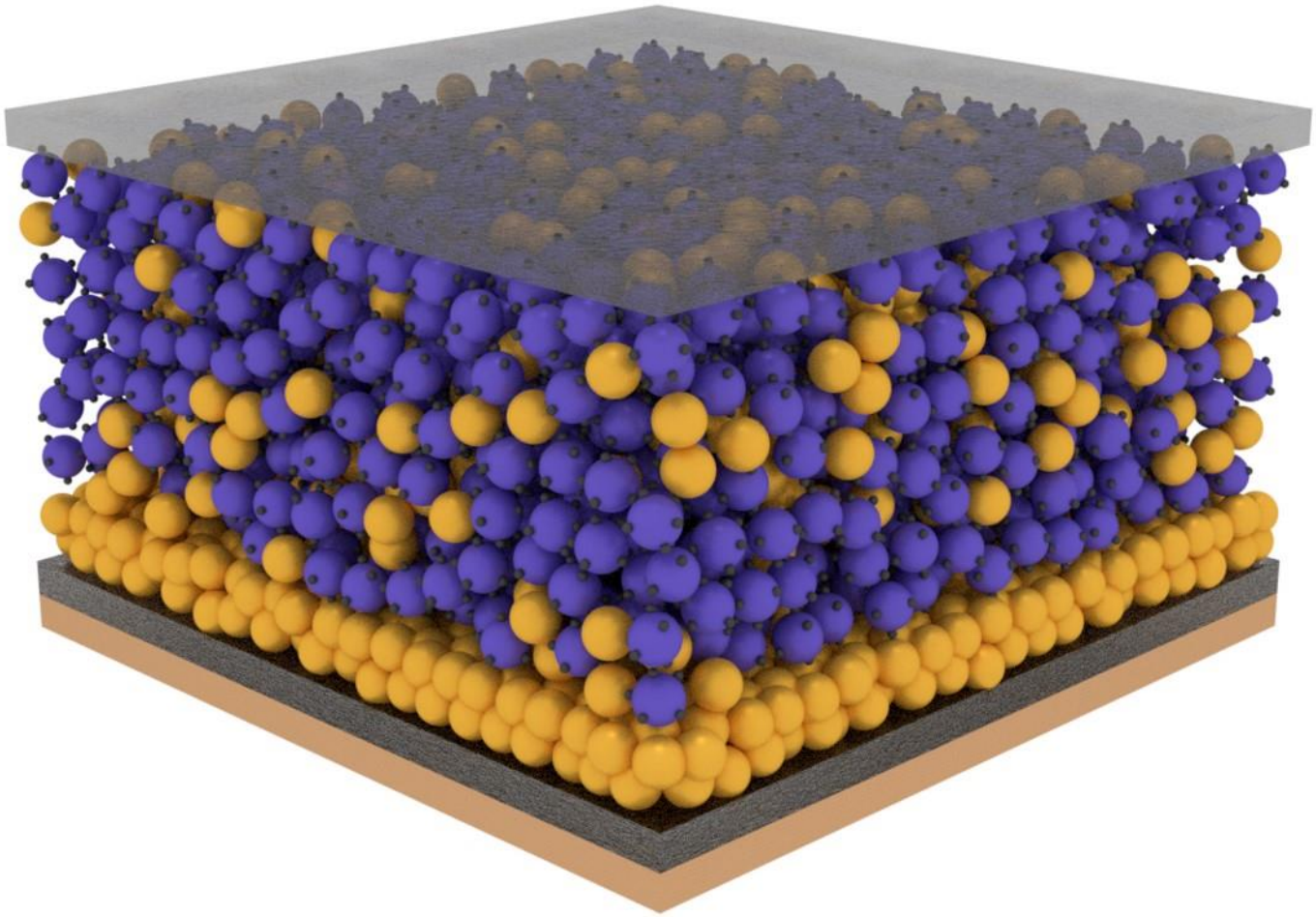
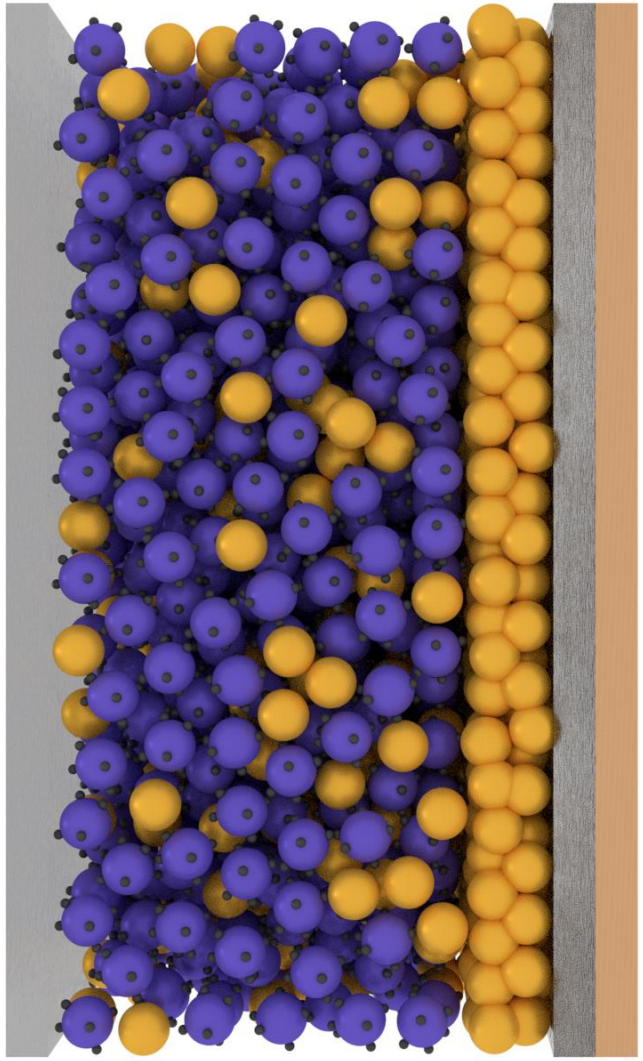
UNIVERSITY OF OXFORD

SOLBAT

# SOLBAT: solid-state metal anodes (day 1)



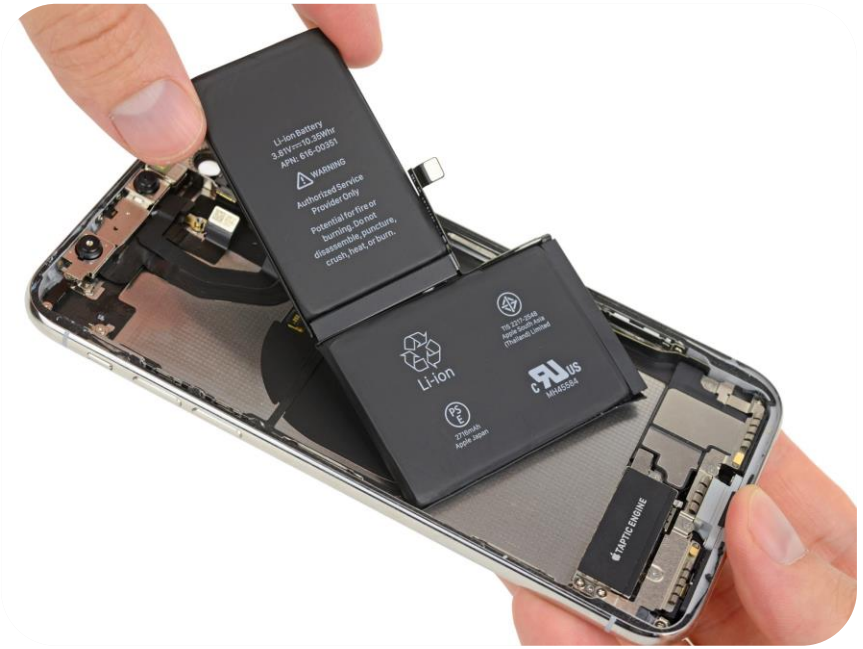
# WHY SOLID STATE?



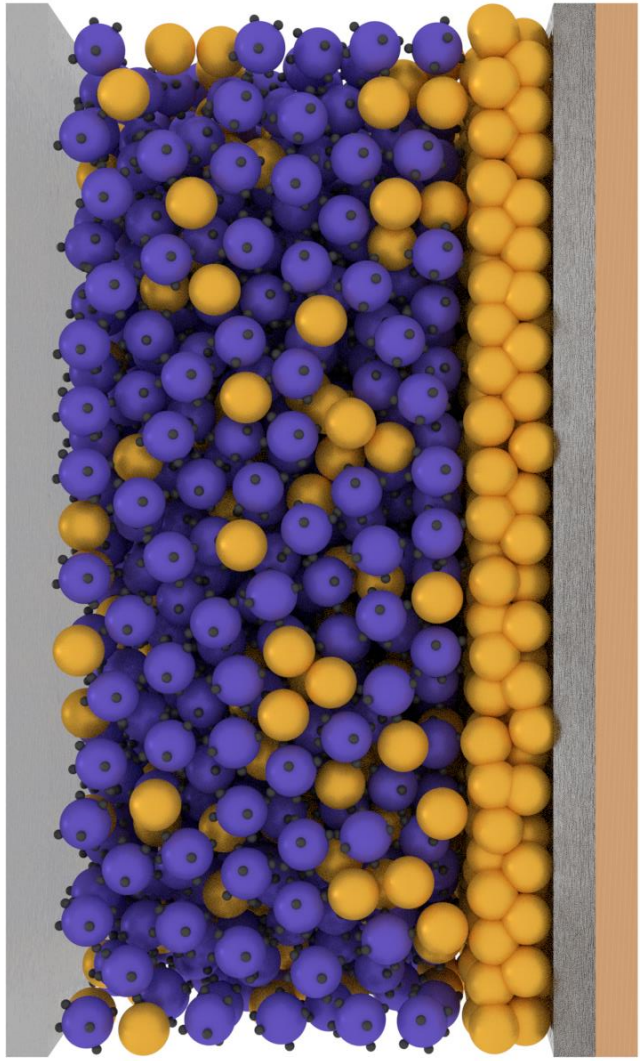
ENERGY

POWER

SAFETY



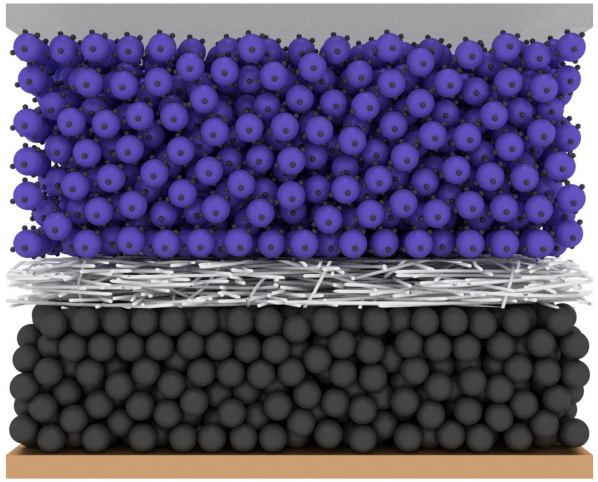
# HOW SOLID STATE?

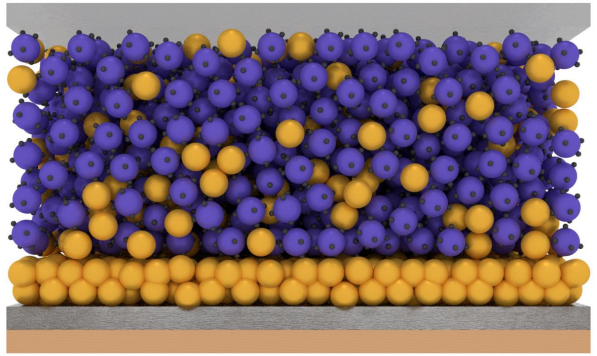


ENERGY

POWER

SAFETY

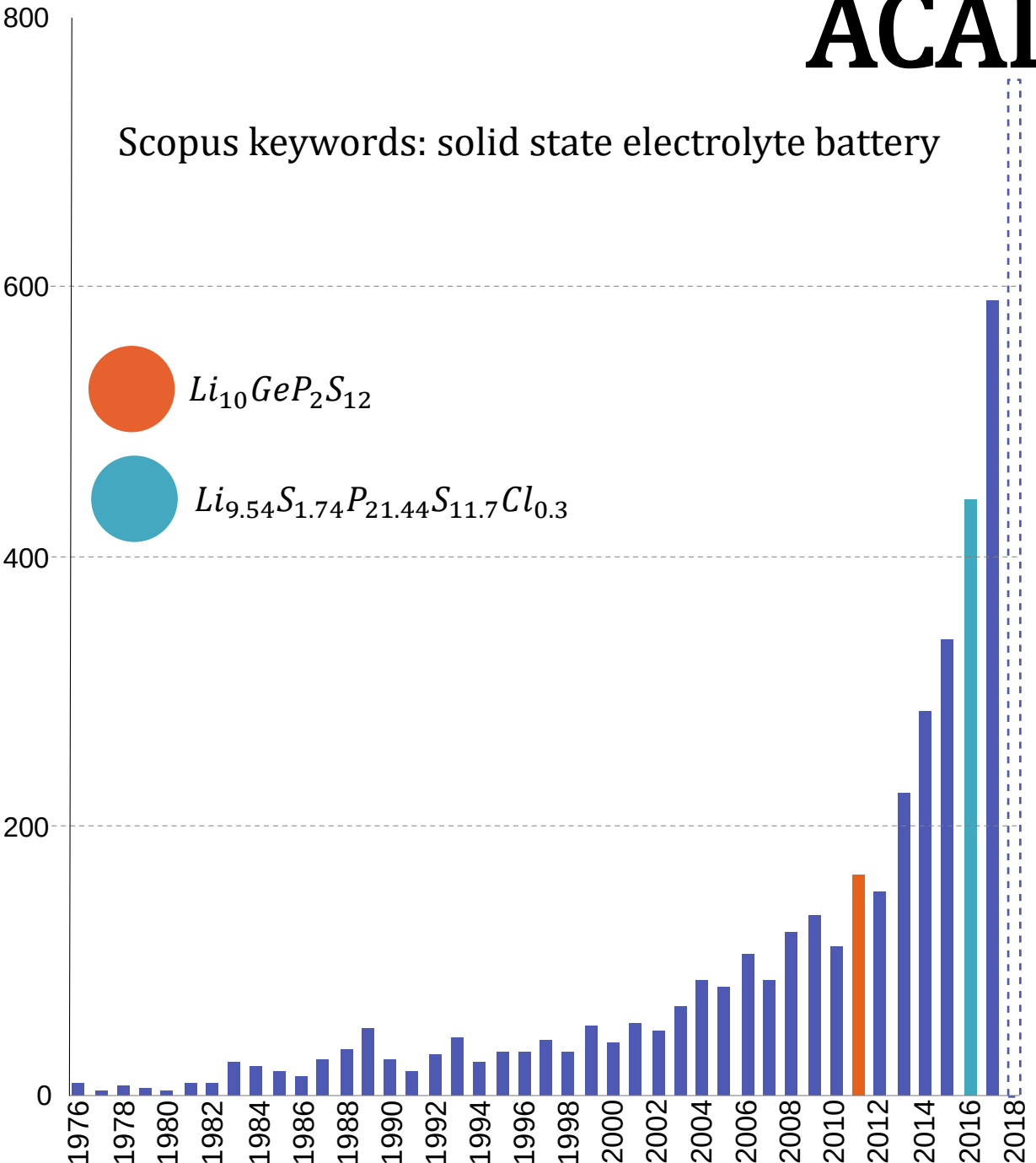


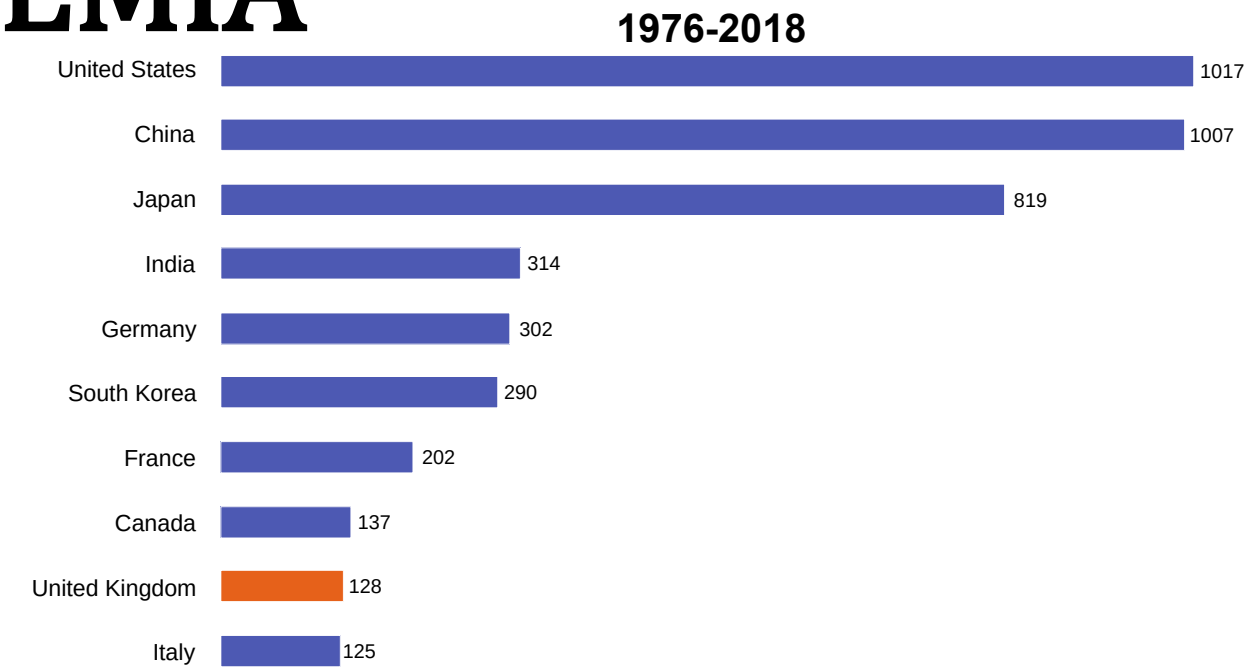


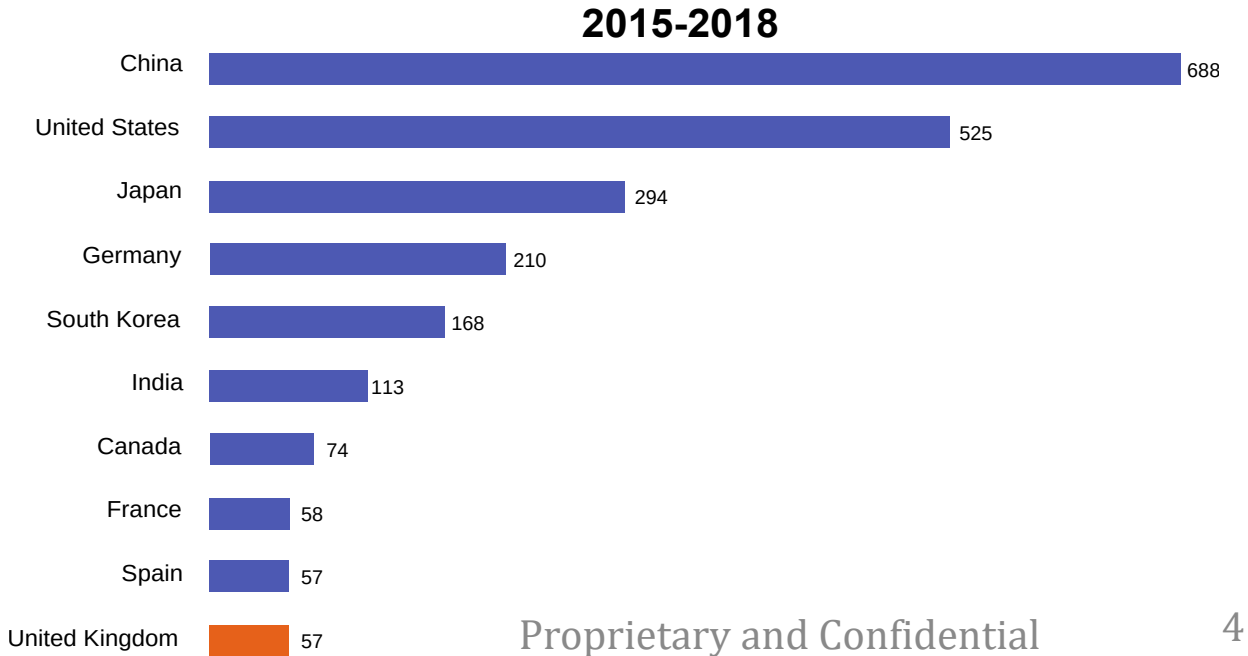
$$t_{Li^+} = \frac{I_{Li^+}}{I_{total}} \sim 1$$

