Scanning Electrochemical Microscopy

V. A Study of the Conductivity of a Polypyrrole Film

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ABSTRACT

The potential dependence of the conductivity of a polypyrrole polymer film was studied by scanning electrochemical microscopy (SECM) operating in the feedback mode, where the steady-state faradaic current at an ultramicroelectrode tip increased or decreased depending on the conductivity of a sample as the tip was moved near the surface of the sample immersed in an electrolyte solution. From the measurement of tip current as the potential of a polypyrrole film was scanned, the region of potential where the film is conductive could be obtained. When a disk-shaped ultramicroelectrode tip (12.5 μm radius) was two-dimensionally scanned above the boundary region of the platinum-polypyrrole substrate (a Pt disk, 1 mm radius, half of which was covered by the polypyrrole film *ca.* 2000Å thick), the tip currents could be used to image the substrate. The effect of tip scanning speed and the substrate potentials were employed to study the conductivity of the polypyrrole film and the diffusion hysteresis in SECM in the feedback mode.

Previous papers from our group described the principles of scanning electrochemical microscopy (SECM) (1), the quantitative theory of the feedback mode (2), and several applications of SECM (3). In SECM an ultramicroelectrode (UME), with a tip radius of the order of 10 μm or less, is moved in close proximity to a substrate of interest in contact with a solution containing an electroactive species. The electrode reaction at the tip gives rise to a tip current that is affected by the substrate. In general, the tip current, i_T, is controlled by electrochemical reactions at the tip electrode and the sample substrate and is a function of the tip/substrate distance, d, and the conductivity and chemical nature of the sample substrate. The measurement of i_T can thus provide information about sample topography (3, 4) and its electrical and chemical properties. In the feedback mode the magnitude of i_T increases with respect to its steady-state value at large distances from the substrate, when the tip electrode is moved close to a conductive substrate, and decreases when the tip electrode is moved close to an insulating substrate (2). In this paper we focus on the variation of i_T caused by changes in the electrical properties of a sample substrate, a film of the polymer polypyrrole (PP), whose conductivity can be changed electrochemically.

It is well known that a reduced polypyrrole film is insulating and an oxidized one is conductive (5-10). Several studies involving *in situ* measurements of PP conductivity have been reported using interdigitated array (IDA) electrodes (8) or sandwich electrodes (9). Following previous SECM experiments with simple substrates, we investigated the potential dependency of the conductivity of a PP film by observing changes in the feedback current. A polypyrrole film was grown on a section of a 2-mm-diameter platinum disk electrode. The tip was held above the PP region and i_T was monitored, as the potential of the Pt-PP substrate (E_S) was changed. We introduce the concept of the SECM T/S cyclic voltammetric curve, in which tip current is recorded *vs.* substrate potential (*i.e.*, i_T *vs.* E_S), which, in this study, shows the transition between the conductive and insulating states of the PP film. Moreover, by scanning the tip across the boundary region between Pt and PP, the topographic structure and PP conductivity could be monitored, as the substrate potential was cycled between oxidized and reduced PP states.

Experimental

Platinum-polypyrrole substrate for SECM.—A PP film (Fig. 1) was grown on a 2-mm-diameter platinum disk electrode, half of which was masked by Teflon tape, by applying cyclic potential sweeps (24 cycles; scan rate = 200 mV/s) between 1.0 and −0.6V *vs.* a silver quasi-reference electrode (AgQRE) (5). The solution was 50 m*M* pyrrole monomer (Aldrich Chemical, Milwaukee, Wisconsin) and 0.2*M* tetrabutylammonium fluoroborate ($TBABF_4$, Southwestern Analytical Chemicals, Austin, Texas) in acetonitrile (MeCN, spectrophotometric grade, Mallinckrodt, Paris, Kentucky). MeCN was equilibrated with a Mallinckrodt molecular sieve (Grade 514GT 4Å); $TBABF_4$ was dried overnight in a vacuum-oven and pyrrole was used as received. A disk-shaped carbon UME tip (5.5-μm radius) and a disk-shaped platinum UME tip (12.5-μm radius) were fabricated as previously described (1, 3, 4).

