Quasi-Steady-State Voltammetry of Rapid Electron Transfer Reactions at the Macroscopic Substrate of the Scanning Electrochemical Microscope

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Abstract

We report on novel theory and experiment for scanning electrochemical microscopy (SECM) to enable quasi-steady-state voltammetry of rapid electron transfer (ET) reactions at macroscopic substrates. With this powerful approach, substrate potential is cycled widely across the formal potential of a redox couple while the reactant or product of a substrate reaction is amperometrically detected at the tip in the feedback or substrate generation/tip collection mode, respectively. The plot of tip current versus substrate potential features the retraceable sigmoidal shape of a quasi-steady-state voltammogram although a transient voltammogram is obtained at the macroscopic substrate. Finite element simulations reveal that a short tip–substrate distance and a reversible substrate reaction (except under the tip) are required for quasi-steady-state voltammetry. Advantageously, a pair of quasi-steady-state voltammograms is obtained by employing both operation modes to reliably determine all transport, thermodynamic, and kinetic parameters as confirmed experimentally for rapid ET reactions of ferrocenemethanol and 7,7,8,8-tetracyanoquinodimethane at a Pt substrate with ~0.5-µm-radius Pt tips positioned at 90 nm–1 µm distances. Standard ET rate constants of ~7 cm/s were obtained for the latter mediator as the largest determined for a substrate reaction by SECM. The various potential applications of quasi-steady-state voltammetry are also proposed.

Scanning electrochemical microscopy (SECM) has evolved as a powerful electroanalytical tool to investigate heterogeneous electron transfer (ET) reactions at electrode/solution interfaces. High versatility and spatial resolution are inherent advantages of SECM against other electrochemical methods.[1, 2] For instance, outer-sphere heterogeneous ET reactions have been studied by SECM to resolve the heterogeneous surface electroactivity of various electrodes and materials. SECM has been also developed to successfully probe inner-sphere heterogeneous ET reactions for the rapid screening of electrocatalysts and photocatalysts in combinatorial arrays. In standard SECM measurements, a disk ultramicroelectrode tip is positioned near a target electrode or material as a substrate to monitor ET kinetics at the local substrate surface under the tip. Typically, tip and substrate electrodes are biased externally to independently control ET rates at the respective electrode/solution interfaces.[3] Alternatively, only an SECM tip is biased to drive and monitor a heterogeneous ET reaction at an unbiased electrode[4] or at an electroactive material on an insulator[5] as a substrate.

Greater understanding of potential-dependent ET kinetics at electrode/solution interfaces is of paramount importance both fundamentally[6] and practically,[7] and relies on voltammetry.[8]

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In fact, voltammetry of heterogeneous ET reactions at the tip of SECM is well established[9] and has been successfully applied to determine large standard ET rate constants, k^0, of up to ~17 cm/s at nanometer-sized tips.[10] In comparison, the SECM measurement of potential-dependent ET rates at substrates is significantly limited. In the traditional feedback mode of SECM (Figure 1a), substrate potential, E_S, is held far from the formal potential, $E^{0'}$, of a redox couple to achieve steady state, where a substrate reaction (R → O + e) is opposite to a diffusion-limited reaction at the tip (O + e → R).[3] A rapid substrate reaction, however, is accelerated enough at E_S far from $E^{0'}$ to be limited by mass transport without reaching a kinetic regime,[11] thereby limiting the largest k^0 value measured by this approach to 0.42 cm/s[12] so far.

In contrast, a rapid substrate reaction is slowed at E_S around $E^{0'}$ to be reversible or even quasireversible. Advantageously, a quasireversible reaction gives both thermodynamic ($E^{0'}$ and kinetic (k^0 and transfer coefficient, α) parameters[13] as demonstrated for quasireversible substrate reactions by employing the feedback mode[3, 11] (Figure 1b) or the substrate generation/tip collection (SG/TC) mode[14] (Figure 1c), where the substrate-generated species, R, is detected at the tip at a diffusion-limited rate. The amperometric tip current in either mode, however, is transient with a reversible or quasireversible reaction at a macroscopic substrate, which results in the time-dependent growth of a mediator concentration gradient around the tip–substrate gap. Eventually, quasi-steady state is reached around the gap with a separation of a few micrometers after a macroscopic substrate is held at a fixed potential for ~5 s[9, 15, 16] or when the potential of a macroscopic substrate is swept very slowly at 2 mV/s.[17] True steady state (not quasi-steady state) can be achieved in the SG/TC mode by employing an ultramicroelectrode as a substrate,[14, 18-20] which restricts the size of examinable substrates.

