



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

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Changing the World's Energy Future

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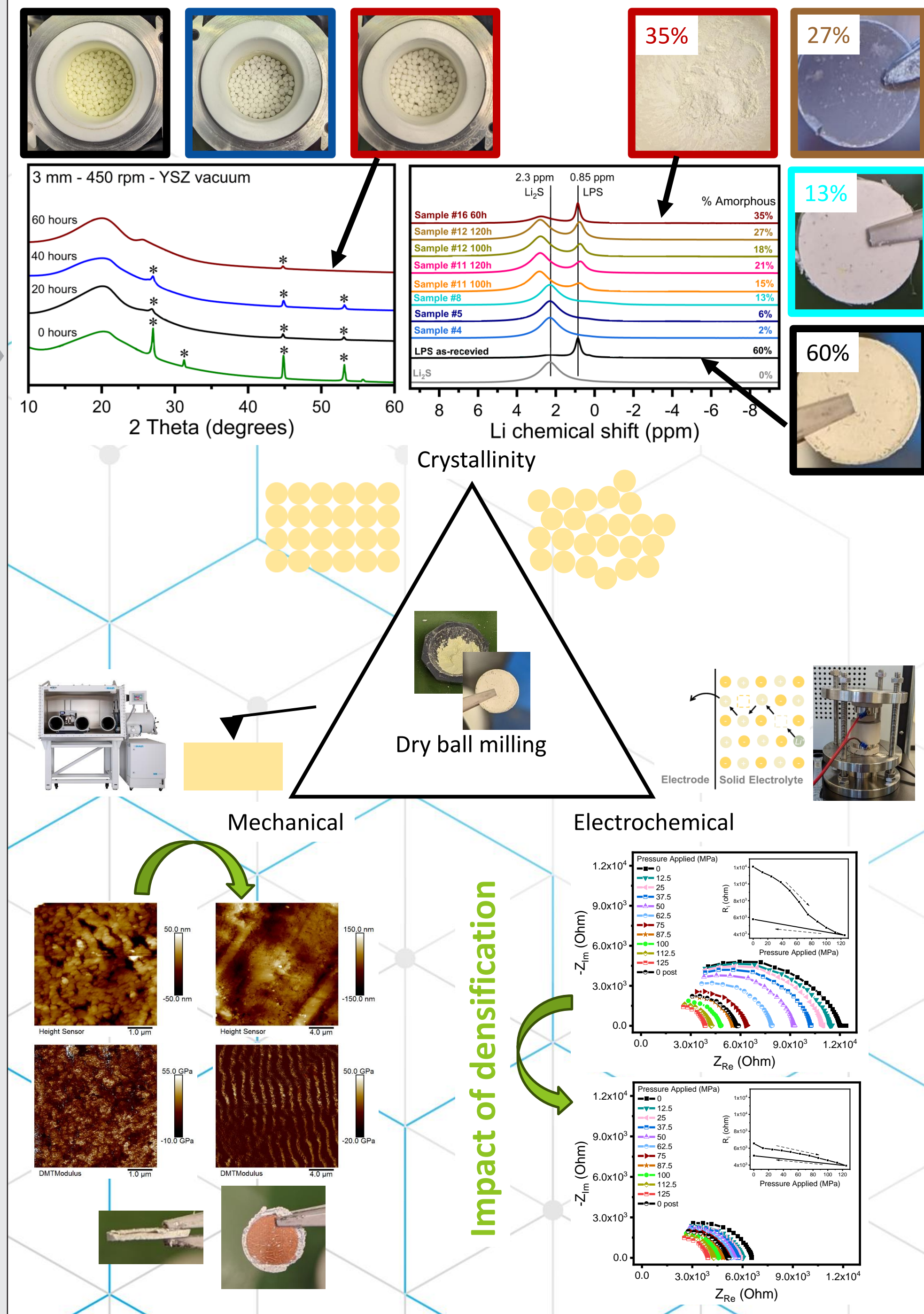
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Presenter:
Corey Efaw

BACKGROUND: Batteries are needed to support the decarbonization movement, especially in the transportation sector (16.2% of all GHG emissions).¹ Lithium metal, solid-state batteries, could address many of the barriers seen in traditional Li-ion, liquid battery chemistries. In this work, *sulfide-based solid-state electrolytes* are synthesized through *dry ball-milling* and examined through various forms of characterization, to better understand the impact of synthesis parameters on make-up and performance.



