Polymer/ceramic Composite Electrolyte for Solid State Batteries

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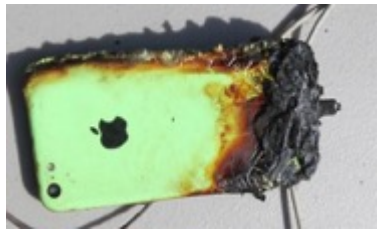
Safety Issues in Current Li-ion Batteries

Safety



How Lithium-Ion Batteries Turn Into Skin-Searing Firebombs

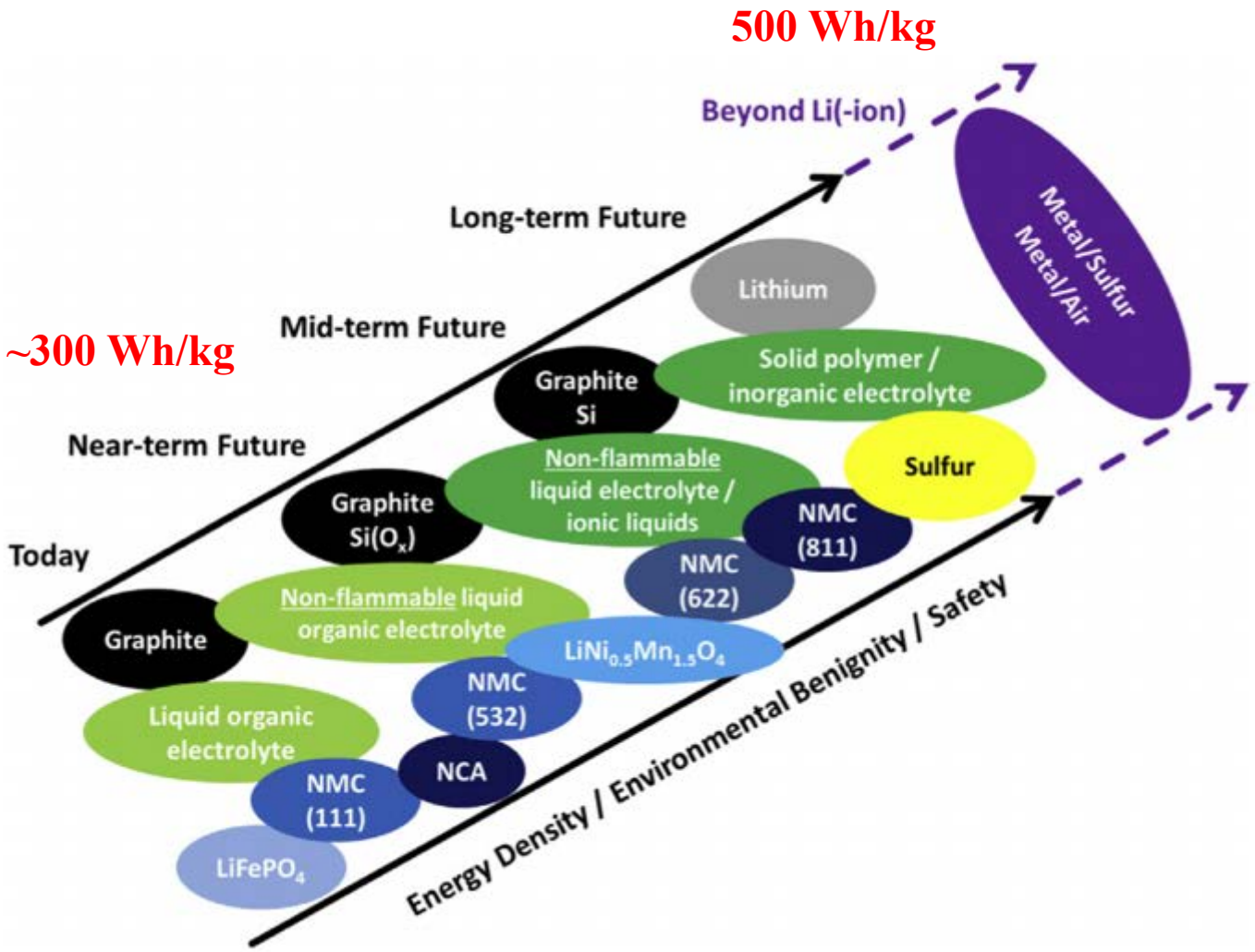
Burning concern: Energy storage industry battles battery fires

Morning Mix

Woman's headphone batteries exploded on flight to Australia, causing burns

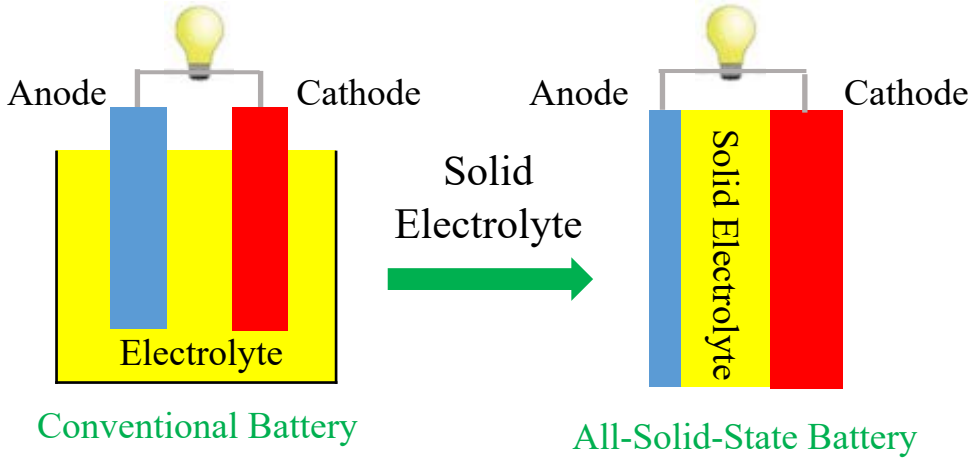
Hyperdrive

Explosions Threatening Lithium-Ion's Edge in a Battery Race



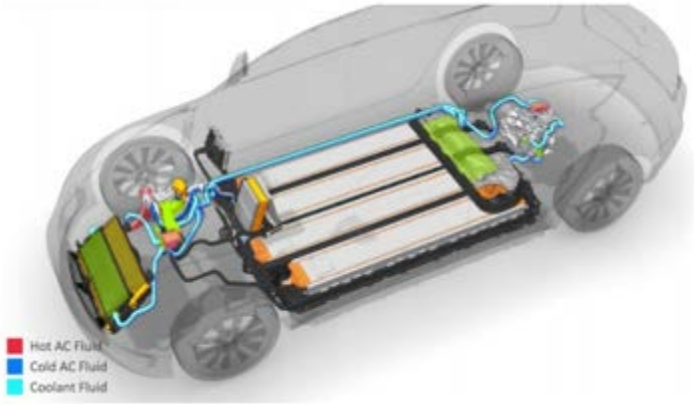
Journal of Power Sources 382 (2018) 176–178

