Development, Characterization, and Testing of Solid-State Electrolytes for Batteries

Corey Efaw
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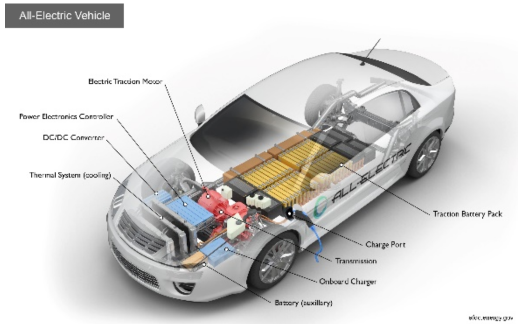
LRS #INL/CON-23-74274

Idaho National Laboratory

The Sales Pitch for Batteries

- Decarbonization!!
  - Roll out an electric vehicle (EV) fleet ASAP
- Untapped, enabling markets
  - eVTOL, aerospace, communications, etc.

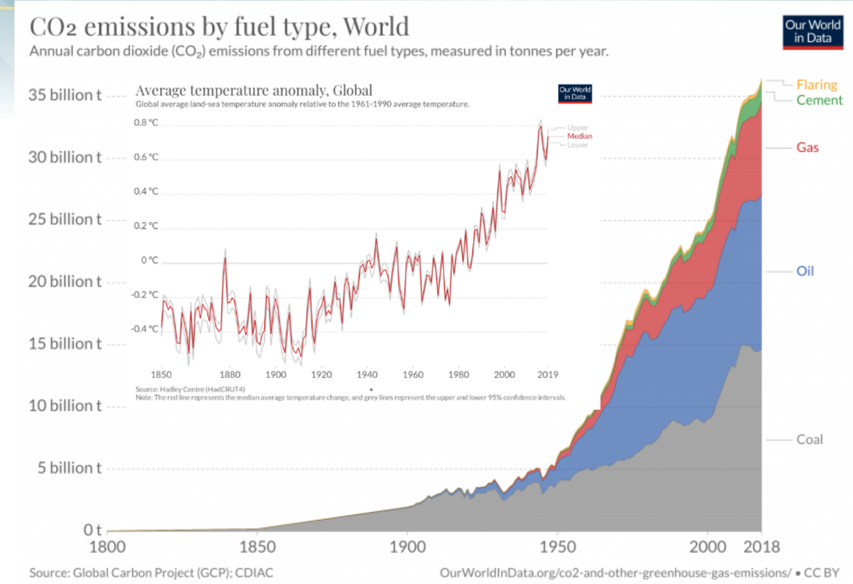


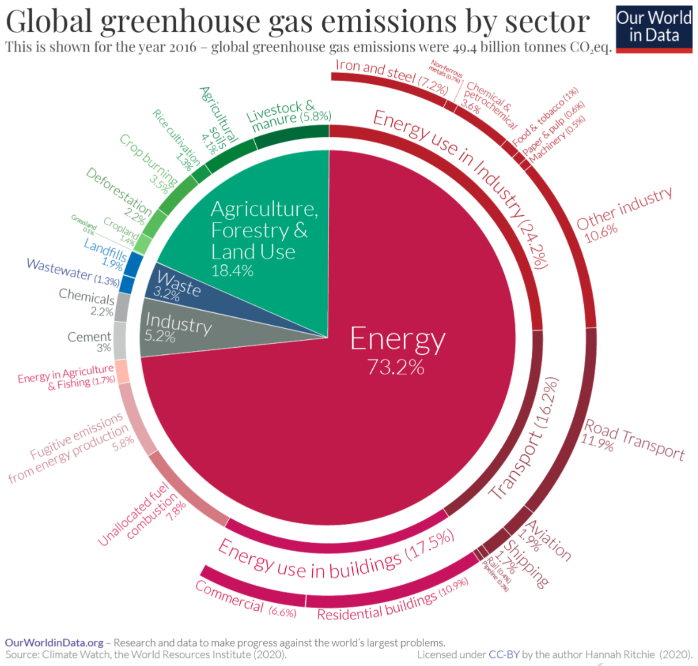
DOE – Alternate Fuels Data Center

Sion Power "Airbus Zephyr"

Heart Aerospace – 19-seat, 400 km (~ 250 miles), all-electric

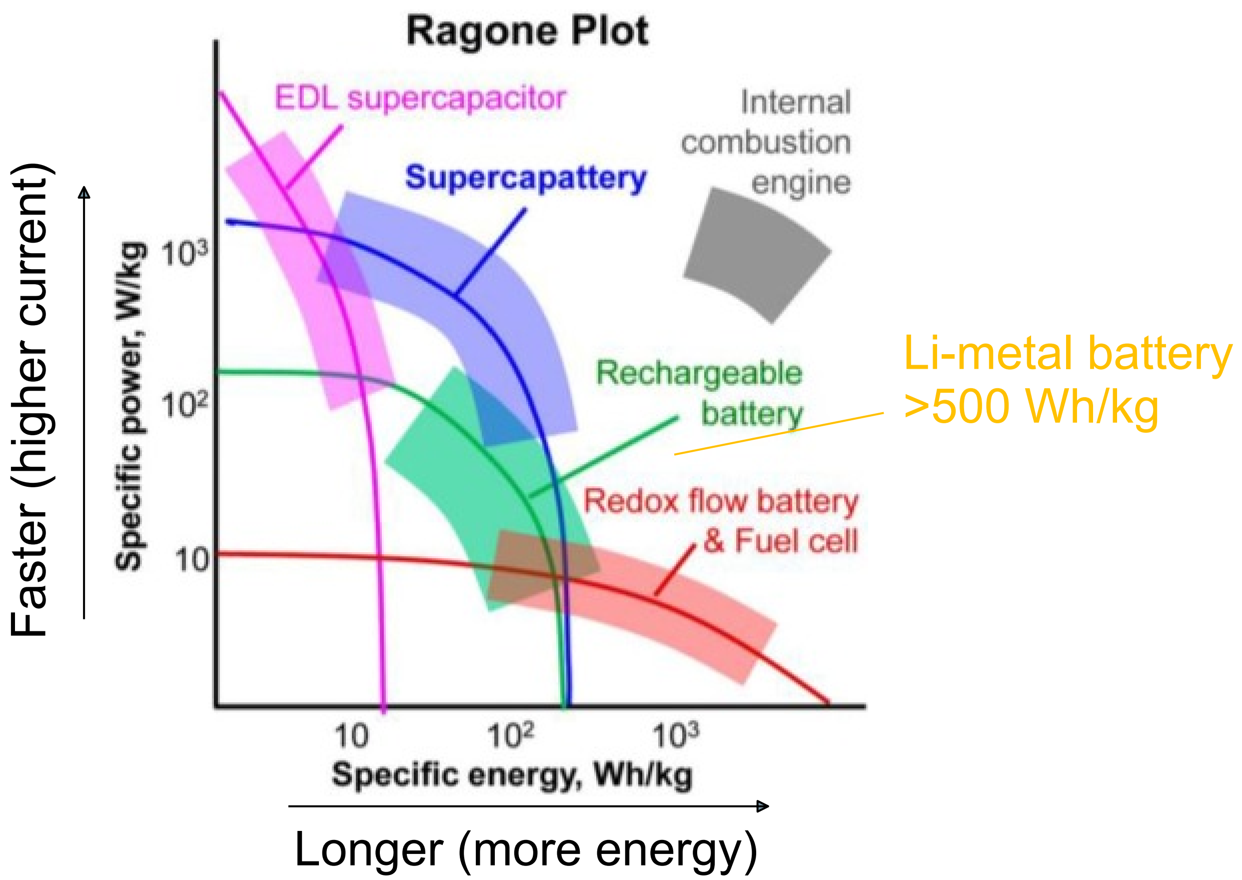
Archer Aviation's "Midnight" eVTOL model

