

A new acceleration factor for the testing of corrosion protective coatings: flow-induced coating degradation

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Abstract For corrosion protective coatings that are designed to give lifetimes of protection that may extend to 50 years, valid accelerated test methods are necessary to develop improved systems and validate performance. Fluid flow over metals has long been believed to influence the corrosion process. Studies have been focused on the effects of flow rate on the corrosion of bare metals. The influence of fluid flow on the degradation of metal-protective coatings has received less attention. This paper describes a preliminary study on the influence of laminar flow on organic coatings. A Hele-Shaw cell and its associated fluid control apparatuses are incorporated into the electrochemical cell setup. The barrier properties of the coating as a function of immersion time and flow rate have been monitored by electrochemical impedance spectroscopy. We observe that the barrier properties of the coating measured electrochemically decrease exponentially with the increasing flow rate. We propose that the flowing electrolyte solution could be used in acceleration tests for the lifetime prediction of organic coatings as the acceleration of failure we have observed does not appear to change the mechanism of failure. Further analysis is proposed to validate immersion flow rate as a universal accelerating parameter for coating failure.

Keywords Flow-induced corrosion, Coatings, Acceleration tests, EIS

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Introduction

The flow-induced corrosion is encountered in engineering equipment involved in marine technologies, as well as in oil and gas production processes. For bare metals, the fluid flow is believed to enhance the corrosion process via the promotion of oxygen transport, electrolyte transport, and mechanical removal of materials. A plethora of studies have been focused on the flow-induced corrosion on the metal surface which is in direct contact with the electrolytic solution.¹⁻⁵ Heitz¹ summarized the technological or engineering approaches since 1950s to the study of the flow-induced corrosion, the mechanism of which was categorized and the prevention strategies were discussed. Mercer and Lombard² comprehensively investigated the effects of temperature, dissolved oxygen content, chloride concentration, as well as the convection incurred by mechanical stirring, on the corrosion behavior of uncoated mild steel in water. They discovered that in chloride containing solutions, the steel mass loss increases with the rotation rate of the specimen. They believe that the stirring of the solution facilitates the transport of oxygen onto the surface of the specimen, and thus eliminates the limitation of the diffusion of oxygen. Wharton and Wood³ investigated the influence of fluid velocity on the pitting corrosion of stainless steel in laboratory environment. Ring electrodes were employed as steel specimens for the experimental tests in a circular pipe; electrochemical noise measurements (ENMs) were utilized to analyze the pit formation. The growth of pits was studied under a variety of flow conditions (the Reynolds number range from 1000 to 75,000). Free⁴ evaluated copper and AISI 1018 steel corrosion on a rotating disk electrode in an acidic environment. The corrosion rate was measured for a variety of solution conditions and compared with the prediction of the mathematical models considering the thermodynamics effects and

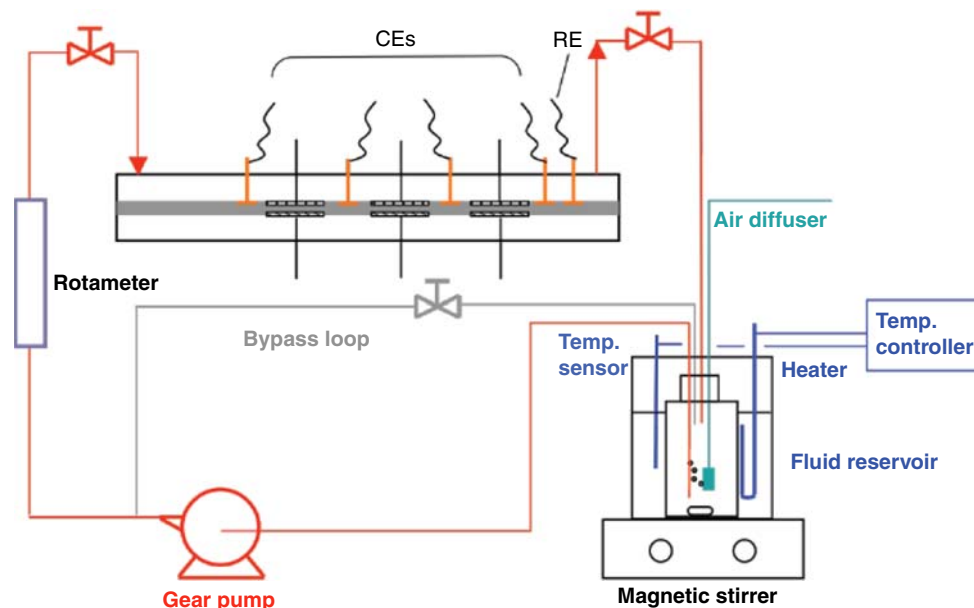


Fig. 1: Schematic diagram of the circulating flow

the mass transport of reacting species. The existence of surfactant inhibitors was also considered in their experiments and mathematical models. Melchers and Jeffrey⁵ reported the field observations of the effect of seawater velocity on the corrosion of mild steel. Consistent with earlier laboratory findings, the overall corrosion increases with the water velocity. The amount of increase in the corrosion is more prominent than the results obtained under laboratory conditions.

