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## WEBINAR

# Exploring Battery Materials: Electrodes, Electrolytes, and Interfaces Thereof

René Windiks  
Materials Design

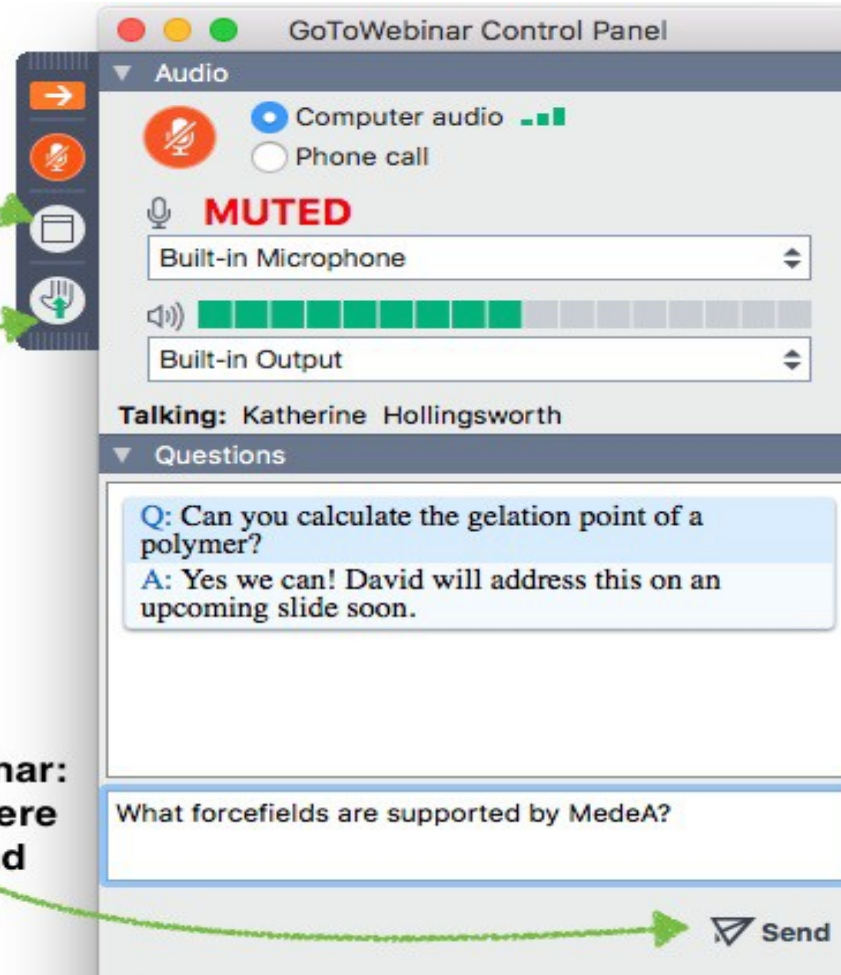
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# Webinar Team

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- ▶ Simulation approaches for batteries: Need for atomic-scale simulations
- ▶ Current Li ion battery technology
- ▶ Specific case examples
  - Properties of the solid electrolyte interface (SEI) of Li ion battery cells
  - Materials for next-generation battery technologies
    - Low-strain cathode materials
    - High-energy density cathode materials
    - Li diffusion in the cathode material NMC311
    - Electrochemical stability of solid-state electrolytes (SSE)
    - Properties of solid polymer electrolytes (SPEs)
- ▶ Summary and Conclusions



# Battery Modeling and Simulations

# Battery Cell Engineering Modeling

## ▶ Multi-physics simulations with mathematical models

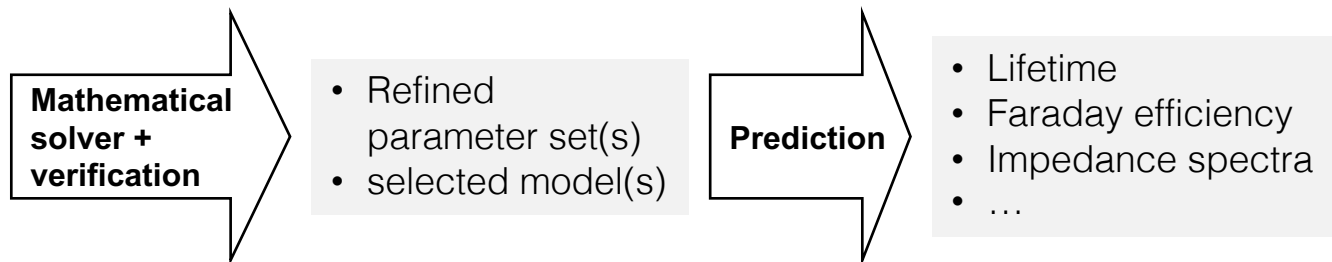
- Newman model
- Single particle model
- Nernst-Planck equation
- Cottrell equation
- Poisson-Boltzmann equation
- Butler-Volmer equation
- ...

requirement: initial **estimate** of parameters of battery components & materials

- diffusivity
- porosity, density, charge carrier concentrations (morphology)
- thermal conductivity
- electronic conductivity
- heat capacity
- reaction & charge transfer rates
- exchange current densities
- ...

## ▶ Workflow

- Measured battery cycling data (e.g. CV curves for relevant charge rates)
- initial set of 15-20 parameters
- selected model(s)

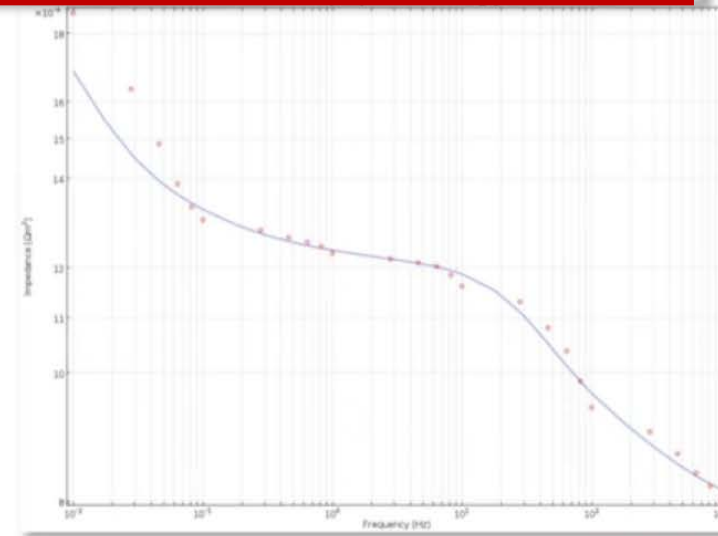
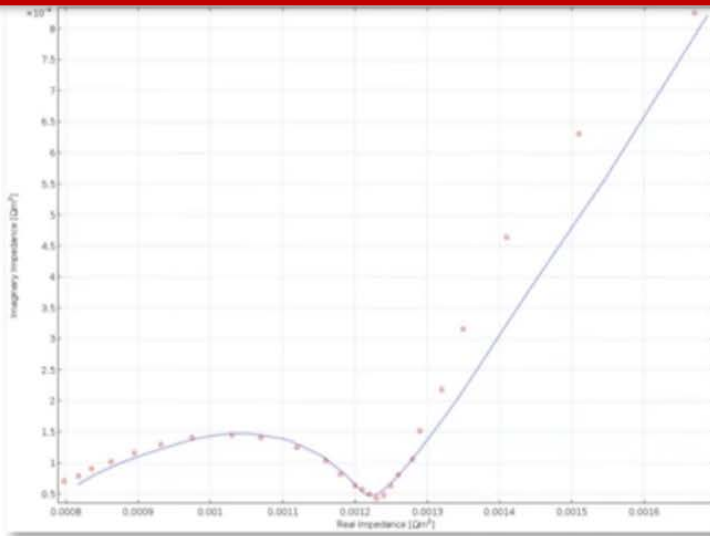


## ▶ Are relevant chemical reactions & processes adequately described?

# Uncertainty in Multi-Physics Simulations

## Parameter Estimation

“With four parameters I can fit an elephant, and with five I can make him wiggle his trunk.”



COMSOL

<https://www.comsol.de/video/intro-to-modeling-lithium-ion-batteries-using-comsol-multiphysics-july-24-2018>

# Advantage of Atomic-Scale Modeling and Simulations

## ► Reliable calculations and prediction of key properties of any battery material

### Materials Fabrication

- Free energies and phase diagrams: miscibility vs separation
- Elasticity: ductility, brittleness, hardness
- Permittivity Dielectric constants
- Piezoelectricity
- Diffusivity
- Thermal expansion
- Heat capacity
- Electronic structures

### Cycling Behavior, Fast Charging

- Ion conductivity
- Electrical conductivity
- Thermal conductivity
- Electrochemical stability vs degradation
- Phase transformation
- Volume change of particles
- Metal plating

### Interfaces of Electrodes, Electrolytes, Coatings, Binders, etc.

- Interphase morphology
- Interfacial contact
- Current density
- Overpotentials
- Inter-diffusion & segregation
- Interfacial stabilities/delamination
- Potential profiles

### Diagnostics & Analysis

- XPS (core level shifts)
- NMR (chemical shifts, field gradients, paramagnetic shifts)
- Powder diffraction patterns
- IR & Raman Spectra
- UV-Vis Spectra



# Current Li-Ion Battery Technology

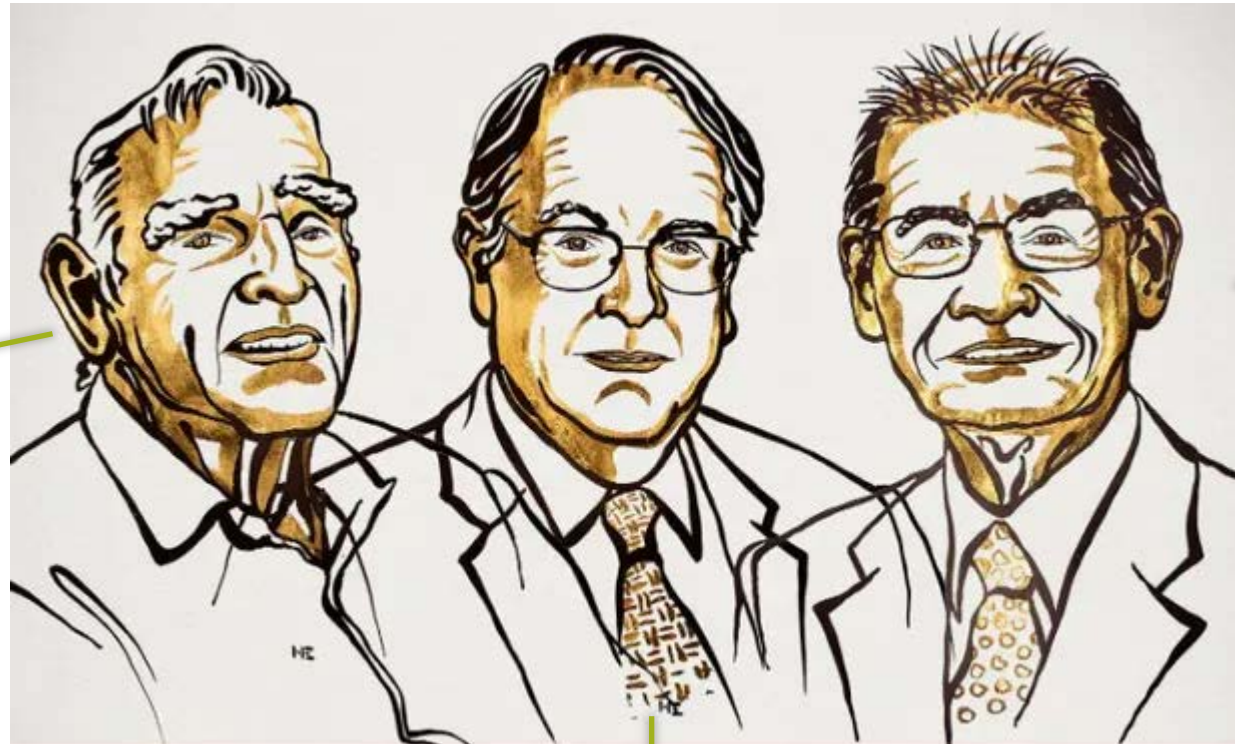
# Nobel Prize in Chemistry 2019 ...

... given to three distinguished and valued researchers whose inventions led to the commercially available lithium-ion battery in 1991

John B.  
Goodenough

M. Stanley  
Whittingham

Akira  
Yoshino



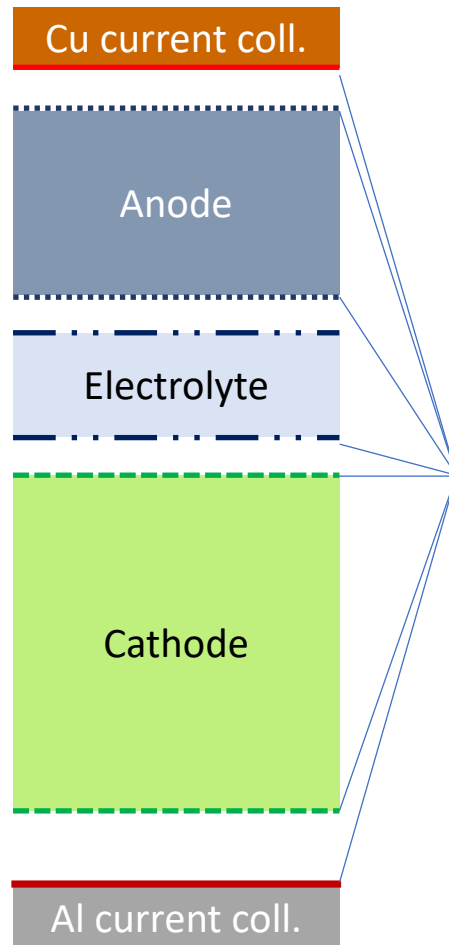
$\text{LiCoO}_2$  intercalation  
cathode

petroleum coke anode  
to intercalate Li ions

Intercalation of lithium  
ion in  $\text{TiS}_2$

# Li Ion Battery Cells: Electrochemical Reactors

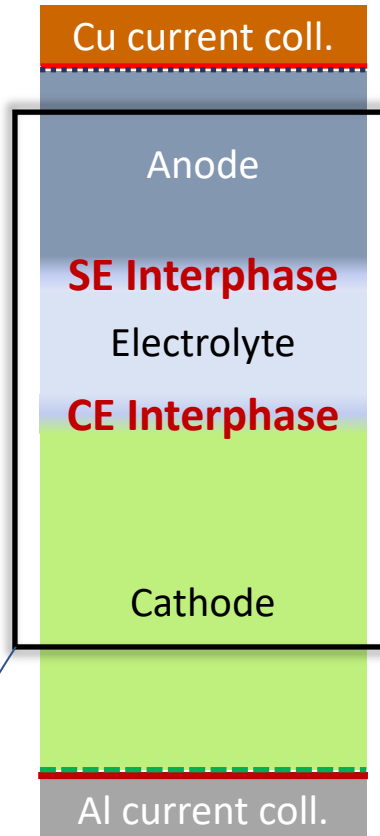
## Individual Components



Passivation layers/Coatings

Assembling

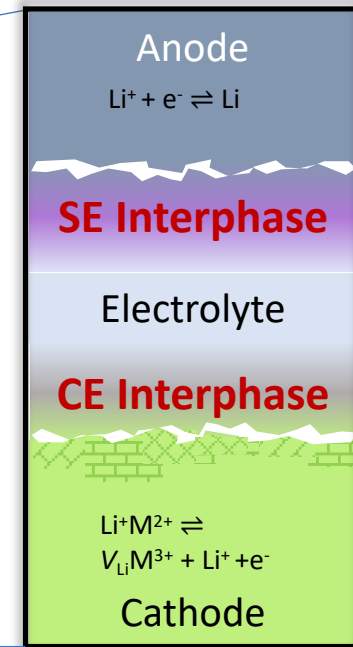
## Initial Cell



Electrochemically active domain

Cycling

## Used Cell



Electrochemical reactions cause

- ▶ Interphases with low  $\sigma_{ion}$
- ▶ Interfacial loss
- ▶ Electrochemical inactive phases
- ▶ Gassing
- ▶ Dendrite formation
- ▶ ...

