



# **Development of Solid State Electrolytes for Li Metal-Based High Capacity Battery**

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**Invited Presentation at 236<sup>th</sup> Electrochemical Society Meeting  
Atlanta, Georgia, October 15, 2019**



# Outline

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- **Introduction/NASA Energy Requirements**
- **Challenges for Li Metal as High Capacity Anode**
- **Solid State Electrolytes for Li Metal Anode**
- **Result Summary**
- **Next Steps/Future Directions**



# Safe and High Capacity Batteries: Important for NASA Missions

- **Batteries provide**

- a versatile, reliable, safe and portable energy source, and are an essential component of the power system of virtually all NASA missions
- Electrical energy storage options for NASA Space missions, such as:
  - Power during spacecraft eclipses
  - Peaking power for high power needs



- **Aeronautics**

- Electrified Aircraft (EA)
- Urban Air Mobility (UAM)

- **Space**

- Moon to Mars and beyond





# Desired Battery Properties for NASA Missions

- **Safe**
- **High in specific energy**
- **Light in weight**
- **Compact in volume**
- **Long in shelf life**
- **Durable in wide temperature ranges and harsh environments**
- **Reliable in meeting mission requirements**

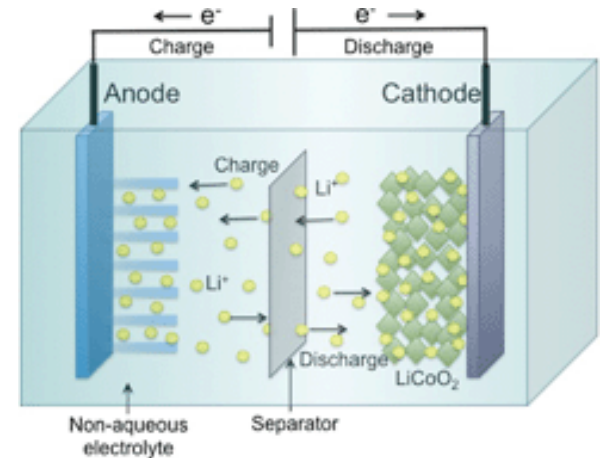




# State-of-Art (SOA) Li-Ion Battery (LIB)

- **LIB Specs:**

- Specific energy: 180-200 Wh/kg
- Specific power: 300 W/kg
- Cycles: 1000s (excellent)
- Temp range: -20°C to 60°C
- Excellent rechargeability



Poulomi, R. et al J. Mater. Chem. A 2015 (6)

Anode: Graphite

Cathode: LiCoO<sub>2</sub>

Electrolyte: Li salt in organic carbonate

- **Limitations:**

- Maximum of energy density <250 Wh/kg
- Electrolyte flammable and fire hazards



# NASA Demands Very High Specific Energy Batteries



## 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 SOA Li-ion chemistries**

➤ Progress in these areas requires advances in safe, very high energy batteries



# Advanced Safe, High Energy Li Batteries

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- **Advanced electrode materials to improve Li-ion battery energy**
  - Anode active materials
  - Cathode active materials
- **Advanced electrolyte to improve safety**
  - Non-flammable additives
  - Ionic liquids
  - Solid state electrolyte
- **Beyond Li-ion battery chemistries**
  - Li-S Chemistry
  - Metal air batteries chemistries such as  $\text{Li/O}_2$



# NASA Programs For Safe and High Energy Batteries Development

- **Advanced Space Power System Program (ASPS), 2009-2014**
  - Partnered with University/Industry for Advanced components development
    - Si as advanced anode - Georgia Tech, Physical Science Inc.
    - NMC as advanced cathode - University of Texas at Austin
    - Low-flammable electrolyte - NASA JPL
    - Fabrication of large format flight-type prismatic cells with Si anode (35Ah) - PSI/Yardney
- **Advanced Energy Storage System (AESS) Project under Game Change Program (2014-2017)**
  - Amprius: Silicon Anode-Based Cells for High Specific Energy Systems
  - University of Maryland (UMD): Garnet Electrolyte-Based Safe Lithium-Sulfur Energy Storage







# Beyond Li-Ion Battery Chemistries

- **Li/S Battery Chemistry:**
  - **Advantages**
    - Very high theoretical specific energy: 2680 Wh/kg
    - Availability: abundance on earth
    - Non-toxic
    - Environmentally benign
  - **Challenges**
    - Poor electronic conductivity
    - Low voltage
    - Li dendrite growth
    - Polysulfide shuttle causing short cycle life
- **Metal-Air Batteries Chemistries, e.g. Li/O<sub>2</sub>**
  - Very high theoretical specific energy (3458 Wh/kg)
  - Air cathode is “open” to environmental
  - Battery depends on environment e.g. O<sub>2</sub>, humidity, air flow, temperature
  - Complex discharge products, high overpotential during cycling
  - Safety, Li dendrite growth



# NASA Energy Storage Related Research for High Capacity Battery Technologies Beyond Li-Ion Chemistries

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- **Advanced Energy Storage System (AESS) Project under Game Change Program (2014-2017)**
  - University of Maryland (UMD): Garnet Electrolyte-Based Safe Lithium-Sulfur Energy Storage
- **Center Innovative Fund (CIF)**
  - Solid Polymer Nanocomposite Electrolyte to enable Li Metal Safe Cycling (FY 16, FY 18)
- **Convergent Aeronautics Solutions (CAS)**
  - LION – Li-Oxygen Battery (FY 17-FY19)
  - SABERS – Solid State Architecture Batteries for Enhanced Rechargeability and Safety (Li/S-Se battery, FY20-FY22)
- **SBIR/STTR Program**
  - Small Business/University for Beyond Li-ion Battery Chemistries and Technologies or Other Unique Technologies to Meet NASA Needs



# Lithium Metal: Ideal Anode for High Capacity Battery

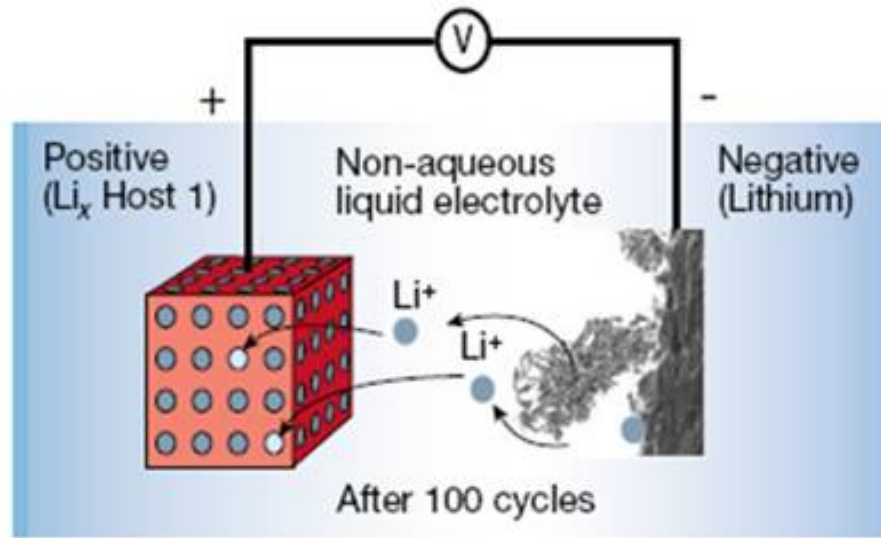
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- **Very high theoretical specific capacity: 3860 mAh/g**
- **Lightest metal: low density ( $0.534 \text{ g/cm}^3$ )**
- **Lowest negative electrochemical potential (-3.040V vs. SHE)**
- **100% active material (no binder is needed)**



