

Particle Dynamics Electromechanical Model of a Cathode Microstructure in All-Solid-State Batteries



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Outline



- ☐ Introduction – state of the art battery technologies
- ☐ Cathode composition and microstructure of all-solid-state batteries – purpose of the modeling
- ☐ Cathode microstructure – particle dynamics electro-mechanical model
- ☐ Modeling capabilities and results
- ☐ Summary

State of the Art Battery Technologies



Addressing NASA needs

- ❑ **Transformational Tools and Technologies (TTT)**
 - Approaches for production of intrinsically safe, high performance batteries

- ❑ **Advanced Air Transport Technology (AATT)**
 - Hybrid electric aircraft with >100 mile range



- ❑ **Revolutionary Vertical Lift Technology (RVLT) - Urban Air Mobility (UAM) Concepts**
 - eVTOL aircraft with >50 mile range



❑ Lithium-Ion

- Highly flammable liquid electrolyte
- Cooling/insulation/fire containment packing requirements
- Safety concerns: thermal runaway and energy uncertainty

❑ Li-S

- Only chemistry known to meet 500 Wh/kg
- Cycle life poor
- Charge/discharge rate insufficient

❑ Solid-State Battery

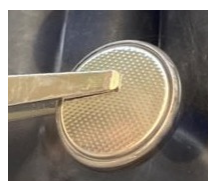
- Non-flammable
- Weight saving design
- Higher operating temperature
- Bi-polar stack design possible
- Low ionic conductivity
- Difficult to fabricate

Current focus is on all solid-state Li-S battery systems

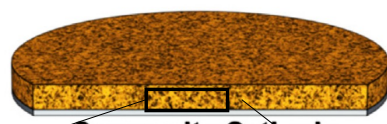
Cathode Composition and Microstructure of All-Solid-State Batteries



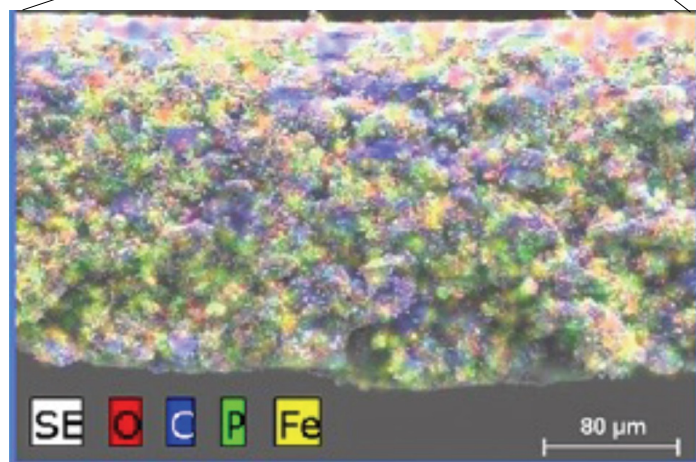
Model cathode microstructure at particle level



Battery Cell



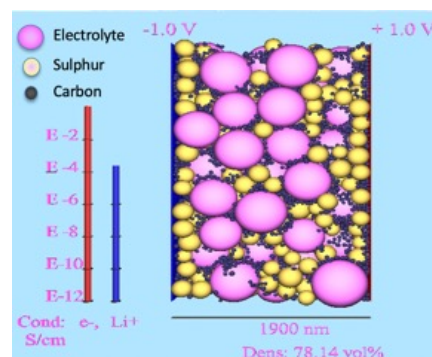
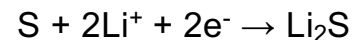
Composite Cathode



Cross-sectional backscattered electrons image of a SE cathode layer

Solid State Cathode constituents:

- ❑ Cathode active material (CAM) - **S, Se, Se_xS_y, Li₂S**
- ❑ Solid electrolyte (SE) with high Li⁺ ionic conductivity -
Ceramic oxide electrolyte LLZO - Li₇La₃Zr₂O₁₂ of ionic cond: 5x10⁻⁴ S/cm
- ❑ Electronic conductive agent (ECA) with high electron conductivity – carbon black (CB), and holey graphene (hG)



