

# Scanning Electrochemical Microscopy. 30. Application of Glass Micropipet Tips and Electron Transfer at the Interface between Two Immiscible Electrolyte Solutions for SECM Imaging

Theodoros Solomon<sup>†</sup> and Allen J. Bard\*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

Electron transfer at the interface between two immiscible electrolyte solutions (ITIES) supported at the tip of a micropipet is demonstrated using the 7,7,8,8-tetracyanoquinodimethane (in 1,2 dichloroethane)/ferrocyanide (in water) system. This micro-ITIES is then used as a probe in scanning electrochemical microscopy for imaging purposes. A micro-ITIES can successfully be used to image surfaces with a resolution comparable to that obtained when using a metallic tip of the same size.

In scanning electrochemical microscopy (SECM), an ultramicroelectrode (UME) tip is brought very close to a surface and is scanned across it. The variations in faradaic currents are used to produce a topographic (three-dimensional) image of the surface. The tip or probe is usually a metallic UME, most frequently a Pt-Ir disk in an insulating glass sheath.<sup>1</sup> A detailed discussion of the principles and techniques of SECM and the different types of tips employed has recently appeared.<sup>2</sup> The resolution attainable in SECM imaging is directly related to the diameter of the tip employed. Fabrication of metallic UMEs in the micrometer range is straightforward but time-consuming, since careful beveling by repeated polishing of the glass sheath surrounding the metal disk must be carried out to make a useful tip. Smaller tips, even down to 10–20 nm, can be fabricated,<sup>2,3</sup> but these are fragile and the yield is modest. Thus we have been interested in devising a method of using a drawn glass capillary (a micropipet) as a tip in a mode analogous to metallic ones. Glass capillaries of sub-micrometer dimensions are easily fabricated on a commercial micropipet puller. We describe here the fabrication and application of such a tip based on electron transfer at the interface between two immiscible electrolyte solutions (ITIES).<sup>4,5</sup>

The principles of this approach are illustrated in Figure 1. A glass capillary is filled with a fairly concentrated aqueous solution (w) of a redox couple (R<sub>1</sub>, O<sub>1</sub>) and a supporting electrolyte. The substrate to be imaged is immersed in an organic liquid (o) that is immiscible with water and contains species O<sub>2</sub> and an electrolyte. As described below, the current is controlled by the rate of

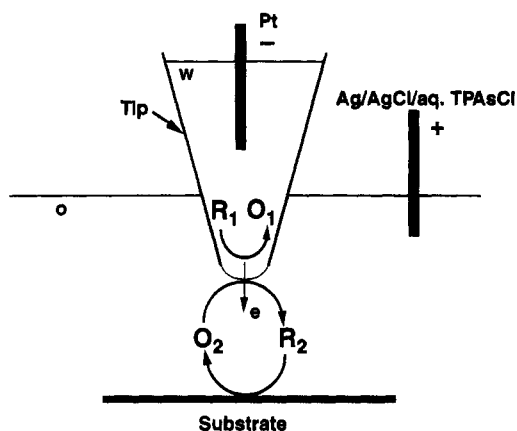


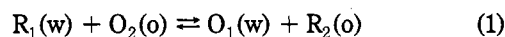
Figure 1. Schematic representation of the principles of SECM with micro-ITIES.

electron transfer at the water/organic solvent interface (the ITIES), which in turn is a function of the feedback between tip and substrate. In electrochemical studies of the ITIES, much work has been done on ion transfer across the liquid/liquid interface, but relatively few studies have been carried out on electron transfer at the ITIES.<sup>4,5</sup> Almost all studies of ion or electron transfer have been carried out at interfaces several millimeters in diameter. Taylor and Girault<sup>6,7</sup> showed that a "micro-ITIES" could be formed at the tip of a micropipet, and they used this interface (10–50 μm diameter) to study ion transfer processes. No previous studies have appeared in which a micro-ITIES has been used to investigate electron transfer between species confined to the two immiscible liquids.

In this article we demonstrate electron transfer at the liquid/liquid interface at the micropipet tip and show that the cyclic voltammetry of a species in the organic layer at such a tip is equivalent to that found at a metal tip. We then demonstrate the use of such a micropipet for SECM imaging.

