All-Solid-State Li-Batteries for Transformational Energy Storage

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Engineering Battery Safety and Reliability

Conventional liquid/polymer electrolytes are flammable

Charred Cells

Charred Boeing 787 Li-battery

Undamaged photo:
-Note 8 Cells and
- battery management Circuitry
-not water cooled

Hoverboard battery fire

Samsung battery fire

Requiring additional system complexity and mass

Tesla battery pack teardown

and still no guarantee

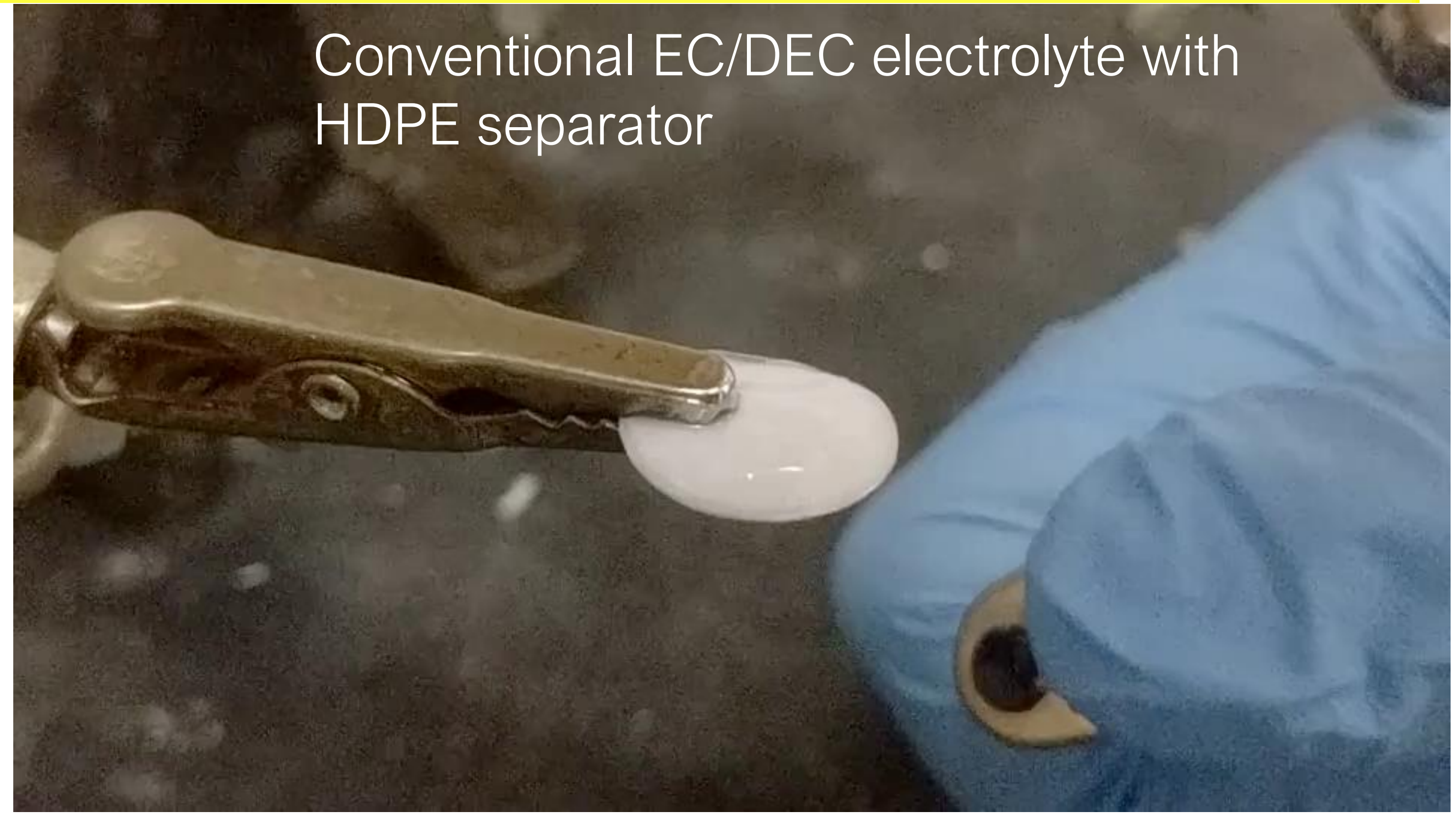
Engineering Battery Safety and Reliability

Conventional liquid/polymer electrolytes are flammable

See CBS News video at:
http://www.ionstoragesystems.com


CBS THIS MORNING
CBS NEWS / November 3, 2016, 7:55 AM

Are scientists on the brink of creating a non-combustible battery?



Ceramic electrolytes are Non-flammable

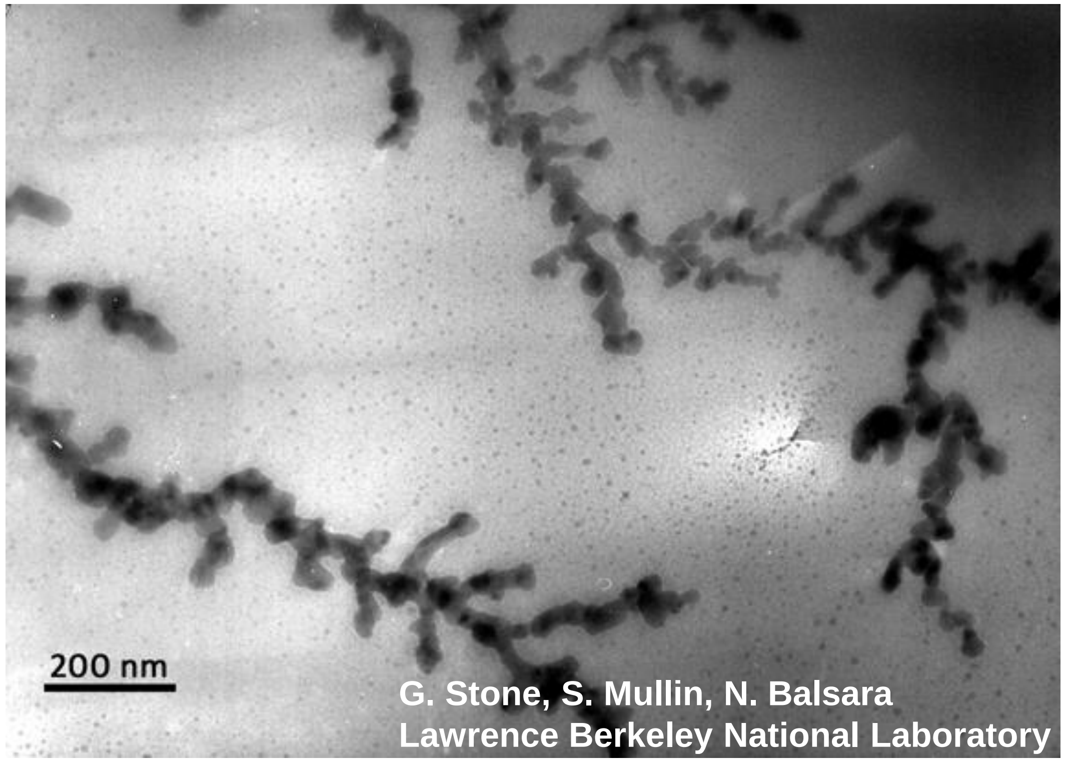
- Negating/reducing thermal control requirements

Increased Energy Density with Li-Metal Anode

Li-metal anodes have 10X the theoretical specific capacity of Li-carbon anodes (3860 mAh/g vs 372 mAh/g)

Conventional liquid/polymer electrolytes are soft and therefore have Li-dendrite problem

They also have electrochemical stability issues with Li-Metal



Ceramic electrolytes are hard, so if sufficiently dense can block Li-dendrite propagation

Some ceramic electrolytes (e.g., Garnet) are also chemically/electrochemically stable with Li-Metal

Li^+ Conducting Garnets

Garnet electrolytes also have comparable RT conductivity (~1 mS/cm) to organic electrolytes

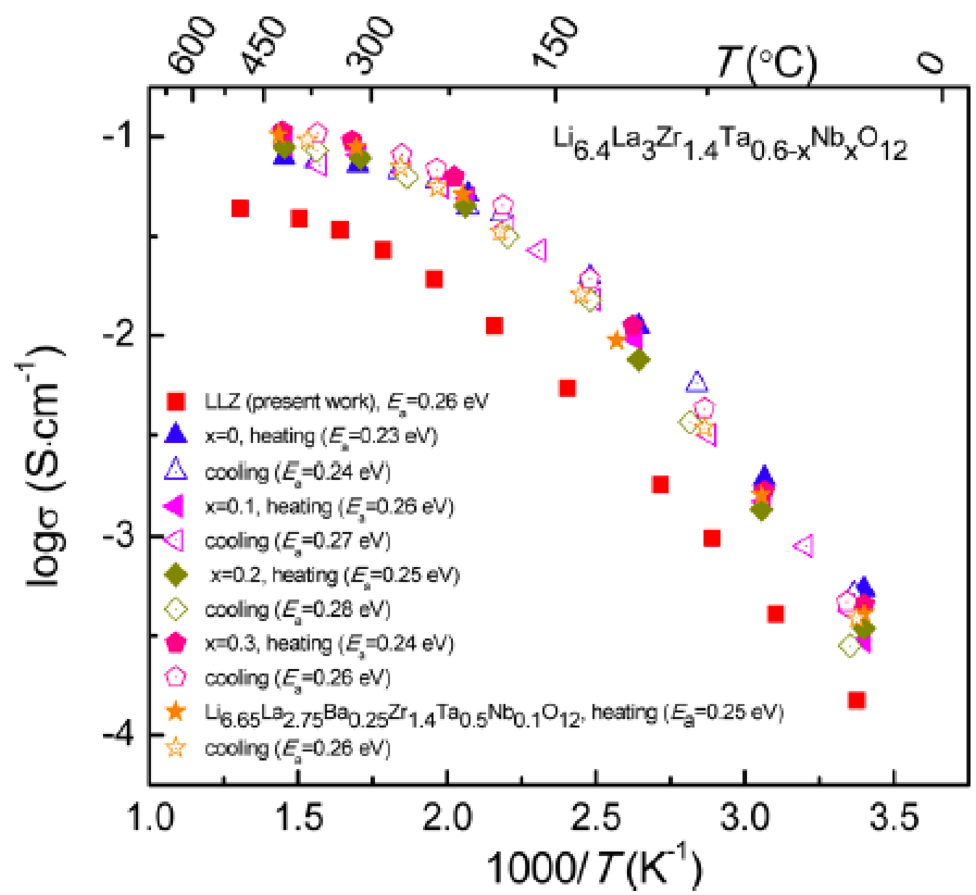
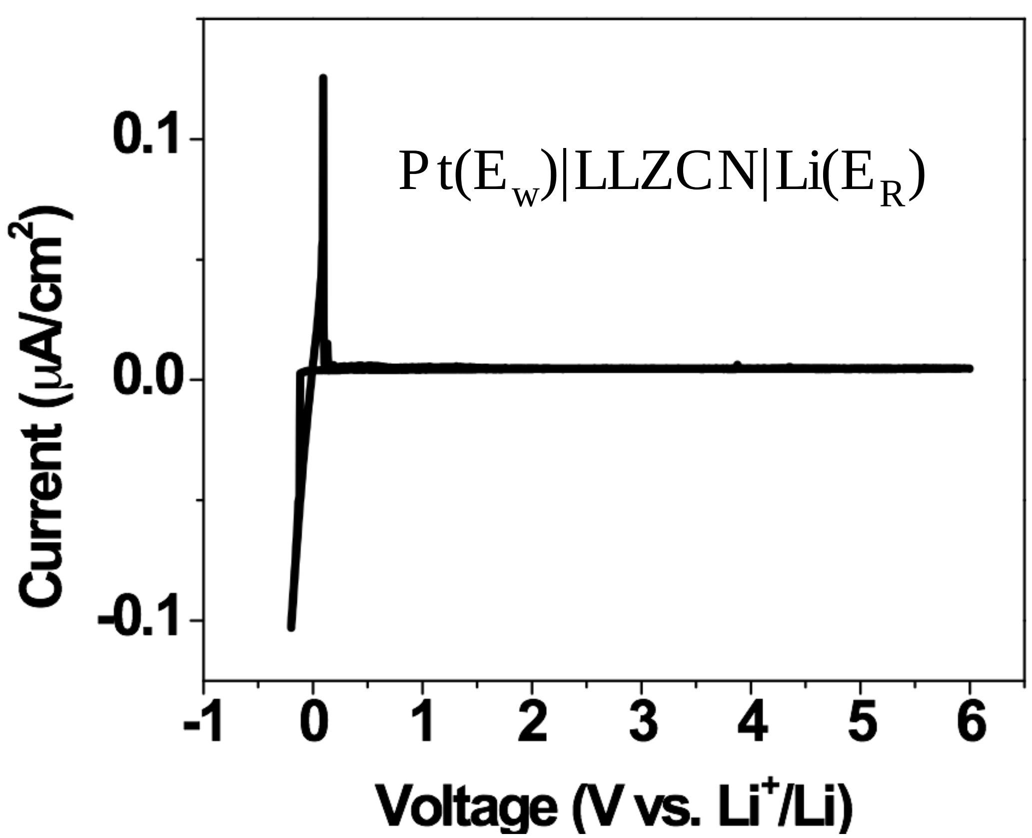


Figure 5. Arrhenius plots for Li-ion conductivity of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ ($x = 0$), $Li_{6.4}La_3Zr_{1.4}Ta_{0.5}Nb_{0.1}O_{12}$ ($x = 0.1$), $Li_{6.4}La_3Zr_{1.4}Ta_{0.4}Nb_{0.2}O_{12}$, $Li_{6.4}La_3Zr_{1.4}Ta_{0.3}Nb_{0.3}O_{12}$, $Li_{6.65}La_{2.75}Ba_{0.25}Zr_{1.4}Ta_{0.5}Nb_{0.1}O_{12}$, and undoped $Li_7La_3Zr_2O_{12}$ (LLZ) prepared at 1150 °C.

Xia Tong,† Venkataraman Thangadurai,*,† and Eric D. Wachsman‡
Inorg. Chem. 2015, 54, 3600−3607



and much wider voltage stability window, from Li-metal to over ~6V

Overcoming Solid State Battery Limitations

So what is limiting successful development of solid-state garnet batteries?

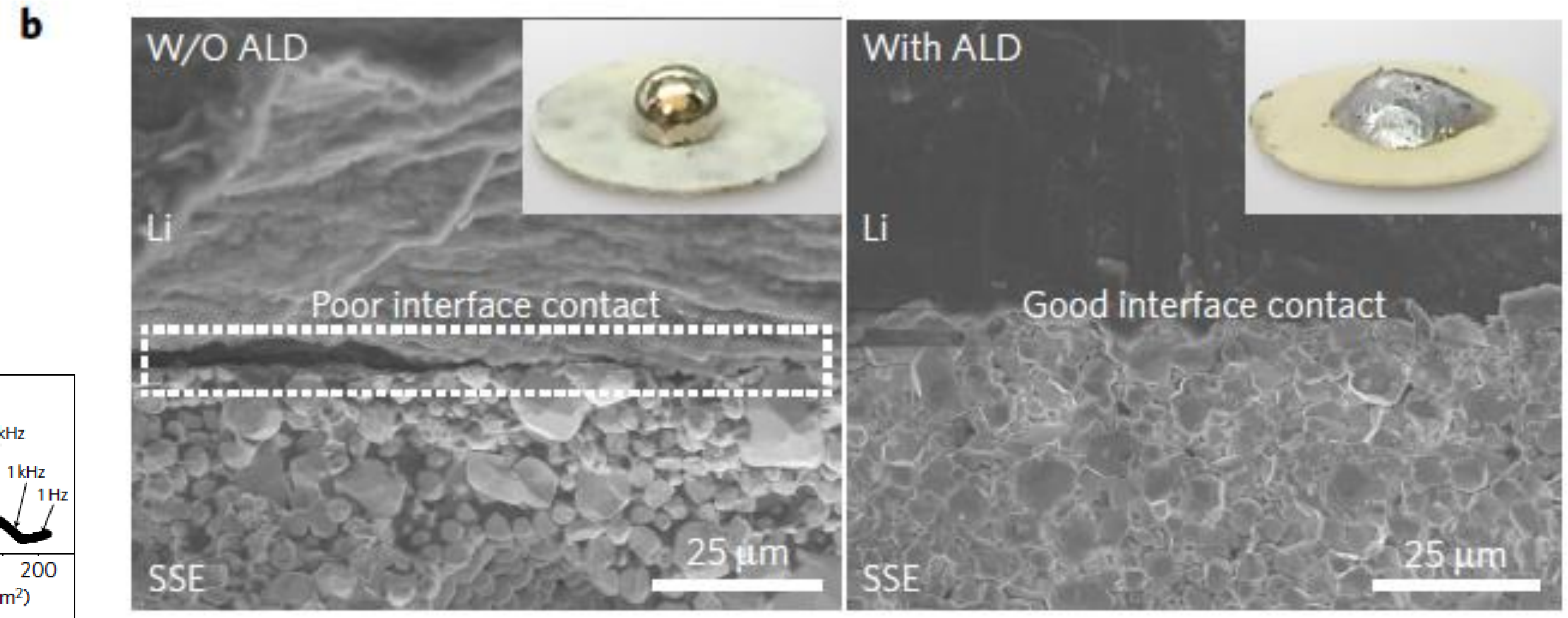
- High specific solid-solid interfacial impedance
- Typical planar geometries have low electrolyte/electrode contact areas
- Typical sintered electrolyte pellets (to obtain sufficient density) are thick and thus have high ASR

Overcoming Li-Garnet Interface Impedance

nature materials | ARTICLES
PUBLISHED ONLINE: 19 DECEMBER 2016 | DOI: 10.1038/NMAT4821

Negating interfacial impedance in garnet-based solid-state Li metal batteries

Xiaogang Han[1†], Yunhui Gong[1†], Kun (Kelvin) Fu[1†], Xingfeng He[1], Gregory T. Hitz[1], Jiaqi Dai[1], Alex Pearse[1,2], Boyang Liu[1], Howard Wang[1], Gary Rubloff[1,2], Yifei Mo[1], Venkataraman Thangadurai[3], Eric D. Wachsman[1]* and Liangbing Hu[1]*



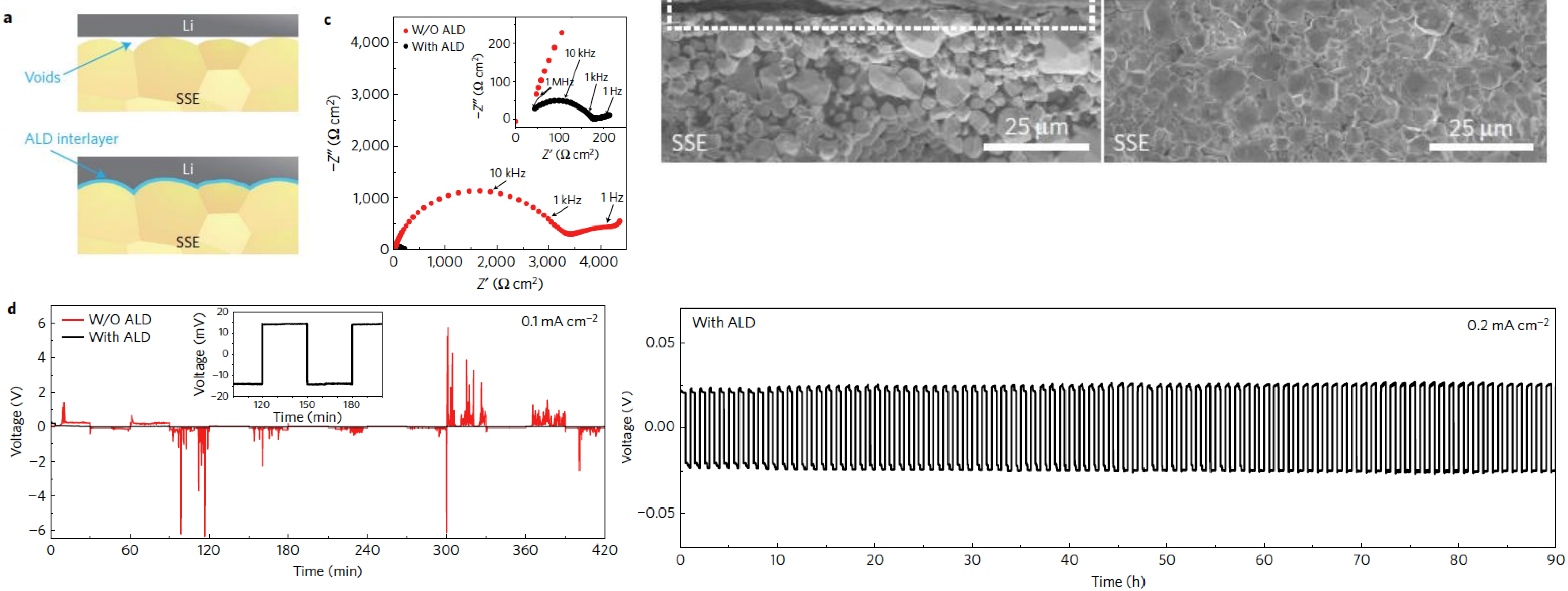


Table 1 | Electrochemical impedance and d.c. ASR for Li/LLCZN/Li cells with and without ALD coating on both sides of garnet SSE.

