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Technical Notes

Selective Insulation with Poly(tetrafluoroethylene) of Substrate Electrodes for Electrochemical Background Reduction in Scanning Electrochemical Microscopy

Joaquin Rodriguez-Lopez, Mario A. Alpuche-Aviles, and Allen J. Bard*

Center for Electrochemistry, Department of Chemistry and Biochemistry, University of Texas, Austin, Texas 78712

We describe a wet process for the fabrication of poly(tetrafluoroethylene) (PTFE)-covered electrodes in which arrays of holes (∼200 μm) are formed. The PTFE coating provides electrical insulation of most of the electrode surface with selected regions exposed for electrochemical experiments. The arrays of microholes can be controllably patterned and filled with precursor solutions using a piezoelectric dispenser. A micrometer spot of electrocatalyst is produced after reduction of the precursor. The application is tested for scanning electrochemical microscopy (SECM) in the tip generation−substrate collection (TG−SC) studies of electrocatalysts. The method is shown to reduce the substrate background currents that are included in the electrochemical signal read from the local perturbation induced with the SECM tip to the substrate in the TG−SC mode of SECM. This background current reduction is consistent with the decrease in the exposed area of the electrode. The general methodology for the fabrication of the substrate electrodes and two proof-of-concept applications in the TG−SC SECM modality are described.

A method for protecting and selectively exposing regions of electrodes to make microarrays is presented. Scanning electrochemical microscopy (SECM) in the tip generation−substrate collection (TG−SC) mode[1,2] has been successfully used in the design and screening of oxygen reduction electrocatalysts.[3−6] Figure 1 shows a schematic of the TG−SC SECM mode. The tip locally generates a species which diffuses across the tip−substrate gap and undergoes an electrochemical reaction at the substrate electrode. For many applications, such as in electrocatalysis research, the substrate electrode consists of an array of spots made of potentially catalytic materials that are deposited onto an "inert" conductive substrate such as glassy carbon (GC). The probe is scanned close to the substrate to produce an image of the electrochemical activity of the substrate by plotting the substrate current as a function of tip position. The activity increases when the probe passes over an electroactive spot, and the spots with more facile kinetics for a given reaction (at a given potential) show higher electrochemical activity, which increases the substrate current.

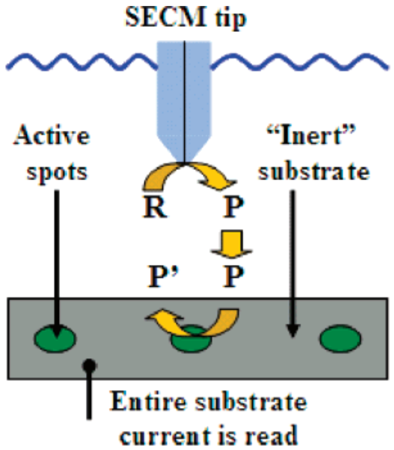

Figure 1. Schematic of a typical tip generation−substrate collection (TG−SC) experiment for electrocatalyst screening. R = reactant (initially in solution), P = product at the tip, and P′ = product after reaction of P at the substrate. P′ and R may be the same species depending on substrate conditions.

Note, however, that the substrate current is the sum of the contributions from the background current of the entire substrate electrode plus the local response induced by the species generated at the tip. Although the substrate is considered to be inert to the electrochemical reaction of interest, there is, in fact, a background current that can be traced to the presence of oxidation or reduction reactions, e.g., due to traces of electroactive impurities or surface processes.

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* Corresponding author. E-mail: ajbard@mail.utexas.edu.

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In practice the background current that is read at the substrate electrode (diameter ~1 cm) can dominate over the response at a given spot generated by the diffusing species produced at the small tip (diameter ~25 μm). Generally, the spots must be small enough and at the same time far apart so that the perturbation at the substrate depends only on the localized interaction between the probe and one single spot. This implies that even if the catalysts are prepared with a relative high density of spots, there will be a contribution from the background of the substrate material as the tip travels from spot to spot. Moreover, in practice it is desirable to have free substrate regions for tip positioning and tip scans to correct the substrate tilt, which increases the exposed substrate area. Background correction is complicated because small changes in the experimental conditions and the history of the substrate electrode can cause the substrate background to drift. To reduce the background one must minimize the exposed area of the supporting electrode (e.g., GC) without compromising the TG−SC experiment. The area of the electrode must be selectively insulated and exposed in only small regions of the supporting electrode that are necessary to provide electrical connection to the spots. This will scale the background current proportionally to the reduction of exposed area.

