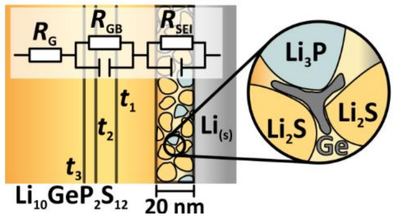
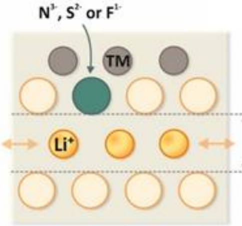
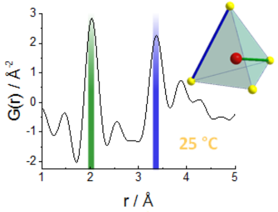
Karlsruher Institut für Technologie







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Solid State Batteries – Cell concepts and electrodes

J. Janek
Physikalisch-chemisches Institut, Justus-Liebig-University Gießen
& BELLA – Batteries and Electrochemistry Laboratory, INT, KIT

- „Solidifying“ lithium ion batteries?
- Solid electrolytes as components of „next gen“ cells?
- Enabling Li metal electrodes?

→ No thin film batteries! → „Thick electrode“ batteries (≈ 10^2 µm)
→ Talk excludes polymer-based batteries

BASF International Network on Electrochemistry

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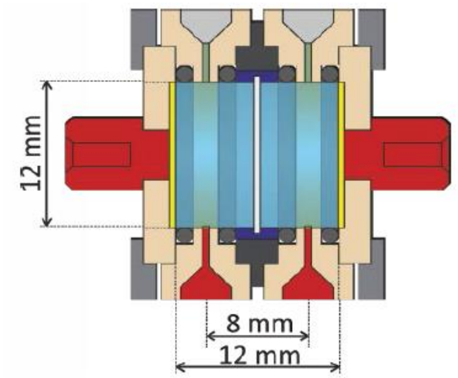
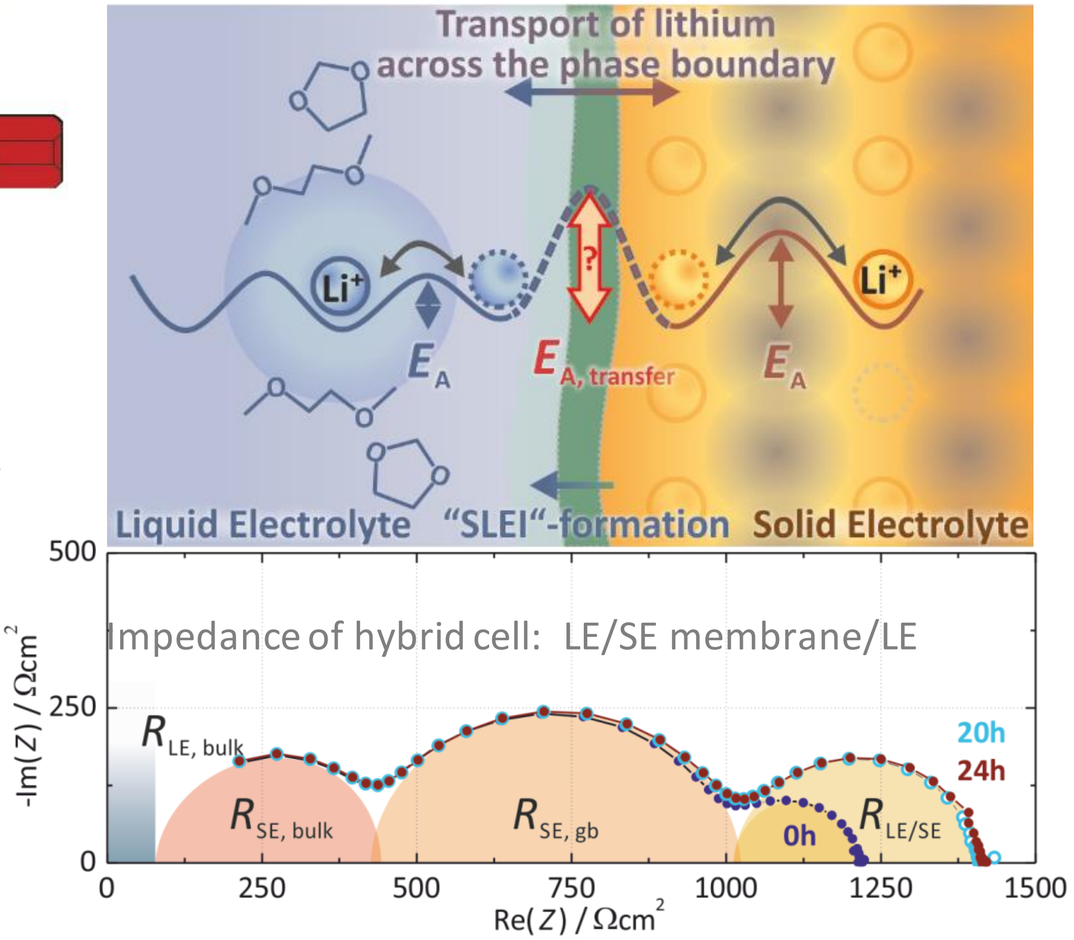
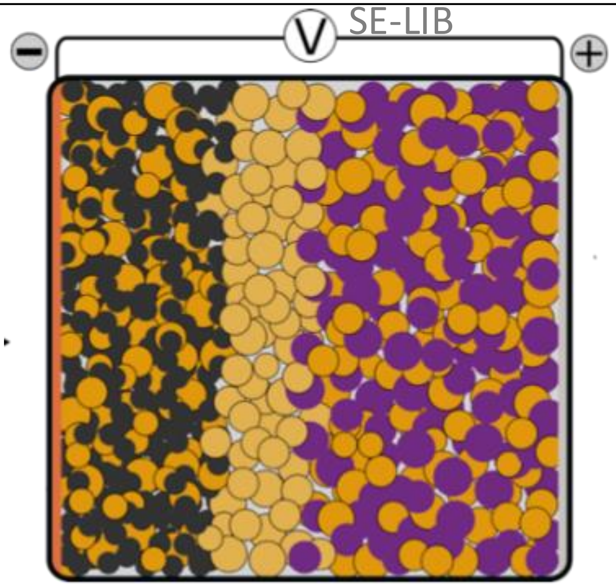
Battery and Electrochemistry Laboratory

Why solid electrolytes? – Avoiding chemical „cross-talk“?



Hybrid solid/liquid cells with separate anolyte/catholyte

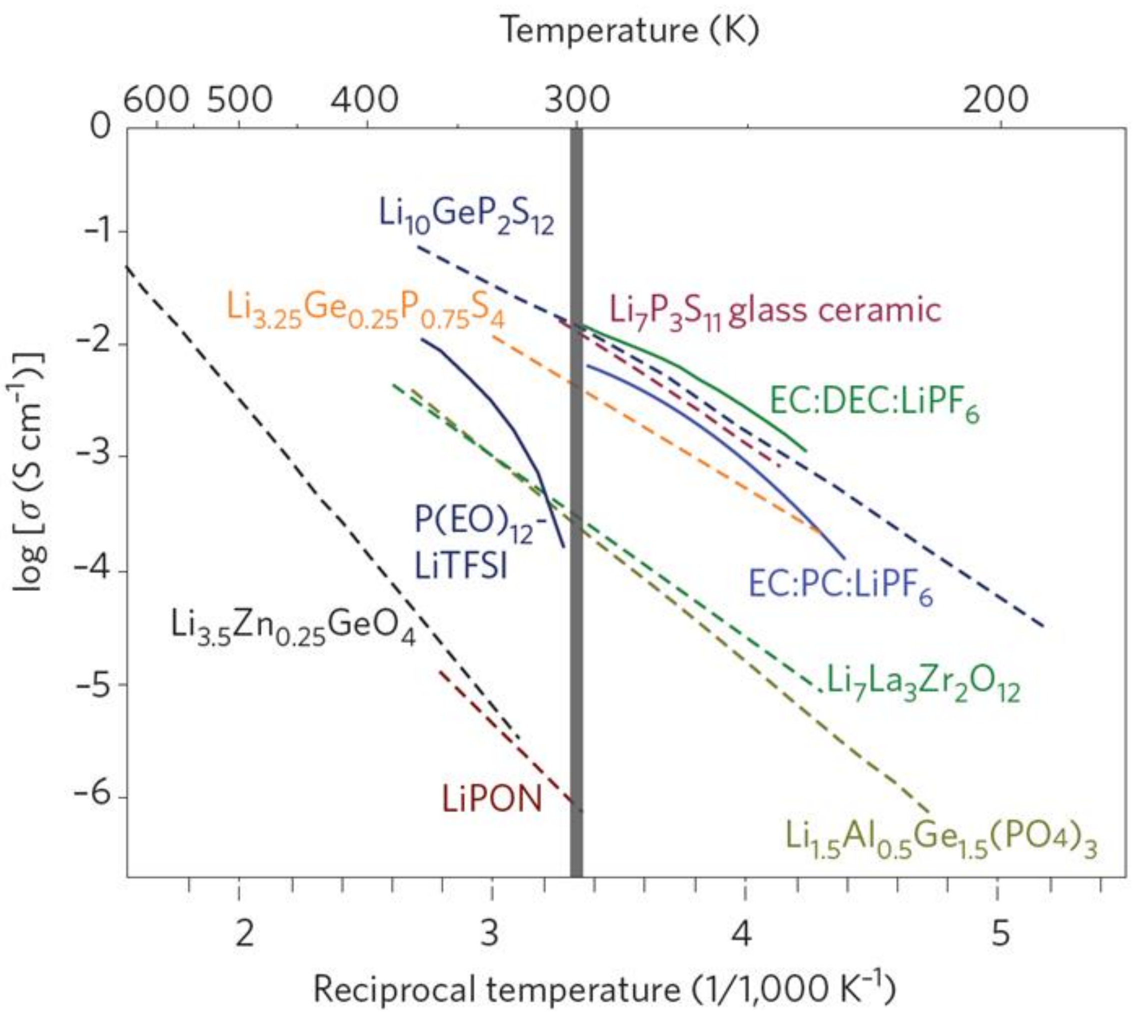




+ Capacity (Li metal anode)?
+ Safety (non-flammable)?
+ Stability (impermeable)?
+ Cycle life (stable)?

- Low rates
- High costs
- Mechanical instability

Solid electrolytes – What are the limits?



How low should the activation barrier be?

If $\sigma_i > 10^{-2}\ (\Omega\ \mathrm{cm})^{-1}$ $\quad (T = 300\ K)$

Boltzmann factor – jump probability

$$\sigma_i = \underbrace{\left[\frac{(z_i F)^2}{6RT} a^2 \nu_0\right] \cdot c_i}\ \cdot \exp\left(-\frac{E_a}{kT}\right)$$

with $\sigma_0 \approx\ 700\ (\Omega\ \mathrm{cm})^{-1}$

then: $\exp\left(-\frac{E_a}{kT}\right) > 1.4 \cdot 10^{-5}$

$E_a <\ 0.29$ eV

Solid electrolytes – What are the limits?

compound	E_a / eV
Li_3OCl (25 mS/cm??)	0.06
$RbAg_4I_5$	0.1
N…	
Li…	
Li_7…	
„LiPON“	0.55
ZrO_2 (9 mol-% Y_2O_3)	1.0

How low should the activation barrier be?

