SAND2017-0810C

Monocarba-closo-polyborate electrolytes for all solid state Li-ion batteries

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1- Sandia Nationa Labs, Livermore, CA; 2 – NIST, Gaithersburg, MD

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Li-polymer batteries deliver high energy, power density

0.4 cm thick
52.3 mAhrs/cm^2
0.26 W/cm^2
>500 Cycles

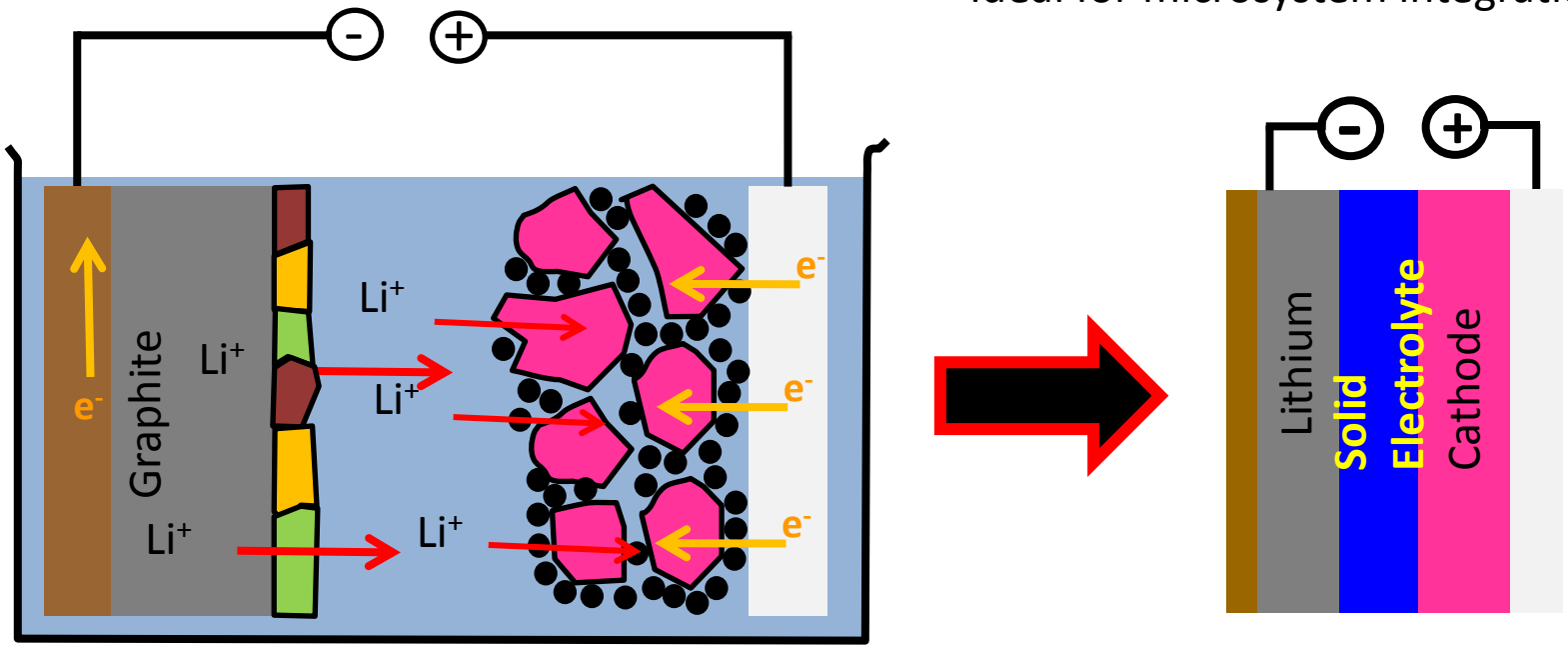
Alaska Airlines Credit Card Reader Fire Causes Emergency Landing

IMPACTING TRAVEL | PATRICK CLARKE | OCTOBER 12, 2015

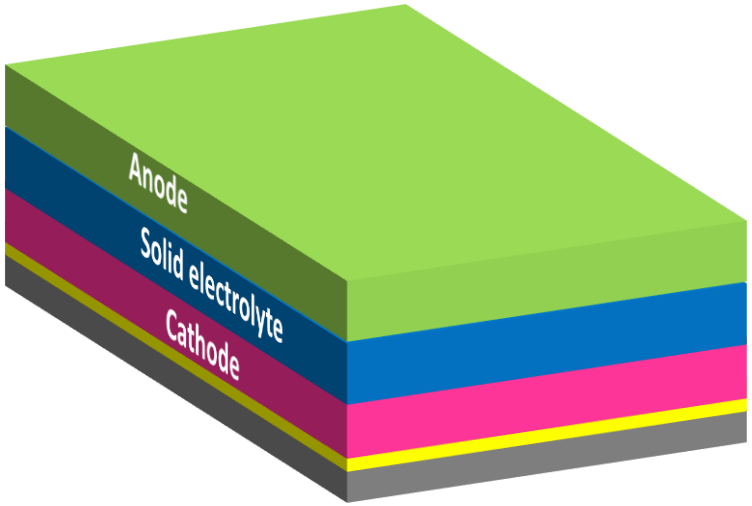
Liquid electrolytes limit battery lifetime, T, V_{OC}, safety

All solid state batteries can:

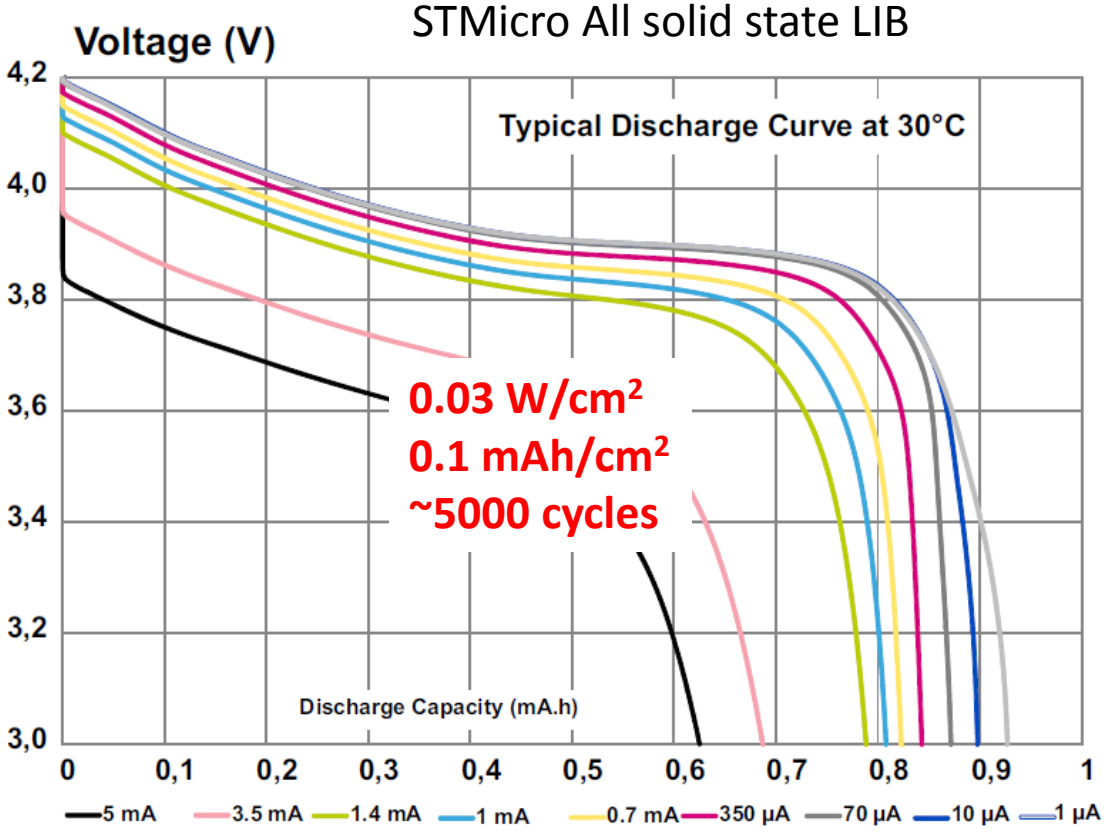
- Simplify packaging, increase Wh/L
- Operate at higher T
- Ideal for microsystem integration



