

A (Very Brief) History of The Battery

Amy L. Prieto
CSU



Alessandro Volta's battery (circa 1800 A.D.): copper and zinc separated by cardboard soaked in brine

However, jars have been discovered outside Baghdad dating to **200 B.C.**:
iron rod, encased in copper, and soaked in vinegar or wine (0.78 V)

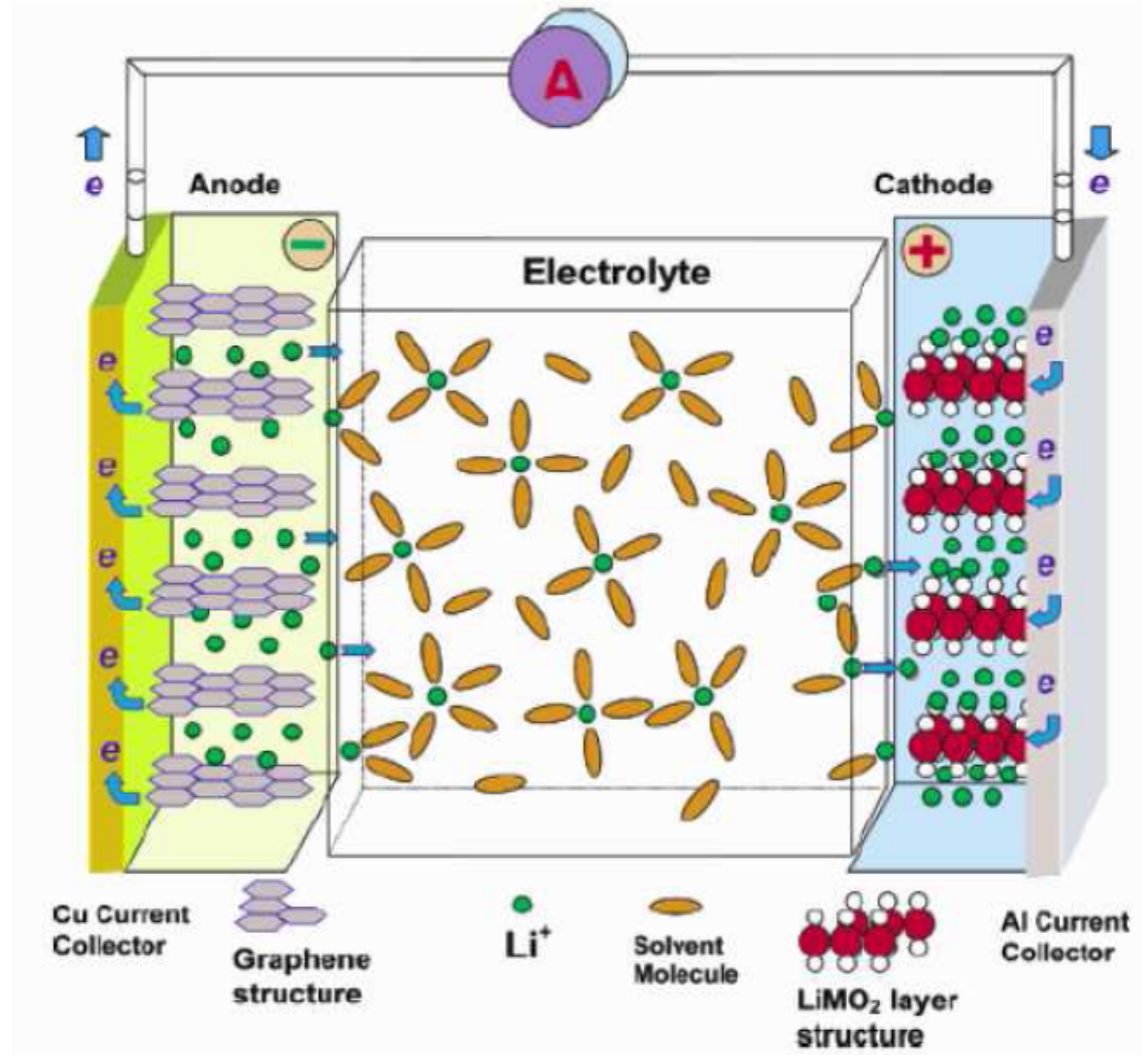
How Batteries Affect Your Life



The Main Components of a Typical Li-ion Battery

Components

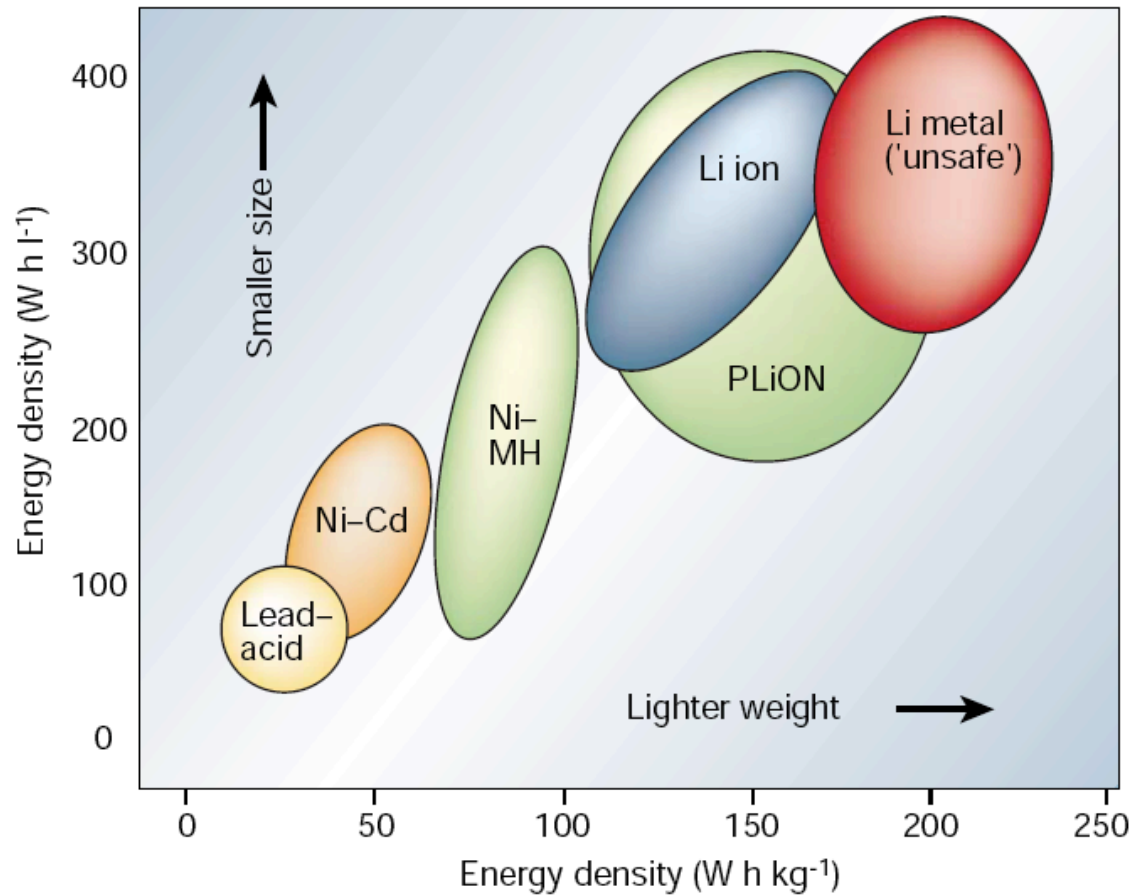
- Anode (Carbon)
- Cathode (LiCoO₂)
- Electrolyte (EC/DMC with LiPF₆)
- Separator (Polypropylene)



Topics to be discussed

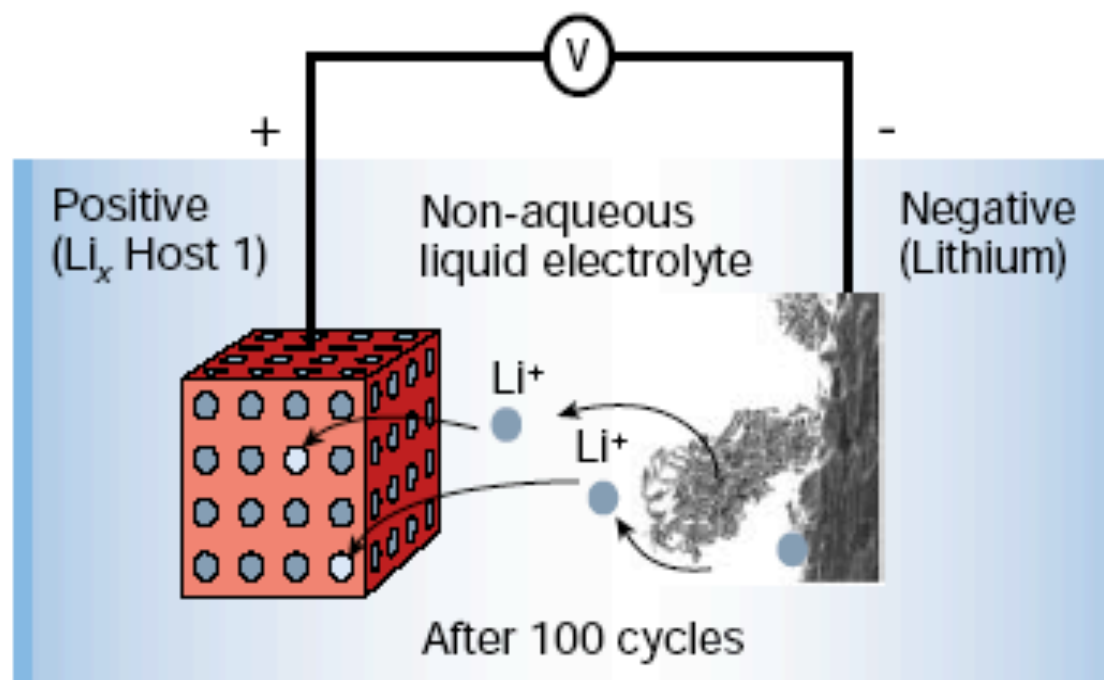
- Stability of Li (dendritic growth)
- Volume expansion challenges in electrode materials (*anodes*)
- Redox reactions in batteries
 - Energy level diagrams, which determine the electrochemical window of a battery
 - Solid-electrolyte-interfaces
- The importance of diffusion rates

Rich Battery Chemistry



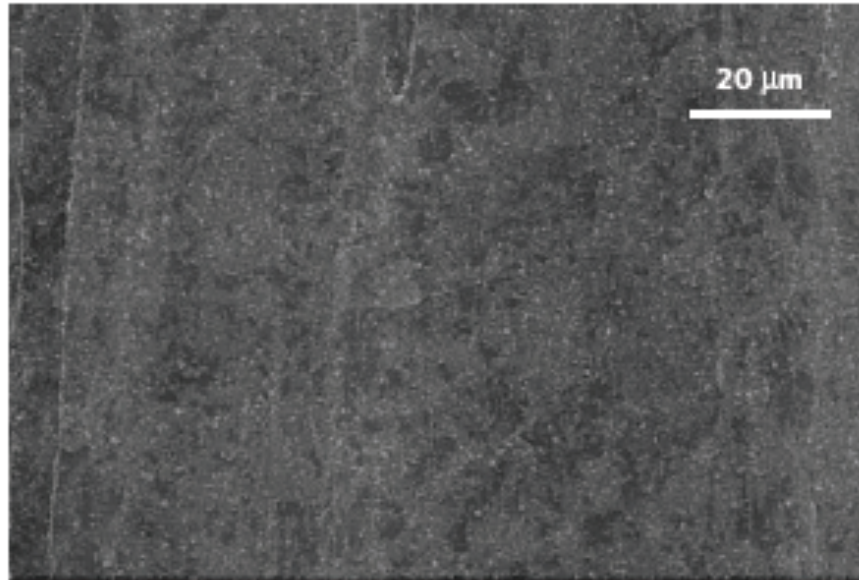
Advantages to Li: light, large electrochemical window

Intercalation Chemistry: Anodes

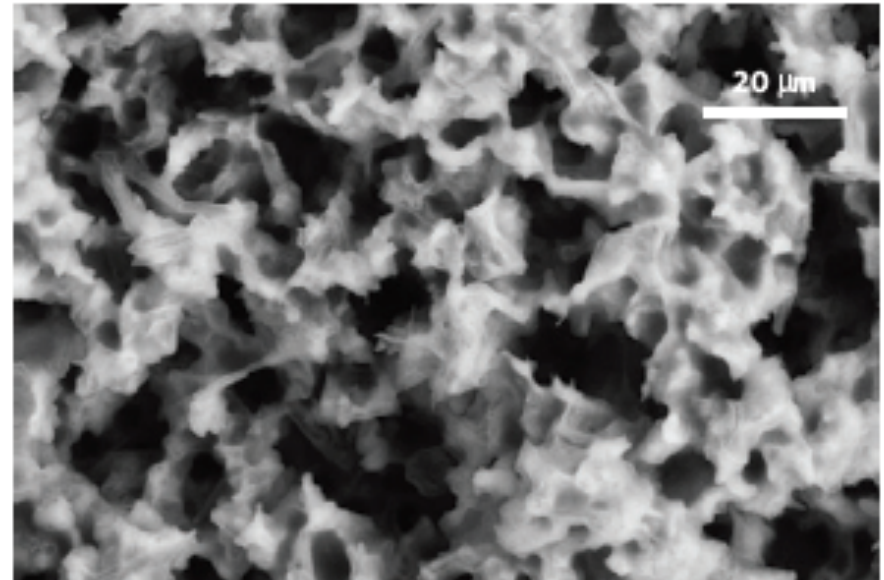


Dendritic growth of Li onto Li metal anodes

Li-Dendrite Growth: Cause of Safety Failures



bare Li

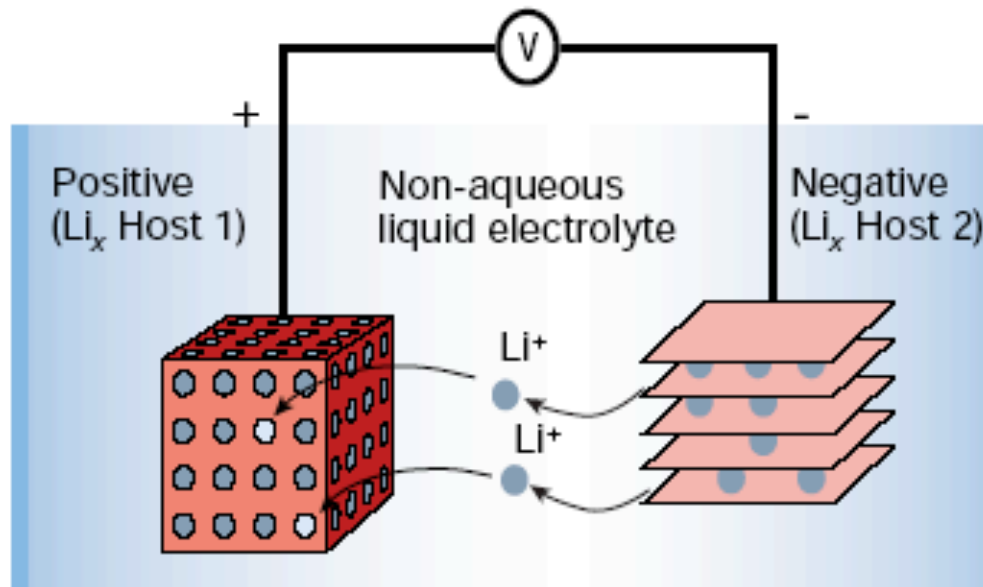


Li surface after charging

- Li dendrites puncture the separator, causing a short
- liquid electrolyte is flammable
- LiCoO_2 cathodes decompose to generate O_2



One solution: Graphite



Current commercial batteries have graphite anodes
trade-off is lower energy density

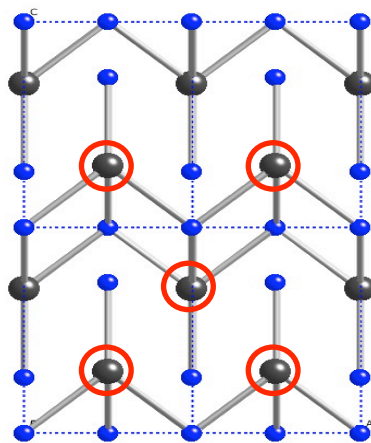
Cu₂Sb

Graphite based materials are the current standard

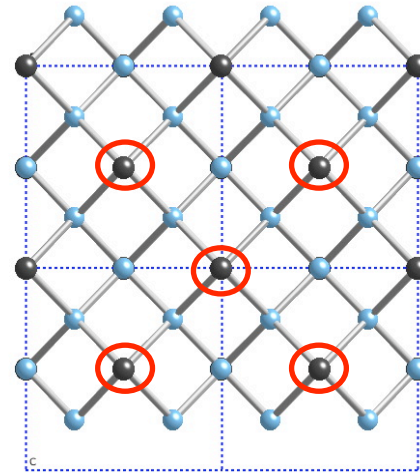
Theoretical capacity of 372 mAh g⁻¹ (818 mAh ml⁻¹) (LiC₆)

