ROUTING AND ACTION

MEMORANDUM

ROUTING

TO:(1) Energy Sciences Branch (ES) (DeLong, Hugh)

Report is available for review

(2) Proposal Files Report No.: -REP Proposal Number: 78035-ES-REP.1

DESCRIPTION OF MATERIAL

CONTRACT OR GRANT NUMBER: W911NF-21-1-0289

INSTITUTION: University of Illinois - Chicago

PRINCIPAL INVESTIGATOR: Robert Klie

TYPE REPORT: Final Report

DATE RECEIVED: 8/18/23 4:58PM

PERIOD COVERED: 5/15/21 12:00AM through 11/14/22 12:00AM

TITLE: Final Report: Acquisition of An In-Situ Electro-Chemical Cell for Multi-Modal Research and Education at UIC

ACTION TAKEN BY DIVISION

(x) Report has been reviewed for technical sufficiency and IS [x] IS NOT [ ] satisfactory.

(x) Based on my technical review, I have identified no OPSEC or Technology Protection concerns that need to be addressed regarding this report.

(x) Perfomance 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 SSL\HUGH.C.DELONG on 8/23/23 4:33PM

ARO FORM 36-E

REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
18-08-2023	Final Report	15-May-2021 - 14-Nov-2022

4. TITLE AND SUBTITLE
Final Report: Acquisition of An In-Situ Electro-Chemical Cell for Multi-Modal Research and Education at UIC

5a. CONTRACT NUMBER
W911NF-21-1-0289

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
060122

6. AUTHORS

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
78035-ES-REP.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Robert Klie
UU	UU	UU	UU		19b. TELEPHONE NUMBER 312-996-6064

RPPR Final Report
as of 23-Aug-2023

Agency Code: 21XD

Proposal Number: 78035ESREP **Agreement Number: W911NF-21-1-0289**

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DUNS Number: 098987217 EIN: 376000511
Report Date: 14-Feb-2023 Date Received: 18-Aug-2023

Final Report for Period Beginning 15-May-2021 and Ending 14-Nov-2022

Title: Acquisition of An In-Situ Electro-Chemical Cell for Multi-Modal Research and Education at UIC

Begin Performance Period: 15-May-2021 **End Performance Period:** 14-Nov-2022

RPPR Final Report
as of 23-Aug-2023

Report Term: 0-Other

Submitted By: Ph.D. Parisa Mirbod
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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1 **STEM Participants:** 1

Major Goals: This DOD Research and Education Program for Historically Black Colleges and Universities and Minority-Serving Institutions Equipment/Instrumentation grant was awarded to to acquire a novel in-situ liquid-cell electro-chemical sample holder for transmission electron and X-ray microscopy to significantly improve the electrochemistry research capabilities at the University of Illinois at Chicago (UIC). The Protochips Poseidon Select Electrochemistry and Heating holder was successfully purchased and installed at UIC in September 2022.

This multi-modal holder became part of the UIC RRC Electron Microscopy Core (EMC) facility, where it is now available to the over 200 annual RRC EMC users of the atomic-resolution aberration-corrected JEOL-ARM200CF and the JEOL-3010 transmission electron microscopes (TEM).

The Poseidon Electrochemistry and Heating holder provides the ideal setup for correlative electron microscopy analyses of liquid/solid interfaces at room and elevated temperatures using the UIC TEM. This holder has several unique features that are not available at any other laboratory in the United States. Specifically, the holder is designed to fit in the atomic-resolution TEMs at UIC providing unprecedented spatial and energy resolution during electro-chemical/catalytic cycling. The holder is also designed to allow for heating the liquid samples up to 150 °C while performing in-situ electro-chemistry experiments, thus allowing, for the first time, to track the morphological changes in multi-valent battery cathodes at or near the atomic scale.

The new holder has enabled new teaching and training opportunities for under-represented students at UIC. UIC is a designated Hispanic Serving Institution, and the PI Klie has established an active undergraduate student visiting program with Tecnologico de Monterrey in Mexico.

Accomplishments: The holder was ordered on June 25, 2021 and delivered in September 2022. This project featured a prototype closed-cell TEM holder and prototype E-chip sample supports to perform a wide range of heated electrochemistry experiments safely inside the TEM with experimental parameters defined by UIC.

