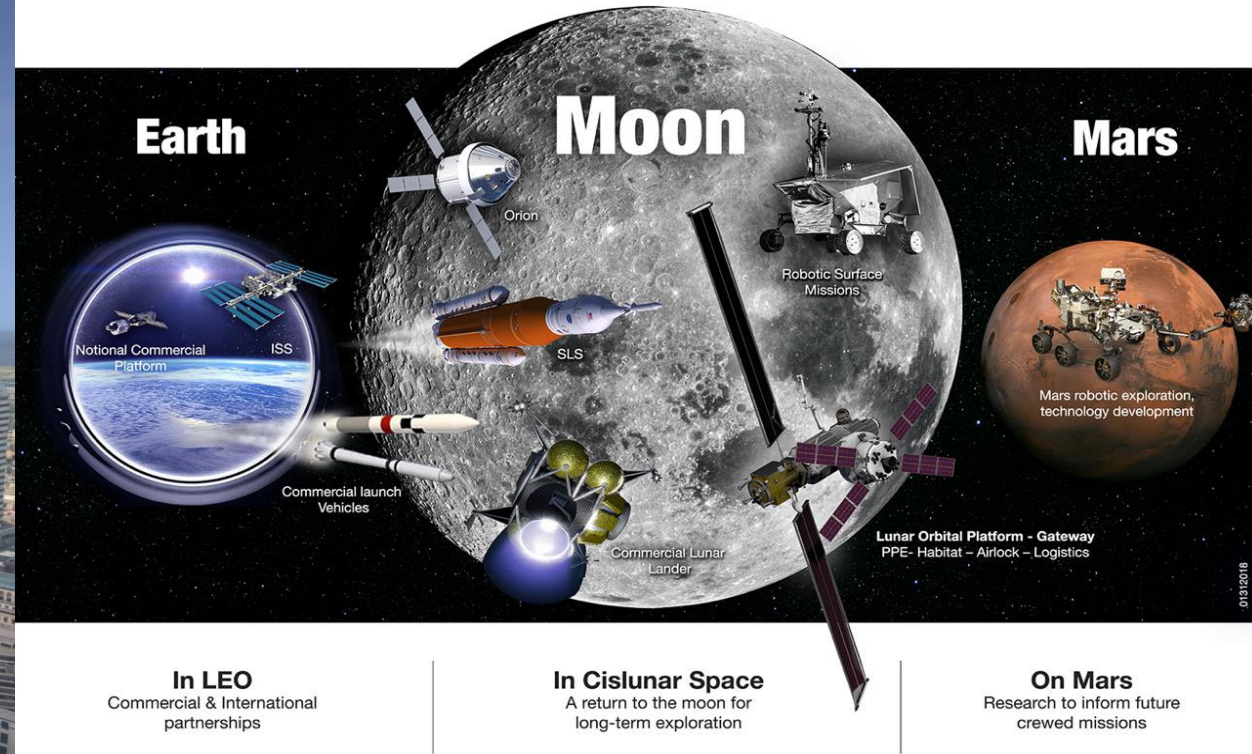


Computationally Guided Development of Components for High Energy Density Solid-State Lithium-Sulfur Batteries



Vadim F. Lvovich¹, Vesselin Yamakov², Rocco P. Viggiano¹, Donald A. Dornbusch¹, John W. Connell³, Yi Lin³

1 - NASA Glenn Research Center, Cleveland, OH 44135 2 - National Institute of Aerospace, Hampton, VA 2366 3- NASA Langley Research Center, Hampton, VA 23681

31st Topical Meeting of the International Society of Electrochemistry , Aachen, Germany, 2022

NASA Demands Very High Specific Energy Batteries and Fuel Cells



Electric Aviation 500 – 750 Wh/kg

- Green aviation – Less noise, lower emissions, high efficiency
- Hybrid / All-electric aircraft – Limited by mass of energy storage system
- Commercial aviation – Safe, reliable, lightweight on-board electric auxiliary power unit



Extravehicular Activities (Spacesuit power) >400 Wh/kg

Required to enable untethered EVA missions lasting 8 hours within strict mass and volume limitations.

Astronaut life support
Safety and reliability are critical
100 cycles



Landers and Rovers, Robotic missions, In- space habitats >500 Wh/kg

Batteries are expected to provide sufficient power for life support and communications systems, and tools including video and lighting

- >100 cycles

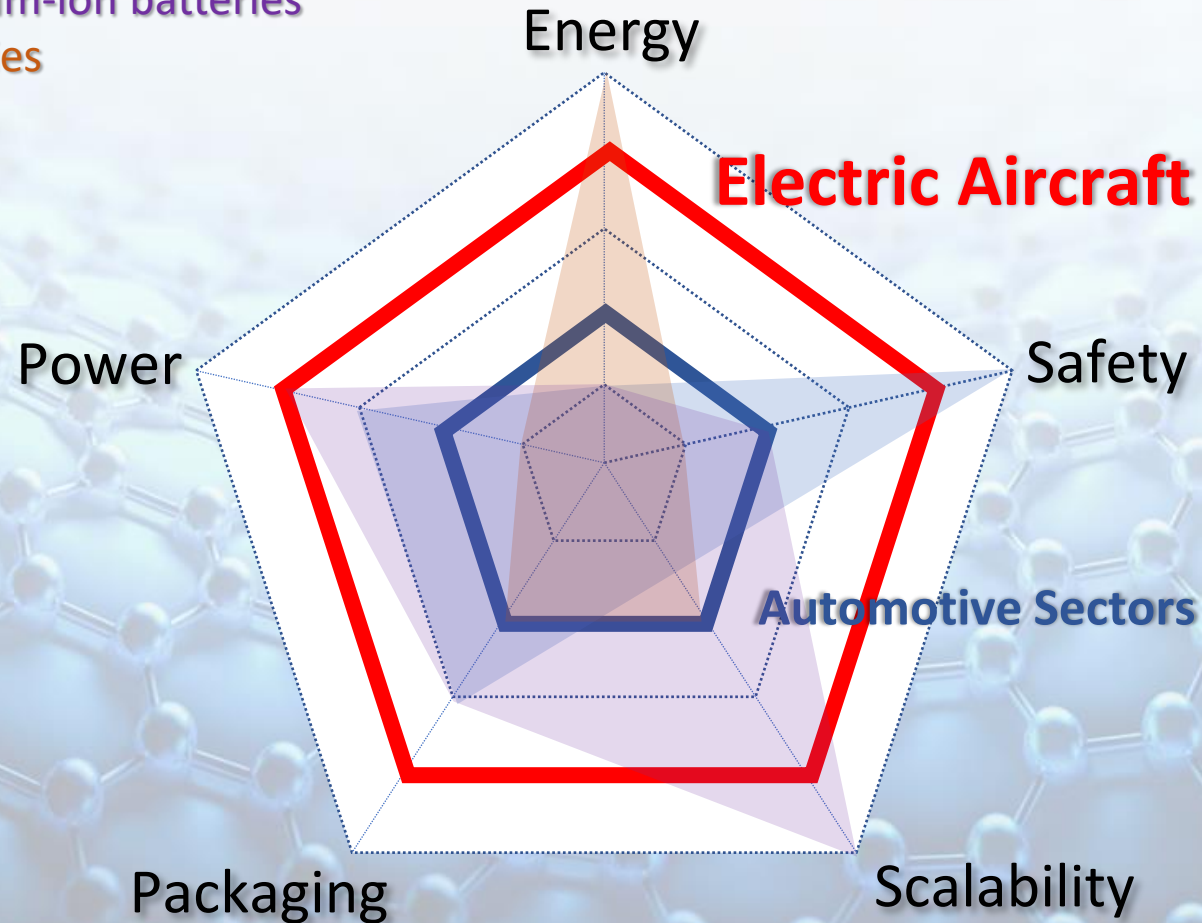
NASA future mission requirements far exceed the capabilities of lithium-ion chemistries

- Progress in these areas requires advances in safe, very high energy batteries and fuel cells