Energy Density of Solid-state Batteries

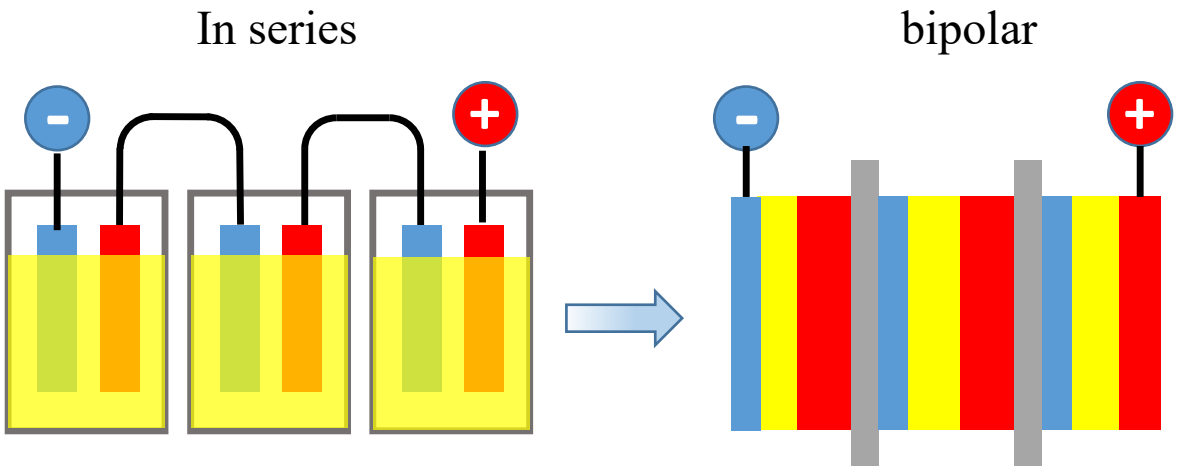


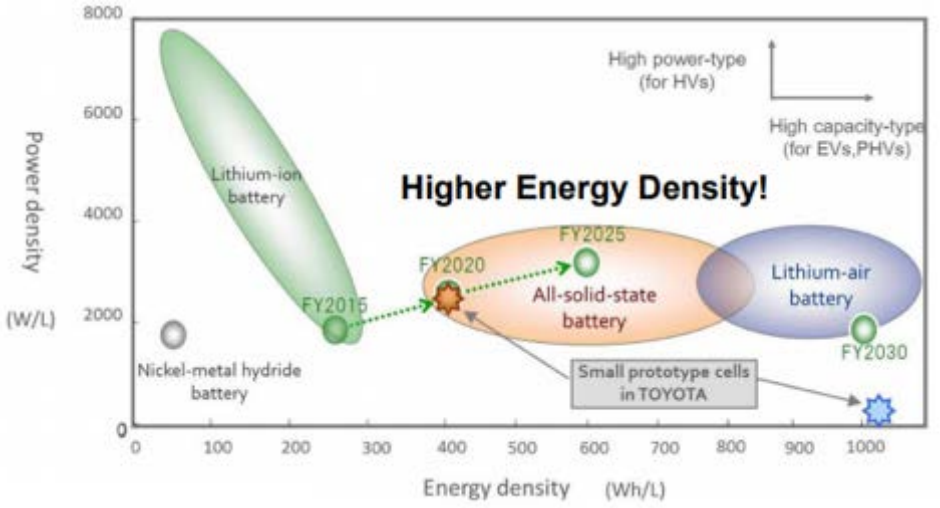
Graphite:
372 mAh/g
820 mAh/cc

Lithium:
3860 mAh/g
2061 mAh/cc



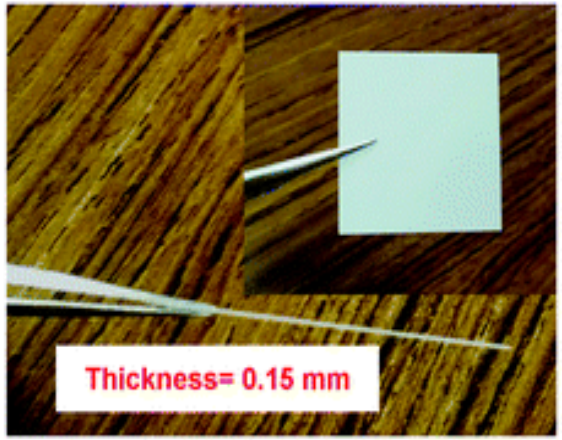
- Simplified thermal management system

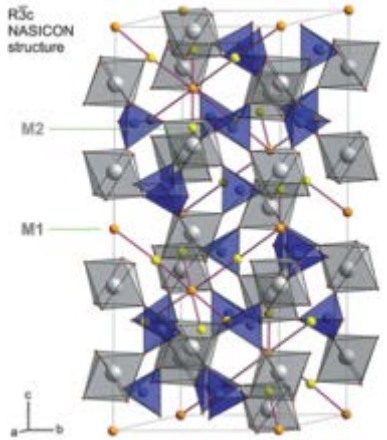




Solid Electrolyte Classes

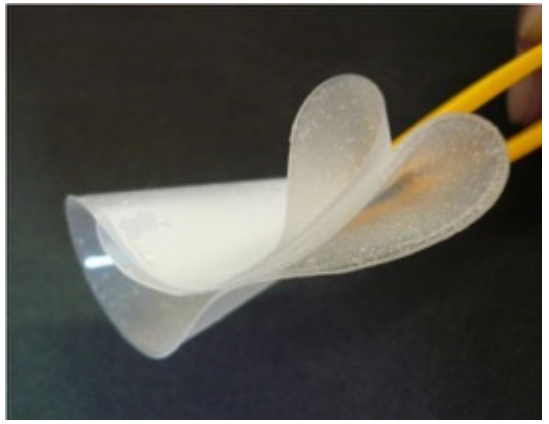
Ceramic Electrolyte

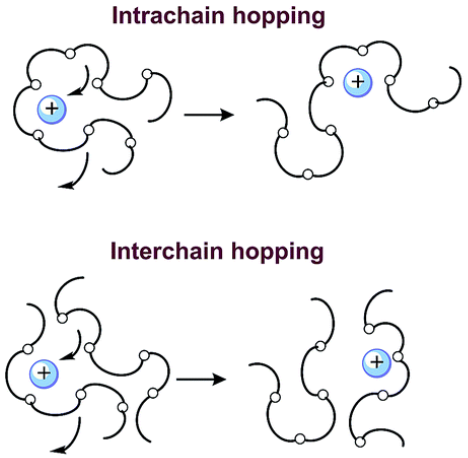




$Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP),
$Li_7La_3Zr_2O_{12}$ (LLZO),
$Li_7P_3S_{11}$ (LPS)
$Li_{10}GeP_2S_{12}$ (LGPS)

Polymer Electrolyte





Poly(ethylene oxide)

Polycarbonates (e.g. polyethylene carbonate)

Poly(FEC)

Polyacrylonitrile (PAN)…..

