Investigating Ink Properties and 3D Printing Process Parameters for Manufacturing 3D Solid State Ceramic Electrolytes

Dylan Cox[1], Hui (Claire) Xiong[*2], Katelyn Shadley[3], Bin Li[4], Kiyo Fujimoto[4]
Oregon State University, Boise State University, University of Idaho, Idaho National Lab

Introduction

Solid state ceramic electrolytes offer numerous advantages over liquid organic electrolytes including . Additionally, these solid ceramic electrolytes allow the use of a lithium metal anode, which dramatically improves energy density[1]. Of these, Lithium Lanthanum Zirconium Oxide (LLZO) is a particularly promising solid electrolyte candidate due to its high ionic conductivity and stability over large temperature and voltage ranges[2]. However, it also has a key limitation in the poor interfacial contact between the electrode and electrolyte which results in a high interfacial impedance[2].

These challenges may be partially or fully addressed by additive manufacturing techniques. Additive manufacturing techniques enable the creation of a battery with a 3D internal structure to improve the surface area and reduce the thickness of the electrolyte. This has the potential to increase both the energy density and power density of the battery.

Background

Building lithium ion batteries with a 3D structure represents a potential way to increase both their energy and power densities. 3D printing is seen as a promising manufacturing method to create batteries with a complex internal structure, but it is unclear which types of 3D printing methods are the most suitable. This project will investigate the suitability of the aerosol jet printing and direct ink writing techniques for 3D printing solid state ceramic electrolytes for 3D lithium ion batteries.

- 3D printing allows a wide range of potential electrolyte geometries to be explored to maximize surface area and interfacial contact.