Coatings have been widely applied on metals to act as a corrosion barrier. The influence of the fluid flow on the barrier properties of the coating thus becomes a great interest in the service lifetime prediction of the coatings. Nevertheless, the mechanism is complicated since the effects of fluid flow are prominent in both the mass transport of water, oxygen, and electrolytes through the coating film and the morphology of the coating itself under fluid forces. Few studies have been contributed in the understanding of the influence of the fluid flow on the degradation of organic coatings protecting metals, although a considerable amount of research has been conducted on the response of the absorbed inhibitors to the fluid flow.⁶⁻⁹ Heeg et al.⁶ employed a rotating cylinder electrode in the study of flow influences on the persistency of inhibitor on C-steel. Zeller III⁷ investigated the protective functions of high-phosphorus electroless nickel on metals under different flow rates created by rotating cylinder electrodes. Hong et al.^{8,9} and others studied the effects of pipe flow on the imidazoline-based corrosion inhibitors. Electrochemical methods have been employed to characterize the inhibitor's protective function in the aforementioned studies. In addition, the mechanical removal of the coating film by strong hydrodynamic forces has been considered by Ruzic et al.¹⁰ Jeffcoate

and Bierwagen¹¹ showed, via electrochemical noise measurement (ENM) and electrochemical impedance spectroscopy (EIS), that the efficiency of the organic coating is significantly reduced by immersion in a flowing electrolyte solution compared with that in a stationary electrolyte solution.* Wei et al.¹² obtained a similar conclusion for fusion-bonded epoxy powder coating systems. However, the influence of the flow rate on the barrier properties of organic coatings was not investigated, and the flow may not always have been the laminar, controllable rates we used.

In this study, laboratory-scale devices have been designed and employed to investigate the fluid flow influence on the electrochemical barrier properties of organic coatings for steel. In the current work, coatings are exposed to laminar channel flow with a variety of controllable laminar flow rates. Electrochemical impedance spectroscopy has been employed to characterize the changes in coating properties after exposure.

Experimental setup

The experimental configuration is shown in Fig. 1. The fluid (a 3.5-wt% NaCl solution) stored in the reservoir is pumped into the test section, in which six coated steel panels are exposed to the electrolyte solution. Those samples are connected with copper wires for electrochemical measurements. Out of the test section, the fluid flows back to the fluid reservoir, where an air

* Mills and Bierwagen did some initial work on examining flow effects as an acceleration factor for corrosion in coated systems (NDSU 1994, Unpublished work).

pump and air diffuser are employed to accelerate the oxygen uptake of the fluid. A gear pump is selected to supply with small flow rates. A bypass loop is employed to control the flow rate. The temperature is maintained using a water bath.

A Hele-Shaw cell is constructed as shown in Fig. 2. An acrylic plastic sheet (shown as the gray part) with

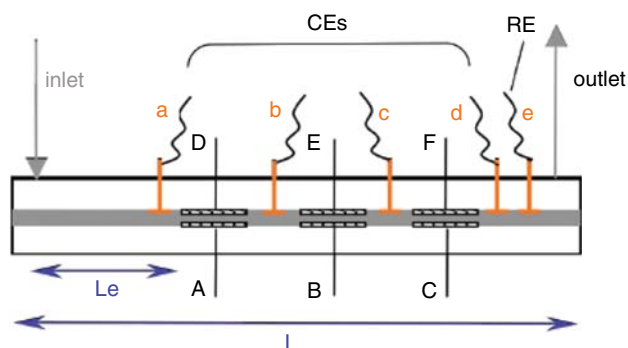


Fig. 2: Configuration of the electrochemical cell

0.25" in thickness is sandwiched by two parallel plates with tubes attached as the inlet and outlet. A 3" × 22" rectangular canal is cut in the middle of the sandwiched acrylic sheet, thus a rectangular channel is formed. As shown in Fig. 2, six coated stainless steel panels are attached to the upper and lower channel walls facing toward the flow. The location of the panels is chosen such that the first pair of panels is 6" away from the solution inlet. This ensures the fluid flow to fully develop before it reaches the sample panels. This long entrance part also serves as a sedimentation section for corrosion products or impurities suspended in the solution in the form of particles. We controlled the flow rate such that the Reynolds number of the flow is <math>Re < 400</math>. (The Reynolds number Re is a dimensionless number characterizing the features of fluid flow. It is expressed as $Re = hU\rho/\mu$, where h is the half width of the fluid conduit, U is the maximum flow velocity, ρ is the density, and μ is the viscosity of the fluid.) Five platinum electrodes are adhered to the channel wall acting either as counter electrodes or the reference electrode. In the EIS tests, a sample, three platinum electrodes and the flowing electrolyte solution work

