

# A Topography Characterization of Organic Coatings Degradation under Flowing Deionized Water

Qixin Zhou, Yechun Wang and Fardad Azarmi

*Mechanical Engineering, North Dakota State University, Fargo 58108, North Dakota, USA*

Received: June 07, 2011 / Accepted: July 06, 2011 / Published: October 10, 2011.

**Abstract:** Flow induced corrosion of organic coatings occurs in a wide variety of industrial and civilian applications such as pipes, heat exchangers, chemical reactors, vehicles, etc. In order to understand the behavior of flow induced organic coating degradation, the coating is exposed to flowing fluids as well as quiescent solutions. The deionized water (DI Water) is chosen as the immersion fluid. The thickness and gloss of the organic coating are measured before and after the immersion. Both optical and atomic force microscopy is used to characterize the topography of the coating surface. The topography study shows that the blisters are formed on the coating surface after coating degradation. The results from Electrochemical Impedance Spectroscopy (EIS) measurement reveal that the coating's impedance modulus decreases more substantially under the flowing condition.

**Key words:** Coating degradation, flowing fluid exposure, topography characterization, deionized water.

## 1. Introduction

One of the primary performance properties of organic coatings is corrosion protection [1]. It is the most common and cost effective approach to protect metallic objects and structures. Organic coatings can generate barriers between the substrate and the environments, which can reduce the transportation of oxygen, water and ions to the coating metal interface [2]. The organic coatings have the ability to impede the current between anodic and cathodic areas of the metal substrate [3].

Flow induced corrosion is a complex system. Flow velocity, flow pattern, solid particles, impact angles all contribute to corrosion process. Recent studies are all related to fluid flow over metals, but the influence of fluid flow in the degradation of metal-protective organic coating has received less attention. The increase in the impact velocity decreased the corrosion resistance of the uncoated mild steel under the erosion-corrosion condition [4]. The effect of flow

induced corrosion on the failure of a tubular heat exchanger was investigated [5]. It was demonstrated that the low velocity of circulating water incurs the settlement of deposits in heat exchanger tubes and eventually the thinning of the tube wall, which are the main cause of the failure of heat exchanger. Flow regimes from laminar to turbulent on the corrosion of stainless steel were studied by Wharton and Wood [6]. Wood's group also investigated the influence of sand concentration and sand size on the erosion-corrosion for different corrosive solutions, velocities and a variety of engineering materials such as stainless steel, carbon steel and nickel-aluminum bronze [7].

In addition, salt solutions are often adopted in corrosion test. Very few works have been using pure water (e.g., deionized or distilled water) and only reported for metallic materials. Previous studies have been reported on the corrosion of copper nickel alloys in distilled water [8], condenser tube materials in distilled water [9], cracking of stainless steel in pure water [10] and localized corrosion inhibition of stainless steel in deaerated pure water [11]. Nevertheless, no study has been carried out for coating

---

**Corresponding author:** Fardad Azarmi, professor, research fields: materials characterization, surface engineering, thermal spray coatings, solid mechanics. E-mail: Fardad.Azarmi@ndsu.edu.

systems immersed in pure water.

Metal protective organic coatings are designed to have a service life time of more than 50 years, accelerated test methods are hence needed to evaluate and validate the performance of the coating. In this study, we investigate flow induced organic coating degradation using deionized water (DI water) as the working fluid. And it is compared with the coating degradation under stationary DI water immersion. The goal of this study is to improve the understanding of organic coating degradation under flowing DI water, since previous work mentioned that flow conditions accelerate coating degradation [12, 13].

The influence of working fluid on organic coating degradation will be presented via topography characterization as the main approach. The optical and atomic force microscopy can closely examine the topography of the coated samples. We will focus on the visualization and discussion of the topographical changes of the coating occurred during degradation. Electrochemical impedance spectroscopy (EIS) has been considered as a valuable tool in the study of corrosion protective coatings. EIS is adopted to predict the lifetime of corrosion protection, rank the coatings systems, and measure the water uptake through coatings [3]. In this paper, EIS is employed as an accessorial measurement method to verify the topography characterization. The details of the EIS study and the correspondent equivalent circuit modeling will be presented in future publications.