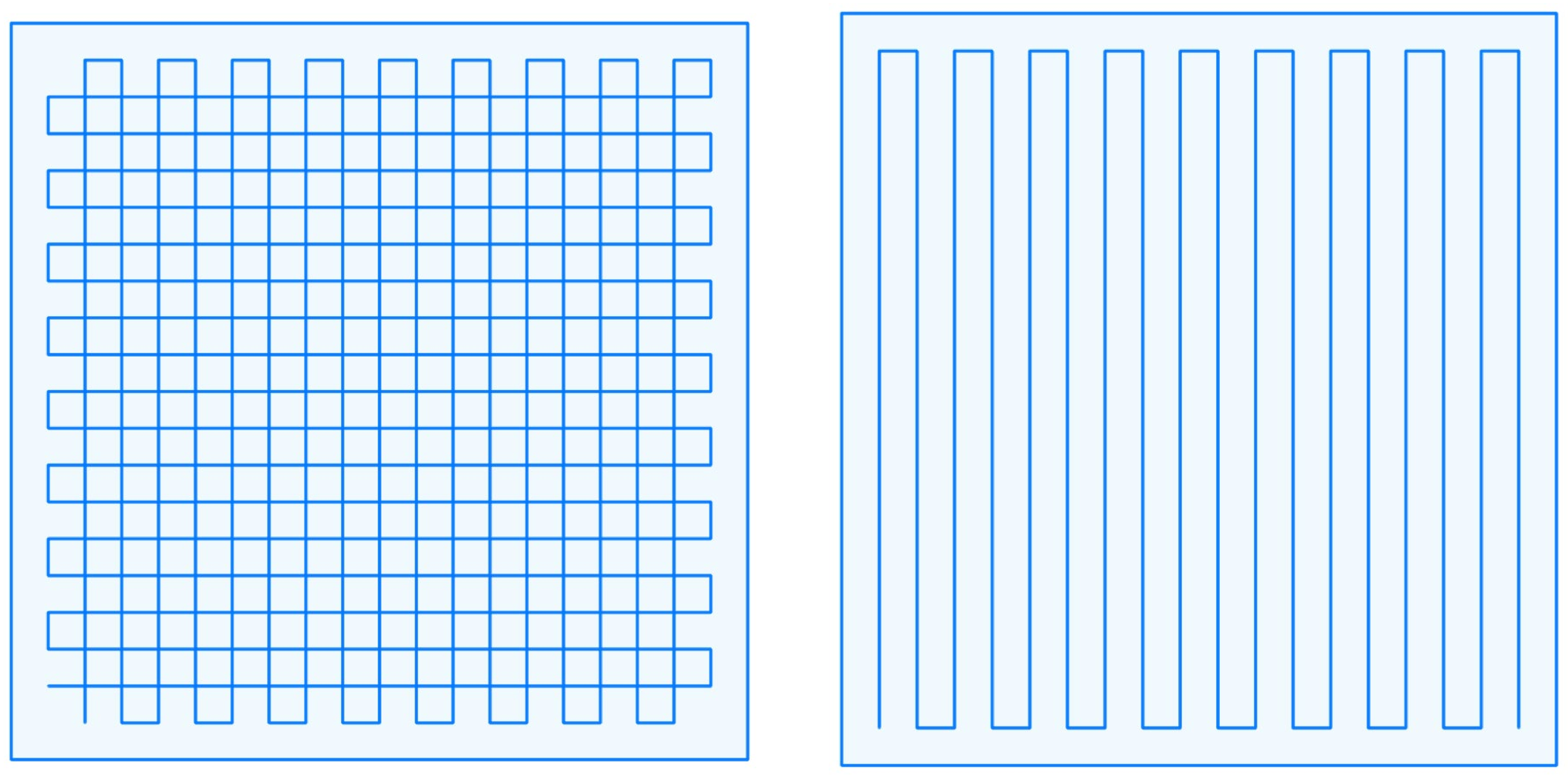
