Materials Issues in Energy Storage

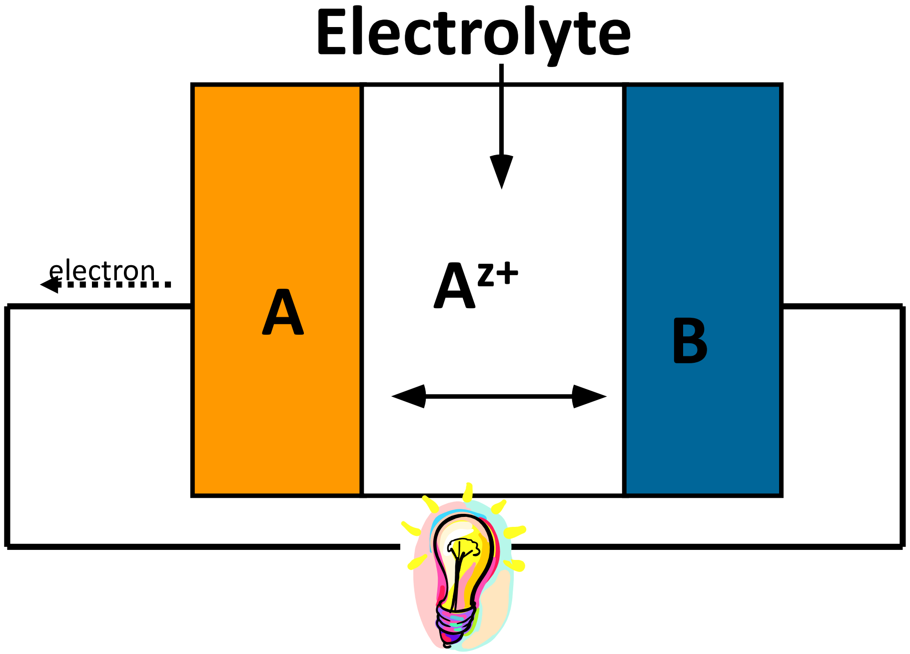
G. Ceder 3/1/2015
APS workshop – San Antonio, TX

Something about myself

- Materials design through computation and experiment
- 20 years in Li-ion. Programs in Na-ion, Li-air, hydrogen, solid-state batteries, and multi-valent intercalation (JCESR)
- Mix of fundamental and applied science
- Work with companies: Bosch, Umicore, Ford, Samsung, Dupont, Duracell, financial industry…
- Feel free to ask questions about science, markets, automotive, grid, Tesla, …

Electrochemical energy storage/generation

Convert chemical energy from a reaction directly into electrical energy

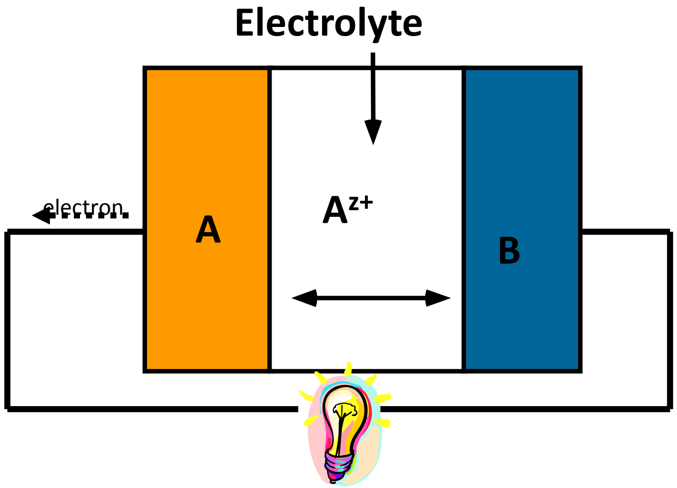


- ☐ A and B want to react
- ☐ Reactants are separated by electrolyte which only allows ionic species A^{z+}.
- ☐ Electrons are forced through outside circuit
- ☐ Complete (exact) conversion of chemical reaction energy (ΔG) into electrical energy

$$-\Delta G = V \Delta q = VzF$$

F = 96 485.3415 s A / mol

Few ions are chosen …



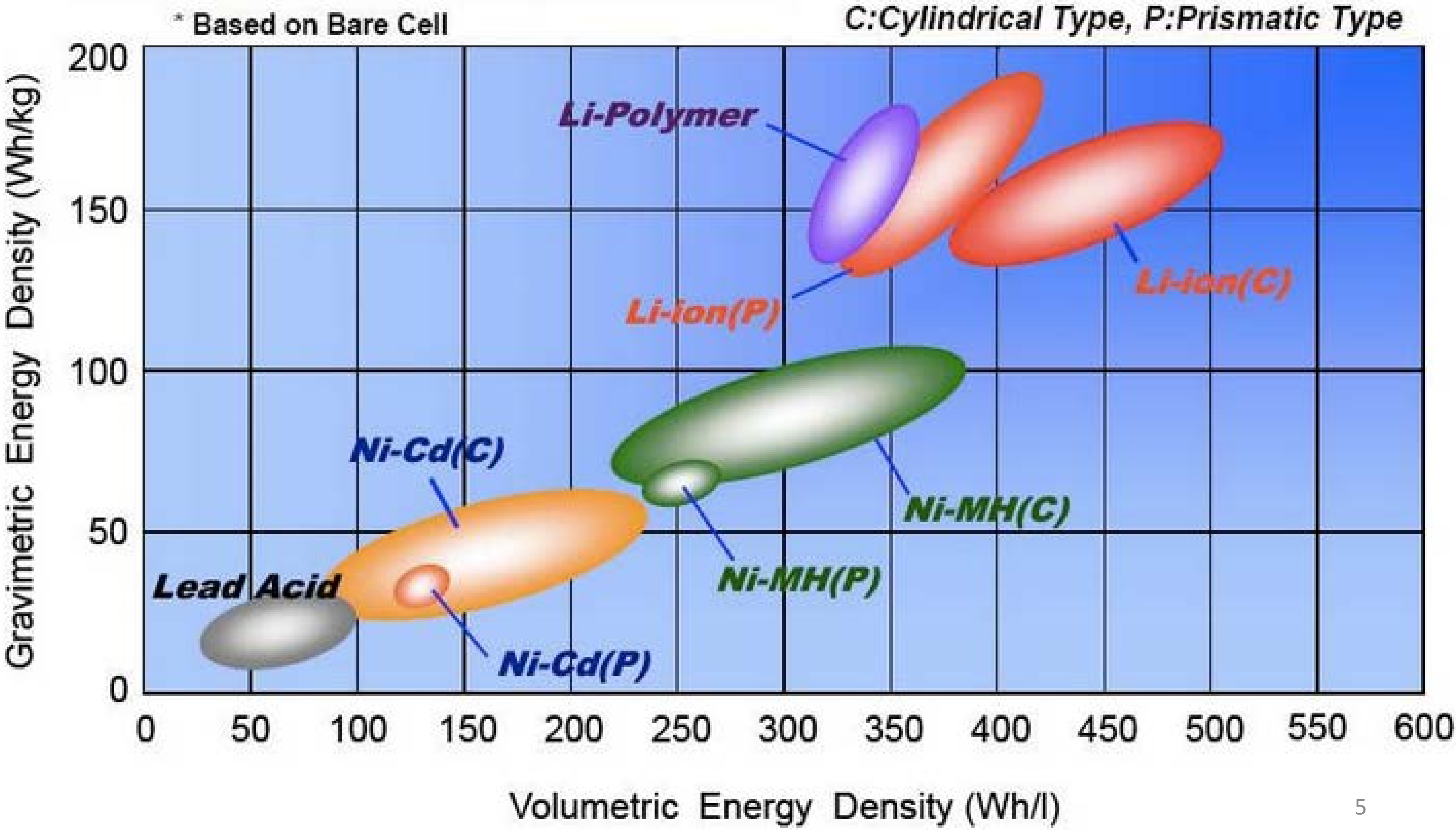
☐ Only limited number of low-valent ions are mobile in electrolytes at room temperature: H^+, OH^-, Li^+, Na^+, K^+, some divalent ions in H_2O.

☐ Need perfectly reversible reactions for rechargeable battery technology

☐ Need control (safety). No spontaneous reactions

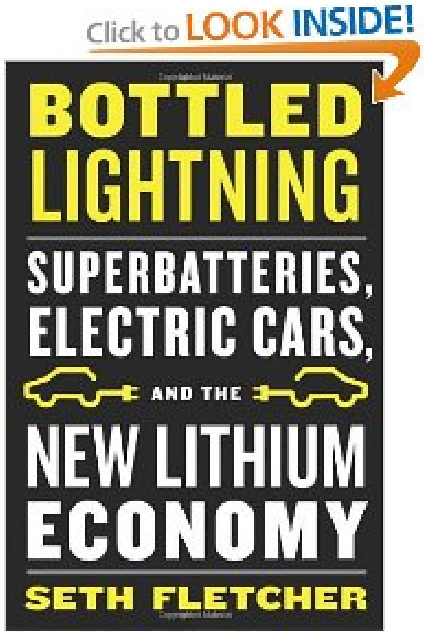
- H^+ (or OH-) is the mobile species in aqueous electrolyte for Pb-acid, NiMH and Ni-Cd batteries
- Li^+ mobile species for Li-ion
- O^{2-} for solid oxide fuel cells
- Mg^{2+}/Ca^{2+} etc. being researched for future technologies (e.g. JCESR)

$$\Delta\varepsilon = -\frac{\Delta\mu}{z}$$

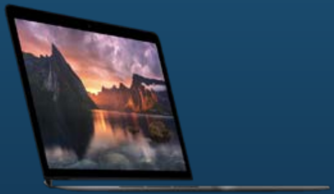
* Based on Bare Cell
C:Cylindrical Type, P:Prismatic Type
Li-Polymer
Li-ion(P)
Li-ion(C)
Ni-MH(C)
Ni-MH(P)
Ni-Cd(C)
Ni-Cd(P)
Lead Acid
Gravimetric Energy Density (Wh/kg)
0
50
100
150
200
Volumetric Energy Density (Wh/l)
0
50
100
150
200
250
300
350
400
450
500
550
600

History

- **1970's** Research into intercalation of ion in materials
- **1976**: Stan Whittingham (at Exxon at the time) shows working of Li metal/TiS_2 cell (rechargeable)
- **1979**: John Goodenough publishes the $LiCoO_2$ cathode
- **1980'ies**: Commercialization of Li/MoS2 cell – and recall due to safety issues
- **1991:** Sony commercializes Li-ion with the carbon anode
- **TODAY:** Cells with several cathode chemistries on the market. $15 Billion market growing rapidly from portables into automotive and grid



Li ion is on the move to take all

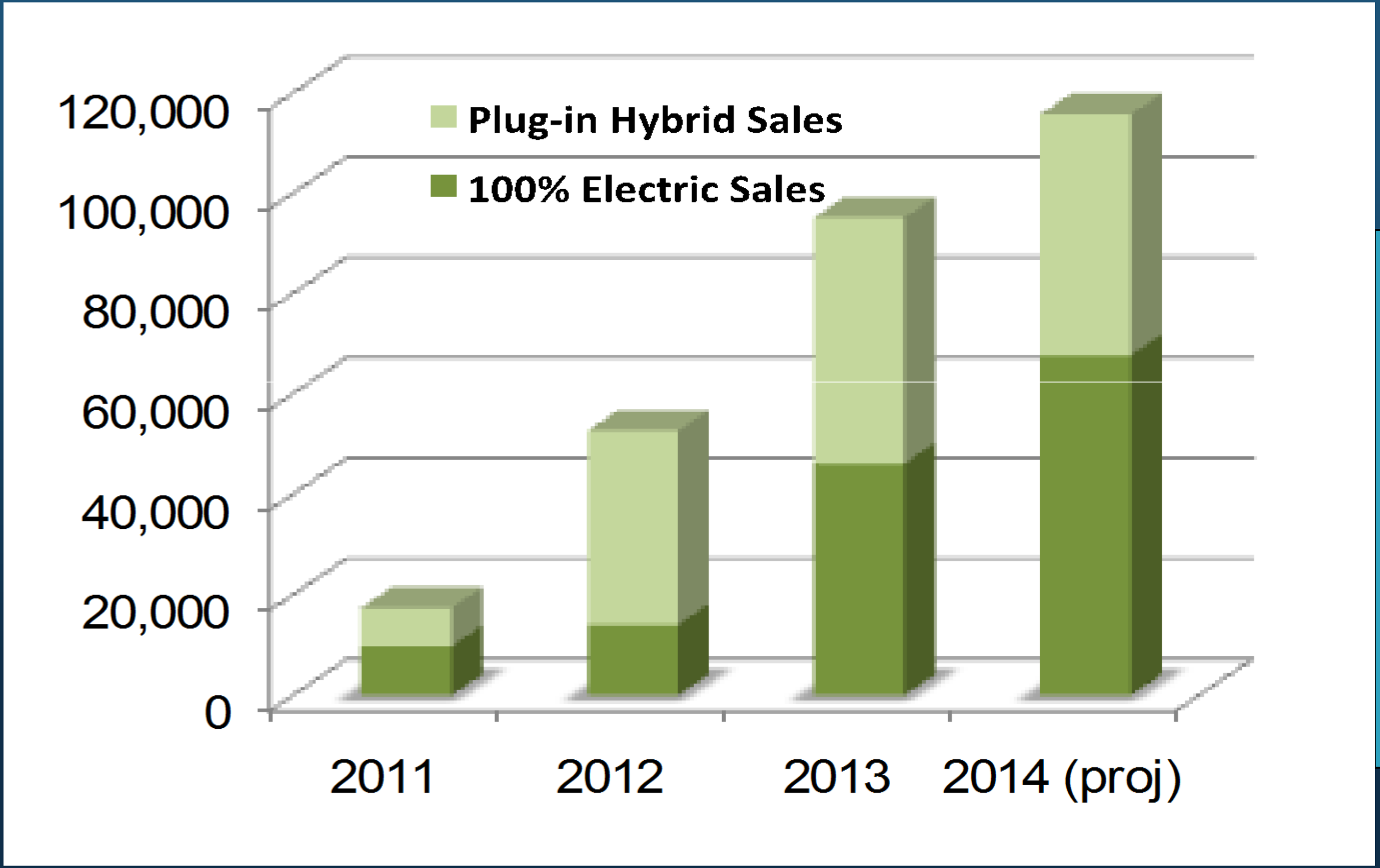


Electronics

Automotive

Grid

Electrified Vehicles are still small part of US car sales, but see substantial growth



World:
320,000
vehicles

Uses ≈12% of Li-ion market

2012	2013	2014 (proj)
Top (> 10k)	Top (> 10k)	Top (> 10k)
Chevy Volt 23k	Chevy Volt 23k	Nissan Leaf 30k
Prius PHV 13k	Nissan Leaf 22k	Chevy Volt 19k
	Model S 18k	Model S 17k
	Prius PHV 12k	Prius PHV 13k
		Ford Fusion 11k

