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LDRD Final Report - In Operando Liquid Cell TEM Characterization of Nickel-Based Electrocatalyst

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Disclaimer

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In Operando Liquid Cell TEM Characterization of Nickel-Based Electrocatalyst

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Abstract

A commercial electrochemistry stage for transmission electron microscopy (TEM) was tested to determine whether to purchase one for the microscopes at Lawrence Livermore National Lab (LLNL). Deposition of a nickel-based electrocatalyst was pursued as a material system for the purpose of testing the stage. The stage was found to be problematic with recurring issues in the electrical connections and vacuum sealing, which has thus far precluded a systematic investigation of the original material system. However, the electrochemical cells purchased through this FS will allow the Lawrence Fellow (Nielsen) to continue testing the stage. Furthermore, discussions with a second vendor, which released a similar electrochemical TEM stage during the course of this FS, have resulted in an upcoming long-term loan of their stage at Lawrence Berkeley National Lab (LBNL) for testing. In addition, low-loss electron energy-loss spectroscopy (EELS) measurements on nickel-bearing electrolyte solutions led to a broader EELS investigation of solvents and salt solutions. These measurements form the basis of a manuscript in preparation on EELS measurements of the liquid phase.

Background and Research Objectives

Electrochemical liquid cell TEM is a young characterization technique with the potential to provide unique insights into a broad range of functional materials in real environments, including numerous programmatic efforts such as energy storage materials, accelerated corrosion, additive manufacturing, and biomimetic assembly. A commercial platform is available for in situ electrochemical experiments in the TEM, but its viability for quantitative measurements across a wide spectrum of materials is unknown. The goal of this study was to test the functionality of this tool through investigating the nanoscale evolution of a nickel-based electrocatalyst, in order to determine the value of acquiring a liquid cell TEM holder compatible with the CM300 and Titan microscopes at LLNL. This new capability at LLNL would provide a characterization platform to directly image, and collect structural and chemical information at the nanometer-scale of, assembly mechanisms, phase transformations, and morphological changes in a variety of liquid-based systems under controlled conditions.

Scientific Approach and Accomplishments

The primary research metrics for this project were studying the deposition and evolution of a nickel-based electrocatalyst in the TEM. To this aim, we tested an analytical electrochemical TEM stage from Hummingbird Scientific by biasing electrodes immersed in a nickel-based electrolyte while imaging in a JEOL 2100F field emission TEM at the Molecular Foundry. Initial biasing tests utilized a Metrohm PGSTAT302N potentiostat. However, because the potentiostat imposes a ground in the circuit and the stage goniometer holds the stage at 5 volts, this setup was found to be incompatible. The setup was thus changed to incorporate a Keithley source meter to manually sweep the relative bias of two electrodes in the electrochemical cell. We experienced recurring electrical issues with the TEM stage due to faulty and fragile electrical connections. Despite repeated repair of the delicate connectors these problems have persisted, precluding the necessary ability to properly bias the electrochemical cell for testing. In addition, the stage exhibited issues with vacuum compatibility, which required it to be sent back to the vendor for repair. In only a few instances did the electrical biasing aspect of the stage function as expected. In these cases we were able to cycle the bias on the electrodes and observe nickel deposition and stripping (Figures 1 and 2).

While the electrical issues in the stage prevented us from making extensive measurements on deposition and evolution of the catalyst material, we were able to capture the deposition and stripping of nickel from solution on a few occasions. A few cycles of this process, controlled by sweeping the electrode bias between +/- 2.2 V, can be seen in Figures 1 and 2 below. In Figure 1 growth can be observed extending laterally from the edge of the electrode in addition to islands nucleating and growing on the top surface of the electrode (most readily seen in the second cycle). However, deposits are also seen on the silicon nitride membranes separate from the electrode, starting around 360 s during the first dissolution sweep and building up throughout the rest of the video. Further work will need to be done to investigate whether this behavior is inherent to the cycling process or is a beam-induced phenomenon.