# Challenges: Li Metal as High Capacity Anode

- Very reactive, parasitic reactions, resulting in low coulombic efficiency (CE)
- Shape changes during cycling, causing capacity loss and poor cyclic-ability
- Dendrite growth causes safety concern



(Tarascon, J. M. et al, Nature, 2001, 414, 359-366)



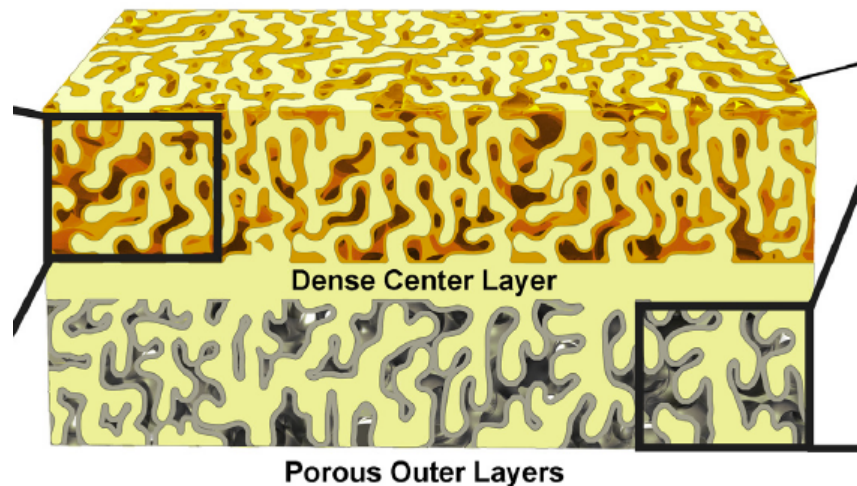
# Solid State Electrolyte: Improve Safety of High Capacity Battery with Li Metal Anode

- **Solid State Electrolyte to Enhance Safety**
  - Attractive approach to enable Li metal anode safety
- **Challenges in Solid State Electrolyte Development**
  - Low ionic conductivity at room temperature ( $<10^{-3}$  S/cm)
  - High contact/interfacial resistance issues
  - Processing/fabrication issues
- **Solid state electrolytes**
  - Ceramic type such as Garnet
    - Trilayer solid state electrolyte (SSE) by UMD
      - funded by NASA AESS program (COR/TM: James Wu)
  - Solid polymer nanocomposite electrolyte
    - funded by NASA CIF (FY 16 & FY 18)
    - (conducted at NASA/Glenn Research Center, PI: James Wu)



# Trilayer Garnet Solid State Electrolyte (SSE)

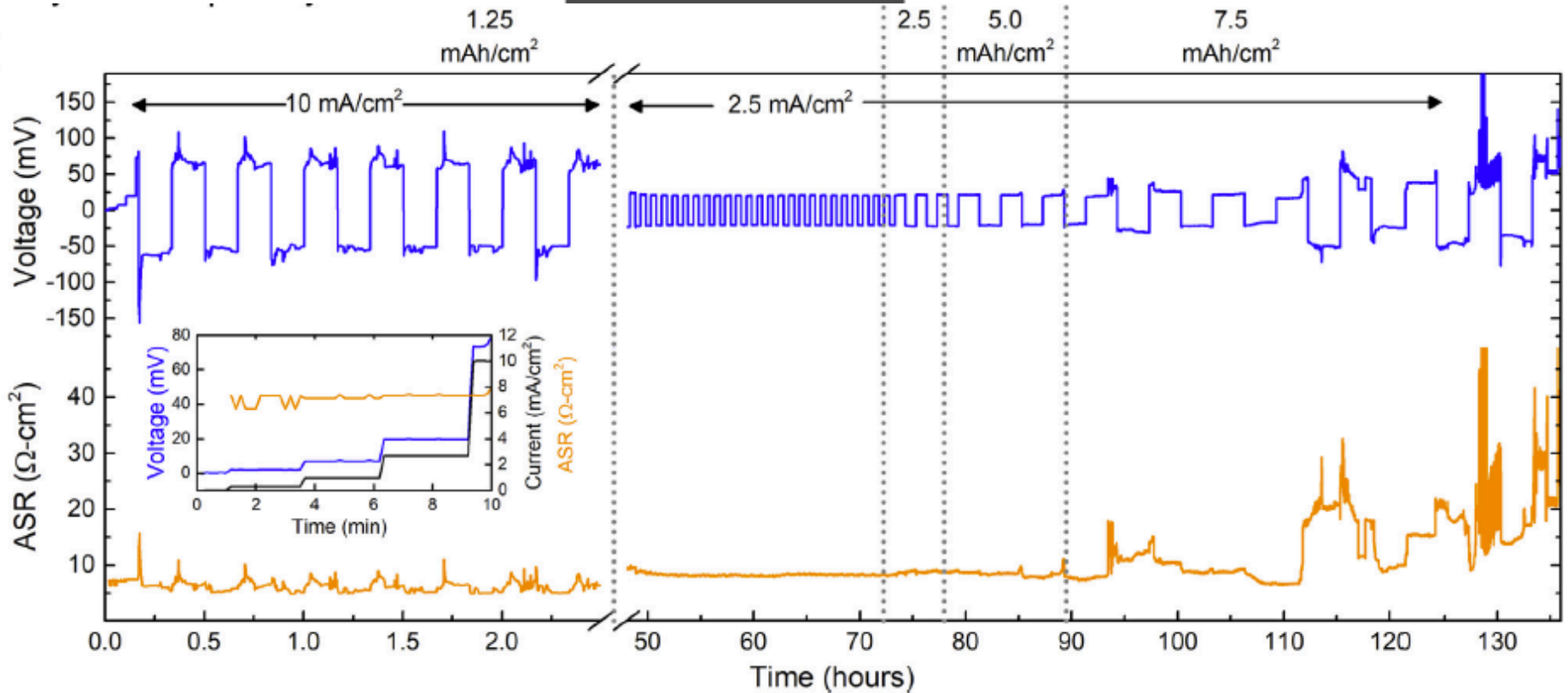
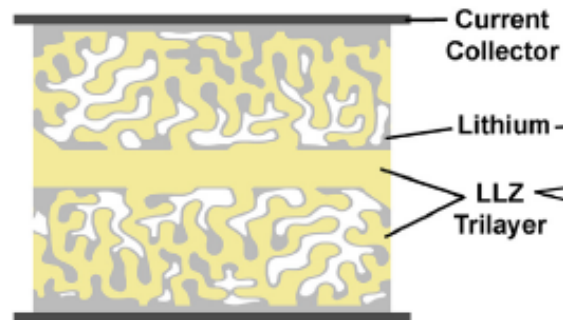
- **Garnet (doped LLZ) as solid state electrolyte**
  - High RT ionic conductivity (  $\sim 1$  mS/cm)
  - Chemically and electrochemically stable with Li metal
- **Trilayer garnet 3D-SSE as a scaffold (developed by UMD)**
  - Porous-dense-porous layer
  - Increase contact surface area between SSE and active materials
  - Lower interfacial resistance & ability to operate at higher current