Solid Electrolyte Classes

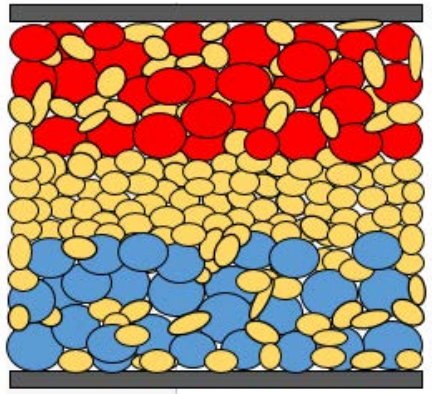
	Conductivity (S/cm)	Cathode Stability	Anode Stability	Processing / Scalability	Air Stability
Sulfides (e.g. $Li_7P_3S_{11}$)	10^{-3} – 10^{-2} at 25 °C				
Oxides (e.g. LLZO)	10^{-4} -10^{-3} at 25 °C				
Polymer (e.g. PEO, PAN)	10^{-5} -10^{-4} at 25 °C, 10^{-3} at 60 °C				

Good OK Not good

Recent Progress

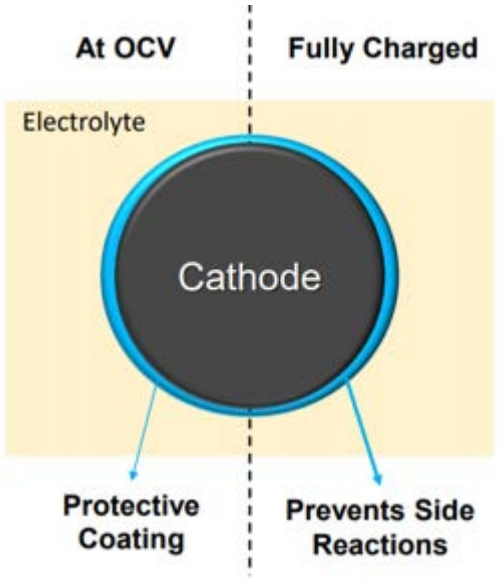
Toyota
NMC/sulfide/graphite

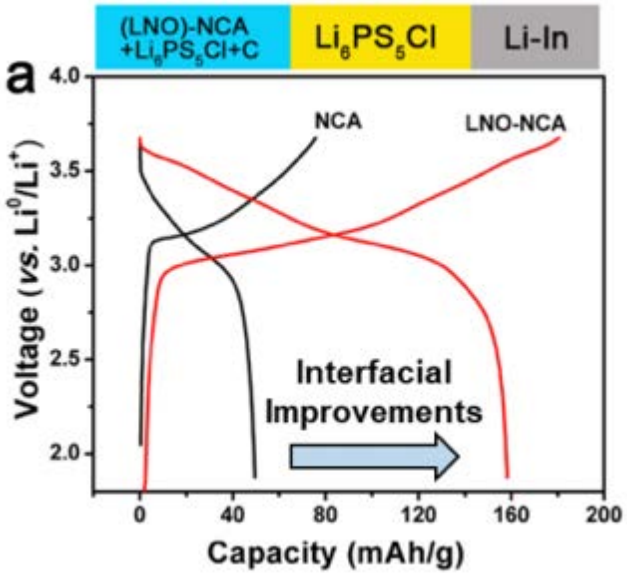
Cathode



Anode

High power
Wide temperature range





Anode stability: Lithium → Graphite or Indium

Potential Challenges:

Scalability, Air stability, Pressure (5-20 MPa)?

http://www.diandong.com/news/9985.html
https://en.wikipedia.org/wiki/Bollor%C3%A9_Bluecar

Courtesy by Shirley Meng

Recent Progress

Bolloré blue car:
$LiFePO_4$/PEO/Li metal batteries

Challenges:

- Working at 70-90 °C
  (low conductivity at RT)
- Low specific energy (~100 Wh/kg)
- PEO is not stable with 4 V cathode

Potential Solutions:

- Interfacial stabilization
- New polymer systems

http://www.diandong.com/news/9985.html
https://en.wikipedia.org/wiki/Bollor%C3%A9_Bluecar

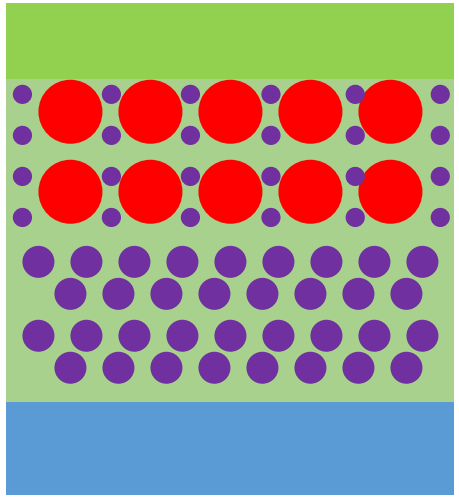
Solid State Batteries with Composite Electrolytes

Al

NMC Cathode

Ceramic/ polymer electrolyte

Lithium

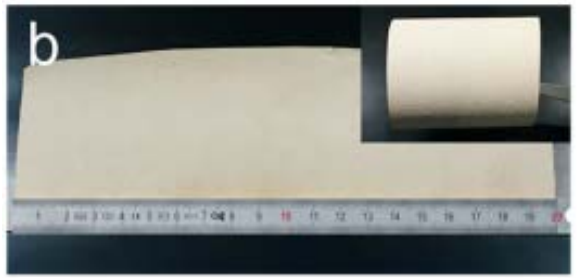


Advantages:

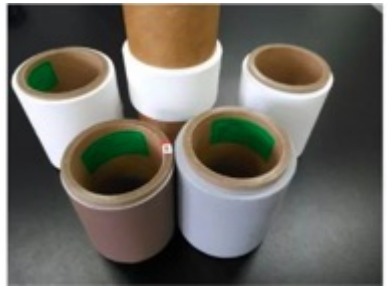
- Easy to process, ultrathin (10-20 μm)
- Enhanced ionic conductivity
- Ceramic fillers suppresses lithium dendrite
- Polymer wets electrode/electrolyte interface.
- A balance between performance & thermal stability

Oxide/PEO (Yang)

Sulfide/polymer (Chen and Meng)

