3D Printed, Low Tortuosity Garnet Framework for Beyond 500 Wh/kg Batteries

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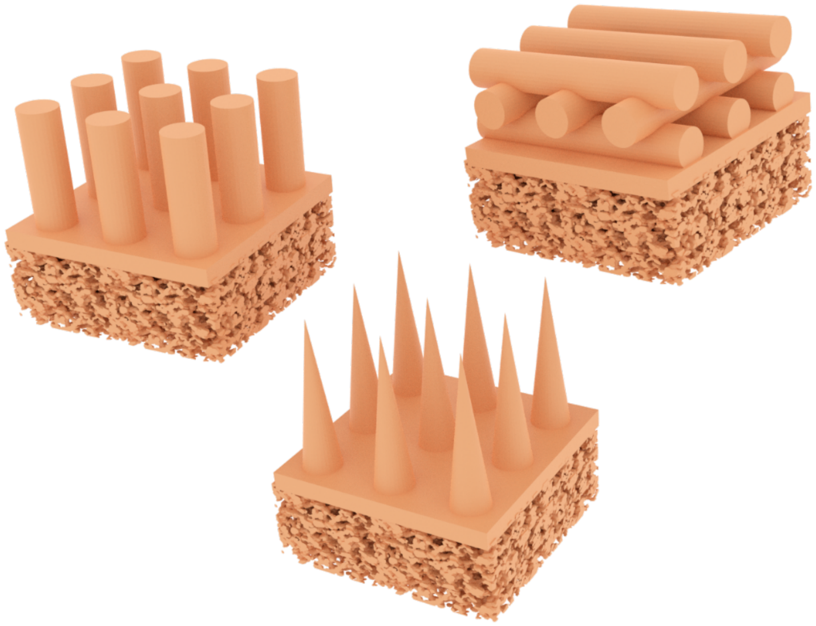
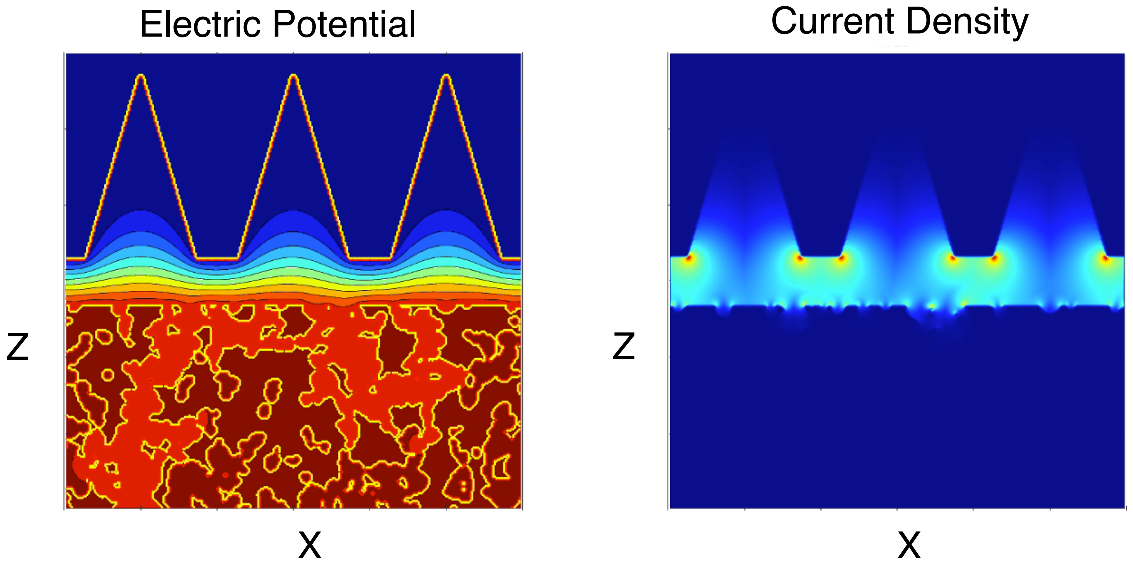
2021 DOE Vehicle Technologies Office Annual Merit Review
June 25th, 2021





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Project ID: BAT504

Overview

Timeline

- Project Start: 10/01/2017
- Project End: 03/31/2021
- Percent Complete: 80%

Budget

- Total Project Funding: $1,333,334
  - DOE Share: $1,200,000
  - Cost Share: $133,334
- FY 2021 Funding received: $0

Barriers

- Garnet electrolytes provide high ionic conductivity and enable Li-metal anodes; however, are typically limited to planar low surface area electrode/electrolyte interfaces.
- Extending interfacial surface area in 3D enables thicker electrodes for higher energy density and potentially increases C-rate; however, solid-state battery transport models don't currently exist.
- 3D printed solid-state electrolytes enable fabrication of controlled architectures for determination of transport models and demonstration of higher energy density and C-rate solid-state batteries

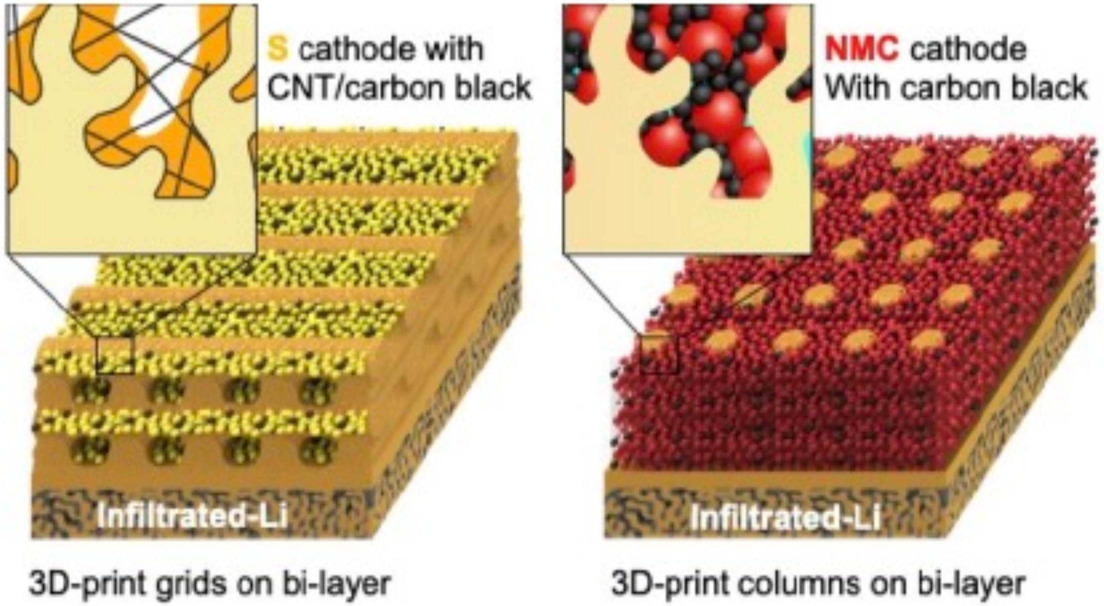
Partners

- Longstanding collaboration with Prof. Venkataraman Thangadurai

Relevance

Objectives

- Develop 3D ordered porous solid-state electrolyte structures that facilitate fast ion transport, enabling thicker electrodes for higher energy density, and higher C-rates for higher power density
- Demonstrate Li-S and Li-NMC batteries with ≥500 Wh/kg for ≥1000 cycles at a C/3 rate



