SOLID ELECTROLYTES FOR NEXT GENERATION BATTERIES

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This presentation does not contain any proprietary or confidential information.

Overview

Timeline

- Project Start Date-Sept. 2010
- Project End Date- Aug. 2013
- Percent complete: 50% complete

Barriers

- Stable solid electrolyte with $\sigma_{Li} > 10^{-4}$ S/cm
- Thin solid electrolyte membrane with enough mechanical strength

Budget

- Funding received in FY10-FY11
  – $70K
- Funding received in FY11-FY12
  – $70K

Partners

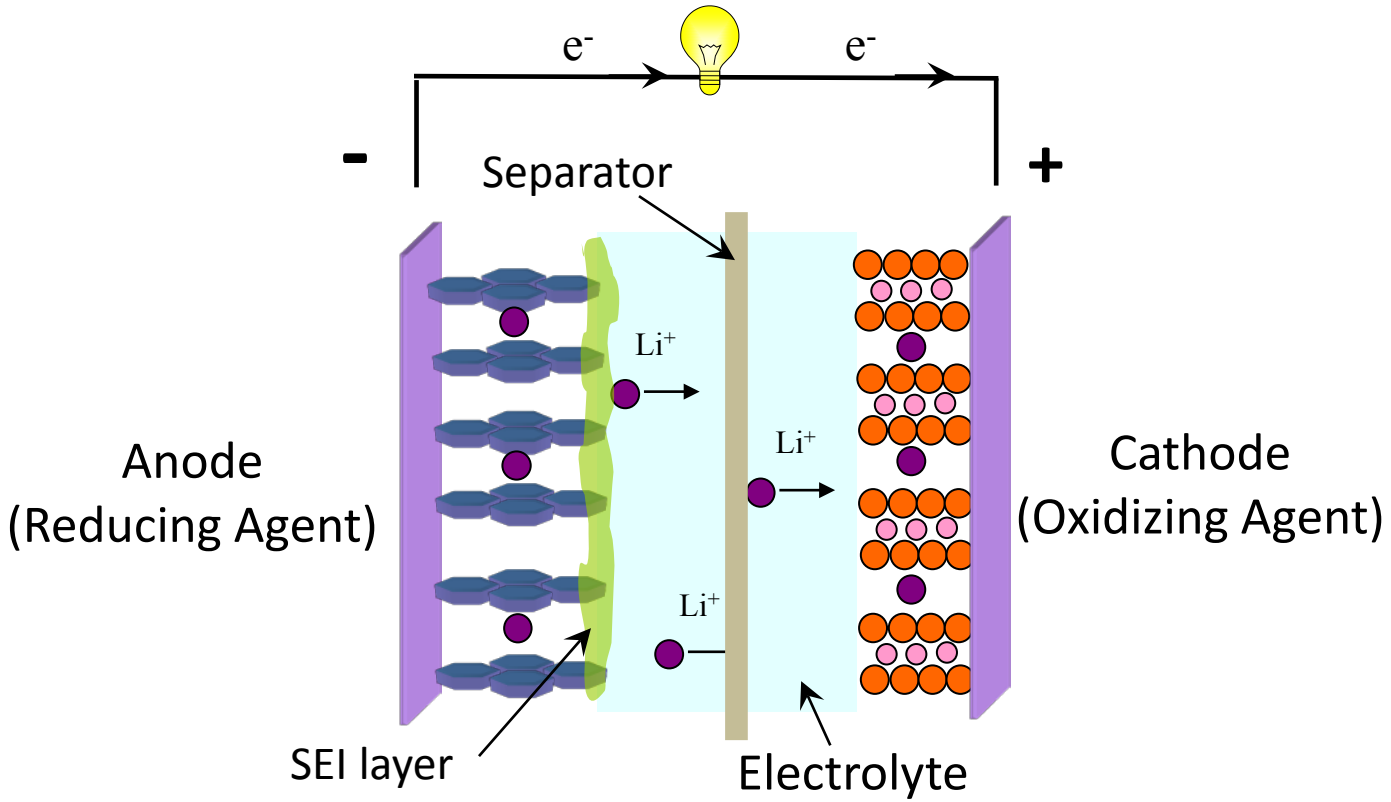
- Oak Ridge National Laboratory

Milestones

- Test liquid-cathode Li battery in which the pH of the cathode solution is alkaline. (Completed)
- Test a composite Li^+-ion solid electrolyte. (Partially completed)
- Test stability of garnet electrolyte in water. (Partially completed)
- Identification of a new Li^+-ion solid electrolyte and/or compounds for a Na^+-ion battery. (Ongoing)

Motivations

A typical State-of-art lithium-ion battery



- Capacity limited by Li solid solution in cathode and loss in SEI layer
- Voltage limited by E_g of carbonate electrolyte.

Why solid electrolyte separator?

