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A Simple and Low-Cost Ultramicroelectrode Fabrication and Characterization Method for Undergraduate Students

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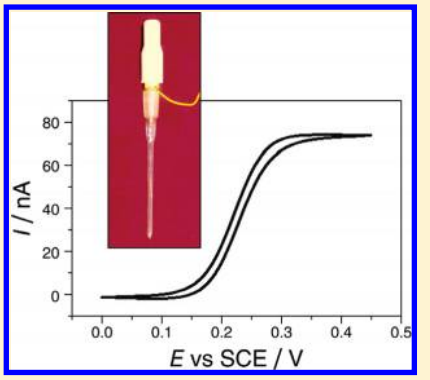
Supporting Information

ABSTRACT: A laboratory experiment is described in which students fabricate disk-shaped gold and platinum microelectrodes with diameters of 10−50 μm by sealing sodalime glass with metal microwires. The electrodes are characterized by performing cyclic voltammetry in aqueous and acetonitrile solution. Commercial microelectrodes are expensive (cost depends on the diameter of electrode) and may deter introduction of voltammetric experiments into laboratory classes at the undergraduate level. The students also fabricate a simple operational amplifier (op amp)-based potentiostat along with a low-current measuring device. This low-cost fabrication helps the students understand the details of instrumentation of a potentiostat with special knowledge in analog electronics. This experiment can be included in the electrochemistry laboratory course for undergraduate students. This experiment can also be incorporated into various undergraduate laboratory courses such as analytical chemistry, general chemistry, biochemistry, physical chemistry, and instrumentational methods of analysis.



KEYWORDS: Second-Year Undergraduate, Upper-Division Undergraduate, Analytical Chemistry, Laboratory Instruction, Physical Chemistry, Hands-On Learning/Manipulatives, Electrochemistry, Laboratory Equipment/Apparatus, Oxidation/Reduction

Ultramicroelectrodes are electrodes with at least one of the dimensions of the order of micrometer or less. Initially, microelectrodes were used for biological and medical research. In early 1980s, Fleischmann and his co-workers at the Southampton Electrochemistry group exploited the versatile properties of microelectrodes in electrochemical studies. The ultramicroelectrodes, owing to their extremely small size, have certain unique characteristics that make them ideal for studies involving high-resistive media, high-speed voltammetry, and in vivo electrochemistry in biological systems.[1] They exhibit a high rate of mass transfer combined with a low ohmic drop and double-layer charging current, which make them a powerful tool for studies of fast heterogeneous kinetics at low concentrations. Owing to the small electrode area, the currents associated with microelectrodes are small, of the order of pA to nA, and the current densities are high.

Microelectrodes make it possible to carry out experiments that are not possible using conventional-sized macroelectrodes. This is due to the considerable difference in electrochemical responses between micro- and macroelectrodes. Because of the small area of microelectrodes, the double-layer capacitance is considerably reduced relative to macroelectrodes. This allows the electrode potential to be changed rapidly, which can be utilized in voltammetric measurements in submicrosecond time scale.[2,3] At normal time scales, cyclic voltammograms obtained with ultramicroelectrodes are different from those of macroelectrodes. The voltammograms are sigmoidal-shaped, analogous to the S-shaped polarograms obtained with dropping mercury electrode or rotating disk electrodes. The rate of mass transport (diffusion) plays an important role in defining the shape of voltammograms. At normal-sized macroelectrodes, the mass transport occurs mostly perpendicular to the electrode surface (planar diffusion). The result is a typical peak-shaped voltammogram for the macroelectrodes. For a reversible redox process, the peak current follows Randles−Sevcik equation[4,5]

$$I_p = (2.69 \times 10^5) n^{3/2} C^* D^{1/2} \nu^{1/2} \quad (1)$$

in which I_p is the peak current density (A/cm^2), n is the electron stoichiometry, D is the diffusion coefficient (cm^2/s) of the electroactive species, C^* is the bulk concentration of the electroactive species, and ν is the scan rate (V/s). On the other hand, for a microelectrode, an S-shaped voltammogram is obtained at lower scan rates, which changes into a peak-shaped one at high scan rates. At lower scan rates, the rate of electrolysis is almost equal to the rate of diffusion, which takes place in a hemispherical fashion as a time-independent process. Hence, it produces steady-state S-shaped voltammogram. At higher scan rates, the rate of electrolysis exceeds the rate of diffusion to a larger extent. At such a fast time scales, redox species take longer time to diffuse. Hence, the current changes with time, and peak-shaped voltammograms are obtained.

