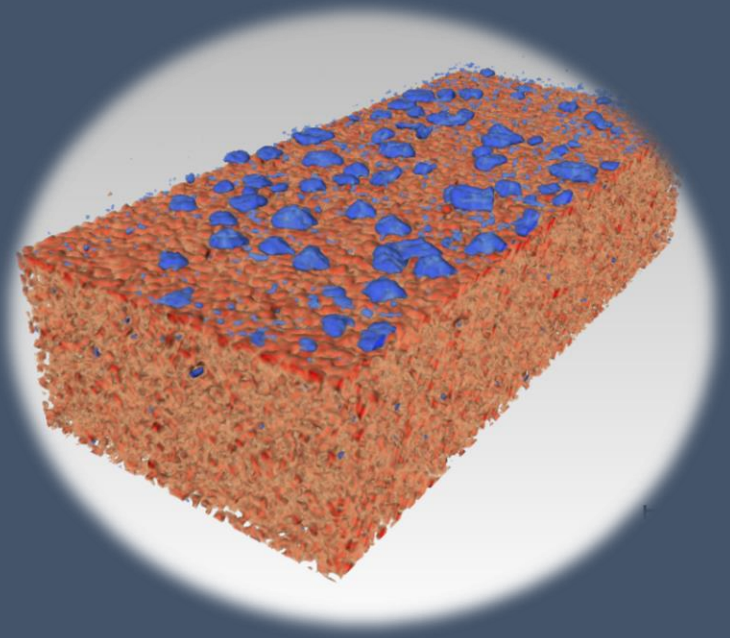
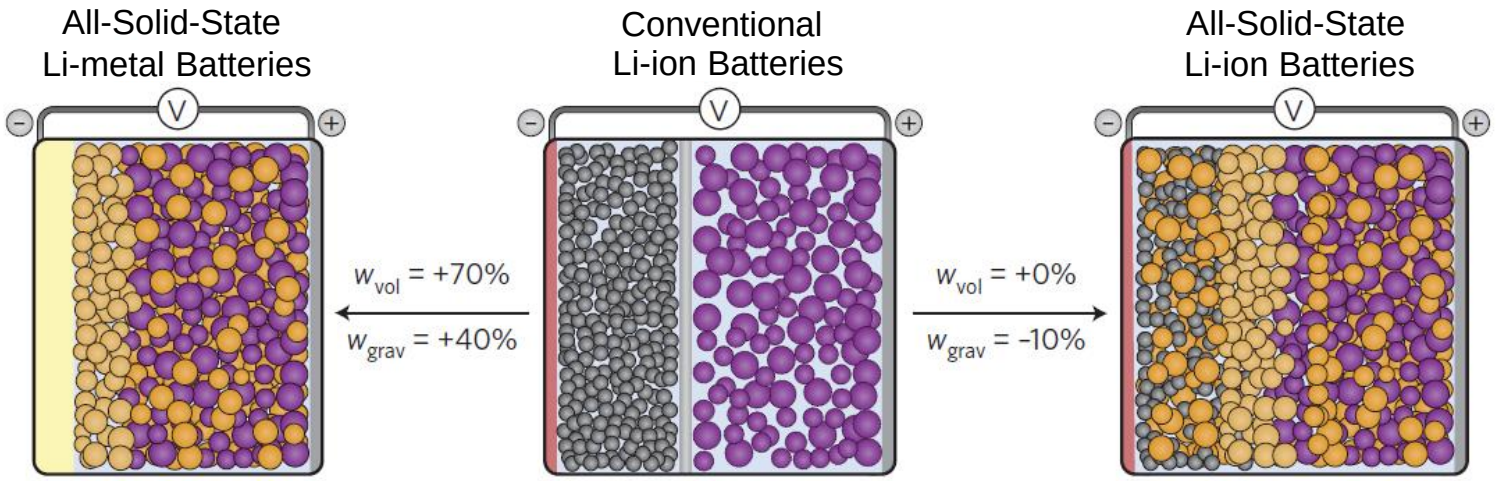
Solid State Batteries
The role of Li metal voids in cell failure

Dominic Spencer Jolly
University of Oxford



THE ALL SOLID STATE LITHIUM BATTERY

from liquid to solid electrolytes



W_{vol} and W_{grav} = **Volumetric and Gravimetric energy densities, respectively**

Zeier, W. G. & Janek, *Nat. Energy* **1,** 1–4 (2016)

Advantages:

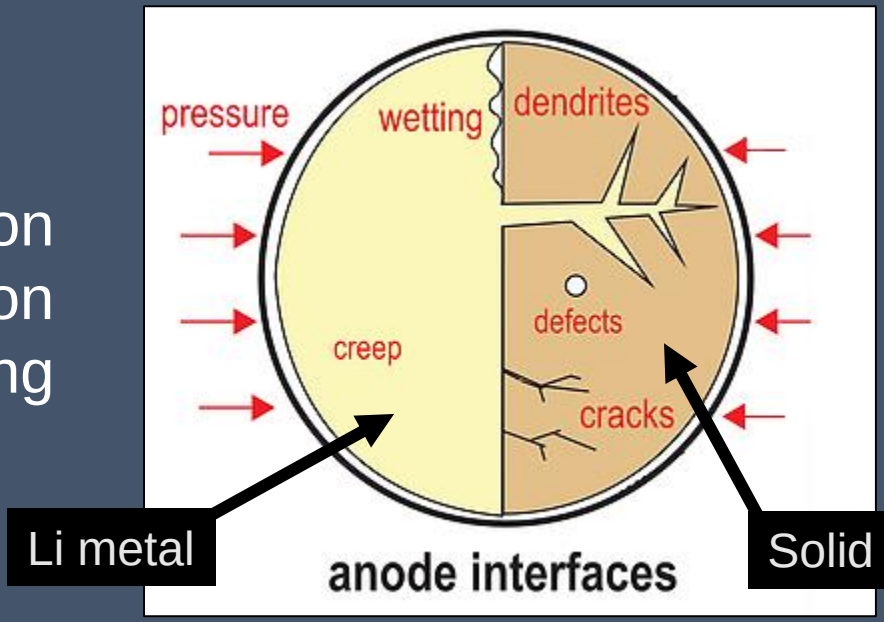
- **Safety – no flammable organic liquid electrolyte**
- **Enable use of Li metal anode - higher energy density**
- **Longer life**
- **Faster charge/discharge**

Energy Density	Current Li-ion	Projected ASSBs
Gravimetric (Wh/kg)	250	500
Volumetric (Wh/L)	700	1300

