Mechanical Properties at the Protected Lithium Interface

Project ID: ES276

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Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

June 2017

This project is jointly funded by DOE and TARDEC through NETL.

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University of Michigan

Overview

- **Timeline**
  - Start: January 2015
  - End: September or December 2017
  - Percent complete 80%

- **Technical barriers**
  - Energy density (500-700 Wh/kg)
  - Cycle life, 3000 to 5000 deep discharge cycles
  - Safety

- **Budget** *This project is jointly funded by DOE and TARDEC.*
  - $340K DOE
  - $540K TARDEC

- **Partners and collaborators**
  - Oak Ridge National Laboratory (lead)
  - Michigan Technological University
  - University of Michigan
  - Collaborators:
    - Nanomechanics, Inc. (Oak Ridge TN)
    - Ohara Corporation, CA

Probing the Li-solid electrolyte interface, from the Li side:

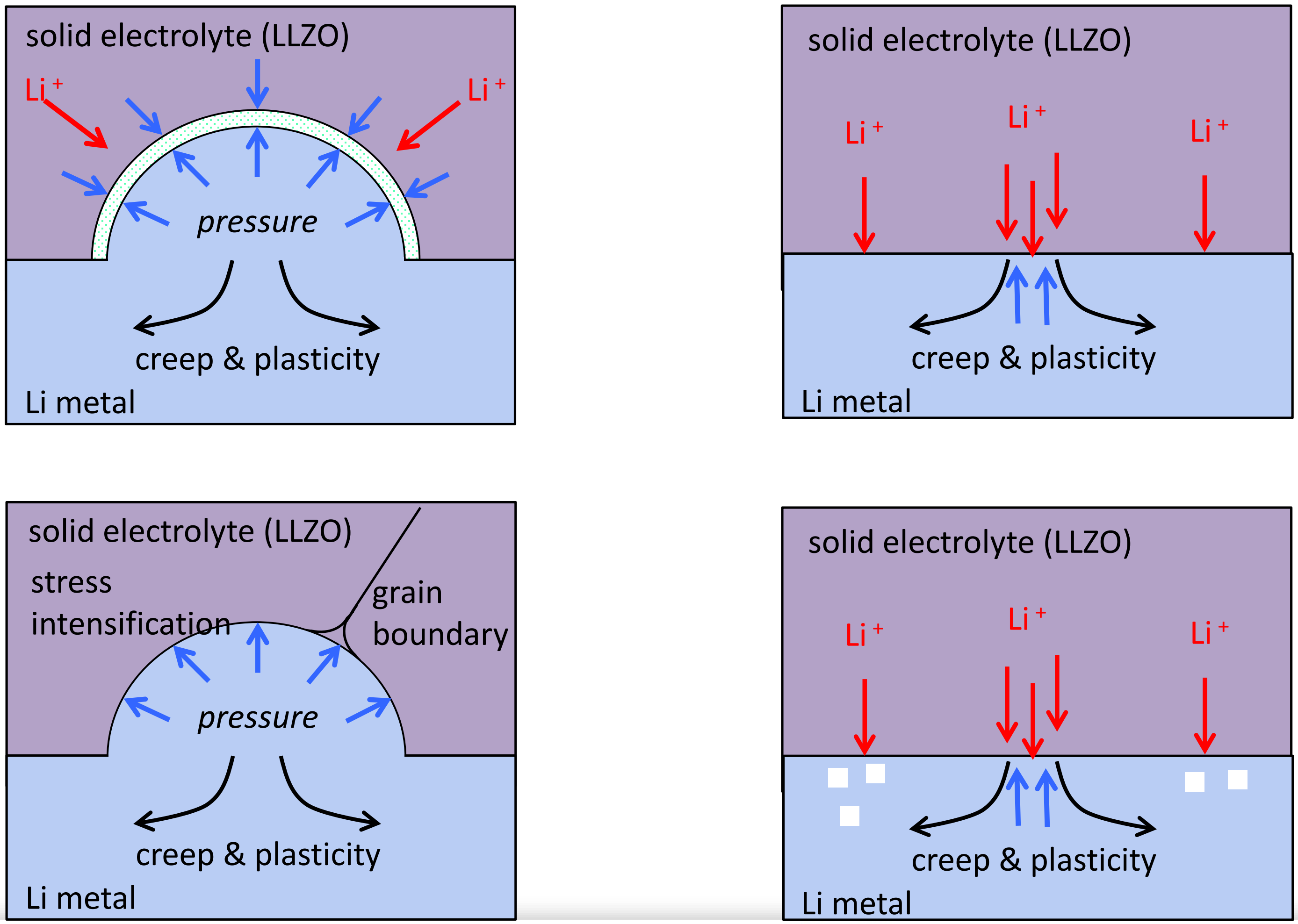
REVELANCE

- **Objectives:**
  - Understand the processes, such as formation of defects and roughening of the Li interface, limiting the cycle life of a solid electrolyte protected lithium anode.
  - Seek new scientific information to reveal the nature of metallic lithium and the lithium/solid electrolyte interface upon rapid and prolonged cycling of the lithium *through the use of mechanical testing,* in addition to typical electrochemical.
  - The goals are to provide:
    - a detailed analysis of candidate solid electrolytes with particular attention to the homogeneity of the interface properties
    - a clear picture of the evolving micro- and defect-structures of the cycled lithium metal.
    - analysis of how lithium must be confined to maintain full capacity
- **Impact:**
  - The expected outcome is a clear interpretation of how the structure of the interface and the defects in the lithium evolve during cycling and how this couples to determine the stability and resistivity of the structure.
  - This will reveal the design rules essential for successful fabrication of the solid electrolyte and packaging in order to maintain full access and efficient cycling of the lithium over many cycles.
  - A safe and energy dense Li anode can only be achieved if there is:
    - Only enough Li to balance cathode, est. 20 µm. (In addition to ~1 µm Li as current collector.)
    - No loss of lithium due to mechanical isolation or side reactions, coulomb efficiency >99.95%.

Objective – Need solutions for two failure processes.

Li shorts through ceramic electrolytes → dead battery
Redistribution of Li during cycling → loss of Li, higher interface resistance

- Inhomogeneity and irregularity of the interface may be relieved by Li flow



Milestones

Milestones: FY15-FY16 Q5-Q8	component	Target:	Status:
Determine elastic properties of battery grade lithium from different sources and preparation, comparing to values from the reference literature	Lithium anodes	Q5	Elastic done. Also plastic deformation
Compare lithium properties, uncycled versus cycled, using thin film battery architecture.	Interface and Li	Q6	Completed
View annealing of defects following a single stripping and plating half cycle, using thin film battery architecture.	Li and interface	Q8	On track, but not with TFB
Milestones FY17 Q9-Q12 next slide			

Comment:
Nanoindentation was intended to be the major method for characterization. As this is proving to be complex, other approaches have been included in the study.

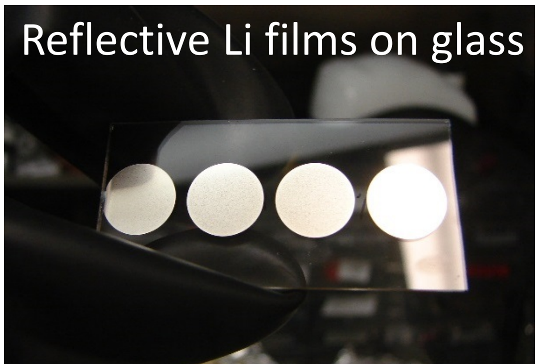
Milestones

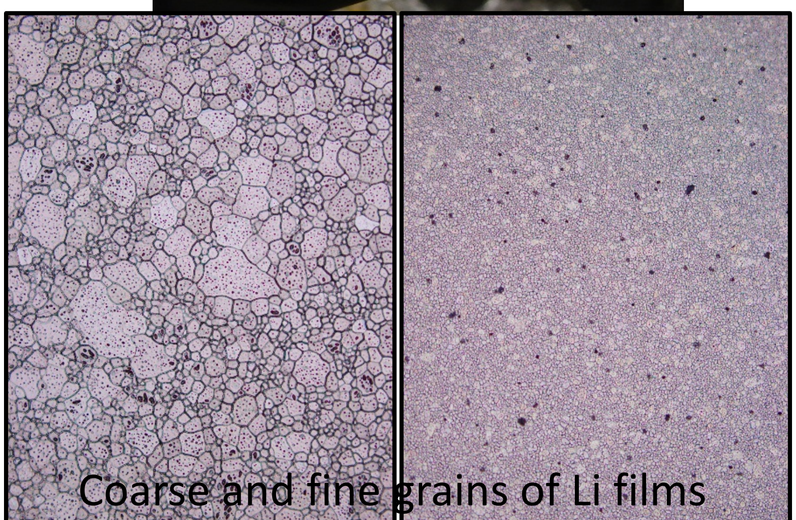
Milestones: FY16-FY17	component	Target:	Status:
Characterize in situ changes in lithium anode from a single stripping and plating half cycle.	Lithium and interface	Q10	Attempts so far not successful
Measure the Li-LLZO interface strength as a function of surface treatment using Instron shear and EIS	Li/LLZO interface	Q11	On track
Examine Li anode in situ during extended electrochemical plating, striping and relaxation to assess defect formation and annealing.	Li battery, with Lipon or LLZO	Q12	Done for TFB, not for LLZO battery
Determine the physical properties of electrolyte failures, the nature of material reduction or lithium incursion/pileup, using indentation or x-ray tomography. Samples from other projects.	Shorted LLZO	Q12	

