Application of Scanning Electrochemical Microscopy to Generation/Collection Experiments with High Collection Efficiency

Chongmok Lee, Juhyoun Kwak, and Fred C. Anson*

Arthur Amos Noyes Laboratories, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

The technique of scanning electrochemical microscopy (SECM) was introduced by Bard and co-workers (1) who have utilized it in a variety of experiments (2). The use of a microelectrode placed close to a substrate electrode to detect electroactive products generated at the latter, as described by Engstrom and co-workers (3, 4), is one attractive application of the SECM technique (1). In previous studies, this type of generation/detection experiment has usually been carried out with the microelectrode used as the detector electrode (1-5). In the present study, a larger (100 \( \mu \)m diameter) substrate...
The electrode is used to detect and collect electrode reaction products generated at a microtip electrode positioned at various distances above the substrate electrode. The collection efficiency (in the sense employed for rotating ring-disk electrodes (6)) of such an arrangement is virtually 100% at easily achievable separation distances. The advantages of carrying out generation/collection experiments with the present apparatus are exemplified with some simple experimental systems. Comparisons with similar recent experiments in which arrays of microband electrodes are utilized (7, 8) are also provided.

**EXPERIMENTAL SECTION**

A carbon microtip electrode with a diameter of 11 μm and a platinum macrodisk electrode with a diameter of 100 μm were fabricated, mounted in glass, and polished according to previously described procedures (1). The carbon and platinum electrodes were employed as the tip and substrate, respectively, in SECM experiments. The miniature electrochemical cell and cell mounting were similar to those described in previous studies (9). The computer-controlled instrument employed in the SECM measurements was based on a previous design (9) with substitution of low-noise operational amplifiers in the bipotentiostat to increase the signal-to-noise ratio in the current measurements and a modification in the programs which control the x-y scanning of the tip electrode so that tip current-tip position data could be acquired and stored separately for scans in the forward or reverse direction across the substrate (10). The separation between the tip and substrate electrodes was determined by comparing the measured and calculated (11) tip current-separation distance data in solutions of Ru(NH₃)₆³⁺ or Fe(CN)₆⁻³.

**RESULTS AND DISCUSSION**

For experiments directed at maximizing the collection efficiency, i.e., the fraction of a reactant generated at a microtip electrode which diffuses to a nearby substrate electrode to be detected by electrochemical oxidation or reduction, one might expect the largest possible substrate electrode to be desirable. However, residual background currents increase with the area of the substrate electrode and substantial increases in signal-to-noise are obtained by limiting the size of the substrate electrode. We found a ratio of the diameters of the substrate to tip electrode of about 10 to provide both good collection efficiencies and acceptable signal-to-noise levels.

To carry out high collection efficiency experiments with substrate electrodes having diameters in the range of 100 μm, it is important to position the microtip electrode above the center of the substrate electrode, as depicted in Figure 1. The necessary positioning of the tip electrode is readily accomplished by employing the SECM instrument to scan the tip electrode across the substrate electrode in solutions containing a reversible, electroactive redox couple according to the procedures described by Kwak and Bard (9). In Figure 2 are shown results from some typical SECM scans in a solution of Ru(NH₃)₆³⁺. The tip was held 11 μm above the plane containing the substrate electrode and scanned across a 200 μm by 200 μm region containing the substrate electrode. The position of the tip electrode was held at −0.5 V vs SCE where the Ru(NH₃)₆³⁺ was continuously reduced to Ru(NH₃)₅²⁺, and the substrate electrode was maintained at 0.2 V so that any Ru(NH₃)₅²⁺ reaching it was oxidized. Very similar behavior resulted when Fe(CN)₆⁻³ was employed as the reactant with the same substrate electrode and potentials set at −0.2 and 0.5 V vs SCE, respectively.

In Figure 2A the current at the tip electrode at each value of x is shown for various values of y with Ru(NH₃)₅³⁺ as the active redox couple. The same data are displayed in a three-dimensional format in Figure 2C. The position of the substrate electrode is clearly defined, and the values of x and y needed to position the tip electrode across the substrate electrode and suppresses the tip current when the tip is above the insulating glass shroud (17).

