In Operando Studies of Advanced Battery Electrodes

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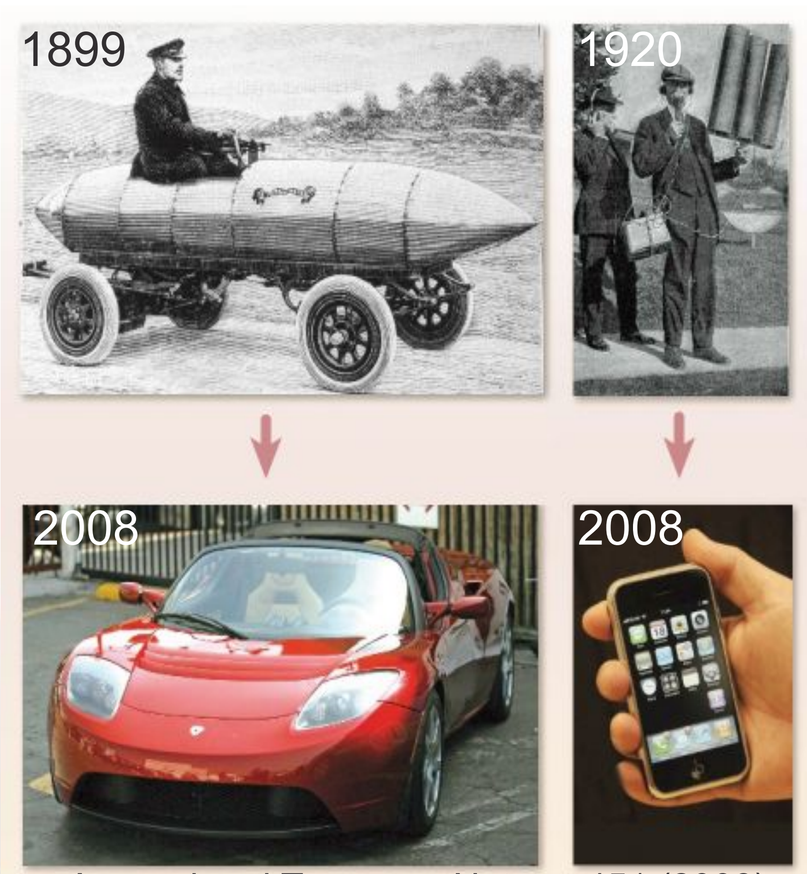
Why batteries?

Economical plug-in hybrid electric vehicle may be best near-term way of reducing our energy related emissions and dependence on foreign oil

National average 9¢/kWh



Armand and Tarascon, Nature, 451 (2008)

- *Lack of good batteries slowed the deployment of electric cars and wireless communication,*
- *Slow progress due to lack of suitable electrode materials and electrolytes…*
- **Electric (and plug-in hybrid) vehicles require a safe, inexpensive, high capacity battery capable of thousands of cycles with little capacity fade**

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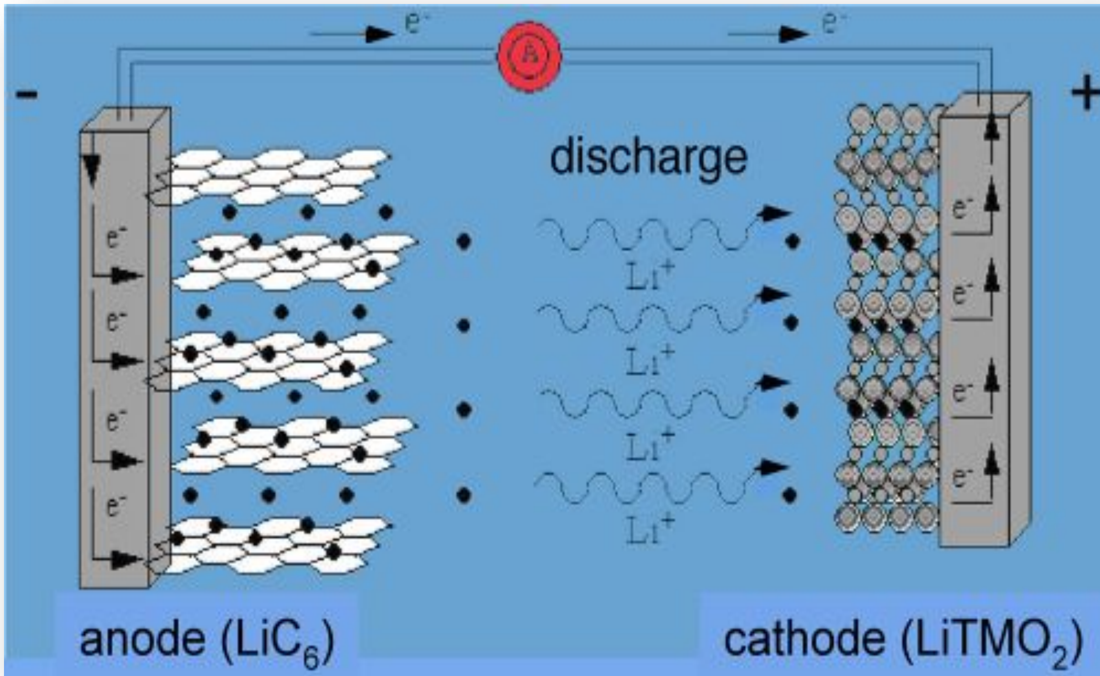
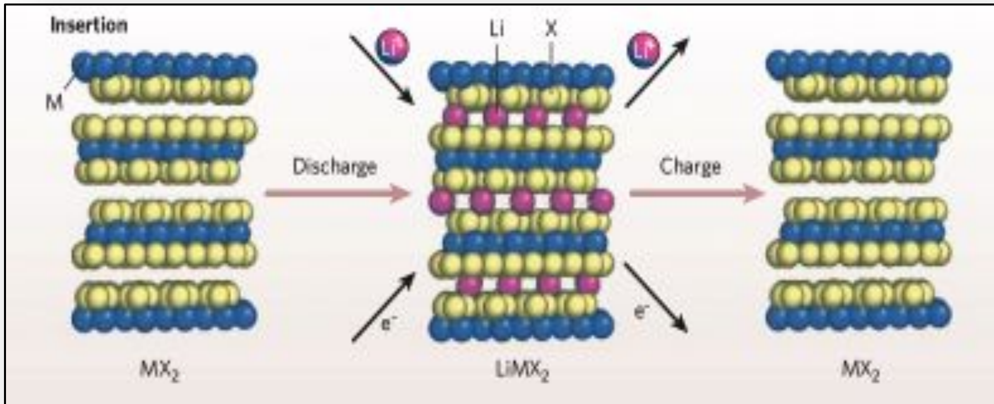
Electrical Energy Storage

Batteries are complex, dynamic devices - involve ion transport, charge compensation, structural changes, metastable phases and instabilities.



• Better batteries requires better understanding of physical and chemical processes occurring during cycling - *to predict and ultimately control capacity (power / energy density), durability (calendar / cycle life), abuse tolerance (safety) and cost.*

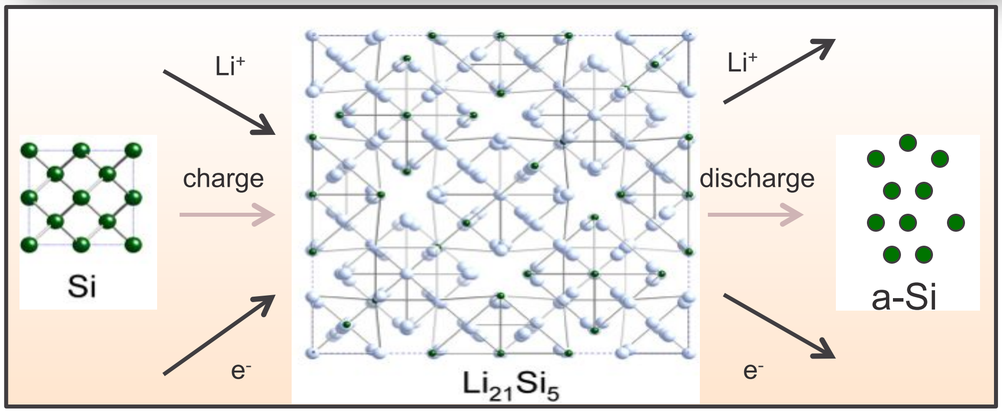
Intercalation and conversion reactions



Intercalation

Li + 6C ↔ LiC_6 (anode)

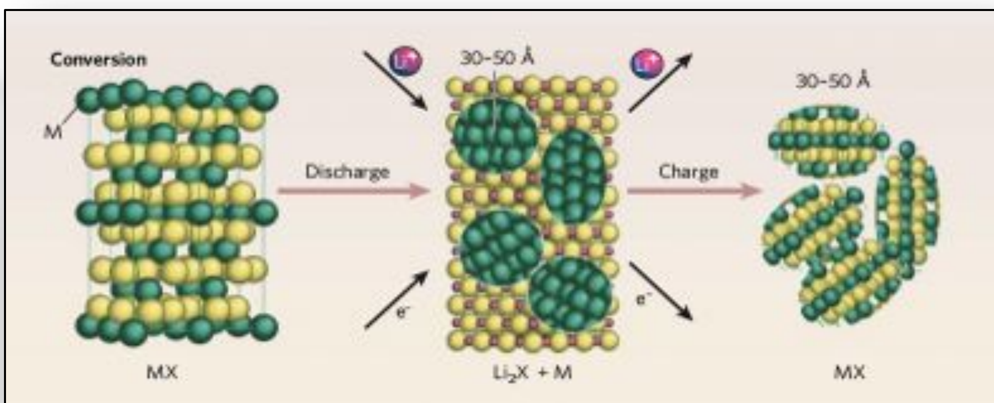
Li+$FePO_4$ ↔ $LiFePO_4$ (cathode)



Alloying

xLi + Si ⟷ Li_xSi (anode)

x = 3.75 - 4.2



Conversion

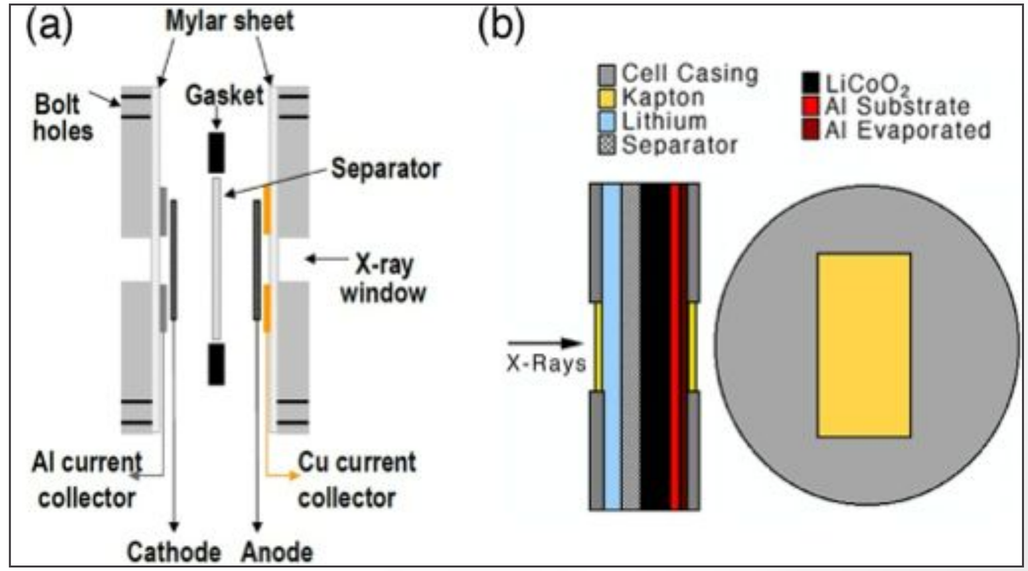
CoO + 2Li ⟷ Co + Li_2O (anode)

FeF_y+ yLi ⟷ Fe + yLiF (cathode)

y = 2 or 3

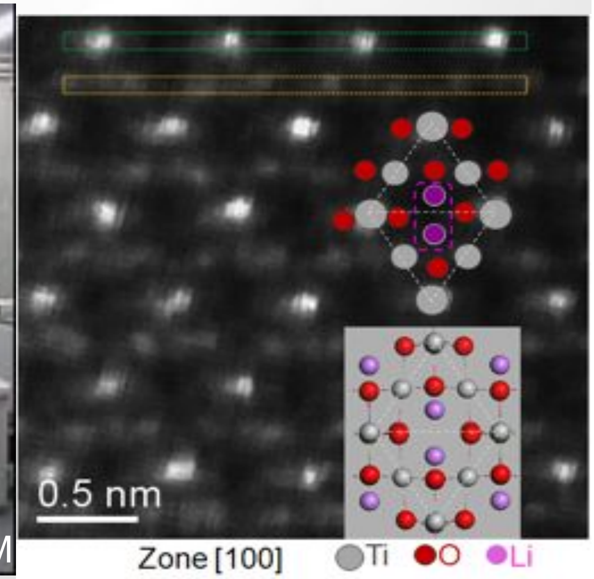
Techniques: *In-situ* synchrotron studies and advanced electron microscopy

Sample holders for in-situ synchrotron studies (XRD, XAS) during cycling.

