Design Principles for Solid Electrolyte–Electrode Interfaces in All-Solid-State Li-Ion Batteries : Insight from First-Principles Computation

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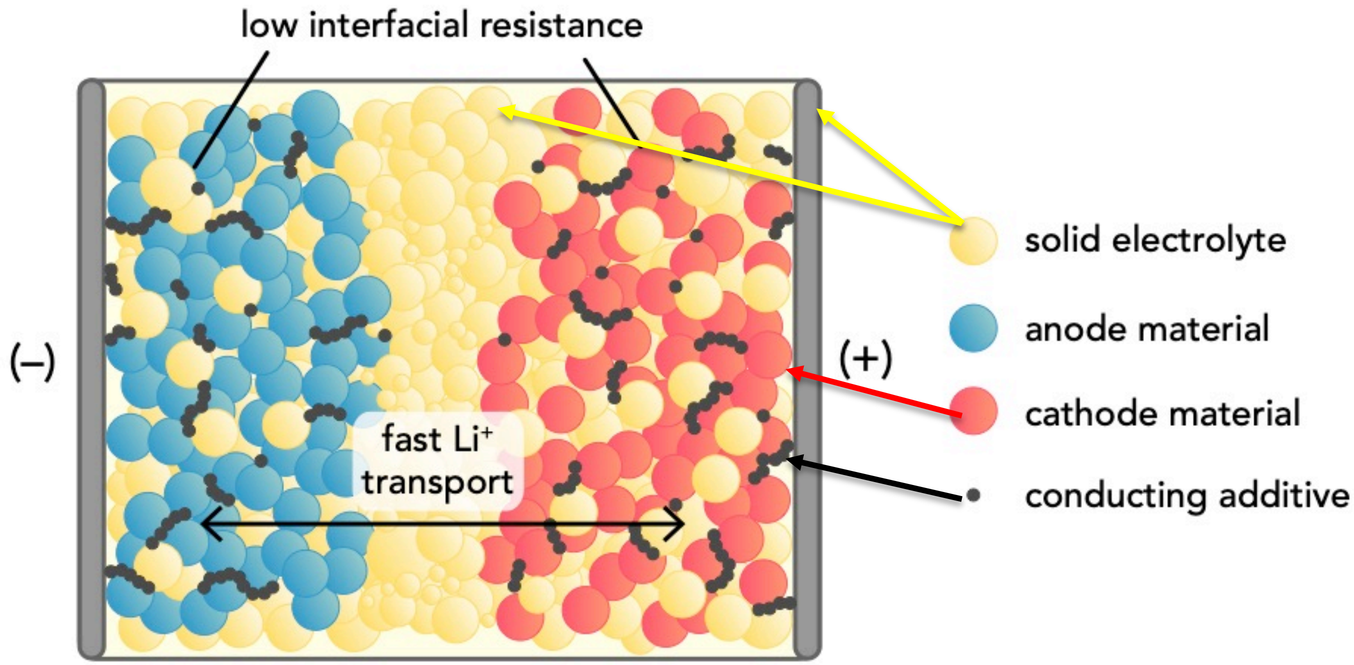
Interfaces challenges in all-solid-state batteries

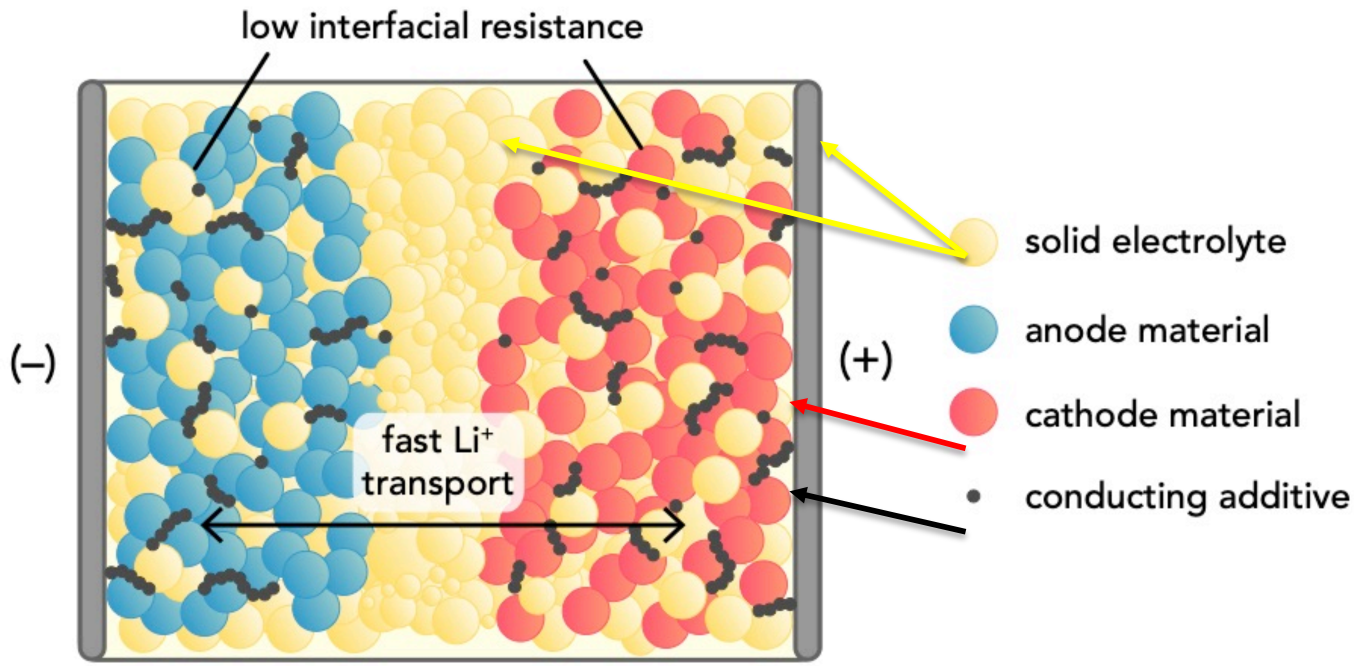


- Critical roles of interfaces in battery performance:
  - Formation of SEI layer ?
  - Interface stability / compatibility. (coulombic efficiency, cycle life)
  - Ionic transport across the interface. (Rate performance)

- What governs interface compatibility in all-solid-state batteries?
- The design principles for compatible interfaces in all-solid-state batteries.

Nolen, Zhu, He, Bai, Mo, ***Joule*** 2018, 2, 2016-2046

Interface Compatibility : Basic Thermodynamics



Factors affecting interface compatibility:

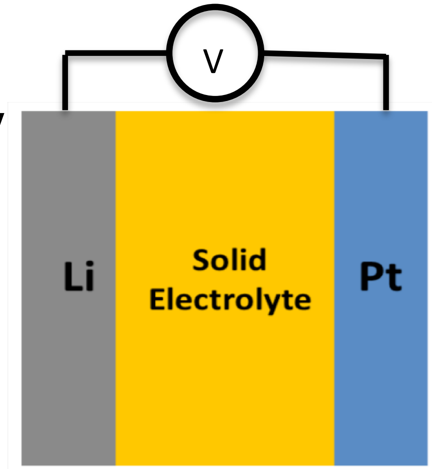
1. Electrochemical window of the solid electrolyte: The reduction / oxidation of the solid electrolyte at applied voltage.
2. Chemical compatibility of interface: Chemical reaction between solid electrolyte and electrodes.
3. Electrochemical compatibility of interface: Electrochemical reaction between solid electrolyte and electrodes (during voltage cycling).

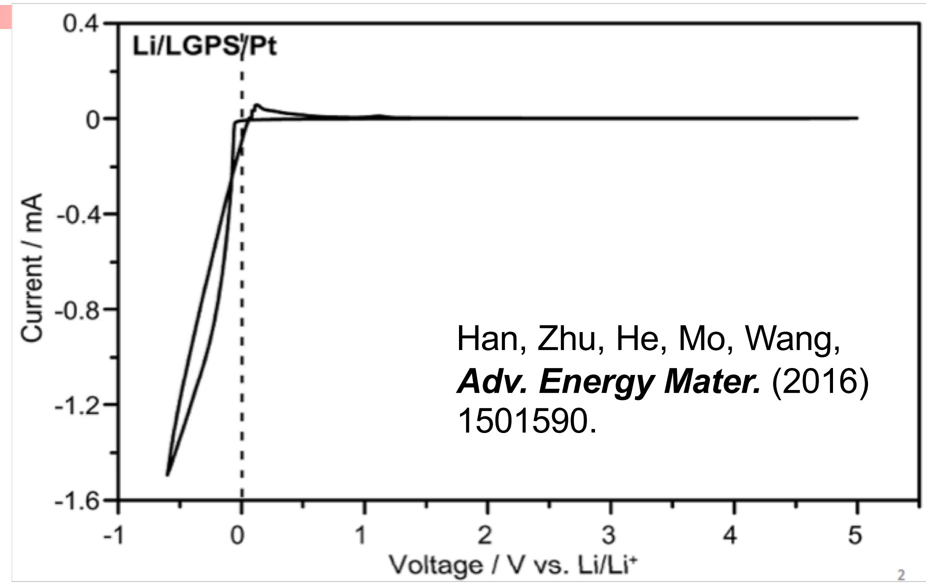
First principles computation to investigate
the thermodynamics of interfaces in all-solid-state batteries.

Zhu, He, Mo, ***J. Mater. Chem. A***, 2016,4, 3253-3266
Nolen, Zhu, He, Bai, Mo, ***Joule*** 2018, 2, 2016-2046

Myth: Solid electrolyte has 0-5V electrochemical window ?

