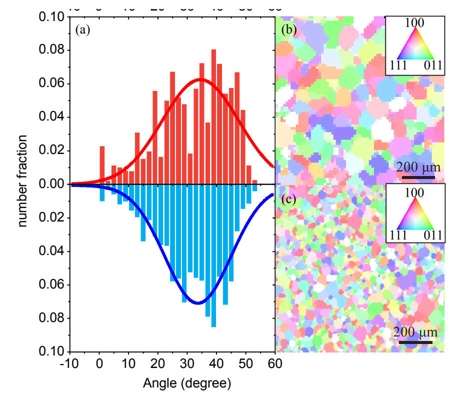
The Future of Solid State Batteries for Electric Vehicles



Marca M. Doeff

Energy Storage and Distributed Resources Division
Lawrence Berkeley National Laboratory
Contact: mmdoeff@lbl.gov

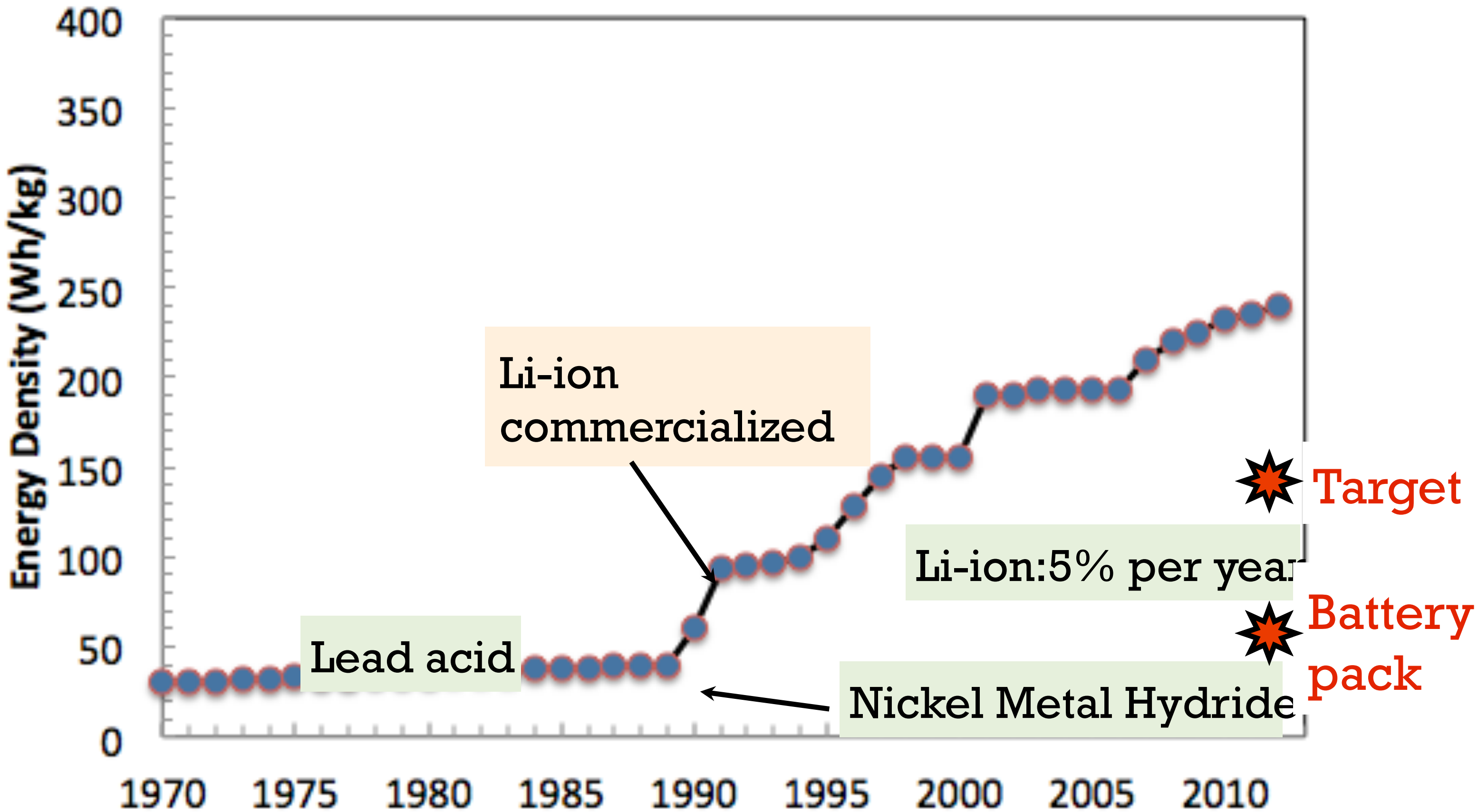
BERKELEY LAB

We are seeing real progress in EVs

Instead of this…

We have…

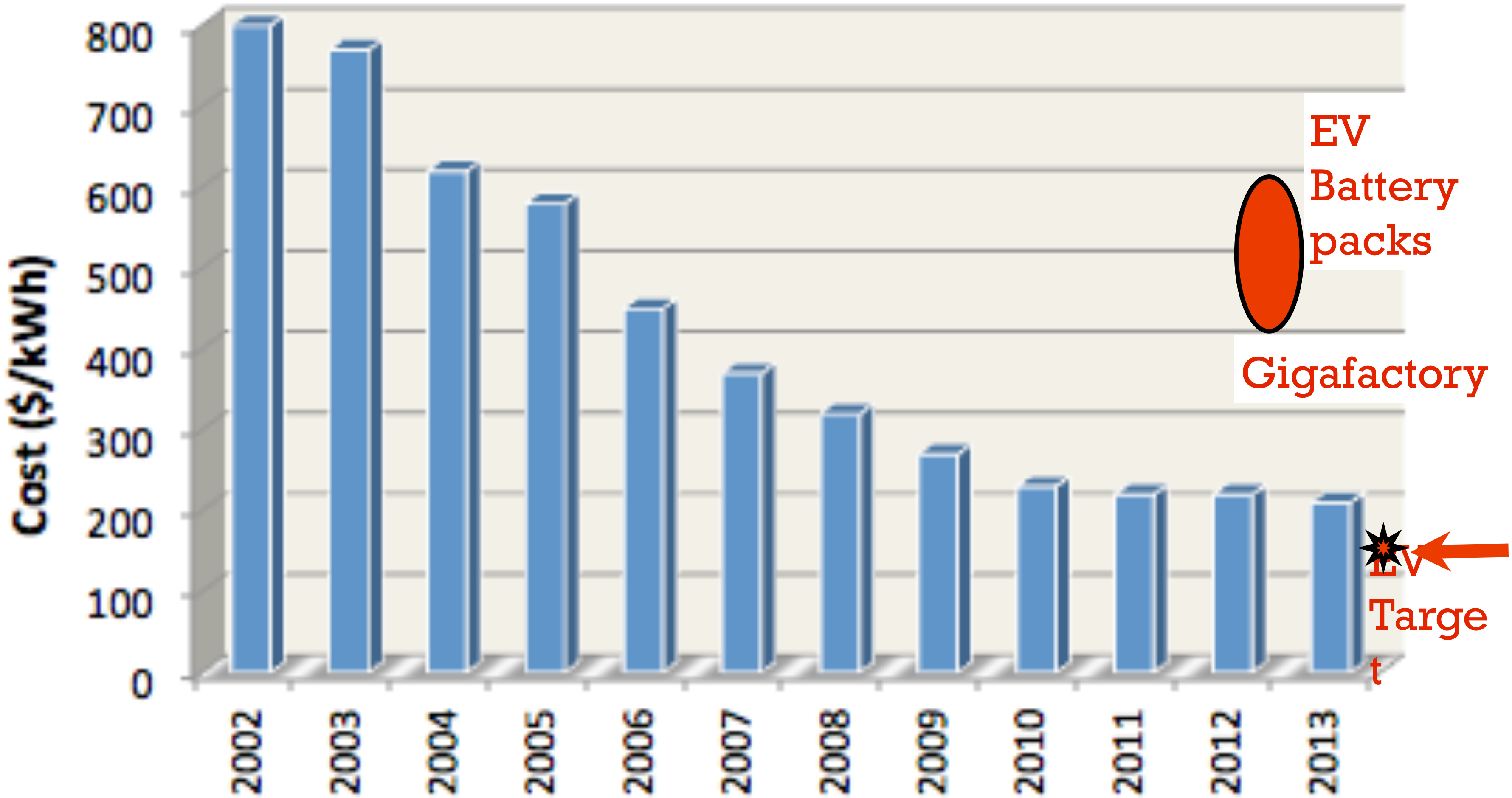
Moore's law for batteries



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

Most improvement from better engineering, rather than new materials.
Practical limit is probably about 350 Wh/kg

