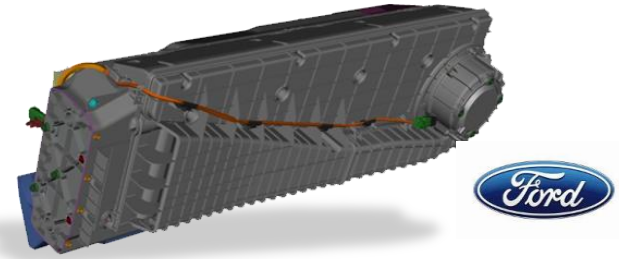
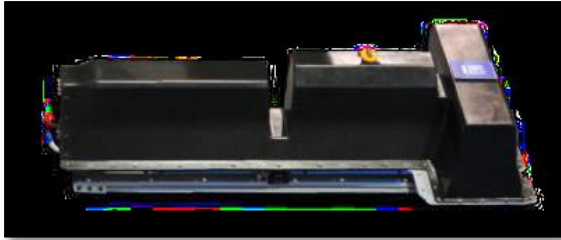


Keeping up with the increasing demands for electrochemical energy storage



Jeff Sakamoto

2015

Top of the learning curve: optimize current technology

2020

Frontiers of Li-ion technology: new materials

2030

Frontiers of energy storage: beyond Li-ion technology



Quantifying the demand for energy storage

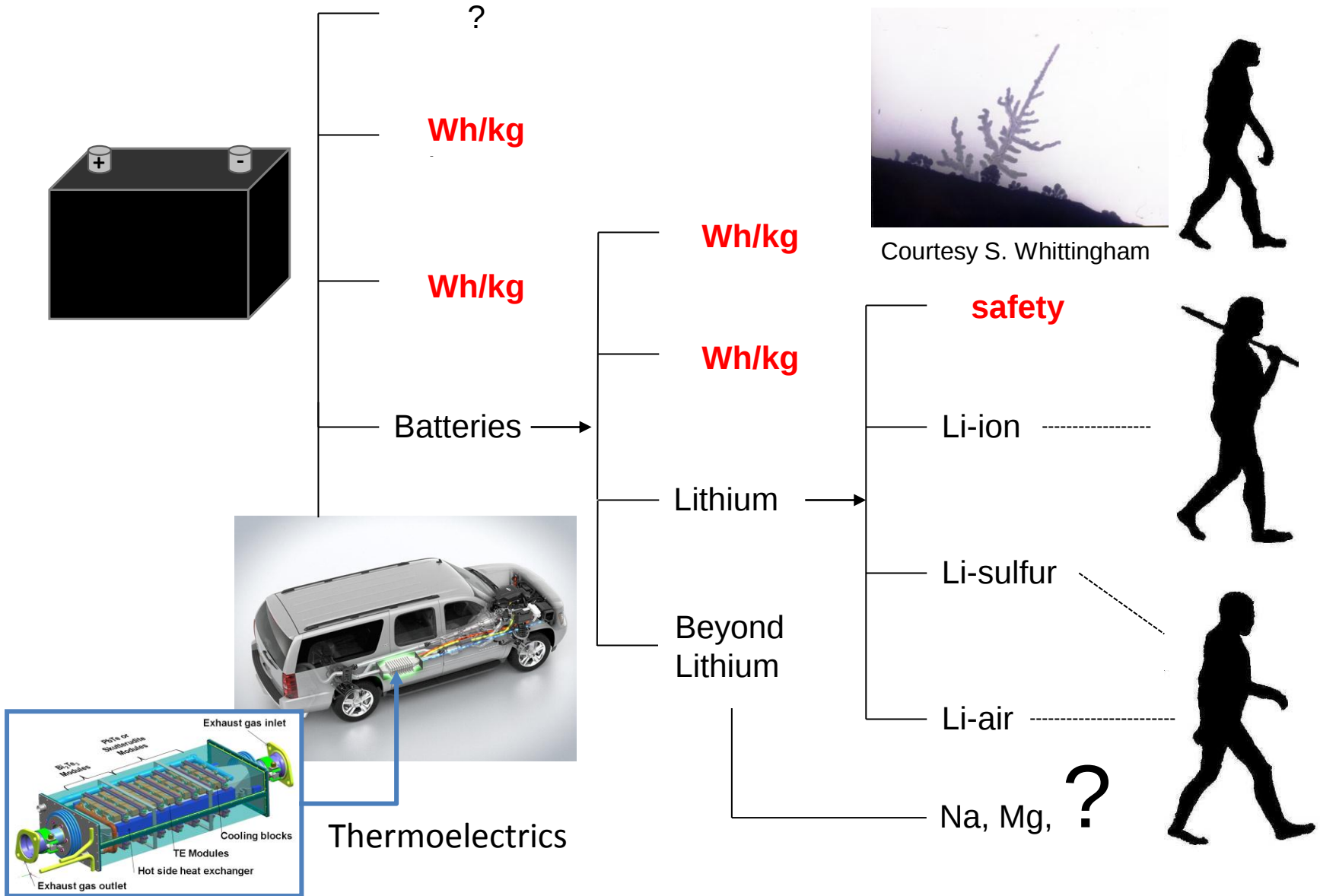
Power: Watts = current·voltage

Energy: Watts·time = Watt·hours

Specific Energy: Wh/kg

Energy Density: Wh/liter

Current and future energy storage tech



Is there enough lithium?

