First Principles Calculations of Existing and Novel Materials

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Project ID: bat054

Overview

Timeline

- Start date: October 2015
- End date: September 2021
- Percent complete: 93%

Budget

- Total project funding

-- FY16	$300,000	-- FY19	$400,000
-- FY17	$537,500	-- FY20	$350,100
-- FY18	$500,000	-- FY21	$460,000

Barriers Addressed

- Energy density
- Cycle life
- Cost

Partners

- none

Relevance/Objectives

Impact:

- To make solid-state batteries we need conductors that have good ionic conductivity, are stable or passivate against anode and cathode, are resistant to Li metal growth, and can be incorporated into the composite cathode.
- Long cycle life, competitive with current Li-ion, requires degradation of less than 10^{-4}/cycle. This requires us to understand all chemical and mechanical parasitic phenomena in a solid-state battery, even those not directly evident in the first few cycles
- Mechanical and their coupling with electrochemical processes need to be quantified to understand the degradation processes in solid-state batteries.

Objectives:

- Understand the fundamental mechanisms by which solid-state batteries degrade
- Understand the role and the nature of chemical reactivity between electrodes and solid electrolyte
- Understand the coupling between mechanical and electrochemical phenomena in degradation of solid state batteries
- Understand the contribution of electronic conductivity to Li penetration through solid electrolytes

Milestones

Date	Milestones	Status
December 2020	Finite T phase diagram of L-P-S system	Completed
March 2021	Develop model for electronic conductivity in solid electrolytes	Completed
June 2021	Evaluate effect of ionic and electronic conductivity on Li plating in solid electrolyte	Completed
September 2021	Develop a valid model for amorphous structure and compare to spectroscopy data	On schedule

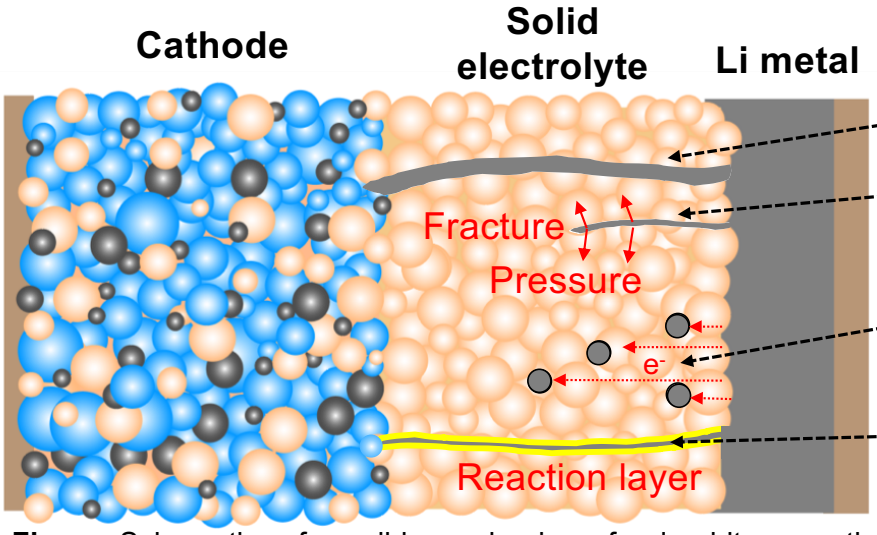
Approach

- Combine continuum transport and mechanics modeling with first principles computations. Integrate experimentally measured variables as needed
- Detailed structural studies using TEM and tomography to visualize breakdown phenomena

Methods

- DFT with GGA and SCAN functional for first principles calculations. Molecular Dynamics for Li-transport
- Phonon calculations with harmonic approximation for vibrational contribution to free energy.
- Continuum equations are derived analytically in the 1D case, and solved numerically with the finite element method in the 3D case.
- TEM for interface visualization and serial FIB/TEM for cathode tomography

Technical Accomplishment: Possible mechanisms for dendrites growth in solid electrolyte (SE)



1. Growth of lithium through connected **porosity**
2. **Stress** intensification leading to propagating fracture through the grains or grain boundaries.
3. Isolated pores: Li deposits inside SE due to **electronic conductivity**.
4. **(Electro)chemical reactivity** leading to SEI formation.

