Capabilities and limitations of direct current and electrochemical impedance mapping in measuring cathodic disbondment of coatings using multi-electrode array

Citation:

CAPABILITIES AND LIMITATIONS OF DIRECT CURRENT AND ELECTROCHEMICAL IMPEDANCE MAPPING IN MEASURING CATHODIC DISBONDMENT OF COATINGS USING MULTI-ELECTRODE ARRAY

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SUMMARY: An electrochemically integrated multi-electrode array has been used to monitor and evaluate the cathodic disbondment of a coating by means of (i) measuring the local electrochemical impedance and (ii) measuring local direct current during its exposure to an aggressive solution under a cathodic protection (CP) potential. The performance of these two measurement methods in determining the disbonded area of the coating has been evaluated by comparing the impedance and current maps measured using the multi-electrode array under different CP potential and different environmental resistivity conditions. The results demonstrate that both current mapping and electrochemical impedance mapping are capable of evaluating the disbonded area of coating at higher level of CP potential (e.g. -1400 $mV_{Ag/AgCl}$) during exposure to a solution with a low resistivity. However, the current maps measured at lower CP potential (e.g. -950 $mV_{Ag/AgCl}$) and measured in a solution with higher resistivity (e.g. 20 Mohm.cm) did not accurately correlate with the cathodic disbondment area of the coating. The electrochemical impedance maps measured at the same conditions, nevertheless, accurately determined the disbonded area of the coating. According to results from this work the electrochemical impedance mapping is found to be more capable of evaluating the cathodic disbondment of coating under different conditions.

Keywords: Coatings, Cathodic disbondment, Multi-electrode array, Direct current, Electrochemical impedance

1. INTRODUCTION
Cathodic disbondment has been widely reported as one of the major failure modes of coating disbondment, especially on coated steel pipelines and other underground coated metal structures which are normally protected by impressed cathodic current or sacrificial anodes [1]. Severe cases of coating cathodic disbondment occurs under excessive cathodic protection (CP) conditions where more products of cathodic reactions such as an alkaline environment (pH between 10 and 14) and hydrogen gas are produced at the macro-defect sites in coatings that damage the interfacial metal/coating bonds [2, 3].

Over the past decades some techniques such as electrochemical impedance spectroscopy (EIS) [3-7] and some extremely meticulous techniques such as scanning acoustic microscopy (SAM) [8-14], scanning kelvin probe (SKP), scanning vibrating electrode technique (SVET) [14-18], and, localized electrochemical impedance

spectroscopy (LEIS) [19-22] have been employed to monitor coating disbondment. However, all these techniques have certain limitations in measuring the cathodic disbondment of thick coatings that are commonly used to protect buried structures such as pipelines. For instance, the authors of current paper reported that conventional EIS has limitations in detecting the disbonded area of defective coatings because global electrochemical impedance measurement is dominated by the low impedance at the coating defect area, and is not sensitive to coating disbondment [23].

One useful and practical tool for studying the cathodic disbondment of coating is multi-electrode array, also known as wire beam electrode (WBE) [24], which allows monitoring the electrochemical parameters from local areas on a coated electrode. Direct current measurement and electrochemical impedance spectroscopy (EIS) have been used previously to study the coating disbondment and degradation [25-26]; specifically it has been used to monitor the cathodic disbondment of a coating with 60 μm thickness by means of current distribution mapping [27]. In a recently published work we employed the multi-electrode array for monitoring the cathodic disbondment of a thick polyester coating (1000 μm) by means of measuring and mapping the "direct current" and "electrochemical impedance" on a polyester coated multi-electrode array [28]. In this paper we report a study aiming at evaluating the efficiency of these two techniques in monitoring the cathodic disbondment of thick coatings under different levels of CP potential and in solutions with different resistivity.

