

ROUTING AND ACTION

MEMORANDUM

ROUTING

TO:(1) Materials Science Division (Stepp, David)

Report is available for review

(2) Proposal Files Report No.: -RIP

Proposal Number: 61487-MS-RIP.1

DESCRIPTION OF MATERIAL

CONTRACT OR GRANT NUMBER: W911NF-12-1-0508

INSTITUTION: Brown University

PRINCIPAL INVESTIGATOR: Pradeep Guduru

TYPE REPORT: Final Report

DATE RECEIVED: 1/14/15 7:30PM

PERIOD COVERED: 9/1/12 12:00AM through 2/28/14 12:00AM

TITLE: Final Report: Acquisition of a Scanning Tunneling Microscope to Enhance Research and Education in Stress-Controlled Catalysis

ACTION TAKEN BY DIVISION

(x) Report has been reviewed for technical sufficiency and IS ☒ IS NOT ☐ satisfactory.

(x) Material has been given an OPSEC review and it has been determined to be non sensitive and, except for manuscripts and progress reports, suitable for public release.

(x) Performance of the research effort was accomplished in a satisfactory manner and all other technical requirements have been fulfilled.

(x) Based upon my knowledge of the research project, I agree with the patent information disclosed.

Approved by NAE\DAVID.M.STEPP on 1/26/15 8:32AM

ARO FORM 36-E

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) 14-01-2015		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Sep-2012 - 28-Feb-2014	
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		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER 611103			
6. AUTHORS Pradeep R. Guduru		5d. PROJECT NUMBER			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Brown University Box 1929 Providence, RI 02912 -9093			8. PERFORMING ORGANIZATION REPORT NUMBER		
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			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 61487-MS-RIP.1		
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13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT We requested DURIP funding to acquire a scanning tunneling microscope (STM) and atomic force microscope (AFM) to enhance the research and educational objectives of the ARO-MURI program currently funded at Brown University on "stress-controlled catalysis." We have acquired an Asylum MFP-3D-SA instrument to, which has been commissioned. We are currently working on developing the in situ electrochemical capability for the instrument to enable real-time surface measurements such as step density, defects and strains during electrocatalytic reactions. We have successfully used the instrument to (i) characterize the surface roughness evolution during					
15. SUBJECT TERMS Scanning Tunneling Microscopy, Atomic Force Microscopy, Catalysis, Strain					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	UU		Pradeep Guduru
					19b. TELEPHONE NUMBER 401-863-3362

Report Title

Final Report: Acquisition of a Scanning Tunneling Microscope to Enhance Research and Education in Stress-Controlled Catalysis

ABSTRACT

We requested DURIP funding to acquire a scanning tunneling microscope (STM) and atomic force microscope (AFM) to enhance the research and educational objectives of the ARO-MURI program currently funded at Brown University on “stress-controlled catalysis.” We have acquired an Asylum MFP-3D-SA instrument to, which has been commissioned. We are currently working on developing the in situ electrochemical capability for the instrument to enable real-time surface measurements such as step density, defects and strains during electrocatalytic reactions. We have successfully used the instrument to (i) characterize the surface roughness evolution during electrochemical de-alloying of Pt-Cu thin films in order to isolate the strain effects on catalysis from those due to surface roughness changes. (ii) We have also characterized thin film catalysts during electrochemical cycling to determine the optimal conditions in which the films retain their integrity. We are currently working on developing an in situ electrochemical cell for the STM/AFM in order to monitor the catalyst surfaces while they are participating in electrochemical reactions. In addition to the MURI related activities, the instrument is made available to other researchers across Brown campus, with preference given to DoD sponsored research projects, thus ensuring broader research and educational impact of the STM/AFM.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

- (1) V.A. Sethuraman, D. Vairavapandian, M.C. Lafouresse, T.A. Maark, N. Karan, S. Sun, U. Bertocci, A.A. Peterson, G.R. Stafford, P.R. Guduru, On the Role of Elastic Strain on Electrocatalysis of Oxygen Reduction Reaction on De-alloyed Pt/PtCu, 2015
- (2) K. Yan, T.A.Maark, V.Sethuraman, P.R.Guduru, A.Peterson. Effect of uniaxial strain on catalytic activity toward hydrogen evolution reaction, 2015.

Number of Presentations: 2.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Pradeep R. Guduru has been appointed as the James R. Rice Professor of Engineering at Brown University in 2014.

Graduate Students

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Names of Under Graduate students supported

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment.

