GLASS-CERAMIC ELECTROLYTES FOR THE NEXT-GENERATION STORAGE

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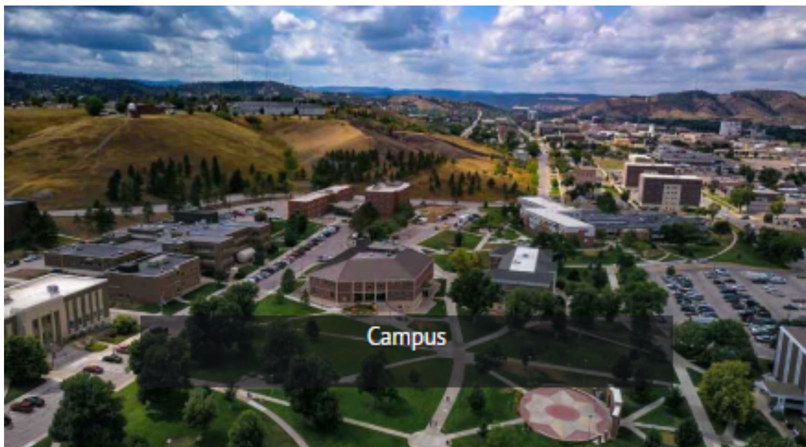
NASA Aerospace Battery Workshop
November
19-21st 2019
Huntsville, AL

SOUTH DAKOTA SCHOOL OF MINES AND TECHNOLOGY HIGHLIGHTS



- Established in 1885
- Wide array of BS, MS, and PhD degrees
- Perfect fit with next-generation ASSB technology

- Sanford Underground Research Facility (SURF) - $1B in 2020
- Ellsworth Air Force Base; Expansion for B-21 project
- NSF IUCRC Center for green solid-state Electric Power Generation and Storage (CEPS)

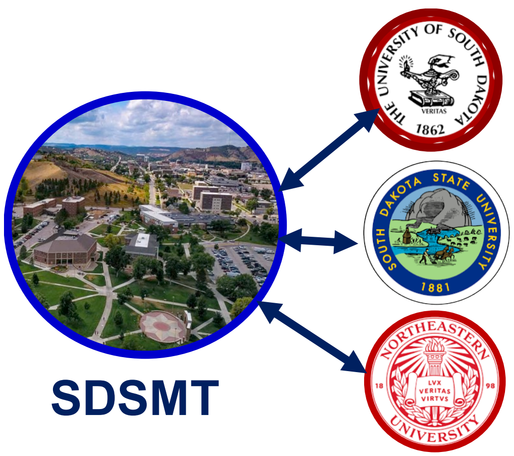
NSF IUCRC CENTER FOR GREEN SOLID-STATE ELECTRIC POWER GENERATION AND STORAGE (CEPS)

- Acceleration of solid-state technology transfer to the market
- Pre-competitive research

CEPS IUCRC

CEPS MEMBERS:

- INDUSTRY
- NATIONAL LABS
- FEDERAL AGENCIES
- THE GOVERNMENT



ACADEMIC CORE:

FOUR UNIVERSITIES

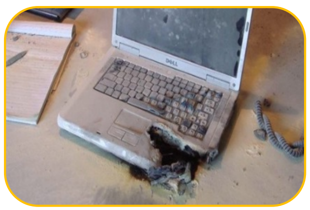
(CURRENT STATUS)

Real time web visitor statistic 09-30-2019

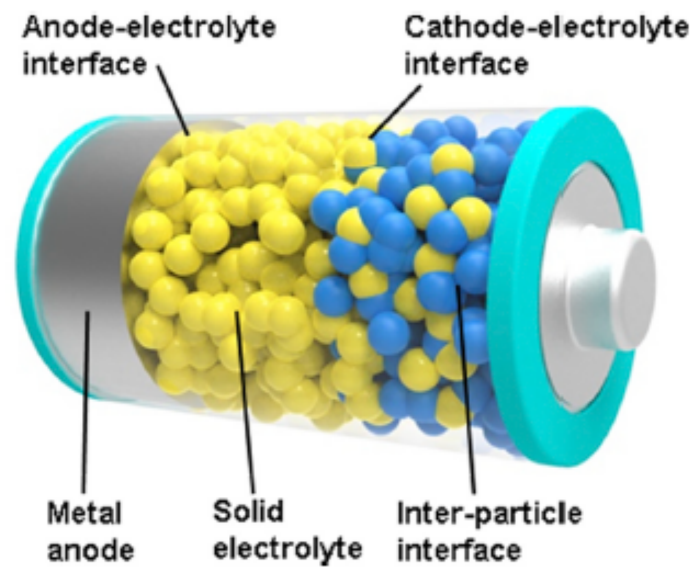
OUTLINE

- **Introduction**
  - Wishlist and expectations
- **Solid-state electrolytes overview**
  - Glass-ceramic vs. ceramic electrolytes
  - Synthesis
- **Antiperovskites**
  - Chemical composition
  - Structure and morphology
  - Li-ion transport mechanisms
  - Doping for lithium storage
  - Electrochemical cells-interfaces

LIQUID VS. SOLID-STATE ENERGY STORAGE WISH LIST



- Safe
- Charge faster
- Cheaper
- Smaller
- Li anode
- Higher voltages
- More power
- Last longer
- Eco-friendly
- Work for all applications

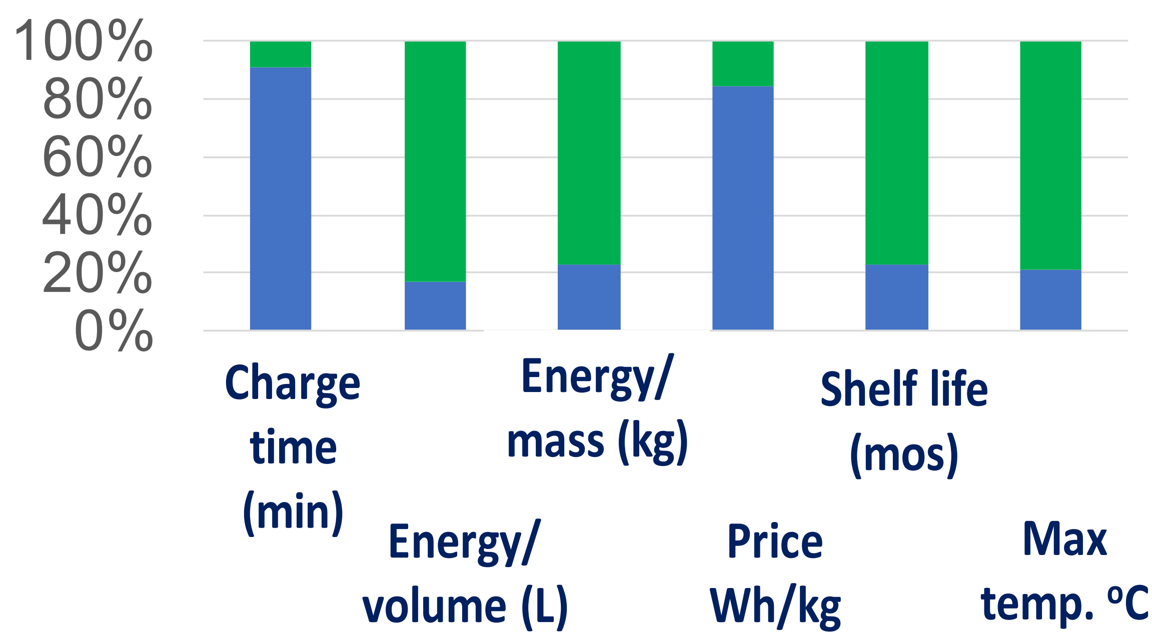


Xu L, et al., Interfaces in solid-state lithium batteries. Joule. (2018) 17;2(10)1991-2015.

EXPECTATIONS FROM SOLID-STATE

- Major consortia/centers focused on energy storage:
  - Joint Center for Energy Storage Research (JCESR)
  - International/national collaborative projects

Lithium Ion Battery with and without liquid

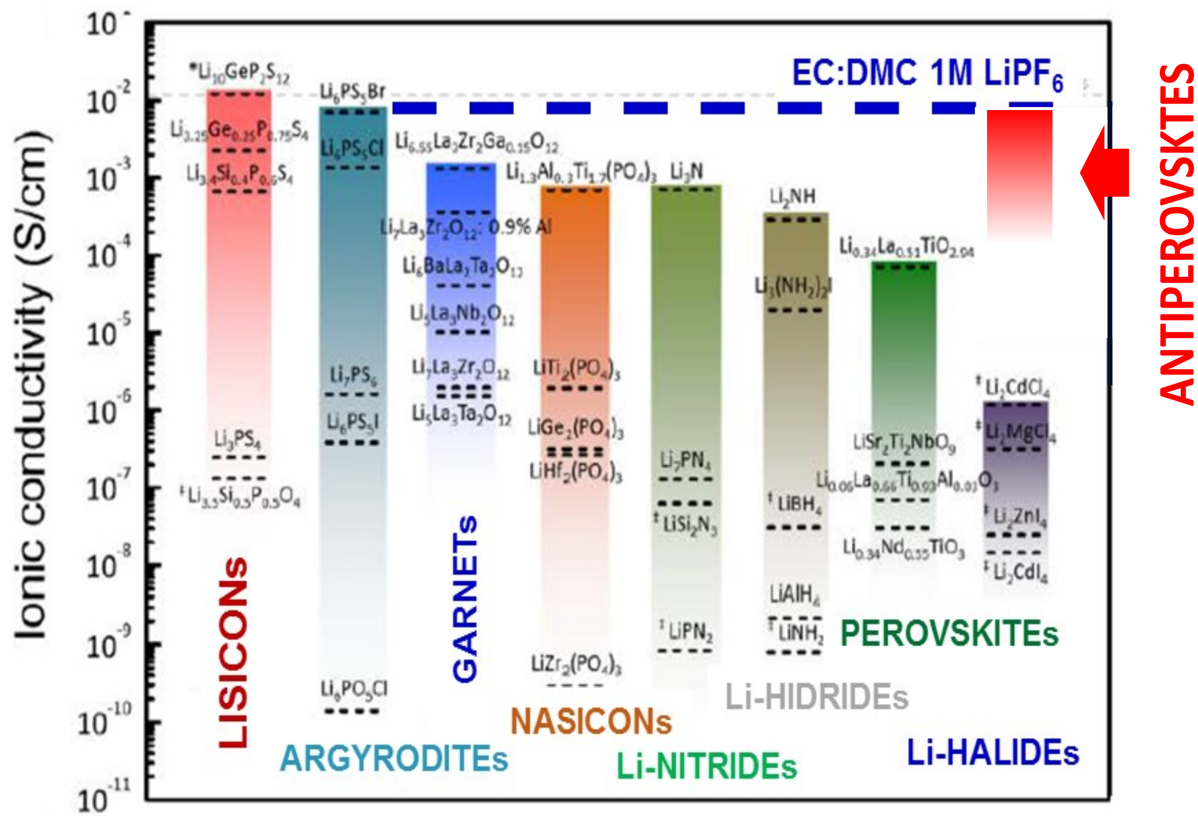


Battery with liquid electrolyte

Battery with solid electrolyte; no liquid electrolyte

SOLID-STATE ELECTROLYTES: BIG PICTURE

- Major problems:
  - Lithium-ion diffusion
  - Grain boundary effects
  - Electrochemical stability
  - Materials cost
  - Processability



Bachman et al., Chemical reviews (2015) 116(1) 140-162.
Wu et al., Ren. and Sust. En. Reviews, 109(2019) 367-385.

