FINAL SCIENTIFIC/TECHNICAL REPORT

REPORT DATE: September 28, 2020

FEDERAL AGENCY	DOE EERE
FOA NAME	Fiscal Year (FY) 2016 Vehicle Technologies Program Wide Funding Opportunity Announcement
FOA NUMBER	DE-FOA-0001384
AWARD TYPE	Cooperative Agreement
AWARD NUMBER	DE-EE0007805

PRIME RECIPIENT	
NAME	Regents of the University of California
TITLE	Sponsored Projects Office
EMAIL	erin.lentz@berkeley.edu
ADDRESS	2150 Shattuck Avenue Room 313 Berkeley CA 947045940
PHONE NUMBER	510-642-0120
TYPE	University
DUNS NUMBER	124726725

PROJECT TITLE	First-principles Modeling and Design of Solid-State Interfaces for the Protection and Use of Lithium Metal Anodes
PRINCIPAL INVESTIGATOR	Gerbrand Ceder

First Principles Modeling and Design of Solid-State Interfaces for the Protection and Use of Lithium Metal Anodes

PROJECT OBJECTIVE

Determine the design principles that control the solid electrolyte/Li electrode interfaces by determining the reaction products stemming from pairing solid electrolytes and Li-metal. A rigorous analysis based on computing electrolyte phase-diagrams closed and open to Li. Li ion transport properties in bulk electrolytes and interfacial products will be assessed through ab initio Molecular Dynamics and Nudged Elastic Band calculations. Simultaneously, a robust framework to identify factors controlling Li-dendrite propagation within solid electrolytes and interfacial products by accounting for irregularities, defects, and grain-boundaries, through a model that includes elements of fracture mechanics, thermodynamics and electrochemistry.

PROJECT IMPACT

The project will lead to understanding of the complex evolution of Li-metal/solid electrolyte interfaces during electrochemical cycling. The understanding of such process is necessary to determine design principles to develop reliable all solid-state batteries.

EXECUTIVE SUMMARY

Li-ion batteries are one of the most advanced energy storage technologies in use today. Li-ion batteries are used in a multitude of applications ranging from consumer electronics, medical devices, sensors and grid storage. However, improving the capacity and energy density delivered by current Li-ion technology requires advanced materials research into novel chemical systems. In this project we have focused particularly in the use of solid-state electrolytes with lithium metal electrodes. Research into all solid-state batteries (ASSB) with Li metal electrodes has significantly expanded in recent years, however most studies reported experimental findings, which left substantial room for theoretical and modeling work as a tool to understand and determine design principles allowing reliable and safe use of ASSBs with Li metal. Among the remaining obstacles preventing reliable use of ASSBs with a Li metal electrode, the stability of the interface between the solid electrolyte and Li metal, and the propagation/dendrite formation of Li metal and resulting mechanical degradation of the electrolyte are key phenomenon that are yet to be fully understood. In the current project we have addressed these two coupled phenomena using first principles calculations and mesoscale continuum modeling. We have obtained chemical and electrochemical stability windows for several solid electrolyte materials. Additionally, from mathematical and numerical modeling of Li protrusion and dendrite initiation during plating and stripping we have determined design criteria in terms of chemical, electrochemical, and mechanical properties and operating conditions for which stable deposition can occur. We also considered the effects of mixed electronic-ionic conduction in solid electrolytes, which has more recently been suggested as another important mechanism involved in ASSB failure. Throughout our work we have successfully addressed important questions necessary for the use of ASSB's. We have determined guiding principles for materials properties and operating conditions necessary to operate ASSB's. And have proposed novel solid electrolyte materials with predicted chemical stability an ionic conductivity. Although this represents significant progress in our understanding, open questions remain in order to fully develop reliable and safely operate ASSBs with Li metal. Future work, building on this project will require further experimental, theoretical and simulation efforts to address remaining questions.

SCIENTIFIC REPORT

The use of bulk reactive metals, such as Li, as negative electrodes in batteries, is a promising way to increase energy density of Li-ion batteries. Furthermore, the use of ceramic and/or glass solid electrolytes to create all solid-state batteries can enable the use of Li metal by preventing unstable propagation of Li dendrites therefore enhancing safety and decreasing capacity fade. Interface chemistry and stability between Li metal and solid electrolytes remains elusive, however the formation of unstable interface products has been identified as the main contribution to limited cycle lifetime and dendrite propagation

Solid Electrolyte Chemistry Selection: Chemical stability, ionic conductivity and mechanical rigidity.

The stability window of electrode, solid electrolyte, and interface products requires construction of multicomponent phase diagrams. From previous work, we have developed theory to construct such diagrams using data available from the Inorganic Crystal Structure Database or data from ab initio calculations. Furthermore, we had also developed a framework for stability analysis to determine electrode/electrolyte interface materials for systems closed and open to Li ion transport. The stability window of materials is determined by the voltage at which lithium is extracted or inserted to the electrolyte. Li deposition at Li-metal electrodes can occur with the reduction of other species, forming a decomposition layer.

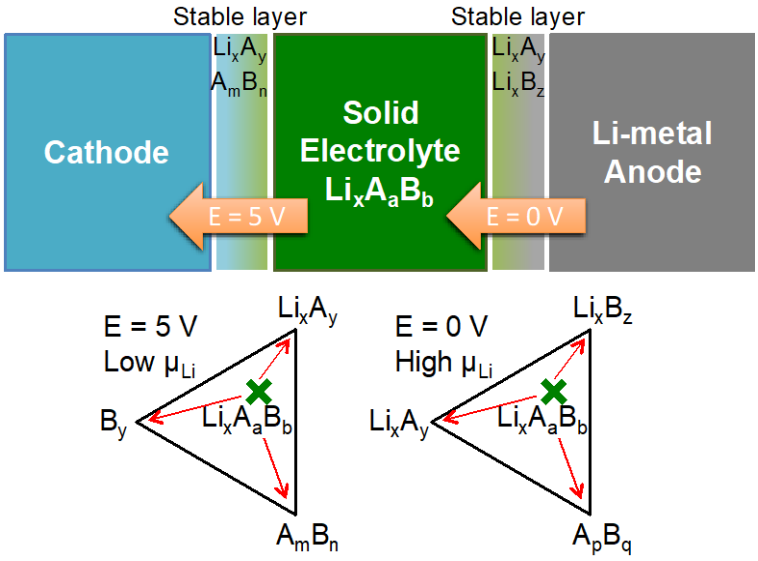

Figure 1. Schematic for the reverse design strategy overlaid on a Li-ion all-solid-state cell. Arrows show the Li chemical potentials which favor Li percolation from the Li-anode (gray) towards the cathode blue. The interfacial

