Enhance Ionic Conductivity & Stability of $La_{2/3-x}\square_{1/3-2x}Li_{3x}TiO_3$ (LLTO) Solid-Electrolyte by Grain Boundary Glass Doping

Yue Zhou, Meng Yao, Greg Collins, **Xingbo Liu**

Department of Mechanical and Aerospace Engineering

West Virginia University

Morgantown, WV 26506 – 6106

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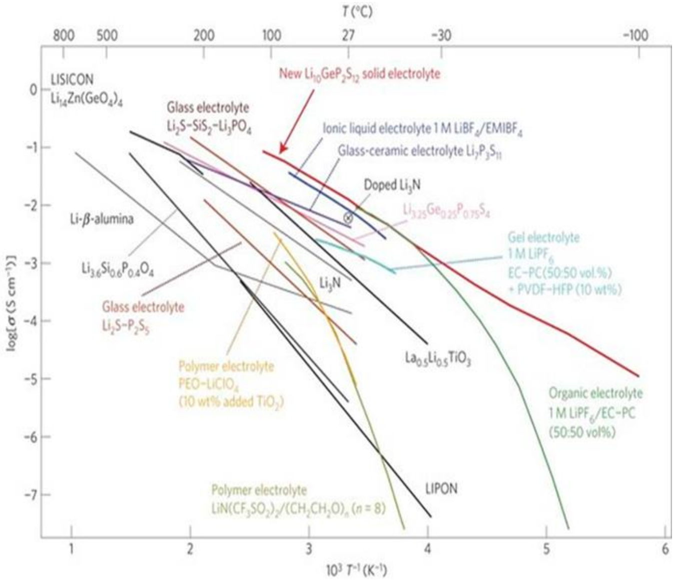
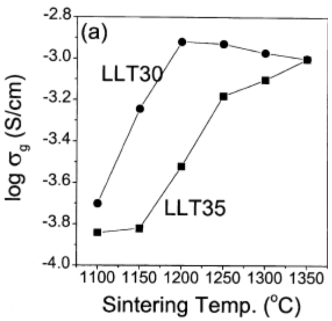
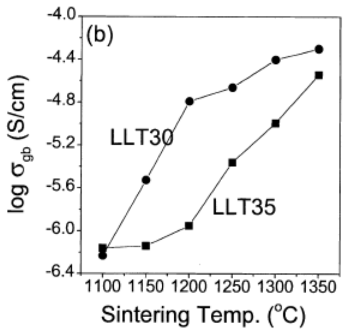
- Dr. Bin Liu / Shanghai University

Background





σ_g $1.8 \times 10^{-4} – 1.3 \times 10^{-3}$ (S/cm)



σ_{gb} $6.5 \times 10^{-7} – 4.1 \times 10^{-5}$ (S/cm)

C.W. Ban, G.M. Choi/Solid State Ionics 140 (2001) 285–292

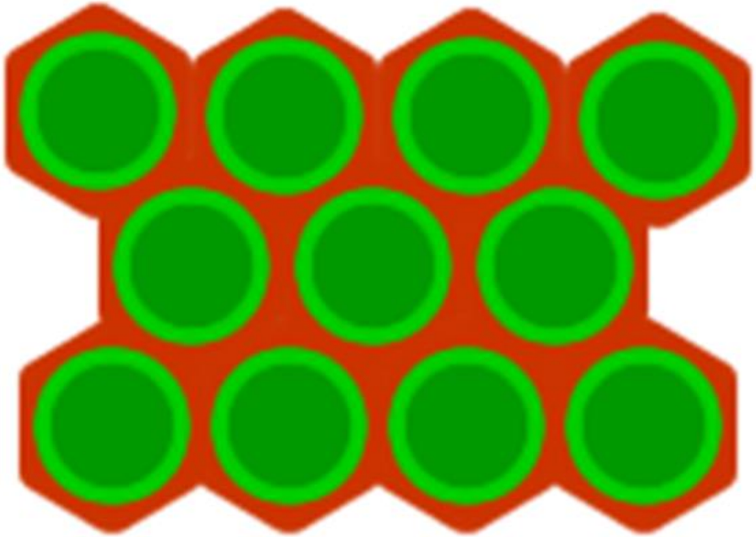
Advantages of solid state electrolytes:

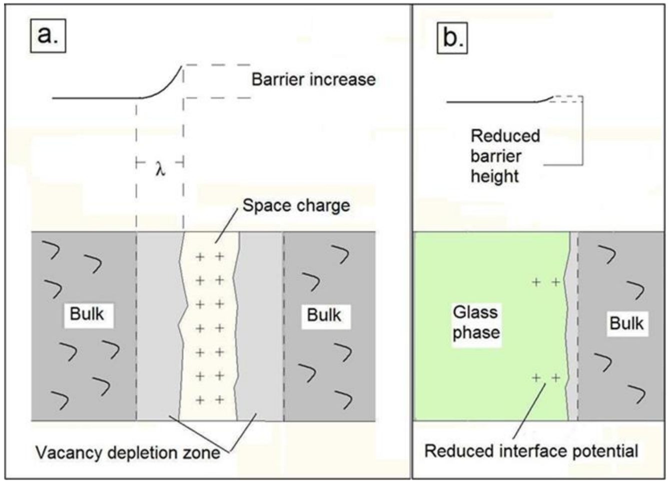
I. Non-flammability
II. Chemical stability
III. Low electric conductivity
IV. Thermal stability

Concerns:

