

An Electrochemical Fabrication Method for Gold and Carbon Ultramicroelectrode

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Au and carbon fiber ultramicroelectrodes have been fabricated by using an anodic electropolishing method. The radii of them were found to be about 450 nm on Au and 240 nm on carbon electrodes from the calculation based on the steady-state limiting currents.

Recently there has been considerable interest in electrochemical studies using microelectrodes.¹⁻¹²⁾ To date, microelectrodes has been applied to various areas such as in vivo electroanalytical studies,³⁻⁵⁾ investigation of nucleation,⁶⁾ fast heterogeneous electron transfer reactions,^{1,7)} rates of chemical reactions coupled to electron transfer,^{8,9)} and studies in highly resistive media.¹⁰⁻¹²⁾ In most investigations, the electrodes with radii greater than 10 μm have been used, since platinum (Pt), gold (Au), and carbon fibers of these sizes are readily available from commercial sources.

Microelectrodes have a number of features which are beneficial for the electrochemical study: The hemispherical nature of the diffusion field gives a steady-state diffusion-controlled limiting current.¹³⁾ The reduced area of electrode results in a diminished charging current and allows the extensions of electroanalytical techniques to samples of a lower concentration and smaller size.¹⁴⁾ The low ohmic drop produced by the microelectrodes eliminates the need for a three-electrode configuration and results in lower system noise.¹⁰⁾ The motivation for reducing the disk electrode radius to sub-micron proportion is that ohmic distortion is virtually eliminated, even in non-aqueous solvents with no supporting electrolyte.

One technique for fabricating sub-micron disk electrodes is to use Wollaston wire, a platinum wire inserted into the center of a large silver wire and drawn to successively small diameter. Bond et al.¹⁰⁾ encased the Wollaston wire in glass, removed the silver by chemical etching, and sealed the glass around the platinum wire. They fabricated platinum disk electrodes with 0.5 μm radius. The Wollaston wire process has recently been extended to form platinum wires of 4 nm radius.¹⁵⁾ It is not clear, however, whether the Bond's technique will be successful with wires of this size. Another approach for fabricating microelectrodes is to use a method of anodic electropolishing that we have already reported for a platinum ultramicroelectrode.¹⁶⁾ The technique has been widely applied for the preparation of the tips in the field electron and ion microscopy¹⁷⁾ and in recording intracellular potentials from single living cells.¹⁸⁾ This method is very

convenient, straightforward and extended to other metals and carbon.

In this study, we extend this method to the fabrication of Au and carbon micro-electrodes. We have investigated various conditions of the anodic electropolishing. Consequently, the most smooth surface of polished Au wire was obtained in an aqueous solution containing concd. HCl : concd. HNO_3 = 1:1 (v/v) and that for carbon fiber was obtained in a 3 mol dm^{-3} KOH aqueous solution. A counter electrode was a thick Pt wire with a diameter of 1 mm and a length of 5 cm. Commercially available Au wire (diameter; $20 \mu\text{m}$) and carbon fiber (UCC Pitch Fiber USC-32S, diameter; $10 \mu\text{m}$) were dipped into each polishing solution and anodically polarized by a periodic square wave of 1-50 Hz using a potentiostat (Solartron model 1186). We have prepared many tips under various conditions and it was found that amplitude of square wave critically affected the shape of the cone and the smoothness of the surface. An increase in the amplitude caused rough structure of the surface. The best amplitude of the waves were about 1.5 V on Au and about 2.0 V on carbon. The polishing current was switched off automatically,¹⁹⁾ when the polishing current decreased rapidly. This method allowed us easily to prepare the tips of a few micrometers. However, the final polishing to obtain a finer wire was carefully carried out by manually applying stepwise pulses.

Figure 1 shows a typical example of a scanning electron micrograph (SEM) of the carbon tips electropolished as described above. The photograph was taken at a magnification of 2000. It can be seen that the radius of the carbon fiber usable for the electrode is less than 500 nm and the surface of the polished carbon fiber is relatively smooth. Using our conditions, fine wires with the radius of this size have been reproduced very easily. Figure 2