GLASS-CERAMIC VS. CERAMIC ELECTROLYTES

Properties	Ceramic, e.g. Garnets	Glass-ceramic $Li_3P_7S_{11}$, $Li_{10}GeP_2S_{12}$, and Na_3PS_4

SYNTHESIS OF LI-ION GLASS-CERAMIC ELECTROLYTES

From aqueous solutions
- Dissolution of inorganic precursors in water
- H_2O evaporation
- Heat-treatment in vacuum for at least 48 hr

Zhao, Daemen, Braga (2012) WO Patent 2,012,112,229.

Pulsed laser deposition
- Composite target from mixed inorganic precursors
- Spray deposition on heated substrate (100-400^{o}C)
- Heat-treatment in vacuum for 48 hr

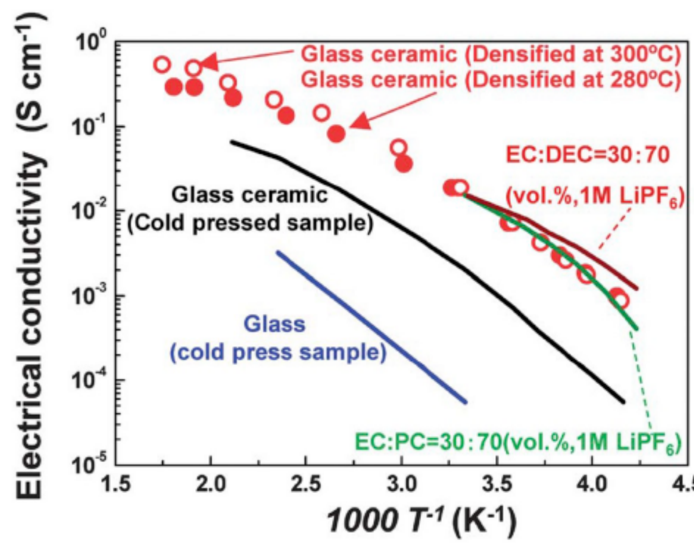
Lu, Daemen, Zhao (2015) US20150364788A1

Spray pyrolysis
- Dissolution of inorganic precursors in water
- Spray deposition on heated substrate (100-400oC)
- Heat-treatment in vacuum for at least 48 hr

Oladeji , US 8,349,498 B2, 2013.

From solid-state precursors
- Mechanical ball milling (~400 rpm; 20 hr)
- Melt quenching/hot-pressing
- Sintering at elevated pressures and temperatures

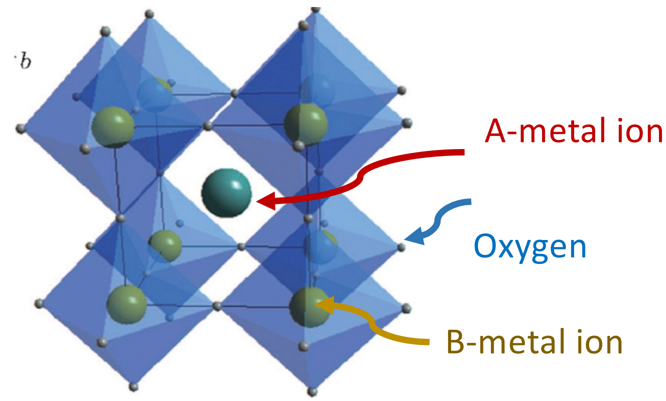
Zhao, Daemen, (2016) US Patent 9,246,188 B2.

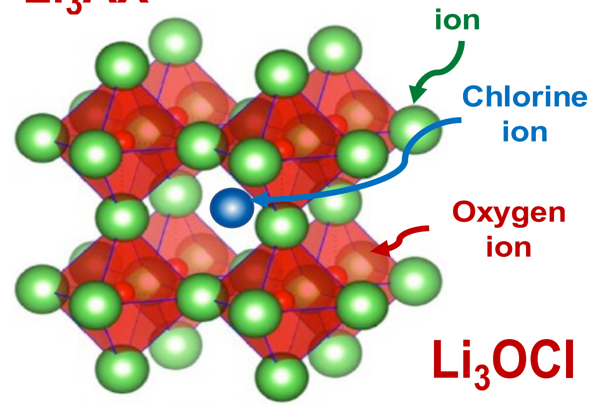


Wu et al., Renewable and Sustainable Energy Reviews, 109(2019) 367-385

ANTIPEROVSKITE FAMILY

- Perovskites: ABO_3 , e.g. $Li_{3x}La_{2/3-x}TiO_3$ (LLTO)
  - $Li_{3/8}Sr_{7/16}Ta_{3/4}Hf_{1/4}O_3$ (LSHT) $\sigma=3.8\times10^{-4}$ S/cm at 25°C; E_a=0.36eV
- Antiperovskites: $ABX_3 = X_3AB$
  - X: metal (Li^+, H^+, group II, or TMs)
  - A: halogen (F^-, Cl^-, Br^-, I^-), chalcogen (S, Se, Te), or a cluster ion
  - B: chalcogen (O, S, Se, Te)
- Lithium-ion transport:
  - Diffusion via interstitial sites
  - Migration through optimum channels
  - Hopping between sites
    - Aliovalent/interstitial substitution
    - Distribution of Li-ions at different sites
    - Distortion /Disorder at sublattices





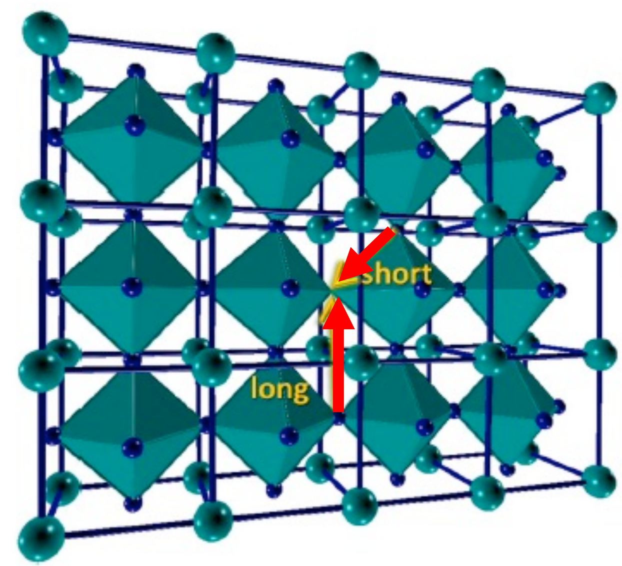
Zhao and Daemen, J. Am. Chem. Soc. 2012, 134, 15042−15047

Li, Goodenough, et al., Angew. Chem. Int. Ed. 2016, 55, 9965 –9968

Zhang et al., J. Power Sources 389 (2018) 198–213

LITHIUM-ION MIGRATION MECHANISMS IN ANTIPEROVSKITES

- Cubic structure promotes 3D Li^+ diffusion
- Two migration mechanisms
    - Through vacancies as charge carriers
    - Interstitial migration
- In LiCl-deficient antiperovskites: interstitial migration is due to charge compensation (increase of interstitial sites)



Mouta et al., Chem. Mater. 2014, 26, 7137−7144
Zhao and Daemen, J. Am. Chem. Soc. 2012, 134, 15042−15047

ROLE OF H_2O in ANTIPEROVSKITE CRYSTAL STRUCTURE FORMATION

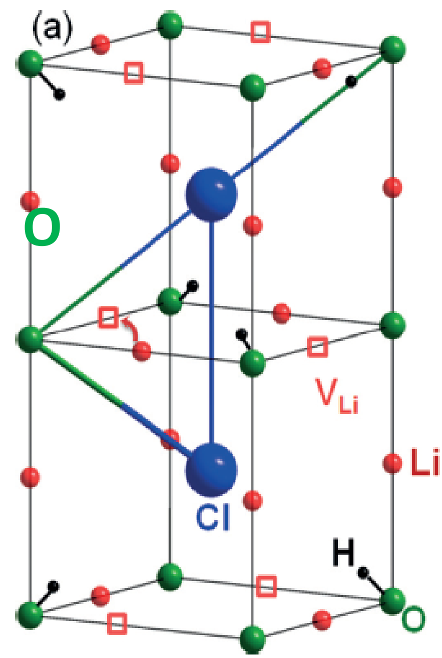
350ºC

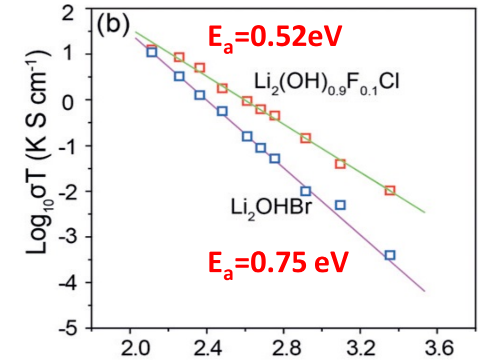
- $2LiOH+LiCl \rightarrow Li_3OCl+H_2O$

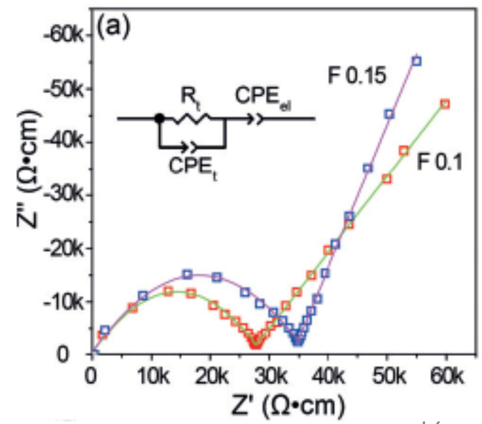
600ºC

- $Li_2O+LiCl \rightarrow$?
- No reaction even at 600ºC
- H_2O plays significant role in formation of cubic phase
- $Li_{3-x}OH_xX$ (X=Cl and Br)