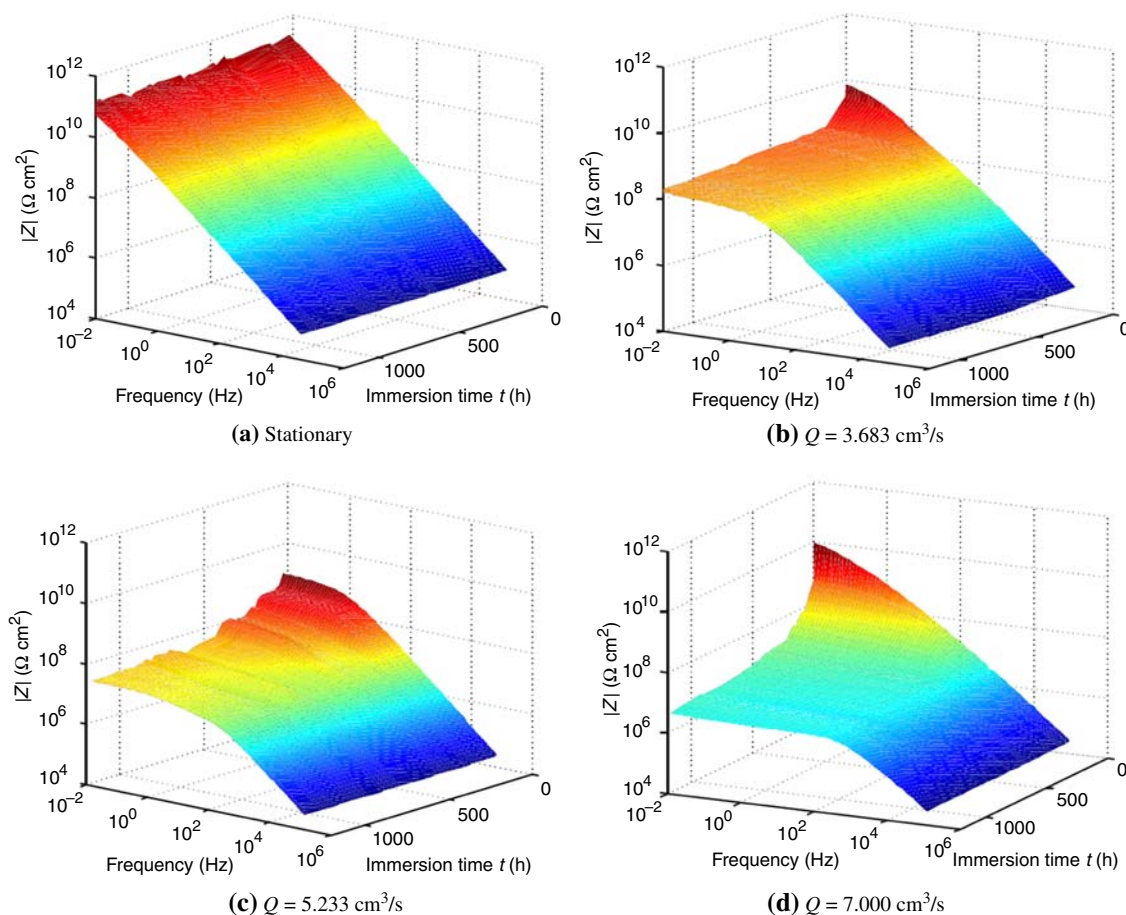


Fig. 3: Impedance modulus as a function of frequency and immersion time for coated steel panels. Panels are immersed in a 3.5% NaCl solution circulating with flow rates $Q = 3.683, 5.233, 7.000 \text{ cm}^3/\text{s}$. The results for the coating immersed in a stationary solution are included for comparison