If $\sigma_i > 10^{-2}\ (\Omega\ \mathrm{cm})^{-1}$ $\quad (T = 300\ K)$

Boltz… …actor
…ability

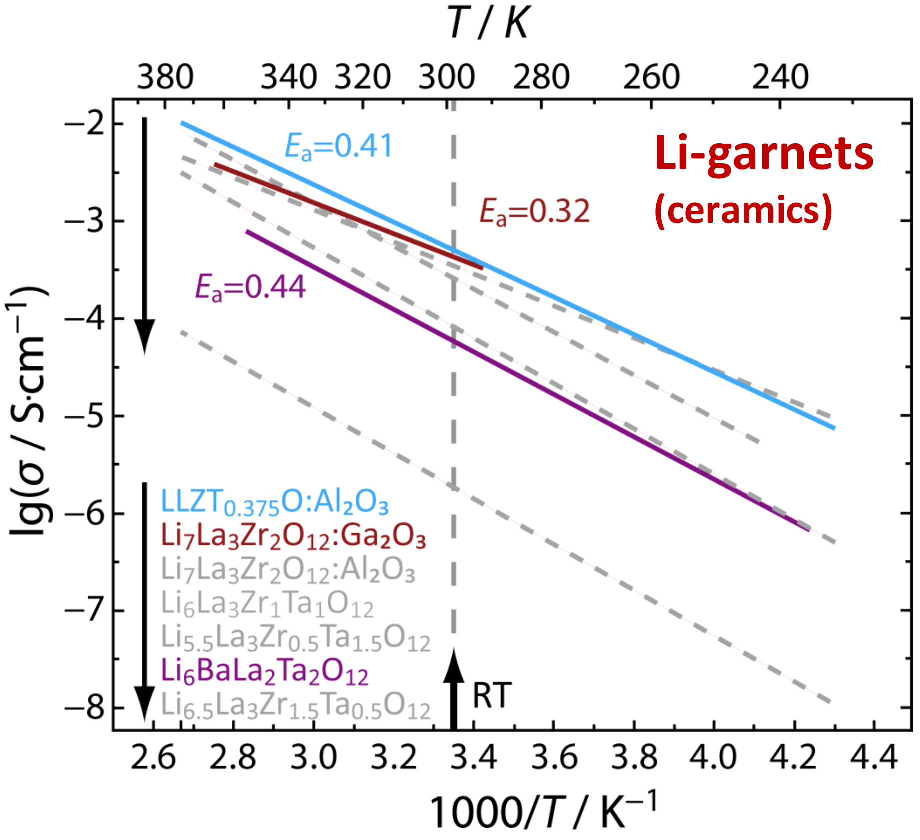
Ionic conductivity of inorganic materials will probably not be limiting.
(BUT: critical influence of microstructure!)

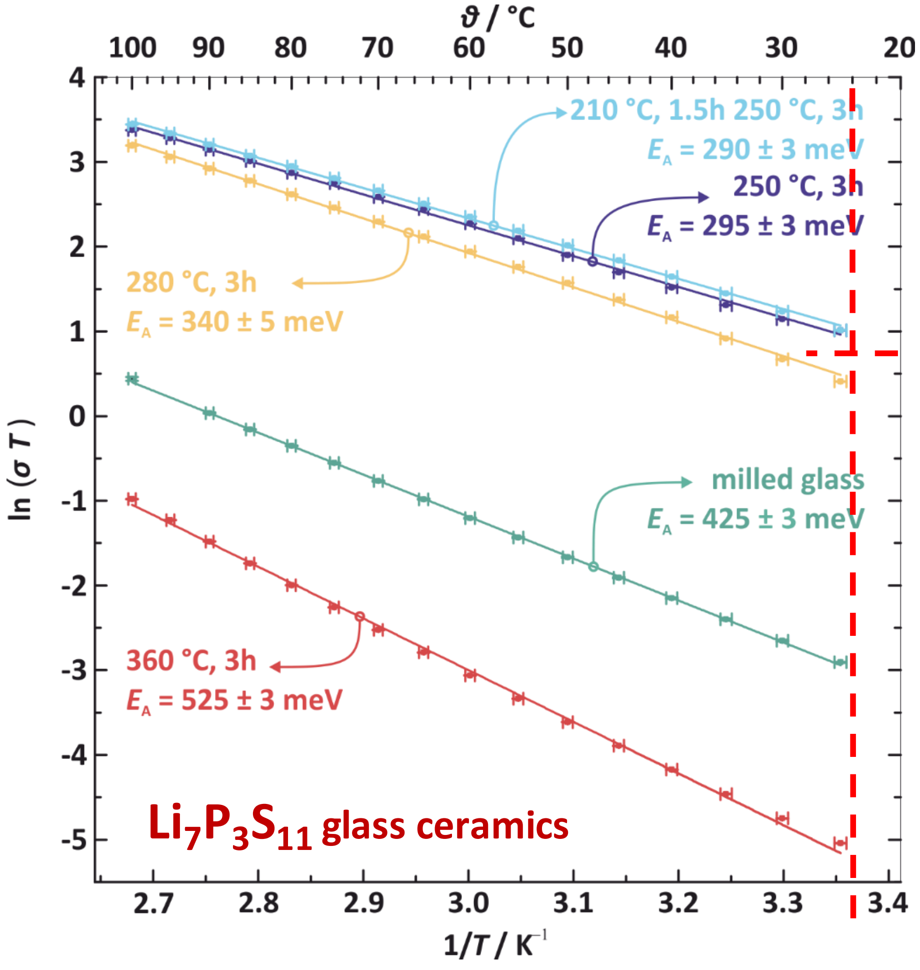
then: $\exp\left(-\frac{E_a}{kT}\right) > 1.4 \cdot 10^{-5}$

$E_a < 0.29$ eV

Solid Electrolytes – Materials and their interfaces

- Best S-based SE: > 10 mS/cm
- Best phosphates: > 1 mS/cm
- Best oxides: < 1 mS/cm

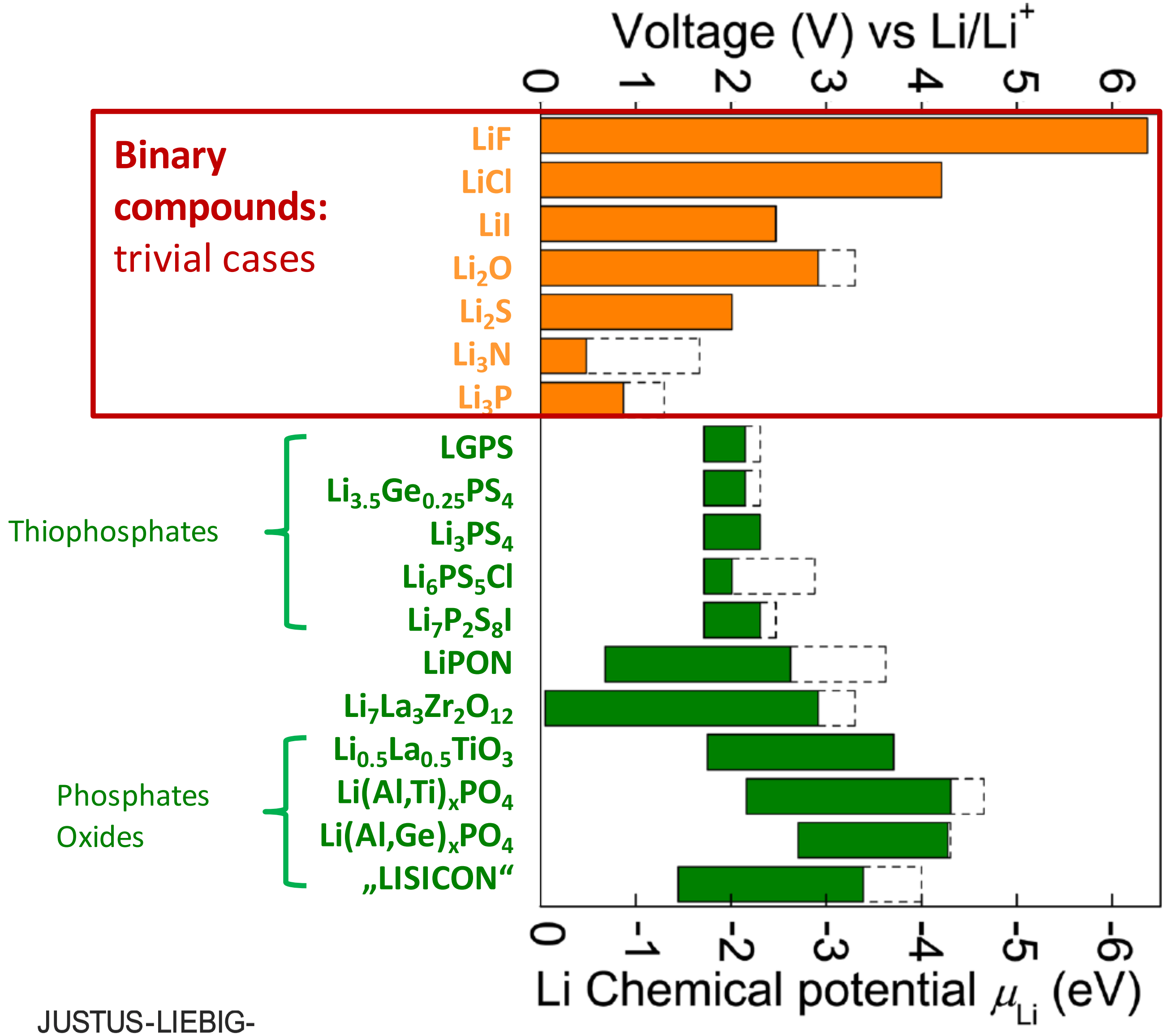


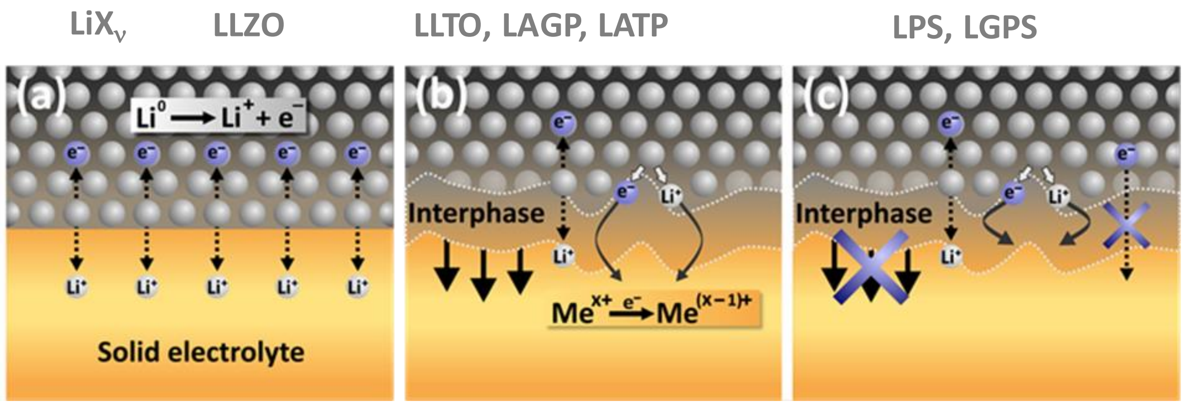


M. Busche, JJ, **L.F. Nazar** et al., Chem. Mater. (2016)

see e. g. work by Kanno and Tatsumisago group

Solid Electrolytes have small thermodynamic stability ranges





(a) Thermodynamically **stable** interface

thermodynamically unstable interfaces

(b) kinetically **unstable** interface (MCI = mixed-conducting interphase)