With the goal of selectively insulating the substrate electrode, the choice of the insulating material is important. Ideally, it should be electrochemically inert and resistant to different chemical and physical environments such as strongly acidic, basic, or nonaqueous solutions, irradiation, and the temperatures used. A few strategies exist on the direct modification of electrodes in order to decrease the background currents;[7−9] however, the materials used in these are not suitable for many studies and we sought to provide a method that would provide poly(tetrafluoroethylene) (PTFE or Teflon)-like materials,[10] which show chemical inertness and resistance to aggressive environments and are commercially available.[11] Electrodes similar to the ones described here have been prepared with photoresist resins,[12] but even mild electrochemical treatments can damage coatings of these, and even with advances in photoresist technology[13] we are unaware of resins that can compete with the stability of PTFE. To our knowledge, no catalytic behavior has been observed in PTFE, and reports of electrochemical modification of this polymer require unusual conditions and setups.[14]

Finally, although the electrodes described in this article are aimed at reducing the background currents in SECM, this approach may be useful in the fabrication of ultramicroelectrodes[15] and in the study of diffusion interactions in arrays.[12,13,16]

EXPERIMENTAL SECTION

Electrochemical Measurements. Solutions were prepared with deionized Milli-Q water. Ferrocenemethanol (FcMeOH, Aldrich) and hexaammineruthenium(III) chloride 99% ($Ru(NH_3)_6Cl_3$, Strem Chemicals, Newburyport, MA) were used as received. The solutions were bubbled with Ar prior to any electrochemical experiment and kept under an Ar blanket during the experiment. All electrochemical measurements were performed using either a CHI900 or CHI900B SECM (CH Instruments, Austin, TX). Substrate electrodes consisted of GC plates 1 mm thick (Alfa Aesar, Ward Hill, MA) cut into squares of either 1 × 1 cm^2 or 1.5 × 1.5 cm^2. They were polished with SiC paper 1200 grit (Buehler, Lake Bluff, IL) and sonicated in MeOH prior to any modification. SECM measurements and imaging experiments were carried out with a 25 μm diameter Pt tip with an RG of 6−7, fabricated as described elsewhere.[1] The counter electrode was a Pt wire. A hydrogen electrode[6] was used for the studies of electrocatalysts, and a Ag/AgCl (saturated KCl) was used for experiments with FcMeOH and $Ru(NH_3)_6Cl_3$; however, all potentials are with respect to a normal hydrogen electrode (NHE). The supporting electrolyte for FcMeOH and $Ru(NH_3)_6Cl_3$ was 0.1 M phosphate buffer prepared by dissolving dibasic sodium phosphate and adjusting to pH 7 with phosphoric acid 85%; for H^+/H_2 TG−SC experiments, 50 mM K_2SO_4 (certified ACS, Fisher) acidified to pH 3 with sulfuric acid (certified ACS Plus, Fisher) was used.

Fabrication of Selectively Insulated Substrate Electrodes. Figure 2A depicts the fabrication steps of the substrate electrodes. In step A1, the pieces of GC are mounted on a metal stage and aligned to a T-shaped piece of metal to allow for repositioning the electrode in the following steps. A piezoelectric microdispenser model MJ-AB-01-60 (Microfab, Plano, TX) with an orifice of 60 μm, controlled by a CHI1550 pico dispenser (CH Instruments, Austin, TX), was used to dispense a 1:1 by volume solution of Microposit 51813 positive photoresist (Rohm and Haas Electronic Materials, Marlborough, MA) and *n*-hexanol (Acros Organics, NJ). The parameters used for dispensing were a jet pulse of 80 V, 50 μs pulse width, and 1 s between pulses. No attempt was made to exploit the photochemical properties of the photoresist; instead we take advantage of the fact that, when dried, it is insoluble in water but is highly soluble in acetone, in which it also swells with an appreciable change in volume. Hexanol is used to reduce the viscosity of the solution, also slightly decreasing the surface tension and the evaporation rate of the photoresist, which is critical for dispensing efficiently without clogging the microdispenser. Arrays of photoresist spots can be designed using this technique (see the Supporting Information for details about the size of the resin spots). After the resin is dispensed, a soft bake at 100 °C for 2 min in an oven is performed on the substrate to allow the resin to dry completely.