Literature is inconsistent to provide sufficient information on dry ball milling of solid-state electrolytes.

x - not documented in text			Milling Media						Grinding Jar			Milling Details							
DOI	Year	mol ratio U ₂ S:P ₂ S 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 ₂ S	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 ₂ S	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 ₂ S	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 ₂ S	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 ₂ S	5	ZrO ₂	3 mm	110	x	22	ZrO ₂	45	510	100	5 min ON, 15 min OFF	x	x	Amorphous below 75mol% Li ₂ S	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/acs.aem.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		

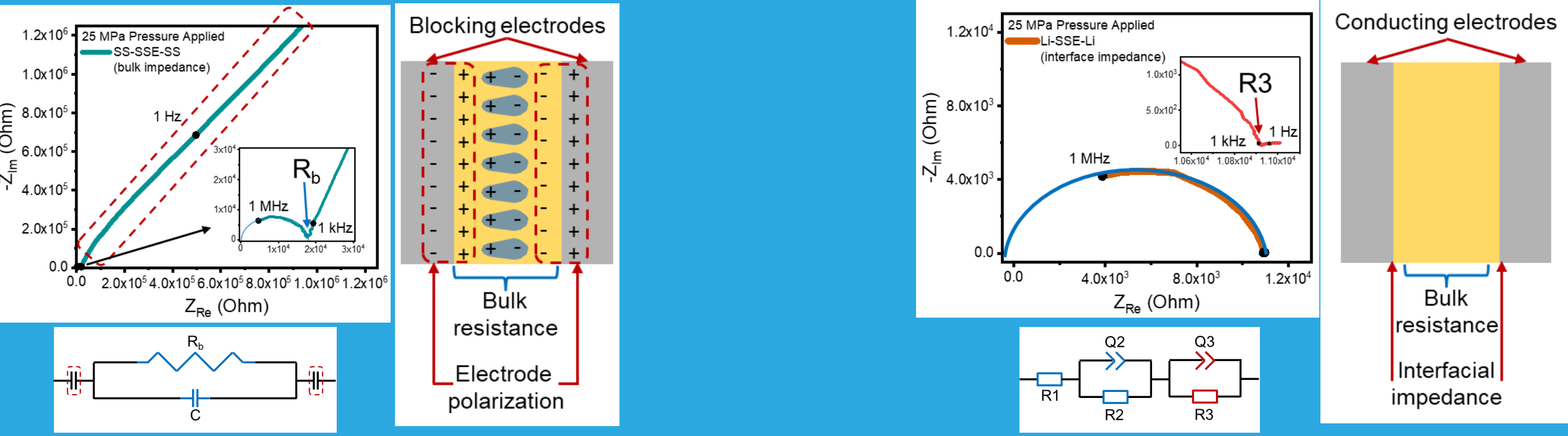
METHODS:

XRD & NMR – XRD provides a go/no-go for crystalline/amorphous presence. NMR is more quantitative.²

Pelletization – 4 metric ton loading done for multiple samples. As-received LPS resulted in lower density (~40±2%), in-house prepared LPS (highly crystalline) samples had much higher density upon pelletization (>60%).

