NATIONAL LAB DISCOVERY SERIES

Ceramic Structures for Solid-State Batteries

Michael C. Tucker

Wooseok Go, Fengyu Shen, Robert A. Jonson, Eongyu Yi, Marca Doeff

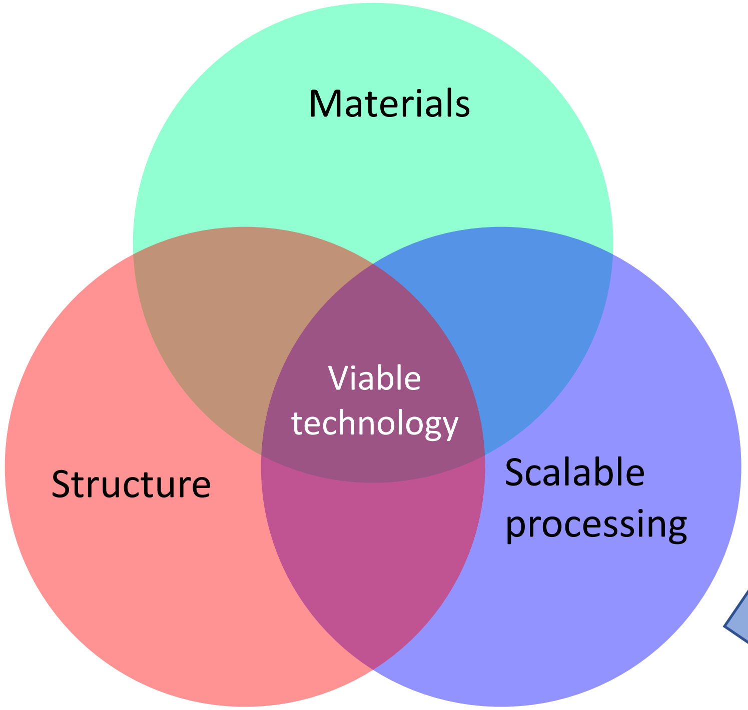
9/17/2024

Energy Conversion Group, ESDR
Lawrence Berkeley National Laboratory, Berkeley, CA, USA

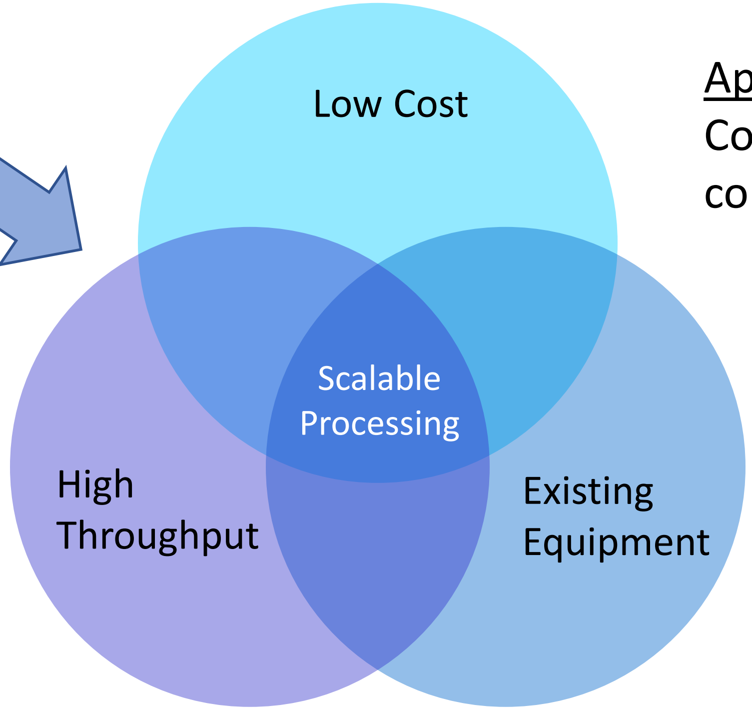
Why Solid State?

- Liquid electrolytes, such as those currently used in electric vehicles, have safety concerns due to their high risk of overheating and flammable liquid electrolyte
- Besides improved safety, solid-state batteries (SSBs) can offer higher energy density and improved stability across a wide temperature range

The Manufacturing Challenge



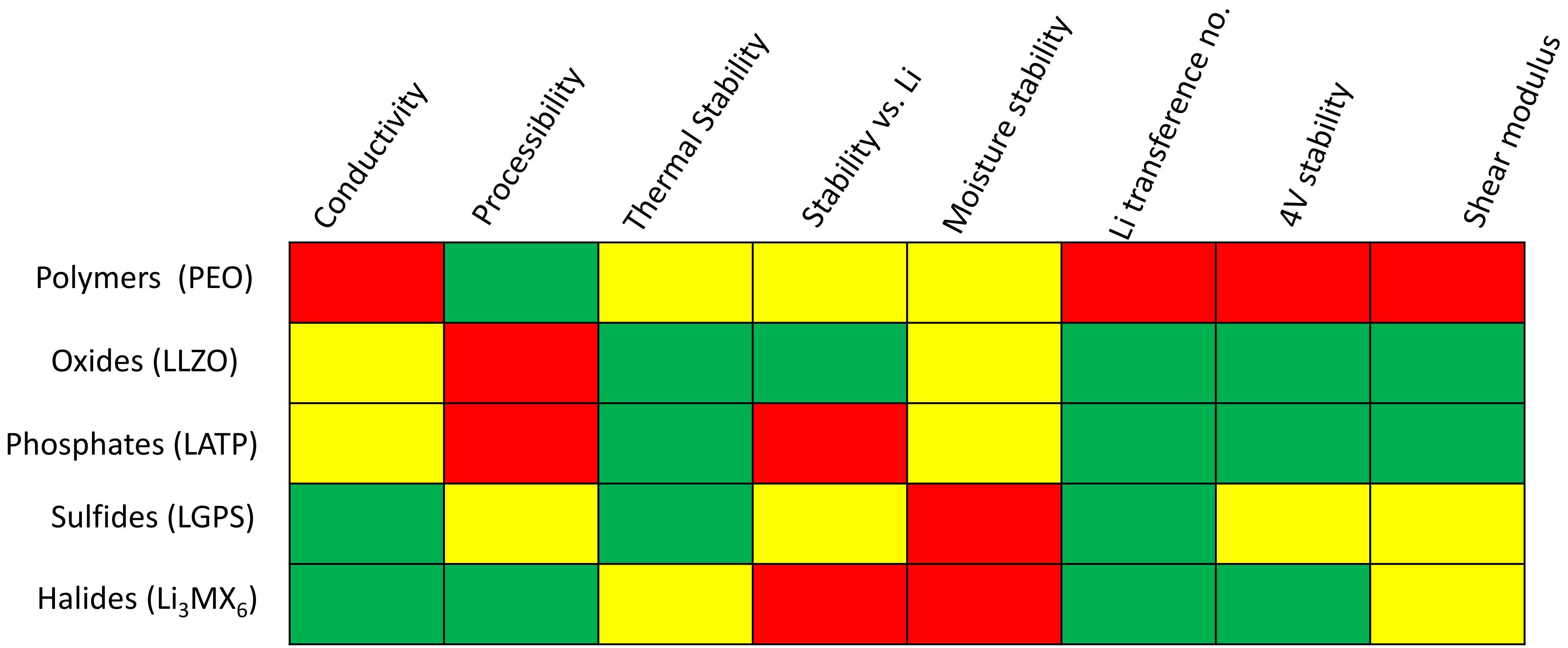
<u>SSB processing challenge and opportunity</u>
- Processing is a bottleneck
- Completely different than existing LiB fabs



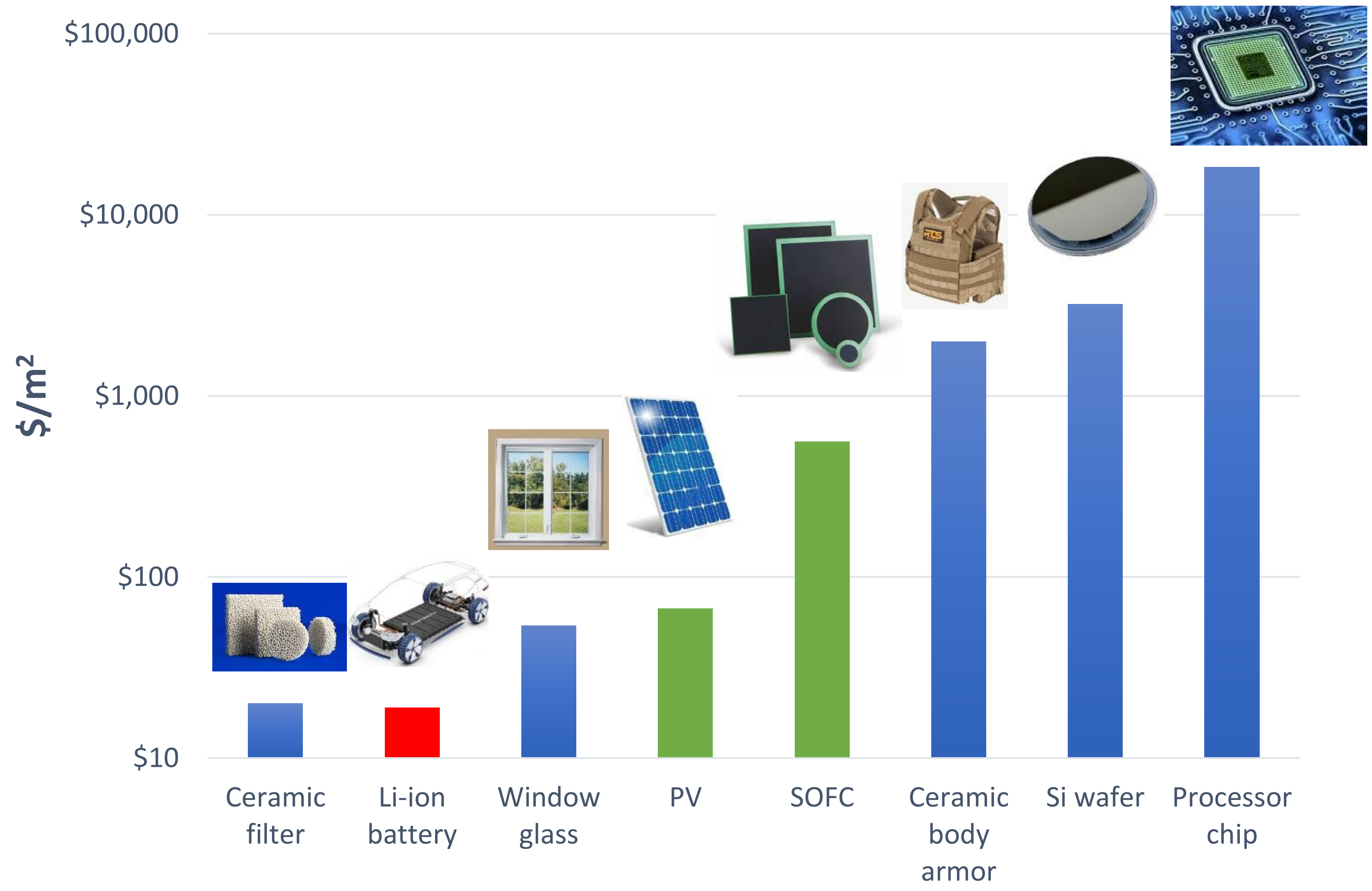
<u>Approach</u>
Couple materials and structural optimization to constraints of low-cost, scalable techniques

<u>Sustainability imposes additional constraints</u>
- Recyclability
- Carbon footprint
- Second life
- Elements used

Processing is Critical



Value Dictates Acceptable Cost



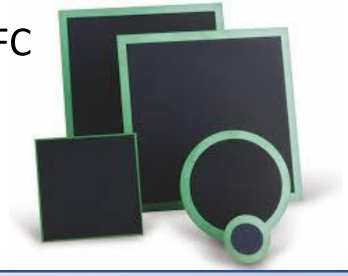
Many manufacturing processes
are simply too expensive for batteries

Aggressively focus on low-cost processing
(in parallel with next-gen materials/structure development)

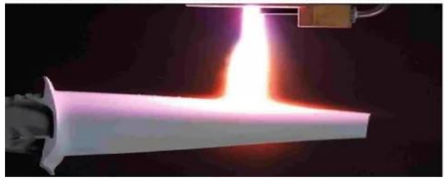
Ceramics Processing Costs

Disposable Filter

SOFC



Thermal Barrier Coating



	$	$$	$$$

Processes: Screen print, Dip coat, Slurry templating — Tapecast — Slot Die — Colloidal spray — Sintering — Thermal spray, 3D printing — Sputtering, CVD, ALD, Plasma spray

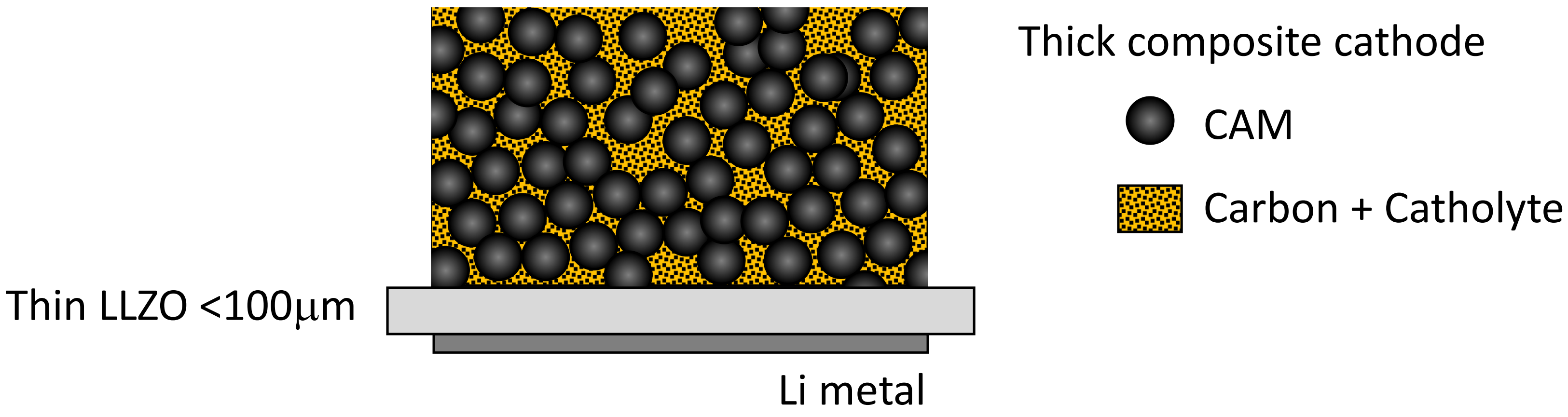
Throughput: Fast/Continuous — Batch — Slow/Single Item

Atmosphere: Air — Dry Room — Glove Box — Vacuum Chamber

Solvents: Water — Benign Solvents — Toxic/Hazardous Solvents

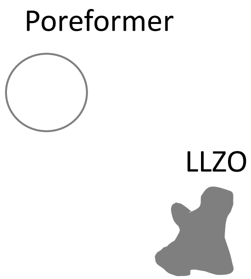
Temperature: <200°C — <900°C — <1150°C — <1400°C — <1600°C