Here we report on novel theory and experiment for SECM to enable quasi-steady-state voltammetry of rapid ET reactions at macroscopic substrates in the wide range of substrate potential around $E^{0'}$. We demonstrate that the amperometric current at a tip, i_T, in either feedback or SG/TC mode maintains quasi-steady state during the cyclic sweep of E_S around $E^{0'}$ when (i) the tip is positioned sufficiently close to a macroscopic substrate and (ii) a substrate reaction is reversible except under the tip. The resulting plot of i_T versus E_S features the retraceable sigmoidal shape of a quasi-steady-state voltammogram although a transient peak-shaped voltammogram is obtained simultaneously at the macroscopic substrate. Advantages of monitoring a substrate reaction as a tip current rather than as a substrate current include the simple measurement and analysis of a quasi-steady-state voltammogram, no charging current at the amperometric tip, high and adjustable mass transport under the tip, and high spatial resolution. Moreover, a kinetic limitation in a quasi-steady-state i_T–E_S voltammogram can be unambiguously discriminated from the effect of ohmic potential drop. Importantly, a pair of quasi-steady-state i_T–E_S voltammograms thus obtained in feedback and SG/TC modes is more informative than each voltammogram and allows for the reliable determination of all transport, thermodynamic, and kinetic parameters as recently demonstrated for steady-state nanopipet voltammetry of a common ion at liquid/liquid interfaces.[21, 22] In contrast to the common-ion approach, a pair of quasi-steady-state i_T–E_S voltammograms is obtained simply by moving tip potential to the feedback or SG/TC region when only one form of a redox couple is initially present in the bulk solution. In the following, we theoretically address requirements for quasi-steady-state i_T–E_S voltammetry by extending the theory of the tip voltammetric counterpart.[9] We also apply quasi-steady-state i_T–E_S voltammetry to the kinetic study of rapid substrate reactions to obtain large k^0 values of up to ~7 cm/s as the largest value determined for a substrate reaction by SECM. Various potential applications of quasi-steady-state i_T–E_S voltammetry are also proposed.

Theory

Model

We simulated i_T–E_S voltammograms under various geometric and kinetic conditions by solving standard diffusion problems for SECM (see the Supporting Information). Specifically, axisymmetric, time-dependent diffusion problems (Figure S-1) were solved by employing COMSOL Multiphysics finite element package (version 3.5a®, COMSOL, Inc., Burlington, MA; a simulation report is attached with the Supporting Information). A current was calculated for the diffusion-limited detection of the original mediator, O, in the feedback mode (Figure 1b) or the substrate-generated species, R, in the SG–TC mode (Figure 1c) to give a pair of i_T–E_S voltammograms at the same tip–substrate distance. Positive tip (and substrate) currents are based on the reduction of the original mediator so that feedback and SG/TC tip responses appear in the upper and lower panels of the following graphs, respectively. The dimensionless flux of species O at the edge of a macroscopic substrate (red dot in Figure S-1) represents a substrate current.

A tip current was obtained in the normalized form (eq S-1) with respect to a limiting current for species O at the tip in the bulk solution, $i_{T,\infty}$, as given by

$$i_{T,\infty} = 4xnFD_O c_O^* a \tag{1}$$

where x is expressed by eq S-2[23] as a function of RG (= r_g/a; r_g and a are outer and inner tip radii, respectively), $n = 1$ for a one-electron process as considered in this model (eq S-6), and D_O and c_O^* are the diffusion coefficient and concentration of the original mediator in the bulk solution, respectively. Features of simulated i_T–E_S voltammograms depend on the following dimensionless parameters

$$L = d/a \quad \text{(dimensionless tip−substrate distance)} \tag{2}$$

$$\sigma = a^2 F v / 4 D_O RT \quad \text{(dimensionless sweep rate for substrate potential)} \tag{3}$$

$$\xi = \sqrt{D_O/D_R} \quad \text{(dimensionless diffusion coefficient ratio)} \tag{4}$$

$$\lambda_O^{'} = k^0 d / D_O \quad \text{(dimensionless standard ET rate constant)} \tag{5}$$

where d is the tip–substrate distance, v is the sweep rate for substrate potential, and D_R is the diffusion coefficient of species R in the bulk solution.

Geometrical Requirements for Quasi-Steady-State Voltammetry

Finite element simulations demonstrate that a quasi-steady-state i_T–E_s voltammogram requires a sufficiently short distance between the tip and the substrate. Figure 2 shows the effect of tip–substrate distance, L, on i_T–E_S voltammograms as simulated for a tip with $RG = 1.5$. In this simulation, a reversible reaction ($\lambda_O' = 125$) for a redox couple with identical

diffusion coefficients ($\xi = 1$) was driven at the whole substrate surface during the cycle sweep of substrate potential at $\sigma = 0.01$. At short tip–substrate distances of $L \leq 0.5$, an i_T–E_S voltammogram in either feedback or SG/TC mode is retraceable on forward and reverse potential sweeps. The retraceable sigmoidal plot of i_T versus E_S corresponds to a quasi-steady-state voltammogram and not a true steady-state voltammogram. In fact, a transient peak-shaped voltammogram results from the plot of substrate current versus substrate potential under the same condition (the inset of Figure 2), confirming a time-dependent change in concentration profiles of redox mediators near the macroscopic substrate (Figure S-2). It is noteworthy that the wide range of substrate potentials in both cathodic and anodic regions far from $E^{0'}$ is applicable under quasi-steady-state conditions to obtain an i_T–E_S voltammogram with the whole sigmoidal shape. In contrast, true steady state is achieved for a reversible substrate reaction only at $E_S - E^{0'} \geq \sim 120$ mV on the forward sweep, where no substrate reaction occurs, i.e., zero current in a substrate voltammogram. Subsequently, only limiting currents in the traditional steady-state feedback mode[3] are observed in this limited potential range.

