



Review

Localized electrochemical characterization of organic coatings: A brief review



Vinod Upadhyay*, Dante Battocchi

Coatings and Polymeric Materials, North Dakota State University Fargo, ND 58102, USA

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ABSTRACT

Local electrochemical techniques such as scanning electrochemical microscopy, scanning vibrating electrode technique, local electrochemical impedance spectroscopy, scanning Kelvin probe technique, and scanning ion-selective electrode technique have gained significant attention in organic coating research. These techniques have enhanced our understanding of the fundamental processes of corrosion at defects and underneath coatings. Each of these techniques employ unique measurement strategy to provide important local information about coatings, their protective properties, defects, and failure mechanisms. In this brief review, the basic principles of these techniques and the nature of information that has been extracted from these techniques to study organic coatings are discussed.

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1. Introduction

Organic coatings are probably the first things that we see in our everyday life. Almost everything that requires protection from corrosion is coated, and organic coatings dominate the usage. They provide barrier to the transport of aggressive species from the environment to the substrate requiring protection in addition to providing other desired functions such as aesthetics and spe-

cialty requirements [1–5]. Commonly used organic coating systems include epoxies, polyurethanes, oils, acrylics, alkyds, polyesters, silicones, phenolics, and amines. Very often pigments and additives are also added to the coatings to improve their performance [1,2,6,7].

Corrosion process is, almost always, electrochemical in nature. Therefore electrochemical characterization techniques are more appropriate and are widely used in understanding the corrosion behavior of structures, and the protective performance of organic coatings. These techniques also circumvent the disadvantages of subjective and qualitative evaluation performed with the exposure testing methods. Widely used electrochemical techniques for coat-

* Corresponding author.

E-mail address: vinodzz@gmail.com (V. Upadhyay).