Electric Vehicles are Changing

Green

Performance

Porsche Panamera

Nissan Leaf

BMW-i3

Prius

Tesla

10 sec

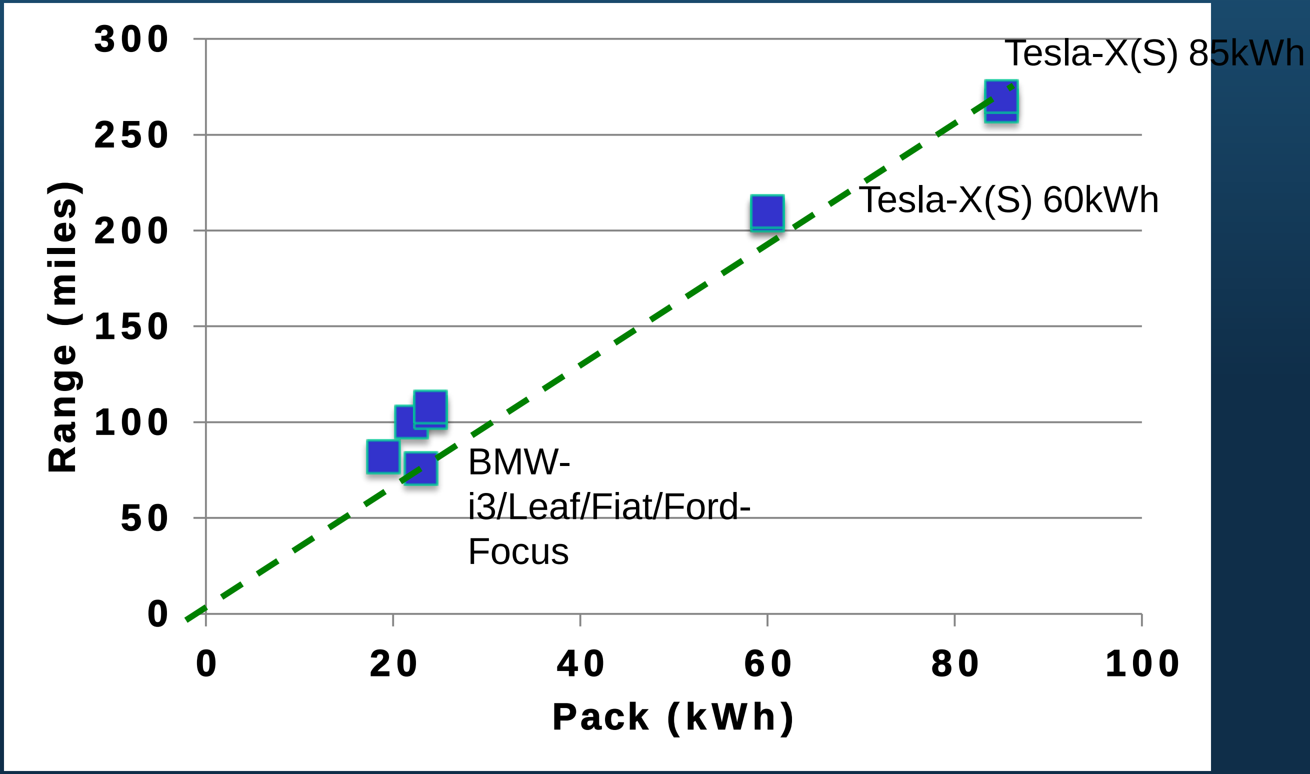
7 sec

5.2 sec

Limited range and range anxiety holds growth back

Driving range is a matter of cost

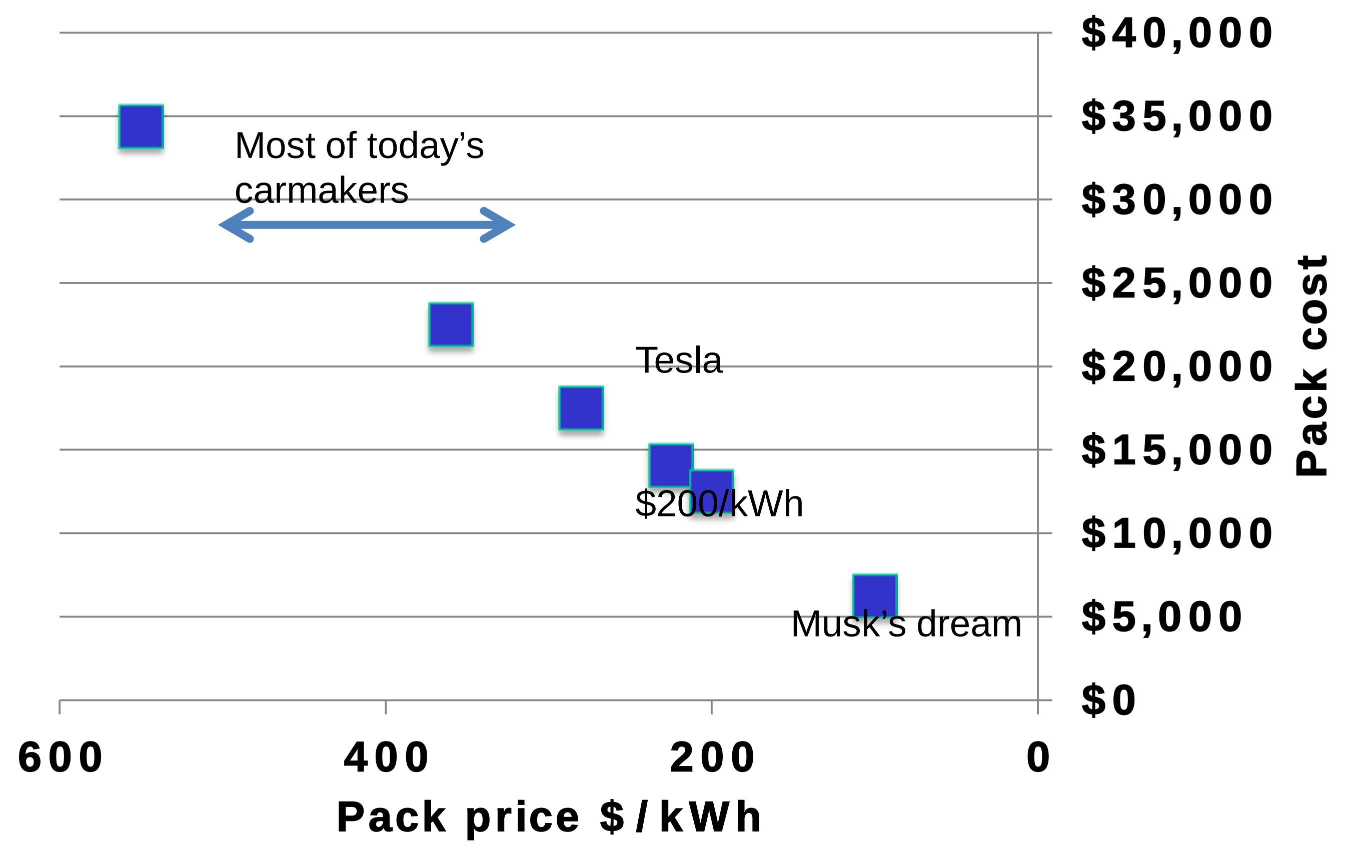
- 3-4 Miles range/kWh of energy storage
- BMW –i3 highest miles/kWh
- 200 miles range requires 50-65kWh pack



Range vs pack size for various EVs

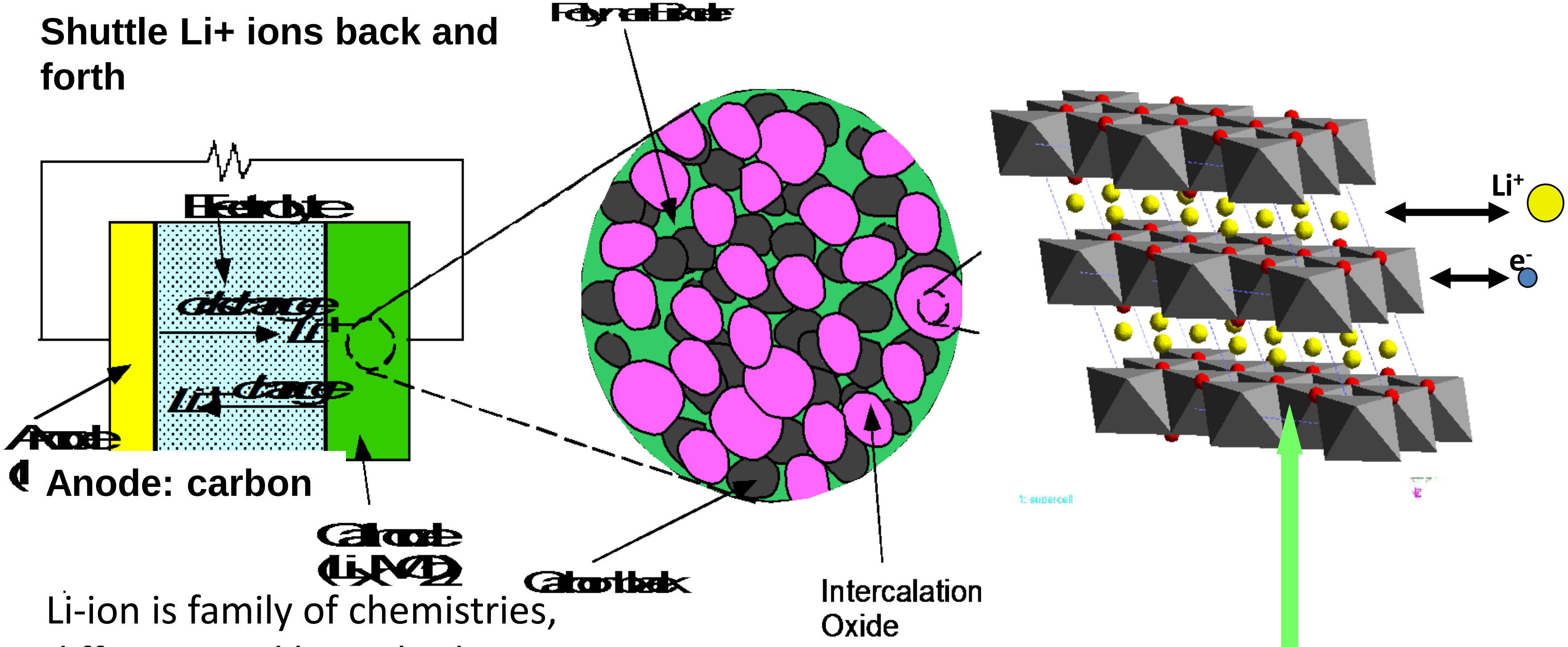
Driving range is a matter of cost

Cost for 250 miles range at 4miles/kWh



Operation of a rechargeable Li battery

Shuttle Li+ ions back and forth



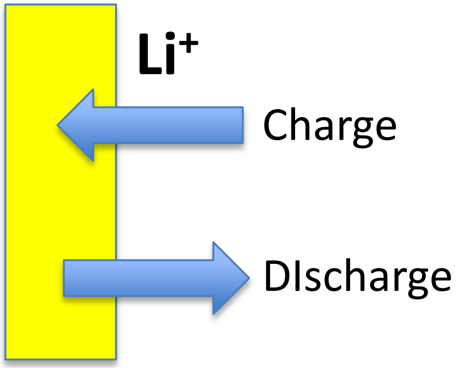
Anode: carbon

Li-ion is family of chemistries, differentiated by cathode

Cathode needs to host and exchange large amounts of Li^+ and electrons at high rate and remain stable

Anode

- Ideal anode would be lithium metal foil.
- Theoretical energy density is ≈ 3,600 mAh/g

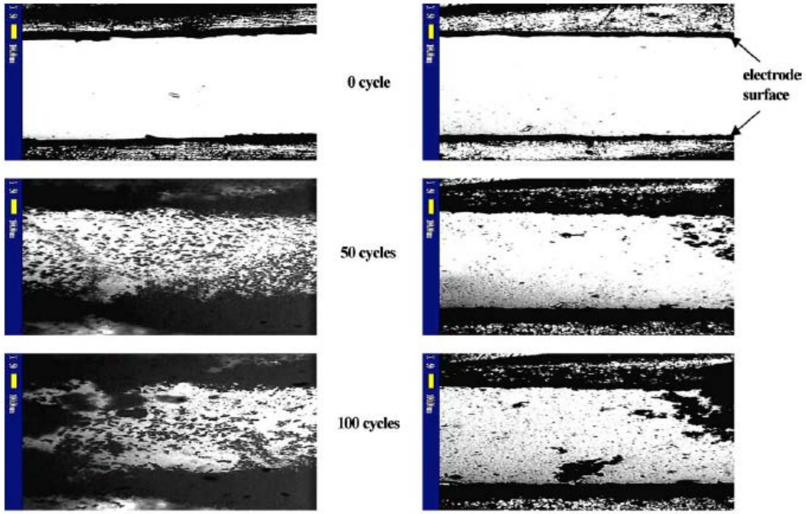


Issues

☐Really need multiple times “excess” Li to have long cycle life (e.g. at 3 times excess theoretical capacity is down to 1,200mAh/g

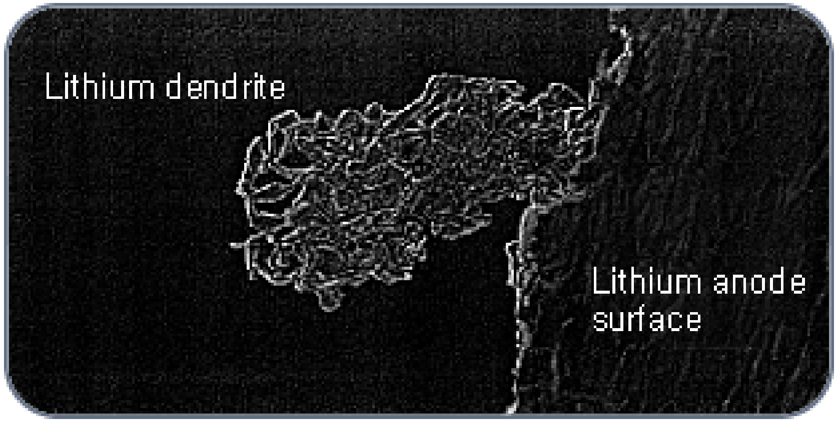
☐Poor Li deposition on charge cycle leads to mossy anode with dendrite formation. DANGER

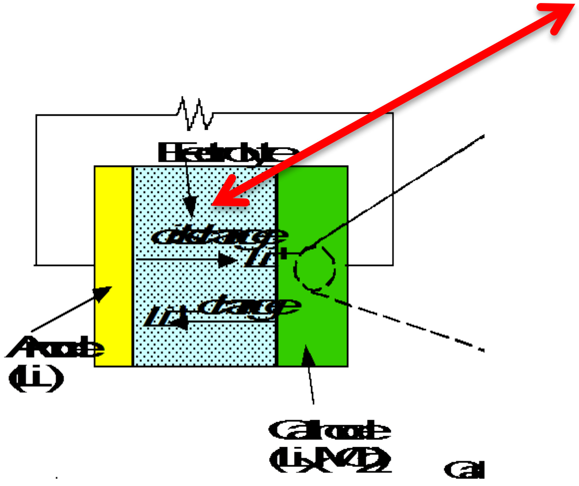
Metallic anode: dendrite formation



(a) Li foil electrode

(b) Li powder electrode





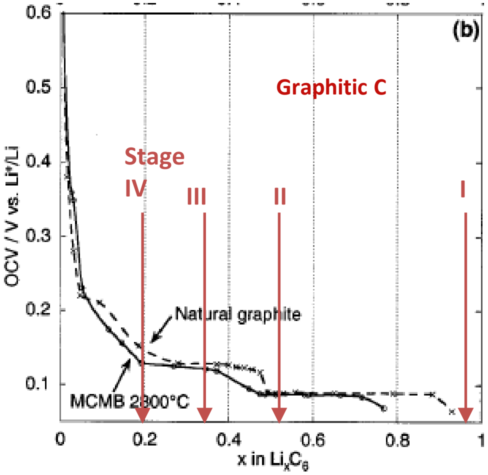
Dendrites grow across the separator and short the cell internally.