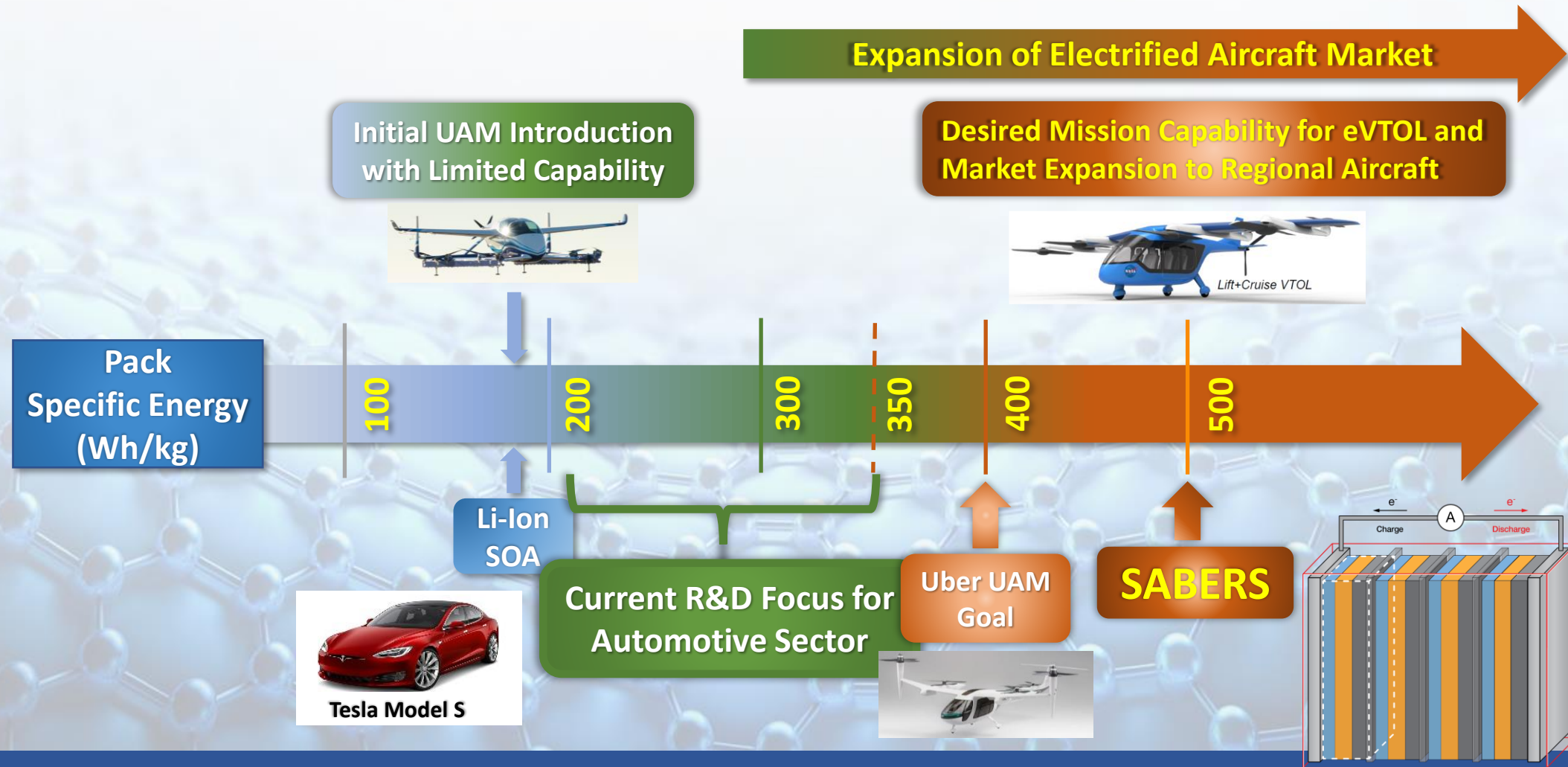
The Big Question

How do we meet **ALL** demanding battery needs of electric aircraft?

- State-of-the-art lithium-ion batteries
- Lithium sulfur batteries
- Solid state batteries

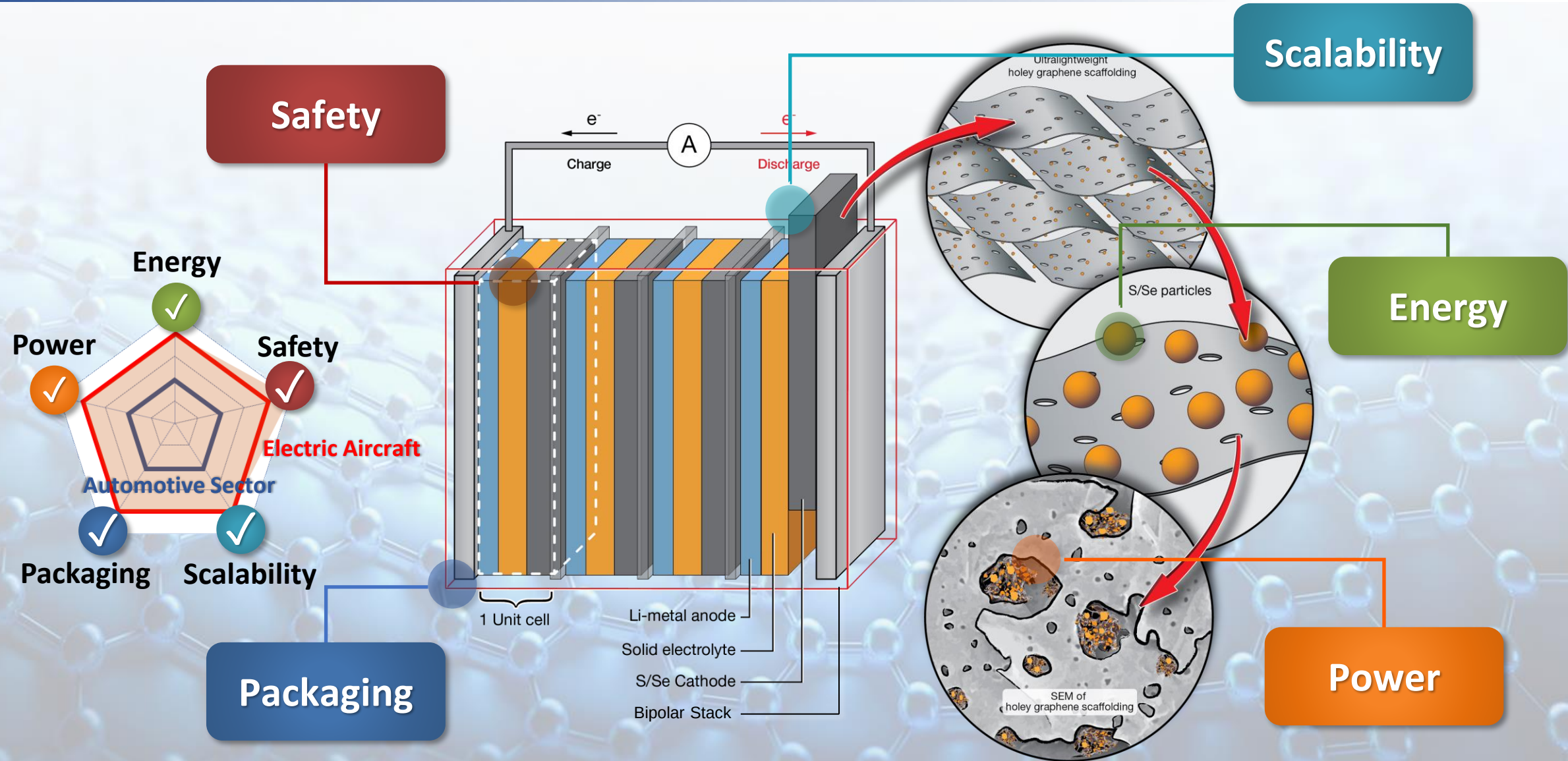


SABERS Focused on Electric Aircraft



❑ Current performance targets for the automotive sector are a battery pack with 250 – 300 Wh/kg

