NECCES
A DOE Energy Frontier Research Center

U.S. DEPARTMENT OF ENERGY | Office of Science

The Limitations to Li-Intercalation Batteries and the Role of Nanomaterials

CCR, Pittsburgh, October 3rd, 2013

M. Stanley Whittingham

State University of New York

Stony Brook University · Binghamton University, State University of New York · Rutgers University · MIT · UC San Diego, Local Impact, National Influence, Global Reach · University of Cambridge · University of Michigan · Berkeley Lab · Brookhaven National Laboratory · Argonne National Laboratory

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NECCES goals:

- Develop a fundamental understanding of how key **electrode reactions** occur, and how they can be controlled,
- What are the intrinsic limitations to **intercalation reactions**? **$LiFePO_4$**
- Gain complete control over **conversion reactions**. **FeF_2, FeF_3, $FeO_{1-y}F_y$**
- Understand the role of overpotential in controlling electrochemical reactions

Improved battery performance will be driven by:

- Understanding how the systems function and why they fail
  - **New characterization (diagnostics) methods will play a key role**
- Reaction mechanisms and new materials
  - **Theory shows options for reaction routes**, and role of overpotential
  - Theory will play a key role in guiding the exploration direction

Redox Intercalation Cathodes for Lithium Ion Batteries Dominate the Battery Storage Market

First Generation (1977):

Layered Sulfides.

TiS_2 - LiAl - Exxon

One Lithium to transition metal ratio

- 480 Wh/kg **(240 Ah/kg)**

EV Show Chicago, 1977

40 years old
Still working

First Commercial Success (1991):

Layered Oxides.

$LiCoO_2$ - **LiC_6** - SONY

0.5 Li to Co cycling - 480 Wh/kg

BAE Systems, Binghamton
11 kWh Li-ion
2000 HEV buses in US 25M miles

Today - 2013:

Mixed layered oxides and **$LiMn_2O_4$** spinel

$Li(NiMnCoAl)O_2$ – electronics, etc

$LiFePO_4$ (& $LiMnPO_4$?)

Power tools, HEV buses, utilities

AES, Binghamton
8-20 MW Li-ion

Intercalation Batteries can be Improved

Most of the Energy is Lost in Cell Construction
(Carbon anode major contributor to loss)

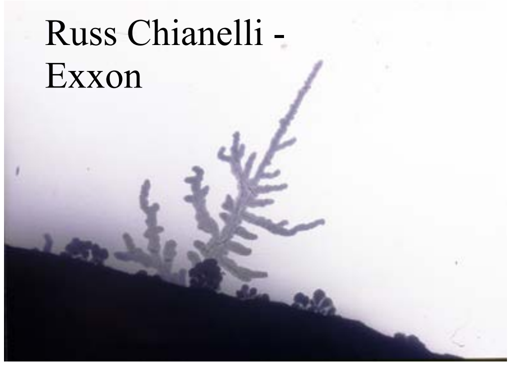
Chemistry	Size	Wh/L theoretical	Wh/L actual	%	Wh/kg theoretical	Wh/kg actual	%
$LiFePO_4$	54208	1980	292	14.8	587	156	26.6
$LiFePO_4$	16650	1980	223	11.3	587	113	19.3
$LiMn_2O_4$	26700	2060	296	14.4	500	109	21.8
$LiCoO_2$	18650	2950	570	19.3	1000	250	25.0
Si-$LiMO_2$ Panasonic	18650	2950	919	31.2	1000	252	25.2

The theoretical values in the table assume only the active components, and no volume or weight for lithium beside that in the cathode.

IEEE Proceedings, Vol. 100, 1518 (2012)

The Anode – Replace Carbon Intercalation
Anode (Li, Na, Mg)

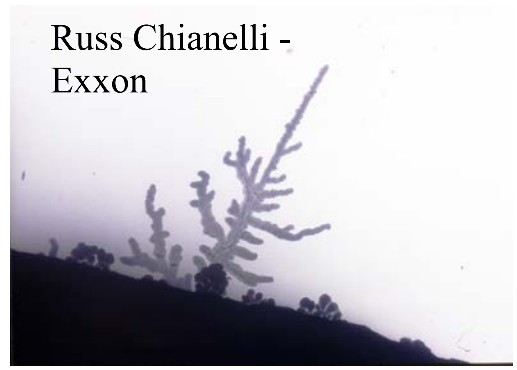
- **The Anode**
  - **Make lithium metal work (Holy Grail)**
    - **+ High capacity**
    - **+2.1 Ah/cc** and >3000 Ah/kg
    - **+ High discharge power**
    - **− Electrodeposition**
      - **− Dendrites "always" form**



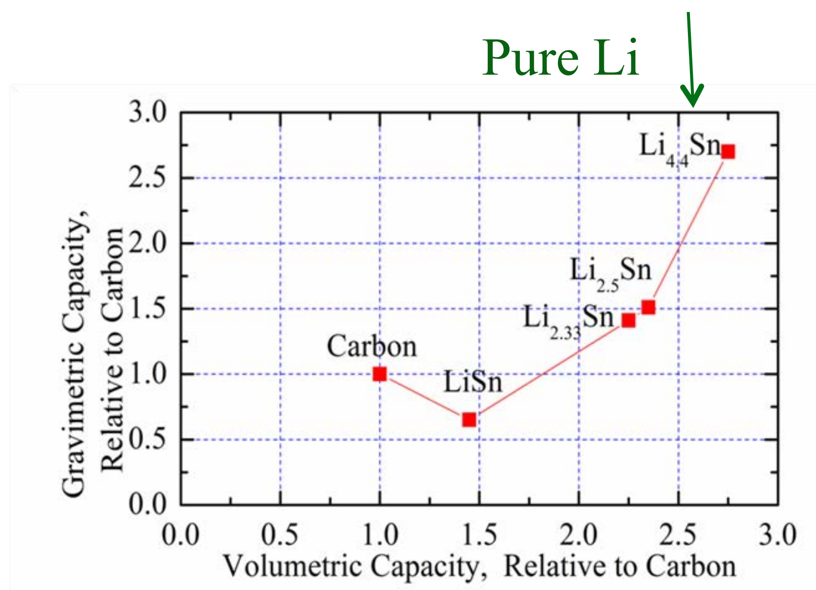
Avestor - AT&T

The Anode – Double Capacity to 1.4 Ah/cc

- **The Anode**
  - **Make lithium metal work (Holy Grail)**
    - **+ High capacity**
    - **+ 2.1 Ah/cc and >3000 Ah/kg**
    - **+ High discharge power**
    - **− Electrodeposition**
      - **− Dendrites "always" form**
  - **Move to tin or silicon**
    - **+ High capacity**
    - **+ Conversion reaction**
    - **− But high expansion and reactivity**

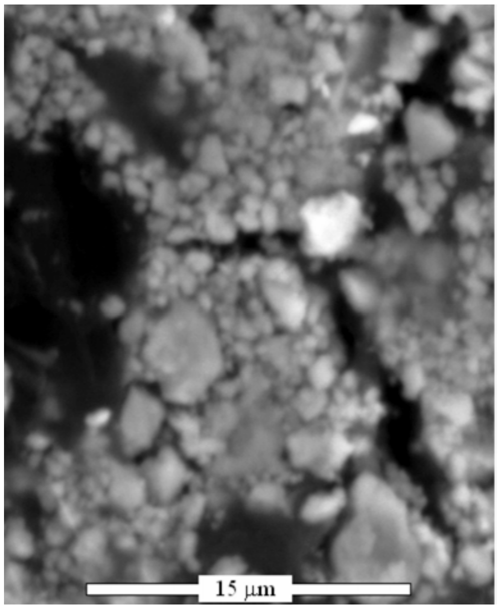


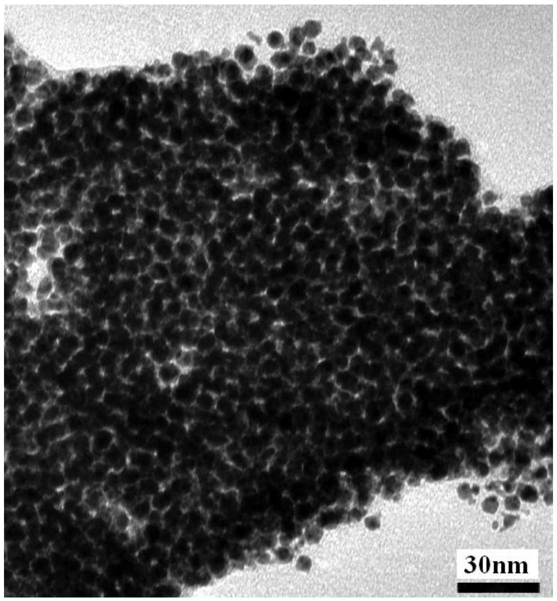
Avestor - AT&T



Nano Amorphous Sn-Co has Promising Electrochemistry
ESL, 10, A274 (2007)