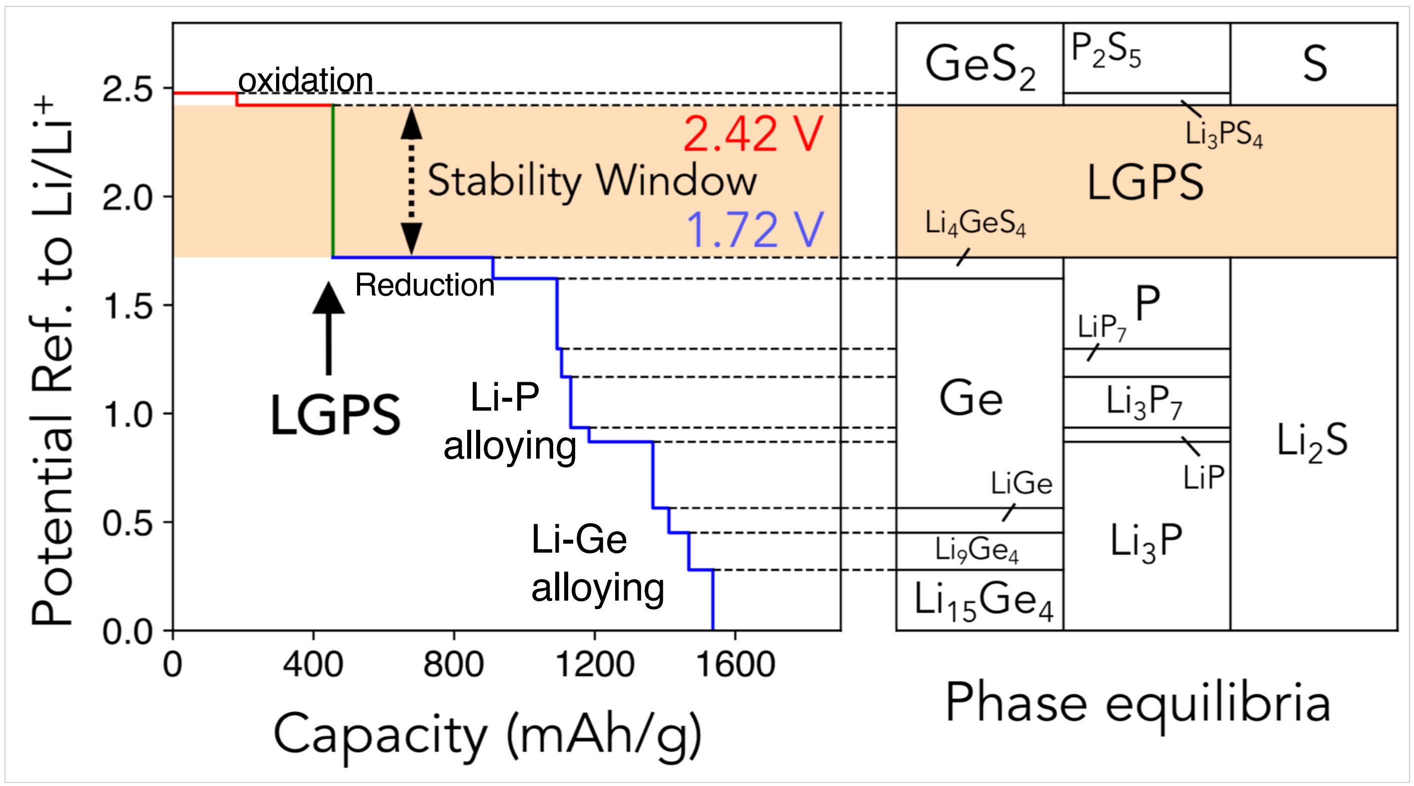
Cyclic voltammetry (CV) using semi-blocking electrodes :
No apparent redox current





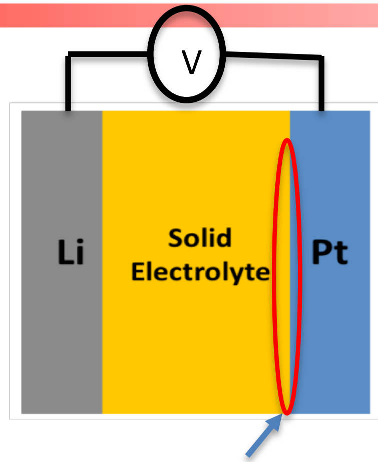
Thermodynamic calculation :

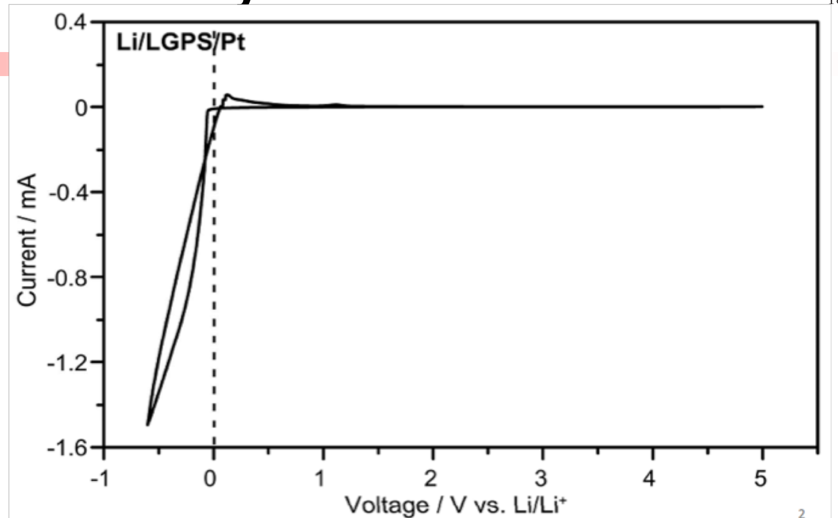
Limited electrochemical window of SE



Measure electrochemical stability of solid electrolyte

Cyclic voltammetry (CV) using semi-blocking electrodes, e.g. Li-LGPS-Pt





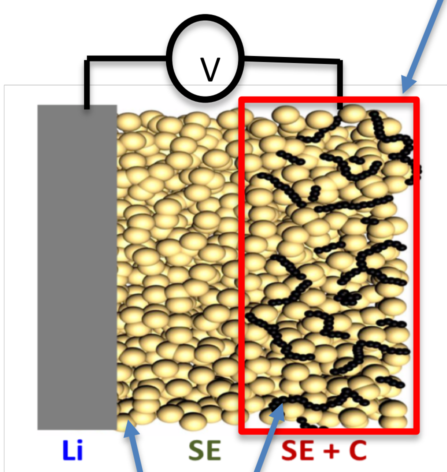
Small contact area; limited kinetics; small redox current to observe.

--> Overestimation of electrochemical window in semi-blocking cell setup

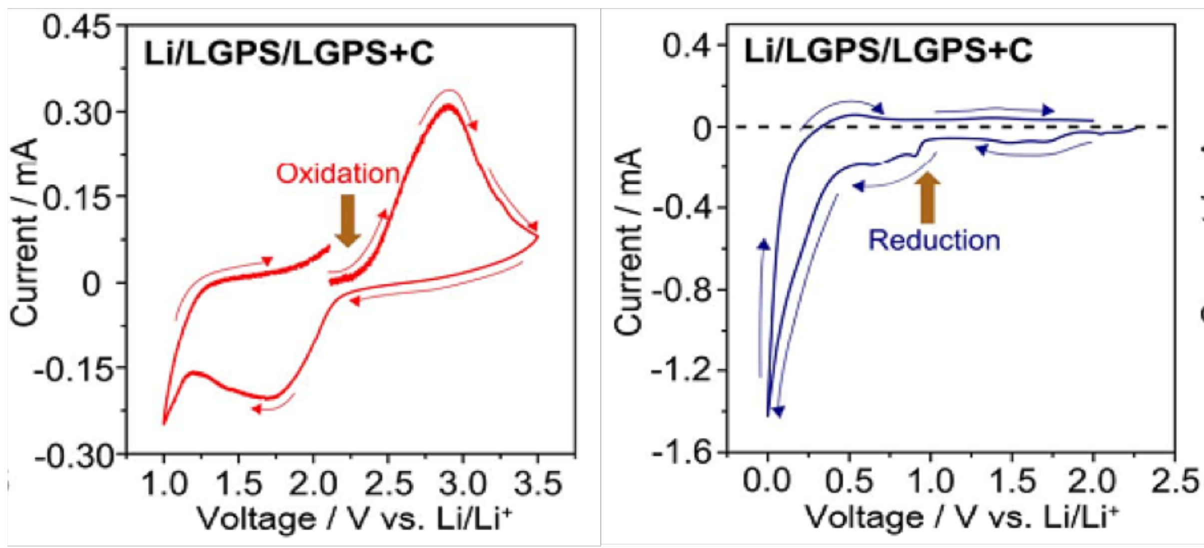
Han, Zhu, He, Mo, Wang, ***Adv. Energy Mater.*** (2016) 1501590.

CV cell using composite electrode mixed carbon: Li-LGPS-LGPS+C

Improve reaction kinetics; mimic real electrode configuration in solid-state battery

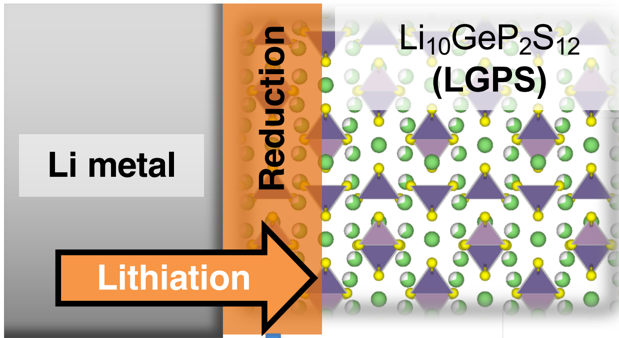


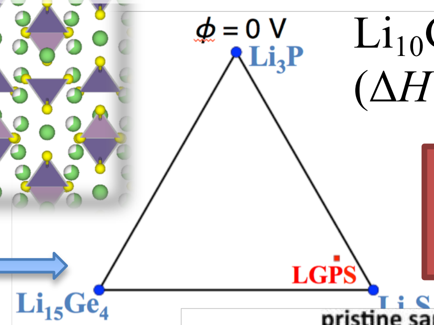
Reaction products become thin layers at the interfaces, affecting cell performance !