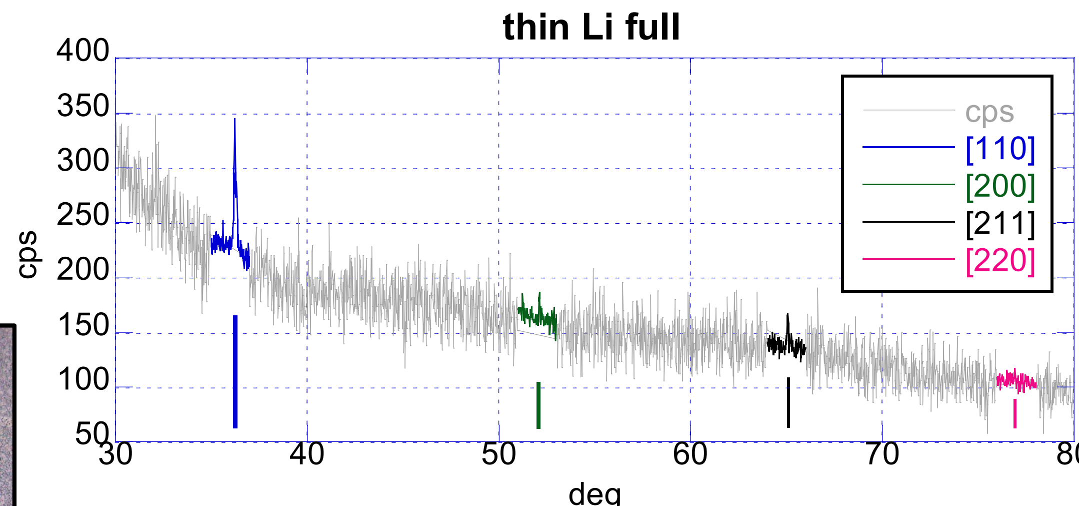
Lithium thin films by vacuum vapor deposition to control the volume, grain size and contact to the solid electrolyte

APPROACH

- Vacuum evaporation → dense films, equiaxed grains (unliked rolled Li).
- Grain size, Li purity, determined by: deposition rate, base pressure, and film thickness.
- Surface reaction/passivation determined by base pressure and Ar glove box purity.
- On clean solid electrolyte, Li coats entire surface with low interface resistance.


Reflective Li films on glass


Coarse and fine grains of Li films



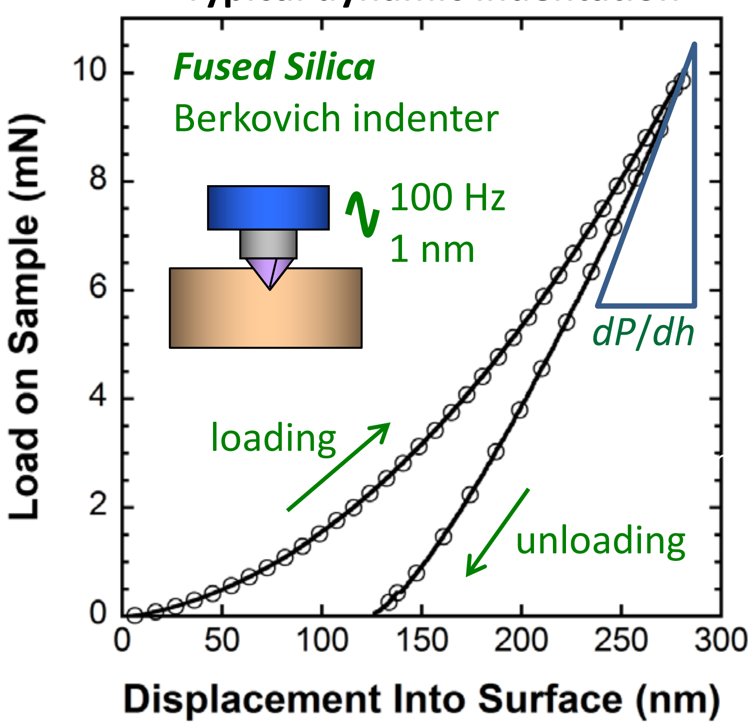
No strong texture found by XRD of Li films

APPROACH

Mechanical behavior of the solid electrolyte (SE), the Li metal, and Li/SE interface by nanoindentation and other methods.

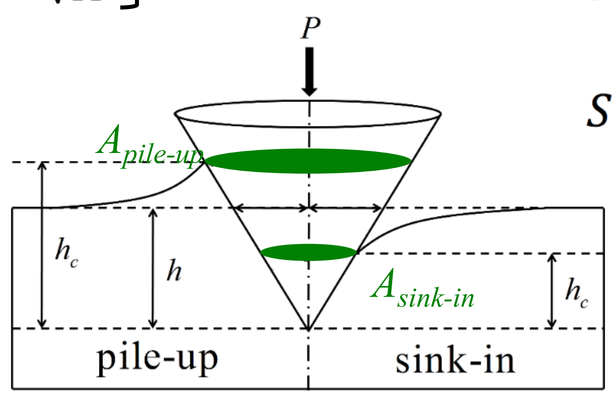
- State-of-the-art nanoindentation techniques: Mechanical properties of thin films, localized properties in individual grains or near grain boundaries; rapid mapping and dynamic methods to examine depth dependent properties & energy dissipation.
- Large indent arrays yield more robust statistics; particularly important for SE and Li.
- Indenter in glove box to minimize surface reactions for both sensitive electrolytes and Li.
- Because E/σ_y and T_H are high, Li's behavior is remarkably complex & unique.

Typical dynamic indentation



$$H = \frac{P}{A}$$ Hardness, the mean pressure the surface can support

$$E \propto \frac{S}{\sqrt{A}}$$ Elastic modulus



Elastic contact stiffness

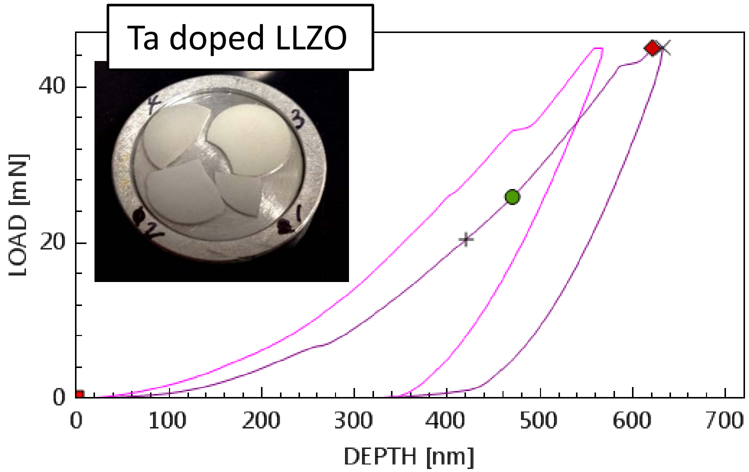
$$S = \frac{dP}{dh}, \text{ or:}$$

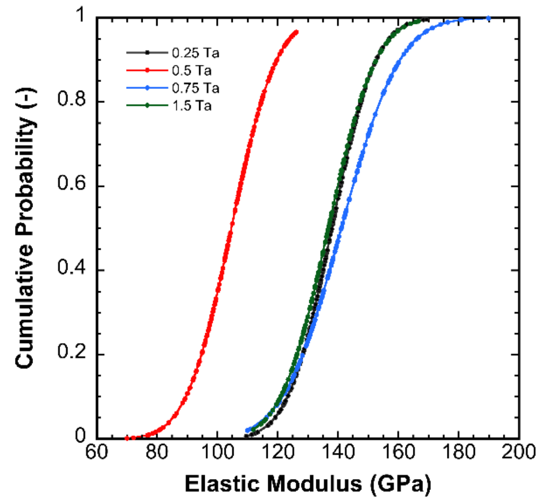
$$S \propto \frac{f_o}{h_o} \cos\delta$$

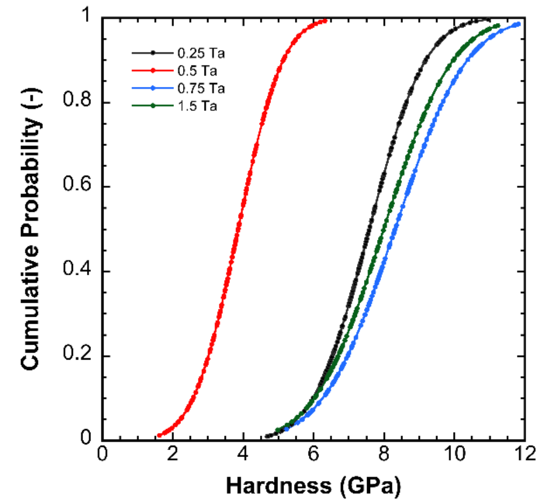
EARLIER WORK

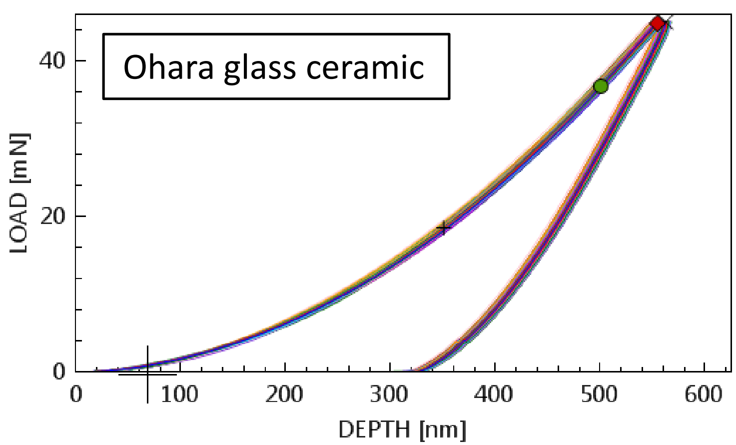
Earlier results from nanoindentation of solid electrolytes.

