

# Lawrence Berkeley National Laboratory

## LBL Publications

### Title

Flexible All Solid State Lithium Batteries Made by Roll-to-Roll Freeze-Casting

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Peer reviewed

## CRADA Final Report Form

Date July 11, 2019

PI Marca Doeff

CRADA No. AWD00003157

LBNL Report Number LBNL-2001224

OSTI Number \_\_\_\_\_

1. Parties: Fisker, Inc. (Participant), University of California/Lawrence Berkeley National Laboratory (Contractor 1) and UT-Battelle, LLC/Oak Ridge National Laboratory (Contractor 2).  
(Identify Parties to the CRADA)

2. Title of the Project: Flexible All Solid State Lithium Batteries Made by Roll-to-Roll Freeze-Casting

3. Summary of the specific research and project accomplishments:  
(Were key major goals of the CRADA achieved?) Yes. The aim of this project was to develop a method for fabricating thick (~ 100  $\mu\text{m}$ ) composite cathodes using freeze-casting, a processing technique for producing porous ceramics. Freeze-casting, developed at the University of California (Contractor 1) and UT-Battelle, LLC (Contractor 2) was used to produce  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO, a solid Li-ion conductor) scaffolds with unidirectional pores. The scaffolds could then be infiltrated with a cathode active material ( $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  or NMC), a conductive polymer and, optionally, carbon black. These cathodes could then be combined with thin dense LLZO electrolyte layers, produced by tape-casting, and thin lithium electrodes to fabricate solid-state lithium batteries that will significantly surpass the performance of traditional LIBs on cost and energy density.

*Note: Final Reports and Forms containing Protected CRADA Information are to be emailed directly to the SPO close out requestor, along with a confirmation of the public release date. Do not submit via eSRA. Also, please do not include any Proprietary Information\* (defined below) in CRADA Final Reports and Forms.*

4. Deliverables:

Deliverables met	Party (LBNL, Participant, Both)	Delivered to Other Party?
Participant will supply nanopowders sufficient for the freeze tape casting work at Contractor 2 (six months after start of project or earlier).	Contractor 1 provided powders so, Contractor 2 could do scale-up work, pending the generation of detailed plans by all	Contractor 1 delivered to Contractor 2.

	CRADA parties	
Participant will deliver a small prototype cell to DOE twelve months after the start of the project.	Contractor 1 will provide cell to DOE.	No.
Contractor 1, Contractor 2, and Participant will submit a report summarizing results to DOE 13 months after the end of the project.	All parties	Yes

5. Identify publications or presentations at conferences directly related to the CRADA?

“Towards Scalable Manufacturing of Solid State Batteries”, Marca M. Doeff, Eongyu Yi, Hao Shen, Guoying Chen, and Stephen Sofie, 236<sup>th</sup> meeting of the Electrochemical Society, Atlanta GA, Oct. 13-17<sup>th</sup>, 2019.

6. List of Subject Inventions and software developed under the CRADA: (Please provide identifying numbers or other information.)

None

7. A final abstract suitable for public release:

(Very brief description of the project and accomplishments without inclusion of any proprietary information or protected CRADA information.)

This project was directed towards understanding scalability and manufacturing issues associated with a novel fabrication method for solid-state lithium batteries initially proposed by Contractor 1 (LBNL). This is based on freeze tape casting (FTC) of Al-substituted  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) to form a porous ion-conducting scaffold, followed by infiltration with cathode active material and other components. The composite electrodes fabricated by this method can then be combined with thin dense layers of LLZO and a lithium foil to complete a solid-state cell. Contractor 1's duties were to determine the best conditions for freeze tape casting of LLZO, and communicate these to Contractor 2 (ORNL) so that they could scale-up the process. Scale-up issues were identified with the first formulation provided to ORNL, but were resolved with the second formulation, and scaffolds were successfully produced at ORNL. Early in the project, hybrid cells were assembled at ORNL using components produced at Fisker (Participant) and could be cycled, although cycle lives were short, probably due to problems associated with the use of liquid electrolyte. The ultimate goal of the project was to produce a functioning completely solid-state cell, which was accomplished at the end of the project, by Contractor 1.

8. Benefits to DOE, LBNL, Participant and/or the U.S. economy.

All solid-state lithium cells have potential safety and energy density advantages over conventional lithium-ion batteries (LIBs). However, commercial solid state batteries with ceramic electrolytes are currently made in thin film configurations, which are costly to manufacture, and fall far short of DOE energy density goals for electric vehicle applications, due primarily to the low areal capacities of the cathodes. Thin film batteries are not suitable for vehicular or other large-scale applications not only due to their high cost, but also because

of the difficulties associated with scaling up the specialized vacuum deposition techniques used to make the devices. The concept of a porous ionic conducting scaffold infiltrated with active material was proposed to address transport limitations associated with using thicker (~100 µm) cathodes in a solid state battery configuration. The FTC method, used to produce the ion-conducting scaffolds, is scalable and low-cost. Thus, two major impediments to solid-state battery operation and manufacture were addressed with this project.

9. Financial Contributions to the CRADA:

DOE Funding to LBNL	\$ 165k
DOE Funding to ORNL	\$ 185k
Participant Funding to LBNL	\$0
Participant In-Kind Contribution Value	\$350k
Total of all Contributions	\$700k

\* *“Proprietary Information” means information, including data, which is developed at private expense outside of this CRADA, is marked as Proprietary Information, and embodies (i) trade secrets or (ii) commercial or financial information which is privileged or confidential under the Freedom of Information Act (5 U.S.C. 552 (b)(4)).*

**CRADA No. NFE-17-06937 Final Report**  
entitled  
**Flexible All Solid-State Lithium Batteries Made by Roll-to-Roll Freeze-Casting**

**Purpose and Background**

In order to commercialize all solid-state lithium-ion batteries (LIBs) for Fisker, Inc. (Participant) for demanding applications such as electric vehicles, low-cost, scalable, and continuous processes for the manufacture of composite cathodes must be developed. Current solid-state devices have thin film formats, which are not competitive with state-of-the-art lithium ion batteries (LIBs) in terms of cost, energy density, or manufacturability. The aim of this project is to develop a method for fabricating thick (~ 100  $\mu\text{m}$ ) composite cathodes using freeze-casting, a processing technique for producing porous ceramics. Freeze-casting, developed at the University of California (Contractor 1) and UT-Battelle, LLC (Contractor 2) will be used to produce  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO, a solid Li-ion conductor) scaffolds with unidirectional pores. The scaffolds will then be infiltrated with a cathode active material ( $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  or NMC), a conductive polymer and, optionally, carbon black. These cathodes will be combined with thin dense LLZO electrolyte layers, produced by tape-casting, and thin lithium electrodes to fabricate solid-state lithium batteries that will significantly surpass the performance of traditional LIBs on cost and energy density.

**Scope of Work**

Contractor 1 will provide information as to the best method of freeze-casting LLZO scaffolds and best formulations for infiltration based on experimentation and characterization including scanning electron microscopy, porosity measurements, X-ray diffraction, AC impedance, and simple DC tests. Using this information, Contractor 2 will fabricate cathode structures consisting of freeze-tape-cast LLZO infiltrated with the other components. Contractor 2 will also investigate the best way to apply the lithium anode to a dense LLZO electrolyte layer made by tape casting. This technology will be transferred to the Participant, who will make a small, prototype solid-state cell at the end of the project. The expected outcome is a roadmap to producing solid-state cells with thick composite electrodes.

