Mechanical and Chemical issues in Solid-State Batteries







Some papers related to this talk

MECHANICS Li Metal Dendrites

- L. Barroso-Luque, Q. Tu, G. Ceder, An Analysis of Solid-State Electrodeposition-Induced Metal Plastic Flow and Predictions of Stress States in Solid Ionic Conductor Defects, J. Electrochem. Soc. 167 020534 (2020)
- Q. Tu, L. Barroso-Luque., G. Ceder. Cell Reports Physical Science 1 (7), 100106 2020

INTERFACE stability

- W.D. Richards, et al. Chemistry of Materials, 28 (1), 266-273 (2016)
- T. Shi et. Al, Characterization of mechanical degradation in an all-solid-state battery, J. Mat. Chem. A, 8, 17399 2020 : DOI: 10.1039/d0ta06985j

COATINGS

- Y. Xiao et al. Computational Screening of Cathode Coatings for Solid-State Batteries Joule (2019), https://doi.org/10.1016/j.joule.2019.02.006. (2019)
- Y-Q. Zhang et al. *Direct Visualization of the Interfacial Degradation of Cathode Coatings in Solid State Batteries: A Combined Experimental and Computational Study,* Adv. Energy Mater., 2020, 1903778, DOI: 10.1002/aenm.201903778 (2020)

REVIEW on INTERFACE STABILITY

• Y. Xiao, Y. Wang, S-H. Bo, J.C. Kim, L.J. Miara, G. Ceder, *Understanding interface stability in solid-state batteries*, Nat Rev Mater. doi:10.1038/s41578-019-0157-5 (2019)

CATHODE LOADING

T. Shi, Q. Tu, Y. Tian, Y. Xiao, L.J. Miara, O. Kononova, G.Ceder, *High Active Material Loading in All-Solid-State Battery Electrode via Particle Size Optimization,* Adv. Energy Mater. 2019, 1902881, DOI: 10.1002/aenm.201902881 (2019)

The competition is highly optimized and requires a very low rate of parasitic reactions

Journal of The Electrochemical Society, 166 (13) A3031-A3044 (2019)

A Wide Range of Testing Results on an Excellent Lithium-Ion Cell Chemistry to be used as Benchmarks for New Battery Technologies

A3031

Jessie E. Harlow, ^{1,2} Xiaowei Ma,^{1,2} Jing Li,^{1,2} Eric Logan,^{1,2} Yulong Liu,^{1,2} Ning Zhang,^{1,2} Lin Ma,^{1,2} Stephen L. Glazier, ^{1,2} Marc M. E. Cormier,^{1,2} Matthew Genovese,^{1,2,*} Samuel Buteau,^{1,2} Andrew Cameron,^{1,2} Jamie E. Stark,^{1,2} and J. R. Dahn ^{0,1,2,**,z}



Need to have $\approx 10^{-5}$ fraction parasitic reaction

Any solid-state battery will have to excel over Li-ion in at least one property, and probably multiple ones

Content for today

- Cathode/SSE electrochemical interface
- Coatings
- Mechanical issues and dendrite propagation

Jeder Group

The electrochemical stability problem on the cathode side

Oxidative Li extraction from the SSE followed by SSE decomposition can occur at every interface that has an electron path to the current collector and an ionic path to the SSE



$$V_{cathode} = - \mu_{Li} = (\mu_{Li} + \mu_{e})$$

- Both Carbon/SSE and SSE/cathode interface are reactive
- Oxidation occurs by Li extraction and removal of electron from the anion
- This is very different from liquid electrolytes

Y. Xiao, L.J. Miara, Y. Wang, G. Ceder, *Computational Screening of Cathode Coatings for Solid-State Batteries* Joule (2019), https://doi.org/10.1016/j.joule.2019.02.006. (2019)

Oxidation limit is set by anion, and modified by its bonding with metals

Cations that move up anion oxidation potential (e.g. through inductive effect) raise the anodic high voltage stability

W.D. Richards, et al. Chemistry of Materials, 28 (1), 266-273 (2016)



Oxidative decomposition is problem for sulfides



W.D. Richards, et al. Chemistry of Materials, 28 (1), 266-273 (2016)

Experimental evidence that sulfide is oxidized at the interface with carbon

Yoon, Kang et al., Scientific reports 8 (2018)



Binding Energy (eV)

When carbon is present, XPS indicates that LGPS is oxidized after first charge.