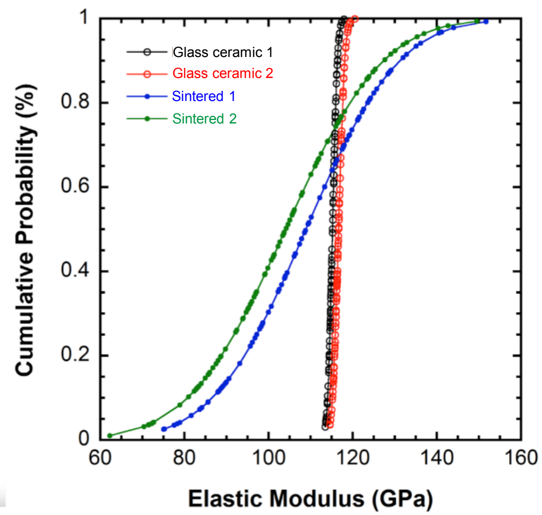
- Elastic & plastic properties of doped $Li_7La_3Zr_2O_{12}$ (LLZO) ceramic electrolytes, and commercial ceramic (sintered) and glass-ceramic plates from Ohara Corp.
- Shorted LLZO, gave no clear indication of weakness.

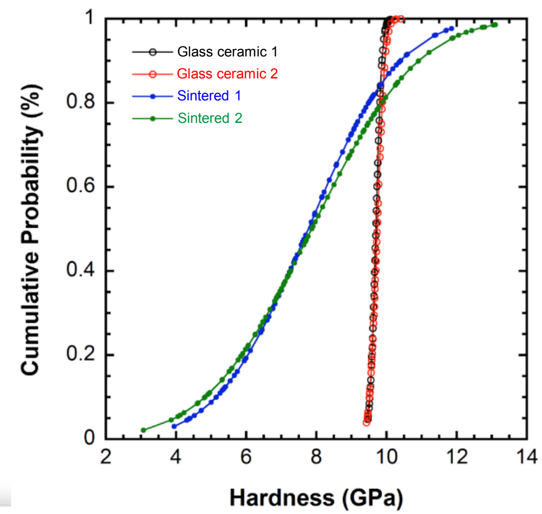








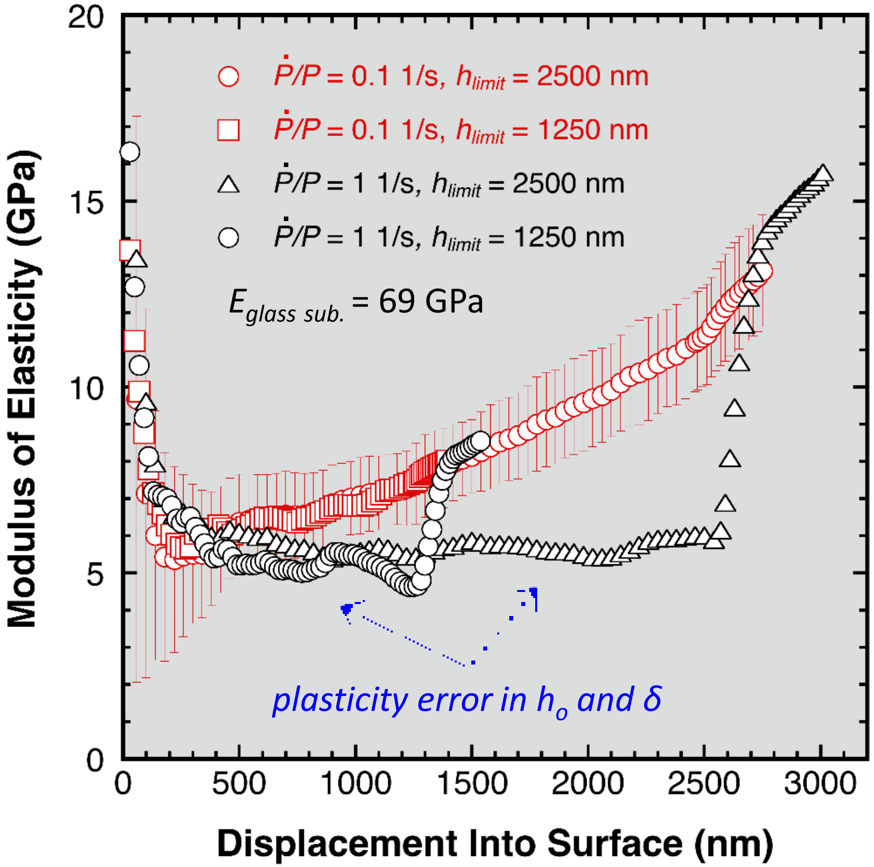


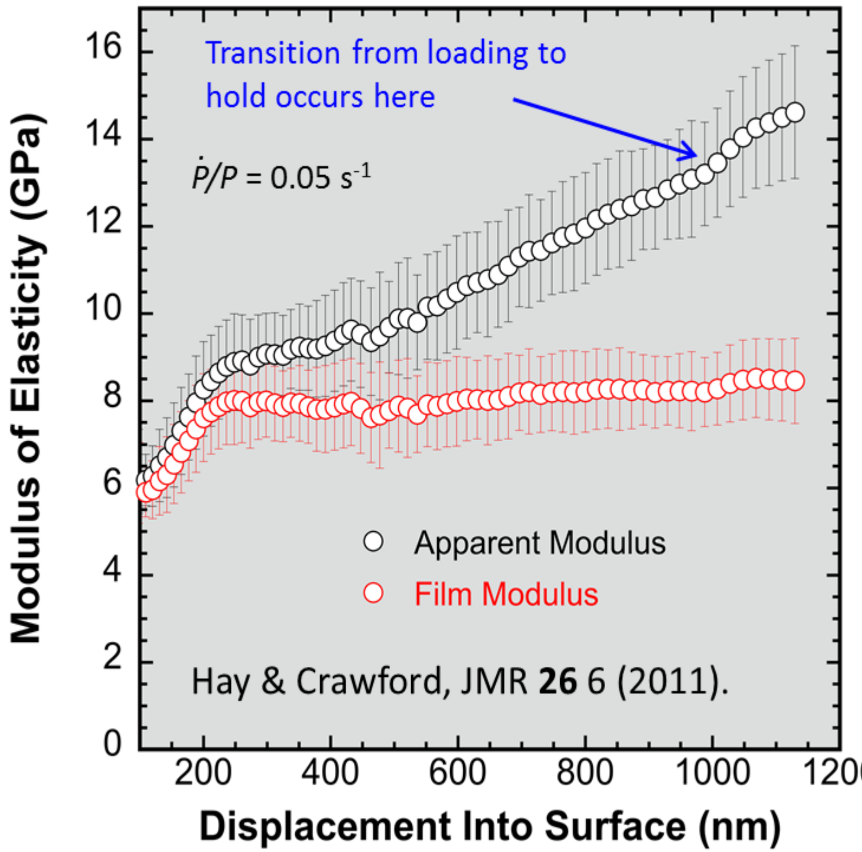


Elastic modulus of Li films on glass via nanoindentation.

ACCOMPLISHMENT

- Dynamic technique can dramatically underestimate E due to Li's extreme E/σ_y .
- At sufficiently slow strain rates relative to the drive frequency, the correct value of E can extracted after removing the substrate effect.
- Measured values agree with literature, approximately 3 to 10 GPa.

