



# Method for visualizing under-coating corrosion utilizing pH indicators before visible damage

Can Berk Uzundal, Burak Ulgut\*

Faculty of Science, Department of Chemistry, Bilkent University, 06800 Ankara, Turkey



## ARTICLE INFO

### Keywords:

Hydrogen permeation  
Corrosion  
Corrosion detection  
Coatings  
Under-coating corrosion  
Defect visualization

## ABSTRACT

A new method for under-coating corrosion visualization is developed. The method detects corrosion through local pH gradients which are visualized by pH indicators. pH gradients are induced in a setup similar to the one popularized by Devanathan. On the uncoated back side of the metal, the sample is cathodically polarized, generating hydrogen gas through electrolysis. The hydrogen generated, diffuses through the metal sample and oxidizes on the anodically polarized painted side wherever the coating develops a defect causing a decrease in the local pH. The local pH is then used in imaging the location of defects through the use of a pH indicator, before any visible corrosion damage occurs on the coated metal sample.

## 1. Introduction

Detecting under-coating corrosion is of importance in assessment of stability and integrity of coated metal samples. When fully coated, metal samples corrode sparingly. Corrosion mainly takes place in regions where cuts, cracks or scratches are present. From these positions corrosion propagates laterally and disrupts coating integrity [1]. Under operational conditions, defects in the coating can result in the failure of the system. Evaluation of coatings and their anti-corrosive properties require facile and non-destructive methods. In the literature, a variety of methods spanning Electrochemical Impedance Spectroscopy (EIS) and Scanning Electrochemical Microscopy (SECM) are present for comparison of various coating materials [2–7]. Moreover, utilizing high frequency waves such as terahertz waves or near-field microwaves, local corrosion can be detected in the bulk scale. These high frequency detection techniques, however, depend on the dielectric differences between the paint, metal and the metal oxide which limits their applications as in the case of aluminum plates where dielectric constants are similar [8,9]. With these high frequency techniques, formation of the metal oxide cannot be visualized before a significant amount of metal oxide forms and the paint swells, thus severely limiting their detection capabilities.

Employing EIS approaches to detect under paint corrosion can deduce the effects of somewhat local changes through changes in the parameters of equivalent circuit models. Yet, the precise location of the change cannot be found on the metal plate. Truly local information on under-coating corrosion can be obtained by SECM. SECM however, requires sophisticated equipment and is not readily available for

routine analysis. Further, scanning large areas in SECM requires a long time and very large equipment. In fact, an SECM study conducted on aluminum alloys which show generation of  $H_2$  and  $H^+$  at regions of coating defects due to exposed metal sites, inspired us in developing our methodology [3,7].

In our methodology, partially inspired by the work of Devanathan, we sought to design our experiment around the  $H^+$  that is generated in the coating defects of the coated sample [10,11]. In the classical Devanathan experiment, a metal plate is fixed in between a two compartment cell (see Fig. 1) where on one compartment  $H_2$  is formed by a cathodic potential while on the other compartment the diffused  $H$  is oxidized into  $H^+$  by an anodic potential. On the latter, the current generated is monitored which yields the diffusion rate of  $H$ . The method since then, is standardized for measurement of diffusion coefficients in metal plates and measurement of metal plate thickness [12]. Recently methods that build on the classical Devanathan experiment to probe the oxygen reduction kinetics at a coating-metal interface was developed [13,14]. Although the reported approach can be used to assess overall coating integrity, local information cannot be deduced. In terms of local resolution, the potential of the Devanathan experiment was demonstrated via Scanning Kelvin Probe Microscopy, where hydrogen permeation through micro-domains of various metals could be discerned [15].

Herein we present a modification to the Devanathan experiment to tap into the local information inherently present through a very simple visualization method: Inspired by the work of Jin et al. where they utilize a pH indicator to visualize local regions of low pH as a result of higher catalytic activity towards methanol decomposition [16], we also

\* Corresponding author.

E-mail address: [ulgut@fen.bilkent.edu.tr](mailto:ulgut@fen.bilkent.edu.tr) (B. Ulgut).

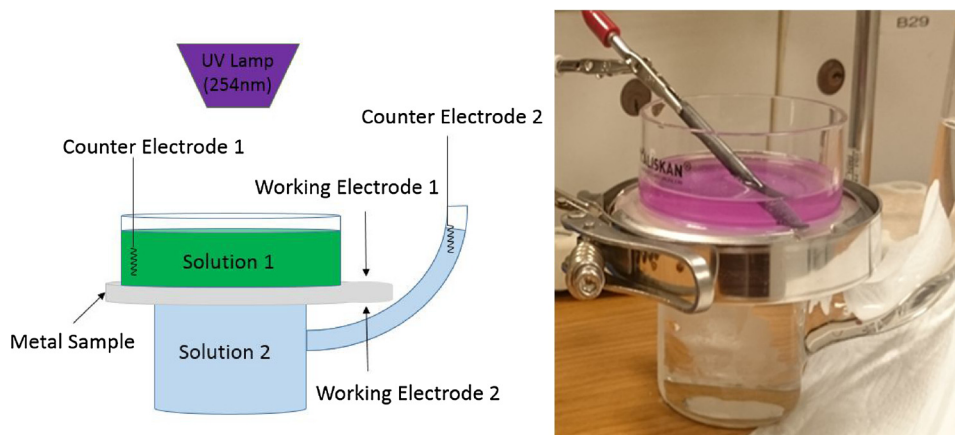


Fig. 1. Schematic representation of the setup (left). The actual setup (right).

add a pH indicator to our two compartment Devanathan setup.