Technology Transfer

Report
**DURIP: Acquisition of a Scanning Tunneling Microscope to Enhance
Research and Education in Stress-Controlled Catalysis**

Grant # W911NF-12-1-0508

Pradeep R. Guduru
James R. Rice Professor of Engineering, Brown University, Providence, RI 02912

Shouheng Sun
Professor of Chemistry, Brown University, Providence, RI 02912

Abstract

We requested DURIP funding to acquire a scanning tunneling microscope (STM) and atomic force microscope (AFM) to enhance the research and educational objectives of the ARO-MURI program currently funded at Brown University on “stress-controlled catalysis.” We have acquired an Asylum MFP-3D-SA instrument to, which has been commissioned. We are currently working on developing the *in situ* electrochemical capability for the instrument to enable real-time surface measurements such as step density, defects and strains during electrocatalytic reactions. We have successfully used the instrument to (i) characterize the surface roughness evolution during electrochemical de-alloying of Pt-Cu thin films in order to isolate the strain effects on catalysis from those due to surface roughness changes. (ii) We have also characterized thin film catalysts during electrochemical cycling to determine the optimal conditions in which the films retain their integrity. We are currently working on developing an *in situ* electrochemical cell for the STM/AFM in order to monitor the catalyst surfaces while they are participating in electrochemical reactions. In addition to the MURI related activities, the instrument is made available to other researchers across Brown campus, with preference given to DoD sponsored research projects, thus ensuring broader research and educational impact of the STM/AFM.

Report Narrative:

We requested DURIP funding to acquire a scanning tunneling microscope (STM) and atomic force microscope (AFM) to enhance the research and educational objectives of the ARO-MURI (grant # W911NF-11-1-0353) program currently funded at Brown University on “stress-controlled catalysis.” We have acquired an Asylum MFP-3D-SA instrument to, which has been commissioned. We are currently working on developing the *in situ* electrochemical capability for the instrument to enable real-time surface measurements such as step density, defects and strains during electrocatalytic reactions. We have successfully used the instrument to (i) characterize the surface roughness evolution during electrochemical de-alloying of Pt-Cu thin films in order to isolate the strain effects on catalysis from those due to surface roughness changes. (ii) We have also characterized thin film catalysts (Ni, Cu, Pt) during electrochemical cycling to determine the optimal conditions in which the films retain their integrity. We are currently working on our goal to develop an *in situ* electrochemical cell for the STM/AFM in order to monitor the catalyst surfaces while they are participating in electrochemical reactions. In addition to the MURI related activities, the instrument is made available to other researchers across Brown campus, with preference given to DoD sponsored research projects, thus ensuring broader research and educational impact of the STM/AFM.

I. Technical specifications of the instrument

We have acquired an The MFP-3D-SA system, which is a high-performance STM/AFM system. Its design uses a single closed-loop scanner to span the range from atomic resolution scans up to micron-scale scans. A control station based on the ARC2 Controller enables a several standard modes and features. The modular hardware and software architecture also supports a range of accessories and allows user-customization for specialized experiments. The system includes:

MFP-3D Head: The standard MFP-3D head contains low-noise cantilever deflection optics, Z scanner, precision engage mechanism, and top-down optics. The key specifications are: noise (A_{Dev}, 0.1Hz-1kHz); inverted optical lever design with low-coherence 860nm SLD (Class 1M) for thermally limited cantilever deflection measurements (DC deflection noise <20pm, A_{Dev}, 0.1Hz-1kHz); cantilever holder compatible with both air and liquid operation, which is especially suited for *in situ* electrochemical experiments.

MFP-3D Scanner: The MFP-3D features closed-loop sample scanning with a low-noise piezo driven flexure stage. Closed-loop operation ensures that the scanner accurately and precisely performs the desired scanning motion. Some key specifications include: Piezo driven flexure stage XY scanner with 90μm scan range, low out of plane motion, and <0.5nm sensor noise (A_{Dev},0.1Hz-1kHz), operates in both open-loop and closed-loop; accommodates large samples, up to 80mm diameter and up to 10mm thick, which is suitable for designing custom electrochemical cells.

MFP-3D Control Station: The MFP-3D Control Station includes the ARC2 AFM controller, high performance workstation and Asylum AFM control software. Some key specifications include: ARC2 controller features 100% digital architecture for the fastest, lowest noise operation; “Hamster” control allows simple, intuitive adjustment of selectable software parameters; highly configurable analog signal access is provided for custom experimentation. An expansion port enables a wide range of optional accessories including temperature control, external magnetic field, and other advanced features.

