STONY
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STATE UNIVERSITY OF NEW YORK

New Materials For and Challenges in Lithium Ion Battery Research

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Basic Research Needs:
Electrical Energy Storage

Grand challenges?

1. Identify the most efficient mechanism(s) for electrical energy storage
2. Find an ideal material combination that will cycle infinitely without capacity loss, for use over a wide range of temperatures.

easy to fabricate, cheap to produce, safe, environmentally friendly, etc.

3. Identify radically different methods or approaches for electrical energy storage … to couple with new/different sources of energy?

New methods of producing electricity may require new battery designs

Control of the local dynamic and structural behavior of materials on the femtosecond-to-years timescale is necessary in order to develop tailor-made energy storage systems with novel properties

INTRODUCTION

How do rechargeable lithium ion batteries (LIBs) work?

Where will they be used and what is the potential short and long term impact?

What are some of the technological requirements for 21st century devices and current problems?

MATERIALS

What are the issues?

Where are the frontiers?

What fundamental scientific breakthroughs required to achieve the materials goals?

Where are the critical information gaps?

New Electrode Materials

New Diagnostic/Characterization Approaches

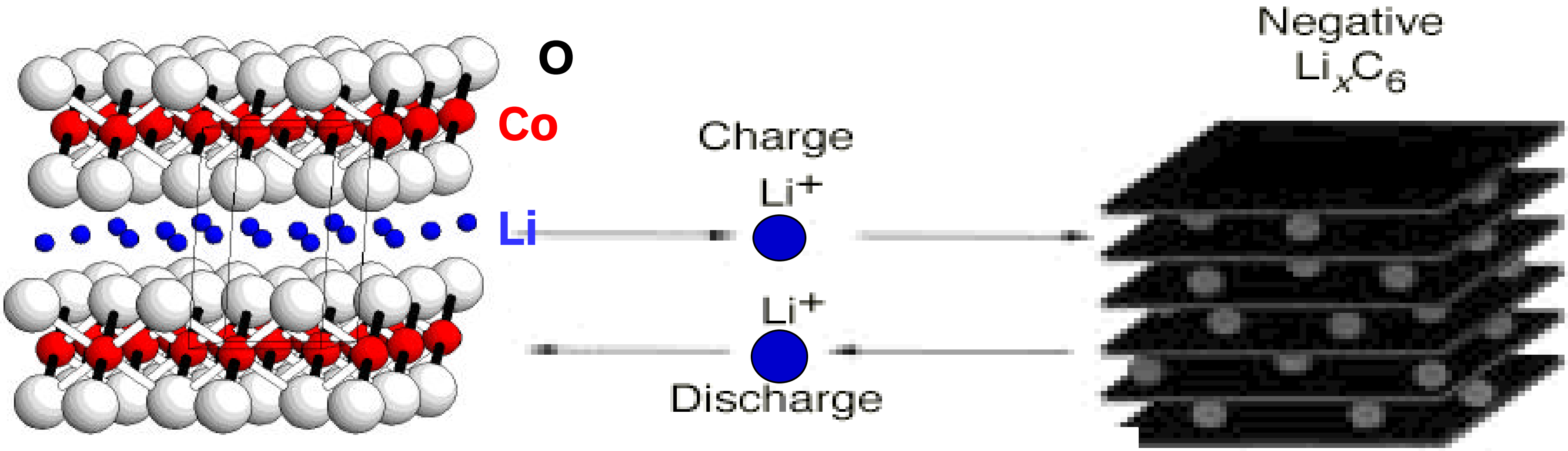
Applications to Layered Materials

MANY OF THESE MATERIALS EXHIBIT A RANGE OF FASCINATING PHYSICAL PHENOMENA – OF BASIC FUNDAMENTAL INTEREST…

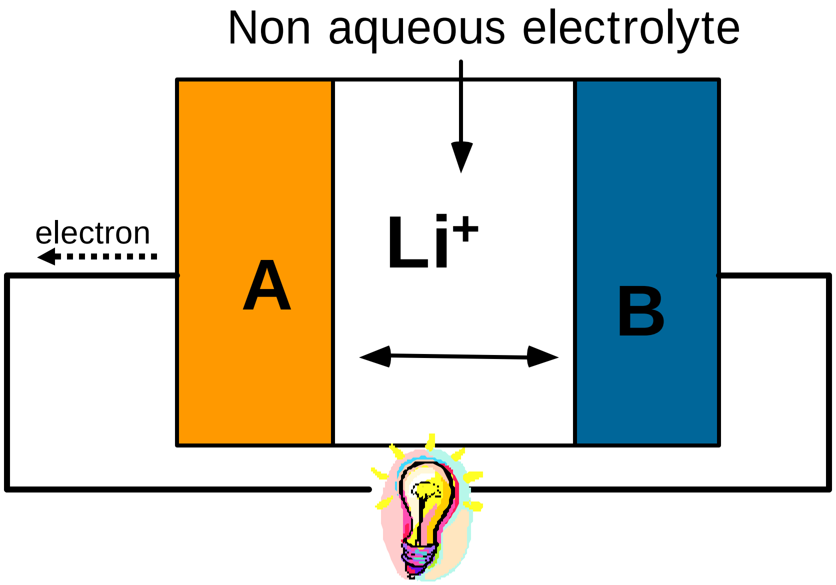
Metal-insulator transitions, charge-ordering, co-operative Jahn-Teller distortions ..

WHICH DIRECTLY IMPACT BATTERY PERFORMANCE

The big advance in this field came with the development of the SONY “Rocking-Chair” battery in 1990

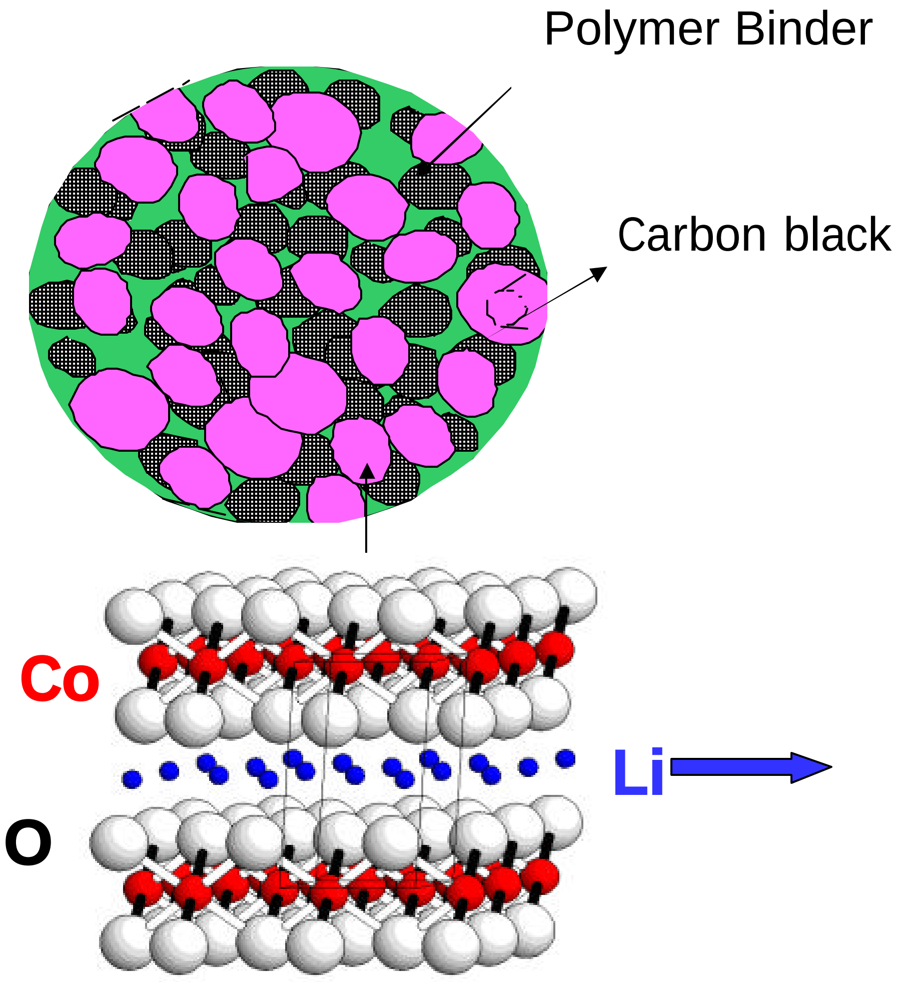


- Lithium shuttles backwards between two layered compounds
- Very high voltage (4 V; cf Ni/Cd @ 1.35 V)
- $LiCoO_2$, J. Goodenough (1980)
- 2ndary host material, Murphy et al., and Scrosati et al. (‘78 and ‘80)



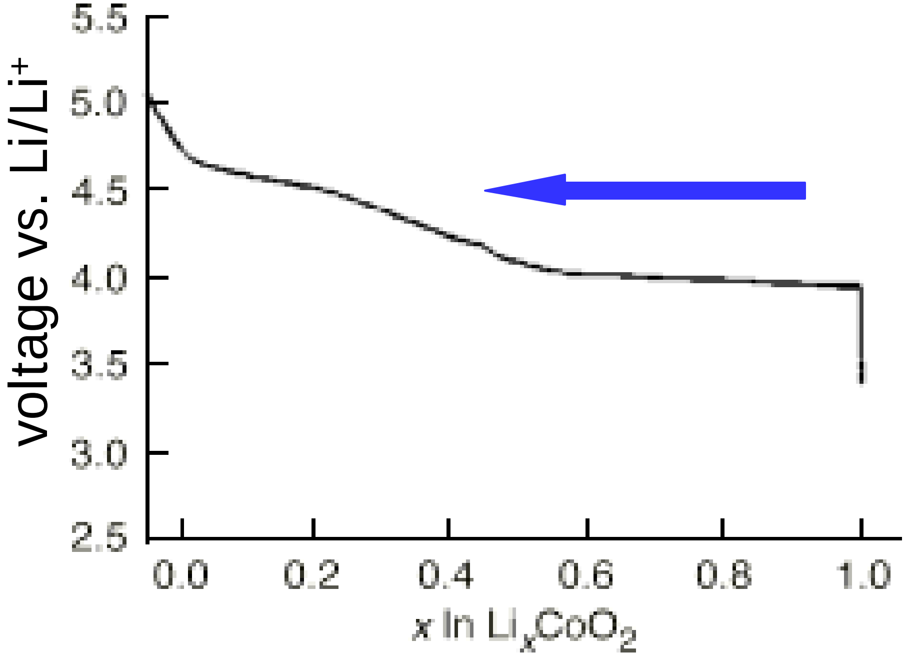
Solid state chemistry at the cathode end...

Positive Electrode
Composite structure



Co^{3+} is oxidized to Co^{4+} on Li removal (deintercalation)

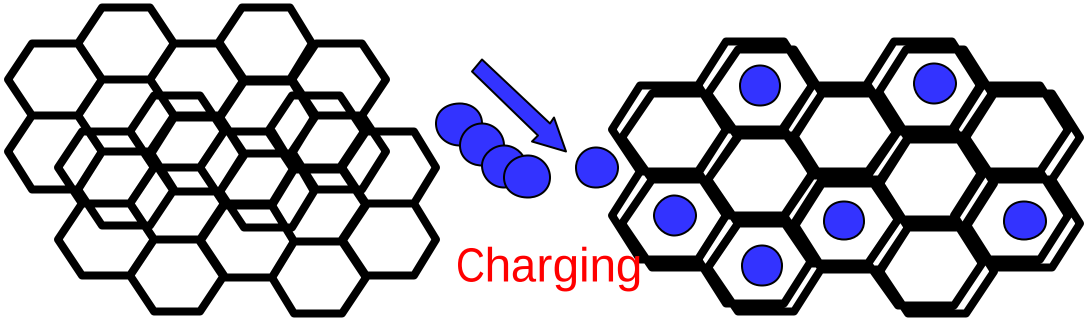
I.e., during charging



Ohzuku *et al.* J. Electrochem Soc. 140, 1862, ‘93

At the negative (anode) end..

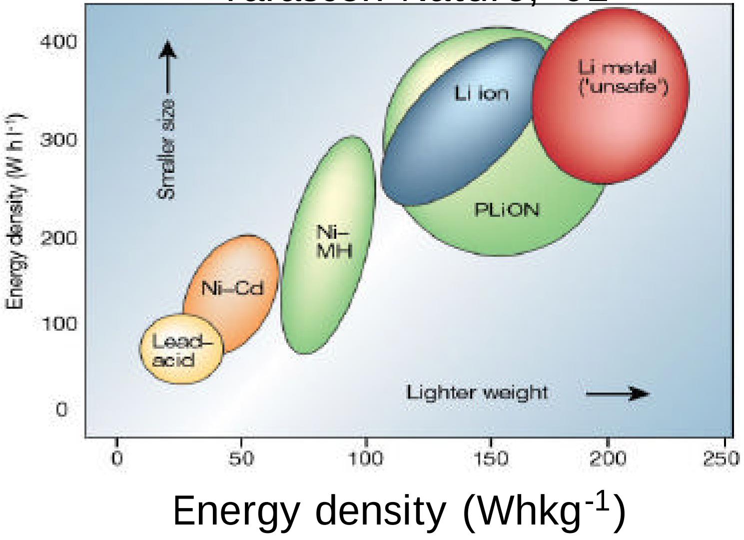
- Graphite anode forms an intercalation compound Li_xC



Requirements for rechargeable batteries:
Reversible electrode chemistry
Large difference in the couples of the two 1/2 cells => High voltages
Light materials => High energy densities
Conducting anode and cathode (current can be removed) => high power densities

	Energy density;	Cycle Life;	Voltage
SONY Cell	90 Wh/kg	500-1000	4V
Pb acid	30	250-500	2V
Ni/Cd	30-35	300-700	1.3V
Ni metal hydride	50	300-600	1.2V

Tarascon Nature, '01



Recent Advances in Portable Technologies and the Proposed Solutions to the Impending Energy Crisis Require Energy Storage Systems: The Various Applications Have Very Different Power Requirements

- Portable Electronics (Cell phones, laptops, PDA, digital cameras)
- Medical Devices

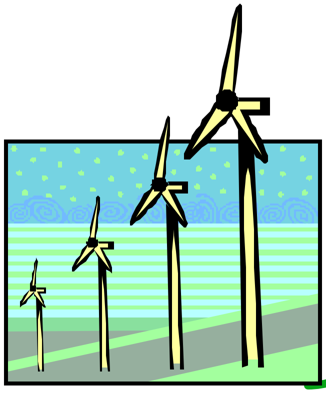
Low Power

(high energy)

- Portable tools
- Back-up power (UPS)

- Power Storage for Renewable Energy
- EVs and HEVs
- Electric bikes/scooters
- “Industrial” EV, forklifts, golf carts

High Power



How will energy storage make impact ?
US Carbon Dioxide Emissions (EIA BAU)
(Millions of tonnes - Carbon)

Slide courtesy G. Ceder

	RESIDENTIAL+ COMMERCIAL		INDUSTRIAL		TRANSPORTATION		TOTAL	
	2005	**2025**	**2005**	**2025**	**2005**	**2025**	**2005**	**2025**
Petroleum	43	48	119	142	526	[illegible]	[illegible]	933
Natural Ga	[illegible]	[illegible]	[illegible]	[illegible]	10	14	252	313
Coal	3	3	55	47	0	0	58	49
Electricity	458	675	182	223	4	6	644	904
TOTAL	624	875	478	562	541	763	1643	2199
		1.7%/yr		0.8%/yr		1.7%/yr		1.5%/yr

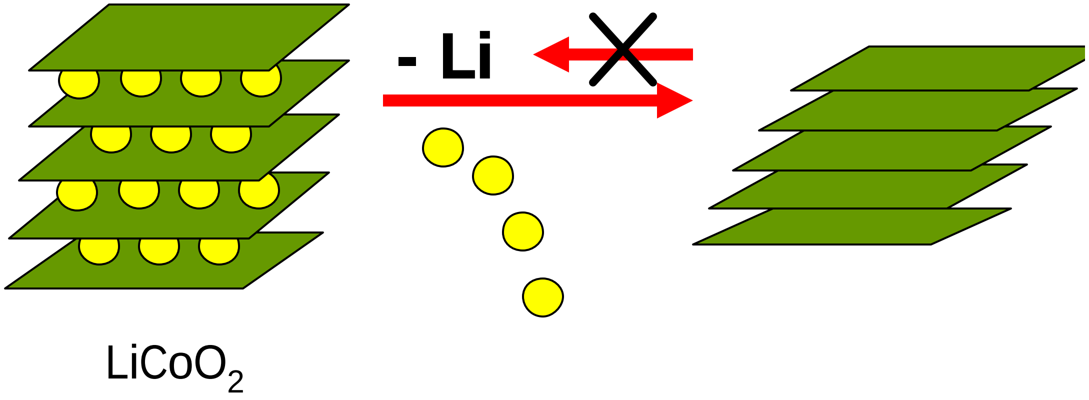
Storage

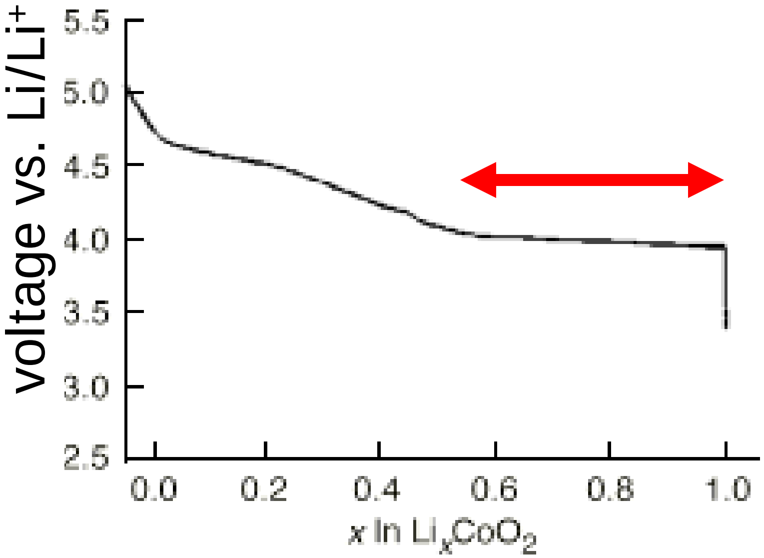
Solar, wind, geothermal + Storage

526 + 458 + 182 = 1166 = 71% of all US CO_2 emissions

Why is more research needed?
Some Major Disadvantages of the $LiCoO_2$ Battery

- COST: Co is toxic and expensive
- MATERIALS RESOURCES: Not sufficient Co globally to meet perceived demands for rechargeables
- I. CAPACITY (how many electrons can be stored): Only 0.5 of the Li can be removed. I.e., low capacity
- II. POWER (rate): V. slow to charge and discharge (low power) - not suitable for E.V.s, H.E.V.s or other high power applications
- III. SAFETY: Li-plating can occur on rapid charging – big issue for EVs/HEVs





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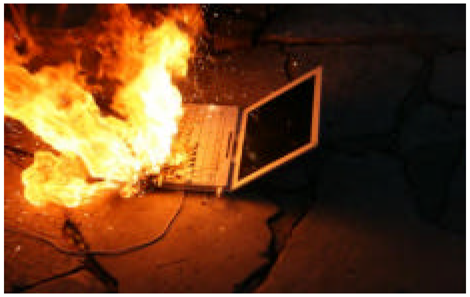
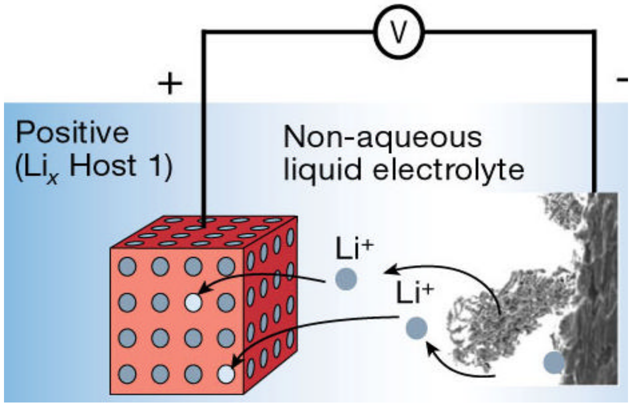
- II. POWER (rate): V. slow to charge and discharge (low power) - not suitable for E.V.s, H.E.V.s or other high power applications
- III. SAFETY: Li-plating can occur on rapid charging; stability at “high” T (thermal runaway) etc.– big issue for EVs/HEVs





-ve
(carbon)

J. -M. Tarascon, Nature ‘01

Improving battery performance will be driven by:

- New materials
- Understanding how the systems function and why they fail

-characterization (diagnostics)

Energy density

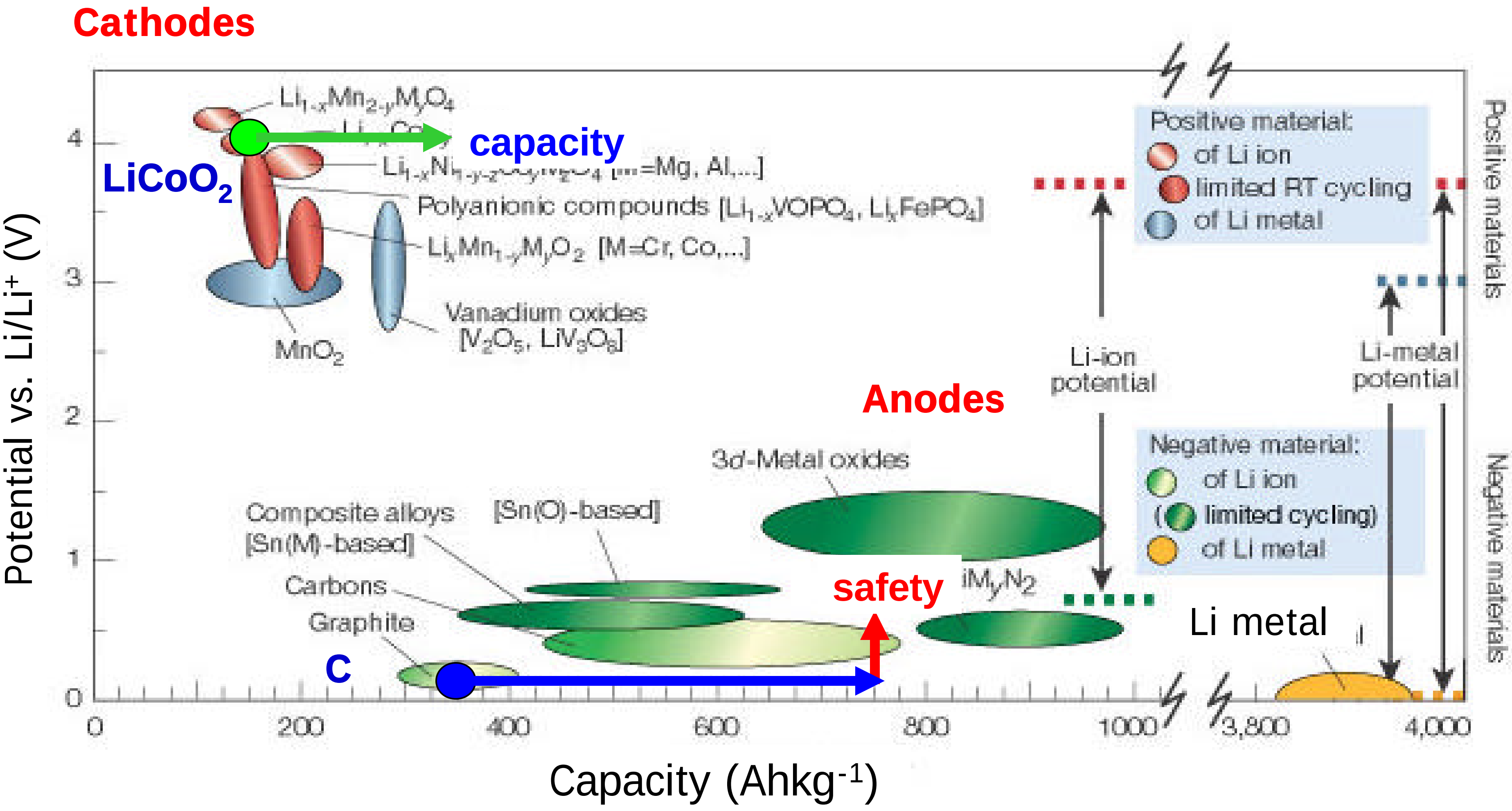
Need to increase the amount of charge stored per unit of material

Power (rate)

Need to increase Li^+ diffusion (and electronic conductivity)

Engineering of cell design

ENERGY DENSITY
New Materials: Voltage vs. Capacity - Status in 2001



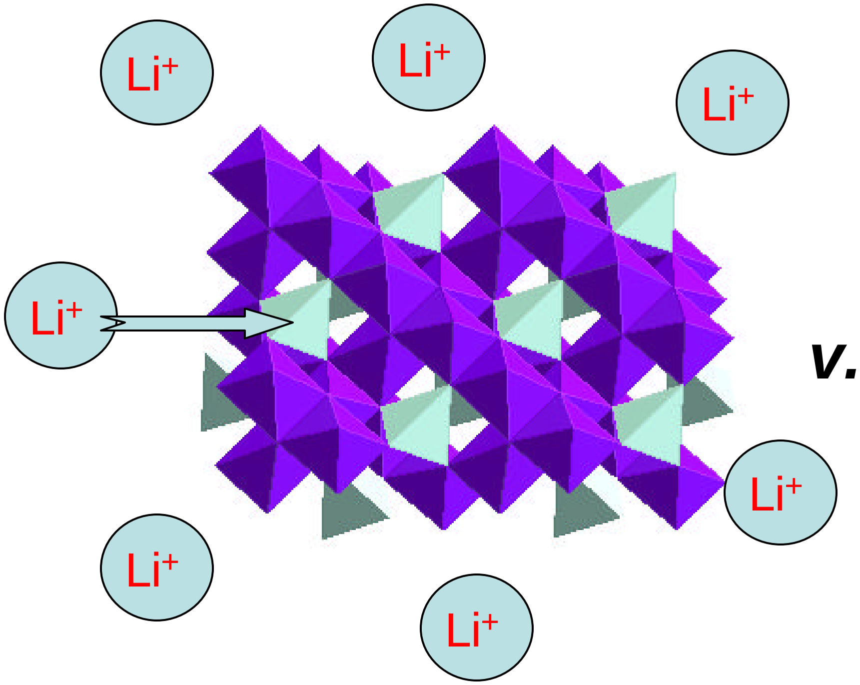
A “few” illustrative examples

J.-M. Tarascon and M. Armand, Nature ‘01

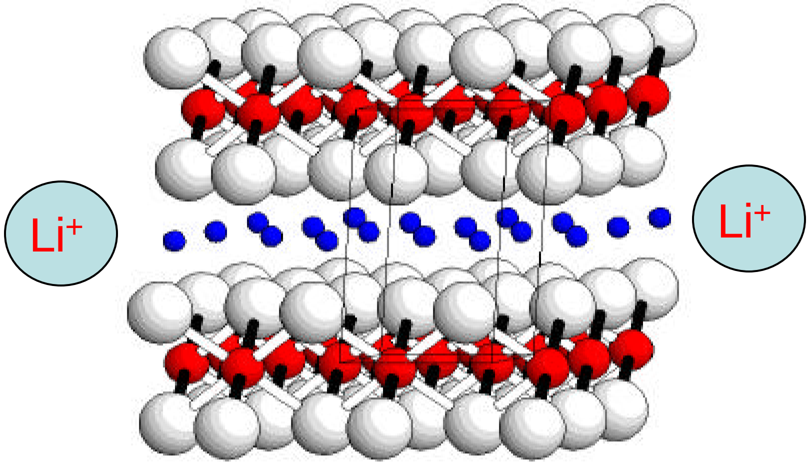
Pushing Back the Frontiers
1. Spinels: Moving to 3-Dimensional Structures

$LiMn_2O_4$ - $Li_{1.05}Mn_{1.95}O_4$

Thackeray, Goodenough



v.s.



