

Corrosion Resistance of Polyurea Polyaspartic Ester Coating in 3.5%NaCl by EIS

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Received: 28 May 2013 / *Accepted:* 17 June 2013 / *Published:* 20 August 2013

Corrosion resistance of polyurea polyaspartic ester (PPE) coating in 3.5% NaCl solution was studied by electrochemical impedance spectroscopy (EIS). A series of impedance spectra of the PPE coating during immersion was measured, and its corrosion resistance was evaluated according to the spectra. The experimental results showed that the PPE coating provided good corrosion resistance in 3.5% NaCl solution and showed excellent protective properties to metallic matrix.

Keywords: polyurea polyaspartic ester coating, EIS, corrosion resistance

1. INTRODUCTION

The performance of coating in a harsh corrosion conditions is directly related to the corrosion extent of a metallic matrix protected by coating, and affect the service life of metal materials. PPE coating is used as a metallic protection coating because it has a lot of excellent advantage, such as instant cure, reaction rate, the high solid content, without solvent volatilization, good weather resistance, color lasting, perfect leveling properties and excellent adhesion etc. Up to new, researches on surface topography, structural morphology and performance of the coatings by aging of salt spray and UV / salt spray cycle have been concerned, few studies have been done on electrochemical behavior of the coating during age by EIS [1-7]. Nevertheless, EIS provides a rapid and convenient technique to evaluate the performance of organic coated metals and has been proven to be a powerful tool in obtaining system specific parameters (coating capacitance, resistance coating, electrical double layer capacitance and charge transfer resistance of coatings) of organic coating and in evaluating the

degradation of a coating on metals. This technique provides quantitative kinetic and mechanistic information which is very useful for developing improved coatings systems [8-11].

In this paper, EIS was used to monitor the degradations of the protective properties of the coating during the immersion in 3.5% NaCl solution. Characteristics of EIS during immersion were gained. Equivalent circuit (EC) models were proposed to interpret the electrochemical impedance data for the present coated systems. The protective properties of the coatings were evaluated and analyzed by electrochemical specific parameters of coating and breakpoint frequency. The result was offered the information of the corrosion resistance and protection properties of the coating in electrochemical parameters.

2. EXPERIMENTAL

(1) Experimental materials

Polyurea polyaspartic ester (PPE)

Q235 ordinary carbon steel

(2) Preparation of samples

Prior to the application of the coatings, the sharp edges of Q235 ordinary carbon steel panels of size 4×4cm were first filed down. The panel surface was then polished with emery paper up to No. 120 and cleaned with acetone. The carbon steel plate was coated with PPE in term of matching order. Coated for only one flat and the interval were 24 hours, thickness of the coating was controlled in about 150 μm. The rear and edge of the panels were protected by applying a thick epoxy film to avoid corrosion. The effective area of the coating was 13cm².

(3) Immersion of sample

The samples were immersed in 3.5% NaCl solution at room temperature. The sample was taken out regularly during immersion and measured by EIS.

(4) EIS Measurement

The electrochemical impedance measurement system of EG&G M388 was used in the experiments. EIS measurement system was composed of a PAR 273 potentiostat and a PAR 5210 lock-in amplifier. The EIS measurements were carried out over a frequency range of 100 kHz to 10 mHz using a 10 mV amplitude sinusoidal voltage. The coated samples were immersed in 3.5% NaCl which served acting as corrosion medium. A three-electrode cell arrangement was used in the experiments. The coated metal panel was the working electrode and a platinum plate served as the counter electrode. The reference electrode was a saturated calomel electrode (SCE). The tested area of working electrode was 13 cm². All the measurements were performed at the open-circuit potential (OCP). The test cells were maintained at 25°C and the NaCl solution was refreshed regularly during the whole test period. The impedance spectra were collected and analyzed for evaluating the protection properties of the coatings.