Cubic Li_2OHCl





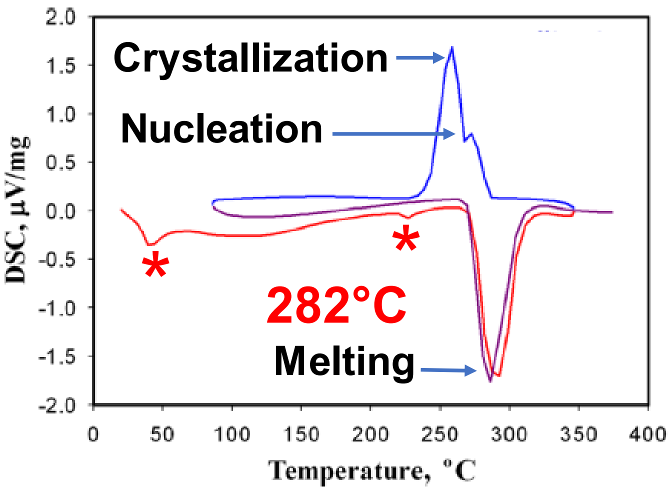


Li, Goodenough, et al., Angew. Chem. Int. Ed. 2016, 55, 9965 –9968

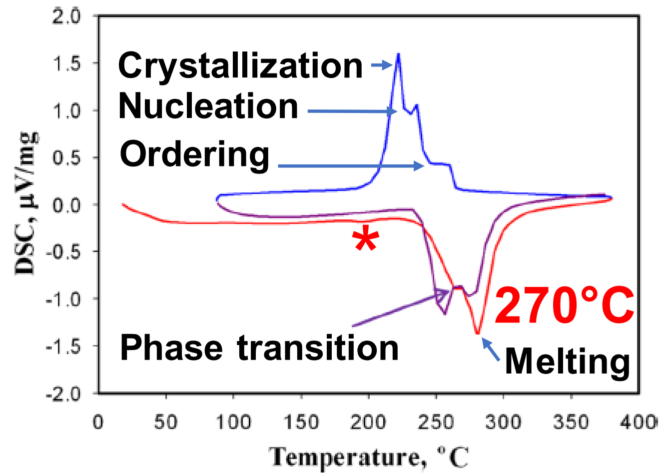
STRUCTURAL AND PHASE TRANSFORMATIONS IN ANTIPEROVSKITES

Differential Scanning Calorimetry (DSC)

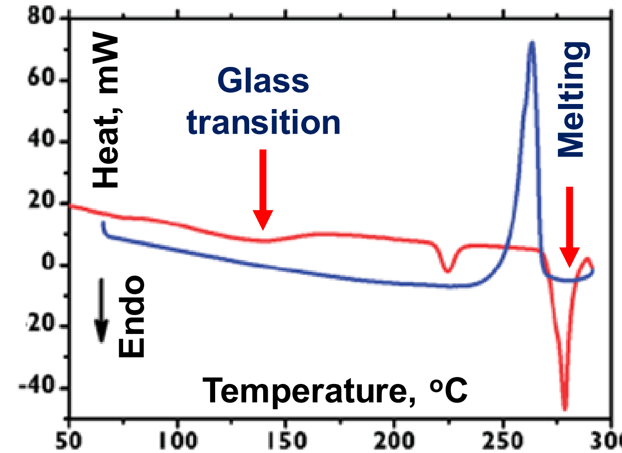
Li_3OCl



$Li_3OCl_{0.5}Br_{0.5}$



$Li_{3-0.01}Mg_{0.005}OCl$



*
- Endothermic peaks due to local disorder- octahedral tilting
- Substitution of halogens is an efficient method of structural manipulation

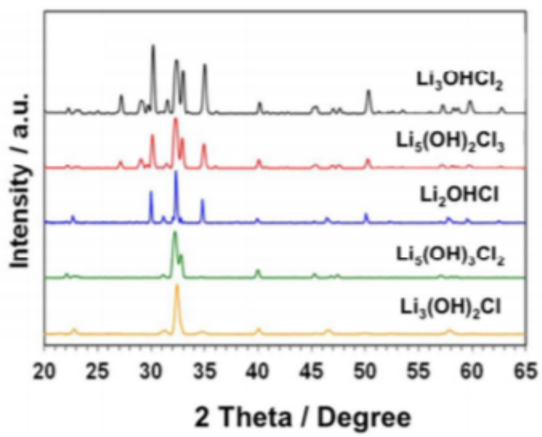
Zhao and Daemen; J. Am. Chem. Soc. 2012, 134, 15047-15042.

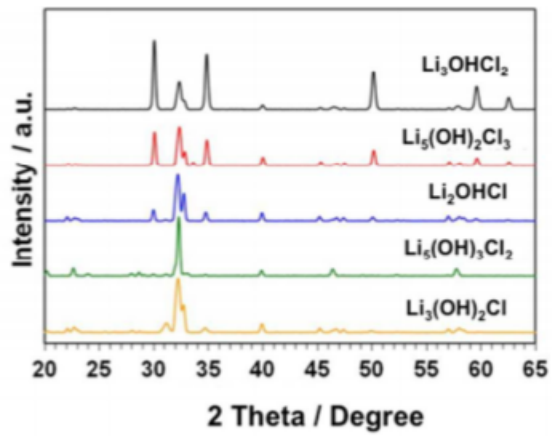
Braga et. al., Mater. Chem. A, 2014, 1–11

EFFECT OF COOLING AND STABILITY IN PRESENCE OF LITHIUM METAL

LiOH : LiCl= 1:2, 2:3, 1:1, 3:2, and 2:1

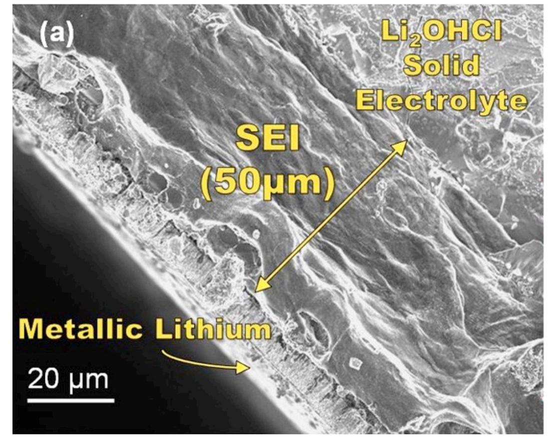
Fast cooling **Slow cooling (8°C/hr)**





$$2Li_2OHCl_{(s)} + 2Li_{(l)} \rightarrow 2Li_2O_{(s)} + 2LiCl_{(s)} + H_{2(g)}$$

- Decomposition of Li_3OCl into precursors in presence of molten lithium



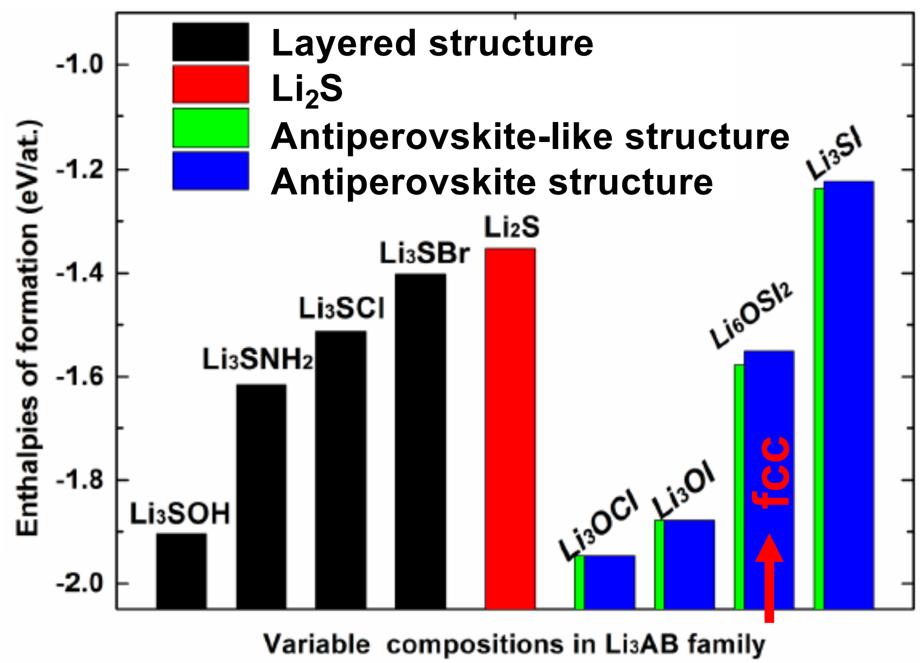
- Superior stability against Li anode
- Extreme conditions above the melting point of Li metal

Z. Hood et al., Li_2OHCl crystalline electrolyte for stable metallic lithium anodes. J. Am. Chem. Soc., 138 (2016) 1768.

ANTIPEROVSKITE DOPING FOR LIB ELECTROLYTES

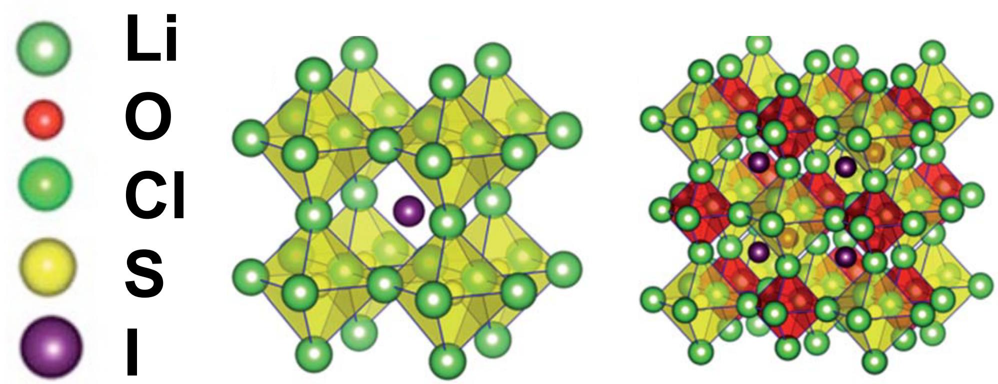
$Li_3O(A_{1-z}A'_z)_{1-\delta}$

Ab Initio Simulation



Wang, et al. J. Materials Chemistry A, 6.1 (2018) 73-83.