Thin Film LIB power, energy limited by Li diffusion

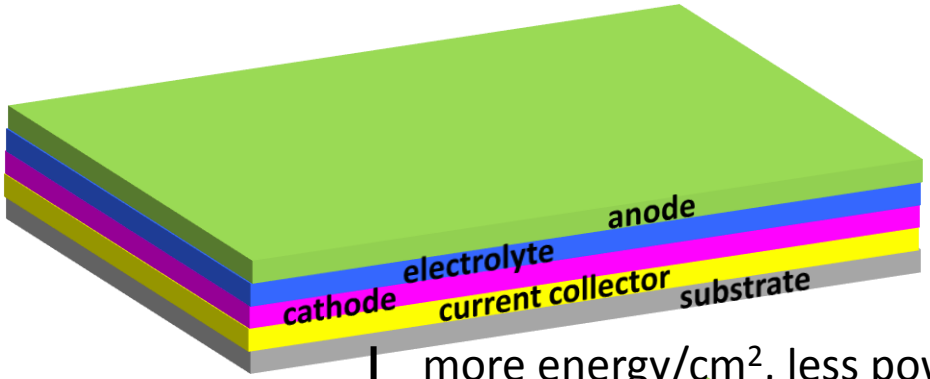


STMicro All solid state LIB

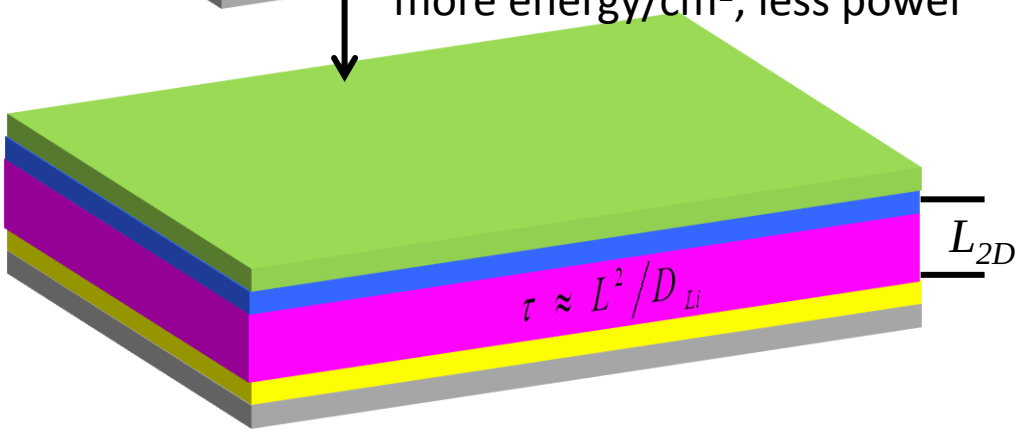


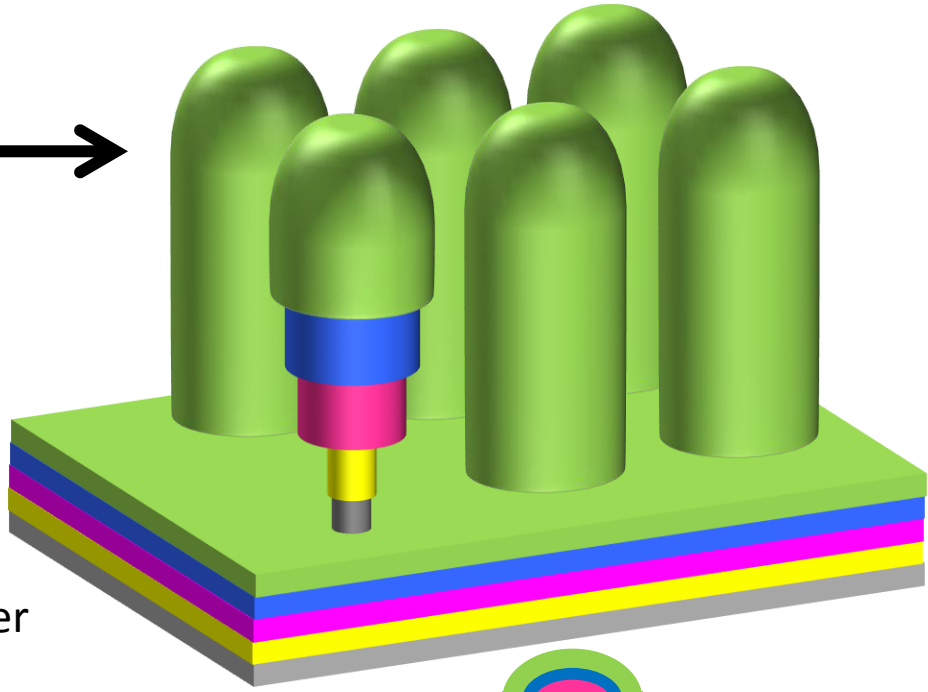
Increase energy, power density w/out new materials?

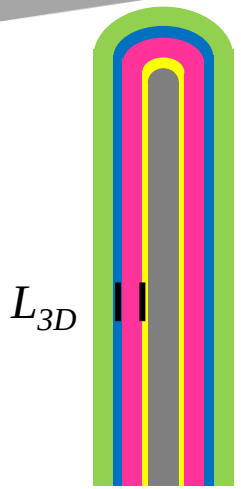
- *Decrease diffusion length*
- *Increase interface area*



