Solid State Composite Electrolyte for Li-ion Batteries

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Acknowledgement

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Outline

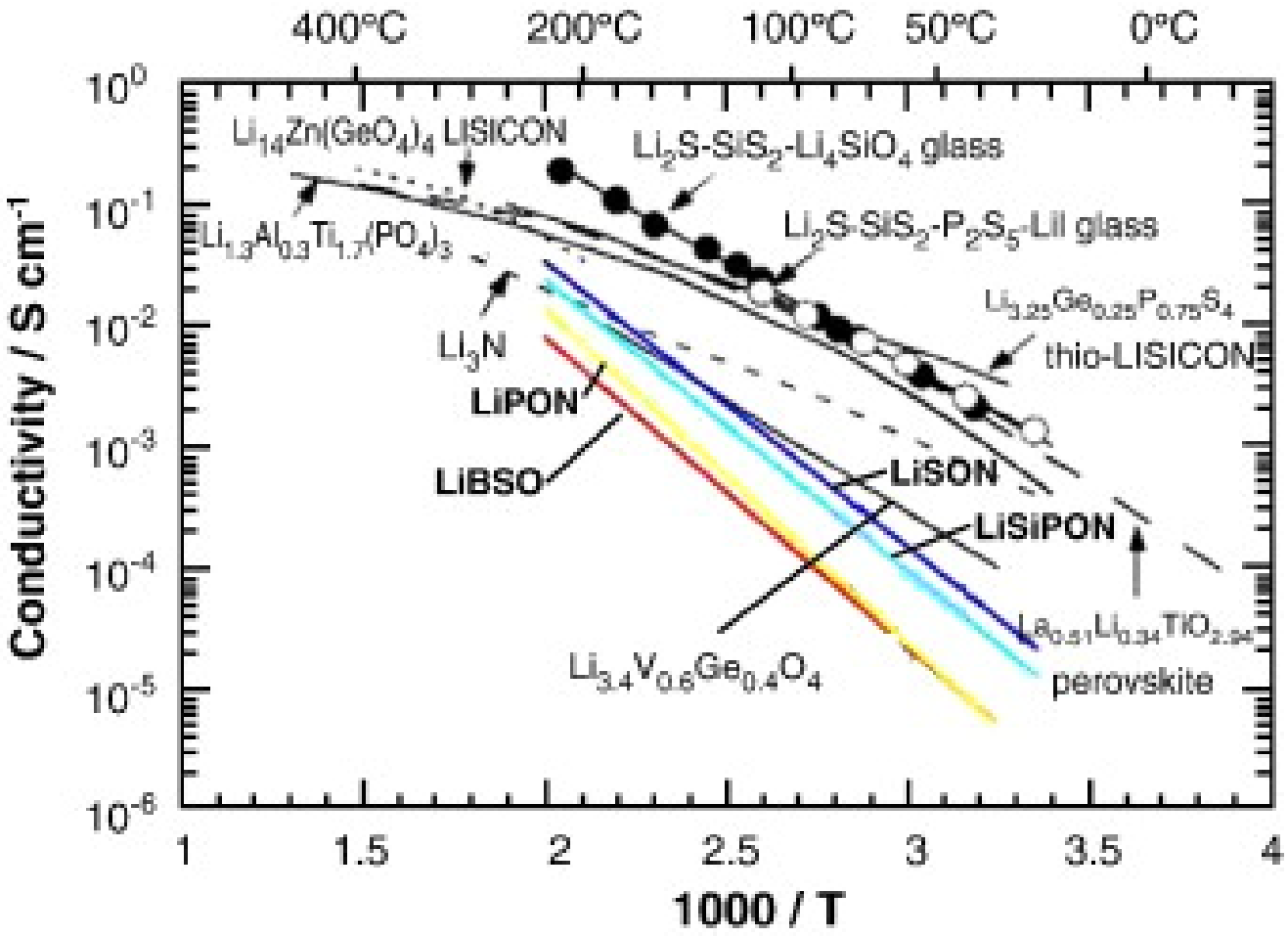
- Background
- Experimental
- Results and discussion
- Conclusions

Background – Concerns of Liquid Electrolyte

- Dangers of explosion and leakage
- Separators and package limiting the miniaturization;
- etc.