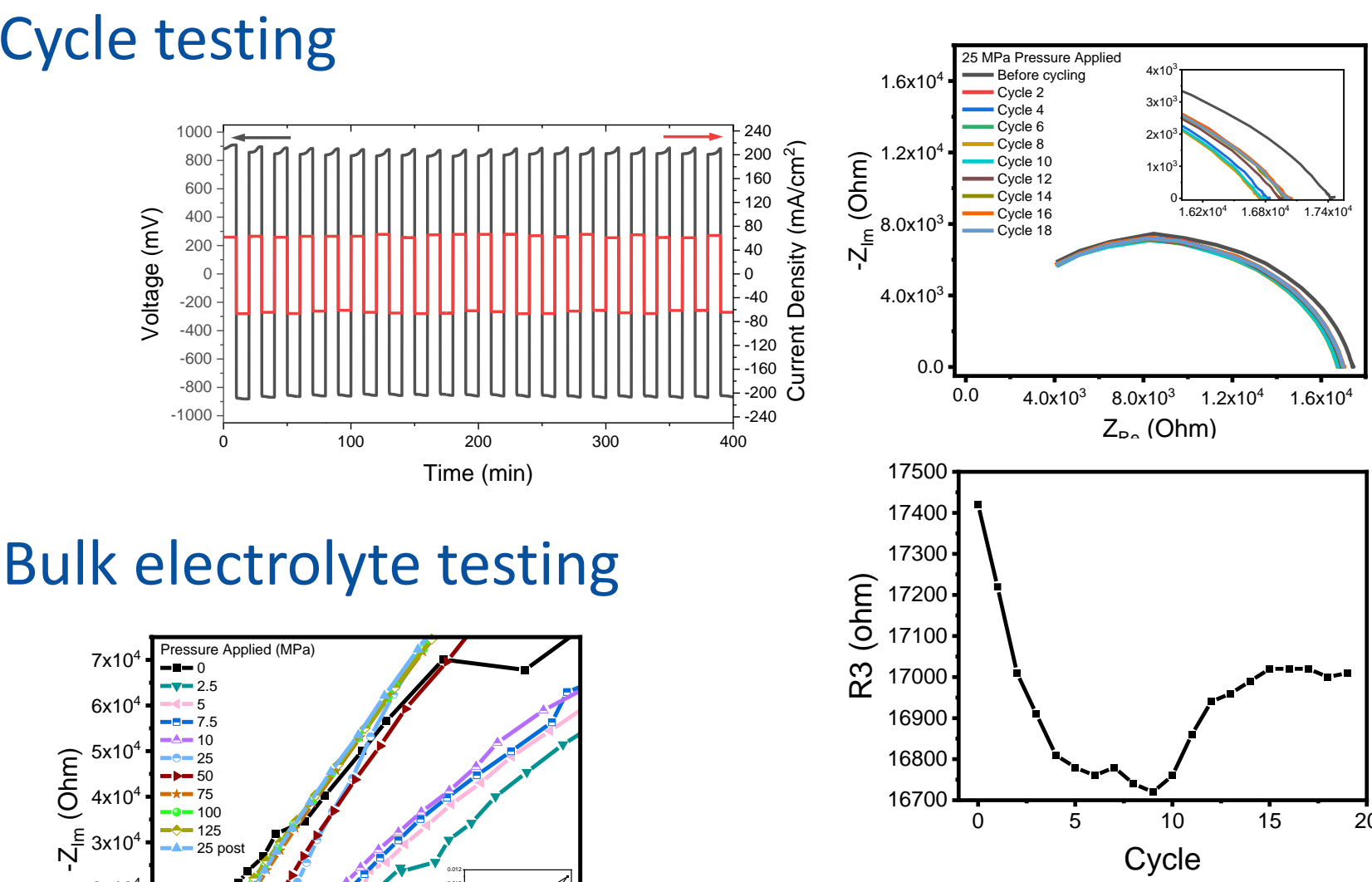
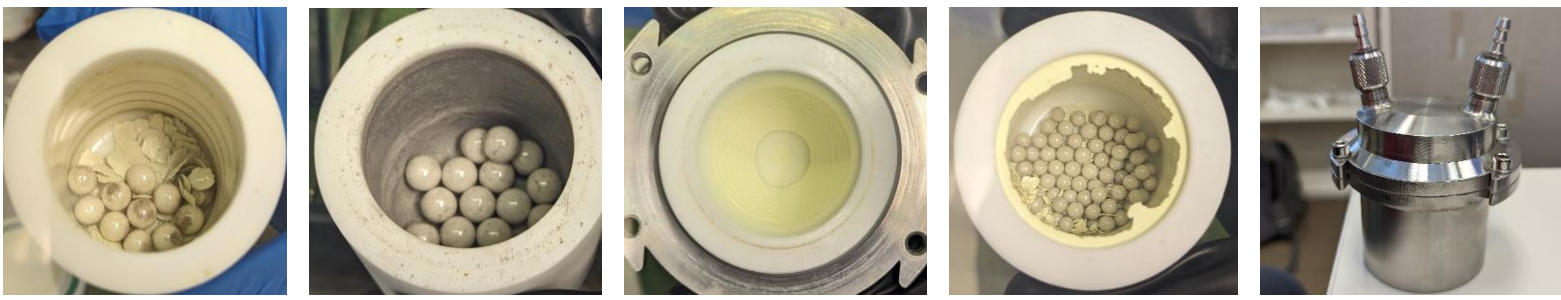
Mechanical testing (AFM – QNM) – Only as-received sample analyzed, both after pelletization and after testing at 1 metric ton load in a symmetric test with SS. Material density changed after operation at high pressure, but mechanical properties did not vary in range.

