BAT539: 3D printing of solid-state Li batteries

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Overview:

Timeline: Jan. 2022 to Jan 2025. 10% completion
Budget: Total $1.125M FY22: $375K

Barriers: (Performance) The integration of ceramic solid state electrolytes (SSEs) into solid state batteries is challenging due to brittleness and air-sensitivity of SSEs, and poor solid-solid contact.

Partners: The simulation group led by Dr. Brandon C. Wood (LLNL) on "Integrated multiscale model for design of robust 3D solid-state lithium batteries"; Dr. Sangil Kim (UIC) on the polymer electrolyte.

Impact: The adoption of a thin separator layer, a thick cathode structure, and a metallic lithium anode will lead to EV batteries with an energy density > 350 Wh/kg for increased mileage per charge. The higher ionic conductivity and suppression of lithium dendrite growth will allow high CCD for fast charging applications. The improved electrode/electrolyte contact will increase battery cycle life for long-term service.

Strategies: 3D printing enables multi-component integration and interfacial engineering, including morphological, chemical and mechanical control.

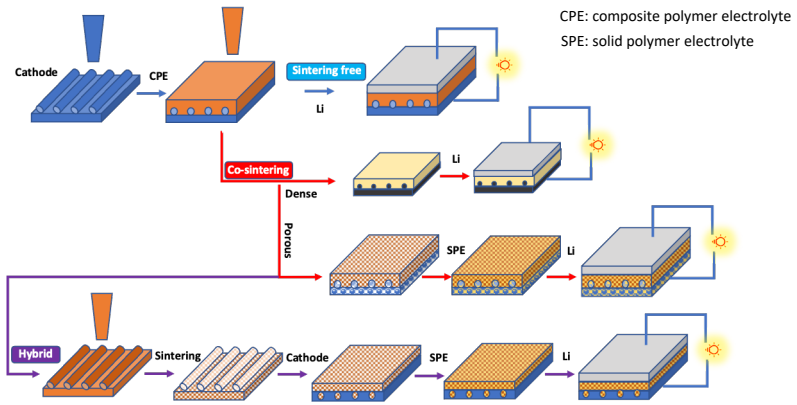
Objectives: (1) Down select three-dimensional (3D) printing and post-processing approaches for SSE/cathode integration, and (2) understand battery failure mechanisms via ex situ and in situ characterization.

FY22 Milestones:

- FY22Q2: Determine the polymer / $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) interfacial chemistry effects on the total ionic conductivity and Li^+ transference number. (Q2, FY 2022; Complete)
- FY22Q3: Improve conductivity and strength of composite polymer electrolytes (CPEs). (Q3, FY 2022; On schedule)
- FY22Q4: Obtain porous co-sintered LLZTO-SSE/NMC/C electrolyte/cathode bilayer structures. (Q4, FY 2022; On schedule)

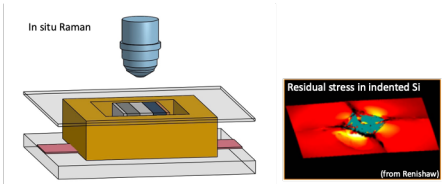
Approach:

- **3D printing-based SSE/cathode integration**

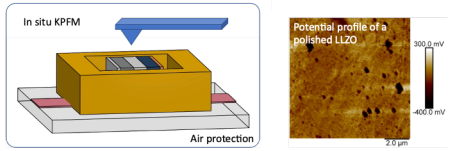


- **In operando characterization**

Raman spectroscopy for chemical/structural/mechanical analysis.

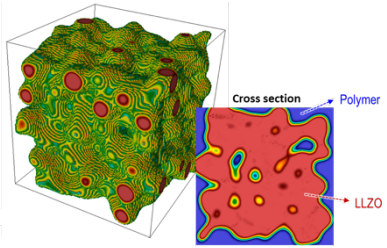


KPFM/SSRM for surface potential and local conductance measurements that reveal space charge layers, degree of lithiation, and rate-limiting processes.



