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DESIGN AND IMPLEMENTATION OF SCANNING ELECTROCHEMICAL MICROSCOPY (SECM) FOR SCANNING OPEN CIRCUIT POTENTIAL SYSTEM ON DAMAGED COATED SURFACES

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ABSTRACT

Scanning Electrochemical Microscopy (SECM) is used for studying the corrosion of metals in fluid environments with high sensitivity. This microscope measures the current in an ultrafine electrode with a radius between a few nanometers to 25 microns when it is in a solution and near the matrix. Scanning of the surface reactions in microscopic scale will be possible by the use of this technique. The scanning electrochemical microscope with sensitivity of 100 μv and 50 μm displacement in longitudinal and latitudinal axes was designed and fabricated in this research. Au and Pt electrodes were used as working and reference electrodes. Producing topographic images of potential variations in area scan is one of the most important outputs of this microscope which images are presented in colorful and 3-dimensional features on the intensity-based potential variations. Some experiments were done by using the fabricated SECM for assessment of corrosion of coated steel. Investigations were carried out on scratched samples. Examination of results of utilizing SECM showed that the potential of scratched surfaces is significantly higher than that in sound surfaces. So it can be deduced that this microscope can detect the initiation of corrosion and nucleation of pits in its initial stages of nucleation in a corrosive solution.

Keywords: scanning electrochemical microscopy, corrosion, defect, reference electrode, Au and Pt electrode and potential.

INTRODUCTION

The SECM is under the Scanning Probe Microscopy (SPM) family. The SECM is used as assessment in corrosion (metal/atmosphere or metal/solution interface), oxidation/ reduction reaction in batteries, photosynthesis in cellular membranes, and decomposition of composite (Figure-1). [1-3]. SECM, as well as the SPM technique, can be used to investigate electrical potential of working surface with accurate position near substrate. In SECM technique, as shown in Figure-2, probe is an Ultra Micro-Electrode (UME) which is performed by a micro or nano-diameter electrode [3-6]. UME and surface of substrate both immersed in an electrolyte solution consisting of a chemical oxidizing agent or reducing species. UME is laterally above the sample surface that can make the topography map of the surface or surface reactivity obtained under inspection [2-4].

It has been reported in studies that this device can be used for inspection often focus on the following issues:

- Detection of small holes and cavities in advance, (electrochemical activation points of the holes are on the germination).
- Monitoring the concentration of production profiles and REACTANTS corrosion.
- Use the needle to determine pinhole formation.

Dissolution of ionic crystal is a phenomenon that can be studied by SECM. UME needle can deplete a chemical specimen with its oxidation or reduction. If any of the basic chemistry is in balance with crystal, it dissolved early as shown in Figure-3. Using the SECM device with high sensitivity, scientists would be able to determine that a solution of copper sulphate crystals in water is occurred in the defect point [6, 7].

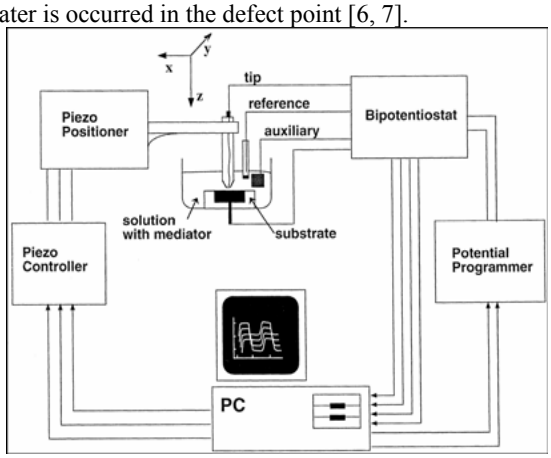


Figure-1. Schematic of scanning electrochemical microscopy SECM [5].