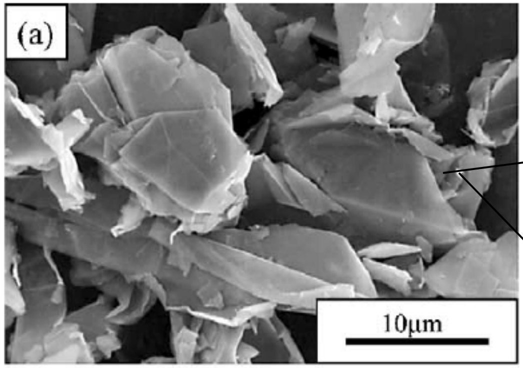
Cells with Li-metal anodes, while they have potential for high energy density, are potentially dangerous

Some small companies are investigating combination of lithium metal with polymer electrolytes

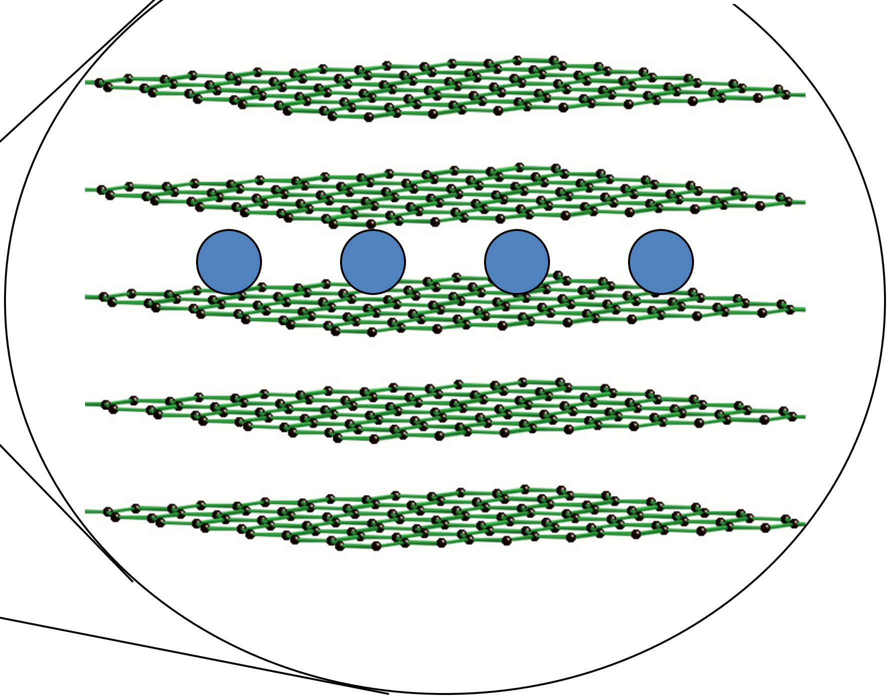
Carbon Anode

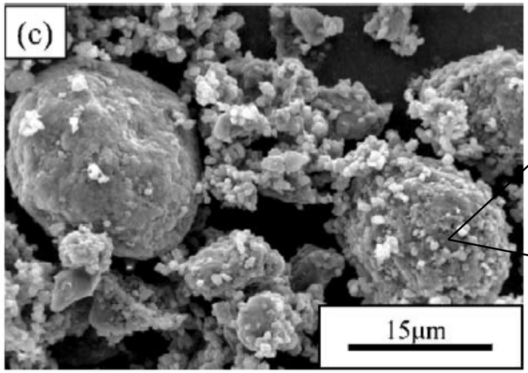
Sony 1991 introduced the carbon anode. Birth of Li-ion technology.





natural graphite

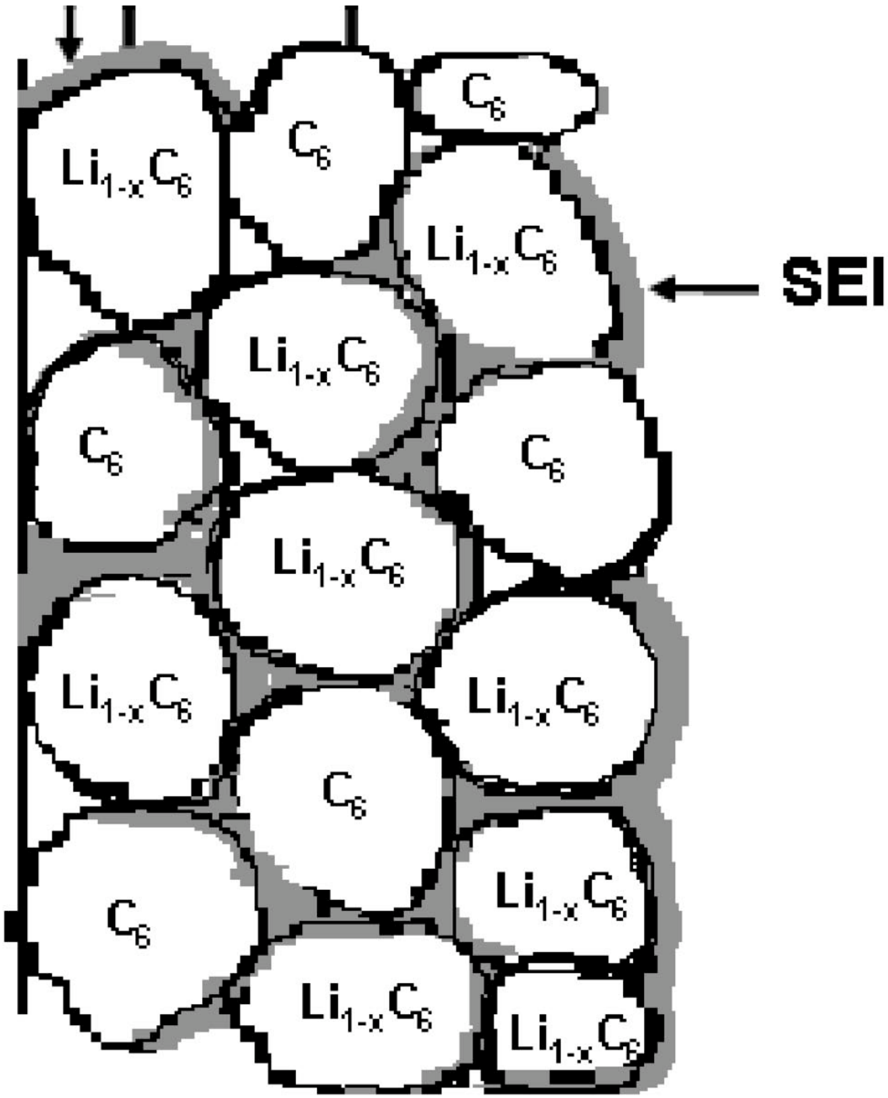




mesophase carbon fiber

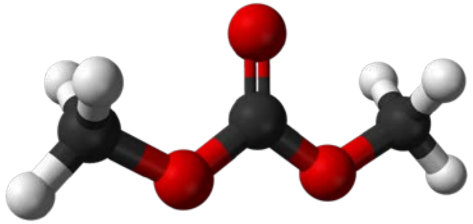
Graphitic carbon can store lithium up to LiC_6 composition (= 372 mAh/g)

Anode passivation



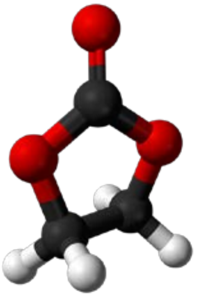
SEI = Solid Electrolyte Interphase

SEI protects carbon from further reaction



dimethyl carbonate (DMC)

Salt = $LiPF_6$



ethylene carbonate(EC)

Desired properties of cathode material

Voltage

Chemical potential of Li

Capacity

Amount of Li that can be reversibly exchanged (without structure collapse)

Rate (ionic)

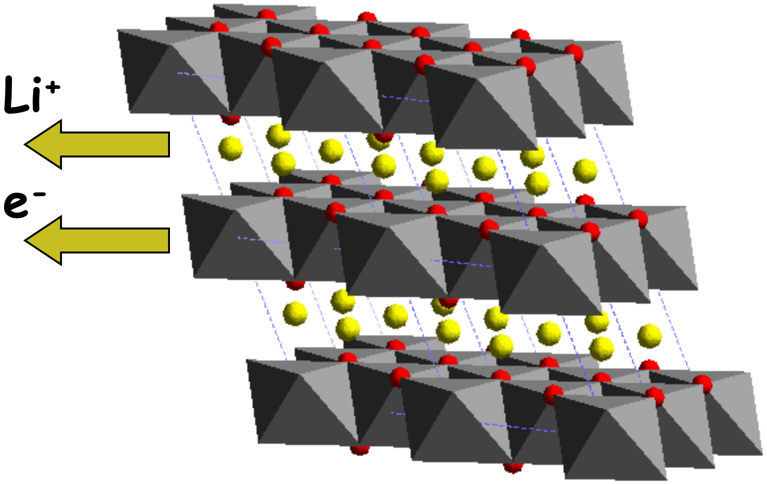
Diffusivity of Li in crystal

Rate (electronic)

Electron mobility in crystal

Capacity retention

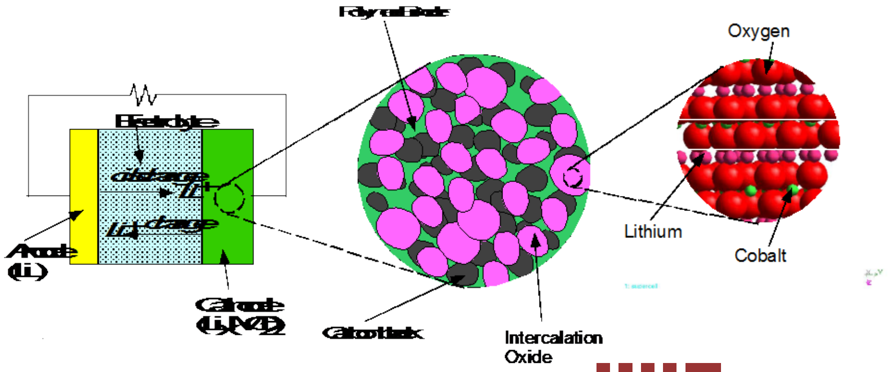
Crystal structure stability (intrinsic and with electrolyte)



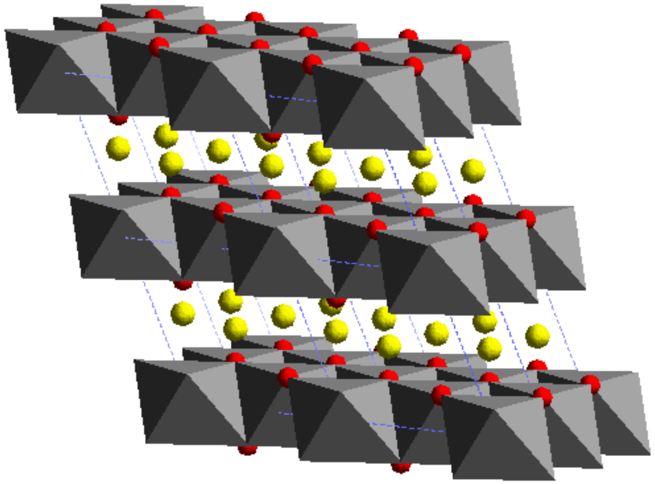
Extract Li^+

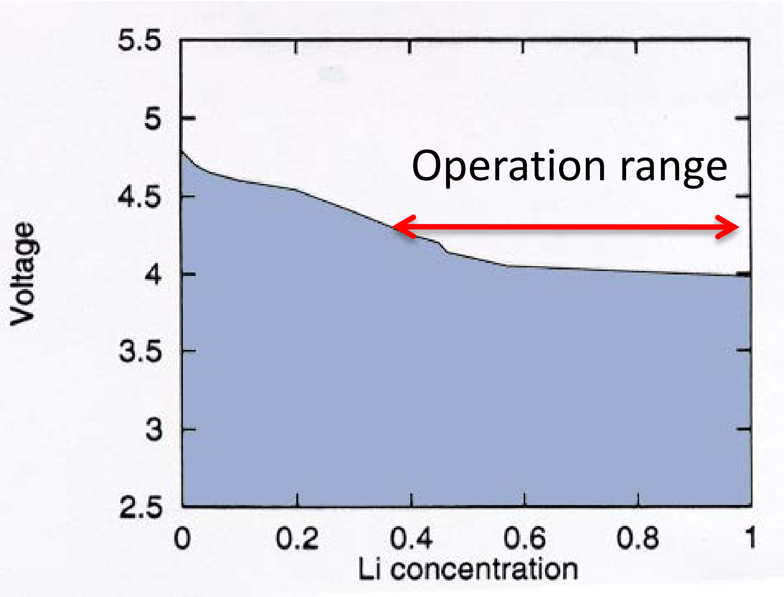
Extract e^-

$$V = - \quad (\mu_{Li} - \mu_{Li}^{ref})$$



The original cathode: $LiCoO_2$

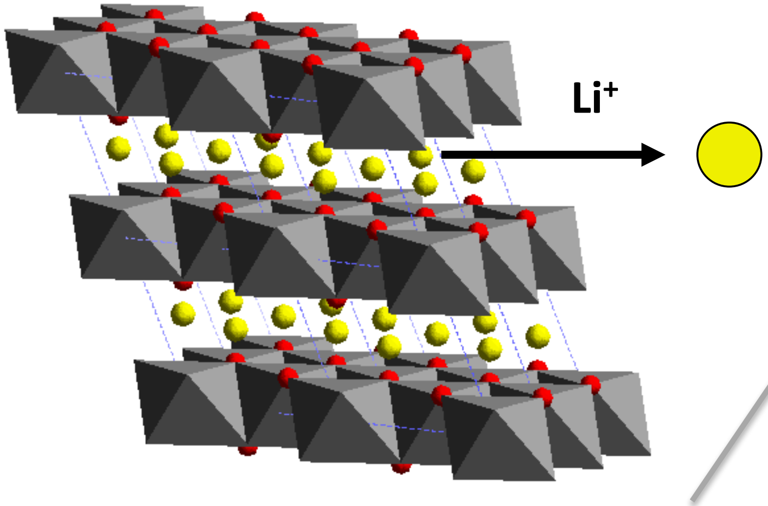




- Was present in 99% of all rechargeable Li-ion batteries from 1991 to mid 90'ies
- Theoretical capacity 278 mAh/g, practical about 170mAh/g
- CONS: Price of Co; lack of safety at high state of charge

The fascinating physics of intercalation oxides

$LiMO_2$



M^{3+} <-> M^{4+}

Li <-> vacancy

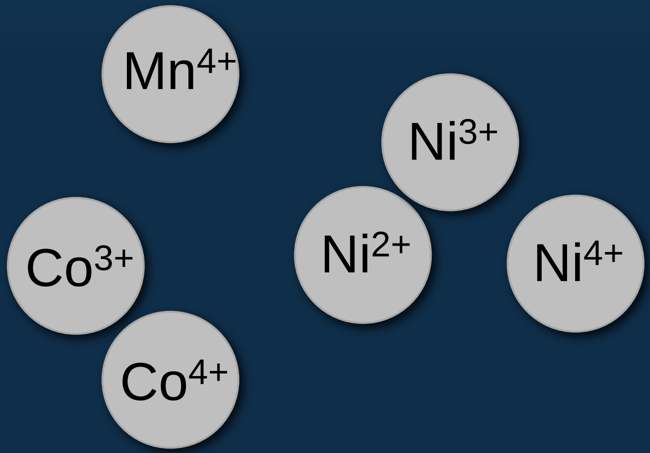
- Metal-insulator (Mott) transition
- Magnetic transitions
- Jahn-Teller distortions
- Charge ordering
- Li-vacancy ordering