Figure: Schematics of possible mechanisms for dendrites growth in the SE

- In past years we have studied mechanisms 2 (stress) and 4 (reactivity). This year we focused on the role of electronic conductivity.

- Electronic conductivity potentially enables plating of lithium metal in the porosity of a solid electrolyte. When Li deposits in a confined pore, stress can build up leading to cracking. Connected cracks can then penetrate the solid electrolyte.

Technical Accomplishment: Developed 3D model for mixed conductivity solid electrolytes including lithium plating in the SE

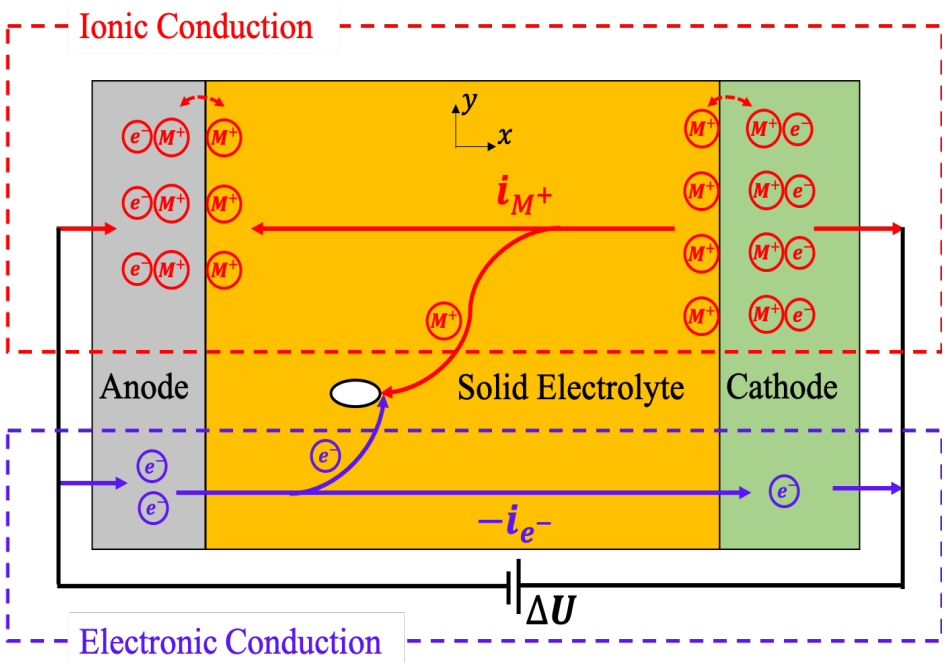


Figure: Schematic illustration of the MIEC model for an SSB cell during charging

1. Transport of Li^+ and e^- in the SE can be described by Ohmic relation:

- Relation of current density ($\boldsymbol{i}_{M^+}$, $\boldsymbol{i}_{e^-}$) and electrochemical potential ($\tilde{\mu}_{M^+}$, $\tilde{\mu}_{e^-}$):

$$\boldsymbol{i}_{M^+} = -\frac{\sigma_{M^+}}{F}\nabla\tilde{\mu}_{M^+}, \qquad \boldsymbol{i}_{e^-} = \frac{\sigma_{e^-}}{F}\nabla\tilde{\mu}_{e^-}$$

- Laplacian equation of electrochemical potential ($\tilde{\mu}_{M^+}$, $\tilde{\mu}_{e^-}$) at steady state:

$$\nabla^2\tilde{\mu}_{M^+} = 0, \qquad \nabla^2\tilde{\mu}_{e^-} = 0$$

2. Charge-transfer kinetics at the Anode/SE and Cathode/SE interface can be described by Butler-Volmer relation:

$$i_n^k = i_{exc}^k\left(e^{\frac{\alpha_a F\eta_k}{RT}} - e^{-\frac{\alpha_c F\eta_k}{RT}}\right)$$

$$F\eta_k = \mu_M^{Electrode} - \tilde{\mu}_{e^-}^{SE} - \tilde{\mu}_{M^+}^{SE} - PV$$

i_n^k is the surface current across the electrode/SE interfaces (k = “anode” or “cathode”).