Li/LLCZN/Li symmetric cell	Bulk/high-frequency ASR (Ω cm^2)	GB/interface ASR (Ω cm^2)	Total EIS ASR (Bulk+GB/interface) (Ω cm^2)	Interfacial EIS ASR* (Ω cm^2)	d.c. ASR (Ω cm^2)	Interfacial d.c. ASR* (Ω cm^2)
W/O ALD	28	3,500	3,528	1,710	N/A	N/A
ALD	26	150	176	34	110	1

*Interfacial EIS and d.c. ASR calculated by subtracting total garnet ASR (108 Ω cm^2) from total EIS and d.c. ASR, respectively, and dividing by interfacial area. GB, grain boundary. Garnet ASR (108 Ω cm^2) was obtained from the EIS garnet conductivity measurement of the Au/garnet/Au symmetric cells.

- Achieved lowest interfacial resistance **~1 Ohm×cm^2**

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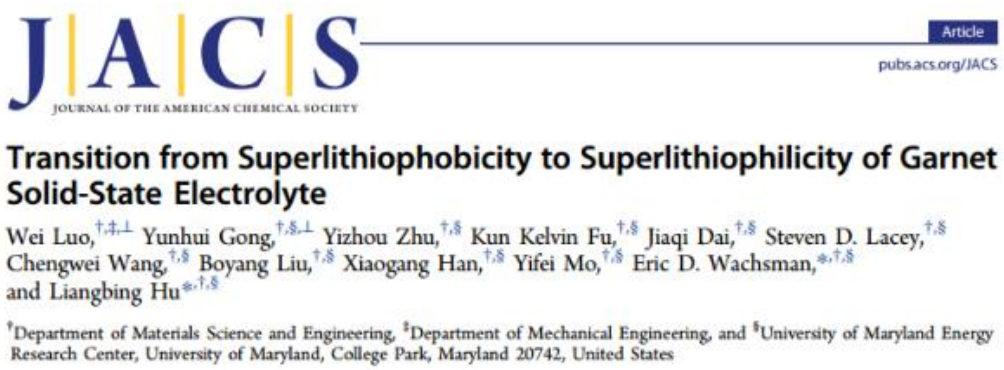
Overcoming Li-Garnet Interface Impedance


JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

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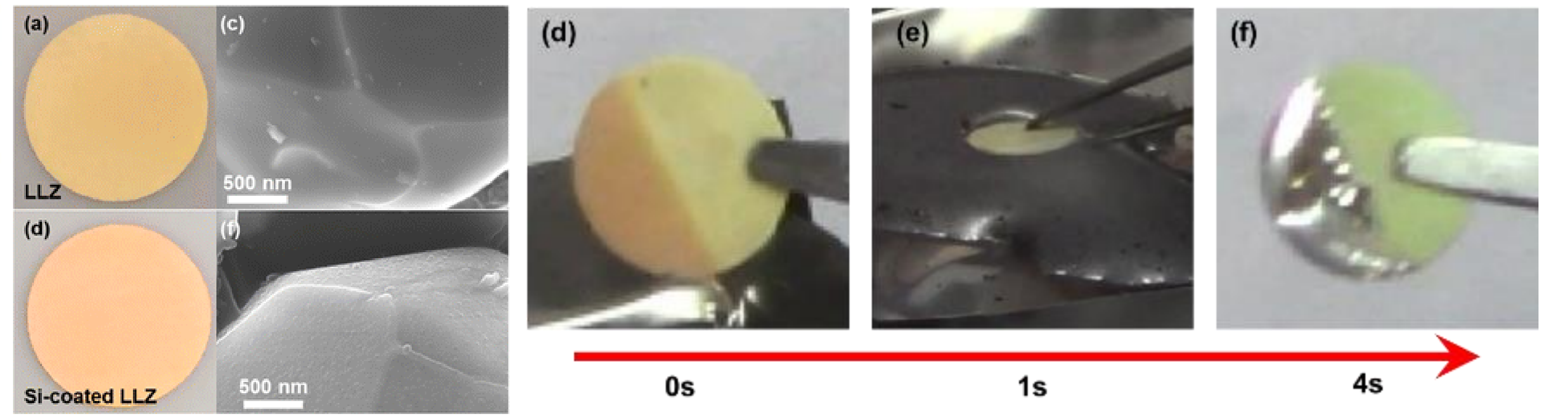
Transition from Superlithiophobicity to Superlithiophilicity of Garnet Solid-State Electrolyte

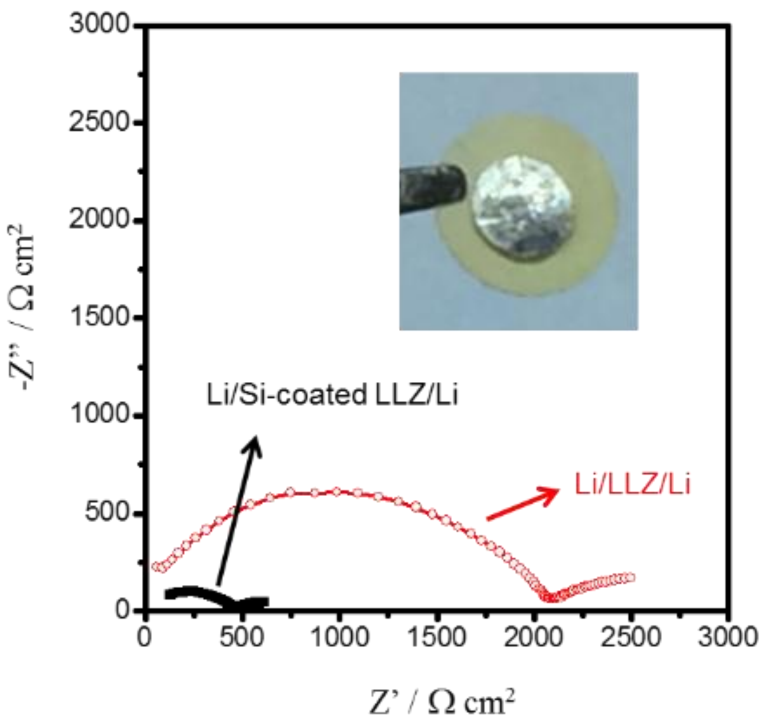
Wei Luo,[†,‡,⊥] Yunhui Gong,[†,§,⊥] Yizhou Zhu,[†,§] Kun Kelvin Fu,[†,§] Jiaqi Dai,[†,§] Steven D. Lacey,[†,§] Chengwei Wang,[†,§] Boyang Liu,[†,§] Xiaogang Han,[†,§] Yifei Mo,[†,§] Eric D. Wachsman,[*,†,§] and Liangbing Hu[*,†,§]

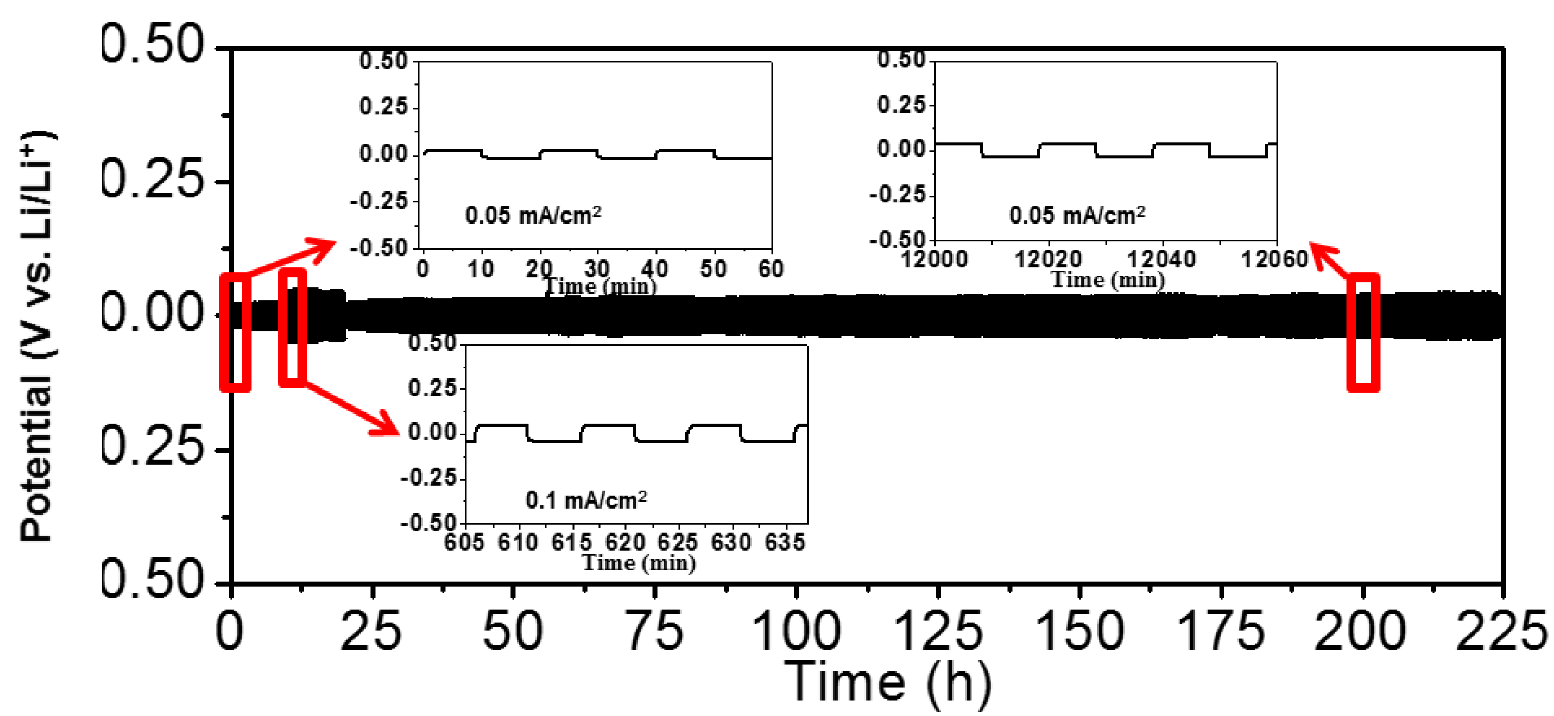
[†]Department of Materials Science and Engineering, [‡]Department of Mechanical Engineering, and [§]University of Maryland Energy Research Center, University of Maryland, College Park, Maryland 20742, United States



Decreased interfacial resistance

Li metal coating on garnet with Si





- Si interface can change garnet SSE surface from lithiophobic to lithiophilic;
- Si interface reduced the interfacial ASR of Li/LLZO to **127 Ohm×cm²**.

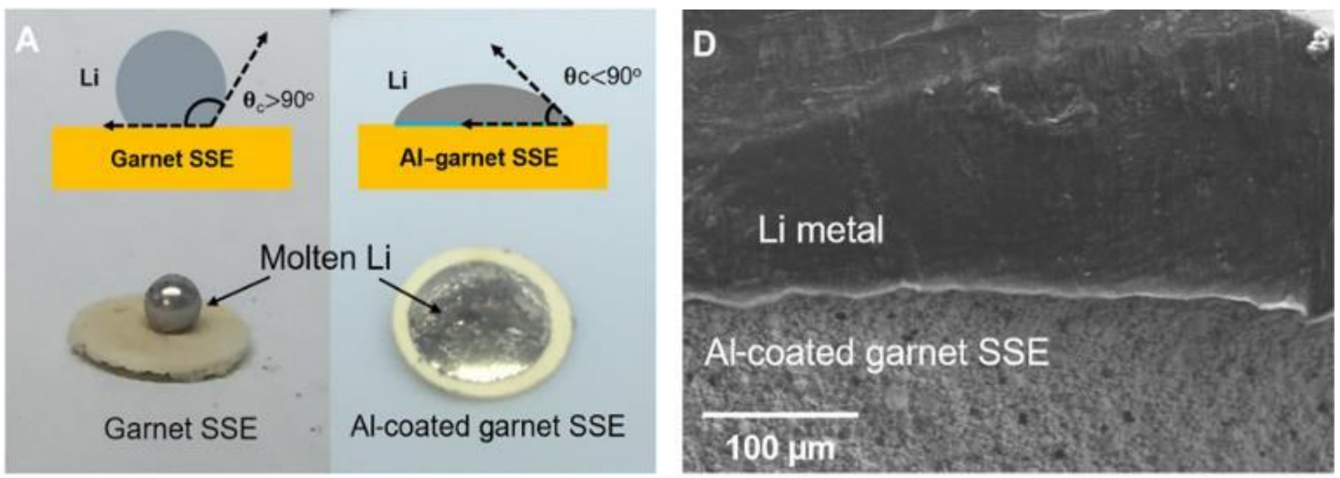
Overcoming Li-Garnet Interface Impedance

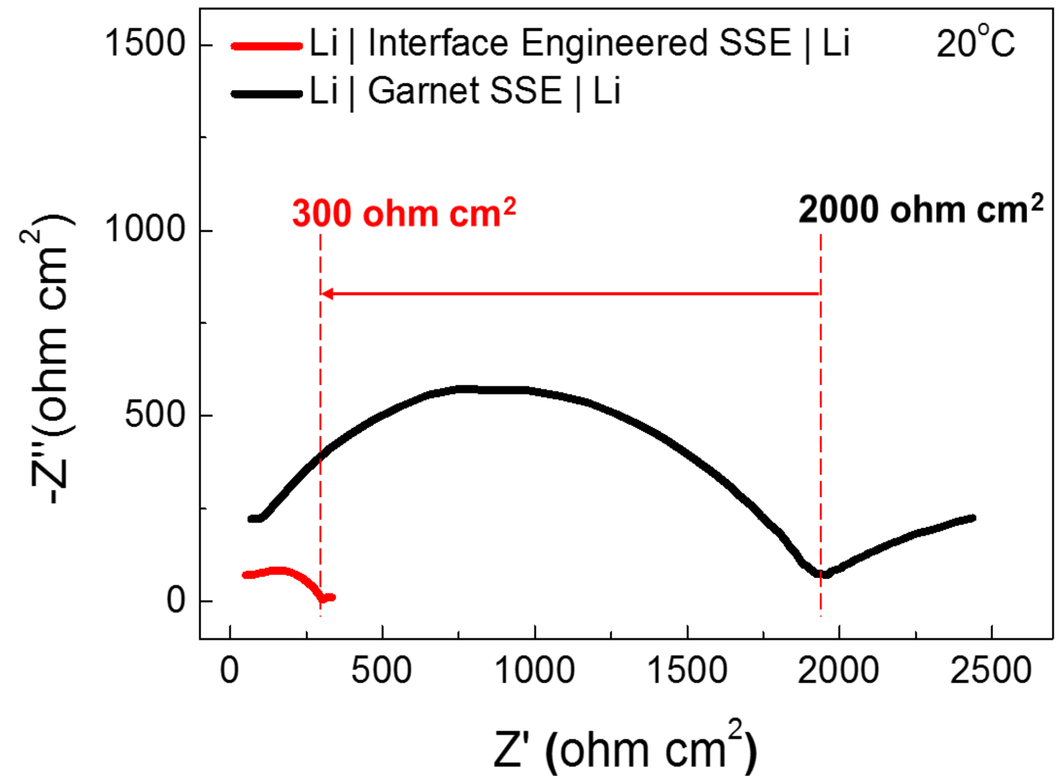
SCIENCE ADVANCES | RESEARCH ARTICLE

APPLIED SCIENCES AND ENGINEERING

Toward garnet electrolyte–based Li metal batteries: An ultrathin, highly effective, artificial solid-state electrolyte/metallic Li interface

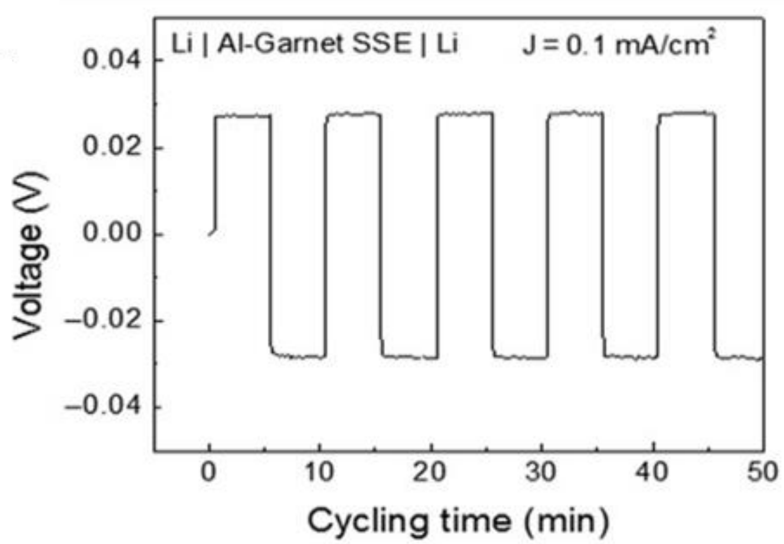
Kun (Kelvin) Fu,[1,2]* Yunhui Gong,[1,2]* Boyang Liu,[2] Yizhou Zhu,[2] Shaomao Xu,[1,2] Yonggang Yao,[2] Wei Luo,[2] Chengwei Wang,[1,2] Steven D. Lacey,[2] Jiaqi Dai,[2] Yanan Chen,[2] Yifei Mo,[1,2] Eric Wachsman,[1,2†] Liangbing Hu[1,2†]

