Materials Science Division Project Safety Review
Safety Analysis Form (03/08)

Date of Submission	03/01/10	FWP No.:	58405

Project Title	Electropolishing TEM samples using perchloric acid/methanol solution This Safety Analysis Form (SAF) supersedes previous version of 4/17/2008.

Is this a (check one) new submission [ ] renewal [ ] supplemental modification [X]

Principal Investigator(s) M. A. Kirk

Other Participants (excluding administrative support personnel) Various EMC users of the IVEM

(Attach participant signature sheet)

Project dates:	Start:	03/01/10	End:	open-ended

This form is to be completed for all new investigations or experimental projects that are conducted in MSD laboratories, and for all ongoing such projects that undergo significant change from their original scope of work, or where there has been an addition of a potentially new hazard not covered in the original review. It is not intended to be used for office work, routine maintenance activities, or administrative tasks.

Experimental work may not be performed until the project safety review has been completed, procedures have been approved, and the work has been authorized (ESH Manual 21.2.3).

The completed form and all supporting documentation is to be submitted to the MSD ESH Coordinator by the principal investigator with sufficient advance notice and information to allow a project safety review prior to the beginning of the experiment. The information will be reviewed by the Division Director, members of the MSD safety review team, and by outside experts (if appropriate) for unresolved safety, health, and environmental issues associated with the proposed work. The principal investigator may be asked to resolve outstanding issues through consultations with the safety review team before the work begins. The information submitted will be reviewed by an independent review team, and final approval will be granted by the Division Director.

This form must be accompanied by a participant signature form once work has been authorized.

The principal investigator must be familiar with the responsibilities of a lead experimenter and the general requirements of the experiment safety review in the Argonne ESH Manual, section 21.2.

Useful references:
Argonne ESH Manual: http://www.aim.anl.gov/manuals/eshman/
Argonne Waste Handling Procedures Manual: http://www.aim.anl.gov/manuals/whpm/
MSD Chemical Hygiene Plan: http://www.msd.anl.gov/resources/esh/
Material Safety Data Sheets: https://webapps.inside.anl.gov/cms/msds/

Table of Contents[1]:

List of Attachments:

MSDS # 35597 for perchloric acid
User's Guide to the EMC Specimen Preparation Laboratory
SOP for using Tenupol with $HCLO_4$-Methanol electrolyte

[1] To update table of contents, right/command click inside table; from resulting contextual menu select "Update field", then "Update page numbers only"

1. Scope of Project (ISM Core Function 1)

1.1 General Description

Provide a general overview description of the project. While scientific background is important, concentrate on an operational description that focuses on the experimental work done in the laboratory.

TEM samples (3 mm in diameter and about 100 μm thick) of Fe, Fe-Cr, and other alloys, are thinned to electron-transparency by electropolishing them in the hood located in laboratory 212/DL126 , with a liquid-nitrogen-chilled solution of 5% perchloric acid, 2.1% water, and 92.9% methanol. The thinned specimens are quickly rinsed in several alcohol baths and then loaded into the IVEM (Hitachi H-9000 NAR TEM), sometimes using Nitrogen gas bagging. The electropolishing solution is mixed by adding the required amount of a commercially-available solution of 70% $HClO_4$ in water to methanol.

1.2 Modules of Project

Describe the various components that make up this project. Components can be pieces of equipment or specific hazardous or complex tasks within the project that require special training to use or perform safely. Indicate locations, even if the project consists of only one component. Indicate custodians for major equipment. Attach designs, drawings, or other useful descriptive material.

This project utilizes the commercial electroplishing apparatus from Struers (Tenupol-5), which is stored in G147. The custodian of this equipment is M. Kirk. An important component is the handling and use of perchloric acid as a portion of the electropolishing solution.

1.3 Project Limits

Define the range of samples, chemicals, physical conditions that you consider covered under this project review. For chemicals and samples include either specific cases that are considered extremely hazardous, e.g. silane, HF, etc., or general classes such as reactive metals, oxidizers, etc. In some cases it may be useful to define the envelope by specifically excluding certain hazard categories.