## THEORY

For the system in Figure 1, the two-phase redox reaction,

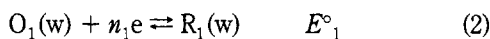


occurs between an aqueous redox couple

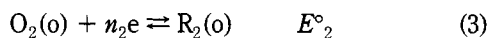
- (6) Taylor, G.; Girault, H. H. J. *Electroanal. Chem.* **1986**, *208*, 179.  
 (7) Stewart, A. A.; Taylor, G.; Girault, H. H. J. *Electroanal. Chem.* **1990**, *296*, 491.

\* Permanent address: Department of Chemistry, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia.

- (1) Wightman, R. M.; Wipf, D. O. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1989; Vol. 15, p 267.  
 (2) Bard, A. J.; Fan, F. F.; Mirkin, M. V. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1994; Vol. 18, p 243.  
 (3) Fan, F.-R. F.; Bard, A. J. *Science* **1995**, *267*, 871.  
 (4) Girault, H. H. J.; Schiffrin, D. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1989; Vol. 15, p 1.  
 (5) Girault, H. H. J. In *Modern Aspects of Electrochemistry*; Bockris, J. O., Conway, B. E., White, R. E., Eds.; Plenum Press: New York, 1993; Vol. 25, p 1.



and a redox couple in the immiscible organic phase (e.g., 1,2-dichloroethane)



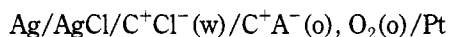
The condition for equilibrium when none of the components of the redox reaction partition into the opposite phase can be expressed as<sup>8</sup>

$$\Delta_o^w\varphi = (E^\circ_2 - E^\circ_1) + (RT/n_1n_2F) \ln \left[ \frac{a_{R_1}a_{O_2}}{a_{O_1}a_{R_2}} \right] \quad (4)$$

where  $\Delta_o^w\varphi = \varphi^w - \varphi^o$  is the potential difference across the interface,  $\varphi^w$  and  $\varphi^o$  are the Galvani or inner potentials in the aqueous and organic phases, respectively, and  $E^\circ_1$  and  $E^\circ_2$  are the standard reduction potentials of each couple in its respective phase which are referred to the same reference electrode in one phase (e.g., the SHE).  $\Delta_o^w\varphi$  can be varied by applying a potential across electrodes immersed in each phase using standard electrochemical instrumentation.

Cyclic voltammetry (CV) for electron transfer to a species ( $O_2$ ) at low concentration in the organic phase at the liquid/liquid interface is generally analogous to that for reduction of  $O_2$  at the metal/liquid interface.<sup>8,9</sup> To employ CV to the interfacial electron transfer reaction, the aqueous phase normally contains a redox couple at a concentration larger than that of the species in the organic phase.<sup>8</sup> One then considers the diffusion of only the species in the organic phase toward the interface. The aqueous phase therefore effectively behaves as a metal, while the species in the organic phase diffuses linearly (at a large planar interface) or hemispherically (at a micropipet) to the interface. The general underlying principles of electron transfer across the ITIES have been presented by Girault and Schiffrin,<sup>9</sup> and only a brief summary applicable to the micro-ITIES will be given below.

Consider first the following conventional electrochemical cell (I),

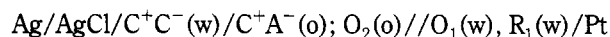


in which a Pt microelectrode is used to study the reduction of  $O_2$  in an organic solvent containing supporting electrolyte  $C^+A^-$ , and a  $Ag/AgCl$  electrode dipped in an aqueous solution of  $C^+Cl^-$  serves as the reference electrode. The potential of cell I at the half-wave potential of a CV wave at the Pt UME is

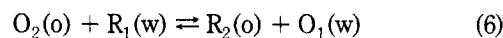
$$E_{1/2}(I) = E^\circ_2 - E_{Ag/AgCl} - \Delta_o^w\varphi_{C^-} \quad (5)$$

where  $\Delta_o^w\varphi_{C^-}$  is the Galvani potential difference (liquid junction potential) between the aqueous (w) and organic (o) phases, as determined by the cation  $C^+$  present in both phases (electrolyte anions  $Cl^-$  and  $A^-$  are constrained to phases w and o, respectively).

