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U.S. DEPARTMENT OF ENERGY

The Future of Energy Storage

Venkat Srinivasan

given by Marca Doeff

Lawrence Berkeley National Laboratory

Disruption has already occurred in the consumer electronics industry

Its happening in electric cars

Instead of this…

We have…

And it will happen on the grid

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ENERGY 11/05/2014 @ 4:56PM | 1,996 views

Storage Industry Celebrates Big Win In California

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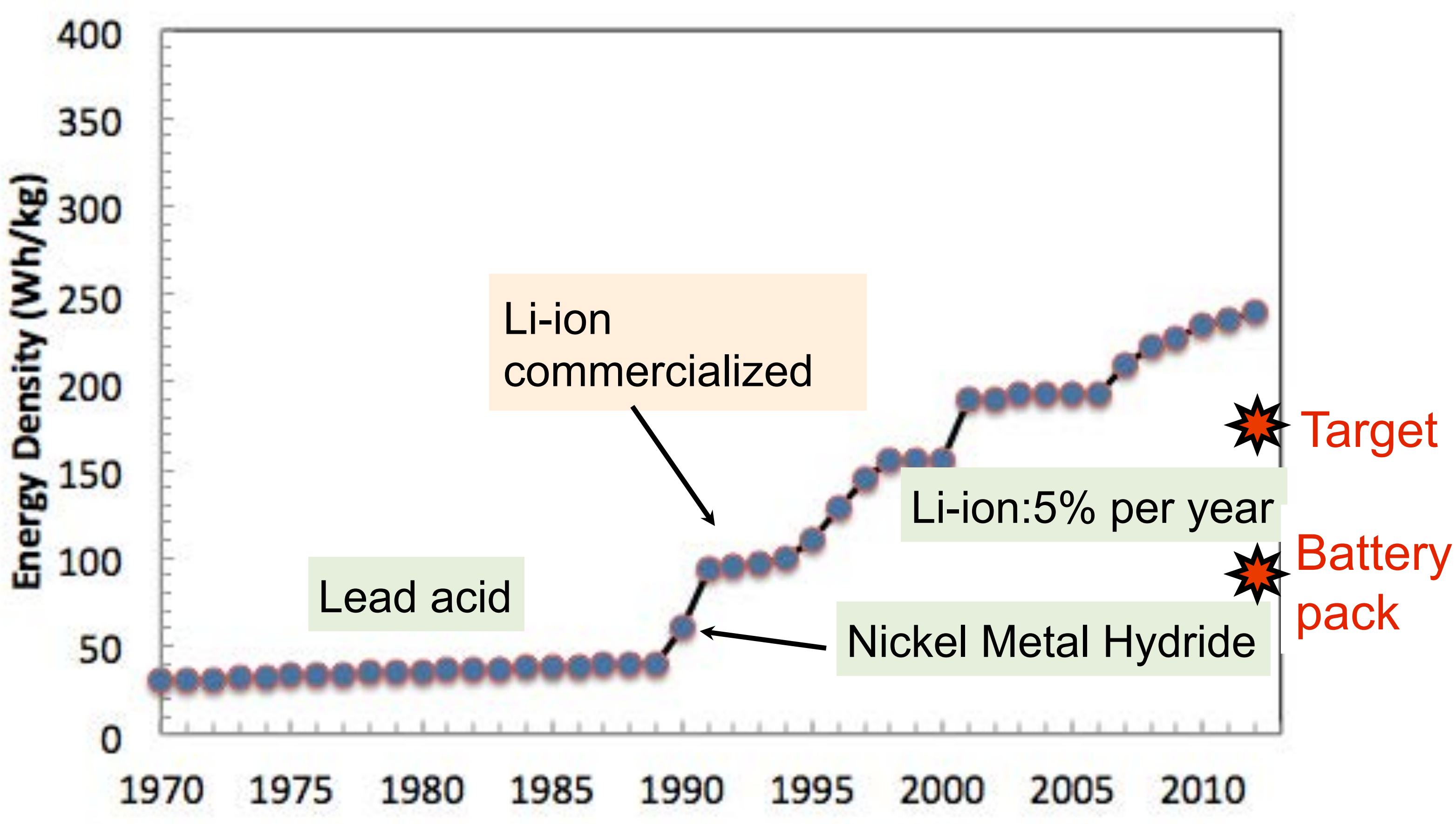
Something rather significant just happened in the energy storage industry: Southern California Edison (SCE) just announced the largest grid-connected storage purchase in the history of the United States. This commitment to purchase 261 MW of storage capability is five times greater than what the utility was required to do under the California Public Utilities mandate.

The companies chosen to provide storage are as follows:

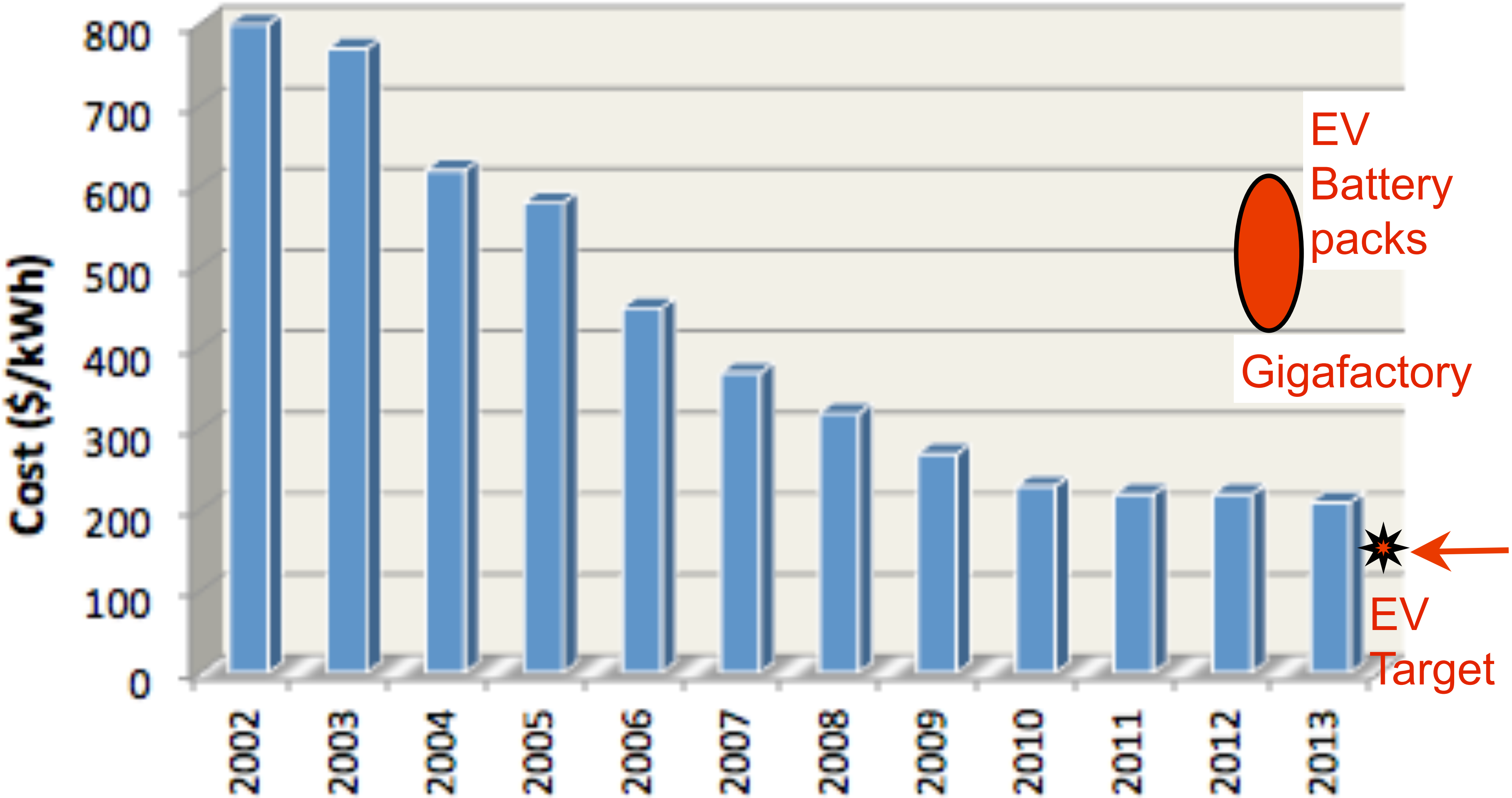
- NRG Energy NRG -0.03% 0.5 MW
- Ice Energy Holdings, Inc. 25.6 MW
- Advanced Microgrid Solutions 50.0 MW
- Stem 85.0 MW
- AES Energy Storage 100.0 MW

Moore's law for batteries



2-5x improvement in energy density needed to achieve range parity with gasoline cars

…and cost remains very high



Batteries at $100-$125/kWh will be the tipping point.

Where does the DOE cost target come from?

- **The car companies feel that the "power plant" cannot cost more than $7500**
- **Assuming a 200 mile car, one needs 60 kWh battery (300 Wh/mile)**
- **Hence, the $125/kWh number ($7500/60 kWh)**

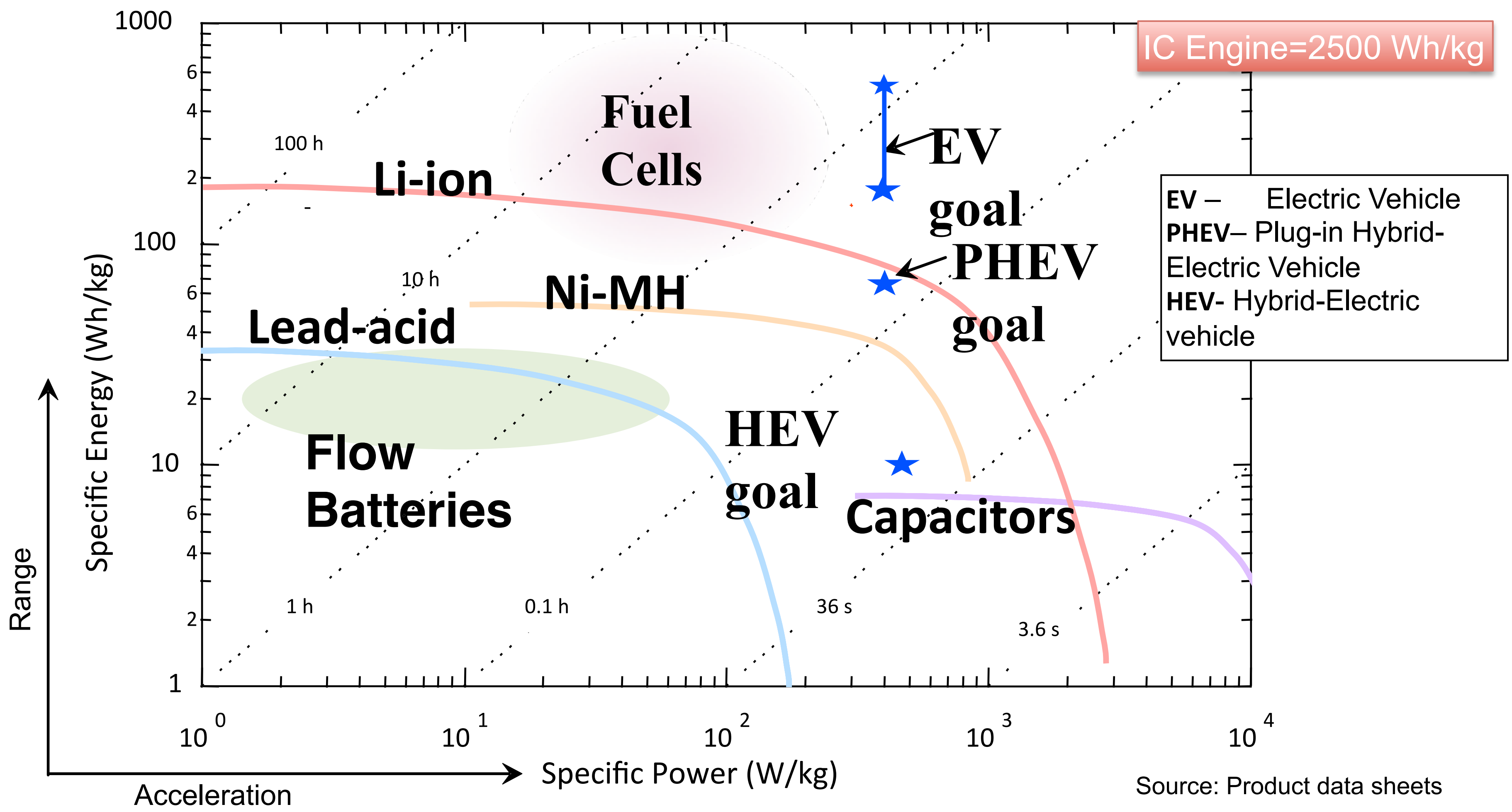
- But what if the consumer demands the same miles as today's vehicle? (350 miles)

- Will need a 90 kWh battery

- Cost target $83/kWh!