The diffusion processes occurring at the ultramicroelectrodes can be understood by solving the diffusion problems for dropping mercury electrodes used in traditional polarography. For a

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spherical electrode (radius r), current is given by

$$i_{\text{spherical}} = nFADC^*[1/(\pi Dt)^{1/2} + 1/r] \quad (2)$$

where $A = 4\pi r^2$ is the area for a spherical electrode and F is the Faraday constant. According to this equation, at longer time scales, the current should be time independent. For a macroelectrode, the current due to semi-infinite planar diffusion is given by the Cottrell equation

$$i_{\text{planar}} = nFADC^*/(\pi Dt)^{1/2} \quad (3)$$

that is,

$$i_{\text{spherical}}/i_{\text{planar}} = 1 + [(\pi Dt)^{1/2}/r] \quad (4)$$

The parameter $(Dt)^{1/2}/r$ will determine when the current will be essentially constant in nature. The expression $i = 4nFDCr$ correlates the steady-state current to the electrode radius r of a microelectrode. Hence, one can determine the dimension of a microelectrode by directly measuring the steady-state current from the S-shaped voltammogram, provided the value of D is known. For a redox reaction with unknown D value, the above expression can be used to determine the diffusion coefficient D. Because the steady-state current is proportional to the bulk concentration of electroactive species, the above expression can also be used in determining unknown concentration of some electroactive species.

Microelectrodes of different geometries such as disks, rings, and bands are commonly found in the literature.[2,5] The fabrication and use of microelectrodes had received little attention in the undergraduate laboratory courses in chemistry as seen from the citation of papers in this *Journal*. The article titled "Electrochemistry at Nanometer-Scaled Electrodes"[6] is the most recent and significant one found in this *Journal*.

Ultramicroelectrodes are available commercially from most companies specializing in electrochemical apparatus, but the cost is high and electrodes of variable diameters are not available. For example, the price of 10 μm diameter platinum and gold microelectrodes from a well-known electrochemical instrument supplier is about U.S. $400. In this article, a simple method of fabricating disk-shaped and inexpensive gold and platinum microelectrodes for undergraduate electroanalytical labroratory course is described. Although, the approach is well-known in various electrochemistry research laboratories, it has not been introduced in undergraduate laboratory programs in chemistry. The electrodes are characterized by performing cyclic voltammetry in an aqueous and a nonaqueous (acetonitrile) solution.

MICROELECTRODE FABRICATION

The main goal of this laboratory experiment is the fabrication of inexpensive microelectrodes of different diameters by sealing glass with metal microwires of required diameters. A wide variety of methods are available for constructing ultramicroelectrodes.[2] Disks, bands, and rings are some of the common geometries of ultramicroelectrodes. The ultramicroelectrode disk is easiest to fabricate and can be made by encapsulating metal microwire in a matrix of glass or epoxy. Stanton et al.[7] described the fabrication of ultramicroelectrodes by sealing microwires into epoxy. Glass is the best choice to be embedded with metal, as it has the properties of good insulation, transparency, inertness, and is easy to polish and seal with metals. Perfect metal-to-glass sealing is an important step in modern scientific glass blowing. To ensure a satisfactory seal, glass must wet the surface of the metal, and the metal must have a coefficient of thermal expansion similar to that of the glass. This will give perfect glass-to-metal sealing without any leakage. Platinum and gold have thermal expansion coefficients of 91 $\times$ 10^{-7} and 143 $\times$ 10^{-7} °C^{-1}, respectively, and the soft glass used here has a thermal expansion coefficient of 92 $\times$ 10^{-7} °C^{-1}. The glass value is suitable for platinum due to the similar thermal expansion coefficients. Although the thermal expansion coefficient of our glass is almost two-thirds that of gold, excellent glass−metal seals have been achieved and fabricated gold microelectrodes show no leakage even when kept in electrolytes for days.