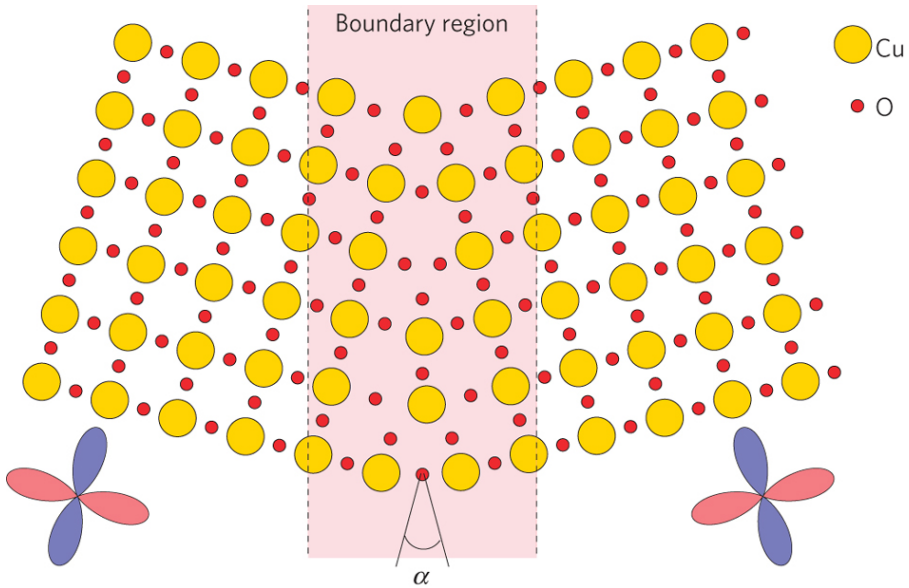
Application of solid electrolyte in lithium-ion batteries

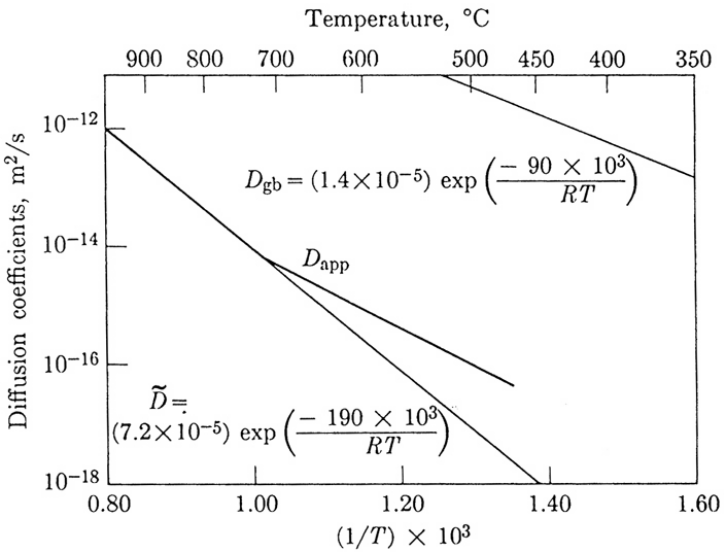
Background – Solid State Li-ion Conductors