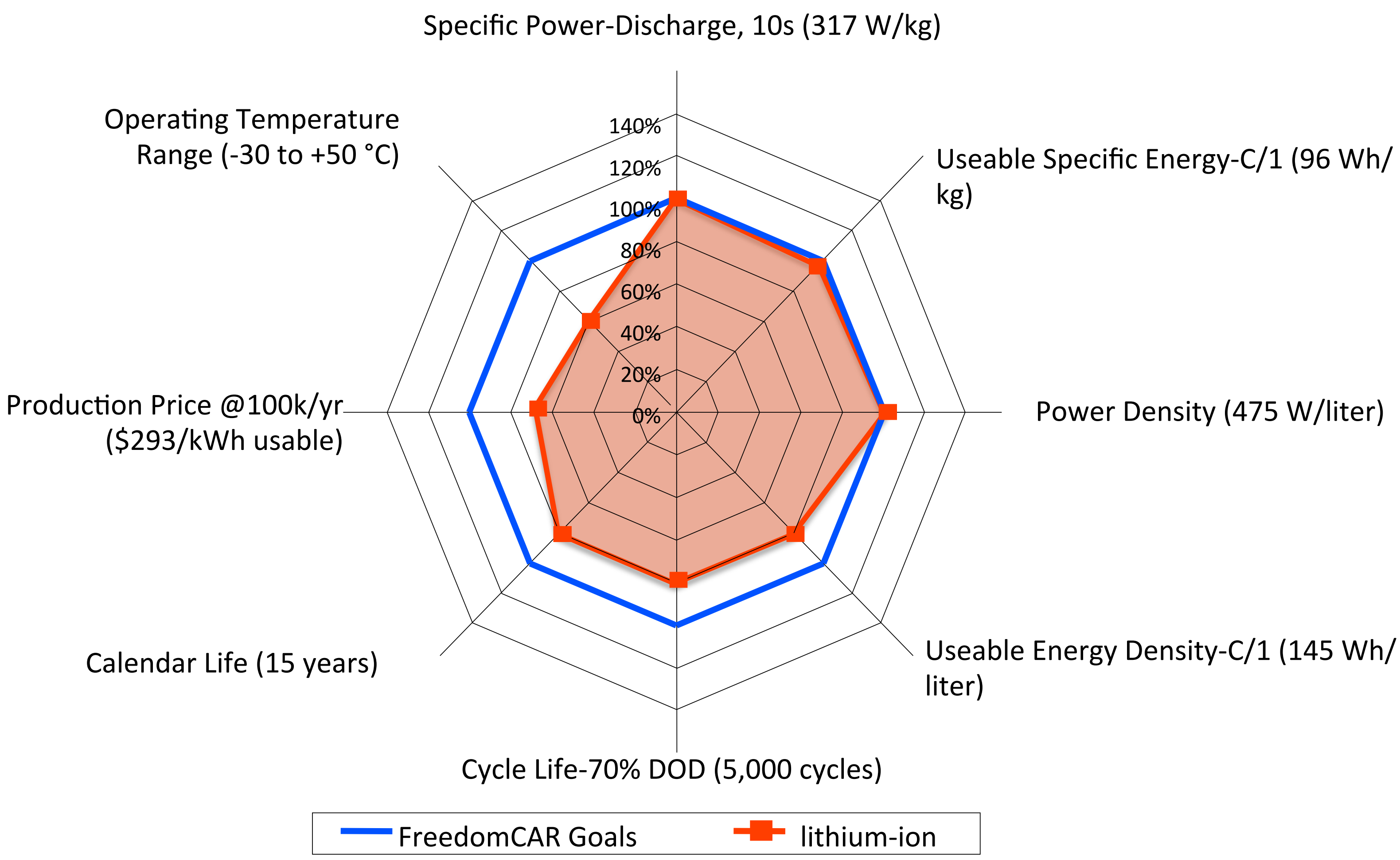
The $125/kWh should be taken to be a target that will allow the tipping point to occur

Energy and power play against each other



But its more than just about energy and power

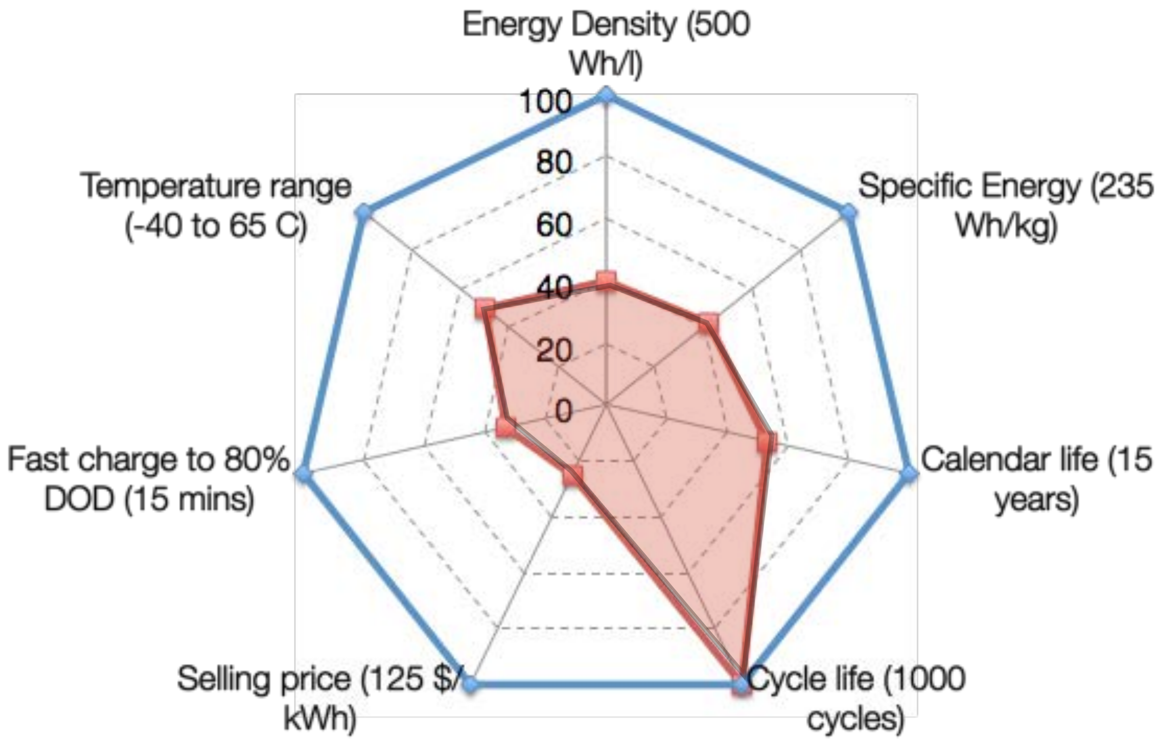
Comparison of Present-day Li-ion Batteries vs. Plug-in Vehicle Goals



Open question: Would the Gigafactory make PHEVs ubiquitous?

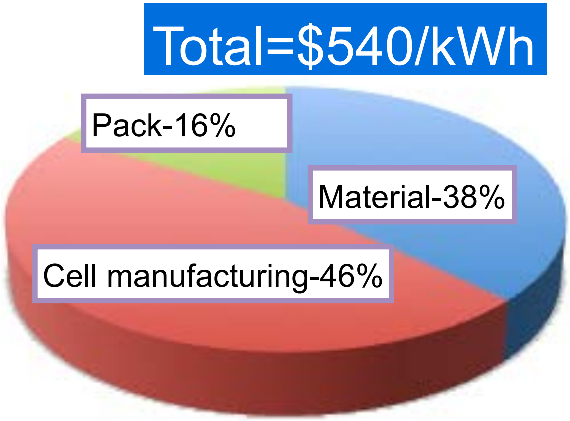
Comparison of Present-day Li-ion Batteries vs. Electric Vehicle Goals

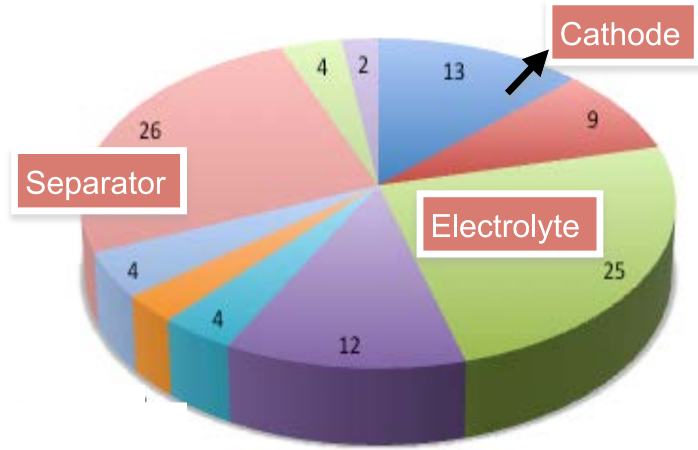
Anode: Graphite, Cathode: $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, Electrolyte: $LiPF_6$ in PC:EC:DEC

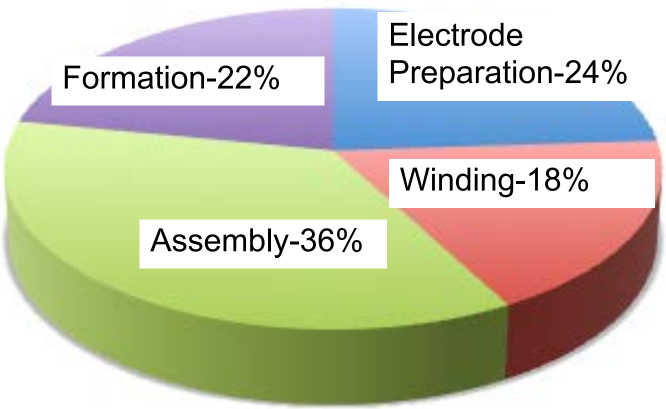


The present feeling is that cost is the main issue. Rest becomes important if cost can be managed.

Where is the cost?