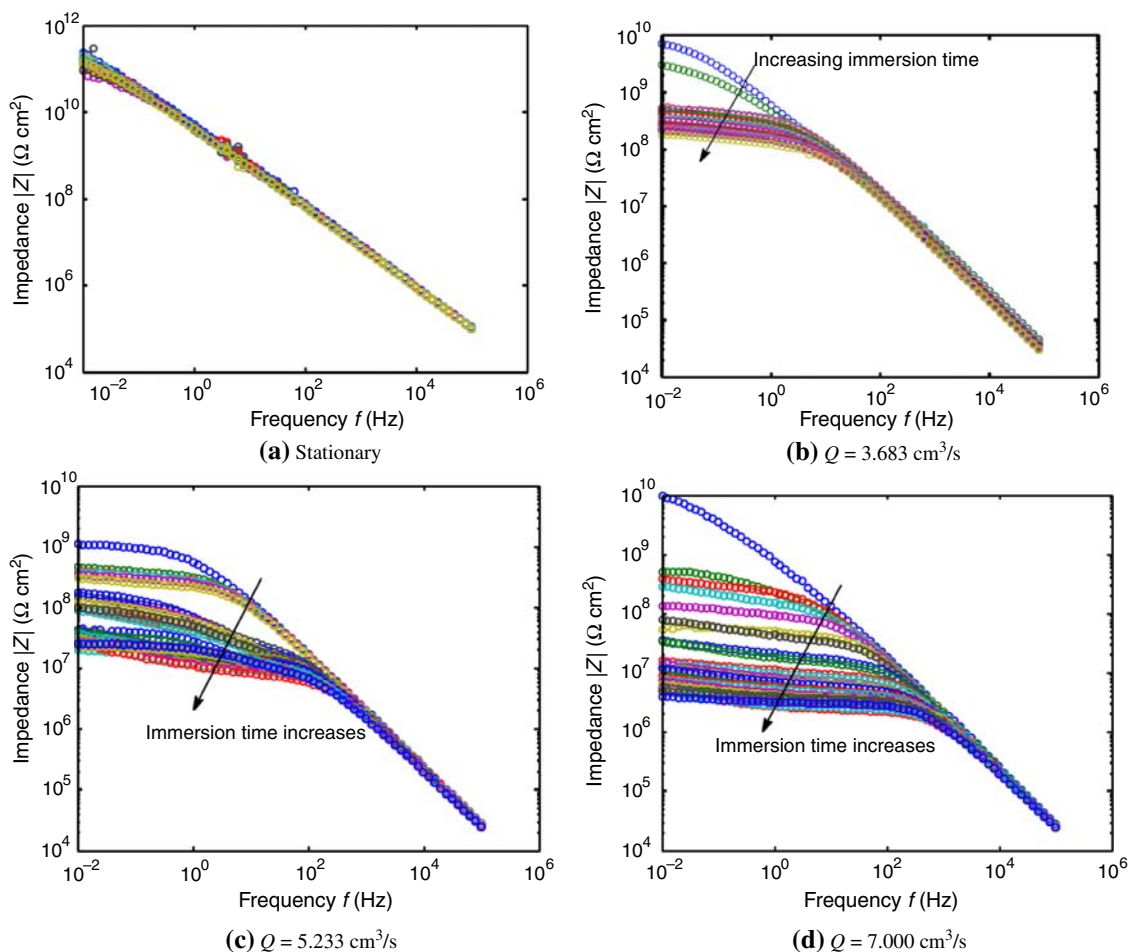


Fig. 4: Impedance modulus as a function of frequency for coated panels at a variety of immersion times. Panels are immersed in a 3.5% NaCl solution circulating with flow rates $Q = 3.683, 5.233, 7.000 \text{ cm}^3/\text{s}$. The results for the coating immersed in a stationary solution are included for comparison

together as an electrochemical cell. For example, when panel A (indicated in Fig. 2) is used as the working electrode, electrodes *a* and *b* are combined and used as the counter electrode; when panel B acts as the working electrode, electrodes *b* and *c* are combined and then employed as the counter electrode. The purpose of this arrangement is to ensure the electrical field around the working electrode to be as symmetric as possible. Electrode *e* always acts as the reference electrode in all cases. This device may also be used in ENMs where the electrochemical cell is completed by the working fluid, a pair of face-to-face panels (e.g., A and D) as the working and counter electrodes, and electrode *e* as the reference electrode.

