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# Scanning Electrochemical Microscopy. 32. Gallium Ultramicroelectrodes and Their Application in Ion-Selective Probes

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**Gallium ultramicroelectrodes for amperometric measurements in scanning electrochemical microscopy were fabricated by introduction of liquid Ga into drawn glass micropipets. Cyclic voltammetry of $Ru(NH_3)_6^{3+}$ and the use of this species for SECM imaging is described. Double-barrel micropipet tips with a Ga amperometric electrode and an ion-selective ($K^+$) potentiometric probe can also be constructed. This probe was used to image the $K^+$ activity near a 20-$\mu$m-diameter lumen of a glass capillary.**

We describe the construction of Ga ultramicroelectrodes (UMEs) and their application in scanning electrochemical microscopy (SECM). SECM[1−3] is a type of scanning probe microscopy (SPM) in which faradaic reactions at the tip (e.g., a UME) are used to study surface properties of different types of samples. In common with other SPM techniques, SECM is based on the high-precision positioning and scanning of a small (nanometers to micrometers) measuring tip over the target surface while data are collected on local surface properties at different measuring tip locations. The basic instrument incorporates a computerized data acquisition unit, and different computer programs with digital filtering and contrast enhancement steps are employed to develop and display the surface image.

Two types of measuring tips are employed in SECM: amperometric UMEs (usually disk-shaped Pt or C electrodes) and potentiometric tips. With amperometric tips, the faradaic current of a selected electrode reaction, in which the UME is held at a given potential with respect to the reference electrode, is measured ($i_T$). The magnitude of $i_T$ compared to the value when the tip is far from the sample surface ($i_{T,\infty}$) is used to determine the tip-to-sample distance ($d$) for both insulating ($i_T < i_{T,\infty}$) and conductive ($i_T > i_{T,\infty}$) substrates.[1−3] Amperometric tips are also used to image surface topography by noting changes in $i_T$ as a function of position. With potentiometric tips, the potential of the electrode with respect to a reference electrode is used to probe the local activity or concentration of a solution component. Potentiometric tips are frequently ion-selective micropipets[4−6] and are used for SECM imaging when a steady-state ion concentration profile exists over the target surface.[7,8] Several different types of potentiometric SECM tips have been utilized.[7−11] With the antimony microdisk SECM electrode,[8−10] both amperometric and potentiometric ($H^+$) measurements are possible, so that approach of the tip to a surface and determination of $d$ can be made in the amperometric mode, before the potentiometric pH measurement. However, with more versatile ion-selective micropipet tips,[11] amperometric determination of $d$ is not possible, because of the high resistivity of ion-selective membranes.

An alternative approach with potentiometric tips is to use a double-barrel structure (e.g., based on $\theta$-micropipets) in which one chamber comprises the desired ion-selective electrode (ISE) and the second an amperometric one.[11] There are well-established procedures for the preparation of double-barrel or multibarrel micropipet ion-selective measuring tips.[4,5] The application of these complex probes is quite common in the life sciences. However, the construction of a double-barrel potentiometric/amperometric tip, especially of a size small enough for high-resolution SECM imaging, is challenging. It is difficult to seal a Pt wire or C fiber in a double-barrel structure while still leaving the second barrel open for filling with the appropriate ion-selective material. Thus, it is of interest to consider the use of a metal of low melting point for the preparation of amperometric microelectrodes.

Mercury is not a good option as an electrode material because it does not wet the glass wall of a micropipet and thus retreats

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from the tip. Gallium, a low melting point (29.78 °C) metal, does wet the glass. The electrochemistry of Ga and the behavior of Ga electrodes in different media have been studied in detail.[12] Investigations with dropping and stationary Ga electrodes showed that electrochemical reduction waves of different metal ions, such as $Ni^{2+}$,[13] $Cd^{2+}$,[14] and $Ga^{+}$,[14] can be obtained on a metallic Ga electrode. Different organic molecules are reduced on a dropping Ga electrode,[12] producing reproducible half-wave potentials. The half-wave potential of certain halohydrocarbons was found to be 0.5 V more positive on a Ga electrode than on a dropping Hg electrode.[15] In the one-electron reduction of methyl iodide on Ga, the formation of an organogallium compound was found.[16]