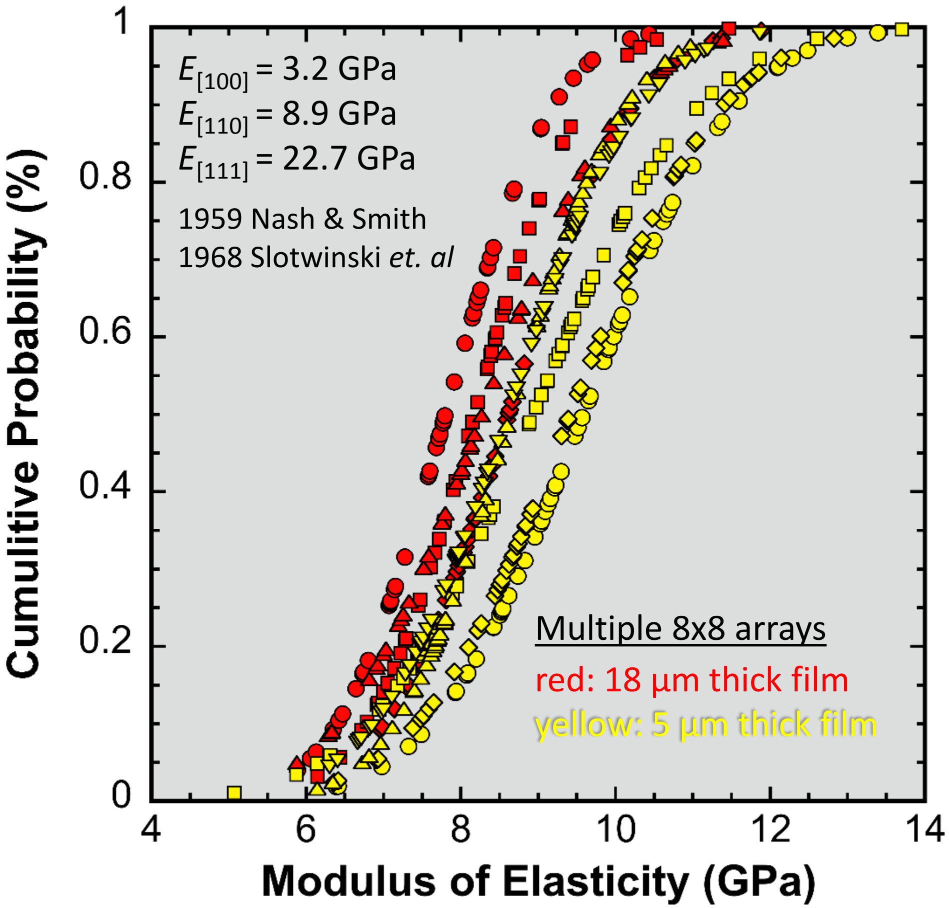


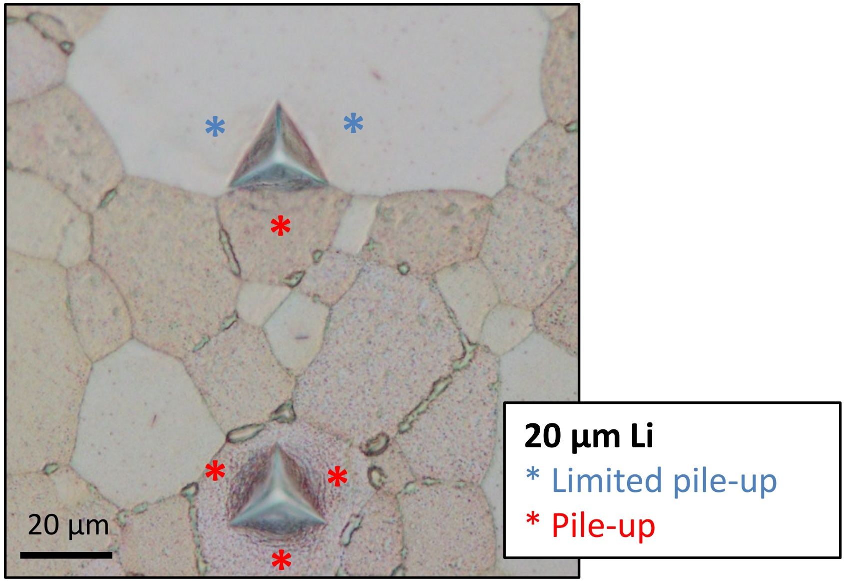


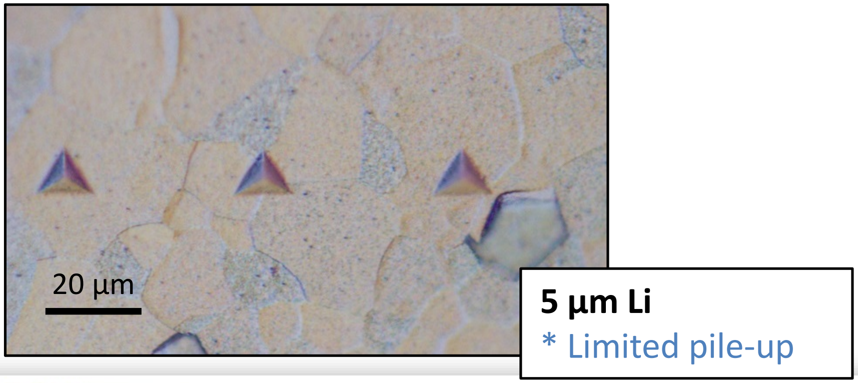
Elastic modulus of Li films on glass via nanoindentation.

ACCOMPLISHMENT

- *E* measured during constant load & hold. *E* exhibits mild texture.
- Deformation is overwhelming accommodated by plasticity.
- Examination of the residual hardness impressions → surface morphology varies from grain to grain and grain boundary to grain boundary.



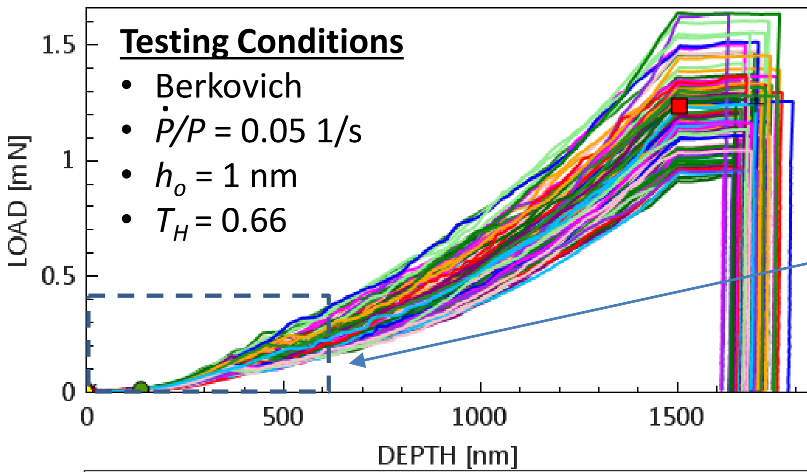


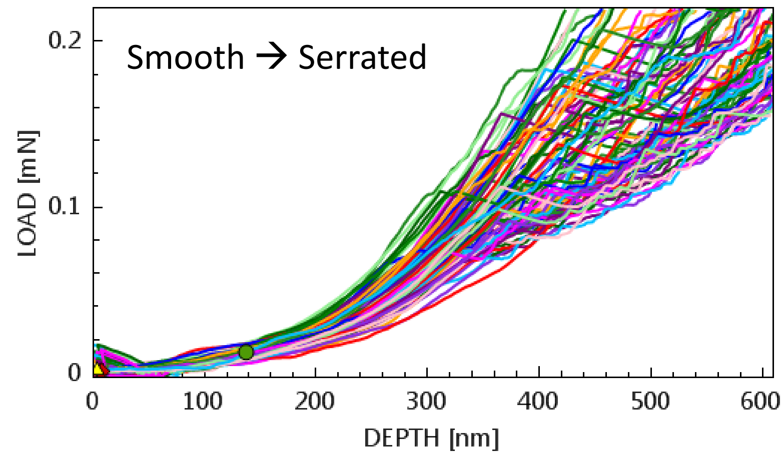


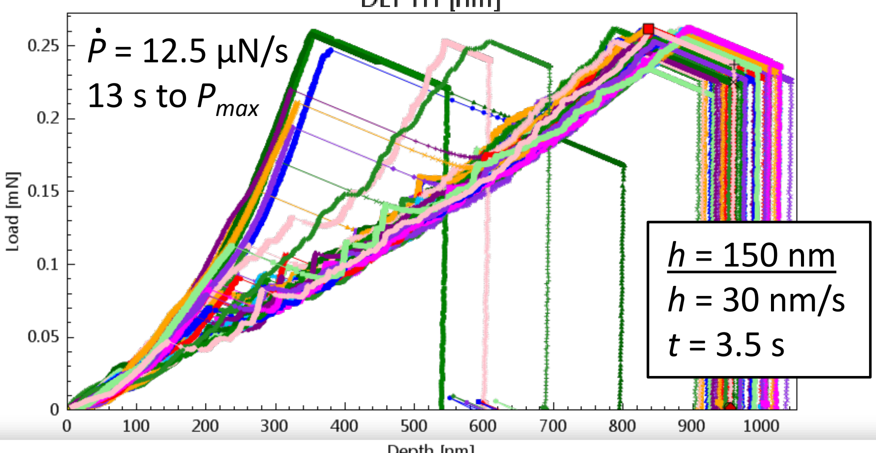
ACCOMPLISHMENT

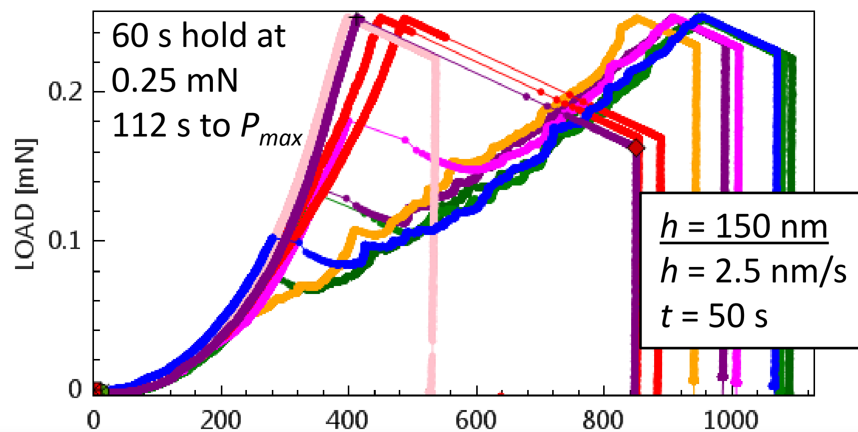
Load displacement curves for Li thin films are unique.

- Distinct deformation regimes: Transition to serrated flow separates regimes of monotonically increasing load & displacement.
- Conjecture: Film's dislocation density initially low. Plasticity near the free surface accommodated by creep. Mechanism exhausts, transitions to stochastic flow via dislocation motion at $\sigma > \sigma_y$.