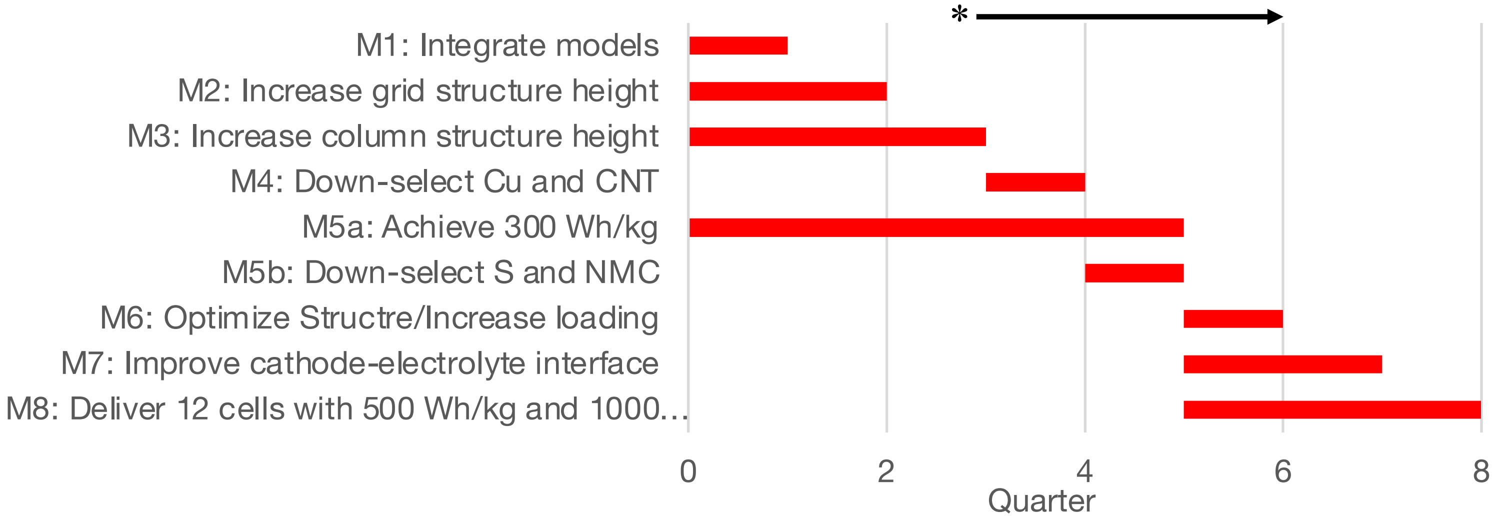
Impact

- Develop structure-property relationships in garnet electrolyte batteries to inform designs for improved performance
- Establish groundwork to help researchers develop batteries for high-demand applications

Approach and Milestones

Approach

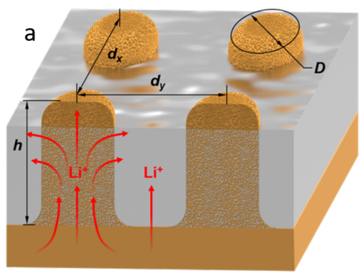
- Develop solid-state ionic and electronic transport models to optimize the structure and experimentally validate models
- Develop 3D printing techniques and fabricate high porosity, low tortuosity $Li_7La_3Zr_2O_{12}$ – garnet (LLZ) structures
- Fabricate and demonstrate high energy density 3D printed solid-state batteries



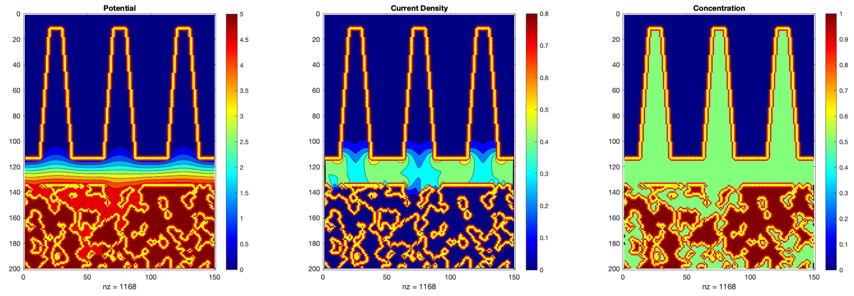
FY19Q1 Milestone: Integrate models to cathode structures **(Completed)**
FY19Q2 Milestone: Increase grid cathode structure height to achieve model design (**Completed**)
FY19Q3 Milestone: Increase column cathode structure height to achieve model design **(Completed)**
FY20Q4 Milestone: Down-select between Cu-porous and C-porous for Li metal anode **(Completed)**
FY20Q5 Milestone: Achieve 300 Wh/kg and down-select between S and NMC cathodes **(In-progress*)**
FY20Q6 Milestone: Optimize structure and increase active loading **(In-progress*)**
FY20Q7 Milestone: Improve cathode-electrolyte interface to achieve >200 cycles with 500 Wh/kg **(In-progress*)**
FY21Q8 Milestone: Deliver 12 cells with an energy density >500 Wh/kg and 1000 cycles **(In-progress*)**

** Campus was closed for 3 months and has only partially reopened, thus experimental results were unavoidably limited resultin in 4 month no-cost extension to July 31, 2021*

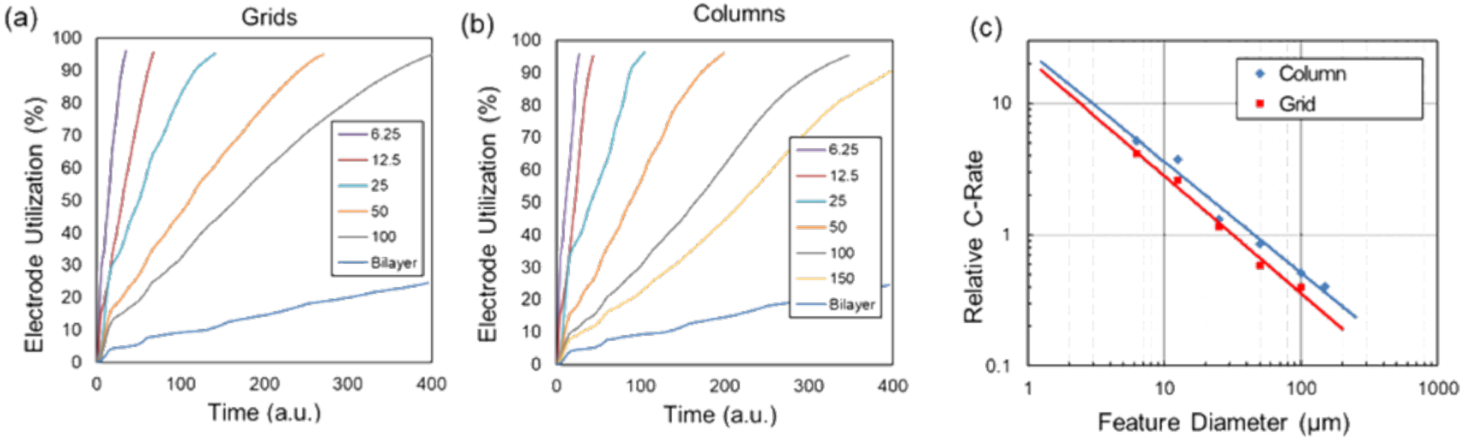
Modeling Solid-State Ionic Transport in 3D Structures

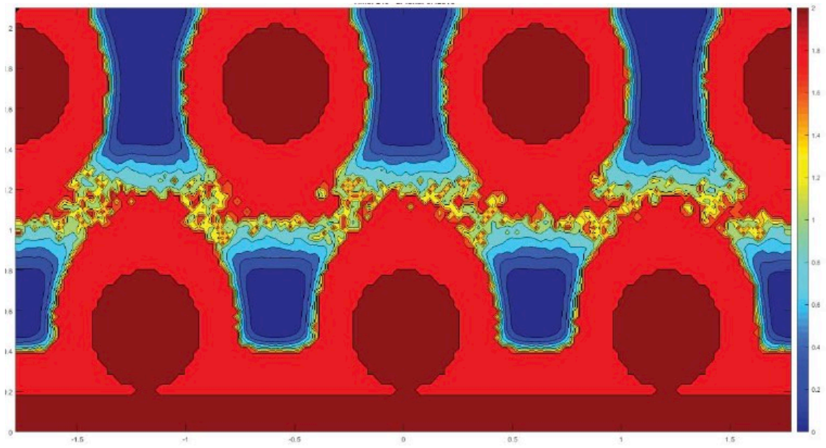


- Developed transport models to predict the utilization of intercalation cathodes such as NMC.
- Current work to model the transport of multiple chemical species in more complex conversion cathodes such as Sulfur



- Model can be applied to any 3D framework – including grid, column, and random porous structures
- Simulations show that finer features with low tortuosity lead to optimal cathode utilization and energy density