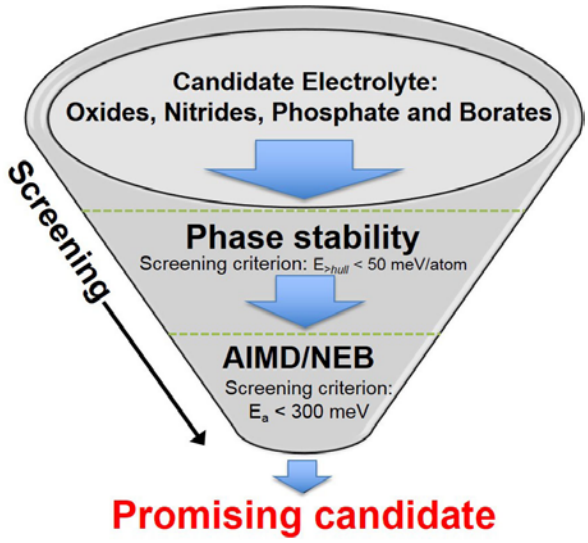

Figure 4. Method adopted here to screen for promising electrolyte materials.

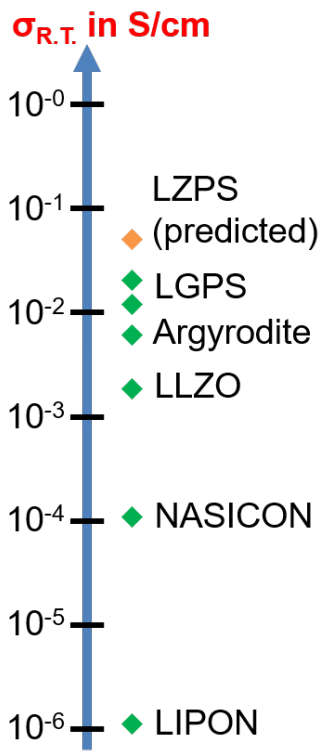

Figure 2. Solid electrolyte materials listed by conductivity.

Using this framework previously developed by our group [Richards et al., *Chem. Mater*, **28**, 266–273 (2016)] to assess the stability of electrode/electrolyte interfaces, we investigated potential solid electrolyte materials (such as oxides, nitrides, phosphates and borates) and selected materials that are stable when in contact with a Li metal anode. Fig. 1 shows the strategy that was implemented to screen for promising solid electrolyte candidate materials that are stable against a Li metal anode.

We developed a model for the **electrochemical stability** of potential solid electrolyte material, based on the framework for stability analysis of electrode/electrolyte interface. We embedded the high component phase diagrams to the calculation of electrochemical stability, as shown in Figure 1, LGPS is used as an example to describe details of this method. According to our current computational results, for the same element M in Li-M-X (X=O or N) ternaries, nitrides exhibit better stability against Li-metal than their oxide counterparts. We attribute this effect of nitrides to their more covalent M-

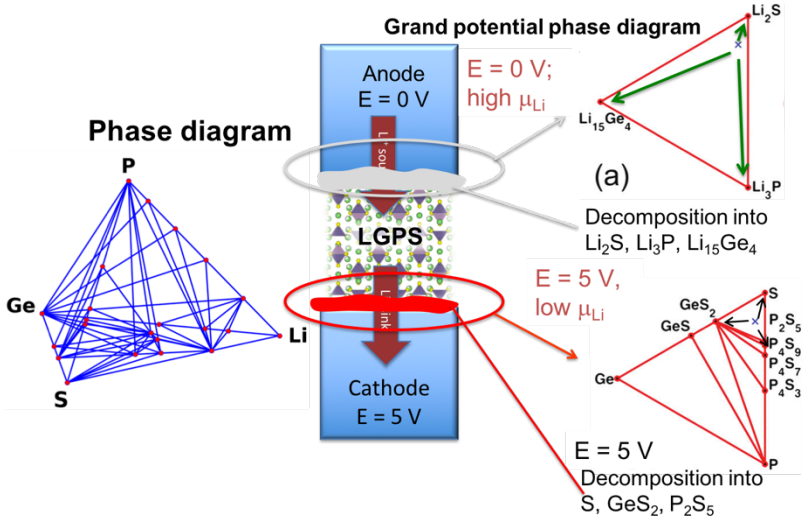

Figure 3. Grand potential phase diagram used in electrochemical stability calculation

N bonding that stabilizes M from being reduced by lithium metal. In terms of decomposition products against lithium metal, lithium metal oxides would form electron conductive phase such as Li-M alloys, making the interface decomposition non-passivating, while in contrast, for N-rich lithium metal nitrides, the nitride/Lithium interface are often self-passivating.

We carried out Li conductivity screening using ab initio molecular dynamics (AIMD) and nudged elastic band (NEB) calculations. The single-vacancy

migration mechanism was first studied using NEB method in a Li nitride material, as shown in figure 1. Li vacancy diffuses in a two-dimensional plane with an activation energy of 284 meV, which is comparable to several state-of-the-art Li-ion conductors. This result indicates that good ionic conductivity could be potentially achieved in these Li nitrides.

By integrating our work on determining chemical and electrochemical stability windows of electrolyte materials against Li metal, we developed a high throughput screening framework which allowed us to explore material/chemical space in search of promising materials. Furthermore, by including Li ion conductivity calculations in the framework, we were able to search for both stable and fast Li conductors. Broadly, our screening framework consisted of computing phase stability from multicomponent phase diagrams, chemical/electrochemical interface stability vs Li, and Li ion conductivity. Using the developed framework, we explored candidate materials including variants of commonly used materials such as oxides and sulfides, in addition to less common chemistries involving phosphates, nitrides, and borates, as shown in Figure 4.