Contractor 1's technical objectives for this project are to determine the best parameters for producing LLZO scaffolds and electrodes made from those scaffolds. Contractor 2's objectives are to first set up a freeze tape-casting apparatus to scale up the manufacture of the LLZO scaffolds and demonstrate that they can be fabricated. Contractor 2 will transfer the cathode formulation developed at the lab scale at Contractor 1 to a benchtop, roll-to-roll (R2R) tape caster located in the DOE Battery Manufacturing R&D Facility at Contractor 2 (BMF). Contractor 2 will also determine the best way to apply the lithium anode to a dense LLZO tape made by tape casting, among three options: 1) thermal bonding/lamination of a lithium foil directly to LLZO, 2) incorporation of a thin (several microns) PEO+lithium salt layer between lithium metal and LLZO to improve adhesion, or 3) sputtering a LiPON layer and lithium metal onto the LLZO. Once the best method is determined, the Participant will assemble a small prototype cell consisting of the LLZO scaffold cathode, a thin dense LLZO layer and a lithium anode and measure the OCV and AC impedance.

**Task 1.** Set up freeze tape-casting unit (Contractor 2)

Contractor 2 will set up a freeze tape-casting unit by the end of the 1st quarter. The Participant will provide advice and expertise on how to procure necessary equipment (the end of this task coincides with Milestone 1).

**Task 2.** Freeze-casting parameters (Contractor 1)

Contractor 1 will determine the best parameters for freeze-casting LLZO, using materials made in-house. Parameters to be explored include solvent type (aqueous vs. non-aqueous), solids loading, amount and type of stabilizing agent (Darvan, gelatin), and binder, cooling and sublimation rates, and calcination temperature and atmosphere. XRD, SEM, and porosity measurements will be used to characterize samples. At the end of the second quarter, Contractor 1 will report the best initial results to Contractor 2 for scale-up using freeze tape casting (coincides with Milestone 2, end of 2nd quarter). Feedback from Contractor 2 will be used to fine-tune the procedure during the 3rd and 4th quarters.

**Task 3.** Electrode optimization (Contractor 1)

Contractor 1 will infiltrate scaffolds with NMC, a conductive polymer such as polyaniline, and, optionally carbon. Freeze-casting results in unidirectional pores in the LLZO scaffold, and capillary action is generally sufficient to draw in powders suspended in solvent to infiltrate pores. In cases where the viscosity of the slurry is increased due to the presence of polymer, a light vacuum is generally sufficient to draw in the mixture. XRD, SEM, AC impedance measurements and simple DC testing (to determine electronic and ionic conductivities) will be used to characterize samples. Knowledge will be transferred to Contractor 2 by the end of the 2nd quarter for scale-up, as part of Milestone 2. Feedback from Contractor 2 during quarters 3 and 4 will be used to further refine the process.

**Task 4.** Cell Component Fabrication (Contractor 2)

Contractor 2 will begin freeze tape casting LLZO scaffolds and infiltrating them using the information that Contractor 1 provides by the 3rd quarter. Contractor 2 will report results of initial attempts to Contractor 1 and Participant, so that procedures can be refined, if necessary.

**Task 5.** Application of Li Metal Anode (Contractor 2)

Contractor 2 will explore the best way to apply lithium to dense LLZO electrolyte layers for use in cells, in consultation with Participant. The dense films will either be made in-house by tape-casting, or contracted out (e.g., to Polymer Innovations, Inc. in Vista, CA is a company specializing in tape casting ceramic films and has experience with LLZO), depending on time constraints. At present, there are three options of interest. These are 1) direct thermal bonding/lamination of lithium to LLZO, 2) application of a thin (several microns thick) layer of polyethylene oxide + lithium salt (e.g., LiTFSI) layer to LLZO, to promote adhesion of lithium and to reduce contact resistance, 3) sputtering of LiPON and lithium onto LLZO. Methods 1 and 2 have the advantages of simplicity and low cost, but may not prevent penetration of lithium metal through LLZO grain boundaries. Method 3 is more complex and expensive, but should prevent dendrites. Another advantage is the considerable expertise that Contractor 2 has with LiPON. A go/no go decision will be made on each of these three approaches by the end of the 3rd quarter.

**Task 6.** Assemble prototype cell and performance test (Participant)

Using components produced by Contractor 2, Participant will assemble a small prototype cell and measure the open circuit potential and AC impedance. This is milestone 4, due at the end of the 4th quarter.

Milestones:

Milestone 1: Set up freeze tape-casting unit (Contractor 2) end of 1st quarter.

Milestone 2: Best initial freeze-casting parameters/electrode optimization (Contractor 1) to transfer to CONTRACTOR 2 for initial manufacture, end of 2nd quarter.

Milestone 3: Best method to apply Li anode to dense LLZO layer (Contractor 2) Go/no go decisions on options outlined below, end of 3rd quarter.

Milestone 4: Assemble prototype solid-state cell and measure OCV (Participant) end of 4th quarter.

**Property Considerations**

No tangible property will be exchanged.

**Estimated Cost and Source of Support**

The contributions by each Party are specified in CRADA Article II, Paragraph C. The flow of funds is summarized below for each Project Year (PY), inclusive of any applicable Federal Administrative Charges (FAC)\*.

Parties	PY 1	Total
DOE's Contribution via Contractor 1:	\$165,000	\$165,000
DOE's Contribution via Contractor 2	\$185,000	\$185,000
<b>Participant</b>		
Funds-In:	0\$	0\$
In-Kind:	\$350,000	\$350,000
Totals:	\$700,000	\$700,000

\*FAC is mandated by Section 3137 of the Strom Thurmond National Defense Authorization Act of 1999 (Public Law 105-261); does not apply if there are no funds-in from Participant.

**Deliverables**

In addition to the minimum deliverables shown in Article X of the CRADA, the following will be delivered:

Participant will supply nanopowders sufficient for the freeze tape casting work at Contractor 2 (six months after start of project or earlier).

Participant will deliver a small prototype cell to DOE twelve months after the start of the project.

Contractor 1, Contractor 2, and Participant will submit a report summarizing results to DOE 13 months after the end of the project.

**Schedule**

Task/Milestone	Work Done By			Project Months			
	Contract or 1	Contract or 2	Participant	1-3	4-6	7-9	10-12
Task 1. Set up freeze tape-casting unit		X	X	X			
Task 2. Freeze-casting LLZO parameters	X			X	X	X	X

Task 3. Optimization of electrode	X	X	X	X	X	X	X
Task 4. Cell Component Fabrication		X	X			X	X
Task 5. Application of Lithium anode		X			X	X	
Task 6. Full Cell Assembly and Test			X				X

## Program Management

The principal investigators for this CRADA are Marca Doeff (Contractor 1), David Wood (Contractor 2), and Fabio Albano (Participant). Participant will assign a program manager that will oversee the project development and ensure that the timeline, milestones and deliverables are met. Participant will also compile quarterly reports for DOE officials to assess progress of the project. Biweekly conference calls will be held between the three parties to ensure timely project progress.

