Modeling of Solid State Batteries

for Advanced Electric Aircraft

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Modeling Team
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Internship students

Great Support from
Yi Lin, Ji Su
Advanced Materials and Processing Branch,

Sandwich Seminar
1/10/23

Outline

☐ **Introduction – Solid-state Architecture Batteries for Enhanced Rechargeability and Safety (SABERS) transformative technology**

☐ **Solid state lithium sulfur (Li-S) batteries – brief overview**

☐ **Modeling cathode microstructure: particle dynamics electro-mechanical model**

☐ **Modeling capabilities and results**

☐ **Summary**

Related Project and Collaborators

LaRC Energy Storage Materials Team

Yi Lin, Ji Su,
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Advanced Materials and Processing Branch,
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NASA Marshall Space Flight Center
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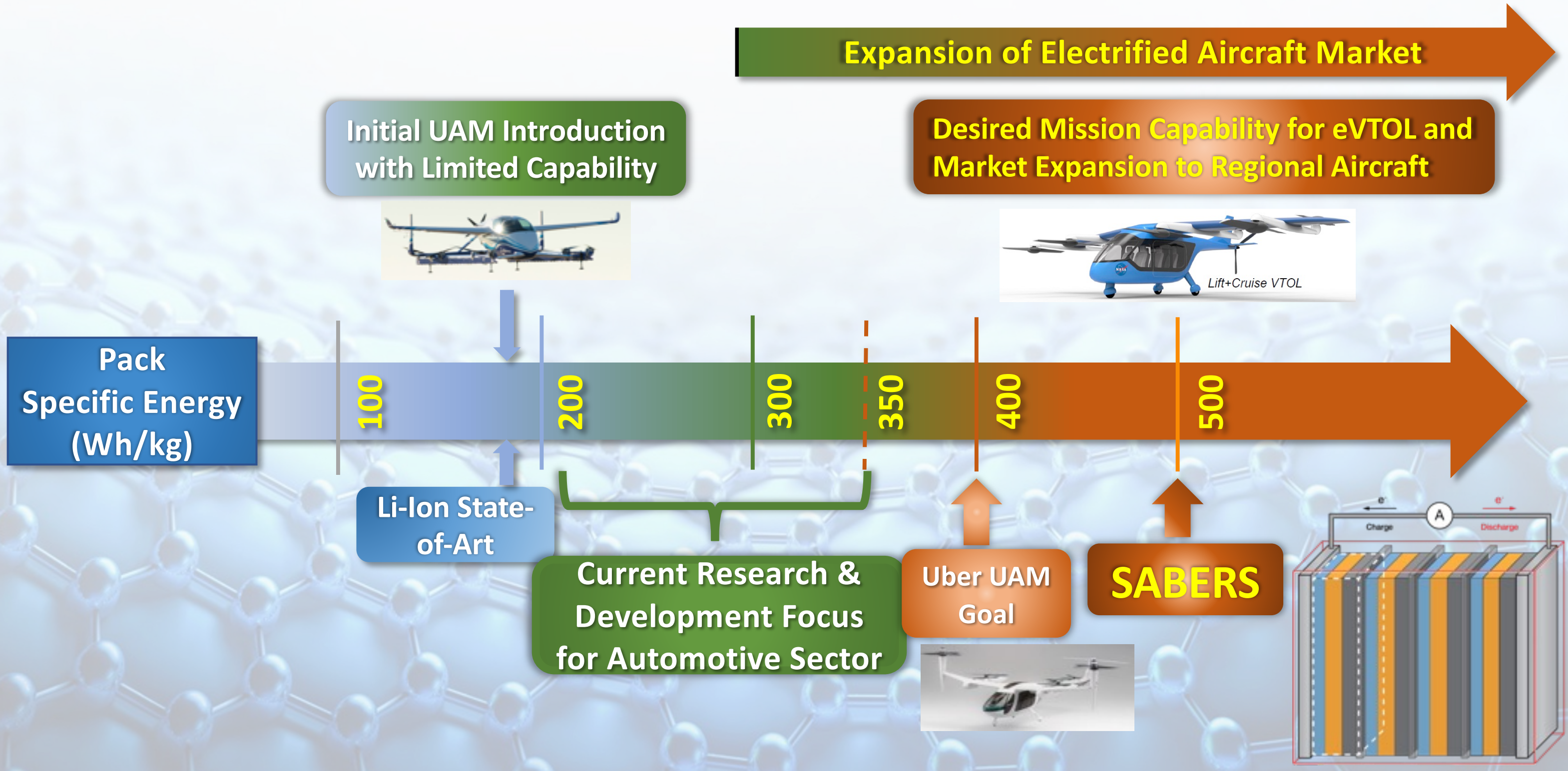
Student Interns in Computational Modeling:

2019-2020: **Christian Plaza-Rivera**
2020-2022: **Brandon Walker; April Rains**
2021: **Justyn Lewis; Malik Satterwhite**
2022: **Prabhat Jandhyala; Sophie Kiley**

SABERS Focused on Electric Aircraft



Expansion of Electrified Aircraft Market

Initial UAM Introduction with Limited Capability

Desired Mission Capability for eVTOL and Market Expansion to Regional Aircraft

Pack Specific Energy (Wh/kg)

100

200

300

350

400

500

Li-Ion State-of-Art

Current Research & Development Focus for Automotive Sector

Uber UAM Goal

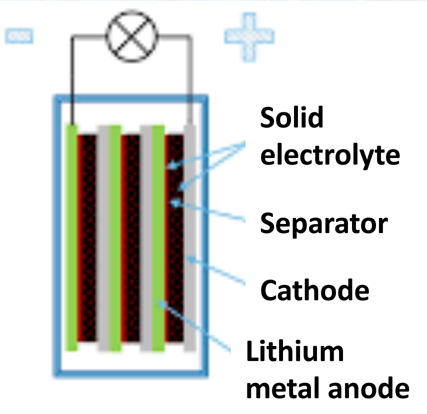
SABERS

UAM – urban air mobility
eVTOL – electric vertical takeoff and landing

State of the Art (SOA) Battery Technologies

- 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

Bi-polar All Solid-State Battery System

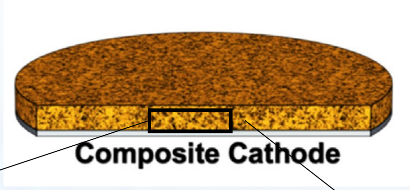


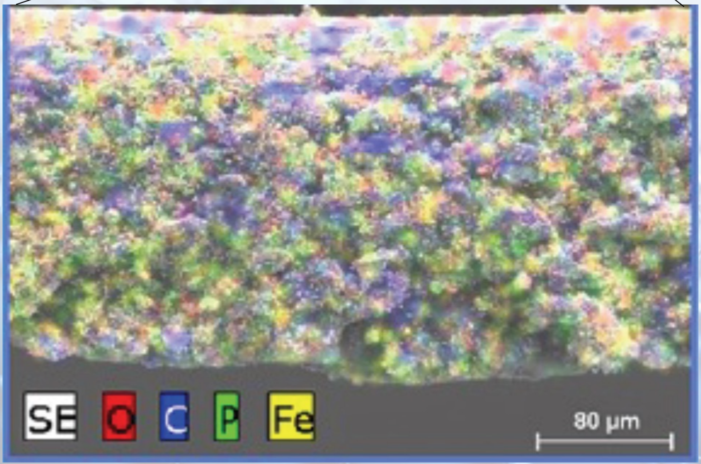
Current focus is on all solid-state Li-S battery systems

Cathode Composition and Microstructure

Model cathode microstructure at particle level

Battery Cell





Cross-sectional SEM image of an SE cathode layer

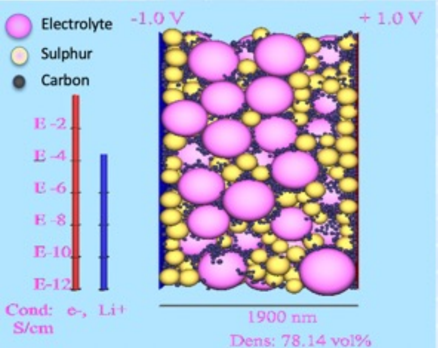
Solid State Cathode constituents:

☐ Cathode active material (CAM) - **S, Se, Se_xS_y, Li_2S**

☐ Solid electrolyte (SE) with high LI^+ ionic conductivity -
Ceramic oxide electrolyte LLZO - $Li_7La_3Zr_2O_{12}$ of ionic cond: $5x10^{-4}$ S/cm

☐ Electronic conductive agent (ECA) with high electron conductivity – carbon black (CB), and holey graphene (hG)

$$S + 2Li^+ + 2e^- \rightarrow Li_2S$$



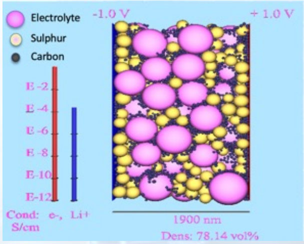
Particle model of an SE cathode

Modeling cathode microstructure can help battery design

Purpose of the Modeling

Superior battery performance strongly depends on optimizing multiple cathode design parameters

Critical parameters for optimal cathode performance:



☐ 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 CA for e^- transport

☐ Li^+ and e^- conductivities of SE and ECA

☐ Mass weight of the components – affects the overall battery weight

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

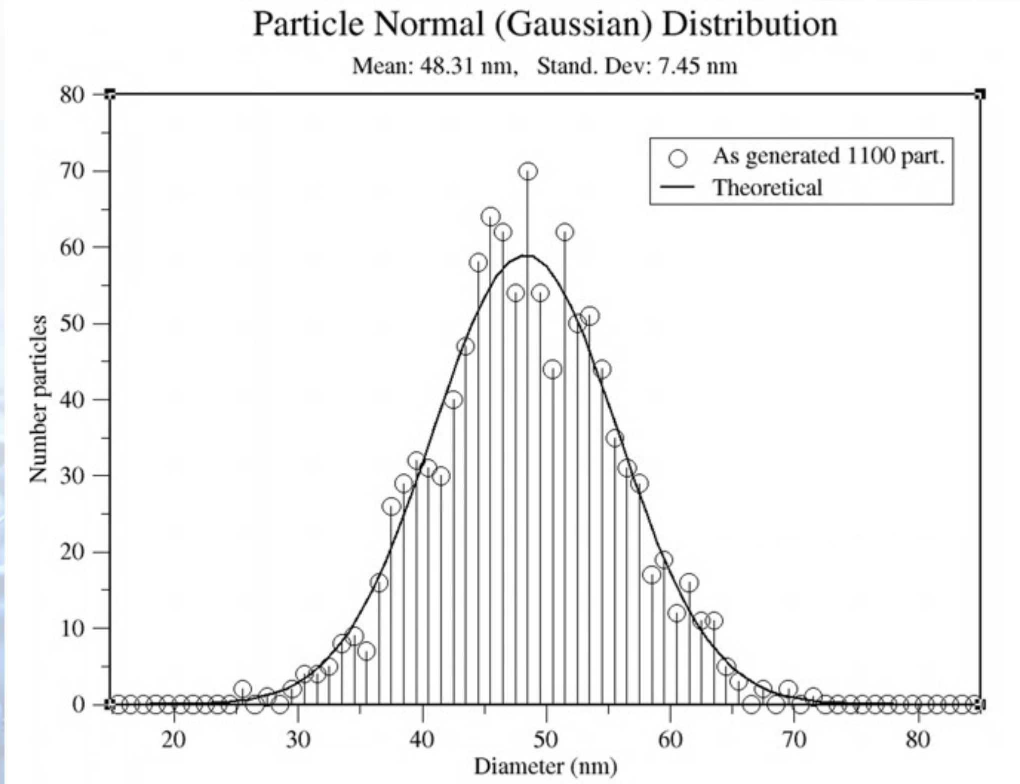
Modeling helps to find the optimal design parameters for superior battery performance

Cathode Model at Particle Level

Solid Electrolyte Sphere Approximation Model (SESAM) (NTR: LAR-19842-1)

Model construction:

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



Robust physics-based electro-mechanical model

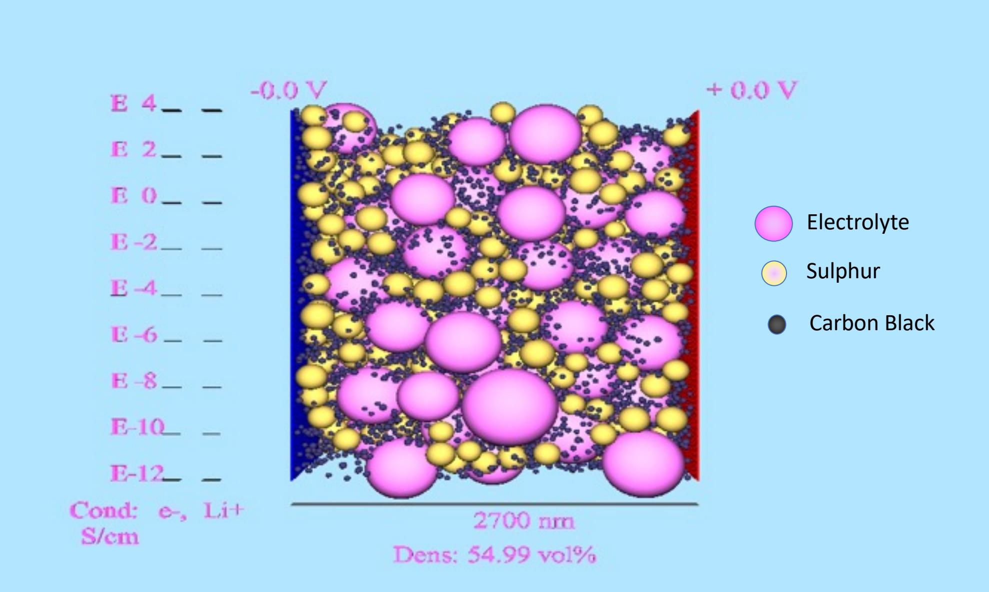
Cathode Model at Particle Level

Solid Electrolyte Sphere Approximation Model (SESAM) (NTR: LAR-19842-1)