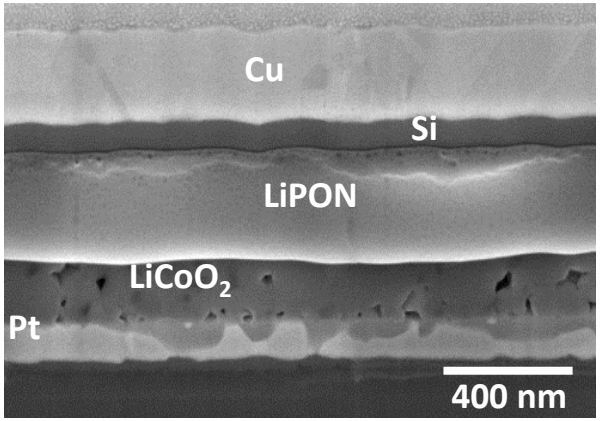
more energy/cm^2, less power

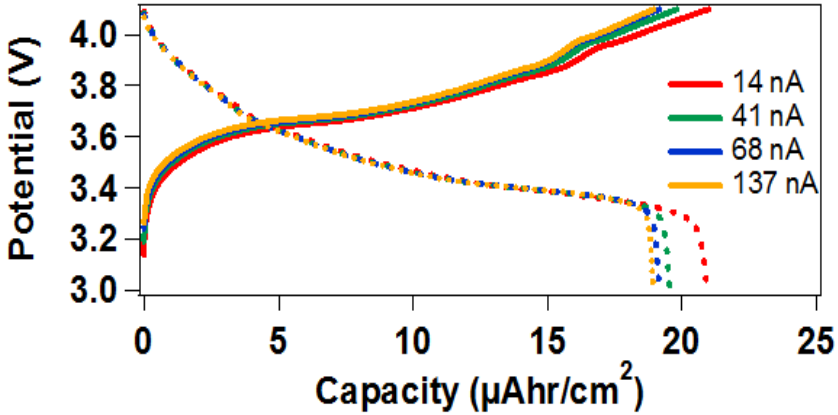


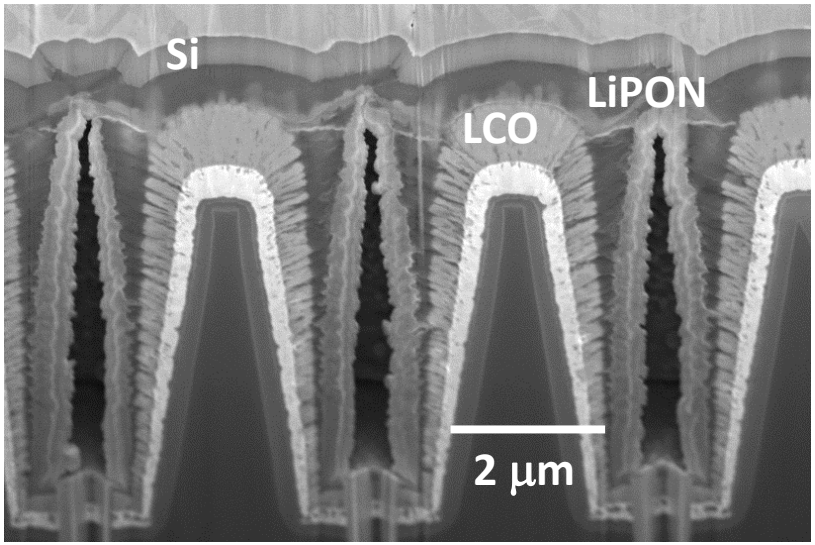


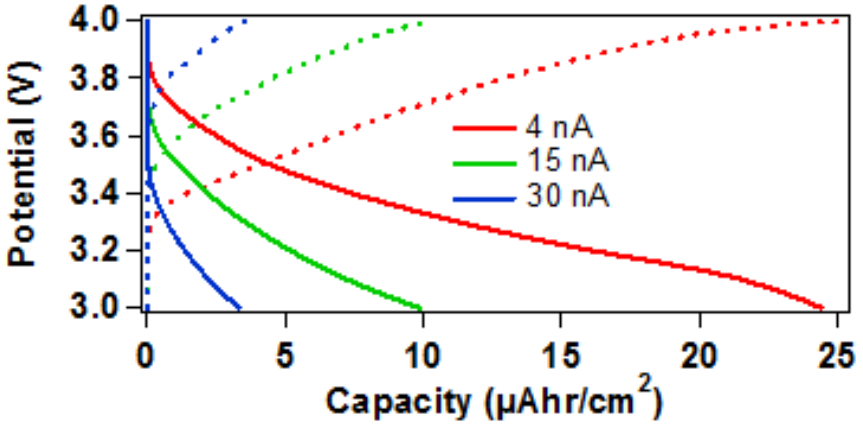


Non-uniformity, low electrolyte conductivity degrade 3D SSLIB performance

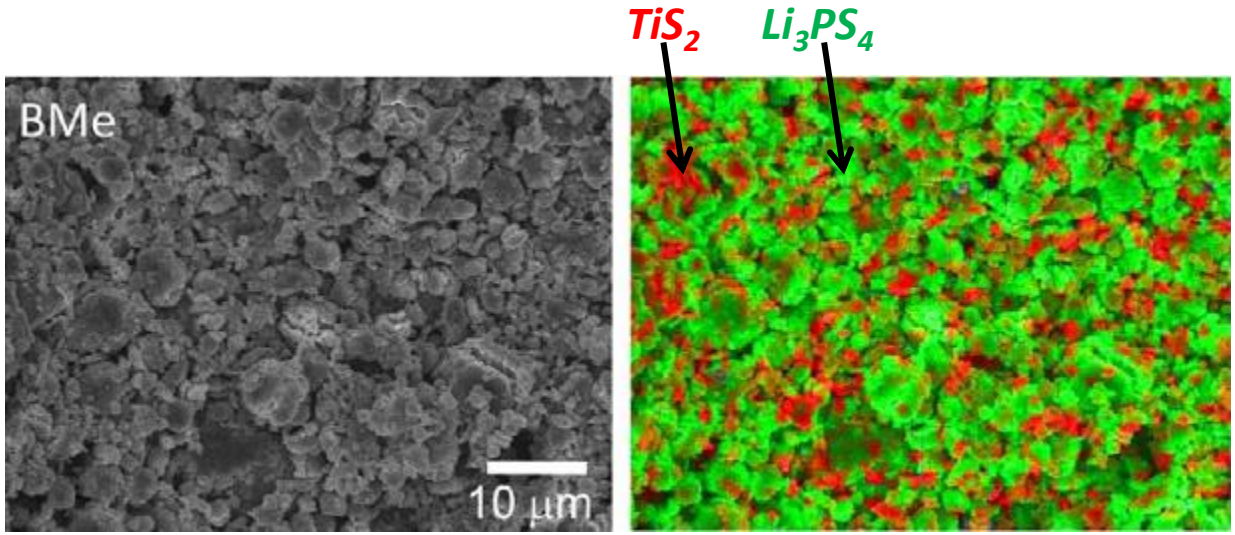




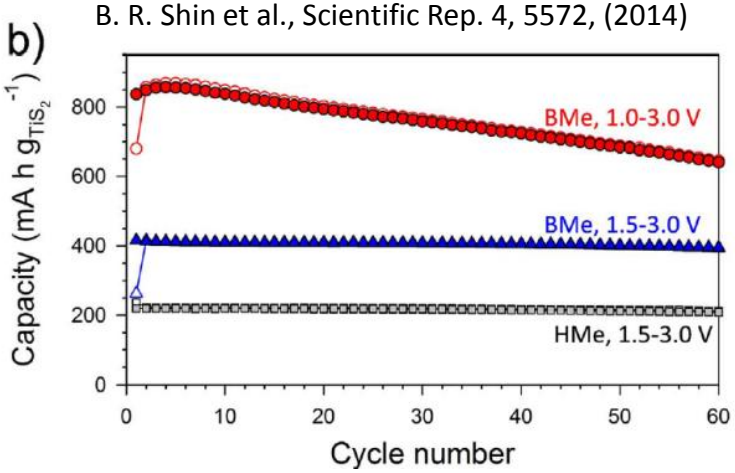


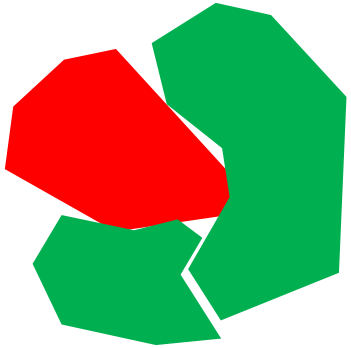


Heterogeneity, interface quality affect composite electrodes

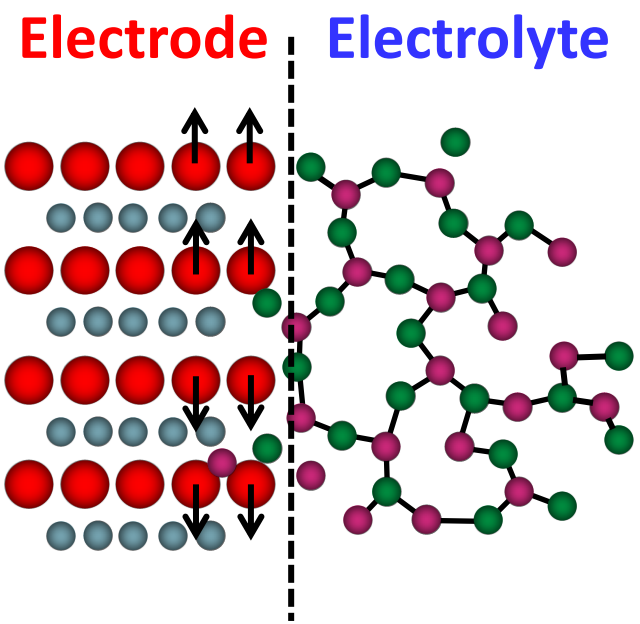


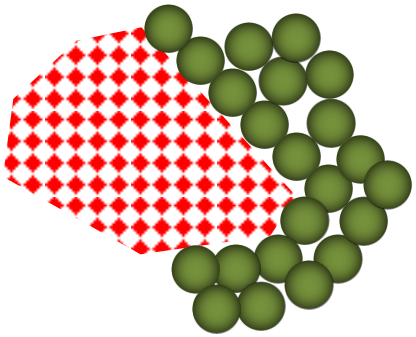
B. R. Shin et al., Scientific Rep. 4, 5572, (2014)



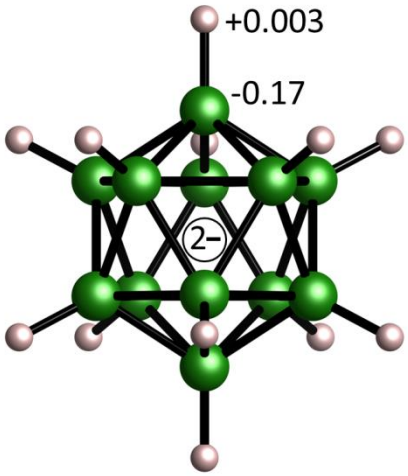


Solid electrolyte with high σ, conformality, compliance, *and* stability needed for composite electrodes

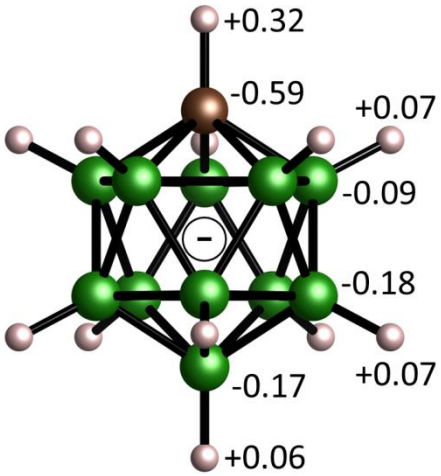




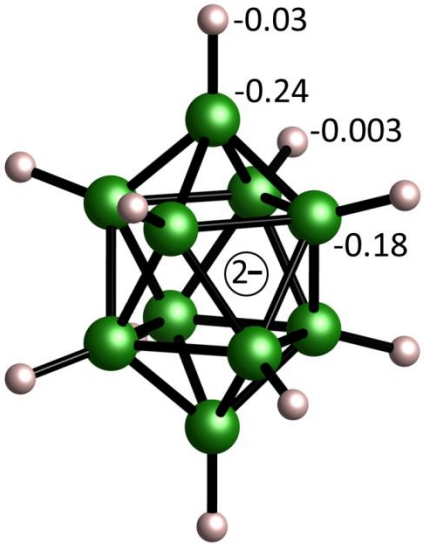
Metal *closo*-(carbo)boranes as solid electrolytes



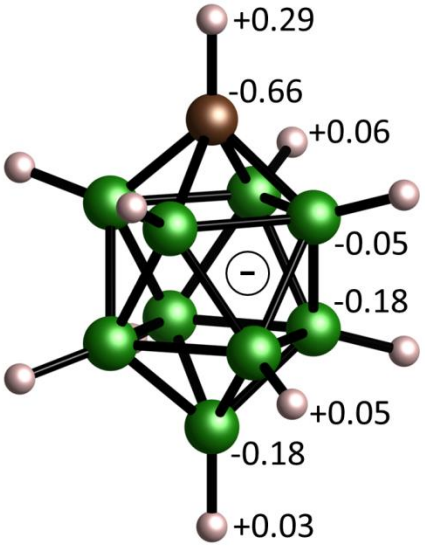
$B_{12}H_{12}^{2-}$



$CB_{11}H_{12}^{-}$



$B_{10}H_{10}^{2-}$



$CB_9H_{10}^{-}$

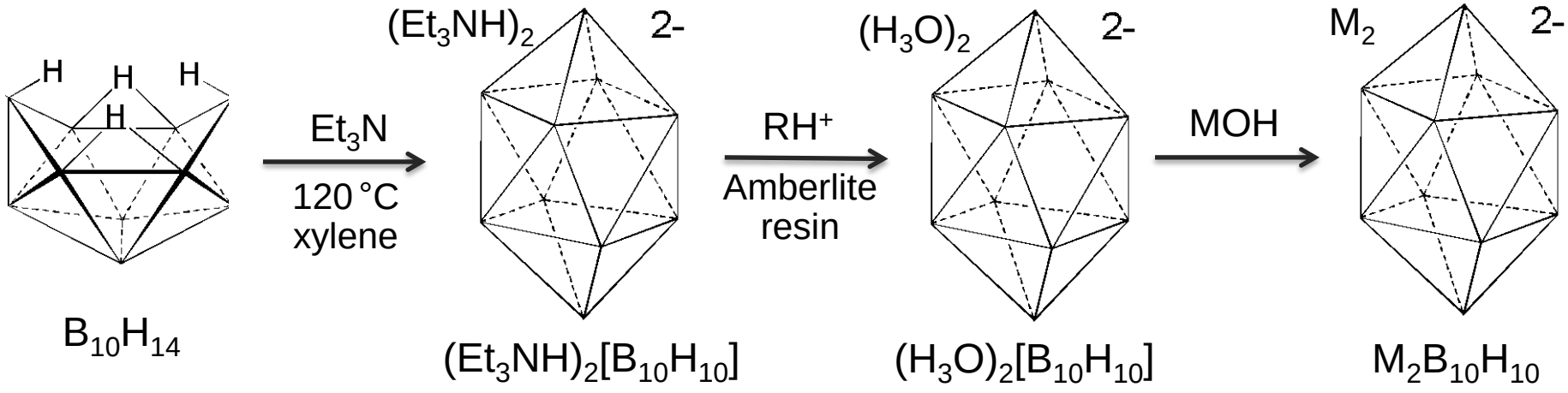
Advantages

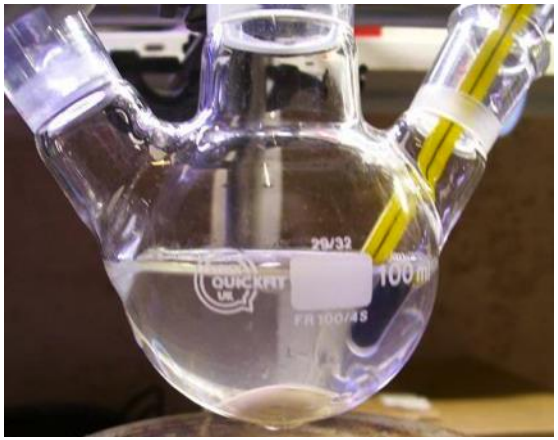
⇒ *Inorganic cage compounds with pronounced aromatic character*