Gallium working electrodes have not found applications in voltammetric chemical analysis, however, and to our knowledge, no previous report of a Ga UME has appeared. Neither the applicable potential window nor the chemical stability of the Ga electrode surface can match the relevant properties of the generally used voltammetric working electrodes, like Pt. However, we felt that a Ga electrode could be employed as a measuring tip in amperometric SECM, since in SECM, solution conditions can frequently be selected with a given electrode material to provide a stable, concentration-dependent, amperometric current at a given working electrode potential. We describe here the preparation and properties of Ga UMEs for SECM applications.

## EXPERIMENTAL SECTION

**Chemicals and Materials.** The chemicals used in the experiments were of reagent grade or better. The ionophores and related compounds used for ISE preparation were obtained from Fluka. Ag wire and Ga metal were purchased from Aldrich (Milwaukee, WI) and Johnson Matthey (Seabrook, NH), respectively. Double- and single-barrel borosilicate glass capillary tubes were obtained from Sutter Instruments (Novato, CA) and WPI (Sarasota, FL).

**Fabrication of Microelectrodes.** Single-barrel Ga microdisk electrodes and double-barrel electrodes with one Ga barrel and one ion-selective barrel were made of borosilicate glass capillaries. Before pipet pulling, the glass tubes were soaked in 1:1 (v/v) mixture of sulfuric acid and 30% hydrogen peroxide for 24 h and then washed thoroughly with doubly distilled water. They were dried at 120 °C for ~30 min, just before pulling. A laser-based puller (Model P-2000, Sutter Instruments) and a conventional puller (Model 720, David Kopf Instruments, Tujunga, CA) were used for making the micropipets.

To fabricate the Ga UMEs, Ga metal was melted in a small glass container in a water bath and then introduced into the glass capillary barrel from the back side with the aid of a syringe. The length of the Ga thread inside the barrel was ~2 cm. The Ga was then forced to the end of the tip by careful centrifuging of the capillary. Periodically, the centrifuge was stopped and the position of the Ga was checked under a microscope. Electrical contact was made by inserting a Pt wire from the back. To solidify the Ga, the electrode was kept in a refrigerator.

In the double-barrel electrodes, the micropipet barrels used for the preparation of ion-selective electrodes were silanized with dimethyldichlorosilane vapor introduced by syringe injection before the introduction of Ga metal into the other barrel. The silanization process was completed by allowing the glass surface to react for 2 h at 120 °C. Silanization of the still empty Ga barrel was avoided by continuously flushing nitrogen gas through it during the ion-selective barrel silanization procedure. The silanizing vapors were removed by suction. After the preparation of the Ga barrel was completed, the ion-selective barrels were back filled with the proper internal filling solution (see below) using a syringe. The tip of the ion-selective barrel was front filled with the corresponding ion-selective cocktail by capillary action and slight suction. A chlorinated Ag wire was inserted to complete the ion-selective microelectrodes.

$K^{+}$-selective microelectrodes used in this study were based on the BME-44 $K^{+}$ ionophore,[17] 2,2′-bis[3,4-(15-crown-5)(2-nitrophenyl)carbamoximethyl]tetradecane (Fluka), with 0.1 M KCl as the internal filling solution. The ion-selective cocktail was prepared by dissolving 5−7% (w/w) ionophore in *o*-nitrophenyl ether and adding 10−70 mol % potassium tetrakis(4-chlorophenyl)-borate (relative to the ionophore).

**Preparation of the Targets.** In the experiments on imaging, an interdigitated gold electrode array (30 $\mu$m thick) deposited on a silica substrate was employed as the target. The actual target was a piece of ~10 × 10 $mm^2$ cut from a thin wafer which was placed on the bottom of the measurement cell.