Gen 1 - Thin free-standing LLZO sheet



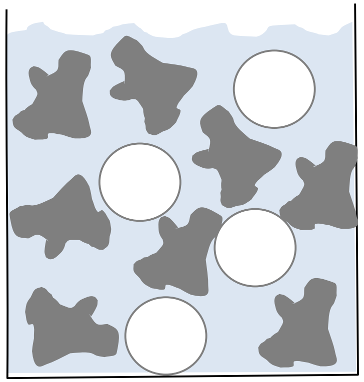
Scalable Processing for Thin Ceramic Sheets: Tape Casting

Powders



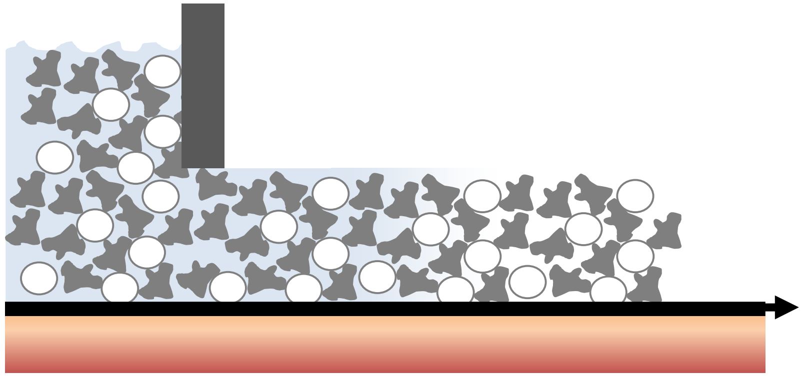
Particle size
Particle shape
Poreformer size
Poreformer shape

Slurry



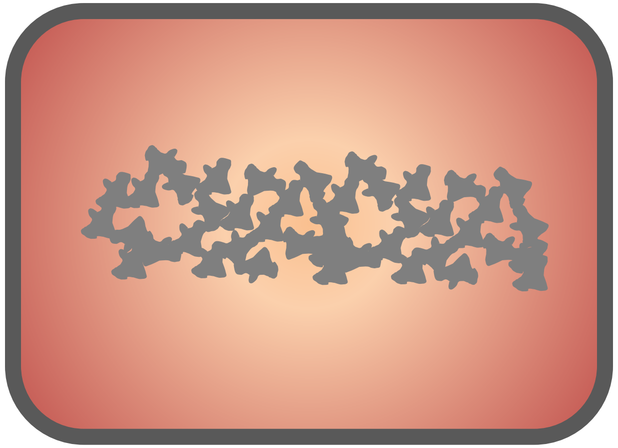
Solvent content
Dispersants
Additives
Milling energy

Tape casting



Thickness
Drying speed
Post-lamination
Casting speed

Sintering



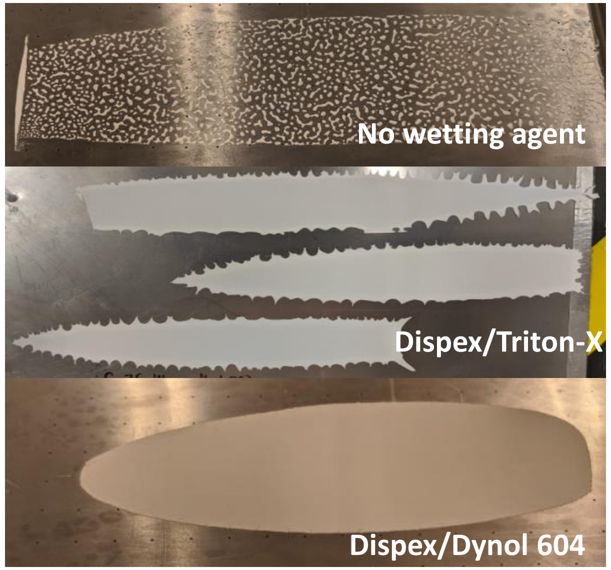
Temperature
Atmosphere
Time

Tape Casting LLZO (2020-061)

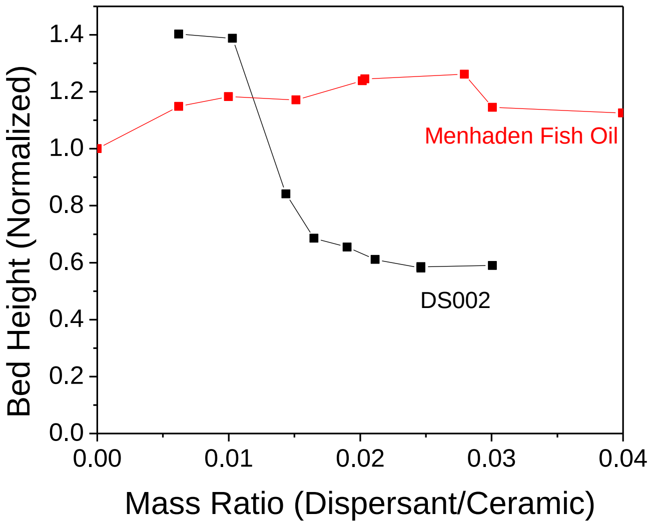
Optimization of aqueous and solvent-based tape slurries
- Wetting agent
- Dispersant
- Binder
- Plasticizer

Binder System	Health/ Safety	Usable	Foaming	Carrier Release	Mechanical Properties	Oxide-Only Density (%)
PVA	Aqueous	Gels				
PII WB4101	Aqueous	Gels	-	-	-	-
Methyl-Cellulose	Aqueous	Yes	Yes Controllable	Controllable De-wetting	Good	40.2
PVB	Ethanol/ Acetone/ Phthalate	Yes	No	Poor	Brittle	44.3
Ethyl-cellulose	Toluene/ Ethanol	Yes	Minor	Good	Brittle	43.9
PII MSB1-13	Toluene/ Xylene	Yes	No	Good	Very Good	41.7

Preventing Dewetting of Aqueous Slurries

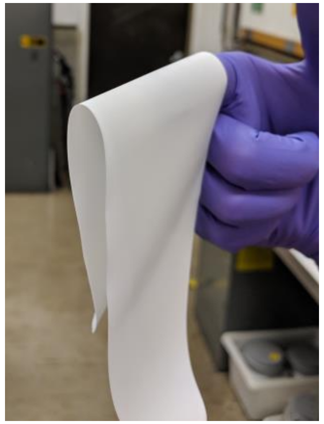


Optimizing Solvent-Based Formulations

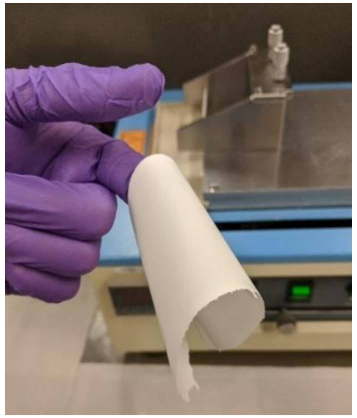


Strong, flexible tapes

Solvent-based slurry

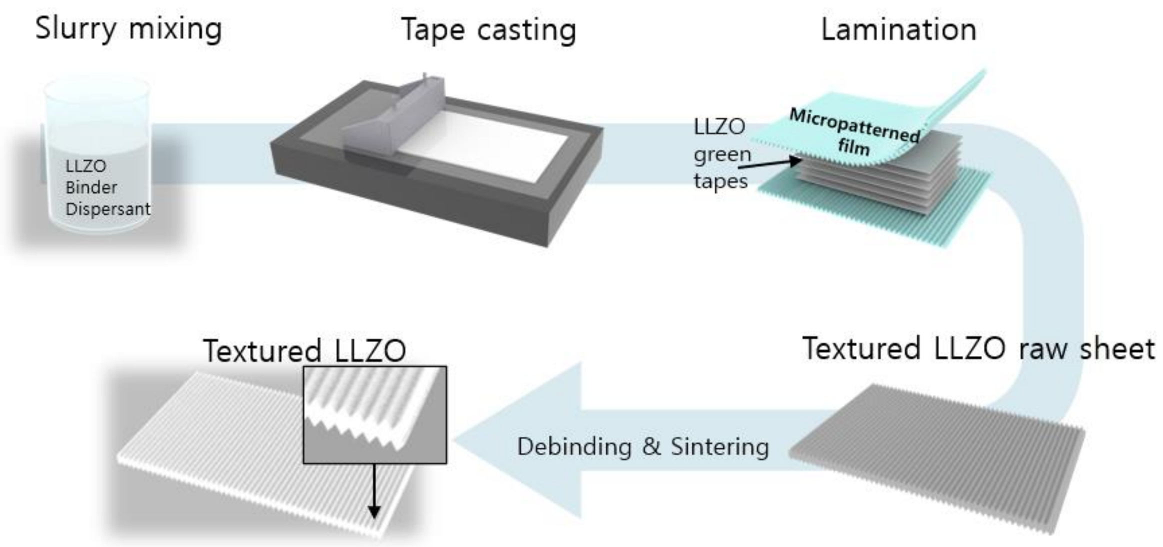


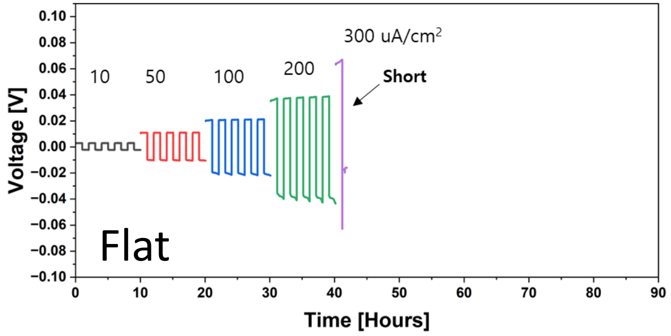
Water-based slurry

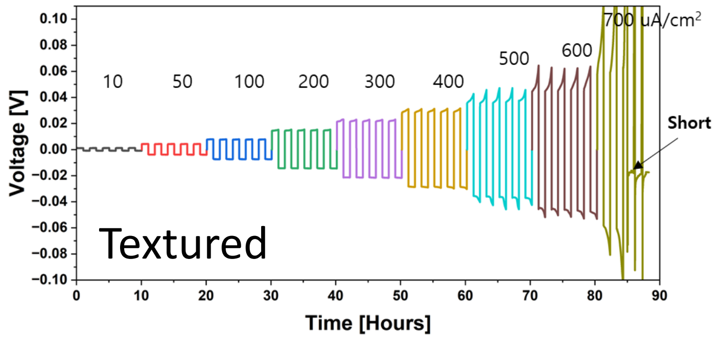


Rob Jonson, M.C. Tucker, et al, Energy and Fuels 35 (2021) 8982-8990

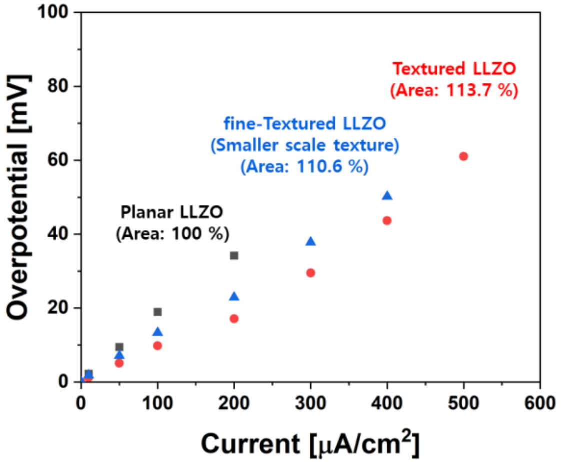
Texturing to Increase Electrode/Electrolyte Interfacial Area (2024-063)

