Composite Cathode Architectures
Made by Freeze-Casting for All Solid-State Lithium Batteries

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Lawrence Berkeley National Laboratory
June 21-25th, 2021

Project ID: BAT506

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Overview

Timeline
• Project start date: April 1, 2019
• Project end date: March 31, 2021
• Percent complete: 100%

Barriers and Technical Targets
• Barriers addressed
  – Energy Density
  – Cost

Budget
• Total project funding: $667k
  – DOE share: $600k
  – Contractor share: $67k
• Funding for FY 2020: $333.5k
• Funding for FY 2021: $166.75k

Partners
• Montana State University
• Mercedes-Benz Research & Development, North America (MBRDNA)
• Project lead: LBNL
Impact
Solid-state-batteries using oxide solid electrolytes promise higher energy density with superior safety. We aim to construct solid-state-batteries with thick composite cathodes paired with lithium metal anodes. The architecture of the developed composite cathode may also provide superior rate performance and low temperature operation compared to lithium-ion batteries.

Objectives
- Produce/characterize Al:Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) porous scaffolds through freeze-tape-casting (FTC).
- Build thick composite cathodes by infiltrating conductor and high energy density cathode materials into the porous scaffolds.
- Construct solid-state-batteries by combining composite cathodes with a dense LLZO layer and a lithium anode.
- Determine processing parameters needed to reach 500 Wh/kg.
<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Description</th>
<th>Owner</th>
<th>Status</th>
</tr>
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<tbody>
<tr>
<td>Dec. 2019</td>
<td>Build bilayer structures for cells, study sintering of bi-layers to achieve full cubic-LLZO phase.</td>
<td>LBNL/MSU</td>
<td>Complete</td>
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<tr>
<td>Mar. 2020</td>
<td>Assemble small cells and test</td>
<td>LBNL</td>
<td>Complete</td>
</tr>
<tr>
<td>Jun. 2020</td>
<td>Vary porosity and morphology in scaffolds and study effects</td>
<td>LBNL/MSU</td>
<td>Complete</td>
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<tr>
<td>Sep. 2020</td>
<td>Optimize infiltration process</td>
<td>LBNL/MSU</td>
<td>Complete</td>
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<tr>
<td>Dec. 2020</td>
<td>Build trilayer structures for cells - stop if infiltration with anode material is too difficult or energy density is too low (go/no-go)</td>
<td>LBNL/MSU</td>
<td>No-go, energy density considerations</td>
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<tr>
<td>Mar. 2021</td>
<td>Assemble small cells from optimized components and test</td>
<td>MBRDNA</td>
<td>On-schedule*</td>
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</tbody>
</table>

* MBRDNA is continuing testing to fulfill cost-share requirements
Approach

- Construct thick composite cathodes by freeze-tape-casting and sintering of LLZO.
- The high porosity scaffolds with directional and continuous pore channels serve as an ideal host for cathode/anode components and aid infiltration during assembly.
- Construct porous/dense bi-layers and porous/dense/porous tri-layers of LLZO.
- Investigate scaffold porosity/pore morphology effect on battery performance.

**Goal:** Achieve high energy density oxide electrolyte based solid-state-batteries using lithium metal anode / high capacity cathode.
Freeze tape cast LLZO scaffold infiltrated with cathode active material, carbon, and organic ionic plastic crystal to make a composite cathode.

<table>
<thead>
<tr>
<th>Capacity/mA.h/g</th>
<th>E vs. V</th>
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<tr>
<td>100</td>
<td>4.4</td>
</tr>
<tr>
<td>50</td>
<td>4.2</td>
</tr>
<tr>
<td>0</td>
<td>4.0</td>
</tr>
<tr>
<td>3.8</td>
<td>3.6</td>
</tr>
<tr>
<td>3.4</td>
<td>3.2</td>
</tr>
<tr>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td>2.6</td>
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</tbody>
</table>

As-assembled coin-cell PEIS

Freestanding tape-cast LLZO dense layer

Technical Accomplishments and Progress

Optimization of porous LLZO layers

MSU work was directed towards optimizing FTC processing. By changing binder, it is now possible to cast large pieces of thinner (~100 µm) LLZO porous layers using 10-15 vol% solids in the slurry. Thinner, highly porous, scaffolds are needed for higher energy density. A bilayer made using the new method is shown at right.
Technical Accomplishments and Progress
Optimization of porous LLZO layers