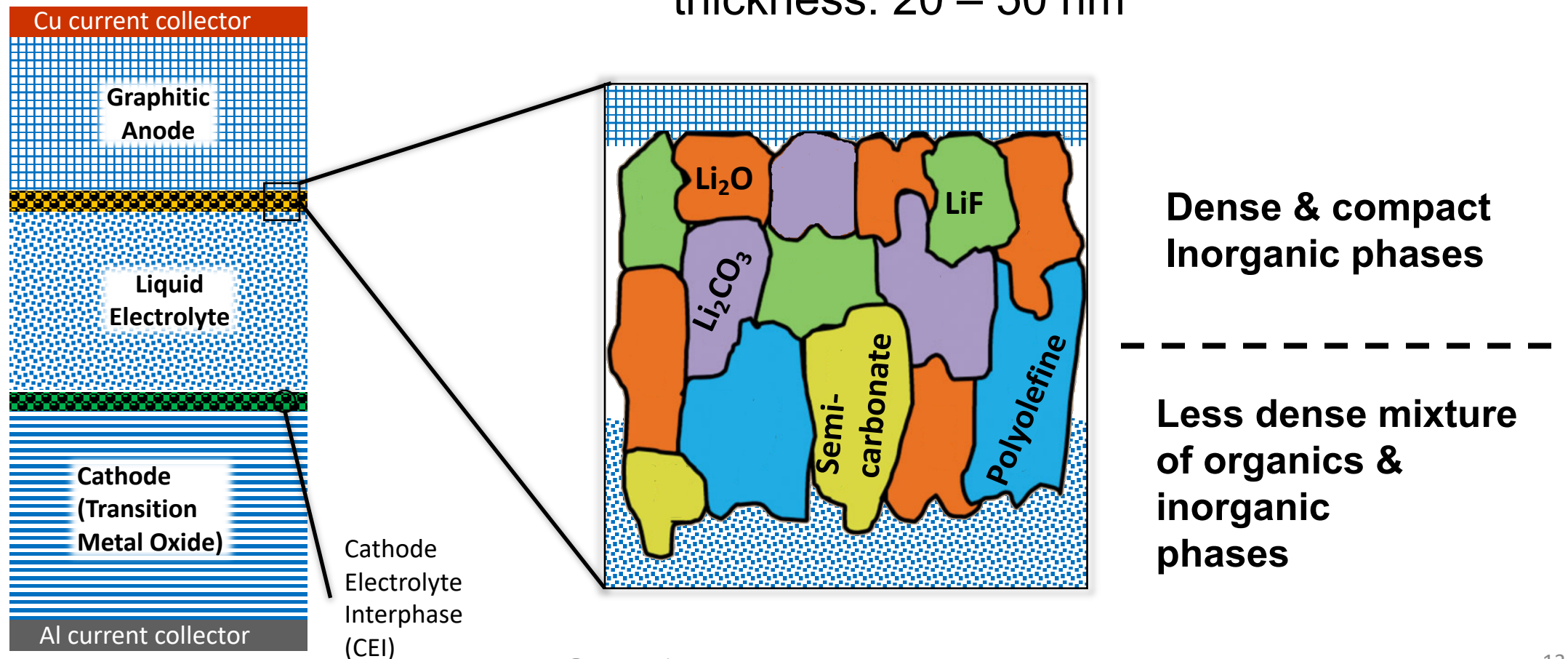
▶ Passive components (binders, etc.) are omitted for clarity

# Interfaces and Interphases in Li Ion Battery Cells ...

... determine performance, life-time, etc.

## ► Li Ion Battery Cell Scheme

► Solid Electrolyte Interphase (SEI) thickness: 20 – 50 nm



# Calculated Properties of SEI Components: $\text{Li}_2\text{CO}_3$

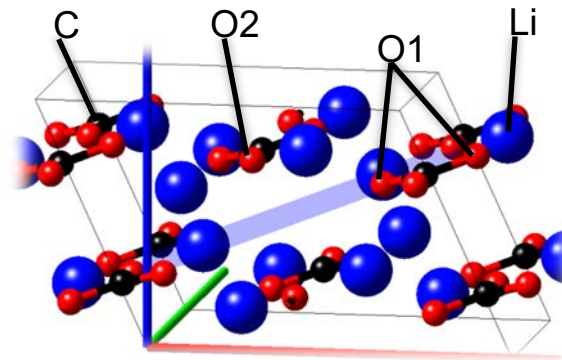
## ► Nuclear Magnetic Resonance (NMR)

**Calc. values** compared with exp. Data [1]

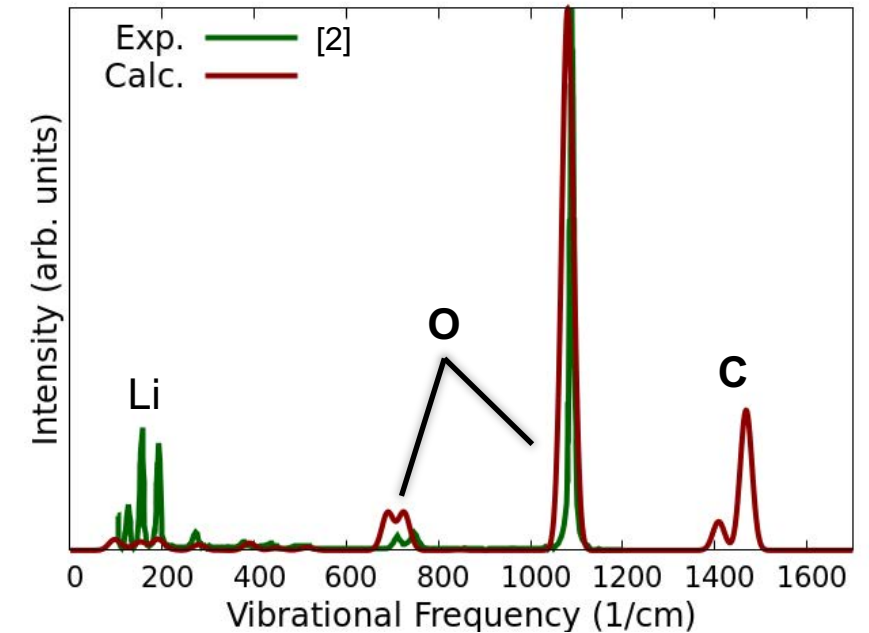
	$C_Q$ (MHz)	$\eta_Q$
$^7\text{Li}$	<b>0.09</b> (Exp. 0.07)	<b>0.6</b> (Exp. 0.8)
$^{17}\text{O1}$	<b>6.9</b> (Exp. 6.9)	<b>0.9</b> (Exp. 1.0)
$^{17}\text{O2}$	<b>7.2</b> (Exp. 7.2)	<b>0.8</b> (Exp. 0.9)

- $|\delta_{\text{iso O1}} - \delta_{\text{iso O2}}|$ :  
**21.5** (Exp. 17.1)[1]

- $\delta_{\text{iso}}$  = NMR isotropic chemical shift
- $C_Q = eQV_{zz}/h$  = quadrupolar coupling constant
- $Q$  = quadrupole moment
- $V_{zz}$  = largest electric field gradient component
- $\eta_Q = (V_{xx} - V_{yy})/V_{zz}$  = quadrupolar anisotropy parameter



## ► IR/Raman spectrum



Medea® InfoMaticA, VASP, Phonon

1. Dunstan, et al. J. Phys. Chem. C 119, 24255 (2015).
2. Jianget al., Phys. Stat. Sol. (A) 211, 206 (2014).

# Other Properties of SEI Components

## ► Calculated values (compared to experimental) data

Material	Bulk Modulus B (GPa)	Shear Modulus G (GPa)	Pugh's Ratio B/G > 1.75 → ductile	Exp. Bulk RT Ion Conductivity $\sigma_{ion}$ (S cm <sup>-1</sup> )
LiF cubic	75 (Exp. 63--93) <sup>[1]</sup>	47	1.6 brittle	< 10 <sup>-32</sup> [3]
Li <sub>2</sub> O cubic	77 (Exp. 57--90) <sup>[1]</sup>	65 (Exp. 70) <sup>[2]</sup>	1.2 brittle	< 10 <sup>-17</sup> [4]
Li <sub>2</sub> CO <sub>3</sub> monoclinic	60	33	1.8 ductile	< 2 10 <sup>-5</sup> [5]
SEI			> 1.75 ductile	

## ► Li<sub>2</sub>O & LiF are very poor Li ion conductors

## ► max. thickness of SEI for diffusion limited current density of $j_{diff} = 1 \text{ A m}^{-2}$ :

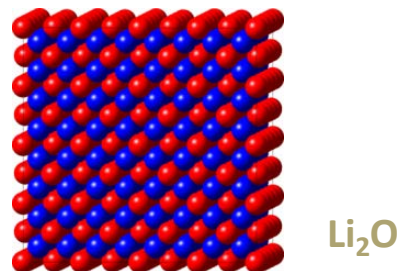
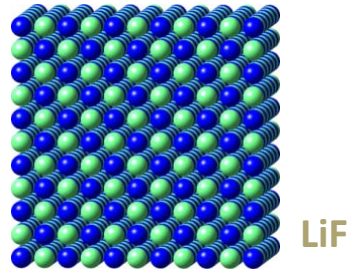
- ~ 0.3  $\mu\text{m}$  (Li<sub>2</sub>CO<sub>3</sub>)
- <10 nm (Li<sub>2</sub>O, LiF)

## ► Why does a 20-50 nm thick SEI work for current densities > 1 A m<sup>-2</sup>?

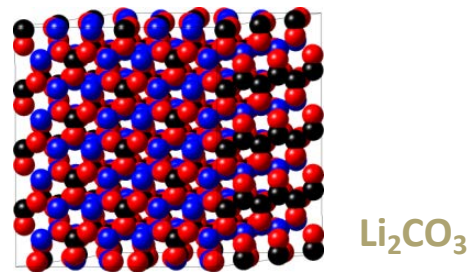
1. Linus Pauling File (LPF) via Materials Platform for Database Science (MPDS.io)
2. Hull, et al., J. Nucl. Mater. 160, 125 (1988).
3. [Pan, Cheng, Qi, Phys. Rev. B 91, 134116 (2015).
4. Omar and Ahmad, Mater. Sci Forum 846, 517 (2016).
5. approximated from  $\sigma$  of Li<sub>2</sub>O<sub>2</sub> and LiO<sub>2</sub> of Kim, et al. Chem. Asian J. 11, 1288 (2016).

# Calculated Ion Conductivity $\sigma_{\text{ion}}$ in Bulk Structures

- ▶ Nernst Einstein relation:  
 $\sigma_{\text{ion}} \propto D_{\text{ion}}$  (ion diffusivity)
- ▶ Einstein Smoluchowski relation:  $D_{\text{ion}} = \Delta r_{\text{ion}}^2 / 6t$ 
  - $\Delta r_{\text{ion}}^2$ : mean square displacement (MSD)
  - $t$ : time
- ▶ Densely packed & compact structures

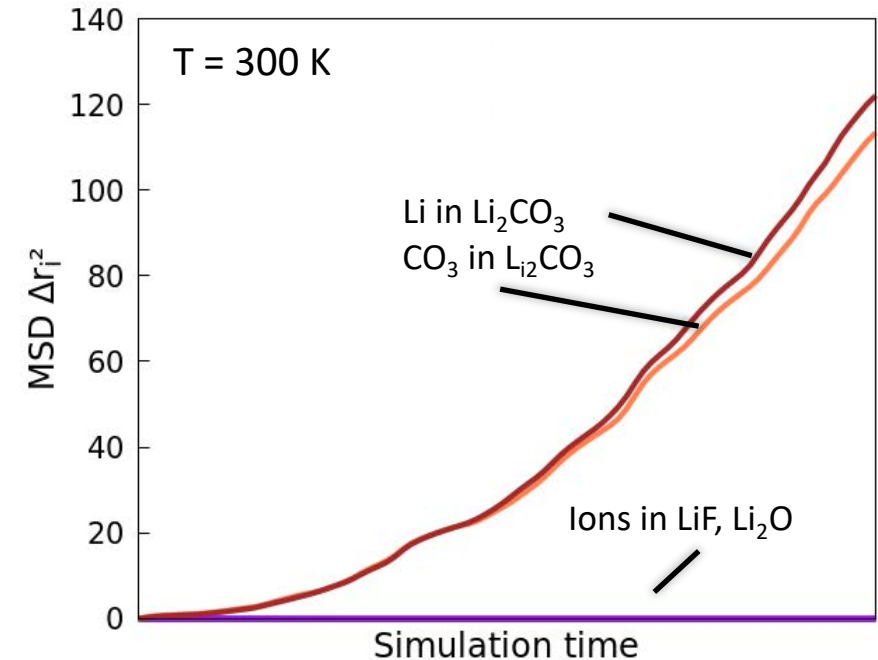


- ▶ “Open” structure



Li – blue  
O – red  
C – black  
F – green

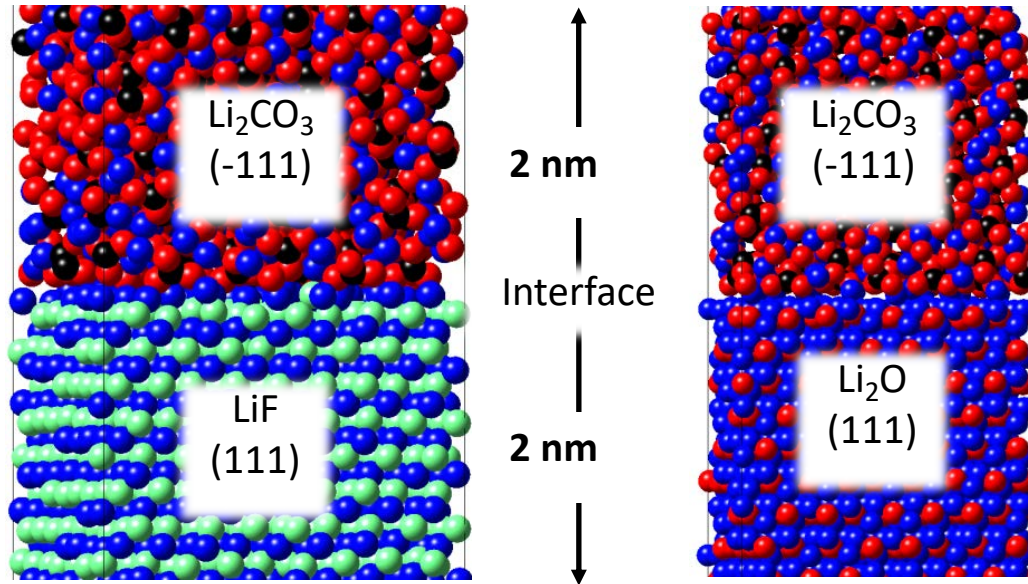
- ▶ MD Simulation of ion self diffusion



- ▶ Transfer number  $t(\text{Li}^+)$  in Li<sub>2</sub>CO<sub>3</sub>  $\approx 0.5$
- ▶ Negligible ion mobility in LiF and Li<sub>2</sub>O