Sample preparation

The stainless steel panels used in the flow chamber are coated with Korabor Aluminum Primer RP140, a chlorinated rubber based coating with aluminum flake

pigment, as well as Korethan Topcoat UT6581, an aliphatic polyester polyurethane resin based finish coat.* Both sides of the panels have been spray-coated with primer and topcoat. Dip coating is employed to protect the edges of the panel. Copper wire is attached onto the steel panel before coatings are applied. To seal the device better, 3M 764 tape is wrapped around the edges and the back of the panel. A 100% silicone rubber sealant made by GE (GE361) is used to attach the panels onto the channel wall. A two-component DEVCON Epoxy (S-35/35345) is employed to seal the holes the copper wire created through the channel wall. Currently, a 3.5% sodium chloride solution is used as the test fluid. We employ a water bath and a temperature controlling system to maintain the system temperature at 25°C.

* The coatings are from KCC Corporation (<http://www.kccworld.co.kr>) and graciously supplied by Dohn Lee.

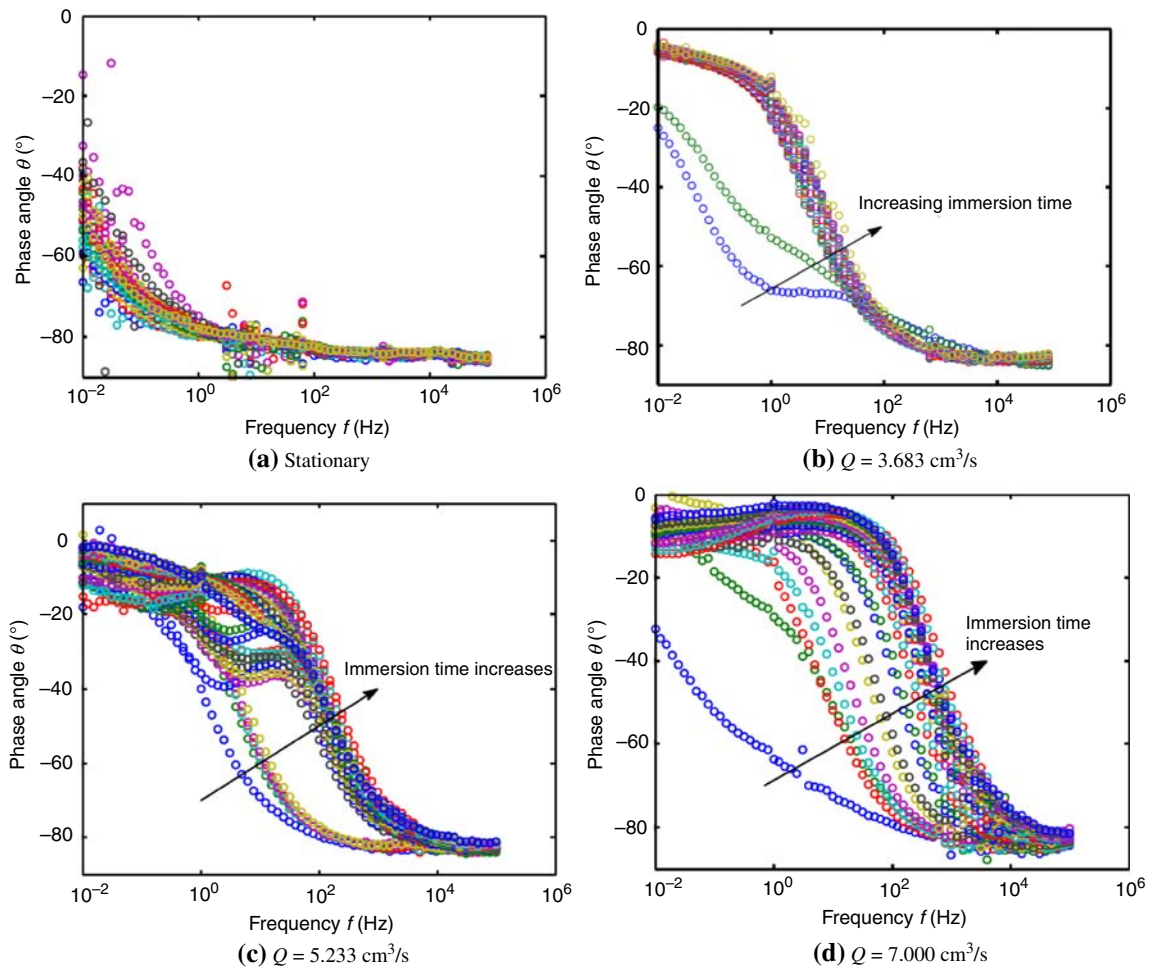


Fig. 5: The phase angle as a function of frequency for coated panels at a variety of immersion times. Panels are immersed in a 3.5% NaCl solution circulating with flow rates $Q = 3.683, 5.233, 7.000 \text{ cm}^3/\text{s}$. The results for the coating immersed in a stationary solution are included for comparison