Challenges of the lithium metal anode/solid-electrolyte interface

Charge

Void formation occurs on stripping

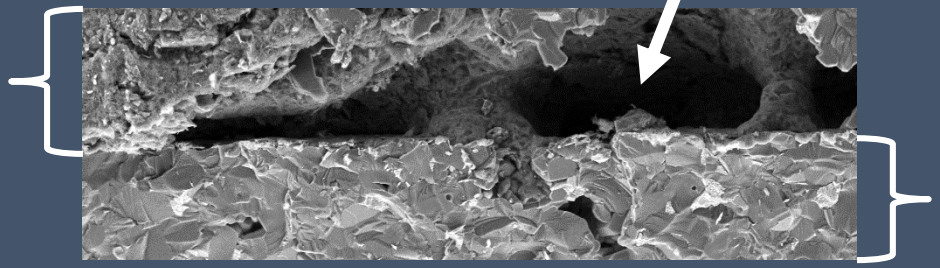


Discharge

Dendrite formation occurs on plating even if ceramic > 95% dense

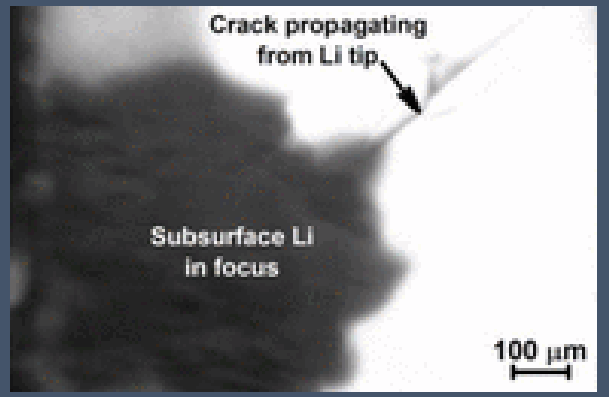
Metal Anode

Interfacial void



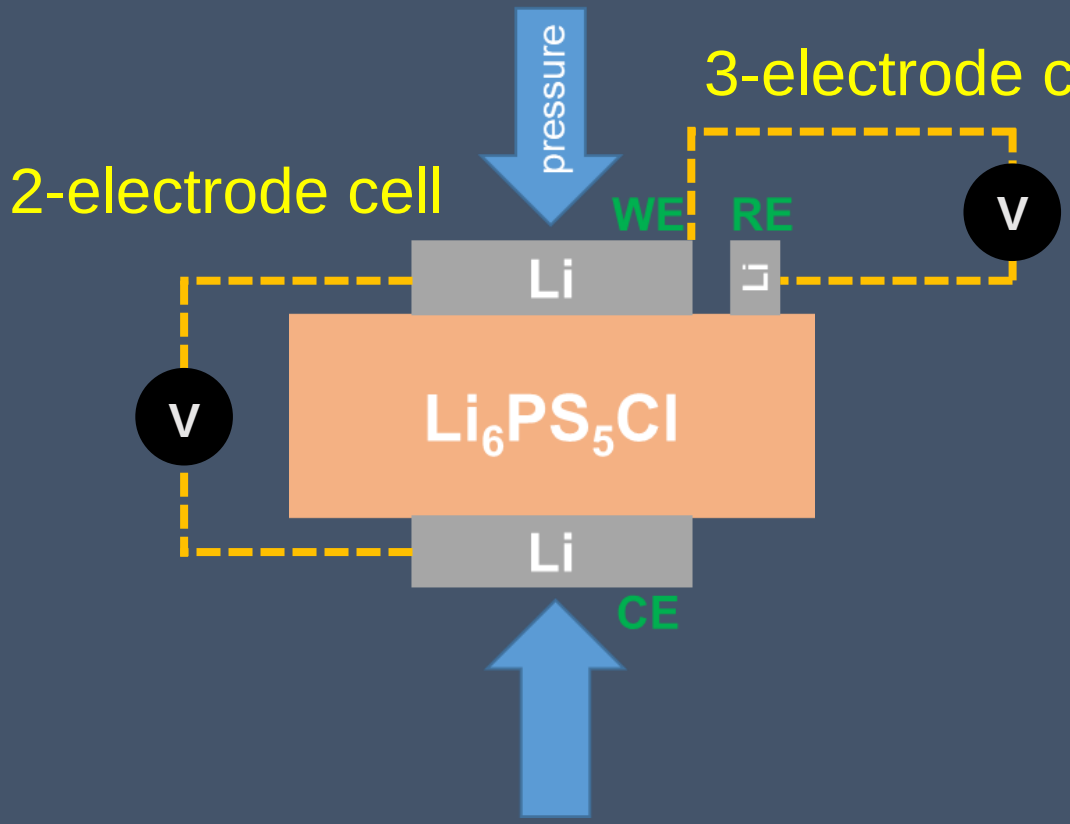
Solid Electrolyte

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

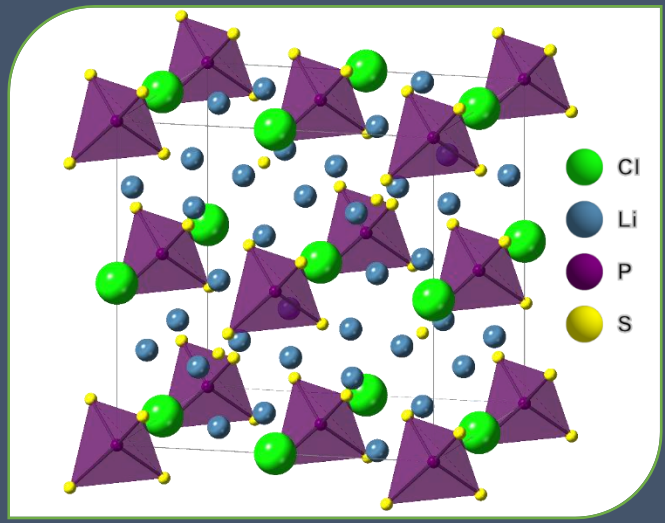


Chiang, et al. *JES,* 2018, 165, A3648.

3-electrode cell – separate stripping from plating



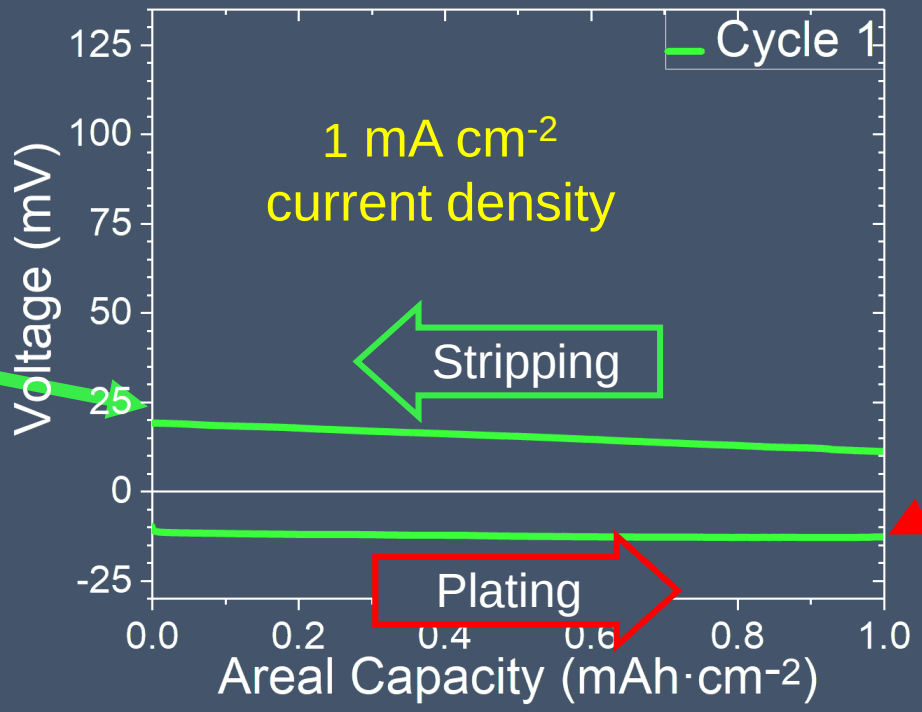
- 3-electrode cell allows separation of Li plating from stripping
- Argyrodite **Li_6PS_5Cl** solid electrolyte:
  - conductivity > 10^{-3} S cm^{-1}
  - soft
- Important to control pressure