Standard modes of operation include full complement of operating modes for fluid and air operation, including; Contact/LFM, AC mode / tapping mode with phase and Q-control, electric force microscopy, surface potential microscopy, magnetic force microscopy, piezoresponse force microscopy, Dual AC and Dual AC Resonance Tracking (DART), loss tangent imaging, force spectroscopy and force mapping, nanolithography, nanomanipulation.

In the Scanning Tunneling Microscopy mode, the system provides tunneling current imaging capability at constant current or constant height, and point spectroscopy (I/V) plots at the desired points. The system includes an STM probe holder with integral pre-amp (gain is 1×10^9 volts/amp).

II. Technical context for the instrument acquisition

Brown University was awarded an ARO-MURI (grant # W911NF-11-1-0353) in 2011 on a project titled: “Stress-Controlled Catalysis via Engineered Nanostructures.” The PIs on this DURIP proposal, **Guduru** and **Sun**, serve as co-PIs on the MURI team, which also consists of multi-scale modelers (**W.A. Curtin**, **G. Lu**) and a materials scientist (**S. Kumar**). The central objective of our MURI effort at Brown is to demonstrate that macroscopic applied loading can be used to actively control and tune catalytic, and by extension many other, reactions through the use of innovative nanoscale material systems. The challenge lies in obtaining sufficiently large changes in surface structure in a controllable mechanical manner, and then isolating strain as the only experimental variable. Two representative projects in which the instrument has been used/ is being used are described below.

(i) The Role of Elastic Strain on Electrocatalysis of Oxygen Reduction Reaction (ORR):

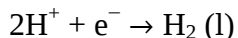
Enhanced catalytic activity of de-alloyed PtCu electrodes towards oxygen reduction (ORR) reaction has been demonstrated in a number of recent investigations in thin-film and core-shell geometries. The enhancement in catalytic activity is typically attributed to electronic interaction between the core and shell constituents as well as epitaxial mismatch strain in the metallic shell. For example, Strasser *et al.* demonstrated enhanced catalytic activity of de-alloyed PtCu core-shell nanoparticles towards ORR, which was attributed to the pseudomorphic compressive strain in the Pt-enriched shell. The magnitude of the strain in the Pt-enriched shell was estimated using lattice-constant measurements (*via* X-ray diffraction). In this project, we have carried out real-time stress and nano-gravimetric measurements during electrochemical de-alloying of thin-film PtCu electrodes. *In situ* stress measurements are made using cantilever-

deflection method, and nano-gravimetric measurements are made using an electrochemical quartz crystal nanobalance (EQCN). Upon de-alloying *via* successive voltammetric sweeps between 0.05 and 1.15 V vs. standard hydrogen electrode (SHE), compressive stress develops in the de-alloyed layer region near the surface of thin-film PtCu electrodes. *In situ* nanogravimetric measurements reveal that the mass of de-alloyed Cu is approximately 210 ng/cm², which corresponds to a de-alloyed layer thickness of 1.23 monolayers or 0.16 nm. From the real-time curvature measurements of the substrate, the average biaxial stress in the de-alloyed layer is estimated to be 4.38 GPa, which corresponds to an elastic strain of 1.62%. We have also carried out density functional theory (DFT) calculations on biaxially strained Pt surfaces to characterize the effect of strain on their ORR activity; the results are found to be in reasonably good agreement with the experimental measurement.

A critical feature of interpreting the changes in catalytic activity in any de-alloyed film is the role of atomic scale surface topography. In addition to strain, changes in atomic scale roughness can also result in change in activity; hence it is essential to characterize the sample surface before and after de-alloying to account for any surface roughness effects. We have employed the STM/AFM acquired under this grant to carry out a systematic study of Pt-Cu surfaces. The RMS surface roughness was seen to increase by approximately 0.1 nm, which revealed that the change in roughness is insignificant and hence the modified catalytic activity can be attributed to the elastic film in the de-alloyed film alone. A manuscript on this work is attached and it is under consideration for publication in the Journal of the Electrochemical Society [V.A. Sethuraman, D. Vairavapandian, M.C. Lafouresse, T.A. Maark, N. Karan, S. Sun, U. Bertocci, A.A. Peterson, G.R. Stafford, P.R. Guduru, *On the Role of Elastic Strain on Electrocatalysis of Oxygen Reduction Reaction on De-alloyed Pt/PtCu*, 2015].