### Outcomes

#### Deliverables

Deliverables met	Party (LBNL, ORNL Participant, Both)	Delivered to Other Party?
Participant will supply nanopowders sufficient for the freeze tape casting work at Contractor 2 (six months after start of project or earlier).	Contractor 1 provided powders so, Contractor 2 could do scale-up work, pending the generation of detailed plans by all CRADA parties.	Contractor 1 delivered to Contractor 2.
Participant will deliver a small prototype cell to DOE twelve months after the start of the project.	Contractor 1 will provide cell to DOE.	No.
Contractor 1, Contractor 2, and Participant will submit a report summarizing results to DOE 13 months after the end of the project.	All parties	Yes, this document

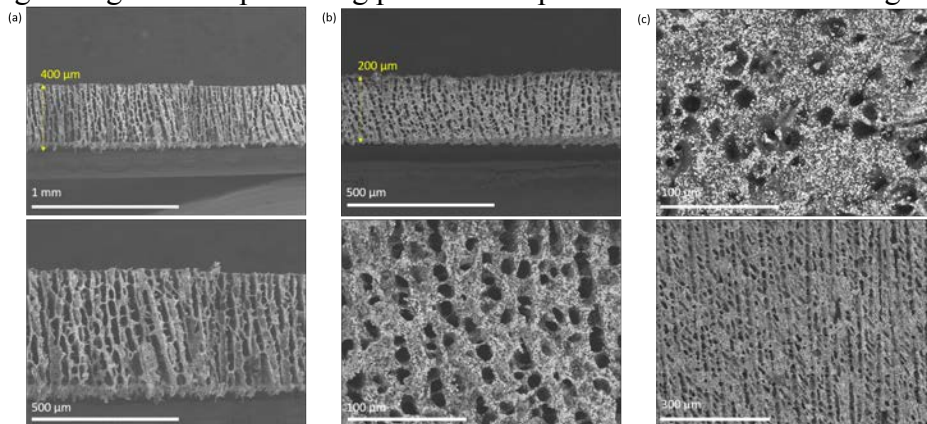
## Results and Discussion

### Quarter 1 LBNL:

Iterations of freeze tape casting based on a formulation shared by Montana State University (collaboration through Battery 500 Seedling project) were performed. Aqueous slurries containing 7.5 – 10 vol.% of LLZO with binder, thickener, along with other additives were freeze tape cast at thicknesses of several hundred microns. Figure 1a and 1b show 7.5 vol.% LLZO slurry freeze tape cast at 400  $\mu\text{m}$  and 10 vol.% LLZO slurry freeze tape cast at 200  $\mu\text{m}$ , respectively. 7.5 vol.% LLZO sample shows higher porosity than the 10 vol.% sample as



expected. Vertical pore alignment was observed in both but with significant bridging among the LLZO pillars, which may interrupt the infiltration of NMC cathode particles. We also found that surface drying during freeze tape casting process was problematic as shown in Figure 1c.



**Figure 1.** (a) Freeze tape cast 7.5 vol.% LLZO slurry. (b) Freeze tape cast 10 vol.% LLZO slurry. (c) Top surface (top) and bottom surface (bottom) of freeze tape cast 10 vol.% LLZO slurry. All images are of green tapes.

The dispersion stability of the LLZO slurry was quite low, such that powder flocculation was observed in 10-20 minutes into casting. The SEM images in Figure 1 are obtained from the initial part of the cast tape. Stability improvement is necessary for a longer cast. pH control approach and other dispersants to replace the currently used Darvan CN were investigated but were unsuccessful at this stage of the project.

PEO based electrolyte and a commercial polymer electrolyte supplied by Fisker were also processed for preliminary testing. These can potentially be used as Li/LLZO interfacial coating material.

#### *Quarter 1 ORNL:*

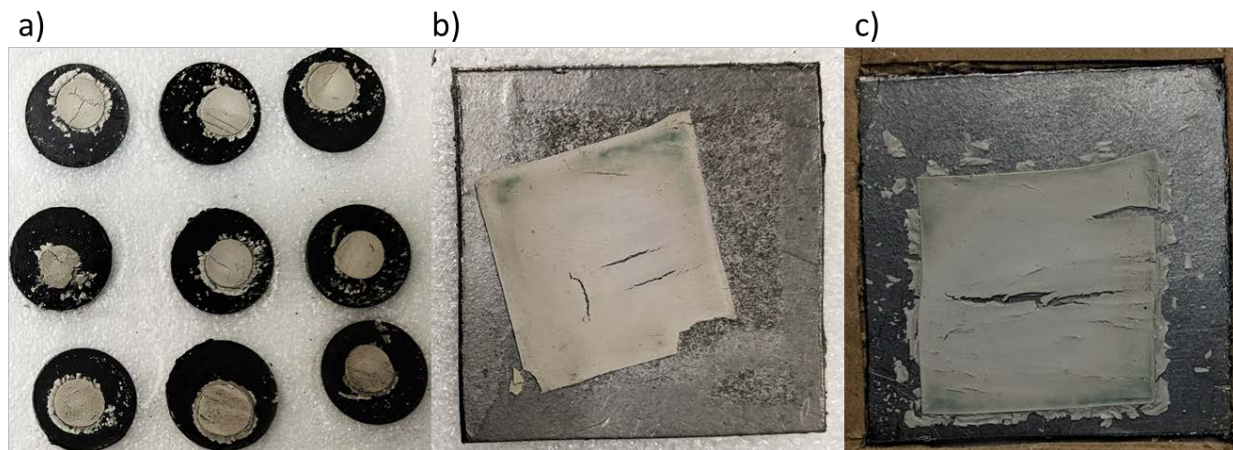
07/20/18: Multiple LLZO bilayers were received from Fisker to assemble and test hybrid (i.e. containing both solid and liquid electrolytes) coin cells and pouch cells at ORNL.

07/20/18-08/31/18: Multiple hybrid coin cells and pouch cells were assembled after infiltrating the bilayers with NMC622 slurry. Performance of the hybrid cells made with regular lithium metal foil and the proprietary thin lithium metal deposited on Cu foil (from AMAT) was compared.

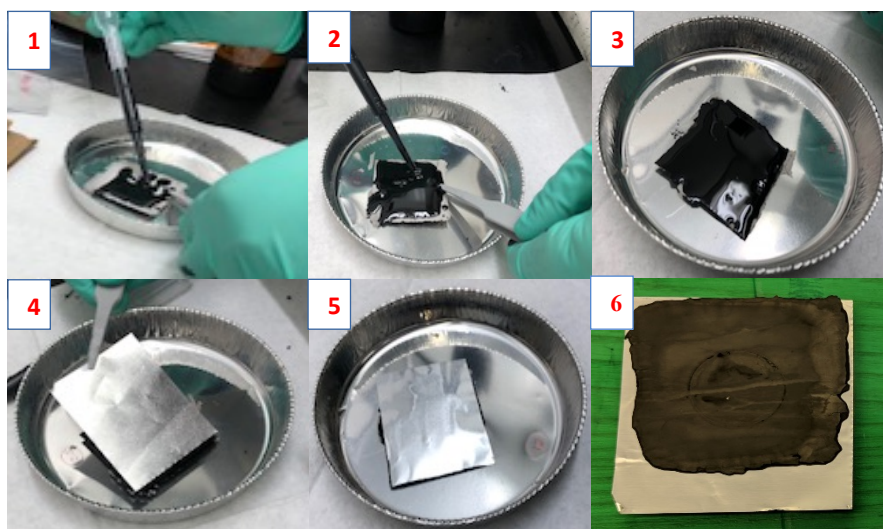
08/07/18: Training and demonstration of the freeze-tape caster at ORNL by Glacigen.

09/13/18: Preliminary recipe of the LLZO slurry for freeze tape casting was transferred from LBNL to ORNL.