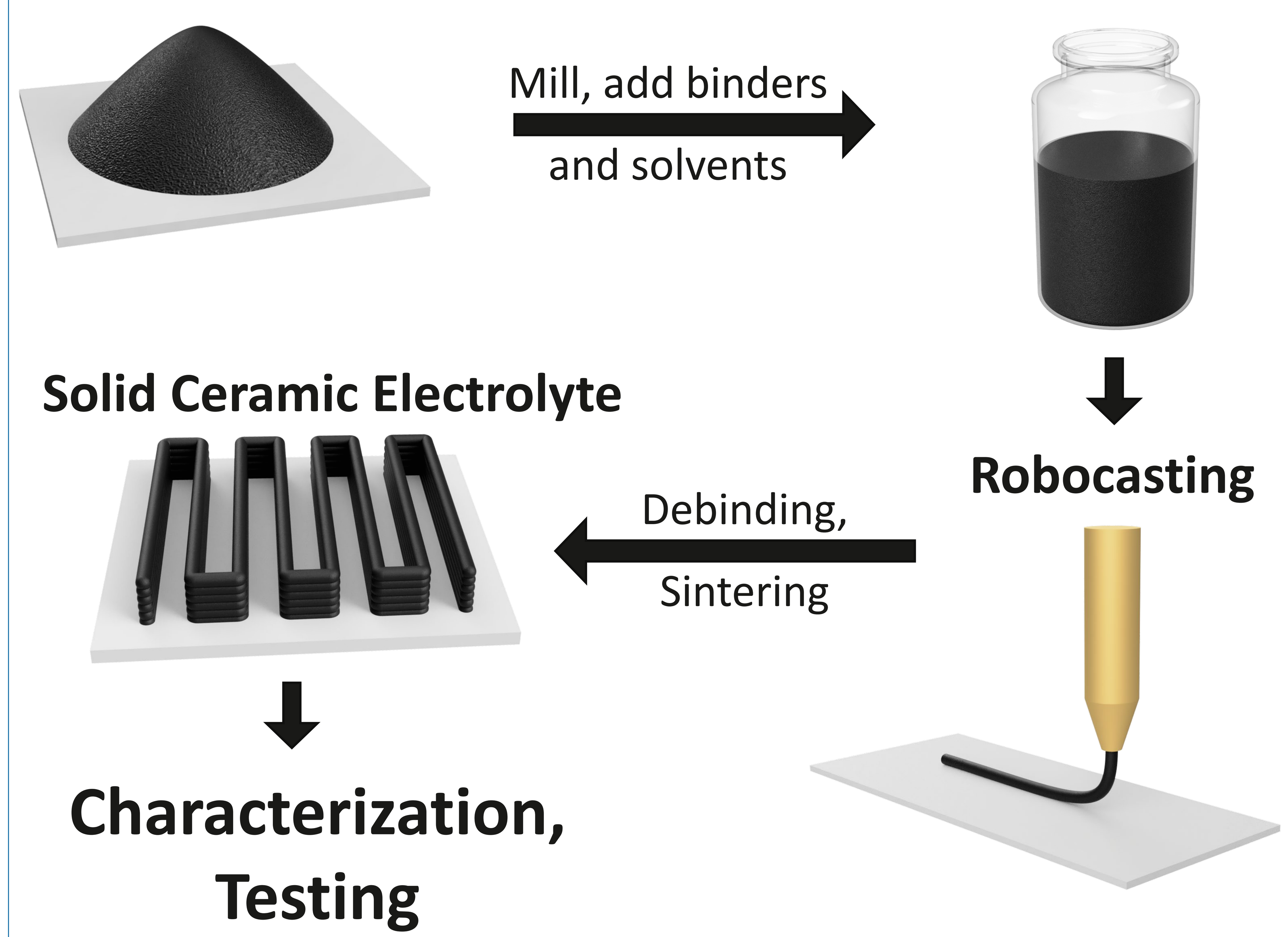


