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Understanding the effects of applied cathodic protection potential and environmental conditions on the rate of cathodic disbondment of coatings by means of local electrochemical measurements on a multi-electrode array

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ABSTRACT

The effect of cathodic protection (CP) potential on cathodic disbondment of a defective coating has been investigated by monitoring the coating disbondment processes during the exposure of coated electrodes to a corrosive solution. The monitoring of coating disbondment was achieved by in situ measurement of local electrochemical impedance and direct current distributions over a multi-electrode array surface under various levels of CP potentials as well as under open circuit potential (OCP). The effects of CP potential and the environmental conditions on the initiation and propagation of coating disbondment have been quantified based on changes in local electrochemical impedance and current distribution maps. The rates of cathodic disbondment have been found to be highly dependent upon the applied CP potential. At OCP and low CP potentials of $-760\text{ mV}_{\text{Ag}/\text{AgCl}}$ and $-950\text{ mV}_{\text{Ag}/\text{AgCl}}$, little or only slight coating disbondment occurred. When the CP potential reached hydrogen evolution potential levels, such as -1100 , $-1200\text{ mV}_{\text{Ag}/\text{AgCl}}$, and $-1400\text{ mV}_{\text{Ag}/\text{AgCl}}$, the rates of disbondment increased significantly. This result indicates that the evolution of hydrogen likely played an important role in accelerating cathodic disbondment of the coating, and that the 'critical potential' at which the hydrogen evolution becomes a significant and dominant electrochemical reaction is important for cathodic disbondment of coatings. It was also found that once the cathodic disbondment initiated under very negative CP potentials, the disbonded distance would spread at an almost constant rate. These results suggest that a practical method of controlling coating disbondment is to ensure that the applied CP potential is below the 'critical potential'.

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1. Introduction

Cathodic disbondment refers to the loss of adhesion of an organic coating to the substrate when a coated steel structure is cathodically protected through impressed current or a sacrificial anode. It is a major form of electrochemically induced organic coating failure that frequently takes place at the metal/coating interface on cathodically protected steel infrastructure such as buried steel pipelines. Cathodic disbondment commences normally at coating defects where the following electrochemical reactions can occur during exposure to corrosive media under a cathodic protection (CP) potential [1–3]:



(dominant at potential less negative than $-1100\text{ mV}_{\text{SCE}}$)



(dominant at potential more negative than $-1100\text{ mV}_{\text{SCE}}$)

Both Reactions (1) and (2) generate hydroxyl ions, resulting in a highly alkaline environment in the vicinity of the coating defect areas. The accepted belief is that this high pH solution can lead to the commencement of cathodic disbondment at a coating defect edge [4]. During the propagation of coating disbondment, the pH beneath the disbonded coating was measured to be greater than 14 [5]. Such high pH driven cathodic disbondment of organic coatings from a steel substrate is considered to arise from three different mechanisms: dissolution of the metal oxide layer, saponification of the polymer coating, or displacement of the coating at the metal/coating interface [6–9]. On the other hand, it has also been suggested that short-lived highly reactive intermediates of the oxygen reduction reaction (superoxides or hydroxyl radicals) might be responsible for detachment of the coating from the metal

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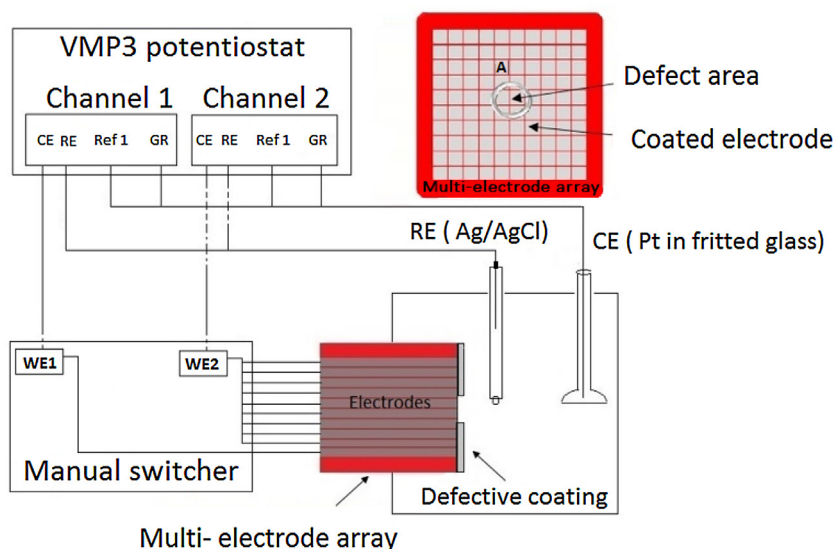


Fig. 1. Schematic diagram of the experimental setup for local EIS measurement under CP.

surface [3,10–12]. All these mechanisms consider that the products of the oxygen reduction reaction (reaction 1) play a key role in cathodic disbondment.