⇒ *Extremely high chemical and thermal stability (e.g. $Cs_2B_{12}H_{12}$ stable up to 800 °C)*

⇒ *Li and Na salts display record high ionic conductivities near room temperature*

Synthesis of *closo*-borate compounds



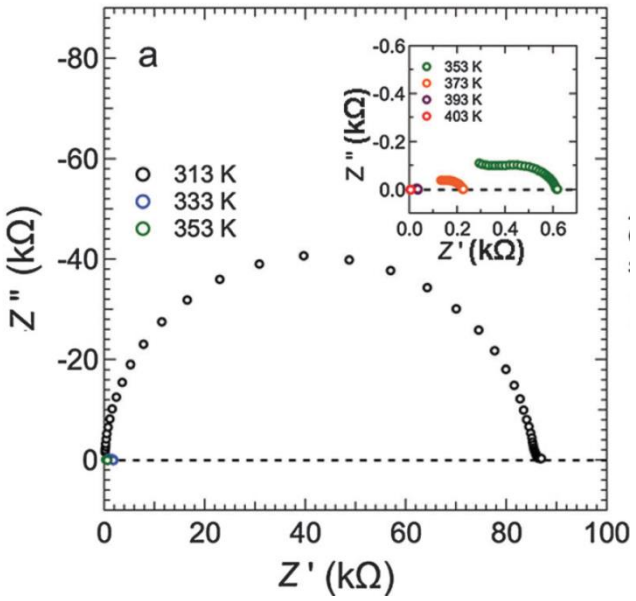


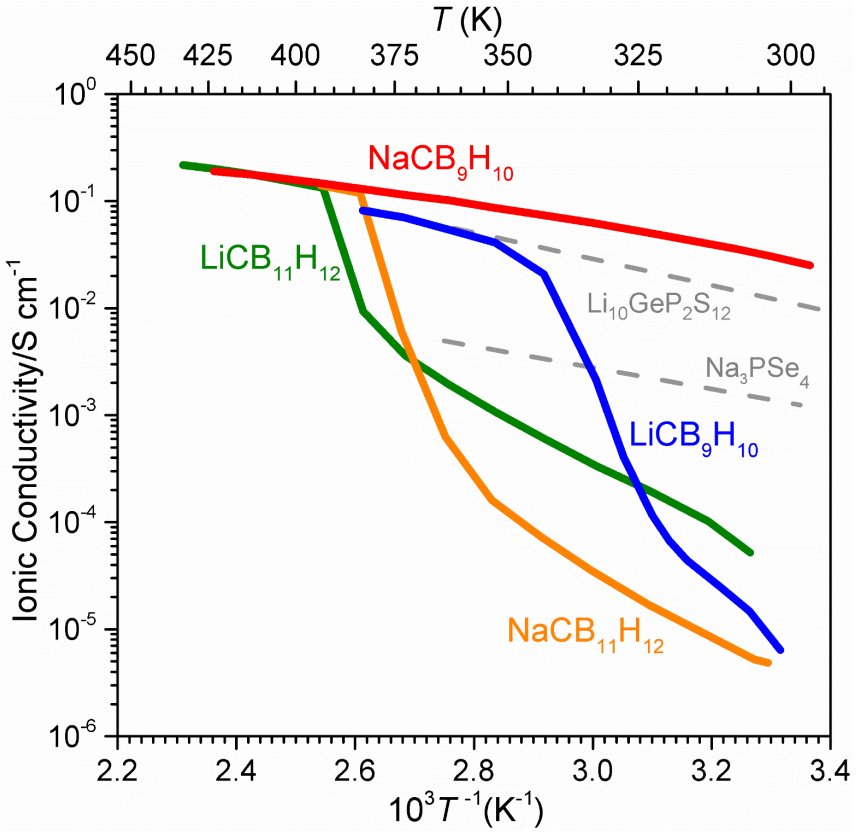
Assembly of closo-decaborate anion

Ion exchange

Water removal

Order-disorder transition in $LiCB_{11}H_{12}$ increases σ

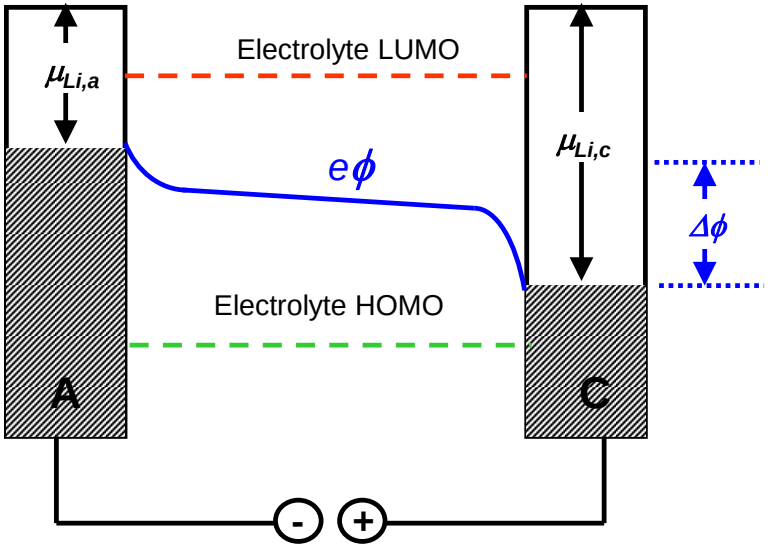


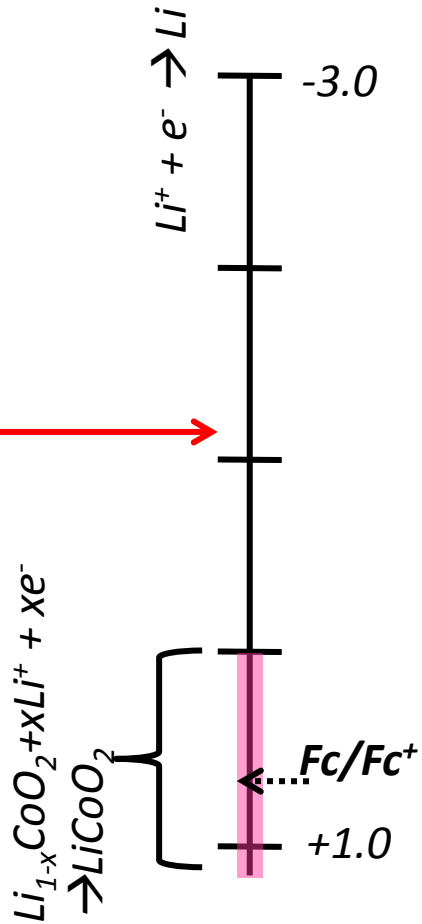


Literature: $LiCB_{11}H_{12}$ stable w.r.t $LiCoO_2$; w.r.t Li→?

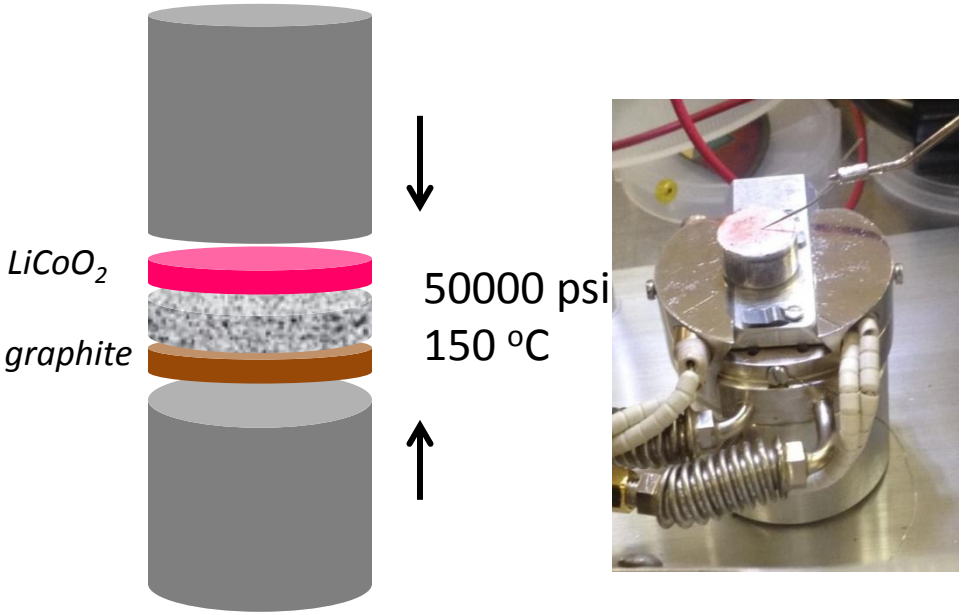
Boere et al., Chem. Eur. J. 19, 1784, 2013

