

Screening of novel anti-corrosion coatings by scanning electrochemical microscopy (SECM)

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Corrosion continues to be a multi-billion dollar problem for the Department of Defense.¹ Current coatings used to prevent electrochemical degradation use hexavalent chromium, but there is now an effort to replace this given it is carcinogenic.² Unfortunately, there is no universally accepted method to test and evaluate potential new coatings. We propose developing a protocol using scanning electrochemical microscopy (SECM) at least screen out poor performers before much time and money is spent on their development.

SECM is a technique developed in the Bard lab at the University of Texas in the early 80's.³ It involves the use of a very small diameter electrode whose electroactive tip is only microns in diameter. The sharpened tip is positioned to within a few tip diameters of a surface which allows the surface to be electrochemically interrogated via a mediator in solution.⁴ This has been extended to study of both corrosion⁵ and film transport properties⁶. It was studies such as these that led us to attempt to use the SECM as a rapid screening tool for various potential anti-corrosion coatings.

The proposed protocol involves, first, mapping the topography of a given area of roughly 100x100 microns by using the negative feedback mode at the insulating surface (figure 1). In this mode, the tip is oxidizing ferrocene methanol in solution. When the tip is within a few tip diameters of a feature, diffusion to the tip is blocked and current decreases. Note in the figure, the current follows the convention of (-) as oxidation. Thus in figure 1, there is a clear plateau feature to the left.

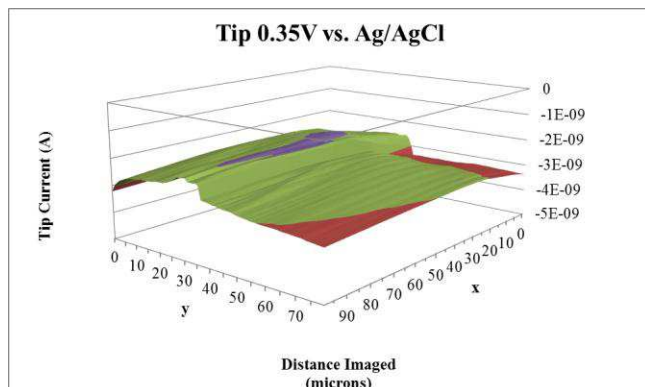


Figure 1: 100 x 100 micron section Solution is 1mM in FcMeOH/0.1 M KNO₃. The Pt tip has a diameter of 25 microns and is 25 microns above the surface.

Then, over the same area, we use the substrate generation – tip collection (SGTC) mode to probe how effective the surface is at passivating the aluminum substrate and curbing diffusion of surface species to/from the substrate. This is done by setting the substrate at potentials increasingly positive of the redox couple in an attempt to produce a species reducible by the tip. Good coatings show little response up to several volts (figure 2).

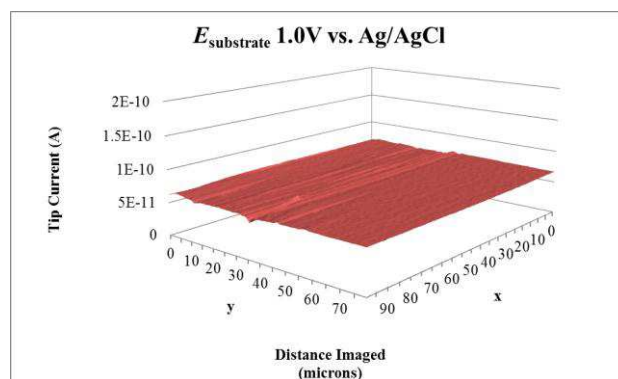


Figure 2: Section similar to Figure 1 showing a good coating with little response.

However, flaws in the coating expose electroactive sites (Figure 3) that may be inferred to be exposed substrate. Blind studies⁷ have shown the technique able to distinguish known best coatings from inferior products so this work will extend to untested coatings and comparisons of various preparations.

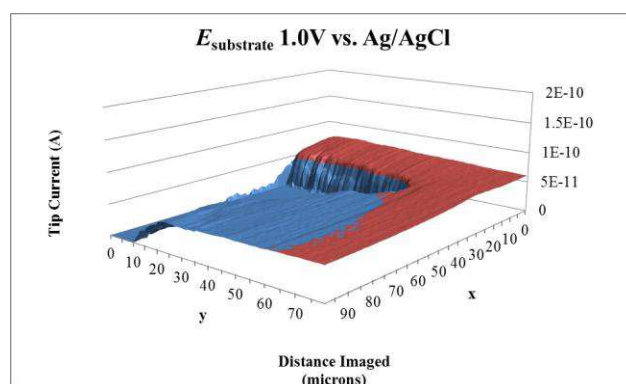


Figure 3: The same section as Figure 1 in the SGTC mode showing an electroactive site.

¹ D. Forman, E. Herzberg, J. Tran, A. Kelly, P. Chang, N. O'Meara, "The Annual Cost of Corrosion for Navy and Marine Corps Aviation Equipment" LMI Government Consulting, Report MEC70T3, May 2008.

² R. Park, L. Stayner, R., "A Search for Thresholds and Other Nonlinearities in the Relationship Between Hexavalent Chromium and Lung Cancer," Risk. Anal., Vol 26, pp. 79-88, 2006.

³ A. J. Bard, Scanning Electrochemical Microscopy, New York, USA, Marcel Dekker, Inc., 2001.

⁴ L. Diaz-Ballote, M. Alpuche-Aviles, D. Wipf, "Fast-scan voltammetry-scanning electrochemical microscopy," J. Electroanal. Chem., vol 604, pp. 17-25, 2007.

⁵ D. Walsh, L. Li, M. Bakare, K. Voisey, "Visualisation of the local electrochemical activity of thermal sprayed anti-corrosion coatings using scanning electrochemical microscopy," Electrochim. Acta, vol. 54, pp. 4647-4654, 2009.

⁶ M. Williams, J. Hupp, "Scanning Electrochemical Microscopy Assessment of Rates of Molecular Transport through Mesoporous Thin-Films of Porphyrinic 'Molecular Squares'," J. Phys. Chem B, vol. 105, pp. 8944-8950, 2001.

⁷ Calhoun, R., Lancaster, F., Microsystems for Measurement and Instrumentation (MAMNA), IEEE Conference Publications, 2012.