Electrochemical testing – Only as-received samples operated in the non-resistive regime. Electrochemical impedance spectroscopy (EIS) was used to measure SSE Bulk conductivity (**R_b**) with an ion-blocking electrodes (SS), while interfacial charge transfer (**R₃**) is characterized with ion-conducting electrodes (Li). Cycling was run in a constant-current design, within a ± 1V range. EIS was measured after each cycle. Artificial solid-electrolyte interphases (SEIs) were tested against pure Li to observe interfacial charge transfer.



OTHER FINDINGS:

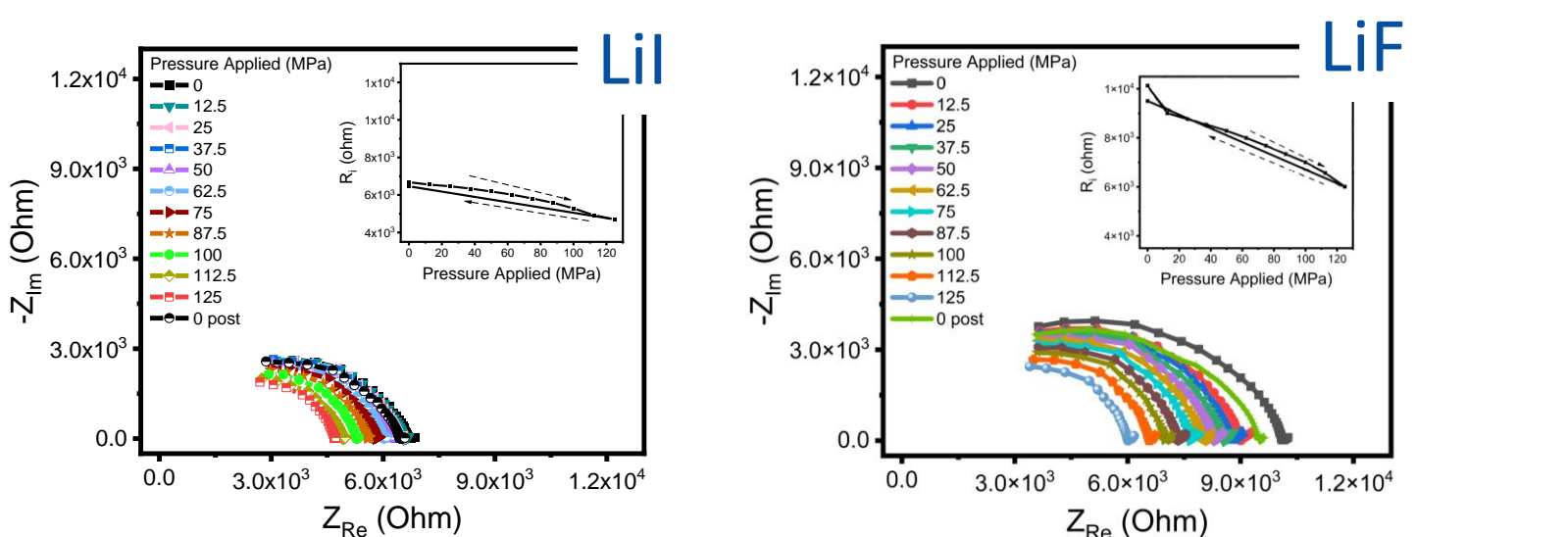
- Milling parameters to consider:
- **Milling rate**
 - 370-540 rpm shows no clear trends
 - **Time**
 - Extending time increases amorphous behavior
 - Extending time also increases “burn effect”
 - **Media**
 - Benefit to use same media as container (YSZ)
 - Size doesn’t reveal any trends...particle size TBD
 - Number of media has no trends
 - **Container**
 - Use of an isolation container is key to achieve higher amorphous content with less time milling
 - Small jar + large media = greater edge adhesion
 - **Cleaning**
 - DMF cleaning + ethanol/DI rinse = reduced adhesion to edges & less flakes
 - Hand milling improves uniform powder size



Bulk electrolyte testing



Artificial Solid-electrolyte interphase (SEI) testing



¹OurWorldInData.org
²Mirmira et al, doi: 10.1039/d1ta02754a

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