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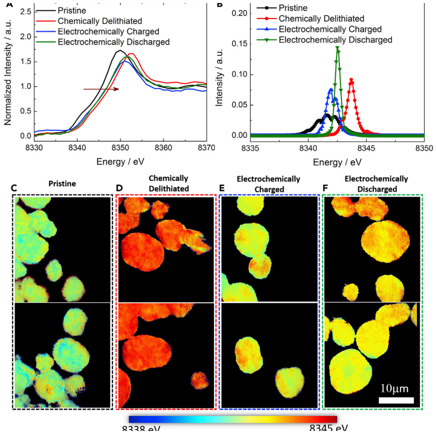
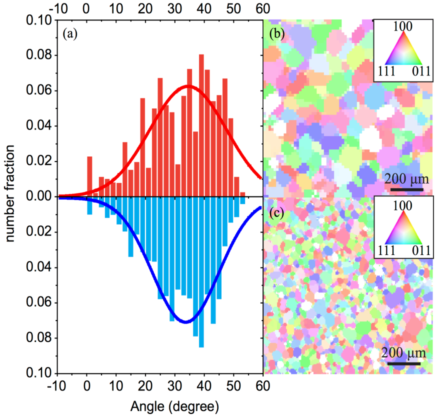
Application of Synchrotron Techniques to Research on Battery Materials





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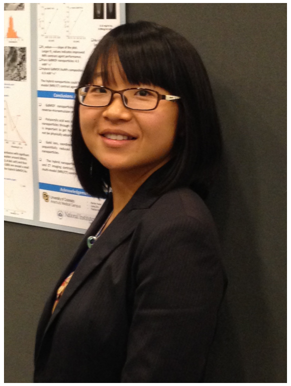
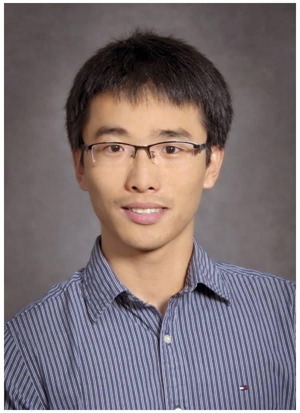
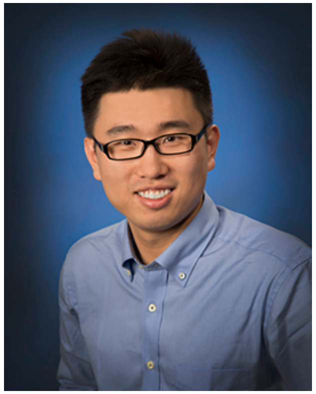
Acknowledgments-Recent NMC work



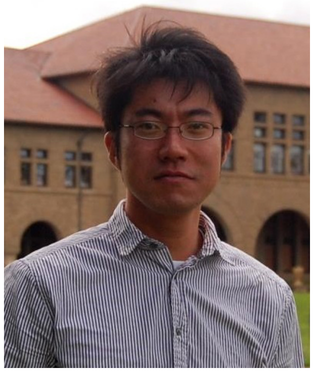
Dr. Chixia Tian
Now at Va. Tech



Professor Feng Lin
Va. Tech

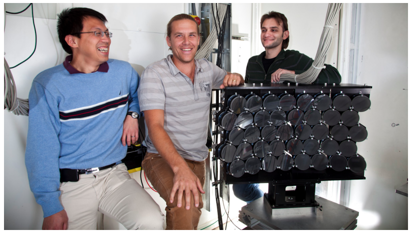


Dr. Huolin Xin
Brookhaven National Lab



Dr. Yijin Liu
SSRL

SLAC NATIONAL ACCELERATOR LABORATORY



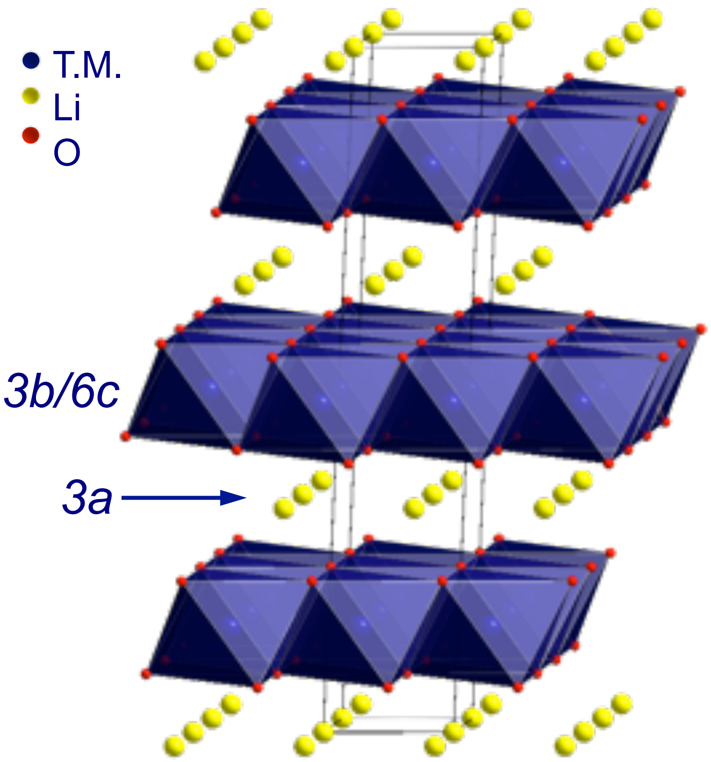
Dr. Tsu-Chen Weng Dr. Dennis Nordlund Dr. Dimosthenis Sokaras

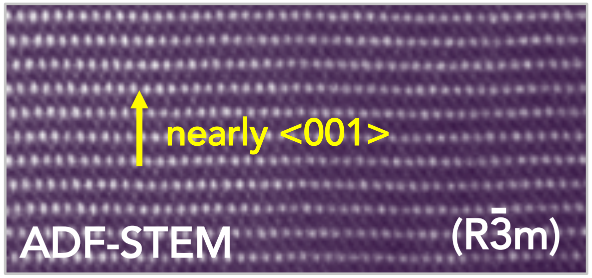
SSRL Beam line Scientists

Funding from the Advanced Battery Materials Research Program, Vehicle Technologies Office, U. S. Dept. of Energy

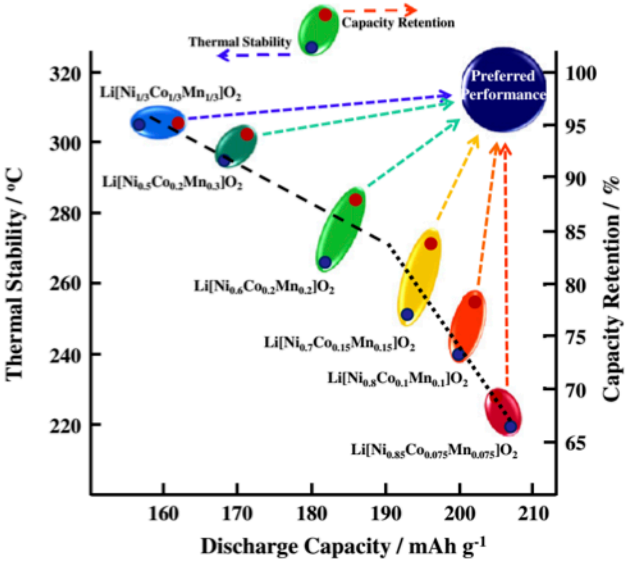
NMC cathodes

- $Li[Ni_xMn_yCo_{1-x-y}]O_2$, NMC ($R\bar{3}m$)
  - Only Ni and Co are electroactive
  - When x=y, Ni^{2+}, Co^{3+}, Mn^{4+} in the pristine state
  - When x>y, $Ni^{2+/3+}$, Co^{3+}, Mn^{4+} in pristine state
  - Move to Ni-rich (x>y) compositions to reduce cost (less Co) and improve practical capacities
  - Lower thermal stability, poorer cycling
  - Can we use higher voltage limits to improve practical capacities?



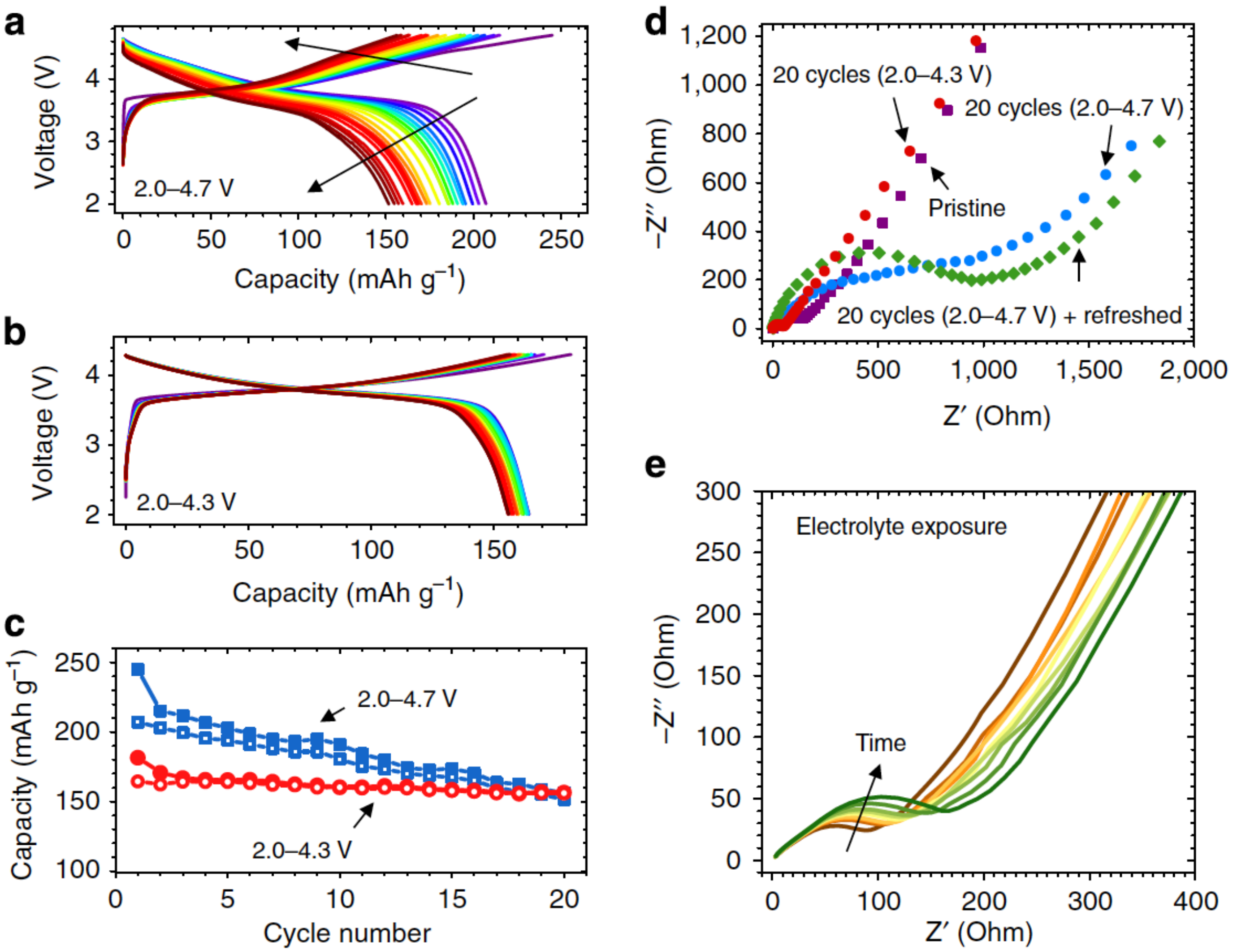


Lin *et al.* Scientific Reports 4, 5694 (2014)



Journal of Power Sources. 233, (2013), 121-130

What Happens during High V Cycling?



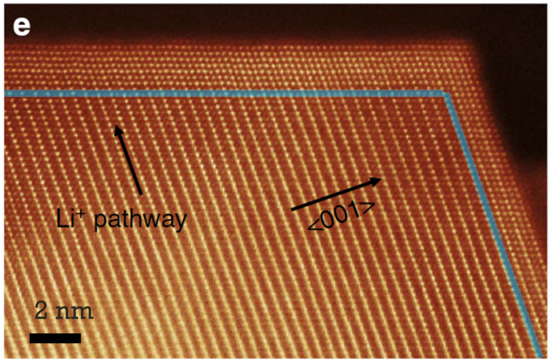
High V cycling of NMC-442 electrodes results in impedance rise and apparent loss of capacity

Lin *et al.* Nat. Commun. 5, 3529 (2014).

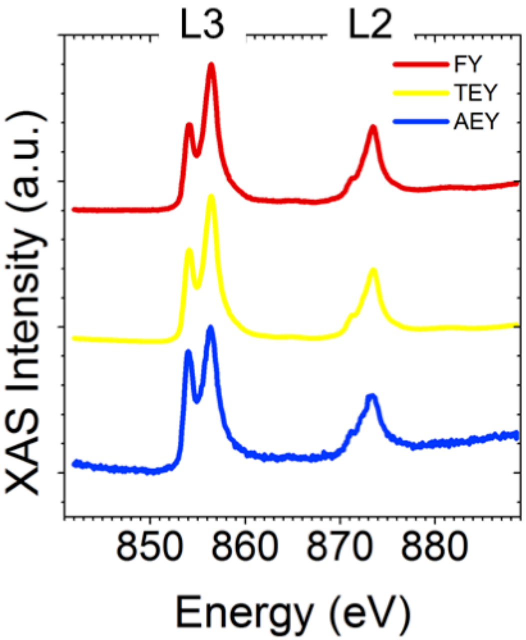
NMC-442, using EC/DMC, 1M LiPF$_6$

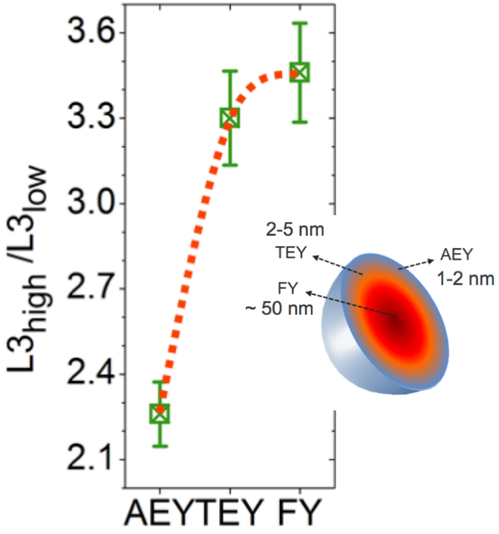
Origins of Losses

Charged (4.7 V vs Li$^+$/Li)

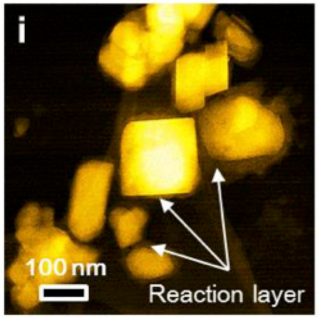


Surface reconstruction to rock salt happens under a variety of conditions

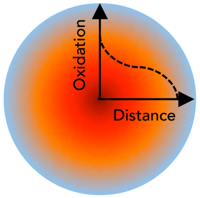


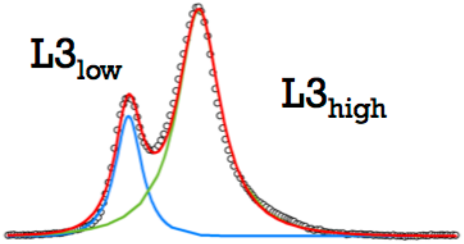


Oxidation state gradient in charged NMC (metals are reduced on surface)



Charging to 4.7V creates a reaction layer (CEI). Not seen after charge to 4.3V

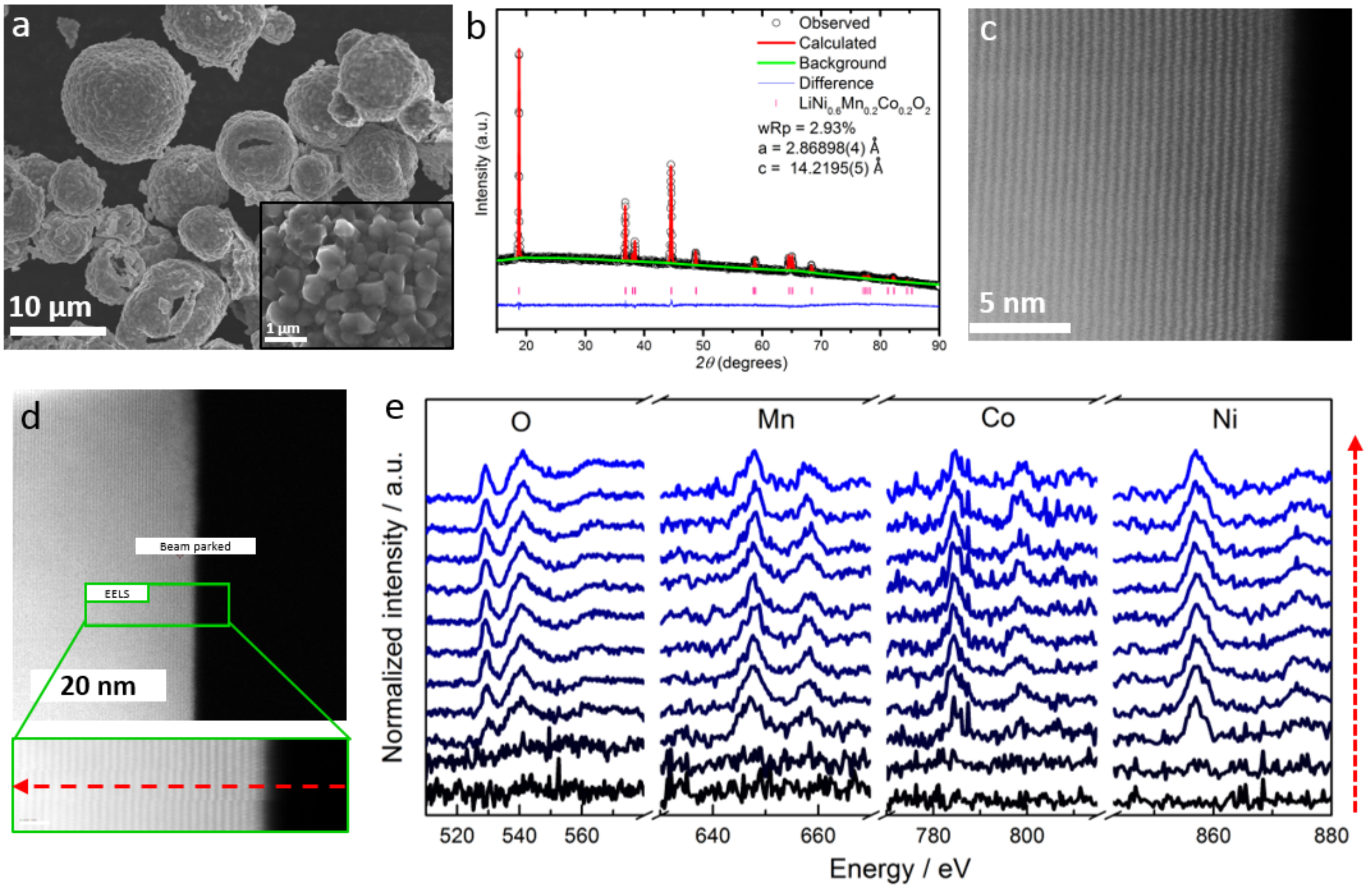




L_{3high}/L_{3low} related to Ni oxidation states

Lin *et al.* Energy Environ. Sci 7, 3077 (2014).
Lin *et al.* Nat. Commun. 5, 3529 (2014).