3-electrode cycling Li/Li_6PS_5Cl 3 MPa

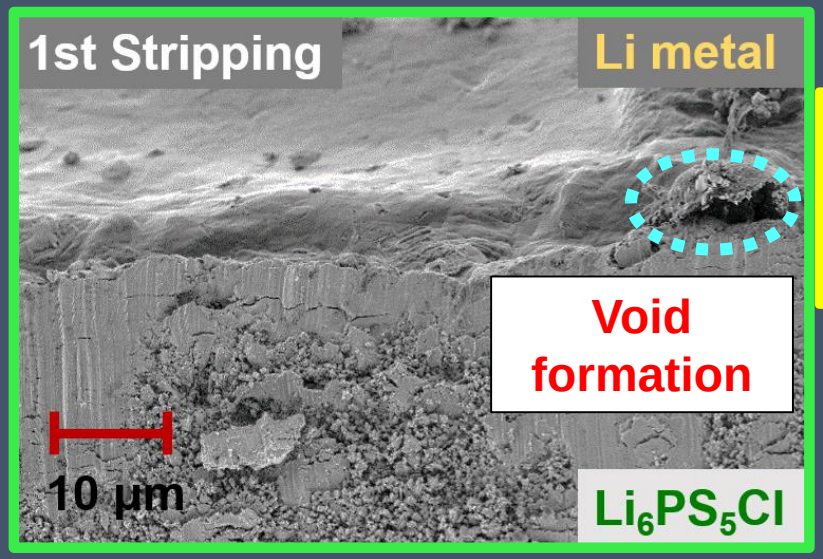
Kasemchainan et al. Nature Materials (2019)

Small polarisation increase on stripping

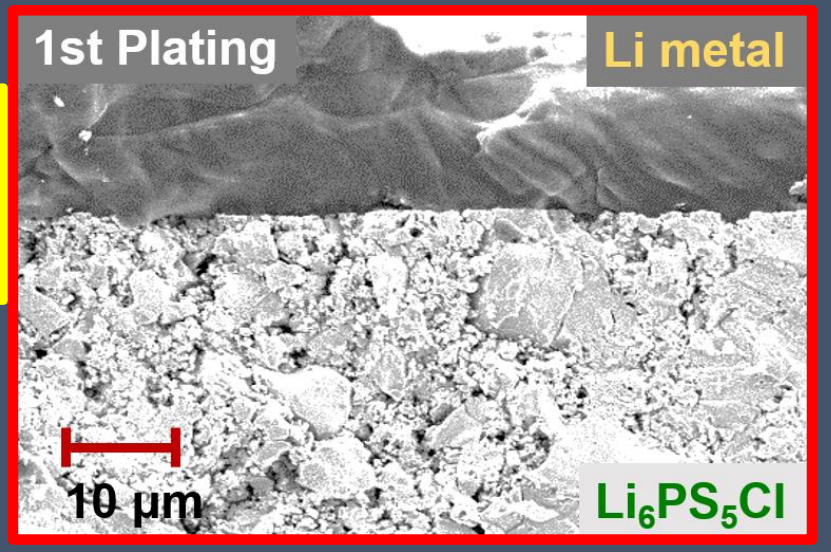


No change in polarisation on plating

Strip/plate 5 µm of Li



SEM cross-sections



3-electrode cycling Li/Li_6PS_5Cl 3 MPa

Significant polarization increase

Eventual dendrite formation

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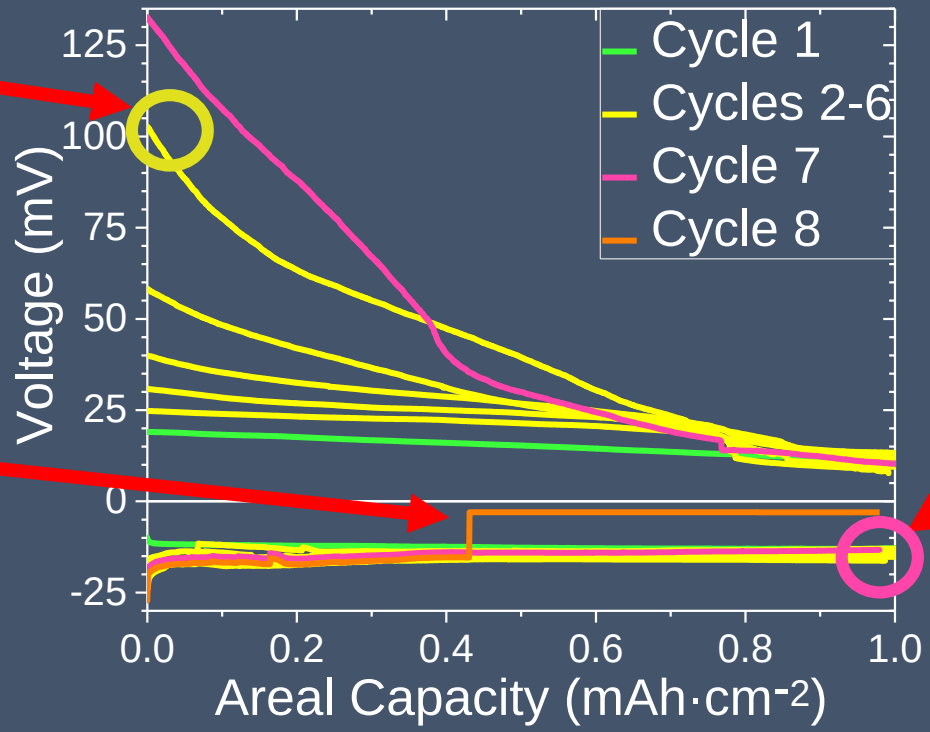
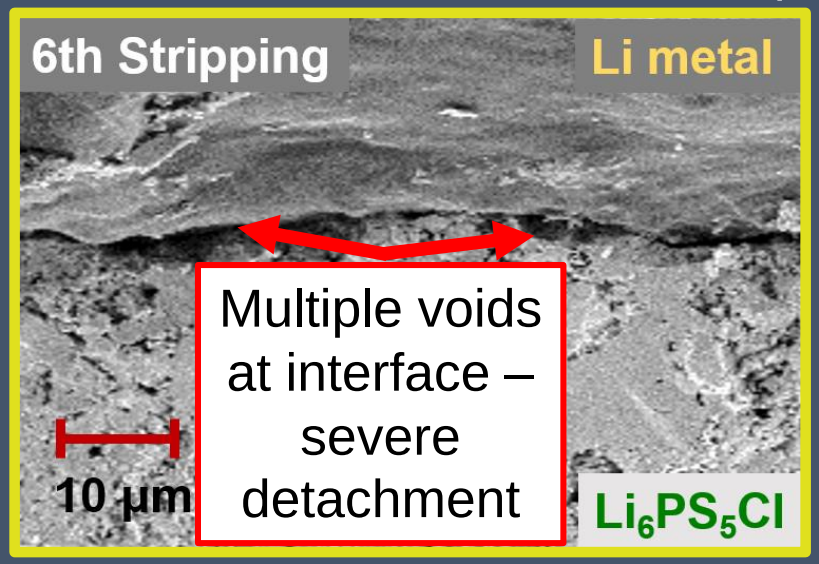
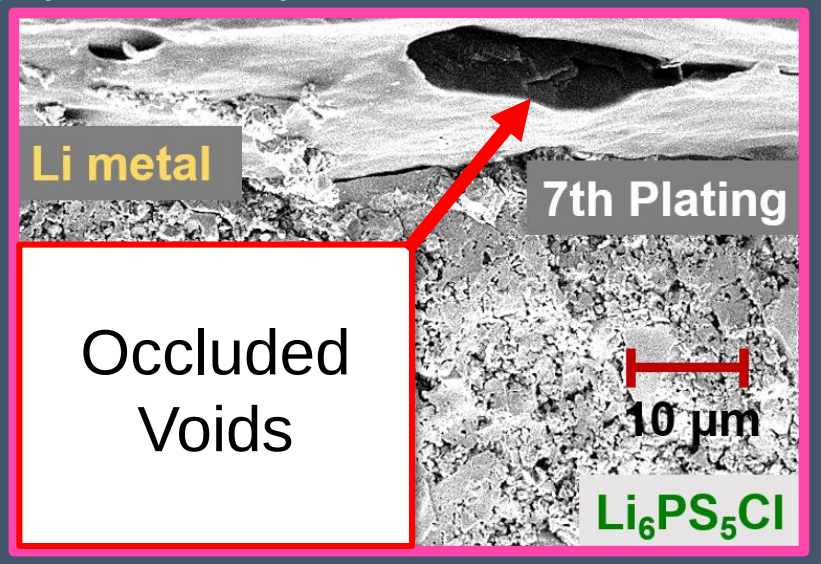
short circuit



