Solid-state electrolytes enabling beyond Li-ion cell chemistries

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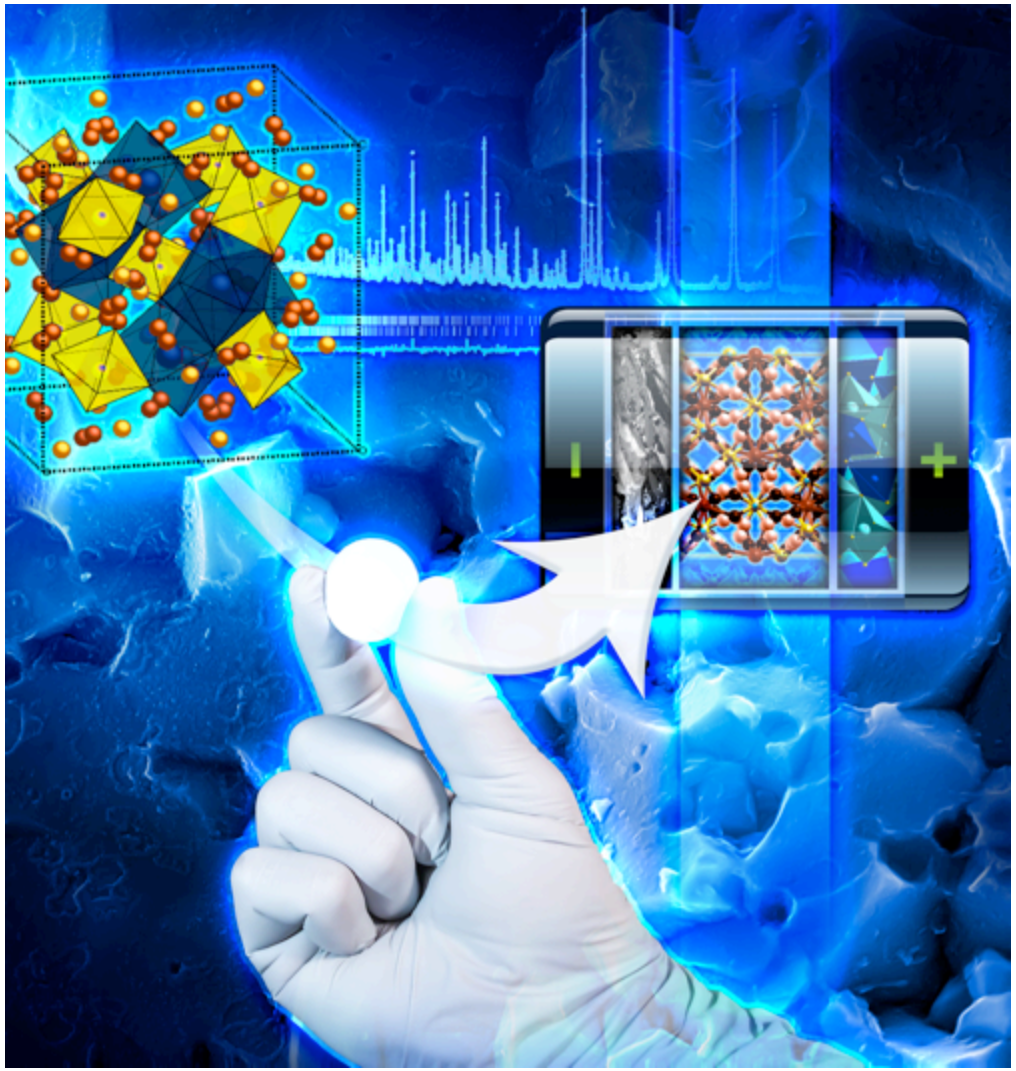
Outline

- Going *Beyond state-of-the-art Li-ion*
- Solid-state battery challenges
    1. Solid-electrolyte stability
    2. Li-Interface transport
    3. Li-Interface stability; short-circuiting
- Summary

Bulk-scale solid-state batteries



+) Could enable Li metal anodes
+) Enable > 5V cathodes
+) No organics to degrade
+) Could be fabricated in air
+) Distributed cell network i/o packs
+) Improved safety
+) Gets better with increasing temp

-) Low temperature performance?
-) Density ~1.8-5X greater than liquid

?) Interface stability & kinetics
?) Mechanical integrity during cycling
?) Large format cell manufacture

Solid-state benefits at the pack-level

1. Solid-state electrolytes could enable robust cell chemistries
2. Less management
3. Less peripheral mass, volume & cost:

Wh/kg
&
Wh/l

Climate Change Committee (2012) Final Report prepared by Element Energy Limited, Cambridge, UK .

Key solid electrolyte selection criteria

1. Fast-ion conductor: $\geq$ 2 x 10^{-4} S/cm at 298K

2. Large electrochemical stability window: 0 to $\geq$ 5V

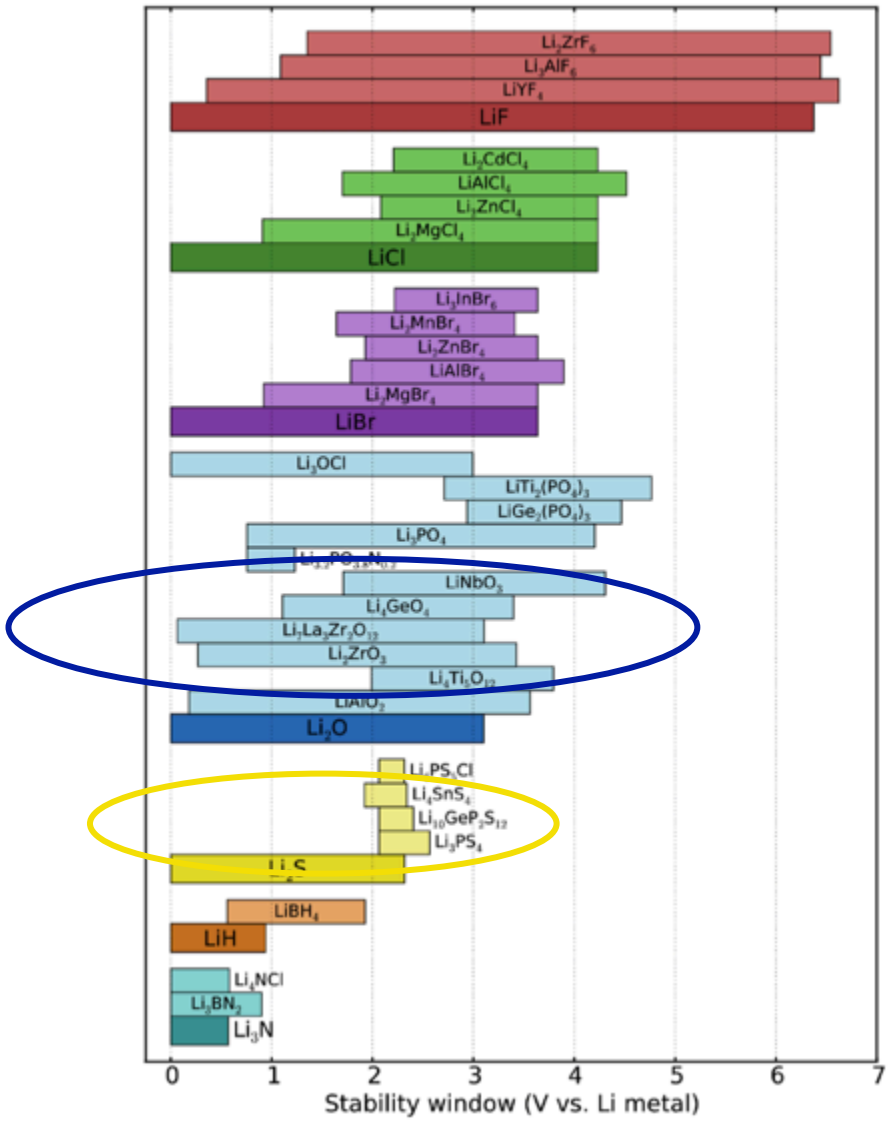
3. Negligible electronic conductivity & large bandgap