- Both material cost and manufacturing costs are important
- It is not obvious that simply finding lower cost materials or finding new ways to assembling batteries will be enough

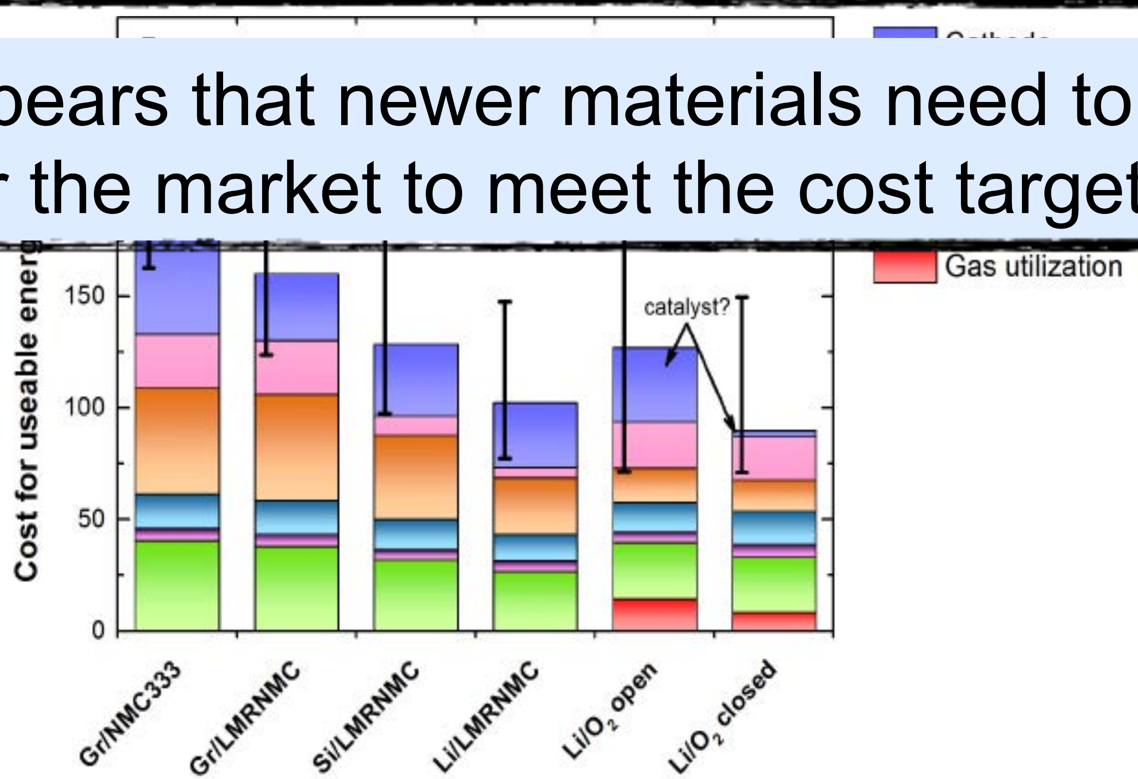
Need to decrease both material cost and manufacturing cost

Cost will go below $200/kWh with today's systems

Tesla's Gigafactory - Synopsis

advanced automotive batteries

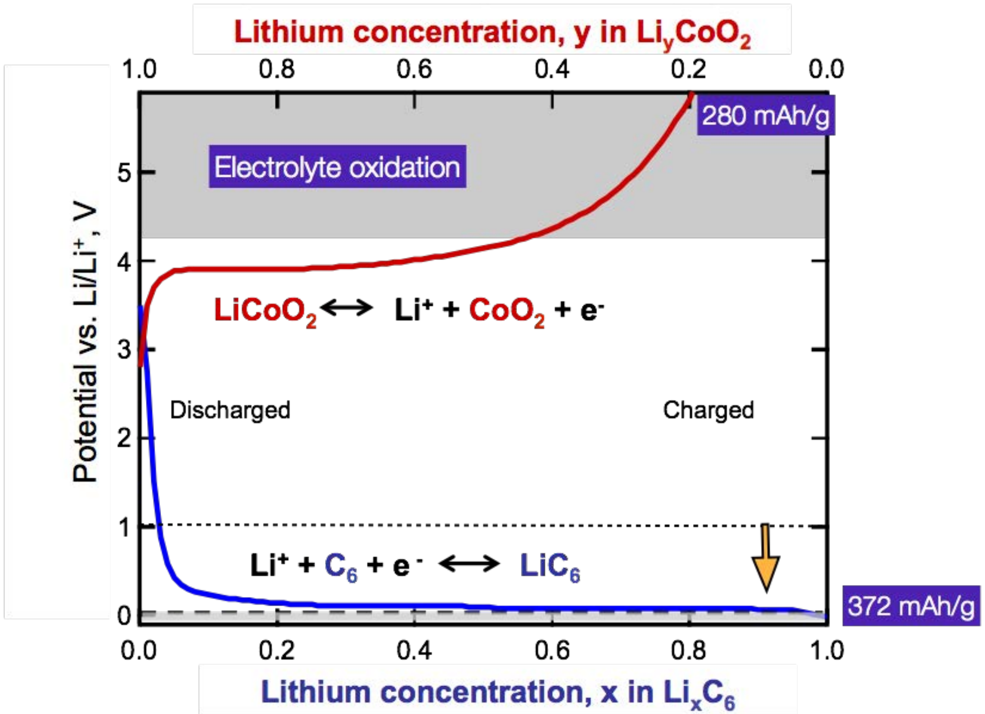
- It represents a huge risk and a tremendous amount of cash investment
- It depends largely on Panasonic's willingness to invest
- If 35 GWh are indeed installed and utilized, our assessment shows that pack pricing for the 2025 time scale could be as low as $167/kWh, $8,400 for a 50-kWh battery and $11,700 for a 70-kWh pack



It appears that newer materials need to enter the market to meet the cost targets

Energy Environ. Sci.,2014, 7, 1555-1563

Approach 1: High voltage cathodes



- Thermodynamics: Need electrolytes that are stable to high voltages
- Kinetics: Need ways to passivate the cathode (coatings)

Consumer batteries are moving to higher voltages. So is Tesla

Meet Tesla's new weapon, a battery scientist

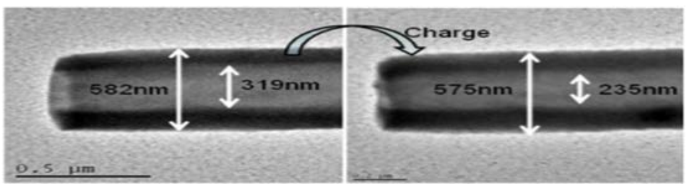
by Kirsten Korosec @kirstenkorosec JUNE 17, 2015, 6:09 PM EDT

"The problem is when you do that [charge it to a higher voltage] the lifetime is compromised," Dahn said in an interview with *Fortune*. "So it's always a trade off between lifetime and energy density."

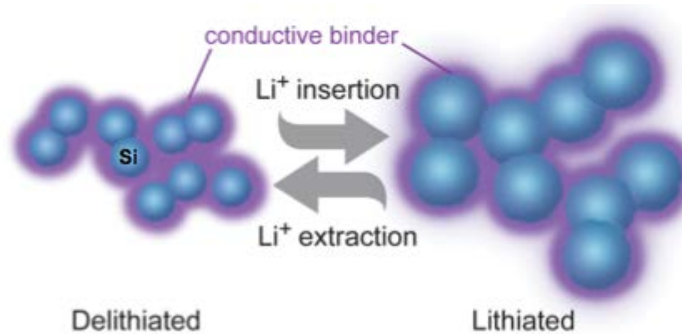
If Dahn can crack this problem—a technically difficult task that requires improving or changing the materials of a lithium-ion cell—he could help Tesla produce cheaper, longer lasting, more powerful batteries. That could have huge financial implications beyond Tesla's electric cars, and could be used in the company's new energy storage products, the Powerwall and Powerpack.

Approach 2: Alloy anodes

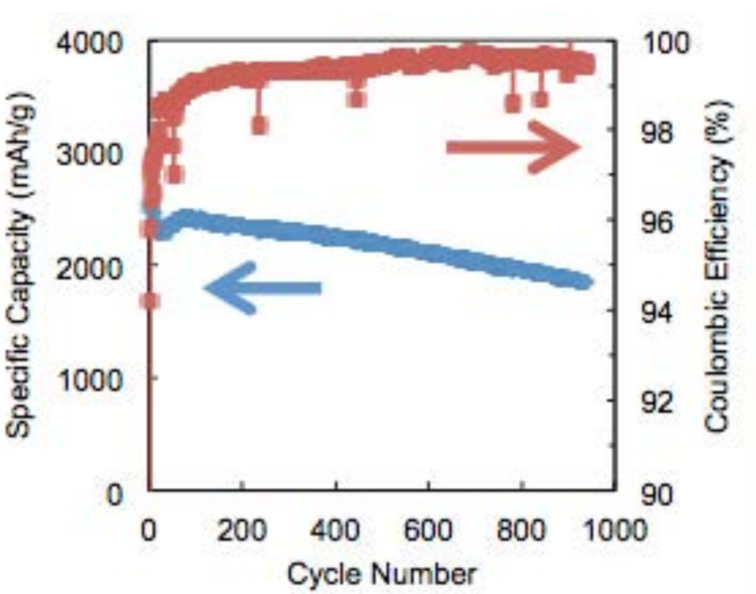
- Alloys, like Li-silicon and Li-aluminum, can intercalate upto 4 lithium per lattice site (graphite intercalates 1 Li for every 6 lattice sites)
- However, to accommodate these lithium ions volume expands more than 300% (graphite expands 10%)



Si nanotube anodes (Yi Cui- Stanford)



Conductive binders (Gao Liu- LBNL)



