3D printing of solid state Li batteries

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Project ID: bat421

6/12/2019

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LLNL-PRES-771468-DRAFT

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

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Overview

Timeline

- Start date: Nov. 2018
- End date: Feb. 2022
- Percent complete: 17%

Barriers

- **Performance**: The integration of ceramic solid state electrolyte into solid state batteries is challenging due to the brittleness, air-sensitivity, and poor solid-solid contact issues.

Budget

- Total project funding:
  - DOE share: $1.125 M
- FY19 Funding: $390K

Partner

- Simulation group:
  - Brandon C. Wood (PI)
  - “Integrated multiscale model for design of robust 3D solid-state lithium batteries”

Relevance

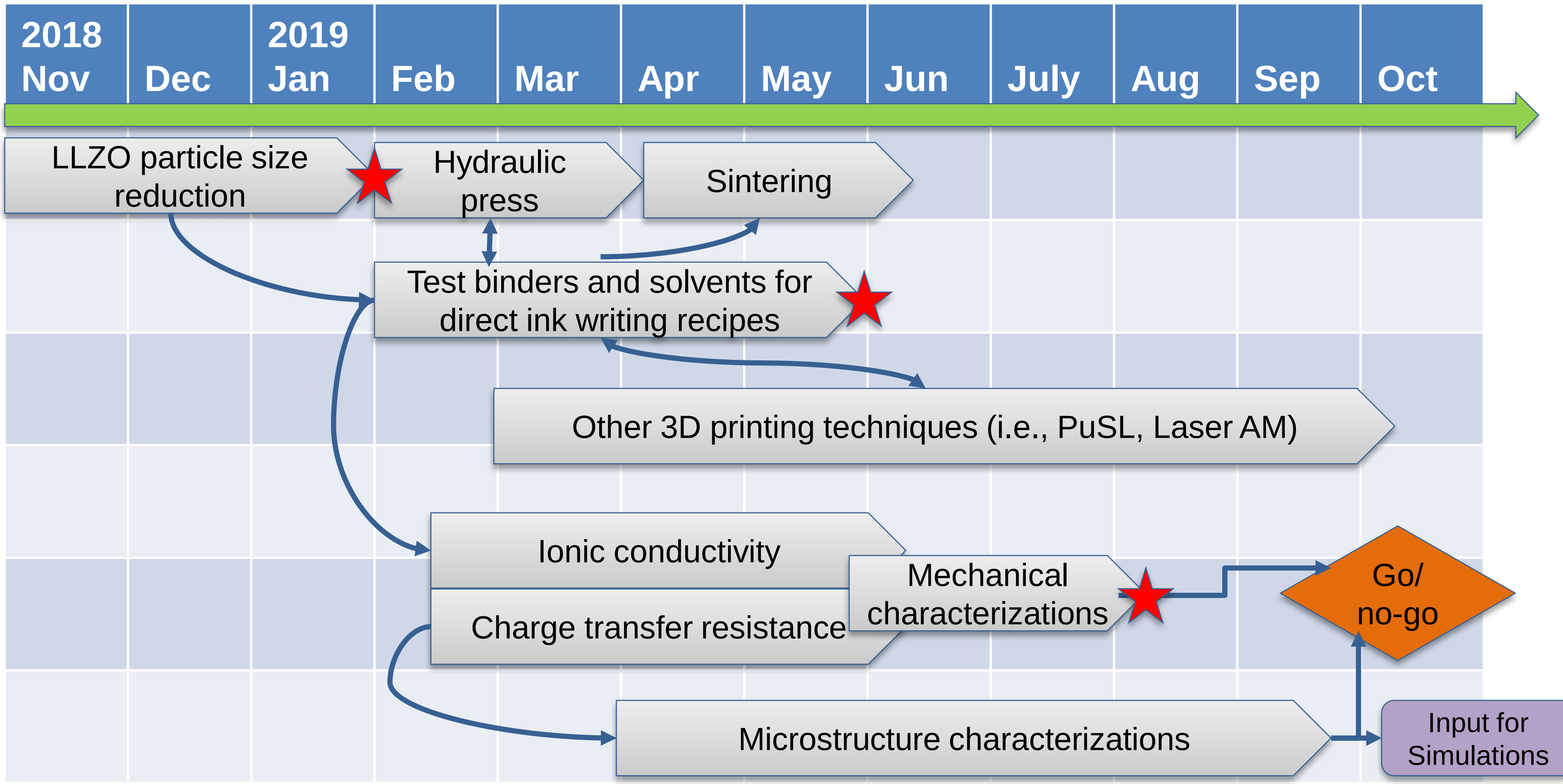
- **Impact**
  - Unlike the well-established roll-to-roll fabrication of conventional Li-ion batteries, the processing of SSBs are unique due to the brittleness of solid state electrolytes (SSEs).
    - Commercial SSE separators are ultrathick, which limited power and energy densities.
    - Free-standing ultrathin ceramic separators are mechanically fragile.
- **Strategies:** 3D printing enables
  - Multi-component integration
  - Interfacial engineering: morphological, chemical and mechanical control
- **Objectives**
  - Tuning microstructures of 3D printed SSE separators
    - Printability & conductivity, grain structure & porosity
  - Process compatibility with cathode printing
    - Sintering conditions and materials selection
  - 3D printing of sintering-free SSE separators
    - SSE/polymer composite