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)



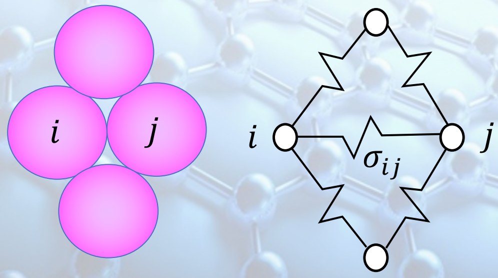
Robust physics-based electro-mechanical model

Cathode Model at Particle Level

Solid Electrolyte Sphere Approximation Model (SESAM) (NTR: LAR-19842-1)

Model construction:

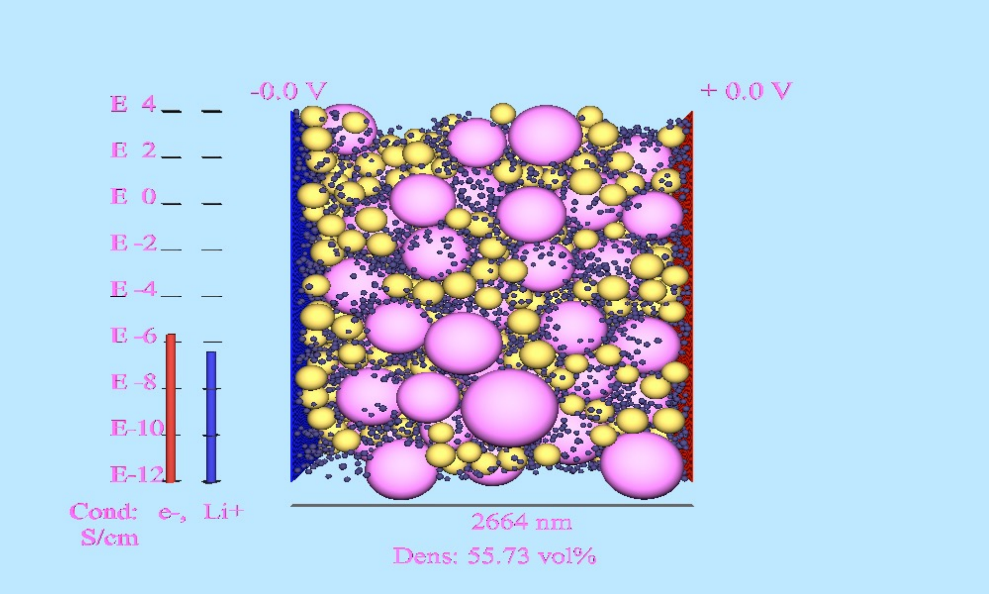
- ☐ **Generate particles of given type (SE, C, S) and given size distribution**
- ☐ **Fills the system box (or RVE) with particles of all types randomly**
- ☐ **Compress the powder composite and measure conductivities**



Solving Kirchhoff's matrix equation gives conductivity

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

Cathode Representative Volume Element (RVE)