Background

Grain Boundaries – Fast Diffusion Pathways



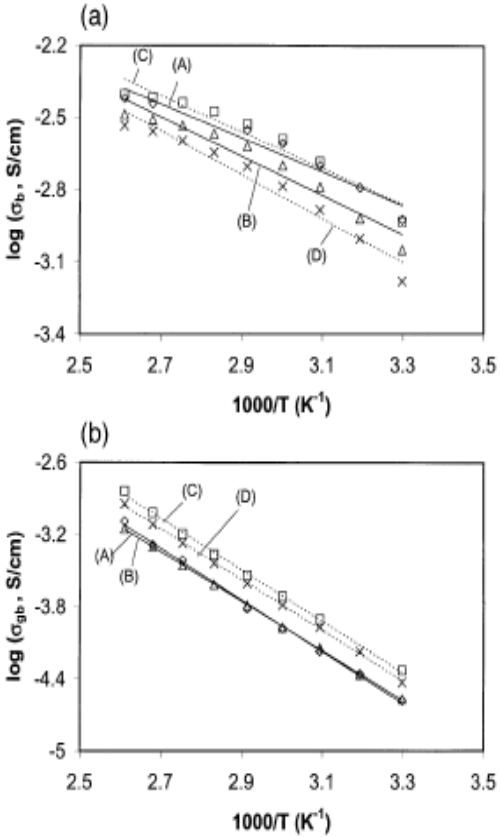


Silver diffusion in poly-crystal copper

Is That Always True?

Background

LLTO



σ_g 8.1X10^{-4} (S/cm)

σ_g 1.8X10^{-4} – 1.3X10^{-3} (S/cm)

σ_{gb} 2.5X10^{-5} (S/cm)

σ_{gb} 6.5X10^{-7} – 4.1X10^{-5} (S/cm)

C.H. Chen, K. Amine/Solid State Ionics 144 2001 51–57

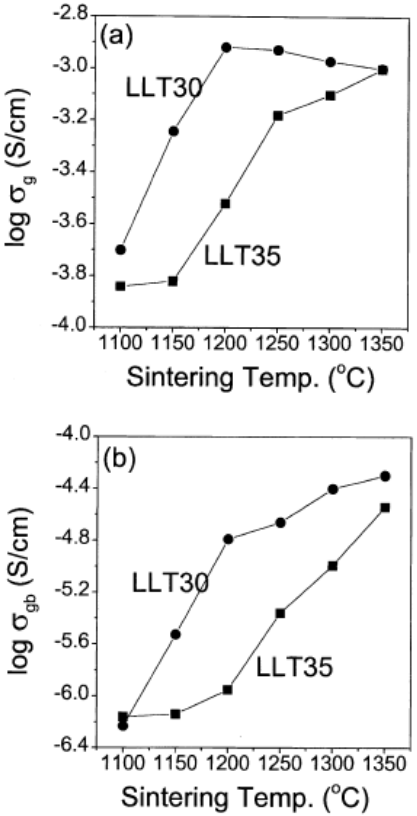
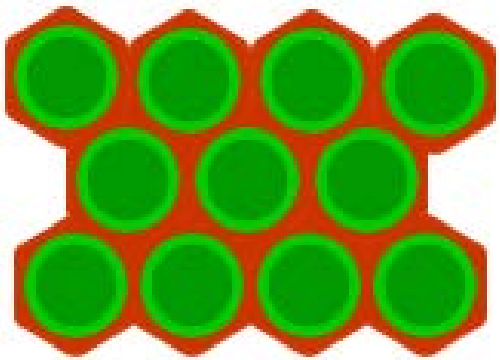


Fig. 5. (a) The grain and (b) the grain boundary conductivity of LLT30 and LLT35 samples with various sintering temperatures at R.T.

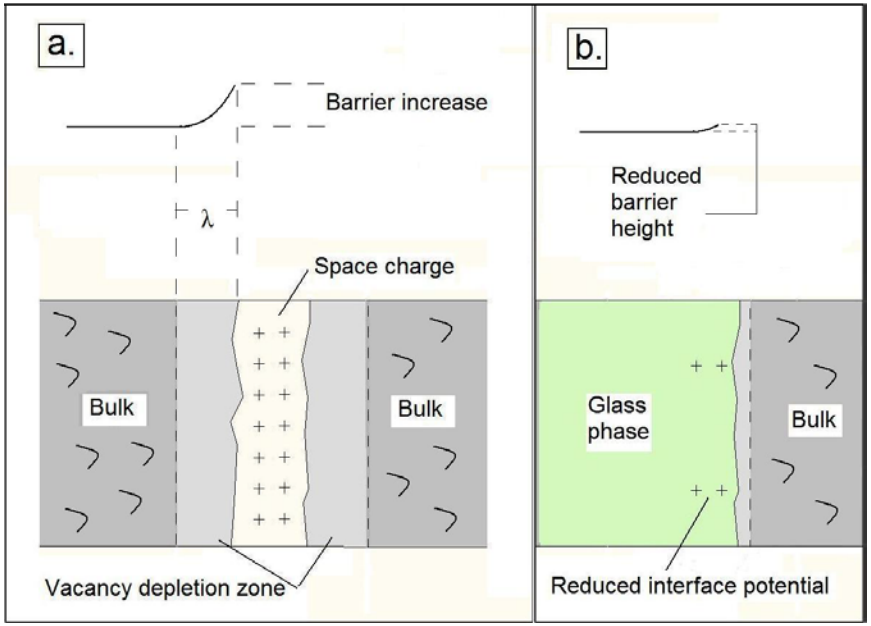
C.W. Ban, G.M. Choi/Solid State Ionics 140 (2001) 285–292