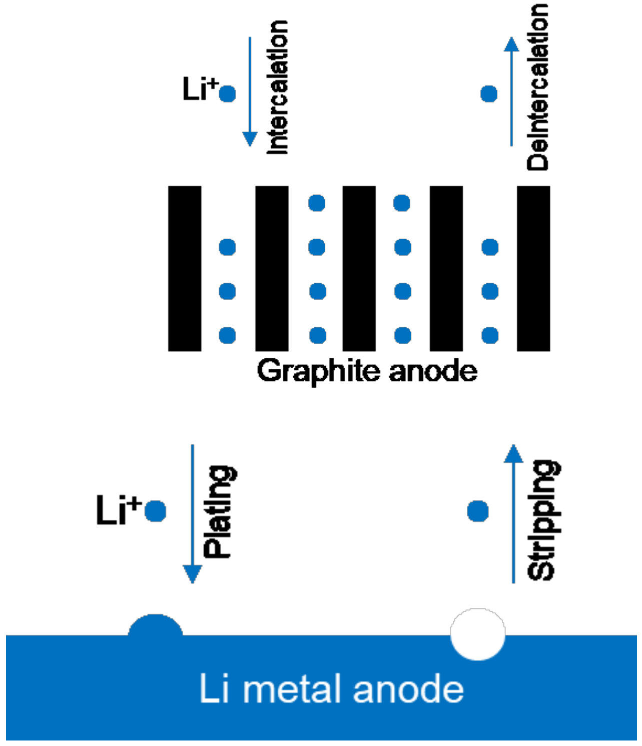




Limitations to Batteries

- Benchmark chemistries are low in energy, but stable
- Next-generation chemistries (Li-metal) are more volatile
  - Inherent instabilities present with plating/stripping (de)lithiation mechanisms



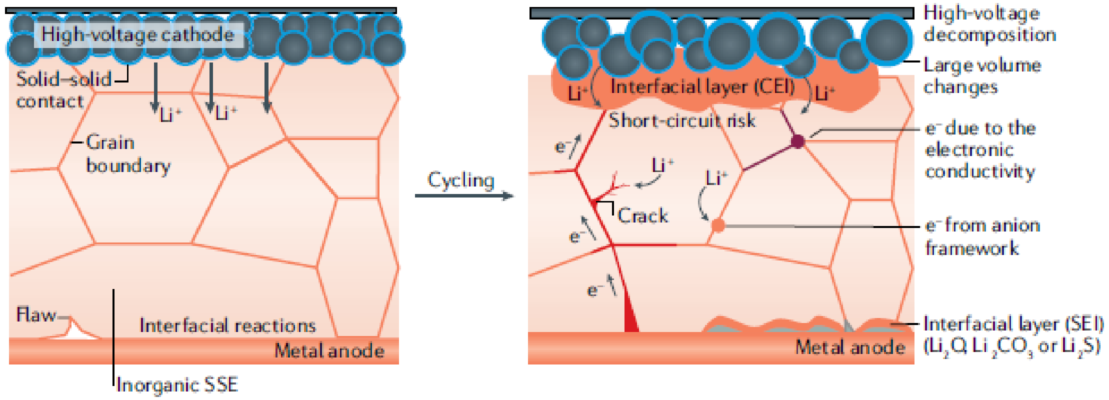


Sulfide-Based Solid-State Electrolytes

+ Improved safety – lack of flammable compounds
+ Provides a physical barrier to dendrites & active material dissolution
+ Electrical insulator & ionic conductor (10^{-3} – 10^{-4} S/cm)

– Requires ultrahigh (> 1 MPa) pressure to reduce interfacial impedances
– Poor stability in humidity ()

Q. Zhao et al, *Nature Reviews* **5**, 229 (2020).

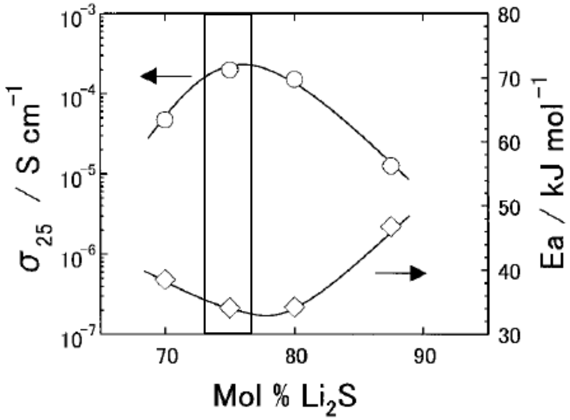


Issues are driven by ionic diffusion kinetics, electrode-electrolyte interfaces, and chemo-mechanical stability.

Material Selection – LPS

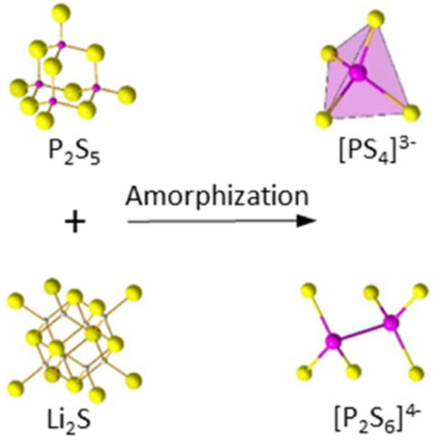
- **75-25 Li_2S-P_2S_5 by mole (LPS)** electrolyte elected as base-material of choice
  - Desire low void & grain boundary LPS – dense & highly amorphous