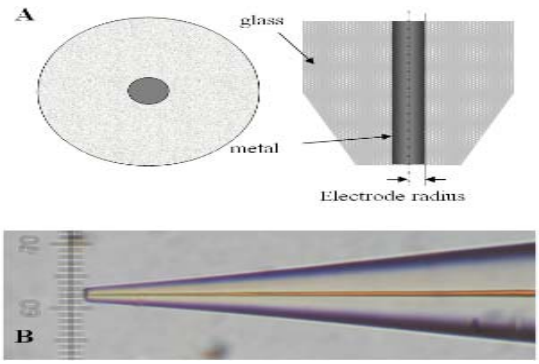


Figure-2. Schematic of sealed tip[5].

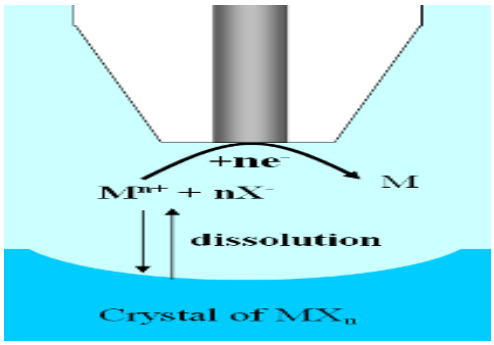


Figure-3. Schematic of reaction between solution and tip [5].

Potentiostat or amperometric is used to amplify the probe signal. After amplification, the signal data would be converted to digital data by an Analogue to Digital Converter (ADC) and so to be stored on a computer. Other important parts of this device include the probe holder, video camera, sample container, stepper motor and other things. [7-9].

Scanning electrochemical microscopy (SECM; the same acronym is used to describe the instrument) has developed into a powerful technique for quantitative investigations of interfacial physicochemical processes, in a wide variety of areas, as considered in several recent reviews [10-14]. This review will provide a background to SECM, with particular reference to its use in characterizing biophysical processes and biomaterials. In the simplest terms, SECM involves the use of a mobile ultramicroelectrode (UME) probe, either amperometric or potentiometric, to investigate the activity and/or topography of an interface on a localized scale. The attractive features of SECM, for the study of biomaterials on a local scale, were recognized soon after the technique was formally established. Early applications included quantitative studies of immobilized enzyme activity and photosynthetic processes on leaves [10-14]. More specifically, when a metal is immersed in a given solution, electrochemical reactions characteristic of the metal-solution interface occur at the surface of the metal, causing the metal to corrode. These reactions create an electrochemical potential, called the corrosion potential or the open circuit potential (measured in volts), at the metal-solution interface. Since the corrosion potential is determined by the specific chemistry of the system, it is a characteristic of the specific metal-solution system.

EXPERIMENTAL METHOD

In this study, the corrosion behavior of carbon steel covered by spray paint examined by SECM equipment. The SECM includes a working electrode and reference electrode with the same principle in which the working electrode (Pt/Au) scans the surface of substrate (i.e. 304 steel coated with paint) and reference electrode sets up in certain position along substrate. The probe movement on the sample surface is performed by an embedded stepper motor. Movement in the direction of X and Y was done with a microcontroller but for the direction of Z, it was done manually. In additional, moving, scanning, getting and saving data, converting analogue to digital and comparing voltage working electrode with reference electrode were done with a microcontroller chip and Bascom program. For better resolution, we used 15-bit analogue to digital convertor. Finally, Matlab program was used for displaying graphically topographic scanning in a computer reading program.

Firstly, coated metal sample was scratched. Then, sample was immersed in container including 3.5% NaCl solution. Then, surface scanning by SECM was done on the scratched surface. As seen in Figure-4 (a, b and c), the middle of coated metal put a small scratch and three pinholes. Two gold electrodes (working and reference electrodes) were used to scan surface dimensions of 15 × 15 mm^2.

Figure-4. Prepared sample for test a) first (1.5×1.5cm^2), b) second (1.5×1.5cm^2) and c) the last sample (2×1.5cm^2).