I. Low ionic conductivities, especially at grain boundaries
II. Manufacturing related issues
III. …

Overall Scientific Approach



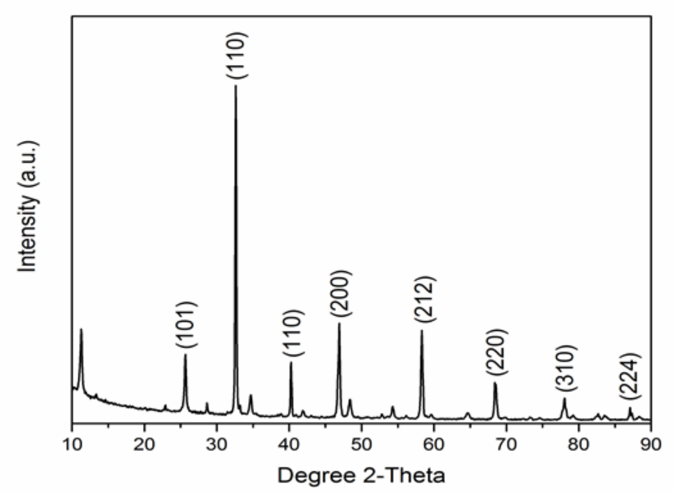


$$\sigma_{tot} = 4e\left(\mu_{bulk} \exp^{-\frac{F+2e\Phi}{kT}} + \mu_{gb} \exp^{-\frac{F}{kT}} \right)$$

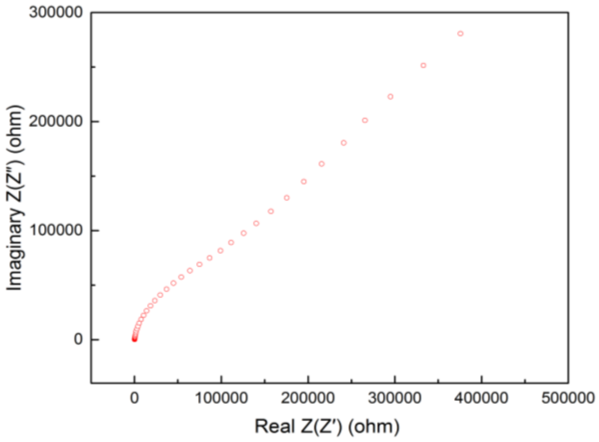
Developing Ceramics-Glass Composites with improved total conductivity and stability

