

# Testing of Acrylic Polyurethane-Coated Carbon Steel for Immersion Service Using Electrochemical Impedance Spectroscopy

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**Abstract:** *This study was carried out on acrylic polyurethane coating deposited on carbon steel substrate. Electrochemical impedance spectroscopy (EIS) was used to investigate the interfacial impedance of polyurethane coated carbon steel and examine the effect of primer application. The coating material was applied using air-spray technique and its thickness varied between 35 & 150  $\mu\text{m}$ . Impedance data were collected using three-electrode cell arrangement while test samples were submerged in aerated 0.5 M NaCl solution at room temperature. A Gamry instrument Reference600 with dedicated EIS300 software served as the Potentiostat for EIS testing of acrylic polyurethane coated carbon steel samples. In order to minimize the external interference, all EIS measurement were carried out in a faraday cage. In the initial stages of testing the coating system proved to have high dielectric properties of the order of giga ohm ( $G\Omega$ ) but this does not persist with time. After three weeks immersion, coating resistance has decreased to lower values and the coating capacitance was of the order of micro-farad; indicative of considerable electrochemical instability. This was for coated samples with and without primer. Determination of the delamination ratio has proved much lower delamination levels (less than 1%) for coated sheets with primer in comparison to those without primer.*

**Keywords:** polyurethane, organic coating, EIS, delamination, immersion testing, capacitance

## 1. Introduction

In corrosion control, the major function of organic coating is to serve as a physical barrier between the metal substrate and reactants present in the aqueous media such as oxygen and aggressive ions. However, the isolation properties of organic coatings are not absolute and degrade with time due to water and ions permeation [1]. The most important property affected by ion diffusion and water permeation through the coating layer is the adhesion to substrate with subsequent electrochemical reactions at the metal/coating interface. The barrier properties of coatings can be improved by increasing coating thickness, using a coating with low porosity, and applying multilayer coatings where pores are not matched geometrically [2]. For all such measures short-term testing is required to evaluate the corrosion behavior of a coating/metal system in a given environment. This might help in the selection of the appropriate metal/coating system for a given set of operational conditions. In the last few decades, electrochemical impedance spectroscopy (EIS) emerged as a powerful non-destructive tool which is widely used to characterize corrosion processes as well as the protective performance of organic coatings in a short time. This can be inferred from the ever increasing number of published literature on the subject over the years. The method has been used by many researchers to test and rank the protective ability of organic coatings (3-6). EIS has many advantages in comparison with other electrochemical techniques. It is a non-destructive tool for the evaluation of many material systems such as coatings, anodized films and corrosion inhibitors [7-9]. The method can provide information on many important corrosion parameters such as corrosion rate, corrosion mechanism and detection of localized corrosion [10-11]. In this work, EIS was used to investigate the interfacial impedance of acrylic polyurethane coated carbon steel sheets, with & without primer application, under full immersion in 0.5 M NaCl solution.

## 2. Experimental Methods

Test samples were in the form of 50x80 mm carbon steel sheets 2 mm in thickness. The surface preparation was carried by sand blasting down to white meal surface finish. Then, coating material was applied using air-spray technique and allowed to cure for two weeks. The coating thickness was measured using Elcometer350 with a precision in thickness range of  $\pm 3 \mu\text{m}$ . The coating thickness was varied between 35 to 150  $\mu\text{m}$ . The thickness results are the mean of ten measurements. After drying time, Test cell was constructed by sticking a plastic 50 mm diameter PVC cylinder on sample sheet and loaded with test solution as shown in fig. 1. The coated samples were classified into two groups: one with primer and the other without primer application.

A Gamry instrument REFERENCE 600 with dedicated EIS300 software served as the Potentiostat for EIS testing of Acrylic polyurethane coated carbon steel samples. This coating is a typical industrial maintenance coating for immersion service. The set of parameters selected for impedance data collection were: 35 mV sinusoidal perturbation at the open circuit potential, a frequency range of  $10^5$  to  $10^{-2}$  Hz and ten data points per decade. The exposed area of test sample was  $15 \text{ cm}^2$ . The corrosion test cell had three-electrode arrangement, as depicted in fig. 2, with graphite rod as the counter electrode, saturated calomel electrode as the reference electrode and the coated steel panel as the working electrode. The prepared EIS setup was used to measure the performance of acrylic polyurethane coated carbon steel samples submerged in an aerated 0.5 M NaCl solution. Every other day, samples were taken for EIS test after one half hour open circuit potential monitoring. EIS data were collected using Gamry Frame-Work data acquisition system version 6.33 and the impedance spectra were displayed and analyzed using Gamry EchemAnalyst

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v5.62. Impedance measurement were carried out in a faraday cage in order to minimize the external interference on the studied system.