Milestones

Tasks, Milestones, and Deliverables	FY19				FY20				FY21			
	1	2	3	4	1	2	3	4	1	2	3	4
Objective 1: Tuning microstructures of 3D printed SSE separators												
1.1: Obtain different particle size distributions of SSE powders												
1.2: Test binders and solvents to adjust the ink quality for 3D printing												
1.3: Measure ionic conductivity and mechanical properties of sintered separators												
1.4: Characterize microstructures of 3D printed separators												
1.5: Explore 3D printing techniques other than DIW												
Objective 2: Compatibilities with cathode printing												
2.1: ALD on ball milled electrolyte/electrode powders												
2.2: Measure thermochemical stabilities of electrolyte-electrode-conductive additive mixtures												
2.3: Monitor the impedance change of the sintered mixtures												
2.4: Run ex-situ/In-situ tomography on cathode(Li)/LLZTO/Li cells												
Objective 3: 3D printing of sintering-free SSE separators												
3.1: Develop polymer/LLZTO recipe for 3D printing												
3.2: Develop polymer-Li salt/LLZTO recipe for 3D printing												
3.3: Measure ionic conductivity and mechanical properties												
3.4: Run ex-situ/In-situ tomography on Li/LLZTO-CPE/Li cells												

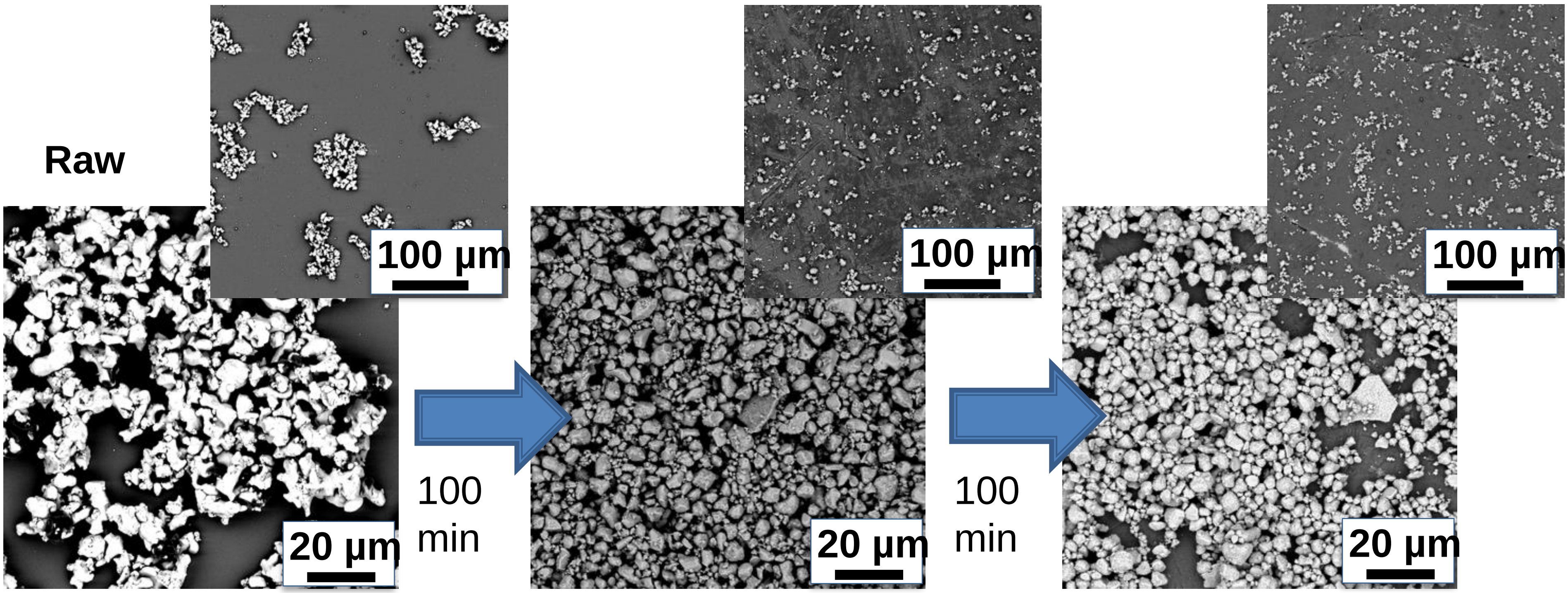
LLZTO: $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$

Approach



- **FY19 Go/no-go Decision:** Be able to 3D print SSE separators with varied feature sizes, microstructures. Achieve < 100 µm feature size, > 10^{-5} S/cm ionic conductivity.