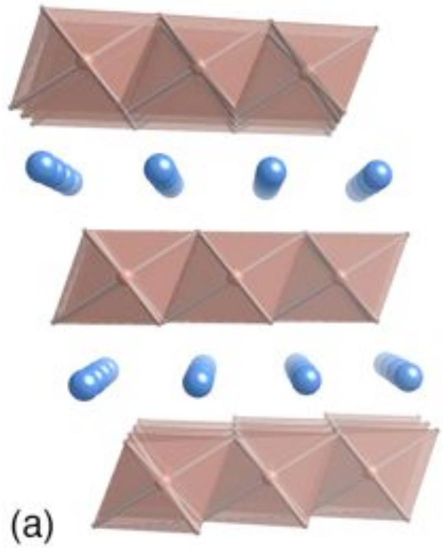


Transmission Electron Microscopy: nanoscale imaging & e-diffraction, Z-contrast, no orientation dependence

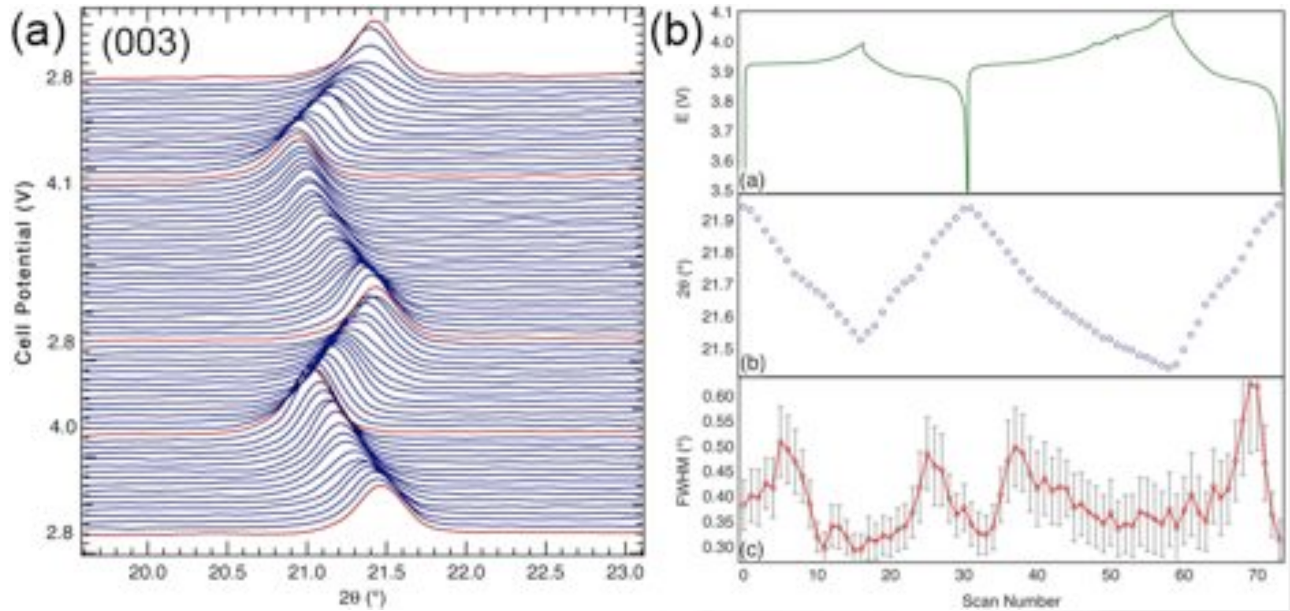
Electron Energy Loss Spectroscopy (EELS) - Sensitive to light elements (e.g., lithium), elemental mapping

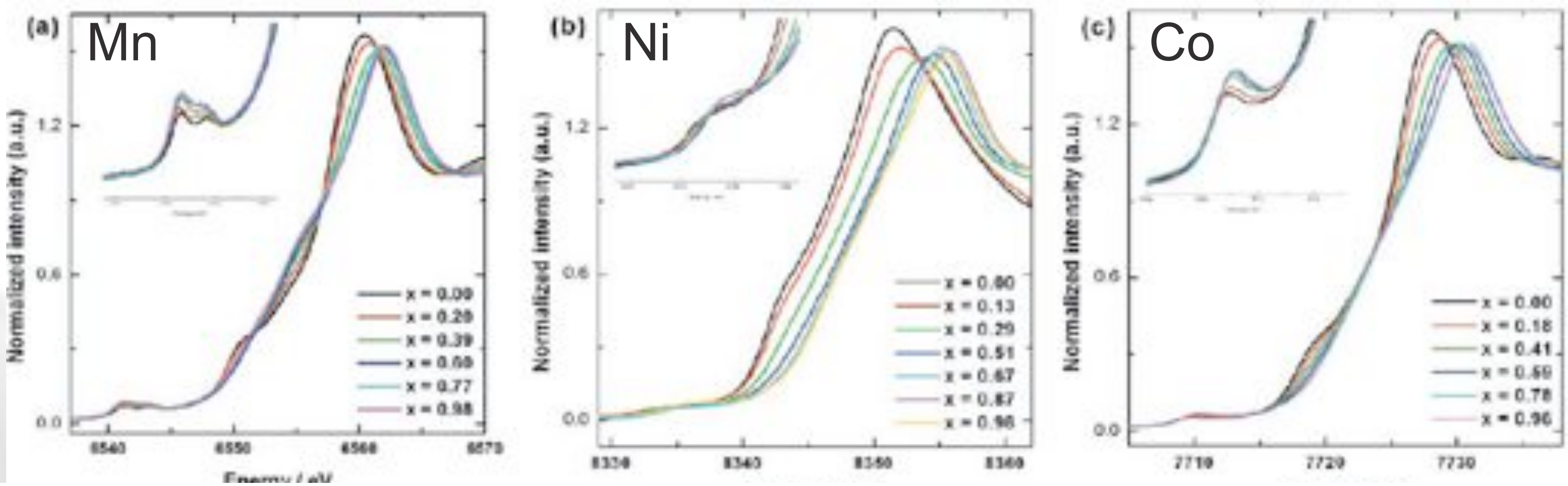


In-situ XRD and XAS at NSLS



$LiCoO_2$



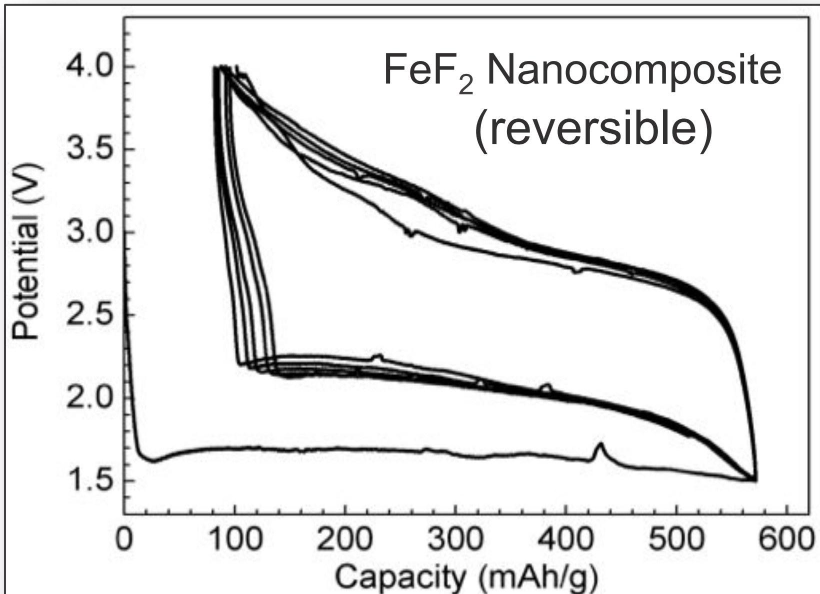


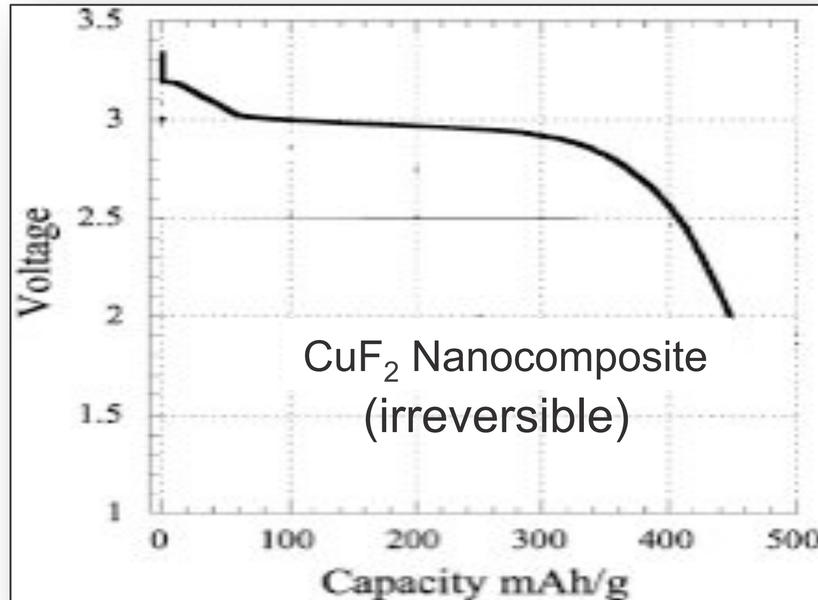
$LiCo_{1/3}Ni1_{1/3}Mn_{1/3}O_2$ (X.Q. Yang et al. BNL)

Conversion reactions: FeF_2 and CuF_2

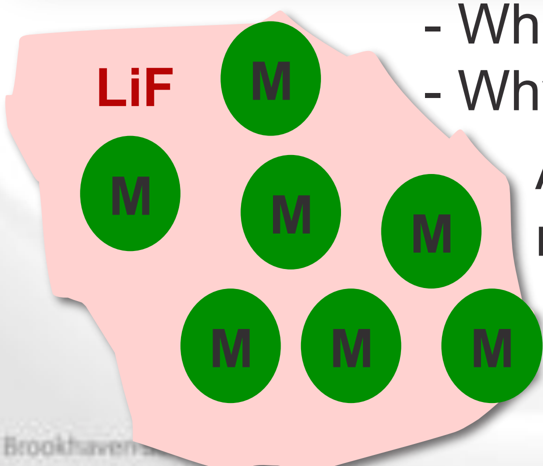
$$FeF_2 + 2Li^+ \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Fe^0 + 2LiF$$

$$CuF_2 + 2Li^+ \xrightarrow{\text{discharge}} Cu^0 + 2LiF$$





F. Badway, et al. *Chem. Mater., Vol. 19, 2007* 4139

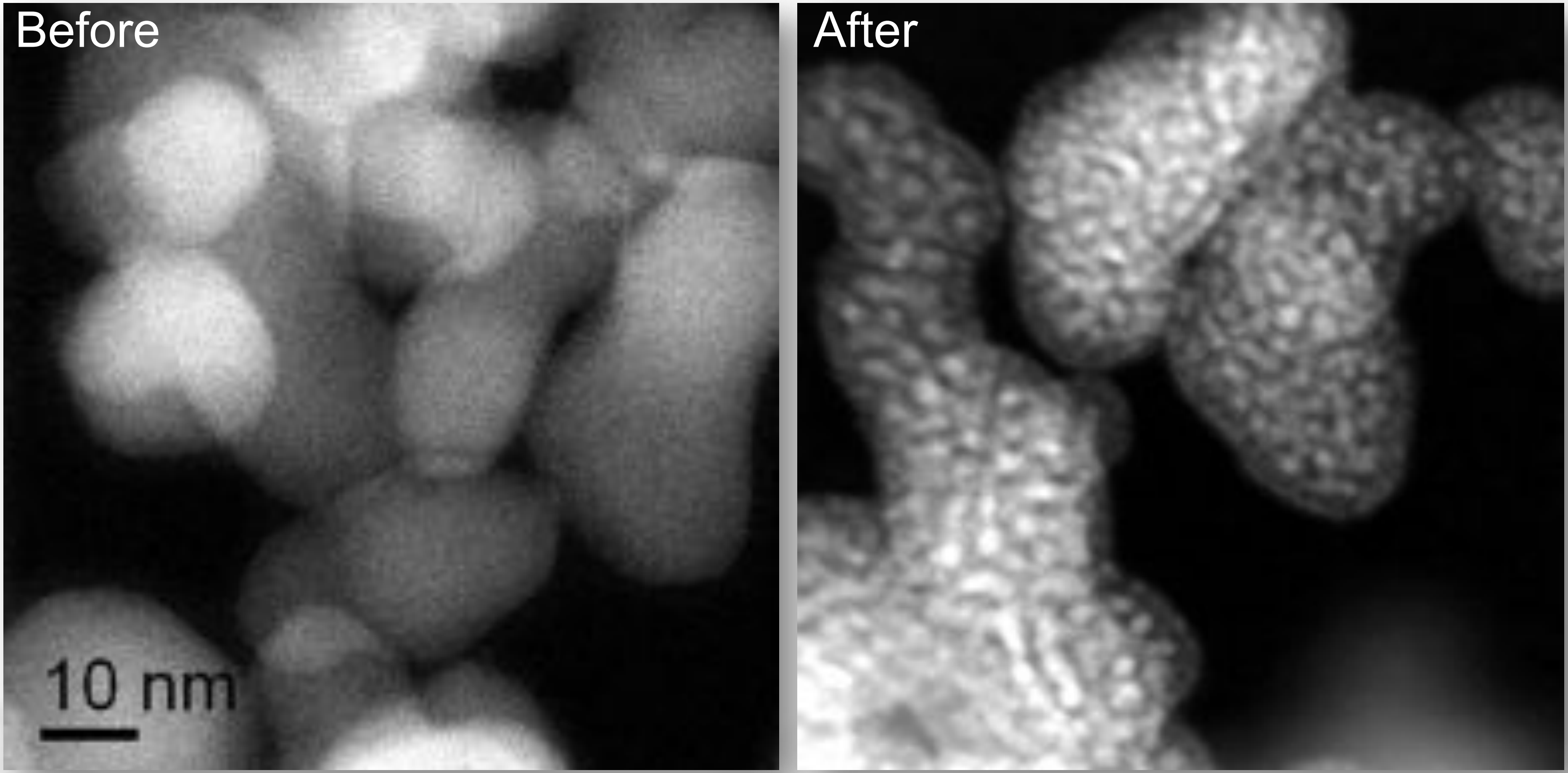


- What is the origin of large hysteresis?
- Why are some systems reversible while others are not?

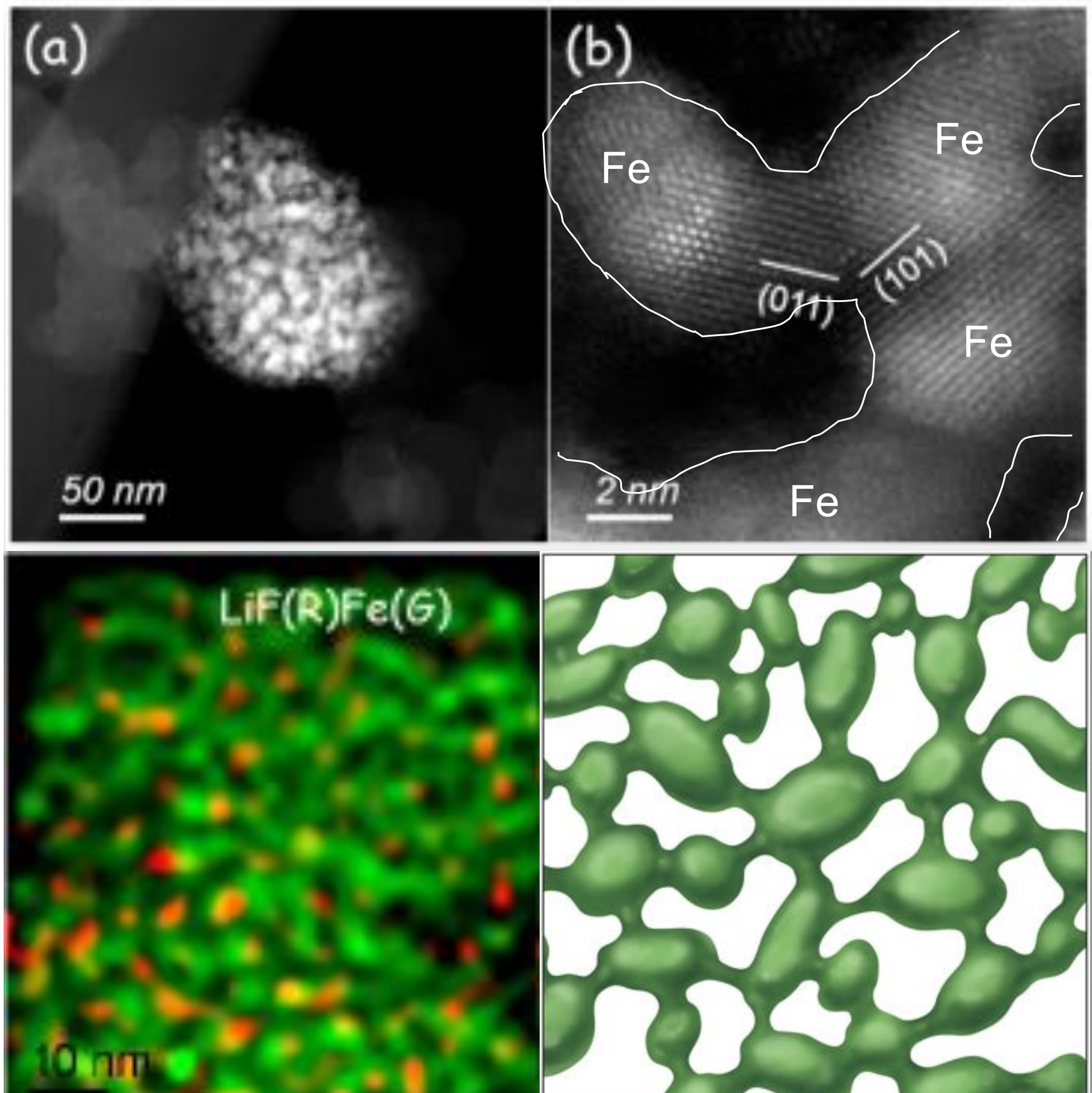
After lithiation electrodes composed of metal nanoparticles (Fe) embedded in insulting (LiF) matrix

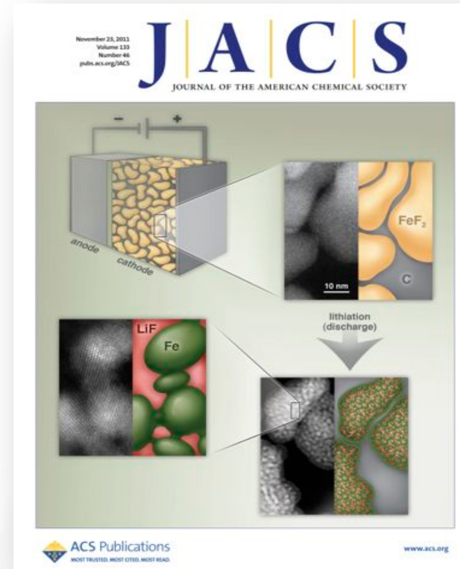
- How do we maintain e- and ionic conductivity?
- What is relationship between parent phase and converted phase?

