Tip generation–substrate collection–tip collection mode scanning electrochemical microscopy of oxygen reduction electrocatalysts

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1. Introduction

The electrocatalytic oxygen reduction reaction (ORR) is the cathode reaction in proton exchange membrane fuel cells (PEMFCs) and alkaline fuel cells (AFCs) and investigations into the ORR have increased substantially as interest in developing fuel cells has accelerated [1–6]. The use of high throughput methods for screening novel fuel cell electrocatalysts has been particularly prominent in recent years and a number of photometric and electrochemical methods have been developed for screening fuel cell electrocatalysts [7–9]. In 2005, Bard introduced a method for screening the activity of novel electrocatalysts for the ORR in acidic media, which was based on tip generation–substrate collection (TG–SC) mode scanning electrochemical microscopy (SECM) [10,11]. An SECM tip is scanned above an array of electrocatalysts while O₂ is evolved at the tip. O₂ then diffuses to each electrocatalyst, where it is reduced. The substrate current is then measured as a function of tip position to identify the most active electrocatalysts. The advantage of using this method over conventional catalyst testing methods is that highly active electrocatalysts can be identified from an array that may contain as many as 60 different compositions within a couple of hours. The convenience of this approach becomes apparent when one considers that electrochemically testing 60 individual electrocatalysts using conventional methods such as rotating ring-disk electrode (RRDE) voltammetry or fuel cell testing could take months and some highly active ORR electrocatalysts have been discovered using this method [12].

A drawback of the screening method as described above is that one cannot determine the product of the ORR at the electrocatalysts. The ORR generally proceeds via either a 4-electron route generating H₂O₂ or OH⁻ (depending on the pH of the electrolyte) or via a 2-electron route generating hydrogen peroxide [13]. In the development of fuel cell electrocatalysts, it is important that the electrocatalysts promote the 4-electron ORR as hydrogen peroxide formation at ORR electrocatalysts reduces the fuel cell power output [14]. There have been some attempts to detect hydrogen peroxide during ORR electrocatalyst screening by SECM and a substrate generation–tip collection (SG–TC) mode SECM-based method for detecting H₂O₂ diffusing from single electrocatalyst spots has been developed by Bard and co-workers [15,16]. Wittstock and co-workers have also developed a transient SG–TC mode SECM method to detect H₂O₂ formation at ORR electrocatalysts [17]. In these methods, substrate potential sweeps or pulses are used to detect H₂O₂ production at the ORR electrocatalysts.

Here, we introduce a new SECM method for screening the activity of ORR electrocatalysts, while simultaneously detecting hydrogen peroxide, that does not require any potential programming of either the tip or the substrate. The basis of our method is a dual function, microring-disk SECM tip, which we use in a novel “tip generation–substrate collection–tip collection” (TG–SC–TC) mode SECM experiment to determine the activity of an Au electrocatalyst.
for the ORR in alkaline media while monitoring the production of hydrogen peroxide at the electrocatalyst surface. The ORR at Au in alkaline media was chosen as it proceeds by a 2-electron reduction to HO$_2^-$, allowing us to demonstrate the principles of our method, which are shown in Scheme 1. O$_2$ is generated at the SECM tip microring at a constant current and diffuses to the electrocatalyst substrate where it is reduced (collected) at a particular potential, generating a substrate current. At the same time, the microdisk within the SECM tip is held at a potential that is sufficiently positive to oxidize HO$_2^-$ at the diffusion-controlled rate, and it collects HO$_2^-$ diffusing from the electrocatalyst. The advantages of using this method are that no potential sweeps or pulses are required to perform the analysis and that the SECM tip can scan electrocatalysts continuously, generating maps containing electrocatalytic and mechanistic information.