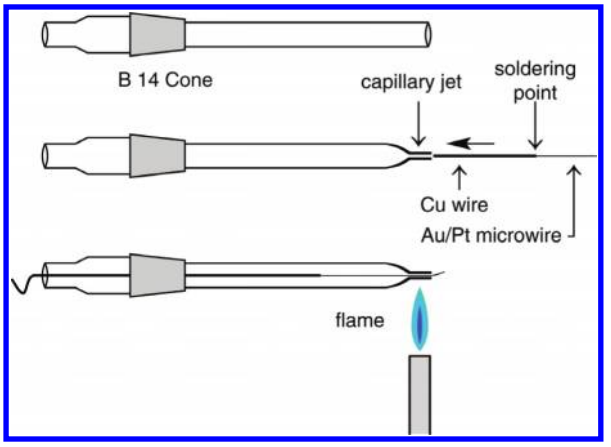

Figure 1. Steps involved in the fabrication of microelectrode. The heavy arrow depicts the direction of insertion of the wire.

A sodalime lamp glass, which is commonly known as soft glass or lamp glass,[8] is available from the fabricators of commercial fluorescent lights. It has a softening point of 700 °C and high percentage of sodium monooxide. The general composition of sodalime lamp glass, from the manufacturers, is SiO_2, 73.5%; Na_2O, 16.3%; CaO, 4.7%; K_2O, 0.3%; Al_2O_3, 1.6%; Sb_2O_3, 0.17%; MgO, 3.4%; and FeO, 0.03%. Similar kinds of soft glasses whose thermal expansion coefficient is close to that of the metals to be sealed may also used.

The following method achieved a perfect metal−glass seal; the steps for the fabrication of ultramicroelectrode are illustrated in Figure 1. The gold and platinum microwires (diameters 10, 12.5, 40, and 50 μm) were obtained from Advent Research Materials, (Oxford, U.K.). A 10 cm length of gold or platinum microwire was soldered with a thin copper wire for electrical contact without any "blob" at the soldered connection, as any blob causes obstruction when drawing the soldered microwire through a narrow capillary jet. The length of the microwire depends on the height of the electrochemical cell along with the cap. The soldered gold or platinum wire was inserted carefully through the fine capillary jet and drawn to the other side and positioned. The wire end just protruded outside the jet capillary. A pinpoint low-temperature flame was set at the burner and the capillary tube was sealed with the gold or platinum wire. High-temperature, broad-flame, and prolong heating may spoil the wire and conduction of heat may sometimes desolder the wire. The sealing must take place from one end progressively to the other end to avoid air trapping between the glass and metal interface, which will weaken the sealing. The other end of the soldered copper wire was folded at the top of the cone and was used as the external electrical contact. However, sealing ultramicroelectrode wires

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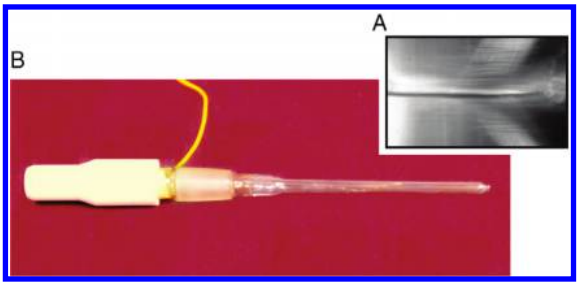

Figure 2. (A) Photomicrograph of the gold microwire−glass seal taken at the tip end of the microelectrode. (B) Photograph of the microelectrode fabricated in the laboratory.

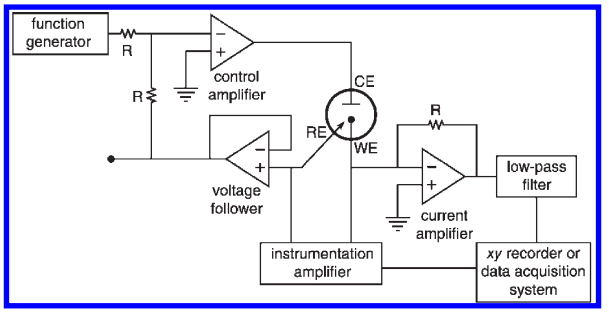

Figure 3. Block diagram of the two amplifier potentiostat used for microelectrode studies.

into glass is not simple and the undergraduate students needed several trial runs before fabricating a usuable ultramicroelectrode. The electrode tip was rendered to disk-shaped by grinding in 1000 grade carborandum, 1500 grade emery paper, and the resulting electrode was smoothed by polishing on a microcloth having a slurry of 1.0, 0.3, and 0.05 μm alumina powder (Buehler) successively. A photomicrograph of the gold microwire−glass seal at the tip end of the fabricated microelectrode is shown in Figure 2A and the photograph of the microelectrode fabricated in our laboratory is shown in Figure 2B. The metal−glass sealing portion was examined under the microscope for any imperfections, although the quality of the electrode should ultimately be assessed electrochemically by cyclic voltammetric studies of standard redox couples such as ferrocyanide/ferricyanide in aqueous media and ferrocene/ferricenium in acetonitrile. From this procedure, many electrodes can be produced with costs on the order of U.S. $5−10 per electrode.