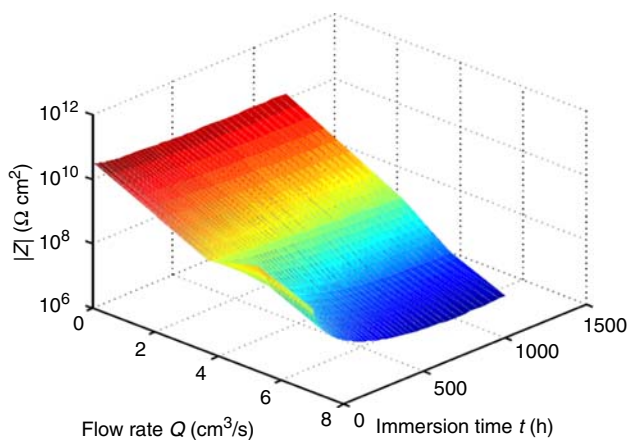


Fig. 6: Impedance modulus at 0.01 Hz as a function of flow rate and immersion time

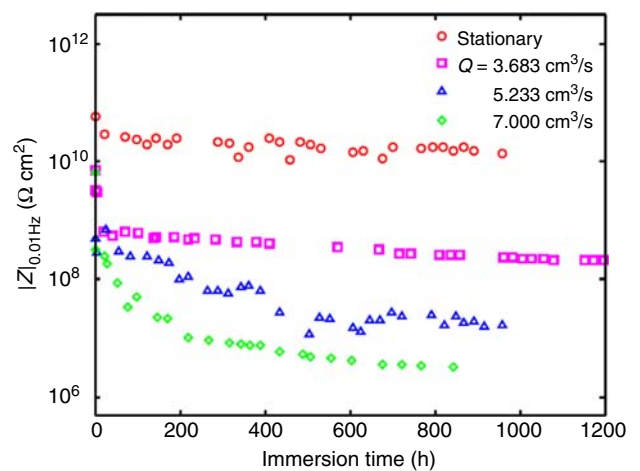


Fig. 7: Impedance modulus at 0.01 Hz as a function of the immersion time. The impedance of the coatings under a circulating 3.5% NaCl solution is compared with that immersed in a stationary NaCl solution

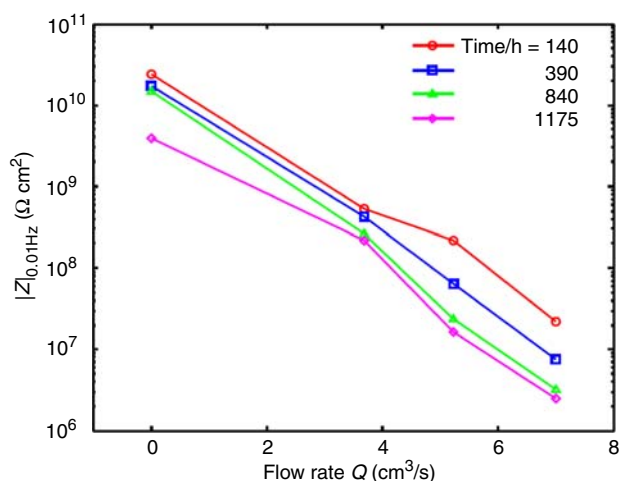


Fig. 8: Impedance modulus at 0.01 Hz as a function of the flow rate at immersion time = 140, 390, 840, 1175 h

Experimental results

Electrochemical impedance spectroscopy data have been collected for panels immersed in the flowing NaCl solution. Three flow rates have been applied: $Q = 3.683, 5.233, 7.000 \text{ cm}^3/\text{s}$. The immersion duration is around 1500 h. In addition, for comparison, panels immersed in an absolutely stationary solution are also considered. (The experimental setup for the stationary situation is the traditional three-electrode electrochemical cell.) As shown in Figs. 3 and 4, the impedance modulus is plotted as a function of the frequency applied in EIS tests as well as the immersion time. We observe that at low frequency (approximately $f < 10 \text{ Hz}$), the impedance modulus $|Z|$ decreases as the immersion time increases, while at higher frequencies the $|Z|$ appears independent on the immersion time. For higher flow rate, $|Z|$ shows a more prominent decrease with time, and the dependence on the immersion time extends to higher frequencies (as shown in Figs. 3d and 4d). The corresponding behavior of the phase angle as a function of the frequency is plotted in Fig. 5 for different flow rates.