The images of the substrate electrode can also be obtained by measuring the current at the substrate as the tip electrode is scanned. The results of this mode of operation are shown in Figure 2B,D. The substrate current is essentially zero until the tip approaches the substrate electrode, which means that the relative changes in the current at the substrate electrode as the tip passes over it are larger than those at the tip electrode where the reduction of Ru(NH₃)₅³⁺ proceeds at all tip positions.

It proved important to limit the scanning rates employed in acquiring the images from substrate currents (Figure 2B,D) to values low enough for the currents measured to approach their steady-state values. For example, images obtained by monitoring substrate currents while the tip was scanned at...
A steady-state profile is generated at the substrate electrode. At which the tip is scanned. The asymmetry is diminished by contrast, the images in Figure 2A,C, obtained with greater than that employed in Figure 2. The asymmetric effects to be observed. For example, in Figure 3 are shown the six contours shown; (C, D) Repeat of A and B while recording the disk currents, which vary between -4.5 and -5.7 nA, for the six contours shown.

50 μm s⁻¹ portrayed an apparently inclined surface with the direction of the inclination depending on the direction of the scan. By contrast, the images in Figure 2A,C, obtained with a tip scanning rate of 10 μm s⁻¹, were independent of the scan direction and closely resembled the images obtained from tip current measurements at both scanning rates.

The current sensitivity and low noise level of the SECM instrument employed in this study permitted some subtle effects to be observed. For example, in Figure 3 are shown a set of isocurrent contours obtained for the tip and substrate electrodes during scans with a separation distance (30 μm) greater than that employed in Figure 2. The asymmetric shape of the pattern obtained for the tip currents (Figure 3A,B) allowed the direction in which the tip was scanned to be established by inspection. The increased separation between the isocurrent lines that results as the tip is moved from positions over the conducting substrate to positions over the insulating glass shroud results from the interplay between the rate of relaxation of the concentration gradients provoked by the crossing of the conductor/insulation interface and the rate at which the tip is scanned. The asymmetry is diminished as the scan rate and the separation distance is decreased, as was observed in a previous study (12). The absence of corresponding asymmetry in the isocurrent contours for the substrate electrode (Figure 3C,D) shows that the substrate currents relax more rapidly than do those at the tip electrode at the separation distance employed. The difference in relaxation times reflects the way in which the layer between the tip and substrate, which is depleted of reactant while the tip is above the insulating glass shroud, is repopulated with reactant as the tip crosses the glass/platinum boundary. Reactant generated at the substrate must diffuse to the vicinity of the tip to establish a new steady-state concentration profile, and this process proceeds less rapidly than the steady-state profile is generated at the substrate electrode.

In attempting to position a microtip electrode over the center of a small substrate electrode it is desirable to avoid conditions (i.e., large separation distances and high scan rates) that give rise to patterns such as those in Figure 3A,B in order to avoid misjudgements about the true center of the substrate.

Figure 3. Current contour maps resulting from scans of the 100 μm diameter platinum-disk electrode by SECM. The experimental conditions were the same as those in Figure 2 except that the tip was positioned to be 30 μm above the center of the platinum disk and was scanned at 50 μm s⁻¹. (A, B) Scan in “forward” and “reverse” direction while recording the tip currents, which vary between 6.8 and 7.0 nA, for the six contours shown; (C, D) Repeat of A and B while recording the disk currents, which vary between -4.5 and -5.7 nA, for the six contours shown.

Figure 4. Generation/collection measurements with the 11 μm diameter carbon-fiber tip electrode positioned above the center of the 100 μm platinum-disk collector electrode. (A) Tip and disk currents as a function of the distance between the two electrodes. Both currents are normalized with respect to the tip current when the separation distance is large (>300 μm). Tip and disk potentials were -0.2 and 0.5 V vs SCE, respectively. The test solution was 5 mM Fe(CN)₆³⁻ in 0.1 M KCl-0.005 M HCl. (B) Collection efficiencies (i.e., disk current/tip current) as a function of separation distance: (1) the system from (A); single (2) or a pair (3) of microband collector electrodes flanking a microband generator electrode (data taken from ref 8). For (2) and (3) the distance is the gap separating the band electrodes.