With the present of carbon, the cell impedance after the first charge increased significantly, mainly from the contribution of the carbon/LGPS interface.

Coating as an effective strategy



Hybridize oxygen in coating to improve oxidation resistance



Uniform amorphous coatings through solution method



Y-Q. Zhang et al, Adv. Energy Mater., 2020, 1903778, DOI: 10.1002/aenm.201903778 (2020)

Experimental confirmation: Comparison of Li-Zr-O coated NMC with Li-borate coated NMC

Cycle life testing in graphite/LPS/coated-NMC solid state cell (0.05 mA cm⁻² between 2.5 and 4.3v) V



Y-Q. Zhang et al, Adv. Energy Mater., 2020, 1903778, DOI: 10.1002/aenm.201903778 (2020)

LZrO coating breaks down after 1st cycle



- After 1st cycle, LZrO coating breaks down. The decomposition product can be indexed to ZrO₂ (Figure b). Li is extracted and some O exchanges with S in SSE. Leads to (Mn,Ni) sulfide compounds
- This is consistent with the computationally predicted reaction

 $Li_2ZrO_3 \rightarrow 2Li + ZrO_2 + O$

- The decomposition of LZrO is attributed to oxidation of O²⁻ at high voltage.
- ZrO₂ was found to distribute
 inhomogeneously on NCM
 surface. STEM-HAADF and EDX
 mapping shows the aggregation of
 decomposition products, where a
 70 nm-thick ZrO₂ layer could be
 observed.

LZrO vs. LBO coating in long-term cycling (50 cycles)



Cathode coating strategy is not perfect

- Imperfection on coating exposes cathode particle to SSE.
- Perfect coating insulates electron conduction path.
- Cathode coating cannot protect SSE/Carbon (or current collector) interfaces.





Chemical Reactivity



- Important for co-sintering of SSE and cathode
- Also important for coatings with SSE

High reactivity at sulfide SSE/oxide cathode interface



Large instability driven by S-O exchange: $LiMO_2 + Li-P-S \rightarrow Li_3PO_4 + M-S > 300 meV/atom driving force$

e.g.: Tsukasaki et al, J. Power Sources, **434**, 226714 2019; Koerver et al, Chem. Mat. **29**, 5574 (2017)

Y. Xiao et al. *Computational Screening of Cathode Coatings for Solid-State Batteries* Joule (2019), https://doi.org/10.1016/j.joule.2019.02.006. (2019)

Oxide coatings are stable with oxide cathodes and have reduced reactivity with sulfides



 However, the oxide coating/sulfide SSE interface still has reactivity > 100 meV/atom, but less than the cathodes themselves.

Y. Xiao et al. *Computational Screening of Cathode Coatings for Solid-State Batteries* Joule (2019), https://doi.org/10.1016/j.joule.2019.02.006. (2019)

-600

Polyanionic oxides have good stability with both oxide cathodes and sulfide SSEs



Polyanionic oxides are more reactive with oxide cathodes than oxide coatings because Li₃PO₄ formation Polyanionic oxides more stable with sulfide SSEs than oxide coatings as they already have a formed PO₄ group

Coating recommendations



Li metal issues

- Dendrite propagation in solids
- Current homogeneity der Group

- L. Barroso-Luque, Q. Tu, G. Ceder, An Analysis of Solid-State Electrodeposition-Induced Metal Plastic Flow and Predictions of Stress States in Solid Ionic Conductor Defects, J. Electrochem. Soc. 167 020534 (2020)
- Q. Tu, L. Barroso-Luque., G. Ceder. Cell Reports Physical Science 1 (7), 100106 2020

Possible mechanisms for dendrites growth in solid electrolyte



1. Connected porosity: Li simply grows through the SE

2. Mechanical: Stress intensification leading to propagating fracture through the grains or grain boundaries.

- 3. (Electro)chemical reactivity leading to SEI formation.
- 4. Isolated pores: Li deposits due to electronic conductivity.