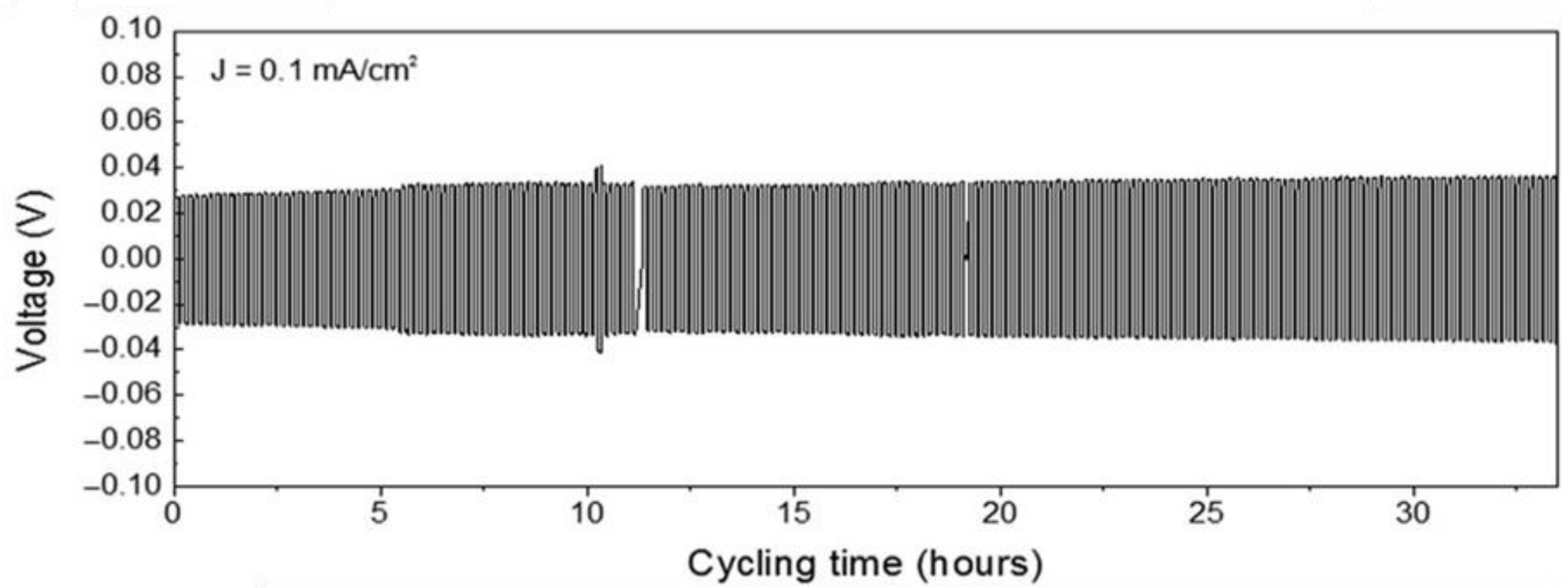




Cycling of Li metal symmetric cell

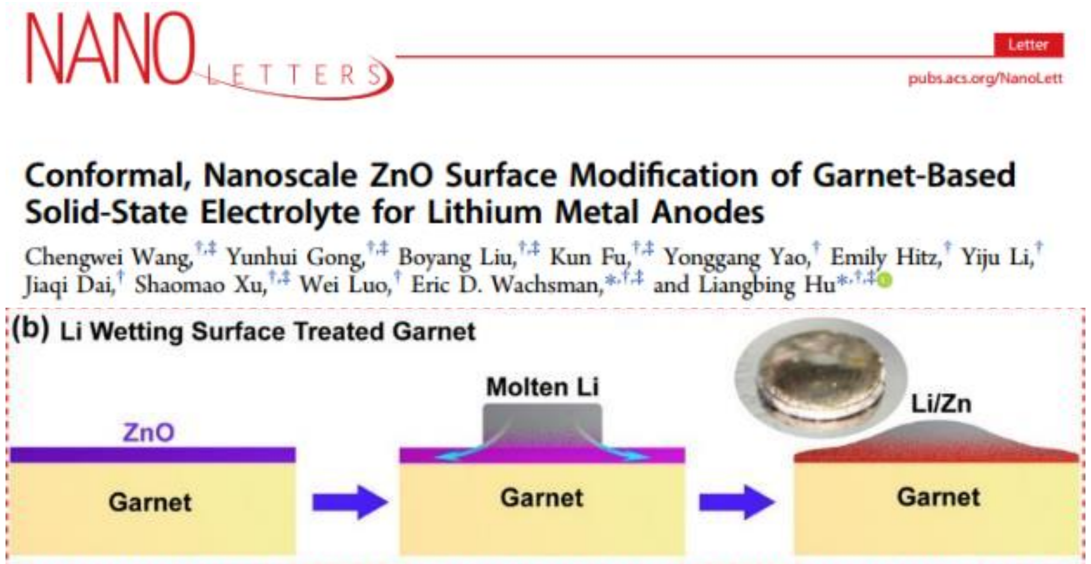
Decreased interfacial resistance

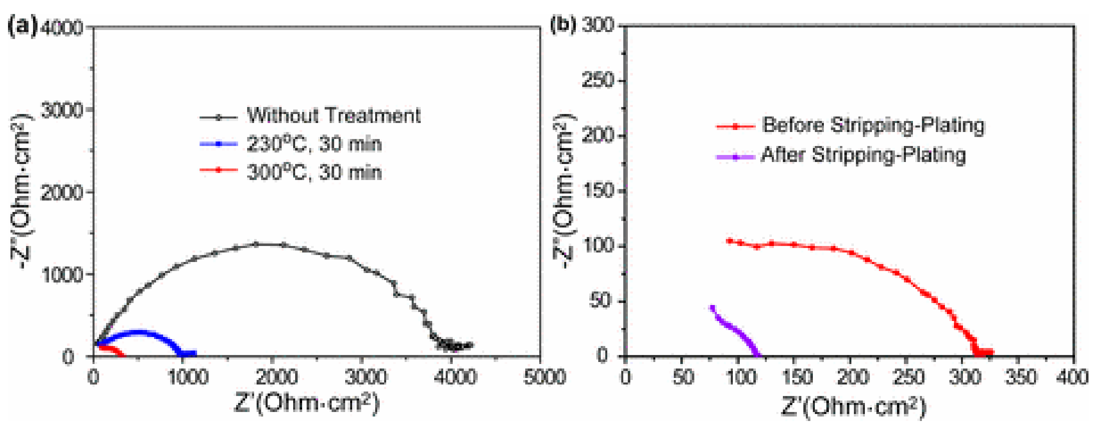




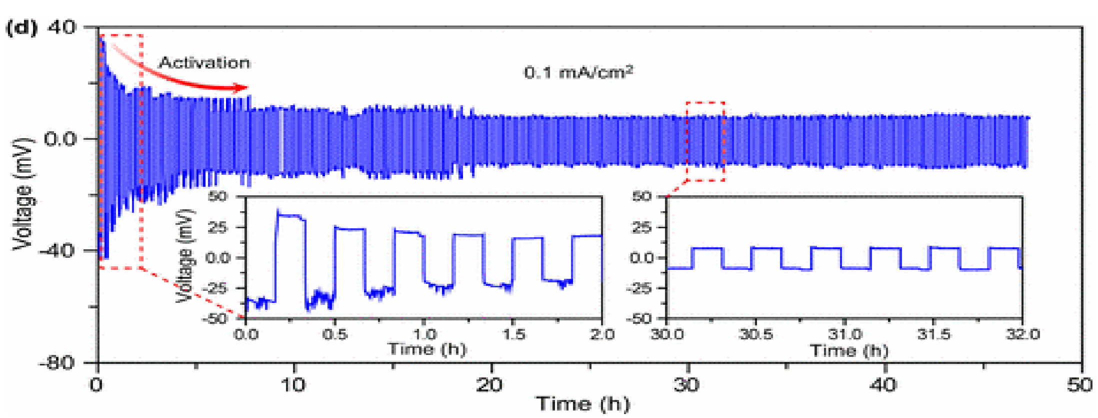
- Interfacial resistance with Al interface: **75 Ohm×cm²;**
- Stable interface with Li metal cycling.

Overcoming Li-Garnet Interface Impedance

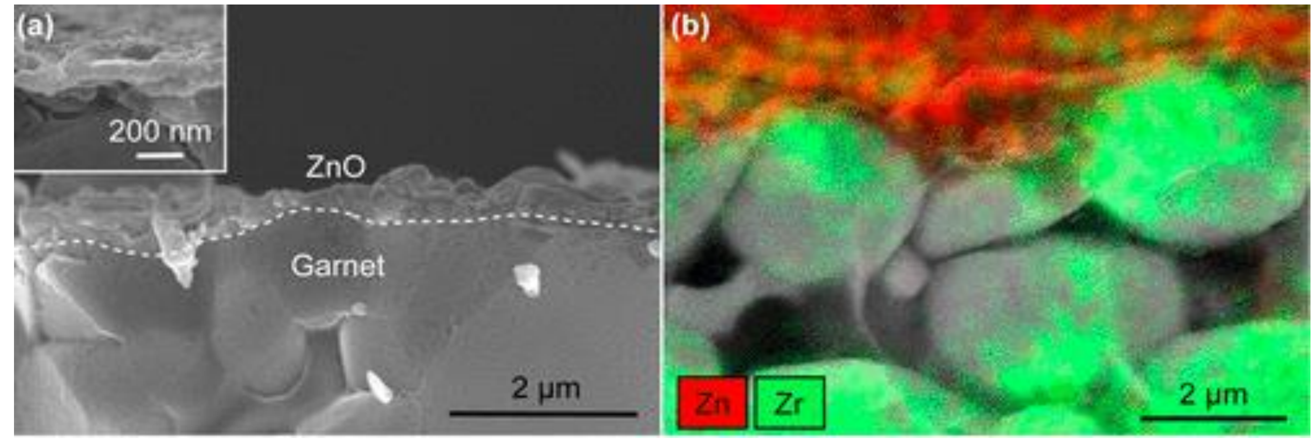




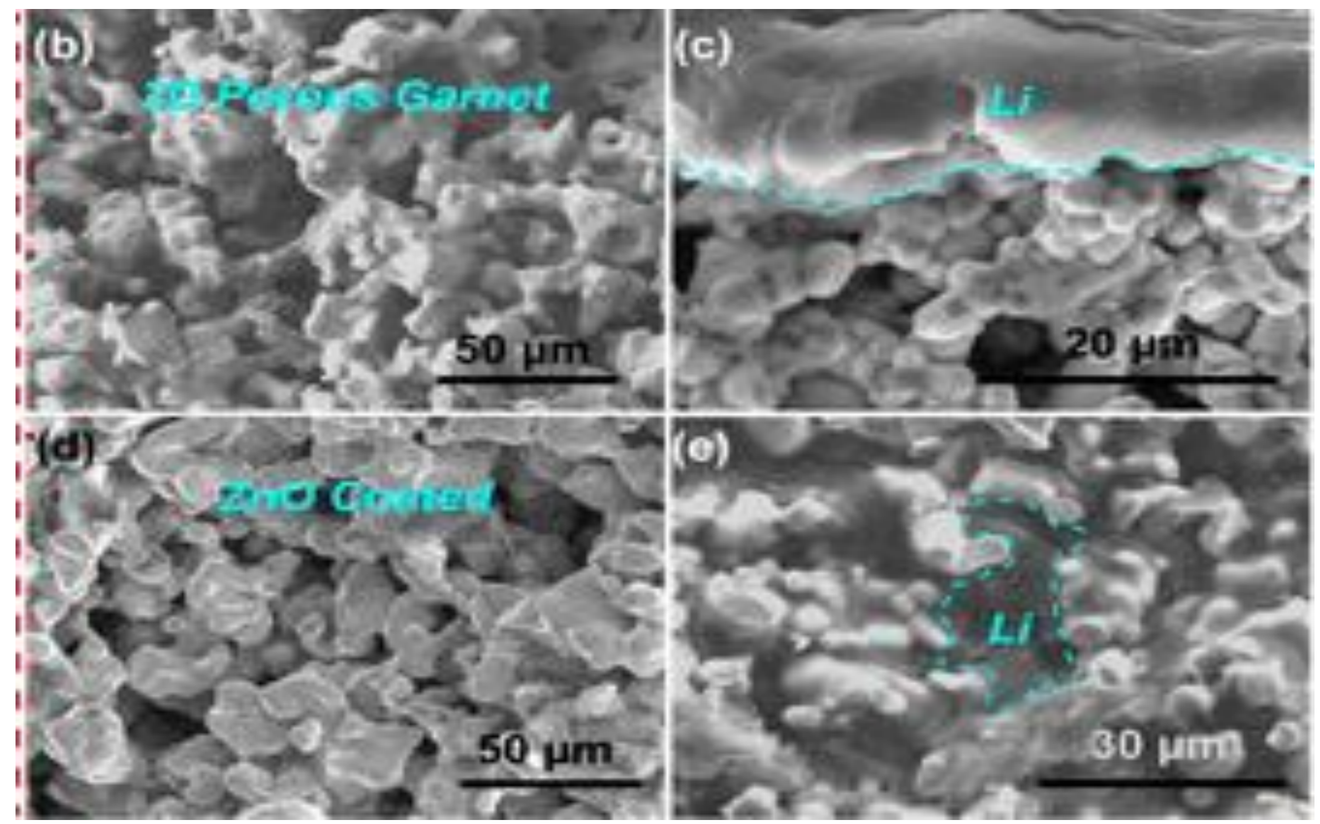
Impedance of Li/garnet/Li with ZnO interface.



Cycling of Li/garnet/Li with ZnO interface.



Li/garnet with ZnO interface

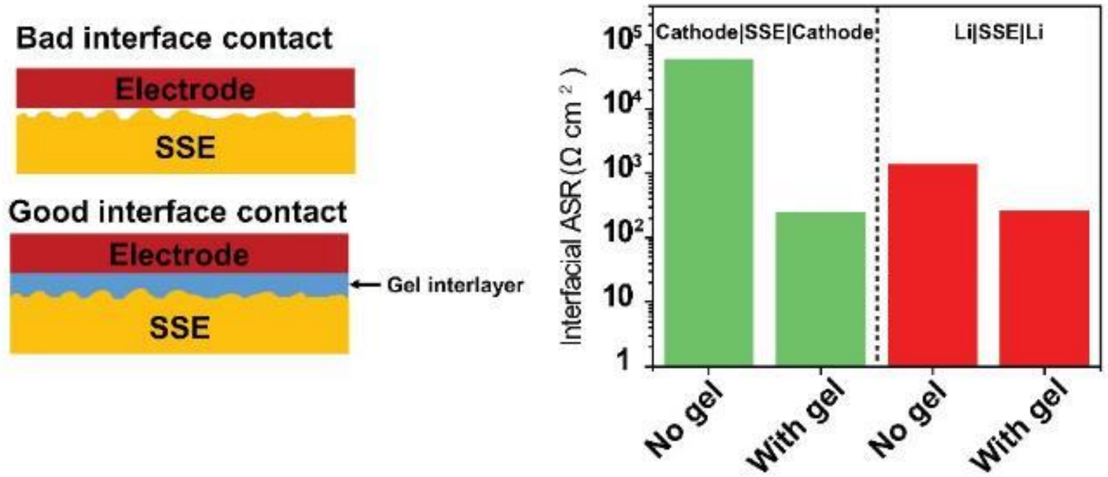


Li/porous garnet with ZnO interface

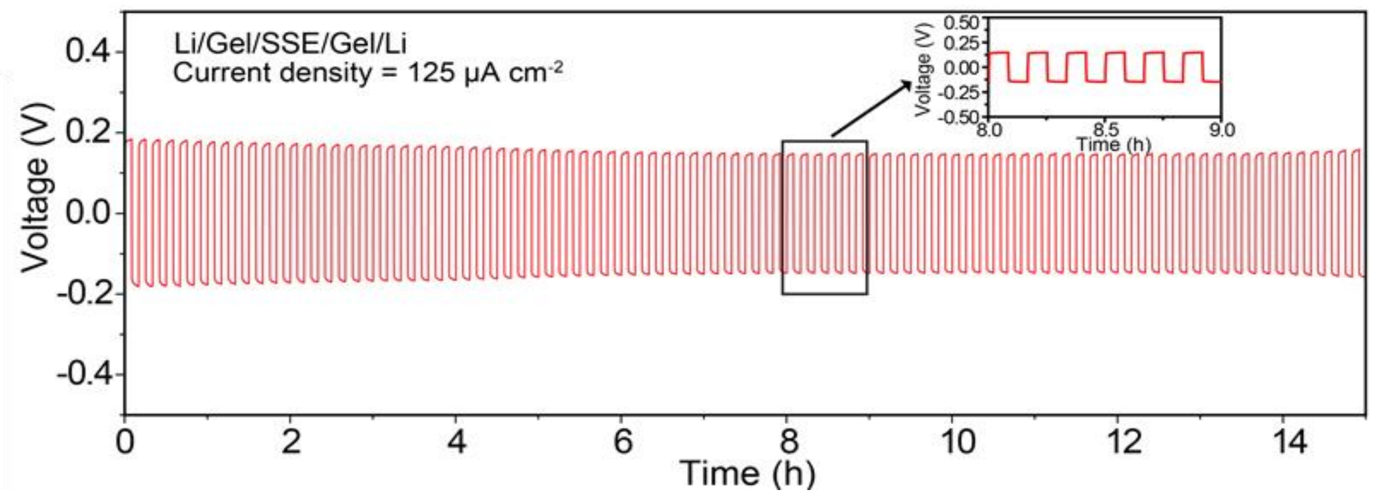
- ZnO interface reduced Li/garnet interfacial resistance to **20 Ohm×cm²**
- Li metal can infiltrate into porous garnet structure

Overcoming Li-Garnet-Cathode Interface Impedance

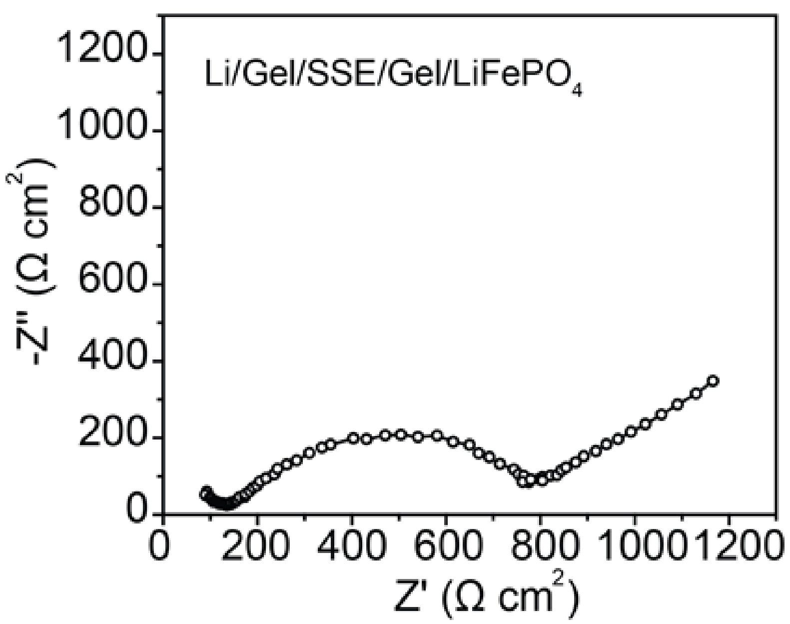
Interface resistance decrease



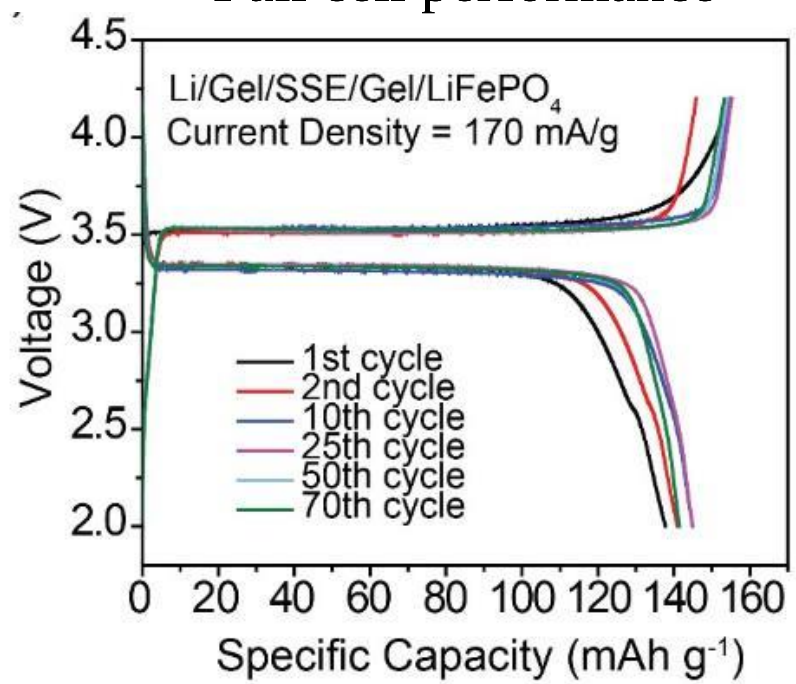
Li metal symmetric cell cycling



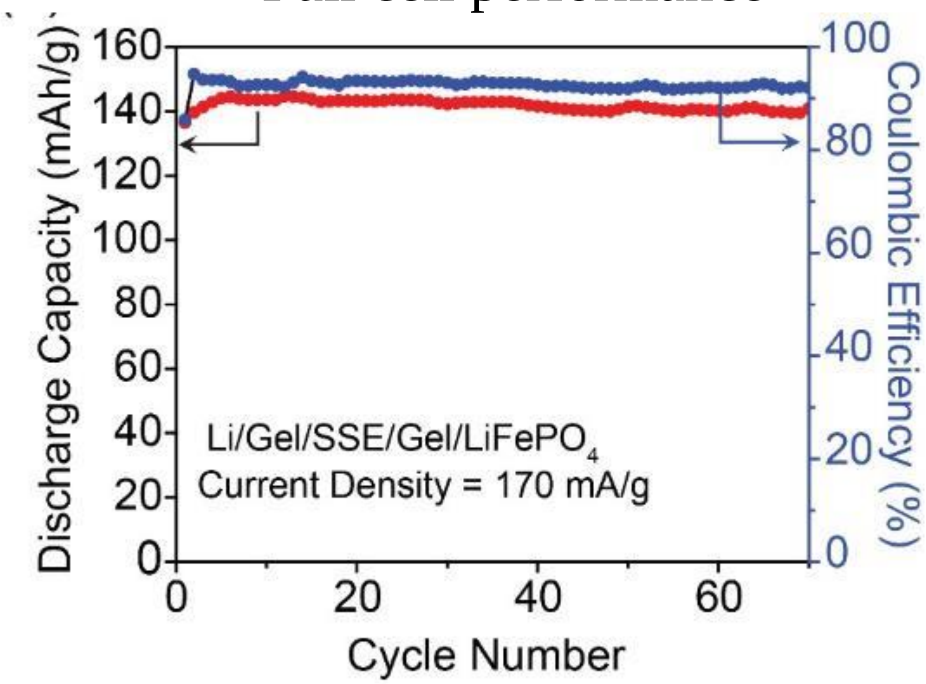
Full cell impedance



Full cell performance



Full cell performance



- Li/garnet interfacial resistance **214 Ohm×cm²**
- Cathode/garnet interfacial resistance **248 Ohm×cm²**
- Stable interface during battery cycling.

