Solid State Composite Electrolyte for Li-ion Batteries

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Acknowledgement

• Dr. Imre Gyuk
• Drs. Vince Sprenkle & Xiaochuan Lu from PNNL
• My postdoc & student in WVU: Dr. Greg Collins, Mr. Yue Zhou
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

Is That Always True?

Silver diffusion in poly-crystal copper
Background

\[ \sigma_g \approx 8.1 \times 10^{-4} \text{ (S/cm)} \quad \sigma_g \approx 1.8 \times 10^{-4} - 1.3 \times 10^{-3} \text{ (S/cm)} \]

\[ \sigma_{gb} \approx 2.5 \times 10^{-5} \text{ (S/cm)} \quad \sigma_{gb} \approx 6.5 \times 10^{-7} - 4.1 \times 10^{-5} \text{ (S/cm)} \]


Overall Scientific Approaches

Developing Ceramics-Glass Composites with improved total conductivity and stability

\[
\sigma_{tot} = 4e \left( \mu_{\text{bulk}} \exp \left( \frac{F + 2e\Phi}{kT} \right) + \mu_{\text{gb}} \exp \left( \frac{F}{kT} \right) \right)
\]
Experimental

Perovskite (LLTO)

Crystal structure of $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$. 
Experimental

Start Materials
- \(\text{La}_2\text{O}_3\)
- \(\text{TiO}_2\)
- \(\text{Li}_2(\text{CO}_3)\)
- \(\text{Al}_2\text{O}_3, \text{SiO}_2, \text{P}_2\text{O}_5\) and/or \(\text{H}_3\text{BO}_3\)

Preparation process
1. Ball milling/Sinter LLTO
2. Ball milling/Sinter glass
3. Grind/mix/press
4. 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$_2$O-B$_2$O$_3$ (.40/.60)}
Results and discussion - EIS

Glass = Li₂O-B₂O₃-SiO₂-Al₂O₃ (.40/.25/.35/0)

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<td>0.0011</td>
<td>0.000053</td>
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<tr>
<td>1%</td>
<td>0.000084</td>
<td>0.001</td>
<td>0.000077</td>
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<tr>
<td>2%</td>
<td>0.00013</td>
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<td>5%</td>
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Results and discussion - EIS

Glass = Li$_2$O-B$_2$O$_3$-SiO$_2$-Al$_2$O$_3$ (.40/.25/.30/.05)

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Results and discussion - EIS

Glass = Li$_2$O-B$_2$O$_3$-SiO$_2$-Al$_2$O$_3$ (.40/.25/.25/.10)

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LLTO/glass with 10% Al$_2$O$_3$
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% Li₂O-B₂O₃-SiO₂-Al₂O₃ can improve GB conductivity by 6 times, and thus 5 times for overall conductivity

Thank you!

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