SABERS Transformative Technology



Combination of unique materials technologies to achieve performance goals

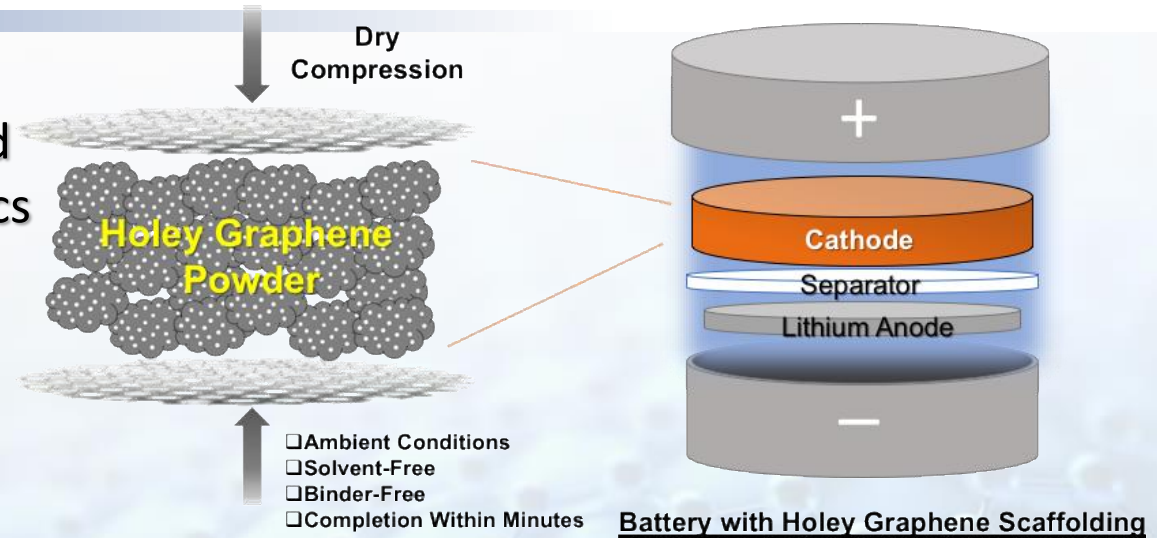
SABERS Cell Components

❑ Unique NASA-developed technology

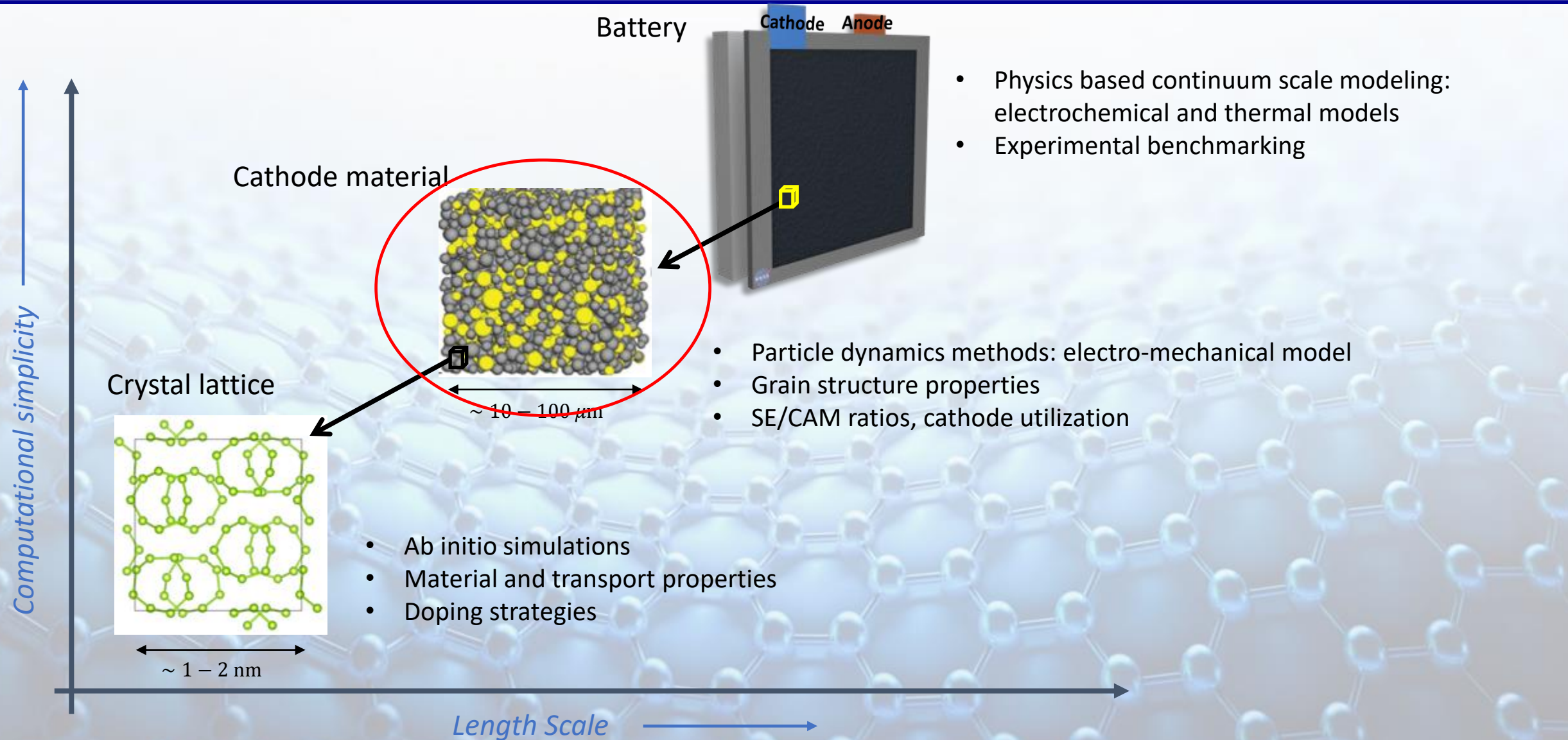
- High conductivity, ultralightweight electrode scaffold
- Through-thickness ion transport enabling fast kinetics
- Enables universal dry electrode processing
- Scalable

- Anode: Li or Li-based alloys
- SE: sulfide (thiophosphate) solid electrolytes
- Cathode:

- A mixture of three with optimal active material content, electrical conductivity from carbon, and ionic conductivity from solid electrolyte (SE); as well as optimal interfaces among three.
- Active material
 - Nonlithiated: S, Se, **SeS_x**
 - Lithiated: Li₂S, **Li₂S_xSe_y**
- SE: sulfide (thiophosphate) solid electrolytes (high ionic conductivity; soft and pressable)
- Carbon
 - Holey graphene (hG)
 - Other carbon additives: Ketjen black, Super P, carbon nanotubes, carbon nanofibers, graphene.



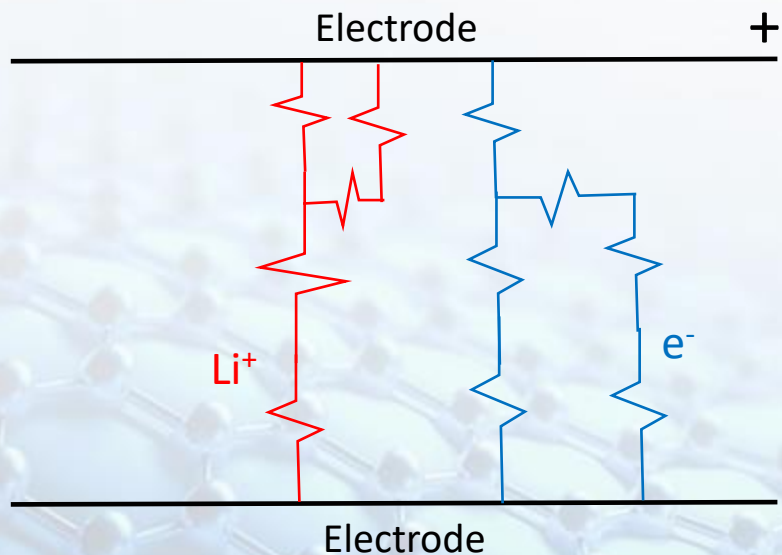
Modeling at Different Scales



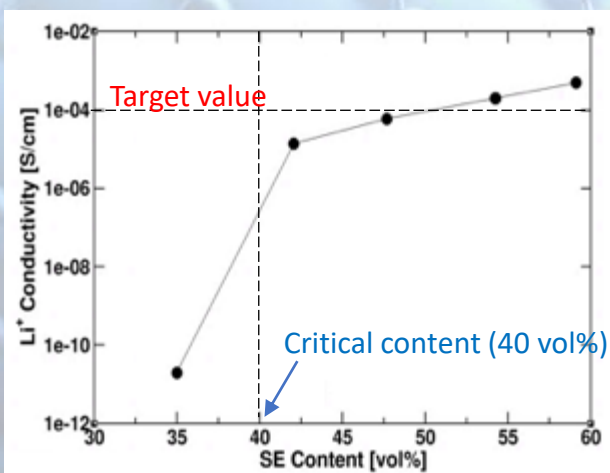
Cathode Model at Particle Level



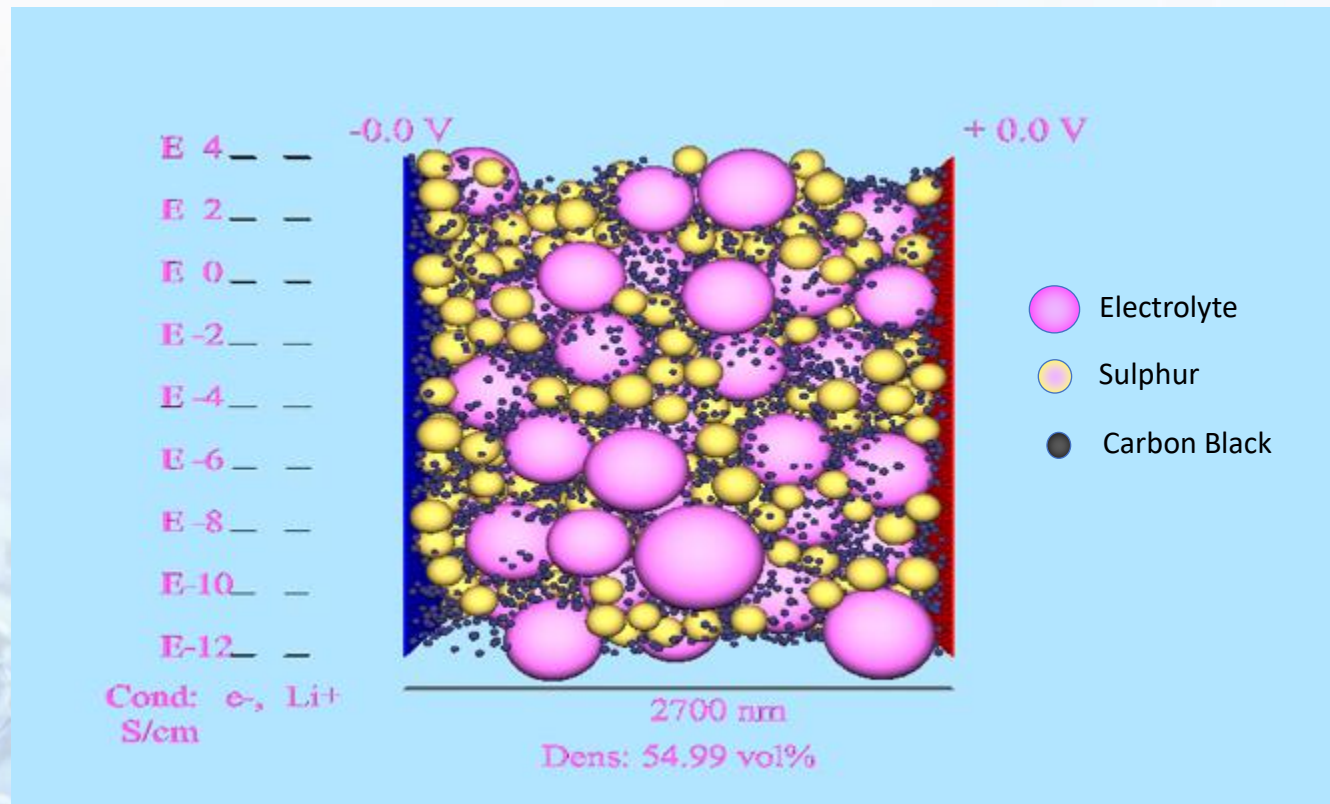
Two electric circuits



Conductivity measurement



Cathode Representative Volume Element (RVE)