# ACADEMIA

Scopus keywords: solid state electrolyte battery

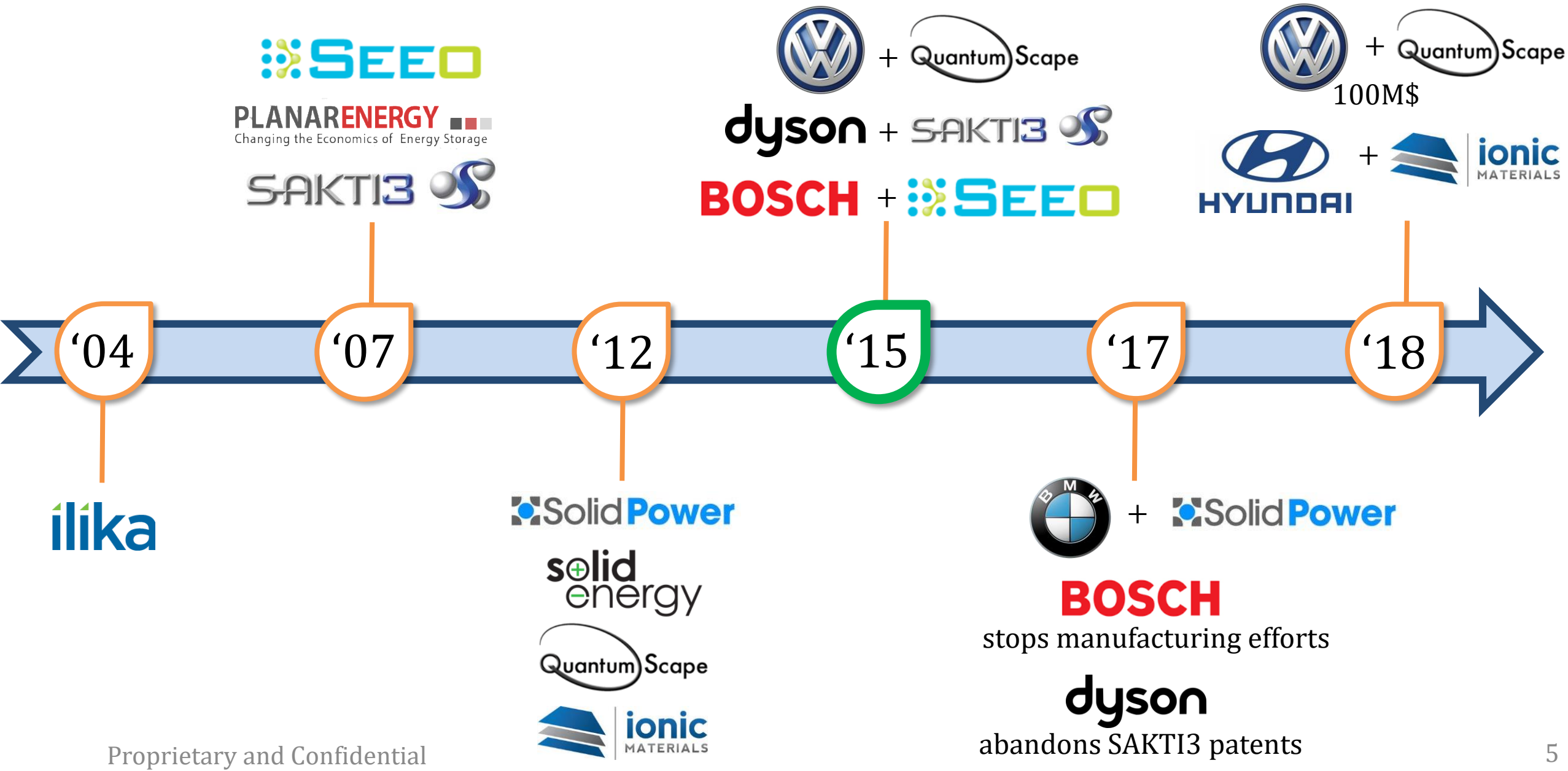


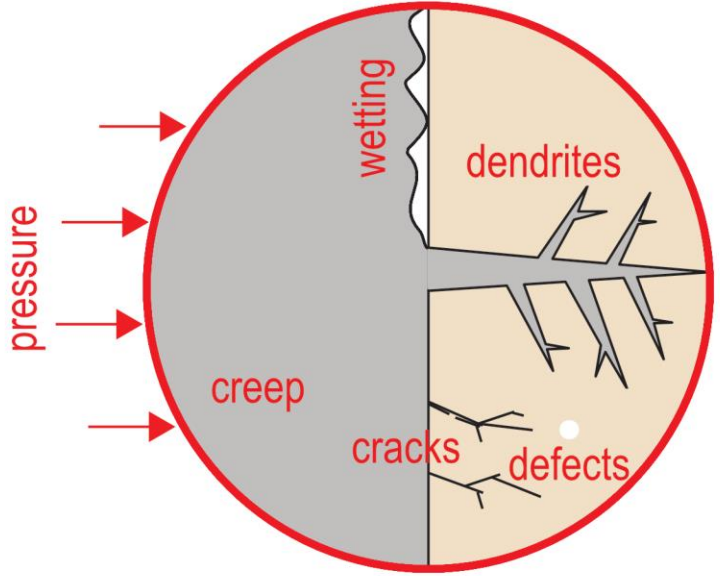




Proprietary and Confidential

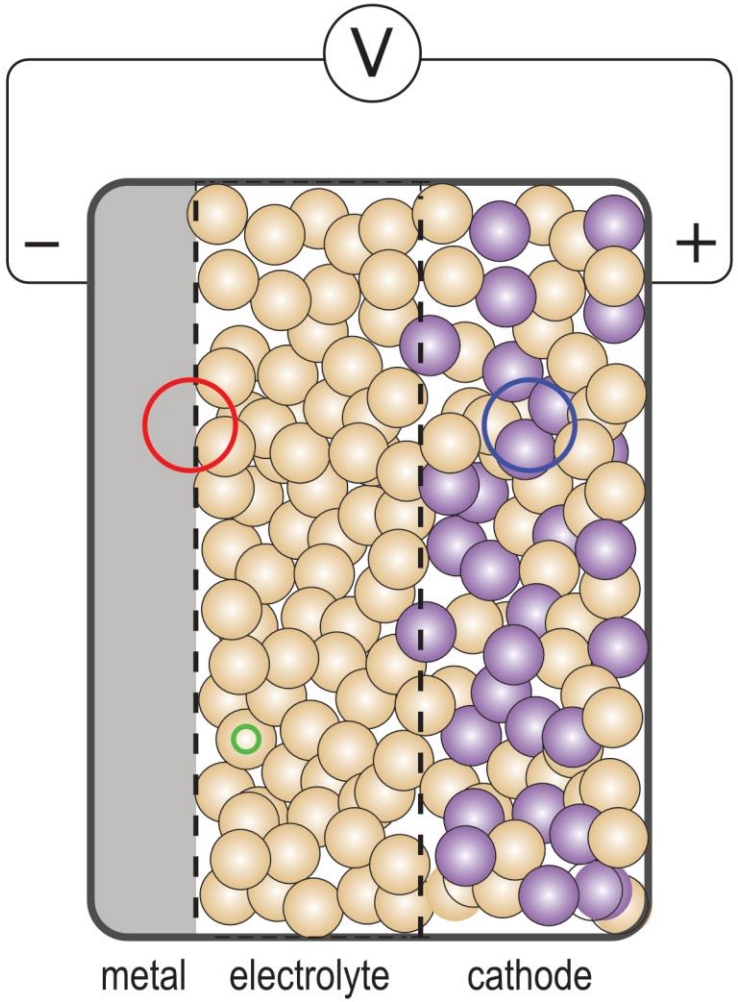
# INDUSTRY

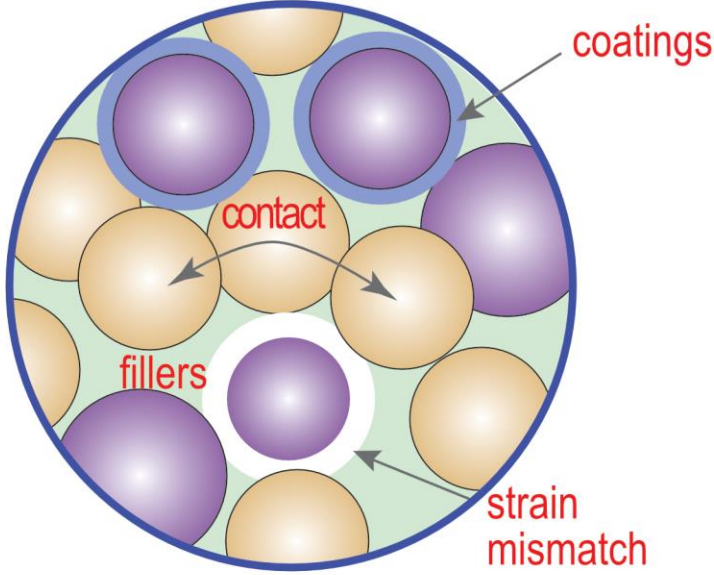

SEEO
PLANARENERGY
Changing the Economics of Energy Storage
SAKTI3
+ QuantumScape
dyson + SAKTI3
BOSCH + SEEO
+ QuantumScape
100M$
HYUNDAI + ionic MATERIALS
'04
'07
'12
'15
'17
'18
ilika
SolidPower
solid energy
QuantumScape
ionic MATERIALS
+ SolidPower
BOSCH
stops manufacturing efforts
dyson
abandons SAKTI3 patents

# SOLBAT

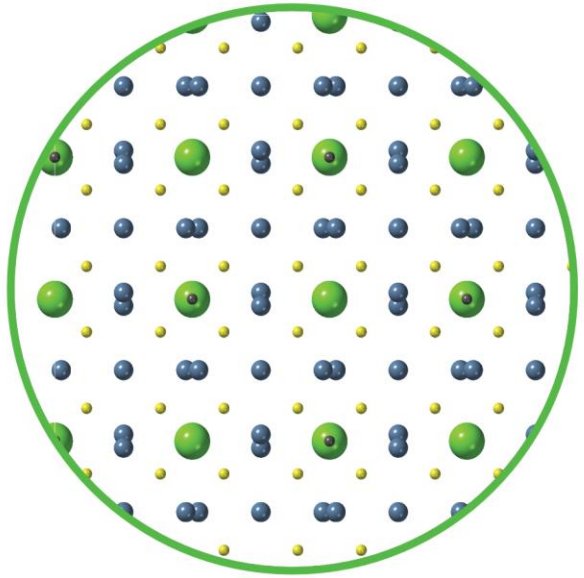



anode interfaces (WP1)

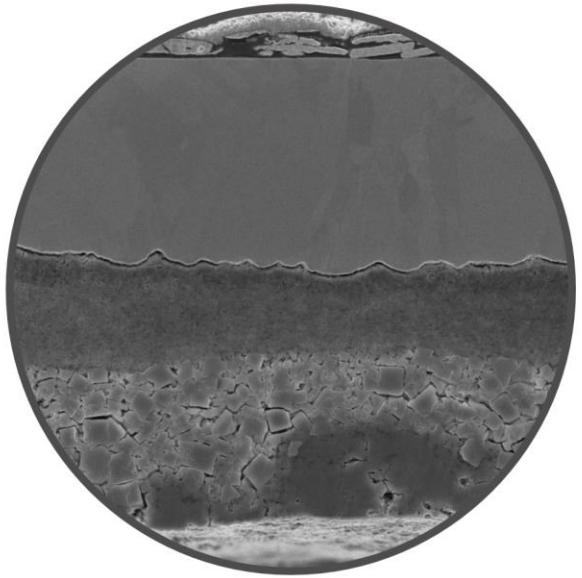



cathode interfaces (WP2)



electrolyte discovery (WP3)

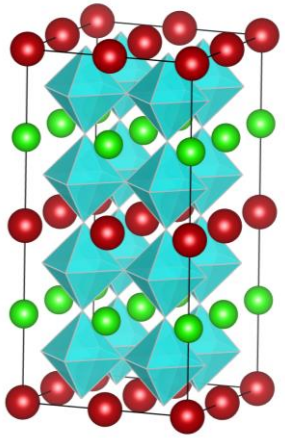


cell fabrication (WP4)

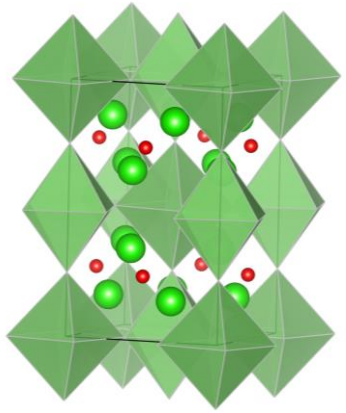
# THE TEAM

- University of Oxford
- University of Liverpool
- The University Of Sheffield.
- University of Cambridge
- University of St Andrews
- UCL

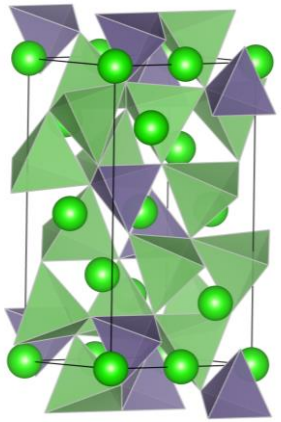
# INORGANIC CERAMICS



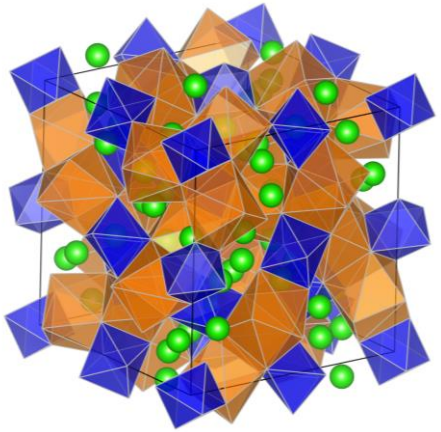
Perovskite (LLTO)
$Li_{3x}La_{2/3-x}\quad{}_{1/3-2x}TiO_3$



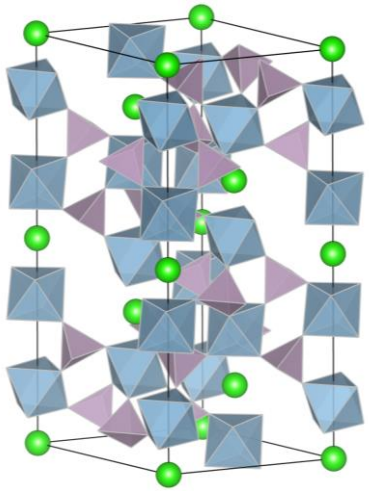
Anti-perovskite
$(Li_3OCl)$



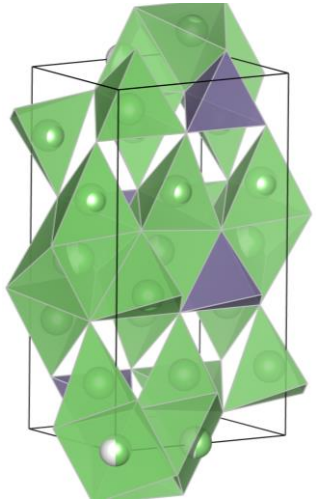
LiSICON
$Li_{14}ZnGe_4O_{16}$



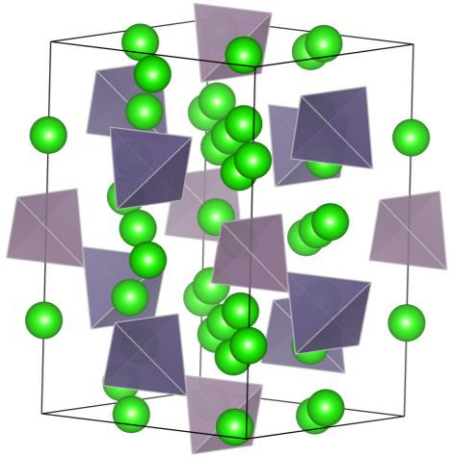
Garnet (LLZO)
$Li_7La_3Zr_2O_{12}$



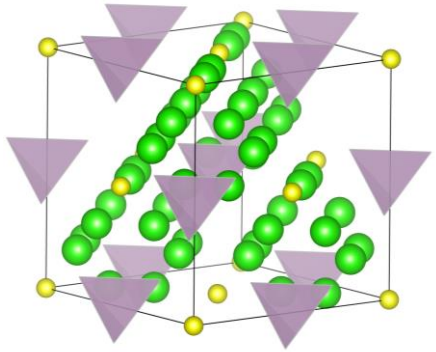
NaSICON $(LAGP)$
$Li_{1.3}Al_{0.3}Ge_{1.7}(PO_4)_3$



Thio-LiSICON
$Li_{4-x}ZnGe_{1-x}PS_4$

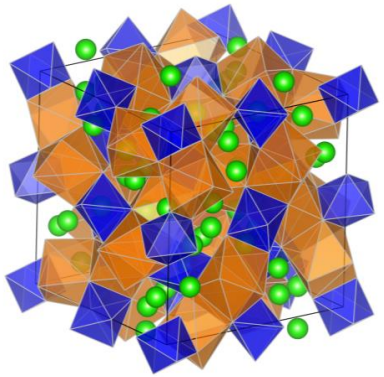
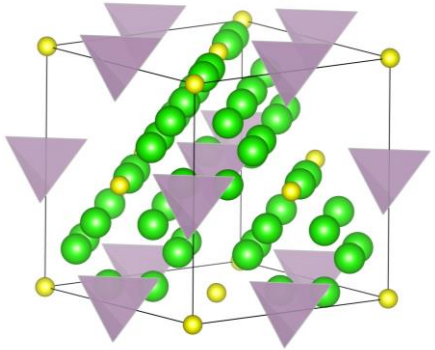


