Electrochemical TEM of Nanostructured Electrodes

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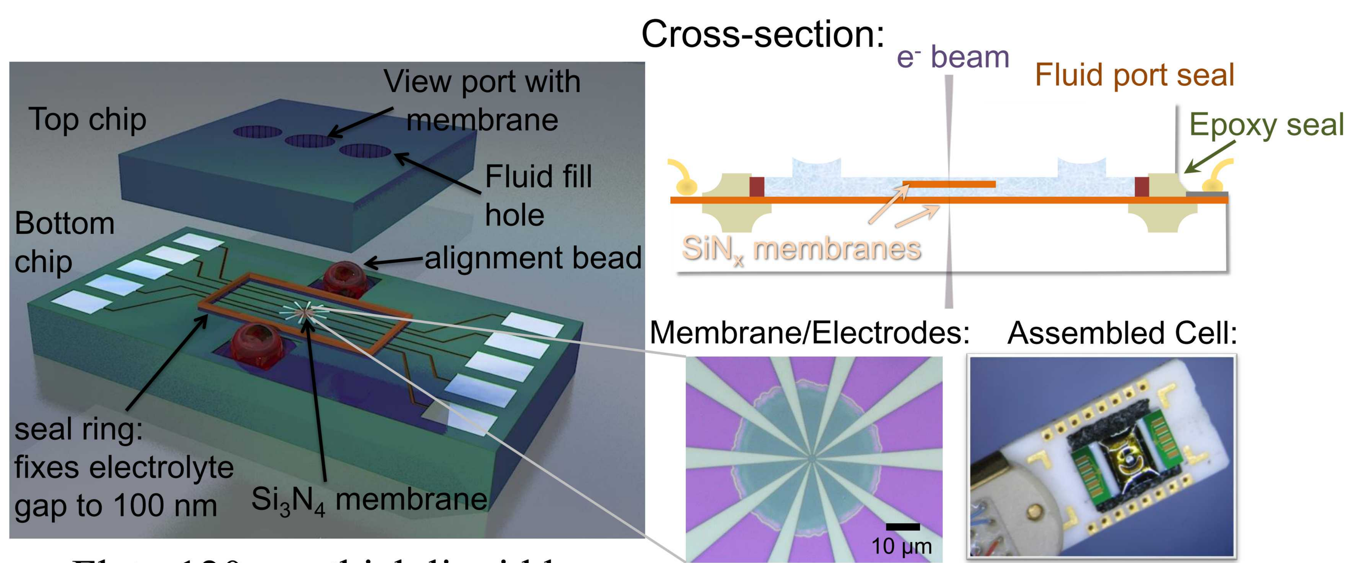
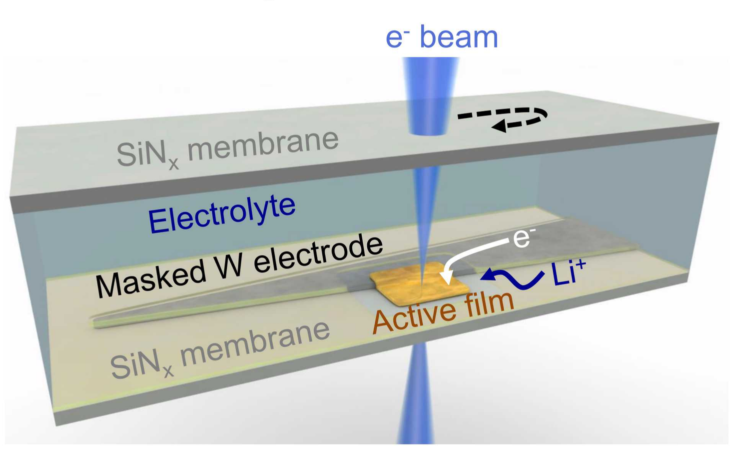
In-Situ Electrochemical TEM of Batteries

High-resolution TEM imaging of nanomaterial electrodes in commercial liquid electrolytes is enabled by a custom microfabricated sealed-cell with electron-transparent membranes. CINT's electrochemical TEM platform is able to test multiple experimental conditions on the same device using a multi-electrode array. Nanoscale electrodes may be cycled under realistic battery conditions while observing the structural and chemical evolution of the materials. Degradation of battery electrodes is being studied using this platform and open-cell techniques for optimization of nanostructured electrode integration into prototype batteries.



