Physical and Mechano-Electrochemical Phenomena of Thin Film Li-Ceramic Electrolyte Constructs

June 24, 2021

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Mechanical Engineering & Materials Science



DE-EE 0008855 bat480

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Overview

Timeline

- Project start date, Oct 1, 2019
- Project end date, Sep 30, 2022
- 50% complete

Barriers

- Performance: enabling Li metal anodes to achieve > 1,000 Wh/I
 - How to protect Li with ceramic electrolyte
- Cost: enabling Li free manufacturing to achieve < \$100/kWh
 - How to demonstrate Li metal anode formation

Budget

- Total project funding: \$1,250k
- DOE share \$1,000k
- \$250k cost share
- \$333k for FY 2021
- \$333k for FY 2022

Partners

• Zakuro Inc.

Relevance

Problem: Significant progress has been made in advancing solid-state electrolyte (SSE) science for use with Li metal anodes. However, commercializing viable solid-state battery (SSB) technology requires translational research.

Goal: This project aims to bridge fundamental and applied research to better understand how SSB cell design and packaging affect performance and durability.

Objective: Advance TRL from 4 (Typical Lab Cell) to TRL 6 (Commercial Cell).

✤ Year 2, study behavior of thin Li.



Major Milestone FY 2021

Long term cycling stability analysis

- Screened approaches to integrate thin Li
- Li must be thin (<18 μm) to achieve 350 Wh/kg (see right; 15 μm = 3 mAh/cm²)
- Down-selected *in situ* Li anode formation as the Li anode integration technique.
- Approach 1: Integrated *in situ* Li anode formation into cell for *operando* visualization cell
- * Approach 2: Study stripping behavior of thin Li





Wang et al. Nature Comm. 2020



Wang, Kazyak, Dasgupta, Sakamoto, Joule, in press.

Approach 1: Operando visualization





Plating at 0.05 mA/cm² for 2.0 mAh/cm² in all cases

Increasing Stack Pressure



Plating at 0.05 mA/cm² for 2.0 mAh/cm² in all cases

Implications for cell design

Factors affecting growth of *in situ* formed anodes:

- Extrinsic factors
 - Stack pressure
 - Plating rate (strain rate) and temperature (Li mech. props.)
- Intrinsic factors
 - Nucleation density
 - Current collector adhesion
 - Lithio-philicity/phobicity of SE, CC
 - Thickness, modulus of CC
 - ➢ Roughness of SE, CC



Remaining challenges and barriers

Mechanics of Interface Delamination

Uniformity of Stack pressure



Implication: mechanistic insight can enable viable Li-free SSB manufacturing.

Approach 2: Study stripping of in-situ plated thin Li



Hypothesis:

- At lower current densities, steady-state stripping is achieved; follows ohmic behavior
- At higher current densities, noticeable deviation from ohmic behavior observed
- Steady-state stripping controlled by the flow of Li metal

Low current density (0.1 mA/cm²) stripping – 10 µm Li



- Void formation is suppressed by the stack pressure at low current density.
- Dramatic increase in ionic-ohmic resistance and blocking behavior indicate Li depletion
- DC polarization and EIS data agree.

Higher current density (0.4 mA/cm²) stripping – 10 µm Li



- Void formation is not suppressed by stack pressure.
- Cell impedance after DC stripping is much smaller than expected based on the voltage profile, but why?
- Li flows to fill voids between end of DC polarization and EIS measurement (~ 5 min), dynamic recovery?

In-operando GEIS during stripping – 0.4 mA/cm2, 10 µm Li



In-operando GEIS during stripping – 0.4 mA/cm², 10 µm Li



- Void formation alone can't justify the dramatic increase in cell impedance.
- Non-linear increase in interface resistance could be due to current focusing effect caused by voids.

Dynamic recovery of voids from Li creep



- Li flow and pressure could cause void collapse within a few minutes after heavy polarization.
- Cell Resistance does not fully recover to the original value, why?
- Lack of re-wetting; voids collapse & Li makes physical contact with LLZO, but is not chemically re-bonded.

Remaining Challenges and Barriers of thin Li stripping



Implication: polarization during stripping likely affects/controls CCD during plating¹⁶

Re-thinking Li mechanics at the interface: hydrostatic stress



- When Li is adhered to the solid-electrolyte interface AND is thin, hydrostatic stress is created.
- Under these conditions, there may be significantly less deviatoric stress to drive plastic deformation and creep.
- This is a different physical environment than what has been assumed.

Summary

- Operando analysis quantified the dynamic evolution of electrode topology during *in situ* Li anode formation:
 - Insight gained can enable viable Li free manufacturing.
- Analysis of thin Li (~ 10 μm) during stripping led to observation of Li dewetting
 - Insight gained can enable stable Li stripping and plating
- The mechanical behavior of commercially-relevant Li thickness (~ 10 20 μ m) is dramatically different that lab-scale > 500 μ m Li thickness
 - Insight gained can enable a better understanding of what controls stripping and plating.

Future work

- Li free manufacturing: better understand the mechanics of current collector delamination and pressure to enable consistent and uniform Li anode formation.
- **Cycling of thin Li anodes:** determine approaches to prevent dewetting during Li stripping.
- **Cathode integration**: demonstrate improved cycling of solid-state Li-S prototypes guided by computation.
- Continue to link project findings with vehicle electrification needs.

Key publication: *Joule* **Perspective**

Transitioning solid-state batteries from lab to market: linking fundamental understanding with practical considerations

Michael Wang, Eric Kazyak, Neil P. Dasgupta, Jeff Sakamoto



Backup slide



Performance and Cycling Specifications

Energy density:

- Stack-specific energy density (no packaging), including components shown in
- NMC 811 with 200 mAh/g and 3.85V avg discharge voltage
- Areal loading of 4 mAh/cm² unless otherwise noted
- 10 um thick current collectors
- 95% relative density in both separator and composite layer
- 25% volume fraction SE in composite unless otherwise noted
- For all cases other than the LLZO/PEO hybrid, composite SE material is the same as separator

Cycle life:

- Only excess Li consumed during initial cycles (cycled capacity limited by cathode capacity)
- Li electrodes dominates inefficiency
- Once excess Li is depleted, capacity fade occurs
- CE assumed to be constant throughout

