



APPLICATION NOTE

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Constant Distance SECM Imaging: Topography-free reactivity imaging of 3D substrates using soft probe SECM

Application Note PAR 106



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Images recorded using constant height Scanning Electrochemical Microscopy (SECM) can suffer from topographical artifacts unless the sample is perfectly flat. Constant distance SECM overcomes these limitations since the probe follows the surface topography ensuring near constant probe – sample separation. The Soft Stylus Probe developed at LEPA-EPFL is one such method and has been successfully applied to a number of substrates with high aspect ratios.

Unlike hard probe contact based techniques, the force of contact of a soft probe is low (approximately three orders of magnitude smaller than hard probe contact based techniques) and therefore is less likely to damage / alter the topography of the substrate during measurement. As such, this technology has successfully measured the activity of soft tissue from melanoma samples.

This application note demonstrates the constant distance mode technique for an insulator / conductor substrate. The sample contained topographic features in the order of tens of microns and up to 5 times larger than the radius of the electrode. It was shown that the structure was electrochemically heterogeneous with some regions corroding faster than others. These electrochemical observations were confirmed with optical microscopy.

Sample Preparation

A typical Swiss 1/2 Francs coin (75% Cu / 25% Ni) was cleaned and roughly polished with a wipe and isopropanol. The sample is ideal for testing contact SECM techniques since it contains a conductive substrate with impacting topographic artifacts.



Figure 1: Test sample - Swiss 1/2 Franc coin

Droplets of a dielectric insulating material were deposited regularly as a grid using an inkjet printer and simultaneous UV photopolymerization (X-Serie CeraPrinter, Ceradrop, France). The resulting micro patterned array is shown in Figure 2.



Figure 2: Swiss 1/2 Francs coin with inkjet printed insulating spots.

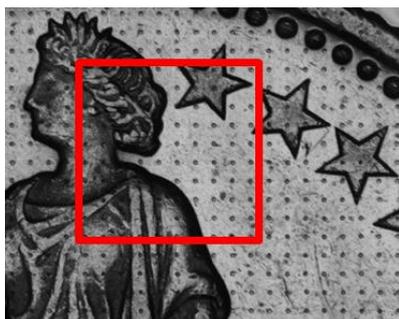


Figure 3: The 3 mm x 3 mm area indicated in red was scanned by SECM.

An area of the coin was selected for analysis and shown in the red box in Figure 3. This section of the coin was chosen since it offered a high degree of image contrast possibilities (curved surfaces, insulating array clearly visible and easily identifiable features such as the star). The topography was analyzed using a Laser Scanning Microscope (LSM). Such topography can also be determined with similar resolution using the VersaScan OSP (optical surface profiler).

Surface Topography Measurements

Surface topography measurements on various parts of the material were made before SECM imaging and the results are shown in Figure 4. It was shown that the microarray of insulator material did not change the topography of the surface. The step height of features in the coin ranged from 130µm to 50µm (see Figure 4 for examples).

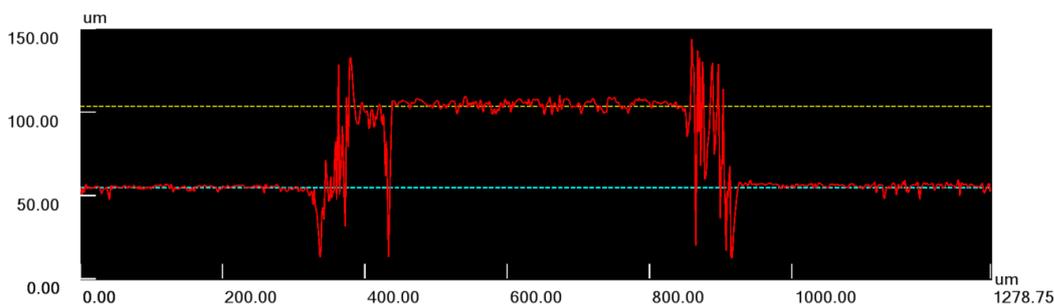
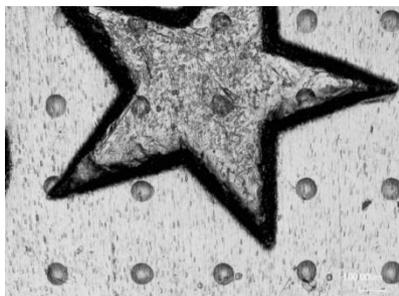


Figure 4: Step height of the star is around 50 µm. Insulating spots have no impact on topography. Data were recorded before the SECM experiment.



SECM experiments

A Soft Stylus Probe with carbon microelectrode and precisely shaped tip was used for all SECM measurements. These probes are exclusive to AMETEK/Princeton Applied Research. Fabrication details can be found in the bibliography at the end of this paper.