Only those participants with sample materials (generally ferritic alloys) that require electropolishing with perchloric solution and minimum air exposure prior to TEM are allowed to use this facility/procedure.

2. Hazard Analysis (ISM Core Function 2)

2.1 Hazard List

Hazard/Issue	Yes	No	Unknown
Does the proposed work, as you perceive it, intrinsically contain the following safety, health, or environmental issues or concerns?			
Chemical Hazards			
Use of toxic chemicals		X	
Use of flammable chemicals	X		
Use of carcinogenic chemicals		X	
Generation of hazardous or toxic wastes	X		
Use of explosive or highly reactive chemicals	X		
Use of strong acids or bases	X		
Use of carbon monoxide gas		X	
Use of hydrogen gas (above 4% concentration)		X	
Use of perchloric acid or perchlorate salts	X		
Use of hydrofluoric acid		X	
Nanomaterials			
Nanoparticles dispersible in air			
Nanoparticles dispersible in liquids			
Biological Hazards			
Work with Biosafety Level 2 or above[2]		X	
Radiological Hazards			
Use of radioisotopes (see section 6)		X	
Exposure to ionizing radiation (excluding radioisotopes)		X	
Generation of radioactive wastes		X	
Physical Hazards			
Use of Class III or Class IV lasers		X	
Use of cryogenic fluids	X		
Use of high magnetic fields		X	
Use of high voltage or high amperage equipment		X	
Electrical work on energized equipment (>50V)		X	
Operation of equipment at high vacuums		X	
Operation of equipment at elevated pressures		X	
Use of compressed gases	X		
Operation of equipment at high temperatures		X	
Hazardous Working Environments			
Working in areas with high noise levels		X	
Potential exposure to climatic extremes		X	
Working at elevated heights		X	
Entering confined spaces		X	
Use of self-contained breathing apparatus or respirators		X	
Work in areas of mechanical hazards		X	
Other (explain)[3]			

[2] Requires review by Institutional Biosafety Committee

2.2 Hazard Details

For all the hazards checked Yes or Unknown, provide specific details, including locations (unless obvious from 1.3). For highly hazardous or energetic chemicals, indicate specific chemicals, quantities used. For physical hazards, give quantitative details (e.g., voltages for electrical hazards, power and wavelengths of lasers).

Hazard	Detail
Flammable chemicals	Methanol and ethanol, 2 liters each.
Hazardous wastes	1. The acid solution (5% perchloric acid, 2.1% water, and 92.9% methanol). 2. Methanol used for washing the equipment and the samples (minute amounts of the acid will be present and, perhaps, some ethanol). 3. Paper towels used for wiping equipment (these towels are segregated in sealed containers and kept wet).
Highly reactive chemical	Perchloric acid is a strong oxidizer. See below for details.
Strong acid	Perchloric acid; see below for details.
Perchloric acid	Typically use <100ml of commercial solution of 70% perchloric acid in water per experiment. Total use of about 6 weeks in a year.
Cryogenic liquid	Liquid nitrogen (several liters/day) used to cool the electropolishing solution to about -30°C.
Compressed gas	Nitrogen gas used for sample handling in gas bag prior to TEM insertion.

2.3 Waste Produced

Describe types and expected quantities of wastes produced by this project (also see 3.6 for the handling of these wastes). Address all applicable major classes (nonhazardous, hazardous/chemical, radioactive, mixed) and the specific types within these classes. Also include wastes that derive from the future decommissioning of equipment (e.g., transformer oils, accumulated debris in reaction chambers) and termination of projects (leftover chemical inventory, samples, materials).

Hazardous/chemical waste: 6 liters/year of the acid solution (5% perchloric acid, 2.1% water, and 92.9% methanol); 8 liters of methanol used for washing the equipment and the samples (minute amounts of the acid will be present and, perhaps, some ethanol); 2 liters of paper towels used for wiping equipment (these towels must be segregated in sealed containers and kept wet).

