

Scanning Electrochemical Microscopy. 60. Quantitative Calibration of the SECM Substrate Generation/Tip Collection Mode and Its Use for the Study of the Oxygen Reduction Mechanism

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The substrate generation/tip collection (SG/TC) mode of scanning electrochemical microscopy (SECM) coupled with linear voltammetry is proposed as a way to quantify reaction intermediates generated in the solution at small substrates (100 μm diameter). The collection efficiency (CE) for SG/TC mode depends on the collector tip radius (a), the tip/substrate distance (d), and the size of the insulating glass sheath surrounding the collector tip (RG). In this work, we present experimental and simulated calibration CE values for different SG/TC geometries. Results of digital simulations in axial 2-D symmetry with the tip approaching a planar substrate are shown and fit experimental results obtained using ferrocenemethanol as a redox mediator very well. This model assumes that the mediator reacts under stationary-state conditions and undergoes diffusion-controlled electron transfer without any heterogeneous or homogeneous kinetic complications. Empirical equations for all SG/TC geometries reported here are provided as a convenient way to predict the maximum CE value for any given distance within the calibration range. Hydrogen peroxide quantification during the oxygen reduction reaction (ORR) at a Hg on Au electrode in acid pH was carried out using the SG/TC mode of SECM to demonstrate the utility of this technique in determining the number of electrons transferred (n) in the ORR. The results ($n = 2.12\text{--}2.19$) clearly point out the predominance of the two-electron pathway over the four-electron pathway when ORR takes place at this electrode material. Therefore, this work presents a powerful alternative to the rotating ring-disk electrode (RRDE) as means of obtaining mechanistic information by calculating the number of electrons transferred during an electrochemical reaction.

The rotating ring-disk electrode (RRDE)¹ has been widely used as a method of studying complex electrochemical reaction mechanisms by detecting intermediates generated during the reaction. The RRDE has been successfully used to study different electrochemical reactions, for example the oxygen reduction reaction

(ORR),^{2–4} which is of importance as the cathode reaction in most fuel cells.⁵ For an efficient fuel cell, it is desirable that oxygen be reduced directly to water in a four-electron reaction (reaction 1) at low overpotential rather than in a two-electron reaction to hydrogen peroxide (reaction 2), and considerable work has been carried out to measure the relative contribution of the $n = 2$ and $n = 4$ paths with different electrocatalysts.⁶



Scanning electrochemical microscopy (SECM)^{7,8} using the feedback mode has become a powerful tool to study kinetics and mechanisms of reactions associated with electrode processes.⁹ Moreover, the SECM generation/collection modes offer significant advantages for steady-state measurements.¹⁰ Our group has already published^{11,12} some work using the substrate generation/tip collection (SG/TC) mode of SECM for the detection of reaction intermediates. In particular, qualitative H_2O_2 detection during the ORR by SECM using an electrically wired enzyme as a tip was carried out; however, it presents several drawbacks because of its limited useful pH range (4.5–7.5) and its low collection efficiency (CE), which does not allow a quantitative measurement of H_2O_2 . This is because only a very small fraction of the species generated at a macroscopic substrate is intercepted by the collector tip. In this work, we present a new approach to quantify

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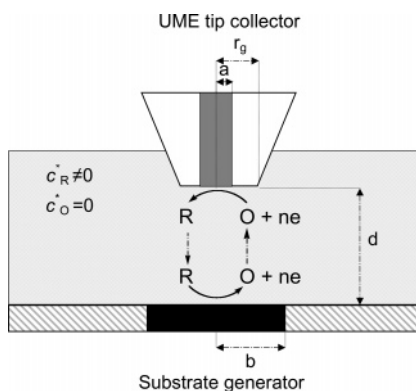


Figure 1. Schematic representation of the substrate generation/tip collection (SG/TC) mode of SECM.

the H_2O_2 produced during a substrate reaction using the SG/TC mode of SECM coupled with simultaneous linear sweep voltammetry (LSV). First, using a standard mediator (ferrocenemethanol), we quantitatively calibrate the SG/TC mode of SECM, for a $100\ \mu\text{m}$ diameter disk substrate, and report the maximum CE as a function of tip/substrate distance (d), tip collector radius (a), and size of the glass sheath surrounding the collector tip (RG). The use of $100\ \mu\text{m}$ diameter substrates allows a relatively high CE at the collector tip (25 and $50\ \mu\text{m}$ diameter), and at the same time, a real approach to experimental applications where such a spot size is readily achieved for many materials. However, we also provide simulated calibration data for larger substrate sizes. We fit the experimental results with the corresponding digital simulation, solved using stationary-state concentration boundary conditions. Finally, we present initial experimental results using this SG/TC experiment for the study of the ORR mechanism. In particular, we report H_2O_2 quantification during the ORR at a Hg on Au electrode in acidic pH using the SG/TC mode of SECM in a manner analogous to the RRDE.