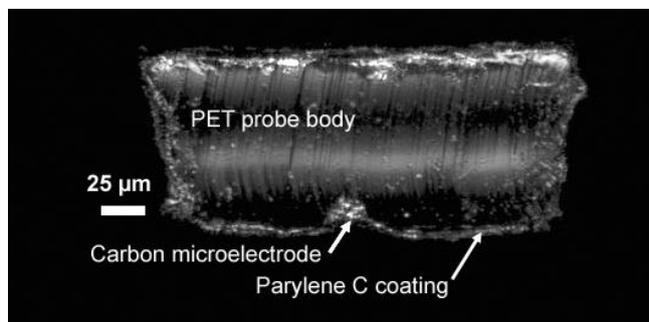


Figure 5: Soft Stylus Probe Cross Section

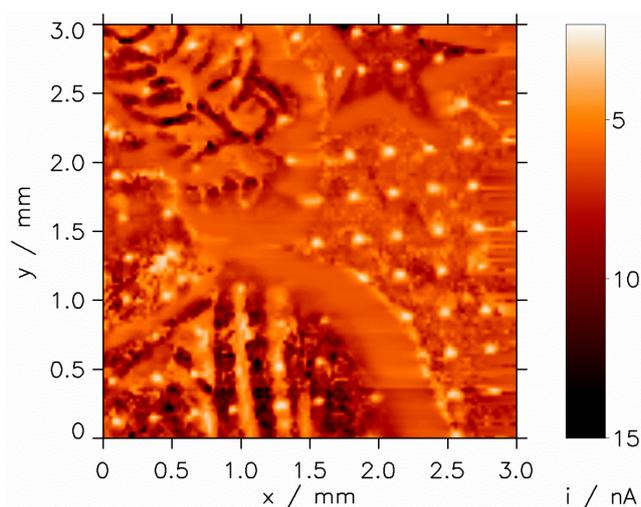


Figure 6: Interpolated feedback mode SECM image. Step size 25 μm . Image time 5 h 3 min. Quasi reference electrode: Ag wire counter electrode: Pt wire, Coin glued on the bottom of a standard SECM cell, Electrolyte solution: 2 mM FcMeOH and 0.1 M KNO_3 , Electrode potential $E_T = 0.4 \text{ V}$ vs. QRE

Constant distance was easily achieved by the simple and robust soft probe design and material properties. The insulating spots on the coin surface were clearly identified as white dots in Figure 6. The reactivity of the coin was heterogeneous (note the change in current) and this is most likely due to the polishing and cleaning of the coin specific exposing high aspect ratio features such as the star. These features showed a higher reactivity (current) in feedback mode imaging. The hindered diffusion current over the insulating spots was equal all over the surface proving constant distance scanning. In contrast with this, the current on the flat conductive area next to the star was not homogeneous reflecting heterogeneous regions of activity. The more highly polished star showed a higher reactivity than the surrounding area. This can also be seen by the accelerated formation of oxides on the star surface after the experiment (Figure 7). This was further confirmed after the insulation spots were removed by abrasion. (Figure 7).

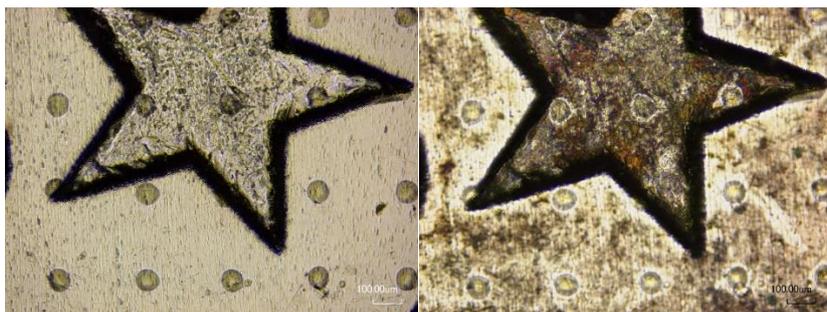


Figure 7: Star on the coin before (left) and after (right) SECM imaging. The more reactive region on the surface on the star suffered stronger from oxidation than the remainder of the substrate. This confirms the higher reactivity of the surface on the star as revealed by SECM feedback mode imaging with the soft stylus probe.

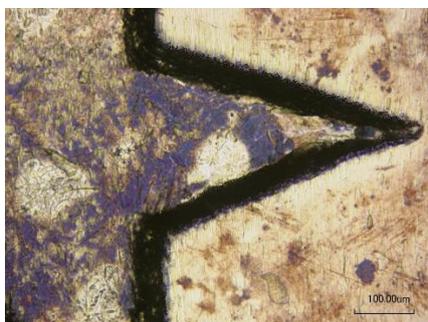


Figure 8: Star on the coin after SECM imaging and cleaning with isopropanol to remove the insulating spots. The parts initially covered with insulation have not been oxidized and represent the initially highly reactive surface in this area.

Conclusions

Constant Distance Mode SECM using Soft Stylus Probe technology was demonstrated to be highly effective at electrochemical activity contrast mapping on a sample with micrometer scale topographic features.



Suggested Reading

1. T.-E. Lin, A. Bondarenko, A. Lesch, H. Pick and F. Cortés-Salazar et al. *Monitoring Tyrosinase Expression in Non-metastatic and Metastatic Melanoma Tissues by Scanning Electrochemical Microscopy*, in *Angewandte Chemie International Edition*, vol. 55, p. 3813–3816, 2016.
2. F. Cortes Salazar, D. Momotenko, A. Lesch, G. Wittstock and H. Girault. *Soft Microelectrode Linear Array for Scanning Electrochemical Microscopy*, in *Analytical Chemistry -Washington DC-*, vol. 82, p. 10037-10044, 2010.
3. A. Lesch, B. Vaske, F. Meiners, D. Momotenko, F. Cortés-Salazar, H.H. Girault, G. Wittstock, *Parallel Imaging and Template-Free Patterning of Self-Assembled Monolayers with Soft Linear Microelectrode Arrays*, *Angew. Chem. Int. Ed.* 51(41) (2012) 10413-10416.
4. Cortés-Salazar, D. Momotenko, H.H. Girault, A. Lesch, G. Wittstock, *Seeing Big with Scanning Electrochemical Microscopy*, *Anal. Chem.* 83(5) (2011) 1493-1499.