- Enabling use of lithium metal anode to increase cell voltage and capacity
- Eliminating irreversible Li loss from cathode side during the first charge
- Enabling use of liquid cathodes with higher capacity than insertion hosts

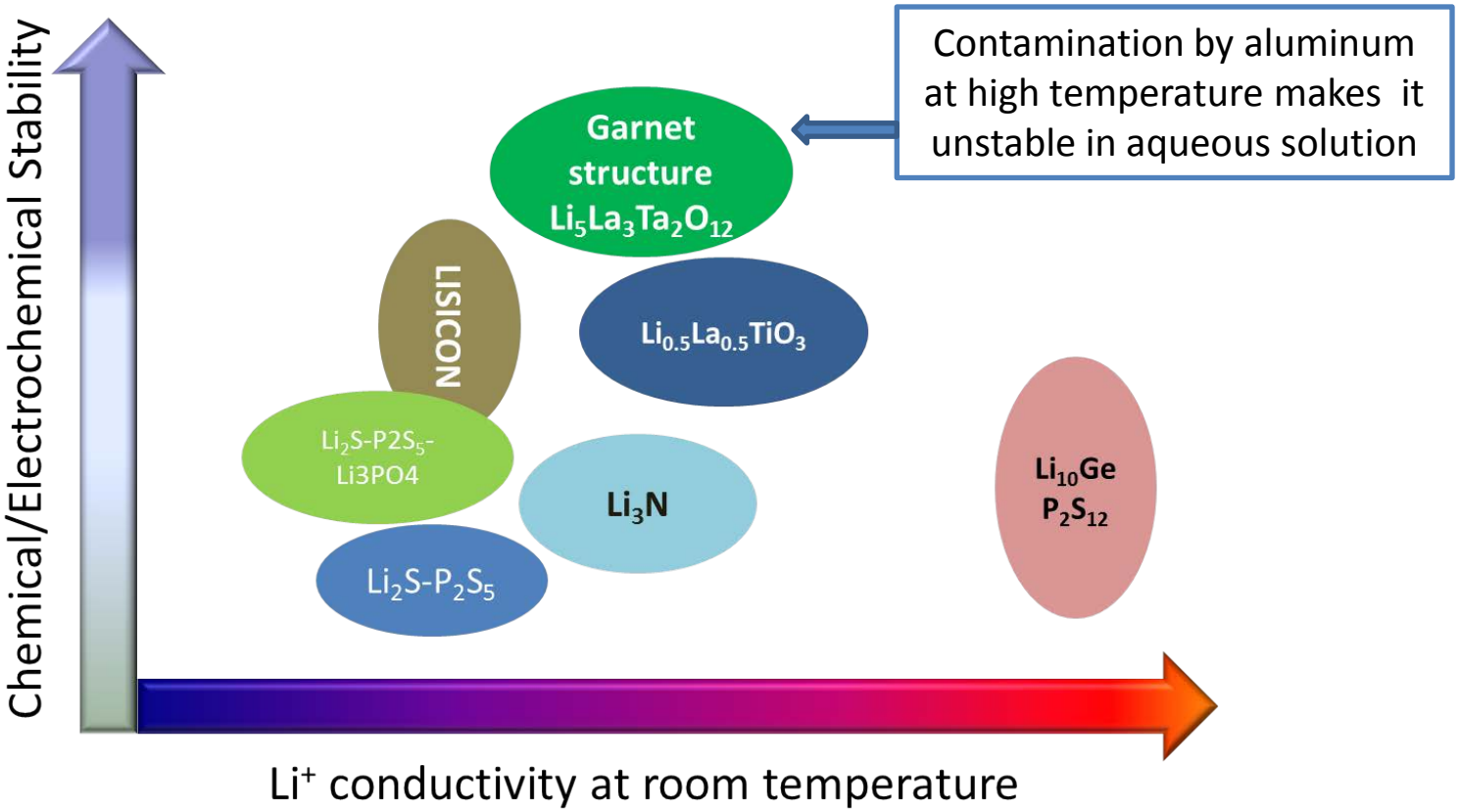
Objectives

Objective: Increase the cell voltage and capacity by using lithium metal anode and a solid electrolyte separator allows varied cathode strategies.

Specific objectives:

- Identify a solid electrolyte with $\sigma_{Li}{}^{+}>10^{-4}$ S cm^{-1} at room temperature that is stable against lithium
- Fabricate a thin, robust and chemically stable electrolyte membrane
- Build a high-voltage cell with a liquid catholyte, a solid electrolyte membrane as separator and lithium metal as anode.