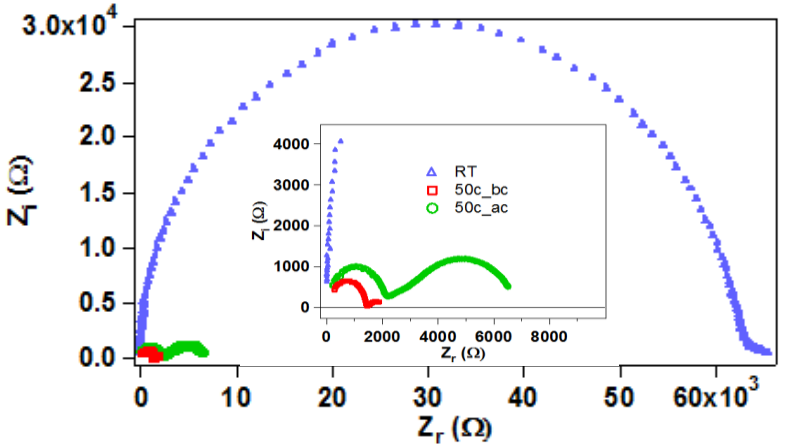
	Oxidation (in SO_2)		Reduction (in MeCN)	
	E_p^{a1} (CV)	E_p^{a1} (SWV)	E_p^{c2} (CV)	E_p^{c2} (SWV)
$[HCB_{11}Cl_{11}]^-$	2.85[d]	2.85	−2.59	−2.57
$[MeCB_{11}Br_{11}]^-$	2.78[e]	2.79	−2.33	−2.29
$[HCB_{11}Br_{11}]^-$	2.76[e]	2.84	−2.31	−2.27
$[HCB_{11}F_{11}]^-$	2.72[f]	2.80	−2.71	−2.66
$[HCB_{11}H_5Br_6]^-$	–[g]	2.63	−2.91	−2.83
$[HCB_{11}Me_5Br_6]^-$	2.29[d]	2.27	−3.32[h]	−3.32[h]
$[HCB_{11}H_{11}]^-$	2.35[d]	2.60	–[i]	–[i]
$[HCB_{11}I_{11}]^-$	2.15[d]	2.15	−1.93	−1.88





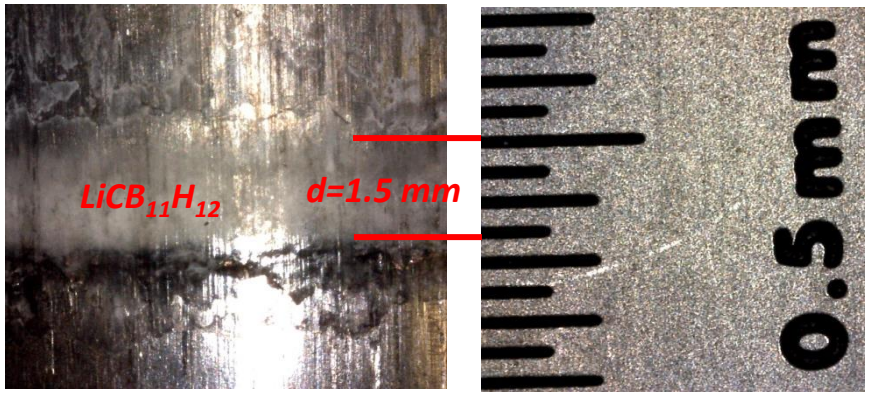
Graphite-$LiCB_{11}H_{12}$-$LiCoO_2$ Solid state battery

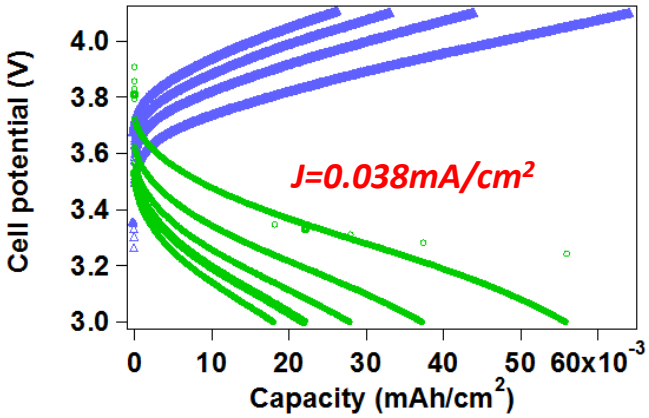




$\sigma(25^oC)=2\times10^{-6}$ S/cm

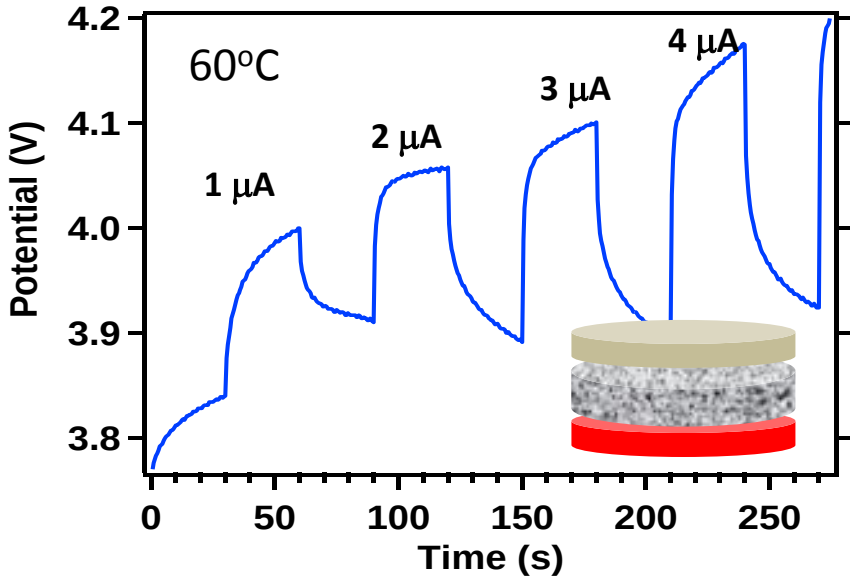
$\sigma(50^oC)=8\times10^{-5}$ S/cm

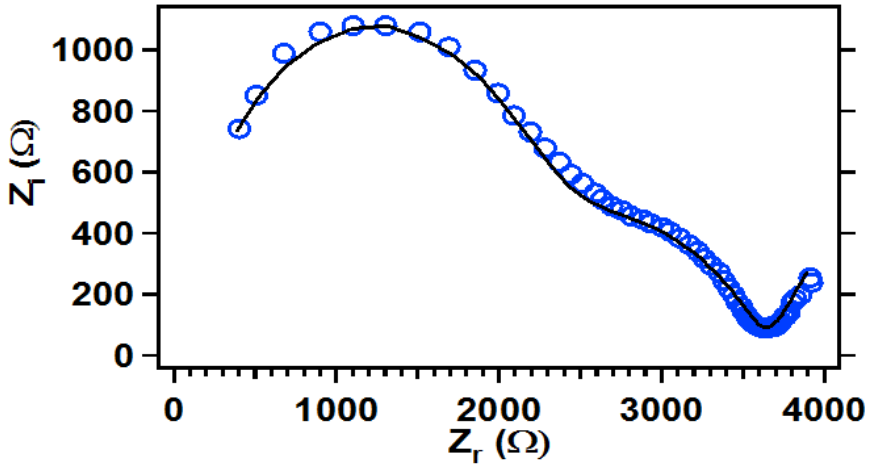


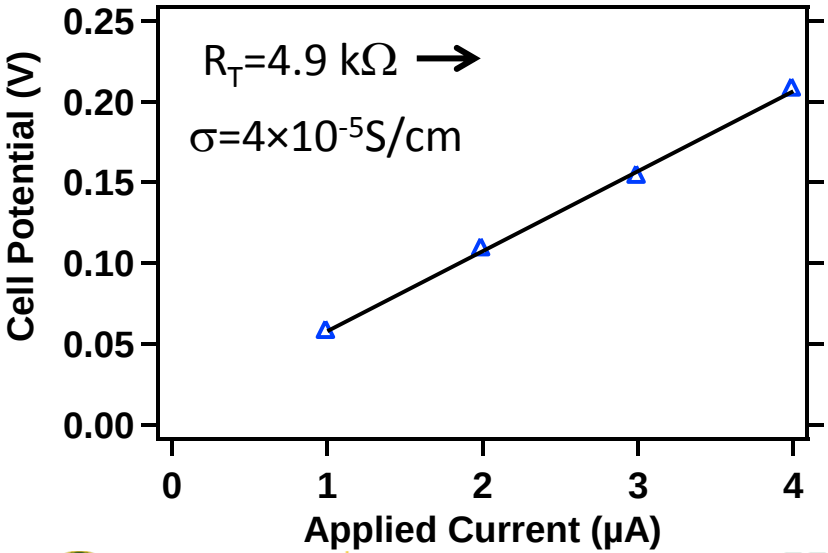


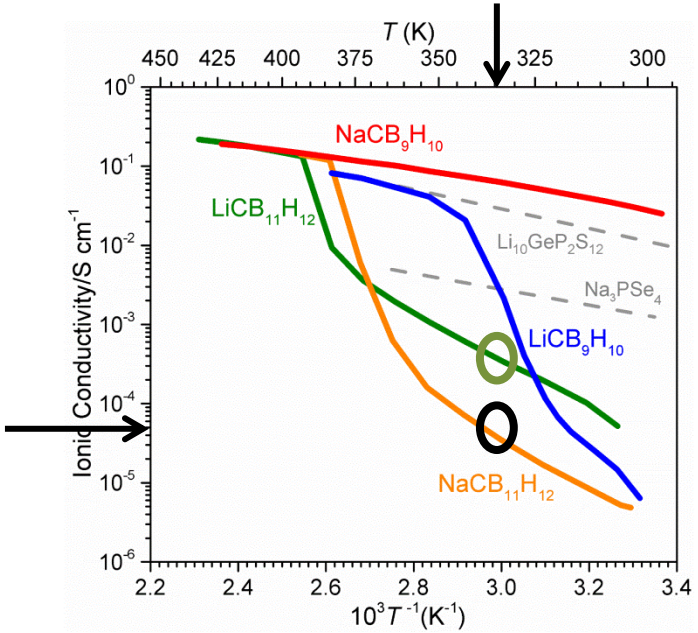
Capacity loss, EIS suggest interfacial reaction; could be address by LiPON passivation