- Li_3OCl→ Li_3SCl adopts a layered structure
- Li_3SCl → Li_3SBr or non-halogen functional groups such as NH_2^- or OH^-
- Substitution of O with S: increase in lattice parameters associated with weakened binding



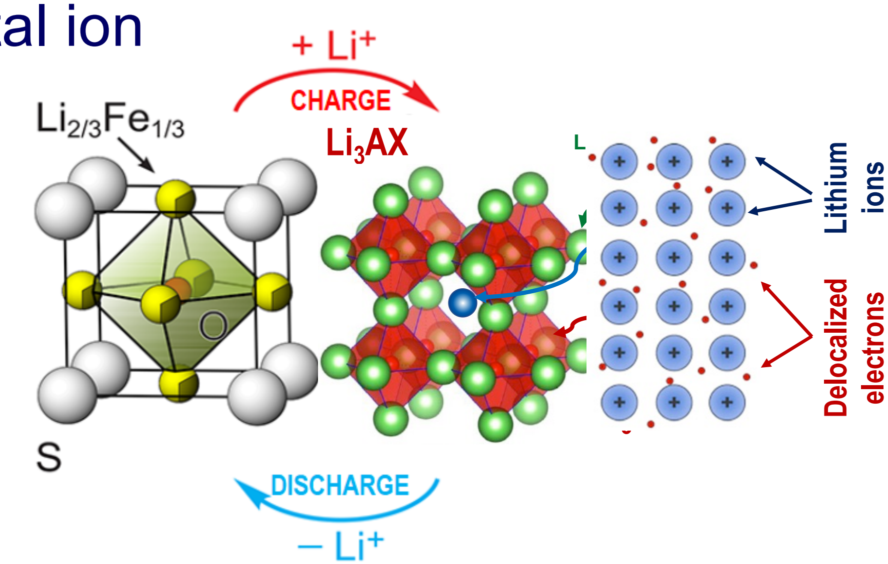
Li_3SI Li_6OSI_2

ANTIPEROVSKITE DOPING FOR LIB CATHODES

- Displacement of Li^+ in Li_3AX for metal ion
- Results in higher Li^+ mobility
- Isotropic 3-D Li^+ migration
- High storage capacity

- Li_2O+ Fe + Ch→(Li_2Fe)ChO
- Ch=S, Se, Te (750^{o}C and 10^{-4}mbar)

- Li_2FeSeO= 163 mAh/g
- Li_2FeSO= 227 mAh/g

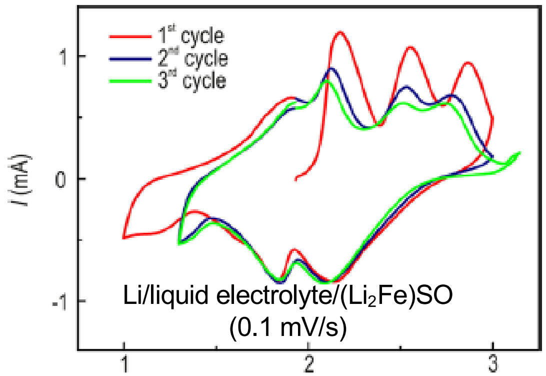


(Li_2Fe)TeO antiperovskite CATHODE

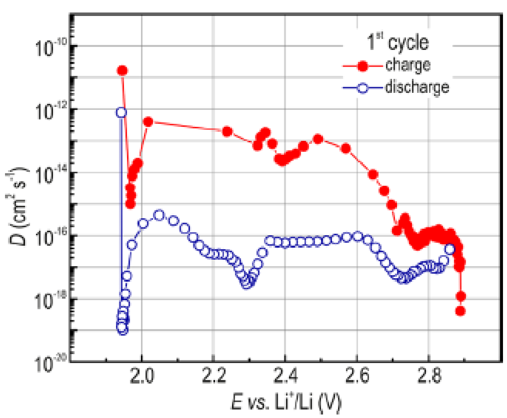
LITHIUM METAL ANODE

Martin Valldor group: Anti-Perovskite Li-Battery Cathode Materials J. Am. Chem. Soc. 2017, 139, 9645−9649

Li-ION STORAGE MECHANISMS IN ANTIPEROVSKITES



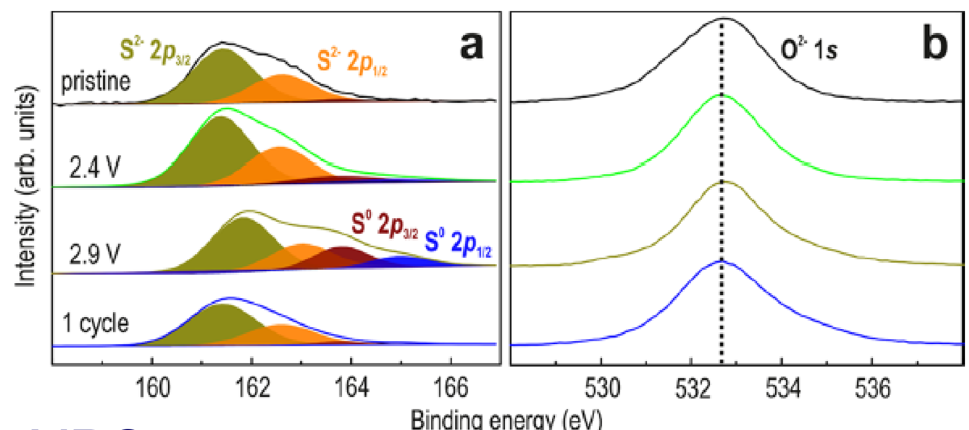
- Few phases during Li extraction/insertion
- Intermediate compound (Li_xFe)SO (x =0.8)



- Li^+ extraction (charging) >> faster than insertion

XANES (Fe K edge):

- Fe valence state: +2/+3
- Upon Li extraction (charging): Fe^{2+} oxidized
- Fe nearest neighbor (Li, Fe): 2.8Å



XPS:

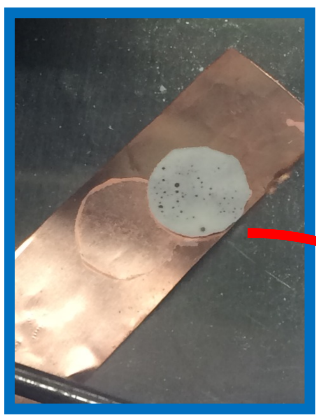
- Partial oxidation of S^{2-}

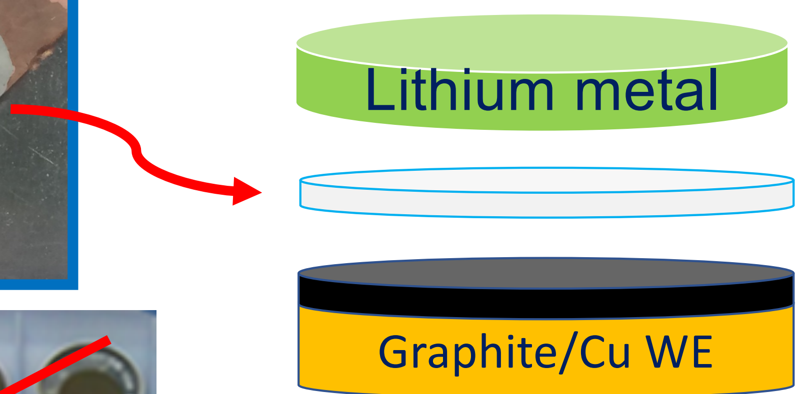
ACS Appl. Energy Mater. 2018, 1, 6593–6599

ANTIPEROVSKITES IN HALF-CELLS

Methods:

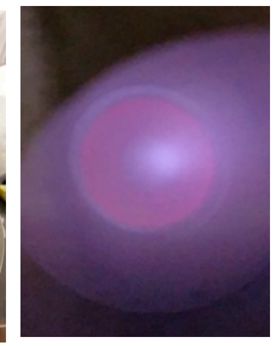
- Delamination
- MS-PVD





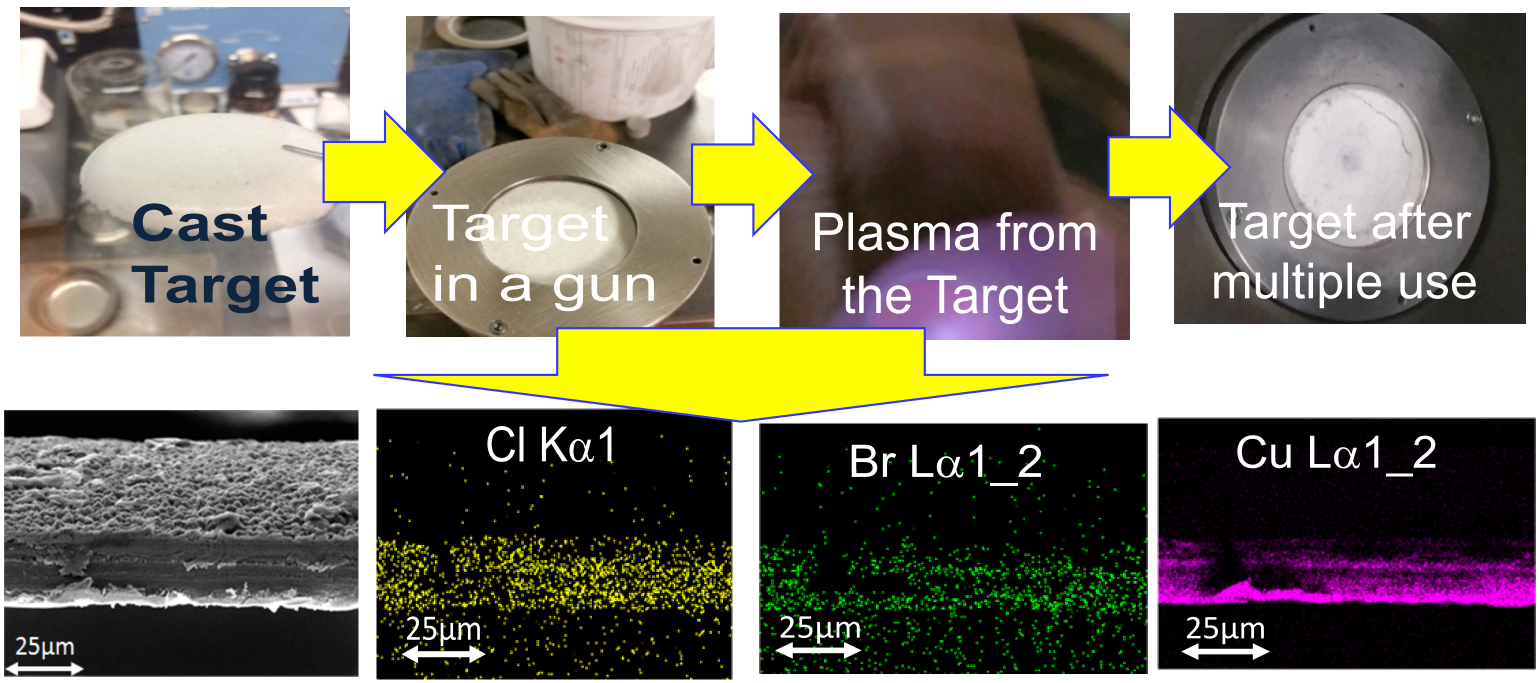
Cast glass-ceramic electrolyte target

Electrolyte target in PVD gun



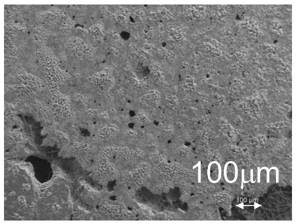
Plasma from the electrolyte target

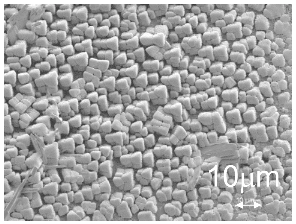
Example: Collaboration between SDSMT and NanoCoatings, Phase II DOD projectPlasma (MS-PVD) for DESIGN of antiperovskites

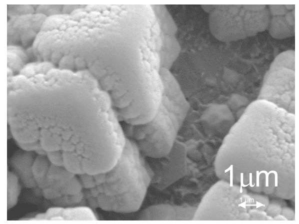


Mechanical and chemical stability of the antiperovskites electrolyte in MS-PVD has been confirmed (DOD Phase I)

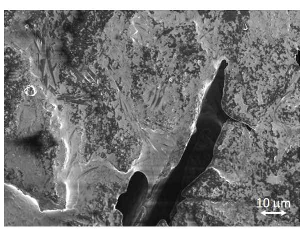
ANTIPEROVSKITE CRYSTAL STRUCTURE IN MOISTURE-FREE ENVIRONMENT

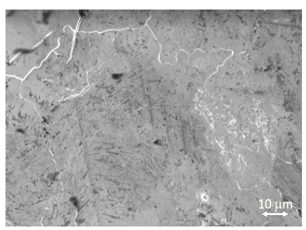




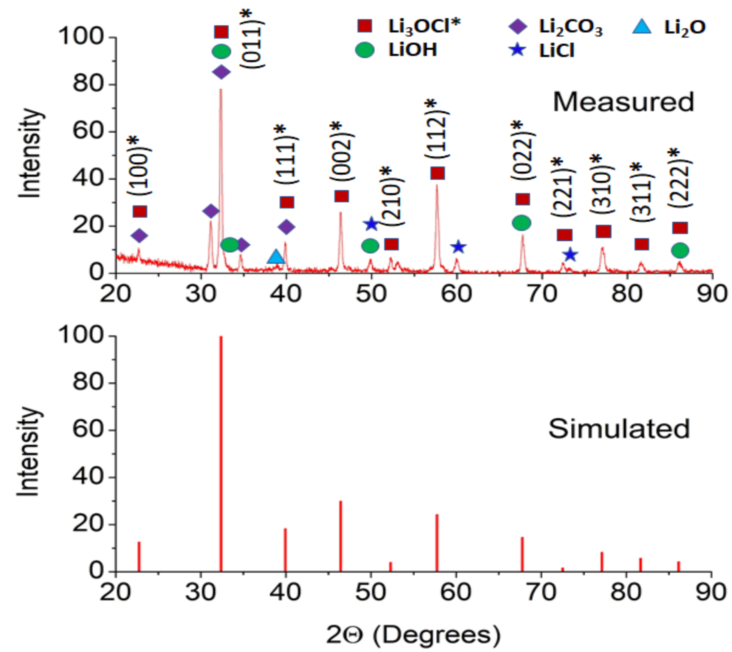


- Slow cooling initiates formation of crystal structure
- Properties similar to sulfides





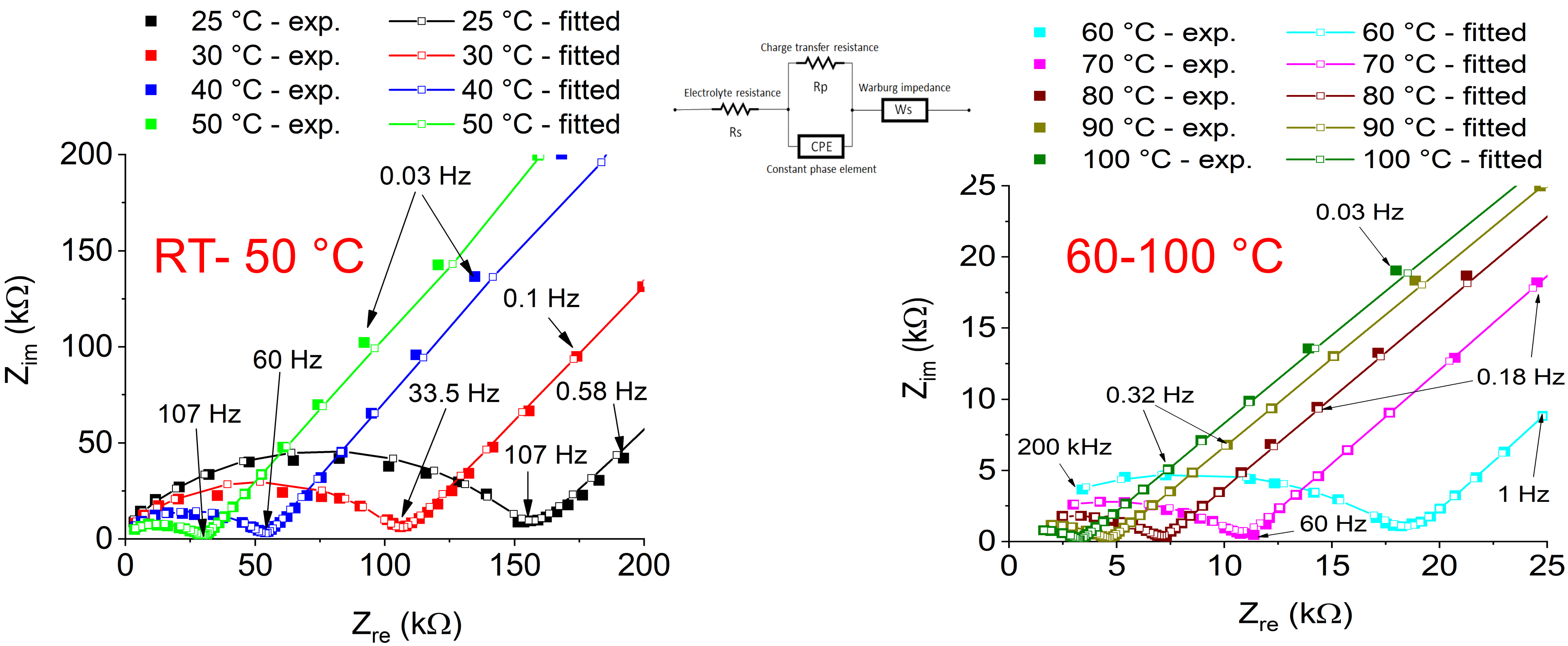
- No compression
- Compression



Dondelinger et al., Electrochim. Acta (2019) 306, 498-505

CONDUCTIVITY AT DIFFERENT TEMPERATURES

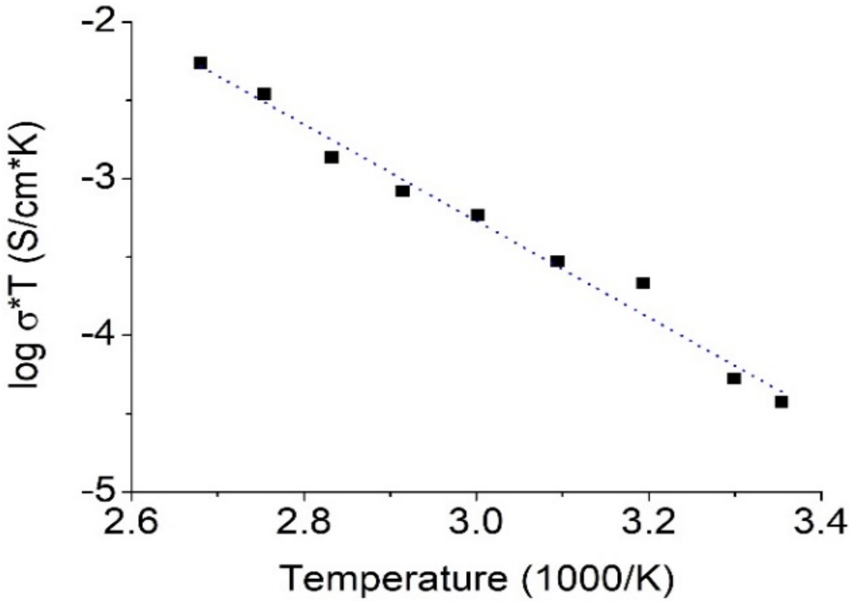
Cu-C/lithium halide/Li metal (0.05V-1.00V)

