Co-extruded Composite Polymer Electrolytes for Solid-State Batteries

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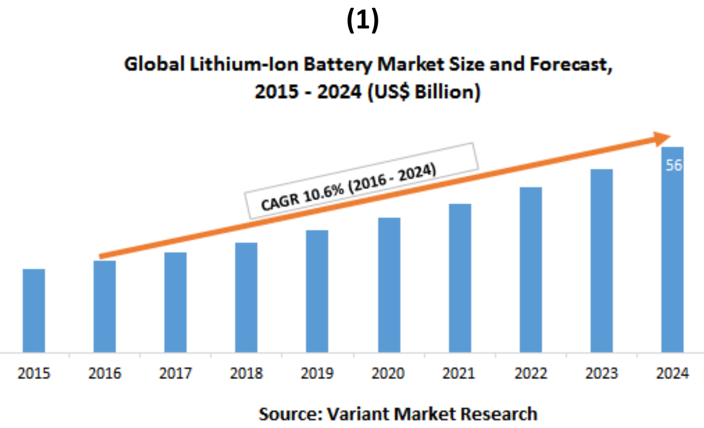
Abstract

Composite polymer electrolytes are exciting alternatives for all solid-state batteries due to their advantages of scalability and overall better mechanical response. This work is evaluating strategies for scalable manufacturing of functionally graded composite polymer electrolytes. A custom-built setup has been made that allows fabrication of co-extruded multimaterial composite polymer electrolytes (CPEs). The project involves performing detailed material and electrochemical characterization of these co-extruded CPE films. The study evaluates two material systems: 75 wt.% LLZO-PEO ($Li_7La_3Zr_4O_{12}$ - Polyethylene Oxide) electrolyte and 25 wt.% LLZO-PEO electrolyte. The configurations include single material films and co-extruded films of both materials with features ranging from 1 mm to 23mm. Ionic conductivity measurements were carried out to evaluate initial control parameters.

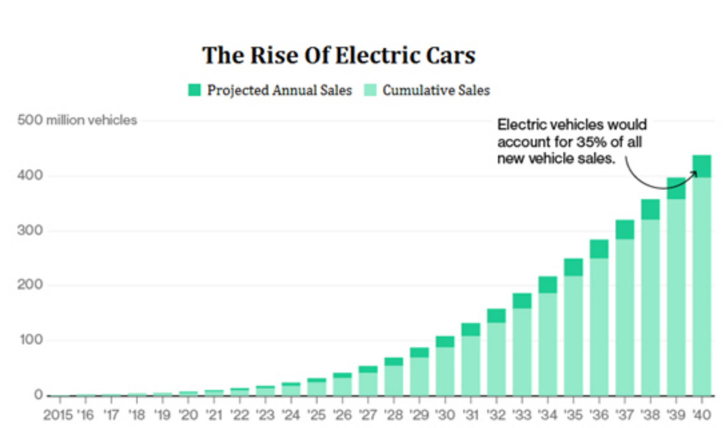
Background & Motivation

(1)



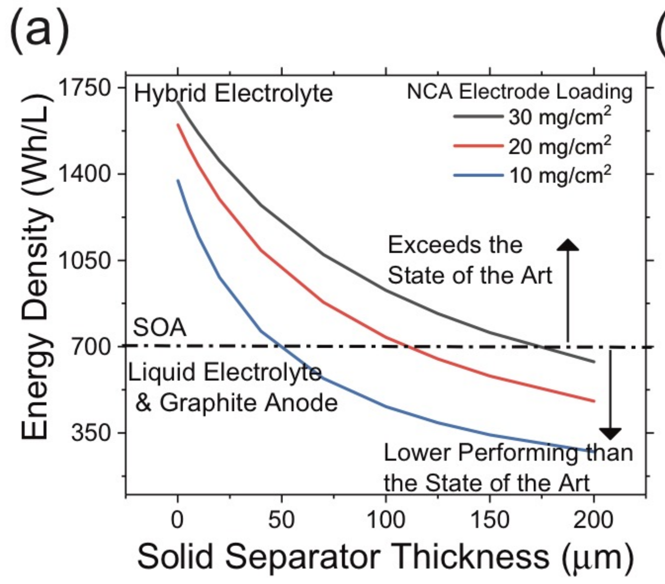
- Demand for Lithium-Ion batteries (LIBs) has been increasing rapidly over the past 10 years
- Wide variety of applications lead to high demand for highly compatible, better, and safer technology