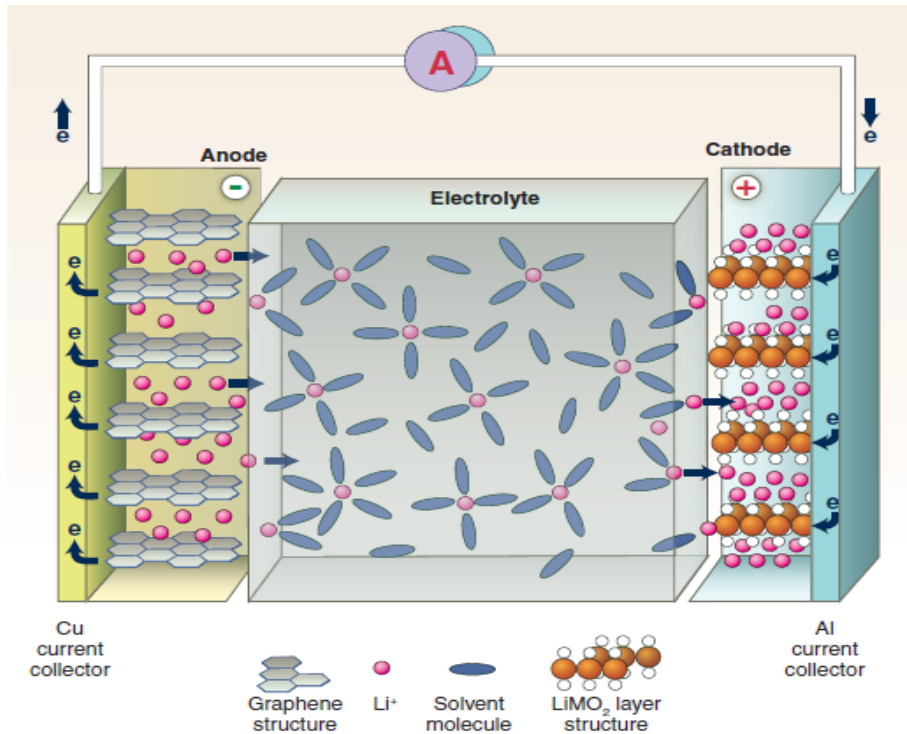


Enough Li for:

- 10^{12} HEV
- 10^{11} PHEV
- 10^{11} BEV

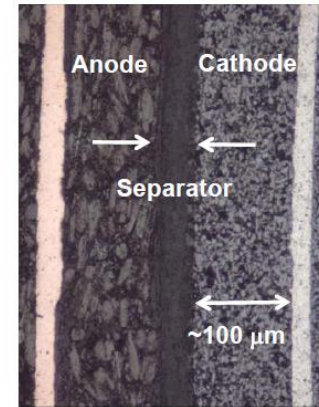
Courtesy of Ted Miller

Current Li-ion: Nuts & Bolts

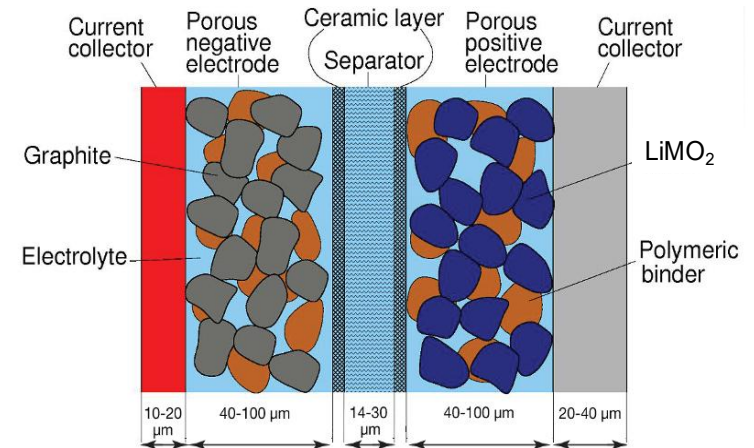


Dunn, B., Kamath, H. and Tarascon, J.-M. 2011. Science 334: 928-935.