LGPS
$Li_{10}GeP_2S_{12}$



Argyrodite
$Li_6PS_5Cl$

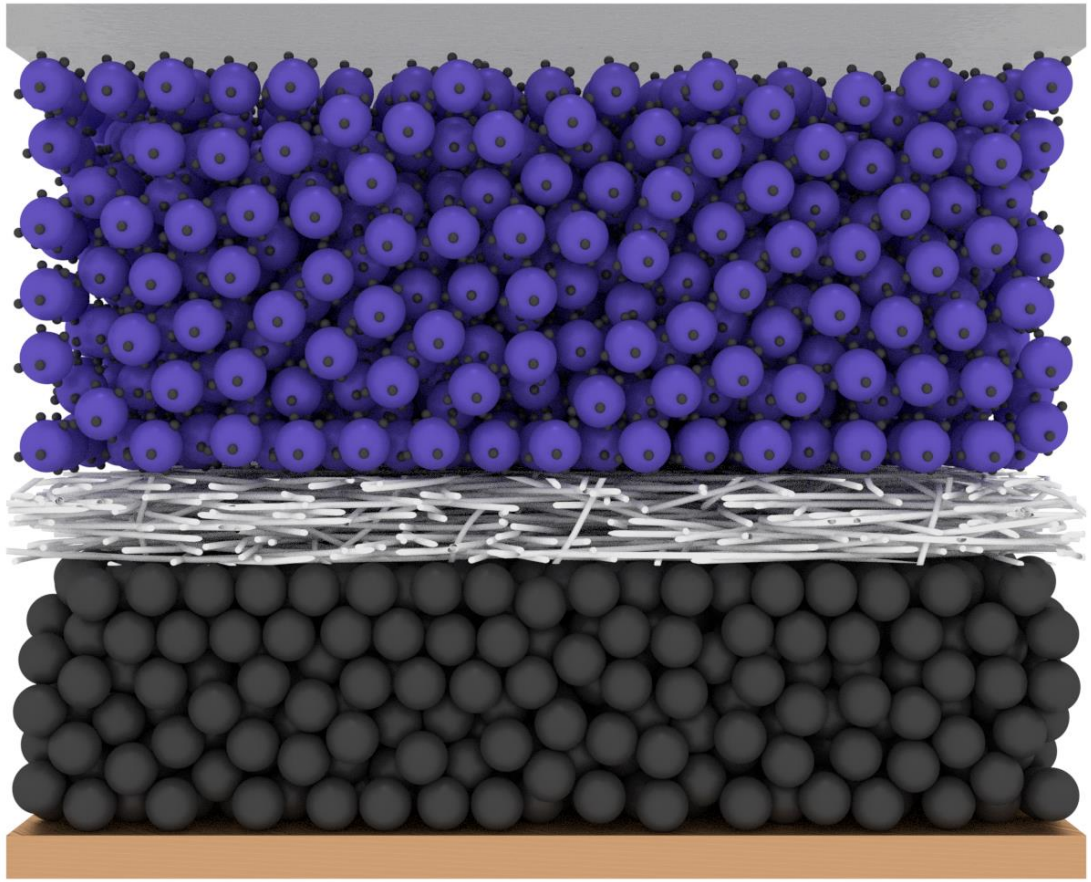
# TWO MODEL SYSTEMS

| | Garnet, $Li_7La_3Zr_2O_{12}$ | Argyrodite, $Li_6PS_5Cl$ |
|---|---|---|
| |  |  |
| $\sigma_{Li^+}$ / S cm$^{-1}$ | $1 \cdot 10^{-3}$ (Ta doped) | $3 \cdot 10^{-3}$ |
| Stability vs. Li metal | stable | ? |
| Electrochemical window | wide | ? |
| $E$ /GPa | 175.1 | 22.1 |
| $G$ /GPa | 68.9 | 8.1 |
| $\rho$ /g $cm^{-3}$ | 4.89 | 1.89 |

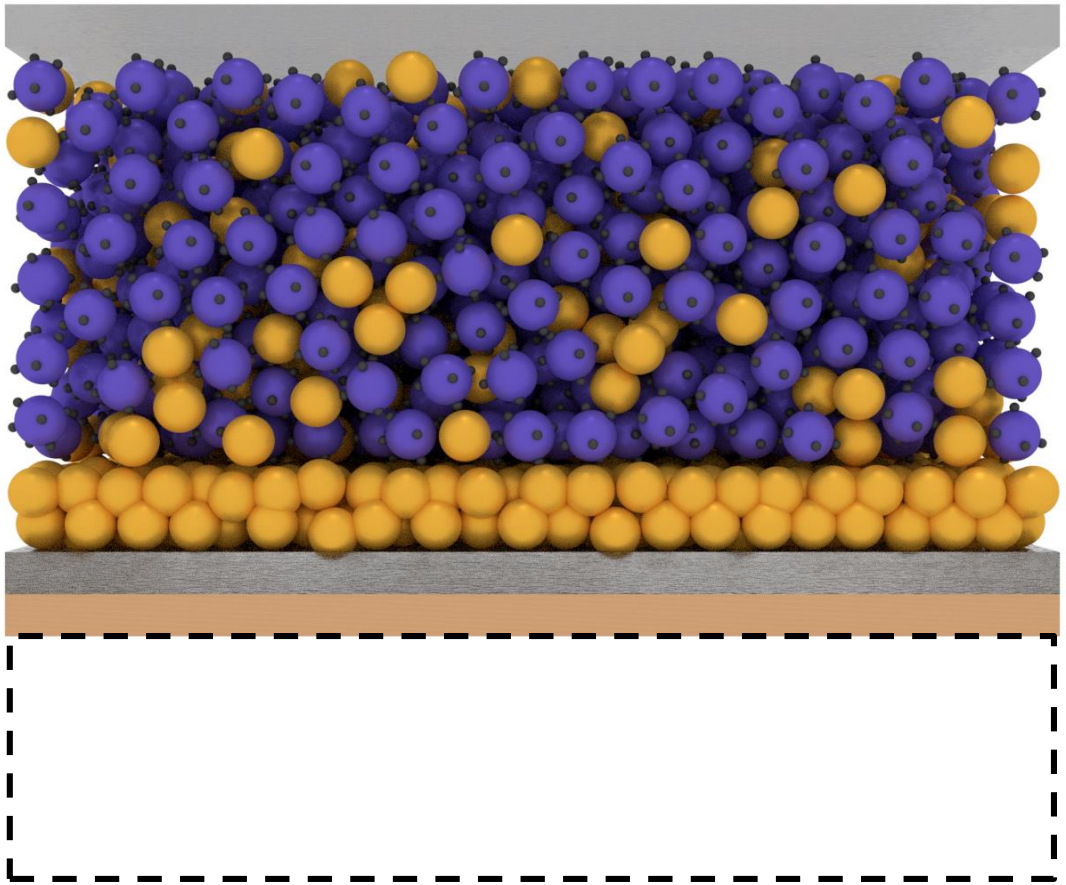
Janek, Nazar, Nan, Maier, Armand, Chen et.al., *New horizons for inorganic solid state ion conductors*, EES (2018)

# TECHNOECONOMICS

**Conventional Li-ion**



**Argyrodite, $Li_6PS_5Cl$**



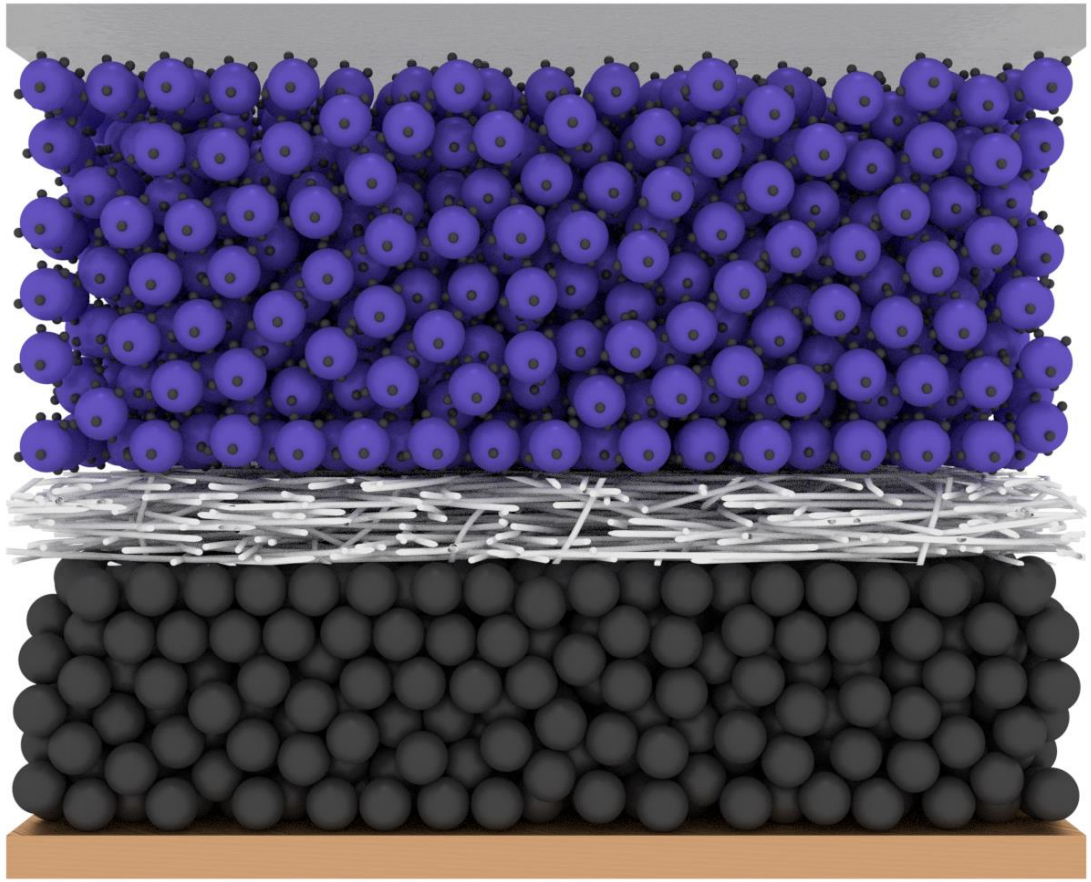
770 $Whl^{-1}$
300 $Whkg^{-1}$

+ 74% vol.
+ 45% grav.

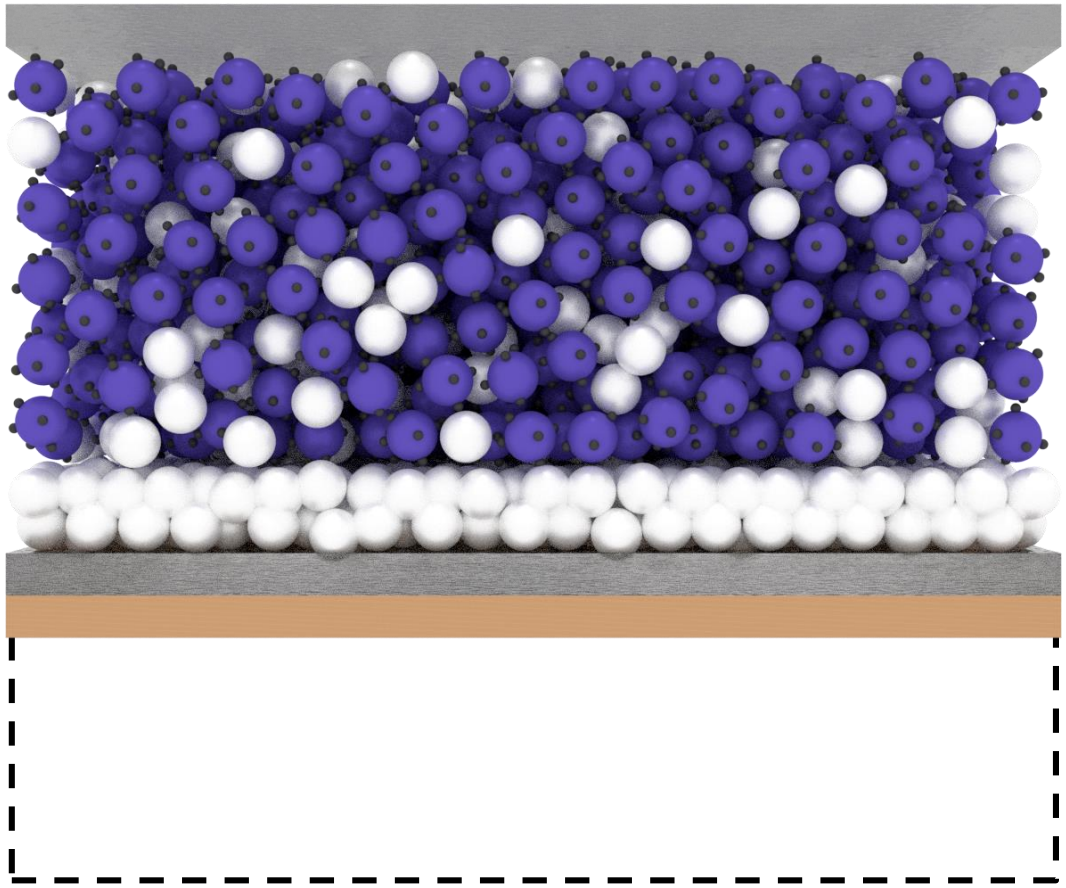
1339 $Whl^{-1}$
434 $Whkg^{-1}$

# TECHNOECONOMICS

**Conventional Li-ion**



**LLZO, $Li_7La_3Zr_2O_{12}$**

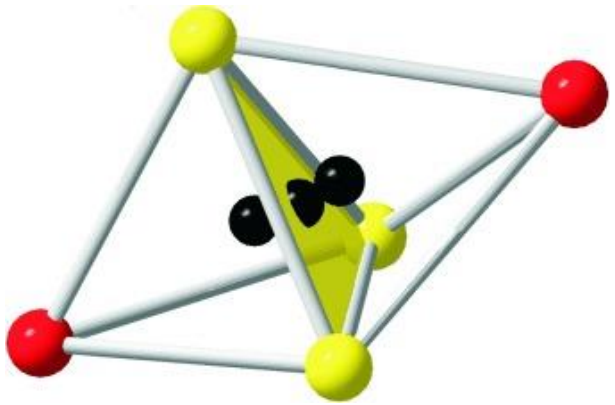


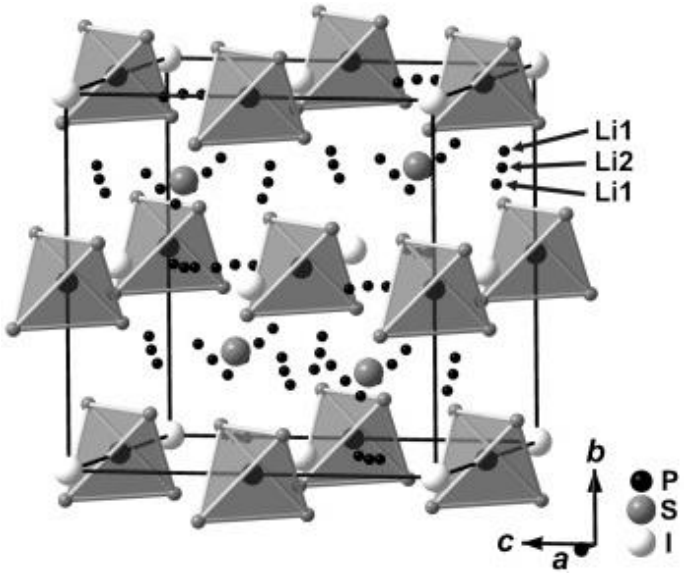
770 $Whl^{-1}$
300 $Whkg^{-1}$

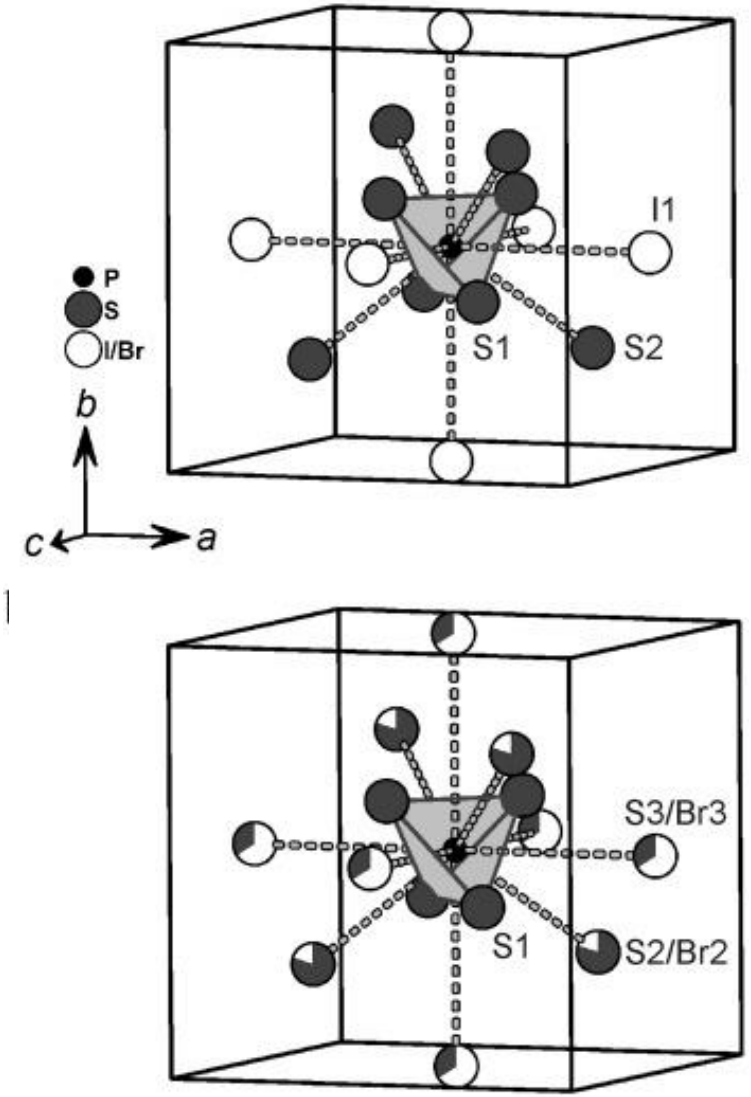
$\xrightarrow[+\ 5\%\ \text{grav.}]{+\ 74\%\ \text{vol.}}$

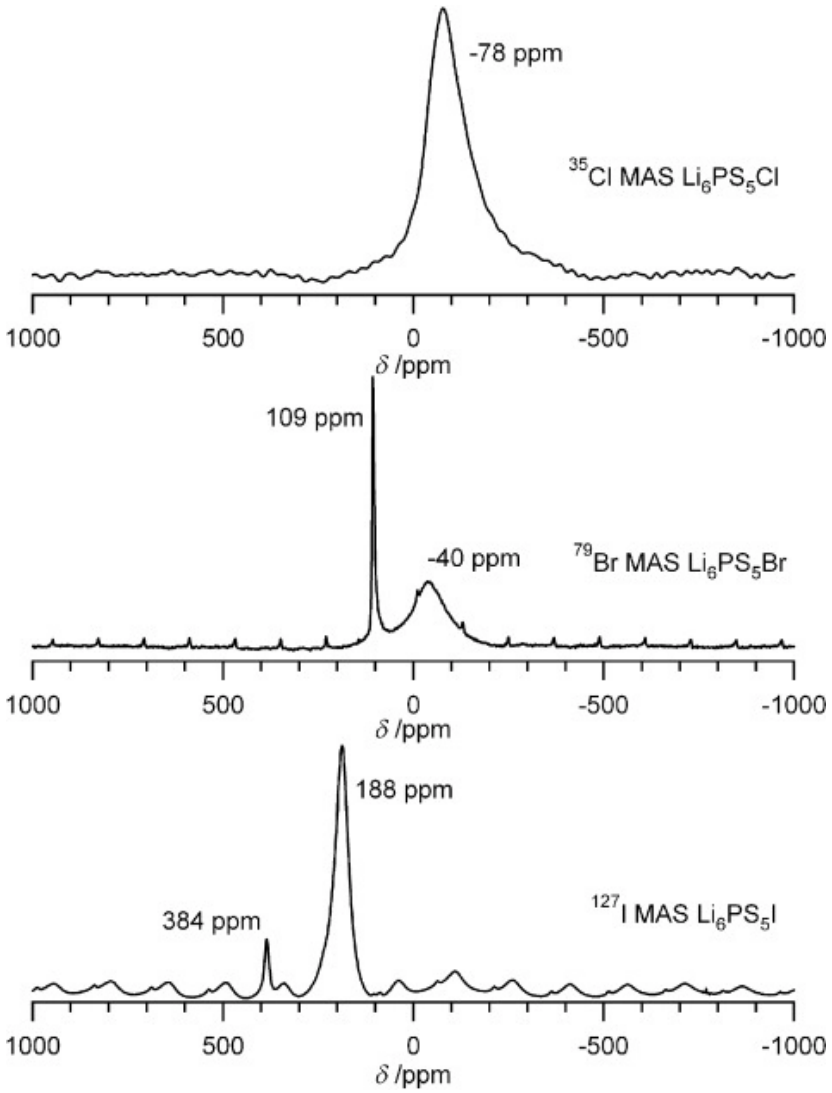
1339 $Whl^{-1}$
315 $Whkg^{-1}$

# ARGYRODITE: HISTORY



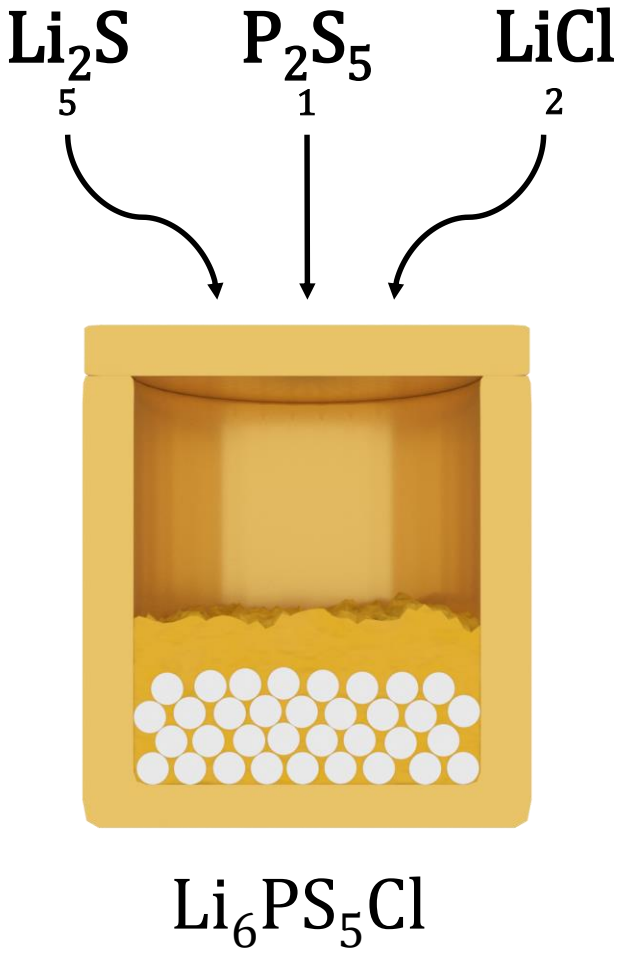



Deiseroth et.al. Angew. Chem. Int. Ed. (2008)