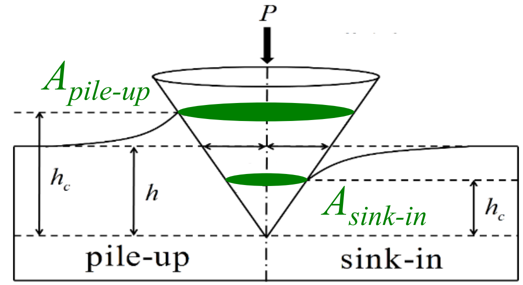


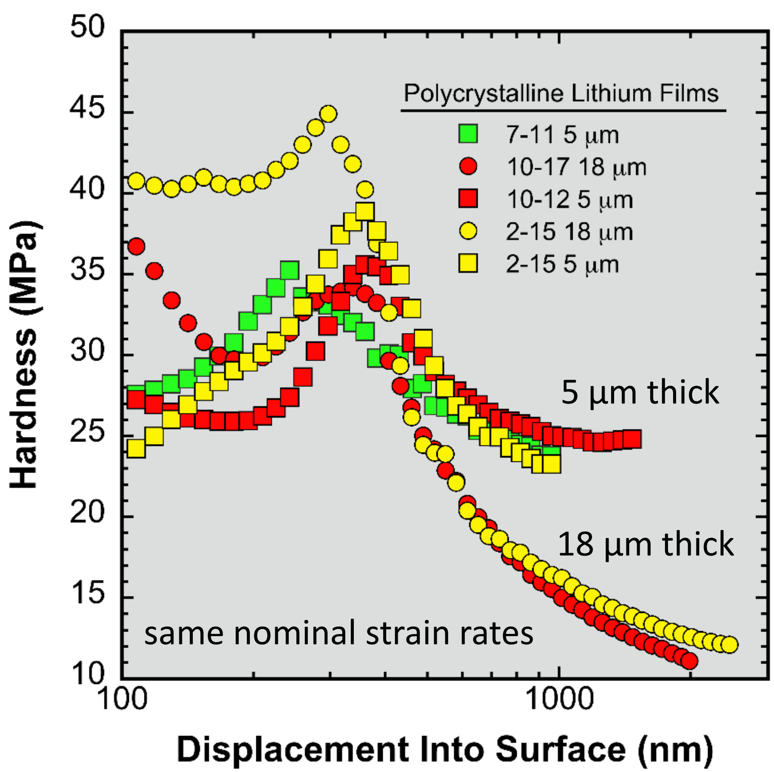
ACCOMPLISHMENT

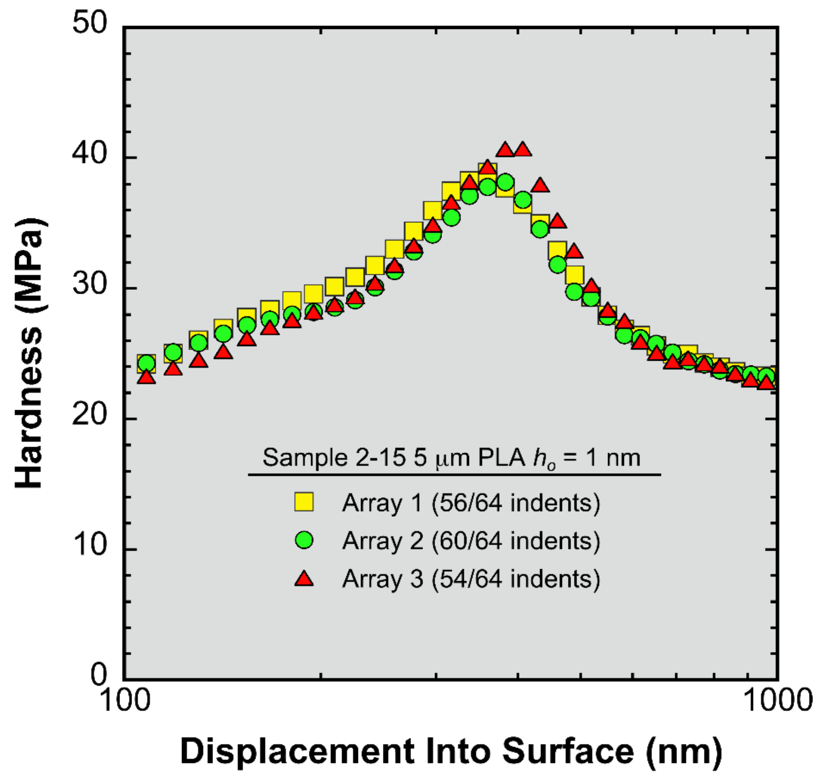
Evaluation of hardness & multiple deformation regimes

- Similar behavior for different film batches & different film thicknesses.
- Highly reproducible for different areas of the same film at the same strain rate.

$H = \frac{P}{A}$ Hardness, the mean pressure the surface can support

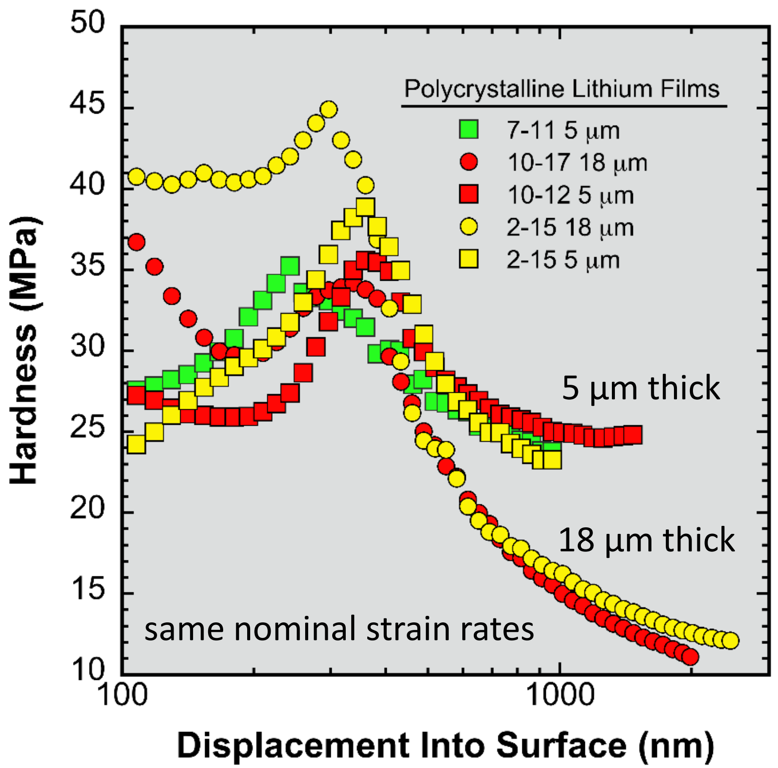


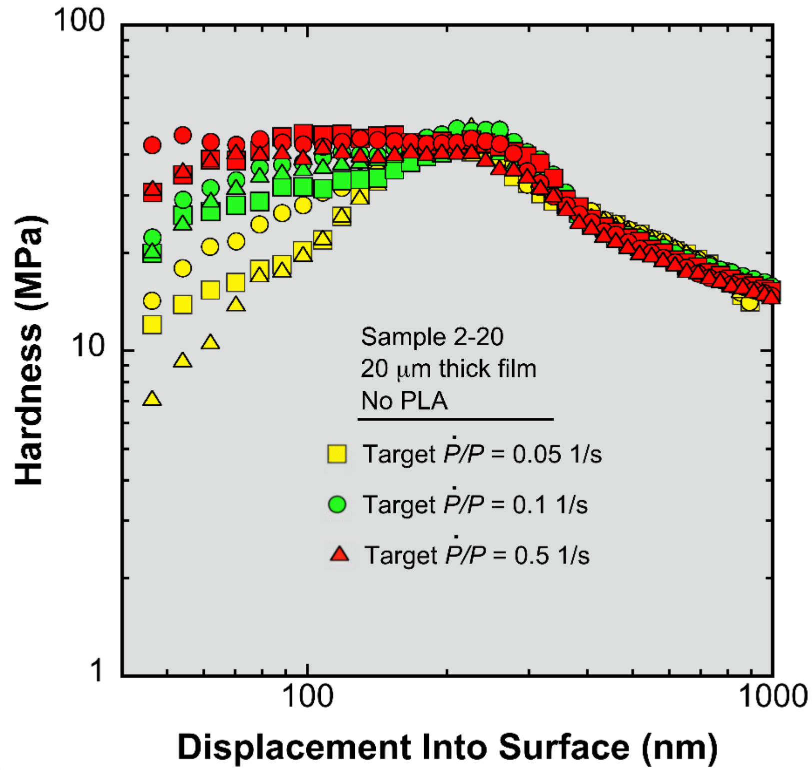




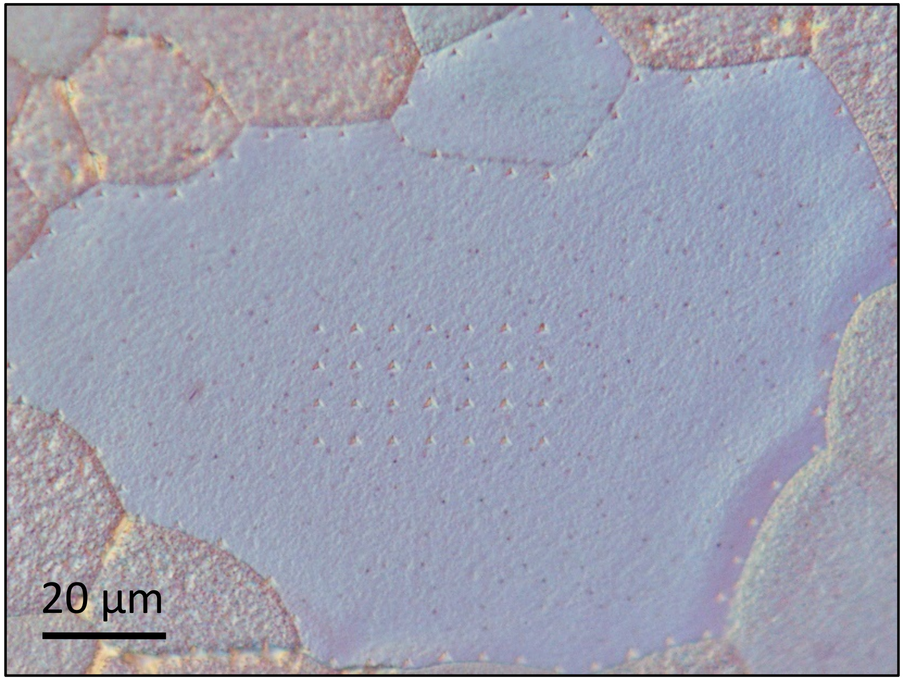
Evaluation of hardness & multiple deformation regimes