## 2. Experiment

### 2.1 Sample Preparation

A primer and a topcoat graciously supplied by KCC Corporation (Seoul, South Korea) have been used in this study. The primer is a chlorinated rubber based coating with aluminum flake pigment and the topcoat is a polyurethane resin based finish coat. Stainless steel panels (Q-Panel Lab Products, Cleveland, OH, USA) are cut into  $3 \times 3$  inches and then abraded with sand paper and cleaned with hexane. The liquid paints are applied by air spraying and cured in room temperature for 24 h.

### 2.2 Experimental Setup

The experimental setup is adopted and modified from which designed by Wang and Bierwagen [13] as shown in Fig. 1. The working fluid is pumped from the fluid reservoir to the test section, and then recycled back to the reservoir. A rotameter maintains the flow rate at  $3.683 \text{ cm}^3/\text{s}$ . The fluid temperature is controlled at  $25 \text{ }^\circ\text{C}$  by a water bath and a temperature controlling system. A flow channel is constructed with plastic sheets. Coated stainless steel panels are adhered to the upper and lower channel walls. The flowing fluid goes through the gap between the two panels facing each other. The platinum meshes are embedded through the plastic plate to the upper channel wall acting either as counter electrodes or the reference electrode. An O-ring glass electrochemical cell is used in the stationary immersion test.

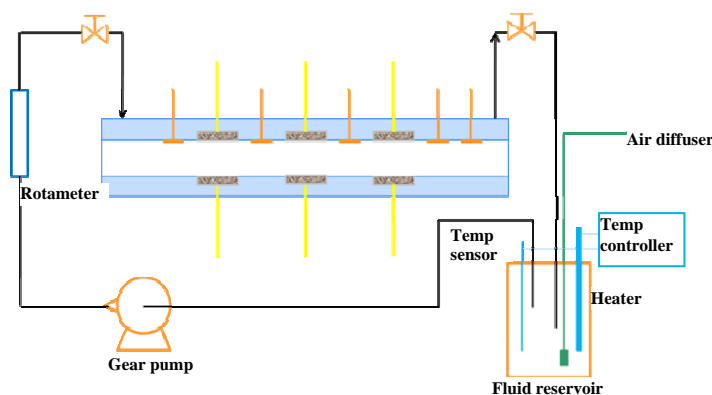


Fig. 1 Schematic diagram of the circulating flow.

### 2.3 EIS Test

The EIS test employs a three-electrode cell. It is composed of a stainless steel panel which is used as the working electrode, platinum electrodes used as the counter electrode on the left and right sides of the test panel, and another platinum electrode near the fluid outlet which acts as the reference electrode. For the stationary immersion a saturated calomel electrode is employed as the reference electrode. The measuring equipment is Reference 600 Potentiostat by Gamry Instruments. Measurements have been taken over a frequency range of  $10^{-2}$  to  $10^5$  Hz with ten points per decade using 15 mV rms AC.

### 2.4 Topography Characterization

An Axiovent 40 MAT (Focus Precision Instrument) is used in this study for optical microscopy. All images are collected over a magnification of  $10\times$  and  $20\times$ , depending on the features present on a given sample. The Atomic Force Microscope (AFM) observation is performed using a Nanoscope IIIa (Digital Instruments, California). All images are obtained in air and collected over a range of scan sizes, which are 100, 50, and 5  $\mu\text{m}$  images each time. Coating thickness and gloss are measured using an Elcometer coating thickness gauge and a NovoTrio statistical glossmeter before and after the immersion respectively.

## 3. Results and Discussion

### 3.1 Topography Characterization of the Organic Coating

#### 3.1.1 Thickness Measurement

The change of the thickness for the two cases is shown in Fig. 2. The coating thickness increases significantly after the immersion in the flowing DI water, while it maintains almost unchanged in

quiescent solution. This is due to the formation of blisters (which can be seen by naked eyes) on the coating surface after the immersion in flowing DI water. However, there are no obvious blisters generated on the coating surface after stationary immersion. It indicates that the flowing fluid causes more substantial surface changes on the coating.