4. Interfacial impedance ~10 - 100 Ω cm^2 $\geq$

5. Critical current density $\geq$ 1 mA/cm^2

1. Electrochemical stability

Calculated thermodynamic stability

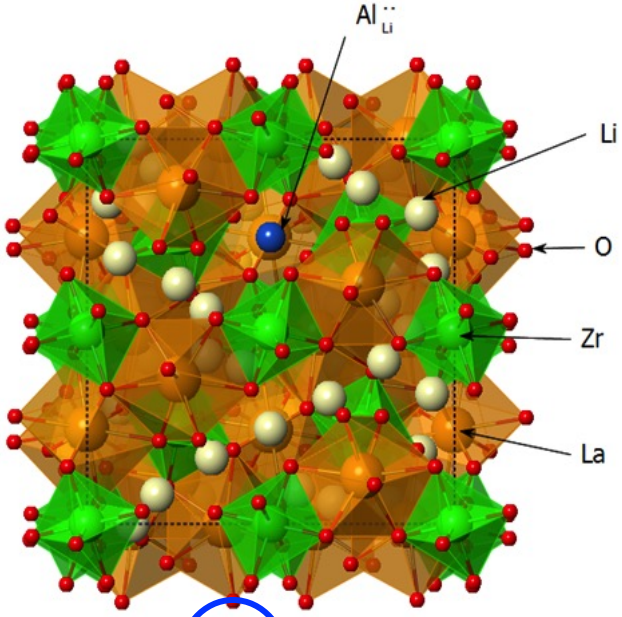


Williams et al. Cedar Group; *Chem Mater 2015*

Case study 1: Garnet-type oxide

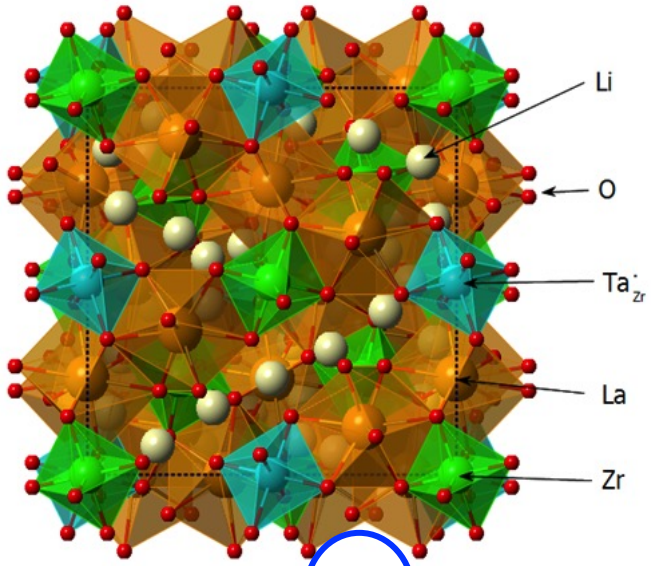
- Is the La-Zr-O framework stable?
- Are the cubic-phase stabilizing dopants stable?