Cu₂Sb improves cyclic stability

Experimental value of 290 mAh g⁻¹ (1914 mAh ml⁻¹)



Cu₂Sb



Li₃Sb

Volume changes are significant

Sn 300%

Si 400%

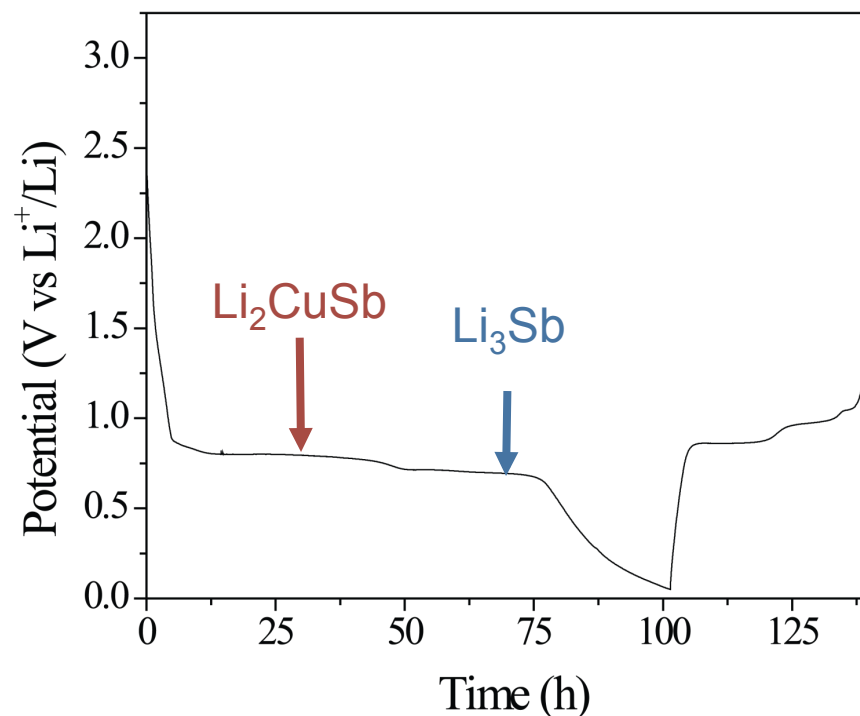
Cu₂Sb 73%

Strong structural relationship between parent and child compound

No danger of plating Li metal

Lithiation of Cu₂Sb

- Lithiation of Cu₂Sb has two main characteristic plateaus:
 - 1st at ~0.8 V vs. Li/Li⁺
 $\text{Cu}_2\text{Sb} \longrightarrow \text{Li}_2\text{CuSb}$
 - 2nd at ~0.6 V vs. Li/Li⁺
 $\text{Li}_2\text{CuSb} \longrightarrow \text{Li}_3\text{Sb}$
- The charge before 0.8 V is due to SEI formation and formation of Li₂O (if oxide is present)



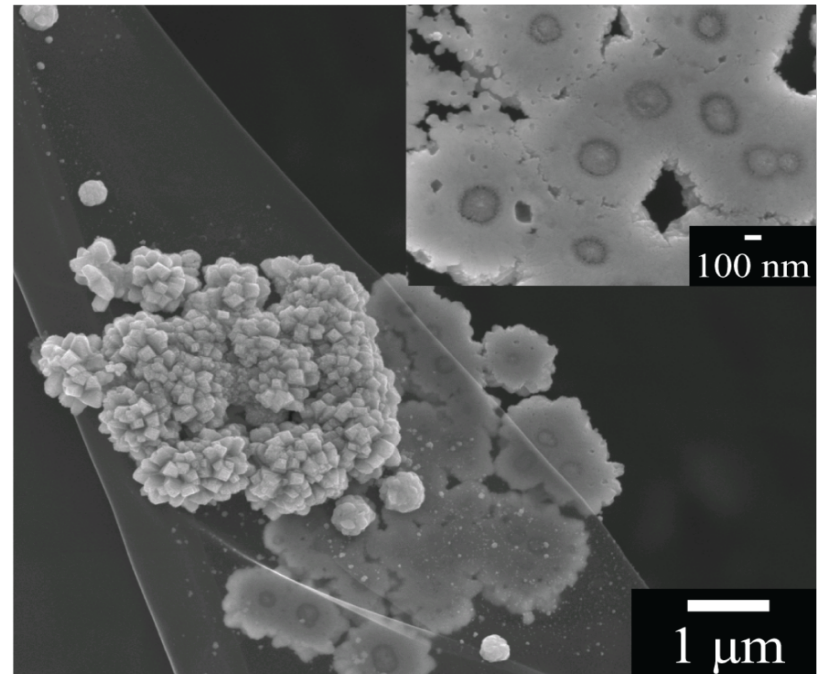
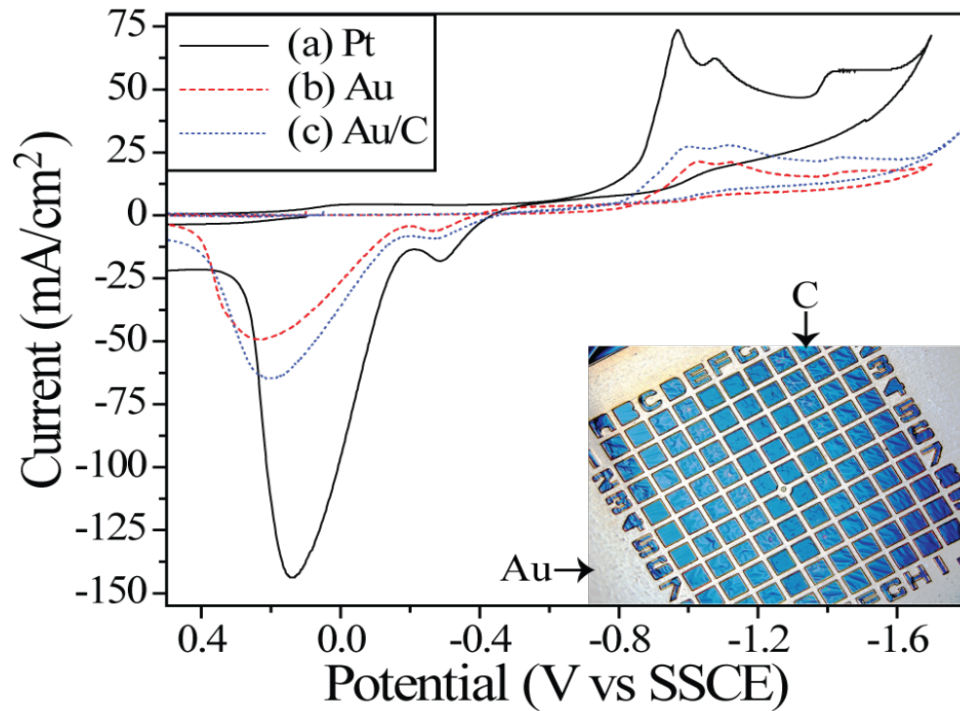
Cu₂Sb thin film

C/100

1M LiClO₄

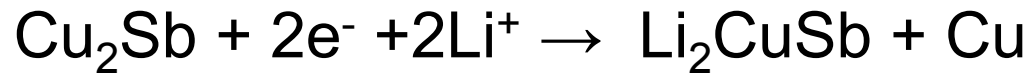
(1:1:1 by vol.) EC:DEC:DMC

Depositing onto TEM Grids

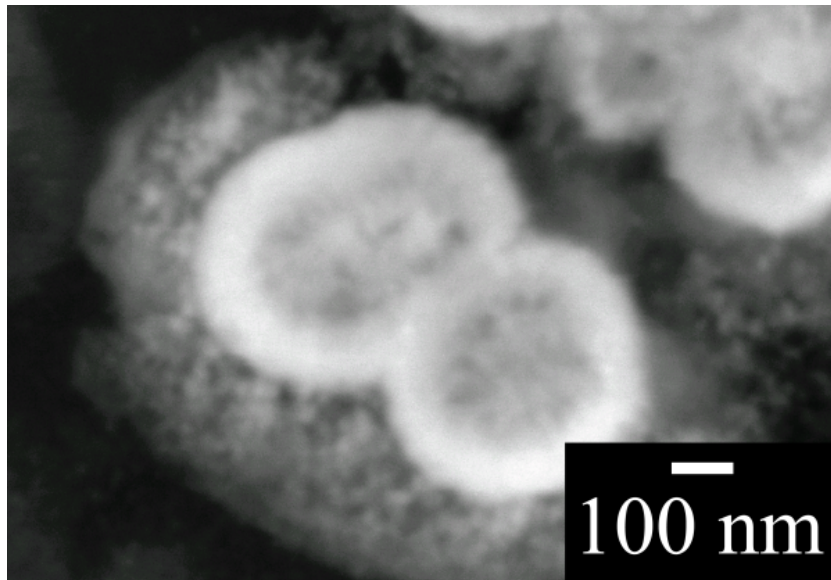


First Charge Plateau

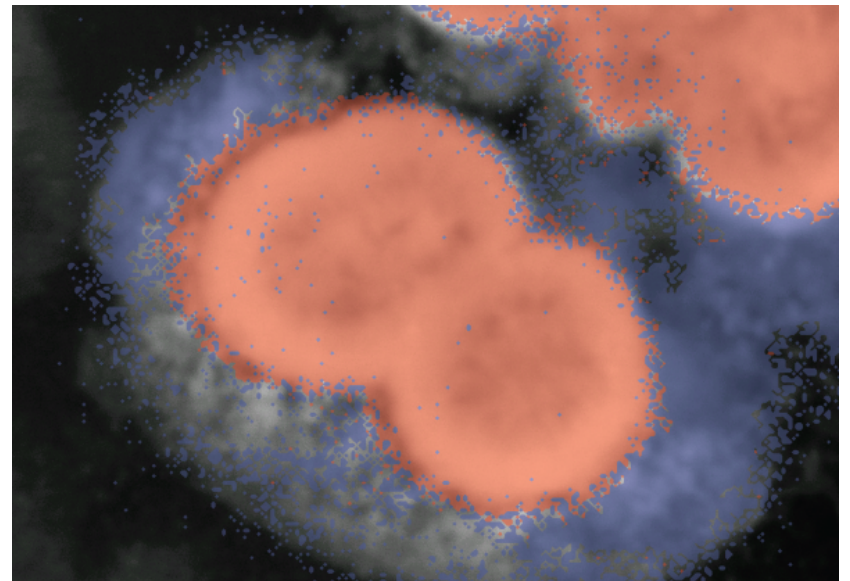
The 1st step in the lithiation process occurs at 0.8 V vs Li/Li⁺



~0.4 mole to 1 mole of Cu per mole of Cu₂Sb is extruded



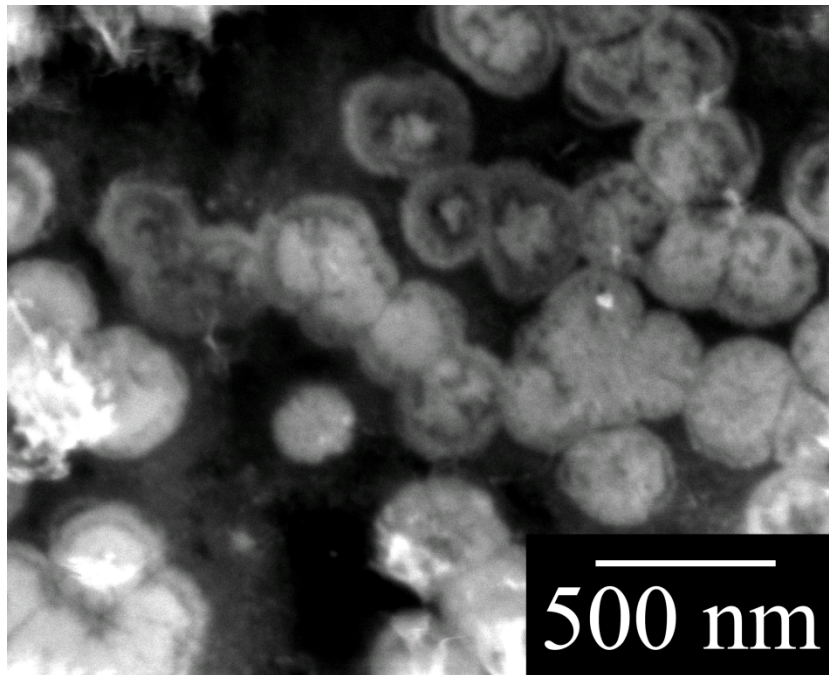
Cu rich
Sb rich
Relative to
Cu₂Sb



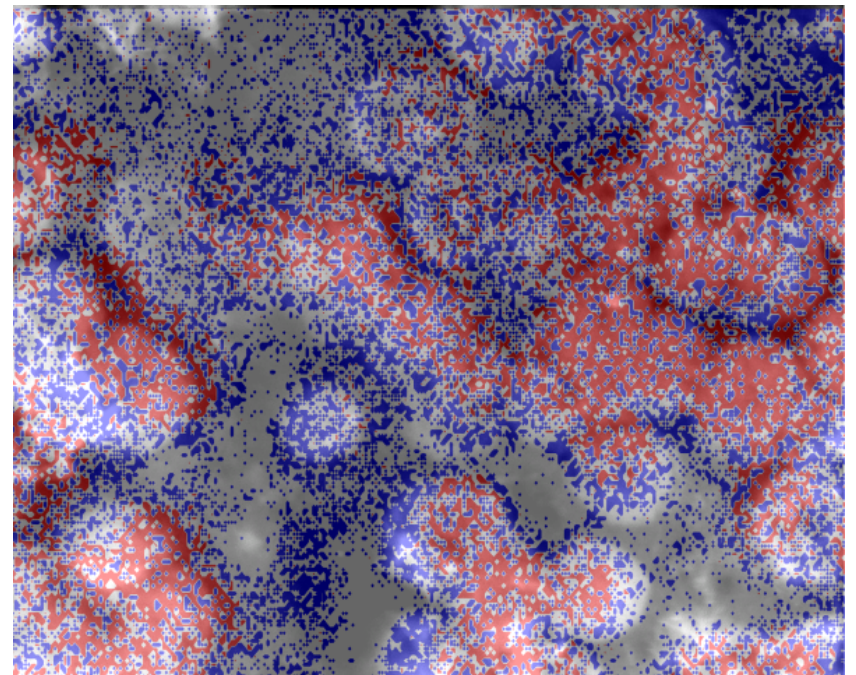
The extruded Cu particles surround the nucleation sites

Second Charge Plateau

The 2nd step in the lithiation process occurs at 0.6 V vs Li/Li⁺



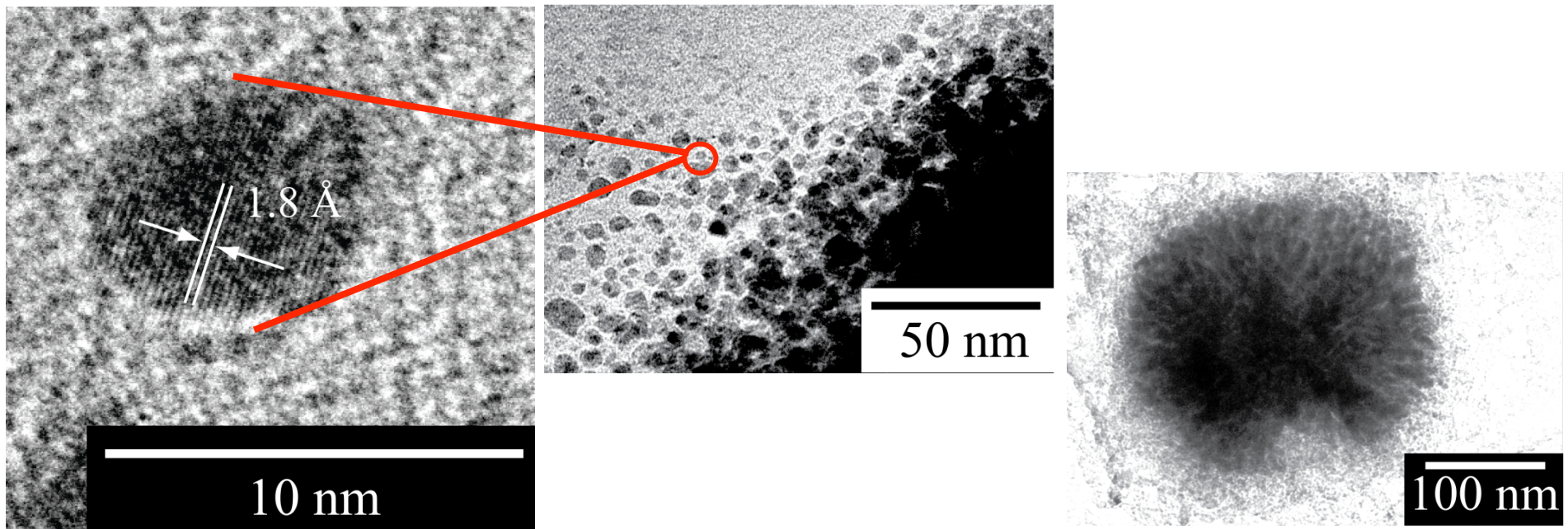
Cu rich
Sb rich
Relative to
Cu₂Sb



Extruded copper is further from nucleation site

Extruded Cu Particles

The extruded Cu is in the form of small < 10 nm particles

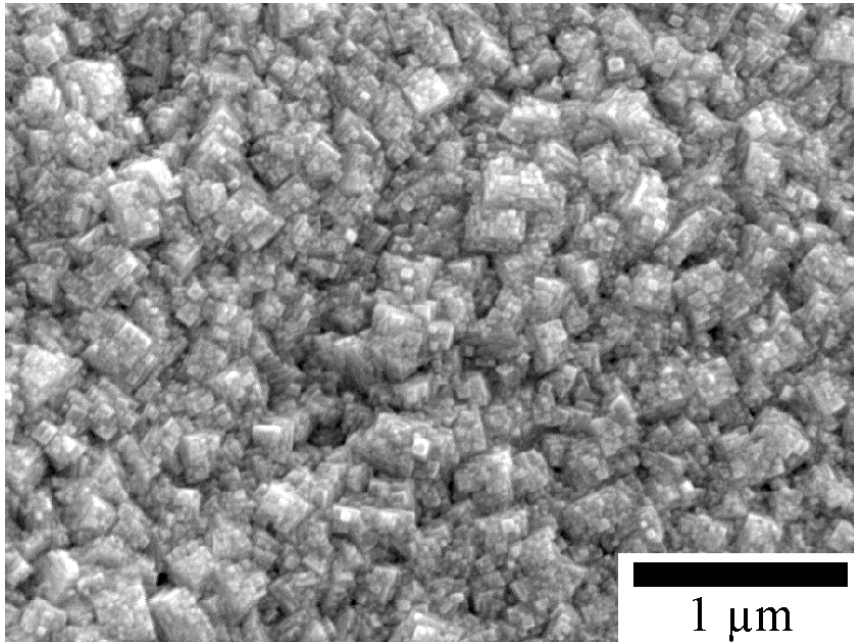


By 0.6 V the Cu particles have traveled from the core and lattice fringes that match Cu(200) are present