3. RESULT AND DISCUSSION

3.1 Evolution of impedance spectra of the coating with immersion time

Fig1.gave the Bode plot of EIS spectra from the coating as the immersion time increased. It was evidence that, after 1 day exposure, a high impedance values at the low-frequency limit 0.01Hz (abbreviated as $|Z|_{0.01}$ below)displayed, which beyond $10^8\Omega\cdot\text{cm}^2$, and the phase angle was almost close to 80° , just one time constant could be observed from the inspection of the impedance spectra. All these indicated that the coating had excellent protection performance, and could effectively protect metals from shielding corrosive medium.

Since being immersed for 20 days, the $|Z|_{0.01}$ of the coating had descended to less than $10^8\Omega\cdot\text{cm}^2$; for 50 days, $|Z|_{0.01}$ had dropped substantially that was little more than $6.8\times 10^7\Omega\cdot\text{cm}^2$. When the coating had been immersed into 3.5%Nacl solution, $|Z|_{0.01}$ had been inferior to $10^6\Omega\cdot\text{cm}^2$, indicating that the coating had lost the capability of protection. With the increasing of immersion time, the values of $|Z|_{0.01}$ decreasing, as well the maximum phase angle shifted to higher frequencies, manifesting that the protective properties of the coating gradually decreased. The reason might be that the electrolyte penetrated the coating and created a path to the underlying surface.

Impedance data at high frequencies usually represented the responses of coating, thus exhibited the coatings characteristics and performance in the solution. The curve of the Bode spectra at the high frequency region overlapped each other as time increasing. That might be due to the saturation of electrolyte permeability, and the capacitance of the coating was no longer increasing substantially.

Two time constants in the impedance diagram eventually occurred after the longer exposure time of 50 days. At this stage of the coating degradation process, electrolyte solution penetrated to the coating/metallic matrix interface, while causing corrosion reactions to the matrix, it also wakened the combine between coating and metallic matrix which resulted in blister or swelling.

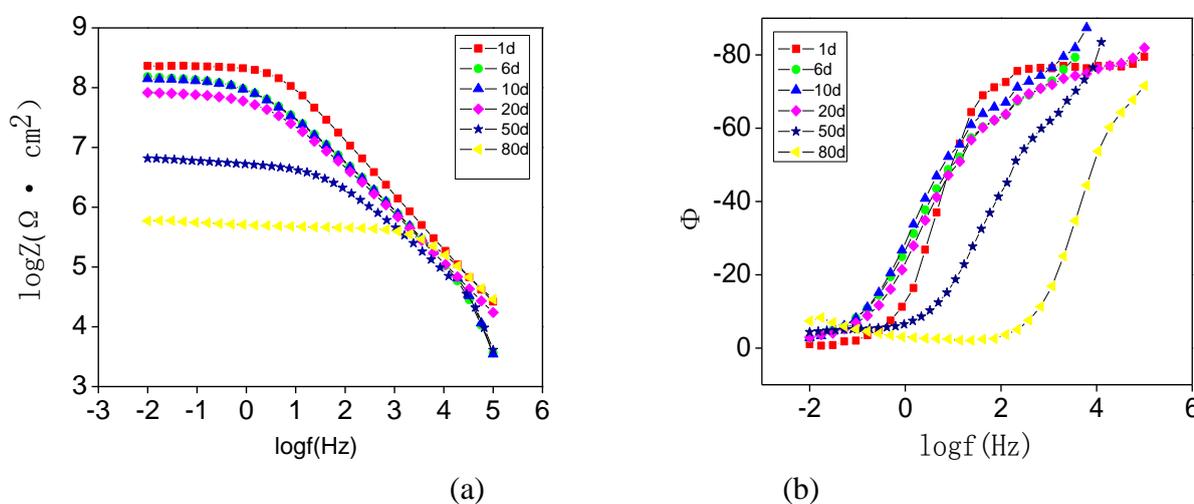


Figure 1. Bode spectra of PPE coating in period of immersion in 3.5% NaCl solution

3.2 Equivalent Electric Circuit (ECC or EC) models for interpretation of the coating

Nyquist plots of EIS spectra from the coating as the immersion time increased were showed in Fig2. A convenient way to evaluate the corrosion properties of the coating was to compare the diameters of the semi-circles in Nyquist plots. The larger the diameter was the better corrosion resistance. It was evident that, EIS spectra showed semi-circle all the while after 1 day, 6 days, 10 days and 20 days exposure, and the diameter of the EIS spectrum decreased gradually as the extension of immersed time, revealing that the corrosion resistance of the coating declined due to the gradually penetrating electrolyte solution. At the same time, it could be simulated by equivalent circuit Fig. 3(a). It must be noted that for taking into account the divergence from the pure capacitive behavior, the capacitance C_c was often substituted by a constant phase (CPE). R_s was the solution resistance and R_c was coating resistance.