SECM experiments.—Instrumental details and operational procedures for SECM were described in a previous paper (3). The bipotentiostat mode (1, 3) was used to apply potentials to tip and substrate. Two potential programmers (PAR 175 universal programmer, Princeton Applied Research, Princeton, New Jersey) and a home-built bipotentiostat (4) were employed to control E_T (the potential of a tip electrode) and E_S (the potential of a substrate) independently. The electrolyte for the SECM studies was an aqueous 10 m*M* $Ru(NH_3)_6Cl_3$ (Aldrich) and 0.1*M* K_2SO_4 solution.

Ellipsometric experiments.—Experimental details for ellipsometry were described previously (11, 12). PP film deposition on a platinum disk electrode (area, 0.176 cm^2) was accomplished by cyclic potential sweeps between 1.0 and −0.6V *vs.* AgQRE in the same solution as that used for the film deposition in the SECM experiment. Ellipsometric measurements were undertaken *in situ* during the film growth at *ca.* 1.0 and −0.6V *vs.* AgQRE, respectively, using a He-Ne laser (wavelength, 632.8 nm) and an angle of incidence of 67°.

Results and Discussion

Ellipsometry.—Ellipsometry was employed to measure the thickness and refractive index of a polypyrrole film. The thickness of the film for SECM studies produced by 24 cyclic sweeps was estimated to be 180 ± 20 nm. The refractive index (at 632.8 nm) of the oxidized form was (1.40 ± 0.05)-*i*(0.35 ± 0.01) and that of the reduced form was (1.70 ± 0.02)-*i*(0.20 ± 0.01). These values reasonably

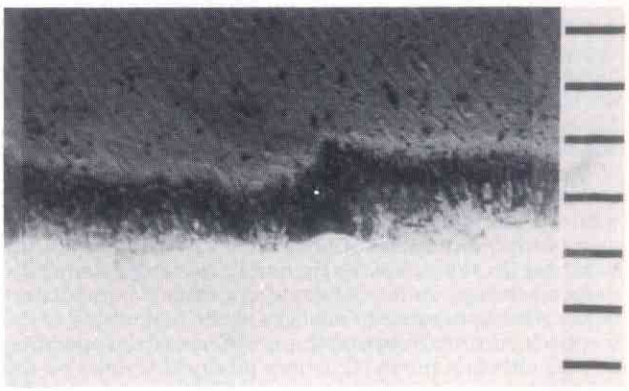

Fig. 1. Optical micrograph of the boundary region of a platinum (lower) polypyrrole (upper) substrate. Tic mark: 10 μm.

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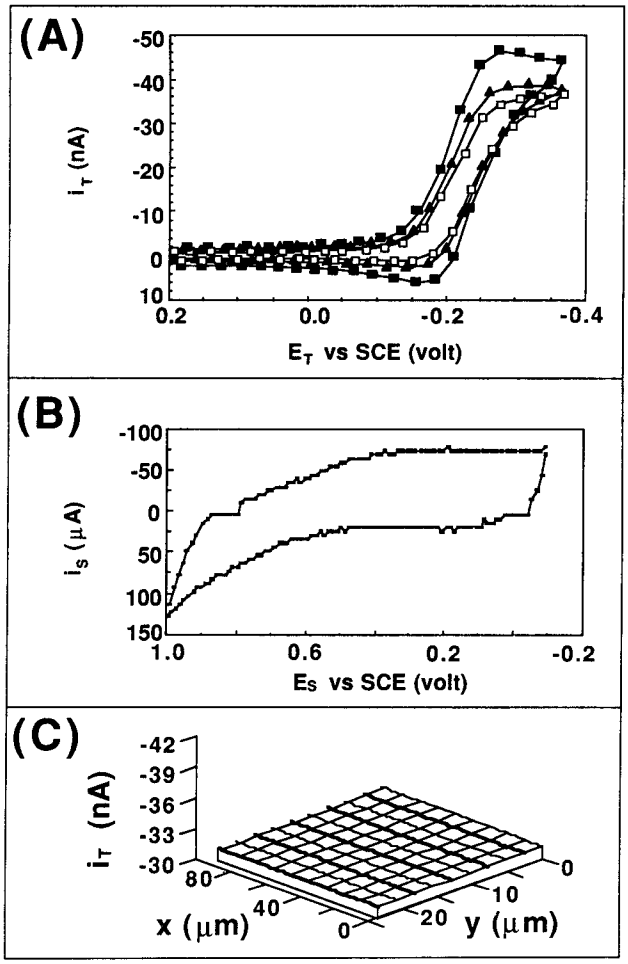