(G. T. Hitz et al. Materials Today 2019, 22, 50-57)



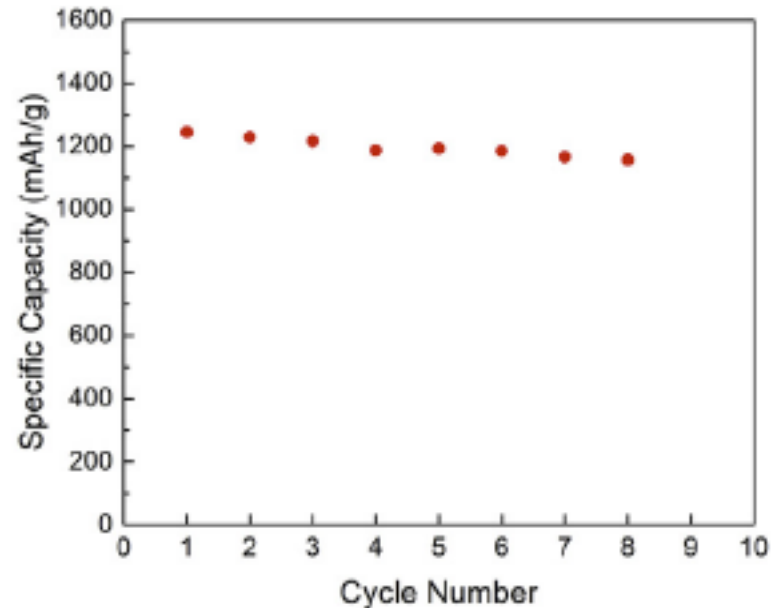
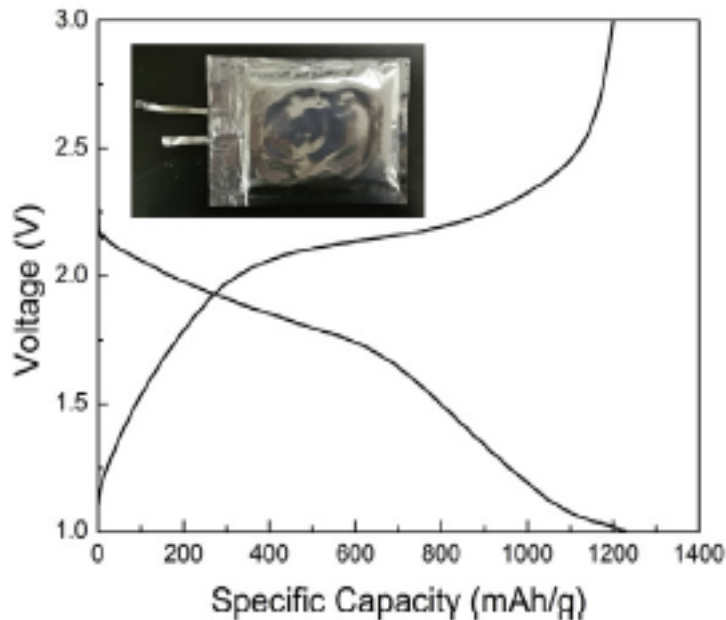
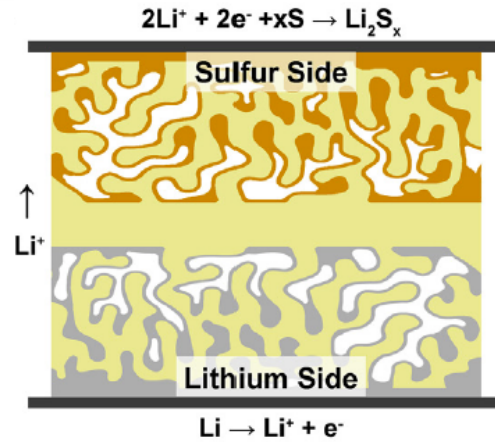
# Li Symmetric Half Cell with Trilayer SSE



(G. T. Hitz et al. Materials Today 2019, 22, 50-57)



# Li-S Full Cell with Trilayer SSE



(G. T. Hitz et al. Materials Today 2019, 22, 50-57)





# Trilayer SSE for Solid State Battery

- Nonflammable, mechanical strong structure
  - High current capability: cycled up to 10 mA/cm<sup>2</sup>
  - Low interfacial resistance: ASR 2 – 10 Ω-cm<sup>2</sup>
  - 1244 mAh/g S without polysulfide shuttling
  - 195 Wh/kg in large-format pouch cell
- a major first step to full scale solid state battery



# Solid Polymer Nanocomposite Electrolyte

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- **Polymer(s) as host matrix, incorporating ionic liquids, Li salts and nanomaterials**
  - ▶ Improve the ionic conductivity
  - ▶ Enhance the mechanical strength
  - ▶ Mitigate Li metal/polymer electrolyte interfacial impedance