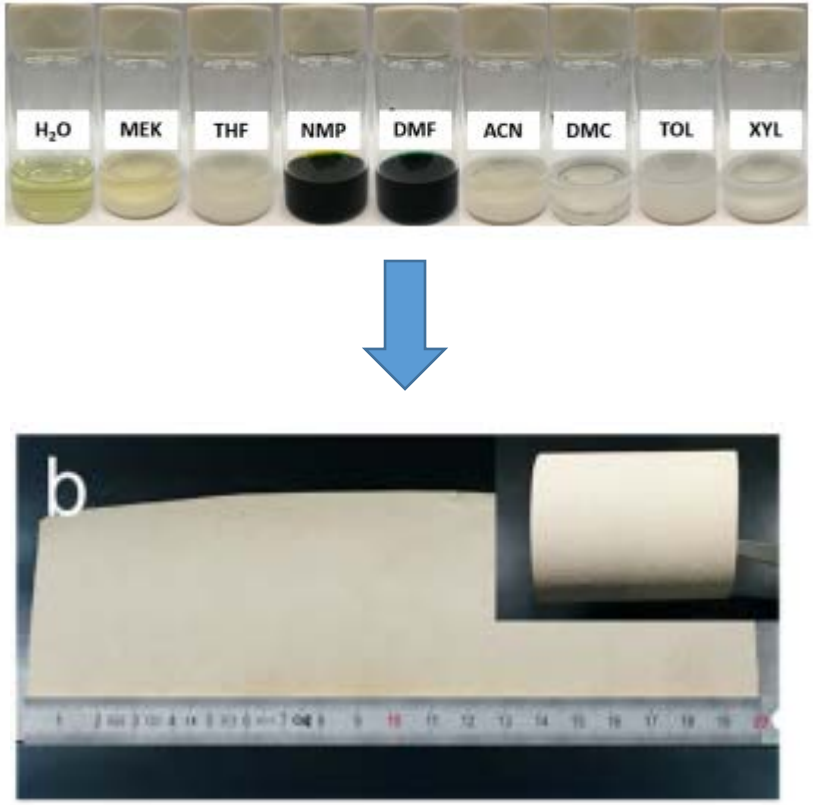


Oxide/Separator (Welion Inc)

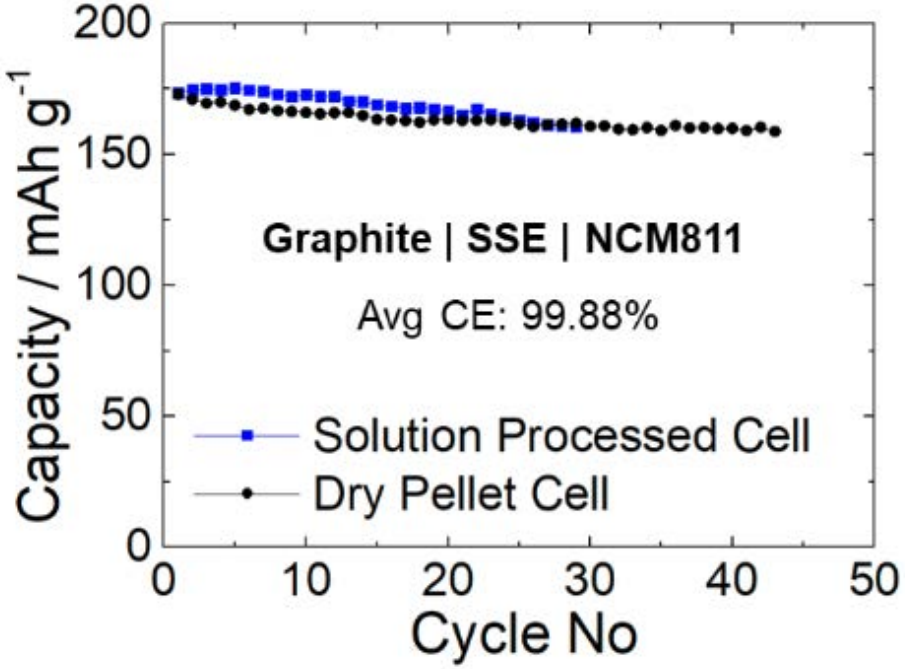


Zheng Chen & Shirley Meng, ACS AEM, 2, 6542 (2019)
Yuan Yang Nano Lett. 17, 3182 (2017), Welion Inc

Polymer/Sulfide Composite Electrolyte



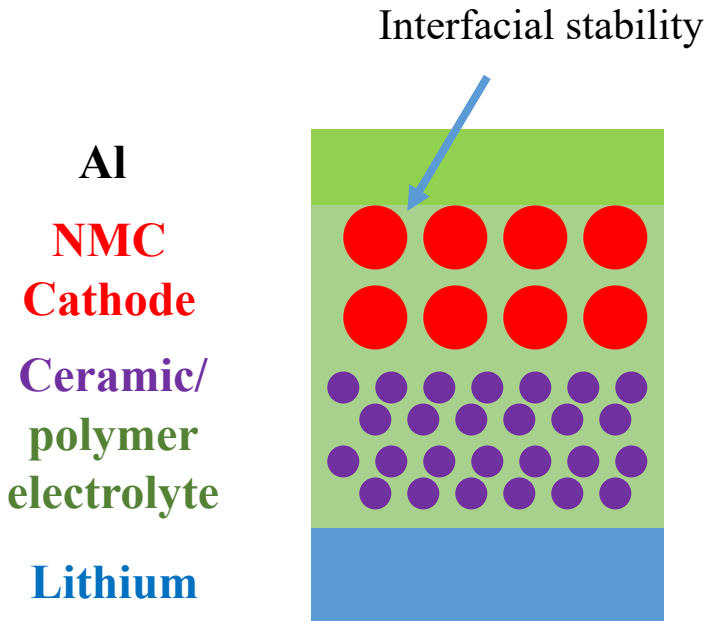
5 % Polymer/ 95% $Li_7P_3S_{11}$ electrolyte