# Enhanced Ion Conductivity due to Interfaces

## ▶ MD Simulations ion mobility in interface models

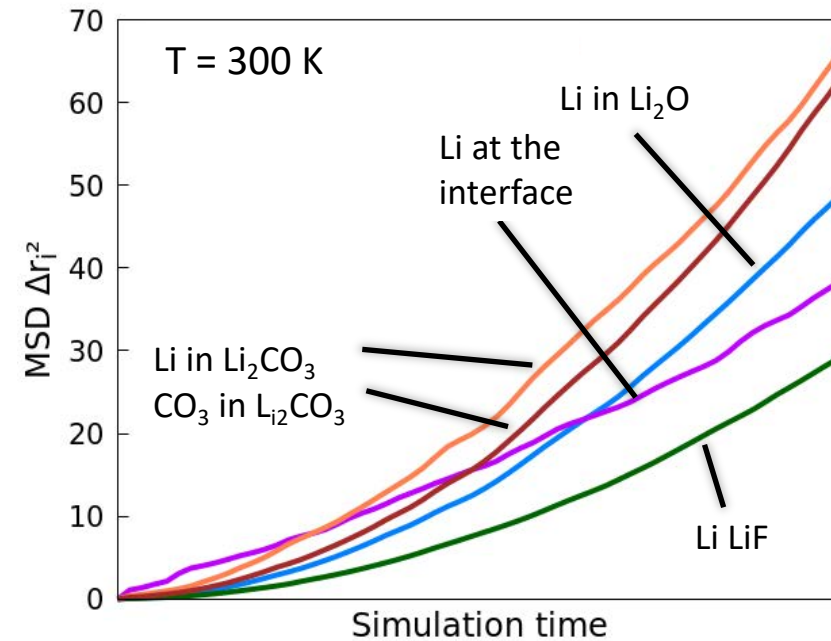


## ▶ Explanation for the enhanced $\sigma_{\text{ion}}^*$ :

- chemical potential of Li is more attractive in Li<sub>2</sub>CO<sub>3</sub> than in LiF and Li<sub>2</sub>O, respectively
- Increased charge carrier concentration near the interface (space charge accumulation): Li<sup>+</sup> in Li<sub>2</sub>CO<sub>3</sub>, Li vacancies in LiF and Li<sub>2</sub>O

\*) Zhang et al., Nano Letters 16, 2011 (2016).

## ▶ MD Simulation of ion self diffusion



- ▶ Li ion mobility in LiF and Li<sub>2</sub>O, respectively, increased by **several orders of magnitude!**

- ▶  $t(\text{Li}^+)$  in Li<sub>2</sub>O and LiF  $\approx 0.5$



# Next-Generation Battery Technologies

# Battery Technologies for the Future

- ▶ New anode materials: Li metal and silicon
  - Good energy density, safety concerns \*)
- ▶ All solids state batteries (ASSBs)
  - Good safety, slow charging & higher cost compared to current technology \*)
- ▶ Lithium-sulphur (Li-S)
  - Good energy density, low lifetime \*)
- ▶ Li-air/oxygen
  - Good energy density, poor lifetime \*)
- ▶ Non-Li charge carriers: Na, K, Ca, Al
- ▶ Organic batteries
- ▶ .....

\*) Daimler AG presentation at CES 2020, Las Vegas, NV



# Solid State Electrolytes (SSEs) for Lithium Batteries

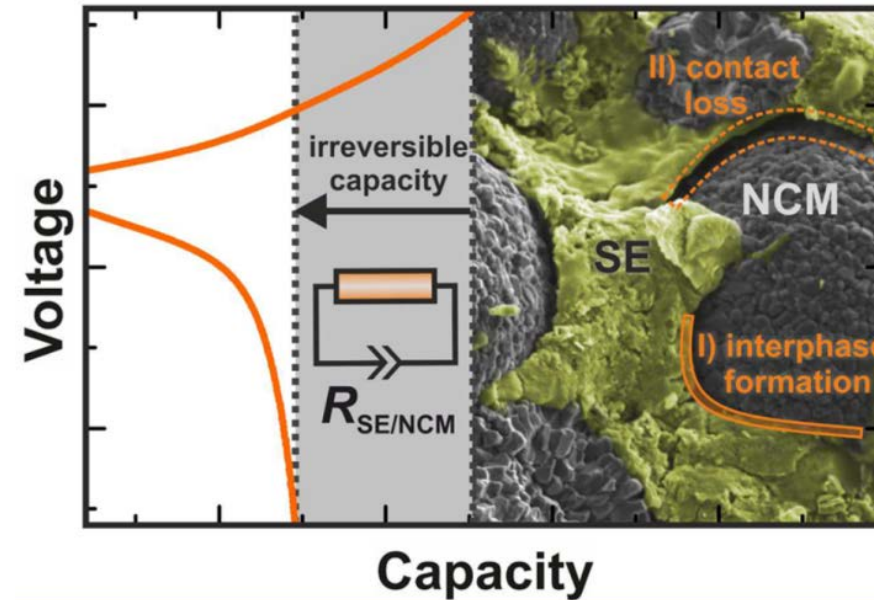
- ▶ Current goal: All solid state LB (ASSLB)
- ▶ Considered as next “technology” for high energy density LBs
- ▶ Key expectation: Extended lifetime & improved safety
- ▶ Issues
  - Rate performance limitations especially below ambient temperatures
  - Interface incompatibility with existing electrode materials
  - Mechanical instability of thin films (metal anode dendrites, cracks → short circuit)
  - Electrochemical instability; e.g. vs. Li metal
  - Cost parity with state-of-the-art liquid organic electrolytes
- ▶ Global R&D emphasis on inorganic ceramics/glasses, polymers, and composites



# Low-Strain Cathode Materials

# Cathode/Solid Electrolyte Interface

- ▶ Materials issues upon charging/discharging (cycling)
  - Formation of kinetically stable interphases (reduction/oxidation products)
  - Contact loss due to cathode particle “breathing” (volume change)
- ▶ Issues lower current density and lifetime of battery cells

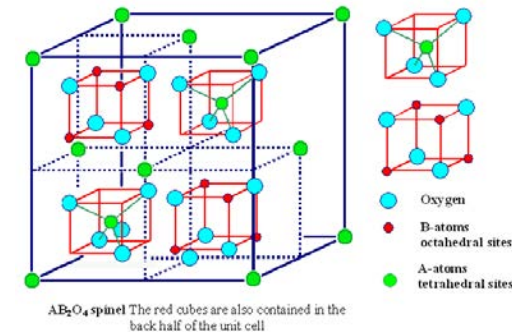
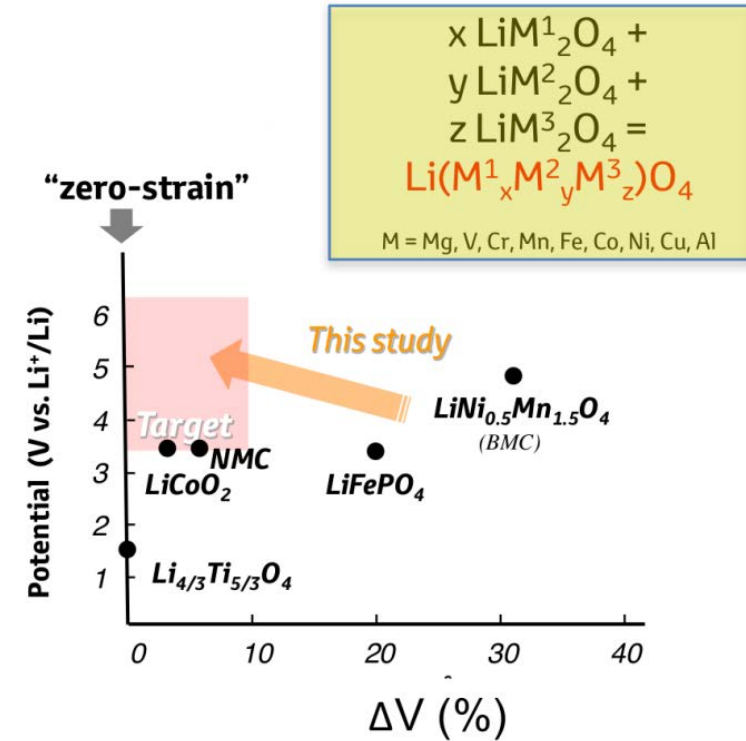


NCM –  $\text{Li}[\text{Ni}_x\text{Mn}_y\text{Co}_z]\text{O}_2$   
SE – solid electrolyte

Koerver, R. et al. Chem. Mater. 29, 5574–5582 (2017) &  
J. Mater. Chem. A 5, 22750–22760 (2017).

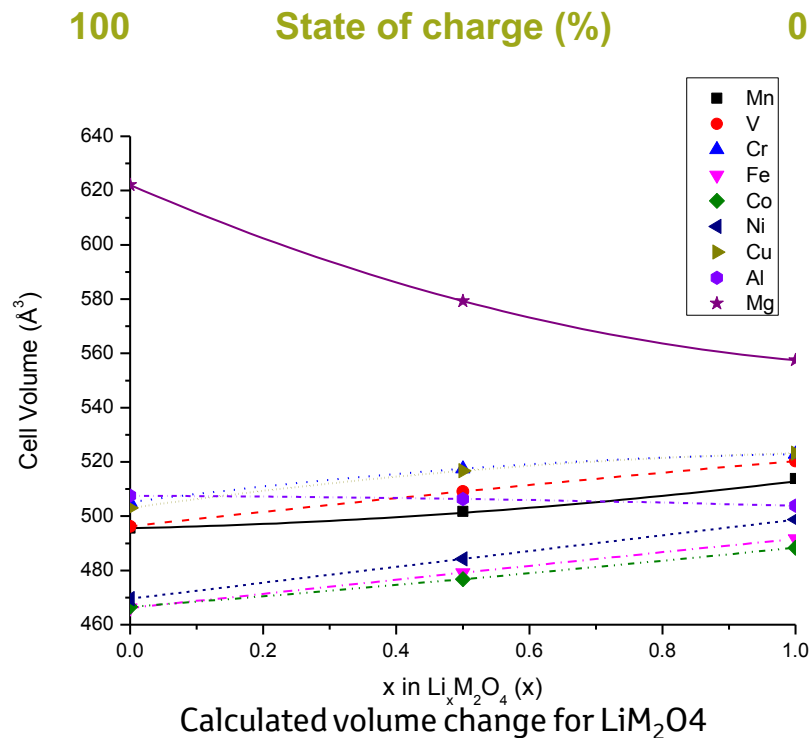
# Low-Strain Cathode Materials For Solid-State LIB

- ▶ No published options for cathode materials (some for anode, as LTO)
- ▶ Deployed *ab initio* modeling to screen various oxide materials with the spinel structure  $\text{LiM}_2\text{O}_4$  to optimize
  - Volume change
  - Lithium electrochemical potential
- ▶ Spinel framework has 3D Li conductivity rather than 2D as in layered TMO → increased ionic conductivity!



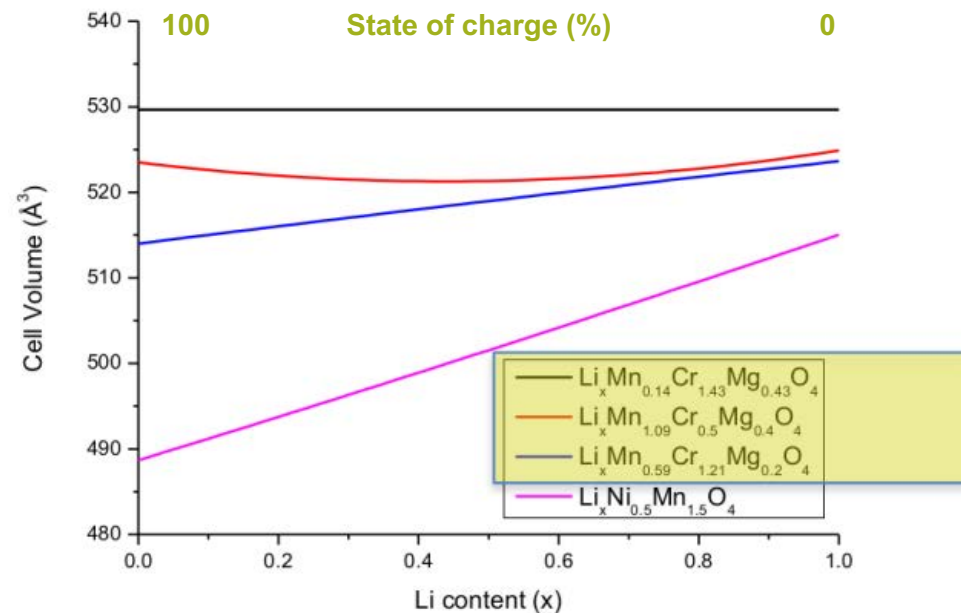
# Optimizing Materials For Low-Strain Cathode

- ▶ Mg is different to selected transition metals as it allows for volume compensation



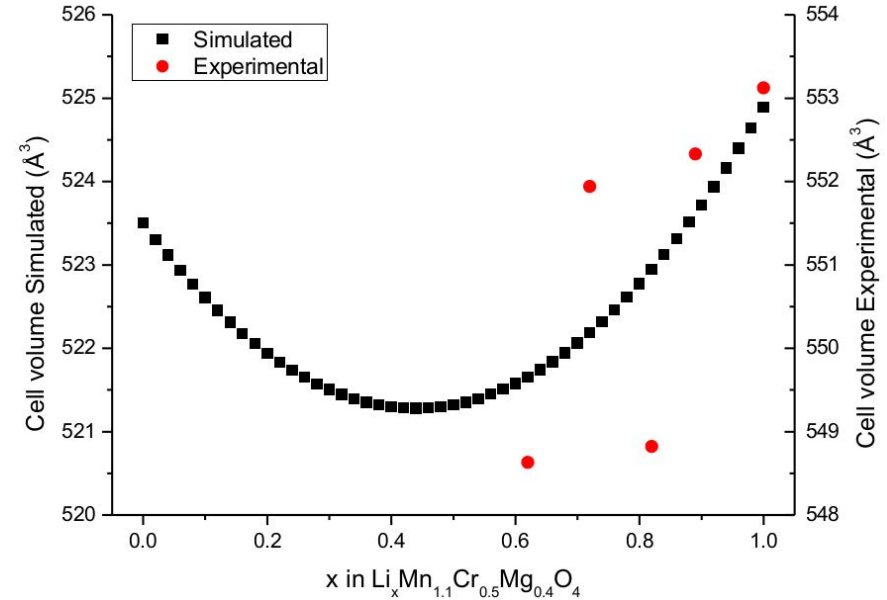
- ▶ Three metals chosen to design the low-strain material

- Mg -- manage volume change
- Mn -- structural stability
- Cr -- compensate electrochemical inactivity of Mg



# Synthesis of Material and Validation

- ▶  $\text{LiMn}_{1.1}\text{Cr}_{0.5}\text{Mg}_{0.4}\text{O}_4$  was synthesized successfully and almost pure
- ▶ This material reacted to delithiation by volume change in the range of max 1% - **very consistent with the model**
- ▶ Two of three materials could not be synthesized in spinel form
  - High Cr-containing spinels are very difficult/impossible to obtain



$$Q_{\max} = 100 \text{ A h/kg @ } 5.0 \text{ V}$$
$$U_{\max} = 500 \text{ W h/kg}$$

- Joint work with Toyota Motors Europe (2016)
- Patent *WO2014191018 A1* with Materials Design® as co-author