For 20% fade

$$\text{efficiency}=100*(1-0.2)^{1/\text{cycles}}$$

For 300 cycles: 99.92%

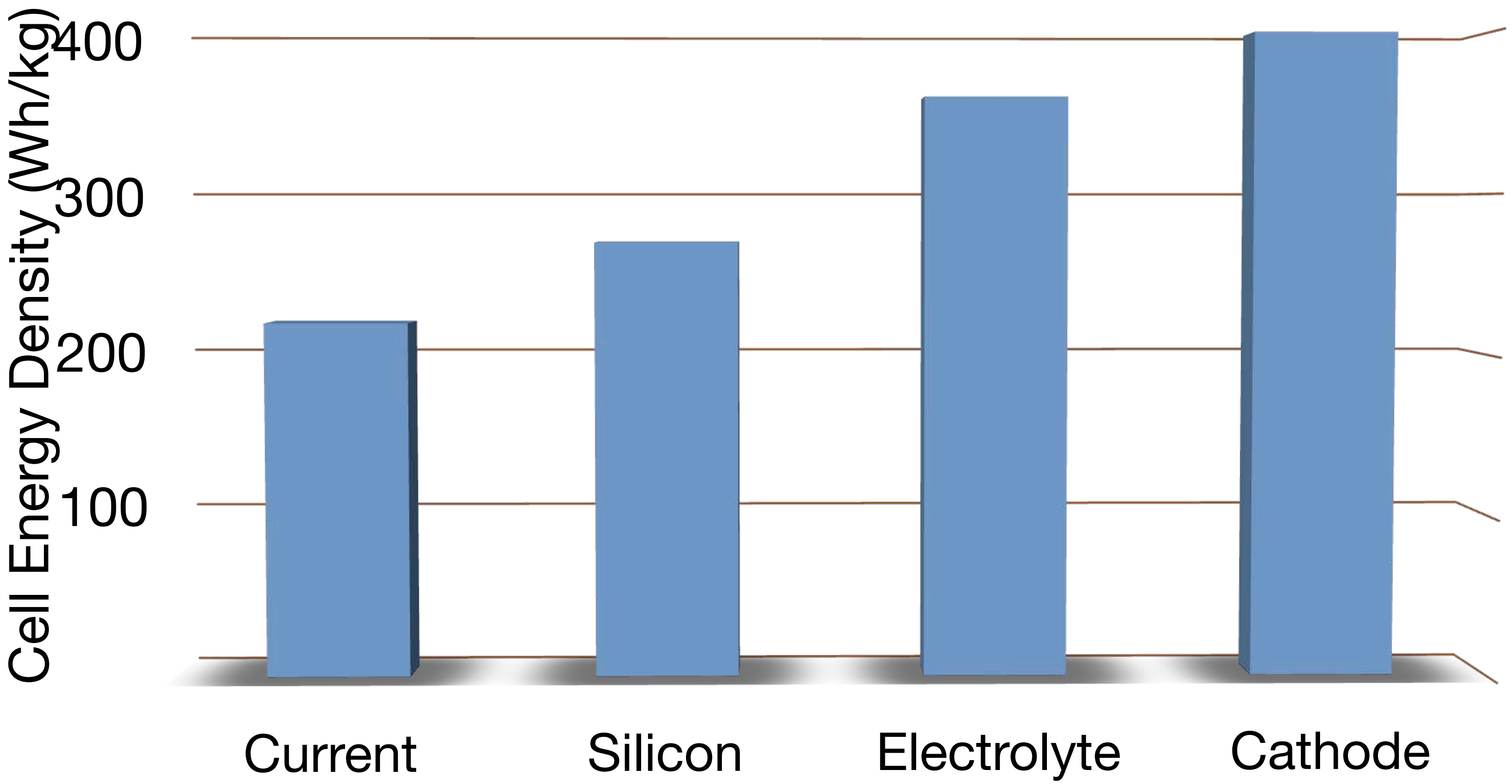
For 3000 cycles: 99.992%

Silicon-graphite mixtures are now entering the market

The energy density improvement is possible without the need to increase the physical size of the battery pack. That's because the lithium-ion battery cells now uses silicon for part of its anode, Musk said. Lithium-ion battery cells typically use graphite for anode. Lots of research has looked into the benefit of using silicon for the anode because silicon can hold a lot more lithium ions. But it also can expand so much that it fractures and becomes unstable. Tesla uses Panasonic's lithium-ion cells.

"It's a baby step in the direction of using silicon in the anode," Musk said during a press conference call. "But we will increasing the use of silicon in the anode.

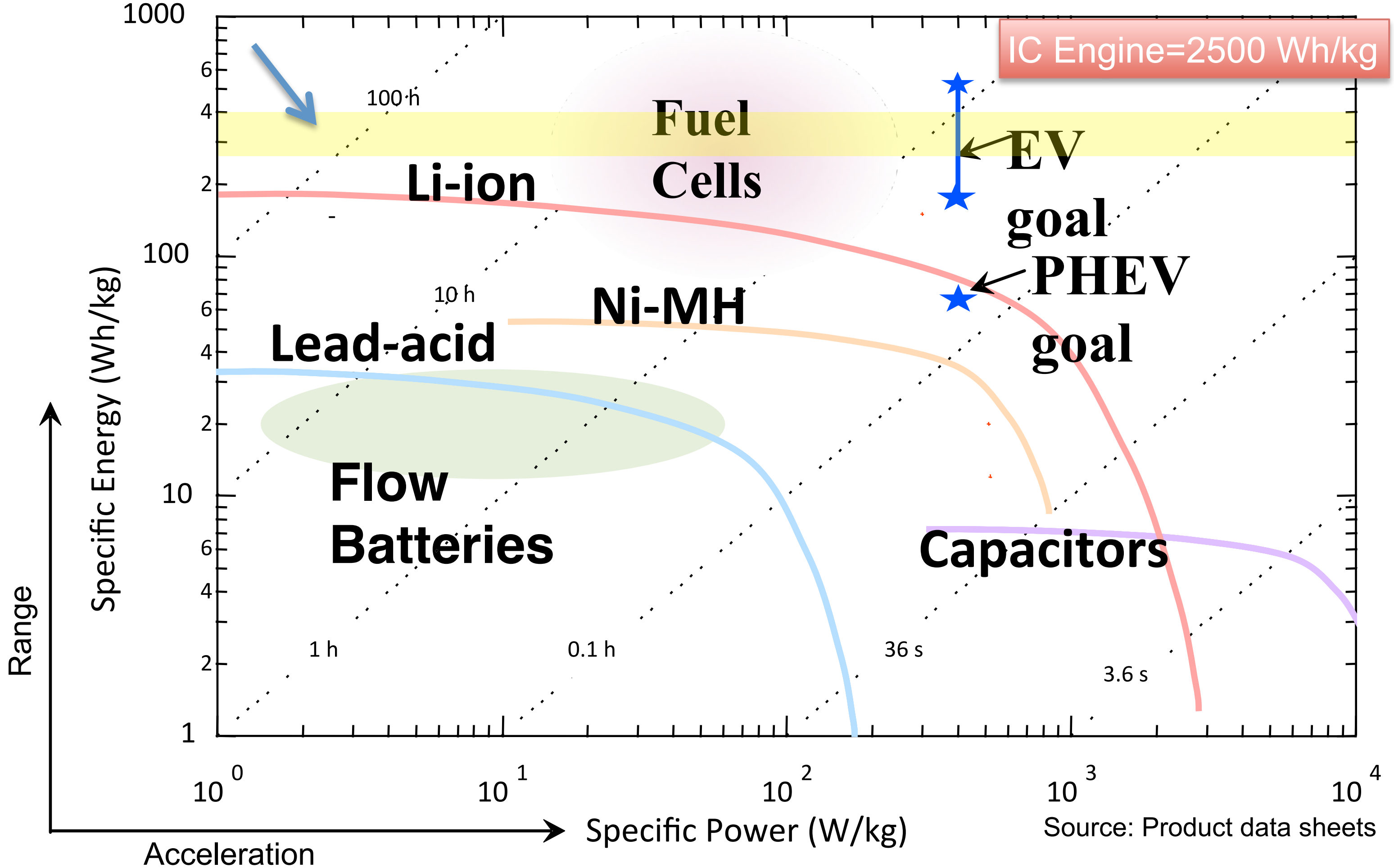
How much can we improve energy with these changes?



- Note: All numbers are at the cell level. Approximately 2x the pack level numbers

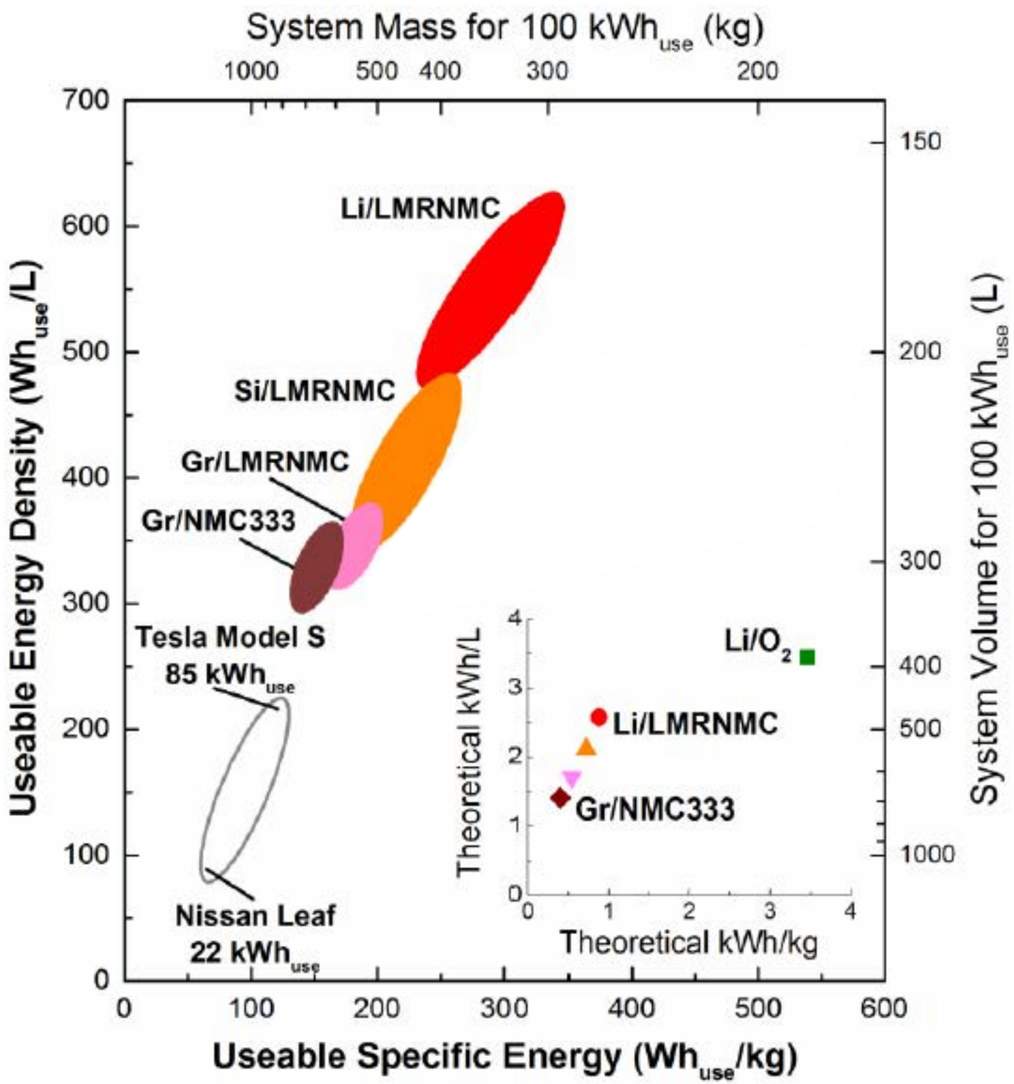
Is this enough?