A. Hayashi et al, *J. Am. Ceram. Soc.* **84** (2), 477 (2001).

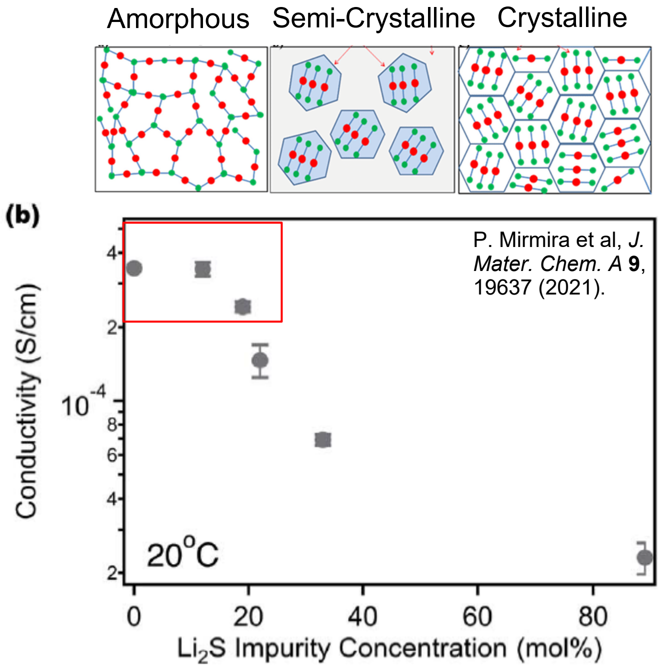


network modifier

network former



$$(\mathrm{P{-}S{-}P + S \rightarrow P{-}S + S{-}P})$$

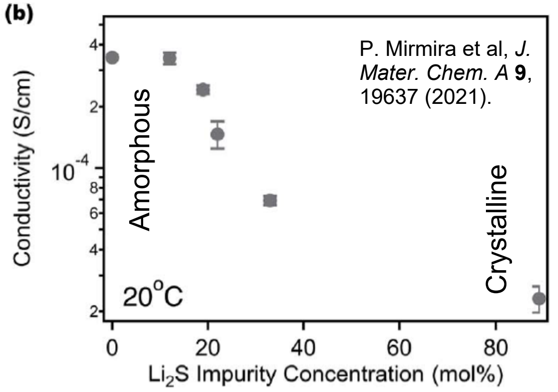


P. Mirmira et al, *J. Mater. Chem. A* **9**, 19637 (2021).

C. Dietrich et al, *J. Mater. Chem. A* **5**, 18111 (2017).

Material Selection & Methods

- **75-25 Li_2S-P_2S_5 by mole (LPS)** electrolyte elected as base-material of choice
  - Desire low void & grain boundary LPS – dense & highly amorphous

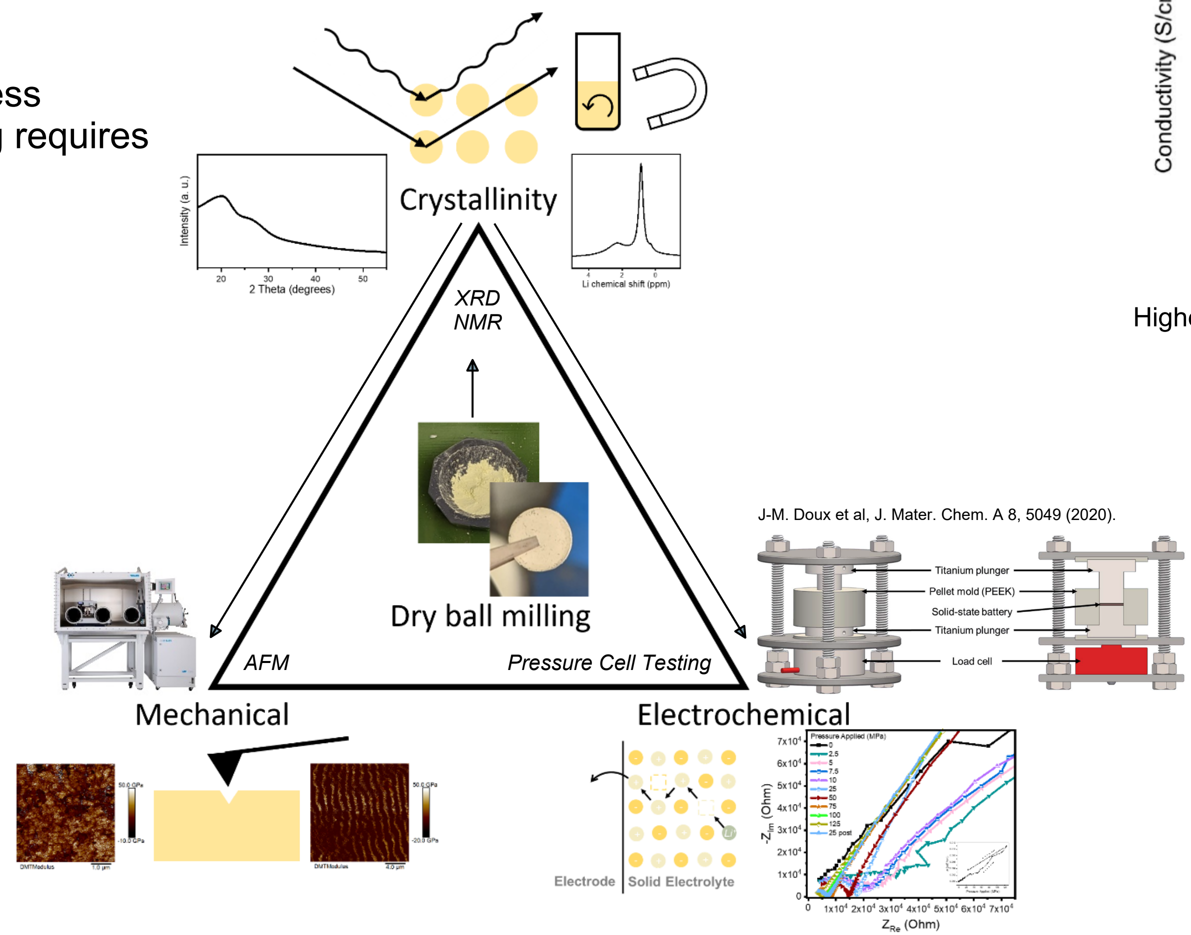


Higher amorphous content → improved conductivity

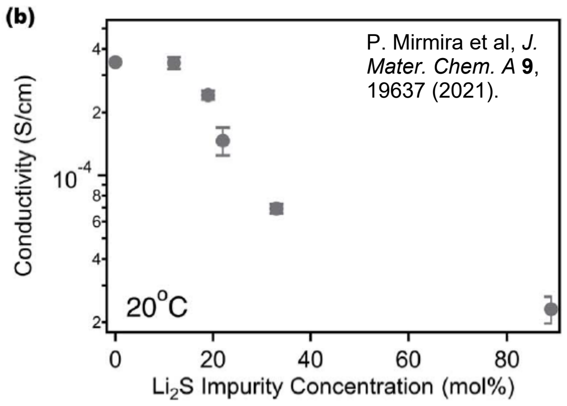
Benefits of dry ball milling
- Lessened overall energy cost on process
- Low temperature – solution processing requires evaporating step of solvents (>100°C)

How do dry ball milling parameters impact different material characteristics?

How does pellet crystallinity impact mechanical and electrochemical performance?