2. Experimental section

2.1. Materials and apparatus

All chemicals were reagent grade and were used as received. Electrochemical measurements were performed using a CHI910B scanning electrochemical microscope from CH Instruments (Austin, TX). The Teflon SECM cell was built in-house and contained an Ag/AgCl reference electrode and an Pt wire counter electrode. Microring-disk SECM tips were fabricated and polished using a P2000 micropipet puller and BV-10 Beveller from Sutter Instruments (Novato, CA). Scanning electron microscopy (SEM) was performed using a Quanta 200 scanning electron microscope from FEI (Eindhoven, The Netherlands). RRDE voltammetry was performed using an MSR rotator and glassy carbon disk/Pt ring RRDE from Pine Instruments (Durham, NC). During O$_2$ reduction/HO$_2^-$ detection measurements, O$_2$ was evolved at the Au microring of the tip at a constant rate by driving a constant current between the Au microring and an Au wire using a battery and a resistor, as described previously [10,11].

2.2. Fabrication of microring-disk SECM tips

Microring-disk SECM tips were fabricated by coating Pt ultramicroelectrodes with Au, sealing the assemblies in an insulating glass sheath and polishing and sharpening. A detailed description of the tip fabrication process can be found in the supplementary content. After fabrication, the tips were characterized using scanning electron microscopy, cyclic voltammetry and scanning electrochemical microscopy.

3. Results and discussion

3.1. Microscopic analysis of microring-disk SECM tips

Fig. 1 shows SEM images of a typical microring-disk SECM tip, which showed a distinct microdisk and microring encased in glass. The radius of the microdisk, $r_e$, was approximately 500 nm, the inner radius of the microring, $a$, was 9.75 μm, the outer radius of the microring, $b$, was 10.5 μm and the radius of the outer glass sheath, $r_g$, was 32 μm. Due to the shape of the Au-coated quartz taper, $a$ and $b$ increased with increasing polishing time and, consequently, $a$ and $b$ differed significantly from tip to tip. However, $r_e$ was approximately 500 nm in all tips as the diameter of the extruded Pt wire within the quartz taper did not vary significantly along the shaft (the extruded Pt did form a very small diameter region near the end of the pulled assembly but this portion had been removed during polishing). Similarly, the Au microring thickness did not vary significantly with changes in the polishing time, as it was approximately 750 nm along the entire length of each tip.

3.2. Cyclic voltammetry using microring-disk SECM tips

Cyclic voltammograms (CVs) were recorded at the microdisk and the microring of an SECM tip in ferrocenemethanol (FcOH)
and representative CVs are shown in Fig. 2A (lower line) and Fig. 2C, respectively. When recording these CVs, “generation–collection” (G–C) experiments were also performed, in which oxidized FcOH generated during the potential sweep at the microring was reduced (collected) at the microdisk (Fig. 2B) and, when the microdisk potential was scanned, FcOH+ was collected at the microring (Fig. 2A upper curve). The CVs recorded at the microdisk and the microring showed steady-state responses typical of that expected for electrochemical reactions at a UME surface. However, during the recording of \( i_{\text{ring,}\infty} \) when the microring was the collector electrode, a significant slope in the CV was observed (Fig. 2A, upper curve). We attribute this slope to some resistance within the Au film, which becomes very apparent when one attempts to record such small currents at such a relatively large microring electrode. The half-wave potential, \( E_{1/2} \), for FcOH oxidation was 0.45 V at each electrode. The steady-state currents at the microdisk, \( i_{\text{disk}} \), and the microring, \( i_{\text{ring,}\infty} \), were 160 pA and 7.5 nA, respectively, which can be compared with theoretical values calculated using Eqs. (1) and (2), respectively [18]:

\[
i_{\text{disk}} = 4nFDC_e\rho
\]

\[
i_{\text{ring,}\infty} = \left( \frac{R_g}{b} \right) \left[ R_g \left( 1 - \frac{a^2}{b} \right)^{4.4} \right]
\]

