Cooperative Research and Development Agreement (CRADA) Final Report

Report Date:
Dec. 13, 2022

In accordance with Requirements set forth in the terms of the CRADA, this document is the CRADA Final Report, including a list of Subject Inventions. It is to be forwarded to the DOE Office of Scientific and Technical Information upon completion or termination of the CRADA, as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Mercedes Benz R&D North America, Inc and Lawrence Berkeley National Laboratory

CRADA number: FP00009062

CRADA Title: Composite Cathode Architectures Made By Freeze-Casting for All Solid State Lithium Batteries

Responsible Technical Contact at Berkeley Lab: Marca Doeff

Name and Email Address of POC at Partner Company(ies):
Tobias Glossmann (tobias.glossmann@mercedes-benz.com)
Sponsoring DOE Program Office(s):
Office of Vehicle Technologies
LBNL Report Number:
LBNL-2001496
OSTI Number:
[SPO to complete]

Joint Work Statement Funding Table showing DOE funding commitment:

DOE Funding to LBNL	$68,372
Participant Funding to LBNL	-
Participant In-Kind Contribution Value	$67,780
Total of all Contributions	$136,152

Provide a list of publications, conference papers, or other public releases of results, developed under this CRADA:

"All-Solid-State Batteries Using Rationally Designed Garnet Electrolyte Frameworks" E. Yi, H. Shen, S. Heywood, J. Alvarado, D. Parkinson, G. Chen, S. W. Sofie, and M. M. Doeff **ACS Applied Energy Materials**, DOI: 10.1021/acsaem.9b02101 (2020).

"A Perspective on Solid-State Batteries with LLZO" Keynote address to the 23rd International Conference on Solid State Ionics, Boston MA July 17-22, 2022.

“A Brief Introduction to Freeze Tape Casting for Solid-State Battery Applications” Manufacturing of Energy Storage Fridays, sponsored by the U. S. Department of Energy Energy Storage Grand Challenge Manufacturing and Supply Chain Subgroup, May 13, 2022.

“Solid State Batteries based on Garnet Architectures” 3rd World Conference on Solid Electrolytes for Advanced Applications: Garnets and Competitors, Virtual Meeting, Oct. 25-26th, 2021.

“Controlled Electrode Architectures for Optimized Battery Performance” 240th meeting of the Electrochemical Society, virtual meeting, Oct. 10-14, 2021.

Provide a detailed list of all subject inventions, to include patent applications, copyrights, and trademarks:
(Patents and patent applications are to include the title and inventor(s) names. When copyright is asserted, the Government license should be included on the cover page of the Final Report)
[PI to complete]

1) “Solid State Batteries Using Architecturally Controlled Rigid and Soft Solid Electrolytes” Eongyu Yi, Marca M. Doeff, Guoying Chen, Stephen Sofie, U.S. Patent Application Serial No. 62/936,737 Nov. 18, 2019.

Executive Summary of CRADA Work:

As part of a Battery 500 seedling project, MBRDNA partnered with LBNL and Montana State University (MSU) to develop solid-state batteries based on an Al-substituted LLZO ($Li_7La_3Zr_2O_{12}$) ceramic ion-conductor. All solid-state lithium batteries are attractive contenders for use as power sources for electric vehicles because of their potential for better safety and higher energy density than state-of-the-art lithium-ion batteries, although they are still at early stages of development. Al-substituted LLZO is one of the most promising solid electrolytes for battery applications based on high ionic conductivity, a wide operating voltage window, and apparent stability vs. reduction by lithium. However, difficulties with processing thin (< 20 um and dense LLZO membranes have hampered development of devices based on this material. It is non-compressible and must be sintered at high temperatures to densify components. It is also difficult to maintain contact between the active cathode material and LLZO in the composite cathodes, which is critical for successful operation. This research project aimed to use novel processing methods to overcome these issues. The end result was the first ever-reported truly all-solid-state battery based on LLZO operating at room temperature without application of exogenous pressure. During the course of the project, we also identified a number of issues that need to be addressed to improve the technology readiness level of this battery.

The procedure is to fabricate a porous LLZO ceramic scaffold using freeze-tape casting methods and co-sinter it with a tape cast thin dense LLZO layer to make a bilayer. A cathode material (either $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ or $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$, hereafter abbreviated NMC-622 or NMC-811), carbon, polyvinylidene fluoride (PVdF) and a secondary solid electrolyte based on succinonitrile complexed with lithium salts is then infiltrated into the porous layer, and lithium metal is attached to the opposite side to form the cell. A number of trouble-shooting configurations that were variants of this procedure were also assembled and tested at LBNL.