Step A2 consists of covering of substrates with PTFE. A 60 wt % dispersion of PTFE in water (Aldrich) was applied dynamically (typical charge of 8 drops/cm^2) using a model EC101 spin coater (Headway Research, Inc., Garland, TX) at a speed of 3000 rpm. The full charge was usually delivered during 10 s and was allowed to remove excess material and spin dry during 50 s. Further air

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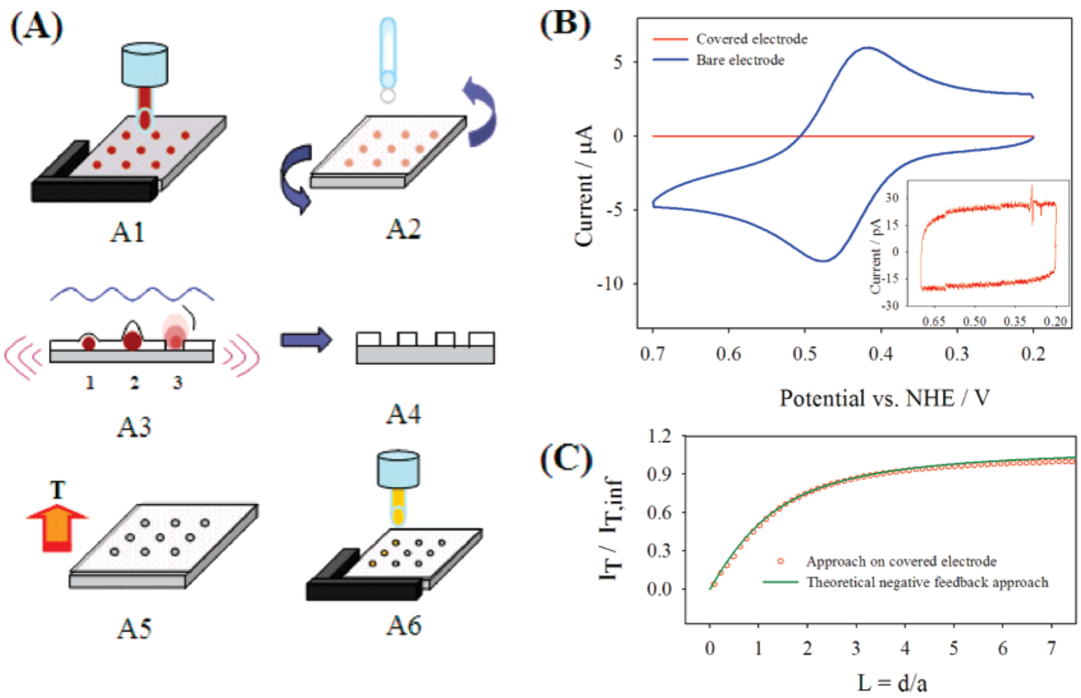

Figure 2. (A) Schematic of the steps required to fabricate the insulated electrodes with an array of holes (detail in text): A1—microdispensing of photoresist array, A2—spin coating with PTFE, A3—opening of spots in an acetone bath, A4—illustration of the side view of an array, A5—sintering of the PTFE layer, and A6—redispensing over the holes with catalyst precursor. (B) Cyclic voltammogram of ferrocenemethanol on a bare and completely PTFE-covered electrode. The inset shows the covered electrode on a different scale. $\nu = 20$ mV/s. (C) Normalized approach curves; comparison between the theoretical response (RG = 10) over an insulator and the experimental approach using ferrocenemethanol as mediator over the PTFE-covered electrode (approach speed 3 μm/s).

drying improved the success rate, but the electrodes must not be oven dried. The dry electrodes are then taken to an acetone bath at room temperature for a short time; this is a critical step in the development of the array of holes. The substrates are rapidly immersed in acetone while strongly agitating them in the bath for about 10 s. During this time, depicted in the progression from steps A3 to A4, the acetone permeates through the PTFE layer, swells the resin, and breaks away the material that is on top of the photoresist spot, leaving a hole. Just enough time is needed for this to happen, and longer exposure can affect the integrity or the PTFE layer. The substrates are then taken out of the bath, and the excess acetone is gently removed by tilting the electrode over a paper wipe.