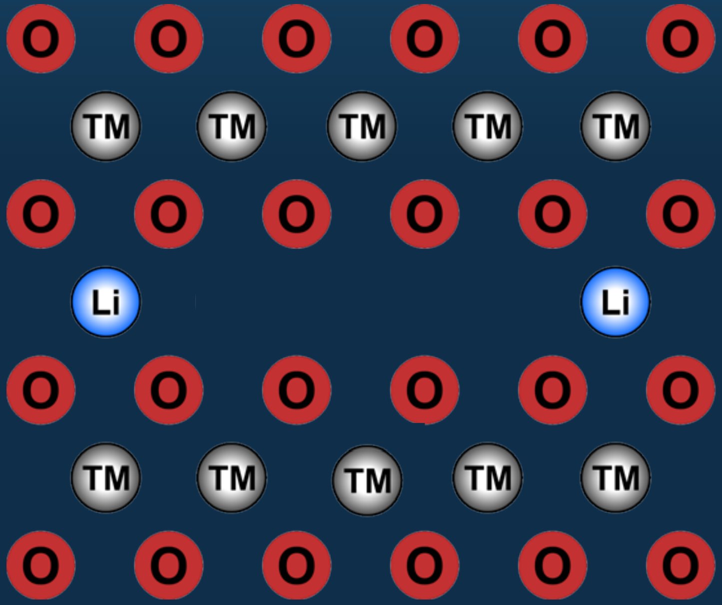
Conventional Li battery cathode materials are layered

LCO -> your laptop

NCA (Ni, Co, Al) -> your Tesla

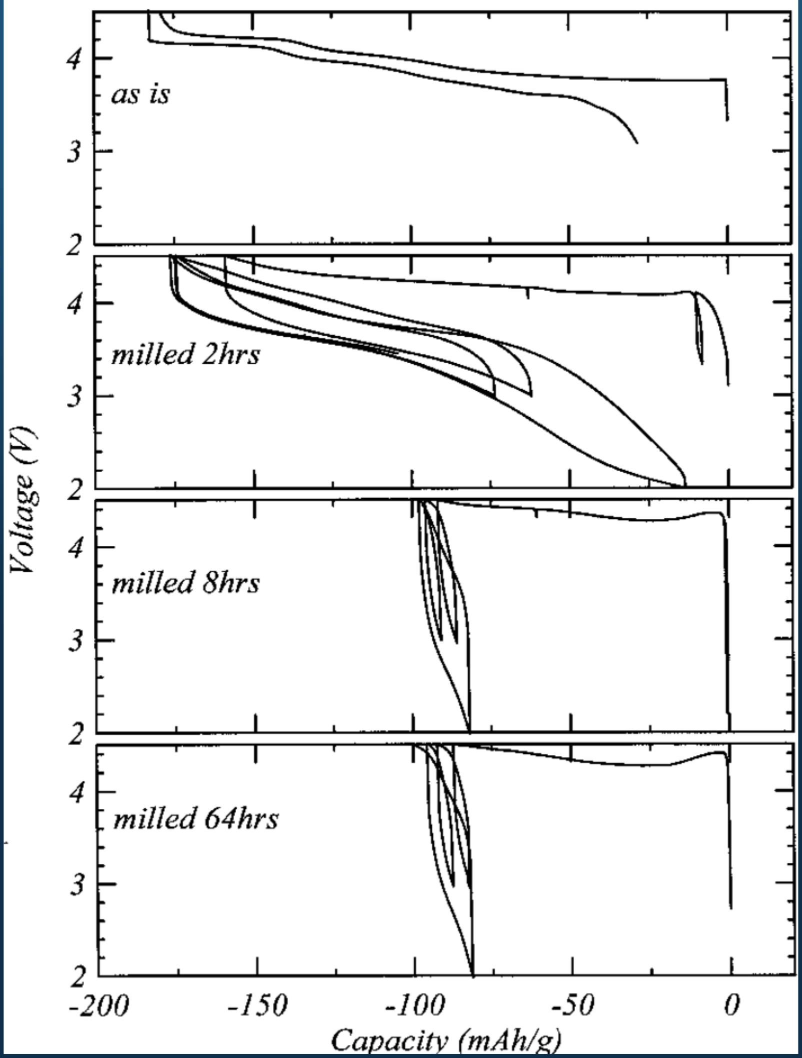
NCM (Ni, Co,Mn) -> my BMW-i3





Disorder systematically decreases performance

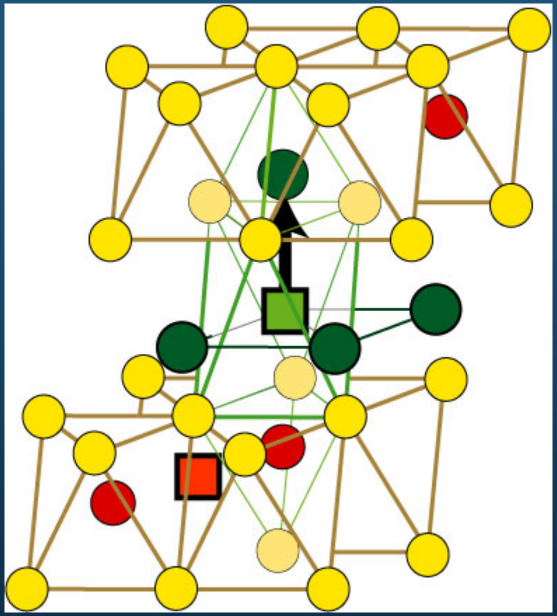
LiNiO$_2$

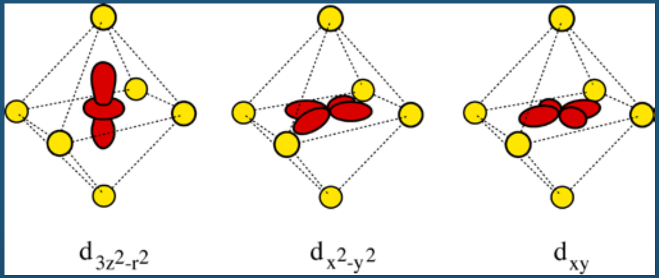


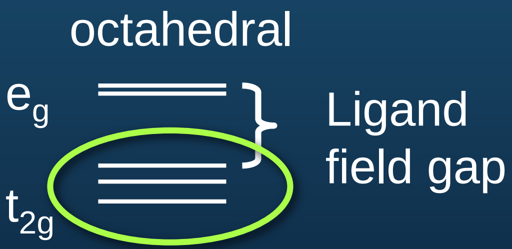
Disorder materials
by ball milling

Obrovac, Mao and Dahn, SSI, 112, p9 (1998)

Tetrahedral site is the activated state as TM migrates into Li layer







octahedral

e_g

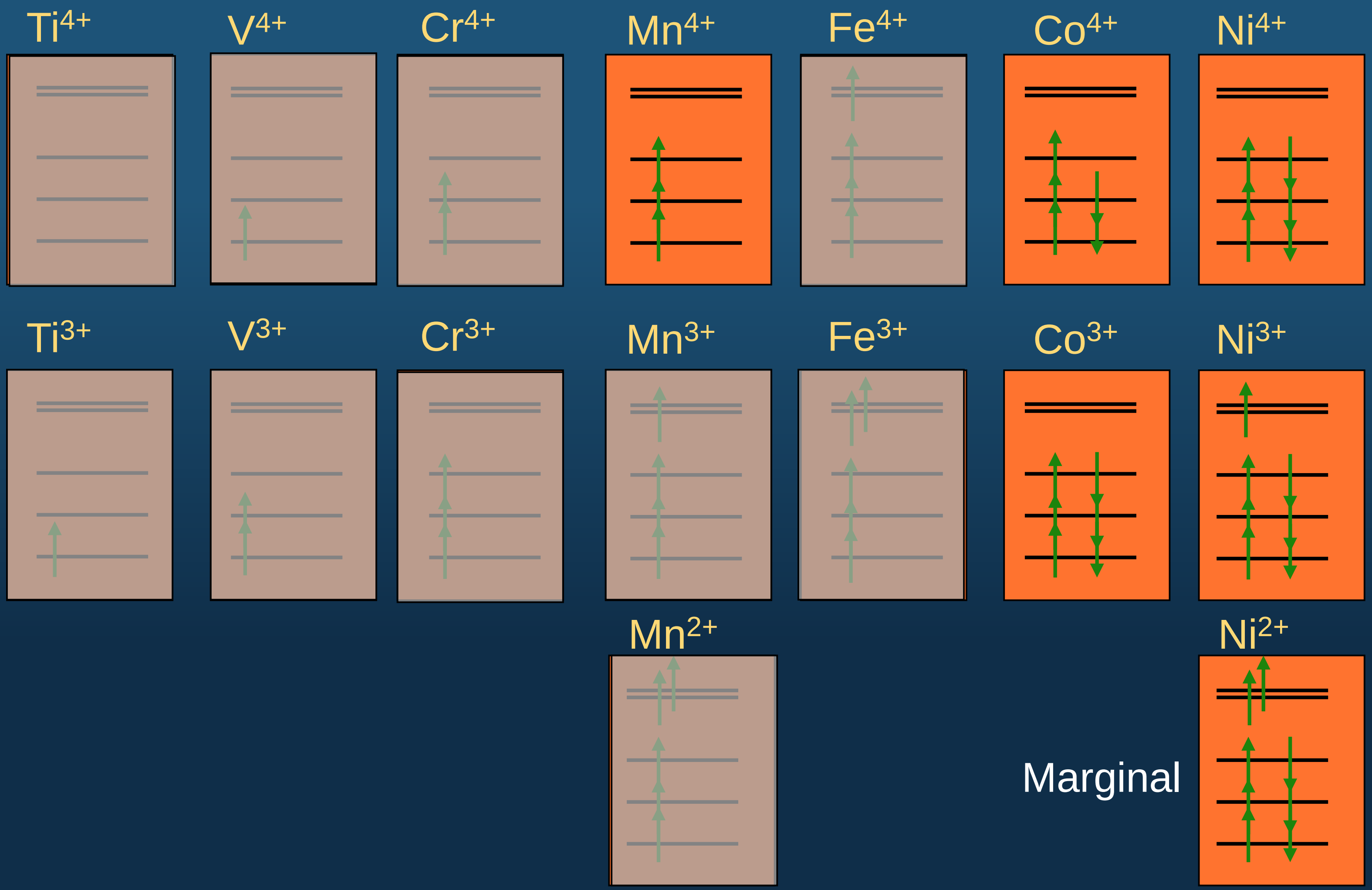
t_{2g}

Ligand field gap

Filling these orbitals favors octahedral occupation

Reed et al. Electrochem. Solid State Lett. (2001)

Electronic structure determines Tet/Oct preference

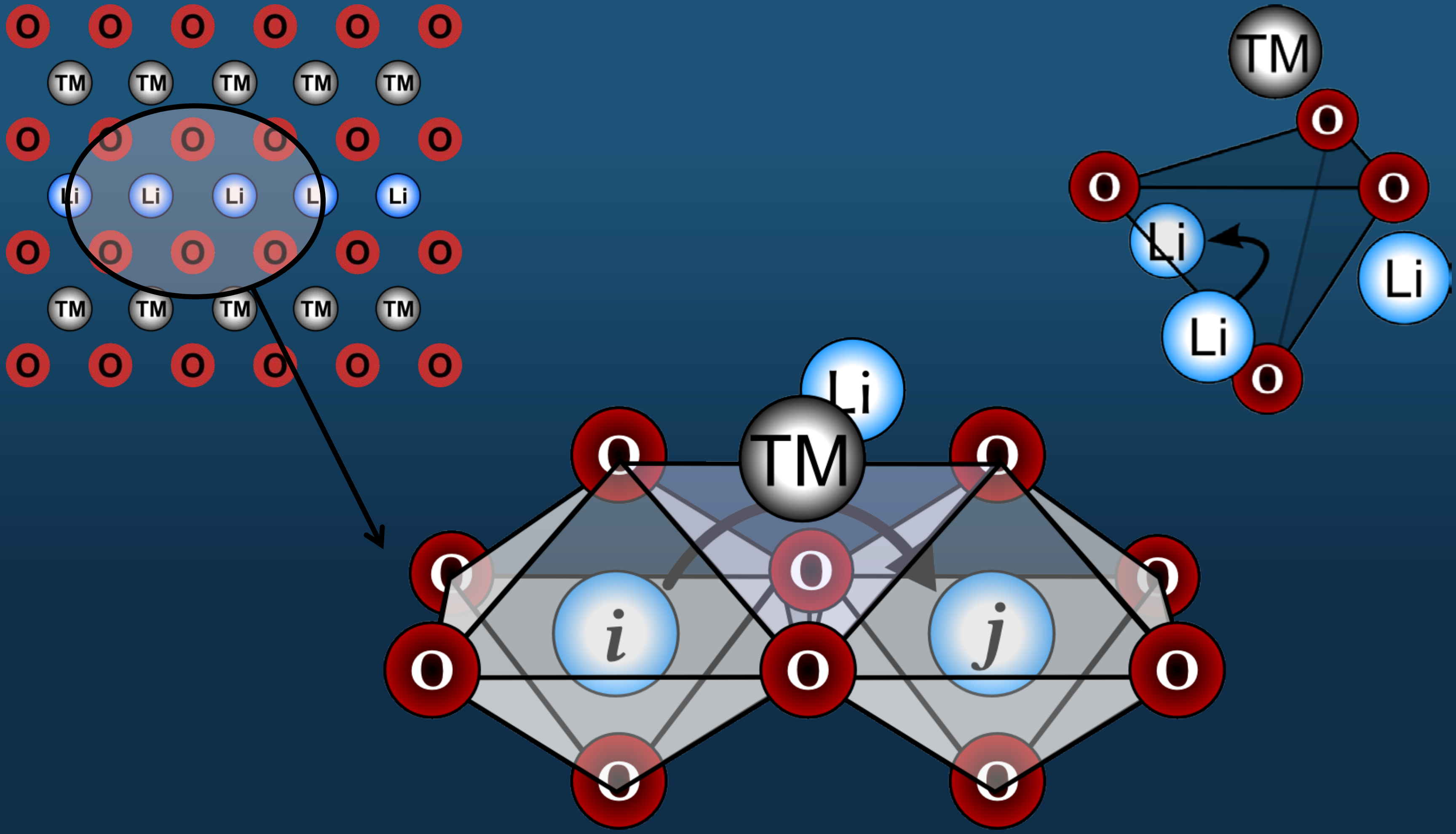


Reed and GC Chemical Reviews, **104** (10), 4513-4533 (2004).
Reed et al. Electrochem. Solid State Lett. (2001)

Why is disorder so bad ?
Same reason we can not achieve theoretical capacity

280 mAh/g is one electron per LiMO2 unit
we achieve max 150-200 mAh/g

Li diffusion mechanism in “rocksalts”