SONY's Tin Anode is a Smart Nanostructure

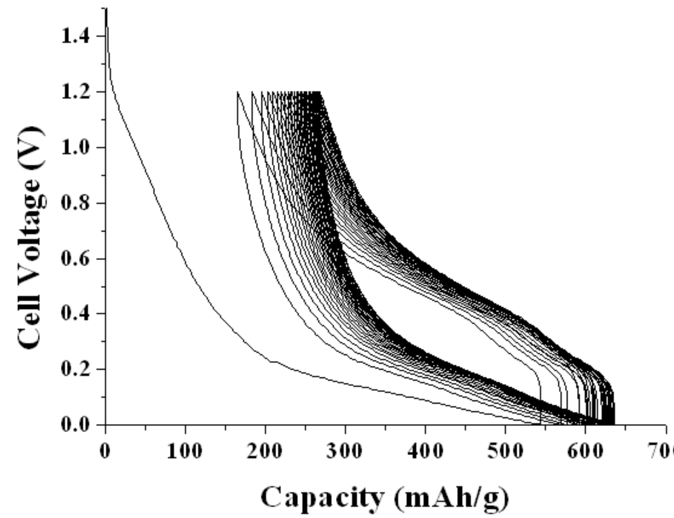


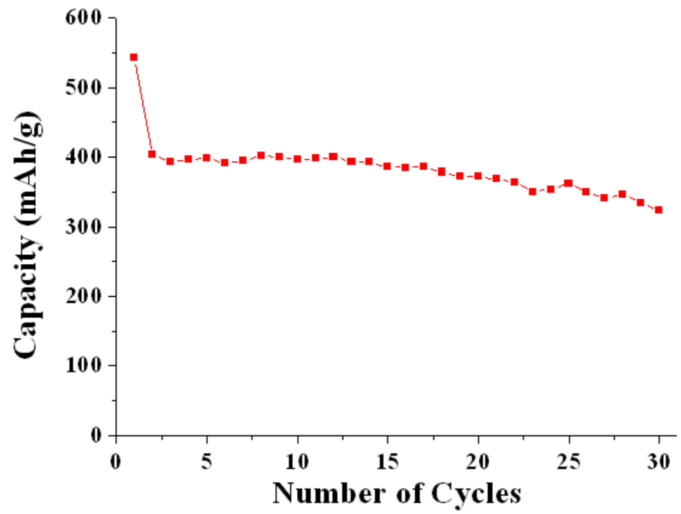


23 % tin; 10.3 % cobalt; y % titanium

$Sn_{1.1}CoTi_y$ + carbon

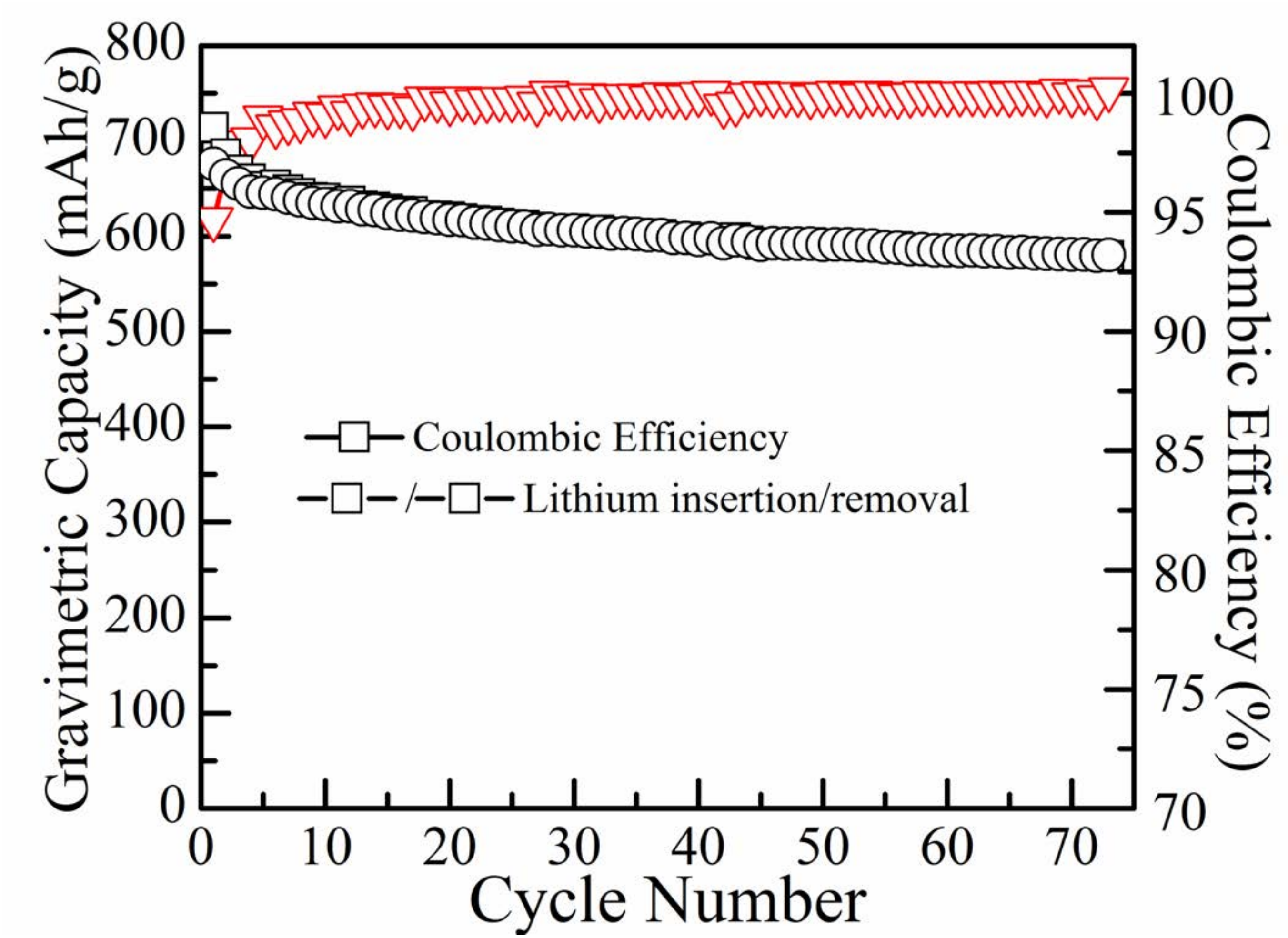
Amorphous-nano





Cobalt free: nano Sn-Fe-C cycles very well

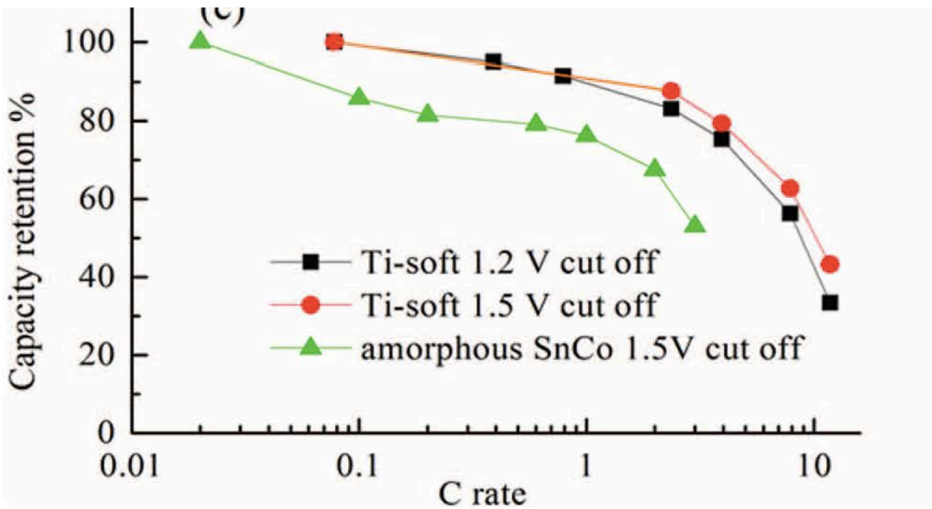
Tin-carbon electrode + Fe as Sn_2Fe



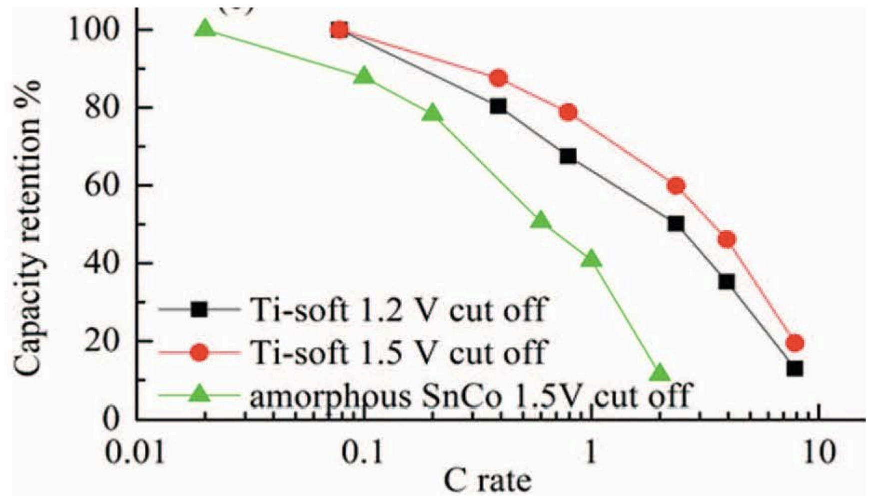
Cobalt gone: nano Sn-Fe-C equally as good
(J. Electrochem. Soc., 158, A1498, 2011)