- Flat ~120-nm thick liquid layer
- Picoampere current control
- Customized 10 electrodes: materials and patterning
- Li incorporation with controlled area

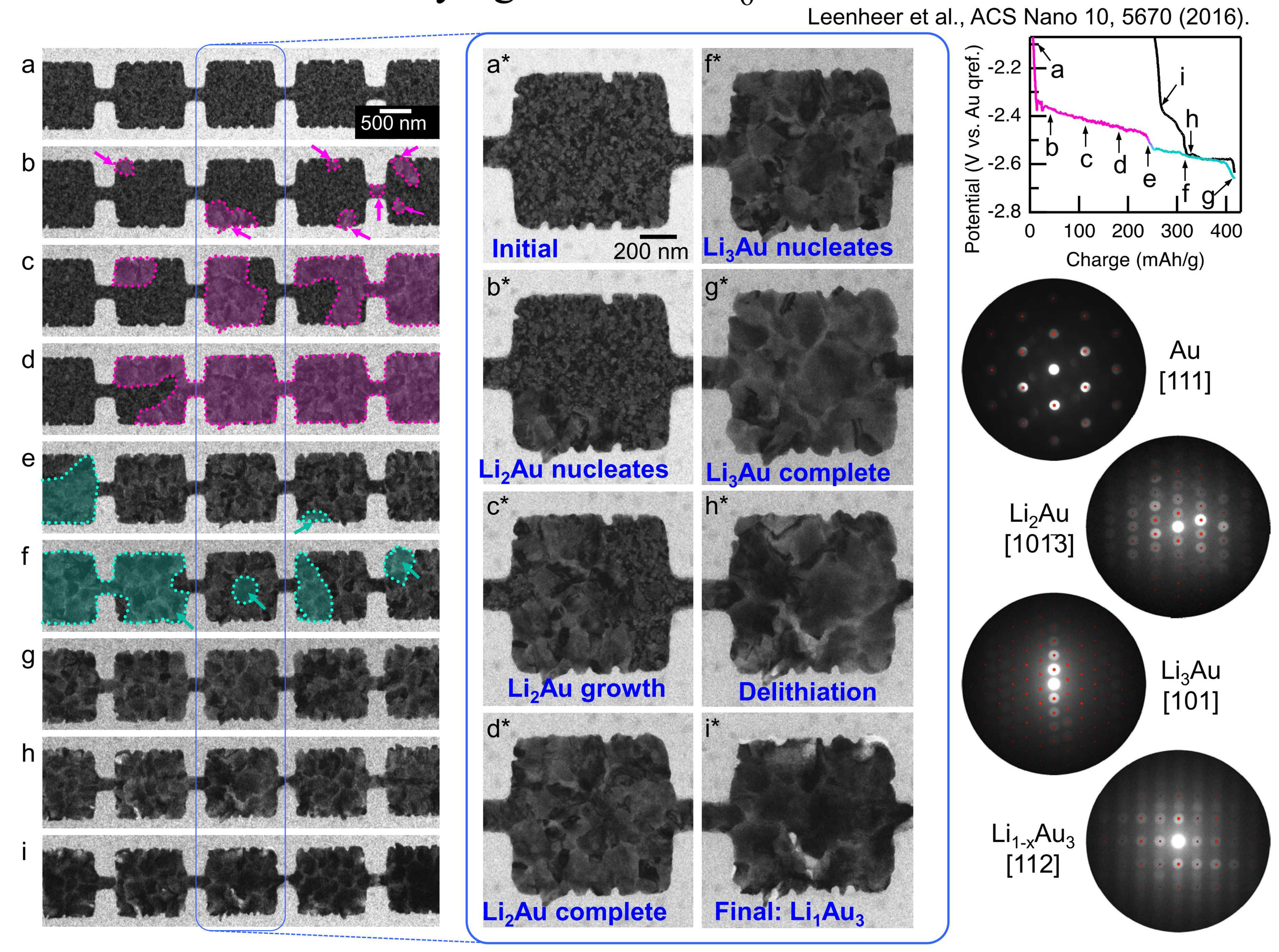


- Active films are patterned down to ~1 µm² to be fully visible in TEM
- Controlled current measurement links images with electrochemical signatures

