BERKELEY LAB
LAWRENCE BERKELEY NATIONAL LABORATORY

U.S. DEPARTMENT OF ENERGY

Recent Advances on Garnet LLZO Solid Electrolytes for Lithium Batteries

Marca M. Doeff, Guoying Chen, Lei Cheng

Energy Storage and Distributed Resources Division

Lawrence Berkeley National Laboratory

Berkeley, CA

Contact mmdoeff@lbl.gov

Acknowledgments-LLZO

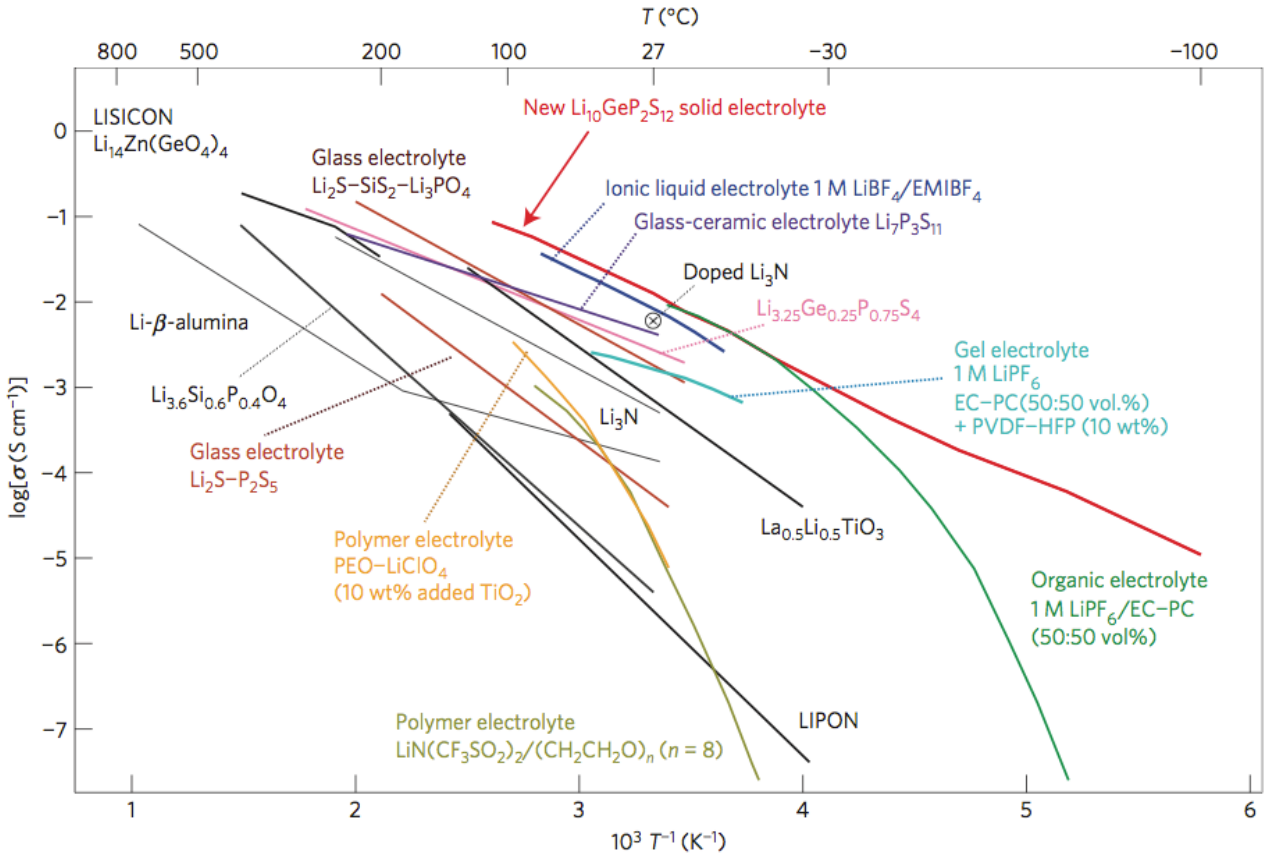
- **DOE Office of Vehicle Technologies for funding under ILIRP and BATT**

Lei Cheng, PhD student
MSE, UCB-Obtained PhD in 2015
now at Quantum Scape

- Tom Richardson (LBNL)
- Jordi Cabana (LBNL, now UIC)
- Guoying Chen (LBNL)
- Vassilia Zorba (LBNL)
- Rick Russo (LBNL)
- Huaming Hou (LBNL)
- Ethan Crumlin (LBNL, ALS)
- Wei Chen (LBNL)
- Ruimin Qiao (LBNL, ALS)
- Simon Lux (LBNL)
- Robert Kostecki (LBNL)
- Zhi Liu (LBNL, ALS)
- Kristin Persson (LBNL)
- Wanli Yang (LBNL, ALS)
- Martin Kunz (LBNL, ALS)
- Nobumichi Tamura (LBNL, ALS)
- Chenghao Wu (LBNL)
- Angelique Jarry (LBNL)
- Yifan Ye (LBNL, ALS)
- Jinghua Guo (LBNL, ALS)
- Miquel Salmeron (LBNL)
- Junfa Zhu (LBNL, ALS)
- Joong Sun Park (LBNL)
- Apurva Mehta (SSRL)

Samantha Catarelli, Uniscan
Daniel Lonsdale, Uniscan
Jaroslaw Syzdek, Bio-Logic

Electrolyte Conductivities

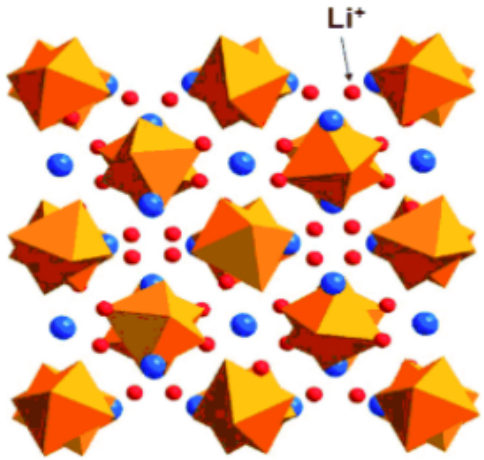


Kamaya et al., Nat. Mater. 10 (2011), 682.

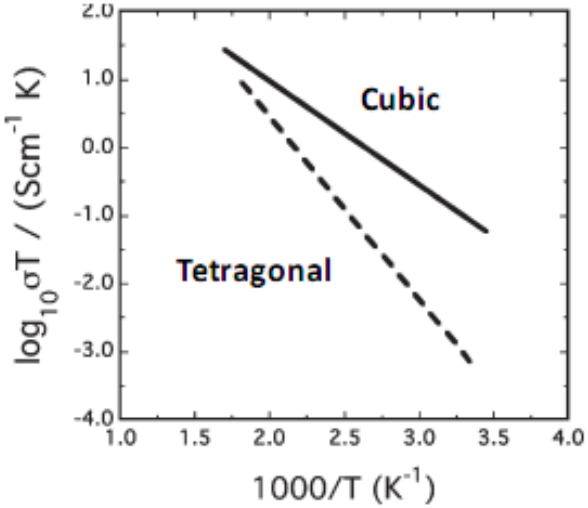
Issues for solid electrolytes:

- Conductivity (single ion conductors)
- Processibility (thin dense films)
- Reactivity (with electrodes, substrates, atmosphere, etc.)

$Li_7La_3Zr_2O_{12}$ 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.

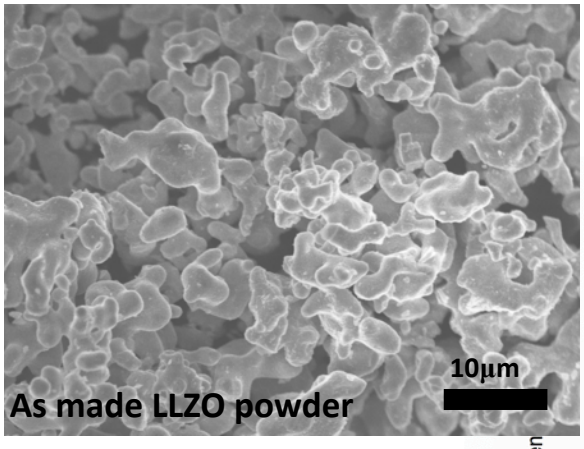
Pros:

- 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

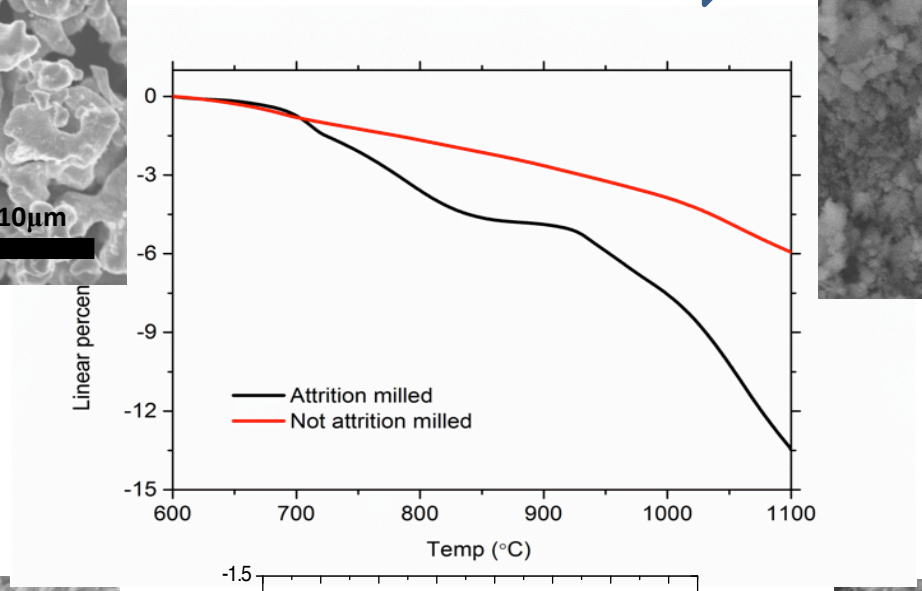
Cons:

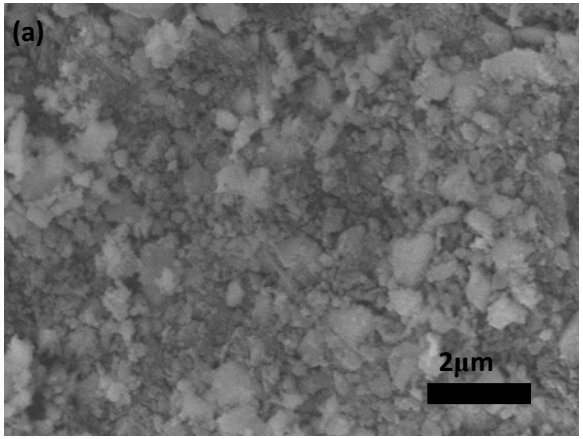
- Difficult to densify
- Reactivity with substrates, moisture, ambient atmosphere
- High interfacial impedances
- Thin films required: for 5 mA/cm^2, voltage drop < 100 mV, needs to be < 200 µm (assuming no contribution from interfacial impedances!)

Densification-particle size matters



Attrition mill



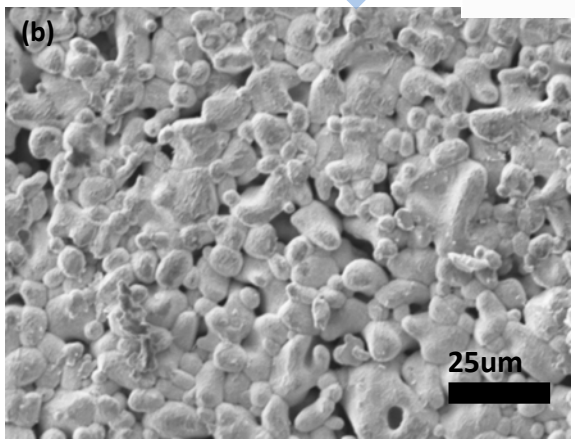


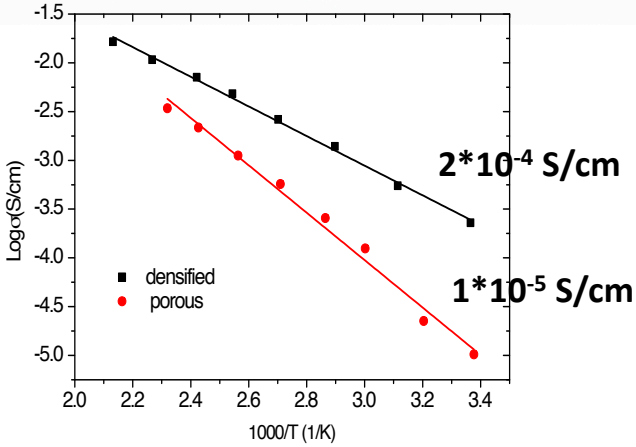
1100 °C sintering (porous)

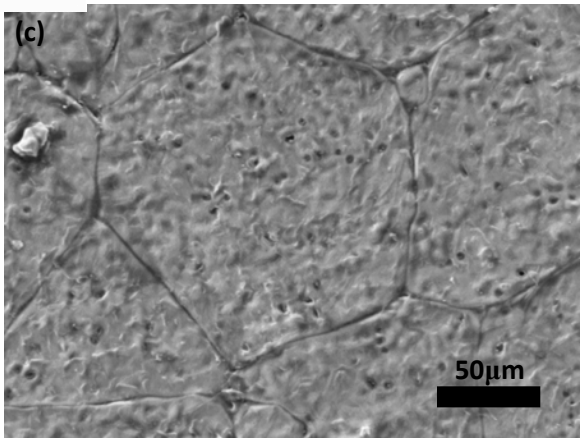
1100 °C sintering (Dense)

