New Electrode Designs for Ultrahigh Energy Density

Yet-Ming Chiang

Massachusetts Institute of Technology

May 11, 2011

Project ID#: **ES071**

Overview

Timeline

- Project start date: May 2010
- Project end date: Dec. 2012
- Percent complete: 38%

Barriers

- Low energy density
- Low rates
- Poor cycle life

Budget

- Total project funding: $555,000
- Funding for FY10: $278,000
- Funding for FY11: $277,000

Partners/Collaborators

BATT collaborators:

- A. P. Tomsia and Q. Fu (LBNL)

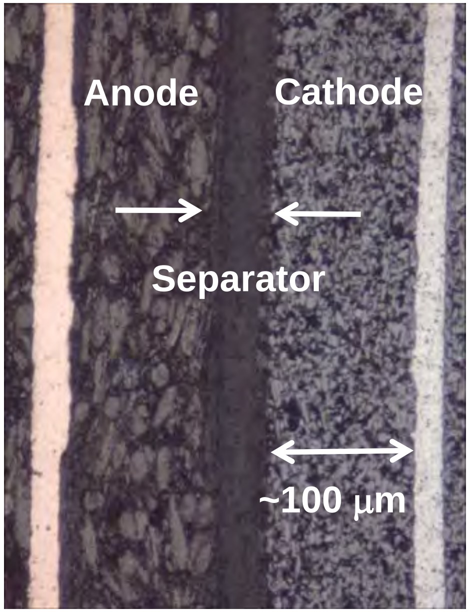
Other collaborators:

- J. Halloran (U. Mich)
- W. C. Carter (MIT)

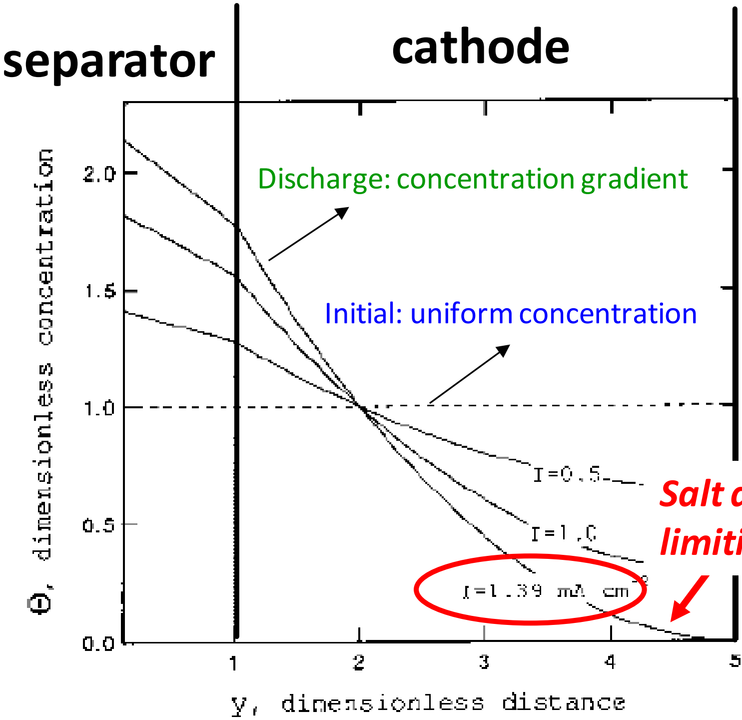
Objectives

- Develop a scalable high density binder-free low-tortuosity electrode design and fabrication process to enable increased cell-level energy density compared to conventional Li-ion technology for a range of electrode-active materials.
- Develop *in-situ* measurements of electronic and ionic transport vs. Li concentration using binder-free sintered electrode design
- Measure transport parameters of high voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ (undoped and doped) in collaboration with BATT researchers in new Ni/Mn Spinel Focus Group

Approach: Problem to be solved



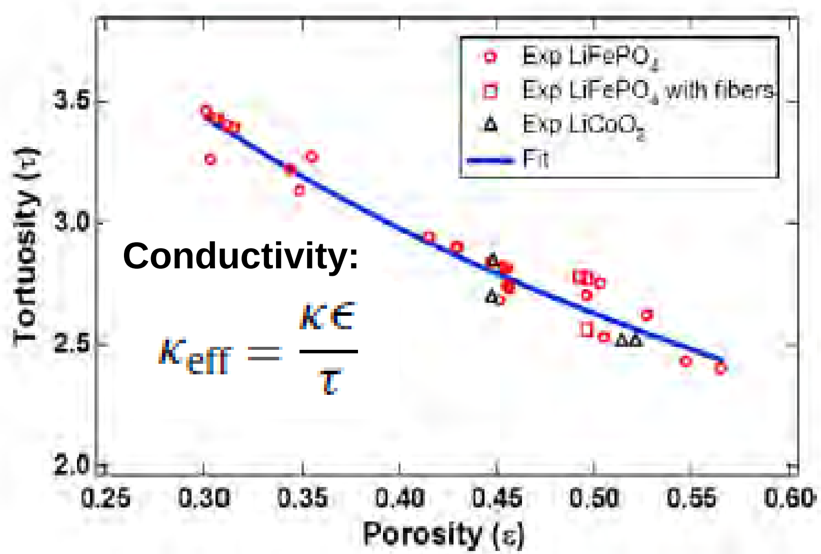
Q.C. Horn and K.C. White, Abstract #318, 211th ECS Meeting, 2007



M. Doyle and J. Newman, *J. Appl. Electrochem., 27, 846 (1997)*

Current Li-ion electrodes have a design compromise driven by manufacturing considerations:

- Calendaring powder-based electrodes for high *active fraction* results in pore networks with high tortuosity, filled with binder /carbon
- Electrodes must then be thin for high rate
- Thin electrodes result in high *inactive fraction* at cell level, lowers energy density
- *A vicious cycle*

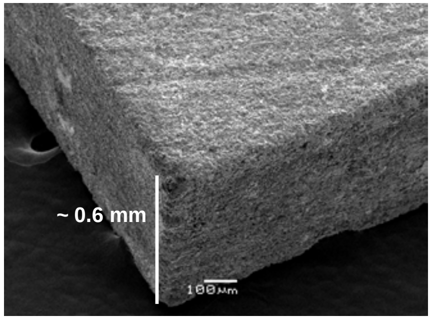


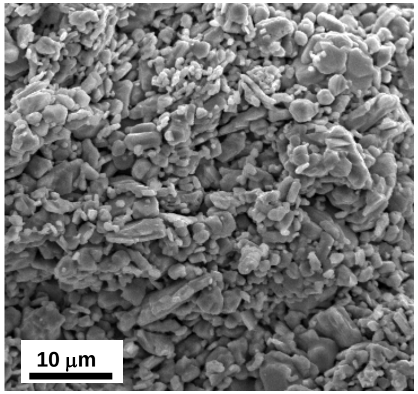
$$\kappa_{\text{eff}} = \frac{\kappa\epsilon}{\tau}$$

I.V. Thorat *et al.*, J. Power Sources, 188, 592 (2009)

Approach: High Density and Low Tortuosity

(1)

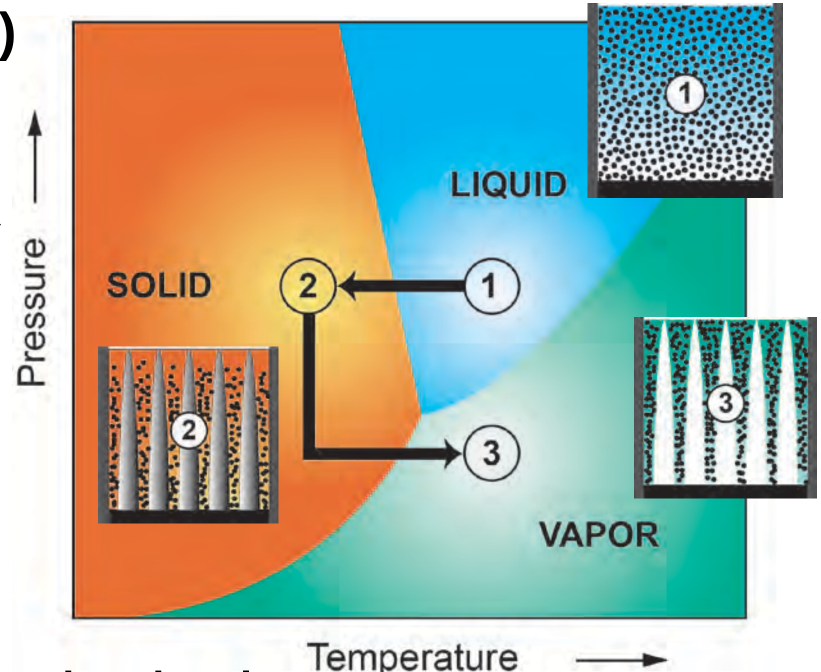




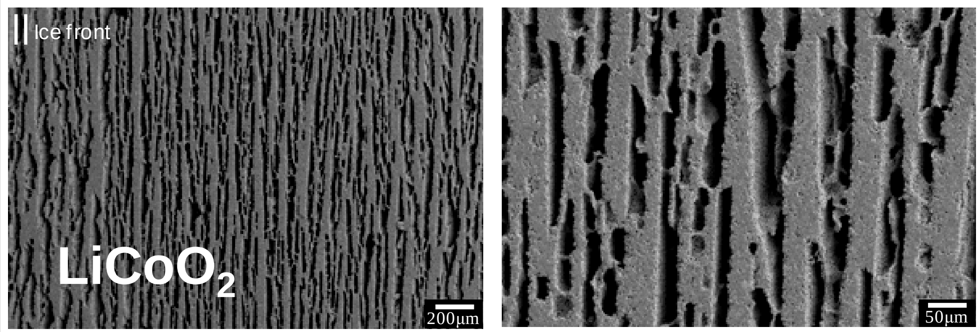
Monolithic cathode
Infiltrated by liquid electrolyte