In step A5 the PTFE layer is sintered. The substrates were heated to 350 °C for 20 min with a heating ramp of 7 °C/min in a F21100 tube furnace (Barnstead International, Dubuque, IA) under a constant Ar flow and allowed to cool down to room temperature. At this point the electrodes are fully functional. Step A6 represents the deposition of a material of interest in the exposed spots. Only minor adjustments are needed to redispense test materials in the spots of the array.

Testing of Insulated Electrodes. Electrodes without holes were tested for pinholes; they were prepared by only spin coating the PTFE and sintering as described above. Electrochemical measurements were done with a 0.3 mM solution of ferrocenemethanol 97% (Aldrich) in 0.1 M phosphate buffer. The area exposed to solution was $A = 3.21 \times 10^{-5}$ m^2 (3.2 mm radius). Approach curves were obtained by using ferrocenemethanol as mediator.

Electrodes with an array of holes without redispensing any other material on top of the revealed holes were tested by SECM imaging and chronoamperometry. The redox mediator used for these measurements was 1 mM hexaammineruthenium(III) chloride. A typical substrate electrode with an array of 29 holes (7 × 4 plus an indicator spot) with a center-to-center distance of 600 μm was used. Each hole had a typical diameter of 175 μm.

For electrocatalyst proof-of-concept testing, Pd spots were prepared by dispensing 0.1 M solution of ammonium tetrachloropalladate(II) 99.995% (Aldrich) in 3:1 V/V water/glycerol in the holes of a developed electrode covered with PTFE. The number of drops on each column of the array was varied, so as to yield the following pattern: column no. 1—20 drops, column no. 2—16 drops, column no. 3—12 drops, column no. 4—8 drops, column no. 5—2 drops, column no. 6—blank, column no. 7—16 drops. The precursor solution was dried at 180 °C under Ar (1 atm) for 1 h, reduced under H_2 (1 atm) at 350 °C for 1 h, and cooled under Ar (1 atm) with heating ramps of 5 °C/min. The electrochemical cell for this case had an area of 6.36×10^{-5} m^2 (4.5 mm radius).

RESULTS AND DISCUSSION

The PTFE layer that is obtained over the GC pieces after sintering shows good mechanical properties; it is possible to manipulate them in the electrochemical cell with only minor damage by accidental scratches. The layer also passes the "Scotch tape" test and is able to resist up to 20 min of sonication in water, after which it starts to peel off from the edges of the GC plate. Figure 2B shows the results of comparing a bare GC electrode with a covered one without revealed holes; for the conditions used, the bare electrode shows a behavior in accordance to the expected currents from the Randles—Sevcik equation for the electrochemistry of ferrocenemethanol (oxidation peak current, $i_{p,a} = -9.6$

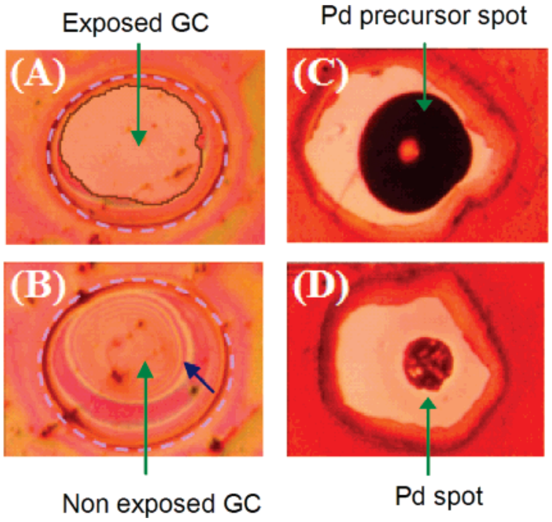

Figure 3. Optical microphotographs, 250 μm × 330 μm, of holes on PTFE-covered electrodes. (A) Revealed spot; the dashed line indicates the original size of the resin spot, and the edge left behind by the removed PTFE is emphasized in brown. (B) Unsuccessful breaking away of the PTFE layer over a resin spot; the dashed line indicates the original size of the resin spot, and the blue arrow indicates light interference rings characteristic of the presence of the PTFE layer. (C) Redispensed drop of Pd solution over a revealed hole. (D) Typical appearance of a Pd spot after drying and reduction under H_2 (350 °C).