where \( R_g = r_g/b \), \( D \) is the diffusion coefficient of FcOH (2.2 × 10⁻⁵ cm² s⁻¹ from UME voltammetry – see the supplementary content for further details), \( i_{\text{disk}}(R_g) \) is the steady-state current at a disk electrode with radius \( b \) (note that \( i_{\text{ring,}\infty} \) is used in this case to differentiate it from the current at the microdisk of the microring-disk SECM tip, \( i_{\text{ring}} \)) and all other constants have their usual meanings. Using SEM analysis, \( r_g \) for this tip was 500 nm, \( b \) was 24 μm, \( a/b \) was 0.97 and \( R_g \) was 2 (which increases \( i_{\text{ring,}\infty} \) by a factor of 1.1 over the value determined using Eq. (1), which applies for disk electrodes with large insulating sheaths) [19]. This estimated geometry resulted in a theoretical \( i_{\text{ring,}\infty} \) of 210 pA from Eq. (1) and a theoretical \( i_{\text{ring,}\infty} \) of 8.3 nA from Eq. (2). The differences between the calculated and experimental values of \( i_{\text{ring,}\infty} \) are most likely due errors in estimation in the tip geometry from SEM analysis. In particular, it was difficult to resolve and measure the microdisk accurately using SEM analysis due to some charging of the surface. One possible way to measure the disk dimensions more accurately could be to use atomic force microscopy, as has been recently demonstrated by Mirkin for nanoelectrodes [20]. However, such analysis is beyond the scope of our work and, as will be discussed below, such slight uncertainties in the tip geometry do not affect the operation of these probes in TG–SC–TC SECM. However, the relatively good agreement between the experimental and theoretical values of \( i_{\text{ring,}\infty} \) indicates that the error in the estimation of the microring geometry using SEM was low.

The collection efficiency, \( CE \), describes the amount of electro-generated material that is collected at the collector electrode (\( CE = \frac{i_{\text{ring,}\infty}}{i_{\text{disk}}} \)). When the microring was the collector electrode, \( CE \) was \( \sim 0.3 \) (\( i_{\text{ring,}\infty} \sim 50 \) pA and \( i_{\text{disk}} = 160 \) pA) and, when the microdisk was the collector, \( CE \) was 0.004 (\( i_{\text{disk}} = 30 \) pA and \( i_{\text{ring,}\infty} = 7.5 \) nA). \( CE \) is a function of the electrode geometry and the higher \( CE \) at the microring is due to radial diffusion of FcOH⁺ from the microdisk towards the microring. When the disk was the collector, \( CE \) was significantly smaller due to the relatively small size of the microdisk and diffusion of FcOH⁺ away from the microring towards the outer edge of the tip. The effects of the microring-disk tip geometry on \( CE \) were not examined in any more detail as our primary interest was in the use of these microring-disk tips for SECM experiments. However, these data clearly show that the diffusion fields at the microring and microdisk can interact with each other (in a generation–collection mode) but, in the following section, we demonstrate that the microring-disk tip can also interact with a substrate electrode in an SECM experiment.

*Fig. 2.* (A) CV recorded at the microdisk of the microring-disk SECM tip in FcOH between 0.2 and 0.65 V vs. Ag/AgCl at 50 mV s⁻¹ (lower line). The first sweep was in the positive direction. The upper line shows the current at the microring (held at 0.2 V) as the microdisk potential was scanned. (C) CV recorded at the microring of the microring-disk SECM tip using the same conditions as in (A). In each case, the solution contained 0.5 mM FcOH in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate, [TBA][PF₆], as supporting electrolyte.
3.3. Scanning electrochemical microscopy using microring-disk SECM tips

Fig. 3 shows an SECM feedback approach curve obtained by recording $i_{\text{m} \text{ng}}$ as a microring-disk SECM tip approached an insulating Teflon substrate in an FcOH solution. Also shown in Fig. 3 is the theoretical response for negative feedback at a microring SECM tip generated using the following equation [18):

$$N_{i_{\text{m} \text{ng}}}^T(L, R_g, r_m, b) = \left[ 1 + \frac{0.28}{L^2 + 1.12 (\frac{a}{b})^{1.43}} \right] N_{i_{\text{m} \text{ng}}}^T(L, R_g)$$