- Li insertion and diffusion can occur in 3D ☺
- Smaller (anisotropic) volume changes in cycling ☺

-Manganese Spinels $LiMn_2O_4$ --> MnO_2+ Li 4V 120 $mAhg^{-1}$

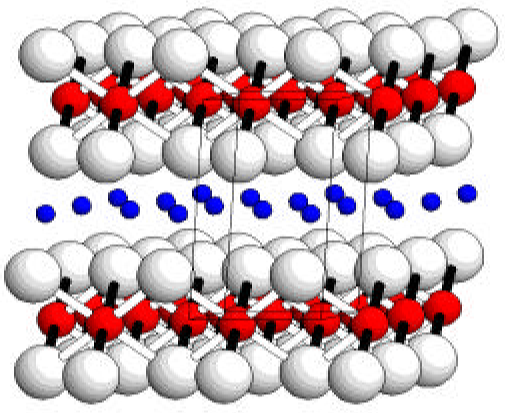
-Cheap, Good electronic conductivity -   high power ☺

- but low capacity (cannot reduce to < $Mn^{3.5+}$, due to JT distortion) and problems with Mn^{2+} dissolution 🚫

•Commercialized in applications where cost is critical

•Zero-strain anode $Li_4Ti_5O_{12}$

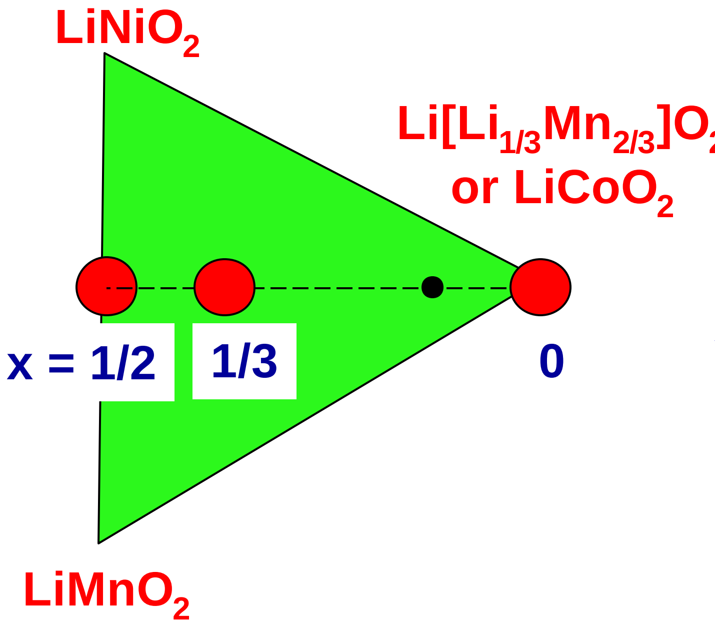
Pushing Back the Frontiers
2. Improving Capacity in Layered Materials



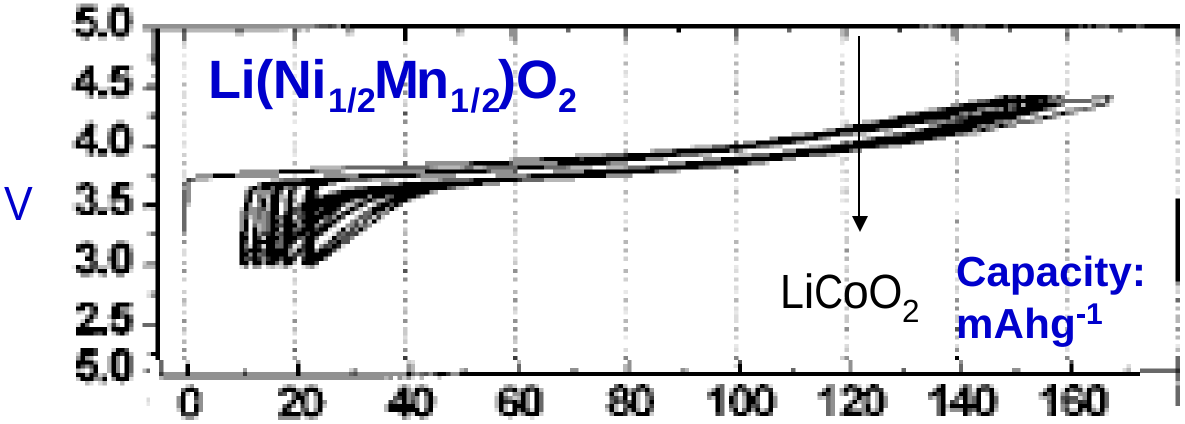
Layered cathode materials have been discovered, where the oxidation/reduction processes involve multiple-electron redox processes

Ni^{2+}-Ni^{4+} (Ohzuku & Makimura, *Chem. Lett.* ‘01; Lu, MacNeil, & Dahn, *Electrochem. Solid St. Lett.*, ‘01)

Cr^{3+} - Cr^{6+} $Li[Li_{0.2}Mn_{0.4}Cr_{0.4}]O_2$ (Ammundsen, ‘01)



200 mAhg-1 to 4.8 V



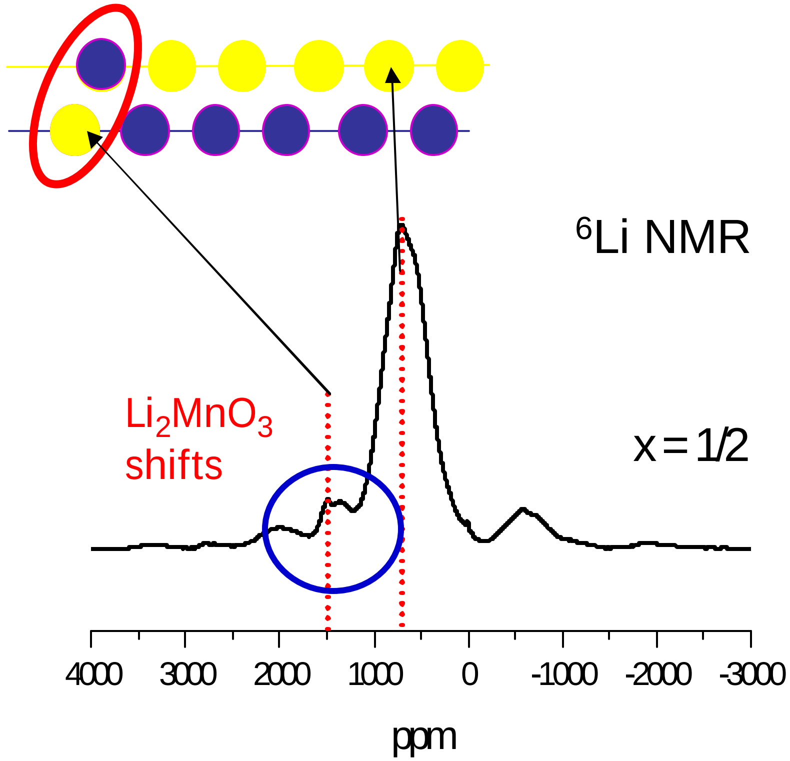
DATA From: Z. Lu, D. D. MacNeil, J. R. Dahn, *ESSL* **4**, (2001) A191-A194.

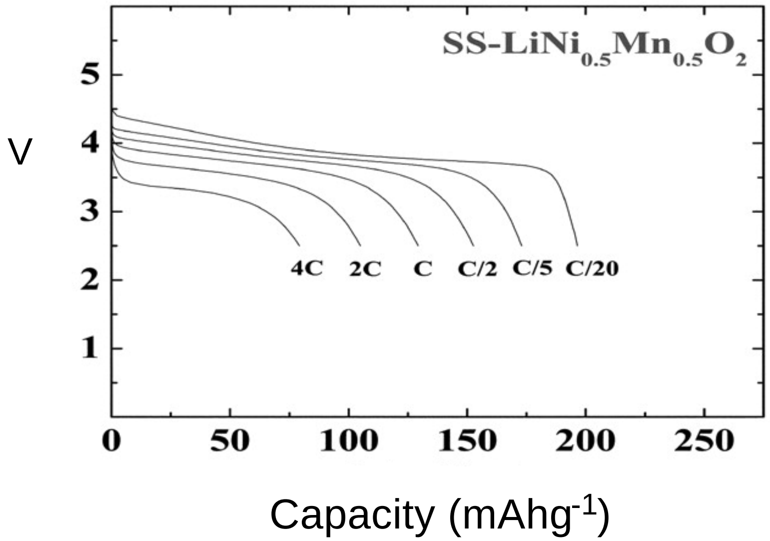
Pushing Back the Frontiers
2. Improving Capacity in Layered Materials

$Li[Co_{1/3}Ni_{1/3}Mn_{1/3}]O_2$: Improved safety of charged phases (Dahn et al.)

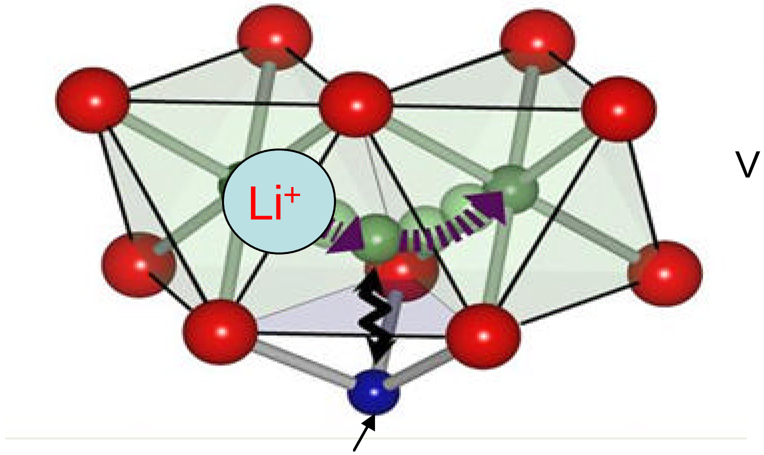
$Li[Ni_{1/2}Mn_{1/2}]O_2$: Problem with Li^+/Ni^{2+} exchange

$Li^+[Ni^{2+}_{0.5}Mn^{4+}_{0.5}]O_2$ ---> $Li_{1-x}Ni_x[Mn_{0.5}Ni_{0.5-x}Li_x]O_2$

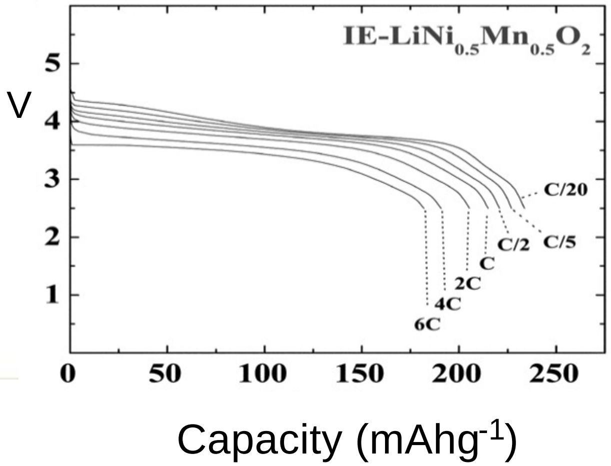


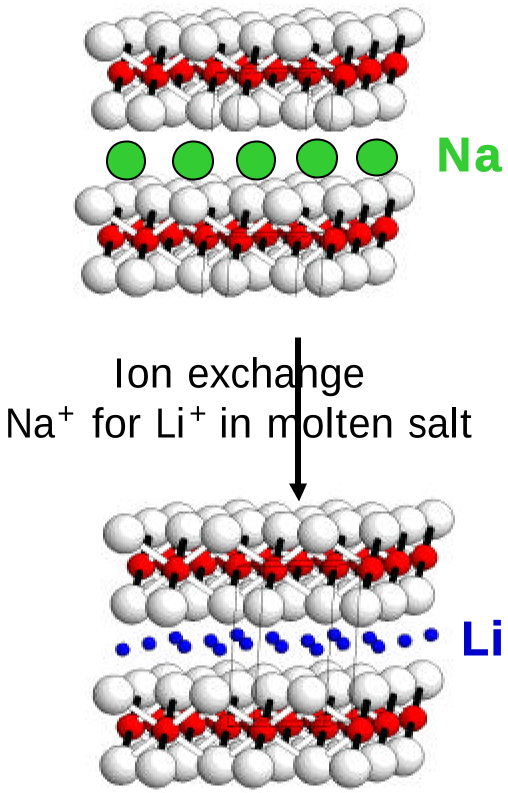


Pushing Back the Frontiers
3. Improving Ionic Conductivity in Layered Materials



activated state for Li motion is close to TM site





Ion exchange
Na^+ for Li^+ in molten salt

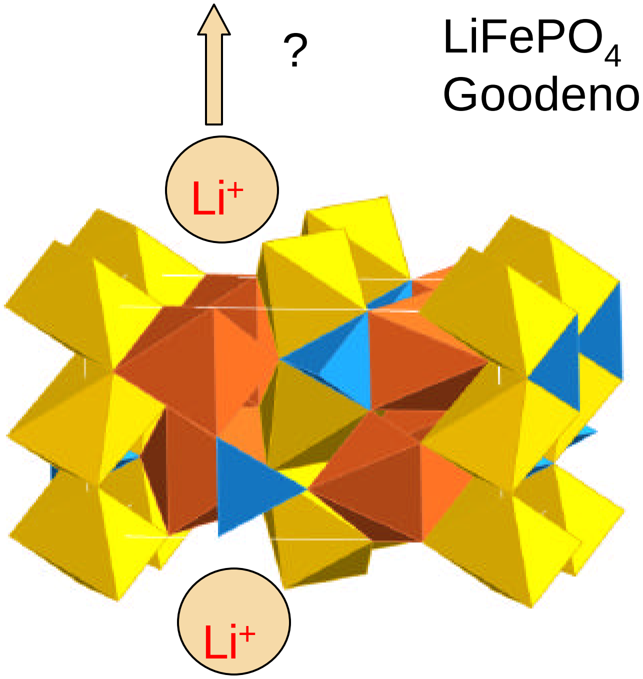
Transition metal	Co^{4+}	Ni^{4+}	Mn^{4+}	Ni^{3+}	Co^{3+}	Cu^{2+}	Ni^{2+}
Activation barrier (meV)	490	490	340	310	310	270	210 ☺

- Lead to high rate $Li(Ni_{0.5}Mn_{0.5})O_2$*

Kang and Ceder., Phys. Rev. '06

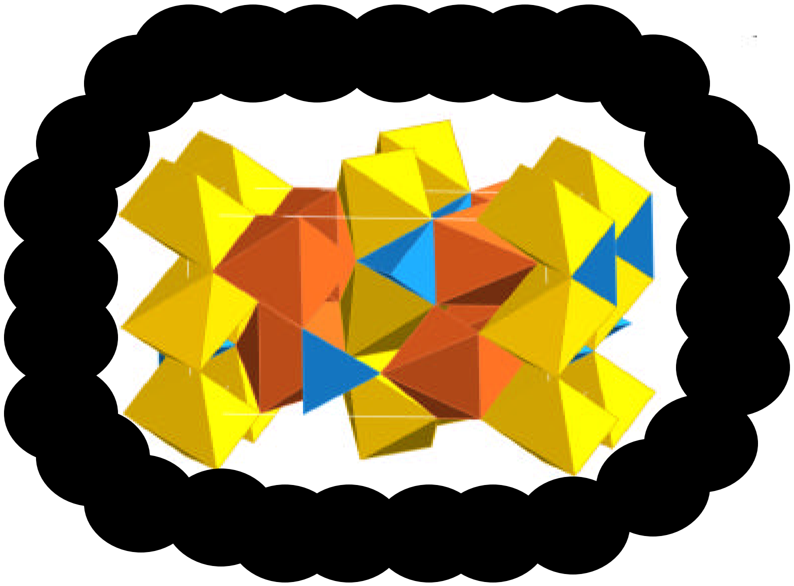
*Kang, Meng, Breger, Grey, Ceder, Science 2006

Pushing Back the Frontiers
4. $LiFePO_4$: Extracting Li From Insulating Materials



$LiFePO_4$
Goodenough

Cheap
Safe
3.4 V



$LiFePO_4 \rightarrow FePO_4$

2-phase reaction
between 2 insulators

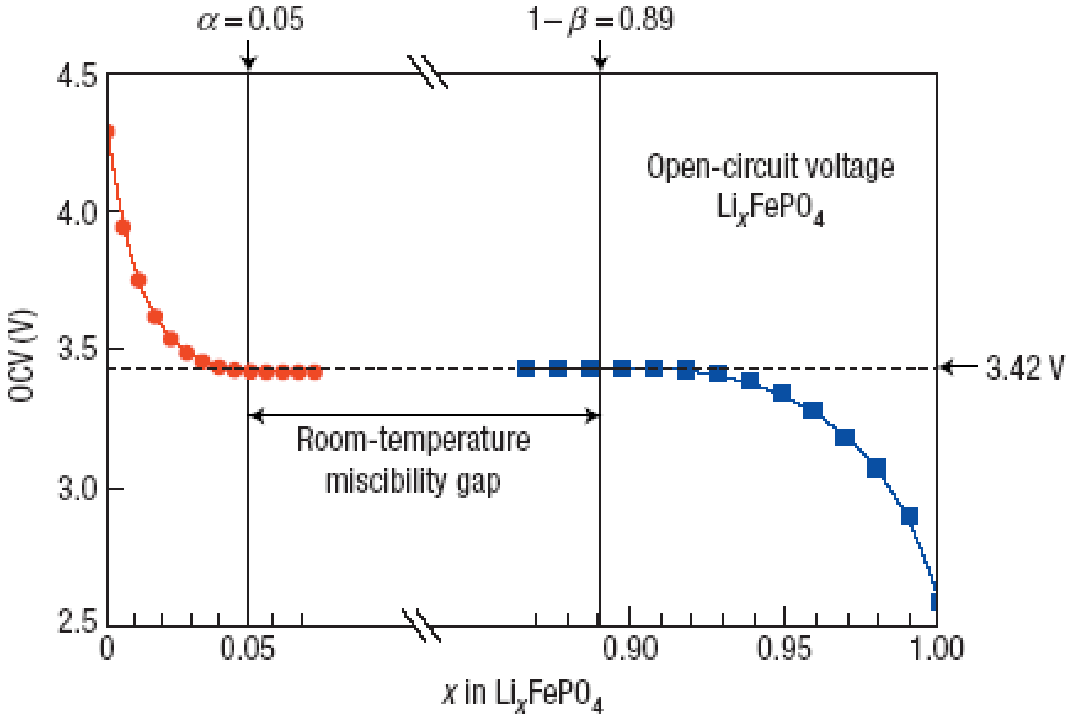
Apply carbon coating ☺
(M. Armand)

What other insulators can be made
electrochemically active?
Fe_2SiO_4 (olivine)
Fluorides
Why does $LiMnPO_4$ fail?

Make nano-materials to reduce
diffusion length
Dope?

A123

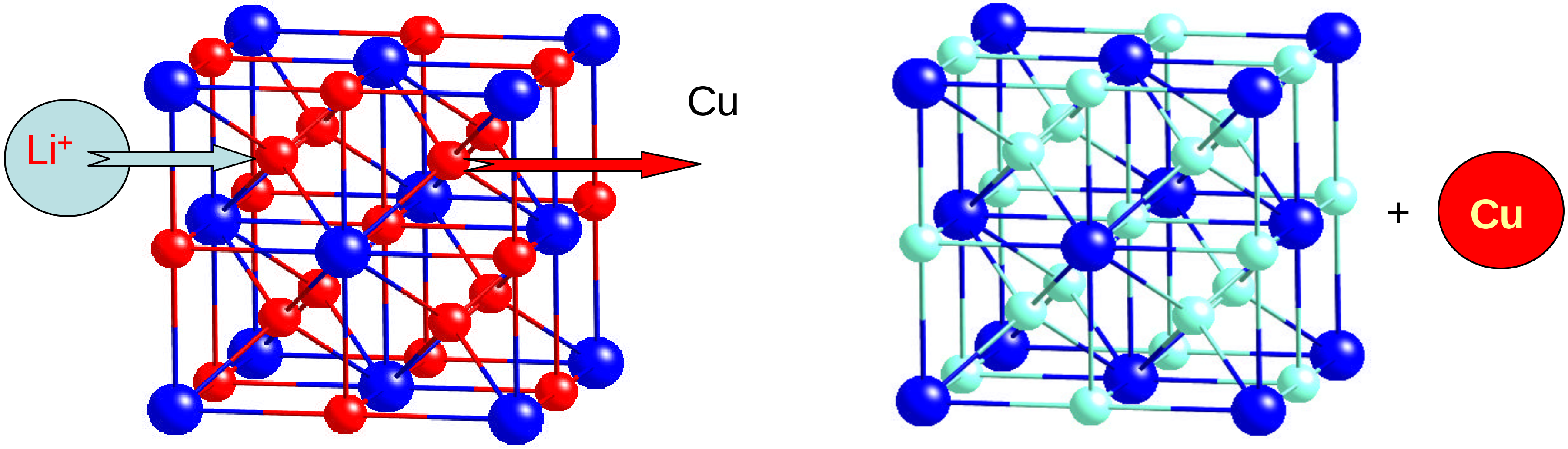
Pushing Back the Frontiers
4. $LiFePO_4$: Extracting Li From Insulating Materials



A. Yamada et al, *Nature Materials*, **5** (2006) 357

Pushing Back the Frontiers:
5. Moving Beyond Intercalation Chemistry

Intermetallic



A. Extrusion:

$InSb + Li \rightarrow Li_3Sb + In$

$Cu_2Sb + Li \rightarrow Li_3Sb + Cu$

“In^{3+}” reduced to In^0

Thackeray, Dahn

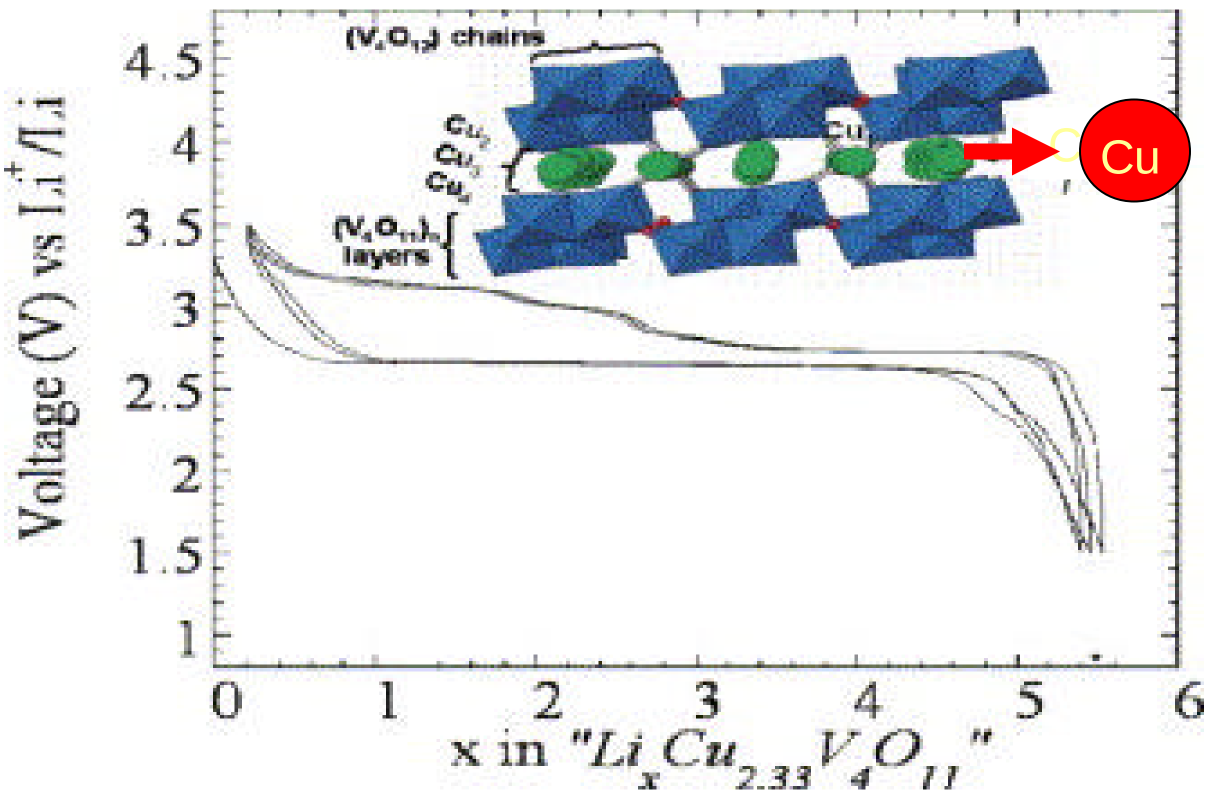
High capacities

Cost of materials?

Enabling chemistry

Reversibility?

Pushing Back the Frontiers:
6. Combining Insertion With Extrusion



Host reduced and metal extruded
=> Higher capacities?

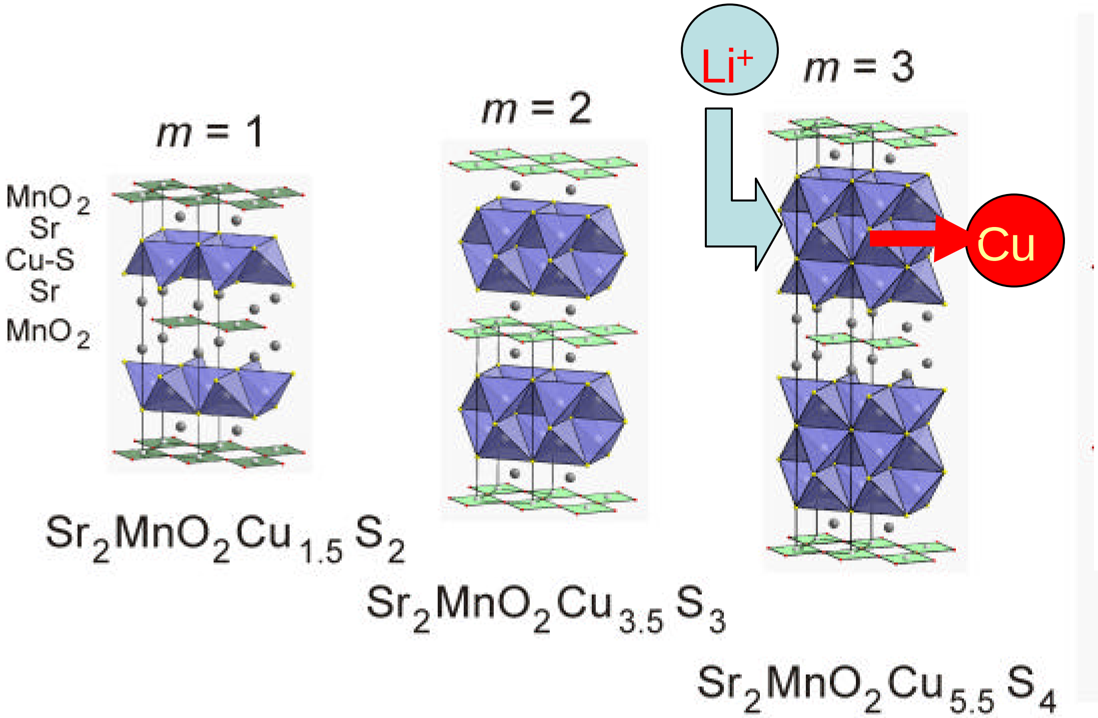
$Cu_{2.33}V_4O_{11}$ + x Li ----> $Li_xCu_{2.33-y}V_4O_{11}$ + y Cu

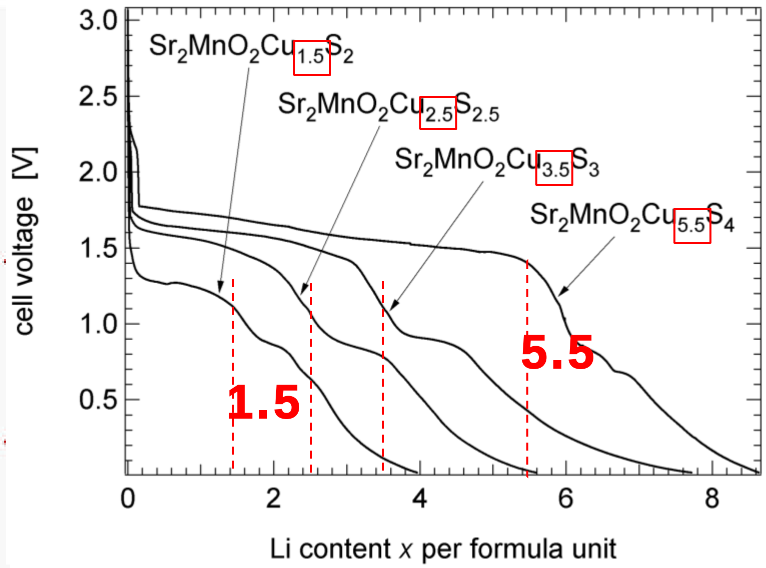
Cu^+ V^{5+} V^{4+} Cu^0

Reversibility?