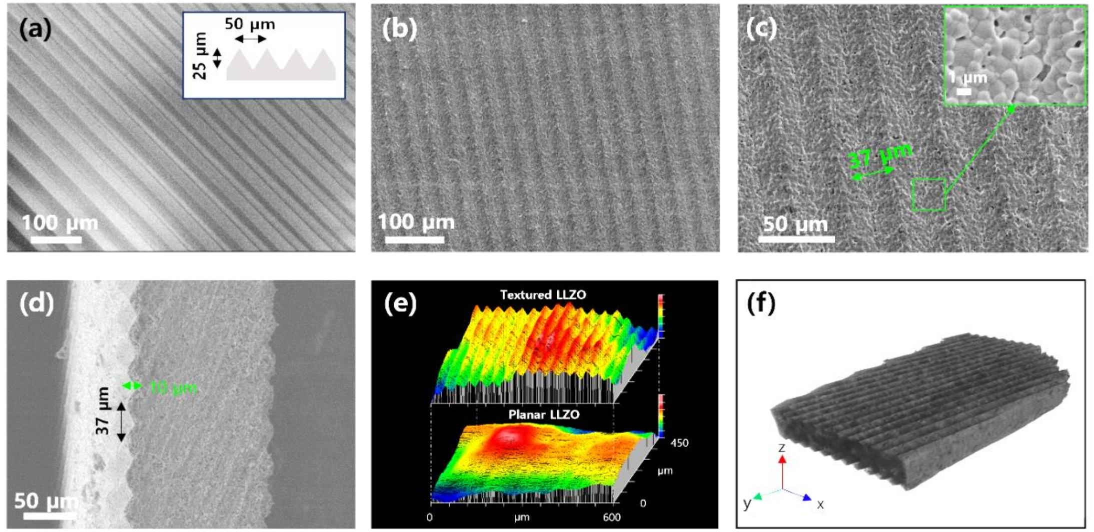




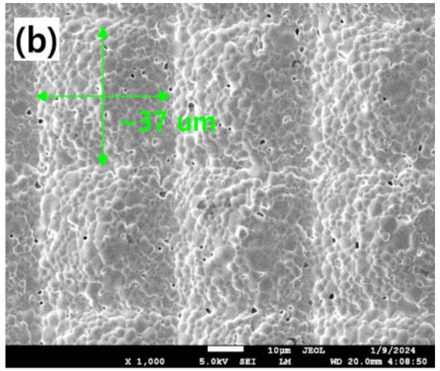


- Increases CCD
- Reduces interfacial resistance

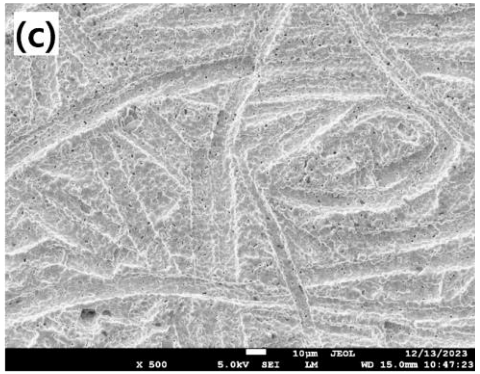




Pressing substrate twice rotating 90º

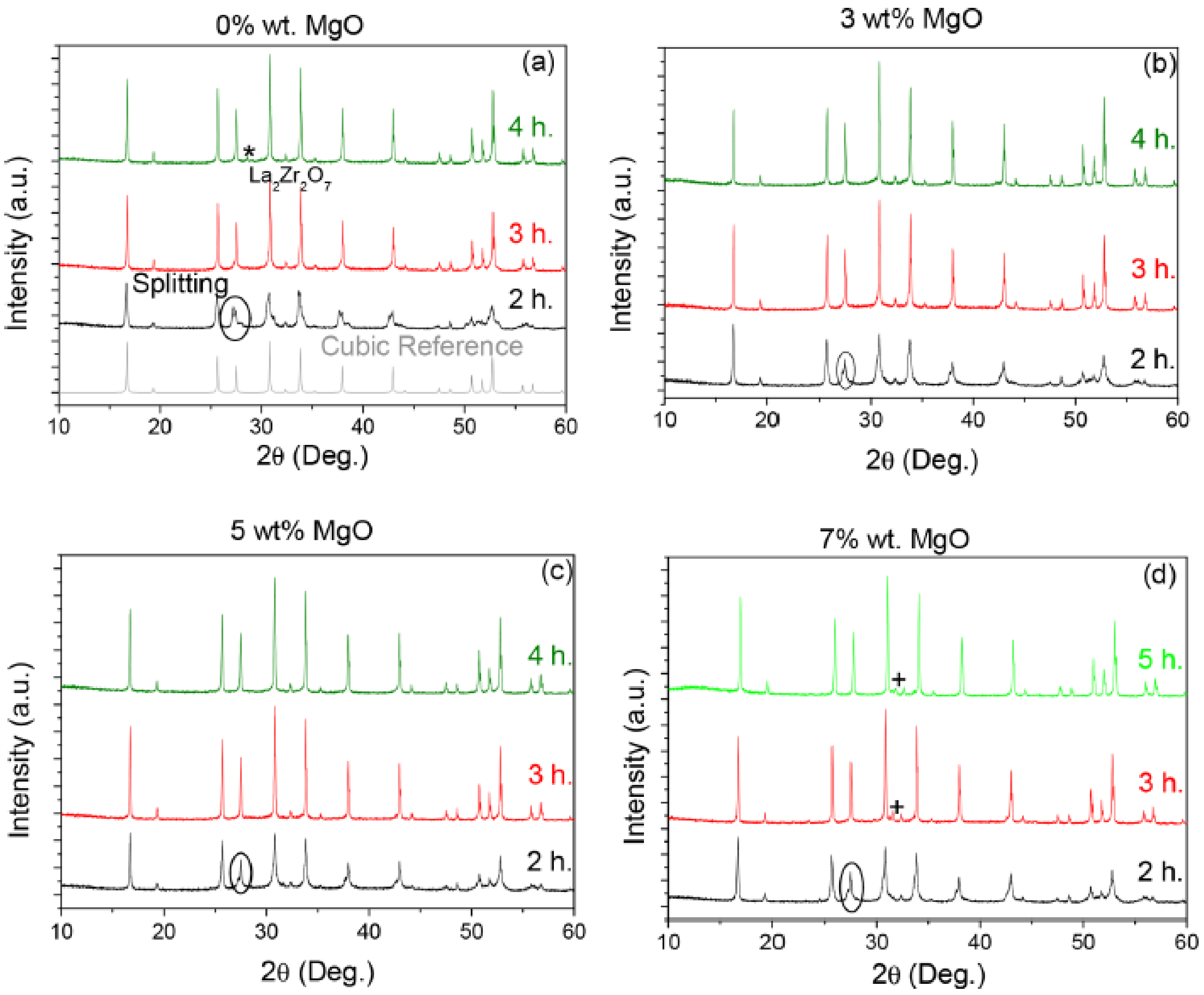


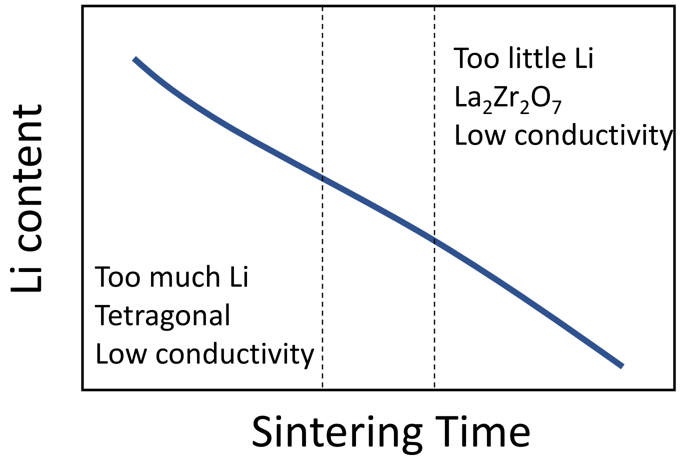
Carbon paper substrate



W. Go, M.C. Tucker, et al. ACS Energy Letters (2024) DOI: 10.1021/acsenergylett.4c00800

Fine-Tuning Li Content (2020-061)



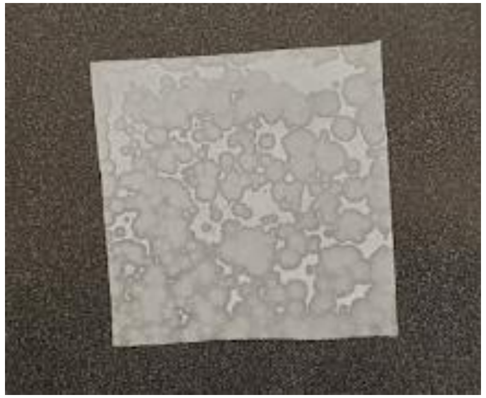


Li content must be managed carefully
- powder composition
- Li additives
- Sintering protocol (time, temp, flow)
- Kiln furniture

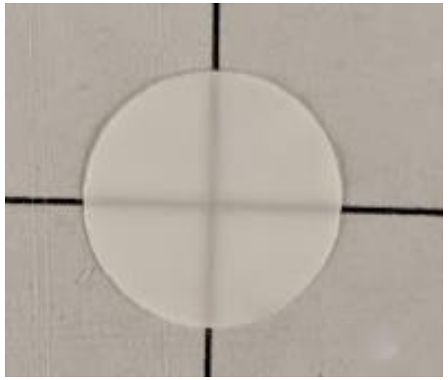
Rob Jonson, M.C. Tucker, et al, Energy and Fuels 35 (2021) 8982-8990

Tape Sintering Optimization (2020-061)

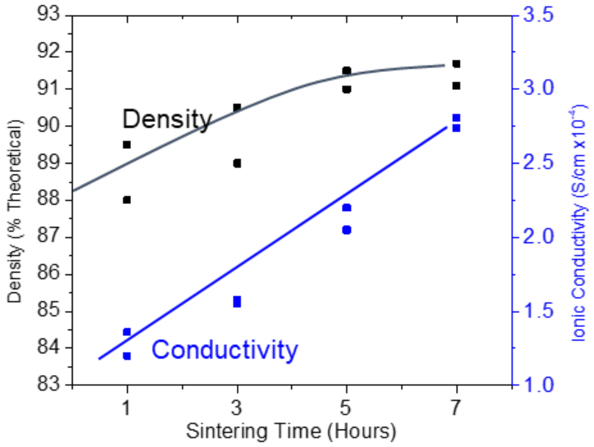
Sintering at 1115°C

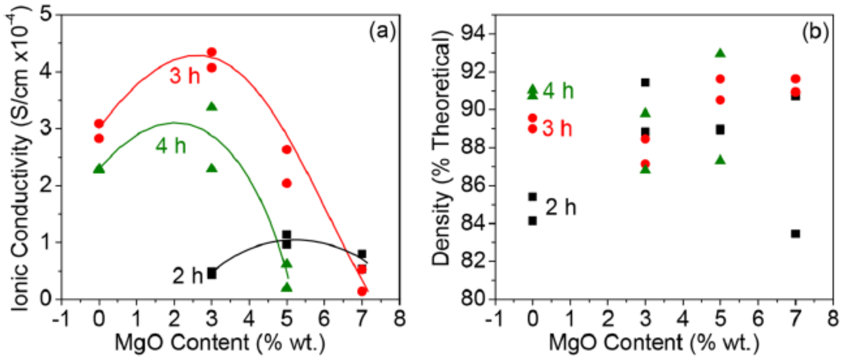


Abnormal grain growth with 5% Li_2CO_3 no MgO



4% Li_2CO_3 4% MgO
Uniform Grains





Optimized Li_2CO_3, temperature, and time for Li content

MgO nanopowder inhibits abnormal grain growth

Thin layers of LLZO are more challenging than pellets
- Li loss
- Abnormal grain growth
- Densification

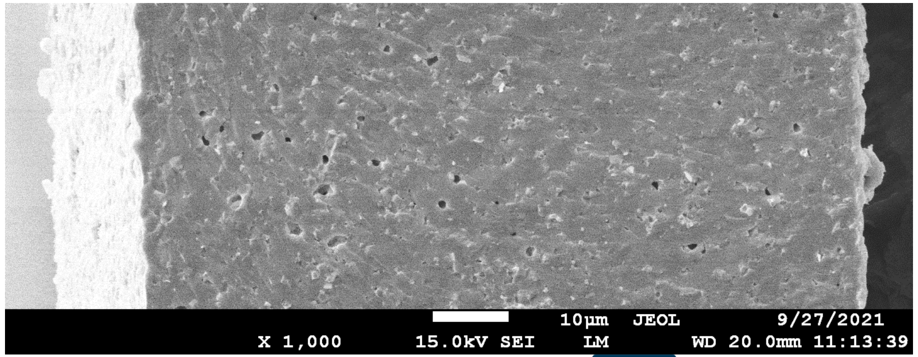
Optimization of processing and additives
- Sintering time, temperature
- Sintering atmosphere
- Kiln furniture materials
- Li_2CO_3 and MgO content

Optimization has achieved

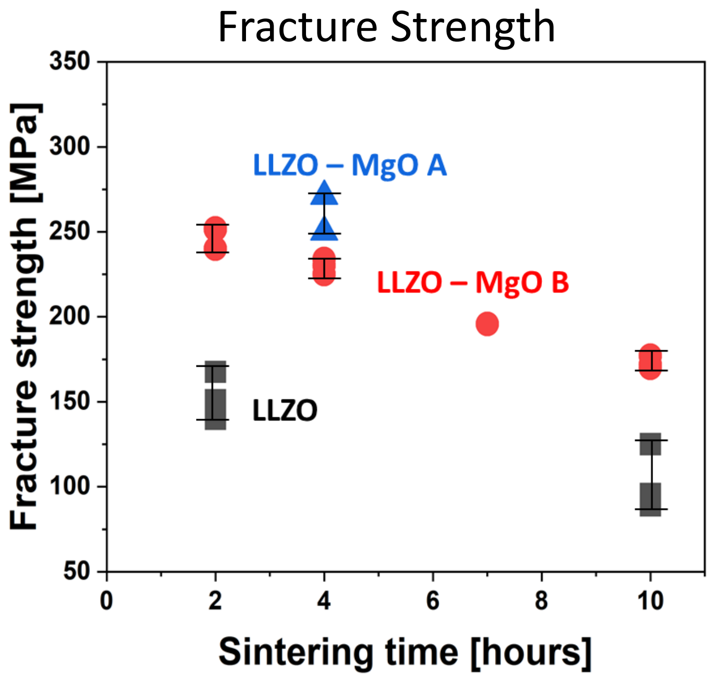
Conductivity >$2x10^{-4}$ S/cm

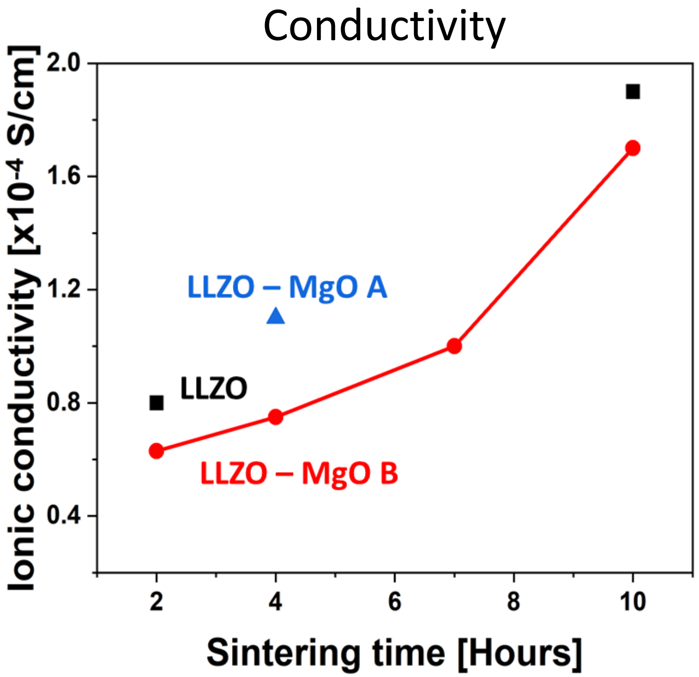
Density >90%

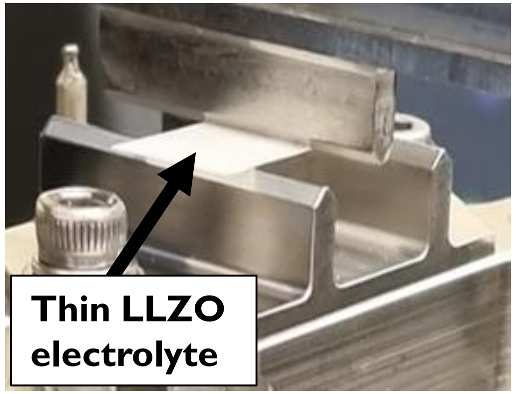
Fine-grained structure



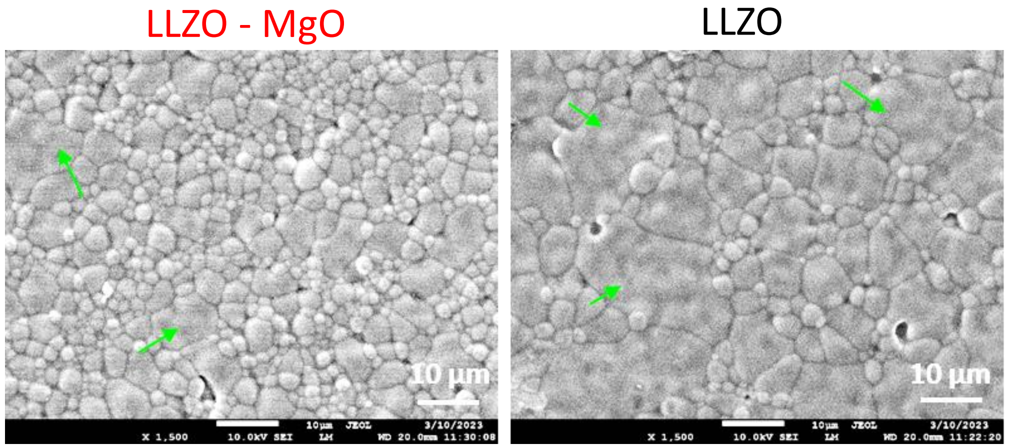
Mechanical Properties - MgO (new IP)