130 °C lower than previously reported for conventional processing

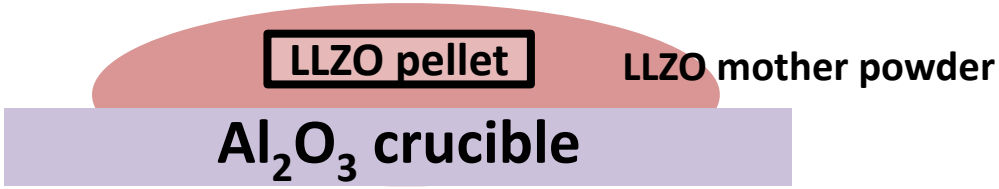
94% density



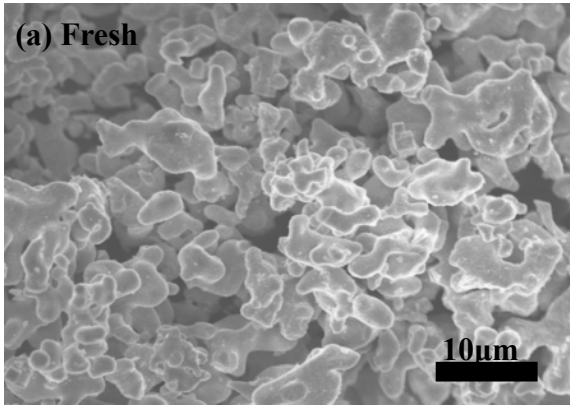


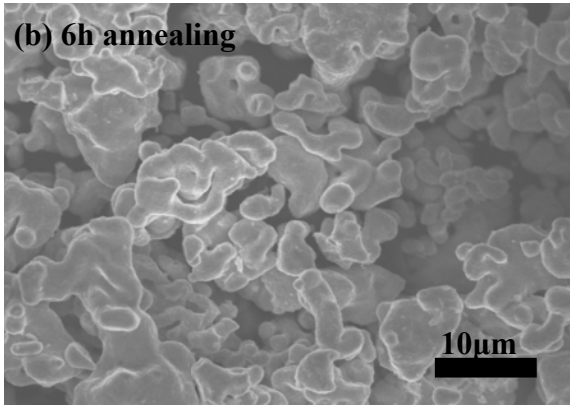


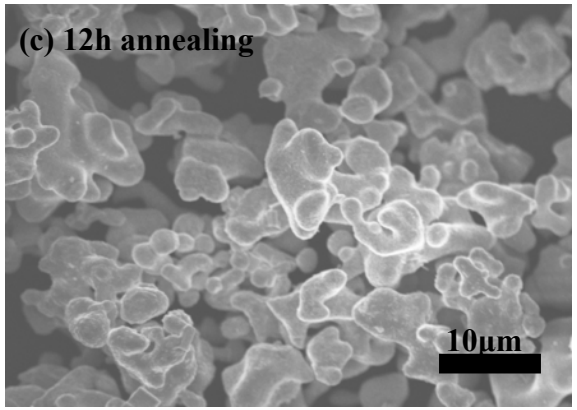
Composition matters



Microstructure of different powder covers



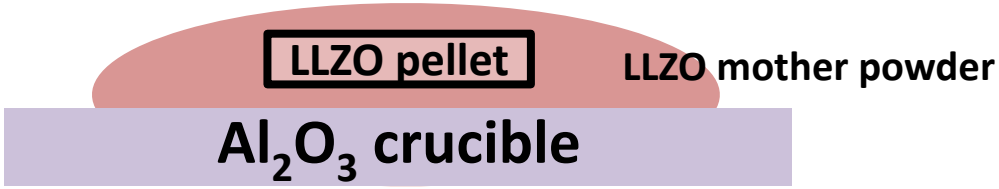




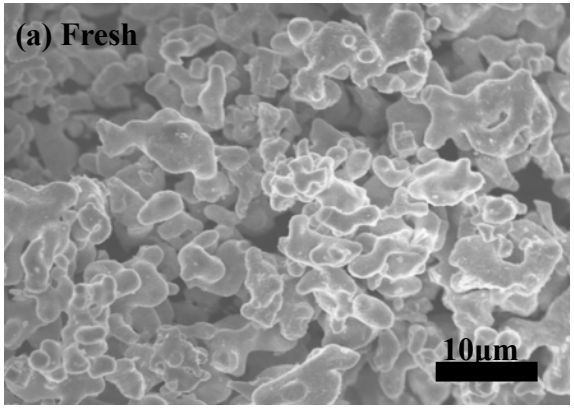
Li content decreases, Al content increases

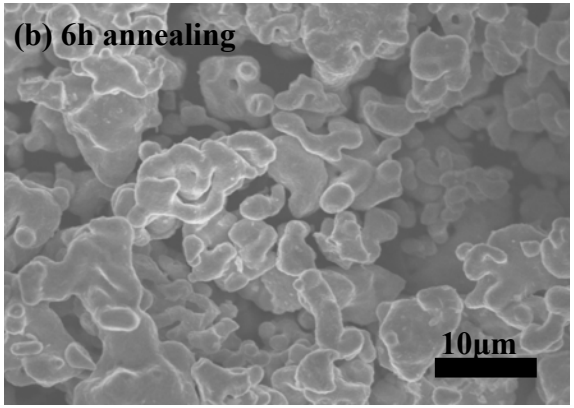
Annealing Time	0h (fresh)	6h	12h
Calculated Formula	$Li_{5.82}Al_{0.30}La_3Zr_{1.93}O_{11.72}$	$Li_{5.61}Al_{0.33}La_3Zr_{1.95}O_{11.70}$	$Li_{5.34}Al_{0.39}La_3Zr_{1.95}O_{11.66}$
Lattice parameter	12.9848 Å	12.9813 Å	12.9653 Å

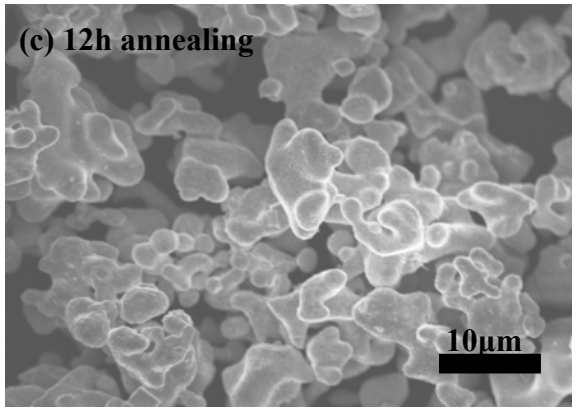
Composition matters



Microstructure of different powder covers

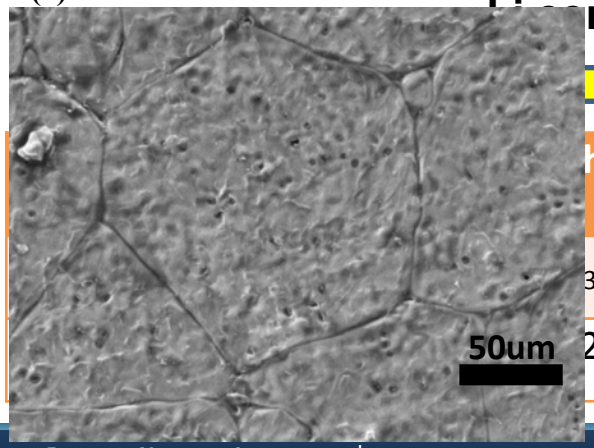




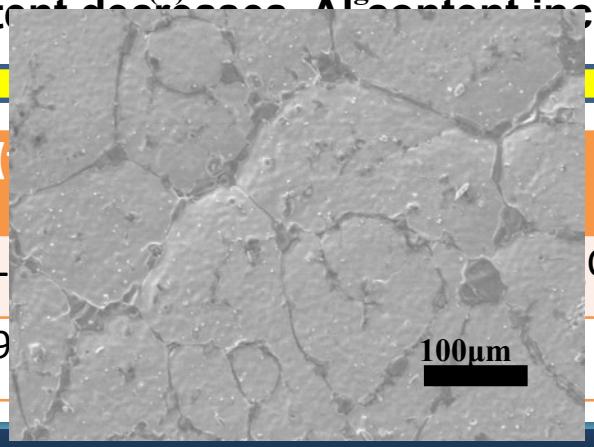


Microstructure of sintered pellet under different powder covers

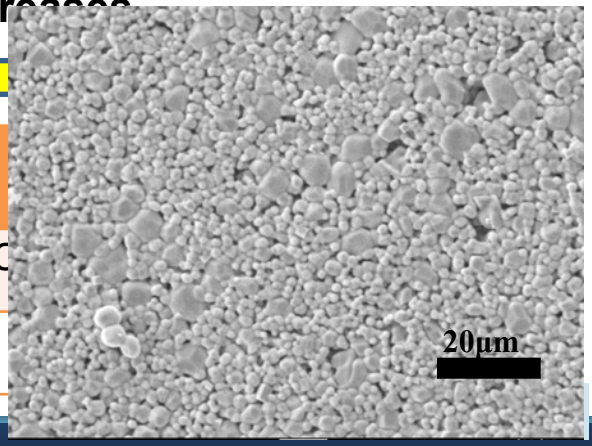
(a) fresh



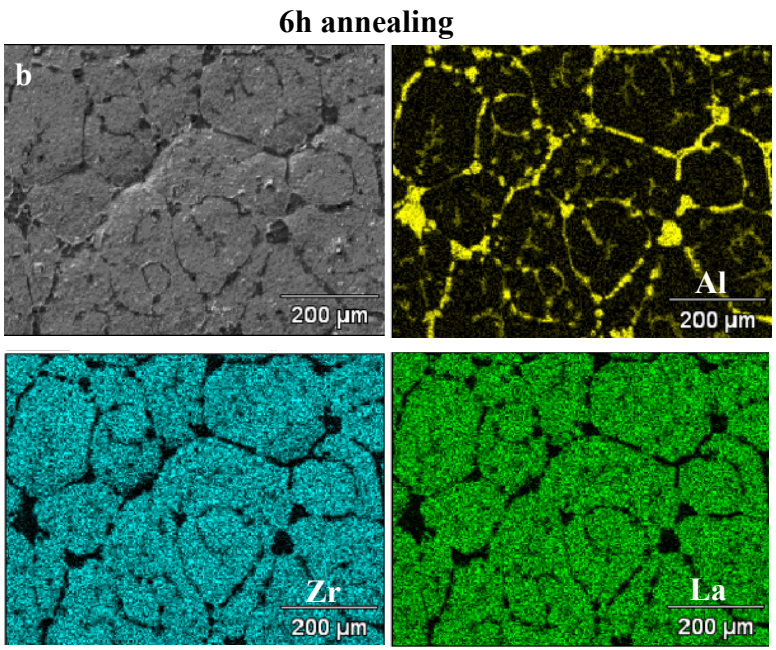
(b) 6h annealing

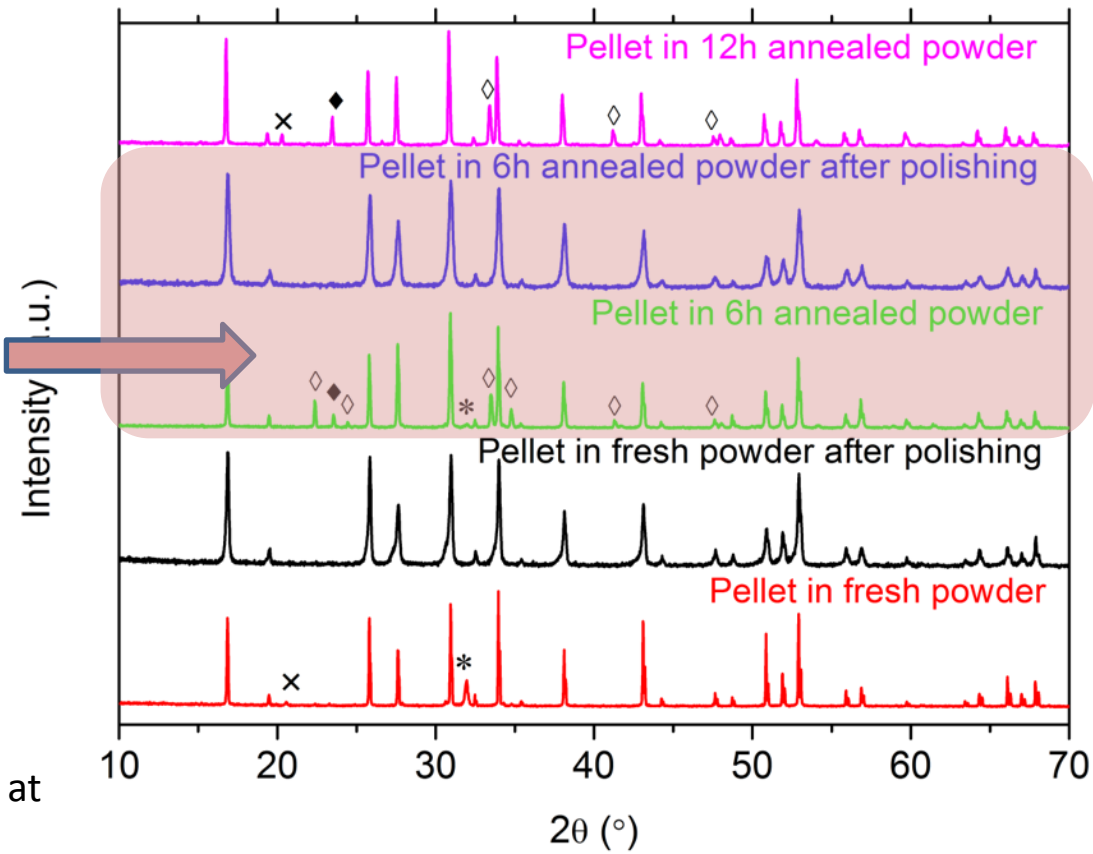


(c) 12h annealing



Surface impurity segregation





Al rich impurities (probably $LiAlO_2$) segregate at grain boundaries in the sample made under the thermally treated powder. There are more surface impurities as well (particularly Al-rich ones), which can be polished away.

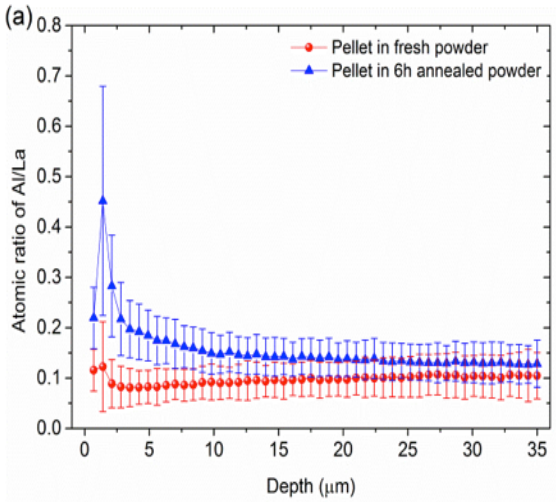
Cheng et al., *J. Mater. Chem. A*, 2, 172 (2014).

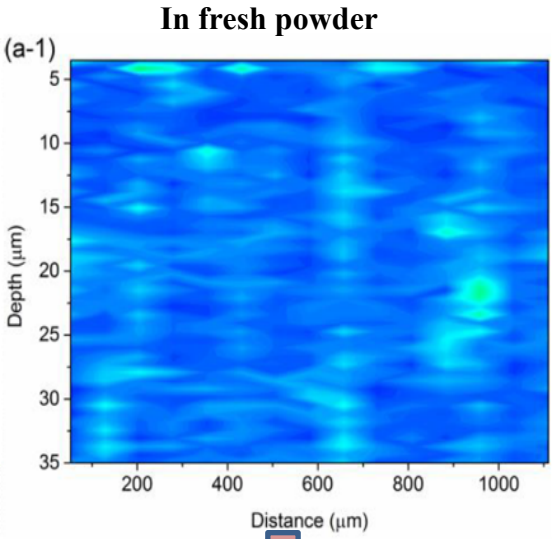
◊$LiAlO_2$(PDF# 018-0714); ♦$LaAlO_3$(PDF# 085-1071); *$La_2Li_{0.5}Al_{0.5}O_4$(PDF# 040-1167); ×Li_2ZrO_3(PDF# 016-0263).

