# A SIMPLIFIED METHOD OF THE PREPARATION AND TESTING OF PT MICROELECTRODES SEALED IN GLASS

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*Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.*

A simplified method was used for the preparation of Pt microelectrodes sealed in glass. Electrodes were fabricated without the help of vacuum and by sealing them in soft glass capillaries. The use of SIAL and SIMAX glass produced microelectrodes with much higher and ill-defined background currents. The regular shape of voltammograms, typical for Pt, can be used as a simple test of the perfection of microelectrodes.

Microelectrodes from platinum, gold, mercury and graphite having one dimension less than 25 μm have been investigated intensely during recent years. Such electrodes consist of metallic disks, cylinders, rings, spherical mercury drops, graphitic fibers, and various arrays of such elements have been fabricated. Compared to electrodes of larger dimensions microelectrodes offer significant advantages in electrochemical measurements.

Due to the predominant spherical diffusion, a steady-state response can be obtained at appropriately low sweep rates of voltammetric experiments. Determination of the rate of heterogeneous electron transfer reaction and the rate constant of the homogeneous chemical reaction can be extended to more rapid processes. The decrease of the IR drop and the favourable ratio of faradaic to charging currents allows the use of microelectrodes in less polar solvents, lower supporting electrolyte concentrations and faster sweep rates.

Several constructions of platinum-disk microelectrodes have been reported[1 - 14]. The procedure involves sealing the platinum micro wire in glass or making a seal of Pt to glass with epoxy. This latter method seems to be simple, but it produces inferior electrodes[4,9]. Traces of epoxy can contaminate the platinum surface in the course of polishing and epoxy cement can be attacked by organic solvents and by strong acidic or alkaline aqueous solutions.

The reported procedures of sealing of Pt micro wires in glass use tubes and capillaries from Pyrex or soft glass for this purpose. A vacuum was usually applied to enable a better adhesion of glass to metal. A detailed description of the fabrication of platinum-disk ultramicroelectrodes has been published by Baer et al.[11].

In our microelectrode fabrication we followed initially this published procedure[11]. We have found, however, that the application of the recommended procedure can result in microelectrodes of inferior quality. The use of Pyrex glass or different glass with a low thermal expansion coefficient can result in microelectrodes with relatively high background currents.

It is known that the Pt wire having a greater coefficient of thermal expansion than Pyrex, must be thin enough when sealed in this type of glass. Such seals will be liquid-tight but are not intended for use with vacuum. Microscopic cracks or leaks between Pt and low-expansion glass can result in the distortion of voltammetric response of microelectrodes, which are apparent mostly at relatively low rates of voltage scan.

On the other hand, Pt in soft glass seals are made easily gas-tight since soft glass and platinum have about the same coefficient of expansion. Microelectrodes fabricated with the use of a soft, high-expansion glass exhibit therefore better quality which is manifested by substantially lower background current in voltammetric investigations.

The sealing of a Pt micro wire in the soft glass required, however, a modification in the described procedure by Baer et al.[11]. Our experience with this altered and at the same time simpler method of the microelectrode fabrication will be described in this contribution.

## EXPERIMENTAL

Platinum micro wires of 6 and 25 μm diameters were used. Both were purchased from Goodfellow Metals Limited (England). The thinner one was delivered as Wollaston wire, where the Pt micro wire is covered by an Ag envelope.

Three types of glass were used for the sealing of Pt micro wire. They differ in the thermal expansion coefficient: SIAL and SIMAX glass (Kavalier, The Czech Republic) had low values of the coefficient ($48 \cdot 10^{-7}$ $K^{-1}$ and $32 \cdot 10^{-7}$ $K^{-1}$, respectively) and a soda lime glass (from the same manufacturer) was a typical soft glass with about the same expansion coefficient as platinum ($90 \cdot 10^{-7}$ $K^{-1}$).

It was found, that electrodes fabricated with the help of vacuum deflation of a light-walled glass tube towards a Pt micro wire exhibited often formation of many small bubbles in glass. These bubbles were concentrated in the close vicinity of the sealed wire and considerably impaired the seal. This effect was apparent mainly in the seal of Pt in a soft glass.

We have tried to avoid this formation of micro bubbles by the preheating of the Pt wire and by a desorption of the gases from the glass capillary. Pt micro wire was heated by the flow of current to a red glow and the capillary with the inserted Pt wire was then heated under vacuum to 300 °C for 3 h. The sealing of the wire in glass then followed without suspension of this vacuum.