Electrochemical & Mechanical Modeling: Assessing Li propagation and electrolyte fracture.

We also used continuum level theory to build mesoscale models of dendrite growth and potential fracture in solid electrolytes. We studied the heterogeneous deposition of lithium at the boundary of Li-metal anode. We hypothesized the performance was highly related to externally applied pressure, the contact area between anode and electrolyte, and the chemical reaction at Li-metal anode/solid electrolyte interface. Several different cases were studied in order to figure out the behavior of lithium metal in confined space and grain boundaries, as shown in Figure 5.

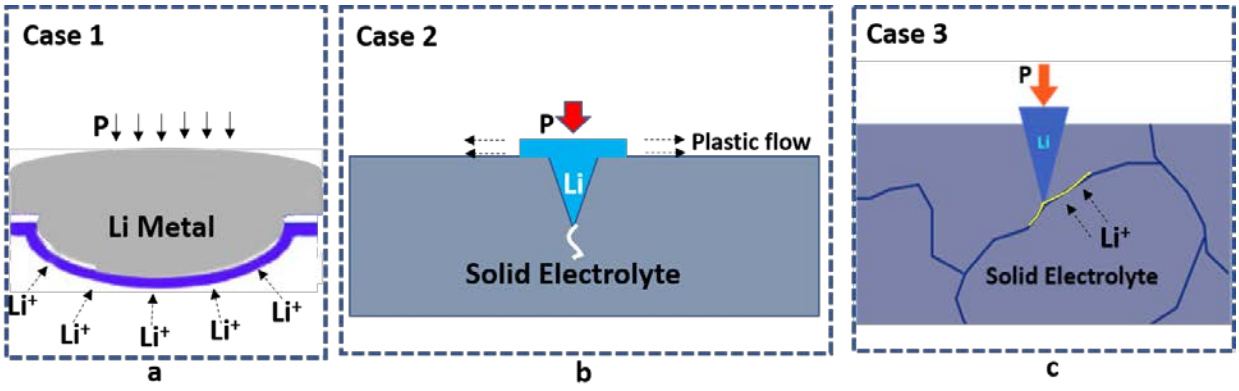

Figure 5. (a) Models that explain the Li dendrite formation, and (b) propagation in crack, and (c) grain boundaries

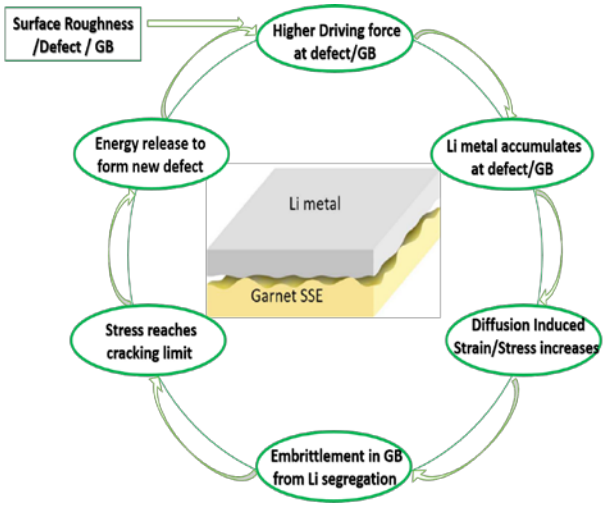

Figure 6. Scheme of the formation and propagation of lithium dendrites during electrochemical cycling of a solid state battery.

As illustrated in Fig. 6, lithium dendrite formation and propagation through solid electrolyte materials may be understood as a combination of multiple physical phenomena, including mechanical effects (such as nonlinear elastic and plastic deformation) and electrochemical effects (such as chemical diffusion and the migration of charged species through the electrode and electrolyte materials subject to a constant electrostatic potential, as well as electrochemical reactions taking place at the solid electrolyte/electrode interface). Dendrite growth is also strongly related to crack propagation in brittle materials. Therefore, a framework combining (electro) chemistry, thermodynamics (interface energy), and fracture mechanics was established in our work.

Furthermore, experimental work has shown that external pressure on a solid-state battery and the interfacial contact quality between lithium metal and the solid electrolyte will affect the overall capacity of battery. In order to quantify the relation between external pressure and interfacial contact, and therefore understand how the contact loss will lead to the formation of dendrites, we developed and built the model shown in Figure 7; As shown in the figure, the contact between lithium metal anode and solid electrolyte is usually not perfect. In order to study the inhomogenous deposition caused by this imperfect contact, we constructed a simplified model to study the relation between surface roughness and interfacial contact. We found that because of the existance of roughness, generated stress and lithium deposition concentration developed and may cause further cracking of the solid electrolyte.

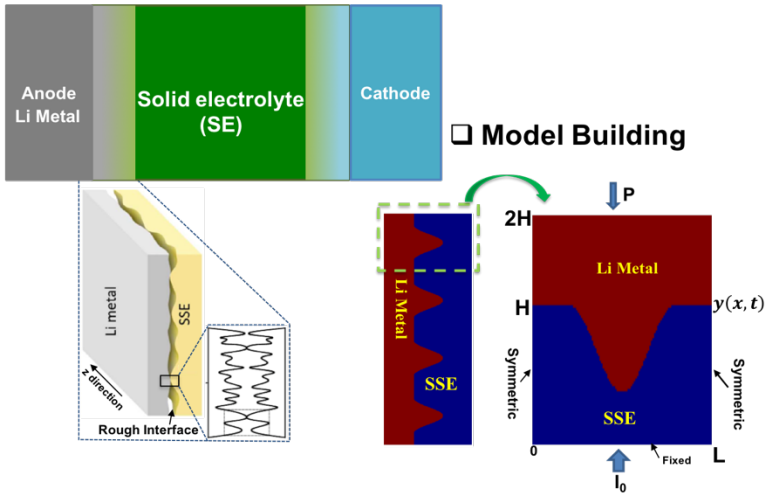

Figure 7. Mechanical model to study contact loss and surface roughness

Experimental work has also shown that solid lithium deposited at the interface is able to crack the surface of the solid electrolyte and penetrate into bulk electrolyte in the form of Li dendrites. In order to crack the relatively hard ceramic material, there must be very large stress concentration at the tip of the cracking area; therefore, it was important to study the critical stress at local areas that yield fracture. In order to quantify the relation between external pressure, surface roughness and critical stress, and understand how the increase of tip stress will lead to the formation of fracture, we constructed a simplified model as shown in Figure 8. We found that because of the existance of roughness, a stress concentration is developed at the tip of the rough surface. The stress developed at these sites can be several orders of magnitude higher than the yield stress of lithium

