# Scanning Electrochemical Microscopy. 47. Imaging Electrocatalytic Activity for Oxygen Reduction in an Acidic Medium by the Tip Generation−Substrate Collection Mode

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The oxygen reduction reaction (ORR) in acidic medium was studied on different electrode materials by scanning electrochemical microscopy (SECM) operating in a new variation of the tip generation−substrate collection mode. An ultramicroelectrode tip placed close to the substrate electrode oxidizes water to oxygen at a constant current. The substrate is held at a potential where the tip-generated oxygen is reduced and the resulting substrate current is measured. By changing the substrate potential, it is possible to obtain a polarization (current−potential) curve, which depends on the electrocatalytic activity of the substrate material. The main difference between this mode and the classical feedback SECM mode of operation is that the feedback diffusion process is not required for the measurement, allowing its application for studying the ORR in acidic solutions. Activity-sensitive images of heterogeneous surfaces, e.g., with Pt and Au electrodes, were obtained from the substrate current when the $x-y$ plane was scanned with the tip. The usefulness of this technique for imaging electrocatalytic activity of smooth metallic electrodes and of highly dispersed fuel cell-type electrocatalysts was demonstrated. The application of this method to the combinatorial chemical analysis of electrode materials and electrocatalysts is discussed.

Intense research is being conducted to lower the cost and improve the performance of proton exchange membrane fuel cells (PEMFCs).[1,2] One of the key issues is the search for better and less costly electrocatalysts for the cathodic reaction, the oxygen reduction reaction (ORR), in acidic media (eq 1).[3,4] The high

$$O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O \qquad (1)$$
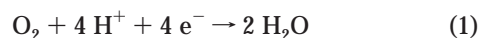
overpotential of present Pt-based catalysts for this reaction and

their easy poisoning are some of the main causes for the diminished performance of these devices.[4−6] On the other hand, although other alternatives such as macrocyclic transition metal complexes,[7] metal oxides,[8] and selenides[9] have been studied, most of the PEMFC cathodes are still Pt-based materials,[10] which are expensive and not widely available for mass consumption. Thus, further improvements will require the development of ORR catalysts that are more active and poisoning-tolerant, as well as involving materials that are less costly and more abundant than the Pt currently used in these catalysts.

Ideally, the design of new electrocatalysts would be carried out by predicting the effect of each component and preparation parameter, since an Edisonian searching would be extremely material- and time-consuming.[11] However, Mallouk et al.[12−15] have recently shown that the search for better fuel cell electrocatalysts can be rapidly performed by a combinatorial chemistry approach. For example, they synthesized spots of a five-component catalyst for methanol oxidation[12,13] and ORR/water oxidation[13−15] that spanned a wide compositional range. They also studied other reactions such as glucose oxidation and colloidal water oxidation catalysts.[16,17] An optical screening method was used, where a

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fluorescent indicator that detects local pH changes in the diffusion layer above the catalyst spot during the reaction allowed them to qualitatively image the electrocatalytic activity.[18] After the most active compositional regions were identified by this rapid screening method, they were characterized by conventional electrochemical methods. A more quantitative method based on the serial measurement of the electrochemical current of each electrode in a 64-electrode array has also been presented.[19] The direct reading of the current was shown to be more sensitive to minor differences in electrode activity than the fluorescent indicator-based pH screening. An elaborate fabrication is required and each spot must be individually connected, via a multiplexing arrangement. Thus, an electrochemical method that allows the sensitivity and quantitative characterization gained in the measurement of electrochemical behavior with the speed of optical detection would be very advantageous.

Scanning electrochemical microscopy (SECM) is a technique with excellent potential for this kind of study, since its capability to detect and to image regions with different catalytic activities is very well known.[20] One of the earliest applications of SECM was the detection of differences in electrochemical activity of heterogeneous materials such as carbon−Au,[21a] copper−lead,[21b] and carbon−Pt[22] composite surfaces. This capability has now been expanded to a wide variety of applications; examples are the detection of precursor points for corrosion[23] and of active sites on oxide surfaces,[24] the imaging of activity from biological materials such as antibodies,[25] enzymes,[26] DNA,[27] and cells,[28] and the analysis of permeation and transport through thin films and membranes.[29] Reactions of interest in fuel cells have been studied by SECM. For example, the conventional feedback mode of SECM was used for studying[30−32] and imaging[33] the activity of materials
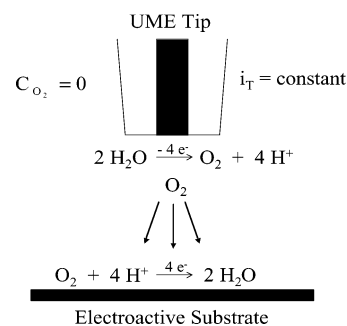

Figure 1. Scheme of the modified TG−SC mode for the study of the ORR in acidic medium.