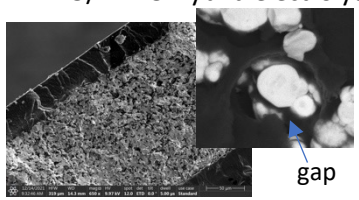
- **Simulation collaboration**

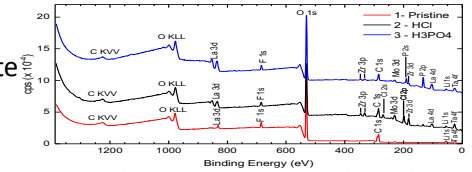
Phase field modeling to reveal ion transport and mechanical properties of hybrid/composite electrolytes.



Recent progress:

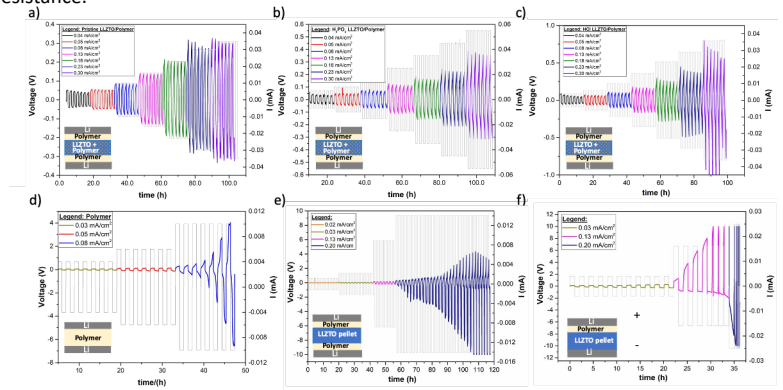
- PEO/LLZTO Hybrid electrolyte





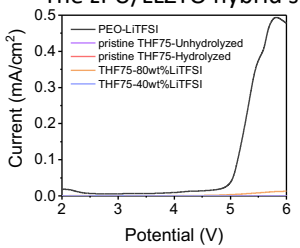
Composition	Total σ_{Li} @ RT (mS/cm)	Total σ_{Li} @ 60°C (mS/cm)	E_a @ 60°C (eV)	t_{Li^+} @ 60°C	CCD @ 60°C (mA/cm²)
Polymer SE	0.0071±0.002	0.12	----------	0.24±0.03	0.13
SPE/ LLZTO/SPE	0.0127±0.0002	0.173±0.027	0.46	0.41±0.07	0.25±0.02
SPE/HCl- LLZTO/SPE	0.017±0.005	0.171±0.056	0.51	0.44±0.02	0.22±0.04
SPE/H_3PO_4-LLZTO/SPE	0.0076±0.0007	0.153±0.051	0.45	0.59±0.01	0.28±0.02

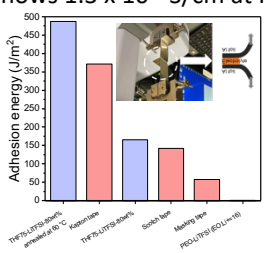
UV curable PEGDA/PEGMEA/PEO/LiTFSI (SPE) infilled LLZTO films show good infilling but relatively weak interfacial bonding strength. Conductivity is higher than SPE but lower than porous LLZTO film itself. Acid treatment reduced Li_2CO_3 content and decreased interfacial resistance.



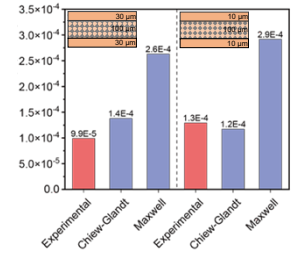
Asymmetric cycling was found for the bilayer and trilayer hybrid cases using well-sintered LLZTO pellets, suggesting one-directional ion transport from SPE to LLZTO.

- A novel zwitterionic polyurethane (zPU) polymer electrolyte developed by our UIC partner shows high EC stability, high ionic conductivity, and superior adhesion energy (low interfacial resistance).
- The zPU/LLZTO hybrid shows 1.3 x 10^{-4} S/cm at RT.





THF75-LiTFSI80wt%-LLZTO



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Run by Dr. Tae Wook Heo at LLNL

Tested by Kun Wang in Dr. Sangil Kim's group at UIC