$Li_7La_3Zr_2O_{12}$



$Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$

e.g. Al substitutes for Li

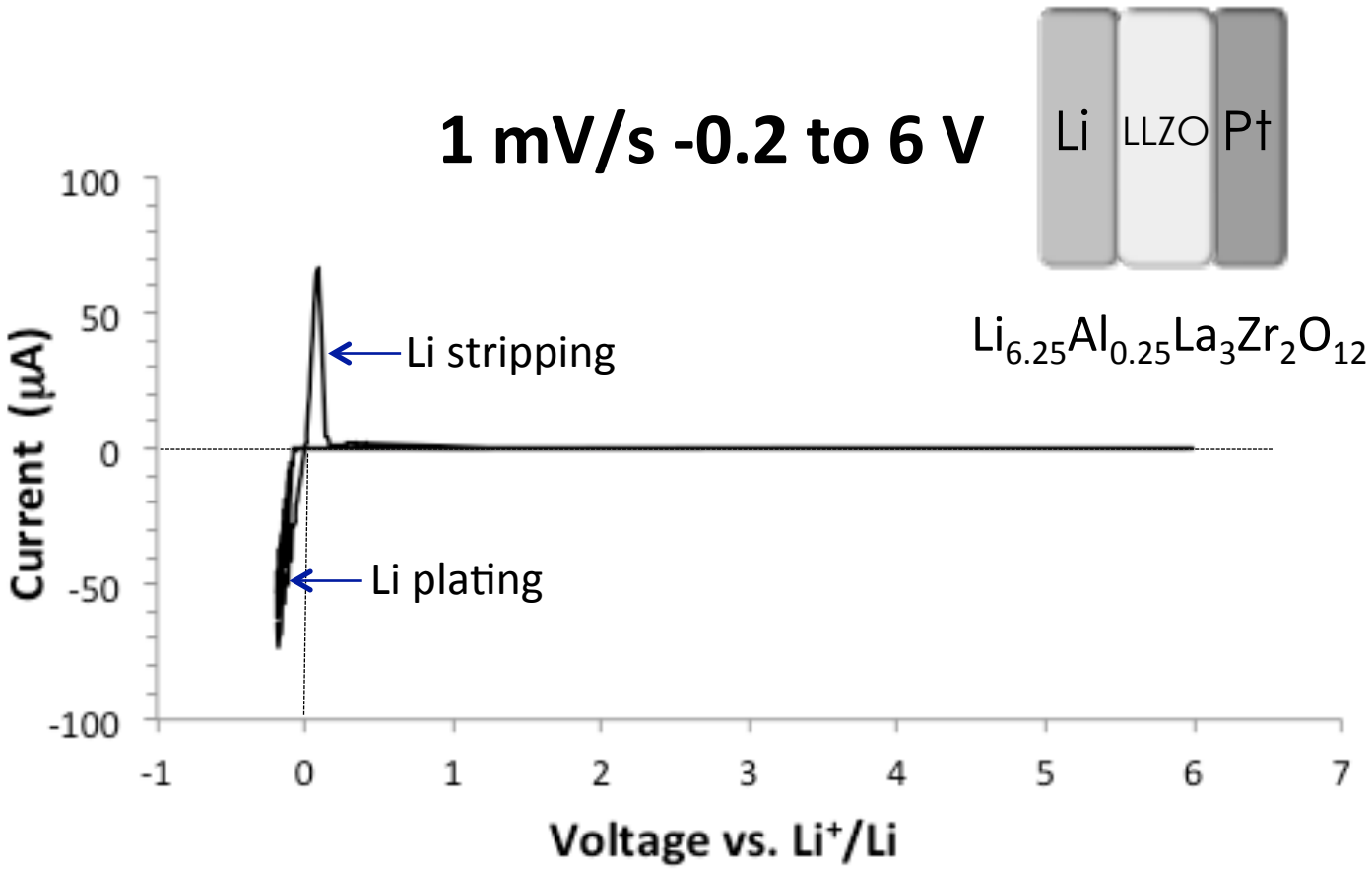


$Li_{6.5}La_3Zr_2Ta_{0.5}O_{12}$

e.g. Ta substitutes for Zr

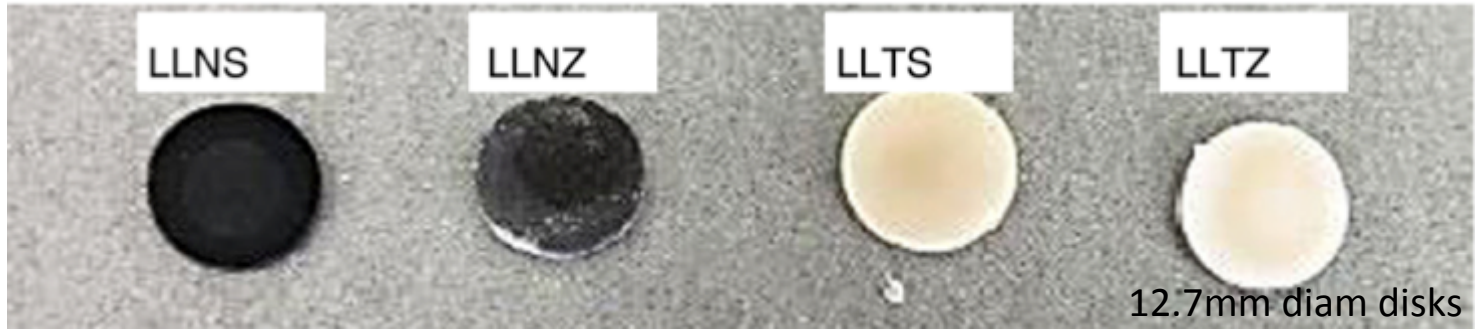
Yu et al. Chem. Mater., 2016, *28* (1), 197–206

Cyclic voltammetry (typical)

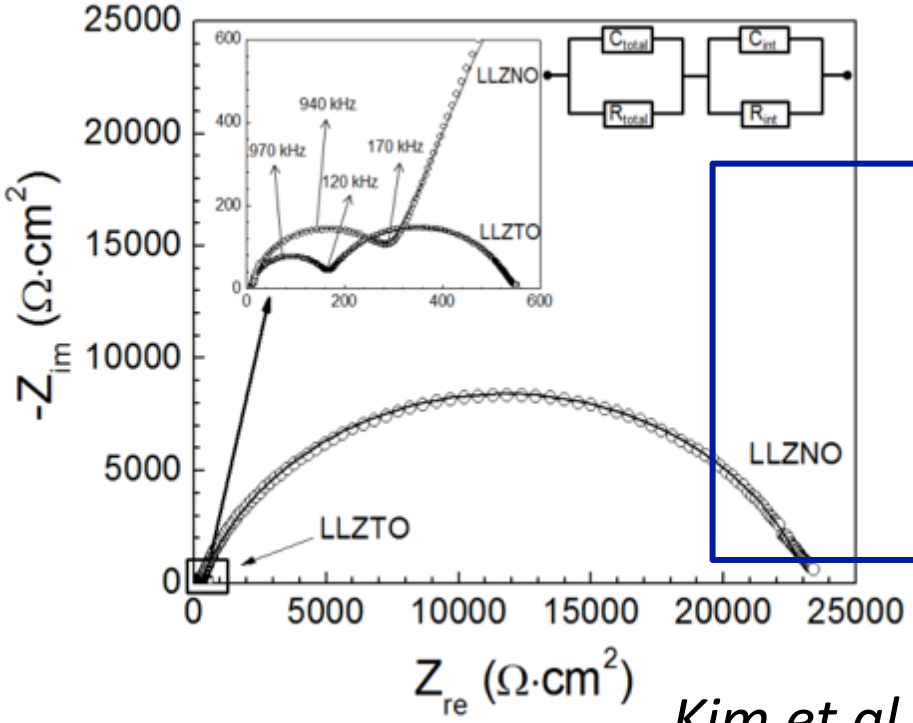


❖Cyclic voltammetry is a preliminary check, but need static tests and precision.

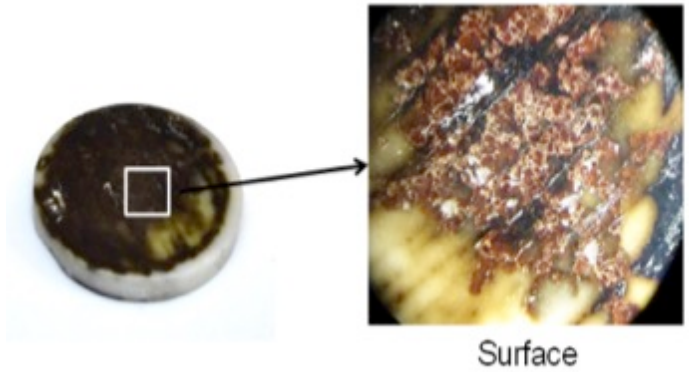
Physical contact with Li: Nb & Ta in LLZO