*Liu, B.; Gong, Y.; Fu, K.; Han, X.; Yao, Y.; Pastel, G.; Yang, C.; Xie, Hua.; E. D. Wachsman.; L, Hu. Garnet Solid Electrolyte Protected Li-Metal Batteries Under minor revision of *ACS Applied Materials & Interfaces*

Overcoming Li-Garnet-Cathode Interface Impedances

Energy & Environmental Science

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

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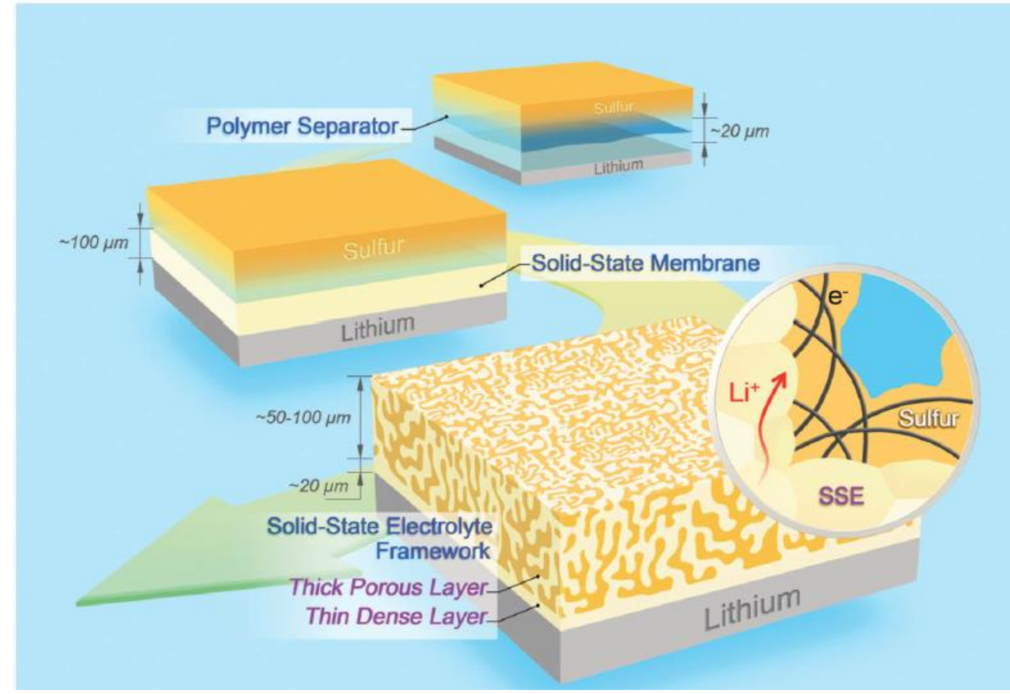
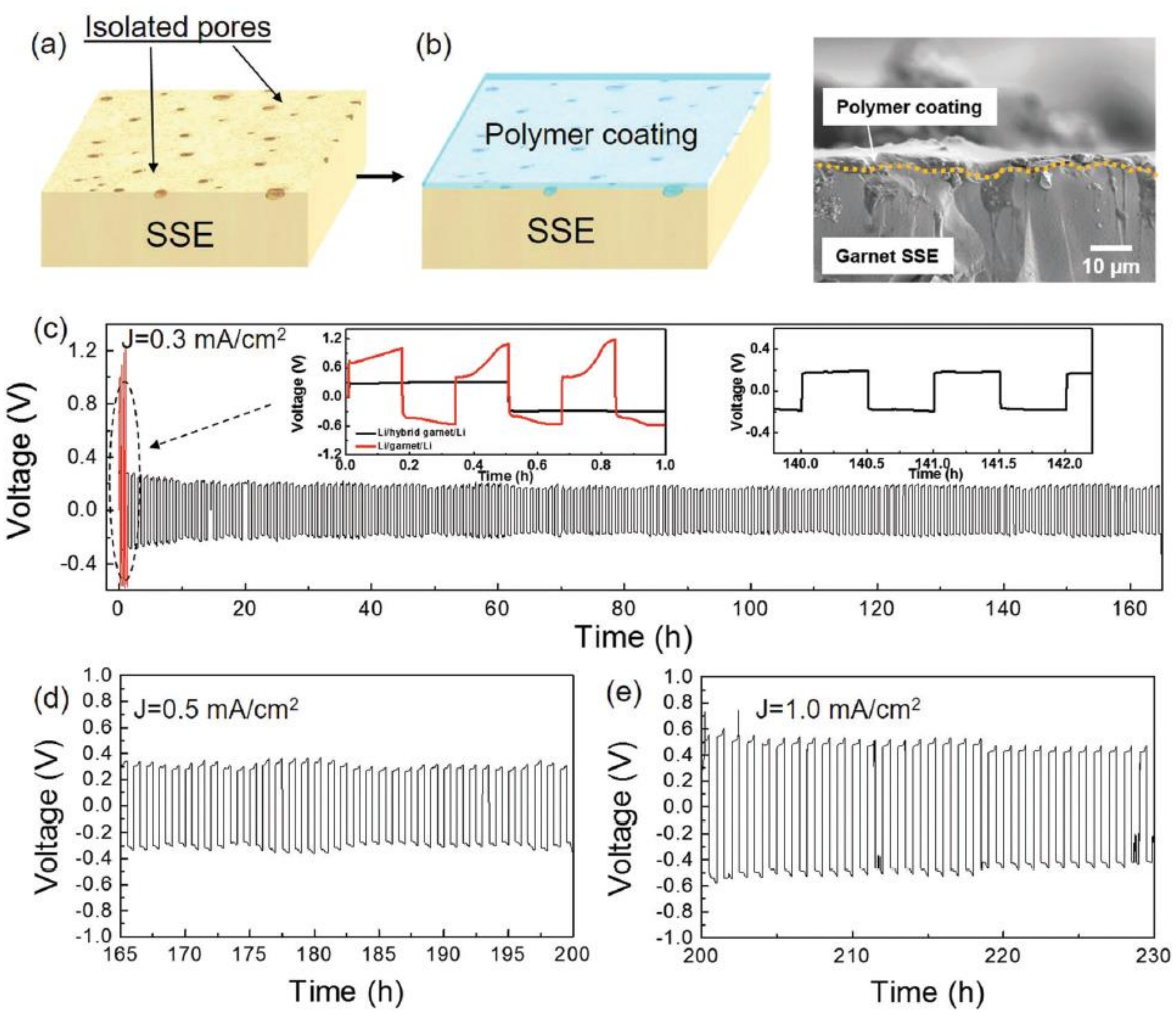
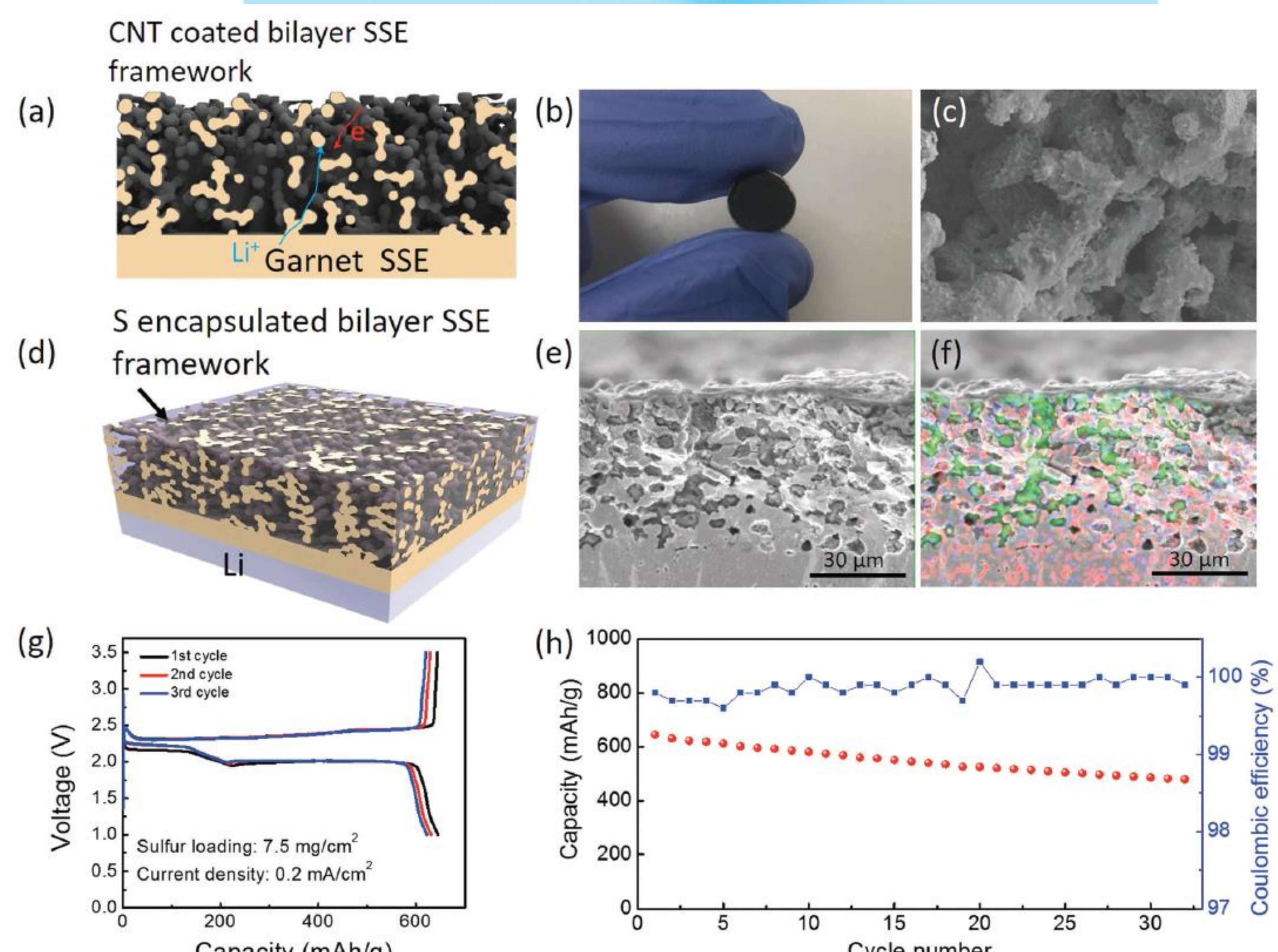
Three-dimensional bilayer garnet solid electrolyte based high energy density lithium metal–sulfur batteries†

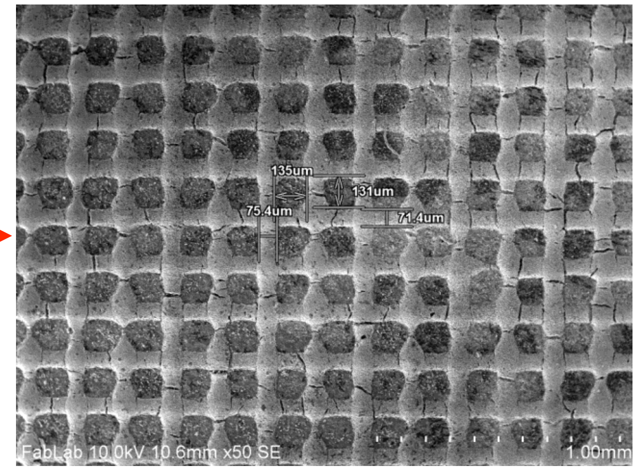
Kun (Kelvin) Fu,‡[ab] Yunhui Gong,‡[ab] Gregory T. Hitz,[ab] Dennis W. McOwen,[ab] Yiju Li,[b] Shaomao Xu,[ab] Yang Wen,[ab] Lei Zhang,[ab] Chengwei Wang,[ab] Glenn Pastel,[b] Jiaqi Dai,[b] Boyang Liu,[b] Hua Xie,[b] Yonggang Yao,[b] Eric D. Wachsman *[ab] and Liangbing Hu *[ab]

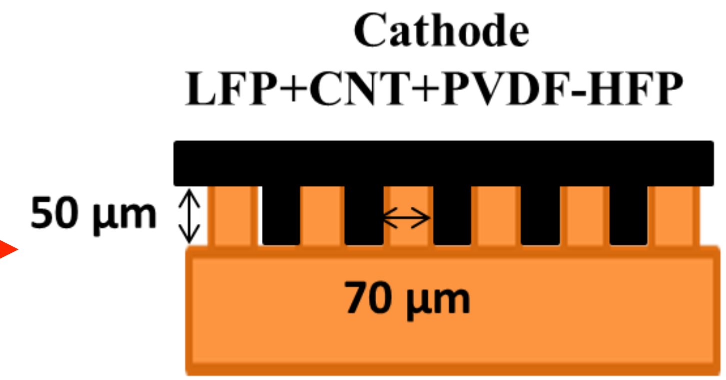




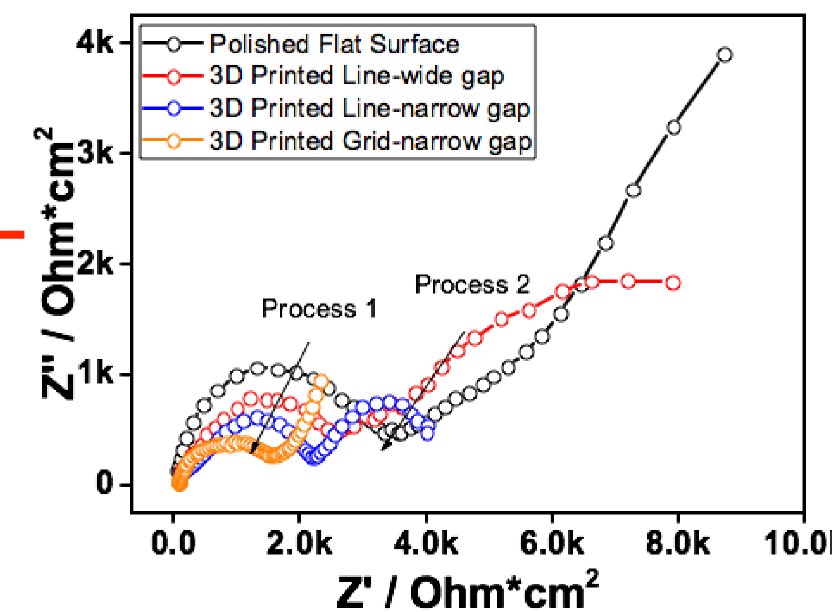


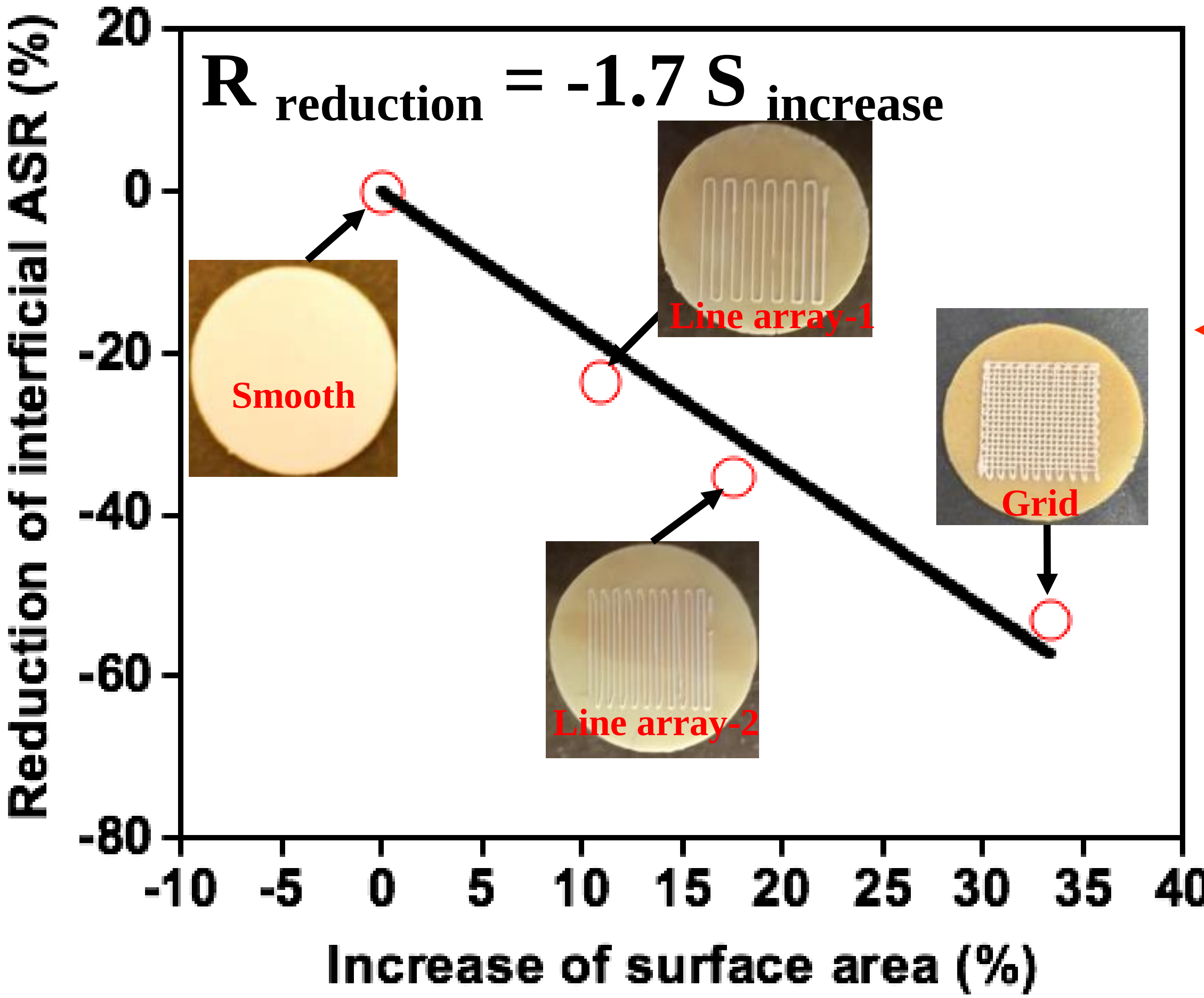
Effect of Solid-Solid Contact Area on Interfacial Impedance





3D printed architecture on garnet surface

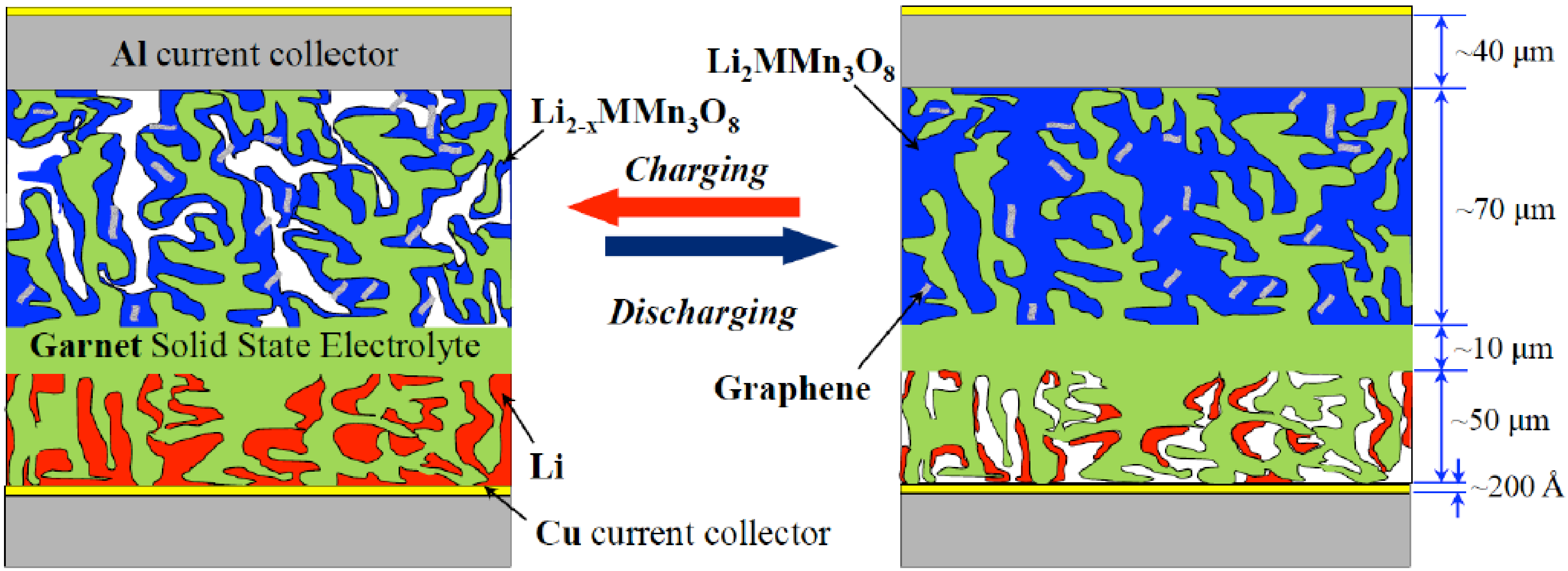




- 52% reduction in interfacial ASR by surface microstructure modification
- Interfacial ASR reduces ~2X increase in contact surface area