for the hydrogen oxidation reaction (HOR) in an acid medium. Highly dispersed catalysts were also tested by SECM for hydrogen evolution[34] and oxidation,[35] and a method of studying the oxidation of methanol by SECM was recently proposed.[33] Furthermore, SECM in the feedback mode can be used for the study of the ORR on Pt in an alkaline medium.[36] In this study, the oxidation of hydroxide ion (which occurs preferentially to water oxidation in an alkaline medium) occurred at the tip and the oxygen thus produced was reduced at a Pt substrate. The feedback current could be used to study the kinetics of the reaction. However, this approach is restricted to a small range of pH, around pH 12, where the oxidation of hydroxide ion at the tip can be used. The ORR in neutral or acidic media cannot be studied by this feedback mode, since the feedback diffusion of the tip reactant (water) will not cause changes in the tip current. A similar situation applies for the HOR in neutral and alkaline solutions. Thus, a different mode of operation of the SECM that does not require the feedback process must be used for this purpose.

In this work, a different SECM alternative that allows the analysis of electrode reactions without the requirement of the feedback process is presented. The proposed technique is a variation of the tip generation−substrate collection (TG−SC) SECM mode.[20,37,38] The principle is shown in the scheme of Figure 1, which illustrates an experiment where the reduction of molecular oxygen to water on the substrate is studied. The substrate potential is fixed at a value where oxygen should be reduced to water. Because the solution contains no oxygen, the substrate current (i_S) is negligible. On the other hand, when an ultramicroelectrode (UME) tip is placed close to the substrate by using the positioning control of the SECM, and a constant oxidation current (i_T) is applied to the tip, water is oxidized to oxygen on the UME, and a constant flow of oxygen is generated at the tip and diffuses to the substrate. The tip current must be sufficiently small to prevent the saturation of the solution by oxygen and the subsequent formation of bubbles. When the oxygen reaches the substrate surface, it is reduced at a reaction rate that depends on

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the substrate potential and its electrocatalytic activity. The substrate current should increase reaching a quasi steady state. This current is governed by the flow of oxygen coming from the UME tip surface, reacting at the substrate, and being lost by lateral diffusion toward the bulk solution. It is possible to measure a collection efficiency (CE), where CE = i_S/i_T, ranging from 0 to 1, depending on a number of factors[37] such as the tip−substrate separation (d), the nature and potential of the substrate, and the RG of the tip (where RG = r_g/a, where a and r_g is the UME and the tip radius, respectively). The main advantage of this mode of operation is that the observed response does not require the feedback process. This property allows one not only to study reactions that are inaccessible by the feedback approach but also to extend the concentration range beyond the low values required to reach diffusion control at the UME tip. The substrate genera-tion−tip collection mode has been used earlier to image electron-transfer kinetics on heterogeneous electrodes.[22] Furthermore, Anson et al.[38] showed that it is possible to get images of electroactive spots (for $Ru(NH_3)_6^{2+}$ and $Fe(CN)_6^{4-}$ oxidation) through the classic TG−SC mode by recording the substrate current as a function of the tip position when an x−y scan of the tip was carried out. Thus, it should also be possible to get images of catalytic activity through this modified mode. Moreover, individual connection to different catalyst spots and multiplexing is not required, since the SECM tip scan provides the needed addressing (as long as the catalyst spots are spaced at a sufficient distance that cross talk among them does not occur), so a single connection to a conductive substrate can be made.

The proposed method was used here to analyze and compare the electrocatalytic activity of different electrode materials for the ORR, with special emphasis on its possible application to combi-natorial analysis. Interpretation of the data for extracting kinetic and mechanistic information will be the subject of further publications.

EXPERIMENTAL SECTION

Preparation of Electrodes. *Tip Electrodes.* UME tips were prepared by the procedure described previously.[20] Briefly, Pt wires (25-μm diameter; Goodfellow, Cambridge, U.K.) were heat-sealed in borosilicate glass capillaries (o.d./i.d. = 2.0/0.9 mm) under vacuum. The bottom cross section was polished with sandpaper until the Pt disk was exposed. Then it was polished with a sequence of alumina powders (from 1.0 to 0.05 μm) and sharpened until an RG of about 8−10 was achieved. The electrical connection between the unsealed end of the wire and a copper wire was made using silver epoxy (Epoxy Technology, Billerica, MA) cured overnight at 120 °C.