FeF_2 before and after lithiation



FeF_2-C nanocomposite: fully lithiated

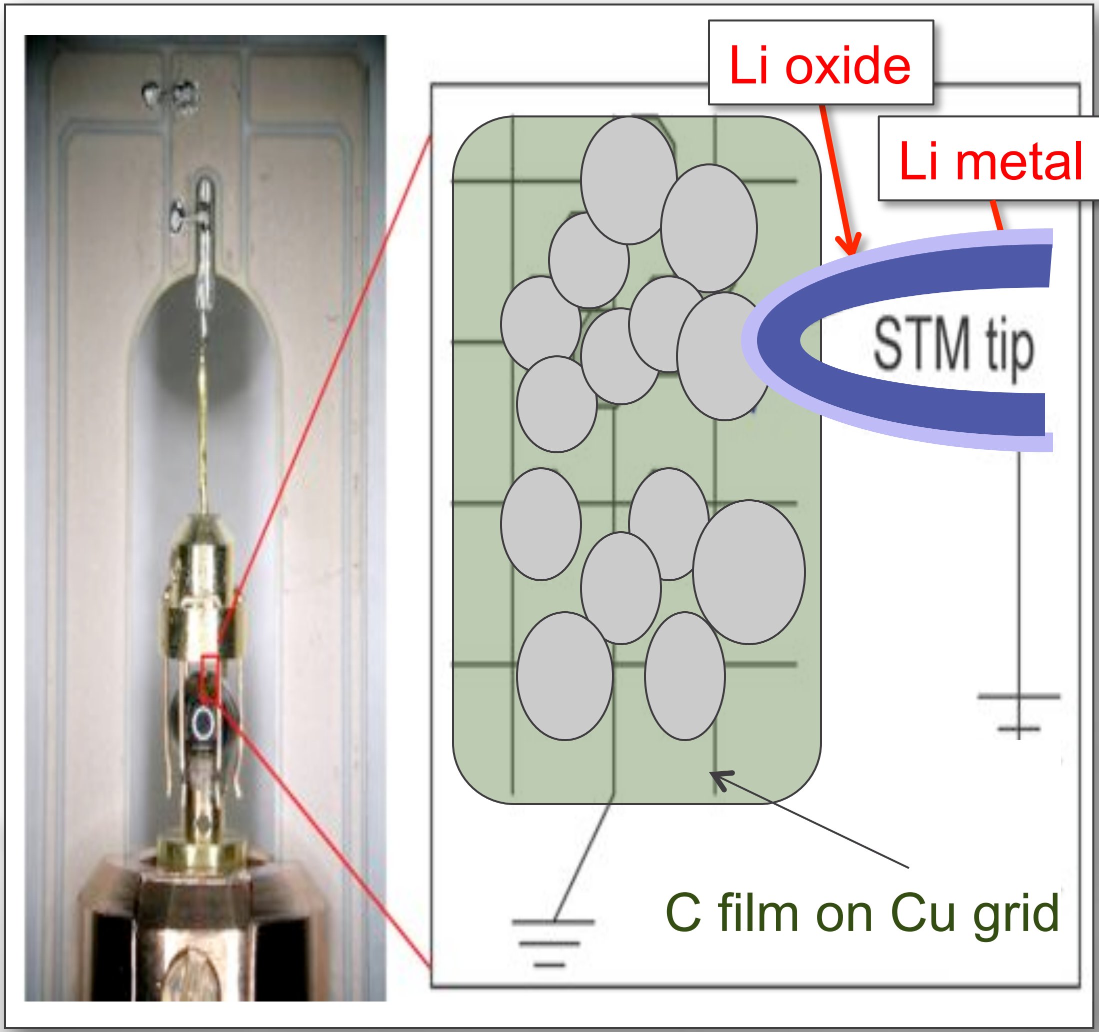


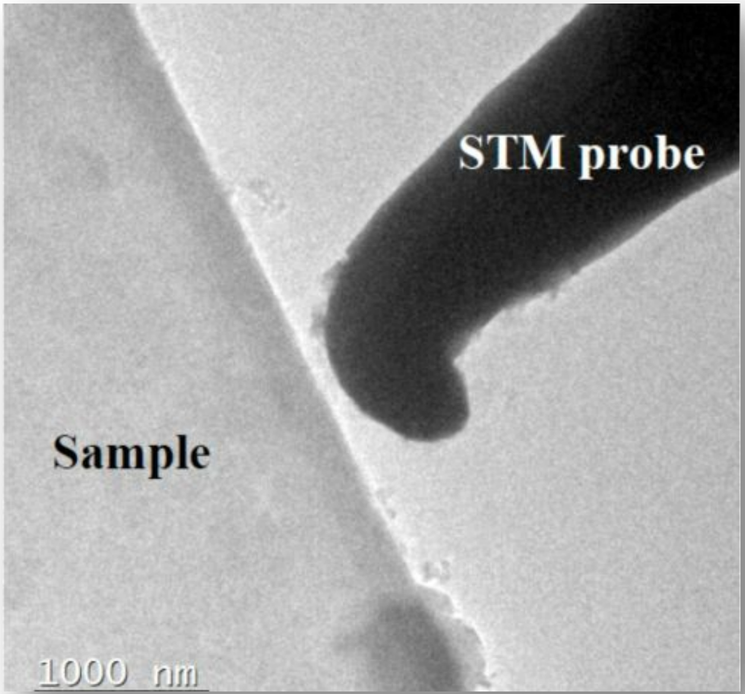


- Upon lithiation particle size decreases to 3-5nm
- Formation of interconnected (bicontinuous) Fe network during lithiation
- Effective conductive matrix for electron transport

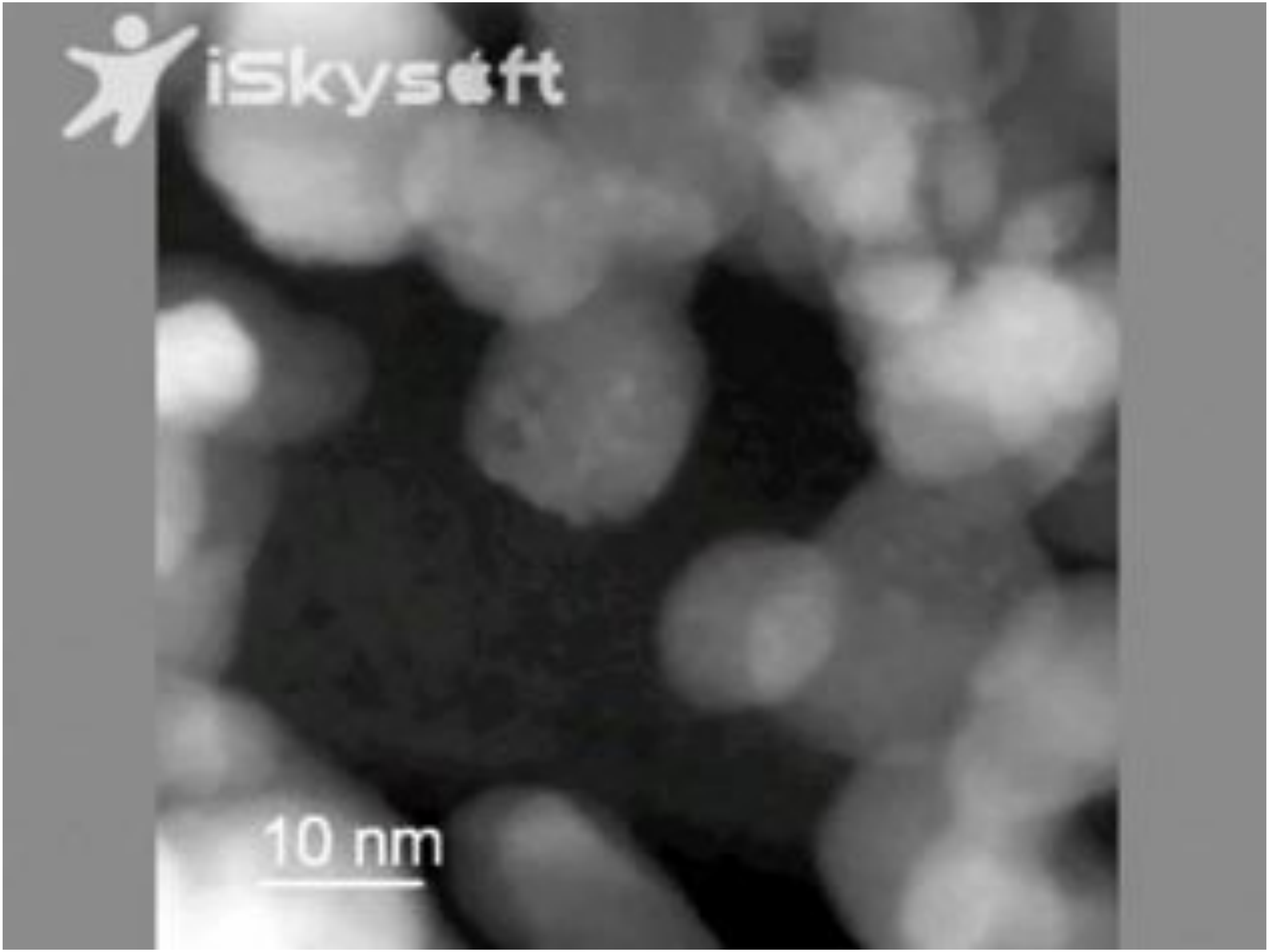
In Situ Studies: Single particle approach

Couple high-resolution imaging with electrochemical measurements

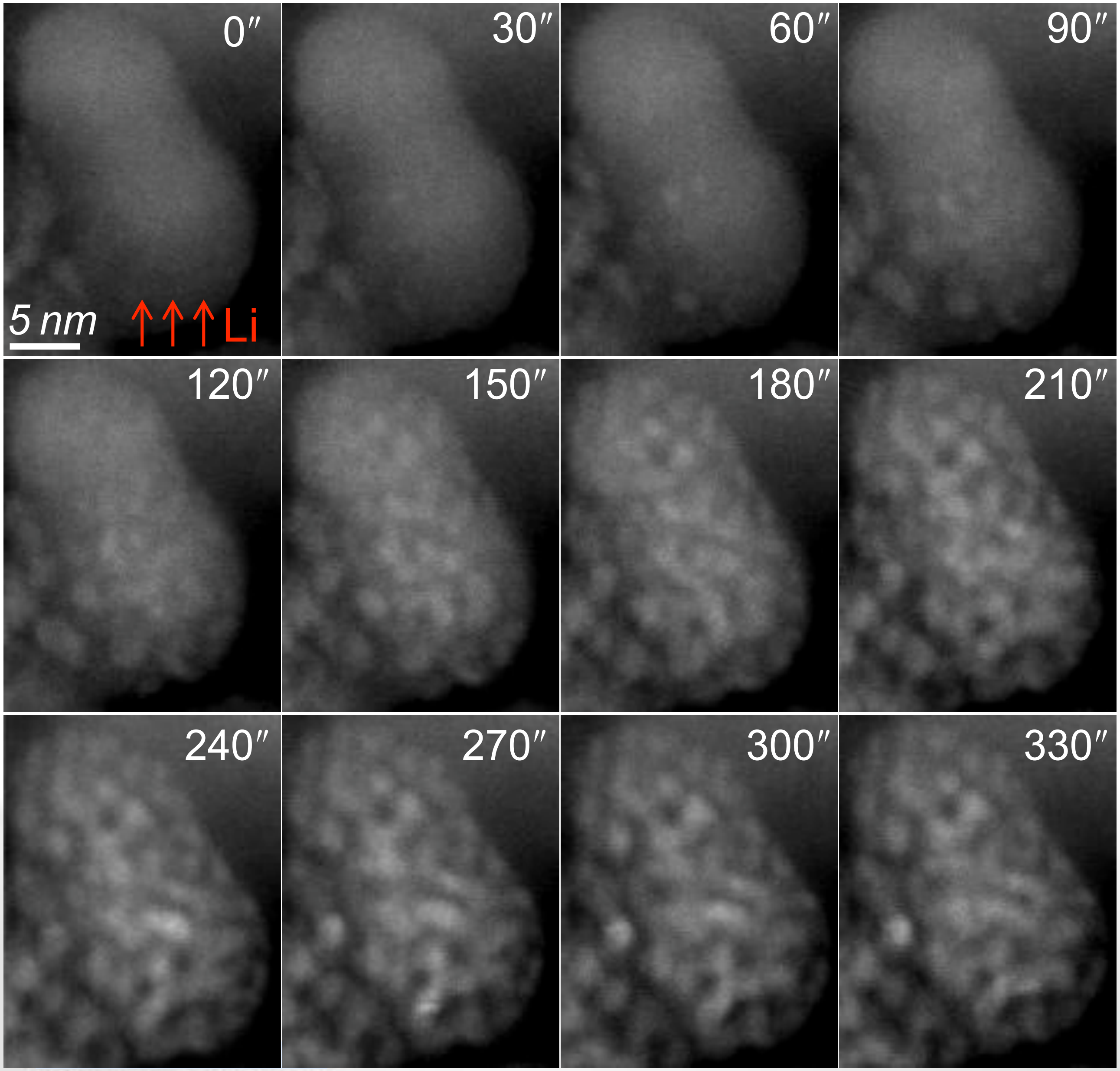




TEM sample holder with piezo-driven STM tip - bias used to measure IV curves on nanoscale


10 nm

Conversion reaction of a single FeF_2 nanoparticle



- Conversion reaction starts from surface and moves inward
- No morphology change after conversion reaction
- Formation of 1-3 nm Fe within FeF_2 domain
- 40-50% volume expansion.