(3)

where $N_{i_{\text{m} \text{ng}}}^T$ is the tip-substrate distance ($L = d/b$, where $d$ is the tip-substrate distance) and $N_{i_{\text{m} \text{ng}}}^T(L, R_g)$ is given by the following equation [21]:

$$N_{i_{\text{m} \text{ng}}}^T(L, R_g) \approx \frac{2.02}{R_g^2} \ln \left( \frac{L + 0.023 R_g}{L - 0.145 R_g} \right) + 1.585 + \frac{a_b}{R_g^2} \left( 1 + \frac{a_b}{R_g^2} \right)$$

(4)

In generating the theoretical SECM feedback approach curve, $R_g$ and $a/b$ were set at 2 and 0.97, respectively (determined using SEM analysis), and the best-fit value of $b$ from Fig. 3 was 22 μm, which agrees reasonably well with that determined using SEM analysis ($b = 24$ μm). It is important to note at this point that, due to the relatively small size of the microdisk compared to the total tip diameter ($r_m$ was usually about a factor of 40 smaller than $r_g$), tilts in the SECM tip as it approached the surface made it impossible for the microdisk to approach the substrate surface to small L. Despite numerous attempts, it was not possible to reliably remove the tilt such that good, reproducible approach curves could be recorded using the relatively small microdisk. One solution to this problem is to reduce the distance between the microdisk and the microring by sharpening the Pt UME prior to coating with Au. However, this sharpening could only be performed by hand, which led to irregularly-shaped microrings and poor tip concentricity. As a result, such a sharpening step was not used and no SECM feedback approach curves were obtained by recording $i_{\text{m} \text{ng}}$ as the tip approached a substrate are presented here. However, as discussed previously, our primary aim was to use these microring-disk SECM tips for generation–collection SECM experiments, which can usually be performed at relatively large $L$. To demonstrate the usefulness of our tips in SECM imaging, SG–TC mode SECM images of an Au disk substrate were obtained by recording $i_{\text{disk}}$ and $i_{\text{m} \text{ng}}$ as the tip was scanned over an Au substrate when in contact with an FcOH solution (Fig. S4 in the supplementary content). These images demonstrate that the microring and the microdisk of the tip can be used independently to record SECM images.

3.4. Tip generation–substrate collection–tip collection SECM at a stationary microring-disk SECM tip in alkaline solution

A microring-disk SECM tip was positioned above an Au substrate in an alkaline solution and a range of microring currents, $i_{\text{m} \text{ng}}$, were applied to evolve O$_2$. In these experiments the relatively larger microring within the tip was used as the generator electrode to maximize the flux of O$_2$ towards the substrate. Fig. 4A shows the responses obtained by recording the substrate current, $i_S$, while the substrate was held at $E_S = -0.5$ V to reduce O$_2$ at the diffusion-controlled rate and Fig. 4B shows the responses obtained by recording the microdisk current, $i_{\text{disk}}$, while the microdisk was held at $E_{\text{disk}} = 0.2$ V to oxidize HO$_2$ at the diffusion-controlled rate (theoretical response for negative feedback at a microring SECM tip by sharpening the Pt UME prior to coating with Au. However, this sharpening could only be performed by hand, which led to irregularly-shaped microrings and poor tip concentricity. As a result, such a sharpening step was not used and no SECM feedback approach curves were obtained by recording $i_{\text{m} \text{ng}}$ as the tip approached a substrate are presented here. However, as discussed previously, our primary aim was to use these microring-disk SECM tips for generation–collection SECM experiments, which can usually be performed at relatively large $L$. To demonstrate the usefulness of our tips in SECM imaging, SG–TC mode SECM images of an Au disk substrate were obtained by recording $i_{\text{disk}}$ and $i_{\text{m} \text{ng}}$ as the tip was scanned over an Au substrate when in contact with an FcOH solution (Fig. S4 in the supplementary content). These images demonstrate that the microring and the microdisk of the tip can be used independently to record SECM images.)
appropriate potentials for O₂ reduction at Au and HO₂ oxidation at Pt were determined using cyclic voltammetry – see Fig. S5 in the supplementary content for details. When \( E_D^{\text{ring}} = 300 \text{ nA} \) was applied, \( i_S \) increased significantly, leveled off at approximately 60 nA above the background current after a couple of seconds and decreased to the background level when \( E_D^{\text{ring}} \) (and O₂ generation) was stopped (uppermost transient in Fig. 4A). The transient response obtained during this experiment was similar to that obtained using TG–SC mode SECM (and disk-shaped SECM tips) to study the ORR in acidic medium [22] and demonstrates that O₂ evolution and collection is possible using the Au microring/Au electrocatalyst substrate system. The evolution of O₂ at the microring at \( E_D^{\text{ring}} = 300 \text{ nA} \) was reproducible and Fig. 5A shows that \( i_S^{\text{ring}} \) could be switched on and off repeatedly and the shape of the O₂ collection transients did not change significantly. The increase in \( i_S \) of approximately 60 nA upon collection of O₂ at the substrate corresponds to a substrate collection efficiency, \( CE_S \), of 0.2. The relatively low \( CE_S \) is due to the large distance between the tip and the substrate, which allows diffusion of most of the electrogenerated O₂ away from the substrate and into the bulk solution (the effect of \( d \) is discussed further below).

