

SHORT COMMUNICATION

SCANNING ELECTROCHEMICAL MICROSCOPY BASED ON ION TRANSFER
ACROSS IMMISCIBLE ELECTROLYTE SOLUTIONS[‡]

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Abstract. A liquid/liquid interface at the tip of a micropipette, and across which ion transfer can take place, is used as a probe for imaging a metal substrate using scanning electrochemical microscopy. Images were obtained that were comparable in quality to those found using metallic ultramicroelectrode probes.

INTRODUCTION

Recently it was shown [1] that a micro-interface between two immiscible electrolyte solutions (micro-ITIES), and across which electron transfer can take place, can be used as a probe for substrate imaging using the technique of scanning electrochemical microscopy (SECM). Under properly controlled conditions, a micropipette containing a concentrated aqueous solution consisting of the oxidized and reduced forms of a redox couple can be regarded as analogous to a metal electrode at which interface an electron transfer can take place. This may then be applied as an SECM probe to image various surfaces. Micropipettes can now be easily constructed using commercial pipette pullers, so that the tedious routine of constructing metal ultramicroelectrodes, with the attendant problems of polishing, securing flat surfaces, etc. can sometimes be avoided.

In an attempt to broaden the versatility of micropipettes for SECM investigations, the possibility of using ion (rather than electron) transfer across the ITIES for SECM imaging was investigated. This preliminary communication reports on the results of SECM imaging using a micropipette and based on the transfer of I⁻ across the water-nitrobenzene interface.

Ion transfer across a liquid-liquid interface supported at the tip of a micropipette (with the aqueous (w) phase being inside the micropipette) has been investigated experimentally and theoretically by Girault *et al* [2-5]. Experimentally, the techniques of linear sweep and cyclic voltammetry have so far been used. The cyclic voltammogram for ion transfer at the tip of a micropipette is highly asymmetric, resulting from the nature of the diffusion process at the interface. Thus, ion transfer from inside the

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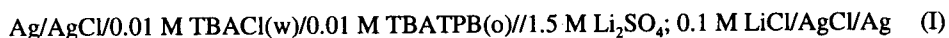
pipette to the organic (o) solution outside (w → o) may be regarded as being controlled by linear diffusion, whereas ion transfer towards the pipette from outside (o → w) is controlled by hemispherical diffusion. The cyclic voltammogram is thus peak-shaped for ion transfer (w → o), whereas a steady state current is observed for ion transfer o → w. As a result, it is often difficult to assess experimentally (using cyclic voltammetry) the reversibility of ion transfer. Furthermore, mass transfer for "ingress" (motion towards the micropipette from outside) is much faster than that for "egress" (motion from inside the micropipette to the solution outside), and hence the return scan for egress/ingress transfer is not clearly discernible in the cyclic voltammogram. For an ingress/egress transfer, the sweep rate dependence of the reverse peak does not increase in the classical manner with the square root of the sweep rate. In spite of such asymmetry, the voltammogram for ion transfer at the micropipette can be used as a basis for imaging in the "generation-collection" mode of SECM operation.

The principle of the generation-collection mode of SECM using a metallic ultramicroelectrode tip to image the surface of a substrate has been reported [6], so only a brief outline will be given of this principle as applied to ion transfer across the micro-ITIES.

In the substrate generation-tip collection mode, an ion that can transfer within the available "potential window" from the organic phase to the micropipette containing the aqueous phase, is electrochemically generated by the substrate, which is placed in the organic phase. The metal substrate is embedded in an insulator. The micropipette is held at the potential corresponding to the steady state current for diffusion of the generated ion from the organic phase to the micropipette tip. As the micropipette is lowered towards the metal substrate, the tip current increases corresponding to an increase in current due to the transfer of this ion from the organic phase to the aqueous phase. If, however, the tip is positioned away from the metal substrate, and above an insulator, no transferable ion immediately reaches the tip, and there is no current due to ion transfer. Thus at the boundary between the metal and the surrounding insulator, the micropipette tip senses a sharp change in current. This change in current is then used for imaging purposes.

