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RPPR Final Report
as of 15-Nov-2021

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STEM Degrees: 0 **STEM Participants:**

Major Goals: This research infrastructure program project has as goal to enable the extension of the diagnostic capabilities used in the MURI “Plasma-driven solution electrochemistry” (PDSE) with high resolution in liquid ex situ Transmission Electron Microscopy (TEM) and enable the development of a first-of-its-kind in situ TEM plasma electrolysis capability inspired by and advancing the state-of-the-art in situ electrolysis TEM studies. This new capability will enable, for the first time, in situ investigations of electrochemical reactions near the plasma-liquid interface leading to the formation of nanomaterials.

The project consists of acquiring a high resolution TEM and a liquid and gas holder compatible with in situ plasma generation.

Accomplishments: Description is provided in attached PDF document.

Training Opportunities: While no personnel was supported on this project, a postdoctoral research sponsored by the MURI "Plasma-driven solution electrochemistry" significantly benefited from extensive training on TEM and in situ TEM holders in the framework of this project.

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

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Project Contribution:
National Academy Member: N

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Partners

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Dr. Daan Hein Alsem - Hummingbird Scientific Inc - Washington. We have extensively worked with Dr. Alsem for ac

I certify that the information in the report is complete and accurate:
Signature: Peter Bruggeman
Signature Date: 11/10/21 11:22PM

Project report

Transmission Electron Microscope (TEM) to Study Plasma-Driven Solution Electrochemistry (PDSE)

The project consists of two equipment purchases: a high-resolution TEM and *in-situ* TEM holders which are described separately below.

High Resolution TEM (Purchase price: $1,133,082)

A high-resolution TEM, ThermoFisher Scientific (formerly FEI) Talos^{TM} F200X G2 analytical (S)TEM, was acquired and delivered in May 2021 to the University of Minnesota. The TEM purchased for this research instrumentation program will be located in a dedicated room with an area of 471 sqf (room 1-208) in Nils Hasselmo Hall which is part of the Characterization Facility (CharFac) of the University of Minnesota. Figure 1 shows images of the renovated room and the TEM. The TEM will be maintained and operated by the CharFac to the benefit of the entire University of Minnesota community as well as external users. Administrative and technical support will be provided through CharFac. While the TEM system was delivered May 2021 at the University of Minnesota, the COVID pandemic has led to delays in the room renovation for the TEM resulting in a delay in the installation of the TEM. The dedicated TEM room is at the time of writing this report fully renovated and fulfilled all technical requirements for the installation. Pictures of the main room and attached utility room are shown in Figure 1(a,b). The ThermoFischer Scientific engineers are scheduled to install the TEM the week of November 15, 2021.

Figure 1 – (a) Picture of the main room in NHH building dedicated for the purchased TEM. (b) Adjacent specially designed utility room for power supplies and other auxiliary equipment for the TEM. (c) Image of the Talos^{TM} F200X G2 TEM purchased on this project.

TEM holders (Purchase price: $366,917.92)

The PI of the project has been intensively working over the last year with the technical team of Hummingbird Scientific, led by Dr. Daan Hein Alsem, to design and fabricate two dedicated TEM holders that are compatible for *in-situ* plasma generation. These two TEM holders are based on Hummingbird Scientific`s design of gas-cell and liquid-cell holders. Both holders required major design modifications to make them compatible with the high voltage required to generate plasma. Figure 2(a-c) show pictures of the new *in-situ* plasma TEM holder and the chip that were designed based on Hummingbird`s gas cell TEM holder.