Substrate Electrodes. Individual smooth Pt and Au disks were prepared by heat-sealing Pt (127-μm diameter; Aldrich, Milwaukee, WI) and Au (100-μm diameter; Goodfellow) wires in borosilicate glass capillaries by the same procedure as for the tips. A substrate containing both Pt and Au disks electrically connected was prepared in the same way using a two-barrel glass tube (o.d./i.d. = 1.50/0.86 mm; Sutter Instrument, Novato, CA). The glassy carbon substrate was the cross section of a cylindrical rod (2-mm diameter; Alfa Aesar, Ward Hill, MA). All these substrates were encased into Teflon cylindrical sheaths, polished with alumina, and ultrasonically cleaned. For a complete cleaning, the Pt and
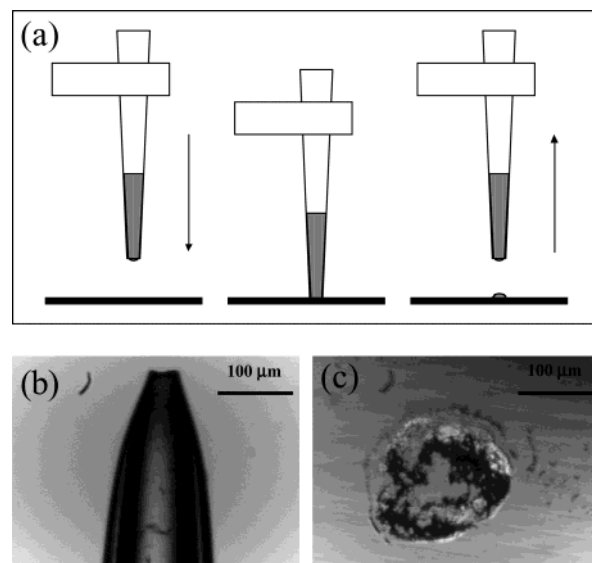

Figure 2. (a) Method used for the deposition of catalyst spots on the glassy carbon support. (b) Optical micrograph of the bottom end of a glass micropipet used for the preparation of spots. (c) Optical micrograph of a typical Pt spot supported on glassy carbon.

Au electrodes were immersed into a solution of hydrogen peroxide (10% v/v) + diluted sulfuric acid for 12 h before the experiments.

Catalyst Spots. Arrays of finely dispersed catalyst spots sup-ported on glassy carbon were used as substrates in this work to demonstrate the application of the proposed method for a combinatorial analysis of materials used in fuel cell-type electrodes. High-density arrays are necessary since the scanned area is very small (no more than 1 cm²). Pt and Ru spots were prepared by reduction of precursors with sodium borohydride[39] following the procedure described for combinatorial analysis.[13] The precursor solutions were dihydrogen hexachloroplatinate(IV) (Alfa Aesar) and ruthenium(III) chloride (Aldrich), both 0.8 M in water. Just before the preparation of the spots, the precursor was mixed with an equal volume of 0.1 M aqueous sodium bicarbonate (Fisher, Fair Lawn, NJ). The reducing agent was 10% w/v aqueous sodium borohydride (Sigma, St. Louis, MO) freshly prepared. Small drops of the precursor solutions were placed on glassy carbon by capillarity, making contact between a precursor-filled micropipet and the carbon support for a few seconds, as shown in Figure 2a. Micropipets with diameters of ∼50 μm were used (Figure 2b); these were made from borosilicate glass capillaries (o.d./i.d. = 1.0/0.58 mm; Sutter Instrument) using a laser-based pipet puller (model P-2000, Sutter Instrument). The puller parameters were as follows: heat 450, fil. 5, vel. 40, del. 200, pul. 200. A slight overpressure was applied inside the pipet by pressing a pipet bulb connected to its top end. For making the arrays, the position of the micropipet was controlled through the piezoelectric inch-worms of the SECM apparatus. After the whole array of precursor spots was obtained, the pipet was discharged, washed several times with water, and refilled with the reducing solution. Then, the reducing agent was dispensed on each spot in the same way as the precursor. The arrays were kept drying at room temper-ature overnight and washed thoroughly with water. The morphol-ogy of each spot was visually examined with an optical microscope
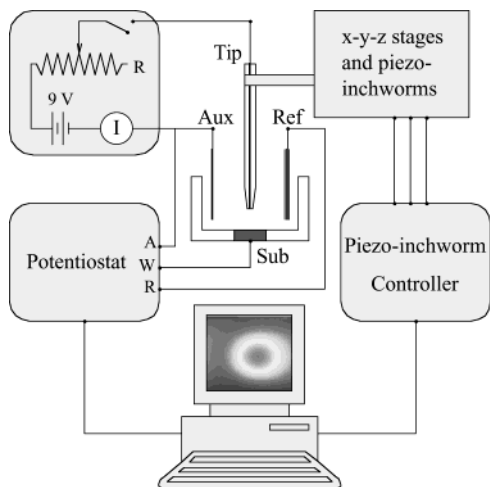
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Figure 3. Scheme of the electrochemical setup used for the TG–SC experiments.

Figure 4. Typical chronoresponses of the substrate current obtained on smooth metallic disks during a static TG–SC experiment; $d = 10$ μm. (I) Pt disk; $i_T = 71$ nA; $E_S = 0.2$ (a), 0.75 (b), and 0.9 V (c). (II) Au disk, $i_T = 76$ nA, $E_S = 0.0$ (d), 0.3 (e), and 0.55 V (f). Up and down arrows signal the moment when the tip is turned on and off, respectively.