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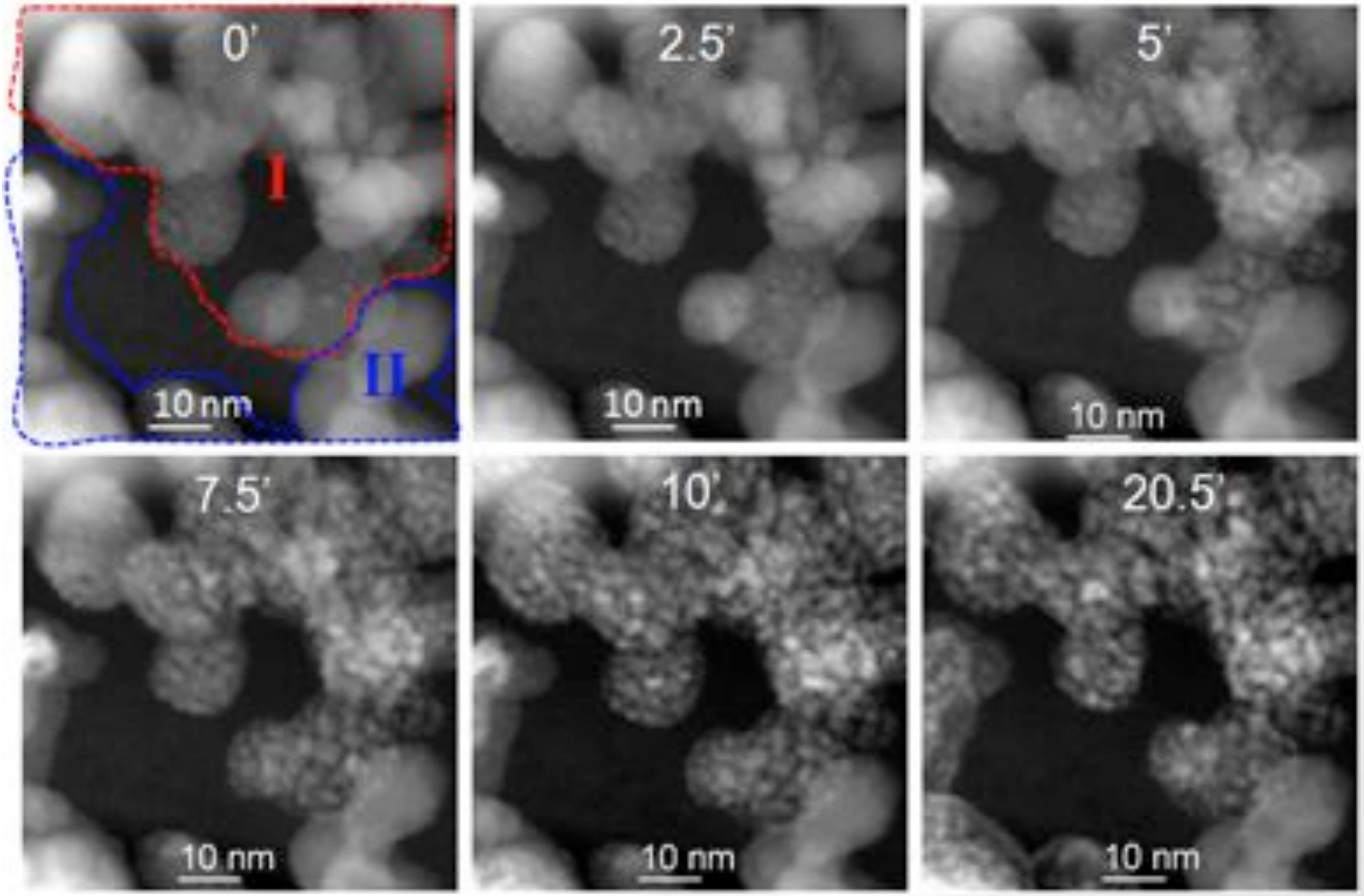
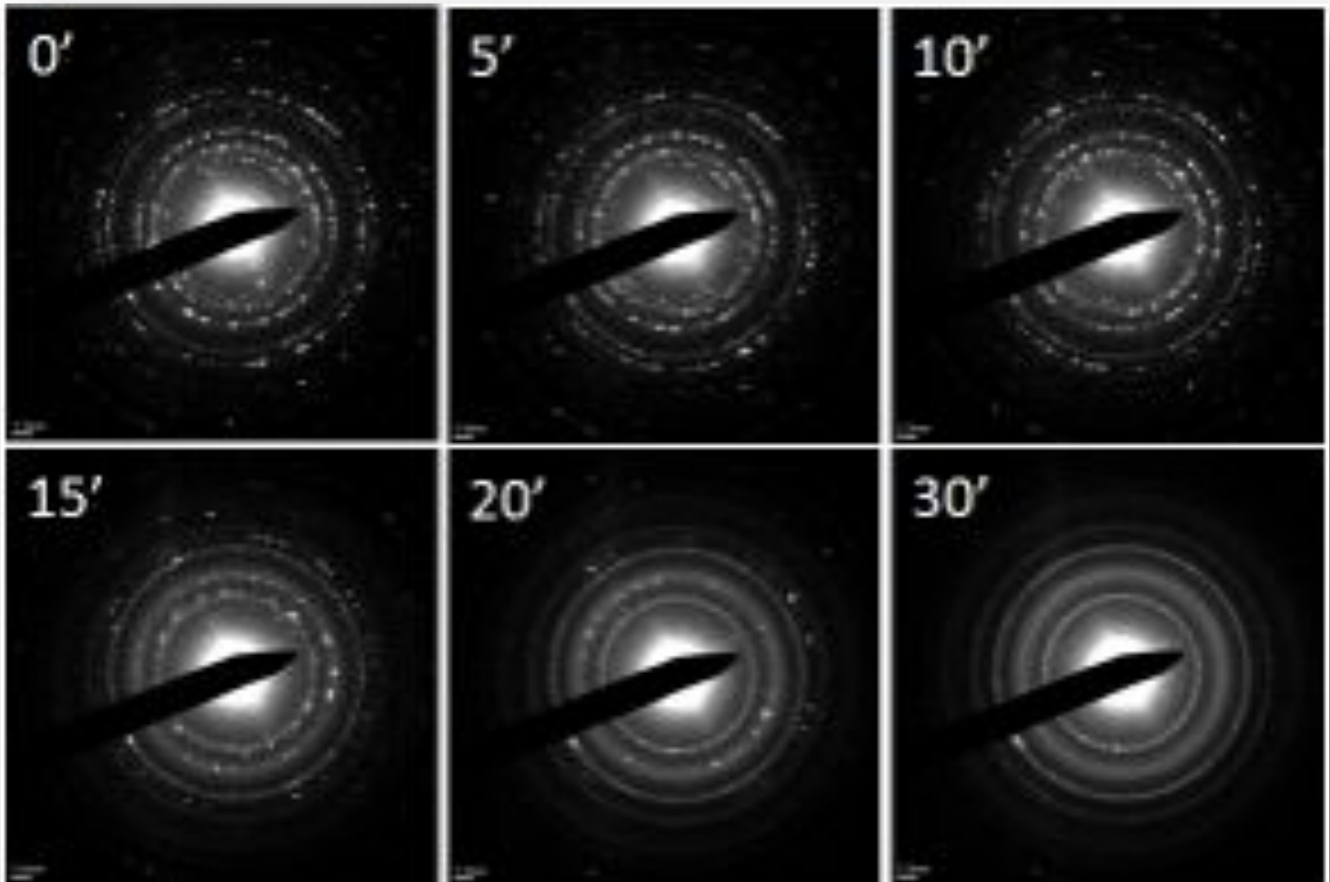
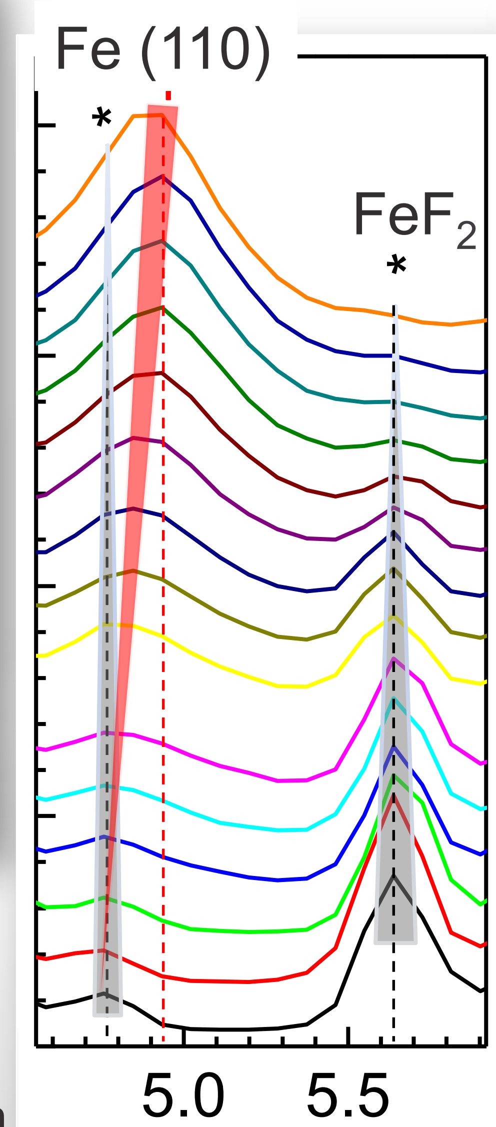
Conversion of a cluster of FeF_2 particles



- Conversion reaction starts from surface (fast Li surface diffusion) and moves inward (slower bulk conversion – size dependent)
- Active and "dead" FeF_2 particles are evident

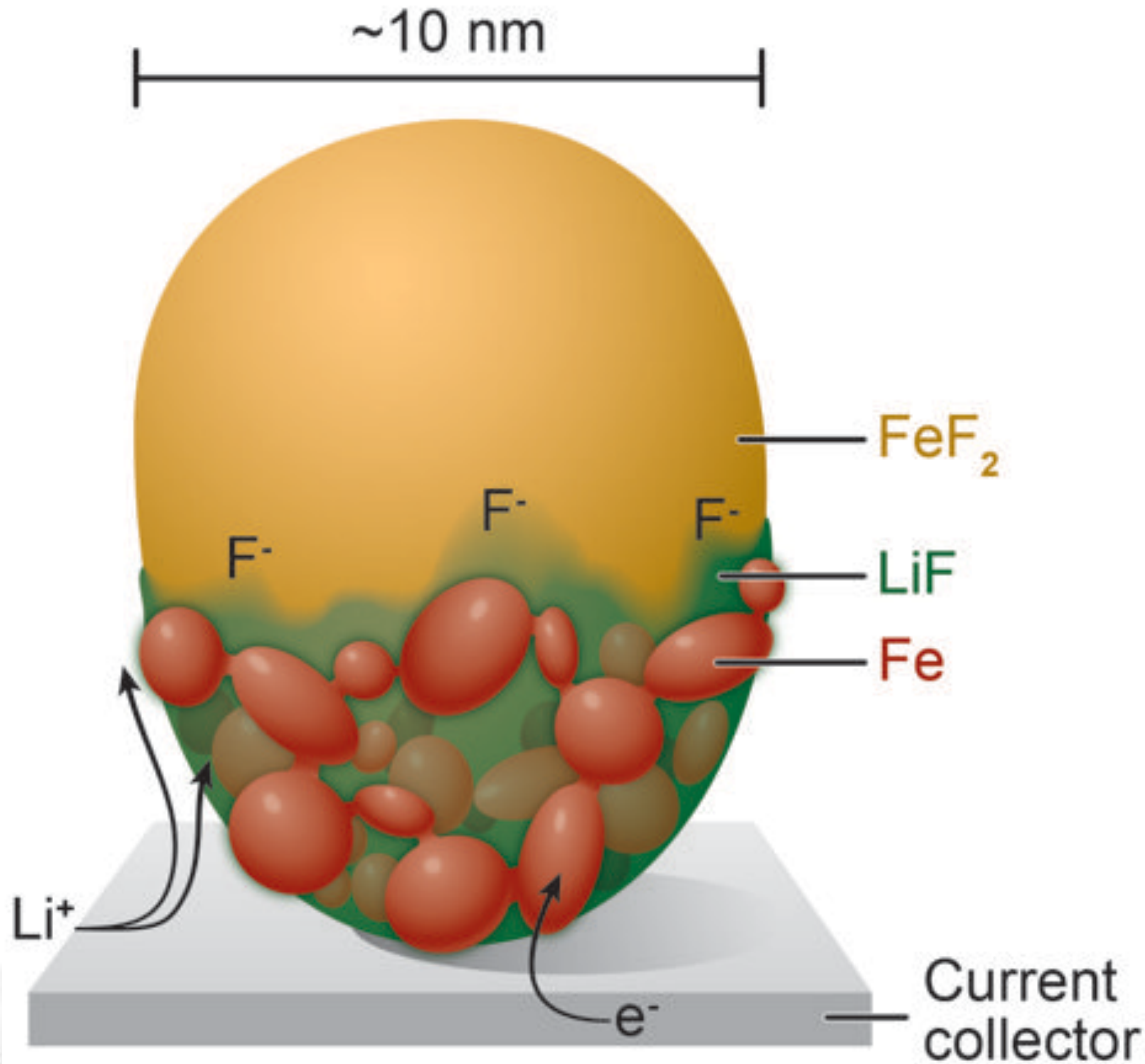
In situ electron diffraction of FeF_2 Conversion





- Time-lapse diffraction patterns used to track structural evolution of FeF_2.
- FeF_2 (210) slowly fades while Fe peaks shift to higher angles indicating Fe lattice decreases during conversion.