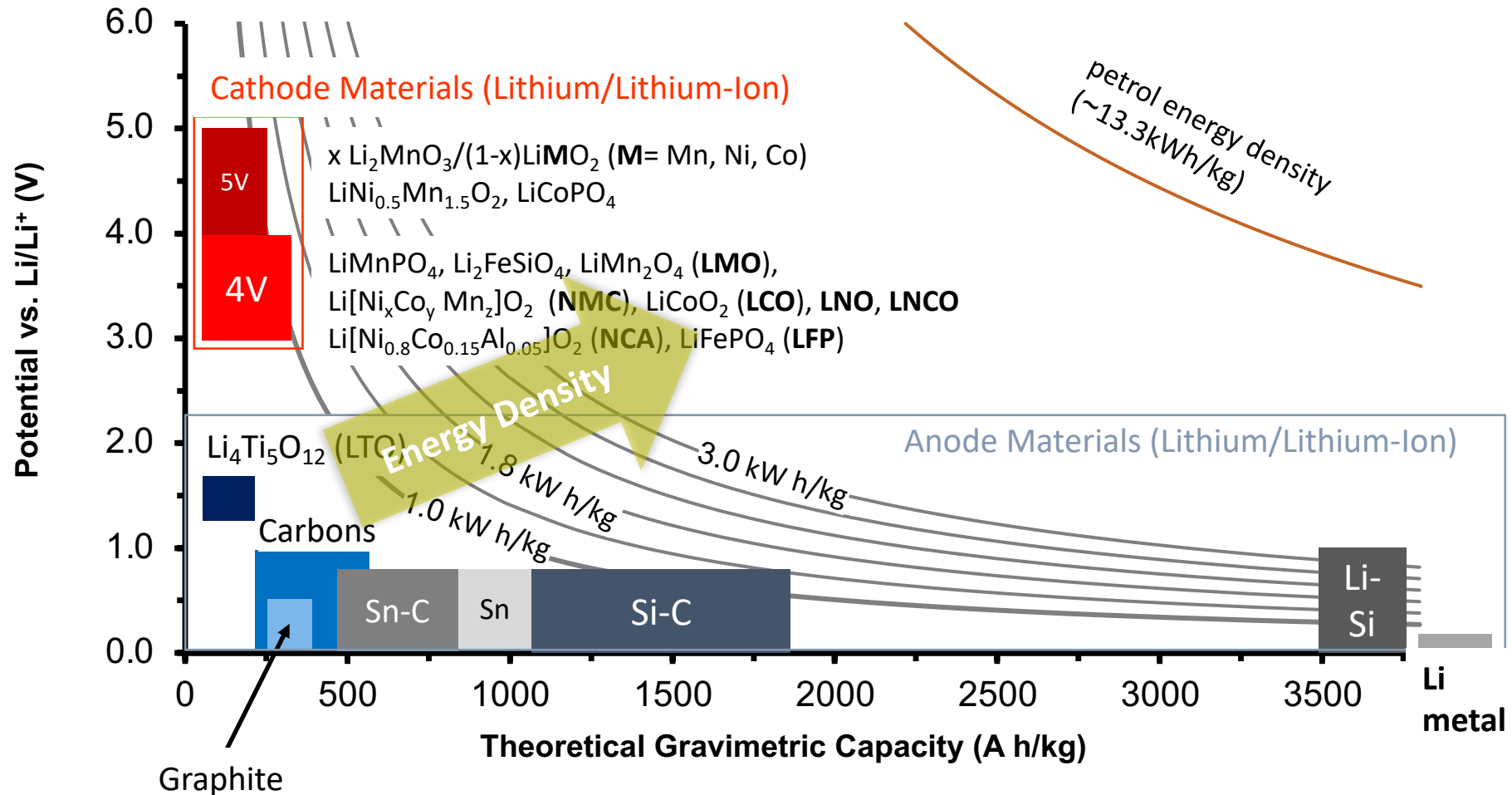




# High-Energy-Density Cathode Materials

# State of the Art LB Electrode Materials

**Gravimetric energy density [kWh/kg]: capacity [Ah/kg] × potential [V]**



According to Martin Winter, AABC Europe 2016

# Computational Screening of Cathode Materials

- ▶ Search for known structures that contain
  - Relevant charge carriers, e.g. Li
  - Elements relevant for electrochemistry, scaffold former and stabilizer
- ▶ Calculate charge carrier densities → maximum theoretical capacities
- ▶ Calculate Li chemical potentials → open circuit voltages

$$V_{OC} = \mu_{Li}(\text{cathode material}) - \mu_{Li}(\text{metal})$$

H																		He
Li	Be											B	C	N	O	F		Ne
Na	Mg											Al	Si	P	S	Cl		Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br		Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I		Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At		Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Rg									

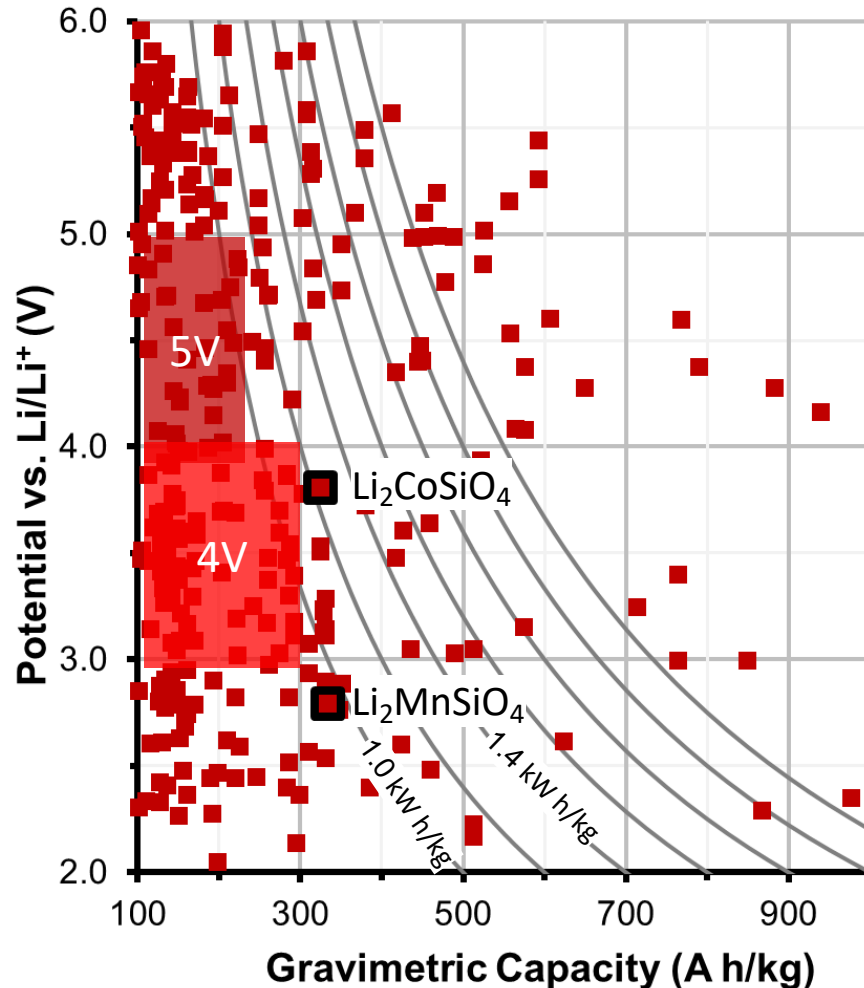
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr



# Design of High Energy Cathode Materials: Proposal

- ▶ Gravimetric energy densities of **existing** & **modified** materials

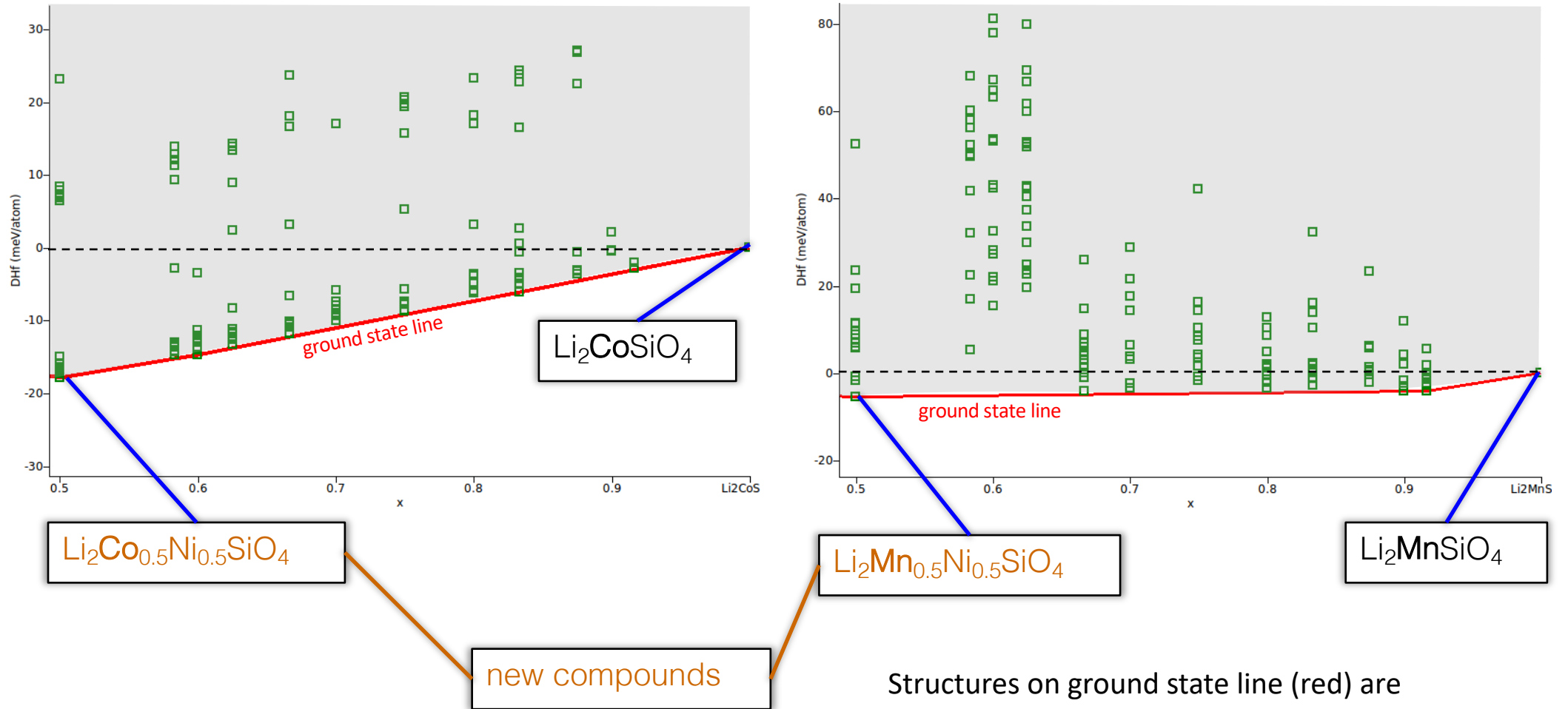


- ortho-silicates Li<sub>2</sub>MSiO<sub>4</sub>
- Energy densities (Wh/g)
  - 1.2 ( $M = \text{Co}$ )
  - 0.9 ( $M = \text{Mn}$ )
- Challenge: Atomic structure of Li<sub>2</sub>Ni<sub>0.5</sub>M<sub>0.5</sub>SiO<sub>4</sub> is unknown

MedeA InfoMaticA  
MedeA High Throughput  
MedeA UNCLE  
MedeA VASP

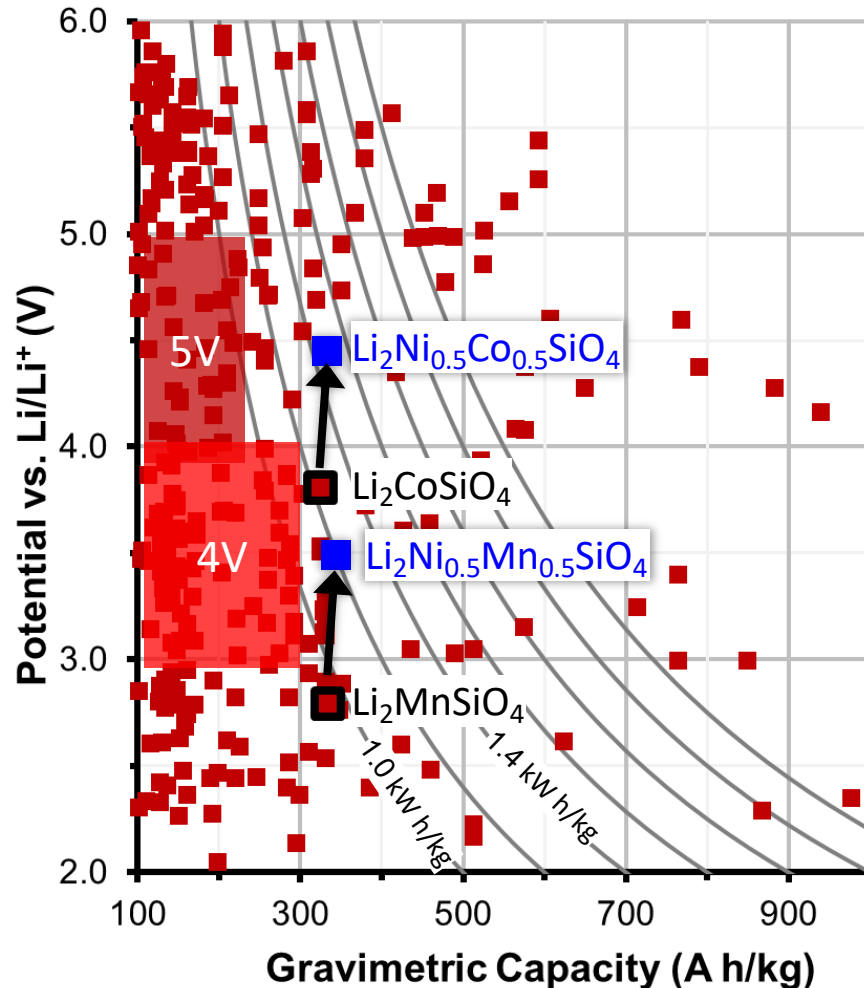
# Calculated $\text{Li}_2\text{M}_{1-x}\text{Ni}_x\text{SiO}_4$ Phase Diagrams

- Step to determine most stable crystal structures of  $\text{Li}_2\text{Ni}_{0.5}\text{M}_{0.5}\text{SiO}_4$



# Design of High Energy Cathode Materials: Result

- ▶ Gravimetric energy densities of **existing** & **modified** materials



- ortho-silicates  $\text{Li}_2M\text{SiO}_4$
- Energy densities (Wh/g)
  - 1.2 ( $M = \text{Co}$ )
  - 0.9 ( $M = \text{Mn}$ )
- Increase energy density by admixing up to 50 mol-% Ni
  - $\text{Li}_2\text{Ni}_{0.5}M_{0.5}\text{SiO}_4$
  - $\text{Li}_2\text{Ni}_{0.5}\text{Co}_{0.5}\text{SiO}_4$