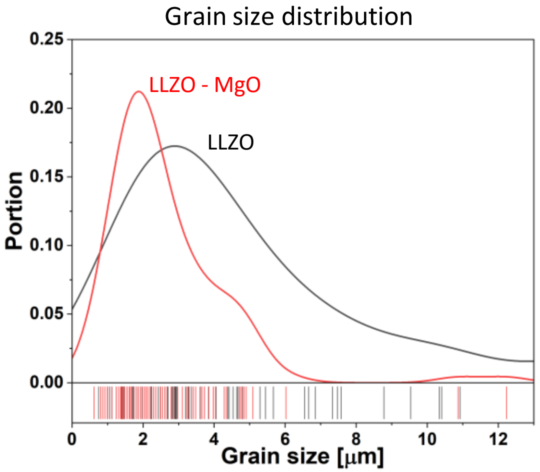






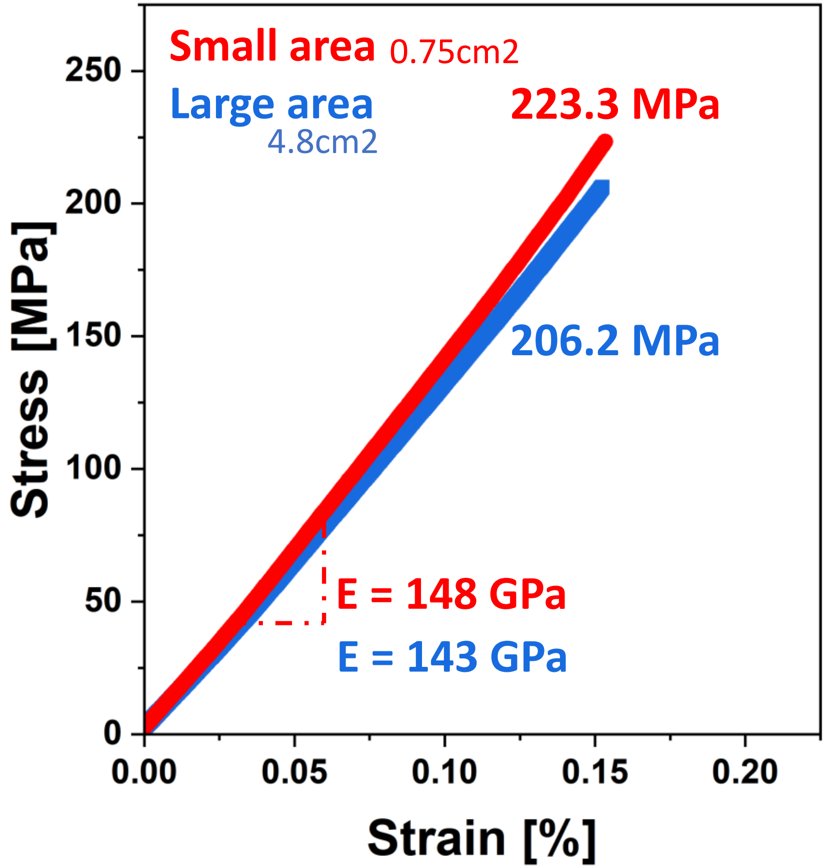
- Test based on ASTM C1161-18
- Fracture strength, Young's modulus



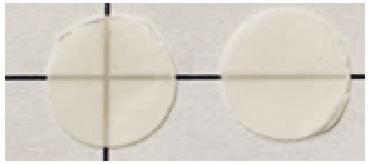


MgO addition
- Prevents abnormal grain growth
- Narrows grain size distribution
- Improves strength ~70%
- Maintains conductivity

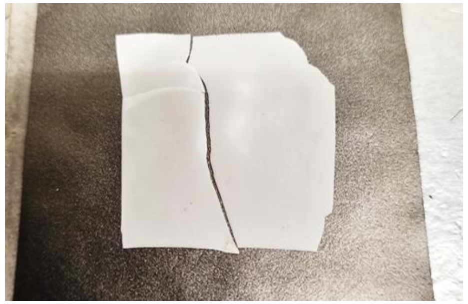
Mechanical Properties - Scale Up of Thin LLZO Sheets



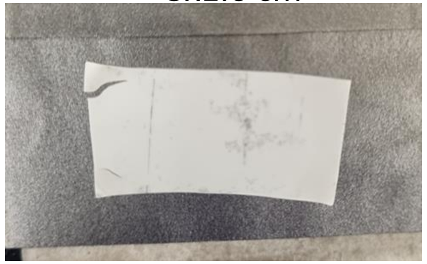
1.2 cm Diameter

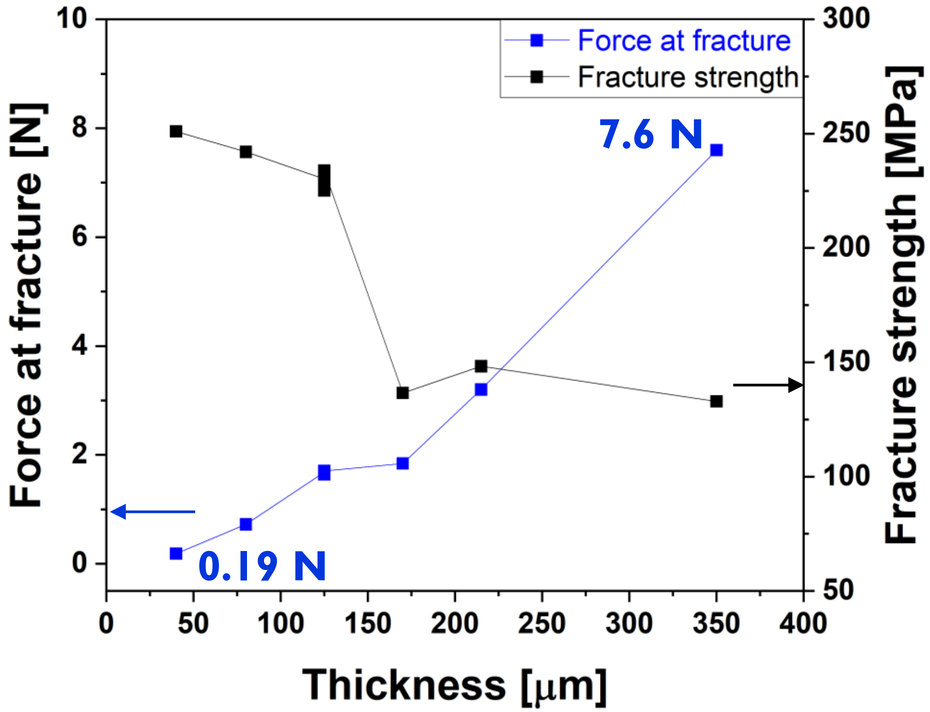


3x3 cm



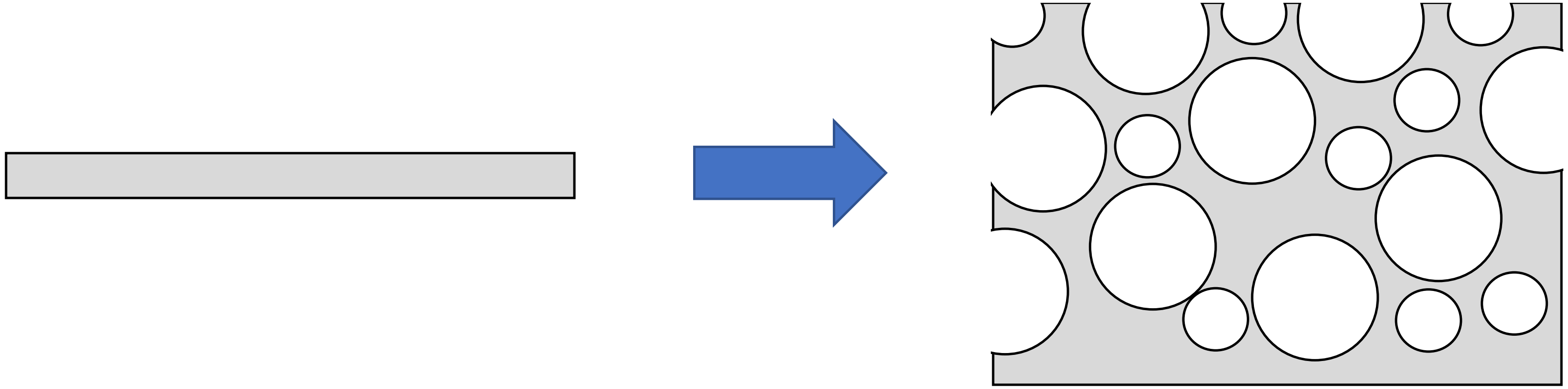
3x1.6 cm





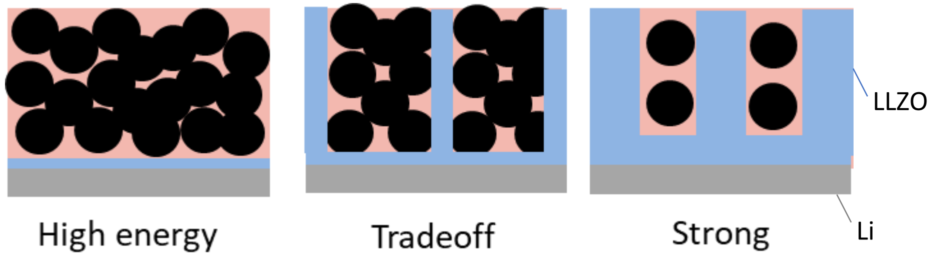
Similar mechanical properties for large and small sheets, but:
- **Large sheets are mechanically too weak** to handle
- Difficult to scale up to large area
- Difficult to reduce thickness lower than 80 μm

Gen 2 - Thin, Dense LLZO Supported on Porous LLZO Scaffold



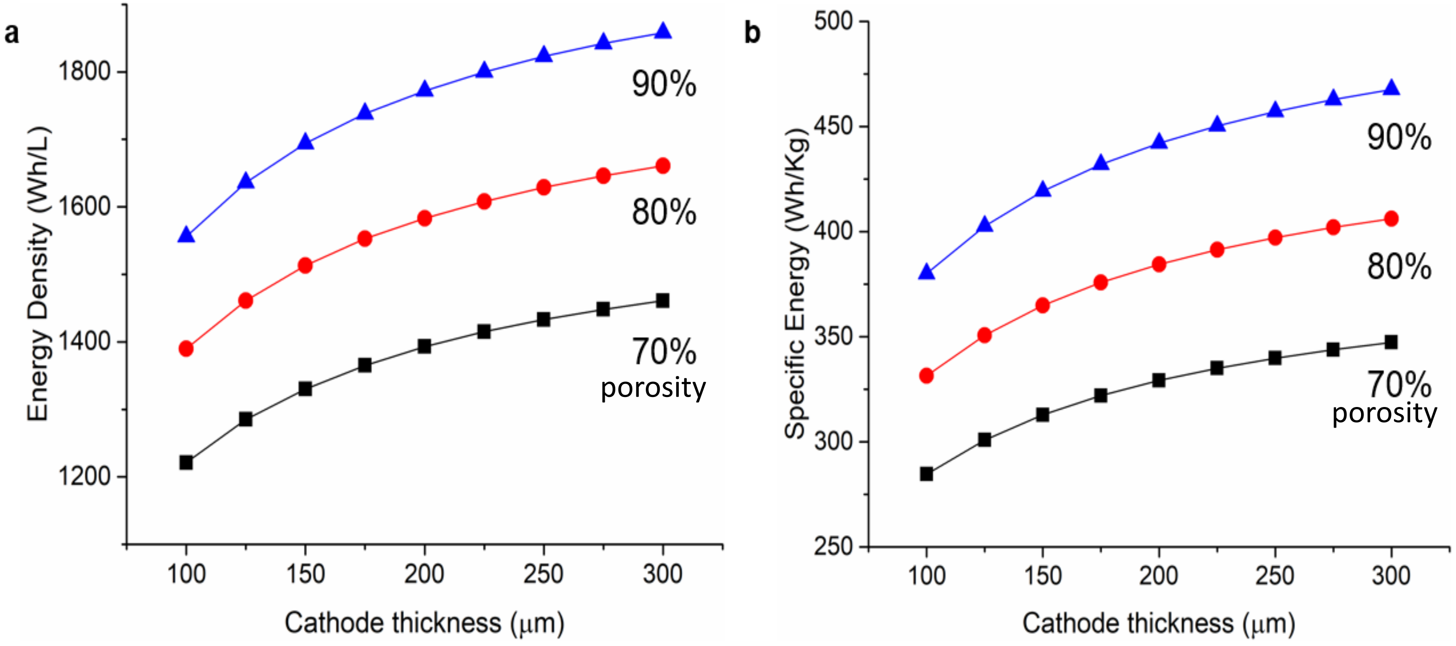
Thin Electrolyte Supported on a Scaffold

500 Wh/kg requires thick cathode, high loading of active material, thin electrolyte
These requirements are in conflict with mechanical requirements
Challenging to achieve with scalable processing



Targets
5-20 μm thick electrolyte
150-300 μm thick cathode
70-90 % Scaffold porosity
70-90% active material in pores

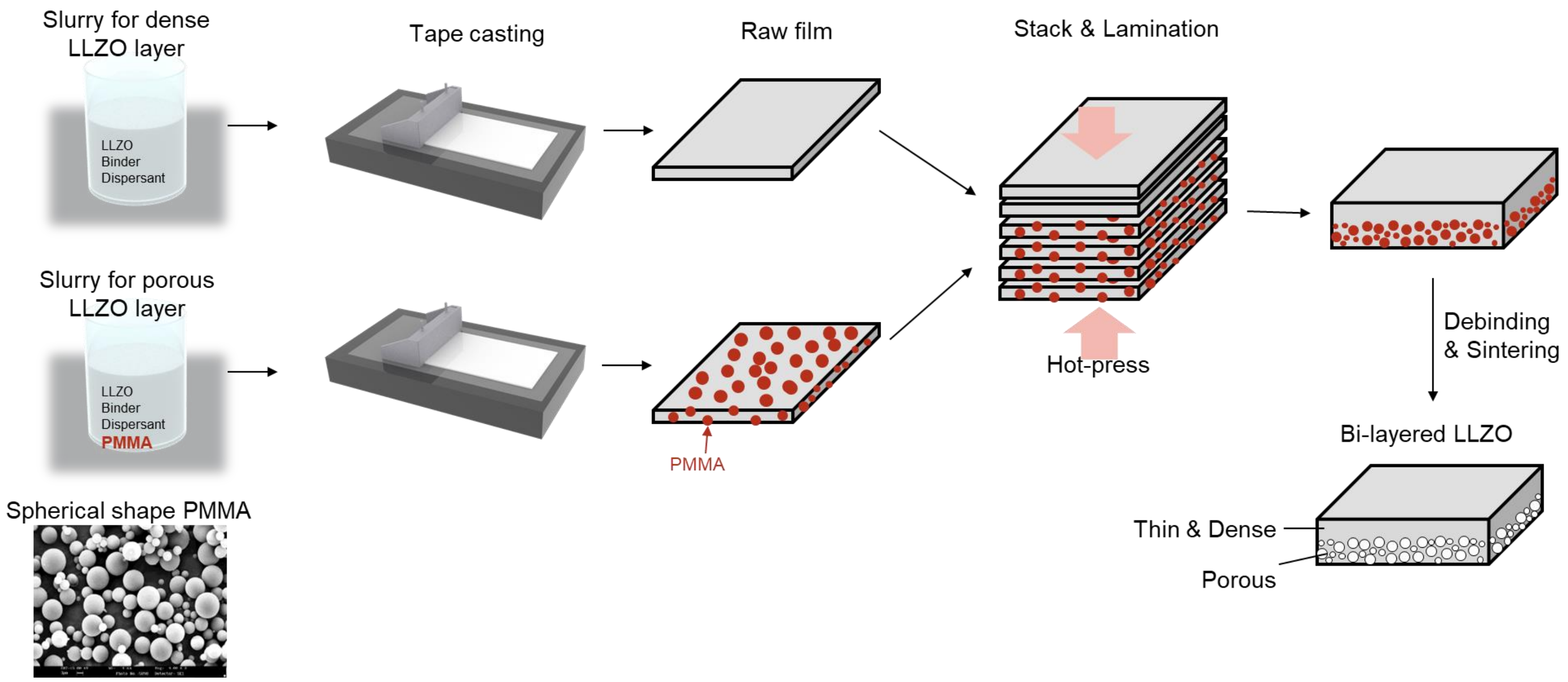
LLZO Scaffold porosity and thickness
20μm electrolyte, 74% NMC-26% SSE-C, C, binder