(c) kinetically **stable** interface (**SEI** = solid electrolyte interphase)

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Graph modified from: Y. Zhu et al., ACS Appl. Mater. Interf. (2015)
S. Wenzel, W Zeier and JJ, JLU (2016)

Physikalisch-Chemisches Institut

Solid Electrolytes form SEI – Kinetic stability!

$$\frac{d(\Delta\xi)}{dt} = \nu \cdot V_m(SEI) \cdot j(Li)$$

Wagner-type approach:
Diffusion-controlled formation of fully covering thin film (mixed-conducting)

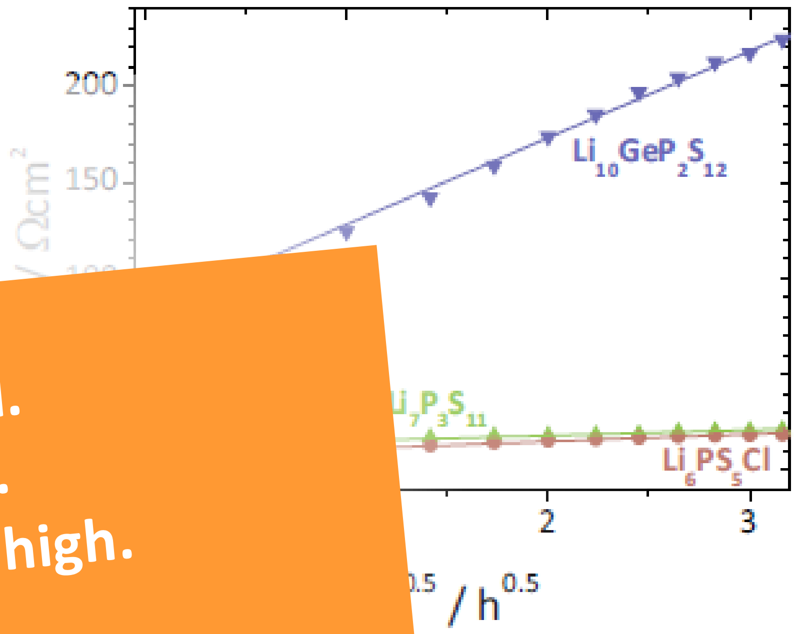
$$j(Li) \cong -L(\text{Li}) \cdot \frac{\Delta\mu(\text{Li})}{\cdots}$$

$$\Delta\xi \, d(\Delta\xi) \cong [\nu V_m \cdots$$

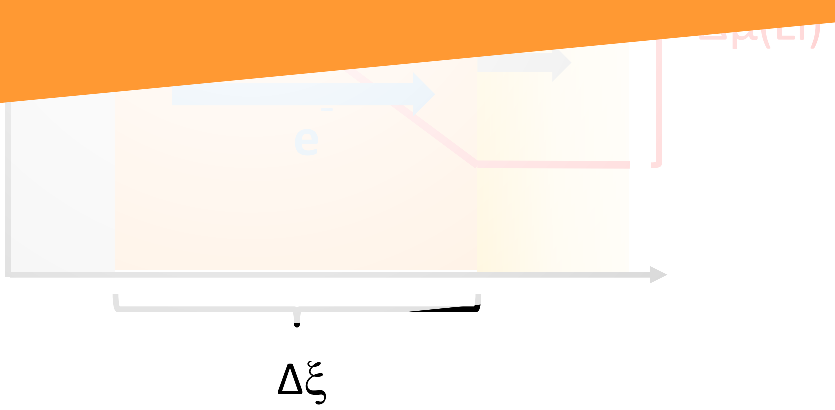
$$(\Delta\xi)^2 = k \cdot t$$

Parabolic rate law – S… dependence of interphase thickness on time

$$k \cong \frac{2\,\nu\, V_m}{F^2} \cdot \overline{\sigma(e^-)} \cdot \mu(Li)^\circ$$



**Most SE form SEI on lithium metal.
Thus: Kinetic stability is required.
SEI may be critical if resistance is too high.**

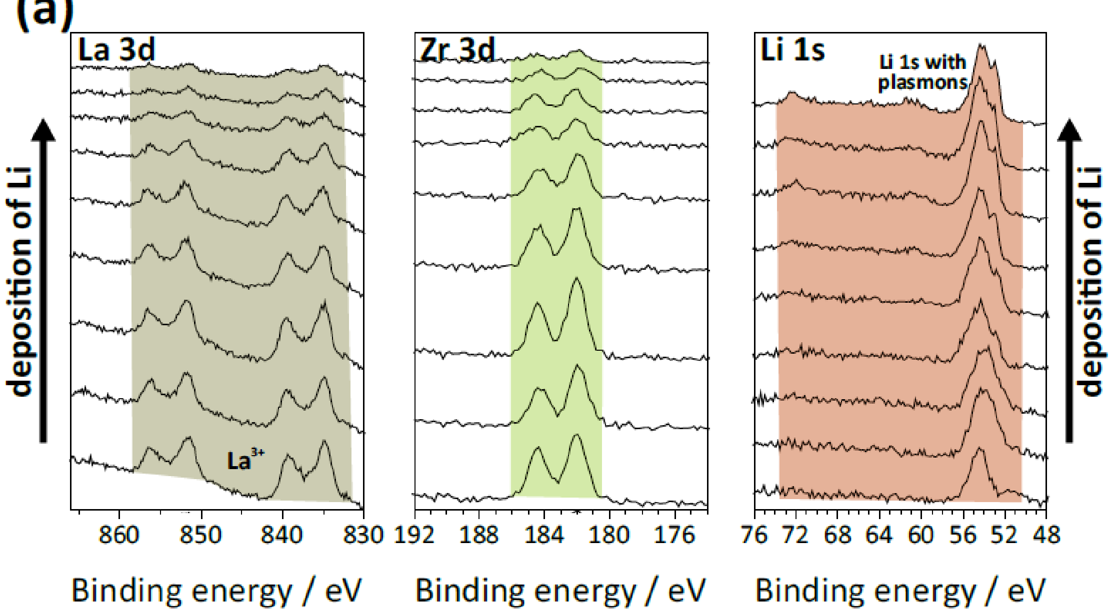


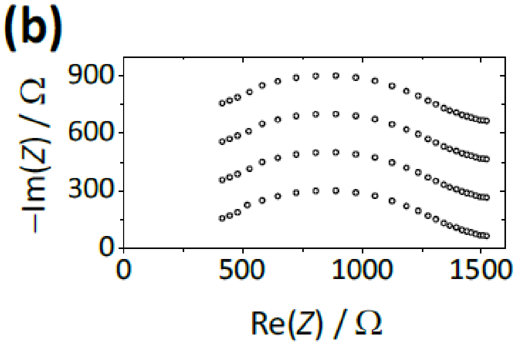
Good solid electrolytes also form a SEI – like liquid electrolytes!

SEI can probably be „designed“.

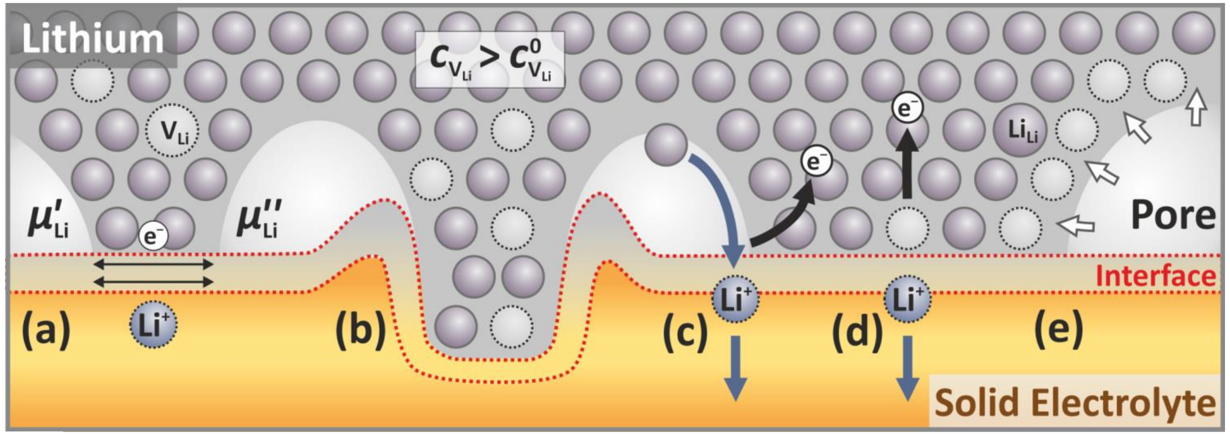
Solid Electrolytes – (Electro-)Chemomechanical instability

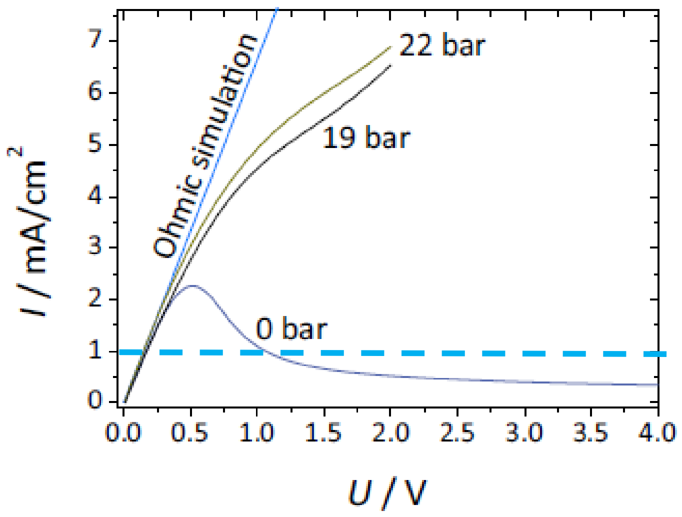
$Li_7La_3Zr_2O_{12}$ – a (the one?) stable SE