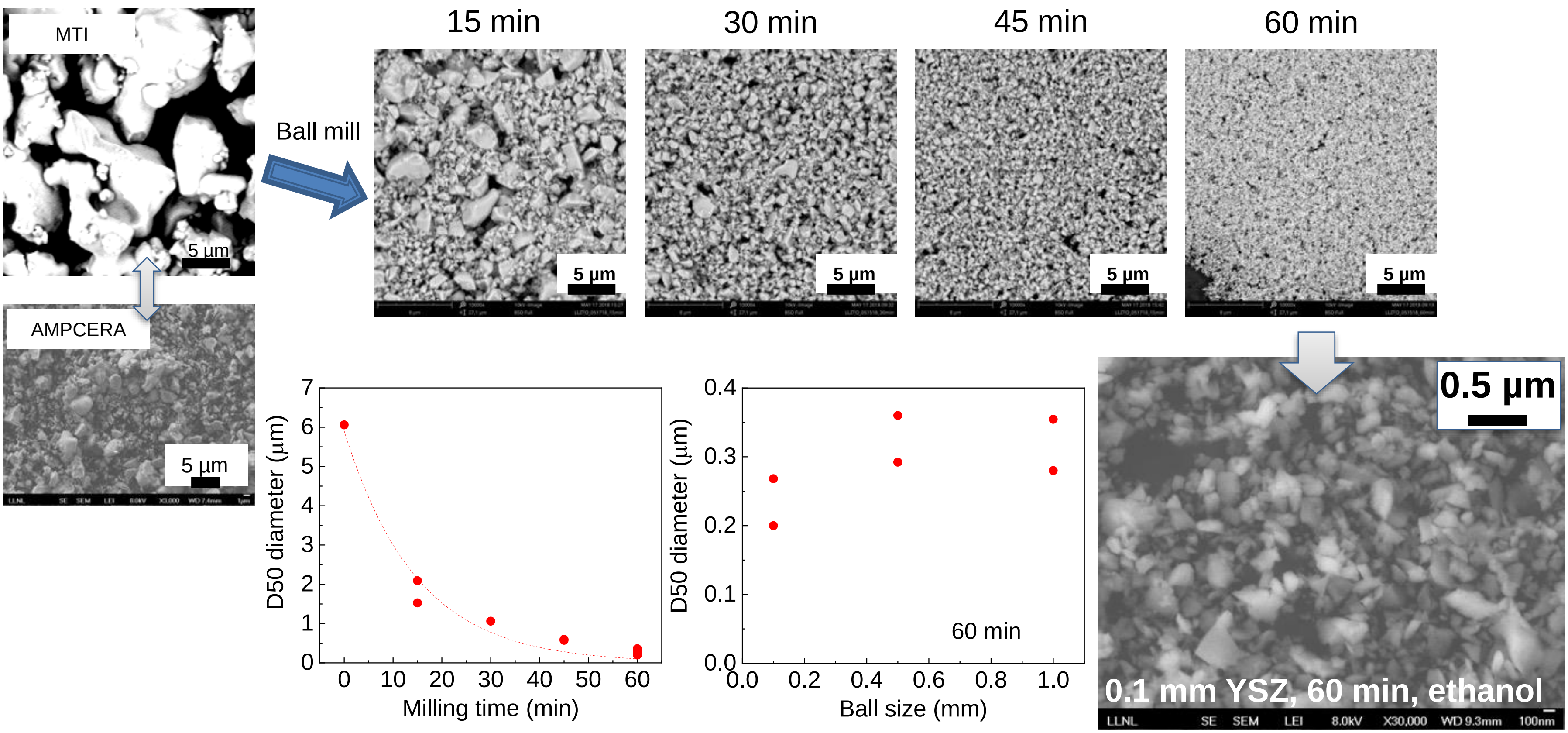
Accomplishments to date – FY19



Conditions: dry mill using SPEX 8000-D mixer mill, 60g 0.1-0.2mm YSZ balls with 10g LLZTO (5μm) powders, 100 min and then another 100 min
Results: Aggregates between particles were broken down to form single particles. Particle sizes