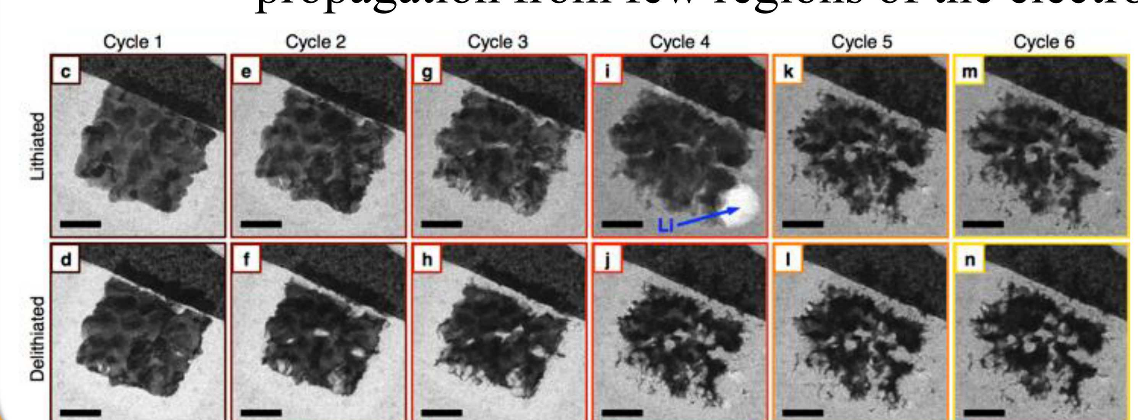
Lithium Alloying: Nucleation and Propagation

- Li-alloying materials also increase anode capacity, but 100 - 300% volume expansion can cause mechanical failure.
- Tracked two electrochemical phase changes in model thin-film material: Au-Li alloying in 1M $LiPF_6$ in 1:1 EC/DMC.

Leenheer et al., ACS Nano 10, 5670 (2016).



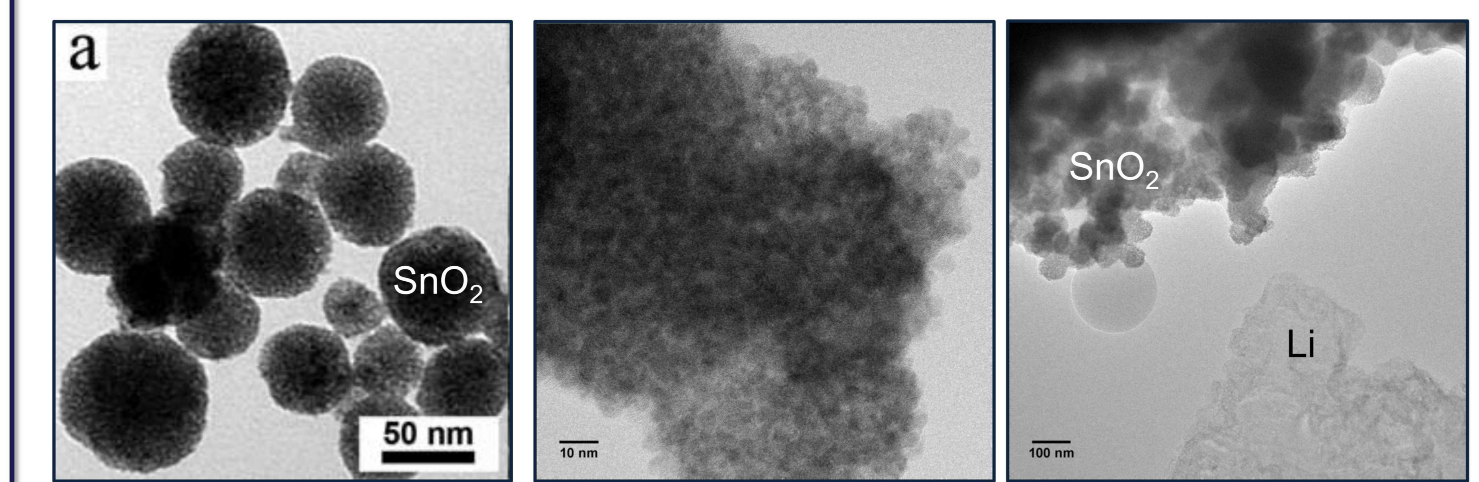
Lithiation in 40 nm Au film showing nucleation and phase front propagation from few regions of the electrode.