Thermodynamic window of LGPS : 1.7 – 2.4 V

Interphase layer formation due to the reaction of Solid Electrolyte



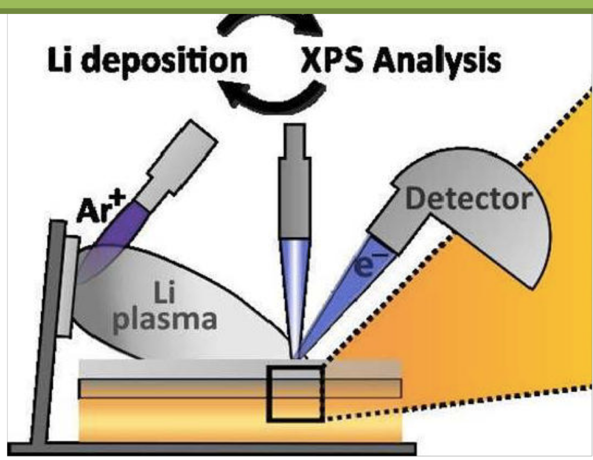


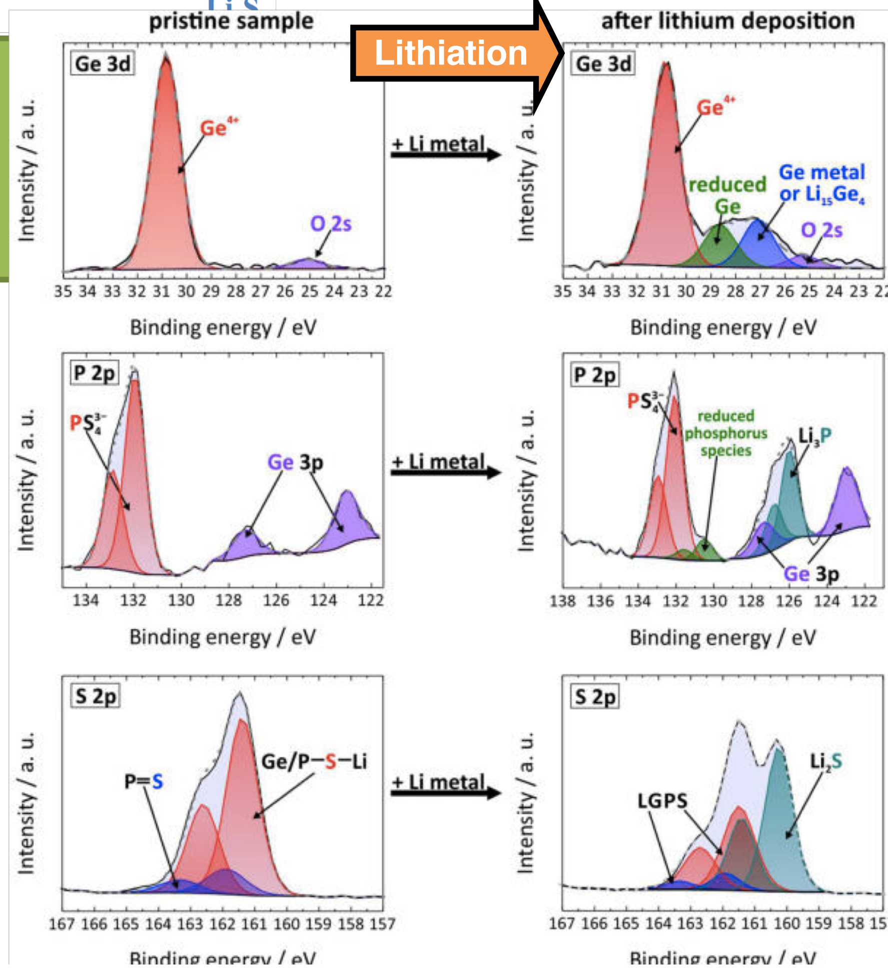
Thermodynamic calculations

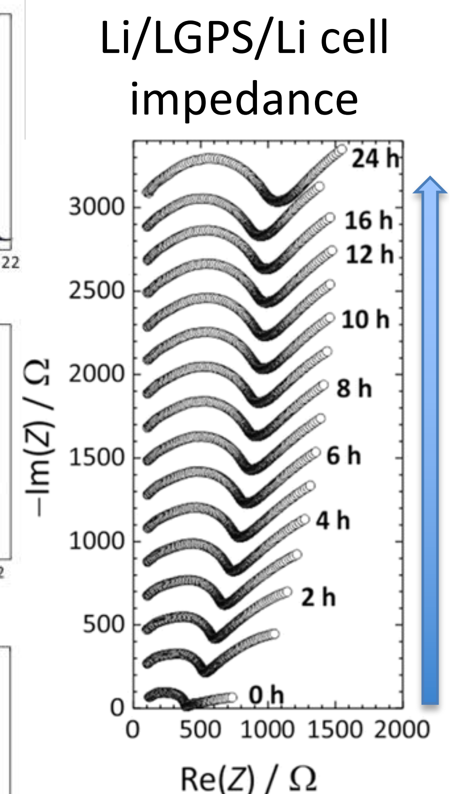
$$Li_{10}GeP_2S_{12} + 23.75\ Li \rightarrow 12\ Li_2S + 2\ Li_3P + 0.25\ Li_{15}Ge_4$$
$$(\Delta H = \mathbf{-31.3\ eV\ /\ -3019\ kJ/mol})$$

Interphase layer formation at the Li-SE interface :
---> High interfacial resistance.

In-situ Characterization confirm the interphase layer formation, agrees with thermodynamic calculations



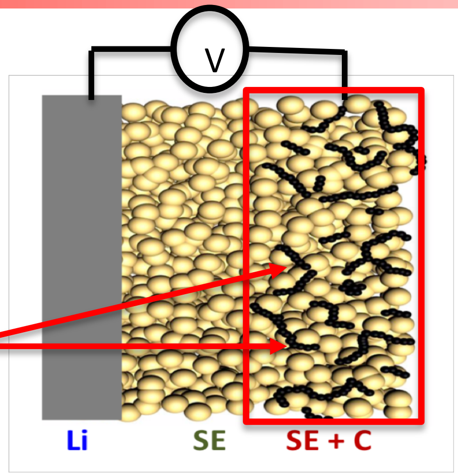


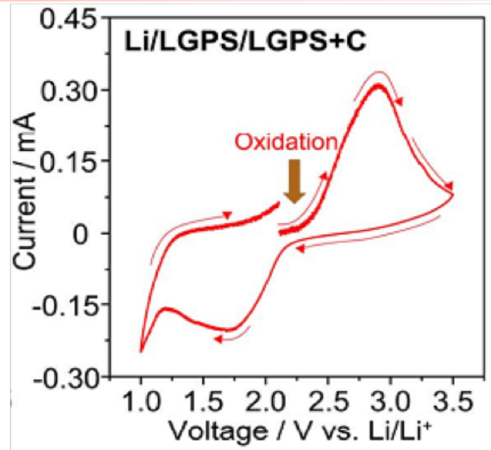


Wenzel, Randau, Leichtweiß, Weber, Sann, Zeier, Janek, ***Chemistry of Materials*** (2016), 28, 2400

Oxidation at cathode interface

Oxidation reaction also lead to interphase layer formation at cathode interface

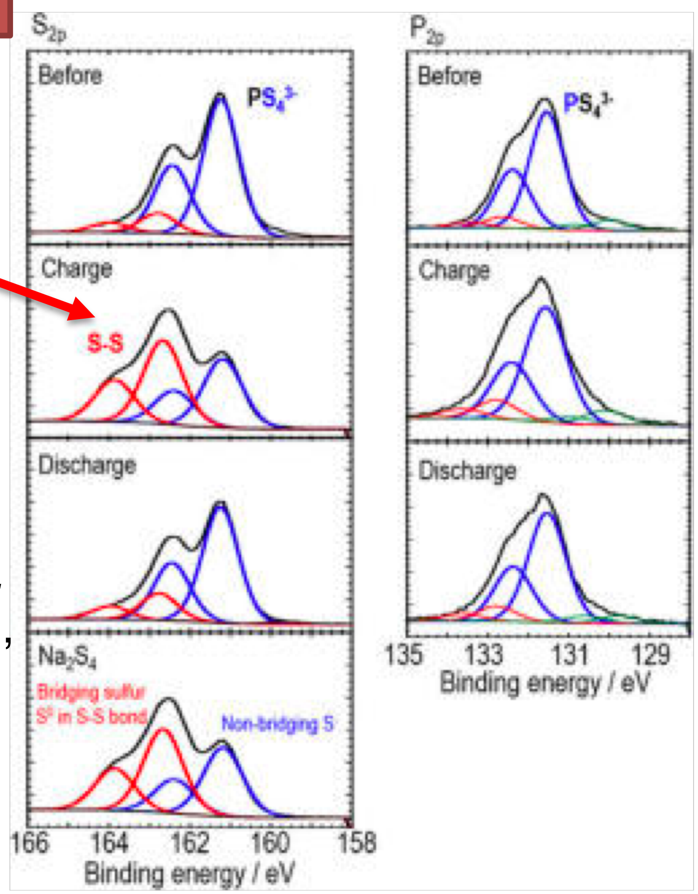


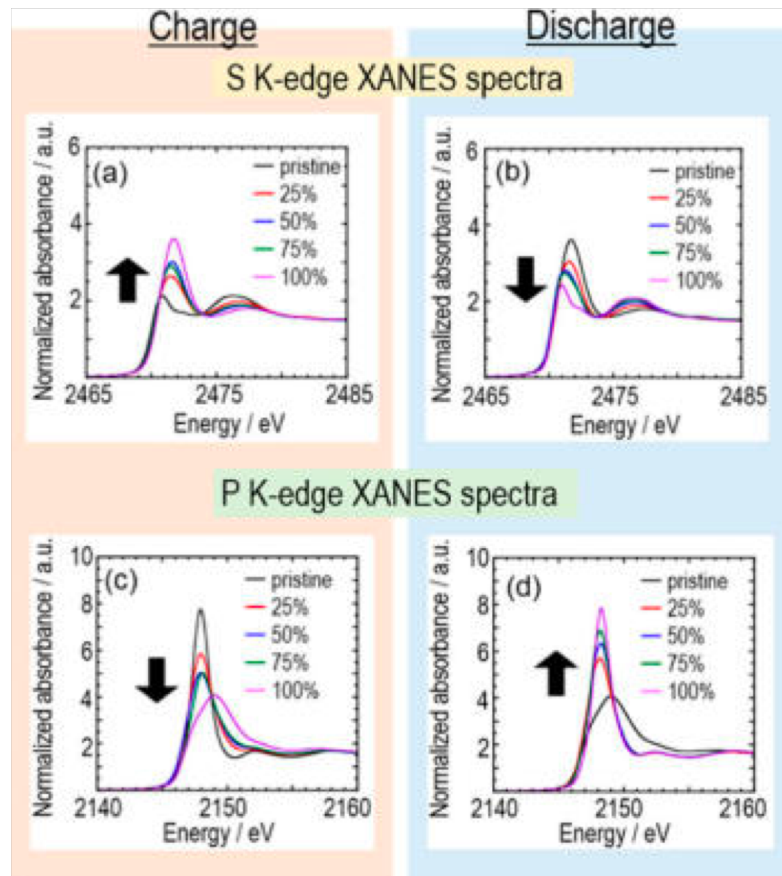


Han, Zhu, He, Mo, Wang, ***Adv. Energy Mater.*** (2016) 1501590.