2.4 Effluents and Emissions

Describe types and expected quantities of materials disposed into the water drains (effluent). Include process water if the amount disposed is unusually large (e.g., constantly running water). See ESH Manual 10.4 for rules regarding disposal of chemicals into the waste water stream. Consult with the building manager for stricter rules due to the condition of drain pipes.

No waste into water drains.

Describe types and expected quantities of gases, aerosols, and other volatile materials emitted to the atmosphere through the ventilation system (incl. hoods)

No gases or aerosols into hood exhaust system or room.

Are all components of this project considered "bench scale research" (NEPA)? Yes __X__ No ______

[3] See ESH Manual 21.3 Appendix A for a more comprehensive list of potential hazards

[Limited in any single experiment, measurement, or test to 5 gal. or 5 lbs of hazardous material, or 1 lb of extremely hazardous material (40 CFR 355)]

2.5 Interaction With Other Projects

Describe possible interactions with other projects (or separate components within the same project) that are carried out in the same or adjacent spaces. Are there incompatibilities of hazards that need to be mitigated by spatial separation or staggered times of operation (e.g. lasers vs. other work in laser access controlled area). Does this project introduce major hazards into a building that are not covered under the current Building Emergency Plan (Bldg. 223 emergency plan on MSD intranet, http://www.msd.anl.gov/resources/esh/ , confer with building managers for other buildings)?

The MSD-SAF-20007 project (TEM/SEM Specimen Preparation) in 212/DL126 uses the same laboratory. A temporary rope barrier is used to keep non-participants away from the hazards that this project introduces to 212/DL126, and the hood is then unavailable for any other work belonging to MSD-SAF-20007.

3. Hazard Control (ISM Core Function 3)

3.1 Design Features and Engineering Controls

For all hazards present, describe the design features and engineering controls applied to control the hazards. Engineering controls include enclosures and barriers that cannot be removed without the use of tools, interlocks, ventilation, software controls, etc. Engineering controls are possible and should be first line of control for all hazard classes (chemical, physical, electrical, biological, radiological).

The chemical work occurs in the east hood in 212/DL126.

3.2 Procedural Controls

For complex hazardous tasks, describe how the hazards are controlled by the work procedure. E.g., specific order of tasks, verification of instrument readings, required use of special tools, and the like.

The hazards in preparing the electropolishing solution are controlled by following the steps in this procedure:

1. The area around the hood must be controlled to keep non-participants away from the acid operations.
2. Wear the proper PPE for handling liquid nitrogen (see section 3.3).
3. Chill the methanol in the hood.
4. Wear the proper PPE for mixing acid solution (see section 3.3).

Add the perchloric acid solution (commercial 70% perchloric acid in water) to the methanol.

3.3 Personal Protective Equipment

List personal protective equipment (PPE) to be worn. Be specific to task or situation, unless it applies to all laboratory work in this project. Remember that safety glasses are not sufficient splash protection against certain chemicals. For gloves, be specific as to type appropriate for the task.

Task/Situation	Personal Protective Equipment
All laboratories	Safety glasses (ANSI Z87.1 compliant)
Cryogenic Handling	Section 4.10.10 of the ES&H Manual requires: • Cryogenic gloves (blue gloves provided by EMC). • Full face shield (provided by EMC). • Trousers without cuffs. • Shoes: closed-toe with non-absorbent material uppers. • Lab coat with buttons fastened (or long-sleeve shirt with cuffs buttoned and the shirt tail outside the trousers).
Mixing/handling acid solution	• Shoes: closed-toe with non-absorbent material uppers. • Full-length pants that will cover the shoes. • Lab coat. • Acid-resistant apron. • Nitrile gloves. • Face shield.

3.4 Training

Indicate the training required for participation in this project. Include Argonne-supplied training (list course numbers and titles), job-specific training (indicate who provides training, how records are kept), and external training (academic requirement, specialized training and/or certification).

The EMC staff will initiate an Argonne Training Profile for those users who are not Argonne employees but who will be working in the EMC more than 10 days per year.