μA with $D = 7.8 \times 10^{-10}$ m^2/s),[17] whereas the covered electrode shows a purely capacitive response. This indicates that the surface of the electrode has been blocked with a decrease in the capacitance of almost 5 orders of magnitude (as evaluated from the capacitive current at 0.3 V vs NHE), demonstrating that this blockage arises not from the loss of activity of the GC but rather from the presence of an insulating layer. From the variation of this capacitive current with scan rate (see the Supporting Information) we estimate this thickness to be on the order of 0.7 μm. Further evidence of the good insulating properties of the layer comes from SECM approach curves on a completely covered substrate shown in Figure 2C. The bare GC electrode shows positive feedback under these conditions (not shown), whereas the approach curve over a PTFE-covered substrate fits the theory for negative feedback for an insulating substrate very well. Such approach curves are also observed on the insulated parts of the electrode after the holes are opened.

Figure 3 shows typical micrographs of the holes that are obtained. Figure 3A shows a hole that has been successfully formed after immersion in acetone; the shape and dimension of the hole correspond well to the size of the dispensed spot of resin. Notice also the clear-cut edges that are left behind after the material on top of the spot has been removed by the swelling of the resin. Provided the protocol described in the Experimental Section is followed, a 100% efficiency in the opening of the holes of an array was achieved (i.e., all the dispensed spots were opened). For comparison, an example of a spot that was unsuccessfully revealed is shown in Figure 3B; the photoresist dissolved, but the PTFE on top of the spot was not removed. This behavior was usually encountered when the PTFE layer was too stiff and impermeable (as happens with oven drying before revealing the spots). Figure 3C shows an example of a drop of Pd solution that was dispensed on a hole. If the orientation and position of the electrode with respect to the dispenser are maintained with the T-shaped piece, it is easy to deliver material reproducibly into each hole of the array. Figure 3D shows an example of the final Pd spot in electrical contact, surrounded by a limited area of the GC substrate exposed to the solution.

Figure 4A shows an SECM image of an array of GC holes. The solution contained 1 mM $Ru(NH_3)_6^{3+}$ which is reduced at the tip to $Ru(NH_3)_6^{2+}$ ($E_T = -0.2$ V vs NHE) while the GC substrate performs the opposite oxidation reaction ($E_S = 0.2$ V vs NHE). At this substrate potential the $Ru(NH_3)_6^{3+}$ is stable ($E_{1/2} = 0.01$ V vs NHE), so an anodic current flows only when the tip passes over active spots on the substrate (holes). Except for some small defects in the PTFE layer that may be the result of isolated drops of resin or tip scratches during positioning, the image proves most of the surface is covered with an insulating layer: there is a homogeneous background of ~1.5 nA and a large contrast between this and the −16 nA of the active spots. Note that, although the background is cathodic (positive current), the signal is about 10 times higher than the background in absolute terms, and this corresponds to a collection efficiency of nearly 100% of the amount produced at the tip ($i_{T,\infty} = 7$ nA, tip−substrate distance $d = 12.5$ μm, so $L = 1$ and positive feedback is ~$2.2i_{T,\infty}$). Figure 4A also indicates that the electrochemistry of the substrate after removal of the resin is intact, thus providing an efficient wet procedure to produce such holes. One apparent drawback of the wet procedure, however, is that by an estimation of the expected positive to negative feedback currents at the SECM tip, the thickness of the insulating layer is of approximately 2 μm. We have not studied the homogeneity of the film, and we focus only in its ability to remove electrochemical background for SECM experiments. The calculated thickness of 0.7 μm from the capacitance of the film could correspond to an average thickness, and in any case, the range of 0.7−2 μm is tolerable for most SECM TG−SC studies.

Figure 4B shows the comparative results of the signal and background levels with and without covering of PTFE. The electrochemical background drops from 91 nA with a bare electrode to 2 nA with a covered electrode with holes, representing a 45-fold decrease in the background current. Following geometric arguments, the ratio between the exposed area of the bare electrode (3.21×10^{-5} m^2) to the one resulting from the product of 29 holes of 175 μm diameter (6.97×10^{-7} m^2) is equal to 46, in close agreement to the observed decrease in the background current.