…and costs are coming down



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

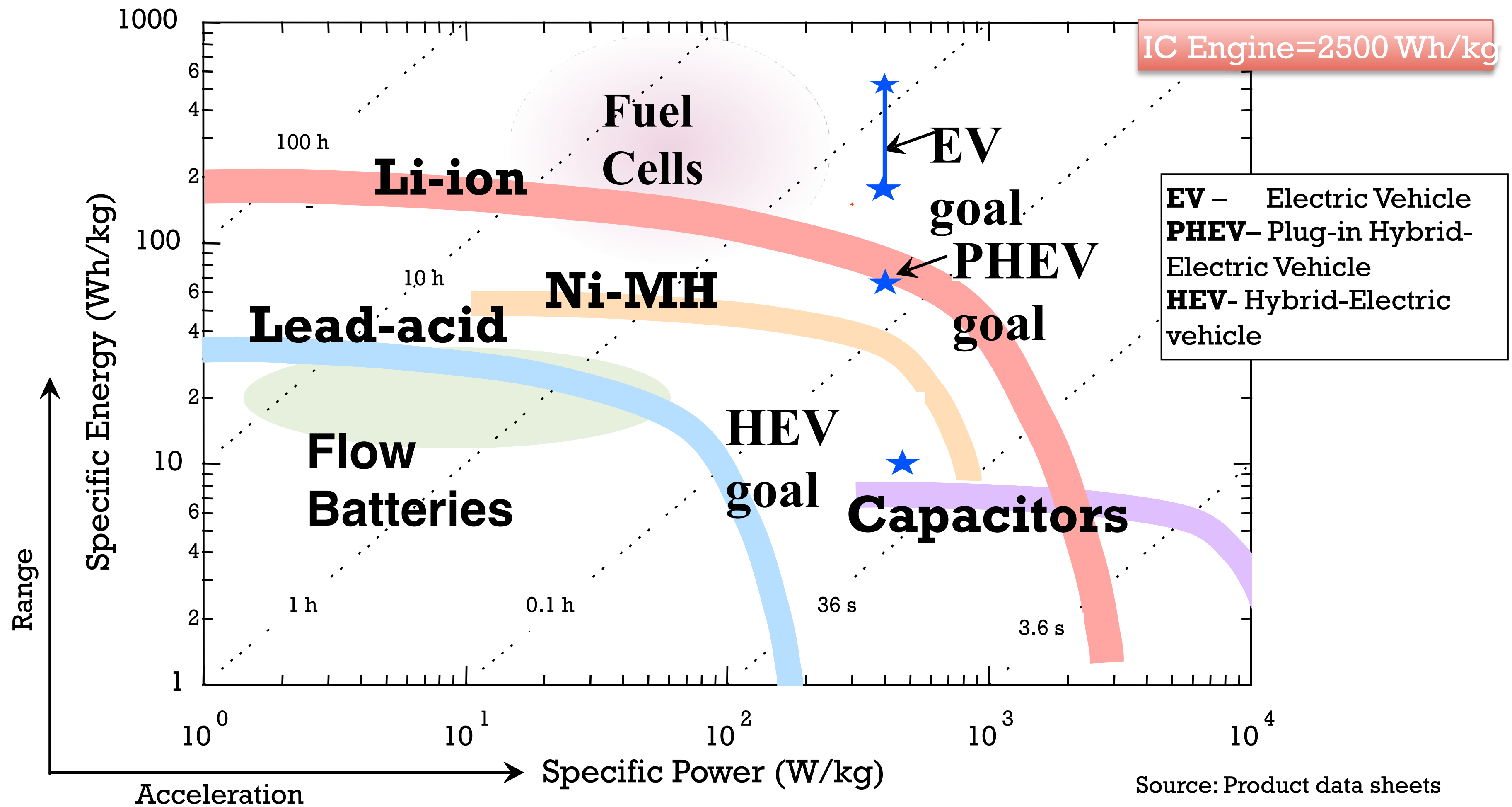
Where does the DOE cost target come from?

- 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!

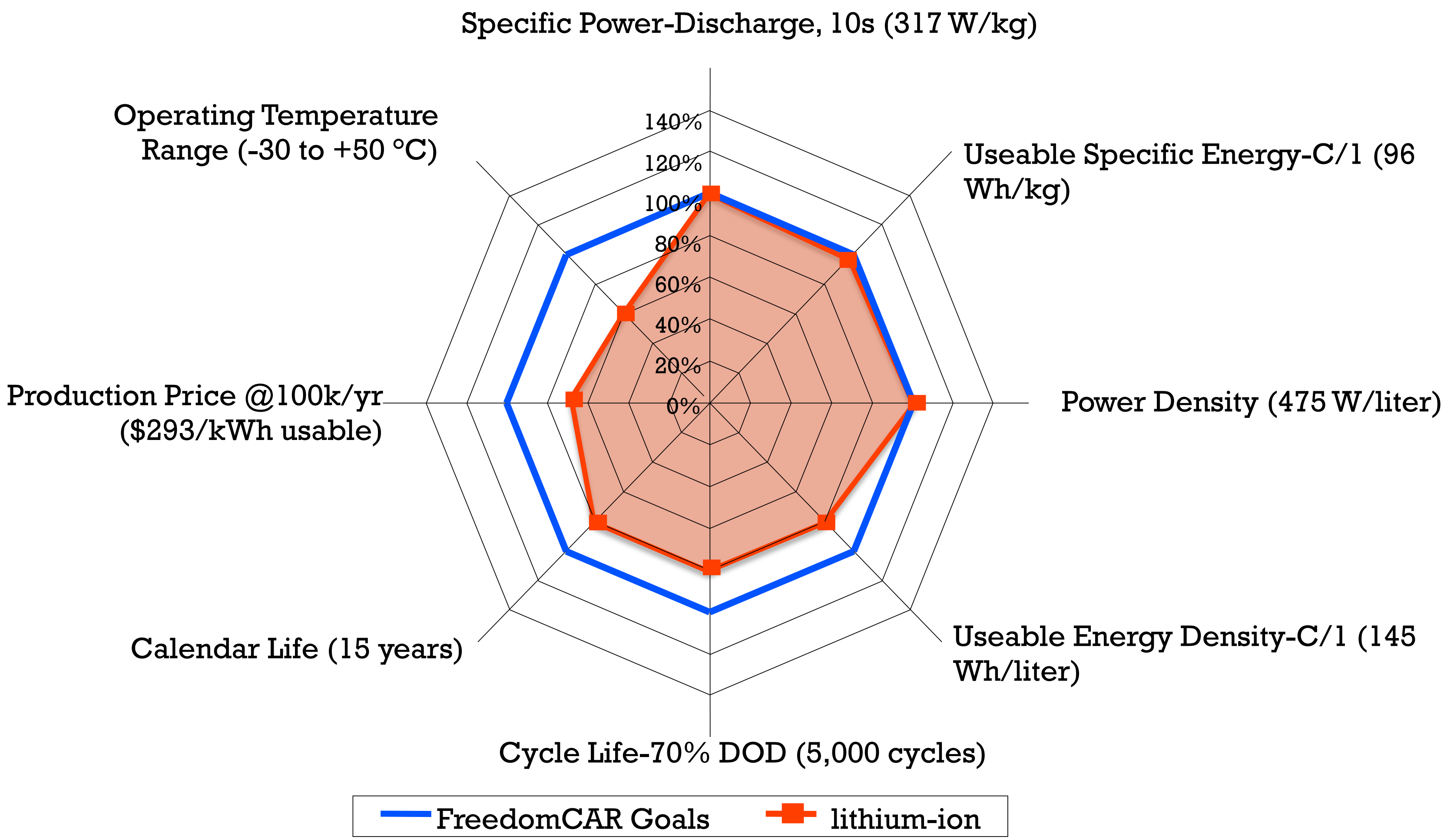
The $125/kWh should be taken to be a target that will allow the tipping point to occur

Energy and power play against each other



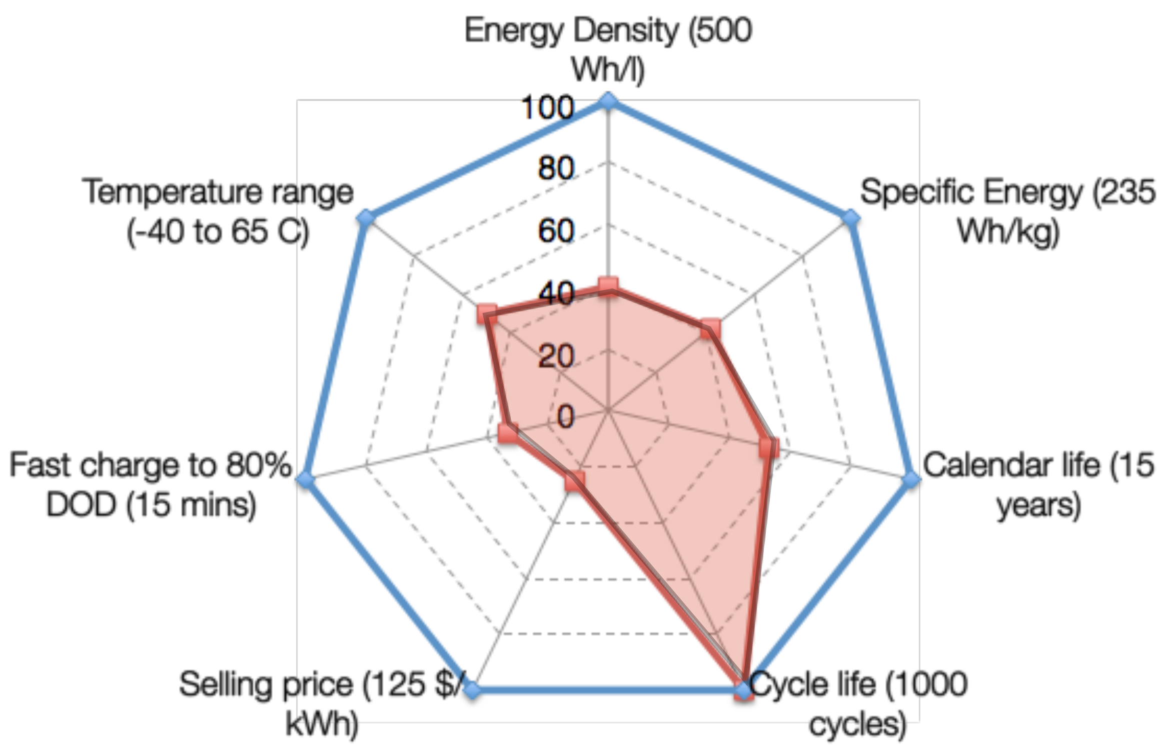
But its more than just about energy and power

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



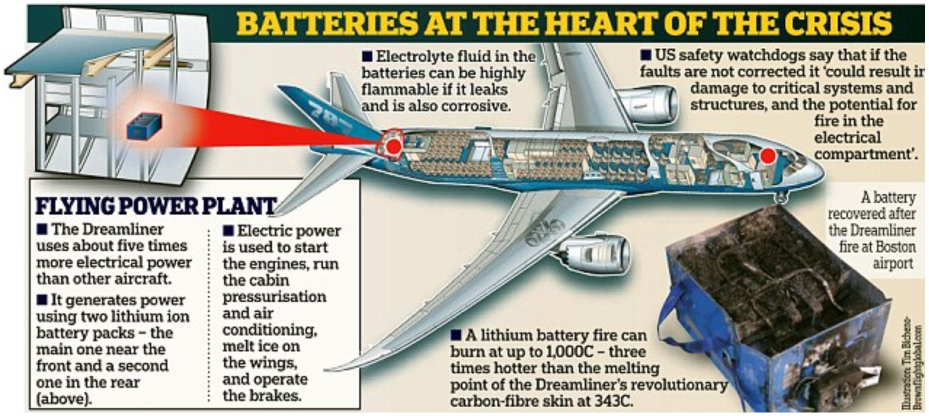
Comparison of Present-day Li-ion Batteries vs. Electric Vehicle Goals

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.