The required Argonne courses for this project are:

- ESH108212, Building 212 Safety Orientation; required of all EMC users
- ESH100U, ANL User Facility Orientation (or ESH100); required of all EMC users
- ESH223, Cyber Security Program Training (or ESH223U); required of all EMC users
- ESH377, Electrical Safety Awareness; required of all EMC users
- ESH574, Chemical Waste Generator

Project participants must receive on-the-job training for this project from Mark Kirk. The training consists of the following:

- Reading the MSDS for perchloric acid, methanol, and ethanol.
- Reading the *User's Guide to the EMC Specimen Preparation Laboratory* to make sure that they are following approved, safe, laboratory practices.
- Consulting with the /DL126 Laboratory Supervisor (Jon Hiller, 2-7904) before they are allowed to prepare specimens by chemical means in 212/DL126 .
- EMC staff (Mark Kirk) will train them to operate the electropolishing equipment and to handle the chemicals in accordance with Argonne's requirements.
- Trainees must go through a period of familiarization under the supervision of an EMC staff member (Mark Kirk), and they must demonstrate to that EMC staff member that they can work safely before they will be allowed to work as an independent participant.
- **The signature of the participant on this SAF indicates that such training has been completed.**

3.5 Chemical Storage

Describe the specific locations where chemicals and gases are stored including type of storage (e.g., flammables cabinet) and how hazardous chemicals are labeled. Include precautions taken for the storage of carcinogens. Indicate who is responsible for keeping the Chemical Management System (barcodes) up-to-date. Attach Material Safety Data Sheets (MSDS) for the particularly hazardous chemicals, and describe where all MSDS are available near the location of the project. The PI must ensure that MSDS for all chemicals used in this project are on file in the Chemical Management System (https://webapps.inside.anl.gov/cms/msds/) and that all participants have ready access to them.

Alcohols are stored in the flammable hazards cabinet in 212/DL126, segregated from acids.

The bottles of 70% perchloric acid are stored under left side of hood in 212/G147, segregated from flammable liquids.

The electropolishing solution shall be stored in a loosely-capped polyethylene bottle inside a secondary container in the east hood in 212/DL126 . The alcohols used for rinsing the TEM samples shall be collected in a polyethylene bottle inside a secondary container in the hood. Waste paper towels that have been used to absorb small amounts of the acid solution or methanol shall be collected in polyethylene bottles or bags for further processing. All containers must be labeled with their contents (names and amounts of the chemicals).

MSDSs are available in the IVEM office, 212/G143, and in 212/DL126.

3.6 Sample Storage and Disposition

Describe how and where samples utilized and produced in this project are stored (and labeled!) while not in active use, how long they will be retained, and how they will be disposed of.

The samples produced by the project are of non-hazardous materials and will be removed from 212/DL126 by the participants.

3.7 Waste Handling

For all hazardous, radioactive, and mixed wastes, describe where and how they are accumulated (include satellite waste area number), and who will be responsible for writing up the waste for disposal by Waste Management. Indicate any special circumstances (special containers, venting, etc.) regarding the safe storage of waste. Address the prevention of incompatible waste mixtures. Include plans for dealing with the waste produced by the future decommissioning of equipment and termination of projects.

Wastes are stored in the the Satellite Waste Accumulation Area # 21200006 in DL126.

The electropolishing solution shall not be diluted and it will be tested with Quantofix® Peroxide 100 Test Sticks for peroxide content prior to giving it to Waste Management.

Jon Hiller is responsible for writing and submitting waste requisitions.

At the end of the job, participants must immediately notify the Lab Supervisor, Jon Hiller (2-7904), and Mark Kirk and work with them to properly label and store the process waste .

3.8 Emergency Management

If this project involves chemical hazards, esp. the use of corrosive chemicals, list locations of eyewash stations and safety showers. Indicate who is responsible for checking eyewash stations weekly.

There is one eyewash station located on the north wall of DL126. Jon Hiller tests this eyewash on a weekly basis. Participants are made aware of its location. The nearest safety shower is located on the east side of corridor D15 between DL136 and DL1394. Building 212 maintenance is responsible for checking the shower.

Include emergency procedures in case of accidents, evacuations, or other hazardous situations. Include egress routes into common areas (hallways), safe shutdown procedures, and other pertinent information. Procedures may be attached. Are all hazard categories posted at the laboratory doors?