were slightly reduced and with much round shape. Additional dry milling does not change much.

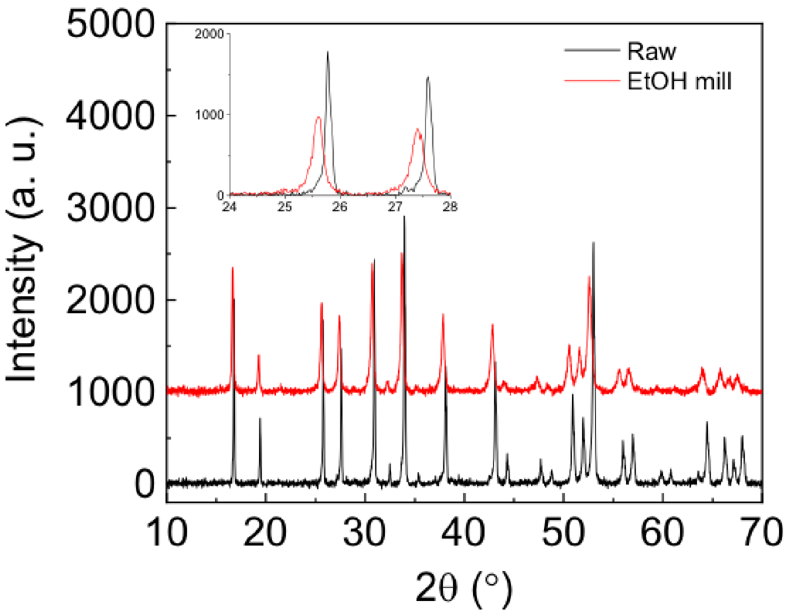
Accomplishments to date – FY19

- LLZTO powders were milled down from 6 µm to 200 nm for particle size effects on printing and sintering. --- **Milestone 1 achieved**