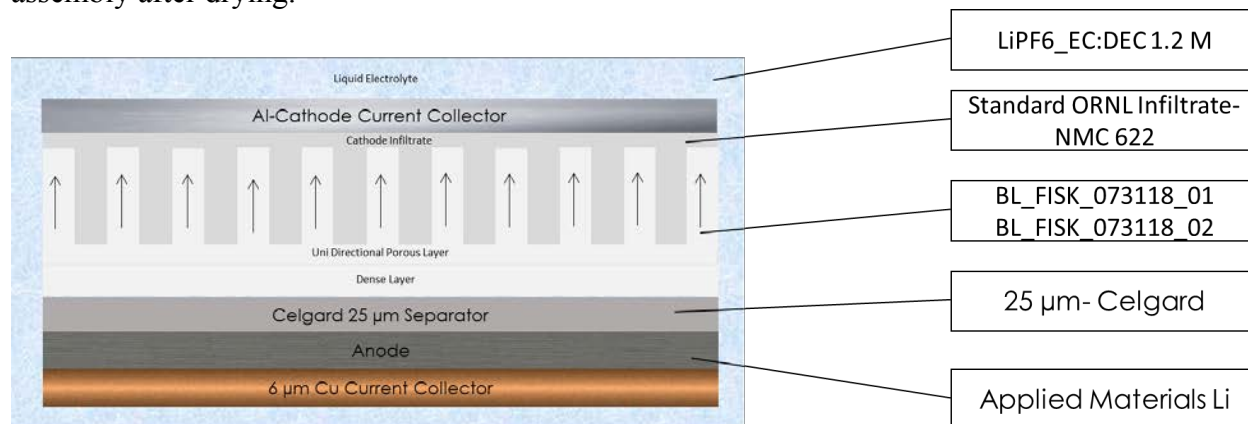
Figure 2 shows photographs of some of the bilayers received from Fisker for hybrid coin cells and pouch cells assembly at ORNL. These scaffolds were infiltrated in our lab with the standard  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC622) cathode slurry via drop casting (Figure 3). Small prototype hybrid pouch cells were assembled using a proprietary lithium thin film from Applied Materials as the anode and the NMC622 infiltrated - porous LLZO scaffold as the cathode. Lithium foil and cathode-LLZO assembly were separated with a Celgard 2325 separator and ~200 mg of liquid electrolyte (1.2 M  $\text{LiPF}_6$  in EC/EMC 3:7 wt.) was added to each hybrid pouch cell. The cell design was provided by Fisker and is shown schematically in Figure 4.



**Figure 2.** Photographs of some of the bilayers received from Fisker for hybrid coin cells and pouch cells assembly at ORNL.

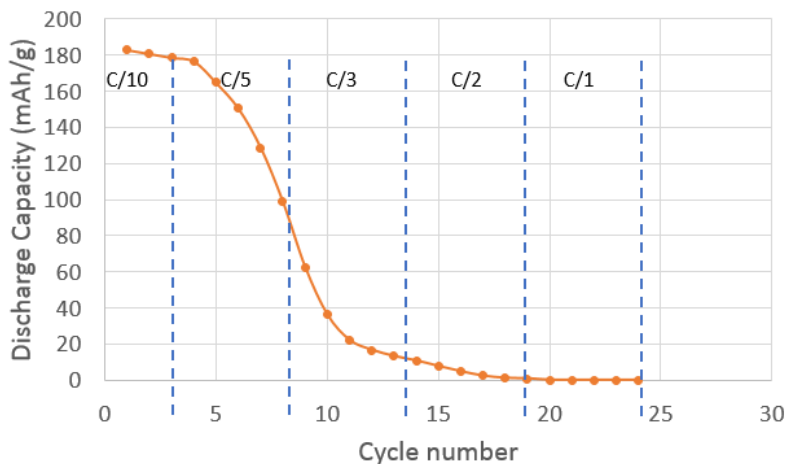


**Figure 3.** Steps 1 to 3 showing cathode slurry infiltration into porous LLZO scaffolds via drop casting. Step 4 & 5 showing attachment of aluminum current collector. Step 6 shows the final assembly after drying.



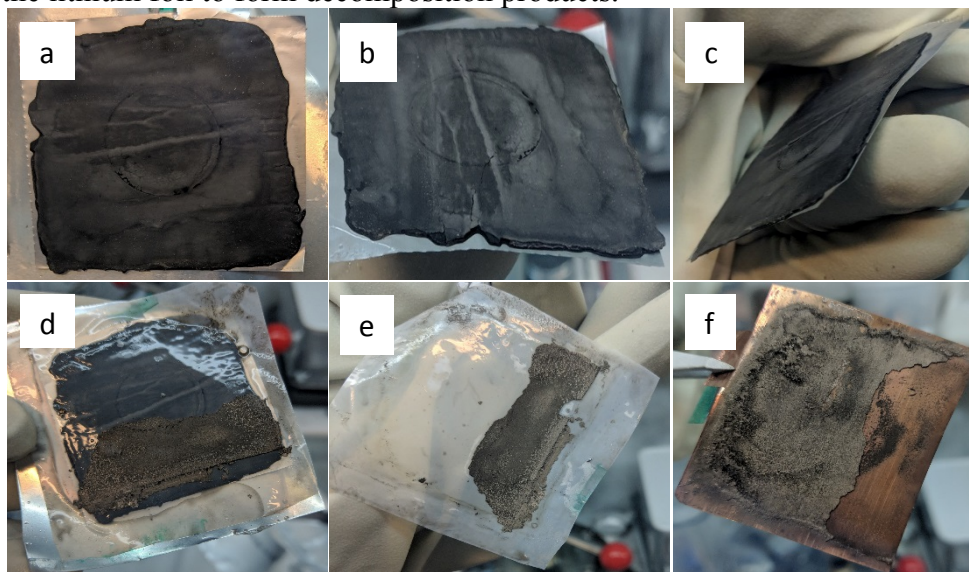
**Figure 4.** Schematic of the hybrid cells made at ORNL.

Figure 5 shows the rate-performance of one of the hybrid pouch cells. The cells were cycled between 2.5-4.35 V with a 2 h hold at the upper cut-off voltage. The cell performed well at the initial low rate cycling (0.1C) to give a specific discharge capacity of  $\sim 180$  mAh g<sup>-1</sup>. However, the capacity declined rapidly as the charge/discharge rates were increased, falling to almost zero at 1C rate. When the cell was cycled again at 0.1C after the 1C cycling, no capacity could be recovered.



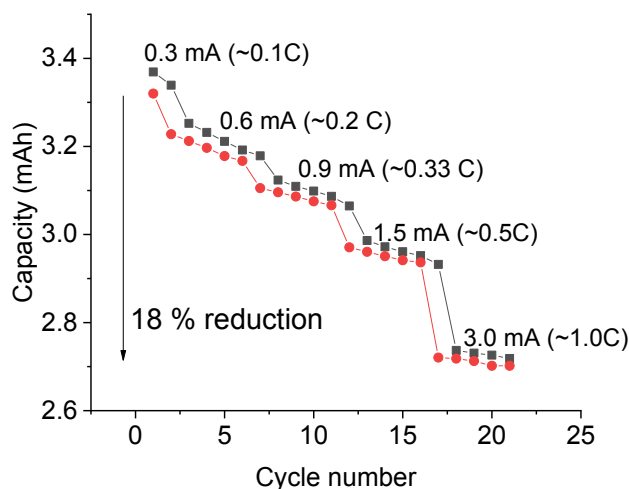
**Figure 5.** Rate performance of a hybrid pouch cell cycled between 2.5 – 4.35 V with a 2 hour hold at upper cut-off voltage.

To test the cause behind this rapid performance decline, the cells were opened, and the components were visually inspected. While the cathode-LLZO assembly showed no apparent degradation such as delamination from aluminum current collector or fracture (Figure 6a-c), the lithium foil showed dramatic color change, delamination from the copper substrate as well as crumbling into smaller pieces (Figure 6d-f). This suggests irreversible consumption of cyclable lithium at the lithium foil to form decomposition products.



**Figure 6.** Photographs of the hybrid pouch cell components after the rate performance test. (a-c) show the cycled cathode-LLZO assembly, and (d-f) show the cycled proprietary lithium foil.