Olympus BH-2 (Olympus Optical Co.). A typical spot is shown in the micrograph of the Figure 2c. Their sizes, with diameters of ~200 μm, were fairly reproducible and they were typically separated by 300 μm.

Electrochemical Measurements. The ORR measurements were made in aqueous solutions of 0.5 M H_2SO_4 prepared by dilution of sulfuric acid (Fisher) with Milli-Q reagent water (Millipore Co., Bedford, MA). To avoid interference due to dissolved oxygen from air, the solutions were deareated by bubbling argon before each experiment, and an argon blanket was kept flowing over the cell during the measurements. All the experiments were made at room temperature. A scheme of the electrochemical setup is shown in Figure 3. SECM Teflon cells were used in all the experiments. A hydrogen reference electrode, made with a platinized Pt wire in 0.5 M H_2SO_4 saturated with H_2 (1 atm), and a Pt wire were the reference and the auxiliary electrodes, respectively. A PC-controlled CHI 900 SECM instrument (CH Instruments, Austin, TX) was used for controlling both the x–y–z piezoinchworms (Burleigh Instruments Inc., Fishers, NY) and the substrate potential. The tip current was controlled with a battery-powered source (9 V) connected between the tip (positive) and the auxiliary electrode.

The UME tip was positioned at a known distance from the substrate by the conventional SECM feedback mode,[20] using the H^+/H_2 couple in aqueous 5 mM H_2SO_4 + 0.1 M K_2SO_4 (Fisher) as a mediator.[30,31] The tip was held at a potential of −0.6 V (complete diffusion control for the H^+ reduction[30,31]), and the approach curve was obtained over the surrounding glass sheath or over the glassy carbon substrate. The negative feedback allowed one to place the tip position close to the substrate surface. Then the solution was changed to 0.5 M H_2SO_4 to do the ORR TG–SC experiments.

Steady-state polarization curves were measured on Pt and Au electrodes. Before each experiment, the Pt and Au disk substrates were electrochemically activated[3] by anodic polarization at 1.4 V (1.6 V for Au) for 60 s, followed by cycling the potential between 1.4 (1.6 V) and 0 V at 0.1 V s^{-1} until reproducible voltammograms were obtained.[40,41] After positioning the UME tip just over the
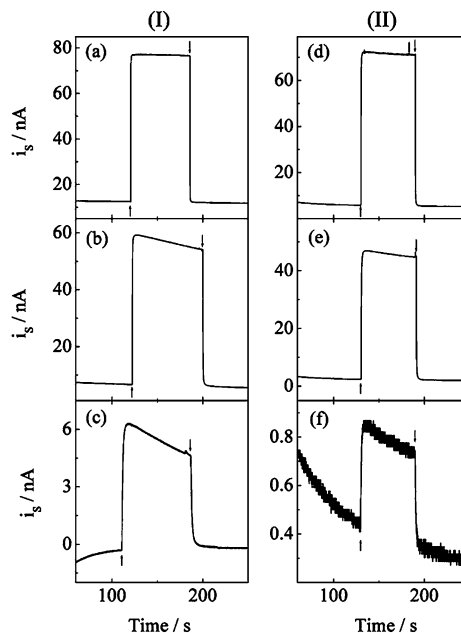
metallic disk, it was placed at a distance of 10 μm. The substrate was then held at a potential where oxygen should reduce ($E_S <$ 1.23 V), and the substrate current was measured. When the background current (coming from reduction/oxidation of impurities in solution) was stable, a constant oxidation current was applied to the UME tip (10 nA $< i_T <$ 220 nA) allowing oxygen to evolve from it. If the current was higher than 220 nA, the formation of oxygen bubbles due to saturation was clearly detected in the substrate response. After a period of 1−2 min, the tip polarization was turned off, but the substrate current was still measured for an additional 2 min to obtain a value for adequate background subtraction.

Images of the substrate activity by SECM in the TG–SC mode using the ORR substrate current were taken. This permitted not only the placement of the tip exactly over the metallic disks for the static measurements previously described but also the screening of surfaces with different electrocatalytic activity. The tip was situated at 30 μm from the substrate, and a constant oxidation current was applied on it. The substrate was held at the desired potential for oxygen reduction and the tip was scanned in the x and y directions while the substrate current was read as a function of the tip position. A quiet time of 120 s was necessary to allow for the stabilization of the substrate background. In most of the experiments, the scan rate was 300 μm s^{-1}.