(2)

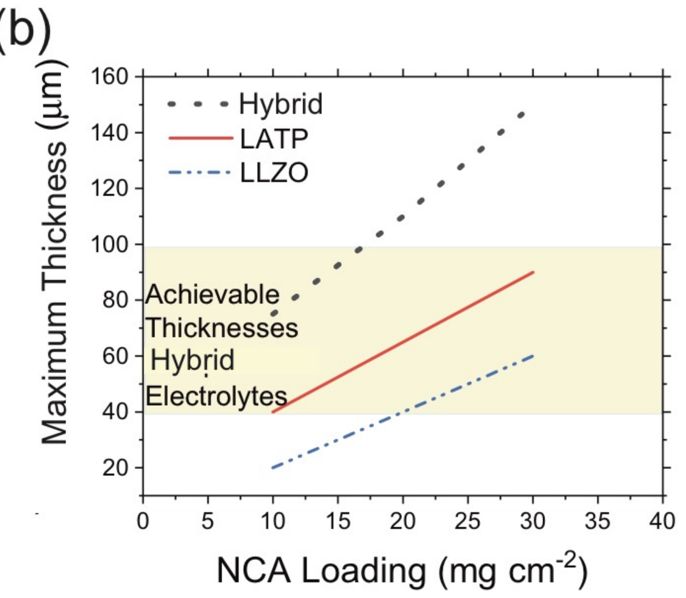


- Increase in demand for electric cars alone means increasing need for rapid battery production
- Use in transportation systems like cars and even planes in the future means batteries need to be safer and more reliable than ever
- Liquid electrolytes used in standard LIBs are highly flammable

(a)