US Patent: 8,865,354 B2; US Patent Application No. 13/693,359

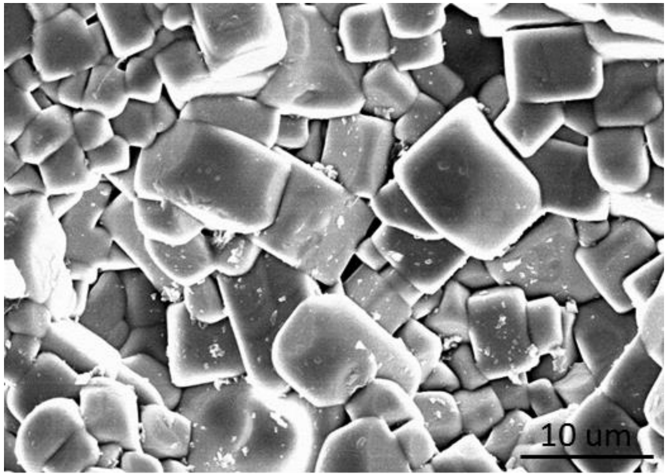
Summary of FY15 Effort



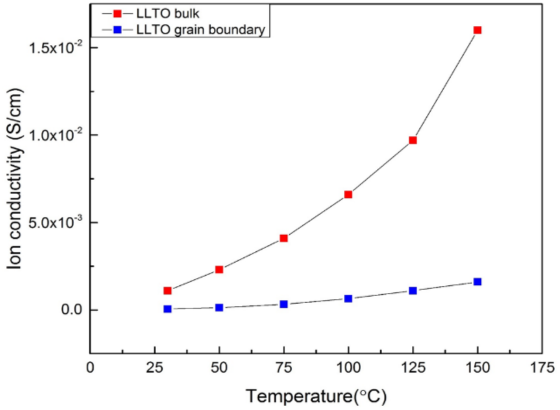
XRD pattern of LLTO we synthesized



Typical EIS of LLTO@30°C

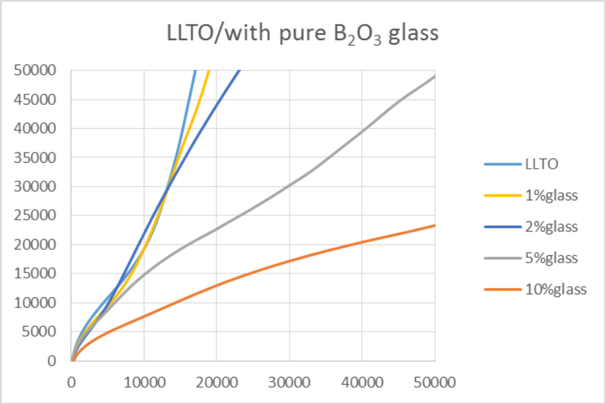


SEM graph of LLTO cross section

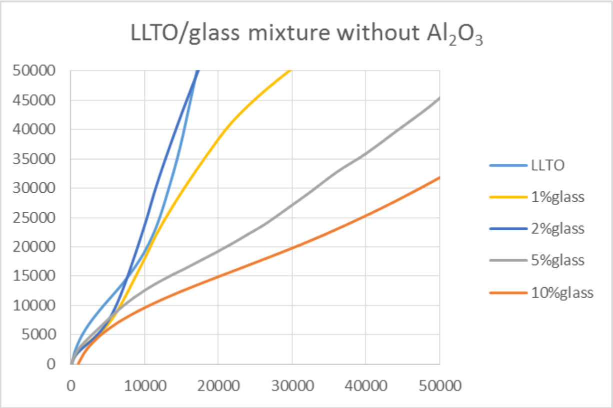


LLTO bulk and GB conductivities at different temperatures

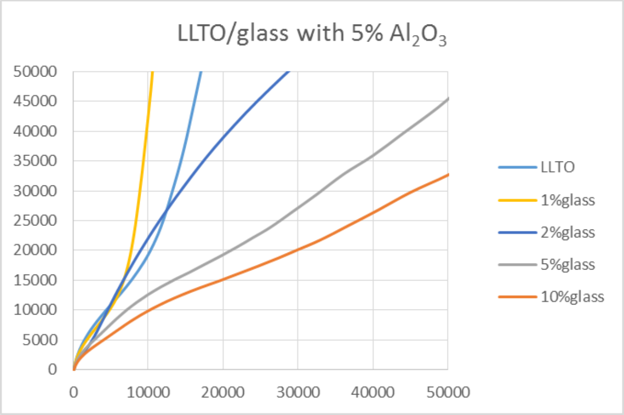
Summary of FY15 Effort



	gb	diff	total
LLTO	0.000056	0.0011	0.000053
1%	0.000071	0.00094	0.000066
2%	0.00012	0.0009	0.000106
5%	0.000014	0.00085	0.000014
10%	0.0000001	0.00025	0.0000001



	gb	diff	total
LLTO	0.000056	0.0011	0.000053
1%	0.000084	0.001	0.000077
2%	0.00013	0.00094	0.000114
5%	0.000074	0.00088	0.000068
10%	0.000027	0.00059	0.000026



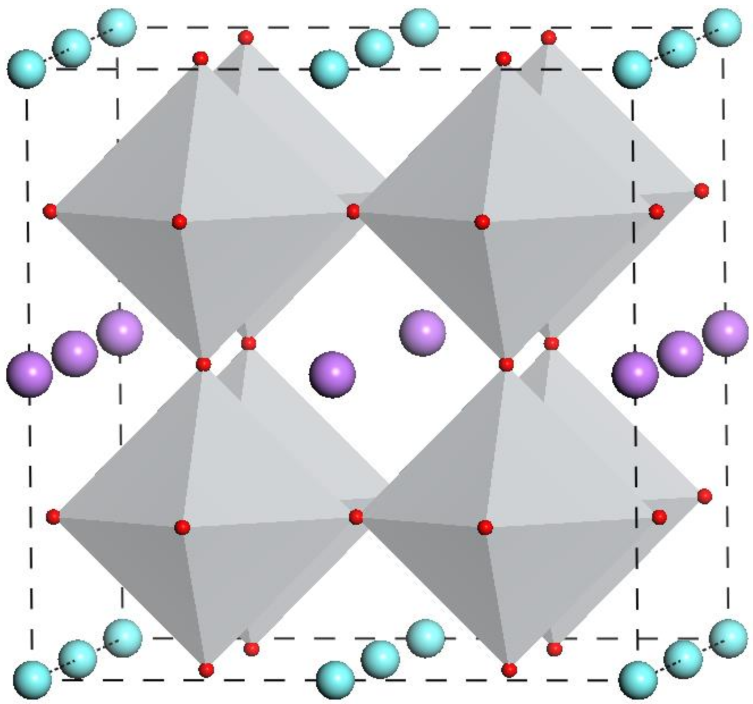
	gb	diff	total
LLTO	0.000056	0.0011	0.000053
1%	0.00013	0.00105	0.000116
2%	0.00034	0.00089	0.000246
5%	0.000086	0.00074	0.000077
10%	0.000021	0.00034	0.000020

Improve GB conductivity by 6 times
Improve overall conductivity by 5 times

Outline

- Fundamental understanding of ionic conduction in LLTO and LLTO/Glass systems
  - Ab initio calculations
  - Experimental characterization in LLTO/Al2O3 system
- Improving microstructures and conductivities by optimizing manufacturing process
- Full-cell assembly & characterization