RESULTS AND DISCUSSION

Smooth Platinum and Gold Electrodes within an Insulating Matrix. Figure 4 shows typical i_S responses for the ORR during a TG–SC experiment on (I) Pt and (II) Au. When the UME tip, held at $d = 10$ μm, is turned on to generate oxygen, i_S

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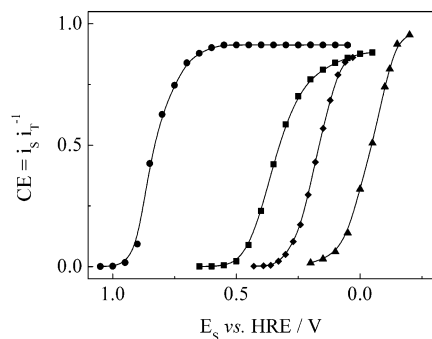(41) Appleby, A. J. *J. Electroanal. Chem.* **1970**, *27*, 325−334.

Figure 5. Polarization curves (normalized respect to i_T) obtained through the TG−SC mode on Pt (●), Au (■), glassy carbon (▲) and Ru (◆) electrodes.

increases almost immediately, reaching a steady-state quickly. In the same way, just a few seconds after the tip is turned off, i_S returns to its background value. After background subtraction, i_S is seen to be high (essentially the same as i_T) on Pt when $E_S <$ 0.6 V, although at more positive potentials it falls quickly and is negligible beyond 0.9 V. A slight decrease in i_S after reaching the steady state is observed when $E_S > 0.6$ V due to deactivation of Pt, which could be associated with changes in the surface state due to incipient oxide formation[42] or adsorption of impurities from the solution.[43] These responses were quite reproducible, indicating that the cleaning treatment regenerated the same initial surface. The substrate current is also high on Au when the potential is less positive, but it falls beginning at a potential above 0.1 V and is very small for $E_S > 0.4$ V. There is a slight drop in the steady-state current at Au in all of the responses, which can be attributed to the known deactivation of Au at these potentials.[41,44] The measured CE at the most negative potential was not 1 even when the tip was very close to the substrate. This could occur because of the faradic efficiencies for the evolution and reduction of oxygen in the UME tip and in the substrate are not 100% due to secondary reactions such as the formation of hydrogen peroxide[44,45] or some oxidation of reducing impurities in the solution at the tip. The dependence of CE (or i_S normalized respect to i_T) on E_S resulting from the previous experiments is shown in Figure 5. The i_S values were taken 5 s after reaching the steady state. The curve for Pt is similar to the classical polarization curve obtained in oxygen-saturated acidic solutions,[3] where the current is diffusion controlled at potentials lower than 0.8 V. On the other hand, the ORR on Au occurs over a wider range of potential under kinetic control, reaching total diffusion control at potentials lower than 0 V, similar to the behavior in oxygen-saturated solution.[44] These curves clearly show the differences in electrocatalytic activity between Au and Pt. Moreover, from the analysis of these responses, it should be possible to extract kinetic information about the electrode reaction. One aspect that needs to be addressed is how the partial (or total) reduction of O_2 to H_2O_2 (a 2-electron pathway) at the substrate, which is known to compete with the 4-electron path on Au and carbon,[44,46] affects the TG−SC response. The ratio

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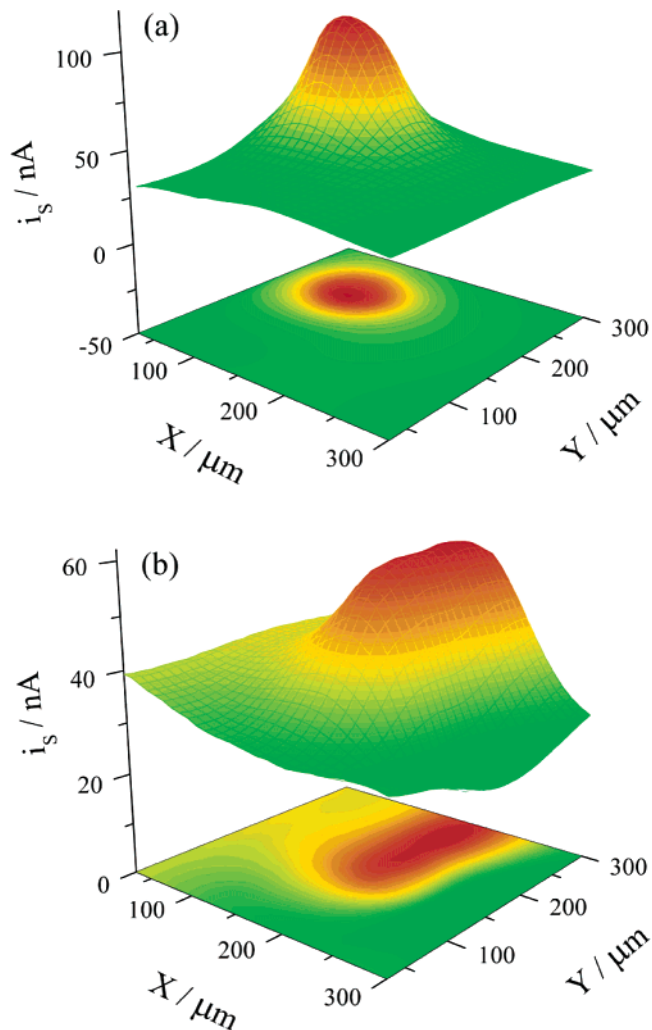
Figure 6. ORR images obtained by the TG−SC mode of a smooth Pt disk (127-μm diameter) embedded in glass: Scan rate 300 μm s^{-1}; $E_S = 0.1$ V. (a) $d = 30$ μm; $i_T = 76$ nA. (b) $d = 5$ μm; $i_T = 36$ nA. In both (a) and (b), the lower figure is a gray scale image where the current is represented by the color and the upper is an actual representation of i_S as function of x−y position.