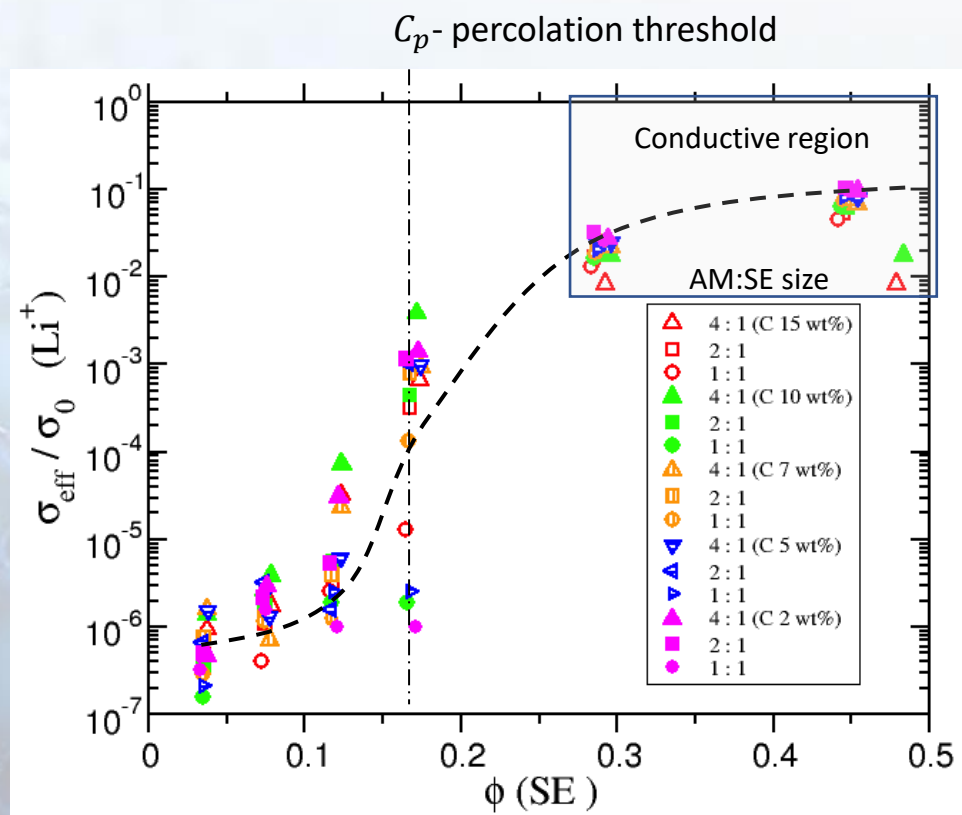
Model construction:

- ☐ 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

Li⁺ - Conductivity vs Cathode Content

Summary of all cathode compositions data

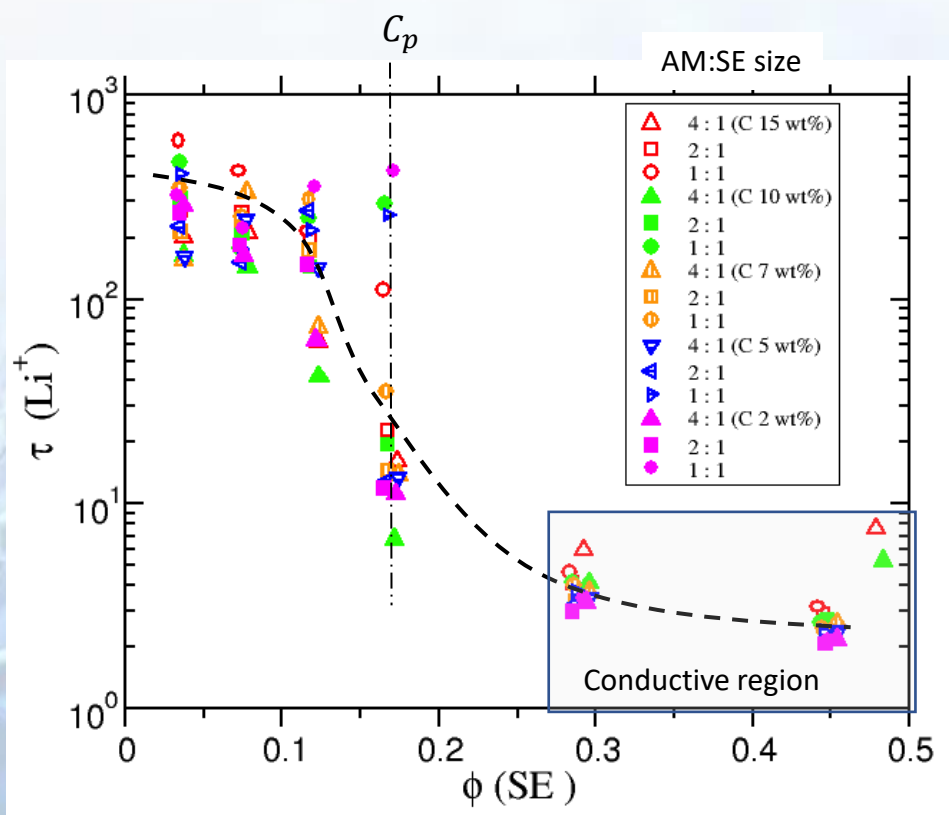
Effective conductivity vs material vol%



Percolation threshold at $C_{p,SE} \approx 17$ vol%

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

Tortuosity vs material vol%



e⁻ - Conductivity

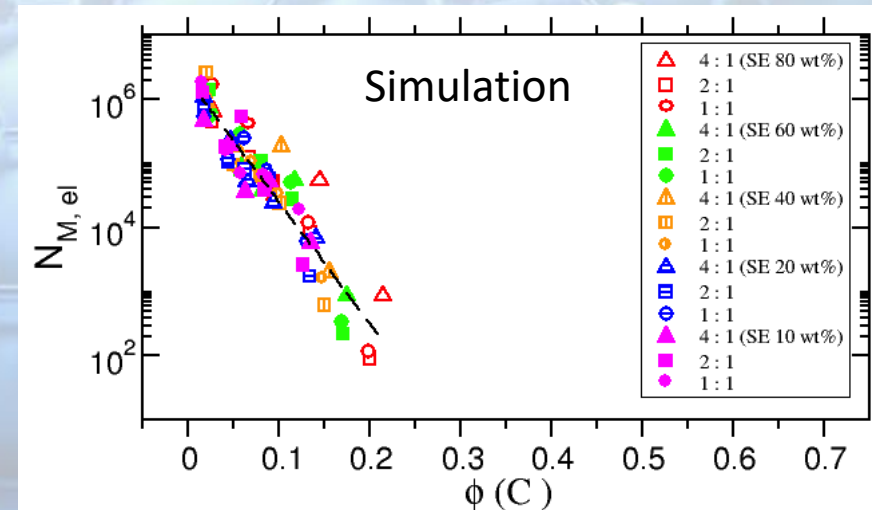
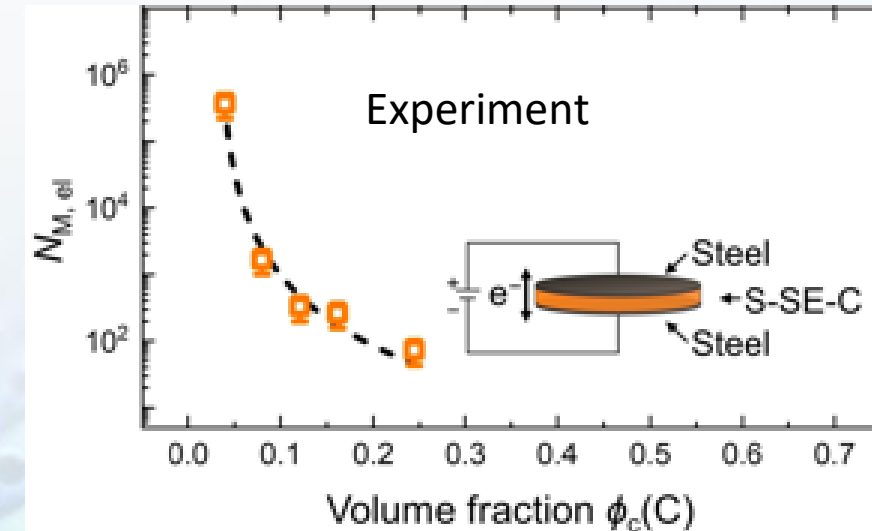
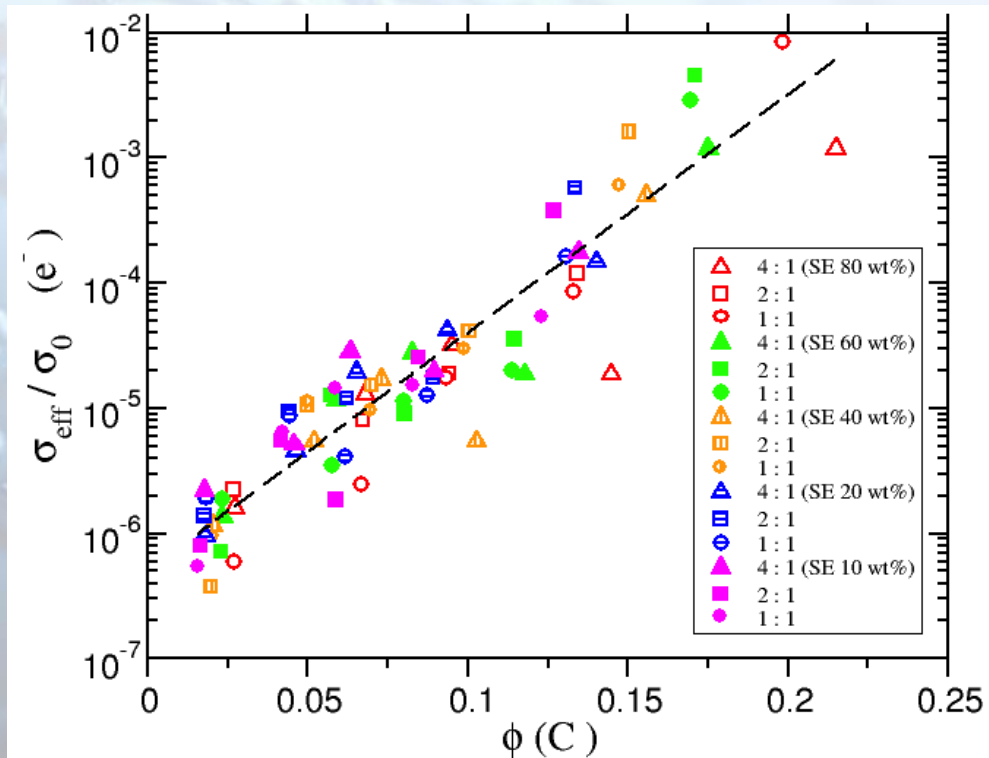