The Pt microelectrode is now replaced by a micropipet containing a Pt wire dipped in a concentrated solution of both  $O_1(w)$  and  $R_1(w)$ , as in cell II below,



where the  $Pt/O_1(w), R_1(w)$  electrode behaves as both a working and a redox reference electrode. On applying a potential difference between the Pt and Ag wires, resulting in a potential drop ( $\Delta_o^w\varphi$ ) across the interface, the redox reaction



will take place. The equilibrium condition is governed by eq 4. In other words, injection of an electron to reduce  $O_1$  at the Pt contact will promote electron transfer from  $R_1$  in the aqueous phase to  $O_2$  in the organic phase at the ITIES to maintain electroneutrality of each phase. When the potential is scanned and the current is recorded, the voltammogram is similar to that at a metal electrode. Since the concentration of  $R_1$  is much larger than that of  $O_2$ , in the absence of interfacial kinetic effects, the current is governed by the diffusion of  $O_2$  to the interface.

At the half-wave potential,  $a_{O_2} = a_{R_2}$ , and hence from eq 4 (with  $n_1 = n_2 = 1$ ),

$$\Delta_o^w\varphi_{1/2} = E^\circ_2 - E^{\circ'}_1 \quad (7)$$

where  $E^{\circ'}_1 = E^\circ_1 + (RT/F) \ln(a_{O_1}/a_{R_1})$  is essentially constant.

The potential of cell II between the Pt and Ag electrodes is given by

$$E(II) = E^{\circ'}_1 - E_{Ag/AgCl} - \Delta_o^w\varphi_{C^+} + \Delta_o^w\varphi \quad (8)$$

At the half-wave potential, combining eqs 7 and 8,

$$E_{1/2}(II) = E^\circ_2 - E_{Ag/AgCl} - \Delta_o^w\varphi_{C^-} \quad (9)$$

and hence (see eq 5),

$$E_{1/2}(I) = E_{1/2}(II) \quad (10)$$

Thus, provided that the micropipet contains the aqueous redox couple at a relatively large concentration, the voltammogram for the interfacial electron transfer at the micropipet should resemble that at the Pt microelectrode, with the half-wave potentials being the same according to eq 10. Hence, the same principle should be applicable for employing the micro-ITIES instead of a metallic ultramicroelectrode for imaging purposes in SECM. For a detailed discussion of the needed conditions for one phase to be regarded as metal-like, see ref 10.

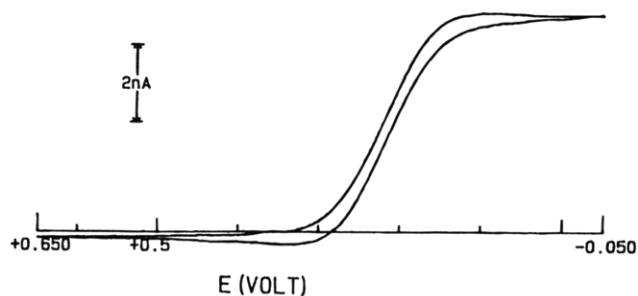
## EXPERIMENTAL SECTION

Micropipets were made from glass capillaries (1.2 mm o.d., 0.68 mm i.d.) using a commercial laser-based pipet puller (Sutter Instruments Co., Model P-2000). The internal diameter of the

(8) Geblewicz, G.; Schiffrin, D. J. *J. Electroanal. Chem.* **1988**, *244*, 27.

(9) Girault, H. H. J.; Schiffrin, D. J. *J. Electroanal. Chem.* **1988**, *244*, 15.

(10) Stewart, A. A.; Campbell, S. A.; Girault, H. H. J.; Eddowes, M. *Ber. Bunsenges. Phys. Chem.* **1990**, *94*, 83.



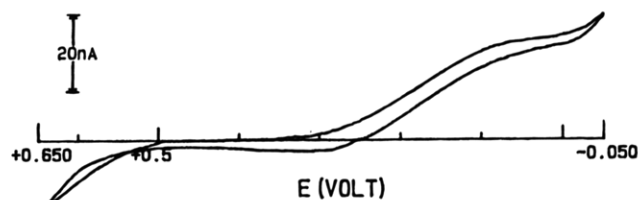
**Figure 2.** Voltammogram for the reduction of 1 mM TCNQ in DCE at a 25- $\mu\text{m}$  Pt microelectrode using cell I. Supporting electrolyte, 1 mM TPAsTPB; sweep rate, 50 mV/s.

micropipet tip was measured with an optical microscope. The composition of the aqueous phase in the micropipet was 1 M  $\text{Li}_2\text{SO}_4$  (Matheson, Coleman and Bell, MCB), 0.40 M  $\text{K}_4\text{Fe}(\text{CN})_6$  (MCB), and 0.01 M  $\text{K}_3\text{Fe}(\text{CN})_6$  (Aldrich) and was prepared from Millipore water. The organic phase composition was 1 mM 7,7,8,8-tetracyanoquinodimethane (TCNQ; Aldrich) and 1 mM tetraphenylarsonium tetraphenylborate (TPAsTPB) (prepared by precipitation from TPAsCl (Aldrich), and NaTPB (Aldrich), followed by recrystallization from acetone) in 1,2-dichloroethane (DCE).