of the currents for both pathways as well as the feedback of the H_2O_2 from the substrate to the tip affects the collection efficiency. These issues are being studied and will be the subject of future communications.

Figure 5 clearly demonstrates that this mode of operation is strongly sensitive to the activity of the substrate material. It would be useful if this sensitivity could be reflected in SECM images, since they would quickly give an idea about the performance of the studied materials. Figure 6a shows the image resulting when i_S is plotted as a function of the tip position when scanning an insulating surface (glass) containing a Pt disk held at a potential where oxygen is reduced. The substrate current increases when the tip passes over the active region, defining the form and size of the disk with good resolution. Steady-state images are obtained despite the high scan rate since the tip size is small and the collection efficiency when the tip is over the substrate is close to 100%. The distance tip−substrate has an effect on the resolution of the image obtained, as can be observed in Figure 6b. A distorted image results when the tip is very close (5 μm) to the substrate during scanning. The elongation along the scanned direction
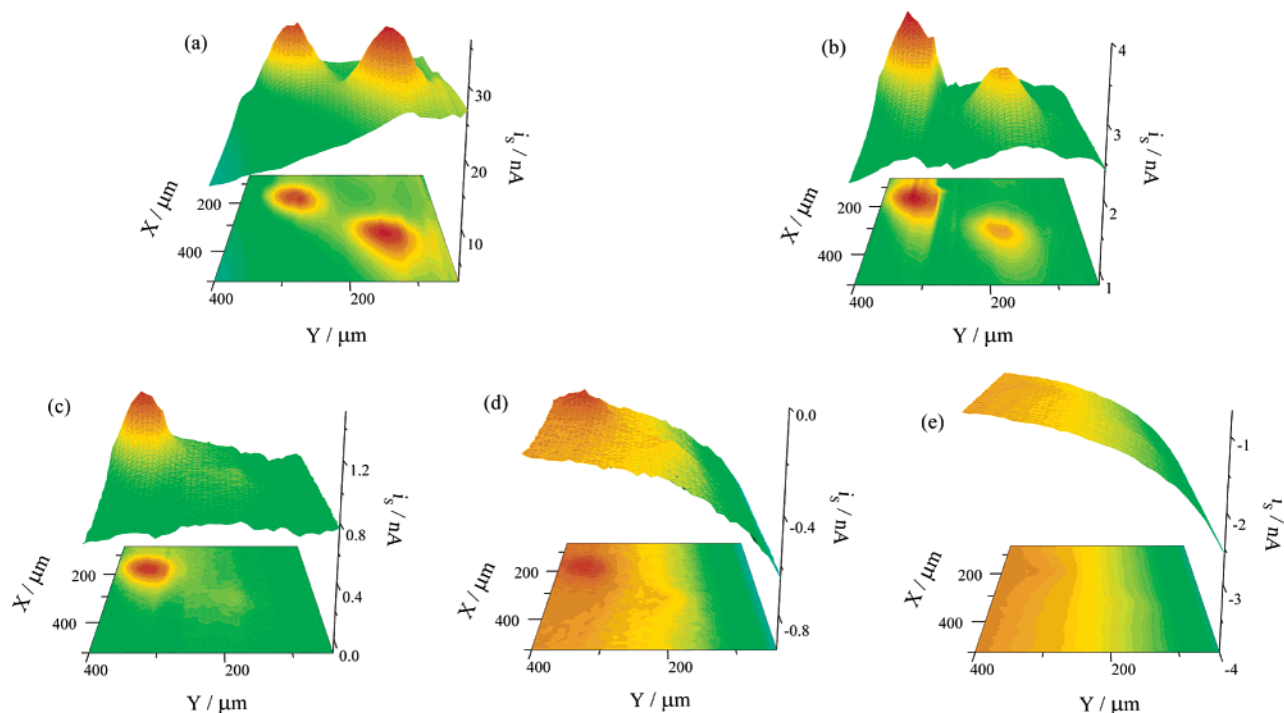
Figure 7. ORR images obtained by the TG−SC mode of smooth Pt (127-μm diameter, left rear) and Au (100-μm diameter, right front) disks electrically connected and embedded in glass: scan rate 300 μm s^{-1}; d = 30 μm; i_T = 15 nA; E_S = 0.1 (a), 0.2 (b), 0.4 (c), 0.7 (d), and 0.9 V (e).