➤ e⁻ conductivity increases exponentially with C wt%

➤ In range with literature results:

MacMullin Number: $N_M = \sigma_0 / \sigma_{eff} = \tau^2 / \phi = 10^2 \div 10^6$

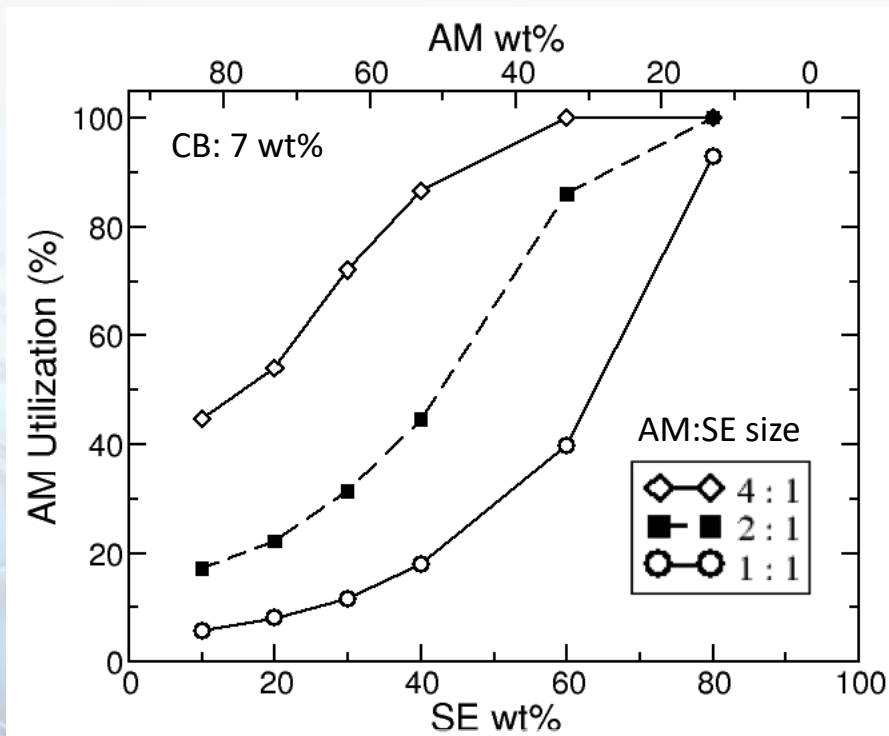
Effective conductivity vs material vol%



Cathode Utilization



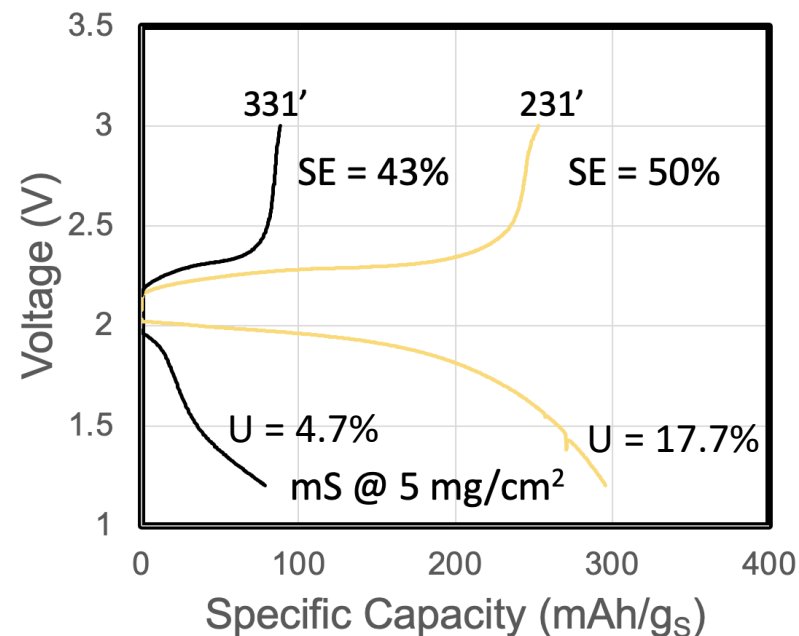
Simulation



Increase of SE Content significantly improves utilization

Experimental data

0.1 C @ 60C



Increase of SE Content significantly improves rate performance & utilization

Experimental data

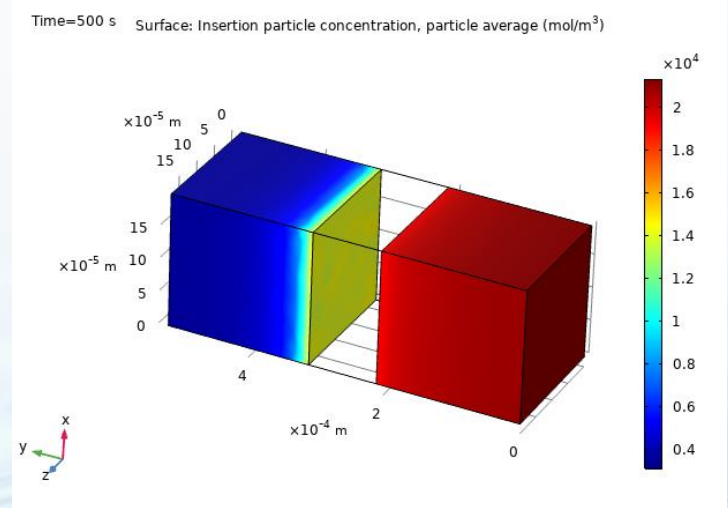
Battery #	Experiment Type	Cathode Type	Total Cathode Weight (mg)	AM Mass Loading (mg/cm ²)	AM Percentage in Cathode (%)	SE Percentage in Cathode (%)	1D Capacity (mAh)	1D Specific Capacity (mAh/g)	Utilization (%)
244	High Rate @ 60C	[(33)1]'-mS	20	5	42.9%	43%	0.311	79.2	4.7%
233	High Rate @ 60C	[(23)1]'-mS	30	5	33.3%	50%	1.161	295.8	17.7%

COMSOL components modeling – Li insertion

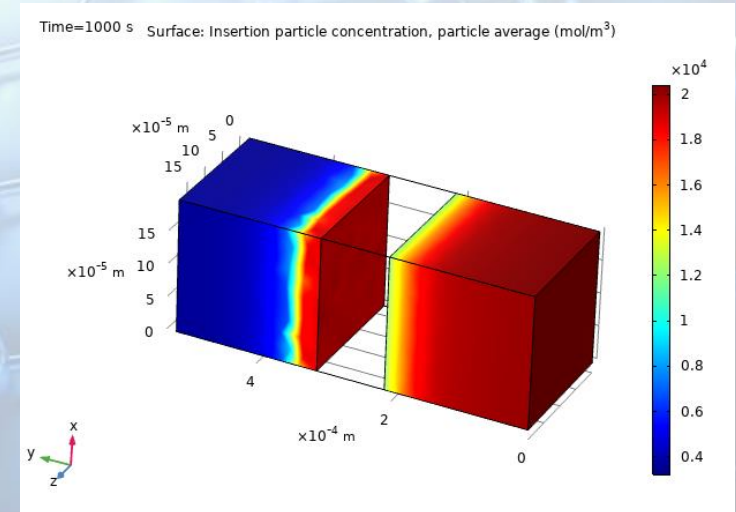
Results for baseline properties for LTO, LiPF6, LFP and 50 A/m² (5 mA/cm²) current density

Electrode		Porous anode	Porous cathode
	Electrical conductivity σ_s (S/m)	100	91
	Solid diffusivity D_s (m ² /sec)	6.8e-15	3.2e-13
	Solid volume fraction ϵ_s	0.65	0.65
	Particle radius r_p (μ m)*	6	4
	Initial lithium concentration $c_{s,init}$ (mol/m ³)*	22852	2649
	Reference concentration $c_{s,ref}$ (mol/cm ³)	22852	21190
Charge transfer interface	Transfer coefficients α_a, α_c	0.5, 0.5	0.5, 0.5
	Reference exchange current density $i_{o,ref}$ (A/m ²)	1	1
Electrolyte	Electrolyte diffusion coefficient D_l (m ² /sec)	7.5e-11	
	Transport number t_+	0.363	
	Activity dependence	0	
	Electrolyte reference concentration $c_{l,ref}$ (mol/m ³)	1000	