The structure of the Au electrode quickly degrades from a thin-film to a raised island structure after only a few cycles at standard charge/discharge rates.

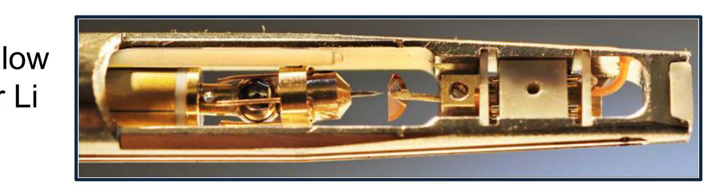
SnO_2 Nanocrystal Aggregate Electrodes

5-6 nm SnO_2 nanocrystals, in 70 – 100 nm aggregate particles were lithium cycled to study electrode degradation of mesoporous structures



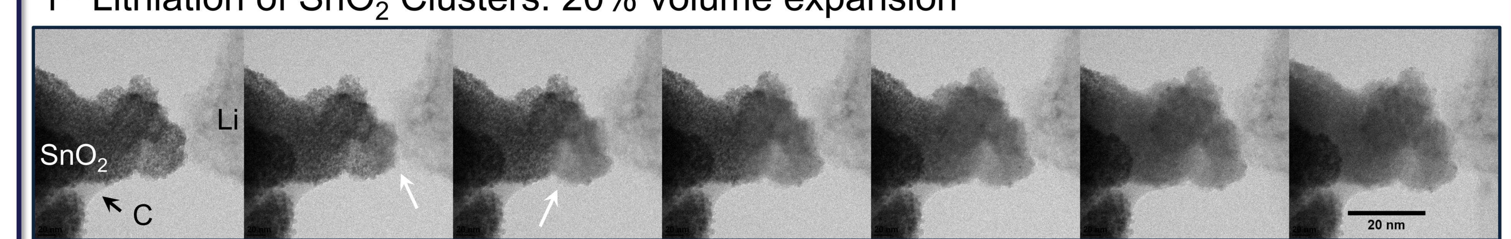
Anumol et al., Nanoscale 2, 1423 (2010).

Open-cell solid-state electrochemical TEM studies allow for tracking the dynamic material cycling behavior for Li insertion and removal from nanocrystal aggregates

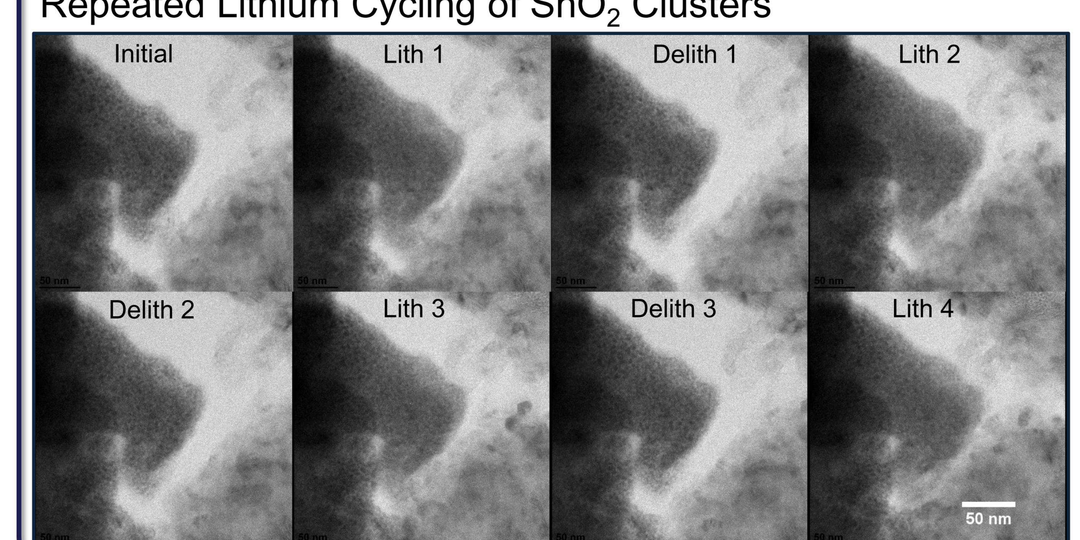


Do the nanocrystal aggregates have residual synthesis materials that could be facilitating Li insertion between nanocrystals? Could nanocrystal aggregates be made into an intact electrode film without the use of a binder?