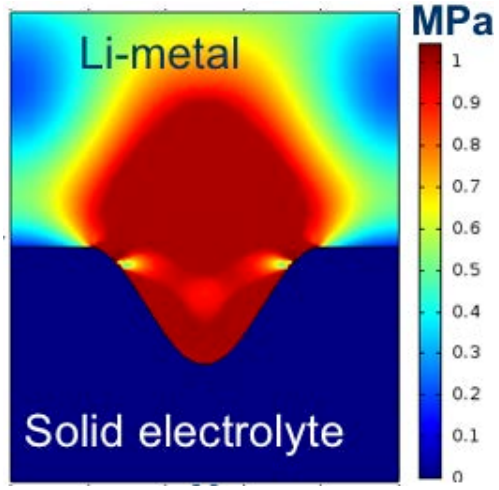

Figure 9. Mechanical model to study stress concentration at rough surface.

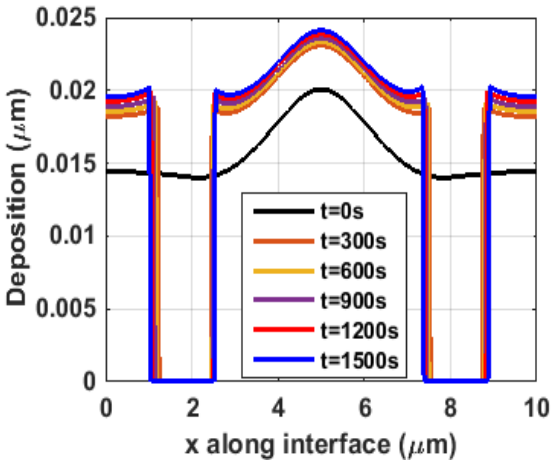

Figure 8. Li deposition at Li metal/SE interface at different charging time.

and approaching the fracture stress of solid electrolyte; such a high stress concentration could further crack the solid electrolyte.

Experimentally it is observed that the interfacial contact between Li metal and solid electrolyte (SE) deteriorates during cycling of a solid-state battery (SSB). Inhomogeneous deposition at a rough interface (or defect) is believed to be one of the main reasons for contact loss and for the nucleation and propagation of dendrites in SSB. We modeled, the Lithium ion transport in the SE, the electrochemical deposition at Li metal/SE interface, and the mechanical balance between Li metal and SE coupled together and solved the model numerically using the Finite Element Method. As shown in Figure 1, Lithium is unevenly deposited along a cosine shape interfaces. Initially, lithium is plated more at the center of the interface than in other areas. After further deposition at the interface Lithium accumulates at the central area and causes the separation of Li metal and SE at the low deposition area. The contact loss at the low deposition area causes an increase in current density at the remaining contact area, which causing even larger Li deposition inhomogeneity. Eventually, more and more contact loss can be observed at the interface, as shown in Figure 9.

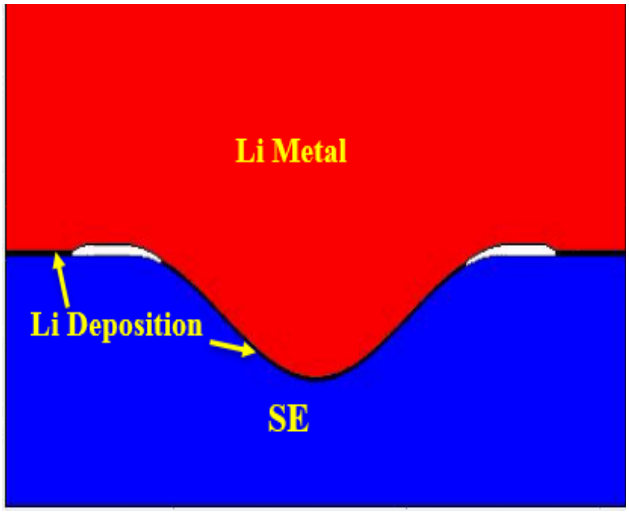

Figure 10. The gap generated at Li metal/SE interface because of inhomogeneous deposition

Interfacial contact loss is determined by several factors, including the back-pressure at the cell boundaries during cycling, the material properties of both Li metal and SE, and the morphology of the interface. A high back-pressure at the boundary can decrease the amount of contact loss. A big enough back pressure can in principle always ensure a perfect interfacial contact during cycling, but too large a back-pressure may also crack the SE and facilitate the growth of dendrites. Our study showed that a lower yielding stress of Li metal can also decrease the amount of contact loss because a softer Li metal means a higher plastic flow along the Li metal/SE interface, which can fill in any

possible gap generated by the inhomogeneous deposition.

In parallel, we additionally developed a theoretical model to account for deposition at sharp cracks. This model accounts for current focusing effects at cracks and allows to determine the corresponding stress state. The current density inhomogeneity from sharp tips can occur additionally to that from interfacial contact loss as we have determined and reported previously. This becomes yet another source for high local deposition currents that can lead to higher stress conditions than depositions at flat interfaces.

The theoretical model quantified the local distortion effects of sharp interfaces on potential, flux lines, and stress increases. Figure 11 shows normalized modelling results for local fields at a sharp defect. Furthermore, the study shows that deposition inhomogeneity at crack can lead to stress states with large deviatoric components that force deposited metal to plastically yield. Hence, we obtained yet more evidence for the critical importance of Li yielding and plastic properties.