## 2. Experimental

### 2.1. Method

Between the two compartments of the designed cell (see Fig. 1), a metal plate (aluminum 2024 of 0.2 mm thickness) is fixed. The bottom compartment is the generator cell where  $H_2$  is generated by a reducing potential, while the above compartment is the detection cell where the diffusing H is oxidized into  $H^+$  by an oxidizing potential. The generator cell contains saturated brine (saturated aqueous NaCl solution) while the detection cell contains brine adjusted to pH 9 or pH 6 (for phenolphthalein or quinine respectively) with NaOH. As the indicator, a couple drops of phenolphthalein or 370 mg/L quinine is added. One separate, floating potentiostat is attached to each compartment in a two electrode configuration where two graphite rods are used as both counter and reference electrodes in a two electrode configuration and the metal sample in the middle is the working electrode for both potentiostats. To the generator cell a negative constant potential is applied while to the detection cell, a small positive potential (0.5 V) is applied to generate  $H_2$  and to oxidize H into  $H^+$  respectively. Magnitude of the potential applied on the generator cell depends on the nature of the metal sample and the ability of the metal to catalyze the hydrogen formation reaction such that the metal surface is covered with hydrogen completely. As the size of the hydrogen bubble increases the current supplied drops since the electrical contact between the metal and the solution is cut off from the generator side. The complete hydrogen coverage ensures a uniform start of diffusion across the metal sample. Routinely, potentials around 10 V were applied. A constant current cannot be imposed on the metal without overloading the potentiostat attached to the generator cell since the hydrogen bubble that forms blocks the current.

Floating potentiostats are an absolute necessity in this setup since a single metal electrode acts as the working electrode of both the generator and detection cells. If two earth grounded instruments were employed, applying different potentials on the two cells would not be possible since the ground in each instrument would be fixed to the same point. Floating the potentiostats allow for the grounds of each potentiostat to be at a different level with respect to the earth ground, allowing the application of different potentials.

In our setup, a Gamry Instruments Interface 5000E was used for the generator cell and a Gamry Instruments Interface 1000E was used for the detection cell.

For experiments conducted using phenolphthalein indicator, a camera was fixed over the electrochemical cell. The fixed camera ensures that background subtraction could reliably be made.

### 2.2. Image processing

To increase the clarity of the images taken with phenolphthalein indicator, a background subtraction routine was utilized. Simply, the images are imported as arrays of RGB values (Red-Green-Blue) into a Python 2.7 environment. Each of the color channels individually are normalized using the following simple formula to account for minor changes in ambient light.

Let “C” be Red, Blue or Green Channel

$$\text{Normalized } C = \frac{C - \min(C)}{\max(C) - \min(C)} * 255$$

Then, using GIMP 2.8 image processing software, the contrast of the background subtracted images were enhanced. The contrast of an image can be thought as the difference between the brightest pixel and the darkest pixel. When the contrast of an image is increased, this difference is enhanced by making the darkest pixel darker while the brightest pixel is made brighter, where all three channels are considered in unison. The contrast enhancement was done to increase the clarity of the images such that colors can be visualized regardless of the medium this article is presented (in print or in web).

For a select case, color reduction was employed to even further enhance the contrast of the images. The GIMP algorithm for color reduction is based on the following simple algebra [17];

Let “C” be the array of values corresponding to Red, Green or Blue channels with floating point values ranging between 0 and 1

$$\text{Color reduced } C = \text{round} \left( \frac{C * \# \text{ of colors}}{\# \text{ of colors}} \right)$$

where “# of colors denote” the number of colors in the color reduced image.

Quantification shown in Fig. 7, is made easier using color reduction where color reduction lumps colors within a close region of color space to a single color. The size of this region is determined by the number of colors specified. Using color reduction, slight off-colors are assigned as pure green and can be accounted for in the quantification. Similar to contrast enhancement, color reduction also increases the clarity of the article in different media.

After normalization and color reduction (where applicable) the first image is subtracted from rest of the images by a simple array operation.

Throughout the article and the supporting information, the images are presented with their originals and their processed version.

In terms of quantification of the color reduced images, a 300-pixel by 300-pixel region was selected (shown in Fig. 7). If all the pixels in the region was purely green, the total green content of the region would be  $300 \times 300 \times 255$  where the color in any channel can be a number ranging from 0 to 255. Thus, summing the green channels of all the

Download English Version:

<https://daneshyari.com/en/article/7105488>

Download Persian Version:

<https://daneshyari.com/article/7105488>

[Daneshyari.com](https://daneshyari.com)