Another proposed mechanism considers the evolution of hydrogen gas as a result of reaction 2 at relatively more negative CP potentials (e.g. more negative than $-1100\text{ mV}_{\text{SCE}}$) to be the driving force of cathodic disbondment processes. It is suggested that cathodic disbondment is due to the mechanical lifting of the coating by the build-up hydrogen gas at the interface of the coating and the steel substrate [13–15]. However this mechanism has remained a hypothesis that has not been investigated nor verified experimentally.

Since all proposed mechanisms of cathodic disbondment are related to cathodic reaction products, the rate of coating disbondment should be affected by the level of CP potential. The effect of applied CP potential have been examined previously by polarizing defective coated samples to a range of negative potentials in test cells designed based on the standard test method usually referred to as ‘cathodic disbondment test’ (CDT) [16–21]. The cathodic disbondment behavior of various coatings after exposure to an aggressive salt solution under a cathodic potential is determined by measuring the radial disbondment distance of coatings after being destructively peeled off from the underlying steel substrate [22]. Using this method, the disbondment behavior of different types of coatings such as liquid epoxy (255–900 μm thickness) [16,18,19], three layer polyethylene (2000 μm thickness) [17], FBE (500 μm thickness) [20] and high build epoxy (150 and 500 μm thicknesses) [21] has been investigated under different levels of potential, from $-500\text{ mV}_{\text{SCE}}$ to $-2500\text{ mV}_{\text{SCE}}$ which covers potential levels at both regions of oxygen reduction and hydrogen evolution. A common finding in all these works is a strong potential dependence of the cathodic disbondment behavior of coatings. By shifting the potential to more negative values, more coating disbondment has been observed. A phenomenon reported by some researchers is the increase in coating disbondment in a non-proportional manner when the CP potential was elevated from a value in the region of oxygen reduction to a value in the region of hydrogen evolution [17,18,20,21]. For instance when the applied CP potential increased from $-1000\text{ mV}_{\text{SCE}}$ (oxygen reduction region) to $-1200\text{ mV}_{\text{SCE}}$ (hydrogen evolution region) the disbonded distance on a defective polyethylene coating of 2000 μm thickness increased from 7 mm to 12.5 mm [17]. The change of the applied CP potential from $-1000\text{ mV}_{\text{SCE}}$ to $-1400\text{ mV}_{\text{SCE}}$ caused a 1.6 times

increase in disbonded area of a 255 μm epoxy coating. A non-linear relationship between the applied potential and cathodic disbondment on epoxy coatings have also been reported by others [20,21]. Little mechanistic study has been carried out to understand and explain this behavior, probably due to the technical difficulties in the in-situ measurement of cathodic disbondment rates.

Although relatively new techniques such as scanning acoustic microscopy (SAM) have been used to provide in-situ information on the effect of the level of CP potential on cathodic disbondment of defective coatings, this method is suited only to investigate the disbondment of thin coatings ($<100\text{ }\mu\text{m}$) [23,24]. Similarly, techniques such as scanning kelvin probe (SKP) and localized electrochemical impedance spectroscopy (LEIS) have limitations in accurately monitoring the cathodic disbondment of thick coatings [25–30]. Currently the investigation of the effect of CP potential on the disbondment of thicker coatings are limited to ex-situ visual observation of the disbonded area of test samples using tools such as a microscopic digital camera. Traditional methods of visual reading of coating disbondment such as the microscopy inspection require the excavation of coated samples from the testing environment and the removal of the disbonded coating film for the examination of coating disbonded areas, therefore they are generally not suitable for studying the kinetics of coating disbondment.

This paper presents an investigation on the effect of CP potential levels on cathodic disbondment of a practically relevant thick coating based on in situ local electrochemical measurement technique using a multi-electrode array [31]. This multi-electrode array method has been previously demonstrated to be capable of monitoring the cathodic disbondment of a defective thick coating [31]. Local electrochemical impedance measurements using an electrode array sensor have been shown to significantly improved sensitivity for monitoring the initiation and propagation of cathodic disbondment of defective coatings [31]. This method facilitates the probing of the commencement of coating disbondment and the gradual changes of disbonded areas under different levels of cathodic protection potential. The main reason that we use multi-electrode array is to enable the in-situ measurement of cathodic disbondment of coatings of any thickness, either opaque or transparent. The multi-electrode method provides a means of in-situ assessment and monitoring of cathodic disbondment kinetics. The resolution of the electrode array maps can be increased, when necessary, by using more and smaller individual electrodes. This capability has enabled research on the influence of different levels

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