#### 3.1.2 Gloss Measurement

The gloss of the coating surface is evaluated to quantify the blistering on the coating surface before and after immersions. Gloss reflects the smoothness of the surface. A mirror-like surface has a high gloss value, while a rough surface shows a lower gloss value. The values obtained from the glossmeter indicate the percentage of the light reflectance on the coating surface with respect to that on a black glass standard at three different grazing angles:  $20^\circ$ ,  $60^\circ$  and  $85^\circ$ . The gloss measurements of the coatings are listed in Table 1. For all three grazing angles, the gloss values decrease after the immersion, which indicates the coating surface is getting rougher and hence the barrier property of the organic coating is reduced. The decrease in the gloss value is much more pronounced for coatings immersed in the flowing DI water. It demonstrates that more blistering takes place for those coating samples.

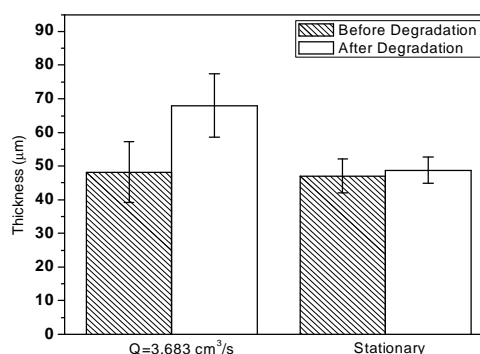


Fig. 2 Thickness of coating samples immersed in DI water with flow rate  $Q = 3.683 \text{ cm}^3/\text{s}$  and stationary immersion.

Table 1 Gloss measurements for coatings immersed in DI water with flow rate  $Q = 3.683 \text{ cm}^3/\text{s}$  and stationary immersion.

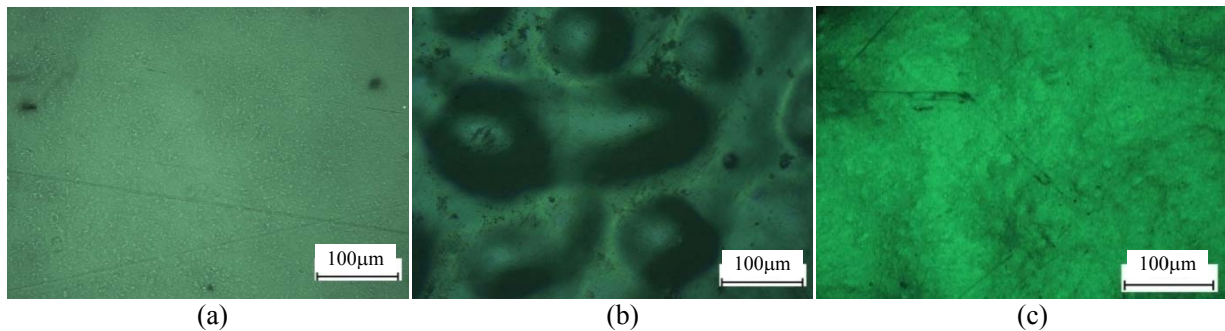
| Degradation condition             | Before degradation |                |                | After degradation |                |                |
|-----------------------------------|--------------------|----------------|----------------|-------------------|----------------|----------------|
|                                   | $20^\circ$         | $60^\circ$     | $85^\circ$     | $20^\circ$        | $60^\circ$     | $85^\circ$     |
| $Q = 3.683 \text{ cm}^3/\text{s}$ | $24.8 \pm 3.6$     | $56.3 \pm 7.5$ | $50.8 \pm 6.4$ | $12.4 \pm 2.8$    | $31.5 \pm 8.3$ | $17.2 \pm 3.1$ |
| Stationary                        | $22.2 \pm 1.0$     | $59.7 \pm 1.6$ | $57.1 \pm 4.1$ | $14.2 \pm 0.8$    | $44.7 \pm 3.9$ | $46.4 \pm 2.2$ |