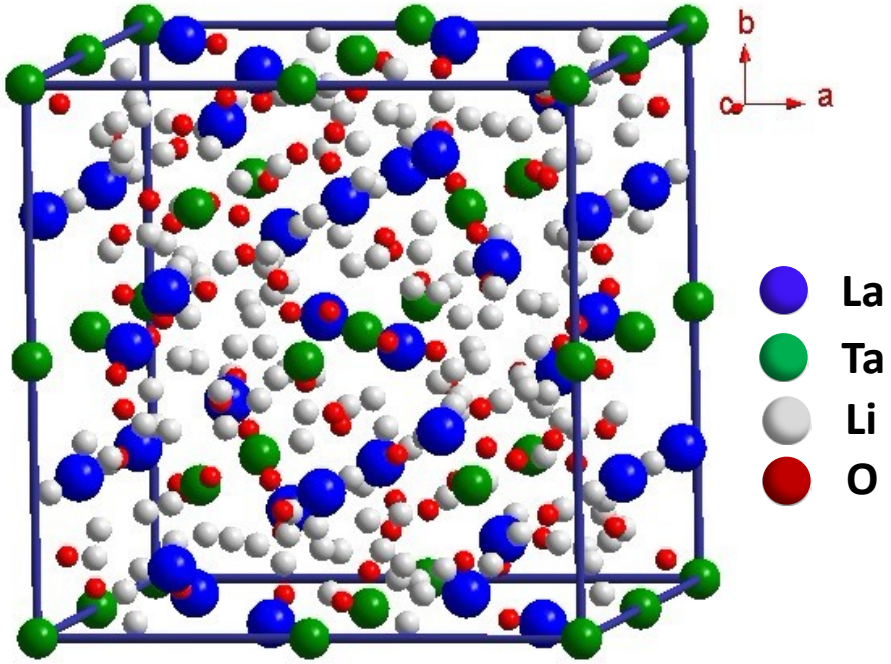
Existing Solid Electrolytes



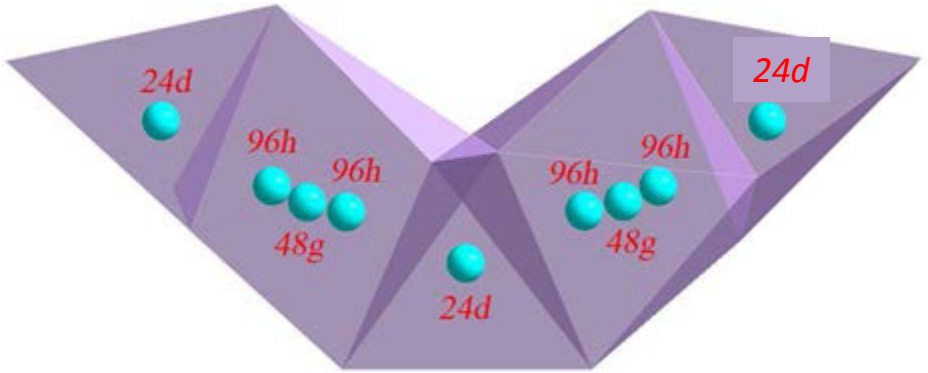
Garnet structure electrolytes are electrochemically stable with a larger window than commercial LISICON® membrane and are not sensitive to water as sulfides, so they are a promising separators for flow-through batteries using aqueous solutions.

Approach

Garnet: $A_3B_3C_2O_{12}$
Garnet framework: $B_3C_2O_{12}$



Interstitial spaces for lithium



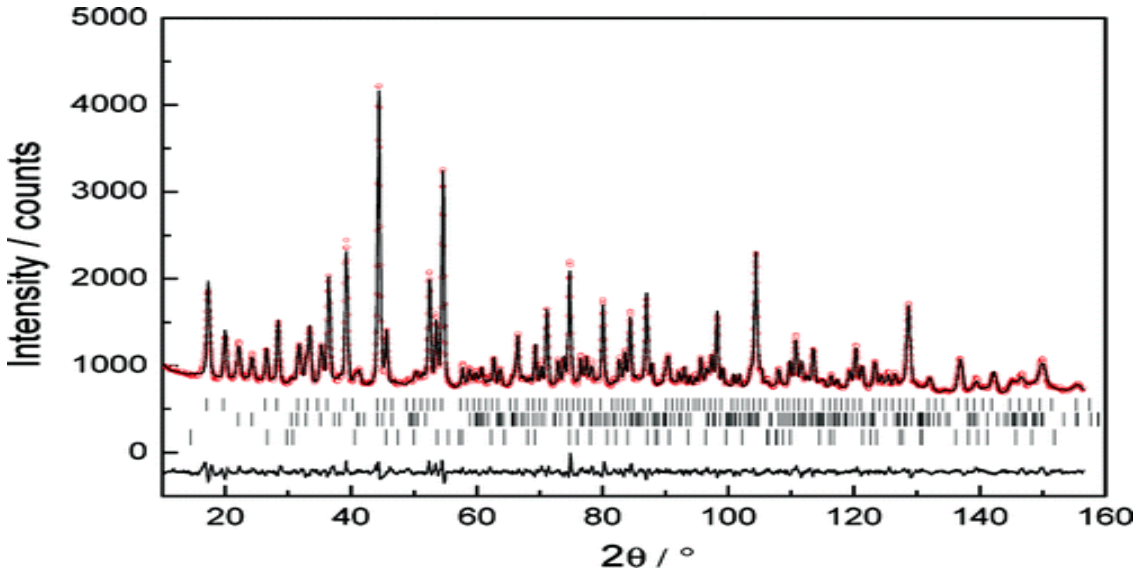
$La_3Ta_2O_{12}$ framework with Li in interstitial space

Tetrahedral sites 24d bridged by octahedra with positions 96h and 48g.