EXPERIMENTAL SECTION

Chemicals. Ferrocenemethanol 97% (Aldrich, St. Louis, MO), K_2SO_4 (Aldrich, St. Louis, MO), H_2SO_4 , 94%–98% trace metal grade, HNO_3 50%–70%, KNO_3 (all Fisher, Fair Lawn, NJ), and $\text{Hg}_2(\text{NO}_3)_2$ dihydrate (Fluka, Steinheim, Germany) were used as received. Deionized water was obtained from a Milli-Q (Millipore) deionizing system.

Electrochemical Measurements and Electrodes. In the SG/TC mode, a redox-active species, O, is electrogenerated from a precursor solution species, R, at a $100\ \mu\text{m}$ diameter substrate electrode. Species O diffuses away from the substrate, and part of it is collected by a tip held at a constant potential where O undergoes diffusion-controlled reduction back into R. Figure 1 shows a scheme of the experiment, where a represents the tip collector radius, b the substrate generator radius, r_g the radius of the tip collector including the glass sheath, and d the tip/substrate distance. Moreover, two more parameters can be defined as a function of a , r_g , and d . They are L the normalized distance ($L = d/a$) and the RG value ($\text{RG} = r_g/a$).

Au and Pt electrodes were fabricated by heat sealing the corresponding metal wire under vacuum in a borosilicate glass capillary.⁸ When ferrocenemethanol was used as a mediator, $25\ \mu\text{m}$ (RG = 6 or 10) or $50\ \mu\text{m}$ (RG = 3 or 6) diameter Au electrodes

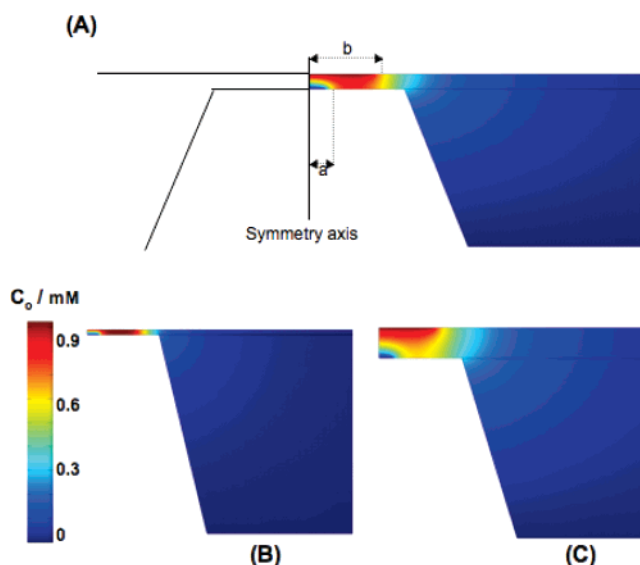


Figure 2. (A) Left side: schematic representation of the nonsimulated portion of space illustrating the way the tip is represented in the axial 2-D geometry. (A) Right side, (B and C): zoom into the simulation result for the concentration profile of species O for $a = 12.5\ \mu\text{m}$, $b = 50\ \mu\text{m}$, $r_g = 75\ \mu\text{m}$, and $d = 19, 5,$ and $34\ \mu\text{m}$, respectively.

were used as collector tips and a $100\ \mu\text{m}$ (RG = 17.5) diameter Au electrode was used as a generator substrate. When oxygen was used as a mediator, a $25\ \mu\text{m}$ (RG = 6) diameter Pt electrode was used as a collector tip and a $100\ \mu\text{m}$ (RG = 17.5) diameter Hg on Au electrode was used as a generator substrate. The Hg on Au electrode was prepared as previously described.¹³ All substrate and tip electrodes were polished with alumina paste ($0.05\ \mu\text{m}$) on microcloth pads (Buehler, Lake Bluff, IL) to yield a flat disk. The substrate electrode was tightened at the bottom of a Teflon cell with a $2.0\ \text{mm}$ diameter aperture via an O-ring.

A reference hydrogen electrode (RHE) was used in all experiments, and all potentials are reported with respect to RHE. A gold wire or a graphite rod $0.5\ \text{mm}$ diameter was used as a counter electrode. All electrochemical measurements were carried out at room temperature in a four-electrode arrangement using the SECM CHI 900B (CH Instruments, Austin, TX), which incorporates a bipotentiostat. First, a SG/TC image was recorded to locate the substrate electrode. Then, the collector tip was placed at the coordinates that showed highest activity in the image, and the center of the substrate was located using scans in the X and Y directions. Finally, the collector tip was positioned at a given distance above the substrate, and a linear scan voltammogram (LSV) of the substrate was taken while the tip potential was held at a constant value where the substrate-generated species reacts under diffusion controlled conditions. A low scan rate, e.g., $2\ \text{mV s}^{-1}$, was used during the substrate potential sweep to allow steady-state concentrations to be achieved. When ferrocenemethanol was used as a mediator, the experimental conditions for the SG/TC image and approach curves along the X and Y directions were $E_{\text{tip}} = 0.3\ \text{V}$ and $E_{\text{subs}} = 0.7\ \text{V}$. The collector tip was positioned at given distances above the substrate using a positive feedback approach curve in the Z direction for each reported distance. When oxygen was reduced, $E_{\text{tip}} = 1.2\ \text{V}$ and $E_{\text{subs}} = -0.3\ \text{V}$; the collector