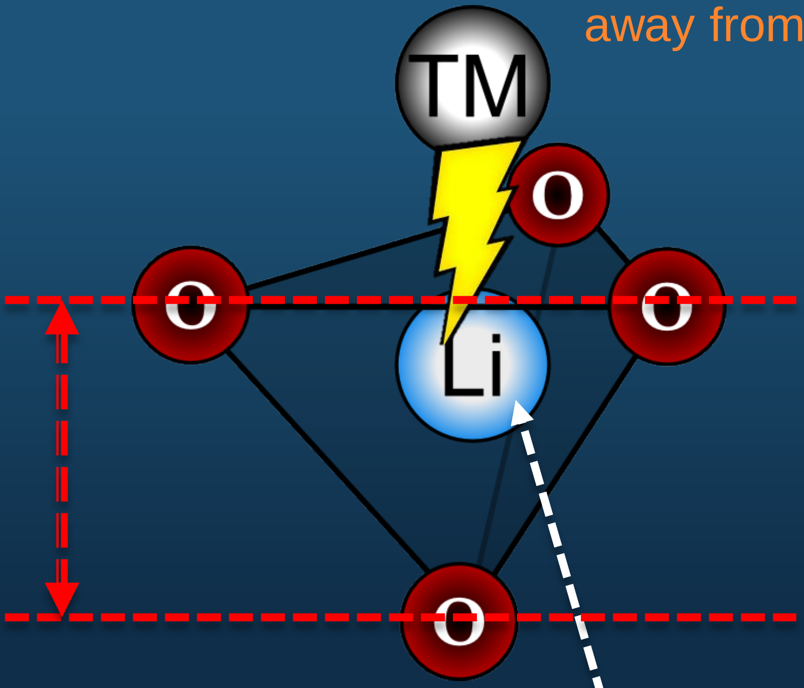


Li hopping from oct to oct site through tetrahedral site

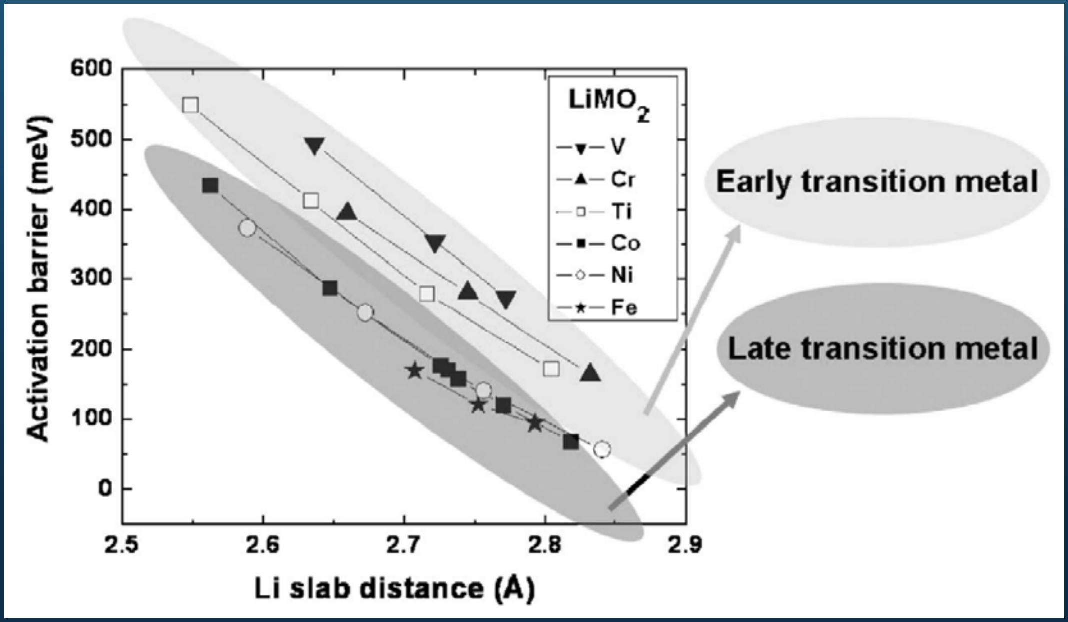
Tetrahedral site is approximately the activated state

In layered oxides one gate-ion is a Transition Metal (TM)

Increase slab spacing allows the TM to relax further away from the Li in the activated state



Activated state



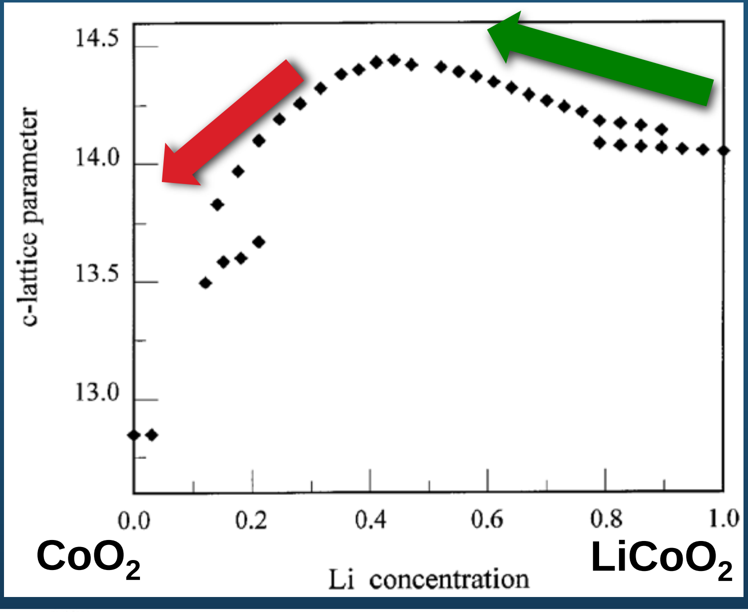
[K Kang and G Ceder
Phys. Rev. B 74 (2006) 094105]

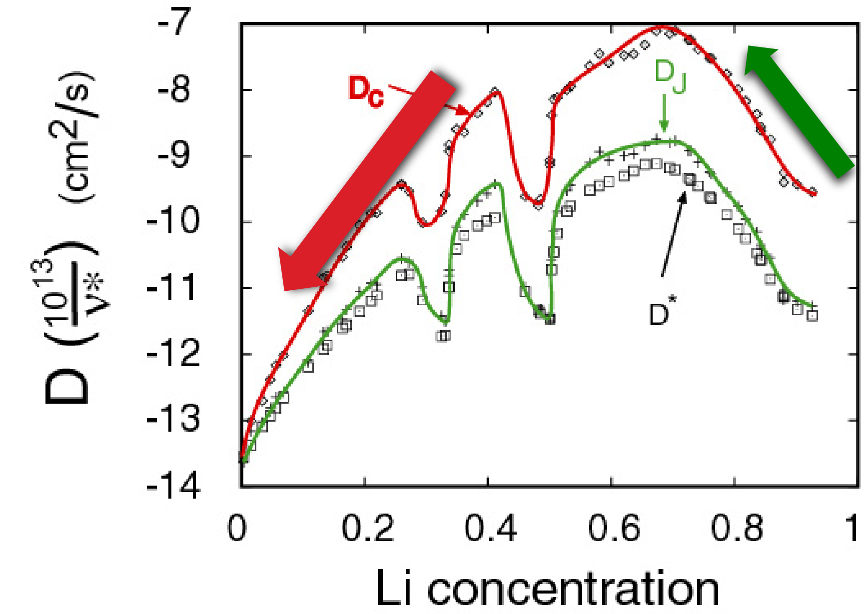
Every 0.1 Å in slab space reduction reduces D_{Li} by more than a factor of 10

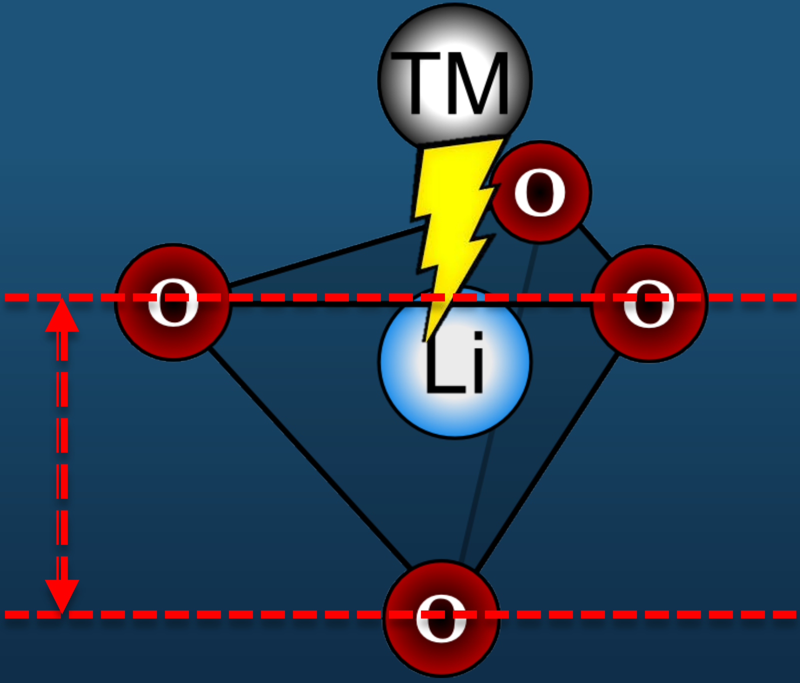
A. Van der Ven, G. Ceder, *Electrochemical and Solid State Letters* **3**, (2000) 301-304.

High delithiation and high lithiation reduces slab distance

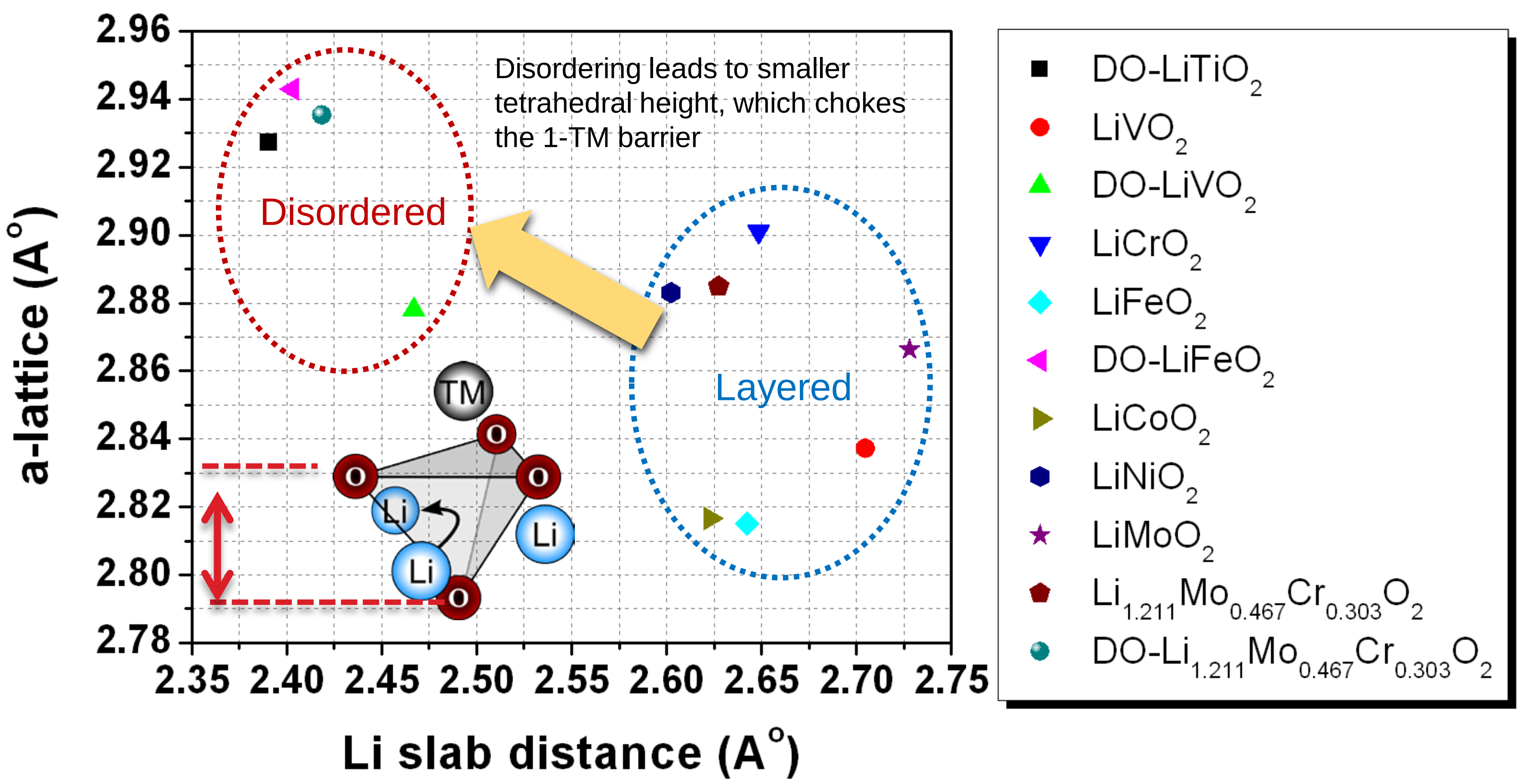
G Ceder, et al, *JOM* 50 (1998) 35.





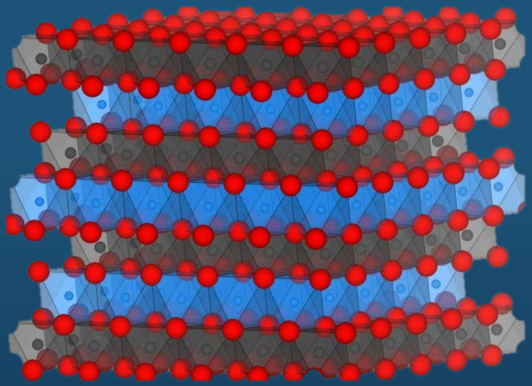


Disorder reduces slab distance



Disordering leads to smaller tetrahedral height, which chokes the 1-TM barrier

Strategies to reach theoretical capacity in cathode oxides

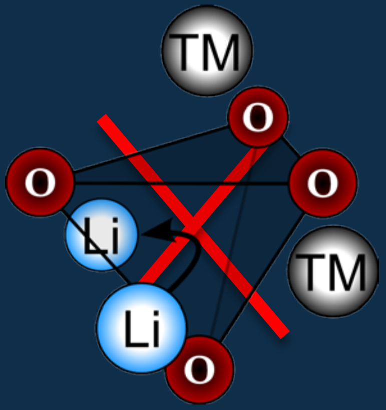


- Pillaring layers ? Not been successful
  (e.g. Work by Nazar and Whittingham)

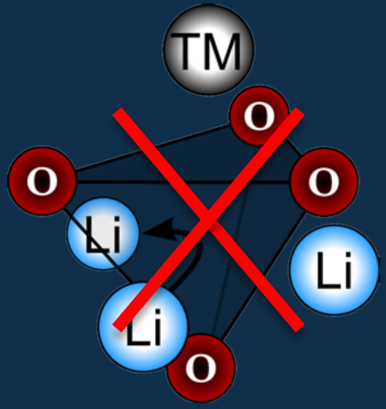
- Can we make a diffusion mechanism that is **less sensitive** to lattice parameter ?