Technical Accomplishment: Developed a full model for potential distribution in the solid electrolyte. Capturing the complexity by which voids near the anode fill and shadow the Li plating on the anode

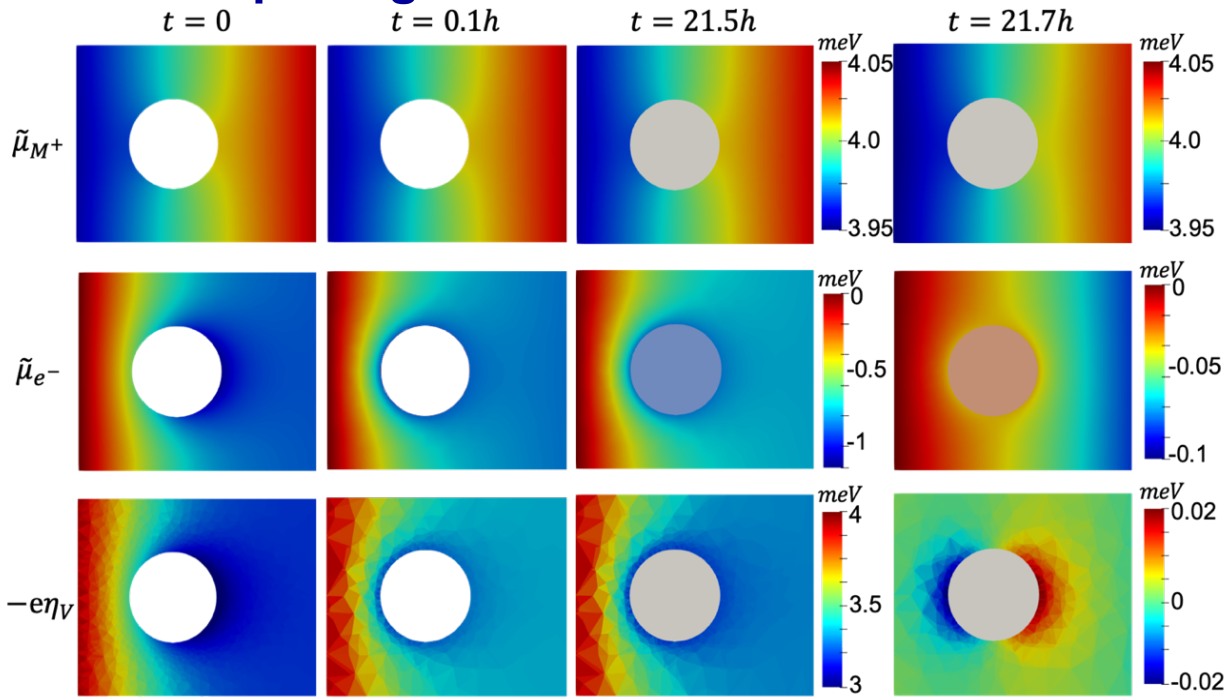


Figure: The distribution of electrochemical potentials near the void area. $\tilde{\mu}_{e^-}$ and $\tilde{\mu}_{M^+}$ are the electronic and ionic potentials. $-e\eta_V = \tilde{\mu}_{e^-} + \tilde{\mu}_{M^+}$ is the plating potential.

The distribution of electrochemical potentials near a void in the SE of a symmetric cell at four specific times. The white color in the first two columns shows that very little metal is deposited in the void. The gray color in the right two columns indicates that the void is fully occupied by Li metal. The left side of each picture is the anode.