Metal anodes: Vacancy injection during anodic dissolution



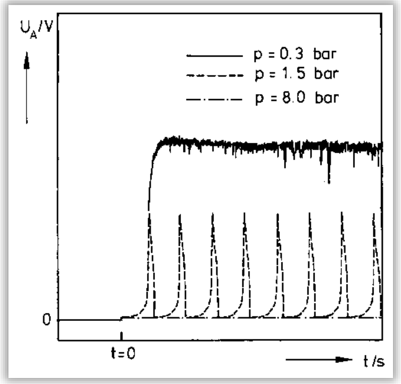


pressure dependence Li anode

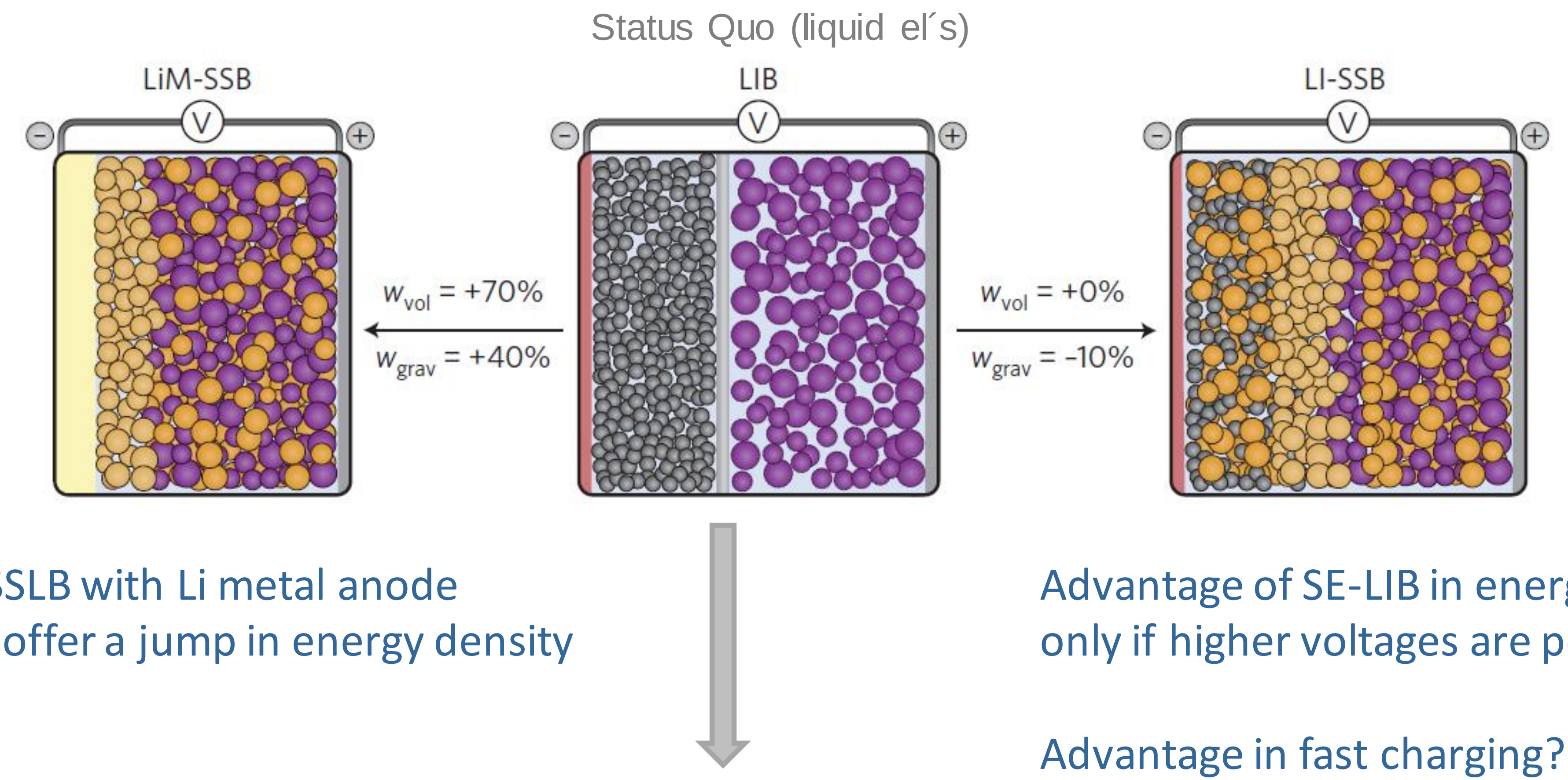
$Li/Li_7P_3S_{11}$

300 K

S. Wenzel (JLU, 2016)



Solid State Lithium (ion) batteries



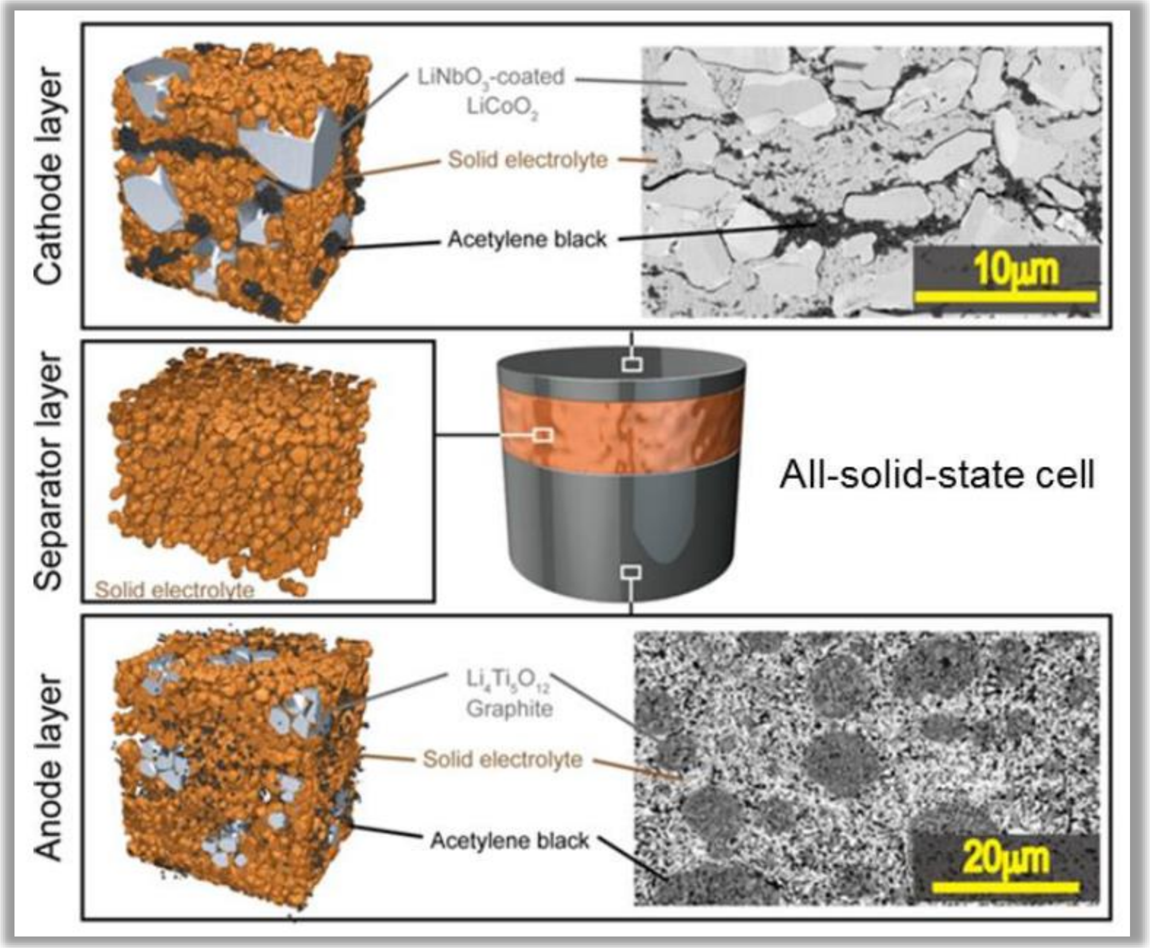
HV-SSLB with Li metal anode may offer a jump in energy density

Advantage of SE-LIB in energy density only if higher voltages are possible.

Advantage in fast charging?

Solid state Li-O_2, Li-S_2 and conversion-type cells?

Solid State LIB (reports by Toyoto MC)

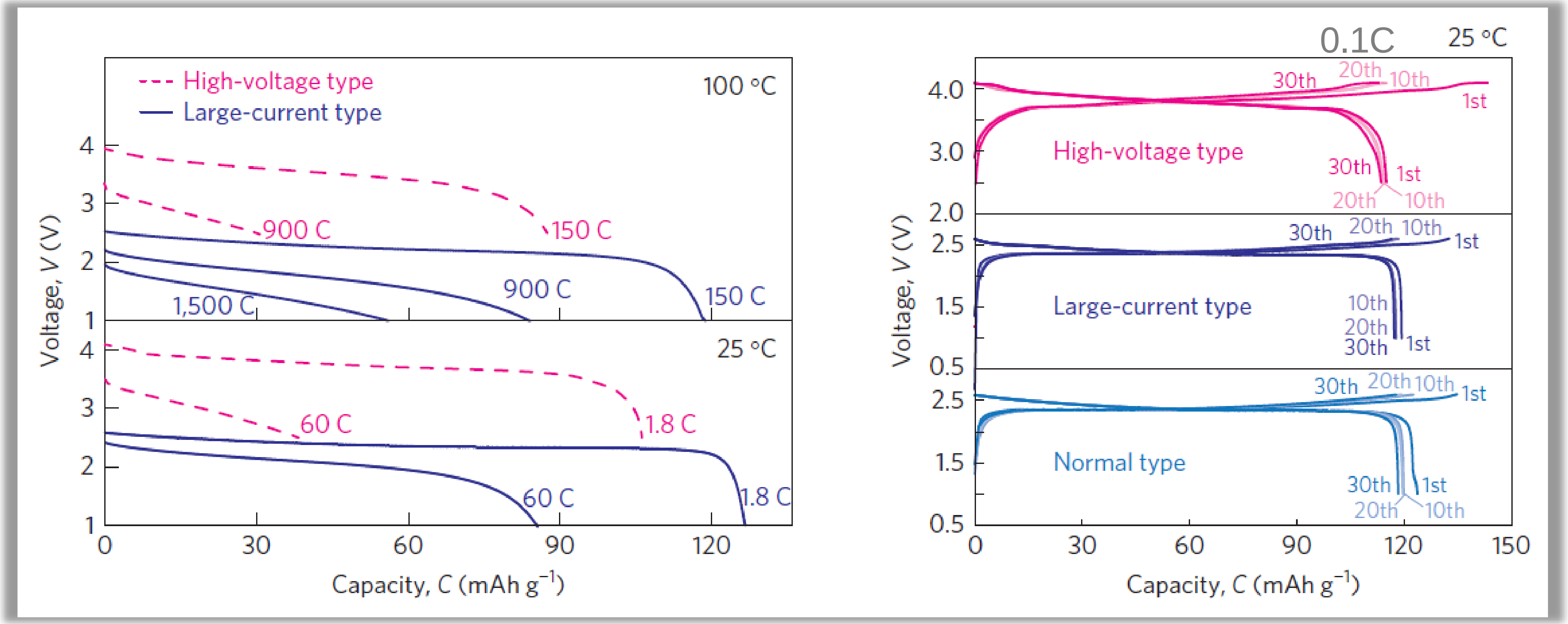


Data taken from Toyota MC

LTO/SE/LCO	C/SE/LCO
28 µm (4.87 mg LCO)	
LCO:SE:AB = 60:34:6	
LCO coated with $LiNbO_3$	
240 µm	
≈ 0.68 mAh/cm²	
103 µm	29 µm
LTO:SE:AB = 30:60:10	C:SE = 40:60
≈ 84 Wh/L	
≈ 40 Wh/kg	

LTO/SE/LCO	**C/SE/LCO**
28 µm (4.87 mg LCO)	
LCO:SE:AB = 60:34:6	
LCO coated with $LiNbO_3$	
If the SE-layer could be reduced to **13 µm**	
103 µm	**29 µm**
LTO:SE:AB = 30:60:10	**C:SE = 40:60**
≈ 370 WL	
≈ 164 Wh/kg	

Solid State LIB (reports by Toyoto MC) – Kinetics as real advantage?