Li3PS4 shows S redox reactions by XPS and XANES

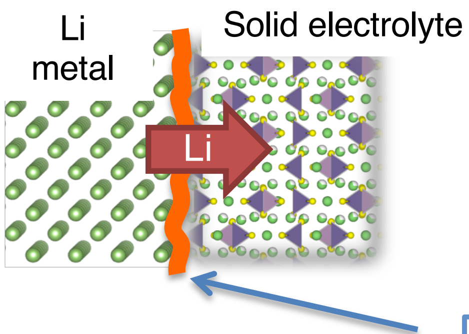
Hayashi et al. *Chem. Mater.*, **2017**, *29* (11), pp 4768–4774



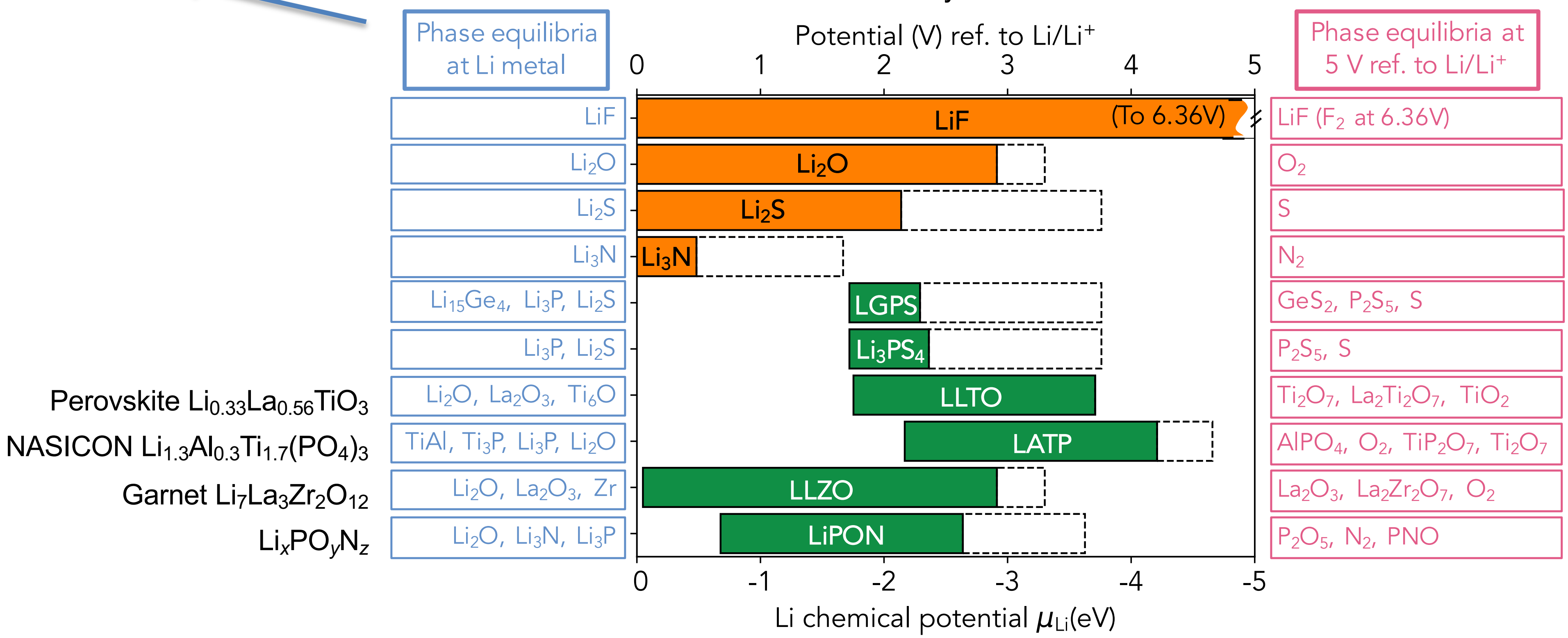


Thermodynamic Intrinsic Electrochemical Window of Solid Electrolyte

- Li binary stable against Li metal
- Sulfide SEs generally have narrow window: due to cation reduction and S oxidation
- Oxide SEs have wider window than sulfides. Oxidation may be kinetically limited.



Electrochemical window of solid electrolyte

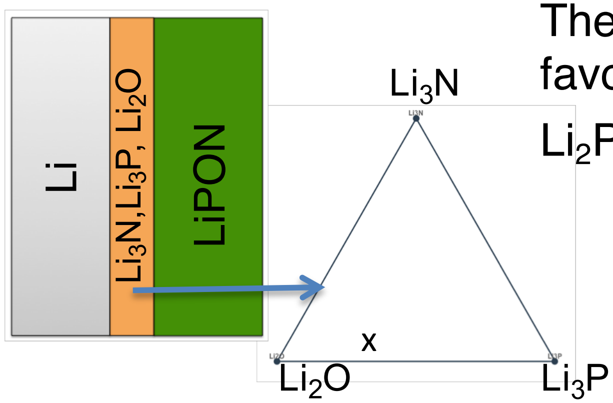


Zhu, He, Mo, ***ACS Appl. Mater. Interfaces,*** 2015, *7* (42), 23685–23693

Nolan, Zhu, He, Bai, Mo, ***Joule***, 2018, 2, 2016-2046

Formation of Passivating Interphase Layer to Enable Compatibility

LiPON is well demonstrated for thin-film solid state batteries.
Li-LiPON is a compatible interface.



Thermodynamics also shows Li reduction is energetically favorable

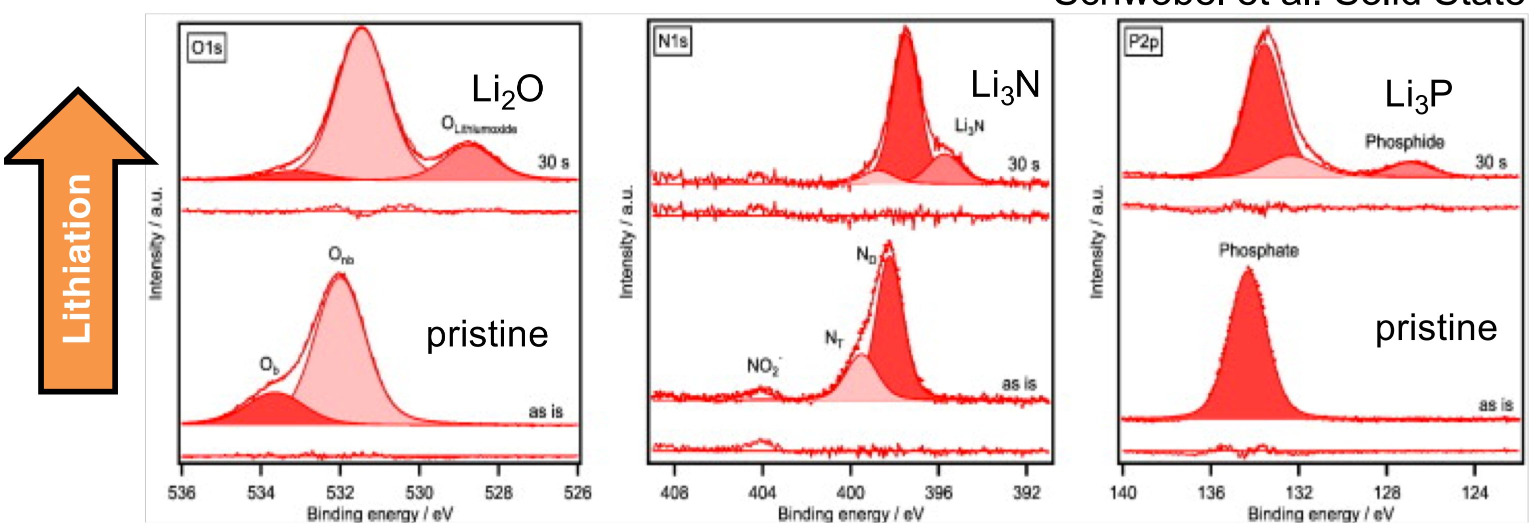
Li_2PNO_2 + 8 Li→ Li_3N + 2 Li_2O + Li_3P (-3.9 eV / 380 kJ/mol)

In situ, spontaneous formation of SEI-like interphase layer

- consisting Li_3P, Li_3N, Li_2O,
- ion conducting but electronic insulating
- **Passivate** the interface of solid electrolyte.

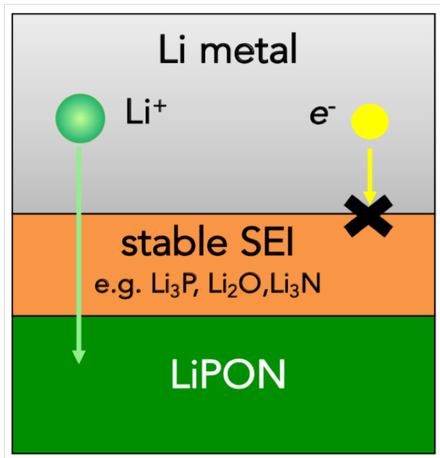
In-situ XPS observed Li reduction of LiPON

Schwobel et al. Solid State Ionic (2016), 273, 51



Design Principles for Li-SE Interface

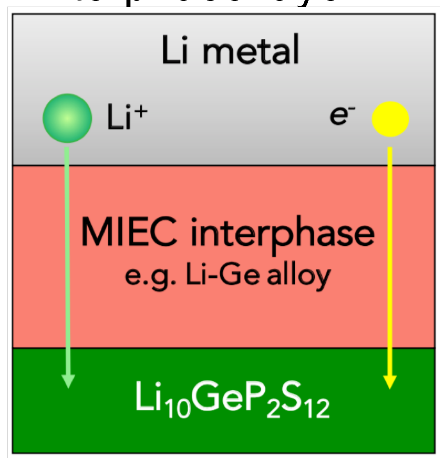
Type 3 interface:
compatible
by forming passivating SEI
layer



e.g.
Li-LiPON

Desired SEI property:
Ion conducting but
electronic insulating

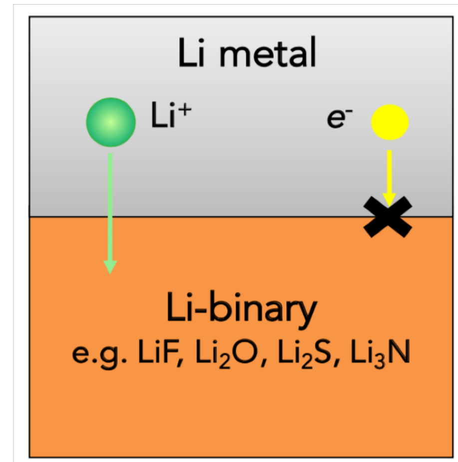
Type 2 interface:
non-compatible
form *mixed ionic and electronic conductor* (MIEC)
interphase layer



e.g.
Li-LGPS,
Li-LLTO, Li-LATP

Avoid !
Decomposition
continue !

Type 1 interface:
compatible
Stable, no decomposition



e.g.
Li-LiF, Li-Li_2O, Li-Li_3N
Li-LLZO (?)