Fig. 5B and the uppermost transient in Fig. 4B show \( i_{\text{disk}}^{\text{ring}} \) (at \( E_{\text{disk}} = 0.2 \text{ V} \)) as \( i_S^{\text{ring}} \) (300 nA) was turned on and off. Upon turning on \( i_S^{\text{ring}} \), a current spike was observed at the disk, which was a brief coupling between the disk and the ring. After the spike, \( i_{\text{disk}}^{\text{ring}} \) increased rapidly, leveled off after a few seconds and then decreased rapidly after O₂ evolution was stopped. The general shape of the current transient obtained when recording \( i_S^{\text{ring}} \) was similar to that obtained by recording \( i_S \), i.e., the current rose upon beginning O₂ evolution, leveled off after a few seconds and then returned to the baseline value when O₂ evolution was stopped. However, the major differences in the increases in \( i_S \) and \( i_S^{\text{ring}} \) during the TG–SC–TC experiment are the sign and magnitude of the current increase and the magnitude of the current increase. First, \( i_{\text{disk}}^{\text{ring}} \) increased negatively while O₂ was evolved at the microring, i.e., an oxidation current flowed due to oxidation of HO₂. Second, \( i_{\text{disk}}^{\text{ring}} \) increased above the background signal by approximately 30 pA during O₂ collection, which represents a collection efficiency at the microdisk (of material from the substrate), \( CE_D \), of approximately 0.0008. This value is obviously significantly smaller than that obtained for \( CE_S \) and is due to the relative sizes of the electrodes. The microdisk within the SECM tip was drastically smaller than that of the substrate, meaning that the vast majority of HO₂ formed at the substrate diffused away into the solution rather than being collected at the microdisk.