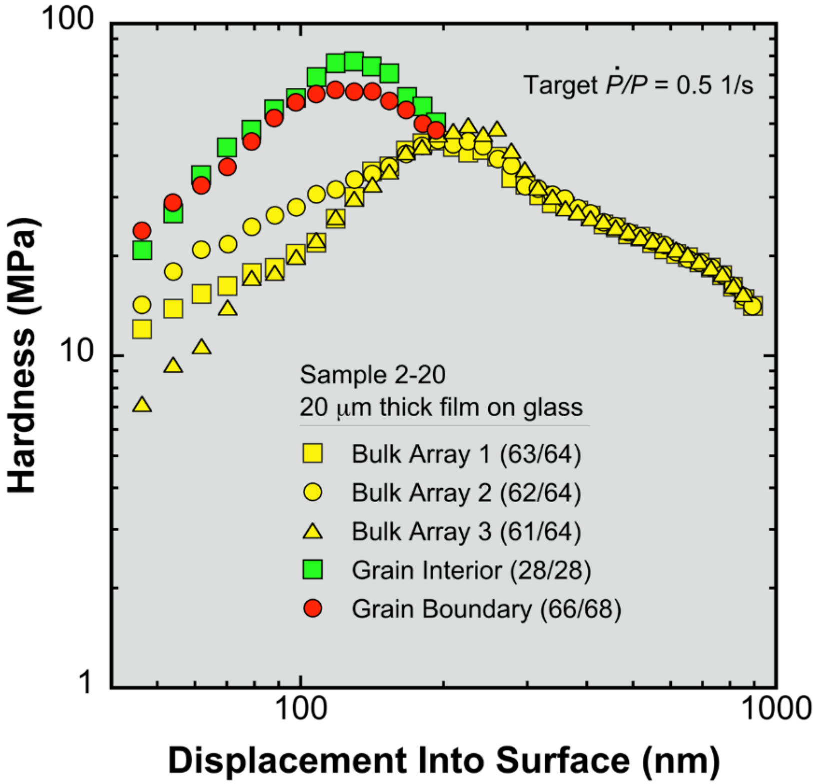
- Similar behavior for different film batches & different film thicknesses.
- Highly reproducible for different areas of the same film at the same strain rate.
- ***Li surface can support more or less pressure depending on the strain rate. The pressure also depends on the length scale (indentation depth).***
- Likely that the strain rate dependent pressure near the free surface depends significantly on the dislocation density and diffusion coefficient.

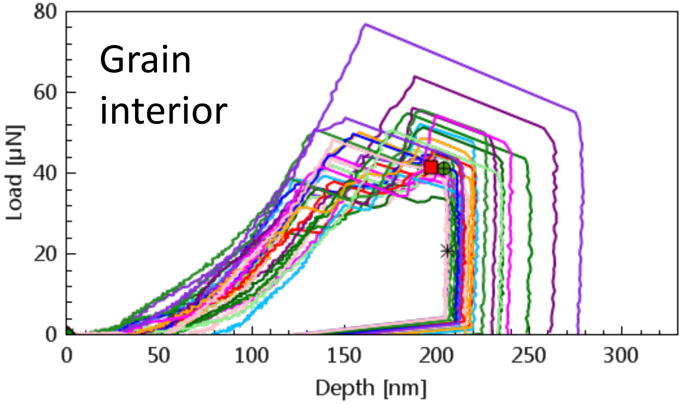


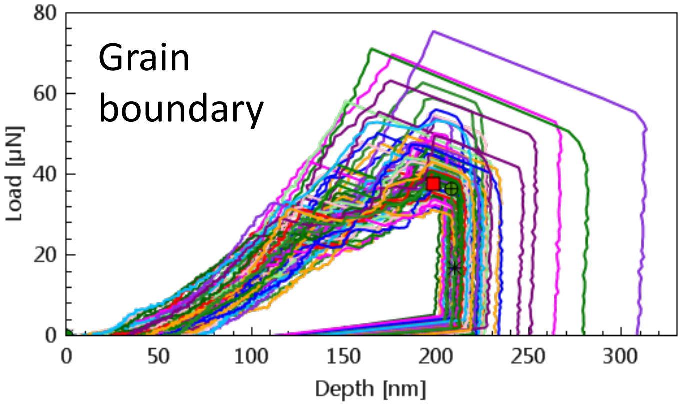


No significant change in load-displacement behavior with respect to indent location relative to grain boundaries









Summary and future work for nanoindentation

1. At high homologous temperatures, the pressure Li can support depends on the strain rate and length scale in a manner that likely reflects the dislocation density and the self diffusion coefficient.

   Significance: Inhomogeneity and irregularity at the SE/Li interface will create localized pressure in the Li, the magnitude of which will be controlled by the current density (strain rate) and Li's ability to alleviate the pressure via diffusional creep, plastic flow or fracture of the SE.

2. The elastic and plastic properties of Li are highly anisotropic. Initial evidence shows only a mild texture effect in *E* with film thickness.

   Significance: Crystallographic orientation may play an important role in determining how localized pressure at the SE/Li interface is controlled.

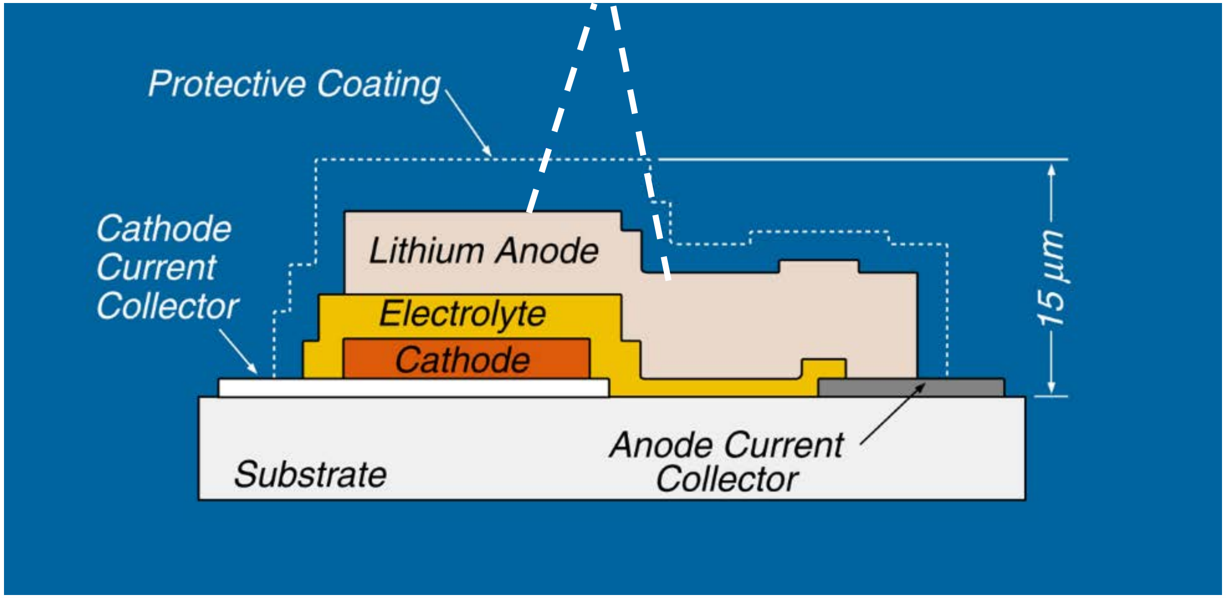
- **Future work:**
    1. Li: Determine the stress exponent at various length scales and temperatures to verify the creep mechanism(s) & estimate the activation volume.
    2. Li: Determine the change in hardness and elastic modulus with crystallographic orientation.
    3. Li: Determine how the hardness changes with cycling conditions.
    4. Li & SE: Perform in-operando cycling & mechanical testing to assess changes in the defect structure at the SE/Li interface.
    5. SE: Assess potential changes in local *E* & *H* relative to the grain boundaries and cycling conditions.

Any future work is subject to change based on funding levels.

A different approach to look at slow redistribution of Lithium upon extended cycling

- Lithium at thin film battery (TFB) differs from the protected Li battery for EVs, yet this may indicate processes for create/anneal of Li defects & redistribution.
  - TFB has Lipon electrolyte.   Not a self supporting ceramic electrolyte.
  - TFB uses less than 1 μm Li per cycle.
  - The TFB is a full cell with cathode, cycled > 3000X.
- Surface is profiled with a contact stylus, not by nanoindentation.