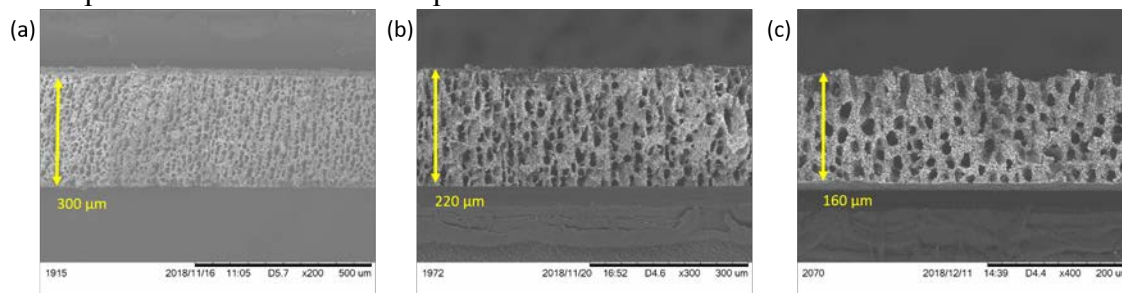
To test this hypothesis, we paired the extracted cathode-LLZO assembly (unrinsed) with regular lithium foil and made hybrid coin cells with fresh liquid electrolyte and Celgard separators. Before assembly, the 4 cm X 4 cm assembly was randomly cut into small pieces using a ceramic scissors so as to fit inside a coin cell. Figure 7 shows the rate performance of one of such cells. In the plot, only absolute cell capacity is presented as it was difficult to estimate the active material loading due to irregular shape of the LLZO-cathode piece. As can be seen, the cell performed significantly better with the discharge capacity reduction of only 18% going from 0.1C to 1C.



**Figure 7.** Rate performance of a coin cell containing a cycled cathode-LLZO piece, paired with a fresh regular lithium metal disc, fresh liquid electrolyte and a Celgard separator. Cell was cycled between 2.5-3.45 V with a 2h hold at upper cut-off voltage.

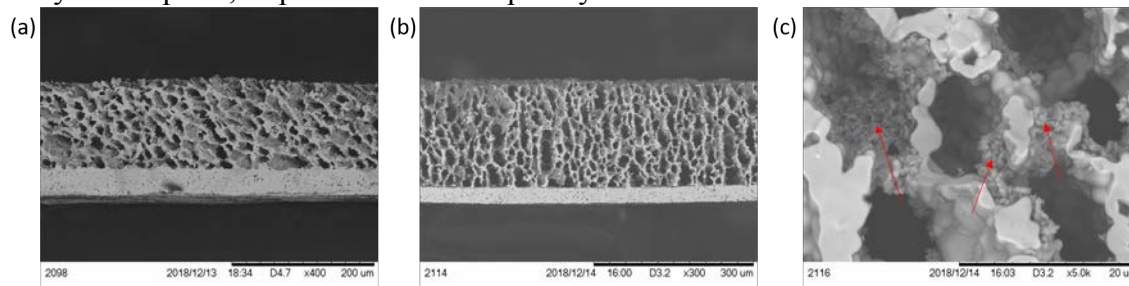
### Q2 LBNL

Through processing variable optimization, freeze tape cast green tapes could be produced at < 200  $\mu\text{m}$ , reaching layer thicknesses suitable for practical application. In order to mitigate the green tape cracking issue during freeze-drying, 10 vol.% LLZO slurries were mainly cast. The slurry stability was improved by introducing a polyacrylic acid dispersant, which allowed the slurry to stay well dispersed throughout the entire casting period. By adjusting the casting speed and the freezing bed temperature, a range of pore sizes could be obtained as shown in Figure 8. Smaller pore sizes result in higher specific surface area, a key factor in mitigating the cathode/electrolyte interfacial impedance. However, optimal usable pore size is dependent on the infiltration process of the cathode components.



**Figure 8.** SEM fracture surface images of freeze tape cast 10 vol.% LLZO slurry produced at various thicknesses and casting speeds. Vertical pore alignment is evident.

Freeze tape cast and tape cast green tapes were stacked and sintered to produce dense/porous bilayers of LLZO as shown in Figure 9a. Cathode components were dispersed in an organic solvent and drop cast onto the porous layer as shown in Figures 9b and c. Red arrows in Figure 9c indicate the infiltrated cathode components. Further optimization for infiltration was necessary at this point, as pores are not completely filled.



**Figure 9.** (a) Sintered dense/porous LLZO bilayer. (b),(c) Cathode component infiltrated bilayer.

### *Q2 ORNL*

10/1/2018: The hybrid cell approach was abandoned because the goal of the project was to produce solid-state cells.

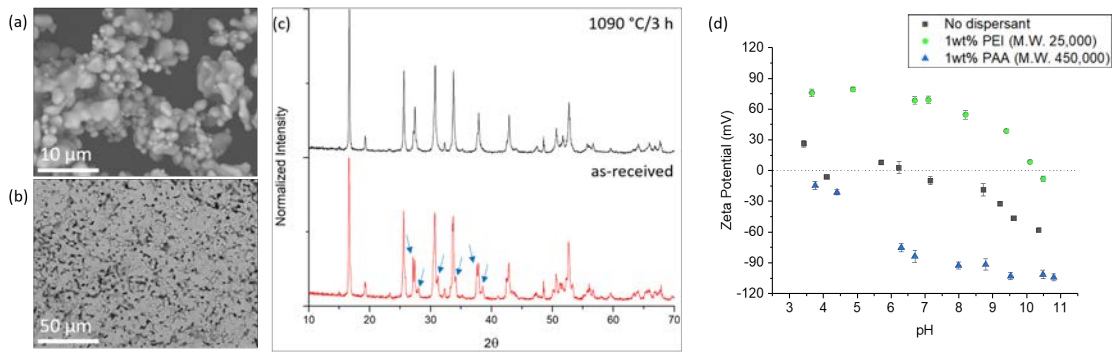
11/05/18: The sputtering unit (Kurt Lesker) to be used for depositing LIPON and lithium metal on LLZO was inspected and repairs/replacements needed on the machine were identified.

Note: Delays were incurred because Participant did not provide commercial LLZO to Contractors 1 or 2, as agreed upon in the SOW.

### *Q3 LBNL*

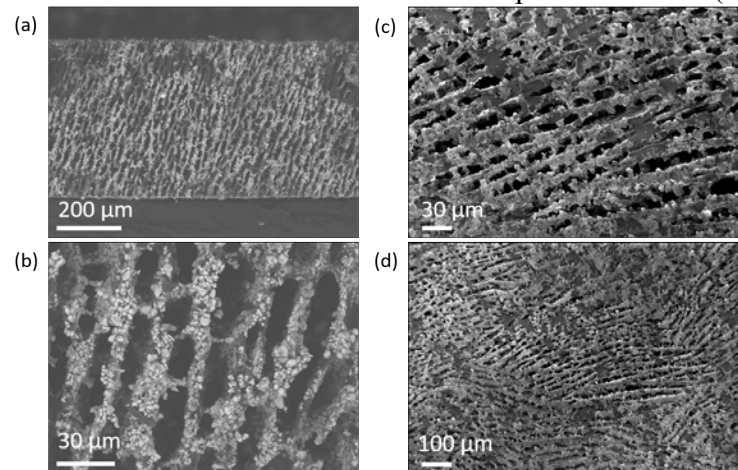
LBNL purchased commercial Al<sup>3+</sup> doped LLZO from NEI for internal use and to send to ORNL for scale-up. NEI is a lower-cost vendor than the original provider (MSE Supplies), and was used due to budgetary concerns. Powder characterization as well as freeze tape-casting experiments followed. As-received powders were several microns in size with majority of them showing necking from calcination (Figure 10a). XRD showed a mixture of cubic and tetragonal LLZO suggesting the powder is Li rich (Figure 10b). It also had a thick (>160 nm) Li<sub>2</sub>CO<sub>3</sub> surface coating layer, as confirmed by XPS, likely due to reaction with atmospheric air. XRD of powder compacts (pellets) heated to 1090 °C/3 h showed smaller t-LLZO peaks, suggesting that c-LLZO can be obtained by blowing off excess lithium while sintering (Figure 10c).