Particle model of an SE cathode

Modeling cathode microstructure can help battery design

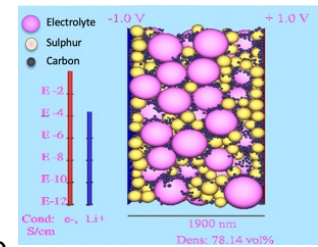


Purpose of the Modeling

Maximize battery performance by optimizing multiple cathode design parameters

Optimal battery design parameters:

- ☐ Grain size of the powder components
 - larger – better conductivity (less interface resistance)
 - smaller – increased power output (larger surface area)
- ☐ Composition ratio between CAM : SE : ECA
 - High amount of CAM, or cathode loading – 50–90 vol%
 - Sufficient, but minimal amount of SE, with good CAM/SE contact to ensure sufficient Li^+ diffusion
 - Sufficient, but minimal amount of ECA for e^- transport



Maximizing battery performance parameters:

- ☐ Li^+ and e^- conductivities of SE and ECA
- ☐ Cathode materials utilization
- ☐ Mass weight of the components – affects the overall battery weight

CAM: S, Se
SE: Ceramic oxide
ECA: Carbon Black

Modeling helps to find the optimal design parameters for superior battery performance

Cathode Model at Particle Level



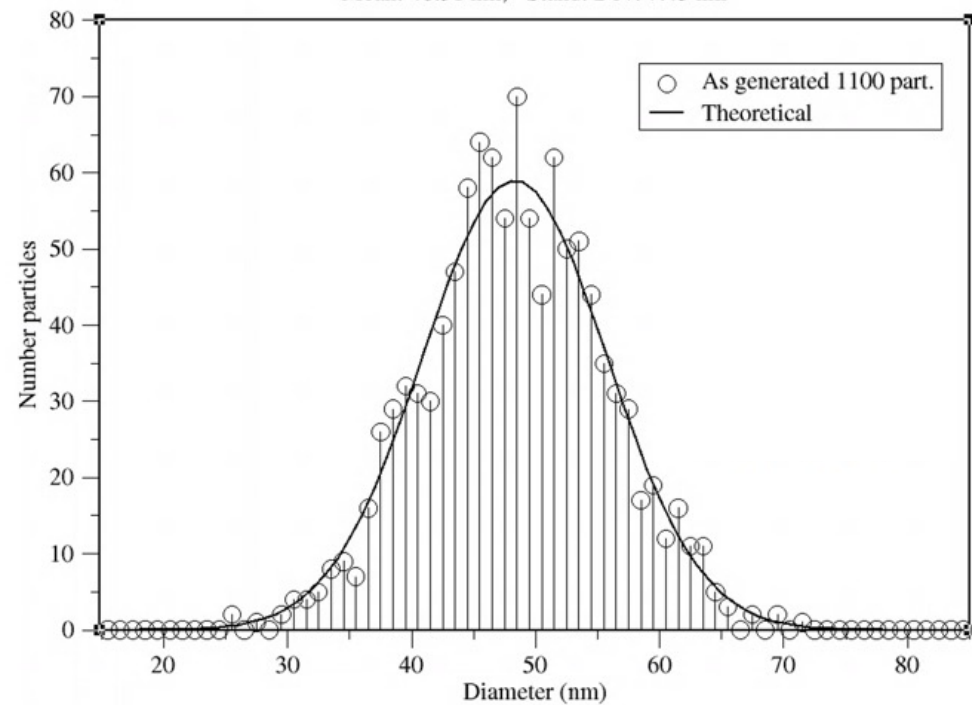
Solid Electrolyte Sphere Approximation Model (SESAM)

Model construction:

- Generate particles of given type (SE, C, S) and given size distribution

Particle Normal (Gaussian) Distribution

Mean: 48.31 nm, Stand. Dev: 7.45 nm



Robust physics-based electro-mechanical model

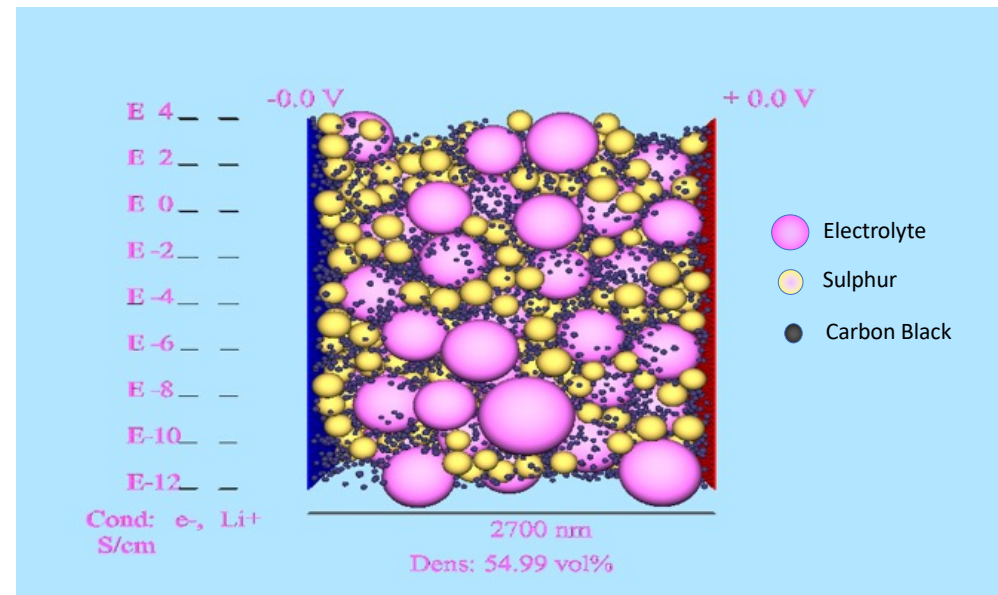
Cathode Model at Particle Level

Solid Electrolyte Sphere Approximation Model (SESAM)

Model construction:

- ☐ Generate particles of given type (SE, C, S) and given size distribution
- ☐ Fills the system box (or RVE) with particles of all types randomly

Cathode Representative Volume Element (RVE)

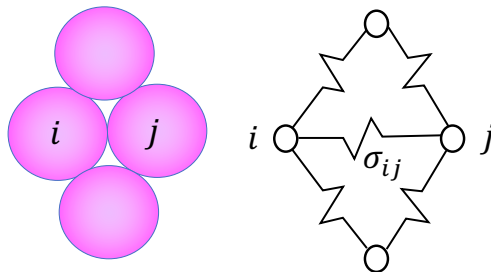


Cathode Model at Particle Level

Solid Electrolyte Sphere Approximation Model (SESAM)

Model construction:

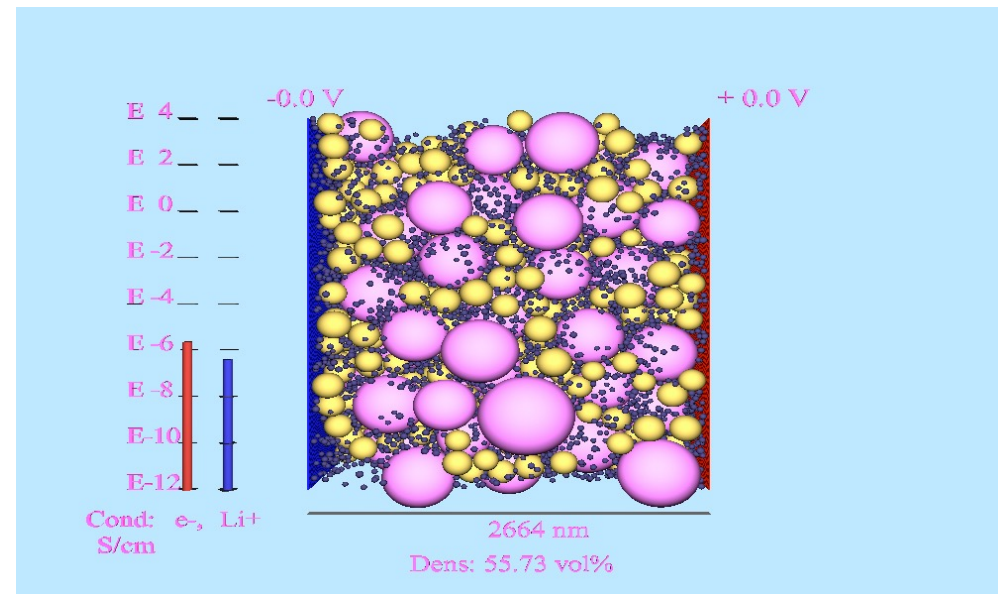
- ☐ Generate particles of given type (SE, C, S) and given size distribution
- ☐ Fills the system box (or RVE) with particles of all types randomly
- ☐ Compress the powder composite and measure conductivities