Binder-free, high density (65-75 vol%) sintered electrodes at 200-700 μm thickness can be cycled at C/5-C/2 rates[1]

(2)

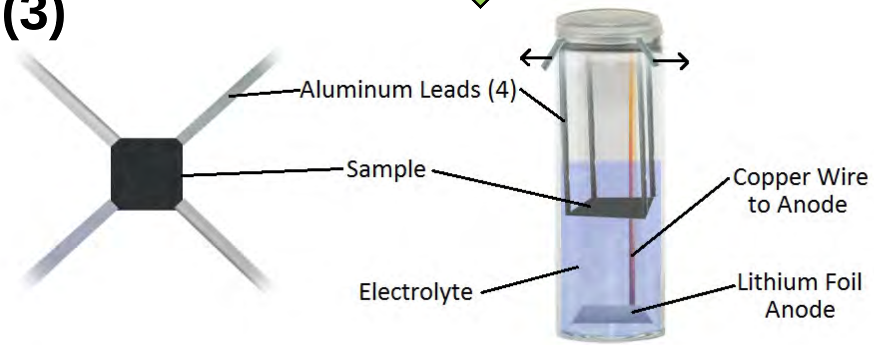


Directional Freeze-Casting



Electrodes with aligned pores of low tortuosity (τ ~1) and high sintered density (60-65 vol%)

(3)



In addition: Binder-free sintered electrodes are ideal format for *in-situ* characterization of electronic and ionic transport vs. Li concentration.

[1]**W. Lai, C.K. Erdonmez, *et al*., *Adv. Mater*., 22, E139-E144 (2010).**

Milestones

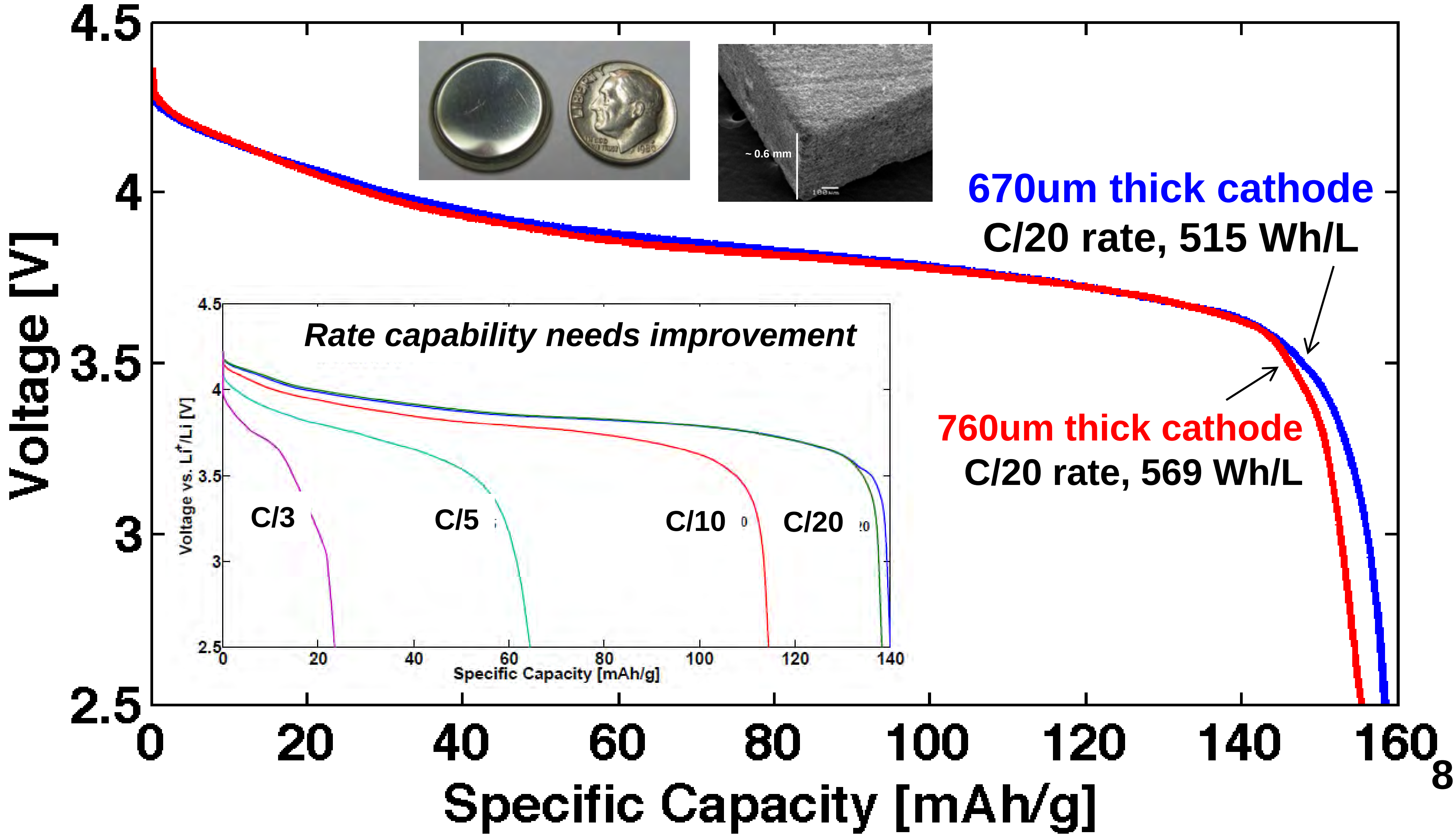
- Report fabrication procedure, structural characterization, and initial electrochemical test data for directional freeze-cast and sintered $LiCoO_2$ electrodes in laboratory scale lithium half-cells. (March 11) **COMPLETED**
- Report results of sintering process development study for high-density additive-free $LiNi_{0.5}Mn_{1.5}O_4$ electrodes. (June 11) **ON SCHEDULE**
- Report electrochemical test data for high-density additive-free $LiNi_{0.5}Mn_{1.5}O_4$ cathodes in laboratory scale lithium half-cells. (Sept. 11) **ON SCHEDULE**

FY10 Technical Accomplishments

- **Demonstrated High Energy Density Potential of Additive-Free Sintered Electrodes at Coin Cell Scale**
- **Developed Freeze-Casting Approach for Fabricating High Density Low Tortuosity Battery Electrodes**
- **Obtained PHEV/BEV-Capable Rate Capability in Freeze-Cast and Sintered $LiCoO_2$ Cathodes**
  - **Demonstrates importance of low tortuosity**
  - **Validates technical approach**
- **Initiated Transport Measurements in Li/Mn Spinel**

FY10: Demonstrated High Energy Density Potential of Binder-Free Sintered Electrodes

- 2016 Coin Cells (half cells) with >500 Wh/L Energy Density
- 74 vol% sintered $LiCoO_2$, no binder or conductor
- *42 mAh/cm²* area capacity is >10x that of conventional electrodes