Li-$LiCB_{11}H_{12}$-$LiCoO_2$ High interface resistance

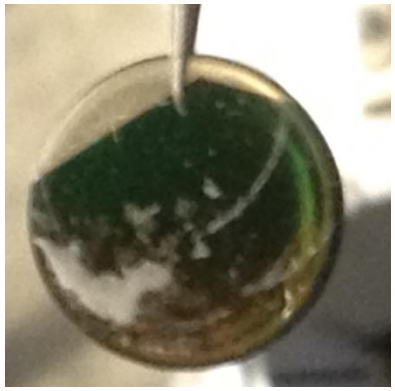


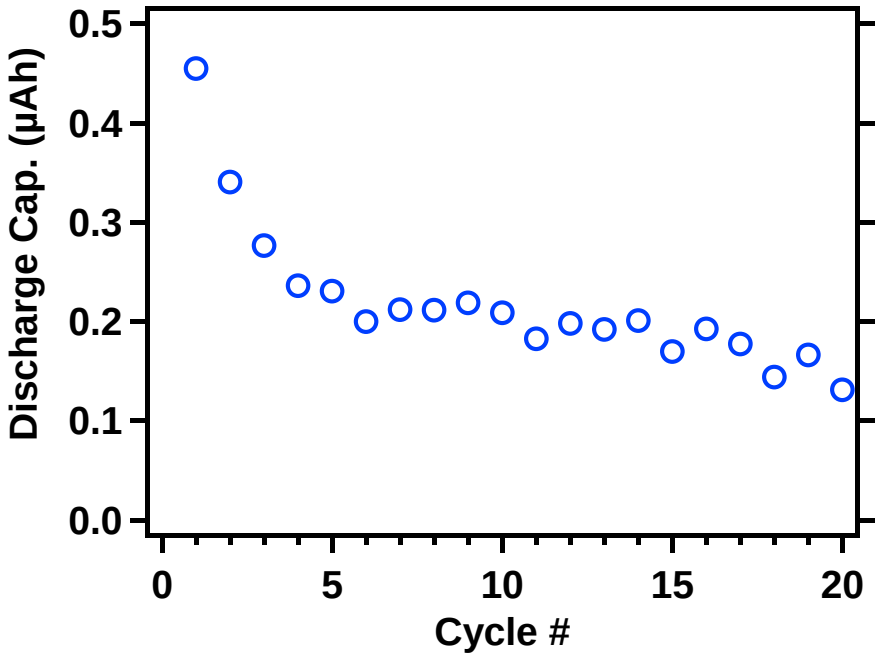






Capacity loss, optical images suggest interfacial reactions

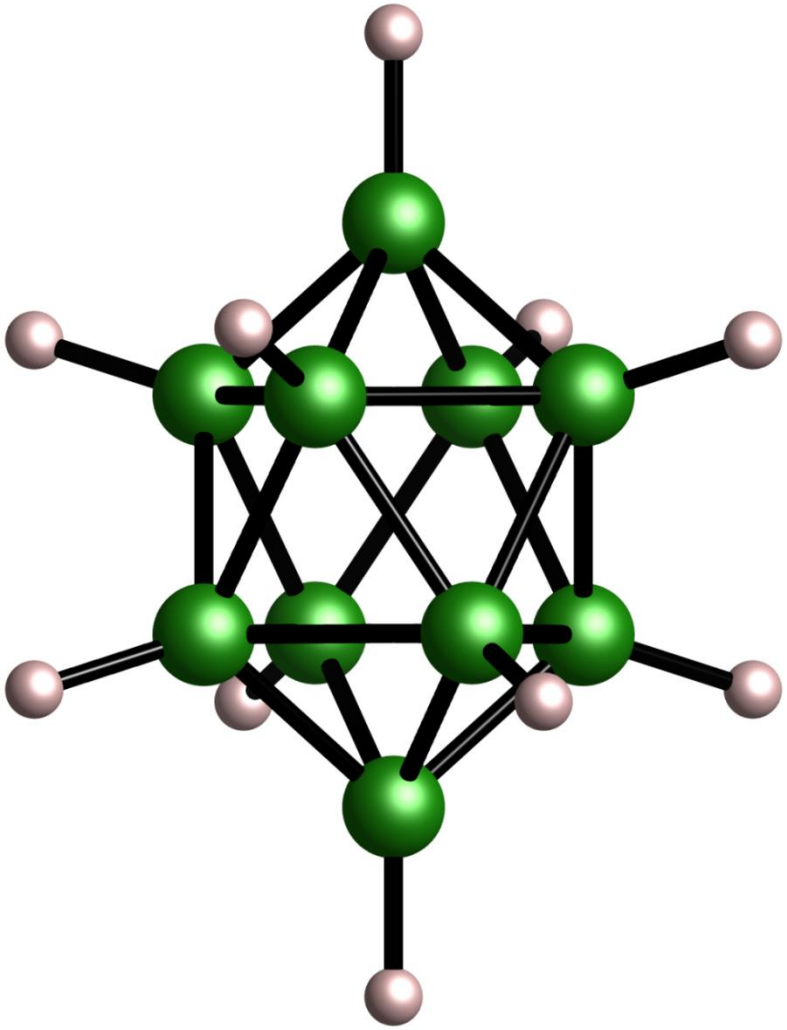


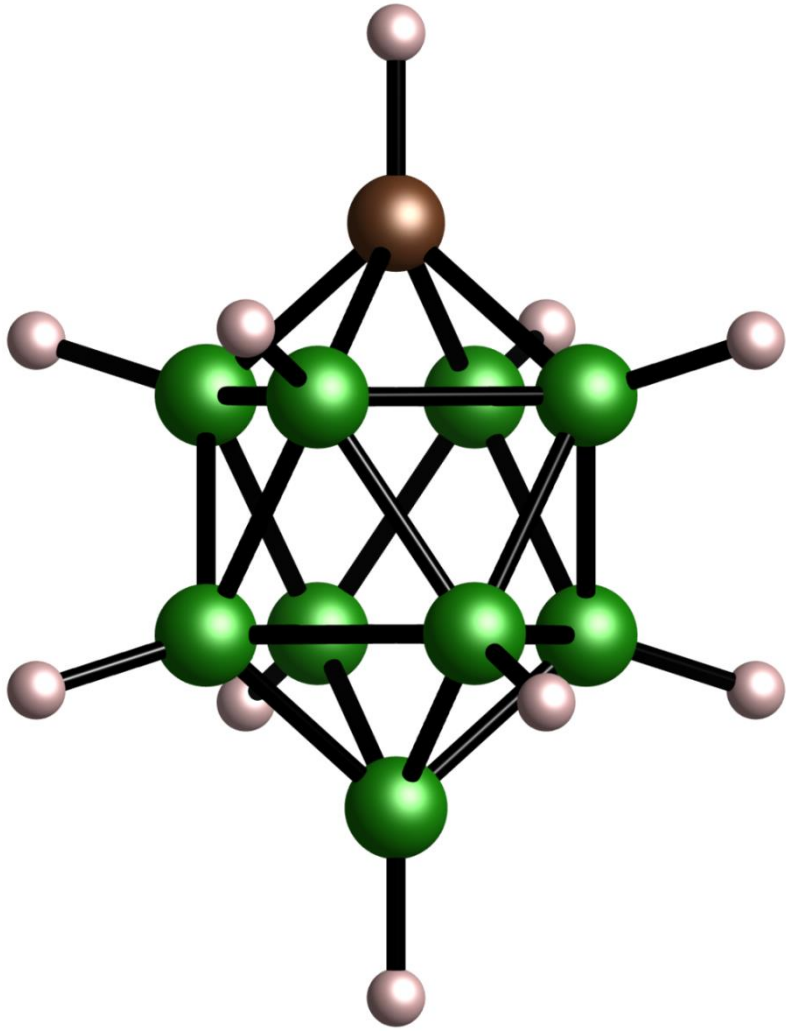


Summary

1. Nanocluster ionic salts may solve solid electrolyte interface challenge:
   - high ionic conductivity
   - conformality
   - strain compliance
2. First $Li/LiCB_{11}H_{12}/LiCoO_2$ battery demonstrated:
   - Interfacial reactions likely
3. Future work:
   - Ultrathin secondary electrolyte for stabilization
   - 3D cathode for high energy and power density

This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, and by Sandia National Laboratories' Laboratory Directed Research and Development (LDRD) Program





$B_{10}H_{10}^{2-}$

$CB_9H_{10}^{-}$

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NEES II NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE

UNIVERSITY OF MARYLAND

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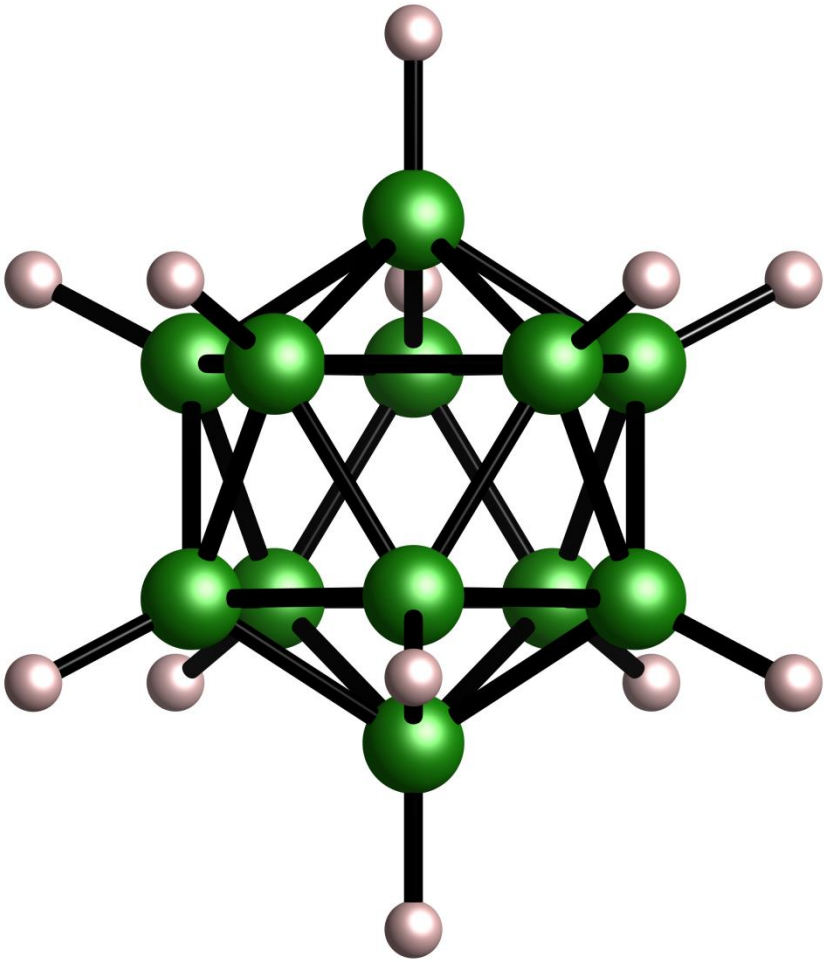