MedeA InfoMaticA  
MedeA High Throughput  
MedeA UNCLE  
MedeA VASP



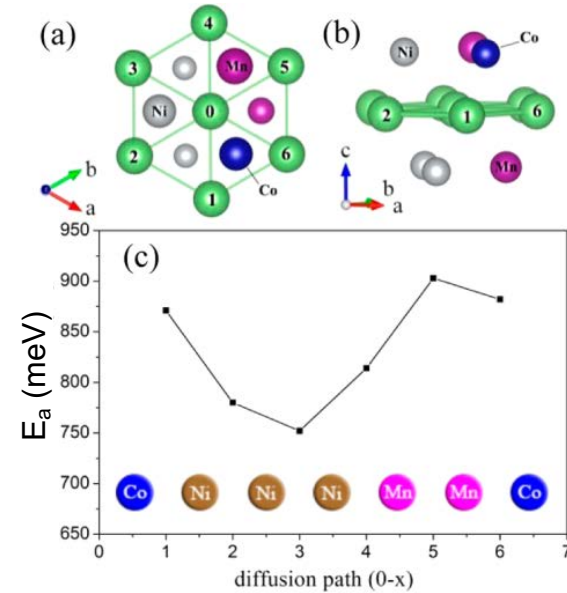
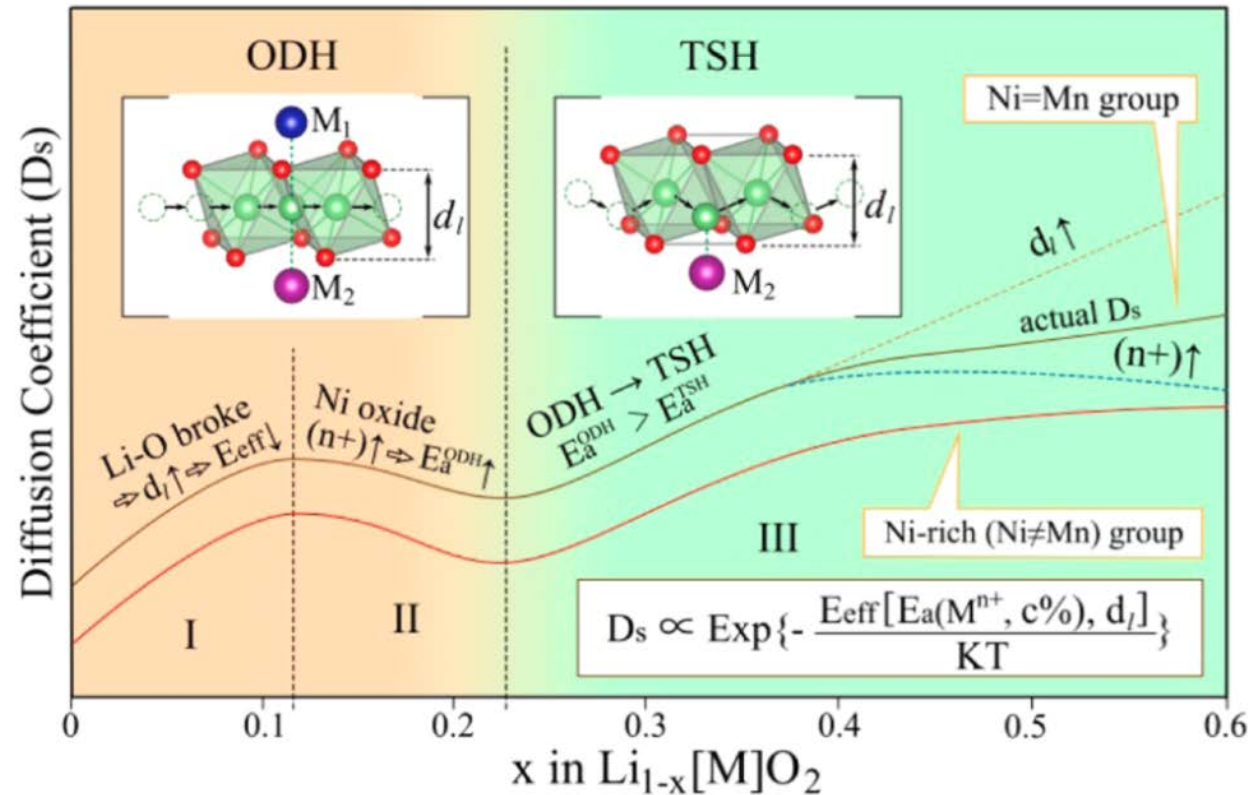
# Lithium Transport in the Cathode

## Material $\text{LiNi}_{3/5}\text{Mn}_{1/5}\text{Co}_{1/5}\text{O}_2$ (NMC311)

# Li Diffusion Mechanisms in the NMC311 Cathode Material

- Characterized Li diffusion coefficient as a function of de-lithiation

- Investigated the diffusion paths and their activation barrier  $E_a$



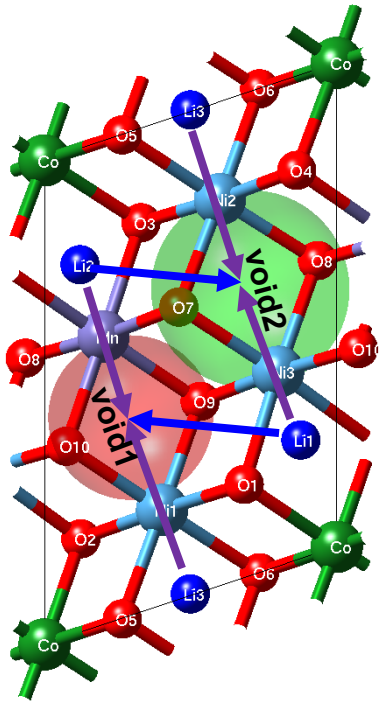
Transition metal	Ni <sup>2+</sup>	Ni <sup>3+</sup>	Ni <sup>4+</sup>	Co <sup>3+</sup>	Mn <sup>4+</sup>
Activation barrier (meV)	357.2	429.7	545.0	510.3	523.1

- Oxygen dumbbell hopping (**ODH**) dominant state of charge (SOC) < 0.22; tetrahedral site hopping (**TSH**) dominant at SOC > 0.33



# Possible Li Diffusion Paths in $\text{Li}_{0.6}\text{NMC311}$ , SOC = 0.4

(a) parent structure



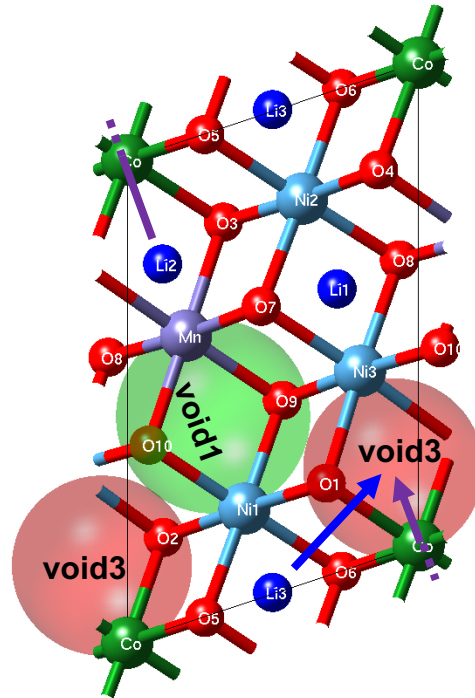
ODH

1. Li1 to void2 via Ni
2. Li2 to void1 via Mn
3. Li3 to void1 via Ni
4. Li3 to void2 via Ni

TSH

5. Li1 to void1 via Ni
6. Li2 to void2 via Mn

Created from (a) by Li1 migration to void2



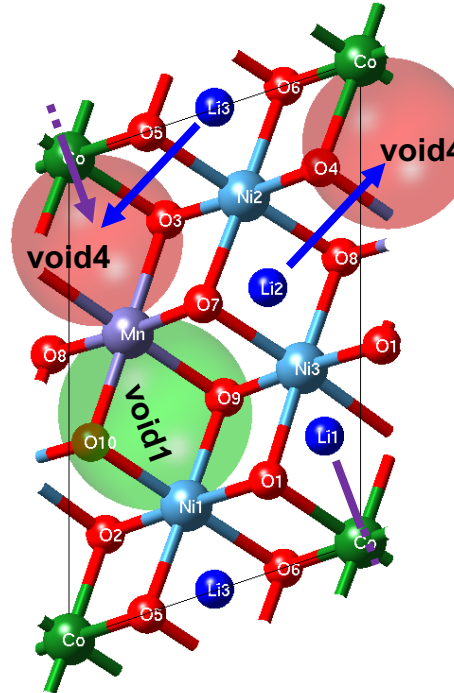
ODH

7. Li2 to void3 via Co

TSH

8. Li3 to void3 to Co

Created from (a) Li2 migration to void2



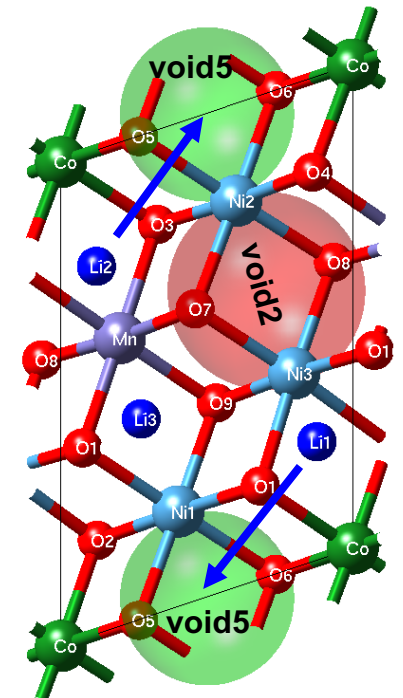
ODH

9. Li1 to void4 via Co

TSH

10. Li2 to void4 via O

Created from (a) by Li3 migration to void1

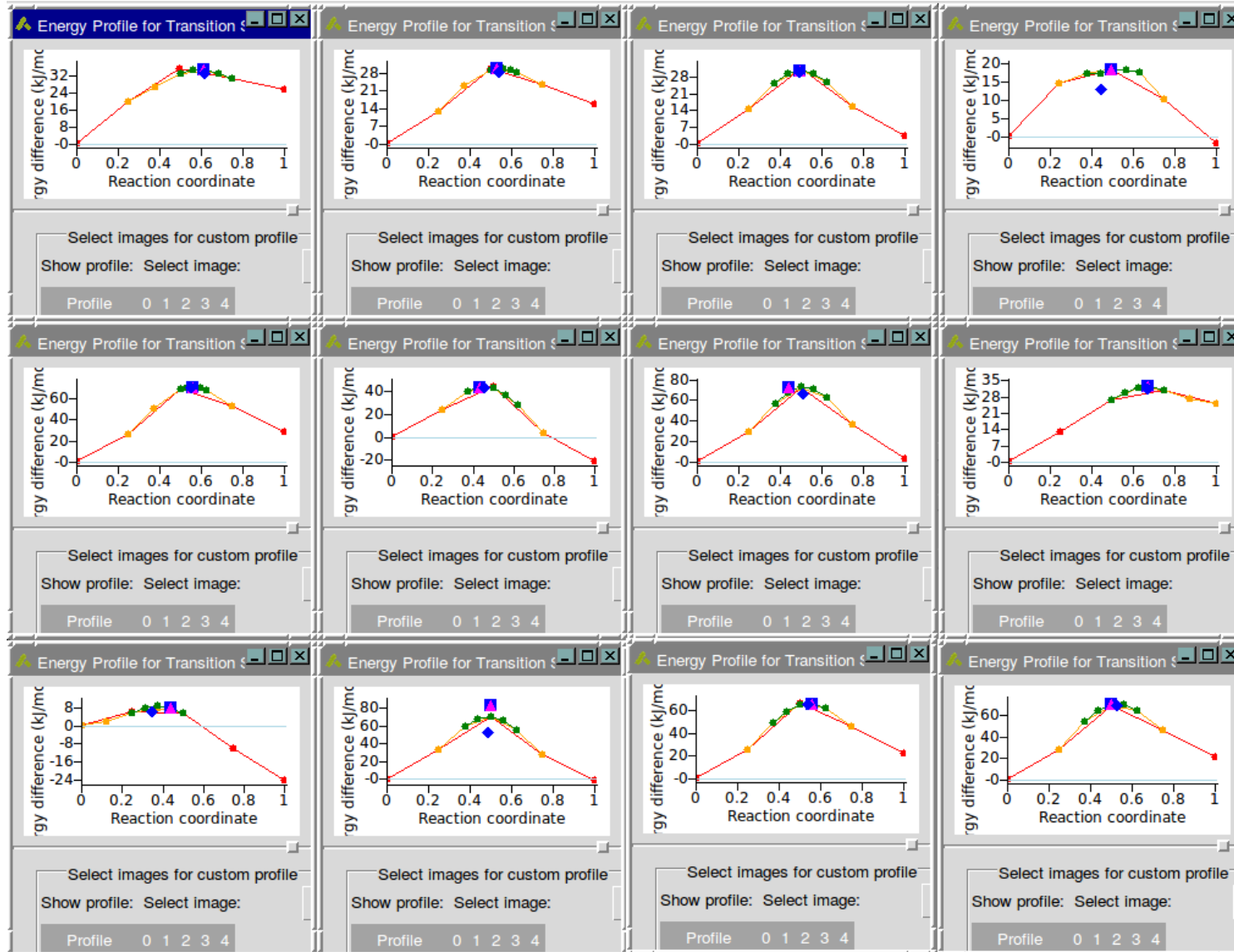


TSH

11. Li1 to void5 "Ni-to-Ni"
12. Li2 to void5 "Mn-to-Ni"



# Calculated Energy Profiles of the 12 Ion Diffusion Paths



- The activation barriers ( $E_a$ ) of the diffusion paths are equivalent of the energies of maximum in the energy profiles

MedeA VASP  
MedeA Transition State Search (TSS)



# Calc. Activation Barriers of Li Ion Diffusion in $\text{Li}_{0.6}\text{NMC311}$

Diffusion Path			Calculated Activation Barrier (meV)
type	Index	Via/to	
TSH	10	O	230
	12	Ni <sup>3+</sup>	230
	5	Ni <sup>2+</sup>	310
	6	Mn <sup>4+</sup>	400
	11	Co <sup>3+</sup>	620
	8	Co <sup>3+</sup>	870
ODH	1	Ni <sup>3+</sup>	310
	4	Ni <sup>3+</sup>	510
	2	Mn <sup>4+</sup>	630
	3	Ni <sup>3+</sup>	680
	9	Co <sup>3+</sup>	791
	7	Co <sup>3+</sup>	1006

- ▶ Trend of calculated activation barriers trend:
  - TSH: O < Ni < Mn < Co
  - ODH: Ni < Mn < Co
  - Results are in excellent agreement with the trend calculated by Wei et al.