### 3.1.3 Optical Microscopy and AFM Measurement

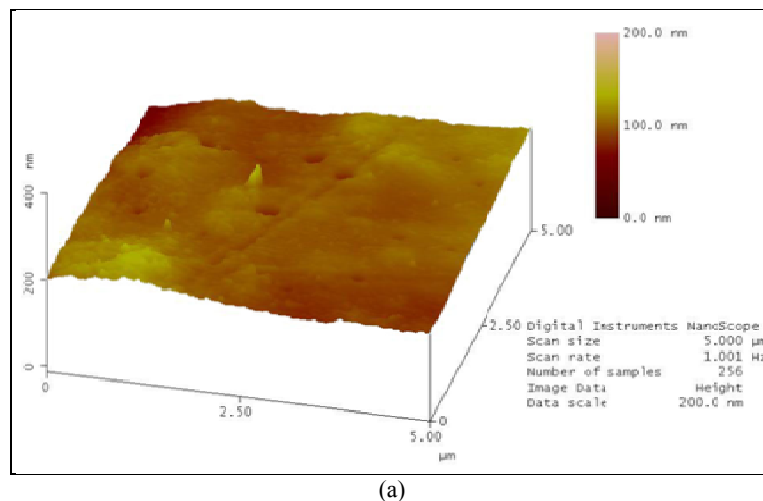
Fig. 3 shows optical microscopy images of the coating surface before and after the degradation. The surface is smooth before immersion. Under stationary immersion, DI water contributes a little to change the coating surface. However, after the immersion in flowing DI water, spherical protuberances appear on the coating surface. These protuberances could be the blisters connecting with each other.

The topography change measured by Atomic Force Microscopy (AFM) is in good agreement with the optical microscopy. As shown in Fig. 4a, the surface is flat before immersion with a small number of tips and holes. After 30 days immersion in the flowing DI water, blisters are formed on the coating surface, as shown in Fig. 4b. The left and right corners of this image are out of the AFM measurement range due to large height. It indicates that blistering on the coating surface is rather severe under the flowing condition. After 30 days

immersion in the stationary DI water, there are some protuberances on the coating surface, as shown in Fig. 4c. Previous work has mentioned that blistering is a common phenomenon in coating degradation representing the initial physical change due to alternating environments [14]. The formation of blistering is usually the first visible indication of insufficient protection by organic coating against corrosion [15]. Blistering may be caused by the permeation of water to coating metal interface due to osmotic pressure [16]. Our study shows that the flowing fluid over the coating surface promotes blistering to a more severe level. This may be explained by the fact that flowing DI water maintains the ion concentration gradient between the bulk solution and the coating by refreshing the fluid on the coating surface and hence the osmotic pressure is maintained throughout the immersion. On the contrary, for coatings in the stationary immersion, the ion



**Fig. 3** Microscopy images for the coating surface before and after degradation, (a) Before degradation, (b) After degradation with flow rate  $Q = 3.683 \text{ cm}^3/\text{s}$  and (c) After degradation under DI water stationary immersion.



(a)