One important area in which these covered electrodes are of use is in electrocatalyst screening by SECM. As shown in Figure 3D, it is possible to obtain arrays of holes in which a material of interest is deposited over the opened GC areas. These electrodes improve the SECM measurements by increasing the signal to background ratios, which is especially important when the background currents are drifting or noisy, and that under some conditions may surpass by orders of magnitude the electrocatalytic response of the deposited material.

Figure 5A shows an SECM image of the electrochemical activity toward H_2 oxidation by Pd spots deposited over a

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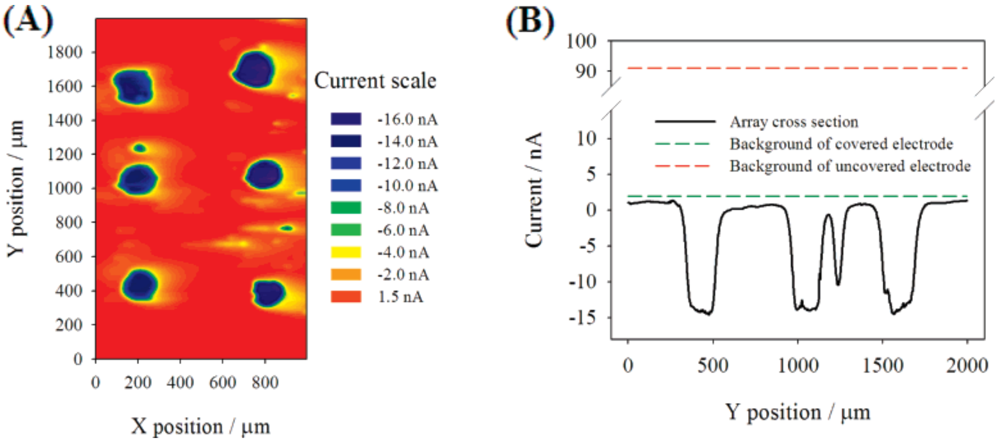

Figure 4. (A) SECM imaging of revealed GC holes on the PTFE-covered substrate: 1 mM $Ru(NH_3)_6^{3+}$ in 0.1 M phosphate pH 7 buffer; 25 µm diameter Pt tip, $d \sim 12.5$ µm. Potentials vs NHE: tip, −0.2 V; substrate, 0.2 V. Tip raster, 240 µm/s; quiet time before imaging, 30 s. (B) Comparison of the electrochemical background signals as obtained by chronoamperometry (steady state after 500 s) to a cross section of (A) at $x = 200$ µm.