Zeta potentials of the powder were measured in the pH range of 3-11 using two dispersants polyethylenimine (PEI) and polyacrylic acid (PAA) (Figure 10d). The results suggested that PAA would be a good dispersant for slurry formulation as the LLZO slurry is highly basic (pH 14+) due to the protonation of LLZO in water. However, the formulated slurry showed rapid powder flocculation and it was empirically determined that the xanthan gum, the thickener, was affecting surface chemistry of the dispersed LLZO powder.



**Figure 10.** (a),(b),(c) SEM/XRD analyses of as-received LLZO powder and LLZO powder compact (pellet) heated to 1090 °C/3 h. Blue arrows indicate t-LLZO peaks. (d) Zeta potentials of as-received LLZO with selected dispersants at varying pH.

In order to achieve viscosities suitable for freeze tape casting, the LLZO fraction was increased from 10 to 14 vol.% in the slurry. Well-aligned LLZO struts were observed in the fracture surface SEM images of the freeze tape cast green tape (Figure 11a,b). The slurry formulation was transferred to ORNL and initial results showed similar pore structures (Figure 11c, d).



**Figure 11.** Freeze tape cast LLZO green tapes. (a),(b), Fracture surface SEM images of green tapes produced at LBNL. (c),(d), Surface SEM images of green tapes produced at ORNL.

### Q3 ORNL

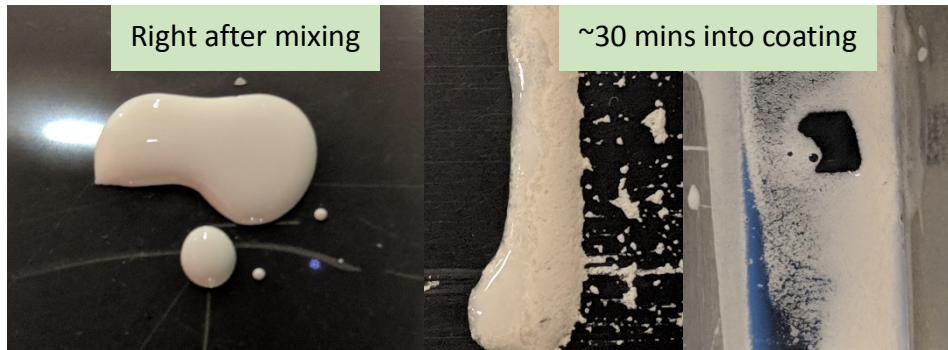
01/18/19: Purchase order for a new chiller for the Kurt Lesker sputtering unit was made. (It was delivered on 04/23/19).

01/31/19: 1.5 kg of commercial LLZO powder purchased by LBNL was received on 01/31/2019. Preliminary LLZO (NEI) slurry formulations were received from LBNL (on 01/13/19 and 03/14/19) and were tried on the ORNL freeze tape caster. Table 1 shows the detailed slurry formulation received on 03/14/19. Slurries at both LBNL and ORNL were made on a small scale (with 4-6 g of LLZO powder) to produce freeze tape cast porous layers which are only two to three inches long. Slurry stability was assessed visually, and the final pore structure obtained was characterized via SEM imaging.

**Table 1.** LLZO slurry recipe for FTC transferred from LBNL to ORNL on 03/14/19.

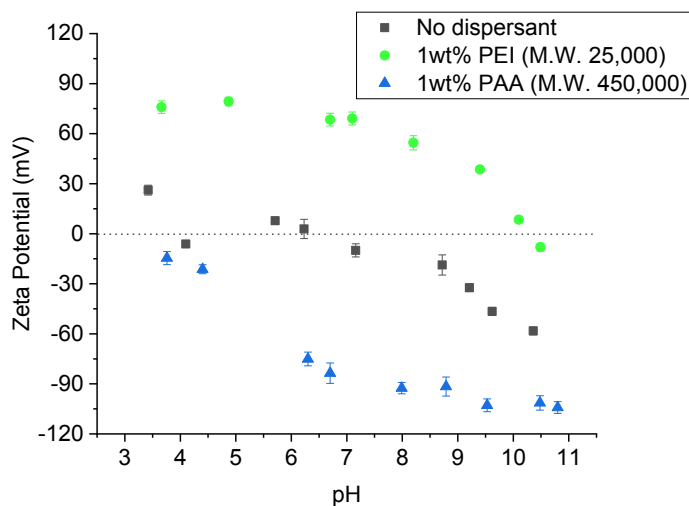
Component	Solids weight (g)	Solution weight if applicable (g)
LLZO (NEI)	6	N.A.
Li <sub>2</sub> CO <sub>3</sub> (20% excess)	0.33	N.A.
PAA450k	0.032	N.A.
HA-12	0.72	1.6
VANZAN (0.2wt%)	0.00545	5.45

As can be seen from Figure 12, the slurry of LLZO showed stability issues. The solids separated from the solvent (water) to form a two-phase mixture within ~30 min after mixing. This is an issue for scaling-up of the freeze tape casting process, as the slurry needs to be stable for several hours, given the slow speed of the freeze tape casting process. A non-homogenous slurry would lead to segregation of LLZO and binder in the final porous layer as well as would affect the final pore structure.



**Figure 12.** Photographs of a LLZO slurry right after mixing (left) and after ~30 mins (right).

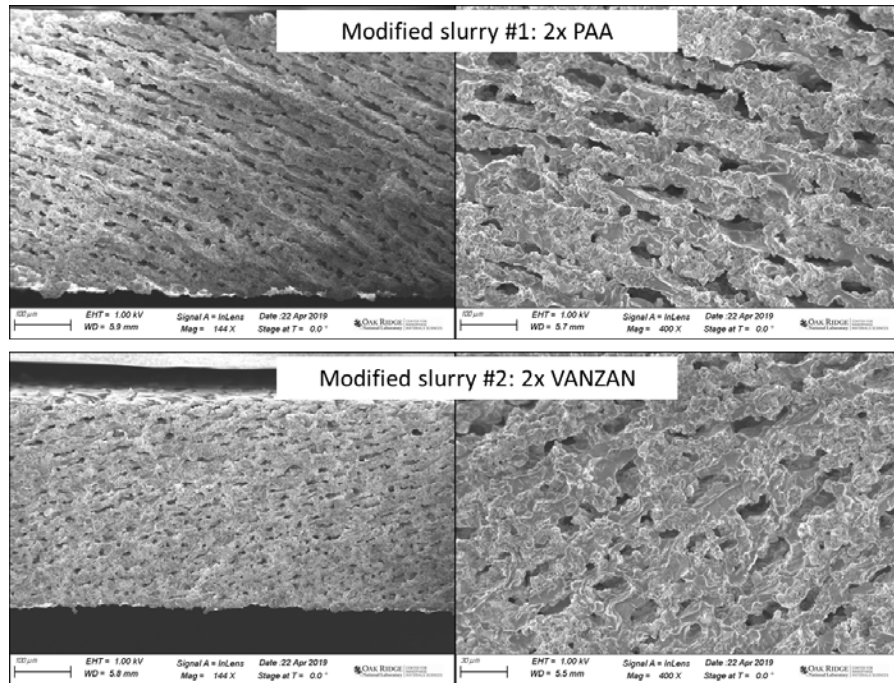
One important characteristic that determines the slurry stability is the surface charge of particles in the dispersion as it provides electrostatic hindrance towards flocculation. To identify a suitable dispersant for the LLZO particles, we measured surface charge of LLZO particles dispersed in water with and without the presence of various dispersants via Zeta Potential measurements (Figure 13) as a function of pH. A cationic dispersant (polyethyleneimine (PEI)), and an anionic dispersant (polyacrylic acid (PAA)) were chosen for the measurements. PAA was also the dispersant in the LBNL slurry recipe. Due to leaching of Li<sup>+</sup>-ions from LLZO when in contact with water, the LLZO slurry is very basic (pH >12). Therefore, a high surface charge at this pH value of 12 would be favorable. As can be seen from the results in Figure 8, PAA would be better than PEI, as the surface charge of LLZO in its presence is < -90 mV. PEI on the other hand would be a better dispersant at a lower pH. These results were communicated to LBNL to help make guided decisions for improving the slurry stability.



