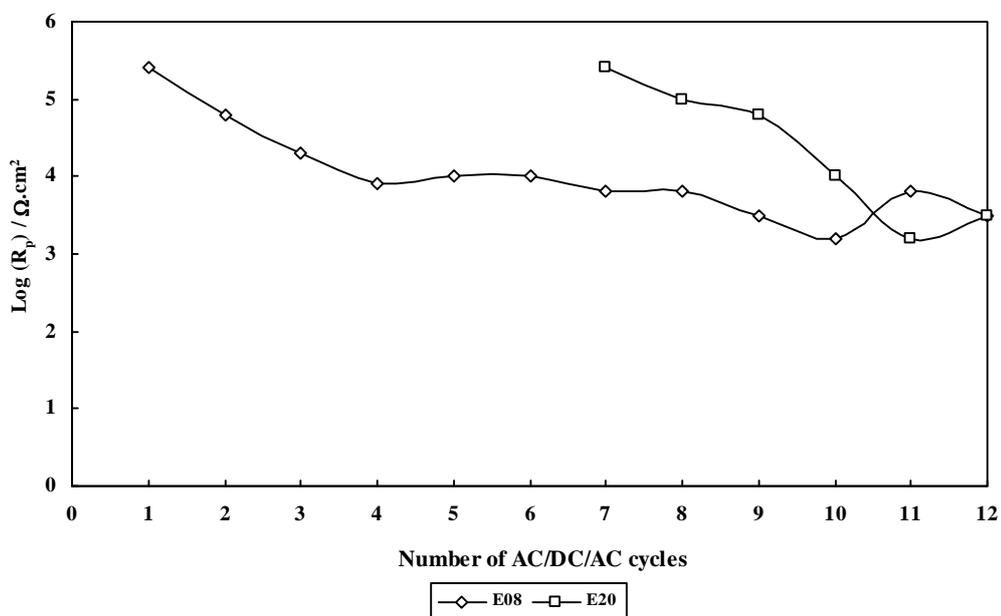


Figure 11: Charge transfer resistance of the electrocoatings after different DC exposure cycles.

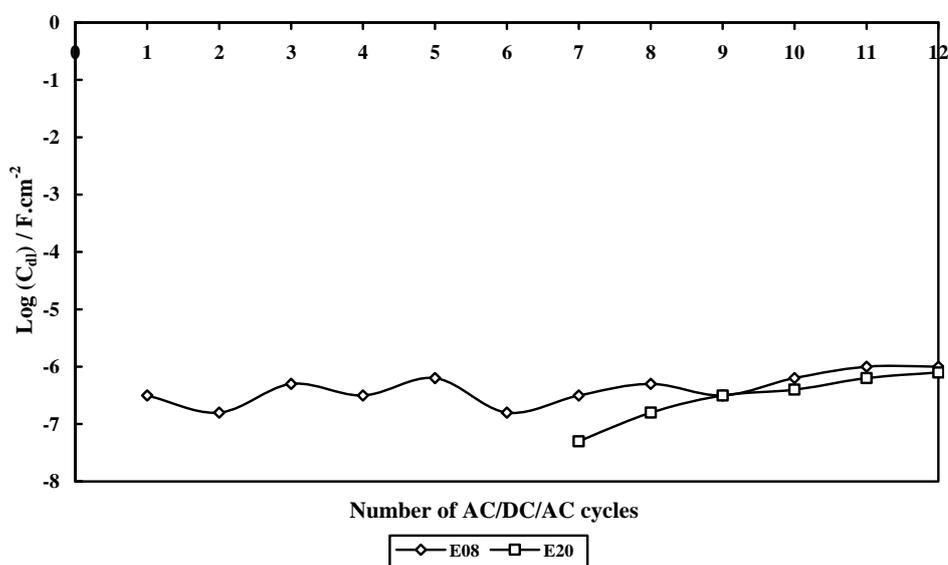


Figure 12: Double layer capacitance of the electrocoatings after different DC exposure cycles.

Generally, according to the results shown in Figures (1) and (2), in the first step of applying -4V for 2 hours (seventh cycle) drastical degradation of coated samples occur. After six cycles of AC/DC/AC test, the magnitude of electrical current density for E20 sample increased about 6 orders. On the other hand, the magnitude of open circuit potential was decreased. The periodic testing at given number of cycles results in the delamination at coating/metal interface. The results indicate that the corrosion at the interface takes place after 6 cycles for E20 sample compared to 3 cycles for E08. Based on barrier property ( $R_{po}$ ) and current density plots, three cycles of -4V DC degraded the E08 sample and the E20 sample was degraded after 6 cycles. For the E20 sample, at the first step of applying -4V for 2 hours, the protective property of coated metal has been failed. As Figure 4 shows, the coating

resistance of the samples are more or less the same during 6 cycles at -4V for 20 min, but in the first step of applying DC voltage (-4V) for 2 hours, the coating resistance declined drastically. So, the duration of applying DC voltage is much more important than cycle numbers. The measurement showed that the barrier properties of the E08 sample was not so good because of the lower electrocoating thickness and lower resistance to diffusion of water and corrosive ions to the electrocoating film in this sample. Comparison of the protective properties of different electrocoated samples is possible by applying -4V DC voltage for a short time (20 min) at the accelerated AC/DC/AC test. This short time (20 min) is not enough to degrade the coating with more dry film thickness (20  $\mu$ m) significantly. In these cases, the longer period of time could be effective.

#### 4. Conclusions

A cathodic electrocoating primer was applied over phosphated normal steel substrates by cathodic electrodeposition. Deposition voltages of 280V and 180V were applied in order to obtain 20 and 8 $\mu$ m dry film thicknesses, respectively. Twelve cycles of AC/DC/AC

test were carried out on each test panel. The DC step conditions of the first six cycles included application of -4 V vs. Ag/AgCl for 20 minutes and the DC step conditions for the other cycles included -4 V vs. Ag/AgCl for 2 hours. Results showed that by increasing

the cycle number of applied potential in AC/DC/AC test, the magnitude of electrical current density was also increased. Applying DC potential created pores at the electrocoating film. The lower film thickness of the electrocoating layer results in the lower barrier properties

of film. On the other hand, applying the DC potential (-4V vs. Ag/AgCl) for longer times (2 hours), developed harsher conditions for degradation of anticorrosive properties of different electrocoating films.

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