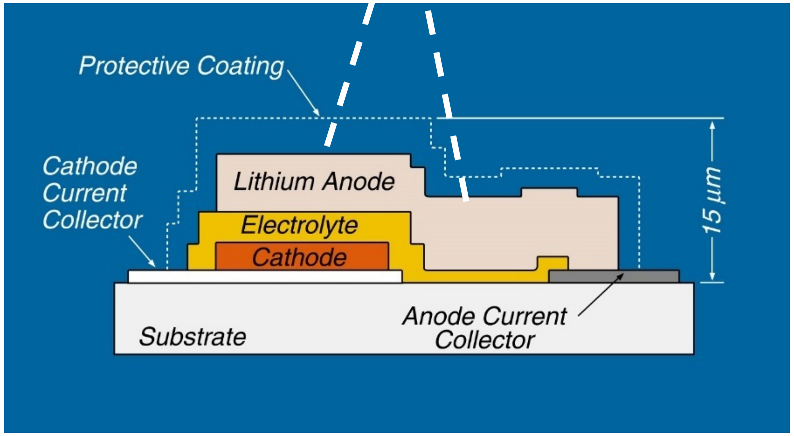
Photograph and profile

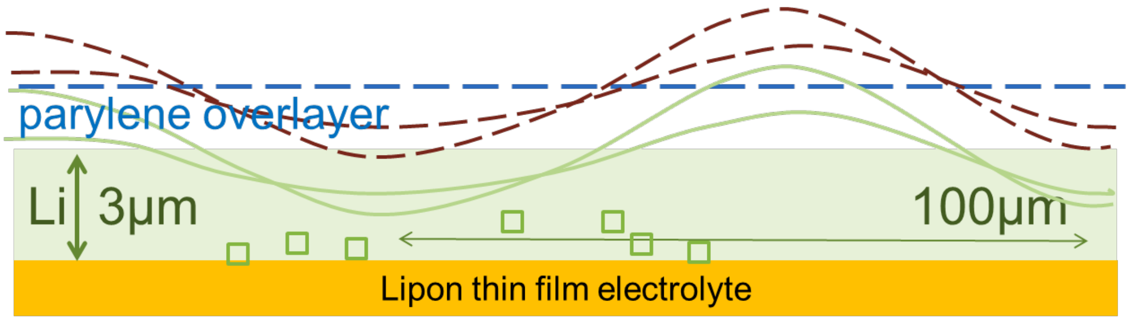


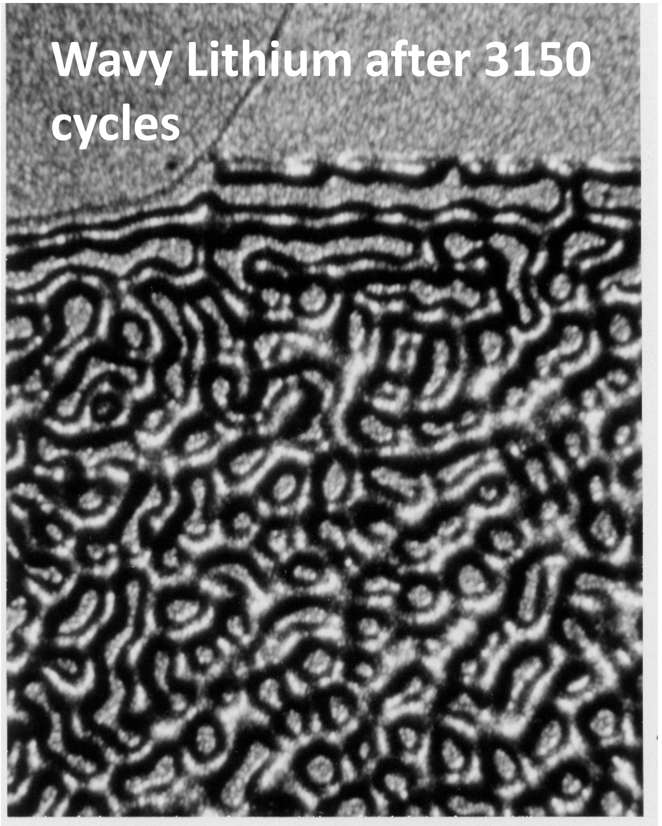
Lithium can redistribute forming long waves across the anode as a result of extended cycling

EARLIER WORK

- Li initially 3um thick, forms ridges 6um thick.
- Parylene protects Li; remains adhered.







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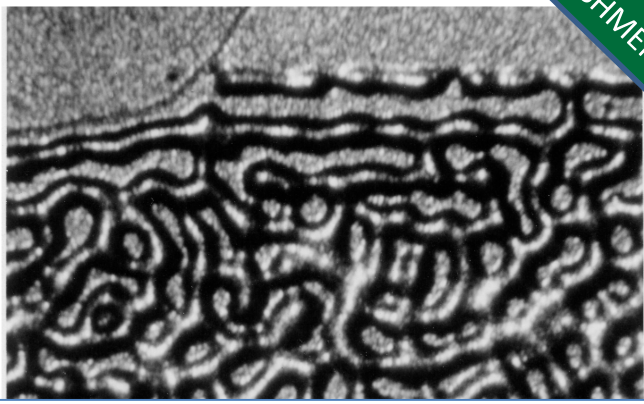
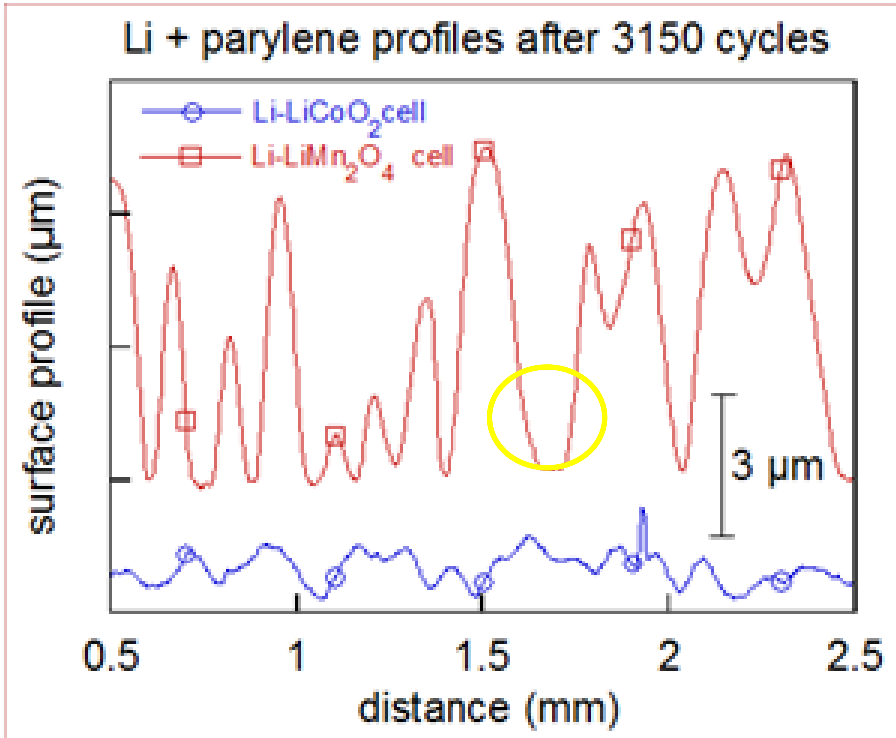
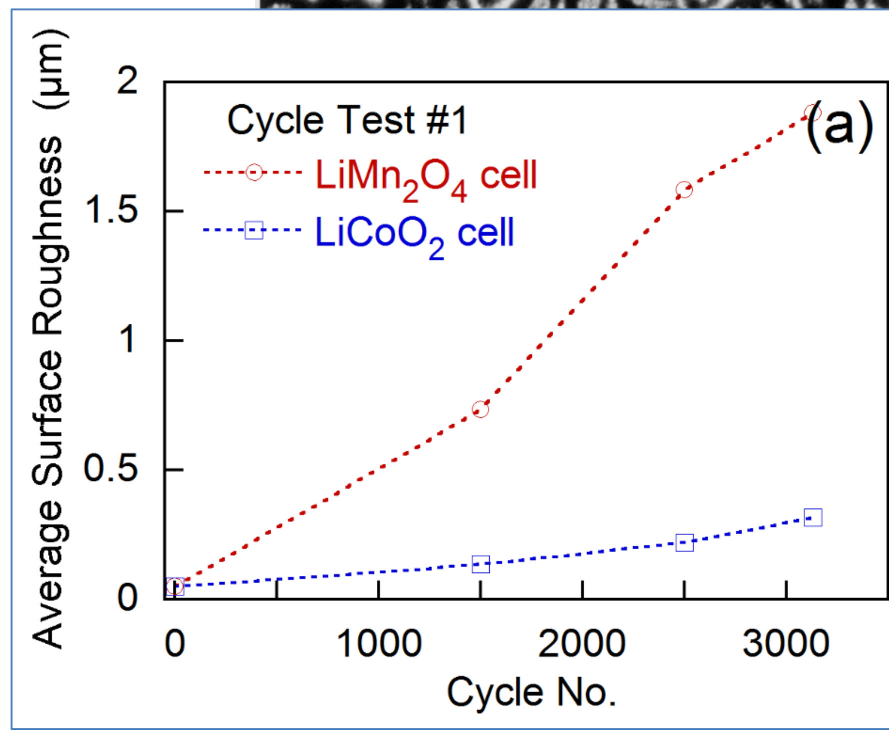
Redistribution of Li is faster with $LIMn_2O_4$ than $LiCoO_2$ cathode

ACCOMPLISHMENT

- Wavy structure is similar for LCO and LMO.
- Li volume is conserved, no evidence of porosity.
- Contact angle at flat valley < 1°.
- Little increase in interface resistance until isolation.