(ii) Modulation of catalytic activity in metal catalyst thin films towards Hydrogen Evolution Reaction:

Hydrogen Evolution Reaction (HER) plays a central role in several energy technologies such as fuel cells and electrochemical energy storage. HER is also an ideal reaction to study the effect of elastic strain since it is a simple reaction with a single electron transfer and the binding energy of the hydrogen atom is known to be an accurate descriptor of the catalytic efficiency of a surface. The half-cell reaction for HER is shown below.



It is well established that the binding strength of hydrogen, expressed as the free energy change of hydrogen adsorption ($G_{\text{B}}[\text{H}]$), is a primary predictor of electrocatalyst effectiveness for the HER, with ideal catalysts having $G_{\text{B}}[\text{H}]$ of ~ 0 . This is often represented by a “volcano plot”, which plots activity versus $G_{\text{B}}[\text{H}]$. On such a plot, the peak of the volcano (maximum activity) occurs at $G_{\text{B}}[\text{H}] \sim 0$, with reduced activity on the left-hand side ($G_{\text{B}}[\text{H}] < 0$) due to too strong H binding, and reduced activity on the right-hand side ($G_{\text{B}}[\text{H}] > 0$) due to binding H too weakly. In this investigation, we showed how a continuous mechanical strain can be applied in situ on various metal thin film catalysts to directly tune the H binding energy and thus the catalytic

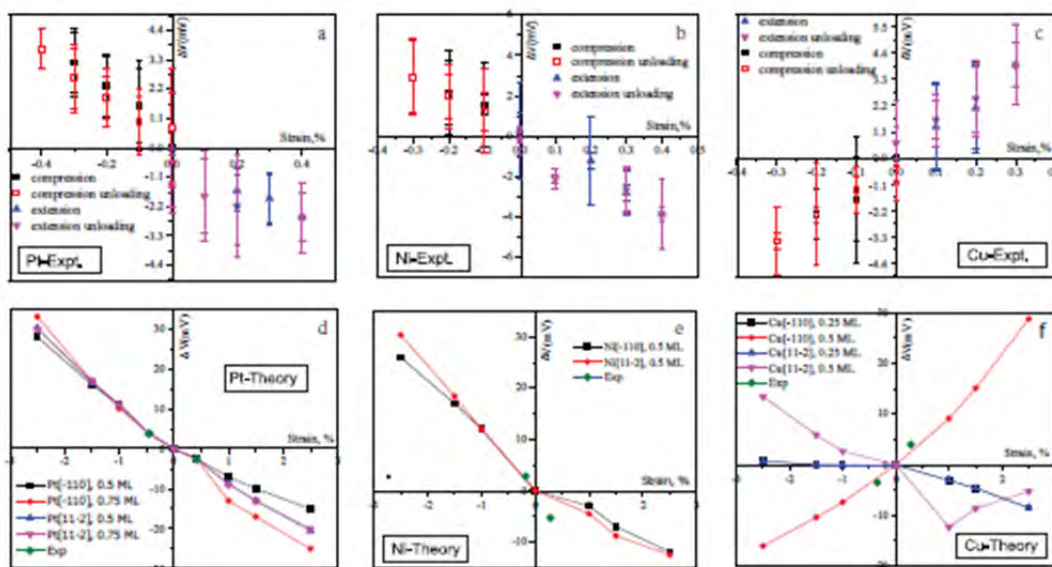


Figure 1. Shift in the threshold potential (ΔV) for hydrogen evolution reaction during a cyclic voltammogram (CV) experiment, which is also a measure of change in the catalytic activity of the surface. The figure shows ΔV vs. strain, experimental results (top) and computational results (bottom) for Pt, Ni and Cu. Good agreement between the experiments and the theory is observed in all cases.

activity of the hydrogen evolution reaction (HER). The HER is often described in terms of a volcano plot, which suggests optimum HER catalysts will have $G[H] = 0$ (the free energy change of hydrogen bonding). In this work, we prepared thin-film catalysts from three regions of the volcano plot — Ni ($G_B[H] < 0$), Pt ($G_B[H] \sim 0$) and Cu ($G_B[H] > 0$) — and subjected them to both compressive and tensile mechanical strain. Since Ni and Cu are on either side of the volcano plot, our computational prediction is that, if compressive strain enhances the catalytic activity of Ni, then it should have the opposite effect on that of Cu by moving the binding energy farther away from the volcano peak. Alternatively, if compressive strain retards the catalytic activity of Ni, then it should have the opposite effect on that of Cu by moving the binding energy closer to the volcano peak. Remarkably, the experimental results are in agreement with this simple picture offered by the volcano plot, i.e., Pt and Ni thin films benefit from compressive strain, which weakens hydrogen binding, while Cu's HER activity is retarded by compressive strain. Just the opposite trend is observed when a tensile strain is applied. The main result of the investigation is shown in Fig. 1, which shows the shift in the threshold potential (ΔV) for hydrogen evolution reaction during a cyclic voltammogram (CV) experiment, which is also a measure of change in the catalytic activity of the surface. The figure shows ΔV vs. strain, experimental results (top) and computational results (bottom) for Pt, Ni and Cu. Good agreement between the experiments and the theory is observed in all cases. However, interpretation of the above experimental results requires careful characterization of the catalyst films to ensure that: (i) the deposited film is continuous, which must be ascertained as the films