- Staggering layers leads to higher energy density by decreasing the longest diffusion distances

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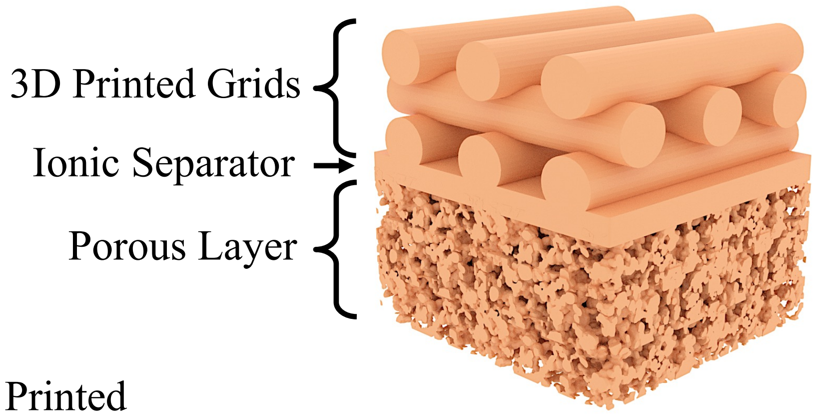
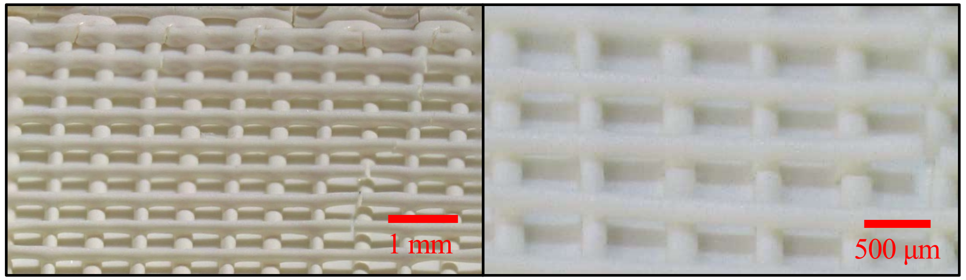
FY19Q1 Milestone: Integrate models to cathode structures (Completed)

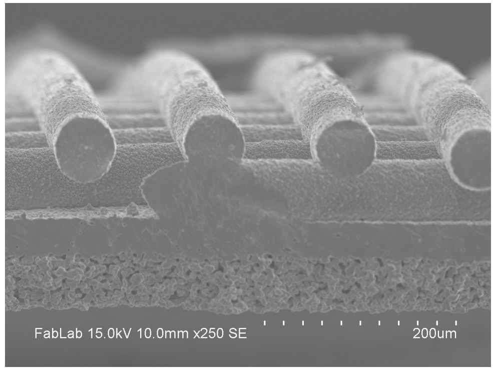
Fabricate 3D High Porosity, Low Tortuosity, LLZ Structures



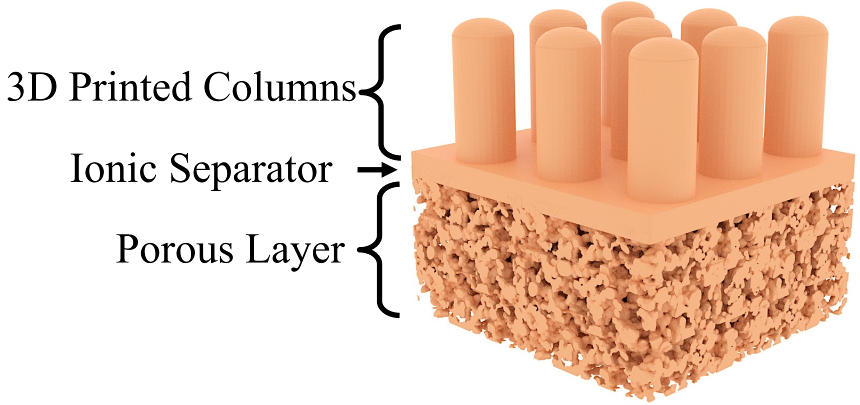
As Printed



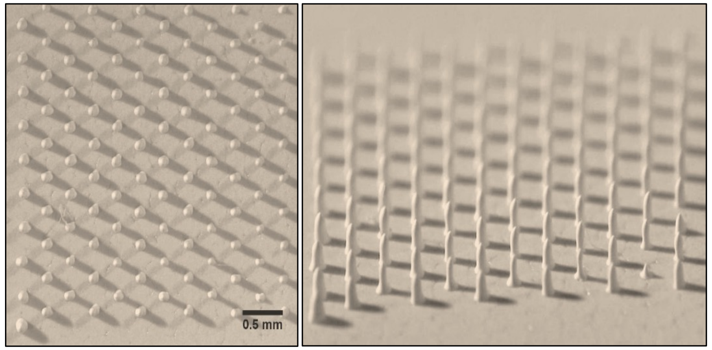
Sintered



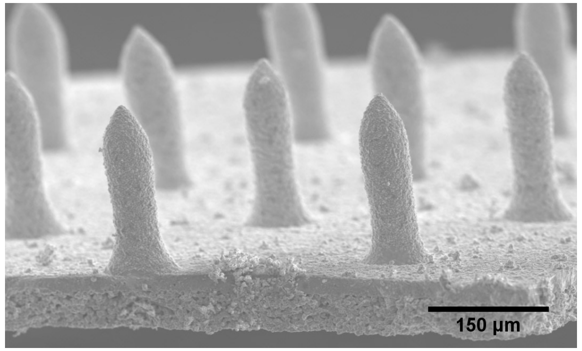
- Achieved sintered ~100 µm LLZ grid height on bilayer garnet structure
- Grid structure has better mechanical strength than columns and can infiltrate sulfur cathodes



As Printed



Sintered



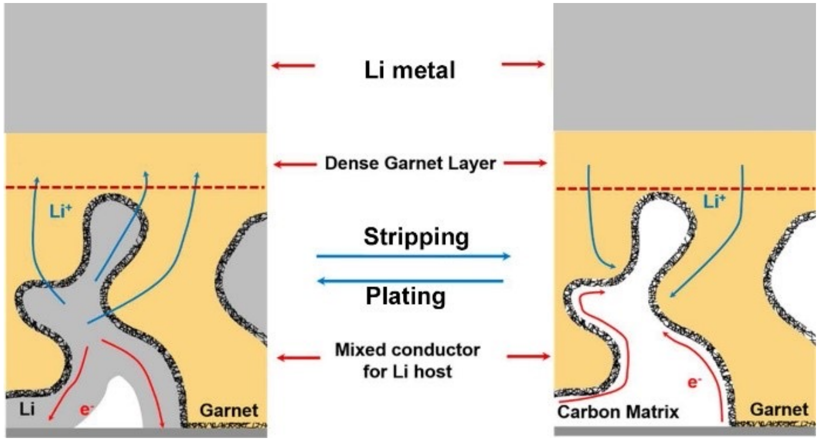
- Columns are easier to fill with cathode material such as NMC because of low tortuosity
- Achieved sintered ~200 µm LLZ column height on bilayer garnet structure

FY19Q2 Milestone: Increase grid cathode structure height to achieve model design (Completed)
FY19Q3 Milestone: Increase column cathode structure height to achieve model design (Completed)

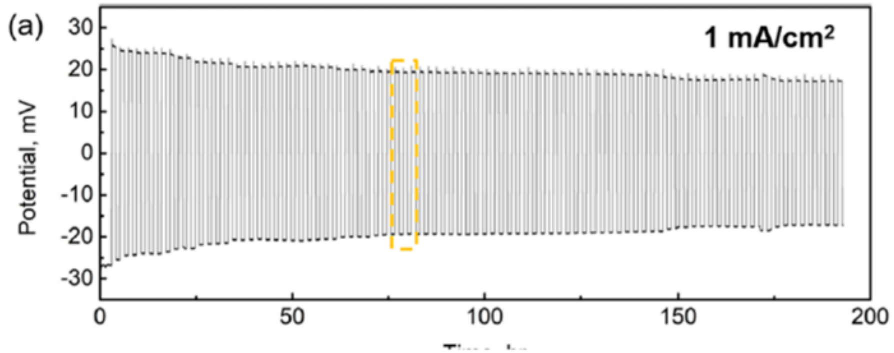
Develop “Li-Free” Solid-State Anodes and Down Select