Targets/Goals

- Define a list of needs and requirements for the system in order to perform desired experiments.
- Design, manufacture, and characterize E-chip sample supports that meet or exceed the performance targets, including maximum temperature, electrical leakage, and broad chemical compatibility with samples/electrolytes at elevated temperature.
- Design, manufacture, and characterize a prototype closed-cell TEM holder compatible with the JEOL ARM200F microscope at UIC that can supply the liquid and electrical signals to the E-chips and samples to help meet or exceed the targets outlined.
- Delivery of the completed system.

Performance and Design Goals

- Compatible with the UHR pole piece for a JEOL ARM200F
- Heating and electrochemistry must be performed simultaneously
- Temperature range: room temperature to 150°C at minimum
- Working, counter, and reference electrode materials: Platinum
- Chemical compatibility with:
  - Acetonitrile
  - Glymes (i.e. Diglyme, Triglyme, etc..)
  - Ethylene carbonate
  - Ionic liquids, such as TFSI- (a.k.a., bis(trifluoromethane)sulfonimide, N(SO2)2(CF3)2)2) anions)

Performance and Design Goals

- Compatible with the following JEOL pole pieces: FHP2, FHP, WGP, UHR, SAP, HRP, HR.

- Not compatible with specific cryo-boxes, please alert Protochips immediately if a cryobox is present.
- Alpha tilt range for UHR pole piece: best efforts to meet standard Poseidon tilt range in UHR
- pole piece of +16° / -9°
- Compatible techniques: S/TEM, EDS, EELS, Diffraction, Aberration Correction
- Number of liquid ports: 2 inlets (enables mixing), 1 outlet
- Heating ramp rate: 5°C/sec

Ability to heat liquids in the holder tip to a minimum of 150°C.

Heat is be supplied using a heating coil patterned on the large E-chip. Forcing DC current through the coil will heat the E-chip, and its temperature will be measured and controlled through its resistance. The E-chips and holder tip is made of thermally conductive materials that can quickly reach a thermal equilibrium after the temperature setpoint is adjusted. A Keithley 2450 power supply, or one similar, is used to deliver current and measure the resistance of the coil, and will be controlled using Protochips' Clarity software for Poseidon Select. The power supply and Clarity software are included in the Poseidon Select Heating Expansion package that will already be onsite at UIC. Protochips exceeds 150°C and characterized the maximum temperature possible within the limits of the E-chip materials, holder materials, and power supply.

Ability to perform nA-scale electrochemical measurements of samples.

E-chips features three electrodes for electrochemistry experiments – a working electrode, a counter electrode, and a reference electrode. At least one of these electrodes is located over a thin silicon nitride membrane window on the E-chip so that it can be viewed in the TEM during experiments. The location and size of these electrodes was reviewed with the team at UIC prior to fabrication. Given the small size of TEM samples and the thin liquid layer between the E-chips, electrochemical measurements in the TEM are usually very low current signals. Accordingly, the E-chips were designed to minimize leakage current between the individual electrodes and between the electrodes and heating coil. A high-resistivity substrate and thick dielectric layers between the electrodes and substrate was used to minimize leakage. A Gamry Reference 600+ potentiostat was supplied with the Poseidon Select Electrochemistry Expansion Package and was already onsite at UIC upon arrival of this system. This potentiostat and its software support most common electrochemistry experiments and has the low-current performance required for electrochemistry in the TEM.

Compatibility with samples and electrolytes.

The materials for the E-chips, including the substrate, metals, and dielectrics was chosen to optimize compatibility with the samples and electrolytes used during electrochemistry experiments with heating. Protochips advised which materials are "known compatible" and "known incompatible", and provide advice for materials whose compatibility is unknown. Safety of the system, the microscope, and the customer are high priorities.

The liquids specified by UIC as performance goals had not been tested by Protochips, but Protochips customers have used most of these without issue. Chemical compatibility testing is highly recommended to be done by UIC, especially on different glymes and ionic liquids, using protocols provided by Protochips prior to introducing the liquid into the holder.