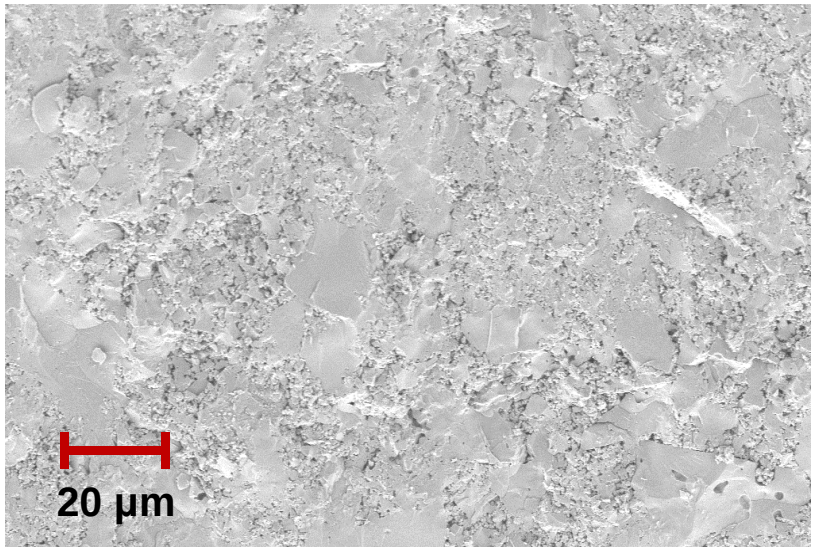
# SYNTHESIS

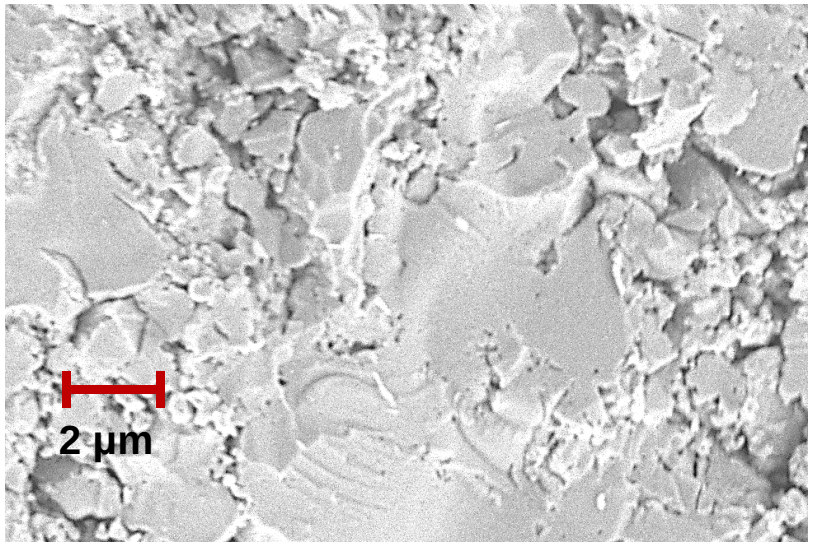


Boulineau et.al. Solid State Ionics (2012)