Doubles the Volumetric Capacity of Carbon

Tin-carbon electrode + Fe as Sn_2Fe



Lithium removal – discharge of cell

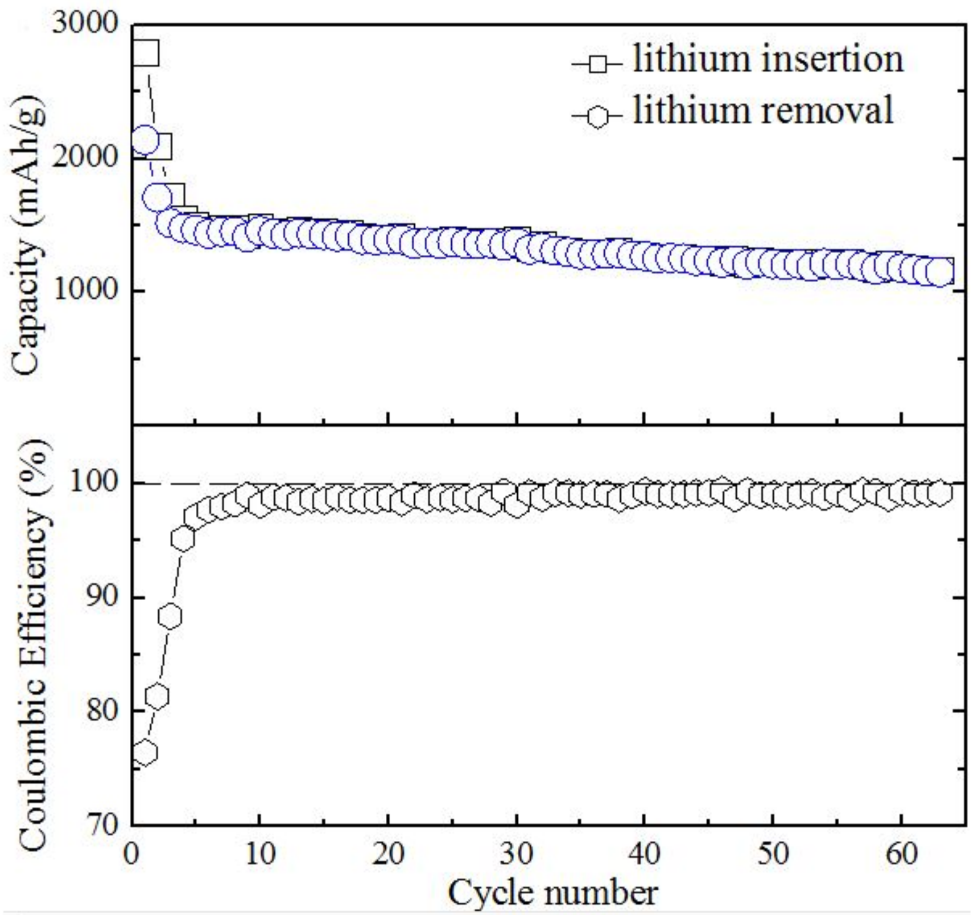


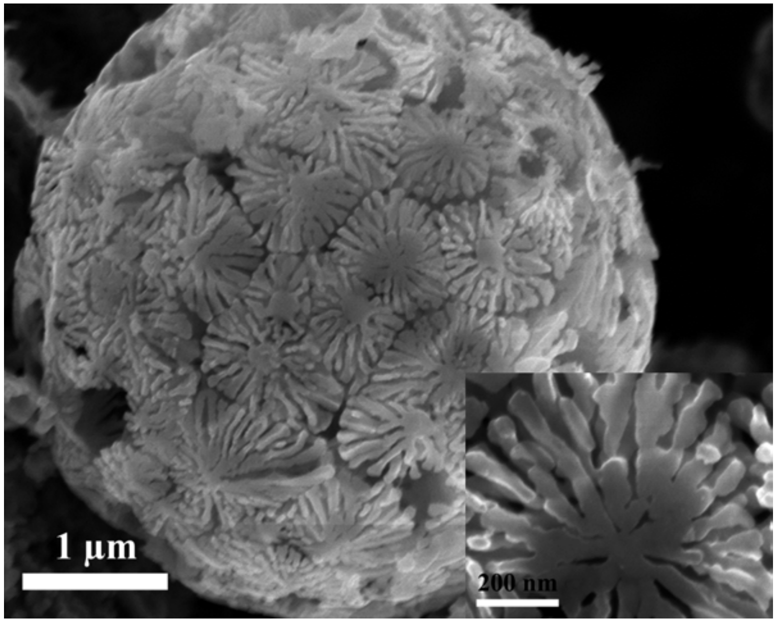
Lithium insertion – charging of cell

Silicon also a possibility, but …
(MRS Commun., 3, 119, 2013)

Silicon anodes formed by leaching from AlSi alloy

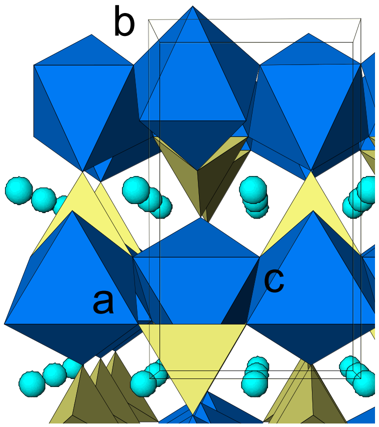
Challenge is lack of achieving > 99.9% efficiency

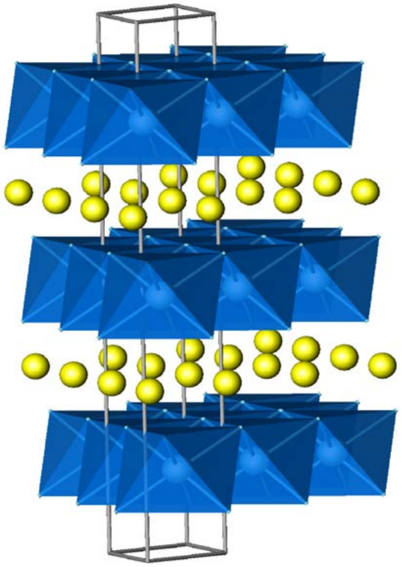




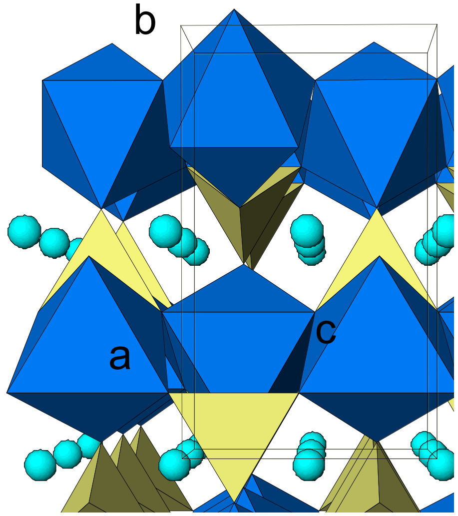
The Cathode – Increase Capacity to 250 Ah/kg

- **The Cathode**
  - **Phosphate & Olivine compounds**
    - + Limited to around 160 Ah/kg
      - + Highest rate when nano, but electronic insulator
      - + What is mechanism?
    - + Two electrons per redox center
      - + 2 Li or 1 Mg
  - **Layered Oxides**
    - + Can one electron per redox center be accomplished?
      - + > 250 Ah/kg
      - + Today ~ 180 Ah/kg

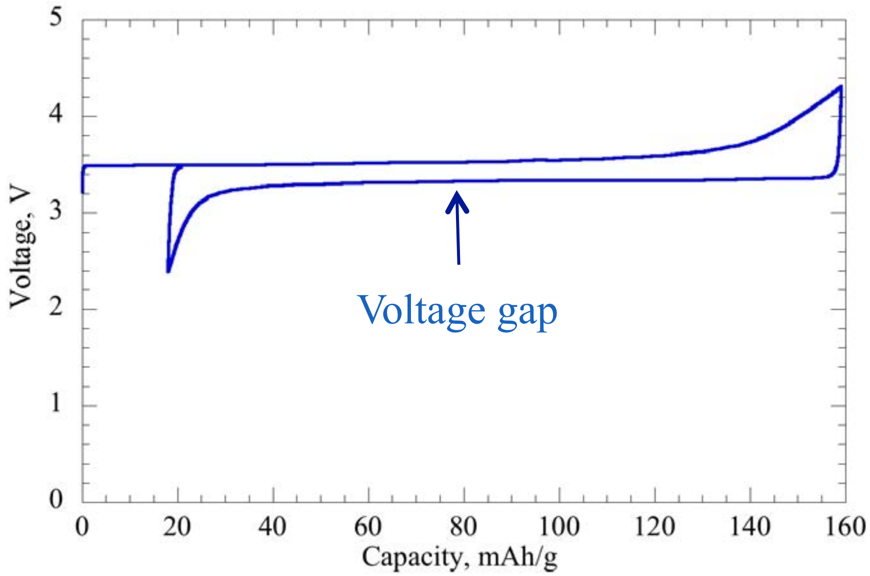


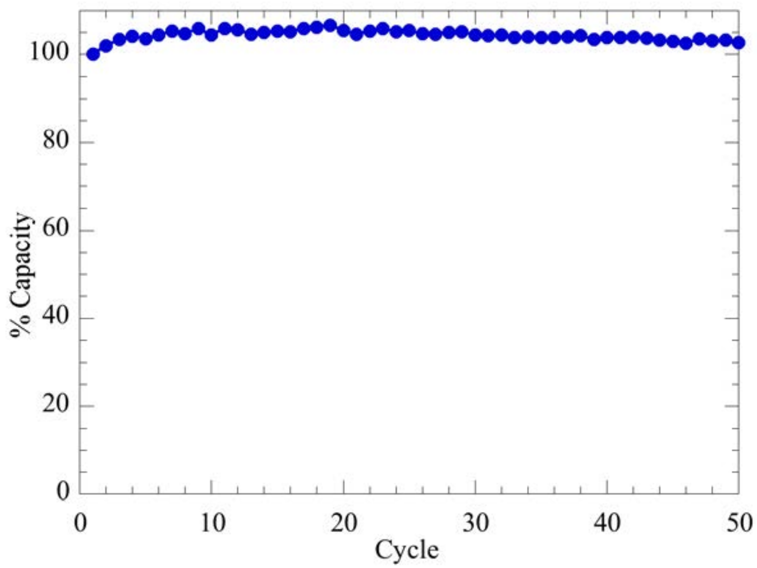


Characteristics of $LiFePO_4$ Electrochemistry



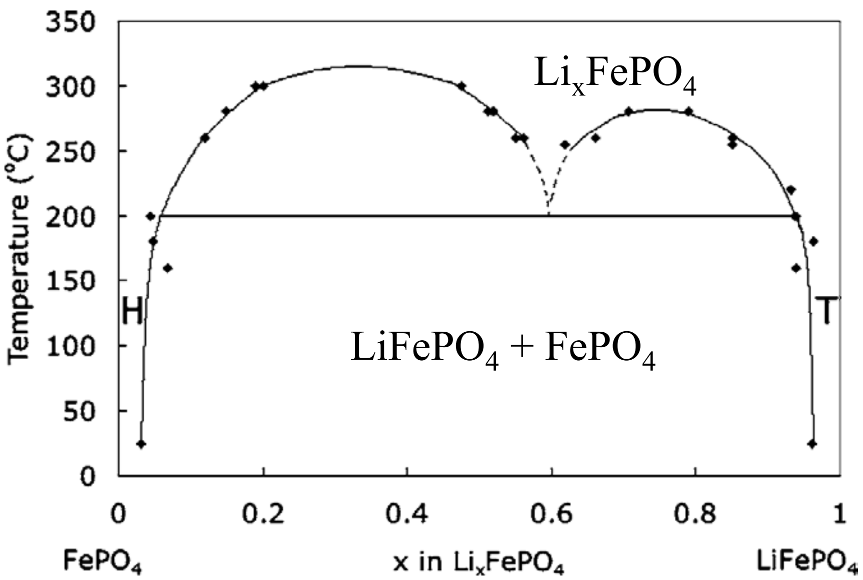
- Electrochemical behavior of **ordered** Olivine
  - **Electronic insulator**
    - Extrinsic conductor added, Fe_2P + C (>650°C)
  - **Two-phase reaction**: $LiFePO_4$ + $FePO_4$ – slow kinetics
    - Plateaus in cycling curves
  - **One-dimensional tunnels** = easily blocked
  - Inconsistent with actual behavior
    - Highest rates, 100% utilization, voltage gap