A quasi-steady-state tip current is obtained at a sufficiently short tip–substrate distance, where concentrations of redox mediators around the tip uniformly and instantaneously follow their concentrations at the substrate surface (Figure S-2), i.e., the tip sees substrate surface concentrations as bulk concentrations. In addition, substrate surface concentrations must quickly reach quasi-steady state at different substrate potentials to give a retraceable i_T–E_S voltammogram.

This requirement is satisfied under local equilibrium conditions at the substrate/solution interface with a reversible substrate reaction (see below). In contrast to the short distance region, concentrations of redox mediators at longer distances from a macroscopic substrate do not instantaneously follow their substrate surface concentrations (Figure S-2). Therefore, longer tip–substrate distances of $L \geq 1.0$ result in unretraceable i_T–E_S voltammograms under the same condition (Figure 2), where a reverse wave shifts toward more extreme potentials with respect to the corresponding forward wave.

We also found that the current at a tip with smaller RG reaches quasi-steady state more quickly under practical conditions with $D_O \neq D_R$ ($\xi \neq 1$). For instance, a tip with $RG = 1.5$ gives quasi-steady-state voltammograms at $\sigma \leq 0.01$ and $L = 0.25$ in a range of $0.5D_O < D_R < 2D_O$ that is typical for aqueous and organic electrolyte solutions (Figure 3a). As σ increases to 0.1 (Figure S-3a), an i_T–E_s voltammogram with $D_O \neq D_R$ slightly deviates from a quasi-steady-state behavior. The requirement of $\sigma \leq 0.01$ for quasi-steady state corresponds to $a \leq 3.3$ μm in eq 3 with $v = 50$ mV/s and $D_O = 5 \times 10^{-6}$ cm^2/s, thereby yielding $d \leq 0.81$ μm at $L = 0.25$. Micrometer- or submicrometer-radius tips with $RG = 1.5$ can readily approach to such short distances from a substrate (see the Results and Discussion). In comparison, significantly smaller σ (≤ 0.001) is required for obtaining nearly quasi-steady-state voltammograms at a tip with $RG = 10$ under the same condition with $D_O \neq D_R$ (see Figure 3b and S-3b for $\sigma = 0.01$ and 0.001, respectively). The requirements of $a \leq 1.0$ μm for $\sigma \leq 0.001$ and $d \leq 0.25$ μm for $L = 0.25$ are difficult to be achieved using conventional tips with large RG (for instance,[24] $a = \sim 0.5$ μm and $RG = \sim 7$ give $L > 0.7$). Overall, an SECM tip with small RG significantly facilitates the quasi-steady-state measurement of an i_T–E_s voltammogram under practical conditions.

This RG effect with $\xi \neq 1$ is explained as follows. When oxidized and reduced forms of a redox couple have unequal diffusion coefficients, transient concentration profiles of these redox mediators in the tip–substrate gap relax toward the final quasi-steady-state profiles by their radial diffusion between the gap and the bulk solution as extensively simulated for tip chronoamperometry in both positive feedback[15] and SG–TC[16] modes. A shorter radial

diffusion distance under a thinner insulating sheath surrounding the tip results in quicker attainment of quasi-steady state.

Requirement of Reversible Substrate Reaction for Quasi-Steady-State Voltammetry

A dimensionless rate constant, λ_O', was varied in finite element simulations to find that a substrate reaction must be reversible except under the tip to obtain the whole i_T–E_s voltammogram under quasi-steady-state conditions. Figure 4 shows i_T–E_s voltammograms for a tip with $RG = 1.5$ as simulated for various λ_O' values with $\alpha = 0.5$, $\sigma = 0.01$, $L = 0.25$, and $\xi = 1$. Quasi-steady-state i_T–E_s voltammograms are obtained only with $\lambda_O' \geq 0.3$ when substrate voltammograms are reversible or nearly reversible at this dimensionless scan rate (Figure S-4). This requirement of a reversible reaction at the exterior substrate surface for quasi-steady-state i_T–E_s voltammetry is explained as follows. When a substrate reaction is reversible, substrate surface concentrations of redox mediators are always equilibrated with time-dependent substrate potentials. In fact, the convolution principle confirms that equilibrium concentrations of species O and R at the exterior substrate surface uniquely correspond to substrate potentials independent of rate and direction of potential sweep (eqs S-15a and S-15b). Eventually, equilibrium surface concentrations immediately control mediator concentrations around a narrow tip–substrate gap (Figure S-2), where local quasi-steady state is maintained during the cyclic sweep of substrate potential. In contrast, i_T–E_s voltammograms for kinetically limited substrate reactions at the exterior surface ($\lambda_O' \leq 0.1$ in Figure 4) are partially unretraceable around their foot.