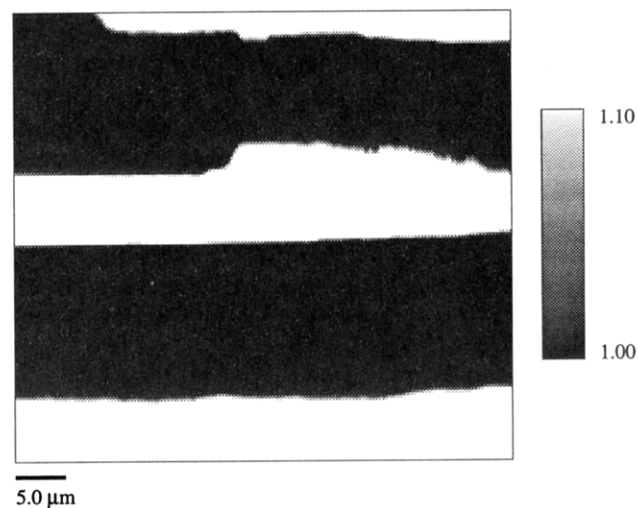
The voltammograms for the reduction of TCNQ at a Pt microelectrode and at a micro-ITIES were recorded using the BAS 100A electrochemical analyzer and the SECM setup described previously.<sup>2,11</sup> Prior to the SECM experiment, the potential of cell II was set to the limiting current region in the voltammogram. The micropipet was first lowered to the surface to be imaged until a positive or negative feedback (on a conducting or insulating part, respectively, of the surface to be imaged) was detected. At this distance from the surface, the micropipet was then scanned laterally over an area of either  $50 \times 50 \mu\text{m}^2$  at a scan rate of 2 m/s or  $100 \times 100 \mu\text{m}^2$  at a scan rate of 10 m/s, depending on the type of surface.

## RESULTS AND DISCUSSION

**Cyclic Voltammetry at the Micropipet.** We first compare the CV of 1 mM TCNQ (species  $\text{O}_2$ ) in DCE containing 1 mM TPAsTPB supporting electrolyte at a Pt microdisk electrode (25  $\mu\text{m}$  diameter) and at a micropipet filled with an aqueous solution of a concentrated redox couple. The CV at the Pt UME (analogous to cell I) (Figure 2) shows a typical, essentially steady-state, ultramicroelectrode voltammogram. When the UME was replaced by a micropipet (25  $\mu\text{m}$  i.d.) filled with an aqueous solution of 0.4 M  $\text{K}_4\text{Fe}(\text{CN})_6$ , 0.01 M  $\text{K}_3\text{Fe}(\text{CN})_6$ , and 1.0 M  $\text{Li}_2\text{SO}_4$  (analogous to cell II), a similar but more drawn-out voltammogram was obtained (Figure 3). The current measured at the micropipet tip is larger than that at a Pt disk of nominally the same dimension. This phenomenon was also observed in the earlier studies of micropipet ITIES,<sup>6</sup> where a 7-fold difference was observed. The authors ascribed this difference to the ITIES not being a perfect disk and thus actually having a significantly larger surface area. The factors governing the shape of the voltammograms for electron transfer at the ITIES have been discussed<sup>10,12,13</sup> and may also include some resistive drop at the micropipet tip. The current increases at the ends of this voltammogram because



**Figure 3.** Voltammogram for the two-phase electron transfer at a micro-ITIES obtained on replacing the Pt microelectrode of Figure 1 by a micropipet containing 1.0 M  $\text{Li}_2\text{SO}_4$ , 0.4 M  $\text{K}_4\text{Fe}(\text{CN})_6$ , and 0.01 M  $\text{K}_3\text{Fe}(\text{CN})_6$ . Sweep rate, 50 mV/s.