Phase Diagram of $LiFePO_4$-$FePO_4$

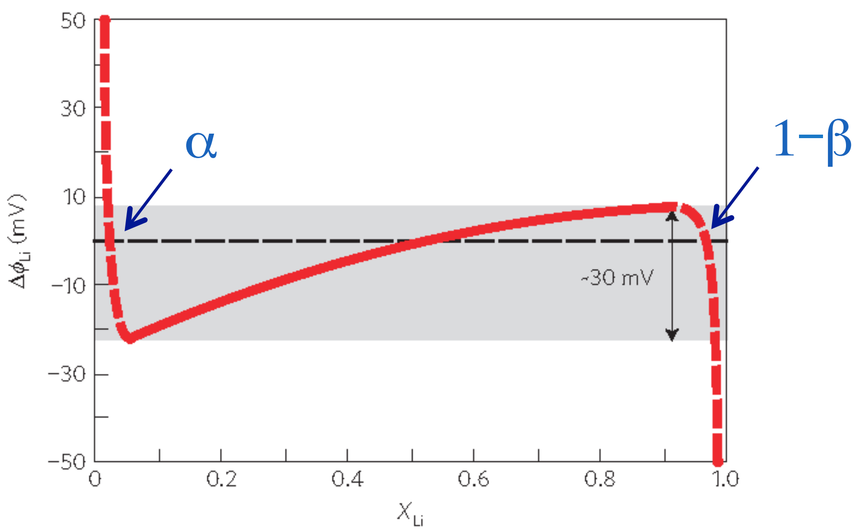
- High rate capability typical of single-phase reaction
  - Li_xFePO_4 for $0 \leq x \leq 1$ (as in Li_xTiS_2)
  - Actual: $Li_{1-\beta}FePO_4$ phase ***to*** two phases ***to*** $Li_\alpha FePO_4$ phase
    - (α and β 0-3%)



Dodd et al, Electro. Soc Ltrs, 2006

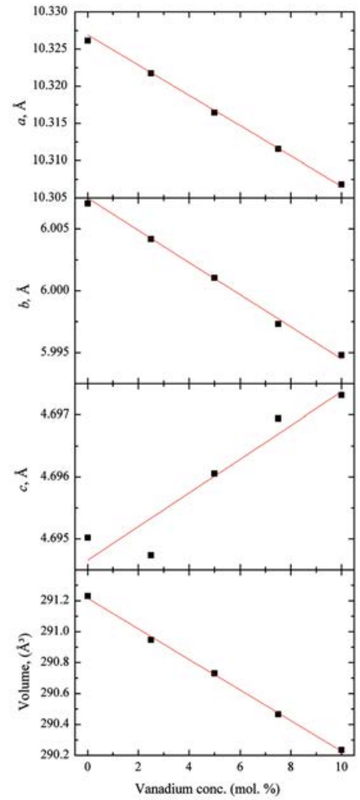
NECCES developed model to explain behavior
(Nature Materials 10, 587, 2011)

- High rate capability typical of single-phase reaction
  - Li_xFePO_4 for $0 \leq x \leq 1$ (as in Li_xTiS_2)
  - Actual: $Li_{1-\beta}FePO_4$ phase ***to*** two phases ***to*** $Li_\alpha FePO_4$ (α and β 0-3%)
- Developed model
  - Metastable single phase (kinetic state)
  - Two-phase on relaxation (thermodynamic state)



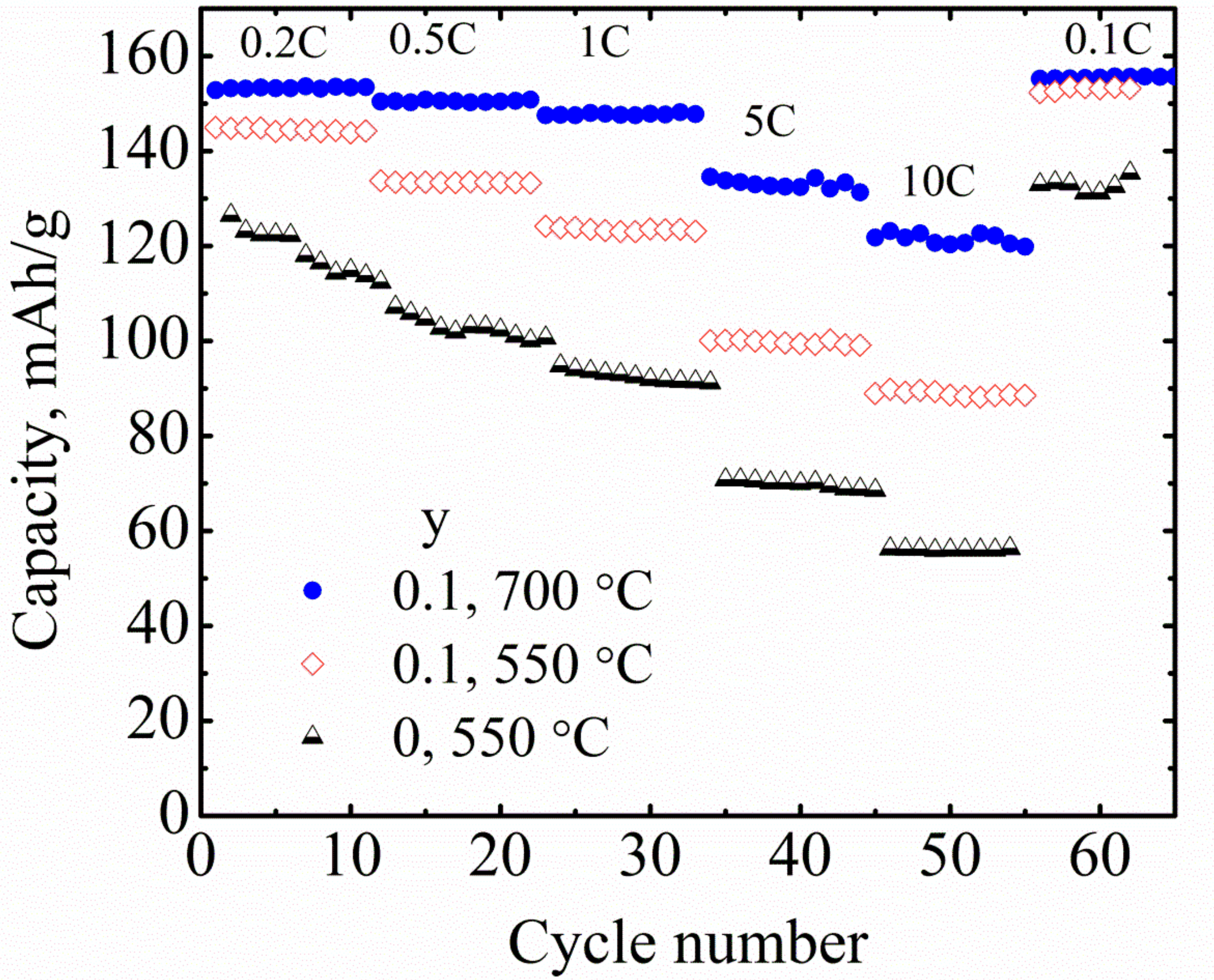
How to Test the Single-Phase Model?

- Single phase model applicable to **nano-size** materials (< 100 nm)
  - Difficult to observe directly (all expts see equilibrium two-phases)
  - Can substitution of some of the Fe or Li give evidence? (adding defects)
    - Substituted aliovalent vanadium, V^{3+}, into the structure (theory says no)
      - **550°C single phase** - solubility f(T)
        - 10% on Fe site
          - Charge compensation by Fe vacancies
      - 700°C + $Li_3V_2(PO_4)$ + Fe_2P



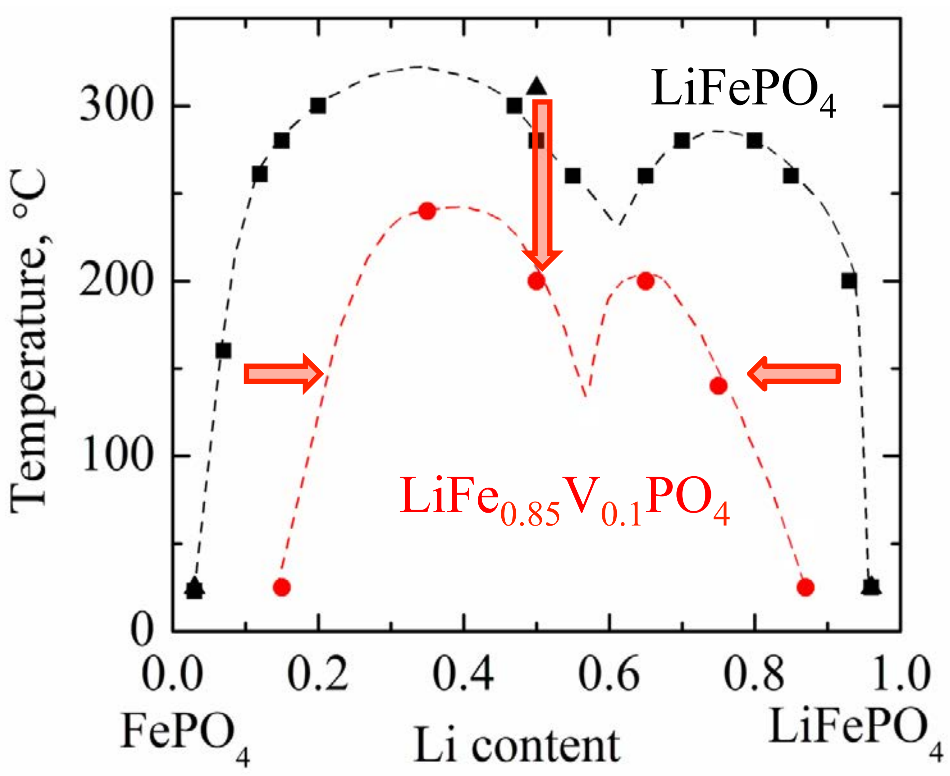
Performance Enhanced by Vanadium Substitution, V^{+}_{Fe}