- “Li-Free” anodes reduce cell mass and cost, and simplify processing for Li-metal anodes

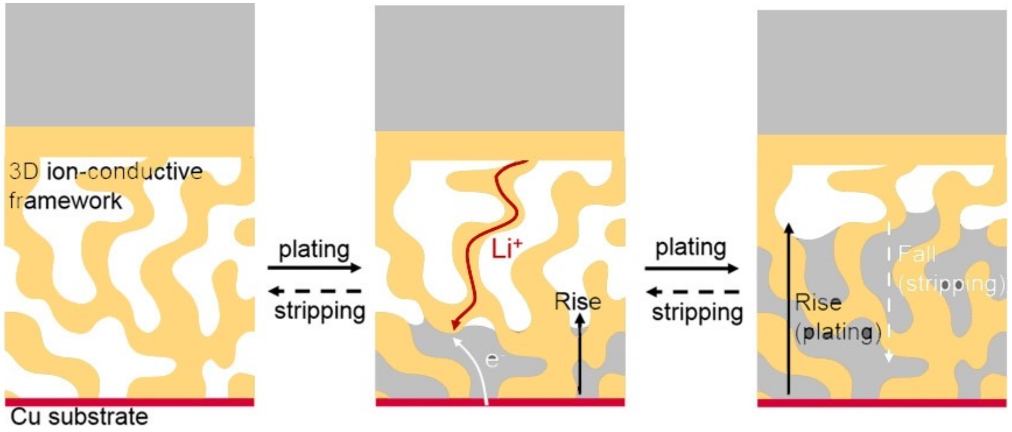
- Conformal coating of CNT inside garnet pores creates mixed electron-ion conducting framework to enable “Li-Free” anodes

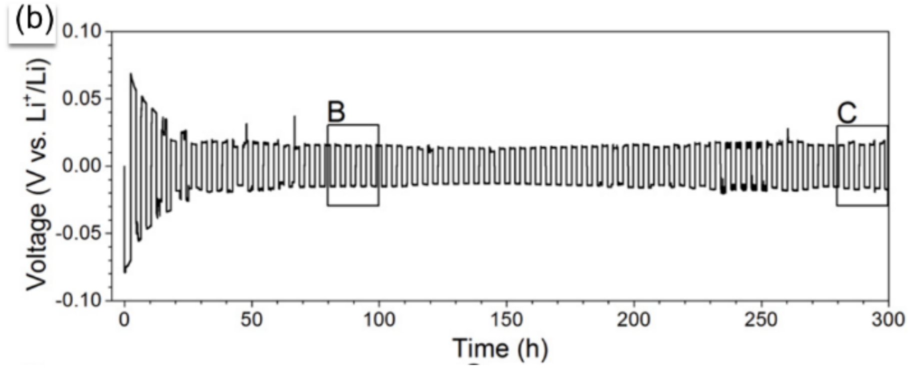


Cycling of cell with CNT current collector at 1 mA/cm^2 (Ref.: Nano Lett. 2018, 18, 3926-3933)



- Sputtered Cu layer on the exterior surface of the porous LLZ layer provides electrical contact for Li deposition and Li rises towards the dense layer during plating





Cycling of cell with Cu current collector at 0.5 mA/cm^2 (Ref.: PNAS, 2018, 115, 3770-3775)

CNT properties preferred for “Li-Free” anodes

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FY20Q4 Milestone: Down-select between Cu-porous and C-porous for Li metal anode (Completed)

Optimize Structure and Increase Active Loading

- Continued to improve 3D printing of garnet solid electrolyte
- Altered printed structure by controlling ink properties
- Achieved a wide range of structures and structural parameters

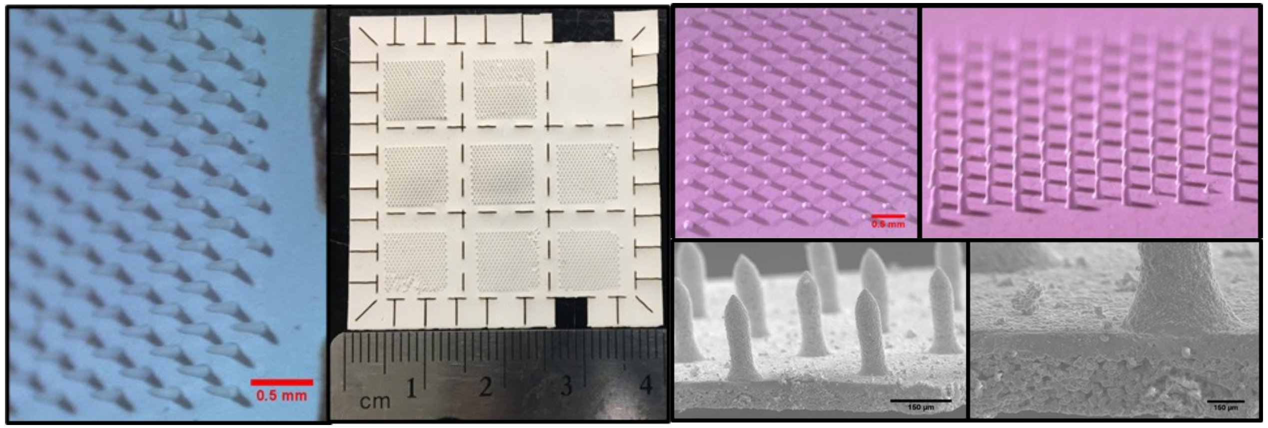
Columns:

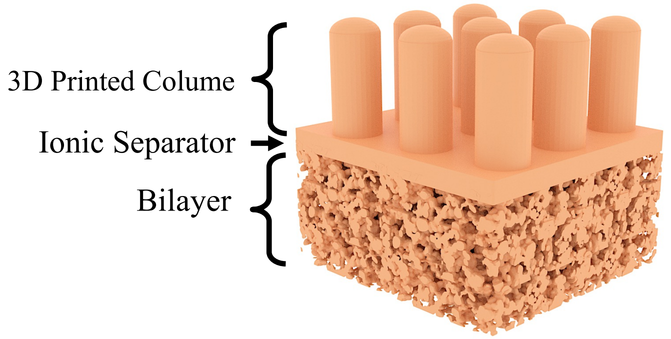
Height/Diameter ratio: 1.4-2.7

Diameter: 56-180

Spacing 237-333 µm

Porosity: 37-94%





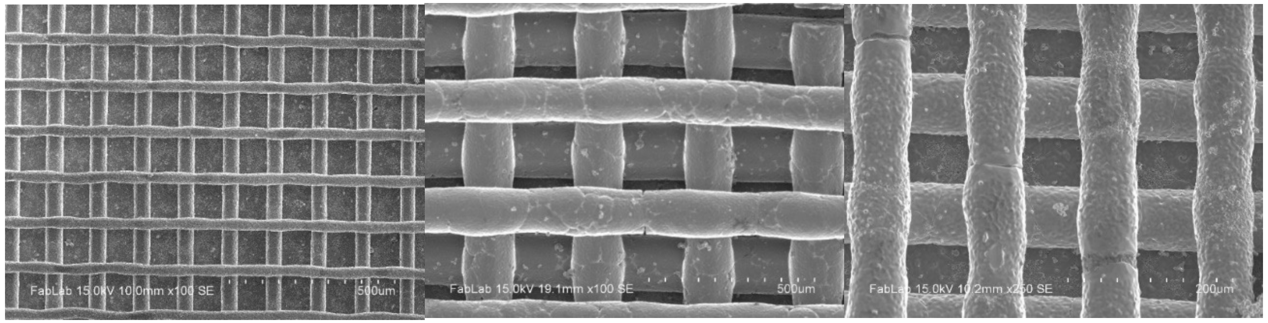
Grids:

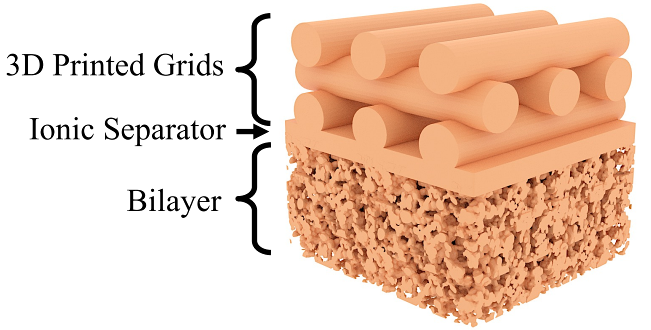
Spacing/Diameter Ratio: 2.0-2.8

Diameter: 50-150 µm

Line Spacing: 140-350 µm

Porosity: 60-70%





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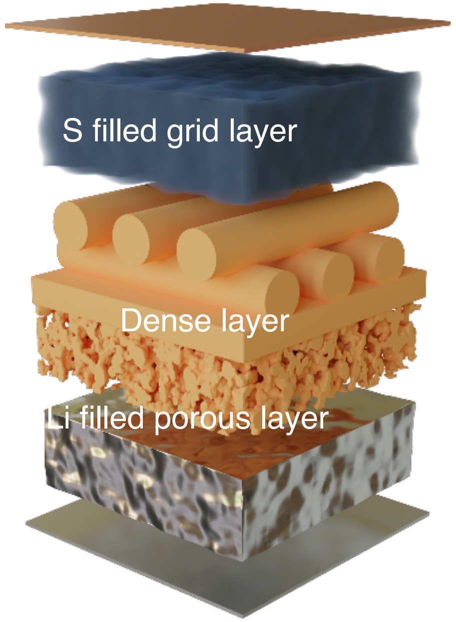
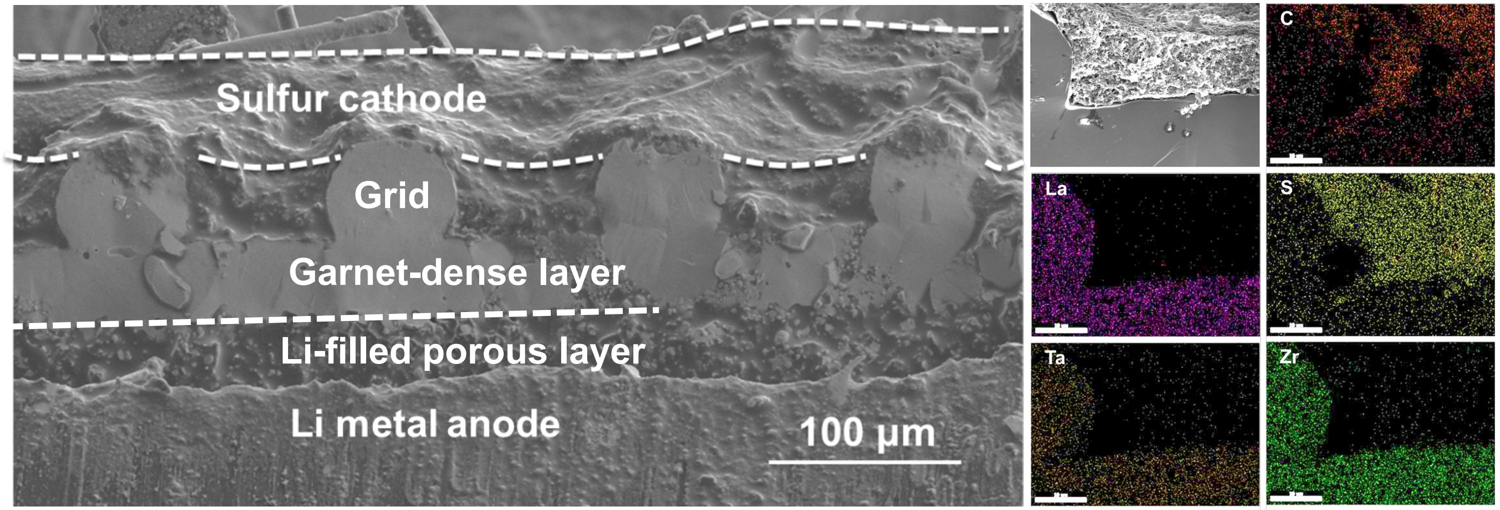
FY20Q6 Milestone: Optimize structure and increase active loading (In-progress)

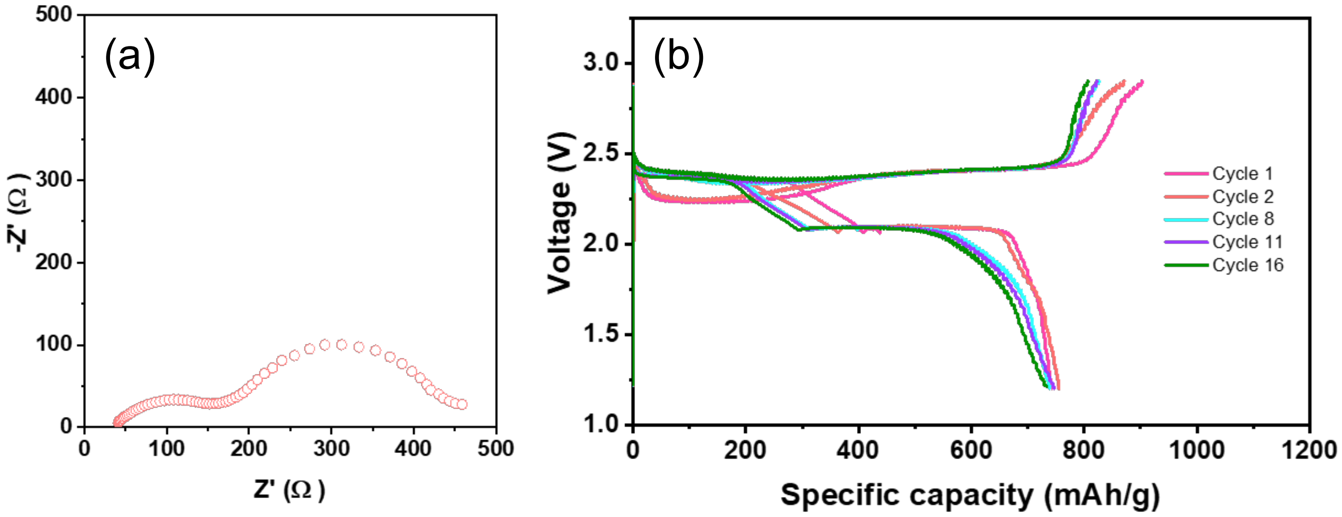
Demonstrate Cells with 3D Printed Grids (Li-S batteries)



