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Scanning Electrochemical Microscopy

X. High Resolution Imaging of Active Sites on an Electrode Surface

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ABSTRACT

The dependence of the SECM feedback current on electron-transfer kinetics was used as the basis for imaging variations in electrochemical activity over a composite surface. A gold phase in a glassy carbon electrode could be imaged due to the differential electrochemical kinetics of the Fe(III)/Fe(II) couple in 1M H₂SO₄.

In this letter, we report the use of the scanning electrochemical microscope (SECM) to image variations in electrochemical activity over an electrode surface. The variation of electron transfer rates across an electrode because of surface heterogeneity is a familiar occurrence in electrochemical systems. This variation arises from the presence of active sites on a less active substrate, e.g., catalyst particles or defect, edge, and kink sites. Active sites can also represent portions of the electrode surface that have not been deactivated by adsorption of passivating species or by the formation of blocking layers. Pre-

vious work has demonstrated that the SECM can be used to image conducting or insulating materials and can also image conducting regions that are embedded in, or overlay, insulators (1). The most useful approach to imaging with the SECM has been the feedback mode. In the feedback mode an ultramicroelectrode tip generates the reduced or oxidized form of a mediator species. As the tip is brought close to a surface, the tip current arising from the electrolysis is perturbed. At an electronically insulating surface, the current is decreased, because diffusion of the mediator to the tip is hindered (negative feedback). However, at a conducting surface, the mediator can undergo the reverse electron transfer (et) reaction to regener-

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ate its original oxidation state. This regeneration of the mediator in the gap between the tip and substrate causes the tip current to increase, giving rise to positive feedback.

We have shown previously that the feedback current at a conducting substrate is sensitive to the rate of et between the mediator and substrate (2). As the et rate decreases, the response changes from that of an ideal conductor to that of an insulator. The quantitative nature of the observed response depends upon the tip-substrate distance, d , and the heterogeneous et rate constant at the substrate (2). This differential response with et rate forms the basis for reaction rate imaging of a heterogeneous electrode surface. We report here images of a composite glassy-carbon (GC)/gold substrate that depend upon the difference in activity of the two phases. We also show that by controlling the potential of the composite substrate, the differences in activity between GC and Au can be minimized or maximized, allowing precise control over the imaging conditions.

The apparatus and tips used have been described previously (2). The mediator for these experiments was Fe(III) ion in an aqueous 1M H₂SO₄ solution. All potentials are reported vs. the Hg/Hg₂SO₄ reference electrode in 1M H₂SO₄ (MSE). A GC/Au composite surface was constructed by first polishing a GC disk electrode (BAS, West Lafayette, Indiana) with 0.05 μm alumina. The smooth GC surface was then firmly pressed against 600 grit carbide paper to form scratches and indentations. Next, gold was plated on the scratched surface by applying a cathodic current of 1.1 mA cm⁻² for 180 s in a commercial plating bath (Transene Company, Rowley, Massachusetts). Finally, the electrode was briefly polished with 0.05 μm alumina. Inspection of the composite surface by optical microscopy showed that about 10-20% of its area was composed of gold regions which formed on the scratched areas. The gold regions were either thin irregular bands 30 to 100 μm long by 2 to 6 μm thick or, more rarely, irregular regions of 5 to 100 μm diameter.

Cyclic voltammograms of the Fe(III) mediator at a scan rate of 100 mV/s at the composite GC/Au electrode are similar to voltammograms reported previously at a GC electrode (2). The contribution of the gold regions was not apparent in these voltammograms. The formal potential for the Fe(III)/Fe(II) couple is +0.02 V vs. MSE under these conditions (2). The heterogeneous et rate for Fe(III) at unactivated GC electrodes is slow, with a standard rate constant of about 10⁻⁶ cm s⁻¹ (2, 3). In contrast, the et rate at Au electrodes has been reported to be 10⁻⁴ to 10⁻² cm s⁻¹ (4, 5); therefore, the gold phase of the composite will be more active. The rate of et at the substrate can be controlled by controlling the substrate potential. This is demonstrated in Fig. 1. Here the tip is a 8 μm diameter carbon-fiber microdisk electrode. The tip potential is held at -0.6 V so that the Fe(III) ion is reduced to Fe(II) at the diffusion controlled rate. Figure 1 shows the current recorded at the tip as it is swept at a close distance, about 2.1 μm, across the same area of the composite surface. At a substrate potential of +0.7 V, the response is relatively flat. The slight slope arises because the composite surface was slightly tilted with respect to the x-y