MedeA VASP

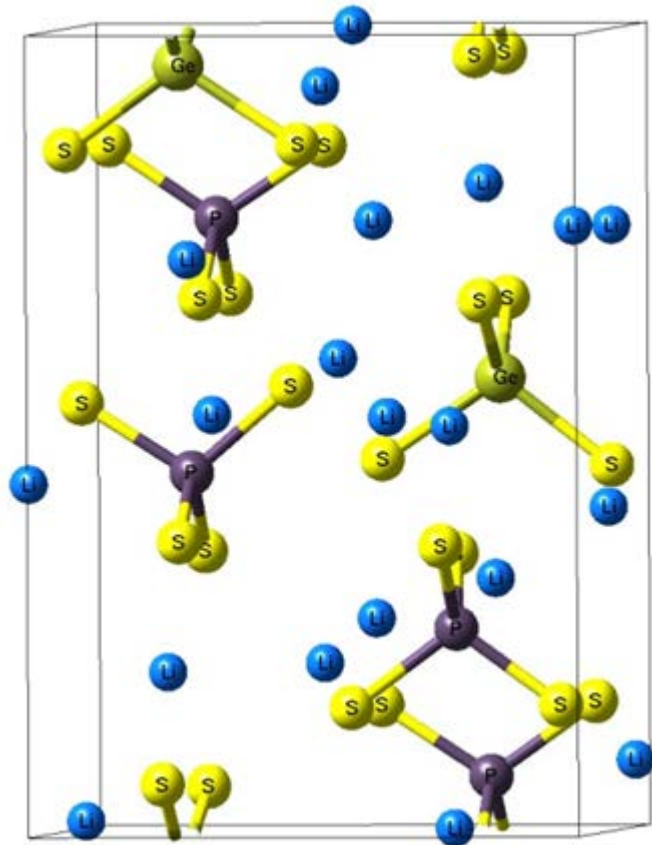
MedeA Transition State Search (TSS)



# Solid Electrolytes

# Solid Electrolytes for Lithium Batteries

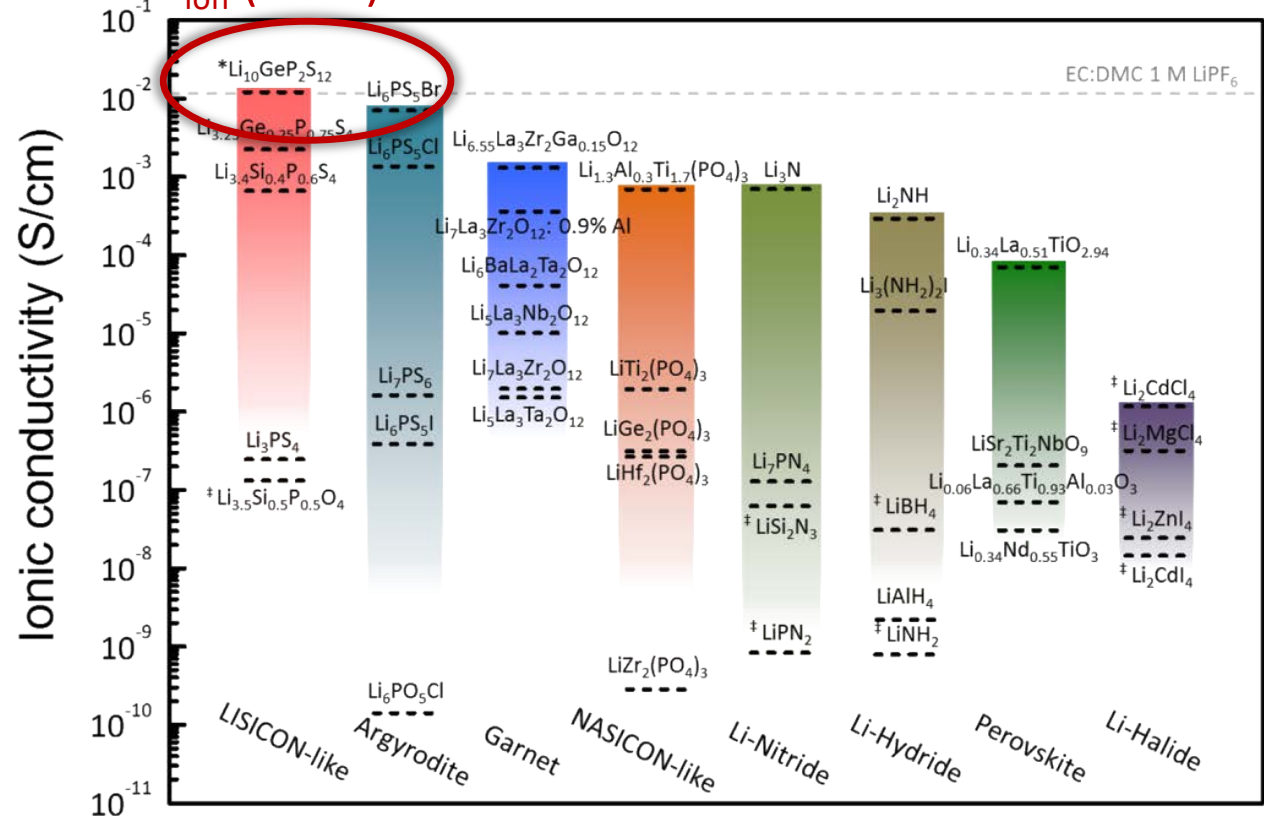
- ▶  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS):  
Prototype with ion conductivity comparable to liquid electrolytes



Crystal structure of LGPS

- ▶ Reported total ionic conductivity of solid-state lithium-ion conductors at room temperature

$$RT \sigma_{\text{ion}} (\text{LGPS}) = 10 \text{ mS cm}^{-1}$$



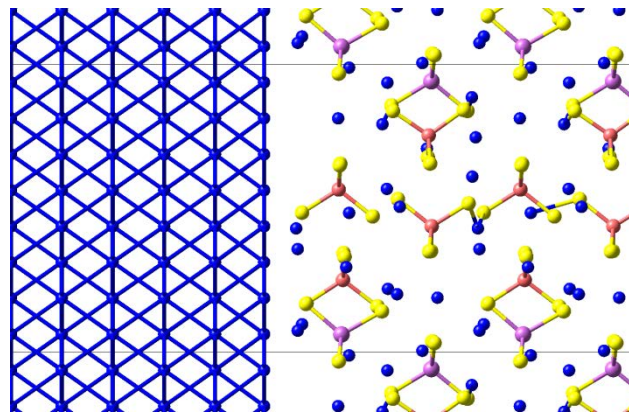
Bachman et al. Chem. Rev. 116, 140 (2016).

# LGPS in Contact with Li Metal: Formation of Interphases

MedeA VASP

- ▶ *Ab initio* Molecular Dynamics (MD) simulations
- ▶ Evolve atoms at T=300K

t = 0 ps

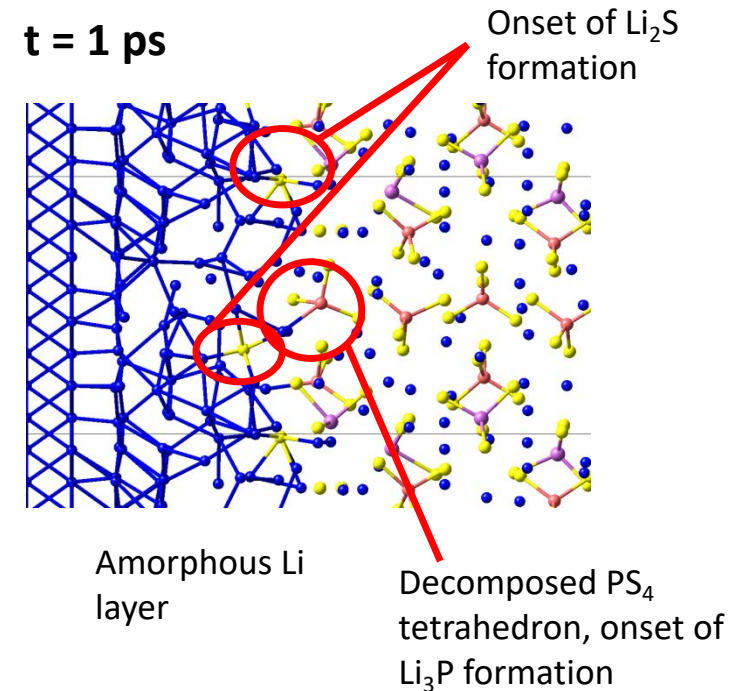


Li metal  
(110) surface

LGPS crystal

Li – blue  
S – yellow  
P – magenta  
Ge – purple

t = 1 ps



Onset of  $\text{Li}_2\text{S}$   
formation

Amorphous Li  
layer

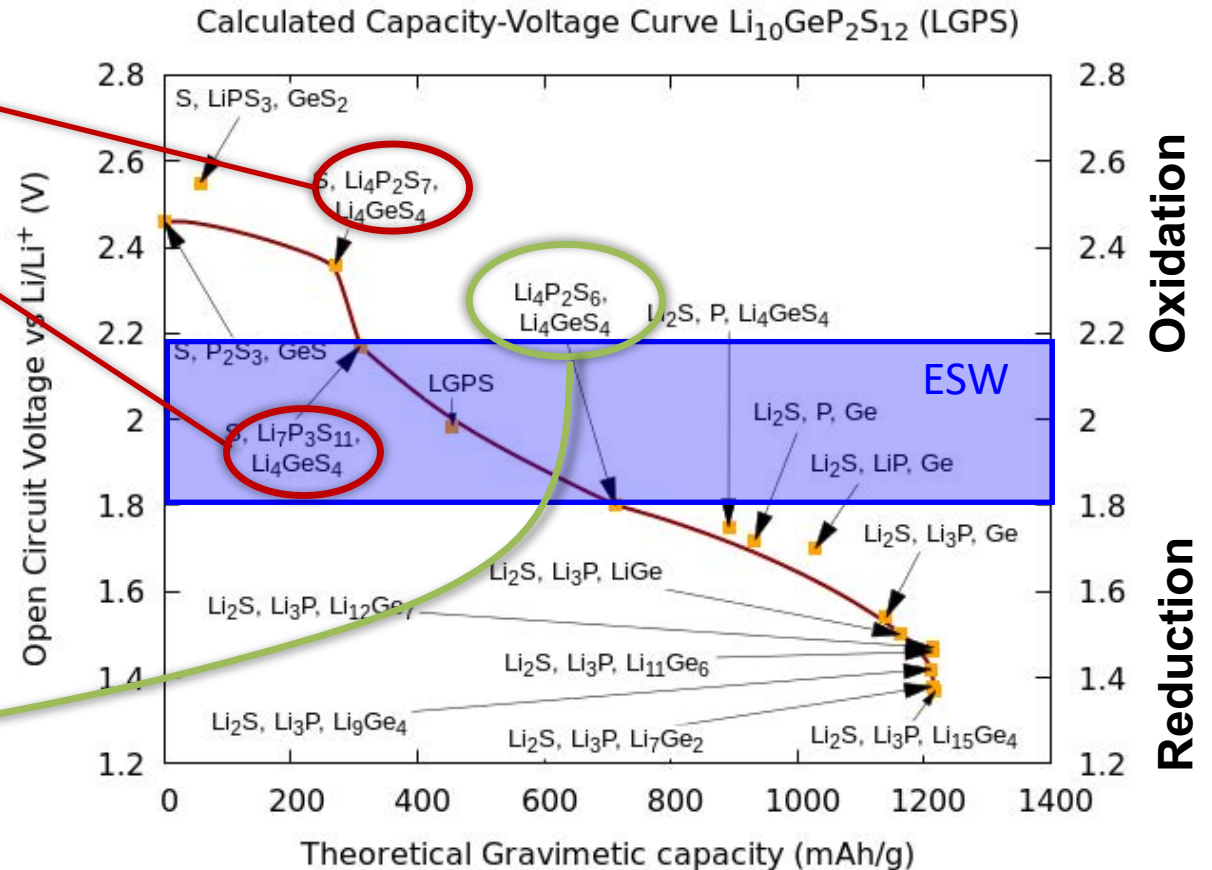
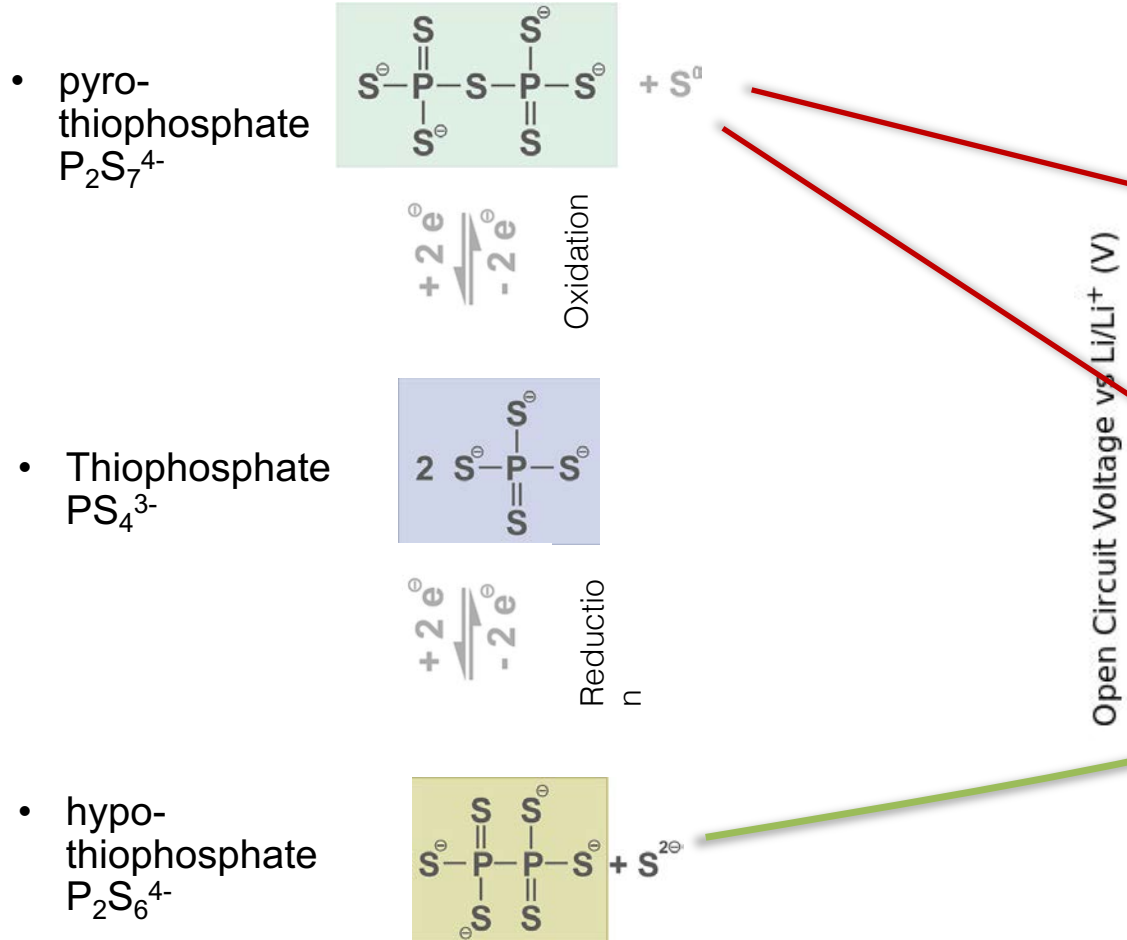
Decomposed  $\text{PS}_4$   
tetrahedron, onset of  
 $\text{Li}_3\text{P}$  formation

- ▶ Simulations show *rapid* decomposition of LGPS at Li anode
- ▶ Onset of rapid formation of  $\text{Li}_3\text{P}$  and  $\text{Li}_2\text{S}$  in agreement with experiments of *Wenzel et al., Chem. Mater. 28, 2400 (2016)*

# Electrochemical Stability Window (ESW) of LGPS

- Thiophosphate redox compounds that are detected in measured X-ray photoelectron (XPS) spectra \*)

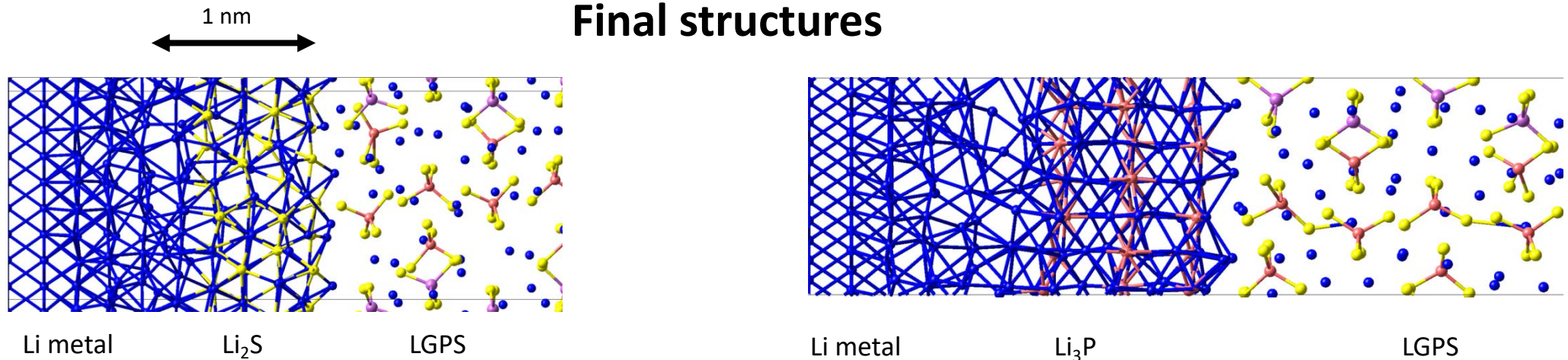
- The calculated ESW of LGPS between 1.8 and 2.1 V Li/Li<sup>+</sup>



\*) Koerver et al. J. Mater. Chem. A 5, 22750 (2017). Dewald et al., Chem. Mater. 31, 8328 (2019).