EXPERIMENTAL

Tetrabutylammonium tetraphenylborate, TBATPB (Fluka), tetrabutylammonium iodide, TBAI (Fluka), tetrabutylammonium chloride, TBACl (Aldrich), iodine (Fischer), nitrobenzene (nb) (Mallinckrodt), lithium chloride (Alpha), lithium sulfate (MCB) were all used as received. Cyclic voltammograms for the cell:



with and without 1 mM I₂ or 1 mM TBAI in the organic phase were taken using the BAS 100 A Electrochemical Analyzer. The set-up for the SECM experiments was the same as that described previously [1]. The micropipettes were constructed from a glass capillary 1.2 mm o.d. and 0.68 mm i.d., and drawn to a sharp tip using a laser-based pipette puller (Sutter Instruments) to a size of 50 μm i.d. For the SECM experiments, a 2 mm diameter Pt disc electrode screwed at the base of a Teflon cell was used as a substrate. A bipotentiostat (Ensmann Instruments) was used in a 2-electrode mode both to generate I₂ from I₂ at the Pt disc, and to set the tip potential corresponding to the I⁻ transfer. Prior

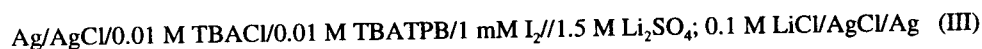
to SECM imaging, the tip potential was adjusted to a value of 0.30 V (Cell I, but with 1 mM I_2 added in the organic phase) and the micropipette positioned on the Pt side of the boundary between the Pt and the surrounding Teflon insulator. The substrate potential was set to a value of -0.45 V (Cell II):



in order to reduce the I_2 to I^- . The micropipette was lowered towards the Pt substrate until a sharp rise in current due to the ion transfer $I(o) \rightarrow I(w)$ is detected. The downward vertical motion was then stopped and the tip scanned in the direction of the insulator until a sharp decrease in current was detected. Thereafter, the micropipette was scanned forwards and backwards over an area of 250 μm^2 (X-axis) \times 100 μm^2 (Y-axis), at a scan rate of 25 $\mu\text{m/s}$ (X-axis) and 10 $\mu\text{m/s}$ (Y-axis).

RESULTS AND DISCUSSION

It was first necessary to select the potential at which I_2 is reduced to I^- at the platinum substrate. From the voltammogram of Cell II, a value of -0.45 V was chosen. Next, it was important to set the potential of the aqueous phase to a value suitable for the transfer $I(o) \rightarrow I(w)$. For this purpose, a study was made of the ion transfer process across the water-nitrobenzene interface supported at the tip of a micropipette using TBAI in the organic phase. The cyclic voltammograms for the supporting electrolytes (Cell I) and for the organic phase containing 1 mM TBAI are shown in Figures 1a and 1b, respectively. It is seen that addition of TBAI to the nitrobenzene solution produces an asymmetric wave which is due to the transfer of I^- . The steady-state positive current corresponds to the transfer $I(o) \rightarrow I(w)$, whereas the peak corresponds to the transfer $I(w) \rightarrow I(o)$. This voltammogram was used to determine the tip potential (at which iodide is transferable) to be used for the SECM experiment. A potential of 0.30 V (see Figure 1b) was selected for this purpose. As expected, the voltammogram was no different from Figure 1a when I_2 was added, (Cell III), since there is now no ion that can transfer across the interface within the available "potential window".



Although the formation of I_3^- in the organic phase is a possibility, this should not create any complication, since the potential of the aqueous phase in the micropipette was set to a value corresponding to the transfer of I^- (as ascertained by the experiment using TBAI). Besides, the potentials at which the two ions transfer across the water-nitrobenzene interface is very different, since

$$\Delta_o^w \phi_{I^-}^o = -0.195 \text{ V}, \quad \Delta_o^w \phi_{I_3^-}^o = 0.242 \text{ V} \quad [7].$$

The SECM image of a part of the Pt disc and a part of the surrounding Teflon insulator is shown in Figure 2. It is seen that the image fairly reproduces the actual situation at the boundary between the two surfaces, thereby proving that ion transfer in the substrate generation-tip collection mode of SECM operation can successfully be used for substrate imaging.