Closed-Cell TEM Holder

Compatibility with the JEOL ARM200F TEM with UHR pole piece

The TEM holder was manufactured for the JEOL ARM200F with UHR pole piece. Standard Poseidon Select tilt range for the UHR pole piece (+16° / -9°) was achieved, however this may be impacted by the design changes necessary to enable the simultaneous heating and electrochemistry function. The holder tip was designed to optimize collection of EDS spectra. All Protochips holders are designed in accordance with strict safety standards provided by the microscope manufacturers. The prototype holder should also be compatible with plasma cleaners, leak check stations, and other equipment designed for use with JEOL TEM holders.

The holder was tested for vacuum before shipping and will meet all other vacuum, flow and mechanical testing criteria set for a standard Poseidon Select system.

Ability to deliver liquids to the sample area between the E-chips

Fluid flow paths for the prototype TEM holder will be unchanged from the standard Poseidon Select TEM holder.

Ability to deliver current to the E-chips

To meet the requirement of simultaneous heating and electrochemistry, the prototype TEM holder requires at least two additional circuit paths connecting the power supply to the E-chip. This includes additional traces and contact pads on the flex circuit as well as additional contact pads on the prototype E-chip. The required connectors at the holder handle may be different than a standard Poseidon Select due to these additional circuits. The holder is compatible with the electrochemistry equipment and heating equipment purchased by UIC. Protochips characterized the maximum temperature possible within the limits of the E-chip materials, holder materials, and power supply, exceeding 150 °C .

Deliverables:

The prototype Poseidon Select holder was shipped with the following accessories:

- Holder stand and tip stand
- 100 pairs of Poseidon Select E-chips for simultaneous heating and electrochemistry
- experiments (enough for at least 100 experiments)
- Protective Pelican case
- Any cabling adapters that may be needed to connect to the heating power supply or
- potentiostat
- Poseidon Select microfluidics and sample prep kit:
  - 1 mL and 5 mL syringe
  - Pipette 0.1 µL - 2.0 µL
  - PEEK tube cutter and T-splitter
  - Evaporating dish
  - Watch glass
  - Luer lock assembly
  - PEEK fittings, nuts, plugs, and adapters
  - 2-pack of gaskets

Training Opportunities: During the grant period, pot-docs and students, as ell as users of the UIC Research Resources Center (RRC) were trained using the new holder. Specifically, Yingjie Yang, a post-doc in Klie's group led the testing and early experiments using the new holder. In addition, Mr. Francisco Lagunas, a graduate student at UIC, who is Hispanic, was trained on the new holder. He graduated in May 2023 and is now a post-doc at Argonne National Laboratory.

In addition, 4 undergraduate students, Emilia Ferral, Clareth Blanco Tencio, Adriana Punera and Nora Greys Zamora. Mr. Ferral graduated with a BS in Physics from UIC earlier this year and has stayed on as a student researcher while preparing his graduate school application. Ms. Punera, Blanco and Zamora are all junior undergraduate student from Tecnologico de Monterrey in Mexico who spend a Semester in the PI Klie’s group as part of a visiting student program. The PI helped set up this program in UIC Physics, which will be expanded to other departments in the College of Liberal Arts & Sciences at UIC. All four undergraduate students are Hispanic.

Results Dissemination: Preliminary results of the holder development and benchmarking were presented at the 2022 Gordon conference and seminar for liquid cell (poster by Yingjie Yang, oral by Robert Klie), the Materials Research Society 2022 Fall meeting (oral by Robert Klie), the American Chemical Society 2022 Fall meeting (poster by Yingjie Yang), the American Physical Society Meeting march 2023 (poster by John Farrell), and the Midwest Microscopy and Microanalysis 2023 Spring meeting (oral by Yingjie Yang).