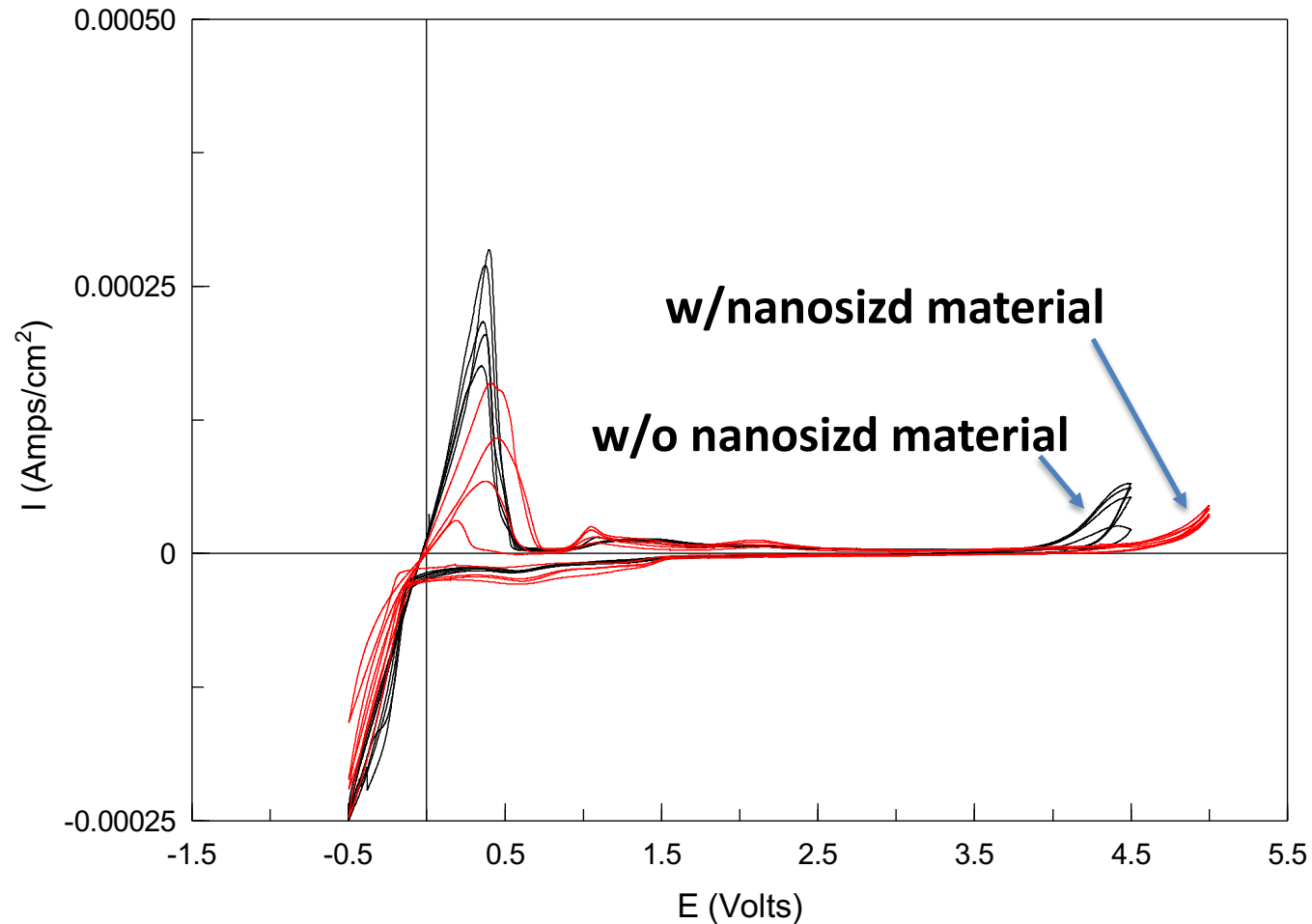


# Impact of Nanosized Material Filler on Solid Polymer Properties

	Ionic Conductivity at RT (S/cm)
w/o Nanosized Fillers	$1.40 \times 10^{-3}$
w/ Nanosized Fillers	$2.02 \times 10^{-3}$

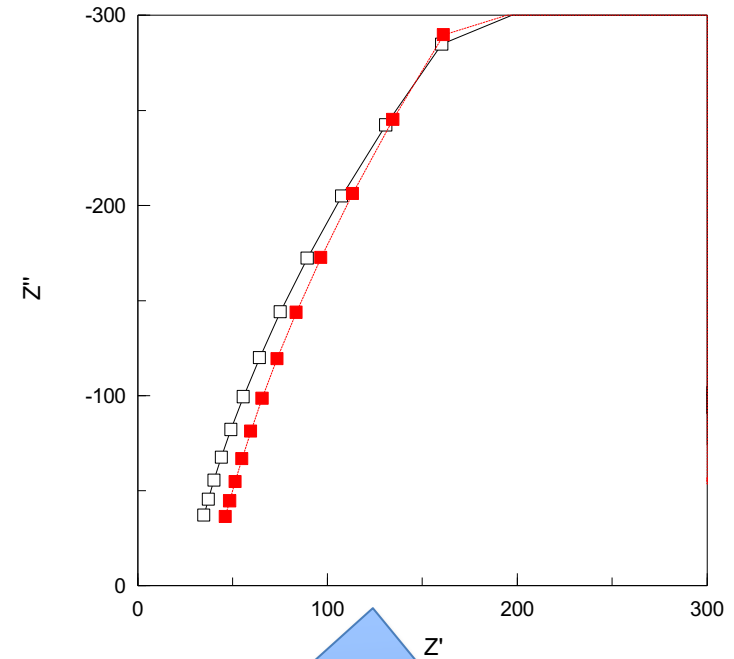
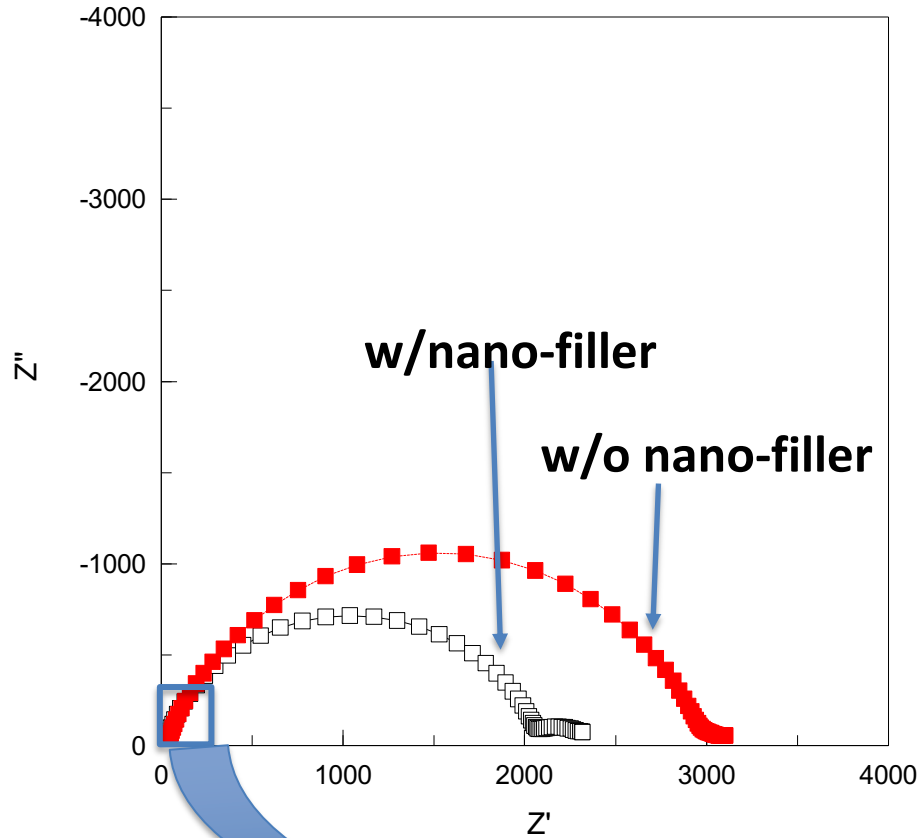