Overall Scientific Approaches

Developing Ceramics-Glass Composites with improved total conductivity and stability

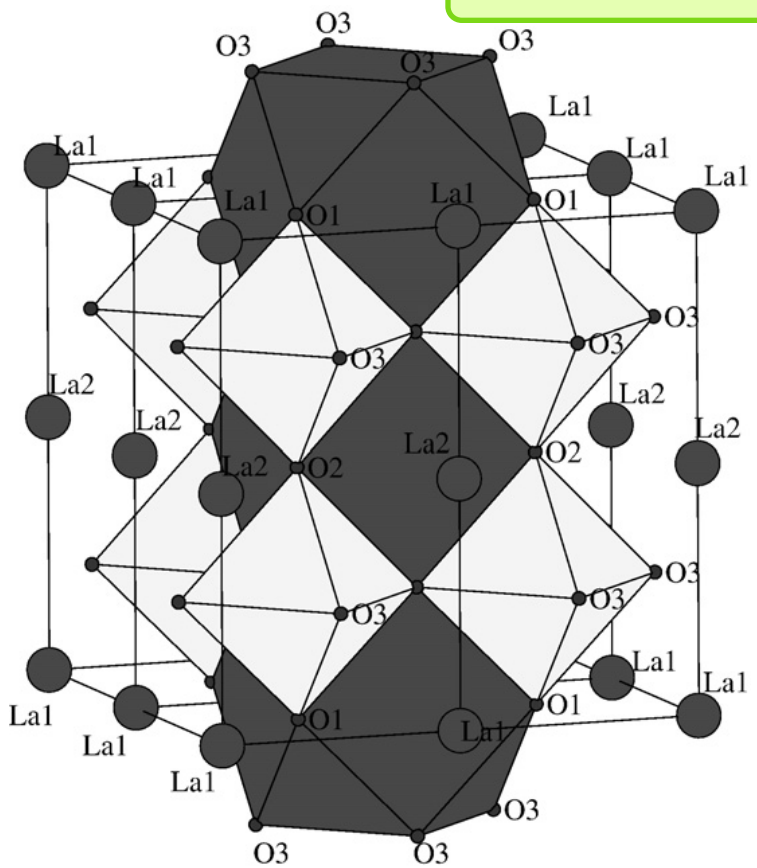


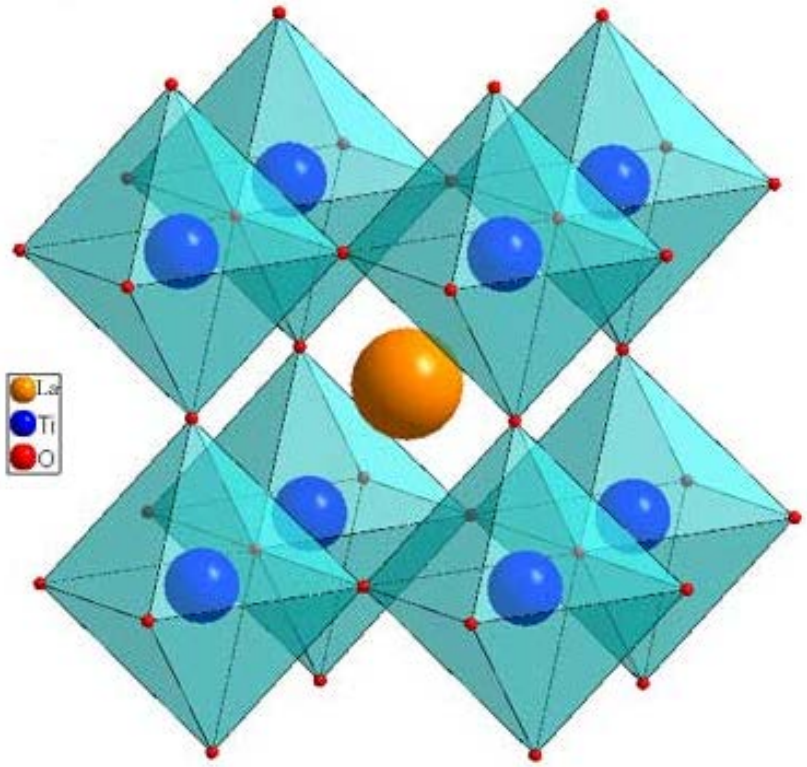
$$\sigma_{tot} = 4e\left(\mu_{bulk}\exp^{-\frac{F+2e\Phi}{kT}} + \mu_{gb}\exp^{-\frac{F}{kT}}\right)$$



Experimental

Perovskite (LLTO)





Crystal structure of $Li_{3x}La_{2/3-x}TiO_3$.