We found, however, that even in this case the seal was often deteriorated by microscopic bubbles. Blank experiments, when the SIMAX glass capillaries and capillaries from the soft glass were sealed in vacuum (about 1 mPa) even in the absence of Pt micro wire, have shown that the formation of gas

bubbles along the seal most probably originate from the thermal decomposition of glass. A parallel experiment using a Pyrex glass capillary resulted in a seal without any bubbles.

On the other hand we proved that seals of our SIMAX or soft glass capillaries under atmospheric pressure were free of any microscopic bubbles.

These results have led us to the application of a procedure for the fabrication of Pt microelectrodes without the use of vacuum in the course of sealing. Such a method is much simpler and in addition can be used for seals in thermally less stable types of glasses.

Typically a 20 cm piece of 3 mm i.d. by 4 mm o.d. clean glass tube was drawn out along a 1 cm section in the middle to a diameter which allows a close passage of the Pt wire. A 1 cm length of the Pt wire in 25 μm diameter (or Wollaston wire with a Pt core of 6 μm diameter) was cut out. At one end of this wire a small hook was made and then the wire was dropped into the glass tube in such a way that it was trapped by its hook in the narrow-drawn section of the tube.

The wire was cleaned with acetone and alcohol. Silver coating from the Wollaston wire was then dissolved with 50 wt.% nitric acid. The glass tube with the wire was carefully lowered so that the acid reached several millimetres below the hook at the end of the wire. The dissolution was complete within 10 or 15 min. The wire was then rinsed with dilute ammonia and distilled water applied on the top of the glass tube. After the rinsing the glass tube with micro wire was dried.

Both ends of the glass tube containing the wire were fitted in vertical position with the hooked end of the wire pointing upwards by means of two metallic clamps (see Fig. 1*a*). The section of the glass tube below the constriction and above the fitting had to be heated to softness in order to relieve the strain in the glass. This procedure will prevent any distortion of the glass in the course of sealing of the micro wire.

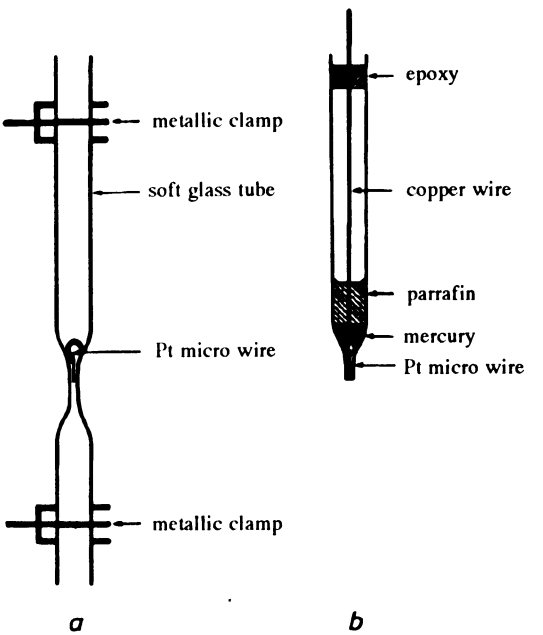


FIG. 1
Diagram of two stages of fabrication of Pt microelectrode. *a* The Wollaston wire in a constricted glass tube, the silver coating at the end of the wire is etched off; *b* the finished microelectrode

The tube was heated by means of an oxygen–natural gas flame. The sealing of the glass tube should start below its constriction and very slowly continue upward along the constriction to the hook in the Pt wire. The location where Pt joins Ag has to be sealed into glass, but the end of the hook should be free to ensure the electrical contact to the micro wire. With a magnifying glass or a microscope it can be verified that the Pt micro wire remains continuous and glass adheres free of bubbles to it.

The glass tube was cut off in the constricted section below the sealed micro wire. The cut surface of glass was ground off by means of a relatively low-grade emery paper (SIA 3/0, Switzerland) to expose a cross-section of the sealed Pt wire. The surface of the exposed disk was then polished, first with high-grade emery paper (SIA 6/0, Switzerland) and then with diamond pastes M10, M5 and M1 (Pramet, The Czech Republic), with the grain size 10, 5 and 0.1 μm, respectively. The electrode was then washed with acetone, distilled water and polished with alumina suspension (Aluminiumoxid Sorte 3, Chemie-Werk Greiz–Dolau, Germany) on polishing cloth and, subsequently, on a wet cloth only to remove the adhering alumina particles. The size of the exposed Pt micro disk and the precision of the polishing was controlled with a metallographic microscope (Zeiss, Germany) with the magnification gradually increased up to 500 times.