SECM device is capable of making surface adjustment that would be scanned up to 4×4 cm2. The probe movement in X and Y direction is under control. The number of achieved data according to motor movement step can be adjusted before starting. The sensitivity of this device is 50 × 60 µm2. Figure-5 and 6 shows the schematic of the device including electronic circuits, mechanical parts, tip and the supply voltage. Also, the output end is connected to a computer system.

Figure-5. A) Gold and b) Platinum tips.

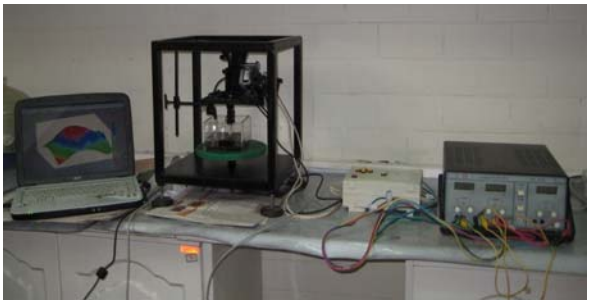


Figure-6. Equipment of SECM device.

RESULTS AND DISCUSSION

Scan results obtained by SECM on steel sample immersed in NaCl solution accurately shows the scratch location that is area under corrosion or oxidation (Figure-7). At time zero, there is no any corrosion or potential changes, but over time (shown in Figures-7a to 7-f) as seen in surface, potential changes are schematically started. Results clearly show that the corrosion rate increased with time (corrosion is related to Cl ions).

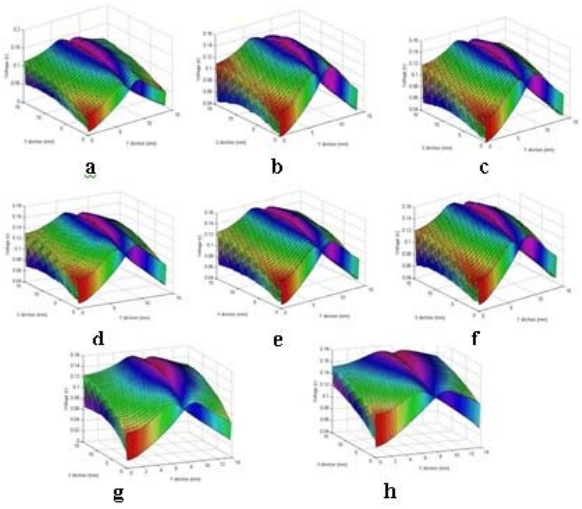


Figure-7. Three-dimensional topographical map of the first sample immersed in 3.5% NaCl solution after a) 30, b) 40, c) 50, d) 60, e) 85, f) 100, g) 130 and h) 170 min.

In the next step, the device was used to scan another sample as shown in Figure-4b. Potential data that was captured from scanning at different times indicates the severity of the corrosion in this area (Figure-8). The results also showed an increased rate of corrosion over time correctly.

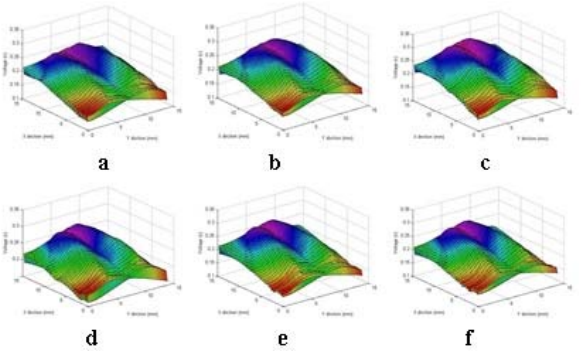


Figure-8. Three-dimensional topographical map of the second sample immersed in 3.5% NaCl solution after a) 40, b) 80, c) 105, d) 125, e) 150 and f) 170 min.