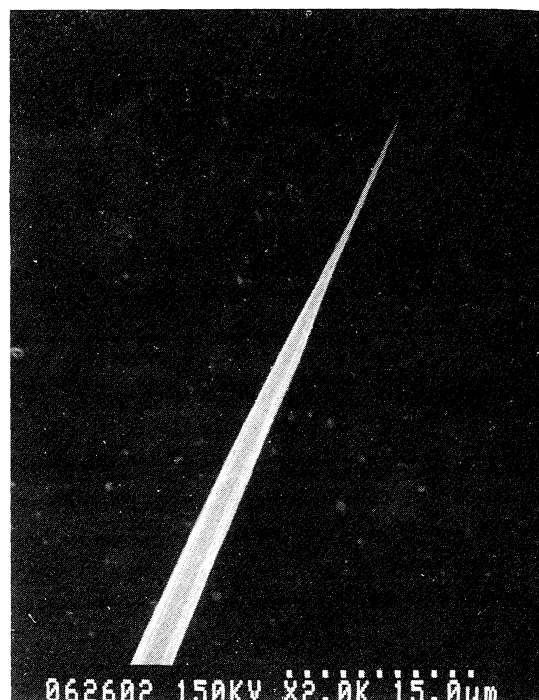


Fig. 1. A scanning electron micrograph of the carbon fiber. The photograph was taken at a magnification of 2000.

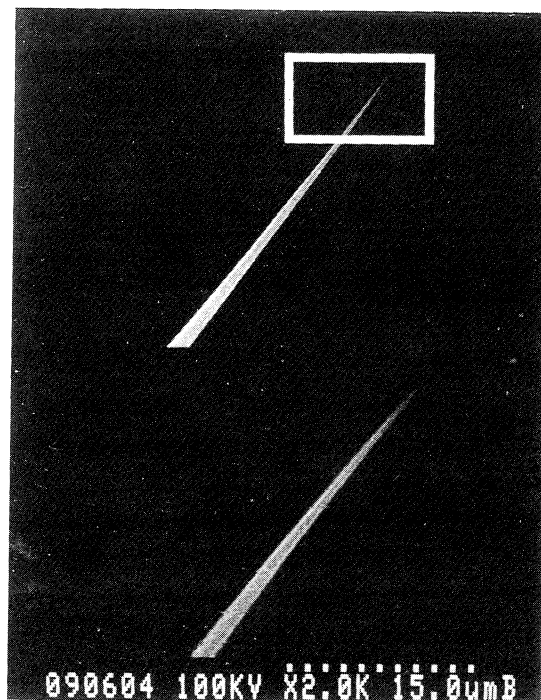


Fig. 2. A scanning electron micrograph of the Au wire. The photograph was taken at a magnification of 2000.

shows a typical example of a SEM image of the Au tip. The photograph was taken at a magnification of 2000. The shape of Au wire tips electropolished was almost the same as that of the carbon fiber. It can be considered that the manufacturing of the present ultramicro-electrode is more useful than that of using Wollaston wire method described by Bond et al.,¹⁰⁾ because this method is available to the carbon and the shape of the fine wires prepared in this study has a tapered cone. The upper portion of the unetched wire was directly soldered to the central conductor of a co-axial cable.

The tips fabricated by electropolishing were covered with SiO_2 thin film by RF sputtering and then sealed into an epoxy resin (Quetol 812; Nisshin EM (Tokyo)) at 60 °C for 24 h. The electrodes in the sealed assembly were exposed by cutting the epoxy resin with a diamond knife (Diatome) attached to an ultra-microtome (Porter-BLUM model MT2-B). Note that the electrode surface is easily renewed by cutting the tip in the present method before each experiment.

Figure 3 shows a typical example of the cyclic voltammogram of 5 mM $\text{K}_4\text{Mo(CN)}_8$ at the carbon microelectrode in a 0.1 M KCl aqueous solution. A two-electrode configuration, not using a potentiostat, was employed for the electrochemical measurements. A saturated calomel electrode (SCE) was used as a counter electrode. Small currents were measured with a high speed current amplifier (Keithley model 427). All measurements were carried out in an aluminum sealed box and the influence of the noise was excluded from the measurements. The half-wave potential,²⁰⁾ $E_{m/2}$, was determined as 0.55 V vs. SCE which is in complete accord with the literature value.²¹⁾ The steady-state diffusion controlled limiting current (I_d) is about 200 pA as shown in Fig.3.