FY10: Applied Freeze-Casting Approach to Battery Electrodes for First Time

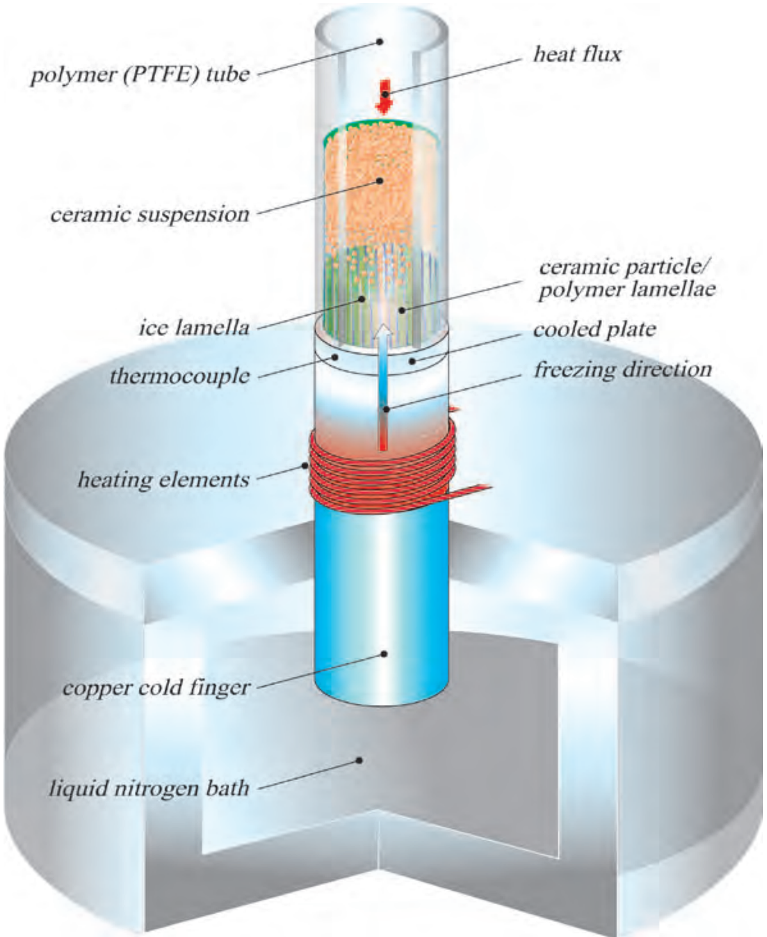
Collaboration:

(1) Freeze-casting done at LBNL (Q. Fu and A.P. Tomsia)

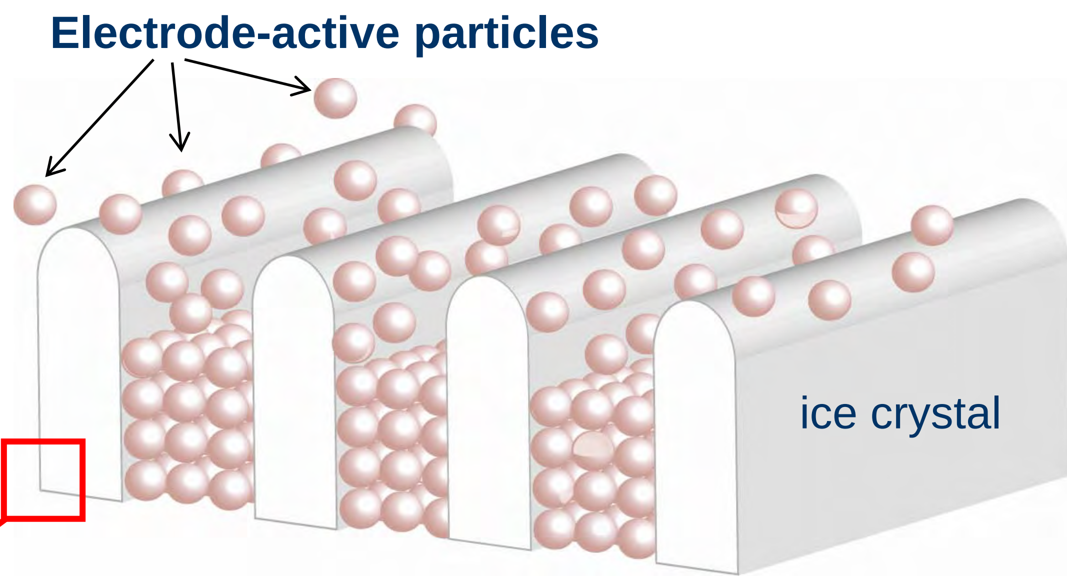
(2) Freeze-casting study explored effects of:
- $LiCoO_2$ solids fraction
- Freezing rate (e.g., 5 C versus 1 C/min)
- Additives to control pore orientation, morphology
- NO additives remaining in electrode after sintering

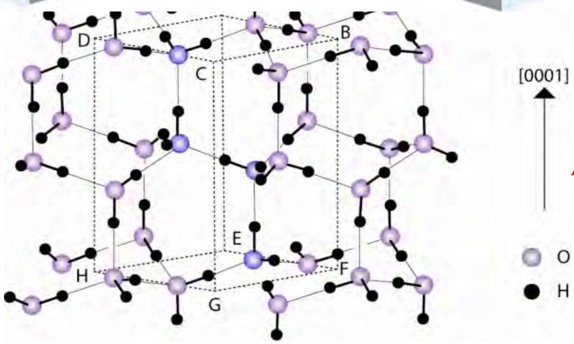
(3) Electrochemical testing done at MIT (A. Ransil, C.-J. Bae, Y.-M. Chiang)

Freeze Casting Of Solid/Liquid Mixtures Produces Lamellar Structures



- **After ice removal, porosity is created where the ice crystals grew**
- **Controlling ice freezing rate dictates morphology of porous scaffolds**