**Figure 1:** Overview of some coated test panels

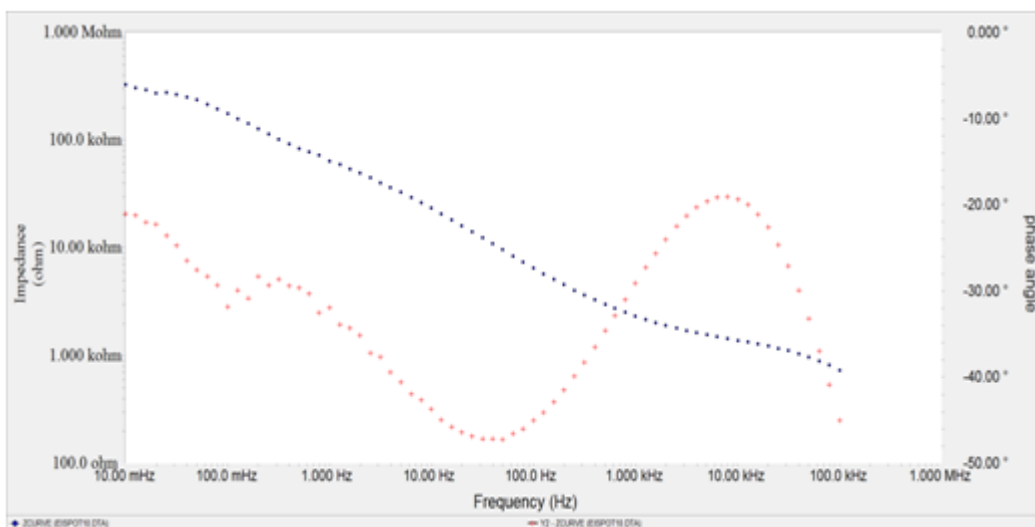


**Figure 2:** Experimental setup for impedance measurement

### 3. Results & Discussion

In the first few days of coating immersion in test solution, the coating has been characterized by its good barrier properties. For all tested samples, coating layer was tight and does not allow water, oxygen or other aggressive ions to penetrate through & reach the metal substrate. The measured coating resistance was of giga ohm ( $G\Omega$ ) order which proves highly dielectric properties of coating layer. This value is three orders of magnitude higher than the commonly accepted one of  $M\Omega$  order [12,13] normally considered as the border resistance used to distinguish barrier coatings from degraded ones.

Following seven days of immersion, the coating impedance decreased by two to three orders of magnitude down to  $400\text{ k}\Omega$  as shown in fig. 3. Here, the impedance data are better displayed as  $\log |Z|$  versus  $\log (f)$  because impedance data changes over many orders of magnitude.



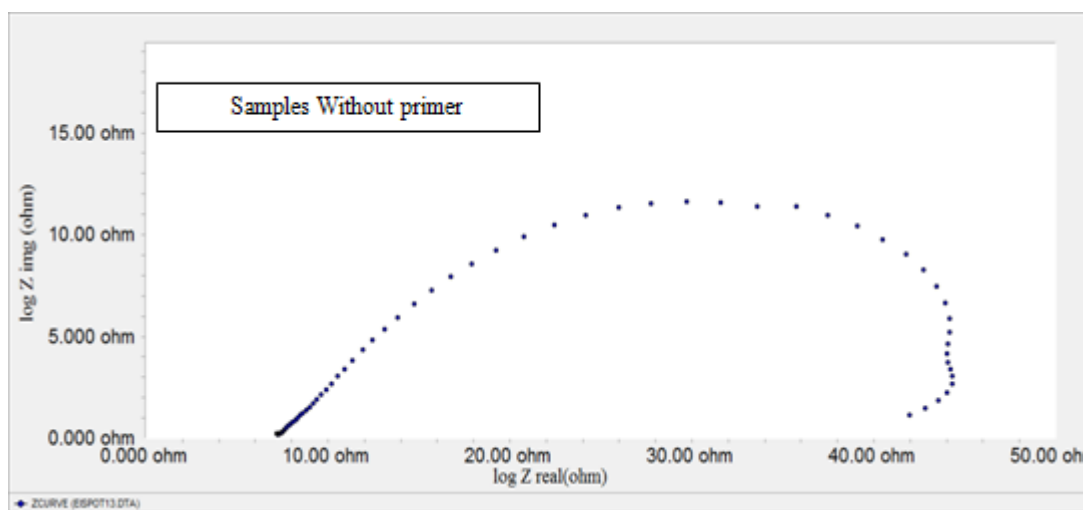
**Figure 3:** Impedance spectrum in Bode format recorded after 7 days of immersion exposure to 0.5M NaCl solution