Structure of LLTO



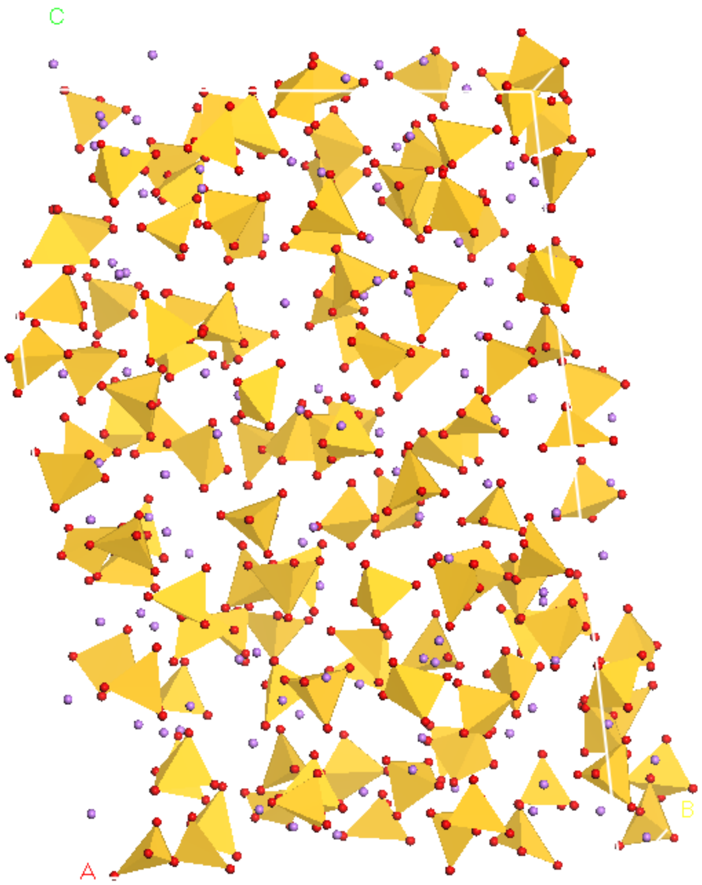
LLTO supercell

Space group: Pm-3m (221)