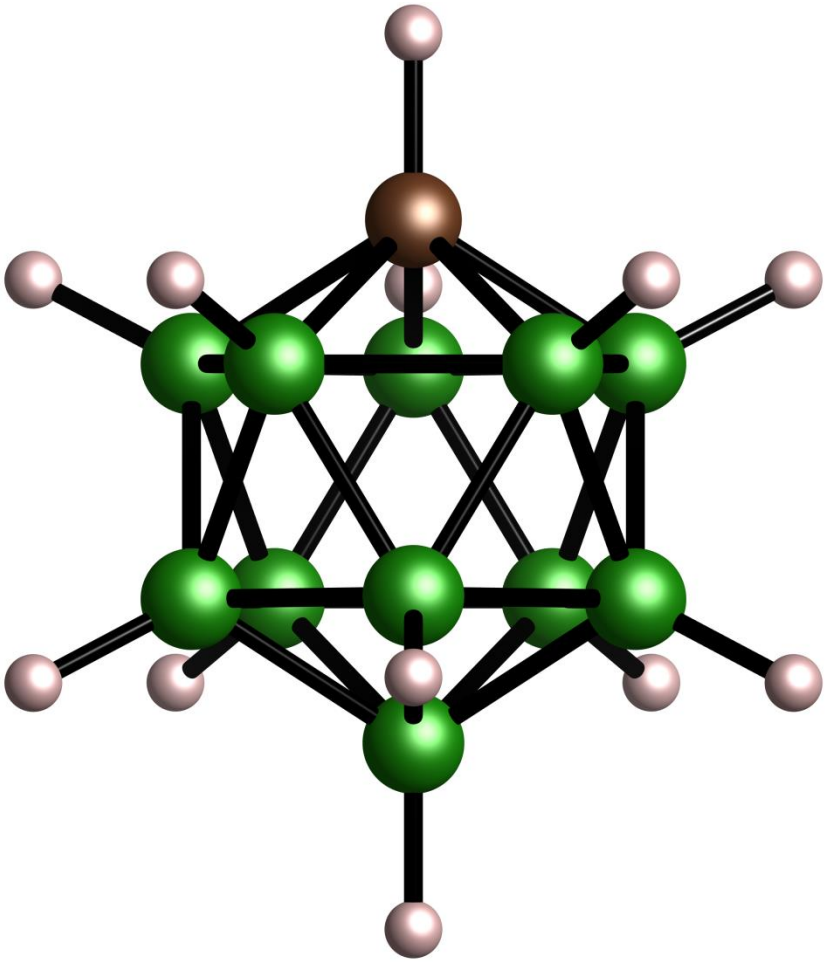

$B_{12}H_{12}^{2-}$ $CB_{11}H_{12}^{-}$

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NEES II NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE

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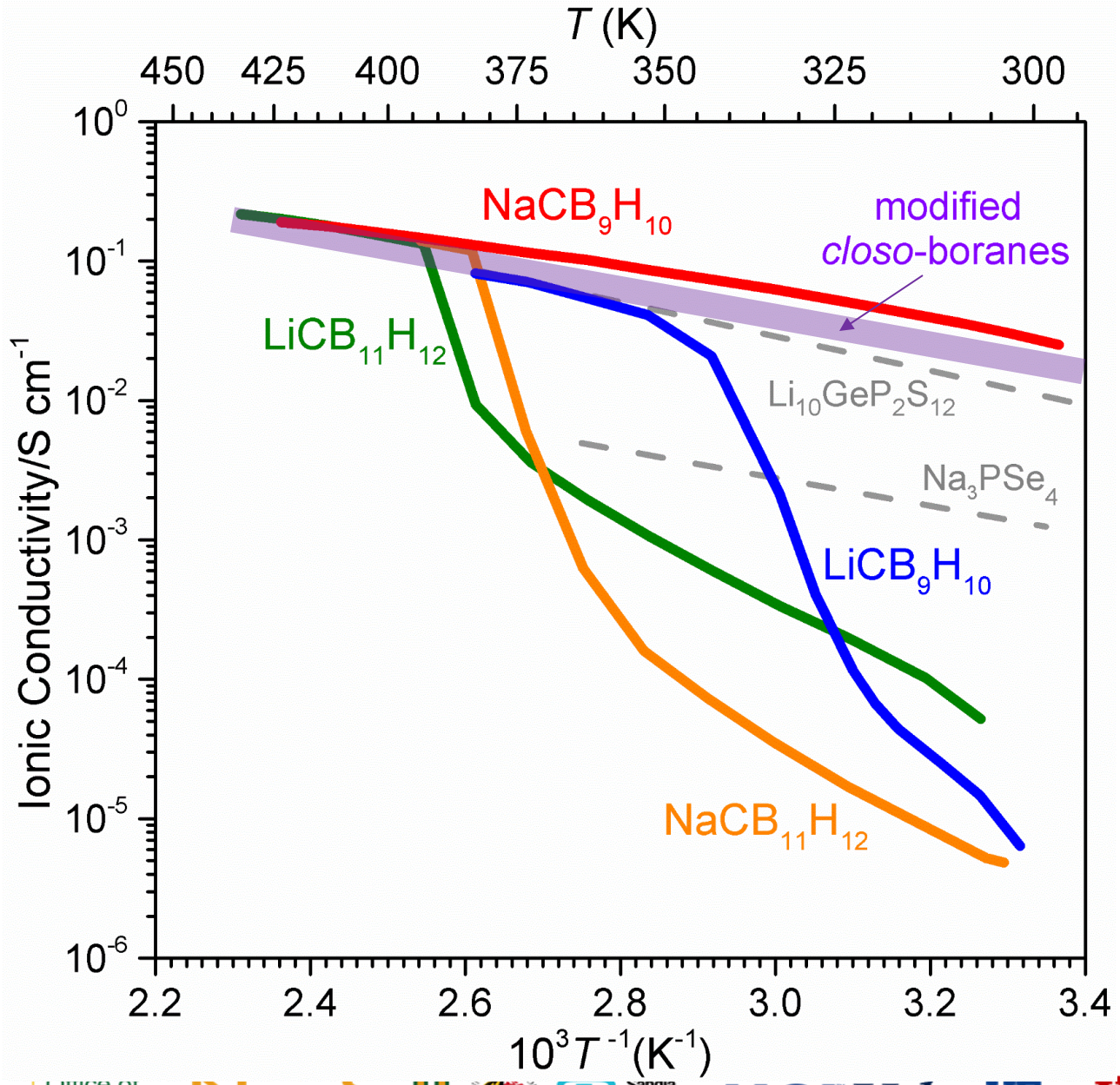
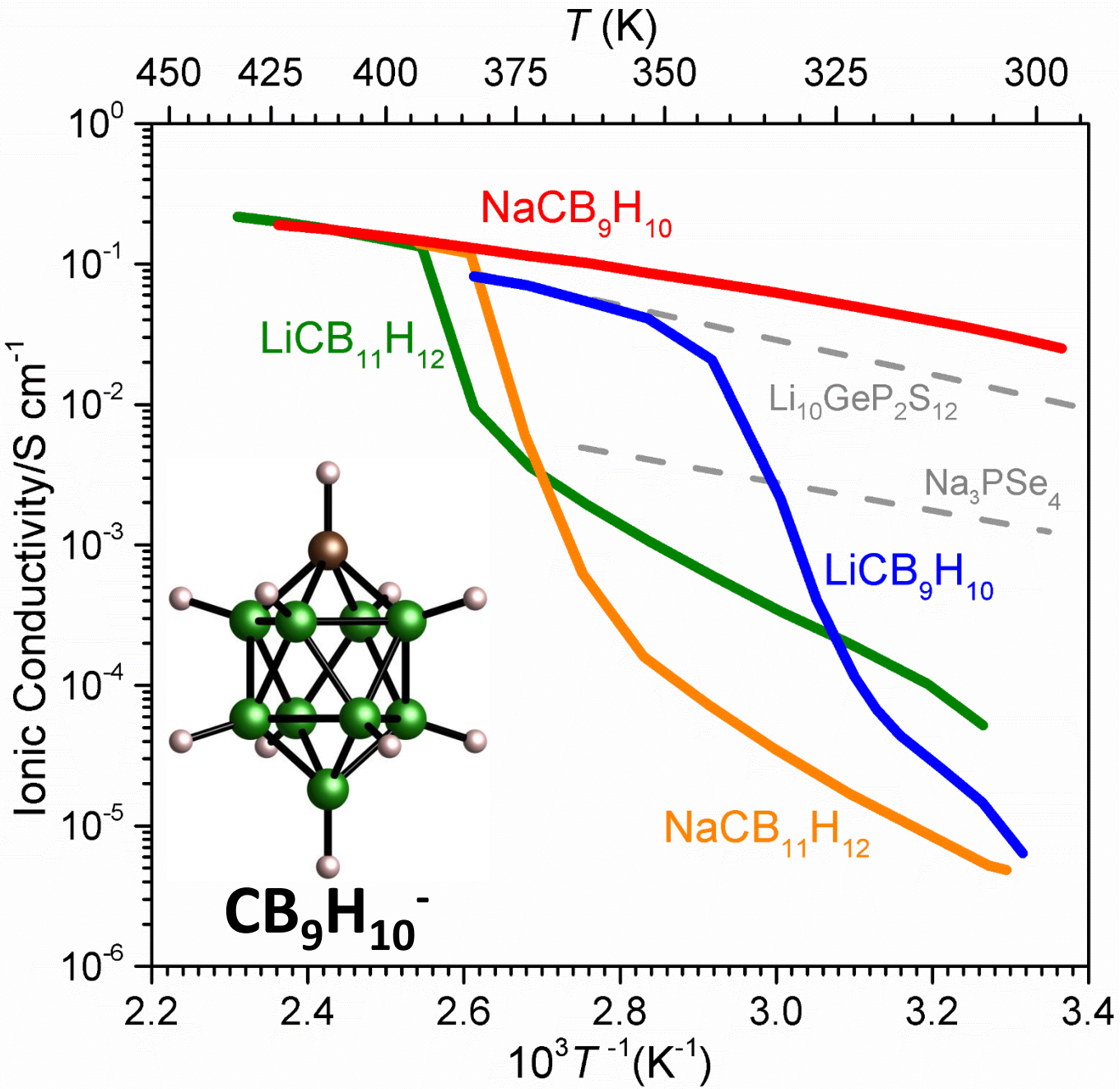
Sandia National Laboratories