500
sec

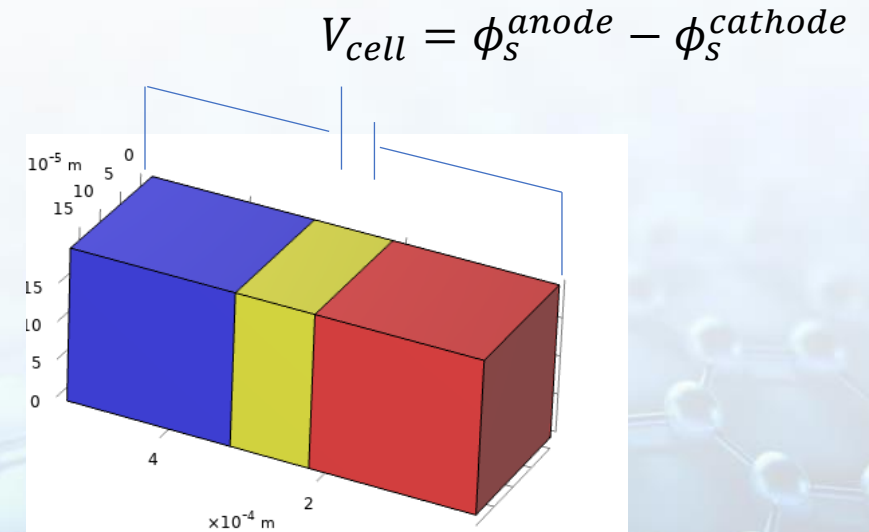
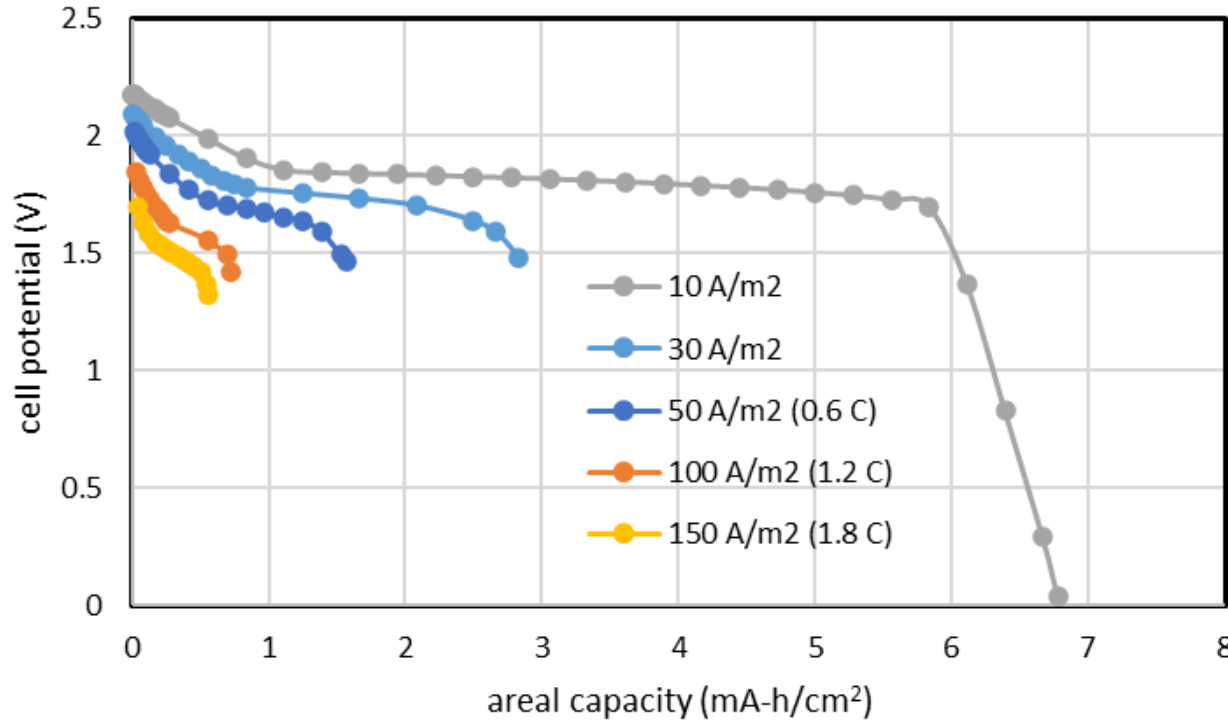


1000
sec



COMSOL components modeling – Li insertion

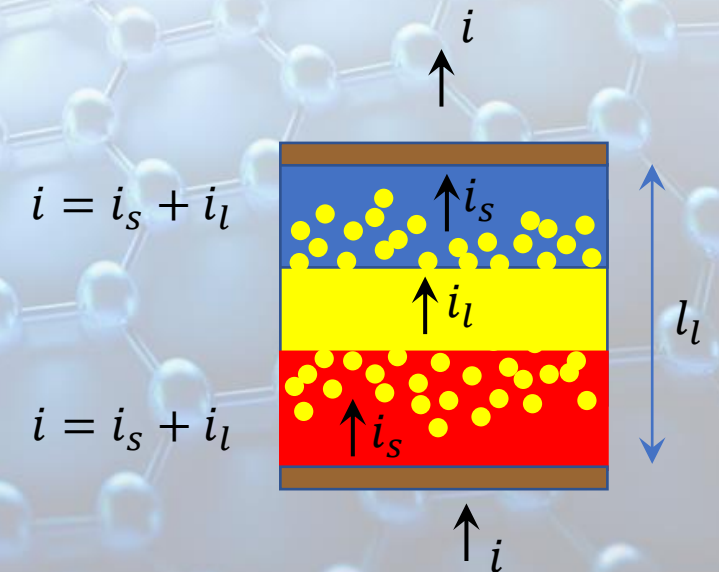
Cell potential versus areal capacity and current density: Baseline properties for LTO, LiPF6, LFP



Areal capacity = $i * t$

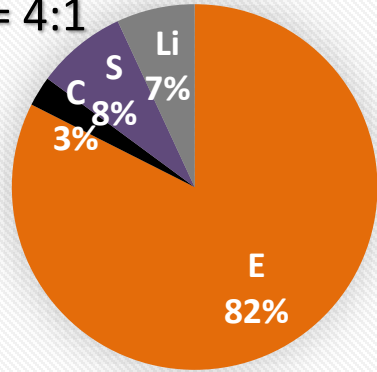
Power density $\rho_{power} = V_{cell} i = (V_{eq} - \eta_d - \eta_{mt} - \eta_{ct}) i$

Overpotentials $\eta_d = \int_0^{l_s} \frac{i_s}{\sigma_{s,eff}} dy$ $\eta_{mt} = \int_0^{l_l} \frac{i_l}{\kappa_{eff}} dy$