Kasemchainan et al. Nature Materials (2019)

No polarization increase

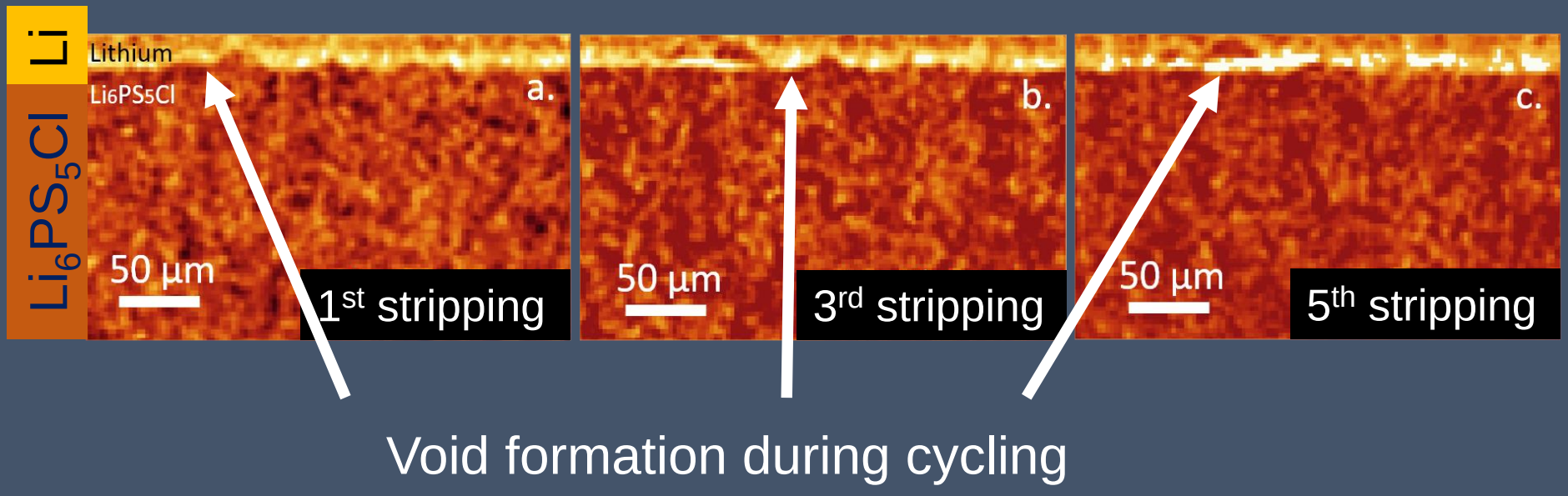




In-situ X-ray computed tomography to reveal void evolution at the interface

Observe void evolution under controlled pressure cycling

Reconstructed virtual cross section from CT



Void formation during cycling

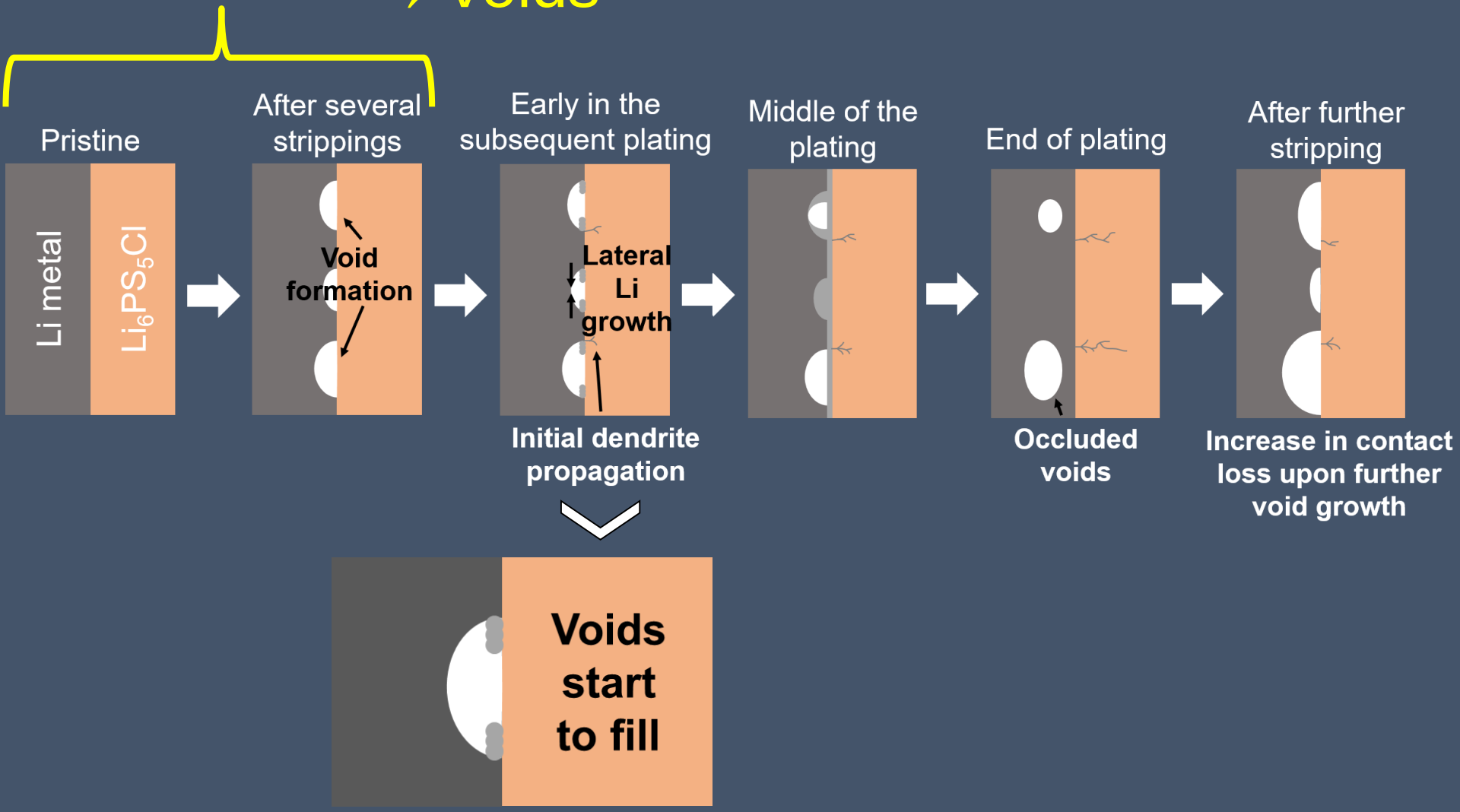
Number and length of voids increase along interface