1st Lithiation of SnO_2 Clusters: 20% volume expansion



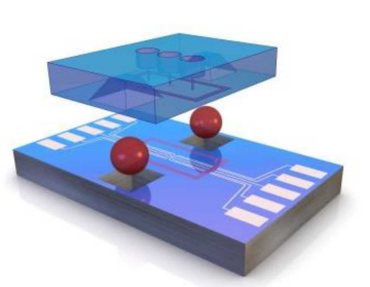
Repeated Lithium Cycling of SnO_2 Clusters



Mesoporous SnO_2 electrode exhibits reproducible cycling of Li to/from the structure with flexible volume expansion

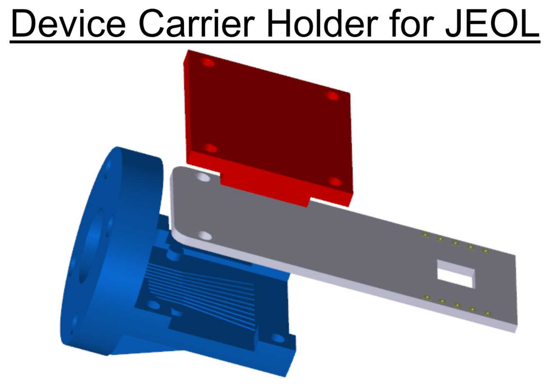
What is the relationship between the flexible volume expansion to nanocrystal size?

TEM Holders for the CINT EChem Platform

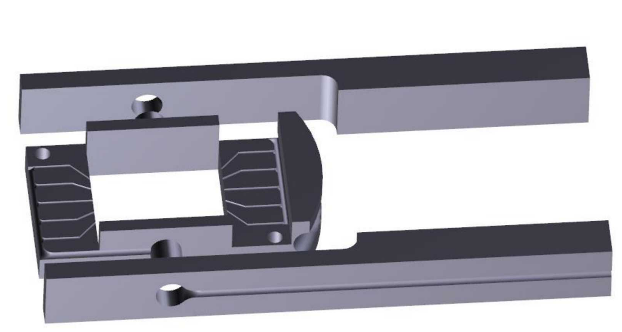


CINT is making prototype TEM holder designs to operate the electrochemical TEM platform within various microscopes and allowing for double-tilt capability.

Device Carrier Holder for JEOL



Double-Tilt Device Carrier Holder

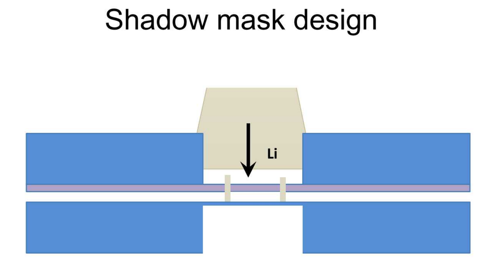


Custom TEM holders will allow for use of the MEMS platform at CINT user's home institutions (Univ. Maryland will receive the first prototype). Integration within CINT allows for testing in the LANL FEI Titan (monochromated & aberration-corrected) and the ion-beam TEM (ion irradiation, precession electron diffraction and cathodoluminescence) for advanced structural, chemical and property measurements of MEMS controlled in-situ experiments.

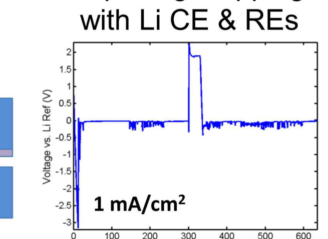
Developments and Future Directions for Nanoscale Battery Testing in the TEM

Integration of Li counter and reference electrodes into the electrochemical platform will provide quantitative voltage measurements