Standard building 212 evacuation procedures are in effect. Participants are required to take EMC101 orientation which covers the 212 evacuation process. Exit doors are posted. Hazard categories are posted on the laboratory door.

3.9 Additional Hazard Control

Describe here any measures of hazard controls that are not already documented in the previous sections.

None

3.10 Guidance Documents

List all documents, publications, and books, that you have consulted in the hazard analysis and control. Include relevant chapters and sections of the ES&H Manual but do not include those chapters that are requirements documents for other documents (e.g., 4.2). The divisional Chemical Hygiene Plan (http://www.msd.anl.gov/resources/esh/) is mandatory reading for all participants in projects that contain chemical hazards.

Hazard	Guidance
flammable chemicals	*Argonne ESH Manual* sections 11.3 and 4.3; MSDS for methanol and ethanol.
hazardous wastes	*Perchloric Acid and Perchlorates*, A. A. Schilt, QD181.C5/S27/1979; MSD Chemical Hygiene Plan; MSDS for methanol, ethanol, and perchloric acid; *Argonne Waste Handling*

	Procedures Manual.
highly reactive chemicals	See guidance for perchloric acid.
strong acids	See guidance for perchloric acid.
perchloric acid	*Perchloric Acid and Perchlorates*, A. A. Schilt, QD181.C5/S27/1979; *Argonne ESH Manual* section 4.3; MSD Chemical Hygiene Plan; MSDS for perchloric acid.
cryogenic fluids	*Argonne ESH Manual* section 4.10
compressed gases	*Argonne ESH Manual* sections 13.1 and 13.2

4. Working Within Controls (ISM Core Function 4)

4.1 List of Work Procedures

List all work procedures relevant to this project

The work procedure for preparing the electropolishing solution:

5. The area around the hood must be controlled to keep non-participants away from the acid operations.
6. Wear the proper PPE for handling liquid nitrogen (see section 3.3).
7. Chill the methanol in the hood.
8. Wear the proper PPE for mixing the acid solution (see section 3.3).
9. Add the perchloric acid solution (commercial 70% perchloric acid in water) to the methanol.

Electropolishing work procedure:

1. A face shield isn't necessary while electropolishing.
2. The electropolishing and sample-rinsing activities shall take place in the hood.
3. Operate the Tenupol according to the SOP and the manufacturer's instructions.

Chemical storage work procedure:

1. The electropolishing solution shall be stored in a loosely-capped polyethylene bottle inside a secondary container in the hood.
2. The alcohols used for rinsing the TEM samples shall be collected in a polyethylene bottle inside a secondary container in the hood.
3. Waste paper towels that have been used to absorb small amounts of the acid solution or methanol shall be collected in polyethylene bottles or bags for further processing.
4. All containers must be labeled with their contents (names and amounts of the chemicals).

Chemical waste handling work procedure:

1. At the end of the job, participants must notify the Lab Supervisor so that the process waste can be immediately transferred to a Satellite Waste Accumulation Area (storage in a flammables storage cabinet may not be necessary depending on the total volume in the SAA).
2. The electropolishing solution shall not be diluted.
3. The electropolishing solution must be tested with Quantofix® Peroxide 100 Test Sticks for peroxide content prior to giving it to Waste Management.

4.2 Dosimetry

List locations where radiation dosimeters must be worn. Indicate if a ring is required in addition to the regular badge, and whether neutron dosimetry (type BGN) or not (type BG) is required. Consult with Health Physics regarding requirements.

Location	Dosimetry Requirement
None	

Identify individuals who will be issued dosimeters.

Name	Ring (Y/N)	Neutrons (Y/N)
None		

4.3 Safety Monitoring Equipment

Describe any equipment that is used to monitor safe working conditions (e.g., oxygen monitors, background radiation alarms). Note that all such equipment must be approved by Industrial Hygiene (or Health Physics for radiological monitoring).

None

4.4 Industrial Hygiene Monitoring

List the periodic Industrial Hygiene sampling that is required based on chemical, biological, or other hazardous materials used in this project.