Literature Gaps



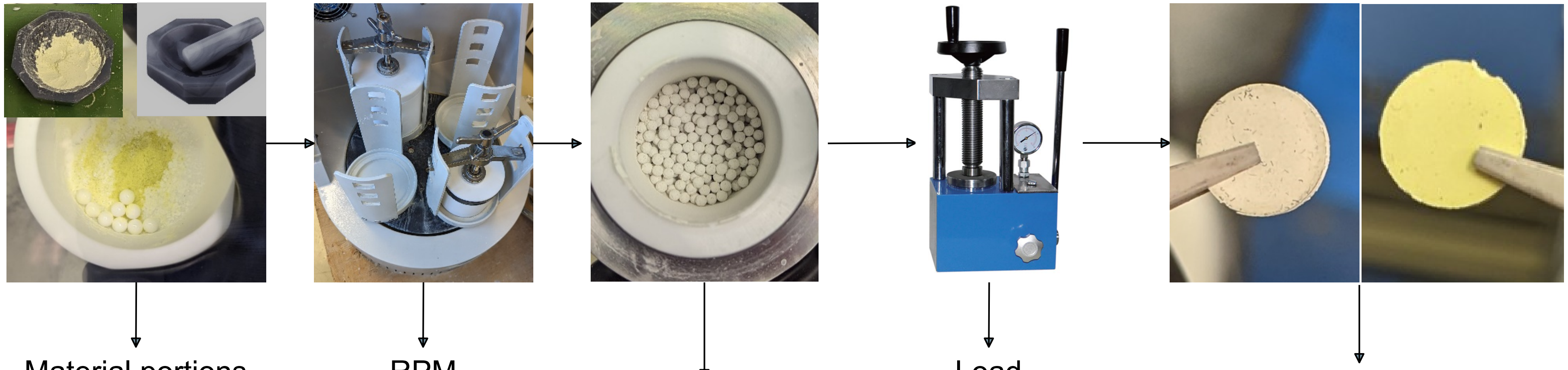
Methods publication in process for *ECS Journal of Solid State Science and Technology* to address literature inconsistencies.

x - not documented in text				Milling Media					Grinding Jar		Milling Details						
DOI	Year	mol ratio Li_2S:P_2S_5	Total active mass (g)	Material	Size(s)	Appx. Mass (g)	Count	Media: active (g:g)	Material	Size (mL)	RPM	Time (hr)	Milling Interval	Hand Milling	Jar Cleaning	Amorphous vs. Crystalline	Notes on Water Prevention
10.1111/j.1151-2916.2001.tb00685.x	2001	75:25	0.5-1	Alumina	10 mm	20	10	10-20	Alumina	45	370	20	Continuous	Y before	x	Amorphous	Milling in a glovebox
10.1016/j.elecom.2009.07.028	2009	70-80% Li_2S	1	ZrO_2	12 & 15 mm	15	1 each	x	ZrO_2	vial (Spex)	x	20	Continuous	x	x	Glass	Milling in a glovebox
10.1016/j.elecom.2009.07.028	2009	70-80% Li_2S	1	ZrO_2	12 & 15 mm	15	1 each	x	ZrO_2	vial (Spex)	x	20	30 min ON, 30 min OFF	x	x	Glass	Milling in a glovebox
10.1039/c0jm01090a	2011	80:20	x	ZrO_2	5 mm	60	160	x	ZrO_2	45	500	20	x	x	x	"Almost amorphous"	x
10.1016/j.ssi.2010.10.013	2011	67-80% Li_2S	x	ZrO_2	4 mm	120	500	x	ZrO_2	45	510	8-24	x	x	x	Glass & glass-ceramic	Dry Ar atmosphere
10.1038/srep02261	2013	75:25	x	ZrO_2	4 mm	120	500	x	ZrO_2	45	510	10	x	Y before	x	Amorphous	Dry Ar atmosphere
10.1016/j.jpowsour.2015.10.040	2015	75:25	1	ZrO_2	4 mm	120	500	x	ZrO_2	45	510	45	x	x	x	Unconfirmed	x
10.1038/nenergy.2016.30	2016	77:23	x	x	x	x	x	x	x	x	x	120	x	x	x	Crystalline	Milling in a glovebox
10.1038/srep21302	2016	67-75% Li_2S	x	ZrO_2	10 mm	32	10	x	ZrO_2	45	370	80	x	x	x	Mixture	Dry Ar atmosphere
10.1016/j.ssi.2015.11.034	2016	70:30	x	ZrO_2	3 mm	x	x	x	ZrO_2	80	510	144	10 min ON, 20 min OFF	Y, every 8h	x		Milling in a glovebox
10.1039/c7ta06067j	2017	50-75% Li_2S	5	ZrO_2	3 mm	110	x	22	ZrO_2	45	510	100	5 min ON, 15 min OFF	x	x	Amorphous below 75mol% Li2S	Milling in a glovebox
10.1149/2.1831712jes	2017	75:25	x	ZrO_2	4 mm	120	500	x	ZrO_2	45	510	10	x	x	x	Glassy	x
10.1038/s41467-018-04762-z	2018	77.5:22.5	x	x	x	x	x	x	Stainless Steel	500	x	20	x	x	x		x
10.1021/acs.jpcc.9b01425	2019	75:25	4	ZrO_2	3 mm	8.5	x	25	ZrO_2	45	510	117	5 min ON, 15 min OFF	x	x	Amorphous	Dry Ar atmosphere
10.1002/aenm.202101111	2021	75:25	x	ZrO_2	10 mm	36	12	x	ZrO_2	x	510	20	15 min ON, 15 min OFF	Y before	x	Crystalline	Sealed with parafilm & tape
10.1039/d1ta02754a	2021	75:25	2-5.2	ZrO_2	5 or 10 mm	32-64	x	6-16	ZrO_2	45	350-510	15-80	0-5 min OFF/hr	Varied	Varied	Amorphous	Screw-top clamp for sealing
10.1021/acsaem.0c02771	2021	75:25	x	x	x	x	x	x	ZrO_2	45	600	10	x	x	x		Milling in a glovebox
This work	22-23	75:25	2	YSZ	1.2-10 mm	20-70	varied	8-24	YSZ or Teflon	45-500	370-850	10-120	Varied	Varied	Varied	Commonly crystalline	Tape or screw-top clamp

Filling the Gaps

- Many preparation parameters affect the resulting SSE makeup
  - What's the best "recipe"?

Access thru Hydr. & Echem Dept.



Material portions
Milling media
Additional processing

RPM
Time
Intervals

Multimodal characterization
XRD, NMR, etc.

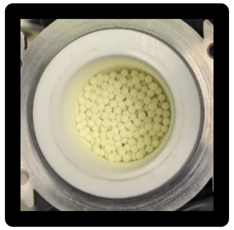
Load
Time

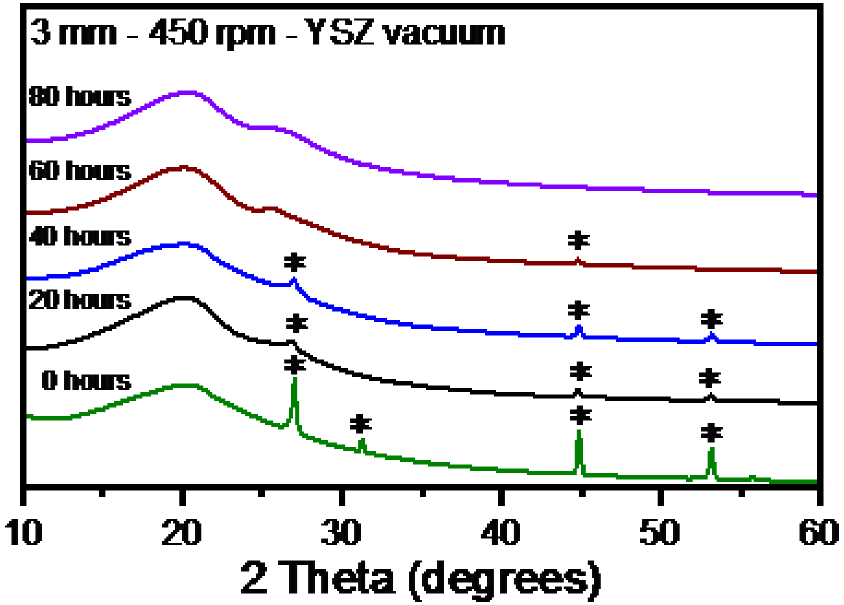
Physical characteristics
Electrochemical testing
Mechanical testing