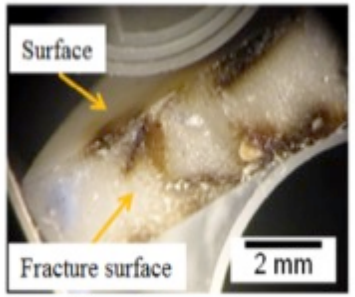


H. Nemori et al. / Solid State Ionics 282 (2015) 7-12



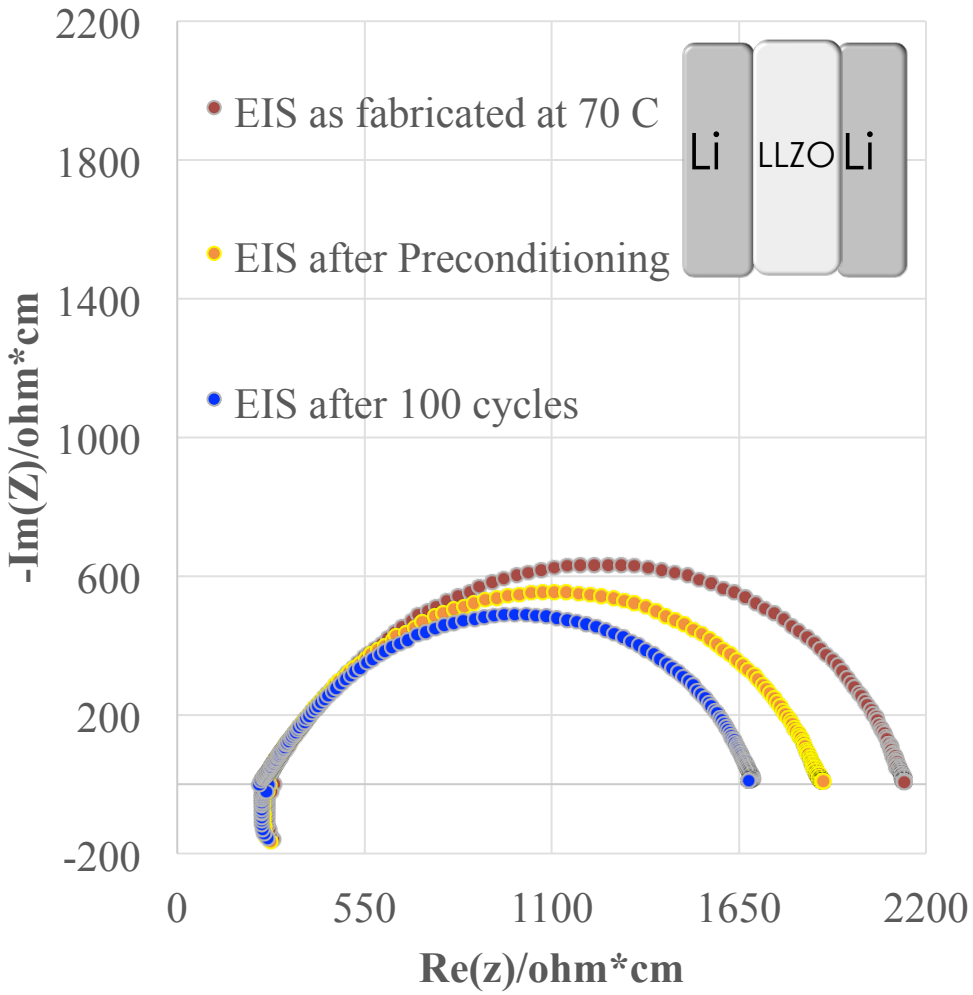
LLZNO



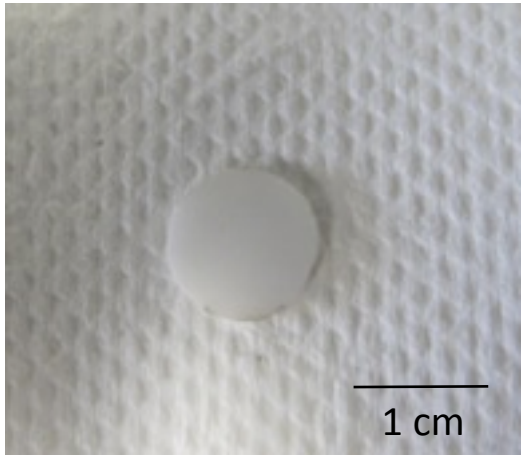


Kim et al. Frontiers in Energy (2016)

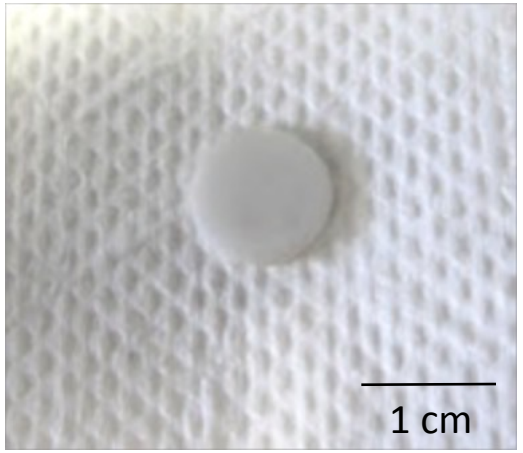
Cycling Li-[$Li_{6.28}La_3Zr_2Al_{0.24}O_{12}$]-Li cells