**Figure 4.** SECM image obtained using a micro-ITIES probe (5- $\mu\text{m}$  tip). Substrate was silicon with parallel platinum bands. Current scale is in units of  $10^{-8}$  A.

of the onset of supporting electrolyte ion transport between the water and DCE solutions. The general agreement of the voltammograms in Figures 2 and 3 and the similarity in the half-wave potentials agree with the model of Girault and Schiffrin,<sup>9</sup> in which, provided the aqueous phase contains a high concentration of the redox species, the voltammogram of electron transfer at the ITIES should reflect only the diffusion of the electroactive species in the organic phase toward the interface. This has previously been observed in four-electrode potentiostatic experiments at large planar interfaces,<sup>8,14,15</sup> where peak-shaped voltammograms were observed. The steady-state behavior seen in Figure 3 is consistent with hemispherical diffusion to the liquid/liquid interface at the micropipet tip.

**SECM Imaging with the Micropipet.** To illustrate the use of the micropipet tip in SECM imaging, scans across test structures (microband arrays) were carried out. These followed previous SECM practice,<sup>2</sup> except that the metal tip was replaced by the micropipet and the sample was immersed in a DCE, 1 mM TCNQ, 1 mM TPAsTPB solution. Figure 4 shows the SECM image of a silicon substrate with somewhat irregular parallel Pt bands  $\sim 5 \mu\text{m}$  wide, taken with a 5- $\mu\text{m}$ -diameter tip. Differences between the negative feedback (insulator) region (dark color) and positive feedback (conductive) region (light color) are clearly seen. The sample for which the SECM in Figure 5 was obtained is the connecting strip consisting of  $\sim 50\text{-}\mu\text{m}$  copper wires on a plastic base from the head of an HP Deskjet printer. The image shows

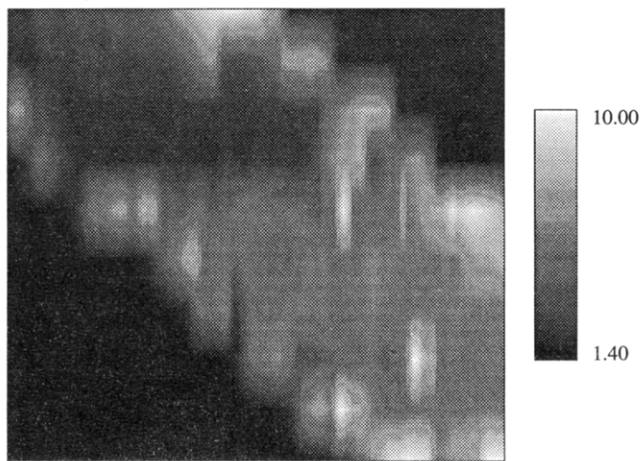
(11) Wipf, D. O.; Bard, A. J. *J. Electrochem. Soc.* **1991**, *138*, 469.

(12) Wei, C.; Bard, A. J.; Mirkin, M. V. *J. Phys. Chem.*, submitted.

(13) Solomon, T.; Bard, A. J. *J. Phys. Chem.*, submitted.

(14) Cunnane, V. J.; Schiffrin, D. J.; Beltran, C.; Geblewicz, G.; Solomon, T. *J. Electroanal. Chem.* **1988**, *247*, 203.

(15) Cheng, Y.; Schiffrin, D. J. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2517.



10.0  $\mu\text{m}$

**Figure 5.** SECM image obtained using a micro-ITIES probe (25- $\mu\text{m}$  tip). Substrate was a corroded strip of copper on a plastic base. Current scale is in units of  $10^{-9}$  A.

the uneven topography of the conductive copper band, presumably caused by corrosion, on the nonconductive substrate.

### CONCLUSIONS

We have demonstrated that micropipet tips can be used for faradaic current imaging in SECM. Several advantages accrue

(16) Fan, F.-R. F.; Bard, A. J. *Science*, in press.

from the use of these tips as compared to metal ones. First, they are much easier to construct, especially for tips with submicrometer diameters. The application of such ultramicropipet tips to probe the liquid/liquid interface is under investigation. Moreover, although very small (nanometer) metal tips can be used in SECM to image insulator surfaces,<sup>16</sup> high-resolution imaging of conductive surfaces by SECM is not possible, because of the onset of tunneling when the tip approaches to within 5–10 nm of the surface. Such tunneling will not occur with glass micropipets. However, the alignment and application of such tips will still be challenging. Another potential problem with such tips is the high resistance of the solution in the very thin region near the tip end, leading to an internal  $iR$  drop and possible limitations caused by rates of electron transfer at the liquid/liquid interface. Further work on the application of micropipet tips for SECM imaging is in progress.

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