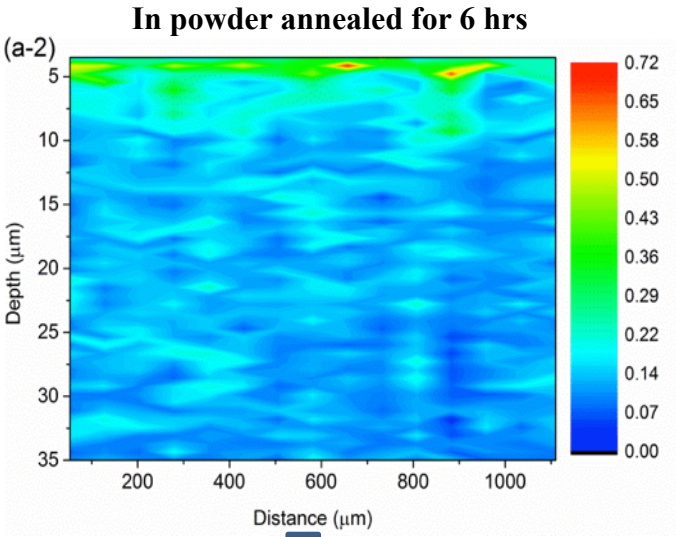
Visualization of impurity distribution-Al/La ratios

1-D depth profile

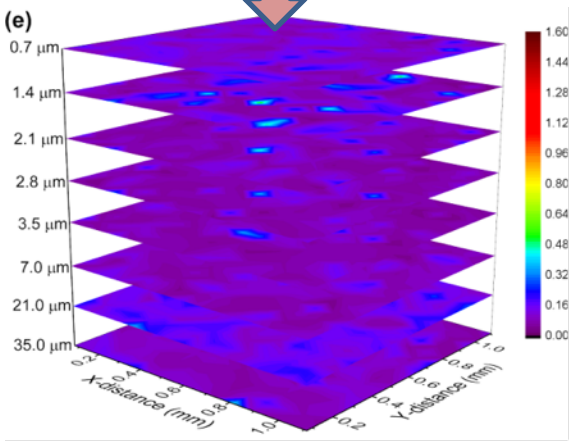
2-D cross section mapping

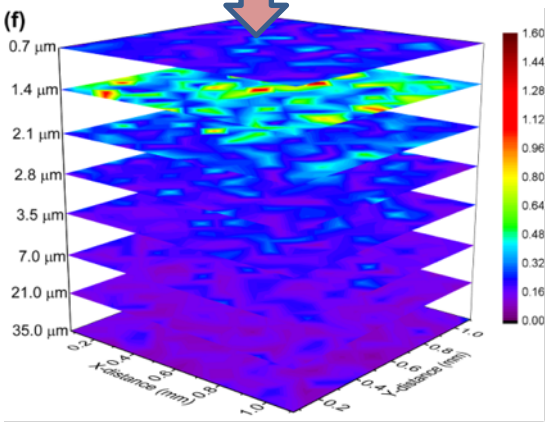






- Using Laser induced breakdown spectroscopy (LIBS) to determine the elemental distribution
- All data showing atomic ratio of Al/La



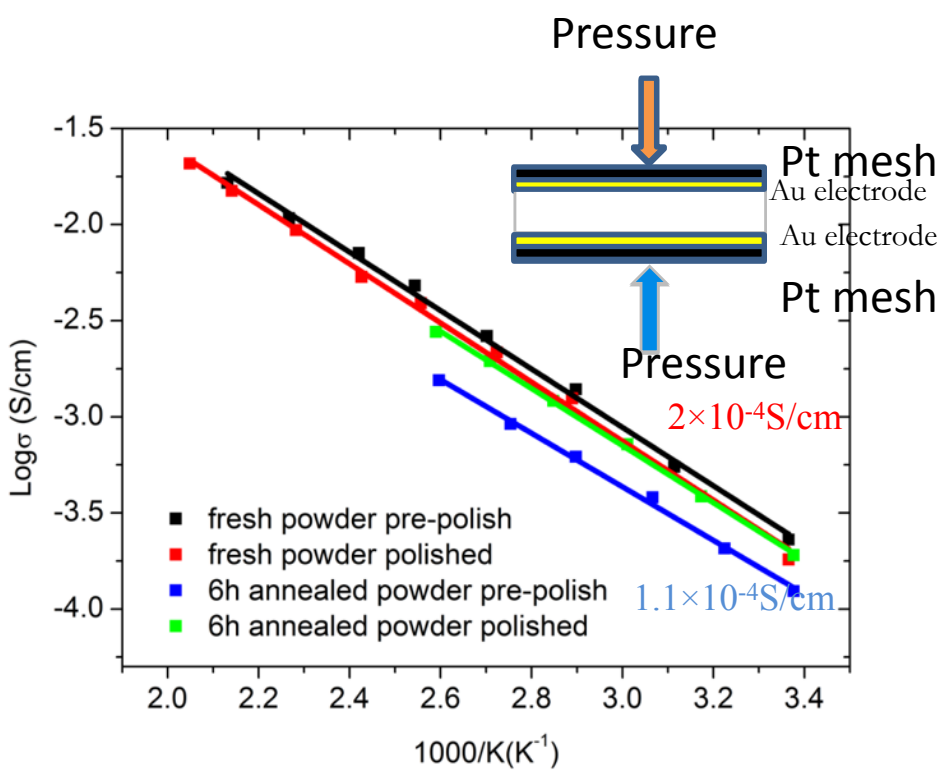


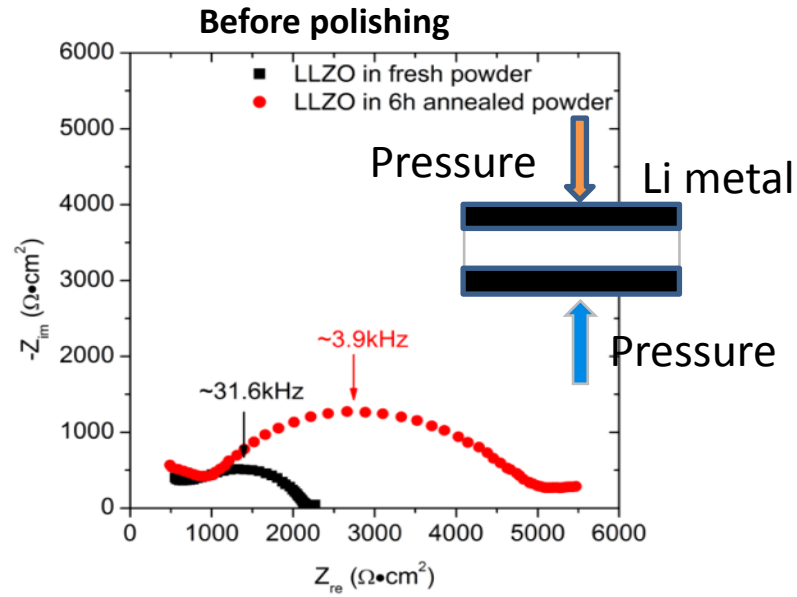
No difference found for Li/La and Zr/La

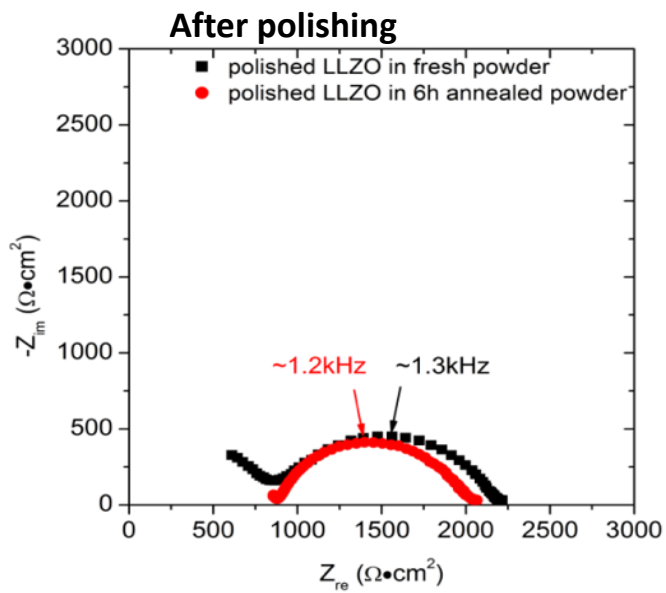
3-D layer stacking

See Hou et al. *J. Anal Atomic Spectroscopy*, 30, 2295 (2015) .

Electrochemical properties

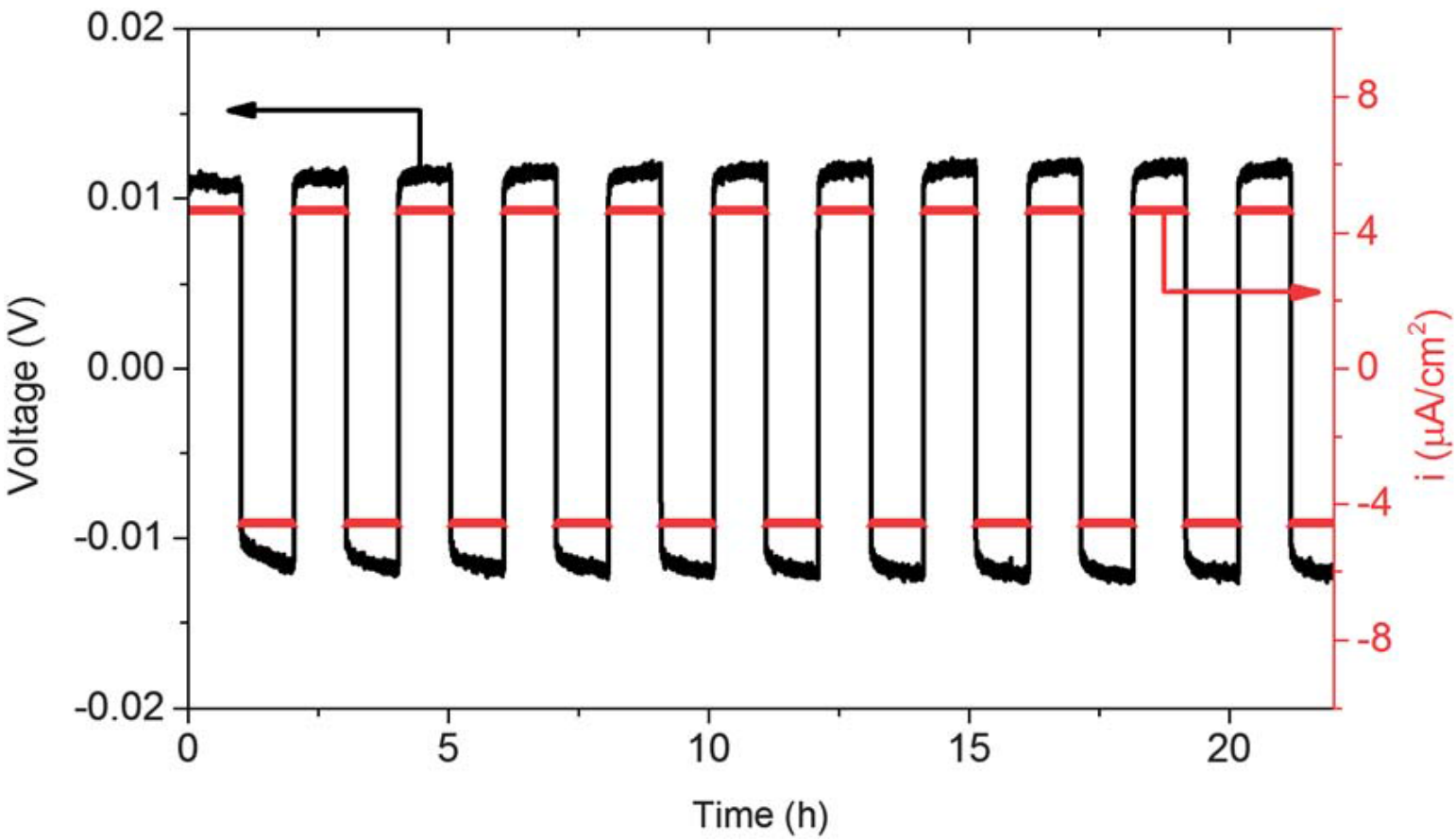






- Small variation in conductivity in general
- Significant difference in interfacial performance

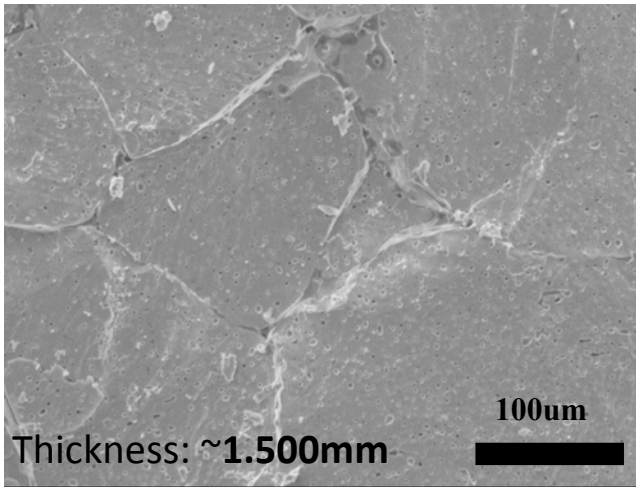
DC cycling



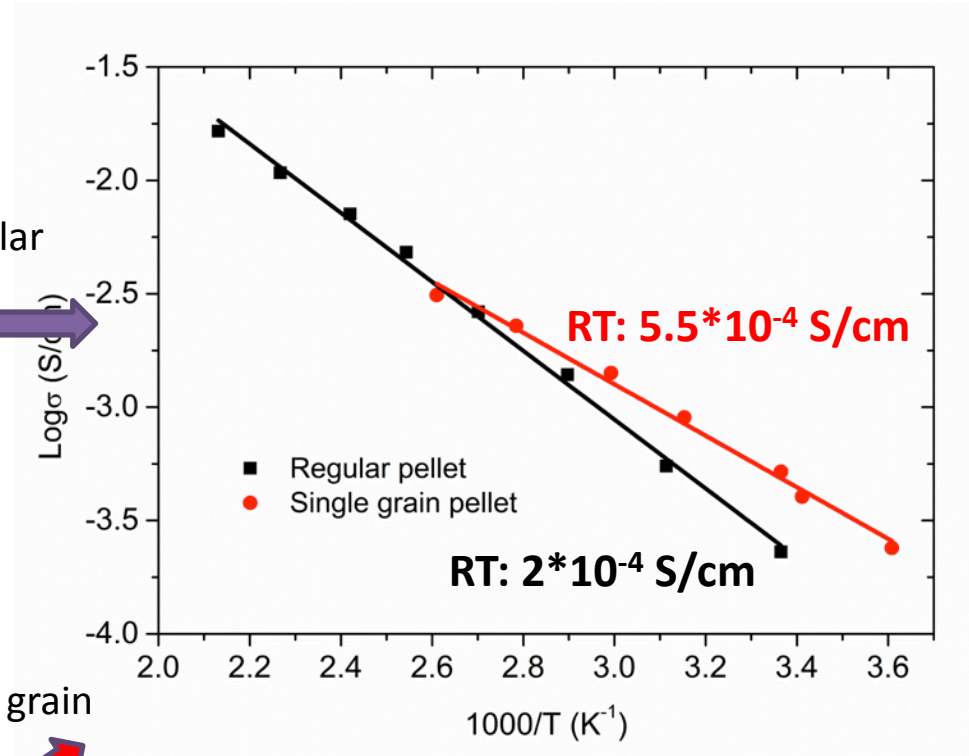
Galvanostatic cycling of a symmetrical cell with lithium electrodes and LLZO sintered in fresh powder at current density of ±4.6 μA cm^2. The LLZO pellet used for this experiment was approximately 1.5 mm thick and 8.0 mm in diameter and was processed in fresh powder without polishing.