- If we **disorder** cations we will get different environments of activated state

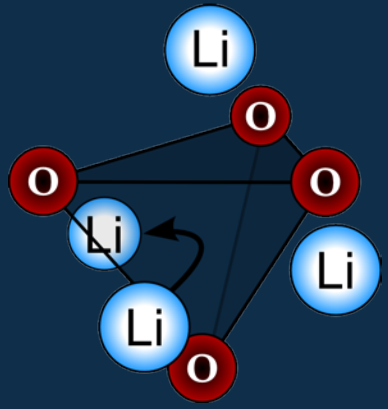
2-TM



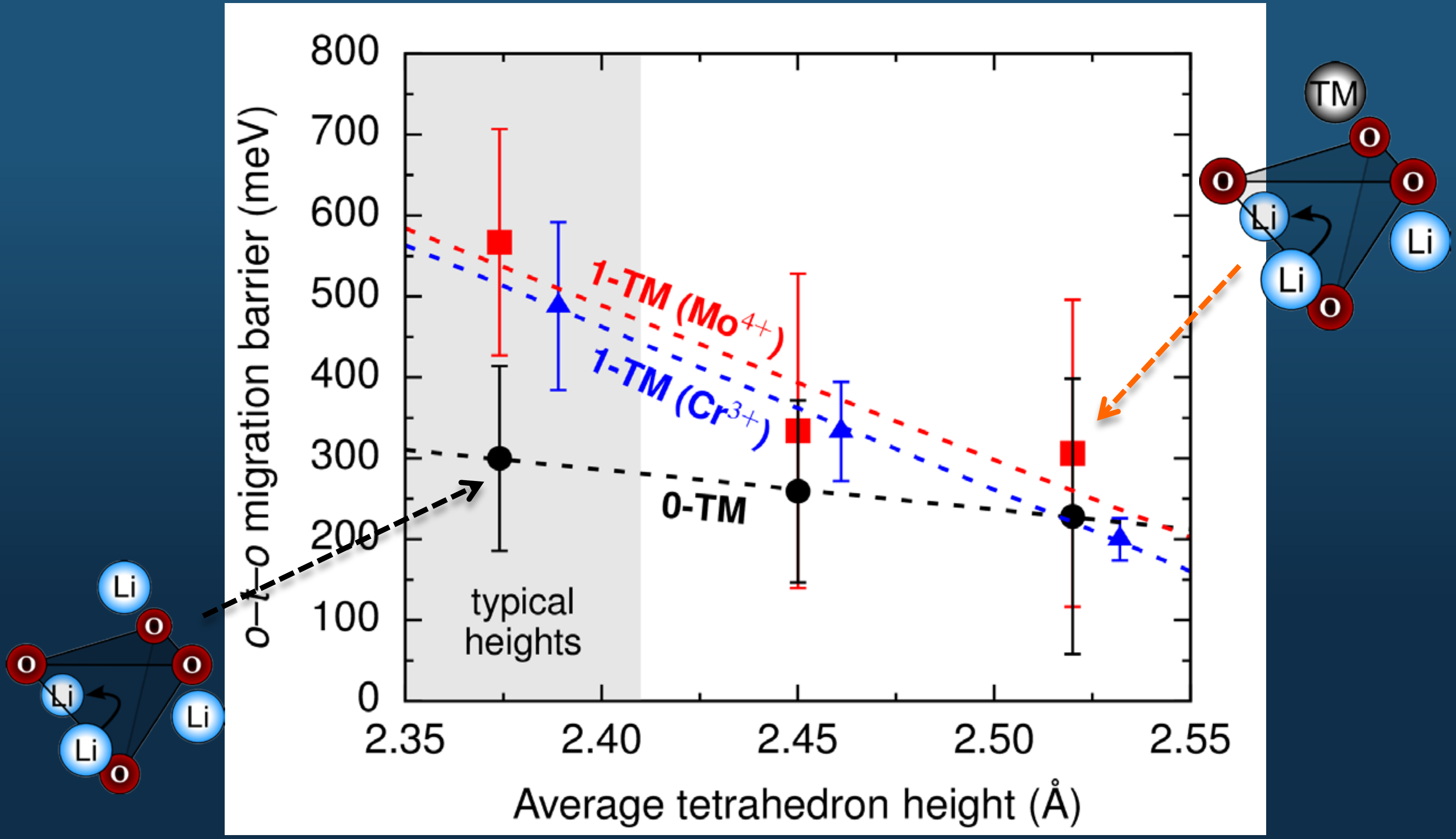
1-TM



0-TM



NEB calculations show that 0-TM channels are much less sensitive to lattice parameter



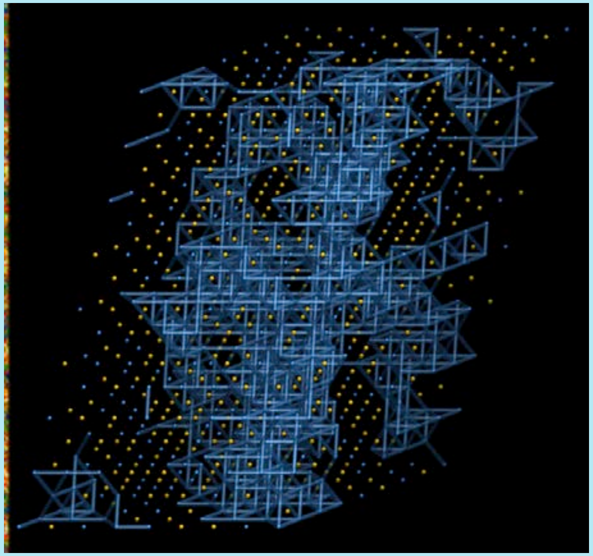
0-TM channels will be active in disordered rocksalts !

Conditions for macroscopic 0-TM diffusion

Is the **concentration of 0-TM channels** sufficient to support macroscopic diffusion?

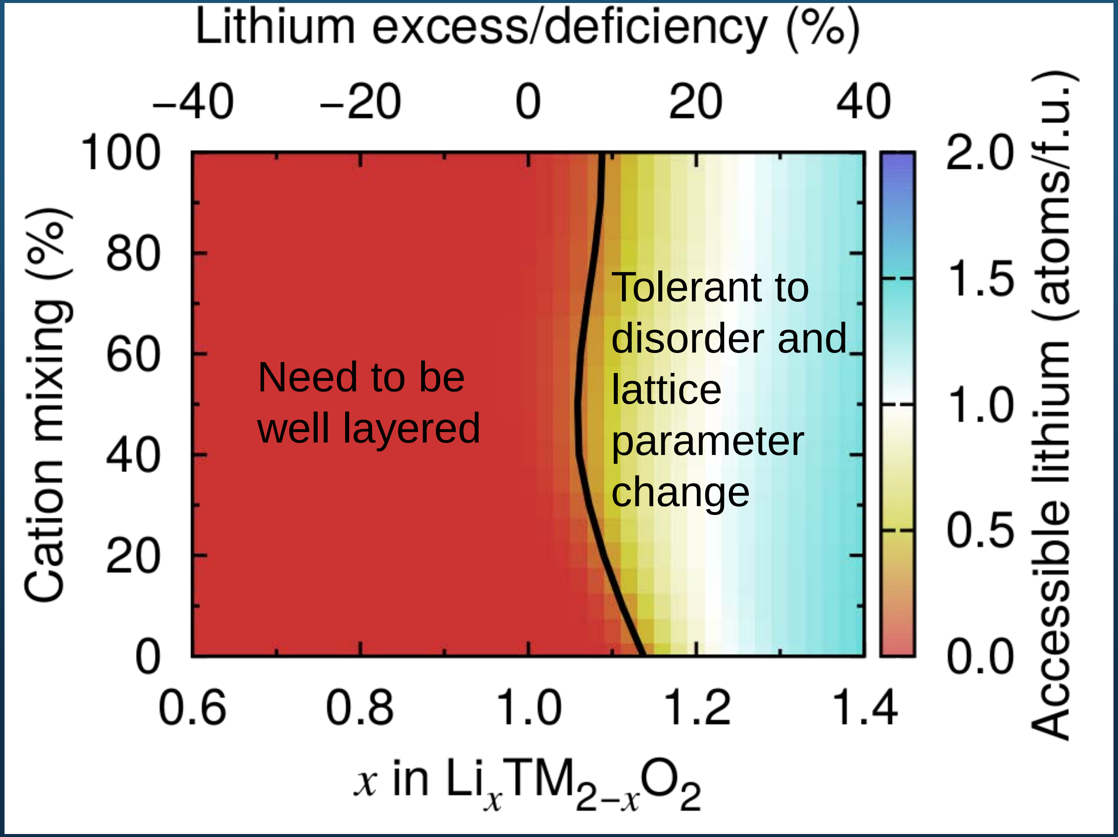
In other words:
When do 0-TM channels form a **percolating network**?

APPROACH



Monte Carlo simulation to find percolation thresholds for 0-TM diffusion channels

Lattice-parameter insensitive Li mobility



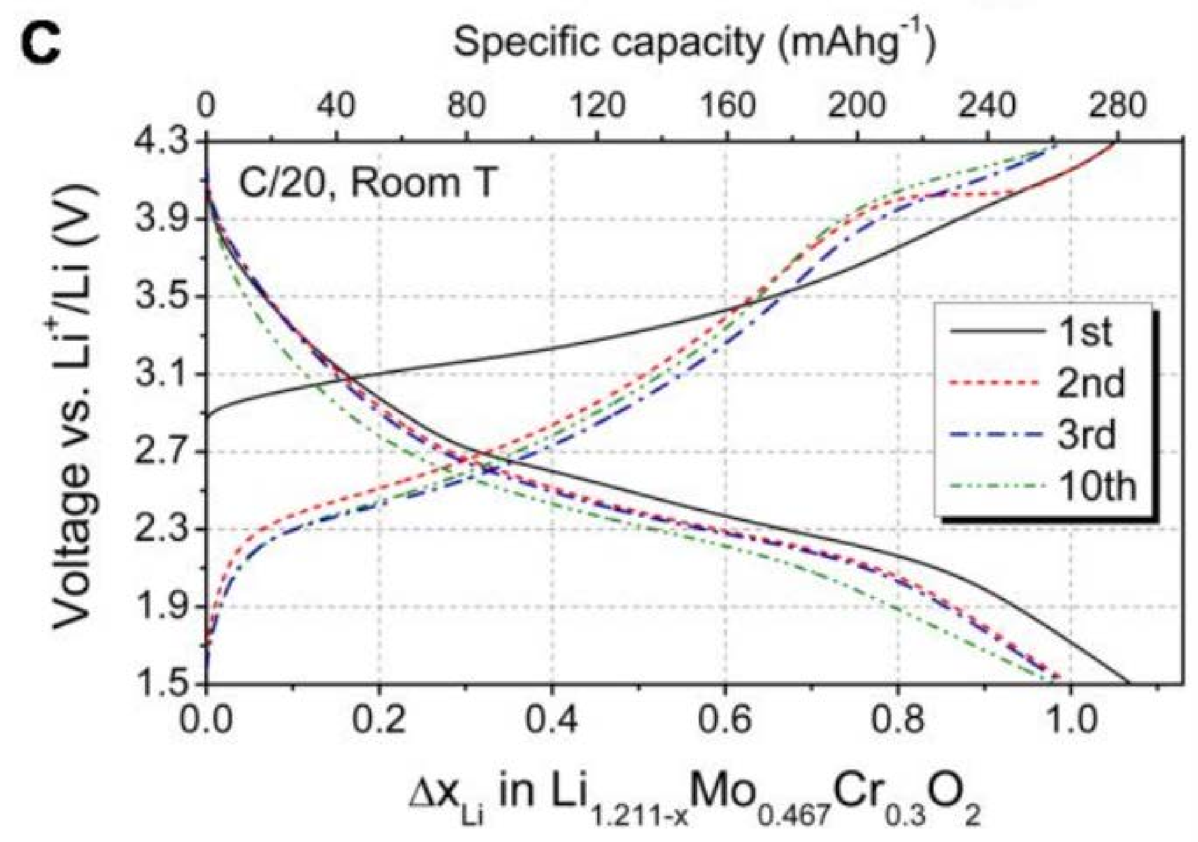
- By adding Li excess > 10% the material achieves an additional Li diffusion mechanism which is insensitive to lattice parameter

$Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$ (LMCO): A Material with near theoretical capacity


$LiMO_2$

280mAh/g

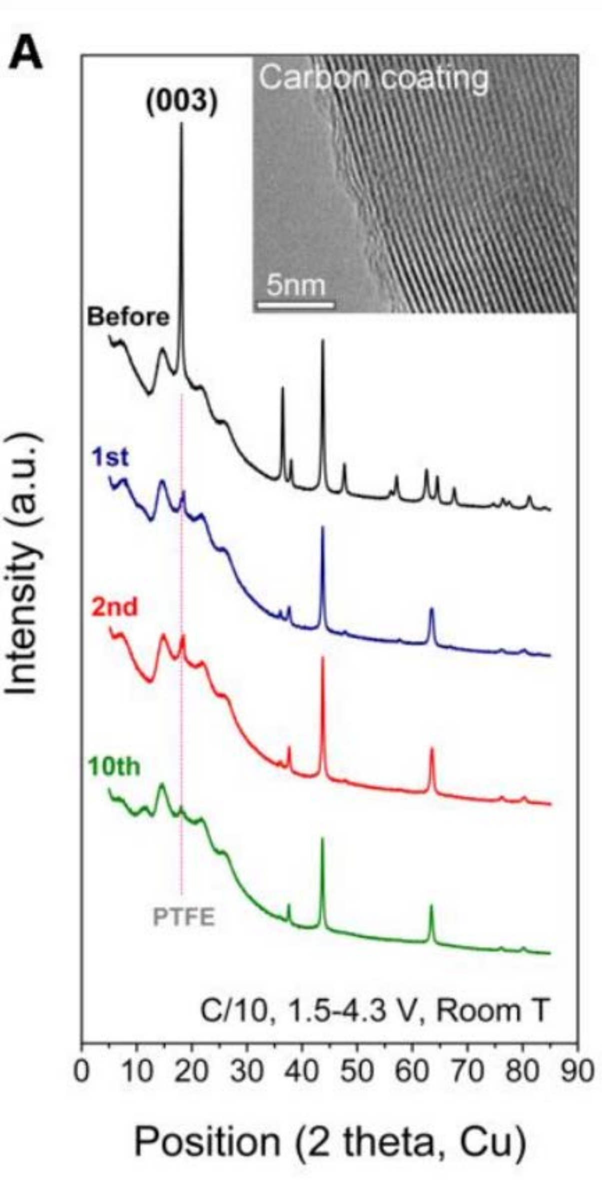
MO_2



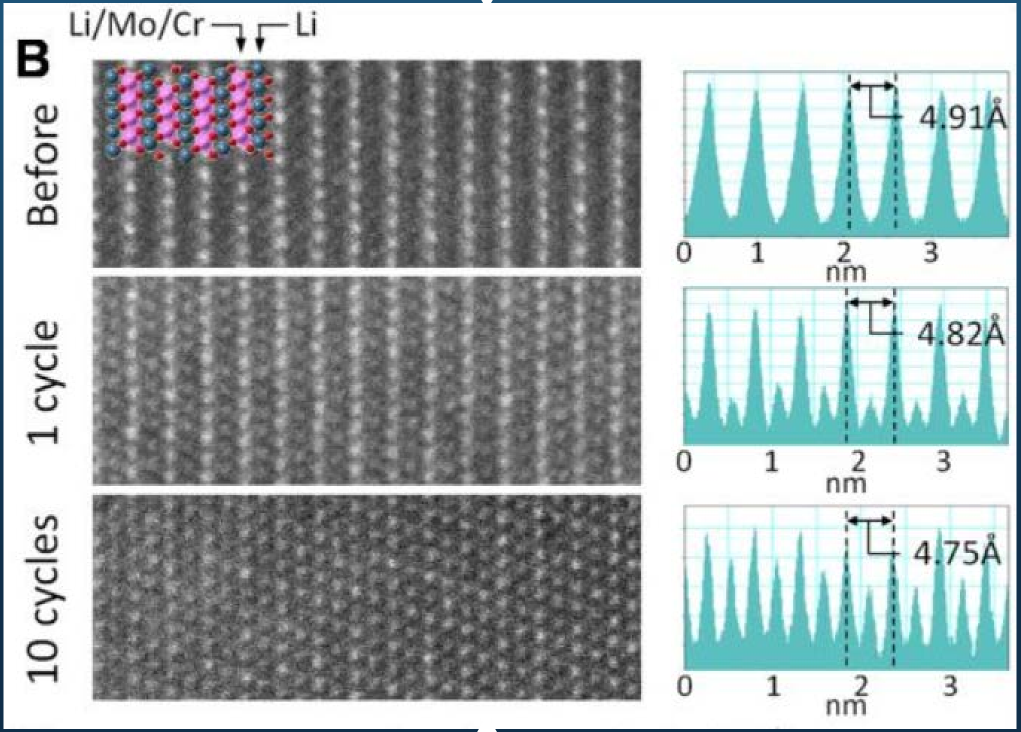
712 Wh/kg
3350 Wh/l
Density = 4.7

J. Lee, A. Urban, X. Li, D. Su, G. Hautier, G. Ceder, *Unlocking the Potential of Cation-Disordered Oxides for Rechargeable Lithium Batteries,* Science, 343 (6170), 519-522 (2014)

$Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$ (LMCO) becomes disordered after a single cycle



well-separated Li and TM layers



intense cation mixing

J. Lee, et al., Science, 343 (6170), 519-522 (2014)

Cathode Challenges

- Design Intercalation Structures that have high stability and high Li mobility over a very large range of Li concentrations and metal valence states

- One solution: cation disordered structures with Li-excess -> need to raise voltage w/o too much oxygen oxidation