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tip was located at a given distance above the substrate using the negative feedback approach curve in the Z direction. In all cases, the corresponding approach curve was fit to the well-established theory for the corresponding RG value.⁸ When ferrocenemethanol was used as a mediator, the experimental conditions of the SG/TC experiment coupled with LSV were E_{tip} held constant at 0.3 V and E_{subs} scanned from 0.3 to 0.7 V at a scan rate of 2 mV s⁻¹ and a deaerated solution containing ferrocenemethanol 10⁻³ M and K₂SO₄ 0.1 M was used. When oxygen reduction was studied, E_{tip} was held constant at 1.2 V and E_{subs} was scanned from 0.5 to -0.4 V at a scan rate of 2 mV s⁻¹ and an oxygen-saturated solution containing 0.5 M H₂SO₄ was used.

RESULTS AND DISCUSSION

Simulation Model. The model for the simulation assumes that the mediator undergoes a simple diffusion-controlled one-electron transfer without any heterogeneous or homogeneous kinetic complications at the tip and substrate. The diffusion problem was solved under steady-state conditions (eqs 1 and 2) using concentration boundary conditions on the substrate (eqs 3 and 4) and the tip (eqs 5 and 6).

$$D_{\text{O}}\nabla^2 c_{\text{O}} = 0 \quad (1)$$

$$D_{\text{R}}\nabla^2 c_{\text{R}} = 0 \quad (2)$$

Boundary conditions at the substrate electrode: $0 < r < b, z = d$, assuming $D_{\text{O}} = D_{\text{R}}$

$$c_{\text{R}}(r, d) = c_{\text{R}}^* \quad (3)$$

$$c_{\text{O}}(r, d) = c_{\text{O}}^* \quad (4)$$

Boundary conditions at the tip: $0 < r < a, z = 0$

$$c_{\text{R}}(r, 0) = c_{\text{R}}^* \quad (5)$$

$$c_{\text{O}}(r, 0) = c_{\text{O}}^* \quad (6)$$

where $c_{\text{R}}(r, z)$ and $c_{\text{O}}(r, z)$ are the steady-state concentrations in cylindrical coordinates of reduced (R) and oxidized (O) species, respectively, and c_{R}^* and c_{O}^* their bulk values. The wall of the tip as well as the glass sheath around the tip and substrate are treated as insulators. For semi-infinite diffusion to hold, the simulation space limits are set to c_{R}^* and c_{O}^* .

Initially, only reduced species R is present in the bulk ($c_{\text{R}}^* \neq 0, c_{\text{O}}^* = 0$), which is consumed to produce the oxidized species O at boundary b (substrate generation); the oxidized product O diffuses across the tip/substrate gap, d , and is collected (reduced) at boundary a (tip collection) to regenerate R, with some O lost by diffusion into the bulk of the solution. The CE is determined by the ratio between the tip current and the substrate current, which, at a given a and b , is a function of d and the tip RG.

Diffusion simulations in axial 2-D symmetry were carried out using the Comsol Multiphysics v.3.2 software (COMSOL, Inc., Burlington, MA). This software uses the finite element method with an exponentially expanding grid to generate a two-dimen-

sional grid according to the principle that the regions of steeper concentration gradient require more grid points than the other regions. In this type of symmetry, only cylindrical coordinates (r, z) are necessary to define the geometry of the problem; thus, the Laplacian operator (∇) is expressed in terms of these variables. A quantitative description of the maximum CE is obtained by extracting the steady-state currents at the tip and substrate electrodes, i_{tip} and i_{subs} , respectively, from the integration of the flux over the boundaries a and b , eqs 7 and 8.

$$i_{\text{tip}} = \int_{r=0}^{r=a} 2\pi n F D_{\text{O}} r \frac{\partial c_{\text{O}}(r, 0)}{\partial z} dr \quad (7)$$

$$i_{\text{subs}} = \int_{r=0}^{r=b} 2\pi n F D_{\text{R}} r \frac{\partial c_{\text{R}}(r, d)}{\partial z} dr \quad (8)$$

where n is the number of electrons transferred ($n = 1$ in this case), F is Faraday's constant (96 485 C/mol), and D_{O} and D_{R} are the diffusion coefficients for the species (assumed, as a good approximation value, equal to 7×10^{-10} m²/s for both species).¹⁴

The simulation dimensions used were tip (collector) $a = 12.5$ μm with $r_{\text{g}} = 75$ μm (RG = 6), $r_{\text{g}} = 125$ μm (RG = 10), or $r_{\text{g}} = 150$ μm (RG = 12); $a = 25$ μm with $r_{\text{g}} = 75$ μm (RG = 3) or $r_{\text{g}} = 150$ μm (RG = 6) with the substrate (generator) with $b = 50, 75, \text{ or } 100$ μm surrounded by an insulating sheath of material equal to the one used in the experiment. The total simulation space had a horizontal dimension of 875 μm and a height of 200 μm in addition to d . The tip/substrate gap represented as d was changed to obtain the CE values along the Z direction while the position of the tip was kept constant (hence, evaluation at $z = 0$ in eq 7). For $a = 25$ μm , 10 different simulation runs were carried out for values of d between 5 and 50 μm . Similarly for $a = 12.5$ μm , d was 2–40 μm . More details about the model are contained in the Supporting Information.