Pristine NMC-622 Synthesized by Spray Pyrolysis

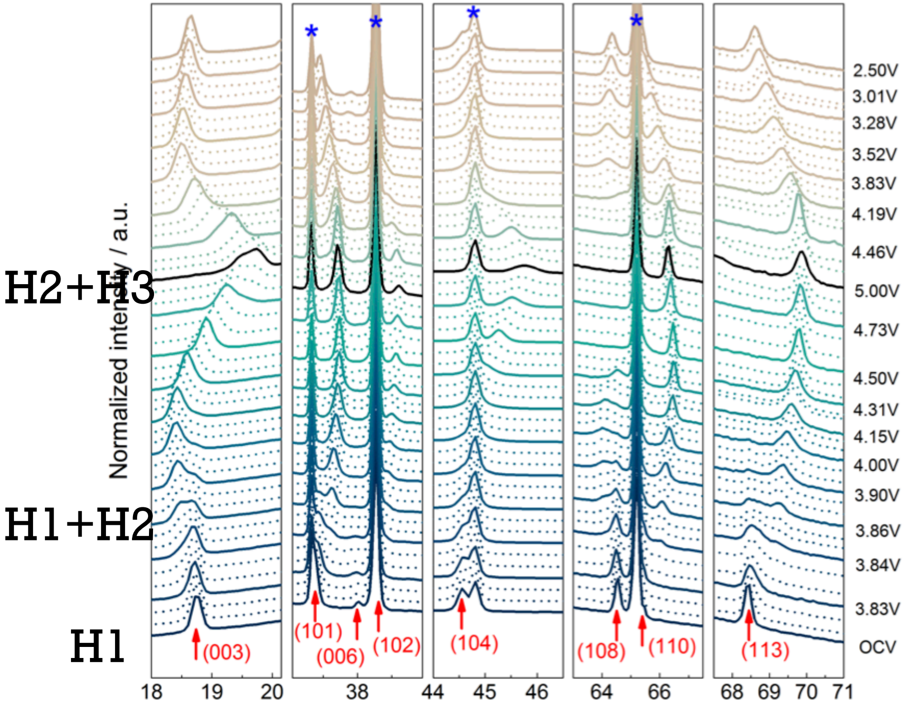


- ❖ Spherical NMC622 particles were prepared by spray pyrolysis
- ❖ *R*-3*m* structure with good crystallinity
- ❖ STEM-EELS data show little change of TM&O oxidation state from surface to bulk

Tian et al., *J. Electrochem. Soc.* 165, A696 (2018).

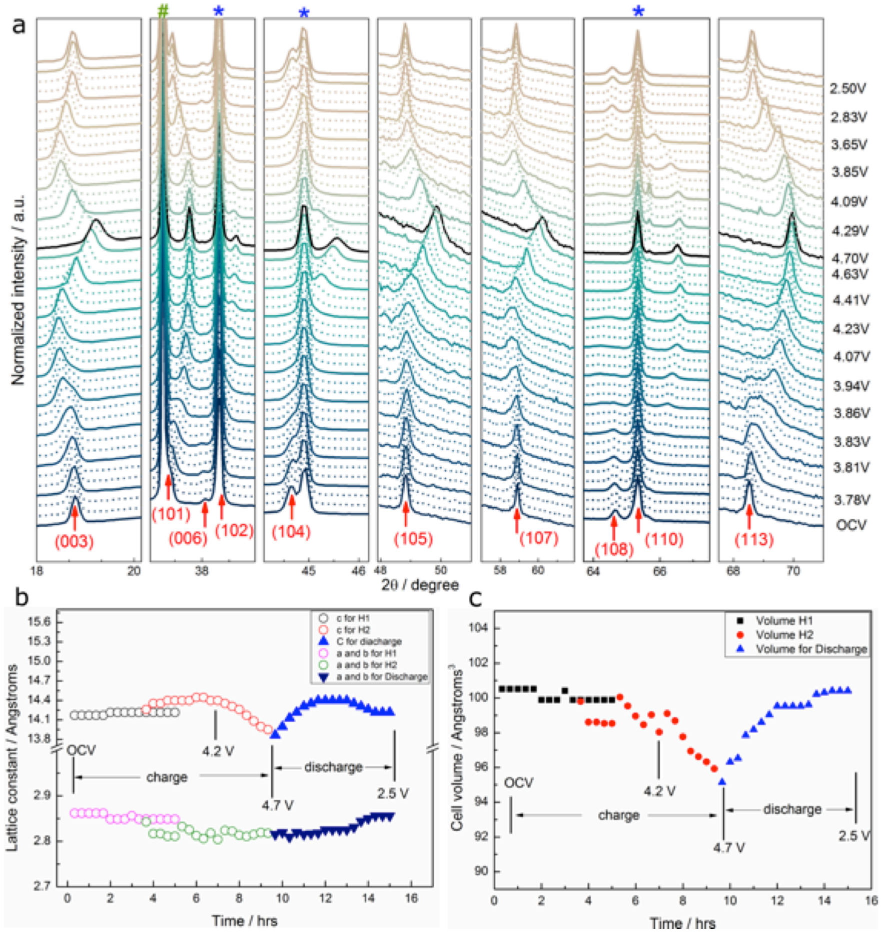
NMC-622 *in situ* XRD

Cycling to 5V

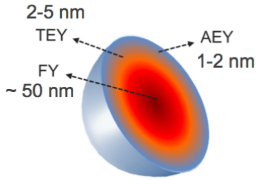


Phase behavior similar to $LiNiO_2$, but H3 transition occurs at potentials higher than the practical voltage range typically used in cells

Cycling to 4.7V

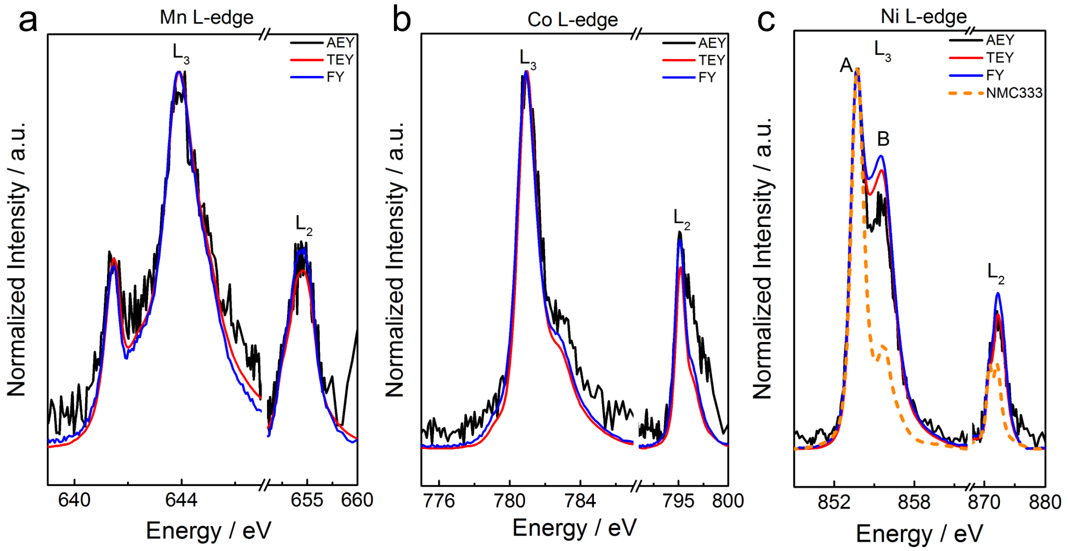


~4% volume change between 2.5-4.7V. Excellent reversibility

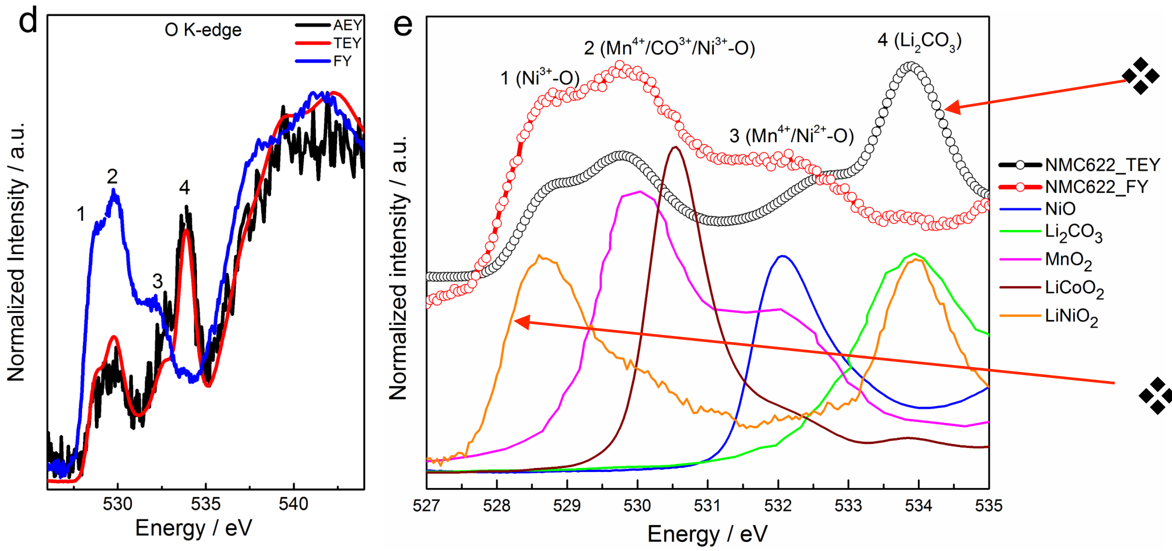


Soft XAS on pristine NMC-622

(TEY and FY modes)



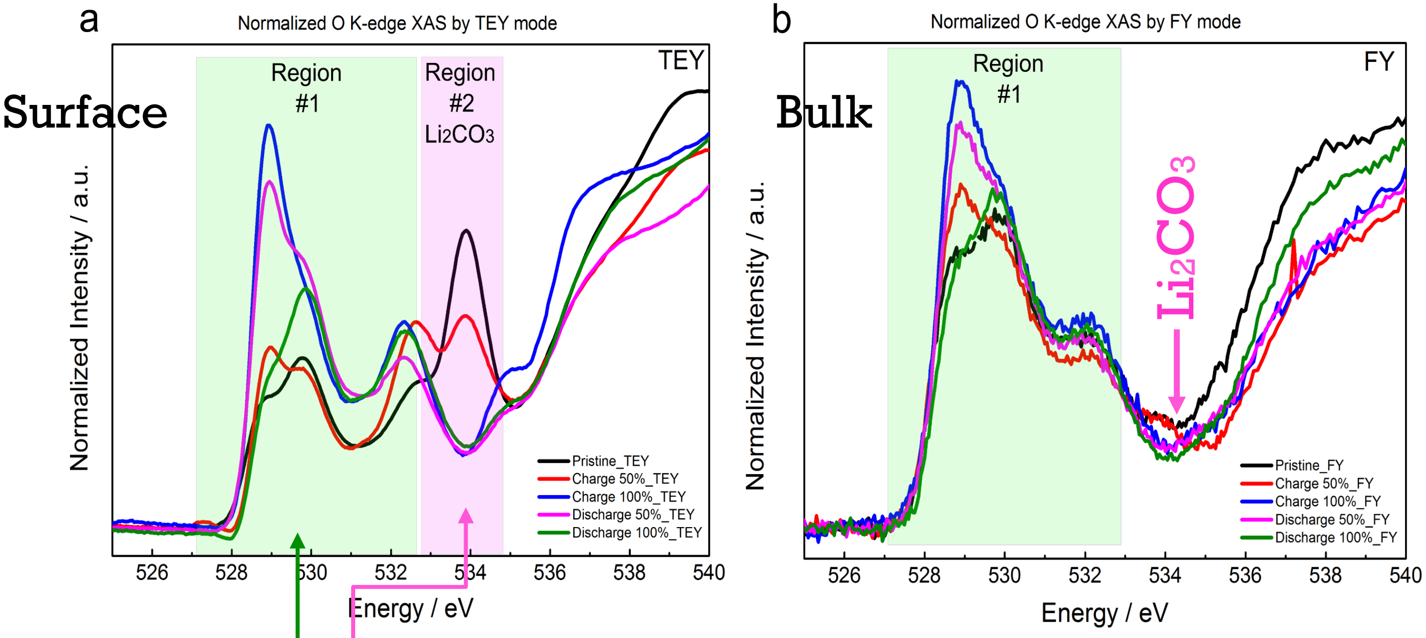
- ❖ Ni is slightly reduced on particle surfaces compared to bulk, Mn and Co are not. Average Ni oxidation state is much higher than 2+, as expected.

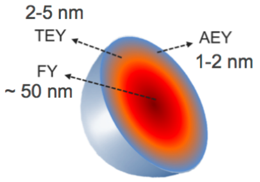


T.M. 3d-O2p states

- ❖ Li_2CO_3 is formed on surfaces-observed in TEY mode (5 nm), not in FY mode (50 nm).
- ❖ Ni^{3+} 3d-O2p presents as a shoulder in pristine material.

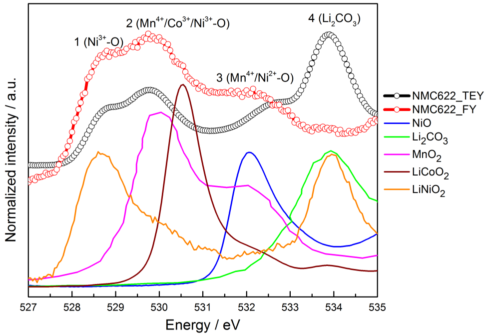
O K-edge soft XAS (TEY and FY modes)





Surface Li_2CO_3 disappears after charging.

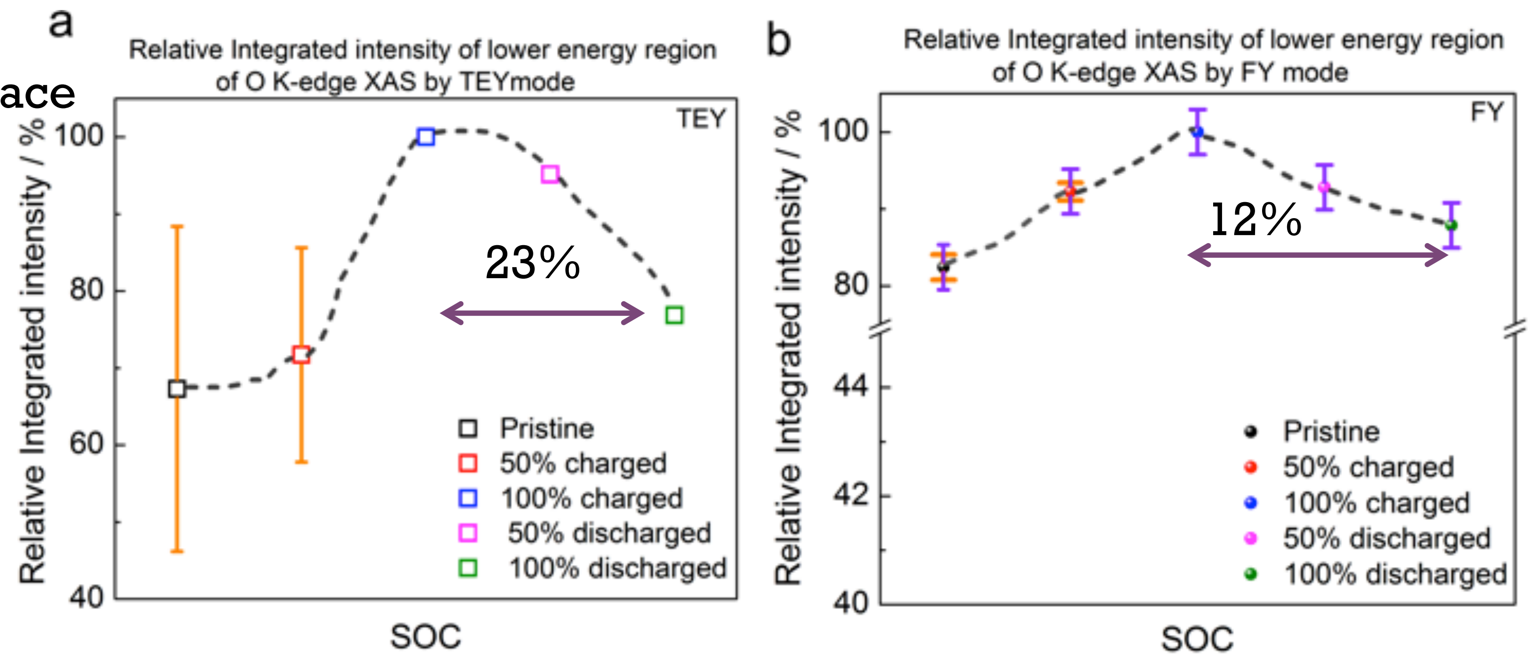
TM3d-O2p peaks increase in intensity and shift during cycling.