INSTRUMENTATION

Cyclic voltammetry was carried out using a homemade potentiostat and also with an EG&G potentiostat (model 263 A) interfaced to a PC through a GPIB card (National Instruments). The fabrication of a simple operational amplifier (op amp)-based potentiostat along with the low-current measuring device can be accomplished by the students.[9] These amplifiers are inexpensive and have excellent sensitivity. The currents normally associated with microelectrodes are of the order of pA to nA. The problems associated with measurement of small currents and elimination of noise can be overcome by the use of ultra low noise, low bias current amplifiers. Though the current amplifier output can be recorded using any inexpensive *xy* recorder, a simple USB-based data acquisition system is recommended for data transfer to the PC and subsequent display. An SRS function generator

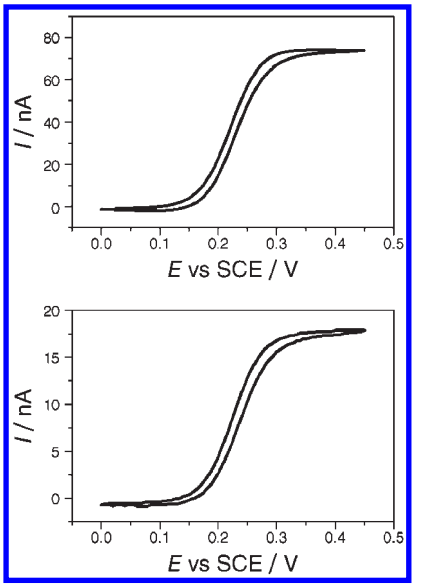

Figure 4. Cyclic voltammograms for 10 mM ferrocyanide with 1 M NaF with (A) 40 μm Au and (B) 10 μm Pt microdisk electrodes. Scan rate: 5 mV/s.

(model DS340, 15 MHz) was used as a voltage source for supplying suitable voltage ramp. The acquired data can be plotted on line using Labview or similar graphical software. The schematic diagram of the experimental setup used for microelectrode studies is shown in Figure 3.

HAZARDS

Acetonitrile may be fatal if swallowed, inhaled, or absorbed through skin; may cause irritation to skin, eyes, and respiratory tract; and is flammable. TBAFB causes irritation, may be harmful if swallowed, and is combustible. Ferrocyanide, ferrocene, and sodium fluoride are extremely hazardous in case of ingestion. Gloves and safety glasses should be worn throughout the experiment. Care must be taken when using the burner to seal the glass.

EXPERIMENT

The experiment including the fabrication of ultramicroelectrodes along with the design of the experimental setup can be completed in three weeks. Students performed this experiment in 4-h lab sessions that met three times a week. The students reported their results in the laboratory notebook. Students worked in groups of 5 and 50 students contributed to the data presented here.

CHARACTERIZATION OF MICROELECTRODE BY CYCLIC VOLTAMMETRY

Platinum, 10 and 50 μm diameter, and gold, 12.5 and 40 μm diameter, microdisk electrodes were fabricated. The electrodes were characterized by performing cyclic voltammetry (CV) of 10 mM potassium ferrocyanide with 1 M NaF in water and also of 1 mM ferrocene in 0.1 M TBAFB/acetonirile solution (TBAFB = tetrabutylammonium tetrafluoroborate). For a disk-shaped microelectrode, a typical sigmoidal voltammogram was observed and the limiting plateau current from CV is given by

$$i_{lim} = 4nFrC^*D \quad (5)$$

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Table 1. Calculated Radius Values for Microelectrodes from Sigmoidal-Shaped Steady-State Voltammograms