Solving Kirchhoff's matrix equation gives conductivity

$$(I_i) = (\sigma_{ij})(V_j)$$

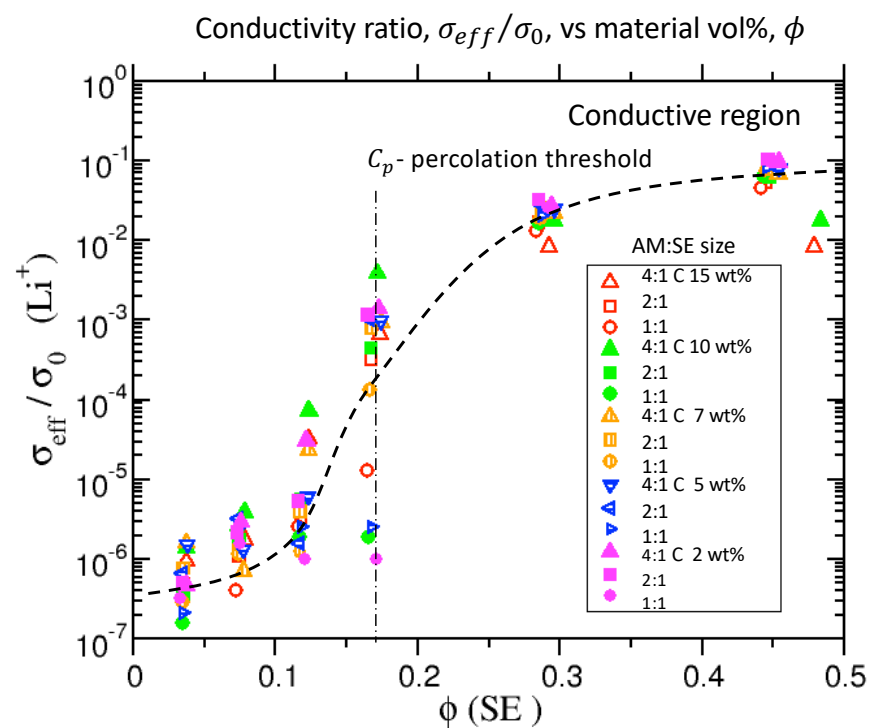
Cathode Representative Volume Element (RVE)



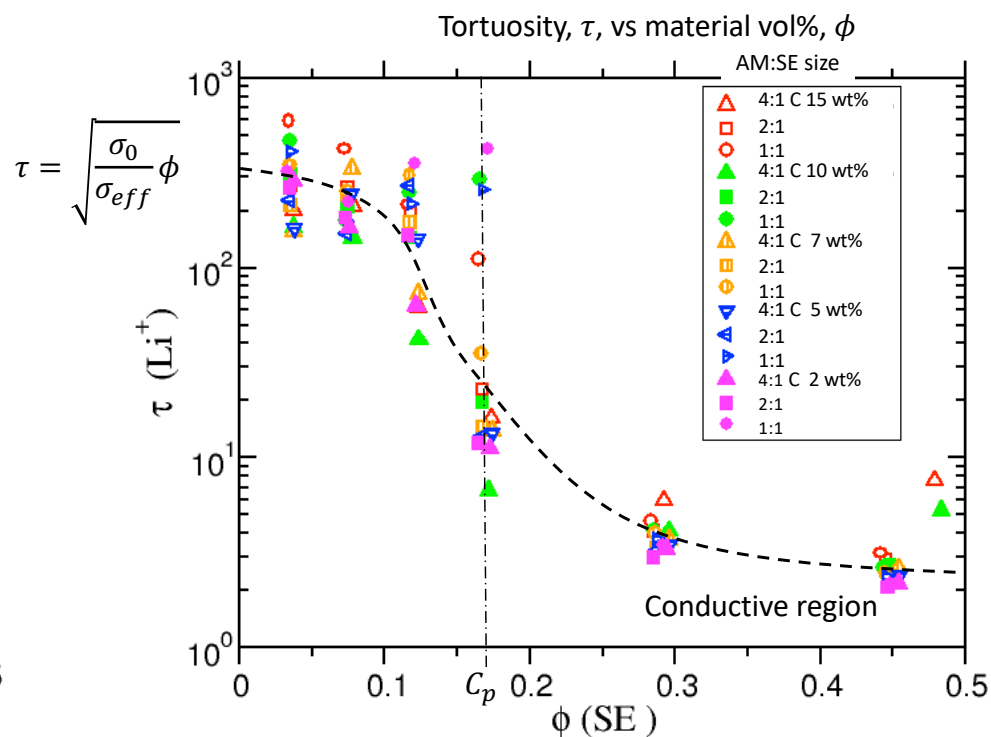
Results: Li⁺ Conductivity vs Cathode Content