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

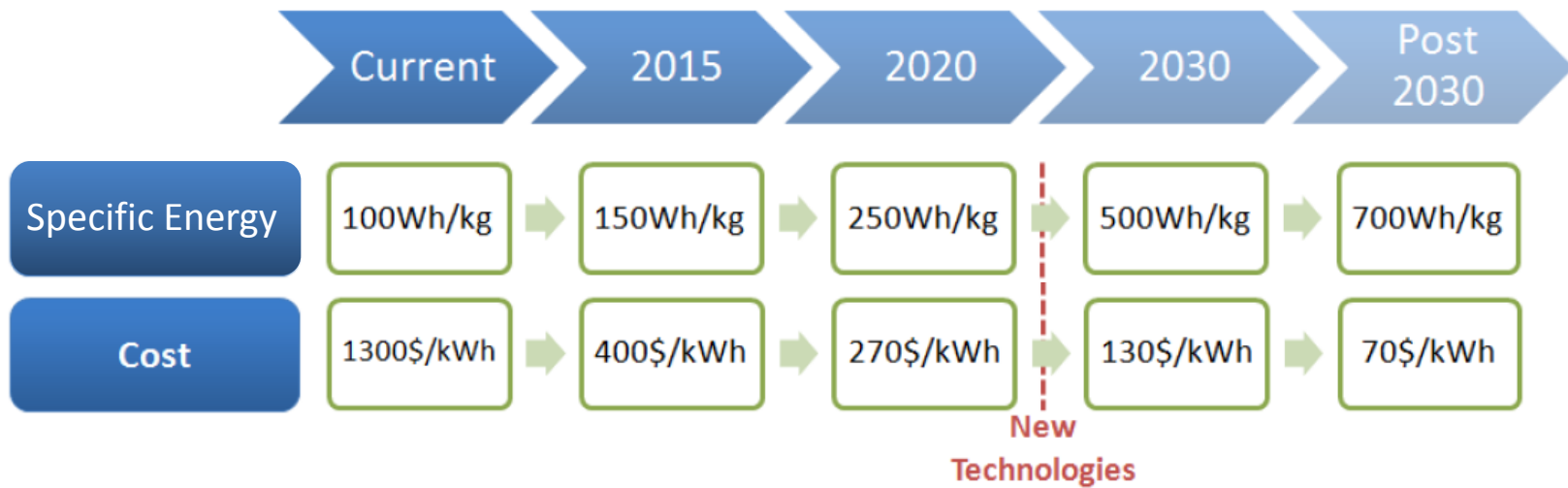


Typical Thickness of Li-ion cell components



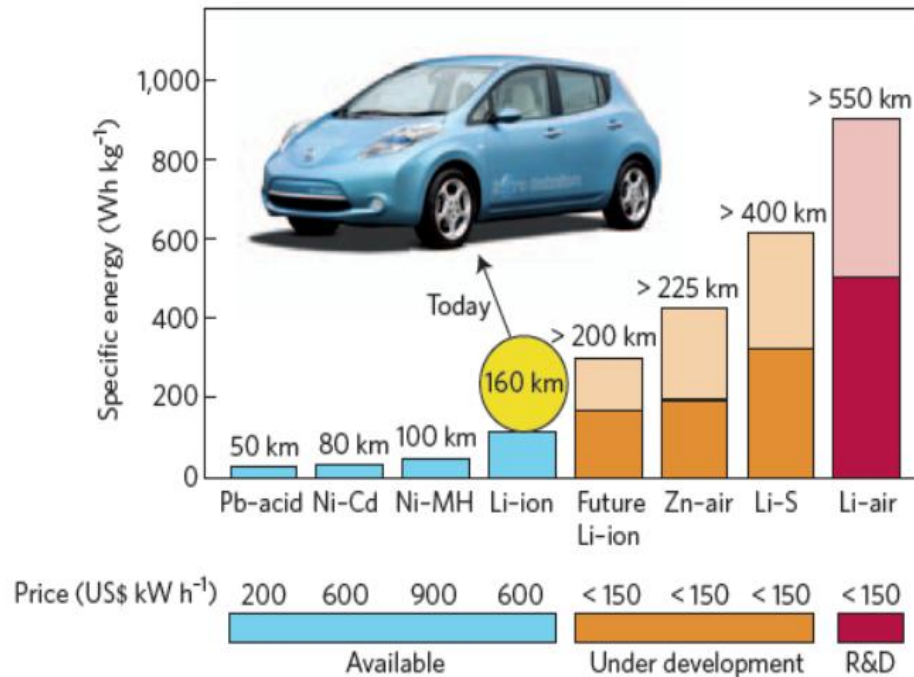
Ponticel, P, 2012,, Society of Automotive Engineers:
Vehicle Electrification: 6-28.

Frontiers of Electrochemical Energy Storage

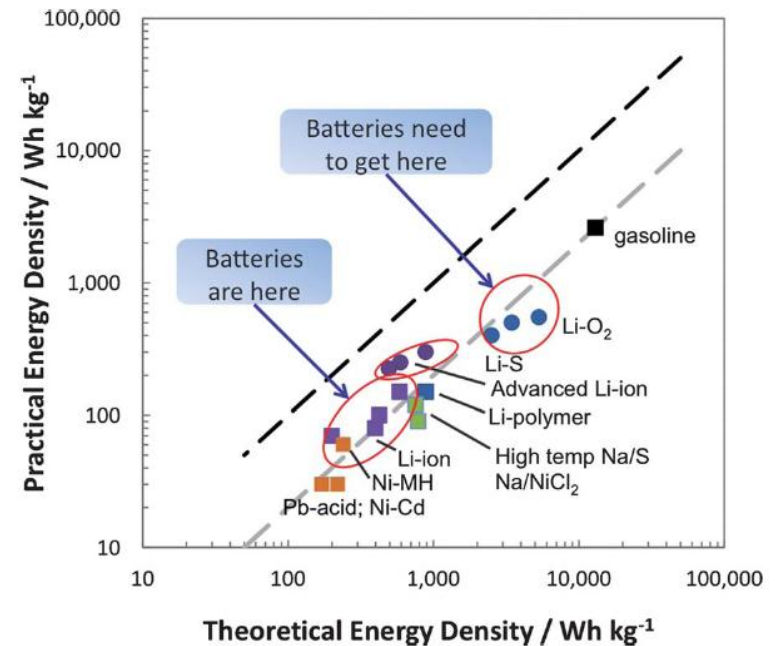


Climate Change Committee (2012) Final Report prepared by Element Energy Limited, Cambridge, UK .

Frontiers of Electrochemical Energy Storage

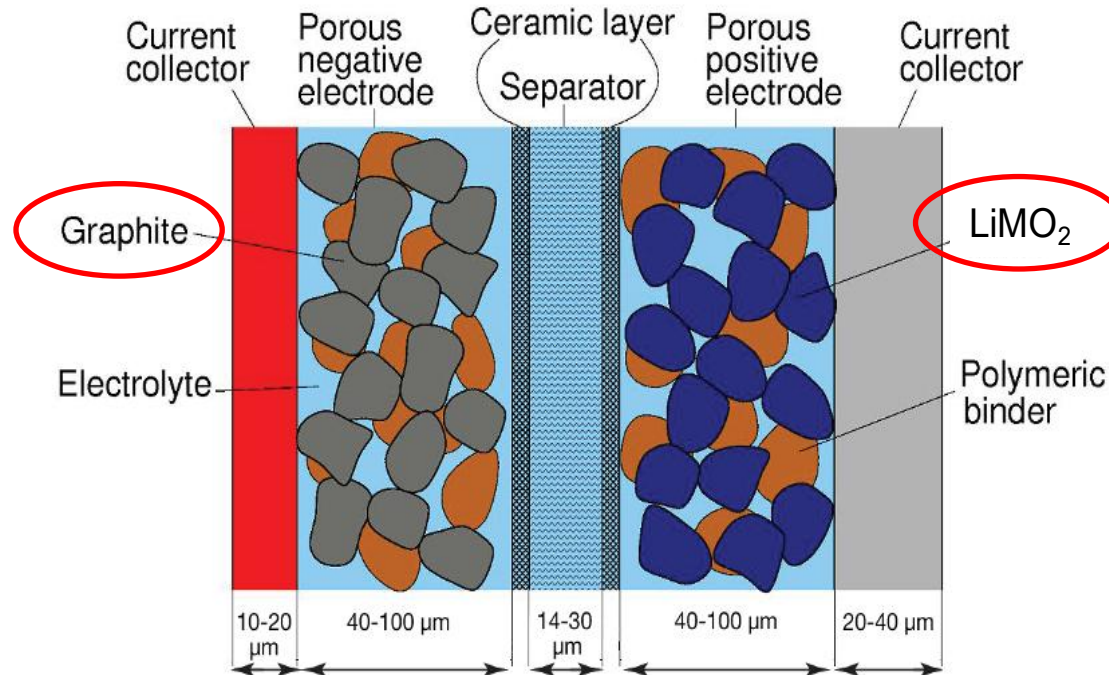


Bruce, P. G., Freunberger, S. A., Hardwick, L. J. and Tarascon, J.-M. 2012. Nature Materials 11: 19-29.