# CHARACTERIZATION

## MICROSCOPY



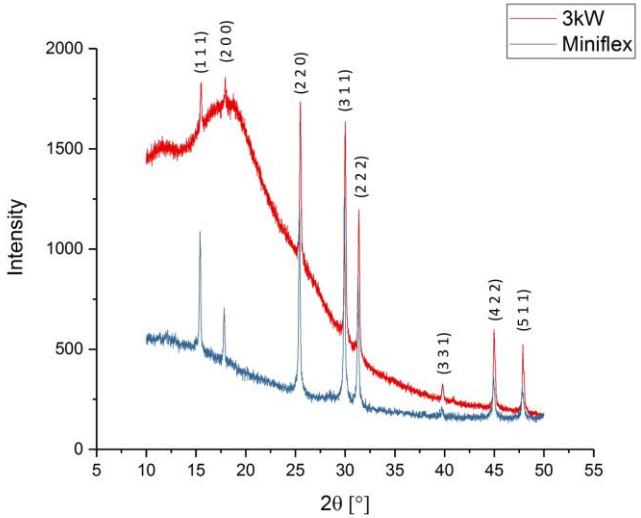

## ELECTROCHEMICAL

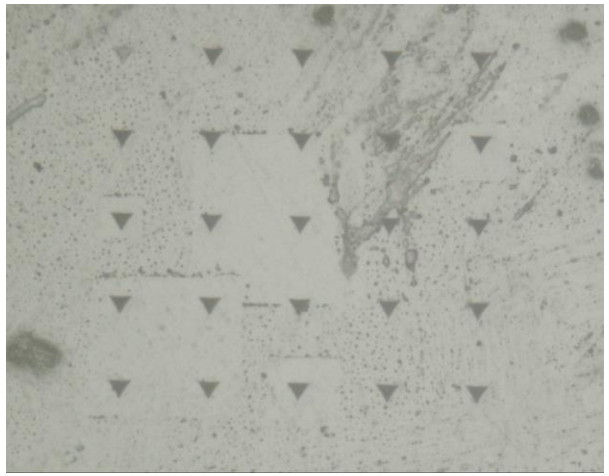
$\sigma_{Li+}$: ~3 mS/cm @ RT

5 mm

HENRY ROYCE INSTITUTE
ATOMS TO DEVICES

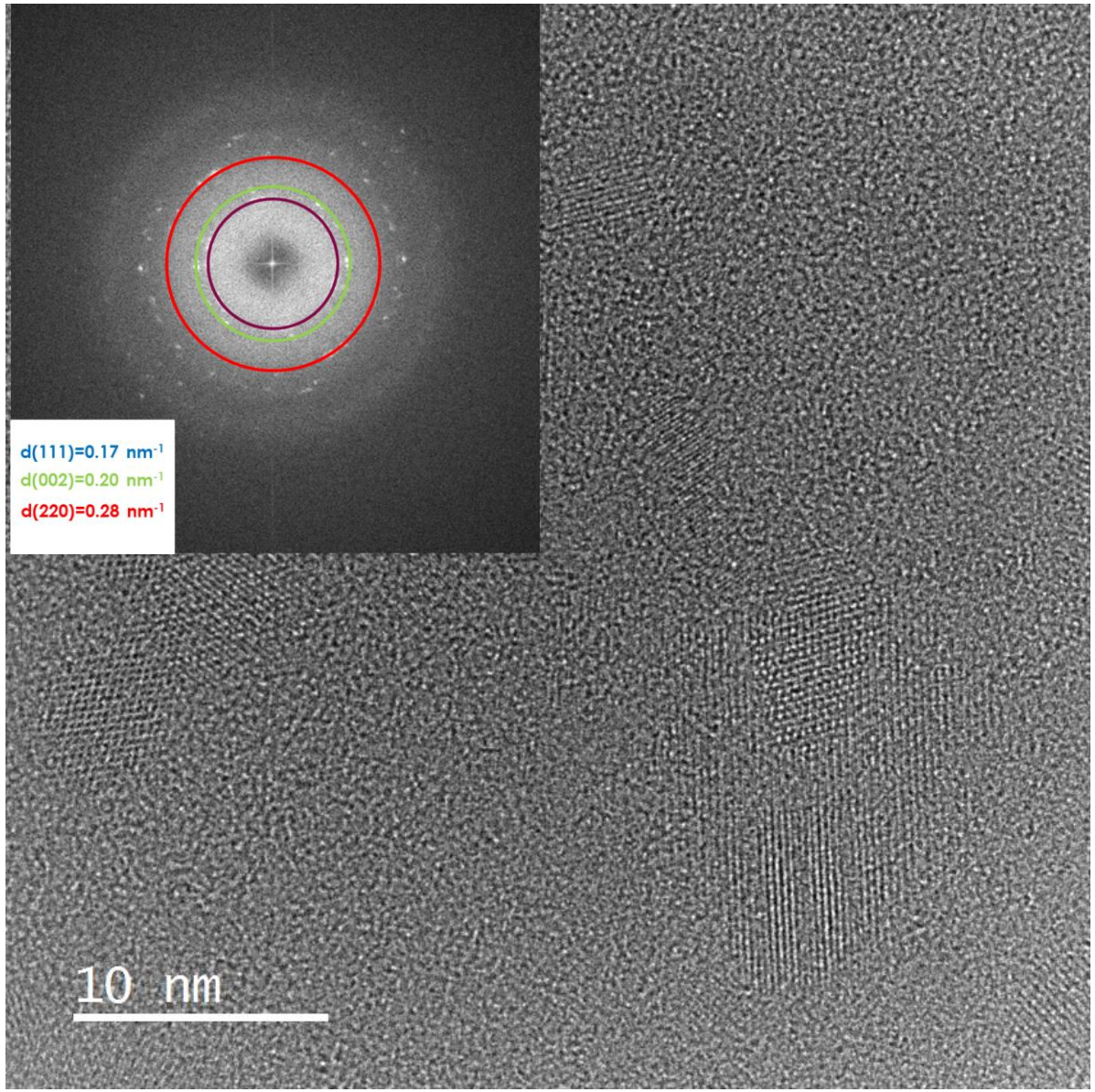
## STRUCTURAL

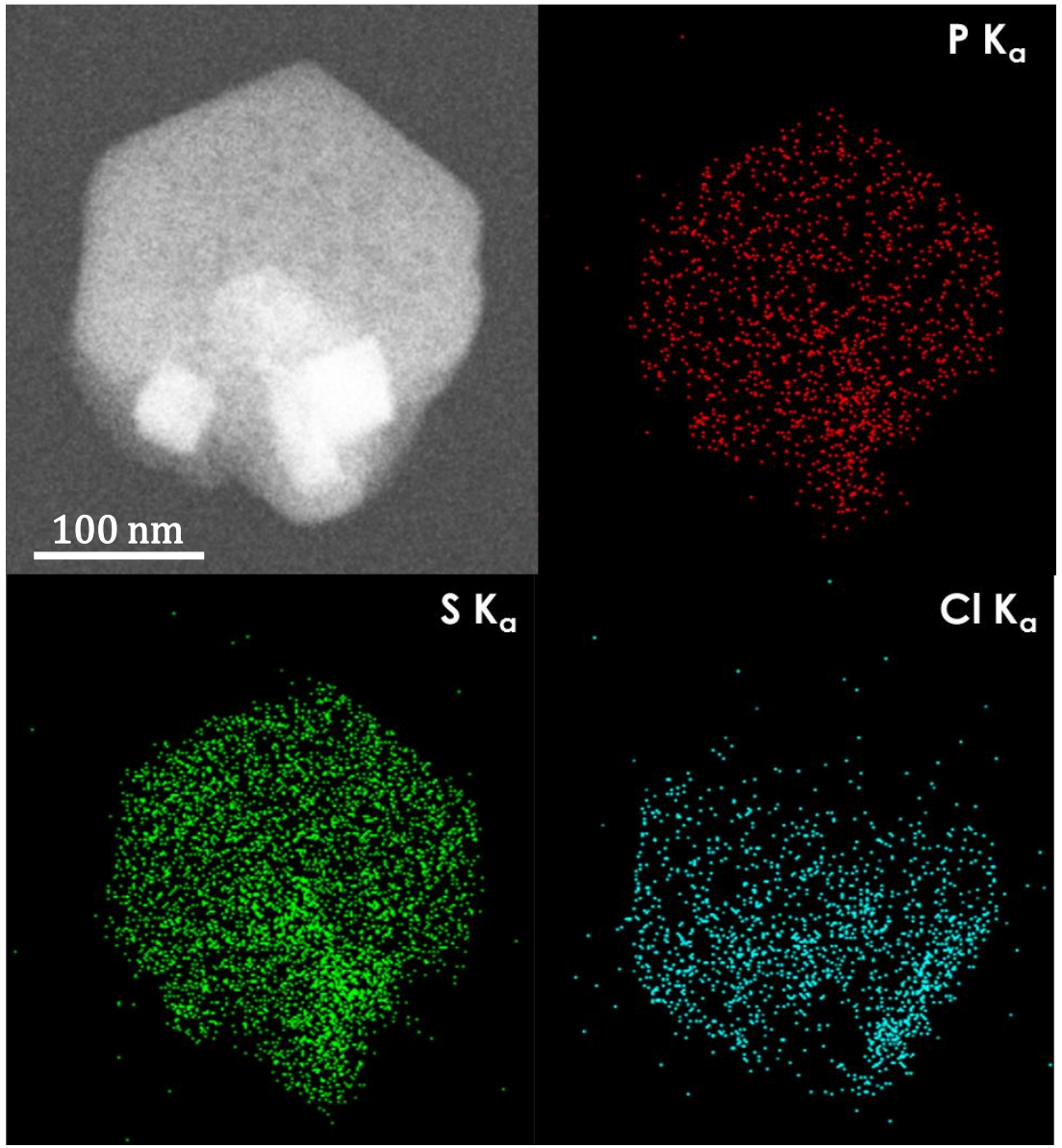


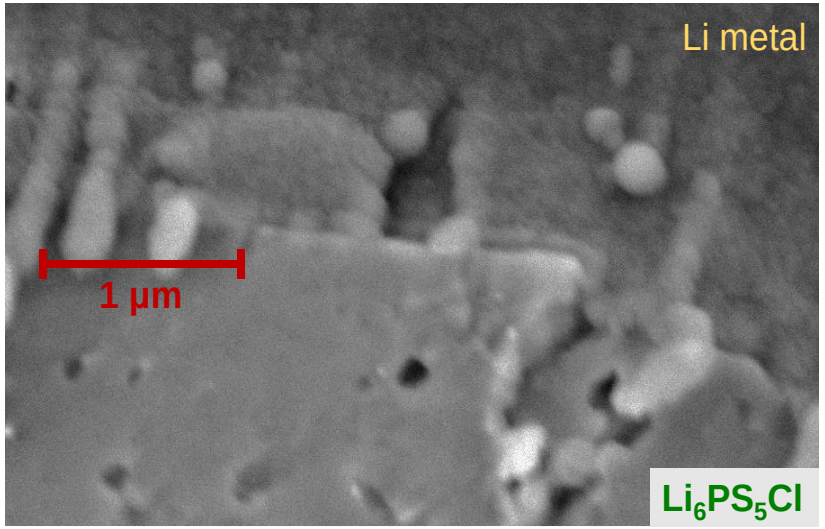
E = 15 ±3 GPa

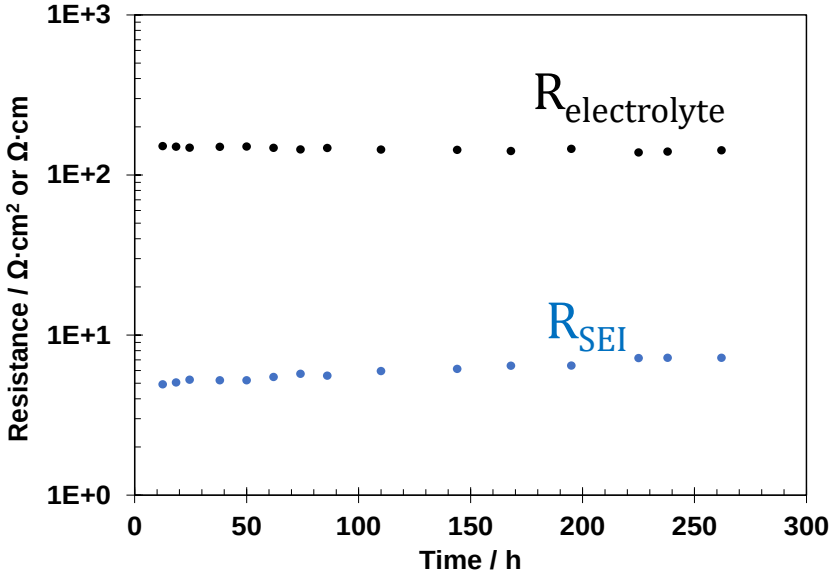
# HIGH-RESOLUTION PHASE CONSTRAST

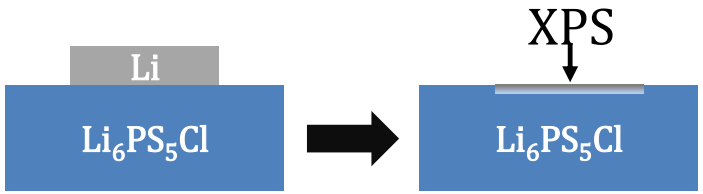


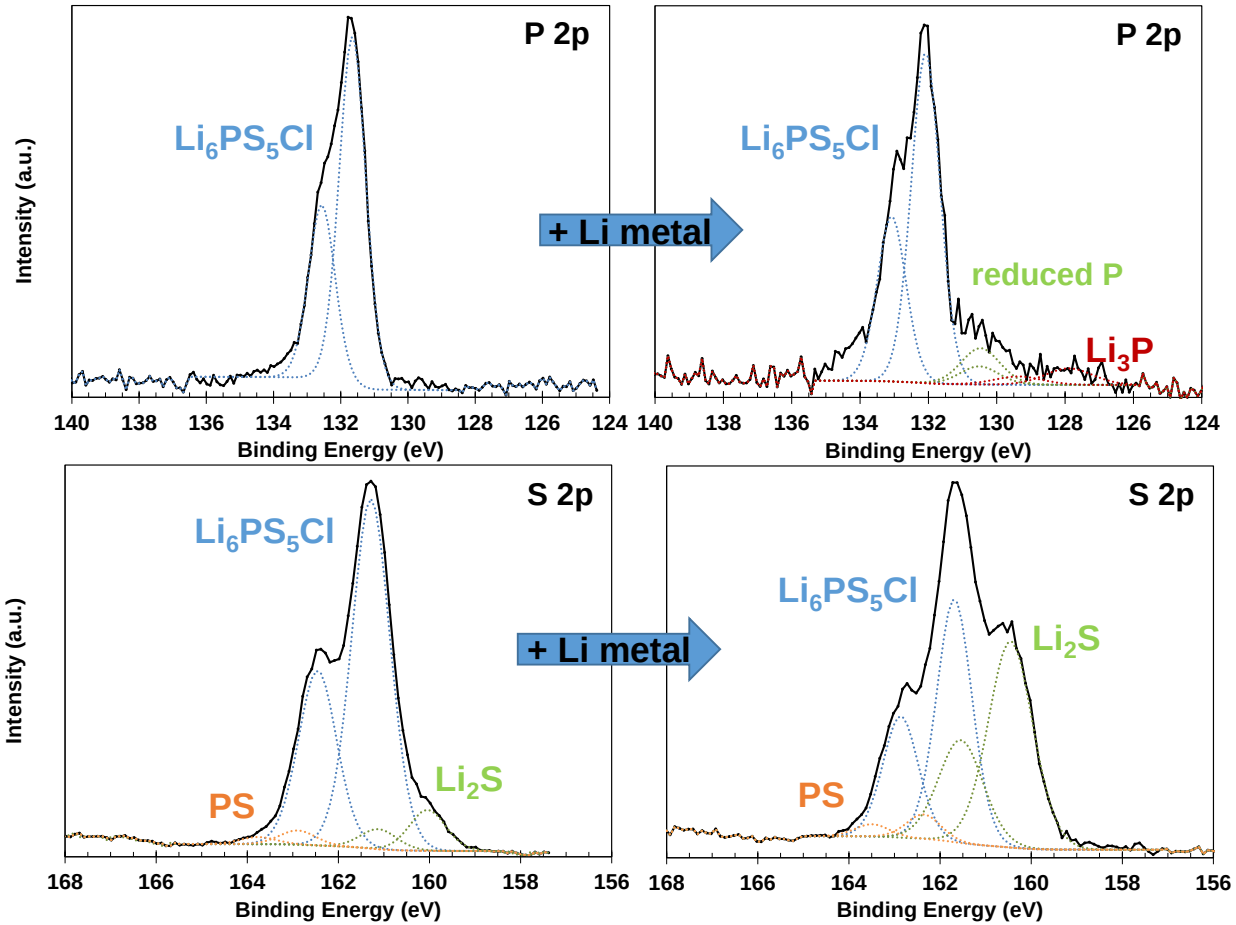



# SURFACE ANALYSIS

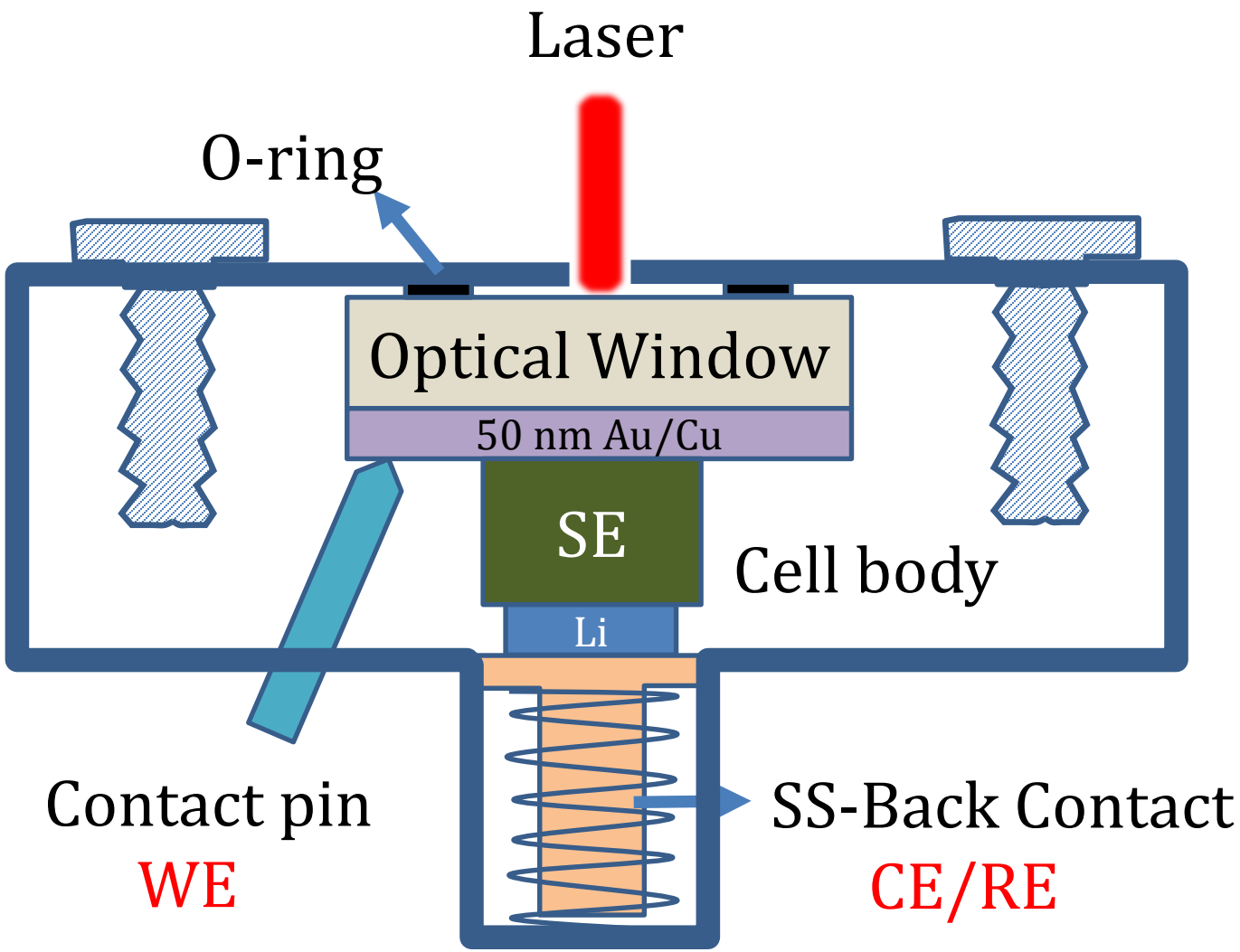


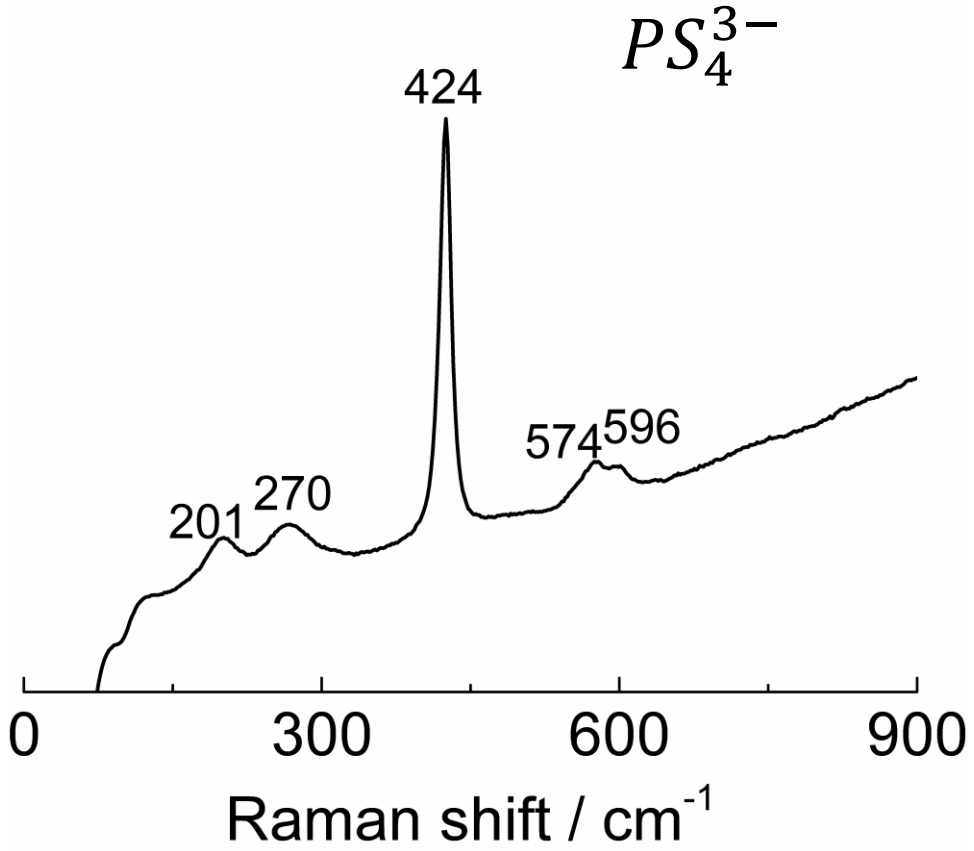



# IN-OPERANDO RAMAN



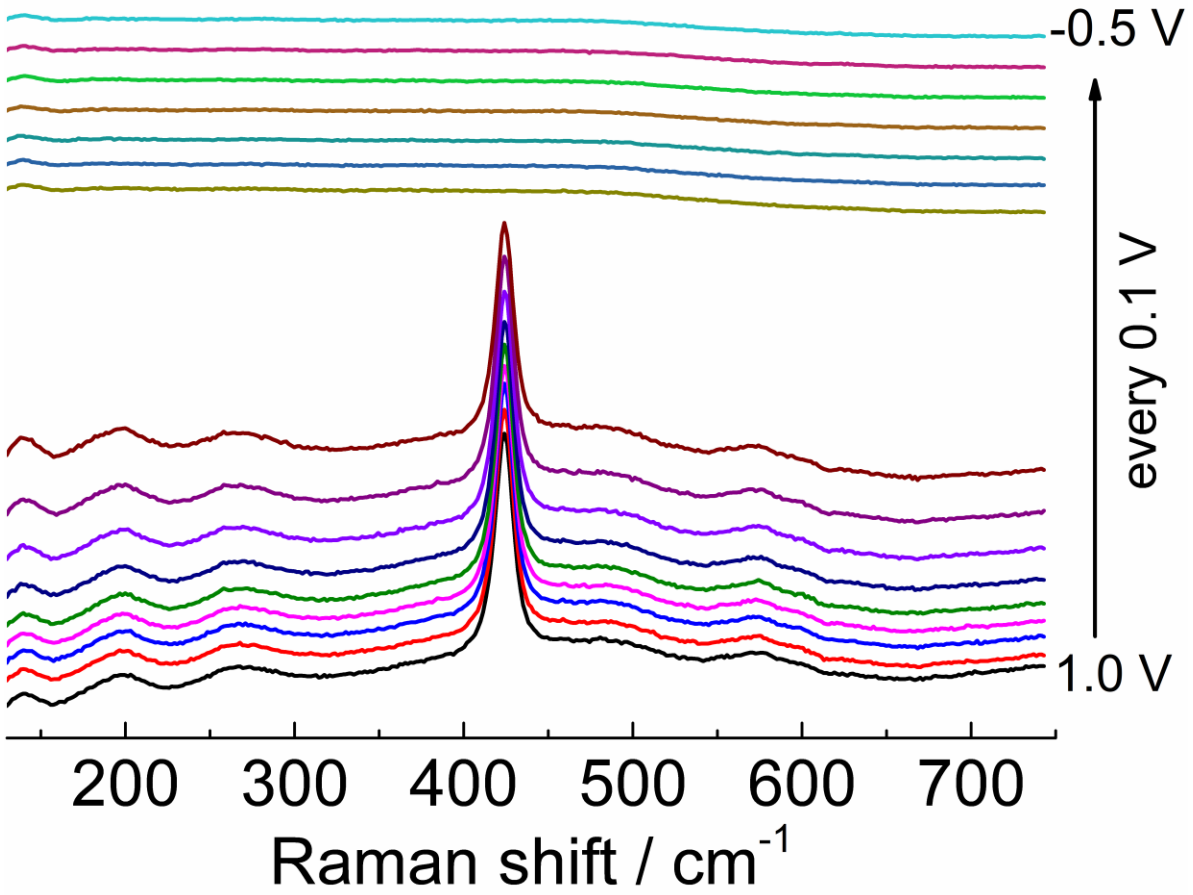

Raman spectra of bare $Li_6PS_5Cl$

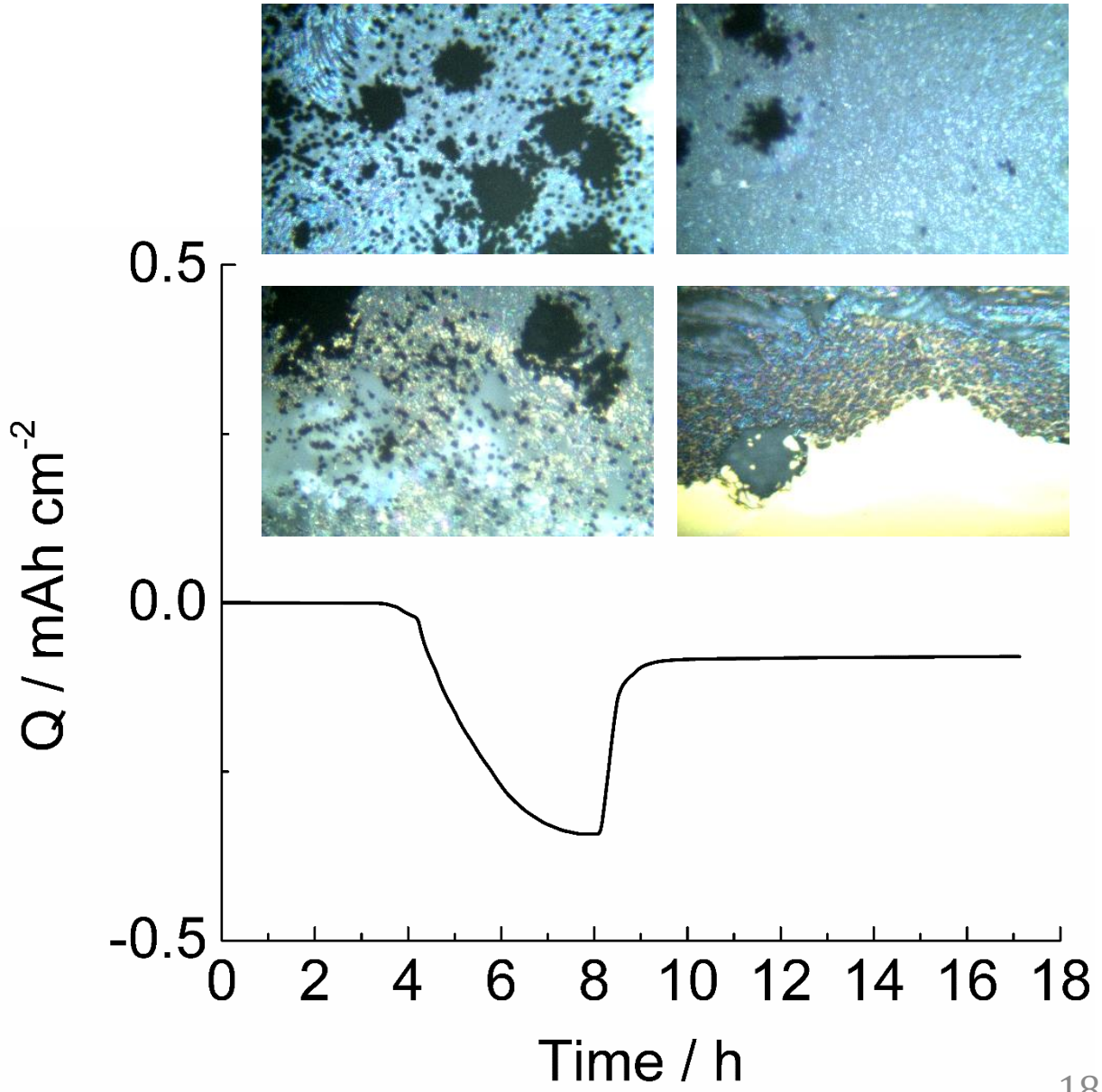



Journal of Power Sources 293 (2015) 941-945

# IN-OPERANDO RAMAN

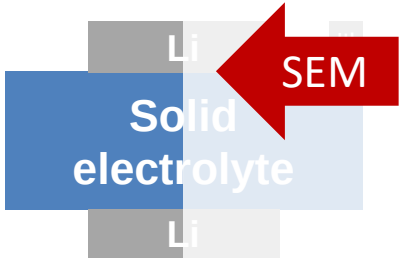
Potentiostatic: 15 minutes hold

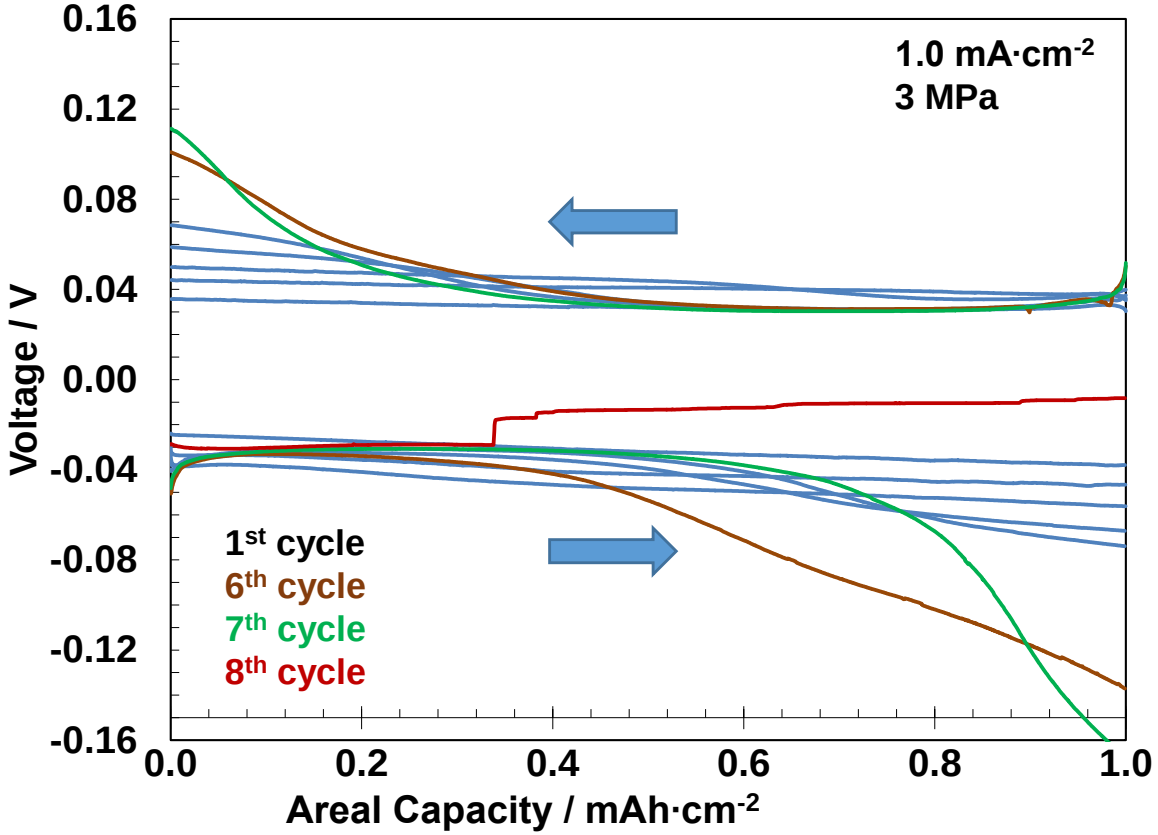


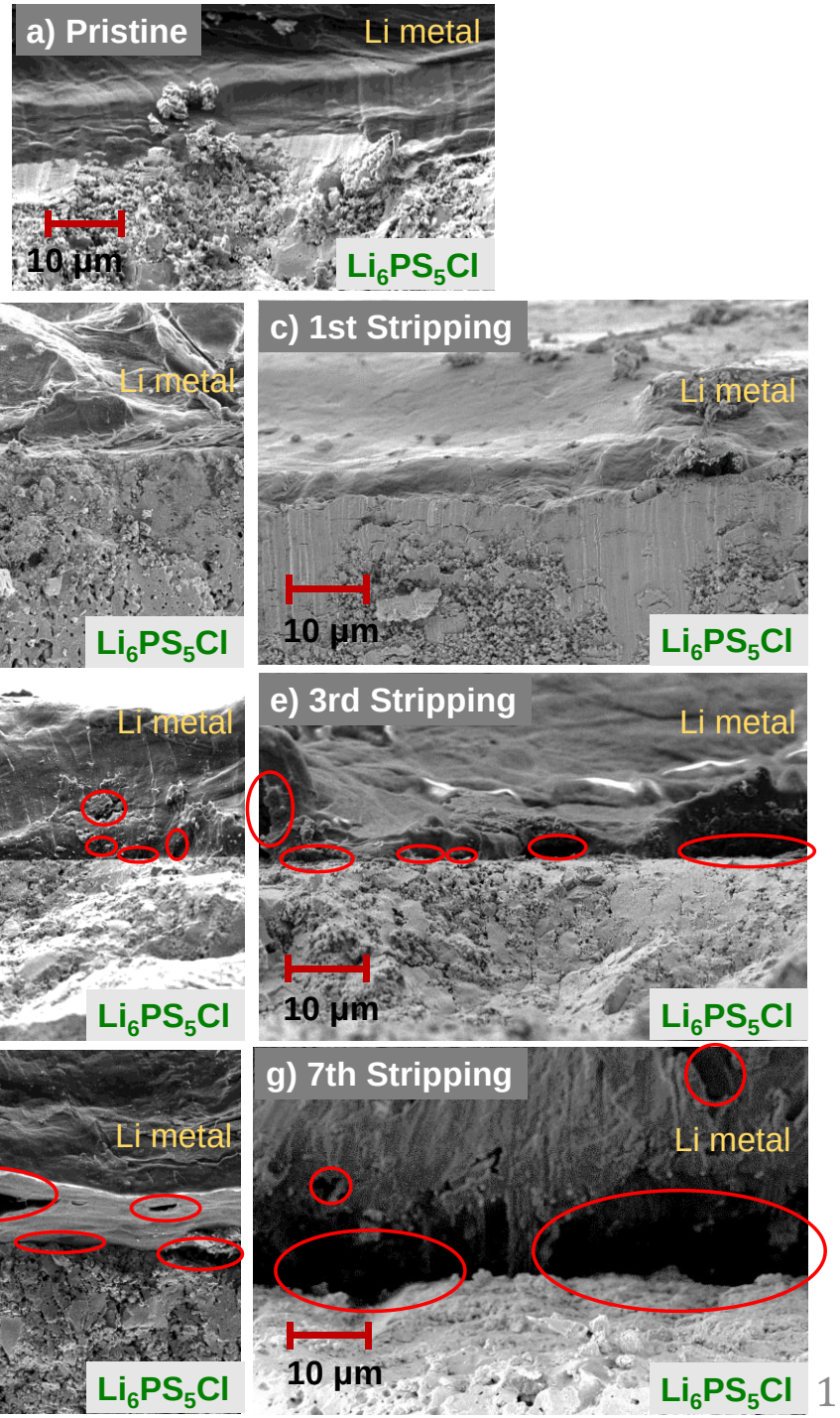