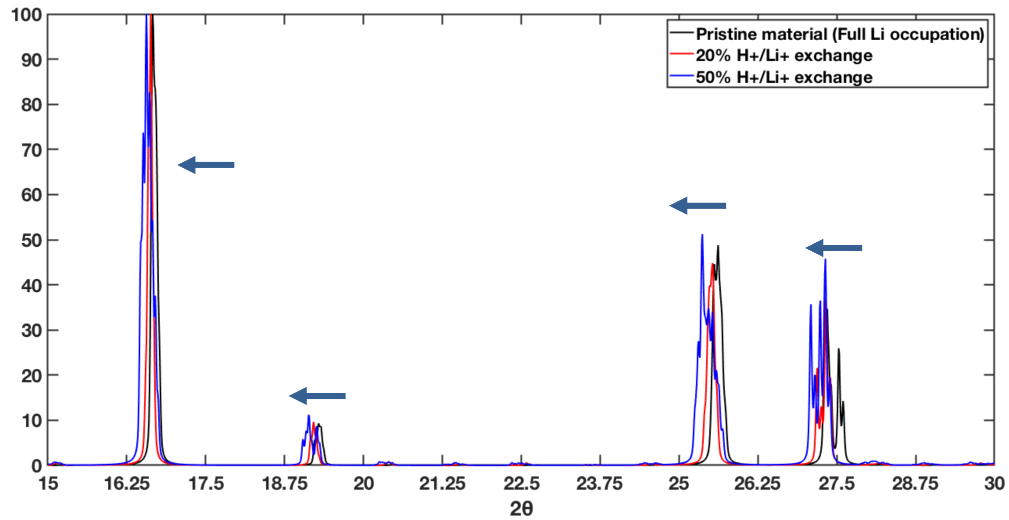


Accomplishments to date – FY19

- **Lattice spacing increase and phase transition** indicate the occurrence of H^+/Li^+ exchange during alcohol-assistant high-energy ball milling.