Simulations for different values of a, d , and RG were carried out in order to compare with the experimental results using ferrocenemethanol as the mediator. Figure 2A shows the assumed model (substrate above/tip below) in axial symmetry, with the variables r and z . Figure 2B,C and the right side of Figure 2A show the steady-state concentration profiles of species O from the simulation for different values of d at constant a and RG. These figures show that as d increases, more species O is able to escape from the tip/substrate gap to the bulk without being collected by the tip; hence, a lower CE is obtained. We observe the same trend for all simulated a values.

Experimental Results. Calibration with Ferrocenemethanol.

We used a well-known single electron transfer mediator (ferrocenemethanol) to calibrate the maximum CE achievable with the SG/TC mode with a 100 μm diameter substrate. This process does not involve further complications such as coupled homogeneous or heterogeneous reactions. In particular, we present CE values as a function of tip/substrate distance corresponding to two different tip radii (12.5 and 25 μm) and two different RG values for each tip radius. Figure 3 shows the tip and substrate currents collected during the substrate potential scan for one of the cases reported here ($a = 25$ μm , RG = 6). The tip current/substrate current ratio, for a given potential in the diffusion-controlled region

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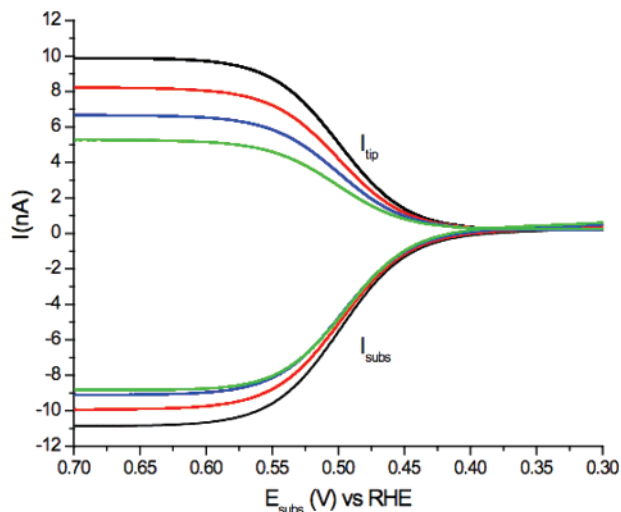


Figure 3. Experimental results of the SG/TC mode of SECM using ferrocenemethanol (R) oxidation at the substrate ($b = 50 \mu\text{m}$) and ferrocenium–methanol (O) reduction at the tip ($a = 25 \mu\text{m}$, $\text{RG} = 6$) for the calculation of CE^{max} as a function of $d/(a/b)$, deaerated solution containing 1 mM ferrocenemethanol and 0.1 M K_2SO_4 . Substrate potential scanned from 0.3 to 0.7 V at 2 mV s^{-1} and tip potential held at 0.3 V. Displayed data corresponds to black line $d = 5 \mu\text{m}$, red line $d = 10 \mu\text{m}$, blue line $d = 15 \mu\text{m}$, and green line $d = 25 \mu\text{m}$.

of the substrate process, gives the steady-state CE value. Therefore, it is easy to see that even at a small distance ($d = 5 \mu\text{m}$, $L = 0.2$, black line in Figure 3), 100% CE is not achieved in this type of experiment. Some substrate generated species inevitably diffuses past the tip into the bulk solution. In contrast, in the previously reported¹⁵ tip generation/substrate collection (TG/SC) mode of SECM using a stable mediator in absence of any other process, CE is essentially 100% for $L < 2$.

All CE values calculated from the experimental data such as those shown in Figure 3 are displayed in Figures 4 and 5 and compared with the corresponding data obtained from the simulations. Moreover, we have included in these figures the polynomial regression line that best fits all 10 simulated values in each case. All four different geometries show good agreement between the experimental and the simulated CE values. According to the simulations, CE values close to 100% should be available in all cases when d is very small, but experimentally those d values are very difficult to reach, especially for tips with large RG values. For this reason, we do not show experimental data for $d \leq 5 \mu\text{m}$. Moreover, Figures 4 and 5 show higher CE values when the RG is bigger at constant values of a , b , and d . This trend exhibited in simulated and experimental results points out the sensitivity of the CE value to the size of the glass sheath surrounding the collector tip. As illustrated back in Figure 2, a lower CE is obtained as more material escapes into the bulk of the solution; if the RG is increased, it is reasonable that more material is trapped in the tip/substrate gap and is thus available to be collected by the tip.