Technical accomplishment

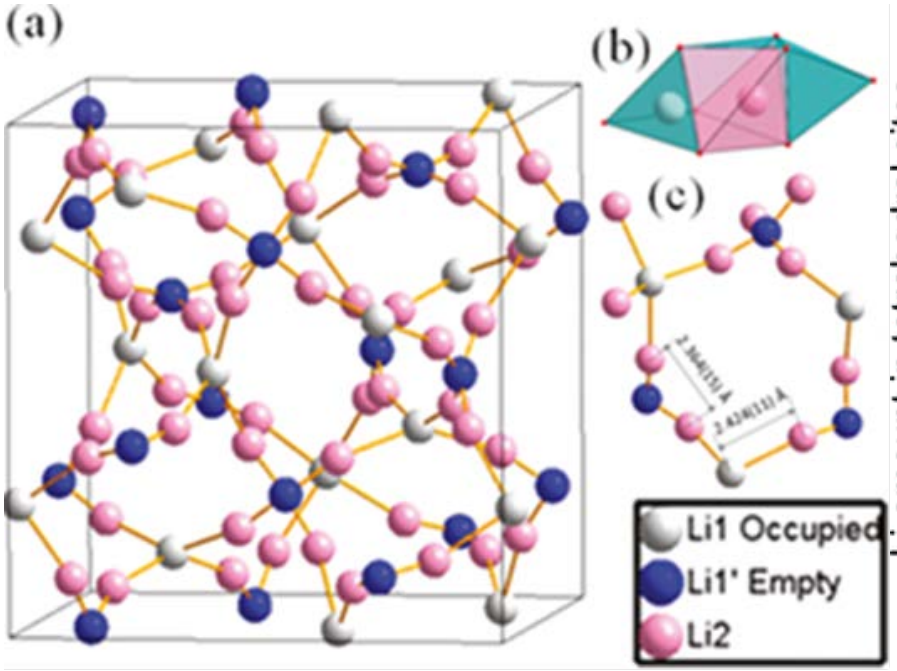
Refined structure parameters of cubic $Li_7La_3Zr_2O_{12}$

Atom	Site	Occupation	X	Y	Z	U_{iso}/U_{eq} (Å^2)
Li1	24d	0.564(12)	3/8	0	¼	0.026(2)
Li2	96h	0.442(3)	0.6802(8)	0.5968(8)	0.1004(9)	0.034(3)
La	24c	1	1/8	0	¼	0.0124
Zr	16a	1	0	0	0	0.0107
O	96h	1	0.28209(10)	0.10070(11)	0.19449(13)	0.0174

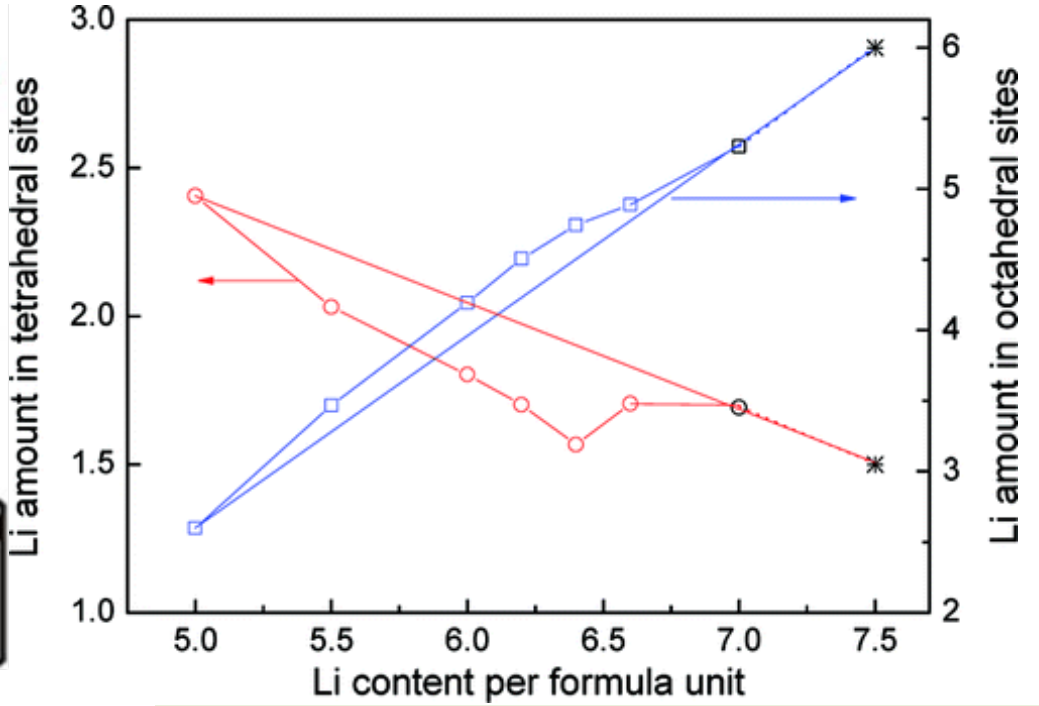


Al-free sample has been prepared via a low-temperature synthesis route.

Neutron diffraction results reveal that lithium barely occupies 48g site in $Li_7La_3Zr_2O_{12}$.