The coatings approach a simple resistor at low frequency. To investigate the behavior of the coating resistance, we plot in Fig. 6 the impedance modulus $|Z|$ at a low frequency ($f = 0.01 \text{ Hz}$) as a function of the immersion time and flow rates. Data for the absolute stationary situation are included for comparison. In Figs. 7 and 8, we also plot in two dimensions the low-frequency impedance modulus as functions of immersion time and flow rate, respectively. As shown, upon immersion the impedance modulus decreases dramatically for panels in flowing electrolyte, while less decrease is observed for coatings in stationary electrolyte especially at the beginning of the immersion. We notice that the low frequency $|Z|$ decreases at a faster rate with time in higher flow rates. We also observe that the low frequency $|Z|$ are smaller by orders of

magnitude for higher flow rates than systems in stationary immersion at long times of immersion. In addition, Fig. 8 explicitly shows the exponential decay in the coating barrier property as the flow rate increases.

An equivalent circuit model has been established as shown in Fig. 9a, to analyze the flow influence on individual model elements, namely, the coating capacitance (C_c), double-layer capacitance (C_{dl}), charge-transfer resistance (R_{ct}), and pore resistance (R_{po}). The software, Zview,* is employed in the data fitting. The value of each component in the circuit model is obtained and plotted as a function of the immersion time, shown in Fig. 10. A Randles circuit model (shown in Fig. 9b) is found to be more applicable for coatings in stationary solution, thus C_c and R_{po} are considered zero in stationary environment. We notice that the pore resistance and the charge-transfer resistance decrease with immersion time. The resistance decreases in a faster manner for higher flow rates. For the coating capacitance and the double-layer capacitance, there is no obvious tendency observed with respect to the immersion time and the flow rate, as may be caused by a model artifact.

Discussion

We believe that the time-dependent decay in the coating barrier property under laminar flow may be caused by: (i) the water invasion; (ii) the diffusion of electrolytes and oxygen into the coating; (iii) the release of corrosion or degradation product from the coating-metal interface into the coating layers; (iv) the mechanical removal of the coatings by fluid shear, which is reflected in the decreased coating thickness; and (v) the modification of the shape of the solution inclusion in the coating as a response to the fluid shear.

The percolation of water into or out of single or multilayer organic coatings has been intensively studied.^{13–20} However, Fick's law of diffusion may not be able to explain the substantial drop in the barrier properties of coatings as we increase the flow rate, since the water concentration in the bulk (dilute) solution is maintained constant despite the different flow rates. The flow rate of the electrolyte solution may have a prominent influence on the diffusion process of ions entering and ions (as corrosion/degradation products) exiting the coating layers, as would be reflected on the values of the coating resistance and capacitance. The ablation on the coating surface over a significant long time may result in the decrease of the coating thickness and barrier properties of coatings. We expect to further investigate the relation between the flow rate and the ablation of the coatings. The modification of the percolation shape by the fluid shear may also contribute to the decay in the barrier properties of coatings. It is apparent that effective medium theory models or their

* <http://www.scribner.com/>

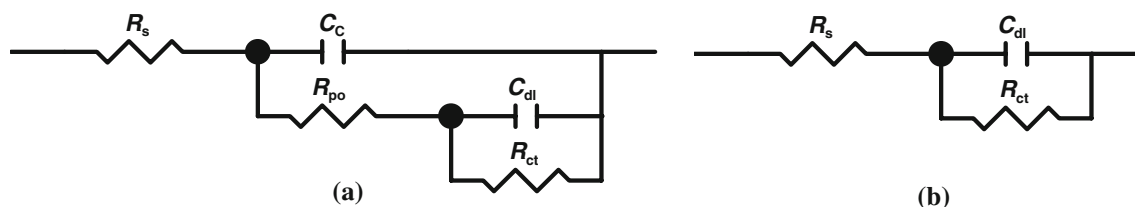


Fig. 9: Equivalent circuit model used for the impedance analysis: (a) circuit model for coating in flowing solution and (b) circuit model for coating in stationary solution