**Figure 13.** Zeta potential of LLZO in the presence/absence of dispersants.

Flocculation in a dispersion can also be retarded sterically by increasing the viscosity. High molecular weight PAA (M.W. 450,000) can act both as a dispersant (discussed above) and a thickener. Xanthan gum (VANZAN) is the primary thickener in the formulation (Table 1). In order to improve slurry stability, we modified the recipe in Table 1 in two ways and observed the slurry stability with time visually. In one case, the amount of PAA was doubled, while in the other the amount of VANZAN was doubled, keeping the rest same. In both cases, slurry stability was significantly improved, and no flocculation was observed after 30 mins. Figure 14 shows SEM images of the cross-sections of the FTC porous tapes obtained with the above two slurry modifications.



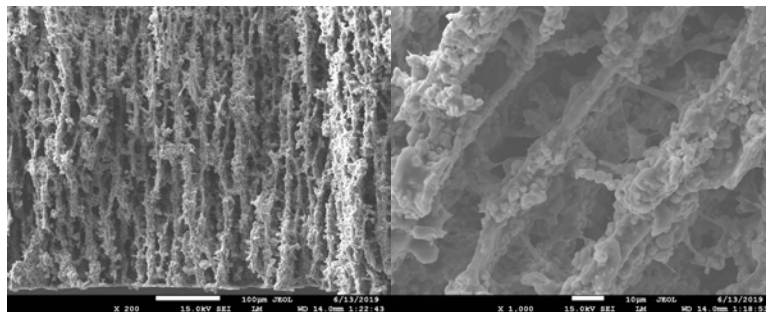


**Figure 14.** SEM images of the cross-sections of the FTC porous tapes obtained with slurries that have either double the amount of PAA (top), or double the amount of VANZAN (both), compared to the original recipe shown in Table 1.

Even though the slurry stability was improved for these cases, the resulting porosity in the freeze-dried tapes was not satisfactory. Pore alignment was not vertical, and pore-size was smaller than what LBNL demonstrated for their recipe, and pore walls were thicker. Ideal case scenario demands vertical pores with almost zero tortuosity and high pore volume with large pores (>20  $\mu\text{m}$ ) for easier cathode infiltration.

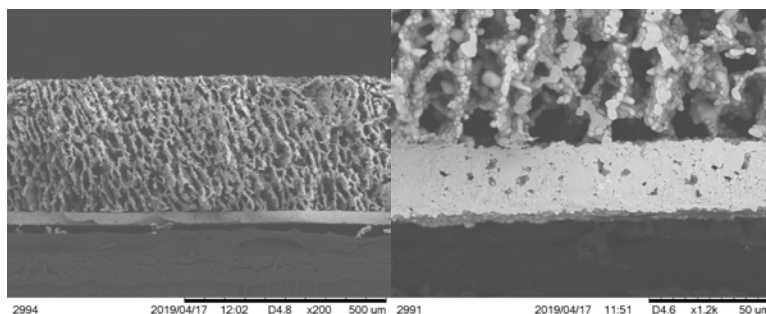
*Q4 LBNL*

Freeze tape casting formulations were further developed using the NEI LLZO powder to achieve improved stability, ice structure, flexibility, and sample uniformity. Acrylic latex emulsion binder with low  $T_g$  (-45  $^{\circ}\text{C}$ ) was introduced to impart flexibility while frozen to prevent sample cracking while freeze-drying. It was possible to freeze tape cast 4'' x 4'' porous LLZO scaffold through slurry viscosity and additive content optimization, which showed good sample uniformity. It is now possible to consistently freeze tape cast LLZO powders from two different vendors.



**Figure 15.** SEM fracture surface images of freeze tape cast NEI LLZO green tape. Vertical pore structures are observed clearly.

Freeze tape cast green tape from above was combined with tape cast green tape provided by Fisker to sinter porous/dense bilayer LLZO architectures. After sintering to 1090 °C/3 h, the two layers are well bonded. The tape cast green tape sintered to high densities with no open pores.



**Figure 16.** SEM fracture surface images of sintered porous/dense LLZO bilayer. The two layers are well connected.

The LBNL postdoc traveled to ORNL to assist with freeze tape casting as there were inconsistencies in the ice structures the two labs were getting. Two postdocs worked side by side along the entire slurry formulation to the freeze tape casting process and were able to reproduce the freeze tape casting results of LBNL at ORNL. Several factors including additive content, mixing method, freeze tape casting parameters were adjusted to fit the ORNL lab condition (e.g. humidity, room temperature, etc.)

#### *Q4 ORNL*

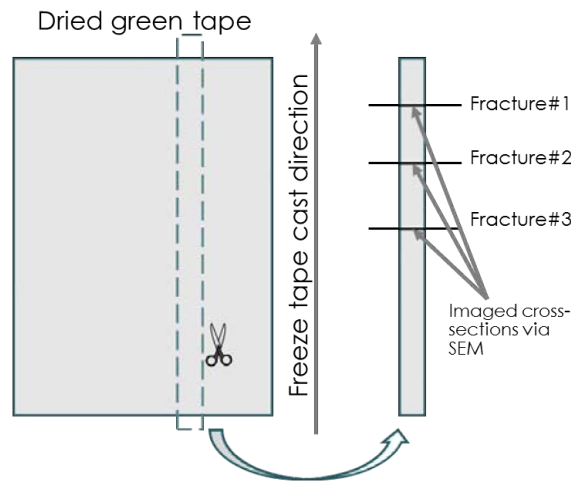
The LBNL postdoc traveled to ORNL to assist with scale-up of freeze tape-casting. The LLZO slurry for freeze tape casting was modified (Table 2) resulting in less flocculation. It also resulted in more flexible freeze-dried green tapes compared to those made from the previous version in Table 1. This slurry recipe is different from the previous version of the recipe in the following aspects: 1) a higher Li<sub>2</sub>CO<sub>3</sub> content (30% excess vs. 20% excess earlier), 2) use of a different emulsion binder (Rovene 97982) in combination with the previously used HA-12 emulsion binder (60:40 ratio), and 3) double the amount of PAA and VANZAN. Rovene 97982 is a soft acrylic emulsion known for its flexibility. Improvement in the slurry stability by doubling the amounts of PAA and VANZAN was observed at ORNL as well (discussed in the previous section). Indeed, during freeze tape casting no visible flocculation was observed for 30-60 mins. Overall, several differences were noted in the way of mixing the slurry components as well as seemingly insignificant things during the casting step, which likely resulted in the inconsistency in the final porous tape structure obtained at LBNL versus at ORNL for the same slurry recipe. Two freeze tape casting runs were performed for the slurry in Table 2 but at different freezing temperatures and line speed.