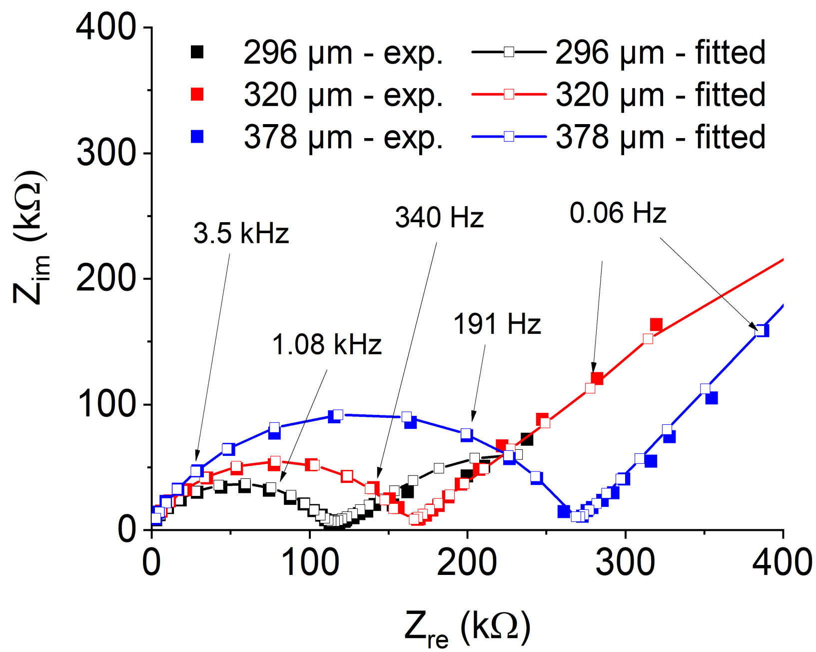


Dondelinger et al., Electrochim. Acta (2019) 306, 498-505

TEMPERATURE AND THICKNESS EFFECTS

Cu-C/Lithium halide/Li metal (0.05V-1.00V)

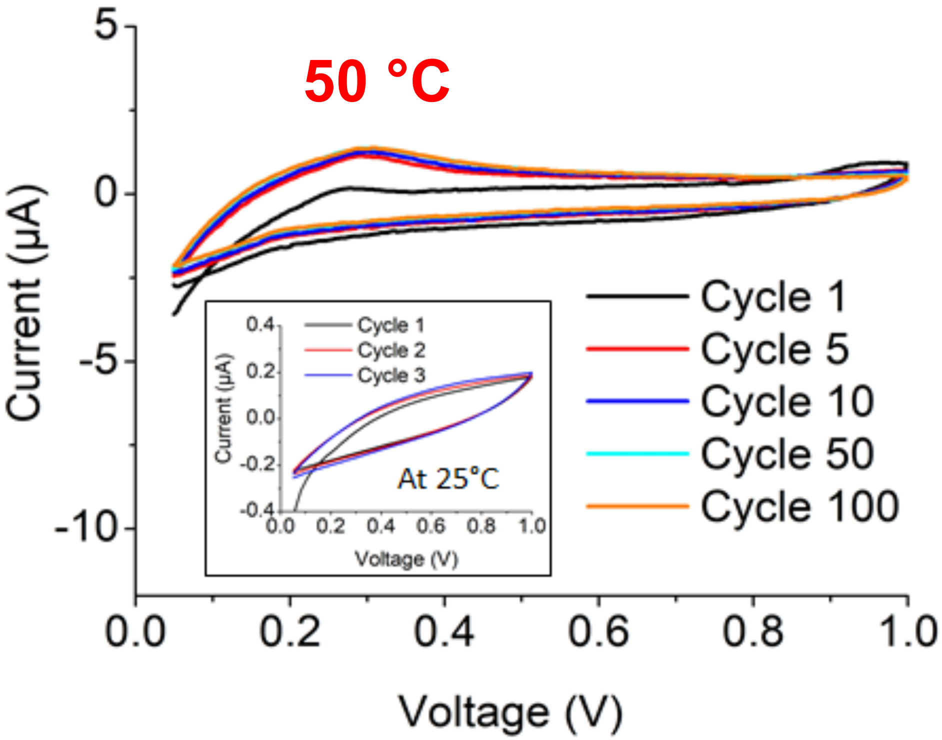


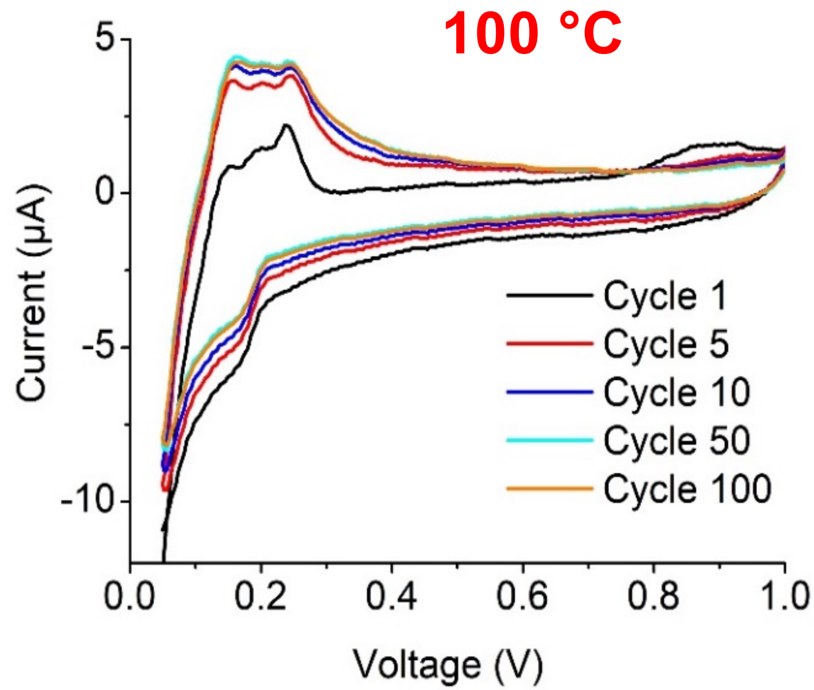


Dondelinger et al., Electrochim. Acta (2019) 306, 498-505

CYCLIC VOLTAMMETRY

Cu-C/Lithium halide/Li metal (0.05V-1.00V)