# LGPS Stability Against Interphases $\text{Li}_2\text{S}$ and $\text{Li}_3\text{P}$

## ► *Ab initio* Simulated Annealing



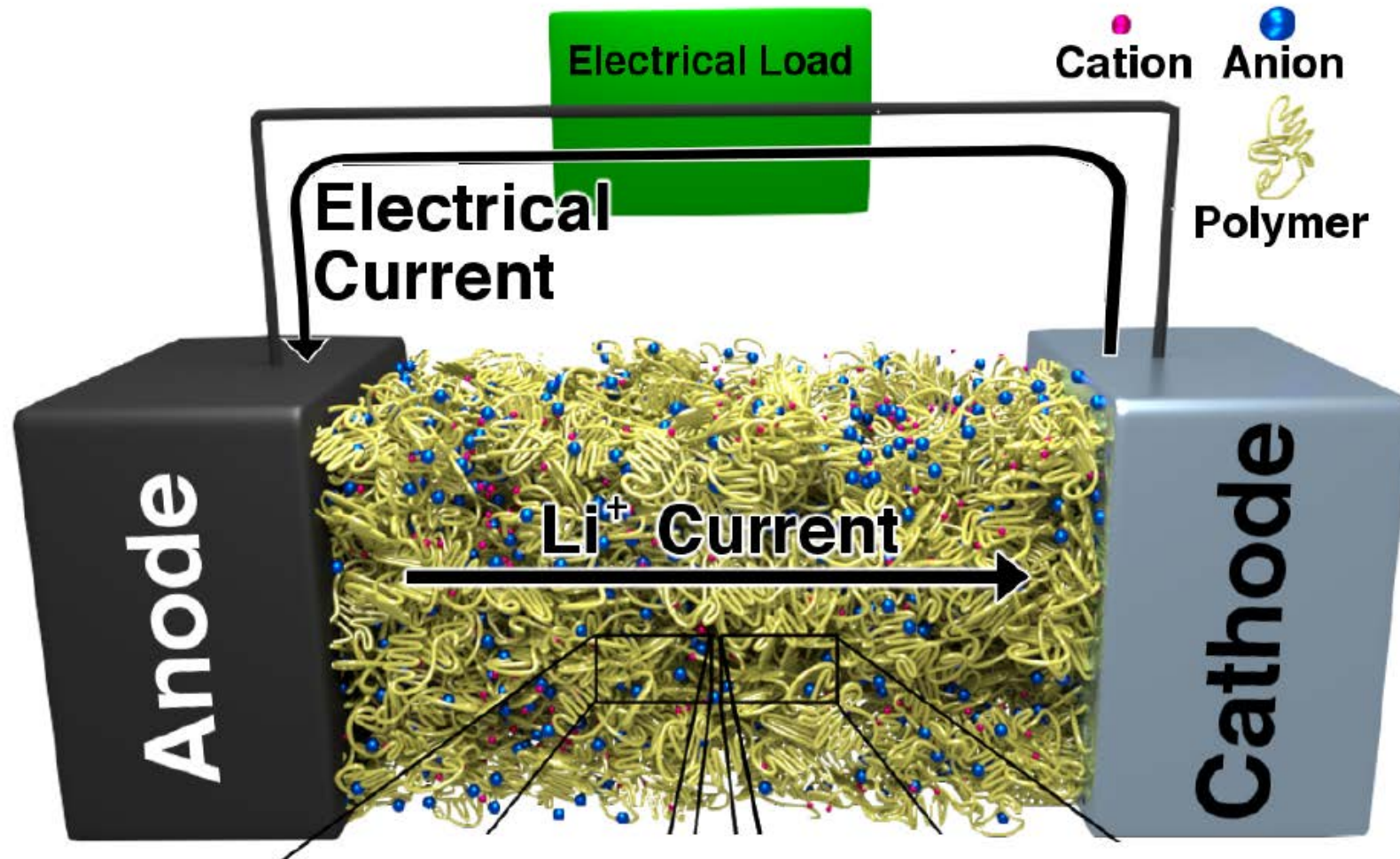
**No  $\text{PS}_4$  or  $\text{GeS}_4$  tetrahedron is ruptured**

Li – blue  
S – yellow  
P – magenta  
Ge – purple

- Interphases are chemically inert against Lithium and LGPS
- Interphases protect LGPS against reactions with lithium

MedeA VASP

# Solid Polymer-Electrolytes (SPEs)

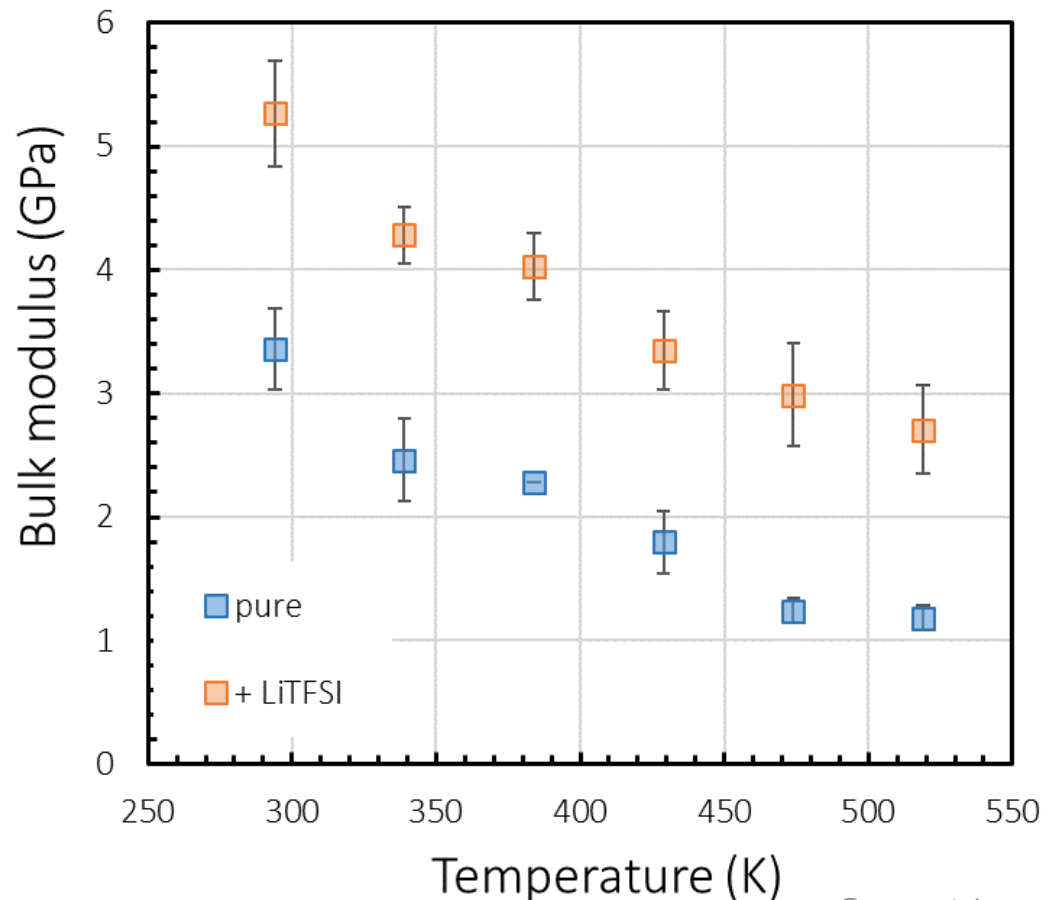




# Calculated Elasticity & Mechanical Properties

Polymer-in-Salt electrolyte

Random copolymer of acrylonitrile (AN) with butyl acrylate (BuA) in  
Li bis(trifluoromethanesulfone)imide (LiTFSI)



## ► Effect of Li salt

At all temperatures, the polymer-in-salt electrolyte is more brittle than the pure polymer

## ► Effect of temperature

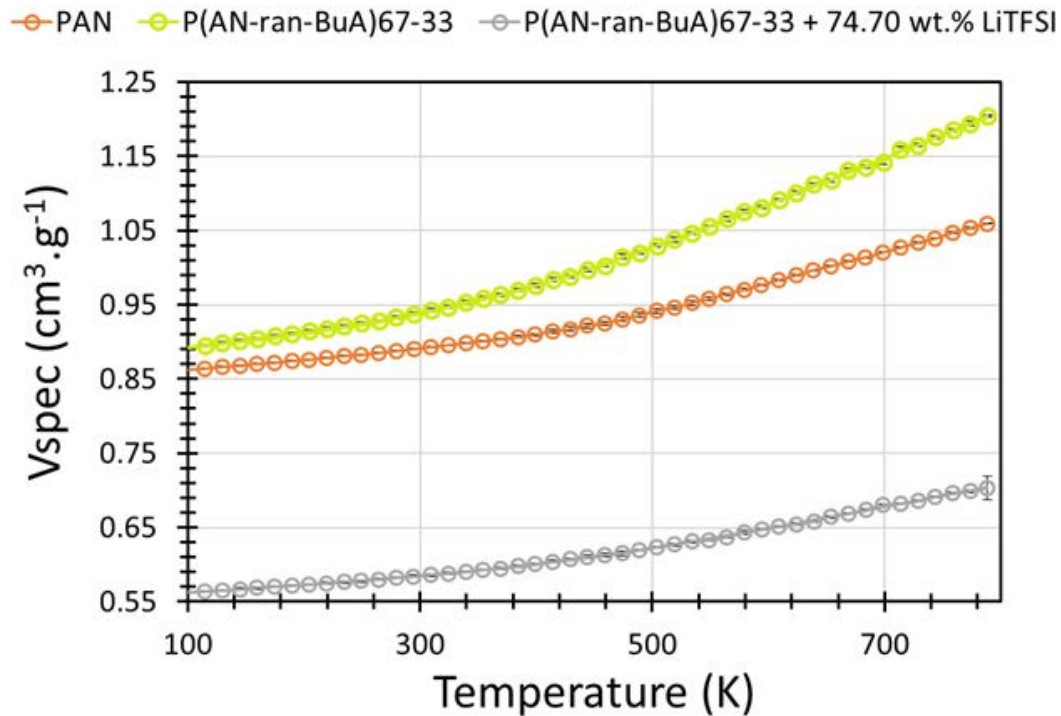
Softening of polymer-in-salt electrolyte and pure polymer with increasing temperature

# Prediction of Glass Transition Temperature ( $T_g$ )

Random copolymer of acrylonitrile (AN) with butyl acrylate (BuA)

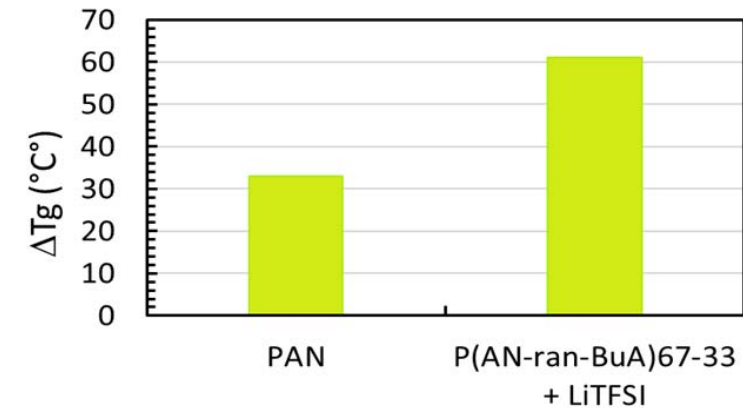
- Pure
- In Li bis(trifluoromethanesulfone)imide (LiTFSI)

Atomistic dilatometry: Calculation of specific volume ( $V_{\text{spec}}$ ) vs temperature ( $T$ )



► The variation of  $T_g$  calculated between PAN and P(AN-ran-BuA)67-33 agrees with the experimental value of 30 K

► Effect of LiTFSI (charge carrier salt): Comparison to the pure copolymer  $T_g$  increases with increasing LiTFSI content

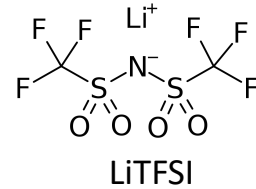




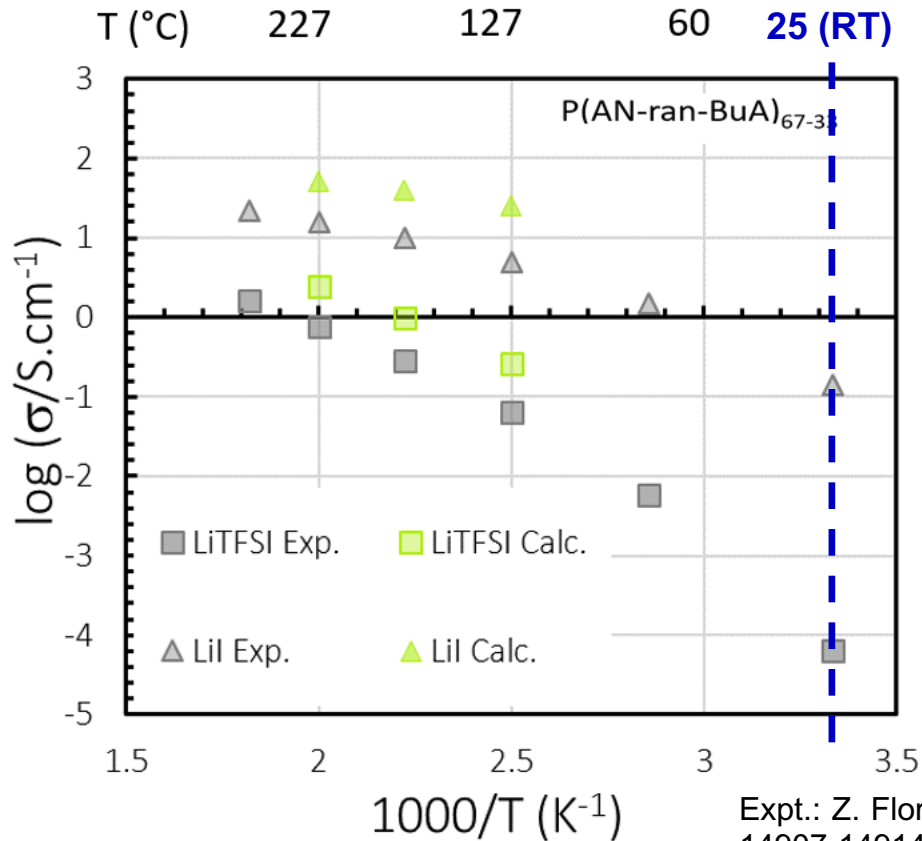
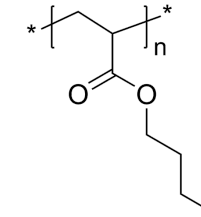
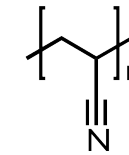
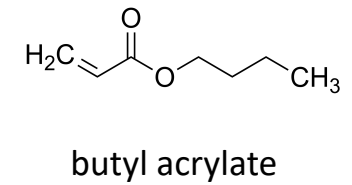
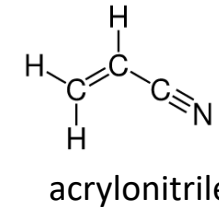
# Morphology Determines Li Ion Conductivity $\sigma_{ion}$