Fig. 2. A) T-cyclic voltammetry (tip current, i_T, *vs.* tip potential, E_T), at three different scan rates (v): (□) 100 mV/s; (▲) 200 mV/s; (■) 500 mV/s, C tip, a = 5.5 μm; B) S-cyclic voltammetry (substrate current, i_S, *vs.* substrate potential, E_S, at v = 10 V/s; C) SECM data (i_T *vs.* position) when the tip electrode (Pt, a = 12.5 μm) is rastered far above a PP substrate, with E_T = −0.375V *vs.* SCE and tip scan speed (S_T) = 23.7 μm/s. Tip substrate distance (d) > 165 μm. In all experiments the substrate was PP deposited on a 1-mm-radius Pt disk electrode and the solution was 10 mM $Ru(NH_3)_6Cl_3$, 0.1M K_2SO_4.

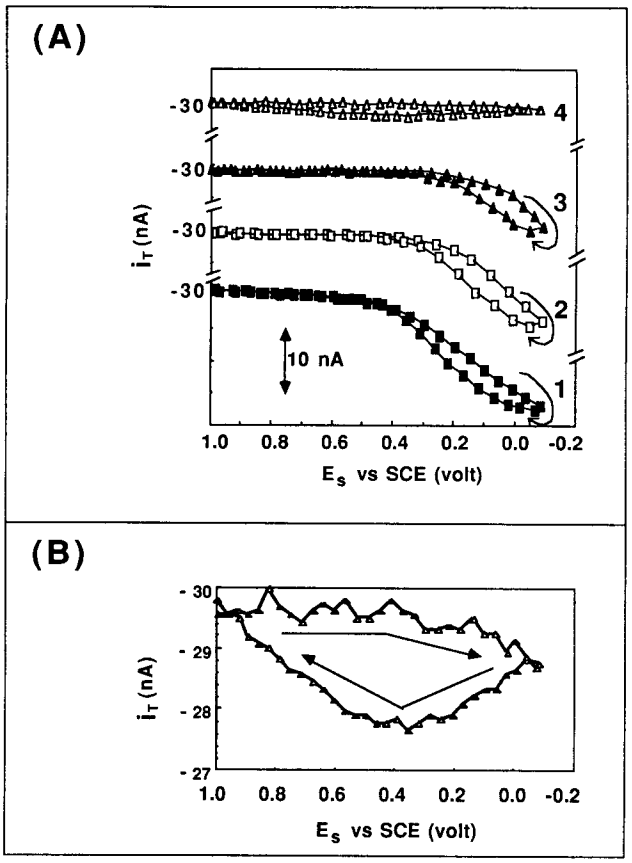

Fig. 3. SECM T/S cyclic voltammetry [tip current (i_T) *vs.* substrate potential (E_S)]. Tip electrode: 5.5-μm-radius carbon UME; E_T, −0.415V *vs.* SCE. Solution: aq. 10 mM $Ru(NH_3)_6Cl_3$ and 0.1M K_2SO_4. Substrate: PP film region of PP/Pt substrate. Tip-substrate distance, d, 6.0 ± 0.5 μm. $i_{T,\infty}$ = 20.5 nA. A) Potential scan rate (v) dependence of i_T *vs.* E_S (1, v = 20 mV/s; 2, v = 50 mV/s; 3, v = 200 mV/s; 4, v = 10 V/s); B) Amplified view of i_T *vs.* E_S at v = 10 V/s.

matched (within 10%) those reported for a PP film grown from an aqueous $NaClO_4$ solution (7). A detailed ellipsometric study of PP growth and conversion is discussed elsewhere (12).