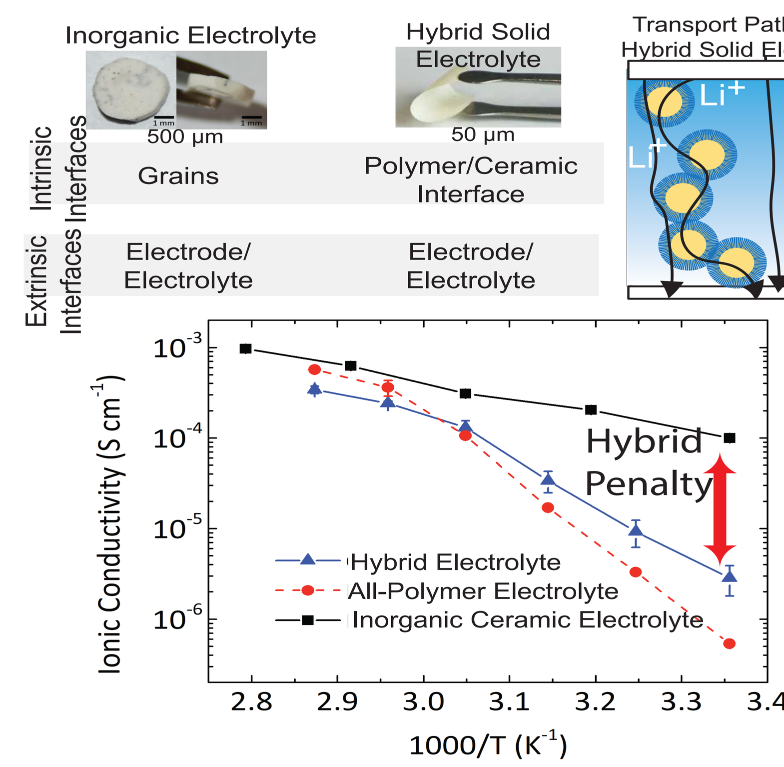


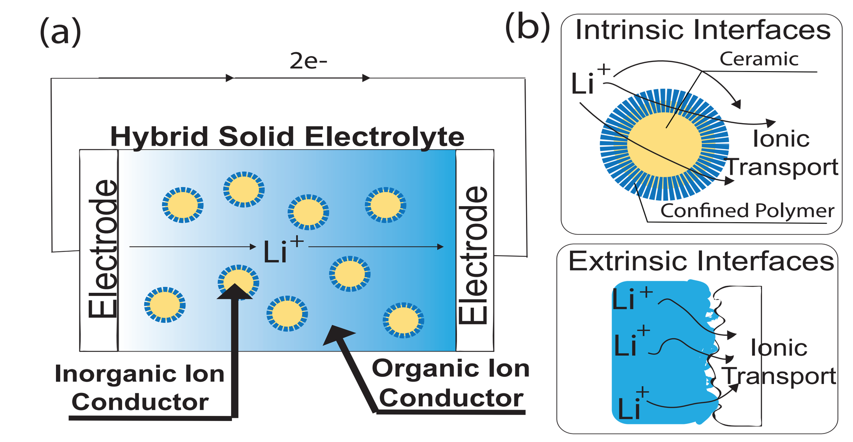
(b)



- The change in energy density as a function of separator thickness is shown in Figure (a). Electrode loading is variable and controllable. Figure (a) provides promising insight that with thin enough solid electrolytes, better energy density than that of the state of the art (SOA) liquid electrolytes can be achieved
  - Solid electrolytes provide a safer and more mechanically sound alternative to organic liquid electrolytes
- The maximum thickness of different solid electrolytes in order to out perform the SOA liquid electrolytes is shown in Figure (b)
  - LLZO and LATP have limitations on how thin they can be made
  - Hybrid electrolytes can achieve the optimum thickness range, allowing for a safer electrolyte to compete with the SOA in performance

Challenges in Hybrid Electrolytes





- Figure (a) - Lithium ion transport through the electrolyte
- Figure (b) - intrinsic and extrinsic interface limitations in solid state electrolytes
  - Intrinsic – Ion travelling through or around the ceramic molecules
  - Extrinsic – Ion travelling between electrolyte and electrode

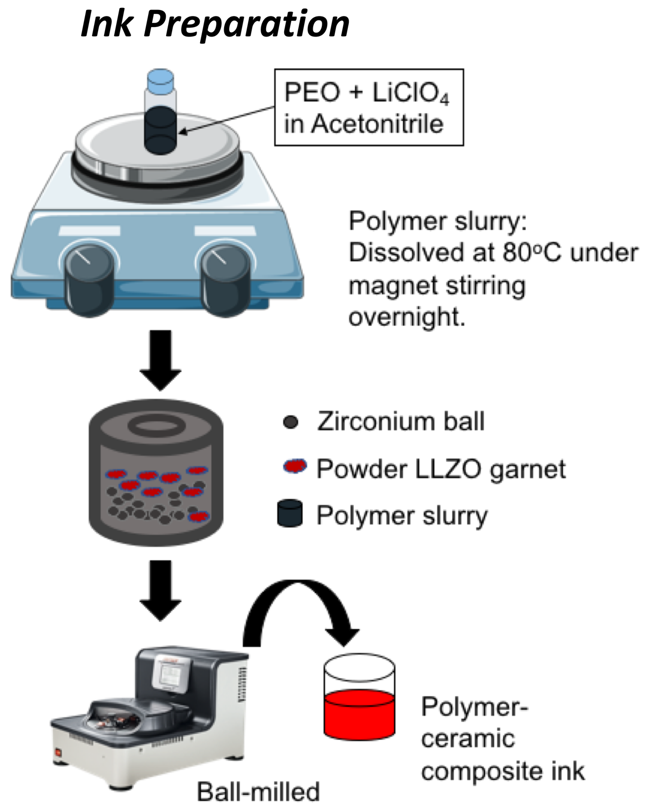
Research Goals

Science goal: **To establish control parameters of co-extruded composite polymer electrolytes**