Positioning by means of the pattern of substrate current contours appears to be preferable in such circumstances. However, we found it difficult to obtain such clear images if much larger substrate electrodes (e.g., 1 mm diameter) were employed because of larger contributions to the substrate current from background or "leakage" currents. Fortunately, it was not necessary to employ larger substrate electrodes in order to obtain high collection efficiencies.

Collection Efficiency Measurements. Once the tip (generator) electrode was positioned over the center of the substrate (collector) electrode, it was of interest to determine how the collection efficiency (as measured by the ratio of substrate current to tip current) varied with the distance separating the tip and substrate. In Figure 4A are plotted the tip and substrate currents (normalized with respect to the tip current obtained when the separation distance is large enough to render the presence of the substrate electrode negligible) vs the distance between the two electrodes. The solution contained Fe(CN)₆³⁻, and the potential of the tip was set at a value where the reduction to Fe(CN)₅⁻ proceeded at a diffusion-controlled rate while the substrate was held at a potential where the Fe(CN)₅⁻ was oxidized back to Fe(CN)₆³⁻. The steady-state current at the tip increased significantly above the constant value obtained at large distances when the separation became less than ca. 10 μm. This behavior is the result of the electrochemical feedback process that has been elucidated in earlier reports (11). The current at the substrate electrode was essentially zero at sufficiently large separations.
(not shown) and increased slowly as the separation decreased until the sharp rise resulting from the electrochemical feedback set in and the tip and substrate currents became nearly equal.

In Figure 4B are plotted collection efficiencies as a function of the tip-to-substrate separation for a solution of Fe(CN)₆³⁻. Attractively high collection efficiencies are obtained. They exceed 0.9 for separations below 20 μm, and even at 100 μm the efficiency is 0.3. Thus, the closely spaced microtip–macrodisk system allows very efficient capture by the disk of species generated at the tip.

Geometrical differences between microband arrays and tip–substrate systems will, of course, produce behavioral differences, but it is of interest to compare these two methods of conducting generation/collection experiments with separation distances in the micron range. Curves 2 and 3 in Figure 4B give the collection efficiencies obtained in a recent study with interdigitated microband electrodes (8). Larger efficiencies were obtained from generator band electrodes that were flanked by two collector electrodes (curve 3) than from a side-by-side pair of microband electrodes (curve 2). The microtip–macrodisk system provides not only larger collection efficiencies but also a reasonable range of separations where the collection efficiency is close to unity and insensitive to small changes in the separation.

Preliminary results of a digital simulation study of the effect of tip geometry and substrate size on collection efficiencies (10) show that collection efficiencies greater than 0.9 are to be anticipated at separation distances comparable to the radius of the tip, even when the substrate and tip have similar radii, so long as the tip is perfectly disk-shaped.

CONCLUSIONS

The experimental system described in this study has several attractive features: Unusually large collection efficiencies are easily achievable, which would be valuable in the detection of short-lived intermediates generated at the tip or in measurements of the kinetics of reactions between species generated at the tip and other reactants present in the solution. Compared with rotating ring–disk or interdigitated microband electrode systems that can be employed for the same purposes, the present system allows a wider range of generator-to-collector distances to be examined by means of the continuously variable micropositioning apparatus. The other techniques would require that a series of electrodes with varying separations be constructed. The fabrication of a macrodisk electrode opposed to adjustable microtip electrode is somewhat simpler than is the construction of ring–disk or interdigitated microband electrode assemblies.

The ability to use substrate currents instead of tip currents to obtain images by means of the SECM technique is another advantage of the present system because it permits successful imaging at large separation distances where the changes in tip current are considerably smaller than the changes in substrate current.

The system described in this study was constructed with the intention of applying it to studies of ionic transport at the surfaces of electrodes coated with polymers and polyelectrolytes. The high collection efficiencies that have been demonstrated should prove useful in quantitative measurements of electroactive species ejected from such coatings when current is passed through them. The results of these experiments will be described in a forthcoming report.

LITERATURE CITED


Received for review January 14, 1991. Accepted April 18, 1991. This work was supported by the National Science Foundation. This is Contribution No. 8379 from the Division of Chemistry and Chemical Engineering.