The good agreement found between simulated and experimental results validates each polynomial regression line for future studies. Empirical equations provide a convenient way to predict the maximum CE value (CE^{max}) for any given distance within the calibration range, assuming a redox process without any homo-

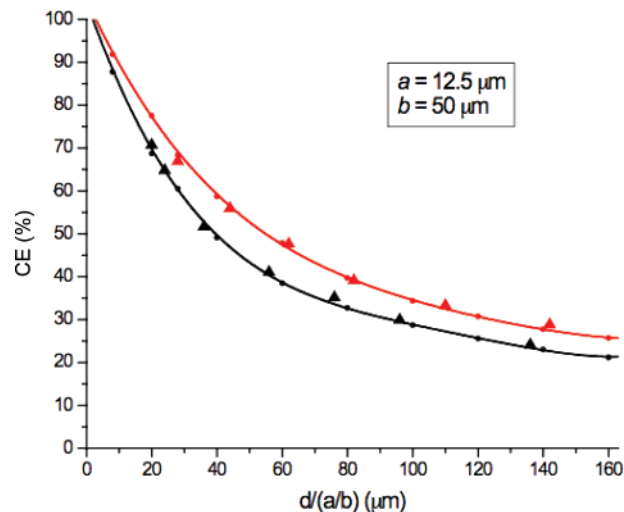


Figure 4. CE values calculated for $a = 12.5 \mu\text{m}$ and $b = 50 \mu\text{m}$. Red line and symbols correspond to a tip with $\text{RG} = 10$, and black line and symbols correspond to a tip with $\text{RG} = 6$. Circles correspond to CE values obtained from simulation, and triangles correspond to CE values obtained from experimental data using ferrocenemethanol as a mediator. Continuous lines correspond to the polynomial regression line for the simulated values.

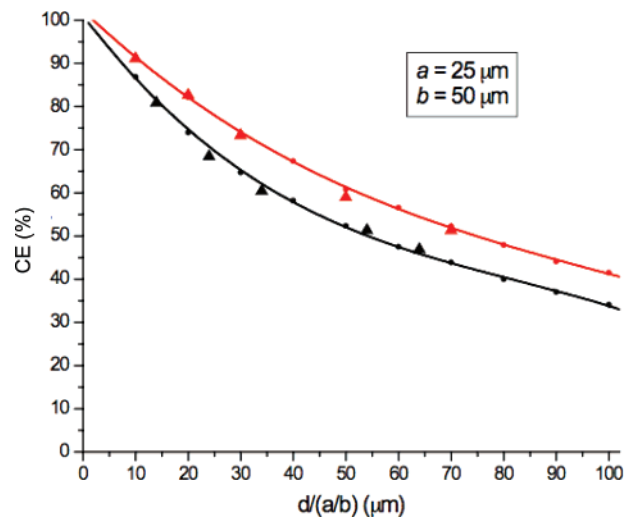


Figure 5. CE values calculated for $a = 25 \mu\text{m}$ and $b = 50 \mu\text{m}$. Red line and symbols correspond to a tip with $\text{RG} = 6$, and black line and symbols correspond to a tip with $\text{RG} = 3$. Circles correspond to CE values obtained from simulation, and triangles correspond to CE values obtained from experimental data using ferrocenemethanol as a mediator. Continuous lines correspond to the polynomial regression line for the simulated values.

geneous or heterogeneous kinetic complications. For this reason, we provide a general equation for each a value, which describes the CE^{max} vs adjusted distance, $d/(a/b)$, behavior. This is given in eq 9 when a is $12.5 \mu\text{m}$ and eq 10 when a is $25 \mu\text{m}$, for CE^{max} (%) and $d/(a/b)$ (μm). The corresponding parameter values for each of those equations are reported in Tables 1 and 2, respectively.

$$\text{CE}^{\text{max}} = A + B\left(\frac{d}{a/b}\right) + C\left(\frac{d}{a/b}\right)^2 + D\left(\frac{d}{a/b}\right)^3 + E\left(\frac{d}{a/b}\right)^4 \quad (9)$$

$$\text{CE}^{\text{max}} = A + B\left(\frac{d}{a/b}\right) + C\left(\frac{d}{a/b}\right)^2 + D\left(\frac{d}{a/b}\right)^3 \quad (10)$$