Conversion process in FeF_2



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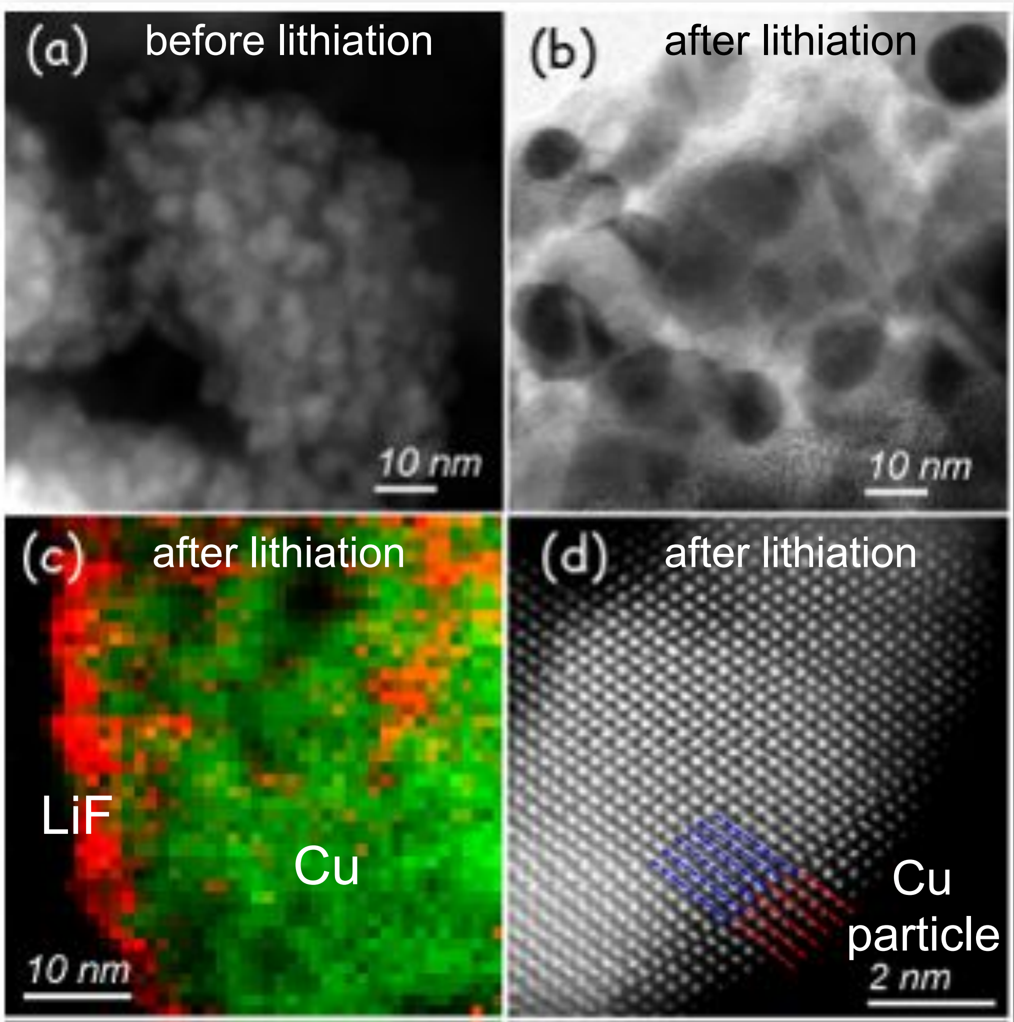
What about other conversion reactions?

CuF_2 conversion occurs ~3.5V: $CuF_2 + 2Li^+ + 2e^- \rightarrow 2LiF + Cu$

- very high energy density 1400 Wh/kg, but **irreversible**



Converted CuF_2: Cu and LiF spatially separated and do not form interconnected network - possibly due to high Cu diffusivity

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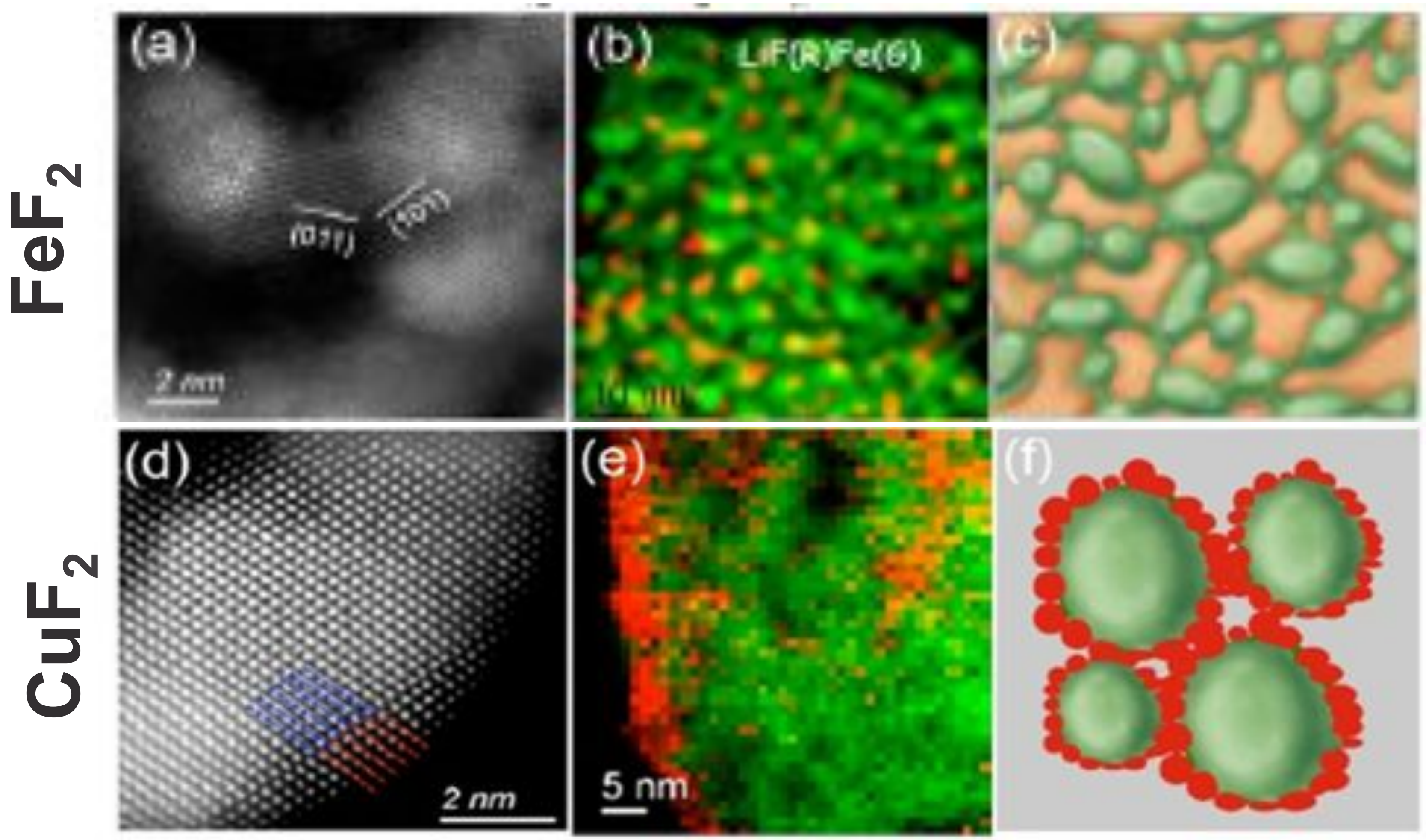
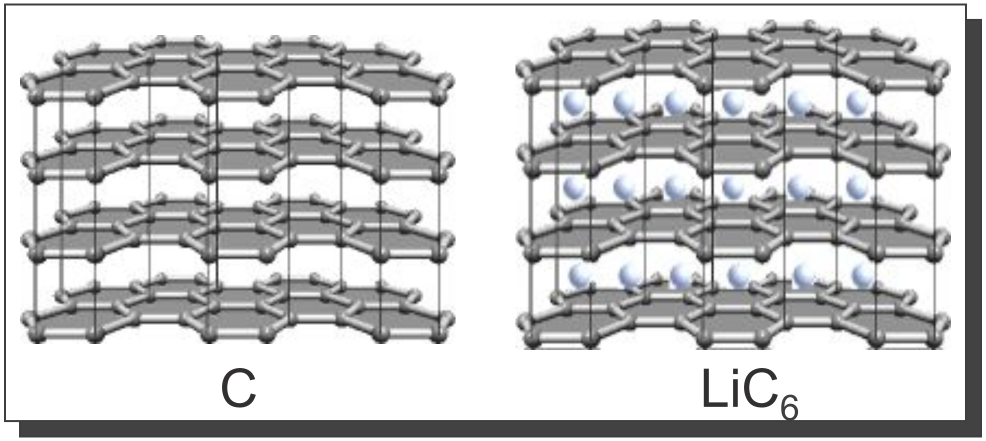
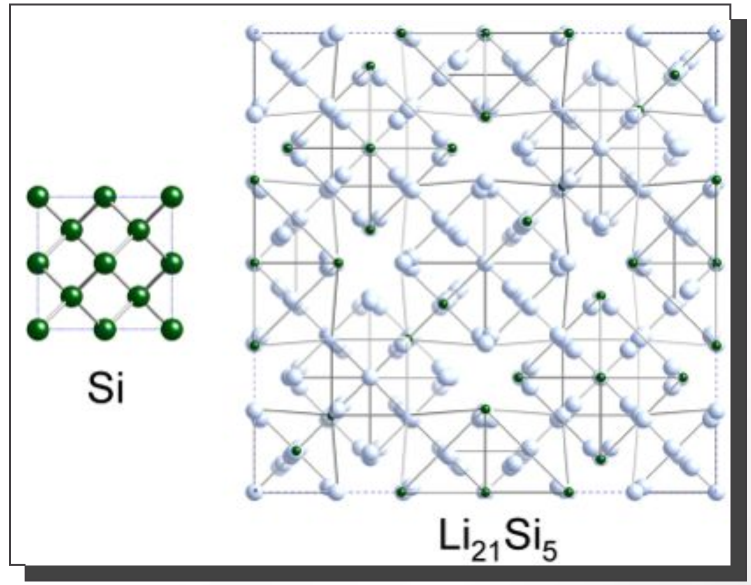
How do cations affect morphology & phase distributions?



- **Can we make a CuF_2 system behave more like FeF_2?**
- Preliminary tests performed by ball milling FeF_2 with CuF_2 in an attempt to prepare nanoscale mixture or possibly solid solution

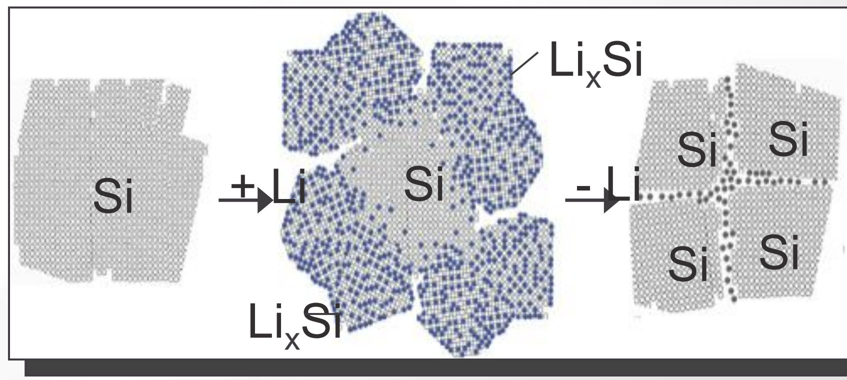
Anodes: intercalation and alloying



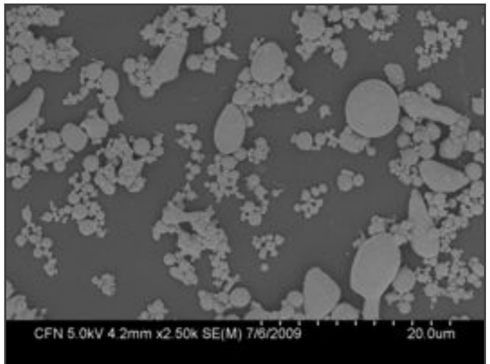


Minimize decrepitation and improve cycle life using nano-scale anodes

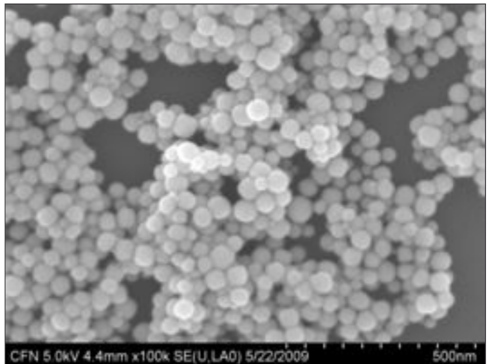
- Short diffusion lengths: $t \propto x^2$
- Fewer heterogeneities and strain gradients mean less decrepitation
- High concentration of grain boundaries and surfaces (low diffusion barrier)
- Nano-dimensions confine elementary defects: no dislocations; no cracking