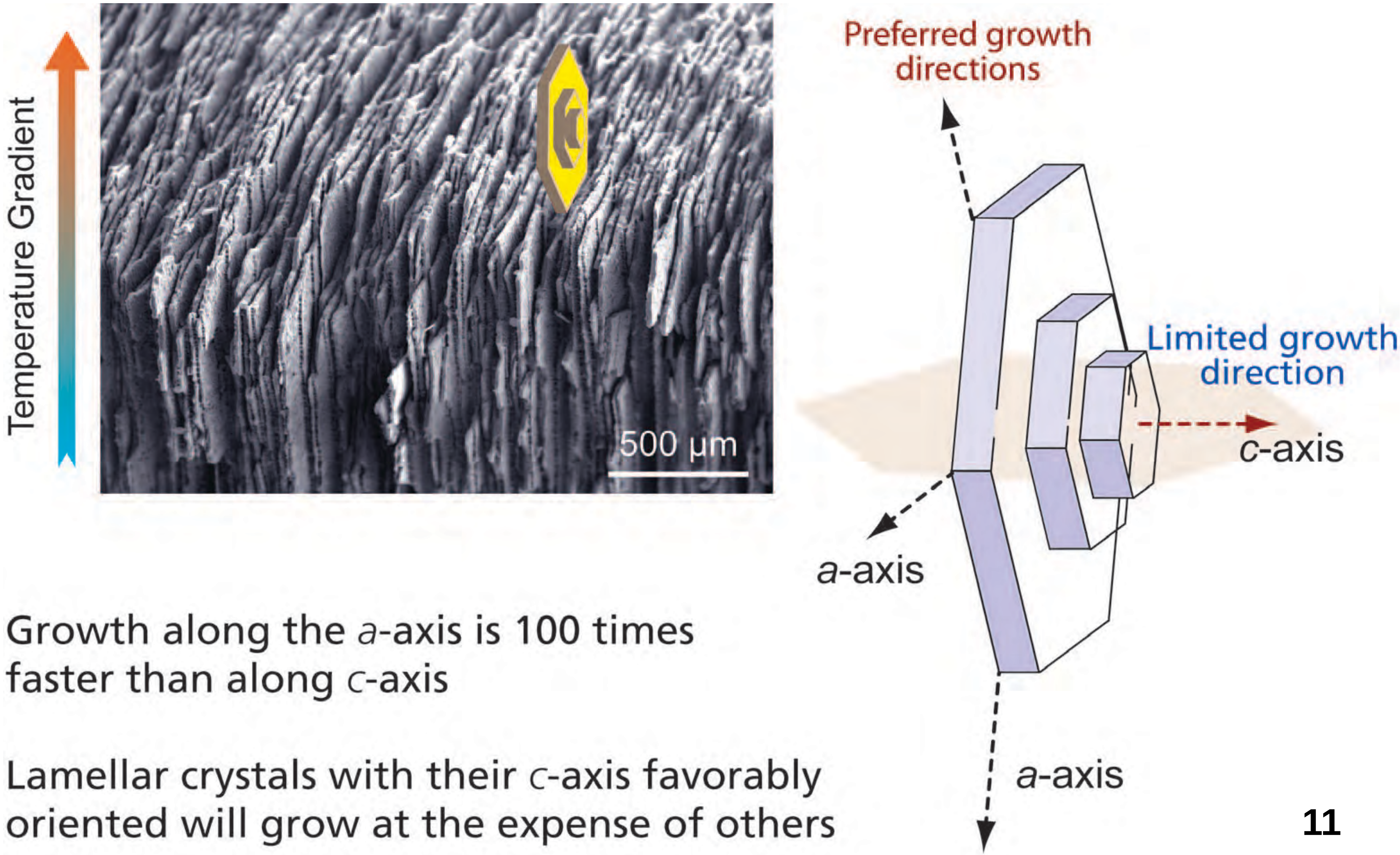




crystal structure of ice

Deville, Saiz, Nalla, Tomsia, *Science*, 2006, Wegst, *Phil. Trans.*, 2010

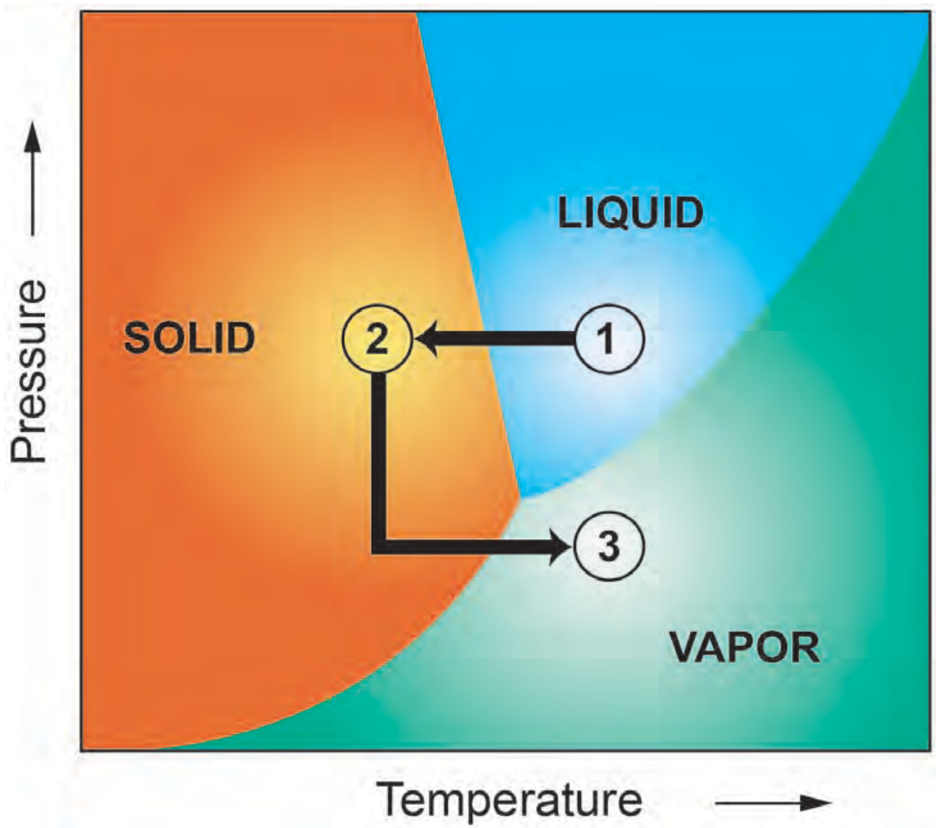
Lamellar Growth Anisotropy Of Ice Can Produce Aligned Electrode Pore Structure

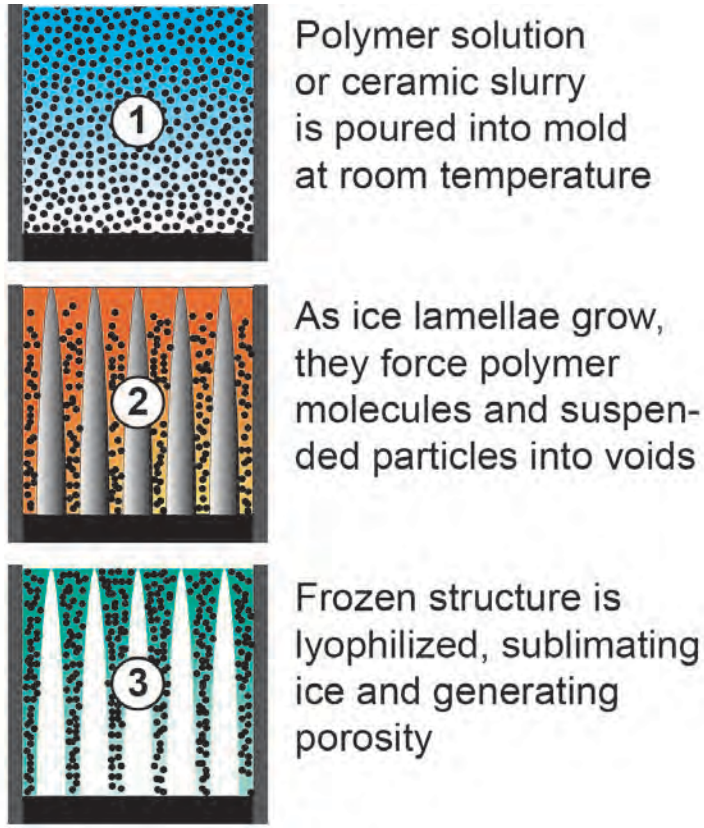


Growth along the *a*-axis is 100 times faster than along *c*-axis

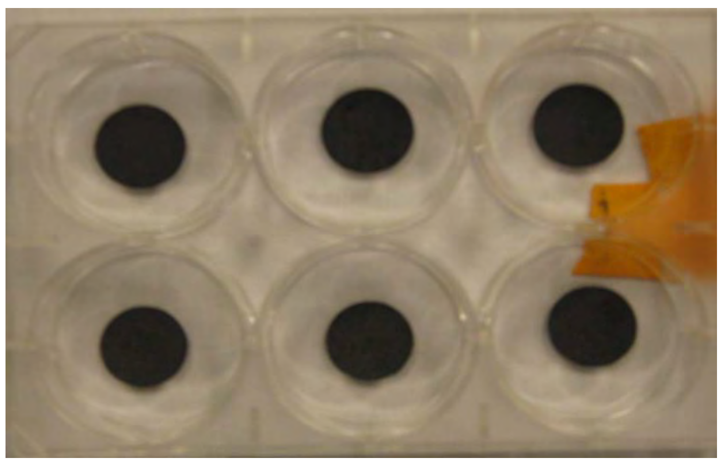
Lamellar crystals with their *c*-axis favorably oriented will grow at the expense of others

Electrode Processing Steps





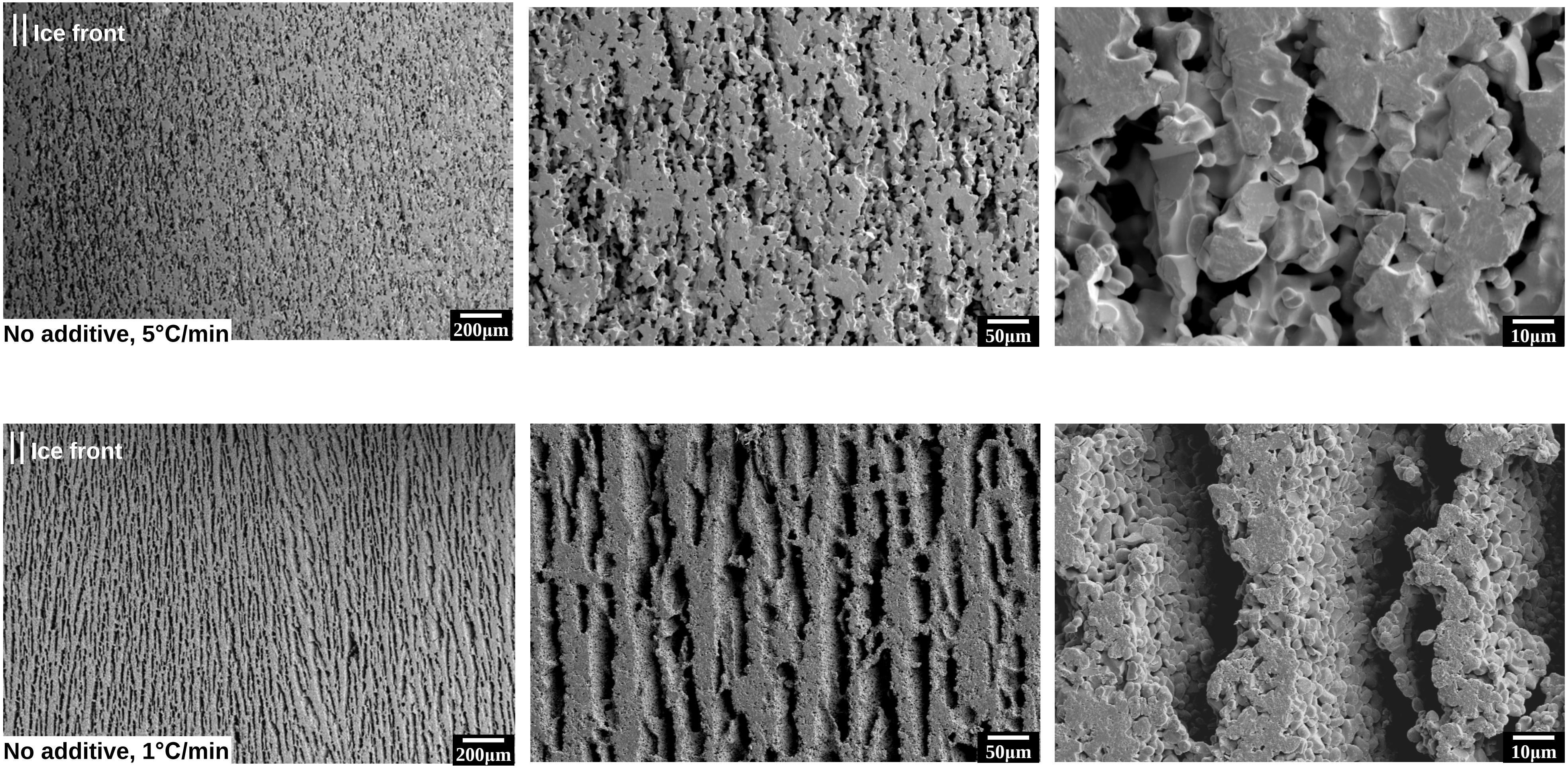
Structure is then *sintered* to produce electrodes for testing:



15 mm dia. electrodes

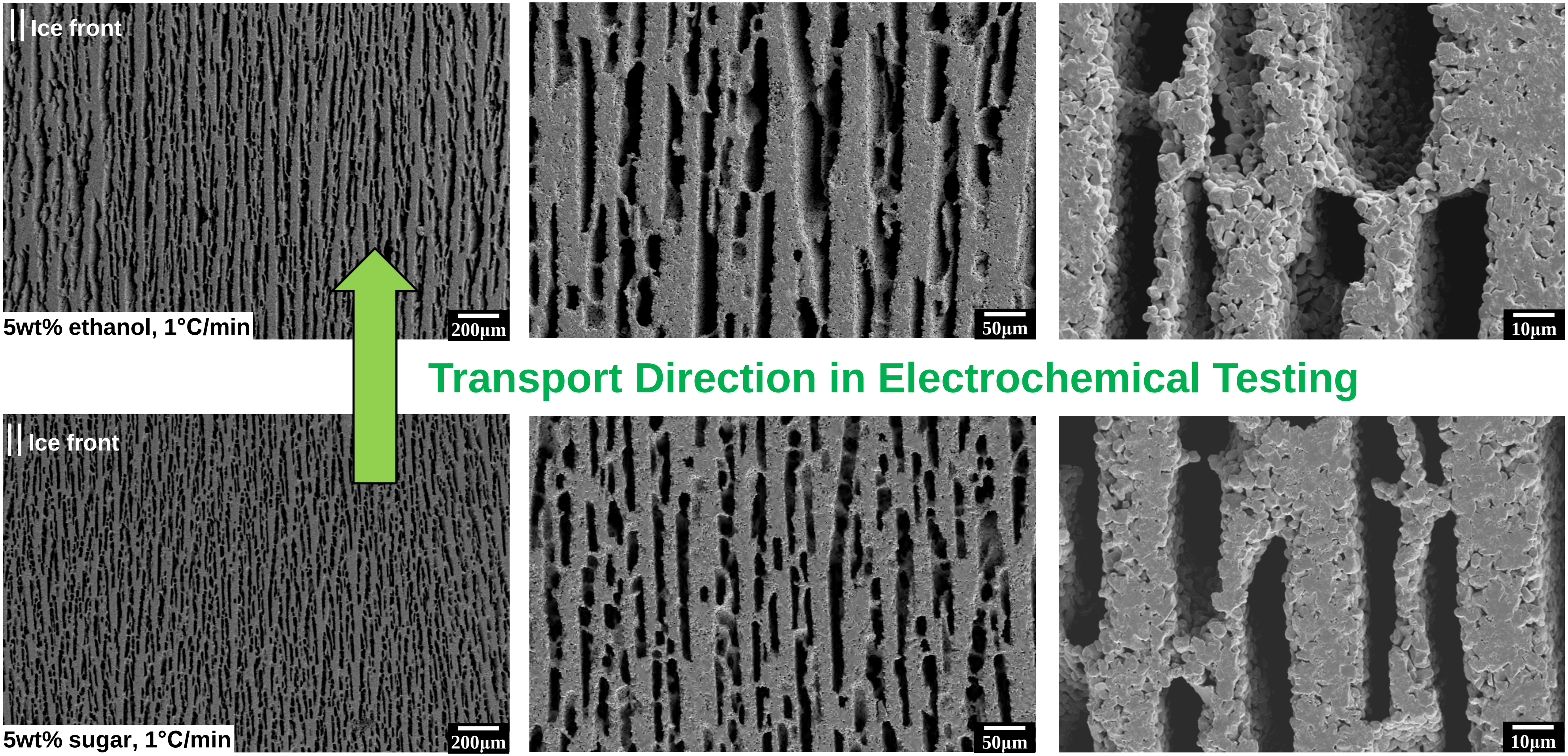
Wegst, *Phil. Trans.*, 2010

Example of Results: Effect of freezing rate



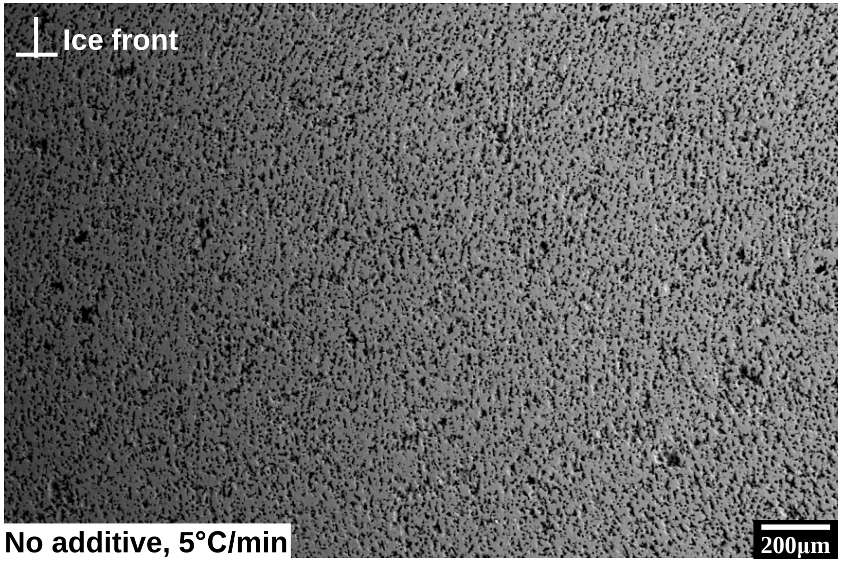
- Freezing rate affects growth rate and growth anistropy of ice Pore former
- Lower freezing rate produces larger pores, lower tortuosity
- Samples are shown after final sintering

Example of Results: Effect of additives

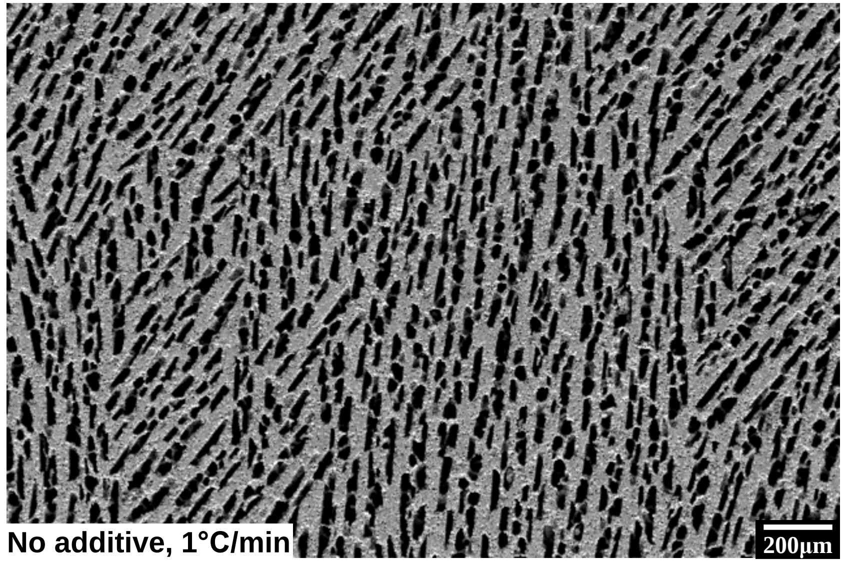


- Hygroscopic additives (alcohol, sugars) influence ice crystal morphology
- Extent of cross-branching (pore channel blocking) can be tuned