These voltammograms with slow substrate kinetics become retraceable at more extreme potentials, where a substrate reaction is diffusion-limited (for more detailed discussion, see Supporting Information). These partially unretraceable i_T–E_s voltammograms are beyond the scope of this work and will be addressed in future work.

Analytical Expressions for Quasi-Steady-State Voltammograms

Quasi-steady-state i_T–E_s voltammograms can be expressed using analytical equations as obtained by extending the theory of the tip voltammetric counterpart[9] (see the Supporting Information for their derivations). When the original mediator O is detected at the tip in the feedback mode (Figure 1b), the quasi-steady-state tip current in the normalized form, $I_{T,O}^{FB}(E_s, L)$, is given by

$$I_{T,O}^{FB}(E_s, L) = \frac{\pi}{2xL(2/\theta_S + 2\theta_S^{\alpha-1}/\lambda_O' + \xi^2 + 1)} + \frac{\xi\theta_S}{\xi\theta_S + 1}\left[I_{T,d}(L) - \frac{\pi}{2xL(\xi^2 + 1)}\right] \quad (6)$$

with

$$\theta_S = \exp[F(E_s - E^{0'})/RT] \quad (7)$$

where $I_{T,d}(L)$ is the normalized tip current under diffusion-limited positive-feedback conditions. In addition, the normalized quasi-steady-state tip current in the SG/TC mode, $I_{T,R}^{ST}(E_s, L)$, is given by

$$I_{T,R}^{ST}(E_S, L) = -\left\{ \frac{\pi}{2xL(2\xi^2\theta_S + 2\theta_S^\alpha/\lambda_O' + \xi^2 + 1)} + \frac{1}{\xi\theta_S + 1}\left[\frac{I_{T,d}(L)}{\xi} - \frac{\pi}{2xL(\xi^2+1)} \right] \right\} \tag{8}$$

Eqs 6 and 8 are valid when a solution initially contains only species O as assumed in this theory section. Alternatively, eqs S-36 and S-38 must be used for feedback and SG/TC modes, respectively, when only species R is initially present in the bulk solution.

These analytical equations agree well (< 1% error) with simulation results for both reversible (Figures 2, 3a, and S-3) and quasireversible ($\lambda_O' \geq 0.3$ in Figure 4) conditions under the tip with RG = 1.5 or 10 when $D_O = D_R$. These equations, however, are less accurate with $D_O \neq D_R$, where the assumption of local mass balance in the tip–substrate gap (eqs S-20 and S-40) is not exact. With $D_O \neq D_R$, the total concentration of redox molecules in the gap at a quasi-steady state is different from their initial total concentration because of their radial diffusion between the gap and the bulk solution.[15, 16] Nevertheless, errors in eqs 6 and 8 increase only up to ~4 % for reversible redox couples with $D_R = 0.5 D_O$ or $2 D_O$ (Figures 3a and S-3b).

Kinetic Analysis of a Pair of Quasi-Steady-State Voltammograms

As recently discussed in detail for steady-state voltammetry,[21, 22] a pair of quasi-steady-state i_T–E_S voltammograms in both operation modes allows for the reliable determination of thermodynamic ($E^{0'}$) and kinetic (α and k^0) parameters even when a substrate reaction under a tip is nearly reversible. The shape of a nearly reversible quasi-steady-state voltammogram depends on kinetic parameters too weakly to reliably determine both kinetic and thermodynamic parameters. For instance, an i_T–E_S voltammogram with a relatively large λ_O' value of 2 and a normal α value of 0.5 nearly overlaps with an i_T–E_S voltammogram with an anomalously large (or small) α value of 0.8 (or 0.2) by adjusting λ_O' and $E^{0'}$ accordingly for either feedback or SG/TC mode (Figures S-6a and S-6b, respectively). Different combinations of λ_O' and $E^{0'}$, however, must be used for curves in different operation modes to be superimposed with each other. This result indicates that the unique combination of thermodynamic and kinetic parameters can be obtained from a pair of quasi-steady-state i_T–E_S voltammograms for a nearly reversible substrate reaction under a tip.

It should be noted that the kinetic analysis of a pair of quasi-steady-state i_T–E_S voltammograms requires $I_{T,d}(L)$ and ξ values as obtained from the corresponding pair of limiting currents in feedback and SG/TC modes. The respective limiting currents are equivalent to $I_{T,d}(L)$ in eq 6 and $-I_{T,d}(L)/\xi$ in eq 8 when the solution initially contains only species O. In contrast, a limiting current of $-\xi I_{T,d}(L)$ is given by eq S-38 for the SG/TC mode when only species R is initially present in the bulk solution. Noticeably, the knowledge of ξ is also required for the determination of $E^{0'}$ from the position of a reversible quasi-steady-state i_T–E_s voltammogram (see Figure 3 for the ξ-dependent shift of i_T–E_s voltammograms).