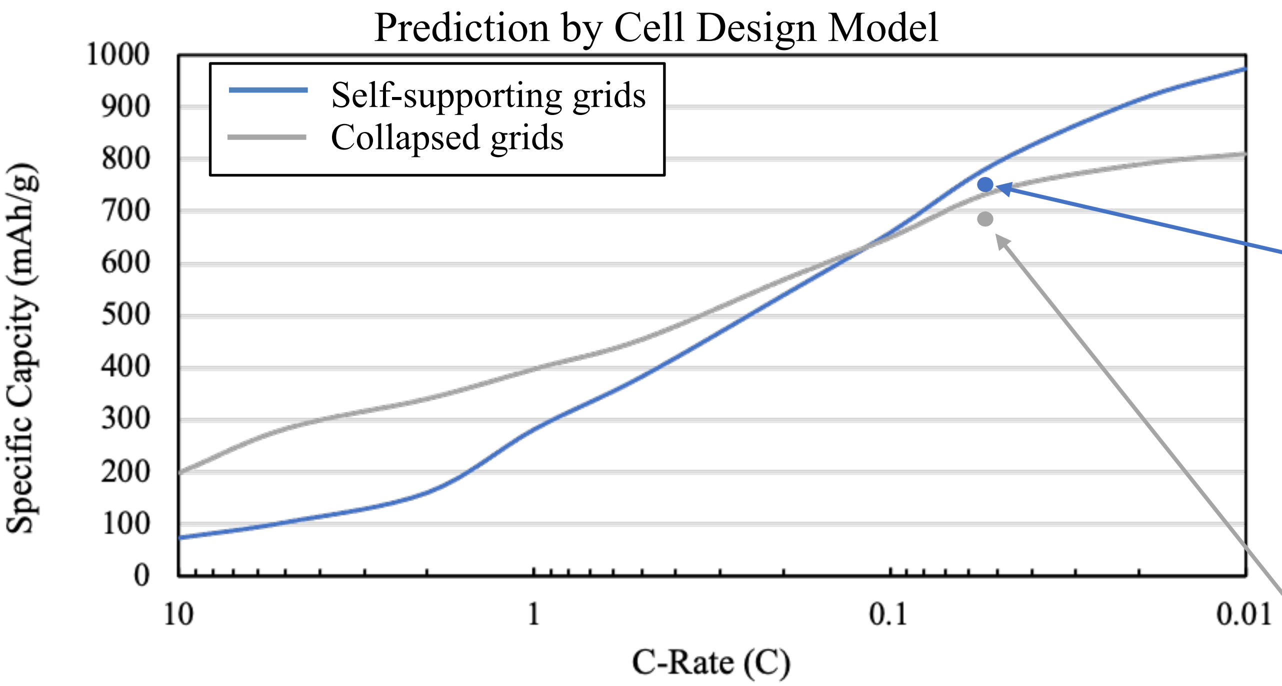


- Li metal is well infiltrated into the porous layer of garnet electrolyte;
- Sulfur/carbon cathode is conformally coated on the printed-grid side.

- The Li-S cell with grids structure (above);
- Electrochemical performance of a Li-S cell at room temperature (RT) with sulfur mass loading of 4 mg/cm^2 and current density of 20 mA/g. (a) EIS of full cell at RT, (b) Voltage profiles of cycles 1-16.



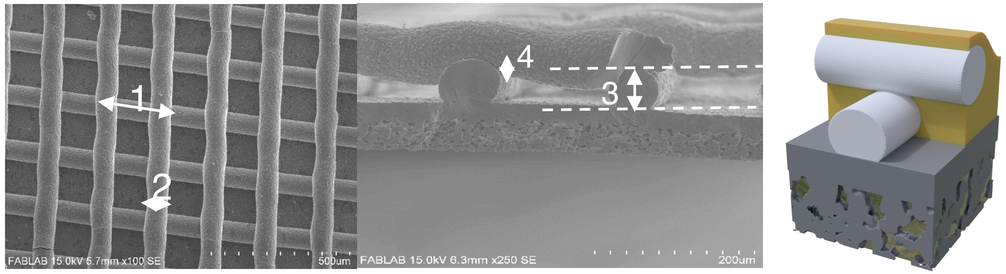
Validating Cell Design Model for Li-S batteries with 3D Printed Grids



- Self-supporting grid performs better at lower c-rates because of the increased surface area and increased access to active material farther from the separator.
- Collapsed structure cycles better at higher c-rates because of the low tortuosity and constriction penalties to effective conductivity.

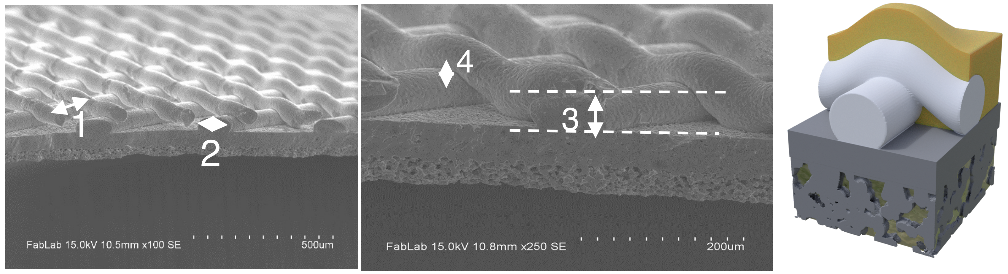
Model Parameters

1. Center to center feature separation – 206.9 um
2. Feature Thickness – 81.2 um
3. First layer Height – 64.0 um
4. Second Layer Overlap – 18.8 um

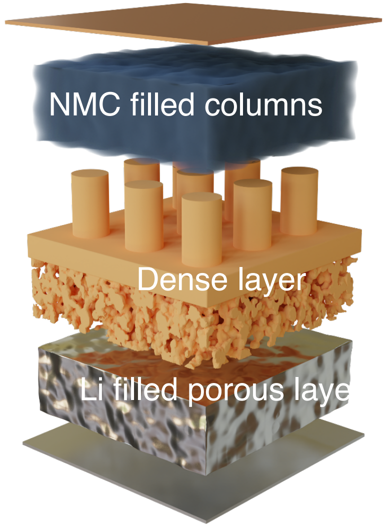


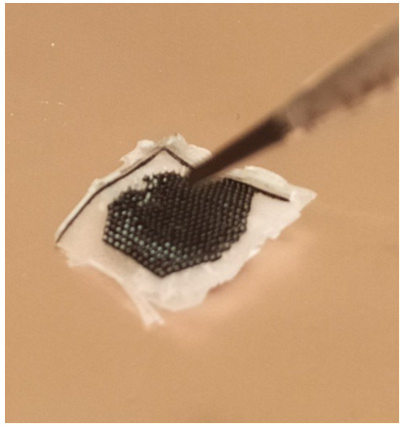
Model Parameters

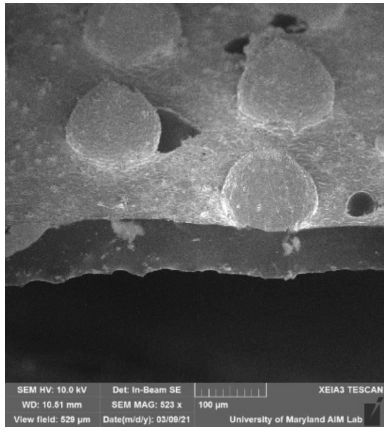
1. Center to center feature separation – 306.0 um
2. Feature Thickness – 80.7 um
3. First layer Height – 38.5 um
4. Second Layer Overlap – 21.2 um

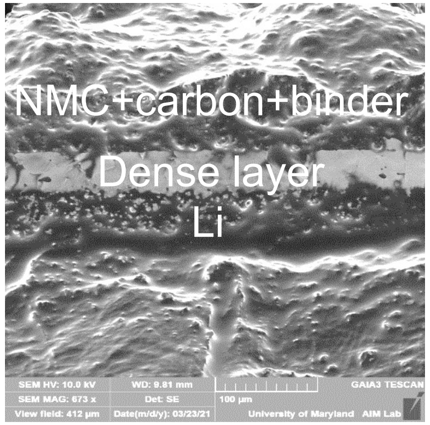


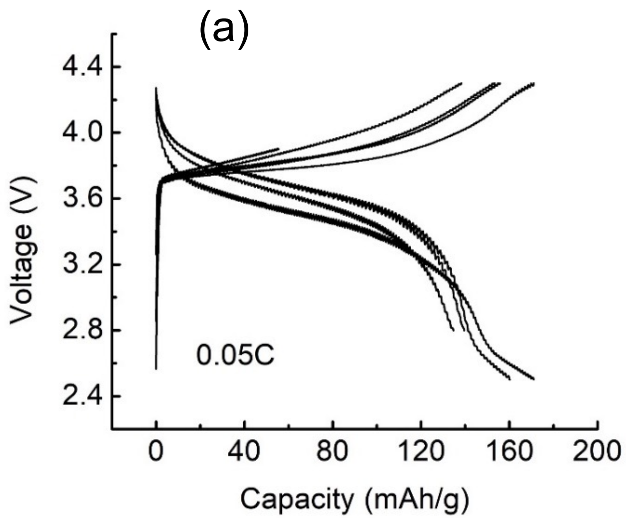
Demonstrate Cells with 3D Printed Columns (Li-NMC batteries)