Morcrette and Tarascon

Pushing Back the Frontiers:
6. Combining Insertion With Extrusion



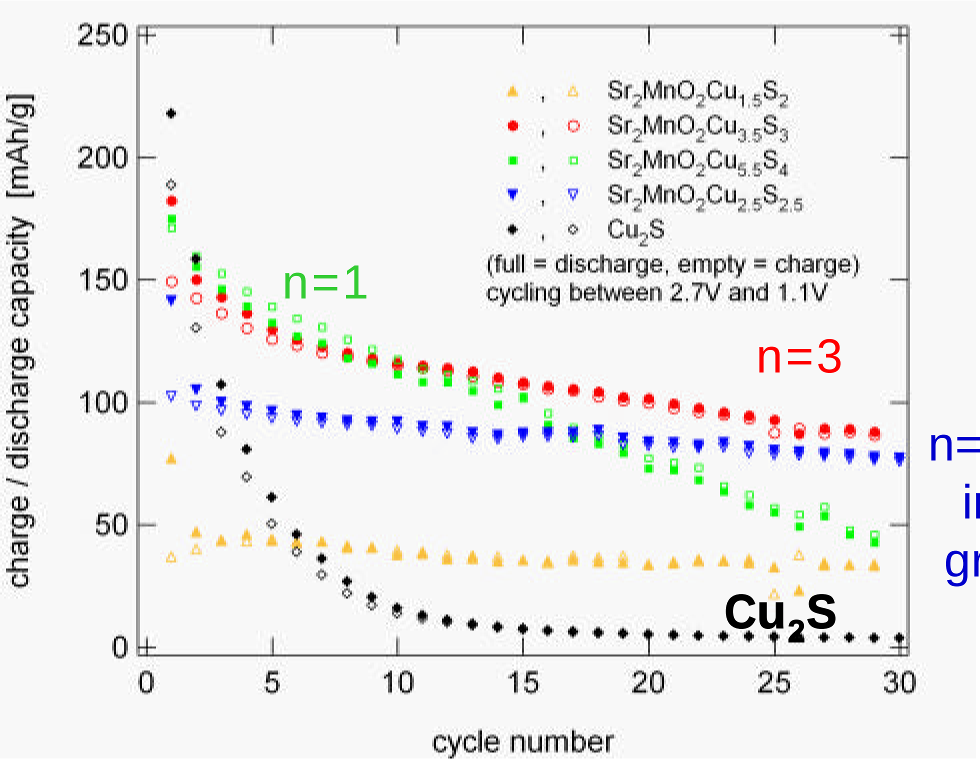


$Sr_2MnO_2Cu_{1.5}S_2$ + 1.5Li -> $Sr_2MnO_2Li_{1.5}S_2$ + 1.5Cu

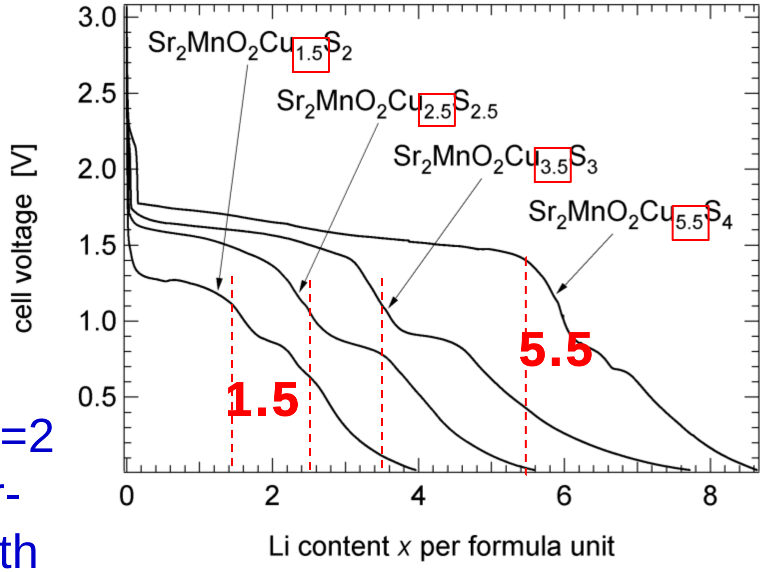
$Mn^{2.5+}$ Cu^{+} Mn^{2+} Cu^{0}

Clarke, Rutt, U. Oxford; S. Indris, J. Cabana and Grey

Pushing Back the Frontiers:
6. Combining Insertion With Extrusion



n=1/n=2 inter-growth



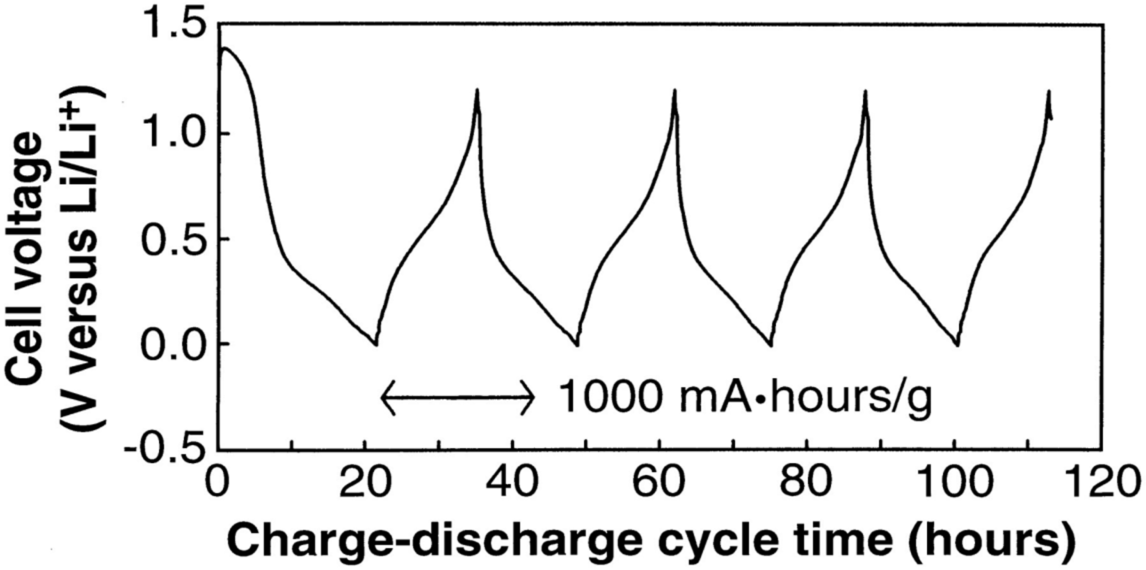
The materials cycle well in *c.f.* to Cu_2S

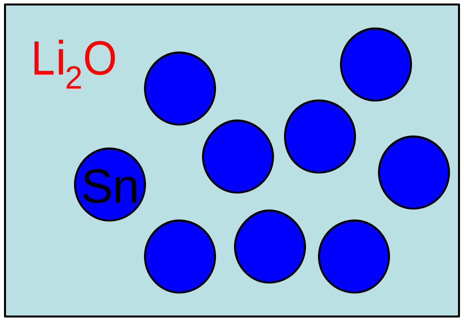
Relatively inert layers help to stabilize electrodes
Rapid Li^+ mobility in sulfide layers

Clarke, Rutt, U. Oxford; S. Indris, J. Cabana and Grey

Pushing Back the Frontiers:
7. Multiple Electron Processes: Nanoparticles and Composites

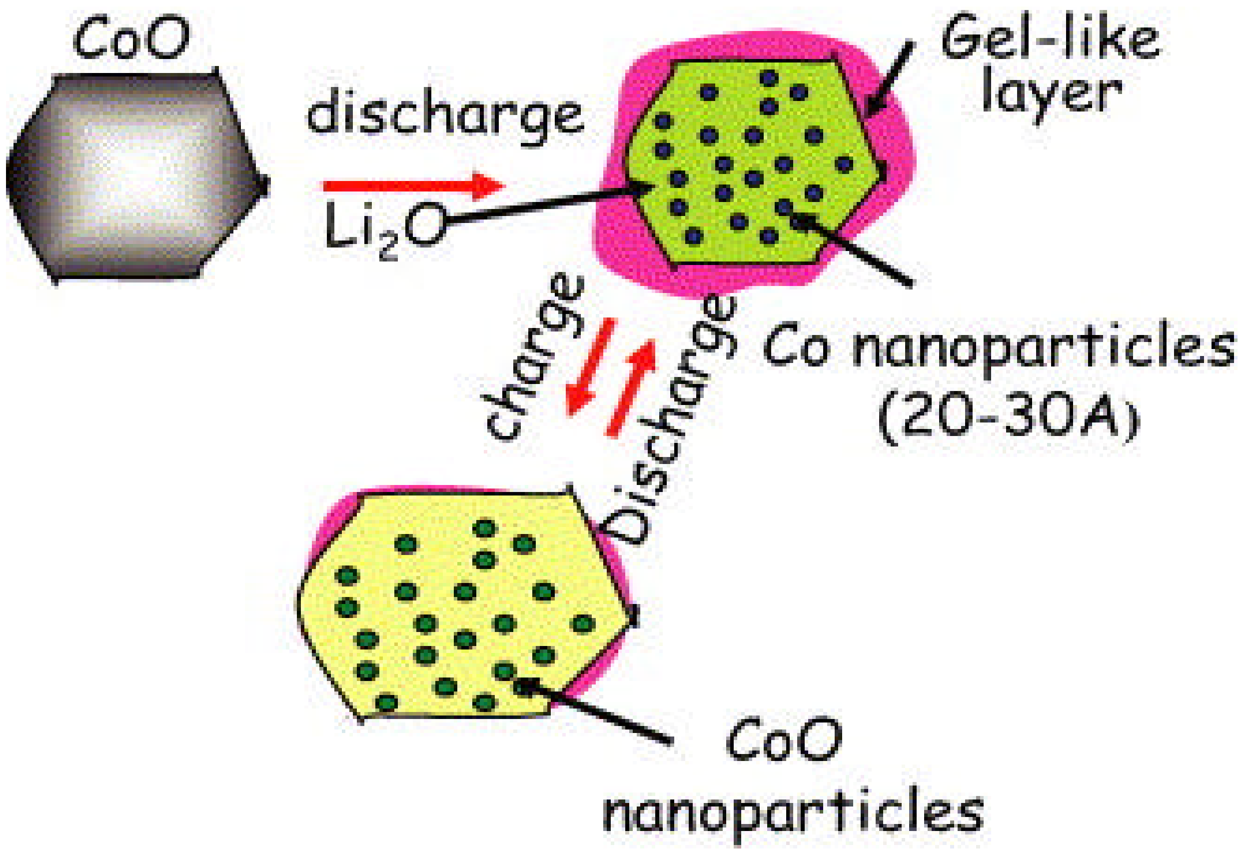
- Metals and alloys show v. high capacities (e.g, Si = 4000 mAhg-1) but suffer from extremely large volume expansions
- => use a composite (of nano particles/domains) to absorb stresses during cycling
- **Tin-Based Amorphous Oxides (TCO):** $Sn_{1.0}B_{0.56}P_{0.4}Al_{0.4}O_{3.6}$ (T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science*, 1997)





TCO : $SnO + SnO_2 \dashrightarrow Li_2O + Sn \dashrightarrow Li_xSn$

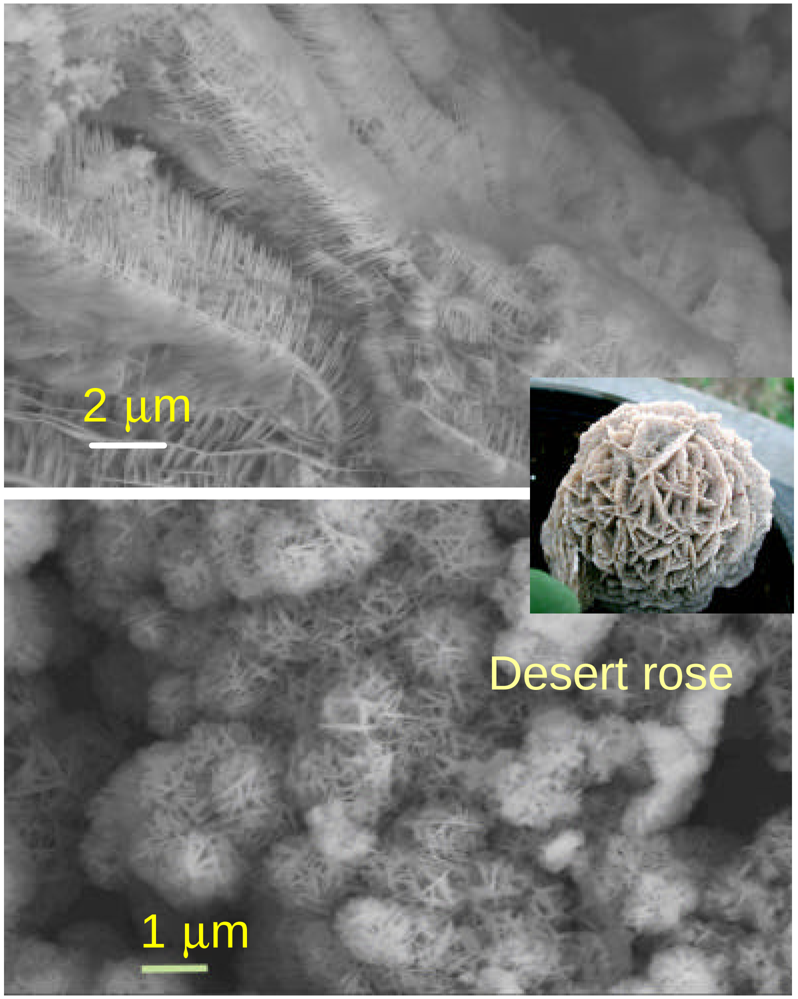
Pushing Back the Frontiers:
7. Multiple Electron Processes: Nanoparticles and Composites



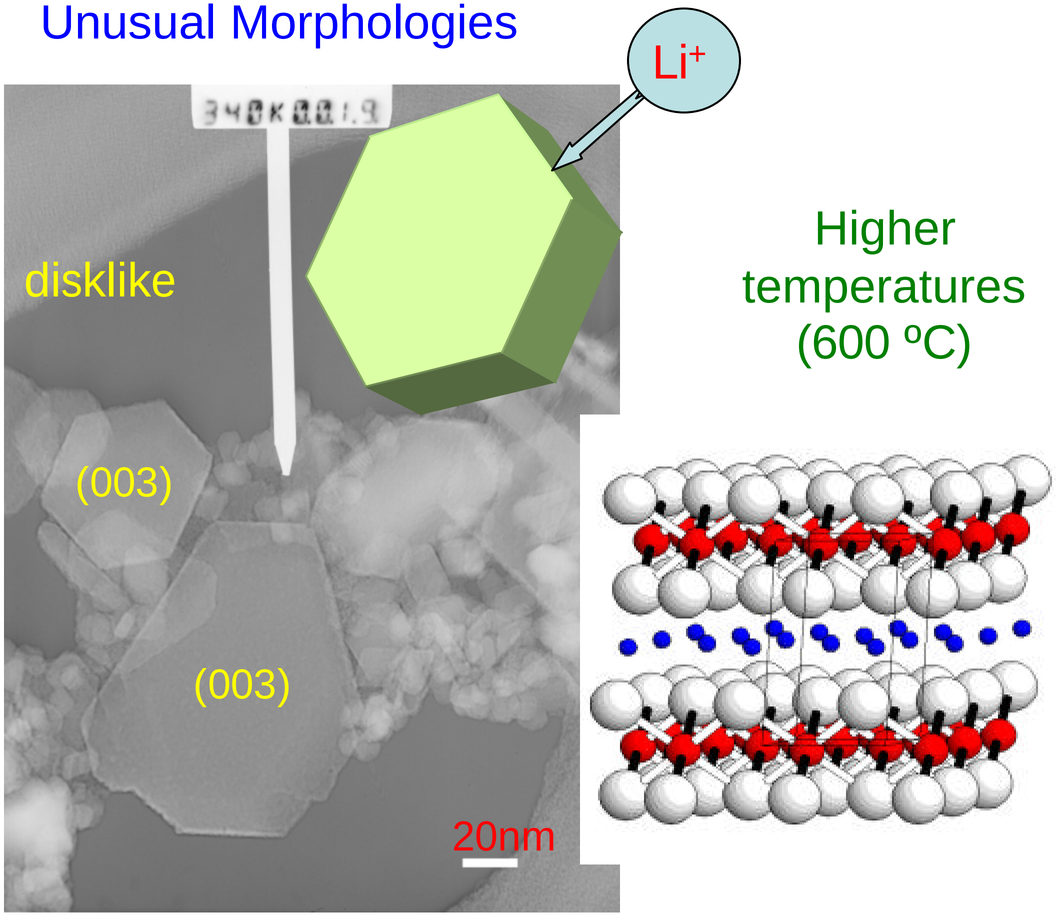
$CoO + 2Li \dashrightarrow Li_2O + Co$ (740 $mAhg^{-1}$)

S. Grugeon… J.-M. Tarascon, 2003

Pushing Back the Frontiers: 8. Design of electrodes: New nanostructures, composites and morphologies



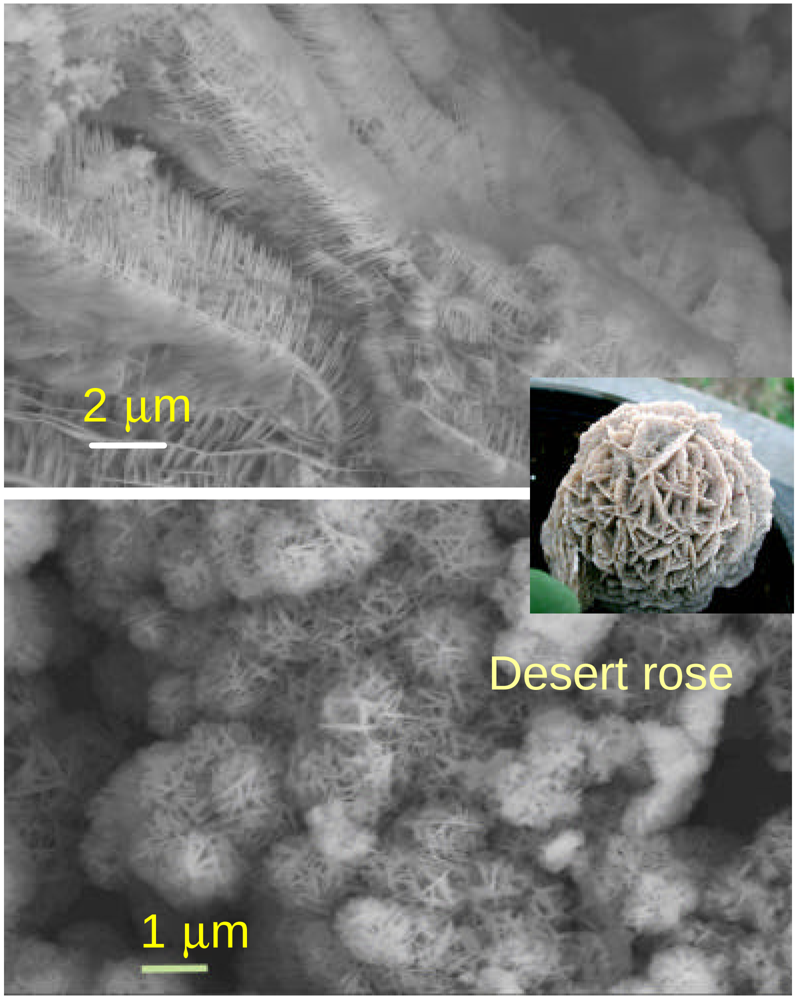
Low Temperature (200 ºC) Molten Salts and Hydrothermal Reactions: Unusual Morphologies

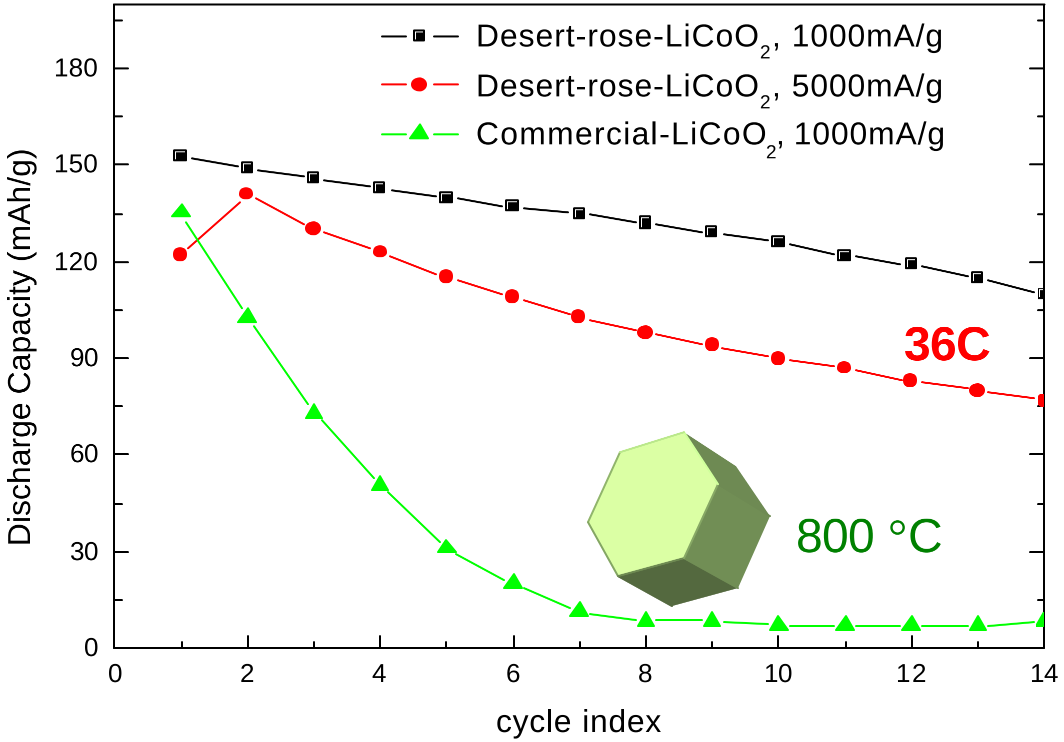


Higher temperatures (600 ºC)

Pushing Back the Frontiers:

8. Design of electrodes: New nanostructures, composites and morphologies





Balls (roses) stay intact in electrode:

- Optimize concentration 010 and 100 surfaces for intercalation
- Particles wired together
- But still issue of capacity fade

How do we go from new materials chemistry to an operating battery?

Improving the materials performance requires a fundamental understanding of how materials function and what structural/electronic properties limit battery performance

1. How do material/cells/batteries function and how and why they (often!) fail

Structures of the materials as they are cycled

Electronic properties and ionic conductivities: How do they change as Li^+ is removed?

2. Identify, and develop a fundamental understanding of, mechanisms for processes relevant to energy storage. For example,

- How does an ion intercalate into and diffuse through a solid and how does this vary with type of surface, bulk structure, metal vs. ionic solid, morphology..?
  (solid solution vs. 2-phase, role of defects, dislocations etc.)

3. Establish *general rules* from these studies to contribute to the materials design process.

- Structure property relationships…
- key material parameters (and their implications for material stability and rate performance).

Identify under what regime the rules or predictions are expected to apply.

4. Challenge the conventional wisdom

- Remove the cartoons (esp. true of nano!)

Optimizing Battery Function Requires that we understand how many components and processes function individually and synergistically

- materials -active (electrodes, additives)
-inactive (separator, current collectors…)
-electrolyte (solvent, salt, additives)
-multiple interfaces (electrolyte/cathode, active material/ binder, electrolyte, carbon within active material…)

- processes -redox mechanism & kinetics
-self discharge
-ageing
-failure mode
-safety, abuse tests

Characterization Techniques (structural, spectroscopic, physical, electrochemical…)

-Combine with simulation & modelling
-in situ
-ex situ

Many parameters:
•need to define issues that are critical to performance and to extract general and specific trends

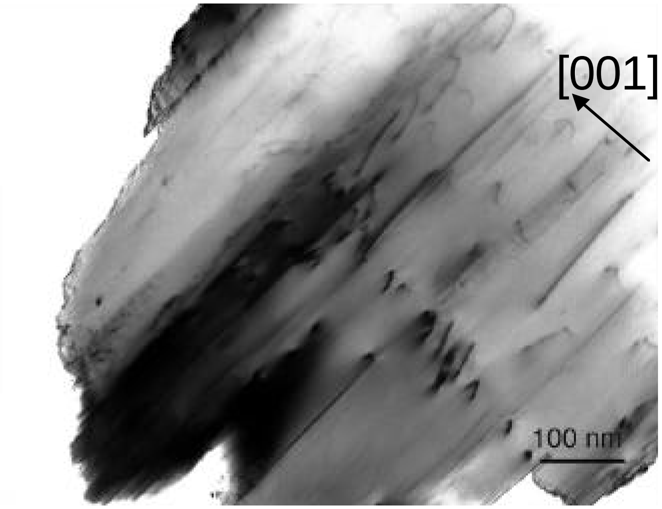
•Batteries are alive and intrinsically complex systems:
need for interdisciplinarity, multi – level approaches

We have little general/fundamental understanding of .... the role that interface structure and chemistry plays in controlling battery performance

Solid - Solid

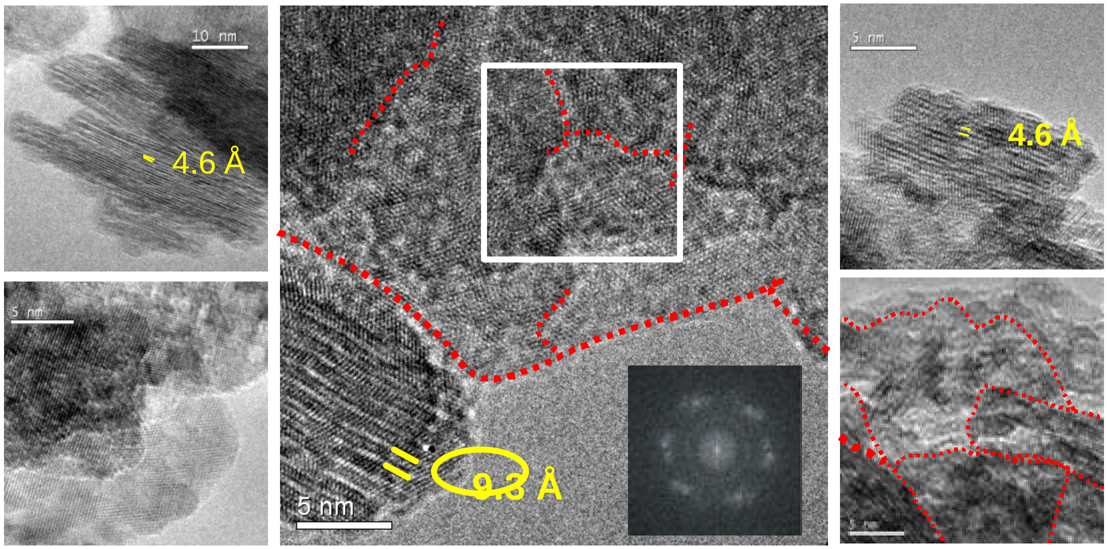
Internal interfaces – **dislocations**, reaction fronts etc.

Dislocations in $LiCoO_2$ (commercial material, uncycled) (H. Gabrish): View perpendicular to the [001] direction.
- Dislocations glide in slabs stacked along [001].



The β-$Ni(OH)_2$ / β-NiOOH transformation (R. Palacin)

$$\beta\text{-}Ni(OH)_2 \xrightarrow{O_3} \beta\text{-}NiOOH \xrightarrow{H_2O_2} \beta\text{-}Ni(OH)_2$$



- What is the role of dislocations in cycling behavior?
- How do they change during cycling, do they adopt an equilibrium configuration?
- Relationship to fracture formation/prevention?

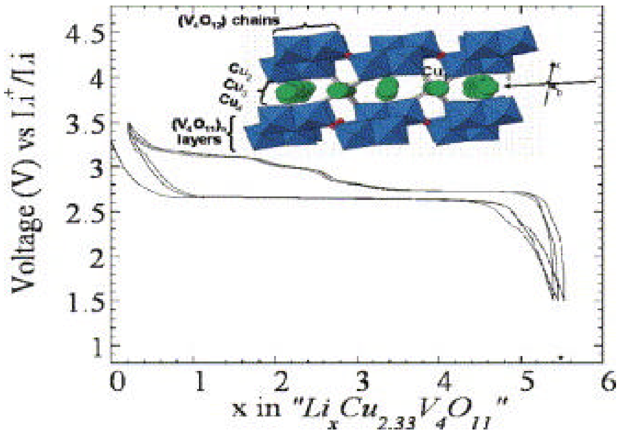
We have very general/fundamental understanding of .... the role that interface structure and chemistry plays in controlling battery performance

Solid - Solid

- Internal interfaces cont.
- How do **reaction fronts** move through solids?
- Does this vary with temperature, overpotential, particle morphology and size?