Safety is a key concern



Boeing Dreamliner

Don't keep live ammo next to your laptop in your pickup truck! (NY Times, Aug. 15, 2006)

Hoverboards

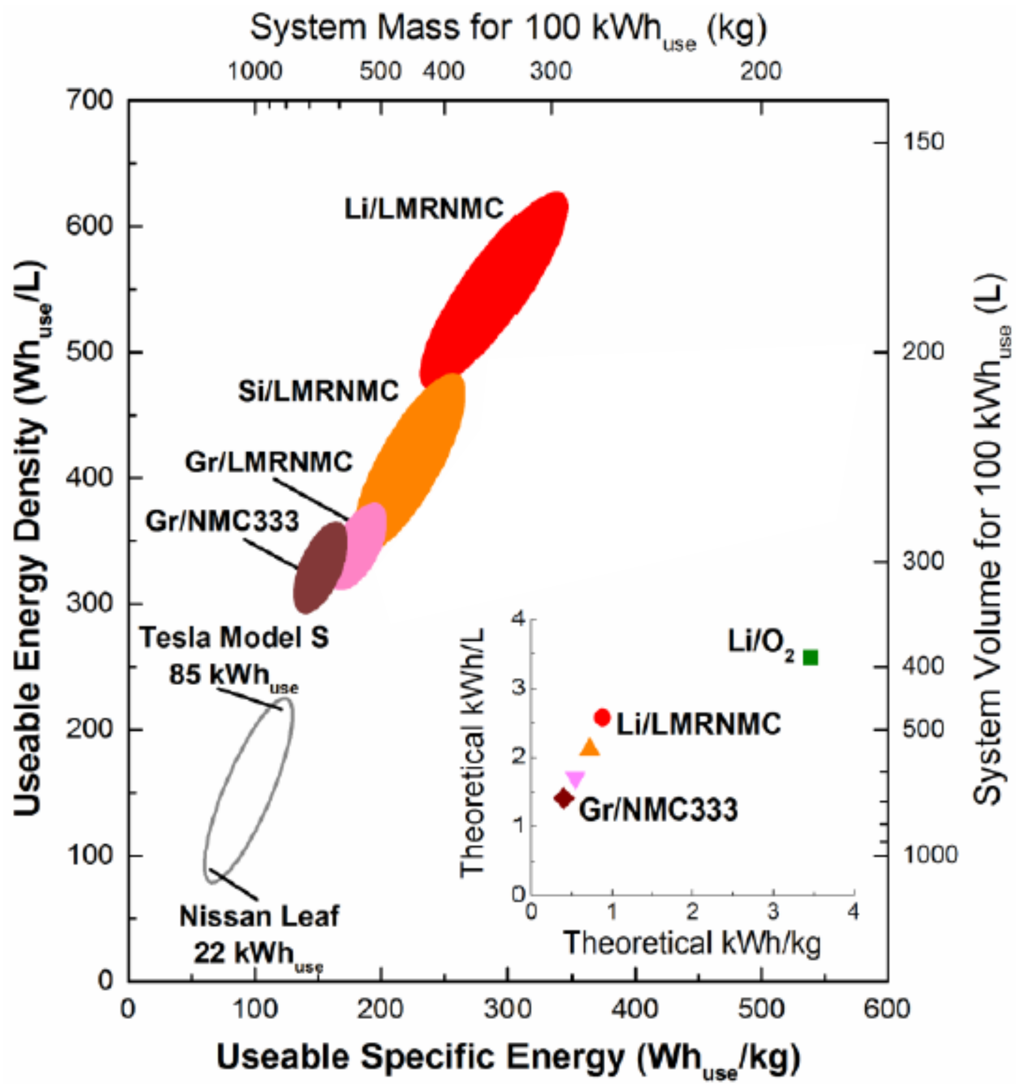
Samsung Galaxy Note 7

Battery Blows Up and Destroys NASA Robot-NASA's RoboSimian robot recently suffered a massive battery explosion.

By Avery Thompson Oct 27, 2016 Popular Mechanics
Lithium-ion batteries going boom have been in the news a lot recently because of Samsung's exploding Galaxy Note 7. But Samsung isn't the only one with an exploding battery problem. NASA's having its own difficulties.

Officials say series of intense fires delayed rescue after Tesla crash; both victims identified
POSTED 2:35 AM, NOVEMBER 3, 2016, BY FOX59 WEB, UPDATED AT 05:32PM, NOVEMBER 3, 2016
INDIANAPOLIS, Ind. — A series of intense fires both large and small prevented rescue crews from reaching the victims of a fiery car crash near downtown Indianapolis early Thursday morning.

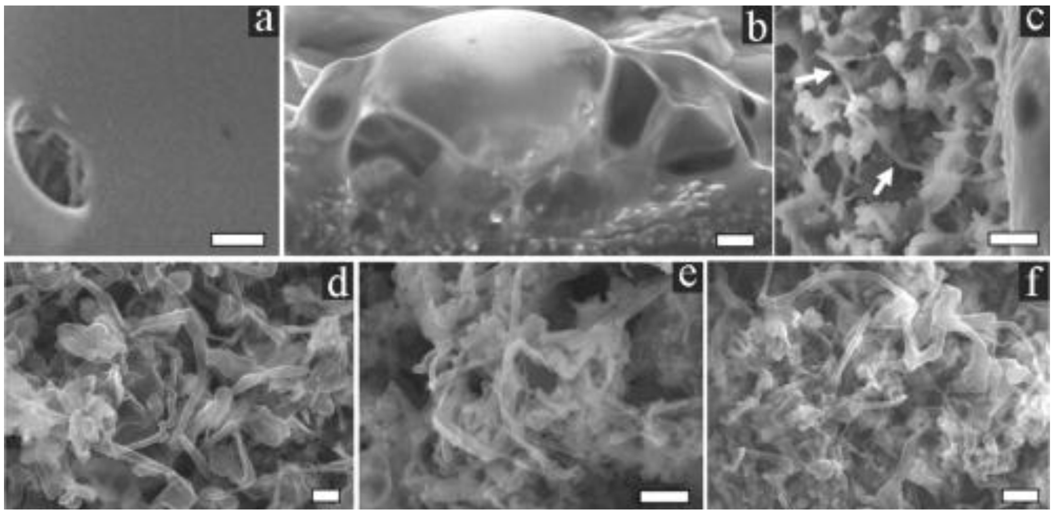
Are Lithium Metal Batteries the answer?

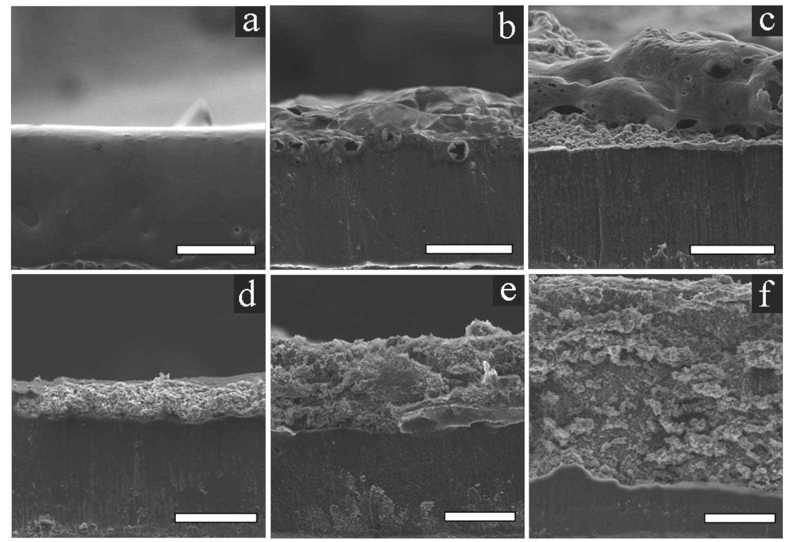


Energy Environ. Sci.,2014, 7, 1555-1563

The Li Metal Electrode is a Challenge

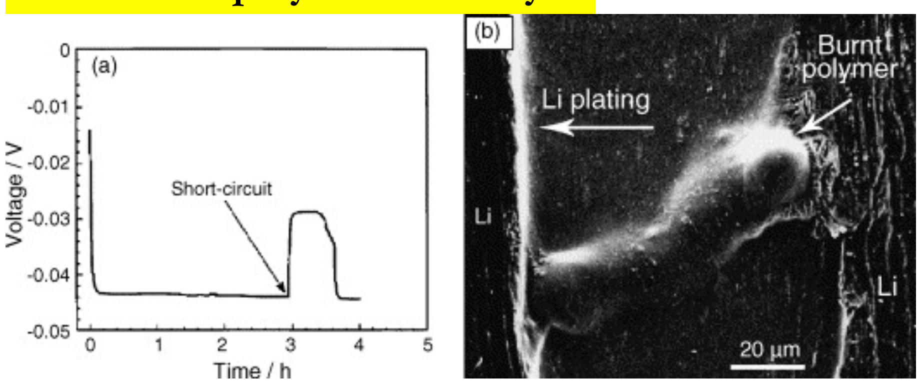
Li metal in conventional Li-ion carbonate electrolytes





Lopez *et al.*, *J. Electrochem. Soc.* 156 (2009), A726.

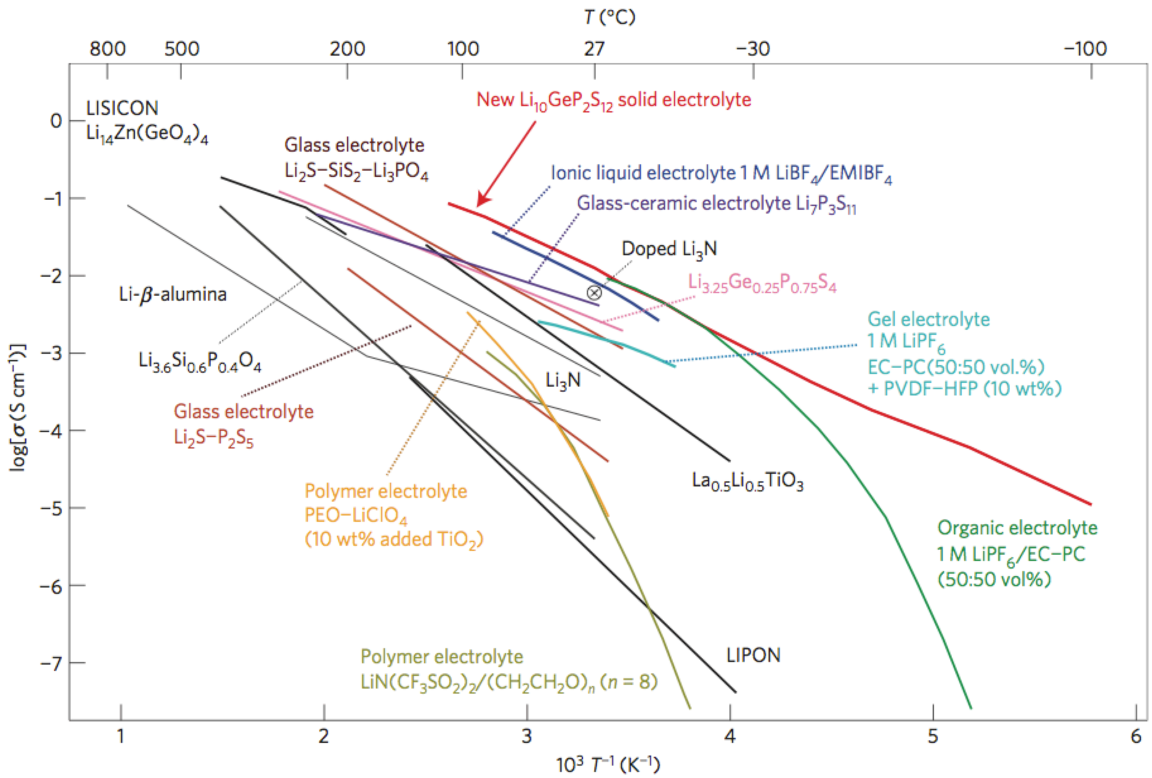
Li metal in polymer electrolyte



Rosso *et al.*, *J. Electrochem. Soc.* 51 (2006), 5334.

