Electrochemical impedance spectroscopy as a tool to measure cathodic disbondment on coated steel surfaces: Capabilities and limitations

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ABSTRACT

The disbondment of protective organic coatings under excessive cathodic protection potentials is a widely reported coating failure mechanism. Traditional methods of evaluating cathodic disbondment are based on ex situ visual inspection of coated metal surfaces after being exposed to standard cathodic disbondment testing conditions for a long period of time. Although electrochemical impedance spectroscopy (EIS) has been employed as an effective means of evaluating various anti-corrosion properties of organic coatings; its application for assessing the cathodic disbondment resistance of coatings has not been sufficiently exploited. This paper reports an experimental study aimed at developing EIS into a tool for in situ measurement and monitoring of cathodic disbondment of coatings. A clear correlation between EIS parameters and the disbonded coating areas has been confirmed upon short term exposure of epoxy-coated steel electrodes to cathodic disbondment conditions; however the degree of this correlation was found to decrease with the extension of exposure duration. This observation suggests that EIS loses its sensitivity with the propagation of coating disbondment, and that in order to achieve quantitative determination of the coating cathodic disbondment localized EIS measurements are required to measure the parameters related to local disbonded areas.

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1. Introduction

Cathodic disbondment is a mode of coating failure that frequently occurs in metal structures such as oil and gas pipelines, which are usually protected by organic coatings in conjunction with cathodic protection (CP). It is generally believed that cathodic disbondment of pipeline coatings is due to a CP induced strong alkaline environment at the coating defects that damages the bonding between coating and metal surfaces [1,2]. Traditional methods of evaluating cathodic disbondment of pipeline coatings in industry are based on the excavation and visual inspection of the pipeline surface. Current laboratory assessment of cathodic disbondment resistance (CDR) of coatings is based on ex situ visual inspection using standard laboratory testing methods such as AS4352, ASTM G8-96 and ISO 15711 [3–5]. Since CDR tests in sand or soil environmental conditions can take a long time, standard laboratory tests usually involve accelerated testing in a corrosive solution which aims to simulate the most aggressive field test condition. For

instance according to the Australian Standard AS4352, a constant current of 3 ± 0.02 mA is applied to a coated steel specimen with an artificial defect of 6 mm diameter immersed in a 3 wt.% NaCl solution. After 28 days of accelerated immersion test, the specimen is removed from the test cell and the coating disbonded area is estimated by stripping the coating from the metal surface using a knife followed by visual inspection of the test specimen [3].

There are a number of limitations associated with the current cathodic disbondment test methodologies. Firstly, these accelerated tests are operating at CP current densities significantly higher than those experienced in practical pipelines; therefore results from these tests may not be representative of long term coating performance under normal pipeline operating conditions. On the other hand it was reported that a high variation in test results could be found from different test samples [6,7]. For instance Holub et al. [6] investigated the performance of coatings under various standard cathodic disbondment test conditions, and noted major issues in test reproducibility and results inconsistency. These are believed to be due to differences in parameters and procedures specified in different CDR test standards. For instance different CDR test standards could apply different test temperatures, different electrolyte type or concentrations, different test duration, and different

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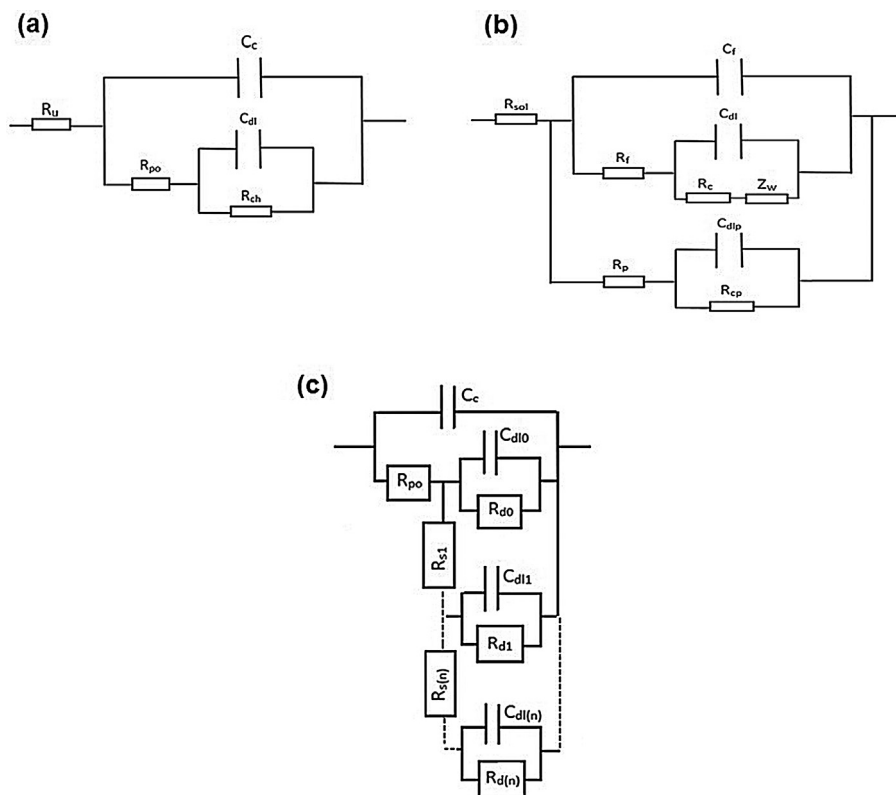*E-mail address:* mike.tan@deakin.edu.au (M.Y.J. Tan).