This degradation of coating film properties could be referred to water and aggressive ions ingress. However, coating still provide protection of substrate at this high impedance value.

With continual immersion, the coating resistance further decreased to lower values. Table 1 presents data on impedance value variation with coating thickness for samples treated with primer and for samples without primer application tested for the same period of time. It can be seen from these data that the prime-coated samples had higher resistance values & thus better barrier properties for water and ions penetration. For the same thickness, the impedance of coated samples without primer had only a small fraction of the impedance of coated samples with primer. But for both types of samples the impedance increases with coating thickness.

**Table 1:** Variation of coating electrochemical impedance with thickness after three weeks- exposure

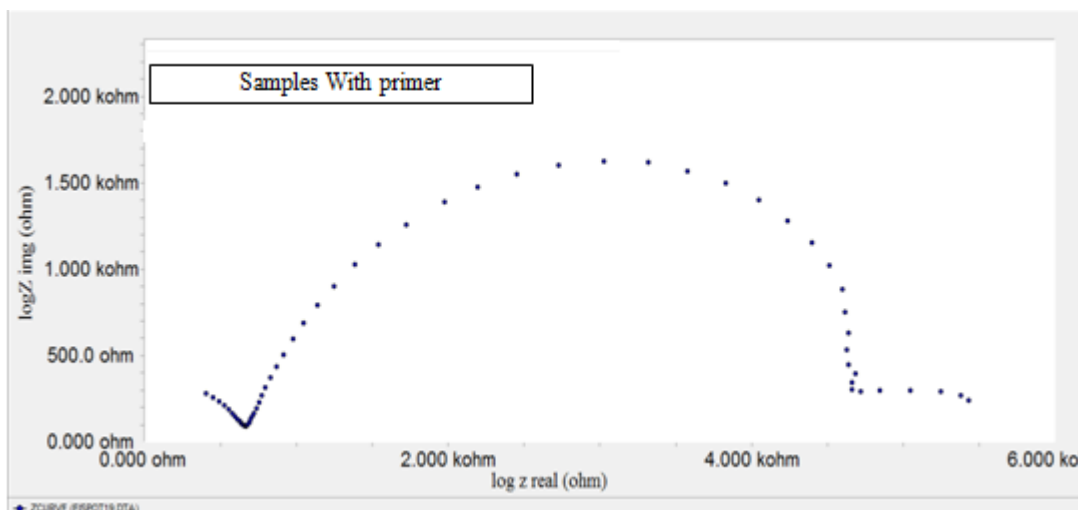
Coated samples with primer			
S.No.	Coating thickness [ $\mu\text{m}$ ]	$ Z $ $\text{k}\Omega$	Remarks
8	35	0.92	Measurements were conducted under stagnant condition in aerated 0.5 M NaCl solution at room temperature.
3	50	1.98	
4	60	2.21	
10	80	2.65	
1	100	4.50	
7	150	5.57	
Coated samples without primer			
14	25	0.017	Measurements were conducted under stagnant condition in aerated 0.5 M NaCl solution at room temperature.
11	35	0.032	
13	50	0.120	
5	65	0.420	
6	150	1.20	