- Generation of current density inhomogeneities leads to dendritic growth.
- Reaction with electrolyte leads to mossy growth and formation of unstable decomposition layers.

Solid Electrolytes



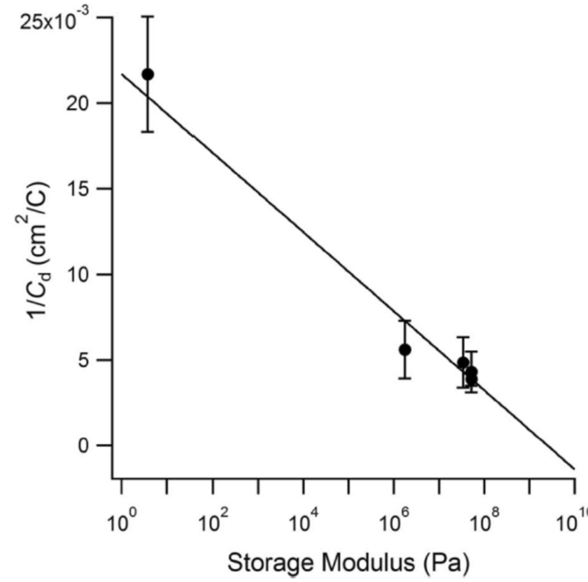


Figure 6. Reciprocal of charge passed to short-circuit ($1/C_d$) versus storag modulus, G′, showing the empirical determination of critical modulus neede to eliminate dendrite growth at current density = 0.17 mA/cm^2 in block copoly mer electrolytes with $r = 0.085$ at 90°C. Critical modulus required to eliminat dendrite growth under the specified conditions is calculated from x-intercep of fit included on plot.

Kamaya *et al.*, *Nat. Mater.* 10 (2011), 682.
Stone *et al.*, *J. Electrochem. Soc.* 159 (2012), A222.

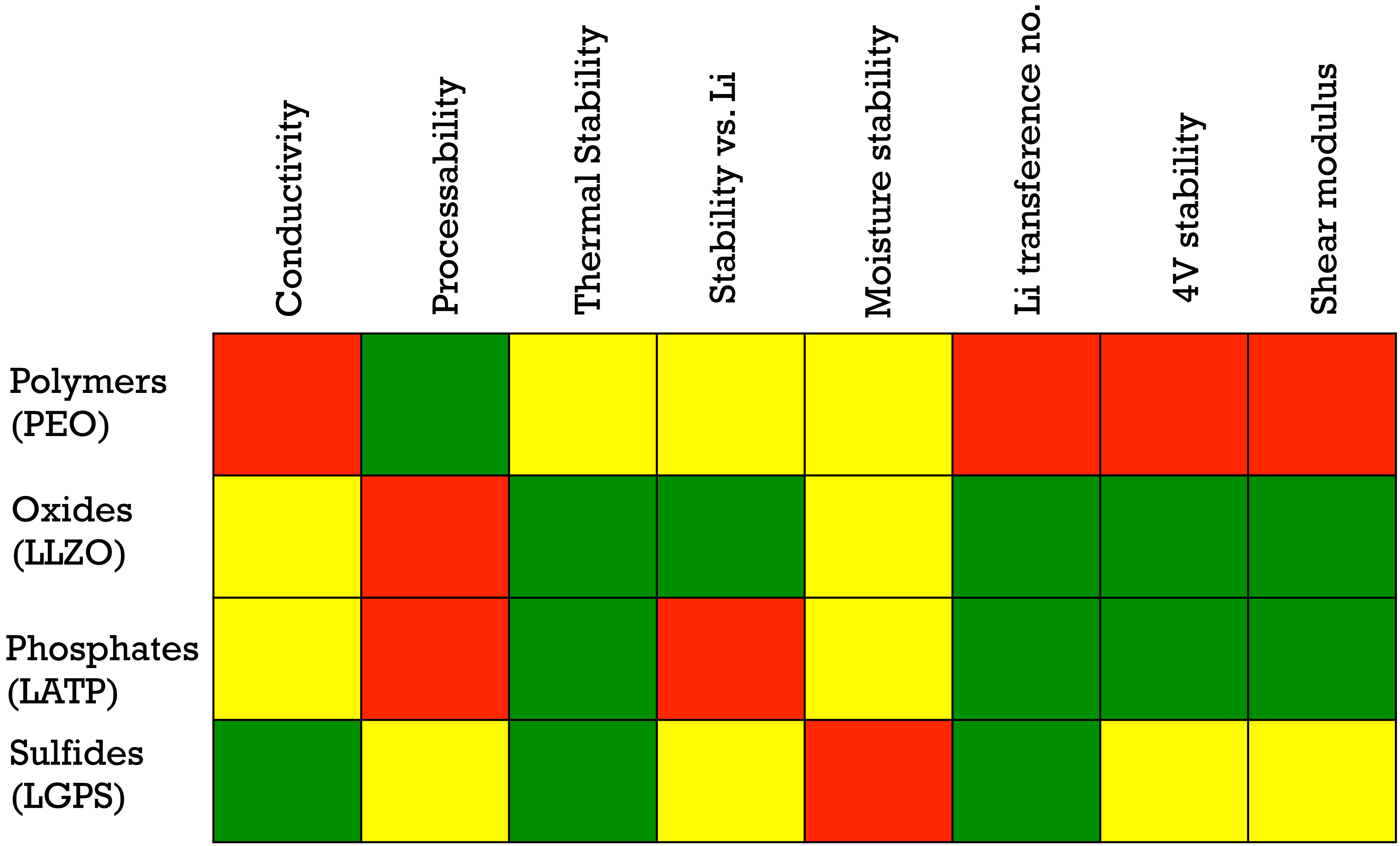
- Replace polymeric separator+liquid electrolyte with solid
  - Homogenizes current density at the Li surface and/or is stiff in order to “push dendrites back”.
  - No flammable electrolytic solution

Wish list for solid electrolytes

- High ionic conductivity (0.2-10 mS/cm at RT)
- Low electronic conductivity
- Stability vs. very reducing Li metal and oxidizing cathode- can use protective layers but this increases cost and complexity
- Processable into thin layers (<50 μm depending on material and cell design) over large areas
- Operate over a wide temperature range
- Low cost
- Promotes safe cycling of lithium (no dendrites)
- Good mechanical properties (can accommodate volume strain)

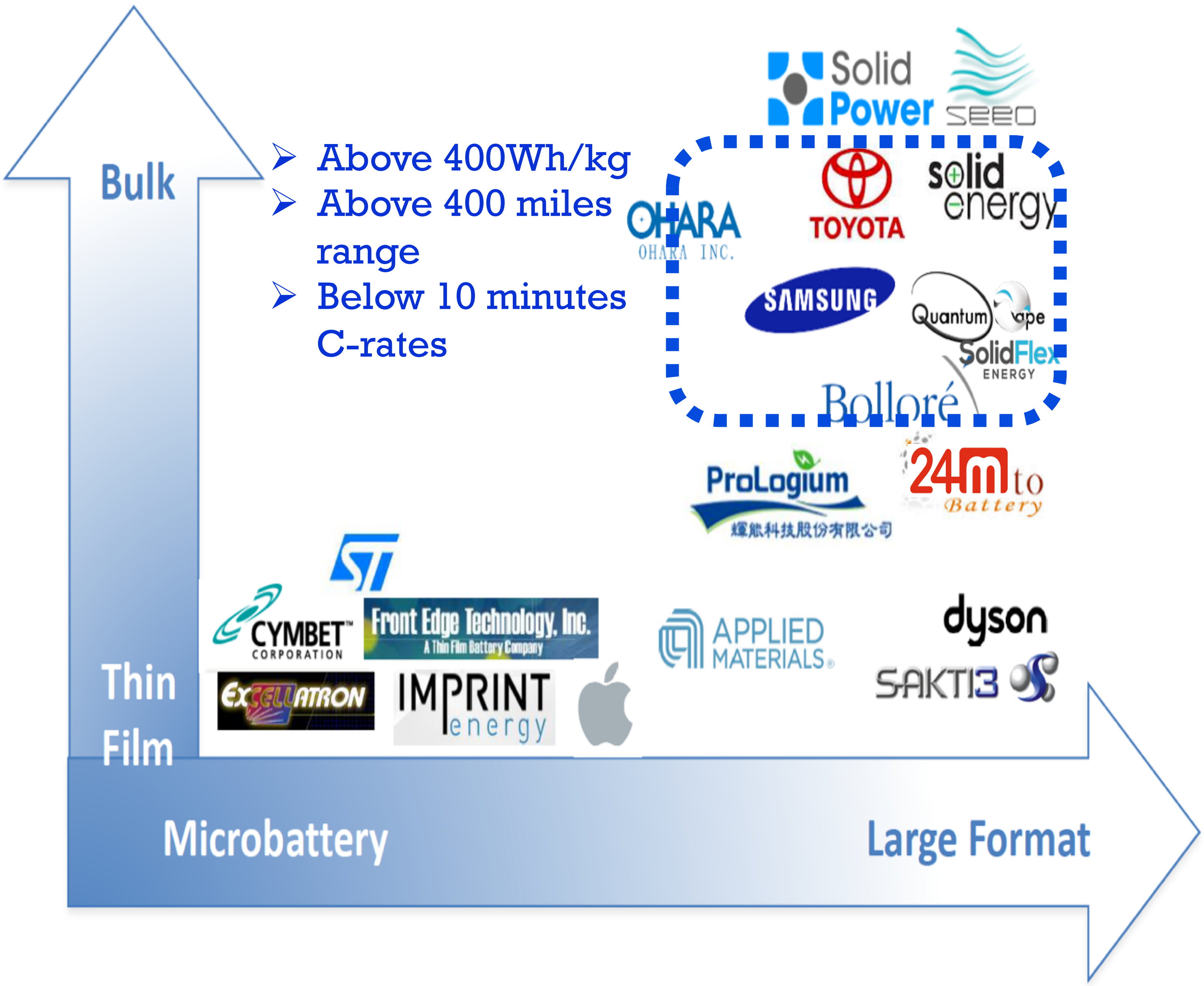
Nothing fulfills all of these requirements to date!