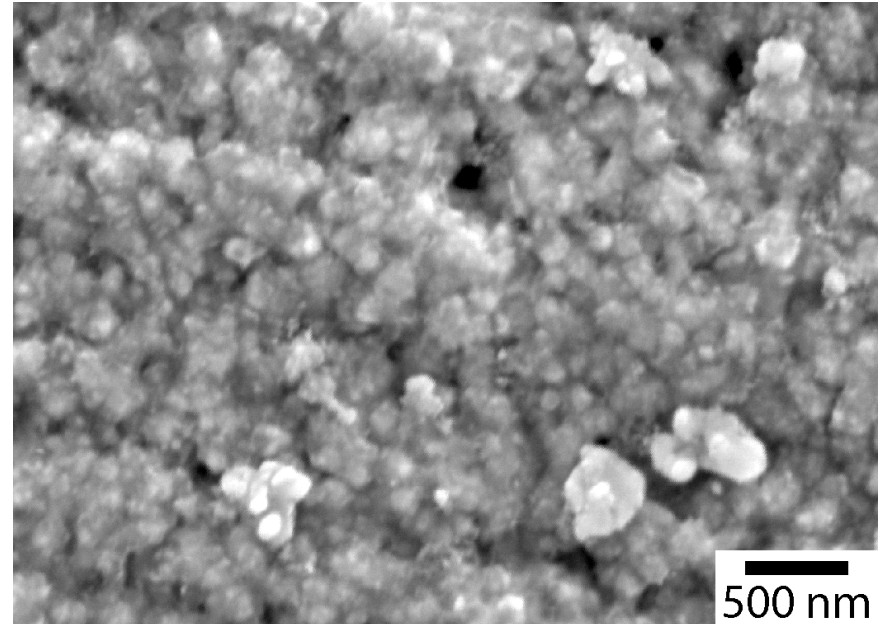
For examples of other systems that extrude metal particles see E. Takeuchi (Ag)

Using a Physical Barrier to Keep the Cu in Contact

Cu_2Sb Film

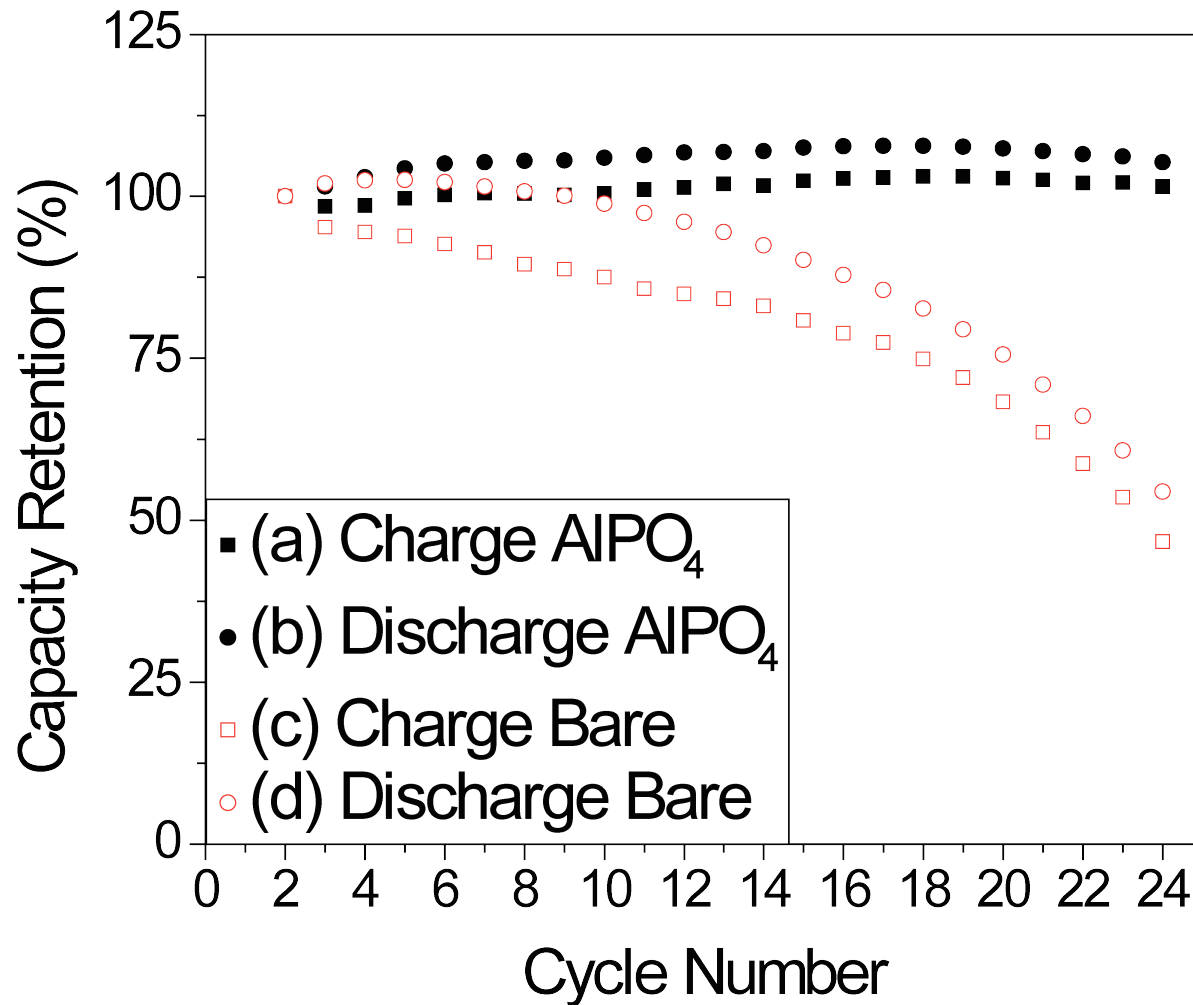


AlPO_4 Coated Cu_2Sb Film



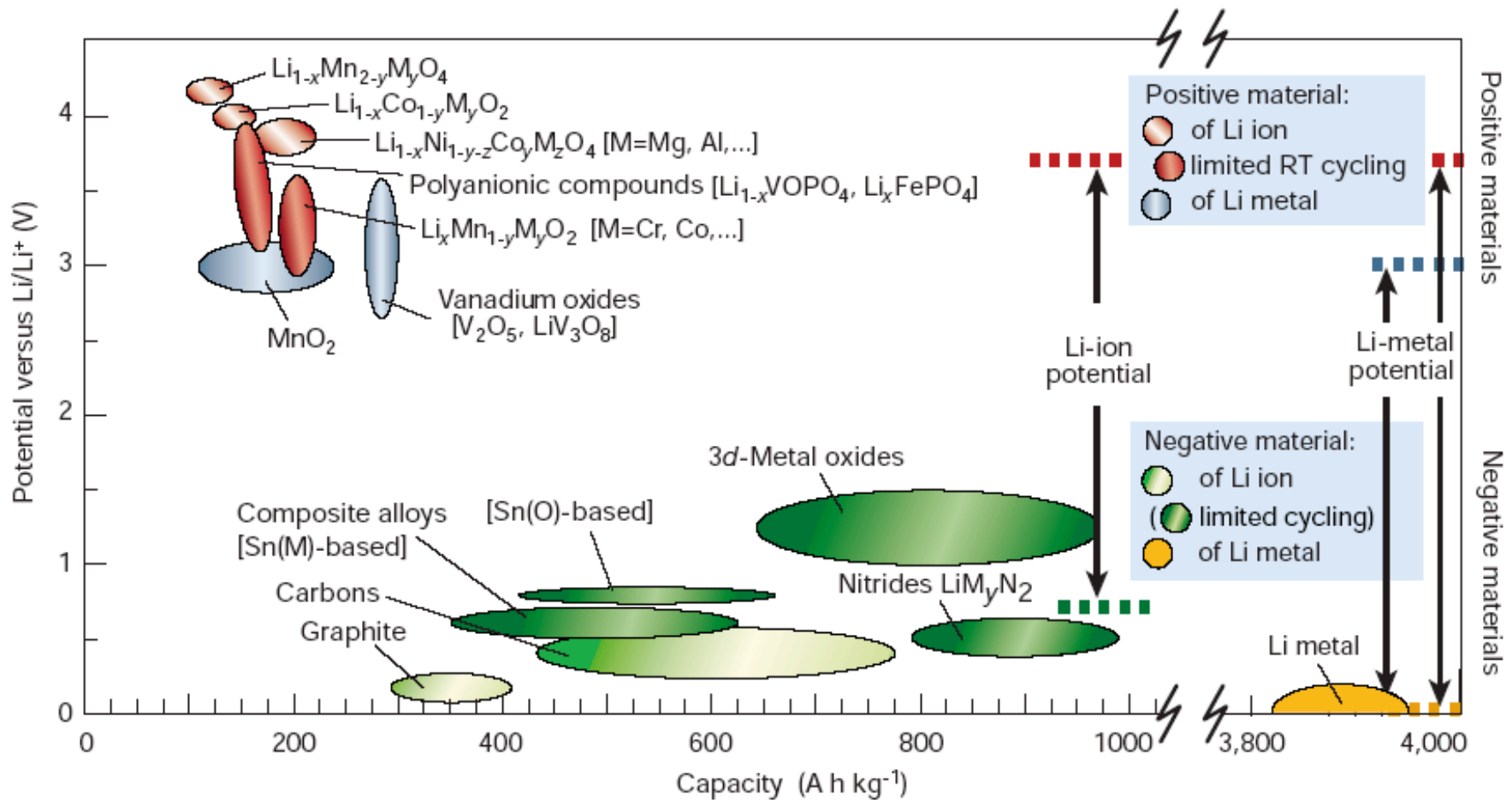
AlPO_4 can be coated onto the Cu_2Sb surface 'electrochemically'

Enhanced Capacity Retention



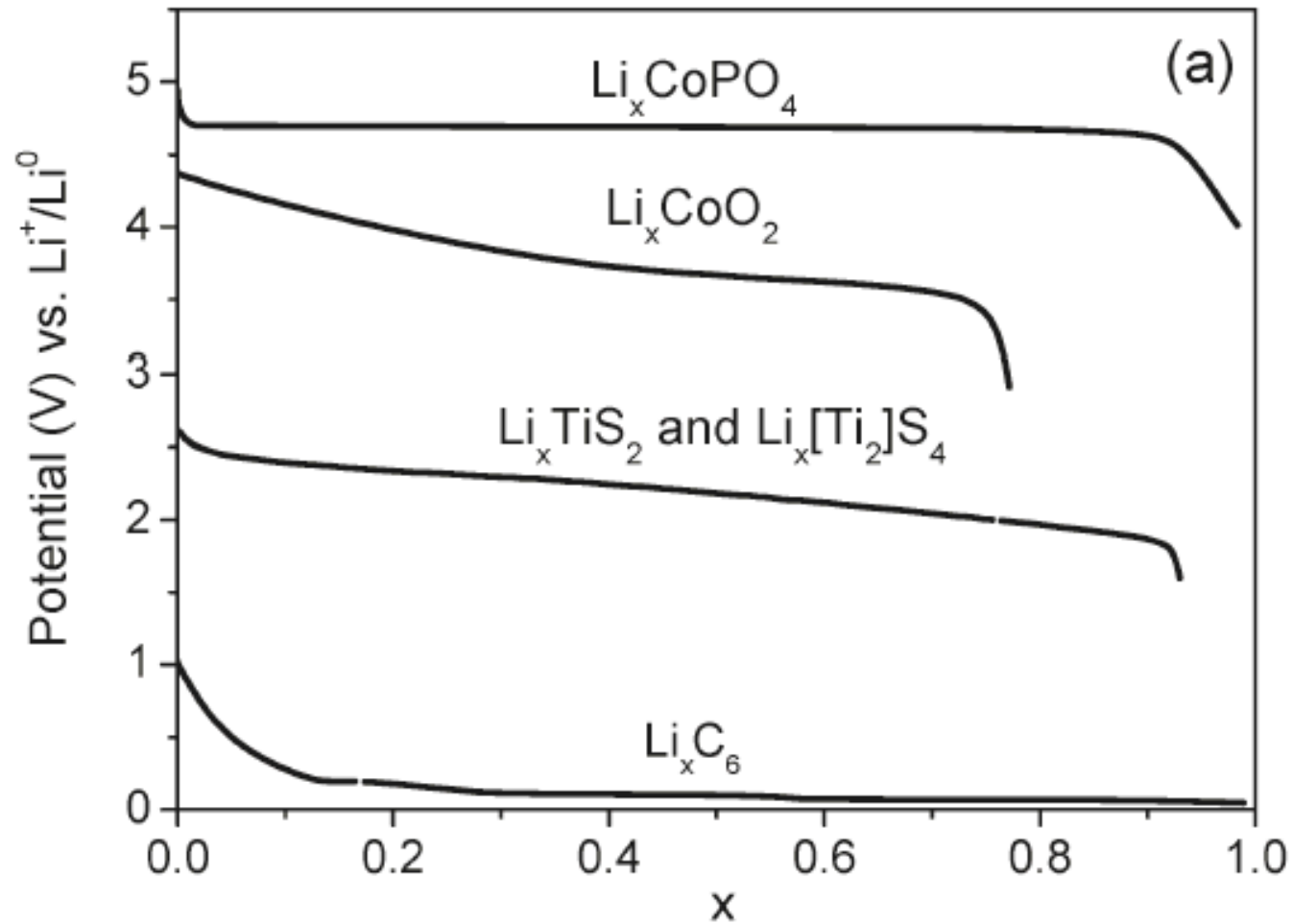
AlPO₄ coated Cu₂Sb films have a higher capacity retention

Different Chemistries

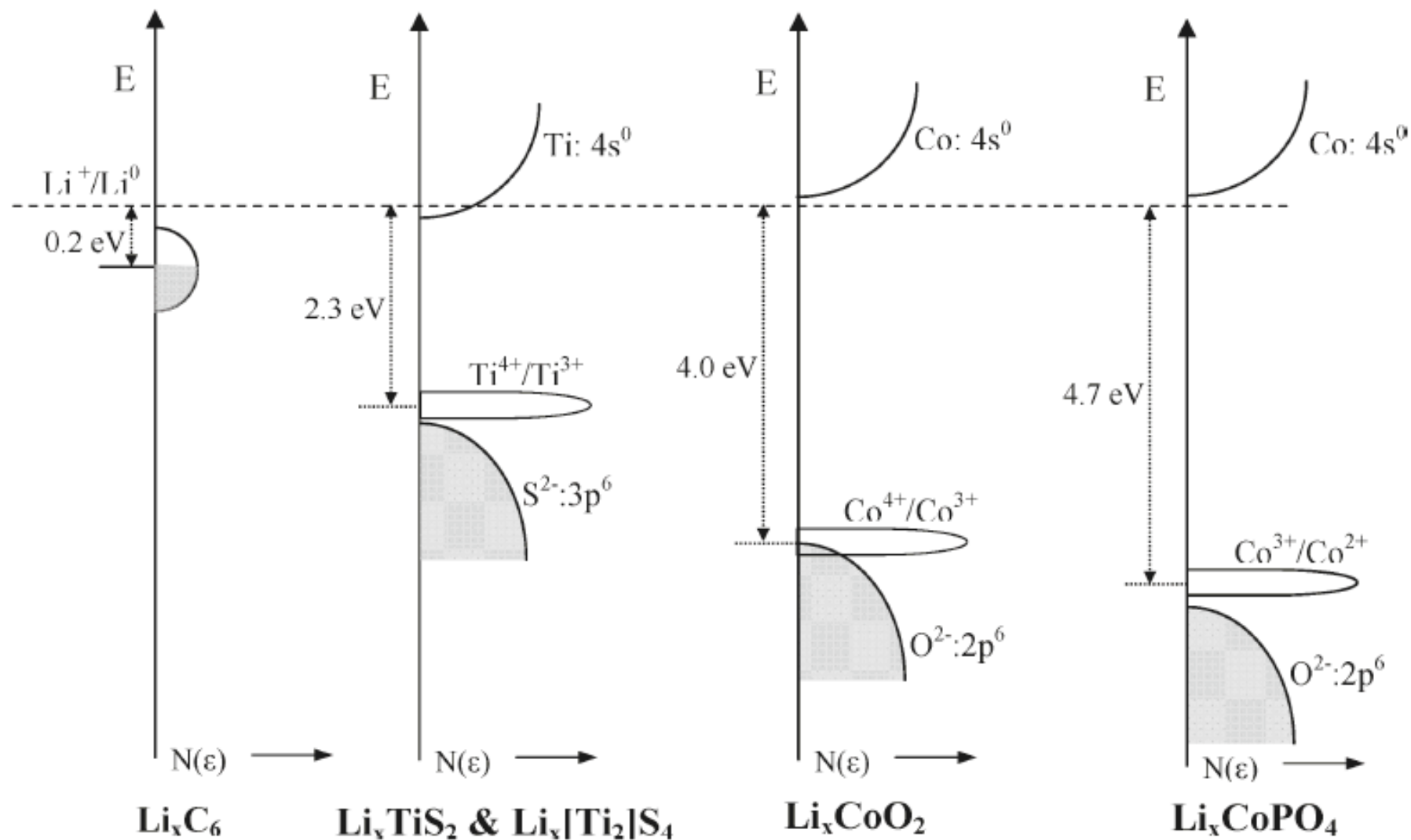


There is still a significant interest in solving the Li-dendrite problem.