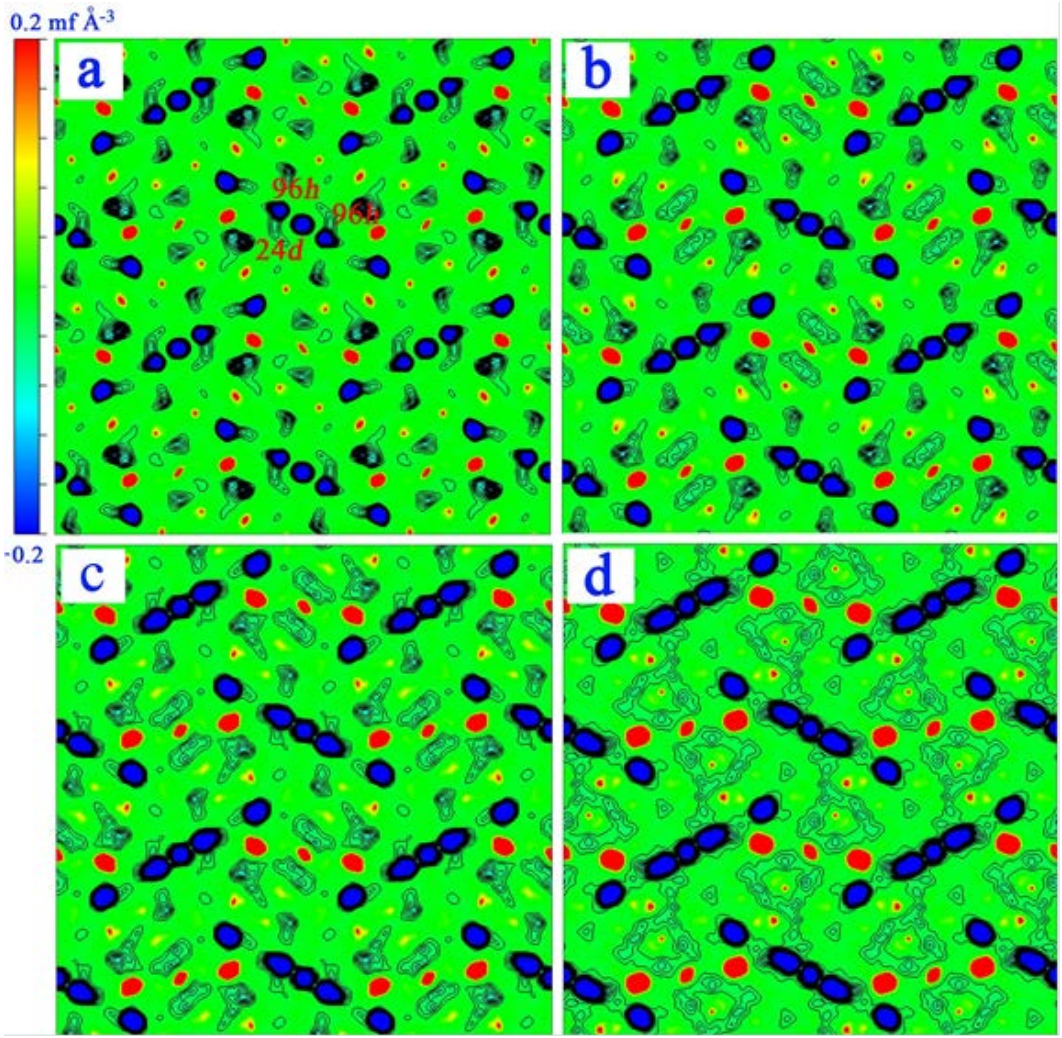
3D connection of Li sites within the interstitial space of the garnet framework with 7.5 Li per formula unit.

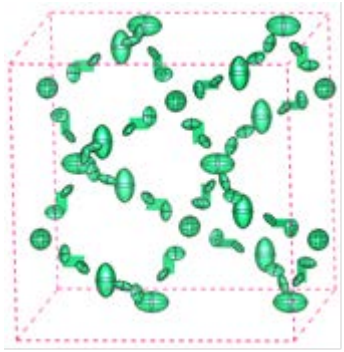


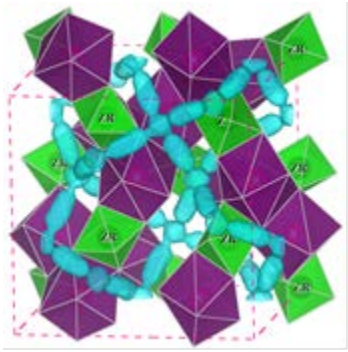
Li site occupancies vs Li content per formula unit from neutron diffraction.

- Short-range order of lithium appears when the Li content per formula unit approximates 7.
- It is noticed there is a transition point near 6.5 per formula unit, so we suspected the maximum lithium conductivity is in this region.