Experimental

Start Materials

- La_2O_3
- TiO_2
- $Li_2(CO_3)$
- Al_2O_3, SiO_2, P_2O_5 and/or H_3BO_3

Preparation process

Ball milling/Sinter LLTO

↓

Ball milling/Sinter glass

↓

Grind/mix/press

↓

Co-fire

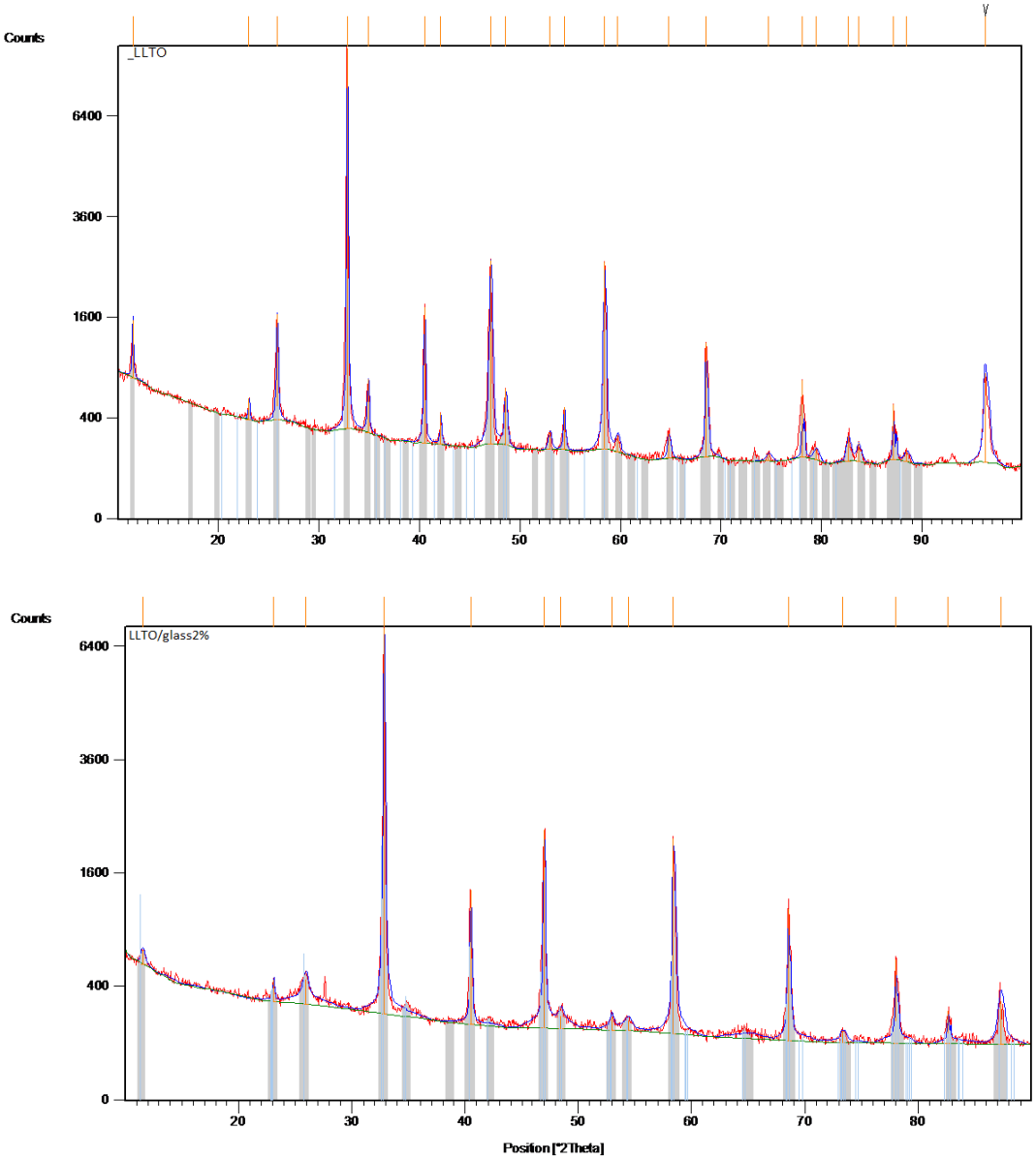
Characterization techniques

- Scanning electron microscopy (SEM)
- X-ray diffraction (XRD)