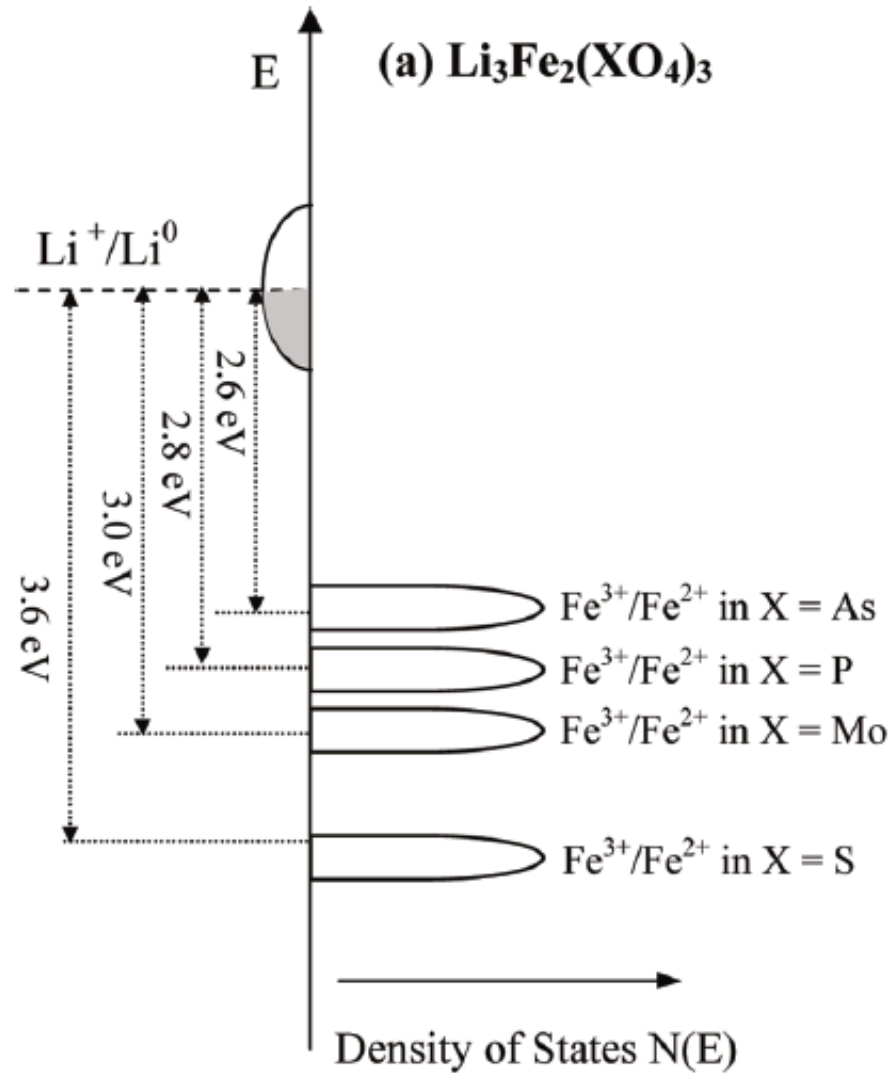
Voltage profiles of common cathodes



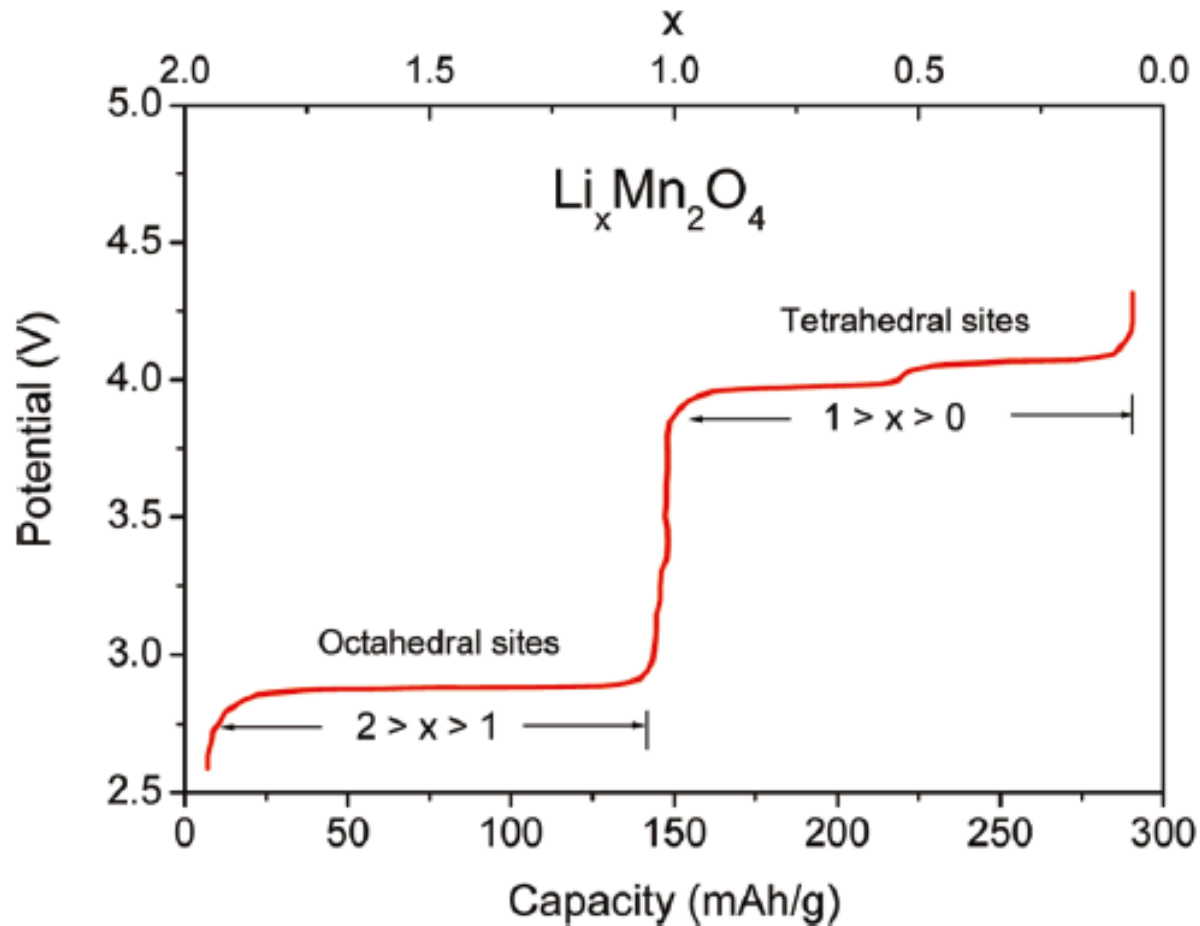
Energy level diagrams



Tunability Using Crystal Chemistry

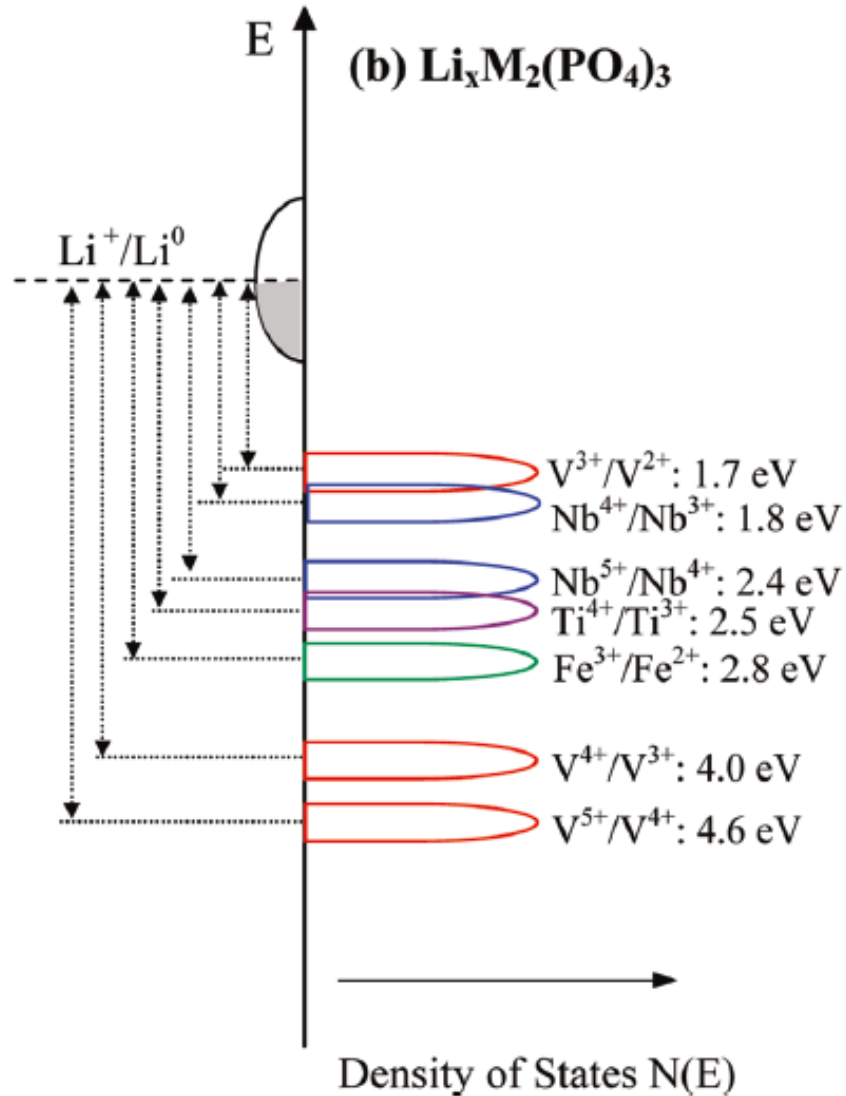


Effect of Geometry



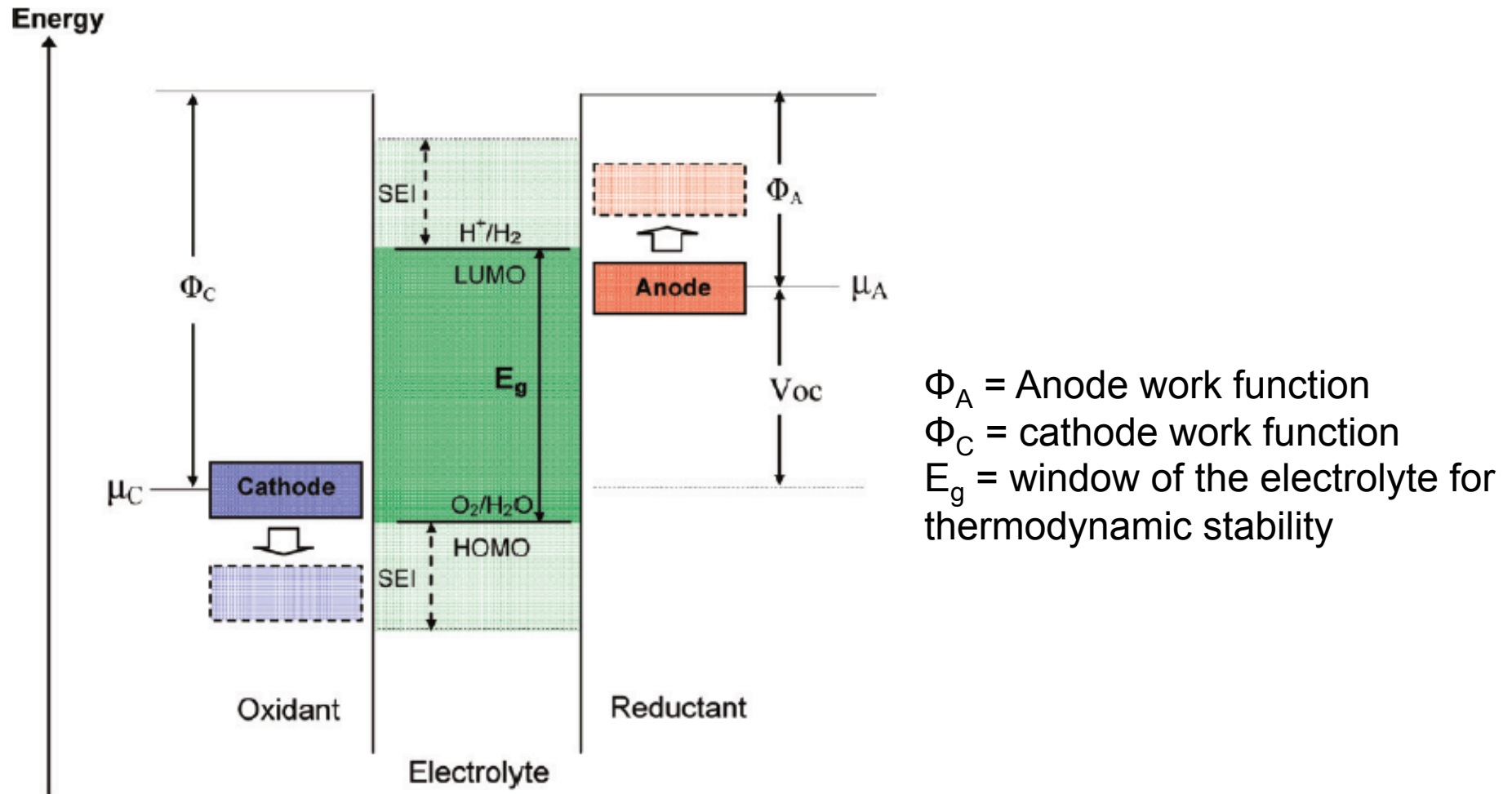
But if you take all of the Li^+ out, the structure collapses and it isn't reversible.