The integrated intensity in region #1 represents the redox activity of the oxygen, since the effective number of holes in the oxygen (through the TM-O interaction) is proportional to this area.

Semi-Quantification of Oxygen Activity-Surface and Bulk

Surface



Bulk

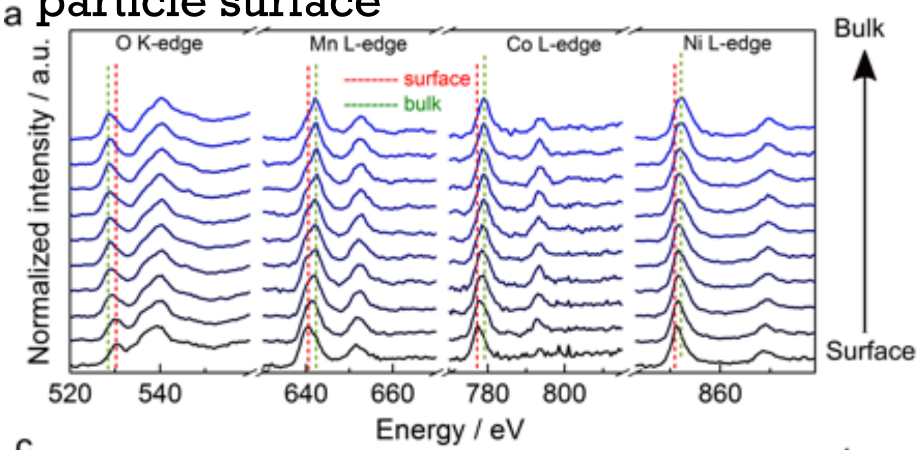
- ❖ Changes are more dramatic in TEY mode than in FY mode=more dynamic changes of hole states on surface.
- ❖ Compare to Ni L-edge results (Ni is more reduced on the surface).

These two sets of data taken together indicate that O on the surface is more active than in the bulk.

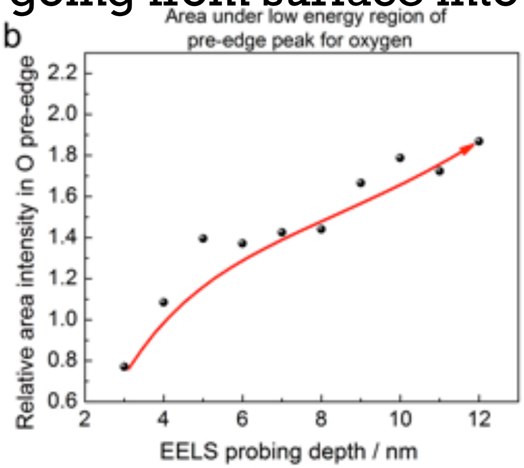
NMC-622 after 50 cycles between 4.7-2.5V

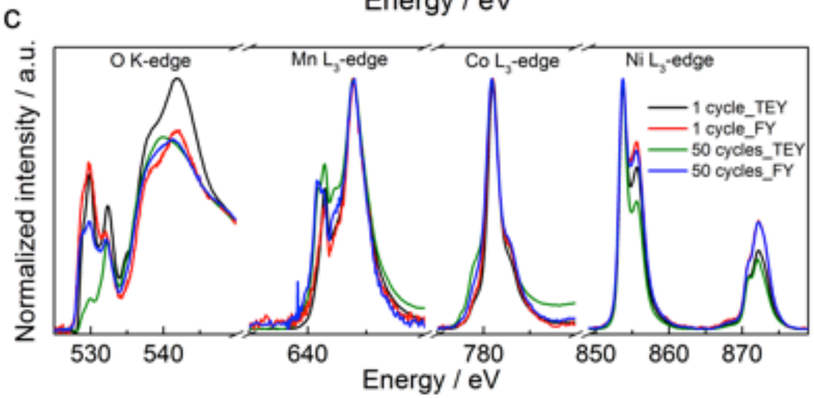
(stopped at end of discharge)

EELS show metals are reduced on particle surface

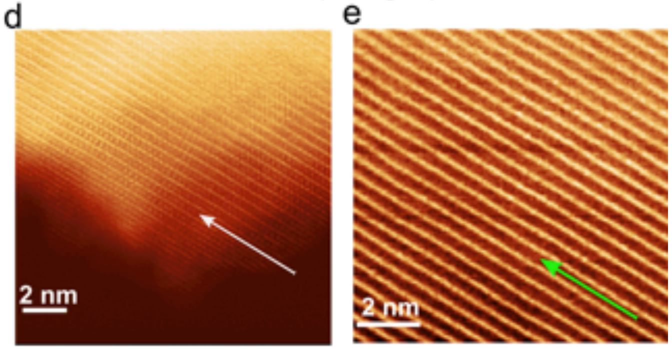


Increased TM3d-O2p hybridization going from surface into bulk





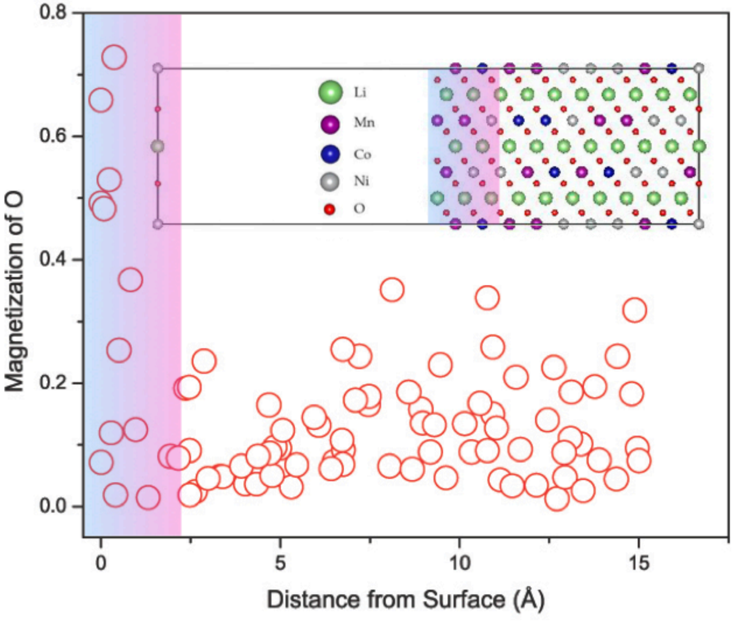
Soft XAS shows reduced T.M. on surfaces



Images show T.M. ions in Li channels

STEM-EELS and soft XAS experiments show that surface reconstruction is significant after 50 cycles

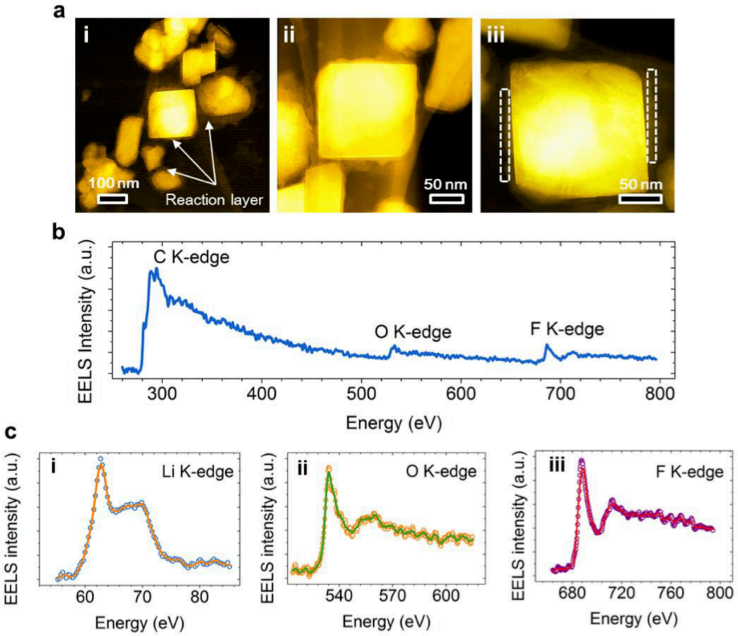
Surface Oxygen Activity and Consequences



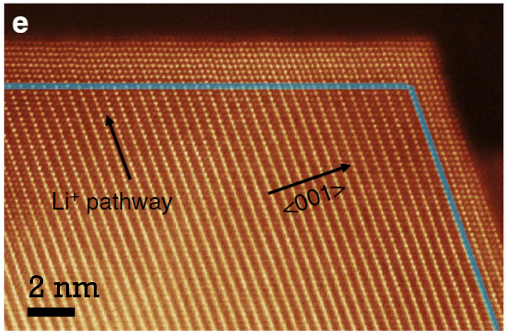
I. Markus, unpublished results

Computational results also indicate that surface oxygen is more reactive than that in the bulk in NMCs. This reactivity explains the strong tendency for surface reconstruction to rock salt to occur under a wide variety of conditions. It may also contribute to reactions at the cathode/electrolyte interface that raise impedance during high voltage cycling.

CEI formation



Surface Reconstruction

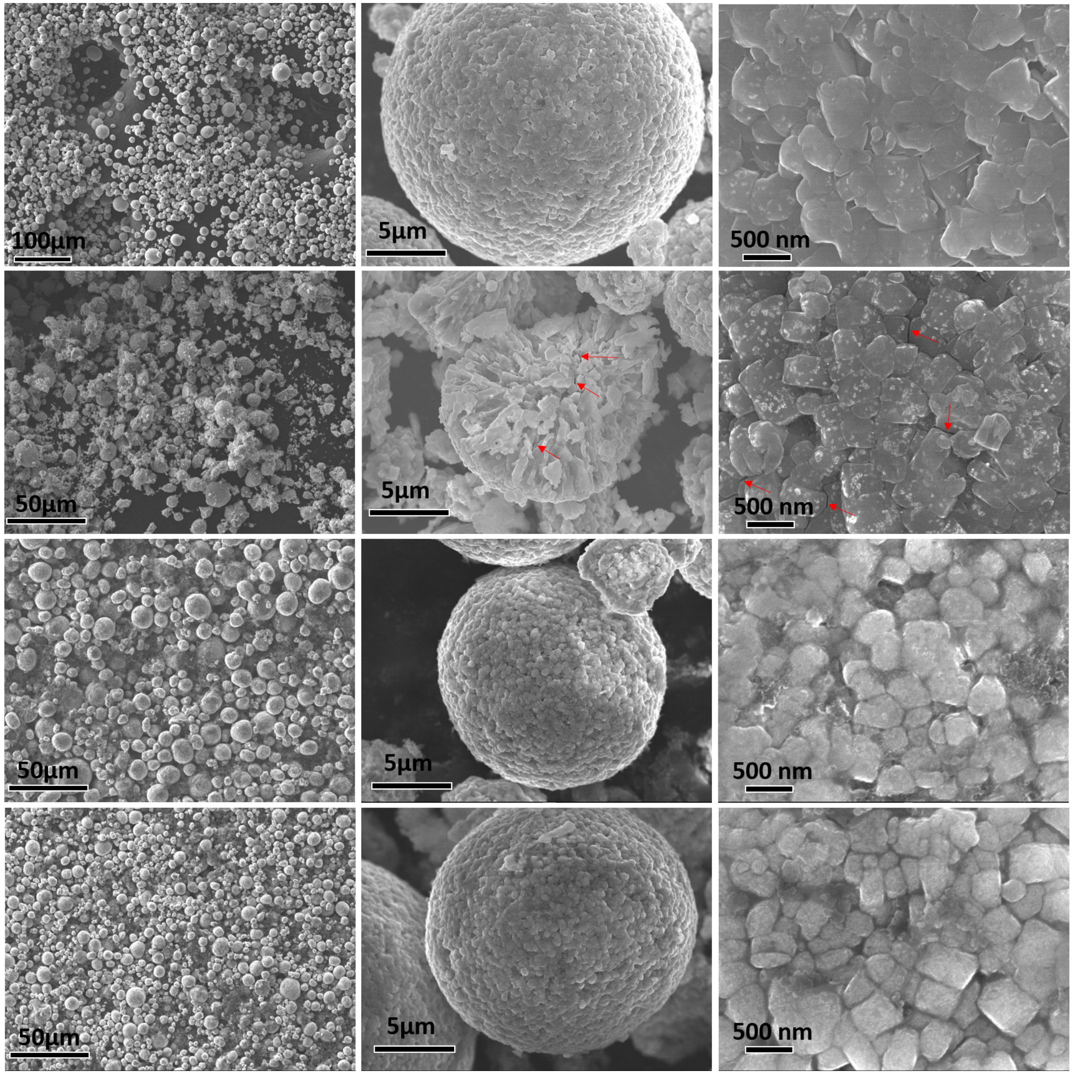


Lin et al. *Nature Commun.* 5, 3529 (2014) and *Energy & Environ. Sci.* 7, 3077 (2014).

Chemical vs. Electrochemical Delithiation

- We often use chemically delithiated materials as models for what goes on during cell charge/cycling.
- Are there differences between chemically delithiated and electrochemically delithiated samples?
- If so, what can these differences tell us?

Morphology changes during delithiation



Pristine

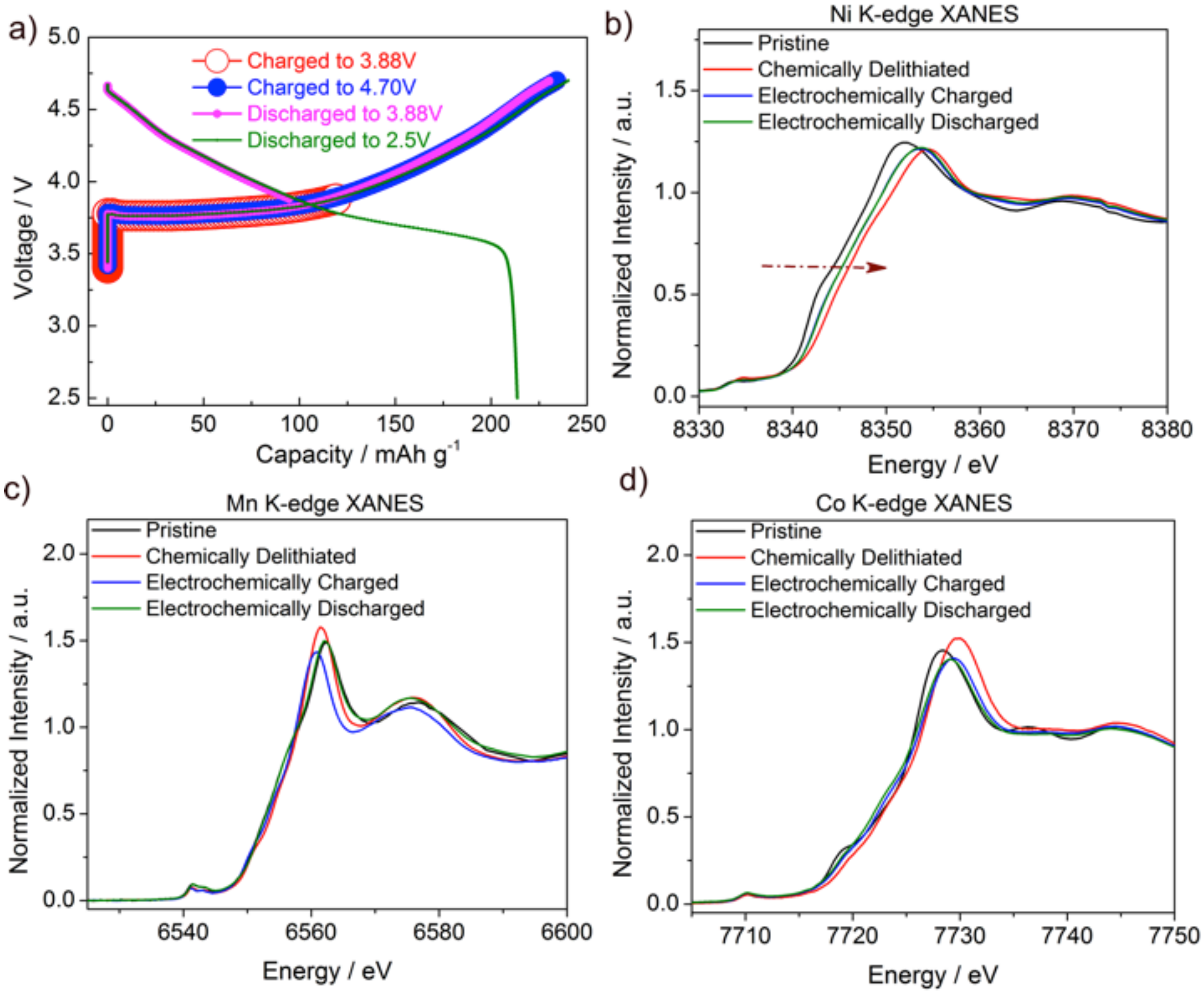
Chemically
Delithiated
($Li_{0.43}Ni_{0.6}Mn_{0.2}Co_{0.2}O_2$)

Electrochemically
charged to 3.88V
($Li_{0.57}Ni_{0.6}Mn_{0.2}Co_{0.2}O_2$)

Electrochemically
charged to 4.7 then
discharged to 3.88V
($Li_{0.51}Ni_{0.6}Mn_{0.2}Co_{0.2}O_2$)