MSU used their expertise in freeze tape casting to optimize the scaffold-making process, and LBNL developed cell making procedures and used advanced diagnostics such as synchrotron micro-tomography to understand the materials properties. MBRDNA assembled cells from components provided to them by either LBNL or MSU and tested them electrochemically. In some cases, already-assembled coin cells were provided to MBRDNA by LBNL. Tests carried out at MBRDNA included impedance spectroscopy, initial charge and discharge, rate capability tests, and extended cycling, all at room temperature. Some cells were de-crimped and subjected to post-mortem analysis after cycling. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) and optical imaging were carried out on the de-crimped cells. MBRDNA provided this data to LBNL. Quarterly reports were submitted to DOE summarizing these efforts and results.

Summary of Research Results:

Figure 1 shows images of solid-state cell components made using the concepts listed above. Also shown is impedance data and several cycles of a Li/LLZO/NMC-622 cell.

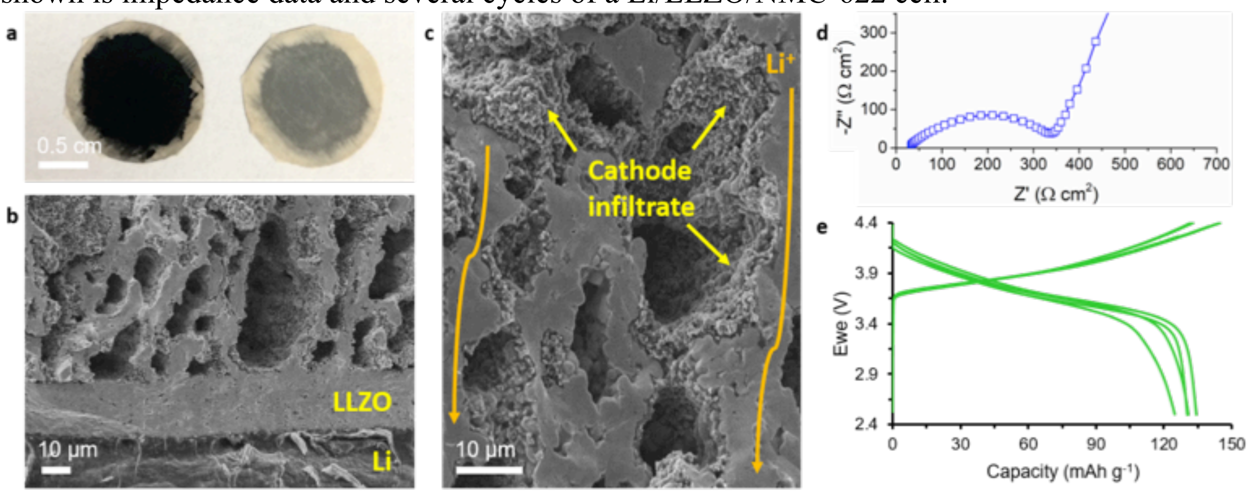

Figure 1. (a) optical images of front and back sides of infiltrated bilayer. (b) SEM image of the cell showing porous scaffold, dense layer, and lithium electrode. (c) SEM image of infiltrated scaffold. (d) Nyquist plot showing cell impedance, and (e) four cycles of a Li/LLZO/NMC-622 cell made at LBNL. Testing was carried out at room temperature with no added pressure or liquids. Modified from reference 1.

MBRDNA was able to verify LBNL's results on solid-state cells (Figure 2) using NMC-811. Extended cycling and rate capability testing at MBRDNA revealed performance limitations. Capacities fell to 60% of the initial value by the 50th cycle. Rate capability was modest, with substantially reduced practical capacities above C/5 rate. Furthermore, active material loadings for these cells were low; it is obvious from the image in Figure 1c that the pores were not completely filled. One unexpected issue that was identified in this project was difficulty infiltrating the scaffolds due to reactivity of LLZO with carrier solvents (a number of trouble-

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1. All-Solid-State Batteries Using Rationally Designed Garnet Electrolyte Frameworks" E. Yi, H. Shen, S. Heywood, J. Alvarado, D. Parkinson, G. Chen, S. W. Sofie, and M. M. Doeff **ACS Applied Energy Materials**, DOI: 10.1021/acsaem.9b02101 (2020).

shooting configurations were carried out to understand this effect). This caused high cell impedance, to the extent that many cells failed.