Lithium pathway in $Li_7La_3Zr_2O_{12}$



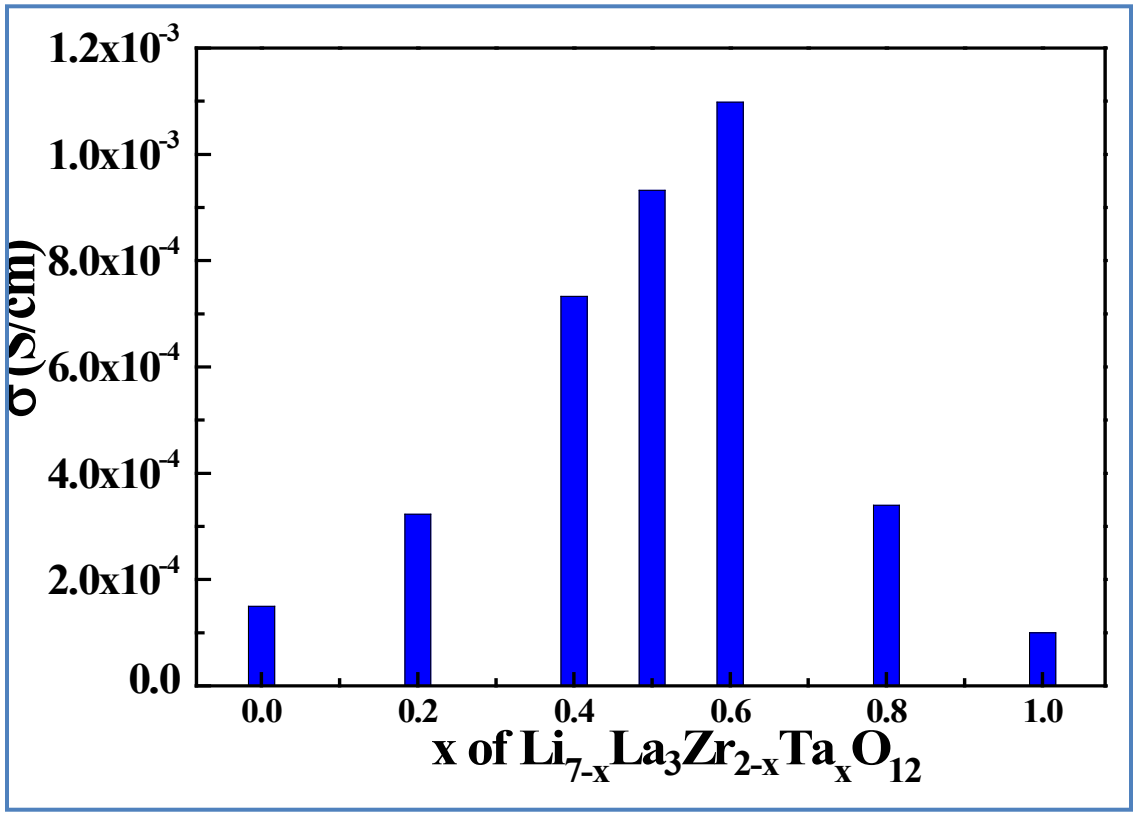




Two-dimensional contour maps sliced on the (001) plane with z = 0.4 at (a) RT, (b) 200, (c) 400 and (d) 800°C, respectively; Li delocalizes along the 3-dimensional chain, Li(24*d*)-Li(96*h*)-Li(48*g*)-Li96*h*)-Li(24*d*) direction, whereas Zr, La and O remain near their original positions.

Accomplished by collaboration with Los Alamos National Laboratory

Optimization of Lithium content



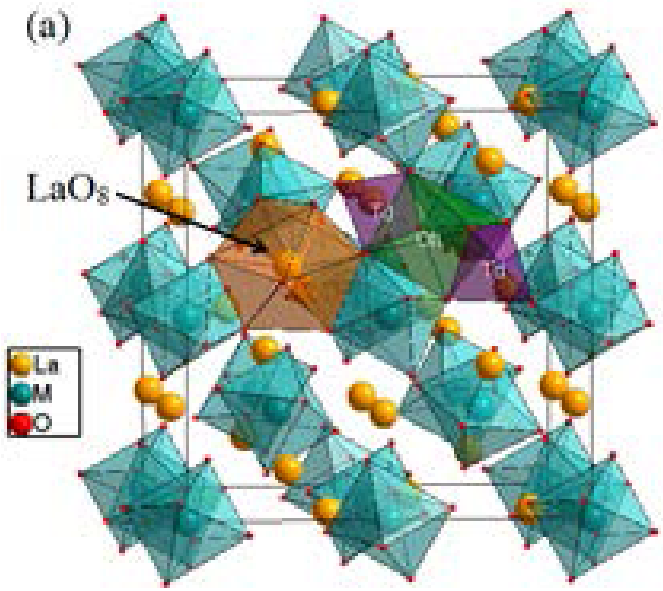
In accordance with prior result results, a maximum $\sigma_{Li+} > 10^{-3}$ S cm^{-1} has been obtained at x=0.6 (nominal composition $Li_{6.4}La_3Zr_{2.4}Ta_{0.6}O_{12}$).

Table 1 Comparison of the lattice parameter and density for $Li_6La_3SnMO_{12}$.

Nominal Composition	Lattice parameter (Å)	Ionic radius of M^{5+} (Å)	Theoretical density (g cm^{-3})	Real density (g cm^{-3})	Relative density (%)
$Li_6La_3SnSbO_{12}$	12.8991	0.60	5.514	4.841	87.8%
$Li_6La_3SnNbO_{12}$	12.8682	0.64	5.373	4.815	89.6%
$Li_6La_3SnTaO_{12}$	12.8693	0.64	5.921	5.266	88.9%

Table 2 Room-temperature ionic conductivity and activation energy for $Li_6La_3SnMO_{12}$ at 20 °C.