Free-standing thin films, a single grain thick

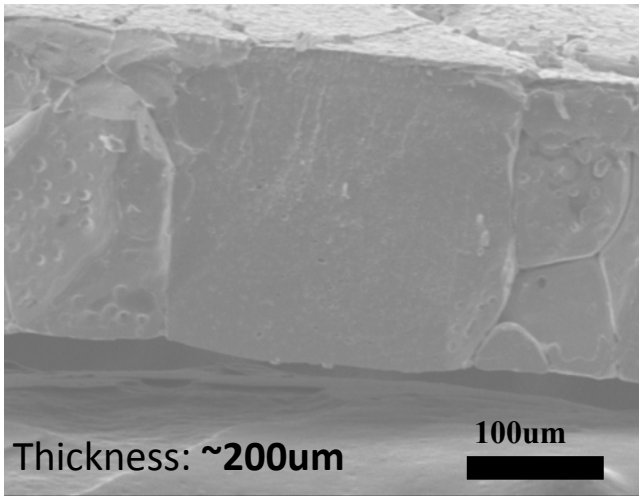
Cross section (fractured)



Regular



Single grain

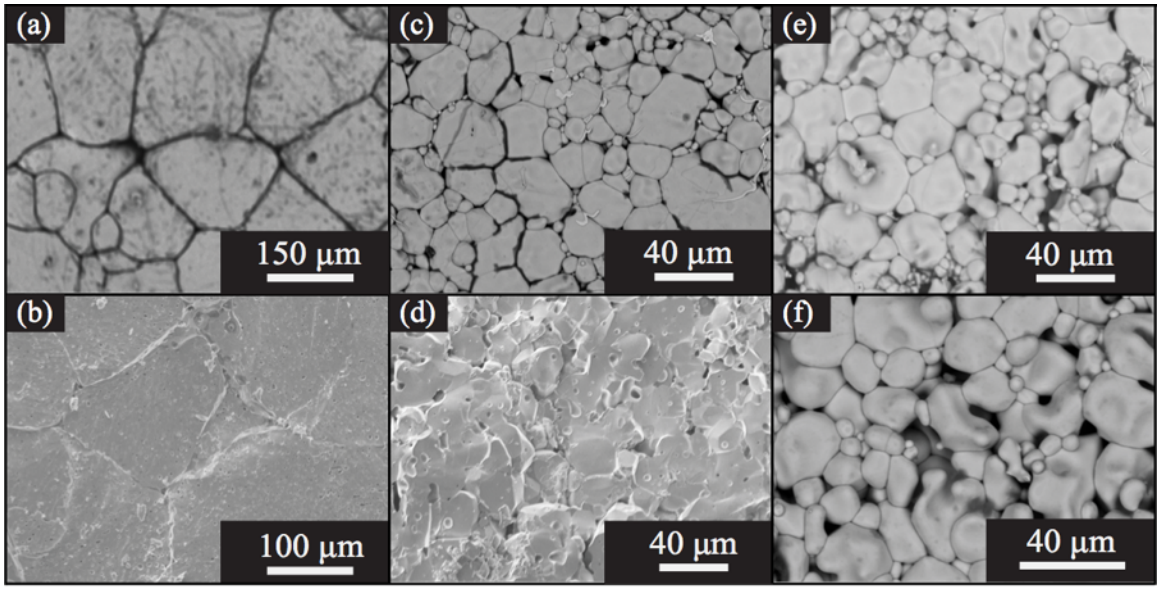


Cheng et al., *J. Mater. Chem. A*, 2, 172 (2014).

Control of Microstructures

surface

cross-section



surface
70% 1 µm
30% 10 µm

surface
50% 1 µm
50% 10 µm

1 µm particles

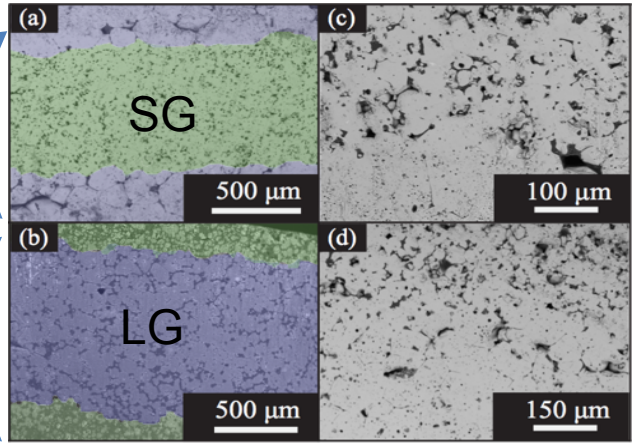
90% 1 µm
10% 10 µm

Not dense

Heterostructures

LG

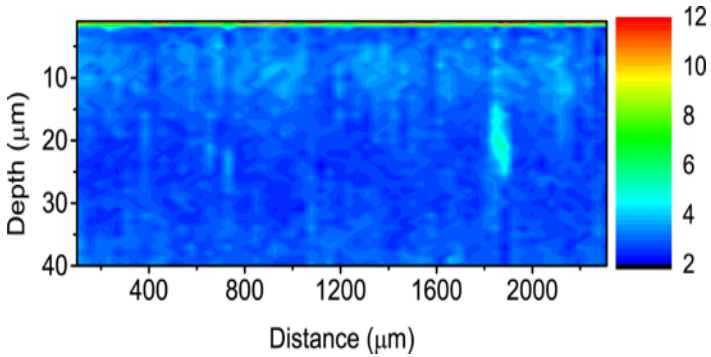
SG



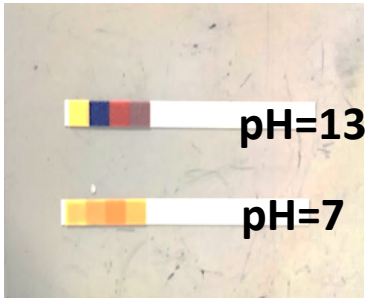
Junctions between large grain and small grain regions

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

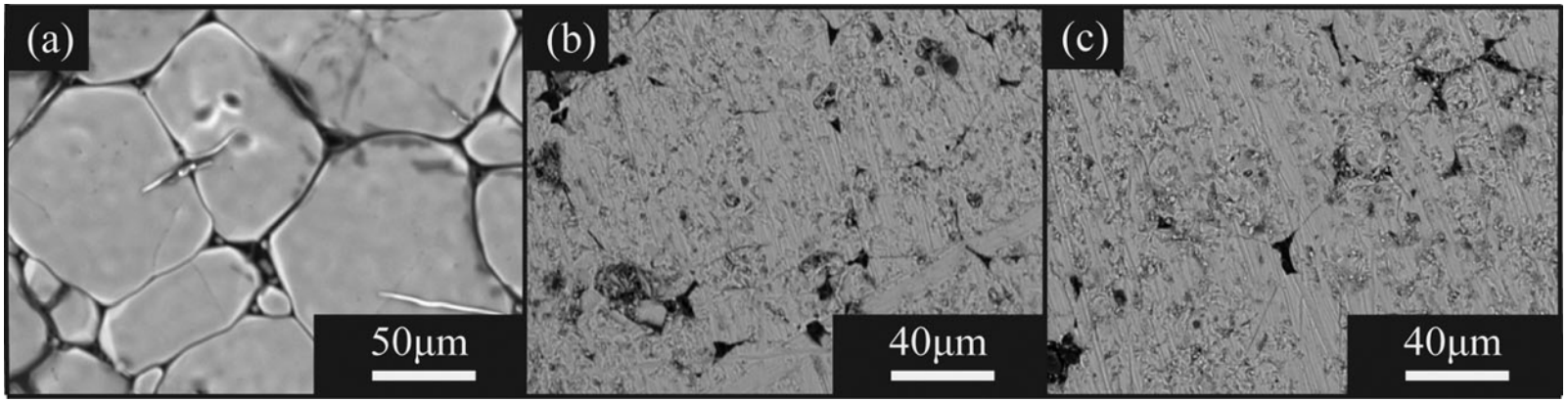
Origins of Interfacial Impedance



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

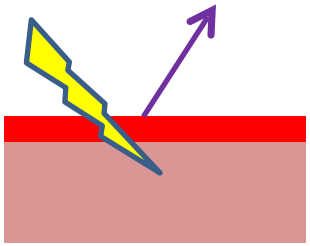
Polished under Ar

Polished under air, exposed to air several days

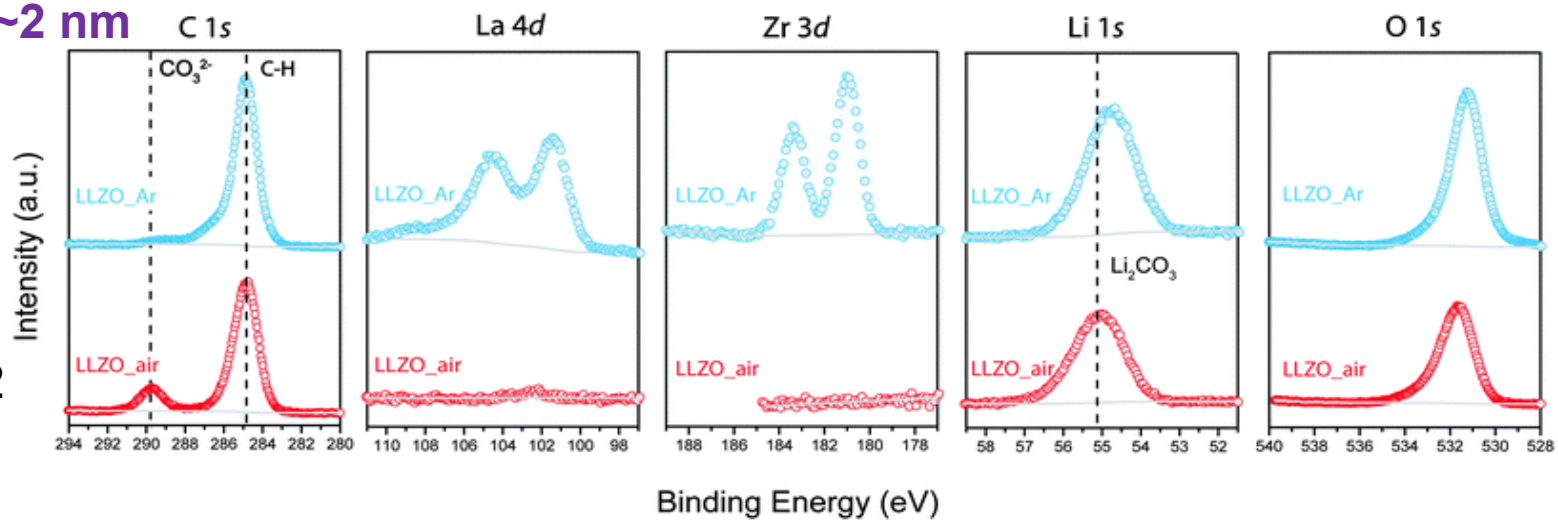
Could high interfacial impedance be related to these observations? Need surface sensitive techniques.