- Li ions in solution destabilize the slurry during freeze casting. This presents a challenge for dispersing LLZO and casting consistency.
- This presents as increased strut bridging (left)-solid regions that interrupt the long-range columnar porosity through the thickness.
- While this makes infiltration of particulates more difficult, it also allows fabrication of very high porosity (>90%) self-supported LLZO structures, needed for high energy density.
Technical Accomplishments and Progress

Optimization of porous LLZO layers and processing

Bilayers with porous layers made from slurries containing a) 10 vol. % LLZO, b) 7.5% LLZO, and c) 5% LLZO.

(a) LLZO with 200 nm ZnO coating. (b) Seamless Li/LLZO interface aided by ZnO coating layer. (c) Porous LLZO coating layer (<10 µm) on dense LLZO.

Higher porosity scaffolds are desirable to maximize energy density. To improve wetting of lithium onto LLZO, ZnO was coated onto a dense LLZO surface using a simple sol-gel process. Previously, gold was sputtered onto LLZO to ensure good contact with lithium metal. This works well, but is not practical except in the laboratory.
Trilayer made with 2 FTC layers. The anolyte needs to be made much thinner to avoid energy density penalties. This is difficult to carry out with FTC.

Drop casting LLZO onto a sintered bilayer (dense+ FTC layer) results in a thinner layer for the anolyte. Fracture surface micrographs of a porous/dense/porous (180/30/30µm) trilayer are shown. Top porous layer (catholyte) is freeze-tape-cast whereas the bottom porous layer (anolyte) is drop-cast.

Tomographic image and pore analysis of porous/dense bilayer. Dense layer was formed by aerosol spraying. Pores taper from 11-16 mm.

A no-go decision was made on the trilayer approach due to the added processing complexity and energy density penalty.
Technical Accomplishments and Progress

**cell troubleshooting**

- Cells contain no liquid of any sort
- No external pressure other than from coin cell components
- Room temperature operation
- No co-sintering-avoids high temperature reactions between components
- **HOWEVER**, Many cells fail prematurely or show low capacity/poor cycling
  - All interfaces needs to be assessed
- Many trouble shooting experiments carried out to find sources of the problem (example below)

Additional cathode slurry placed on top of scaffold to improve adhesion between cathode and current collector. This lowers cell impedance. Cell cycles, but capacity is lower than expected and fading occurs. One problem is that polycrystalline NMC needs to be ground so that it can be infiltrated, causing degradation. Other pain points may be possible deleterious interactions between LLZO and succinonitrile (SN, organic ionic plastic crystal) electrolyte as well as other interfaces.

C/10 cycling
Technical Accomplishments and Progress

cell troubleshooting, continued

Original cell build procedure

- Sinter bilayer
- Deposit Au on dense layer
- Vacuum infiltrate cathode slurry
- Melt bond lithium
- Melt infiltrate SN electrolyte
- Assemble coin cell

Troubleshooting configuration

- Sinter bilayer
- Deposit Au on dense layer
- Melt bond lithium
- Melt infiltrate SN electrolyte
- Place tape cast electrode infiltrated with SN on top
- Assemble coin cell

LLZO surface degraded by carrier solvent? Reaction between LLZO and SN?

Fill scaffold pores only with SN to see if reactivity is a problem or if it is the carrier solvent.
Technical Accomplishments and Progress

original procedure, using DMC as carrier solvent

- Many carrier solvents tried
- Rigorous air exclusion
- Many cell failures
- Water in solvents a problem or direct reactivity with LLZO (see Gupta et al. J. Power Sources, 474 (2020): 228598
- DMC works, but cathode materials not well-dispersed.
- Poor dispersion may be responsible for high initial impedance, lower than expected initial capacity
- Still see capacity fading
Better results in troubleshooting configuration suggests reactivity between SN and LLZO is less important than issues with carrier solvent.

LLZO needs to be protected from contact with most carrier solvents.