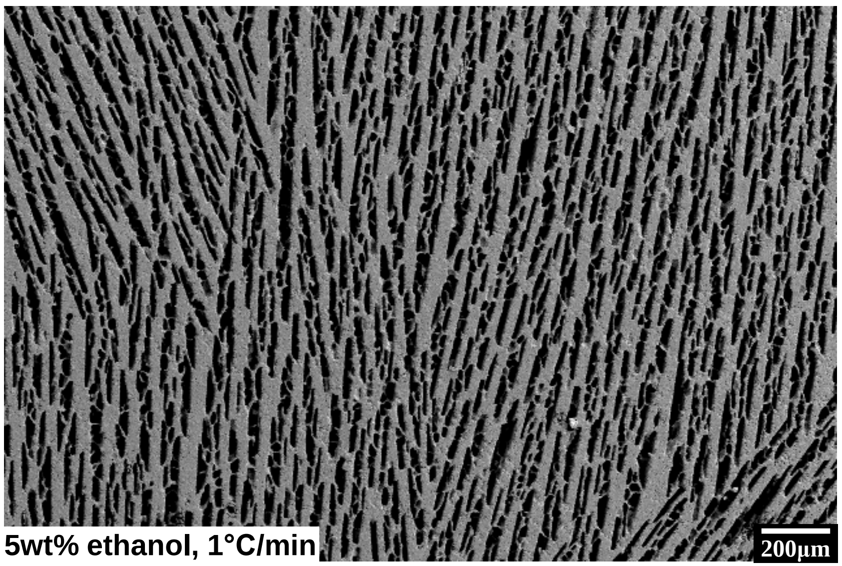
Sample Cross-Sections Perpendicular to the Freezing Direction Also Show Some Alignment



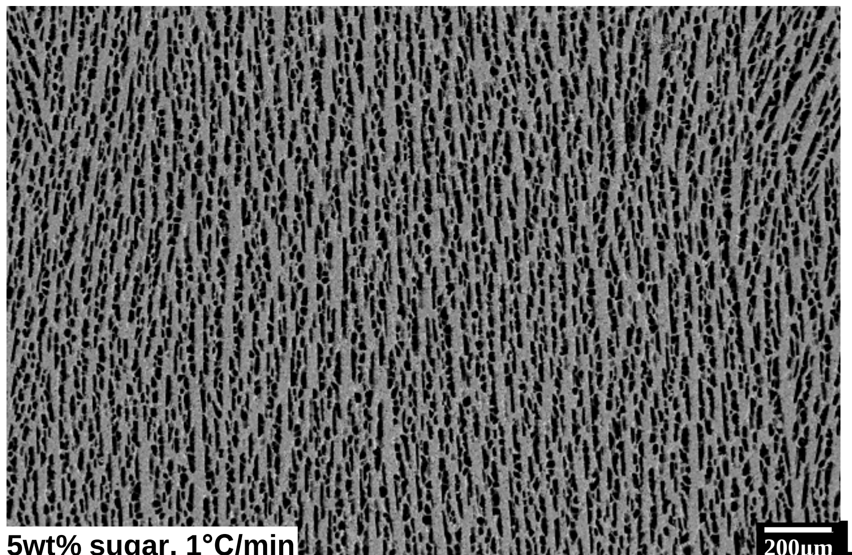
No additive, 5°C/min



No additive, 1°C/min



5wt% ethanol, 1°C/min

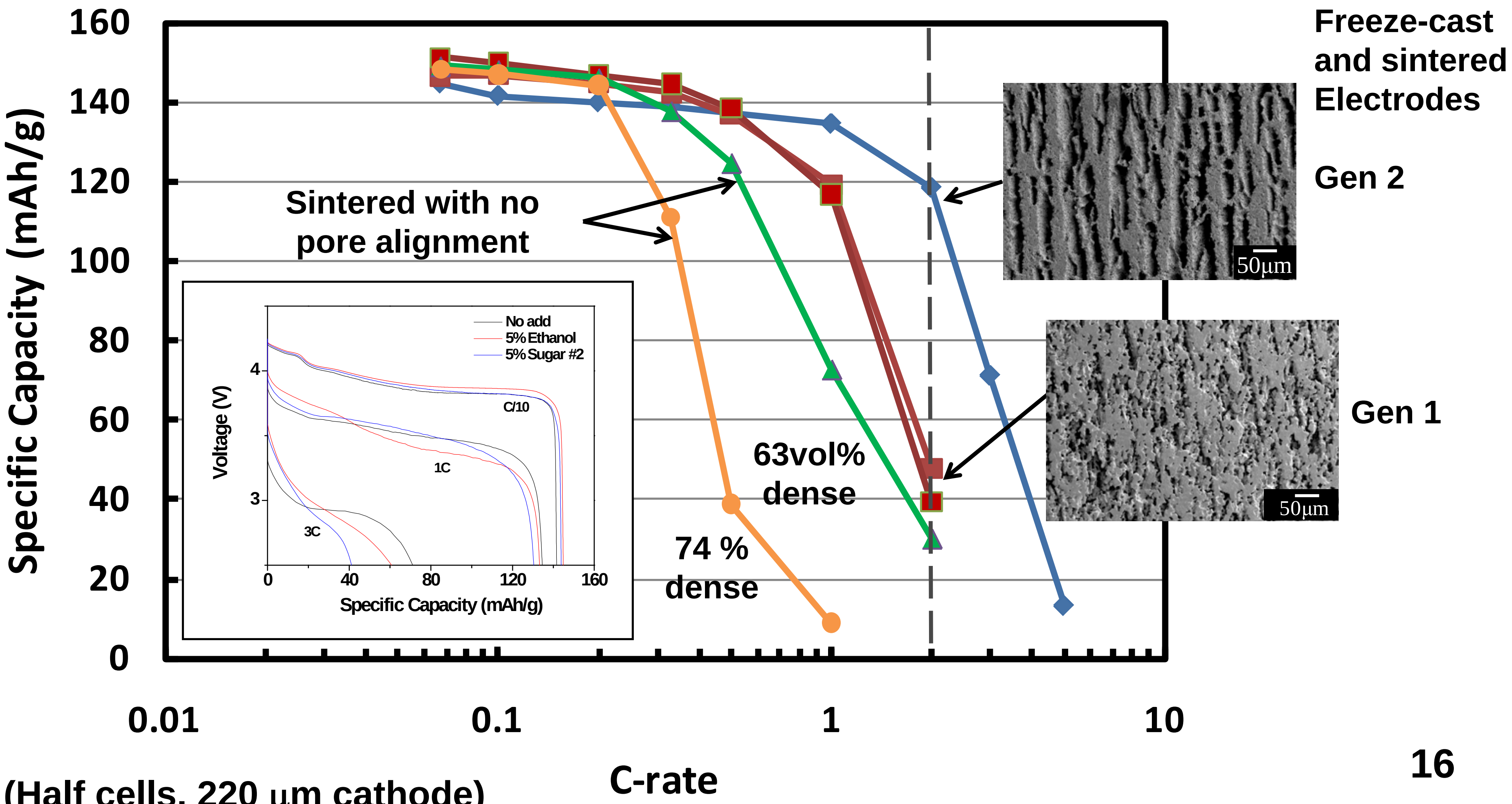


5wt% sugar, 1°C/min

15

Results Summary: Increase in Rate Capability Observed for Low Tortuosity Microstructures