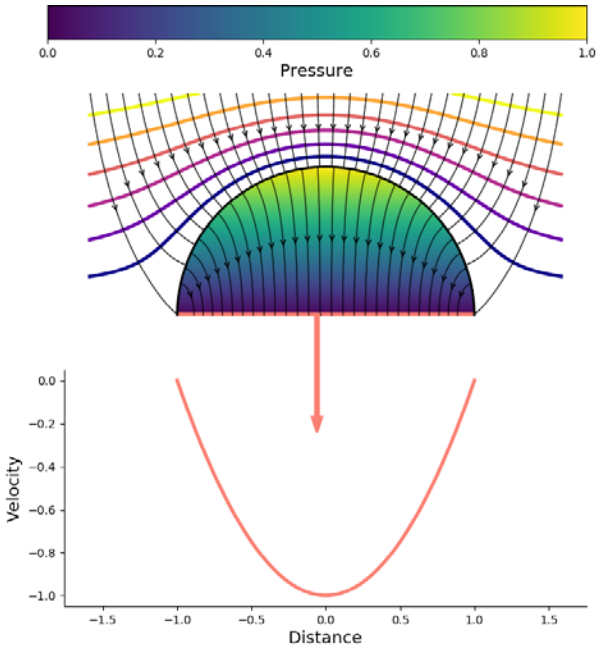

Figure 11. Crack tip normalized ion flux, potential, and pressure field.

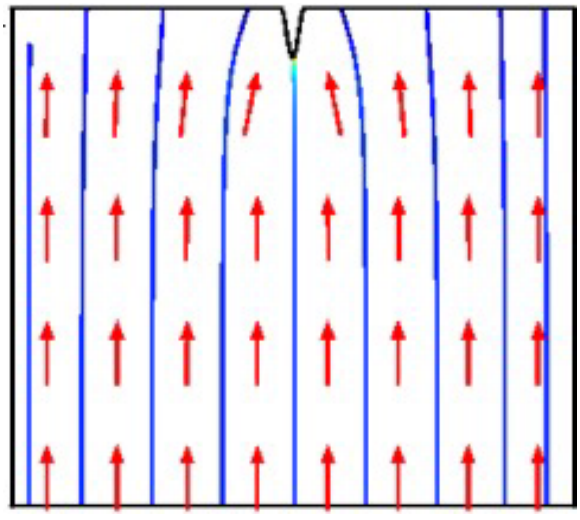

Figure 12. Current density distribution near the crack on the surface of solid electrolyte.

Furthermore, the role of high ionic conductivity is an important aspect in determined possible stress states. High ionic conductivity can exacerbate current *hotspots*, but it also plays a role in potential ion redistribution, which becomes another stress relief mechanism present in our theoretical study. Thus, continued development of this theoretical framework allowed us to determine critical values for material properties (i.e. Electrolyte conductivity, Electrolyte elasticity and fracture toughness, Li yield) that play an important role in Li propagation and cell performance.

The geometry of the initial defect on Li metal/SE interface is usually characterized by roughness measurements, which are commonly defined by several key parameters: (1) arithmetical mean length (the average length of defects on a rough surface), (2) density of peaks (represents the number of

peaks per unit area, determining the width of the defect), and (3) Kurtosis (represents shape of the defect, the bigger this value, the sharper the defect is).

For perfect single crystal solid electrolytes (SEs), the existence of initial surface defects (including initial crack or void) is one of the main factors thought to enable Li-dendrite propagation. As shown in Figure 12, a small size surface defect would cause current density concentration, which would further lead to Li accumulation near the defect and SE fracture underneath the defect tip. The shape of the initial defect can also affect the current density distribution, as shown in Figure 13. With the same defect size, different shapes show the same maximal value of current density but different distributions: the smoothest distribution for a semi-circle shape defect while the sharpest distribution for a cosine shape defect.

Initial defects (such as initial crack/void) on the surface of SEs with lengths ranging from $10nm$ to $1\mu m$ are usually inevitable. To prevent the penetration of Li dendrite into SEs, surface engineering methods can be employed to make defects "shallow and wide." For example, mechanical polishing can reduce the defect length, surface corrosion and etching may increase defect width or change defect shape. Especially for initially narrow and long defects, a small increase of defect width or decrease of defect length can notably homogenize the distribution of current density, and therefore decrease the amount of Li accumulation near defects.

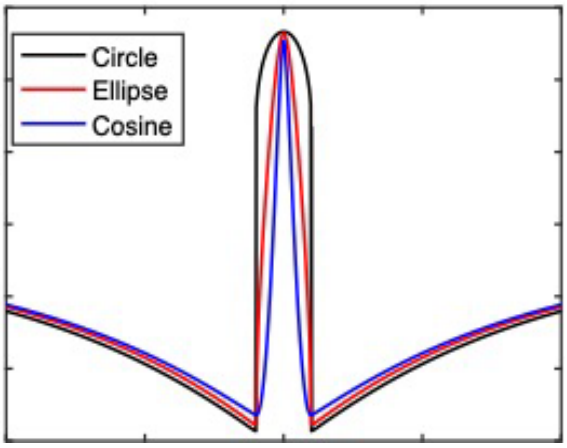

Figure 13. Normal current density distributions along interface of three different

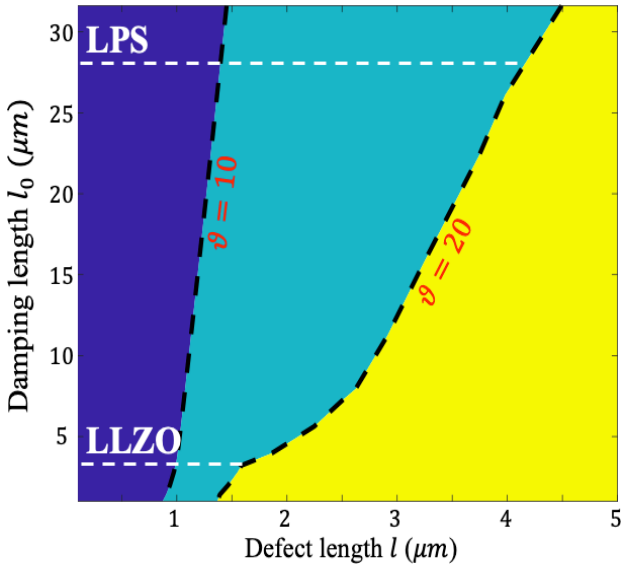

Figure 14. Deposition stability θ as a function of defect length and damping length of different SE materials.