Figure 1: Geometries that were printed

Project Goals

- Demonstrate the feasibility of printing ceramic LLZO electrolytes using Robocasting and Aerosol Jet Printing techniques
- Quantify the printing parameters that yield electrolytes that best meet the performance targets needed for 3D lithium ion batteries
- Develop consistent and repeatable process parameters to print electrolytes of varying sizes and geometries
- Minimize material wastage

Methods



Results

Figure 2: LLZO electrolyte ink, batch 1

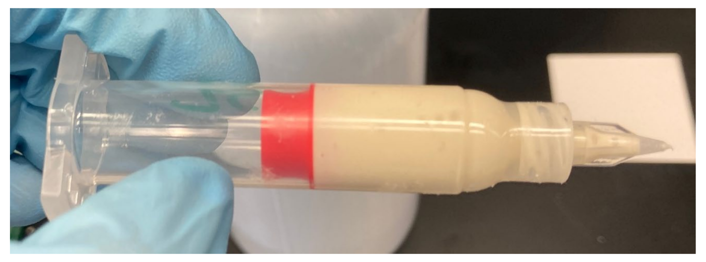


Figure 3: Ink before dispensing

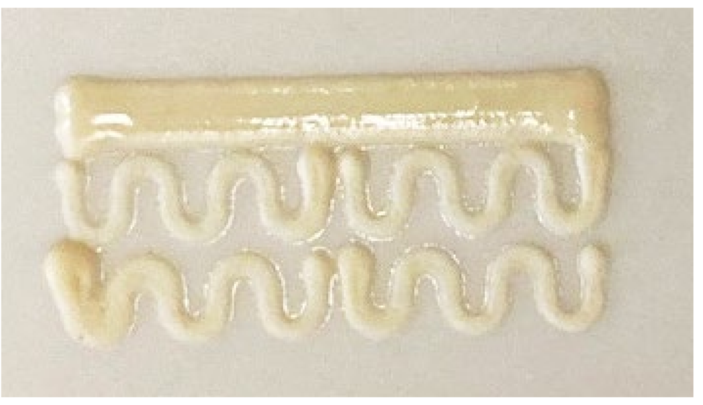


Figure 4: Completed calibration pattern

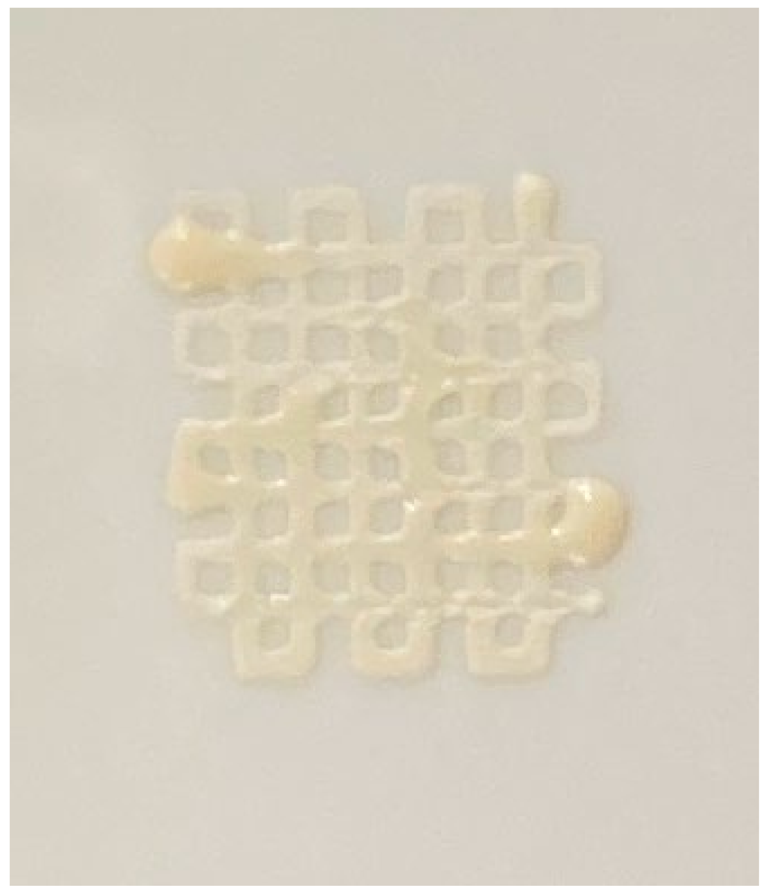


Figure 5: Printed grid pattern

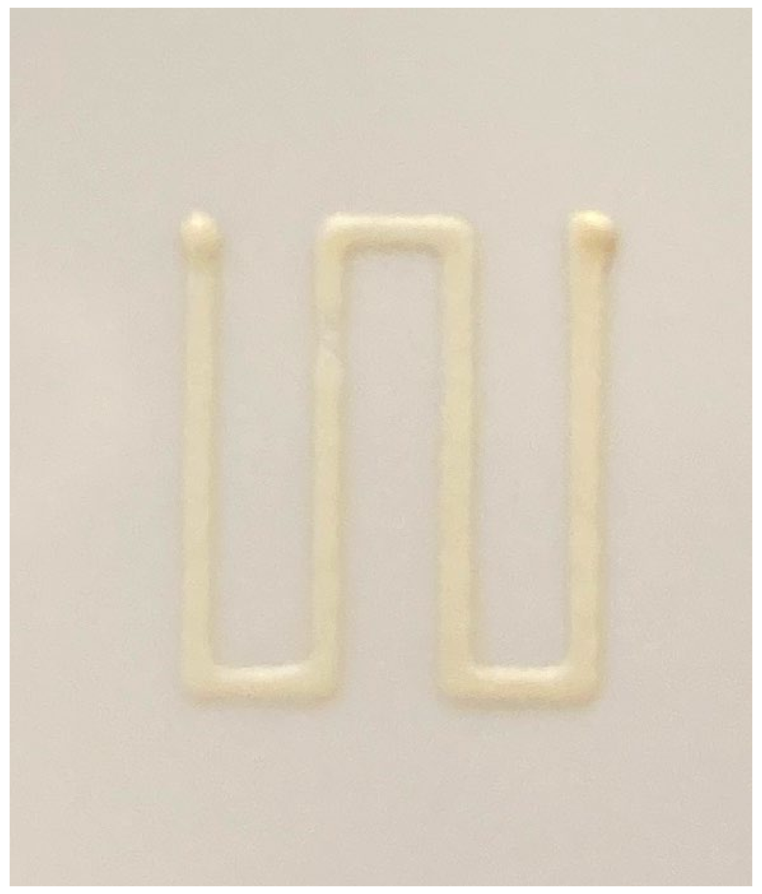


Figure 6: Printed z-pattern

Structural Characterization

SEM imaging will allow the changes in microstructure that result from the printing and sintering processes to be characterized.