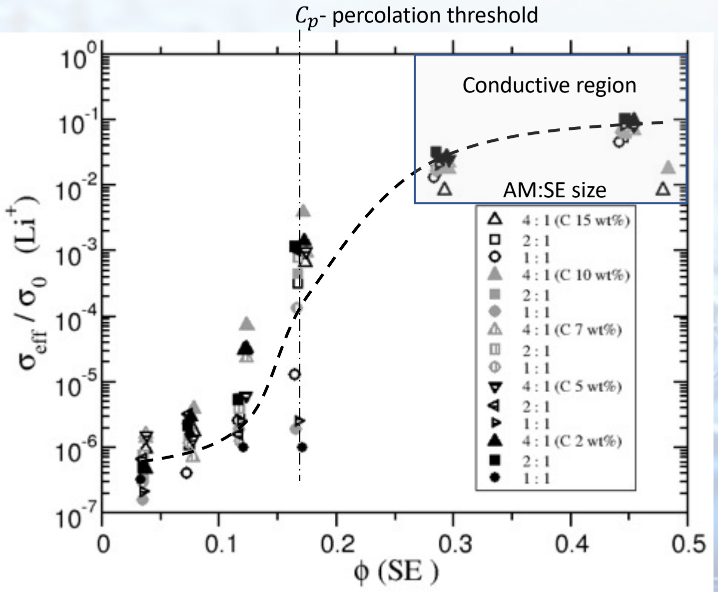


Robust physics-based electro-mechanical model

Results: Li$^+$ - Conductivity vs Cathode Content

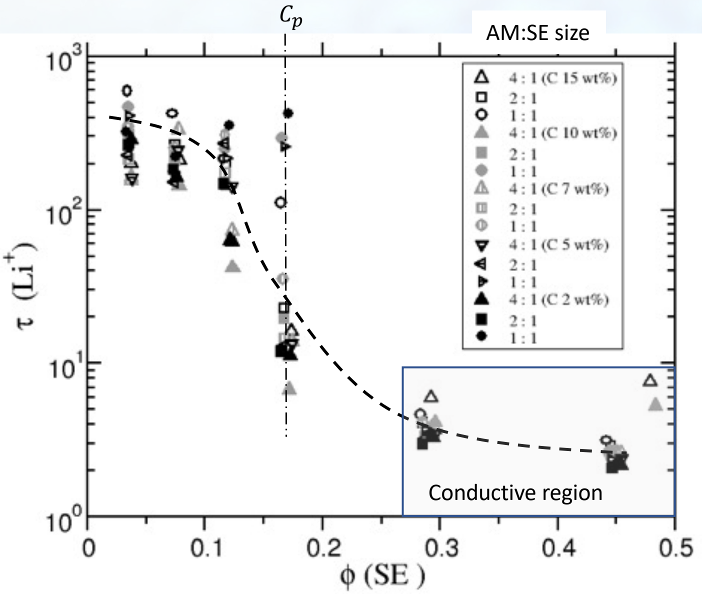
- ➢ Percolation threshold at $C_{p,SE} \approx 17$ vol%
- ➢ High conductivity at $C_{SE} > 30$ vol %
- ➢ No noticeable dependence on CAM:SE size ratio (SE size was constant = 100 nm)
  - ▪ Effect on size could be expected when SE size changes (to be performed)

Conductivity ratio, σ_{eff}/σ_0, vs material vol%, ϕ



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

Tortuosity, τ, vs material vol%, ϕ



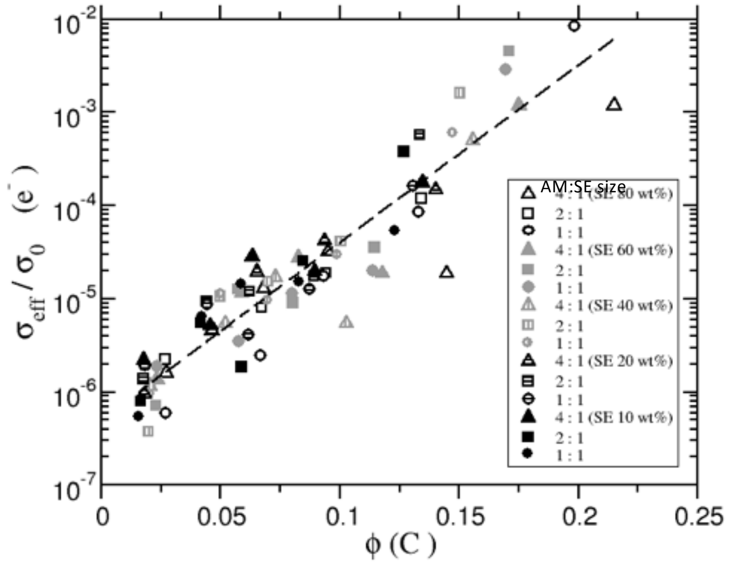
σ_{eff}- effective conductivity; σ_o- conductivity of a fully dense material

Prediction of Li$^+$ and e$^-$ conductivities helps design optimization

Results: e$^-$ - Conductivity

- e$^-$ conductivity increases exponentially with CB wt%
- τ – values are in agreement with literature results: ~ 10
  MacMullin Number: $N_M = \sigma_0/\sigma_{eff} = \tau^2/\phi = 10^2 \div 10^6$