In the experiments in which a potassium ion image was recorded, a dc current driven ionic migration was used to create the target ion concentration profile. In this case, the target was made of a U-shaped glass tube with a capillary at one end (with a tip diameter of 1−25 $\mu$m). After complete filling with a 0.1 M KCl solution, the U-tube with the capillary was inserted into the cell through a hole in the center of the cell base. The cell contained 0.1 M NaCl as background electrolyte. Two Ag/AgCl wires, one in the noncapillary end of the U-tube and the other in the bulk solution of the cell, were used to apply the electrophoretic current. The electrodes were connected with appropriate polarity to the dc current generator.

**Instrumentation.** The SECM setup has been described in detail elsewhere.[8] A CE-1000 micropositioning device (Burleigh Instruments, Fishers, NY) connected to a PC via a DAC was used to control the movement of three piezoelectric inchworm motors. The electrochemical cell, with the target of interest placed in the middle of the cell base, was mounted on a horizontal stage, and the microelectrode measuring tip was mounted on a three-axis translation stage that allowed submicrometer scale tip positioning. An EI-400 bipotentiostat (Ensman Instruments, Bloomington, IN) was used for potential control and current measurements, and the potentiometric measurements were made with a home-built high-impedance voltmeter. An agar gel salt bridge with 0.01 M NaCl electrolyte was used to connect the reference electrode chamber to the cell.

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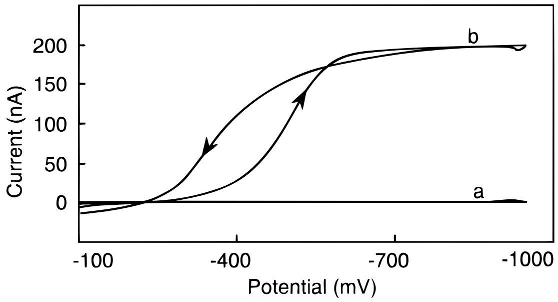

Figure 1. Cyclic voltammograms of a 70-$\mu$m-diameter Ga UME in (a) 0.1 M KCl and (b) 2 mM $Ru(NH_3)_6Cl_3$/0.1 M KCl solutions. Reference electrode, SCE; scan rate, 50 mV/s.

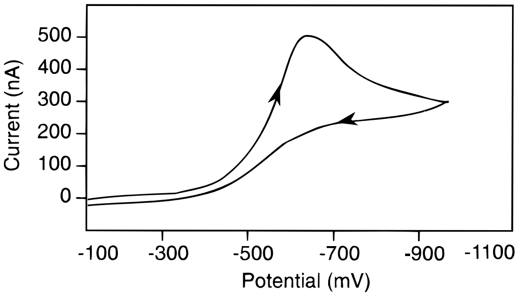

Figure 2. Cyclic voltammogram of a 70-$\mu$m-diameter Ga UME in a 2 mM $Ru(NH_3)_6Cl_3$/0.1 M KCl solution. Reference electrode, SCE; scan rate, 1 V/s.

In some of the measurements with the single-barrel Ga working electrodes, a PAR Model 174A polarographic analyzer (Princeton Applied Research, Princeton, NJ) and a one-dimensional ($z$) electrode-positioning device was employed. The latter-was based on a type M-MFN25PP translation stage (Newport Corp., Irvine, CA).

A BAS 100B electrochemical analyzer (BAS, West Lafayette, IN) was employed to perform the voltammetric measurements. For the electrochemical characterization of micropipet ion-selective electrodes, a home-built high-impedance voltmeter was used.[8]

## RESULTS AND DISCUSSION

**Ga Voltammetric Ultramicroelectrodes.** The potential range accessible with a Ga electrode in aqueous solutions is determined by the overpotential for proton reduction (hydrogen gas formation) on the cathodic side and by complicated passivating oxide film formation processes on the anodic side. According to Szabó,[18] the hydrogen overpotential depends on the extent of water adsorption. The less water that adsorbs on the electrode surface, the higher the overpotential. A clean liquid Ga surface provides the highest overpotential, while the oxide film, which increases the amount of water adsorbed, decreases the hydrogen overpotential. Since solid Ga adsorbs more water, the overpotential is usually smaller on solid than on liquid Ga surfaces. The formation of different gallium oxide films delays anodic Ga dissolution. This passive film formation appears in cyclic voltammograms recorded with stationary Ga electrodes.