Li plating side

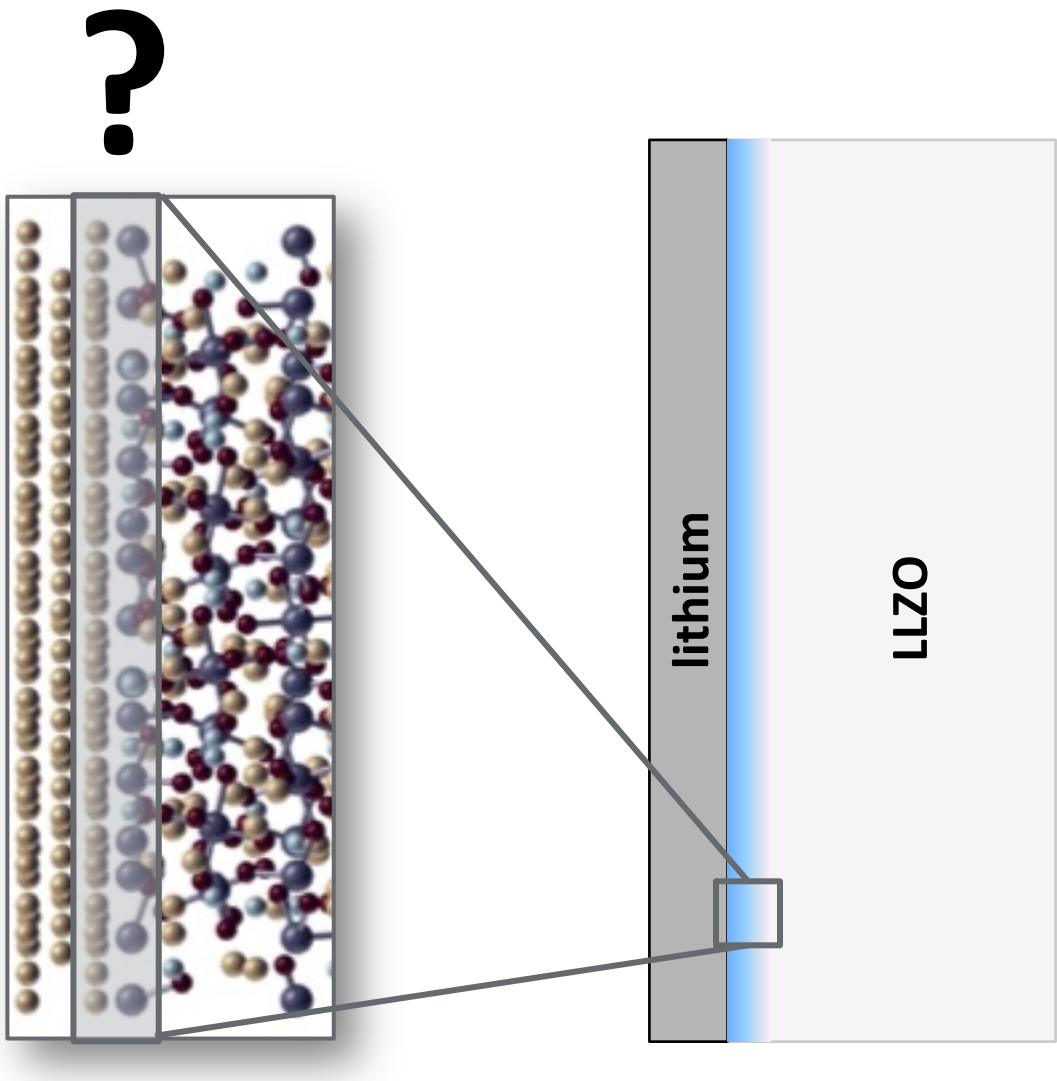


Li stripping side

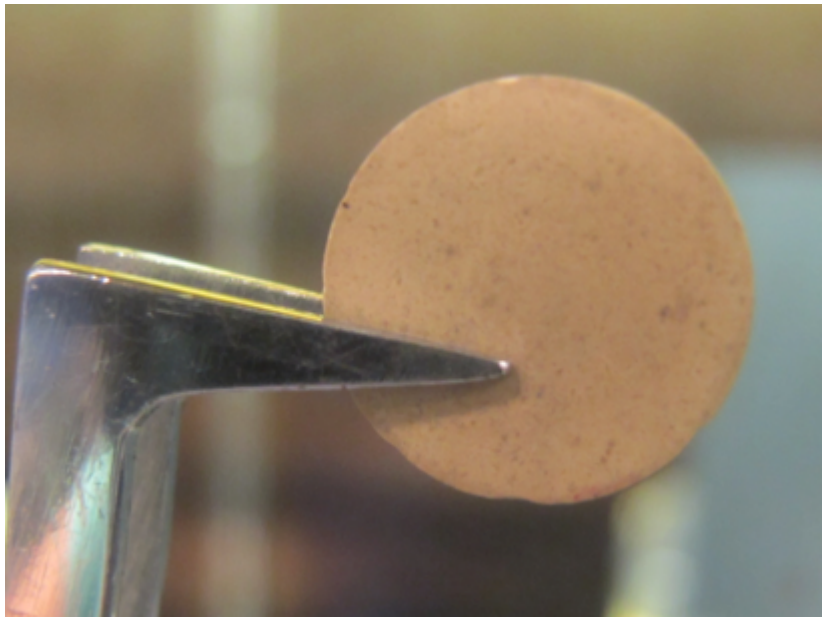


❖ No obvious evidence of instability

Li / LLZO / Solid-state Sulfur-based cathode


?
lithium
LLZO

Case study 2: Li-P-S glass ceramic



Li-P-S glass ceramic membrane: 75 Li_2S – 25 P_2S_5

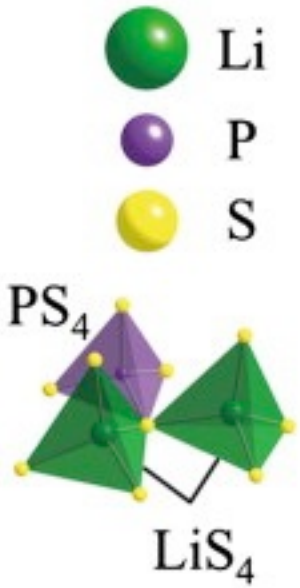


Image from Homma *et al.* (Kanno Group)
Solid State Ionics 2011

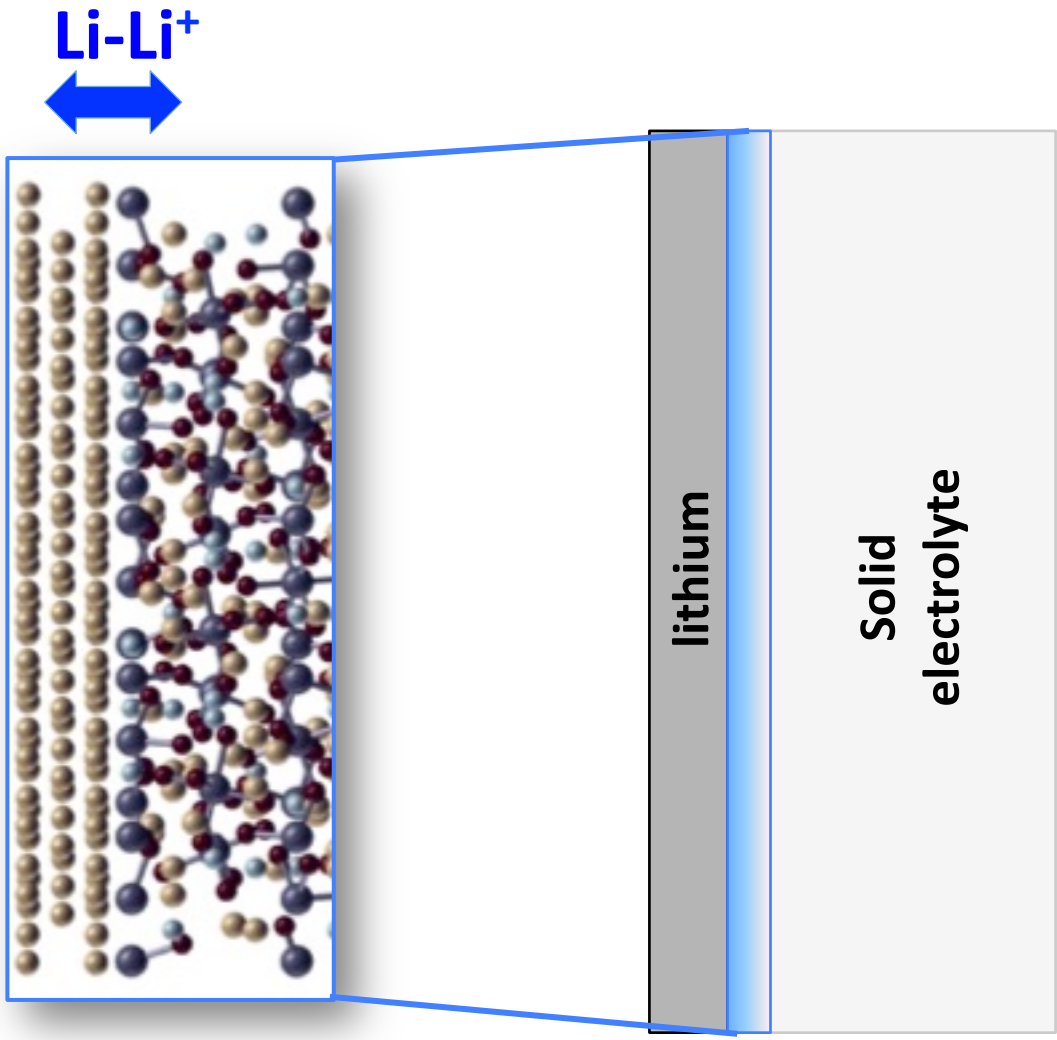
R. Garcia & J. Sakamoto (UM)
F.Mizuno, T. Arthur, and R. Zhang (Toyota)