# Cyclic Voltammetry: Solid Polymer Electrolyte





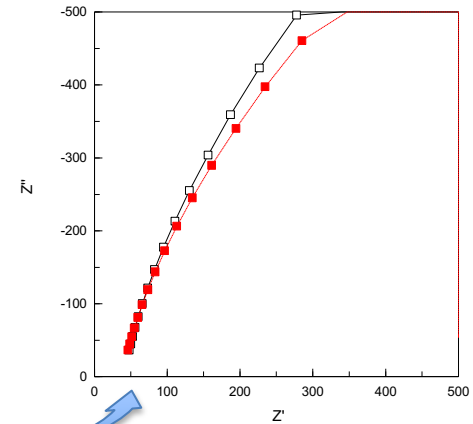
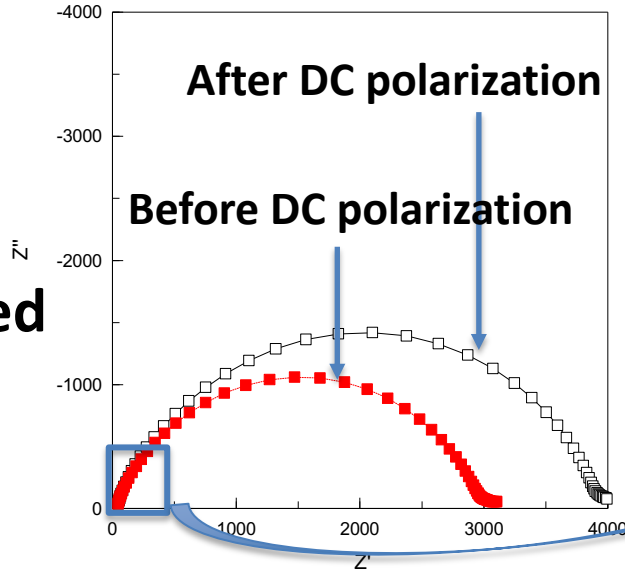
# Impedance of Li Metal/Solid Polymer Electrolyte Interface



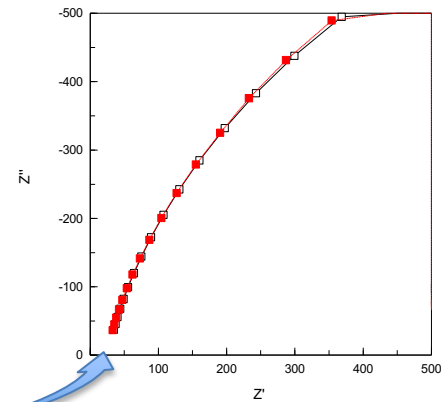
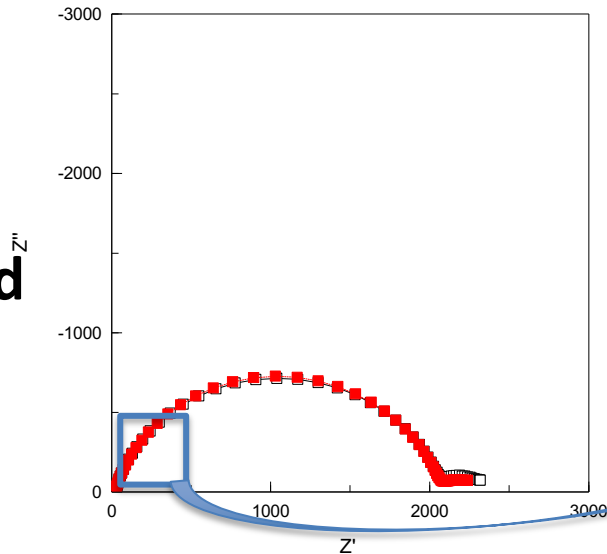