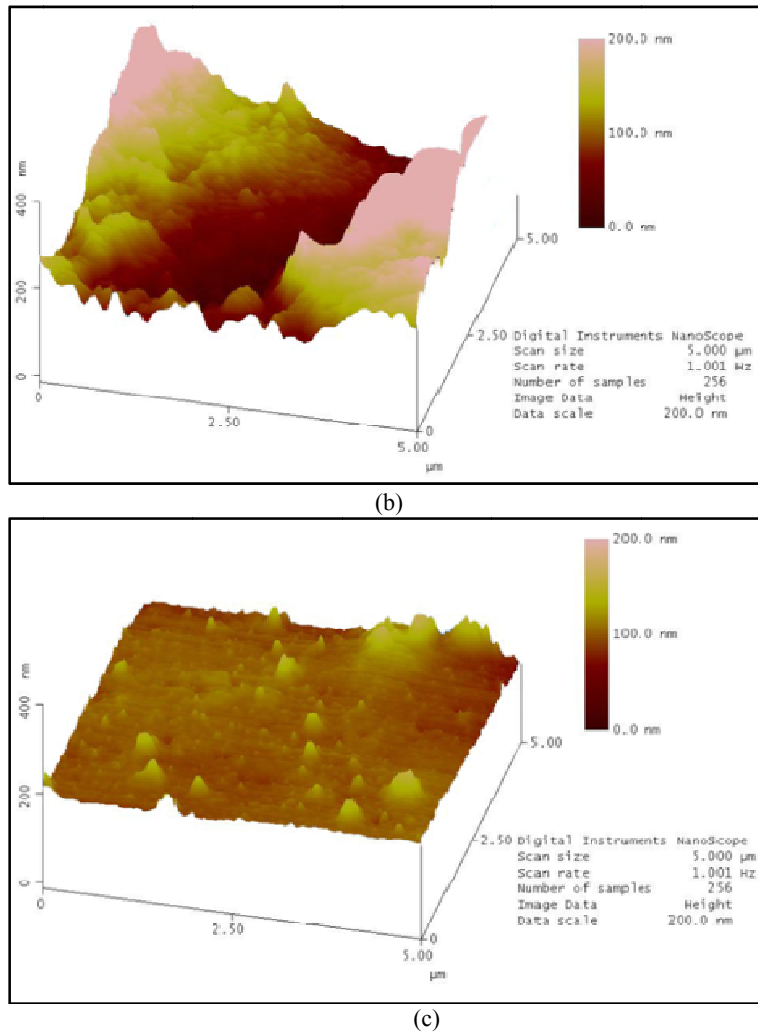


Fig. 4 AFM images for the coating surface topography before and after degradation, (a) Before degradation, (b) After degradation with flow rate  $Q = 3.683 \text{ cm}^3/\text{s}$  and (c) After degradation under DI water stationary immersion.

Table 2 Roughness of coatings immersed in DI water with flow rate  $Q = 3.683 \text{ cm}^3/\text{s}$  and stationary immersion.

|          | Before degradation | After degradation $Q = 3.683 \text{ cm}^3/\text{s}$ | After degradation stationary |
|----------|--------------------|---|------------------------------|
| RMS (nm) | 118.15             | 147.58  | 124.52                       |
| Ra (nm)  | 92.26              | 102.61  | 96.67                        |

concentration gradient decreases due to diffusion so that the osmotic effect diminishes as the diffusion achieves steady state.

The AFM device is equipped with topographic analysis software capable of measuring both values of square roughness (RMS) and average roughness (Ra). These roughness values are all obtained from  $100 \mu\text{m}$  images of the coating surface before and after the immersion, and the average values are listed in Table 2. It is clear that the roughness of the coating surface has increased after the degradation. Flowing condition

contributes more to increase the surface roughness due to blistering. The blistering also results in the increasing coating thickness as well as the decreasing gloss.

### 3.2 EIS Tests

To provide information in the electrochemical properties of the coatings, Electrochemical Impedance Spectroscopy (EIS) data are collected for coated panels immersed in the flowing fluid as well as the stationary immersion. The impedance modulus as a function of the

applied frequency in EIS tests is shown in Fig. 5 at flow rate  $Q = 3.683 \text{ cm}^3/\text{s}$ . A similar plot for the coated panel immersed stationary in DI water is shown in Fig. 6.

In a general way, the impedance modulus decreases with exposure time, showing a loss of protective properties of the coatings. The decrease rate for the impedance modulus is larger in the beginning of the immersion, and then followed by a relatively slower decrease (as shown in both Fig. 5 and Fig. 6). Due to good quality of the coating samples which contain no pinholes or air bubbles, the decrease of impedance modulus indicates the water uptake into the coating layer.

The EIS data at low frequency can be a strong predictor of the corrosion resistance of coating samples [17]. To illustrate the change in the coating's barrier property (e.g., coating degradation) over time, the relative impedance modulus as a function of time is shown in Fig. 7. The relative impedance modulus is obtained by normalizing the impedance modulus at 0.01 Hz with the modulus at initial immersion. This variable describes the relative decrease in impedance modulus at the low frequency during the immersion either in flowing fluid or stationary immersion. The relative impedance modulus decreases faster and more pronounced under flowing DI water than stationary

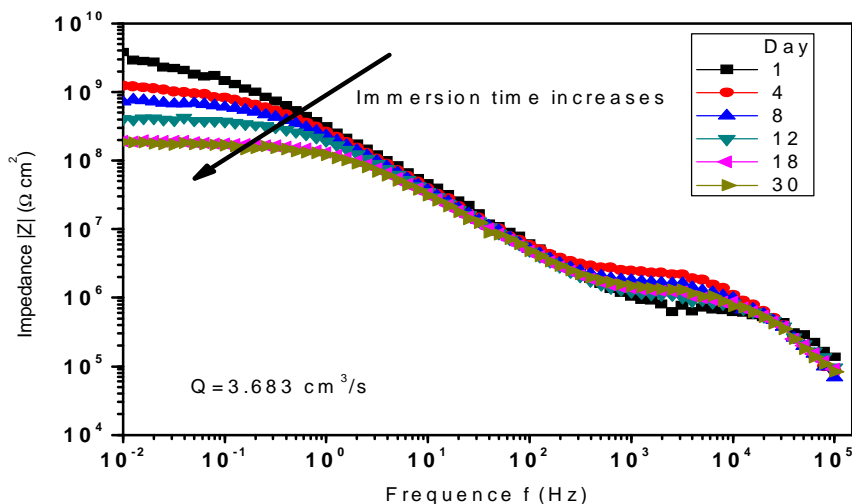


Fig. 5 Impedance modulus as a function of frequency for coating samples immersed in DI water with flow rate  $Q = 3.683 \text{ cm}^3/\text{s}$ .