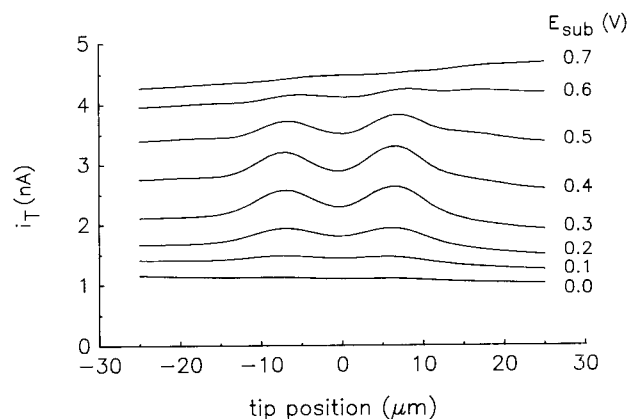


Fig. 1. Line scan of a region of the composite GC/Au surface for the substrate potential held at various potentials (as labeled). The mediator is 2.0 mM Fe(III) in 1.0M H₂SO₄. The tip is an 8 μm diameter carbon-fiber disk held at a potential of -0.6 V. Tip-substrate separation is 2.1 μm and tip scan speed is 10 μm s⁻¹.

scanning plane of the tip. The flat response indicates that the surface is uniformly active with no topographic features, since at this potential both the GC and Au phases will oxidize the tip-generated Fe(II) back to Fe(III) at nearly diffusion-controlled rates. As the substrate potential is decreased, a pair of features from the Au phase are observed in the line scan. At these intermediate potentials the Au surface has a larger rate of et than the GC phase; thus, the Au phase shows a larger feedback response. At a potential around 0.0 V the line scan again is almost flat. Here the et rates at both phases are close to zero and little feedback occurs. The features observed at intermediate potentials are not well resolved, with gaussian-shaped profiles. This is likely due to the tip having a larger diameter than the size of the Au sites. The fact that the Au phase is incompletely resolved also implies that the current arising from the Au phase is lower than expected; this would suggest that the scans would enjoy greater contrast with better resolution resulting from the use of a smaller tip. Although no attempt was made in these preliminary experiments to improve the resolution, sub-μm resolution with the SECM is possible (6, 7).

SECM images of the composite surface are shown in Fig. 2A and 2B. For these images, the current, measured as a 10 μm diameter Pt tip was rastered above the surface, was converted to a gray-scale intensity. Figure 2A shows the result of a scan over a 200 × 130 μm region of the composite with the composite potential held at a voltage of +0.55 V vs. MSE. Figure 2B shows the identical region but with a composite potential held at +0.8 V. The bright regions in Fig. 2A represent higher tip currents at the gold sites and are due to the more rapid et rates compared to the darker GC sites. In Fig. 2B the et rates at both phases are at diffusion limit and so the phases are indistinguishable. Note, however, that topographic features are common to both images; for example, the round depression in the upper right of both images is due to a small pit in the GC surface. Also note that the change in the background level from lower right to upper left is due to a slight tilt in the sample. Examination of the composite surface by optical microscopy confirmed that the imaged regions indeed contained gold phases of the same shape and orientation as on the SECM image, and showed the small pit in the GC as well.

The SECM can be used to examine, at high resolution, differences in electrochemical activity at surfaces. The magnitude

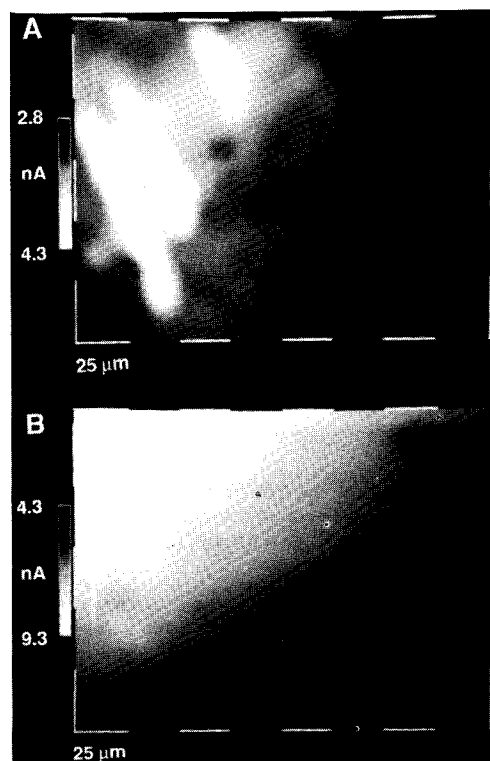


Fig. 2. Gray scale images of identical regions of the composite GC/Au surface. The tip is a 10 μm diameter Pt disk held at -0.45 V, tip scan speed is 10 μm s⁻¹. Imaged region is 200 × 130 μm. Note the different current scales. (A) Substrate potential is +0.55 V. (B) Substrate potential is +0.8 V.

of the current feedback as a function of potential and position can be used to assign rates of et at various locations on a surface (2). Moreover, the imaging conditions can be "tuned" to the particular electrode by choice of substrate potential, redox mediator, and solution conditions. Imaging of et transfer processes at other types of surfaces, e.g., on substrates undergoing corrosion or passivation reactions or biological substrates should also be possible.

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