Conductivity ratio, σ_{eff}/σ_0, vs material vol%, ϕ



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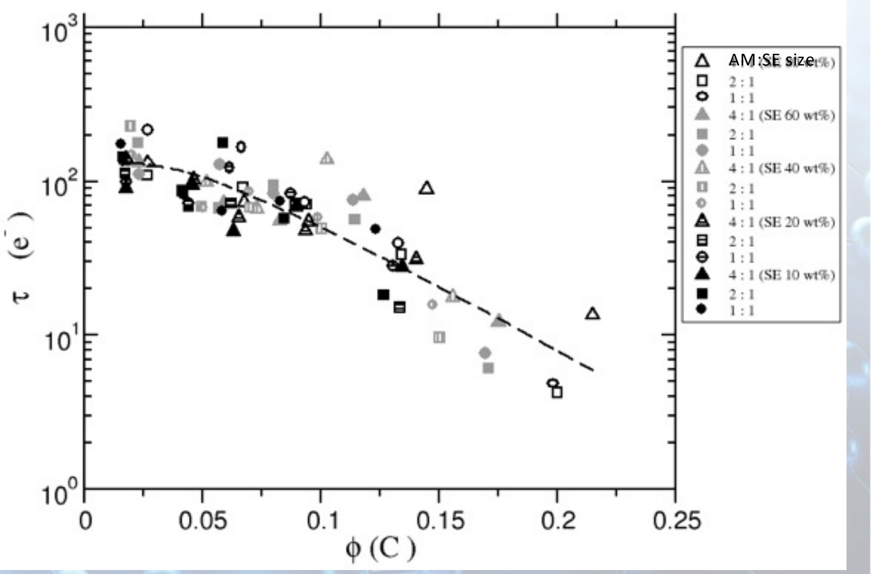
Tortuosity, τ, vs material vol%, ϕ



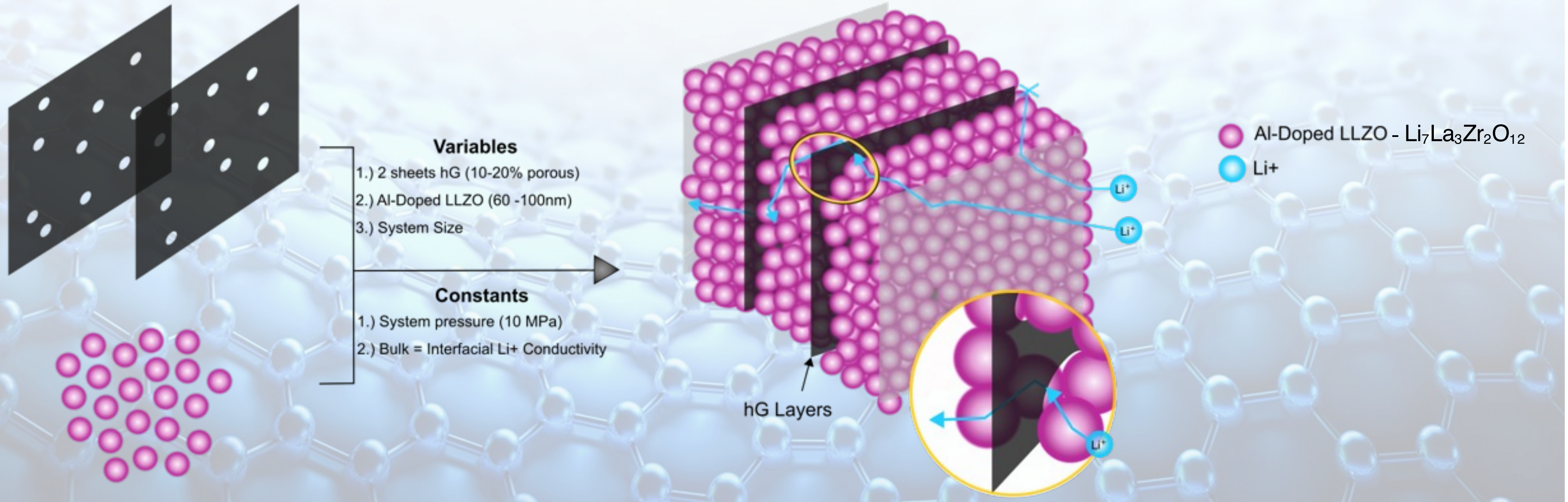
σ_{eff} - effective conductivity; σ_o - conductivity of a fully dense material

Prediction of Li$^+$ and e$^-$ conductivities helps design optimization

hG Model

hG allows for:

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



Variables

1.) 2 sheets hG (10-20% porous)
2.) Al-Doped LLZO (60 -100nm)
3.) System Size

Constants

1.) System pressure (10 MPa)
2.) Bulk = Interfacial Li+ Conductivity

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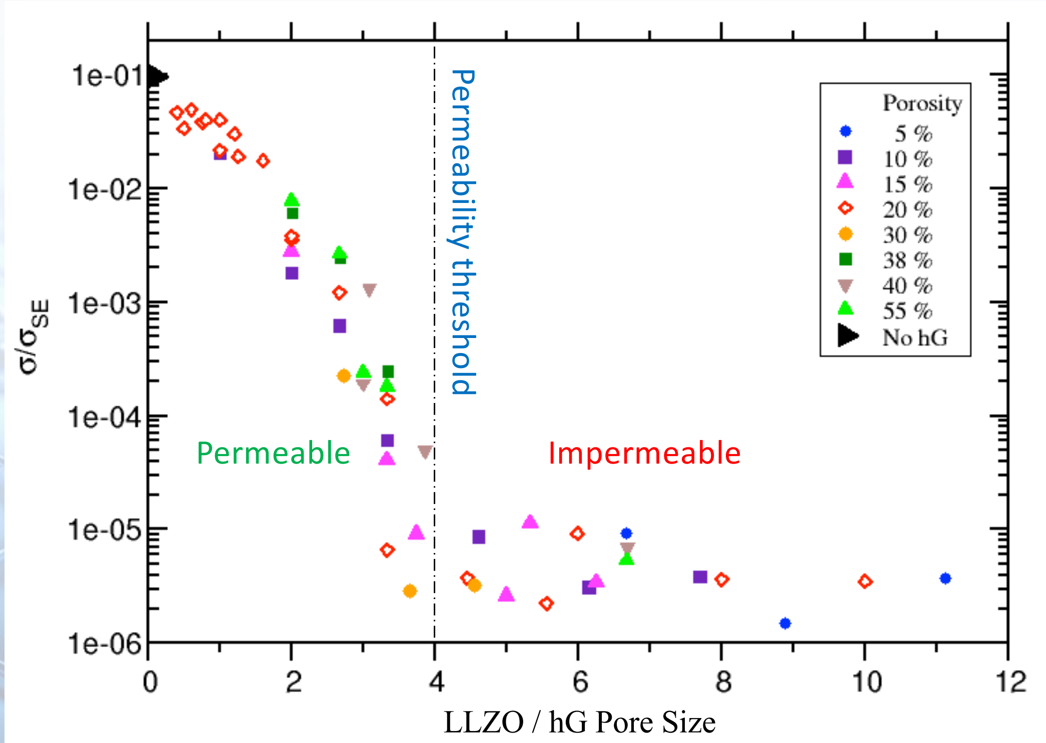
hG is expected to significantly improve battery performance

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

hG vs CB as Conductor Material

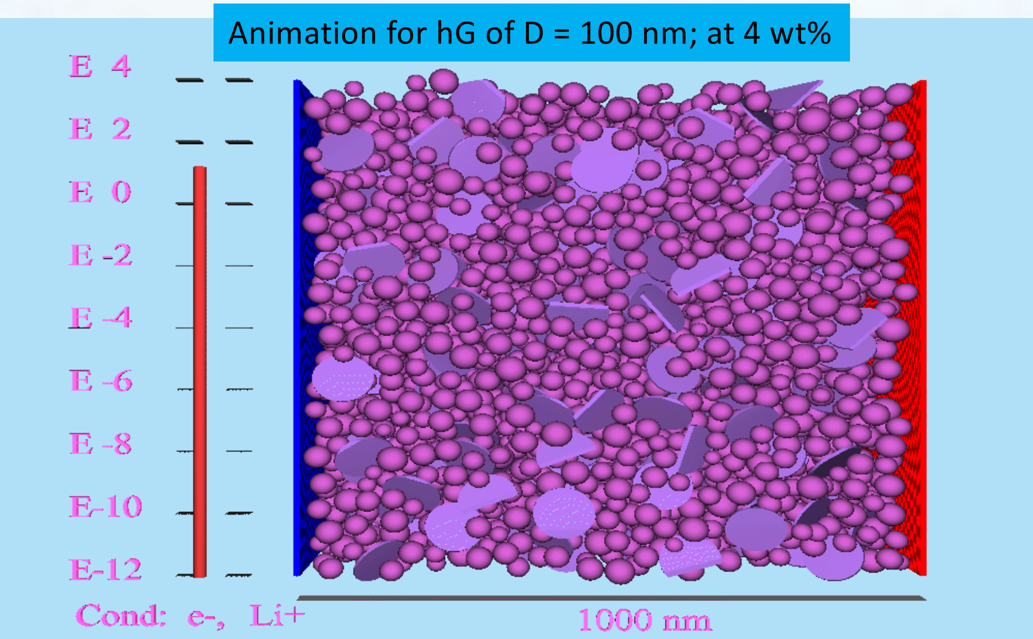
Purpose

- Study how hG size and wt% affect Li^+ and e^- conductivities to optimize cathode utilization and battery performance
- Compare hG vs CB as conductors for Li-ion and e- conductivities