In the last step, sample scanning was done after creating an artificial pitting on the coated surface (Figure-4c). Sample was exposed to the NaCl solution. In the beginning, the corrosion was started in two points due to more expansion area (Figure-9a), and then with the past time, third point was started with the small peak (Figure-9b) since this point is smaller than the two last points. As it can be seen in Figure-9a and 9-b, two points from all three points clearly showed that in the initial moment corrosion occurred. The third point has lower corrosion rate and its effect is less intense as shown. As it can be seen in Figure-9, after 2 and 2:30 hours of immersion, the corrosion rate in the pitting area is higher due to the high pitting corrosion rate on the inside.

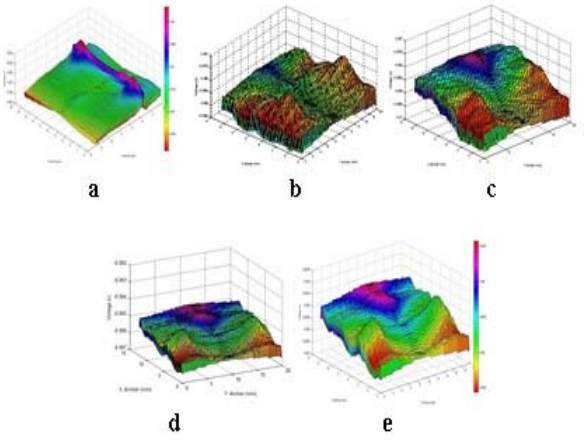
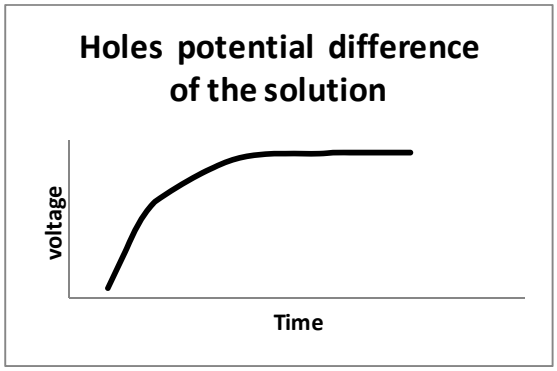


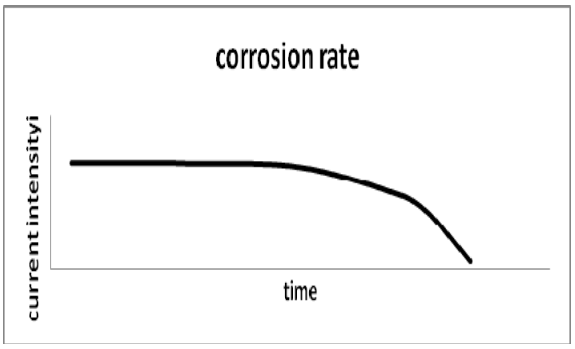
Figure-9. Three-dimensional topographical map of the second sample immersed in 3.5 % NaCl solution after a) 30, b) 80, c) 120, d) 150 and e) 170 min.

This device followed an electrochemical process and measured potential base on point to point measurement of surface with working electrode versus reference electrode. Surface potential is the representative of surface topographic properties which can give significant information and effective surface characteristics. It can be concluded that the corrosion rate and the potential difference at active pitting area are high compared to other places.

Over time, the corrosion rate decreased in pitting area due to corrosion product formation (Figure-10).



(a)



(b)

Figure-10. Potential difference and corrosion rate in pitting area.

CONCLUSIONS

Artificial pitting and scratched area on coated sample will be anodic in corrosion phenomena. The potential in anodic part will be differed from cathode part which is critical to be monitored. The results showed that our home-made SECM was able to scan potential and accordingly corrosion rate in scratched and pitting area accurately. Corrosion rate was increased versus time in defected area in initial time. As shown, potential of pitting is increased and this device can detect it.

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