Can Li crack a Solid Electrolyte ?

- Li is a very soft metal: yield stress is ≈ 1 MPa
- Assuming Li can crack a SSE is asking if jelly can crack concrete ?



Can stress intensification at the crack tip be large enough to fracture the SSE ?



Porz, et al, Adv. Energy Mater. 2017, 7, 1701003

DATA taken from Q. Tu, L. Barroso-Luque., G. Ceder. Cell Reports Physical Science 1 (7), 100106 2020, and refs therein

Electrode Type	SE	Young's modulus (GPa)	Fracture Toughness $(MPa \cdot m^{1/2})$	
	LPS	19.5±0.9	0.25±0.04	
Li-Metal ($\sigma_{\rm v} = 0.8MPa$	LLZO	150.3±2.2	1.25±0.20	
E_{Li} =7.8 GPa) (4)	LLTO	203	1.08±0.20	
	LATP	115	1.1±0.30	
Na-Metal ($\sigma_{y} = 0.2MPa$	Na_3PS_4	19	~0.25	
$\begin{array}{c} E_{Li}=10 \text{ GPa} \\ (23) \end{array} \beta - alumina \end{array}$		260	2.2	

Metal protrusion in SSE focusses current: concept



Increased deposition rate at crack tip needs to push Li metal towards the anode -> results in increase pressure at crack front

Model



- Continuum PDE model for coupled deposition and electrode metal plastic flow.
- Approximations:
 - Isotropic ionic transport in SE
 - Metal viscous flow.
 - Planar crack geometry.
 - Model 1: No feedback between stress in crack and Li transport in SSE
 - Model 2: Feedback between stress in crack and Li transport in SSE

Solution with no mechanical coupling between Li transport in SE and electrochemistry leads to very large possible pressures



L. Barroso-Luque. Q. Tu, G. Ceder. 2020 J. Electrochem. Soc. 167 020534

Coupling of the mechanical stress to the transport equations limits the pressure increase in a significant way



For $\sigma_{Li+} > 0.1 \text{mS cm}^{-1}$ and reasonable pseudo viscosities for Li, screening length is tens of microns. Smaller defects are essentially "invisible" for the current.

Importance of High Ionic Conductivity in Solid Electrolytes: Screening

As the conductivity of the SE increases, the equipotential lines act like there is no defect, hence there is no current focusing and no stress build-up



Limiting value (maximum) Pressure that can be achieved for flaws below the screening length

$$\Delta P(l) \approx \frac{\alpha z_{+} Fl}{\sigma_{+} V_{m}} i_{0} \qquad \stackrel{\text{egg}}{\underset{\Delta \Phi}{\text{Limetal}}}$$

L. Barroso-Luque. Q. Tu, G. Ceder. 2020 J. Electrochem. Soc. 167 020534

Materials Design & Cell Operation Criteria

closed form equation for the stress intensity factor

$$K_I \approx \beta_1 \left(\frac{z_+ F i_0}{\sigma_+ V_m}\right) L^{3/2} + \beta_2 P_0 L^{1/2}$$

Safe operating zones for current density and stack pressure for SSE with 1MPa $m^{1/2}$ fracture toughness and a 10µm flaw



Current homogeneity: effects of conductivity, ASR, and stack pressure

Local current density is not the same as overall current density. The more inhomogeneity, the higher local current density can be.

How to reduce current inhomogeneity ?

Evaluate effects of stack pressure, ionic conductivity, and areaspecific-resistance on interfacial deposition inhomogeneity



Q. Tu, L. Barroso-Luque., G. Ceder. Cell Reports Physical Science 1 (7), 100106 2020

Models for charge transport

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



 i_n is the normal current density passing across the electrode/SE interfaces.