Experiments with Ga UMEs showed that a reproducible voltammetric reduction wave can be obtained for $Ru(NH_3)_6Cl_3$ as an electroactive component. The applicable potential window in 0.1 M KCl is 0.1 to $-1.5$ V vs SCE. In Figure 1, cyclic voltammograms recorded with a Ga microelectrode (70-$\mu$m diameter) in deoxygenated solutions are shown. Curve a was taken in the background electrolyte (0.1 M KCl) and curve b was recorded in a 2 mM $Ru(NH_3)_6Cl_3$/0.1 M KCl solution at a scan rate of 50 mV/s. Voltammograms recorded in solutions of the same composition at a higher scan rate (1 V/s, Figure 2) show that, in contrast to the behavior on other solid electrodes like Pt, the $Ru(NH_3)_6Cl_3$ reduction is quite irreversible. By selecting an electrode potential more negative than $-0.6$ V, stable steady-state $Ru(NH_3)_6Cl_3$ concentration-dependent amperometric currents can be recorded with the Ga UME barrels over a concentration range of 0.1$-$1 mM. The equation of the regression line of the amperometric current vs concentration function is $i$ (nA) $= 1.45 \times 10^4$ (M) $- 0.56$ with a regression coefficient of 0.998.

The Ga electrode surface is often coated with an oxide film. To see how this film affects the effective surface area, the areas of Ga UMEs of different sizes were compared with a Pt microdisk electrode. The geometric area was estimated with an optical microscope, while the electrochemical (geometric) surface area was determined by comparing the steady-state amperometric current of 2 mM $Ru(NH_3)_6Cl_3$ at a Ga microelectrode set at $-0.7$ V vs SCE with the amperometric current measured under the same conditions with a platinum microdisk electrode of known surface area [determined from a voltammogram recorded in 0.1 M $K_4Fe(CN)_6$ solution]. The effective area ratio of the Pt microelectrode to Ga was ~1.4, suggesting blockage of portions of the Ga electrode by oxide film. The fact that this electrode with a large diameter for an ultramicroelectrode shows steady-state behavior at this scan rate suggests the active (oxide-free) zones are distributed across the surface to form a random array, although we cannot eliminate the possibility of some leakage at the Ga/glass interface.

**Ga SECM Tips.** To evaluate the utility of the Ga microelectrode as a voltammetric SECM tip, negative and positive feedback effects on a Ga electrode were studied. Accordingly, amperometric tip currents were monitored while the electrode (a double-barrel configuration with a 22-$\mu$m-diameter Ga disk) approached insulating (Teflon) and conductive (Pt) targets in a 5 mM $Ru(NH_3)_6Cl_3$/0.1 M KCl solution (Figure 3). The current had a constant value ($i_{T,\infty}$) when the electrode was far from the target surface, but increased in the proximity of a conducting surface (positive feedback) or decreased on approach to an insulating surface due to the blocking of the analyte diffusion (negative feedback) as predicted by SECM theory with voltammetric tips. In Figure 3, the theoretical approach curves (solid line) and the experimental points are in fair agreement. The slight discrepancy between the experimental and theoretical curves can be attributed to the nonideal (disk) geometry of the double-barrel configuration.

The utility of a Ga measuring tip to the determination of the tip-to-target distance via approach curves demonstrates that these tips are applicable to topographic imaging with chemical information. To prove this, a one-dimensional amperometric current vs $x$ distance curve is shown in Figure 4. This curve was recorded over an interdigitated gold electrode array on a silica surface keeping the measuring tip at a constant distance $d$ of 25 $\mu$m from the surface, while the tip was scanned in the $x$ direction. The