Fig. 4A and B also show the effect of decreasing \( i_{\text{disk}}^{\text{ring}} \) on \( i_S \) and \( i_{\text{disk}}^{\text{ring}} \). When \( i_S^{\text{ring}} \) was decreased from 300 nA to 5 nA, \( \Delta i_S \) and \( \Delta i_{\text{disk}}^{\text{ring}} \) (where \( \Delta \) is the absolute increase in the steady-state current upon evolving O₂ at the microring) decreased linearly demonstrating that a wide range of currents could be applied to the ring, changing the amount of O₂ generated at the Au microring (the linear relationships are shown in Fig. S6 in the supporting information). The effect of \( d \) on \( i_S \) and \( i_{\text{disk}}^{\text{ring}} \) was also determined and both \( \Delta i_S \) and \( \Delta i_{\text{disk}}^{\text{ring}} \) decreased rapidly with increasing \( d \) (Fig. 6). At \( d = 60 \mu \text{m} \), the signal due to O₂ collection at the microdisk was negligible (Fig. 6B). However, O₂ could be collected at \( d = 75 \mu \text{m} \) (Fig. 6A). These effects were due to the relative dimensions of the Au substrate and the Pt microdisk within the SECM tip. As the tip was moved further from the substrate, the microdisk collected significantly smaller portions of the expanding diffusion field due to HO₂ buildup at the substrate but a significant amount of the O₂ diffusing from the microring was detectable at the relatively large substrate as the Au microring moved away from the surface. The loss of both the \( \Delta i_S \) and \( \Delta i_{\text{disk}}^{\text{ring}} \) signals as the SECM tip was moved away from the substrate have implications for screening electrocatalysts for the ORR; it is important that screening is performed at relatively small \( L \) to ensure that any HO₂ generated on electrocatalyst surfaces is detected. Of course, this behavior also demonstrates clearly that the transient responses obtained at both the substrate and the microdisk are due only to diffusion of the electroactive species between the tip and substrate.

3.5. Effect of the applied substrate potential on substrate collection and disk collection currents

The effects of \( E_S \) on \( i_S \) and \( i_{\text{disk}} \) was examined while the SECM tip was positioned close to the Au substrate and Fig. 4C and D shows a series of transients recorded at different \( E_S \) values. Graphs of \( \Delta i_S \) and \( \Delta i_{\text{disk}}^{\text{ring}} \) vs. \( E_S \) are shown in Fig. 7A and B, respectively. Upon changing \( E_S \), measurable \( \Delta i_S \) values were obtained only at \( E_S < -0.3 \text{ V} \), i.e., the onset potential for O₂ reduction at the Au substrate was \(-0.3 \text{ V} \) (Fig. 7A). As \( E_S \) was made more negative, \( \Delta i_S \) increased reaching a limiting value at approximately \(-0.5 \text{ V} \). Comparison of this “polarization curve” obtained using SECM with a polarization curve for O₂ reduction obtained using RRDE (Fig. S7 in the supplementary information) shows that O₂ reduction began at a slightly more negative potential at the Au substrate than at an Au-coated glassy carbon RRDE assembly, presumably due to the higher inherent activity of the Au nanoparticles for O₂ reduction.
and/or better cleanliness of the Au nanoparticles. Fig. 7B demonstrates that HO\textsubscript{2} was detected at the microdisk within the SECM tip at all substrate potentials where O\textsubscript{2} reduction occurred, in agreement with the RRDE data (Fig. S7 in the supporting information).