Changing the transition metal



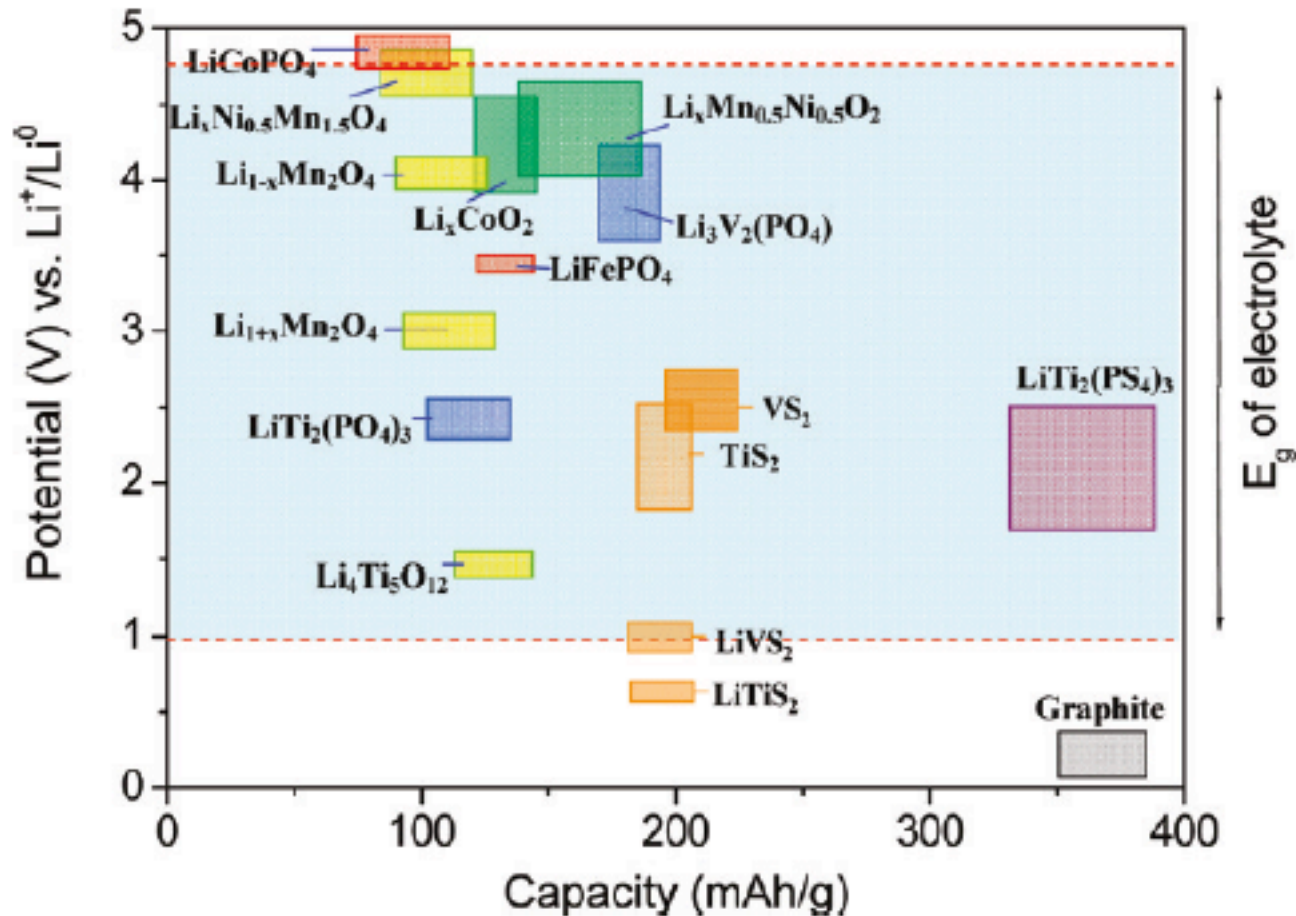
The challenge is that when you make the voltages large, you have to worry about unwanted reactions with the electrolyte

Liquid Electrolyte Stability



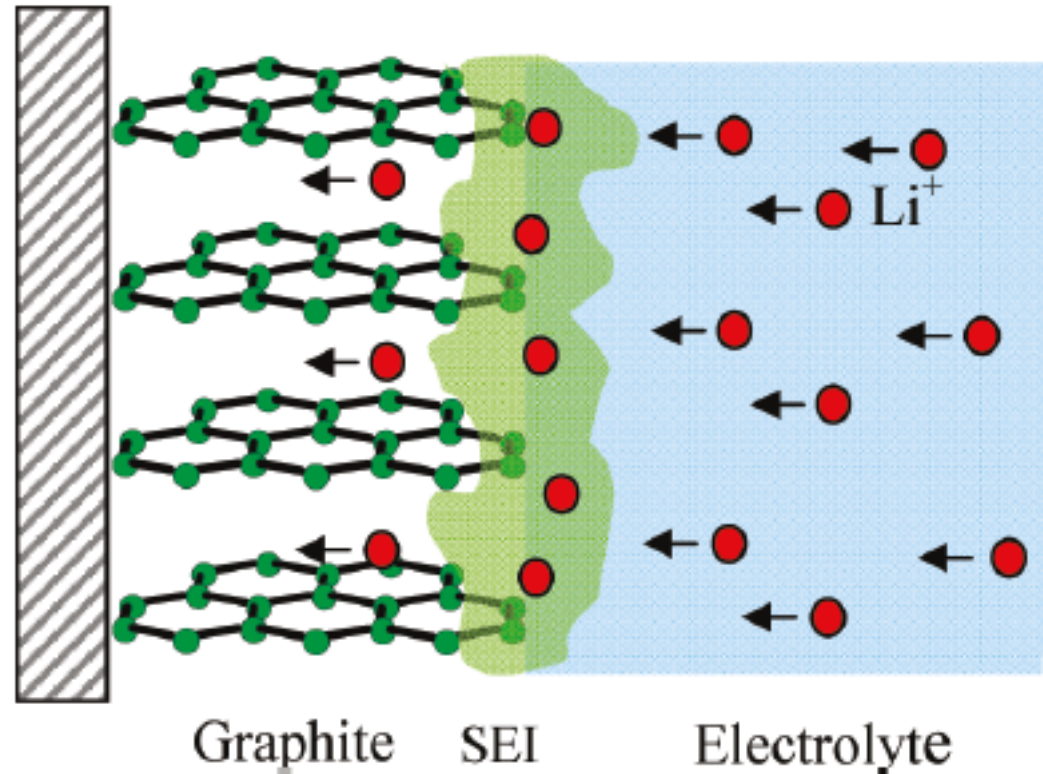
*The kinetic stability of a battery is due to the formation of a stable **solid electrolyte interface (SEI)***

Voltage window of the electrolyte



Voltage versus capacity relative to the window of 1 M LiPF_6 in EC/DEC (1:1)

Generic Cartoon of the SEI



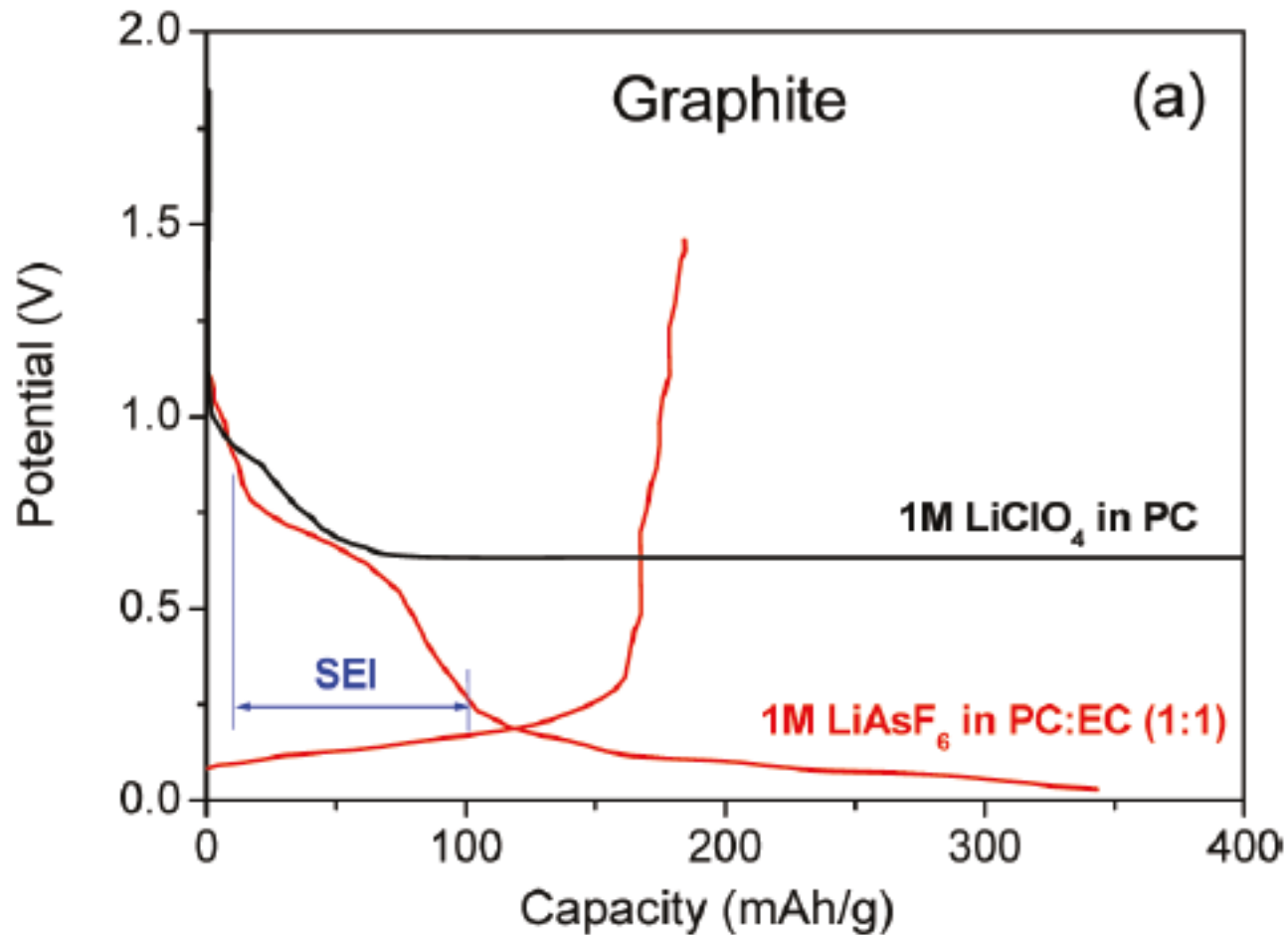
The SEI is still poorly characterized, although people have developed ways to control its growth with the addition of various additives

Summary of electrolytes

Table 1. Nonaqueous Electrolytes for Li-Ion Batteries

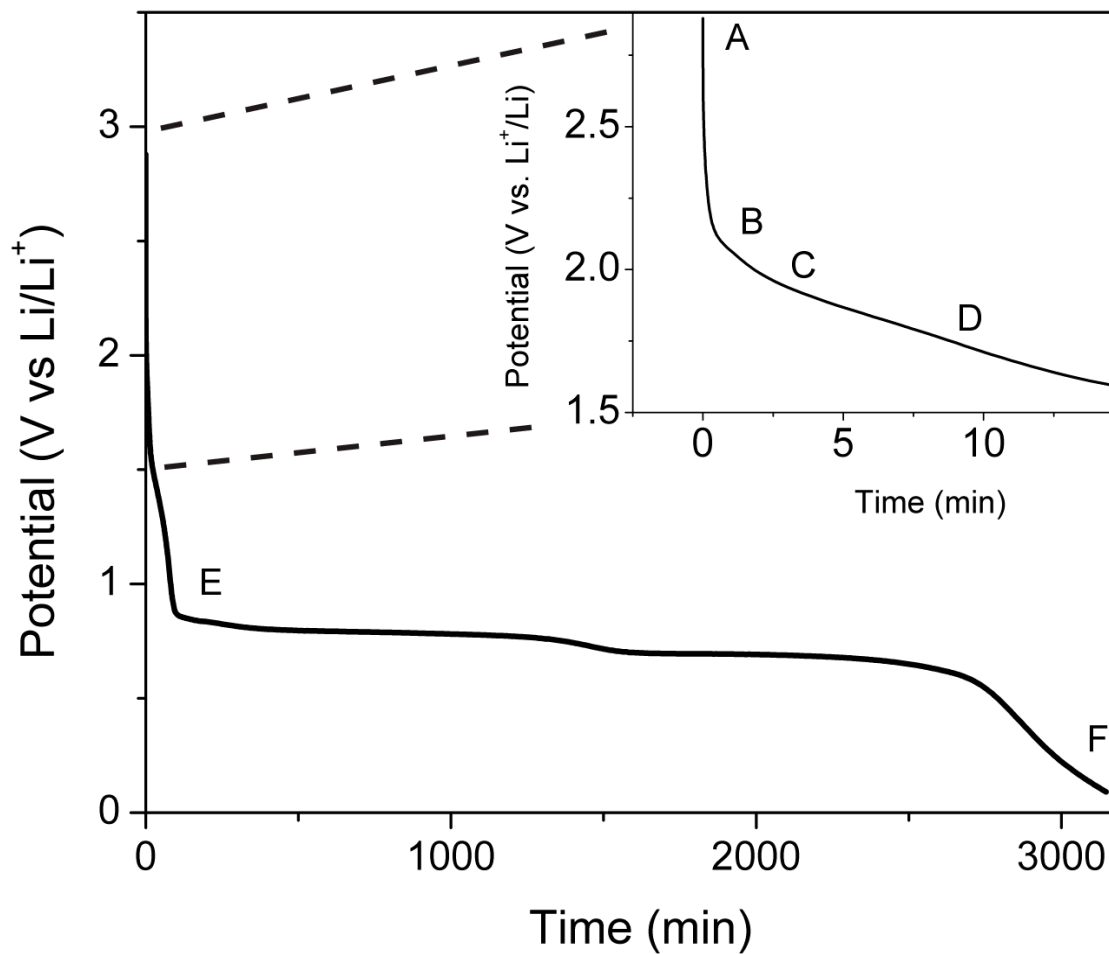
Electrolytes	Example of classical electrolytes	Ionic conductivity ($\times 10^{-3}$ s/cm) at room temp	Electrochemical window (V) vs Li^+/Li^0		Remark
			Reduction	Oxidation	
Liquid organic	1M LiPF_6 in EC:DEC (1:1)	7^3	1.3^7	4.5^6	Flammable
	1M LiPF_6 in EC:DMC (1:1)	10^3	1.3^7	$> 5.0^3$	
Ionic liquids	1M LiTFSI in EMI-TFSI	2.0^{15}	1.0^{15}	5.3^{15}	Non-flammable
	1M LiBF_4 in EMI- BF_4	8.0^{15}	0.9^{16}	5.3^{16}	
Polymer	LiTFSI-P(EO/MEEGE)	0.1^{24}	$< 0.0^{24}$	4.7^{24}	Flammable
	LiClO_4 -PEO ₈ + 10 wt % TiO_2	0.02^{26}	$< 0.0^{26}$	5.0^{26}	
Inorganic solid	$\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ ($x = 0.75$)	2.2^{28}	$< 0.0^{28}$	$> 5.0^{28}$	Non-flammable
	$0.05\text{Li}_4\text{SiO}_4 + 0.57\text{Li}_2\text{S} + 0.38\text{SiS}_2$	1.0^{30}	$< 0.0^{30}$	$> 8.0^{30}$	
Inorganic liquid	$\text{LiAlCl}_4 + \text{SO}_2$	70^{20}	-	4.4^{20}	Non-flammable
Liquid organic + Polymer	$0.04\text{LiPF}_6 + 0.2\text{EC} + 0.62\text{DMC} + 0.14\text{PAN}$	4.2^{38}	-	4.4^{38}	Flammable
	$\text{LiClO}_4 + \text{EC} + \text{PC} + \text{PVdF}$	3.0^{39}	-	5.0^{39}	
Ionic liquid + Polymer	1M LiTFSI + $\text{P}_{13}\text{TFSI} + \text{PVdF-HFP}$	0.18^{43}	$< 0.0^{43}$	5.8^{43}	Less flammable
Ionic liquid + Polymer + Liquid organic	56 wt % LiTFSI- $\text{Py}_{24}\text{TFSI} + 30$ wt % PVdF-HFP + 14 wt % EC/PC	0.81^{44}	1.5^{44}	4.2^{44}	Less flammable
Polymer + Inorganic solid	2 vol % LiClO_4 -TEC-19 + 98 vol% $95(0.6\text{Li}_2\text{S} + 0.4\text{Li}_2\text{S}) + 5\text{Li}_4\text{SiO}_4$	0.03^{46}	$< 0.0^{46}$	$> 4.5^{46}$	Non-flammable
Ionic liquid + Liquid organic ¹⁹		-	-	-	Non-flammable