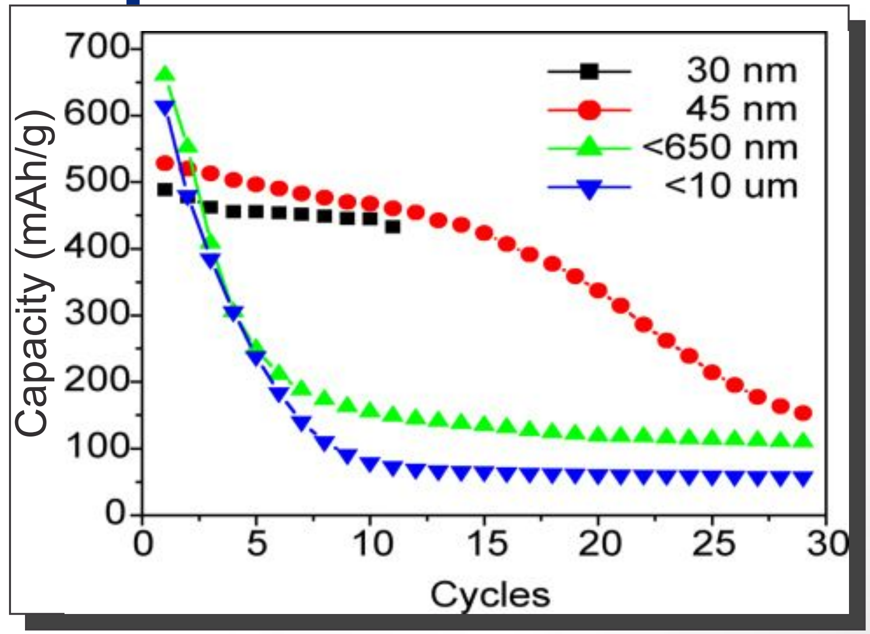
Cycling Tin-based nanoparticles

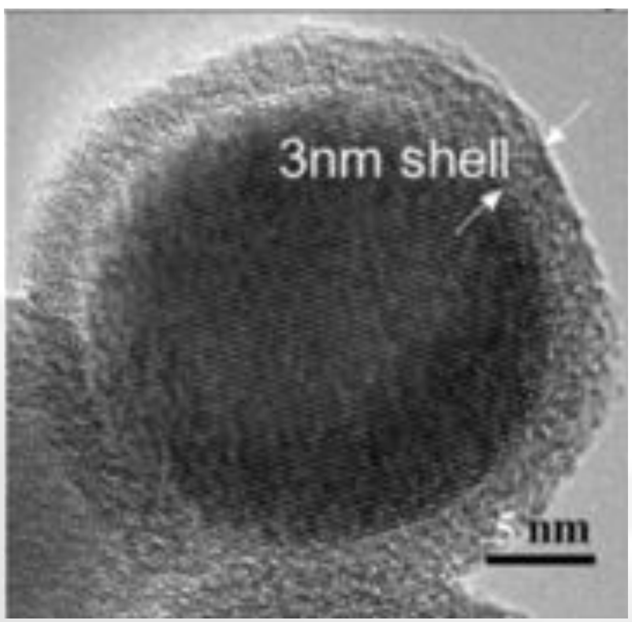


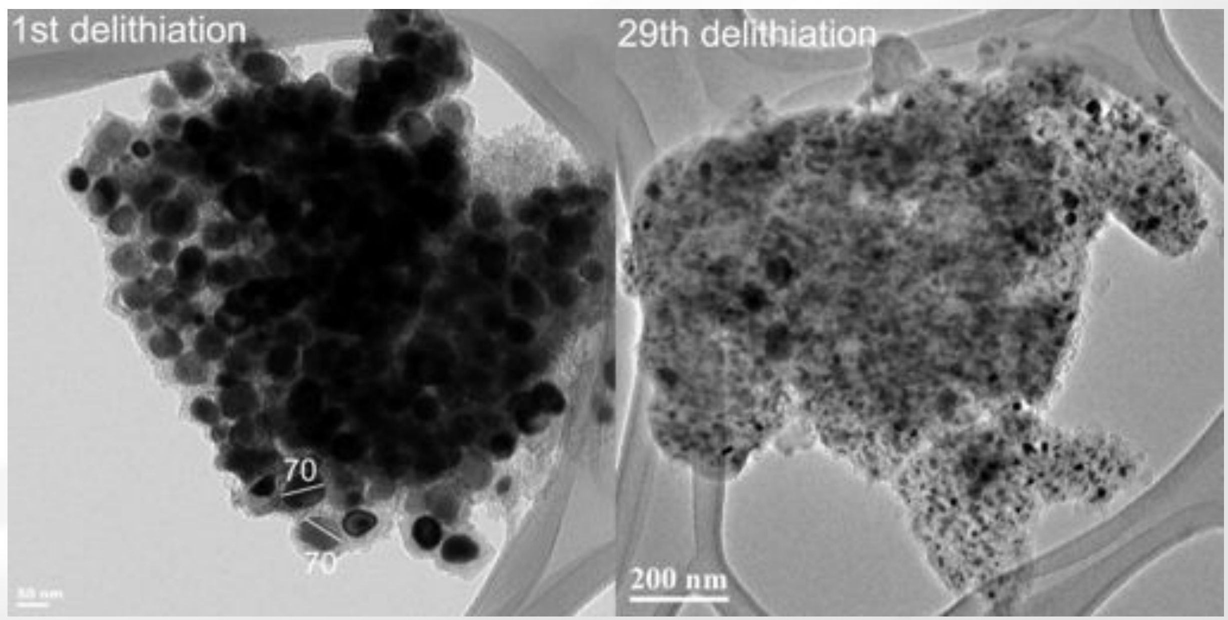
Tin <10 μm (Alfa)



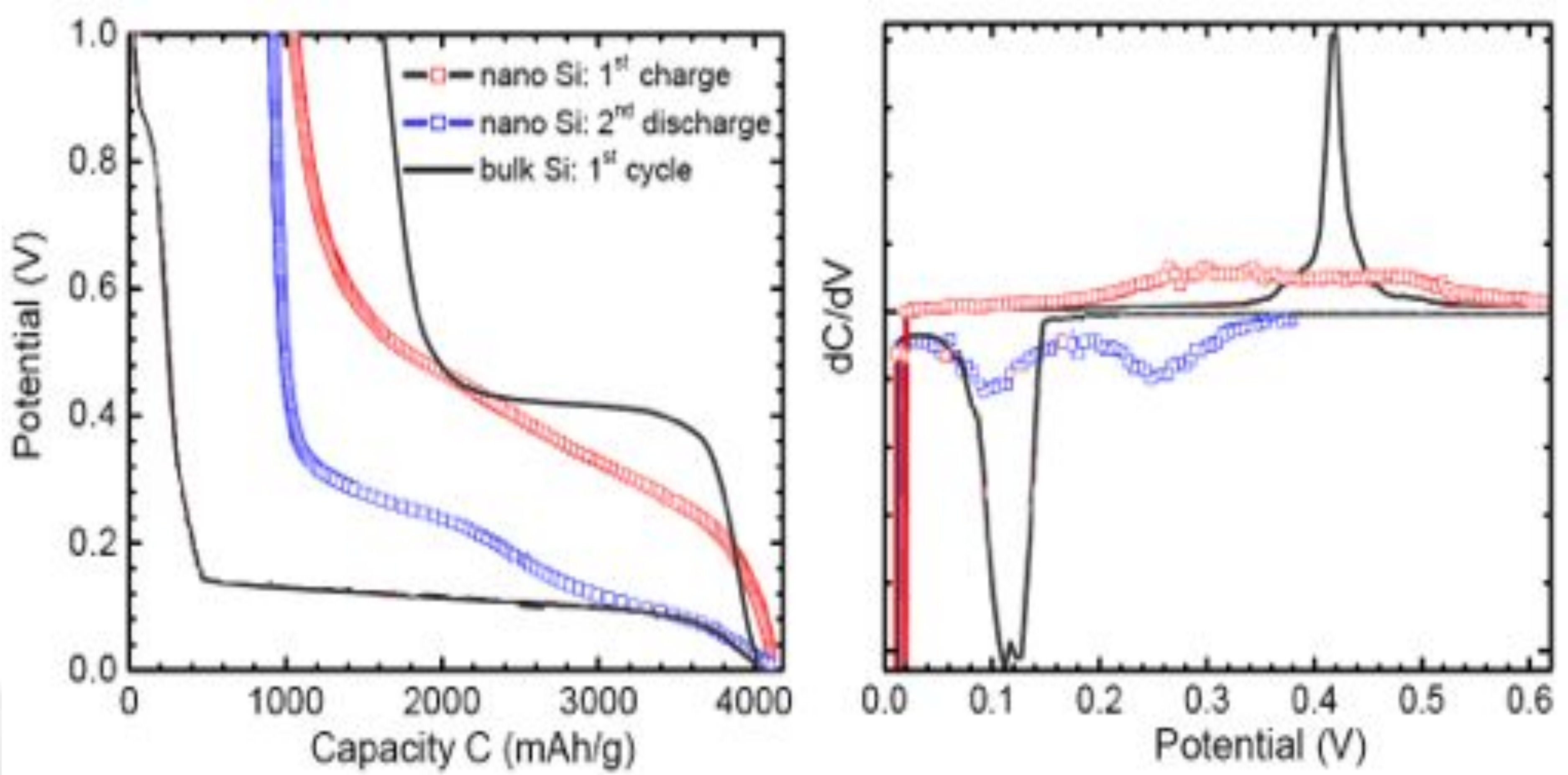
Tin 45±11nm



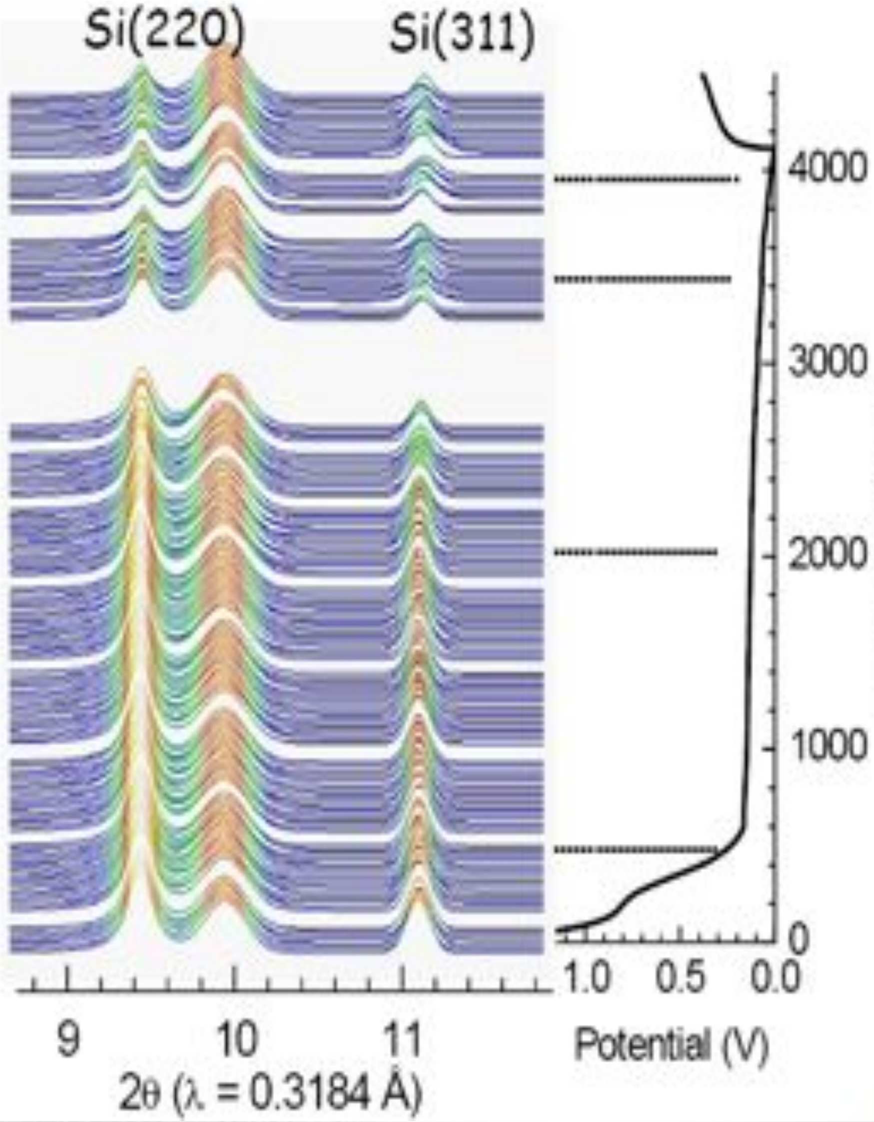


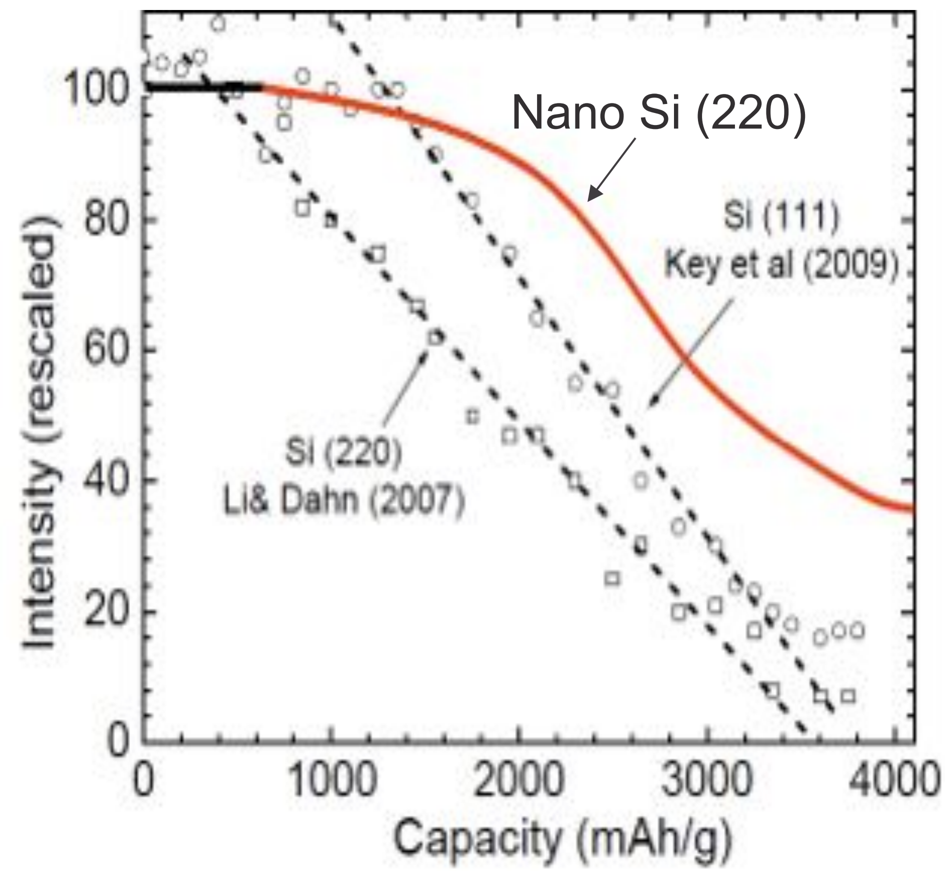


Si voltage profile: nano vs. bulk



in-situ XRD nano-scale Li_xSi





Bulk Si: intensity drops linearly

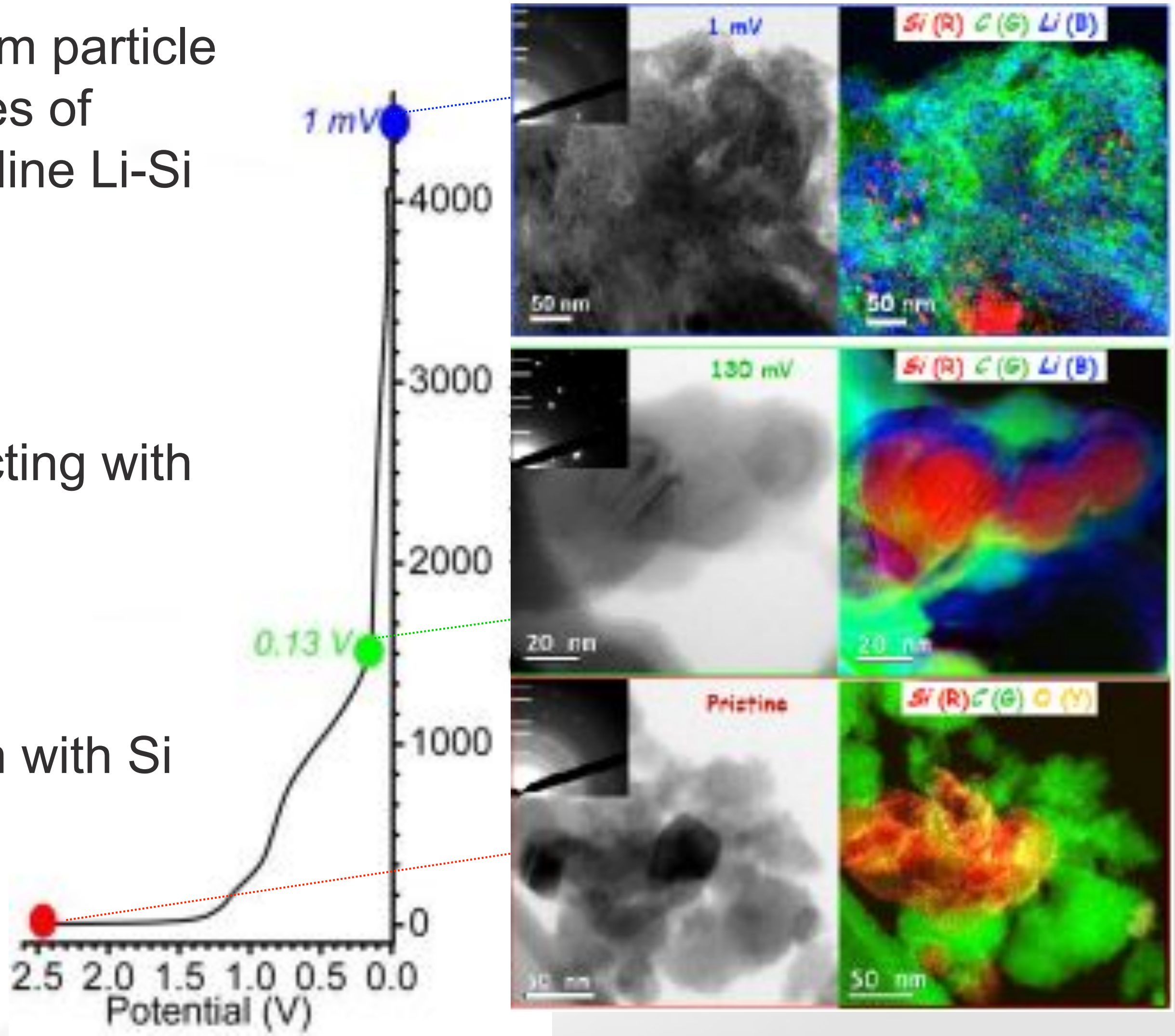
Nano Si: intensity is initially constant then drops quickly