**C/10 cycling**
Technical Accomplishments and Progress

troubleshooting configuration with NMC-811

- Better results with troubleshooting configuration extends to NMC-811 cathodes.
- Not yet clear what gives rise to inefficiency and capacity fading
MBRDNA cell testing in troubleshooting configuration

C/20, NMC-811

Rate data

C/2/2 cycling

MBRDNA received cells from LBNL and was able to reproduce results and carry out testing. Initial cycling is good, but fading is evident over time (impedance rise occurs). Reasons for this are not yet clear. Rate may be limited by planar lithium electrode. MBRDNA will continue testing using components from MSU to complete cost-share requirement.
Responses to Previous Year Reviewers’ Comments

- “The approach for fabricating a porous electrode with connected channels using freeze-tape casting is very innovative for solid-state LLZO Li batteries. However, the reviewer stated that how to reduce the interface resistance between LLZO and the cathode active materials, especially after cycles, still needs to be addressed.”
  - We thank the reviewer for the positive comments, and agree that the cathode/LLZO interface is a major contributor to overall cell impedance. Some work this year was directed towards understanding its origins.

- “A porous LLZO layer with controlled pores was fabricated on a dense LLZO layer. The reviewer noted that it is still hard to fill all the pores with solid active materials. The contact between LLZO and active materials are hard to maintain during cycles. The cycle life and energy density of the cell still need to be addressed.”
  - Troubleshooting was carried out extensively this year to understand the challenges of this system. MBRDNA was able to reproduce LBNL’s results.

- Optimization of the pore size and cathode particle size can increase the overall loading. The reviewer wondered if a theory and modeling effort can help to determine the pore size, geometry, and volume fraction of the active material, etc.
  - We hope to incorporate a modeling effort in follow-up work, as well as to use single crystal NMC, if it possible to obtain it.
Collaboration and Coordination with Other Institutions

<table>
<thead>
<tr>
<th>Collaborator</th>
<th>Role</th>
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<tbody>
<tr>
<td><strong>Montana State University (Stephen Sofie)</strong></td>
<td>Freeze-tape-casting processing parameter screening/optimization. Collaborate on overall ceramic processing and cell build activities.</td>
</tr>
<tr>
<td><strong>Mercedes Benz R&amp;D North America (Tobias Glossmann)</strong></td>
<td>Overall battery testing including industry protocols.</td>
</tr>
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</table>
At present, infiltration is the biggest challenge. Deleterious interactions between many carrier solvents and LLZO presented unexpected problems. In some cases, this may be addressed by rigorous drying of solvents (adventitious water may degrade LLZO), but in other cases, direct reaction between solvent and LLZO is the issue.

Reasons for capacity fade and coulombic inefficiencies during cycling are not yet clear and could arise from many causes. More trouble shooting is needed.

Rate capability is somewhat limited, most likely by the planar lithium electrode.
Proposed Future Research

- Project officially ended on 3/31/2021.
- MSU will continue to provide components to MBRDNA so that they can continue testing as part of the cost share agreement.
- We are looking for opportunities to continue this work. We made a lot of progress during the course of this project, but uncovered many challenges that need to be addressed.
Summary

• To the best of our knowledge, these are the ONLY examples of truly solid state batteries using LLZO in a practical form factor operating at room temperature. NO co-sintering, NO external pressure applied, NO liquids, NO heating

• Many challenges revealed by this study
  – LLZO is sensitive to water, reactivity with carrier solvents revealed
  – Infiltration is more difficult than anticipated due to these factors
  – Source of capacity fading, inefficiencies not yet clear, many possibilities
  – Rate capability is probably limited by anode at present

• Troubleshooting configuration is not practical in the real world
  – A simple alternative is a composite electrode containing SN electrolyte cast on a dense LLZO layer, but structure will be fragile, and we lose advantages of low tortuosity
  – Original configuration is still attractive, but we need to find a way to protect LLZO from carrier solvent
    • Consider cathodes that can be melt-infiltrated (sulfur)
    • Protect LLZO with, e.g., ALD coating of h-BN (see Rajendran et al. Chem. Mater. https://doi.org/10.1021/acs.chemmater.1c00747)
Publications and Presentations


- “All-Solid-State Batteries using Li$_7$La$_3$Zr$_2$O$_{12}$ Garnet Electrolyte Framework” Marca M. Doeff and Eongyu Yi Virtual PRIME meeting 2020, Oct 4-9, 2020 (invited).