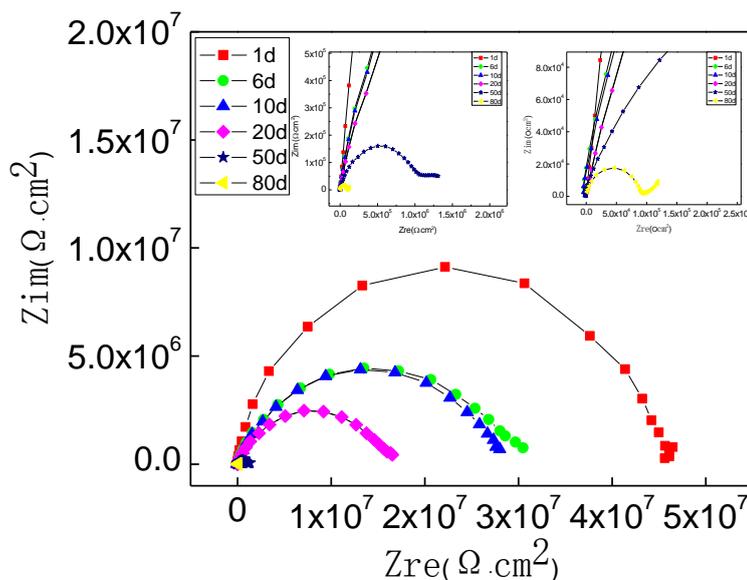


Figure 2. Nyquist spectra of PPE coating in period of immersion in 3.5% NaCl solution

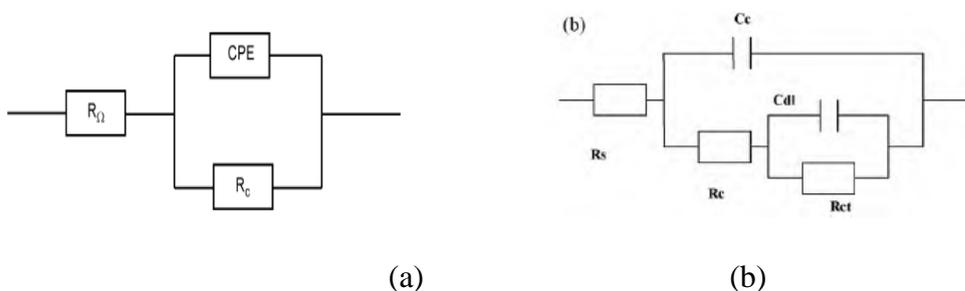


Figure 3. Equivalent circuits for the PPE coating in 3.5% NaCl solution at different stages

With the immersed testing going on, in addition to a circular arc occurred in the high frequency part, there was a diagonal lines in short frequency region (showed in Fig.2), indicating that the

corrosion medium had reached the coating/matrix interface and the matrix corrosion had occurred. For EIS data simulation, a general equivalent circuit model in Fig.3 (b) was used to describe two sub-electrochemical interfaces. The dielectric properties of the coating was displayed by a pair of elements of CPE-c (c means coating) and R_p in parallel replaces. Another pair of CPE-s (S means substrate) in parallel was adopted to describe the charge transfer process at coating/matrix interface pinholes.

3.3 Variations of corrosion electrochemical parameters with immersion time

3.3.1 Coating resistance and coating capacitance

Coating resistance (R_c) could reflect the penetration capacity of coating anti-corrosive, so it was used to evaluate the protective performance of the coating [12].