Depth profiling with Synchrotron XPS and s-XAS

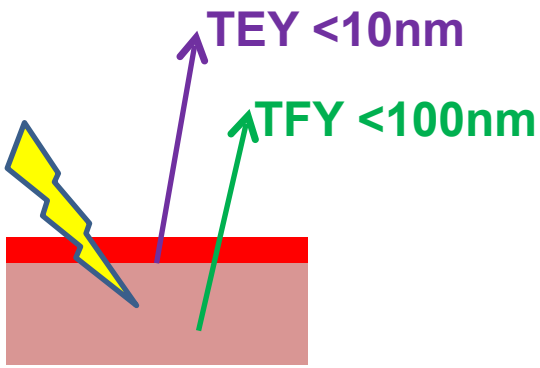
Photoelectron ~2 nm



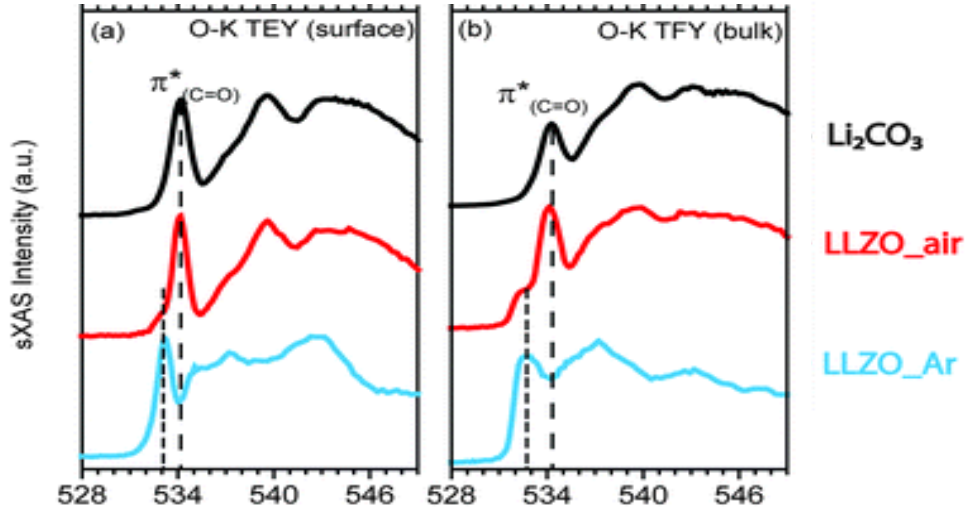
ALS BL 9.3.2



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

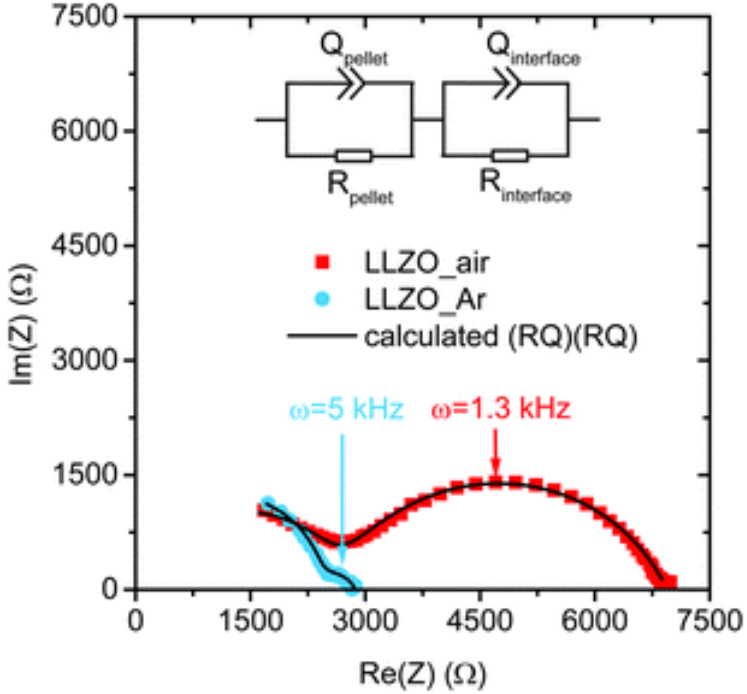


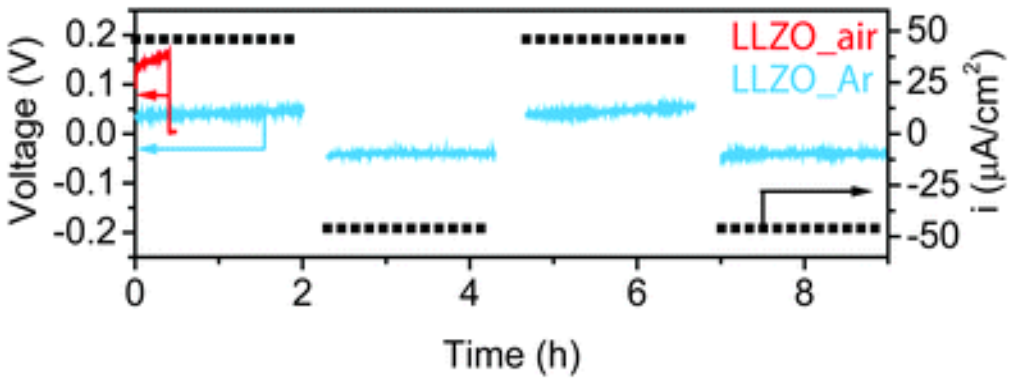
ALS BL 8.0.1



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

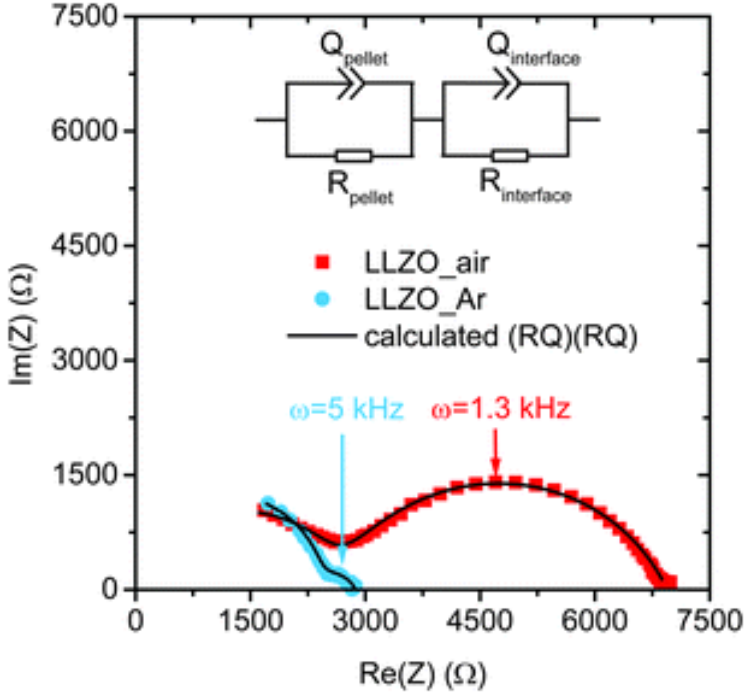
Lower interfacial resistance in the absence of surface Li_2CO_3

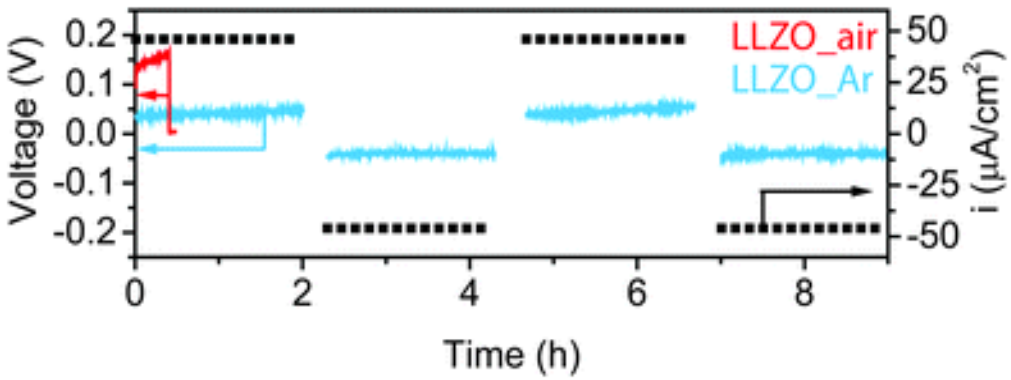




Item	Pellet Resistance	Interfacial Resistance	Interfacial ASR
LLZO_air	2652 Ω	4307Ω	960 Ω·cm^2
LLZO Ar	2355 Ω	491 Ω	109 Ω·cm^2

Lower interfacial resistance in the absence of surface Li_2CO_3

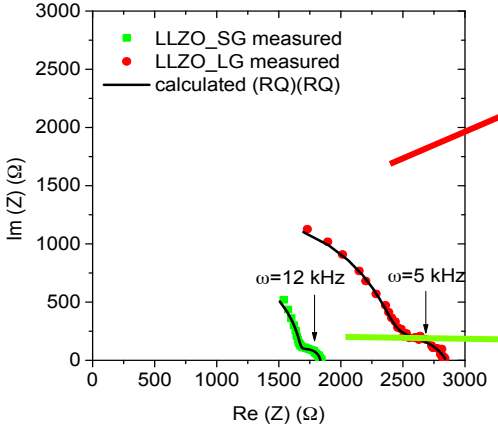


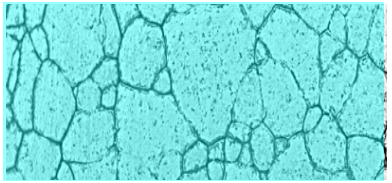


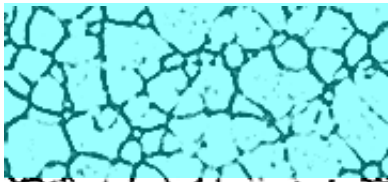
109 Ω·cm² is still not good enough to be practical

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)

Influence of Microstructure on Interfacial Impedance







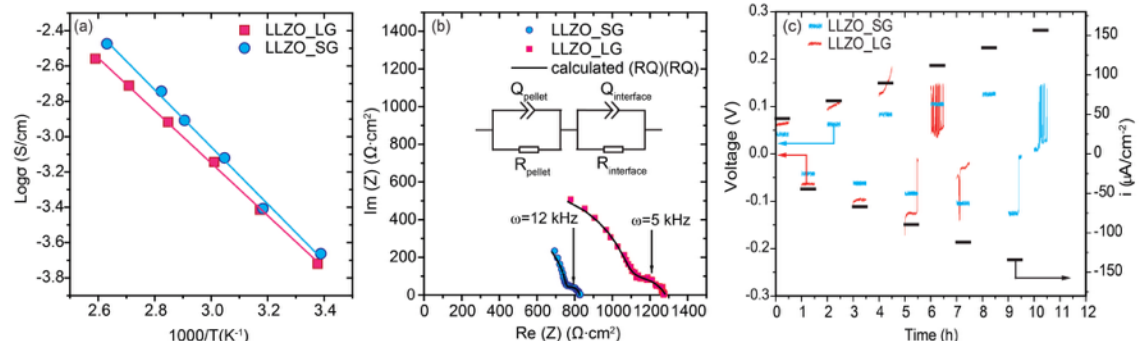
Removal of Li_2CO_3 layer and manipulation of microstructure lowers interfacial impedance, making LLZO a practical option for cells.

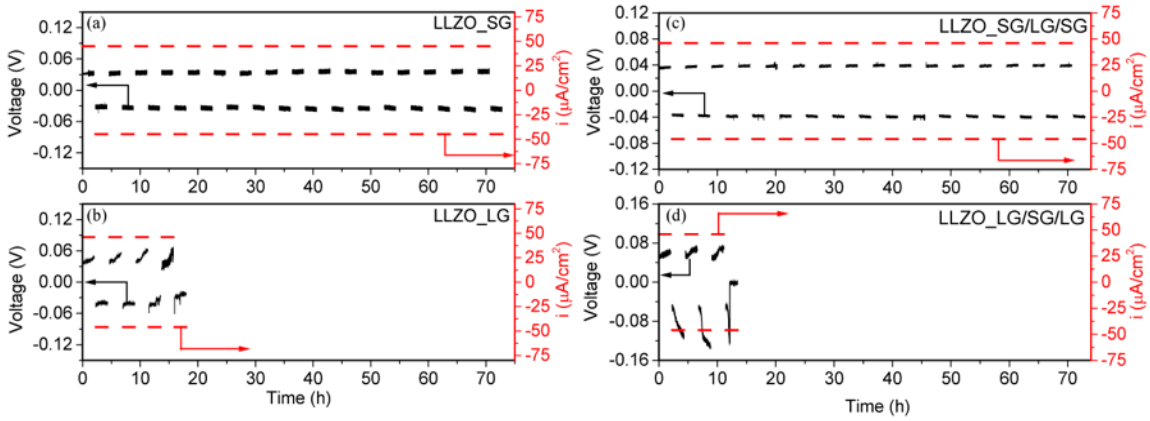
Item	Total Conductivity	Bulk Resistance	Interfacial Resistance	Area specific interfacial resistance
LLZO_LG	2.0×10^{-4}S/cm	2335 Ω	566 Ω	127 Ω·cm^2
LLZO_SG	2.5×10^{-4}S/cm	1672 Ω	161 Ω	37 Ω·cm^2

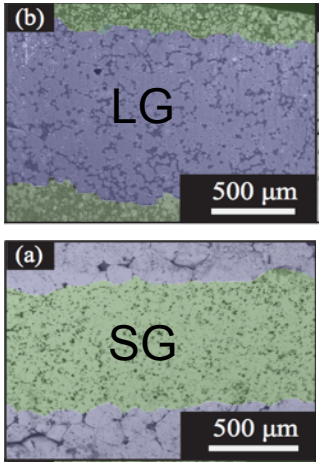
Lowest ASI
ever reported for LLZO!

Effect of Interfacial Impedance and Microstructure on Electrochemistry

Li/LLZO/Li cells



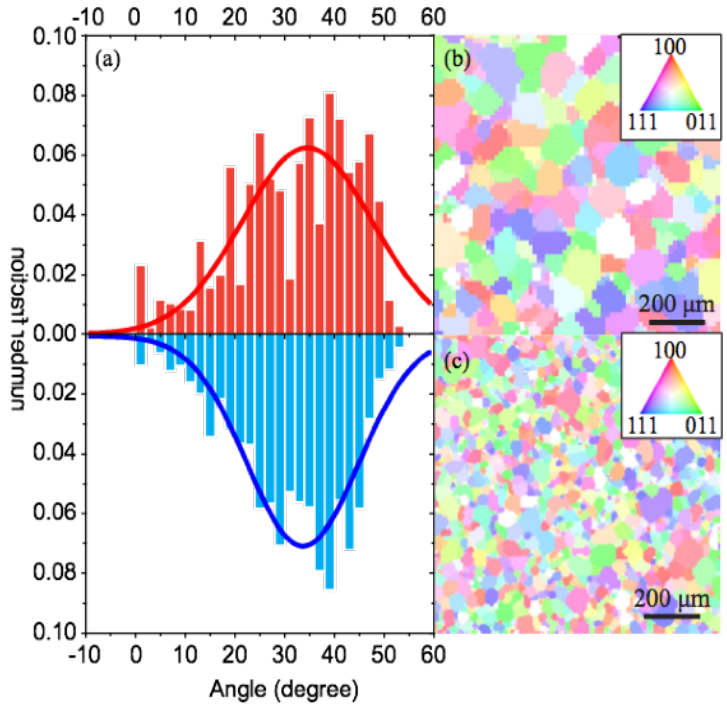




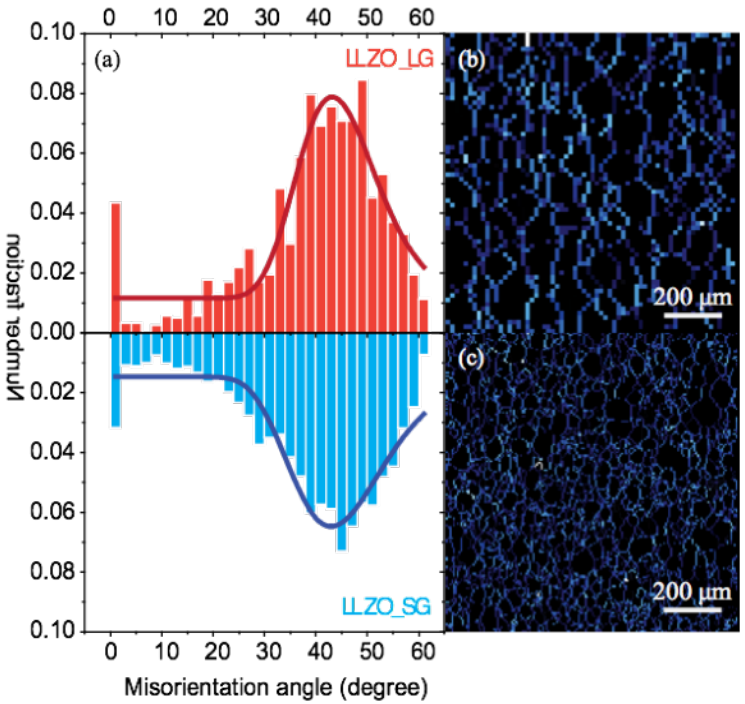
- Small grained samples have lower interfacial impedance and cycle better in stepped or constant current experiments
- Heterostructures with small grains on the outside (closest to Li electrodes) perform better than those with large grains on the outside.
- Surface microstructure is very important!
-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

Grain Orientation Mapping

High-resolution Synchrotron Polychromatic X-ray Laue Microdiffraction.