SECM T/S cyclic voltammetry (i_T vs. E_S).—Several different forms of cyclic voltammetry (CV) can be carried out with SECM. In tip (T) CV, the tip potential (E_T) is scanned and the tip current (i_T) measured, with the substrate held at a potential E_S. Typical T-CV results for the solution employed in these studies (10 mM $Ru(NH_3)_6^{3+}$, 0.1*M* K_2SO_4) are shown in Fig. 2A. Substrate (S) CV involves a scan of E_S *vs.* substrate i_S (Fig. 2B). These two CV modes (T-CV and S-CV) are used to check the electrochemical response of the tip electrode and the substrate before topographic scans. Tip/substrate (T/S) CV involves monitoring i_T *vs.* E_S, with E_T maintained at a given potential and the tip held near [within a distance of about one tip diameter (2)] the substrate. In this mode the tip monitors electrochemically induced changes in the substrate at locations immediately below the tip, because of changes in the magnitude of the feedback current. Note that this is different from operation in the collection mode (1), where products formed on the substrate are analyzed at the tip.

T/S cyclic voltammograms at different scan rates for a 5.5-μm radius C UME tip above the PP region of the substrate are shown in Fig. 3. In the T/S CV the tip was held at −0.415V, where $Ru(NH_3)_6^{3+}$ is reduced to the 2+ form, and E_S was first held at +0.70V, where the PP is in the oxidized, conductive form, and i_T was monitored as the distance between tip and substrate, d, was decreased. Under these conditions any $Ru(NH_3)_6^{2+}$ that diffuses to the PP surface is oxidized to the 3+ form, which diffused back to the tip to lead to an enhanced i_T value compared to the value when the tip is far from the substrate, $i_{T,\infty}$ (20.5 nA). The theoretical current-distance relationship, $i_T/i_{T,\infty}$ *vs.* a/d, where a is the tip radius, for a conductive substrate (2) could then be applied to obtain the absolute tip/substrate distance, d, by nonlinear curve fitting. The T/S voltammetric experiment was then executed at a d of 6.0 ± 0.5 μm (d/a = 1.1 ± 0.1). The voltammetric curves (i_T *vs.* E_S) in Fig. 3 show the transition between the conductive state and insulating state of a polypyrrole film. In the positive potential region (E_S: 0.4 to 1.0V *vs.* SCE), $|i_T|$ is bigger than $|i_{T,\infty}|$ because of positive feedback from the conductive PP substrate. When E_S < 0.0V, i_T is smaller than $i_{T,\infty}$, because the substrate is in an insulating condition and blocks the diffusion of $Ru(NH_3)_6^{3+}$ to the tip (1-3). The region 0.4 < E_S < 0.0V *vs.* SCE represents a transition region where the PP undergoes a change from conductor to insulator. All curves show a hysteresis in this transition region, even at the relatively slow scan rate (v) of 20 mV/s.

The hysteresis arises from two processes. The major contribution in this potential region is the rate at which PP is oxidized and reduced (9, 10). This can be seen in the S-CV (Fig. 2B) and has been demonstrated previously, *e.g.*, by dynamic conductivity measurements on 13.3-μm-thick PP film during scanning of the potential of two sandwich electrodes (9) and steady-state ac measurements (10). There is, however, also a diffusion temporal hysteresis in SECM experiments, because of the finite time required for a species to diffuse from the substrate to the tip (*ca.* d^2/D). This effect will be most important at high scan rates. For example, at v = 10 V/s, (Fig. 3B), the film was reduced when E_S was