1. Electrochemical stability (brief summary)

- Cyclic voltammetry is not sufficient; chronoamperometry is more precise and representative
- Surface analysis is tricky, but necessary to characterize stability
- Need to consider electrochemical and electronic stability
  - Thermodynamics predicts phase stability – electronic band gap helps predict how fast decomposition can occur

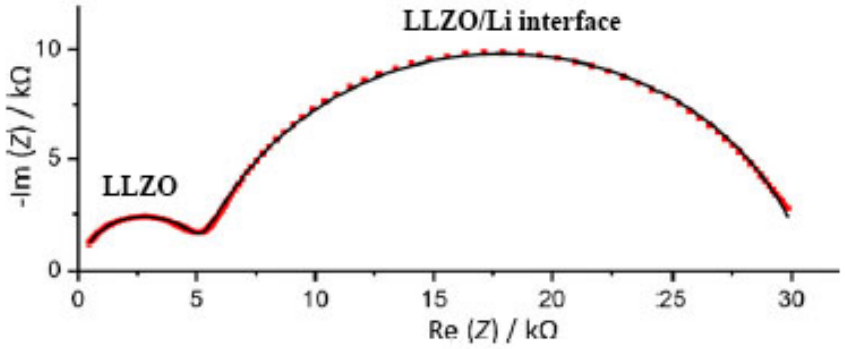
2. Interface kinetics (static)

Li-solid electrolyte interface kinetics



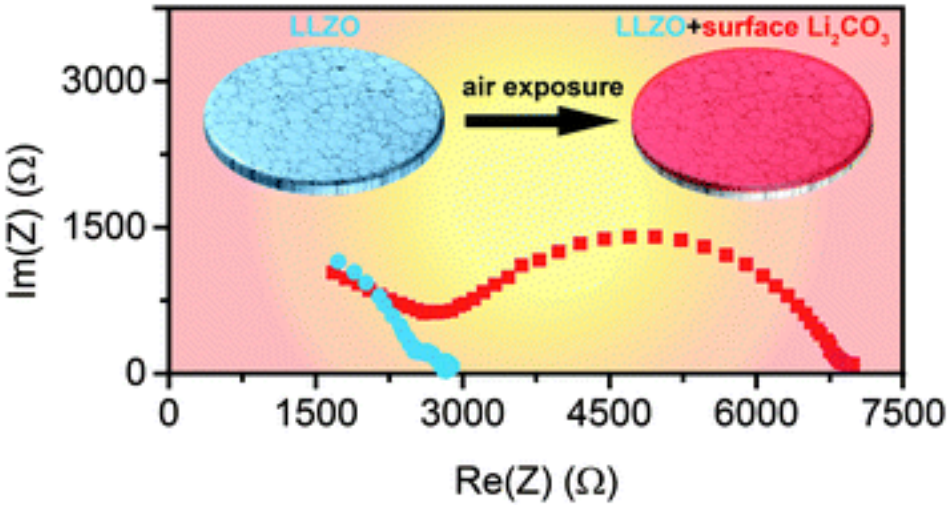
Need to keep surfaces clean

Large interface resistance?

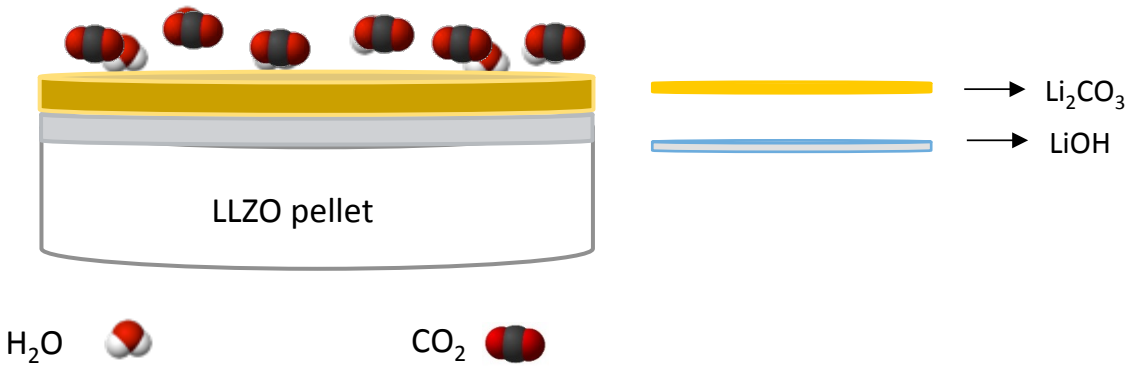


H. Buschmann, *et al.*, J. Power Sources 206, 236 (2012).

Artifacts from air exposure?



L. Cheng, *et al.*, Phys. Chem. Chem. Phys. 16, 18294 (2014).



❖ LLZO reacts with air to form LiOH and Li_2CO_3

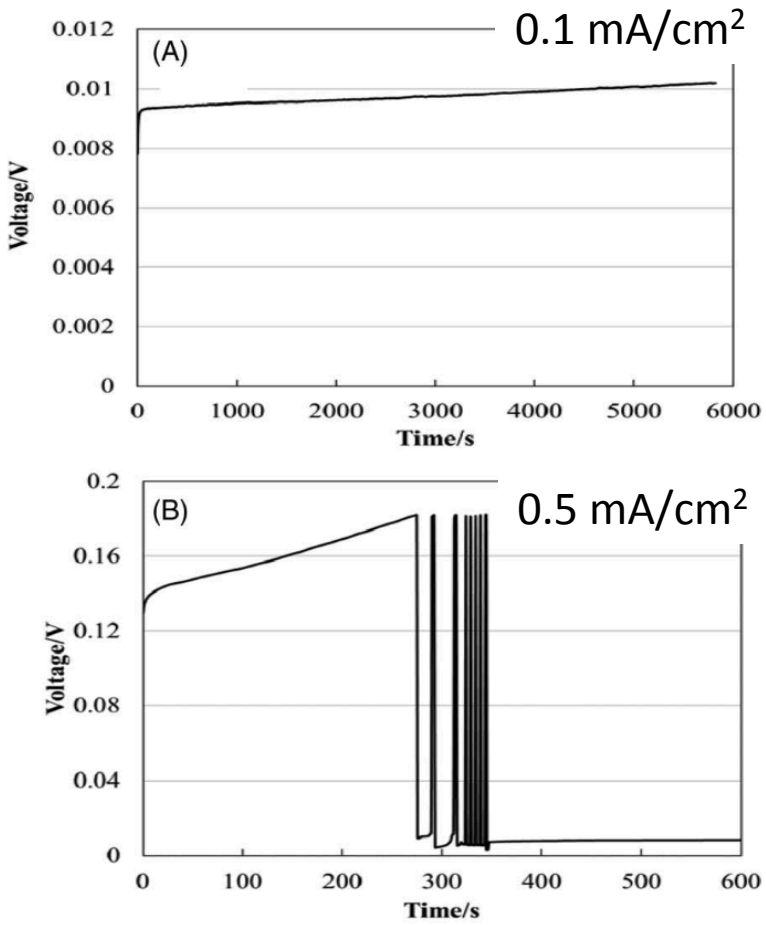
2. Interface kinetics (brief summary)

- Oxide electrolyte processed in air; must not assume surfaces are clean
- LPS glass ceramic electrolyte may form beneficial SEI
- Both oxides and sulfides show reasonably low impedance when paired with metallic Li; this is a significant achievement.