Cell parameter: 3.8717Å

Li:La:□=3:4:1

Structure of Oxide Glass



Glass: SiO_2-B_2O_3-Li_2O

Ensemble: NPT

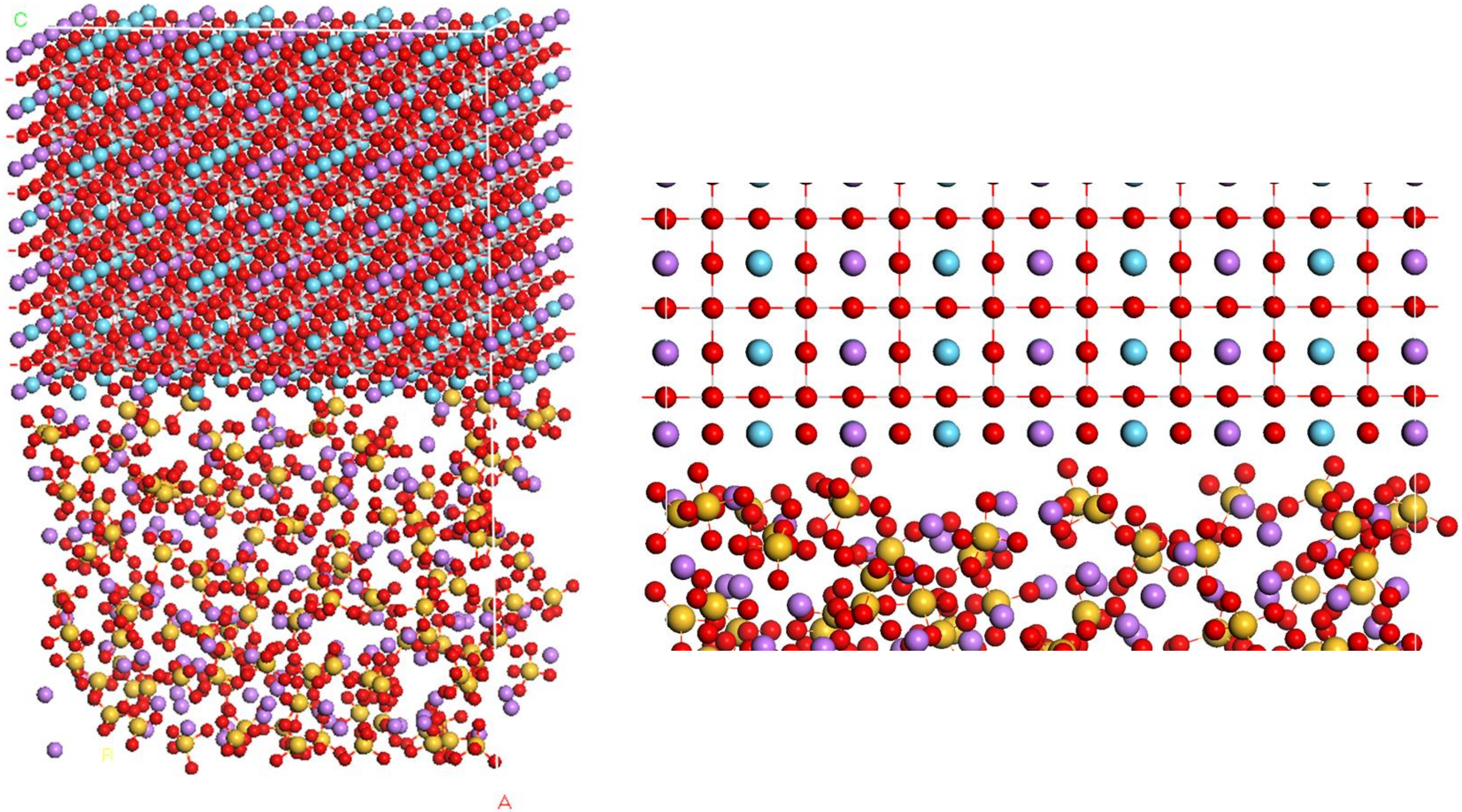
Temperature: 3000K

Pressure: 0.1GPa

Number of steps: 10000

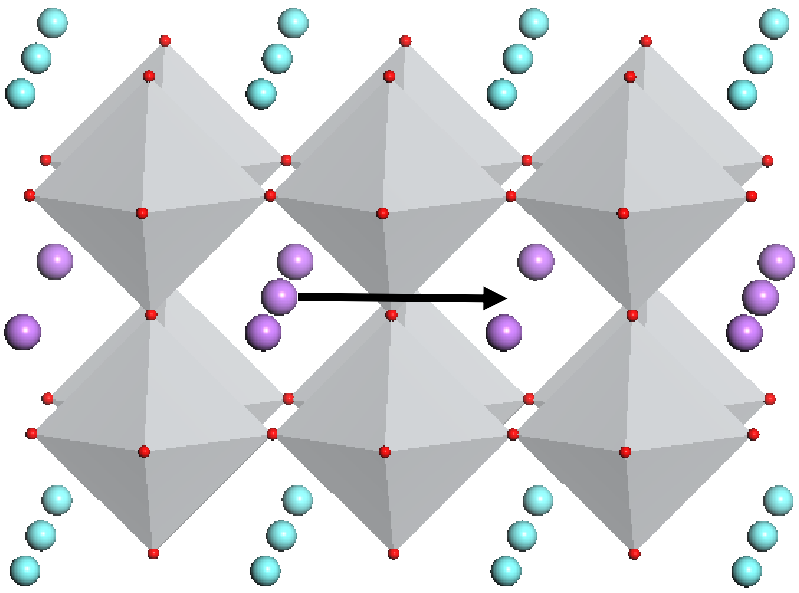
Time step: 1fs

Structure of LLTO/Oxide Glass Interface

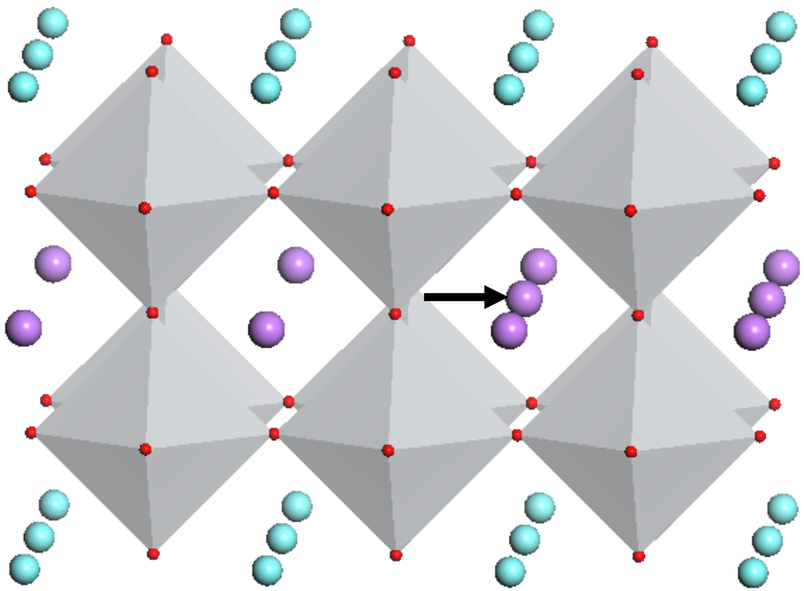


LLTO/oxide glass interface

Lithium ion diffusion pathway

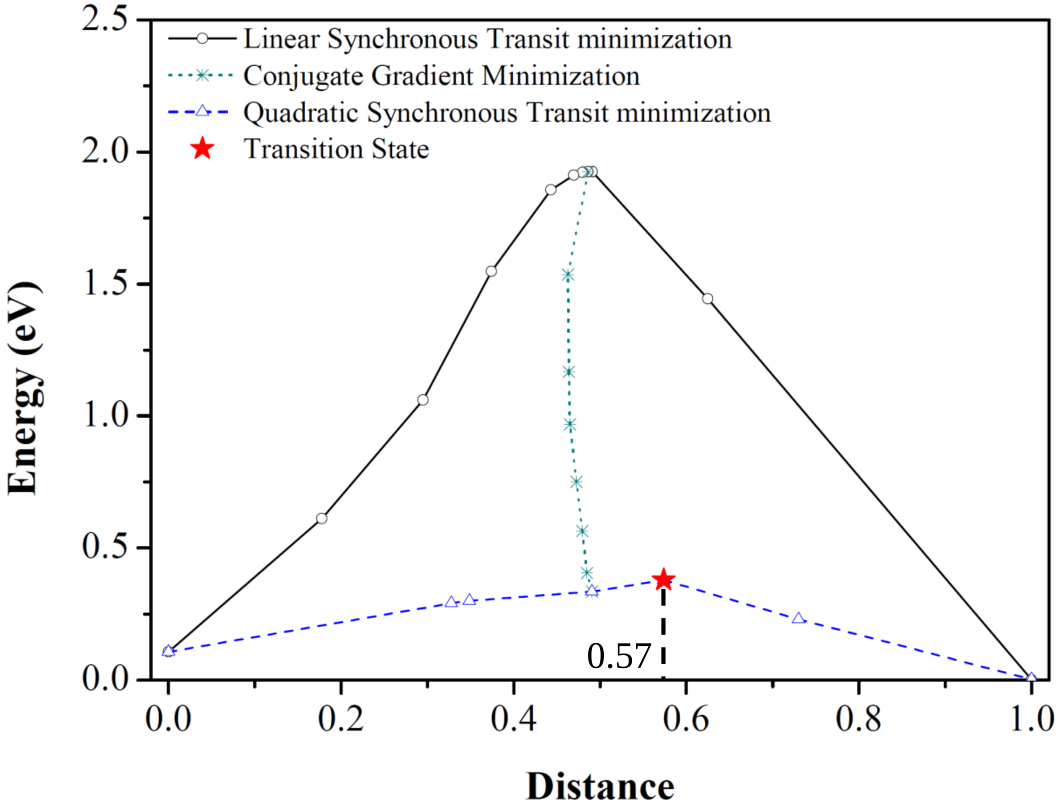