Experimental Section

Chemicals

Ferrocenemethanol (FcMeOH, Aldrich, Milwaukee, WI) was recrystallized twice from hexane prior to use. All aqueous solutions were prepared with 18.3 MΩ·cm deionized water (Nanopure, Barnstead, Dubuque, IA). 7,7,8,8-Tetracyanoquinodimethane (TCNQ, Aldrich)

was recrystallized twice from acetone. Tetrabutylammonium (TBA) perchlorate (Aldrich) was used as organic supporting electrolytes in anhydrous acetonitrile (Aldrich).

SECM Measurements

Approximately 0.5-μm-radius Pt tips with small RG of 1.5–2.5 (Figure S-7c) were fabricated and characterized as described in the Supporting Information. A tip was brought within a short distance of <1 μm from a Pt substrate by monitoring the tip current in the positive feedback mode and was positioned at a fixed distance from the substrate during i_T–E_s voltammetry using a commercial SECM instrument with inchworm motors (CHI 900, CH Instruments, Austin, TX). An SECM stage was placed on a vibration isolation platform (model 63-533, TMC, Peabody, MA). The bipotentiostat of another SECM instrument (CHI 910B, CH Instruments) was employed to simultaneously monitor tip and substrate currents during the cyclic sweep of substrate potential. Positive currents at the tip and substrate correspond to the oxidation of 0.5 mM FcMeOH in 0.2 M NaCl or the reduction of 0.1 mM TCNQ in 0.1 M TBAClO$_4$. Subsequently, feedback and SG/TC tip responses for both mediators consistently appear in the upper and lower panels of the following graphs, respectively.

A 2.5-mm-radius Pt disk electrode (Pine Research Instrumentation, Raleigh, NC) was employed as a substrate. The Pt substrate was polished with alumina paste slurry (0.05 μm) on microcloth pads (Buehler, Lake Bluff, IL), and sonicated three times in deionized water for 5 min, in H$_2$SO$_4$ containing 3 % H$_2$Cr$_2$O$_7$ for 10 min, and again in deionized water for 15 min. A 125 μm-radius Ag wire (99.9 %, Aldrich) was coated with AgCl to serve as an aqueous reference electrode. Inner and outer compartments of a double junction non-aqueous Ag reference electrode (BASi, West Lafayette, IN) were filled with acetonitrile solutions of 0.1 M TBAClO$_4$ with and without 0.01 M AgNO$_3$, respectively.

Results and Discussion

Reversible ET Reaction of FcMeOH

A 0.48-μm-radius Pt tip with RG = 1.5 was employed to obtain quasi-steady-state i_T–E_S voltammograms for FcMeOH at a 2.5 mm-radius Pt substrate (solid curves in Figure 5). Either in the feedback or SG/TC mode, a sigmoidal i_T–E_S voltammogram on the forward sweep of substrate potential completely overlaps with that on the reverse sweep. In contrast, simultaneously measured voltammograms at the macroscopic substrate are peak-shaped and transient (the inset of Figure 5). These results confirm that the retraceable i_T–E_S voltammograms were mainly obtained under quasi-steady-state conditions.

True steady state was achieved only at E_S < ~40 mV on the forward sweep of substrate potential when the oxidation of FcMeOH at the substrate was negligible as estimated from the substrate voltammogram. Only limiting currents were obtained under the true steady-state conditions as employed for the traditional feedback mode,[3] where the range of applicable substrate potentials is significantly limited. Noticeably, FcMeOH gives a reversible voltammogram at the macroscopic Pt substrate (with a peak separation of 60 mV in the inset of Figure 5), which is required for obtaining a quasi-steady-state i_T–E_S voltammogram.

A pair of limiting currents in feedback and SG/TC modes at the same tip–substrate distance was analyzed to determine all transport parameters (d, D_{FcMeOH^+}, and D_{FcMeOH}). An enhanced limiting current in the feedback mode is equivalent to a total positive feedback current of $I_{T,d}(L)$ in eq S-36, thereby yielding tip–substrate distances of L = 0.19–2.4 in eq S-3 (d = 91 nm–1.1 μm for a = 0.48 μm). Interestingly, quasi-steady-state voltammograms were obtained at a long tip–substrate distance of L = 2.4 with the minimal tip-current

enhancement of ~10 %. This result confirms that quasi-steady state does not require a feedback distance and is achieved at tip–substrate distances where concentrations of redox mediators uniformly and instantaneously follow their equilibrium substrate-surface concentrations (Figure S-2). Moreover, limiting currents of $-\xi I_{T,d}(L)$ in the SG/TC mode (eq S-38) at different tip–substrate distances give consistent ξ values of

$\sqrt{D_{FcMeOH^+}/D_{FcMeOH}} = 1.06 \pm 0.02$, thereby yielding $D_{FcMeOH^+} = 8.8 \times 10^{-6}$ cm^2/s for D_{FcMeOH} $= 7.8 \times 10^{-6}$ cm^2/s as determined from $i_{T,\infty}$ at well characterized tips using eq S-37.

