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 2016

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

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Overview

Timeline

- Start: January 2015
- End: December 2017
- Percent complete 40%

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.
 - Contract value \$1000K
 - \$340K FY15 DOE
 - \$540K FY16 TARDEC

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





NANOMECHANICS, INC.

THE UNIVERSITY of TENNESSEE



KNOXVILLE COLLEGE of ENGINEERING



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

• 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*, rather than 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 *
 - No loss of lithium due to mechanical isolation or side reactions, coulomb efficiency >99.95%.

(* except for +1 µm Li to serve as current collector)



PELEIANCE

Milestones

| Milestones: FY15-FY16 | component | Target: | Status: |
|---|----------------------|---------|--------------|
| Four nano-indentation maps showing grain boundary regions of the crystalline LLZO and the glass ceramic material from Ohara | Solid electrolyte | Q2 | \checkmark |
| Two or three indentation studies with as-fabricated, air reacted and polished surfaces | Solid electrolyte | Q3 | \checkmark |
| Demonstrate capability to transfer and then map viscoelastic properties of Li films and rolled lithium foils | Lithium anode | Q4 | \checkmark |
| Determine elastic properties of battery grade lithium from different sources and preparation, comparing to values from the reference literature | Lithium anodes | Q5 | Near done |
| Compare lithium properties, uncycled versus cycled, using thin film battery architecture. | Interface | Q6 | On track |
| View annealing of defects following a single stripping and plating half cycle, using thin film battery architecture. | Active interface | Q8 | On track |



Nano-indentation has not previously been applied to evaluate lithium or its contact with solid electrolytes.

- Use state-of-the-art nano-indentation techniques for: probing small volumes and grains, rapid mapping for statistics, dynamic probe for changes with depth surface to support.
- Well controlled atmosphere for sample preparation and testing.
- Progress from individual materials \rightarrow changes when cycled \rightarrow in-situ active interface.



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Approach strategy:

- Important that Li sample is thin, as for balanced cell.
- Microscope used to view surface and residual impression
- Elastic modulus, hardness & energy dissipation determined as
- a function of depth and strain rate using harmonic tip oscillation



• Force is controlled Displacement is measured >achievable resolution < 0.25 nm Indenter shaft Indenter tip Fused silica standard

Standard reference material

10

8

Hardness (GPa)

- Determine frame stiffness & indenter tip area function
- **Deviation in hardness** near surface due to tip geometry.

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Study of ceramic versus glass-ceramic electrolytes. Glassy phase provides a more uniform material.

- Li electrolytes from Ohara Corp. based on Nasicon-structure
 - Striking difference for sintered Ohara ceramic versus Ohara glass-ceramic
 - Sintered ceramic varies to near 200nm from surface; glass-ceramic is homogeneous, similar to fused silica
 - Automatic map of 100 indents. Data aggregated for 300-500nm depth



Accomplisingen

Lithium Lanthanum Zirconate (LLZO) garnet electrolyte, has high modulus to suppress dendrites

- Results for 98.9 % dense samples, deeply polished surface just before indent
 - Weak variation with: depth, different spots across surface, and sample to sample.
 - Modulus agree with those from pulse echo and DFT.
 - Shear modulus of LLZO far exceeds that of Li, so dendrites are mechanically suppressed (following Monroe and Newman).



| Al doped -LLZO | E (GPa) |
|------------------|-----------------|
| DFT (298 K) | 154.5 |
| Pulse Echo | 146.1 ± 0.8 |
| Nano-indentation | 150.3 ± 2.2 |
| Ta doped -LLZO | F (GPa) |
| | - (0. 0) |
| DFT (298 K) | 147.2 |
| Pulse Echo | 139.9 ± 2.1 |
| Nanoindentation | 153.8 ± 2.7 |

S. Yu, R. D. Schmidt, R. Garcia-Mendez, E. Herbert, N. J. Dudney, J. B. Wolfenstine, J. Sakamoto, and. D. Siegel Published in *Chem. Mater.*

ACCOMPLISINGENT

For the Lithium Lanthanum Zirconate (LLZO) garnet electrolyte, surface preparation & density are critical

- Compared to last slide, these results are for less dense, lightly polished surface, exposed to air for tests.
 - Strong variation with depth, different spots across surface, and sample to sample.







Postmortem measure of shorted LLZO indicates that near shorts, material has statistically higher modulus.

- Post cycling, Li removed from surface revealing dark areas, the sites of shorts.
- Mapping surface areas, near dark streaks the surface is statistically harder.
- Need to repeat with Ar protection and indent image.



Pulse echo is used to detect Li dendrites and microcracks in LLZO, in addition to measuring the elastic modulus

- Shown earlier, elastic modulus from pulse echo agrees with indentation and DFT.
- When Li⁺ current is driven high enough to cause short:
 - Dark streaks penetrate through LLZO
 - A decrease in wave-speed by transverse pulse-echo is observed before actual short is detected.
 - Magnitude of change in wavespeed is consistent with formation of microcracks.