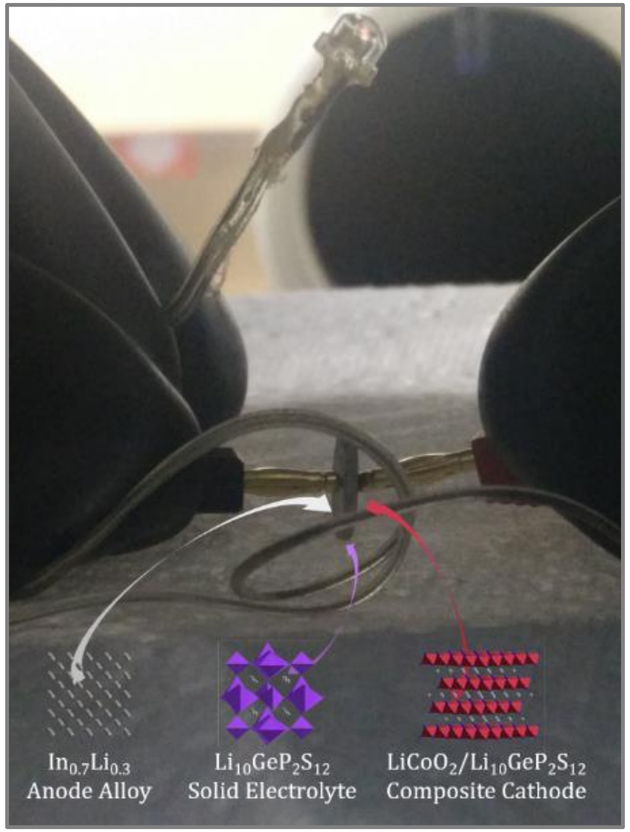
High-voltage type: C/SE/LCO

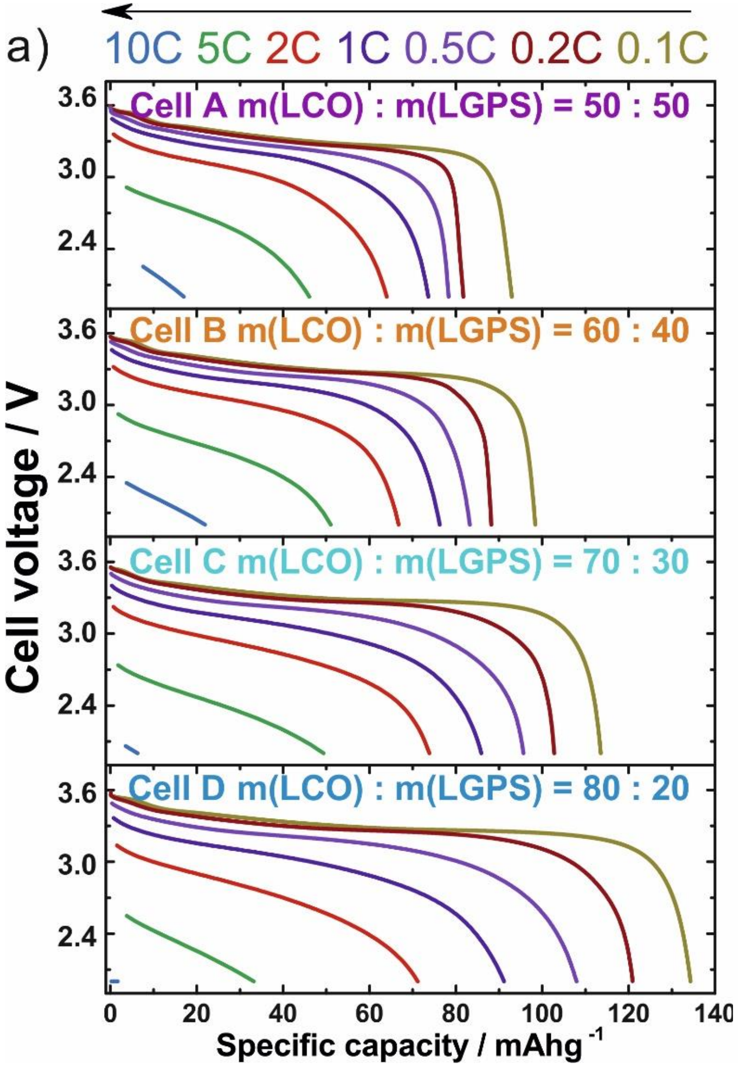
Large-current type: LTO/SE/LCO

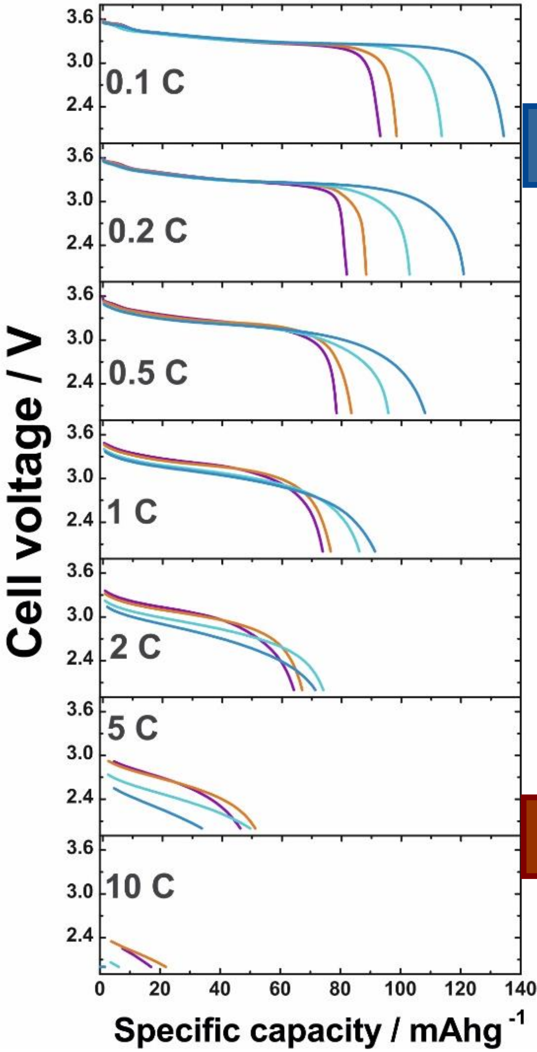
(no information on applied pressure!)