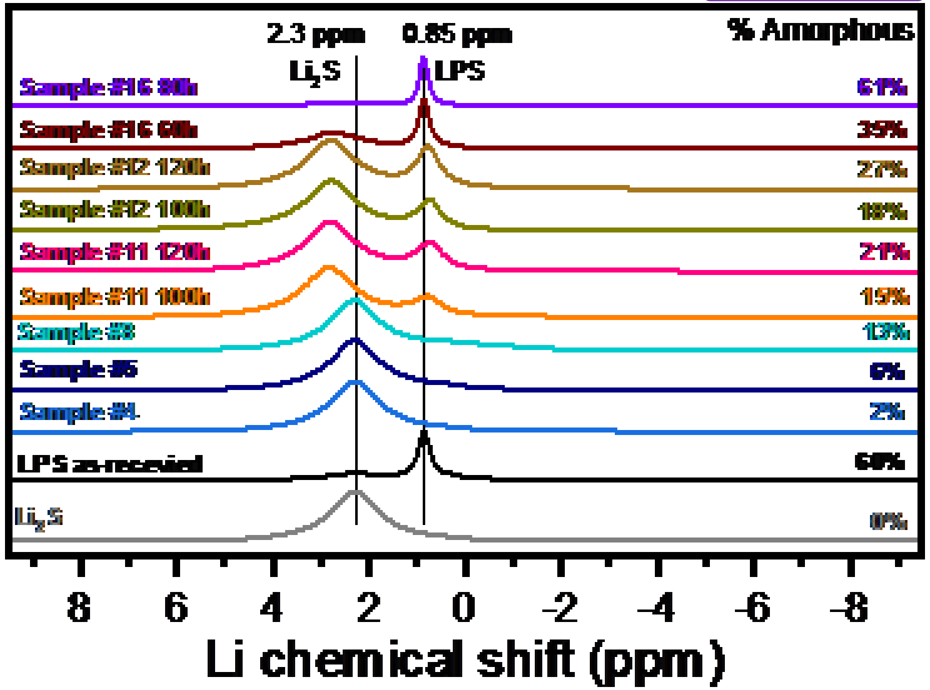
Impacting factors: ***crystallinity***, ***physical characteristics*** *(color, pellet density, etc.)*, and ***e-chem capabilities***

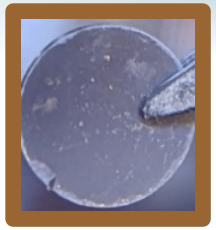
XRD & NMR

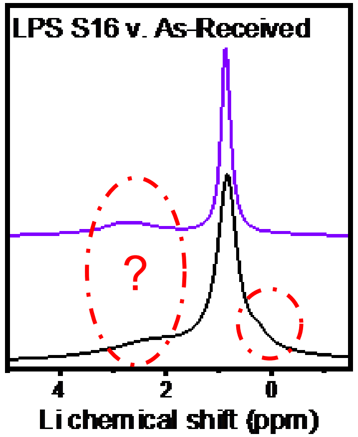
- XRD as a good go/no-go tool
- NMR for quantitative analysis









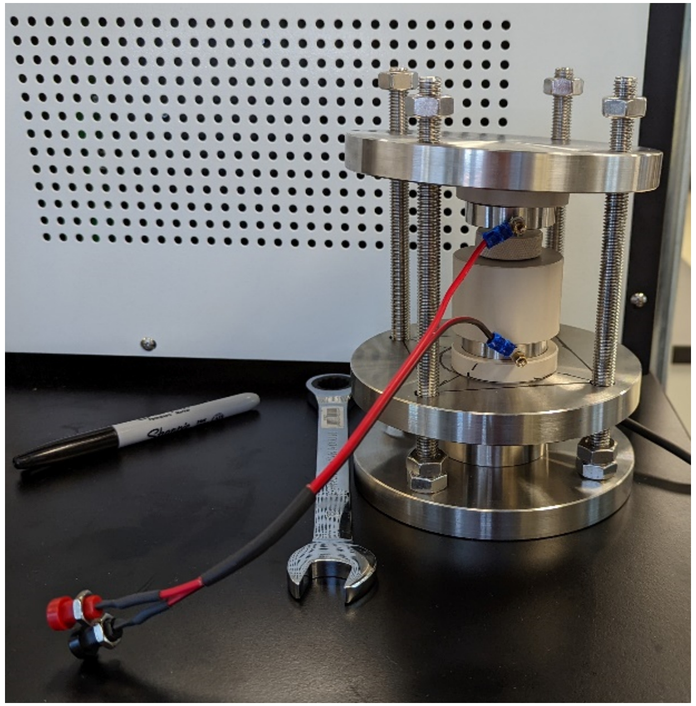


P. Mirmira et al, *J. Mater. Chem. A* **9**, 19637 (2021).

NMR accessed in collaboration with Dr. Corey Pilgrim

Cell-Level Testing

- PEEK Split Cell to run ionic conductivity tests & symmetric cell tests
  - Evaluate impacts of pressure
  - Add modified interfaces (i.e., artificial SEIs) to lithium foil – LiI & LiF



J. Lau…B.S. Dunn, *Adv. Energy Mater.* **8**, 1800933 (2018).

*"…two most promising methods for stabilizing the interface: the **compositional tuning of sulfide** solid electrolytes and the use of **artificial SEIs**"*

J-M. Doux et al, J. Mater. Chem. A 8, 5049 (2020).