All quasi-steady-state i_T–E_S voltammograms thus obtained for FcMeOH are indistinguishable from theoretical voltammograms for reversible ET reactions at the whole surface of a macroscopic substrate (closed circles in Figure 5), thereby yielding consistent $E^{0'}$ values of 157.8 ± 0.5 mV vs Ag/AgCl. These $E^{0'}$ values agree with half-wave potentials of reversible tip voltammograms in the bulk solution and also with averages of anodic and cathodic peak potentials of reversible substrate voltammograms. The half-wave potentials and the averages of peak potentials, however, are based on the convolution of $E^{0'}$ and ξ and are equivalent to $E^{0'}$ only when $\xi = 1$. In contrast, $E^{0'}$ and ξ are separately obtainable from positions and limiting currents of a pair of quasi-steady-state i_T–E_S voltammograms, respectively. This feature of quasi-steady-state i_T–E_S voltammetry will be useful for the study of redox couples with unequal diffusion coefficients, e.g., in room temperature ionic liquids.[25]

Reversible i_T–E_S voltammograms for FcMeOH are consistent with a large k^0 value of ~7 cm/s for this mediator at nanometer-sized Pt tips (25–290 nm radius) as determined by tip voltammetry,[10] where tip potential was swept to oxidize FcMeOH while substrate potential was fixed for the diffusion-limited reduction of FcMeOH$^+$. This k^0 value is 7–8 times larger than the largest mass transfer coefficients of $D_{FcMeOH^+}/d = 0.95$ cm/s and $D_{FcMeOH}/d = 0.84$ cm/s at the shortest tip–substrate distance of 91 nm in Figure 5, which is larger than or barely comparable to tip–substrate distances of 18–122 nm required for obtaining kinetically limited nanotip voltammograms for FcMeOH.[10] Nevertheless, it should be mentioned that our quasi-steady-state approach moves the range of applicable substrate potentials within ± 120 mV from $E^{0'}$, which is comparable to the range of tip potentials required for slowing the nearly reversible oxidation of FcMeOH at the Pt nanotips to determine the large k^0 value. Overall, these comparisons indicate that the upper limit of measurable k^0 values at substrates by quasi-steady-state i_T–E_S voltammetry should be comparable to that at tips by tip voltammetry when the same tip–substrate distance is employed.

Nearly Reversible ET Reaction of TCNQ

The one-electron reduction of TCNQ at a 2.5-mm-radius Pt electrode was investigated using a 0.53-μm-radius Pt tip with $RG = 1.9$ (solid curves in Figure 6).

Quasi-steady-state i_T–E_S voltammograms thus obtained for TCNQ changed from reversible to nearly reversible as the tip was positioned closer to the Pt substrate, where tip–substrate distances were determined from limiting currents of $I_{T,d}(L)$ in the feedback mode using eq S-3. At relatively large distances of $L = 1.9$ and 0.92, the i_T–E_S voltammograms fit well with the corresponding reversible voltammograms (closed circles) as obtained from eqs 6 and 8 to give a $E^{0'}$ value of -88 mV vs Ag. In contrast, the i_T–E_S voltammograms at shorter tip–substrate distances of $L = 0.30$ and 0.18 are broader and shifted toward more extreme potentials in comparison to reversible voltammograms (dotted curves). The experimental voltammograms in both feedback and SG/TC modes fit very well with theoretical curves for nearly reversible substrate reactions under the tip (closed circles), thereby yielding a normal α value of 0.5 and $\lambda_O' = 4.0$ and 2.5 at the respective distances in addition to the same $E^{0'}$

value of −88 mV. The $\lambda_o^{'}$ values correspond to consistent k^0 values of 5.1 and 5.3 cm/s, respectively, which supports the reliability of this kinetic study. In contrast to reversible FcMeOH (Figure 5) with $k^0 =$ ~7 cm/s,[10] similar k^0 values for TCNQ result in a kinetic limitation at similar tip–substrate distances because of larger diffusion coefficients of TCNQ and its anion radical in acetonitrile as determined from limiting currents of $-I_{T,d}(L)/\xi$ in the SG/TC mode (eq 8). Specifically, $\xi = 1.13 \pm 0.05$ thus obtained is comparable to a literature value of 1.03[9] and gives $D_{TCNQ^{\bullet}-} = 1.6 \times 10^{-5}$ cm^2/s for $D_{TCNQ} = 2.0 \times 10^{-5}$ cm^2/s as determined from $i_{T,\infty}$ at well characterized tips using eq 1.