Elemental mapping of Li-Si

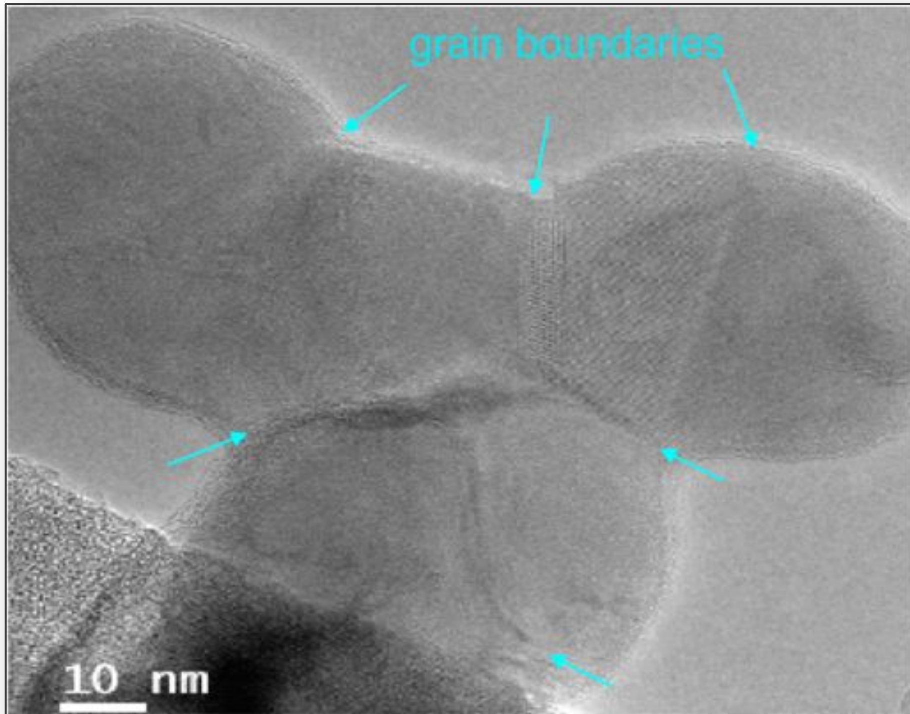
Below 50 mV: Large ~50 nm particle break up into ~5 nm particles of amorphous Li-Si; no crystalline Li-Si is formed (unlike bulk Si)

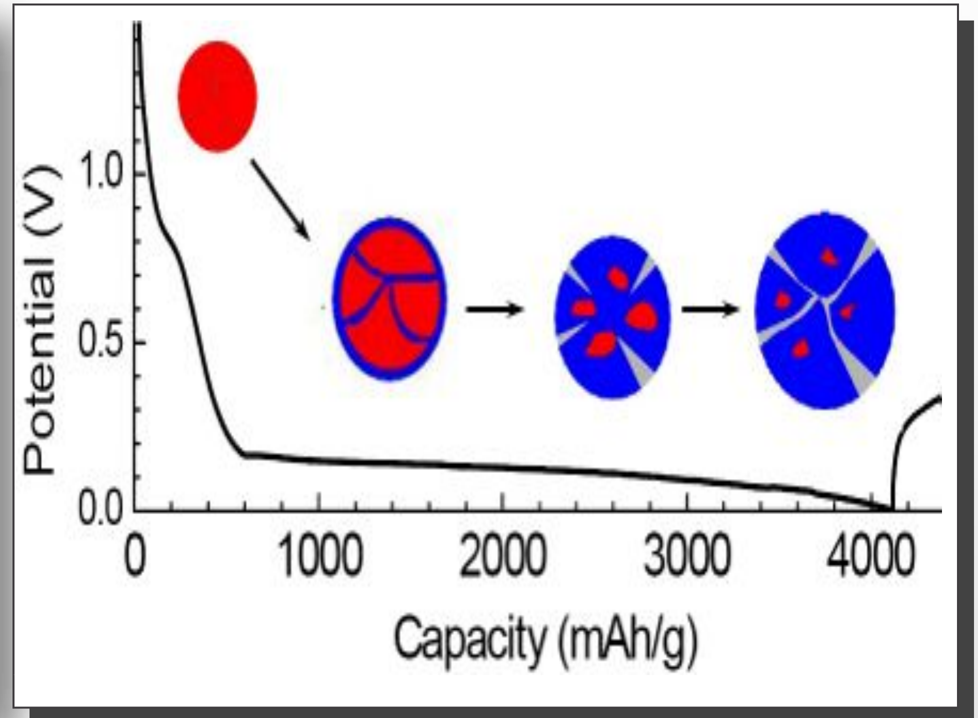
130 - 50 mV: Li begins reacting with Si from the surface inward

Above 130 mV: no reaction with Si



Lithiation mechanism in nano-scale silicon



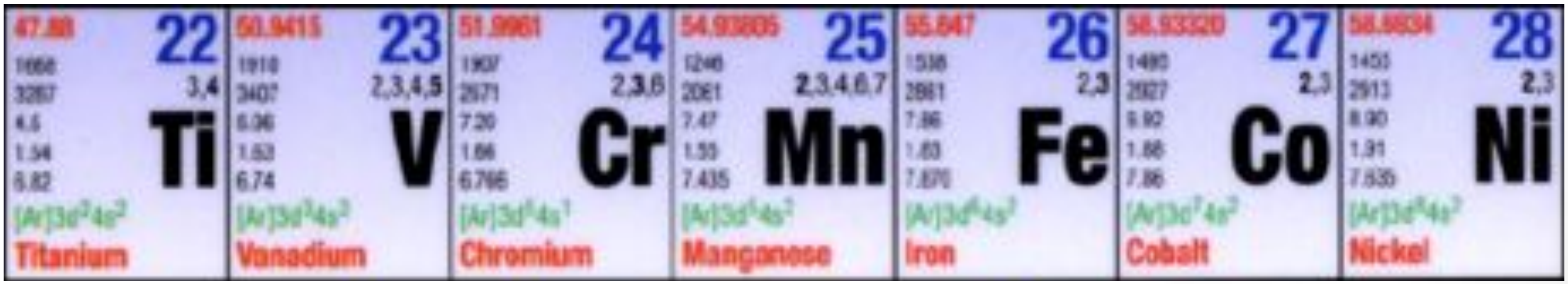


- TEM-EELS and *in-situ* XRD suggest lithiation of surfaces and grain boundaries occurs first followed by bulk lithiation.

- The lithiation mechanism is more obvious due to abundance of surfaces and grain boundaries in nano-scale silicon.

High Capacity Cathodes: Breaking the one-electron barrier

All of the most common lithium cathodes ($LiMO_2$, $LiMPO_4$) use one electron per metal (e.g. Co^{3+}/Co^{4+})

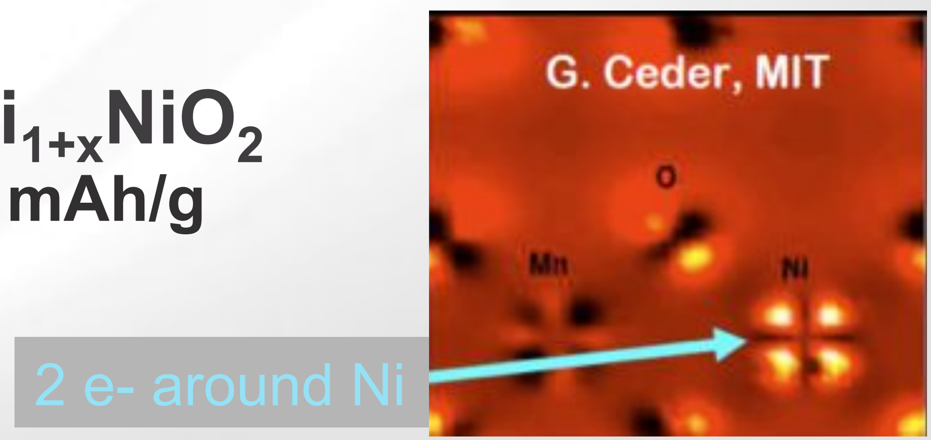


In this case the theoretical capacity is limited to ~300 mAh/g, but practical limit is probably 220-250mAh/g

Much higher capacities are possible in materials that will undergo multiple redox steps:

$$Li^{+} + 2e^{-} + Li_xNiO_2 \rightarrow Li_{1+x}NiO_2$$

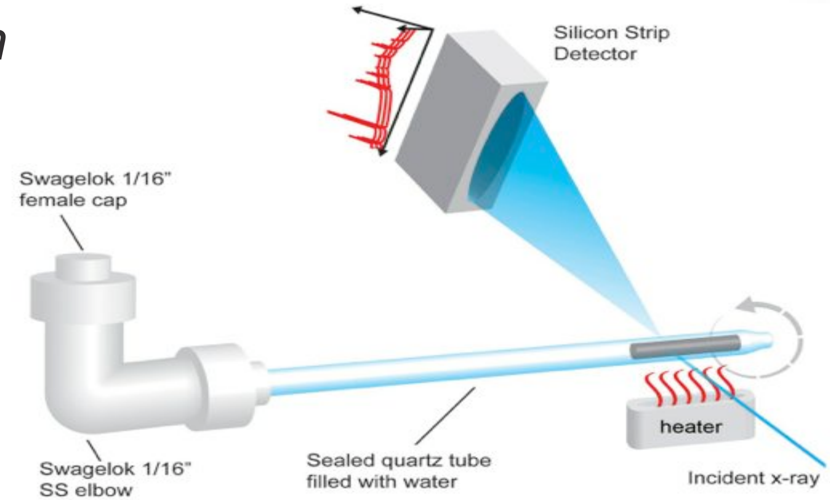
Theoretical capacity: **600 mAh/g**

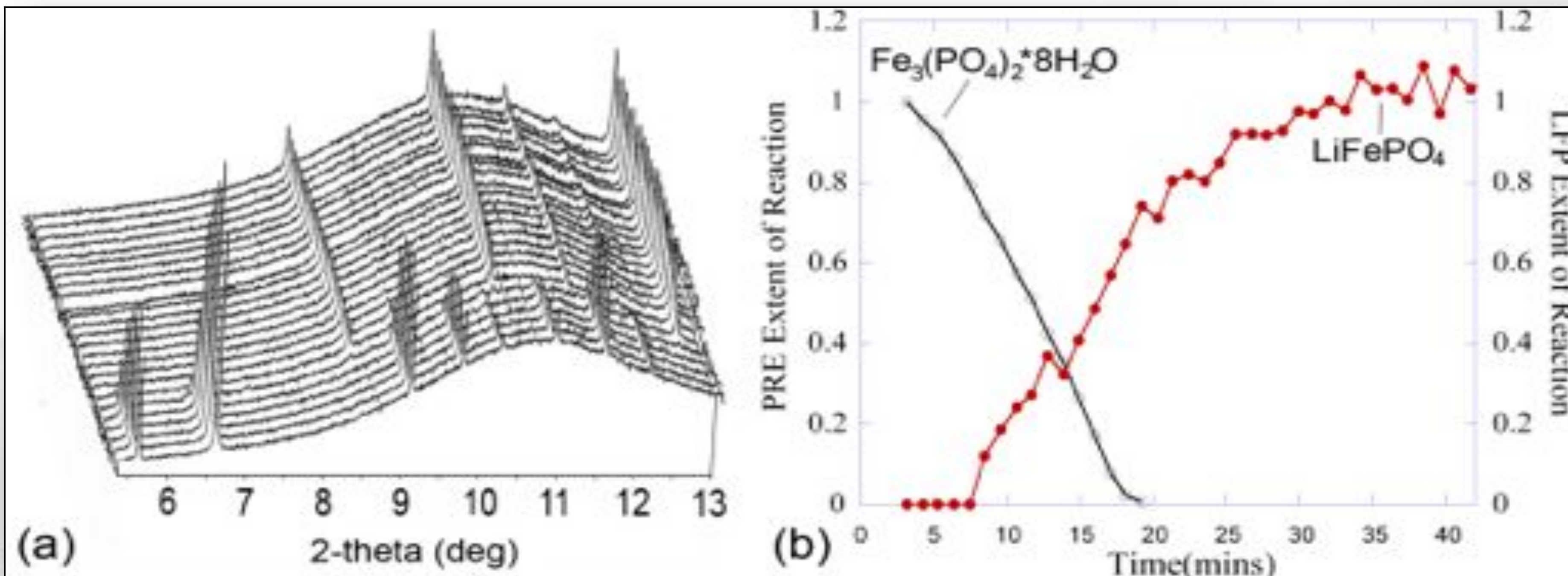


In-situ Synthesis of Lithium Electrodes

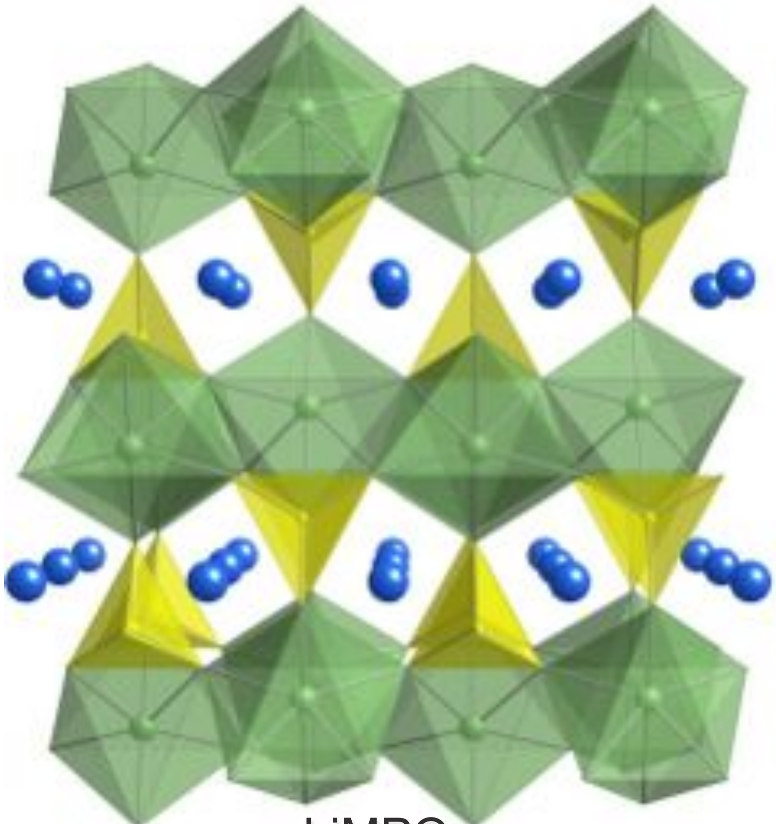
More recently, we have been developing *in situ* synthesis reactors to investigate the complete synthesis reaction