Li /Li_6PS_5Cl interface
Current density = 1.0 mA cm^{-2}
Capacity = 1.0 mAh cm^{-2}
Pressure = 3 MPa

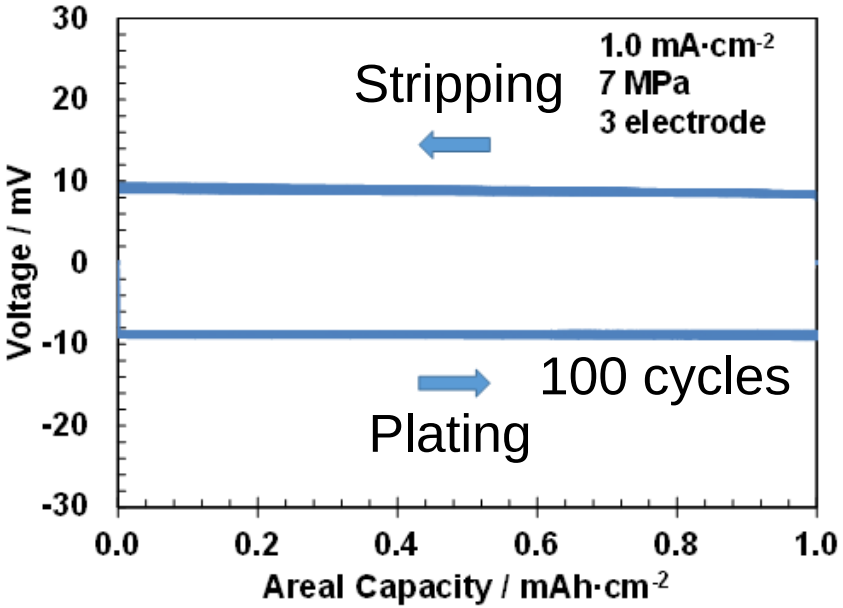
Influence of void formation on cycling

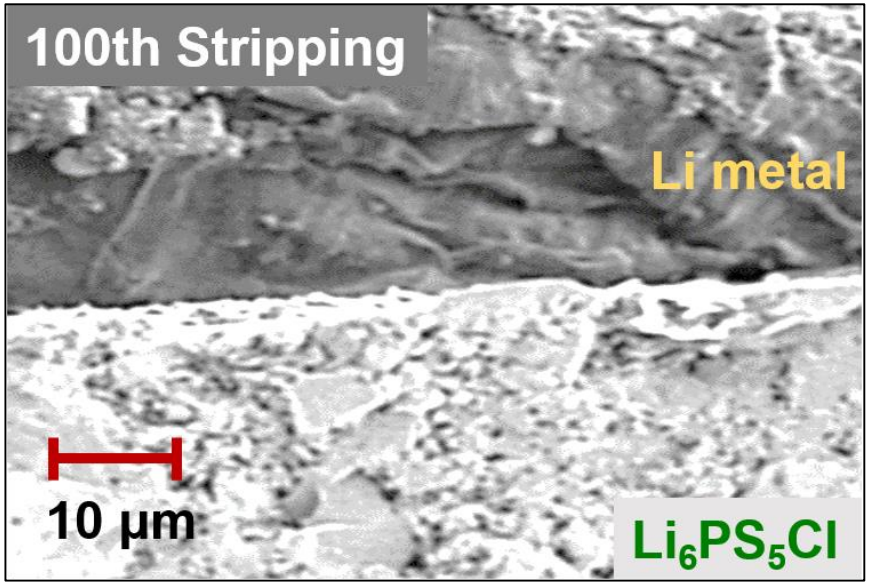
$J_{Li\ diffusion} + J_{Li\ creep} < J_{Li+\ migration}$

$\rightarrow$ voids



3-electrode cycling Li/Li_6PS_5Cl 7 MPa





High pressure → Conformal interface

- Strong pressure dependence – creep of Li metal to interface
- Pressure >> yield strength of Li: 0.81 MPa [1]

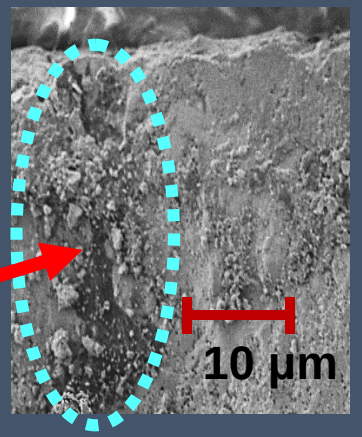
[1] Masias, A., Felten, N., Garcia-Mendez, R. et al. *J Mater Sci* (2019) 54: 2585

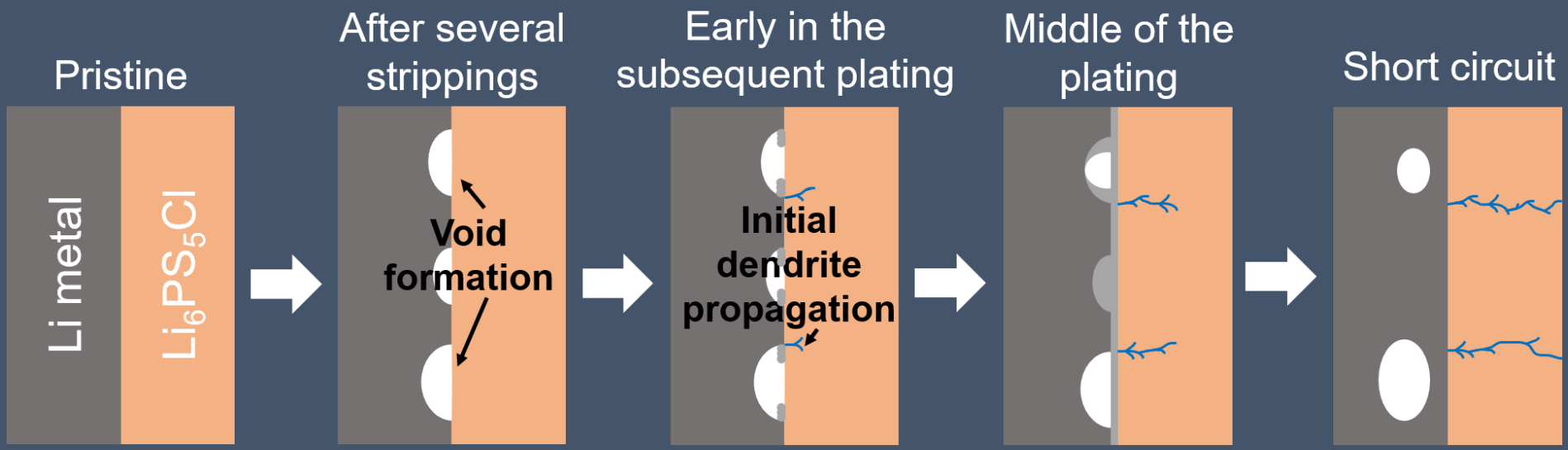
Implications for failure of solid state batteries