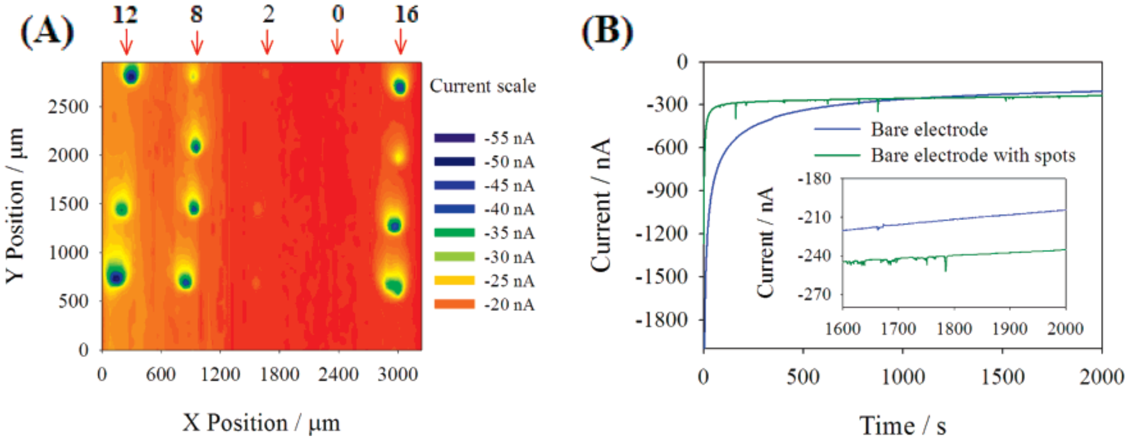

Figure 5. (A) SECM image of H_2 oxidation over Pd spots deposited onto an array of GC holes. Potentials vs NHE: tip, −0.5 V ($i_T = 43$ nA); substrate, 0.8 V. Tip raster: 240 µm/s, quiet time of 600 s before the start of image. Numbers on top of the image represent the drops of Pd solution deposited over each hole (only columns 3−7 are shown). The 25 µm diameter Pt disk tip was positioned at $d = 35$ µm. (B) Chronoamperometric curves of uncovered electrodes with and without spots; potential vs NHE, 0.8 V. The inset shows the two curves at long times in a different scale. Solution: 50 mM K_2SO_4 at pH 3.

selectively insulated GC electrode such as the ones described in this note. In brief, the tip reduces H^+ in solution (pH = 3) to H_2 at a constant flux ($i_T = 43$ nA), which is oxidized at the Pd spots ($E_S = 0.8$ V vs NHE) and thus generates an anodic response. Two main differences from this and the experiment shown in Figure 4 are that the GC substrate at the potential and conditions used (e.g., highly oxidizing potential and acidic medium) will undergo surface oxidation and the presence of metallic spots will increase the effective area, and this contributes to the background current of the substrate. Comparison of the background in the SECM image in Figure 5A (∼ −20 nA) to the anodic response in Figure 5B for a bare GC electrode (∼ −220 nA) under the same conditions shows that the background is reduced by about a factor of 10. The ratio of the exposed area from the bare electrode (6.36×10^{-5} m^2) to the one exposed by the holes in the covered electrode (6.97×10^{-7} m^2) would predict a background reduction of a factor of 91. Figure 5B shows that despite the drifts on the background on either a bare GC plate or one with Pd spots (without PTFE), it is possible to attribute this discrepancy to the presence of the Pd spots. This means that even if the current coming from the oxidation of GC is suppressed 91-fold (i.e., the GC background in the SECM image should be ∼ −2 nA), the contribution from oxidation at all of the Pd spots could well account for the −20 nA background observed in the SECM image; this number is in the same range as the difference between the two curves shown in the inset of Figure 5B at long times. The presence of metallic spots thus limits the practical reduction in background coming from the array. Despite this, Figure 5A is an improved SECM image under the conditions of the experiment and not only because of the 10-fold decrease in the background. For instance, the background drift from the substrate electrode is approximately −5 nA during the whole experiment, and with an analytical signal of −30 to −35 nA coming from hydrogen oxidation at the spots, it corresponds to a signal-to-noise ratio of ∼6, which allows for straightforward detection of the electrocatalytic activity of the spots, a feature not attainable in traditional TG−SC SECM electrocatalyst experiments under these conditions.

CONCLUSIONS

We have developed a method for making substrate electrodes for SECM screening in which the background currents can be reduced at least 1 order of magnitude, and often much more. Enhancing the signal to background ratio of the electrochemical response of the substrate electrode has been demonstrated in the TG−SC mode. The suggested technique allows one to create arrays of holes on a PTFE-insulated GC substrate to reduce the exposed area of the substrate exposed to the working solution and thus decrease the background current. Such a decrease is consistent with the reduction in the area in calibration experiments. When the metallic spots are deposited, their background contribution makes the signal to background ratio smaller than expected, although an enhancement in the image contrast is produced by reducing the impact of the background drift and size. The PTFE layer over the electrodes is chemically and electrochemically inert for most purposes and mechanically stable. The procedure described is also relatively simple, relatively inexpensive, and easy to carry out.

A final remark on the utility of the technique described in this work is the possibility of using it for the fabrication of microelectrode arrays of materials that are not easy to manipulate or to obtain as microwires. Commercial microdispensers with smaller end diameters are available, which may allow the reduction of the dimensions of the holes. The possibility of integrating these microholes into arrays also suggests their use to study array diffusion interactions or other generation−collection experiments.[12,13,17]

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SUPPORTING INFORMATION AVAILABLE

Protocol used to estimate the thickness of the insulating layer of PTFE over the GC electrodes and the size of the holes. This material is available free of charge via the Internet at http://pubs.acs.org.

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