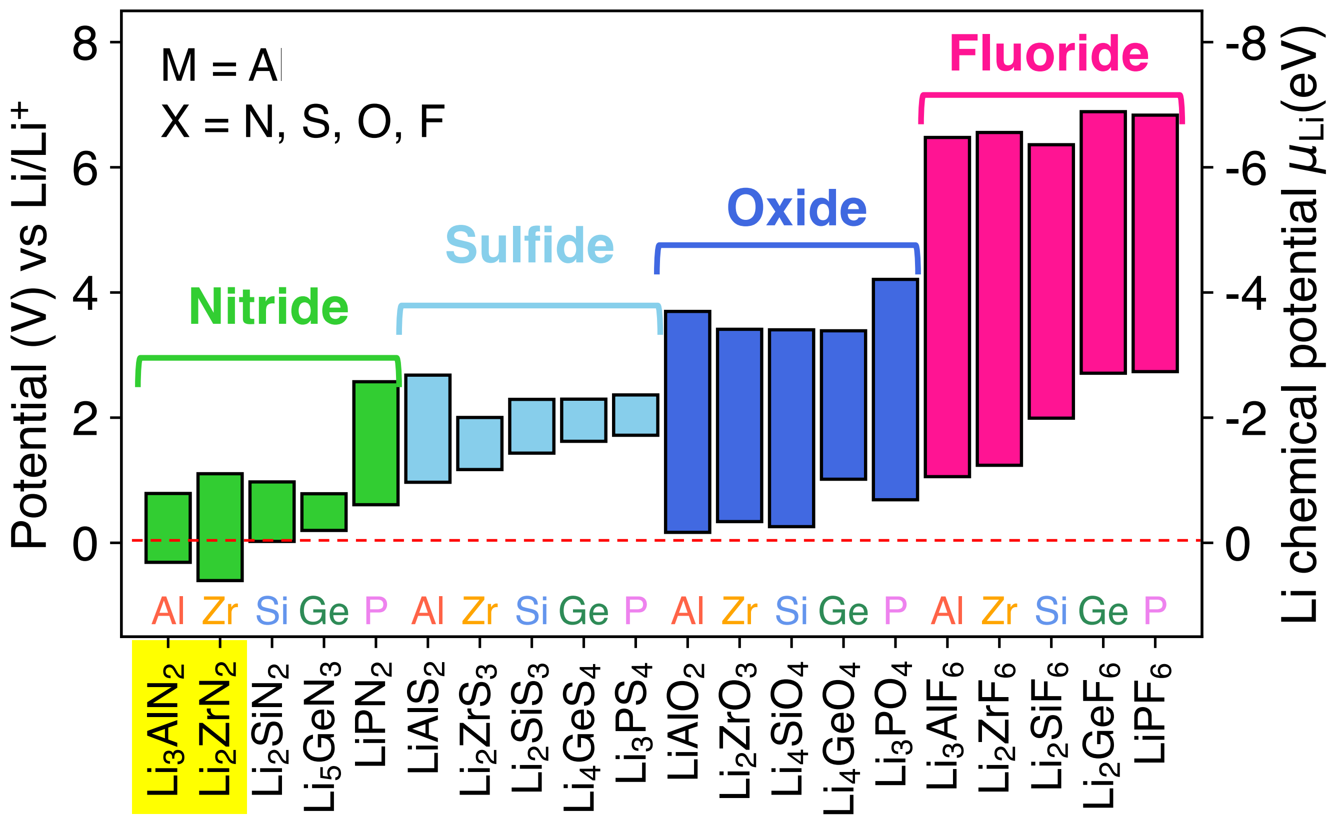
Good but rare

Can we predict / discover some?

Wenzel, Leichtweiss, Kruger, Sann, Janek, ***Solid State Ionics***, 2015, 278, 98–105.
Zhu, He, Mo, ***J. Mater. Chem. A***, 2016,4, 3253-3266
Nolan, Zhu, He, Bai, Mo, ***Joule***, 2018, 2, 2016-2046

What materials chemistry are stable against Li metal ?

Electrochemical stability window of example Li-M-X compounds.



Some Nitrides are Li metal stable and electronic insulating.
Can be used for protecting Li metal.

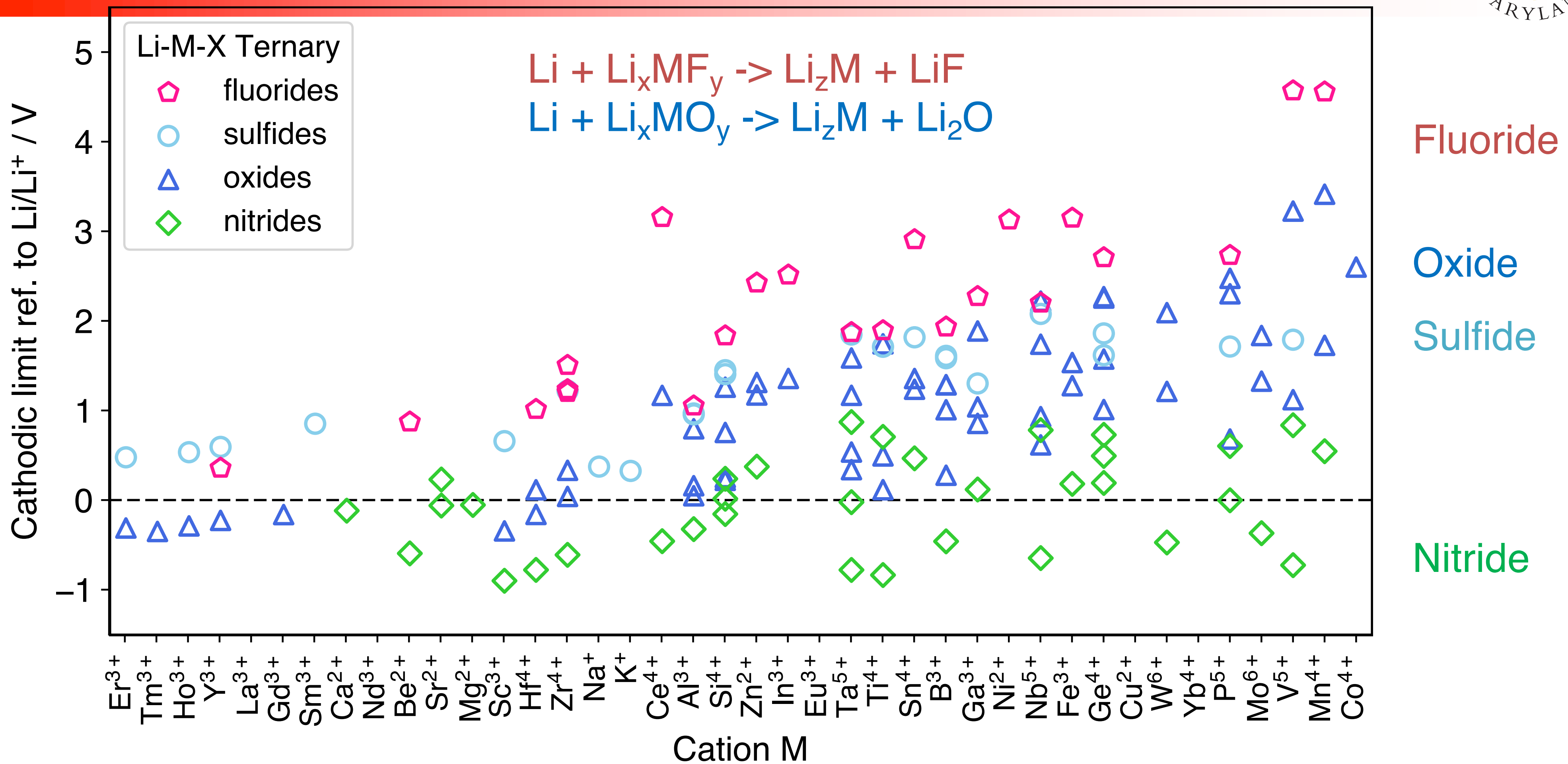
General trend of electrochemical window

Cathodic limit (Reduction):
Nitride < **Oxide** ~< **Sulfide** < **Fluoride**
Cations lead to Li reduction and MIEC interphase (non-compatible), except some nitrides.

Anodic limit (Oxidation):
Nitride < **Sulfide** < **Oxide** < **Fluoride**
Anion oxidation.

Zhu, He, Mo, ***Advanced Science*** (2017) 1600517

Nitrides have unique thermodynamic stability against Li metal



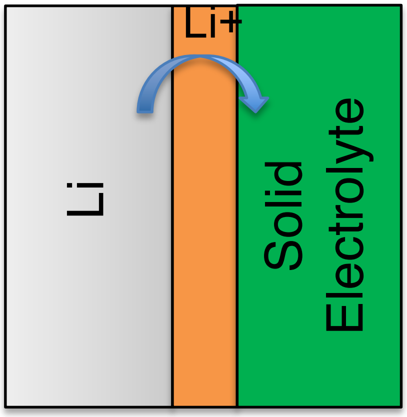
- Most Li-M-X oxides, sulfides, halides are reduced by Li metal. Most form MIEC interphase due to the reduction of metal cations M. (Not passivate)
- **Nitrides** have unique thermodynamic stability against Li metal.

Computation predicted nitrides chemistry to stabilize Li metal

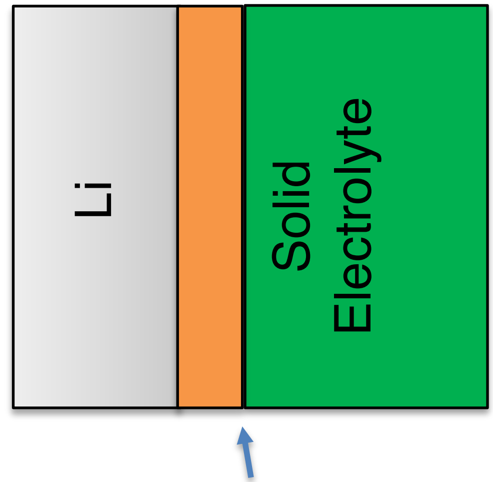
Zhu, He, Mo, ***Advanced Science*** (2017) 1600517

Strategies for Li metal stable interface

Apply artificial SEI layer as coating



Spontaneously formed stable SEI layer



Coat Li-stable artificial SEI

- Li binary: Li_3N (others have low ionic conductivity)
- Li-stable nitrides

In-situ spontaneously form SEI layer.