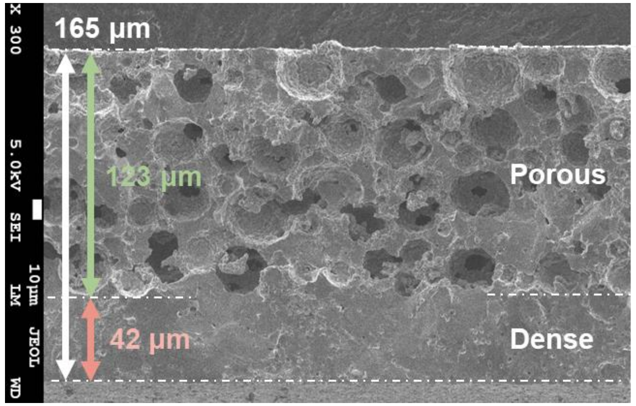


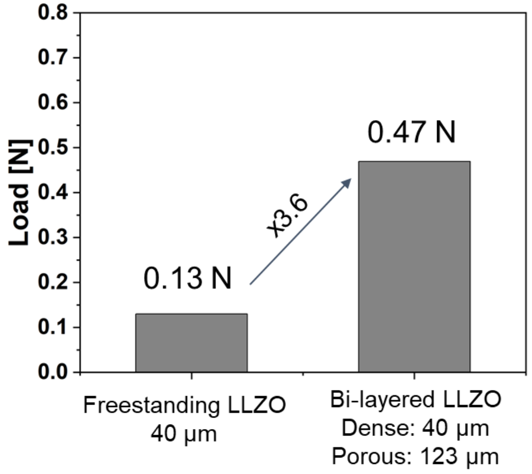
NMC cathode (180 mAh/g, 3.8V), filling fraction 74% of porous LLZO layer. Al and Cu current collectors included, secondary soft solid phase included, 20% excess Li, 20 μm thick LLZO dense layer.

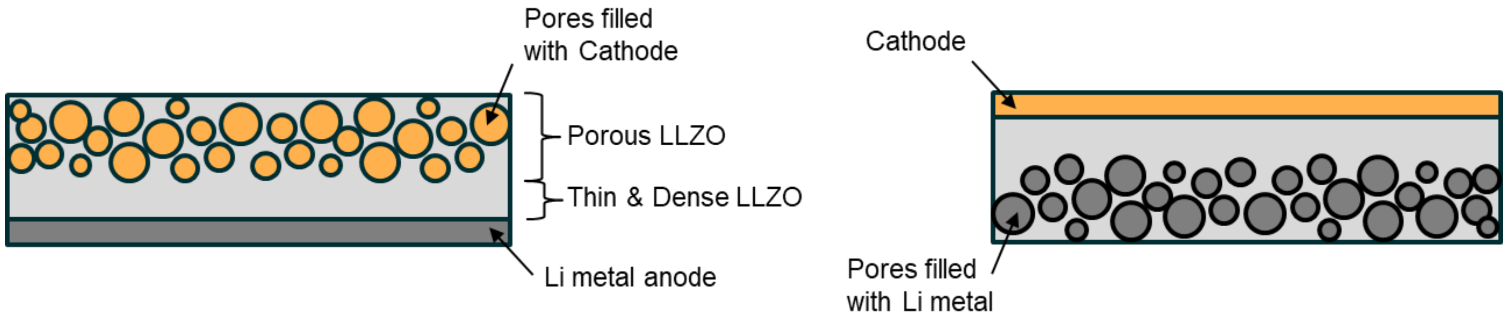
E. Yi, M. Doeff, et al., ACS Appl. Energy Mater. 2020, 3, 1, 170–175

Porous/Dense Bi-layer Tape Casting





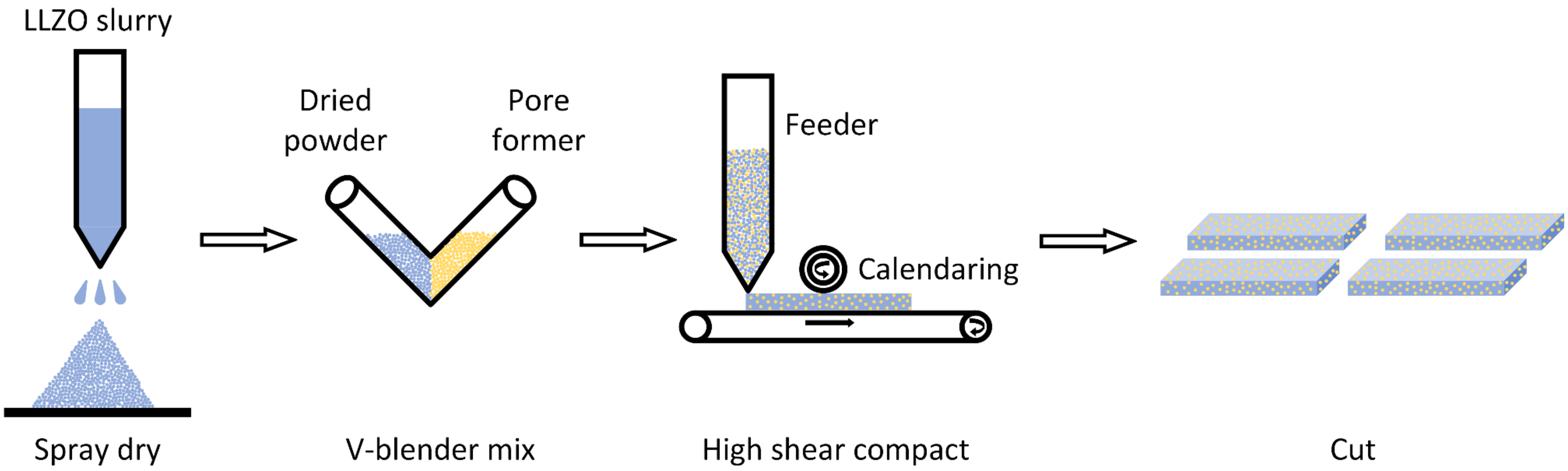


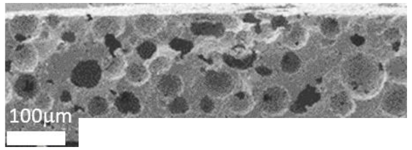


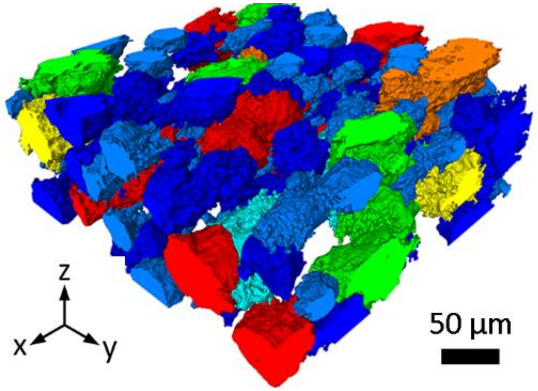
Thin electrolyte for low impedance

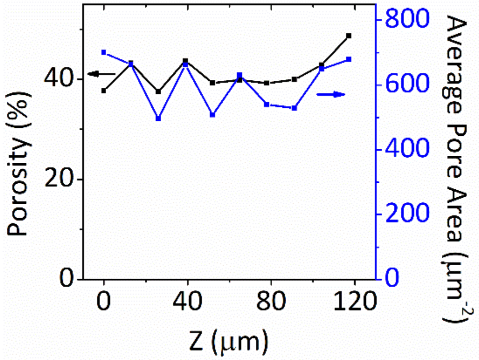
Porous support for mechanical strength

High Shear Compaction (Ragan Technologies) (2020-117)









Tapes with high quality and excellent dimensional tolerance

Uniform porosity

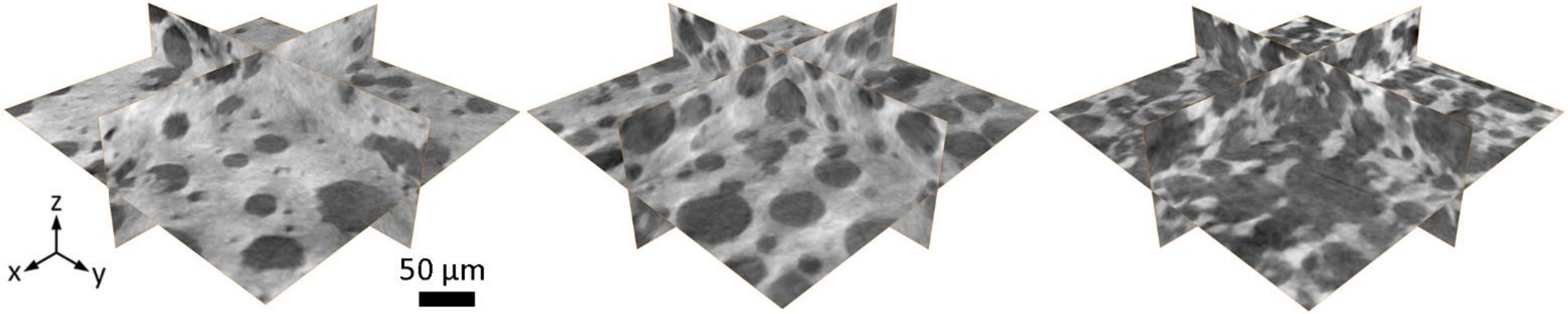
Thick electrode scaffold - 150 μm to 2mm

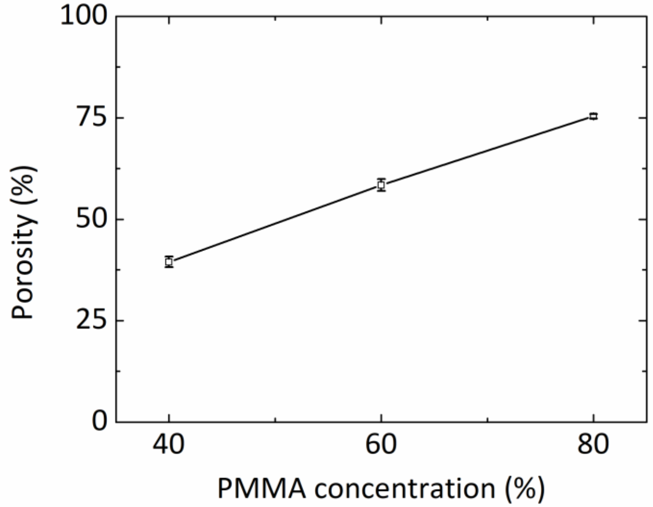
Aqueous processing

F. Shen, M.C. Tucker, et al., J. Amer. Ceram Soc. 105 (2022) 90-98

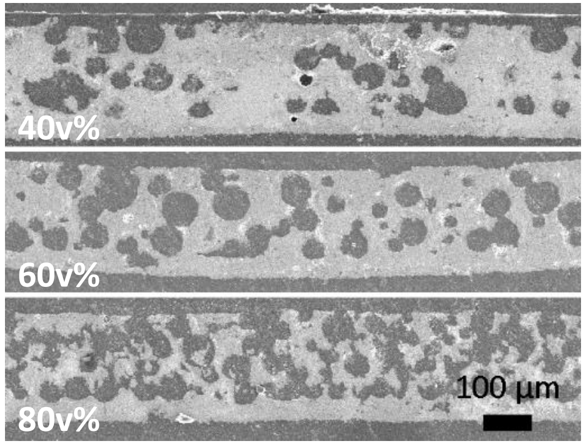
High Shear Compaction (2020-117)