- ❖ Chemical delithiation leads to disconnection in the secondary particles

Electrochemistry and hard XAS

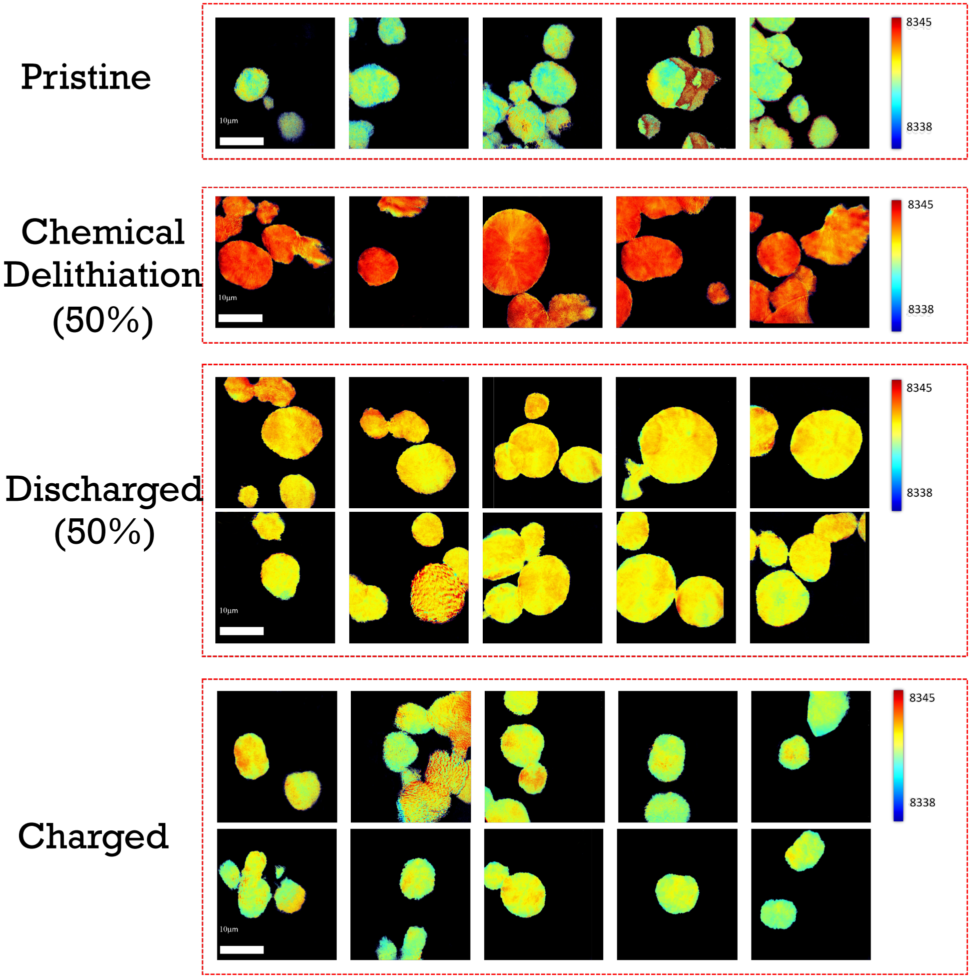


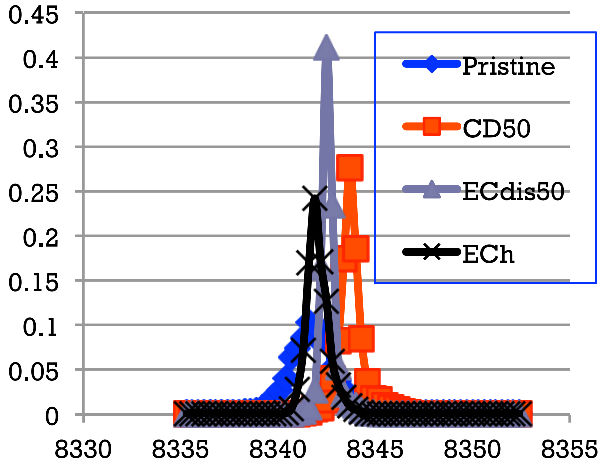
Shifts in Ni K-edge consistent with oxidation of Ni and estimated stoichiometries. Some participation of Co. Mn is inert.

Tian et al., Joule, submitted

SOC (Ni K-edge) mapping of NMC Samples

Ni 2D Transmission X-ray Microscopy (TXM)

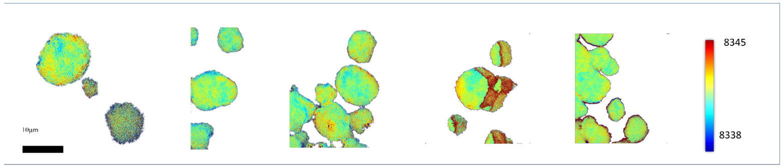




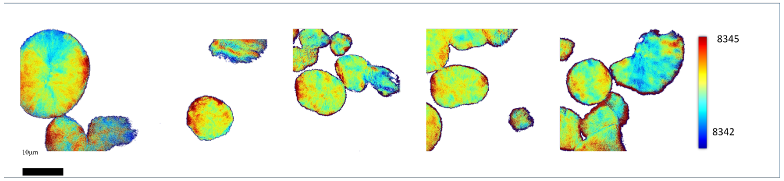
- ❖ Pristine commercial NMC shows inhomogeneities in Ni valence state distribution within and between secondary particles.
- ❖ Chemical delithiation and electrochemical charge lead to overall oxidation and homogenization of Ni valence state.
- ❖ The absolute Ni valence state (SOC) varies between chemically and electrochemically treated samples as expected.

Homogeneity of NMCs' SOC under different conditions-Different scaling reveals heterogeneity

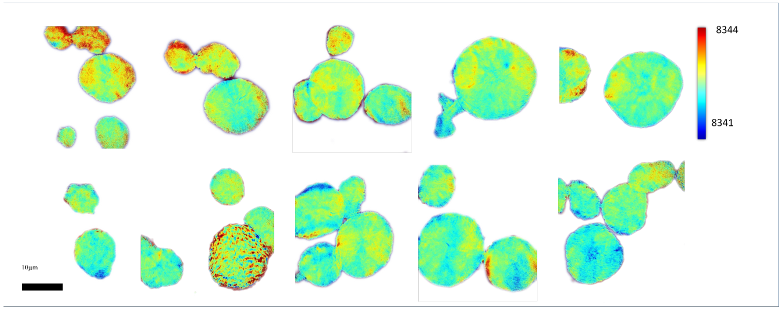
Pristine



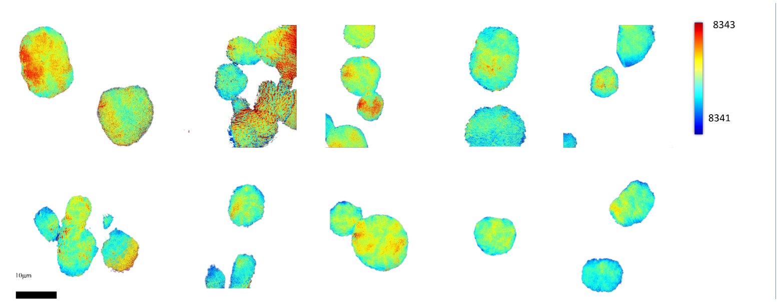
50% Chemical Delithiation



50% discharged



50% Charged



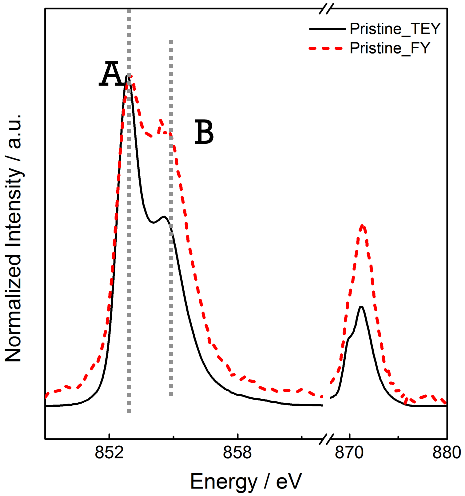
- Finer tuning reveals heterogeneity in both chemically and electrochemically treated samples
- Reasons for heterogeneity differ

- Electrochemical method--- volume-change-induced stress/localized overcharge

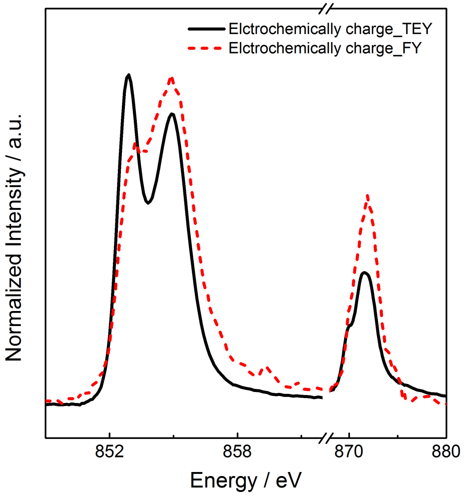
- Chemical delithiation--- Mechanical force induced fracture of secondary particles introduces fresh surfaces, which are less oxidized.

Ni L edge soft XAS (TEY and FY)

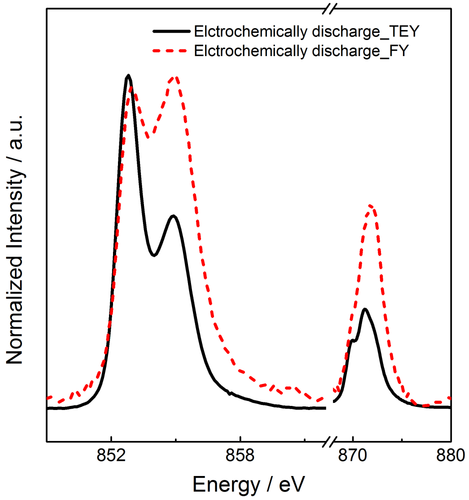
Pristine



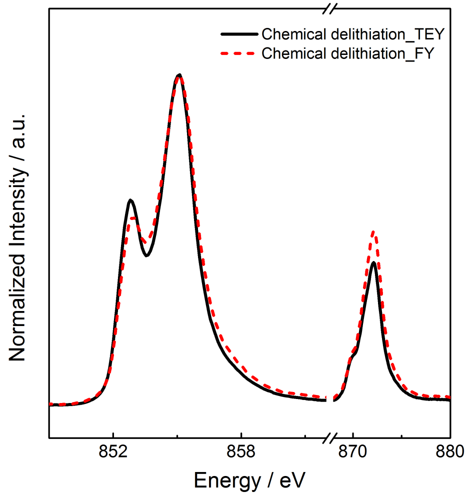
Charged (0.25 cycle)



Discharged (0.75 cycle)



Chemical delithiation



Peak B/A Intensity ratio	Pristine	50% charged	50% discharged	Chemical delithiation 50%
TEY	0.56	0.87	0.57	1.64
FY	0.83	1.28	1.04	1.78
Difference	0.27	0.41	0.47	0.14

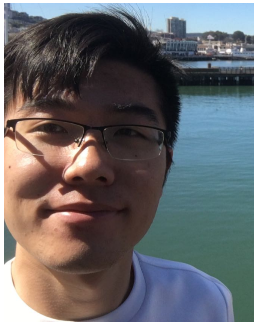
- Electrochemically treated samples show significant surface reduction in comparison with chemically delithiated ones. This suggests exposure to electrolyte plays a role in surface reconstruction.

Summary-NMCs

- Differences in the surface and bulk redox activity of O and Ni in NMCs during cycling result in increased reactivity of surface oxygen
  - This, in turn, is responsible for surface reconstruction to rock salt
  - Oxygen loss
  - Formation of reaction layers on particle surfaces during cycling to high V, resulting in impedance rise
- A comparison of chemically and electrochemically delithiated samples reveals heterogeneities in both samples, although the causes are different
  - Chemically delithiated-cracks from mechanical damage
  - Electrochemically delithiated-disconnection of primary particles due to volume changes
- Surface reconstruction is less evident in chemically delithiated samples
  - This suggests that interactions with the electrolytic solution in electrochemical cells play a significant role in this phenomenon
  - You need something to oxidize!

Acknowledgments-LLZO work

Lei Cheng, PhD 2015
Now at Bosch



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Xi'an Jiatong University

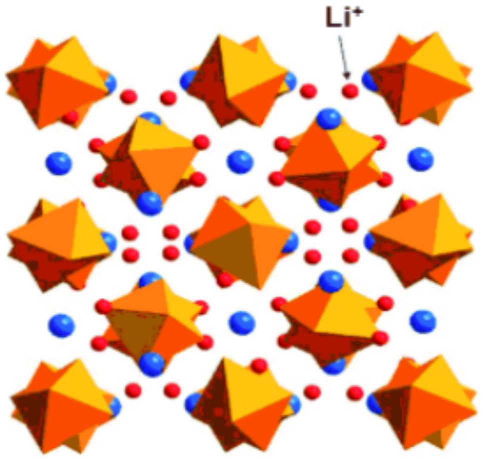
Dr. Eongyu Yi
Current postdoc

Fabio Albano
Fisker

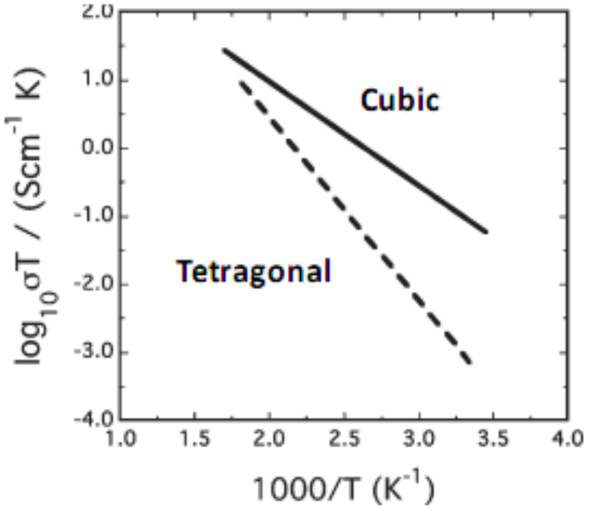
Stephen Sofie, MSU

Funding from ILIRP program, then BATT/ABMR. Freeze-casting work funded as Battery 500 seedling project-VTO, DOE Synchrotron work done at ALS, LBNL

$Li_7La_3Zr_2O_{12}$ and variants: garnet structure



Murugan et al. Angew. Chem. Int. Ed. 2007



Geiger et al. Inorganic. Chem. 2008

Al added to stabilize the cubic phase.

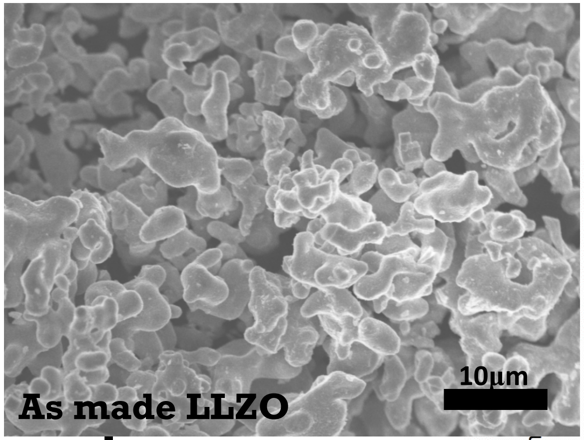
Pros:

- High lithium ionic conductivity for cubic phase (>10^{-4} S/cm at R.T.)
- No reaction observed when contacted directly with molten lithium
- Oxides should be easier to work with than sulfides

Cons (as of ~2014):

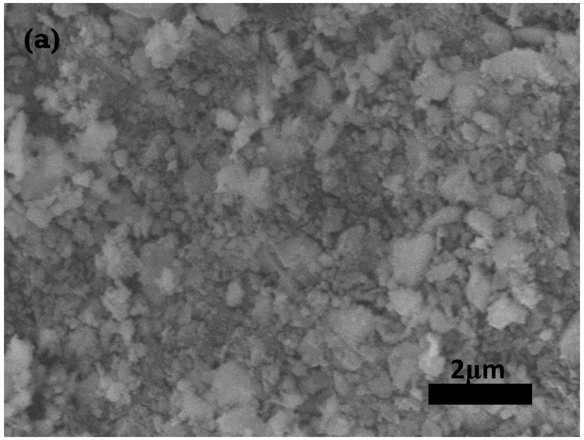
- Difficult to densify
- Reactivity with substrates, moisture, ambient atmosphere
- High interfacial impedances
- Thin films required: for 5 mA/cm^2, voltage drop < 100 mV, needs to be < 200 μm (assuming no contribution from interfacial impedances!)