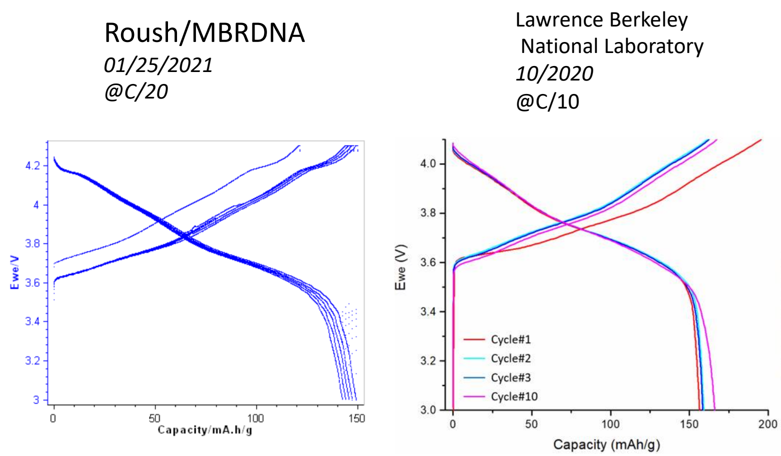

Figure 2. Initial cycles of solid-state cells tested by MBRDNA (left) and LBNL (right). The MBRDNA cell contained NMC-811 as the cathode material, while the LBNL cell contained NMC-622. Both cells contained a succinonitrile-LiTFSI/LiBOB catholyte and were tested at room temperature and ambient pressure.

Post-mortem analysis of a cycled cell, carried out by MBRDNA revealed that the structure of the bilayer remained intact and lithium remained attached to the dense layer. Thus, mechanical failure or detachment of lithium are not the causes of the capacity fading. It is possible, however, that disconnection of active material from either the secondary electrolyte or the LLZO is a contributing factor. More work needs to be done to understand the factors that contribute to the cycling behavior. The rate capability limitations can be addressed by increasing the contact area between the lithium and the dense layer so that the effective current density is lowered. This can be done, for example, by using a porous layer on the anode side that is infiltrated by lithium. To maximize the energy density, this porous layer needs to contain as little LLZO as possible and only a slight excess of lithium (in other words, it should be very thin and very porous). In all likelihood, a different method of fabricating porous LLZO needs to be used for this layer, as it is difficult to make very thin (<100 um) LLZO porous layers. Future work will be directed towards improving infiltration, and optimizing the scaffold-making process for both the cathode and the anode side.

APPENDIX A (Reference Only)

This appendix has been developed by DOE to assist DOE Labs in drafting the ***Executive Summary*** *and* ***Summary of Research Results*** *sections of the CRADA Final Report.*

Executive Summary of CRADA Work:

Include a discussion of 1) how the research adds to the understanding of the area investigated; 2) the technical -effectiveness of the materials, methods or techniques investigated or demonstrated, and their economic feasibility, if known; and 3) how the project is otherwise of *benefit to the public. The discussion should be a minimum of one paragraph and written in terms understandable by an educated layman.*

Summary of Research Results:

- *INCLUDE, IF APPLICABLE: "This product contains Protected CRADA Information, which was produced on [DATE] under CRADA No. [##-####] and is not to be further disclosed for a period of [up to and not to exceed] five (5) years from the date it was produced except as expressly provided for in the CRADA."*
- *Summarize project activities for the entire period of performance, including original hypotheses, approaches used, problems encountered, any departure from planned methodology, and an assessment of their impact on the project results. Incorporate technical data, e.g. facts, figures, analyses, and assumptions used during the life of the project to support the technical conclusions of the work. It is acceptable to incorporate the technical data by reference to other publicly available sources, such as a publications or other reports, but not websites. Provide a comparison of the actual accomplishments with the goals and objectives of the project. Where possible, the summary should cover each task listed in the Statement of Work (SOW) and should note any deviations from the project plan, or lack of technical data.*
- *Identify products, potential applications, and technology transfer activities developed under the CRADA, including those completed and anticipated at the time of the report. These include, but are not limited to: 1) networks or collaborations fostered; 2) technologies/techniques/methodologies; 3) other products that reflect the results of the project, such as commercial products, internet sites, data or databases, physical collections, audio or video, software, models, educational aid or curricula, and instruments or equipment.*

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