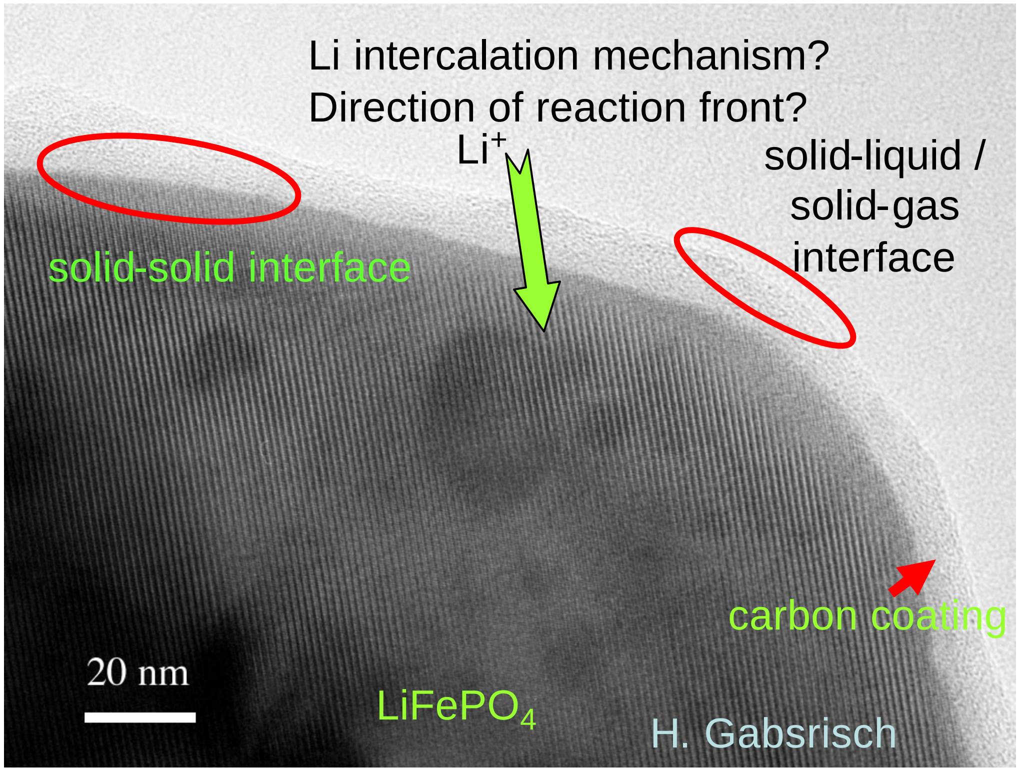
2 phase reactions:
e.g., $LiFePO_4$ Li diffusion

Conversion/extrusion reactions:
e.g., CoO, InSb, $Cu_{2.33}V_4O_{11}$, BiOF..
Cation and anion diffusion



Active – binder/carbon, Electode-SEI interfaces

Electrode-**Solid State Electrolyte** Interfaces



Li intercalation mechanism?
Direction of reaction front?

We have little general/fundamental understanding of .... the role that interface structure and chemistry plays in controlling battery performance

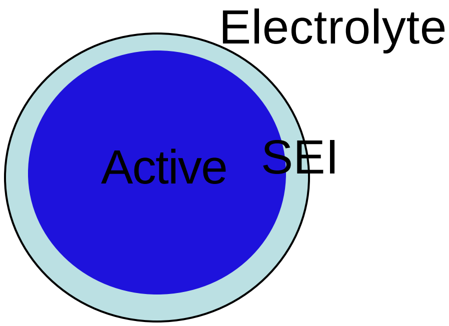
Solid – Liquid

Electrode-Electrolyte Interfaces, SEI-Electrolyte *and* Surfaces

- What does the surface structure of a working electrode look like and how does it change during charge/discharge?
- Is surface reconstruction important (esp. in aqueous media)?
- How do new electrolytes, salts and additives affect the particle surfaces and interfaces
- How do electrolytes and electrolyte salts interact with the particle surfaces? (Effect of different surfaces, surface defects?) How does this affect SEI formation?

Does the electric double layer model bear any relationship to reality?

New characterization methods should be able to answer this question..



The processes in which the electrolyte is involved are only partially understood, but key for battery performance and life.

And of course Solid – Gas and Liquid – Gas interfaces

Li-air etc

We have little general/fundamental understanding of .... the role that interface structure and chemistry plays in controlling battery performance

We need to develop new methodologies for the study of interfaces with particular attention to those involving the electrolyte: (need for more interaction with organic chemists?)

- Advance molecular-level surface electrochemistry to determine the identity or chemical functionality and spatial arrangement (orientation) of surface species at the surface (in presence of electrolyte)

- Probe and characterize charge transfer and mass transport processes

- Understand the thermodynamic, structural, mechanistic and dynamic aspects of interfacial reactions at the atomic- and nano-scale

We have little *systematic* understanding of .... the role that *size* and morphology plays in controlling battery performance

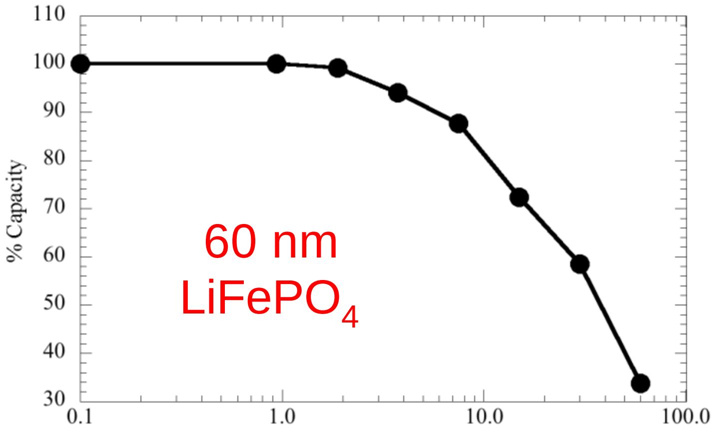
•We need to understand interactions and effects at the nano-to-atomic level and the consequences (positive and negative) of utilizing nanoparticles and composites

Are the different properties due to due electronic or surface structure effects?

Or diffusion path lengths?

or is it simply due to non-stoichiometry?

Pseudocapacitive effects?



M. S. Whittingham, J. Mater. Chem., in press (data from Kim & Kim)

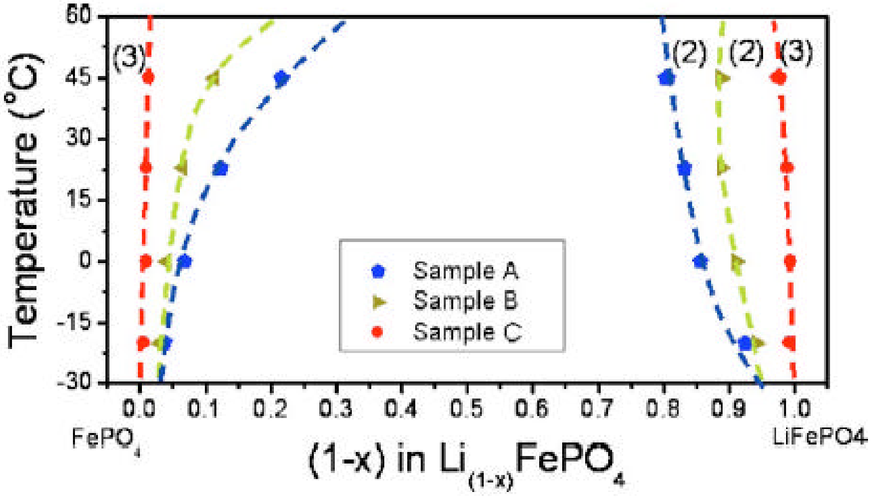
Transport?

Structural relaxation?

Electronic?

Limits of solution altered as f(size)
Yamada and Chiang

We have little *systematic* understanding of .... the role that *size* and morphology plays in controlling battery performance



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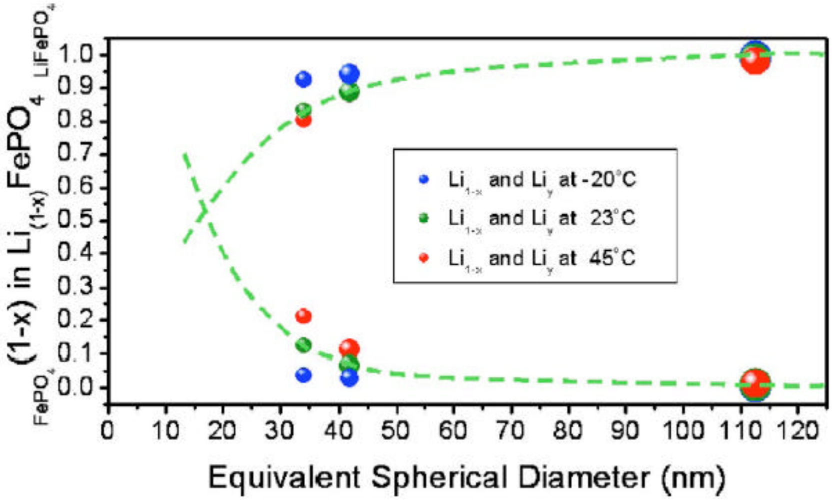
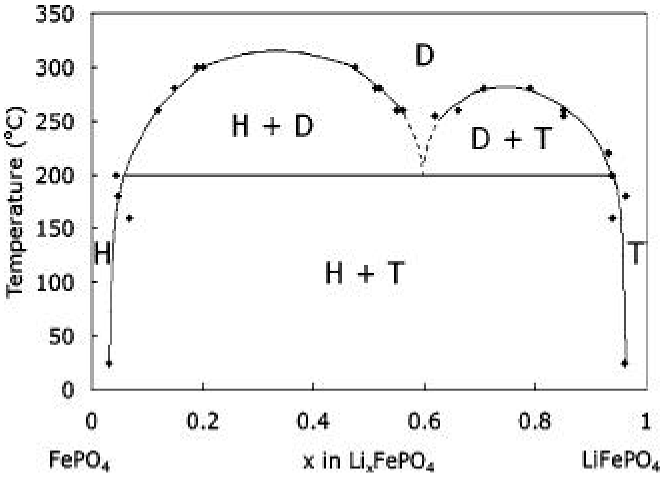




Y-M. Chiang et al, *Electrochem. Solid-State Lett.*, **10** **(**2007) A134

J. Dodd et al *Electrochem. Solid-State Lett.*, **9** **(**2006) A151

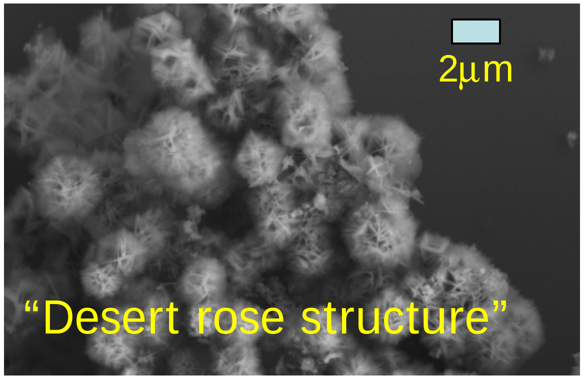
We have very little *systematic* understanding of …. the role that *size* and morphology plays in controlling battery performance

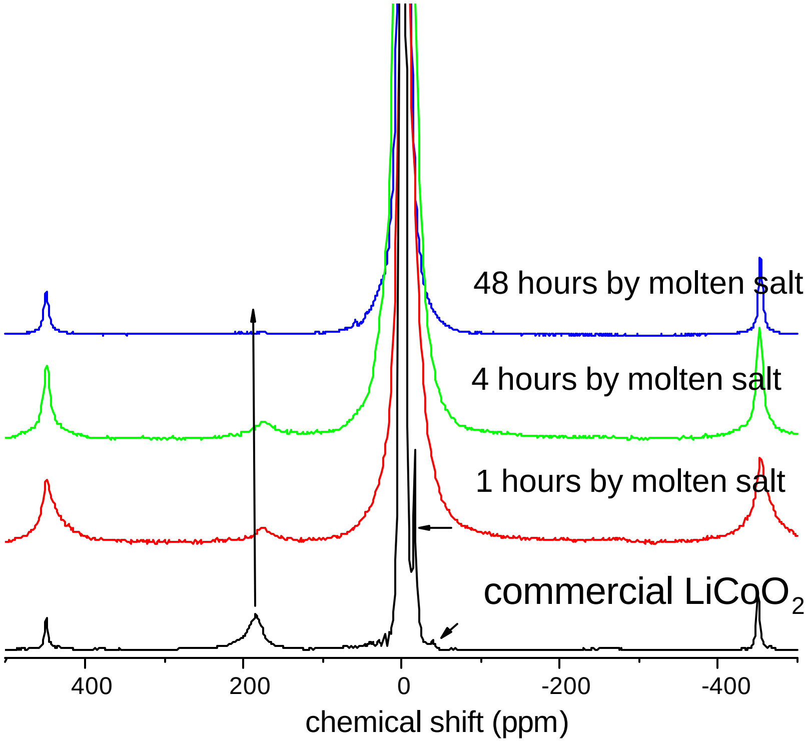
Are the different properties due to

.. diffusion path lengths?

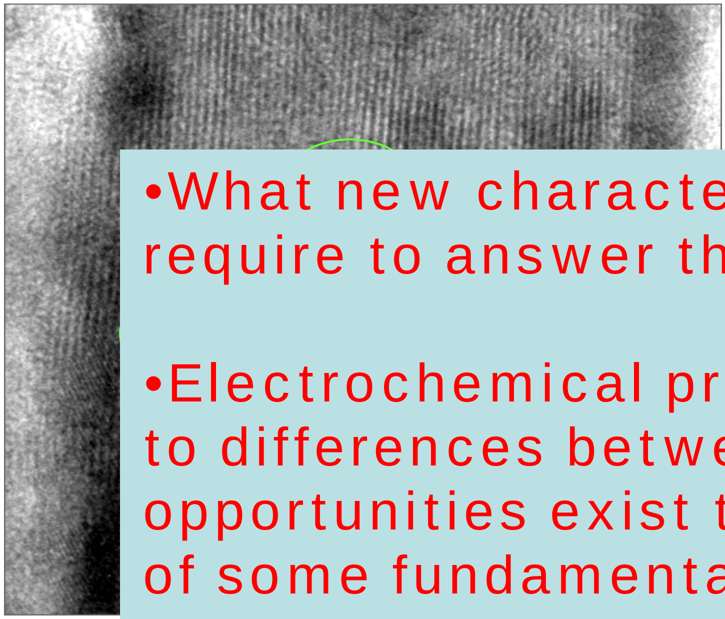
or is it simply due to non-stoichiometry?

- Maximize active surface +minimize Li^+ diffusion length
- Wire particles together (hyper-branched morphology)





We have very little *systematic* understanding of .... the role that *size* and morphology plays in controlling battery performance



Dislocations observed at high potentials associated with the O3 – O1 transition (H. Chen, C. P. Grey)

- Are the different faults and structural transformations different at the nano-

- What new characterization methods do we require to answer these questions?

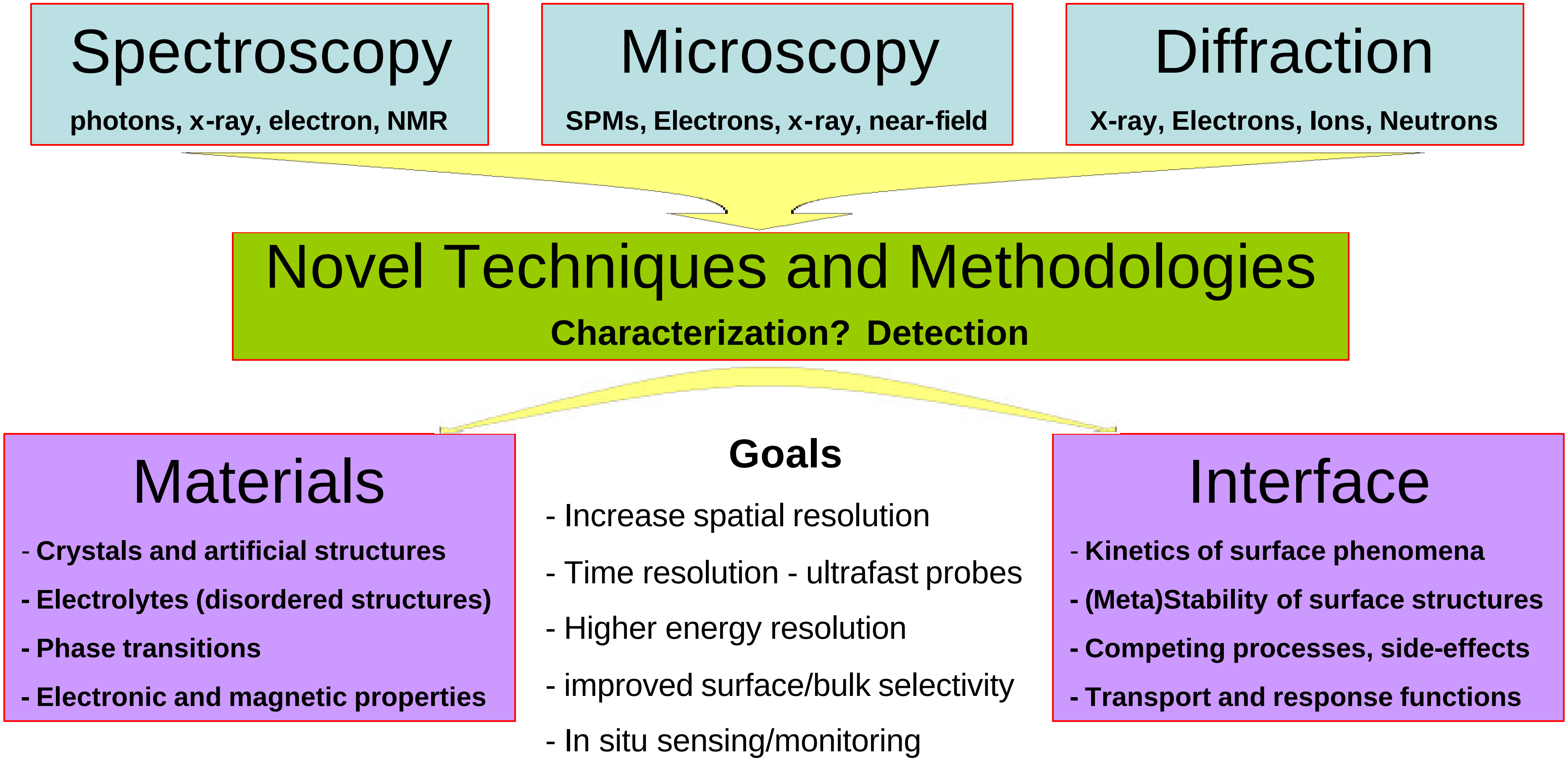
- Electrochemical profiles are extremely sensitive to differences between bulk and nanomaterials – opportunities exist to contribute to understanding of some fundamental physics/chemistry

What happens when particles are dominated by surface effects?

- Coatings – how do they work?

What new methods should we develop?

Non-destructive and in situ analysis at the highest resolution, greatest selectivity, and ultimate detection limits are the primary goals in this field



Spectroscopy

photons, x-ray, electron, NMR

Microscopy

SPMs, Electrons, x-ray, near-field

Diffraction

X-ray, Electrons, Ions, Neutrons

Novel Techniques and Methodologies

Characterization? Detection

Materials

- **Crystals and artificial structures**
- **Electrolytes (disordered structures)**
- **Phase transitions**
- **Electronic and magnetic properties**

Goals

- Increase spatial resolution
- Time resolution - ultrafast probes
- Higher energy resolution
- improved surface/bulk selectivity
- In situ sensing/monitoring

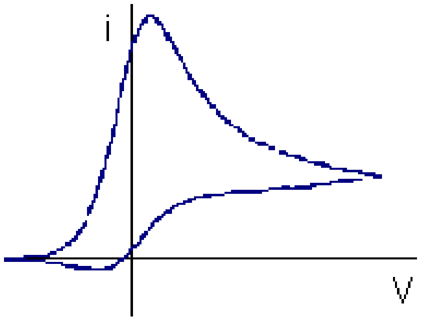
Interface

- **Kinetics of surface phenomena**
- **(Meta)Stability of surface structures**
- **Competing processes, side-effects**
- **Transport and response functions**

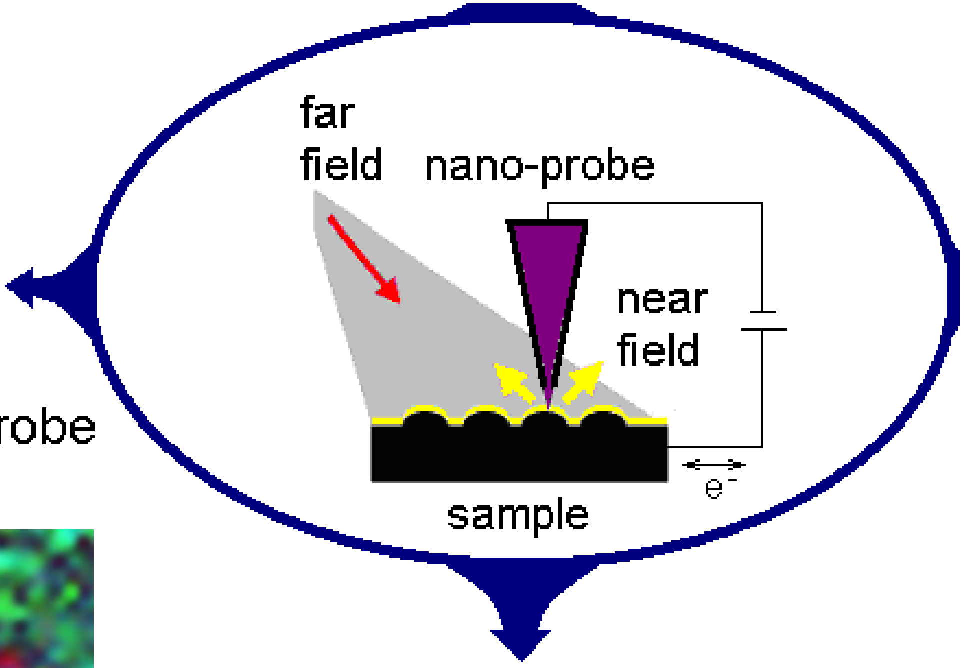
Combination of spectroscopy/diffraction and microscopy imaging to study elementary excitations at high spatial resolution will lead to development of dedicated techniques to study materials and electrode/electrolyte interfaces in energy storage systems

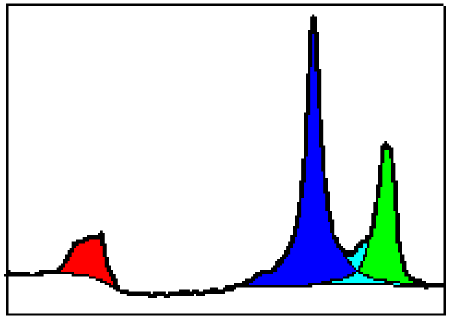
What new methods should we develop?

(In situ) Imaging + Spectroscopy



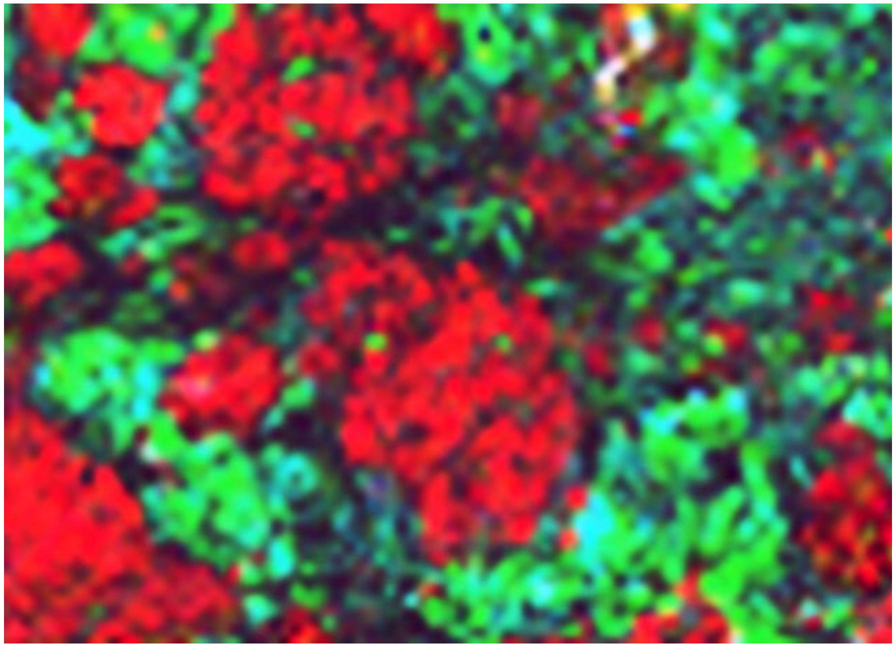
Local Electrochemical Probe





Local Structure

Raman map

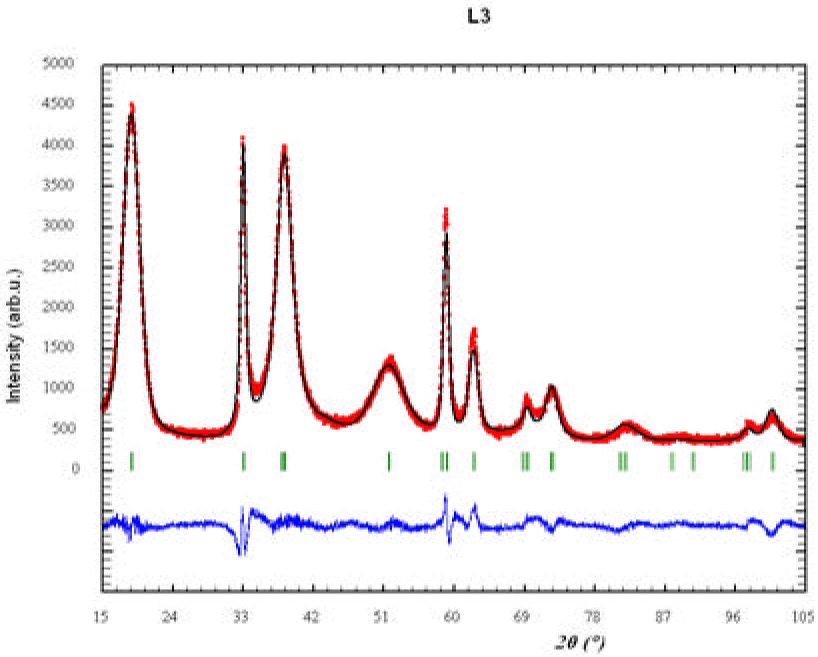


R Kostecki

What new methods should we develop?