# Nano-filler Stabilizes Li Metal/Solid Polymer Interfacial Impedance

w/o  
Nanosized  
Fillers

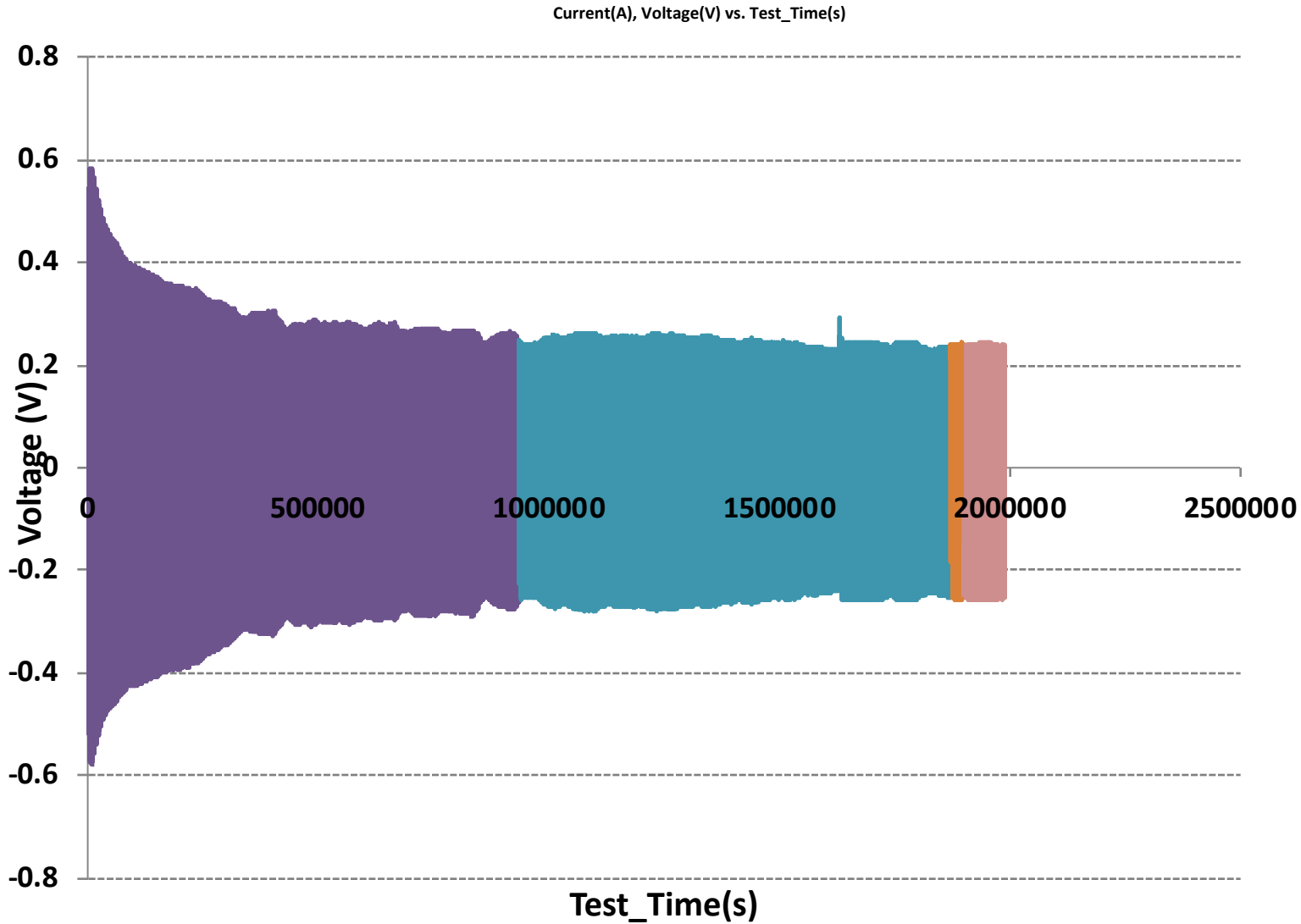


w/  
Nanosized  
Fillers





# Lithium Metal Cycling in Symmetric Cell Using Solid Polymer Nanocomposite Electrolyte

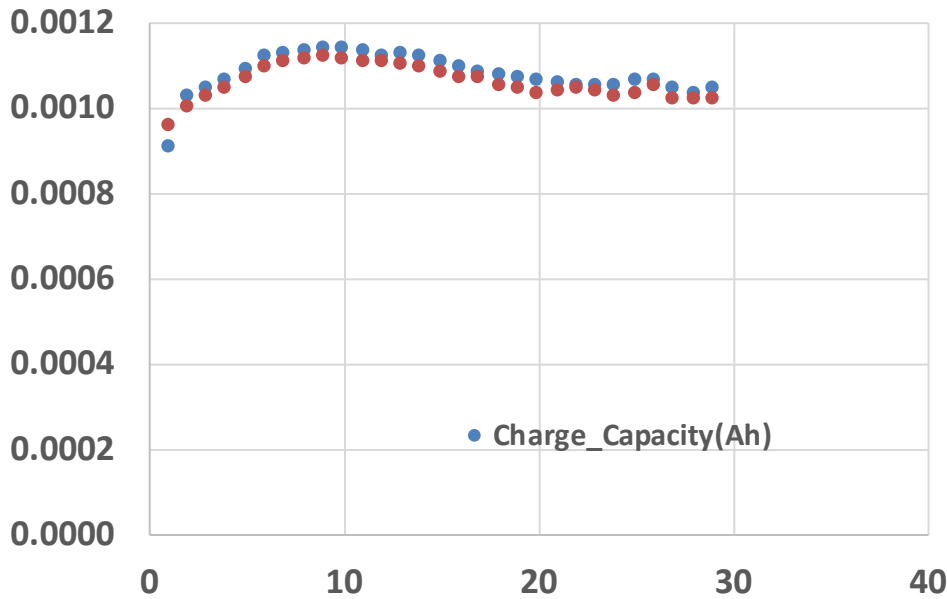


>1000 cycles at symmetric cells



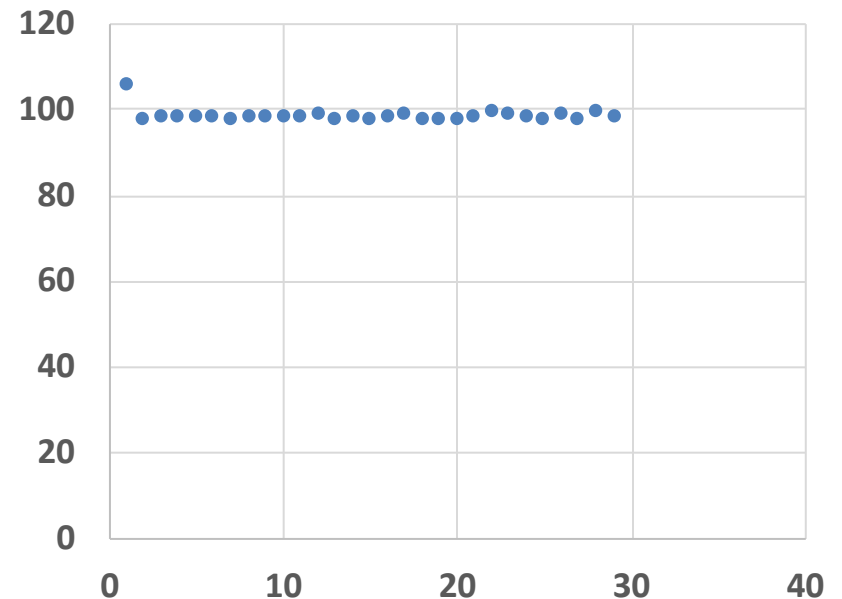
# Lithium Metal Cycling in Full Cell Using Solid Polymer Nanocomposite Electrolyte

Full Cell Cycling: NMC vs. Li Metal



Cycle #

Columbic Efficiency (CE)



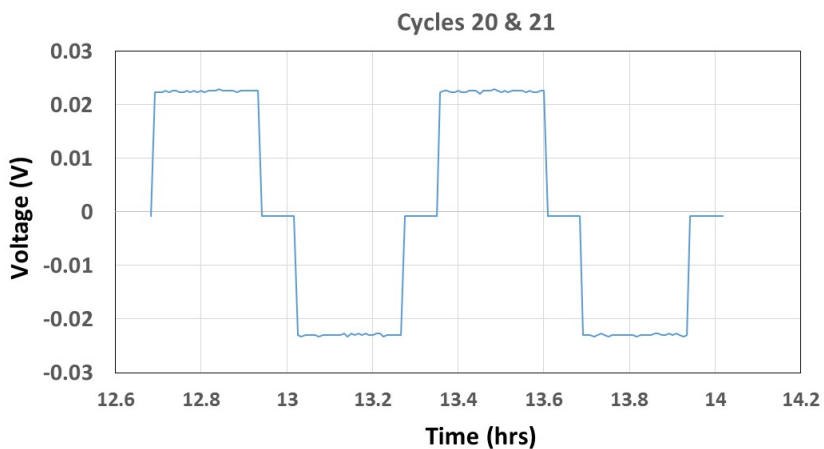
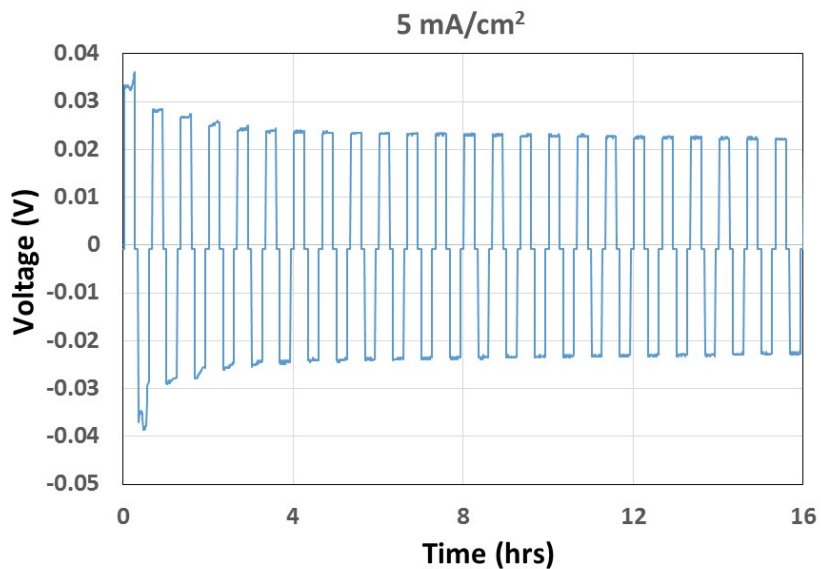
Cycle #