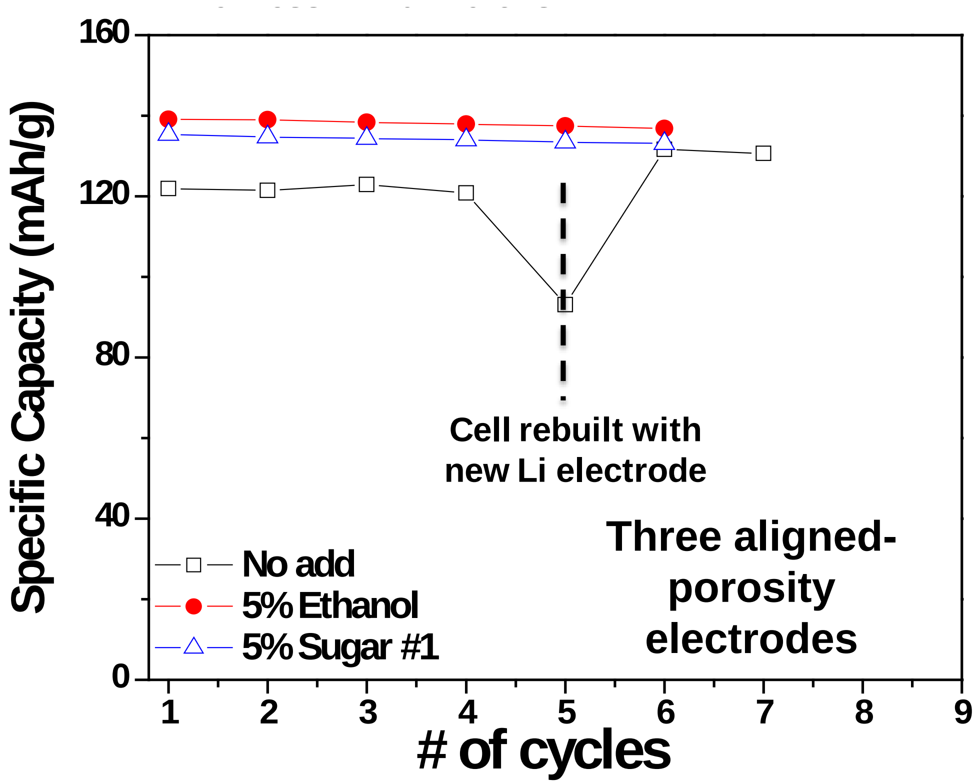
- Validates technical approach
- High utilization at cycling rates (~2C) for PHEV and EV



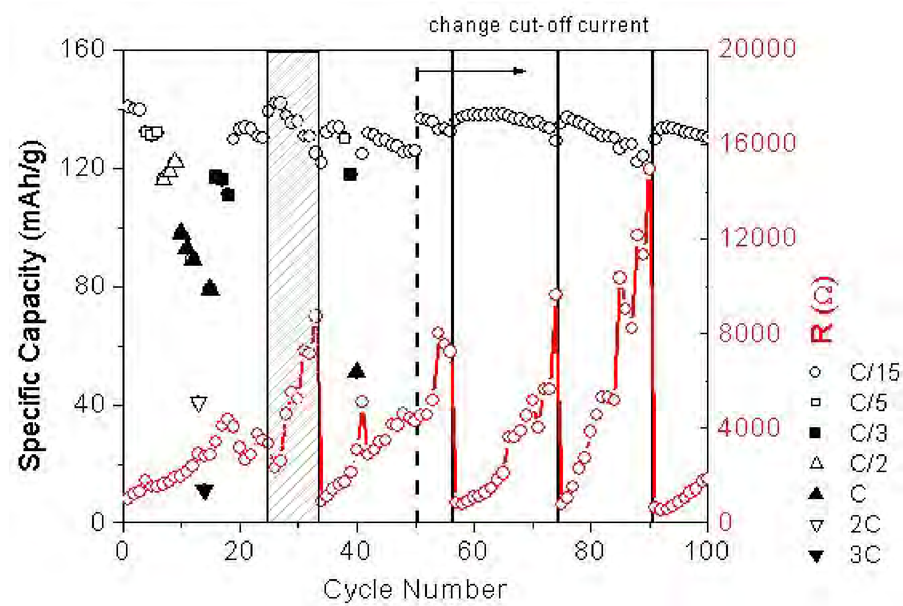
(Half cells, 220 μm cathode)

Preliminary Cycling Data for Low Tortuosity Electrodes

- Li electrode limits life in half-cells (area capacity 10-40 mAh/cm^2)
- Periodic replacement of Li electrode allows continued cycling
- Previous tests have shown stable cycling to ~100 cycles
- *Electrode mechanics* are important



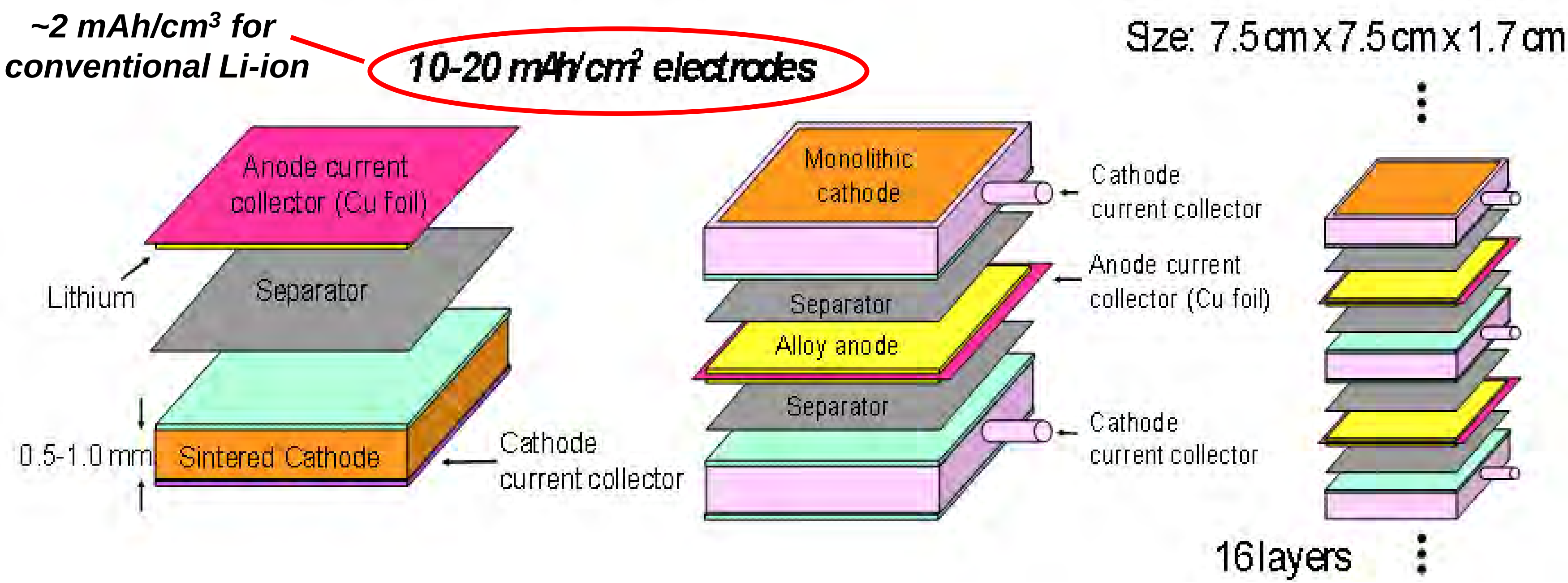
Current tests



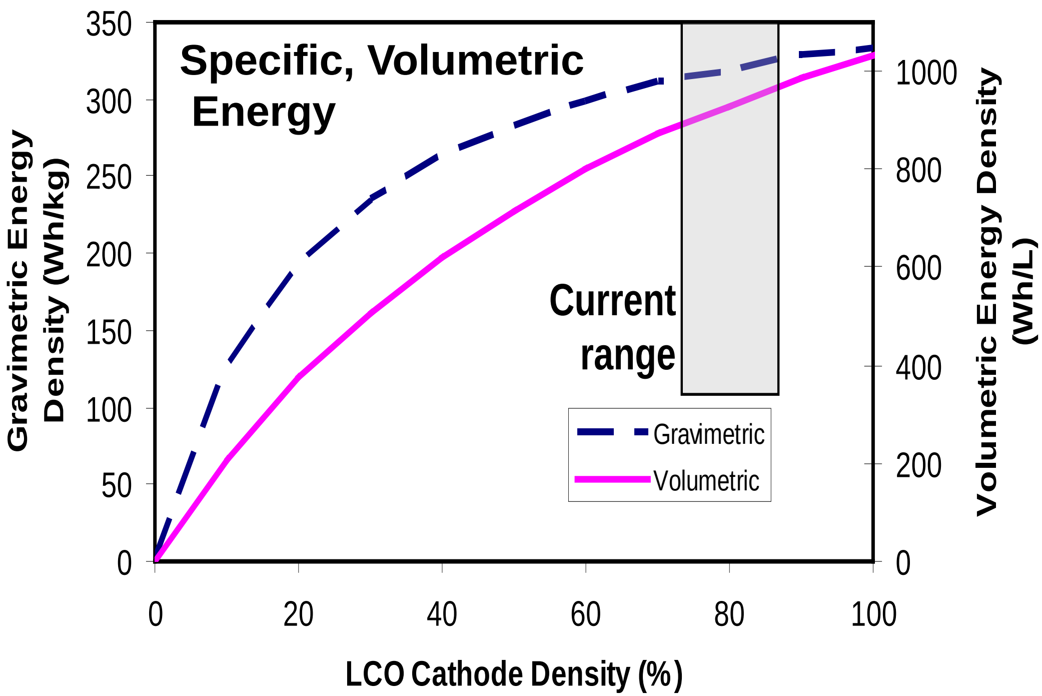
Previous results[1] showed stable cycling of 260 um thick sintered $LiCoO_2$ cathode in a lithium half-cell. Solid vertical lines correspond to cycles when lithium anode and electrolyte were replaced. Note impedance rise during cycling due to lithium metal electrode. (4.25V charging except for shaded region where 4.3V used)