ASSB – Composite cathode design

Li/In | LGPS | **LCO**/LGPS







Electron paths determine capacity

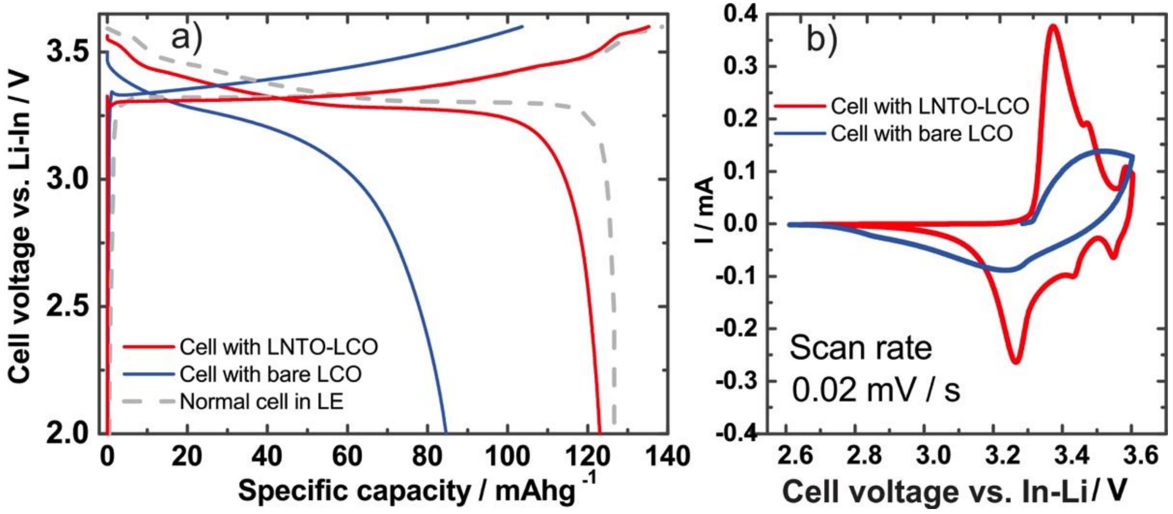
$m_{LCO} : m_{LGPS}$

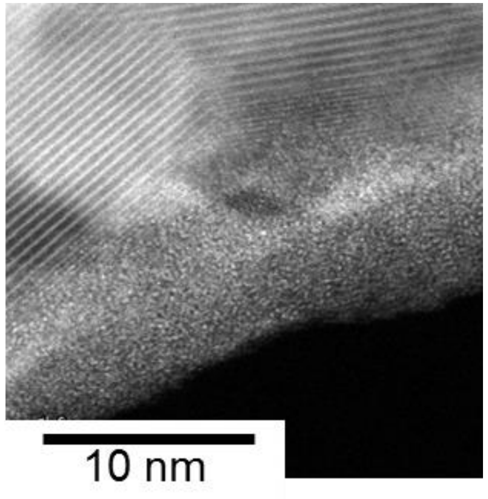
- 80 : 20
- 70 : 30
- 60 : 40
- 50 : 50

Ionic paths determine capacity

W. Zhang, JJ et al., submitted (2017)

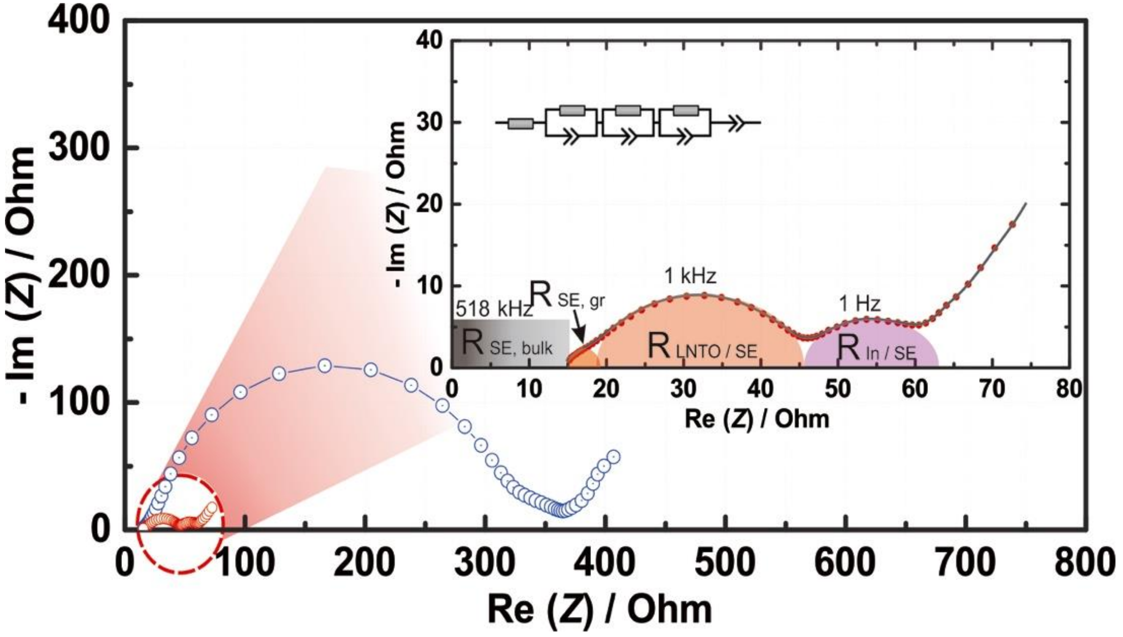
ASSB – Importance of coating the active materials





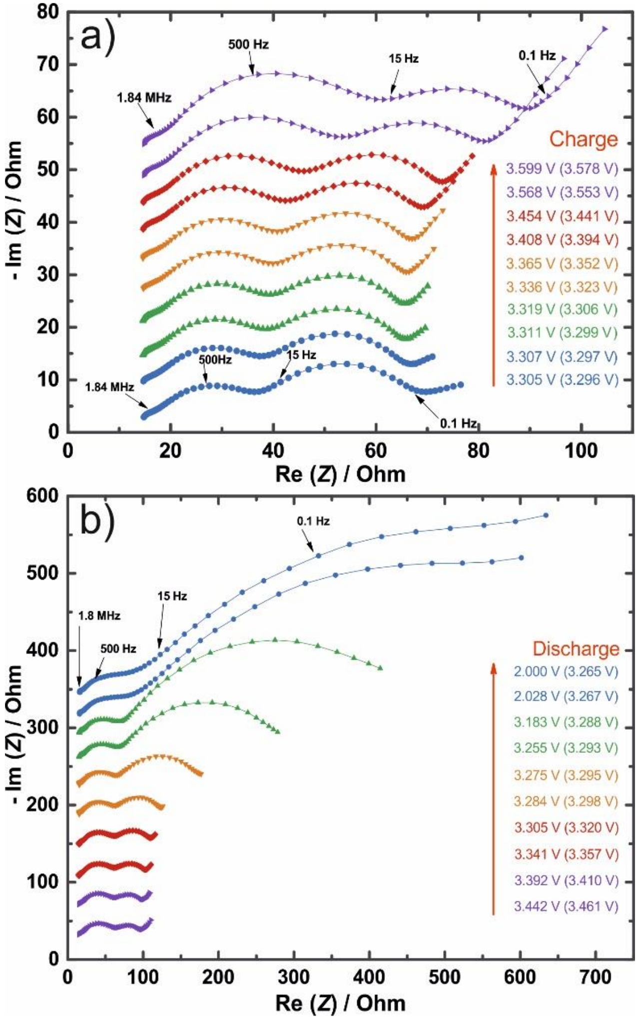
Fast deterioration and large interfacial resistance if oxides are in direct contact with the sulfide solid electrolyte.

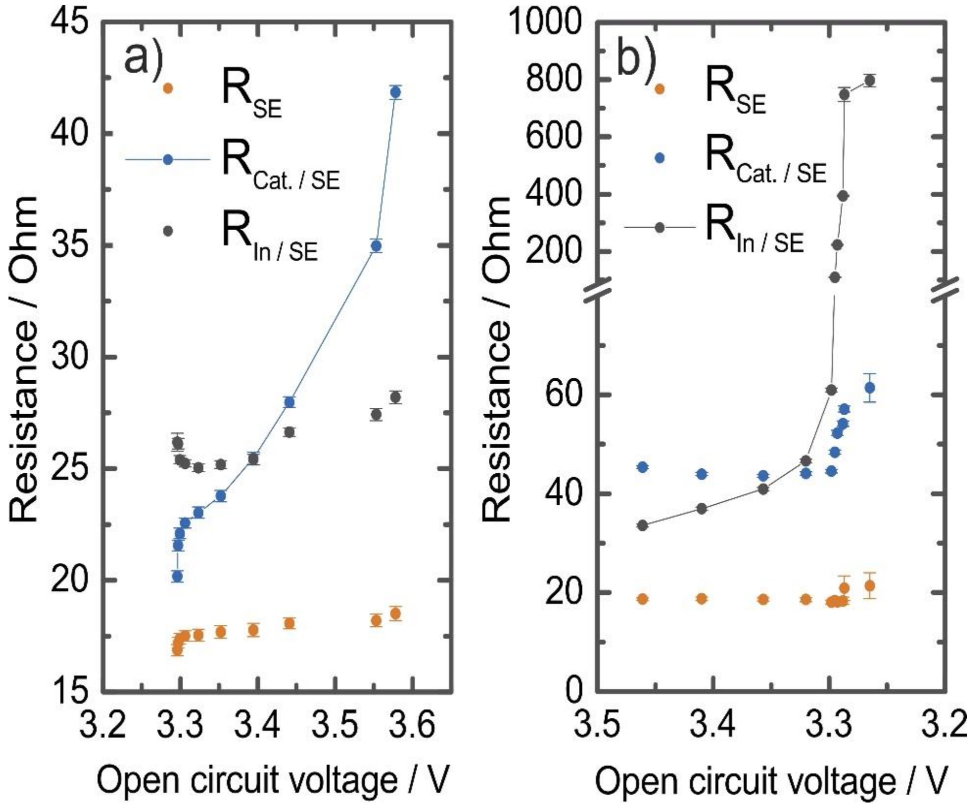
Amorphous coating necessary.



ASSB – Detailed analysis of impedance as function of SOC

Wenbo Zhang (PhD student)



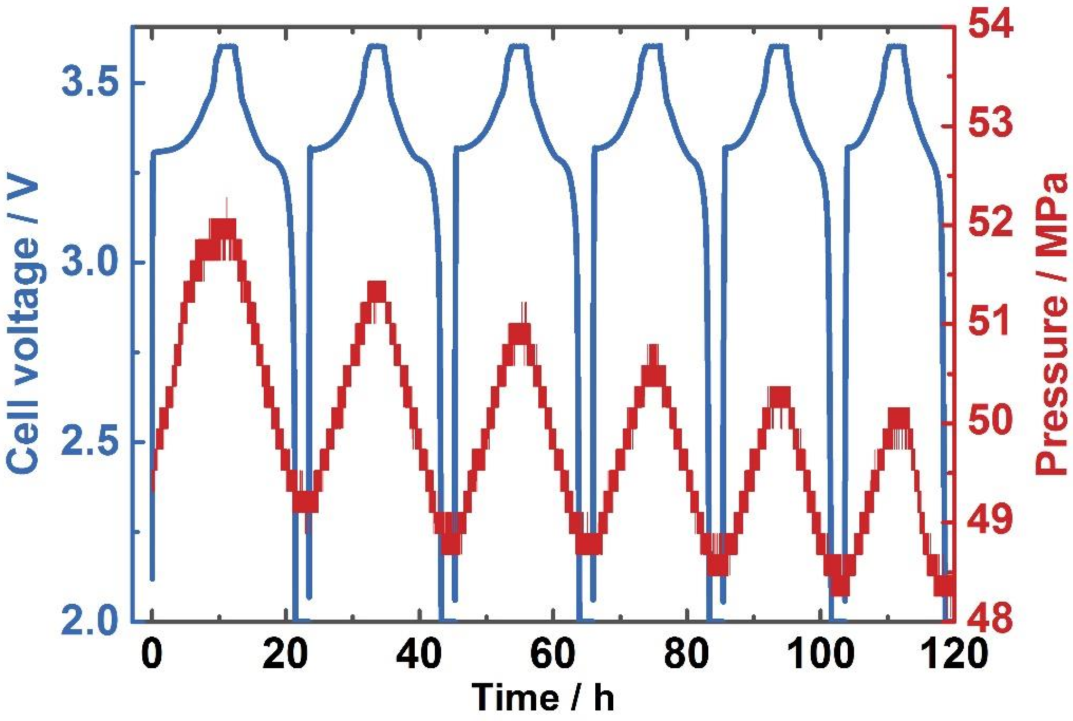


Growing Cathode/SE interfacial resistance due to particle cracking from volume changes.

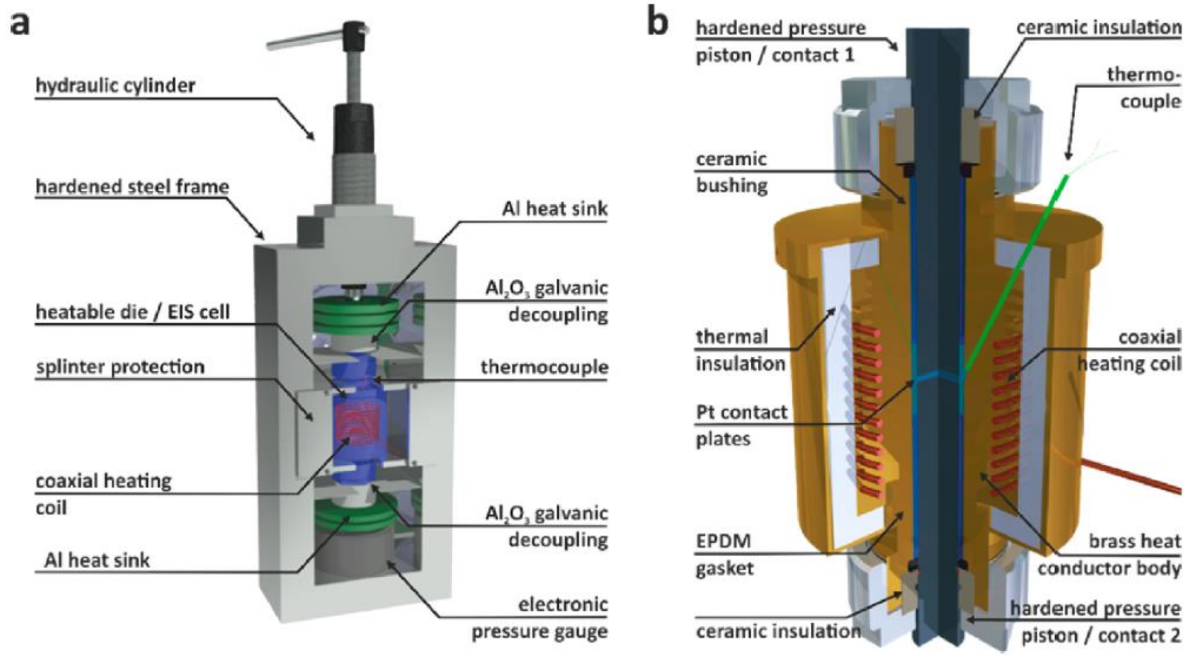
Strong increase of metal/SE interfacial resistance.