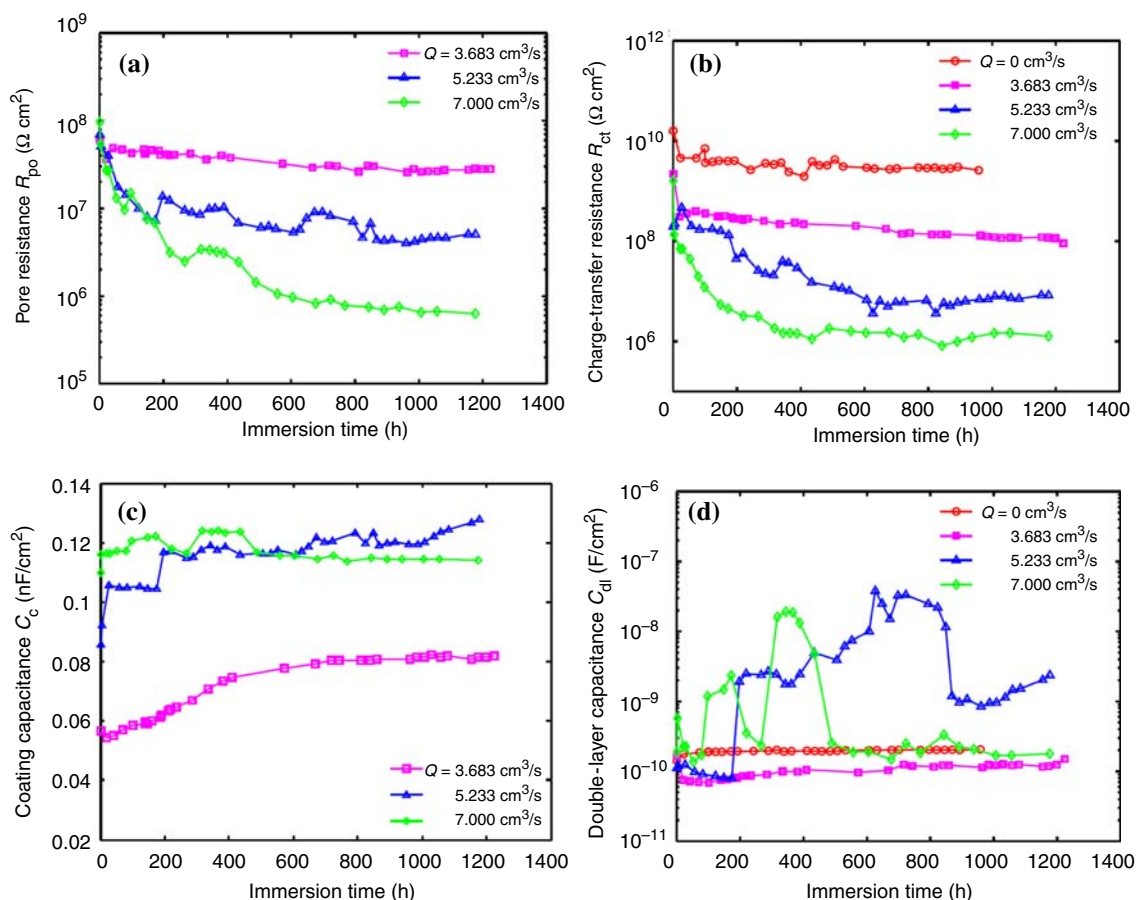


Fig. 10: Circuit model components vary as functions of time for flow rates $Q = 0, 3.683, 5.233, 7.000 \text{ cm}^3/\text{s}$

equivalent must be invoked to fully explain the transport behavior of composite coatings materials.¹⁶ Stafford et al.¹⁷ have shown that the aspect ratio between the length and width of the water inclusions in the coating influences the coating resistance by orders of magnitude. Mathematical models for the aforementioned processes will be established to explain the experimental findings in further investigation.

Conclusions

The influence of laminar flow on the barrier properties of coatings is investigated in this study. Laboratory-scale

devices have been designed to conduct the EIS measurements while the samples are immersed in flowing electrolyte solution with a variety of flow rates.

The impedance spectra show a time-dependent decrease in the coating barrier property. In addition, by varying the flow rate, we are able to observe the influence of the fluid flow on the impedance spectra. By investigating the low-frequency impedance modulus, we notice an exponential decay in the modulus as we increase the flow rate. This finding indicates that manipulating the flow rate could contribute in acceleration tests used in the service lifetime prediction for coatings. By establishing equivalent circuit models, we observe that coating resistance decreases as the flow rate and immersion time increase. The possible causes

for the exponential decay in the coating barrier properties under the increasing flow rate have been discussed.

These results are for only a single coatings system, but other work done in this laboratory¹¹ has shown very similar results for a different coatings system, and other unpublished work here indicates a significant increase in coating failure rate with flowing immersion vs stationary immersion. This work is preliminary in nature, and requires further experimental and theoretical analysis to utilize completely the methods and results described in this paper. However, the results are reproducible, and show some immediate utility as a screening protocol for rapidly comparing the relative barrier performance lifetimes of coatings over metals. Further work is necessary to validate immersion flow rate as a universal accelerating parameter for coating failure as has been shown for temperature as an accelerating factor.²¹ We are currently trying to expand our quantitative understanding of degradation accelerating factors in other studies from this laboratory.^{22,23}

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