SSBs fail because of critical stripping current (CCS)
not plating current (CCP) as thought previously

Above CCS:

Increase in voiding with cycle number – contact loss
→ increase in local current density at interface
→ reach critical current for **dendrite formation**
→ dendrite propagating through solid electrolyte





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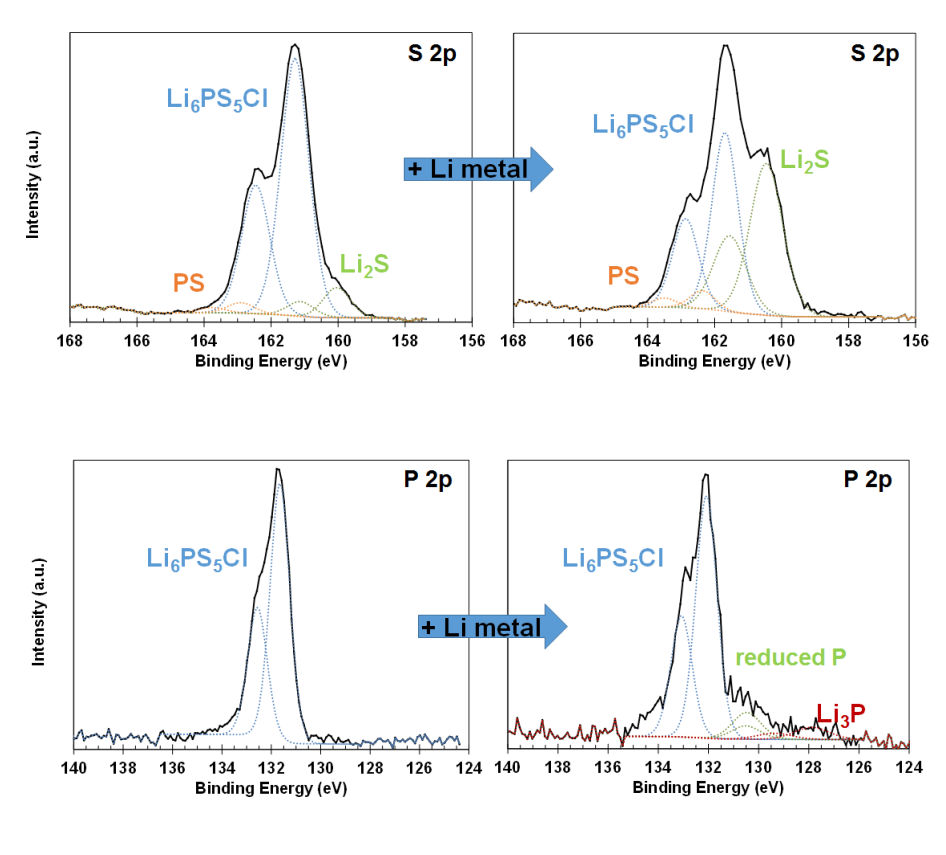
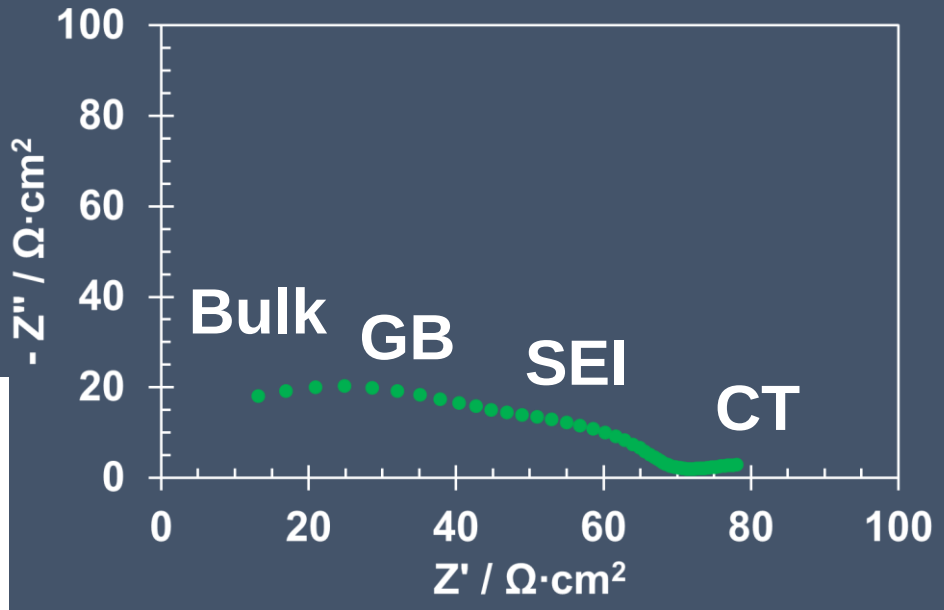
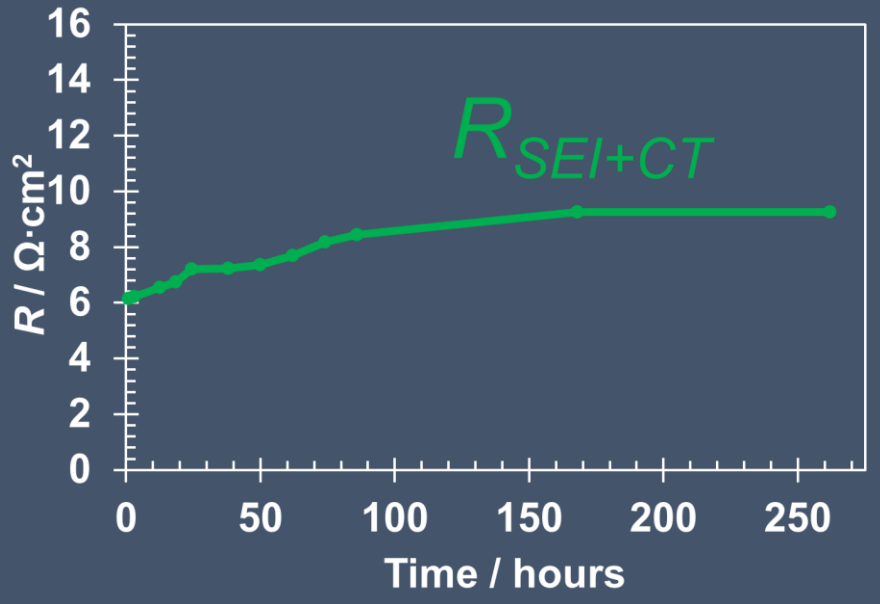
Li/Li_6PS_5Cl Interfacial Stability