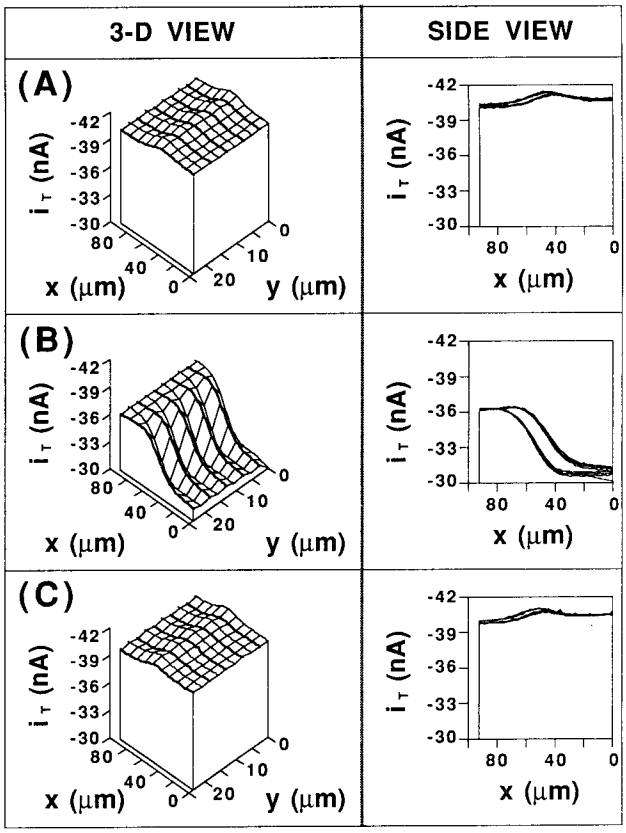

Fig. 4. SECM x-y scans for a tip electrode moved over the boundary region of the PP/Pt substrate [tip/substrate distance (d): 22 μm]. Tip electrode: 12.5-μm-radius Pt UME at E_T = −0.375V *vs.* SCE. Solution: aq. 10 mM $Ru(NH_3)_6Cl_3$ and 0.1M K_2SO_4. Tip scan speed in the x-y direction (S_T): 23.7 μm/s. A) E_S = +0.7V *vs.* SCE, T_M = 19 min; B) E_S = −0.1V *vs.* SCE, T_M = 34 min; C) E_S, +0.7V *vs.* SCE, T_M = 48 min, where T_M is time elapsed after experiment in Fig. 2C determining $i_{T,\infty}$.

scanned in the negative direction, but the effect on i_T was delayed, because Ru(III) generated at the substrate at more positive potentials was still in the vicinity of the tip and diffused to it to contribute to i_T. The current only showed a decrease somewhat later, when E_S was scanned in the positive direction, because of the time required to reach steady-state feedback. Note this SECM diffusion hysteresis will even occur with a substrate showing very rapid electron transfer reactions at the interface (*e.g.*, a Pt electrode) and simply represents the rate at which a steady-state concentration profile is attained upon perturbation of the substrate potential.

Since the theory for transient SECM has not yet been developed, we cannot resolve these two processes. However, such time dependent effects will be of less importance at smaller v and d. This diffusional hysteresis and the rate of PP redox process may account for the slight difference between the potential transition region found here (0-0.4V *vs.* SCE) and that reported previously (8-10) (0 to −0.2V *vs.* SCE), although the different anion in the two investigations may also be a factor.

Topographic (x-y) scans.—Both the topography and conductive nature of the substrate can be probed by x-y scans above the region where the boundary between the Pt and the PP lies (Fig. 1). Such scans were carried out with a 12.5-μm-radius Pt tip held at E_T = −0.375V *vs.* SCE, a potential selected by T-CV with the Pt tip, at d > 165 μm. In this case, $i_{T,\infty}$ was 31.3 ± 0.2 nA. $i_{T,\infty}$ showed some variation for the same electrode upon repolishing and was remeasured before each set of topographic scans. At this value of d, an x-y scan shows no features (Fig. 2C). Such a scan is useful, however, because it demonstrates stability of the electrochemistry at the tip, *e.g.*, the absence of adsorption or filming, which can cause a decrease in i_T.

After measuring $i_{T,\infty}$, the successive experiments shown in Fig. 4 and 5 were carried out over a time span of less than 80 min. The times after this measurement of $i_{T,\infty}$ are noted in the figure captions. By moving the tip toward the substrate while rastering the tip in the x-y directions and monitoring i_T (E_T = −0.375 and E_S = +0.7 *vs.* SCE), we could locate the PP/Pt boundary region even for the PP in the oxidized (conductive) state, as shown in Fig. 4A. The i_T value away from the PP/Pt boundary was 40.0 nA, corresponding to $i_T/i_{T,\infty}$ = 1.3 ± 0.02, or from the theory of SECM with positive feedback, d/a = 1.76 ± 0.08 or d = 22 ± 1 μm. The small bump at the boundary region probably represents some peeling away of the PP film from the Pt substrate in the immediate vicinity of the masking (Teflon) tape edge during the polymerization reaction. The essential equality of i_T over the Pt and PP regions shows that the oxidation of the +2 to the +3 Ru species occurs with equal facility over both regions. When E_S was switched to −0.1V *vs.* SCE, i_T decreased when the tip was above the PP region (Fig. 4B). In this case the PP was insulating, so that the $Ru(NH_3)_6^{2+}$ that reached the PP surface was not reoxidized, while oxidation continued at the Pt. Note that $|i_T|$