Where do we stand presently?



Solid State Battery Companies

- Above 400Wh/kg
- Above 400 miles range
- Below 10 minutes C-rates



Li/polymer batteries-Bolloré Bluecar

Bolloré Bluecar

3 door city car
Range≈90-160 miles per charge
Li/PEO-type/$LiFePO_4$ battery
Battery must be heated to work
(poor conductivity of electrolyte)
Low cell V (~3.5V) due to LFP electrode
(Poor oxidative stability of the polymer)

Battery	
Volume (L)	300
Weight (kg)	300
Specific Energy	100 Wh/kg
Energy Density	100 Wh/L
Electrical Specifications	
Energy	30 KWh
Peak Power	45 kW (30s)
Peak Power Density	150 W/L
Nominal Voltage	410V
Thermal Characteristics	
Internal Temp.	60-80°C
Ambient Temp.	-20°C-160°C

Thin-film batteries (Infinite Power Solutions)

LiPON electrolyte
Conductivity ~10^{-6} S/cm
Requires vacuum processing
Too expensive for EVs

THINERGY
Solid-State, Rechargeable, Micro-Energy Cells (MECs)

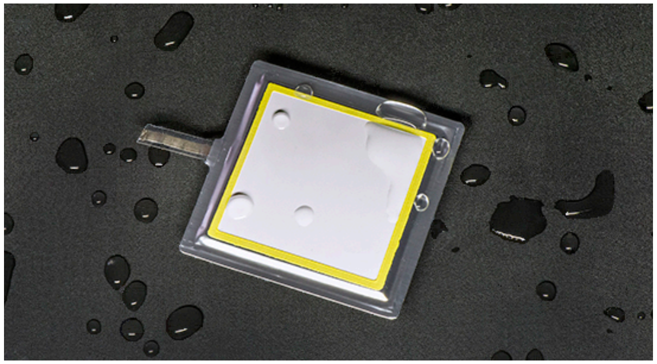
	Units	MEC225	MEC220	MEC201	MEC202
Open Circuit Voltage (OCV)	V	4.1	4.1	4.1	4.1
Package Size/Footprint [1]	in. mm	0.5 x 0.5 12.7 x 12.7	1.0 x 0.5 25.4 x 12.7	1.0 x 1.0 25.4 x 25.4	1.0 x 2.0 25.4 x 50.8
Package Thickness	in. mm	0.007 0.17	0.007 0.17	0.007 0.17	0.007 0.17
Typical Internal Resistance	Ω	260	120	45	20
Maximum Continuous Current	mA	7	15	40	90
Nominal Capacity Options	mAh	0.13	0.3 0.4	0.7 1.0	1.7 2.2
Equivalent Energy in Joules	J	1.8	4 5.5	10 14	24 32
Typical Recharge Time to 90% (at 4.1V CV)	Min.	15	15	15	15
Operating Temperature Range	°C	-40 to +85	-40 to +85	-40 to +85	-40 to +85
Operating/Shelf Life	Years	>15	>15	>15	>15
Recharge Cycles [2]		100,000	100,000	100,000	100,000
Typical Charge Loss/Year		2%	2%	2%	2%
Supersedes [3]		MEC125	MEC120	MEC101	MEC102

All performance metrics measured at 25ºC. See product data sheets for more details.
[1] Does not include connection tabs. Total dimensions of supported tab area is 11.2mm x 2.5mm along one edge of device.
[2] Under typical application usage modes.
[3] MEC200 Series devices require a different PCB pad layout design than MEC100 Series (Not a direct replacement).
Updated 6/26/2012 | DS1016 v.1.6

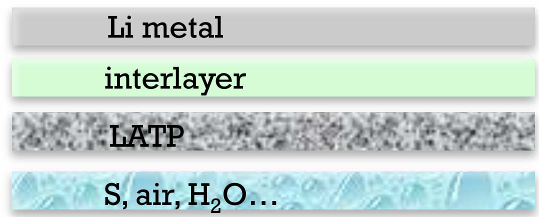
Small form factors (mAh)
Low E.D (~35 Wh/L)-thin + Thick substrates
Excellent cycling

Suitable for small applications (sensors, RFID, etc.

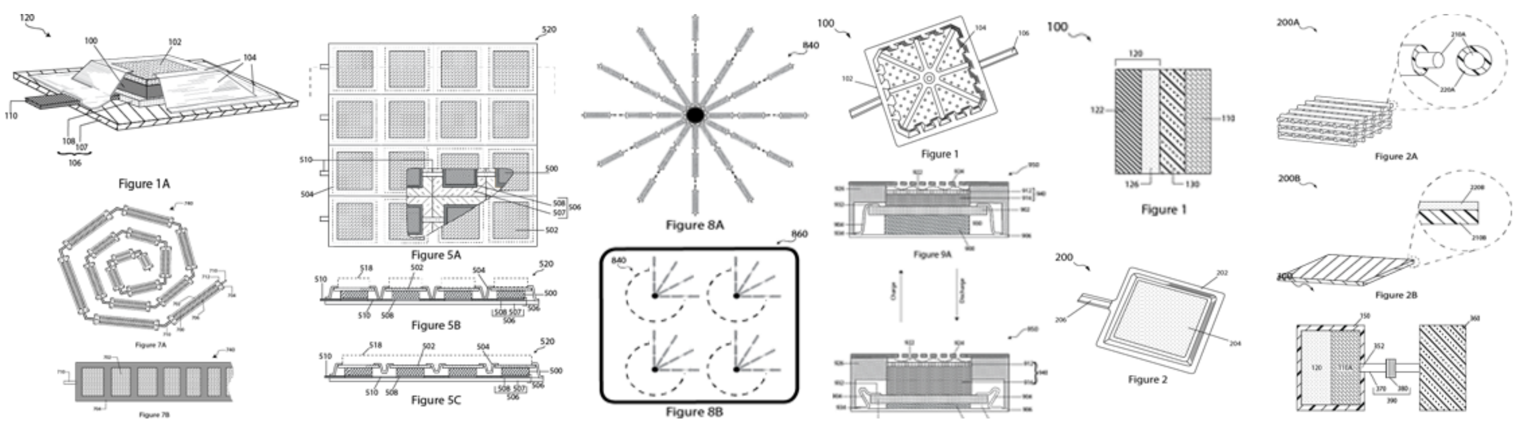
Hybrid Batteries-PolyPlus Battery Company



Protected Lithium Electrode



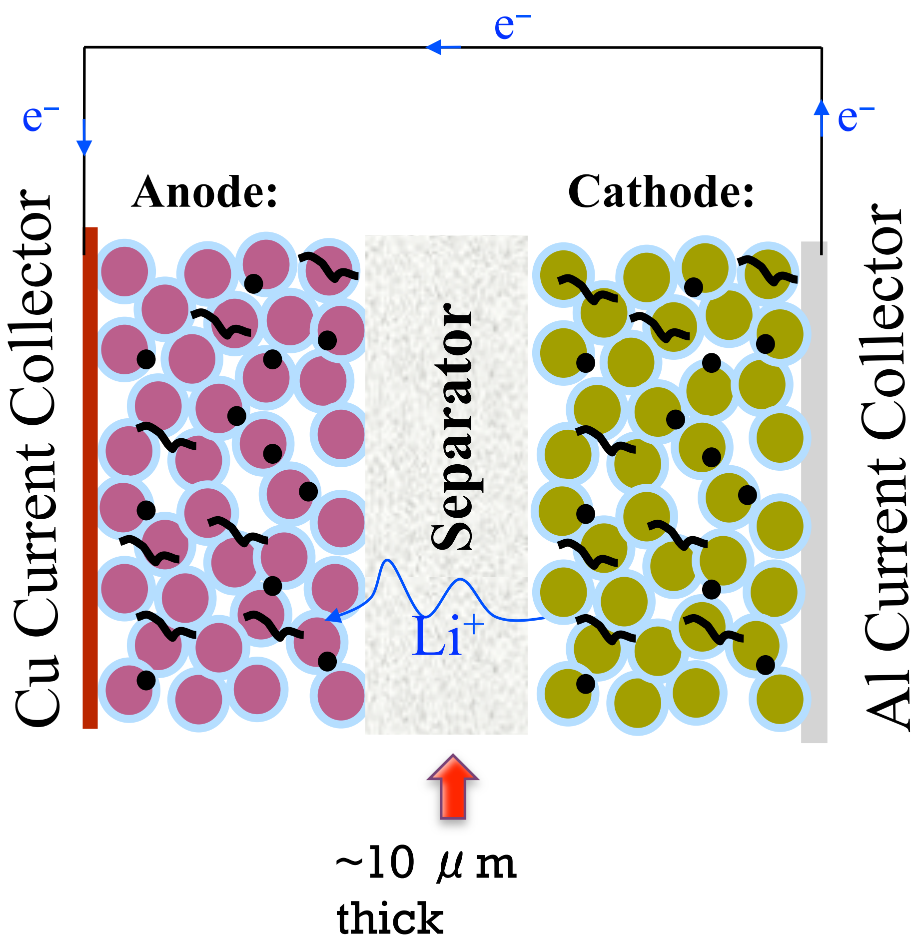
Projected E.D. of aqueous Li/S battery 600 Wh/L, 400 Wh/kg
LATP reduced by Li, requires interlayer
New ARPA-E project using glass electrolytes