Simulation Setup

Electrolyte:
Al-doped LLZO
E = 150 GPa
$\boldsymbol{\nu} = 0.25$
$\boldsymbol{\sigma}_{SE}$ = 1 mS/cm
D = 40 nm
Conductor:
hG: D:
50, 100, 200, 400 nm
System size:
1000 x 1000 x 1000 nm
P: (1 ÷ 100 MPa)

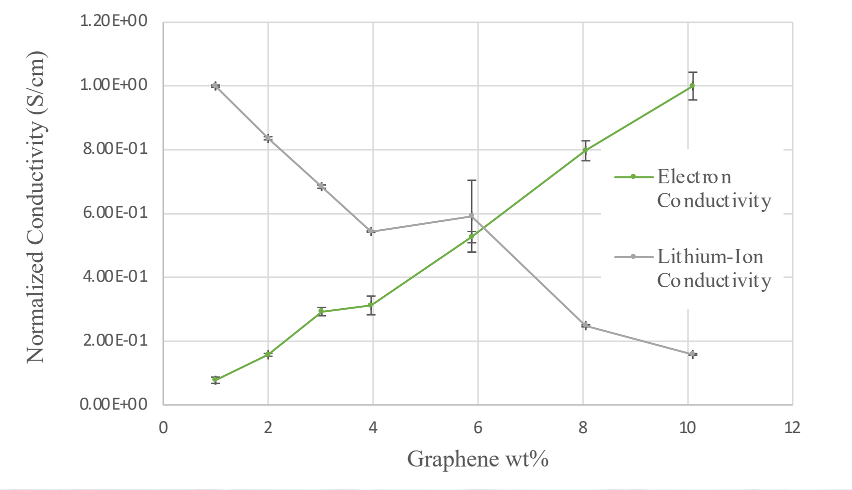
Animation for hG of D = 100 nm; at 4 wt%



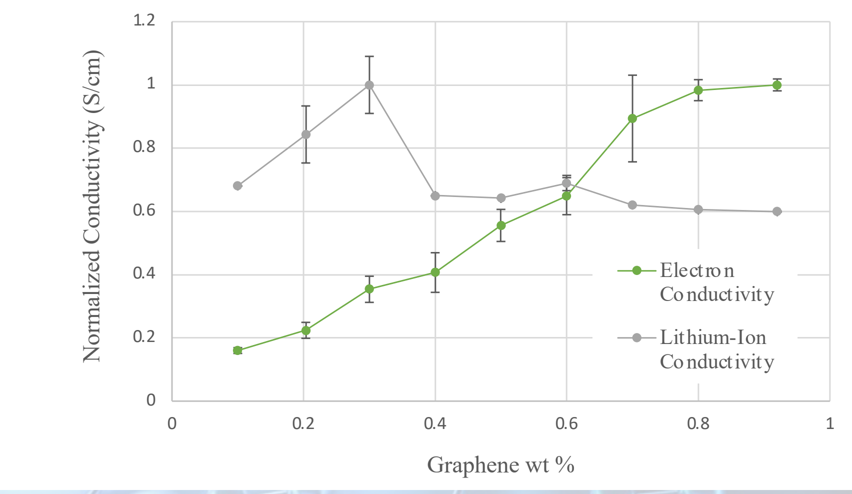
First time explicit modelling of hG disks inserted in electrolyte powder

Electron vs Lithium-Ion Transport of hG

Diameter 100 nm



Diameter 50 nm



- As weight percent increases, electron conductivity increases while lithium-ion conductivity decreases

Addition of hG particles provides increased e$^-$ conductivity, but may significantly inhibit Li$^+$ transport

Summary

- ☐ **During the CAS-SABERS project a particle dynamics solid-state cathode model has been developed for optimizing multiple cathode design parameters:** (NTR: LAR-19842-1)
  - **Grain size of the cathode powder particles**
  - **Cathode powder composition**
  - **Cathode utilization**

- ☐ **The model was used to study Li^+ and e^- conductivities as functions of cathode composition and particle size**

- ☐ **The addition of hG as a conductor material has been studied in terms of its effect on Li^+ and e^- conductivities**

If Enough Funding is Available

Develop a large scale (possibly multiscale) "digital twin" battery cell model to

- ☐ **Incorporate:**
  - **Anode, interface, and cathode composition**
  - **Ion transport from anode to cathode and inside the cathode**
  - **Electrochemical reactions in the cathode**

- ☐ **Predict and validate through experiment:**
  - **Cathode utilization**
  - **Power output**
  - **Charge – discharge parameters**

- ☐ **Improve and accelerate the design of battery development for advanced electric aircrafts**