- *i_{exc}* is the exchange current density at the interfaces.
- η is the surface overpotential: the drop of electrochemical potential of Li^+ ($\tilde{\mu}_{Li^+}$) at the electrode/SE interface.
- 2. Transport of Li^+ in the SE can be described by Ohmic relation:
 - Relation of current density (i_{Li^+}) and electrochemical potential $(\tilde{\mu}_{Li^+})$:

$$\left| \mathbf{i}_{Li^+} = -\frac{\sigma_{Li^+}}{F} \nabla \widetilde{\mu}_{Li^+} \right|$$

• Laplacian equation of electrochemical potential $(\tilde{\mu}_{Li^+})$ at steady state:

$$\nabla^2 \tilde{\mu}_{Li^+} = 0$$

Higher ionic conductivity of SE reduces Li deposition inhomogeneity



Q. Tu, L. Barroso-Luque., G. Ceder. Cell Reports Physical Science 1 (7), 100106 2020

Higher area-specific-resistance (ASR) reduces Li deposition inhomogeneity



Q. Tu, L. Barroso-Luque., G. Ceder. Submitted to Cell Reports Physical Science

Can define "damping length" which is length scale over which inhomogeneity can be removed

Definition of damping length

$$l_0 = \frac{\sigma_{Li} + RT}{i_{exc}F} = \sigma_{Li} + \cdot ASR$$

$$\sigma_{Li} + : \text{ lonic conductivity}$$

$$ASR: \text{ Area specific resistance}$$

$$\Box \text{ Current inhomogeneity near defect}$$

Typical SE material

SE	i _{exc} (mA cm ²)	ASR $(\Omega \ cm^2)$	$\sigma_{Li} (mS / cm)$	l ₀ (μm)
LPON	1.2	21	10^{-3}	0.2
LLZO	12.5	2	0.1	2
LPS	1	25	0.5	125

Tsai, Chih-Long, et al. *ACS applied materials & interfaces*8.16 (2016): 10617-10626.

Sharafi, Asma, et al. Chemistry of Materials 29.18 (2017): 7961-7968.

Q. Tu, L. Barroso-Luque., G. Ceder. Cell Reports Physical Science 1 (7), 100106 2020

Stability factor at anode interface

10

8

6

4

2

0

-0.02

-0.01

0

Coordinate near defect $(10^3 \mu m)_{36}$

0.01

LPS

LPON

0.02

Stress is concentrated near the defect area at the interface

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• Contour of pressure near the defect

Stress components (MPa)

Pressure

VonMises

Stress

Х

- MPa stack pressure
 I i metal
 I i metal
 - Large pressure at the defect area. Pressures exceed yield stress (due to hydrostatic components)

Plastic Deformation of Li under 3MPa

The VonMises stress determines the plastic flow of Li metal at the interface.

Less contact loss is developed with larger stack pressure and lower yield strength of Li metal



Effect of yield strength when stack pressure is 1MPa





Summary: Mechanical effects in conductors

- Electrochemical degradation of SE and coatings occurs. Stable coatings can be designed by maximizing the anion covalency (polyanion systems, low Li content in coating, etc.) NMC with such optimized borate coating has improved cycling. Carbon/SE is also active interface.
- Chemical reactivity is driven between S <-> O exchange (for sulfide SE and oxide cathode) or Li₃PO₄ formation for phosphates in contact with SE with high Li content.
- Stress concentration at the front of a **Li dendrite** does not grow unlimited but feeds back to transport of Li in SSE. Increased pressure raises potential, which in turn reduces current focusing on the dendrite. Purely mechanical cracking does not seem very likely in conductors with typical fracture strength and reasonable conductivity.
- For SSE with good conductivity defect **screening length is tens of microns** and maximum pressure developed is limited. High ionic conductivity is not only important for impedance lowering, but it also limits the buildup of stress concentration.
- **Current homogeneity** improved by higher ionic conductivity, increased ASR, stack pressure higher than a few times Li yield stress.

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