Alloy anodes (10x capacity but lower V
High V cathodes (2x capacity, higher V)



Source: Product data sheets

If Li metal were successful, options open up



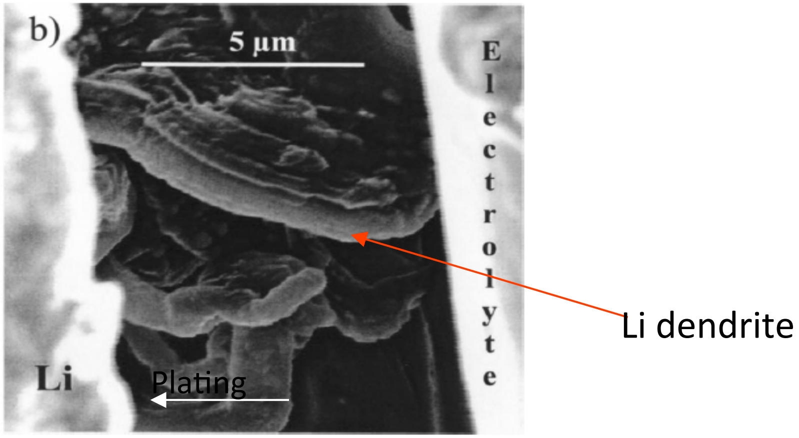
Energy Environ. Sci.,2014, 7, 1555-1563

Approach 3: Lithium metal anodes

- During charge, Li plates on the anode

- The surface of the anode has irregularities on a nanometer scale

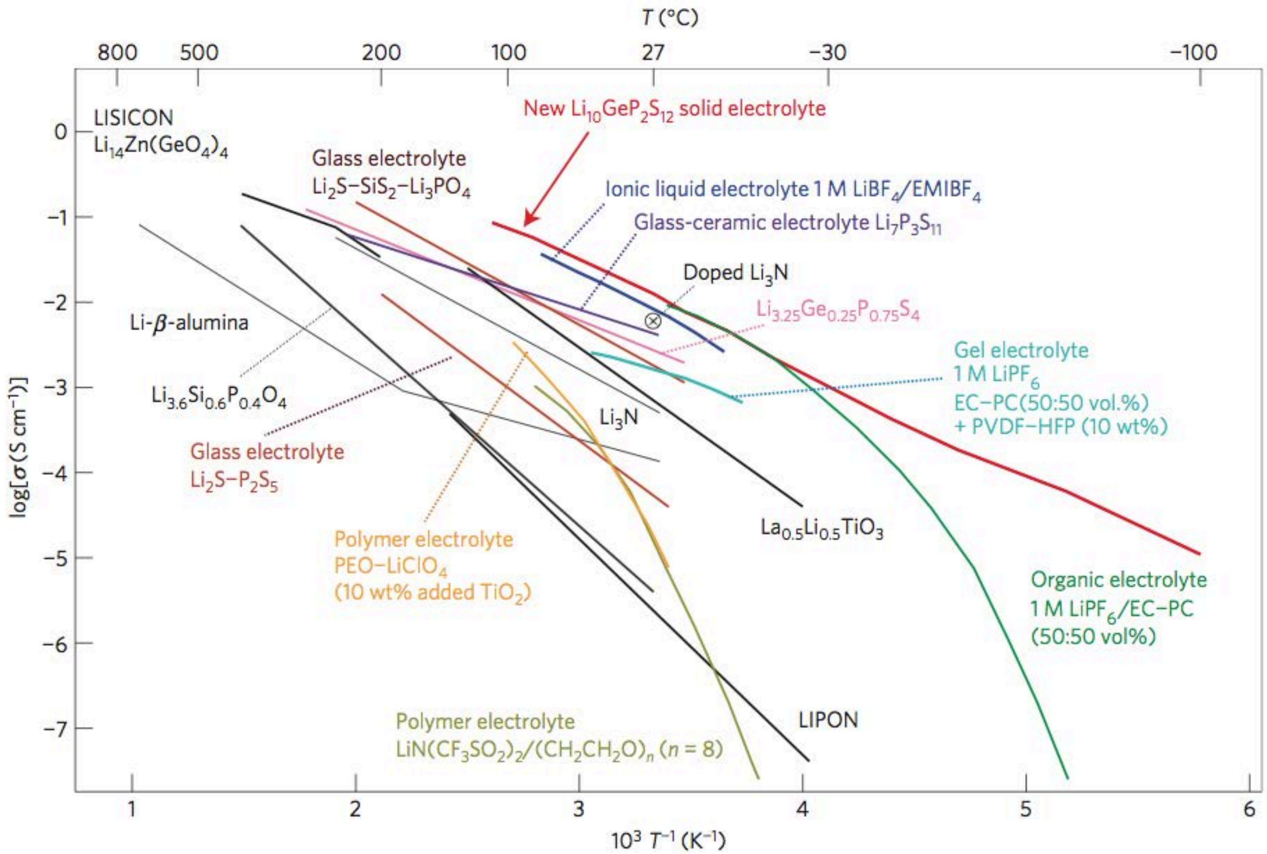
- It has been seen that the plating is not uniform (deposition occurs on protrusions) and leads to formation of dendrites
  - This leads to cell shorting and failure
  - In addition, the growth can break from the surface, thereby isolating material, leading to capacity fade



Source: Dollé et al., Electrochem. Solid State Lett., 5, A286 (2002)

One solution may be to use a protective ceramic electrolyte

Electrolyte Conductivities

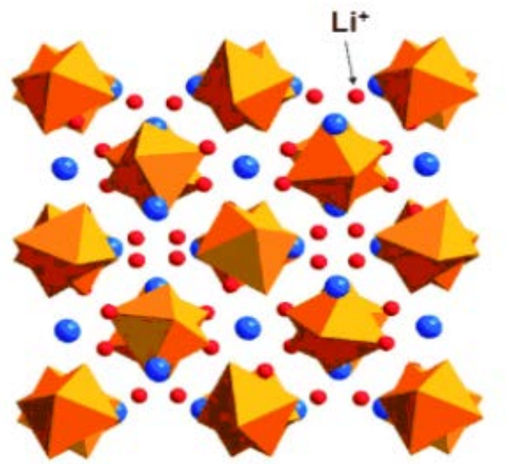


Kamaya et al., Nat. Mater. 10 (2011), 682.

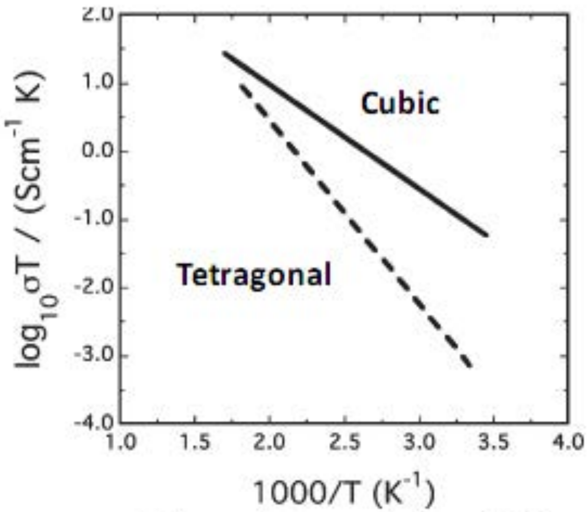
Issues for solid electrolytes:

- 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.

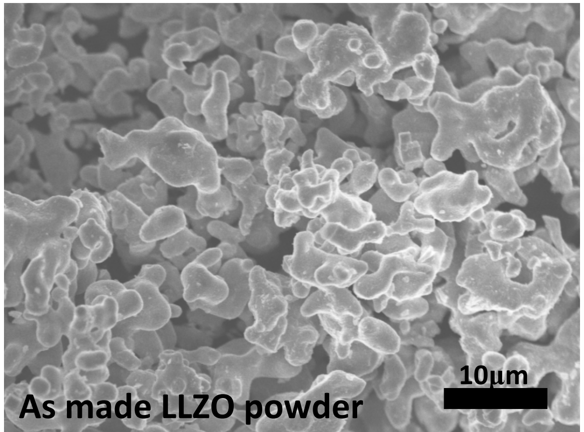
Pros:

- 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

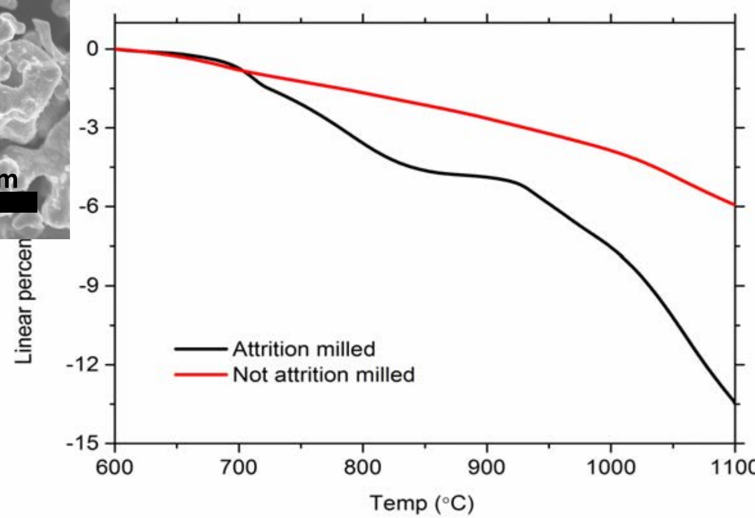
Cons:

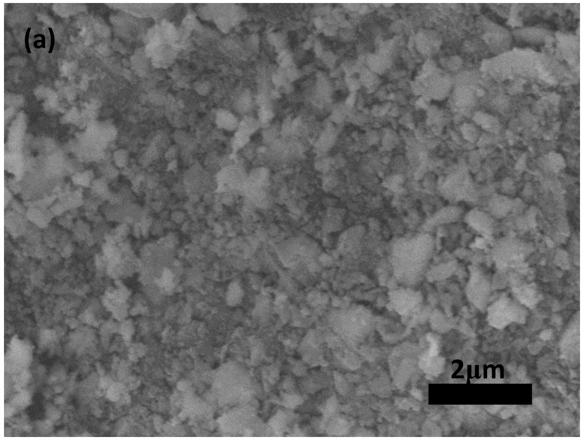
- Difficult to densify
- Reactivity with substrates, moisture, ambient atmosphere
- High interfacial impedances
- Thin films required: for 5 mA/cm^2, voltage drop < 100 mV, needs to be < 200 µm (assuming no contribution from interfacial impedances!)

Densification-particle size matters



Attrition mill



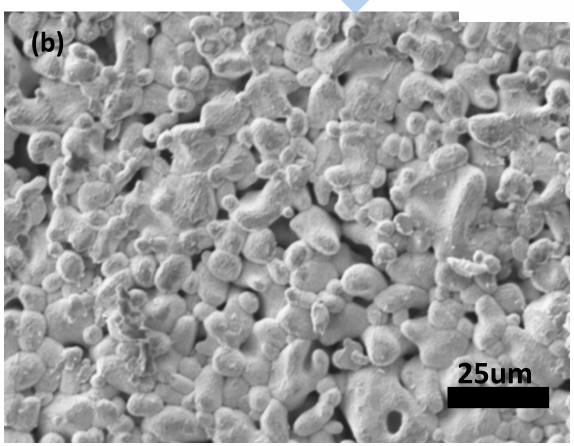


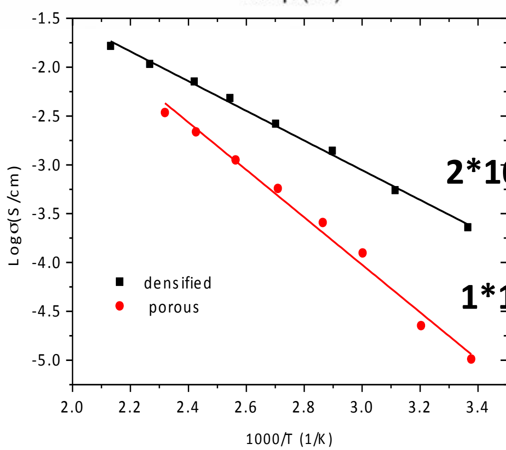
1100 °C sintering (porous)

1100 °C sintering (Dense)