SEI Formation on the First Cycle



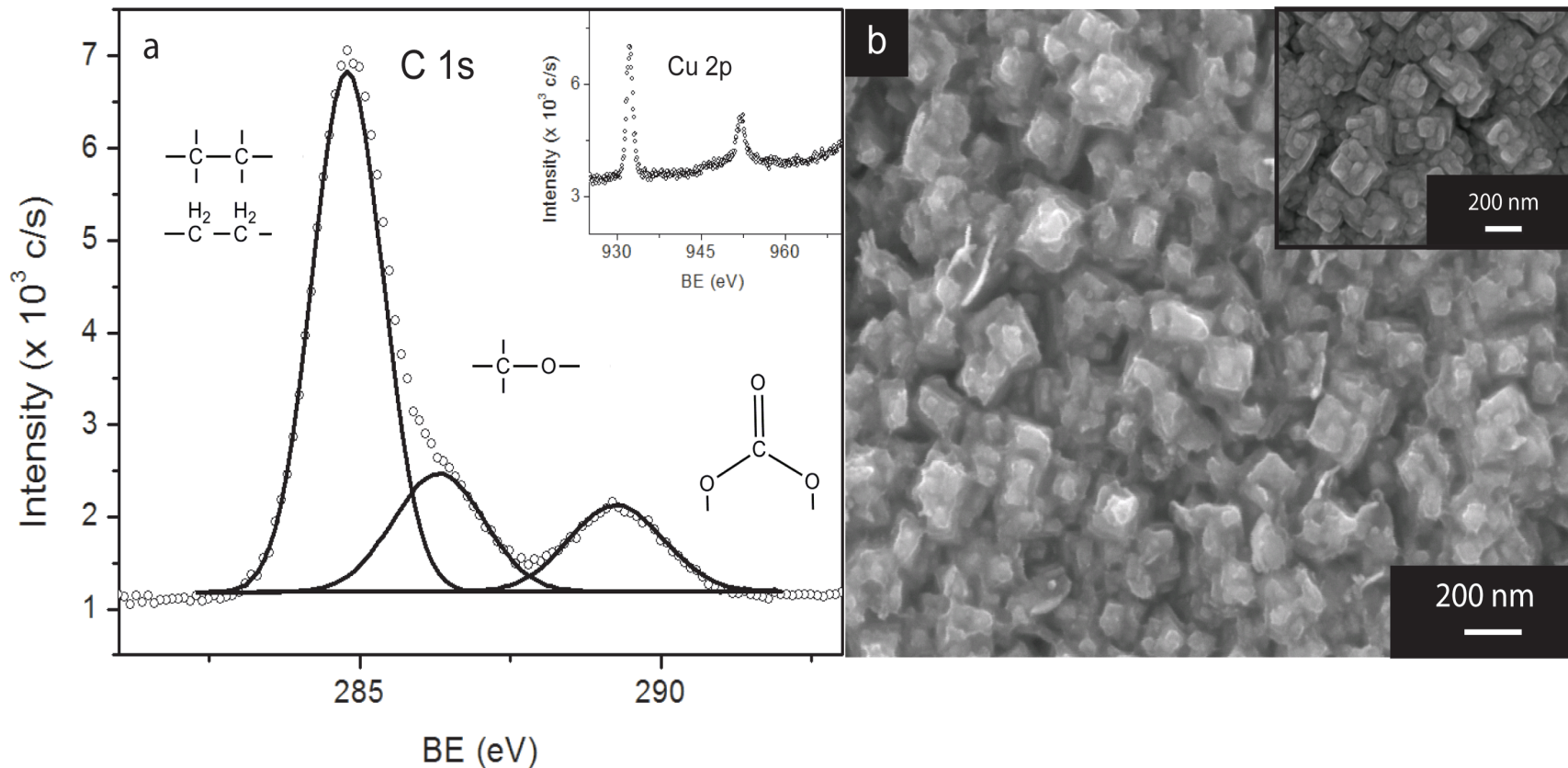
Industrial batteries are cycled several times before they are sold:
forming process

Back to Cu_2Sb



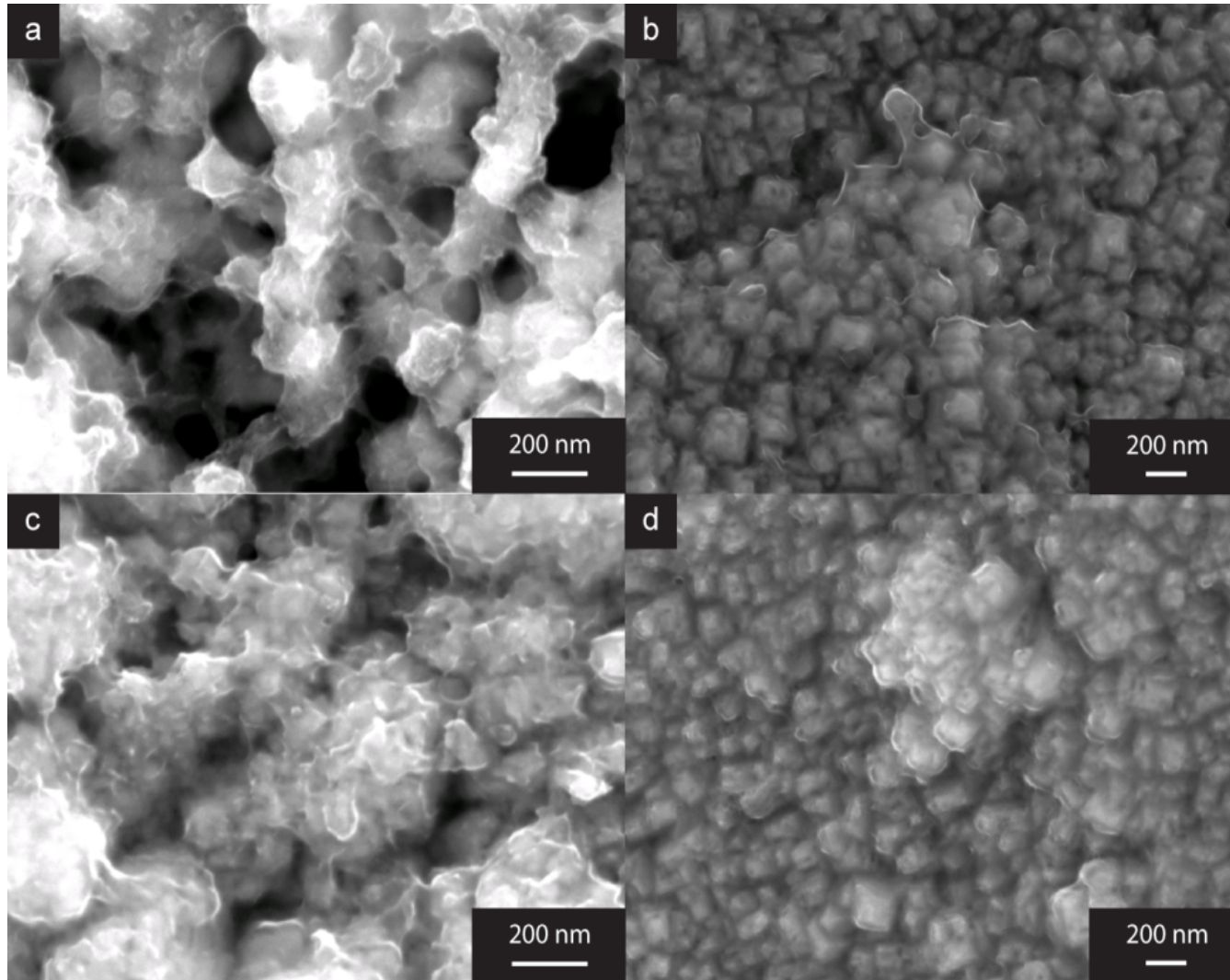
Cu_2Sb electrochemical half-cell galvanostatically charged at $10 \mu\text{A cm}^{-2}$ in a 1M LiClO_4 EC/DEC/DMC (1:1:1) electrolyte solution

Decomposition of Liquid Electrolyte on Cu₂Sb



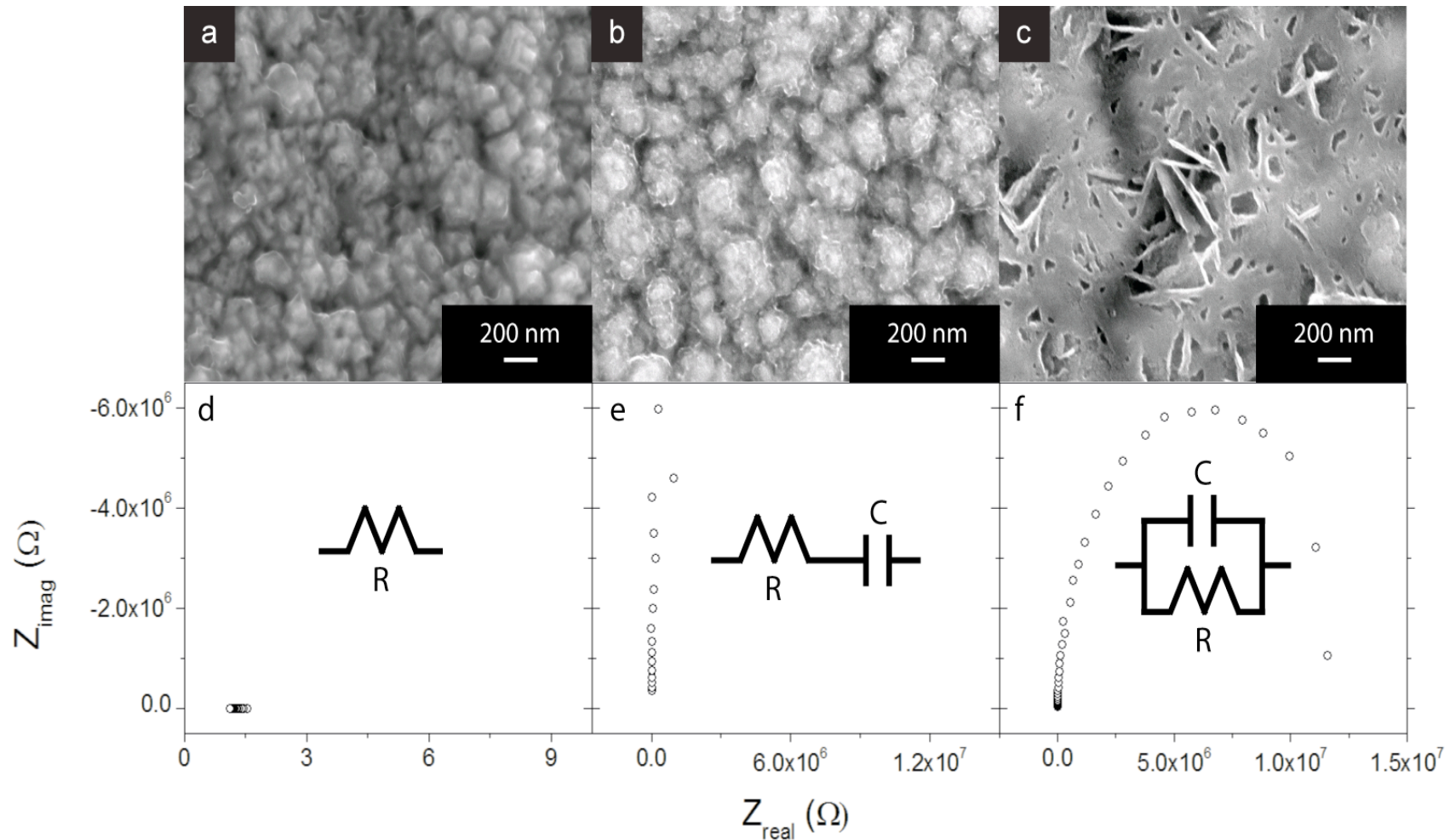
(a) XPS HRES C 1s and Cu 2p (inset) spectra of a Cu₂Sb electrode charged to 1.8 V vs Li/Li⁺
(b) SEM micrographs of the SEI layer formed on the surface of the Cu₂Sb. The cubic morphology of the bare electrode (inset) is still present under the SEI layer

Potential Range is Important in Morphology



SEM micrographs of an SEI grown in the MPR for (a) 5 cycles and (c) 20 cycles. The SEI formed in the HPR for (b) 5 cycles and (d) 50 cycles.

Potential Range is Important in Performance



High potentials

intermediate potentials

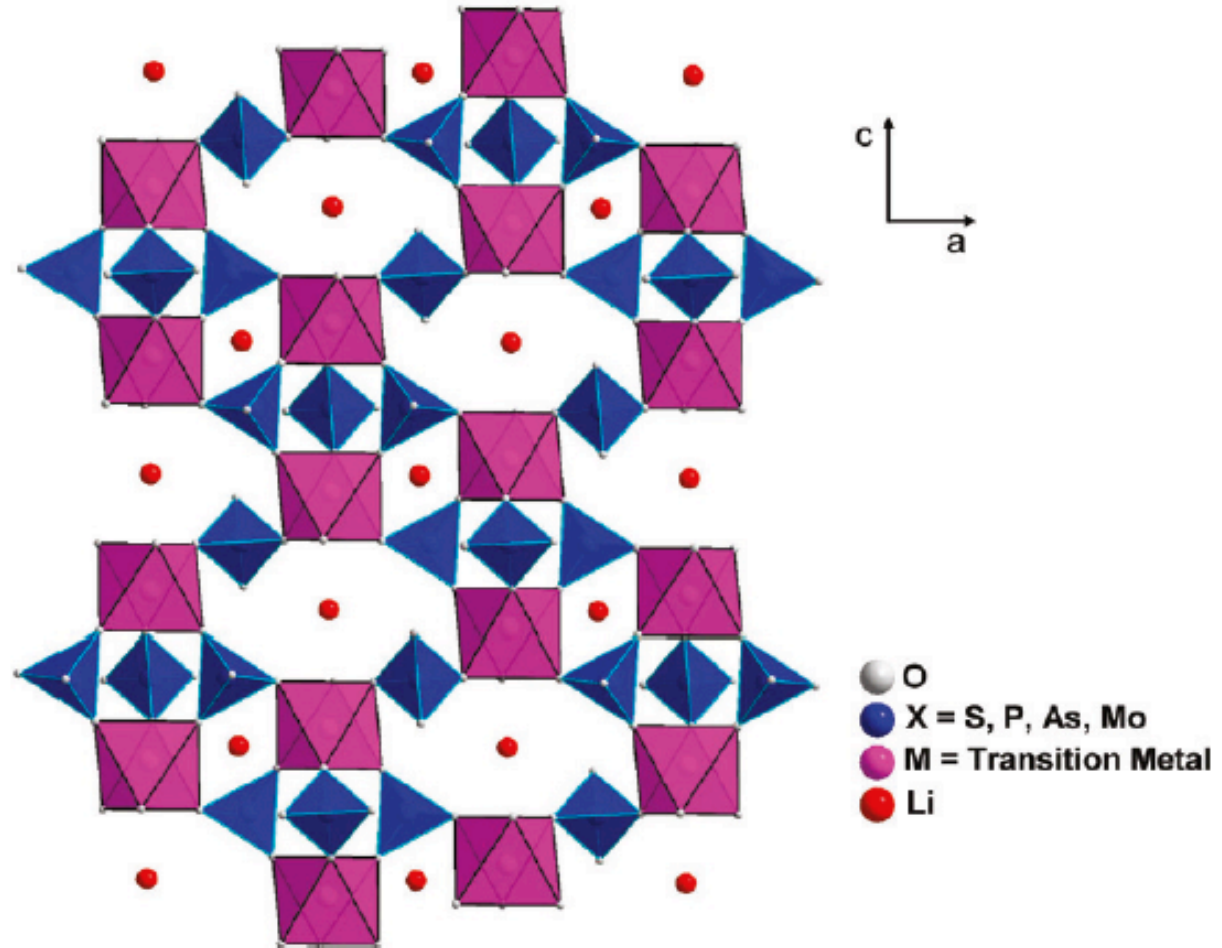
low potentials

Take Home Messages Thus Far

- Stability of Li (dendritic growth)
 - This hasn't been solved on Li metal anodes, and is a significant safety hazard
 - Alternative anode materials can be safer, but you lose on energy density and voltage
- Volume expansion challenges in electrode materials (*anodes*)
 - Mechanical pulverization is a problem in all electrode materials, but especially in dense intermetallics
 - structural similarities between the parent and child compounds can be used to reduce the overall volume changes
- Solid-electrolyte-interfaces
 - Big voltage windows lead to redox reactions with the electrolyte
 - **Interfaces are critical in batteries!**
- *The importance of diffusion rates*