Electrical contact with the Pt micro wire was made by the addition of a small amount of mercury which covered the exposed hooked end of the wire inside the glass tube. A 1 mm thick copper wire was put in contact with the mercury and a paraffin layer introduced into the glass tube sealed the copper wire and mercury in. The upper end of the copper wire was fixed at the top of the glass tube by means of epoxy resin. A schematic drawing of the final stage of the electrode fabrication is shown in Fig. 1*b*.

Voltammetric experiments with the microelectrodes were done in a three-electrode cell using a potentiostat (Wenking Model ST 72, G. Bank, Germany), programmed voltage generator, picoammeter (Keithley Model 485, U.S.A.) and an X–Y recorder (NE-240, EMG, Hungary) with preamplifier, connected to the analog output of the picoammeter. A well grounded shielding of the electrochemical cell was used to suppress disturbing pick-ups.

Voltammetric measurements were done in a solution of 0.5 M $H_2SO_4$ deoxygenated with argon. A mercurous sulfate (in 0.5 M $H_2SO_4$) reference electrode was used (potential +680 mV vs SHE).

## RESULTS AND DISCUSSION

It can be seen in Fig. 2 that both Pt micro wires with the diameter of 25 and 6 μm, respectively, can be sealed in soft glass by means of the described procedure to produce well functional microelectrodes. Cyclic voltammograms with these electrodes in $H_2SO_4$ gave typical responses of Pt electrodes even in the region of low rates of potential scans. These microelectrodes have relatively low values of their roughness factor in the range of 3 – 5, which do not increase markedly during the time of scanning.

On the contrary the sealing of the Pt micro wire into a glass with a lower coefficient of expansion (e.g. in SIAL or SIMAX) resulted in microelectrodes with much higher and ill-defined background current.

Such substantially higher background currents can be explained by the gradual filling of the capillary micro space between Pt and the low-expansion glass with electrolyte and oxygen. The cathodic reduction of oxygen proceeds in these micro leaks in the condition of considerably higher ohmic resistance which apparently shifts the potential

of this electrode reaction. The resulting parasitic currents can be quite high and can distort the voltammetric curves of such electrodes predominantly at low sweep rates of between 10 and 200 mV/s. This disadvantageous behaviour of such electrodes can result in the deterioration during the time of scanning and seriously interfere with applications of microelectrodes sealed in SIAL or SIMAX in electrochemical study of transient effects.

The difference in behavior of microelectrodes sealed in a soft glass and in a low-expansion glass is less distinct in measurements of steady state responses, where background currents on microelectrodes play less important roles. On the contrary, voltammetric studies of such electrodes accentuate any imperfections in the sealing of Pt micro wire in different types of glasses. Regular voltammograms for low scan rate, typical for Pt electrodes in the region of the surface oxide formation and reduction, can be used therefore as a simple test of the perfection of microelectrode fabrications.

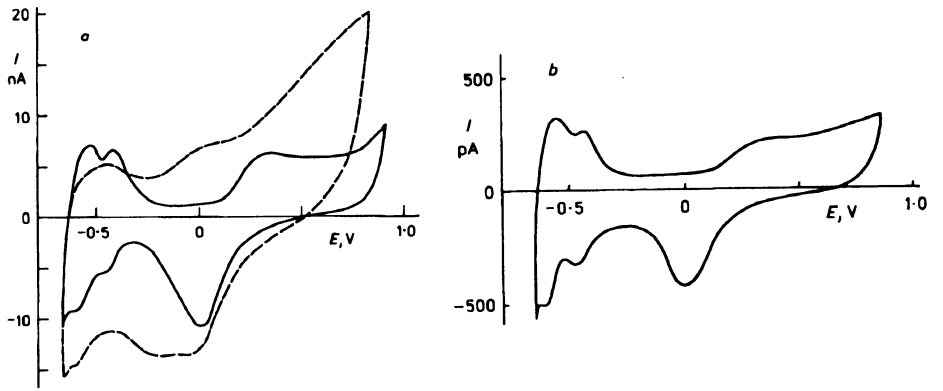


FIG. 2
Cyclic voltammogram for Pt microelectrode, diameter 25 μm (*a*) and 6 μm (*b*). Scan rate (mV/s): 200 (*a*), 20 (*b*). Supporting electrolyte 0.5 M $H_2SO_4$. Electrode sealed in: a soft glass (——), SIAL glass (– – –). Potential values given vs mercurous sulfate reference electrode

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