- Percolation threshold at $C_{p,SE} \approx 17$ vol%
- High conductivity at $C_{SE} > 30$ vol %



σ_{eff} - effective conductivity; σ_0 - conductivity of a fully dense material



$$\tau = \sqrt{\frac{\sigma_0}{\sigma_{eff}}} \phi$$

Prediction of Li⁺ conductivities helps design optimization

Pressure Dependence of Ionic Conductivity

Simulation Setup

Electrolyte:

$\text{Li}_6\text{PS}_5\text{Cl}$ (LPSC)

$E = 22.1 \text{ GPa}$

$\nu = 0.37$

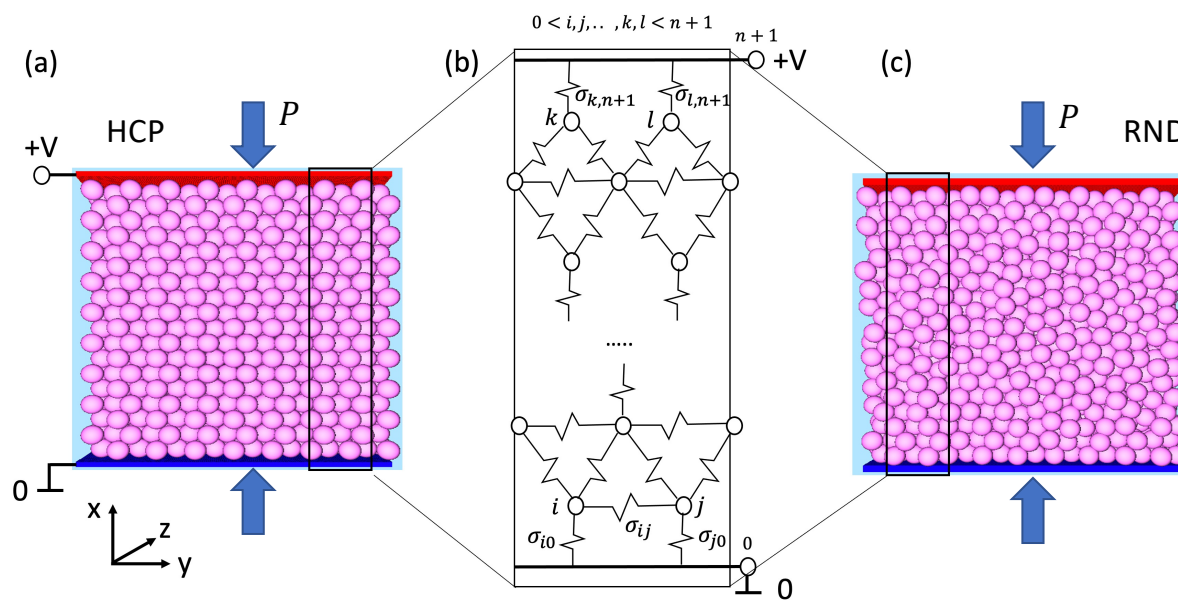
$\sigma_{\text{SE}} = 1.6 \text{ mS/cm}$
(fitted value)

$D = 30 \text{ nm}$

System size:

$600 \times 600 \times 600 \text{ nm}$

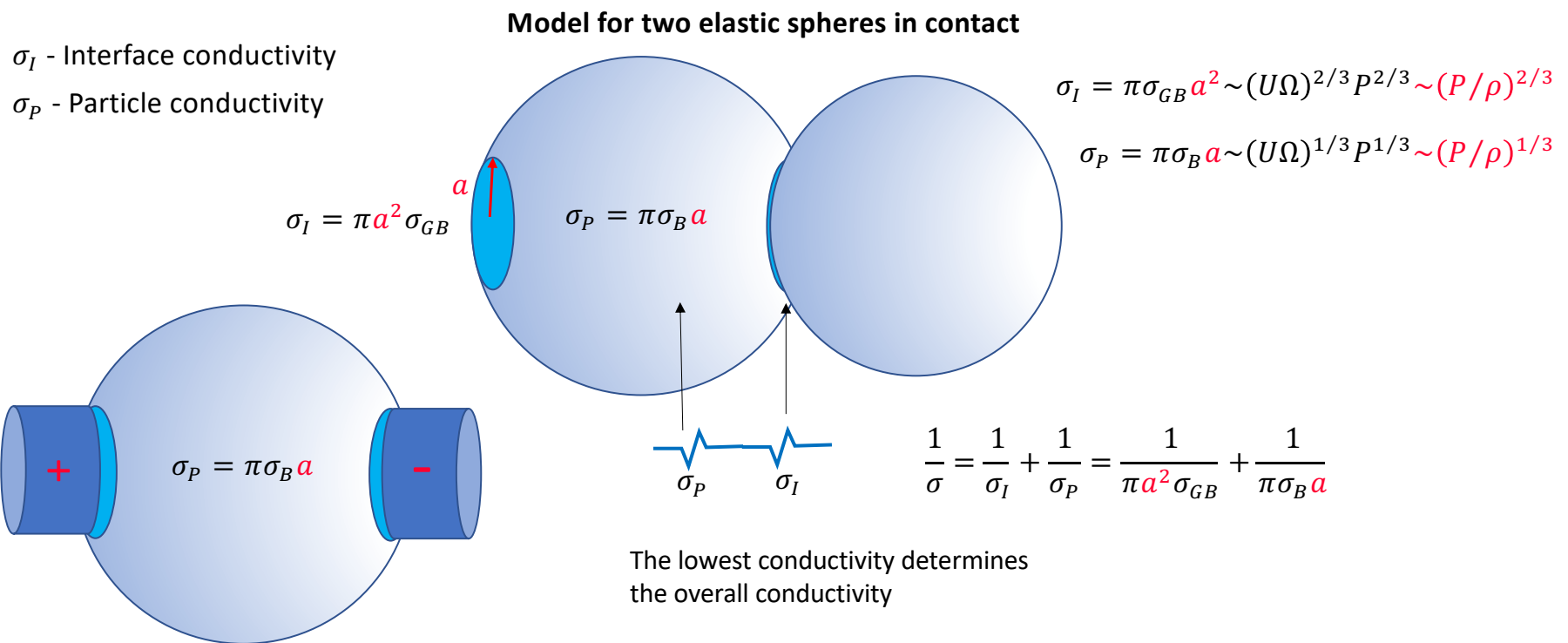
$P: (1 \div 100 \text{ MPa})$



- Regime I: $\sigma_{\text{B}} = 10^5 \sigma_{\text{SE}} \gg \sigma_{\text{GB}} = \sigma_{\text{SE}}$
- Regime II: $\sigma_{\text{B}} = \sigma_{\text{GB}} = \sigma_{\text{SE}}$
- Regime III: $\sigma_{\text{B}} = \sigma_{\text{SE}} \ll \sigma_{\text{GB}} = 10^5 \sigma_{\text{SE}}$

Pressure Dependence of Ionic Conductivity

Theoretical Analysis



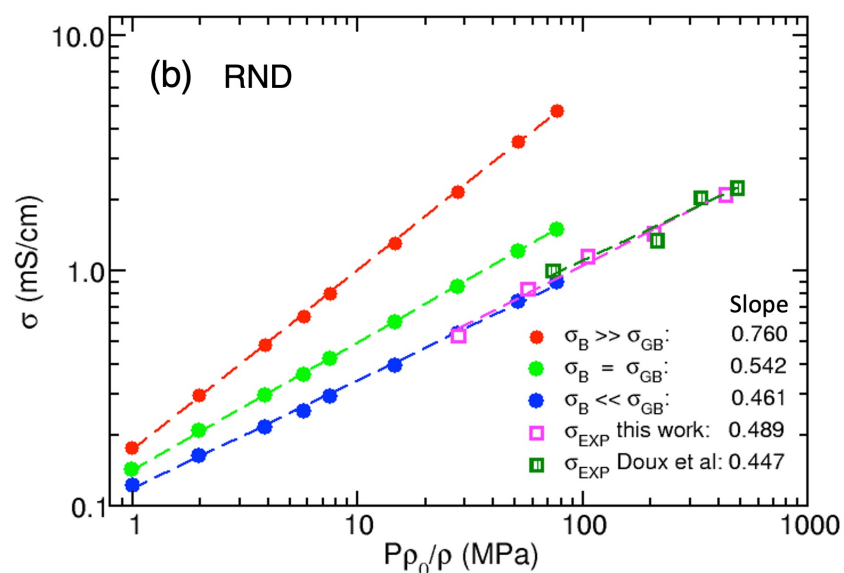
Grain boundary conductivity and bulk conductivity scale differently with contact radius