According to previous equivalent circuit (Fig.3), analyzing the coating impedance spectroscopy (Fig.1 or Fig.2), R_c and C_c of the coating were gained. The coating resistance R_c reflected the anti-penetrating ability of the coating to electrolyte solution was the important parameters to evaluate corrosion resistance properties of the coating, C_c was coating capacitance, when the electrolyte solution penetrated into the coating, the dielectric constant of coating would change, which made C_c change, so C_c was relate to the diffusion behavior of electrolyte solution in the coating.

It could be seen clearly from Fig. 4 that the coatings resistance R_c gradually decreased and C_c gradually increased with the increasing of immersion time from general trend. The result showed that C_c increased quickly in the initial period of immersion and then declined slowly to a stable value, indicating that the homogeneity of coatings decreased along with the water uptake process. The values of coating resistance (R_c) decrease dramatically in the first stage, after which only small decreased occurs.

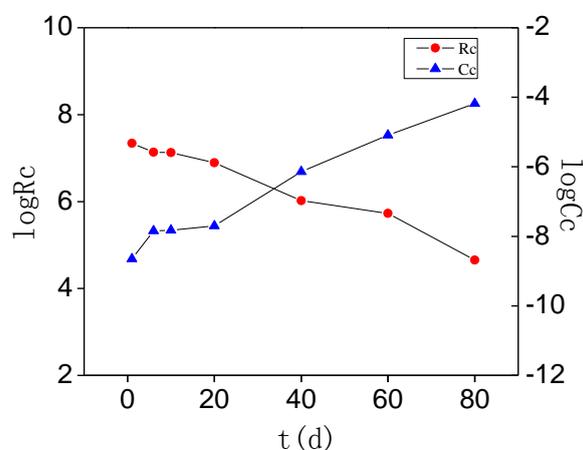


Figure 4. Time dependence of R_c and C_c of the coating

The variation tendencies of C_c and R_c demonstrated that the water permeation in the coatings mainly took place in the initial immersion period. After that, the water gradually reached a saturation

state. These results indicated that the coatings porosity increased gradually as immersion continued, more transmission medium had penetrated gradually into coating through the micro-porous of coating and had gradually been induced pathway [13].

According to general experience, metallic corrosion under the coating had started when values of R_c was below $10^6 \Omega \cdot \text{cm}^2$. The values of coating resistance (R_c) just reached to $5.16 \times 10^6 \Omega \cdot \text{cm}^2$ for 50 days of immersion in 3.5% NaCl solution. If the immersion test continued to carry out, the medium had arrived at the metal surface through the coating, and thereby the electrochemical reaction had generated at a short immersion time, which indicated that the water quickly permeated in the coatings, and the water permeation could promote ions conductivity in the coatings, leading to coating resistance apparently declined in the initial immersion period [14]. After that, the values of coating resistance (R_c) for the coating apparently declined down to only $1.430 \times 10^4 \Omega \cdot \text{cm}^2$ at 80 days and the coating basically lost the protection function All these indicated the coating had excellent protection ability to occurrence of metallic corrosion in 3.5%NaCl.

3.3.2 Coating porosity

In addition, the coating porosity, as a significant parameter, was attained to evaluate or forecast the aging regular of coating.

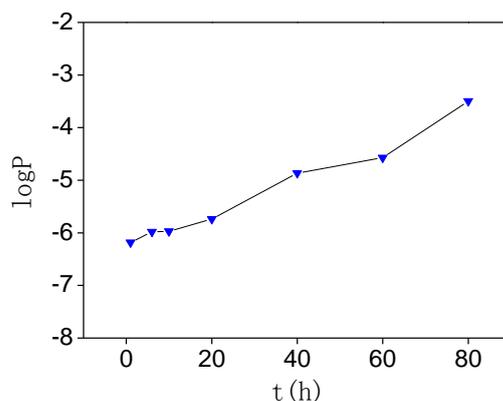


Figure 5. Porosity at different time of exposure to 3.5% solution

It was defined as the ratio of the initial theory volume resistance to actual volume resistance.

$$P = \frac{R_{pt}}{R_p} \quad (1)$$

$$R_{pt} = \frac{d}{A\kappa} \quad (2)$$

In equation, d was behalf of the coating thickness, A was the coating area, κ stand for conductivity of electrolyte, which is $2.34 \times 10^{-3} \Omega^{-1} \cdot \text{cm}^{-1}$ for 3.5%Nacl solution. Variations of coating porosity and equivalent parameters in different aging condition were shown in Fig.5.