Solid State Li Battery (SSLiB)

Use SOFC approach to advance SSLiB's



Low-cost multi-layer ceramic processing developed for fabrication of thin SOFC electrolytes supported by high surface area porous electrodes

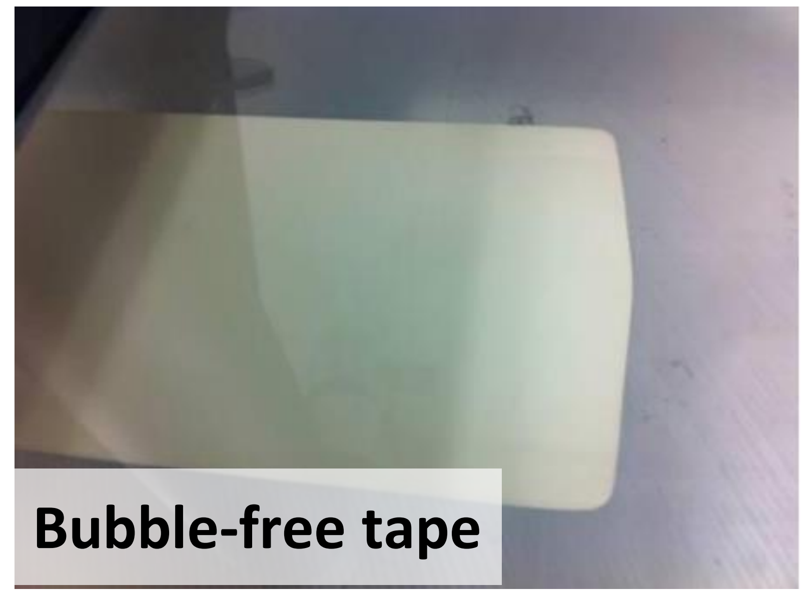
- Electrode support allows for thin ~10μm solid state electrolyte (SSE) fabrication
- Porous SSE scaffold allows use of high specific capacity Li-metal anode with no SEI
- Porous 3-D networked SSE scaffolds allow electrode materials to fill volume with a smaller charge transfer resistance and no electrode cycling fatigue
- Pore filling mechanism removes external dimensional changes with cycling and resulting mechanical issues

Solid State Li Battery (SSLiB)

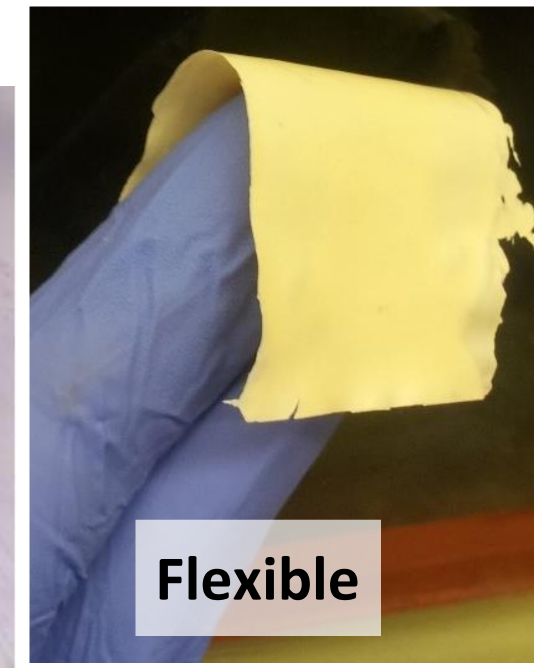
Use SOFC approach to advance SSLiB's

Based on commercially scalable tapecasting process

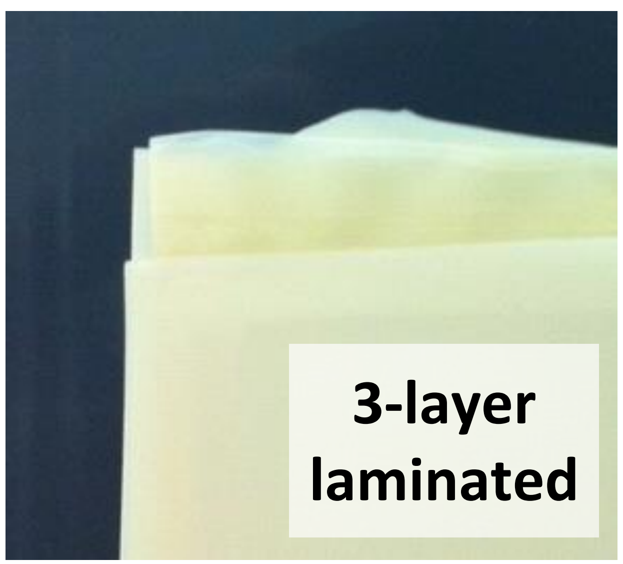
- Cast ~150 um green scaffold tape
- Cast ~20 um green electrolyte tape
- Laminate trilayer green structure
- Cut to size
- Sinter



Bubble-free tape



Flexible



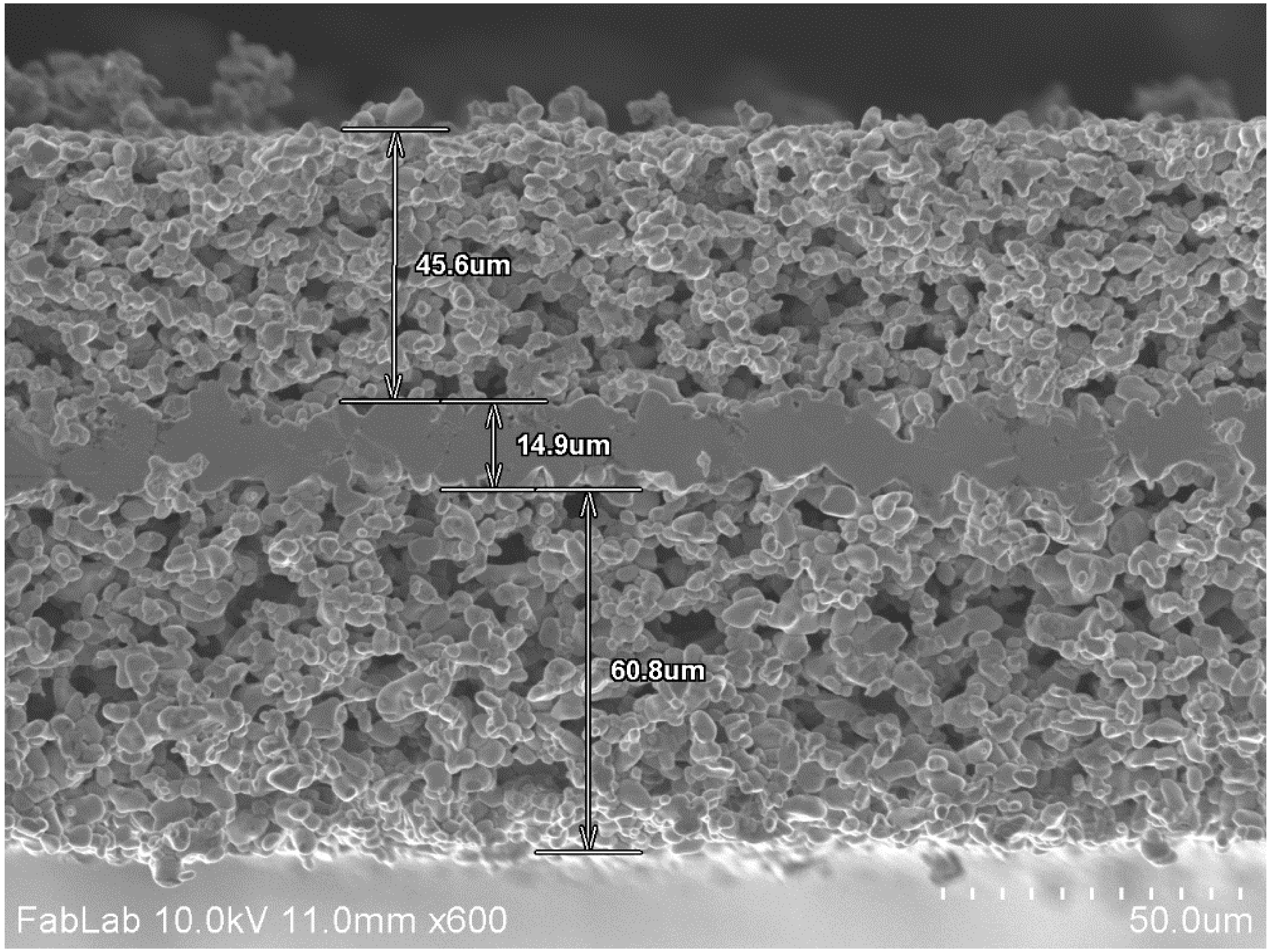
3-layer laminated

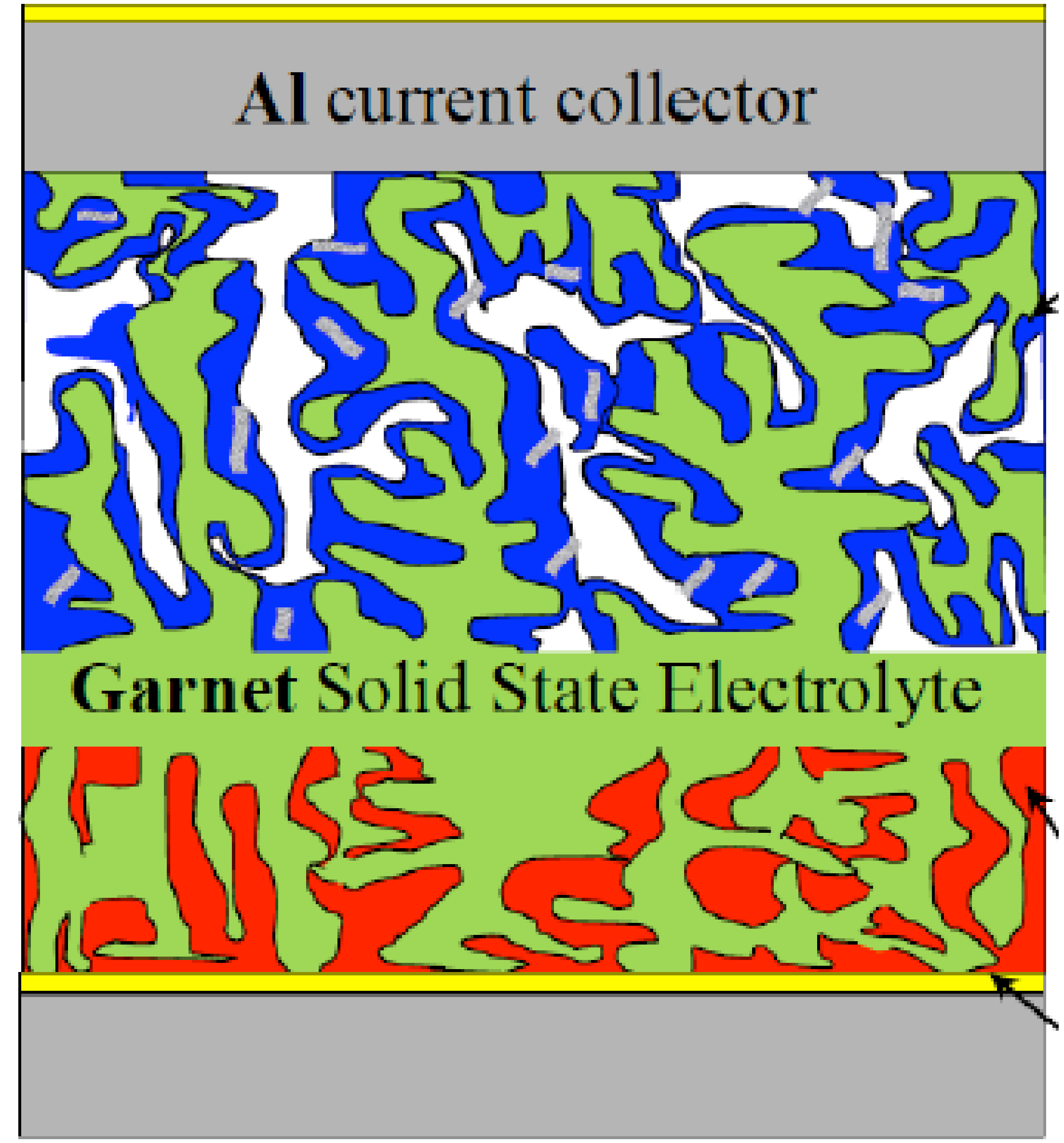
1" punch

Sintered to 0.8" diameter

Sintered to 100 um thickness

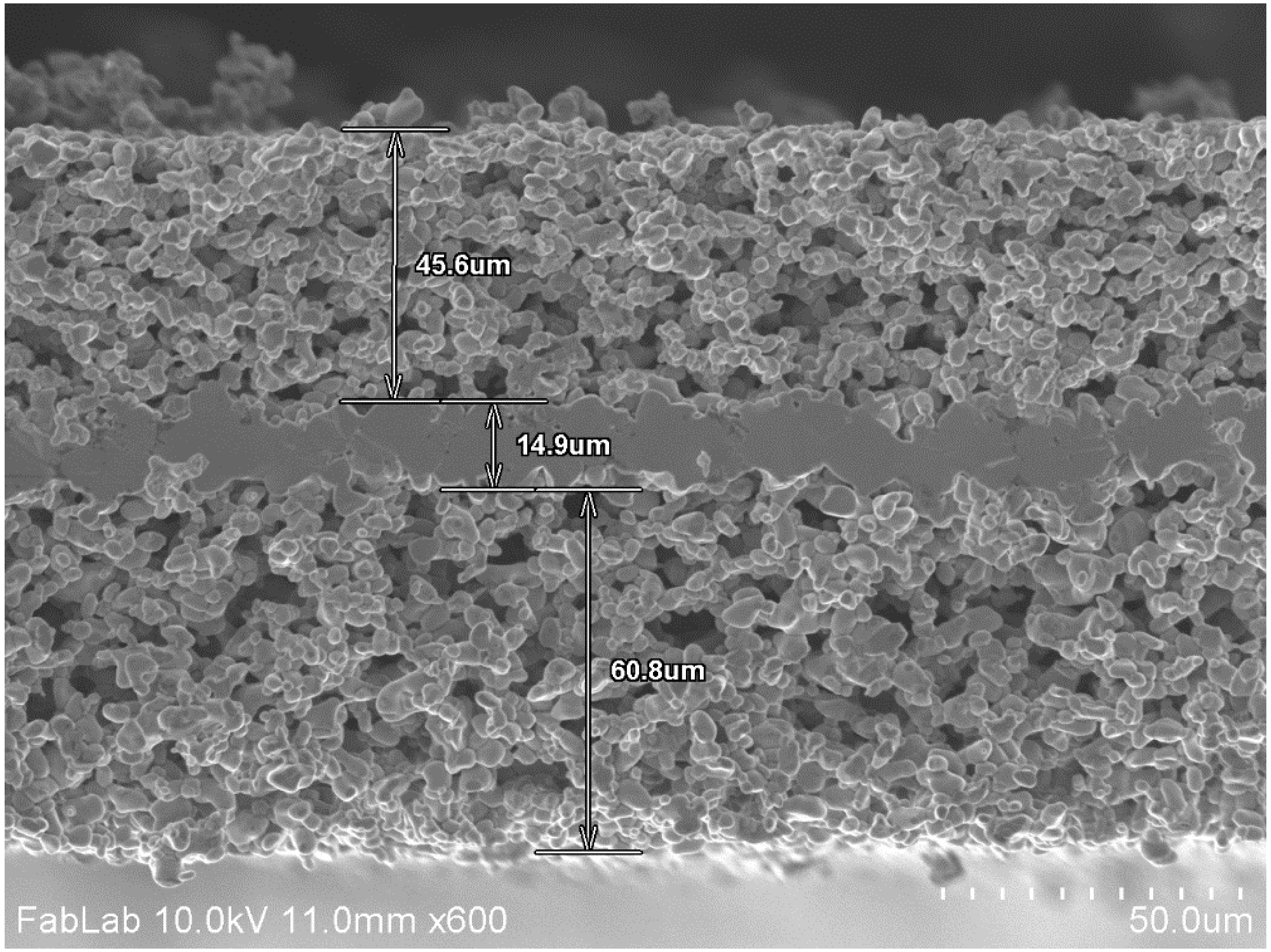
Solid State Li Battery (SSLiB)

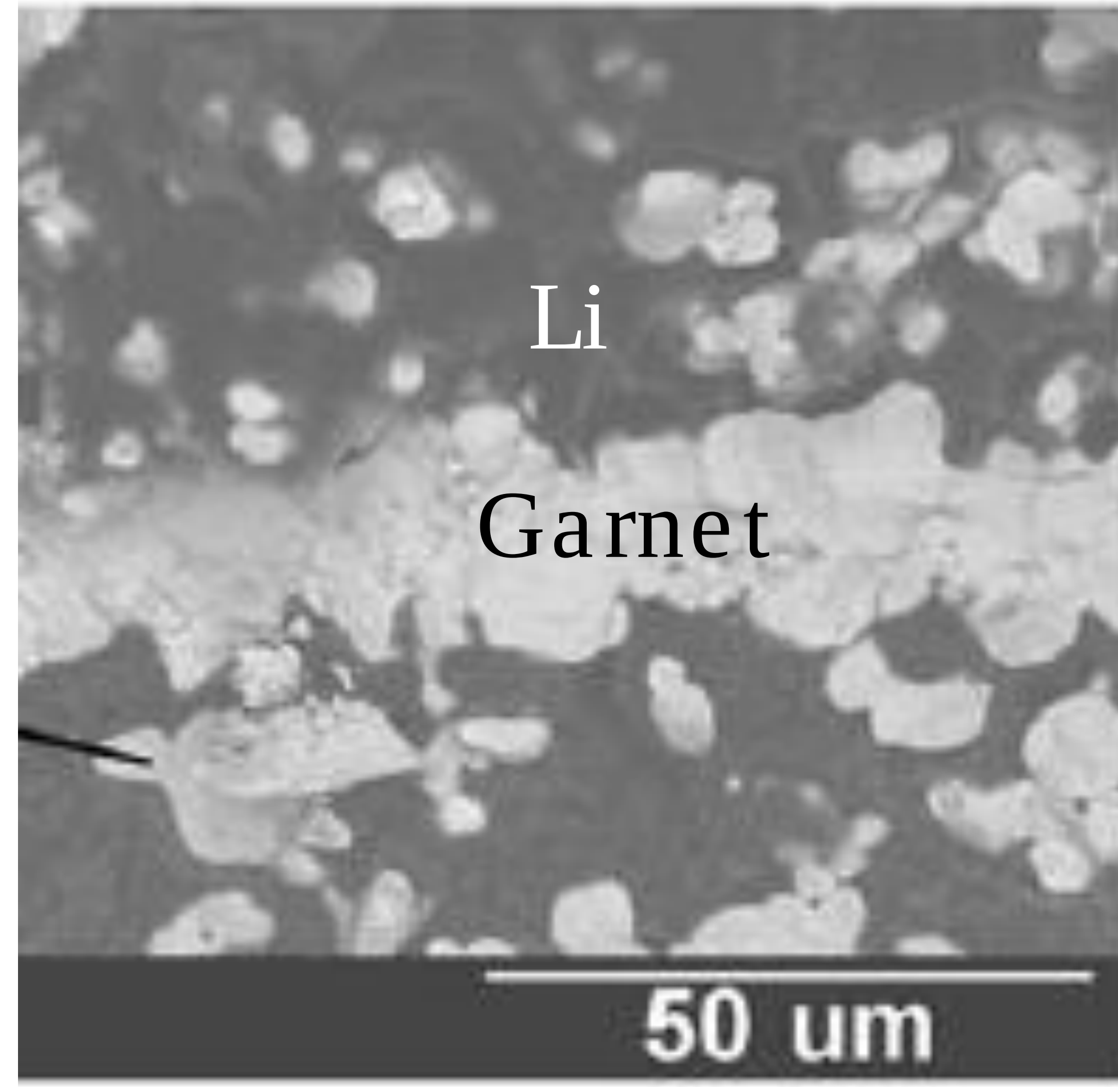




- Thin dense central layer has low ASR and blocks dendrites
- Porous outer layers provide structural support and can be infiltrated with electrodes to provide large electrolyte/electrode interfacial area