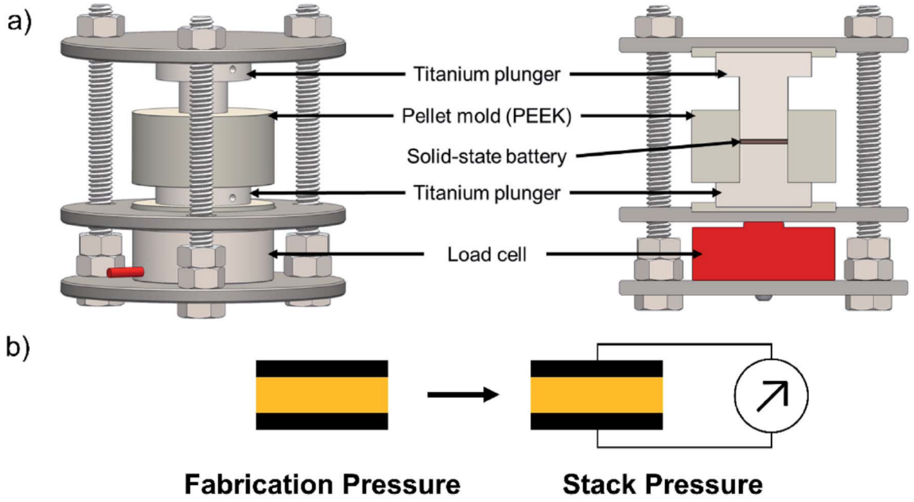
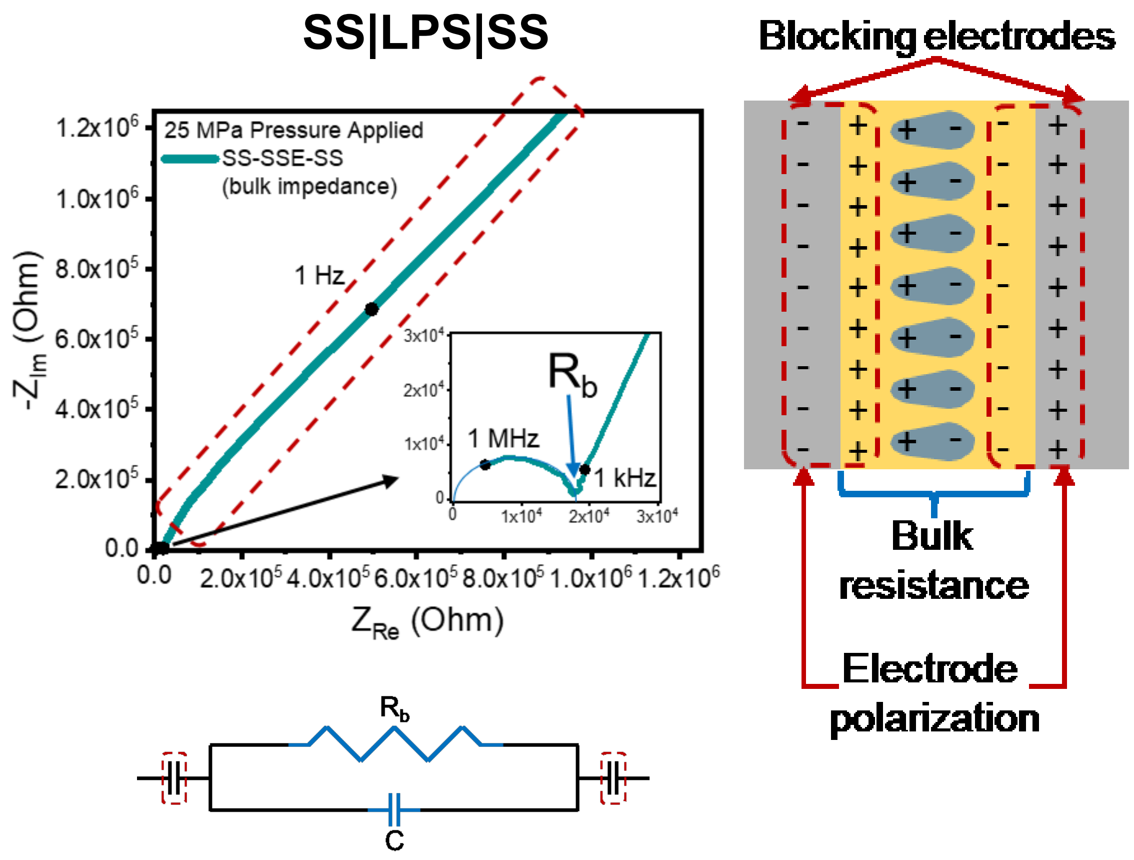


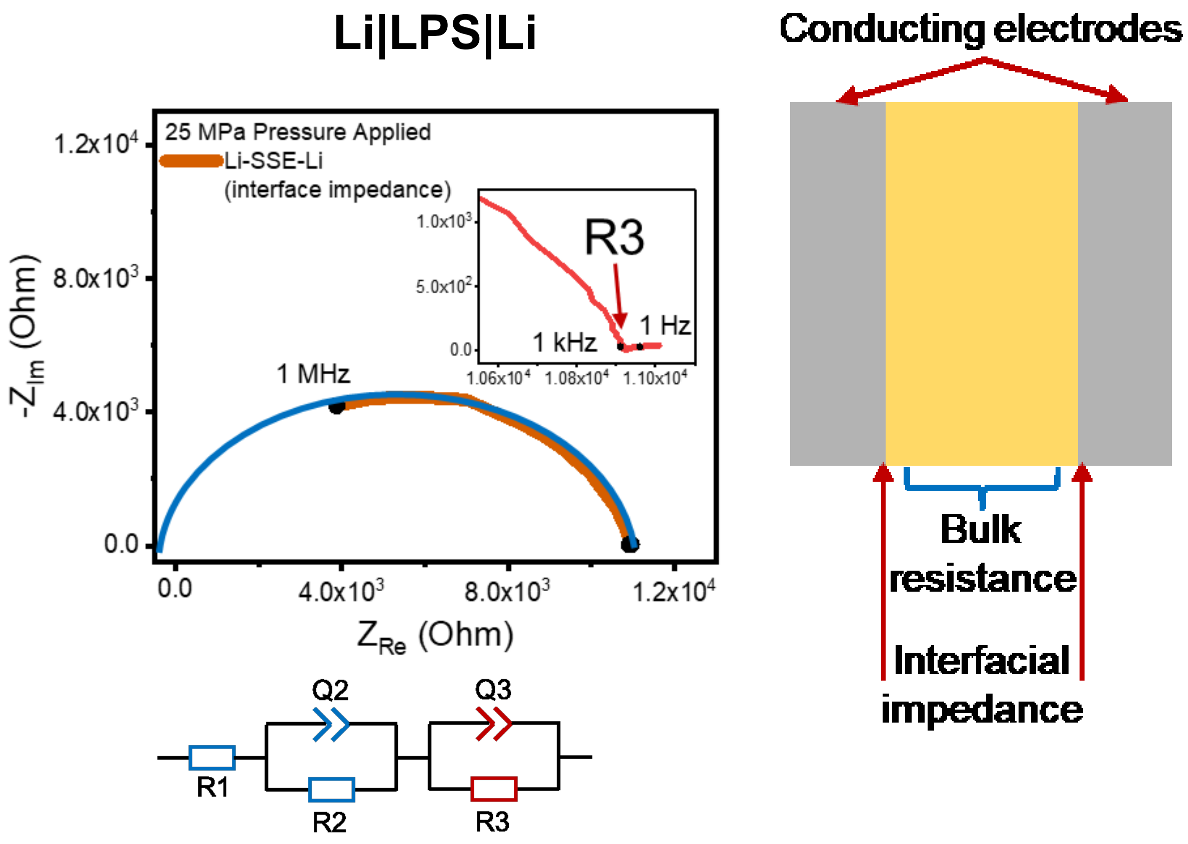
Fig. 1 (a) Design of the solid-state battery holder with a load cell to monitor the stack pressure applied to the battery during cycling and conductivity measurements. (b) For conductivity measurements and battery cycling, pellets are first prepared by applying uniaxial pressure as the fabrication pressure using a hydraulic press and are then cycled in the battery holder at the predetermined stack pressure.

Cell-Level Testing: EIS

- Ion-blocking vs. ion-conducting electrodes
  - Different characteristics to evaluate!