UCI Yale UF UNIVERSITY OF FLORIDA

THE UNIVERSITY OF UTAH

MICHIGAN STATE UNIVERSITY UCLA

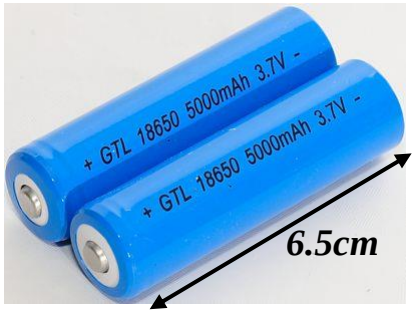


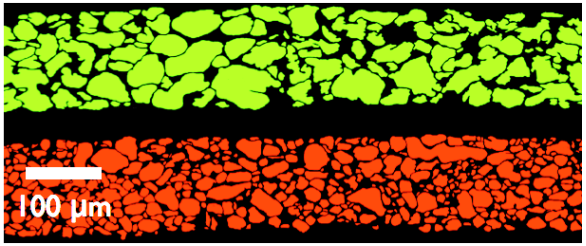

T (K)
450
425
400
375
350
325
300
Ionic Conductivity/S cm-1
10^0
10^-1
10^-2
10^-3
10^-4
10^-5
10^-6
NaCB9H10
LiCB11H12
Li10GeP2S12
Na3PSe4
LiCB9H10
NaCB11H12
CB9H10-
2.2
2.4
2.6
2.8
3.0
3.2
3.4
10^3 T^-1 (K^-1)

‘Holy Grail’: Beat Liquid Electrolyte Battery Performance

Liquid

5000-2000 mAh

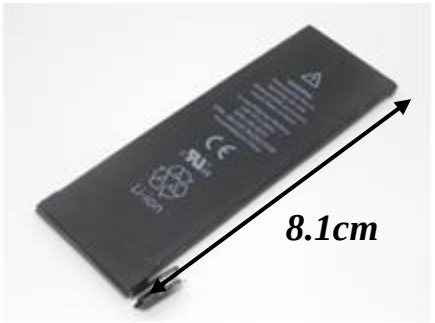


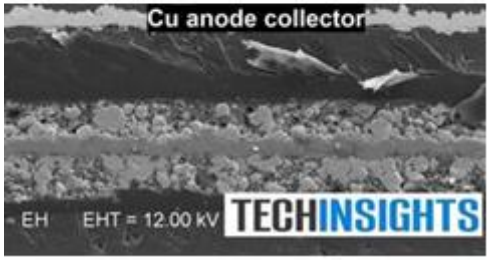


LiCoO2/graphite Li ion battery M. C. Smith et al., J. Electrochem. Soc. 2009

Polymer

~2000 mAh (0.4cm thick)

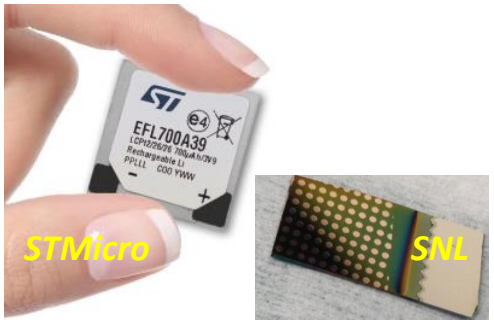


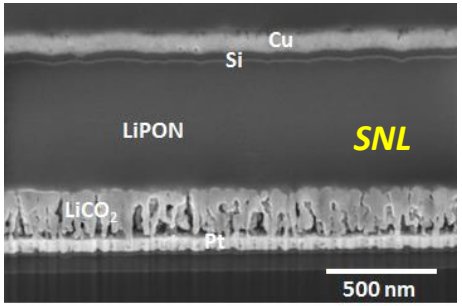


Apple iPhone Li-polymer battery

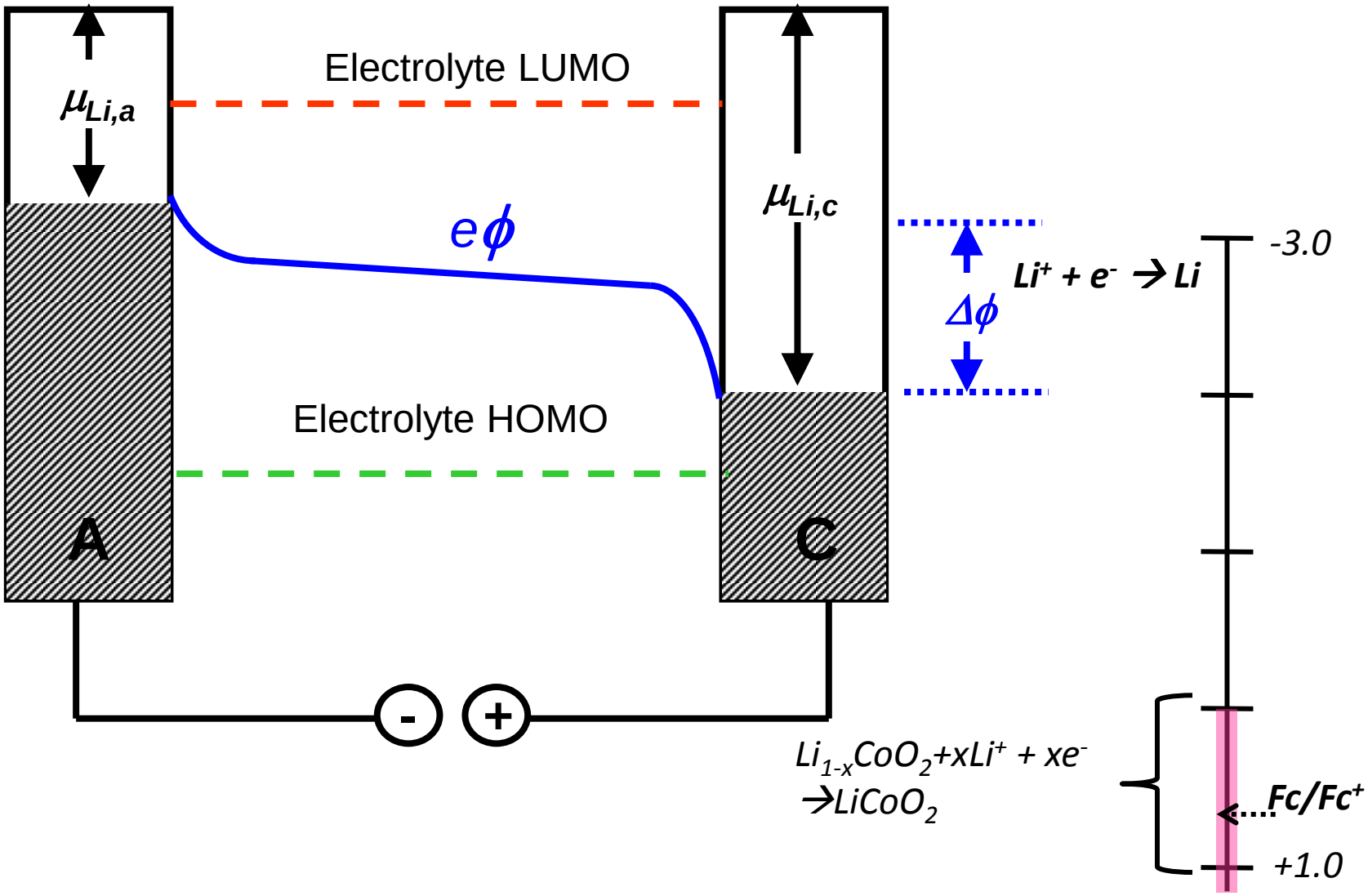
Solid state inorganic

0.7 mAh (0.02cm thick)





Thin film solid state Li-ion battery (SNL)


Electrolyte LUMO
$\mu_{Li,a}$
$\mu_{Li,c}$
$e\phi$
$\Delta\phi$
$Li^+ + e^- \rightarrow Li$
Electrolyte HOMO
A
C
-
+
$Li_{1-x}CoO_2 + xLi^+ + xe^-$
$\rightarrow LiCoO_2$
-3.0
Fc/Fc$^+$
+1.0

Electrochemical (in)stability