

Benign making of sharp tips for STM and FIM: Pt, Ir, Au, Pd, and Rh

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BRIEF REPORTS AND COMMENTS

This section is intended for the publication of (1) brief reports which do not require the formal structure of regular journal articles, and (2) comments on items previously published in the journal.

Benign making of sharp tips for STM and FIM: Pt, Ir, Au, Pd, and Rh

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Sharp tips for various modern microscopies, such as field-ion microscopy (FIM) and scanning tunneling microscopy (STM), can be prepared by electropolishing in solutions which are relatively innocuous for the environment as well as the researcher, compared to the often hazardous solutions still in widespread use. We have made measurements of polishing times as a function of solution and voltage parameters and we report conditions for electropolishing sharp tips of Pt, Ir, Au, Pd, and Rh using relatively benign solutions. © 1995 American Vacuum Society.

I. INTRODUCTION

Several microscopies rely on sharp electron or positive ion sources (tips), or neutral points, for achieving high resolution, and the technical literature is replete with articles devoted to descriptions of techniques for preparing such tips. Harsh, noxious, and dangerous-to-use electrolytes are often recommended for electropolishing some materials. Thus, for example, aqueous solutions of KCN are often used for making sharp tips of Pt, Ir, Au, Rh and their alloys, and HCl/HNO₃, with or without a CCl₄ layer, for Pd.¹⁻³ Occasionally, more benign electrolytes are suggested, such as KCl+HCl+H₂O for Pt.² A recent review⁴ addressed a variety of relevant techniques and included a discussion of electrolytes for Pt-Ir tip making, in which the use of CaCl₂, NaCl, or KCl was suggested.

This work was done to establish, in a systematic manner, some relatively benign electrolyte solutions, concentrations, and voltages suitable for making sharp tips of Pt, Ir, Au, Rh, and Pd. Since the use of dc voltages is known to be ineffective in electrolytically dissolving these metals, we only used ac voltages. The processes which occur under such conditions are rather complicated, typically involving oxidation, reduction, and random gas bubble formation, as well as diffusion of anions and cations and the formation and flow of reaction products. Understanding the detailed mechanisms of tip formation was not our motivation for the work; rather, we wanted to define approximately some parameters for reproducibly making sharp tips from selected metals. We find that the most convenient method for making sharp tips is a two-step process,⁵ with the second step done under an optical microscope at about $\times 500$ to $\times 600$ magnification. The first step is intended to make a smooth and approximately sharp tip (about a micron in diameter with a full apex cone angle less than about 20°). These tips are then fabricated into very sharp tips with a selected cone angle during the second step. The work presented here is a study of the first step, but we have also generally done the second-stage sharpening for each of the metals as well, and an example is given for Pd.

II. EXPERIMENTAL APPROACH

A selection of electrolytes was made on the basis of past experience and the literature. Thus, we mainly used aqueous solutions of CaCl₂, NaCl, KCl, NaBr, and occasionally tried HCl or another electrolyte. Only ac voltages were used.

For CaCl₂, NaCl, KCl, NaBr, the electrolyte solution concentration was determined by adding water to initially saturated (at room temperature) stock solutions. This is a relatively simple procedure, but it should be remembered that the actual amounts of active chemicals in the solutions depend on the solubilities of the particular chemicals. For example, a 10% solution of CaCl₂ has a Cl ion concentration 1.75 times greater than in a 10% solution of NaCl.

The tip-making procedure, in a conventional way, was to immerse a clamped wire 3 mm into the electrolyte, and to apply a measured voltage between the wire and a graphite counter-electrode. The time required for completion of the process, that is when no further electrolytic activity occurred, was determined by visual observation or by the electrolytic current reaching zero.⁶

All of the tips were examined with an optical microscope. In addition, a conventional scanning electron microscope was used to look at some tips, and a low-temperature field ion microscope was used to test the sharpness in more detail for Pd. At least one tip of each metal made using each electrolyte was also fine-polished by microzone electropolishing⁴ to demonstrate the use of the electrolytes for making tips with sub-100 nm apex radii.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The reaction rates generally increased with increasing voltage, as expected, and this led to completion times which decreased with voltage until excessive gas evolution and consequent frothing caused an increased area of liquid and metal, resulting in increased completion times. The completion times tended to decrease with increasing electrolyte concentration, with a few surprises in detail, but then to increase at high chloride concentrations, for example, above about