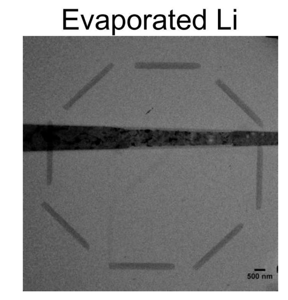
Shadow mask design



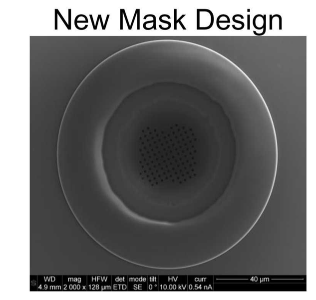
Li plating stripping with Li CE & REs



Evaporated Li

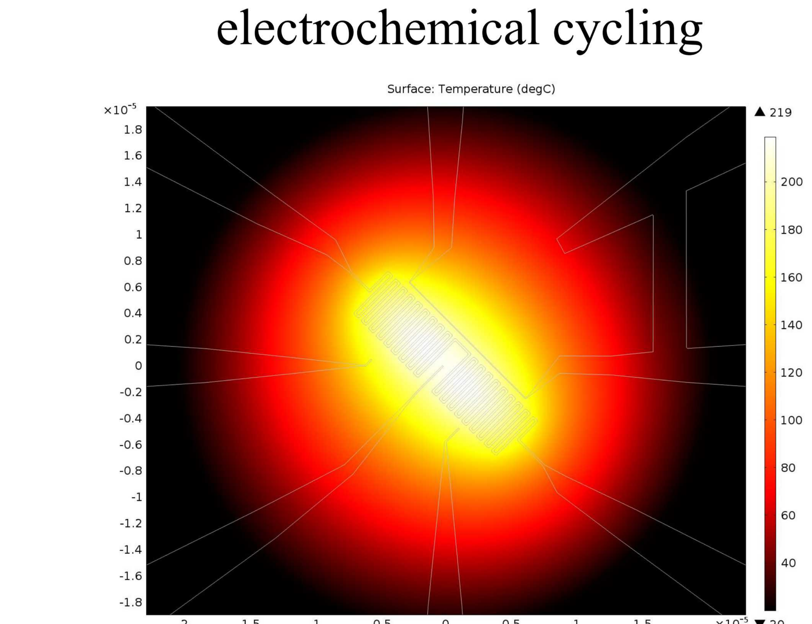


New Mask Design



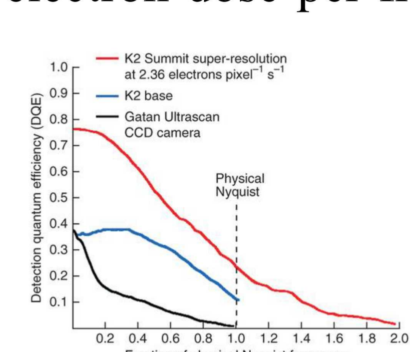
Shadow mask lid for pristine Li evaporation of Li electrodes demonstrates quantitative data. Open fill ports in the lid are used to create large counter and reference electrodes.

Elevated temperature control during electrochemical cycling

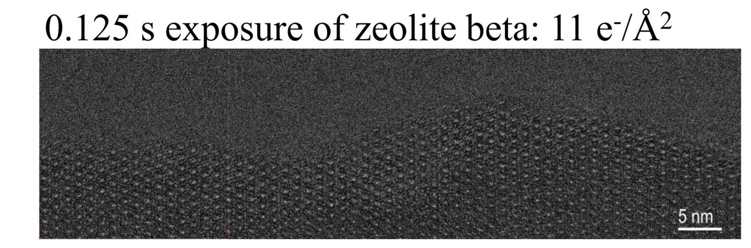


Electron beam lithography can be used to pattern a resistive heater and sense lead about 3 electrodes on the electrochemical TEM platform. This design has the ability to apply/measure temperatures above 100°C for temperature-driven battery degradation mechanisms.

Direct Electron Detection: Increasing resolution without increasing the electron-dose-per-frame



0.125 s exposure of zeolite beta: 11 e⁻/Å²



Beam-sensitive materials, battery electrolytes, require low-dose imaging to mitigate radiolysis damage which can distort structural results for in-situ TEM testing. CINT has purchased a direct electron camera for 7k x7k quality, low-dose and high-frame rate imaging (1,600 fps). Camera is to be delivered to CINT this week.

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NEES NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE

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