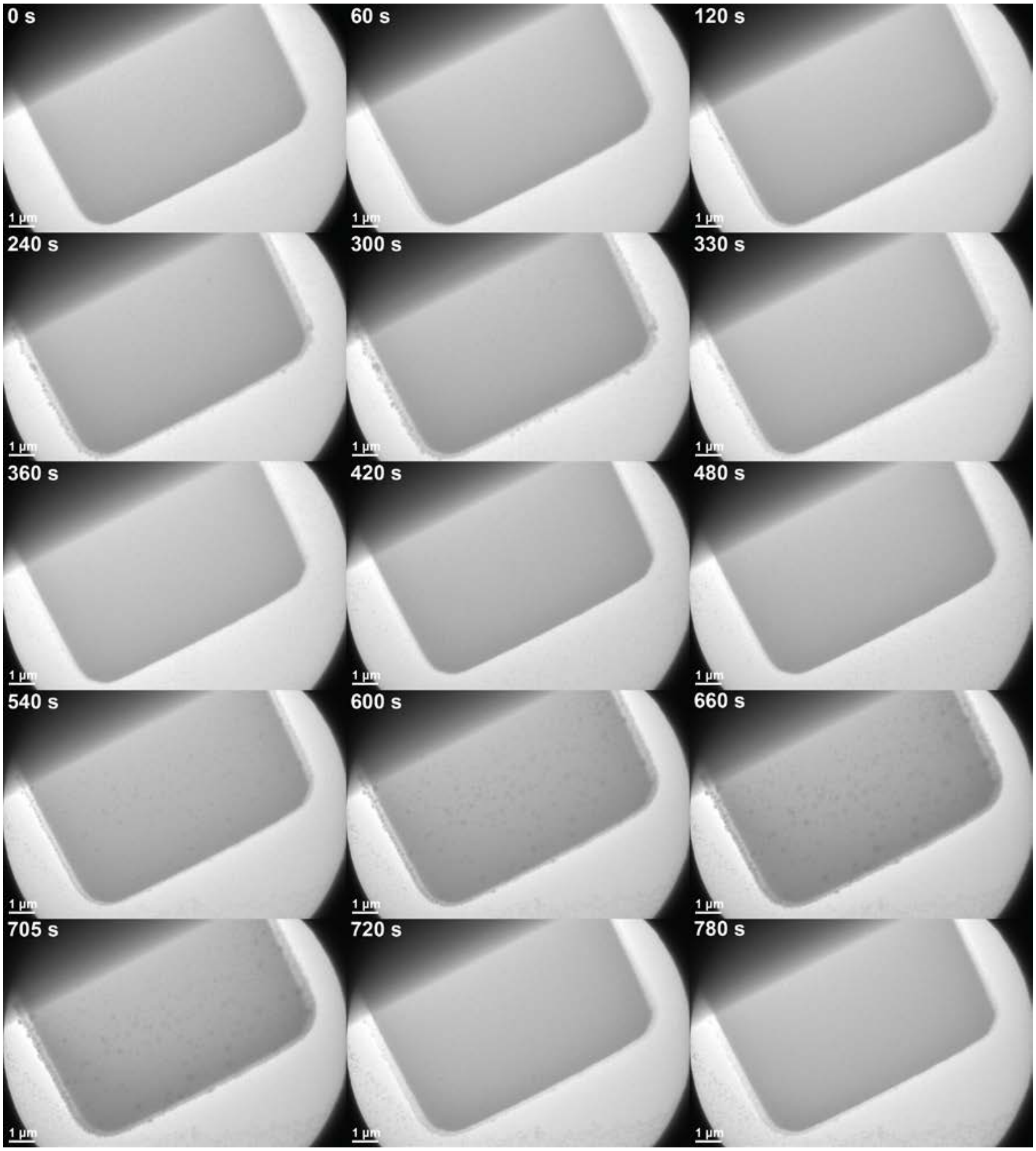

Figure 1. Selected frames from in situ TEM video show two cycles of nickel deposition and stripping from electrode as the bias is swept between +/- 2.2 V.

Figure 2 below shows a higher magnification view of the same cycling process, with just a section of the active electrode area in view. As with

Figure 1, both lateral growth and islands on the top surface of the electrode can be seen growing and dissolving over time as the bias is again swept between +/- 2.2 V.