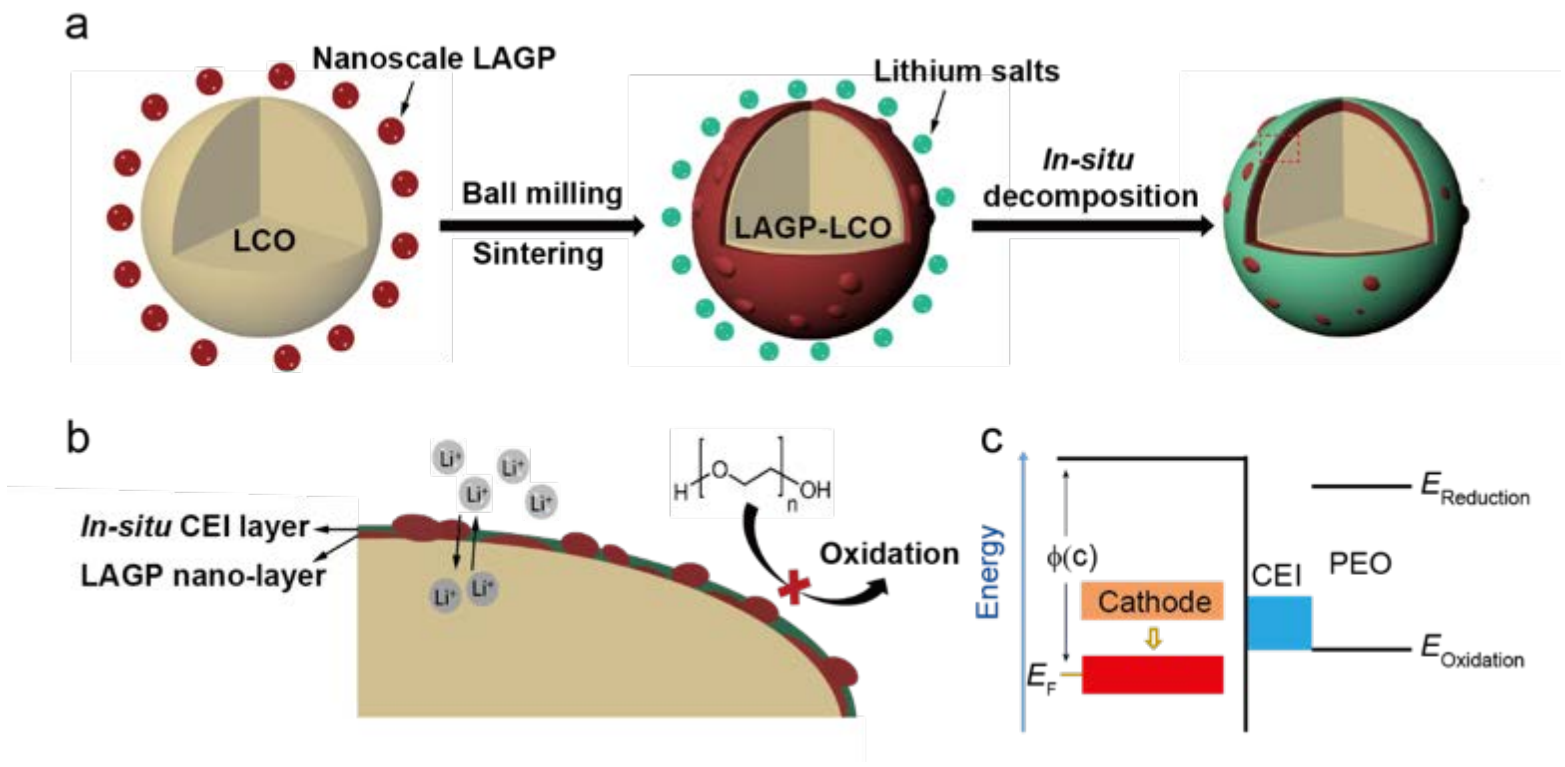


Courtesy by Zheng Chen

Zheng Chen & Shirley Meng, ACS AEM, 2, 6542 (2019)

Double Layer Coating to Stabilize 4 V cathode/PEO interface





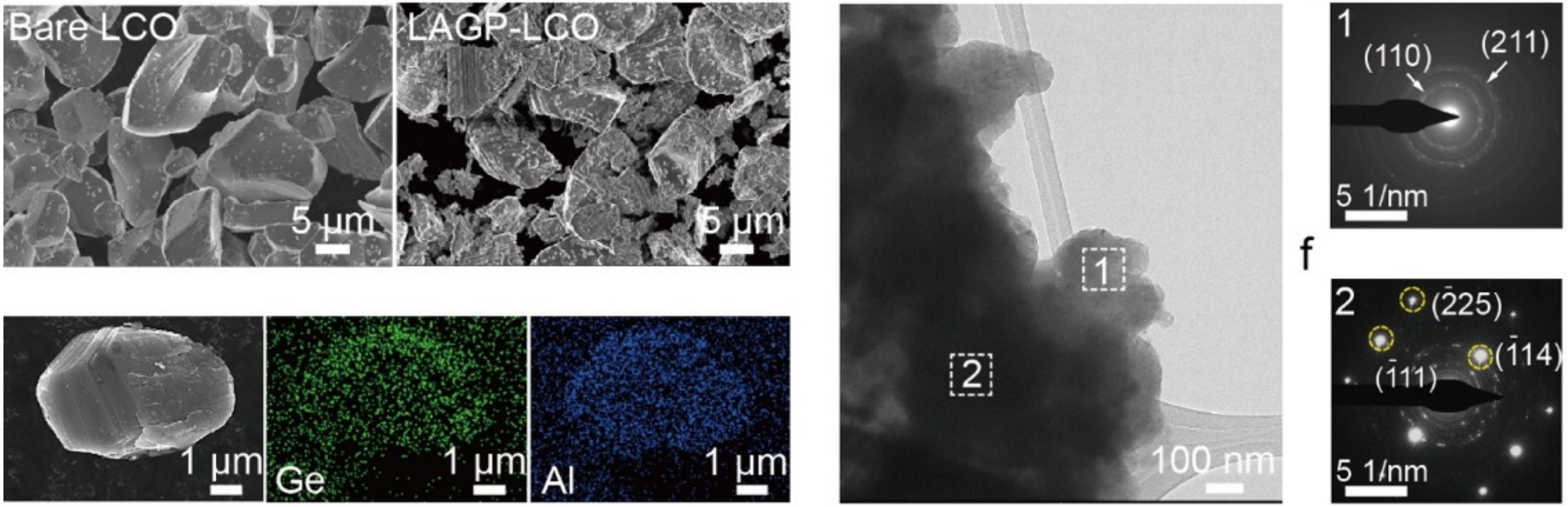
LAGP: $Li_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$

LAGP suppresses the decomposition of PEO,

The weak points are further protected by salt decomposition (e.g. LiDFOB, LiBOB)