Initial structure of LLTO



Final structure of LLTO

Lithium-Diffusion Pathways in LLTO



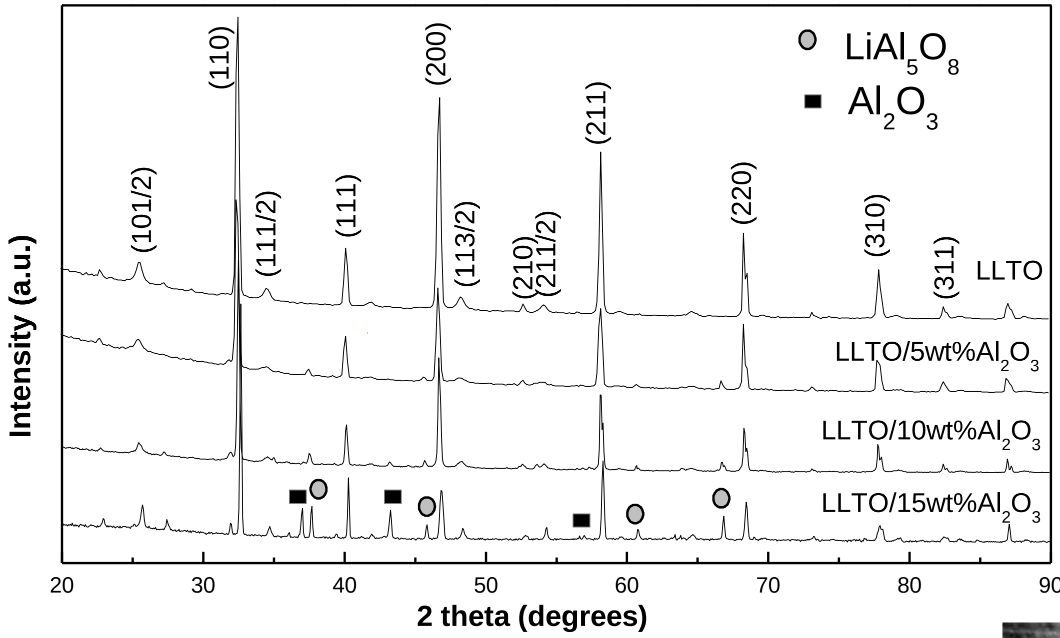
Barrier from reactant:

0.27 eV

Barrier from product:

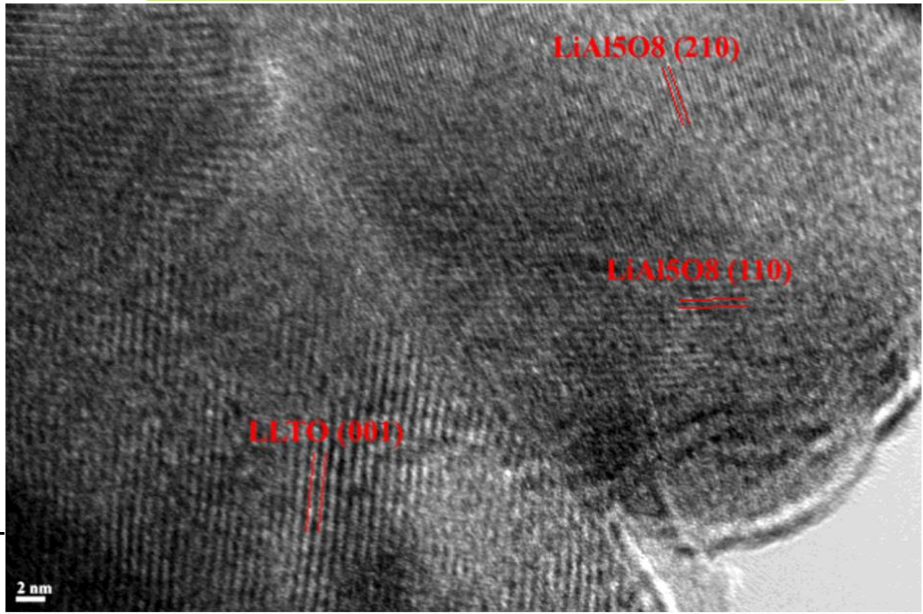
0.38 eV

Effect of Al_2O_3 on LLTO-base Electrolytes



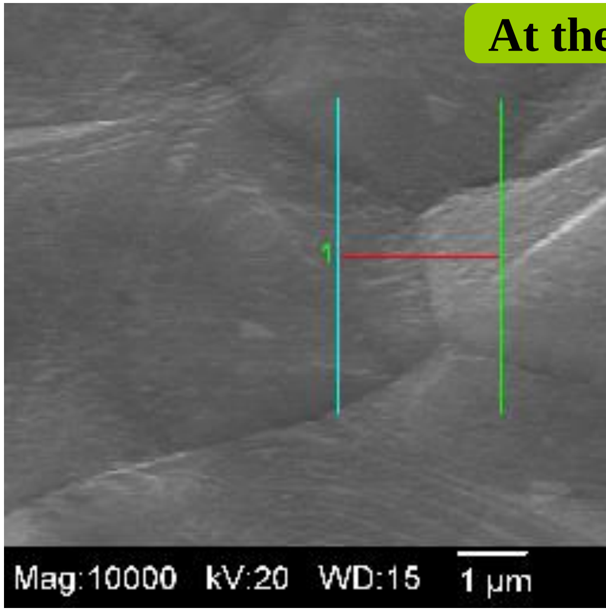
XRD patterns of LLTO/Al_2O_3 composite electrolytes using different amounts of Al_2O_3

