High Energy Ball Mill Tape Casting and Porosity Effects

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Abstract

$Li_7La_3Zr_2O_{12}$ (LLZO) and mixed ion and electron conducting (MIEC) garnet were prepared with high energy ball milling. Milled powers were cast into tapes and then pressed into trilayered porous-dense-porous solid electrolytes with LLZO dense tapes and MIEC porous tapes of 56%, 65%, 75%, and 85% porosity. Percentages come from the mass percent of pore former of the total MIEC mass. Only one trilayer was successful due to inconsistent sintering. Further testing needs to be done to determine the cause of the inconstancies.

Introduction

Solid state batteries:

- Higher potential energy density
- Block Li metal dendrites due to their high shear moduli

Garnet solid electrolytes:

- Wide electrochemical window
- High ionic conductivity
- High chemical and electrochemical stability

(Alexander et al., 2023)

Figure 1: Porous-dense-porous garnet trilayer

Methods

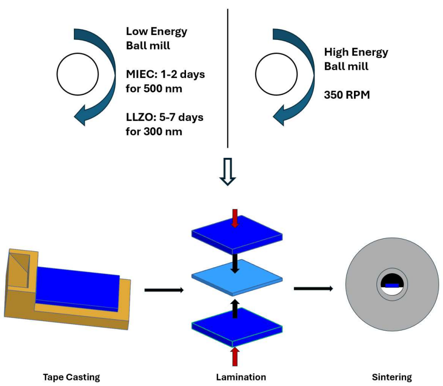
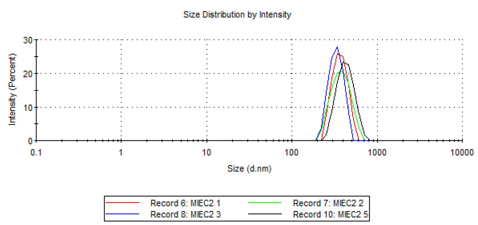


Figure 2: After high energy ball milling (HEBM) a mixture of powders, binders, pore formers, and plasticizers are tape casted to make flat layers of material for battery layer stacking. Layers are stack and laminated under pressure at elevated temperature to form multi-layered electrolytes. Sintering post lamination removes plasticizers, pore former, and binder from laminated tapes.

High Energy Ball Mill Trends



Z-Avg Mean (nm)	Z-Avg St.Dev (nm)
490.4	17.94

Figure 3: ~500 nm particle size achieved for MIEC in one hour

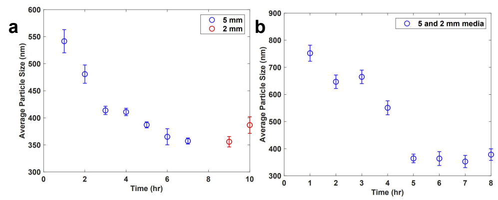


Figure 4: (a) Single media milling of LLZO for 10 hours with switch from 5 mm to 2 mm media at hour 9 and (b) mixed media milling of LLZO for 8 hours

XRD

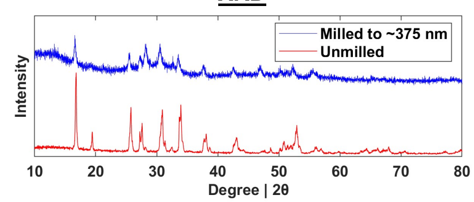


Figure 5: XRD of LLZO before and after milling with the milled sample intensity multiplied by 3 where XRD after HEBM shows contamination of LLZO possibly with praseodymium from milling after MIEC.

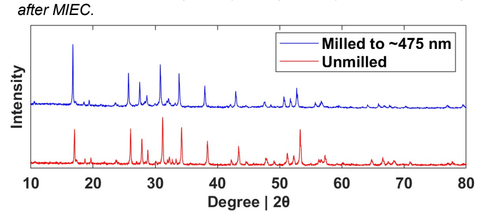


Figure 6: XRD of MIEC before and after milling with good peak matching suggesting no contamination

Trilayers with Different Porosities

Four different porous tapes were made: 56%, 65%, 75%, and 85%. To increase porosity, it was necessary to increase binder amounts otherwise tapes will crack. Porous-dense-porous trilayers were made. Of the four trilayers, only one trilayer was successfully sintered, the 65% porous trilayer. All trilayers were sintered with the same temperature profile indicating that the furnaces are out of calibration and/or the different porosities exhibits different sensitivities to temperature.

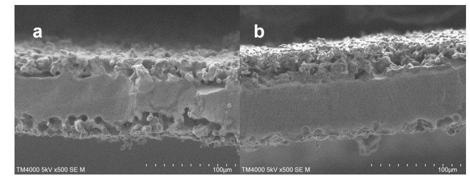


Figure 9: Over sintering leads to pore collapse, as can be see in the (a) 56% porous and (b) 75% porous trilayers. Pore collapse leads to a densification of the porous MIEC sections of the trilayer. Pore collapse leads to poor infiltration of anodes and cathodes into the MIEC

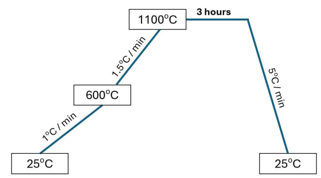


Figure 7: Furnace temperature profile for sintering of all trilayers. Sintering is done under 100 mL/min O_2 flow.

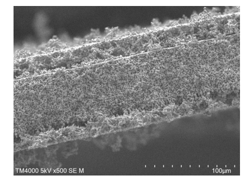


Figure 10: 85% porosity post sintering shows incomplete sintering with uncomplete densification of the dense layer and incomplete removal of binder and pore former in the porous layer.

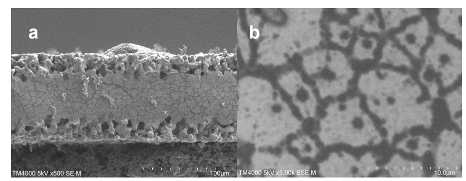


Figure 8: First tape made with contaminated LLZO (a) shows full tri-layer with unexpected grain boundaries in dense layer and (b) back scattering electron scan shows a lighter element in the grain boundaries this is potentially due to praseodymium infiltrating the garnet

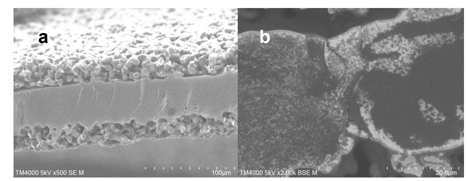


Figure 11: (a) 65% porous successful trilayer where (b) one big grain separates in the dense layer which could cause a short in a full cell as dendrite can more easily penetrate a grain boundary than the fully densified LLZO.

Conclusions

1. High energy ball milling reduces time spent milling. The required particle size for MIEC is achieved in one hour. The required particle size for LLZO takes about 5 hours to achieve. The particle size bottomed out at roughly 350 nm.
2. To increase the porosity, when mixing the slurry, the amount of binder should be increased with the amount of pore former to maintain the proportion of binder to pore former.

Future Work

Further experiments should be done to verify phase of LLZO post milling by HEBM LLZO with an uncontaminated jar. The calibration of the furnaces should also be investigated. Following this, trilayers of different porosities can be made, and porosity can be correlated to conductivity.

References

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Acknowledgements

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