

AN ELECTROPOLISHING CELL AND PROCEDURE TO PREPARE CORRELATED TEM/APT SAMPLE HOLDERS FOR PRESOLAR GRAINS. P. Bhadharla and J. B. Lewis, Laboratory for Space Sciences, Physics Department, Washington University, St. Louis, MO 63130. USA. Email: pranav.bhadharla@wustl.edu

Introduction: Presolar silicon carbide (SiC) grains are the most extensively studied type of presolar grain [1,2], but the size fraction under 200 nm in diameter is less well-characterized than larger grains due to limitations of the instruments used to study the isotopes, trace elements, and subgrains that inform our understanding of where the SiC grains formed. Work is ongoing to adapt atom-probe tomography (APT), a mass spectrometry technique with sub-nm spatial resolution, for study of presolar SiC [3–6]. APT can be correlated with transmission electron microscopy (TEM) analysis [7] to characterize and confirm sample morphology, crystallography, grain boundaries, and subgrains. A commonly used sample holder for these correlated analyses is a Cu half-grid with narrow posts (Figure 1). However, the posts on commercial half-grids need to be refined so they are thin enough to properly mount an APT sample (2 μm base diameter, Figure 2) [7]. Electrolytic polishing or anodic dissolution, commonly known as electropolishing, is an effective thinning process. Electropolishing requires a conductive specimen that is used as an anode in a circuit. The specimen is immersed in an acidic solution through which a current runs, sharpening the specimen through an electrochemical process [8]. When electropolishing half-grids, there are many different factors that must be controlled to ensure the posts are polished to the proper thickness, without etching or pitting. These factors include voltage, molarity of the acidic solution, and time of electropolishing. Voltage and current density are the determinants of etching, polishing, or pitting [8]. Too low of a voltage etches the half-grid while too high causes pitting. Using available lab and shop resources we developed a low-cost electropolishing cell and procedure, designed for ease of use and reproducibility, to support correlated TEM/APT experiments.

Method: Our initial electropolishing cell consisted of a Hewlett Packard Harrison 6205B Dual DC Power Supply that was being run in constant voltage mode, a sample holder with a cable terminal and a copper holder, phosphoric acid, methanol, a variable height holder for a 50 mL beaker, Omni Probe Cu 5 Post Lift-Out Grids with 40 μm nominal thickness, a cathode made out of a U-shaped strip of stainless steel with a cable terminal and two electric cables (Table 1). Eventually, a multimeter and two more cables were added to obtain a more specific reading. It is important to note that the multimeter measured the voltage drop across not just the half-grid but also the electrolyte and electrode. A cable was attached from the power source to the sample holder which held the half-grid. The holder was designed with nonconductive PVC parts surrounding a

feed-through for the wire. A smooth-jaw alligator clip plugged into a ball and socket, allowing for precise orientation of the half-grid in relation to the electrode. The clip could be removed for easy grid loading and unloading. The half-grid was submerged into a solution of phosphoric acid and distilled water. After each trial, the half-grid was submerged in a 10 ml beaker to clean it. The half-grid was the anode in this circuit.

It was important to use the correct voltage, current, and molarity of acid so that the half-grid did not sharpen too quickly. If the polishing times were too short, the uncertainty was large, leading to results that were hard to reproduce consistently. An 8.5% solution followed by a 10% solution was used based on literature recommendations for Cu electropolishing to help obtain a current that would not etch or pit the specimen [8]. There were two ways to change the current: changing the voltage or the molarity of the solution. While changing the voltage typically caused less uncertainty because it was only dependent on the uncertainty of the multimeter, it was also possible to maintain a constant voltage while changing the current by adjusting the molarity of the electrolyte. After polishing, half-grids were observed under an optical microscope. If the outcome of the polishing was unclear, the half-grids were attached to carbon tape and imaged by secondary electron microscopy (Figure 2). A series of trials were run, with varying voltage, electrolyte molarity, and polishing time (Table 1). Starting in trial four a multimeter was used.

Results: The first trial produced a half-grid that was slightly wider than ideal but still usable for sample mounting of liftouts for TEM/APT samples. However, this particular procedure was not reproducible with high success. At higher voltages, more uncertainty was introduced into the measurement due to the time it takes to disengage the circuit. This led directly to a low success rate. Lowering the voltage allowed for longer polishing times, which gave significantly more consistent results (Table 1). In the end, the optimal polishing time was one minute and fifteen seconds, which produced half-grid posts thinner than 10 μm . Methanol proved to be the best solvent to clean half grids. Without methanol dipping, a greenish-blue residue was left on the sample by the phosphoric acid, while acetone dipping damaged the half-grids.