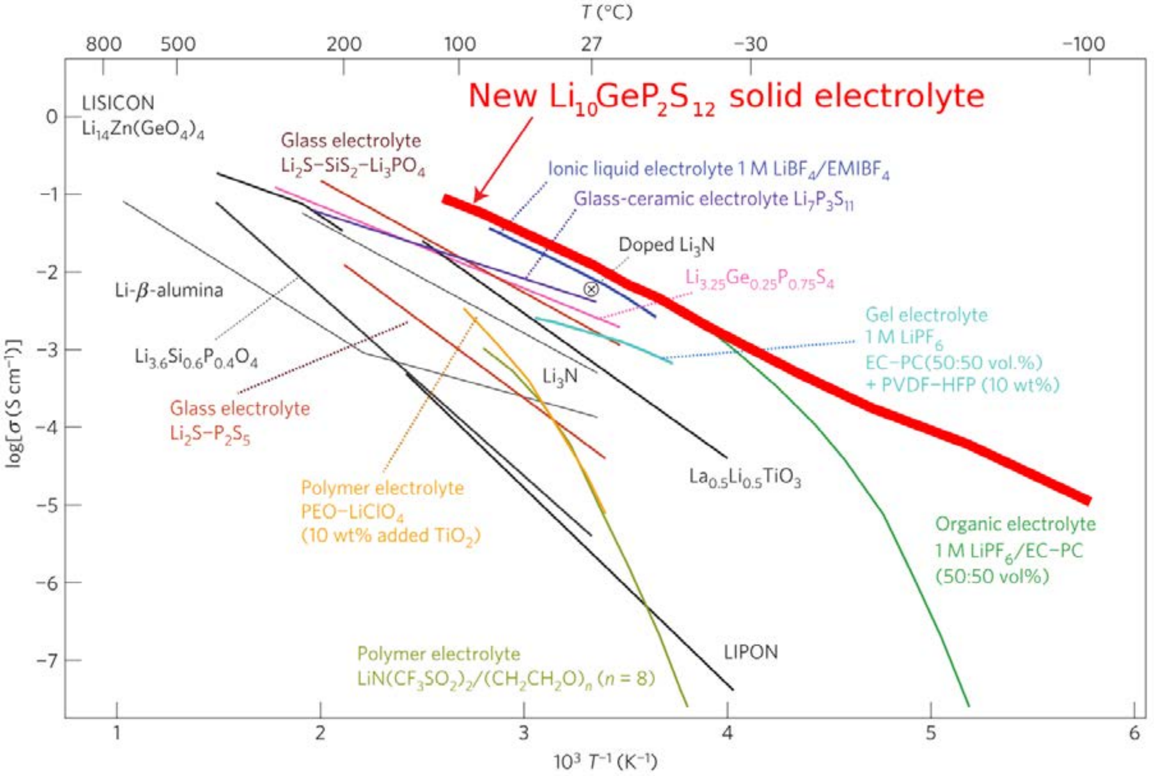
New Directions

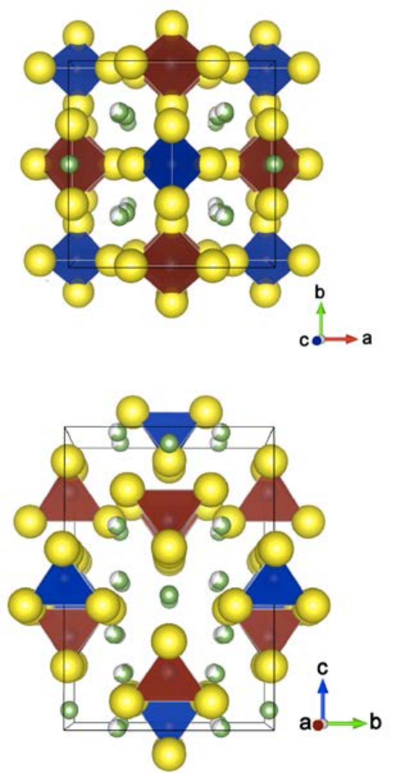
Solid State Electrolytes for Safe Li-ion Batteries

- Highly charged cathode material is oxidizing
- Thermal event can release oxidant form cathode and ignite electrolyte

Solid state inorganic electrolyte ?

$Li_{10}GeP_2S_{12}$: a new superionic conductor





- conductivity: 12 mS/cm @ 25 °C $E_a \approx 240$ meV

ISSUES

- Cost of Ge
- Moisture sensitivity of sulfides

N. Kamaya et al., A lithium superionic conductor. Nat. Mater. **10**, 682-686 (2011)

Digression: How is a battery made today ?

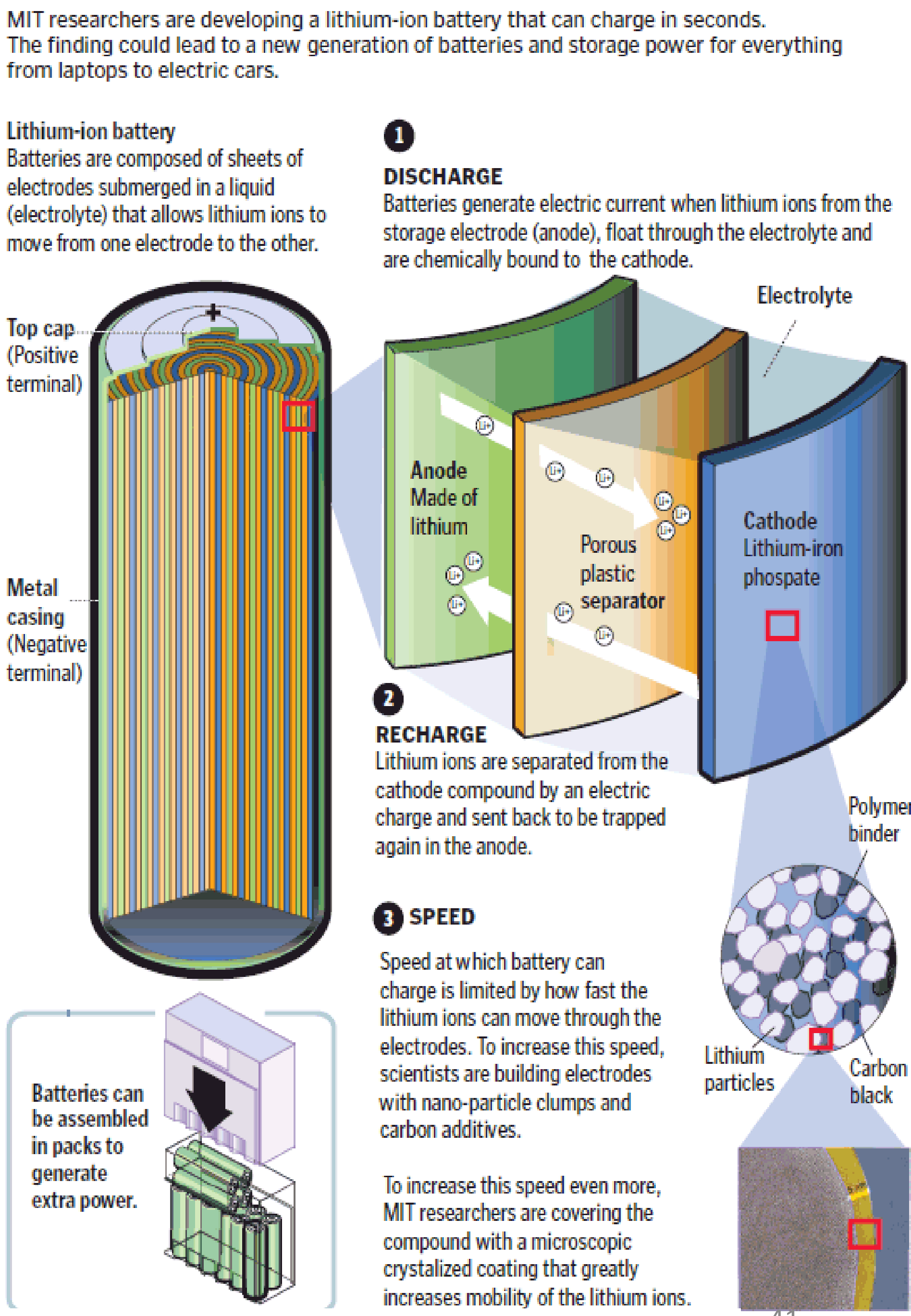
Cell Construction

Conductivity of Li in organic electrolyte is much less than protons in water

Cells are wound

Prismatic cells are folded and have better packing density for automotive

Electrodes are 100 to 400 μm thick, separator is 20 - 100μm


MIT researchers are developing a lithium-ion battery that can charge in seconds. The finding could lead to a new generation of batteries and storage power for everything from laptops to electric cars.

Lithium-ion battery
Batteries are composed of sheets of electrodes submerged in a liquid (electrolyte) that allows lithium ions to move from one electrode to the other.

1 DISCHARGE
Batteries generate electric current when lithium ions from the storage electrode (anode), float through the electrolyte and are chemically bound to the cathode.

2 RECHARGE
Lithium ions are separated from the cathode compound by an electric charge and sent back to be trapped again in the anode.

3 SPEED
Speed at which battery can charge is limited by how fast the lithium ions can move through the electrodes. To increase this speed, scientists are building electrodes with nano-particle clumps and carbon additives.

To increase this speed even more, MIT researchers are covering the compound with a microscopic crystalized coating that greatly increases mobility of the lithium ions.

Batteries can be assembled in packs to generate extra power.

Figure courtesy of Boston Globe

ZARRACINA/GLOBE STAFF

Form factors

Cylindrical 18650 is most commoditized cell

Fully automated winding machines

Prismatic somewhat more expensive, but preferred for some applications for stacking efficiency

Prismatic

Cylindrical

18650

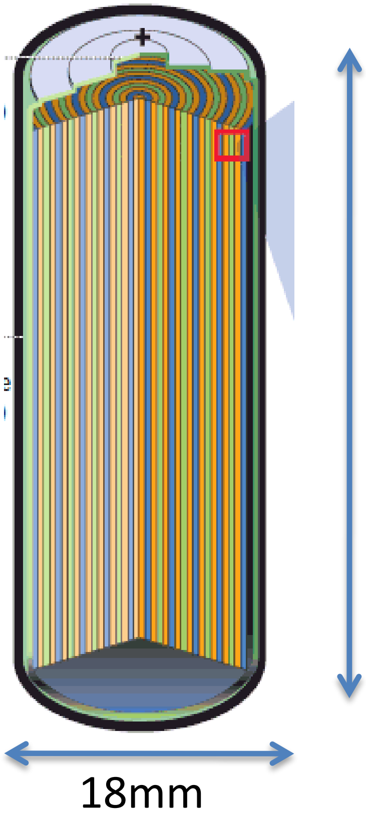
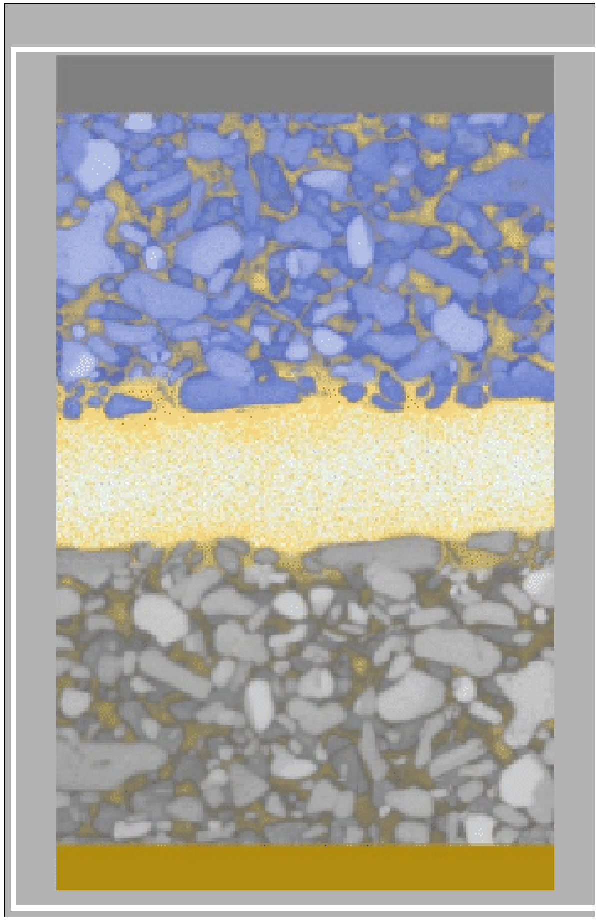
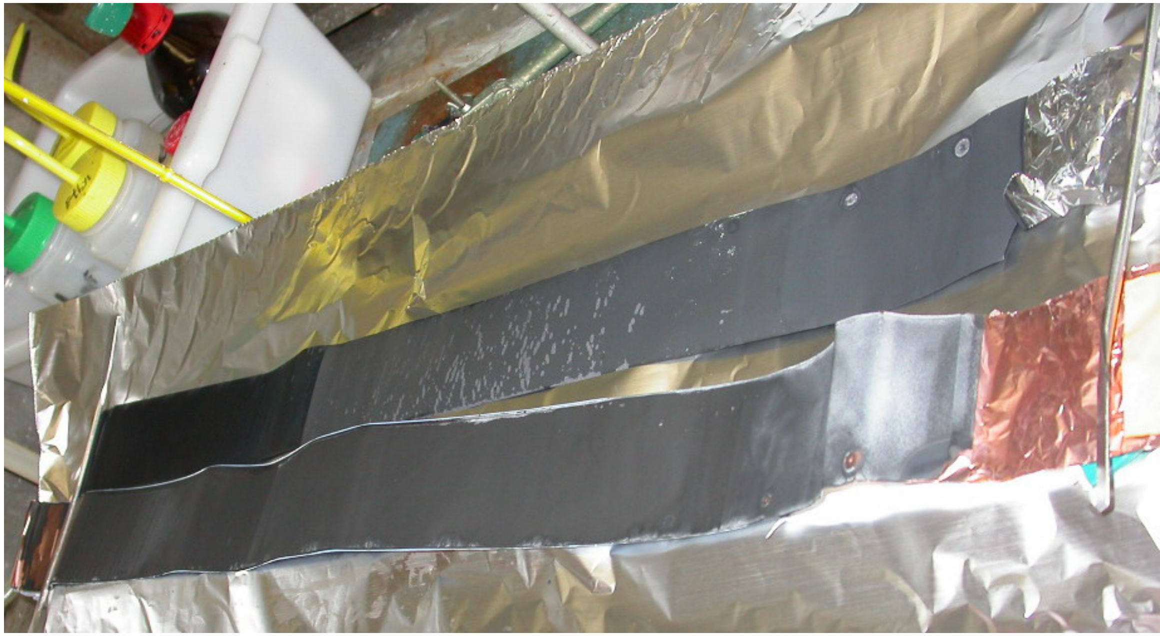


Figure courtesy of Boston Globe

Electrode film





Issues in Solid State Batteries

- Are there limits to solid state conductivity of Li+ ions ?

- How do we engineer a cell that can be made to scale at high speed and low manufacturing cost ?

- How do we characterize, predict, and control solid-state interfaces through mechanical and chemical changes ?

A really hard problem …

Can we diffuse multi-valent ions at room temperature ?