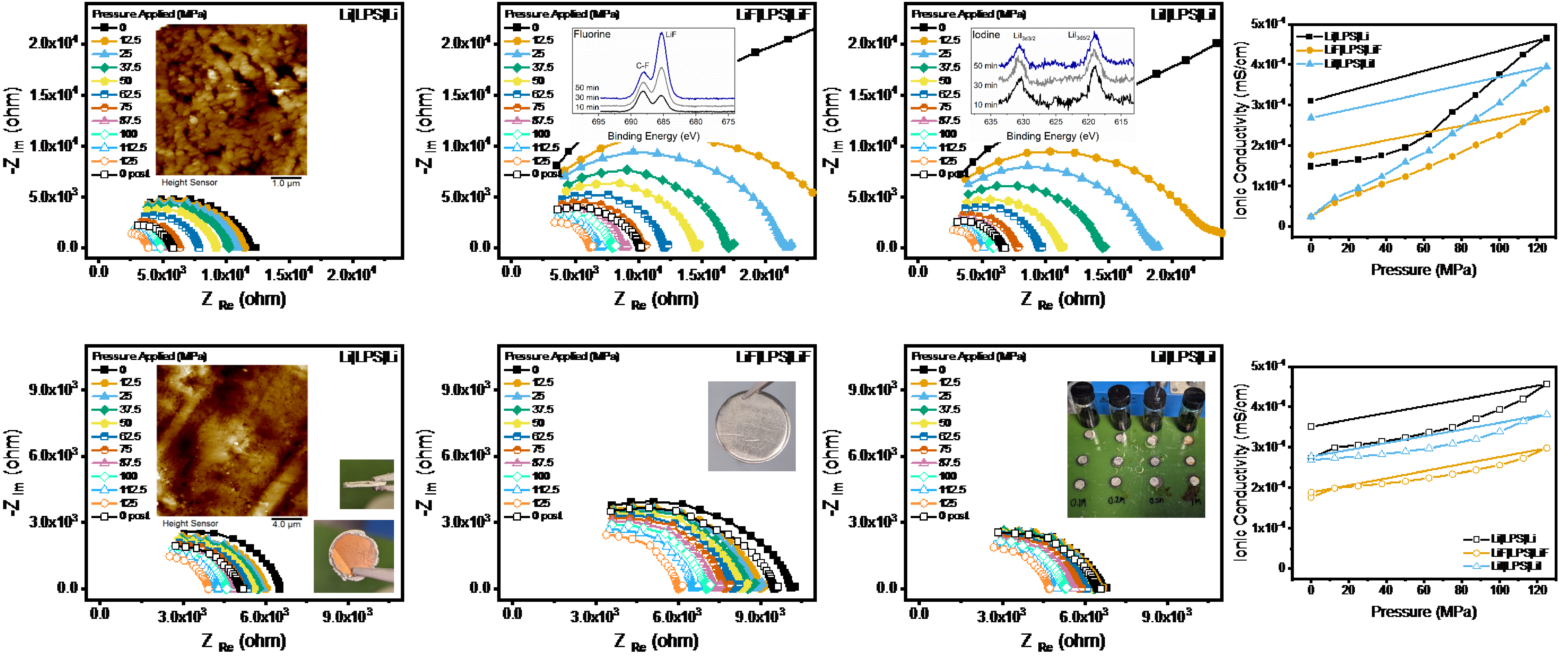


SSE bulk conductivity



Interfacial charge transfer

Cell-Level Testing: Artificial Coatings/SEIs



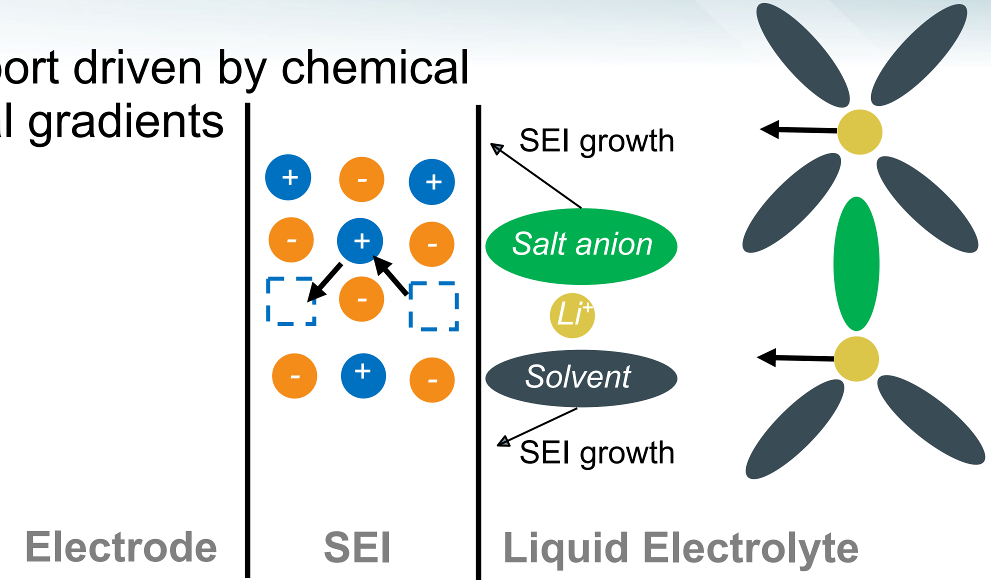
I wish to acknowledge the ancestral and unceded land of the Shoshone and Bannock peoples on which this research was conducted.

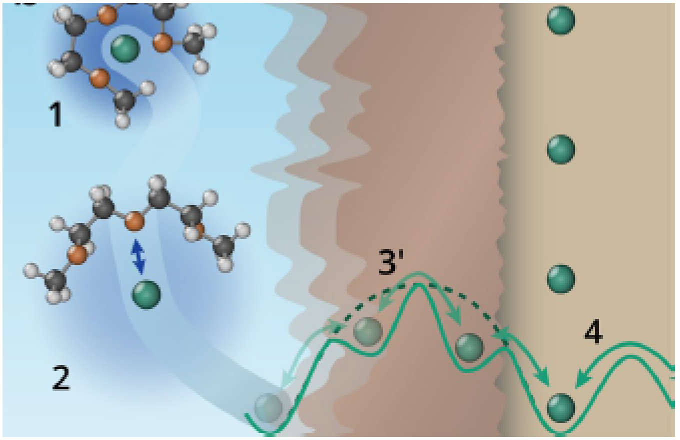
Other acknowledgments:

- LDRD funding under DOE Idaho Operations Office Contract DE-AC07-05ID14517
- The entire LDRD program office and support staff
- Coworkers (INL) Corey Pilgrim, Pete Barnes, Bor-Rong Chen, Bumjun Park, Boryann Liaw, Bin Li, Eric Dufek, Josh Gomez, Dong Ding, (Boise State) Paul Davis, Elton Graugnard, JD Hues, (CAES) Yu Lu, Jeremy Burgener

Questions?