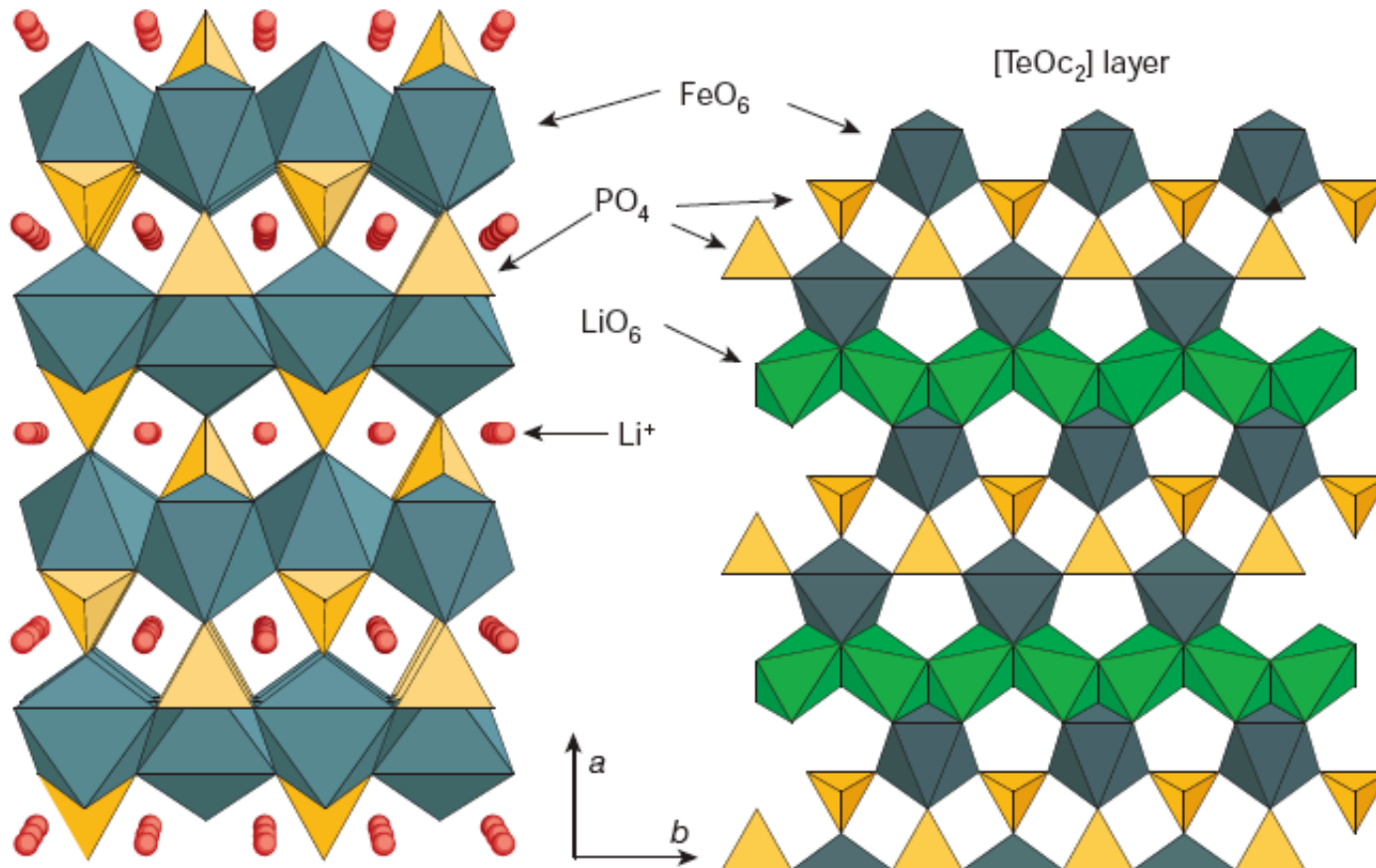
Framework Structures: NASICON

MO_6 octahedra
linked to XO_4
tetrahedra



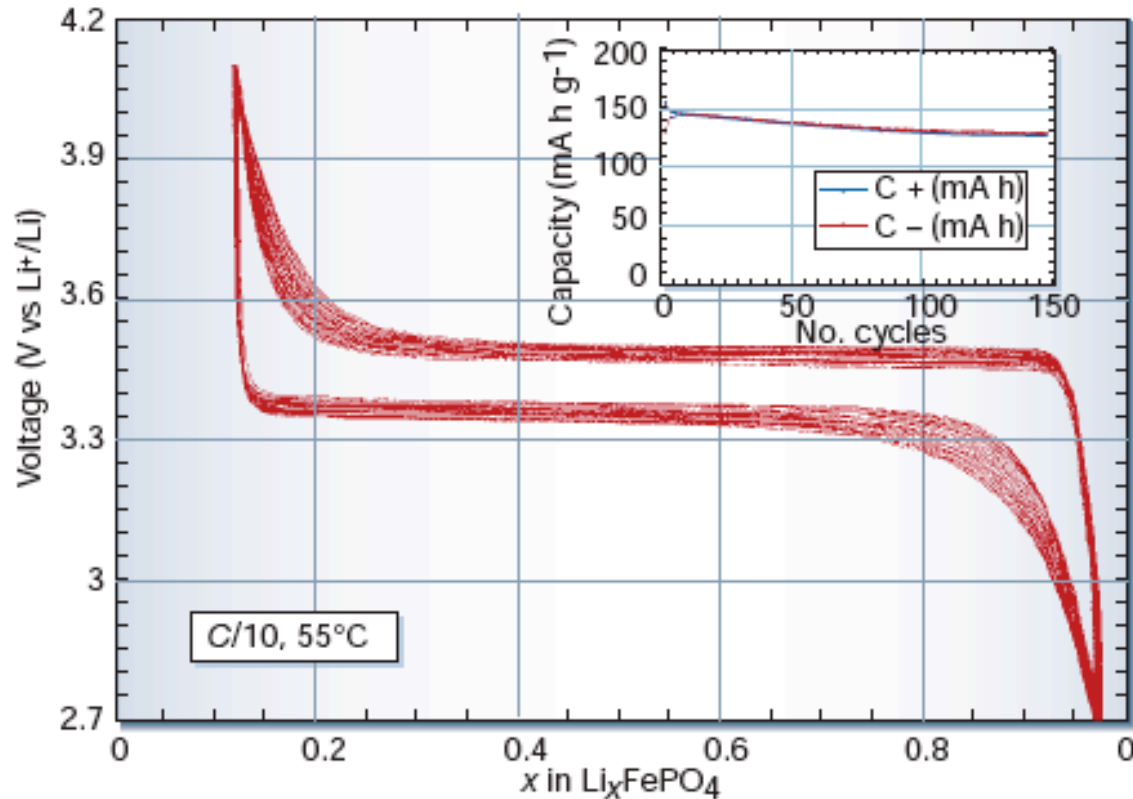
The diffusion rates of Li^+ ions into solid state structures is critical for *how fast* your battery will charge and discharge.

A123's Cathode Material: LiFePO_4



Li⁺ ions in 1D channels.

Charging Behavior: Must be Mixed With Carbon



C rate = capacity/time,
or C/n denotes the rate at
which a full charge or
discharge takes in hours

Advantages: stable over a wide composition range

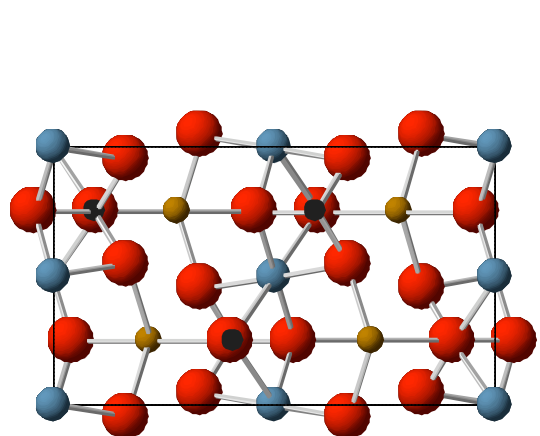
A Current Example: Kang and Ceder

Battery materials for ultrafast charging and discharging
Nature **2009**

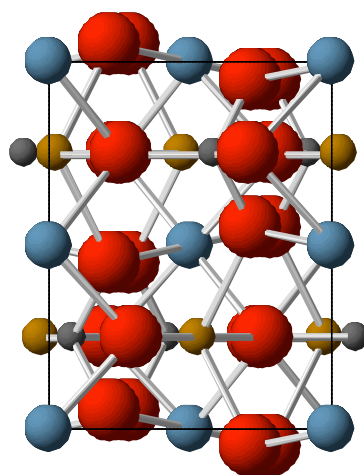
The storage of electrical energy at high charge and discharge rate is an important technology in today's society, and can enable hybrid and plug-in hybrid electric vehicles and provide back-up for wind and solar energy. It is typically believed that in electrochemical systems very high power rates can only be achieved with supercapacitors, which trade high power for low energy density as they only store energy by surface adsorption reactions of charged species on an electrode material¹⁻³. Here we show that batteries^{4,5} which obtain high energy density by storing charge in the bulk of a material can also achieve ultrahigh discharge rates, comparable to those of supercapacitors. We realize this in LiFePO_4 (ref. 6), a material with high lithium bulk mobility^{7,8}, by creating a fast ion-conducting surface phase through controlled off-stoichiometry. A rate capability equivalent to full battery discharge in 10–20 s can be achieved.

Diffusion of Li^+ is Direction Dependent

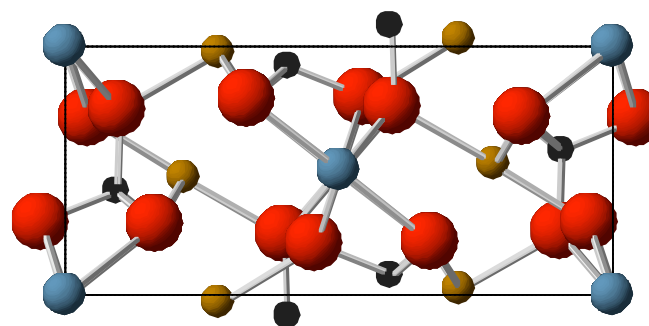
Kang and Ceder explained that Li^+ ions move into the bulk of LiFePO_4 primarily through the ***[010] direction***. The oxygen is shown in red, lithium is blue, phosphorous is grey, and iron is mustard yellow.



[001]



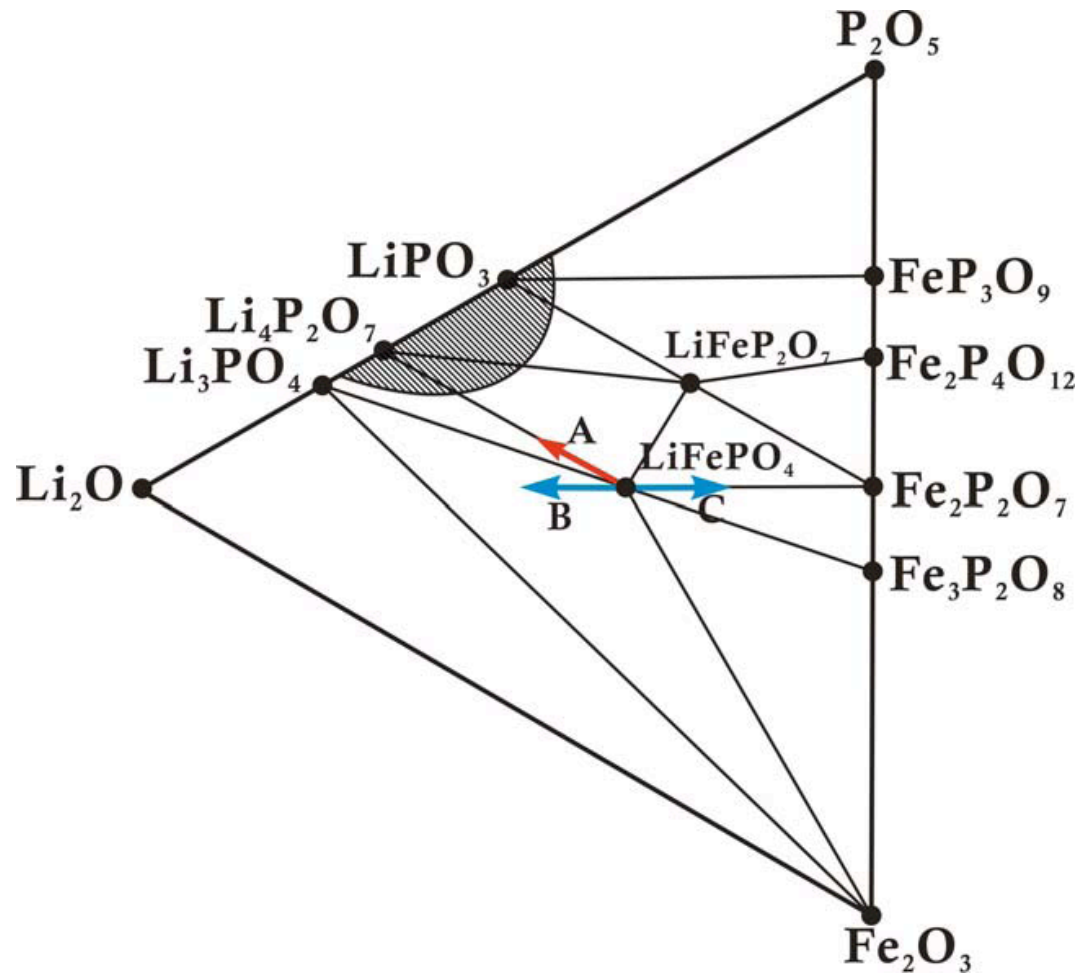
[100]



[010]

[010] has fairly open channels....ideal for cation diffusion

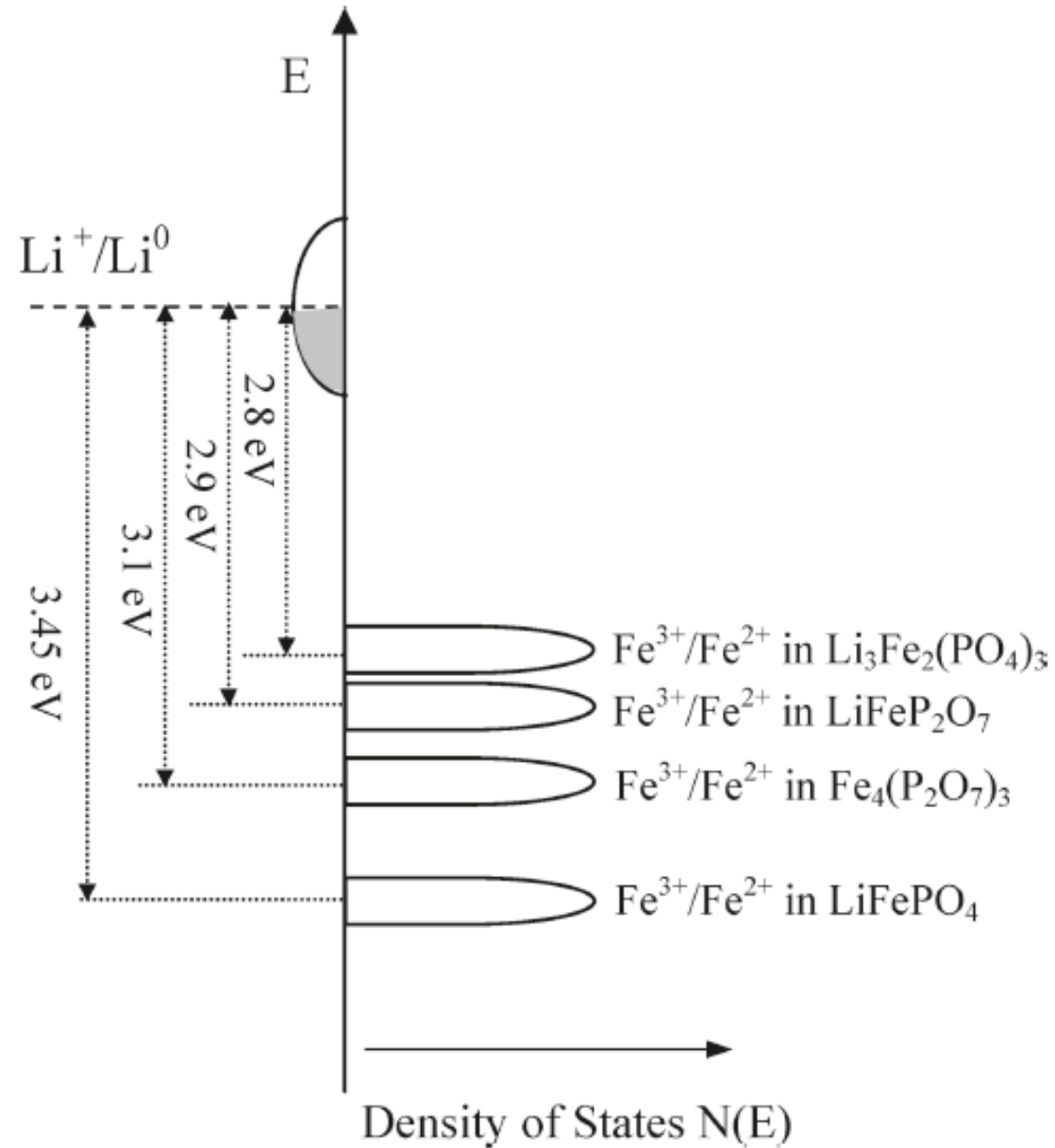
Ternary Phase Diagram



A: poorly crystallized lithium phosphate (good Li conductors)

B: Li-excess or **C:** Li-deficiency leads to Fe-oxides or Fe-phosphates

Control of Composition is Really Important!