RECOMPLISHNEN'S





A. Sharafi et al., *J Power Sources* 302 (2016) 135–139.



Robert D. Schmidt and Jeffrey Sakamoto, in press, Journal of Power Sources.



Indentation approach has been modified for Li metal due to its extreme propensity for plastic deformation.

• Li films: 5-20 μ m on glass substrate. Protected from air, but thin "crust" at surface.



- First measurements (left) by dynamic indentation. Load at different strain rates (1/sec vs 0.1/sec), hold then unload.
 - Very little elastic recovery
- Newer approach (below) normal loading interrupted with 5, 20s holds



Phase angle measures dissipation of mechanical energy. Can it be related to defect formation?

- The phase angle is a direct measure of dissipated mechanical energy; so this may be a **useful** metric enabling the characterization of key defect processes.
- Most materials deform elastically for ~1nm displacement, giving a phase angle ≈0. Not the case for lithium metal.



- This dynamic indentation method (left) is polluted with experimental artifacts.
- It is impossible to overcome Li's plasticity with: 100Hz drive, ~1nm oscillation, and excessive indenter velocity.
- Alternative dynamic methods are being developed.





APISHATEN.

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Elastic modulus and hardness determined from first tests shows reasonable agreement with literature.

Estimate of E (v = 0.362)

- Most viable depth range: 200-300 nm
- Minimized effects of surface contaminants and the substrate
- Literature reports 4.9-8 GPa

Estimation of H (flow stress)

Strong depth dependence

RCCOMPLISINGENT

- 0.018 GPa during hold
- No reports in the literature



New load-time history enables more reliable measurements of the phase angle

Distinct advantage:

 More accurate measurements of the phase angle and stiffness (E) can be made at the end of each hold segment because the indenter velocity goes to 0 nm/s



New load-time history enables more reliable measurements of the elastic modulus (~8 GPa) and hardness (~15 MPa) with displacement from surface.



Compared to the 1st test (slide 14), here:

- the modulus is much less depth dependent and slightly higher in magnitude,
- the hardness is generally lower, but meaningful comparisons are difficult due to the potential for extreme strain rate sensitivity.



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Proposed Future Work

Challenges, Risks and Mitigation

 We have hypothesized that changes in the elastic and plastic mechanical properties will reveal information of the Li defects and interface adhesion. This needs to be demonstrated and there is risk that the interpretation will be complex.

Remainder of FY16 for solid electrolytes

- Repeat statistical evaluation of LLZO before and after shorting with improved samples, polishing, and environmental control.
- Measure the properties of additional ceramic solid electrolytes with attention to grain features and surface coating.

• Remainder of FY16 for lithium metal

- Measure the hardness (flow stress), modulus and phase angle of lithium thin films comparing uncycled and cycled Li films using thin film (low capacity) batteries.
- Measure the properties of lithium as a function of depth to characterize changes near the buried Li-SE interface.
- FY17
 - Prepare functional cells with LLZO solid electrolyte disks for cycling about 20µm of Li while monitoring the elastic and plastic properties with time, depth, and variation along interface area.



FUTURE WORK

Collaboration and coordination

COLLABORAN 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.



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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

- Values for elastic modulus and hardness for Ohara electrolytes, LLZO electrolytes, and Lithium metal revealing the material homogeneity and effect of surface reactions.
- Baseline studies for equilibrated Lithium thin films identified better approaches to ____ extracting the plastic and elastic properties.
- Pulse echo studies provided the elastic properties of LLZO and evidence for microcrack and lithium dendrite formation at high current density.
- **Future work** Work will progress from study of individual materials to changes when small amounts of Li are cycled in a thin film battery, and 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.



Response to previous reviewer comments - none. This is first review.



Technical backup slides

Backup slides provide more information on the nano-indentation technique.



Background: Dynamic nano-indentation analysis - Elastic modulus, hardness & energy dissipation extracted as a function of depth



THE BASICS

- Load (P) is controlled
- Displacement (h) is measured
- Lock-in amplifier controls the dynamic load & gives the displacement and phase angle
- Hardness H is max load (P) divided by contact area (A)
- The stiffness (S) is slope upon unloading (dP/dh)
 OR the continuous (harmonic) stiffness is obtained from the dynamic response as a function of displacement.
- The reduced modulus (E_r) follows, β being a constant ~1, and Young's modulus (E_s) with Poisson's ratio (v).
- When H and E are constant (independent of depth), P/S² is independent of h and A.



Background: Elastic modulus, hardness & energy dissipation in Li films as a function of depth and strain rate via nanoindentation



23 Presentation name