Chemistry of Materials 23, 4733 (2011)



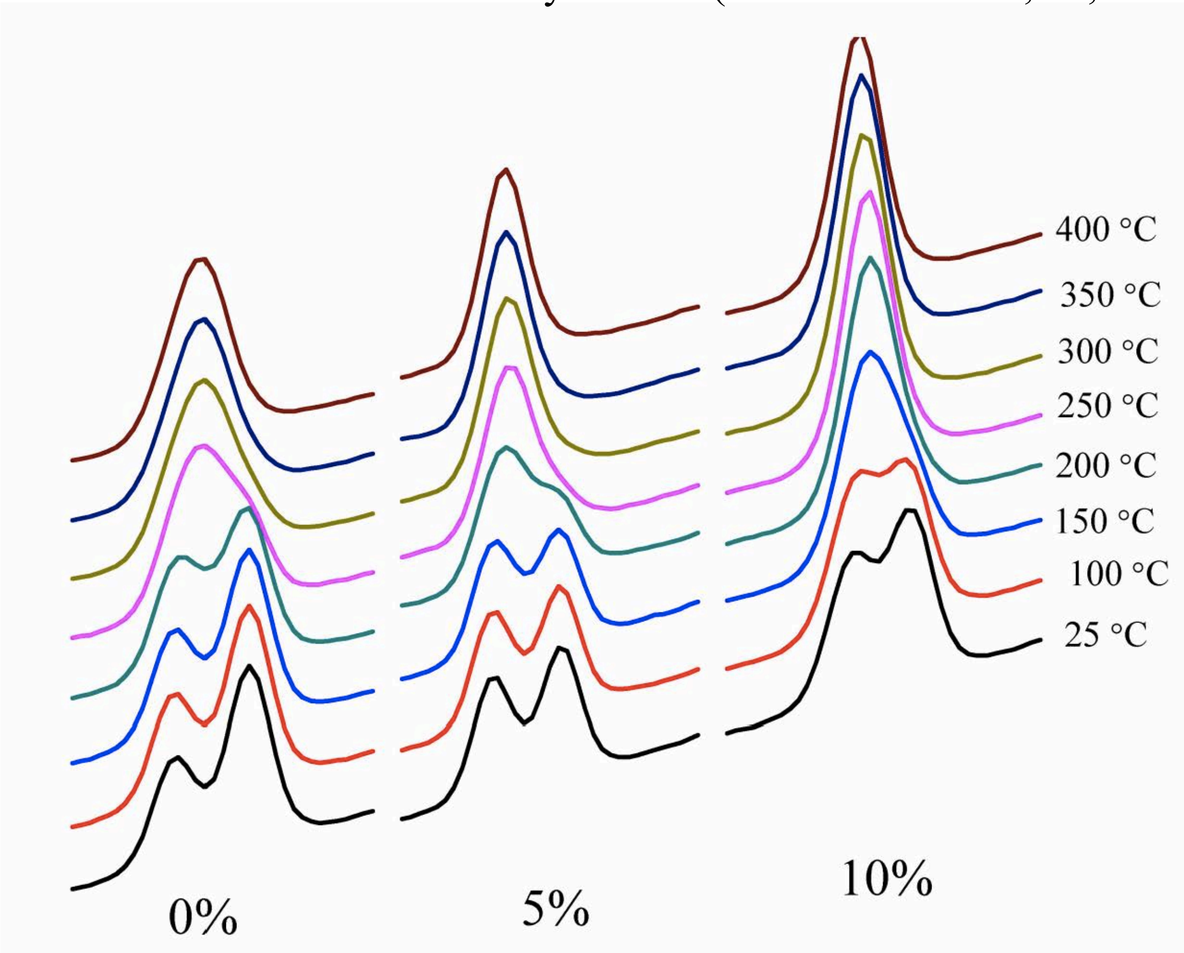
Vanadium Substitution increases Single-phase Reaction
(Chem. Mater. 25, 85, 2013)

- Ideally single phase reaction
  - Expected to be two phase, only $LiFePO_4$ and $FePO_4$ present
  - Preferred, just Li_xFePO_4
    - No nucleation energy for new phase



$Li_{0.5}FePO_4$ Solid Solution Temperature is a Function of Vanadium Content

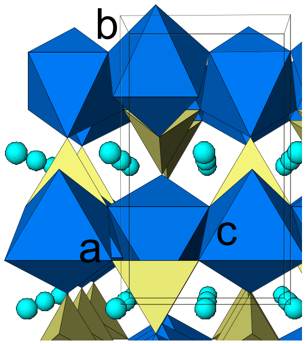
In-situ study at BNL (Chem. Mater. 25, 85, 2013)

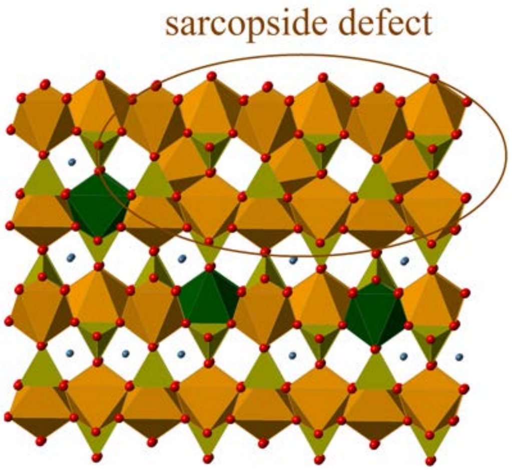


- Transformation of the *200* peak
- Solid solution formation temperature decreases with increase in vanadium content
- Vanadium substituted $LiFePO_4$ behaves as a solid solution electrode, rather than as a 2-phase system

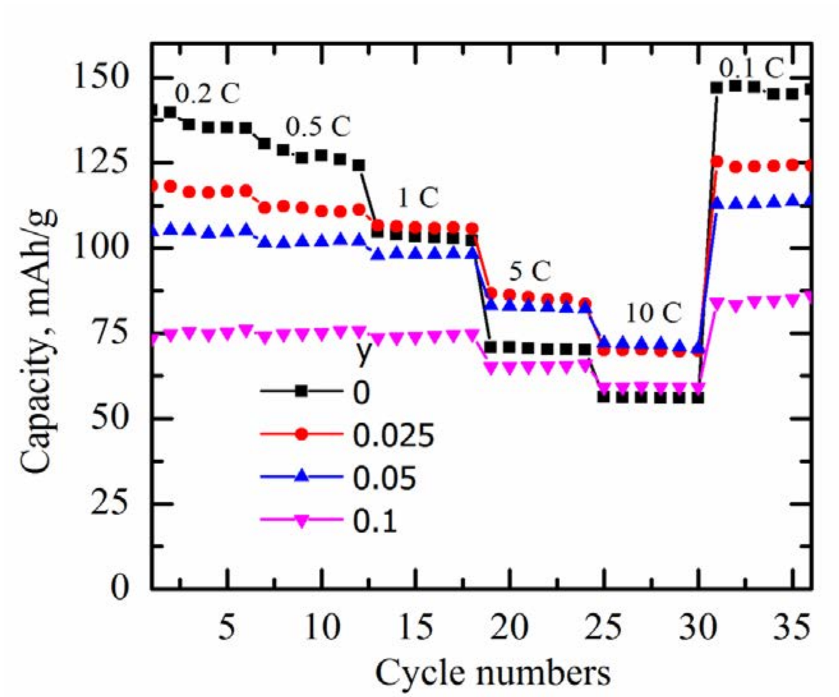
Substitution on the Li Site can occur, M^{y+}_{Li}
(Chem. Mat., 25, 2691, 2013)

- **M +Fe > 1 > Li in $Li_{1-ny}M_yFePO_4$**
  - Vanadium used (very different neutron scattering to Fe)
    - + X-ray diffraction
      - + Fe site totally occupied by transition metal; Li site has metal
    - +Neutron diffraction
      - + Fe site contains Fe + V
      - + Li site contains Li + Fe + vacancies
    - **– Tunnels blocked by Fe?**
  - **+ High rate capability found**
    - **+ Tunnels not blocked**
    - **+ Fe must be present in clusters**
      - **+ Sarcopside regions likely**
      - **+ V ≠ sarcopside, so explains V_{Fe}**

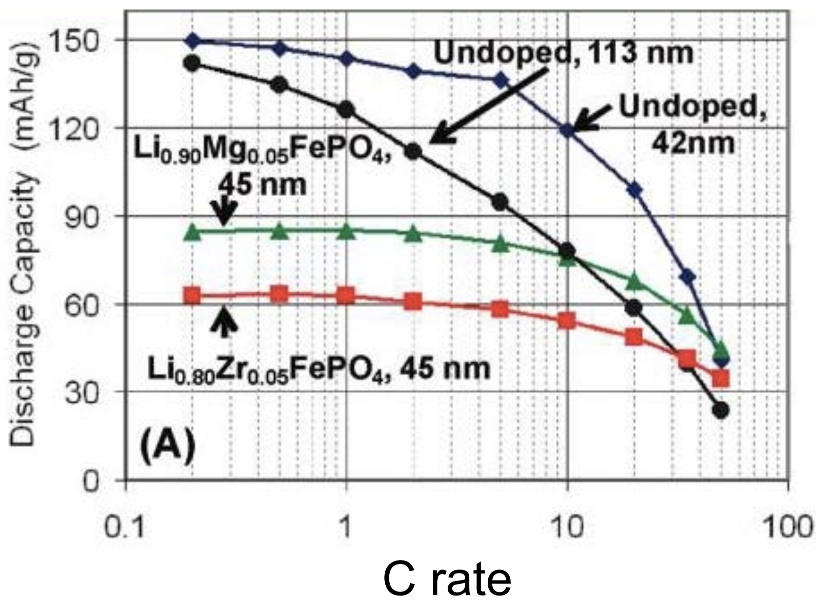




Contrast: Substitution on the Li site enhances high rate capability but kills the capacity, M^{y+}_{Li}