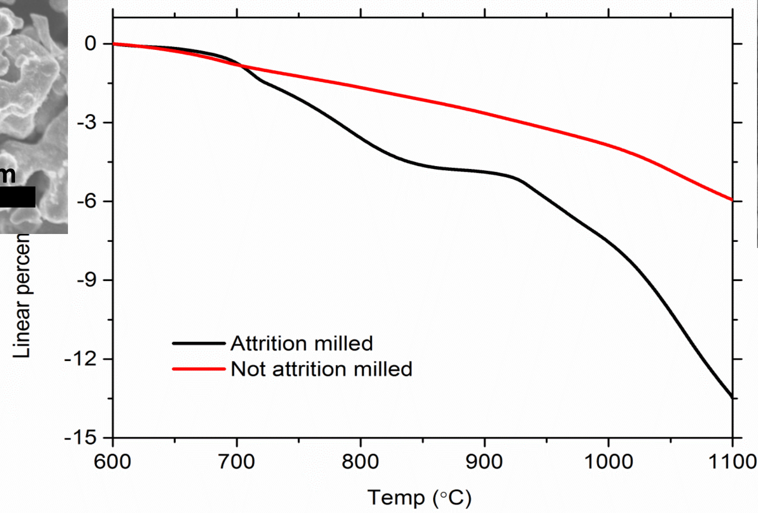
Densification-particle size matters



As made LLZO powder

Attrition mill



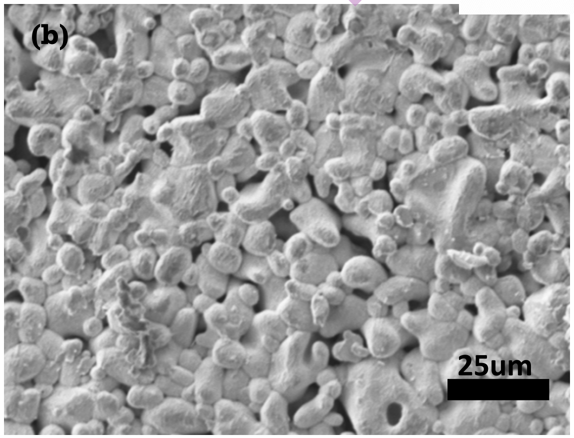


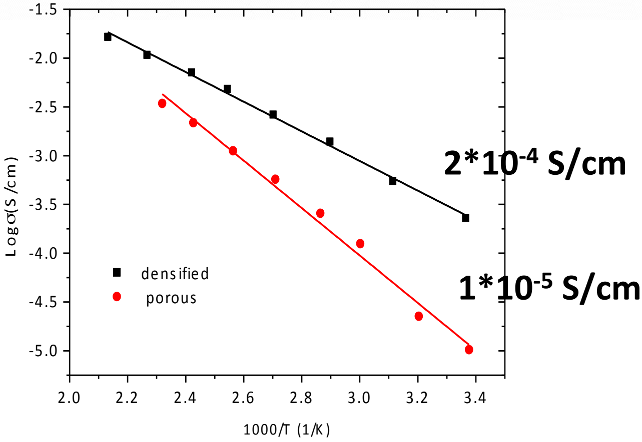
1100 °C sintering (porous)

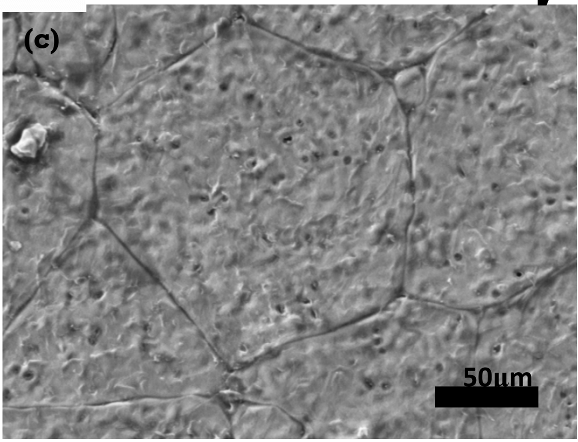
1100 °C sintering (Dense)

130 °C lower than previously reported for conventional processing

94% density

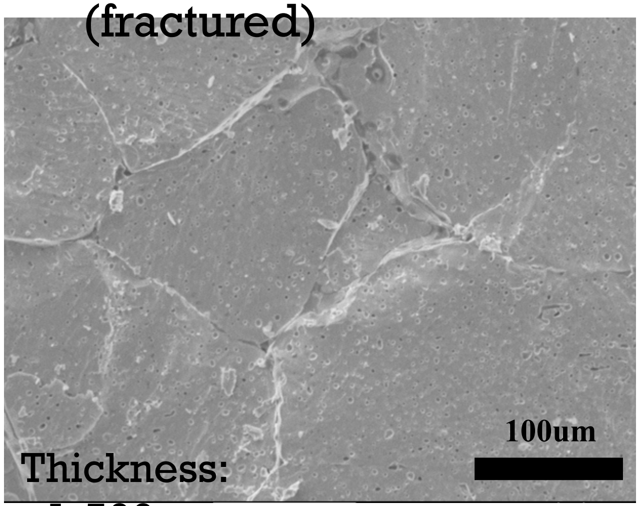






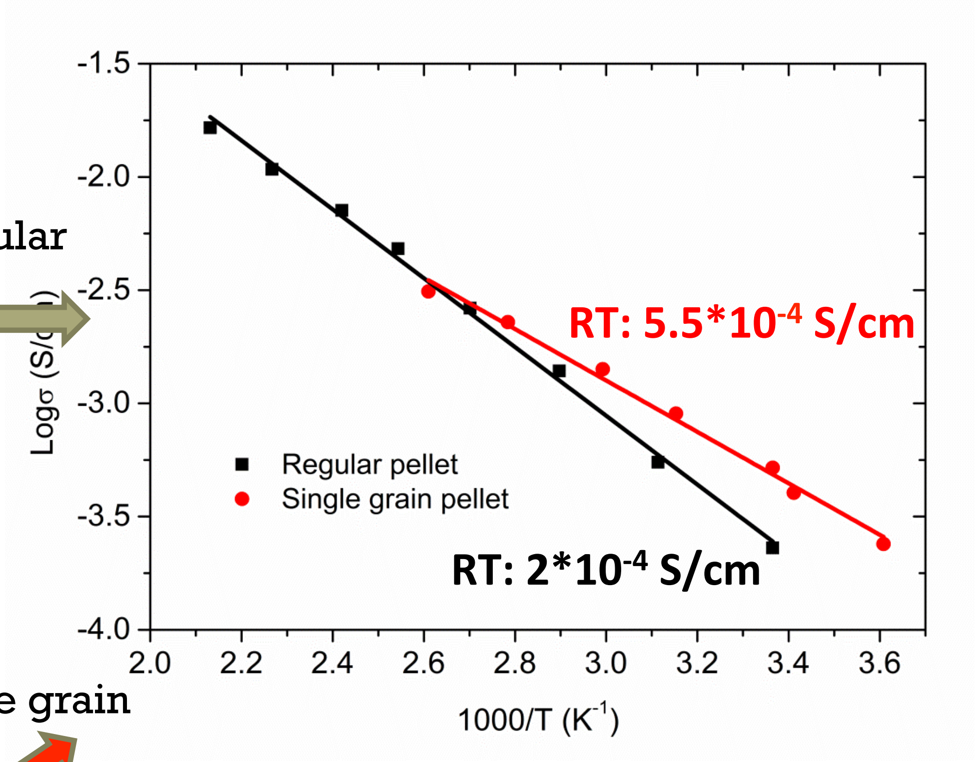
Free-standing thin films, a single grain thick

Cross section (fractured)



Thickness: ~1.500mm

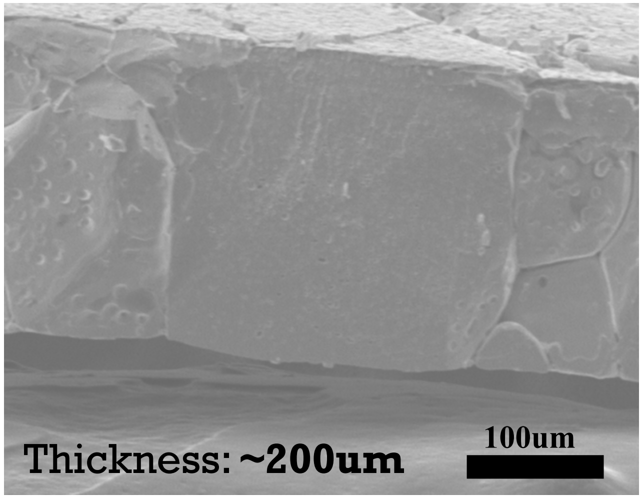
Regular



RT: 5.5*10^{-4} S/cm

RT: 2*10^{-4} S/cm

Single grain



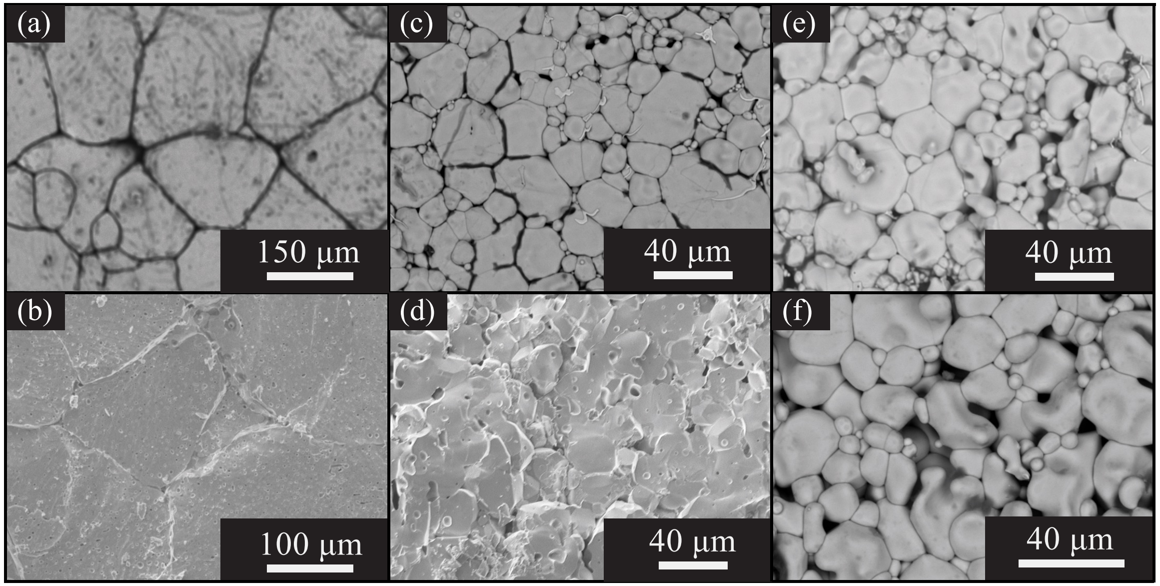
Thickness: ~200um

Cheng et al., *J. Mater. Chem. A*, 2, 172 (2014).

Control of Microstructures

surface

cross-section



surface

70% 1 μm
30% 10 μm

surface

50% 1 μm
50% 10 μm

1 μm particles

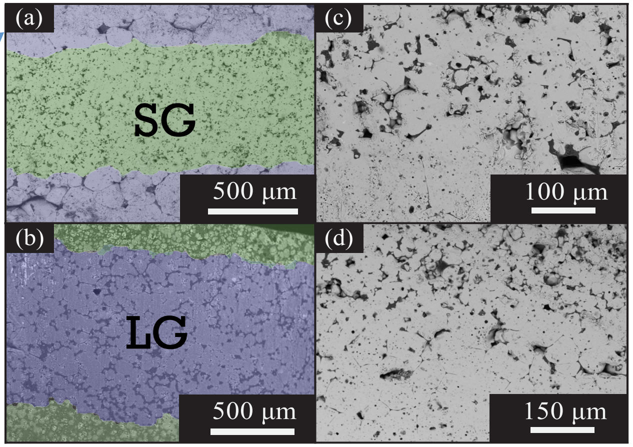
90% 1 μm
10% 10 μm

Not dense

LG

Heterostructures

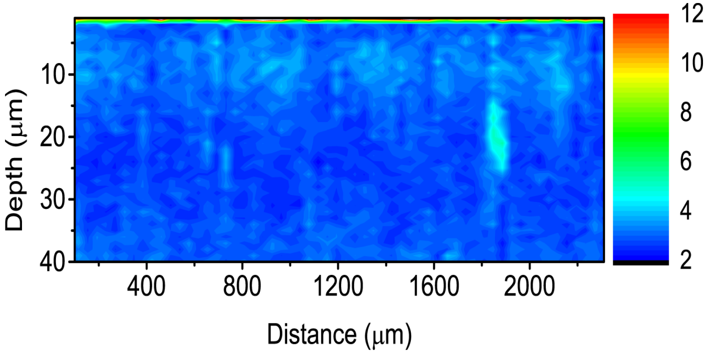
SG



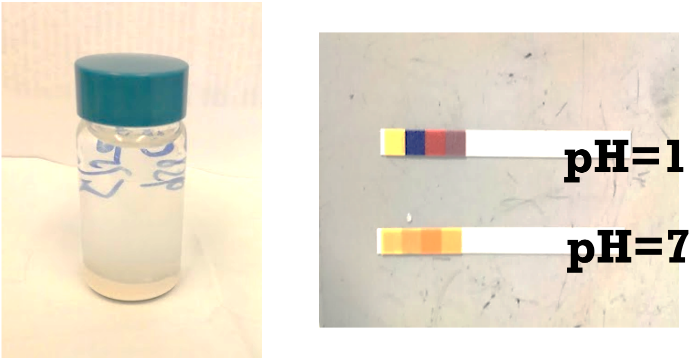
Junctions between large grain and small grain regions

Cheng et al., *ACS Applied Mater. & Interfaces* 7, 2073 (2015).

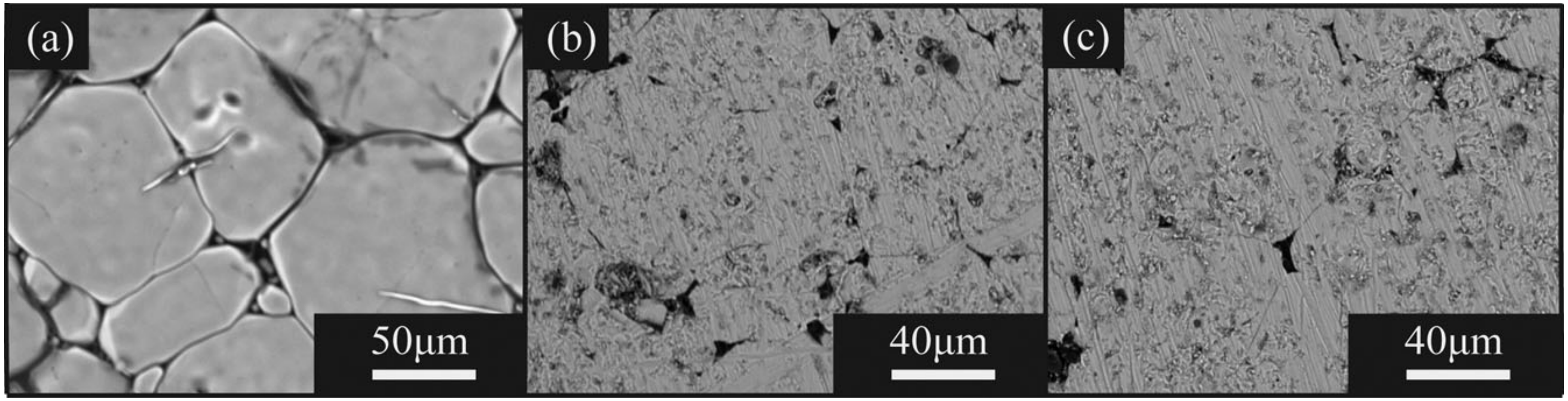
Origins of Interfacial Impedance



LIBS: Li/Zr ratio of a sample exposed to air for several months- ~ 1 μm thick Li-rich layer forms



LLZO reacts in water to form a basic solution



As-sintered

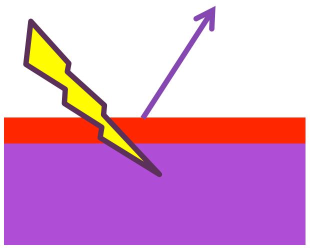
Polished under Ar

Polished under air, exposed to air several days

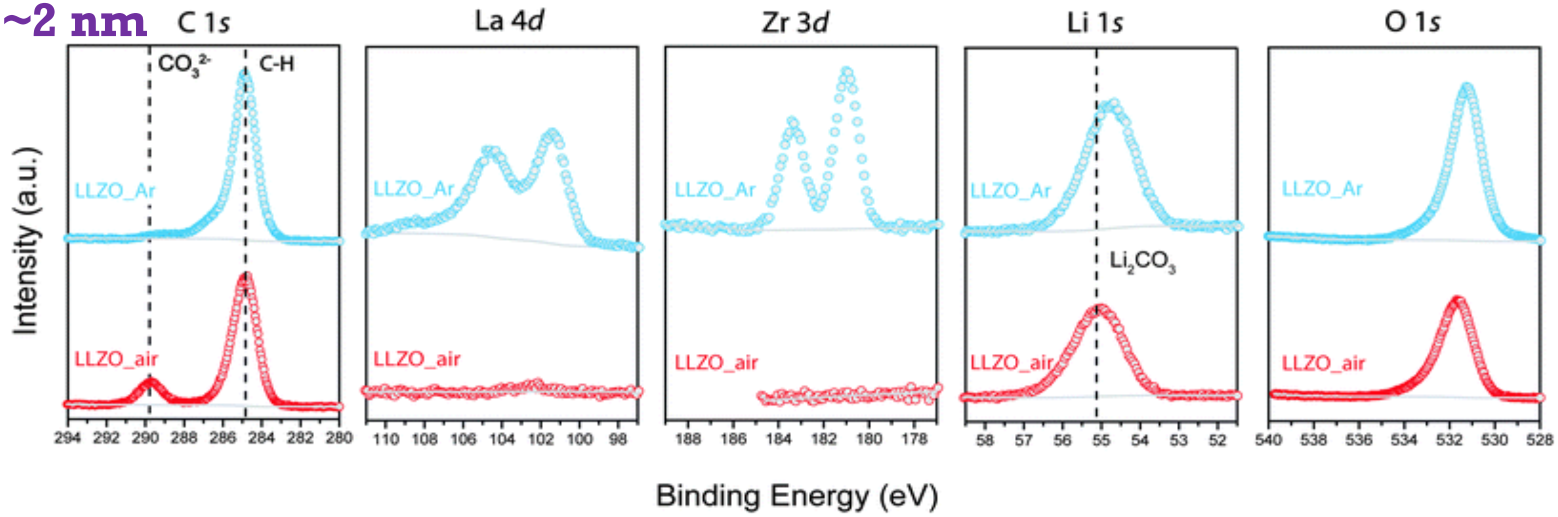
Could high interfacial impedance be related to these observations? Need surface sensitive techniques.