Technical Accomplishment: Developed a full model for potential distribution in the solid electrolyte. Results show that only a small portion of SE is susceptible to Li plating

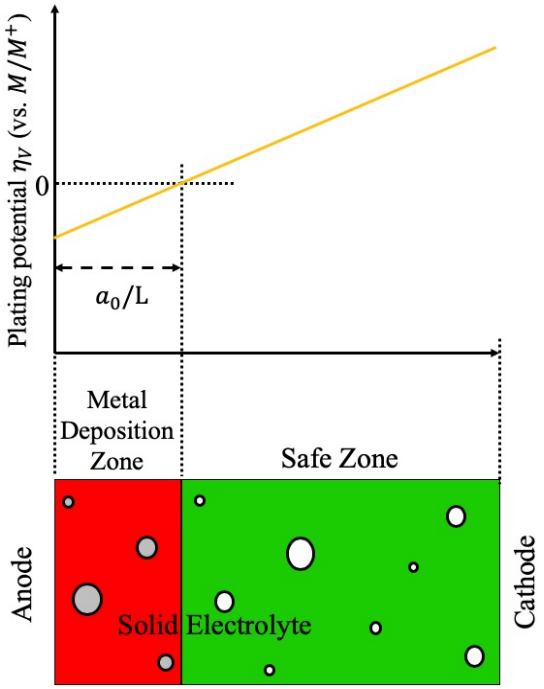


Figure: Schematic illustration of the metal deposition in voids of the SE.

Fraction of electrode thickness susceptible to Li plating

$$\frac{a_0}{L} \approx \frac{\eta_A - V_A}{\eta_A + \eta_C + (V_C - V_A)}$$

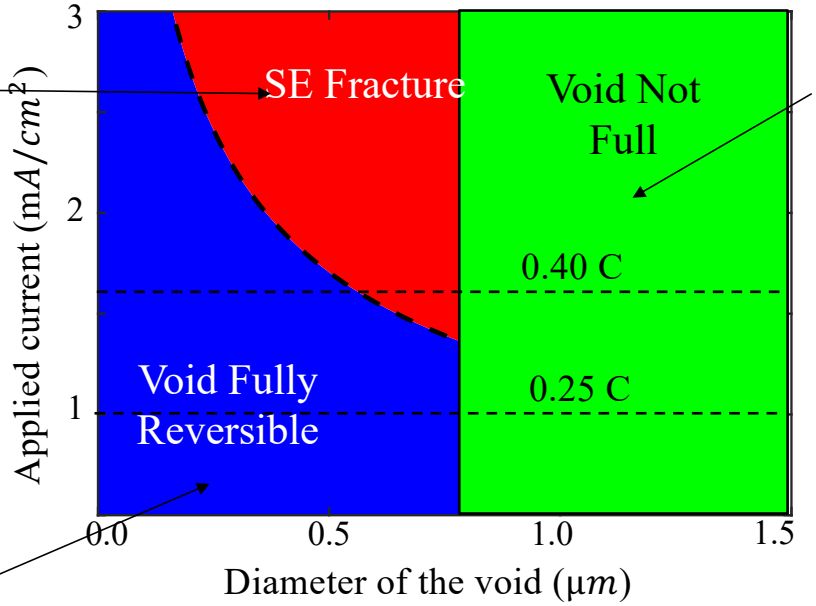
V_A and V_C anode and cathode voltage
η_A and η_C: overpotentials at anode and cathode

- Results show that symmetric Li cells are NOT a good testing vehicle to study Li metal deposition in SE as half of SE is exposed to Li plating conditions, which is very different from a real cell
- In a realistic cell with $V_C > V_A$ and $V_C - V_A >> \eta_A + \eta_C$ only a small part of SE near anode is exposed to plating conditions. If this part can be protected, Li plating in the SE can be stopped.