probably can be attributed to some oxygen still staying between the glass sheath of the tip and the substrate when the UME already is several micrometers away. This effect is less noticeable when tips with small RG values are used or the scans are done with the tip not being very close to the substrate (d > 10 μm for tips with RG = 8−10). From the curves in Figure 5, for a given tip−substrate distance, the increase in the i_S values observed in the images should depend on the nature and potential of the substrate electrode. When a substrate containing both Pt and Au disks simultaneously held at the same potentials is scanned, the images of Figure 7 are obtained. In the region of potentials where the ORR is totally under diffusion control on both metals (E_S < 0.1 V), there are no differences between the i_S values coming from each disk. In the range of 0.1 V < E_S < 0.4 V, the difference in electrocatalytic activity between Pt (still totally active) and Au is clearly seen. At higher potentials (E_S > 0.4 V), the activity of Au is essentially zero while Pt still continues reducing oxygen until E_S > 0.8 V, where it also loses activity. The background current varied slightly during the scan and depended on the substrate potential. The source of this current is uncertain and probably arises from the reduction or oxidation of impurities and oxide formation or reduction on the substrate. These results demonstrate that the imaging capability of the proposed SECM mode can be used to visually identify materials with different electrocatalytic activity for the ORR and provide means for fast surface screening.

Catalyst Spots on a Conductive Support. One of the advantages of the combinatorial analysis of electrocatalysts by SECM is the greater ease in the preparation of electrodes since they are all connected through a single conductive matrix, thus, avoiding the problem of having to provide individual wires to each test spot. This matrix should be almost inactive for the reaction

under consideration, so carbon, which is not catalytically active, is a good choice. The ORR TG−SC polarization curve obtained on a glassy carbon electrode is shown in Figure 5. There is almost no oxygen reduction current for potentials more positive than 0 V, so this substrate is clearly a good support for the catalyst spots. The design of SECM instruments allows one to scan small geometric areas, typically no more than 1 cm². Thus, it is imperative to arrange the catalyst spots in the form of high-density microarrays, with spot sizes and separations of no more than 200 and 300 μm, respectively. To make these arrays, a setup that dispenses very small quantities of precursor solution (only tenths of pL) with a precise dispenser motion controller is required. In this work, the solutions were dispensed by means of capillarity making contact between the bottom of a micropipet and the carbon support, as described in the Experimental Section. The method worked fine for the purposes of this work since very simple arrays were necessary to demonstrate the applicability of the proposed screening technique. Commercial microarrayers that are used in bioassays can, in principle, be used for similar purposes.