Thackeray, M., M., Wolverton, C. and Isaacs, E. D. 2012. Energy and Environmental Science 5: 7854-7863.

Typical Thickness of Li-ion cell components



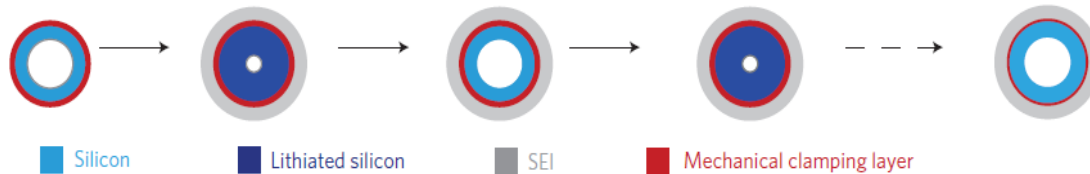
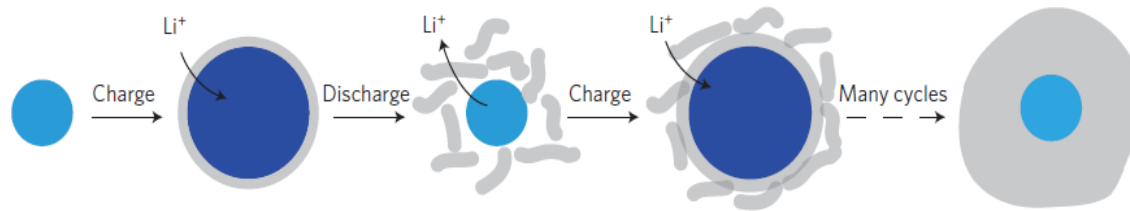
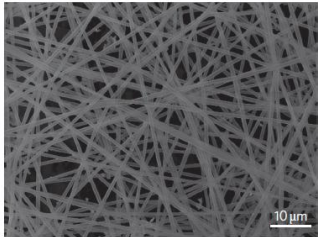
Ponticel. P, 2012. Society of Automotive Engineers: Vehicle Electrification: 6-28.

Electrode capacity: how much Li/mass (mAh/g)

Anode: alloy vs. intercalate Li

Graphite anode = ~ 330 mAh/g (theoretical = 372 mAh/g)

Si anode = ~ 1000 mAh/g (theoretical > 4000 mAh/g)



Cui et al. (2012) *Nature nanotechnology letters*.



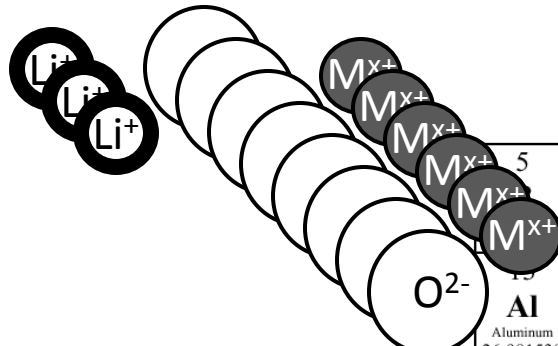
Gorilla Glass®

- +) Si is abundant & cheap
- +) Increase in capacity
- +) Low voltage

- ?) Cycle life; 300% volume change
- ?) Cost of manufacturing nano Si

The Periodic Table of the Elements

1 H Hydrogen 1.00794																	2 He Helium 4.003																	
3 Li Lithium 6.941	4 Be Beryllium 9.012182																	10 Ne Neon 20.1797																
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050	13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80									
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29	55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	58 Ce Cerium 140.12	59 Pr Praseodymium 140.90768	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92532	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	<																													