Technical Accomplishment: Developed criteria to determine when SE voids crack by Li plating

Three-dimensional cell modeling: Depending on the current density, and size and location of voids voids either crack, reversibly fill and empty with Li, or do not fill completely.

Increased current density and larger void size leads to fracture



Very large voids do not fill completely

CONSEQUENCE: While long time sintering densifies a sample, it usually also leads to **fewer but larger voids**. This can aggravate Li penetration by transforming small voids into larger ones that are more susceptible to cracking

Very small voids cannot build up enough pressure to crack SE. Limiting pressure is reached in them where further deposition stops

Technical Accomplishment: Proposed solutions to protect against internal Li plating in SE

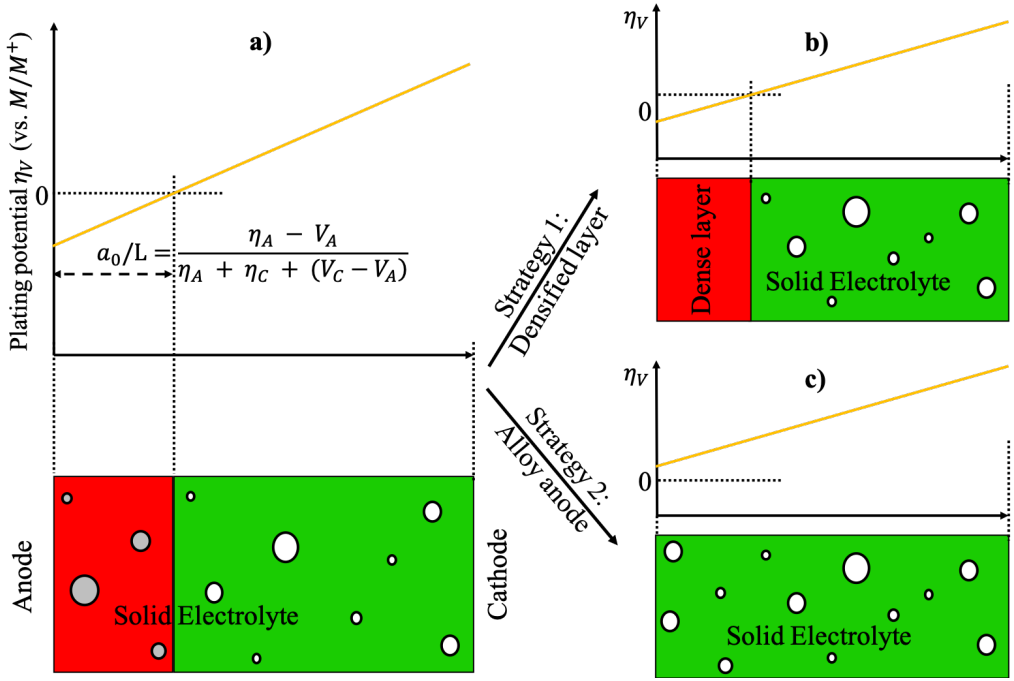
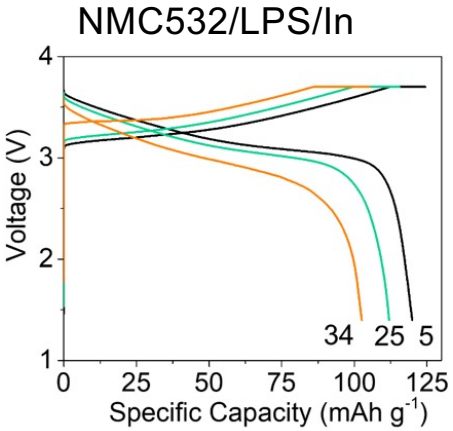