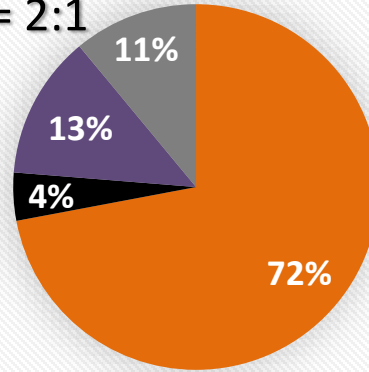
Projected Cell Energy Density

E:Cathode = 4:1
197 Wh/kg



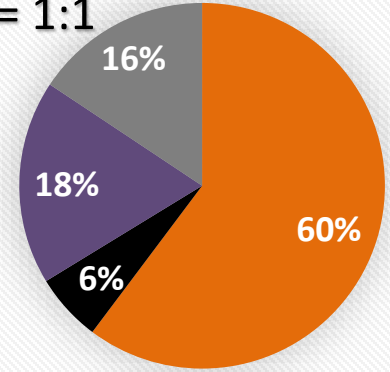
■ E ■ C ■ S ■ Li

E: Cathode = 2:1
313 Wh/kg



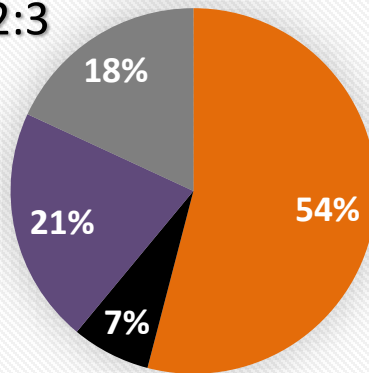
■ E ■ C ■ S ■ Li

E: Cathode = 1:1
441 Wh/kg



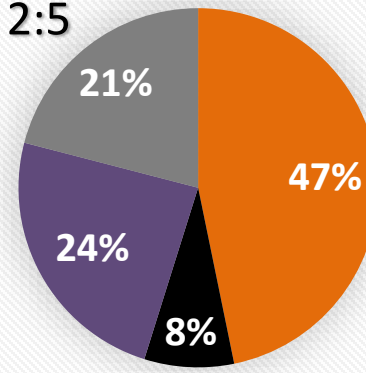
■ E ■ C ■ S ■ Li

E:Cathode = 2:3
508 Wh/kg



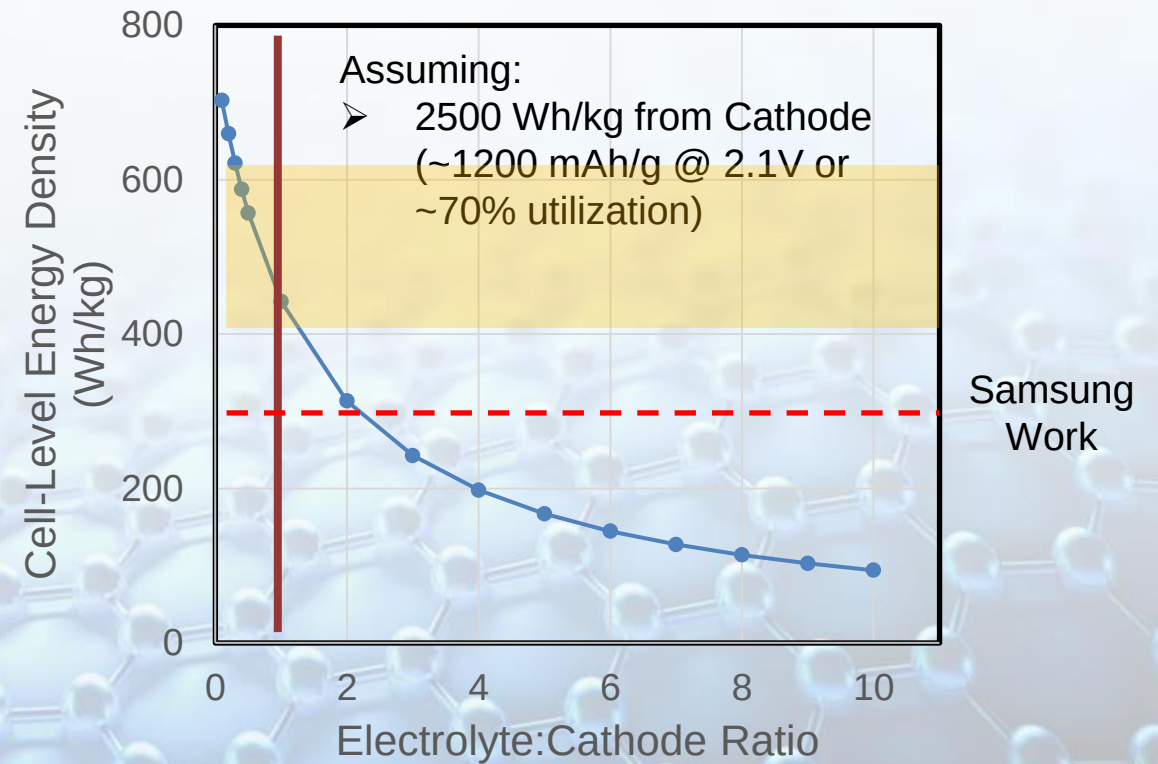
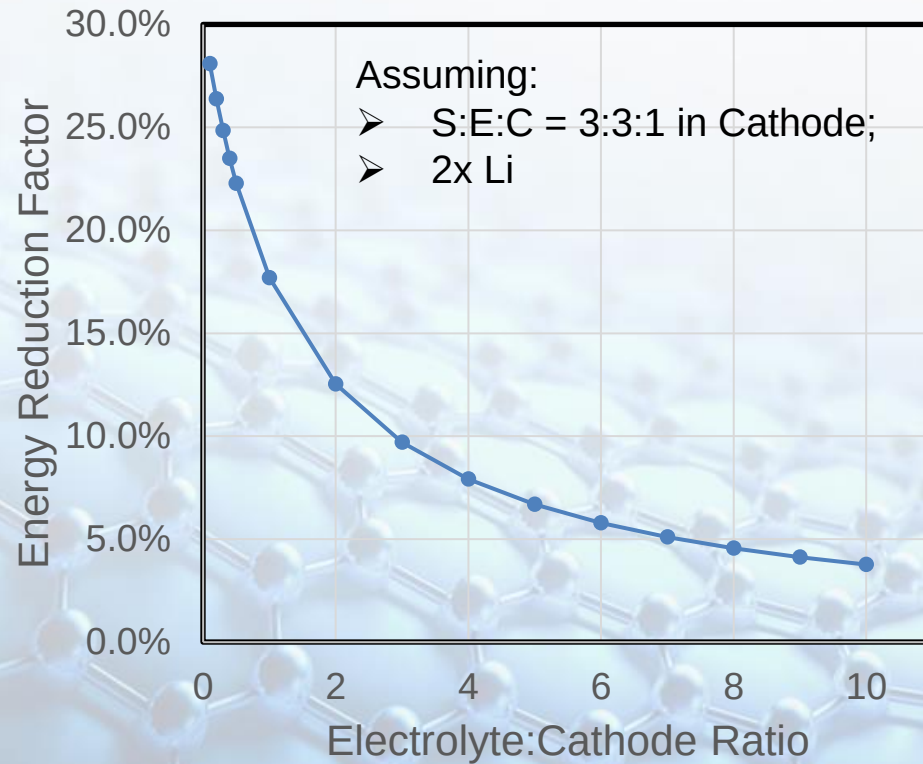
■ E ■ C ■ S ■ Li

E:Cathode = 2:5
586 Wh/kg



■ E ■ C ■ S ■ Li

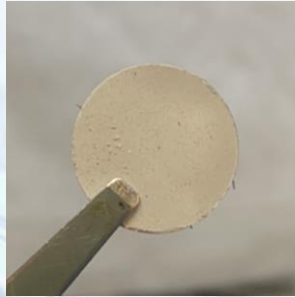
Reaching 500 Wh/kg at Cell Level with Dry Press



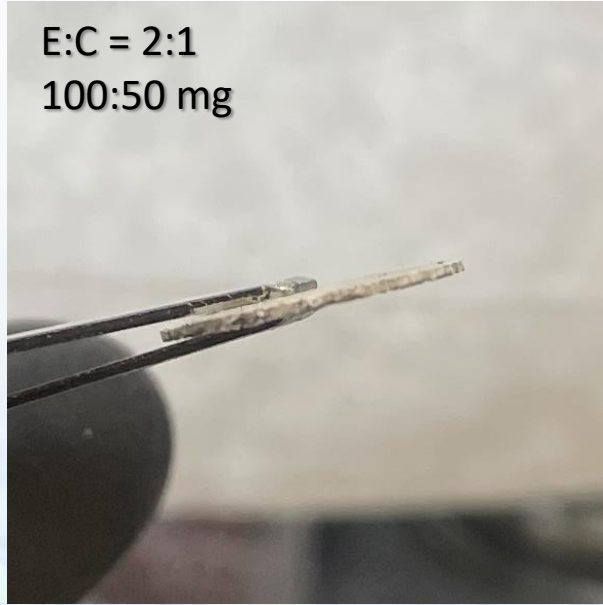
- Thinnest dry-press LPSC currently achieved experimentally: ~20 mg/cm²
- High mass loading can dilute the requirement of absolute electrolyte thickness and also help with the pack-level energy density
- To reach 500 Wh/kg, it would require, for example, a minimum S mass loading of 8.6 mg/cm² @ E:Cathode = 1:1
- Higher mass loading would lead to lower rate and utilization

Dry Pressed Cell Components

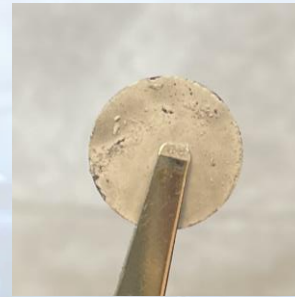
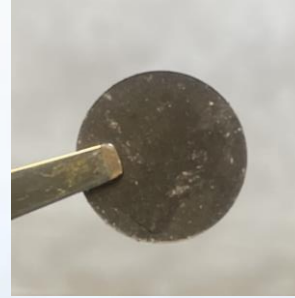
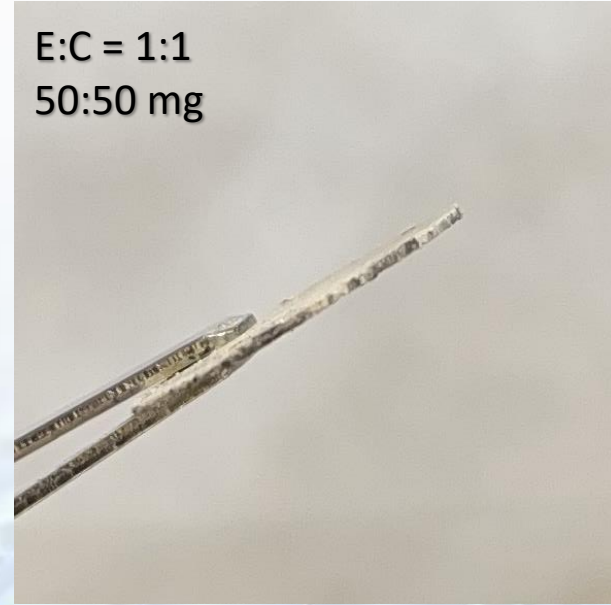
E:C = 4:1
200:50 mg



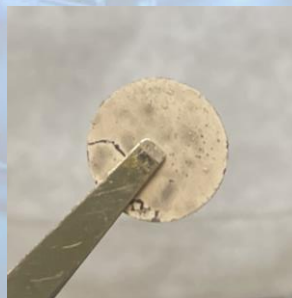
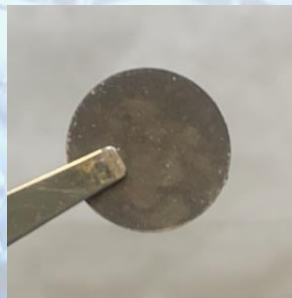
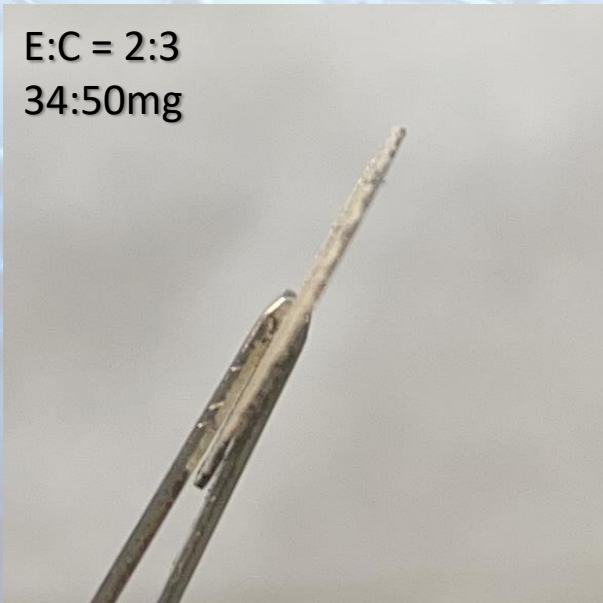
E:C = 2:1
100:50 mg