We used our models to investigate the combined mechano-transport issues resulting from the deposition of Li from a solid state conductor with flaws and irregular surface contact by integrating the transport equations with mechanical models for the materials that incorporate elasticity, plasticity, and fracture. Figure 14 shows the Li deposition stability, which measure the inhomogeneity of current as contour plot against the length of a defect emanating from the Lithium anode and the damping length of the SE. The damping length is a materials property of the SE, related to ionic conductivity and exchange current density of the SE with Li metal, that quantifies the ability of the SE to dampen deposition

instability caused by surface irregularities. Li deposition is more stable when the defect length decreases and the damping length increases. An SE with large damping length (such as LPS) creates more stable deposition than an SE with small damping length (such as LLZO) when their surface roughness is similar. An SE with larger damping length can tolerate worse surface quality.

Similarly, the effect of stack pressure is also a critical aspect in determining deposition stability. Most solid-state batteries use an applied stack pressure to retain good interfacial contact upon cycling. Internal stress from the stack pressure can provide a driving force for Li deformation and help to retain contact when an uneven Li surface forms due to uneven deposition. Low stack pressure may result in insufficient Li deformation and cause interfacial contact loss, while large stack pressure leads to severe stress concentration and causes Li infiltration into pores/GBs of the SE where it may cause fracture if the stress intensity factor is above the limit of the fracture toughness of the SE. Therefore, a "mechanical stability window" of the stack pressure (shown in Fig. 15) is available to prevent both contact loss and SE fracture. For solid-state battery systems with different combination of metal electrodes and SEs, the required mechanical stability window for stack pressure can be very different. In general, smaller stack pressure is needed in a Na-metal system than in Li-metal system to maintain intimate contact because of the lower yield strength of Na-metal compared to Li-metal. Oxide-SE systems can withstand much larger stack pressure than sulfide-SE systems because of their much larger moduli and fracture toughness.

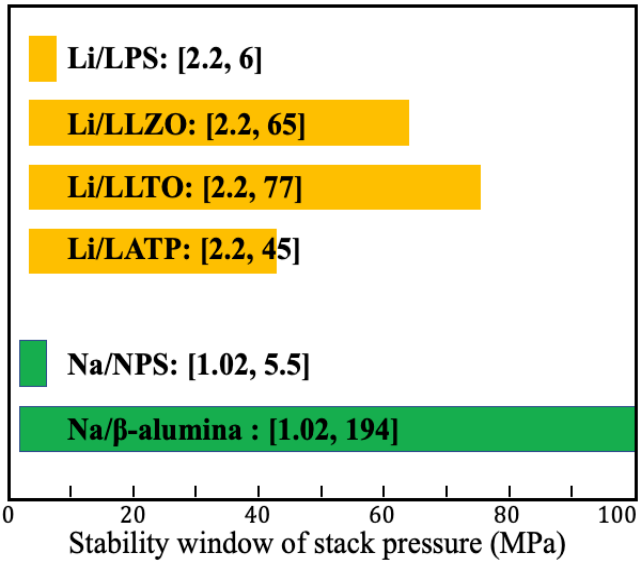

Figure 15. The mechanical stability window of the stack pressure for different SSB systems.

From further investigations of the combined mechanical and chemical phenomena at play during solid state electrodeposition, we quantitatively identified ionic conductivity and conductor fracture toughness as key material properties that control the extent of stable deposition where no fracture-based failure is expected to occur. Figure 16 shows how increased ionic conductivity can reduce the total stress intensity factor (SIF) for a set of given operating conditions. Another feature to notice from Figure 16 is that the applied stack pressure

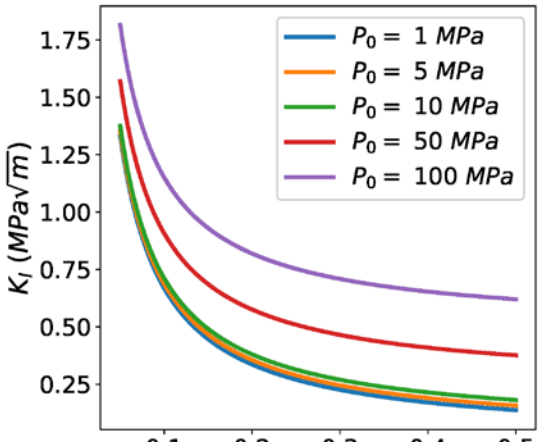

Figure 16. Stress intensity factor (SIF) at a flaw tip of length 20 μm for a ionic conductivity of σ+ = 0.1 mS/cm with 1 mA local current density, as function of the ionic conductivity for different values of applied stack pressure.

directly increases the SIF value and so can bring its magnitude above the solid electrolytes fracture toughness. Thus, a high enough stack pressure can raise the SIF for a metal filled flaw to the critical value and initiate fracture from purely mechanical means as a result of the increase in hydrostatic pressure of the metal.

Using our model treating local stress states that arise from deposition at sharp flaws and fracture criteria based on a SIF values, we calculated the extent of stable deposition regions with respect to charging current density and operating stack pressure. Figure 17 shows the extent of stable deposition regions, and how ionic conductivity and fracture toughness affect the extent of these regions. The ionic conductivity has a stronger effect in increasing the maximum local current densities that can be accommodated. In contrast the fracture toughness plays a more important role in setting the maximum stack pressure that can be used during operation. Ionic conductivity and fracture toughness are shown to be key electrolyte properties that can be optimized to increase the size of subcritical regions and therefore ensure stable deposition in solid state batteries with a reactive metal electrode.