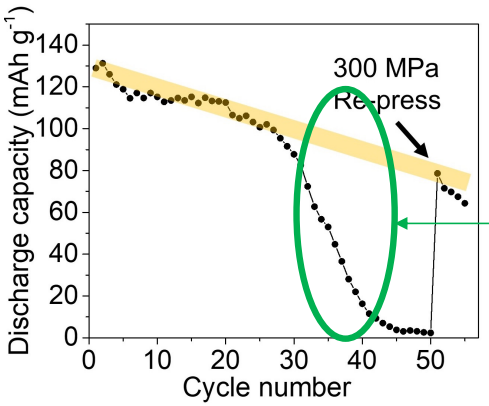
Figure: Two strategies to prevent against internal Li plating in the SE

Our insights and modeling lead to two proposed solutions to protect a SE against internal Li metal growth

1) Thin densified layer on the anode side. Only the region where the potential is favorable to Li plating needs to be protected, either with a thin extrinsic coating, or to ensure that the SE is most dense on the anode side
2) Raising the anode voltage even slightly above the potential of Li metal would protect all of the SE against Li metal growth.

Technical Accomplishment: Visualizing mechanical failure in composite cathode through tomography (collaboration with M. Scott NCEM)





Sudden capacity drop caused by mechanical issues in cathode. Repressing cathode restores capacity

Figure: Electrochemical tests of the SSB cell before and after re-pressing.