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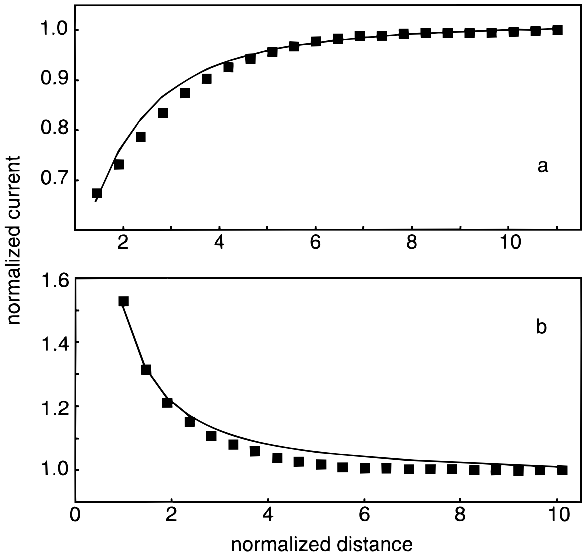

Figure 3. Approach curves (tip current vs distance) for a 22-$\mu$m-diameter Ga SECM tip in a 5 mM $Ru(NH_3)_6Cl_3$/0.1 M KCl solution. The tip potential was $-0.6$ V vs Ag/AgCl reference electrode. The symbols are experimental and the solid lines are theoretical data. (a) Pt surface; (b) Teflon surface.

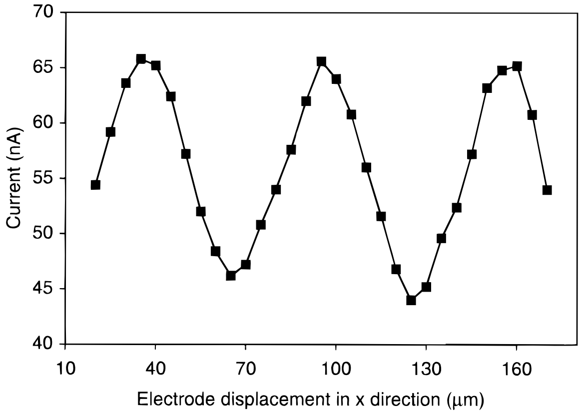

Figure 4. One-dimensional SECM scan of a gold grid with a 30-$\mu$m-diamter Ga tip in a 2 mM $Ru(NH_3)_6Cl_3$/0.1 M KCl solution. Tip potential, $-0.7$ V vs SCE.

measuring tip potential was $-0.7$ V vs SCE, and the test solution contained 2 mM $Ru(NH_3)_6Cl_3$ and 0.1 M KCl as a background electrolyte. The higher currents result from positive feedback over the gold; over the insulating silica, diffusion-blocking negative feedback dominates and the current decreases. Because the diameter of the tip is of the order of the Au band width, the resolution in this experiment is not high and rounding of the current above the conductive bands is seen. An *xy* plane image of the same target is shown in Figure 5. The image was made with a 22-$\mu$m-diameter Ga electrode tip at a potential of $-0.6$ V immersed in a 5 mM $Ru(NH_3)_6Cl_3$/0.1 M KCl solution. As shown in Figure 5, the effective resolution in a gray-scale image can sometimes be improved by the proper selection of the current levels to shade intensity.

**Ion-Selective Double-Barrel Tips.** When an ISE is prepared in the second barrel of the double-barrel Ga electrode, this tip can be advantageously employed in SECM. The Ga barrel is used to probe target distance and for active topographic imaging, while the ion-selective barrel is used for potentiometric ion-selective imaging. Figure 6 shows a $K^+$ image recorded over a 20-$\mu$m-diameter opening of a tube from which a steady flux of $K^+$ was driven by electric current through the measuring cell. The image was made with a double-barrel tip containing a $K^+$-selective electrode barrel in the following way. After rough positioning of the electrode over the target, a 5 mM $Ru(NH_3)_6Cl_3$/0.1 M KCl solution was introduced into the cell and the tip was positioned over the glass (insulating) portion around the target lumen. The tip then was moved toward the glass, and the tip-to-target distance was determined by fitting the experimental amperometric approach curve to the theoretical one. After this step, the solution in the cell was replaced with 0.1 M NaCl solution as a background electrolyte and the potentiometric working mode was activated. A constant current intensity was applied between the two Ag/AgCl wires placed on one side of the U-tube and in the cell to provide migration of $K^+$ from the lumen of the glass tube to the measuring cell. The ISE barrel was connected to the high-