Discussion: The tests of our cell demonstrate it can achieve proper thinning of TEM half-grids with a procedure that takes only a few minutes, and can be easily reproduced, including by different users. Reducing the rate of polishing enough to extend the optimal polish-

ing time is key to minimizing the effect of timing uncertainties. Use of a multimeter in the system adds significantly to the precision with which the voltage can be measured. A methanol wash is important to prevent acid buildup on the grids. Our cell is easy to assemble for use and disassemble for storage. It is also important to note that this is a relatively cost effective, flexible, and accessible approach.

Electropolished half-grids are sharp enough that a few minutes of focused ion beam milling produces a flat post of about 2 μm in diameter, ready for attachment of any FIB liftout for correlated TEM/APT.

Outlook: Once samples are mounted we will introduce the half-grids into a standard TEM holder for analysis. Liftouts of small, <200 nm diameter presolar SiC grains from meteorite sections are the first application for which the electropolished half-grids will be used to enable correlated TEM/APT, but any liftout for APT can be mounted on these sample holders

The electropolishing cell itself can be adapted for polishing or thinning of other samples, given a conductive sample.

References: [1] Hynes K. M. and Gyngard F. (2009) *LPS XL*, Abstract #1198. [2] Zinner E. (2014) *Treatise on Geochemistry v1*, Elsevier, 181–213. [3] Stadermann F. J. et al. (2010) *LPS XLI*, Abstract #2134. [4] Heck P. R. et al. (2010) *LPS XLI*, Abstract #2112. [5] Lewis J. B. et al. (2014) *77th Meteoritical Society Meeting*, Abstract #5367. [6] Lewis J. B. et al. (2018) *LPS XLIX*, Abstract #1174. [7] Gorman B. P. et al (2008) *Microsc. Today* 16(4), 42–47. [8] Zipperian D. C. (2011) *Metallographic Handbook*, PACE Technologies, 129–138.

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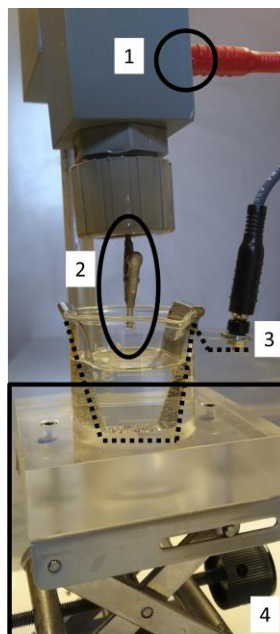


Figure 1: Electropolishing Cell (not including the power source or the multimeter). (1) Cable terminal for the sample holder. (2) Sample Holder. (3) U-shaped stainless steel strip (dashed line) with a cable terminal. (4) Variable height beaker holder.

Table 1: Polishing Trials

Trial Number	% H_3PO_4 ($\pm 0.5\%$)	Voltage ($\pm 5\%$) ¹	Current ($\pm 5\%$)	Time (± 0.5 s)	Results of posts
1	8.5%	3.7 V	20 mA	4.5 s	Usable. Too dull
2	8.5%	3.7 V	20 mA	4.5 s	Dull
3	8.5%	3.7 V	20 mA	6.2 s	Usable. Too dull
4	10%	1.5 V	25 mA	60.0 s	Sharp. Too short
5	10%	1.5 V	25 mA	50.0 s	Dull
6	10%	1.5 V	23 mA	90.0 s	Burnt off
7-10	10%	1.5 V	23 mA	75.0 s	Ideal sharpness

¹Voltage measured by power supply for Trials 1–3, and by multimeter across grid, electrolyte, and cathode for Trials 4–10.

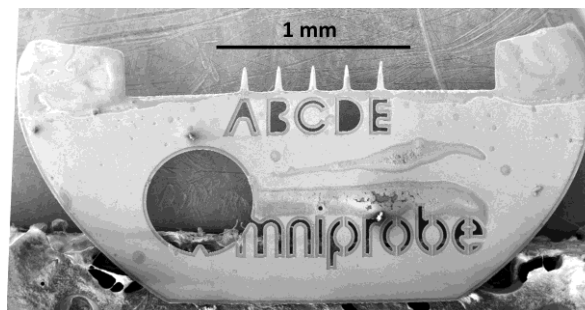


Figure 2: SE image of half-grid Trial 1 (see Table 1) after sharpening, attached to carbon tape. Posts are still too dull but may be usable.