Figure 8 shows the image obtained by scanning an array of Pt spots supported on glassy carbon. Although there is a bigger background current (due to the large conductive area), the spots can be clearly identified by the increase in i_S. However, the responses are slightly different on some of the spots than at others, even though they were prepared under the same experimental conditions. These differences result from adhesion problems of the catalyst particles on the glassy carbon surface that cause variation in the density of Pt particles at each spot. This is a known problem that has been solved by using porous supports such as carbon paper.[13] On the other hand, the height of the spots plays a role in the TG−SC imaging, though this is less important than in the feedback mode, since the TG−SC mode is less sensitive
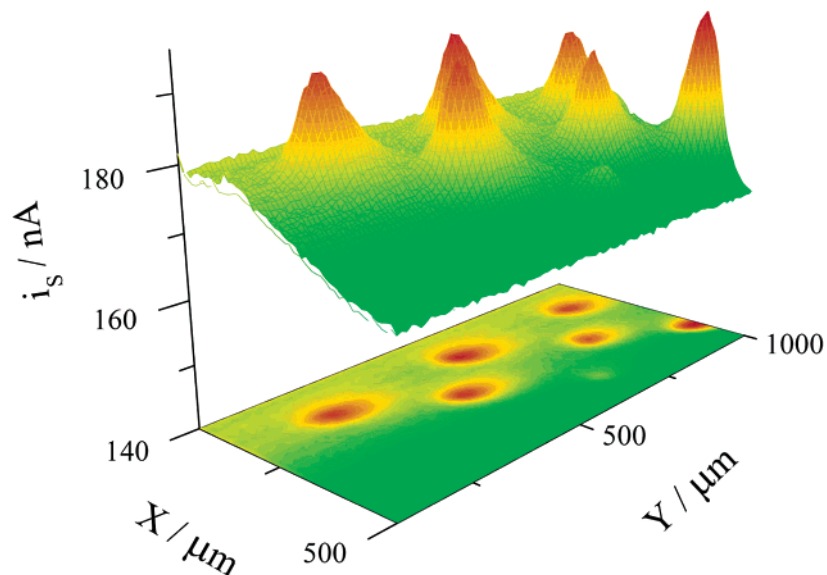
Figure 8. ORR images obtained by the TG−SC mode of an array of Pt spots supported on glassy carbon: scan rate 300 μm s^{-1}; $d = 30$ μm; $i_T = 22$ nA; $E_S = 0.1$ V.
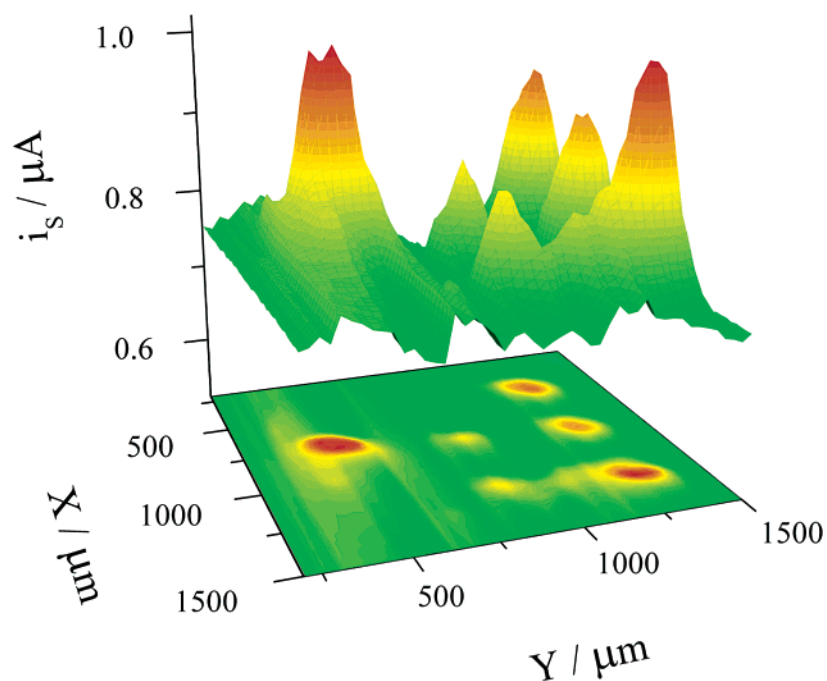

Figure 9. ORR images obtained by the TG−SC mode of an array of Pt (left spot and right row) and Ru (middle row) spots supported on glassy carbon: scan rate 600 μm s^{-1}; $d = 30$ μm; $i_T = 210$ nA; $E_S = 0.1$ V.

to the tip−substrate distance. A way to minimize this effect is to improve the reproducibility of spot preparation, which will lead to similar spot morphologies. To demonstrate that this technique can distinguish differences in the nature of highly dispersed catalysts, an array of Pt and Ru spots was imaged. As can be seen in the polarization curve obtained on a Ru spot deposited on glassy carbon (Figure 5), this metal has a poorer ORR activity than Pt, which also is clearly visualized in the images shown in Figure 9, despite the adherence and height problems previously mentioned.

These results demonstrate the applicability of this method for the fast screening of supported-catalyst activities. However, other considerations must be addressed before using this technique for combinatorial analysis. The procedure used for obtaining the supported spots needs to be optimized for the rapid preparation

of large multicompositional arrays. Likewise, several parameters must be carefully controlled to reach good reproducibility. A good alternative could be to use a more appropriate device for the dispensing of solutions, for example ink-jet microdispensers. On the other hand, porous supports would enhance the adherence of catalyst particles, and thus, one could be sure that the density of particles is almost the same on all the spots. However, the larger the substrate conductive area is, the higher the background current will be. This is a difficult problem, since the increment in i_S will be lower than 0.2 μA (at maximum i_T), stable and small background currents are required to image the spots. Options such as masking the substrate with a nonconductive film before the spot deposition, the application of a chemical/electrochemical pretreatment to the smooth glassy carbon substrate to increase

the adherence and passivate the surface or the use of other smooth, less active, and potentially more adherent substrates, are being explored.

CONCLUSIONS

SECM can be used for the screening of electrocatalytic activity for the ORR in acidic medium of different electrode materials by working in a modified TG–SC mode. Its applicability for studying both individual smooth microdisks embedded in an insulator sheath and highly dispersed materials supported on a nonactive conductive matrix was demonstrated. The analysis is reasonably fast and requires only very small quantities of catalysts. On the other hand, the preparation of catalyst arrays is simple and can be automated. All these properties make the method extremely attractive for its application to combinatorial analysis of multi-component electrode materials. One important advantage of this technique is that the variable utilized to test the catalytic activity is simply the oxygen-reduction current, which is a quantitative and direct parameter about the performance of the analyzed materials in real devices.