JCESR

JOINT CENTER FOR
ENERGY STORAGE RESEARCH

Magnesium technology would benefit significantly from metal anode

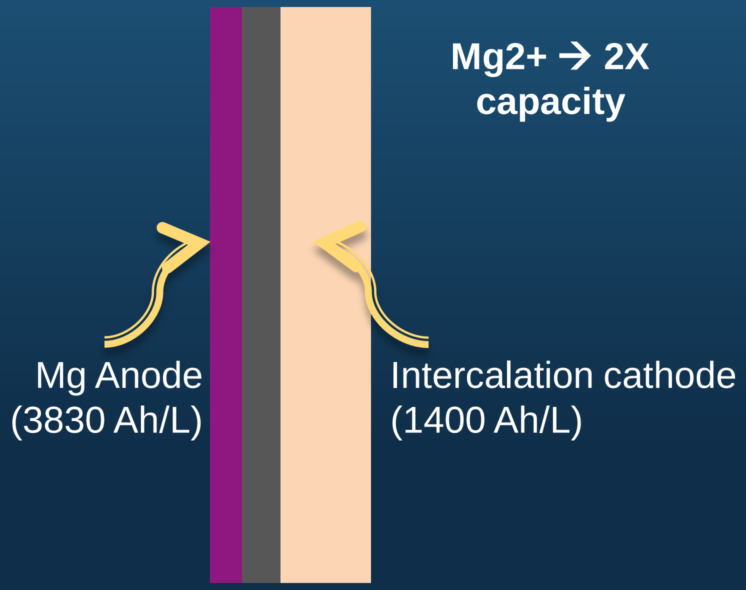
Even if cathode only has equivalent capacity

Commercial Li-ion Battery

Carbon Anode (700 Ah/L)

Oxide Cathode (700 Ah/L)

Magnesium Equivalent



Mg2+ → 2X capacity

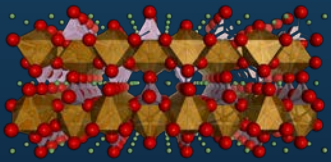
Mg Anode (3830 Ah/L)

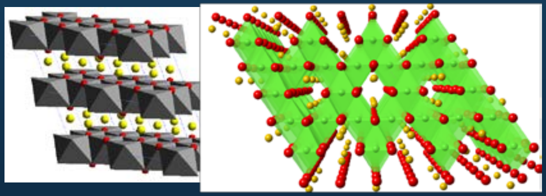
Intercalation cathode (1400 Ah/L)

Why Modeling: Lessons from Lithium Cathodes

Li-intercalation

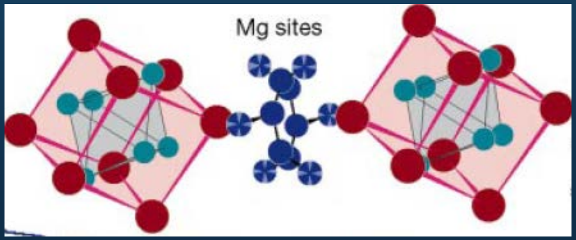
- After more than 40 years of research only a handful of functioning high energy density Li cathode materials – even less commercially available





MV-intercalation

- More difficult than Li-ion. Since 2000 only one well functioning cathode (Mo_6S_8)



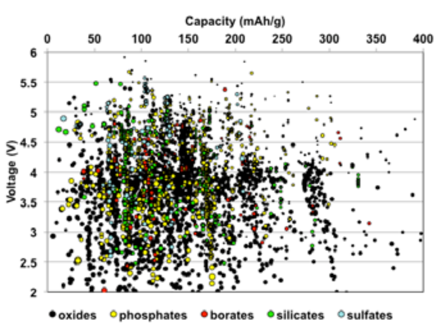
Need computational machinery to pre-screen and direct towards promising design directions

The Materials Project: Vision

www.materialsproject.org

Kristin Persson: Director of the Materials Project

Compute the basic properties (“genes”) of materials across the world of compounds and disseminate that information to the materials community to enable rapid materials searching and design.



Provide well curated, well integrated data

BERKELEY LAB
Lawrence Berkeley National Laboratory

University of California San Diego

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Gerbrand Ceder
Shyue Ping Ong
Evgueni Chtykov

DTU

California Institute of Technology 1891

The University of Wisconsin Madison

NERSC National Energy Research Scientific Computing Center

er
ia
ier

Argonne National Laboratory

Duke University

University of California, Berkeley

Mark Asta

NUS National University of Singapore

Stefan Adams

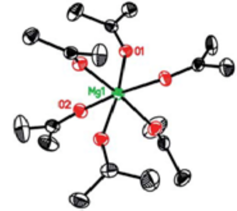
UK University of Kentucky

Alan Dozier
Matthew J. Beck

UCL
Université Catholique de Louvain, Belgium

Geoffroy Hautier

Joint Center for Energy Storage Research (JCESR)



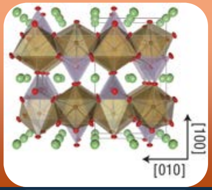
Electrolyte Genome

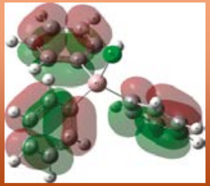
A design platform for novel electrolytes and redox-active molecules

Computational structural/chemical/property data for 10^4-10^5 solvents, salts, and redox molecules; organized for interactive searching and design

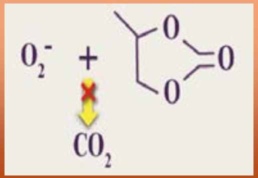
Prioritized target property list for each thrust

Multivalent Intercalation



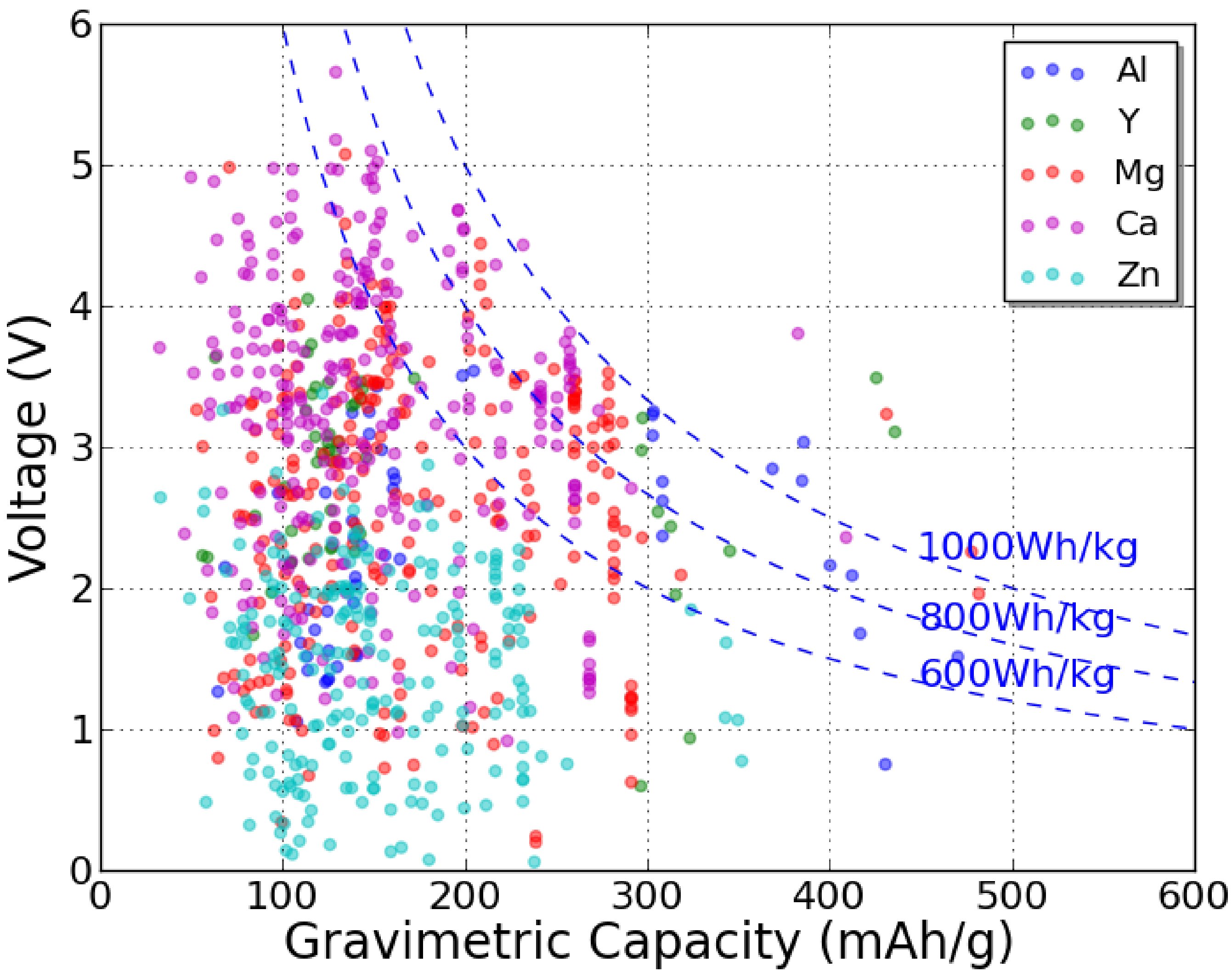


Chemical Transformation

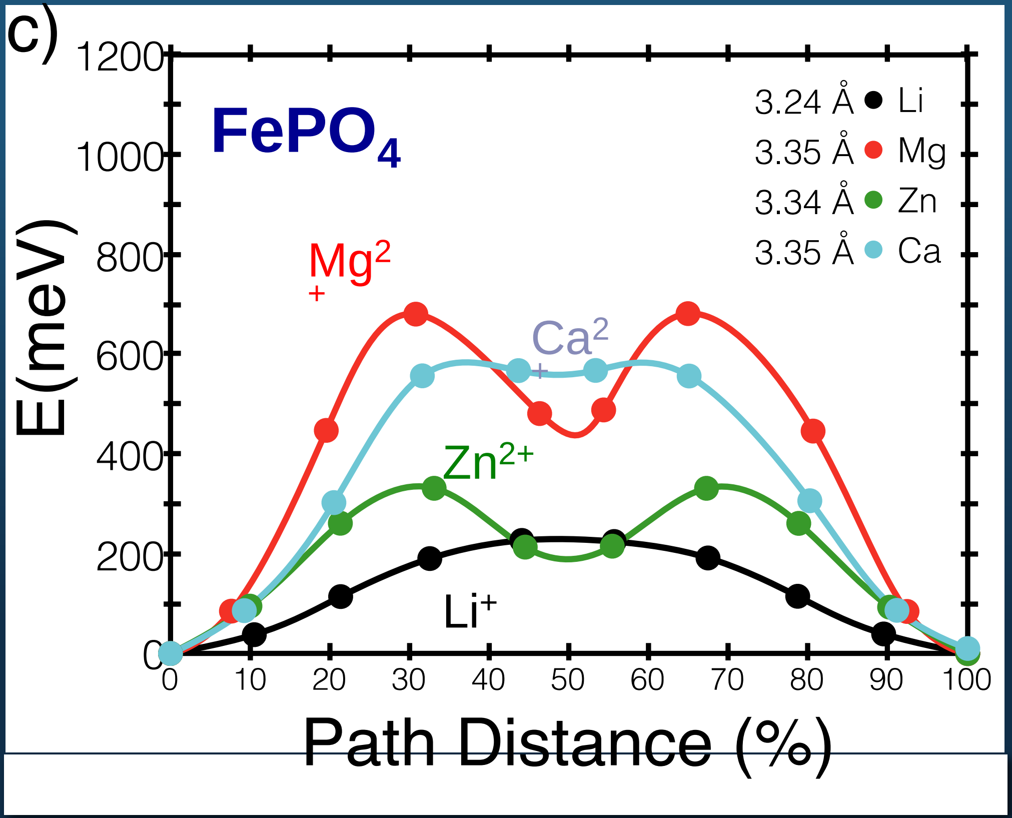


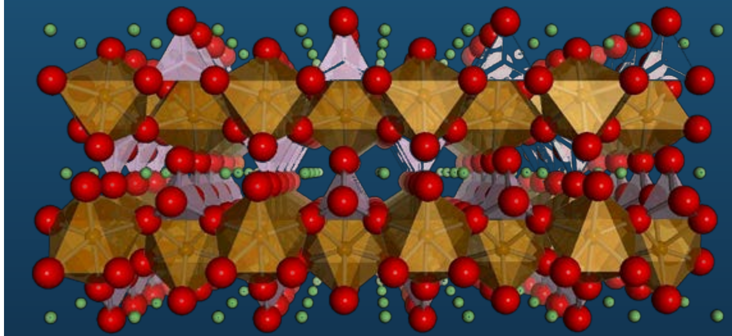
Non-Aqueous Redox Flow

Materials Project: Voltage + stability screening



Good diffusers for lithium are not necessary good for MV





- Mg^{2+} not likely to work
- Ca^{2+} borderline
- Zn^{2+} OK

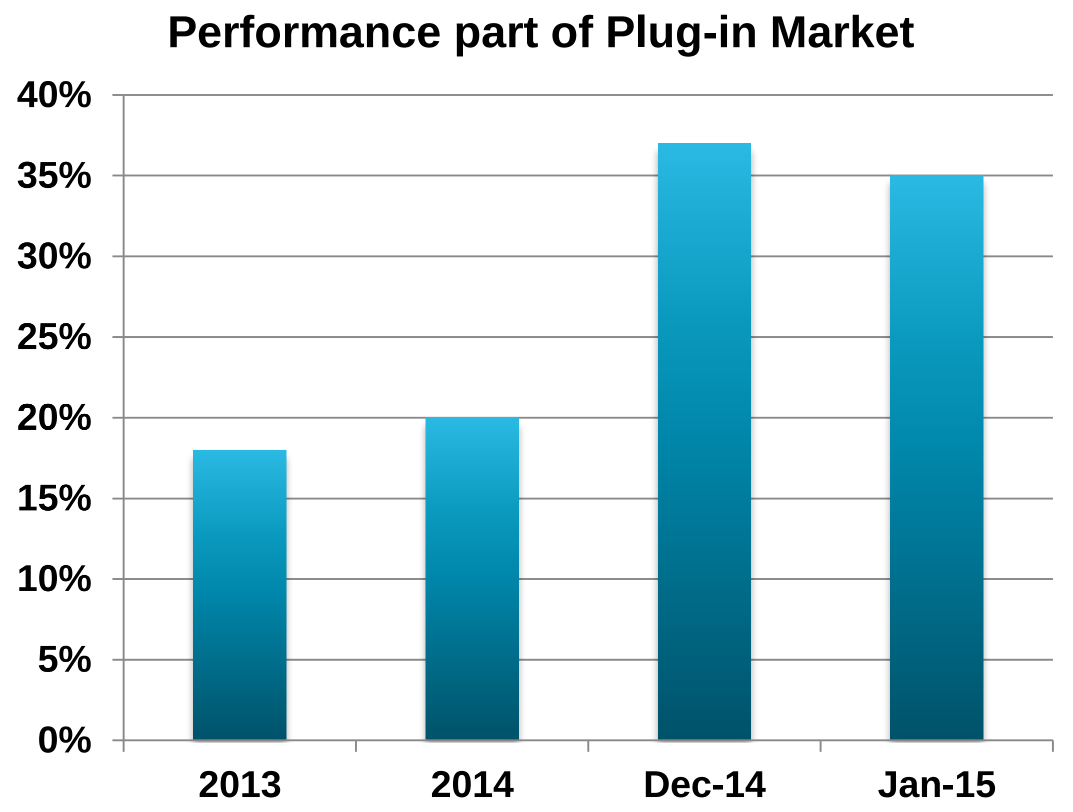
My thanks

Grid Energy Storage Projects Around the World

Lithium-Battery Grid Storage Projects (700 MW total ≈ 2-3 GWh)

California mandate: 1.3 GW by 2022 (≈ 5GWh)

Performance part of market is growing



Top 4 for Jan 2015 (US)

Tesla-S	**1100**
Nissan Leaf	**1070**
BMW-i3	**670**
Chevy Volt	**542**

Performance segment = Tesla, BMW, Porsche

BMW i8

- Plug in Hybrid
- 0 – 60mph in ≈ 4.4 secs
- Power 96 kW (electric) + 170 kW(IC)
- Sells above retail price (> 2,000 sold as of Jan 2015)