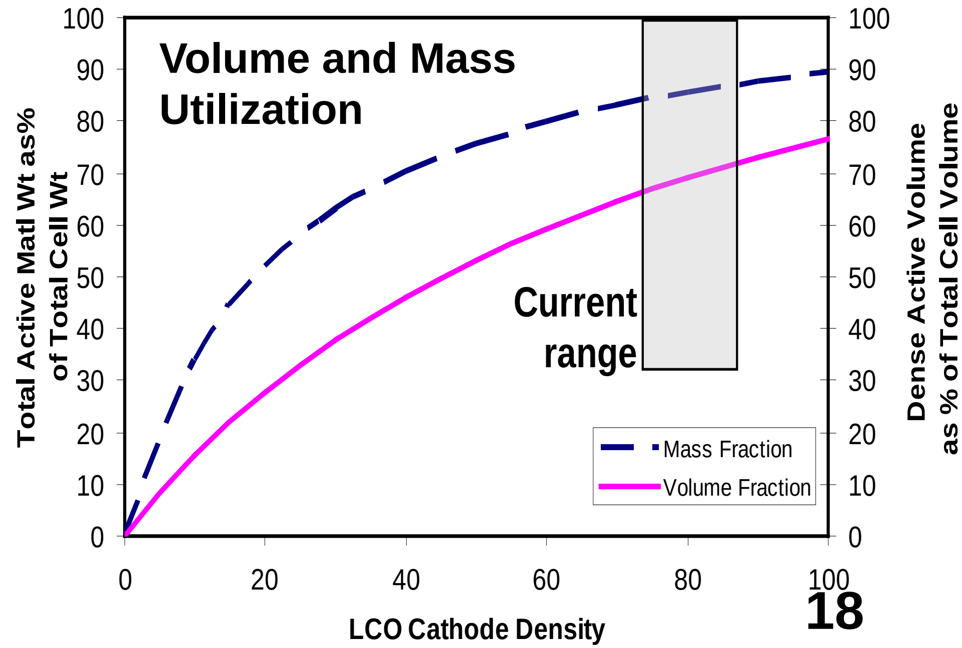
[1]W. Lai, C.K. Erdonmez, *et al.*, *Adv. Mater*., 22, E139-E144 (2010).

Ultimate Goal: Ultrahigh Energy Density PHEV/BEV Cells



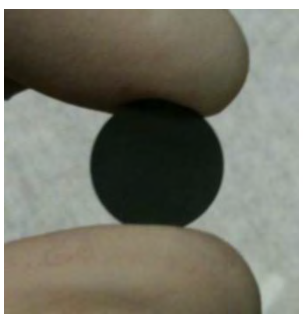
24 Ah cell
800 Wh/L
300 Wh/kg
($LiCoO_2$/C)

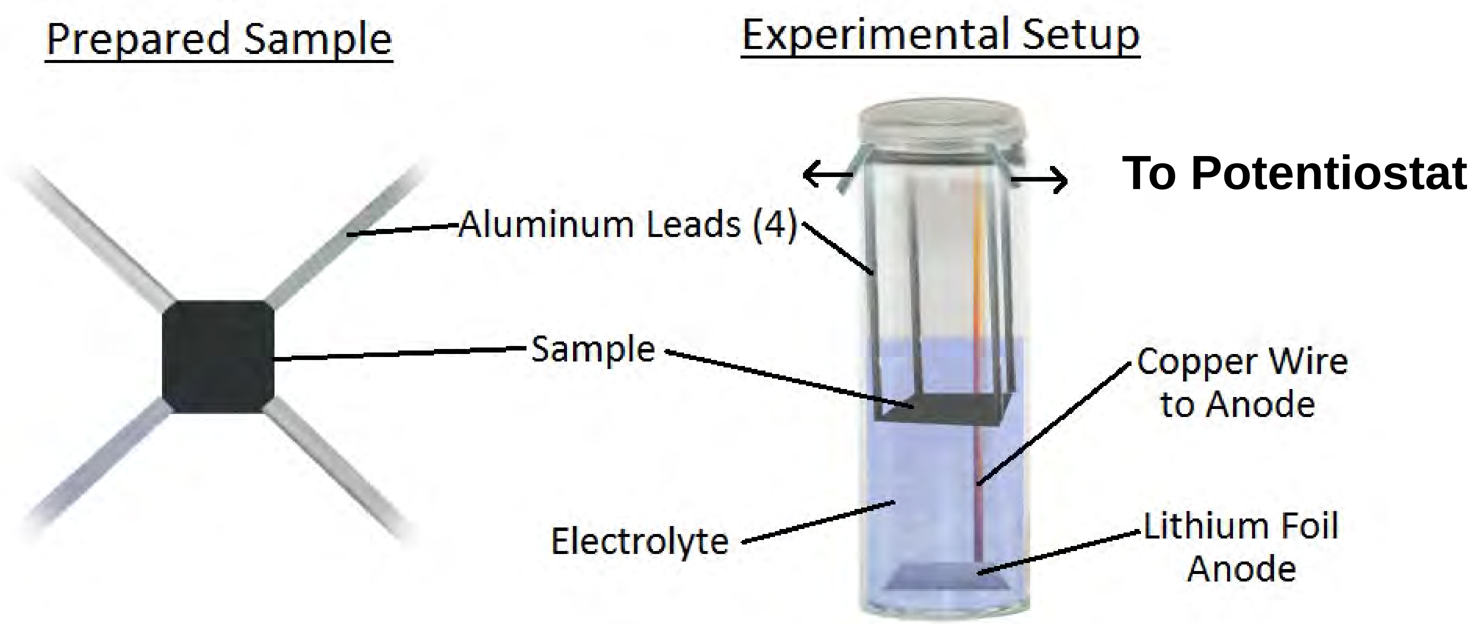




Transport in High Voltage Ni/Mn Spinel

- Sintered electrodes are nearly ideal for *in-situ* measurements of electronic and ionic conductivity during electrochemical titration
  - High sintered density + mechanical stability allows large sample cross-section to be maintained while permitting facile electrochemical titration
  - 4-pt measurement initially, either van der Pauw or linear configuration, to obtain electronic conductivity vs. Li content
  - 2-pt ac measurements with blocking/non-blocking electrodes to separate electronic and ionic conductivity





Collaboration and Coordination with Other Institutions

BATT Collaborators on Electrode Fabrication:

- A.P. Tomsia and Q. Fu (LBNL) – Directional freeze-casting

Collaborators Outside BATT:

- J. Halloran (U. Mich) – Co-extrusion fabrication of electrodes

BATT Coordination within **High Voltage Spinel Transport Group**:

- YMC is Team Leader for *Transport Phenomena Focus Group*
- Other BATT Investigators in Focus Group:
  - G. Chen, R. Kostecki (LBNL) – crystal growth and microcontact meas.
  - K. Perssons (LBNL) – Lithium transport
  - V. Srinivasan and V. Battaglia (LBNL) – Porous electrode measurements
  - R. Manthiram (U. Texas) – Compositional design

Proposed Future Work

FY11:

- Complete optimization of low tortuosity sintered $LiCoO_2$ electrodes as model system
- Establish baseline data for sintered Li/Mn spinel electrodes
- Fabricate and test low tortuosity Li/Mn spinel electrodes
- Validate additive-free sintered electrodes as testbed for conductivity measurement s
- Measure electronic conductivity vs. Li stoichiometry in Li/Mn spinel

FY12:

- Identify high capacity *anode* options to match cathode
- Transition to small prismatic cell tests
- Measure ionic conductivity vs. Li stoichiometry in Li/Mn spinels

Summary

- This project challenges the calendered powder-based electrode paradigm that today dominates lithium-ion battery design and manufacturing but greatly limits energy density and cost
- Our goal is to achieve high active material density while also having low pore tortuosity, in a material of adequate electronic conductivity
- Freeze-casting + sintering has been demonstrated to be capable of producing high density single phase $LiCoO_2$ cathodes with 2C rate capability
- Sintered single-phase electrodes also allow *in-situ* measurement of transport in active materials as lithium is titrated
- Efforts under this project are broadening to high voltage Ni/Mn spinel