Imaging + Diffraction

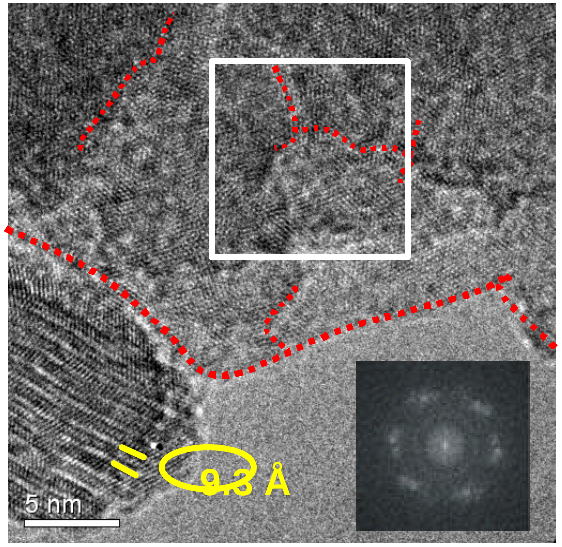
- The simultaneous use of a combination of techniques may help overcome inherent limitations of the individual method



Both diffraction and TEM data were required to solve the structure of β–NiOOH (R. Palacin)

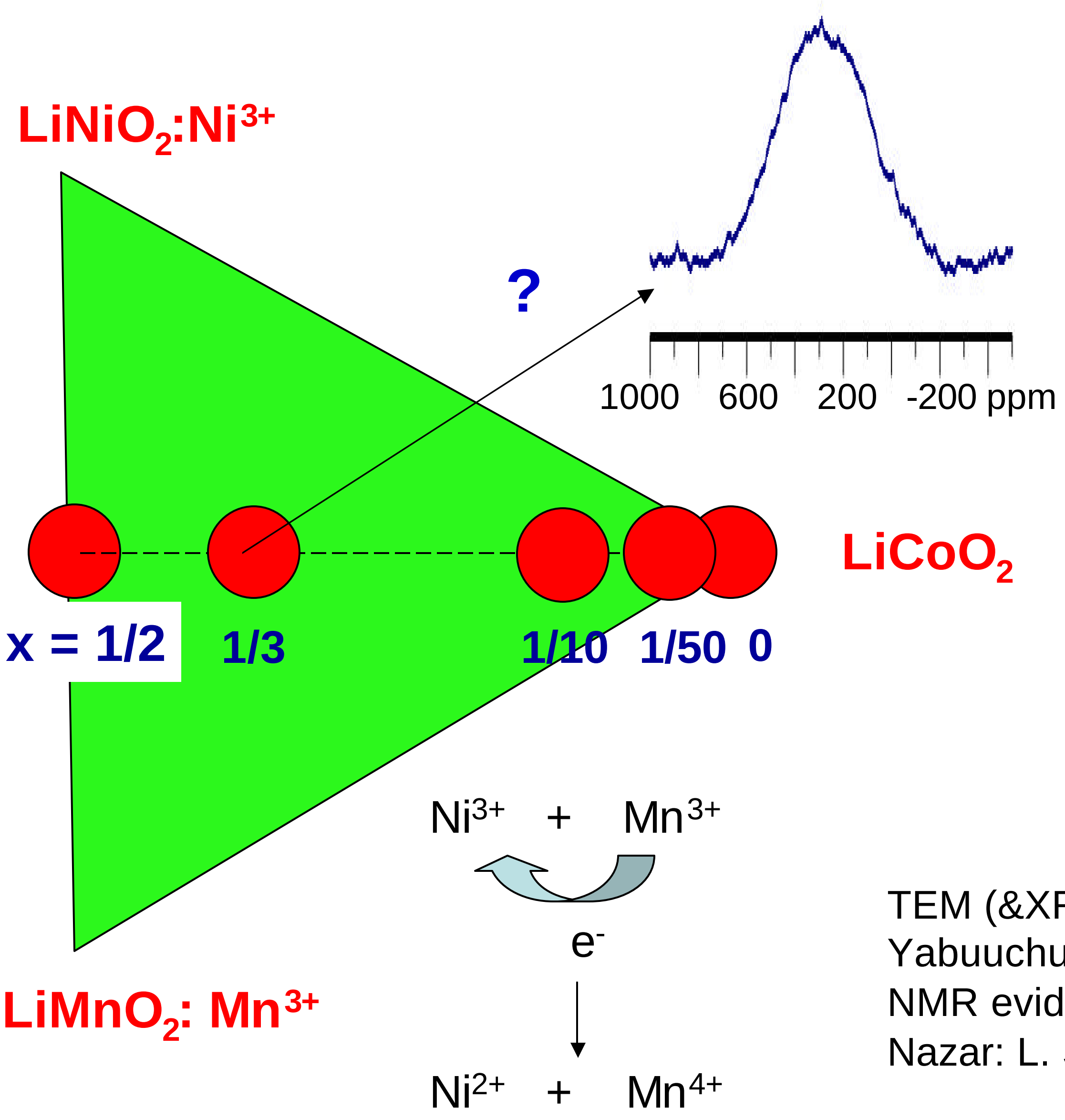
But, more method development work still needed to e.g., distinguish between strain-broadening and stacking faults

TEM : 117 Å x 50 Å



Diffraction + *Local* Structural Probes

Cation Ordering, Oxidation State and Electrochemical Properties of $Li[NiMnCo_{(1-2x)}]O_2$



$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ Ohzuku & Makimura, ‘01

$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ Lu, MacNeil, & Dahn, ‘01

“Solid solution” 1st investigated in detail by Lu and Dahn

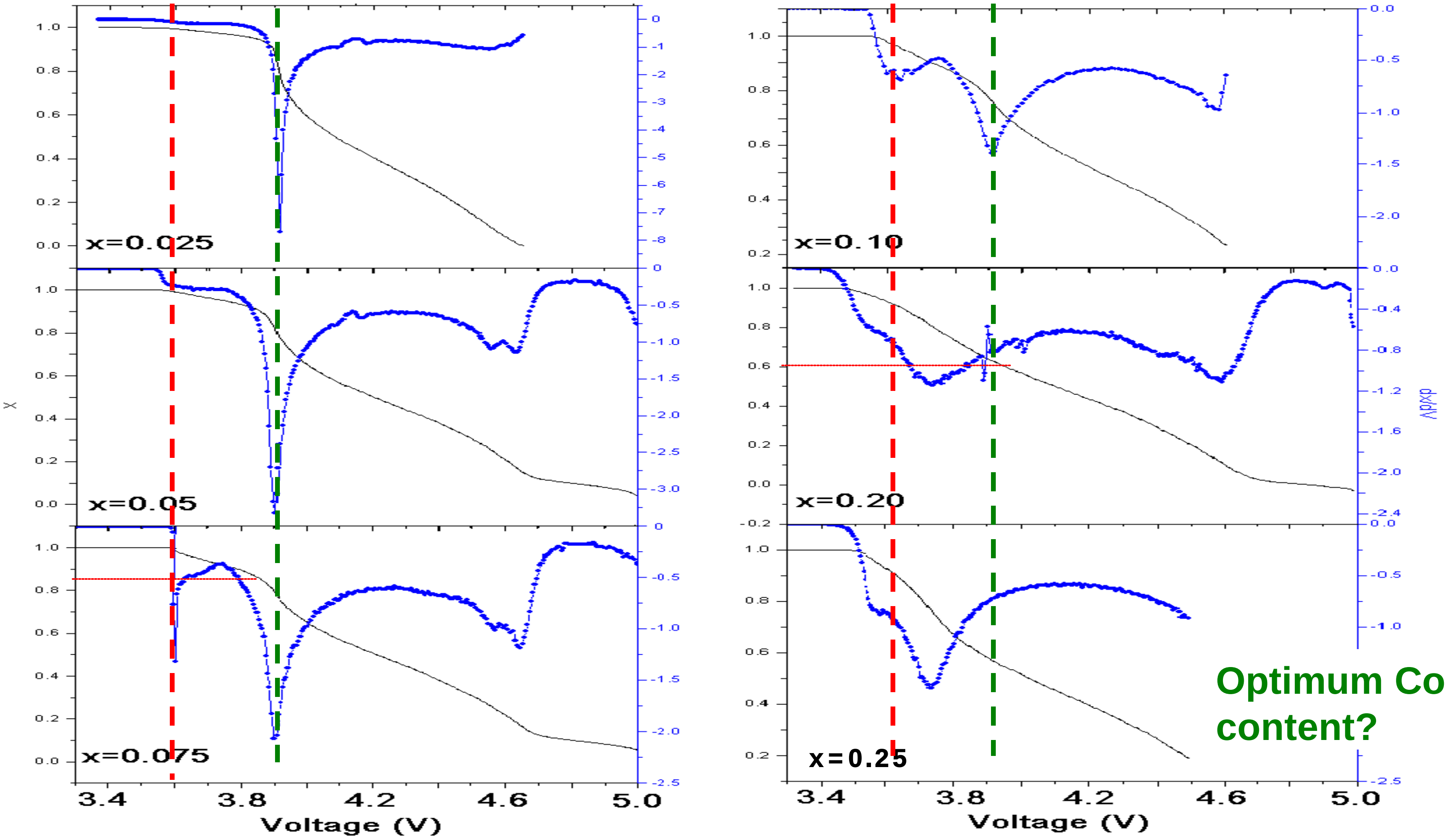
Ni and Mn clustering?
Ni and Mn oxidation state?
Effect of this on electrochemistry

TEM (&XRD) evidence for ordering (Koyama, Yabuuchu.. and Ohzuku; JES **2005**, **2004)**)
NMR evidence for local clustering (Goward and Nazar: L. S. Cahill et al., *Chem. Mater.*, **2005**)

$Li[Ni_xMn_xCo_{(1-2x)}]O_2$: Effect of Ni/Mn content on electrochemical performance?

Co^{3+} - Co^{4+} MIT?

Formula: $Li_y [Ni_xMn_xCo_{1-2x}]O_2$

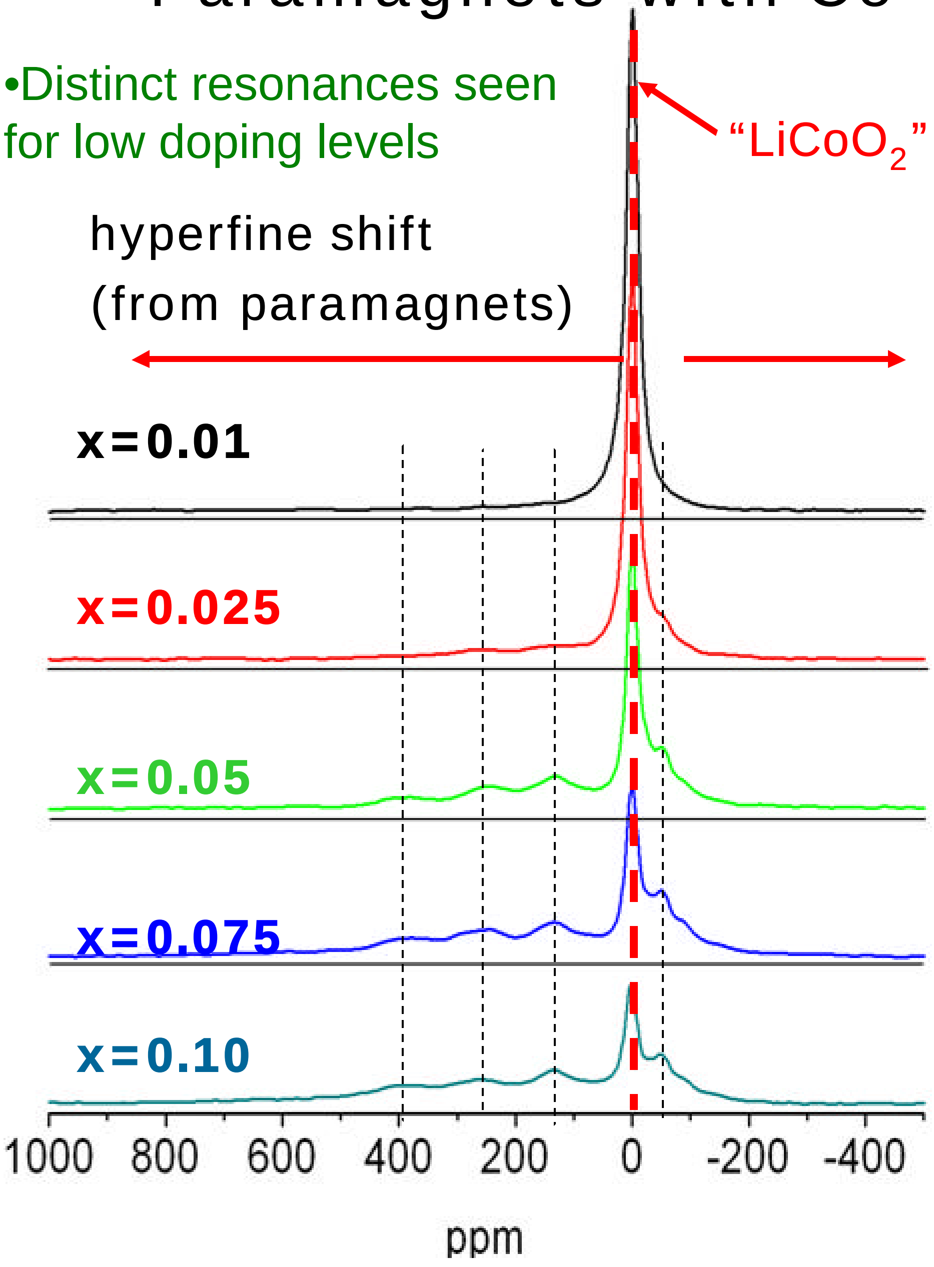


Optimum Co content?

Ni^{2+}? ›Ni^{4+} or Ni^{2+} -> Ni^{3+} -> Ni^{4+}?

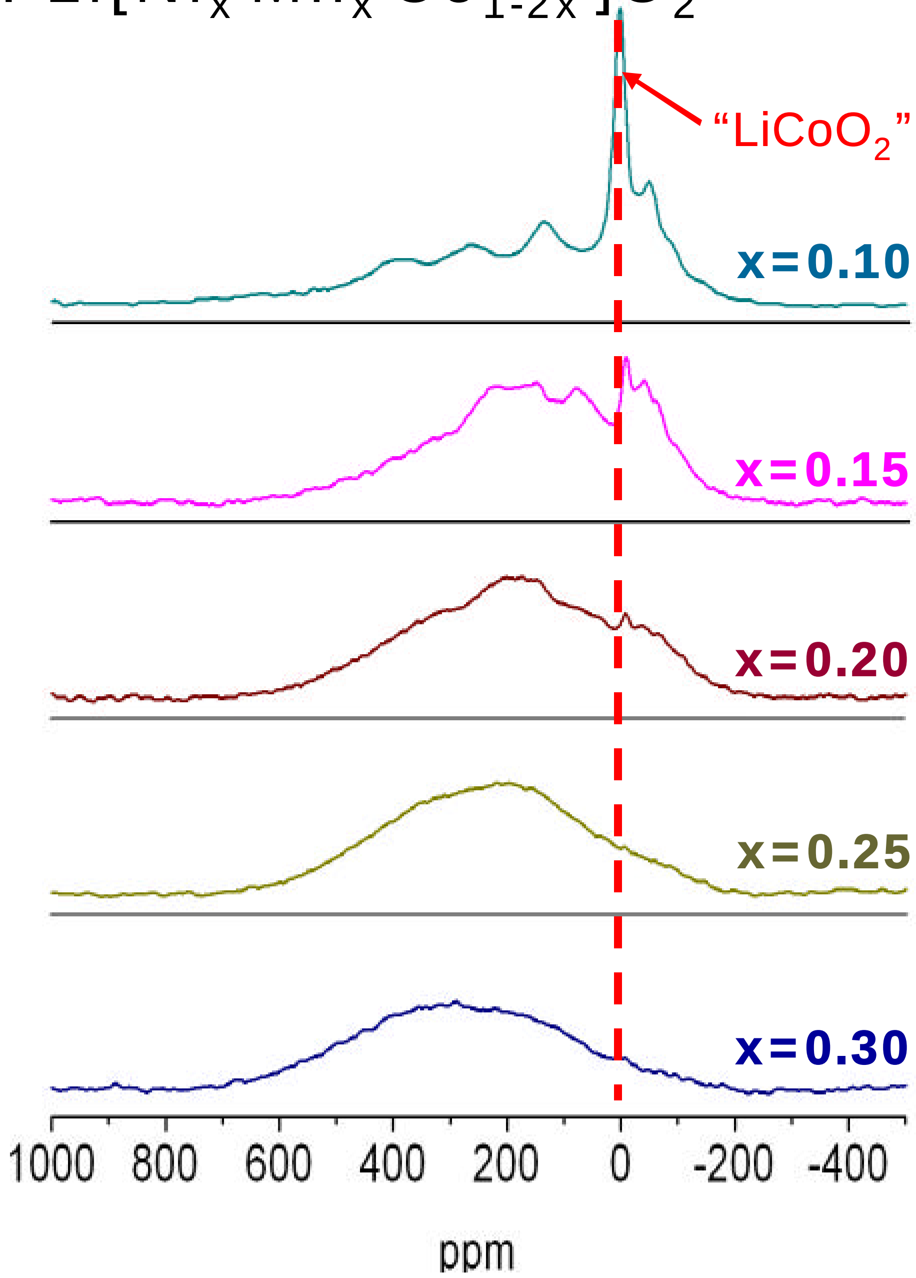
Simplify NMR Analysis by Diluting Paramagnets with Co^{3+}: $Li[Ni_{x'}Mn_{x'}Co_{1-2x'}]O_2$

- Distinct resonances seen for low doping levels



hyperfine shift (from paramagnets)

"$LiCoO_2$"



"$LiCoO_2$"

How can we assign the peaks?

- Hyperfine shifts in dilute systems are additive:

  90° Ni^{2+}-O-Li: ~ -10 to -15 ppm;

  180° Ni^{2+}-O-Li: ~ 170 ppm;

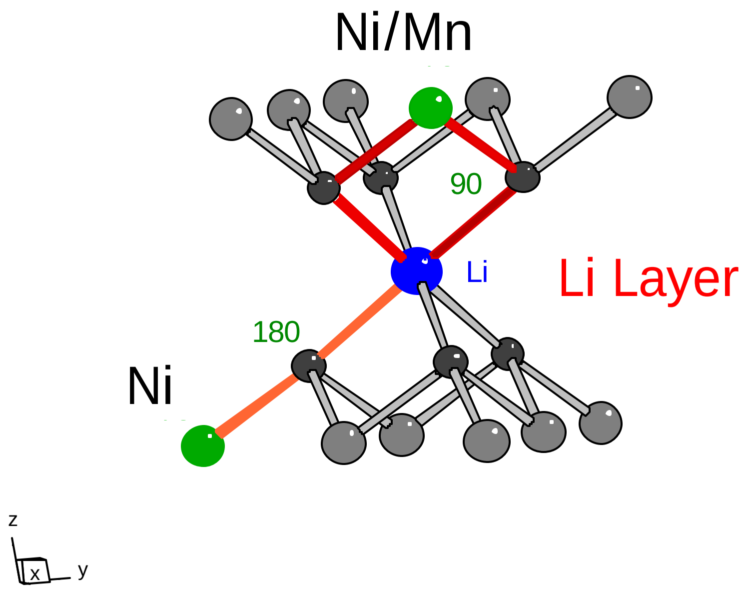
  90° Mn^{4+}-O-Li: ~ 120 – 150 ppm;

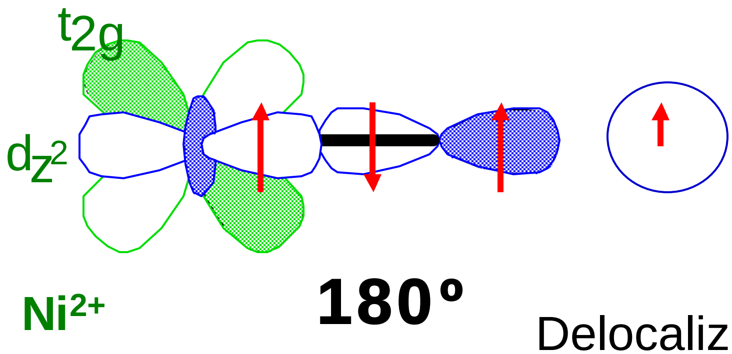
  180° Mn^{4+}-O-Li: ~ -60 ppm;

  Co^{3+}: 0 ppm.

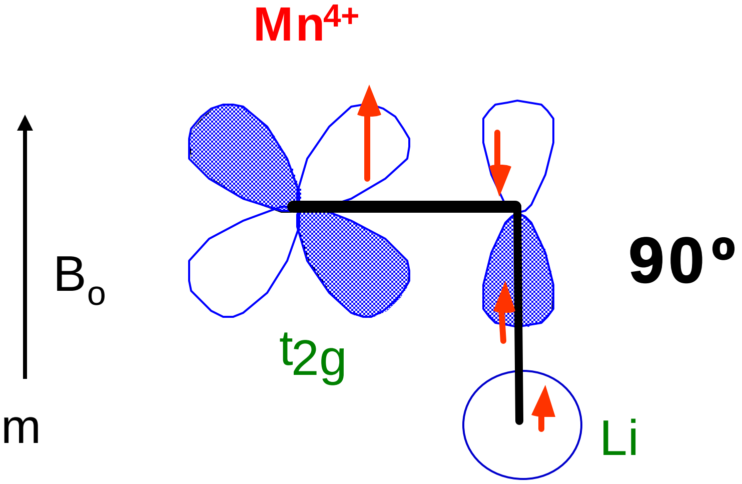
  e.g. $Li(Ni_1Co_5)^{1st}(Mn_1Co_5)^{2nd}$

  Shift = 2(-10) + (-60) = -80 ppm

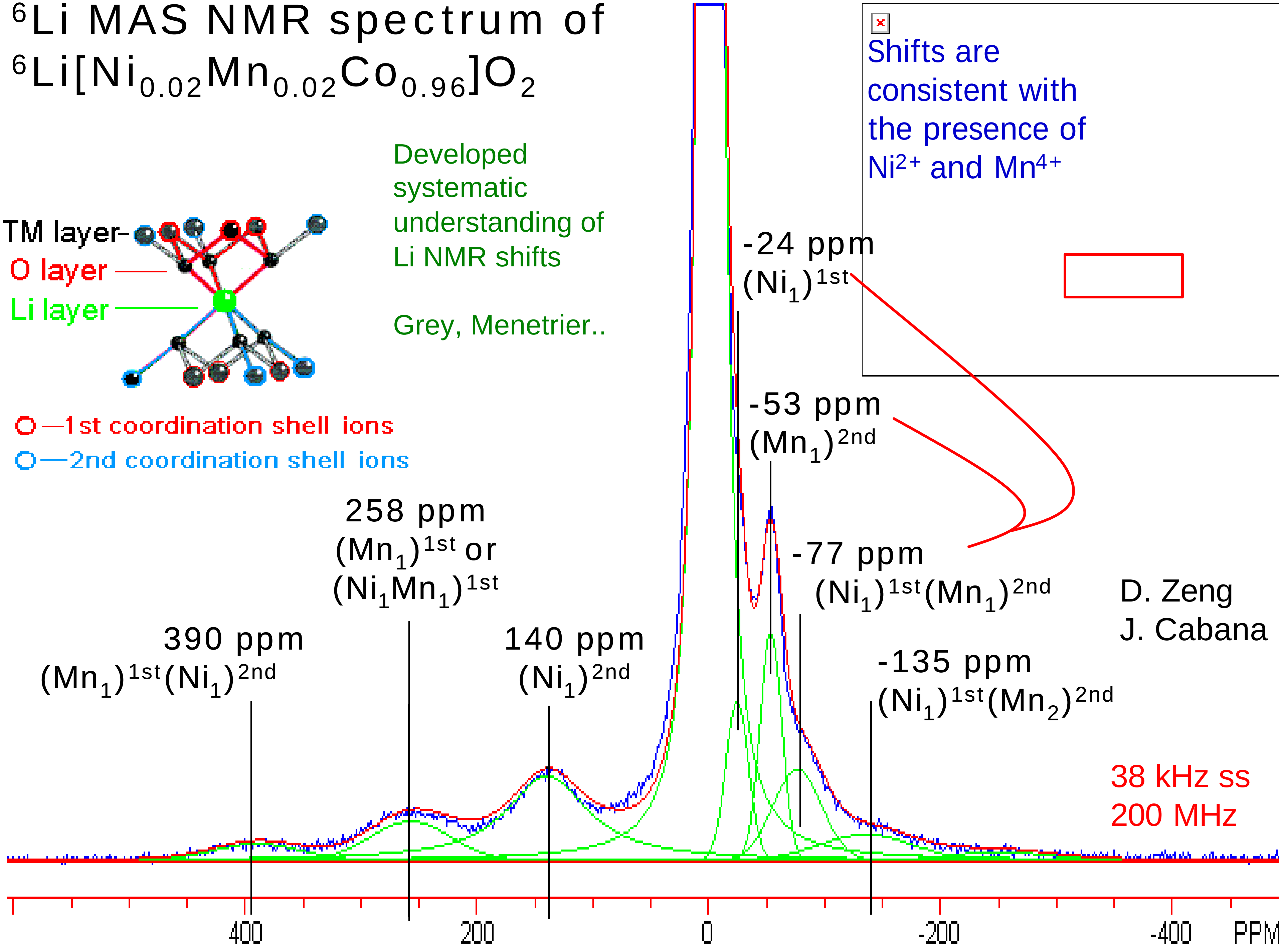




Delocalization mechanism



^{6}Li MAS NMR spectrum of $^6Li[Ni_{0.02}Mn_{0.02}Co_{0.96}]O_2$



Developed systematic understanding of Li NMR shifts

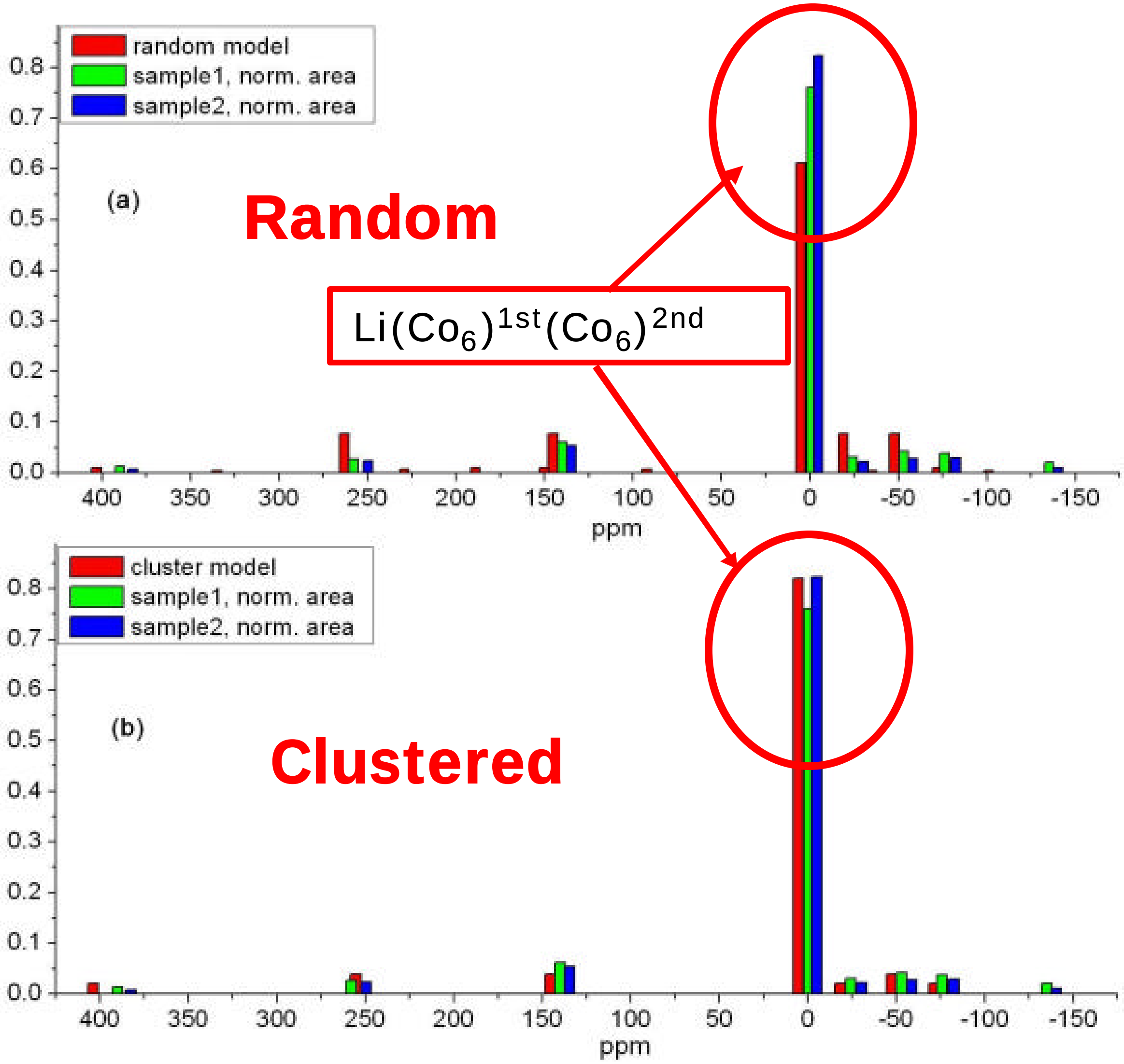
Grey, Menetrier..