We carried out quasi-steady-state i_T–E_S voltammetry for TCNQ at various lateral tip positions over the Pt substrate to obtain k^0 values in the range of 3–7 cm/s (data not shown), which quantitatively reveals the heterogeneous electroactivity of the macroscopic Pt surface. These k^0 values are larger than values of ~1 cm/s for TCNQ at Pt nanotips as determined by tip voltammetry.[10] We ascribe this difference to a more rough surface of a polished Pt macroelectrode,[26] which is confirmed by the direct contact of smooth Pt tips with Pt protrusions at the substrate surface (Figure S-9) and also by the observation of numerous spikes based on tunneling current between the tip and the protrusions near the contact distance (Figure S-10). Overall, the k_0 values as obtained by i_T–E_S voltammetry in this work are effective values. These effective values are still much smaller than a value of ~2×10^3 cm/s as expected from the Marcus theory for TCNQ with a large self-exchange rate constant of 4×10^9 M^{-1} s^{-1}.[10]

The k^0 values of up to ~7 cm/s thus determined for TCNQ by quasi-steady-state i_T–E_S voltammetry are much larger than a k^0 value of 0.42 cm/s for the H$_2$ oxidation at a Pt substrate,[12] which had been the largest k^0 value determined for a substrate reaction by SECM. In comparison to the previous SECM studies of substrate ET kinetics, sharper tips with smaller a and RG were employed in this work to achieve shorter tip–substrate distances and, subsequently, higher mass-transport conditions. In addition, the determination of the large k^0 values for TCNQ requires quasi-steady-state conditions. The intrinsically rapid reaction of TCNQ at a Pt substrate must be slowed at E_S within ± 120 mV from $E^{0'}$ to observe a kinetic limitation (Figure 6). In contrast, only limiting currents are obtained for this rapid mediator under traditional steady-state feedback conditions, where substrate potential must be positive enough with respect to $E^{0'}$ to avoid significant TCNQ reduction at the substrate ($E_S - E^{0'} > 120$ mV on the forward potential sweep as estimated from the reversible substrate voltammogram in Figure 6). Moreover, the reliability of this kinetic measurement is improved significantly by employing both feedback and SG/TC modes under quasi-steady-state conditions. Finite element simulations of nearly reversible substrate reactions under the tip, e.g., $\lambda_o^{'} = 2.0$ in Figure S-6, indicate that a pair of quasi-steady-state voltammograms is essential for the reliable determination of both thermodynamic and kinetic parameters for TCNQ with large $\lambda_o^{'}$ (= 4.0 and 2.5 in Figure 6).

Finally, a good overlap between forward and reverse waves of a kinetically limited i_T–E_S voltammogram for TCNQ confirms the negligible contribution of an iR drop between substrate and reference electrodes to substrate potential. In contrast to the kinetic effect, the iR drop effect depends on the direction of the cyclic sweep of substrate potential to shift forward and reverse waves toward opposite directions, thereby yielding an unretraceable voltammogram under quasi-steady-state conditions. In fact, retraceable i_T–E_S voltammograms were obtained for TCNQ at a low concentration of 0.1 mM, which reduces the iR drop. Importantly, an i_T–E_S voltammogram at this low concentration is well defined because an amperometric tip current is free from a charging current and is enhanced by the efficient mass transport of redox mediators between the tip and the substrate. In contrast, a charging current is significant in the corresponding substrate voltammogram (the inset of

Figure 6). Overall, no information from a substrate voltammogram is needed for the analysis of a quasi-steady-state i_T–E_S voltammogram while the respective voltammograms provide global and local information about the electroactivity of the Pt substrate.

Conclusions

We developed a novel SECM approach to enable quasi-steady-state voltammetry of rapid ET reactions at macroscopic substrates. The wide range of substrate potentials is applicable under quasi-steady-state conditions to cover both cathodic and anodic regions far from $E^{0'}$, one of which reaches the limited range of substrate potentials employed in the traditional steady-state feedback mode.[3] Subsequently, a pair of quasi-steady-state i_T–E_S voltammograms is obtained in both feedback and SG/TC modes to enable the separate and reliable determination of all transport (D_O, D_R, and d), thermodynamic ($E^{0'}$), and kinetic (α and k^0) parameters. This quasi-steady-state approach requires a short tip–substrate distance and a reversible reaction at a macroscopic substrate except under the tip to be intrinsically suitable for the kinetic study of a rapid substrate reaction, which can be slowed at substrate potentials around $E^{0'}$ and probed both cathodically and anodically under high mass-transport conditions. In fact, k^0 values of up to ~7 cm/s for TCNQ as obtained by this approach are the largest determined for a substrate reaction by SECM. A larger k^0 value will be determinable by narrowing the tip–substrate gap, which requires a smoother substrate or a smaller tip as demonstrated for the tip voltammetric counterpart.[10]