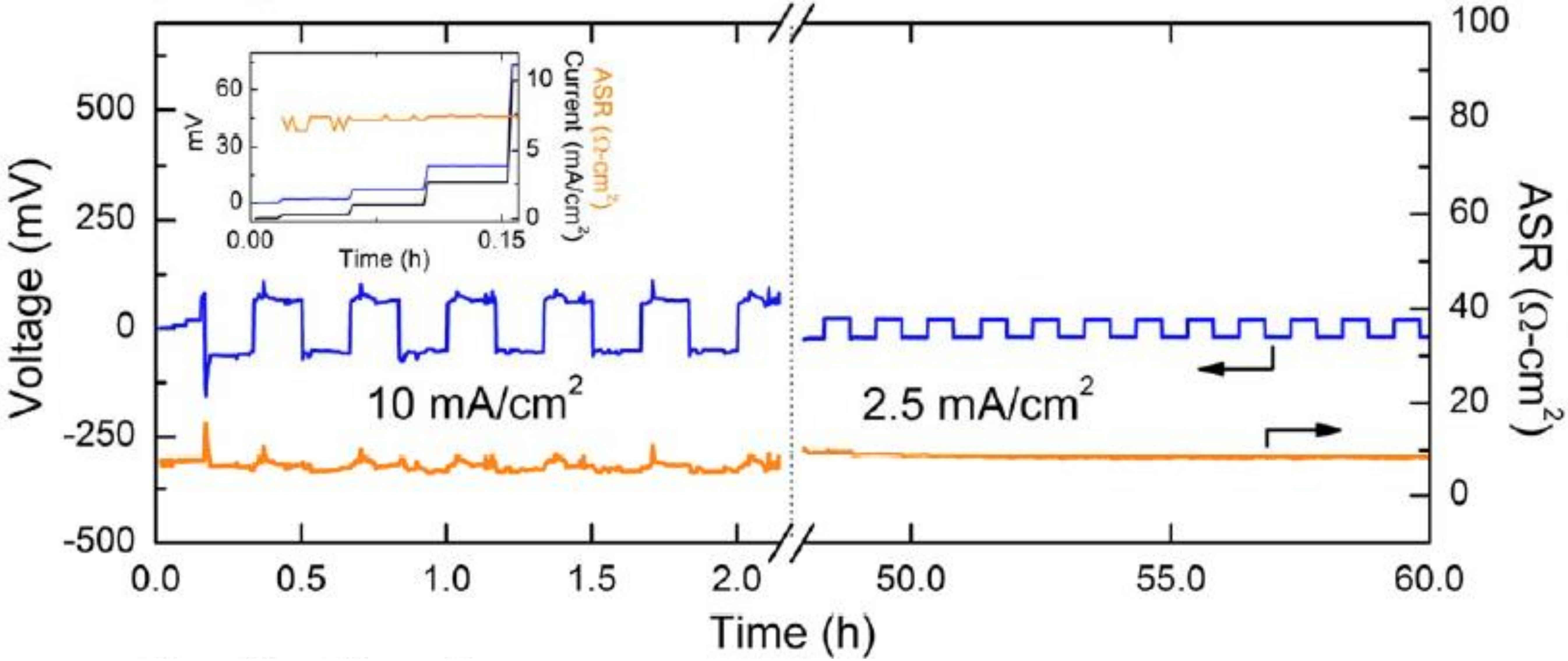
Solid State Li Battery (SSLiB)





- Thin dense central layer has low ASR and blocks dendrites
- Porous outer layers provide structural support and can be infiltrated with electrodes to provide large electrolyte/electrode interfacial area
  - Porous region can be readily filled with Li

Li Cycling of Tri-Layer Garnet



- Stable high current density **10 mA/cm²** plating/stripping cycling at 1.67 mAh/cm² Li per cycle for 16 hours then 2.5 mA/cm² for another 60 hours
- Low ASR (7 Ohm cm²) and no degradation or performance decay

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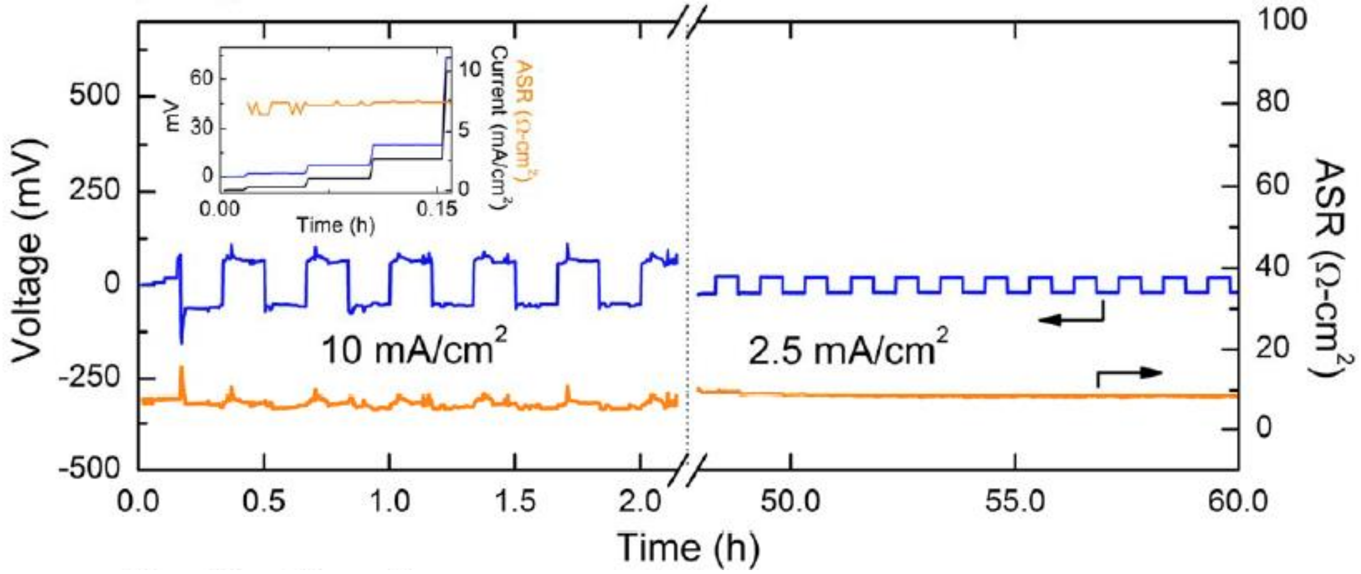
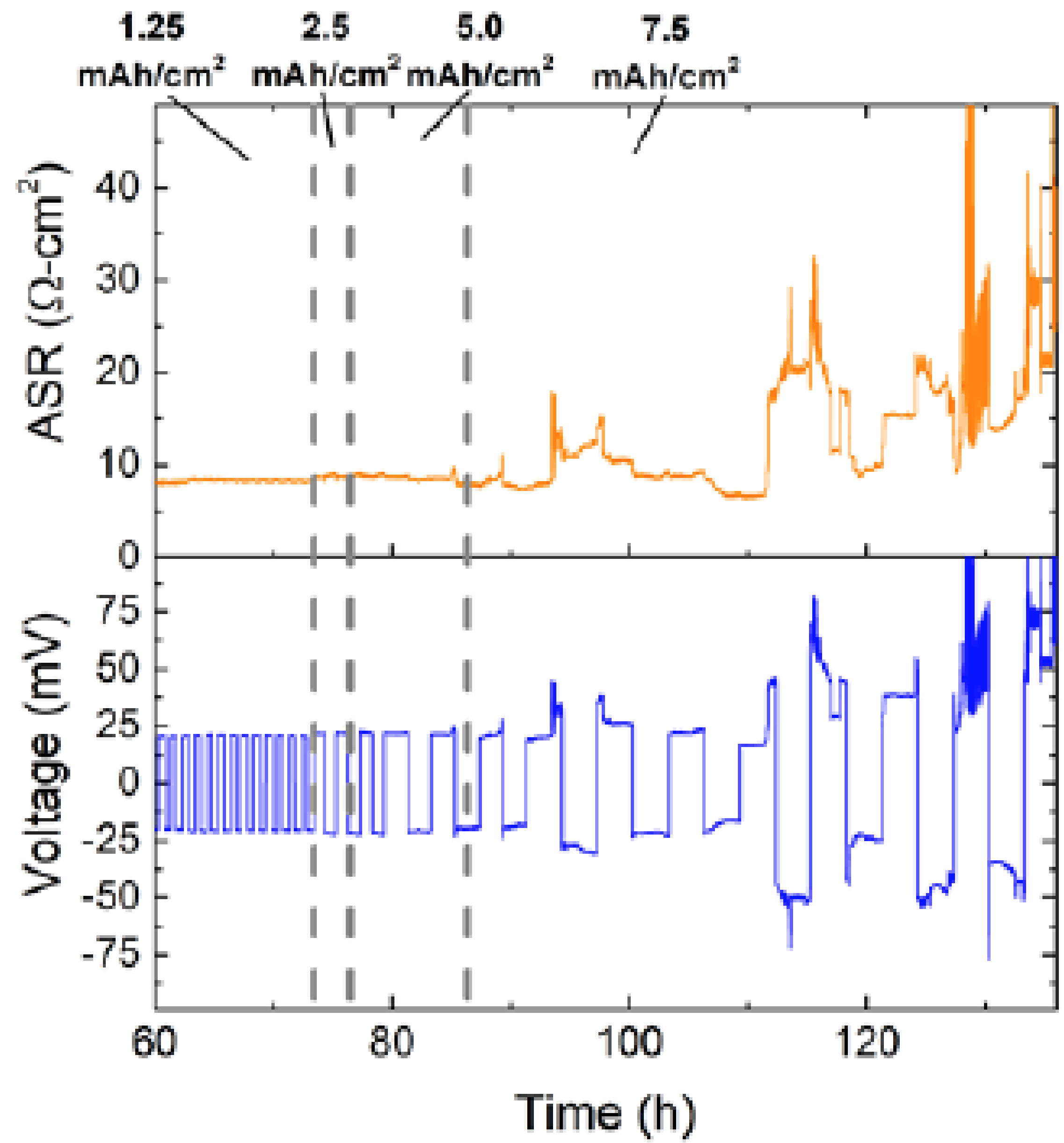
Li Cycling of Tri-Layer Garnet



- Stable high current density **10 mA/cm²** plating/stripping cycling at 1.67 mAh/cm² Li per cycle for 16 hours
- Low ASR (7 Ohm cm²) and no degradation or performance decay

- Can increase Li capacity per cycle until garnet pore capacity (~6 mAh/cm²) is exceeded without increase in ASR
- At 7.5 mAh/cm² Li is depleted from pores and ASR increases and cycling becomes unstable as expected
- Li exhaustion results confirm no dendrites



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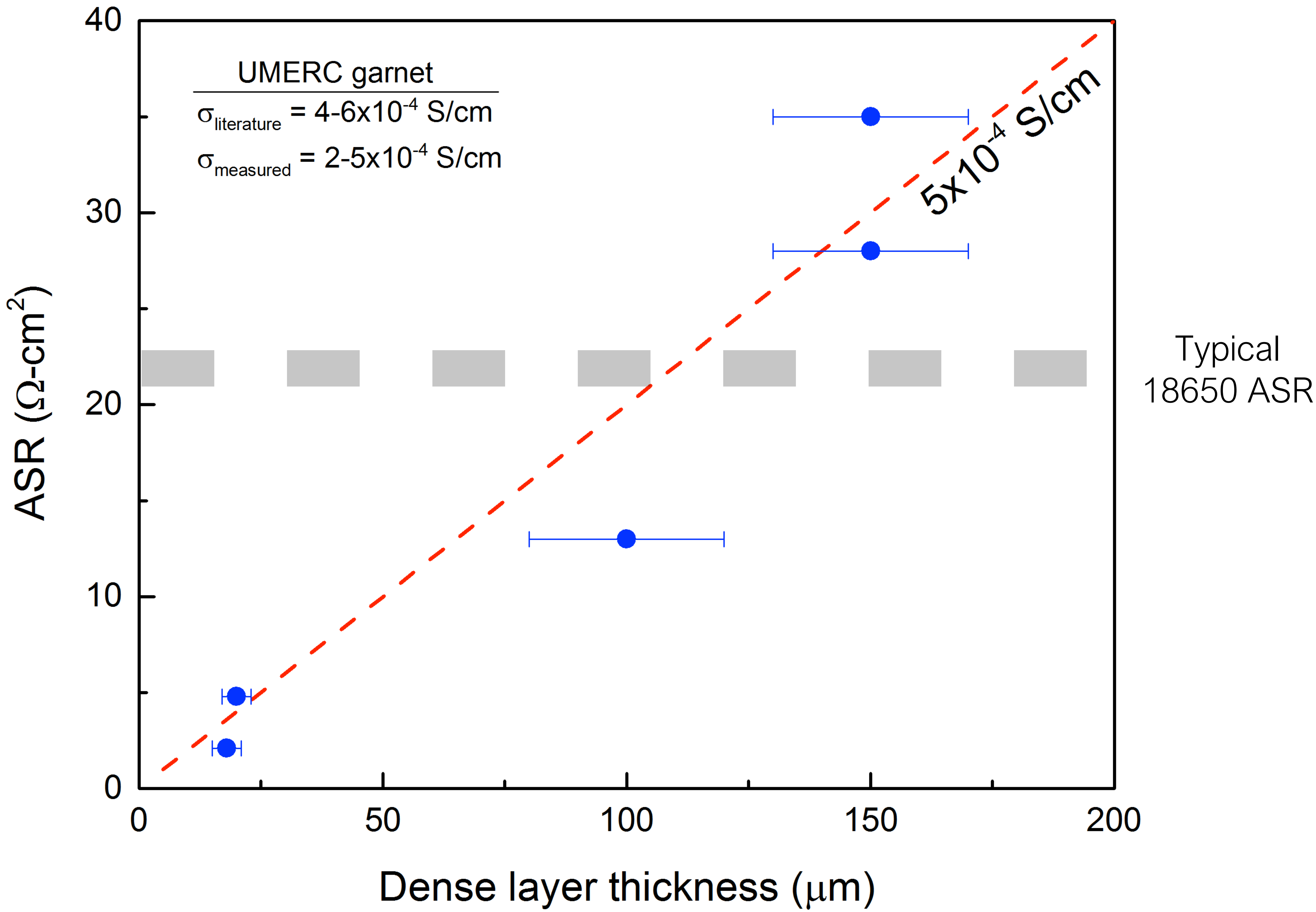
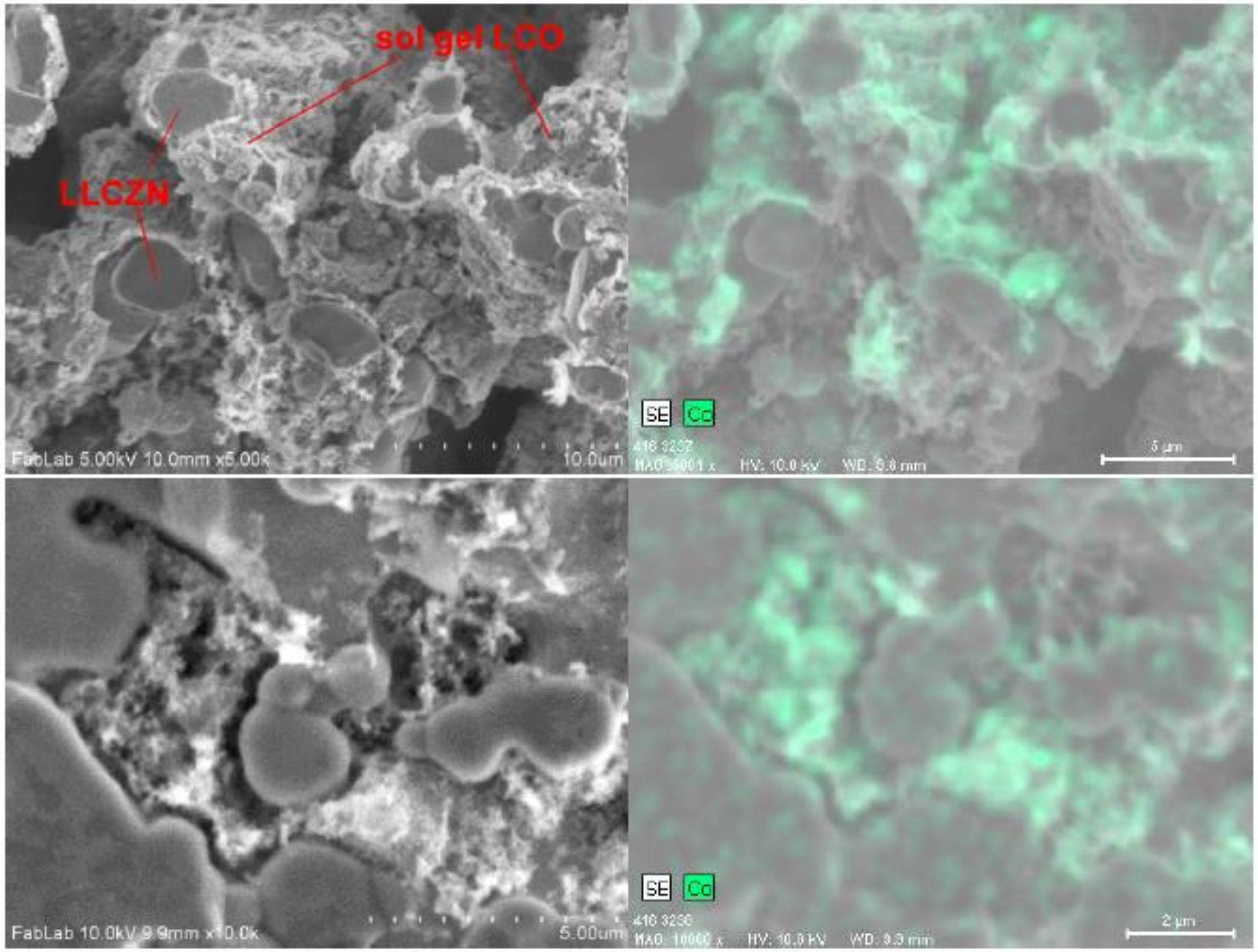
ASR as Function of Layer Thickness