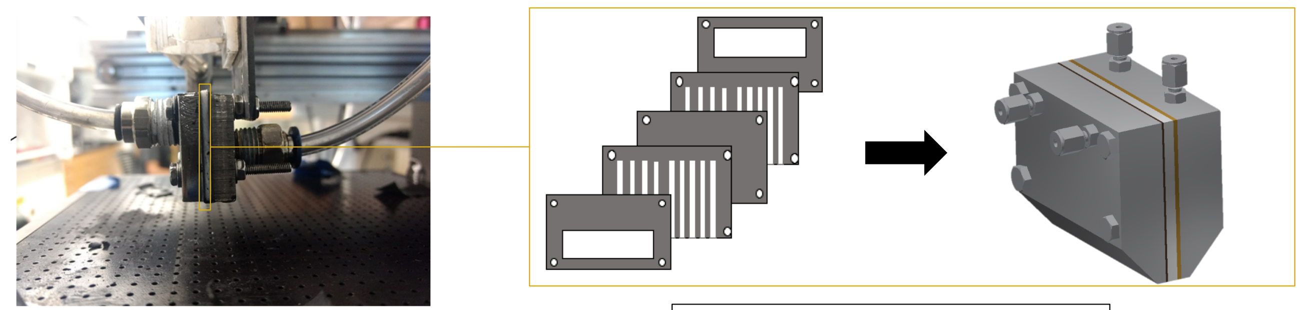
Engineering goal: **Investigate hybrid electrolytes as a viable alternative to state of the art liquid electrolytes**