40 vol% poreformer | 60 vol% | 80 vol%

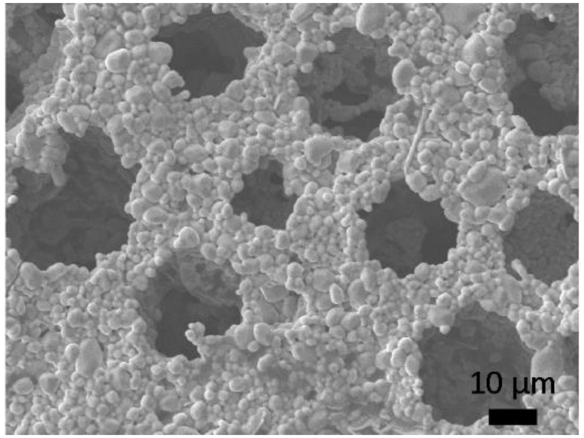




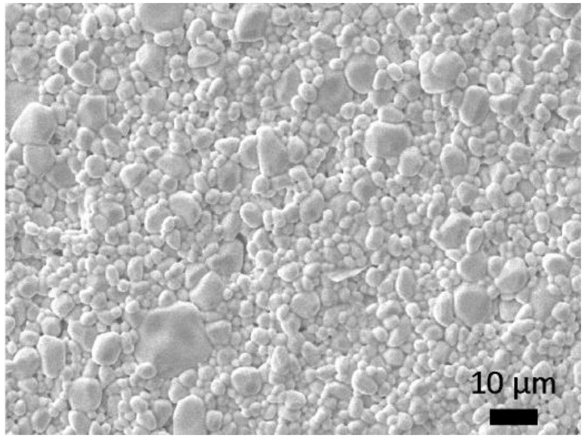
Cross section



Top view



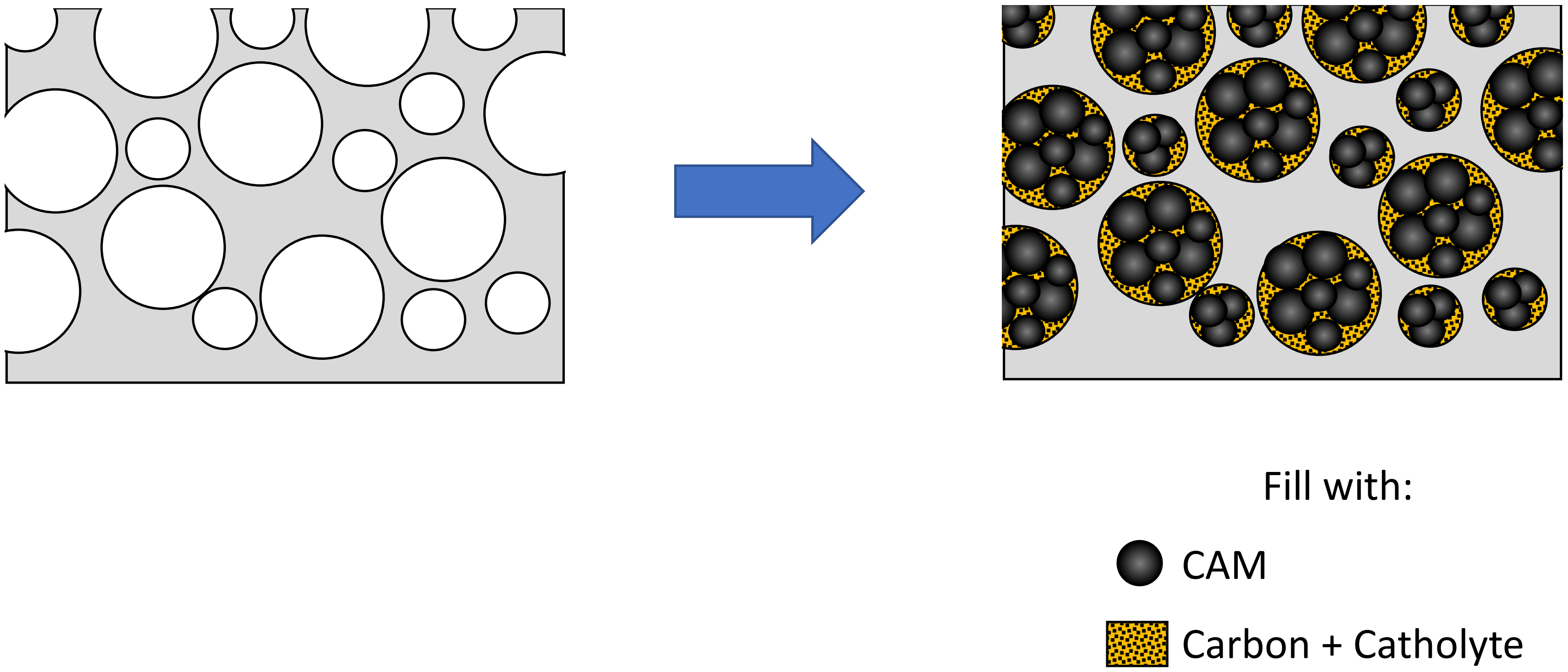
Bottom view



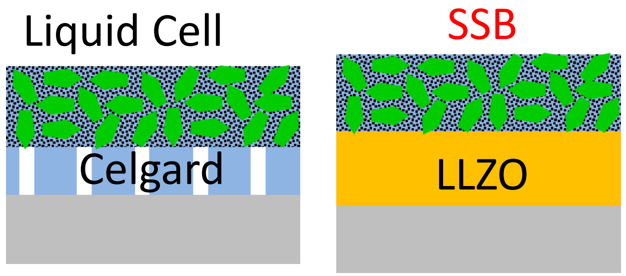
Easy bilayer processing

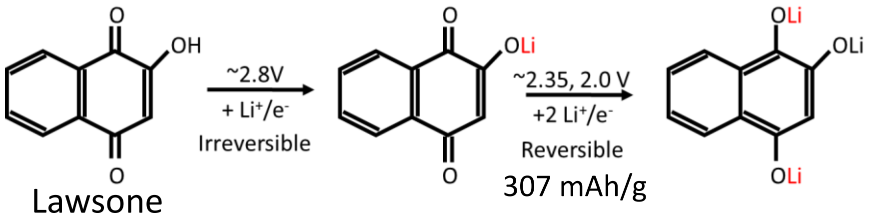
Tunable pore size and porosity

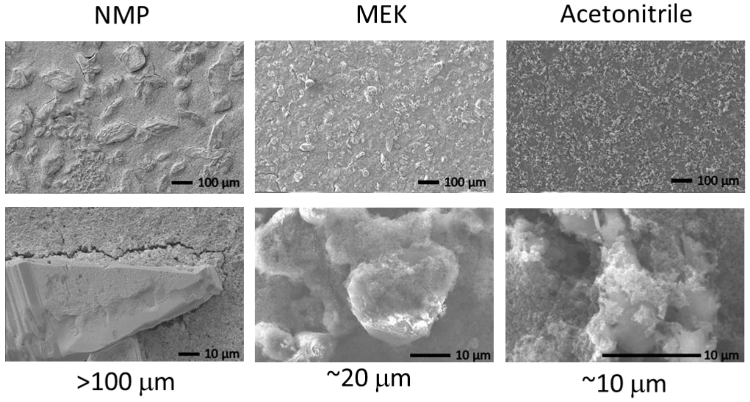
Infiltration of Cathode into Porous LLZO

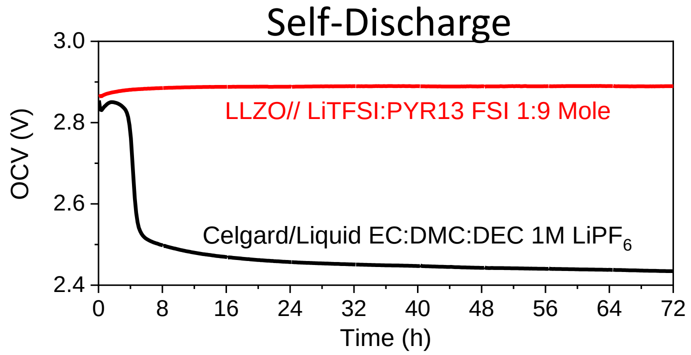


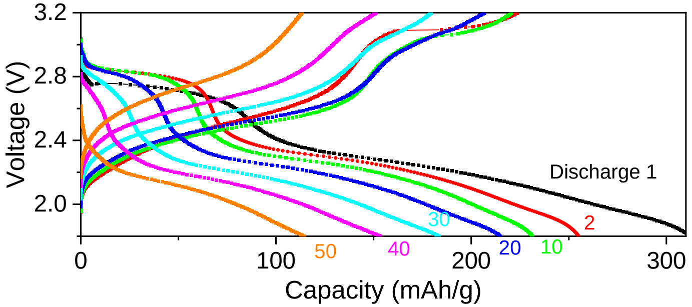
Organic Cathodes for Solution Processing (2022-130)

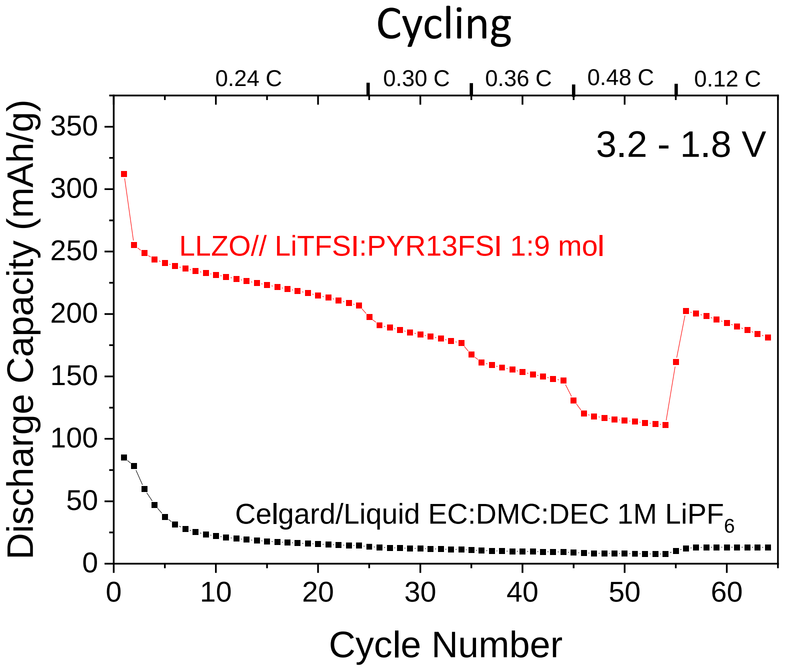












Lawsone dissolves in solvents (including liquid electrolyte)

Solid LLZO separator blocks crossover, enabling retention of capacity

→ Solvent evaporation rate →

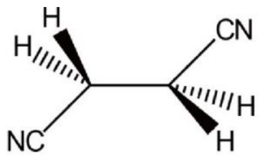
← Lawsone particle size ←

→ Ionic/electronic access to bulk →

R.A. Jonson, V.S. Battaglia, M.C. Tucker, ACS Appl. Energy Mater. 2023, 6, 745−752

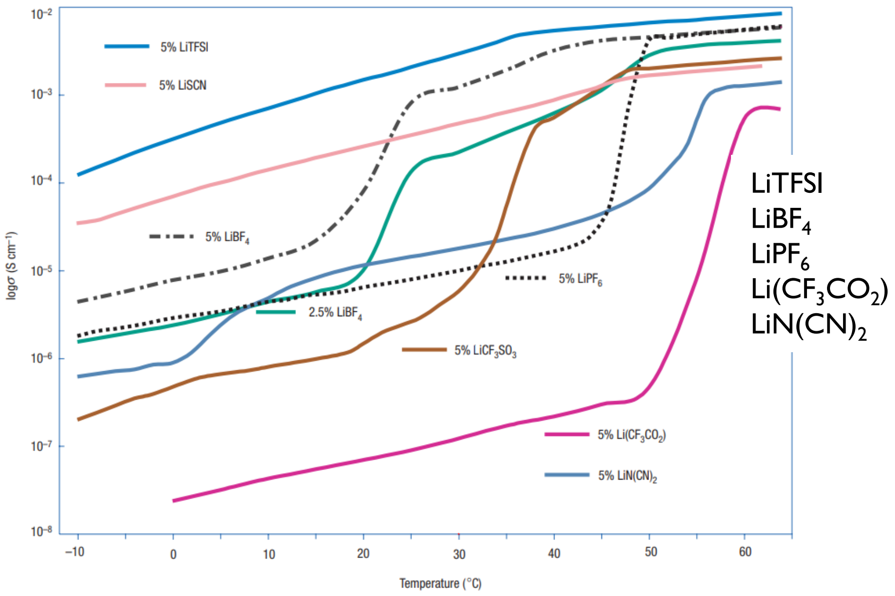
Melt-Processable Catholyte

Succinonitrile (SN) + Li salts as SSE



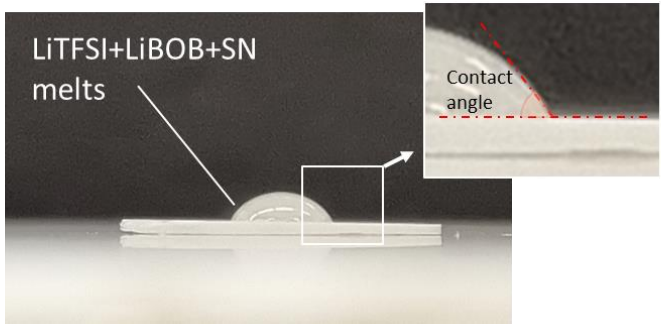
- $C_2H_4(CN)_2$
- Waxy colorless solid at room temperature
- Melting point: 57 °C (134.6 °F)
- Boiling point: 266 °C (510.8 °F)
- **Li salts can be dissolved to have Li-ion conductivity**

Succinonitrile + Li salts

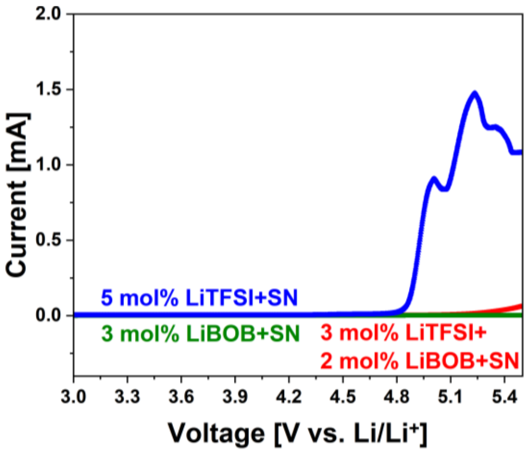


Nature Materials 3, 476–481 (2004)

3:2 mol% LiTFSI-LiBOB



	LiTFSI+SN	LiBOB+SN	LiTFSI+LiBOB+SN
Oxidative stability (vs. Li/Li^+)	> 4.7 V	> 5.5 V	> 5.0 V
Ionic Conductivity [S/cm]	3.46×10^{-3}	5.58×10^{-5}	1.87×10^{-3}
Electronic Conductivity [S/cm]	1.53×10^{-8}	3.79×10^{-9}	9.75×10^{-9}



LIBOB-limited solubility

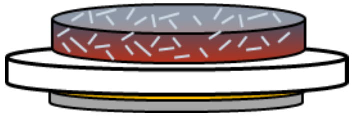
LiTFSI - lower oxidation potential

Mix - improved properties

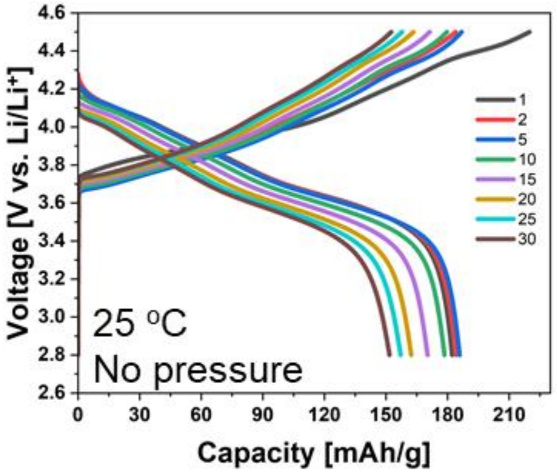
W. Go, M.C. Tucker, M. Doeff, J. Electrochem. Soc. 171 (2024) 20524

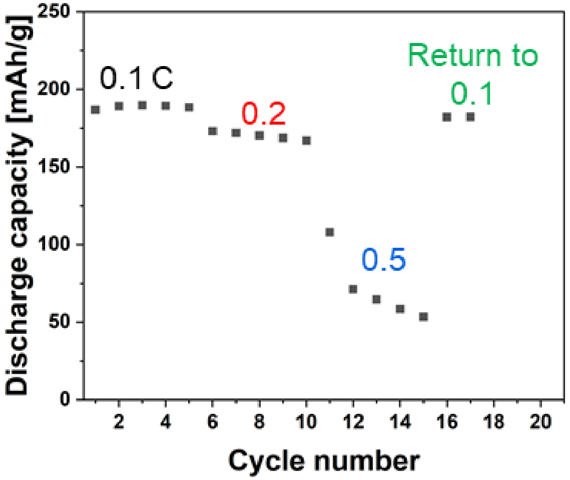
Cell Performance - SN-LiTFSI-LiBOB Catholyte