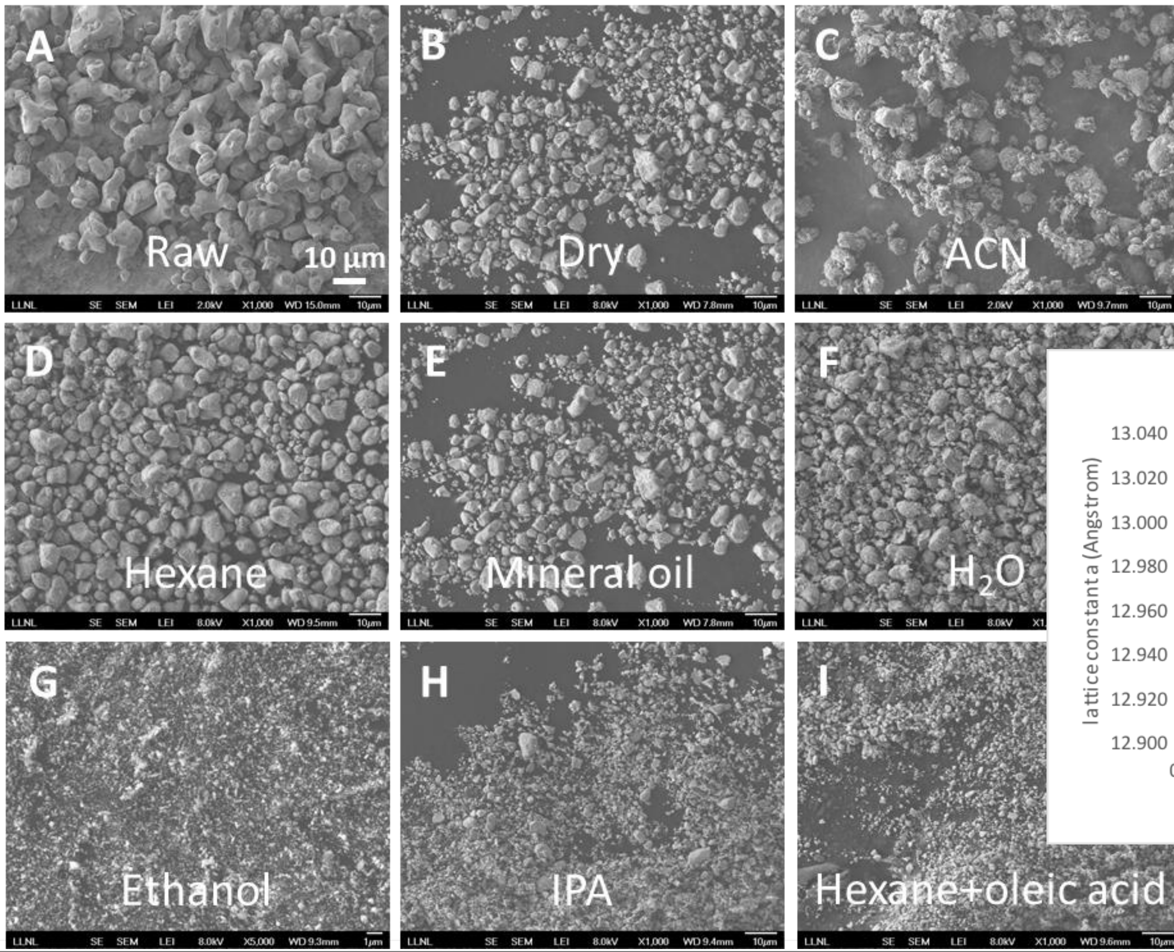


- **First principle calculations** confirm the expansion of unit cell after H^+/Li^+ exchange.

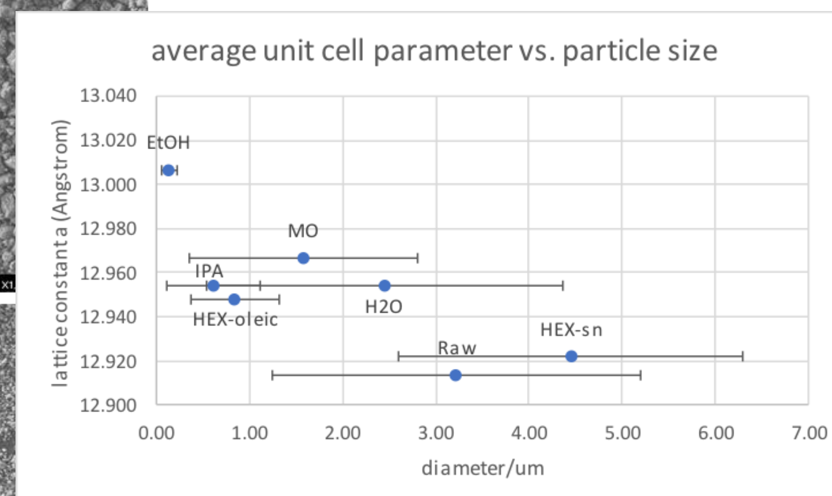


Accomplishments to date – FY19

- New ball milling conditions were developed to minimize H^+/Li^+ exchange while still obtain reduced particle sizes.