Depth profiling with Synchrotron XPS and s-XAS

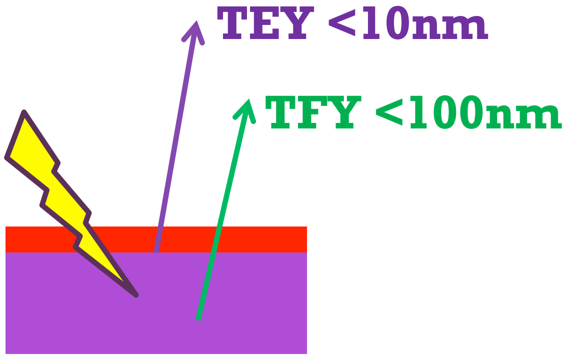
Photoelectron ~2 nm



ALS BL 9.3.2



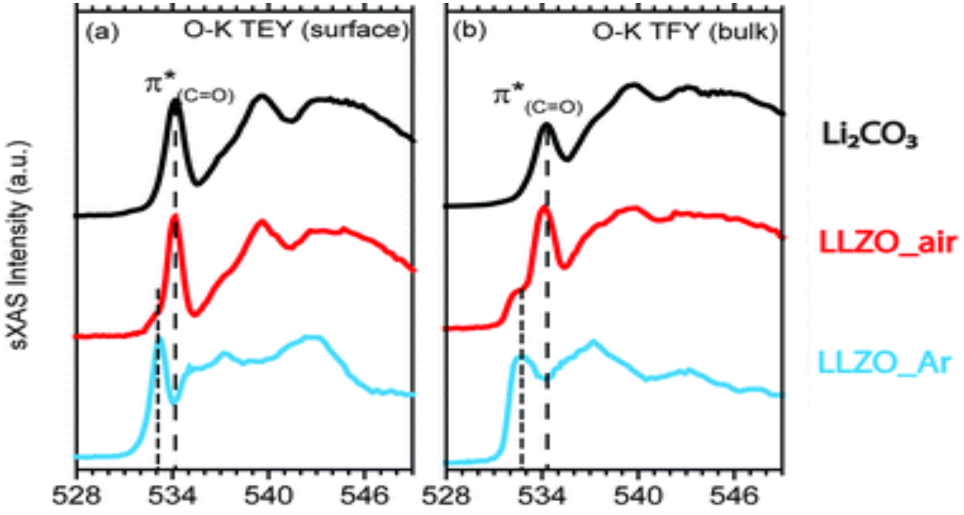
XPS: lower bound estimation of the Li_2CO_3 thickness: >2 nm



TEY <10nm

TFY <100nm

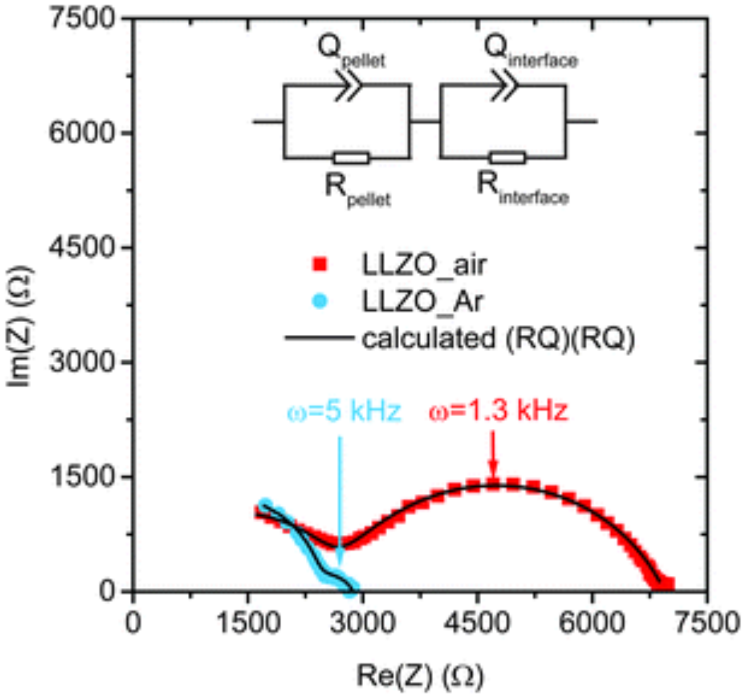
ALS BL 8.0.1

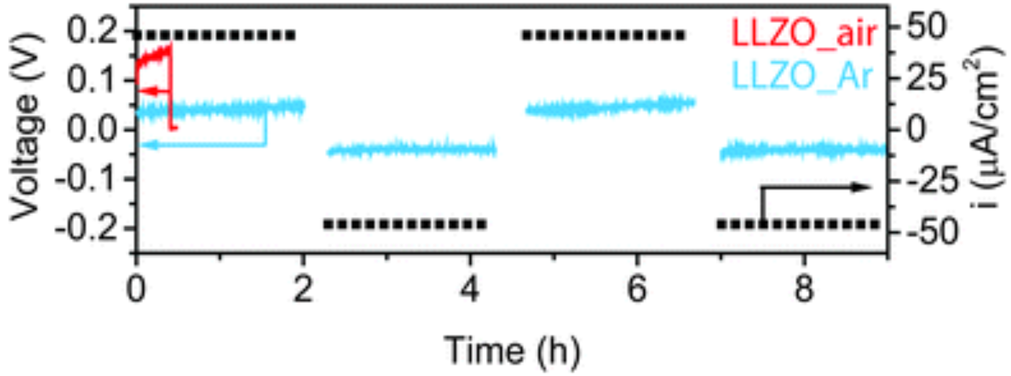


sXAS: upper bound estimation of the Li_2CO_3 thickness: <100 nm, likely ~10 nm

Cheng et al. PCCP, 16, 18294 (2014).

Lower interfacial resistance in the absence of surface Li_2CO_3



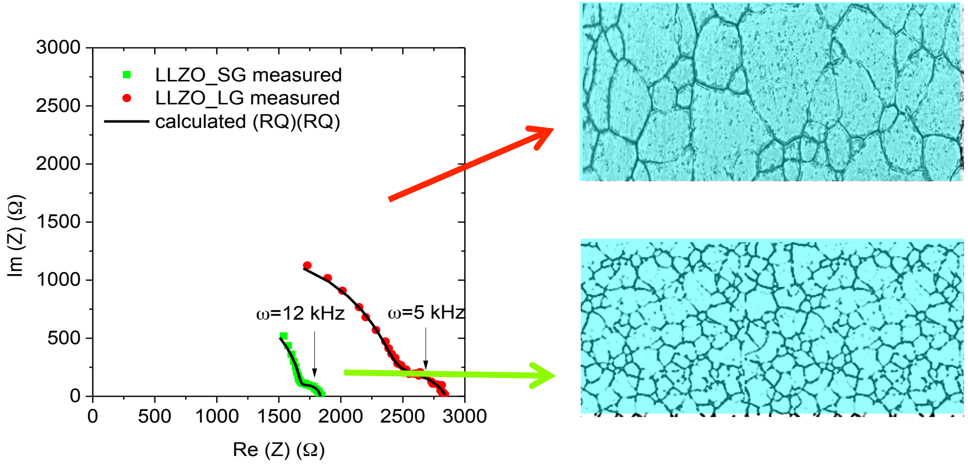


109 Ω·cm² is still not good enough to be practical

At current density of 10mA/cm², (10 mAh/cm² area capacity at 1C rate),
the interfacial resistance should be less then 10 Ω·cm² (0.1V loss at interface)

Name	Pellet Resistance	Interfacial Resistance	Interfacial ASR
LLZO_air	2052 Ω	4307 Ω	960 Ω·cm²
LLZO Ar	2355 Ω	491 Ω	109 Ω·cm²

Influence of Microstructure on Interfacial Impedance



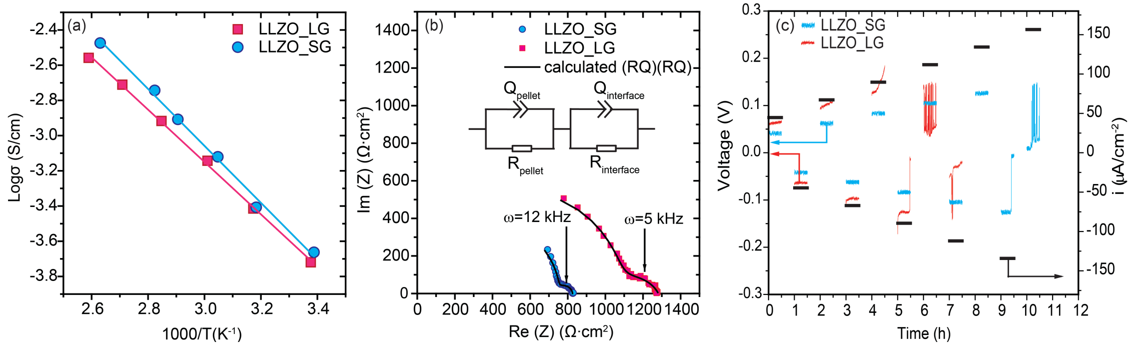
Removal of Li_2CO_3 layer and manipulation of microstructure lowers interfacial impedance, making LLZO a practical option for cells.

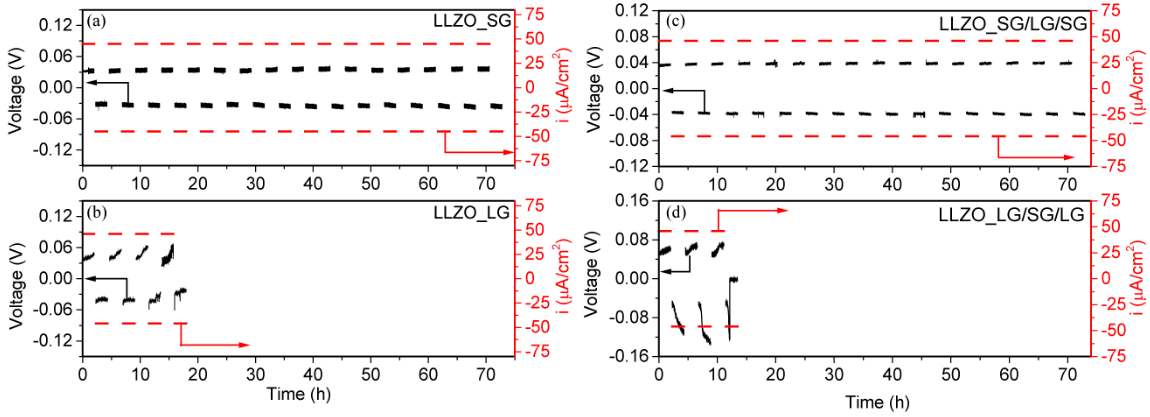
Item	**Total Conductivity**	**Bulk Resistance**	**Interfacial Resistance**	**Area specific interfacial resistance**
LLZO_LG	2.0×10^{-4}S/cm	2335 Ω	566 Ω	127 Ω·cm^2
LLZO_SG	2.5×10^{-4}S/cm	1672 Ω	161 Ω	37 Ω·cm^2

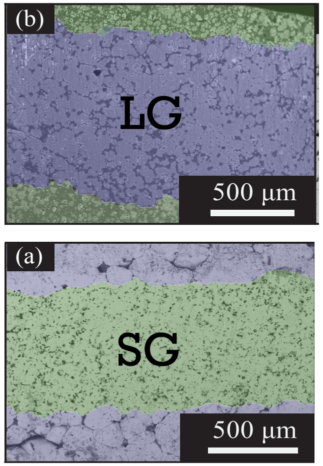
Much lower ASI!

Effect of Interfacial Impedance and Microstructure on Electrochemistry

Li/LLZO/Li cells



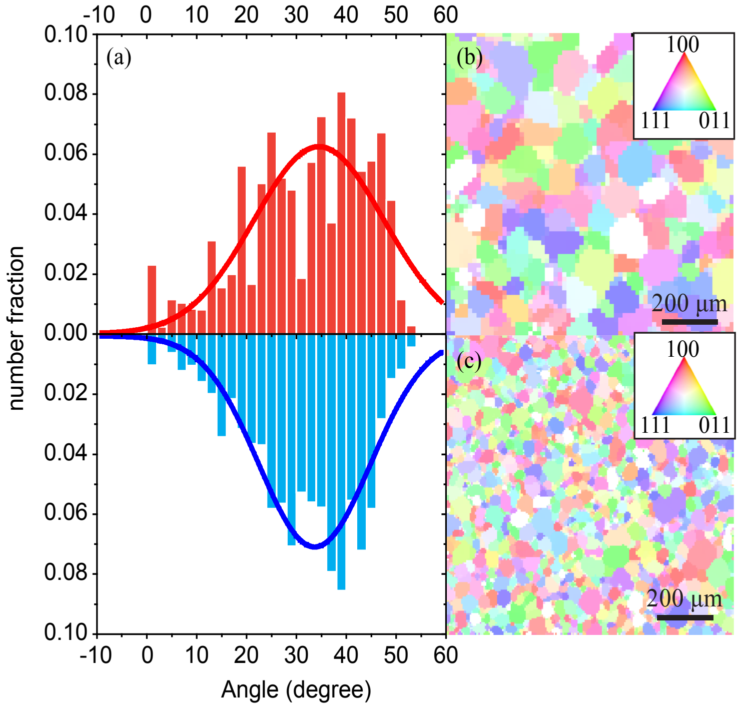




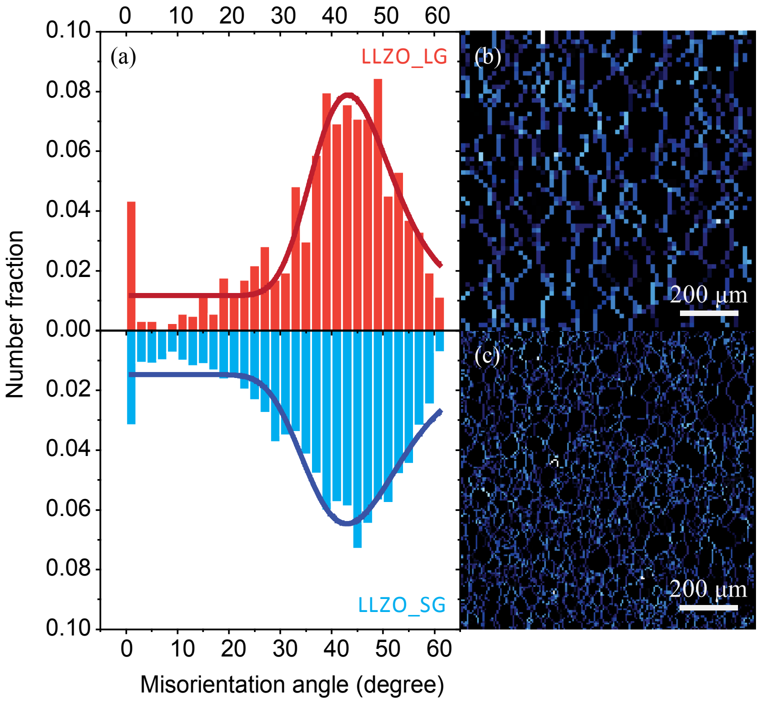
- Small grained samples have lower interfacial impedance and cycle better in stepped or constant current experiments
- Heterostructures with small grains on the outside (closest to Li electrodes) perform better than those with large grains on the outside.
- Surface microstructure is very important!
- BUT, could the difference be due to grain orientation effects?

Grain Orientation Mapping

High-resolution Synchrotron Polychromatic X-ray Laue Microdiffraction.



Grain orientation mapping



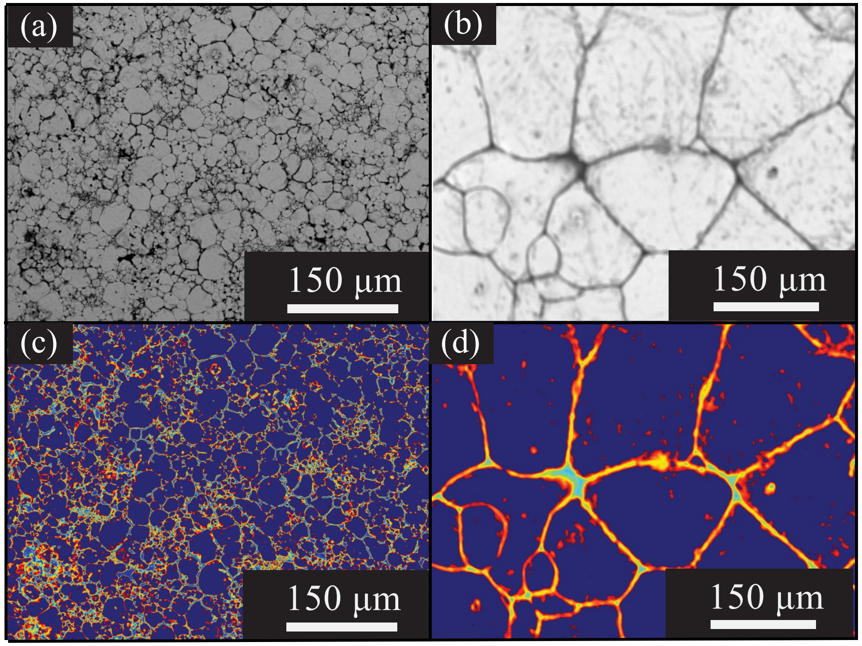
Misorientation angle mapping

- No differences in grain orientation or misorientations between samples➔Differences have to do with grain boundaries