Grain orientation mapping

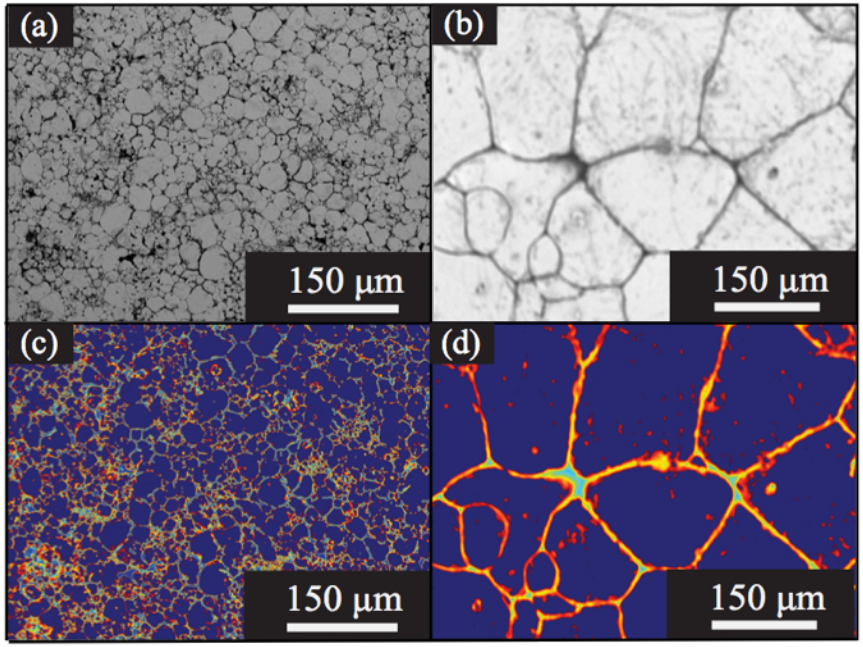


Misorientation angle mapping

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

Visualization of Grain Boundaries

Small grains



Large grains

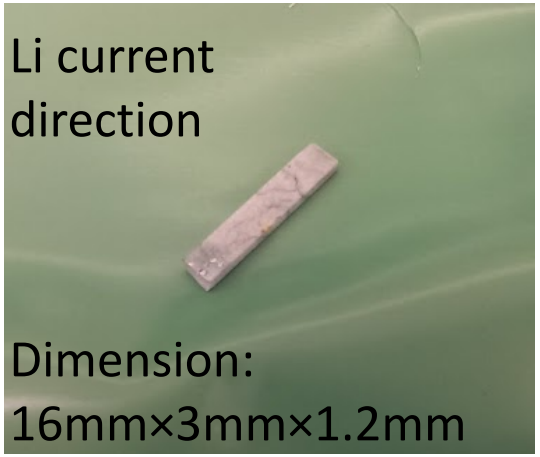
32%

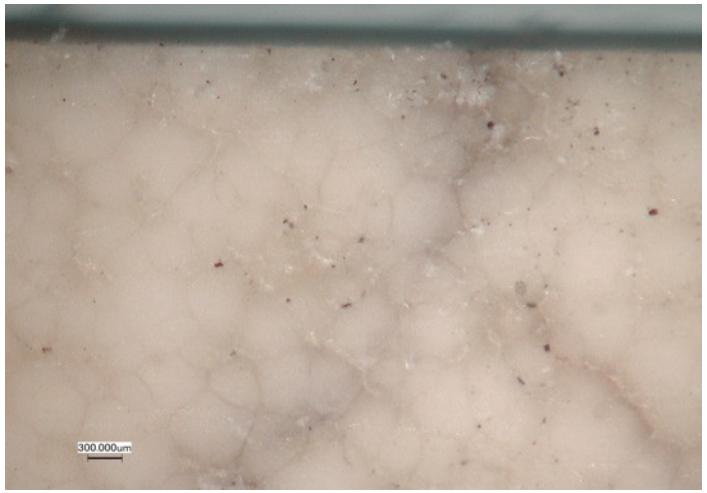
16%

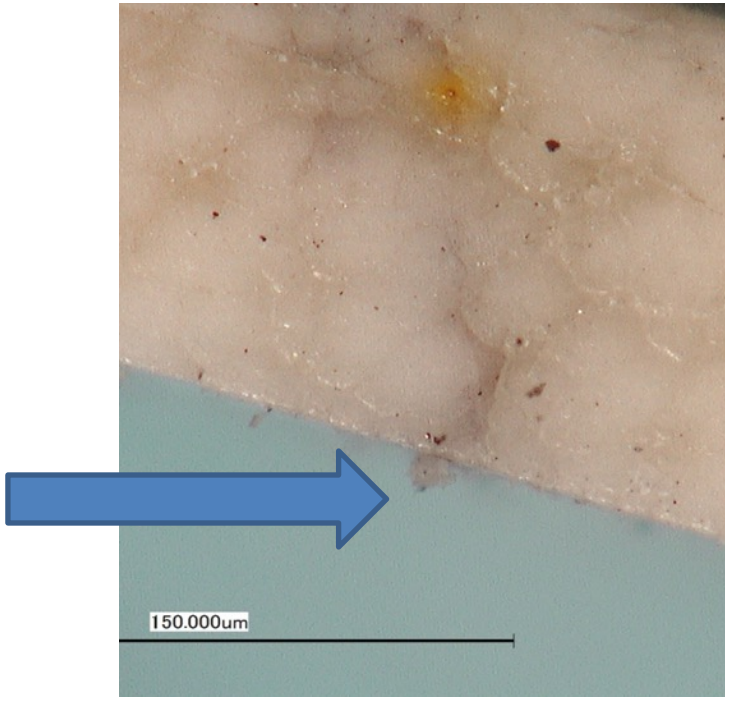
Area fractions of grain boundaries

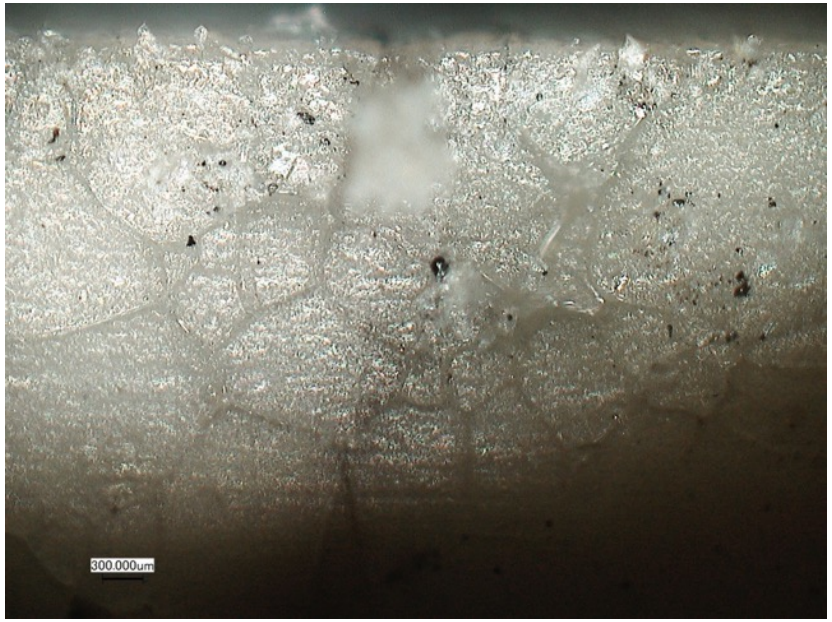
Increased area fraction and tortuosity of grain boundaries in small-grained samples dissipate current and ameliorate the current focusing that leads to dendrite formation.