Fig. 1. Equivalent circuits proposed for analyzing the data collected from coated metal specimen [20,22,24].

CP techniques (e.g. CP under either constant potential or constant current). Indeed Smith et al. [8] noted that testing under high temperature conditions may not be a suitable accelerated testing method. In addition, current CDR test methods are designed for laboratory testing and hence are not transferrable to in situ monitoring of the disbondment of pipeline coatings.

In situ measurement and monitoring of the initiation and propagation of cathodic disbondment in field conditions would be desirable, however this would require techniques that are able to measure the dynamic and localized changes of parameters associated with these processes. Over the past decades the advent of advanced microscopic and scanning probe techniques, such as the scanning Kelvin probe technique [9–12], has facilitated substantial research aimed at measuring localized coating disbondment occurring at the interface between coating and the metal surface; however these scanning probes are laboratory based. They are not readily applied in practical testing of thick pipeline coatings as they require the scanning of a coated surface by positioning micro-sized sensors extremely close to the surface (e.g. 100 μm) [13].

Electrochemical impedance spectroscopy (EIS) is a technique that has been used for decades to measure and monitor the degradation of organic coatings by quantitatively measuring the resistances and capacitances of coated electrodes in an electrochemical cell [14–20]. The Nyquist plots of coated metals have characteristic behavior dependent on the state of the coating, thereby making it possible to follow the penetration of an electrolyte into the coating and to detect the initiation of corrosion at the metal/coating interface [21]. For instance when the electrolyte permeates the coating and reaches the metal surface, the typical single capacitive arc response of an high impedance intact coating would be replaced by one or more semi-circles and a Warburg impedance (typified by a line with the slop of 45°) that indicate the existence of different electrode processes with various time constants as well as a diffusion process on the coated metal surface.

Analysis of impedance data can be used to quantitatively determine both resistances and capacitances of a coated electrode surface in an electrochemical cell if an appropriate equivalent circuit is used to help with the physical interpretation of the impedance data. Each element of the equivalent circuit models a specific function of the electrode/electrolyte interface.

Over the past decades many different equivalent circuits have been proposed to interpret the complex impedance behavior of coated metals. The most commonly used equivalent circuit for describing a degraded organic coating on a metallic substrate is shown in Fig. 1a [20]. In this circuit R_u (or R_s) is the resistance of the electrolyte or the uncompensated resistance between the working electrode (WE) and reference electrode (RE); C_c is the capacitance of the organic coating; R_{po} is the pore resistance of the coating and R_{ch} is the charge transfer resistance (or polarization resistance) of the metal substrate beneath the coating. The R_{ch} has been related to disbonded area under the coating through an equation, $R_{ch} = R_{ch}^o/A_d$, where A_d is the disbonded area under the coating and R_{ch}^o, represents the area specific magnitude of this parameter for bare metal [20]. Also, if coating disbondment occurs, water could reach the metal surface and a double layer forms. Therefore, changes in C_{dl} can be related to the disbonded area of the coating. Based on this assumption the C_{dl} is also related to the area (wet area) under the coating through the equation, $C_{dl} = C_{dl}^o A_d$, where A_d is the disbonded area under the coating and C_{dl}^o is the area specific magnitude of parameter for bare metal [20].

Another attempt of studying coating disbondment using EIS was made by Hirayama and Haruyama [22] who proposed the model shown in Fig. 1b to fit the EIS data from degraded coatings containing pores. In this model a parallel circuit for coating pores is combined with the circuit for the pore-free part of a coated steel substrate. In this model R_{sol} is the solution resistance, C_f and R_f are the capacitance and ionic resistance of the coating, respectively; C_{dl} and R_c represent the double-layer capacitance and the charge