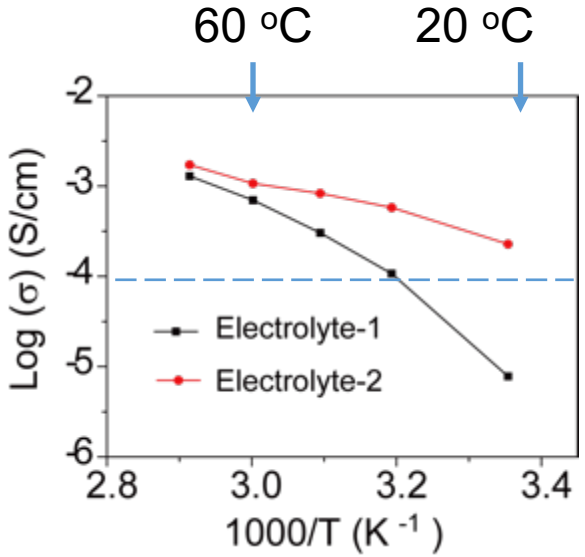
Yuan Yang et al., accepted

LAGP coating on $LiCoO_2$



Granular LAGP coating is formed on LCO by ball milling

PEO and PEO/LLZO electrolyte



Liquid electrolyte

1 M $LiPF_6$ in ECDEC

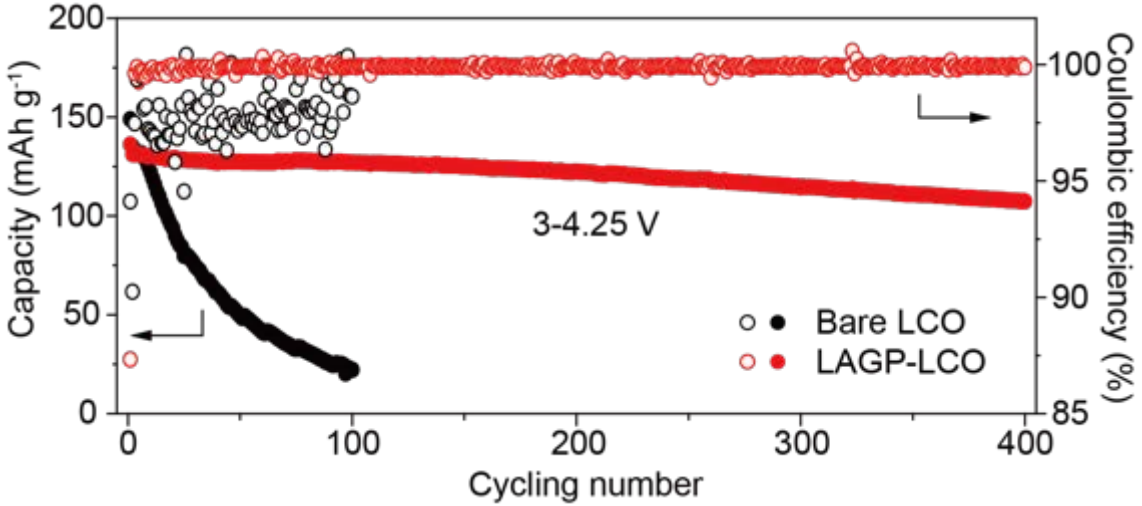
Electrolyte 1: 0.5 M Tri-salt in PEO-10K + PEG500 (1:1)

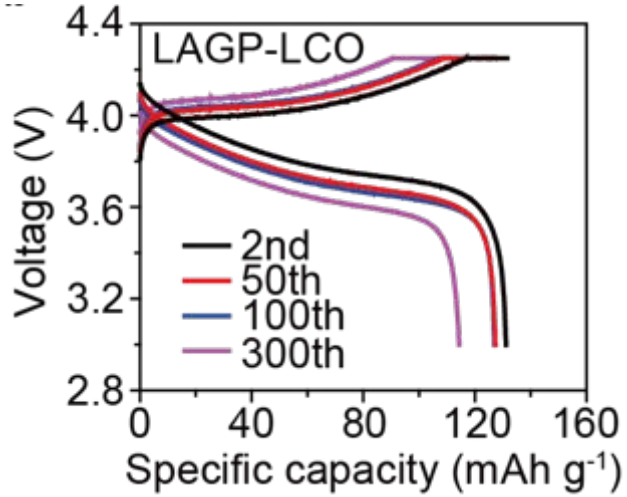
Electrolyte 2: Electrolyte 1 + LLZO

Tri-salt = LiTFSI+LiBOB+$LiPF_6$

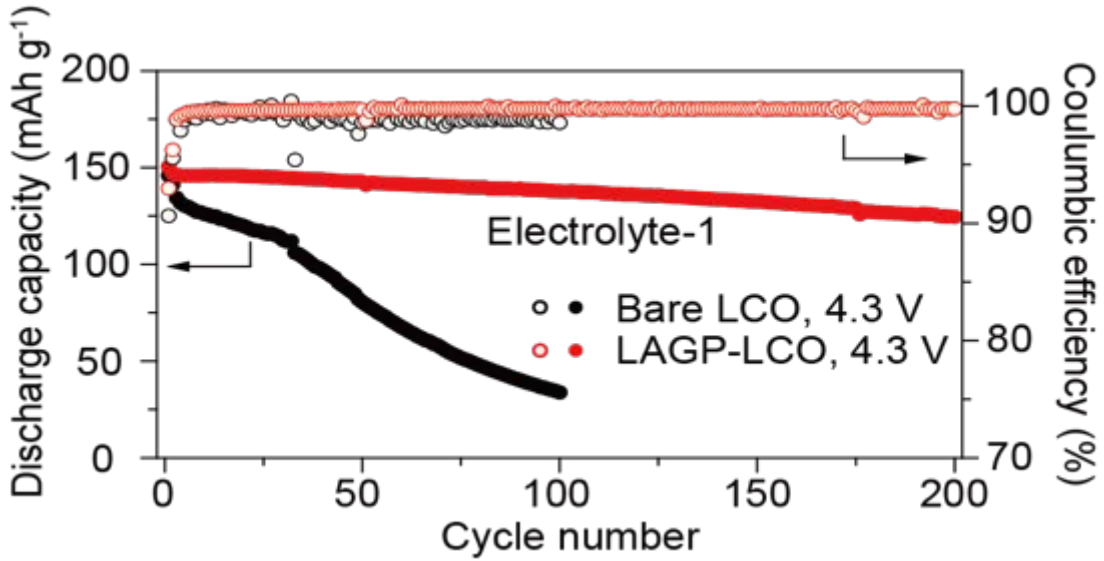
Ignition Test

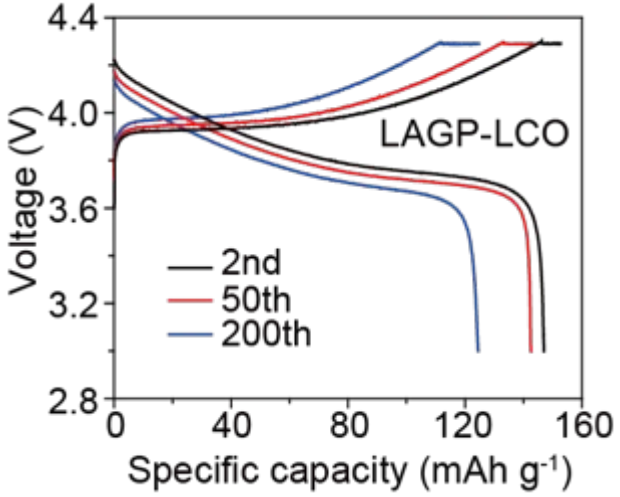
Cycling performance of $LiCoO_2$/PEO/Li cell at 60 °C





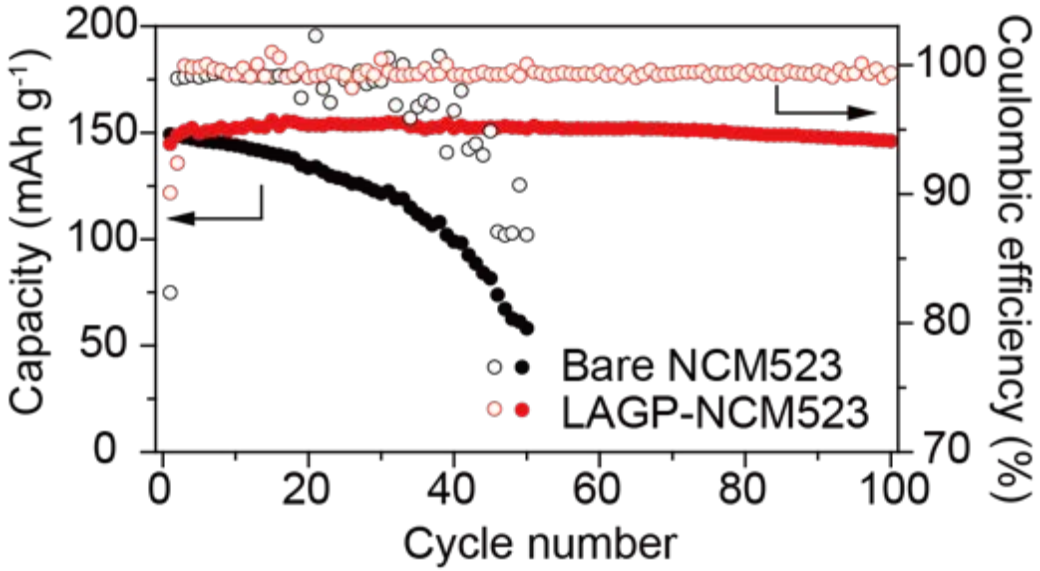
1 mAh/cm² 3.0 - 4.25 V,
82% / 400 cycles,
CE is ~99.9%
C: C/3, DC: C/2