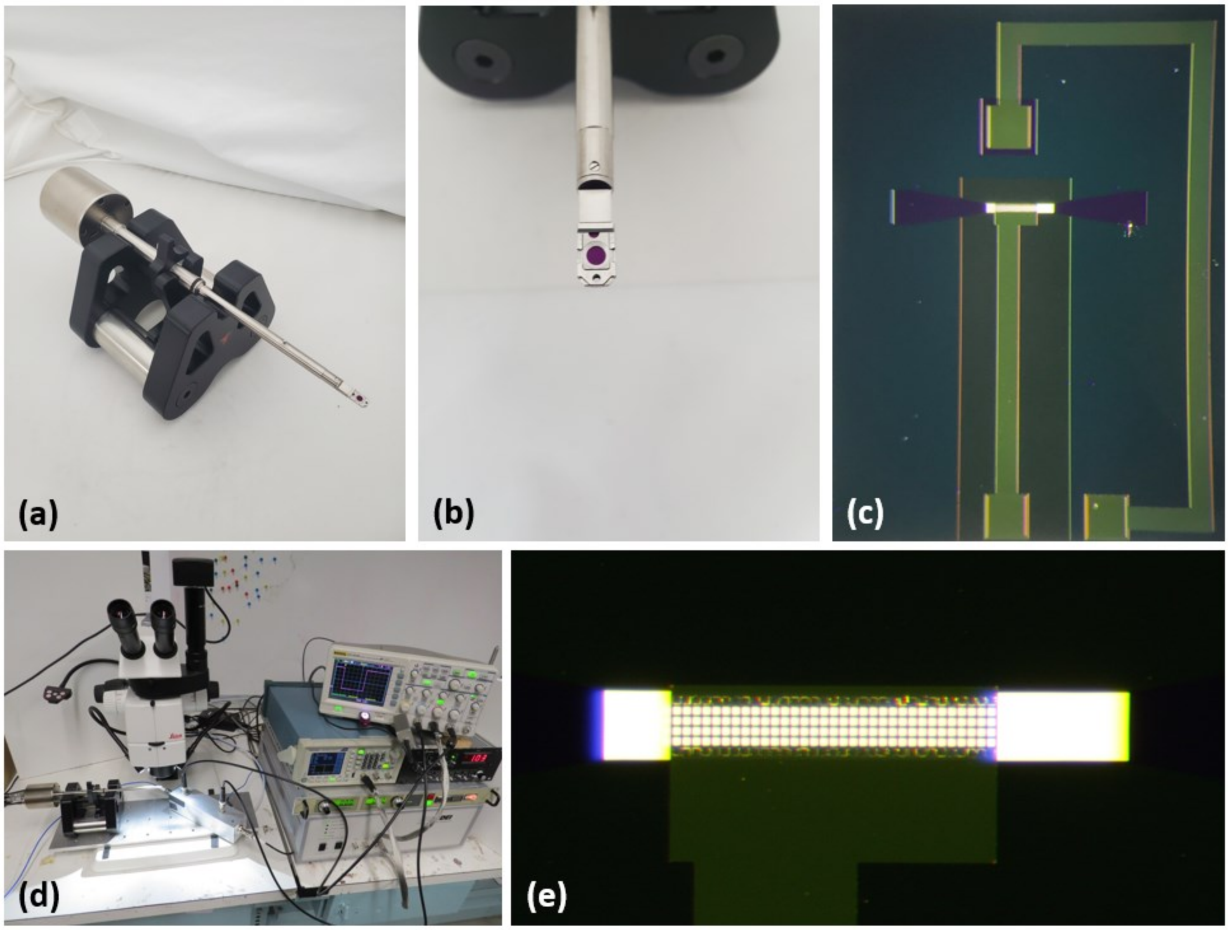

Figure 2 – Images of the new *in-situ* plasma TEM holder based on the gas-cell TEM holder design of Hummingbird Scientific. (a) Overview picture of the holder, (b) zoom in picture of the front end of the holder containing the gas-cell chip, (c) microscopic image of the chip constituting the upper wall of the gas-cell and containing electrodes enabling plasma generation, (d) TEM holder coupled to voltage generation and gas delivery systems during testing in our High Temperature and Plasma Laboratory, and (e) optical microscopy image of the electrode pattern in the chip window area (the square electron pattern has a dimension of 5 μm).

The new *in-situ* gas-cell holder has been tested with voltages up to 600 V which enables the generation of plasma in the gas-cell with a thickness similar to the Paschen minimum of He and Ar. Extensive tests informed us about a list of needed improvements of the chip design (which are consumables) and they are currently being implemented in the second round of chip design. The holder is anticipated to enable the study of PDSE during nanoparticle synthesis after the introduction of a liquid droplet in the cell. In addition, the gas-cell should enable the study of plasma-nanostructured surface interactions similar to the previously reported work by Prof. Eden and co-workers, although under much more controlled gas conditions.