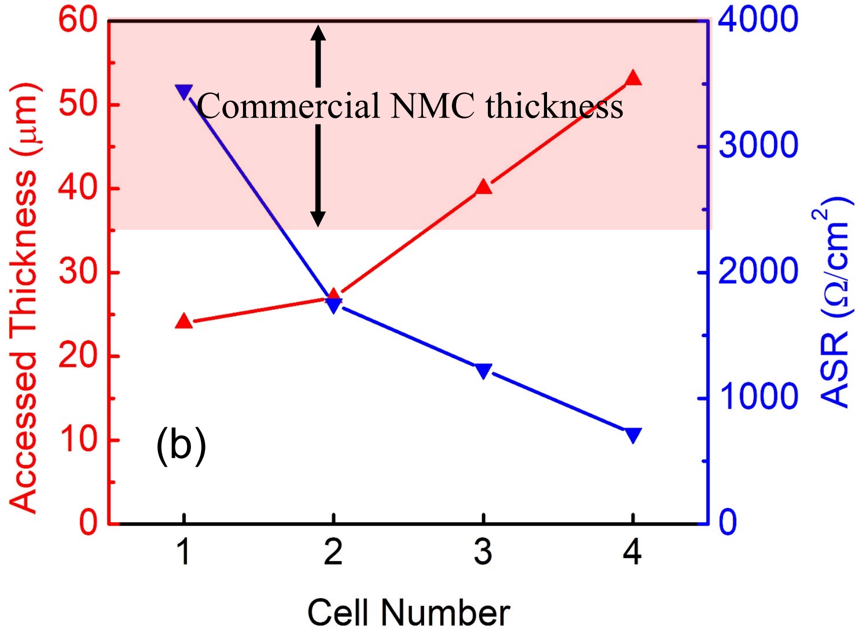








- Solution based NMC infiltration method (left); NMC infiltrated ~75 µm tall columns (middle); Li-NMC cell with column structure (right).
- Electrochemical performance of a Li-NMC cell tested at RT with NMC mass loading of ~1.5 mg/cm^2 and 0.05C (a)
- Continued improvement in processing and microstructure reduced cell impedance of as-deposited NMC
- Lower cell impedance leads to higher capacity due to greater calculated accessible thickness - assuming achievable specific capacity of 180 mAh/g (b)
- Achieving comparable accessible thickness to commercial calendered NMC cathodes (b)



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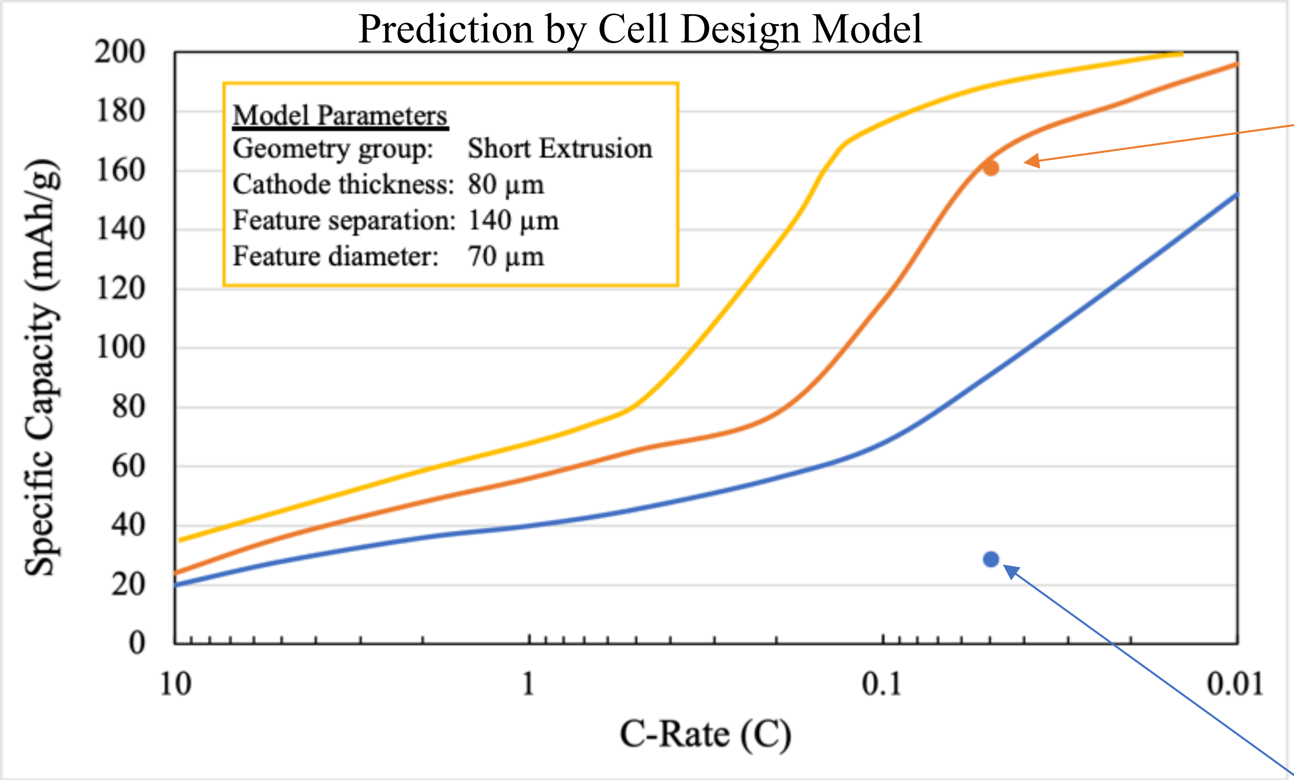
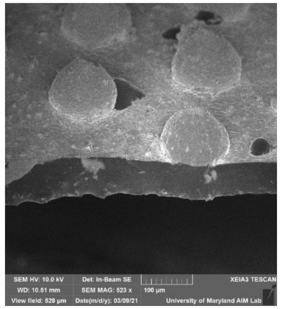
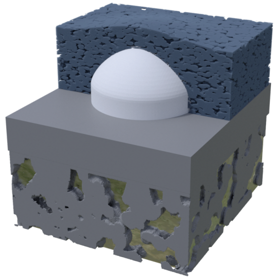
Validating Cell Design Model for Li-NMC batteries with 3D Printed Columns



<u>Model Parameters</u>

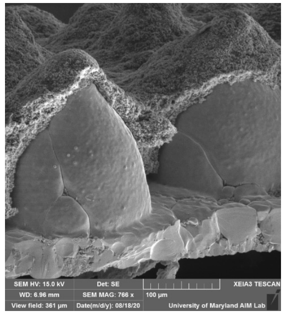
Geometry group:	Short Extrusion
Cathode thickness:	80 µm
Feature separation:	280 µm
Feature diameter:	140 µm

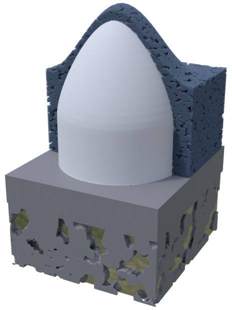




<u>Model Parameters</u>

Geometry group:	Long Extrusion
Cathode thickness:	210 µm
Feature separation:	280 µm
Feature diameter:	180 µm