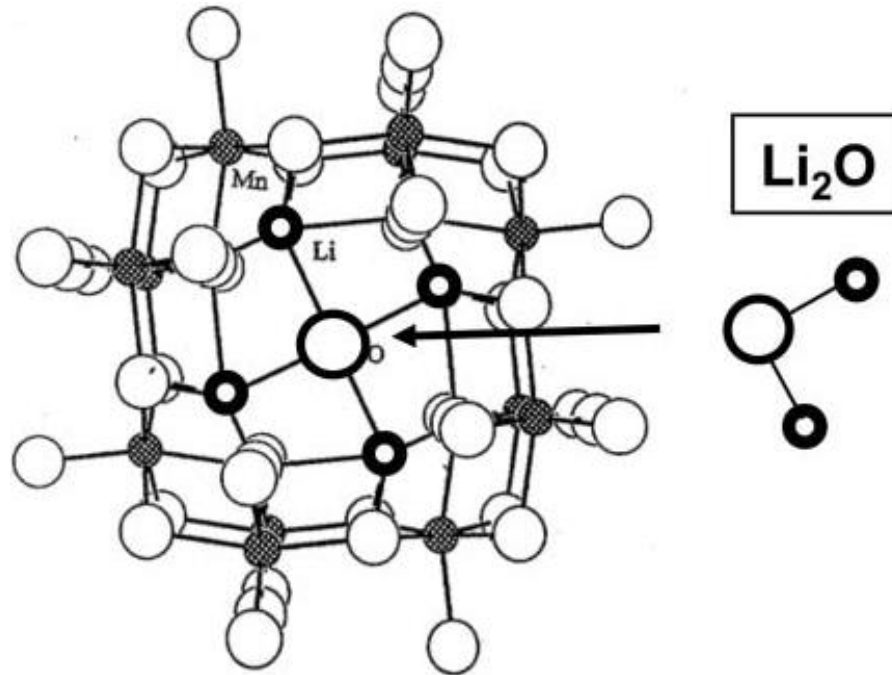
Theoretical

$\text{Li}_1\text{MO}_2 \sim 280 \text{ mAh/g}$

Practical

$\text{Li}_{0.5}\text{MO}_2 \sim 140 \text{ mAh/g}$



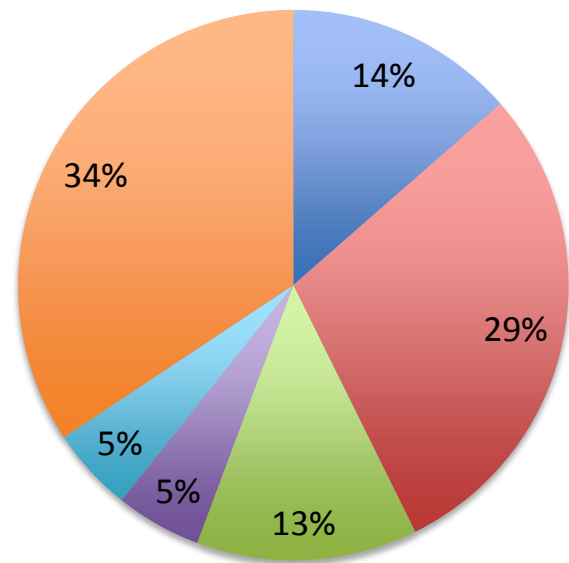


Li₂MnO₃-stabilized Li₁MO₂: ~ 286 mAh/g

Layered cathodes: Thackeray *et al* Argonne National Lab.

+) Doubling of capacity
+) No new elements

?) Slow kinetic/power
?) Crystallographic stability
?) Charged @ > 4.5V: no electrolyte



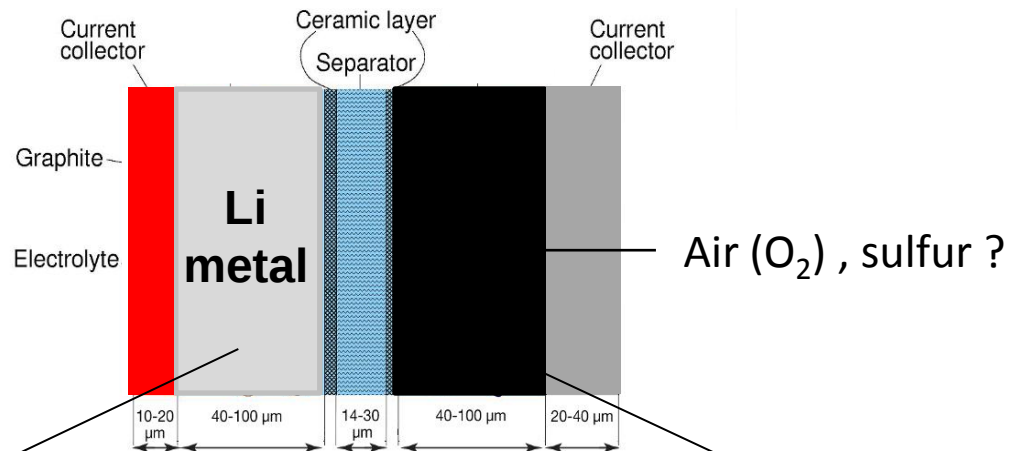
■ Active Anode ■ Active Cathode
■ Inactive Anode ■ Inactive Cathode
■ Separator ■ Housing

Adapted from: Johnson, B.A. & White, R.E.
Journal of Power Sources **70**, 48-54 (1998).

2030

Frontiers of energy storage: beyond Li-ion

(> 400km range, <\$150/kWh)



++ 3375 mAh/g (10X over graphite)

++ Li-Sulfur 2,500 Wh/kg Theoretical

++ Li-O₂ 3,500 Wh/kg Theoretical

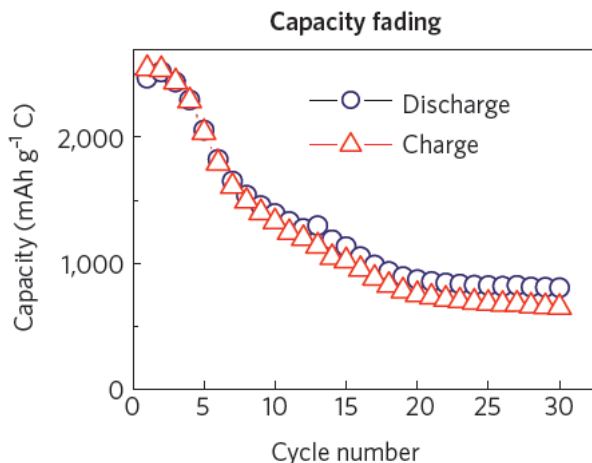
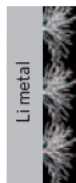
2030

Li-O₂ dry (>500 km range, < \$150 kWh)

Anode

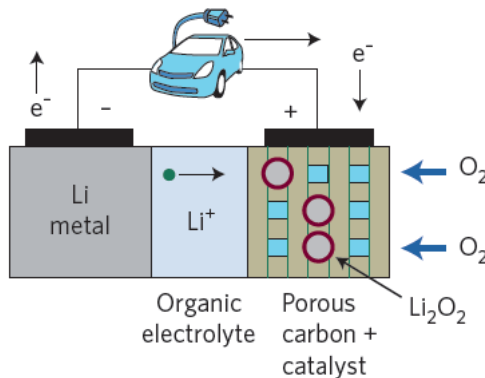
Problems of Li metal

- Dendrite formation
- Cycling efficiency
- Requires stable solid-electrolyte interphase
- Safety issues



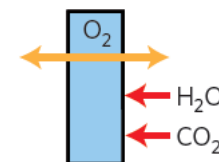
Bruce *et al.* 2012. Nature Materials 11: 19-29.

Discharge



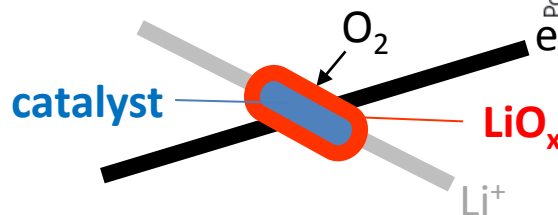
Cathode

Cathode needs a membrane to block CO₂ and H₂O, while allowing O₂ to pass.