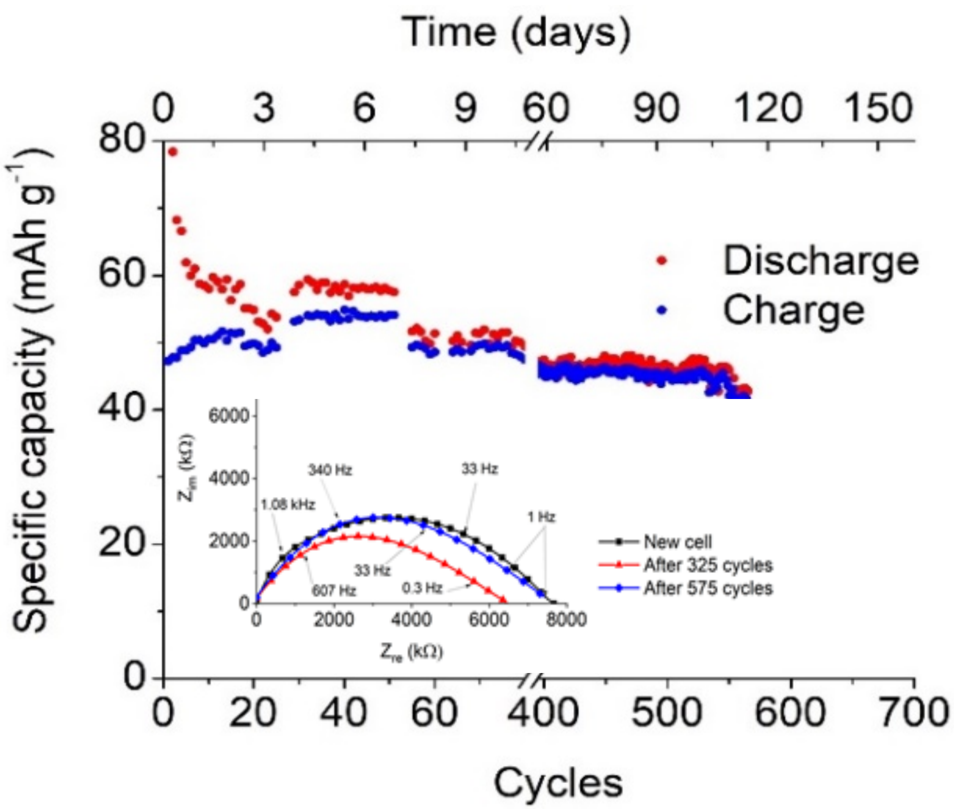


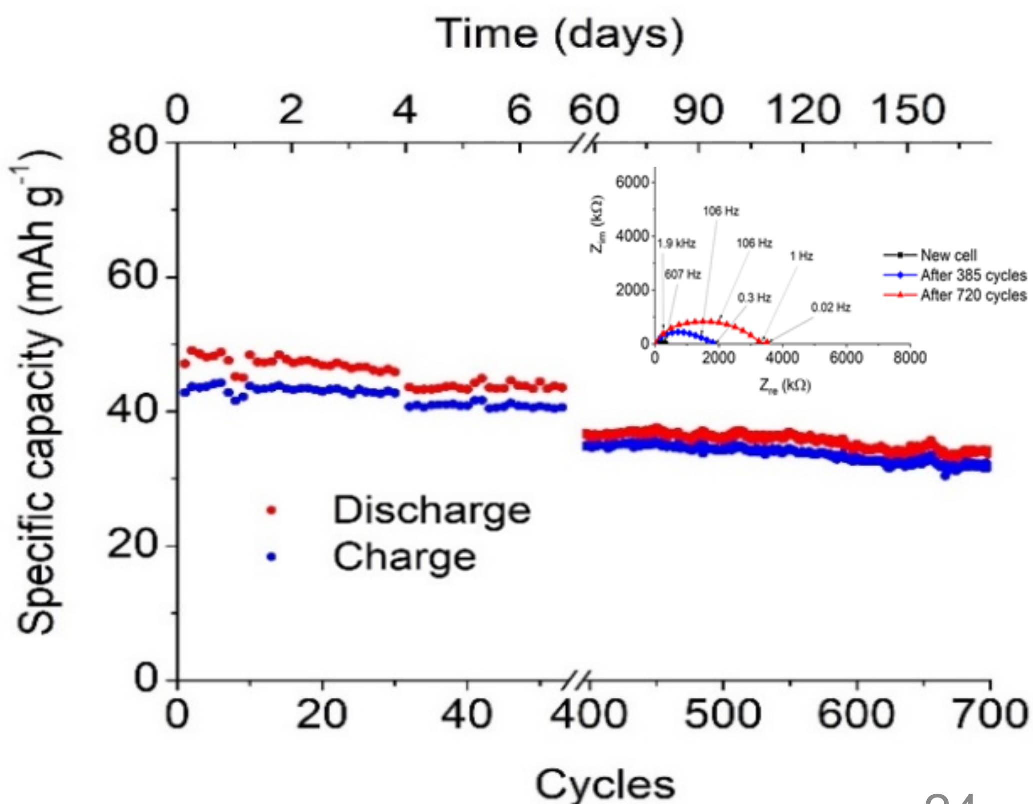


Dondelinger et al., Electrochim. Acta (2019) 306, 498-505

ELECTROCHEMICAL STABILITY VS. LITHIUM

Cu-C/electrolyte/Li metal (0.05V-1.00V)

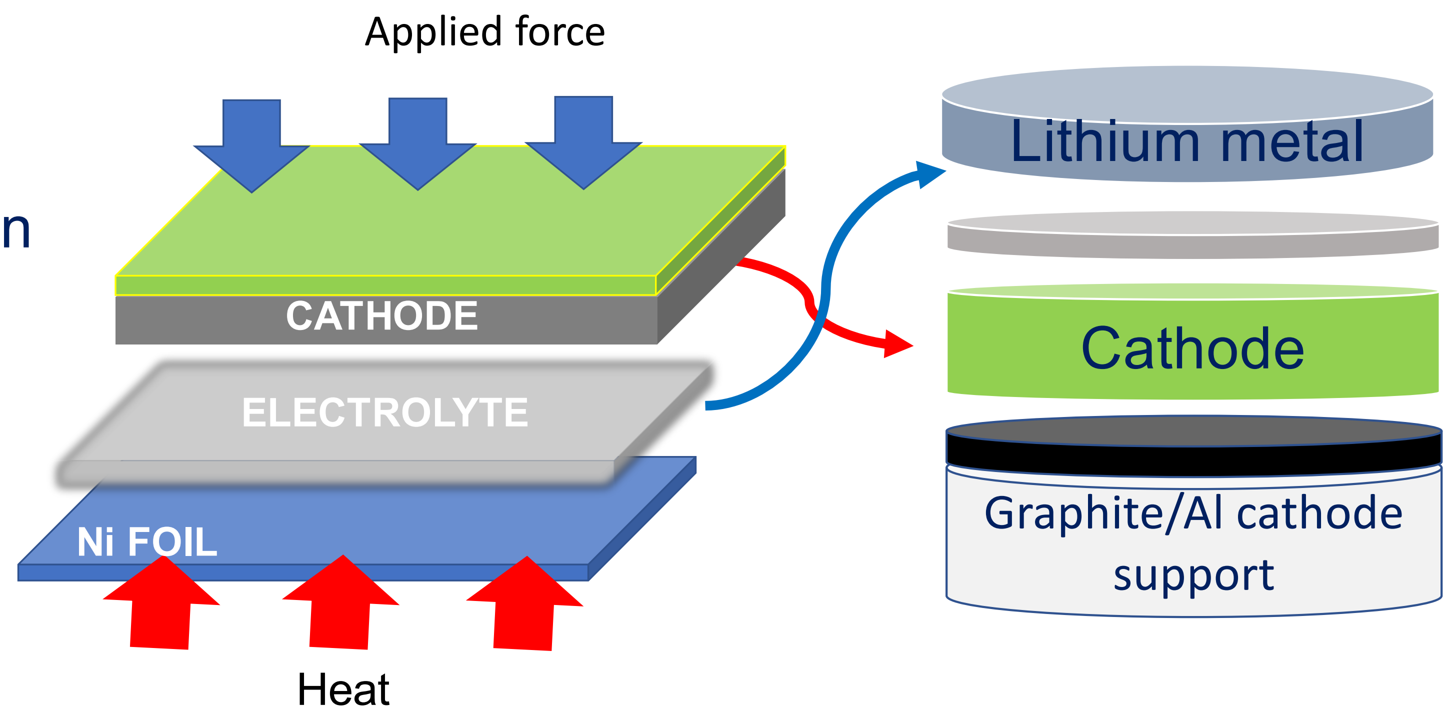




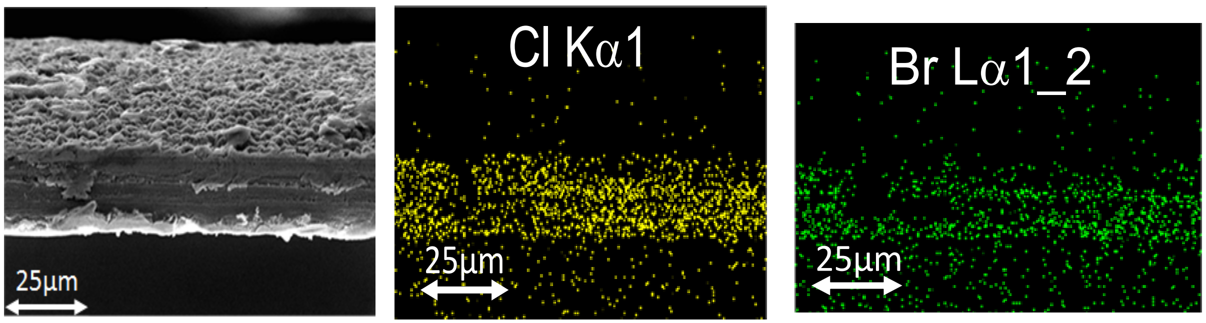
ANTIPEROVSKITES IN FULL CELLS

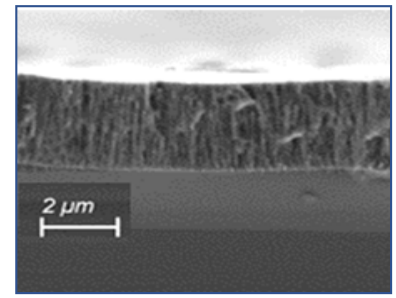
Methods:

- Delamination
- MS-PVD

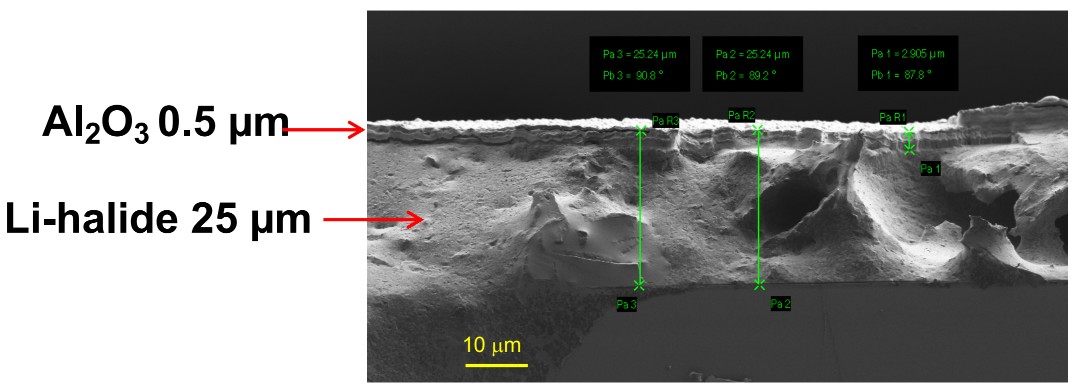


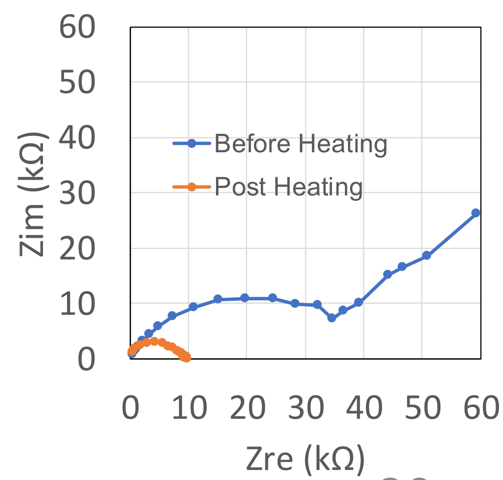
DEPOSITION BY PLASMA-ENHANCED PVD





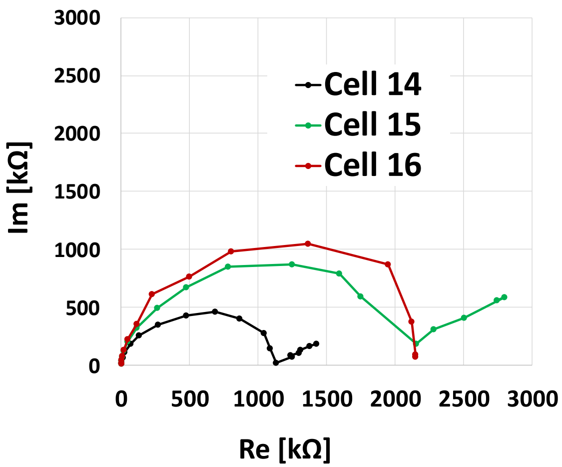
Cathode columnar structure from the cathode target