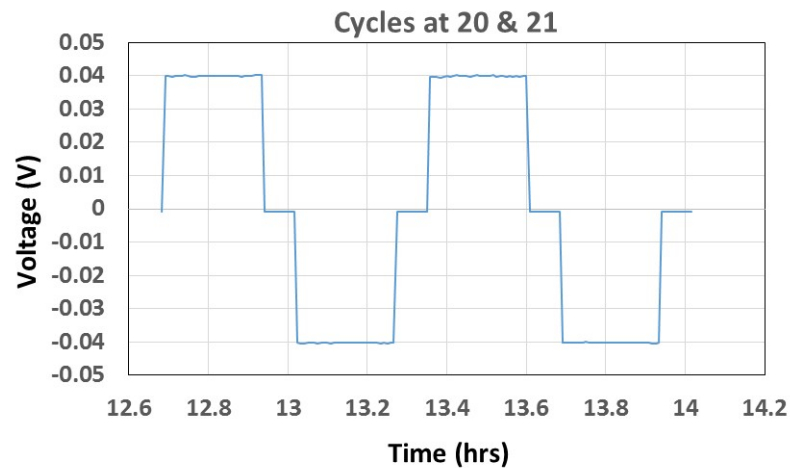
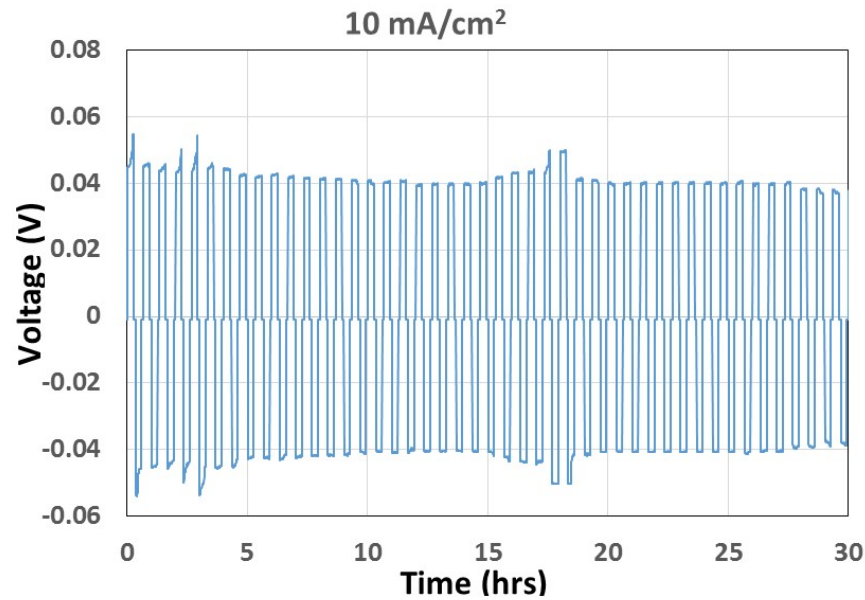


# Voltage Profile vs. Time at Symmetric Cell Cycling

## 5 mA/cm<sup>2</sup>



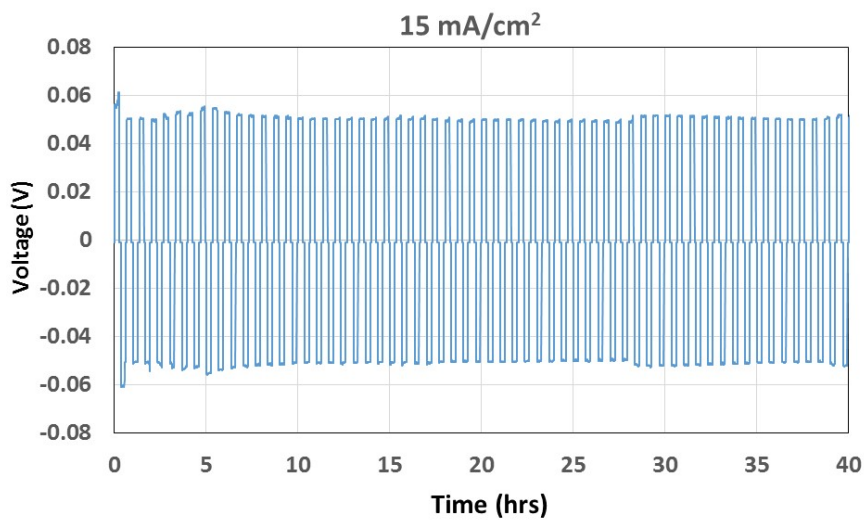
## 10 mA/cm<sup>2</sup>



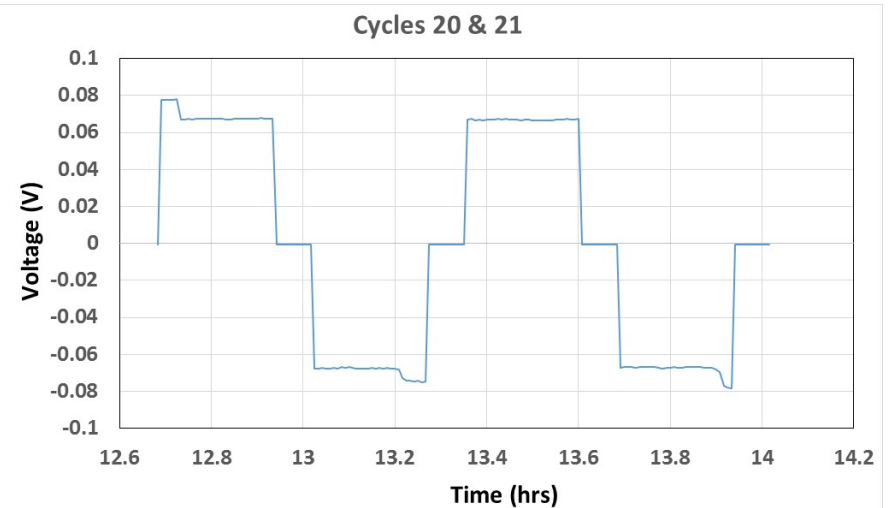
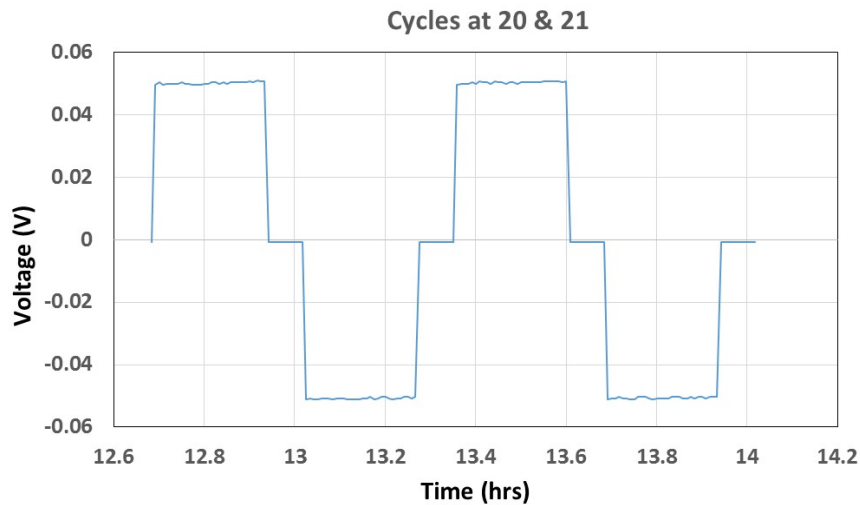
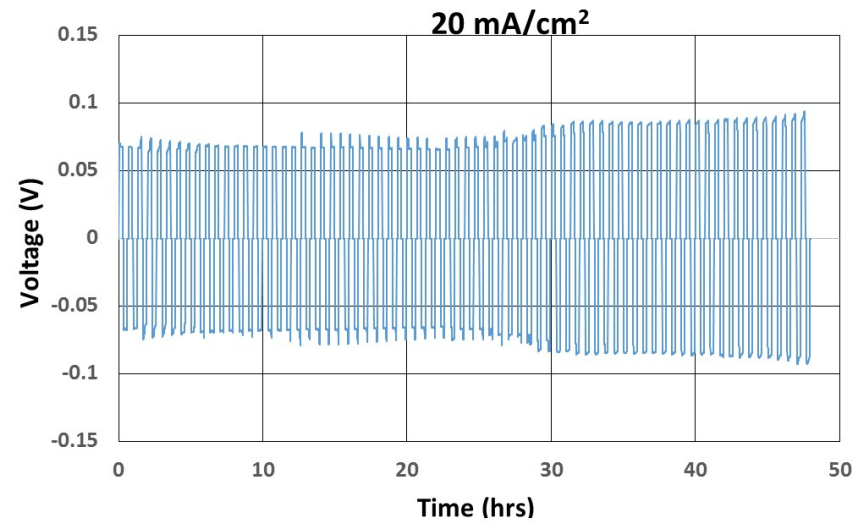