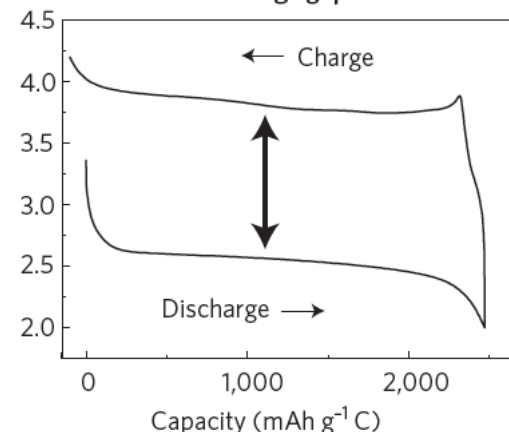


Electrolyte

- Stability
- Conductivity
- Volatility
- O₂ solubility, diffusivity



Voltage gap



Porous cathode design

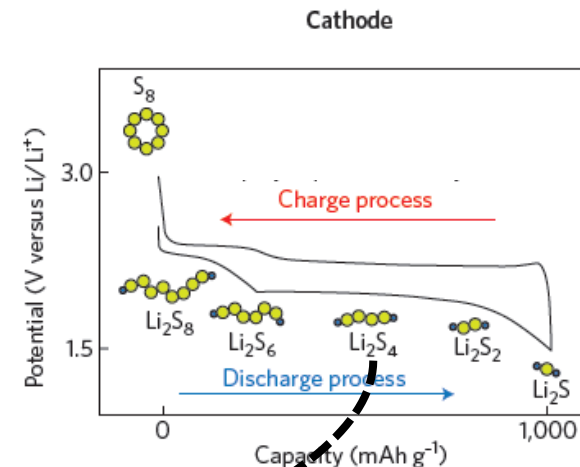
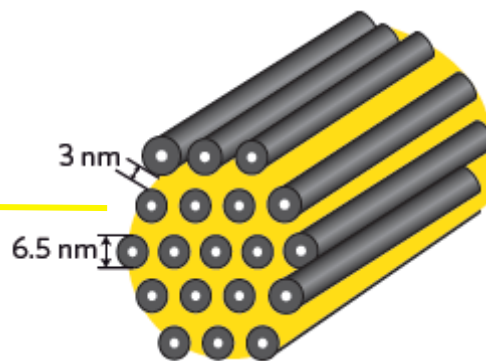
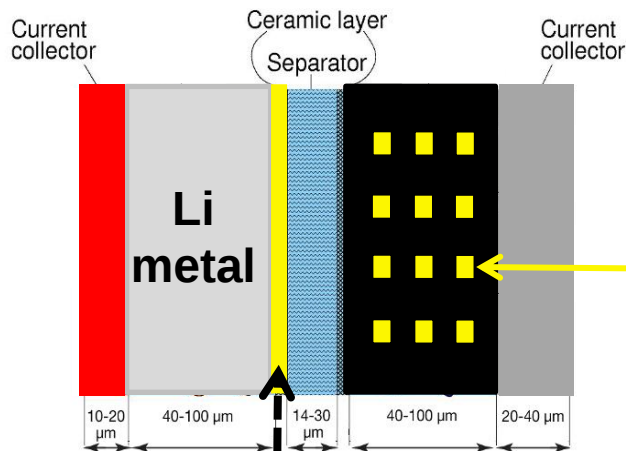
- Pore size, distribution
- Catalyst — type, distribution, loading

+++) High Specific Energy
+) O₂ is ubiquitous

?) Must separate O₂
?) Kinetics/Power/Hysteresis
?) Li metal anode stability

2030

Li-Sulfur (>400 km range, < \$150 kWh)



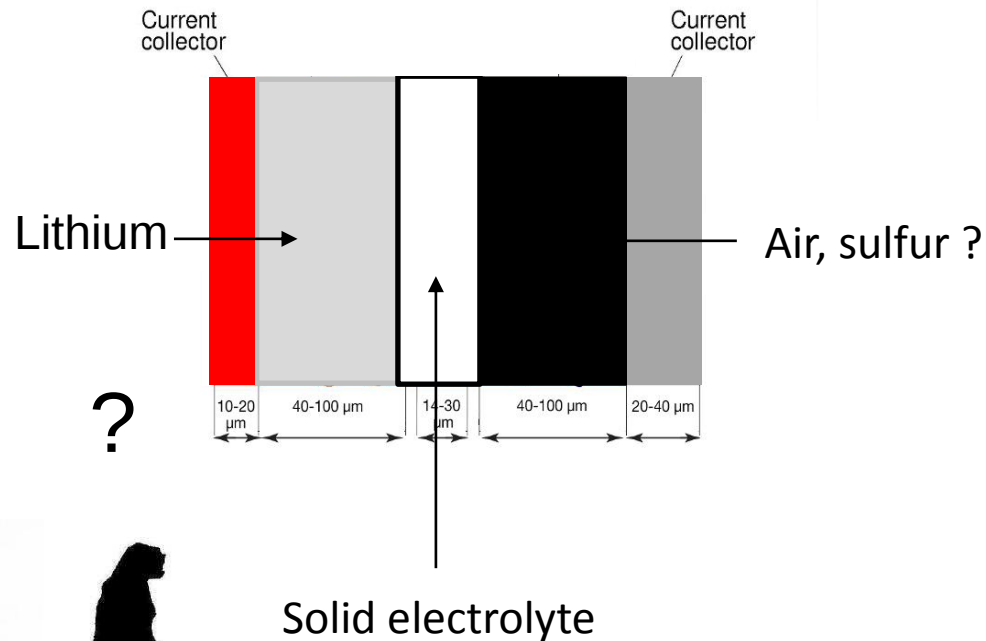
Bruce et al. 2012, Nature Materials 11: 19-29.

Ji, X. and Nazar, L. F. 2010, J. Mater. Chem., 20, 9821-9826.