1 mAh/cm² 3.0 - 4.3 V,
85% / 200 cycles,
CE is ~99.8%
C: C/3, DC: C/2

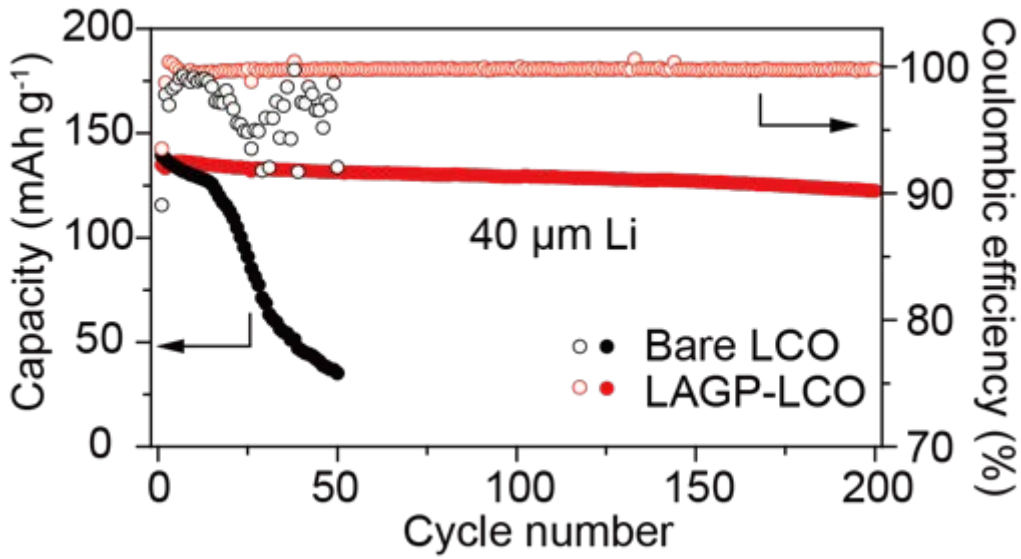
Performance with NCM and thin lithium



NCM523/Li (3-4.25 V)