2. EXPERIMENTAL

The schematic of the employed multi-electrode array (custom-made by Proficiency Contracting Pty. Ltd) with a slight modification to the old generation of multi-electrode array is shown in Figure 1. The multi-electrode array consists of 100 closely packed (gap size: 0.10 ± 0.05 mm) and isolated square shaped electrodes of carbon steel 1020 (2.44 mm x 2.44 mm). The terminals of the wire bundle can be connected together to simulate a one piece electrode. The working surface of the array electrode was polished using 600 and 1200 grit SiC paper and was washed with acetone. The transparent polyester coating (Barnes Products Pty. Ltd.) was prepared by mixing unsaturated polyester resin with 1 wt.% methyl ethyl ketone peroxide (MEKP) as a curing catalyst. The coating was applied on top of a sample of multi-electrode array by brushing. Coated sample was dried at room temperature for 7 days. The measured dry film thickness using a digital Elcometer thickness gauge was 1000±20 μm. An artificial defect of 5 mm diameter was drilled at the center of the coated samples by flat ended bit to reach the metal surface. The coated multi-electrode array was inserted and fixed into an electrochemical cell that was filled with aqueous solution of 3 wt.% NaCl solution. Potential of -1400 mV$_{Ag/AgCl}$ was applied to the sample using a VMP3-300 potentiostat (Bio-Logic Science Instruments) through a platinum wire inserted in a fritted glass with pore size of 10-15 micron as counter electrode. During application of the CP potential the electrodes were connected at the terminals through a connector. Sample was exposed to solution under CP for 600 hours.

As shown in Figure 1, to perform in-situ local EIS measurement on each electrode, the terminal of the array electrode was connected to a manual switcher enabling the measurement of EIS on each of the electrodes (as WE1 in Figure 1), while it was disconnected from the other 99 coupled electrodes (as WE2). In order to perform an in-situ EIS measurement on WE1 and simultaneously controlling the CP potential on the WE2, two potentiostat channels of the VMP3 instrument (Bio-Logic Scientific) in CE to ground connection mode was used (details of connections elaborated in Figure 1). Using channel 1, the same CP potential as test potential is applied to WE1 until the response current is stable, following by measuring EIS at the same CP potential. Simultaneously, CP was applied to WE2 to ensure cathodically protecting rest of 99 electrodes. The EIS was measured with a perturbation potential of ±10 mV in the frequency range of 100 KHz to 300 mHz.
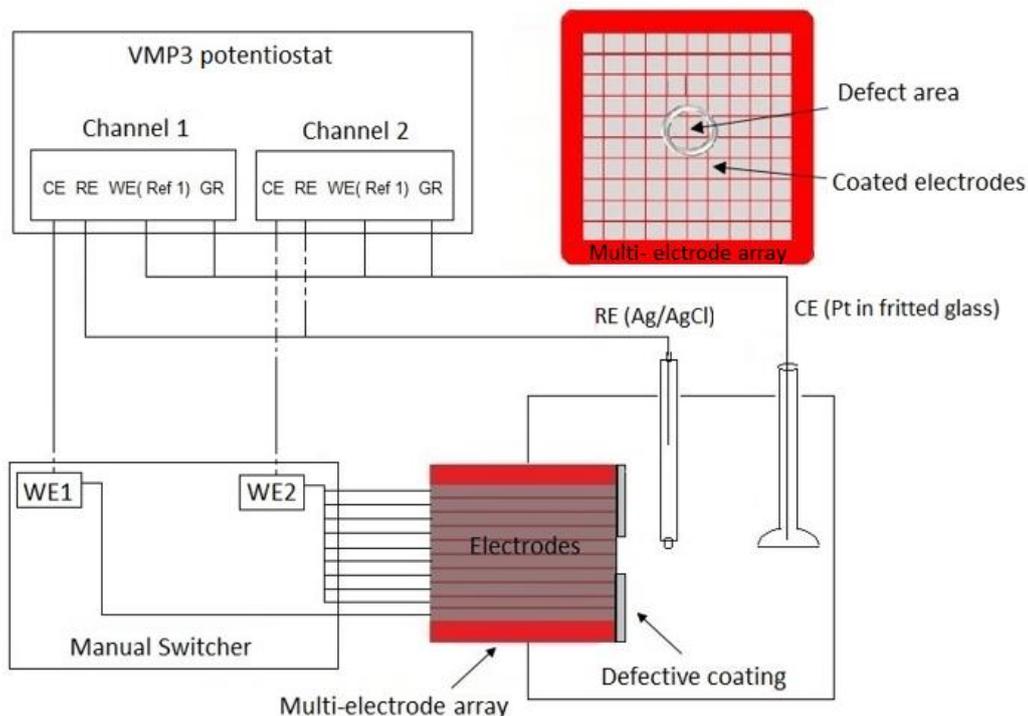
Figure 1 Schematic diagram of the experimental setup for local EIS measurement under CP