130 °C lower than previously reported for conventional processing

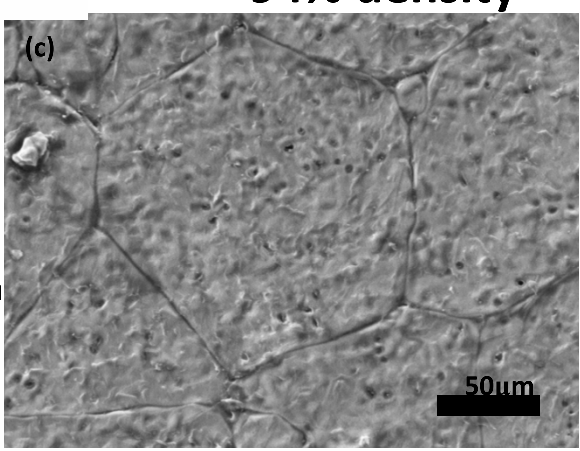
94% density





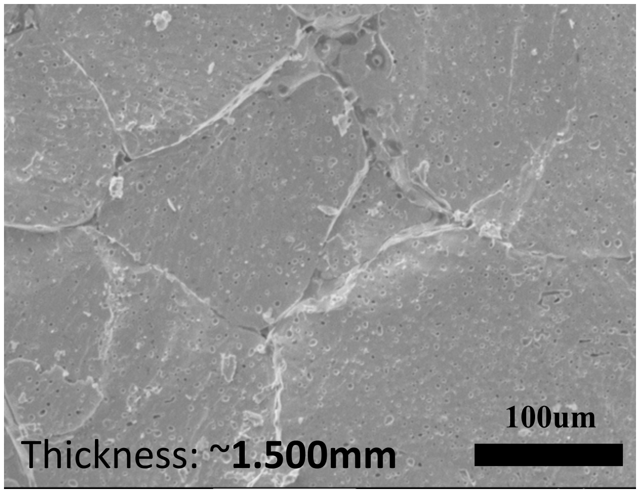
2*10^{-4} S/cm

1*10^{-5} S/cm



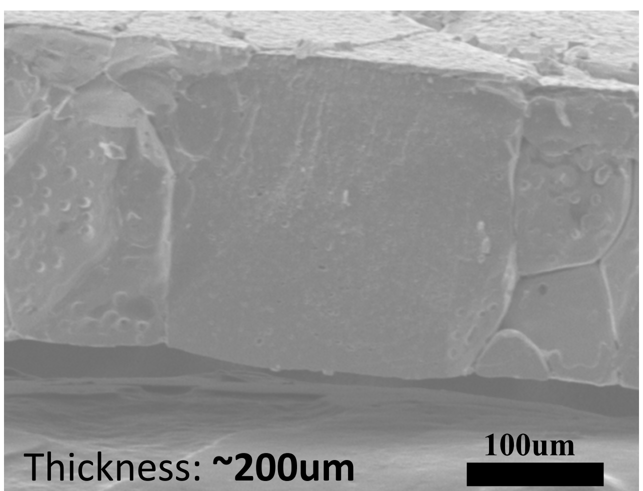
Free-standing thin films, a single grain thick

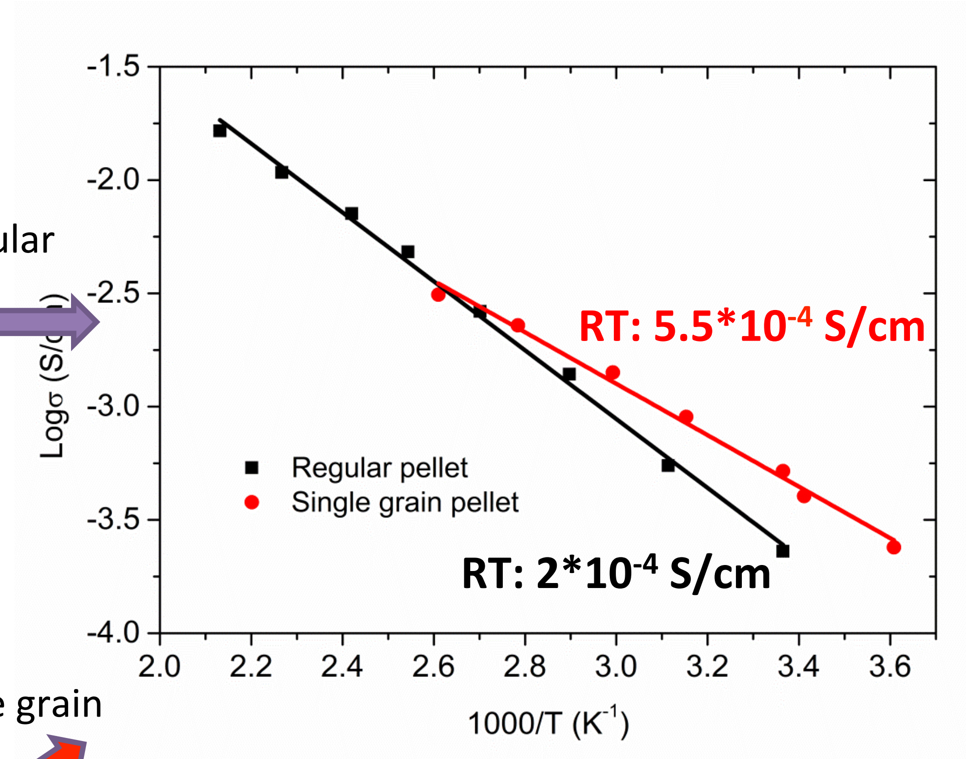
Cross section (fractured)



Regular

Single grain



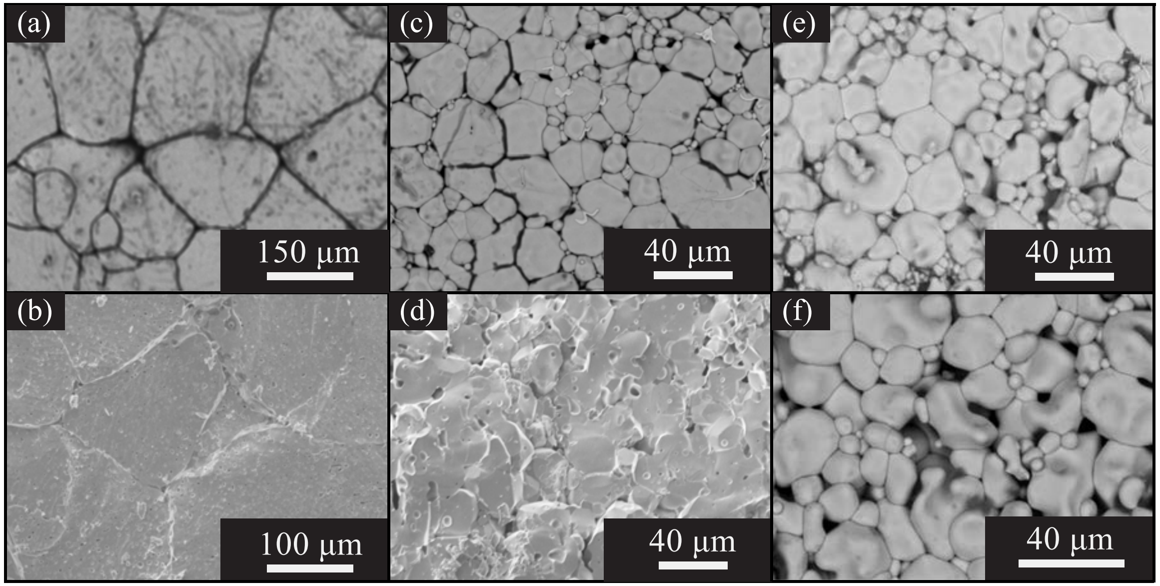


Cheng et al., *J. Mater. Chem. A,* 2, 172 (2014).

Control of Microstructures

surface

cross-section



surface
70% 1 µm
30% 10 µm

surface
50% 1 µm
50% 10 µm

1 µm particles

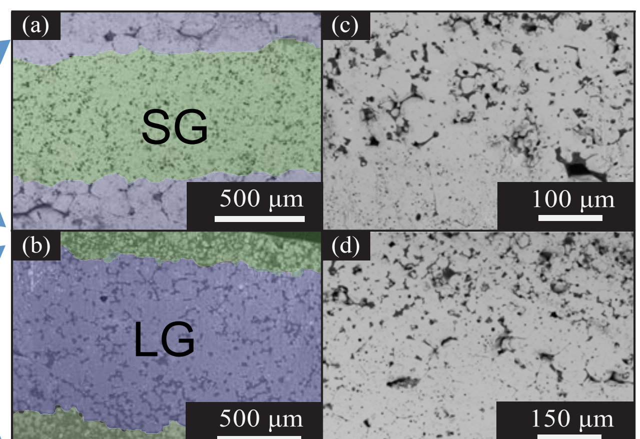
90% 1 µm
10% 10 µm

Not dense

LG

Heterostructures

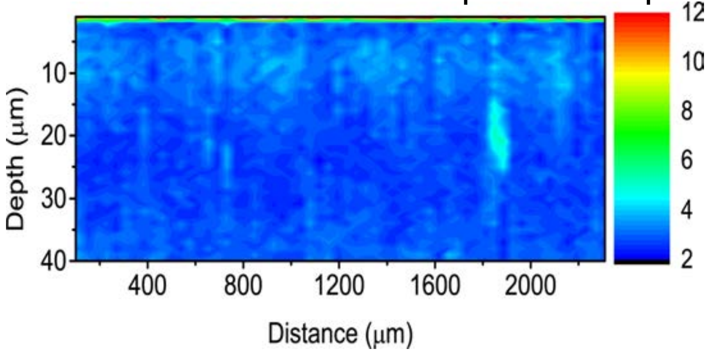
SG



Junctions between large grain and small grain regions

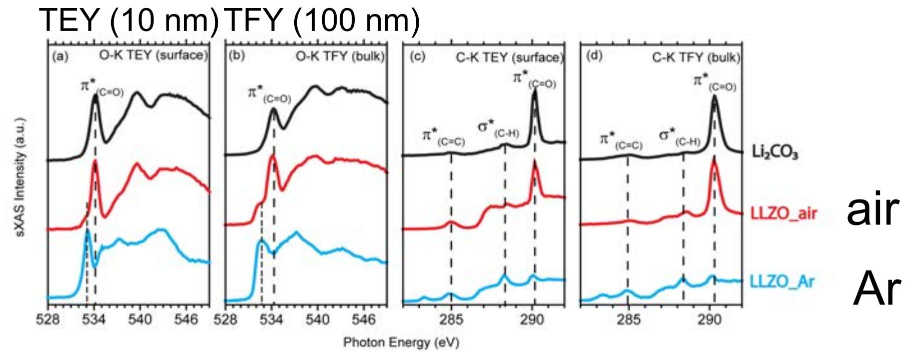
Origins of Interfacial Impedance

LIBS: Li/Zr ratio of air-exposed sample



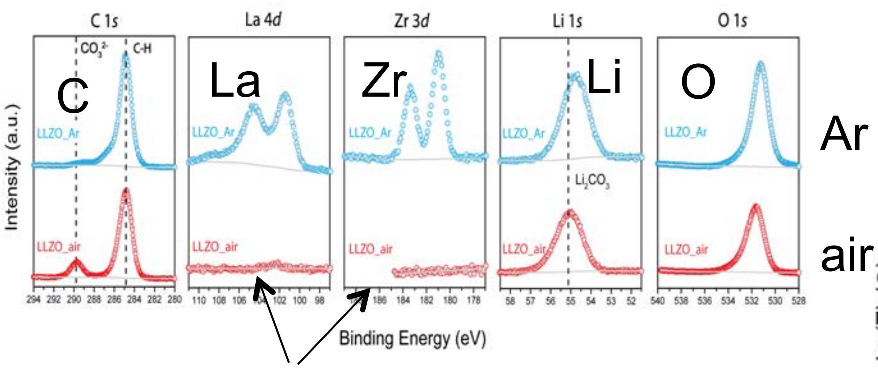
~ 1 µm thick Li-rich layer on sample exposed to air for several months