Co-extrusion: Multimaterial coating

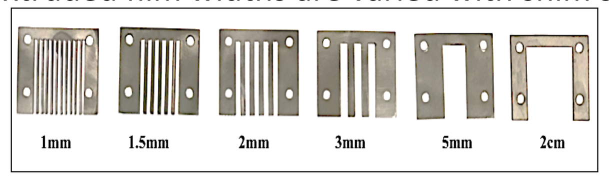
Ink Preparation

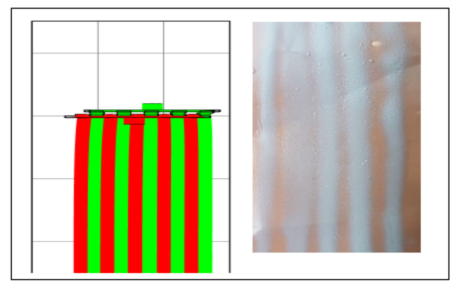


Custom-made slot-die system



Co-extruded film widths are varied with shim size



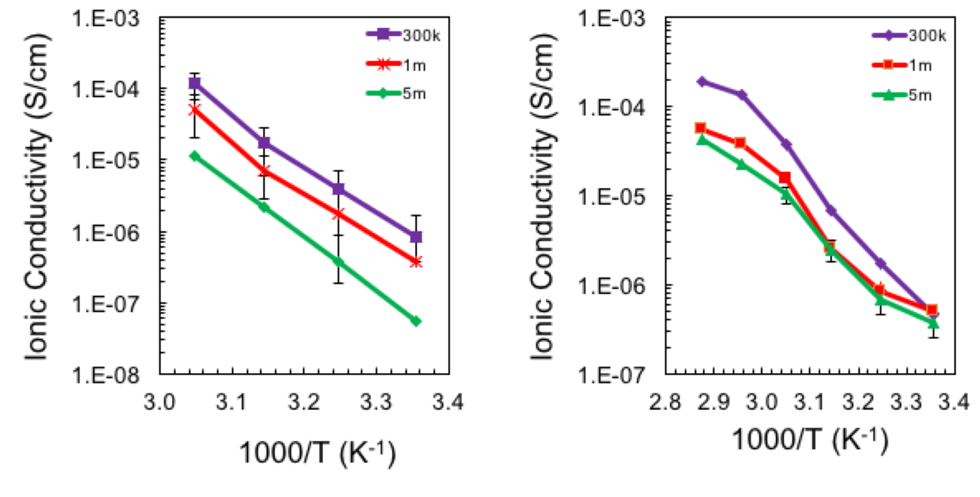


Co-extrusion of 2mm width membrane onto copper foil

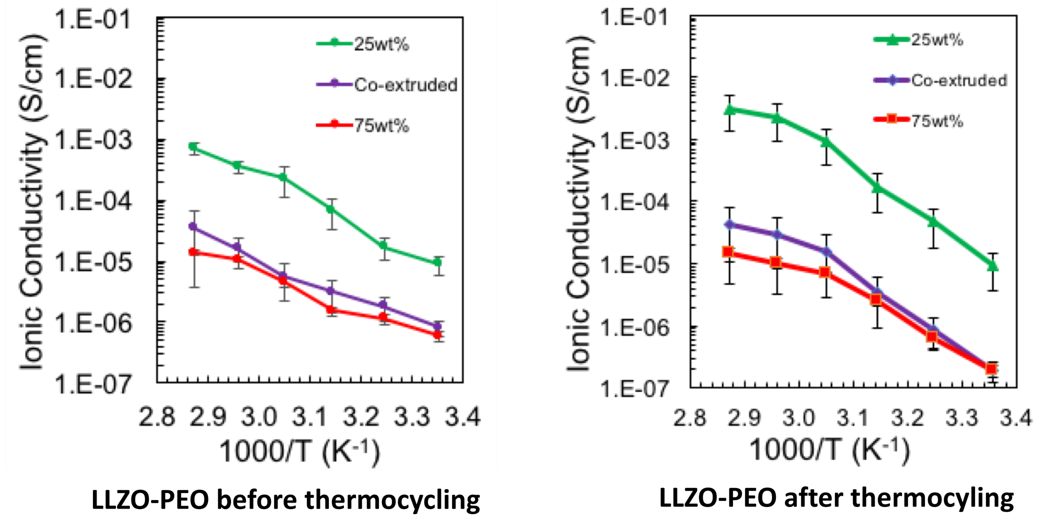
- Independent controlling of feed and position
- Pneumatically controlled ink-feeding to the co-extrusion platform
- Individual mass flow rates were controlled by digital pressure controllers
- Coating speed of 10-1800 mm/min can be studied over 200 mm of coating length.

Composite Polymer Electrolytes

Ionic conductivity measurements were collected using Electrochemical Impedance Spectroscopy with a stainless shim set-up (1 MHz - 100 Hz).