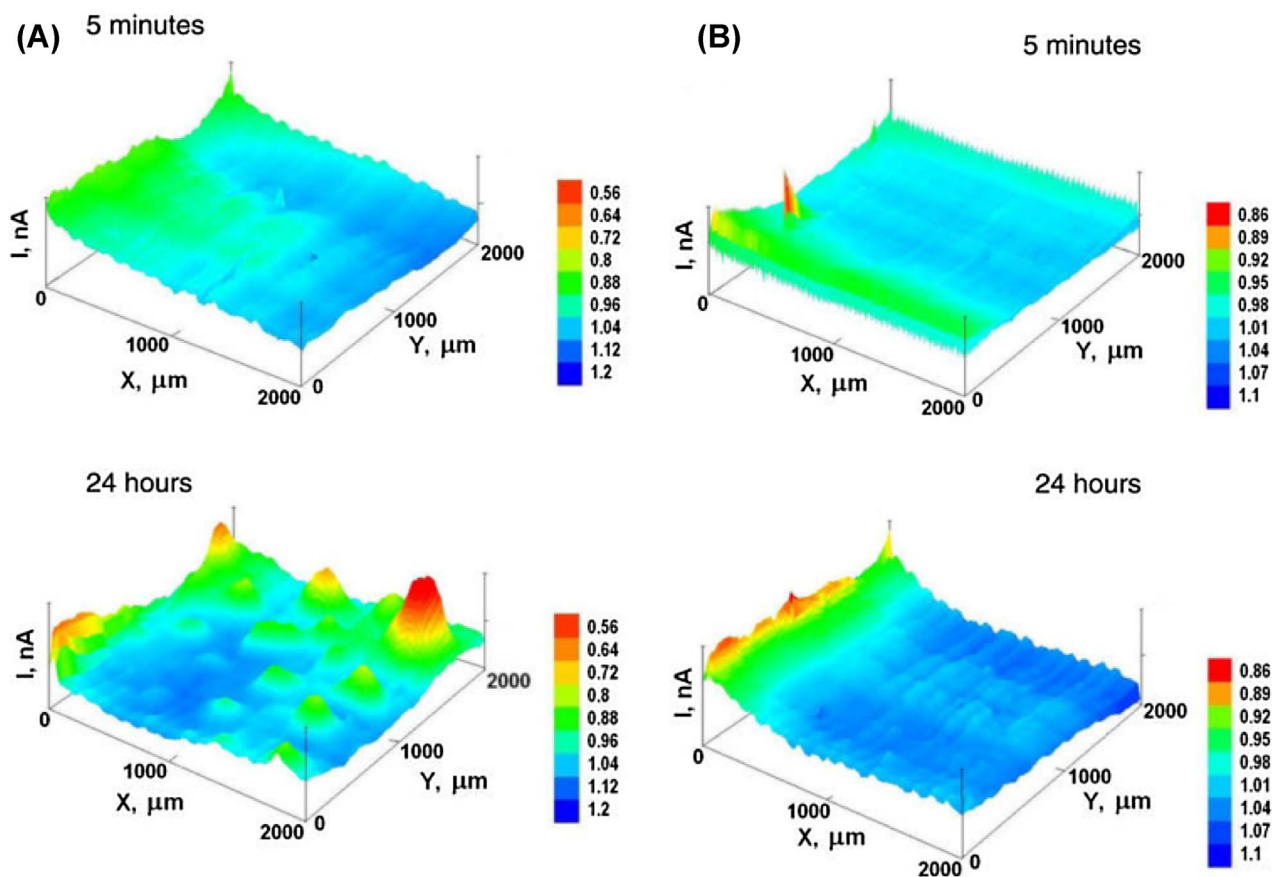


Fig. 1. SECM measurement on a polyurethane coated carbon steel plate. Tip-substrate distance: 15 μm . Scan rate: 30 $\mu\text{m}\cdot\text{s}^{-1}$. Tip potential: +0.50 V vs. Ag/AgCl/KCl (saturated) reference electrode. Values of Z axis: current, nA. The figures represent an area of 2000 $\mu\text{m} \times 2000 \mu\text{m}$ in X and Y directions. From top to bottom: 5 min, 24 h immersion in the test solution in (A) 0.1 M KCl + 0.5 mM ferrocene-methanol and (B) 0.1 M K_2SO_4 + 0.5 mM ferrocene-methanol [49]. [Reprinted with permission from Elsevier™].

ing studies are electrochemical impedance spectroscopy [8–14], electrochemical noise method [15–19], voltammetry [20–25], and DC techniques [26–31]. While these techniques are quantitative they are in essence an integral, surface averaged, global methods. Their response to a perturbation corresponds to a surface averaged measurement ascribable to the behavior of the whole measured surface. Very often, values generated by normalization of the data from these techniques might not be an exact characteristic of the coating, as the intact undamaged areas are also accounted for during normalization procedure, whereas corrosion might occur only at few small defect spots. This implies that global measurement techniques may not provide accurate assessment of coating properties. Large areas of measurement with small defect spots will provide more error compared to smaller areas of measurement. In addition, global measurement techniques also cannot locate exact defect spot, or provide localized corrosion mechanism(s). To overcome these limitations localized electrochemical techniques have been developed and their usage has gained momentum in the last two decades.

Among the widely used local electrochemical techniques applied to organic coating research are the scanning electrochemical microscopy (SECM), scanning vibrating electrode technique (SVET), local electrochemical impedance spectroscopy (LEIS), scanning Kelvin probe technique (SKP), and scanning ion-selective electrode technique (SIET). Scanning reference electrode technique (SRET) has largely been replaced by SVET owing to their similar measurement strategies [32]. In this brief review we provide some information on these techniques and on their applications in the localized study of organic coatings.

2. Local electrochemical techniques for organic coating characterization

2.1. Scanning electrochemical microscopy (SECM)

SECM is a very useful technique that can provide topographic and chemical information about a wide range of sample surfaces in solution. A significant advantage of this technique is its high spatial resolution and its capability to identify chemical species in localized corrosion processes [33,34]. SECM can be classified into three types, namely amperometric SECM, potentiometric SECM [35–38] (also referred to as scanning ion-selective electrode technique (SIET), and treated separately in Section 2.6), and AC-SECM [39,40]. Depending upon the nature of information required they can either be used singly, or in conjunction with other techniques.

Amperometric SECM measures faradaic current associated with electrochemical reactions at the substrate and/or the tip, and have been successfully employed to characterize coatings and corrosion processes. Measurement cell consists of a non-vibrating microelectrode (ultra-microelectrode tip/probe) and the sample substrate under investigation (whose potentials can be controlled using a bi-potentiostat) in addition to an auxiliary electrode, and a reference electrode. Samples can be conductive, semi-conductive, or insulating in nature. The microelectrode probe is either held stationary, or moved across the sample surface during measurement. The nature and property of the substrate is determined by the response of the tip current resulting from the electrochemical reaction at the tip and/or the substrate surface. Detail and historical information about SECM can be found in references [33,34,41–45]. More recent

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