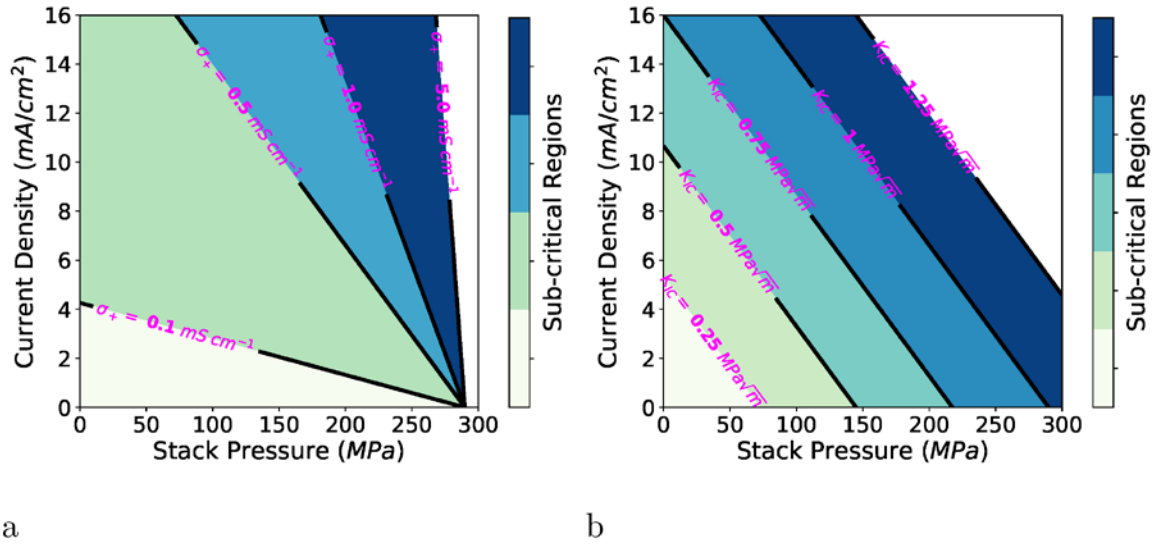

Figure 17. (a) Sub-critical regions for 10 µm flaw in an ionic conductor with 1 MPa√m fracture toughness, and (b) ionic conductor with conductivity σ+ = 0.5 mS/cm. Stable regions are denoted by the color corresponding to the materials property value in addition.

Finally, we studied the effects of mixed ionic and elecotronic conduction. When a solid electrolyte has ionic and electronic conductivities, both the conduction cation M^+ and electrons can migrate inside the SE. During the charging process of the SSB cell shown in Figure 18, M^+ ions migrate like an "ionic conductor" from the cathode to the anode with partial current density $\boldsymbol{i}_{M^+}$ (red lines); meanwhile, electrons conduct as an "electronic conductor" from the anode to the cathode with partial current density $\boldsymbol{i}_{e^-}$ (blue lines). The "ionic conductor" and "electronic conductor" can be treated as an equivalent circuit that are connected in parallel under the same externally applied potential drop ΔU. Charge-transfer reactions (stripping at the cathode-SE interface, plating at the anode-SE interface, metal deposition at the

void-SE interface) can be described by the Butler-Volmer relation. Both the ionic (M^+) and the electronic conduction (e^-) in the SE are assumed to follow Ohmic relation.

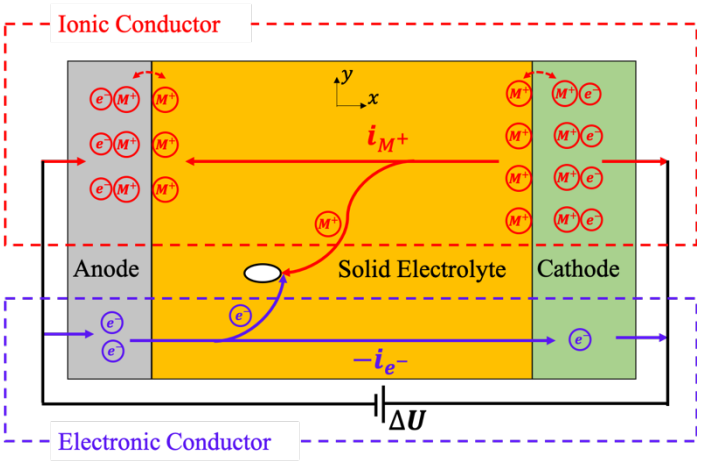

Figure 19. Schematic of the mix ionic-electronic conductor model for a full SSB cell during charging.

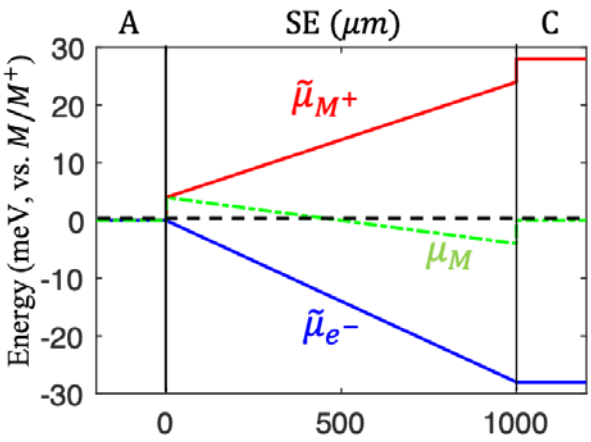

Figure 18. The potential distribution in the SE in a symmetric cell.