Redox System	Type of Microelectrode	$r_{calculated}$[a]/μm
10 mM ferrocyanide with 1 M NaF in water	50 μm diameter platinum microelectrode	27.5
10 mM ferrocyanide with 1 M NaF in water	10 μm diameter platinum microelectrode	5.1
10 mM ferrocyanide with 1 M NaF in water	12.5 μm diameter gold microelectrode[b]	7.1
10 mM ferrocyanide with 1 M NaF in water	40 μm diameter gold microelectrode[c]	21.1
1 mM ferrocene with 0.1 M TBAFB in acetonitrile	40 μm diameter gold microelectrode[c]	29.1
10 mM ferrocyanide with 1 M NaF in water	12.5 μm diameter gold microelectrode[b]	6.5
10 mM ferrocyanide with 1 M NaF in water	40 μm diameter gold microelectrode[c]	20.5
1 mM ferrocene with 0.1 M TBAFB in acetonitrile	40 μm diameter gold microelectrode[c]	22.1

[a] These data are from the experiments conducted by ~50 students. The error values are ±1%. [b,c] Corresponds to different electrodes fabricated using wire of identical radius.

where i_{lim} is the steady-state limiting current (A), F is Faraday constant (96,500 C), and r is electrode radius (cm). By measuring the limiting current from steady-state sigmoidal-shaped voltammogram, r can be determined, provided the values of C^* and D are known. Sigmoidal-shaped voltammograms were observed in all the experiments indicating microelectrode characteristics. The cyclic voltammograms were reproducible even after 24 h in the solution, indicating good metal−glass sealing without any leakage (for example, a 10 μm diameter platinum microelectrode exhibited almost the same steady-state current value of 18 nA for the ferrocyanide redox system even after 24 h in the same solution). The cyclic voltammograms for 10 mM ferrocyanide with 1 M NaF with 40 μm Au and 10 μm Pt microdisk electrodes are shown in Figure 4. The radius of microelectrode was determined using eq 5. In determining r values, the following diffusion coefficient values (D) from the literature at 25 °C[10−12] were used.

$$D_{ferrocyanide/water} = 9.2 \times 10^{-6}\ cm^2/s$$

$$D_{ferrocene/acetonitrile} = 2.4 \times 10^{-5}\ cm^2/s$$

The calculated r values for different microelectrodes obtained from the steady-state voltammograms are shown in Table 1. The difference between the measured radius of the fabricated microelectrodes and radius of the commercial microelectrodes provided by the manufacturer is between 1 and 2%. The difference of measured radius for two different electrodes fabricated using wire of identical radius was not so significant (Table 1). This observation suggests that the microelectrodes fabricated by this technique are reproducible. The electrodes were shown to have similar characteristics to their commercial counterparts.

CONCLUSIONS

A microelectrode-based voltammetric technique is described for the undergraduate chemistry curriculum. The homemade potentiostat as well as the fabricated microelectrodes enhance the undergraduate chemical education by introducing students to this important technique. This homemade potentiostat as well as the microelectrodes were successfully operated in the laboratory. By setting up a low-cost homemade microelectrode and potentiostat, this important electroanalytical technique became more accessible to students at the undergraduate level. Fabricated gold microelectrodes can be used to study the barrier properties of alkanethiol SAM as shown in the Supporting Information. Finally, it is important to mention here that Sur et al.[13] had studied the in situ microwave activation of electrochemical processes by self-focusing intense microwave radiation into a region close to electrode−electrolyte interface by placing metal microelectrodes inside a microwave cavity. They also demonstrated extreme faradaic current enhancement up to 3 orders of magnitude for various redox systems using a 25 μm Pt microelectrode, which can act as an "antenna" to enhance the microwave effect considerably in the vicinity of microelectrode surface.

ASSOCIATED CONTENT

Supporting Information

Instructions for the students; data from fabricated gold microelectrodes studying the barrier properties of alkanethiol SAM. This material is available via the Internet at http://pubs.acs.org.

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(9) Op Amp CA 3140 for the control amplifier and voltage follower and AD 515 (Analog Devices) as current amplifier can be used for the fabrication of the potentiostat. AD 515 is a low-noise amplifier, having ultra low bias current of 75 fA, with low offset and thermal drift, and is ideal for measuring very low currents. However, measurement of such low currents is beset with the problem of line frequency (50 Hz) and its harmonic noise. Excellent signal-to-noise ratio can be obtained by using

an optional unity gain sallen key type low-pass filter having a cutoff frequency of 1 Hz. Low noise, low-drift Op Amp AD 743 (Analog Devices) can be used for fabricating the low pass filter.

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