Nominal Composition	σ_{Li} (S cm^{-1})	E_a (eV)
$Li_6La_3SnSbO_{12}$	0.22×10^{-4}	0.504
$Li_6La_3SnNbO_{12}$	0.35×10^{-4}	0.503
$Li_6La_3SnTaO_{12}$	0.42×10^{-4}	0.498
$Li_6La_3ZrTaO_{12}$[3]	1.8×10^{-4}	0.420
$Li_6La_3ZrNbO_{12}$[4]	~1.5×10^{-4}	~0.40

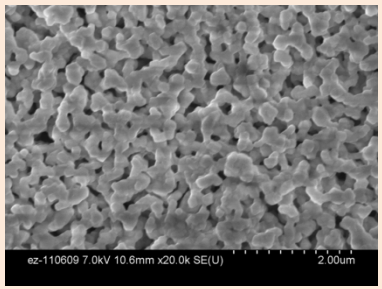


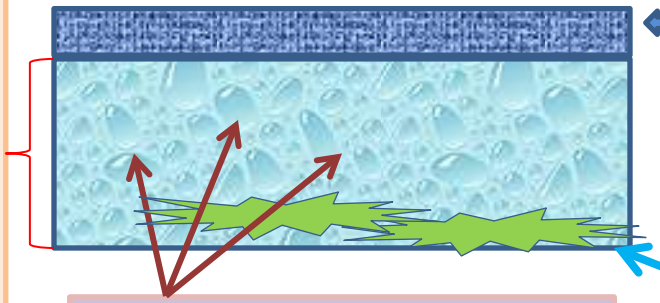
Comparison of the Li^+ conductivities of the garnets show a clear trend to higher Li^+ conductivity the stronger the covalent bonding within the garnet framework; this effect is more important than the size of the interstitial volume within which the Li^+ ions move. Stronger covalent bonding within the framework reduces the strength of the oriented Li bonding in the interstitial space.

Make the solid-electrolyte membrane thin and strong

- Deposit a thin layer on a porous substrate that allows carbonate electrolyte to pass through.
- Make polymer/solid-electrolyte composites that are stable and flexible.

porous substrate (Al_2O_3 ,YSZ…)





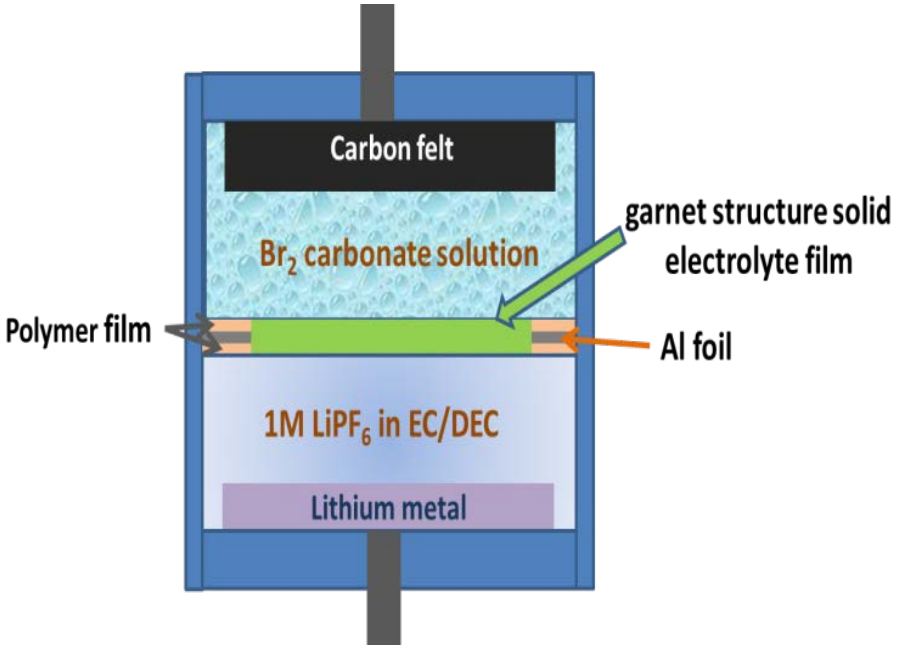
Dense thin layer of garnet electrolyte deposited via PLD