XPS shows that Li_6PS_5Cl is reduced by Li to form mainly Li_2S & Li_3P



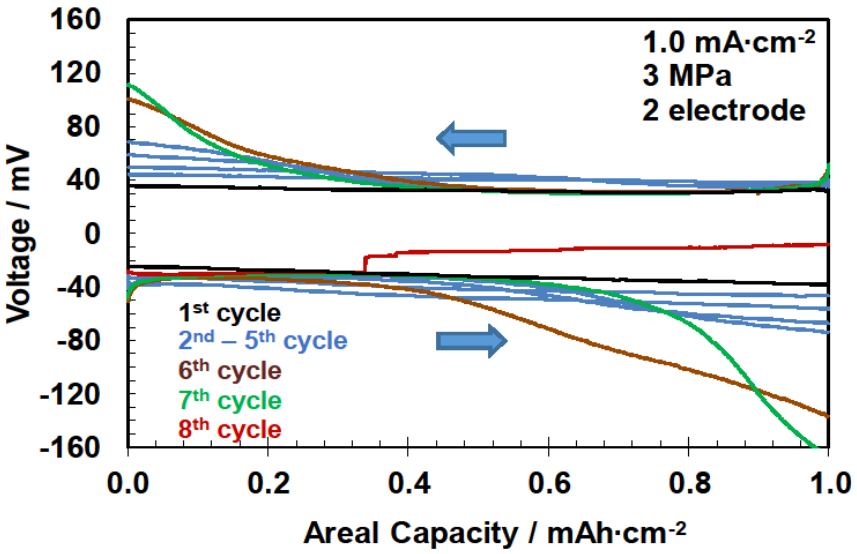


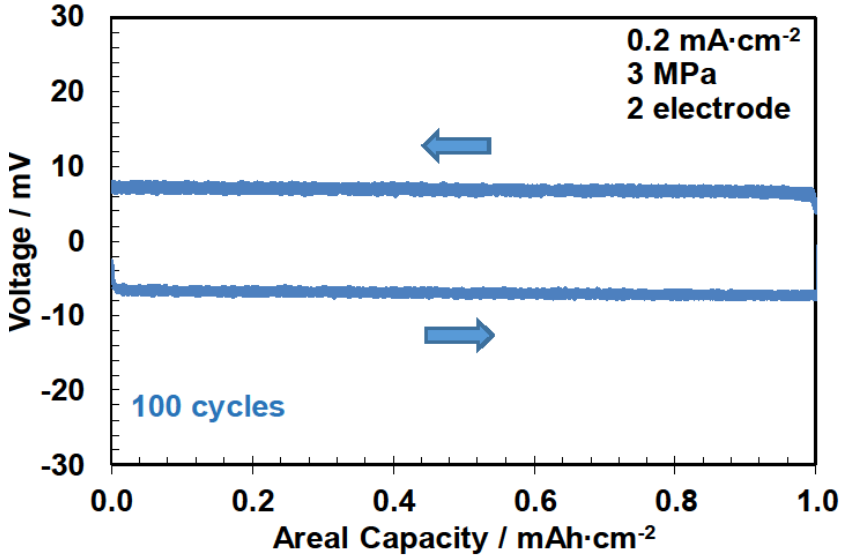


2-electrode $Li/Li_6PS_5Cl/Li$ cells

Current > critical stripping current
Current < critical plating current
cell failure