Shifts are consistent with the presence of Ni^{2+} and Mn^{4+}

D. Zeng
J. Cabana

38 kHz ss
200 MHz

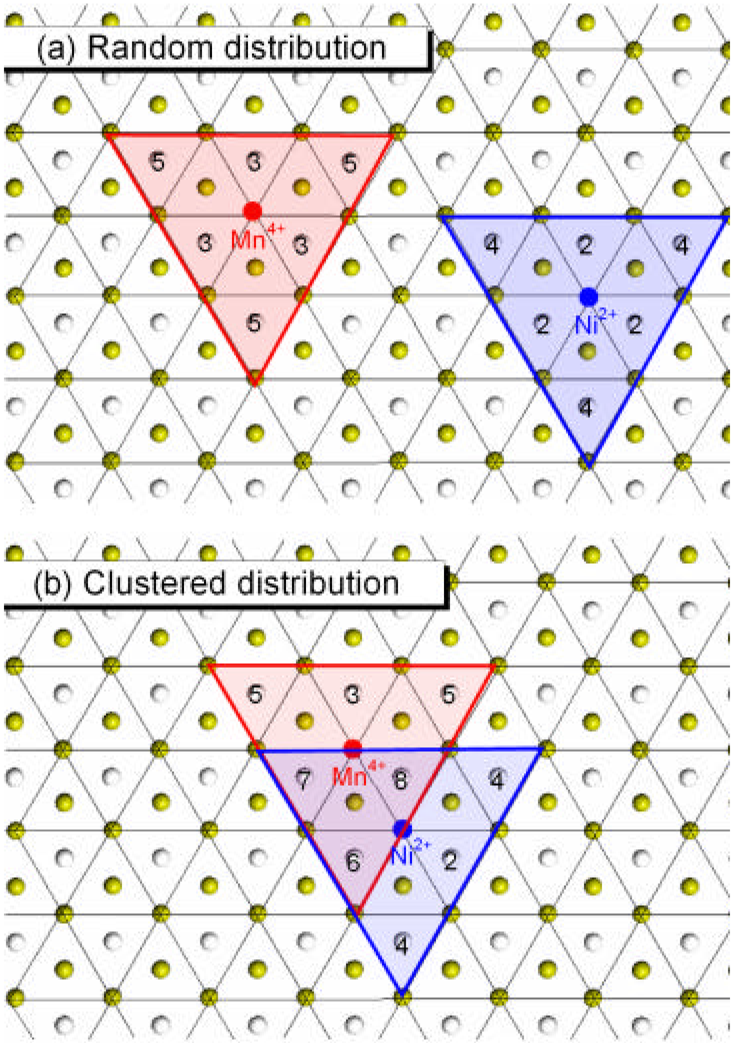
The Ni and Mn are clustered, even in $Li[Co_{0.96}Ni_{0.02}Mn_{0.02}]O_2$



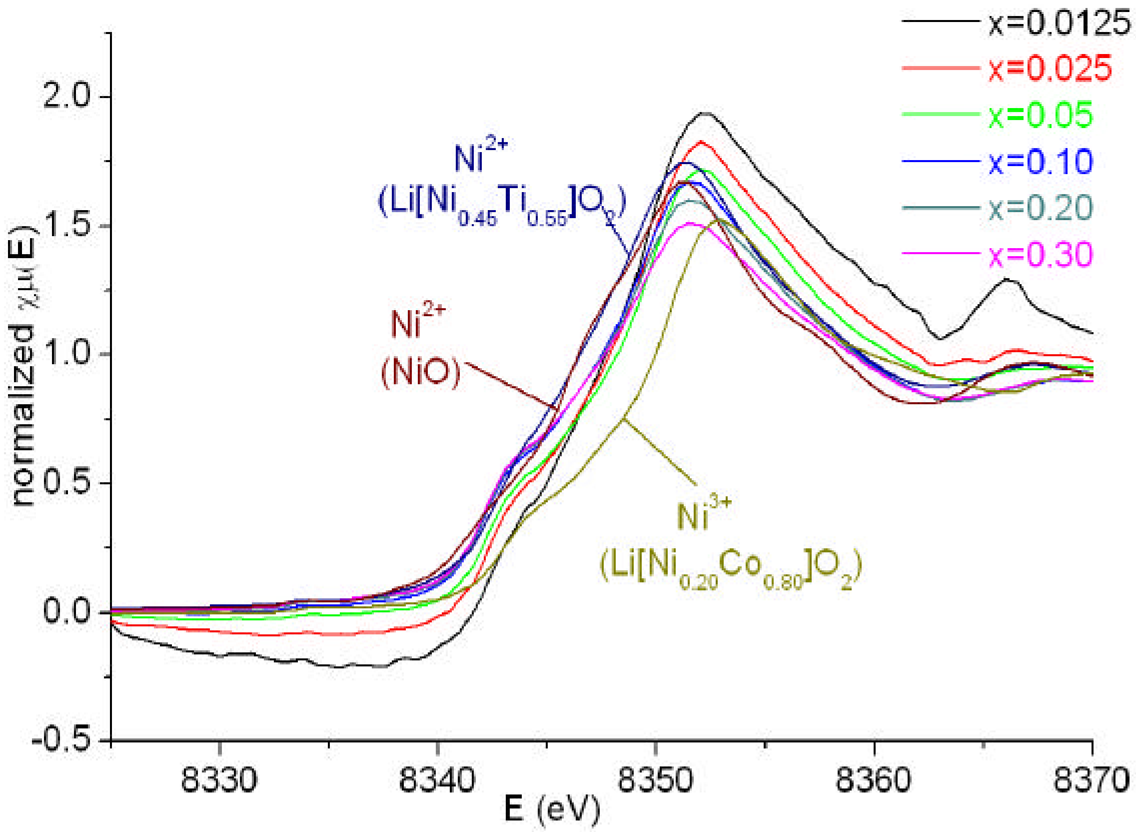
Random

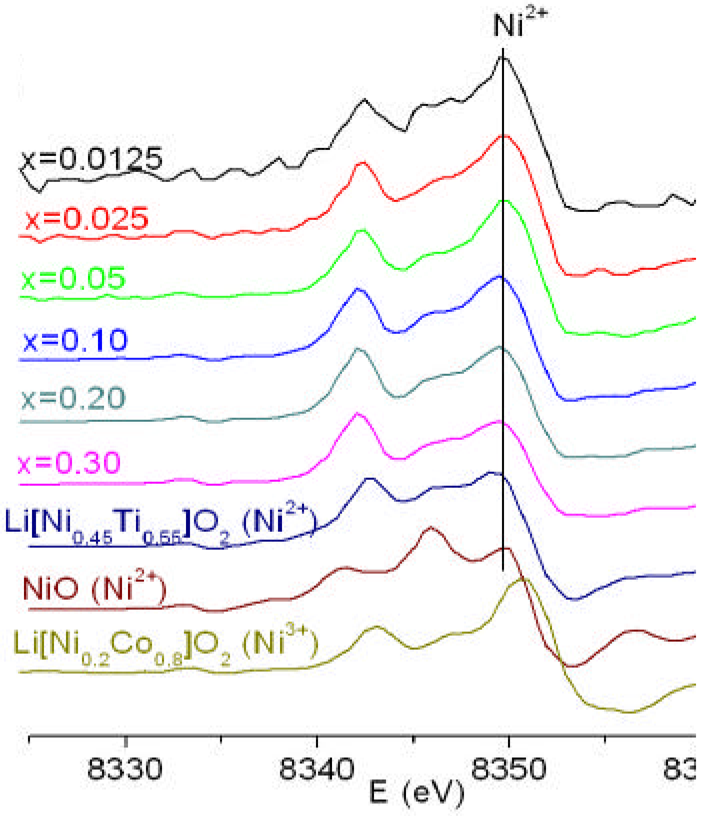
$Li(Co_6)^{1st}(Co_6)^{2nd}$

Clustered



XAS Confirms that the Transition Metals Remain as Ni^{2+}, Co^{3+}, Mn^{4+} Throughout the Series

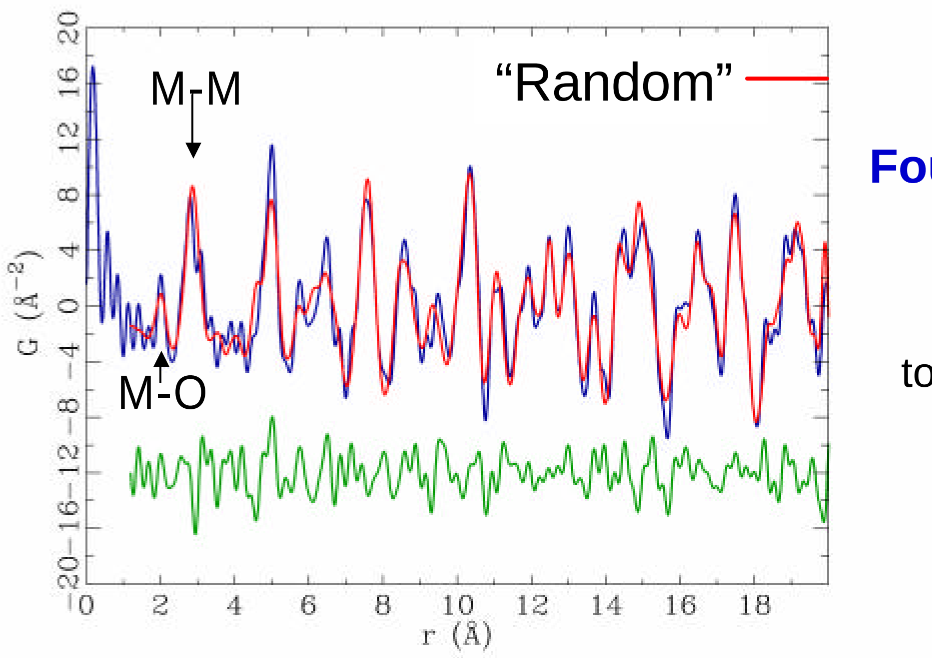




Ni K edge

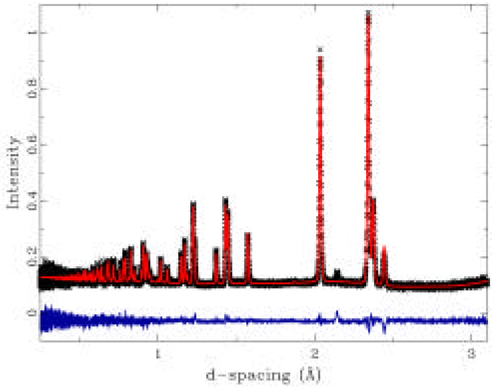
Pair Distribution Function (PDF) Analysis can be used to investigate cation clustering in higher doped samples, e.g., $Li[Co_{1/3}Mn_{1/3}Ni_{1/3}]O_2$

Igami, Billinge, Proffen, Chupas (Grey)

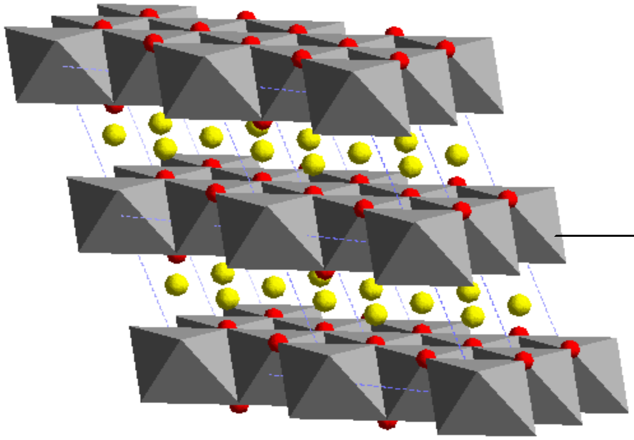


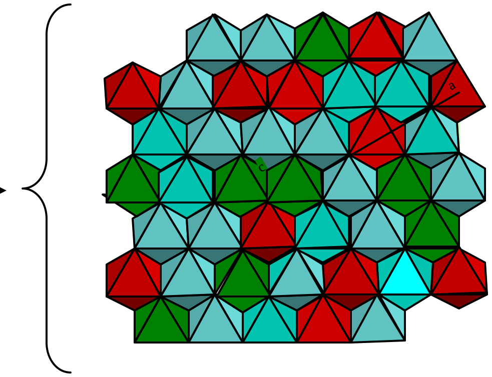
Fourier Transform

to give g(r) - radial distribution function



$$g_C(r) = \frac{1}{r}\sum_i \sum_j \left[\frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0$$

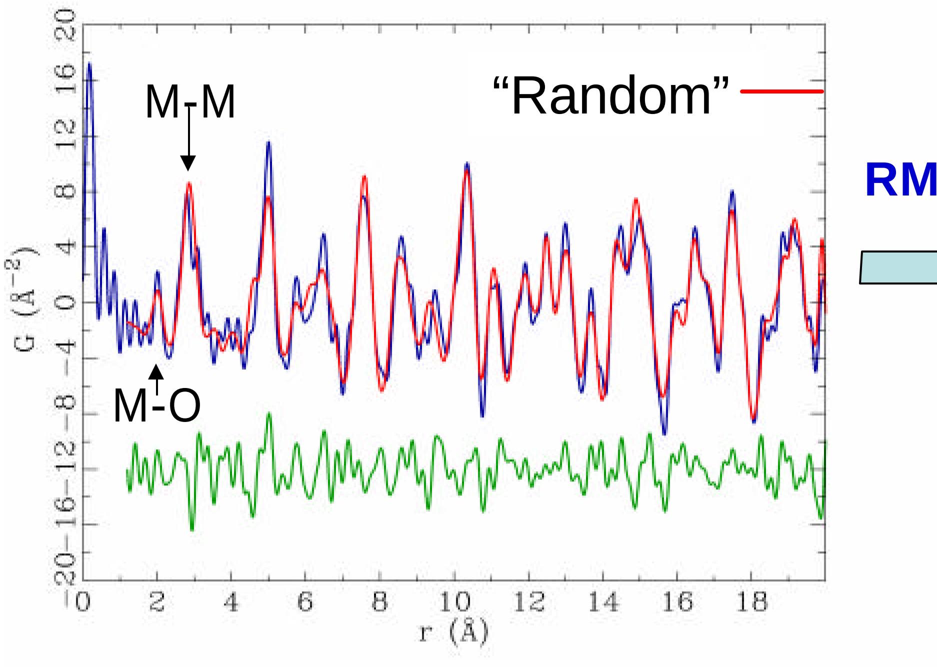




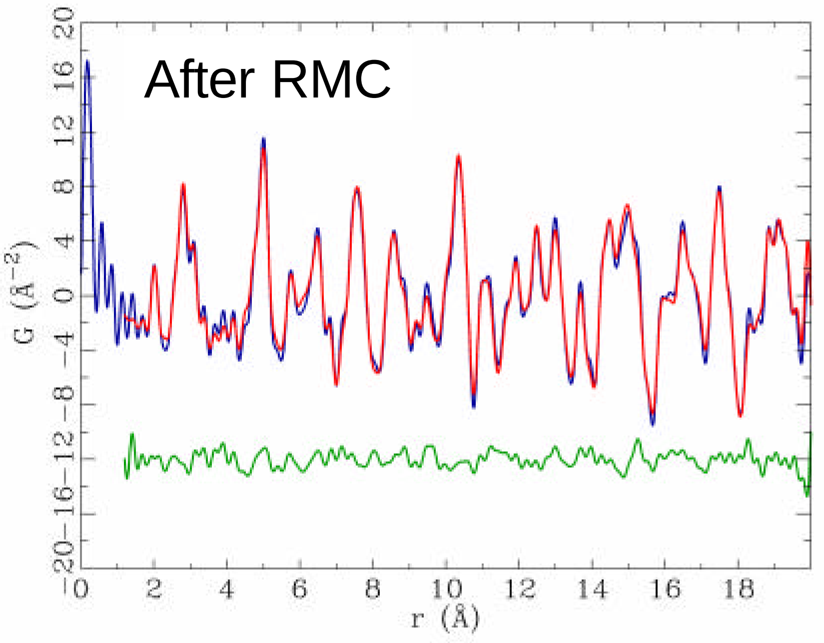
Coherent scattering lengths (fm):

Ni: 10.30
Li: -2.22
Mn: -3.75
Co:2.49

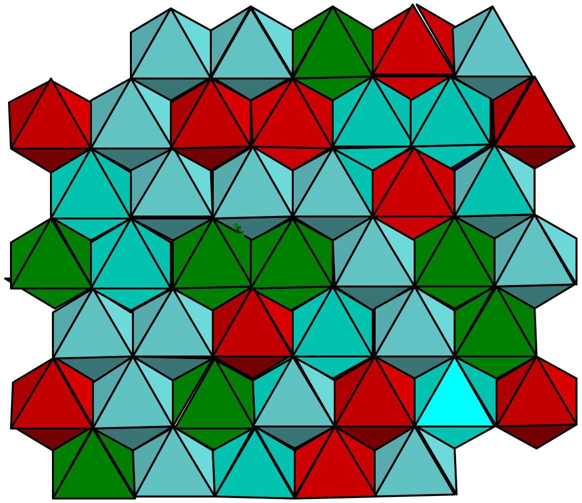
Pair Distribution Function (PDF) Analysis can be used to investigate cation clustering in higher doped samples, e.g., $Li[Co_{1/3}Mn_{1/3}Ni_{1/3}]O_2$



RMC



Giant cluster of 2400 atoms



Coherent scattering lengths (fm):

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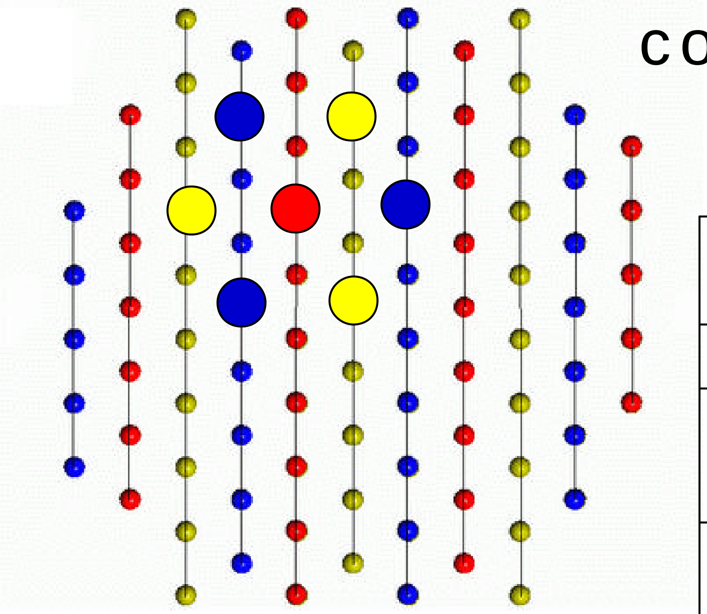
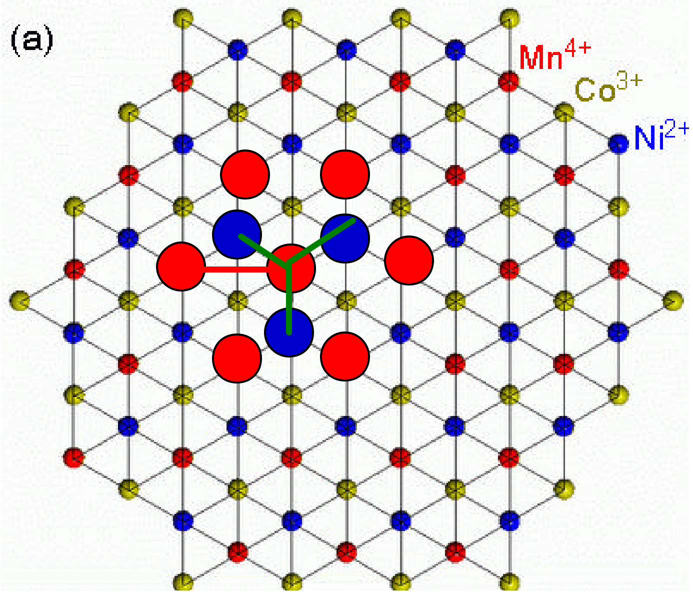
Li: -2.22

Mn: -3.75

Co:2.49

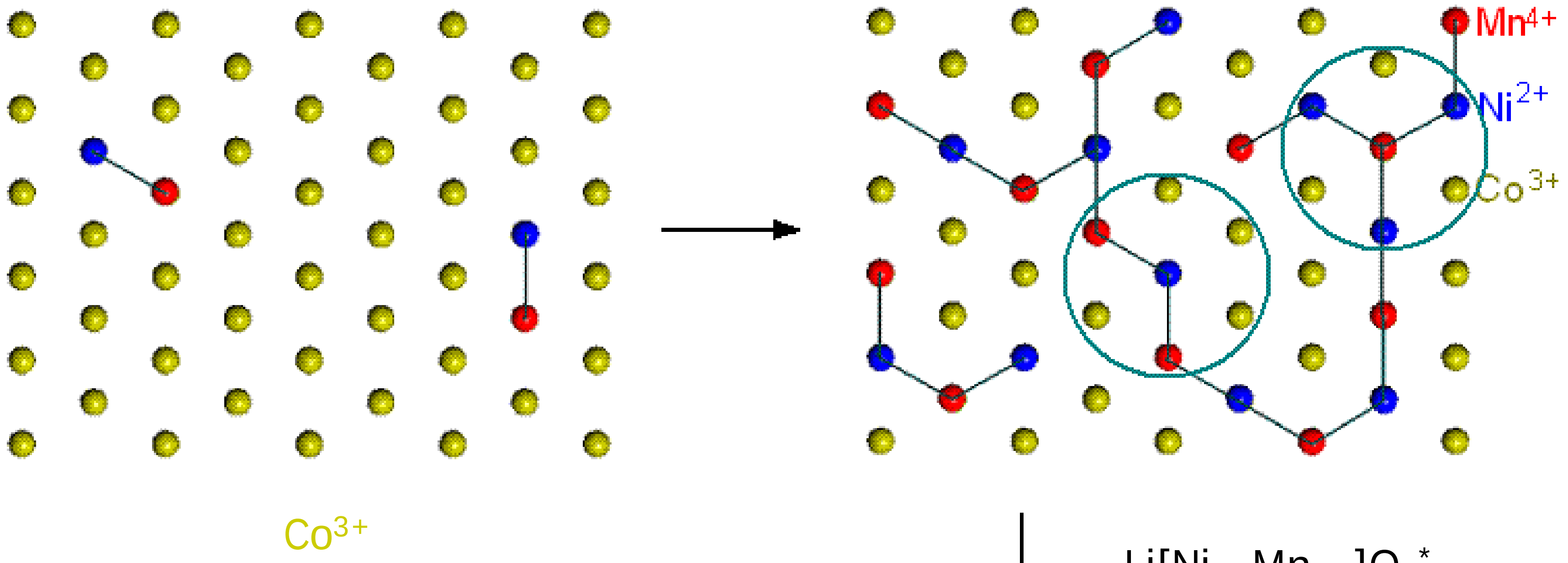
Co disrupts the Ni-Mn ordering; but weak correlations persist





1st coordination shell						
	RMC results		Possible Models			
	Before “Random” (%)	After (%)	Random	[v3 ×v3]R30º-Superlattice	Parallel cation chains	Zigzag
%Ni-Ni pairs	11.8	9.1	11.1%	0	16.7%	22.2%
%Ni-Mn pairs	24.4	28.4	22.2%	33.3%	16.7%	11.1%
%Mn-Mn pairs	12.0	9.6	11.1%	0	16.7%	22.2%
%Ni-Co pairs	20.4	21.7	22.2%	33.3%	16.7%	11.1%
%Mn-Co pairs	20.3	21.1	22.2%	33.3%	16.7%	11.1%
%Co-Co pairs	11.2	10.1	11.1%	0	16.7%	22.2%
Total	100	100	100%	100%	100%	100%

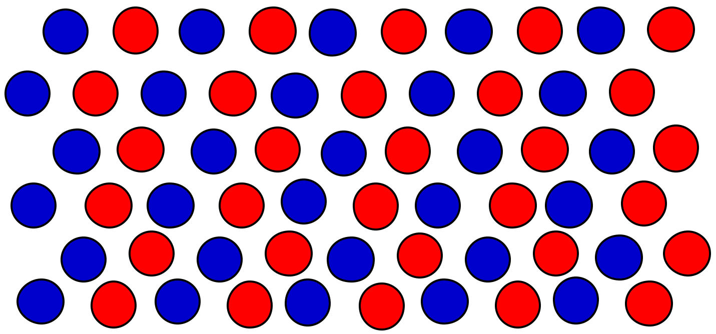
Co disrupts the Ni-Mn ordering; but weak correlations persist



v3 ×v3: Only simple ordered scheme that maximizes Ni-Mn contacts in 1st shell – this results in increased Ni-Ni and Mn-Mn contacts in the 2nd shell

*Kang, Breger, Grey and Ceder, Science '06; J. Mater. Chem. '07;

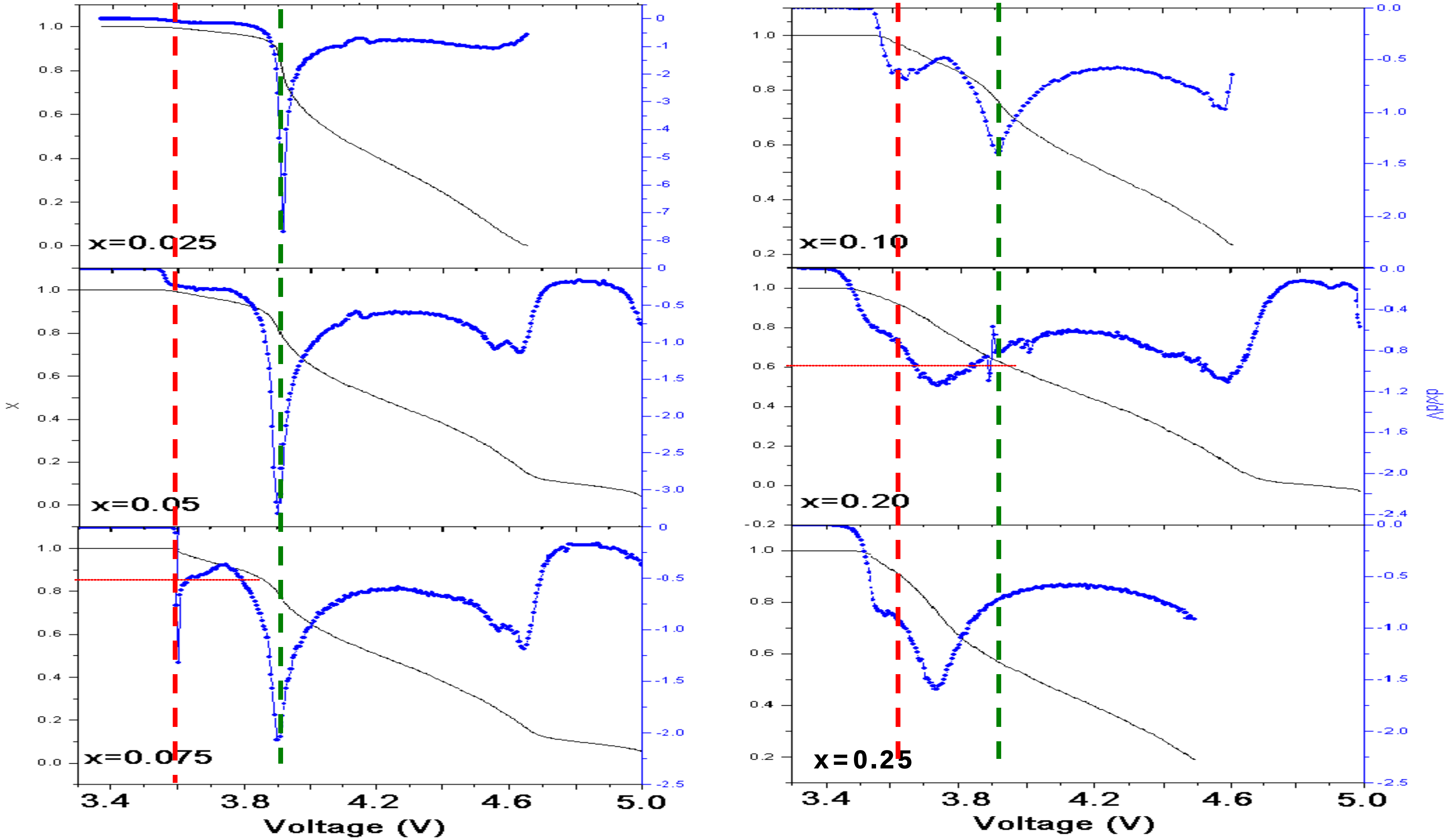
$Li[Ni_{0.5}Mn_{0.5}]O_2$*
derived from
$Na[Ni_{0.5}Mn_{0.5}]O_2$



Effect of Ni/Mn Concentration and Ordering on Electrochemical Performance

Co^{3+} - Co^{4+} MIT?