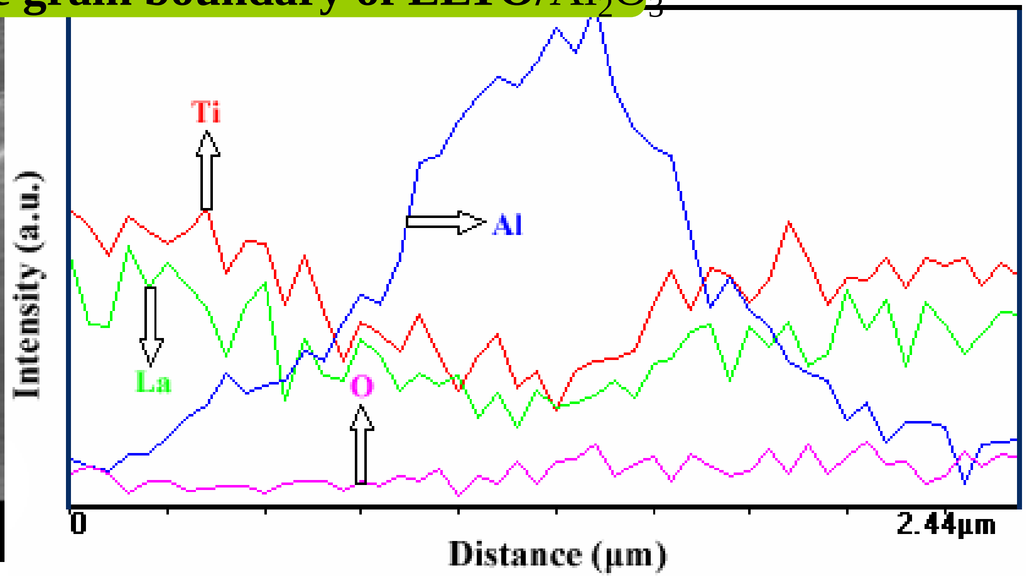
HRTEM Image of LLTO/Al2O3 grain boundary

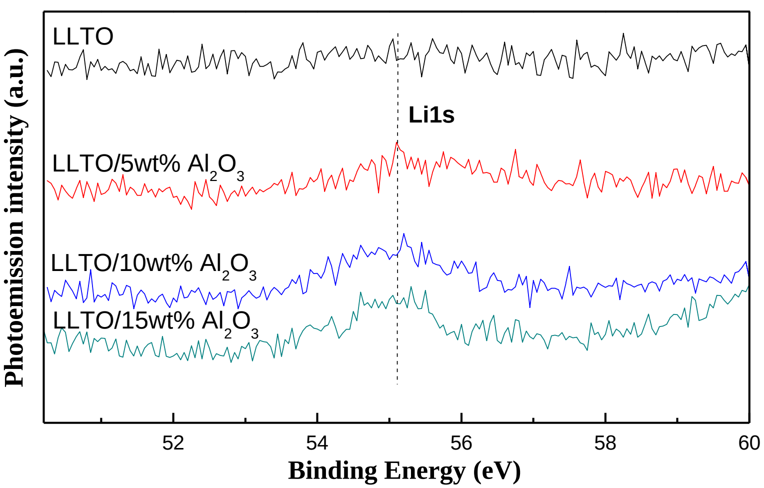


Effect of Al_2O_3 on LLTO-base Electrolytes

At the grain boundary of LLTO/Al_2O_3

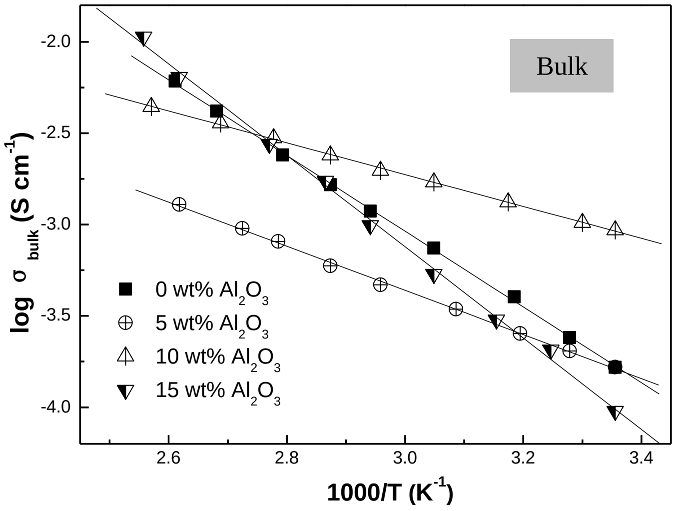


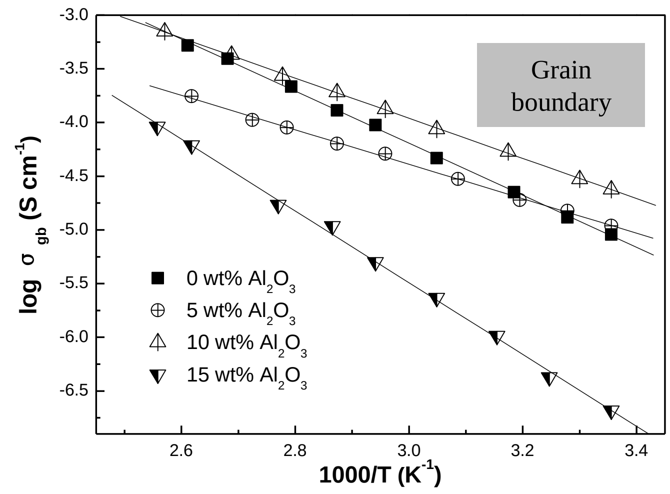




- Pure LLTO – Li 1s (54eV)
- LLTO-Al_2O_3 – Li 1s (55.2eV)
- Possible reduction of Li_2O evaporation