- Electrochemical impedance spectroscopy (EIS)

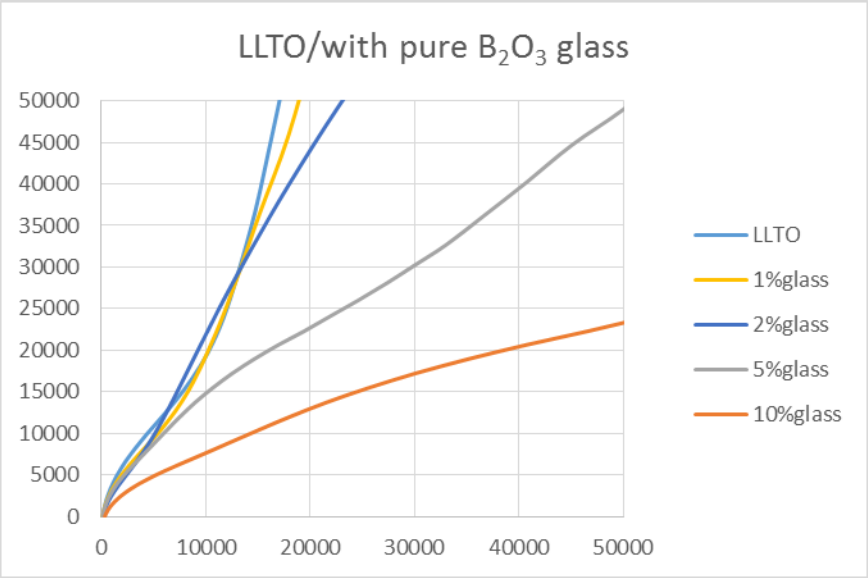
Results and discussion - XRD

- Some loss of intensity for the smaller peaks but the major peaks near 33, 47 and 59 degrees remain unchanged.

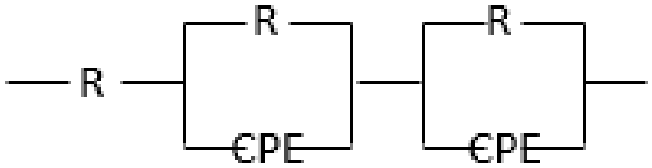
- No observed shifting of peak position indicating no change to the LLTO composition during sintering with glass.