ARPA-E Ionics Awards-Summer 2016

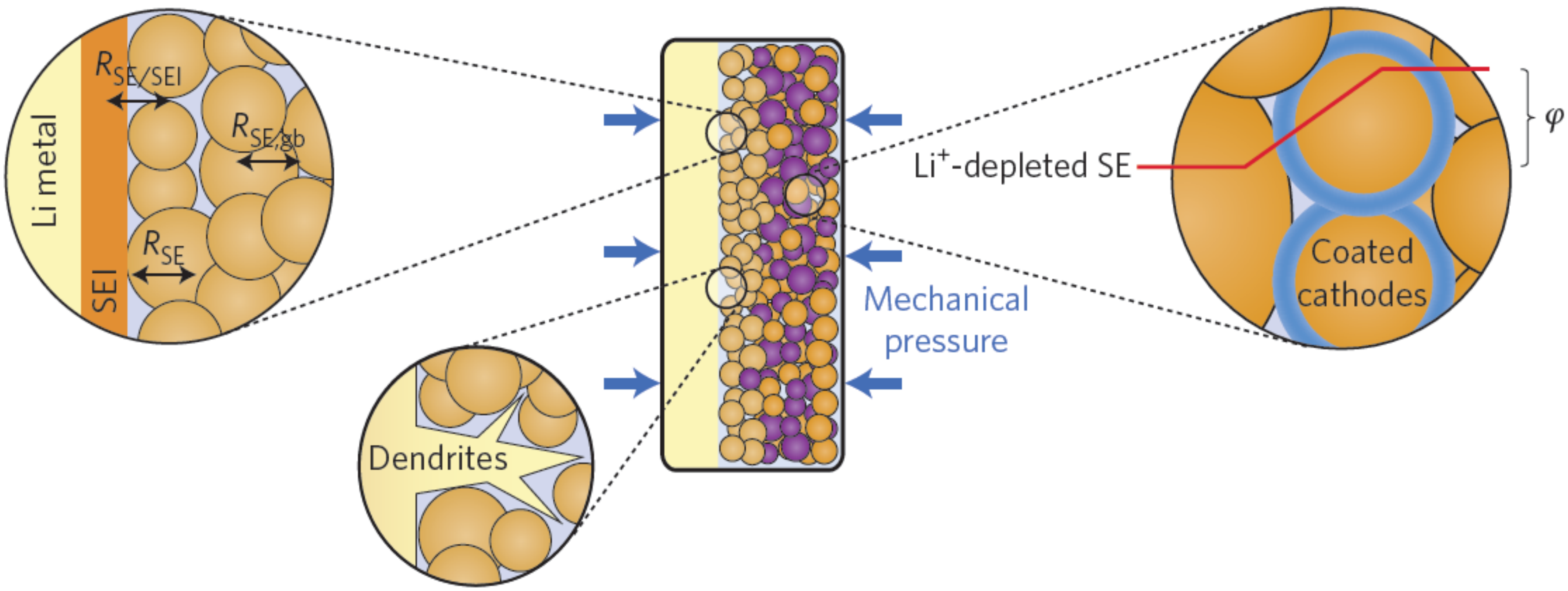
- 24M-Cambridge, MA "Large Area Lithium Electrode Sub-Assemblies (LESAs) Protected by Self-Forming Microstructured Polymer-Inorganic Single-Ion Conducting Composites
- Ionic Materials-Woburn, MA "Novel Polymer Electrolyte for Solid State Lithium Metal Battery Technology"
- Iowa State University-Ames, Iowa "Development and Testing of New, High-Li^+ Ion Conductivity Glassy Solid Electrolytes for Lithium Metal Batteries"
- Oak Ridge National Laboratory, Oak Ridge, TN "Metastable and Glassy Ionic Conductors (MAGIC)"
- Pennsylvania State University-University Park, PA "Cold Sintering Composite Structures for Solid Lithium Ion Conductors"
- PolyPlus Battery Company-Berkeley CA "Flexible Solid Electrolyte Protected Li Metal Electrodes"
- Sila Nanotechnologies-Alameda, CA "Melt-Infiltration Solid Electrolyte Technology for Solid State Lithium Batteries"
- University of Colorado Boulder-Boulder, CO "Flash Sintering System for Manufacturing Ion-Conducting Solids"

What do we need-Lessons from a Typical Li-ion Cell



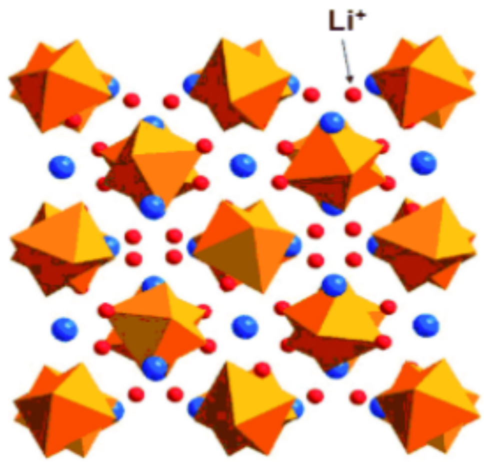
- Electrodes are porous composites (active material+binder+ optional conductive additives).
- Typical porosity (filled with electrolyte solution) ~ 25 vol.%.
- Typical thicknesses (depends on cell design) 20-100 μm.
- For energy-thicker electrodes, for power-thinner electrodes
- Composites are needed to offset low conductivities of active materials
- Separators are very thin and are wet with a few μL/cm^2 of solution

Solid State Battery Cell Design considerations and challenges

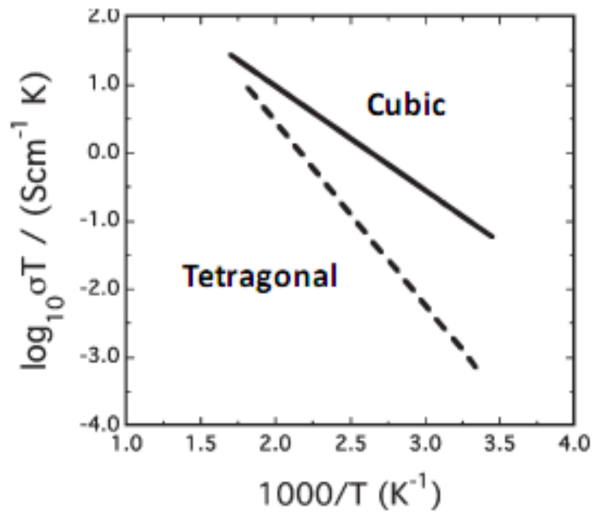


Janek and Zeier, *Nature Energy*, article 16141, 1, (2016).

$Li_7La_3Zr_2O_{12}$ 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.

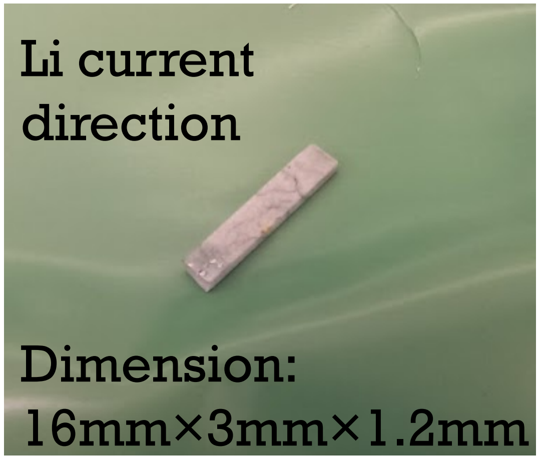
Pros:

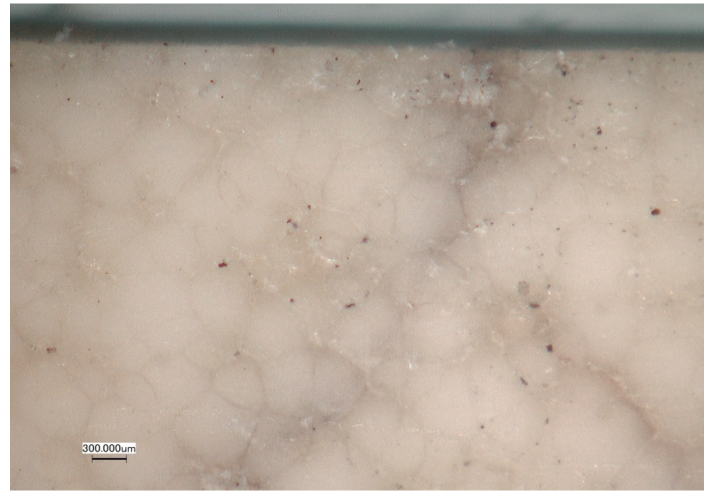
- High lithium ionic conductivity for cubic phase (>10^{-4} S/cm at R.T.)
- No reaction observed when contacted directly with molten lithium
- Oxides should be easier to work with than sulfides

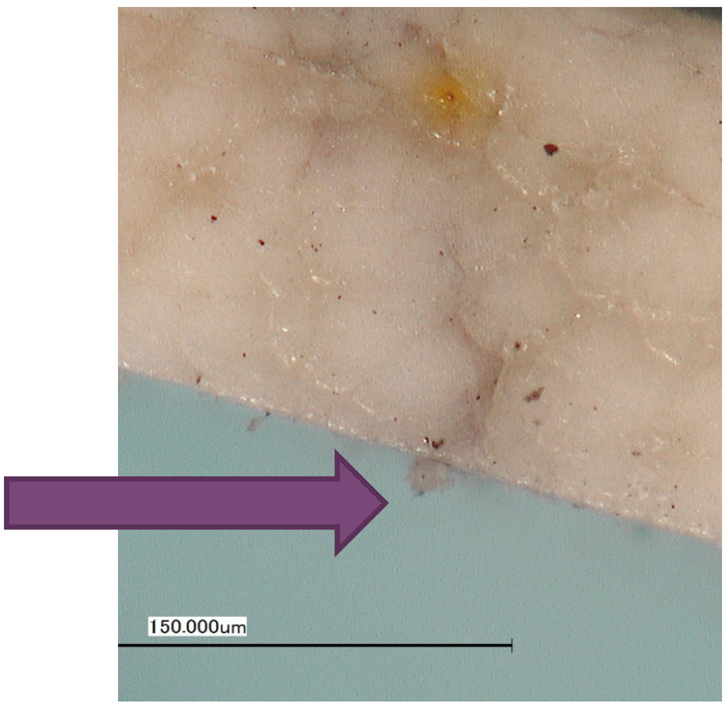
Cons:

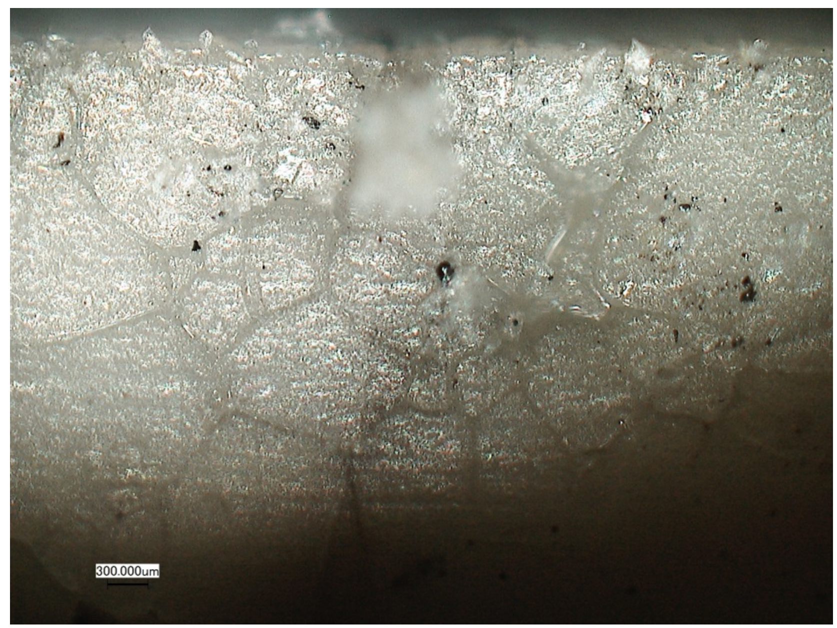
- Difficult to densify
- Reactivity with substrates, moisture, ambient atmosphere
- High interfacial impedances
- Thin films required: for 5 mA/cm^2, voltage drop < 100 mV, needs to be < 200 μm (assuming no contribution from interfacial impedances!)