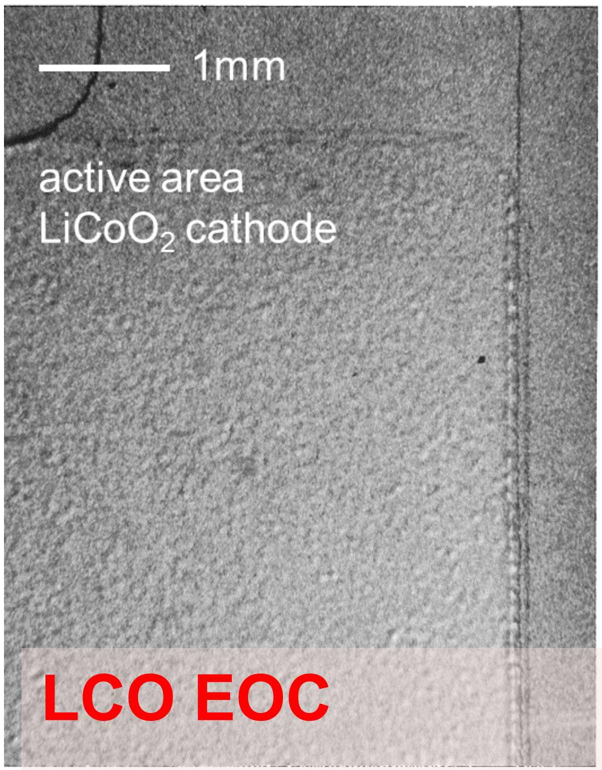


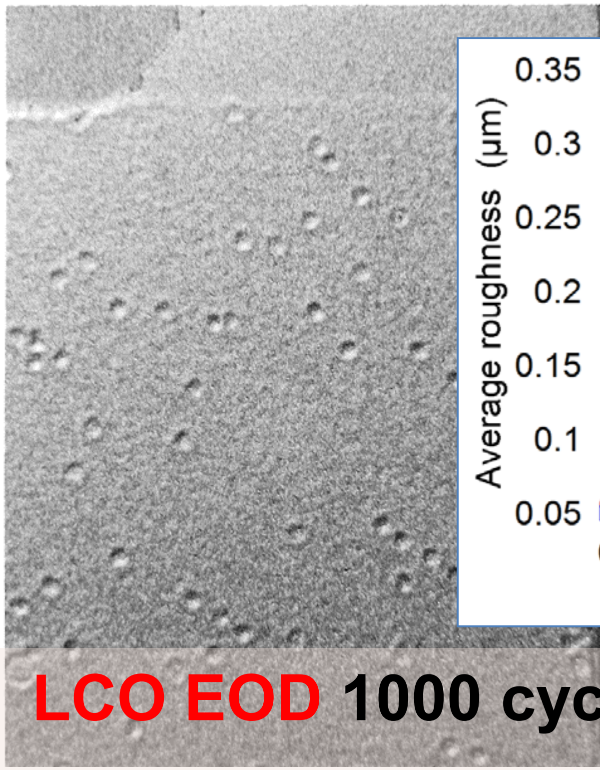


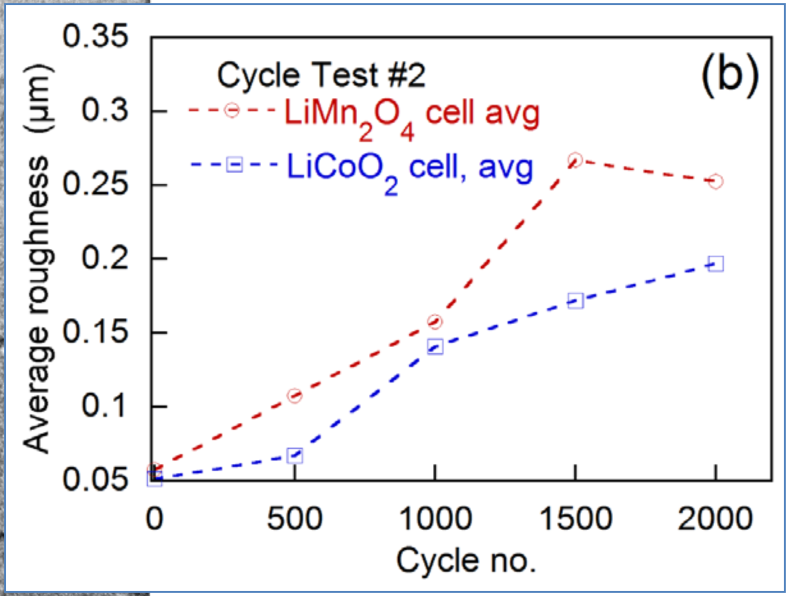


Lithium topology evolves differently if voltage hold occurs at EOC versus EOD

- Hold at end of charge → wavy.
- Hold at end of discharge → smooth with rare and random array of dimples.
- Consistent with diffusion of lattice defects, generated during Li plating, away from interface during holds.

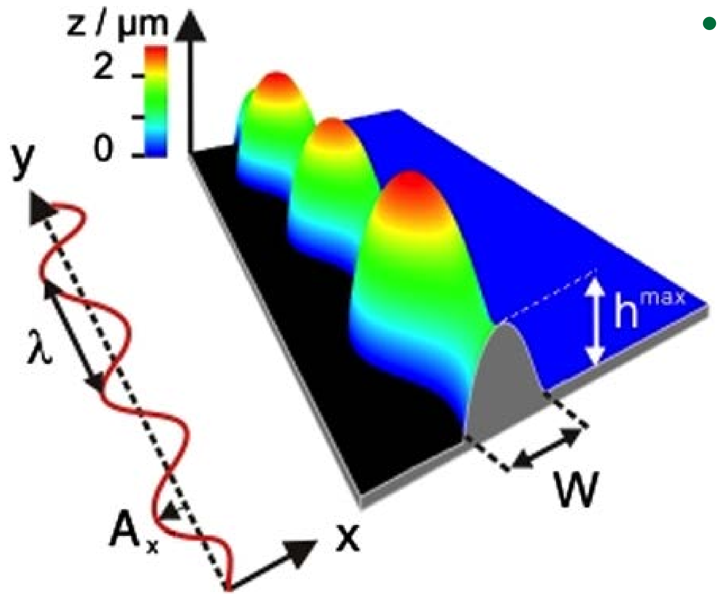






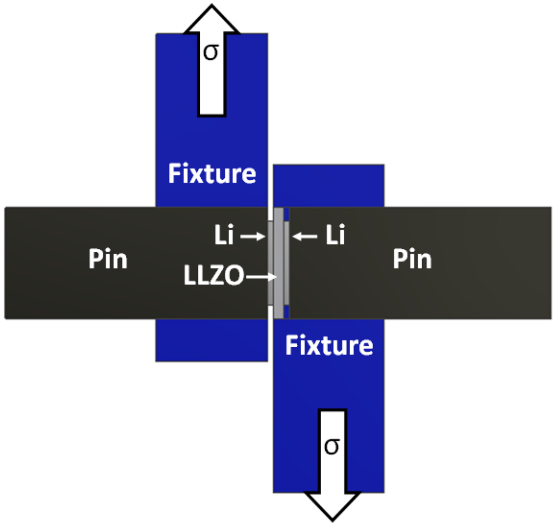
Analysis suggests gradual dewetting and/or Rayleigh instability of the thin Li film

- Tentative analysis – similar to "fingering" of receding metal films when heated, as shown from literature (below).
  - For thin film battery, "flow" of Li is *through the film* during cycling; Flow is *along* interface for dewetting studies.
- Anticipate that similar effects may occur at end of discharge when cycling solid electrolyte protected Li anode, as the Li film will be thin.



N Bhandaru,… A Sharma, Langmuir 31 (2015) 3208

- Lap shear strength tests underway at Univ. Michigan to assess the Li/SE interface adhesion



Proposed Future Work

Any future work is subject to change based on funding levels.

FUTURE WORK

- **Challenges, Risks and Mitigation**
  - No systems examined so far exactly match the required Li cycling, either for range of thickenss (3↔30µm), or current density or extended cycling. However understanding more about defect and dislocation behavior in Lithium will provide fundamental knowledge to make projections.
  - Li // Li performance may not accurately reflect a battery with intercalation cathode, but full cells add complexity.
- **Remainder of project for solid electrolytes**
  - X-ray tomography to image Li dendrites in LLZO solid electrolytes.
  - Another attempt to map grain structure and elastic properties comparing grain boundaries to interior.
- **Remainder of project for lithium metal**
  - Complete assessment of creep regimes for Li films.
  - Continue effort for nano-indentation of functional Li/LLZO/Li cells during active stripping/plating and relaxation. Establish if this will be useful probe for future studies.
  - Measure the Li/solid electrolyte adhesion using lap shear and contact angle tests.
- **Future challenges**
  - Just the beginning. Fully understanding the behavior of lithium upon cycling will require ongoing efforts.

Collaboration and coordination

- Coordination includes frequent shipping of samples, development of new methods and fixtures, and sharing of knowledge of interface reactions gained in other BMR programs. Collaborative effort is expected to increase as the indentation techniques and facility are fully demonstrated.

Response to reviewer comments

- No reviewer comments were submitted from AMR 2016 poster session.

Michigan Engineering, University of Michigan: Ceramic synthesis, hot pressing, pulse echo facilities along with J. Sakamoto's BMR studies of LLZO stability with Li anode and air.

Oak Ridge National Laboratory: Li films, ceramic and polymer electrolytes and battery structures. Dudney coordinates.

Michigan Tech, Create the Future: Nano-indentation facilities and E. Herbert's expertise in methods and analysis of material properties.

Nanomechanics, Inc.: Inventors/manufactures of NanoFlip and iNano hardware and software. Warren Oliver and Phani facilitate new studies.

Summary

COLLABORATIONS

- **Relevance** Achieving high energy density using metallic lithium requires that the lithium capacity is cycled with 100% efficiency. Any roughening or creation of pores in the lithium may lead to loss of active lithium, increased resistance, or failure of the electrolyte.
- **Approach** Generally cycling of lithium is investigated electrochemically. Here we are testing the mechanical properties of both the solid electrolyte and the lithium itself. This should provide not only important materials characterization, but a real-time measure of how lithium moves in response to cycling through a solid electrolyte.
- **Accomplishments**
  - Li films were deposited with control of the grain size.
  - Accurate determination of the elastic modulus and hardness have been accomplished with statistical analysis of the uniformity. Hardness depends on the strain rate and length scale indicative of dislocation structure.
  - Redistribution of the protected lithium upon extended cycling of a thin film battery has been evaluated in terms of lithium defect creation and diffusion.
  - Tools to determine the Li/solid electrolyte interface adhesion and wetting have been setup with initial results.
- **Future work** Work will culminate with cycling of near 20µm of Li on a self supporting solid electrolyte membrane.
- **Collaborations** – Collaboration with Nanomechanics is critical to utilizing the full capability of the indentation technique, particularly for lithium which presents experimental challenges.

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