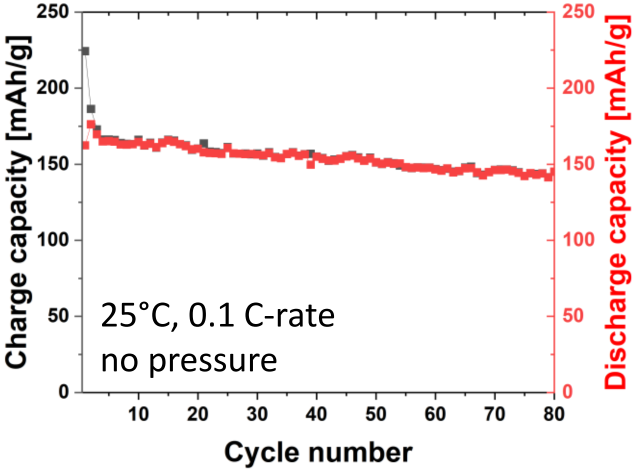
Thin free-standing LLZO ~80μm



	CAM	Catholyte	CM
Ratio [wt%]	54.4	39.0	6.6







Composite cathode

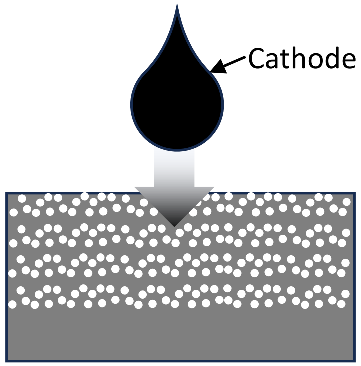
- Mixture of active material, solid catholyte, and conducting material
- $LiNbO_3$ coated NMC 811
- LiTFSI+LiBOB+Succinonitrile mixture ratio 3:2:95 [mol%], **solid** @ R.T.
- Carbon black

Functional solid cathode/catholyte

Deposited as melt (no solvent, high loading)

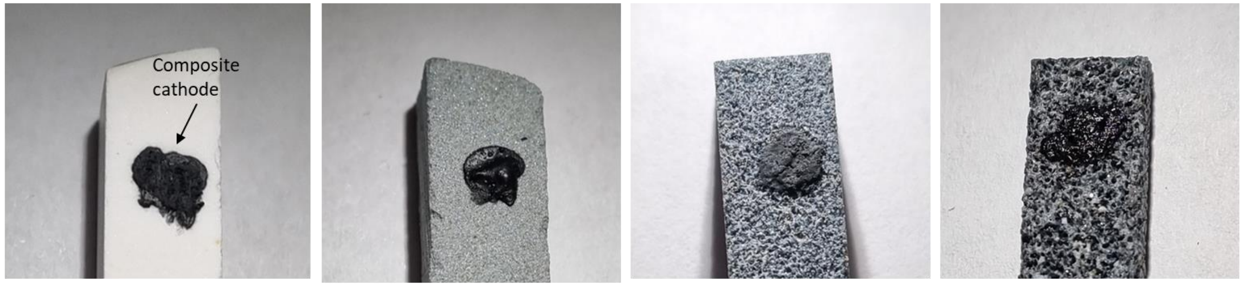
No stack pressure

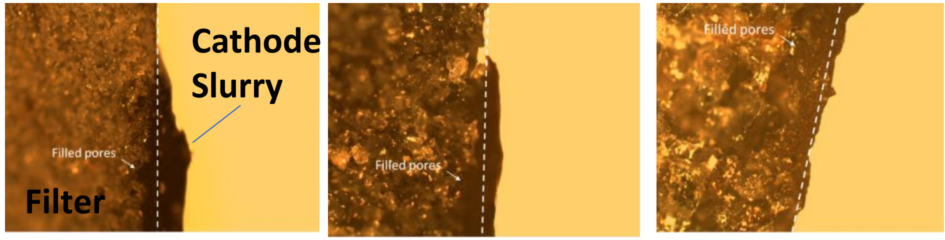
Cathode Slurry Infiltration is Challenging



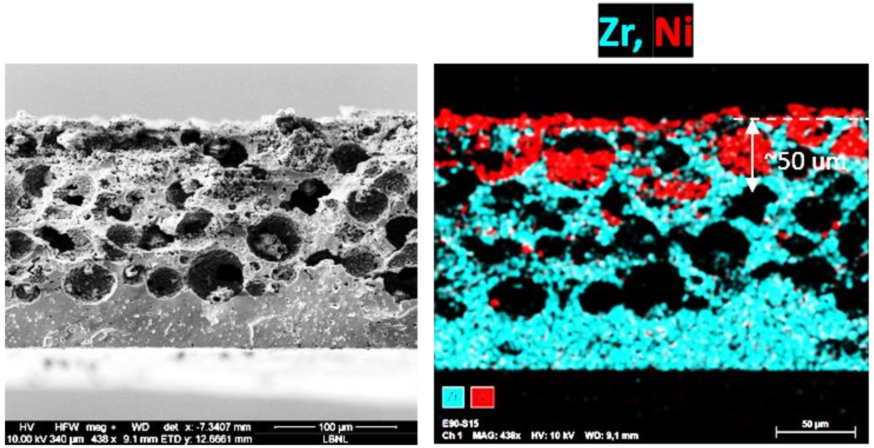
- Cathode infiltration
  - Cathode active materials are not easily infiltrated into the porous support

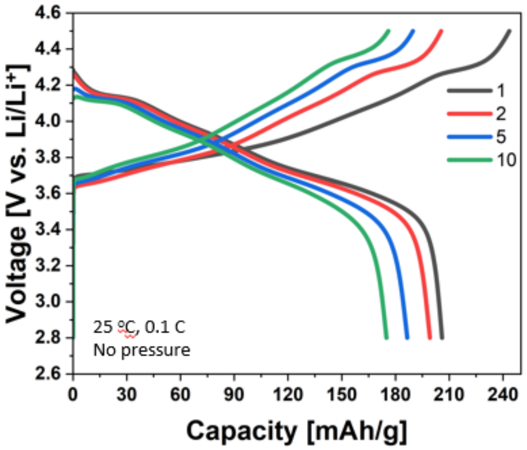
3 um pores | 10 um | 50 um | 120 um

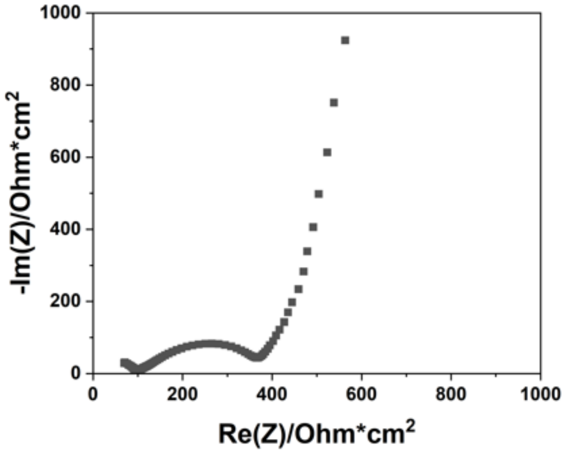




Bilayer LLZO



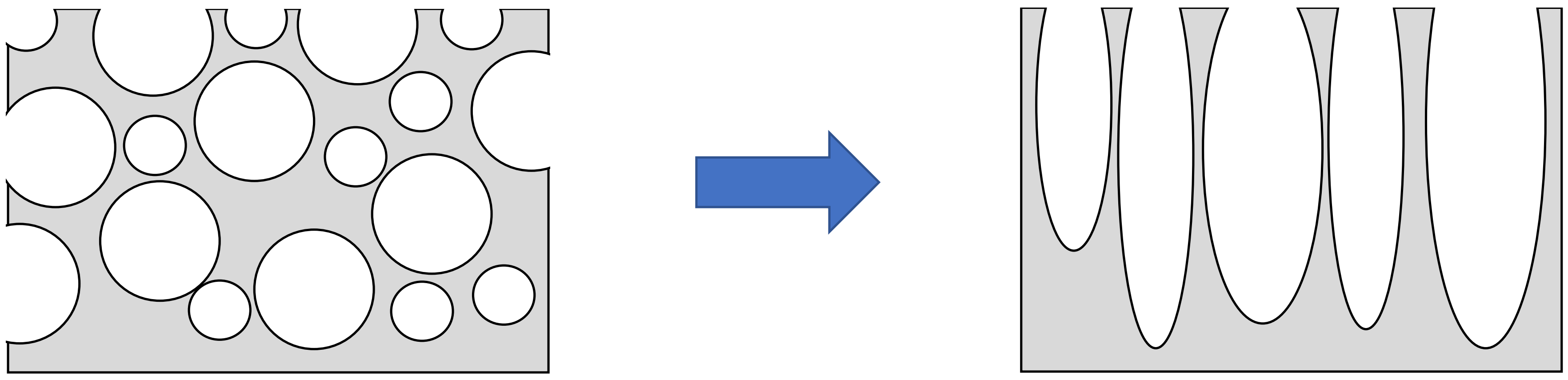




Minimum pore size for NMC cathode infiltration 50-120 μm

Pores must be well-connected

Gen 3 - Porous LLZO Support with Low-Tortuosity Pores

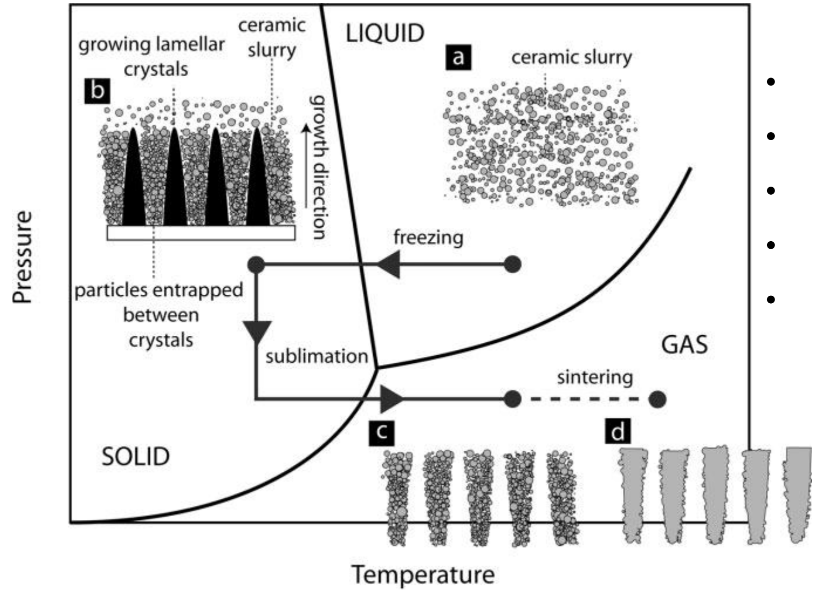


Cathode infiltration enabled by:

- Open faces
- Line-of-sight pores
- Large pore diameter

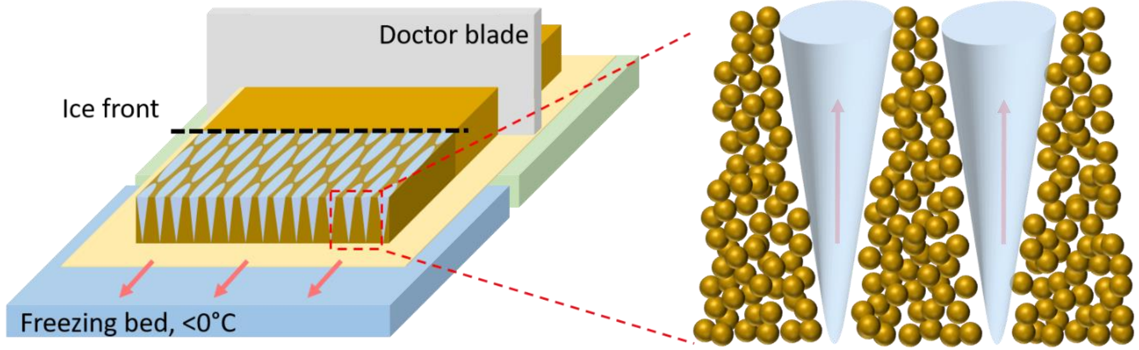
Freeze Tape Casting (2019-177)

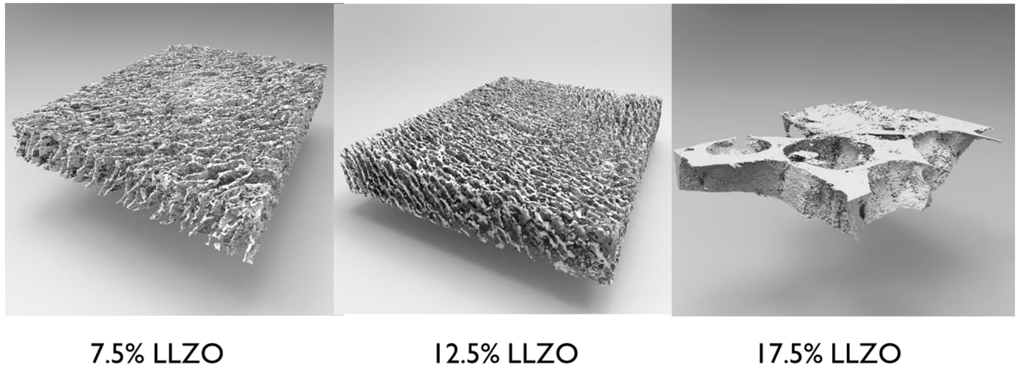
S. Deville, *Adv. Eng. Mater.*, 2008

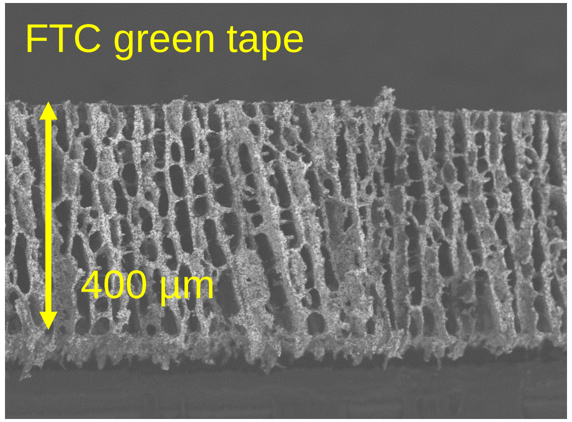


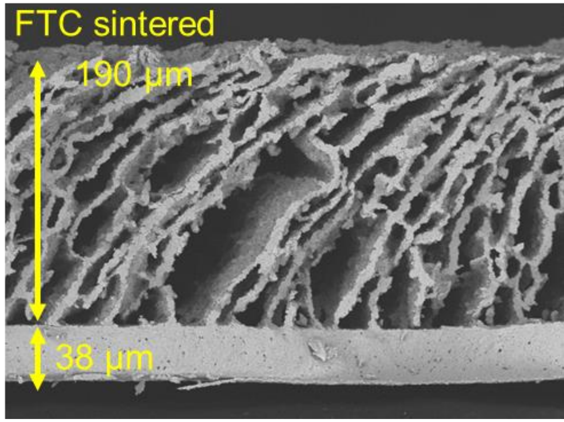
- Solvent type
- Solid loading
- Freezing temp. / cooling rate
- Additive type / concentration
- Particle properties