Optical Evidence of Dendrite Formation via Grain Boundaries



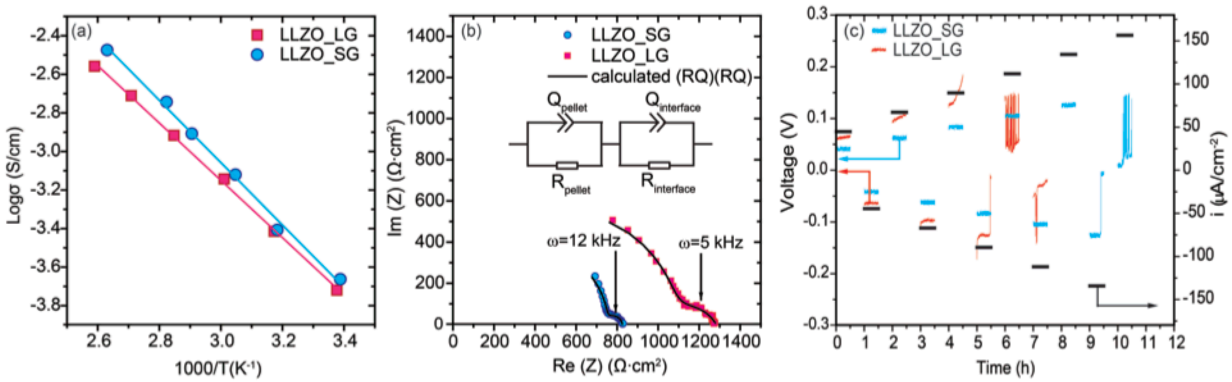


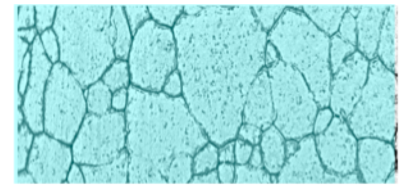




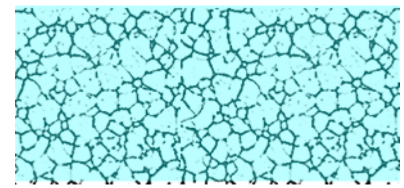
Microstructural Engineering to Improve Resistance to Dendrites

Li/LLZO/Li cells





Large grains (~200 μm)



Small grains (~20 μm)

sample	Total Conductivity	Bulk Resistance	Interfacial Resistance	Area specific interfacial resistance
LLZO_LG	2.0×10^{-4}S/cm	2335 Ω	566 Ω	127 Ω·cm²
LLZO_SG	2.5×10^{-4}S/cm	1672 Ω	161 Ω	37 Ω·cm²

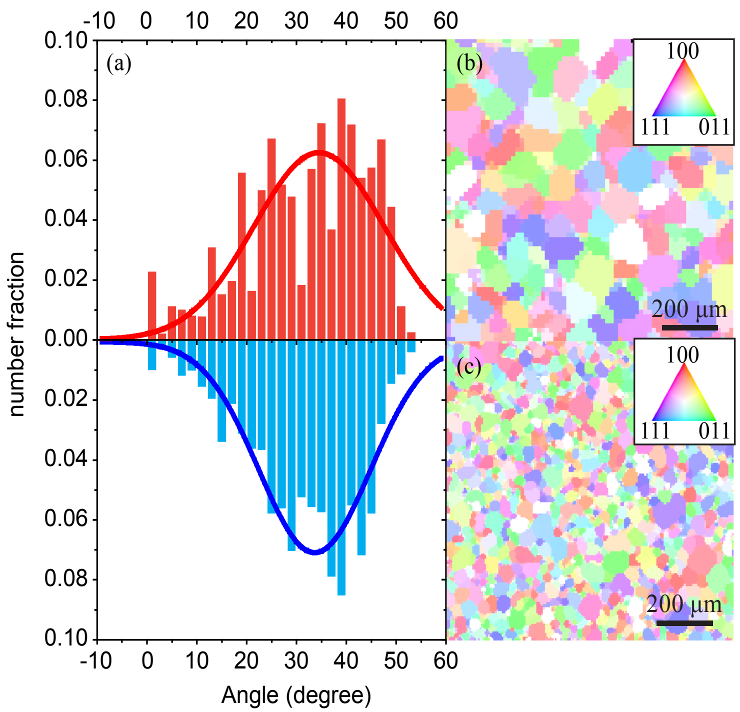
Lowest ASI
ever reported for LLZO!

Why does the small-grained sample have higher conductivity, lower interfacial resistance, and a higher critical current density?

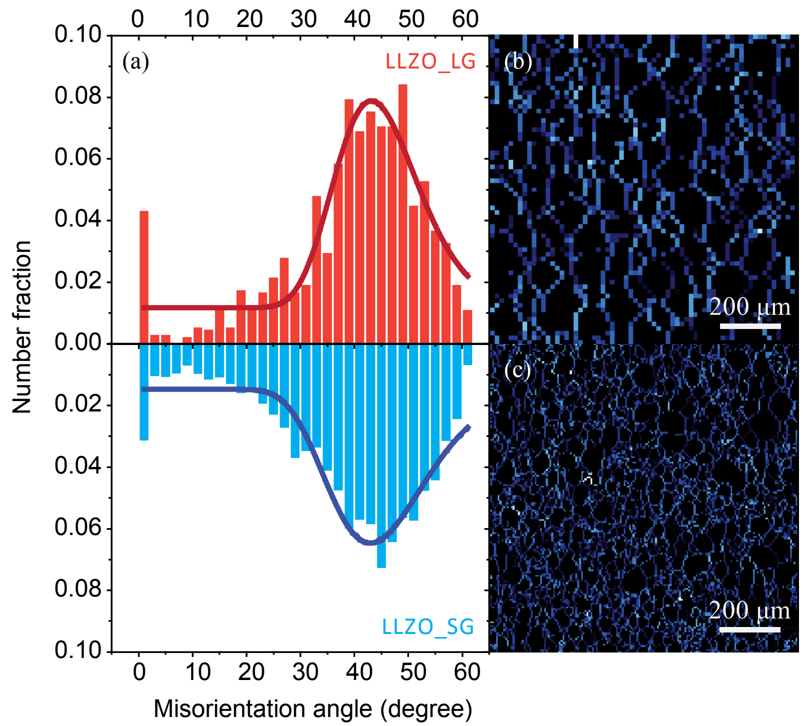
Cheng et al., *ACS Applied Mater. & Interfaces* 7, 2073 (2015).

Grain Orientation Mapping

High-resolution Synchrotron Polychromatic X-ray Laue Microdiffraction.



Grain orientation mapping



Misorientation angle mapping

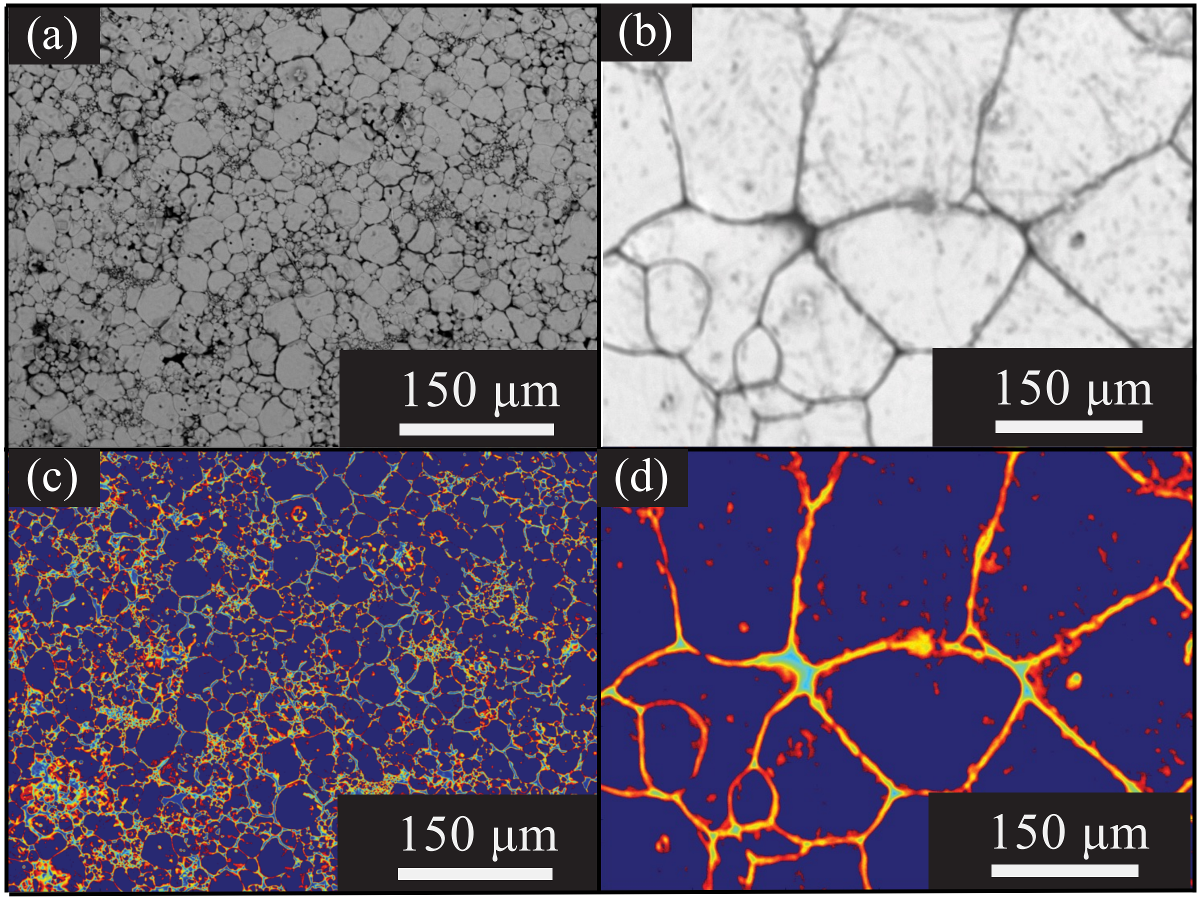
- No differences in grain orientation or misorientations between samples➔Differences have to do with grain boundaries