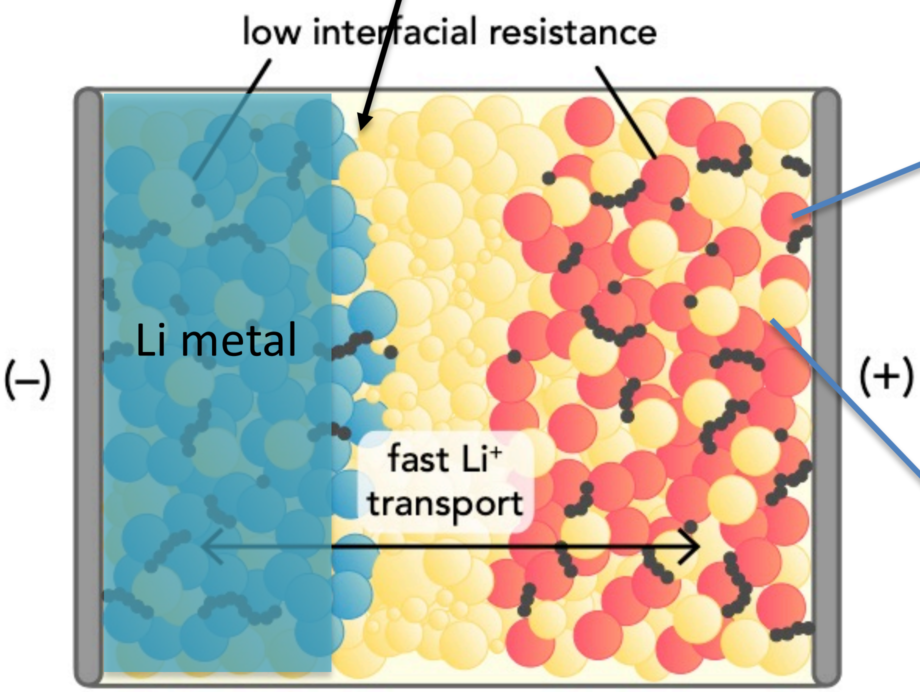
- SE with no metal cation: e.g. LiPON, LPS class, LPS halogen-doped , etc.
- Nitrogen doping can form stable Li metal nitride to protect metal from reduction

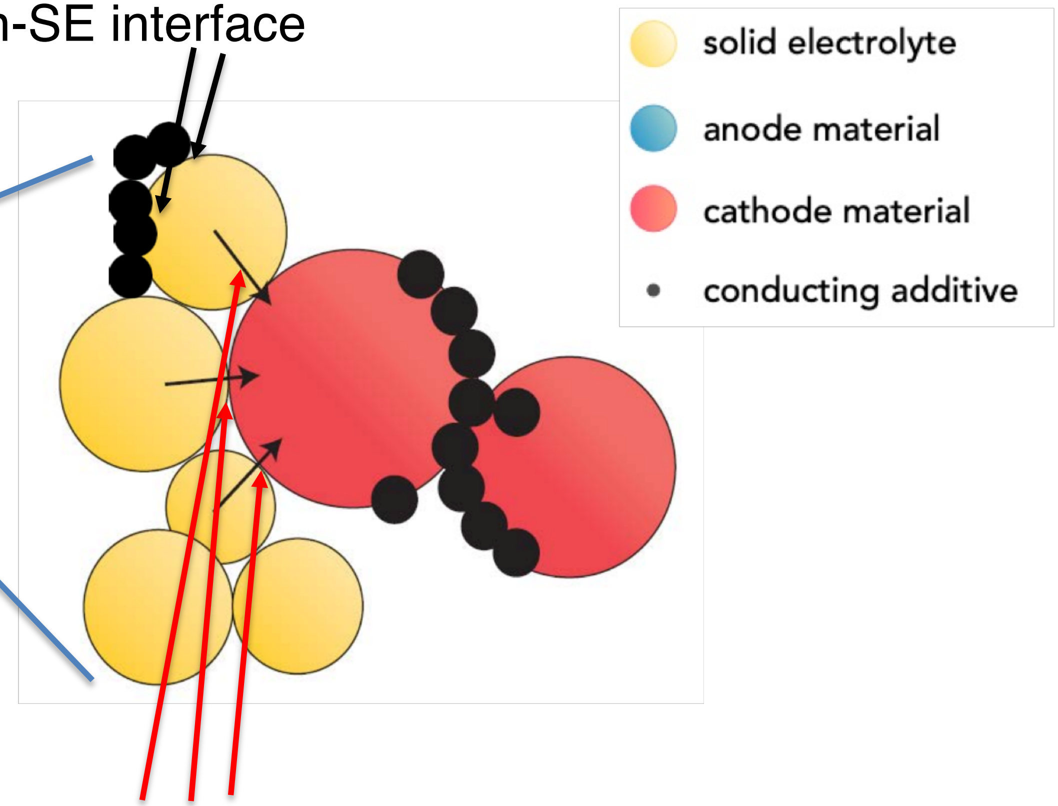
Interphase layers should be Ionic conducting but electronic insulating

Zhu, He, Mo, ***Advanced Science*** (2017) 1600517
Nolan, Zhu, He, Bai, Mo, ***Joule***, 2018, 2, 2016-2046

Interface Compatibility : Basic Thermodynamics

Electrochemical window of the solid electrolyte
→ Decomposition at metal anode interface
→ Decomposition at carbon-SE interface





Chemical compatibility of interface: <u>Chemical reaction</u> between solid electrolyte and electrodes.
Electrochemical compatibility of interface: <u>Electrochemical reaction</u> between solid electrolyte and electrodes (during voltage cycling).

Zhu, He, Mo, ***J. Mater. Chem. A***, (2016),4, 3253-3266
Nolen, Zhu, He, Bai, Mo, ***Joule*** (2018), 2, 2016-2046

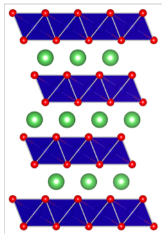
Tian, .., Ceder ***Energy Environ Science*** (2017)

Evaluate Interface Stability from Computational Database

How to evaluate interface stability from thermodynamics

- **Chemical stability**: whether there is an exothermic reaction to form other phases
- **Electrochemical stability**: whether there is an exothermic reaction at applied potential

Cathode, $LiCoO_2$



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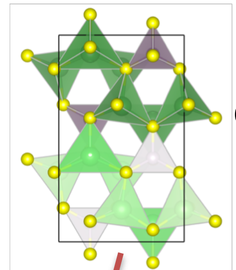
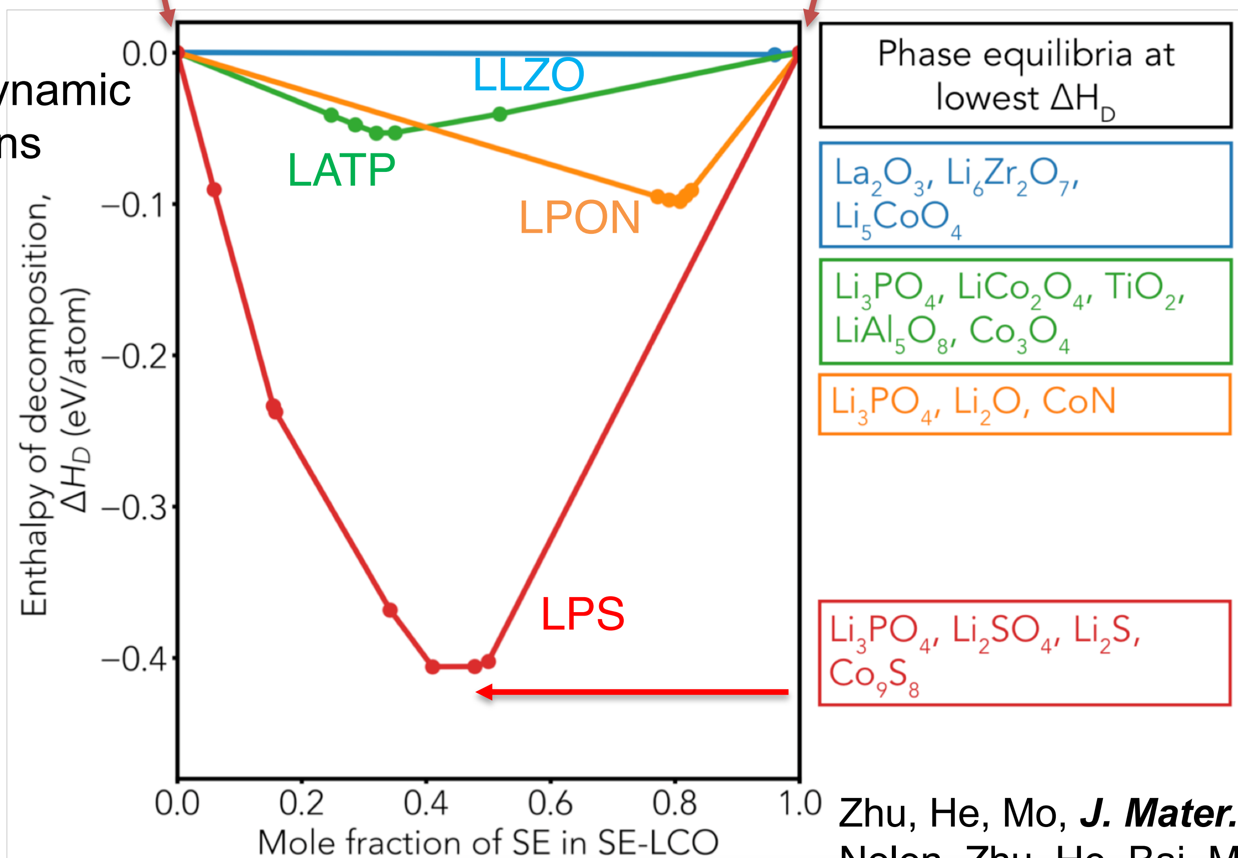


Solid electrolyte e.g. Li_3PS_4

Thermodynamic calculations



Oxide-LCO still unstable thermodynamically. Better than sulfide SEs.

Sulfide-LCO highly unstable. Favorable reaction.