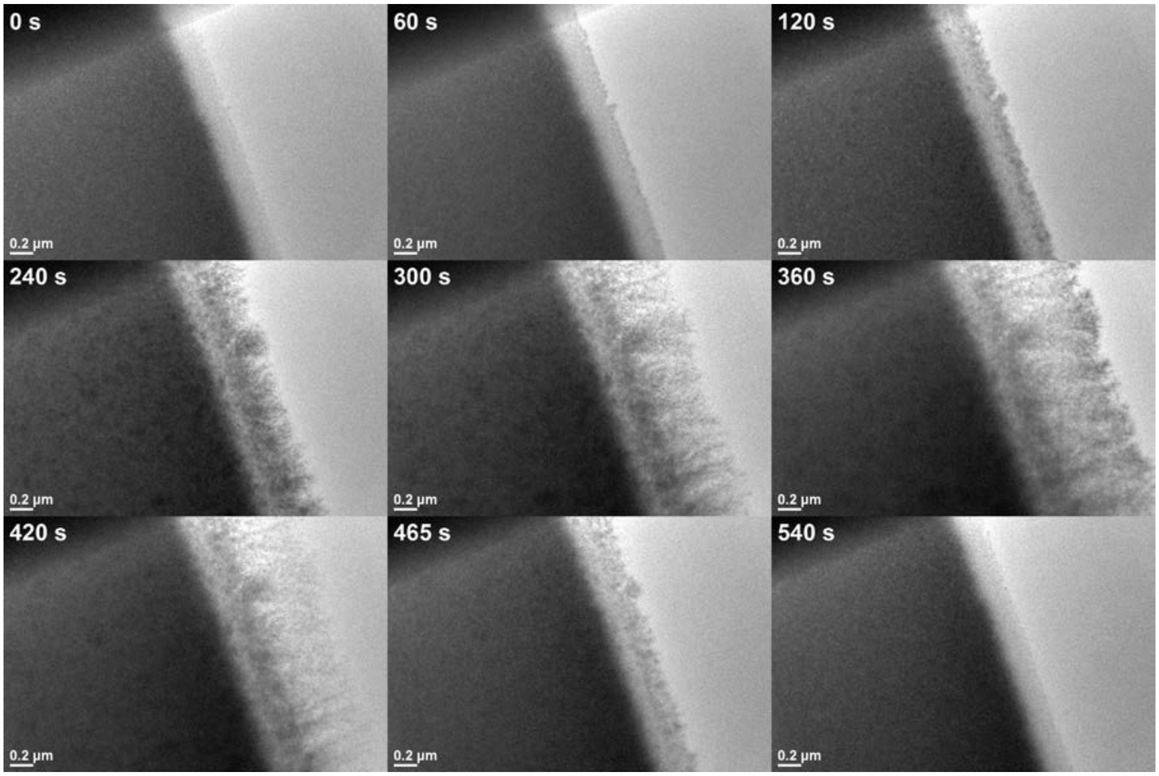

Figure 2. Selected frames from in situ TEM video show higher magnification view of nickel growth and dissolution on the electrode as the bias is swept between +/- 2.2 V.

Ancillary objectives included independent ex situ measurements of the stage and electrochemical cell performance. A measurement jig for the electrochemistry cell was designed and machined at LBNL, compatible with an existing probe station. However, due to the problems with the stage detailed above, the importance of testing the cell independent of the stage has not yet come to the fore.

During the course of the electrochemical tests, EELS measurements were made of the deposited layer and nearby solution, in part to try to obtain a chemical signature of the material and its nearby environment. Very little exists in the literature on liquid phase EELS signatures, beyond a handful of spectra of water and a few other solvents. In the nickel electrolyte solution used for electrodeposition, we found distinct low loss features in the EEL spectrum which led us to look at a set of different salt solutions, as shown below in Figure 3. Analysis of this data is ongoing and we expect that it will form the basis of a manuscript on liquid phase EELS measurements, a subject that is largely absent from the in situ TEM literature, likely to be tailored to a journal such as Microscopy & Microanalysis.