The limiting current (I_d) at a microdisk electrode is expressed by the following equation,^{13,20)}

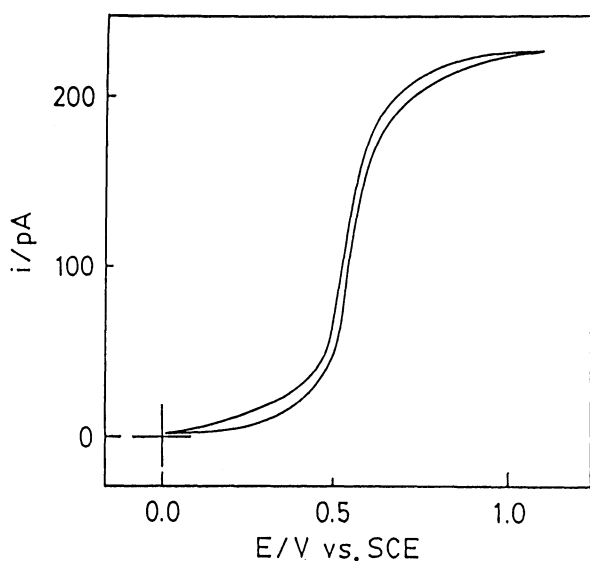


Fig. 3. Cyclic voltammogram of 5 mM $\text{K}_4\text{Mo(CN)}_8$ in 0.1 mol dm^{-3} KCl at a carbon ultramicro-electrode. Scan rate is 50 mV/s.

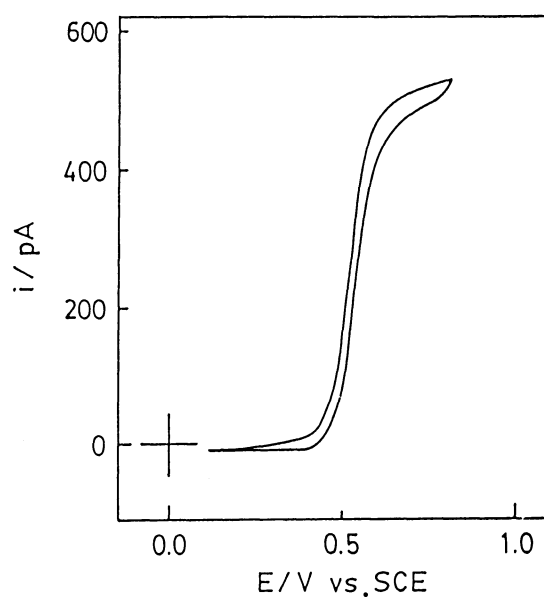


Fig. 4. Cyclic voltammogram of 5 mM $\text{K}_4\text{Mo(CN)}_8$ in 0.1 mol dm^{-3} KCl at an Au ultramicro-electrode. Scan rate is 50 mV/s.

$$I_d = 4nFCDa \quad (1)$$

where n is the number of electrons transferred, F the Faraday constant, D the diffusion coefficient of the electroactive species, C its concentration, and a the radius of the microdisk electrode. From Eq. 1, the radius of the carbon microelectrode shown in Fig.3 was calculated as 240 nm using the diffusion coefficient of $4.6 \times 10^{-6} \text{ cm}^2/\text{s}$ obtained in potential-step chronoamperometry on an usual disk electrode with a diameter of 2 mm. The standard rate constant, k^0 , of $\text{Mo}(\text{CN})_8^{4-}$ is reported as 0.5 cm/s.²¹⁾ It is noteworthy that a plot of $\log[(I_d - I)/I]$ vs. potential (E)¹¹⁾ showed a slope of 65 mV, close to the predicted value, 59 mV, for a reversible electron transfer. But the small deviation from the Nernstian behavior may be the influence of electron-transfer rate on the electrode. Recently, Aoki et al. reported a theory of stationary current-potential curves on microelectrodes for quasi-reversible and total irreversible electrode reactions.²²⁾ Figure 4 shows a typical example of the cyclic voltammogram of the Au microelectrodes in the same solution. The radius of the Au microelectrode is calculated to be about 450 nm from Eq. 1.

The above results and previous paper¹⁶⁾ demonstrate clearly that the method discussed here provides a standard approach for the fabrication of the ultra-microelectrodes. More recently, the Pt ultramicroelectrode in radius of about 10 nm was fabricated in our laboratory. The measurement of the fast heterogeneous electron-transfer rate constant from a steady-state voltammogram will be possible on such an ultramicroelectrode by using the theory of Aoki et al.²²⁾ The details will be published elsewhere.

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