Optical Evidence of Dendrite Formation via Grain Boundaries





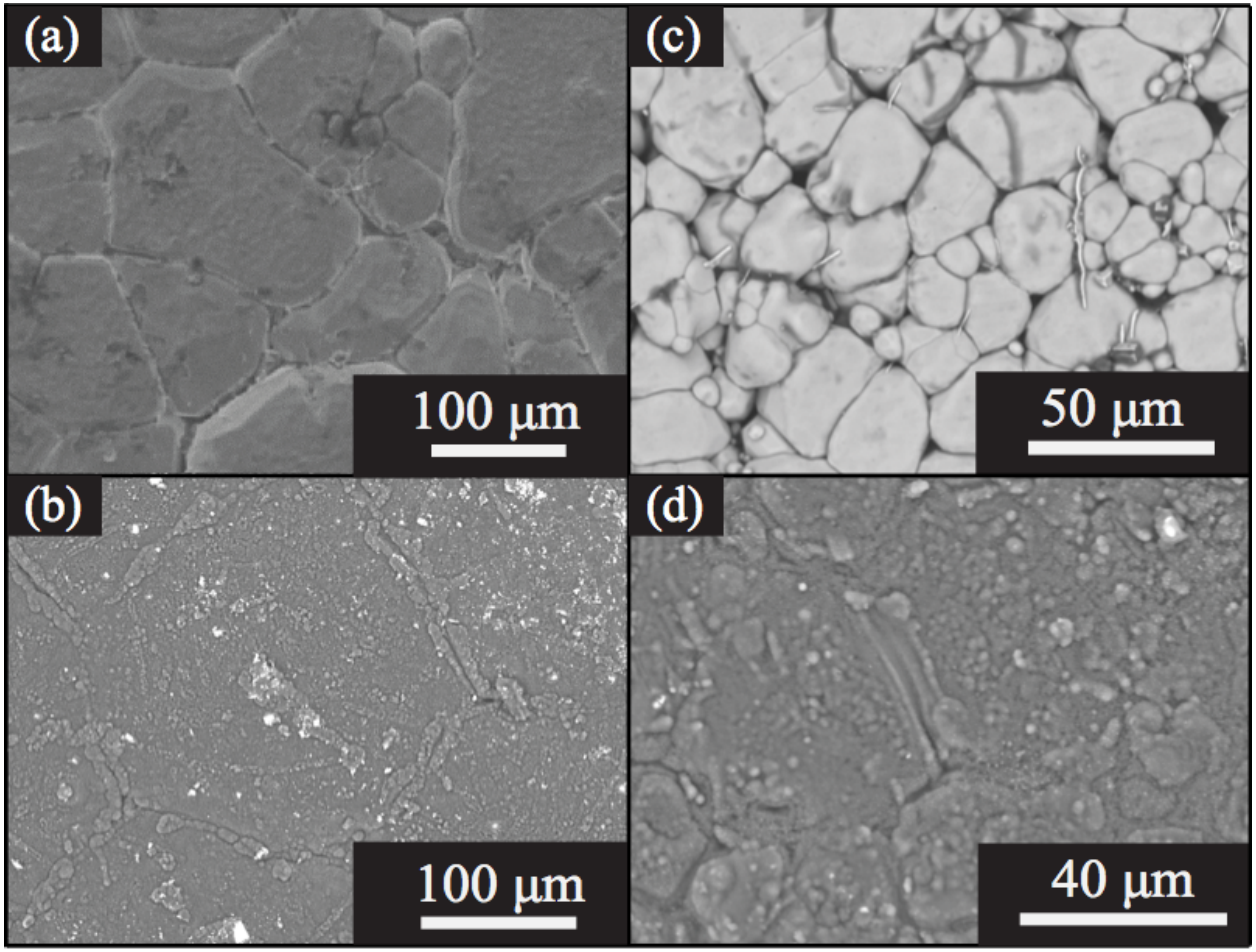




Aging of LLZO Pellets in Air

Pristine

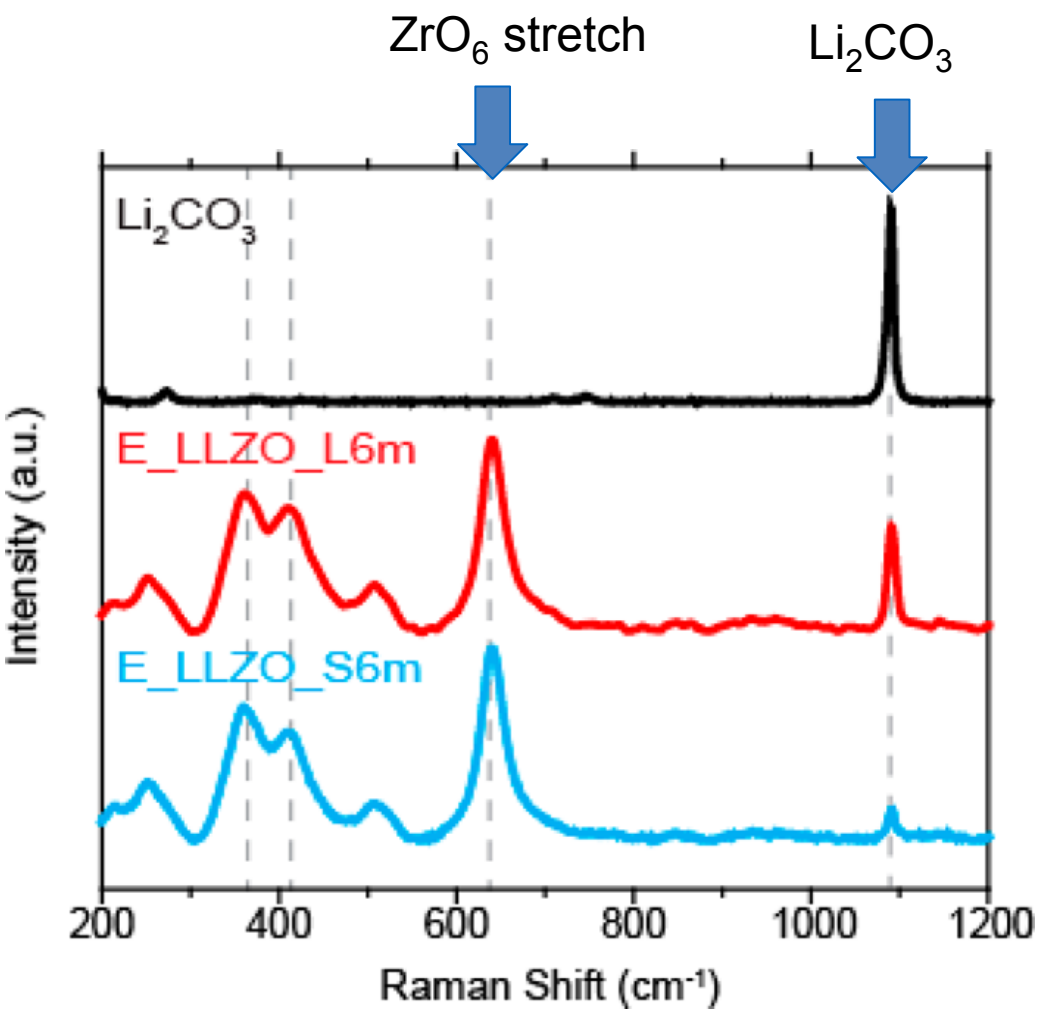
6 months
air exposure



Large-grained sample

Small-grained sample

Effect of Microstructure on Li_2CO_3 Formation-Raman



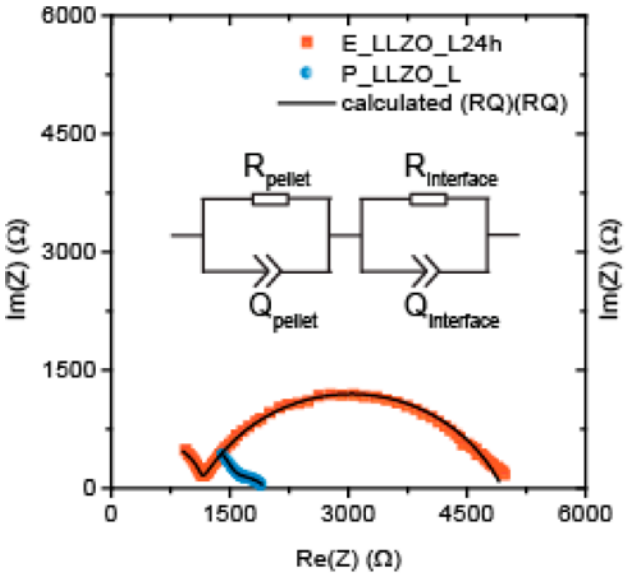
A typical Raman spectrum

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

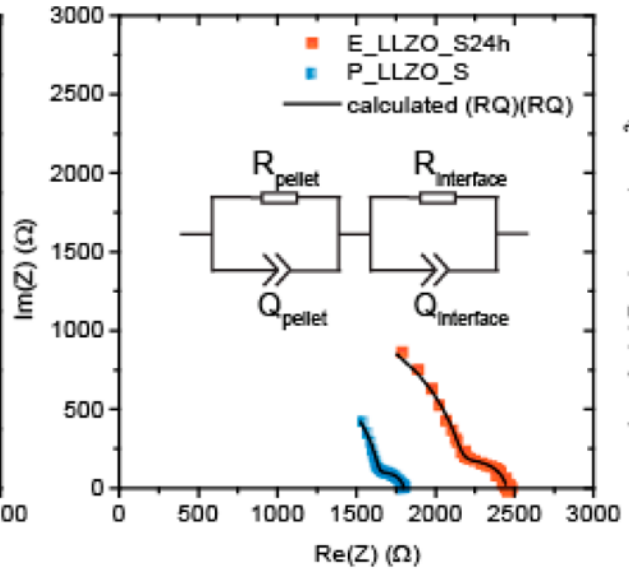
Data averaged over 15 points

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

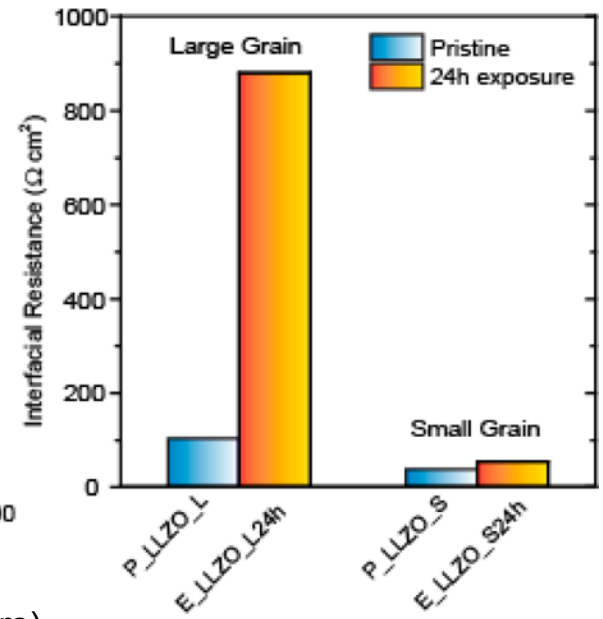
Grain size and Interfacial Impedance-24 hrs of exposure



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 L-edge sXAS experiments

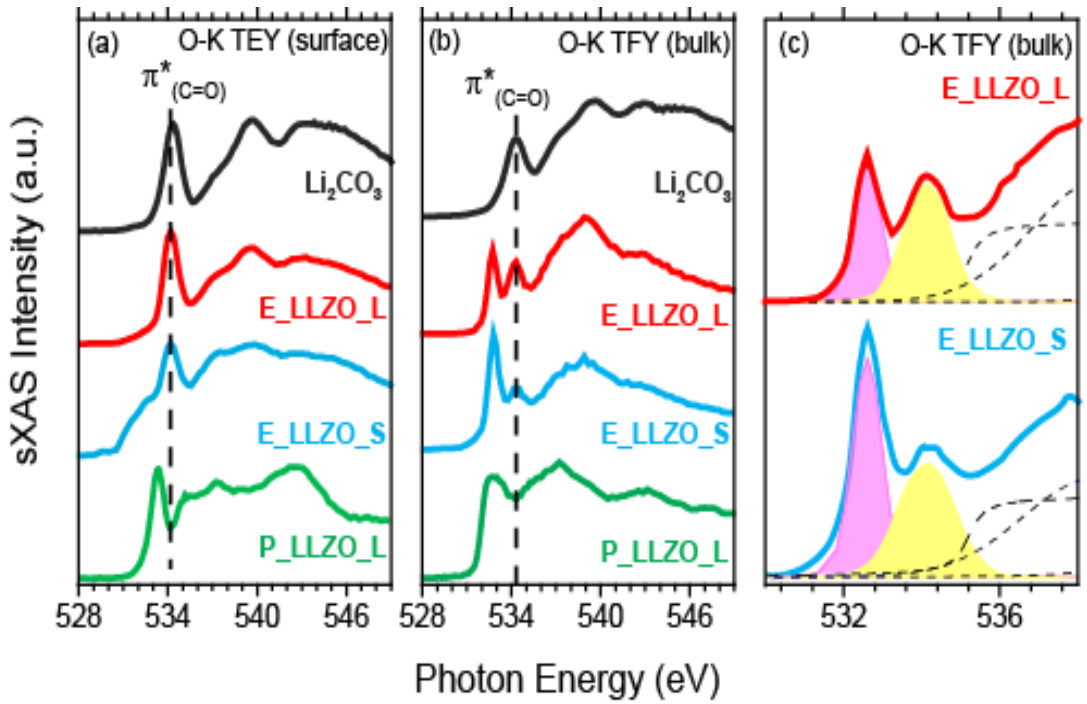
TEY (<10 nm) TFY (<100 nm)

Li_2CO_3

Air exposed LG

Air exposed SG

Pristine



Li_2CO_3/LLZO ratio

LG=1.33

SG=0.96

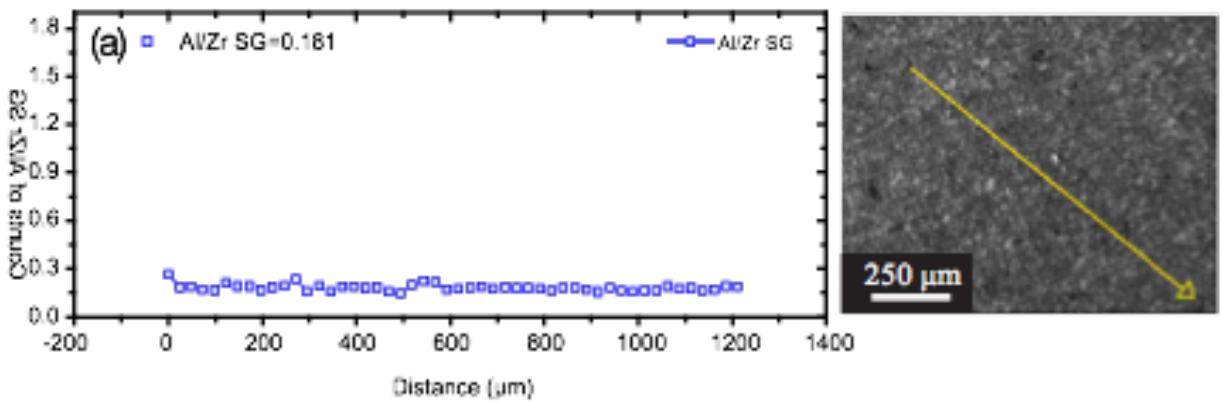
Lattice oxygen is still visible in SG sample in TEY mode, Li_2CO_3 layer is less than 10 nm thick.

Li_2CO_3 layer on LG sample is at least 10 nm thick

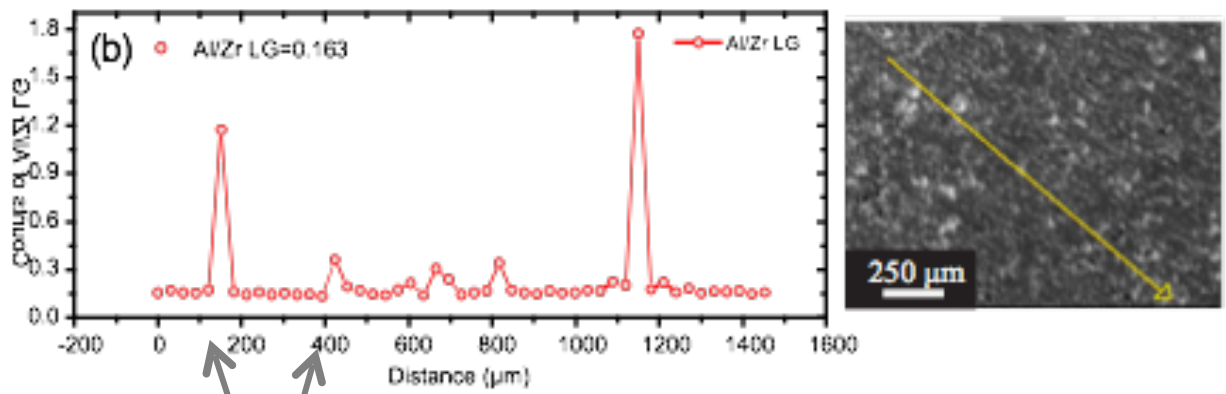
Why does Microstructure Affect Rate of Li_2CO_3 Formation?

EDS line scans, Al/Zr ratios

Small-grained



Large-grained

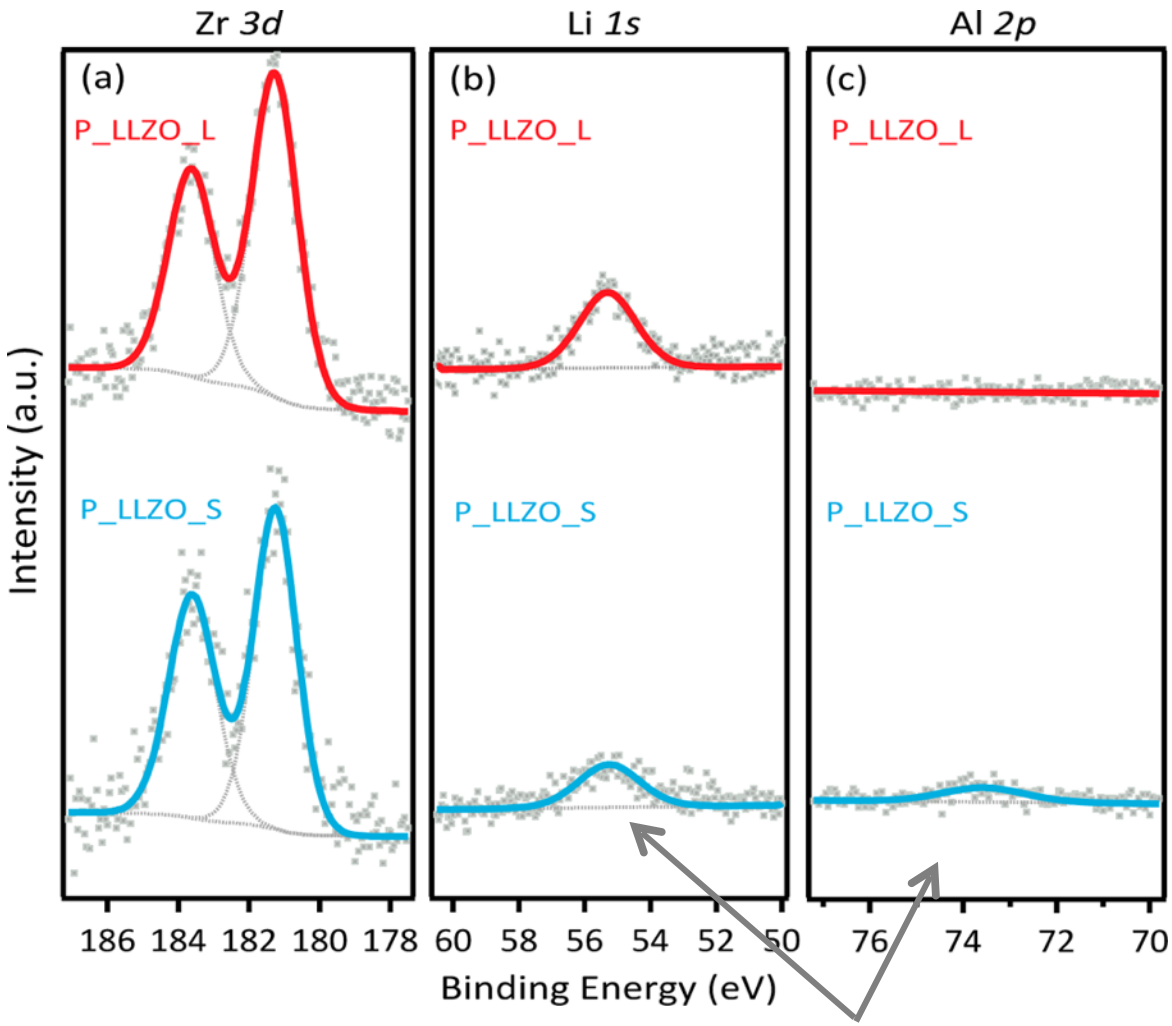


Al spikes every 200 μm!
Suggests Al enrichment at grain boundaries

Synchrotron XPS Experiments

Pristine LG

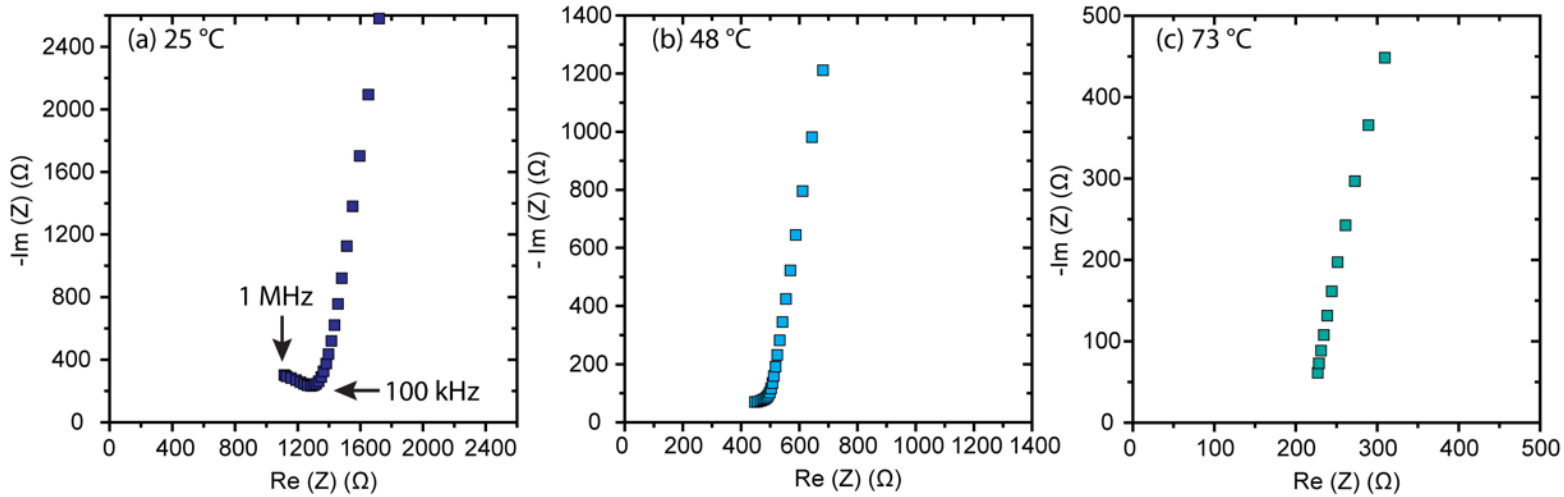
Pristine SG



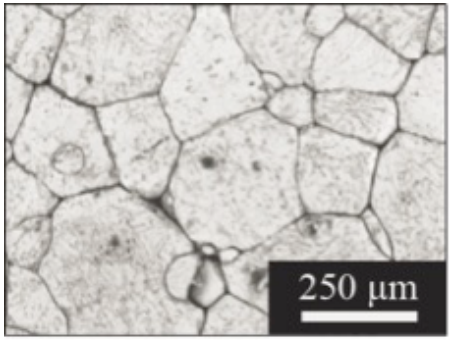
More Al and less Li at surface (grain)=lower reactivity

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

A Closer Look at Grain Boundaries



EIS data on an Au/LG-LLZO/Au cell



pristine LG-LLZO pellet

It's often difficult to deconvolute grain and grain boundary impedances! We need a technique that allows us to obtain more information about grain boundaries readily.