None

4.5 Medical Surveillance

Identify individuals who will be placed in a medical surveillance program as a result of their participation in this project.

None

4.6 Working Alone

Indicate which tasks of this project are of sufficiently low hazard that they may be carried out by a participant working alone, in particular off-hours. Alternately, it may be more convenient to list the tasks that are prohibited while working alone. Note if different rules apply to specific qualification levels among the participants (e.g., students).

No one will work alone on this project.

Prohibited working-alone tasks:

1. Electropolishing, etching, or chemical polishing with acids/bases
2. Mixing corrosives (acids and bases) to form a working solution

5. Feedback (ISM Core Function 5)

5.1 Records Kept

Identify types of records kept with this project that are useful in recreating and improving on the tasks within this project. In particular, include types of records that can be consulted if a task is unsuccessful or produces an unexpected result (in the scientific or operational sense). This could include lab notebooks, datasheets, computer data, instrument logs, images, etc.

Task/Situation	Record Kept
Electropolishing	Users lab notebooks

5.2 Reporting

It is understood that technical results are reported to the outside world in scientific publications, presentations, and technical reports, and to the sponsor in program reviews, contractor meetings, and progress reports. Identify here the channels utilized to report the *operational* experience within the project, division, Argonne, or across the DoE complex. This should include emergency notifications, line management notifications, Lessons Learned (good or bad), group meetings (may serve as pre- or post-job briefings) and other communication channels.

Emergency	1. Call 911. 2. Notify the laboratory supervisor, Jon Hiller (2-7904 or hiller@anl.gov). 3. Notify the EMC director, Dean Miller (2-4108 or miller@anl.gov). 4. Notify the 212 building manager, John Herman (2-6348 or 630-918-9784). 5. Notify the MSD division director, Michael Pellin (2-3510 or pellin@anl.gov). 6. Notify the MSD ESH coordinator, Urs Geiser (2-3509 or ugeiser@anl.gov).
Unplanned events or unexpected results that could affect worker safety and health, the environment, the general public, or Argonne's reputation	Stop work if danger is imminent. Immediately notify the laboratory supervisor, Jon Hiller (2-7904 or hiller@anl.gov).

6. Radioactive Materials Summary

This section to be filled out only if this project utilizes radioactive materials

What isotopes and amounts will be involved?

Isotope	Physical Form[a]	Total Quantity Involved[b]	Quantity Typically Used in a Single Experiment[b]

[a] Physical form could be salt, powder, liquid, gas, etc.
[b] Specify units (dis/min, Ci, etc.).

Provide a schedule for the necessary radiation monitoring.

Where will the experiment be performed? (Identify all laboratories to be used, as well as hoods and/or glove boxes.)

What special provisions will be made for waste disposal?

Are additional or modified emergency plans required? ________ Yes ________ No

If so, identify appropriate changes and additions.

Will the experiment involve special nuclear materials? ________ Yes ________ No

Has the appropriate signage for experimental areas been approved by Health Physics? ________ Yes ________ No

Have radiation monitors been ordered for all researchers? ________ Yes ________ No

Estimate the total external radiation dose equivalents from this work (in person-rems): ________________________

____

Health Physics Name Signature Date

7. Certification, Review and Approval

7.1 Certification

It is my belief that I have identified all the hazards relating to this work, and that by following the procedures outlined above the Materials Science Division and Argonne National Laboratory will be exposed to an acceptable level of risk. I will make this document available to all participants of the project.