Formula: $Li_y\ [Ni_xMn_xCo_{1-2x}]O_2$

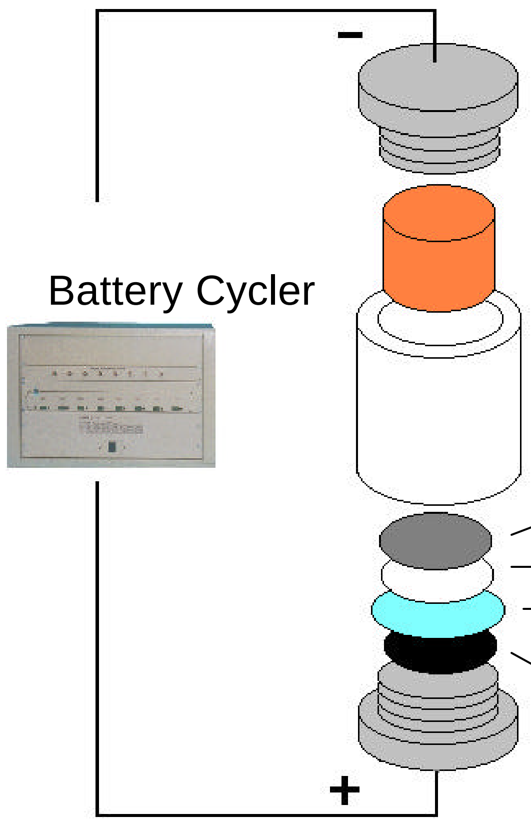


Ni^{2+}? ›Ni^{4+} or Ni^{2+} -> Ni^{3+} -> Ni^{4+}?

Following the Electrochemical Process

Swagelock-type Cell

Battery Cycler



End Bolt

Copper Plunger

Swagelock

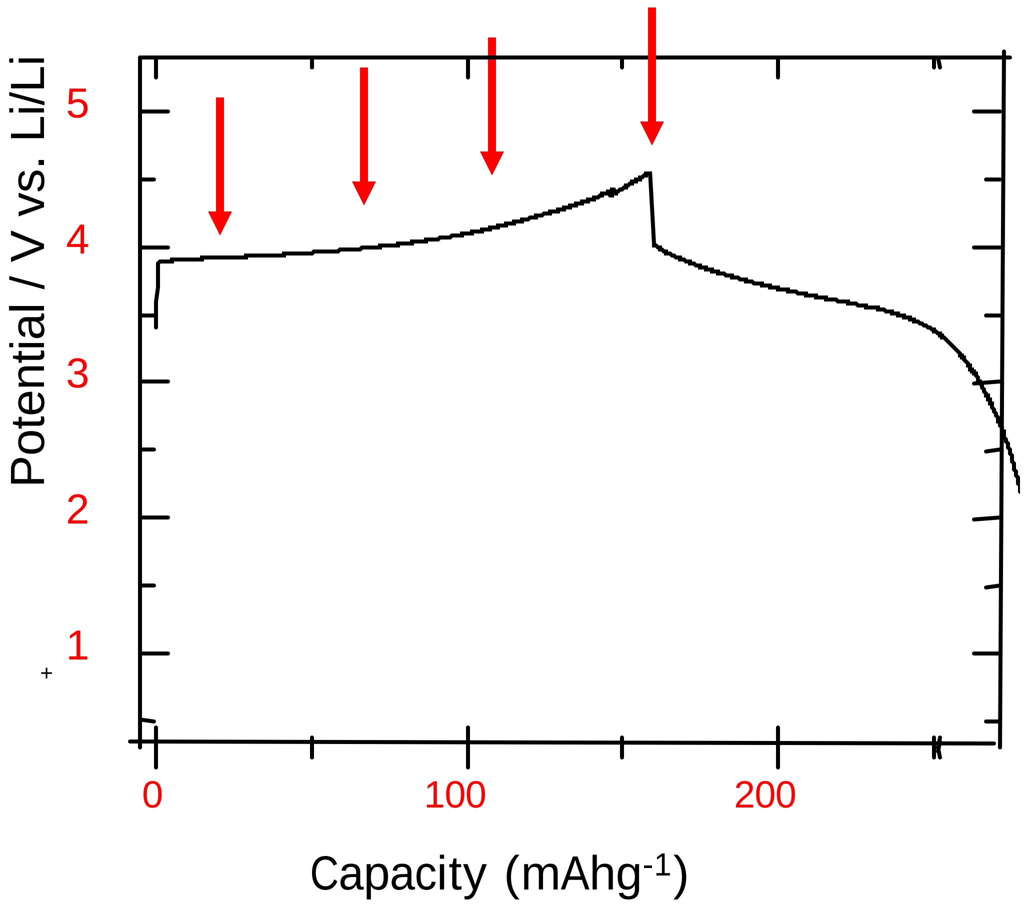
Li Anode

Filter Paper

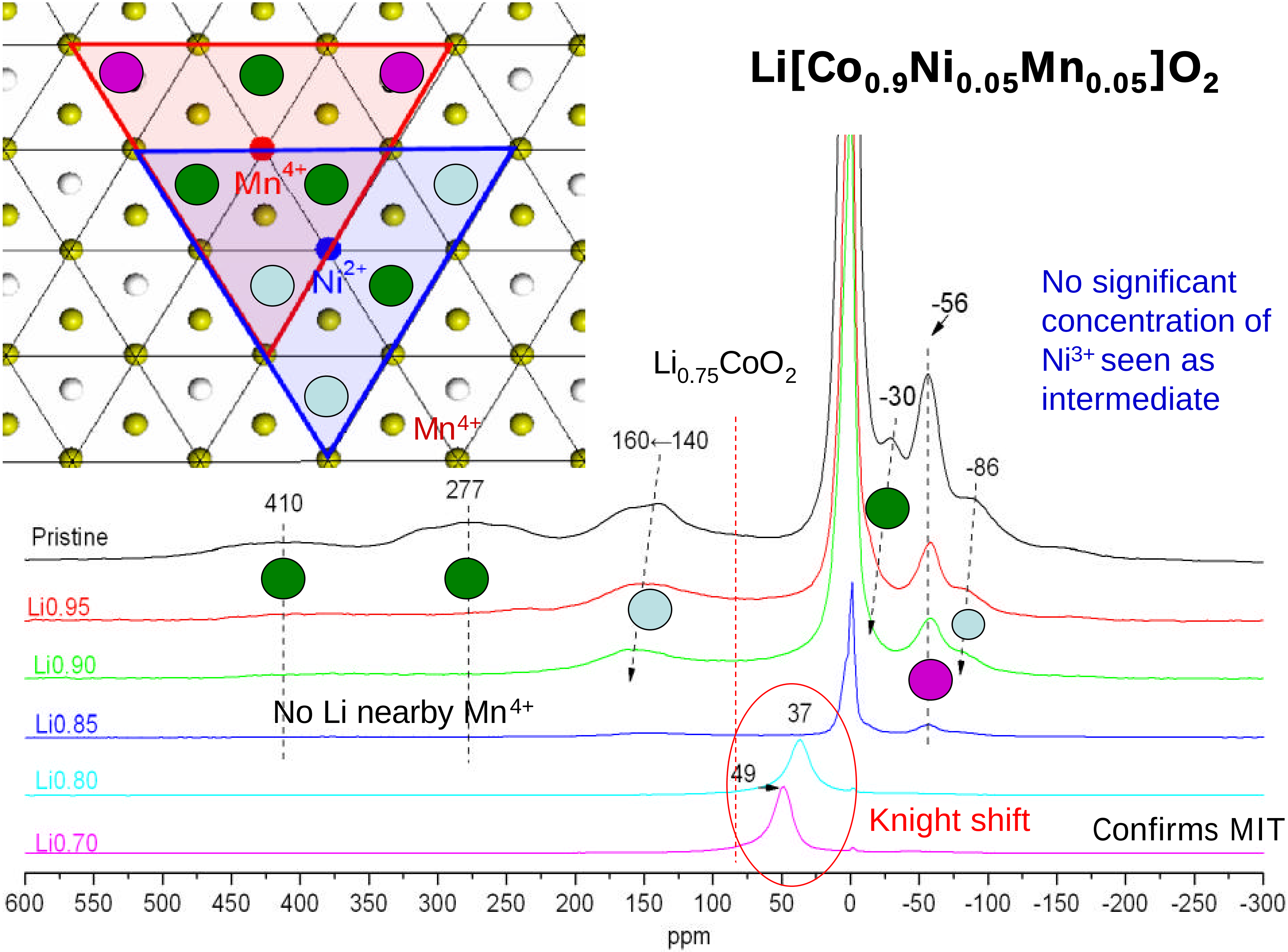
Polypropylene Separator

$LiMn_2O_4$ Cathode

End Bolt



$Li[Co_{0.9}Ni_{0.05}Mn_{0.05}]O_2$



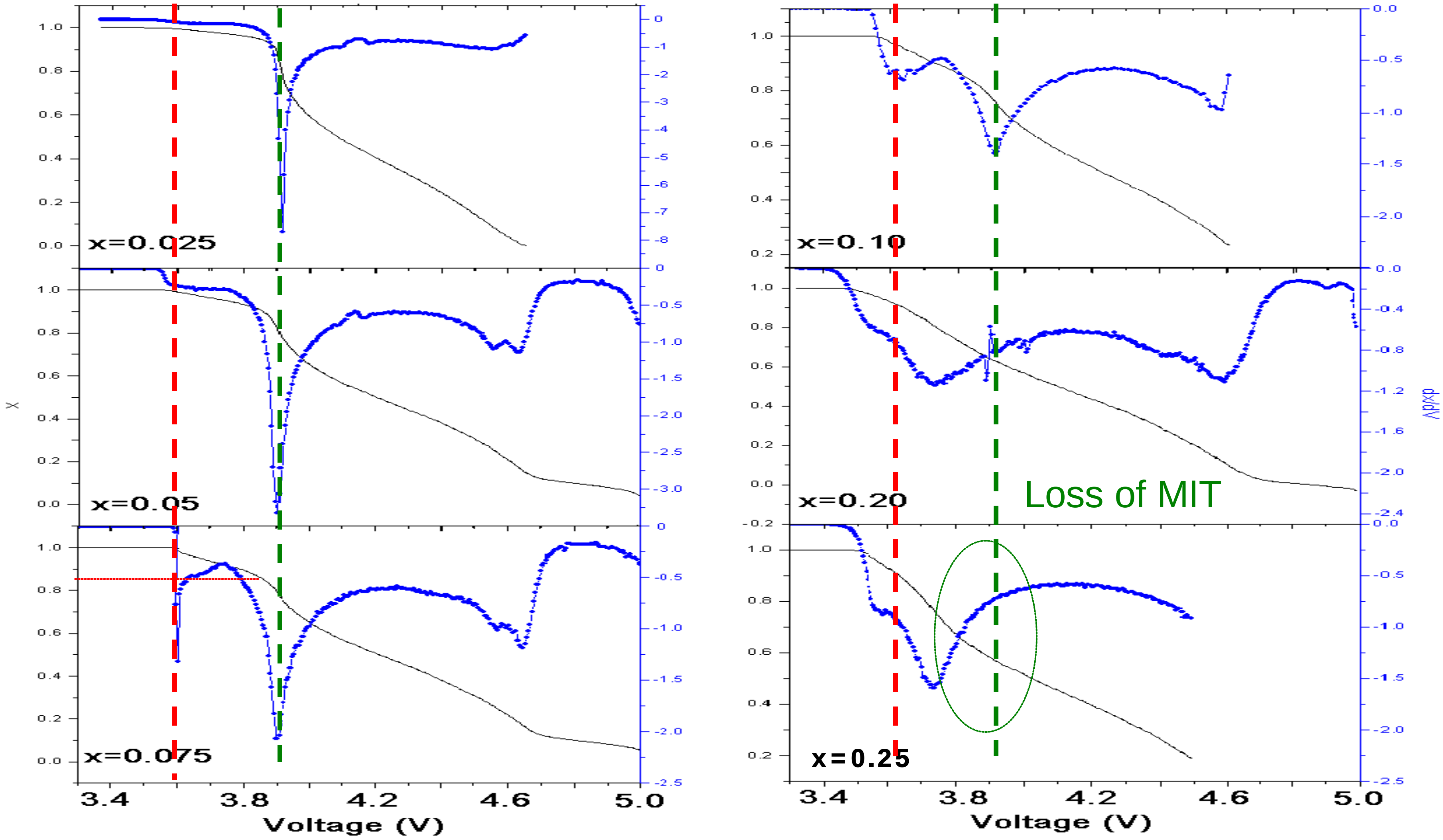
No significant concentration of Ni^{3+} seen as intermediate

Confirms MIT

Cause of the Loss of Metal-to-Insulator Transition

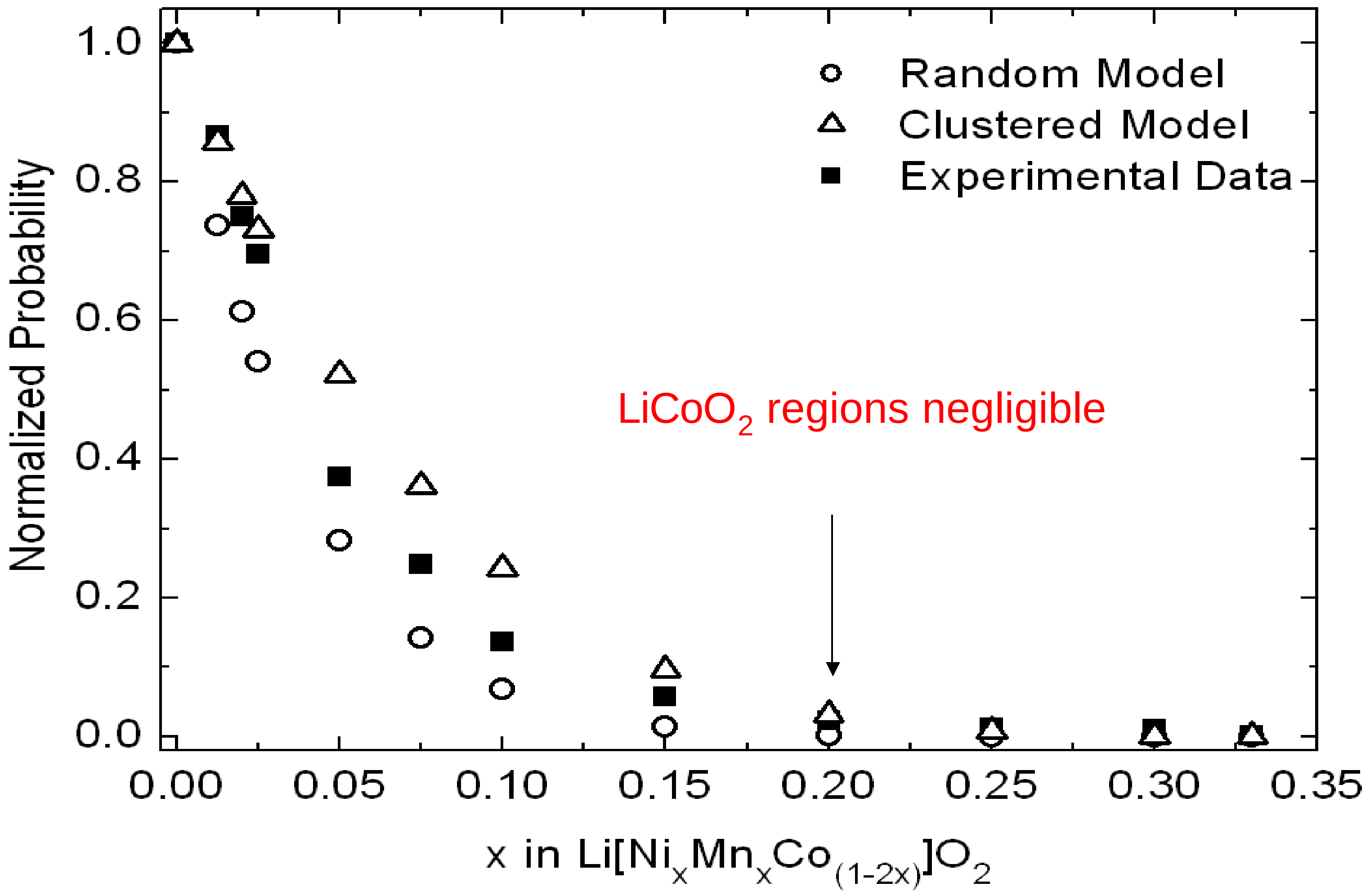
Co^{3+} - Co^{4+} MIT?

Formula: $Li_y\ [Ni_xMn_xCo_{1-2x}]O_2$



Ni^{2+}? ›Ni^{4+} - correlates with Ni content

Loss of “$LiCoO_2$” signal correlated with loss of Metal-to-Insulator Transition

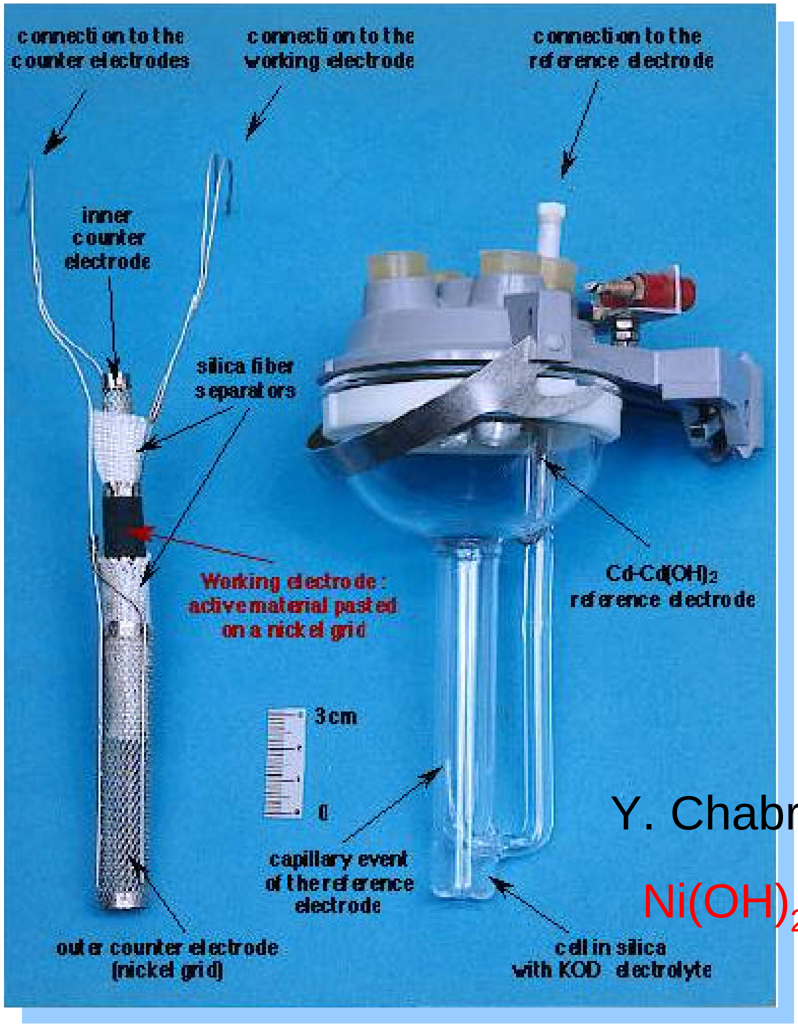


$LiCoO_2$ regions negligible

What new methods should we develop?

Insitu Methodologies

X-ray and XAS studies now routine



Y. Chabre

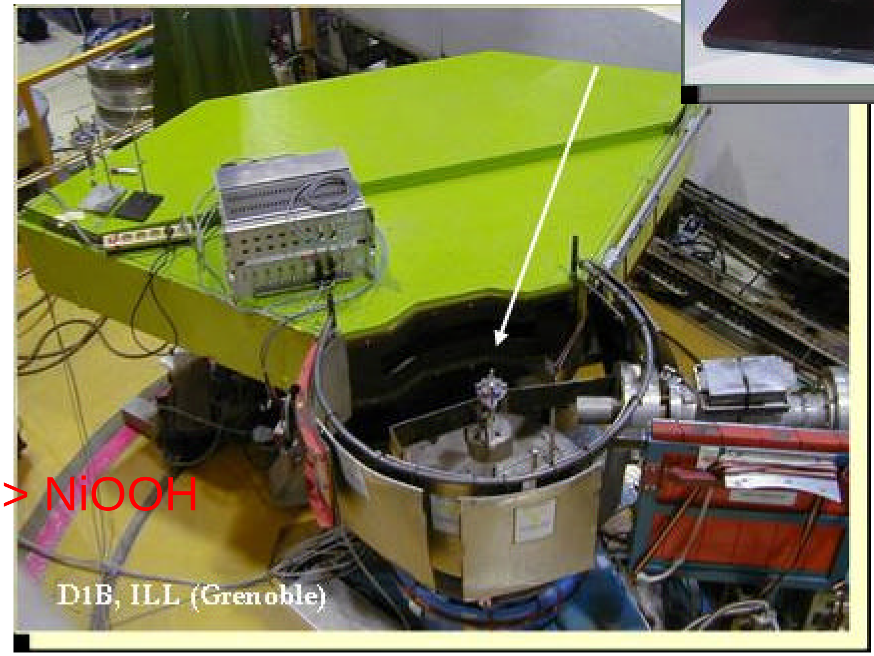
$Ni(OH)_2$ -> NiOOH

Make use of new DOE facilities investments

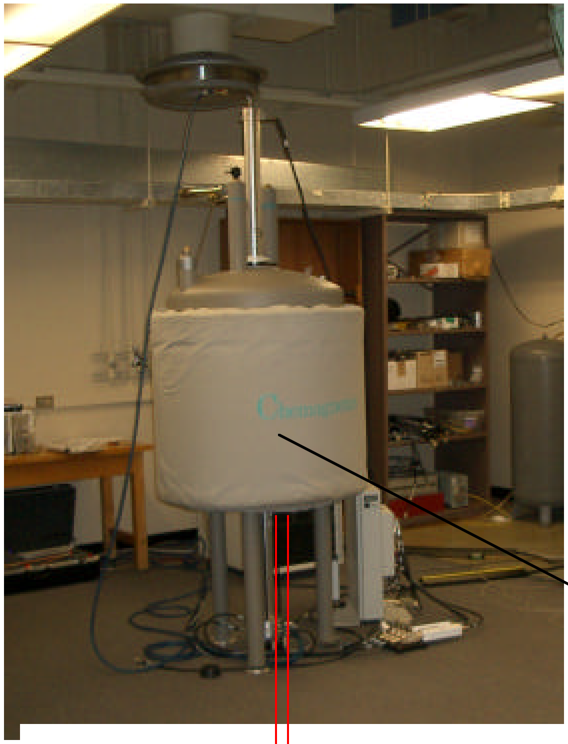
Neutron diffraction – follow the Li (and H/D)

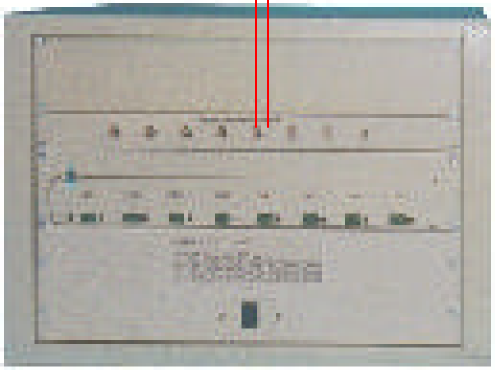
But .. sample size issues
access to beamtime
insensitive technique

DOE investment in Oakridge neutron facilities
-> more time available in US
-> design of smaller cells possible

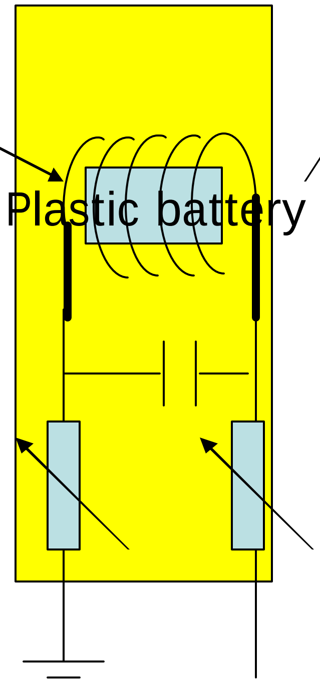

D1B, ILL (Grenoble)

Advanced Diagnostic Methods: *In situ* NMR

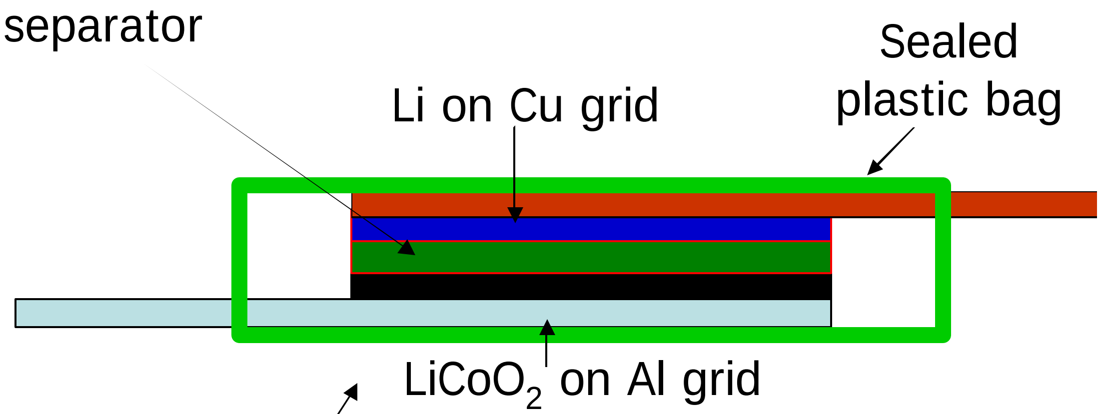




Battery Cycler



Plastic battery



separator

Li on Cu grid

Sealed plastic bag

$LiCoO_2$ on Al grid

Chevallier, F.; Letellier, M.; Morcrette, M.; Tarascon, J. M.; et al.; *Electrochem. Solid State Lett.* **'03,** 6, A225.