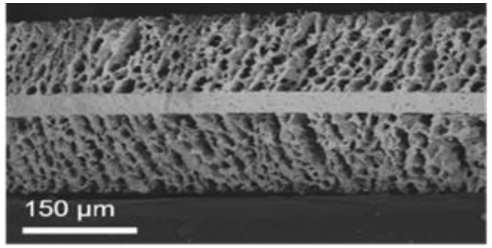
  (size, morphology, zeta-potential)









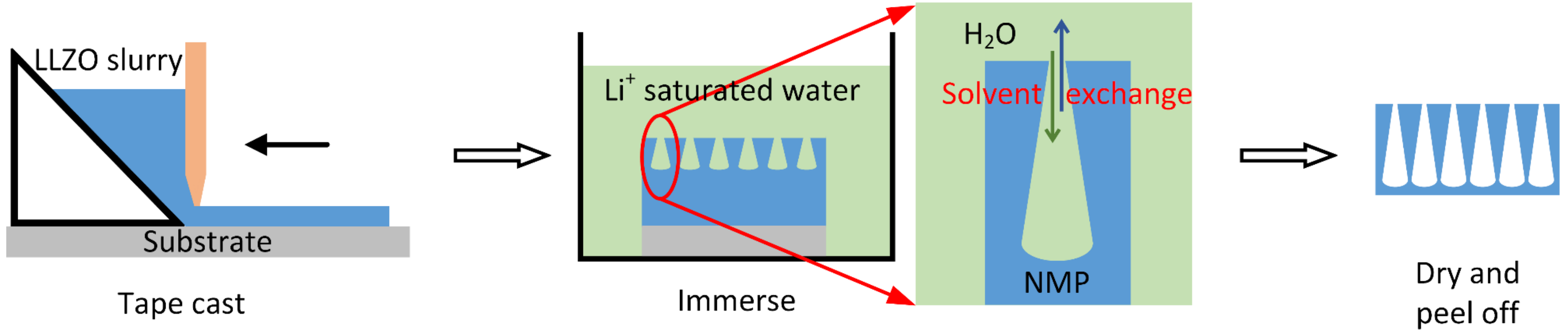


Bilayers and Trilayers with porous LLZO made by FTC
Dense LLZO made by tapecasting

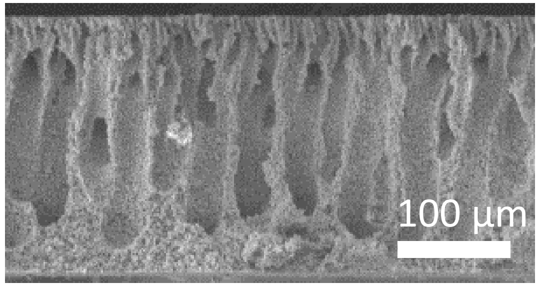
E. Yi, M.Doeff, et al., ACS Appl. Energy Mater. 2020, 3, 1, 170–175

Shen et al., ACS Appl. Mater. & Interfaces, DOI: 10.1021/acsami.9b11780 (2019).

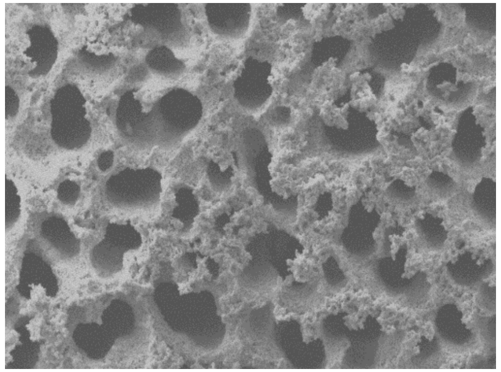
Phase Inversion Tape Casting (2020-117)

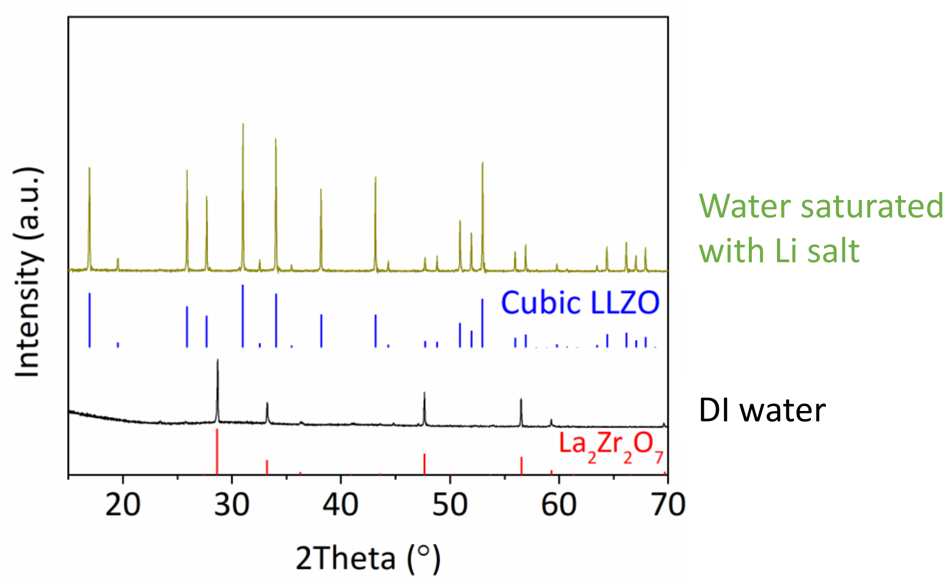


Cross Section



Electrode surface





Li-saturated water prevents leaching of Li from LLZO

Pores do not penetrate bottom of tape

- automatically forms electrolyte/electrode bi-layer

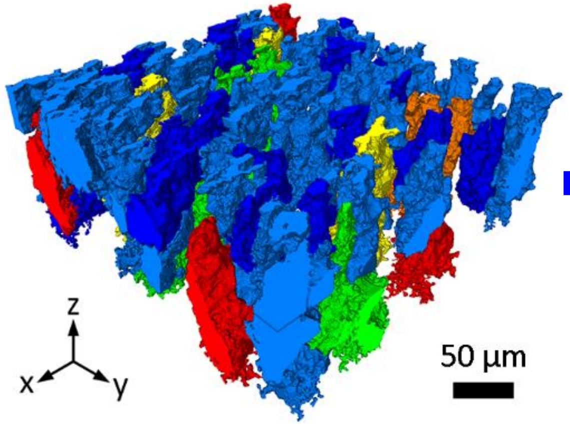
Tunable with temperature and solvent system

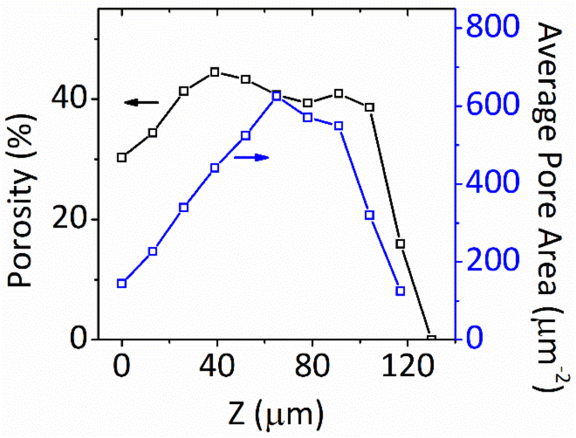
Vertical straight pores

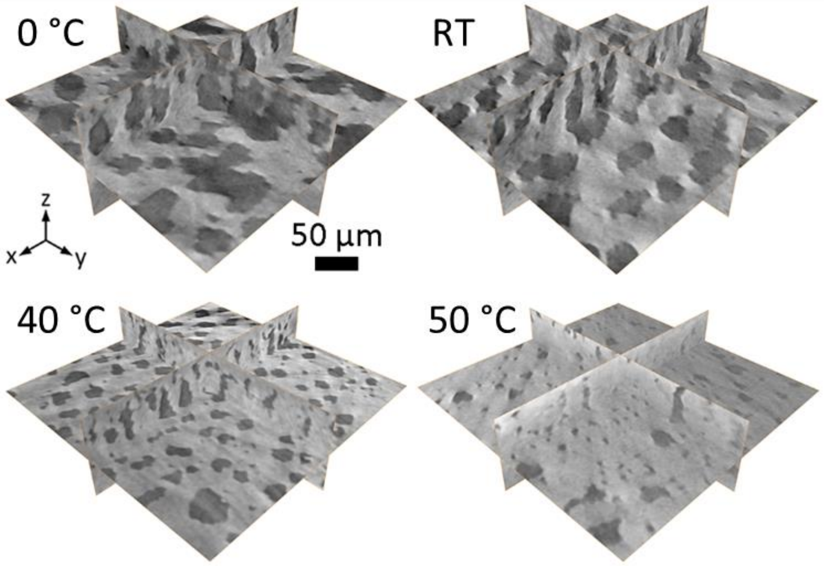
F. Shen, M.C. Tucker, et al., J. Amer. Ceram Soc. 105 (2022) 90-98

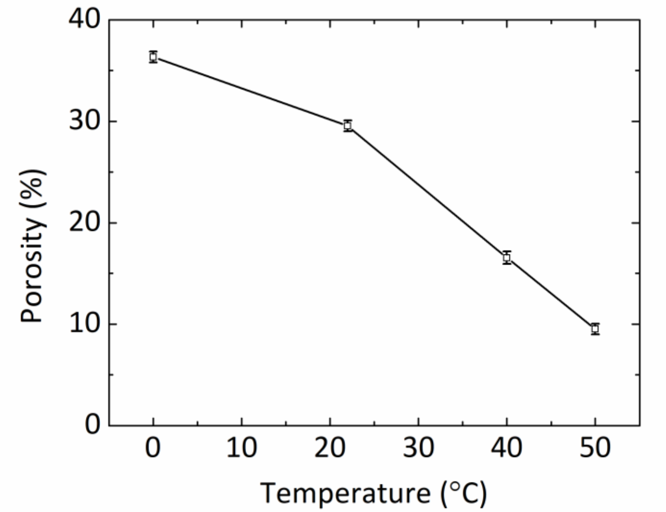
Phase Inversion Structure

(2020-117)







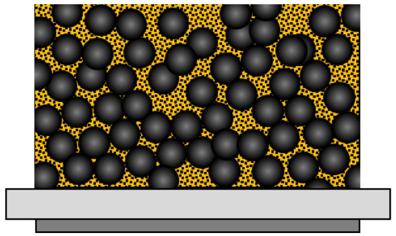


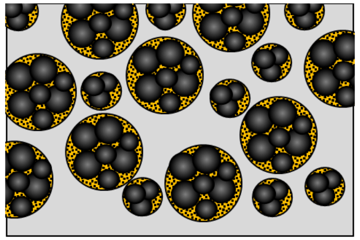
Larger pore size at lower water temperature

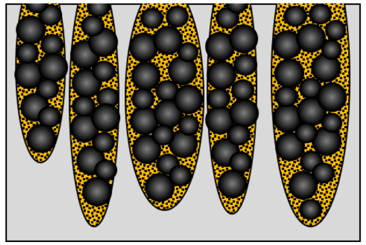
- Water bath temperature: 0 °C

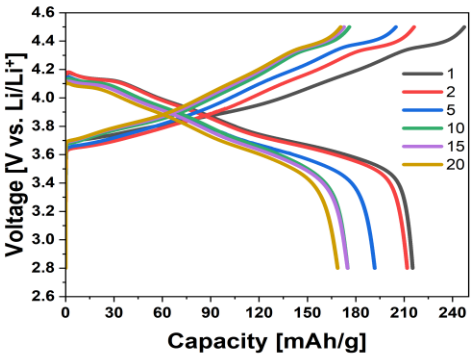
Higher bath temperature increases the solvent exchange kinetics and limits the growth of pores

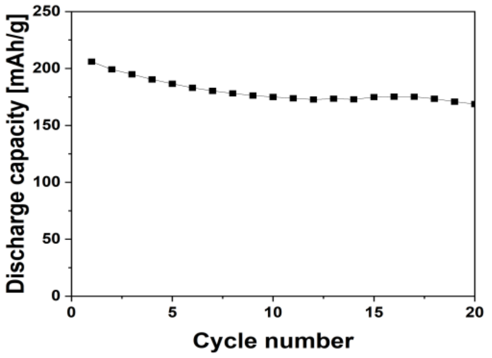
Summary











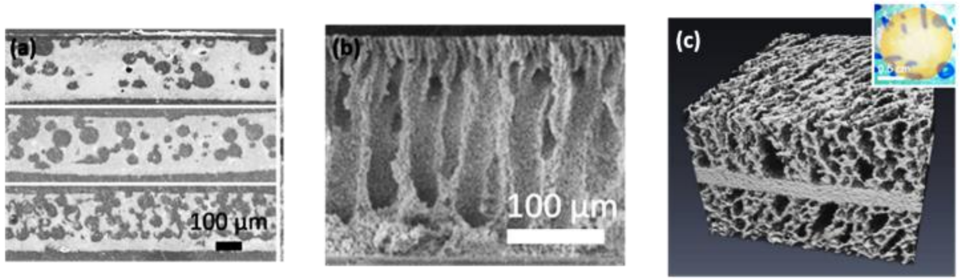
“Solid State Batteries Using Architecturally Controlled Rigid and Soft Solid Electrolytes” Eongyu Yi, Marca M. Doeff, Guoying Chen, Stephen Sofie, US 12,009,475

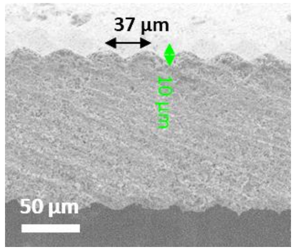
“Binder systems and methods for tape casting lithium garnet electrolytes” Robert Jonson, Michael Tucker, US 11,929,459

“Methods of fabricating porous ceramic electrodes for solid state battery applications” Michael Tucker, Fengyu Shen, US 11,942,622

“Battery with an Organic Cathode and a Solid Electrolyte” Robert Jonson, Michael Tucker, US20240162441A1

.....and more on the way





LLZO processing:

- Tape casting
- Texturing
- High Shear Compaction
- Phase Inversion
- Freeze Tape Casting

Cathode deposition:

- Solution casting organic CAM
- Slurry casting polymer catholyte
- Slurry casting OIPC catholyte

Funding and Acknowledgements

BERKELEY LAB
Lawrence Berkeley National Laboratory

LDRD

U.S. DEPARTMENT OF ENERGY
Energy Efficiency & Renewable Energy

VTO
Simon Thompson

ALS
ADVANCED LIGHT SOURCE

BATTERY 500 CONSORTIUM

STATE OF CALIFORNIA ENERGY COMMISSION
CALIFORNIA ENERGY COMMISSION

MOLECULAR FOUNDRY
RESEARCH MADE POSSIBLE BY MOLECULAR FOUNDRY
foundry.lbl.gov

ROLL TO ROLL CONSORTIUM
U.S. DEPARTMENT OF ENERGY
Hydrogen and Fuel Cell Technologies Office