3.6. Imaging ORR electrocatalysts with simultaneous HO\textsubscript{2} detection

While the detection of the products of electrocatalytic reactions (H\textsubscript{2}O\textsubscript{2} or HO\textsubscript{2}) coming from a single ORR electrocatalyst spot on a substrate surface might be useful for studying individual electrocatalysts, the real advantage of SECM screening of electrocatalysts is that a large number of electrocatalysts can be screened in a very short time. Therefore, it is very important to ensure that O\textsubscript{2} reduction at electrocatalyst spots, and electrochemical detection of hydrogen peroxide, is possible when the tip is scanned across a catalyst surface. Fig. 8 (left column) shows a series of SECM images of an Au electrocatalyst obtained by evolving O\textsubscript{2} at the microring and recording \(i\textsubscript{s}\) as \(E\textsubscript{S}\) was made more negative. At the most positive potential, O\textsubscript{2} reduction at the Au substrate did not occur, yielding a blank SECM image. However as the potential was made more negative (from 0.0 V to −0.75 V) the Au substrate appeared in the SECM images. In each case, the image obtained by recording \(i\textsubscript{s}\) was a good representation of the Au disk surface, i.e., the diameter of the disk in the SECM image agreed with the diameter of the Au disk determined using optical microscopy and cyclic voltammetry. As \(E\textsubscript{S}\) was made progressively more negative, \(i\textsubscript{s}\) for O\textsubscript{2} reduction in the image increased and leveled off to a \(\Delta i\textsubscript{S, image}\) value (i.e., the increase in \(i\textsubscript{s}\) when the tip was over the Au substrate compared to when it was over the glass sheath of the substrate) of approximately 6 nA when \(E\textsubscript{S}\) reached −0.5 V. This imaging data is similar to that obtained previously using TG–SC mode imaging of ORR electrocatalysts [10,22], i.e., recording \(i\textsubscript{s}\) as a function of tip position and \(E\textsubscript{S}\) can yield insights into the electrocatalytic activity of electrocatalytic surfaces. The right column in Fig. 8 shows the images obtained by recording \(i\textsubscript{disk}\) as the microring-disk SECM tip was scanned over the Au substrate (while the microdisk was held at 0.2 V to oxidize HO\textsubscript{2}). At the most positive \(E\textsubscript{S}\) value, a blank image was observed indicating that no HO\textsubscript{2} was detected (as expected as no O\textsubscript{2} reduction occurred at this potential). However as \(E\textsubscript{S}\) became more negative, an anodic increase in \(i\textsubscript{disk}\) was observed as the tip passed over the Au substrate. As was also the case when recording \(i\textsubscript{s}\) during SECM imaging, \(\Delta i\textsubscript{disk, image}\) (i.e., the increase in \(i\textsubscript{disk}\) as the tip passed over the Au substrate over that when the tip was over the glass sheath) increased as \(E\textsubscript{S}\) was made more negative. This demonstrates that O\textsubscript{2} reduction at Au in alkaline media yields HO\textsubscript{2} between −0.2 V and −0.7 V, in agreement with the RRDE data (Fig. S7 in the supporting information) and Fig. 7B.
While these results demonstrate that microring-disk SECM tips can be used to obtain both mechanistic and electrocatalytic activity data from substrates (at the same time) while scanning a microring-disk SECM tip above an electrocatalyst surface, there is one important factor that must be considered when attempting to use these tips in combinatorial ORR electrocatalyst screening, i.e., the ability to quantify the H$_2$O$_2$ formed during the ORR. The amount of peroxide formed will only be measurable if $C_{Ed}$ and $C_{Es}$ are known and one possibility is to calibrate $C_{Ed}$ and $C_{Es}$ for each tip and electrocatalyst using model redox mediators prior to performing any screening experiments. However, this would be very difficult due to the expected interference from adjacent electrocatalyst sites within an array and it is not obvious that a “calibration” experiment is possible in our system, which contains three separate active electrode surfaces, using a single model redox species. However, it is possible that modeling of such TG–SC–TC experiments could allow one to quantify the amount of electroactive H$_2$O$_2$ formed during the ORR and that a complete knowledge of the tip and electrocatalyst substrate dimensions, the tip-substrate distance, and the microring, microdisk and substrate currents could be used to determine the amount of H$_2$O$_2$ produced at an electrocatalyst surface. Even without such quantitative measurements, we suggest that these microring-disk SECM tips will be useful for qualitatively screening large numbers of ORR electrocatalysts for their electrocatalytic activity and that a complete knowledge of the tip and electrocatalyst substrate dimensions, the tip-substrate distance, and the microring, microdisk and substrate currents could be used to determine the amount of H$_2$O$_2$ produced at an electrocatalyst surface. Even without such quantitative measurements, we suggest that these microring-disk SECM tips will be useful for qualitatively screening large numbers of ORR electrocatalysts for their electrocatalytic activity while simultaneously determining whether individual electrocatalysts predominantly catalyze either the 2-electron reduction or the 4-electron reduction of O$_2$. Of course, we anticipate that the microring-disk SECM tips formed using our method will have applications beyond that described in this paper and other investigations using these SECM tips are under way.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jelechem.2012.06.024.

References