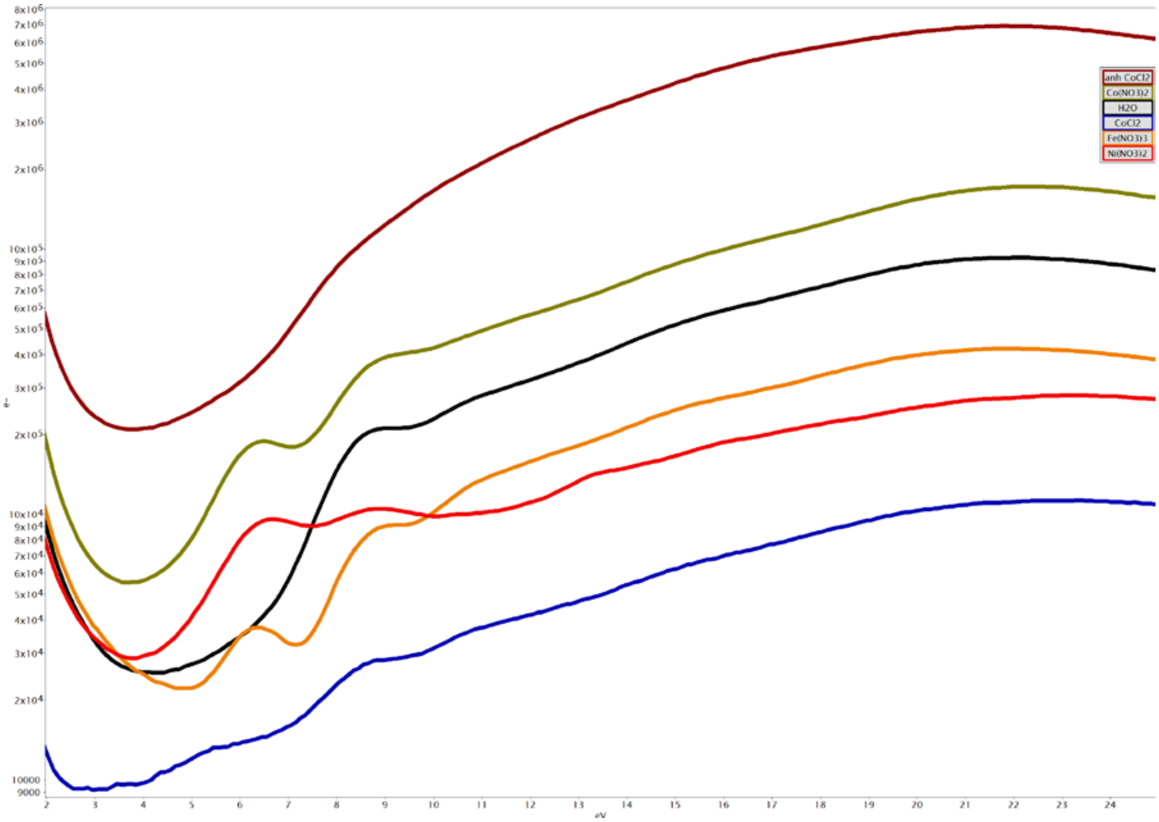

Figure 3. Unprocessed low loss EELS spectra from electrolyte solutions and water show distinct features that appear in the electrolyte solutions.

During the course of the project, a competing vendor (Protochips) released an updated model of their electrochemical TEM stage which addressed our previous concerns with their liquid stages. Through meetings with them at conferences (Materials Research Society, Microscopy & Microanalysis) and on-site at LBNL, we have arranged for the future loan of a stage for testing at LBNL, tentatively scheduled for early 2017.

Impact on Mission

This project was designed to look at the utility of purchasing a commercially available electrochemical TEM stage for LLNL, which would be compatible with the existing Titan and CM300 microscopes. Such electrochemical measurements would dramatically benefit programs investigating energy storage materials, accelerated corrosion, additive manufacturing, and biomimetic assembly.

However, with the demonstrated lack of consistent functionality, the results suggest that at this time it would not be worthwhile to purchase this stage. However, the negotiated future loan of a competing stage for testing at LBNL may result in that stage being suitable.

Conclusion

Recurring problems with the TEM stage precluded any extensive investigations into deposition or aging of the nickel-based electrocatalyst. The current lack of consistent functionality under typical operating conditions makes the stage a poor candidate for purchasing at LLNL. However, continued research by Lawrence Fellow Nielsen at LBNL using the remainder of the supplies purchased under this FS may find that the stage functions with further modifications. Additionally, the future long-term loan of a competing stage at LBNL for testing may determine that another vendor’s product is a viable solution.

EELS measurements on low-loss signatures from solvents and electrolyte solutions are being analyzed. Further measurements will be made with the aim to compile a manuscript for publication on quantitative chemical measurements of the liquid phase in TEM.