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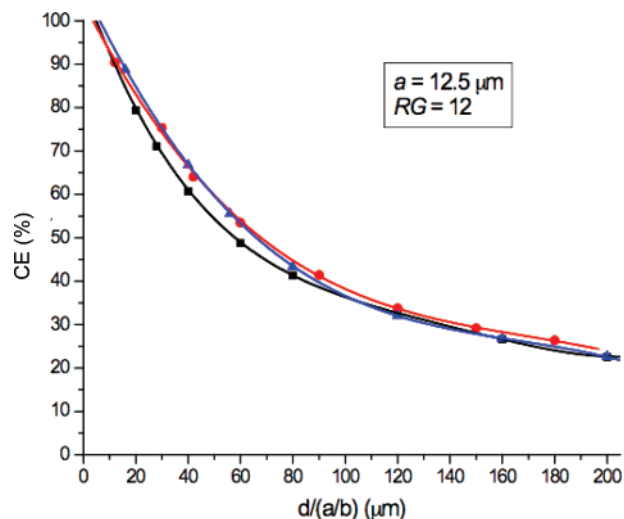


Figure 6. Simulated CE values calculated for $a = 12.5 \mu\text{m}$, $\text{RG} = 12$, and $50 \mu\text{m} \leq b \leq 100 \mu\text{m}$. Black squares correspond to a substrate with $b = 50 \mu\text{m}$, red circles correspond to a substrate with $b = 75 \mu\text{m}$, and blue triangles correspond to a substrate with $b = 100 \mu\text{m}$. Continuous lines correspond to the polynomial regression line for each set of simulated values.

Table 1. Empirical Parameter Values and Correlation Coefficient (R^2) for Equation 9 with $a = 12.5 \mu\text{m}$, $\text{RG} = 6-10$, and $b = 50 \mu\text{m}$

RG	A	B	C	D	E	R^2
6	103.38	-2.1681	0.02585	-1.485×10^{-4}	3.22×10^{-7}	0.9998
10	104.07	-1.641	0.01574	-7.85×10^{-5}	1.57×10^{-7}	0.9998

Table 2. Empirical Parameter Values and Correlation Coefficient (R^2) for Equation 10 with $a = 25 \mu\text{m}$, $\text{RG} = 3-6$, and $b = 50 \mu\text{m}$

RG	A	B	C	D	R^2
3	101.01	-1.6114	0.01583	-6.43×10^{-5}	0.9994
6	102.17	-1.1589	0.00814	-2.64×10^{-5}	0.9997

With this SECM approach, unlike feedback simulations, there are four parameters of importance: a , b , d , and RG . Moreover, the range of practical b -values that allow one to obtain steady state at the substrate is limited to about $100 \mu\text{m}$; at larger values one must examine the time-dependent behavior. Among the geometries treated by eqs 9 and 10, two cases show curves that are nearly the same, i.e., with $a = 12.5 \mu\text{m}$ with $r_g = 125 \mu\text{m}$ and $a = 25 \mu\text{m}$ with $r_g = 75 \mu\text{m}$. Thus, almost the same CE^{max} can be obtained at half of the tip/substrate distance using double the area at the tip collector but with about half of the glass shield. In Figures 6 and 7 we present additional simulated data for the SG/TC mode of SECM that display some common trends and increase the scope of these empirical equations. They show a good convergence of the corresponding polynomial fitting equations for three different substrate sizes ($b = 50, 75$, and $100 \mu\text{m}$) keeping constant values of a ($12.5 \mu\text{m}$ in Figure 6 and $25 \mu\text{m}$ in Figure 7) and r_g ($150 \mu\text{m}$) in all cases. It is important to point out that this merging behavior is only observed when the glass shield of the tip is significantly larger than the substrate size. The corresponding parameter values valid in eqs 9 and 10 that fit the polynomial

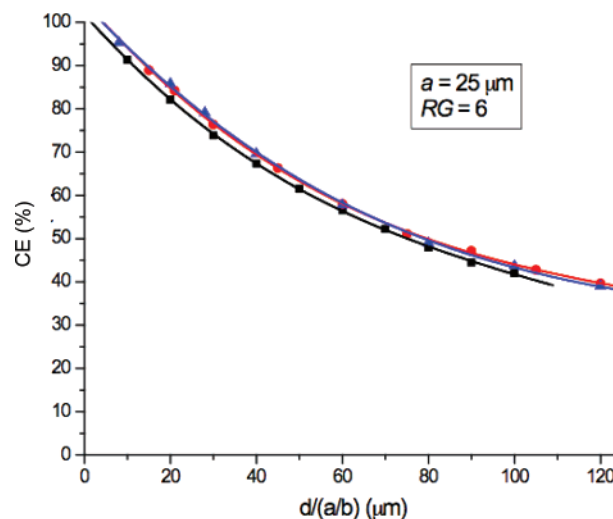


Figure 7. Simulated CE values calculated for $a = 25 \mu\text{m}$, $\text{RG} = 6$, and $50 \mu\text{m} \leq b \leq 100 \mu\text{m}$. Black squares correspond to a substrate with $b = 50 \mu\text{m}$, red circles correspond to a substrate with $b = 75 \mu\text{m}$, and blue triangles correspond to a substrate with $b = 100 \mu\text{m}$. Continuous lines correspond to the polynomial regression line for each set of simulated values.

regression in all the simulated data shown in Figures 6 and 7 are available in the Supporting Information. While these curves provide the needed data for a range of tips and substrates, others can be obtained using the simulation described; the program details are given in the Supporting Information.