Honors and Awards: The PI Klie was named a 2023 University Scholar based on his past research performance The PI Klie was named Head of the Department of Physics in January 2023

Protocol Activity Status:

RPPR Final Report
as of 23-Aug-2023

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Robert F Klie
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Yingjie Yang
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Francisco Lagunas
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Adriana Punaro
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Nora Greys Zamora
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Emilio Ferral
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Clareth Blanco
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

RPPR Final Report
as of 23-Aug-2023

Partners

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I certify that the information in the report is complete and accurate:
Signature: Robert F Klie
Signature Date: 8/18/23 4:58PM

DOD HBCU/MI Final Program Report

PI: *Robert F Klie*
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This DOD Research and Education Program for Historically Black Colleges and Universities and Minority-Serving Institutions Equipment/Instrumentation grant was awarded to acquire a novel in-situ liquid-cell electro-chemical sample holder for transmission electron and X-ray microscopy to significantly improve the electrochemistry research capabilities at the University of Illinois at Chicago (UIC). This multi-modal holder became part of the UIC RRC Electron Microscopy Core (EMC) facility and is now available to the over 200 annual RRC EMC users of the atomic-resolution aberration-corrected JEOL-ARM200CF and the JEOL-3010 transmission electron microscopes (TEM).

The goal of this proposal was to purchase a liquid-cell electrochemistry holder from Protochips, Inc., specifically the Poseidon Heating with Electrochemistry holder, which provides the ideal setup for correlative electron and X-ray analyses of liquid/solid interfaces at room and elevated temperatures using the UIC TEMs. This holder has several unique features that are not available at any other laboratory in the United States. Specifically, the holder was designed to fit in the atomic-resolution TEMs at UIC providing unprecedented spatial and energy resolution during electro-chemical/catalytic cycling. The holder was also designed to allow for heating the liquid samples up to 150 °C while performing in-situ electro-chemistry experiments, thus allowing, for the first time, to track the morphological changes in multi-valent battery cathodes at or near the atomic scale.

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- Any cabling adapters that may be needed to connect to the heating power supply or
- potentiostat
- Poseidon Select microfluidics and sample prep kit:
    - 1 mL and 5 mL syringe
    - Pipette 0.1 µL - 2.0 µL
    - PEEK tube cutter and T-splitter
    - Evaporating dish
    - Watch glass
    - Luer lock assembly
    - PEEK fittings, nuts, plugs, and adapters
    - 2-pack of gaskets

The purchase of the in-situ liquid-cell S/TEM sample holder with simultaneous capabilities of electrochemistry and heating has been completed. Both heating and electrochemistry functions are realized, through an updated design of the contact pad and the MEMS chips, as shown in Figure 1. Figure 1 (a) shows the sample holder placed on a stand, fully assembled outside of the electron microscope. The cable extending from the end of the holder enables the heating capability, three liquid ports connect to the inner tubing of the holder and the tip where the chips are assembled. Figure 1 (b) shows compatible MEMS chips with 5 contact pads, three are assigned to electrochemistry leads and two heating leads.

Figure 1: Photo of (a) the in-situ liquid cell holder with simultaneous heating and electrochemistry and (b) the MEMS chips compatible with the new holder design.

The schematics of the MEMS top chip is shown in Figure 2. Only the middle square, which overlaps with the matching small chip, is exposed to electrolyte. When the electrolyte is sandwiched between two chips, it is confined by silicon nitride membranes and the spacers made of the dielectric material SU-8. The electrodes are made of Pt, which is patterned onto the Si frame and silicon nitride window, and they are only exposed to the electrolyte where silicon nitride is (not exposed where SU-8 is).

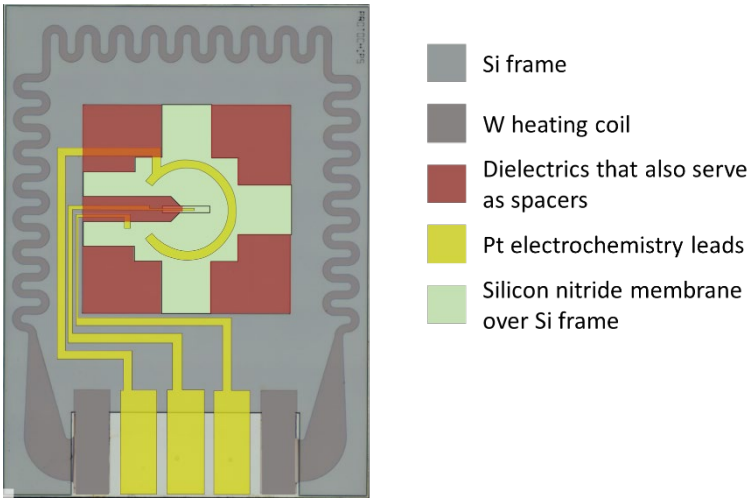

Figure 2: Schematics of the MEMS chip.