Investigate composite cathode microstructure with FIB/TEM

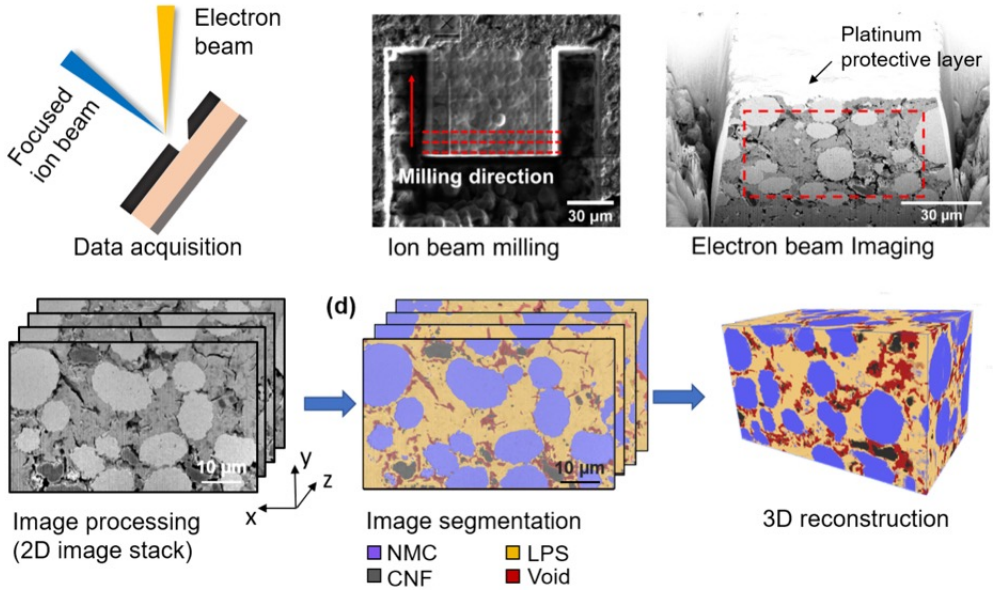


Figure: Workflow for FIB–SEM tomography

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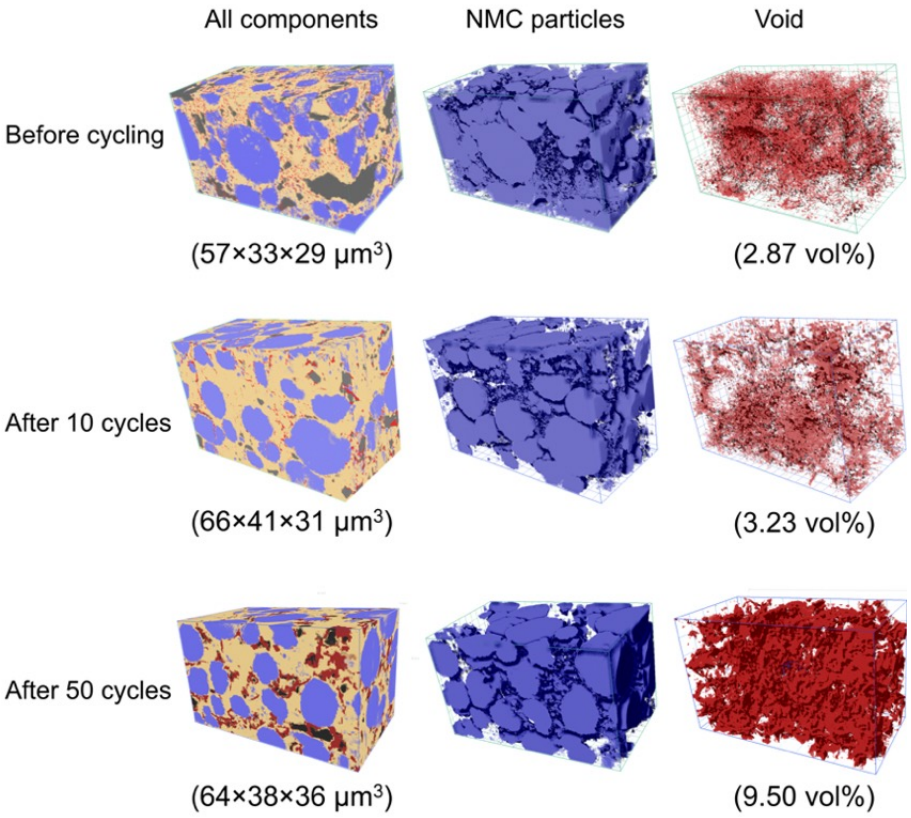

Figure: Reconstructed 3D structures of cathode composite

Possible Solutions

Compliant microstructures by using several design handles:

1) Adding elastomers
2) SSE particle size (smaller will behave more fluid-like)
3) Low strain cathodes

Responses to Previous Year Reviewers' Comments

This program was not reviewed last year

Contributors and Collaborators

Gao Liu : investigation of solution processed LPS

Mary Scott (NCEM): Investigation of coating stability and mechanical breakdown when cycling in a solid-state battery

Srinath Chakravarthy: Samsung research: modeling of electronic conductivity

Remaining Challenges and Barriers

- none

Proposed Future Work

- Since our work shows that only a small fraction of the SE near the anode is vulnerable to the initiation of Li plating, we will investigate how additional layers near the anode can modify the potential and mechanics so as to prevent Li metal penetration.
- We will model and investigate recent experimental results that argue that small amounts of lithiating metals (such as Ag) can homogenize the current and lead to stable Li metal deposition without Li penetration of the electrolyte.
- Continue our investigation of coatings and quantify how much protection they provide for chemical reaction between the SE and cathode

"Any proposed future work is subject to changes based on funding levels."

Summary

- We have previously investigated and demonstrated chemical reactivity between cathodes, coatings and the SE, and mechanical stress concentrations around Li metal growth in the SE.
- This year we focused on mechanical aspects in the composite cathode, and on the role of electronic conductivity in the SE
- If electronic conductivity is present in the SE, a small region near the anode becomes vulnerable to Li plating. The size of this region is proportional to the anode overpotential, and hence to the local current density. Once plating and void cracking occurs in this area, the anode front propagates and deeper regions in the SE can become susceptible to plating
- There is a critical void regime for cracking. Very small voids do not build up enough pressure to crack and large voids never fill. Intermediate voids crack by filling and pressure build up.
- Our results point at the importance of a dense near-anode SE or barrier layer to prevent Li metal propagation
- We demonstrated using serial FIB/TEM tomography that mechanical issues, due to the volume expansion of cathode particles leads to decohesion between the cathode particle and the surrounding SE resulting in capacity loss.