Visualization of Grain Boundaries

Small grains

Large grains



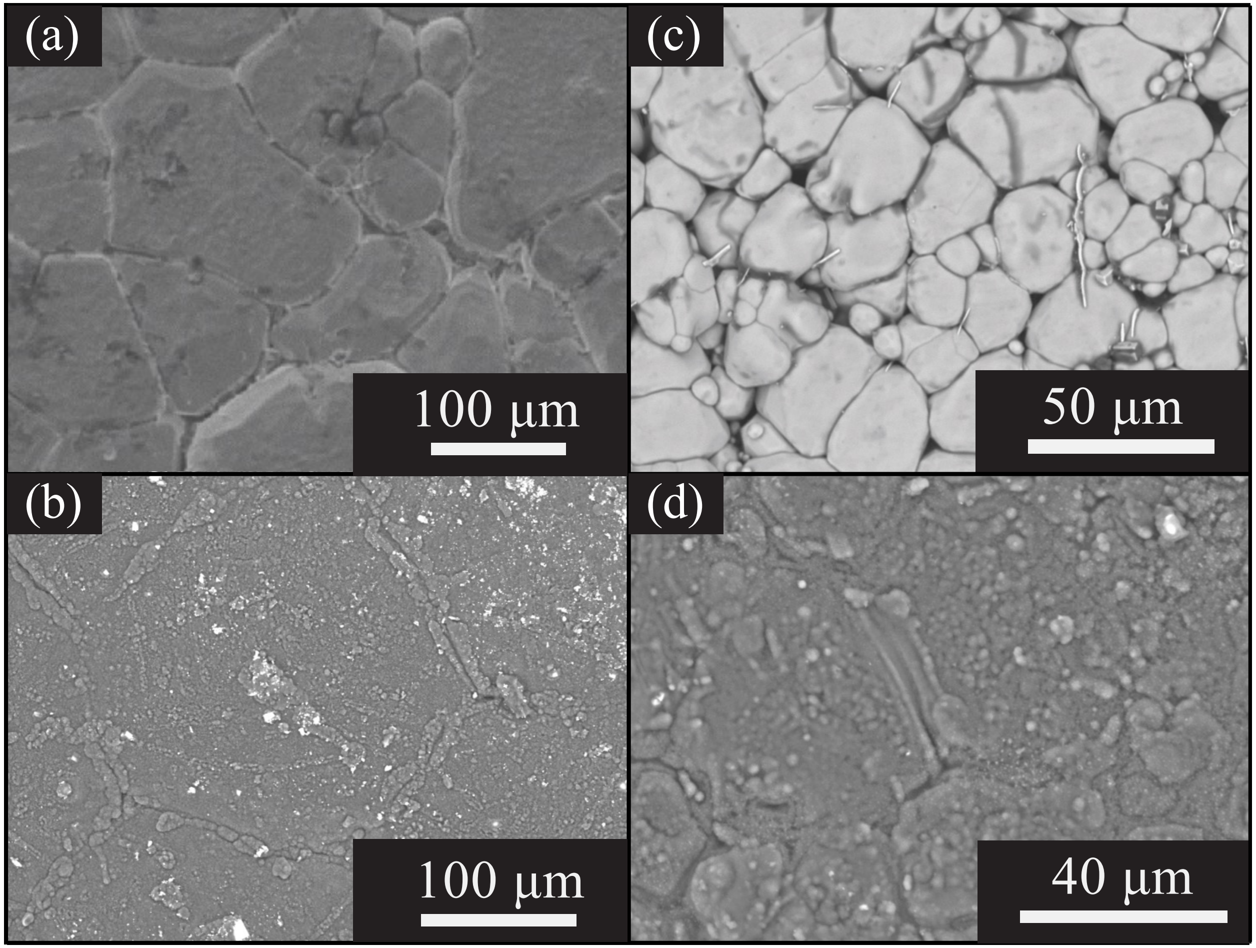
32%

16%

Area fractions of grain boundaries

Increased area fraction and tortuosity of grain boundaries in small-grained samples
dissipate current and ameliorate the current focusing that leads to dendrite formation.

Aging of LLZO Pellets in Air



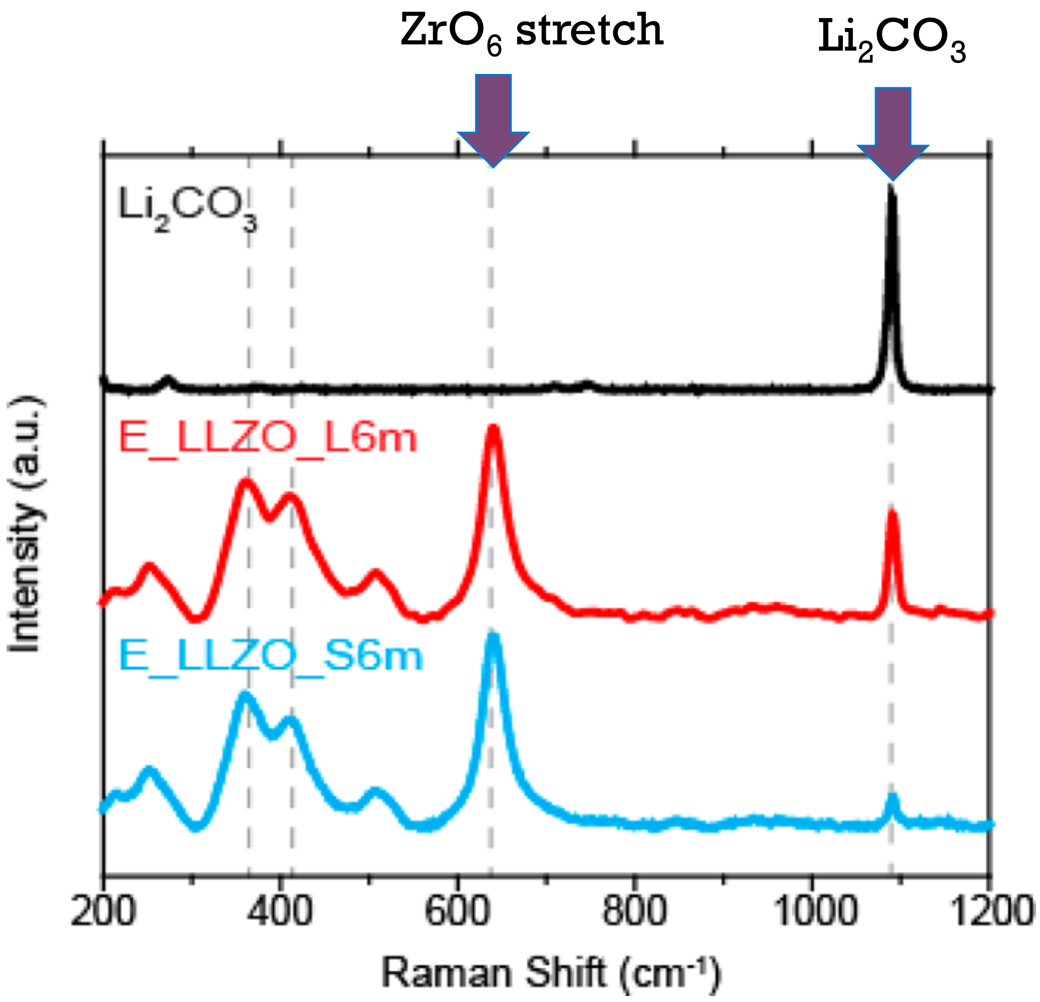
Pristine

6 months
air exposure

Large-grained sample

Small-grained sample

Effect of Microstructure on Li_2CO_3 Formation-Raman



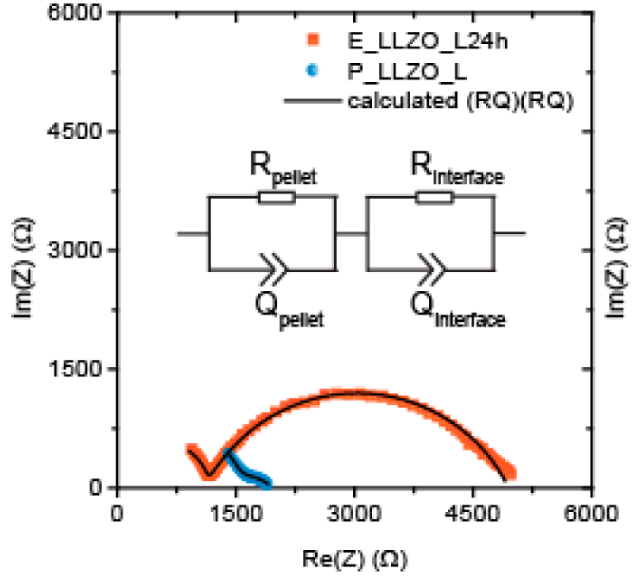
A typical Raman spectrum

Cheng et al., *ACS Applied Mater. & Interfaces*, *7*, 17649 (2015).

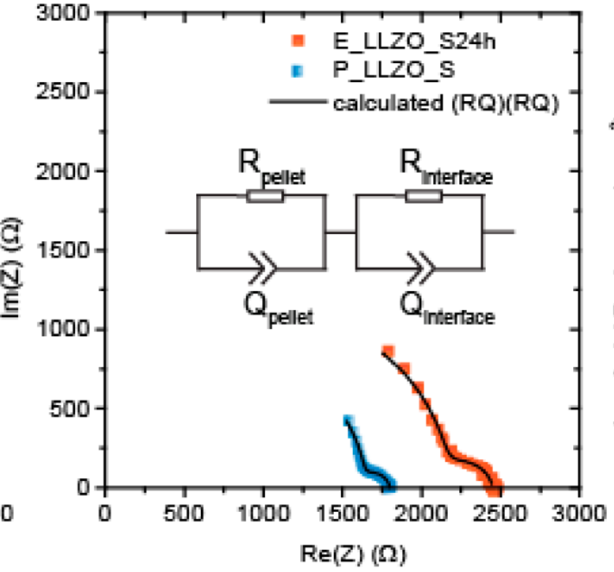
Sample	**Average Li_2CO_3/ LLZO peak ratio (%)**
LG-LLZO, six months	9.3±2.4
SG-LLZO, six months	4.9±1.2

Data averaged over 15 points

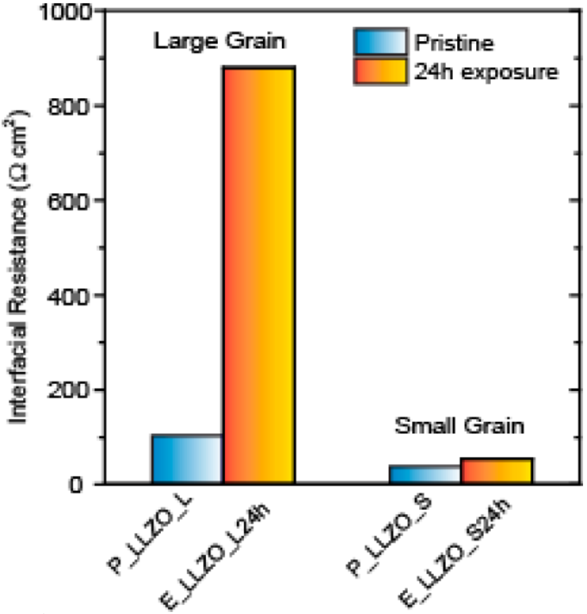
Grain size and Interfacial Impedance-24 hrs of exposure



Pristine and air-exposed (24 hrs) large-grained LLZO



Pristine and air-exposed (24 hrs) small-grained LLZO



Large-grained LLZO is much more sensitive to air than small-grained!

Soft XAS results-24 hours of exposure

O K-edge sXAS experiments

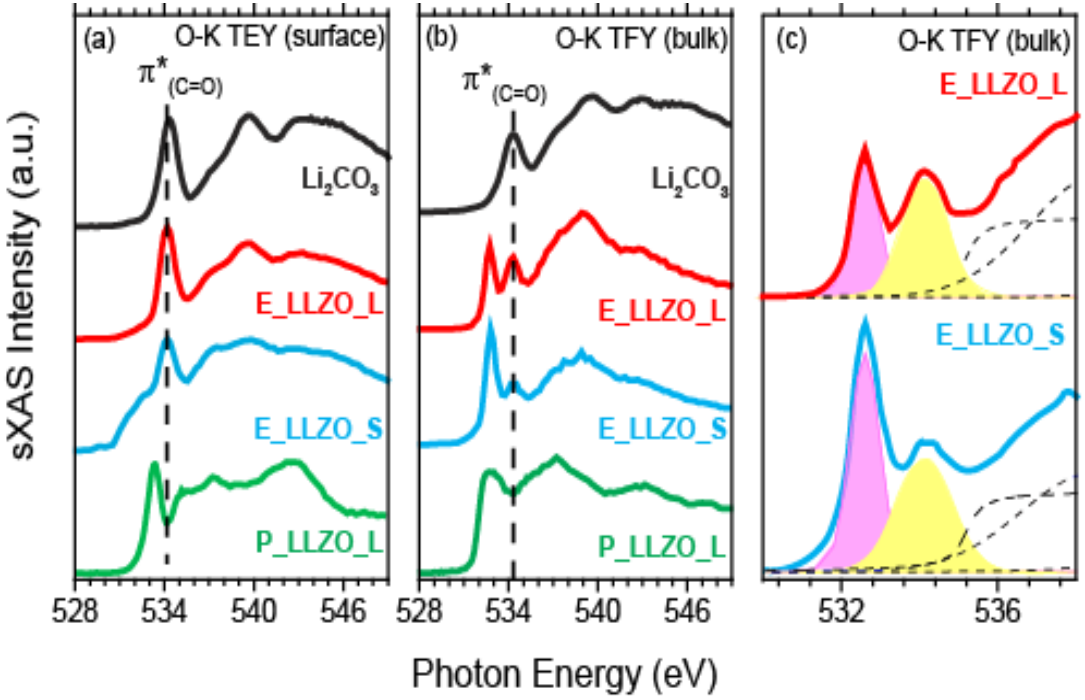
TEY (<10 nm) TFY (<100 nm)

Li_2CO_3

Air exposed LG

Air exposed SG

Pristine



Li_2CO_3/LLZO ratio

LG=1.33

SG=0.96

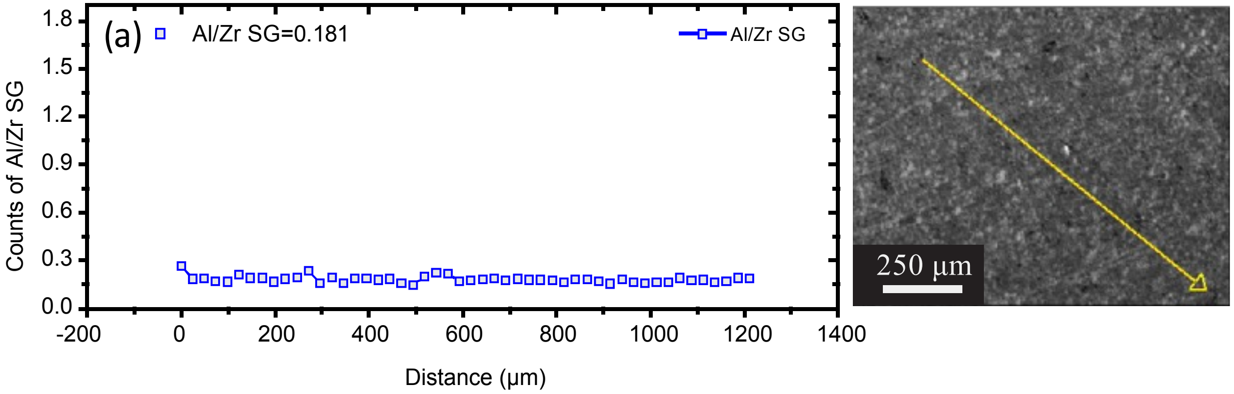
Lattice oxygen is still visible in SG sample in TEY mode, Li_2CO_3 layer is less than 10 nm thick.

Li_2CO_3 layer on LG sample is at least 10 nm thick

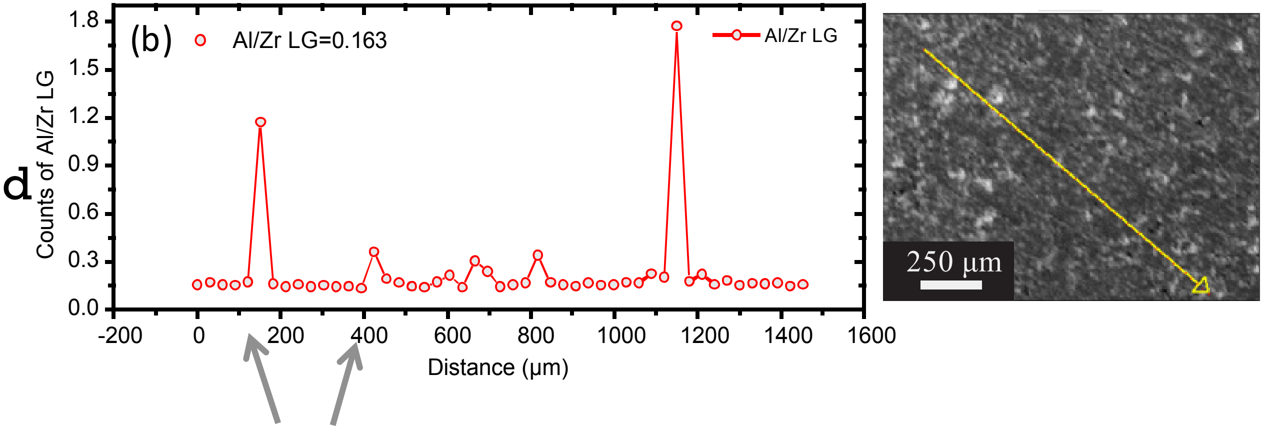
Why does Microstructure Affect Rate of Li_2CO_3 Formation?