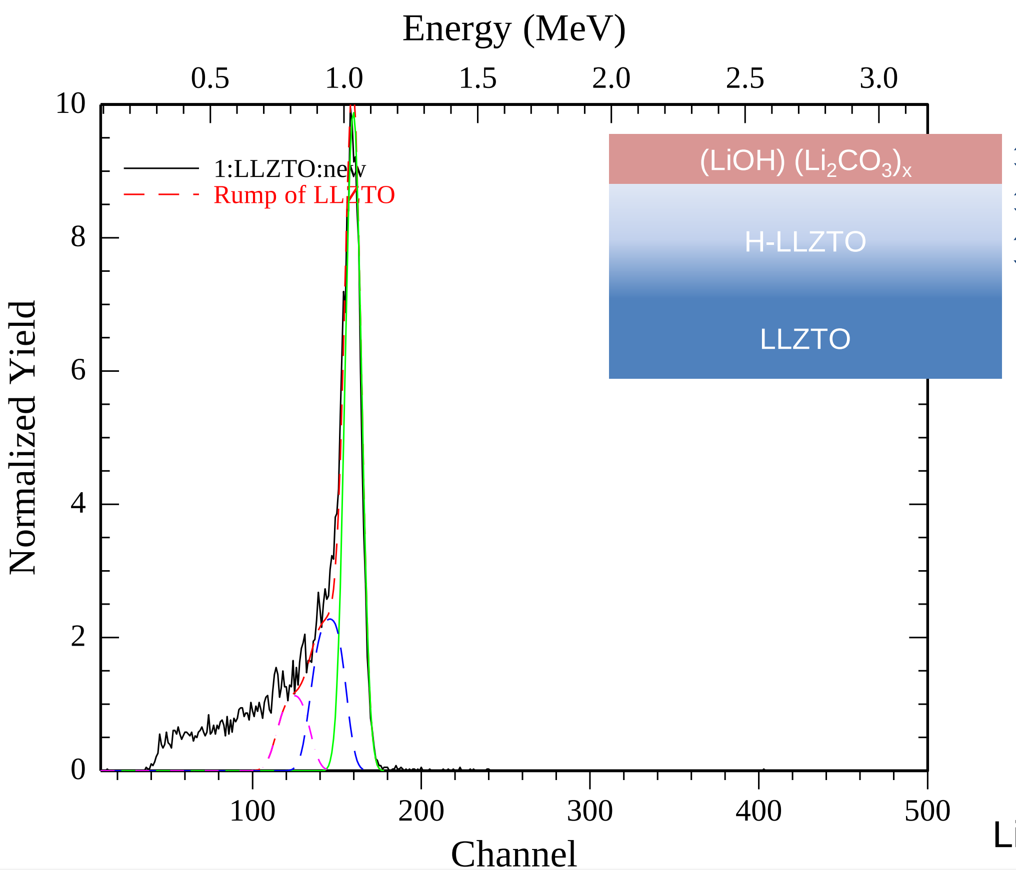


- Milling efficiency:
  - Suspension stability
  - Viscosity
- Li loss:
  - Reactivity
  - Solubility

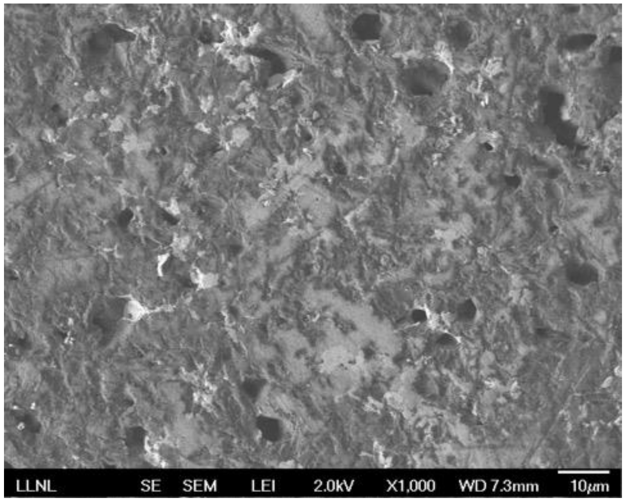


Accomplishments to date – FY19

- Elastic recoiling detection analysis gives quantitative H distribution in the sub-surface region of the air-exposed LLZTO pellets, which can reveal H^+/Li^+ exchange kinetics.



90 nm $LiOH \cdot Li_2CO_3$
130 nm $Li_{5.9}H_{1.1}La_3Zr_{1.4}Ta_{0.6}O_{12}$
110 nm $Li_{6.4}H_{0.6}La_3Zr_{1.4}Ta_{0.6}O_{12}$

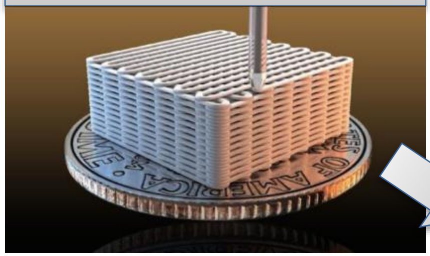


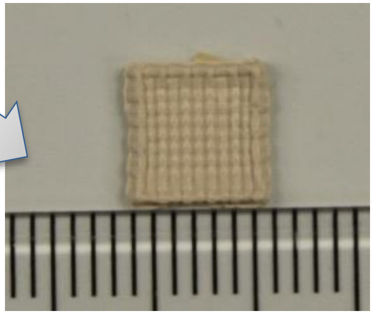
$LiOH/Li_2CO_3$ contaminates show darker color.