W. Zhang, JJ et al., submitted (2017)

ASSB – Mechanical pressure oscillations (Li-In/LGPS/LCO)



(galvanostatic cycling condition (C/13))

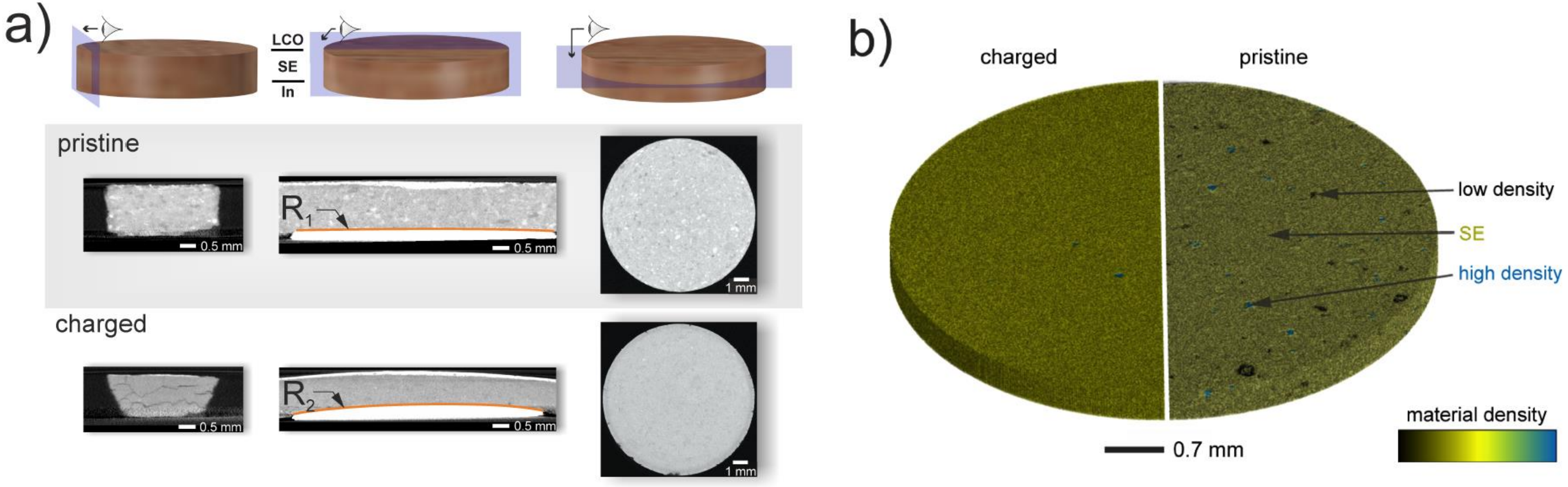


Increasing pressure during charging and decreasing pressure with discharge.

Charging → Anode & LCO expand

ASSB – Mechanical phenomena and failure

X-ray tomography (HZB, Berlin)

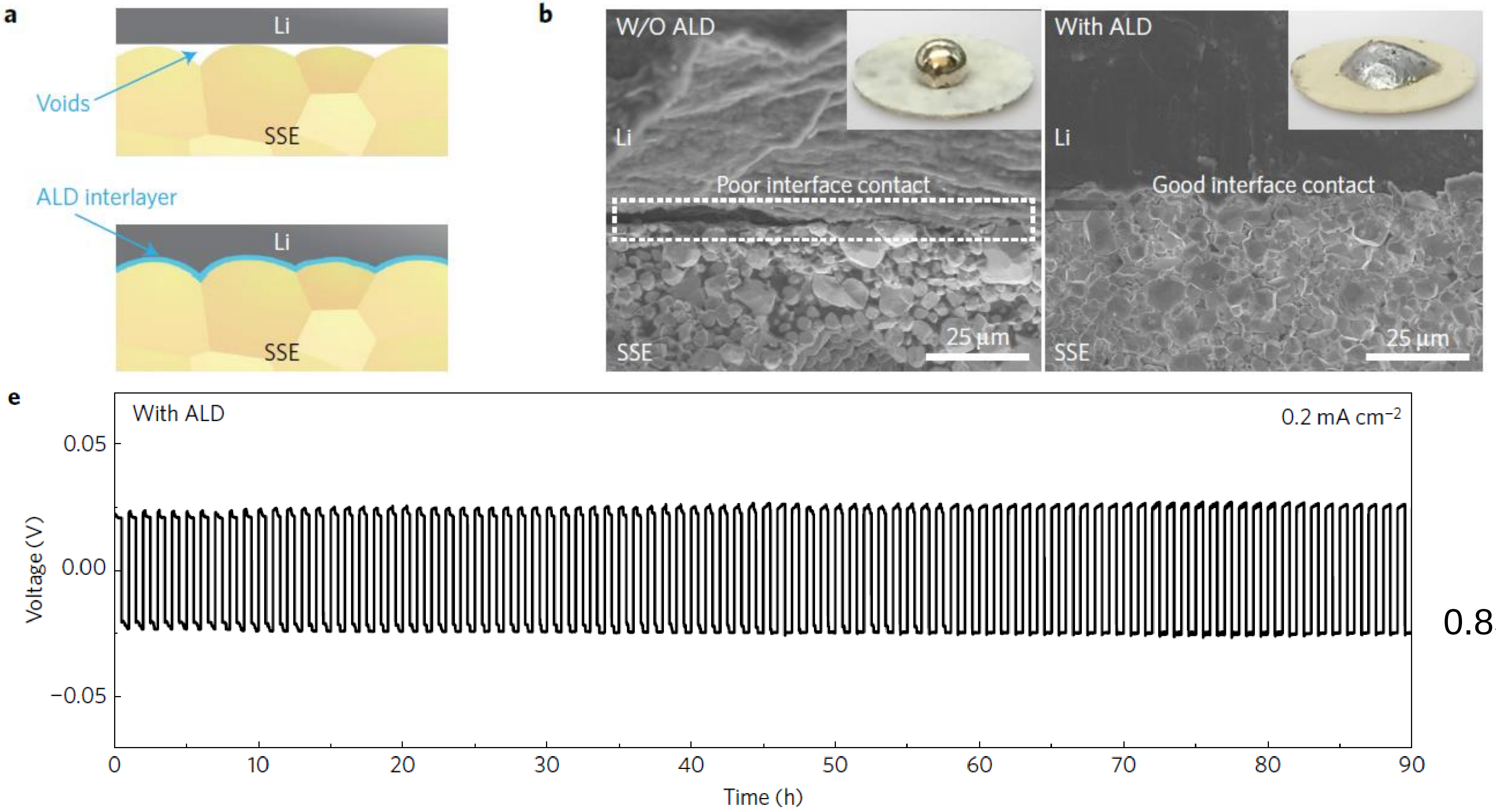


Mechanical strain during operation leads to battery cracking, bending and solid electrolyte consolidation.

Electro(chemical) expansion during cycling in SSB may severely hinder long-term battery performance.

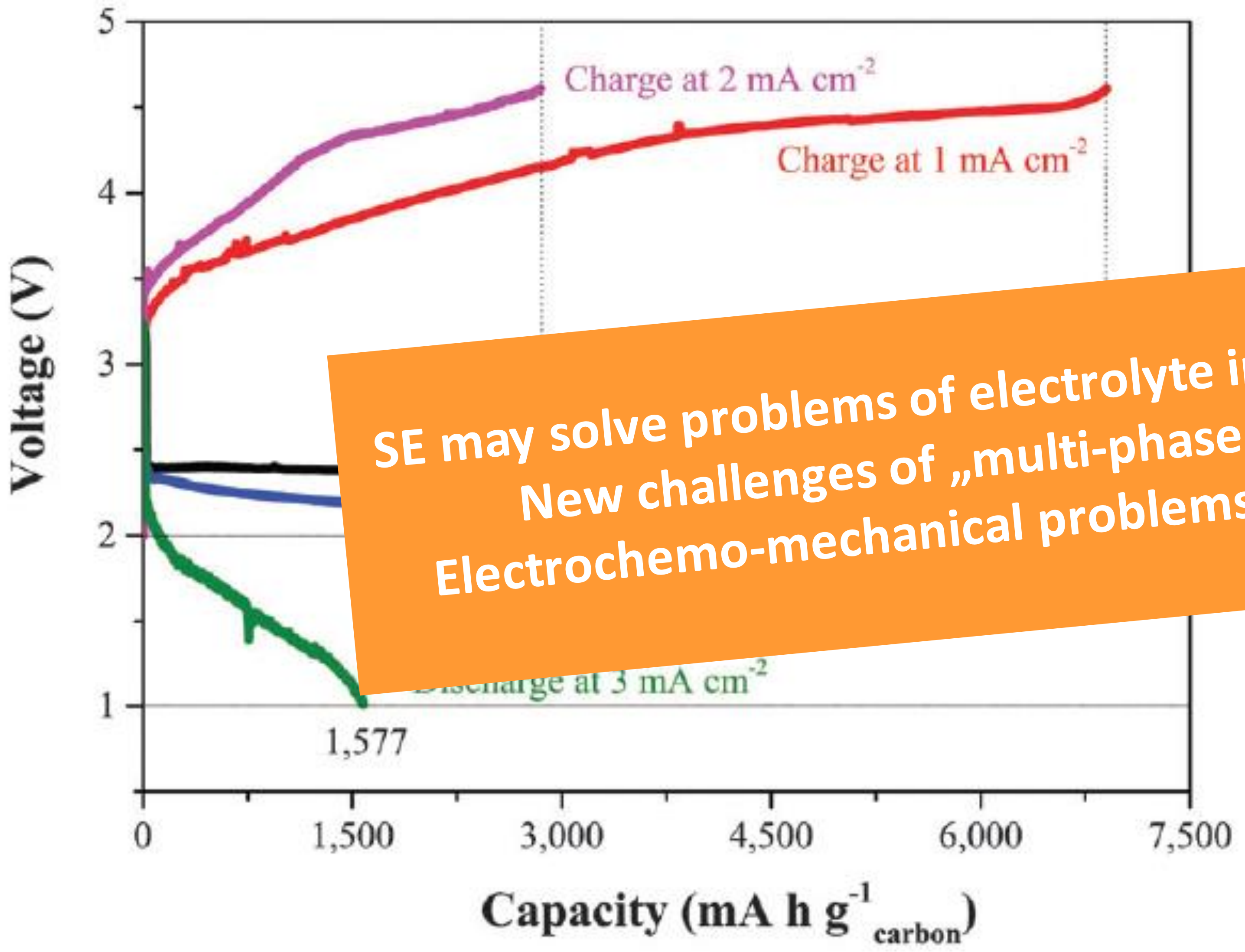
→ **Chemical „design“ & strain-optimized „design“ of cell required**