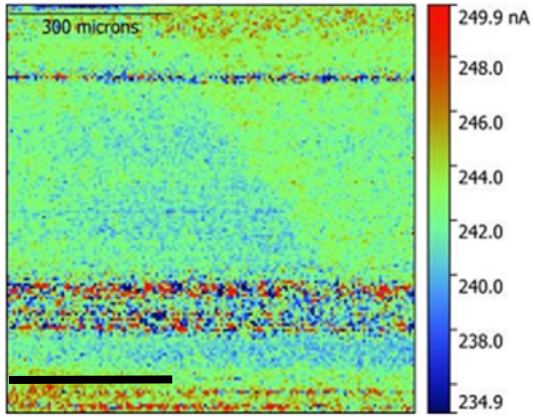
ic-ac-Scanning Electrochemical Microscopy

- Intermittent contact alternating current scanning electrochemical microscopy.
- Allows measurement of sample topography and spatially resolved impedance separately and simultaneously.
- Sample is immersed in a non-reactive conductive medium (e.g., a salt solution).
- A Pt ultramicroelectrode is used as the probe.
- Same degree of contact with the sample is maintained, regardless of topography (mechanical interaction of tip with sample).
- Measurement is of the sample impedance+that of the thin layer of electrolytic solution above it.

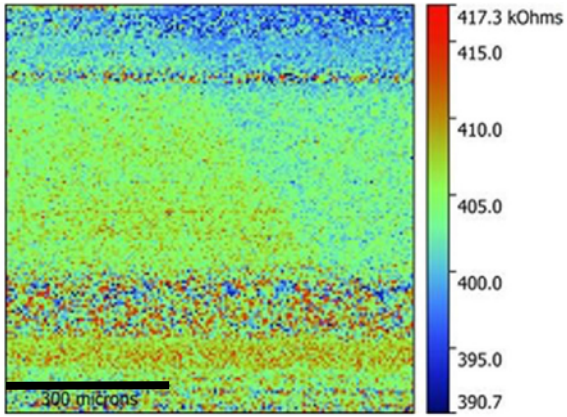
Bio-Logic ic-SECM470

Proof of concept ic-ac-SECM experiment

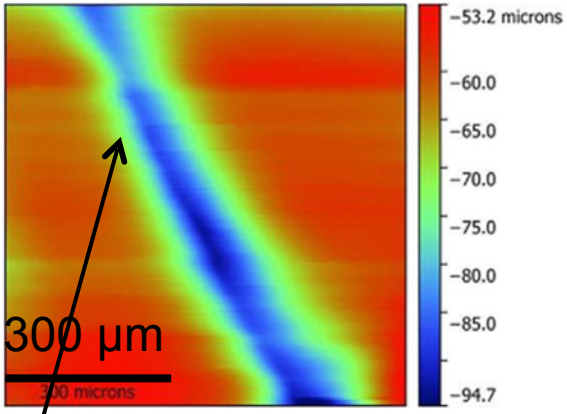
A 650 µm x 650 µm area smooth Teflon blank with a scratch in it, immersed in 0.1 M TBA-ClO_4 in PC.



ac current magnitude



Impedance magnitude



Topography

Little variation seen in impedance in spite of topography change (just noise!)

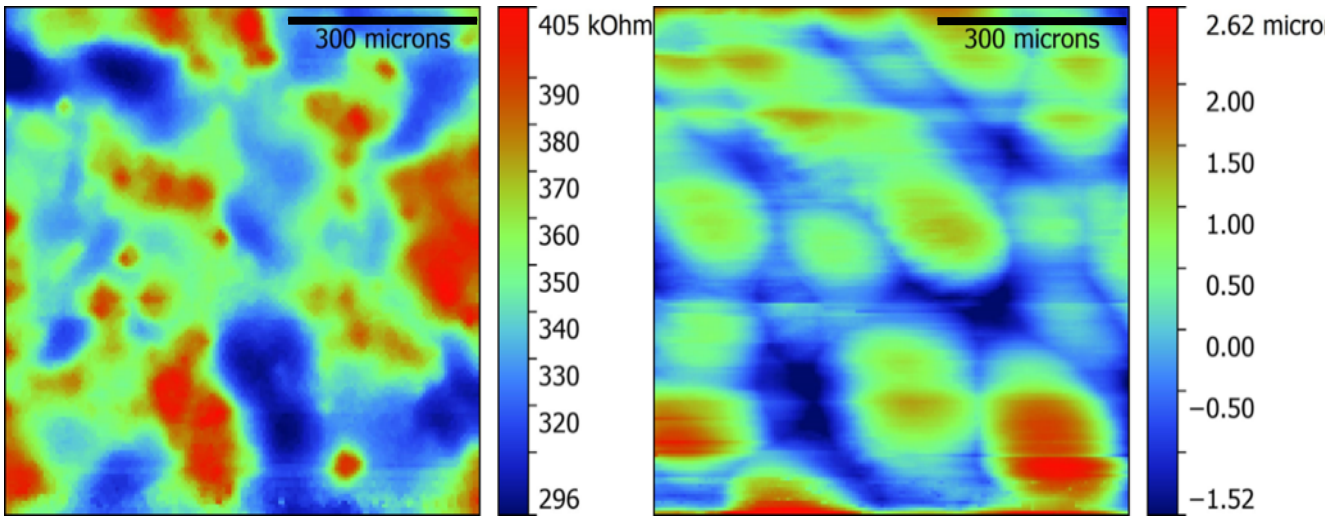
10 µm Pt probe can easily distinguish features ~100 µm across and <50 µm deep.

Catarelli et al. **Frontiers in Energy Research**, DOI: 10.3389/fenrg.2016.00014 (2016).

A First Look at an LLZO Pellet using ic-ac-SECM

650 µm x 650 µm area

300 µm

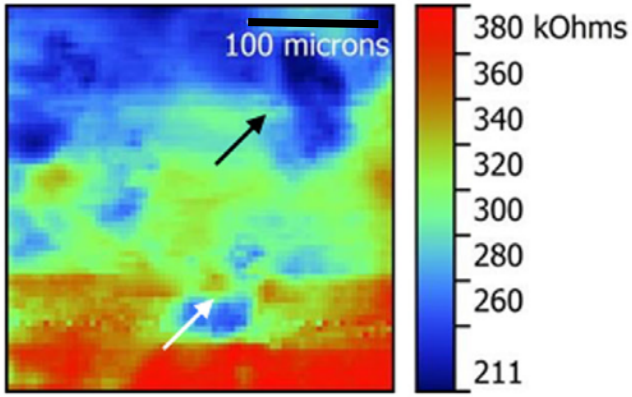


Raised areas (probably grains) roughly correspond to areas of lower impedance

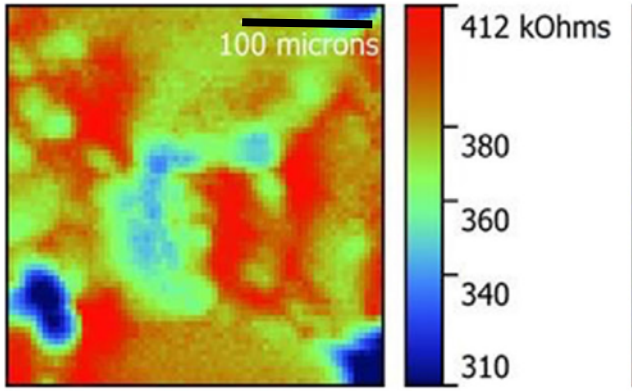
Is cross-talk an issue?

ic-ac SECM experiments on LLZO samples

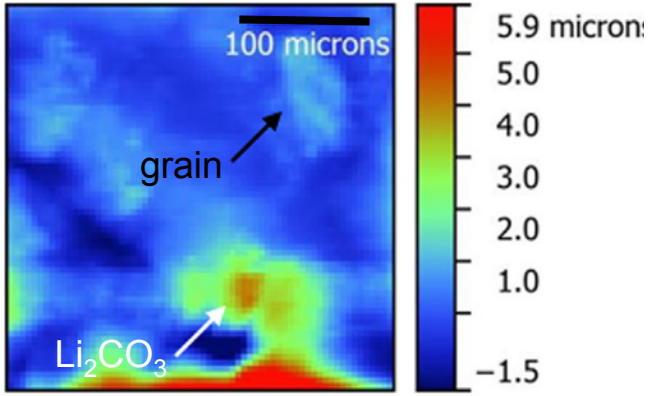
325 µm x 325 µm areas



Impedance

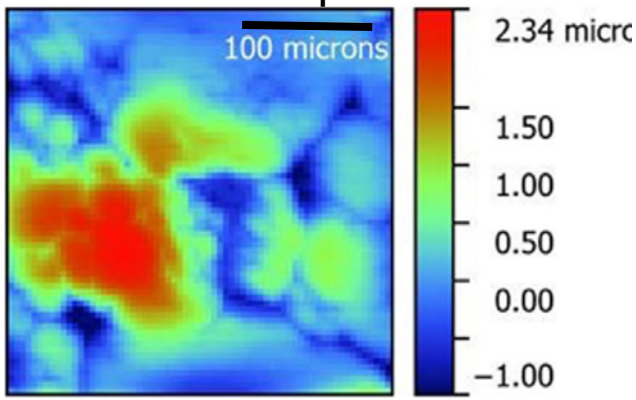


100 µm



Topography

100 µm



Unpolished sample exposed to air

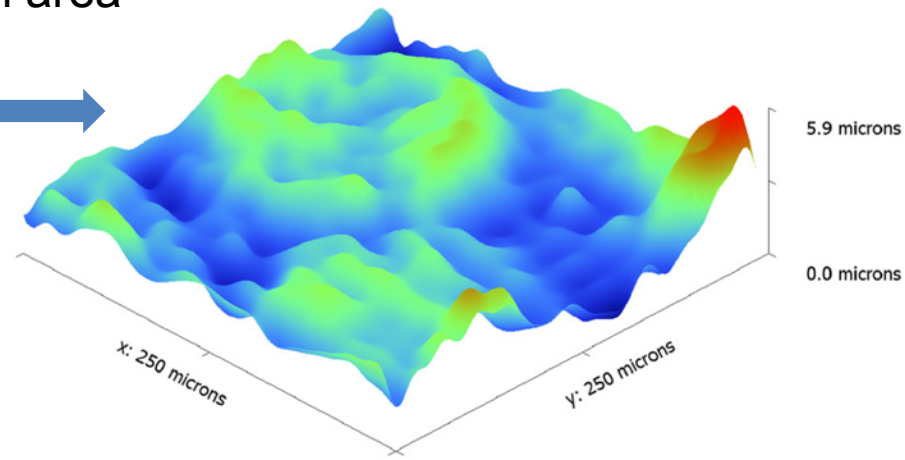
Polished sample (lower topography)

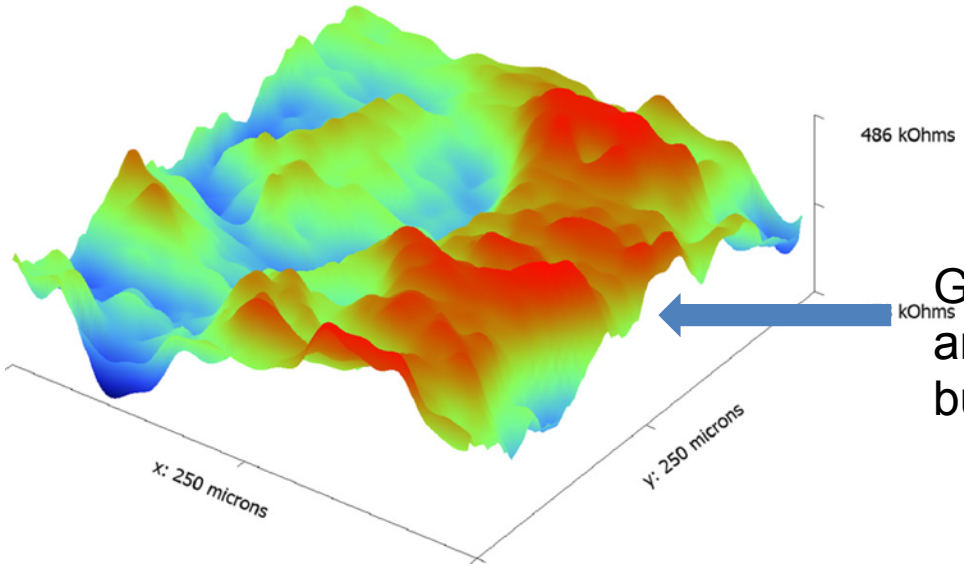
Generally, lower impedance does correspond to higher spots (grains). However, in the unpolished sample, there are some smaller high impedance high spots, possibly, Li_2CO_3 particles.

Zeroing in on a LLZO Grain

250 µm x 250 µm area

A raised grain





Grain boundaries are less conductive, but vary!

Summary

- LLZO can be densified using classical "shake and bake" ceramic techniques, but the details matter (particle size, thermal history of power cover).
- Dendrites still happen, but critical currents depend on surface microstructure (smaller grains are better).
- High interfacial resistance is caused by small amounts of Li_2CO_3 on pellet surfaces. Removing or preventing this surface impurity reduces the interfacial resistance to low values.
- The microstructure, sensitivity to air (Li_2CO_3 formation) and interfacial properties are interrelated.
- Grain boundary chemistries vary depending on processing variables.
- Grain vs. grain boundary impedance-perhaps not a simple question!