For measuring and mapping the local direct current, the electrode's terminal of the array electrode was connected to a grid switching and signal measurement instrument (CPE Systems Pty. Ltd.) equipped with an automatic switcher and a zero resistance ammeter with the resolution of ±3 nA in current measurement. The automatic switcher was programmed to maintain 99 electrodes connected to the WE1 terminal while leaving the remaining electrode connected to the WE2 terminal. After a certain sampling time, the electrode connected to WE2 was changed following by a pre-determined scanning sequence that sweeps the whole array. For measuring the current under cathodic protection conditions, the CP potential of -1400 mV$_{Ag/AgCl}$ was controlled over the all electrodes as working electrode by VMP3 potentiostat using a typical three electrodes setup. The zero resistance ammeter (ZRA) which was internally connected between WE1 and WE2 measured the current with a sampling rate of 10 reading per electrode. After 600 hours the current and electrochemical impedance were measured on the same sample under -950 mV$_{Ag/AgCl}$ while exposure to aqueous solution of 3wt.% NaCl (with resistivity of 20 ohm.cm) and also under -1400 mV$_{Ag/AgCl}$ while exposure to distilled water (with resistivity of 20 Mohm.cm).

3. RESULTS AND DISCUSSION

Figure 2 shows the maps of amplitude of electrochemical impedance (|Z|$_{300mHz}$) and maps of current distribution (i) which were obtained by means of measuring the local parameters at CP potential of -1400 mV$_{Ag/AgCl}$ over the coated multi-electrode array during different exposure of sample to solution with resistivity of 20 ohm.cm under CP potential.
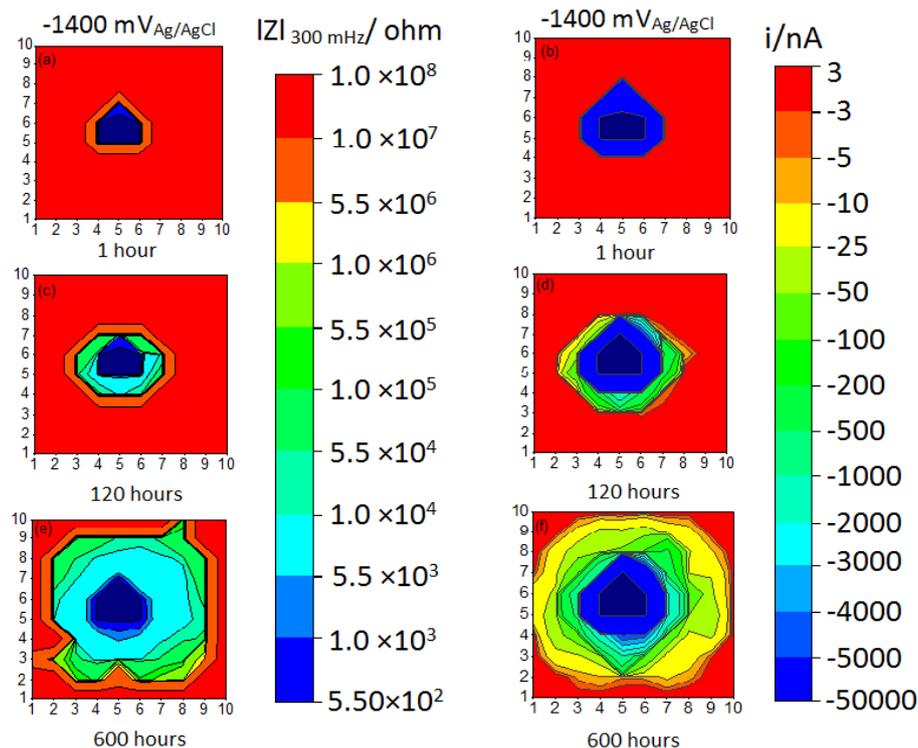
Figure 2 Maps of electrochemical impedance : (a, c, e) and direct current (b, d, f) measured at CP potential of -1400 mV$_{Ag/AgCl}$ on coated multi-electrode array after with a defect after 1, 120 and 600 hours exposure to solution with resistivity of 20 ohm.cm.