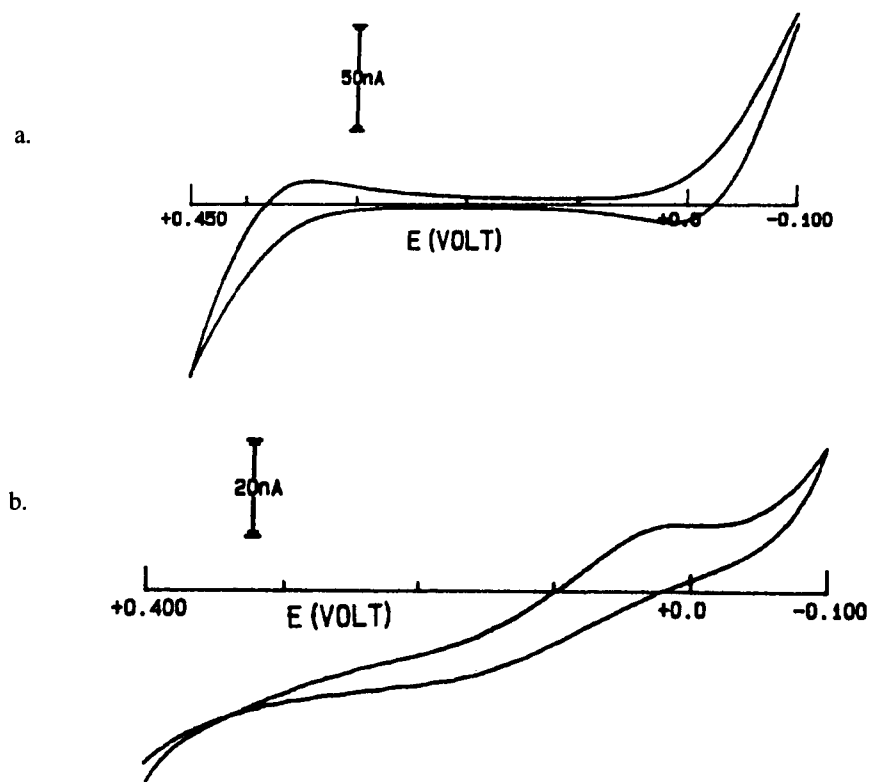


Figure 1. (a) Cyclic voltammograms of the cell: Ag/AgCl/0.01 M TBACl(w)/0.01 M TBATPB(nb)//1.5 M Li₂SO₄; 0.1 M LiCl/ AgCl/Ag (sweep rate 25 mV/s); (b) same as (a), but with addition of 1 mM TBAI in the organic (nb) phase (sweep rate 10 mV/s).

A few remarks may be made about the application of this technique. Most ions whose $\Delta G_{tr}^{o\ w-o}$ are tabulated in the literature are not electroactive, and hence cannot be generated at the substrate, (e.g. ClO₄⁻, tetraalkylammonium ions, etc.). A few, even if they are electroactive, have values that lie beyond the available potential window (e.g. Br⁻, Cl⁻, etc.). However, there are some ions that act as mediators for electron transfer which can be used for ion transfer studies. Examples are the viologens; in fact, the transfer of methyl and heptyl viologens across the water-nitrobenzene interface has been

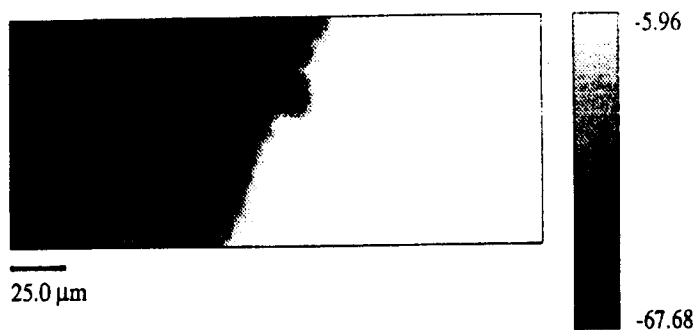


Figure 2. SECM image of a Pt disc (white zone) embedded in Teflon. Tip potential: 0.30 V; substrate potential -0.45 V (1mM I₂ added in the organic phase).

reported [8]. Another is Ru(bpy)₃²⁺, which is not only electroactive, but also transfers across the water-nitrobenzene interface with a standard Gibbs energy of transfer close to that of TBA⁺.

In conclusion, micropipettes that support liquid-liquid interfaces across which electron or ion transfer can take place, can have broad usefulness as probes for SECM imaging. Future work will report on their use for imaging a variety of substrates, including e.g. interdigitated electrodes.

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