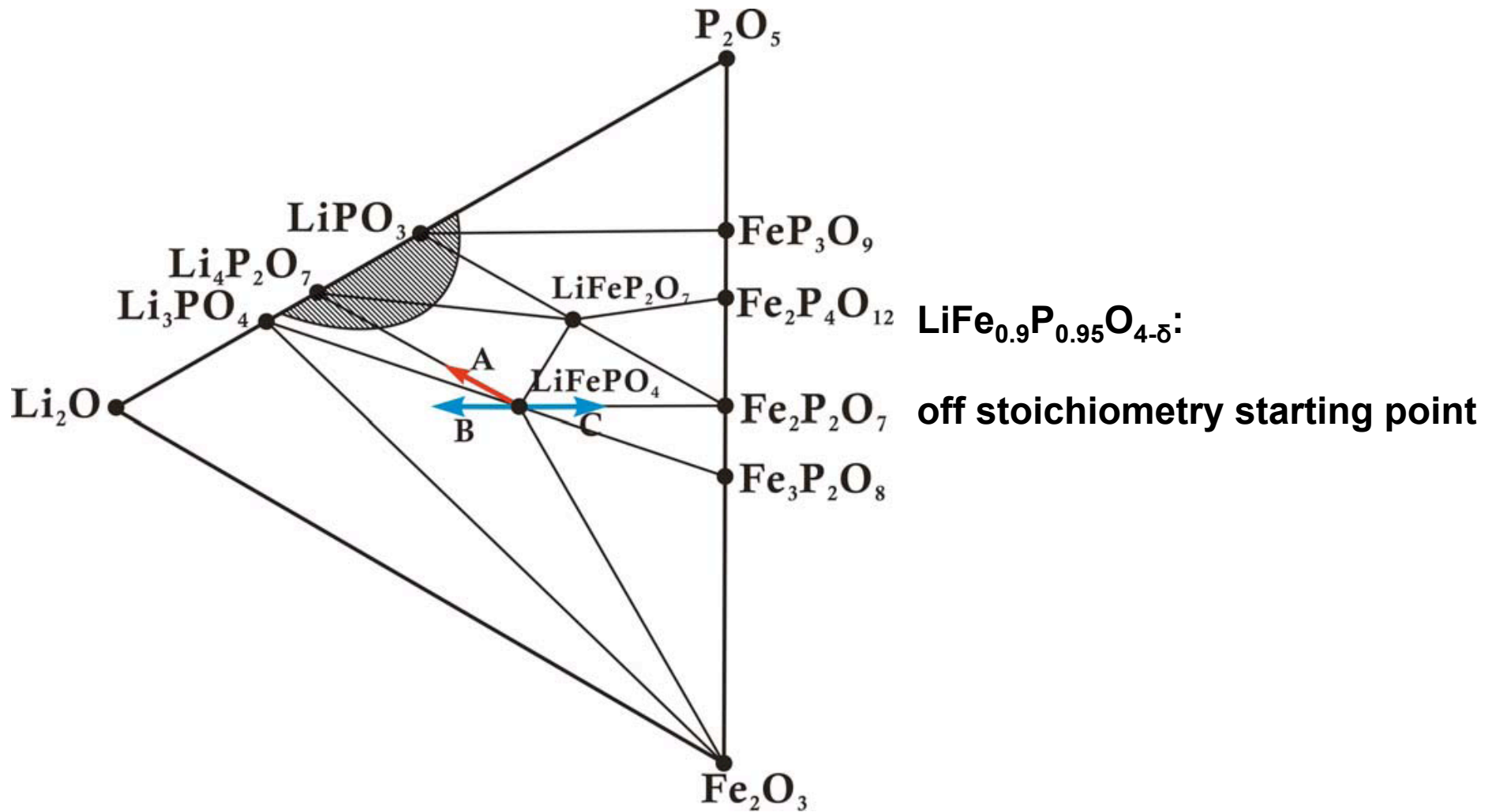
Making A 'Coated' Battery Material

Our synthesis strategy has been to create an appropriate off-stoichiometry in the starting materials so that the coating constituents phase-separate from LiFePO_4 as it forms during the heat treatment, thereby creating the active storage material and coating in a single process. Here we describe results with an iron:phosphorus deficiency ratio of 2:1 (for example $\text{LiFe}_{1-2y}\text{P}_{1-y}\text{O}_{4-\delta}$, $y = 0.05$), as indicated by arrow A in Supplementary Fig. 1. We note that the more common one-to-one iron:phosphorus deficiency (arrow B in Supplementary Fig. 1, equivalent to lithium excess²²) creates a mixture of Li_3PO_4 and iron oxides, which are not likely to conduct well under the synthesis conditions used to prepare LiFePO_4 .

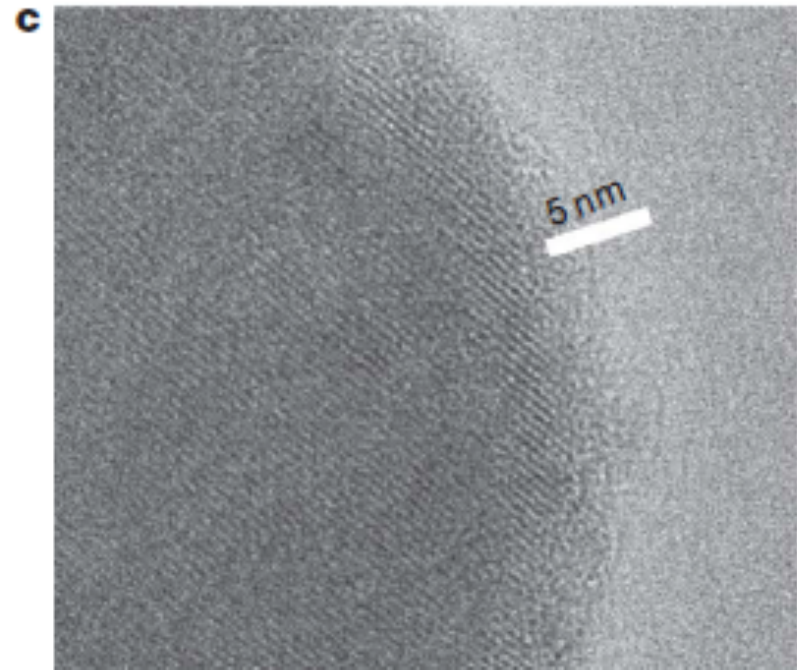
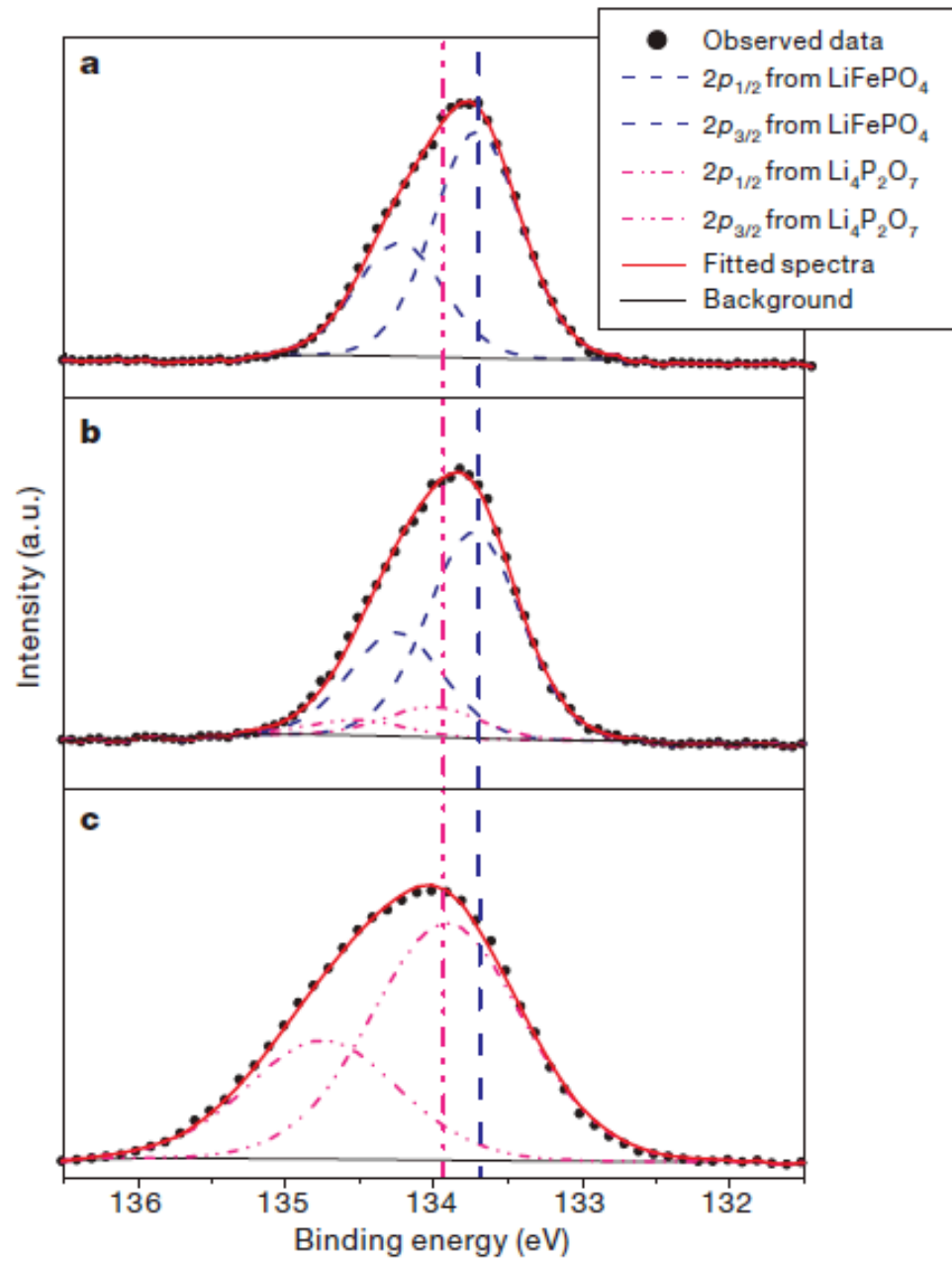
Synthesis

$\text{LiFe}_{0.9}\text{P}_{0.95}\text{O}_{4-\delta}$ was synthesized by ball-milling Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ in appropriate amounts, heating the mixture at 350°C for 10 h and then heating at 600°C for 10 h under argon. X-ray diffraction (Fig. 1a and Supplementary Fig. 2) shows that despite the off-stoichiometric starting mixture, stoichiometric LiFePO_4 forms with lattice parameters ($a = 10.3134 \text{ \AA}$, $b = 6.002 \text{ \AA}$ and $c = 4.691 \text{ \AA}$) very similar to those reported in the literature²³.

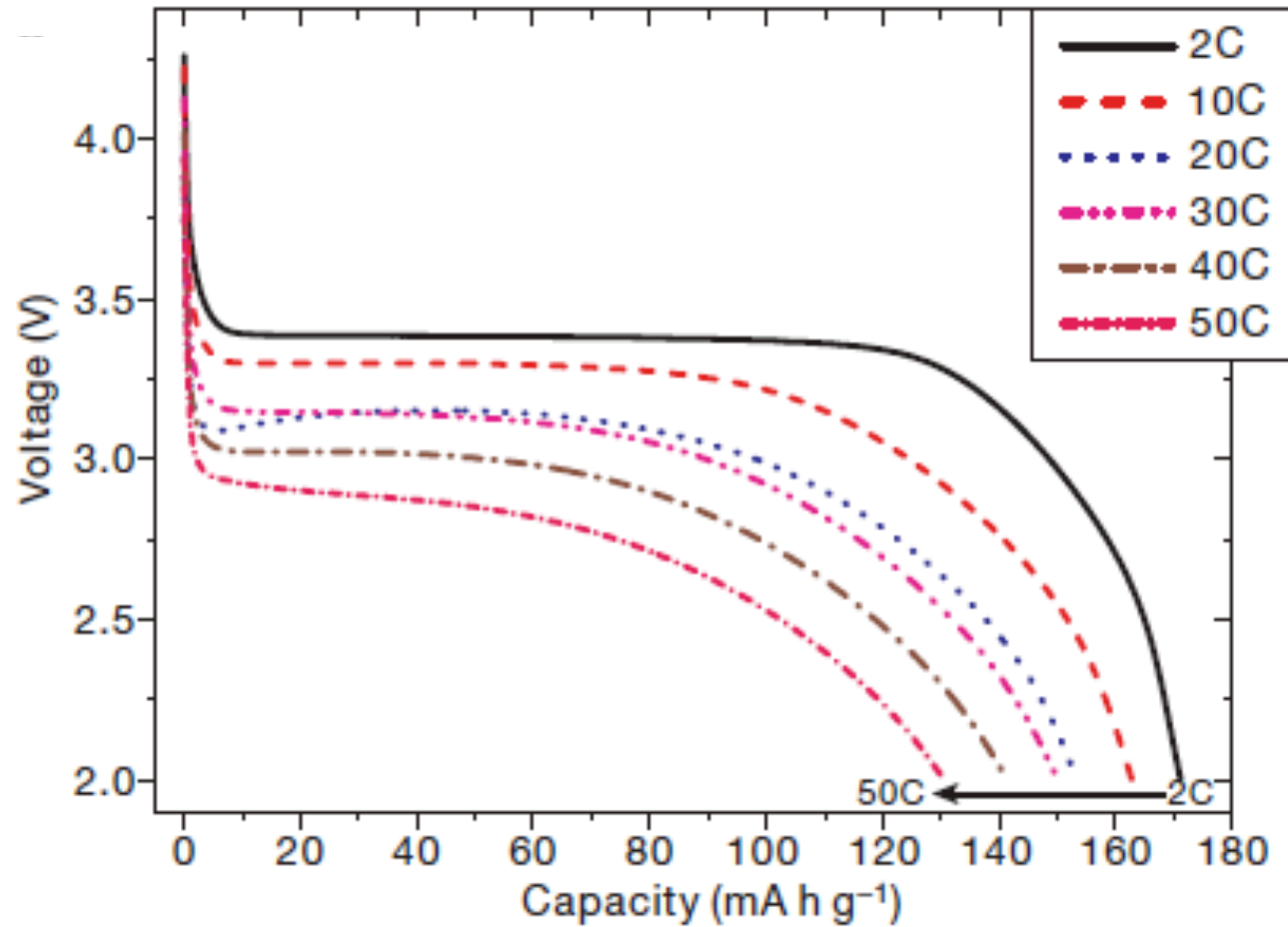
Aiming for LiFePO_4 and $\text{Li}_x\text{P}_y\text{O}_{1-\delta}$



Data for Surface Coating



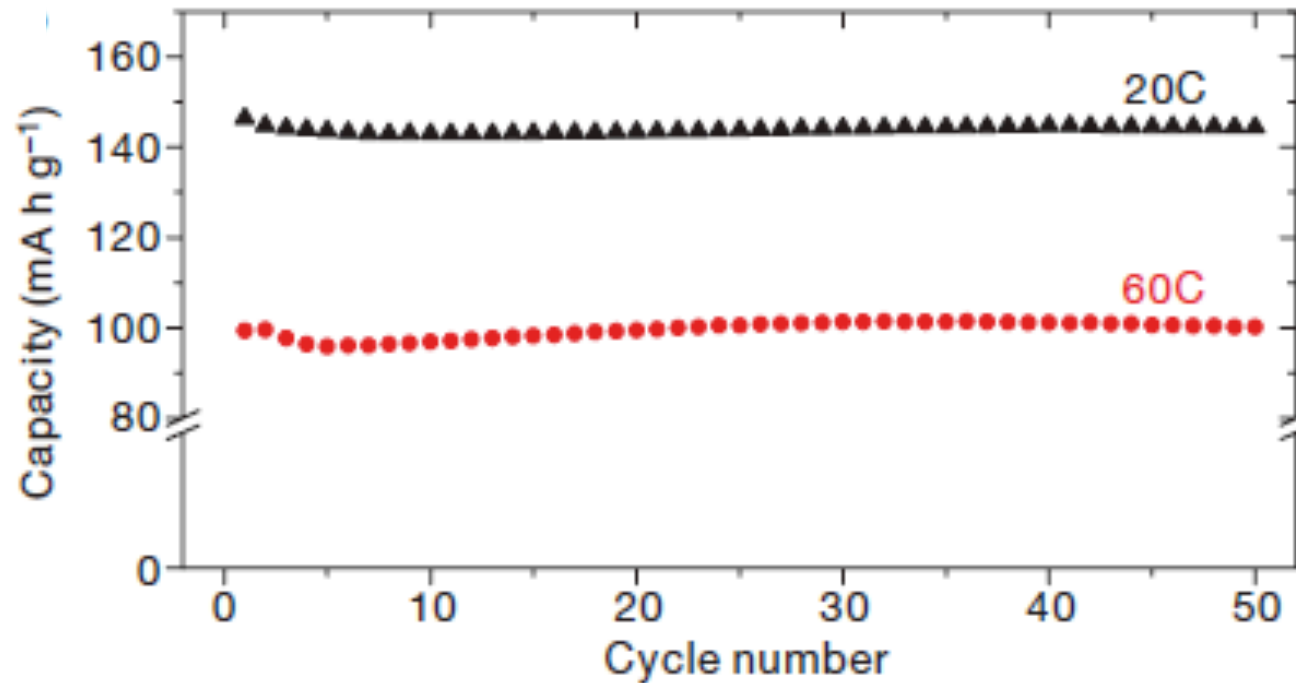
Incredible Rate Performance



The capacity retention is really impressive at high rates.

50C is completely discharged in 72s

Cycle Life at High Rates



You still see a capacity loss at high rates, but it's among the best performing fast rate materials currently known.
competitive with supercapacitors

Final Take Home Messages

- *Stability of Li (dendritic growth)*
 - *This hasn't been solved on Li metal anodes, and is a significant safety hazard*
 - *Alternative anode materials can be safer, but you lose on energy density and voltage*
- *Volume expansion challenges in electrode materials (anodes)*
 - *Mechanical pulverization is a problem in all electrode materials, but especially in dense intermetallics*
 - *structural similarities between the parent and child compounds can be used to reduce the overall volume changes*
- *Solid-electrolyte-interfaces*
 - *Big voltage windows lead to redox reactions with the electrolyte*
 - ***Interfaces are critical in batteries!***
- *The importance of diffusion rates*
 - *Can improve diffusion by nanostructuring (Prof. Bruce)*
 - *Structural features are critical*

Questions? You can reach me at alprieto@lamar.colostate.edu