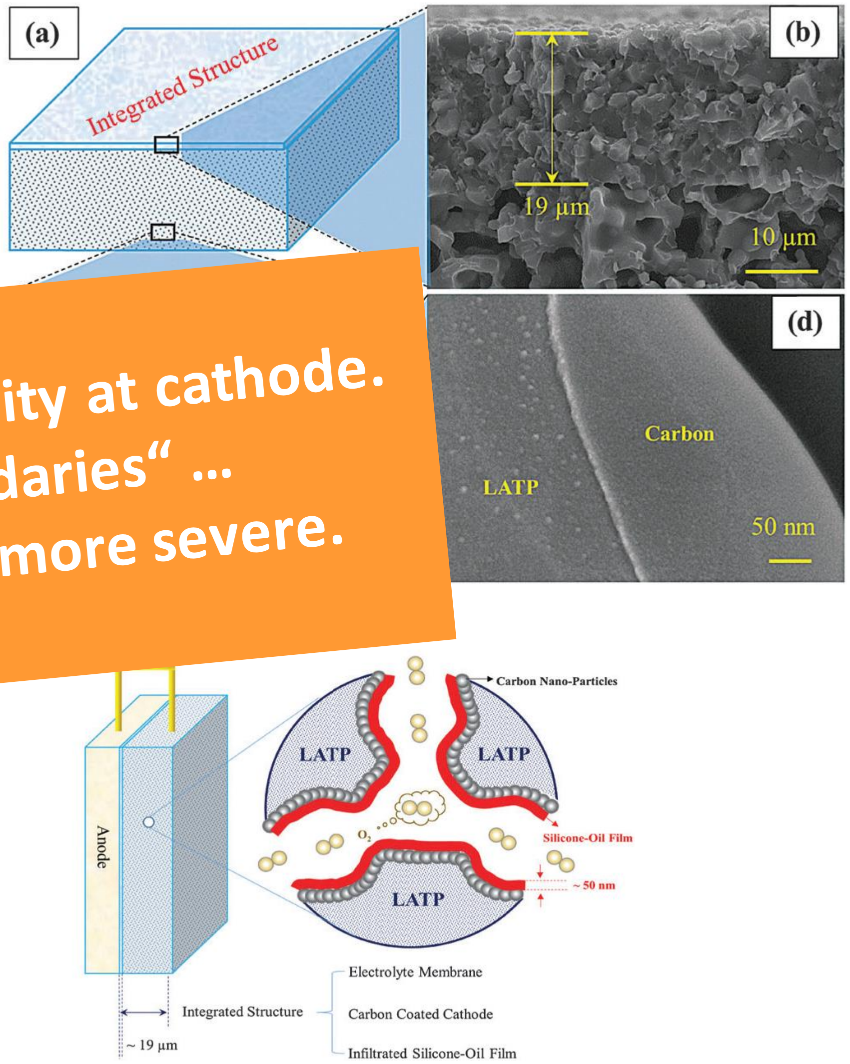
Advances in lithium metal anodes (Wachsman group, Maryland)



0.85 µm Li / cycle

Solid state Li-O_2 cells

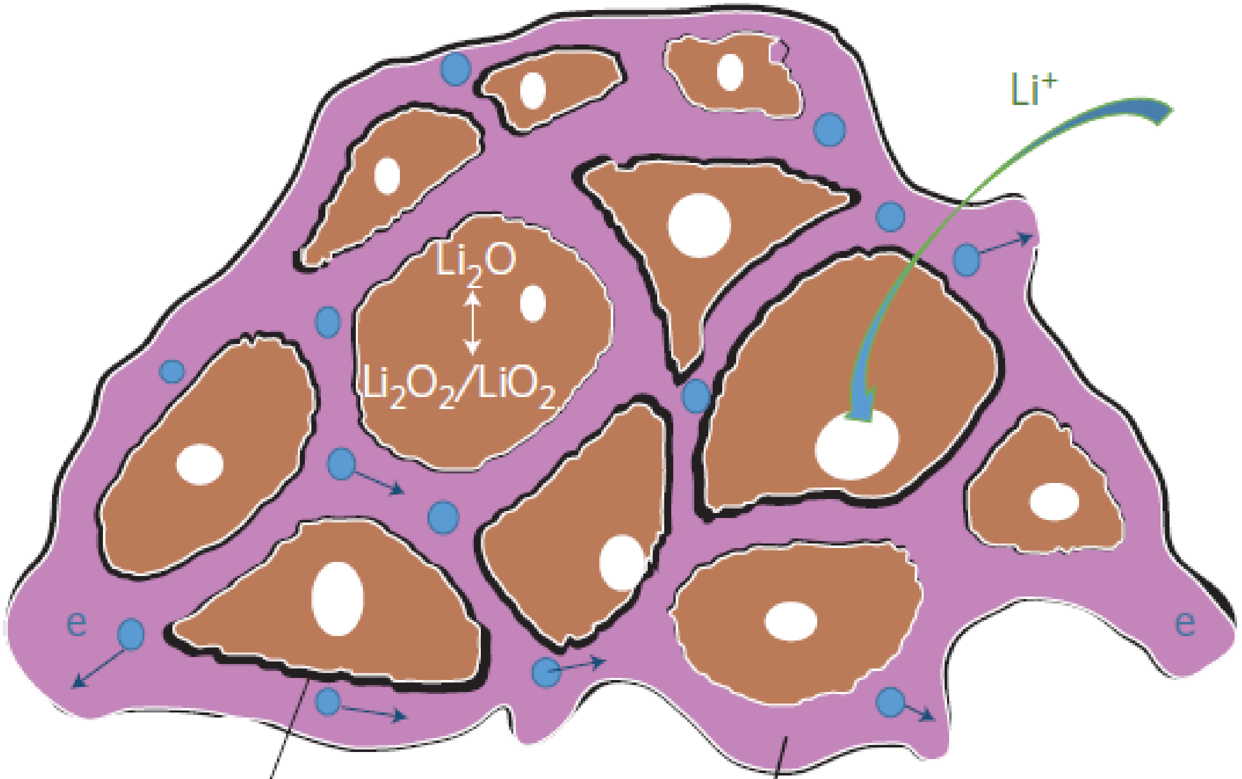




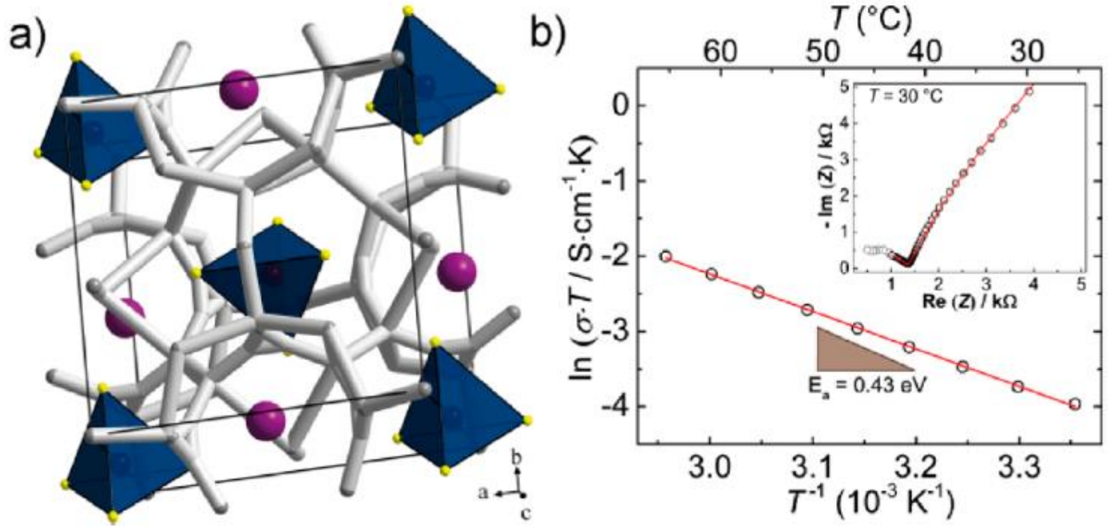
SE may solve problems of electrolyte instability at cathode.
New challenges of „multi-phase boundaries“ …
Electrochemo-mechanical problems even more severe.

K.M. Abraham and Z. Jiang., J. Electrochem. Soc., *143* (1), **1996**, 1

Combined cation and anion redox chemistry (in SSLB)?



Last but not least … Processing of SE…



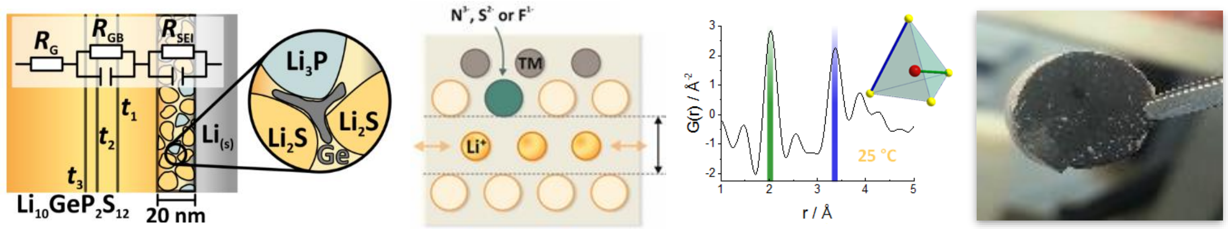
Precursor-based formation of crystalline SE:

$$3Li_2S + P_2S_5 \xrightarrow[RT]{DME} 2Li_3PS_4\cdot DME$$

$$Li_3PS_4\cdot DME + LiI \xrightarrow[RT]{DEM} Li_3PS_4\cdot DME\cdot LiI \xrightarrow[-DME]{200^\circ C} Li_4PS_4I$$

Z. Zhu, K. Amine et al, Nat. Ener. 1 (2016) 1038

S. Sedlmaier, JJ et al. Chem. Mater (2017), in print



Solid State Batteries – Cell concepts and electrodes

Summary

- Fast and exciting progress in inorganic SE
- Solid/solid interfaces are a problem – but solutions appear as possible
- Electrochemo-mechanical coupling yet not sufficiently understood
- Reversible (high capacity, 20 µm) Li metal anode still not proven
- Fast kinetics may be real advantage – not energy density

→ SSLB are not a short term target – long term approach required

BASF International Network on Electrochemistry

Thanks

JUSTUS-LIEBIG-UNIVERSITÄT GIESSEN

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HESSEN

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BASF The Chemical Company

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P. Novak, S. Komaba, I. Krossing

BELLA Battery and Electrochemistry Laboratory

BELLA – Batteries and Electrochemistry Laboratory, KIT, Karlsruhe

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Dr. Joachim Sann
Dr. Johannes Keppner
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…