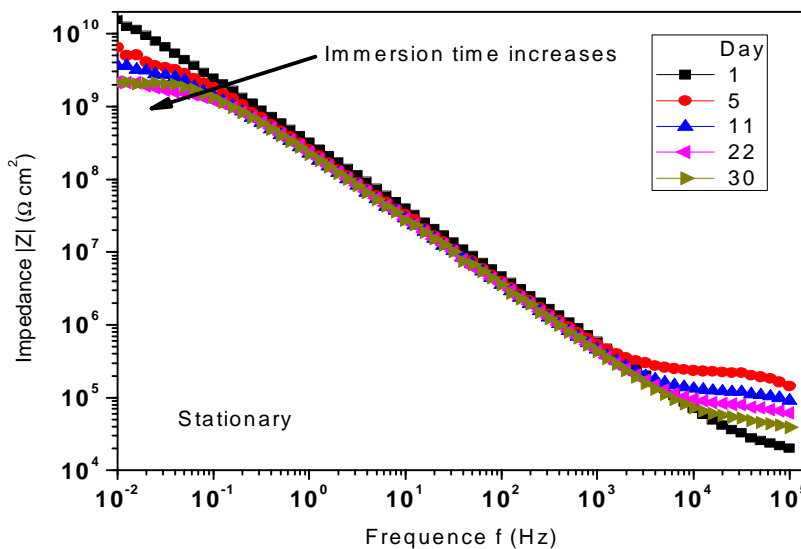


Fig. 6 Impedance modulus as a function of frequency for coating samples immersed stationary in DI water.

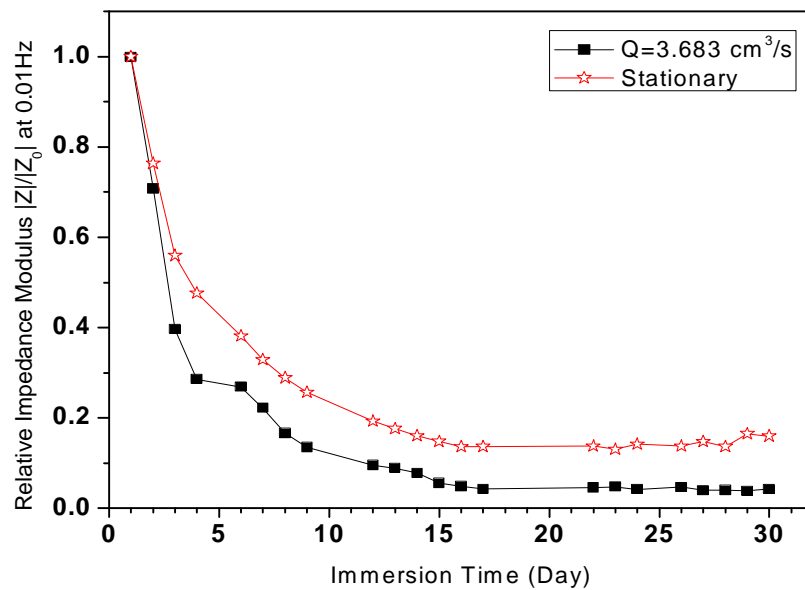


Fig. 7 Relative impedance modulus as a function of immersion time for coating samples immersed in DI water with flow rate  $Q = 3.683 \text{ cm}^3/\text{s}$  (squares) and stationary immersion (stars).

immersion. The rapid decrease rate indicates that flowing fluid enhances the water permeation of coating metal interface. It is in agreement with the results from optical microscopy and AFM images (Figs. 3 and 4) that flowing fluid promotes blistering, since blistering is formed as a consequence of the penetration of water.