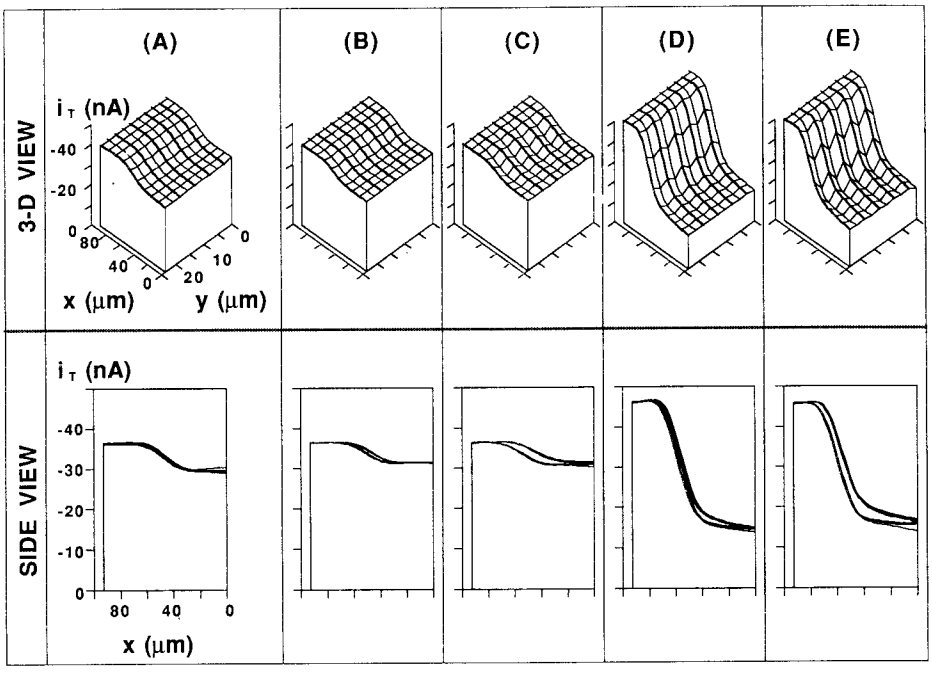

Fig. 5. Effect of tip scan speed, S_T, and distance, d, on SECM response. Same conditions as Fig. 4B, E_S −0.1V *vs.* SCE. A) S_T, 2.2 μm/s; d, 22 μm, T_M = 46 min; B) S_T, 7.2 μm/s, d, 22 μm, T_M = 31 min; C) S_T, 23.7 μm/s, d, 22 μm, T_M = 34 min; D) S_T, 7.2 μm/s, d, 13 μm, T_M = 73 min; E) S_T, 23.7 μm/s, d, 13 μm, T_M = 67 min, where T_M is time elapsed after the experiment in Fig. 2C to determine $i_{T,\infty}$.

over platinum (at −0.1V *vs.* SCE) in Fig. 4B also decreased about 10% from that when E_S = +0.7V *vs.* SCE (Fig. 4A), because at −0.1V, oxidation of $Ru(NH_3)_6^{2+}$ is not a totally diffusion-limited process as it is at +0.7V *vs.* SCE. Note also that although i_T with the tip above the PP region decreased upon switching to −0.1V, i_T was only slightly smaller than $i_{T,\infty}$ (31.3 nA), as opposed to the results in Fig. 3, where $i_T < i_{T,\infty}$ (20.5 nA).