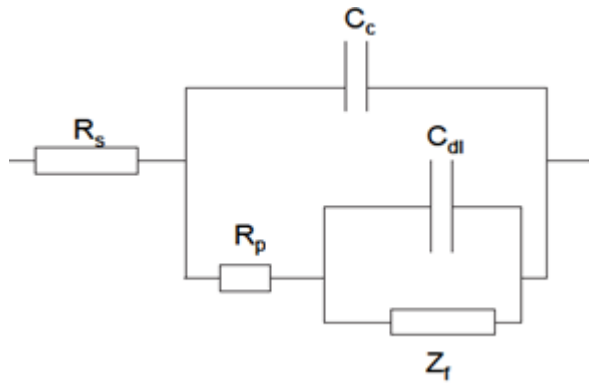
**Figure 4:** Nyquist plot for Acrylic polyurethane coated carbon steel in 0.5 M NaCl solution

The experimental impedance spectra presented in figures 4 and 5 were interpreted on the basis of equivalent circuit model of fig. 6 using Gamry Echem Analyst software. Based on relatively low measured impedance values read from figures 4 and 5, it can be assumed that corrosion reactions has started at the metal/electrolyte interface under the coating or at the base of the pores in the coating. Thus, an electrical element related to the newly created interface has to be included in the equivalent circuit. This is illustrated in

Fig. 6 which is the most common equivalent circuit model for coated metals [14-16] that exhibit some degree of degradation. In this model,  $R_s$ : the electrolyte resistance,  $R_p$ : the pore resistance,  $Z_f$ : an electrical element representing the electrochemical reactions at the metal/electrolyte interface,  $C_c$ : the coating capacitance,  $C_{dl}$ : the double layer capacitance.



**Figure 5:** Nyquist plot for Acrylic polyurethane coated carbon steel with primer in 0.5 M NaCl solution



**Figure 6:** Electrical equivalent circuit of a coated metal in contact with an electrolyte

A comparison between the behavior of polyurethane coating in presence and absence of primer application is presented in figures 4 & 5 Nyquist plots; where the impedance is represented by its real and imaginary components. For coated samples with primer Fig. 5, the radius of the semicircle = 2 k $\Omega$ , thus the  $R_p$  = 4 k $\Omega$

$R_s + R_p = 5.416$  k $\Omega$  therefore  $R_s = 1.416$  k $\Omega$

$$C_{dl} = \frac{1}{2\pi f_{max} R_p} = 0.5 \mu F$$

The coating capacitance;  $C_c$

$$C_c = \frac{1}{2\pi 10^4 |z|_{10kHz}} = 247 \mu F$$

The analogous values for coated samples without primer fig. 4 are:

$R_s + R_p = 42$  &  $R_s = 7 \Omega$

$R_p = 35 \Omega$

$C_{dl}$ : the double layer capacitance:

$$C_{dl} = \frac{1}{2\pi(50)(35)} = 90.1 \mu F$$

$C_c = 2.14 \mu F$

More corrosion resistant coatings normally have capacitance values of the order of pico-farad. The estimated coating capacitance in these measurements are in the micro-farad range; an indication of relatively poor corrosion protection for the studied system. However, the measured values for samples with primer are much higher than the estimated values for samples without primer.

Based on a theoretical value of the double capacitance  $C_{dl}^0 = 20 \mu F/cm^2$  and the exposed surface area of 15 cm $^2$ , a delamination ratio  $D$  was calculated. From this ratio the delaminated area at which corrosion is assumed to occur is calculated as:

$$A_{corr} = Ax D = A \frac{C_{dl}}{C_{dl}^0}$$

Therefore for samples with primer:  $A_{corr} = 0.025$  cm $^2$

For samples without primer :  $A_{corr} = 4.51$  cm $^2$

This means that the delaminated area of coating for coated samples with primer is only a small fraction ~ 0.17% of

exposed area of the electrode whereas the delaminated area is 30% of the exposed electrode surface area for samples without primer application.

#### 4. Conclusions

Electrochemical impedance spectroscopy is a useful technique in predicting lifetime expectancy of organic coatings for immersion service. Moreover, the technique can give quantitative information on coating performance compared to classical test methods such as salt spray test. It was possible to obtain quantitative information on coating disbondment of the studied system in presence & absence of primer use. Much lower coating delamination levels, less than 1%, were determined for coated sheets with primer. The gradual degradation of coating dielectric properties with longer immersion periods was confirmed by the level of measured coating capacitance which was in the micro-farad range for both coating systems with and without primer application.

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