Random copolymer of acrylonitrile (AN) with butyl acrylate (BuA) in

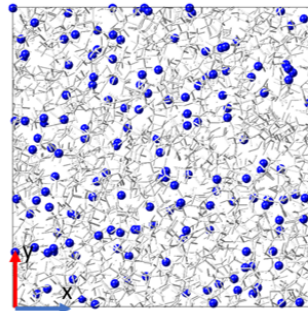
- Li bis(trifluoromethanesulfone)imide (LiTFSI)
- Li iodide (LiI)



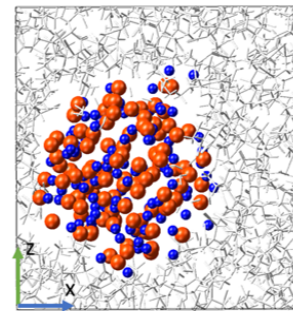
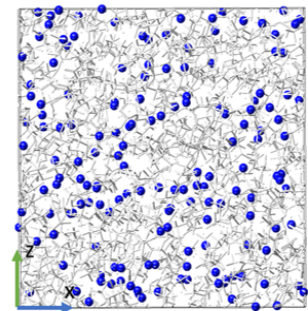
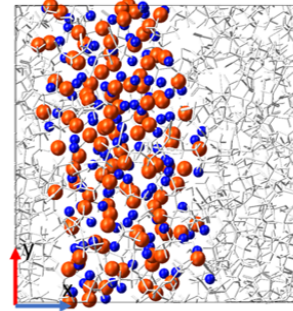
Li<sup>+</sup> I<sup>-</sup>  
Lithium iodide



74.70 wt.% LiTFSI



48.6 wt.% LiI



Side view

Top view

► Molecular dynamics (MD) simulations yield that LiTFSI is dispersed in the polymer matrix

► In the presence of LiI, MD simulations reveal a phase separation leading to anisotropic diffusion and good RT  $\sigma_{ion}$

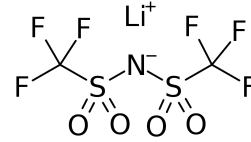
► MD simulations in an electric field cause heating, which is used to determine  $\sigma_{ion}$

Expt.: Z. Florjanczyk *et al.*, J. Phys. Chem. B 108 (2004) 14907-14914

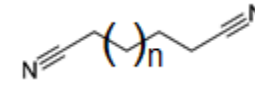
R. Windiks, B. Minisini, and A. Mavromaras, Advanced Automotive Battery Conference, Wiesbaden (2020)

# Calculated Electrochemical Stability

Plasticized random copolymer of acrylonitrile (AN) with butyl acrylate (BuA) in Li bis(trifluoromethanesulfony)imide (LiTFSI)

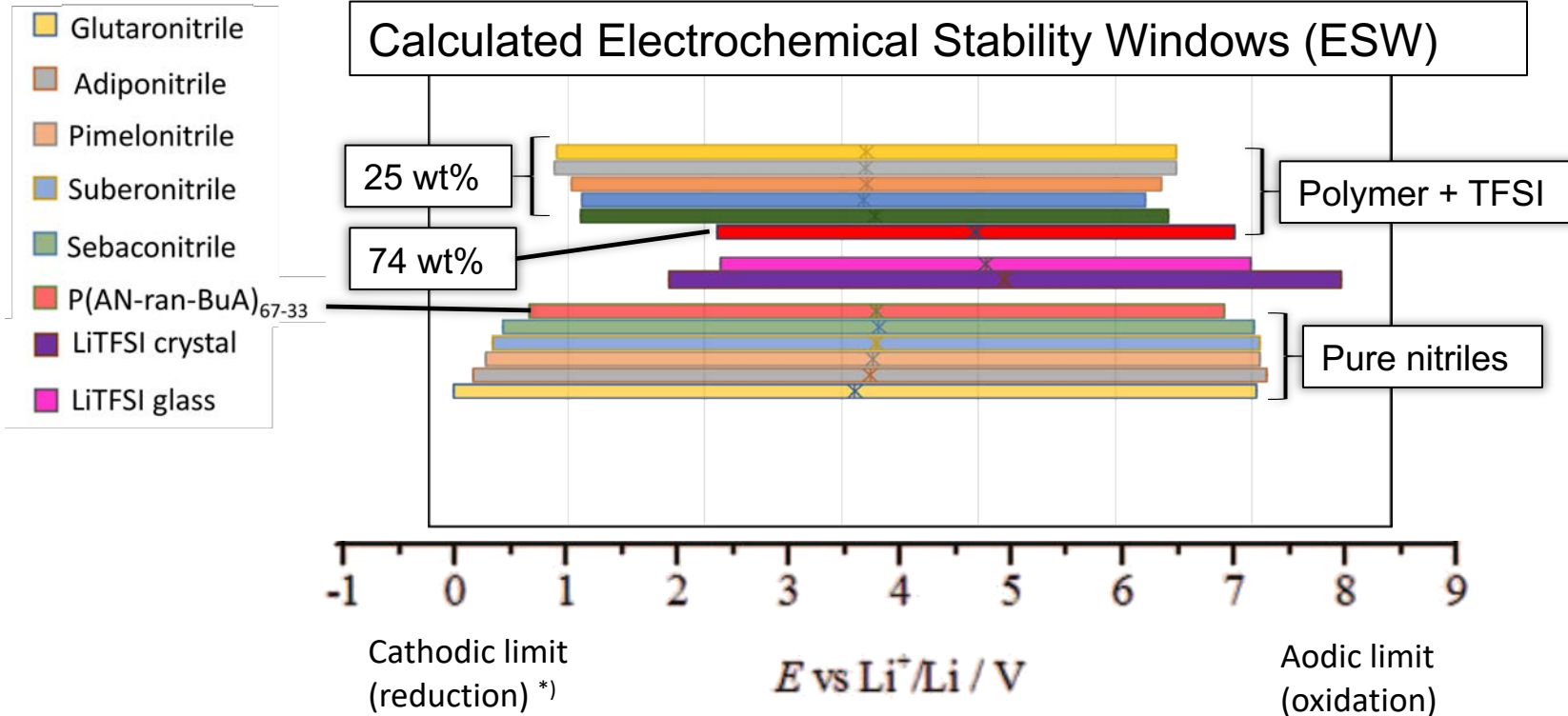


LiTFSI



Organic nitriles

		n
Glutaronitrile	(GLN)	3
Adiponitrile	(ADN)	4
Pimelonitrile	(PMN)	5
Suberonitrile	(SUN)	6
Sebaconitrile	(SEN)	8



- ▶ ESW of pure acrylonitrile/butyl-acrylate copolymer is narrower compared to pure dinitrile solvents
- ▶ LiTFSI salt considerably reduces the ESW of the polymer
- ▶ With 74 wt% LiTFSI, the ESW of the polymer-in-salt electrolyte is very similar to the ESW of pure, amorphous LiTFSI

\*) Calculated cathodic limits of ESWs are calibrated against exp. value of adiponitrile (ADN),  $E \approx 0 \text{ V vs Li/Li}^+$   
 Electrochem. Soc., 160 (6) A838-A848 (2013)

R. Windiks, B. Minisini, and A. Mavromaras, Advanced Automotive Battery Conference, Wiesbaden (2020)

# Conclusions

- ▶ Atomic-scale modeling used to address current engineering needs in battery R&D
- ▶ Virtually created and tested novel materials concepts
  - High-throughput screening of altered structures of cathode materials
  - Optimal composition for low-strain cathode materials
  - Examine electrochemical stability of electrolytes against electrodes
- ▶ Assess key properties prior to synthesis
  - State-of-charge dependent Li transport in electrodes and electrolytes
  - Elasticity and ion conductivity of solid polymer electrolytes
- ▶ Atomic scale modeling supplies reasonable initial parameter sets for
  - synthesis
  - engineering battery simulations
  - ...

# Key Properties for Batteries ...

## ► ... available from atom-scale modeling/simulations for any material

### Materials Fabrication

- Free energies and phase diagrams: miscibility vs separation
- Elasticity: ductility, brittleness, hardness
- Permittivity Dielectric constants
- Piezoelectricity
- Diffusivity
- Thermal expansion
- Heat capacity
- Electronic structures

### Cycling Behavior, Fast Charging

- Ion conductivity
- Electrical conductivity
- Thermal conductivity
- Electrochemical stability vs degradation
- Phase transformation
- Volume change of particles
- Metal plating

### Interfaces of Electrodes, Electrolytes, Coatings, Binders, etc.

- Interphase morphology
- Interfacial contact
- Current density
- Overpotentials
- Inter-diffusion & segregation
- Interfacial stabilities/delamination
- Potential profiles

### Diagnostics & Analysis

- XPS (core level shifts)
- NMR (chemical shifts, field gradients, paramagnetic shifts)
- Powder diffraction patterns
- IR & Raman Spectra
- UV-Vis Spectra

# Online Training and Demo

Atomistic Simulations of Battery Materials  
with *MedeA*

Next Tuesday, August 25, 2020

USA/EUROPE:

9:30 am EST/3:30 pm CEST


INDIA/CHINA/JAPAN:

7:00 pm IST/ 9:30 pm CST/ 10:30 pm JST

Emailed information coming soon!

All MedeA tutorials are available  
at <http://my.materialsdesign.com/tutorials>

\*Training and Demo available to customers  
Who are currently on maintenance



Online Training and  
Demonstration:  
Using *MedeA* to  
Explore Battery Materials

A world map with a dark blue background and glowing yellow city lights. Overlaid on the map are several bright blue nodes connected by thin, curved lines, representing a global network. The text is centered over the map.

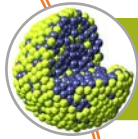
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GOING GLOBAL  
October  
[www.materialsdesign.com/ugm-2020](http://www.materialsdesign.com/ugm-2020)**



# MedeA 3.1 Webinars



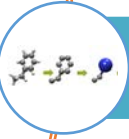
June 2020: Elasticity and Beyond – Predicting Mechanical Properties with *MedeA*, by Ray Shan



June 2020: Diffusion by Erich Wimmer and Benoît Minisini



July 2020: VASP 6 by Martijn Marsman



July 2020: Mesoscale Modeling by Jörg-Rüdiger Hill



August 2020: Exploring Battery Materials...by René Windiks



September 2020: *MedeA* 3.1 by Marianna Yiannourakou, Walter Wolf and Jörg-Rüdiger Hill



# Materials Design Exploring Battery Materials Webinar Links

## ► **MedeA modules mentioned in today's webinar**

- <https://www.materialsdesign.com/builders>
- <https://www.materialsdesign.com/compute-engines>
- <https://www.materialsdesign.com/property-modules>
  
- [MedeA Interface Builder](#)
- [MedeA VASP](#)
- [MedeA Amorphous Materials Builder](#)
- [MedeA Thermoset Builder](#)
- [MedeA LAMMPS](#)
- [MedeA Diffusion](#)
- [MedeA HT Launchpad](#)
- [MedeA UNCLE](#)
- [MedeA MT](#)
- [MedeA Transition State Search](#)

## ► **UGM**

- <https://www.materialsdesign.com/ugm-2020>

## ► **Webinar: Live and Recorded**

- <https://www.materialsdesign.com/webinars>

## ► **Publications**

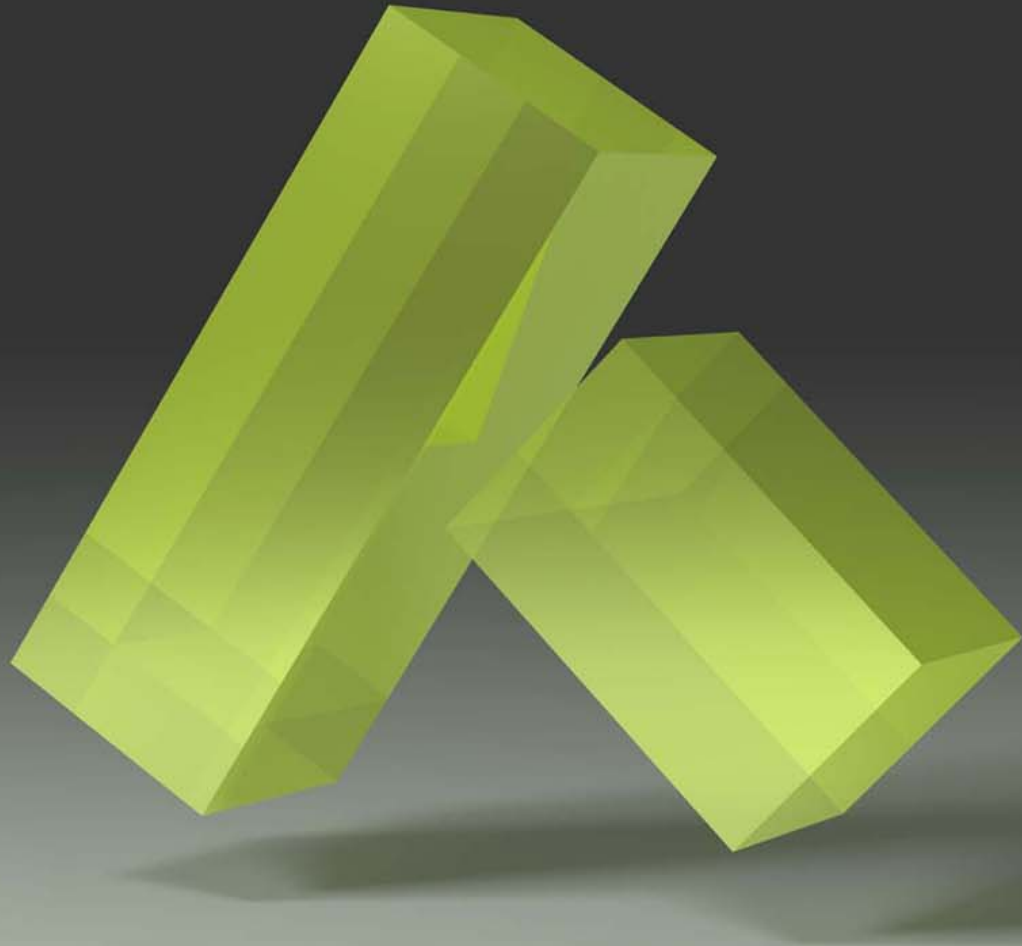
- <https://www.materialsdesign.com/Publications>

## ► **Application Notes**

- <https://www.materialsdesign.com/application-notes>

## ► **For questions or comments contact**

- Katherine Hollingsworth
  - [khollingsworth@materialsdesign.com](mailto:khollingsworth@materialsdesign.com)



# *Medea*

Innovation by Simulation