The reasons for the difference in results between these two experiments is that the tip was relatively closer in Fig. 3 (d/a = 1.1) compared to d/a = 1.76 in Fig. 4. Thus, hemispherical diffusion of $Ru(NH_3)_6^{3+}$ to the tip was not as hindered by the insulating PP. Moreover, in the Fig. 4 experiment, some lateral diffusion of $Ru(NH_3)_6^{3+}$ generated at the Pt area may occur to increase i_T. Finally, the PP film might not be completely insulating and some oxidation of $[Ru(NH_3)_6]^{2+}$ might occur. When E_S was changed back to +0.7V *vs.* SCE (Fig. 4C), i_T over the PP region was restored to the levels in Fig. 4A, because the PP became conductive again. In Fig. 4A and 4C, i_T with the tip over the PP is very slightly larger than i_T over the Pt. The thickness of the PP film, 0.2 μm, is negligible compared to the tip-substrate separation, 22 μm. However, a small amount of tilt of the substrate with respect to the scanning plane of the tip (tilt angle ~1.7°) would produce such a small difference.

The effect of the rate of scanning the tip over the surface (S_T) with E_S constant at −0.1V (insulating region) on hysteresis in i_T caused by delays in attaining steady-state mass transfer is illustrated in Fig. 5. In Fig. 5A, where S_T = 2.2 μm/s, no diffusion hysteresis is detected. However, the other results in Fig. 5 taken at larger S_T-values show hysteresis in i_T during back-and-forth scans over the Pt/PP boundary region. The SECM data in Fig. 5 show a sigmoidal current shape in the x direction rather than an abrupt boundary, because the UME tip employed here had a rather large diameter (25 μm), so that the response represents a convoluted one over the Pt/PP boundary, which also extended over a finite width (*ca.* 11 to 16 μm) (see Fig. 1). Thus, when the tip was moving from the Pt to the PP, i_T decreased. However, it took a finite time to deplete $Ru(NH_3)_6^{3+}$ at the UME and to reach the steady state for the feedback mode of the insulating substrate. In the reverse movement, *i.e.*, when the tip was moving from PP to Pt, i_T increased. Now a finite time was required to supply $Ru(NH_3)_6^{3+}$, which had been depleted around the UME when it was over the PP region. This phenomenon will be called "diffusion hysteresis," because it originates only from the rate of diffusion of the electroactive species, as compared to the hysteresis seen in Fig. 3, which originates from both diffusion and the rate of substrate redox processes.

Approximate transient delays were estimated from the extent of hysteresis in the scans on traversing the Pt-reduced PP boundary in opposite directions (*i.e.*, the side view scans in Fig. 4 and 5). The distance, Δx, between a forward and back y-scan was measured at a current halfway between the Pt and PP current levels. This could be converted to a time from the known value of S_T. The time delays for the different values of S_T and d were as follows: 0.26 ± 0.02s for S_T = 23.7 μm/s and d = 22 μm; 0.30 ± 0.09s for 7.2 μm/s and 22 μm; 0.11 ± 0.01s for 23.7 μm/s and 13 μm; 0.17 ± 0.10s for 7.2 μm/s and 13 μm. The hysteresis time width decreased with smaller d. However, as S_T was decreased, a smaller hysteresis (distance width) was found (compare side view of Fig. 5A to 5C). This diffusional hysteresis is less important when smaller tips (and hence smaller d-values) are employed [see results in Ref. (3), where a tip with a = 5 μm was used]. Since there has been no theoretical treatment for transient SECM (*i.e.*, "diffusion hysteresis"), only rather qualitative statements can be made about the experimental data. The time delays probably also depend upon the size and geometry of the tip electrode.

Conclusions

The SECM technique was employed to study the potential dependence of the conductivity of a polypyrrole film by detecting the feedback current signal to a tip electrode. In this study we used the SECM tip as a sensor to detect the local electrochemistry occurring at a sample substrate that was composed of two kinds of electrode material (*i.e.*, platinum and polypyrrole) as the potential of a substrate was changed. The results found in the intermediate potential range, *i.e.*, for potentials between the completely oxidized (conductive) form and the completely reduced (insulating) form of PP suggest that the feedback current might be used to gauge the electrochemical kinetics of a substrate electrode. Thus we can view the completely oxidized form of PP to represent reversible heterogeneous electron transfer kinetics and the completely reduced one to represent very slow heterogeneous electron transfer. Moreover, this study suggests that the SECM can be used to distinguish different sites on a substrate material by changing the electrode potential as well as by varying the electroactive species in the electrolyte solution.

Acknowledgments

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