It is clear that the current and impedance maps measured after 1 hour exposure (Figure 2) are characterized with a small area at the centre of maps with current values more negative than -3 nA and impedance values $<1\times10^2$ ohm correlating to electrochemical activity of metal surface of defect area. The defect is surrounded with areas of high impedance $> 1\times10^7$ ohm and very small current values close to zero, which are related to areas with intact coating. By extending the exposure time to 120 hours the impedance values on sites around the defect area drop to values between 1×10^7 ohm and 5.5×10^3 ohm (Figure 2c) along with forming similar sites on current maps with values more negative than -3 nA (Figure 2d); these areas form around the defect upon cathodic disbondment of coating and access of solution to metal surface through disbonded gap between coating and metal surface. By extending the exposure time to 600 hours the propagation of disbonded area is elaborated on maps of current and impedance (Figure 2e and Figure 2f). These results clearly indicate that both techniques of electrochemical impedance and current mapping performed at CP potential of -1400 mV$_{Ag/AgCl}$ while exposure to a solution with low resistivity (20 ohm.cm) are efficient in detecting and monitoring the cathodic disbondment of coating.

In order to understand the performance of these techniques in different exposure environments and under different CP conditions, the disbonded area on the sample with disbonded coating after 600 hours was evaluated by measuring local impedance and current at CP potential of -950 mV$_{Ag/AgCl}$ while keeping the sample exposed to solution with resistivity of 20 ohm.cm (Figure 3c and Figure 3d) and also by measuring both electrochemical impedance and current on sample at -1400 mV$_{Ag/AgCl}$ while exposure to solution with a high resistivity of 20 Mohm.cm (Figure 3e and Figure 3f). These results can be compared easily with the former measurement performed at potential of -1400 mV$_{Ag/AgCl}$ while exposure to low resistivity solution of 20 ohm.cm (Figure 3a and Figure 3b).

Comparing the maps obtained by means of local measurements under different conditions have shown that the current maps measured at lower CP potential of -950 mV$_{Ag/AgCl}$ in lower solution resistivity and also the current

maps measured at higher CP potential of -1400 mV$_{Ag/AgCl}$ in higher solution resistivity are characterized with major areas with current values <-3nA (Figure 3d and Figure 3f). This means that although according to current and impedance maps of Figure 3a and Figure 3b, most parts of polyester coated electrode has been disbonded during 600 hours of exposure, current mapping at lower CP potential and higher solution resistivity did not correlate with the cathodic disbondment area of the coating accurately. On the other hand, the electrochemical impedance mapping measured at the same conditions of lower CP potential and higher solution resistivity (Figure 3c and Figure 3e) were successful in accurately evaluating of disbonded area of sample.
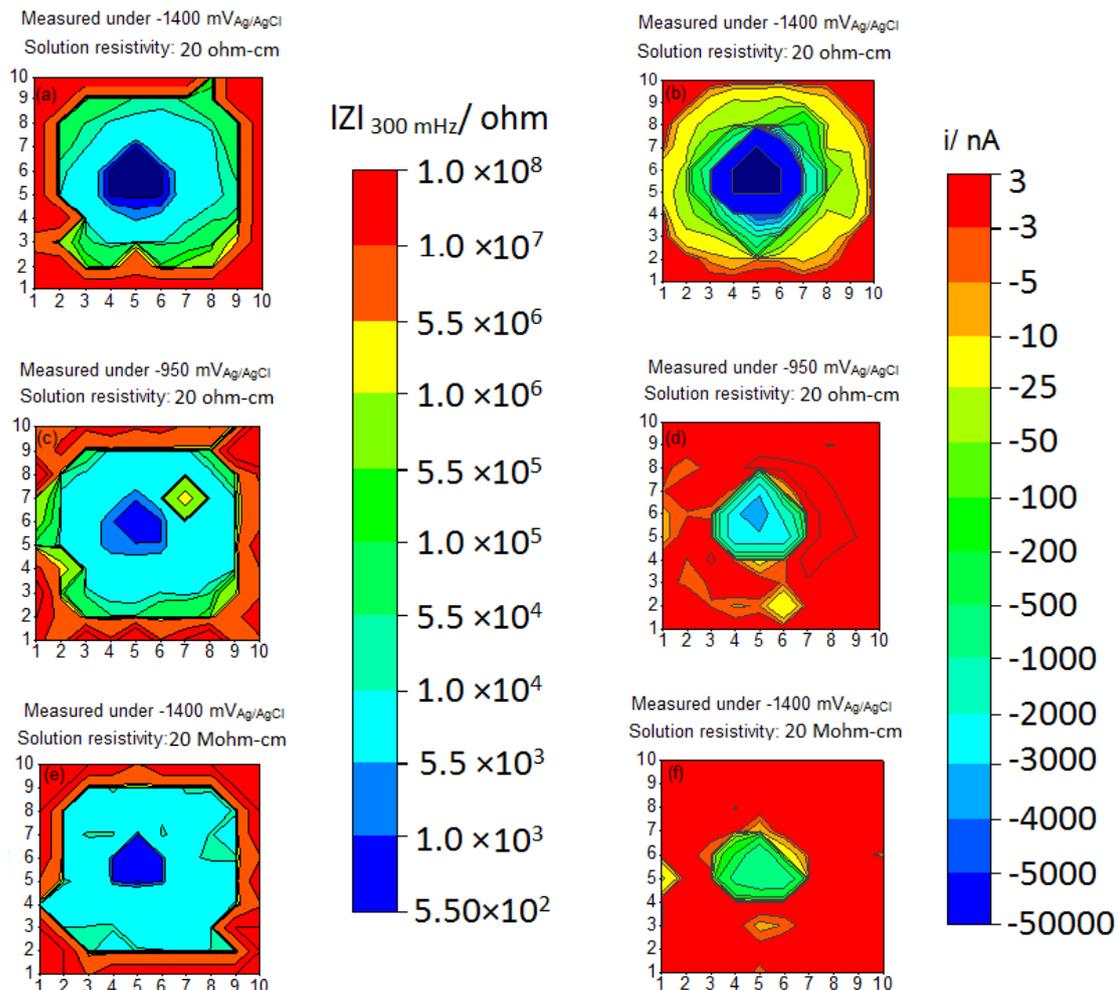