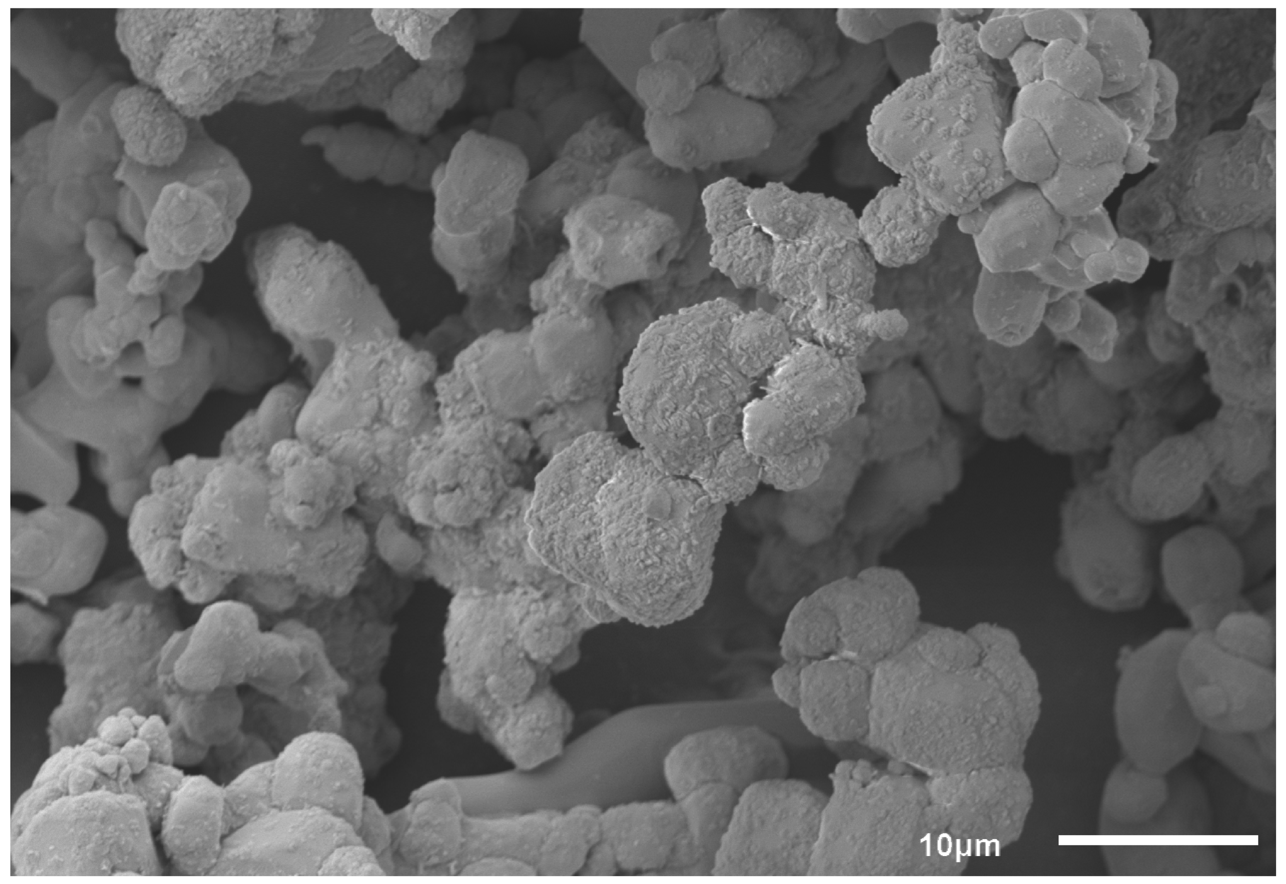


Figure 7: SEM image of unprocessed LLZO powder, 2kx magnification

XRD analysis will allow any changes in crystal structure during the process to be measured.