Soft XAS

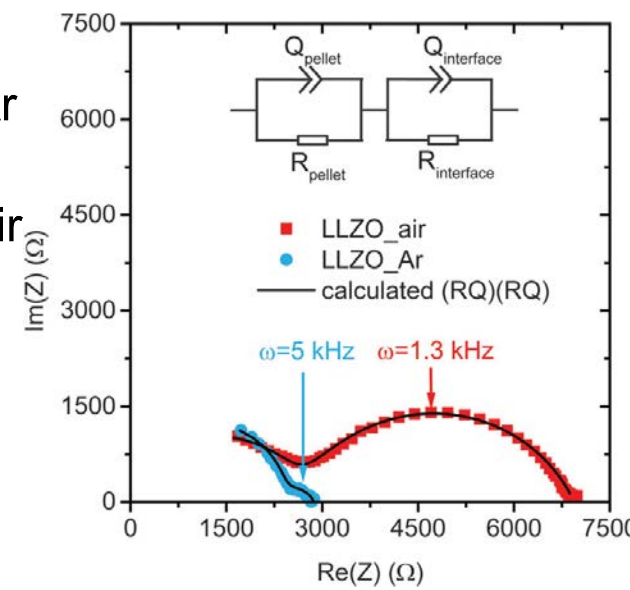


Evidence of Li_2CO_3 formation on sample exposed to air, but still see LLZO in TFY mode (thickness <100 nm)

Synchrotron XPS data



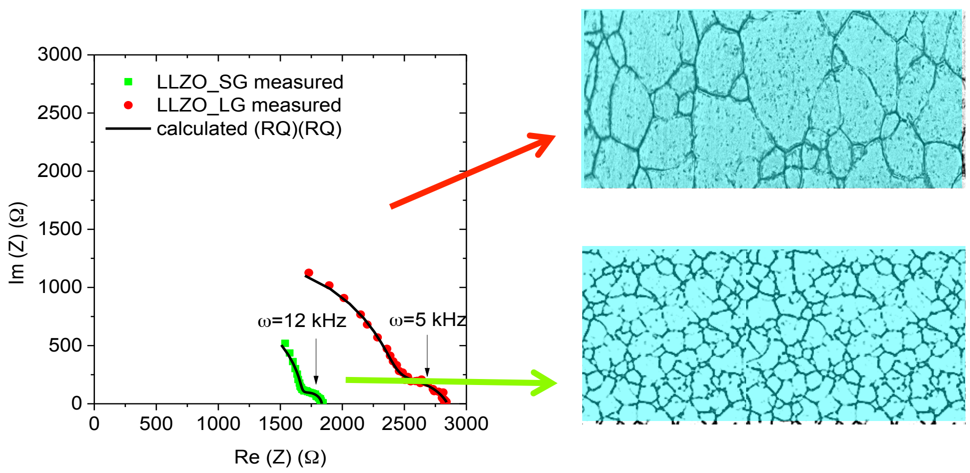
Li_2CO_3 formation on sample exposed to air several days is thick enough to block La, Zr signals (>3 nm thick)



Samples polished under Ar to remove Li_2CO_3 have much lower interfacial resistance

Cheng et al., *Phys. Chem. Chem. Phys*. 16, 18294 (2014).

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.

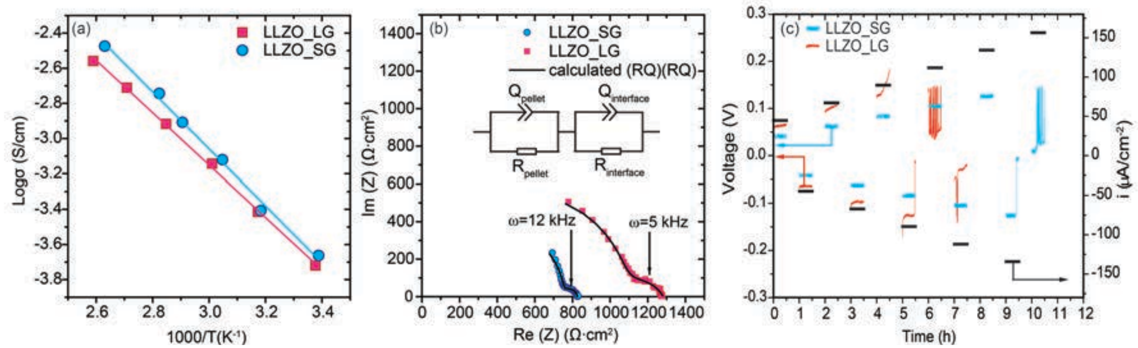
Item	Total Conductivity	Bulk Resistance	Interfacial Resistance	Area specific interfacial resistance
LLZO_LG	2.0×10^{-4}S/cm	2335 Ω	566 Ω	127 Ω·cm^2
LLZO_SG	2.5×10^{-4}S/cm	1672 Ω	161 Ω	37 Ω·cm^2

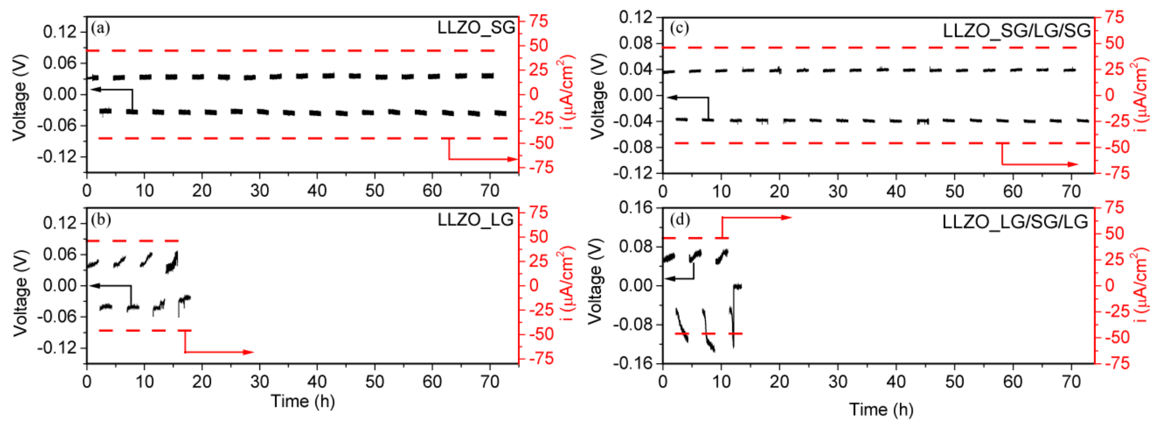
Lowest ASI
ever reported for LLZO!

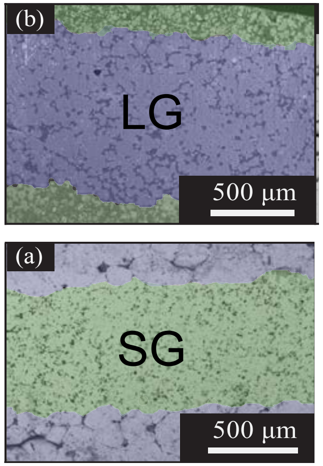
Cheng et al., *ACS Appl. Mater. & Interfaces*, 7, 2073 (2015).

Effect of Interfacial Impedance and Microstructure on Electrochemistry

Li/LLZO/Li cells





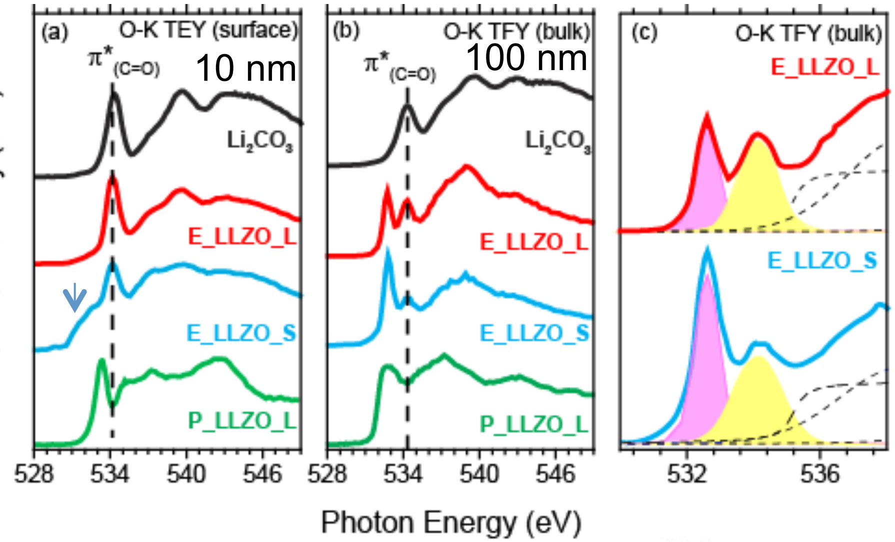


- Small grained samples have lower interfacial impedance and cycle better in stepped or constant current experiments
- Heterostructures with small grains on the outside (closest to Li electrodes) perform better than those with large grains on the outside.
- Surface microstructure is very important!

A Closer Look at the Effect of Microstructure on Li_2CO_3 Formation

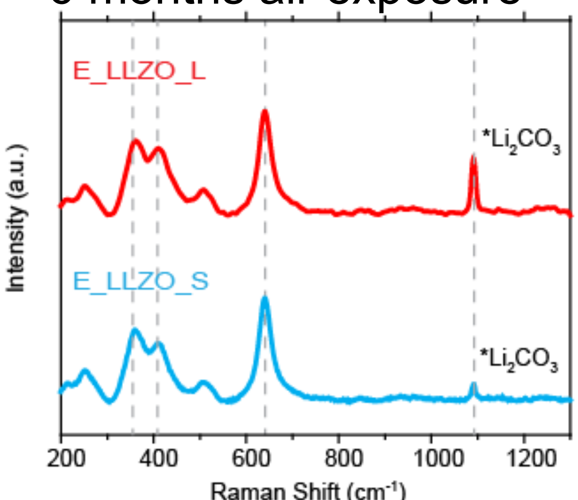
O L-edge sXAS experiments

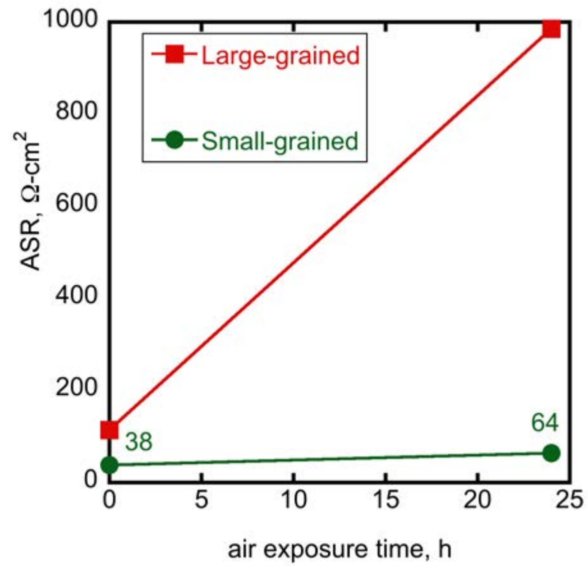
Large-grained
24 h air exposure
Small-grained
24 h air exposure
pristine