Accomplishments to date – FY19

- Two 3D printing techniques
  - Direct Ink Writing (DIW)
  - Paste projection micro-stereolithography (Paste PuSL)
- Advanced sintering
  - Densification achieved in 20 seconds via laser sintering

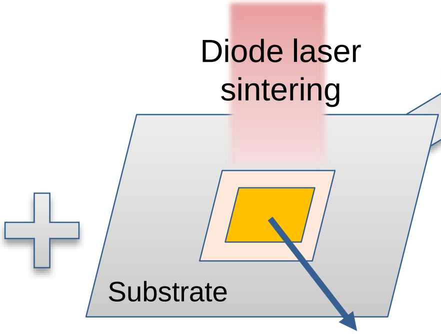
DIW

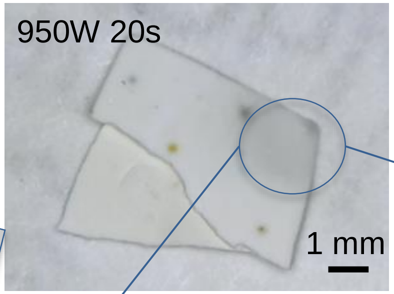


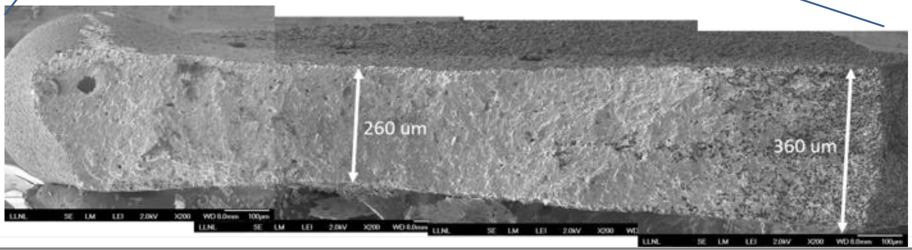


LLZTO-BM30. 200um nozzle. Before sintering.

Paste PuSL







Responses to Previous Year Reviewer's Comments

- This project is a new start.

Partners/Collaborators

- Project Lead – Brandon Wood (bat426)
  - “Integrated multiscale model for design of robust 3D solid-state lithium batteries”

Remaining Challenges and Barriers

- **Ink recipes for 3D printing** need to be developed. The optimal ink recipes and sintering conditions of the printed LLZTO films need to be examined so that high densification and tunable microstructures can be achieved.

- **Surface condition** is critical for the reduction of charge transfer resistance. A method that can effectively avoid or remove the surface Li_2CO_3 contamination layer shall be developed especially for thin film and 3D form factors in which case mechanical polishing is inapplicable.

- **Intimate incorporation of cathode/Li** electrodes with LLZTO electrolyte shall be developed to avoid undesired side reactions that could impede ionic transport.

Proposed Future Research

- **FY19**
  - — **(Q2 milestone):** Down select SSEs, binders and solvents for the 3D printing (**on-going**)
  - — **(Q3 milestone):** Determine post processing conditions for good ionic conductivity and mechanics
  - — **FY19 Go/no-go Decision:** Be able to 3D print SSE separators with varied feature sizes, microstructures. Achieve < 100 µm feature size, > 10^{-5} S/cm ionic conductivity

- **FY20**
  - — Ink development for cathode/anode printing
  - — Thermochemical stabilities of mixtures of electrolyte-active materials-conductive additives
  - — Evaluate half-cell stability and failure mechanisms

Summary

- Accomplishments
  - LLZTO powders with varying particle sizes and degree of H^+/Li^+ exchange have been successfully prepared using high energy ball milling.
  - ERDA reveals the H^+ distribution and H^+/Li^+ exchange kinetics.
  - High density and ionic conductivity have been achieved for hydraulic pressed and then 1100 °C sintered LLZTO pellets.

- Future work
  - Develop 3D printing inks
  - Determine sintering conditions
  - Measure ionic conductivity, charge transfer resistance, and cycling stabilities

Background image: LLZTO crystal ball after laser melting