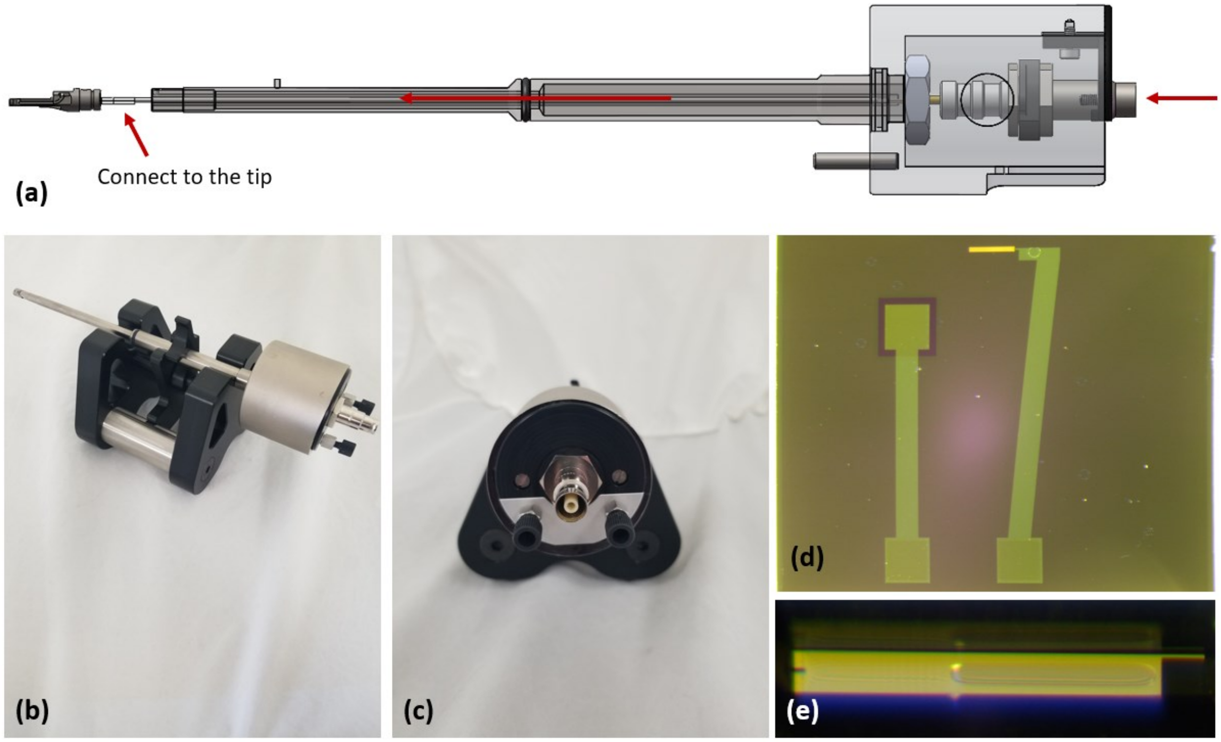

Figure 3 – Images of the second *in-situ* plasma TEM holder based on the liquid-cell TEM holder design of Hummingbird Scientific. (a) Cross sectional schematic of the holder illustrating the design with removable tip and high voltage compatibility, (b) overview image of the new liquid-cell plasma holder, (c) the back of the liquid-cell plasma holder showing newly designed high voltage connection, (d) optical microscopy image of the chip with electrodes forming the lower part of the liquid cell, and (e) image of a bubble forming in the cell enabled by a pulsed voltage which will be used for plasma generation.

Figure 3 shows the newly developed second *in-situ* plasma TEM holder based on the liquid-cell TEM holder design of Hummingbird Scientific. The holder allows continuous flow of solution through the cell that can be monitored. To enable plasma generation in the cell with a thickness of a few 100 nm, we require a higher voltage compared to the gas phase cell. The cell was designed for 3 kV operation and the critical components of the holder have been tested to withstand such high voltages. This requirement, in addition to the ability to disassemble the tip for cleaning of the system after use with different liquids, required major changes to the original liquid-cell design. We incorporated new capability to this holder that allows us to run it also as a gas-cell holder and perform experiments at voltages above 1 kV, when needed. As plasma generation in the liquid state requires excessively large voltages, the generation of plasma in the liquid will be proceeded by bubble formation that can be achieved in the liquid-cell holder by pulsed voltage generation as shown in Figure 3 (e). At the time of writing this report, final tests of the initial chip design are performed (which are consumables) and additional improvements will be implemented in the second round of chip design.

Outlook: Development of the *in-situ* plasma-solution electrolysis TEM capability will be completed within the framework of the MURI "Plasma-driven solution electrochemistry", which broadens the capabilities existing *in-situ* electrolysis TEM methods. It has the potential to provide a treasure trove of new fundamental insights that will provide unique experimental benchmark information for theoretical work, in particular on nucleation theory, and plasma-liquid interaction modeling that are currently performed within the MURI "Plasma-driven solution electrochemistry".