Solid State Li_{metal}/Garnet/LCO Battery

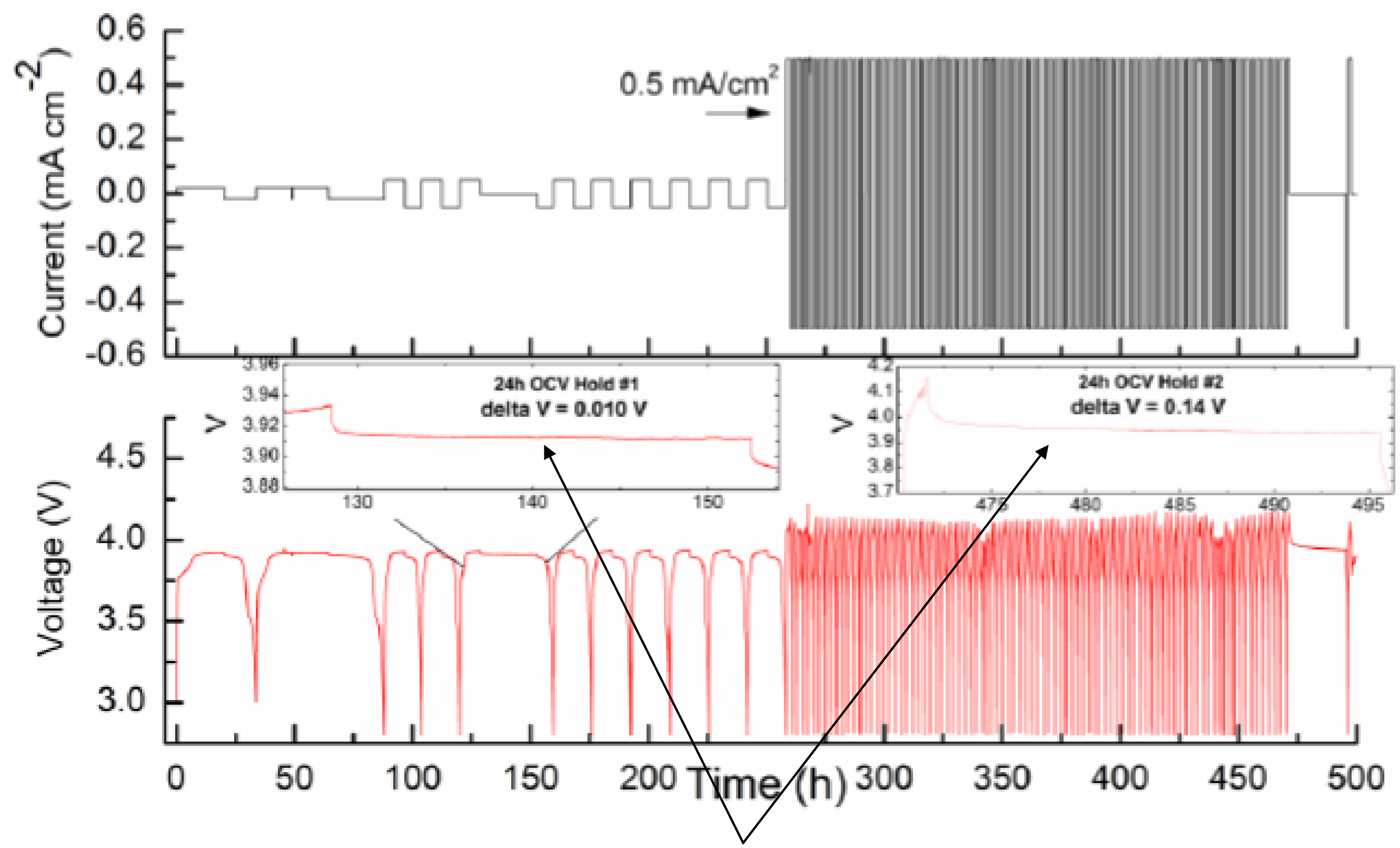
These Li_{metal}/garnet structures provide a transformative battery solution for a wide range of cathode chemistries



Infiltrated LCO as well as a number of cathode materials into the porous garnet structure

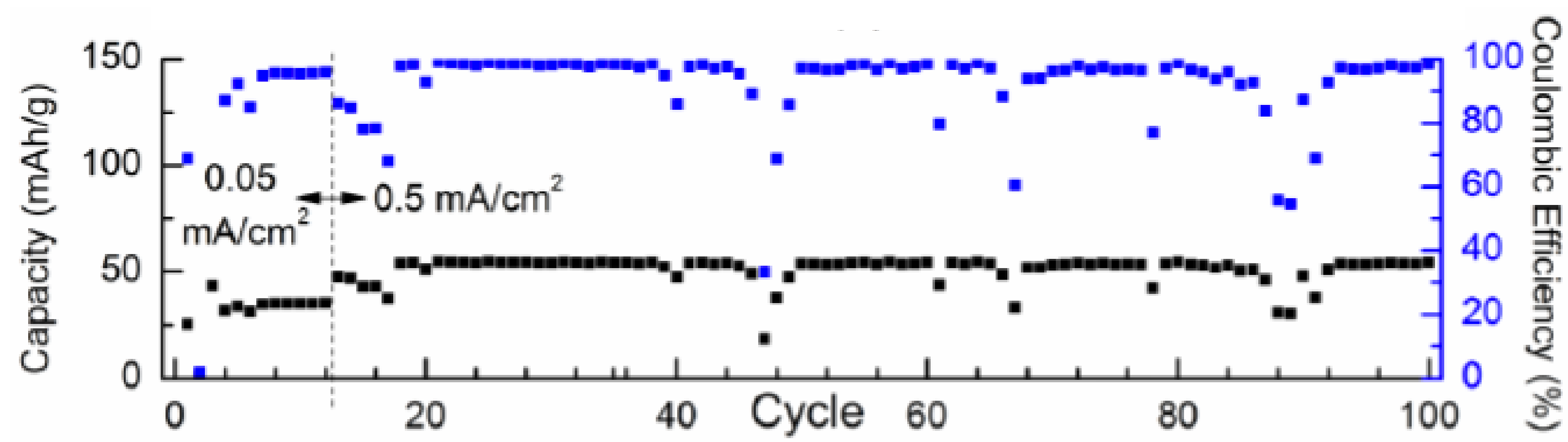
Solid State Li_{metal}/Garnet/LCO Battery

These Li_{metal}/garnet structures provide a transformative battery solution for a wide range of cathode chemistries



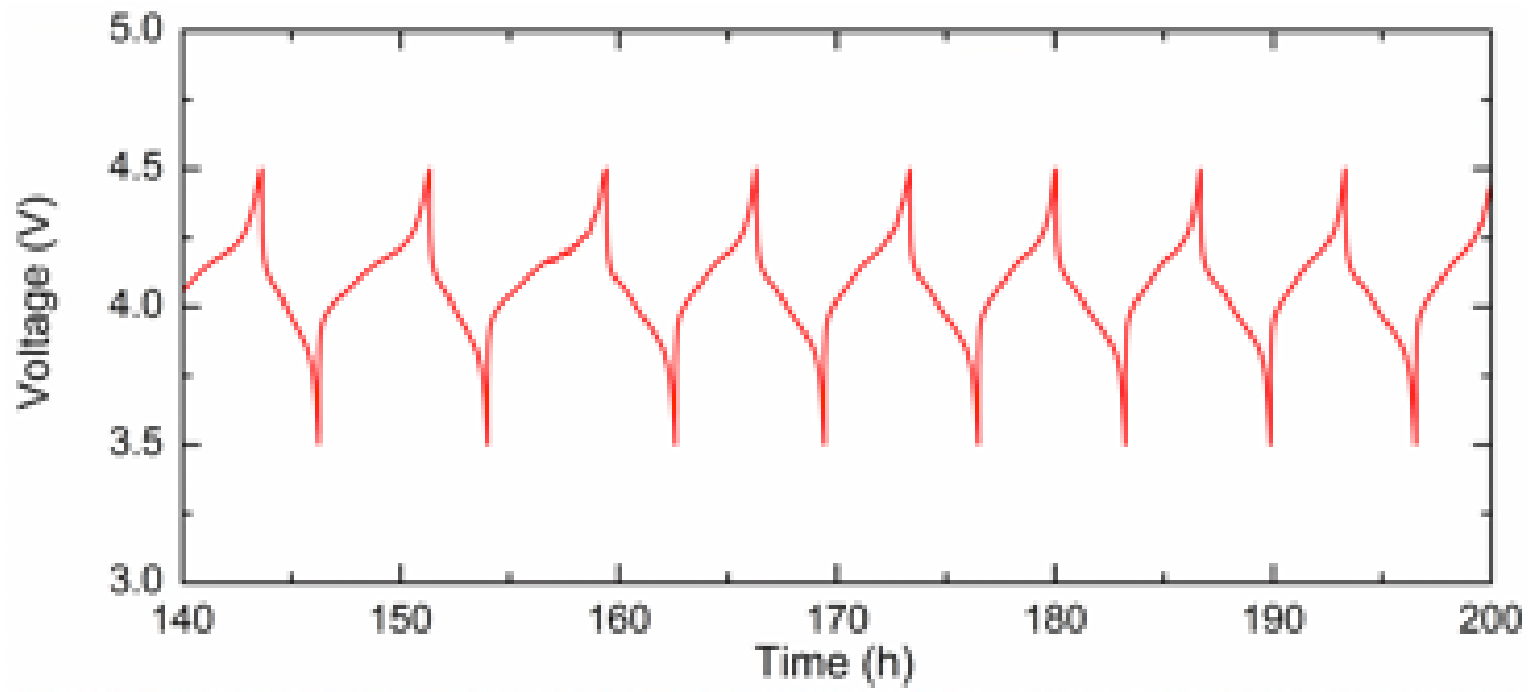
- Stable open circuit voltage for 24hrs confirms no dendrite shorting

- 100% coulombic efficiency and no capacity fade



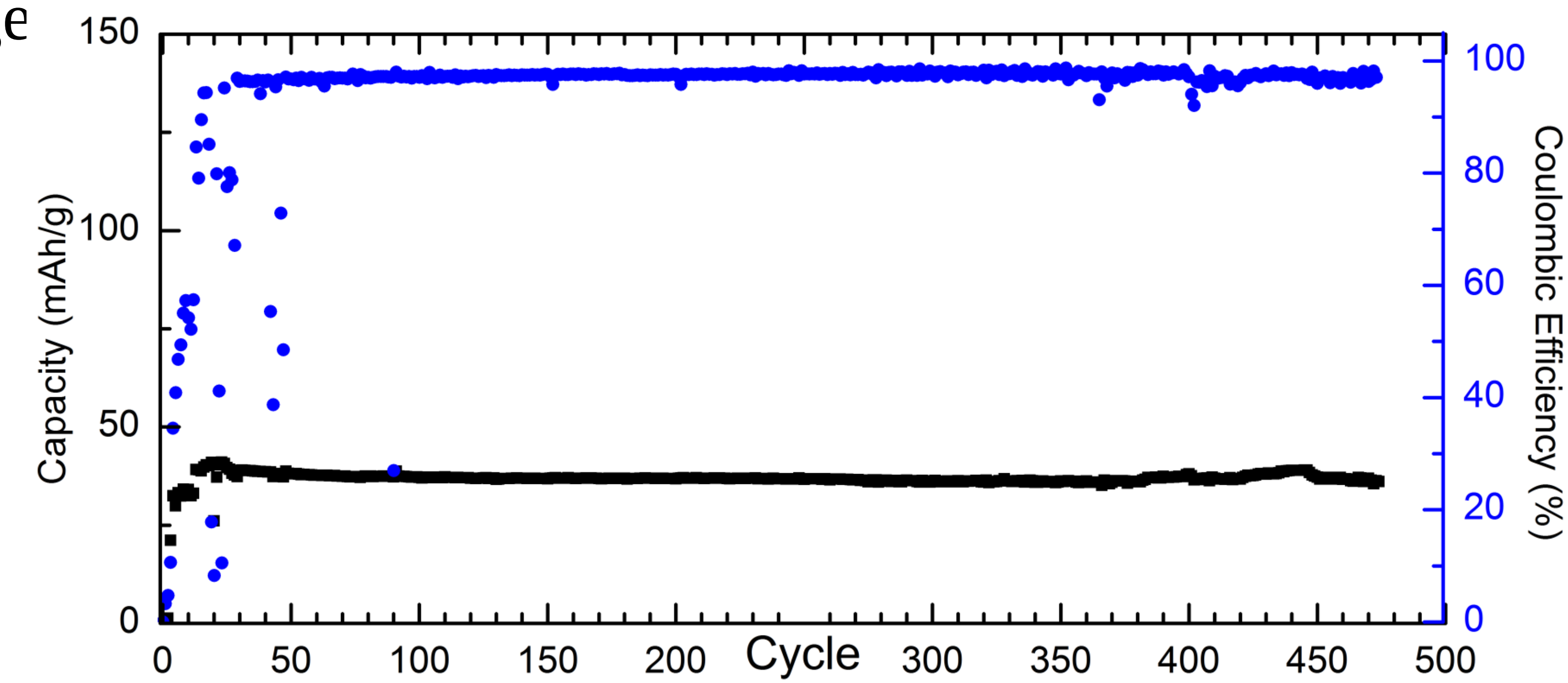
Solid State Li_{metal}/Garnet/Spinel Battery

$Li_xMn_2O_{4-y}(Cl_z)$ cathode

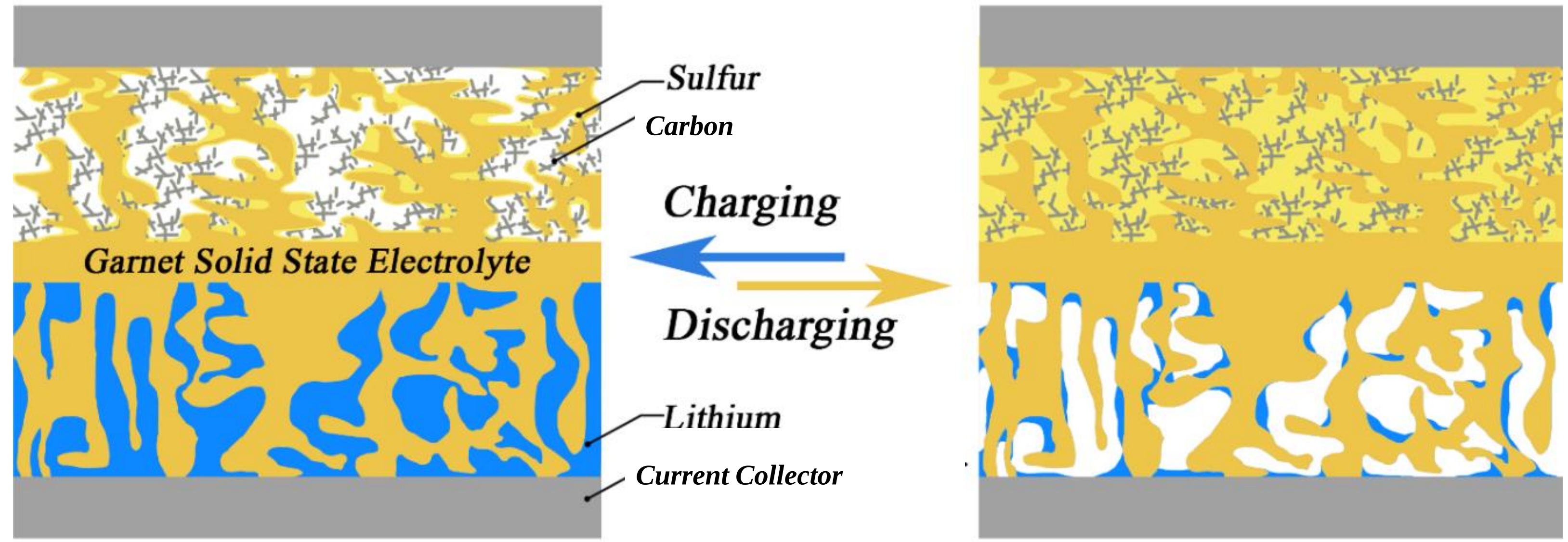


These Li_{metal}/garnet structures provide a transformative battery solution for a wide range of cathode chemistries

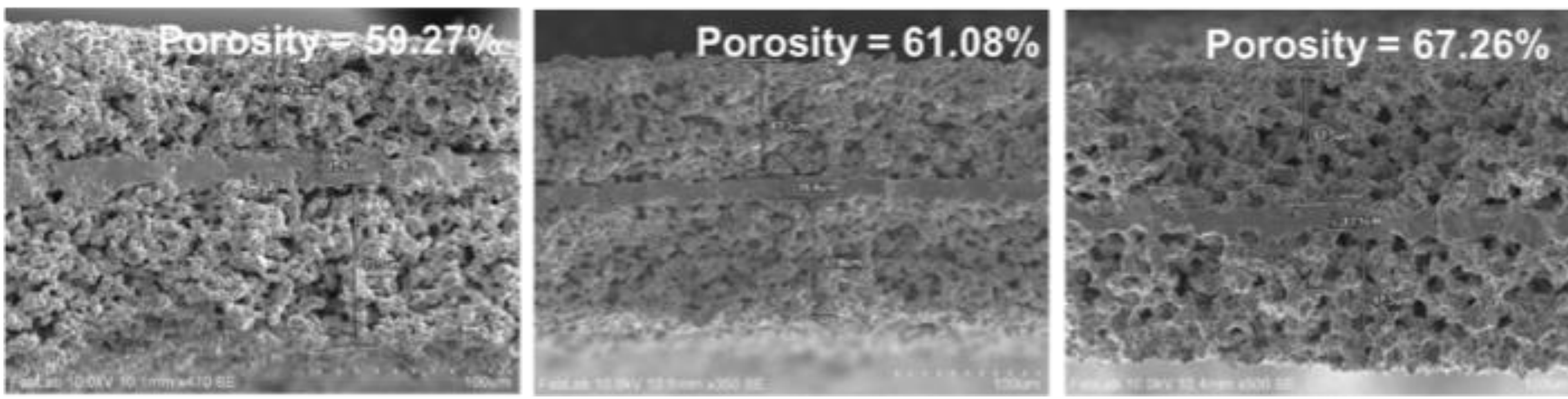
- 100% coulombic efficiency and no capacity fade for 480 cycles



Solid State Li_{metal}/Garnet/Sulfur Battery

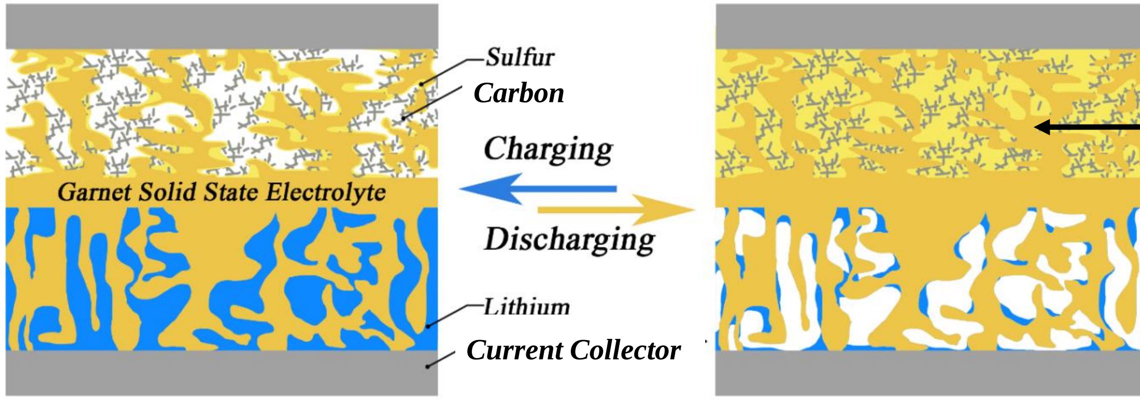


- **Increased electrode porosity from initial ~50% to design ~70%**



- **Increased electrode thickness and capacity matching anode/cathode layers**

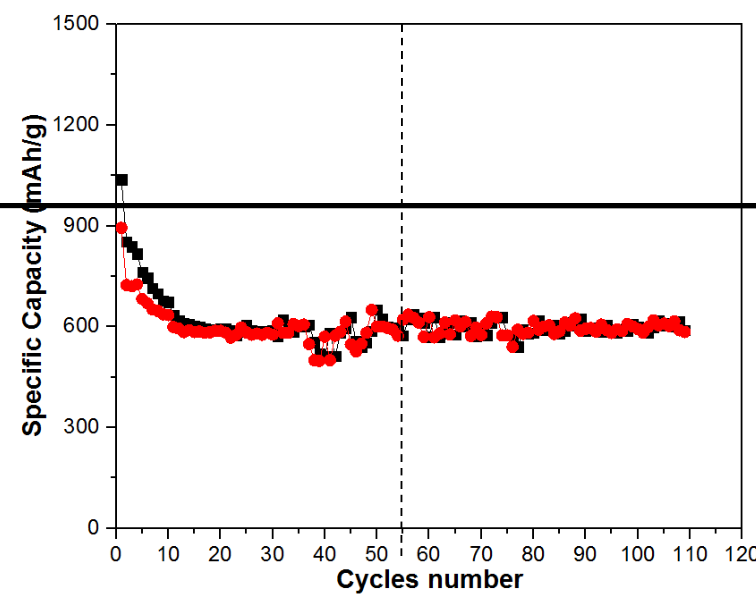
Solid State Li$_{metal}$/Garnet/Sulfur Battery