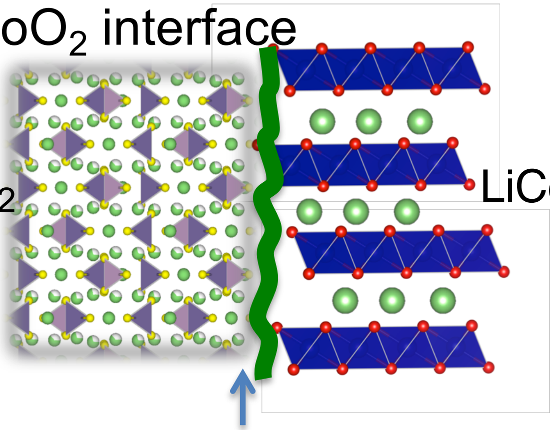
MATERIALS PROJECT

Zhu, He, Mo, ***J. Mater. Chem. A***, 2016,4, 3253-3266
Nolen, Zhu, He, Bai, Mo, ***Joule*** 2018, 2, 2016-2046

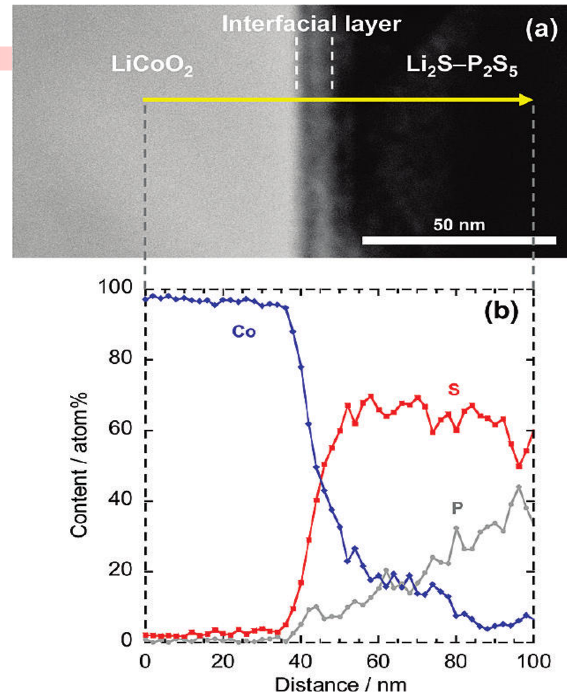
Sulfide SE – cathode interface : Not compatible

For LGPS-$LiCoO_2$ interface

$Li_{10}GeP_2S_{12}$



$LiCoO_2$



Sakuda *et al.* **Chem. Mat.** 22, 949 (2010)

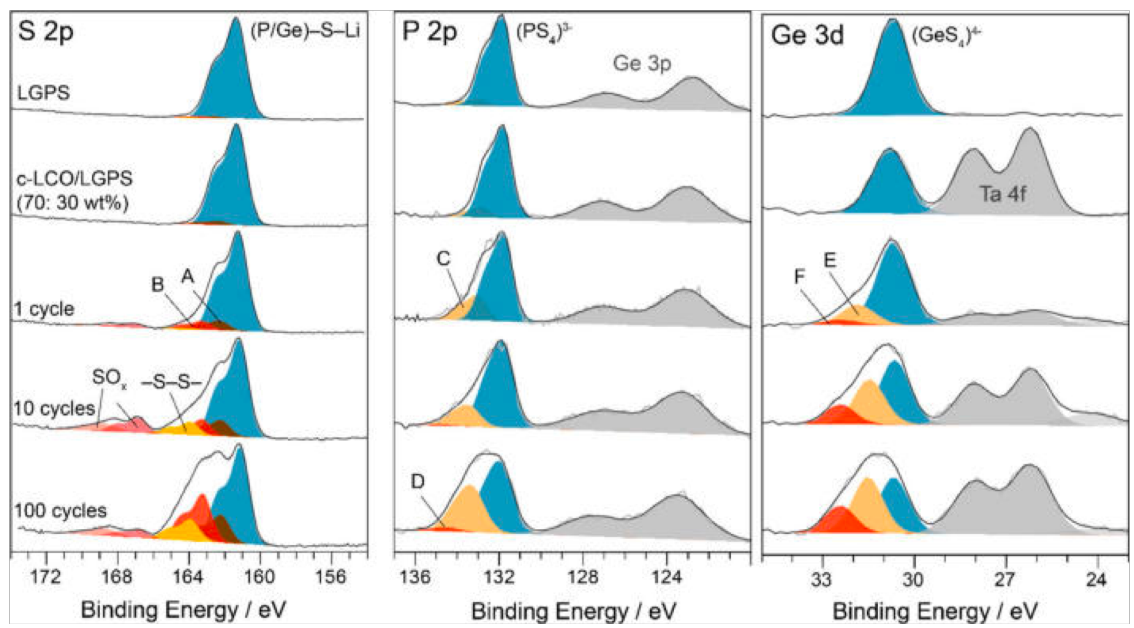
$Li_{10}GeP_2S_{12} + LiCoO_2 \rightarrow Co_9S_8 + Li_2S + Li_2SO_4 + Li_3PO_4 + Li_4GeO_4$

(ΔH = **-0.35 eV/atom**)

- The formation of interphase layers is highly favorable.
- Electronic conductive Co_xS_y lead to MIEC interface
- non-compatible interface

ΔH = **<-1 eV/atom at >4V**

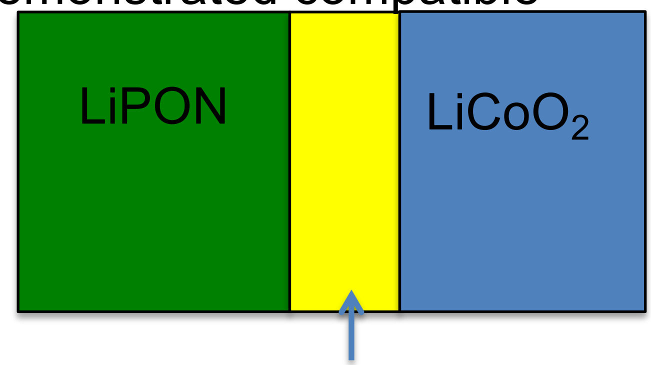
- Voltage drives the interface reaction



Janek et al. ACS Appl. Mater. Interfaces, **2017**, *9*, 35888

Interface reactions for LiPON - Cathode

LiPON-$LiCoO_2$ interface:
demonstrated compatible

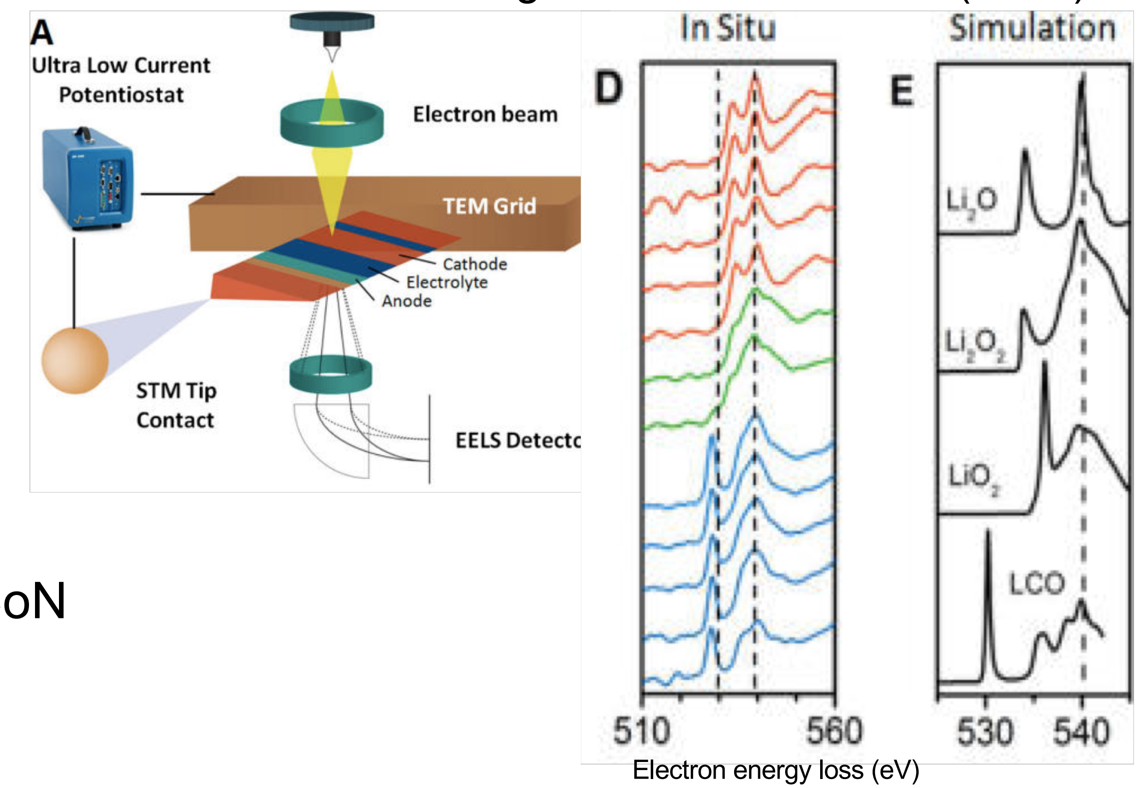


Li_3PO_4, Li_2O, Li_2O_2,
CoN_x, CoO_x, Li_xCoO_y

LiPON+ $LiCoO_2$ ➔ **Li_3PO_4** + Li_2O + CoN
(ΔH = **-0.1 eV/atom**)

ΔH = **-0.17 to -0.48** eV/atom
At applied voltage of 4.2V to 5.0V

Y. S. Meng *et al.* **Nano Letters** (2016)

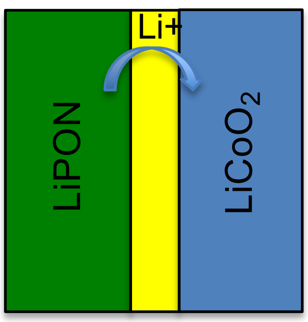


Compatible interface
Electronic insulating but ion conducting interphase formed to stabilize the interface
-> Form **SEI**-like passivation
-> Self-Limiting decomposition
-> Decent interfacial Li+ transport.

Zhu, He, Mo, ***J. Mater. Chem. A***, 2016,4, 3253-3266

Design Principles for SE-Cathode Interface

Type 3. Stable SEI
Compatible
LiPON-LCO

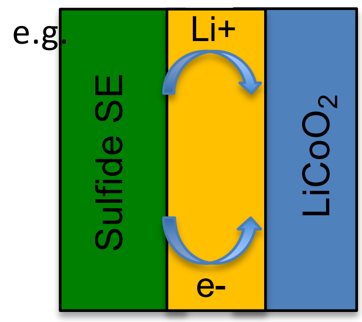


Li_3PO_4, etc.

Electronic insulating interphase formed
-> Limited decomposition
-> Form **SEI**-like passivation
-> Decent interfacial Li+ transport.

Desired SEI property: Ion conducting but electronic insulating

Type 2. MIEC interphase
Incompatible
Sulfide SE-LCO



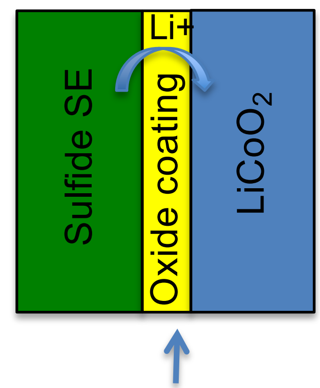
Co_xS_y, etc.

Electronic conductive interphase formed
-> Sustained decomposition.
-> Thick interphase layer.
-> High interfacial resistance.

Avoid ! Decomposition continue !

Can we fix Type 2 interface?