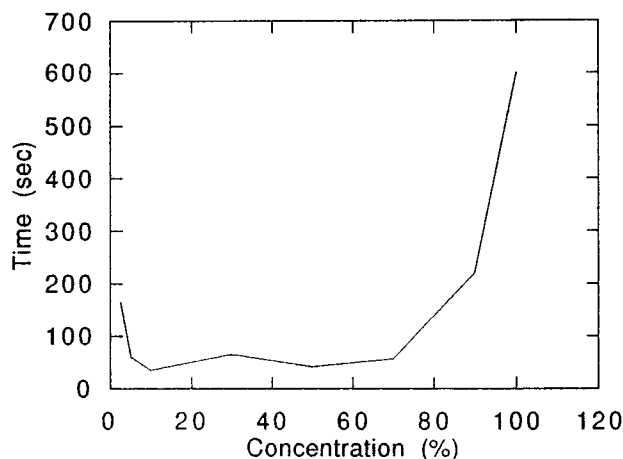


FIG. 1. Electropolishing time vs CaCl_2 concentration for 0.125 mm Pt, at 20 V.

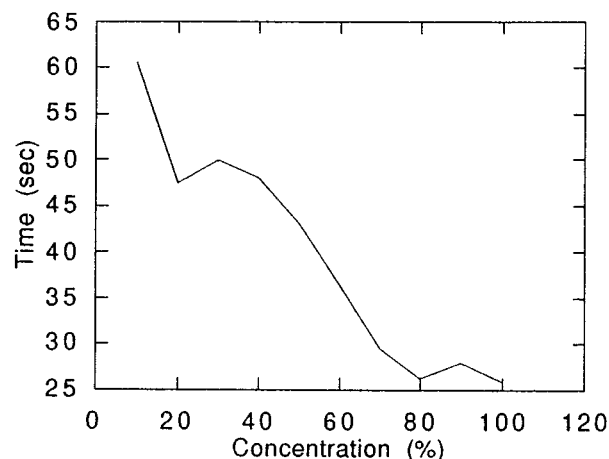


FIG. 2. Electropolishing time vs NaCl concentration for 0.125 mm Pt, at 20 V.

65% sat. CaCl_2 . The quality, judged by smoothness, apex cone angle, and sharpness of the resulting tips, varied over the regimes of composition and voltage, and for this we cannot generalize. Instead the results for individual metals are given and discussed below. We use the term “good tip” in this report to designate a tip which, in the optical microscope at a magnification of $\times 600$, appeared to be smooth and regularly tapered to a tip diameter of about one micron or less, or one which is smooth, regularly tapered to a diameter of about a micron, and terminates in a ball-end. Both of these shapes are suitable for easy second-stage polishing to very sharp points by microzone electropolishing.

IV. THE INDIVIDUAL METALS

A. Platinum

Experiments were done using 0.125 and 0.25 mm diam Pt wires and it was found that good tips could be produced with electrolytes of CaCl_2 , NaCl , KCl , and NaBr in certain solution concentrations. Typical results for time-to-completion of the electropolishing action as a function of electrolyte solution concentration are shown in Fig. 1 for 0.125 mm Pt in CaCl_2 solution at 20 V. Figure 2 shows a plot of time-to-completion versus concentration for making Pt tips in NaCl at 20 V.

Good results for Pt in CaCl_2 were obtained at voltages from 20 to 30 V in solutions of 30%–50% saturated concentration. For NaCl , good results were obtained at 30–40 V and solution concentrations of 10%–90% saturation, and for CCl at 20–30 V and solutions of 30%–50% saturation. For NaBr , we used 0.250 mm diam wire and got good results almost exclusively at 30 V in solutions of 30%–100% saturated concentration.

It is interesting to note that the electropolishing rate for Pt in the chloride electrolytes we tested appears to be related directly to the chloride ion concentration, independent of the cation.

B. Iridium

Ir wire with 0.075 mm diameter was electropolished in the same set of solutions used for Pt, and gave similar results. However, Ir polished more slowly than Pt; typically, the time required for making an Ir tip from the 0.075 mm diam wire was about the same as the time required for making a Pt tip from the 0.125 mm diam wire.

C. Gold

Au wire of 0.203 mm diameter was electropolished in the same set of electrolytes. However, we note that NaBr solutions gave only negative results. Good Au tips were obtained at 30–40 V for CaCl_2 solutions of 10%–50% saturation, and at (almost exclusively) 10 V for NaCl solutions of 30%–100% saturation. For KCl , we tested only 70% and 90% saturated solutions, and good tips were obtained at 10 V. Figure 3 displays scanning electron microscopy (SEM) micrographs of a good tip. Significant deviations from such smoothness were not considered acceptable.