Cyclic voltammetry (CV) experiments of copper stripping and plating were conducted successfully both in the ex-situ testing unit and in an electron microscope in-situ, at room temperature and elevated temperatures up to 80 ºC. Figure 2 (a) and (b) shows the CV curves recorded during in-situ tests at room temperature and 40 ºC, respectively. Images showing the stripping and plating of Cu were recorded in the electron microscope simultaneously. Examples of visualized stripping and plating at 40 ºC and 60 ºC are shown in Figure 2 (c) and (d), which were recorded in TEM mode. The dark contrast at the bottom-left corner of the images is contributed by the Pt electrode on the electron-transparent silicon nitride window of the MEMS chip, and the changing contrast on the edge of the Pt electrode are the Cu metal plating during a CV cycle.

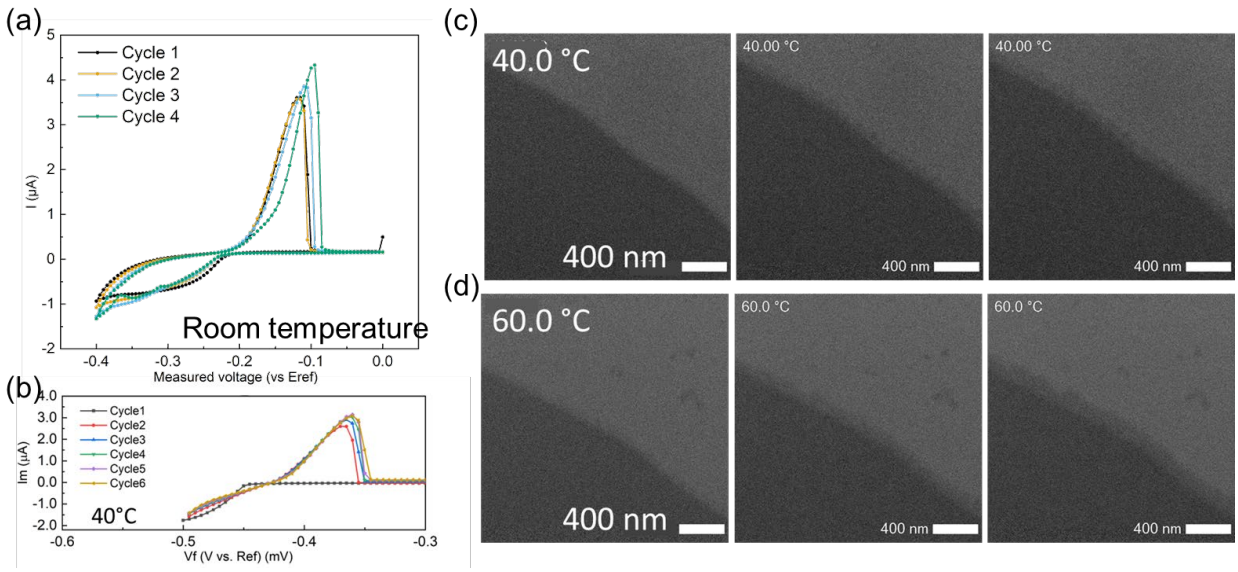

Figure 3: (a) Room temperature and (b) 40 ºC cyclic voltammetry measurements of Cu stripping and plating; Electron images recorded in different stages of stripping and plating at (c) 40 ºC and (d) 60 ºC.

Preliminary results of the holder development and benchmarking were presented at the 2022 Gordon conference and seminar for liquid cell (poster by Yingjie Yang, oral by Robert Klie), the Materials Research Society 2022 Fall meeting (oral by Robert Klie), the American Chemical Society 2022 Fall meeting (poster by Yingjie Yang), the American Physical Society Meeting march 2023 (poster by John Farrell), and the Midwest Microscopy and Microanalysis 2023 Spring meeting (oral by Yingjie Yang).