Results and discussion - EIS

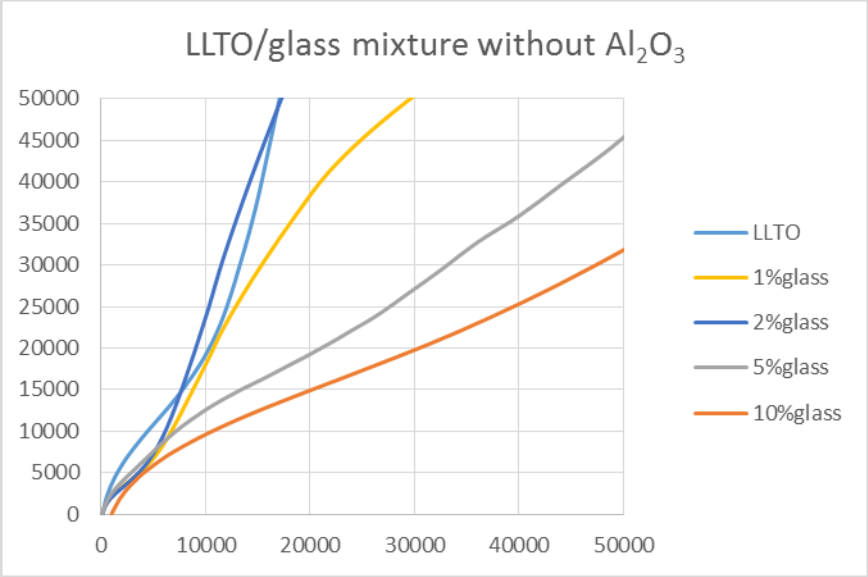


Glass = Li_2O-B_2O_3 (.40/.60)

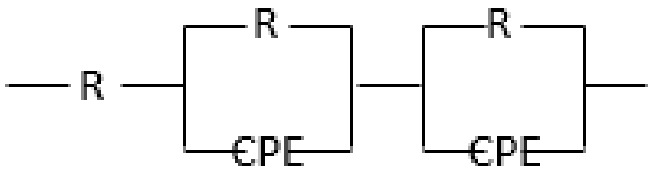


	gb	diff	total
LLTO	0.000056	0.0011	0.000053
1 %	0.000071	0.00094	0.000066
2 %	0.00012	0.0009	0.000106
5 %	0.000014	0.00085	0.000014
10 %	0.0000001	0.00025	0.0000001

Results and discussion - EIS

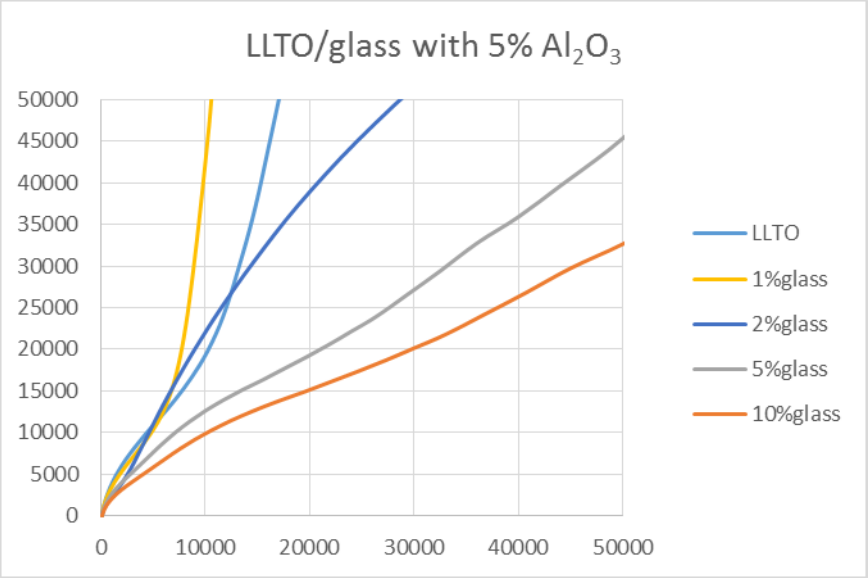


Glass = Li_2O-B_2O_3-SiO_2-Al_2O_3 (.40/.25/.35/0)