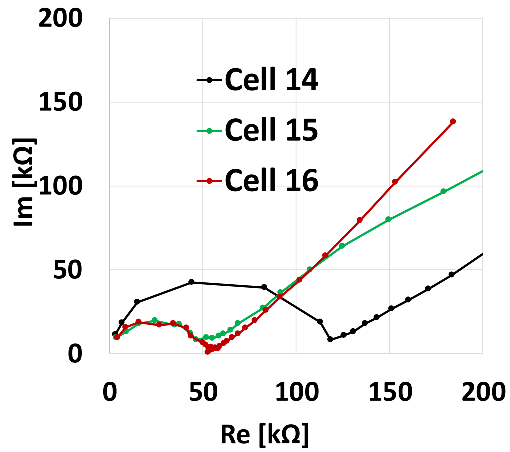


AC IMPEDANCE VS. TEMPERATURE AFTER CELL ASSEMBLY

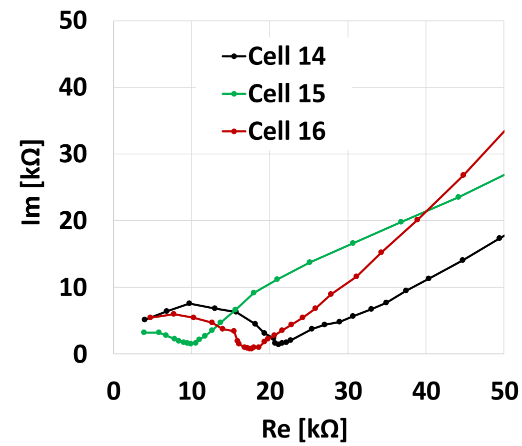
Al-C/LFP (90%), C(10%), Li_3ClO/ Li_3ClO/ Lithium



Room Temperature



50°C



100°C

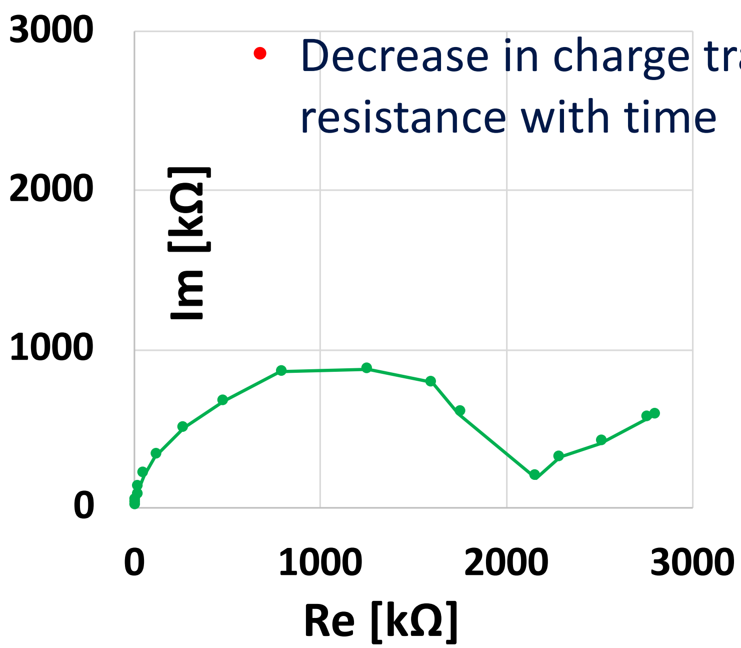
- Decrease in charge transfer resistance with temperature

COMPARICON: AC IMPEDANCE BEFORE AND AFTER CELL EXPOSURE TO HIGHER TEMPERATURES

Al-C/LFP (90%), C(10%), Li_3ClO/ Li_3ClO/ Lithium

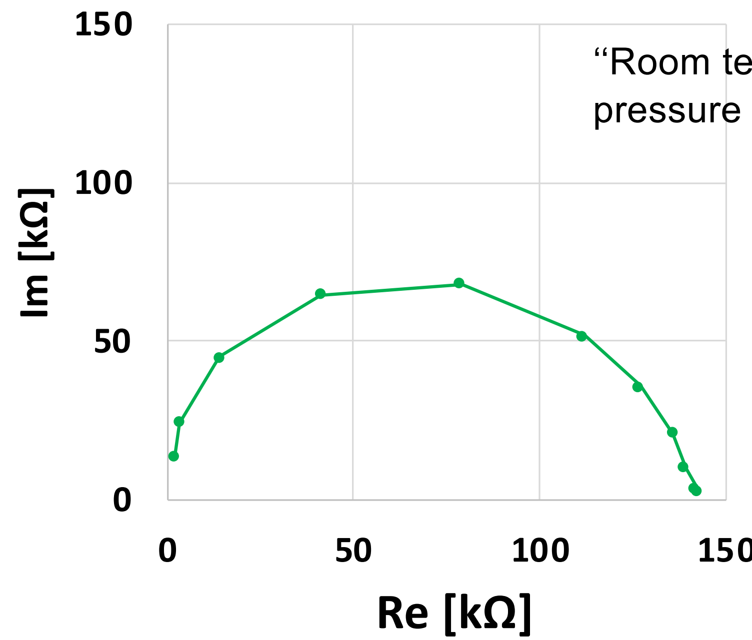
Before testing

- Decrease in charge transfer resistance with time



After exposure to 100^{o}C

"Room temperature pressure sintering"



Sakuda A et. al., . Sulfide solid electrolyte with favorable mechanical property for all-solid-state lithium battery. Scientific reports. (2013) 3:2261.

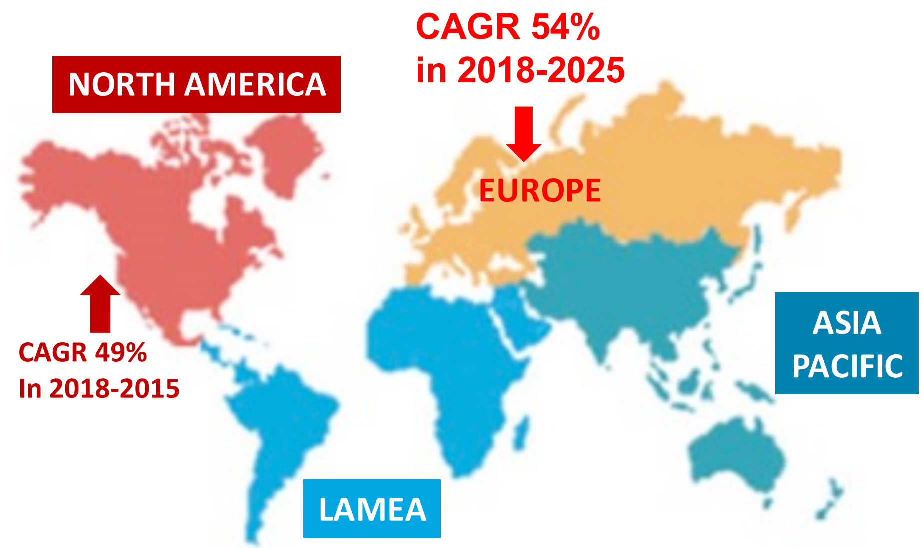
INDUSTRIAL RELEVANCE OF ANTIPEROVSKITES

	Garnets, e.g. LLZO*	Antiperovskites
Melting/processing T	$400^{o}C$** high	$250\text{-}300^{o}C$ low
Cost, $ per kg	6950	~100
Morphology	Grain boundary effects	Amorphous
Conductivity at RT (Sm/cm)	3×10^{-5}- 10^{-3}	2×10^{-3} (PLD)->10^{-1}***
Electrochemical stability in presence of Li metal*	Yes, red. potential 0.05V	Yes, impede formation of dendrites
Sensitivity to moisture and CO_2	Yes and CO_2	Moisture
Electrochemical window	>5V	>5V
Band gap	Appr. 6.4 eV****	5.0◊ - 8.5 eV***

*The lowest reduction potential (0.05 V) and the least favorable decomposition reaction energy (0.02 eV/ atom) at 0 V.
**Pfenninger et al., Nature Energy, 4, (2019) 475–483.
*** Cluster ions, e.g. BH_4^+***** Thompson, ACS Energy Lett., 2 (2017) 462−468.
◊ Zhang, Phys. Review B, 87 (2013) 134303.

CONCLUSIONS: WHAT NEEDS TO BE ADRESSED

- Coupled morphological, electrochemical, and mechanical behavior of antiperovskites
- Origins of spatial/temporal variations at the interfaces, both cathode and anode to move this technology forward



GLOBAL SOLID-STATE LI-ION BATTERY MARKET POTENTIAL FORECAST BY REGION

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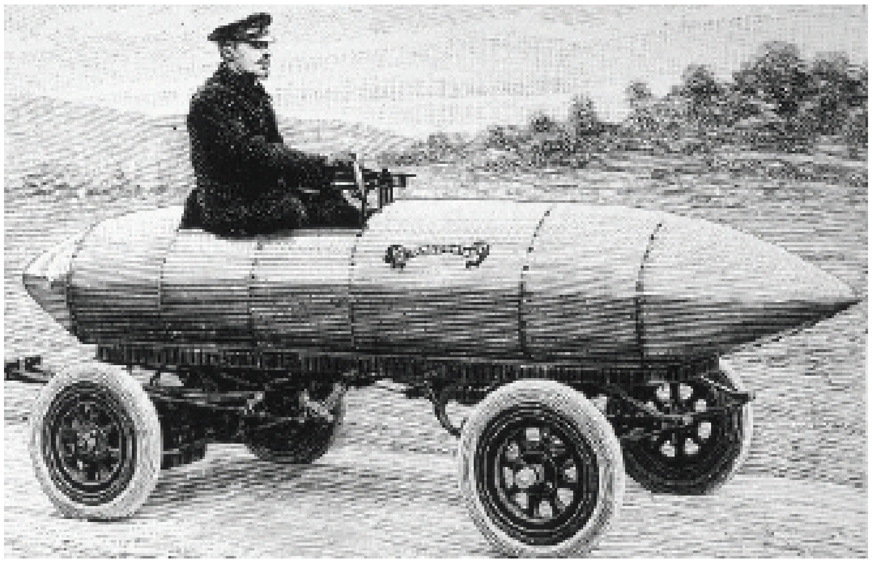
QUESTIONS



1899, Belgium
Car with a lead-acid battery
Speed: 67 mph

2019, Ford F-150
Fully electric truck with a lithium-ion battery; Power: tows 1.25 million lb. train