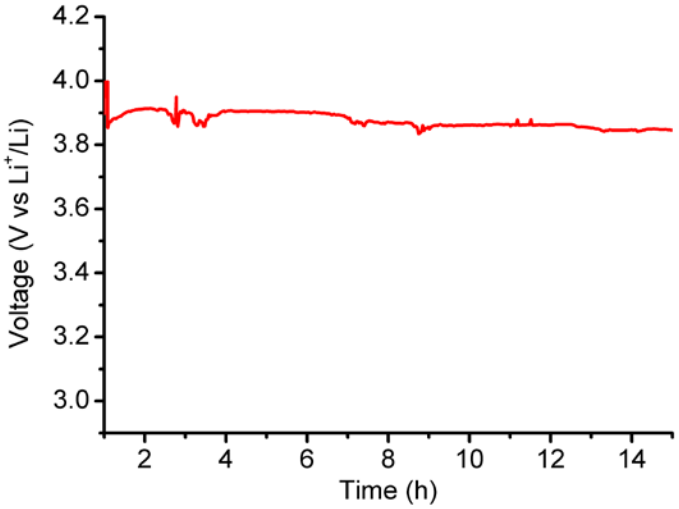
Lithium dendrites

Organic electrolyte (EC, DEC, DMC, PC…) in pores

PLD and spin-coating are accomplished by ORNL

A lithium-bromine battery using a garnet solid electrolyte separator

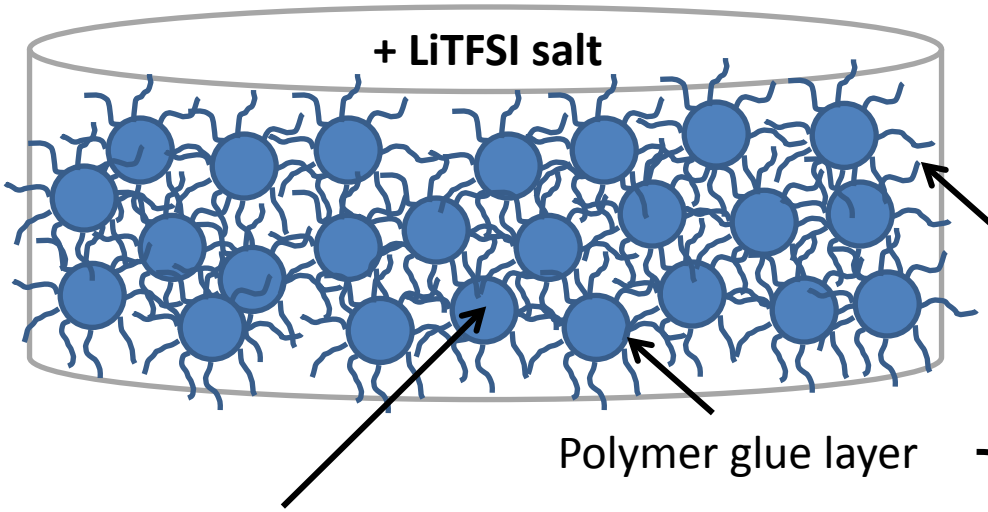


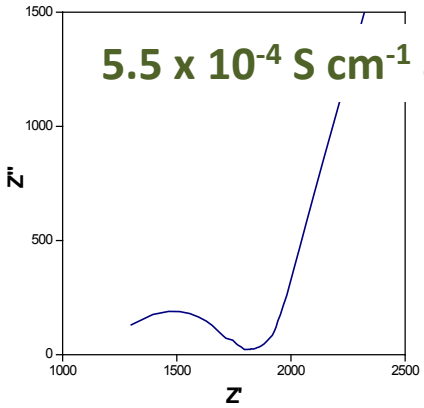


Garnet solid electrolyte is stable in bromine carbonate solution
Bromine can be a very promising liquid catholyte for flow-through battery owing to its high open circuit voltage (4V) and high capacity (335 mAh/g) that is much higher than insertion compounds.

Garnet/Polymer composite solid electrolyte

1. Garnet/PEO composite electrolyte for Solid State Battery





5.5×10^{-4} S cm^{-1} at R.T.

pH ~ 7 in water
with polymer protective layer

New Finding

2. Water-stable Garnet Solid Electrolyte

Long-term stability at high pH/temp. condition
Compatibility of the structure with organic electrolyte
Lithium-ion permeability

Summary

- A low-temperature synthesis route has been developed to prepare aluminum-free $Li_7La_3Zr_2O_{12}$ garnet electrolyte and the lithium distribution in cubic $La_3Zr_2O_{12}$ garnet framework has been resolved. A maximum of 7.5 Li per formula unit has been predicated from neutron diffraction results.
- A high lithium conductivity higher than 10^{-3} S cm^{-1} has been achieved by optimizing the lithium content in $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (σ_{Li+} =1.1*10^{-3} S cm^{-1} at x=0.6)
- Comparison of the Li^+ conductivities of the garnets ($Li_6La_3SnMO_{12}$, M= Sb, Nb, Ta, Zr) shows a clear trend to higher Li^+ conductivity the stronger the covalent bonding within the garnet framework; this effect is more important than the size of the interstitial volume within which the Li^+ ions move.
- A thin garnet electrolyte membrane on a robust porous substrate has been fabricated in collaboration with ORNL and tested in a flow-through battery.
- Polymer/garnet electrolyte composites are under development to fabricate flexible electrolyte membranes.
- A high voltage and high capacity lithium-bromine battery has been built with a garnet electrolyte separator, indicating a promising development of next-generation batteries with solid electrolytes.

Future Work

- Aluminum-free garnet electrolyte will be further studied to understand the lithium transport in garnet framework and its stability in water.
- Porous substrates with different composition and pore size will be studied for supporting the thin electrolyte membrane to optimize its conductivity.
- The Composition of polymer/garnet electrolyte composites will be optimized to obtain higher conductivity.
- The performance of polymer/garnet electrolyte composites in aqueous/nonaqueous electrolyte will be studied.
- The battery configuration of lithium-liquid cathode flow-through batteries will be further developed.