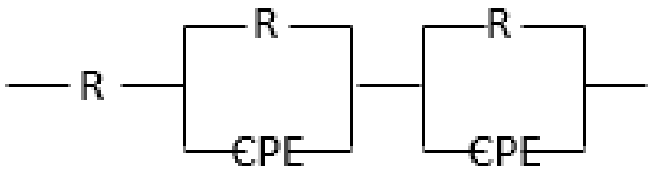


	gb	diff	total
LLTO	0.000056	0.0011	0.000053
1 %	0.000084	0.001	0.000077
2 %	0.00013	0.00094	0.000114
5 %	0.000074	0.00088	0.000068
10 %	0.000027	0.00059	0.000026

Results and discussion - EIS

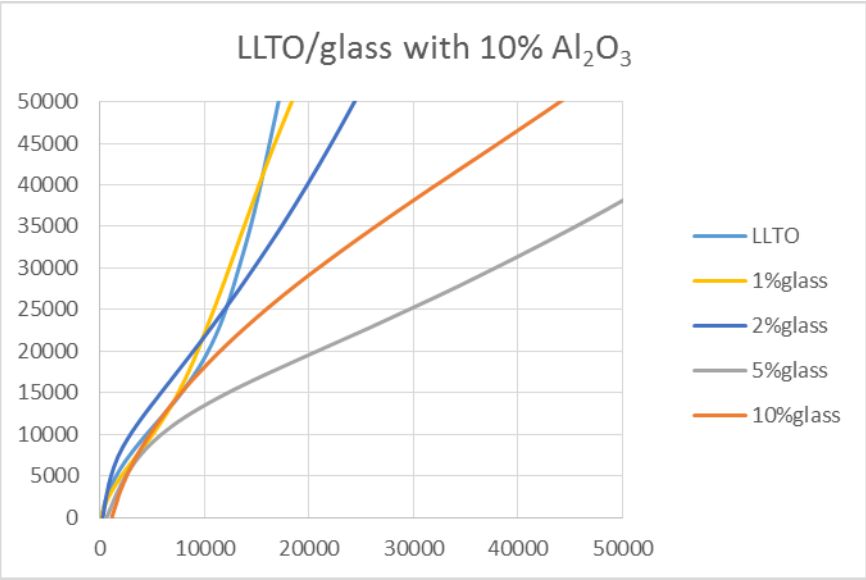


Glass = Li_2O-B_2O_3-SiO_2-Al_2O_3
(.40/.25/.30/.05)

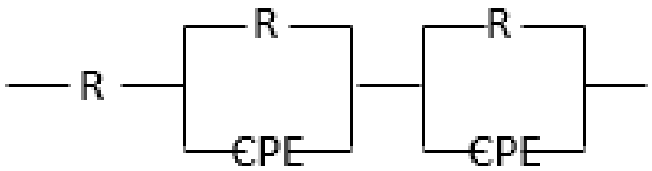


	gb	diff	total
LLTO	0.000056	0.0011	0.000053
1 %	0.00013	0.00105	0.000116
2 %	0.00034	0.00089	0.000246
5 %	0.000086	0.00074	0.000077
10 %	0.000021	0.00034	0.000020

Results and discussion - EIS



Glass = Li_2O-B_2O_3-SiO_2-Al_2O_3 (.40/.25/.25/.10)



	gb	diff	total
LLTO	0.000056	0.0011	0.000053
1 %	0.000047	0.00088	0.000045
2 %	0.000031	0.00085	0.000030
5 %	0.000008	0.00055	0.000008
10 %	0.000003	0.00024	0.000003

Conclusions

Low grain boundary conductivity is the RLS for LLTO

Ceramic-glass composite can significantly improve the GB conductivity, thus overall conductivity.

So far, our best results show adding 2% Li_2O-B_2O_3-SiO_2-Al_2O_3 can improve GB conductivity by 6 times, and thus 5 times for overall conductivity

Patent: US 8,865,354 B2

Thank you!

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