Detection of Hydrogen Peroxide Intermediate in Oxygen Reduction. To prove the feasibility of this SG/TC mode of SECM for the quantification of reaction intermediates, we present some experimental results for the H_2O_2 collection during the ORR at a Hg on Au electrode. Before starting the discussion on the experiment, we examine several factors to decide which of the four geometries discussed above is more suitable to carry out the H_2O_2 collection. Desirable features are high CE, small d to collect a relatively unstable intermediate like H_2O_2 , and low sensitivity to small changes in d coming from the inherent uncertainty of the tip positioning above the substrate. Taking into account all these factors, we decided to use a $12.5 \mu\text{m}$ radius, $\text{RG} = 6$, Pt tip as a collector that allowed us to reach $d = 10 \mu\text{m}$ easily. This represents a short substrate/tip transit that allows rapid H_2O_2 collection, while keeping a high CE^{max} (49%) and at a flatter region of the corresponding CE^{max} vs $d/(a/b)$ curve (black line in Figure 4), thus producing a less sharp dependency of CE with d .

Figure 8 shows the experimental tip and substrate currents collected using the SG/TC mode of SECM during the ORR at a Hg on Au electrode. It is well-known that at this potential at mercury, reduction of oxygen produces H_2O_2 exclusively in a two-electron reaction (reaction 2). In this case, in contrast with the general case sketched in Figure 1, the initial redox-active species in solution is O (O_2) and it can be reduced at a $100 \mu\text{m}$ diameter substrate electrode possibly following two different pathways shown in reactions 1 and 2; however, only reaction 2 electrogenerates the intermediate R (H_2O_2). The tip collector is held at a constant potential where R (H_2O_2) undergoes diffusion controlled oxidation to convert back into O (O_2). Therefore, the CE achieved will depend on the preference of the substrate material to follow reactions 1 or 2 and provides valuable mechanistic information

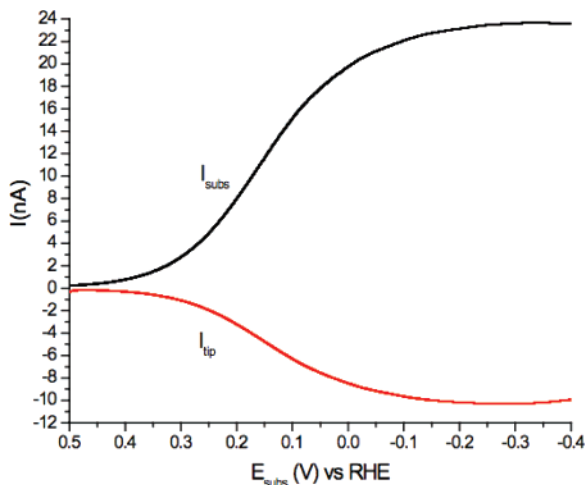


Figure 8. Experimental results of the SG/TC mode of SECM for H_2O_2 collection during ORR at the Hg on Au substrate electrode ($b = 50 \mu\text{m}$), oxygen saturated 0.5 M H_2SO_4 . Substrate potential scanned from 0.5 to -0.4 V at 2 mV s^{-1} , and the Pt tip potential held at 1.2 V. Tip conditions: $a = 12.5 \mu\text{m}$, $\text{RG} = 6$, and $d = 10 \mu\text{m}$.

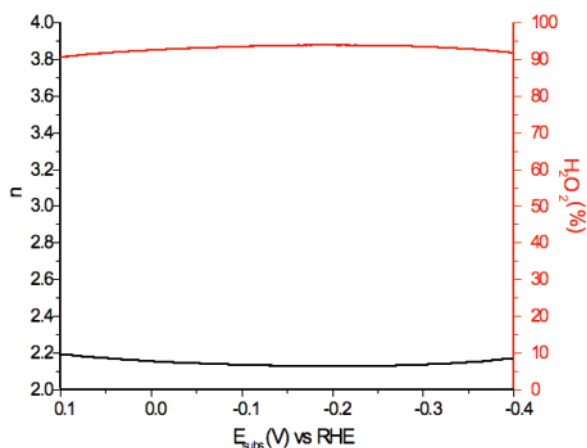


Figure 9. Number of electrons transferred (n , black line) and percentage of H_2O_2 generated (red line) during ORR at the Hg on Au substrate electrode measured using the SG/TC mode of SECM.