Omenya et al, Chem Mater., 25, 2691, 2013

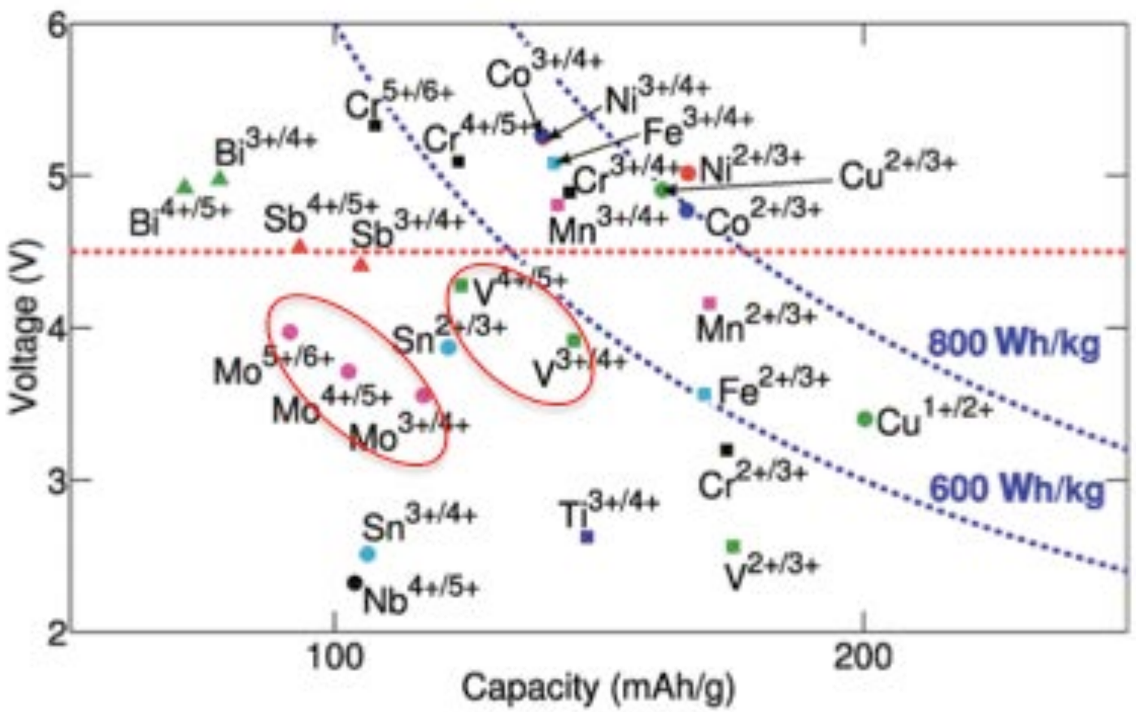


Meethong et al, Chem Mater., 22, 1088, 2010

What about other Phosphates?
Need 2e per Redox Center for > 700 Wh/kg

- $VOPO_4$ is one possibility, ….
- Pyrophosphates do not appear to be feasible for more than 1 Li
- What other systems?
- **Ceder study not encouraging.**

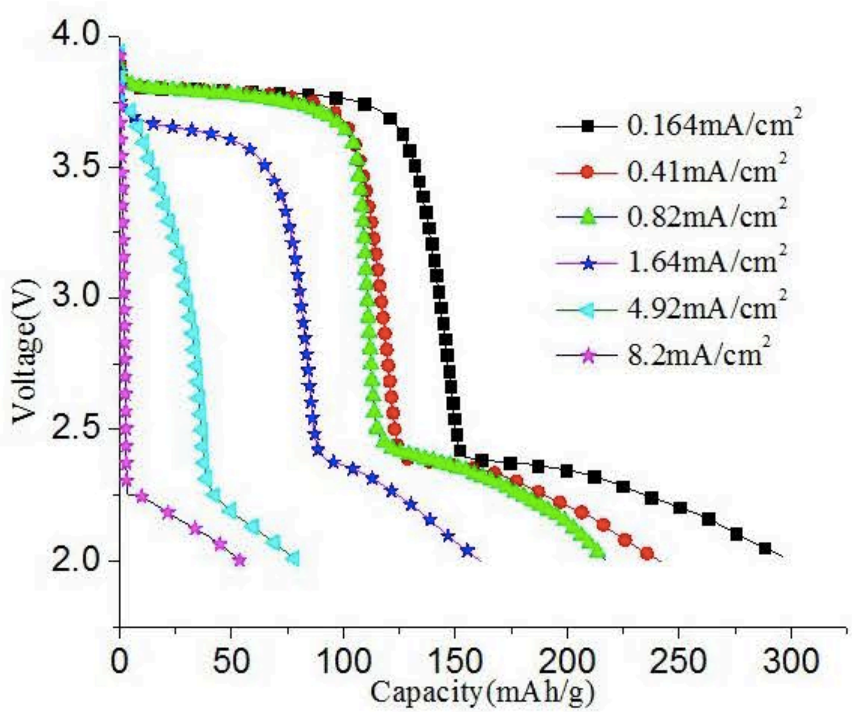
  (Chemistry of Materials, 23, 3495, 2011)