Effect of Al_2O_3 on LLTO-base Electrolytes



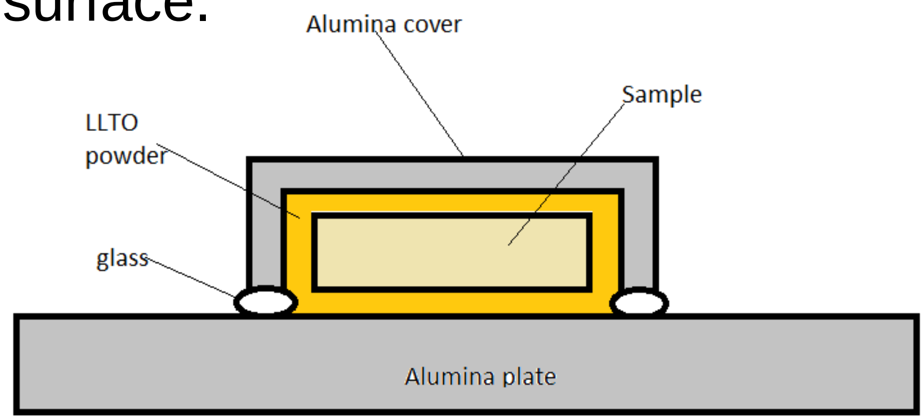


Al_2O_3 content (wt %)	σ_{bulk} (S cm^{-1})	σ_{gb} (S cm^{-1})	$E_{a,\ bulk}$ (eV)	$E_{a,\ gb}$ (eV)
0	1.65×10^{-4}	9.03×10^{-6}	0.41	**0.48**
5	1.66×10^{-4}	1.09×10^{-5}	0.24	**0.32**
10	9.33×10^{-4}	2.38×10^{-5}	0.17	**0.37**
15	**9.56×10^{-5}**	**2.08×10^{-7}**	**0.50**	**0.66**

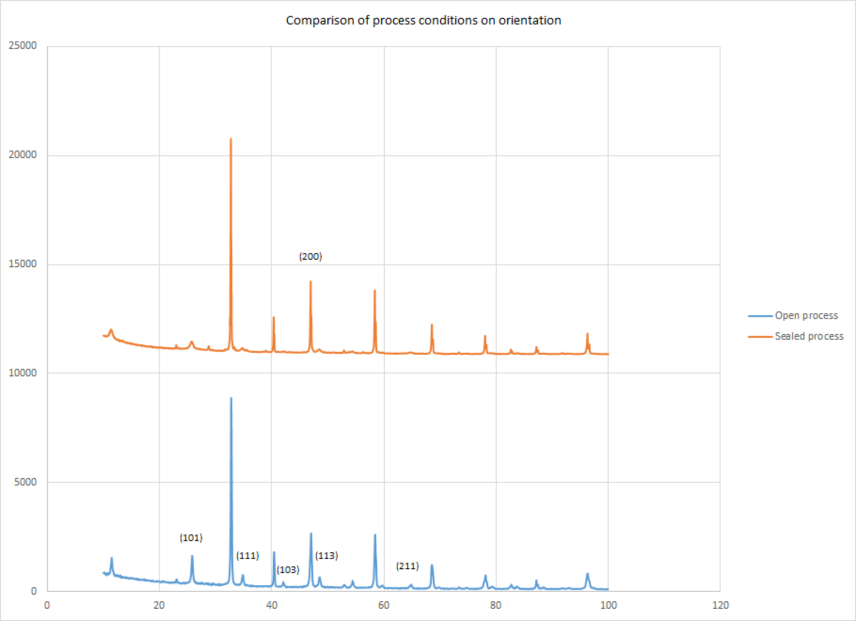
Improving Conductivity by Optimizing Manufacturing

- The vapor pressure of Li is found from the following relation:

  298 K to m.p.: $\log (P/\mathrm{Pa}) = 10.673 - 8310 / (T/\mathrm{K})$
- The vapor pressure at 1150 °C is found to be ~ 10X that at 900 °C.
- The sample is surrounded by LLTO powder and is sealed under a ceramic cover. The melting temperature of the glass is 850 °C so the glass seal is in a molten state during the sintering process. This is to prevent fracture of the ceramic or failure of the seal surface.



Improving Conductivity by Optimizing Manufacturing



Conductivities	GB (S/cm)	Diff (S/cm)	Total (S/cm)
Open Sample	0.00034	0.00089	0.000246
Sealed Sample	0.00039	0.00090	0.000272

Activation Energies	GB (eV)	Diff (eV)
Open Sample	0.33	0.31
Sealed Sample	0.32	0.31

- Dominant Peak (102)
- Decrease in the (101), (111), (103), (113) and (211) peaks
- Increase in the (200) peak
- Cell distortion caused by the Ti atom plays a key role in the Li hopping mechanism

Future Work

- Fundamental Understanding of Li-diffusion in the LLTO and Composite Electrolyte
- Investigation of the Li Conduction at Electrolyte/Electrodes Interface
- Explore Other Solid-Electrolytes
- Develop Realistic Battery Manufacturing & Assembling Processes

Thank You