# EFFECT OF PRESSURE

## 1.0 mA/cm$^2$ 1.0 mAh/cm$^2$ 3 MPa

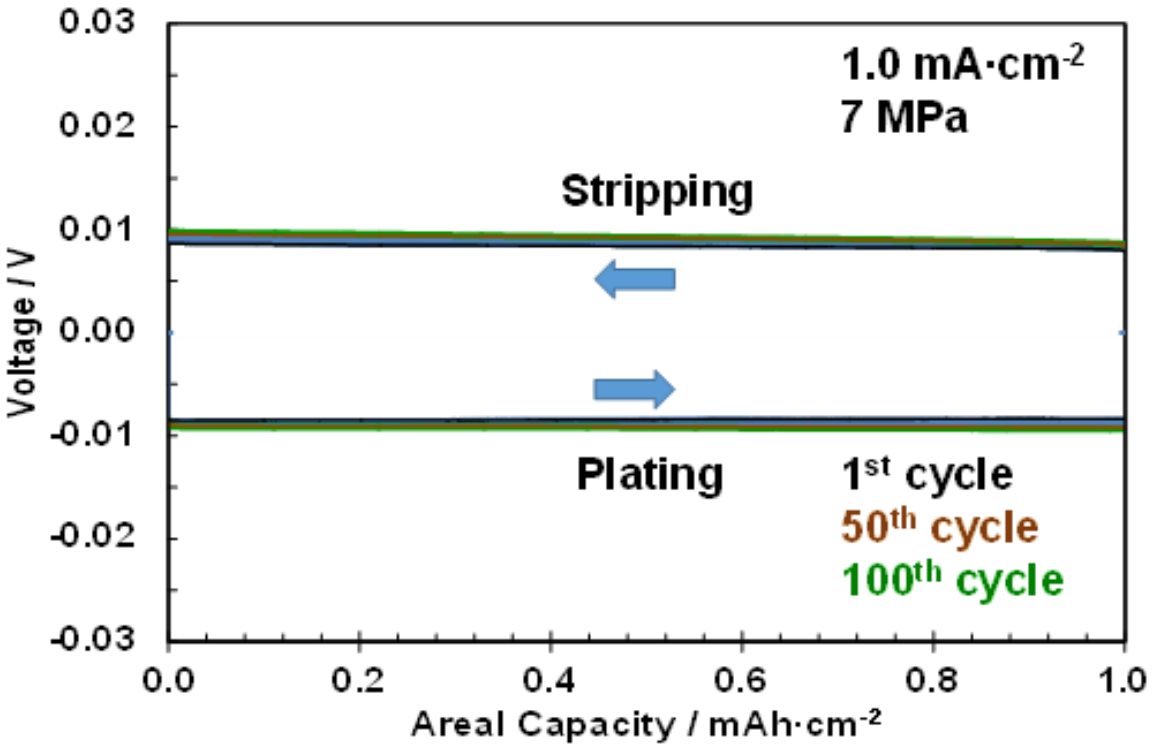


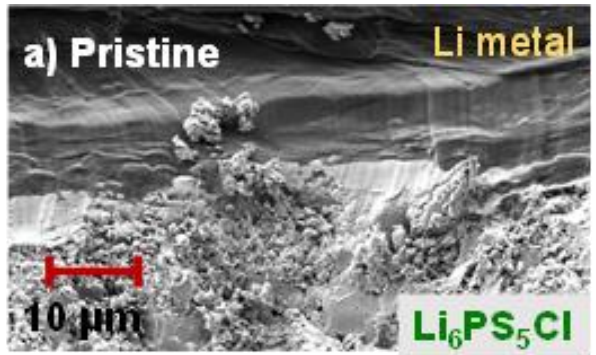



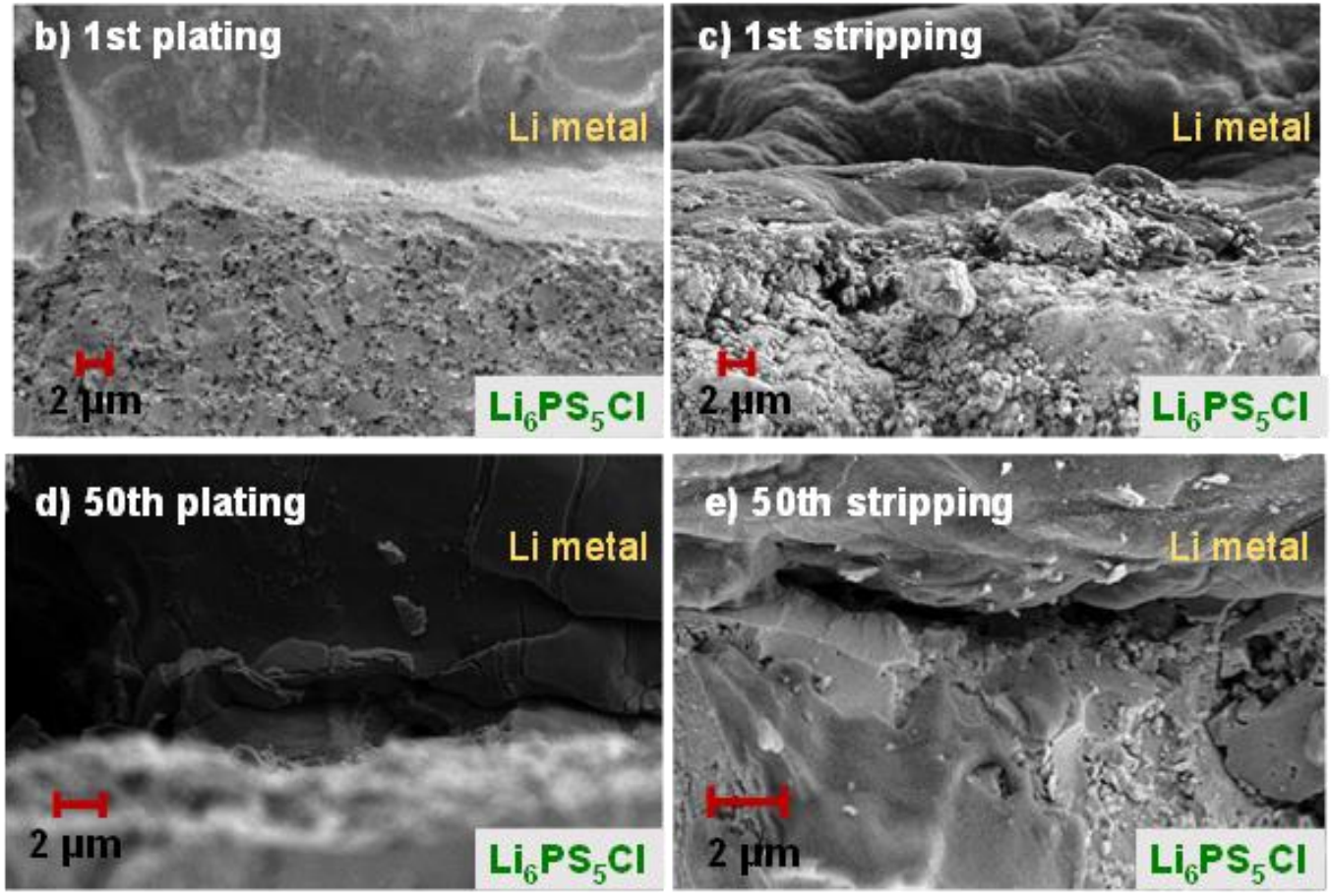



# EFFECT OF PRESSURE

## 1.0 mA/cm$^2$ 1.0 mAh/cm$^2$ 7 MPa



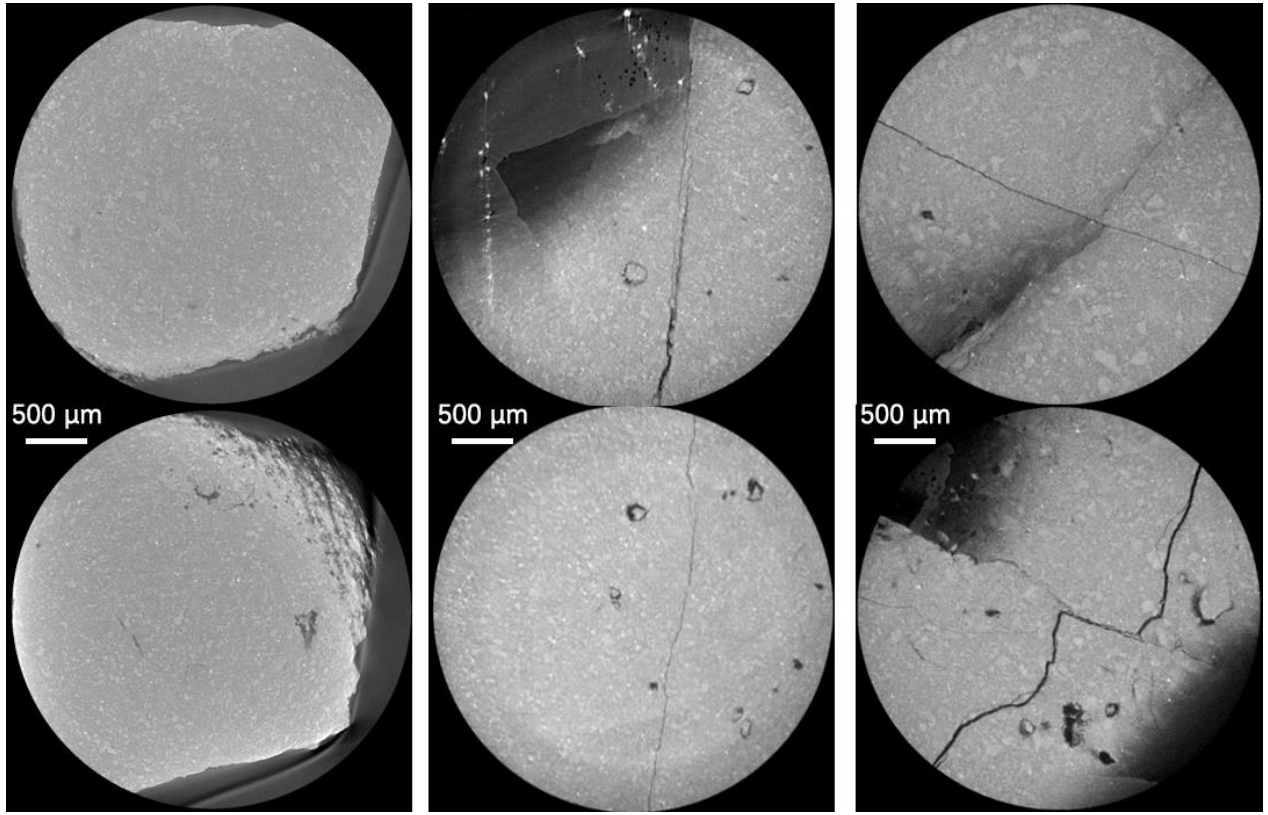
# X-RAY TOMOGRAPHY

## Effect of Current Density on Failure
## 7MPa

1mA/cm$^2$,
50 cycles

2mA/cm$^2$
failed in 3 cycles

3mA/cm$^2$
failed within 1 cycle



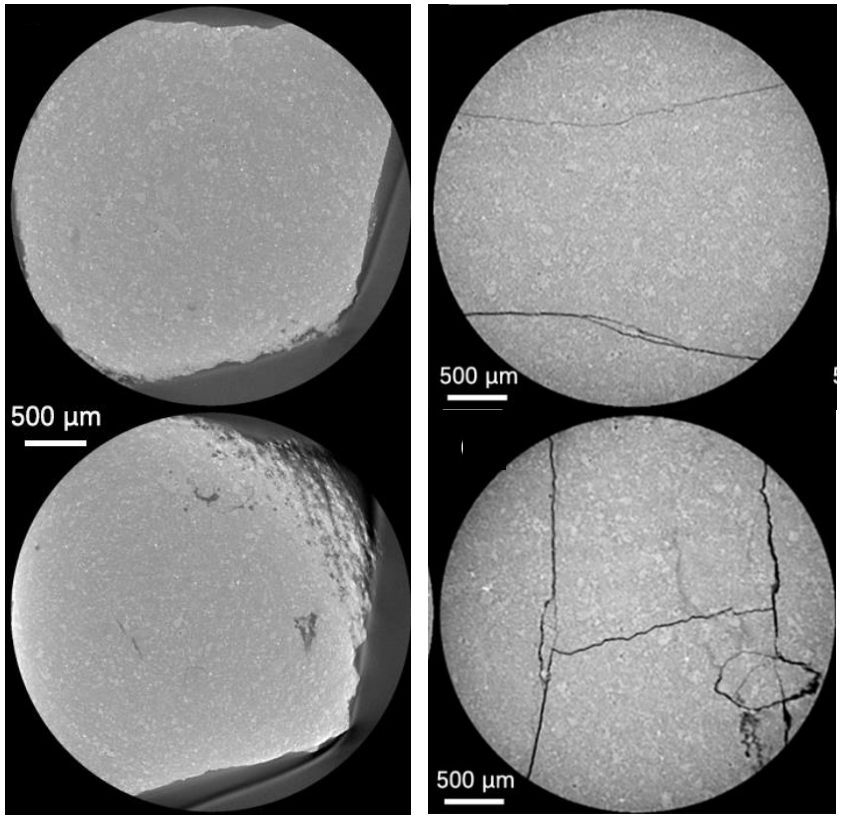

## Effect of Applied Pressure on Failure
## 1mA/cm$^2$

**7MPa**
50 cycles

3MPa
8 cycles, shorted

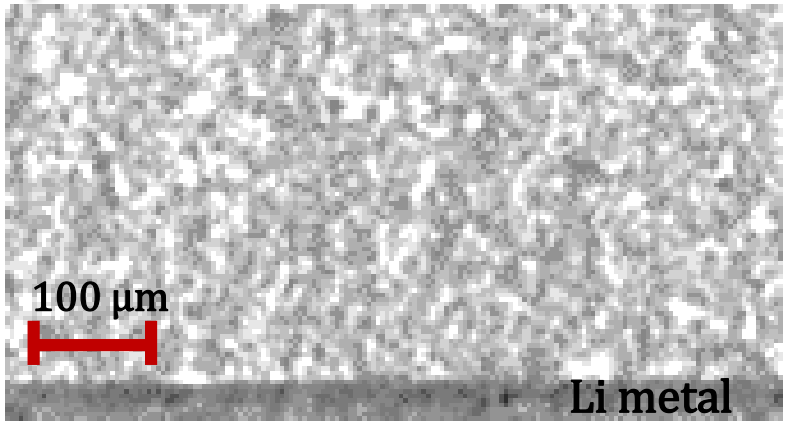
Top

Bottom

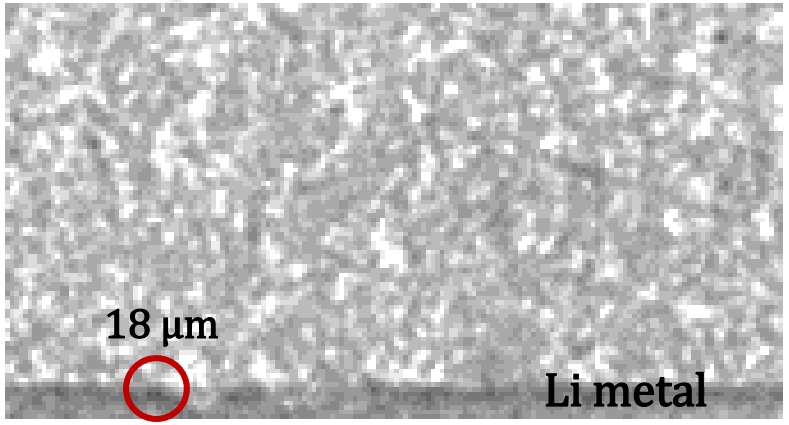


# VOID EVOLUTION

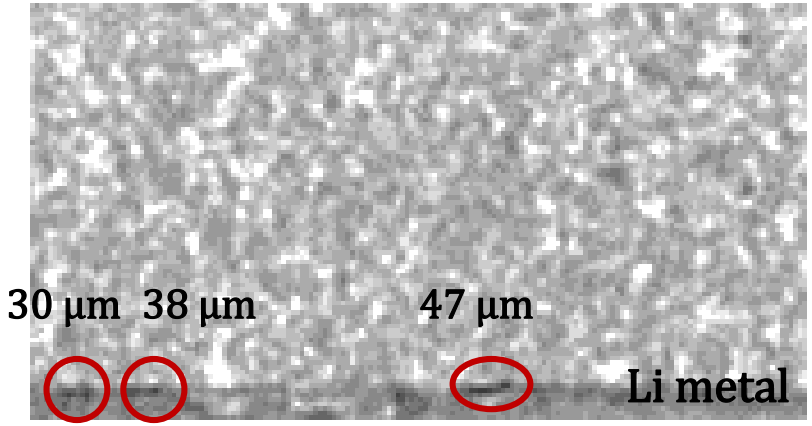
pristine



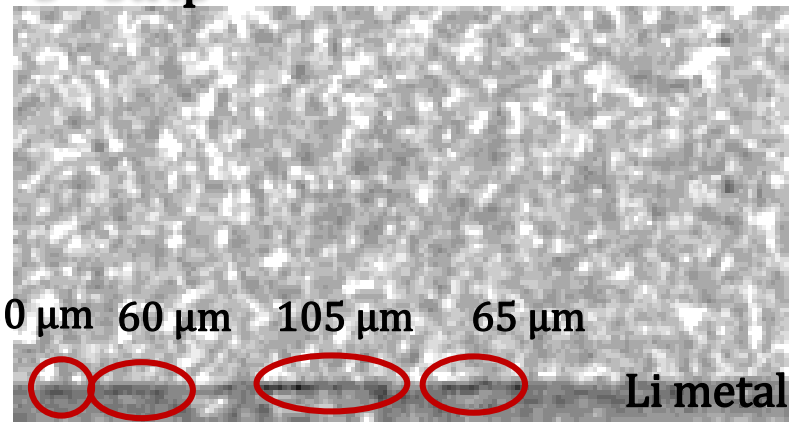

1st strip



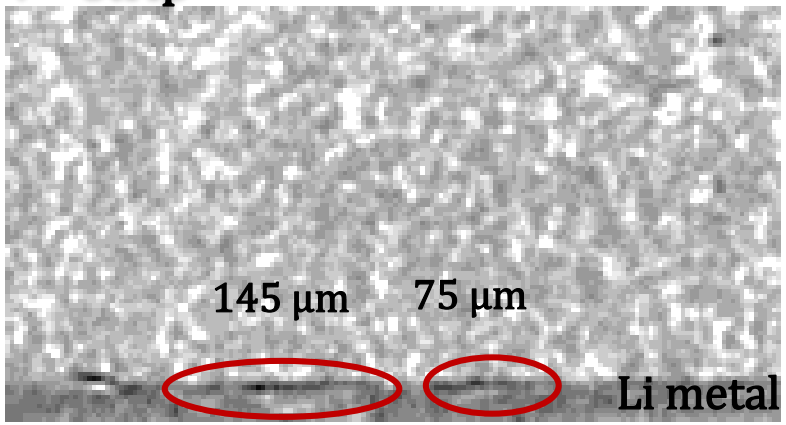

3rd strip




5th strip

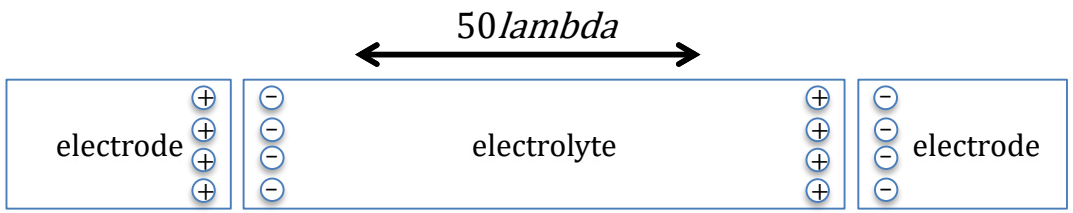



7th strip

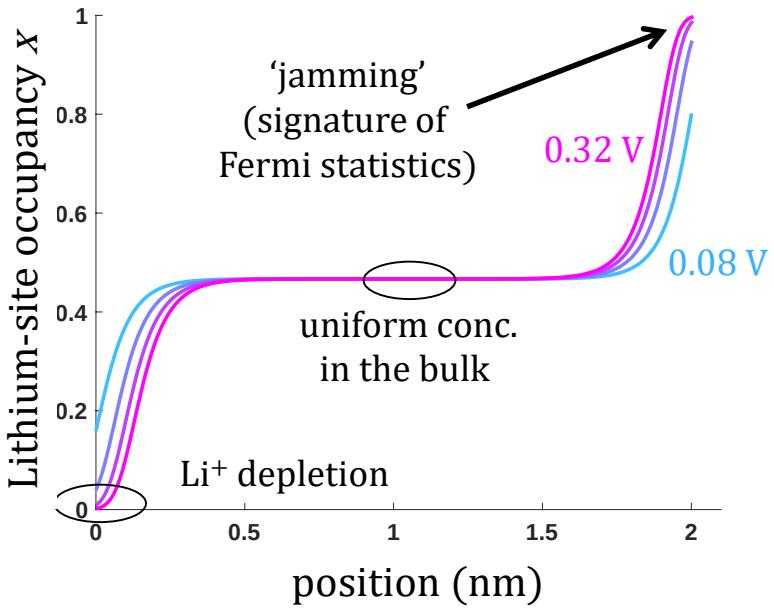


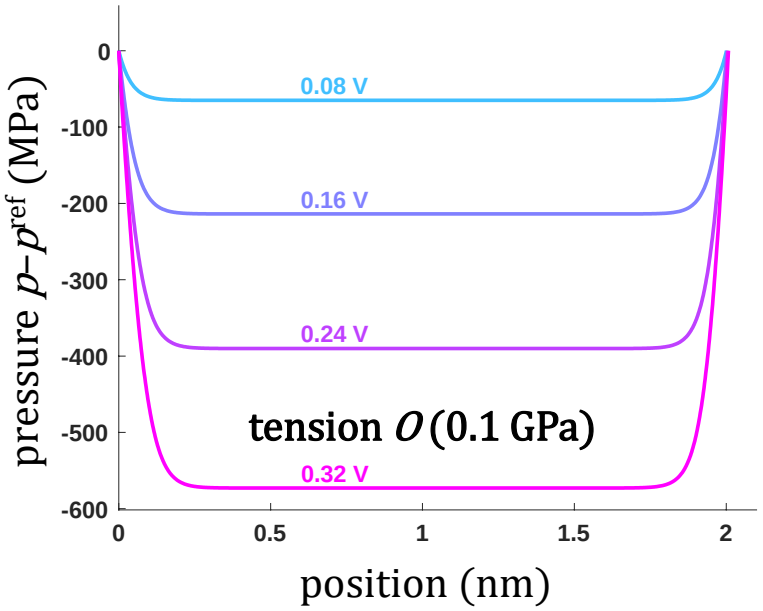