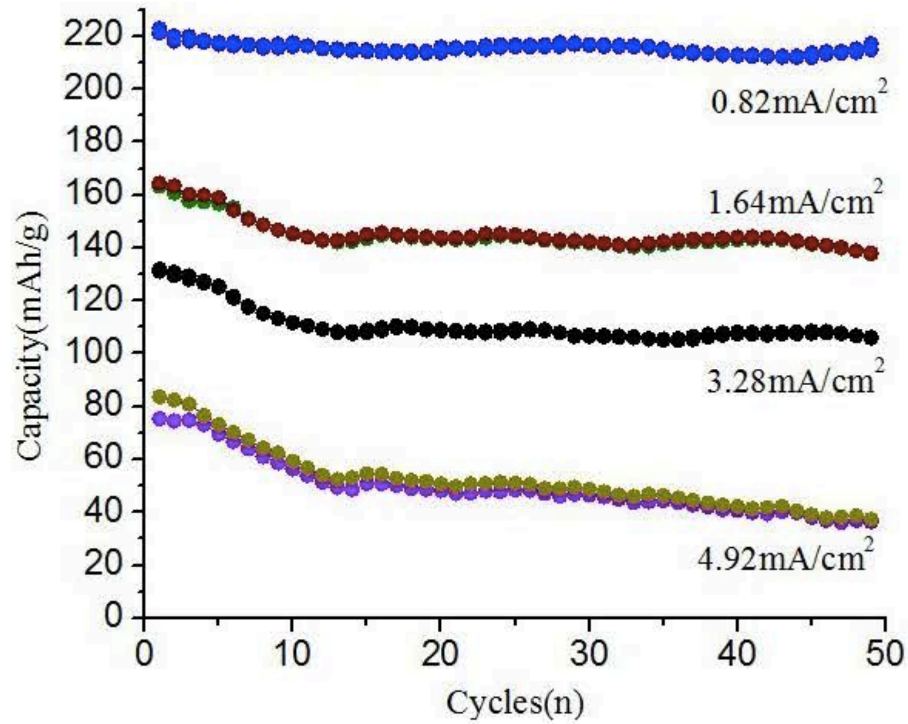


$VOPO_4$ can be cycled over the two lithium despite significant lattice changes

J. Electrochem. Soc., 160, A1777 (2013)

Zehua Chen

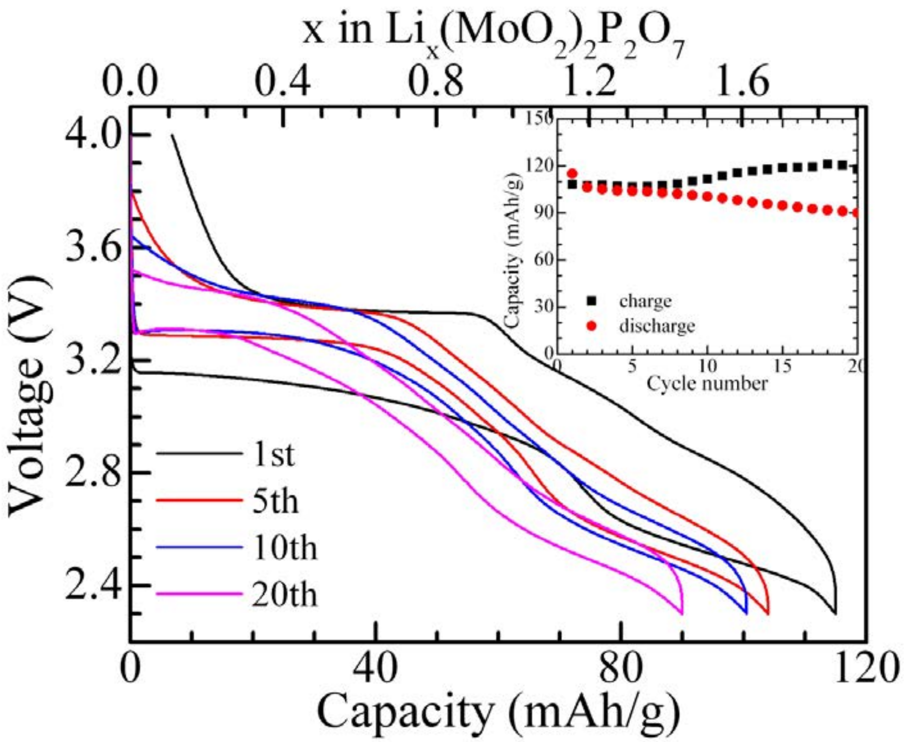




Mo-Phosphates show reversibility

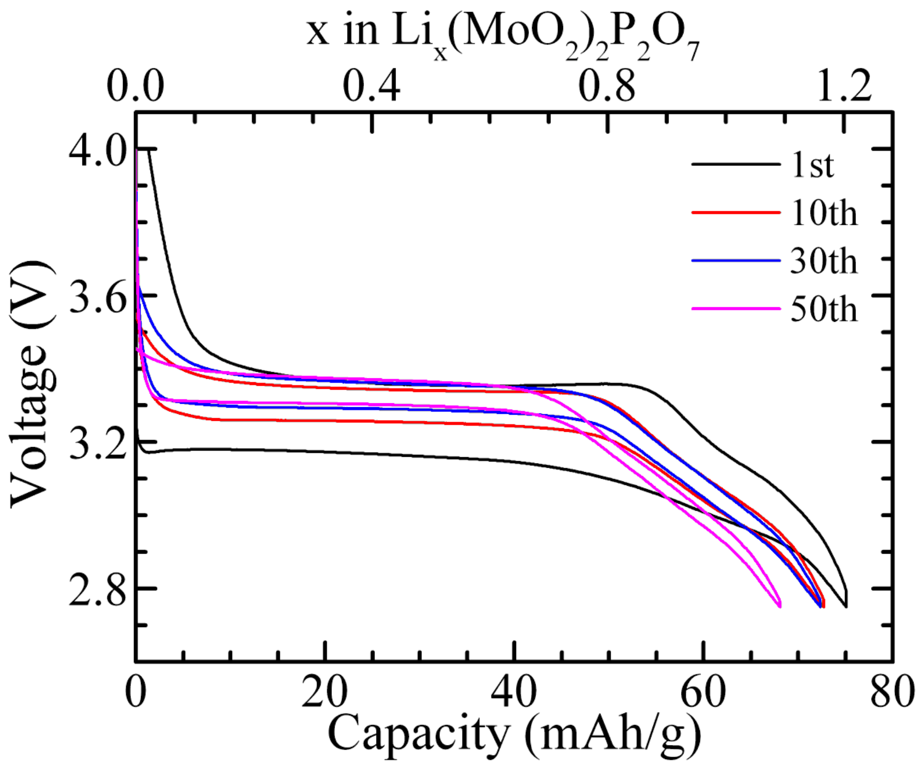
Chem . Mater., 25, 3513 (2013)

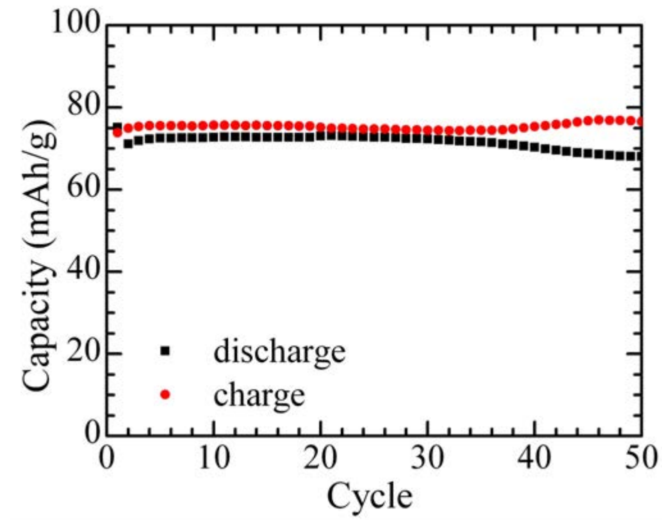
Molybdenum pyrophosphate reacts with close to 2 Li per formula unit

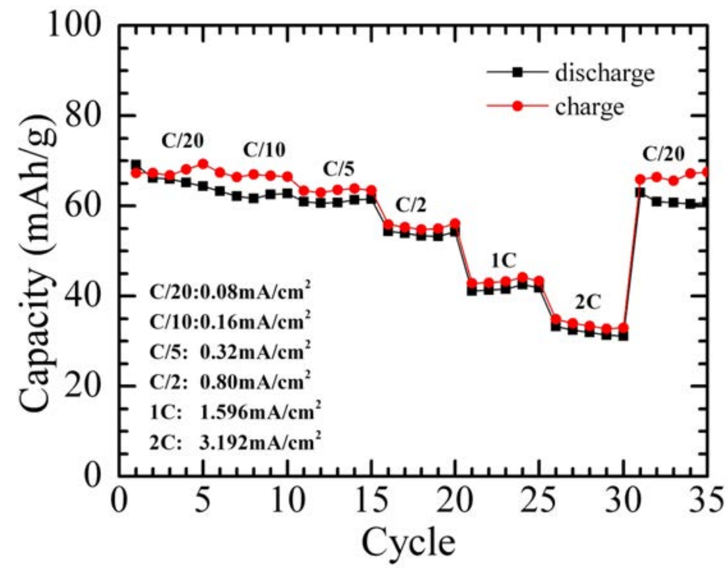


2.8V cut-off improves Mo-Phosphate reversibility

Chem . Mater., 25, 3513 (2013)

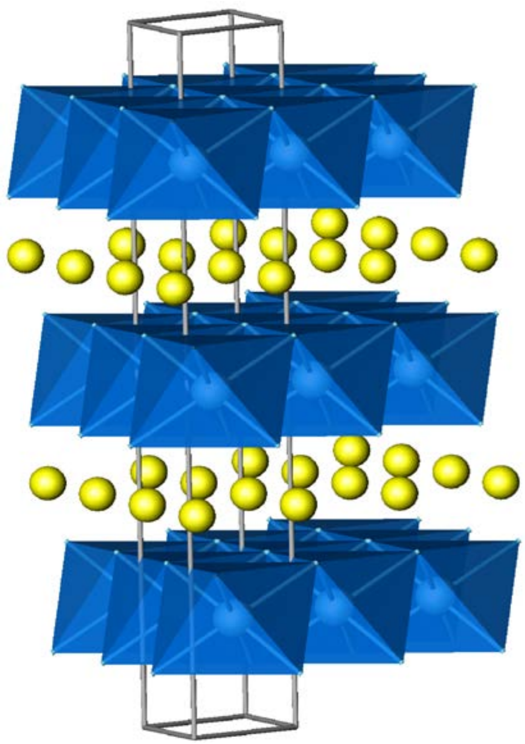






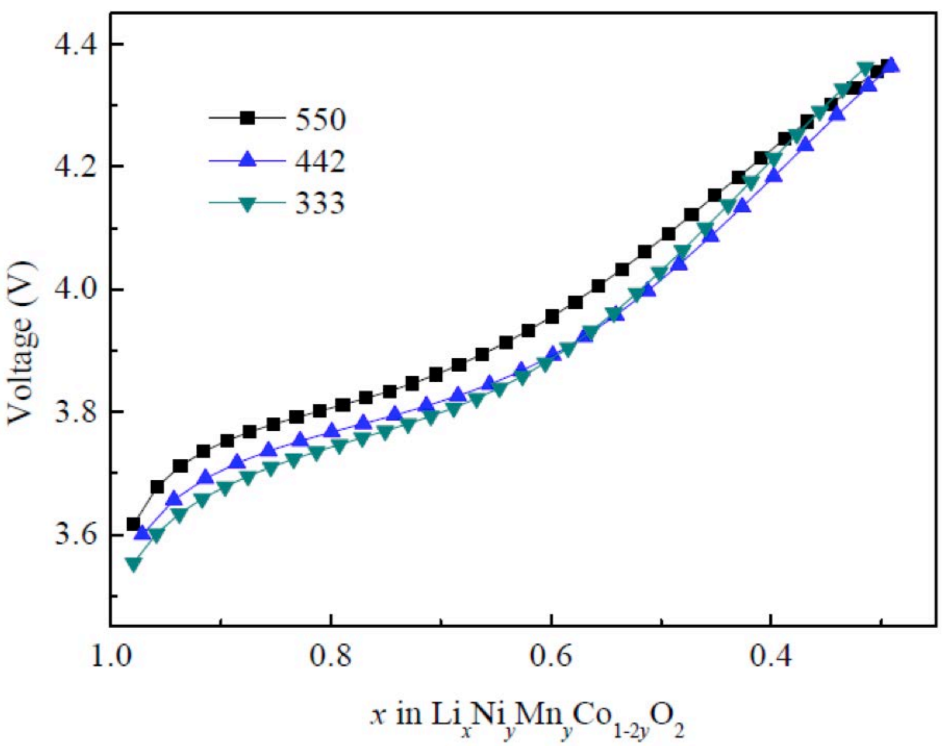
Limits of Layered $Li[LiNiMnCo]O_2$
Why can we not get 250 Ah/kg = 1 Li/M?

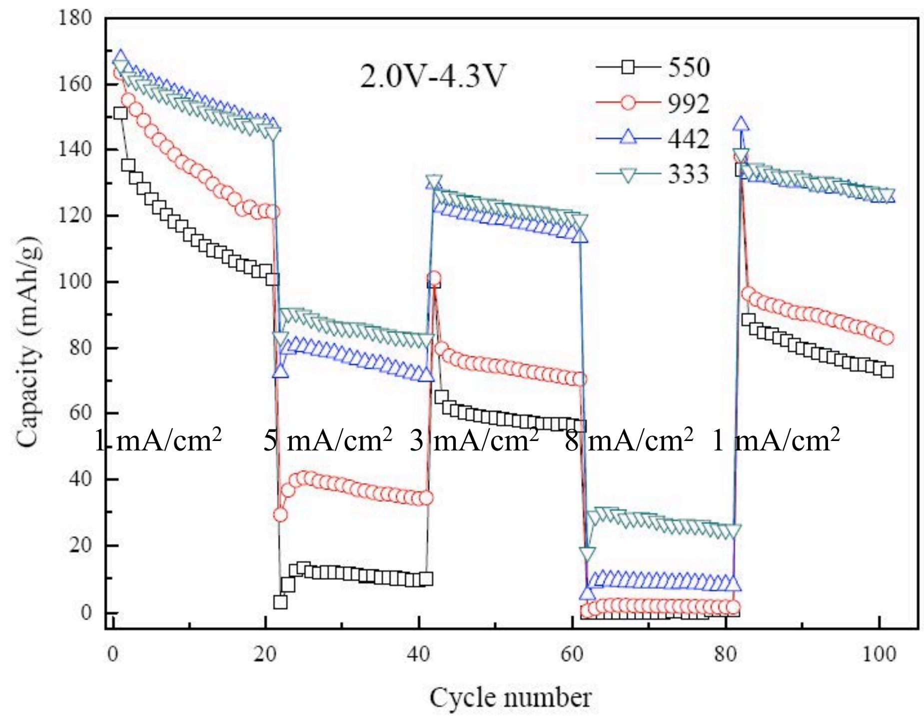
- **What is ideal chemical composition?**
- **Stoichiometric $Li[NiMnCo]O_2$**
  - **Always some Ni/Li exchange (except for high cobalt content)**
  - **A little Ni stabilizes structure against conversion to one block (1T)**
  - **How much Co can be reduced without hurting rate caability**