# Symmetric Cell Cycling w/Various Current Densities

## 15 mA/cm<sup>2</sup>

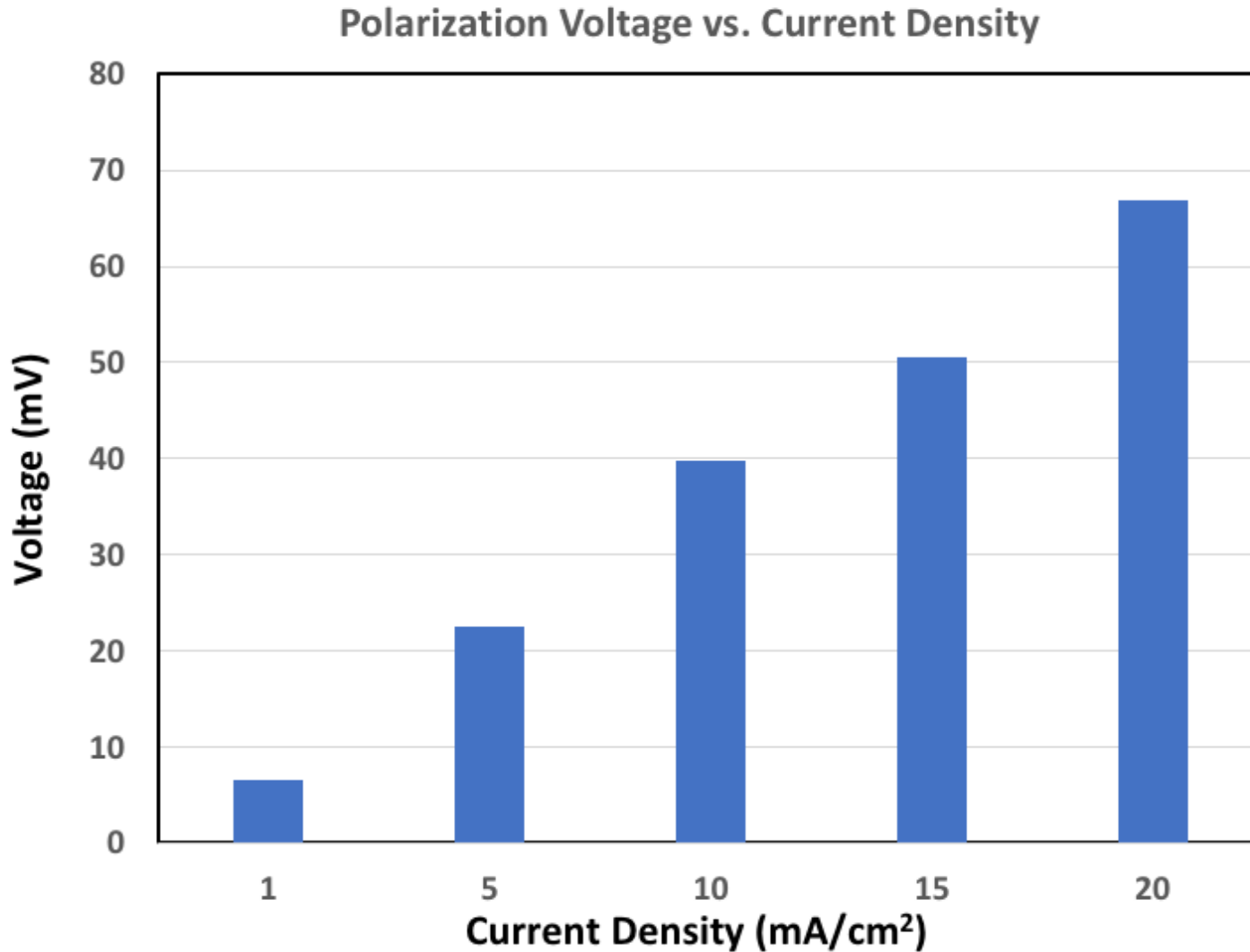


## 20 mA/cm<sup>2</sup>





# Polarization Voltage vs. Current Density (Li/Li Symmetric Cell)





# Solid Polymer Nanocomposite Electrolyte

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- Freestanding and flexible thin film
- High ionic conductivity at RT
- Nanomaterials help stabilize the Li/electrolyte interface
- Improve cycleability of Li plating/stripping at high current densities w/small overvoltage polarization (up to 20 mA/cm<sup>2</sup> with <90mV)
- Solid polymer nanocomposite electrolyte is an alternative and promising approach to enable Li metal cycling safely



# Summary/Next Steps

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- Solid state electrolyte is an attractive and promising approach to enable Li metal cycling to enhance the safety
- The low ionic conductivity and high interfacial resistance for solid state electrolytes have been addressed by approaches such as a microstructured trilayer solid electrolyte design or solid polymer nanocomposite electrolyte
- Optimization for the design of solid state electrolyte to maximize the energy density with practical electrode loading, scale up the fabrication, and reduction of production cost need to be addressed in the future development.



# Acknowledgements

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- UMD team of Garnet Electrolyte-Based Safe Li-S Energy Storage, led by Profs. Eric Wachsman (PI), Liangbing Hu (Co-PI) and Chungsheng Wang (Co-PI).
- NASA Advanced Energy Storage System (AESS) Project under Game Change Program
- NASA Center Innovative Fund (CIF) Program



**Thank you!**

**Any Questions?**