# ELECTRO-CHEMO-MECHANICS

Guanchen Li



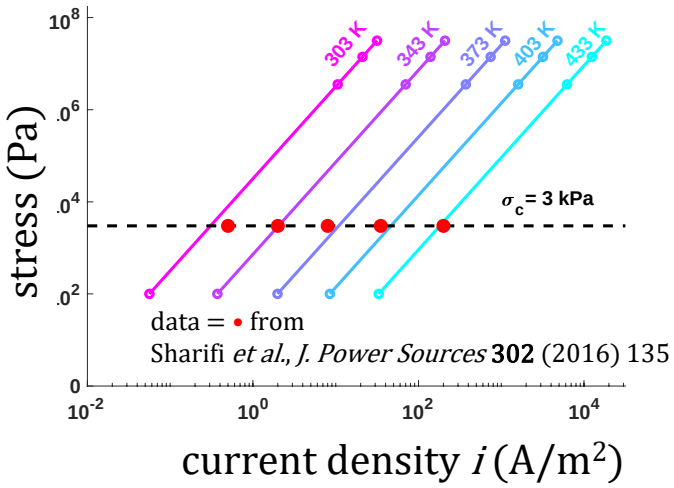

## Transport model output




Space charging (screening) in double layers produces large forces at the interface

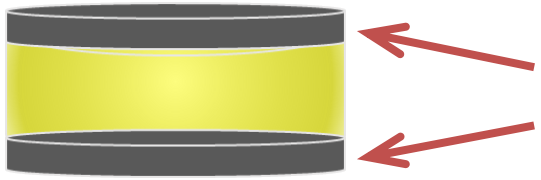
'Critical current' or 'critical stress'?




A simple predictor:

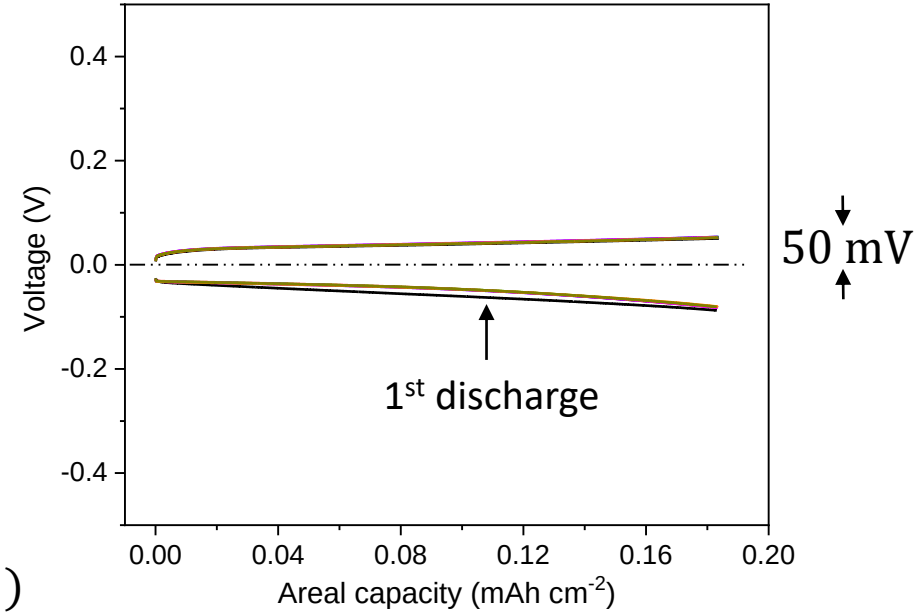
$$i_c \propto R_{int}^{-1} \cdot C_{int}^{-1} \cdot d^{-0.5} \cdot \left(2\gamma_{Li|SE} - \gamma_{GB}\right)^{0.5}$$

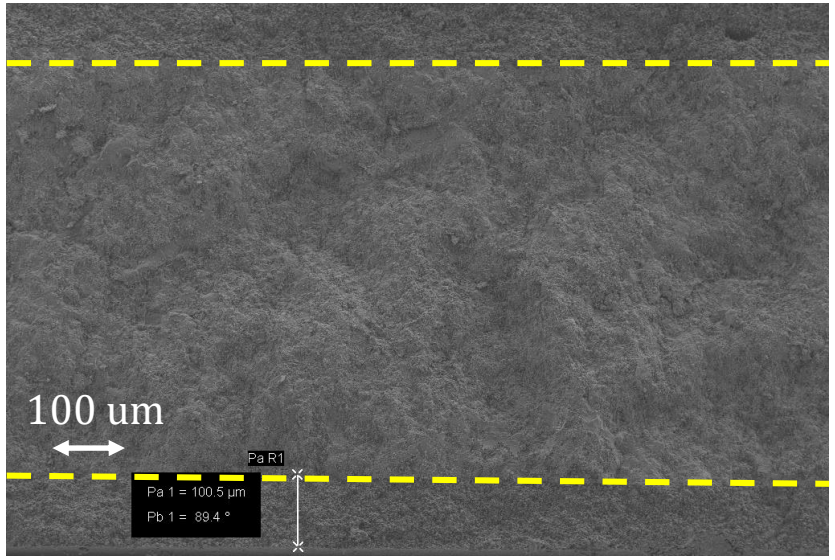
# ALL-SOLID-STATE: LTO| $Li_6PS_5Cl$|LTO



$Li_{4+x}Ti_5O_{12}$/**$Li_6PS_5Cl$**/Super P
(3:6:1, mass)

Stack pressure: 2.5 MPa
Current density: 0.1 mA·cm$^{-2}$ (0.1 mA g$^{-1}$)

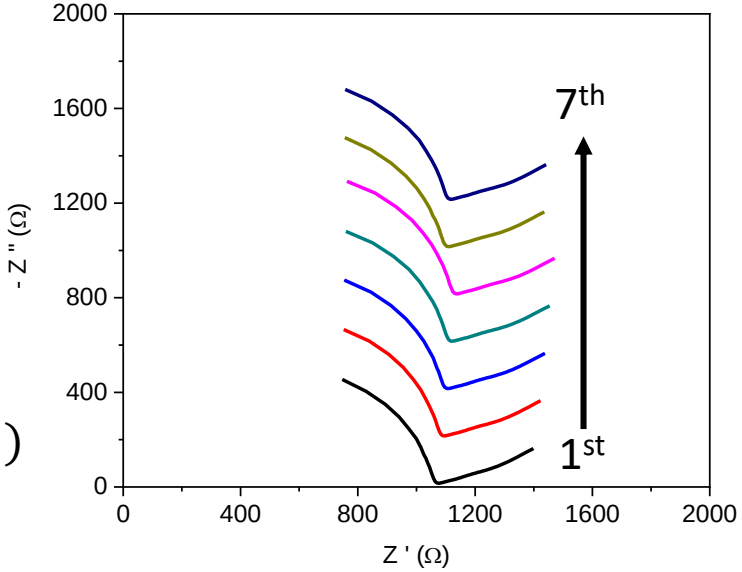



PreLTO : LiPSC : C (3: 6: 1 by mass )
100 um

$Li_6PS_5Cl$ 588 um

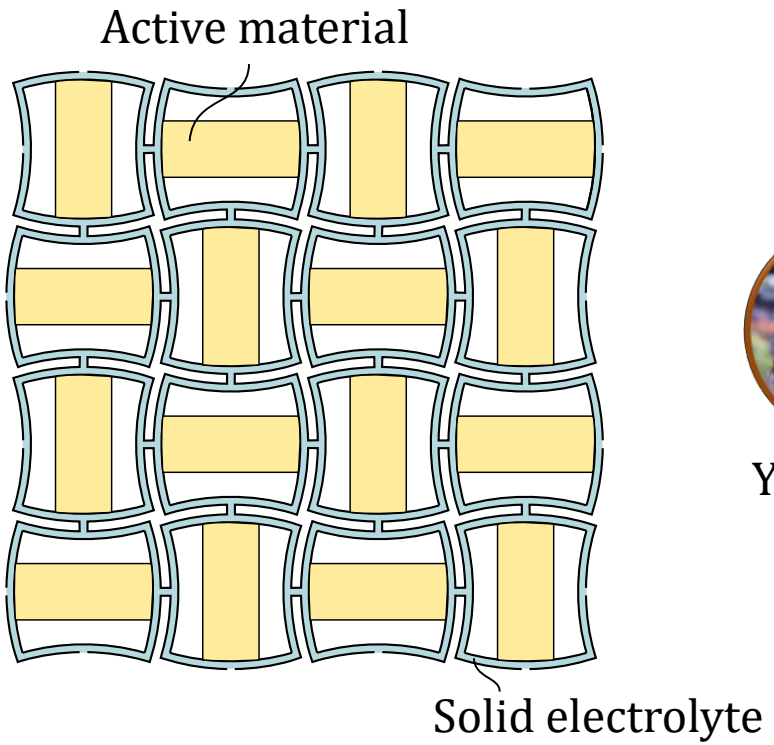
PreLTO : LiPSC : C (3: 6 : 1 by mass )
100 um



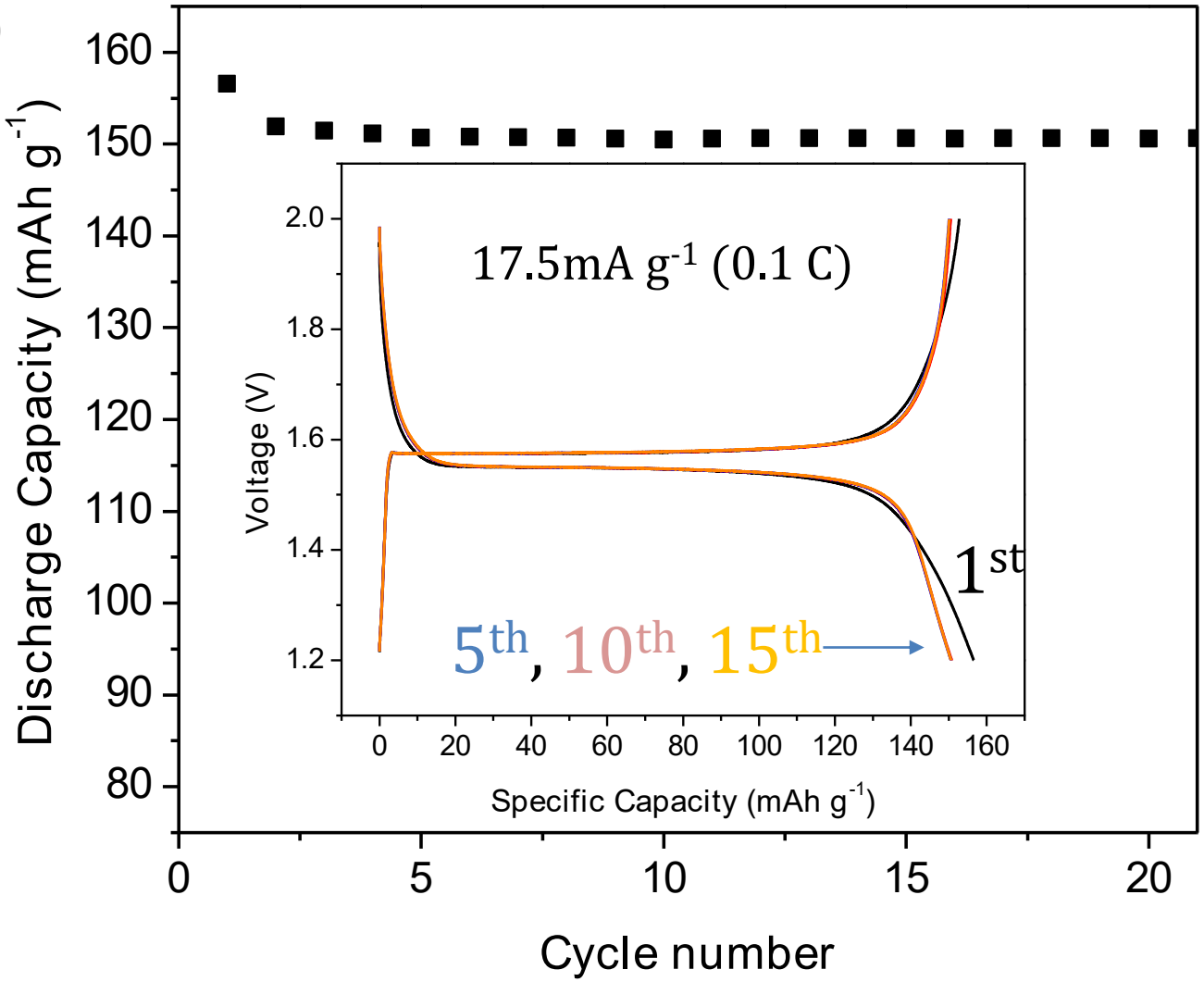
# ALL-SOLID-STATE: LTO| $Li_6PS_5Cl$|Li

$Li_{4+x}Ti_5O_{12}$/**$Li_6PS_5Cl$**/Super P
(Cathode =3:6:1, mass)