about the substrate material where the ORR takes place. It is possible to obtain the CE for the H_2O_2 produced following the same type of data treatment as the one used when ferrocenemethanol was the mediator. This approach allows one to determine the number of electrons transferred (n) during the ORR (eq 11) and the percentage of H_2O_2 generated as a product during the ORR (eq 12). Equation 11 is obtained by substituting the disk current, ring current, and RRDE CE factor (N) for the substrate current (i_{subs}), tip current (i_{tip}), and CE^{max} obtained from the calibration curve, respectively, into the expression used by the traditional mechanistic study of the ORR carried out by RRDE.¹⁶ Thus, the value of n gives a quantitative measure of the relative importance of reactions 1 and 2 in the ORR. Figure 9 shows the percentage of H_2O_2 generated (red line) and the n value (black line) during the ORR as a function of substrate potential. These results were obtained by substituting the experimental tip and substrate currents reported in Figure 8 into eqs 11 and 12. CE^{max}

in this case corresponds to 49% and can be calculated from eq 9 with $d = 10 \mu\text{m}$, $a = 12.5 \mu\text{m}$, and $b = 50 \mu\text{m}$.

$$n = \frac{4i_{\text{subs}}}{\left[i_{\text{subs}} + \left| \frac{i_{\text{tip}}}{\text{CE}^{\text{max}}/100} \right| \right]} \quad (11)$$

$$\text{H}_2\text{O}_2(\%) = \left[\frac{4 - n}{2} \right] 100 \quad (12)$$

The results displayed in Figure 9 point out a clear predominance of the two-electron pathway (reaction 2) when the ORR takes place at the Hg on Au electrode, since the n value is in the range (2.12–2.19). This agrees with the earlier results for the ORR at the dropping mercury electrode¹⁷ and a more recent report,¹⁸ where using a mercury film rotating disk electrode and according to the Levich equation, the first O_2 reduction wave at neutral pH proceeds with $n = 2$. Therefore, the results shown in Figure 9 indicate that the ORR at the Hg on Au electrode does not undergo further electroreduction (reaction 3) or decomposition of the H_2O_2 (reaction 4) in this potential range, in contrast with the behavior of some other electrocatalytic materials, such as Pt or Pd, where the four-electron pathway predominates.^{6,19}



The small discrepancy between the expected $n = 2.00$ reported in the literature for ORR at mercury electrodes and the actual value reported in this manuscript $n = (2.12\text{--}2.19)$ might be attributed to the formation of some platinum oxide at the Pt collector tip during the H_2O_2 oxidation, which is carried out at 1.2 V. The platinum oxide catalyzes H_2O_2 decomposition in acidic solutions into O_2 and H_2O (reaction 4),²⁰ leading to a smaller tip current and a larger n -value. This is a frequent problem in RRDE studies as well, since both techniques usually use a Pt electrode as the H_2O_2 collector. To minimize this problem, a freshly polished Pt collector tip was held at a potential negative enough to reduce platinum oxide before carrying out the H_2O_2 quantification. In comparing SECM and RRDE for studies of H_2O_2 production in the ORR, the SECM should be more convenient, since it allows variation of d (compared to the fixed ring-disk spacing) and simple replacement of the ORR substrate (compared to replacement of the disk material). Moreover, the CE is larger in SECM than in most convenient RRDEs, improving the precision of the measurement. Studies are in progress with other metal and alloy electrodes for the ORR using this technique.

CONCLUSIONS

Most of the SECM experiments that have been introduced are mainly focused in the feedback and TG/SC modes. Relatively few papers have treated the SG/TC mode;^{11,21} most of them using a macro size substrate as the generator, which rules out any

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quantitative measurement of collection efficiency, since only a very small fraction of the generated species is intercepted by the collector tip and time-dependent behavior of the substrate becomes important. We present here a new technique to quantify reaction intermediates based on the SG/TC mode of SECM using small substrates ($\leq 200 \mu\text{m}$ diameter) that allow stationary-state reaction conditions. The experimental results using ferrocenemethanol as a mediator for this SG/TC experiment have been validated by digital simulations carried out using the Comsol Multiphysics software. Both experimental and simulated results assume simple diffusion-controlled electron transfer for the mediator without heterogeneous or homogeneous kinetic complications.

The calibration results (CE vs $d/(a/b)$) presented here for different SG/TC geometries overcome the quantitative measurement problem, a classical drawback of the SG/TC mode. These results also point out the important effect of the collector tip radius and RG in the maximum CE value achievable. Thus, the empirical equations provided here represent a convenient way to predict the maximum CE value for any given distance within the calibration range.

The feasibility of this new technique to quantify reaction intermediates has been tested by determining the amount of H_2O_2 produced in the ORR. This is useful in the evaluation of the reaction pathways of a given material (e.g., $n = 2$ or $n = 4$ for the ORR) as has been classically studied by the RRDE. In particular, we have applied the SG/TC mode of SECM to H_2O_2 quantification

at a Hg on Au electrode in acidic pH. The results obtained ($n = 2.12\text{--}2.19$) clearly point to the predominance of the two-electron pathway (reaction 2) and suggest the possible occurrence of catalytic decomposition of H_2O_2 at a small amount of platinum oxide formed on the tip during the quantification. This SG/TC mode of SECM can be applied to study the ORR at other electrocatalytic materials and has several advantages compared to the RRDE technique, for instance, achieving higher CE values and sensitivity and using nonconvective conditions during the experiment.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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