It was been seen that, the porosity values of the coating became more negative when immersion continued, which indicating that the protective nature of the coating was altered because of the diffusion of corrosive species through the coating. Then as the coating swelled, more transmission medium had penetrated gradually into coating through the micro-porous of coating and had gradually been induced pathway, the coating porosity gradually increased in the later stage of corrosion, which was different from the behavior of coating capacitance.

3.3.3 Evolution of the breakpoint frequency f_b

Microscopic defects area for Organic Coatings were closely related to its protective properties, thus it was very important confirming the organic coating defects area. Defects area of Organic coatings could be analyzed and confirmed by Breakpoint Frequency Method [15-16]. The breakpoint frequency f_b (frequency for a 45- phase angle) was correlated with the relative increase of electrochemically active surface area [17]. The relative increase in defective area could be determined from the increase of f_b [18]. That was to say, it depended directly on the defect area at the interface of organic/metal. So, f_b was proved to be a useful parameter for evaluation of extent of dimension in organic/metal system. The porous of coating surface and reaction of the coat / metal interface or relevant information could be gained by f_b changed with immersion time, thus the protective properties of the coating could be evaluated by f_b and researched damage process of coating. Their relationship was as follows:

$$f_b = K(A_t / A_0) \quad (3)$$

In equation, f_b was breakpoint frequency, $K=1/2\rho\epsilon\epsilon_0$, A_t was defect area, A_0 was size of coating area, ρ was a resistivity of the coating itself, ϵ was dielectric constant of water in coating, ϵ_0 was the dielectric constant of vacuum.

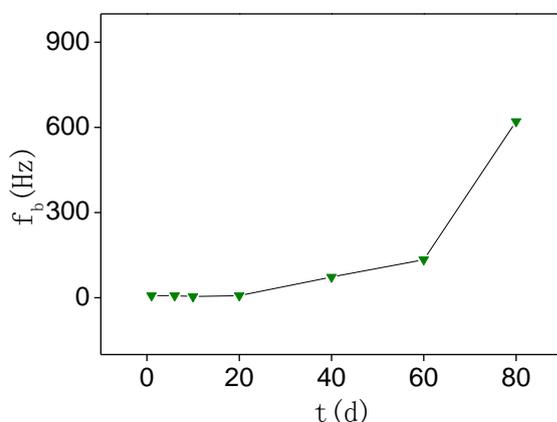


Figure 6. Evolution of breakpoint frequency with immersion time of the coatings

When the electrolyte solution penetrated into the coating, the value of ρ declined and the value of ϵ would increase, the compensation role made it possible that K could be regarded as a constant. Therefore, the coating defects area was proportional to the breakpoint frequency (f_b) [17]. Under

normal circumstances, the breakpoint frequency f_b (frequency for a 45- phase angle,) could be gained easily, it was no need for complex data processing, and f_b was at high frequency so it need not measure time-consuming for the low frequency data. Therefore, breakpoint frequency had become a rapid method for evaluation of the performance of coating.

The breakpoint frequency f_b of coating could be used to speculate the changes of coating defects area. The breakpoint frequency f_b during the immersion time (t) was presented in Fig. 6 by analyzing impedance spectroscopy of the coating, the f_b of the coatings shifted to higher frequencies with immersion time. It could be seen from Fig.6, the trend anti-corrosion performance of the coatings was gradually deteriorated. But breakpoint frequency f_b of the coating increased slower, which indicted that the shortcomings of the coating was smaller, its anti-media penetration ability was better, and it exhibited a excellent anti-corrosion performance.

4. CONCLUSIONS

EIS showed that the PPE coating had a higher coating resistance, lower coating capacitance and lower coating porosity, good permeation resistance to medium, and exhibited an excellent anti-corrosion performance in 3.5% NaCl solution.

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