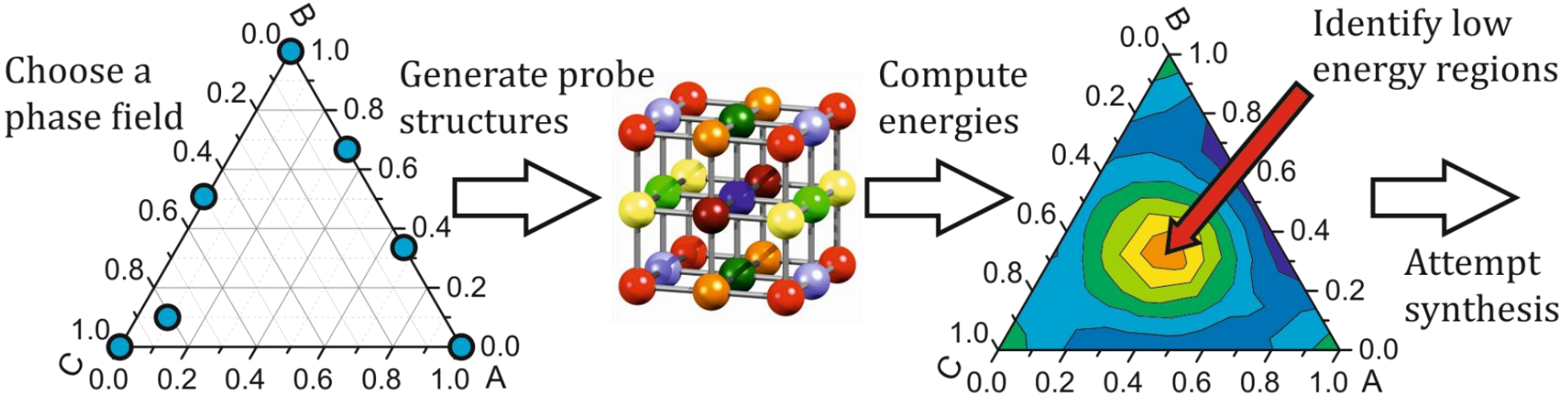
Li metal



Ying Zhao

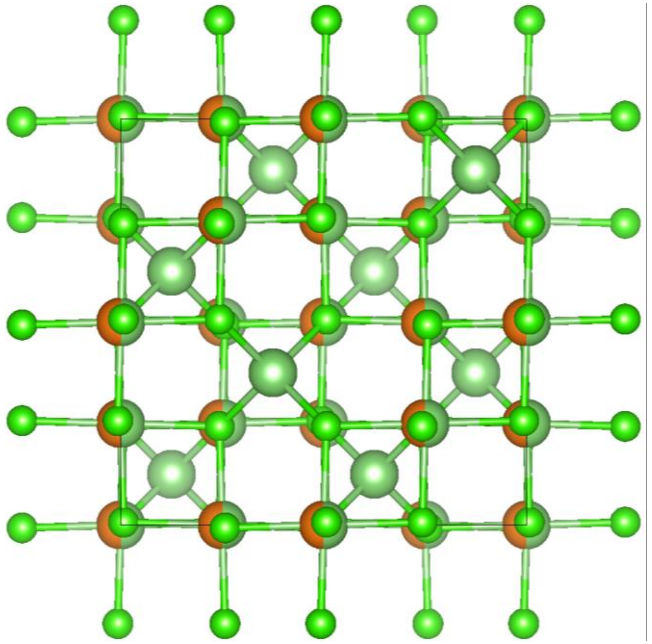


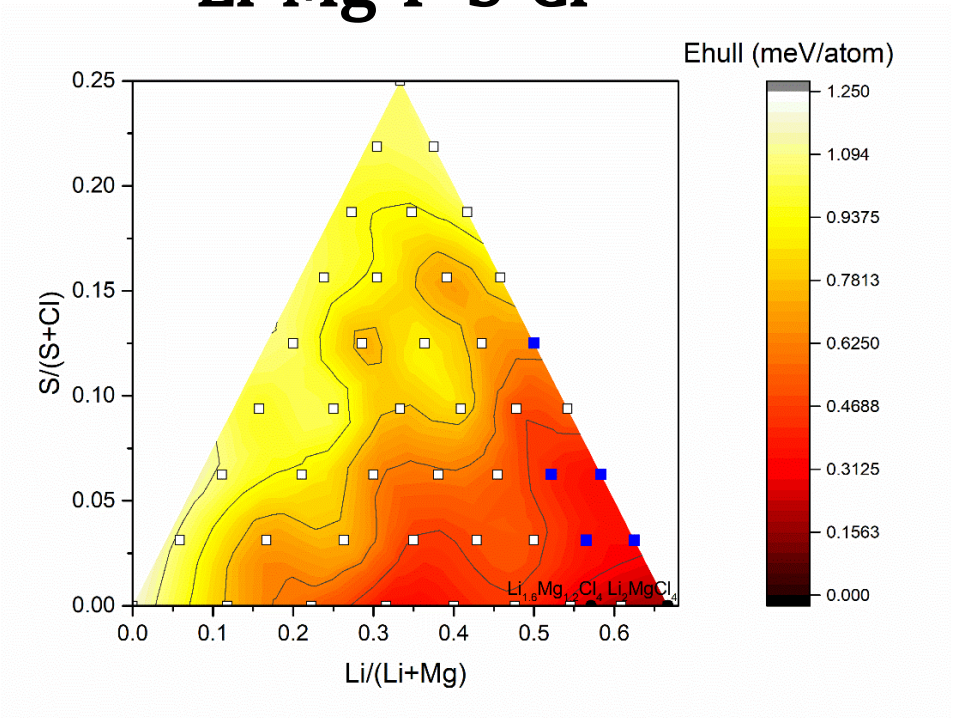
# PROBE-STRUCTURE BASED DISCOVERY

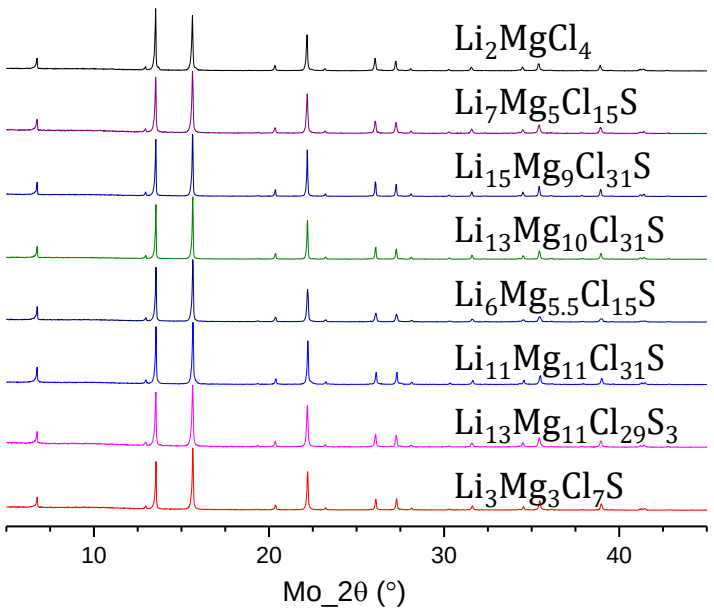


Paul Sharp

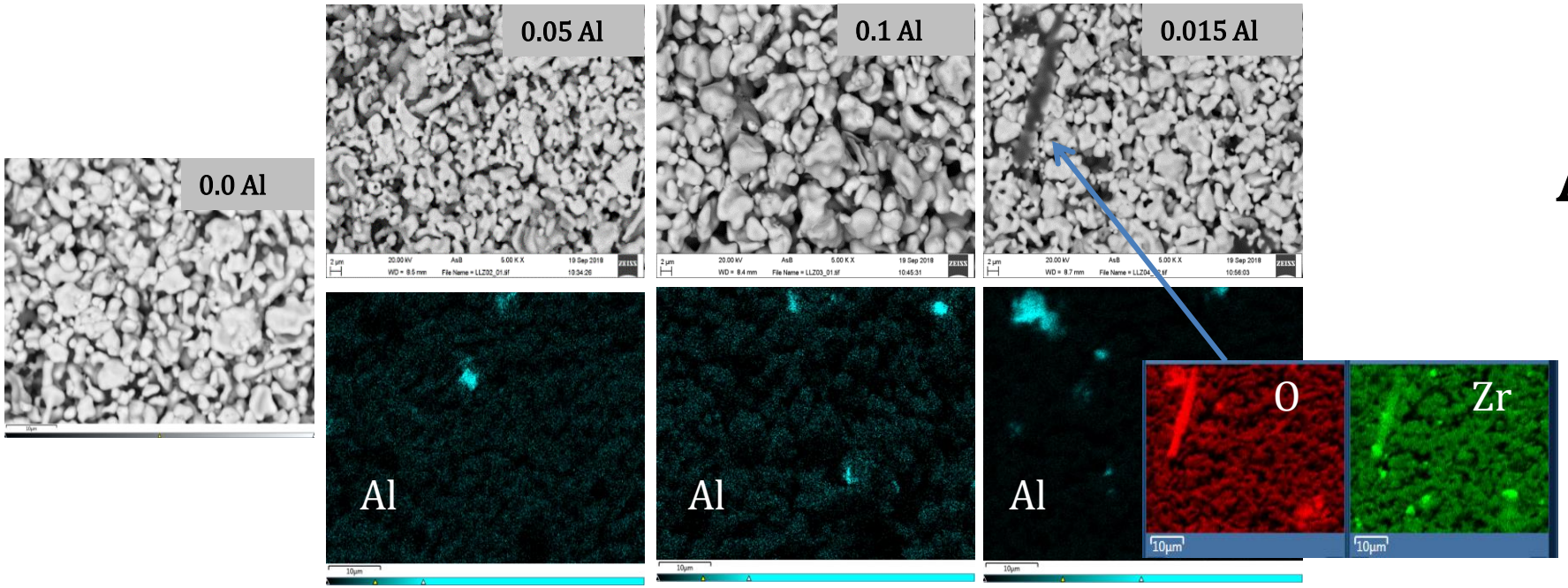
## Li-Mg-P-S-Cl



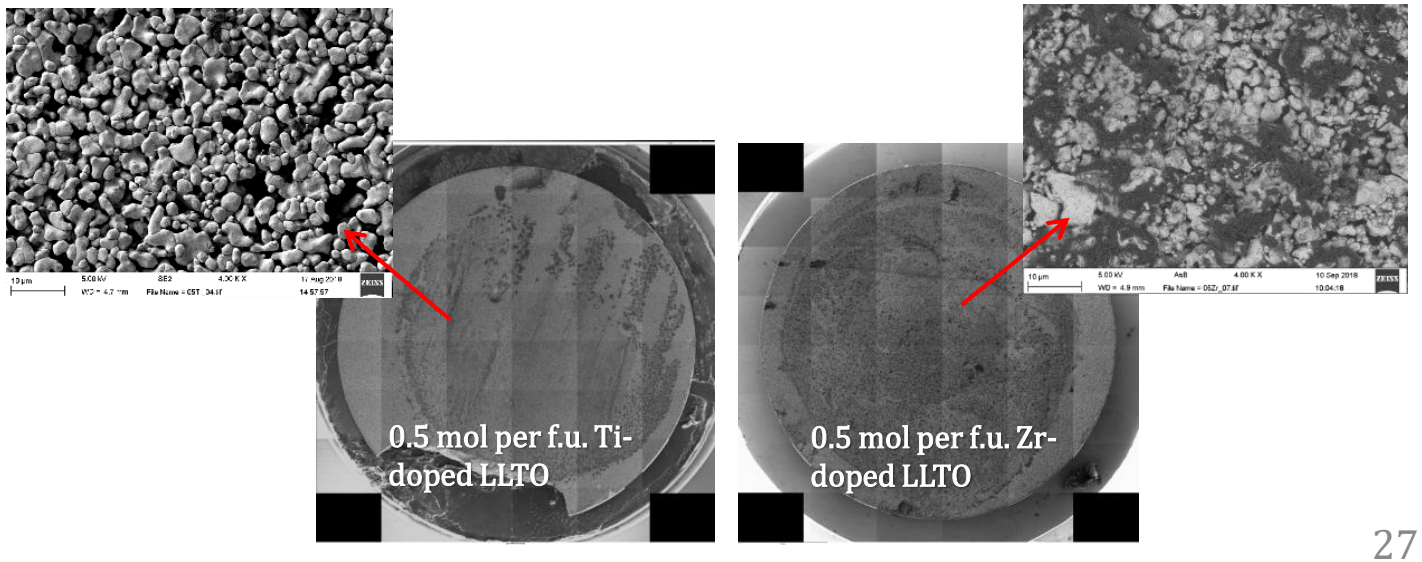


# OXIDES: LLZO

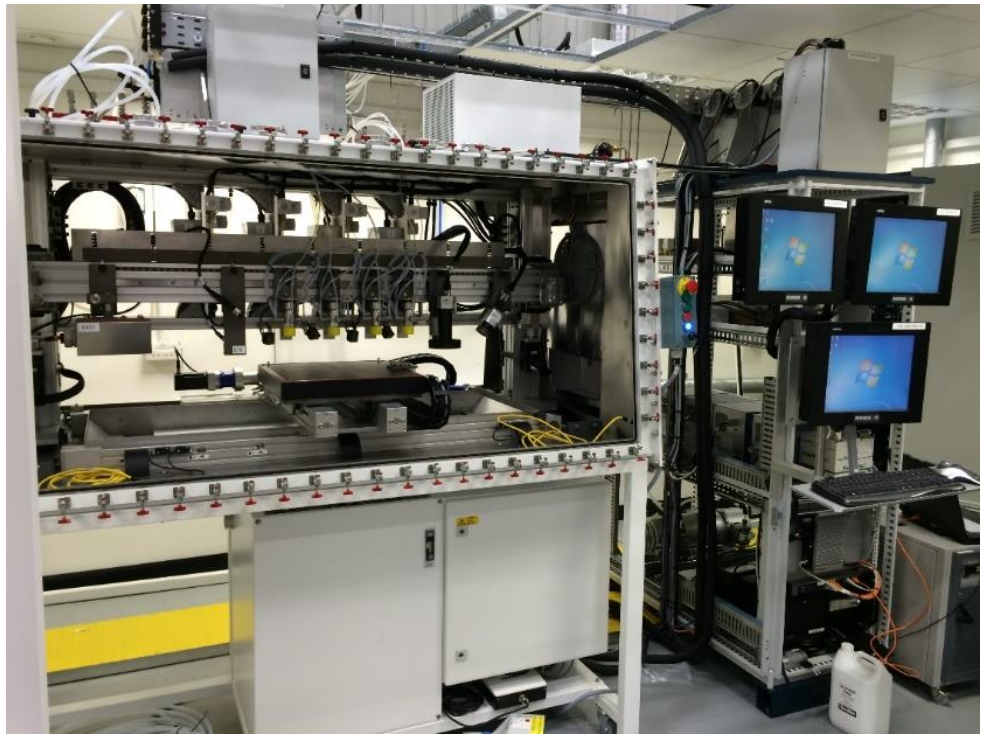


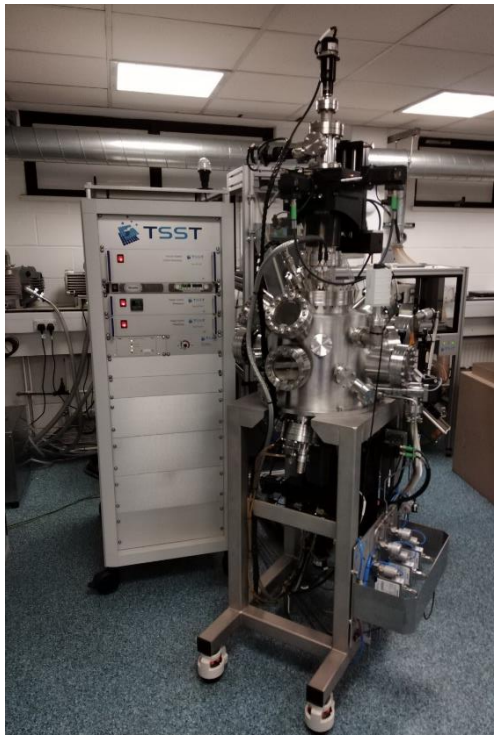

Al-doped LLZTO

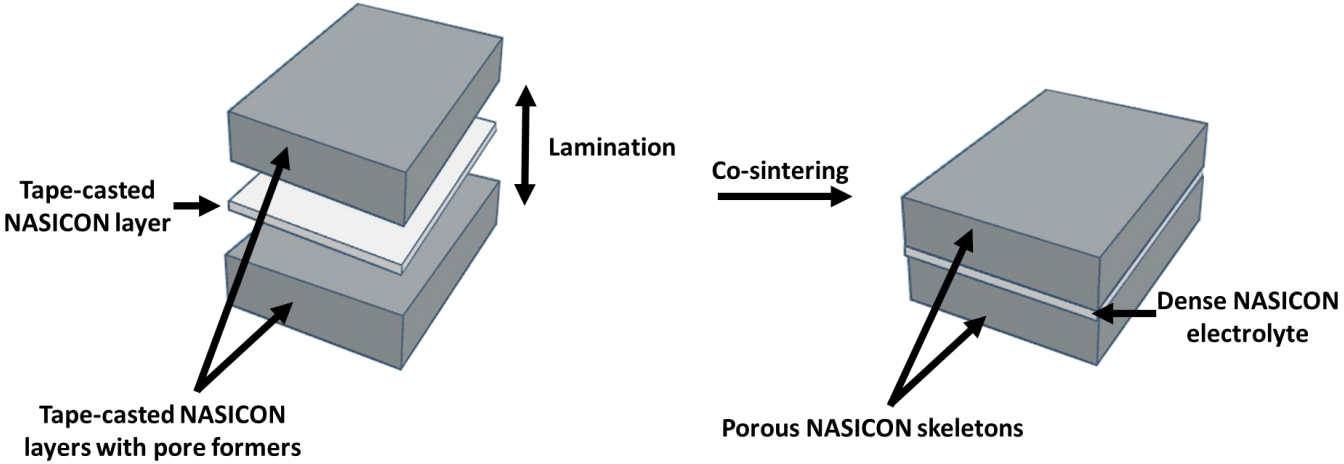



Ti and Zr-doped LLTO

# DEVICE FABRICATION





Mihkel Vestli

# INDUSTRIAL INTERACTION

Morgan Advanced Materials

JAGUAR

LAND ROVER

TOSHIBA

NISSAN

oxis ENERGY

PRAXAIR

CORNING

ilika

HONDA

TOYOTA

# PDRA PRESENTATIONS

Dr. Guanchen Li
Prof. Monroe's group
University of Oxford

**Dendrite nucleation in polycrystalline lithium-conductive ceramics**

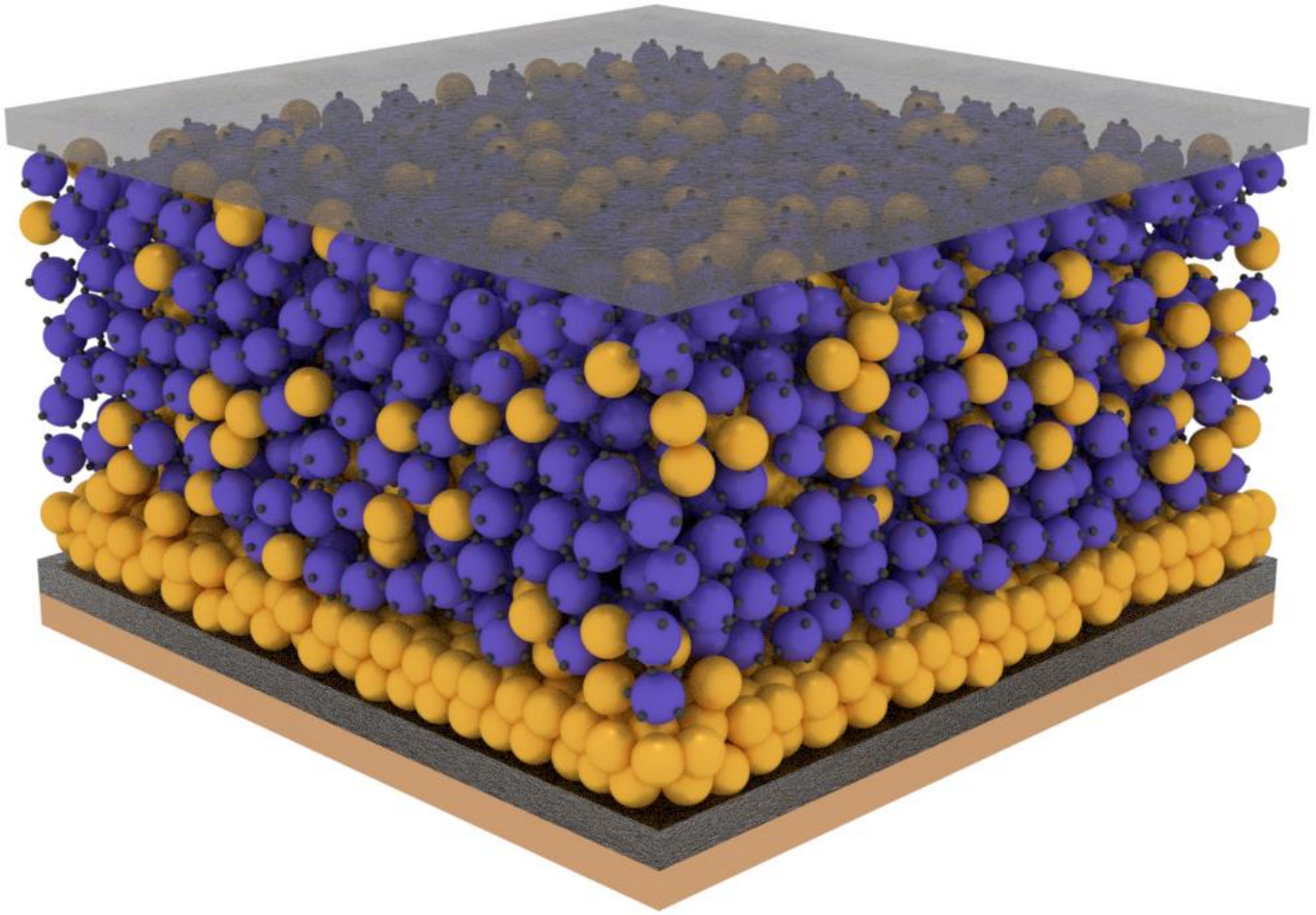
Dr. Ying Zhao
Prof. Fleck's group
University of Cambridge

**Towards an Optimized Composite Cathode Structure**

Dr. Paul Sharp
Prof. Rosseinsky's group
University of Liverpool

**Using Probe Structures to Explore the Li-Mg-P-S-Cl Phase Field with ChemDASH**

Dr. Mihkel Vestli
Prof. Irvine's group
University of St. Andrews

**Tape-casting of NASICON-based solid state battery**

# SOLBAT: solid-state metal anodes (day 1)