EDS line scans, Al/Zr ratios

Small-grained



Large-grained



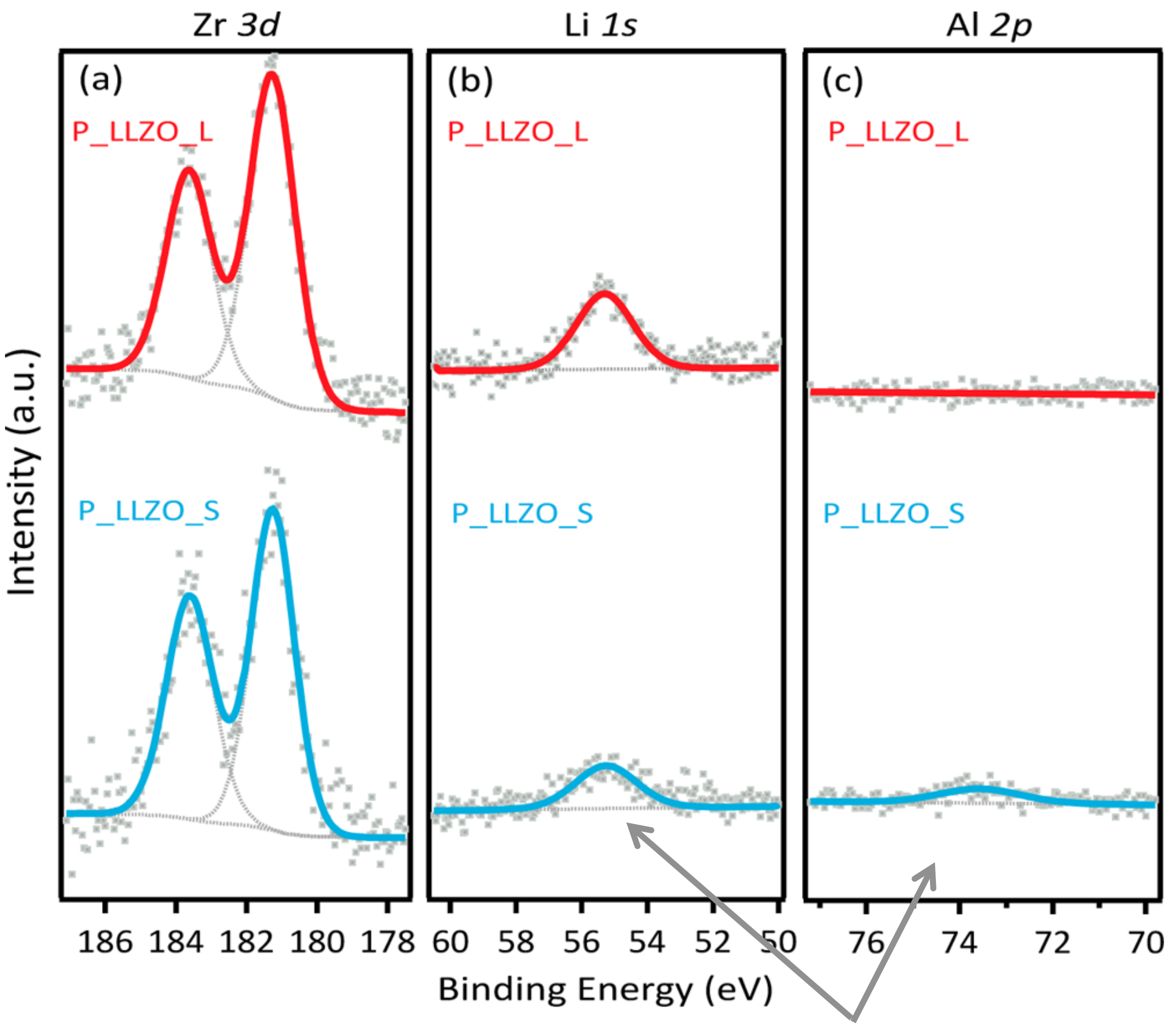
Al spikes every 200 μm!

Suggests Al enrichment at grain boundaries

Synchrotron XPS Experiments

Pristine LG

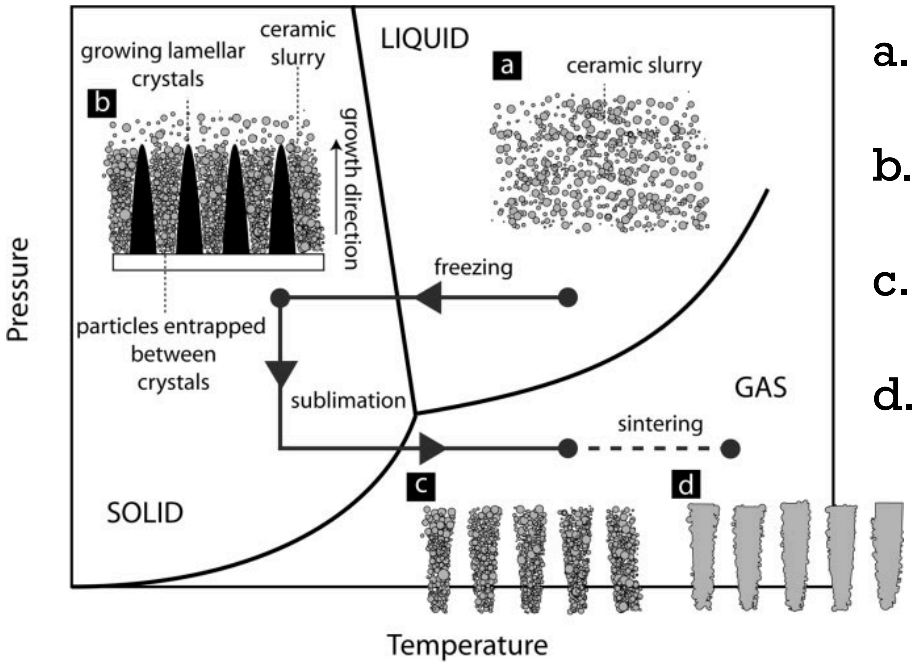
Pristine SG



More Al and less Li at surface (grain)=lower reactivity

Footprint about 1.1.x1.1 mm, probing depth ~2 nm (depends on element)

Freeze-casting, a route to composite electrodes for solid state batteries?



Schematic of freeze-casting process
Deville, *Adv. Engin. Mater.* 10, 155 (2008).

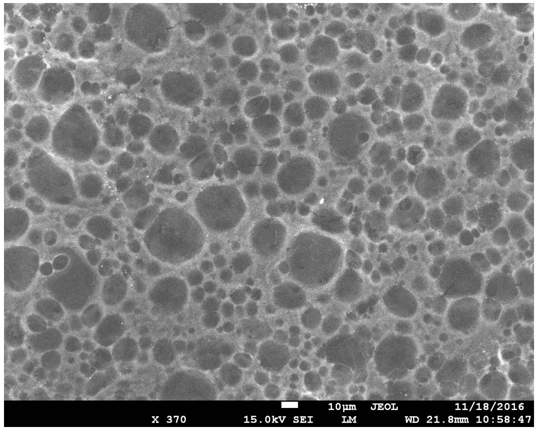
a. Freeze liquid suspension (ceramic slurry)
b. Formation of lamellar crystals takes place
c. Sublime away frozen solvent under controlled conditions
d. Sinter porous ceramic green body to strengthen pore walls

e. Fisker/MSU/LBNL innovation- Infiltrate with cathode active material and conductive polymer to make composite cathode.

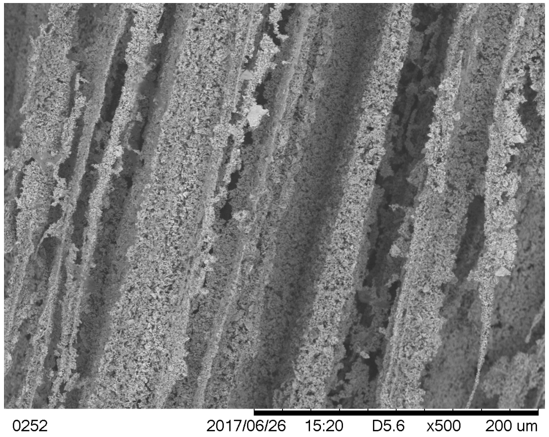
M. Doeff et al., U. S. Provisional Patent Application Serial No. 62/627,347 titled "FABRICATION OF THICK COMPOSITE ELECTRODES WITH UNIDIRECTIONAL PORES FOR SOLID-STATE BATTERIES," filed 7 February 2018.

LLZO Porous Scaffolds

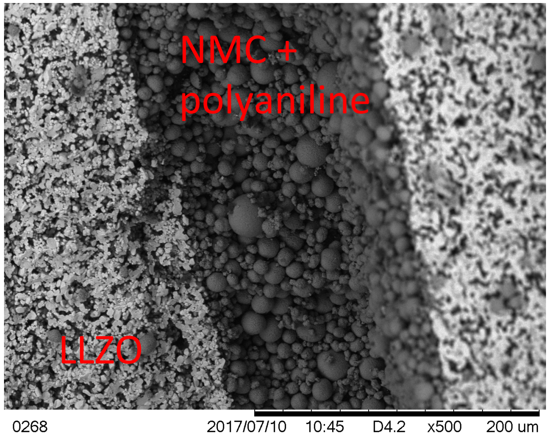
Freeze-casting in progress



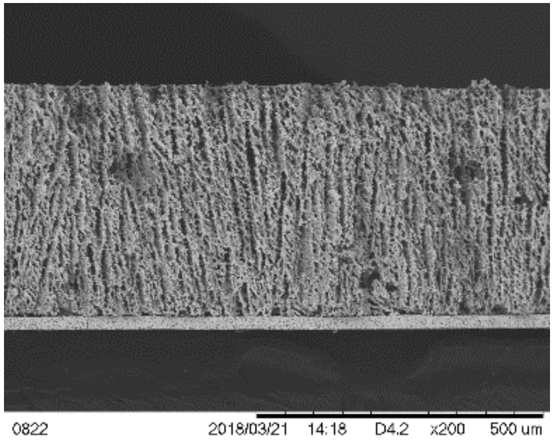
Green body, 25% solids



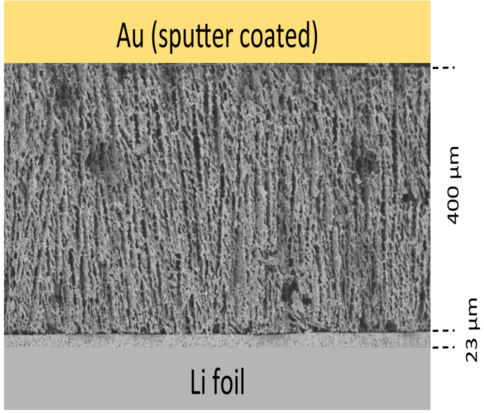
Porous scaffold, 71% porosity



Pore, infiltrated with NMC/polyaniline

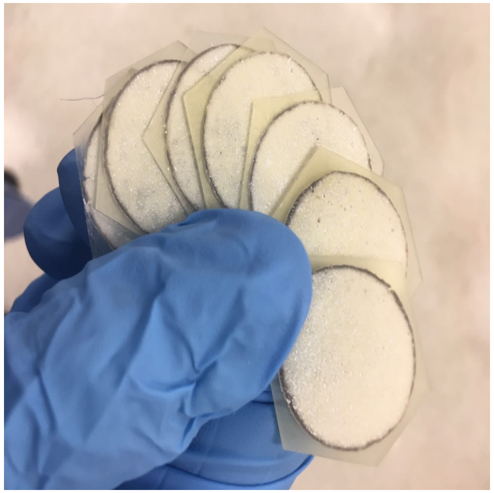


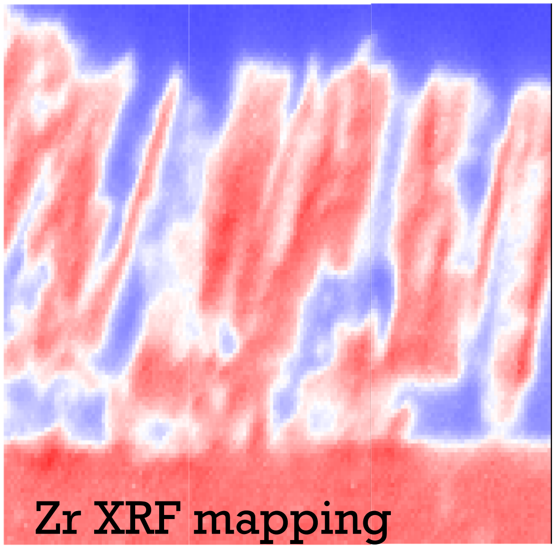
Bilayer, dense LLZO +scaffold

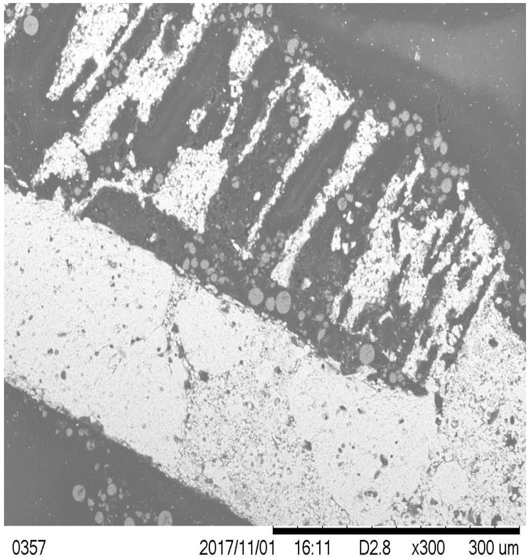


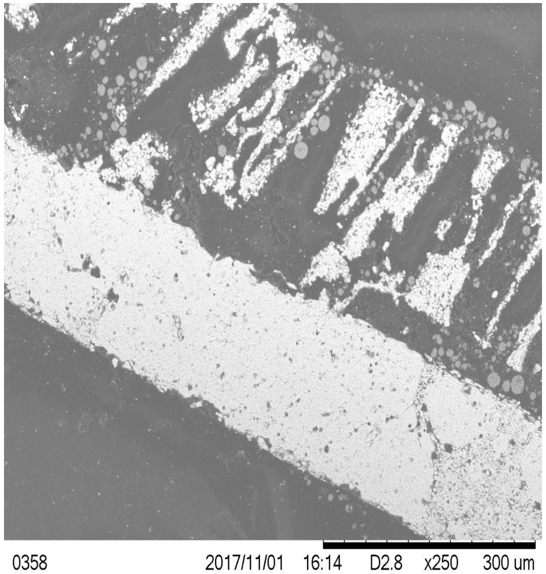
Test cell, schematic

+ Imaging using Synchrotron XRF





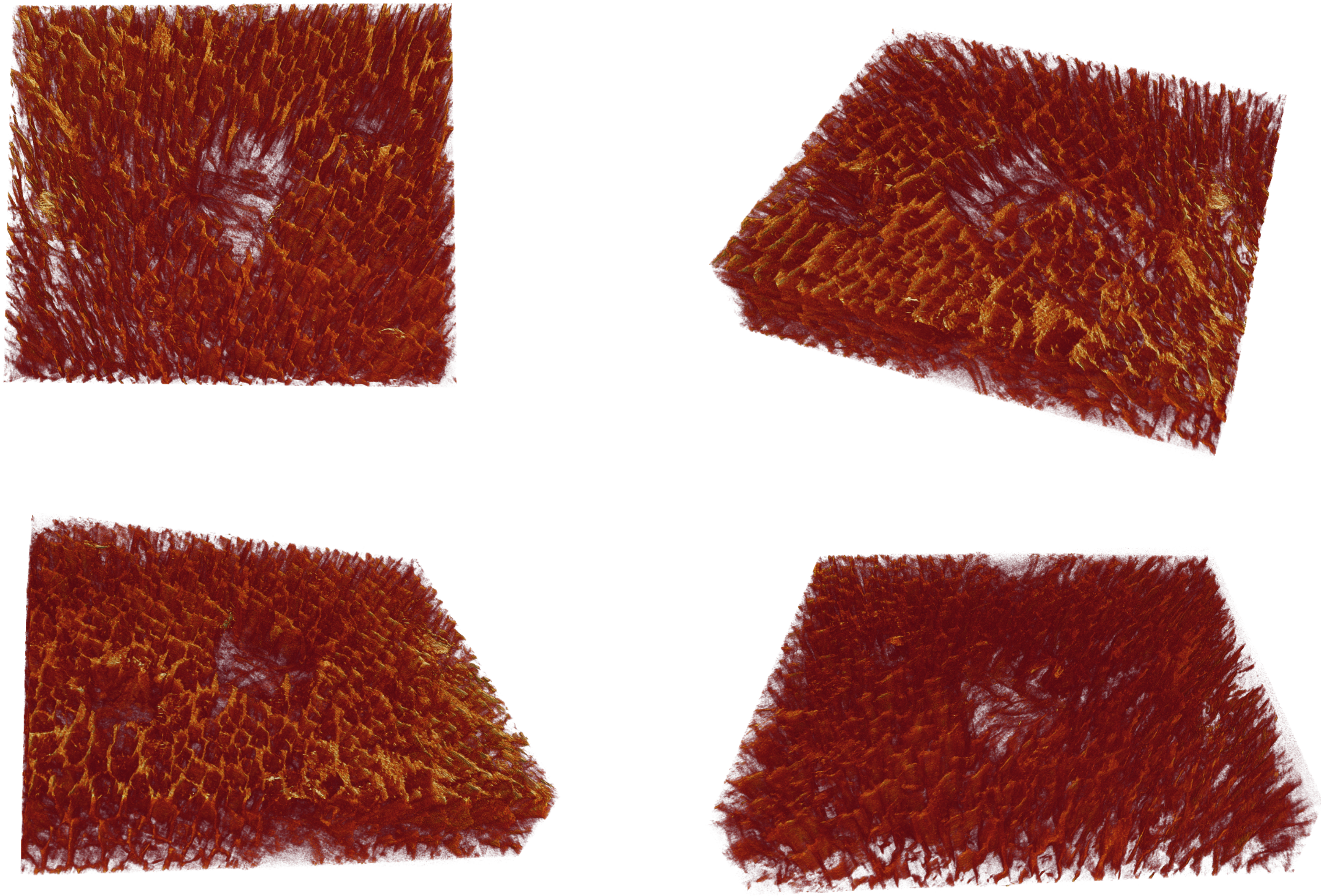




+

Synchrotron Tomography

- 3D model reconstruction for LLZO



Summary-LLZO

- Properties of LLZO (conductivity, critical current density etc.) are highly dependent on the microstructure.
- A surface layer of Li_2CO_3 is responsible for high interfacial impedance at the lithium electrode. Remove this layer to improve electrochemistry.
- Freeze-casting of LLZO, followed by infiltration of active material and polymer may be a scalable and low cost route to production of composite cathodes for solid state cells.
- We are now starting to use synchrotron techniques (tomography and XRF) to obtain information (e.g., porosity) about LLZO scaffolds.