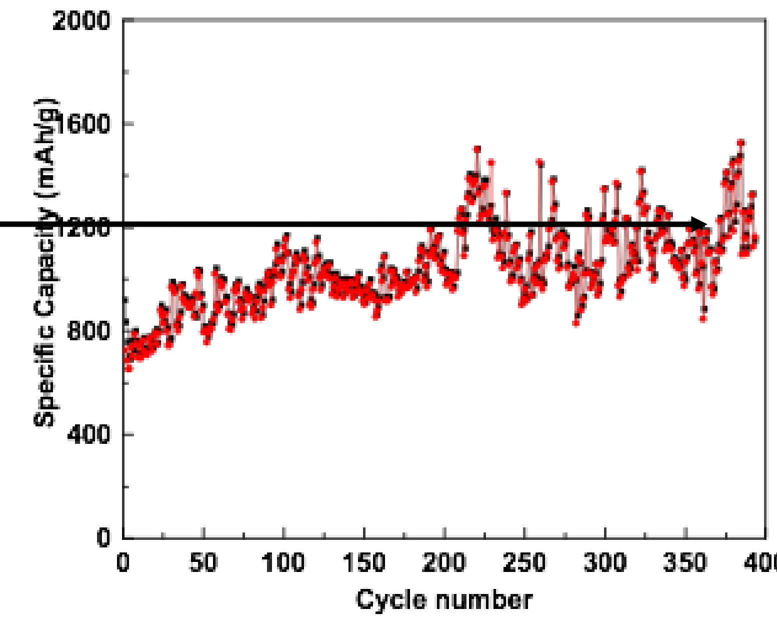


- Evaluated several techniques and increased Sulfur loading from initial ~1 mg/cm^2 to ~8 mg/cm^2

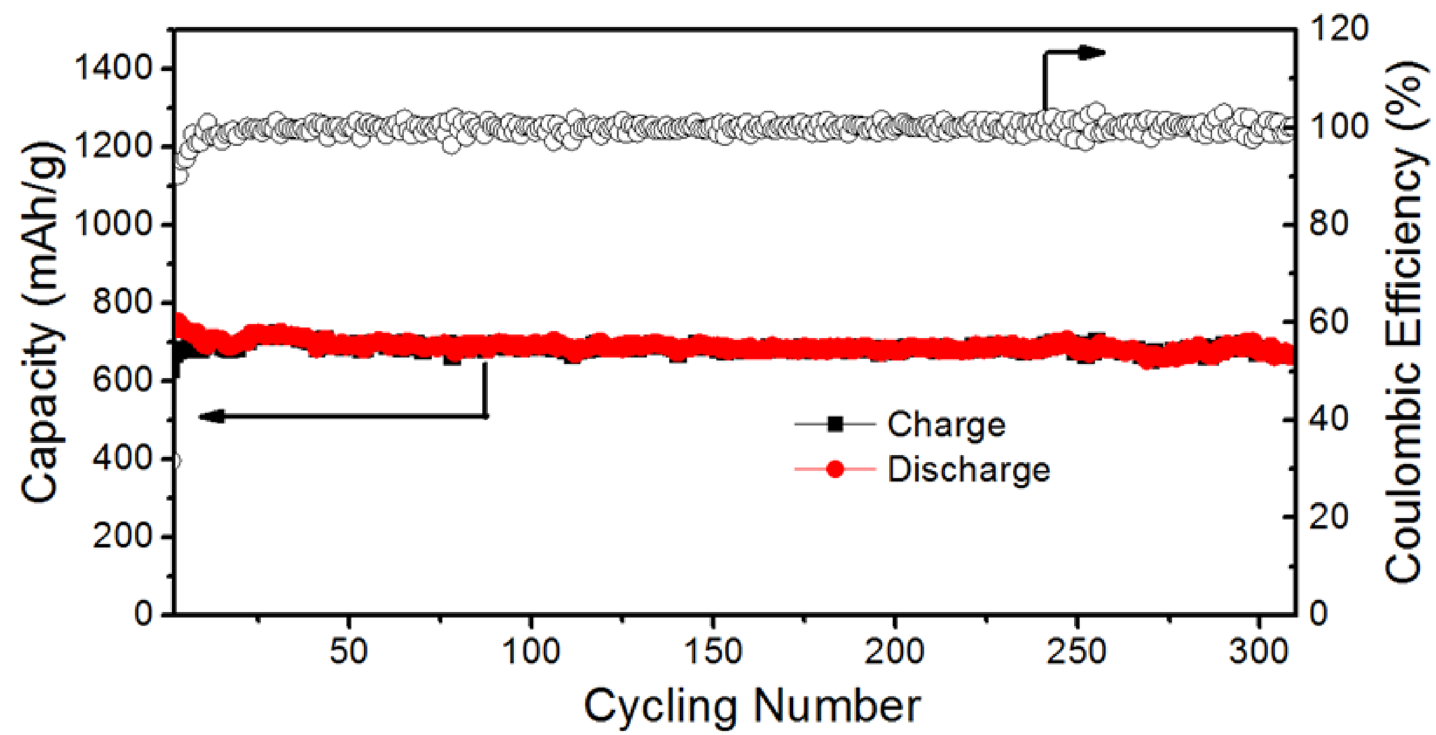
- Increased Sulfur utilization achieving over 1200 mAh/g-s

and continue driving toward theoretical (1600 mAh/g-s)





- Increased cell cycling stability
  - 100% Coulombic efficiency
  - No capacity fade after 300 cycles

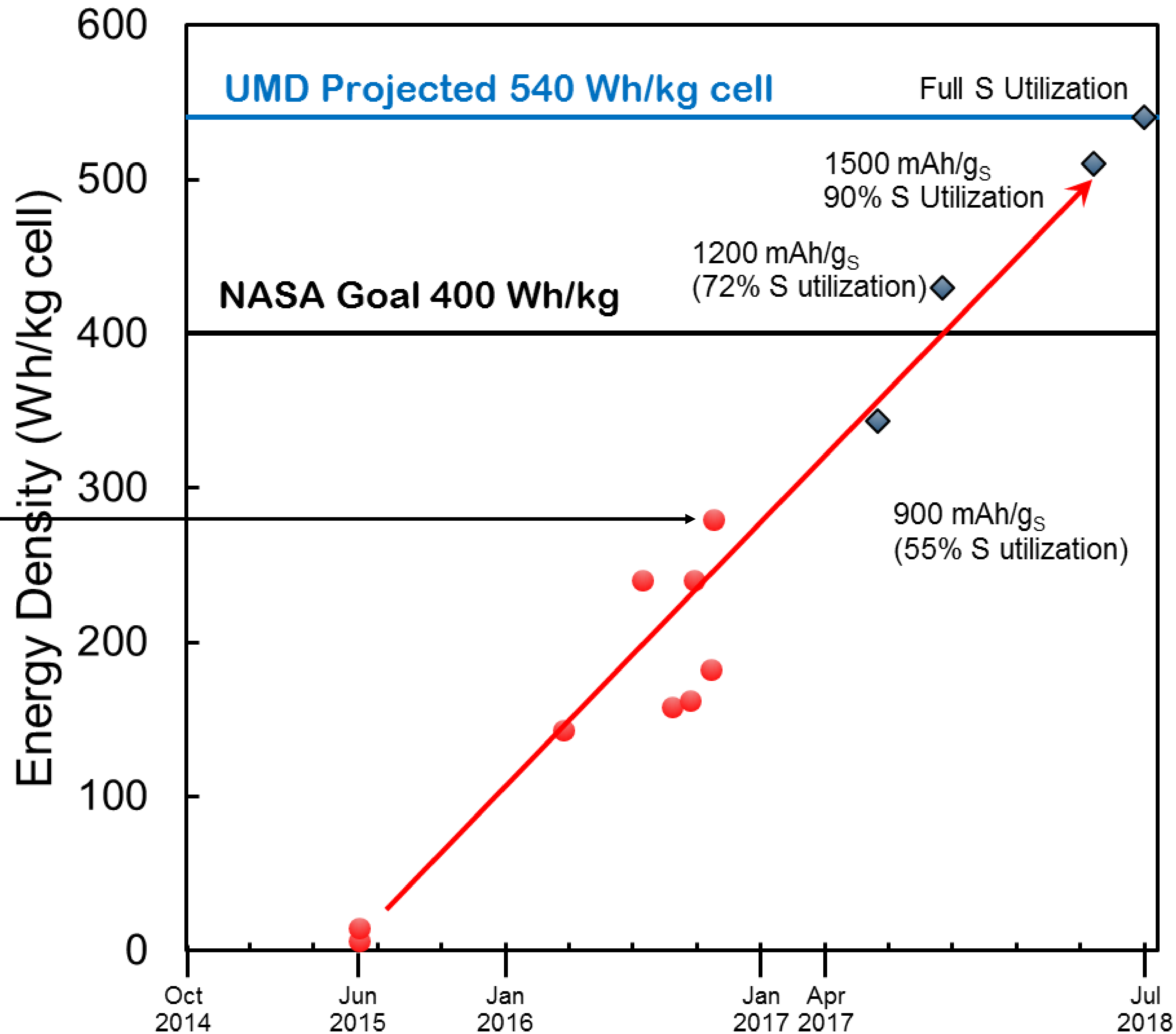


Solid State Li$_{metal}$/Garnet/Sulfur Battery

- In very short time we dramatically increased RT cell energy density based on **total cell mass**

- High RT energy density **~280Wh/kg-total cell** already achieved

- Projected to achieve **~540 Wh/kg-total cell** by increasing Sulfur utilization with current structure



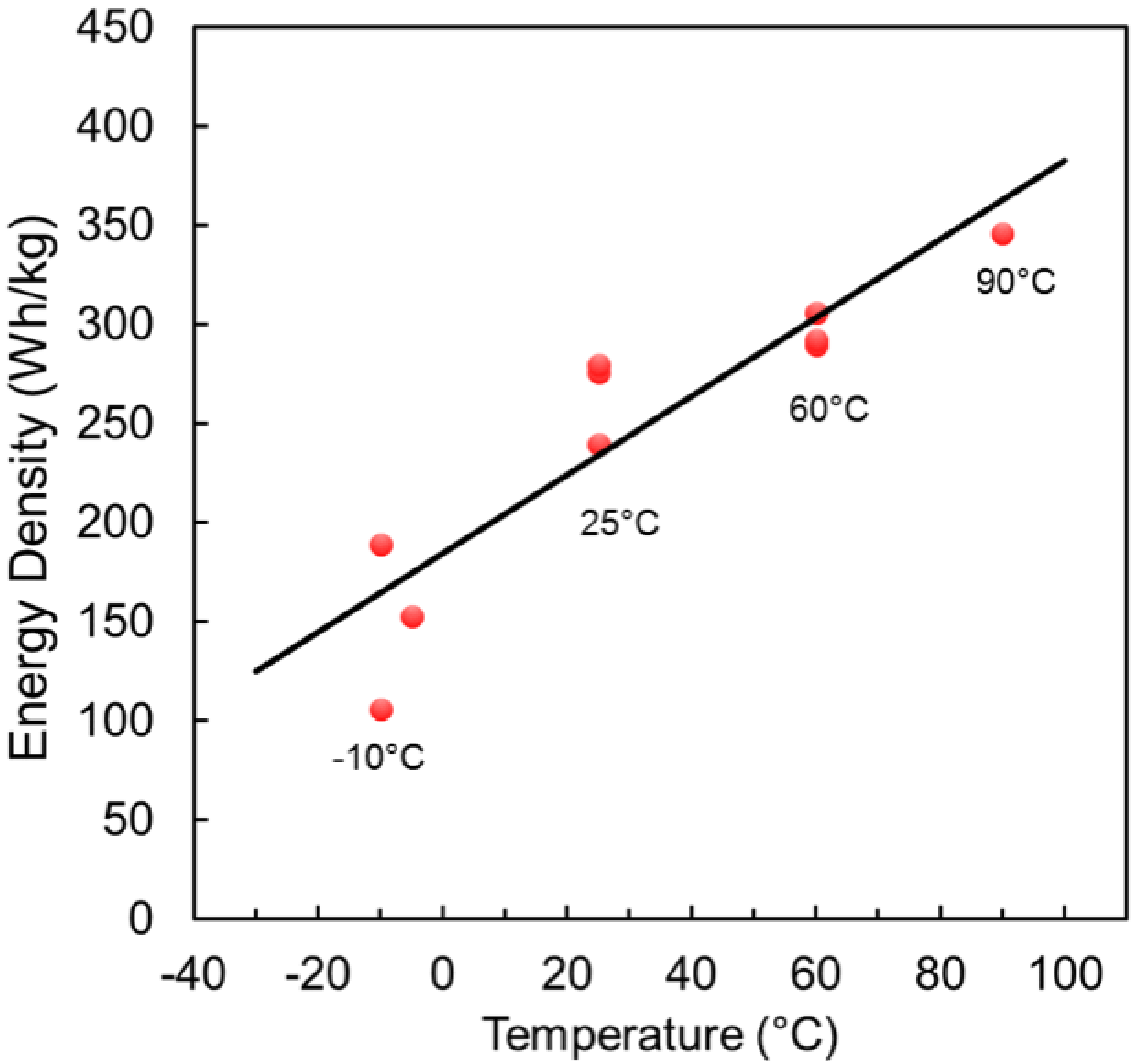
Solid State Li$_{metal}$/Garnet/Sulfur Battery

• Wide operating temperature range with low activation energy

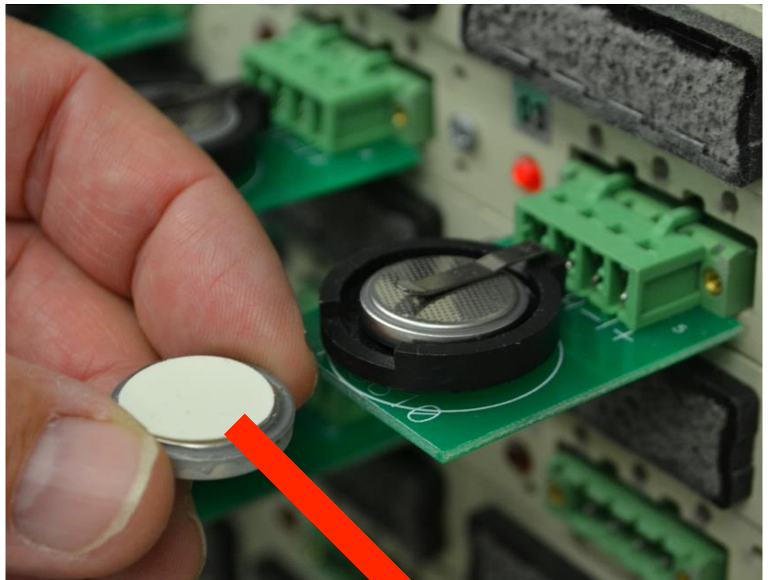
• Energy Density based on **Total Cell Mass**

• Significant increase in energy density with increasing temperature

• **350Wh/kg-total cell** achieved at 90°C

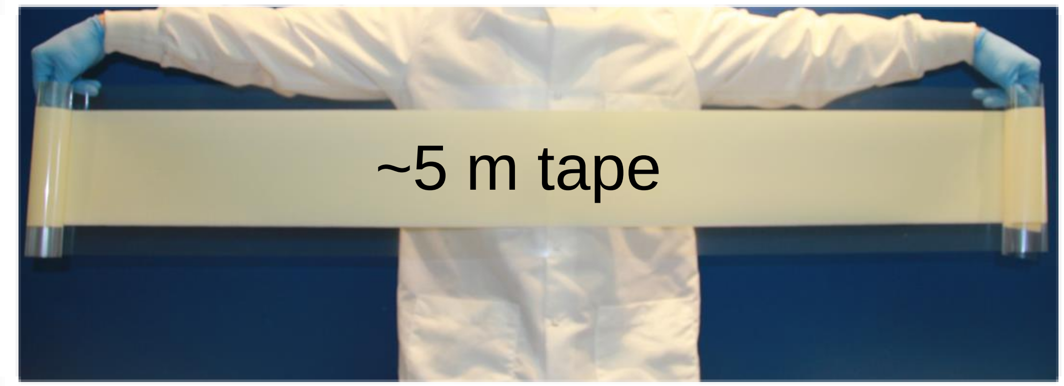


Solid State Li Battery (SSLiB) Scale-up

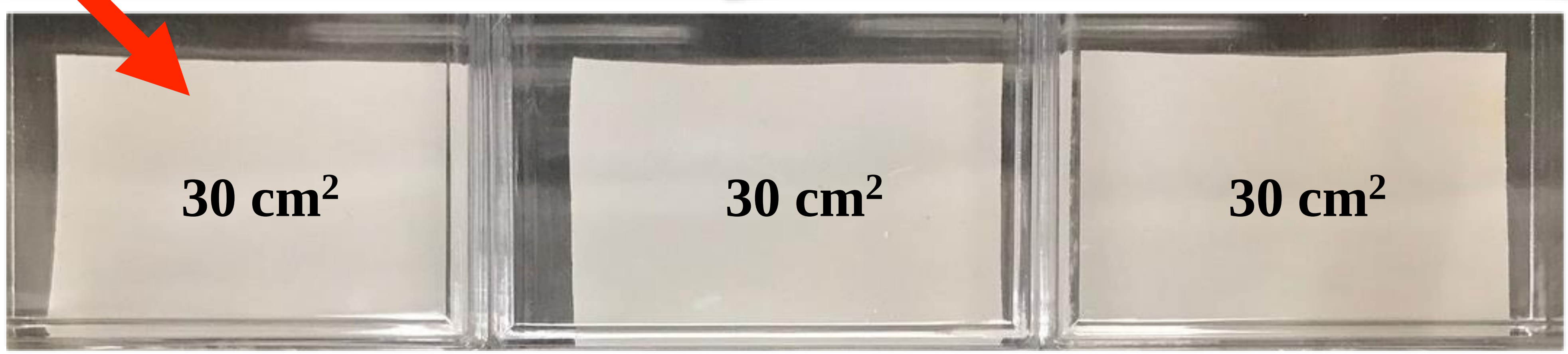


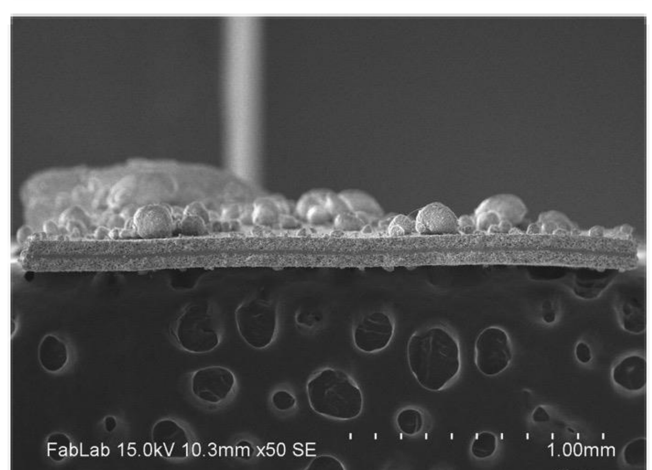
We are scaling up to full format 30 cm^2 cells for commercialization by Ion Storage Systems using developed SOFC fabrication techniques

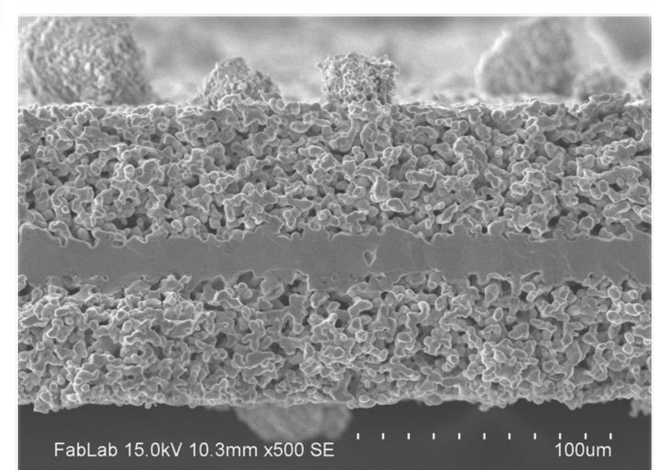
Tapecasting Scale-up



Sintered Full Format Trilayer Electrolytes







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Acknowledgement

Liangbing Hu, Venkataraman Thangadurai, Yifei Mo, Chunsheng Wang, Greg Hitz, Dennis McOwen,Yunhui Gong, Lei Zhang, Tanner Hamman, Matthew Limpert, Griffin Godbey, Zhaohui Ma, Jack Evans Gritton, Kun Fu, Chengwei Wang, Xiaogong Han, Huili Liu, Boyang Liu, Jiaqi Dai, Chunpeng Yang

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Robust Affordable Next Generation EV-Storage (RANGE)
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