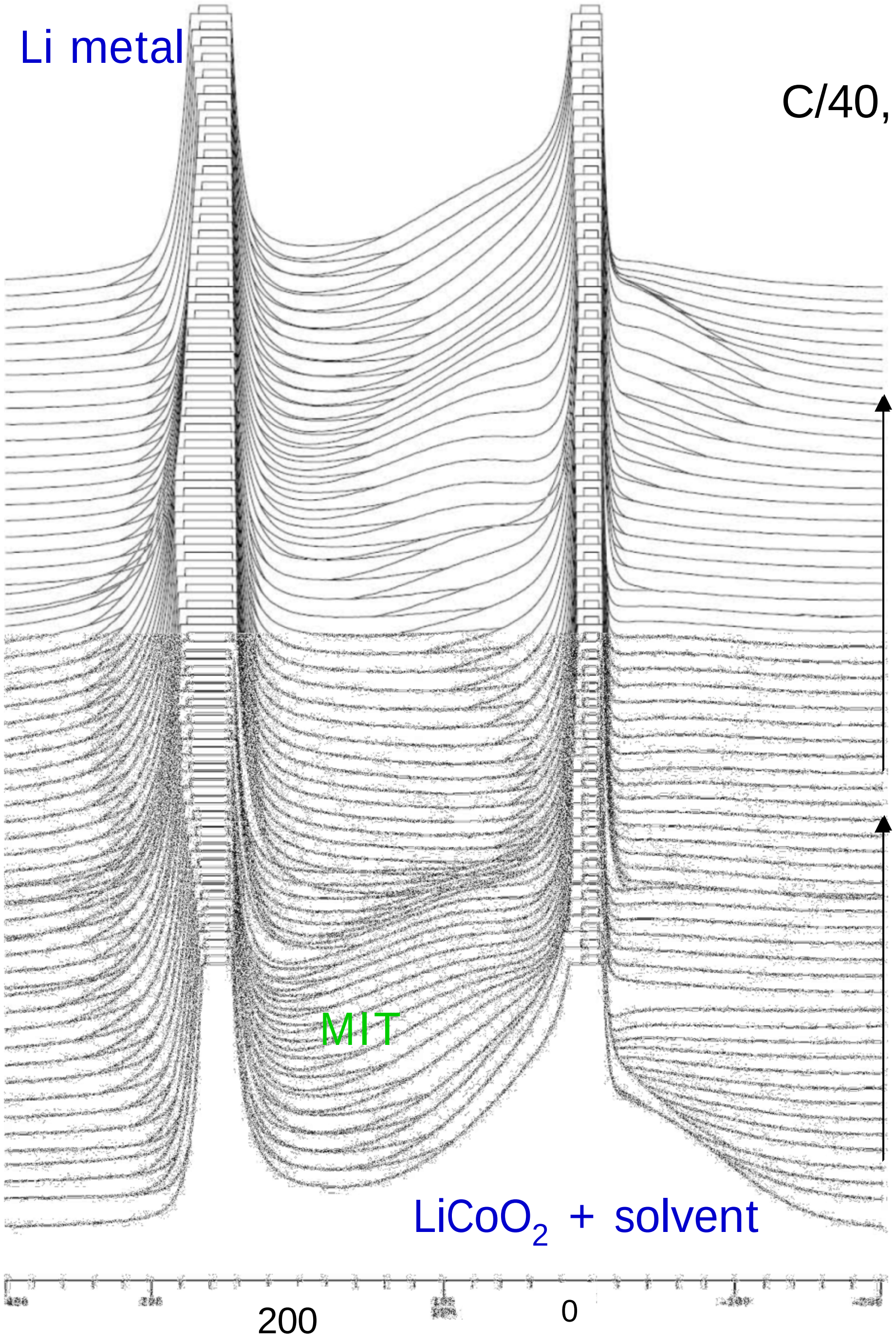
Challenges: *all in progress*

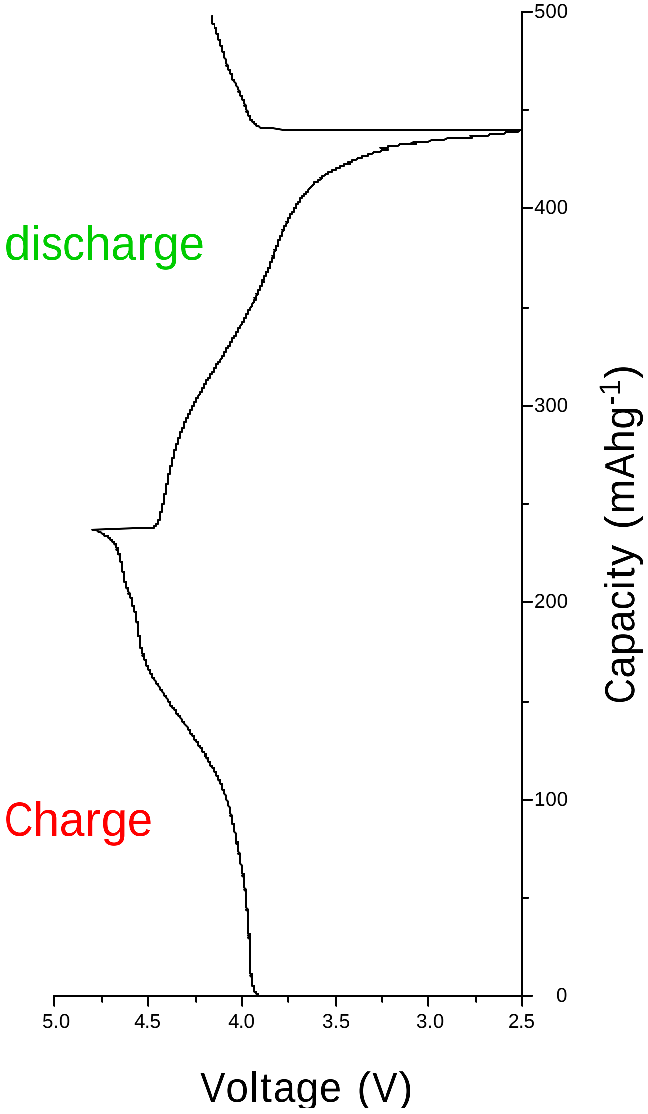
- Develop high resolution MAS NMR approaches
- Separate different NMR signals in static NMR expt.
- Synchronize NMR spectroscopy and e-chem. to monitor fast dynamics

B. Key, R. Battacharya

Commercial $LiCoO_2$

C/40, 2.5V-4.8V, alternating 0.2 and 0.02 s recycle delays





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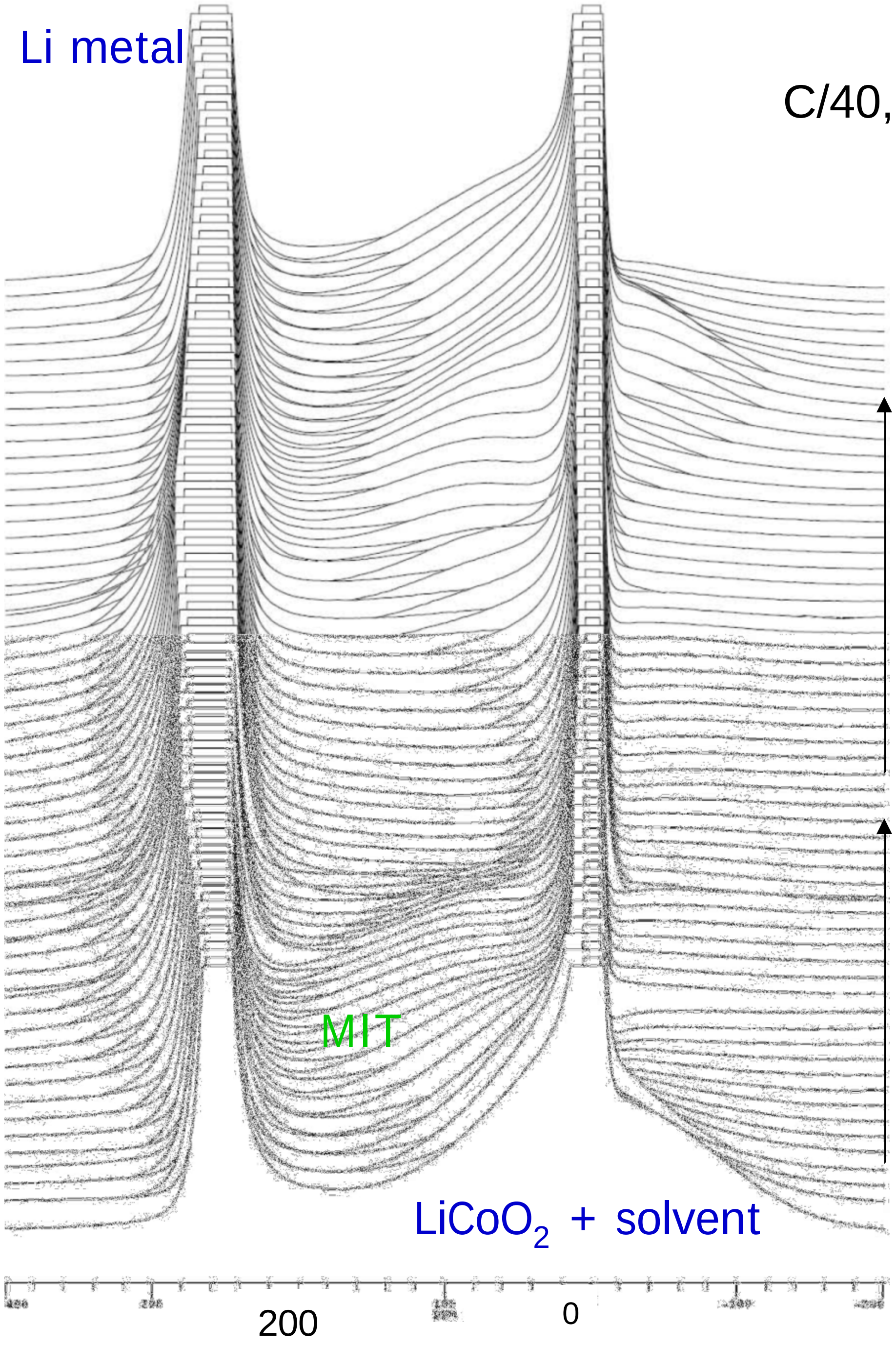


Implemented:

- Automated peak picking and integration routine – dealing with large amount of data
- GITT experiments
- Pulsed mode experiments – follow response to high C pulses in real time

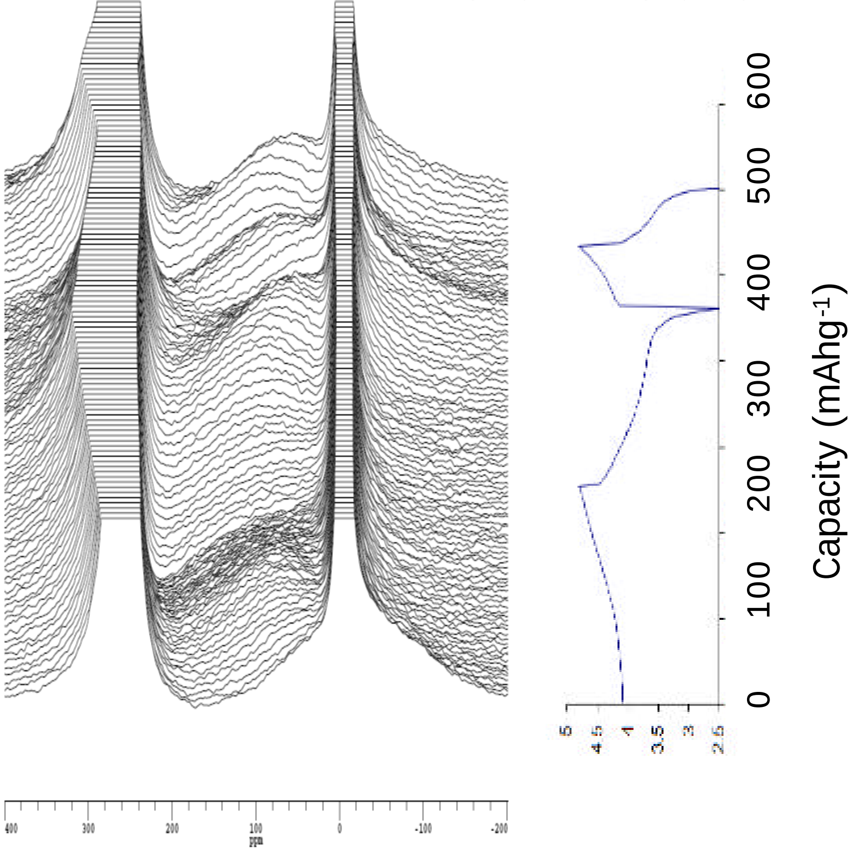
“easy” to perform studies as f(T) – i.e., low and high T studies

“Desert Rose” $LiCoO_2$
C/2 rate 1st cycle,
1C rate 2nd cycle

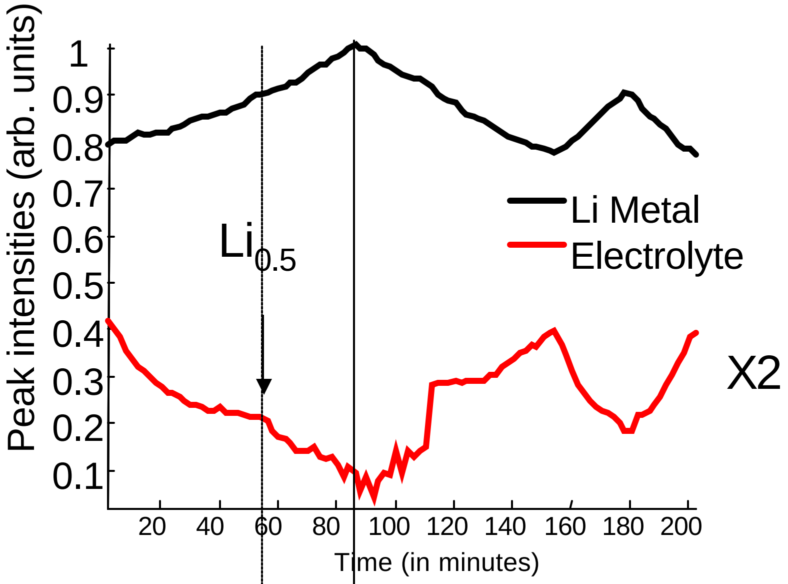
(actual capacity for 2nd cycle is twice the x-axis capacity),
NMR spectra - 1 a minute – 0.5 s record to date

in-situ ^{7}Li static NMR.

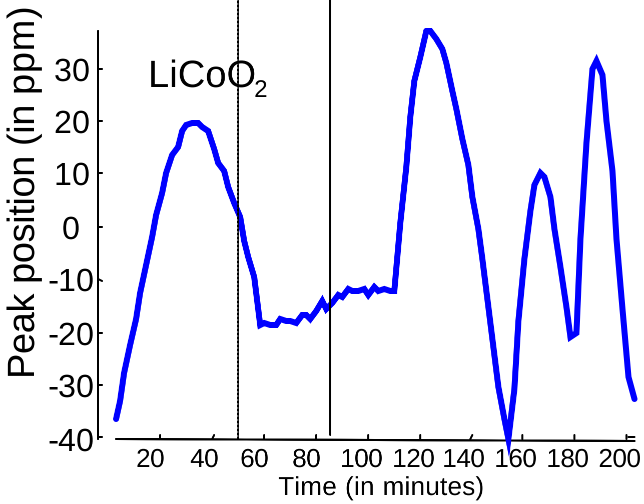
Automated peak picking and integration routine – dealing with large amount of data



Peak intensities as a function of time



Peak position as a function of time



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(actual capacity for 2nd cycle is twice the x-axis capacity),

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Automated peak picking and integration routine – dealing with large amount of data

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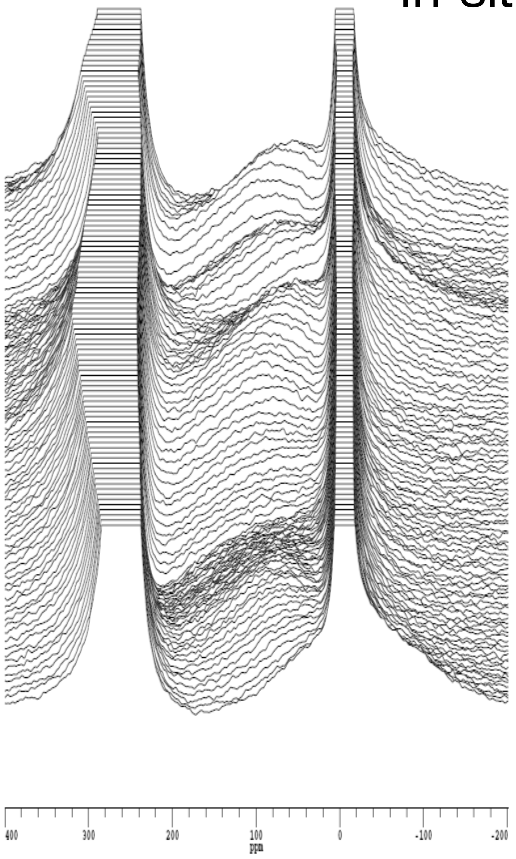
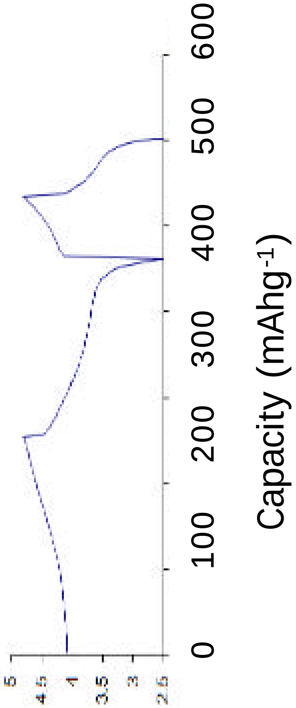
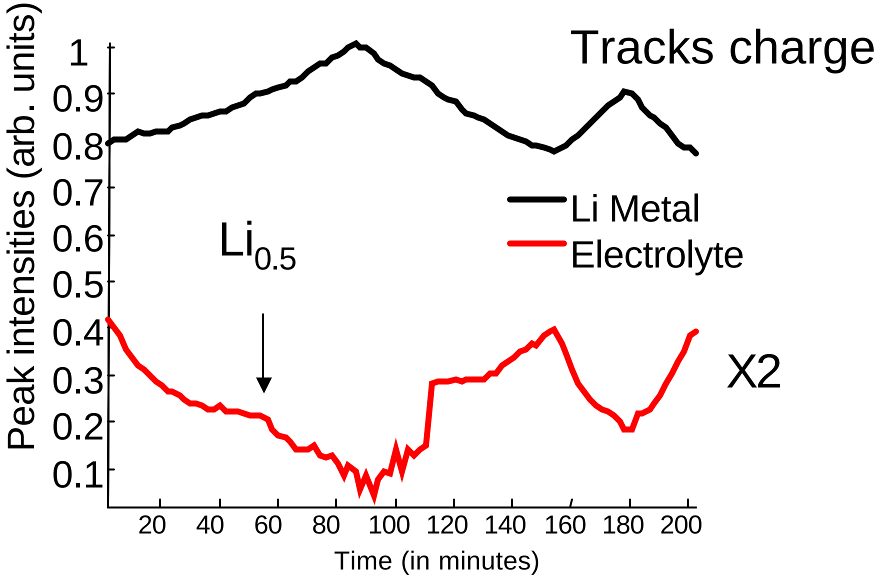
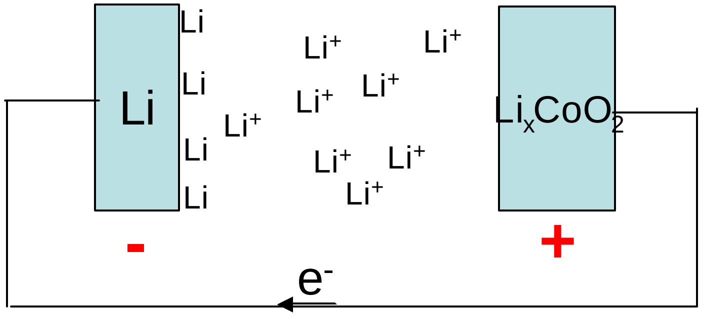




Peak intensities as a function of time





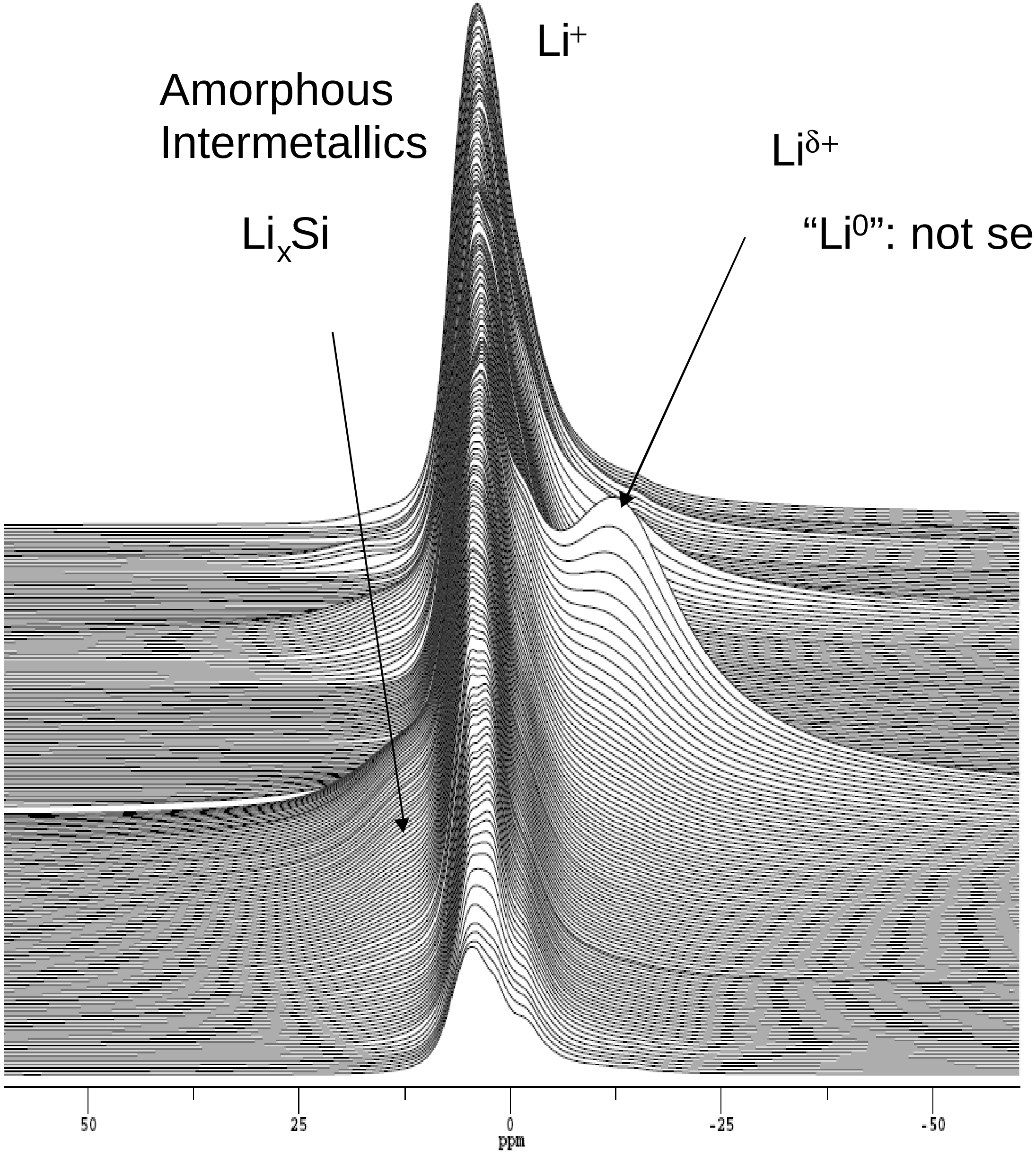
Differences in rate performances of 2 ½ cells, at high rates, lead to electrolyte conc. changes –
Creates overpotential…

In situ observation of Si cycling

Extremely high *theoretical* capacity

Si → Li_xSi → $Li_{3.75}Si$

Amorphous Xstalline



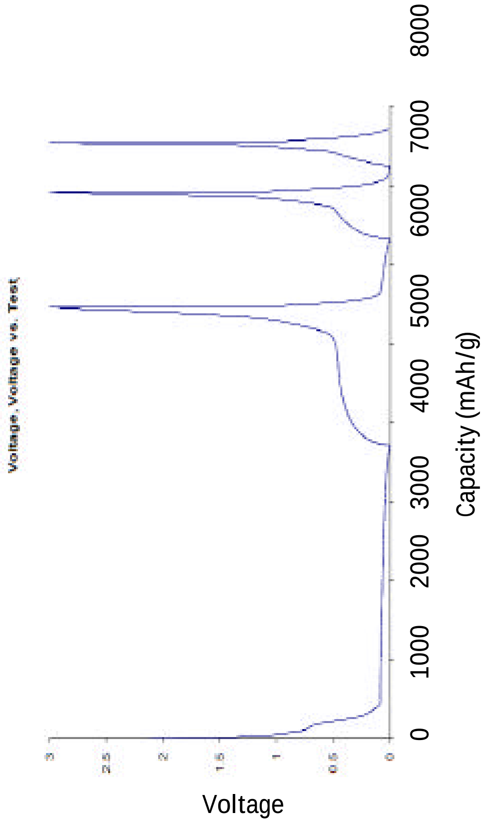
Li^+

Amorphous Intermetallics

Li_xSi

$Li^{\delta+}$

“Li^0”: not seen in ex-situ studies



What new methods should we develop?

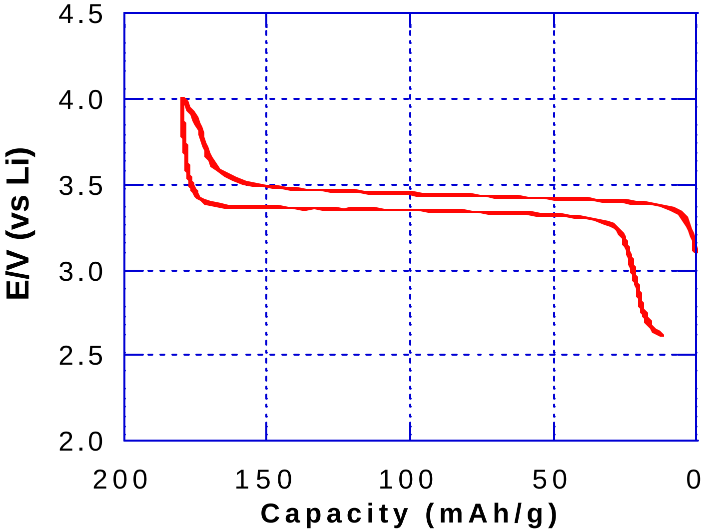
Electrochemistry under extreme conditions

High T electrochemistry

- Fundamental studies
- Different chemistries

High T solid
solutions
Thermodynamic
properties

LiFePO$_4$ 250ºC
in molten LITFSI



Modified swagelok cell

R. Palacin, J. –M. Tarascon

Conclusions

- A wide variety of different materials have been identified or synthesized that push the battery chemistries beyond that of the SONY cell.

- Multi-electron systems (capacity), 3 dimensional structures (rate), extrusion (capacity), nanoparticles, insulating materials, new morphologies, metal-organics…

- Pushing back the materials frontiers requires that we understand how the batteries/materials function and how and why they fail.

- New Diagnostic techniques have been developed to follow changes in local structure, sequences of electrochemical events, and oxidation state

- NMR spectra are very sensitive to local structure and electronic structure;
- Pair distribution function analysis methods are sensitive to order around the metals

- Applied to understand how $Li[Co_{1-2x}Mn_xNi_x]O_2$ functions

However…

Much work is still required to produce a *safe (cheap) lithium-ion battery* for HEV, Plugins and EVs

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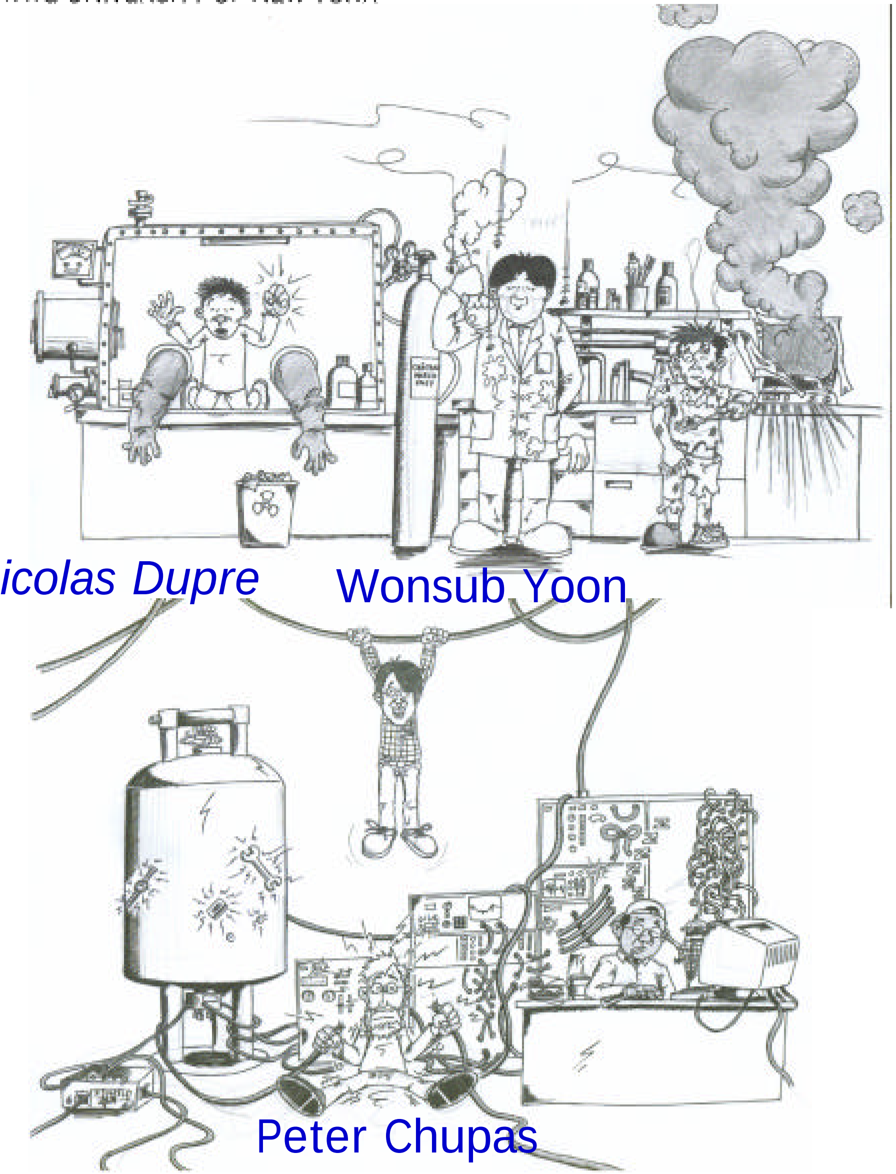
Acknowledgements

CEMS

NSF (DMR) and DOE
(FreedomCAR)



Nicolas Dupre

Wonsub Yoon

Peter Chupas

Meng Jiang
Julien Breger
Hailong Chen
Dongli Zeng
Jordi Cabana
Young Joo Lee
Sylvio Indris

MIT: Gerd Ceder
Shirley Meng
Dany Carlier (Bordeaux)
Kisuk Kang
Yang Shao-Horn

Oxford
Oliver Rutt
Simon Clarke

Thanks also to:
Heike Gabrisch
(University of New Orleans)
Robert Kostecki
(Lawrence Berkeley National Lab.)
and Rosa Palacin
(CSIC, Barcelona, Spain)