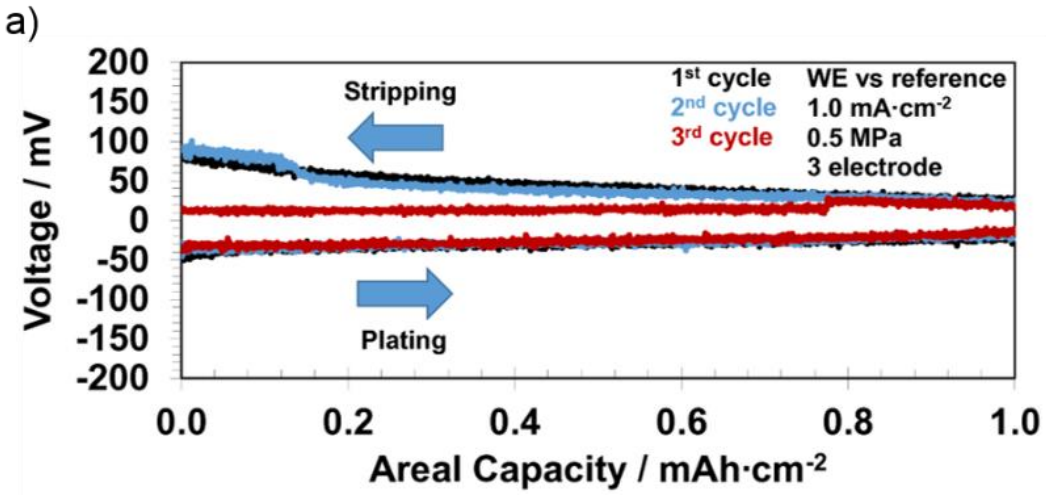
Current < critical stripping current

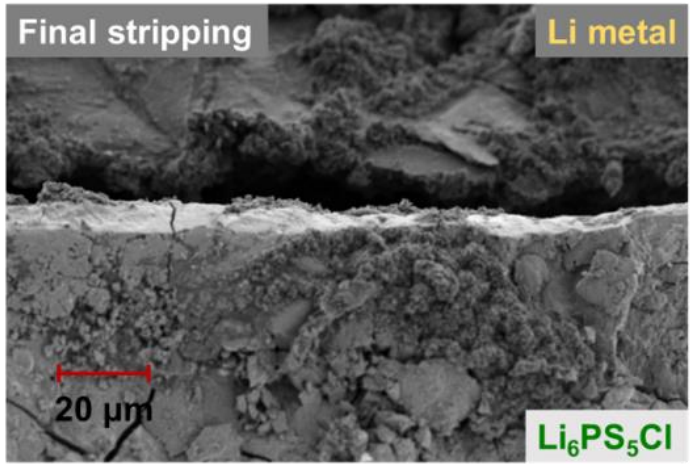




increasing **polarization**
followed by **short circuit**

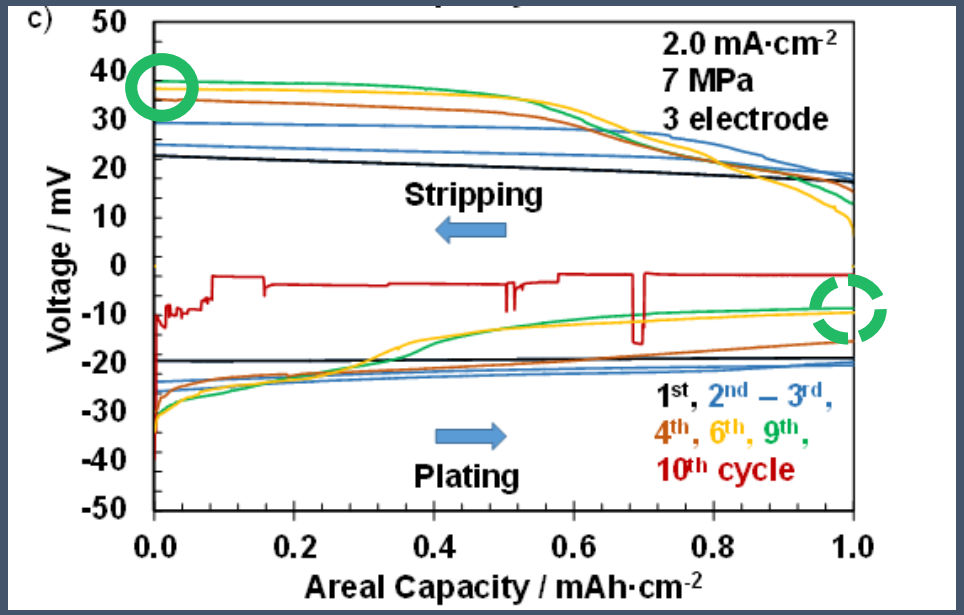
$J_{Li\ diffusion} + J_{Li\ creep} < J_{Li+\ migration}$ → **cell failure**





Voltage vs charge passed for a 3-electrode cell on Li metal plating and stripping at the Li / Li_6PS_5Cl interface at a pressure of 0.5 MPa and a current density of 1.0 mA·cm^{-2} SEM cross-section of the Li / Li_6PS_5Cl interface after the final stripping.

3-electrode cycling Li/Li_6PS_5Cl 7 MPa 2 $mAcm^{-2}$



Reduced polarization

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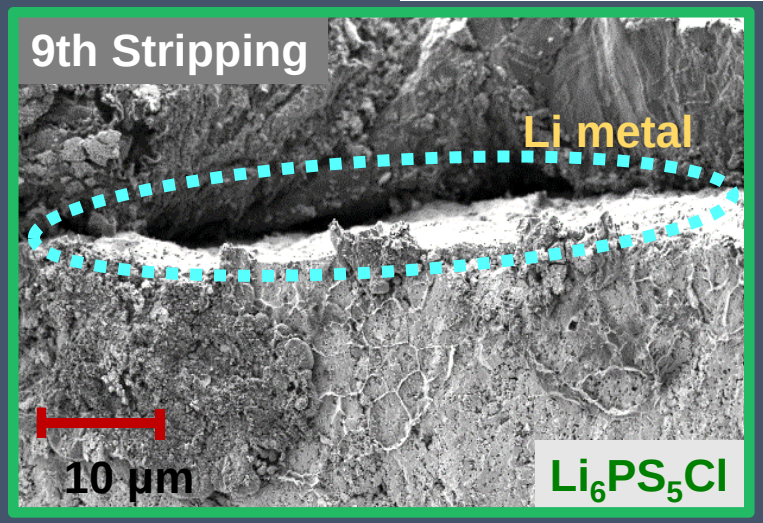
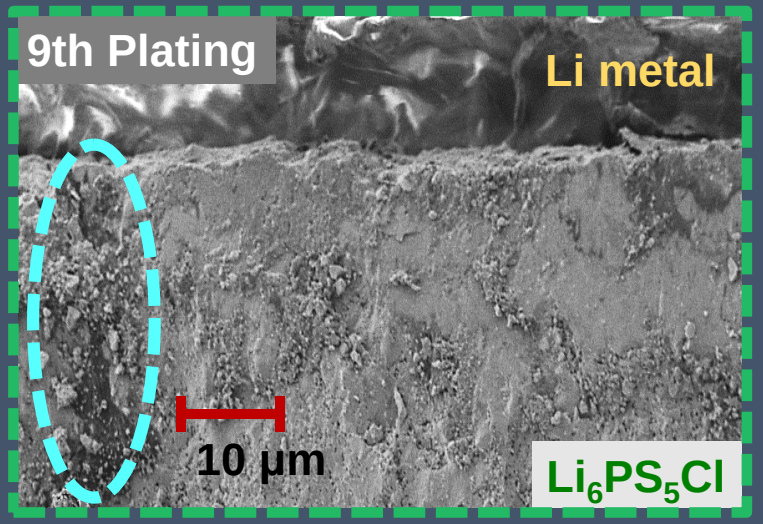
dendrite formation



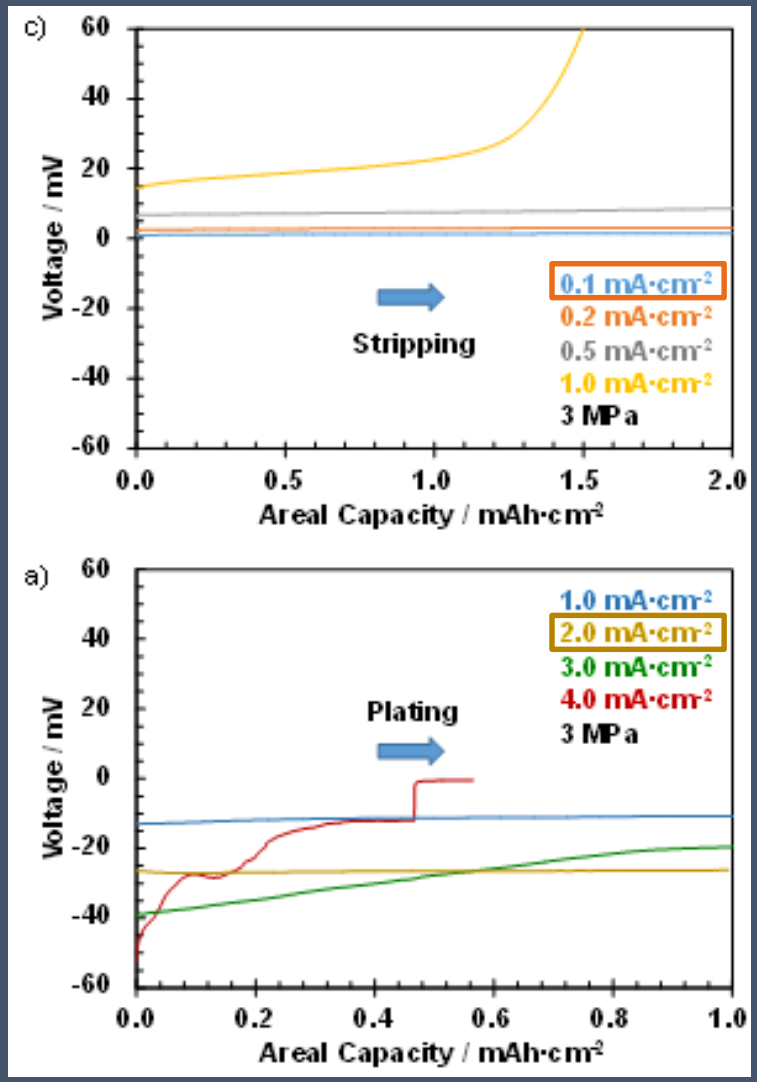


At 7 MPa and 2 mA cm^{-2}: $J_{Li\ diffusion} + J_{Li\ creep} < J_{Li+\ migration}$ → cell failure

Critical current determination

Stripping

Plating



CCS < CCP