M A Kirk 4/18/08

Signature, Principal Investigator Date

7.2 Reviewers and Review Comments

List reviewers for this project and indicate (co-)coordinator/chair(s)

	Jon Hiller (chair)
	Loren Thompson
	John Pearson

Hazard level and review process used: High hazard/complexity X Low hazard/complexity ____

Review team comment

Should Be Considered Medium Hazard No out standing issues

7.3 Environmental Compliance (NEPA)

The NEPA review is usually carried out in conjuction with the funding proposal that supports this project, prior to this safety review. Environmental Compliance Representative (ECR) comment:

No outstanding environmental issues

Urs Geiser [signature] 4/17/08

ECR Name Signature Date

7.4 Approvals and Authorization

The review team has reviewed the safety of this project and recommends its approval:

[signature] 4/18/2008 [signature] 4/18/08

Chair/Co-chair signature Date Co-chair signature Date

Division director check one:

Approval of this project safety review authorizes this work to begin	X
Separate work authorization is required (specify):	

I approve this project safety review:

George Crabtree [signature] 4-17-08

Division Director Signature Date

Argonne NATIONAL LABORATORY

Experimental Change Control Document

ECCD- M S D - 2 0 0 ~~X X~~ 0 3 - 2 0 0 9 - 0 0 3 - C 0 0 1

Division	Sequence	Year	Module #	Change #
M S D	2 0 0 ~~X X~~ 0 3	2 0 0 9	0 0 3	C 0 0 1

1 Original Module

Attach this form to the document to be changed. Next, Use Microsoft WORD functions to accept all changes in the module package under question. Then use track changes to record the changes requested for each module. Only this changed portion will be reviewed.

1.1 Summary of Changes

Because MSD-SAF-20007 perchloric acid work has been excluded from G147, that work has been transferred to DL126, and the SAF has been edited to reflect that change. MSD-SAF-20007 has been added to section 2.5, Interaction with Other Projects.

2 Authorization

Change Authorization:

Limits to Authorization:		
Marquis A. kirk	Marquis A. Kirk	3/1/2010
(Print Name) Experiment Lead	Signature	Date
Urs Geiser	[signature]	3/9/2010
(Print Name) ESH Coordinator	Signature	Date
Michael Pellin	[signature]	3/10/2010
(Print Name) Lead DD	Signature	Date

$HClO_4$-METHANOL ELECTROPOLISHING PROCEDURES

Authors: Carolyn Tomchik, Mark Kirk, and Pete Baldo
Date: 4/8/2008 (revised 3/9/2010)

Material Preparation for electropolishing

Samples are mechanically thinned to approximately 50-100mm, punched into 3mm disks, and the resulting ridge polished off. A final polish with grit-800 silicon-carbide paper is sufficient. Samples are stored under anhydrous methanol until they are electropolished to minimize oxidation.

Optimal polishing conditions

Controlled Parameters
Electrolyte: 5% perchloric acid ($HClO_4$, 70% in water, Fisher A22961LB 1 lb bottle) in 95% anhydrous methanol (CH_3OH, Fisher Optimima A454SK4 (4 liter coated bottle)
Temperature: -44 to -50 ºC maintained through the addition of liquid nitrogen (LN_2)
Voltage: 30V (or up to 32V)
Flow Rate: 30 flow units (or between 25 and 40) on a full scale of 50, adjusted until the two jets meet in a small disc while at temperature.
Flow Mode: sf
Light Sensitivity/Stop Value: set at 800

Dependent Parameters
Current is allowed to fluctuate freely and ranges from 50 to 130 mA. Polishing time is also allowed to vary and ranges from ~27 to 250 s.

Mixing of electropolishing solution

The P.I. (Mark Kirk) must be present before any mixing of electrolytic solutions. The electropolishing solution is mixed directly in the electropolishing basin as follows. First the required amount of anhydrous methanol is poured into the basin. **Warning: You must make sure the methanol is cooled to LN_2 temperature before adding the perchloric acid!** Then, LN_2 is poured into the methanol until the solution reaches a temperature below ~ -50ºC. Once the methanol has cooled, measure the perchloric acid is measured and added to the cold methanol. The solution is pumped through the electropolisher to allow the temperature to equilibrate, and LN_2 added to the basin as needed to maintain the temperature.