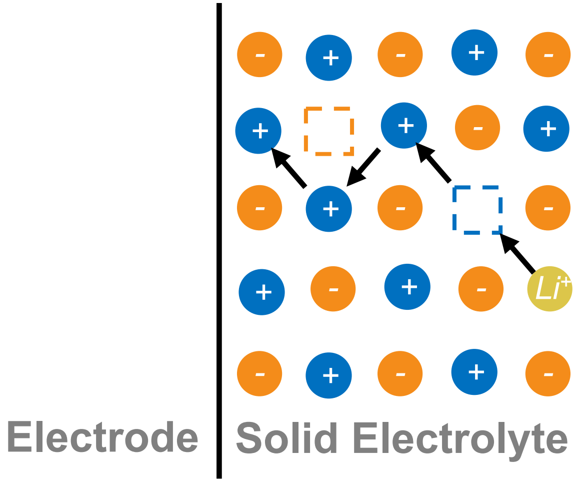
Liquid electrolytes – transport driven by chemical and electrochemical potential gradients



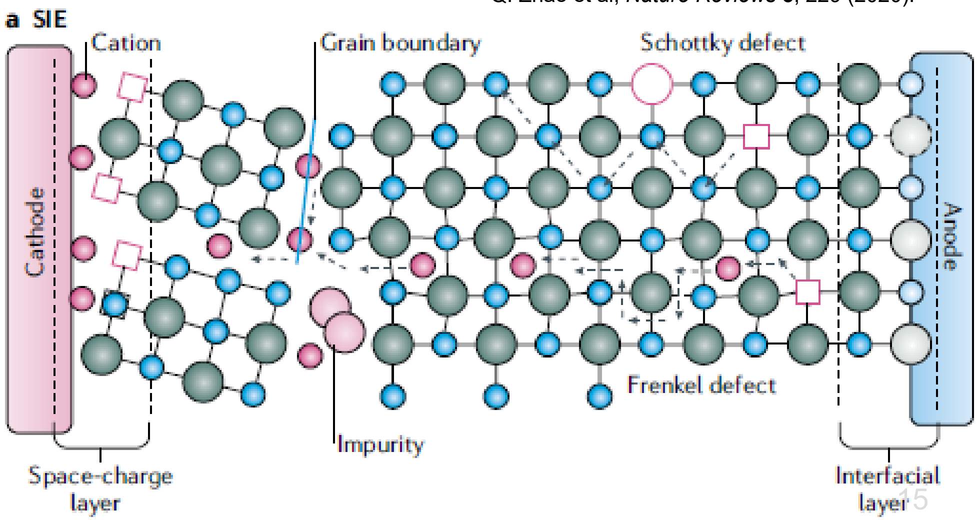


M. Weiss et al, *Electrochemical Energy Reviews* **3**, 221 (2020).

Solid electrolytes – transport driven by charge mobility and concentration

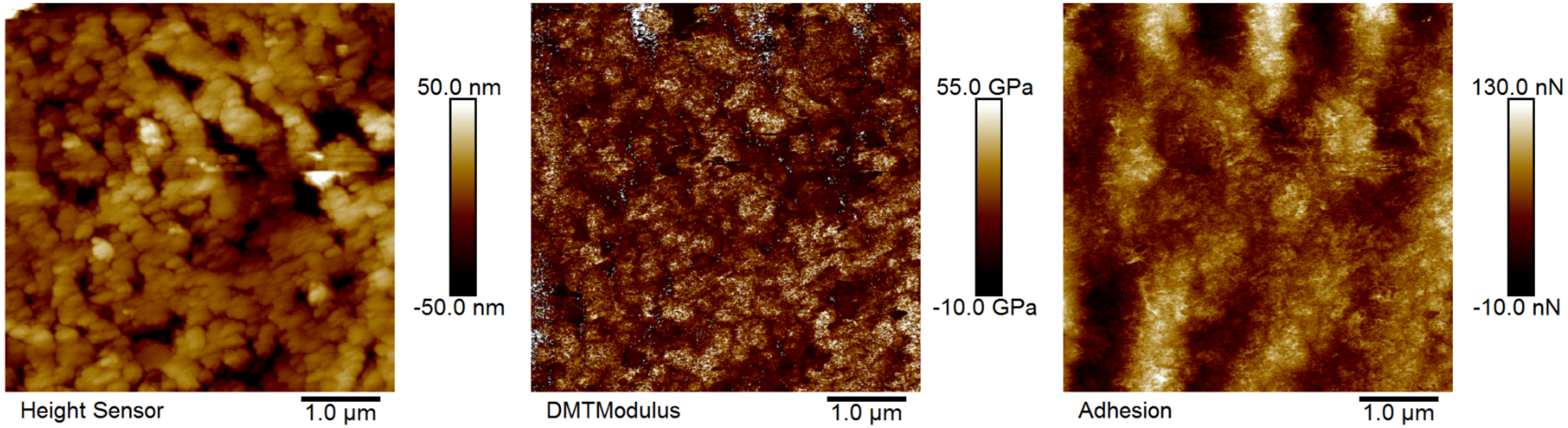


Q. Zhao et al, *Nature Reviews* **5**, 229 (2020).

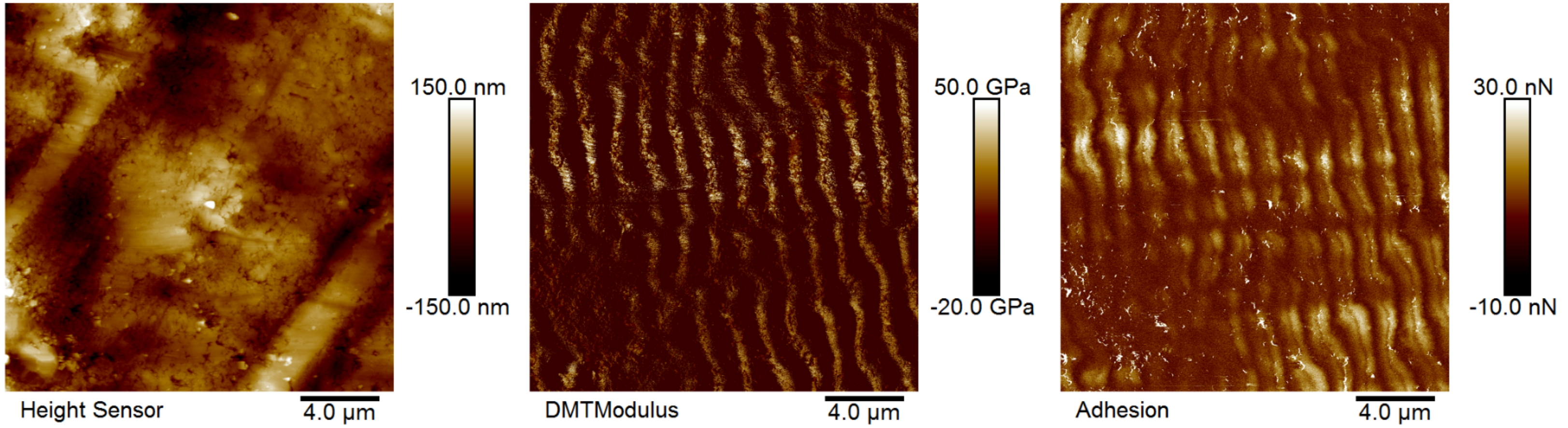


C.M. Efaw, Boise State University, (2021), Dissertation defense, doi: 10.12122/td/1912/boisestate.

Post pelletization



Post 125MPa load



Cycle Testing – Li|LPS|Li