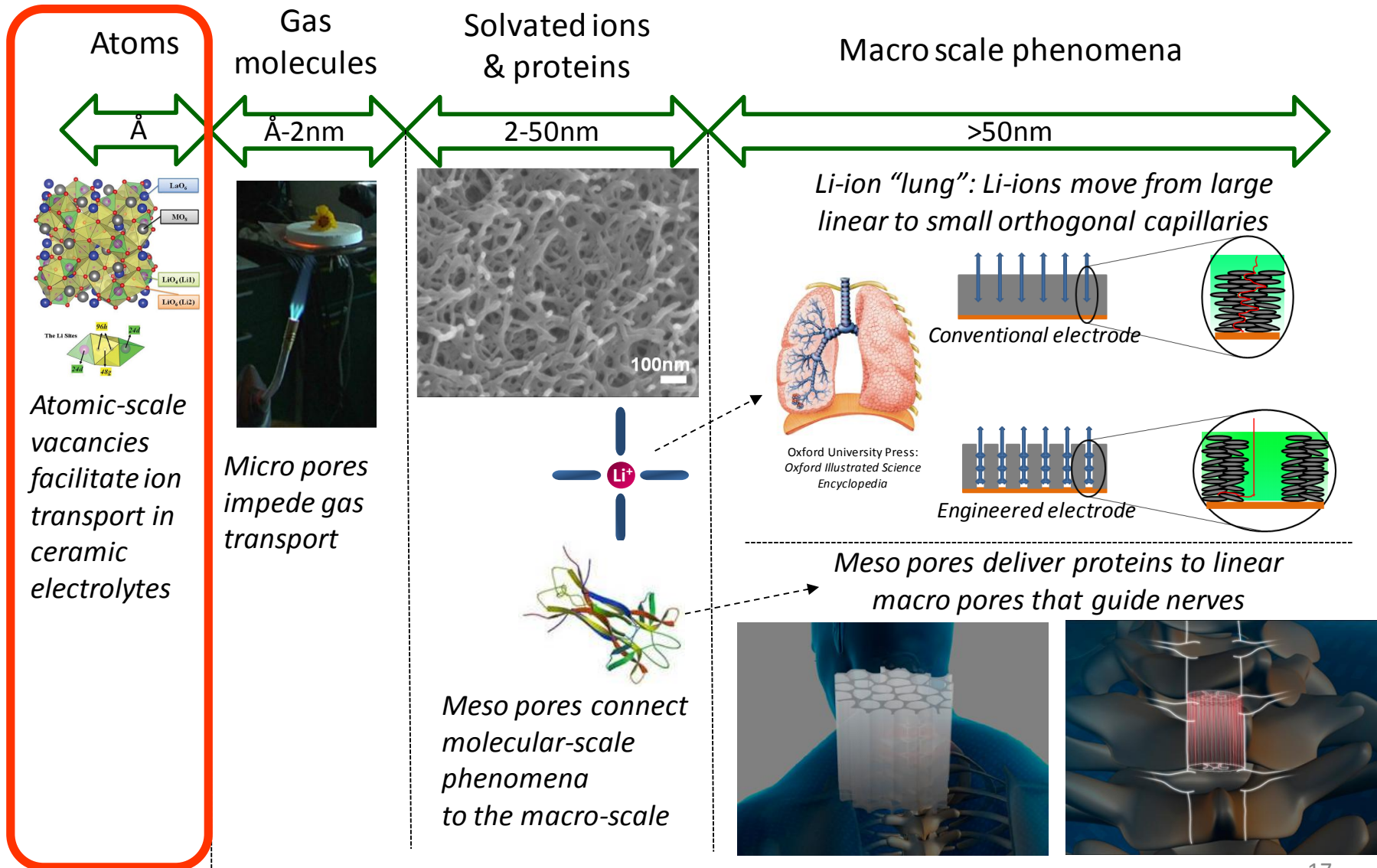
- +) High specific energy
- +) Cheap, abundant
- +) Light
- +) 2 Li for every S (Li_2S)

- ?) cycling
- ?) Sulfur conductivity
- ?) Li metal anode stability

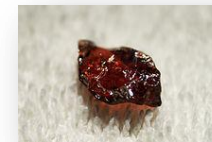
Beyond Li-ion



Sakamoto Group: *Engineering nothing*



Ceramic electrolyte: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet



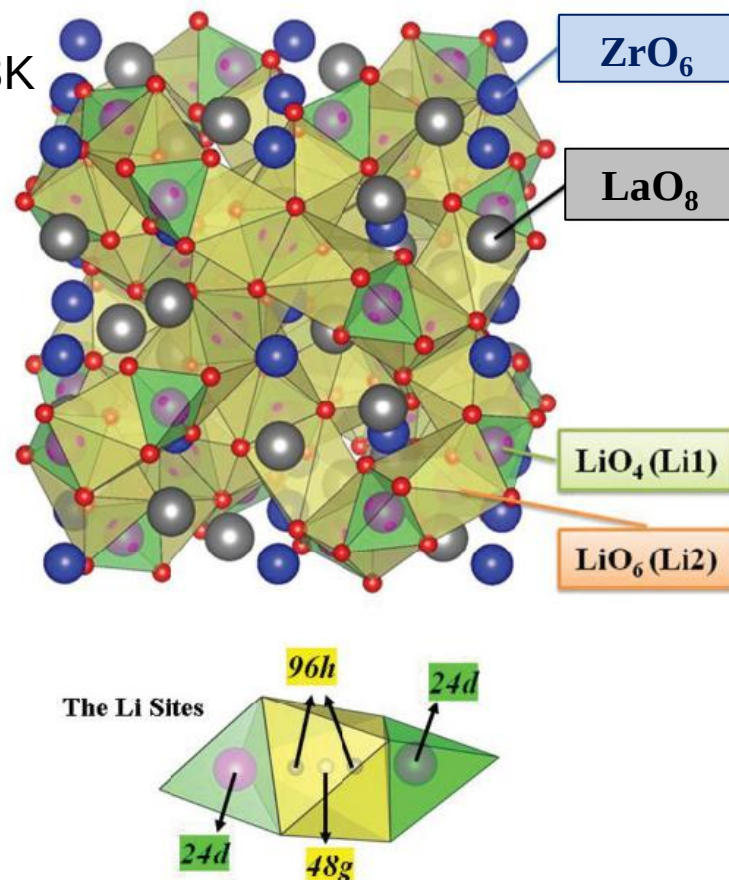
Advantages

- Li Conductivity similar to liquid electrolytes @ 298K
- First bulk, oxide electrolyte stable against Li
- Stable up to 9 V
- Can be synthesized/processed in ambient air