Sample handling after polishing

Immediately after the electropolishing is completed, the TEM disk, still in the holder, is put into a beaker of LN_2-cooled anhydrous methanol (~ -60 ºC) in order to stop the acid etching. The TEM disk, once removed from the holder, is then rinsed in a series of three cold baths - first in anhydrous methanol, then ethanol, and finally anhydrous methanol. Careful sample handling is imperative at this stage. When the holder is first put into the beaker of methanol, it should be done so smoothly, perpendicular to the water surface. Do NOT swish the holder back and forth: the solution moving through the hole in the sample will cause bending near the hole edge. To facilitate easy transfer between the baths, the sample, once removed from the holder, is placed on a small piece of filter paper. The filter paper is then easily picked up and moved between the baths with forceps. Efforts are made to always insert and remove a sample perpendicular to the solution surface so that it "cuts" the surface tension, rather than allowing solution to pool on the top – this helps minimize bending. Samples are stored under anhydrous methanol until they are loaded into the sample stage and microscope (within a few minutes), or until they are loaded under nitrogen gas.

Sample mounting in nitrogen gas bag

If further precaution minimizing air exposure of samples is required, mounting of sample in microscope holder and insertion into microscope under nitrogen gas is possible. A glove bag has been modified to accommodate nitrile gloves for better physical control. After tweezers, sample under alcohol in small dish, microscope sample holder, and small thin bag are inserted into glove bag, several purges with nitrogen gas are then followed by sample mounting. Sample stage end, now with sample, is covered with small bag before removing from glove bag. Sample stage is pushed through small bag as inserted into microscope. Air exposure is thus limited to a few seconds. Generally, this is a two person procedure.

SAFETY CONSIDERATIONS

Handling LN_2 and perchloric acid

A small dewar is used to transfer LN_2 to the electropolisher basin. When filling the dewar from the LN_2 tank, insulated cryogloves and a face shield are used. A lab coat, long pants, and closed shoes are worn at all times. Rubber gloves per the MSDS and safety goggles are used throughout the polishing process, as contact with the perchloric acid solution occurs when removing each sample from the polishing holder. Gloves are changed often, generally after each sample. Perchloric acid is ALWAYS poured into the diluting solution (alcohol or water), never the other way around. All work with perchloric acid is done under a fume hood (this includes electropolishing!). The fume hood is all metal and, is rinsed often to prevent buildup of perchloric residue. Undiluted perchloric acid is always stored in secondary containment away from organic chemicals or materials with which it can be reactive. Area is controlled access with caution pedestals and tape. In an emergency, eyewash is by the sink, dial 911 or have someone do it for you. Fire extinguisher is located on the east side of the D15 corridor between DL132 and DL134.

Cleaning the electropolisher after use

The electropolisher is rinsed after each use to remove any residual acid and return it to ~neutral pH (this also helps preserve the parts). Rinses can be conducted with methanol or ethanol and a final rinse can be done with baking soda and water if the electropolisher is going to be stored for a while. To rinse, fill the basin with methanol and turn on the pump for a few minutes. Generally at least 2 rinses are required. The solution and surfaces in the electropolisher are checked for neutrality with pH paper. Beakers, Petri dishes, thermometers, and anything else in contact with the perchloric solution during polishing are rinsed with ethanol or methanol. All rinse waste (except any final neutral water-baking soda solution) is regarded as acidic electropolishing solution (see the following section on waste).

Waste storage

Do not attempt to neutralize the waste electropolishing solution or rinsing solution. All perchloric-methanol waste is put in a labeled waste storage container (with all contents clearly noted on the label, 4-liter Nalgene heavy-duty HDPE bottle Fisher No. 029234) by itself. No other waste is put in this container (only methanol, perchloric,). Polishing solution can be stored separately from the waste rinse and reused for up to 1 week or approximately 10 samples. Used rinse methanol is stored in a separate labled storage container. Under no circumstances is perchloric solution or waste rinse put down the drain. At the end of the week, used electropolishing solution and rinse methanol should be turned over to Pete Baldo. He will declare it waste, place it in the DL126 Hazardous Waste Accumulation Area, and initiate hazardous waste pickup. Contents of the two bottles must be clearly marked. In the interim, small amounts of waste in storage containers are kept away from organic chemicals and materials in secondary containment.

Materials Safety Data Sheets

For additional information about safe handling and storage of perchloric acid, see the MSDS at https://webapps.inside.anl.gov/cms/msds/