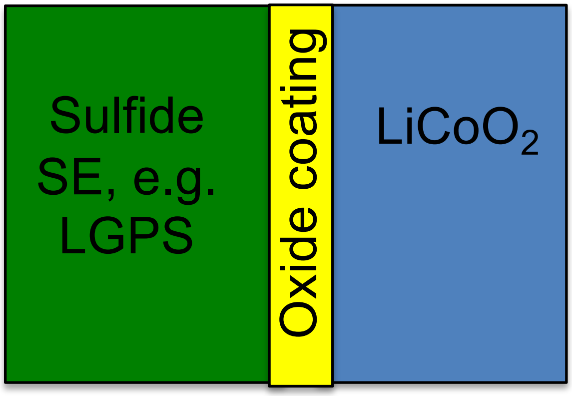
Mitigation strategy:
Converting to Type 3 by **coating**



Oxide coating layer,
(e.g. $LiNbO_3$, Li_3PO_4, etc.)
serves as artificial SEI

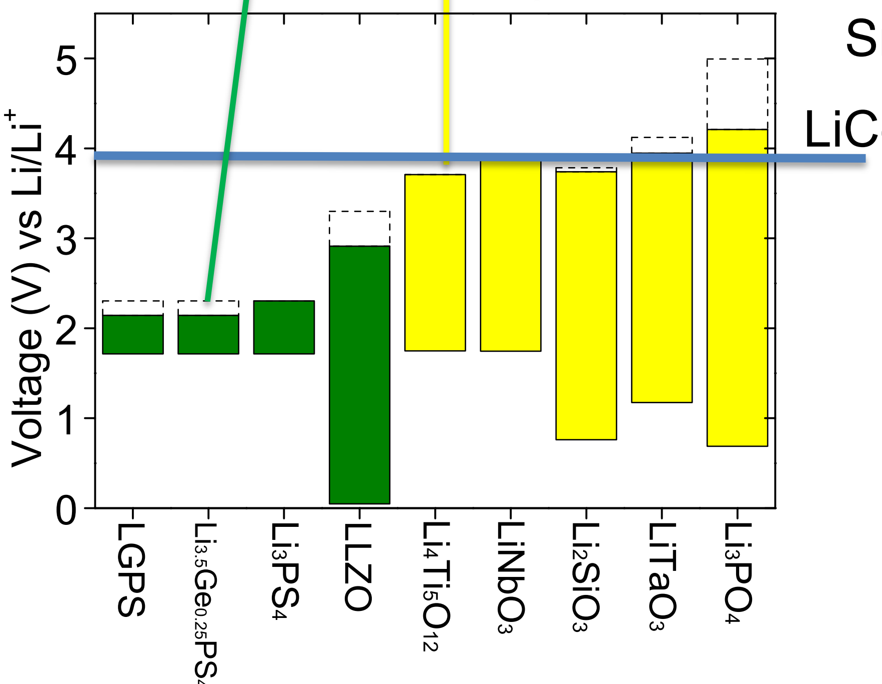
Zhu, He, Mo, ***J. Mater. Chem. A***, 2016,4, 3253-3266
Nolen, Zhu, He, Bai, Mo, ***Joule*** 2018, 2, 2016-2046

Coating Enables Cathode Interface Compatibility



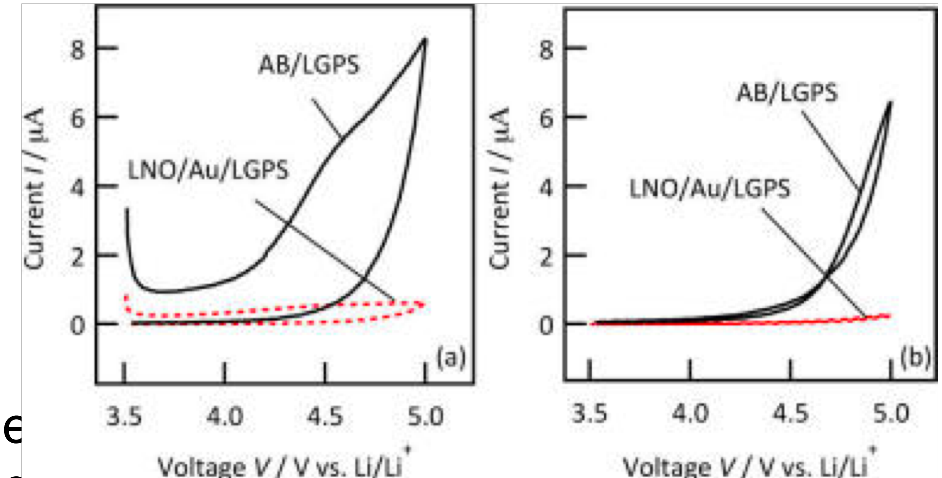
Chemically compatible both SSE and cathode

Small E_{decomp}

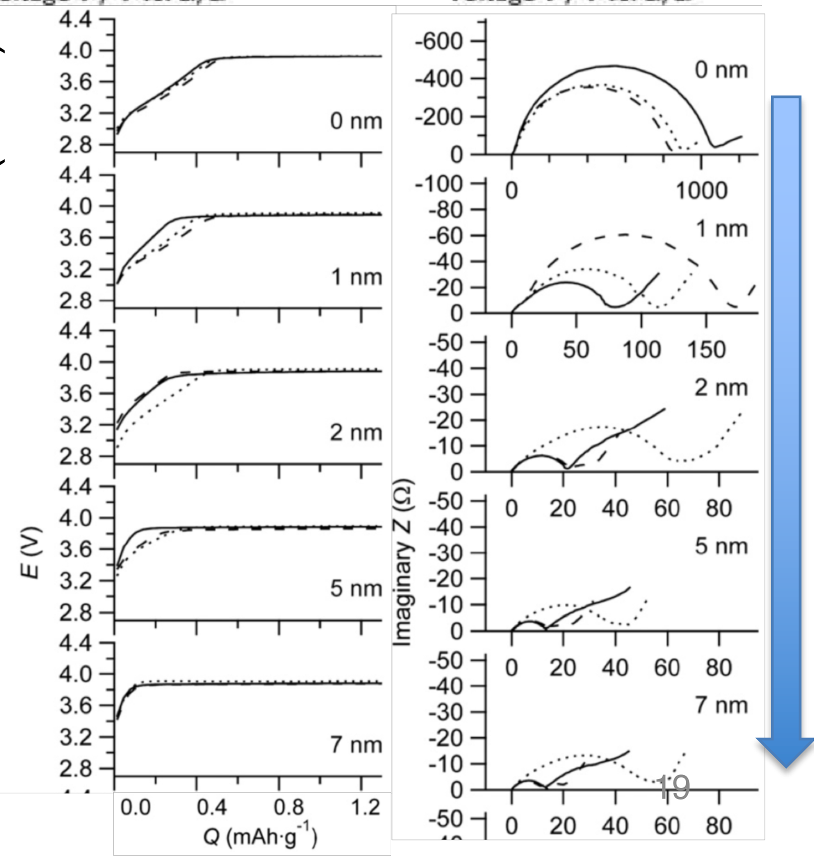


- Has Li+ carriers for ion transport
- Electronic insulating (Type 3)

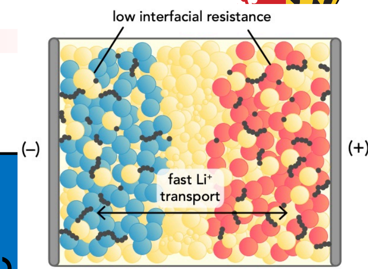
Kanno et al. Chem. Mater. 2016, 28, 2634



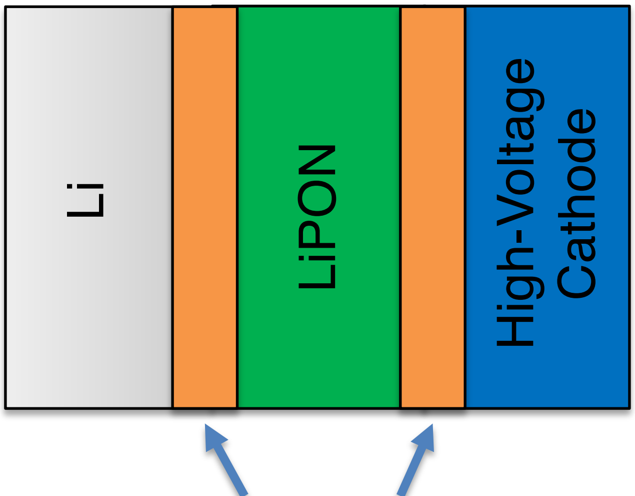
Takada et al. Solid State Ionics (2008)



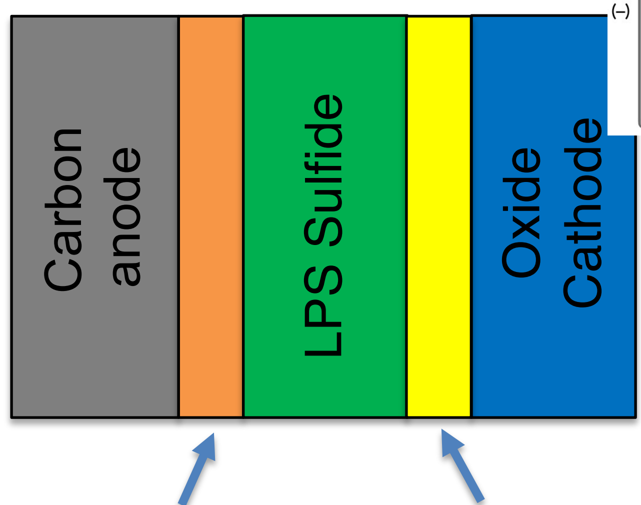
Resolving interface compatibility in all-solid-state battery



Current success cases:



Spontaneously formed
stable SEI layer



formed
SEI layer

Artificial
coating layer

Strategies for resolving interface issues:

- Optimize and design SE to form stable SEI (e.g. LiPON) – good interfacial compatibility.
- Applying thin coating layer as artificial SEI (e.g. $LiNbO_3$ coating on sulfide SE)
- Novel interfacial engineering to spontaneously form stable SEI.

Nolen, Zhu, He, Bai, Mo, ***Joule*** 2018, 2, 2016-2046

Conclusions

First principles Computation Methods

- First principles computation techniques were developed to evaluate the interfacial equilibria of solid materials. The computation framework can be transferable to any heterogeneous interfaces.

Electrochemical stability of solid electrolyte

- Most solid electrolyte materials have limited electrochemical window, and are not thermodynamically stable against Li metal, cathode, or at high voltage.
- The decomposition and reactions of solid electrolyte form interphase layers between the solid electrolyte and the electrode.
- The interphase layer plays a key role in passivating the solid electrolyte. The interphase layer is an origin of high interfacial resistance.

Implications for all-solid-state battery

- Interface engineering is the key to achieve good cell performance.
- Develop compatible materials combinations to optimize interfaces.
- Apply thin coating layers to enable interface compatibility.

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Materials Project

MATERIALS PROJECT

pymatgen

Computational resources:

- XSEDE: NSF TG-DMR130142, TG-DMR150038
- University of Maryland supercomputers
- Maryland Advanced Research Computing Center (MARCC)