The quasi-steady-state approach developed in this work will find various applications beyond the study of rapid substrate reactions. For instance, the separate assessment of transfer coefficient for cathodic and anodic reactions will be important when double layer or Marcus–Hush effect is significant.[6] A voltammetric SG/TC measurement with a macroscopic substrate at quasi-steady state is complementary to the true steady-state counterpart with an ultramicroelectrode substrate as recently developed for the SG/TC study of short-lived intermediates.[19, 20] Quasi-steady-state i_T–E_S voltammetry at different lateral tip positions results in multiple images of a heterogeneous substrate surface based on topography (d), intrinsic electroactivity (k^0), and ET mechanism (α). Moreover, a tip can be scanned at the just outside of feedback distances from a substrate at quasi-steady state to enable the feedback-free, direct imaging of the "surface concentration" of a target species generated or consumed at a substrate electrode. The imaging of an electrode surface concentration contrasts to the SG/TC imaging of a mediator concentration far from a substrate[18] and, interestingly, rather resembles the surface plasmon resonance imaging of electrode reactions,[27] which probes concentrations of both forms of a redox couple at the electrode surface.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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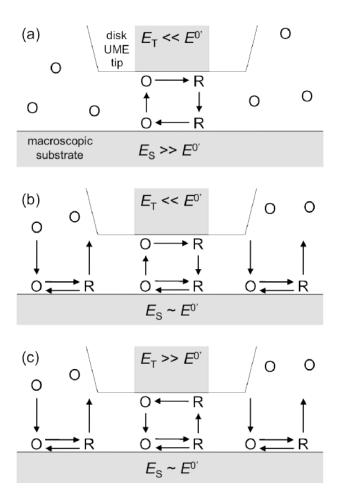27. Shan XN, Patel U, Wang SP, Iglesias R, Tao NJ. Science. 2010; 327:1363. [PubMed: 20223983]

Figure 1.
Scheme of SECM measurements in the (a) steady-state feedback mode, and in (b) feedback and (c) SG/TC modes for a reversible or quasireversible substrate reaction.
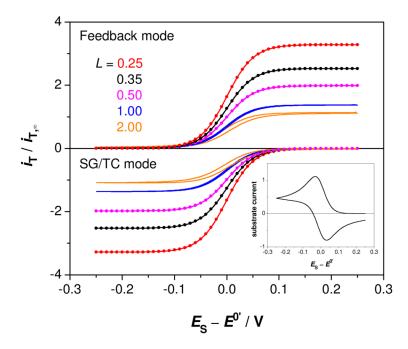
Figure 2.
Reversible i_T–E_S voltammograms simulated for various tip–substrate distances (solid curves). Closed circles represent eqs 6 and 8. The inset shows a simultaneously simulated reversible voltammogram at the substrate.

Figure 3.
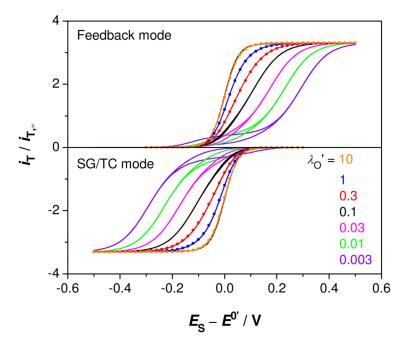Effect of D_R/D_O on reversible i_T–E_S voltammograms simulated for $L = 0.25$ (solid curves). Closed circles represent eqs 6 and 8.

Figure 4.
Effect of normalized standard ET rate constant, $\lambda_O{}'$, on simulated i_T–E_S voltammograms (solid curves). Simulated reversible curves are represented by black dotted lines, which nearly overlap with curves for $\lambda_O{}' = 10$. Closed circles represent eqs 6 and 8.

Figure 5.
Quasi-steady-state i_T–E_S voltammograms for FcMeOH (solid lines). The tip was held at 0.35 or 0.05 V vs Ag/AgCl for feedback or SG/TC modes, respectively. Substrate potential was cycled at 50 mV/s. Closed circles represent reversible theoretical voltammograms (eqs S-36 and S-38). The inset shows a reversible voltammogram as simultaneously measured at the substrate.
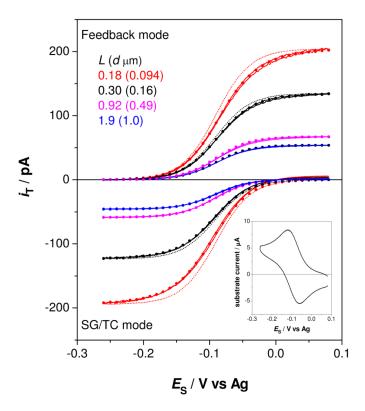
Figure 6.
Quasi-steady-state i_T–E_S voltammograms for TCNQ (solid curves). The tip was held at −0.235 or 0 V vs Ag for feedback or SG/TC modes, respectively. Substrate potential was cycled at 50 mV/s. Closed circles and dotted lines were obtained from eqs 6 and 8. The inset shows a reversible voltammogram simultaneously measured at the substrate (with a peak separation of 61 mV).