S. Ohta, T. Kobayashi, T. Asaoka, J. Power Sources 196 (2011) 3342.



E. Rangasamy, J. Wolfenstine and J. Sakamoto, *Solid State Ionics*, **206**, 28-32 (2011).

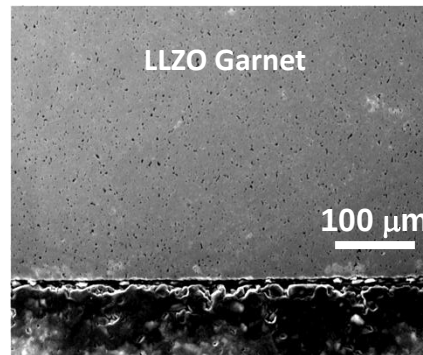
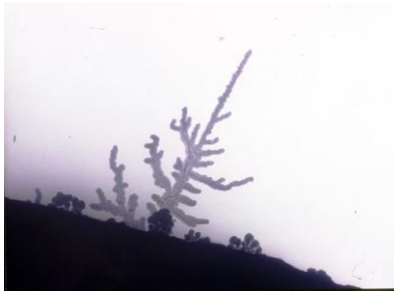


Xu *et al.* PHYSICAL REVIEW B 85, 052301 (2012)

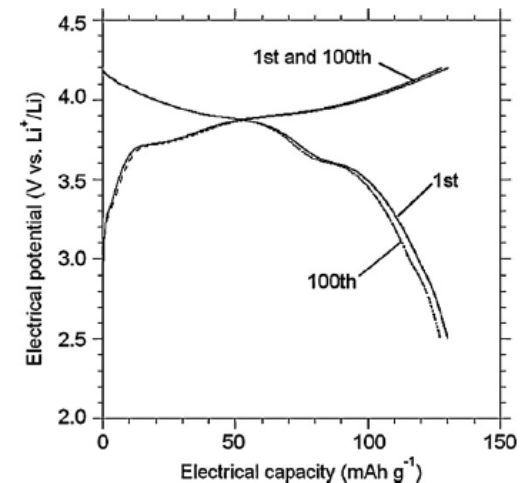
First Report: R. Murugan, V. Thangadurai, W. Weppner, *Angew. Chem. Int. Ed.* **46** 7778 (2007).

Towards cycling Li metal anodes

?

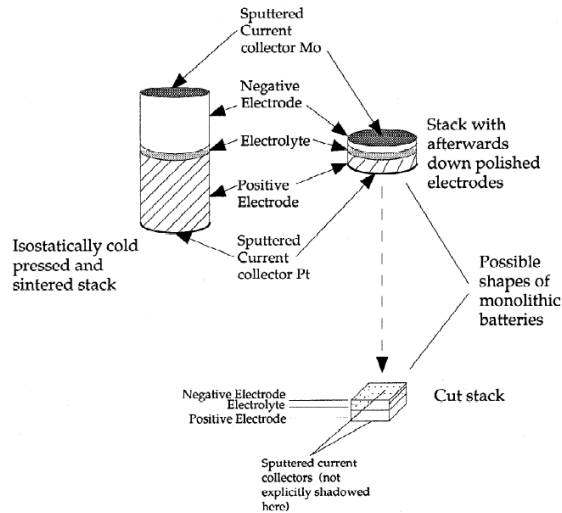


Sakamoto group, cycled LLZO



S. Ohta *et al.*, *Journal of Power Sources*, vol. 196, no. 6, pp. 3342-3345 (2011).

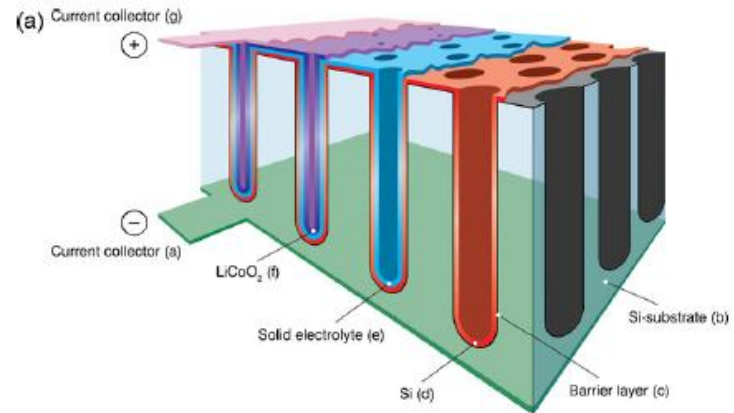
Solid-state, All Ceramic Batteries



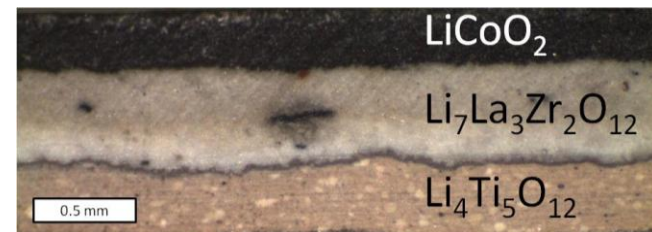
Substrate with windows for embedding of chips

Chips

Weppner *et al.* (1999)



Notten *et al.* Phillips (2009)



Sakamoto group (2011)

- +) No organics to degrade
- +) Synthesized and fabricated in air
- +) Significant reduction in packaging
- +) Non-flammable
- +) Gets better with increasing temp

- ?) Interface integrity
- ?) Kinetics/Power
- ?) Thermomechanical stresses

Conclusions

1. Energy density (Wh/kg) must increase by ~4X
2. Cost (\$kWh) must decrease by ~4X
3. 2020 goal: integrate new materials into current Li-ion
4. 2030 goal: must go beyond Li-ion requiring:
 - Li metal anodes
 - New cathodes
 - Li-O₂
 - Li-Sulfur
5. Opportunities
 - New solid and liquid electrolytes
 - Electrode and battery designs
 - Additive manufacturing
 - Predictive analysis
 - Packaging