**Table 2.** LLZO (NEI) slurry recipe for FTC transferred from LBNL to ORNL on 06/13/19.

Component	Solids weight (g)	Solution weight if applicable (g)
LLZO (NEI)	6	N.A.
Li <sub>2</sub> CO <sub>3</sub> (30% excess)	0.495	N.A.
PAA450k	0.065	N.A.
HA-12	0.36	0.96
Rovene 97982	0.36	0.64
VANZAN (0.2wt%)	0.011	5.5

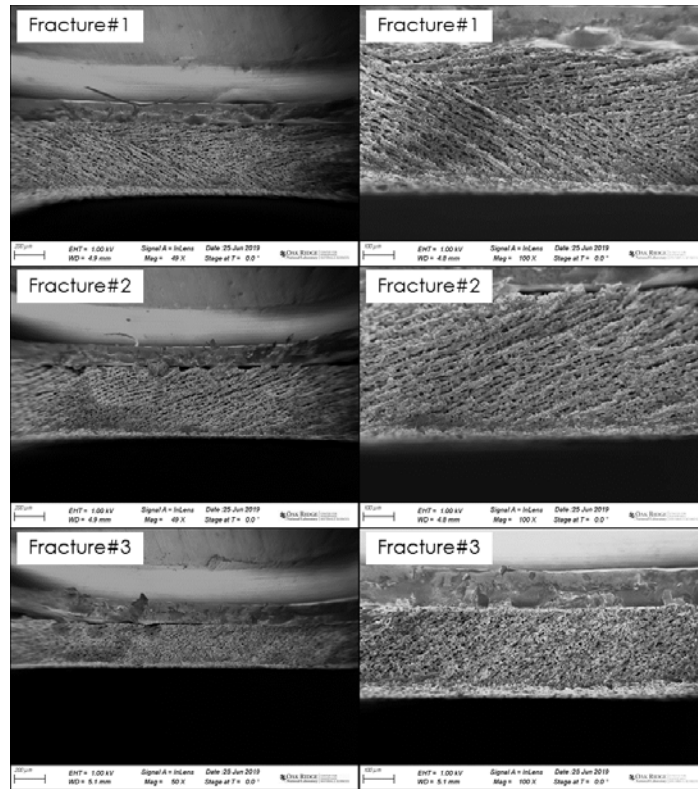
Run#1: FTC done at 20% speed and -13 °C freezing bed temperature.

Figure 17 schematically shows the areas that were characterized via SEM. A thin strip parallel to the FTC direction was cut from the middle of the dried tape. The tape was fractured by bending at three locations, each one further from the front edge of the tape. This was done to assess the areal uniformity of the porosity. It is typically expected that the area further from the front edge would have much less developed porosity as it would be freeze cast later compared to the area closer to the front due to slurry stability/drying issues.



**Figure 17.** Schematic showing the areas of the tape that were characterized via SEM.

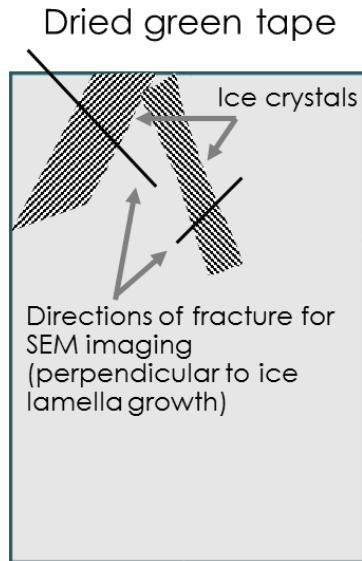
Figure 18 shows the SEM of the three cross-section areas at 50x and 100x magnifications. Porosity can be seen throughout the width of the tape. Pores appear to be oriented somewhat off from normal, but may be an artifact of sample preparation for the SEM imaging. To see perfectly vertical columnar walls, the fracture should be perpendicular to the lamellar growth. Ideally, the ice lamellar growth should occur in the FTC direction, however for a variety of reasons ice growth occurs in random directions throughout the tape.



**Figure 18.** SEM of the cross-sections from three different areas of the LLZO FTC green tape obtained with run #1.

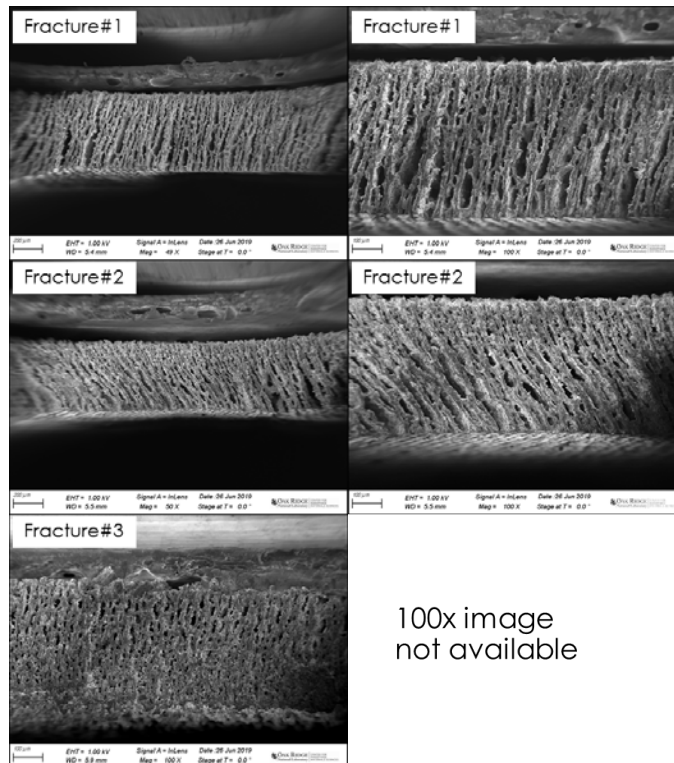
Run#2: FTC done at 15% speed and -11 °C freezing bed temperature.

The slurry recipe in Table 2 was used. FTC conditions were changed to have higher freezing bed temperature (-11 °C v. -13 °C) and slower line speed (15% vs. 20%). The higher temperature was used to increase the size of the ice crystals and obtain larger pores. For SEM imaging, sample was fractured in the direction perpendicular to the ice lamella growth to observe the columnar structure. This is shown schematically in figure 19.



**Figure 19.** Schematic highlighting the difference in the way the run #2 tape was fractured for SEM imaging the cross-sections compared to run #1 tape (schematically shown in Figure 9).

Three such perpendicular fractures were made, and the obtained cross-sections were imaged via SEM (Figure 20). As can be seen, the vertical columnar structure can be observed in some areas. However, the areal uniformity of such porosity still needs to be greatly improved. The fracture#3, for example, does not have a similar columnar porosity as the others.



**Figure 20.** SEM of the cross-sections from three different areas of the LLZO FTC green tape obtained with run #2.

Application of lithium metal anode on LLZO dense layers using the sputtering unit (Kurt Lesker) at ORNL

Due to unanticipated delays in bringing the Kurt Lesker sputtering unit to operational status, these studies could not be performed.

### **Summary**

In spite of the fact that not all the milestones were achieved for this project, due to technical difficulties and difficulties acquiring materials needed for the project, considerable progress was made towards the goals. A main goal was to understand how to scale-up the freeze tape cast process for fabrication of LLZO scaffolds, the first step in making solid-state cells with thick composite electrodes. One of the contractors will present results at an upcoming Electrochemical Society meeting, and publications are under consideration.