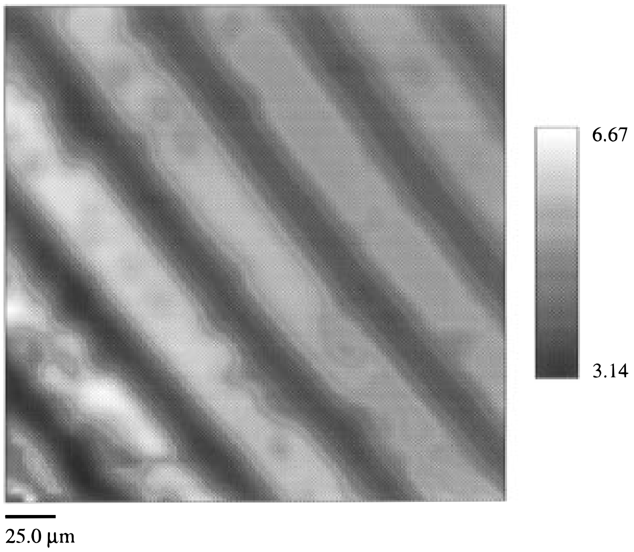

Figure 5. SECM topographic image of a gold grid with a 22-$\mu$m-diameter Ga tip in a 5 mM $Ru(NH_3)_6Cl_3$/0.1 M KCl solution. Tip potential, $-0.6$ V vs saturated Ag/AgCl electrode; tip scan rate, 10 $\mu$m/s. Current scale is in units of $10^{-8}$ A.

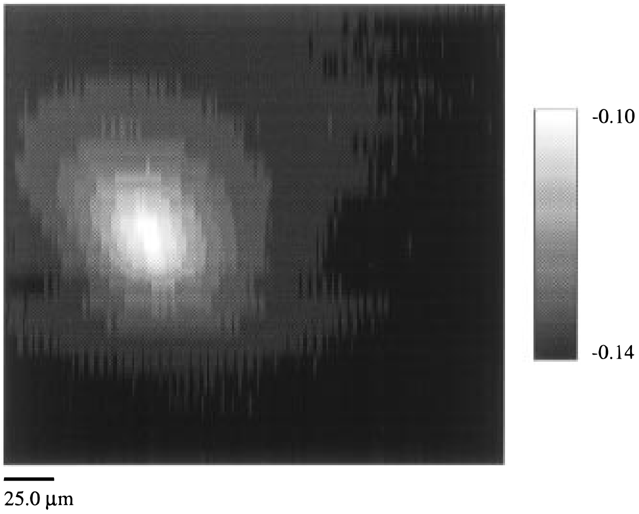

Figure 6. Image of $K^+$ concentration profile over a source of a 30-$\mu$m-diameter micropipet filled with 0.1 M KCl at a height of $\sim$20 $\mu$m. Tip diameter, 18 $\mu$m; scan rate, 5 $\mu$m/s; bulk concentration inside the micropipet, 0.1 M KCl; outside, 0.1 M NaCl; applied potential across target U-tube, 0.9 V. Potential scale in units of V.

impedance voltmeter, and the tip was scanned in the *xy* plane at a known *z* distance from the surface. In the image, the white color indicates higher potassium ion concentrations.

## CONCLUSIONS

Because of its limited potential range and easy passivation, Ga is not usually used as a voltammetric electrode metal. However, ultramicroelectrode tips for SECM can be prepared conveniently by melting the Ga and forcing it into a small-diameter glass micropipet. The $Ru(NH_3)_6^{3+}$ reduction wave provides a useful marker for SECM distance measurements. Ga is especially convenient as an amperometric positioning electrode in a dual-barrel configuration with a potentiometric probe electrode.

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