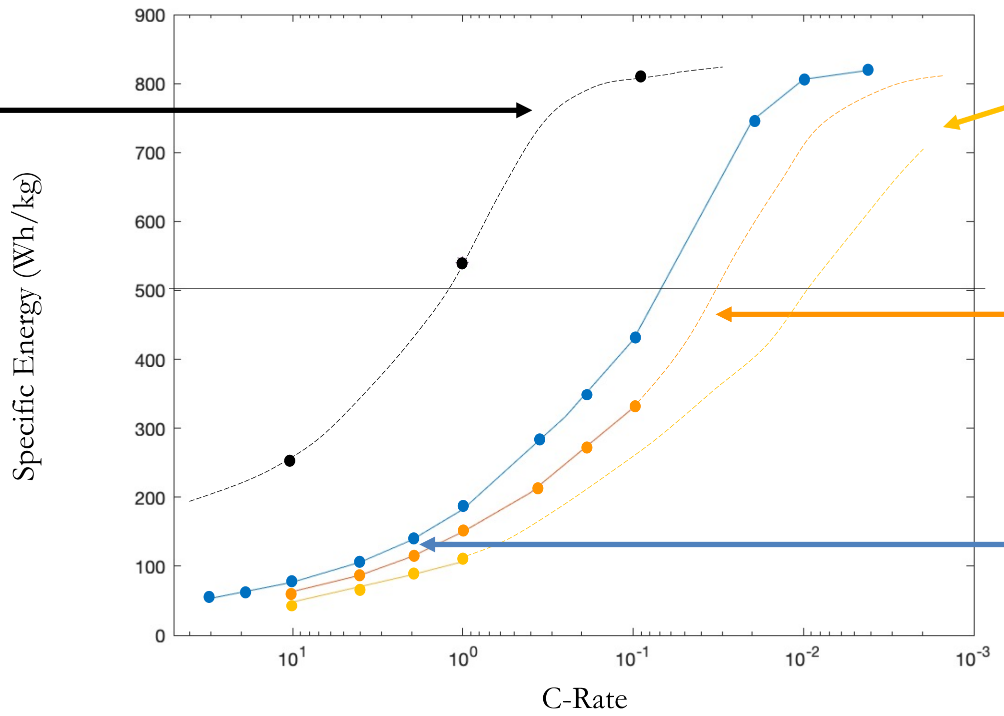




- Shorter columns behave as predicted by the model.
- Taller structures are more likely to have poor contact and worse performance from NMC detaching at the interface
- Validated model provides path to optimize structure

Design Criteria - Energy Density for Different Structures & C-Rates

Model Parameters
Geometry group: Column
Cathode thickness: 100 µm
Feature separation: 75 µm
Feature diameter: 28 µm



Model Parameters
Geometry group: Column
Cathode thickness: 200 µm
Feature separation: 400 µm
Feature diameter: 120 µm

Model Parameters
Geometry group: Column
Cathode thickness: 200 µm
Feature separation: 200 µm
Feature diameter: 60 µm

Model Parameters
Geometry group: Column
Cathode thickness: 150 µm
Feature separation: 100 µm
Feature diameter: 40 µm

- S-shape correlation is observed between C-rate and Specific Energy.
- Design 3D printed structure based on the model prediction

  -Curve shifts to the left (500 Wh/kg achieved at higher C-rates) with decreased print feature dimensions.

  -This includes both feature diameter and inter-feature separation.
- Developing first solid-state battery performance models to provide critical design criteria for achieving 500 Wh/kg energy goal as function of C-rate

FY20Q5 Milestone: Achieve 300 Wh/kg and down-select between S and NMC cathodes (In-progress)

FY20Q6 Milestone: Optimize structure and increase active loading (In-progress)

Response to Previous Year Comments

Approach - *This work has demonstrated the effectiveness of using 3-D structures of garnet-type, solid-state, superionic Li-ion conductors in the electrode. The project has extended the 3-D structure in both the anode and cathode. The 3-D approach is realized with 3-D printing techniques. Due to the extended surface area, a 3-D based, solid-state electrode is a reasonable approach to achieve high energy density on the cathode side and to slow down Li-dendrite formation on the anode side. The reviewer remarked that 3-D printing is also a scalable approach for future manufacturing. One aspect that the PIs need to consider is the brittleness of the garnet materials. The ceramic materials and 3-D structures lack flexibility for scaling up to a larger and multi-layer battery.* - Thank you and we agree brittleness is a significant issue. We have found in separate work that this can be addressed with appropriate cell packaging.

This project is well designed with three approaches to overcome the technical barriers, such as low interfacial surface area for the thick electrode and poor rate capability for solid-state batteries. The reviewer found this project addresses such critical problems with well-designed approaches. – Thank you

Most of the approach looked fine to the reviewer. However, the PIs did not respond to the questions posed by the reviewers, thus making it very difficult to evaluate their work. - Thank you and sorry for not responding to questions. I was not aware there were questions or procedure to respond and when I found out the site was already closed so I never saw the questions.

Technical Accomplishments - *The PIs have made significant progress this year. A 3-D printing method was successfully used to make the 3-D electrodes of two different structures. The electrodes with 3-D structures demonstrated performance improvement in the testing cells. Modeling is successfully used to understand the current and field distribution to aid the 3-D structure design. Electrodes with high loading of ~4 mAh/cm2 of the cathode were fabricated and tested at 60°C at reasonable current density of 30 mA/g (~C/5).* - Thank you

According to the reviewer, excellent progress has been made in the overall project. This project showed several technical accomplishments. These achievements are quite impressive for reaching the overall goals of this project. The reviewer saw these technical achievements and progress as excellent against performance indicators. – Thank you

The achievements are good; however, it was difficult to clarify several of them as the PIs were nonresponsive to the reviewers' questions. - Thank you and sorry for not responding to questions. I was not aware there were questions or procedure to respond and when I found out the site was already closed so I never saw the questions.

Collaboration and Coordination Across Project Team - *The project seemed very well coordinated to the reviewer, and there is one collaborator; The PI of this project has very good collaborations; This is mainly a university project with professors at the University of Maryland.* - Thank you.

Response to Previous Year Comments

Proposed Future Research - *The reviewer commented that the PIs showed an excellent plan for the final year of the project.* - Thank you.

The proposed future work is focused on the 300-Wh/kg and 500-Wh/kg battery fabrication and testing. These are important directions for this project, according to the reviewer. The future work also provided numerical goals to accurately measure the performance enhancement. The PIs need to define clearly how the 300 Wh/kg and 500 Wh/kg are calculated. Is this a cell-level number including all components or just the cathode anode and electrolyte? What is the cell capacity, besides energy density? - Thank you. These are based on cathode, anode, and electrolyte as currently testing ~1 cm^2 in coin cells.

Future work for this project is well planned, and the milestones for the remaining time of this project are well thought out and a logical continuation of earlier milestones. According to the reviewer, a problem with the future plan is the lack of detailed approaches to achieve the overall goal of this project. - Thank you. These are based on cathode, anode, and electrolyte as currently testing ~1 cm^2 in coin cells.

Relevance - *This project is relevant and supportive of DOE objectives to develop an affordable, high-energy-density battery for electric vehicles. There is still a challenge to achieve all solid-state batteries with long cycle life and good rate capability; This project is well designed to address such challenges. The reviewer found this project to be very relevant to DOE objectives in energy storage—a high-energy-density, safe, and long cycle-life battery;*
The plan stated in the Summary slide goes along with the objectives of the Battery500 program. - Thank you.

Resources - *The reviewer said that resources are sufficient for the work performed and planned. The resources of this project are sufficient to achieve the milestones on time. The team seems to have the proper equipment, and visits to the team's laboratories corroborate this. However, the funding seemed somehow high to the reviewer.* – COVID lab closure negatively impacted financial resources and we had to take no-cost extension.

Remaining Challenges and Upcoming Work

- Demonstrate energy (300 Wh/kg) density for Li-S or Li-NMC cells with stable cycling
- Optimize 3D structures to improve loading
- Improve cathode-electrolyte interface to achieve >200 cycles with 500 Wh/kg
- Demonstrate high energy (500 Wh/kg) density for Li-S or Li-NMC cells with over 1000 cycles

Proposed Future Research

FY21

- Demonstrate energy (300 Wh/kg) density for Li-S or Li-NMC cells with stable cycling
- Improve cathode-electrolyte interface to achieve >200 cycles with 500 Wh/kg
- Demonstrate high energy (500 Wh/kg) density for Li-S or Li-NMC cells with over 1000 cycles

Summary

FY20

- Demonstrated 3D printed LLZ full cell fabrication and testing
- Achieved high aspect ratio column structures, ~200 µm tall
- Achieved tall (~100µm) grid structures with 50 µm diameters and a separation of 150 µm
- Down selected "Li Free" anode structure to CNT coated pores vs external Cu current collectors

FY21

- Achieve 300 Wh/kg and down-select between S and NMC cathodes
- Optimize structure and increase active loading
- Improve cathode-electrolyte interface to achieve >200 cycles with 500 Wh/kg
- Deliver 12 cells with an energy density >500 Wh/kg and 1000 cycles