More Li_2CO_3 for large-grained sample

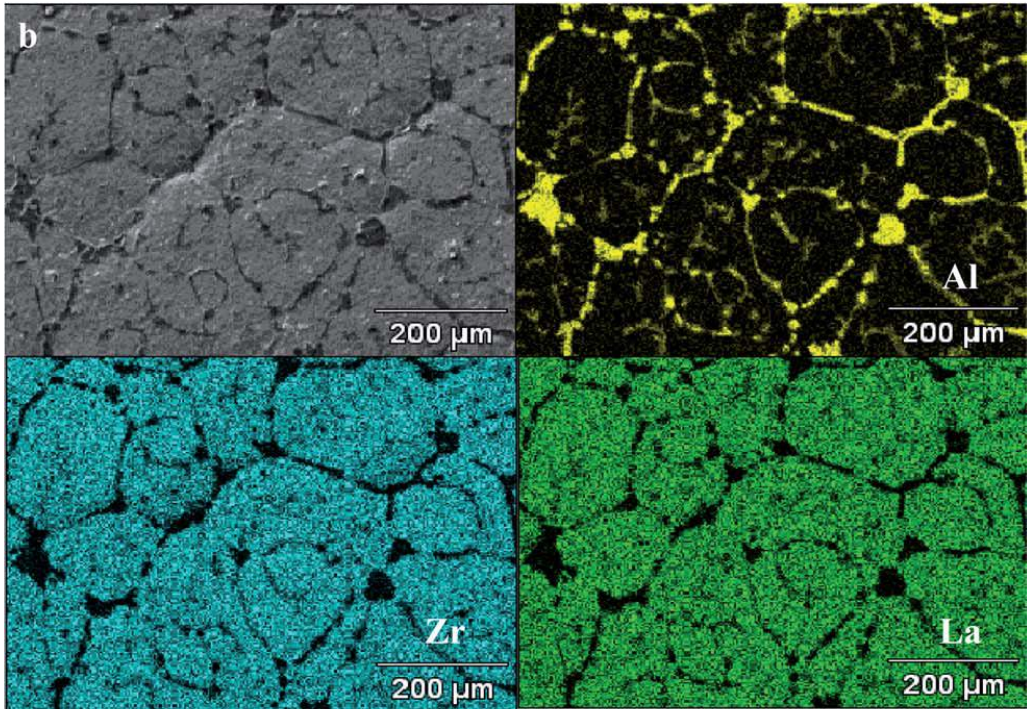
Raman spectra
6 months air exposure





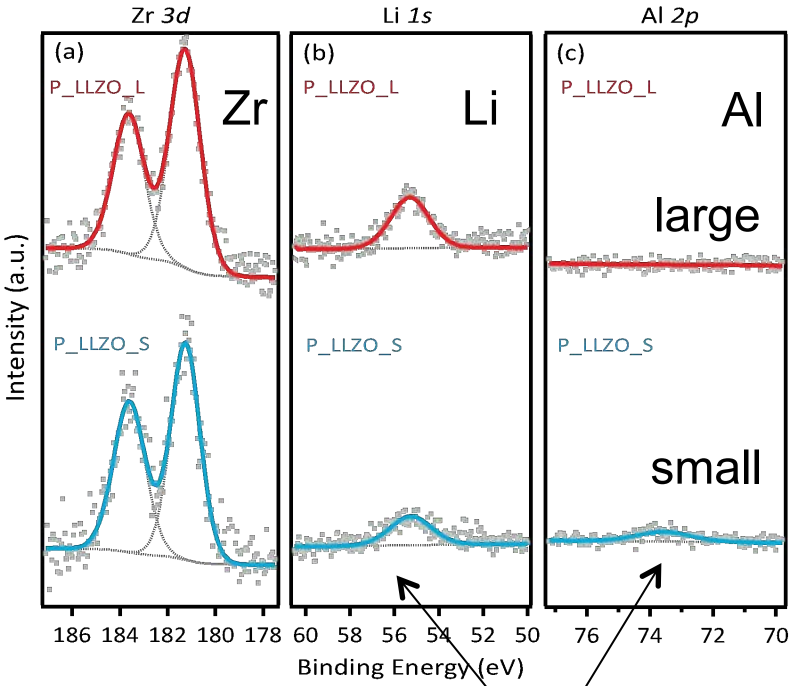
Cheng et al., ACS Applied Mater. Interfaces 7, 17649 (2015).

Why does the Microstructure Affect Rate of Li_2CO_3 Formation?



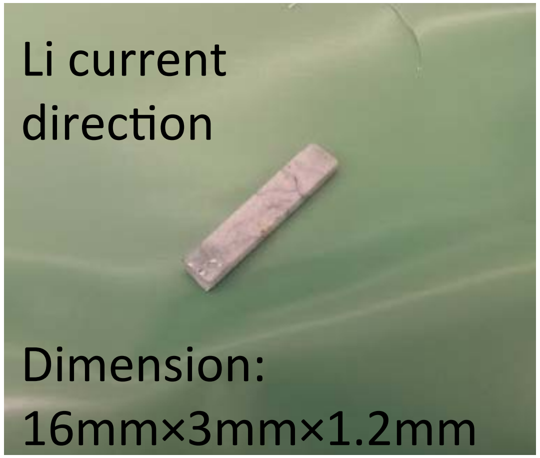
Liquid sintering mechanism for large-grained sample depletes Al from bulk and concentrates it in grain boundaries.

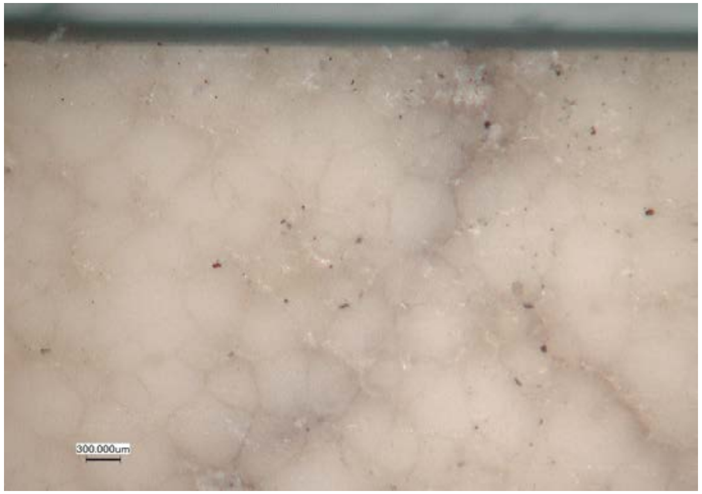
XPS Spectra (surface sensitive)

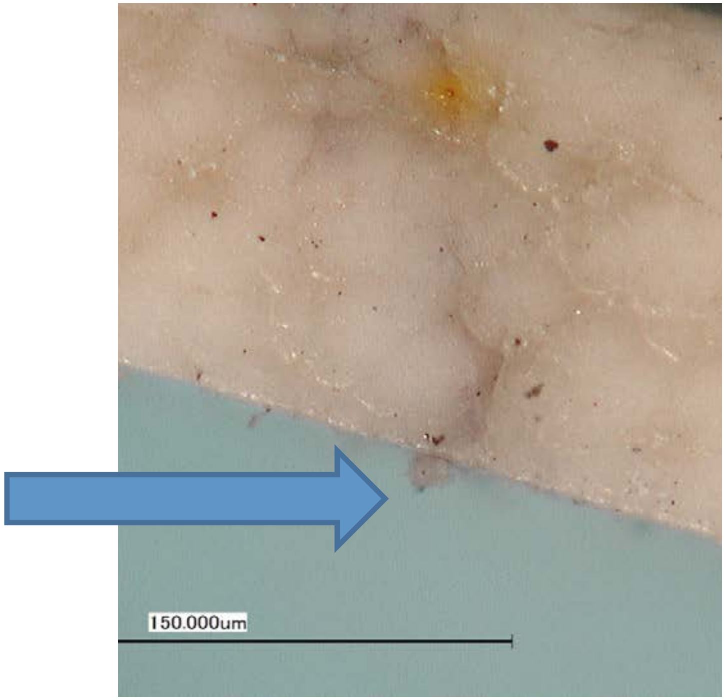


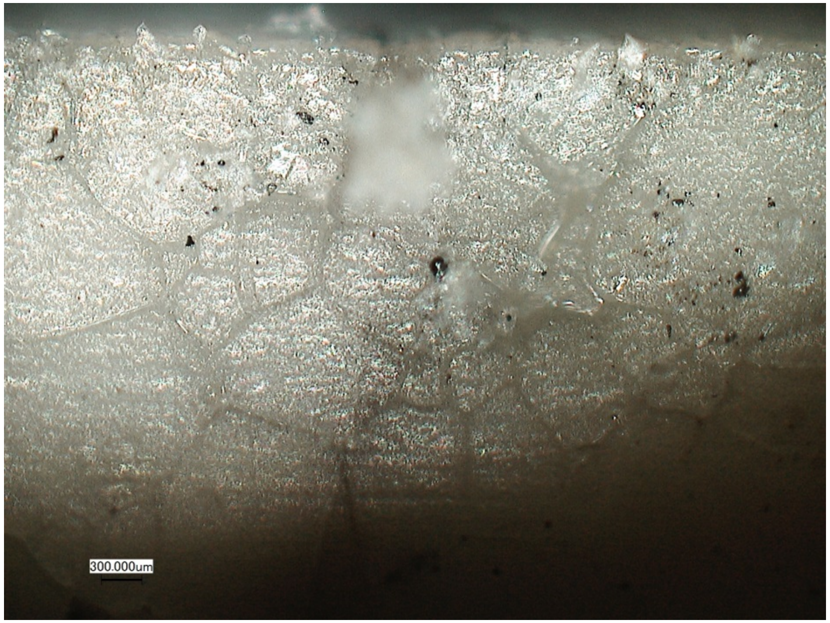
More Al and less Li at surface of small-grained sample, less reactivity with water.

Optical Evidence of Dendrite Formation via Grain Boundaries





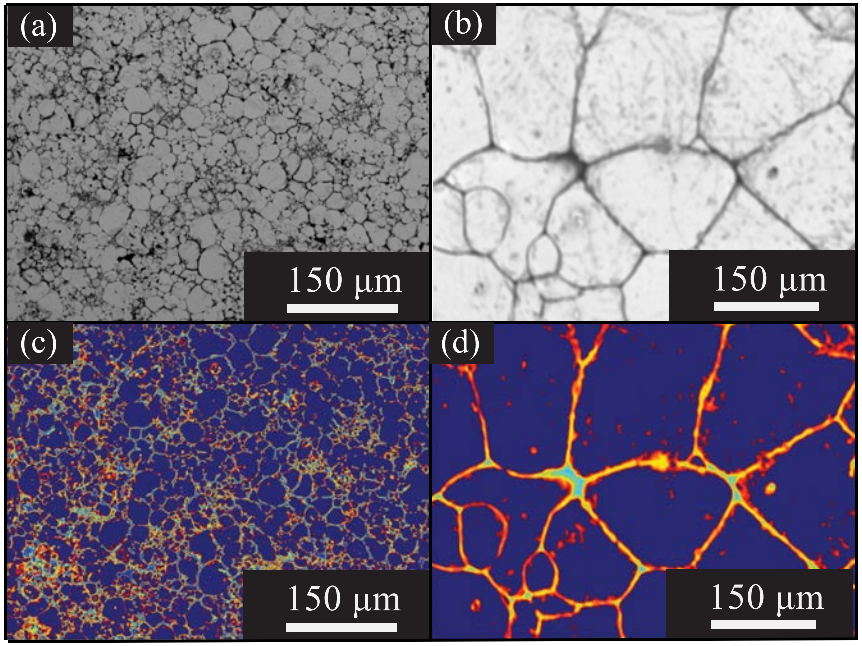




Visualization of Grain Boundaries

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.

Summary

- **There has been remarkable progress in battery technology over the past 25 years, thanks to Li-ion batteries.**
- **We are at the cusp of a revolution; rapidly decreasing costs and incremental improvements in materials for Li-ion batteries have brought us close to vehicle goals-new materials and manufacturing techniques could push us over the finish line.**
- **The next revolution could come with lithium metal batteries, but we need to ensure their safety and long cycle life**
- **Ceramic electrolytes may be the answer, but we need to pay close attention to microstructure and interfaces!**

Thank you for your attention

Also, thanks to DOE-OVT who funds us through various battery programs

Title