- **Mn-rich/Li-rich $Li_{1+y}[NiMnCo]_{1-y}O_2$**
  - **Best opportunity for 250+ Ah/kg**
  - **What are the limitations?**

What is best composition? Cycling at constant current suggests that 442 composition has best overall capacity

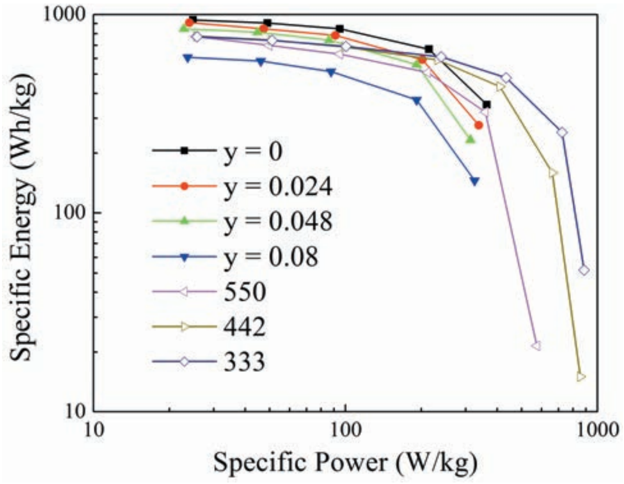


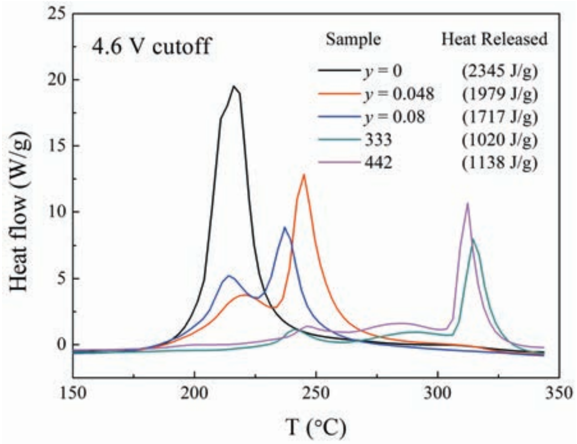


- **Maximum capacity at 4.4 volts is 197 Ah/kg and 180 at 4.3 volts charging**
  - **≤ 20% Co maybe optimum**
- **Charging above 4.5 volts needed to achieve > 220 Ah/kg**
  - **Unstable oxygen-releasing materials**

Can the high Mn $Li_2MnO_3/LiMO_2$ phases deliver?
(JECS, 159, A116, 2012)

- **Poor rate capability**
  - Coupled with a much larger potential change during discharge
  - Lead to lower energy storage than NMC at practical power levels
- Surprisingly **poor thermal stability**
  - Similar to NCA
  - Can be improved by Al substitution
    - But causes further power and energy losses
  - Why are these high Mn phases unstable?
- Low tap density in some cases
  - Function of synthesis method
    - ANL-Binghamton (G. Zhou et al 2012)
- Can the voltage fade be mitigated?
  - Conversion to spinel-like phases
    - Meng et al (Energy & Env. Sciences 2011)



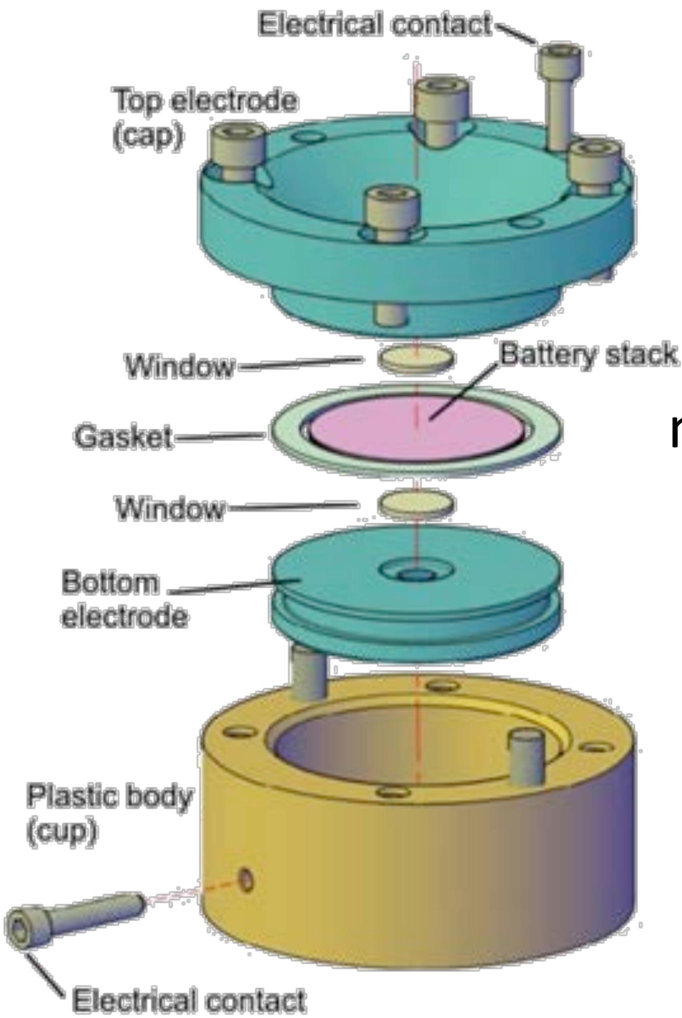


$Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08-y}Al_yO_2$

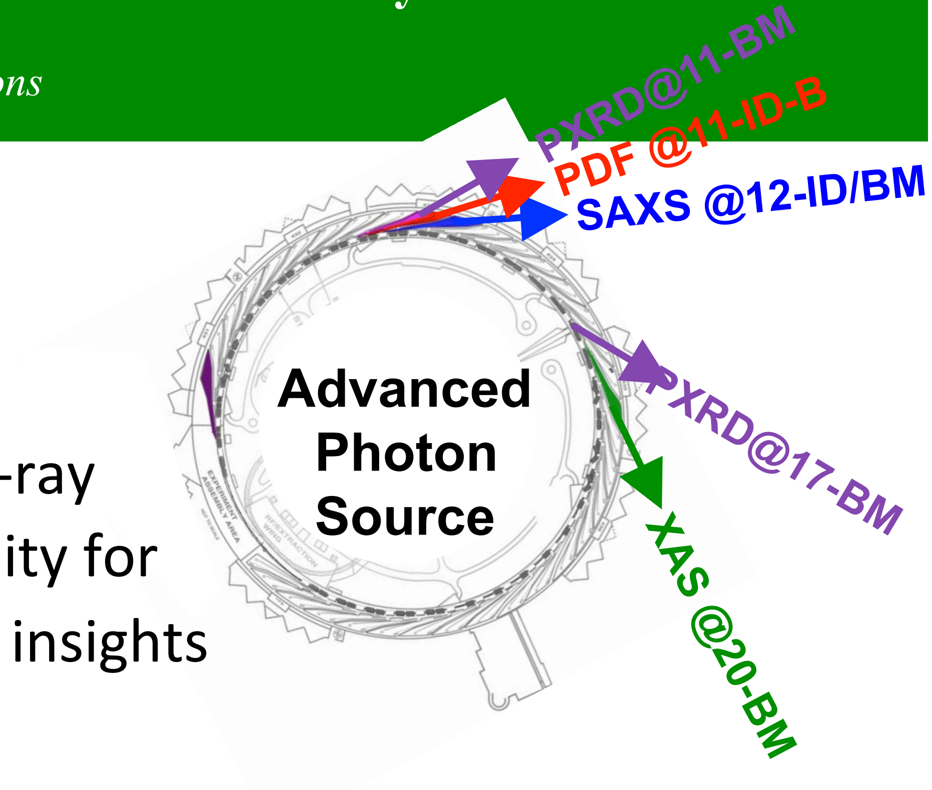
AMPIX cell: Argonne Multi-Purpose In-Situ X-Ray Cell

Chapman et al: J. Appl. Cryst. **2012**, *45*,1261

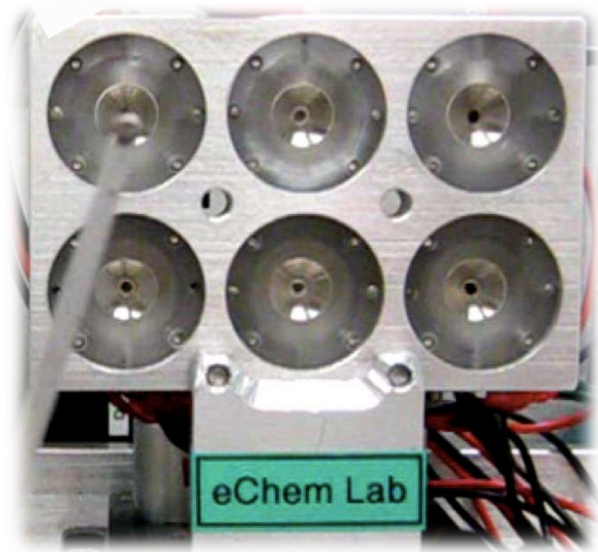
A Transmission-Geometry Electrochemical Cell for
In-Situ X-ray Scattering and Spectroscopic Investigations



Broad X-ray compatibility for multi-modal insights



Multiplexing capabilities for high-throughput



Coin-cell substitute

Patent pending   NECCES EFRC-supported

Conclusions and What's Next

- **Li-ion intercalation batteries**
  - **Approach 800 Wh/kg** (excluding C anode) (200 Ah/kg x 4 V)
    - + **Lab experimental data**
      - + **Cost, beyond raw material, is an issue**
      - + **Find low cost manufacturing methods**
  - **Understand challenges faced by 2e / redox site**
    - **2 Li or 1 Mg**
  - **Volumetric capacity hurt by:**
    - Carbon anode, carbon and binder in cathode
    - Use of nanomaterials
  - **Anticipated limits of intercalation cells (complete cells):**
    - **1500 Wh/L at C rate; 400 Wh/kg at C rate**