- Identify intermediate phases
- Quantify reaction kinetics
- Track defects
- Ultimately, reactor will be used to synthesize new Li electrode materials

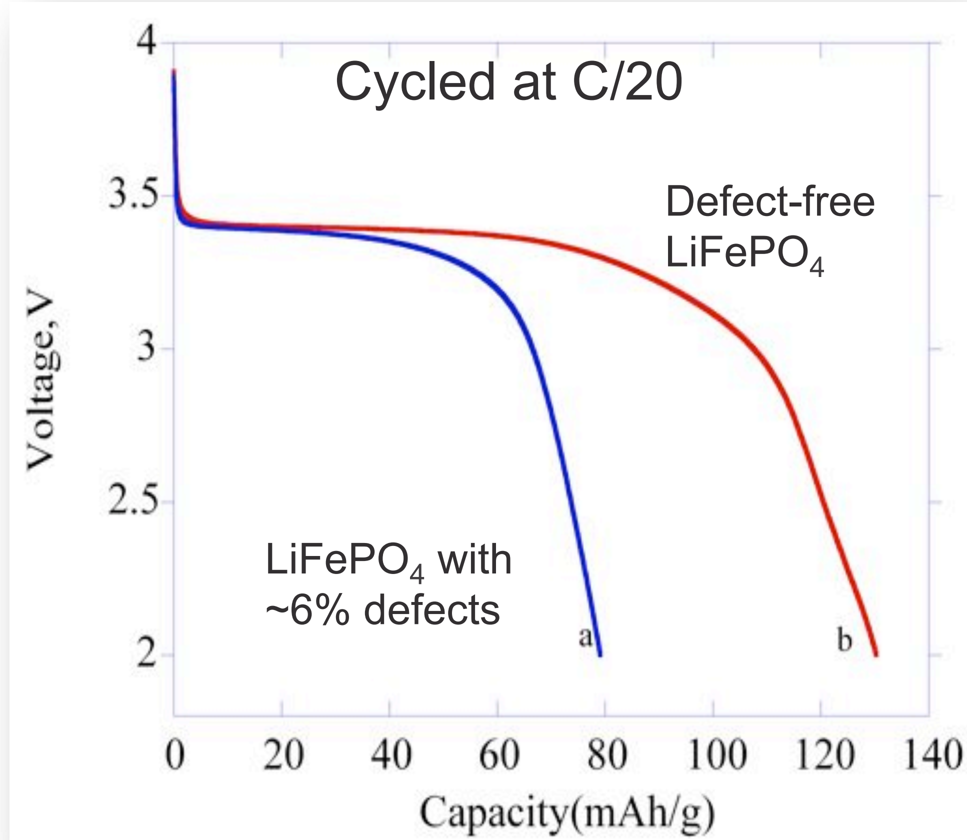




$LiMPO_4$ (Olivine) and antisite defects

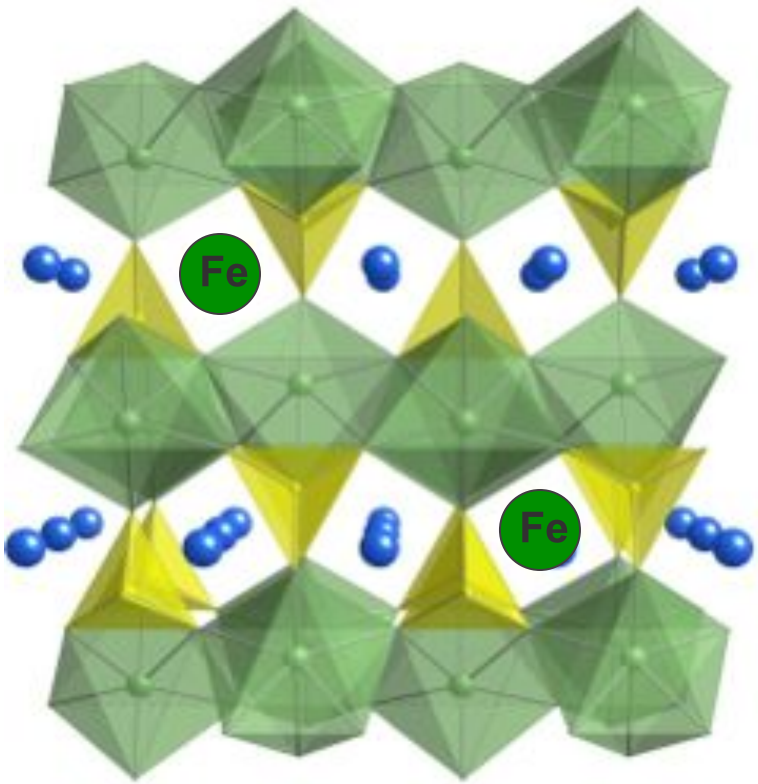


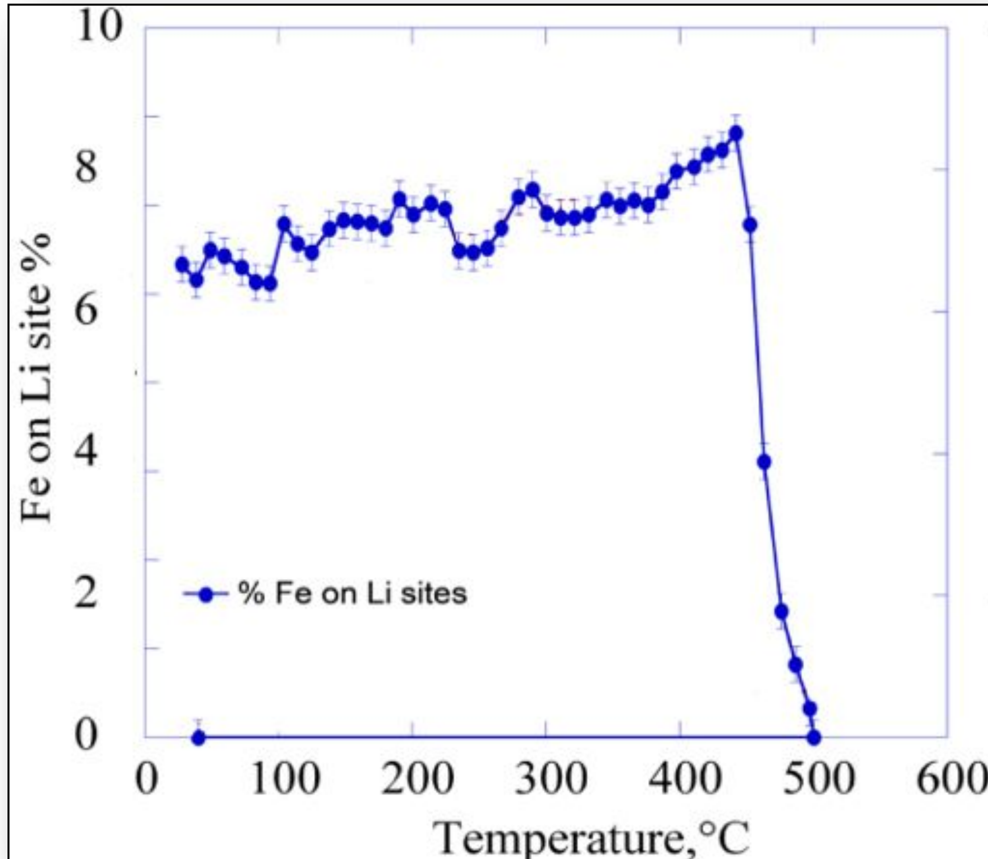
$LiMPO_4$



- Olivine cathodes ($LiMPO_4$) are more stable than layered metal oxides, but Li motion occurs in 1D. Antisite defects (Fe on Li site) limit Li transport
- Reducing anti-site defects improves performance

Characterizing antisite defects in $LiFePO_4$



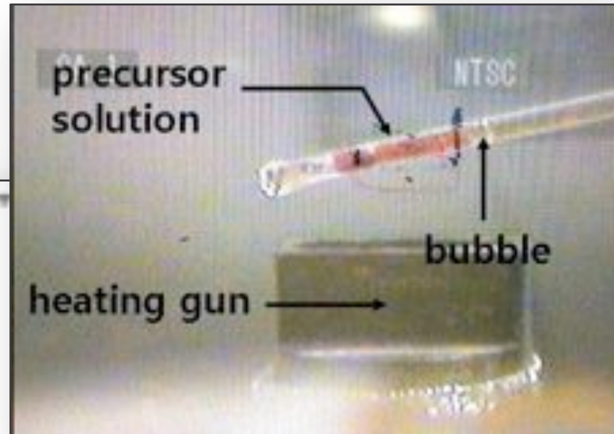


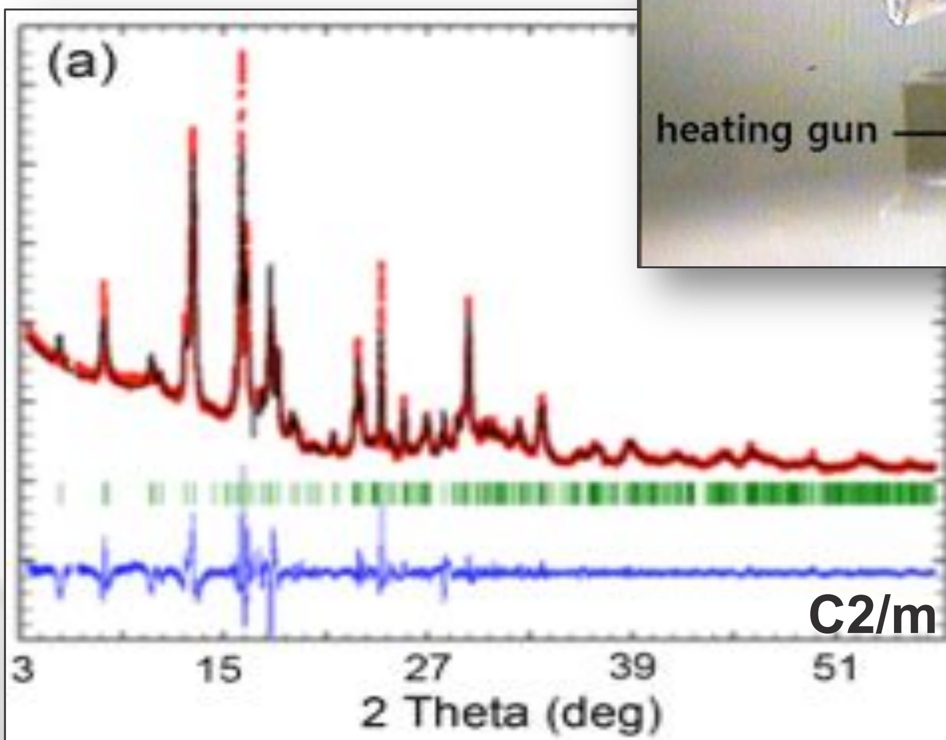
Little is known about anti-site defect concentration and effect of synthesis temperature - at what temperature do the defects disappear?

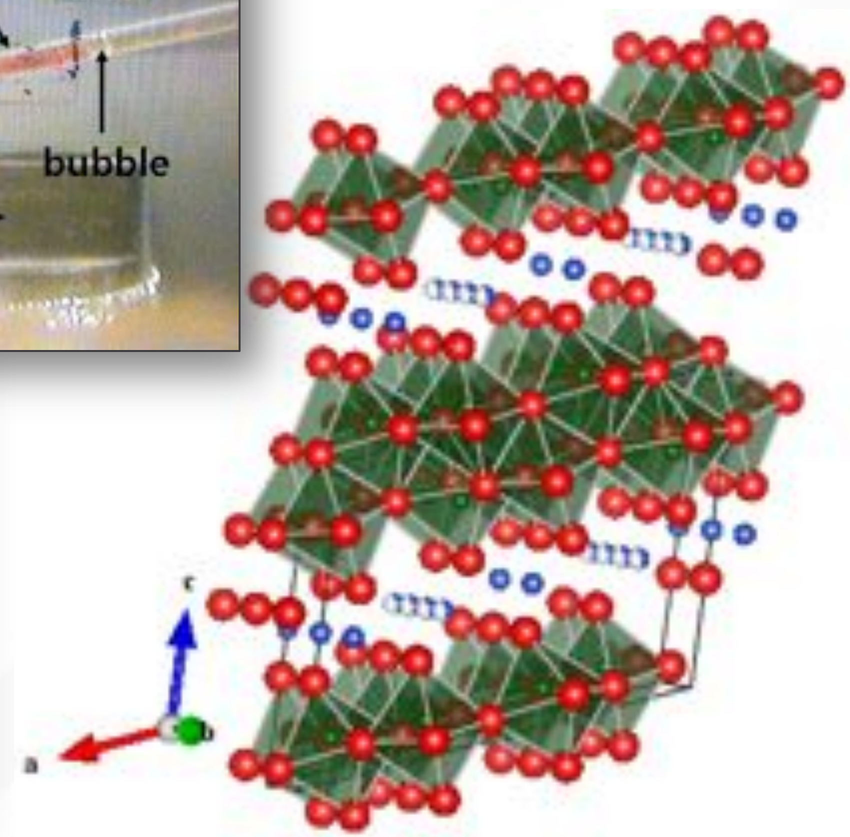
time-resolved XRD indicate that anti-site defects are eliminated above 450°C

Hydrothermal Synthesis of ε-$Cu_{0.95}V_2O_5$

$Cu(NO_3)_2 \cdot 3H_2O + V_2O_5$ + acetophenone → $Cu_{0.95}V_2O_5$ + *byproducts*
(*reducing agent*)







Input for SRX team

- **What experiment would like to do?**
  - Map phase distributions (structural and/or chemical information) in battery electrodes.
- **What should the sample environment look like?**
  - Ex situ samples are powders coated on Al foil. In situ samples are typically coin cells with Kapton window.
- **Which elements with absorption edges in the energy range covered by SRX (4.65keV to 22keV) are of interest?**
  - 3d transition metals (Ti - Cu)
- **What is more important - high spatial resolution (<100nm) or a large sample area (mm w/ sub-μm resolution)?**
  - Both would be useful, but large sample area is probably more important since we can get high resolution with TEM if need be.
- **Which of the techniques available at the SRX beamline would be absolutely crucial for your experiment?**
  - X-ray absorption imaging
  - X-ray spectromicroscopy
  - X-ray microdiffraction

In situ studies??

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NY BES+ New York Battery and Energy Storage Technology Consortium