1 mAh/cm^2 0.3 C, 60 ^{o}C

93.8%/100 cycles

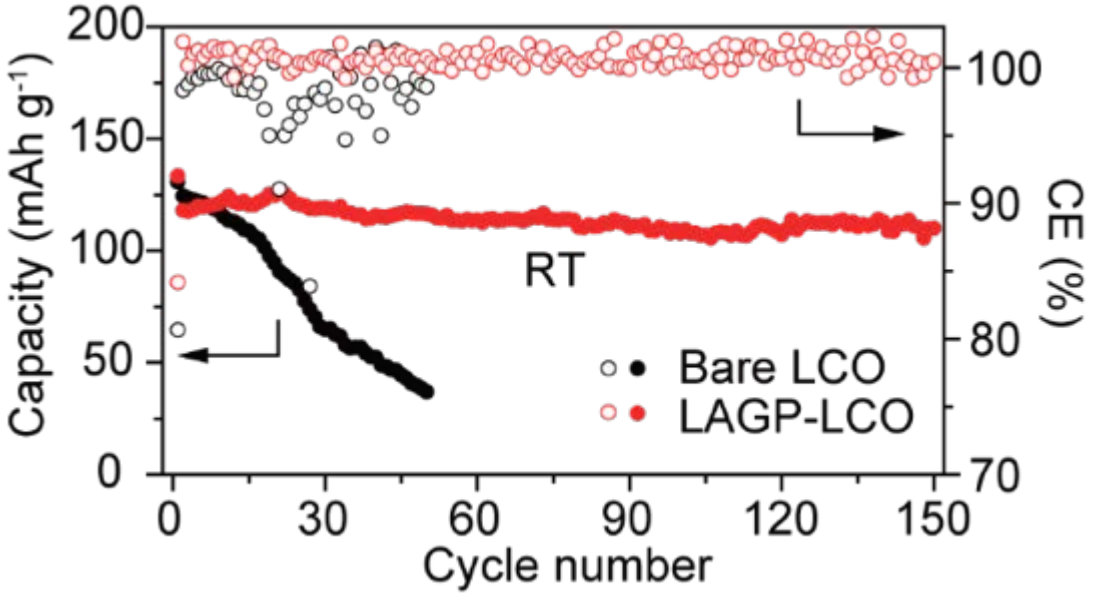


LCO/Li

1 mAh/cm^2 0.3 C, 60 ^{o}C

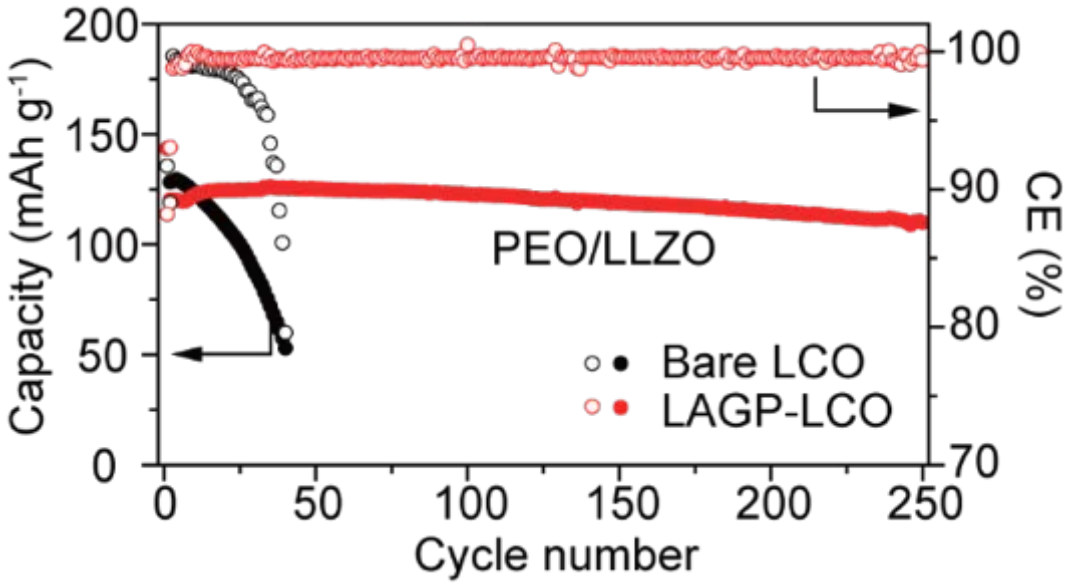
88%/200 cycles

Performance at RT and Composite Electrolyte



RT, 0.5 mAh/cm^2
0.2 C, **90.8%**/100 cycles

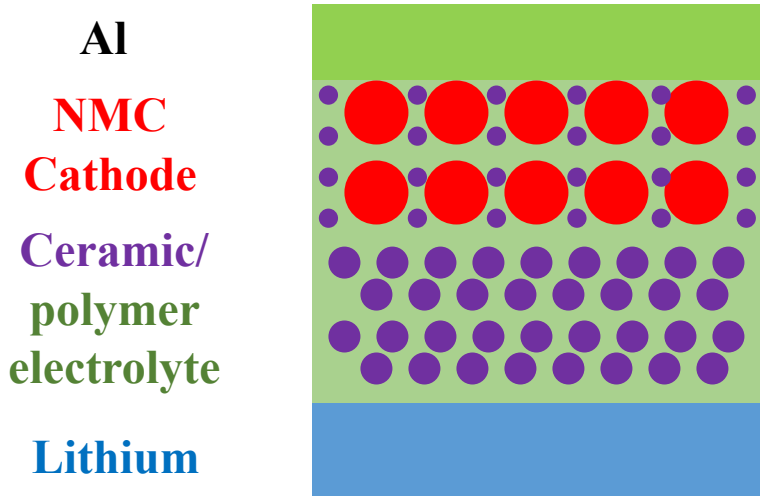
25 wt% EC/PC plasticizer



60 °C, 1 mAh/cm^2
0.5 C, **87.2%**/250 cycles

PEO/LLZO electrolyte

Summary



- Scalability, interfacial stability/impedance, conductivity are critical factors to evaluate solid state batteries
- Composite electrolytes could combine advantages of both ceramic and polymer electrolytes
- PEO/4 V cathode is a possible combination.

Acknowledgement

THANK YOU!

Questions?

Collaborator

Xi Chen (Columbia)
Xavier Roy (Columbia)
ei (Columbia)
Li (CUNY)
ui Xiao (BNL)
anari Waluyo (BNL)
n Lin (BNL)
Xiaoqing Yang (BNL)

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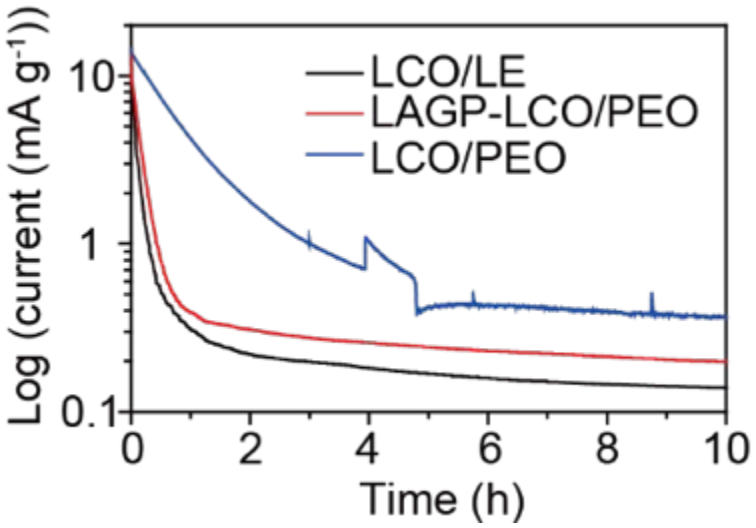
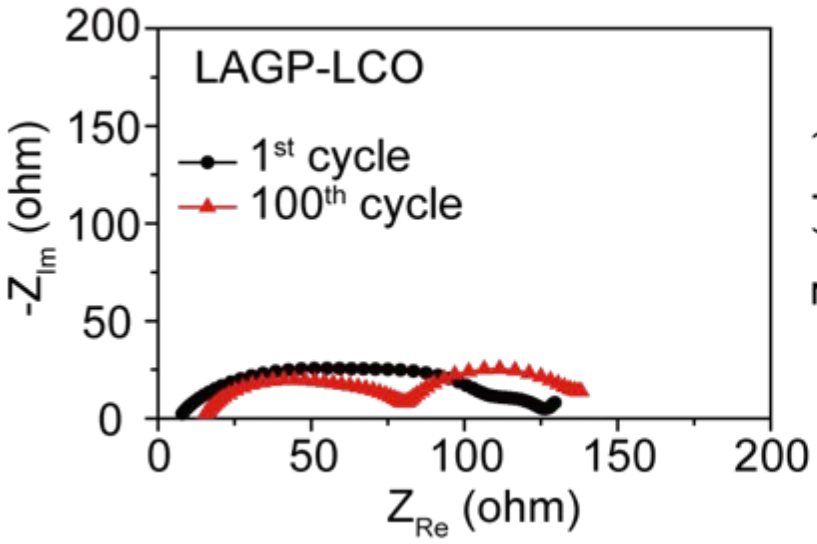
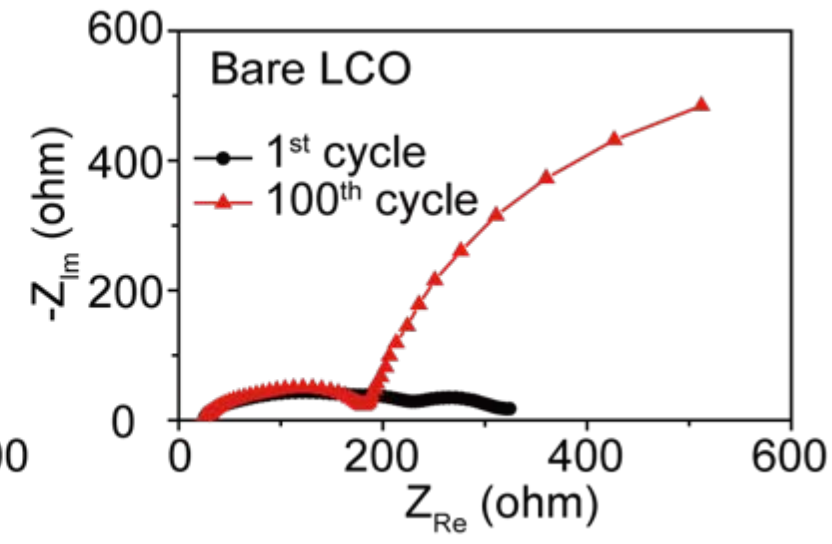
Understanding the Protection Mechanisms







- Leakage current in LAGP-LCO approaches carbonate electrolyte (LE) when held at 4.3 V
- EIS shows that the degradation arises from the ion diffusion in the cathode.

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