The 1D solution shown in Figure 19 represents the ideal case when the structure and material are homogeneous, which can provide general trends for all potentials in the SSB cell. Under the galvanostatic condition with constant charging current, the electronic potential $\tilde{\mu}_{e^-}$ decreases from the anode to the cathode without potential drop when crossing the electrode/SE interface; Contrarily, the ionic potential $\tilde{\mu}_{M^+}$ increases from the anode to the cathode and with a potential drop when crossing the electrode/SE interface. This drop at the interface provides overpotential needed for the stripping and plating. The partial current densities $\boldsymbol{i}_{e^-}$, $\boldsymbol{i}_{M^+}$ are proportional to the gradient of their potentials. The summation $\tilde{\mu}_{e^-} + \tilde{\mu}_{M^+}$ (green-dash line) in the SE determines the overpotential for metal deposition in the SE. The metal deposition will happen only when this value is positive, or say when this value is above the chemical potential of M in the metallic phase (black-dash line). Therefore, metal deposition will happen in voids with location within half of the SE thickness in the symmetric cell.

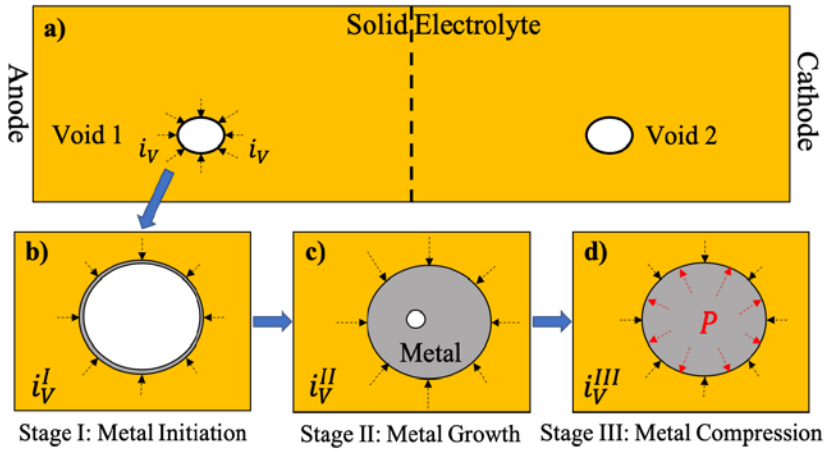

Figure 20. Schematic illustration of different stages of metal deposition in the void.

Li metal can be deposited within voids inside the SE when

the surface overpotential at the location of the void is large enough. Figure 20 presents a schematic illustration of the metal deposition process in the voids. Before cell cycling, no *Li* metal is present in the voids. If the surface overpotential requirement is satisfied, a thin layer of *Li* metal is plated on the surface of the void at an initial deposition rate (Stage I: metal initiation). After initiation stage, the void is gradually filled by *Li* metal at a higher deposition rate (Stage II: metal growth). After the void is fully occupied by *Li* metal at the end of the growth stage, the hydrostatic pressure (*P*) starts to build up as new *Li* metal continues to be deposited into the confined space. The increase in hydrostatic pressure in turn reduces the surface overpotential and decreases the deposition rate until no more metal can be inserted (Stage III: metal compression).

The *Li* metal deposition in the confined void leads to an increase in the hydrostatic pressure in the metal, which further decreases the overall deposition overpotential and the deposition rate in the void. As shown in Figure 21, the pressure is zero before the void is completely filled by the *Li* metal, but shortly after the void completely filled, the pressure rapidly increases to a stable maximal value within several minutes. The horizontal black line represents the critical pressure that the SE material can withstand before fracture. For a given SE material (such as LPS, LLZO) and SE microstructure (such as porosity, pore size), different maximal hydrostatic pressure can be developed under different applied current density. When the applied current density is large enough (such as > 1 mA/cm^2 shown in Figure 2), the developed hydrostatic pressure in the Li metal is higher than the critical pressure allowed for the SE, which will cause fracture of the SE. More deposition will happen in the newly fractured area due to the higher curvature, which leads to further fracture and propagation of *Li* metal.

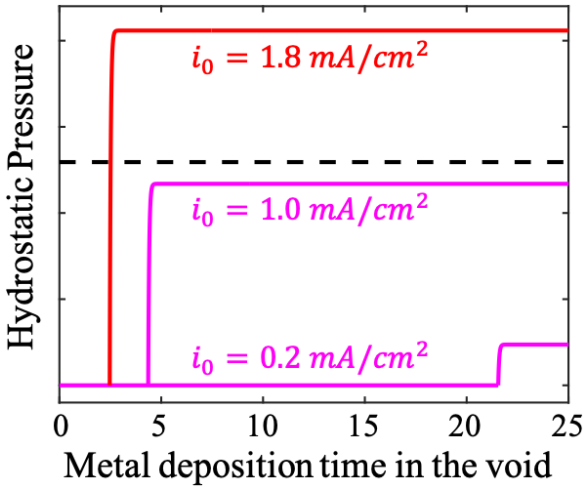

Figure 21. Pressure developed in the metal under three applied current densities.

Publications

- Qingsong Tu, Tan Shi, Srinath Chakravarthy, Gerbrand Ceder. Understanding Metal Deposition in Solid Electrolyte due to Mixed Ionic-Electronic Conduction. To be submitted.
- Barroso-Luque, L., Tu, Q. & Ceder, G. An Analysis of Solid-State Electrodeposition-Induced Metal Plastic Flow and Predictions of Stress States in Solid Ionic Conductor Defects. *Journal of The Electrochemical Society* **167**, 020534 (2020).
- Tu, Q., Barroso-Luque, L., Shi, T. & Ceder, G. Electrodeposition and Mechanical Stability at Lithium-Solid Electrolyte Interface during Plating in Solid-State Batteries. *Cell Reports Physical Science* **1**, 100106 (2020).
- Ouyang, Bin, et al. "Computational investigation of halogen-substituted Na argyrodites as solid-state superionic conductors." *Chemistry of Materials* 32.5 (2020): 1896-1903.
- Bauers, Sage R., et al. "Ternary nitride semiconductors in the rocksalt crystal structure." *Proceedings of the National Academy of Sciences* 116.30 (2019): 14829-14834.

- Zhang, Yubo, et al. "Efficient first-principles prediction of solid stability: Towards chemical accuracy." *Npj Computational Materials* 4.1 (2018): 1-6.
- Xiao, Yihan, et al. "Understanding interface stability in solid-state batteries." *Nature Reviews Materials* (2019): 1-22.