Pressure Dependence of Ionic Conductivity

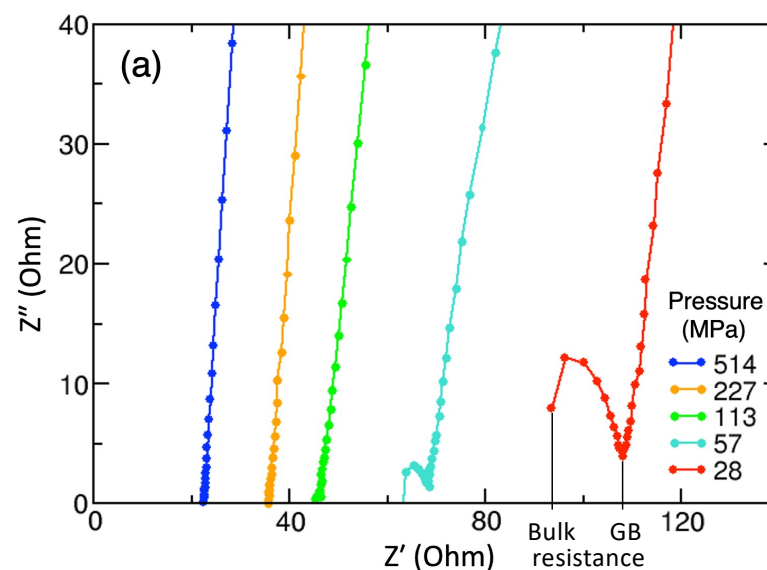


Simulation Validation for $\sigma(P)$

Pressure dependence: simulation vs experiment



Electrochemical impedance spectroscopy

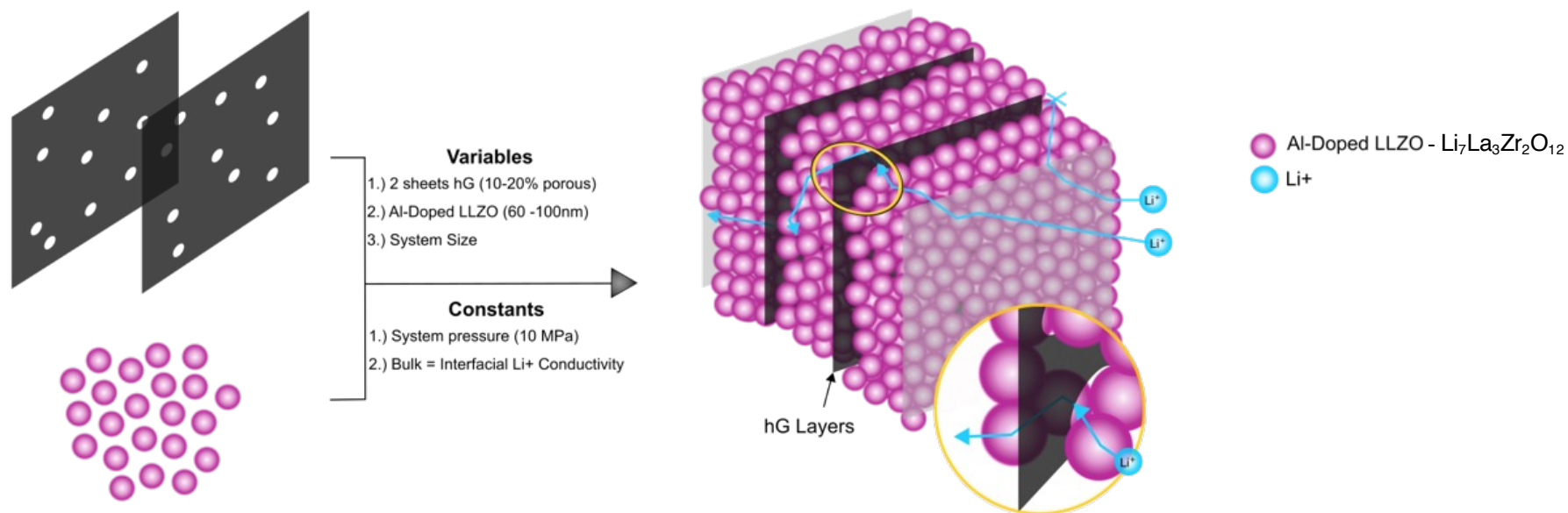


Experiment closest match with Regime III $\sigma_B \ll \sigma_{GB}$: Very good contact conductivity

hG Model

hG allows for:

- ❑ High active material content (up to 90 wt%)
- ❑ High mass loading: high areal capacity
- ❑ Excellent current collector– cathode contact



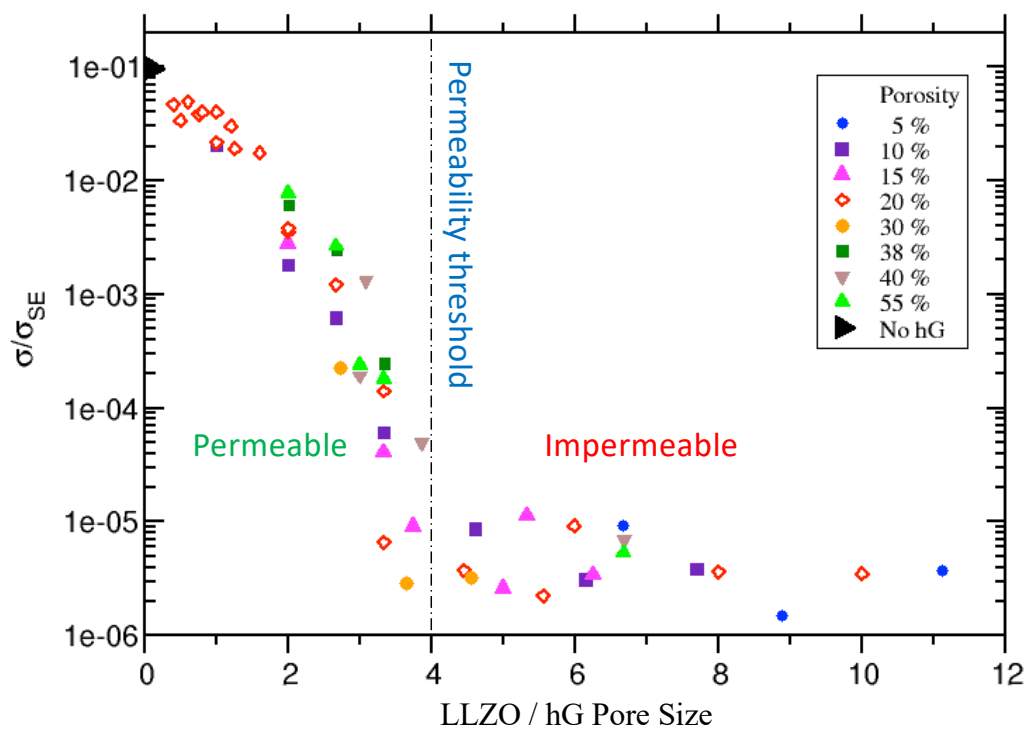
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hG is expected to significantly improve battery performance

Modeling hG Li⁺ Permeability



Universal permeability diagram



Hole size [nm]: 9 – 200
Porosity [%]: 5 - 55

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hG is transparent for Li⁺ when SE particles are smaller than 4-times the pore size

Summary



- ❑ A particle dynamics solid-state cathode model has been developed for optimizing multiple cathode design parameters:
 - Grain size of the cathode powder particles
 - Cathode powder composition
 - Cathode utilization
- ❑ The model was used to study Li^+ conductivities as functions of cathode composition and stack pressure
- ❑ Critical porosity threshold for Li^+ permeability through hG pores was found

Acknowledgements



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