D. Palladium

It has been known for many years¹ that sharp tips of Pd can be made by electrolytic polishing in an HCl/HNO_3 mixture, and this established electrolyte was recently rediscovered.³ In the present work, Pd wires of 0.1 and 0.25 mm diameter were electropolished in aqueous solutions of NaCl , KCl , CaCl_2 and HCl , and in HCl in glycerine.

First-stage electropolishing in these solutions was straightforward, although we found that HCl in glycerine generally gave the smoothest tips. As stated above, we generally use microzone electropolishing for fine sharpening in a second stage. However, from our experience, we are confident that sharp Pd tips could be produced in a single-stage procedure, either by finding the appropriate solution concentration, voltage, and immersion depth, or by reducing the voltage as the sharpening process proceeds. We find the two-stage procedure to be more convenient, in general, allowing more control of the electrolytic process, including the easy use of different solution concentrations in the two stages, if

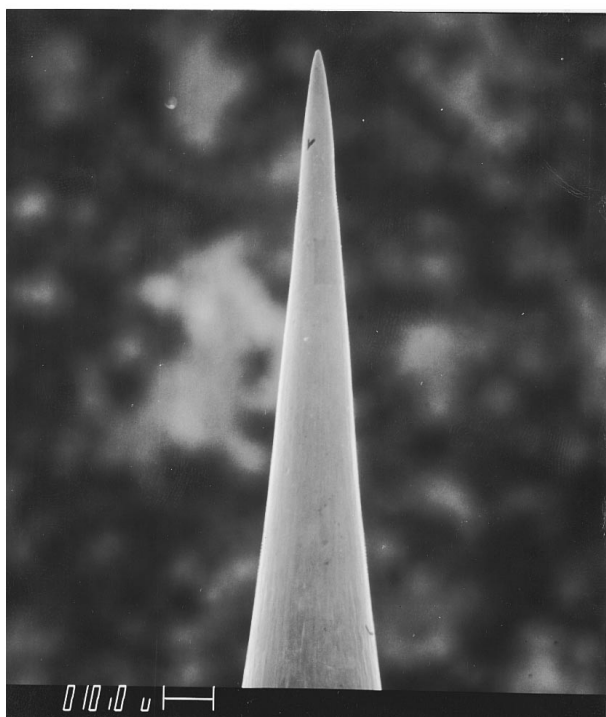
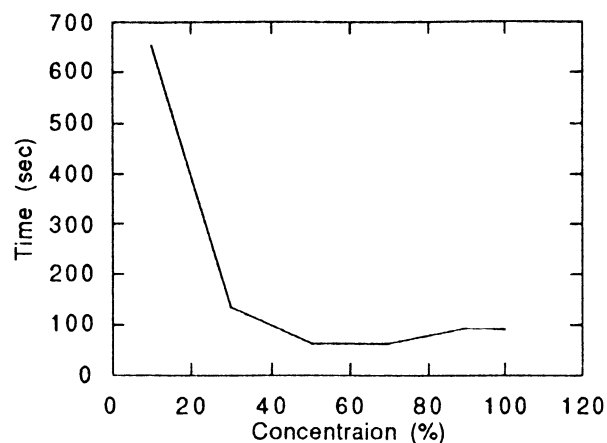


FIG. 3. Electropolishing Au (0.203 mm diameter) in CaCl_2 . (Upper) Time vs solution concentration, at 35 V; (lower) SEM micrograph of a good tip, 650 \times , electropolished in 10% CaCl_2 at 30 V.

desired. The most controllable results for Pd were obtained by using a more dilute solution than that used in the first stage (as is generally done in the second stage), or by using the same or lower concentration solution with a current-limiting resistor in the voltage circuit. In Fig. 4, we show an SEM micrograph and a neon field ion micrograph of sharp Pd tips as an example of electropolishing (both stages) in HCl /glycerine. Good Pd tips were obtained (first stage) at 10–40 V for 10%–100% saturated. NaCl , at 30 V for 20% saturated. KCl (explored less systematically), at 15–25 V for 35% saturated CaCl_4 and at 10 V for 38% HCl in water or in glycerine.