ALS BL 12.3.2

Visualization of Grain Boundaries

Small grains

Large grains

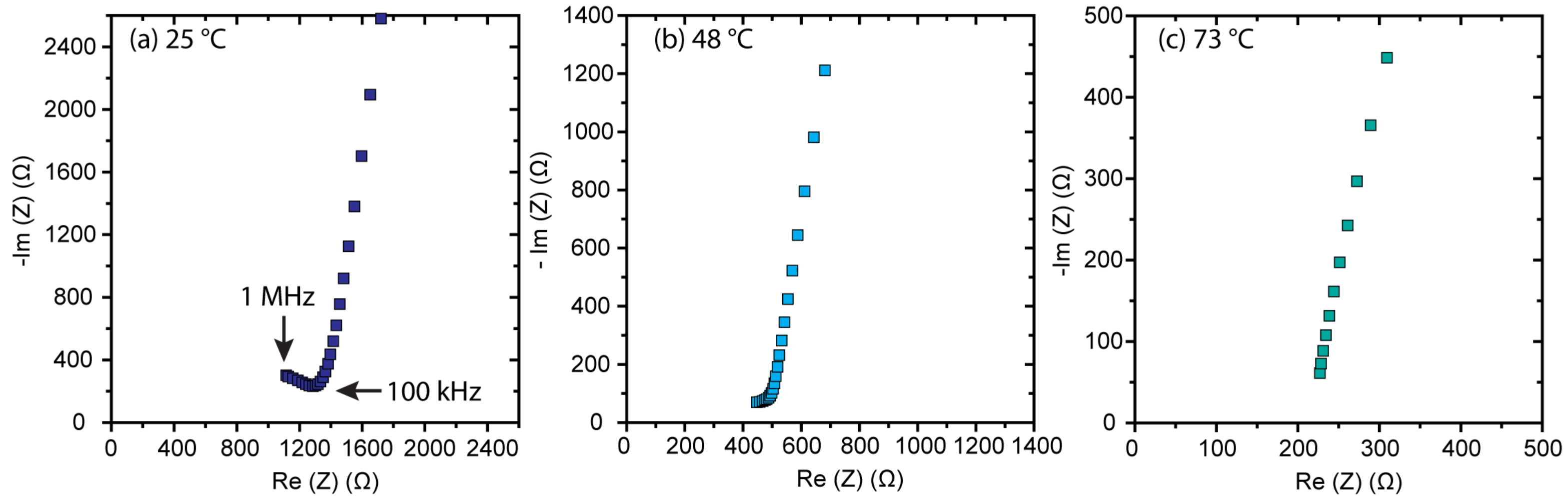


32%

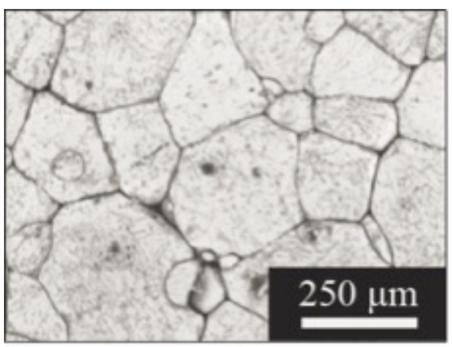
16%

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

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.

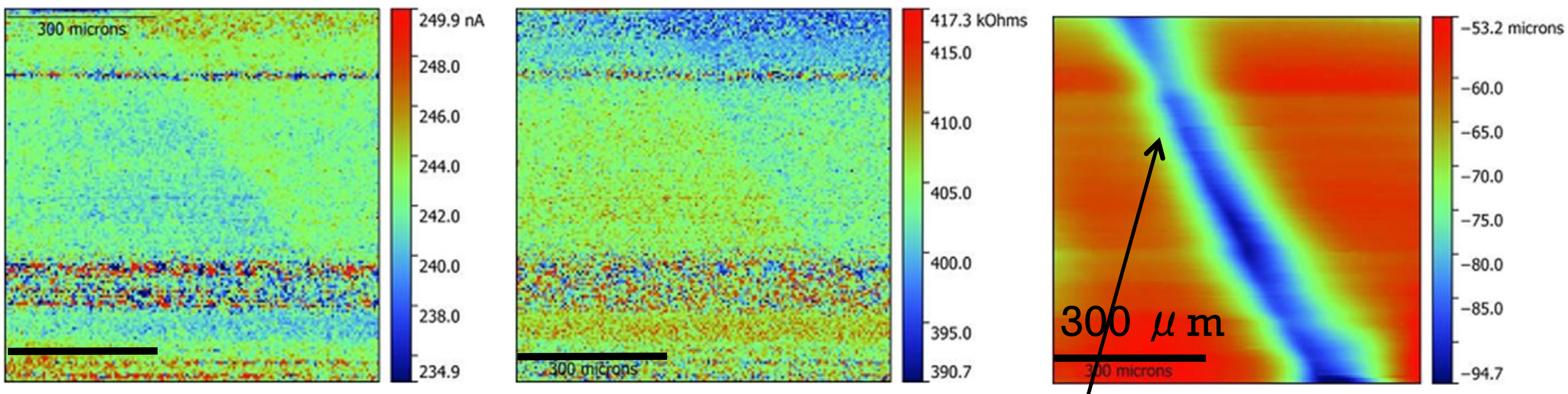
ic-ac-Scanning Electrochemical Microscopy

- 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!)

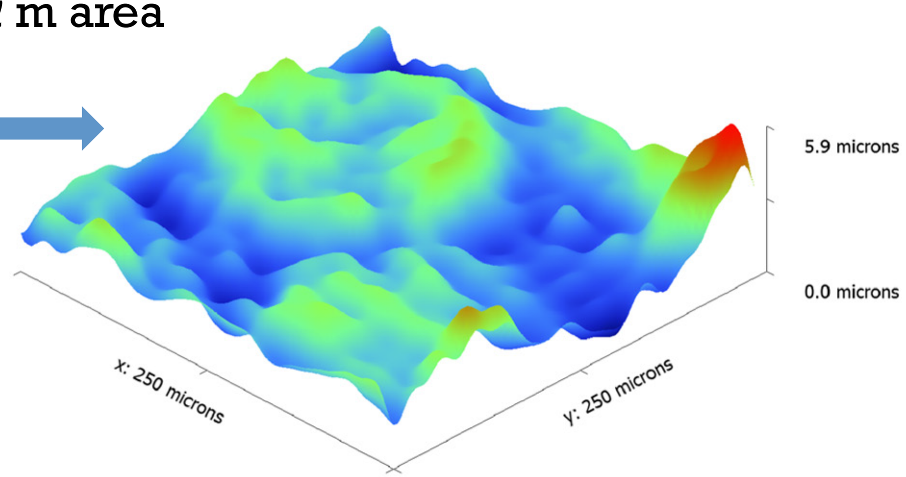
10 μm Pt probe can easily distinguish features ~100 μm across and <50 μm deep.

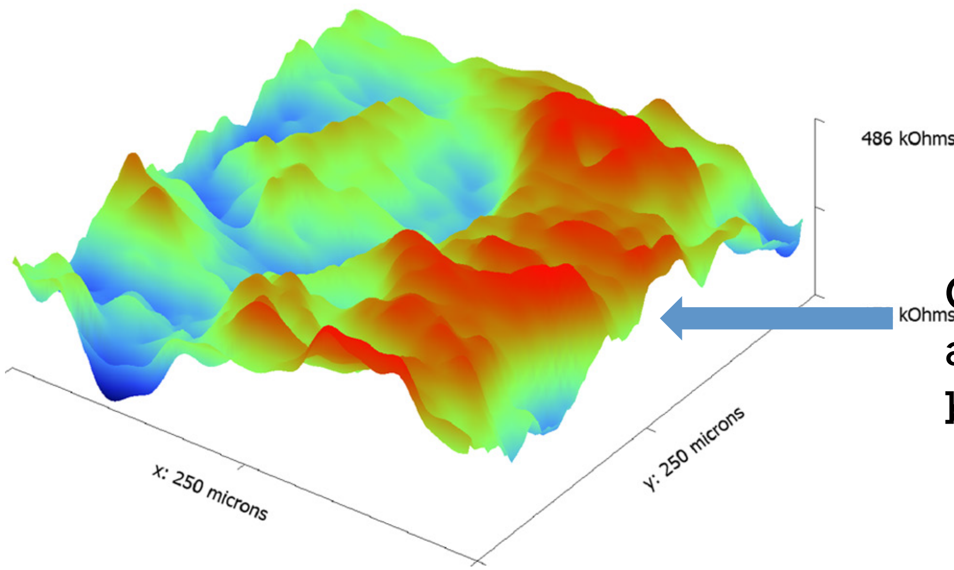
Catarelli et al. **Frontiers in Energy Research**, DOI: 10.3389/fenrg.2016.00014 (2016).

Zeroing in on a LLZO Grain

250 μm x 250 μm area

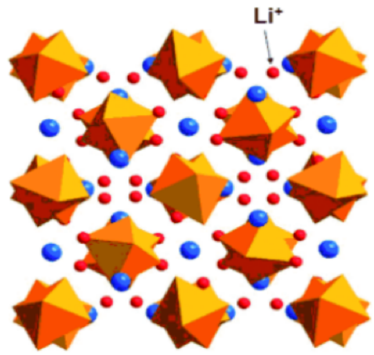
A raised grain





Grain boundaries are less conductive, but vary!

Thank you!



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