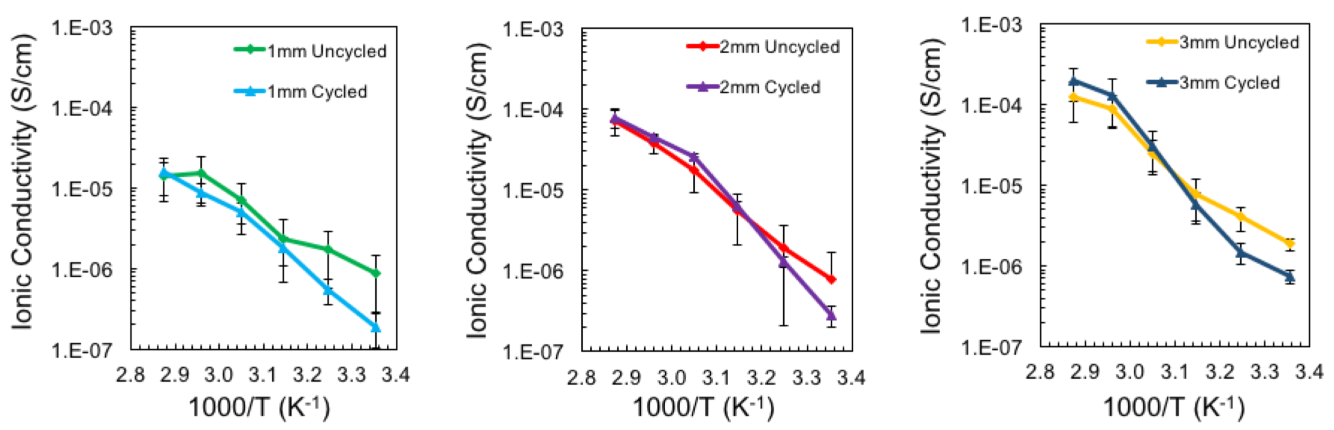


- Ionic conductivity increases when LLZO garnet is added to the polymer
- 300K g/mol PEO has higher ionic conductivity values in both instances, pure and with LLZO

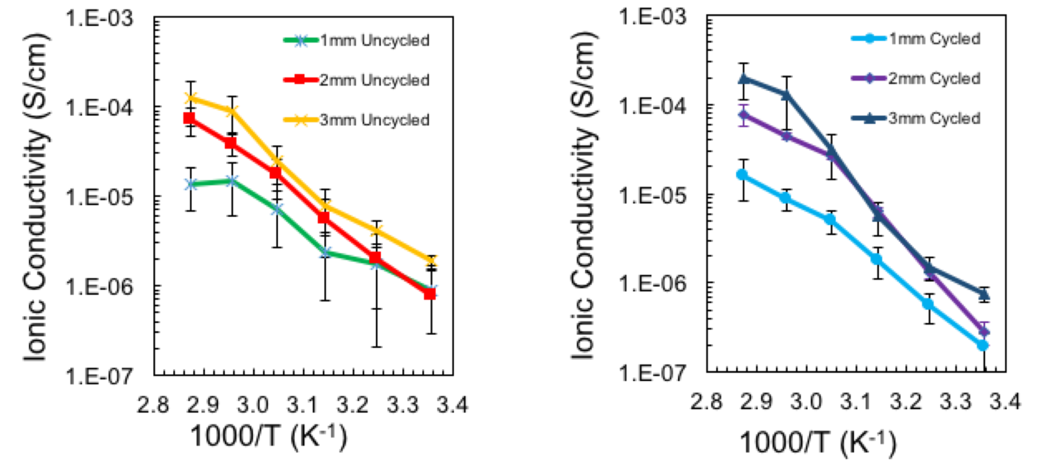


- Samples were thermocycled to 90 °C (10 °C increments with 25 minute pause)
- Thermocycling does not show improvement in the ionic conductivity
- Co-extruding improves the ionic conductivity of the lower ceramic loading matrix

Effect of Co-extrusion Width



Co-extruded LLZO-PEO



Before Thermocycling **After Thermocycling**

- Co-extrusion width improves ionic conductivity
  - 3 mm > 2 mm > 1 mm
- Thermocyling does not have significant impact on ionic conductivity

Conclusion & Future Work

- Co-extrusion as a material engineering process shows significant improvement in mechanical properties of hybrid electrolytes
- Further material characterization such as transference number measurements, critical current density, and spectroscopy needed for comprehensive understanding of ink systems
- Further testing using half cell and full cell
- Thermocyling control tests determine its effect on ionic conductivity

References

1. Variant Market Research, 2018.
2. Bajpai, P. (2016, March 21). The Rise of Electric Vehicles: By The Numbers.
3. Dixit, M. B., Harkey, B. A., Shen, F., & Hatzell, K. B. (2018). Catalyst Layer Ink Interactions That Affect Coatability. Journal of The Electrochemical Society, 165(5), F264-F271.
4. Hatzell, K. B., Dixit, M. B., Berlinger, S. A., & Weber, A. Z. Understanding inks for porous-electrode formation. Journal of Materials Chemistry A. (2017).
5. Mccloskey, B. D. The Journal of Physical Chemistry Letters 2015, 6 (22), 4581–4588

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