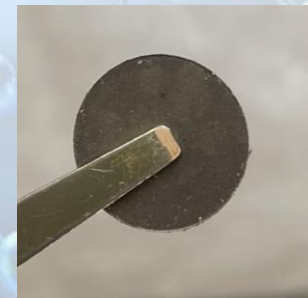
E:C = 1:1
50:50 mg



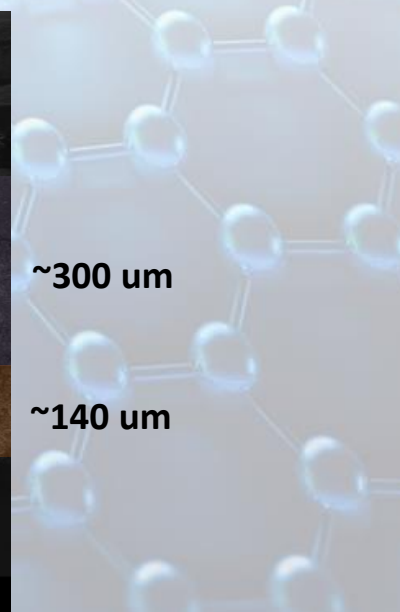
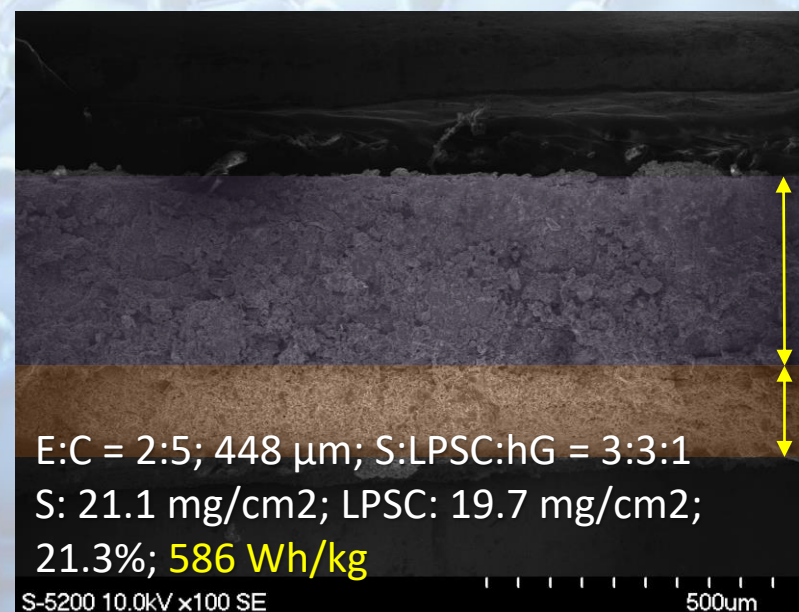
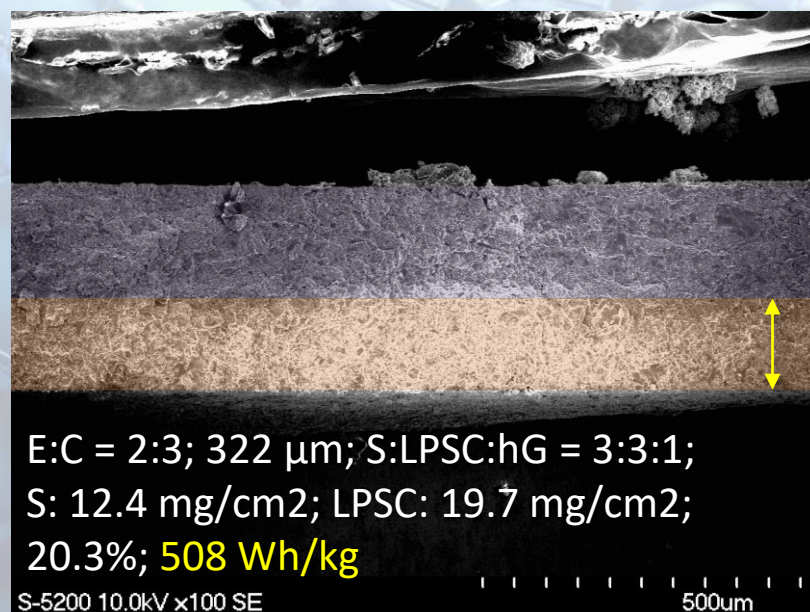
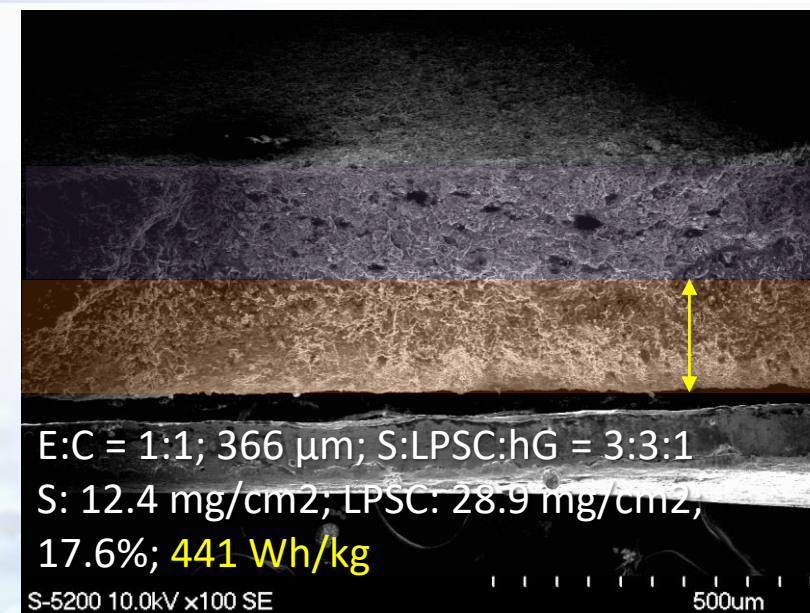
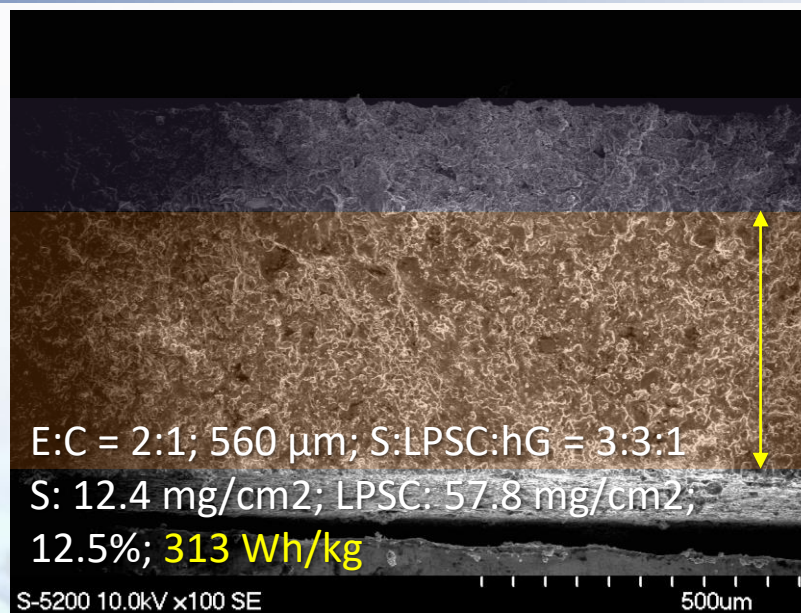
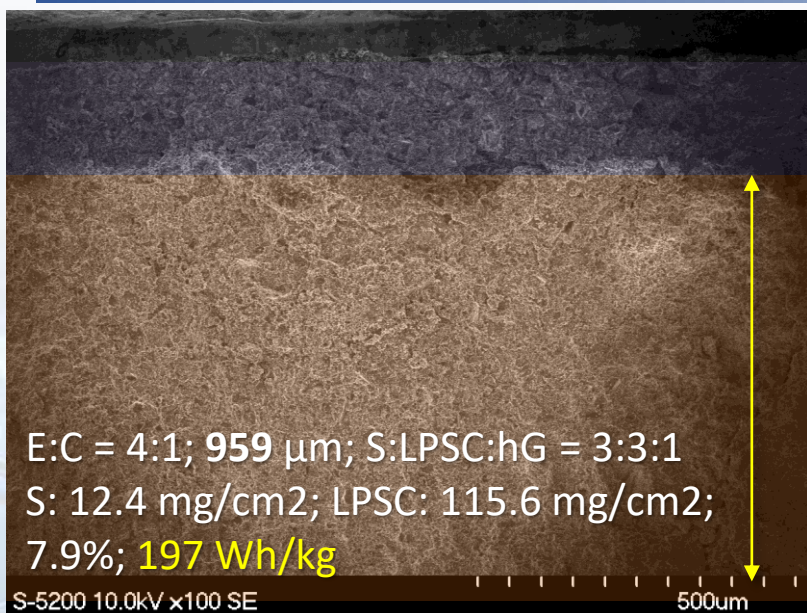
E:C = 2:3
34:50mg



E:C = 2:5
34:85mg



Dry Pressed Solid-State Cells



Feasibility Summary

- **Key parameters to achieve desirable interfaces and interphases**
 - Improving Li-S solid state cell performance is a multi-faceted challenge;
 - Cathode composition optimization is a critical independent task, however there are equally critical challenges associated with anodes and solid electrolytes.
- **Holey graphene as an advantageous carbon additive for dry-pressed solid-state S cathodes**
 - Holey graphene exhibited much better performance than carbon black as the scaffold carbon
- **Toward 500 Wh/kg**
 - It is possible to achieve 500 Wh/kg with dry-press despite fabrication challenges;
 - Reducing electrolyte layer thickness and improving S loading may be simultaneously advanced to achieve 500 Wh/kg.