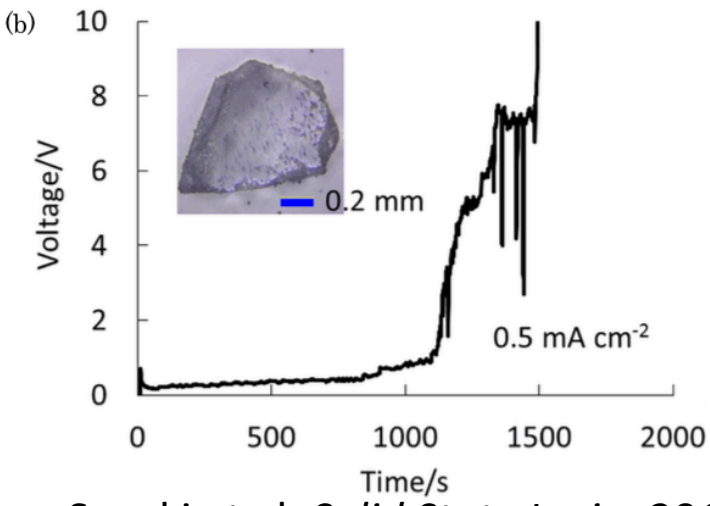
3. Interface stability (dynamic)

Short-circuiting in Li/LLZO/Li cells

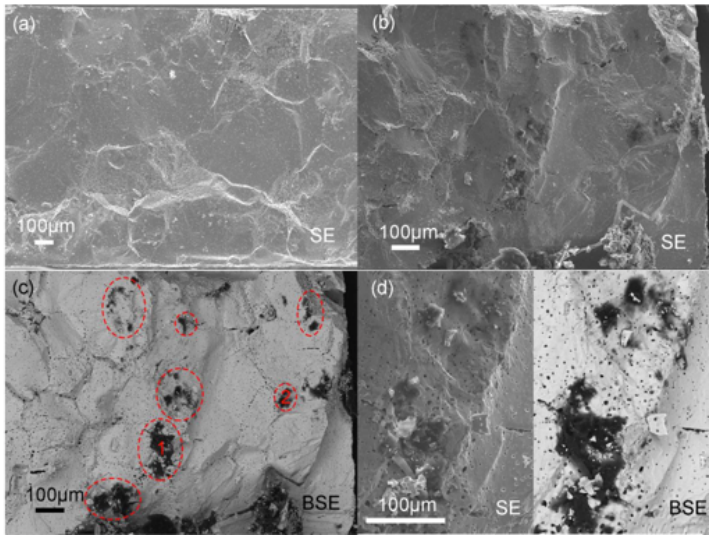
Li/LLZ/Li cells



Ishiguro et al. (Imanishi Group) *J. Electrochem Soc.* 2013

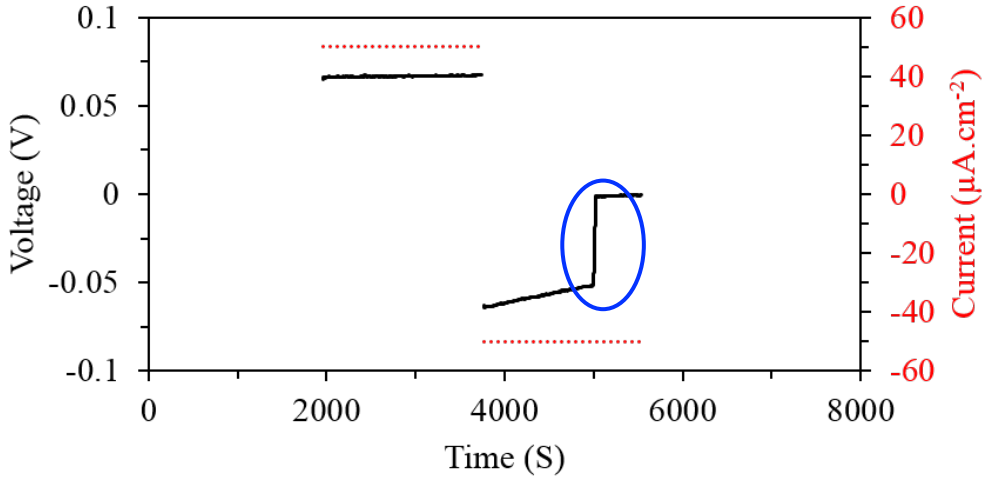


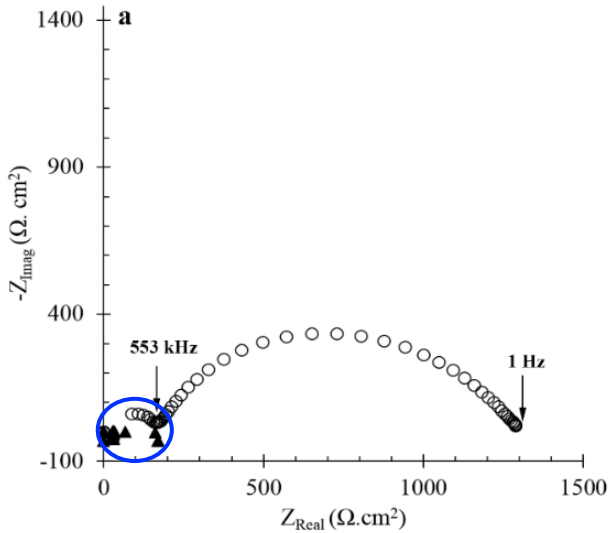
Suzuki et al. *Solid State Ionics* 2015

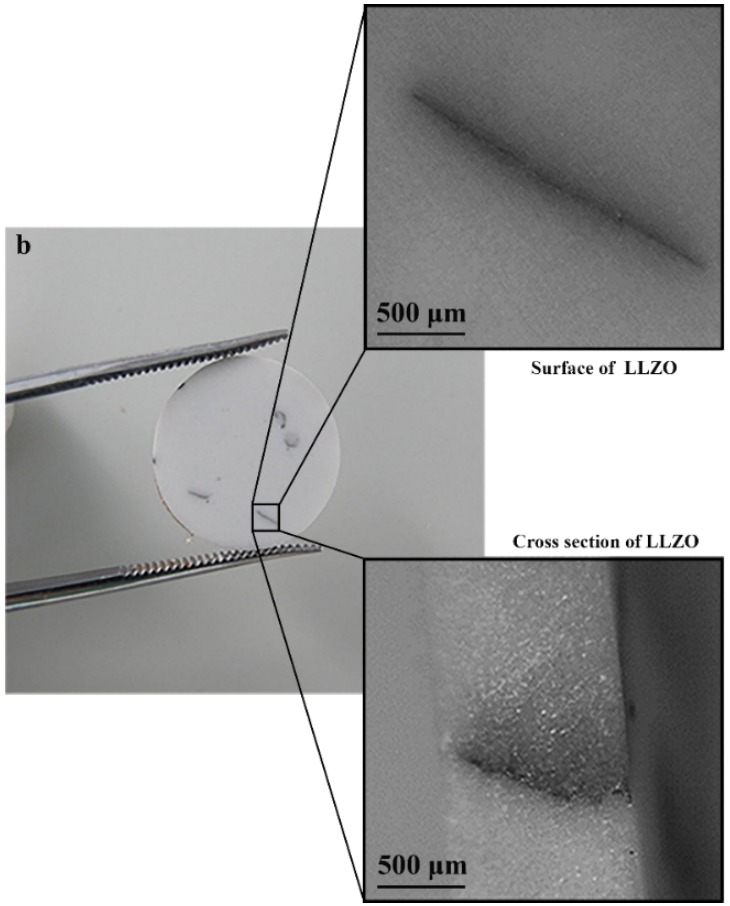


Ren et al. (Nan Group) *Electrochem. Comm*. 2015

Critical Current Density (CCD) at 30 °C







Sharafi, et al. *J. Power Sources* 2016

- At room temperature, CCD (0.05 mA/cm^2) identified as a deviation from Ohmic behavior and a dramatic drop in cell potential.

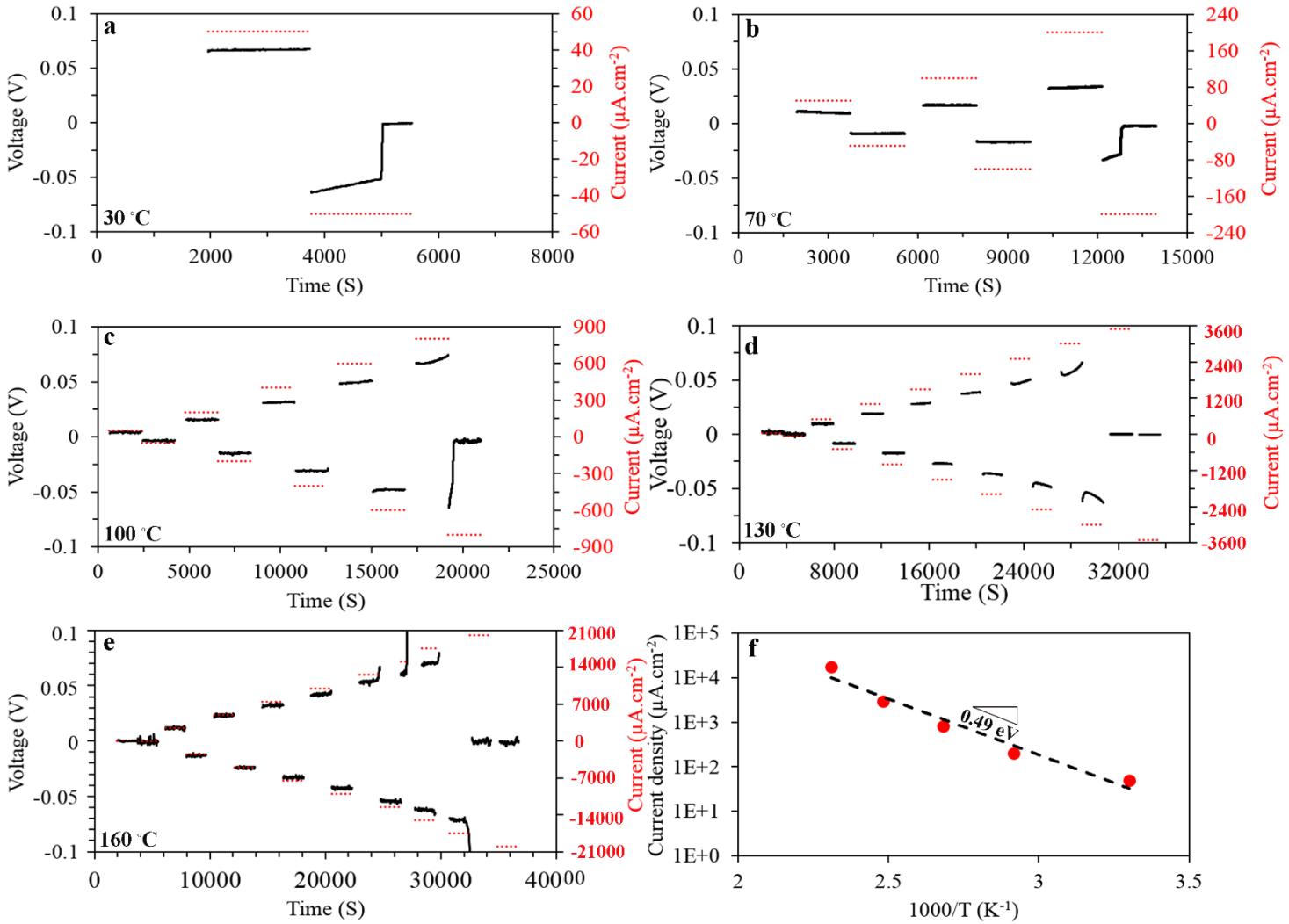
Correlation between $R_{Li\text{-}LLZO}$ and CCD: 30 to 160 °C

1. CCD increased with increasing temp
2. At 160 °C, CCD = 20 mA/cm²

R_{bulk} & $R_{grain\ boundary}$ ↓ as Temp ↑

*$i_{critical} = A/\eta l$

A = mater. elastic & fracture properties
η = viscosity of the solid metal anode
l = crack length



Sharafi, et al. *J. Power Sources* 2016

*Virkar, et al. *Proc.Fast Ion Trans. in Solids* 1979

Li filament short-circuiting (brief summary)

- How big of a problem is this?
- Critical current density of ~ 0.2 mA/cm^2
- Charging a 2 mAh/cm^2 cell takes <u>10 h</u> for 100% DOD
- Currently, these cells are un-optimized/un-engineered
- Rome wasn't built in a day

Summary

- Benefits of Solid-State are clear
- A couple of SSE are promising
- SSE could enable metallic Li
- Discussed three key challenges:
  1. Interface stability – SEI formation?
  2. Interface transport – Solid Li anode kinetics are promising – need to keep interfaces clean
  3. Stability during charging – filaments form when charging at high rates
- Still no obvious show stoppers, but we need to try to find them and address them