Figure 3 Maps of electrochemical impedance and direct current measured over coated multi-electrode array after 600 hours measured under -1400 mV$_{Ag/AgCl}$ while exposure to a solution with resistivity of 20 ohm.cm (a, b); measured under -950 mV$_{Ag/AgCl}$ while exposure to a solution with resistivity of 20 ohm.cm (c, d); measured under -1400 mV$_{Ag/AgCl}$ while exposure to a solution with resistivity of 20 Mohm.cm (e, f).

4. CONCLUSIONS

Both techniques of electrochemical impedance and current mapping over the coated multi-electrode array surface have been found to be capable of detecting, monitoring and evaluating the cathodic disbondment of a defective polyester coating with 1000 μm thickness exposed to a low resistivity solution (20 ohm.cm) under CP potential of -1400 mV$_{Ag/AgCl}$ during 600 hours exposure. However current mapping performed on the sample at lower CP potential of -950 mV$_{Ag/AgCl}$ and in a solution with higher resistivity (20 Mohm.cm) appear to be not efficient in evaluating the real disbonded area of the coating. In contrast, the electrochemical impedance maps

collected at the same measurement and environmental conditions accurately evaluated the disbonded area. These findings elaborate that electrochemical impedance mapping performs more efficiently than direct current mapping in measuring and evaluating the cathodic disbonded area of coating under different conditions of measurement and environmental exposure.

5. ACKNOWLEDGMENTS

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Fariba Mahdavi graduated from the University of Kashan in Iran and worked on anti-corrosion coatings for 6 years before studying for a Master degree at the University Putra Malaysia. She is currently third year PhD student at Deakin University in Australia. Her PhD research focuses on developing a new methodology based on advanced electrochemical techniques for measuring, monitoring, and, understanding the cathodic disbondment of pipeline coatings.

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Professor Maria Forsyth completed her PhD in January 1990 at Monash University and moved to Northwestern University to take up a Fulbright Fellowship in the area of solid electrolytes for lithium batteries. On her return to Melbourne she worked at DSTO for a year before joining the Department of Materials Engineering as a Lecturer in 1993. In 2001 she was awarded an ARC Professorial Fellowship and is currently the Chair in Electromaterials and Corrosion Sciences at Deakin University, within the Institute for Technology Research and Innovation (ITRI). She is co-author of over 280 refereed journal papers, has delivered over twenty invited talks in the last 5 years and has over 7000 citations at present