E. Rhodium

Recently, one of the authors (A.J.M.) prepared a few rhodium tips for field-ion microscopy (FIM) experiments in

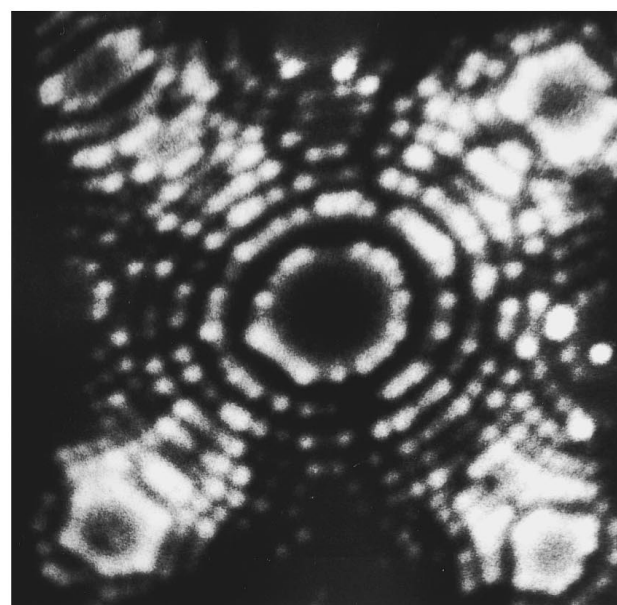


FIG. 4. Pd tips after two stages of electropolishing in HCl /glycerine. (Upper) SEM micrograph, $\times 1000$ magnification and (lower) neon FIM micrograph of another tip, $\times 5\,000\,000$ magnification. The average tip radius is 15 nm.

another laboratory (with M. Naschitzki at the Fritz-Haber-Institut der Max-Planck Gesellschaft, Berlin, Germany). The starting material was 0.125 mm diam rhodium wire. First-stage electropolishing was done in 70% saturated NaCl at 25 Vac, and then microzone electropolishing was done in 33% saturated NaCl at 5–10 Vac. The entire process required about 20–30 min.

V. A CLARIFICATION

It was suggested earlier⁴ that one of us (A.J.M.) “prefers to use a solution of about 50% CaCl_2 by volume in water”

for making Pt–Ir tips. This was innocently based on experience in making a fast-polishing solution by pouring coarse granular CaCl_2 into a beaker, up to the half-volume mark, and then adding water. If fine-powdered CaCl_2 is used instead, the solution will be too concentrated.

VI. SODIUM BICARBONATE

An interesting series of observations was recently made by one of us (A.J.M.). Aqueous solutions of 50%–100% sodium bicarbonate, NaH_2CO_3 , packaged for consumer use, were shown to function very well as electrolytes for making sharp tips of Pt, Pt–Ir, and also W, using ac voltages. First-step polishing of 0.25 mm diam Pt–Ir, for example, using a 50% saturated solution at 32 V, produced a smooth tip in 220 s, and a similar result was obtained using 0.25 mm diam W wire at 21–35 V; the tip-making times were 135 and 63 s, respectively. Second-state electropolishing⁵ to produce very sharp tips was done using a 5%–10% saturated solution at about 7 V, under an optical microscope. It is very interesting that these solutions did not noticeably attack the Au wire, which allowed use of the Au wire to contain the electrolyte in the second-stage electropolishing procedure.

VII. CONCLUSIONS

It is practical to make sharp tips of Pt, Ir, Au, Pd, and Rh by electrolytic polishing in relatively benign solutions. We have presented solution concentrations and voltages which gave us good results with the metals listed. We note that the solutions we report store well for long periods of time. Electropolishing of sharp tips using ac voltages is accompanied by some complex processes and is dependent on several parameters. Impurities in the chemicals used are but one example. The results we have given, therefore, should be taken as an approximate guide and actual voltages should be chosen by a few quick trials with the selected electrolytic solution, wire diameter, and immersion depth.

¹E. W. Mueller, *Z. Elektrochem.* **61**, 43 (1957).

²E. W. Mueller and T. T. Tsong, *Field Ion Microscopy Principles and Applications* (Elsevier, New York, 1969).

³L. Huang and Y. H. Lee, *Rev. Sci. Instrum.* **64**, 3022 (1993).

⁴A. J. Melmed, *J. Vac. Sci. Technol. B* **9**, 601 (1991).

⁵A. J. Melmed and J. J. Carroll, *J. Vac. Sci. Technol. A* **2**, 1388 (1984).

⁶R. J. Morgan, *J. Sci. Instrum.* **44**, 808 (1967).