#### 4. Conclusions

This paper studies the degradation of organic coatings under flowing and quiescent DI water immersion. Flowing fluid contributes more to the change of the topography of the coating surface due to its enhancement of blister formation. The increase in coating thickness and loss of gloss are resulted from the blisters generated on the coating surface after immersion in flowing DI water. The EIS test shows that coating's impedance modulus decreases more substantially under the flowing condition, which reveals flowing fluid accelerates the water penetration into the coating layer. Thus, based on both topography measurements and EIS results, it can be concluded that the flowing DI water degrades the barrier properties of organic coatings more aggressively. And the flowing DI water over the coating surface can be used as an

accelerated factor to predict the service lifetime of organic coatings.

#### Acknowledgments

The authors acknowledge the support by NASA ND EPSCoR, NSF EPS-0447679, and NDSU Advance FORWARD program sponsored by NSF HRD-0811239. Qixin Zhou acknowledges the support of the Presidential Doctoral Graduate Fellowship of North Dakota State University.

#### References

- [1] G.P. Bierwagen, Reflections on corrosion control by organic coatings, *Prog. Org. Coat.* 28 (1996) 43-48.
- [2] Q.L. Thu, G.P. Bierwagen, S. Touzain, EIS and ENM measurements for three different organic coatings on aluminum, *Prog. Org. Coat.* 42 (2001) 179-187.
- [3] G.P. Bierwagen, D.E. Tallman, J. Li, L. He, C.S. Jeffcoate, EIS studies of coated metals in accelerated exposure, *Prog. Org. Coat.* 46 (2003) 148-157.
- [4] M.M. Stack, T.M. Abd El Badia, Mapping erosion-corrosion of WC/Co-Cr based composite coatings: particle velocity and applied potential effects, *Surf. Coat. Technol.* 201 (2006) 1335-1347.
- [5] K. Ranjbar, Effect of flow induced corrosion and erosion on failure of a tubular heat exchanger, *Mater. Des.* 31 (2010) 613-619.
- [6] J.A. Wharton, R.J.K. Wood, Influence of flow conditions

- on the corrosion of AISI 304L stainless steel, *Wear* 256 (2004) 525-536.
- [7] S.S. Rajahram, T.J. Harvey, R.J.K. Wood, Erosion-corrosion resistance of engineering materials in various test conditions, *Wear* 267 (2009) 244-254.
- [8] T. Hodgkiess, D. Mantzavinos, Corrosion of copper-nickel alloys in pure water, *Desalination* 126 (1999) 129-137.
- [9] D. Mantzavinos, T. Hodgkiess, S.L.C. Lai, Corrosion of condenser tube materials in distilled water, *Desalination* 138 (2001) 365-370.
- [10] Z. Lu, T. Shoji, Y. Takeda, Y. Ito, A. Kai, S. Yamazaki, Transient and steady state crack growth kinetics for stress corrosion cracking of a cold worked 316L stainless steel in oxygenated pure water at different temperatures, *Corros. Sci.* 50 (2008) 561-575.
- [11] C.R. Alentejano, I.V. Aoki, Localized corrosion inhibition of 304 stainless steel in pure water by oxyanions tungstate and molybdate, *Electrochim Acta* 49 (2004) 2779-2785.
- [12] C.S. Jeffcoate, G.P. Bierwagen, Electrochemical comparison of coating performance in flowing vs. stationary electrolyte, *ACS Symposium Series* 689 (1998).
- [13] Y. Wang, G.P. Bierwagen, A new acceleration factor for the testing of corrosion protective coating: flow-induced coating degradation, *J. Coat. Technol. Res.* 6 (2009) 429-436.
- [14] X. Yang, D.E. Tallman, G.P. Bierwagen, S.G. Croll, S. Rohlik, Blistering and degradation of polyurethane coatings under different accelerated weathering tests, *Polym. Degrad. Stab.* 77 (2002) 103-109.
- [15] W. Funke, Blistering of paint films and filiform corrosion, *Prog. Org. Coat.* 9 (1981) 29-46.
- [16] J.H. Park, G.D. Lee, H. Ooshige, A. Nishikata, T. Tsuru, Monitoring of water uptake in organic coatings under cyclic wet-dry condition, *Corros. Sci.* 45 (2003) 1881-1894.
- [17] G.P. Bierwagen, L. He, J. Li, L. Ellingson, D.E. Tallman, Studies of a new accelerated evaluation method for coating corrosion resistance: thermal cycling testing, *Prog. Org. Coat.* 39 (2000) 67-78.