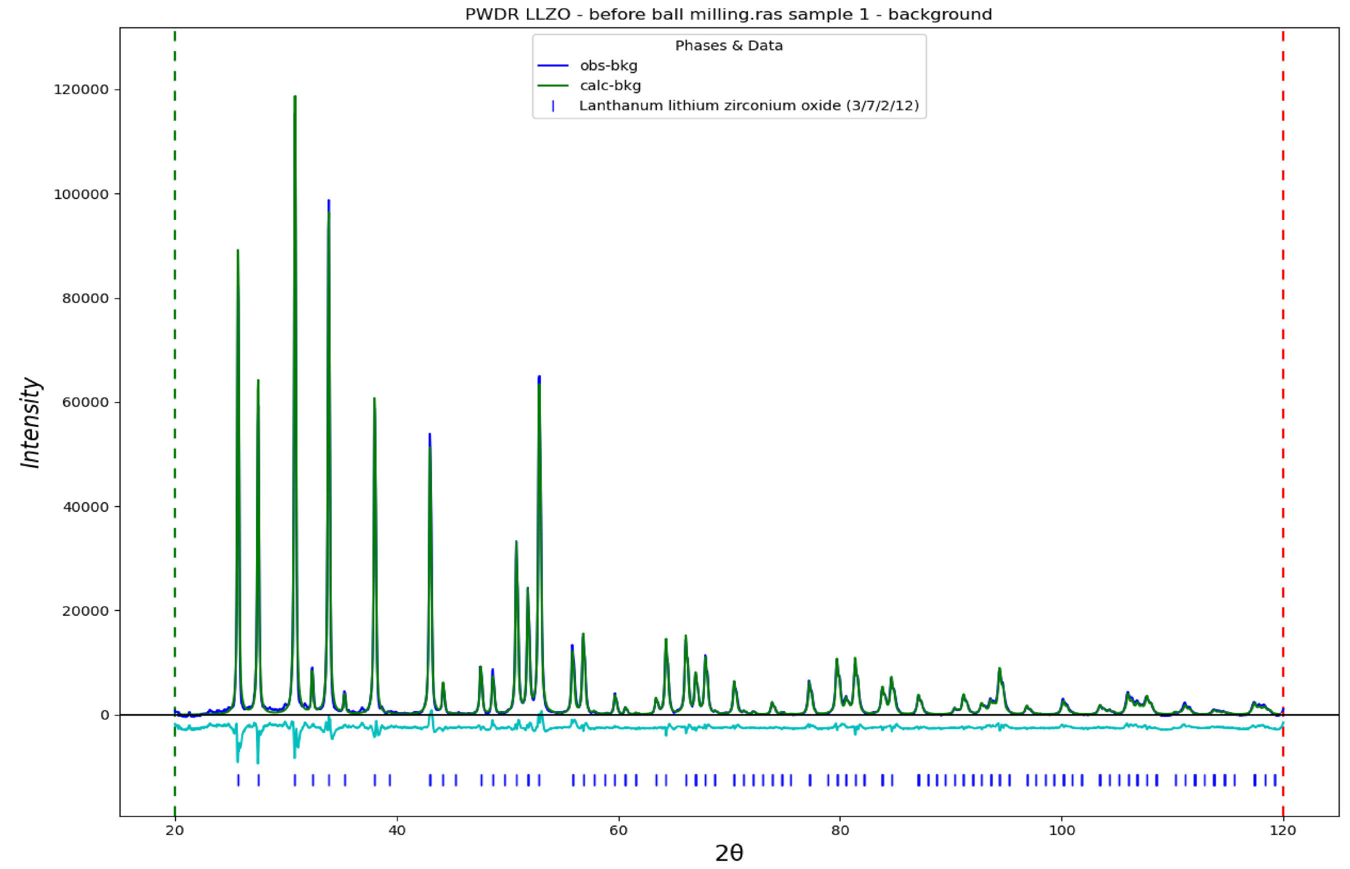


Figure 8: XRD patterns of unprocessed LLZO powder

Going Forward

- Total solids loading was lower than targeted
- Rheological properties of ink need to be more consistent
- Bubble formation led to unpredictable over and under extrusion
- Process parameters need to be tuned for longer lines
- Printing multiple layers needs to be investigated further
- Sintering parameters need to be quantified
- Material wastage needs to be further minimized
- Other printing processes can be evaluated

This project has funding and support from the NSF Center for Advanced Energy Studies REU Program, the Center for Advanced Energy Studies facility, Boise State University, and Idaho National Lab

References:
1. W. Luo, Y. Gong, Y. Zhu, K. K. Fu, J. Dai, S. D. Lacey, C. Wang, B. Liu, X. Han, Y. Mo, E. D. Wachsman, L. Hu, J. Am. Chem. Soc. 2016, 138, 12258.
2. Thangadurai, V.; Narayanan, S.; Pinzaru, D. Chem. Soc. Rev. 2014, 43, 4714 DOI: 10.1039/c4cs00020j