are very thin (20 nm or thinner). A discontinuous film with island morphology would not be able to transmit the strain applied the underlying substrate to the film effectively. (ii) The roughness evolution during CV cycling needs to be measured to ensure that the measured shift in the potential is due to the elastic strain alone. (iii) It is essential to ascertain that the film does not undergo microscopic damage (delamination, cracking, etc.) during CV cycling in order to facilitate interpretation of the experimental data. The STM/AFM system has been used to carry out a systematic characterization of the film under different electrolyte environments. After investigating a variety of electrolytes and concentrations, we have determined that 0.1M NaOH solution is idea for maintaining the surface integrity of the films; all experimental data reported correspond to this electrolyte. This work is currently under consideration for publication in Nano Letters (K.Yan, T.A.Maark, V.Sethuraman, P.R.Guduru, A.Peterson. *Effect of uniaxial strain on catalytic activity toward hydrogen evolution reaction*, 2015).

(iii) Development of Electrochemical STM

We have an ongoing effort to develop the capability to carry out surface science measurements with the STM on surfaces undergoing electrochemical reactions, in order to directly observe the effect of externally applied elastic strains. Electrochemical STM is recently developed and still evolving technique, which is also quite challenging compared to the traditional UHV (ultra high-vacuum) based STM techniques. A schematic of the experimental setup for electrochemical STM is shown in Fig. 2. Development of liquid based STM technique represents a significant advance in surface science measurements, with potential to measure strain effects on the surface electronic structure changes in real time during electrochemical

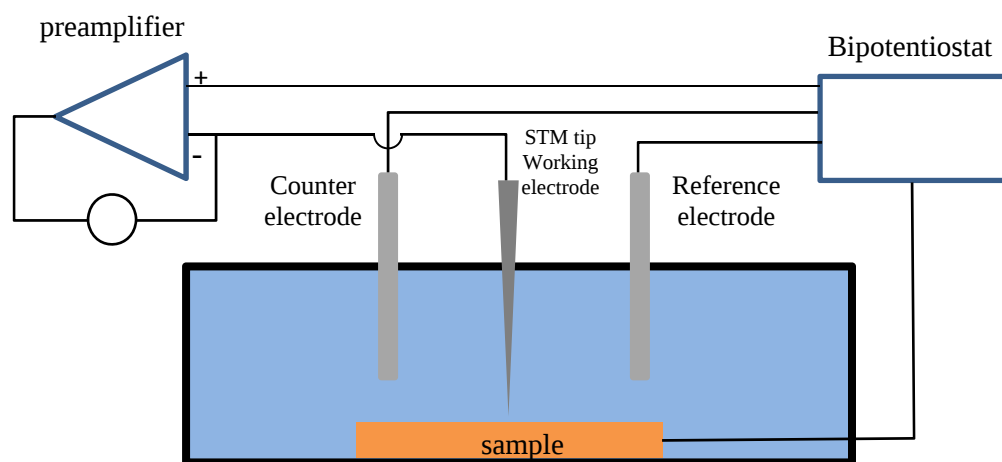


Figure 2. Schematic illustration of an electrochemical scanning tunneling microscopy setup. from: Yagati et al. 2014, "Modern Electrochemical Methods in Nano, Surface and Corrosion Science", June, 2014.

reactions, combined with strains. This is an ongoing effort and we hope to report our progress in due course elsewhere.

III. Summary

In conclusion, we have acquired and commissioned an STM/AFM system under the DURIP grant (W911NF-12-1-0508). The system has been used to support our going ARO MURI work on stress controlled catalysis; systematic studies of thin film catalyst films have been carried out to determine the roughness evolution during de-alloying of Pt-Cu films, which was measured to be 0.1 nm. We have also characterized catalyst thin films and surface morphology changes under a variety of electrochemical conditions in order to determine the ideal conditions in which the films retain their integrity, so the effect of externally applied strains on the catalytic activity can be studied in isolation.