In-situ Solvothermal Synthesis of Novel High-Capacity Cathodes

Feng Wang
Brookhaven National Laboratory

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ES183

Overview

Timeline

- Project start date: April, 2012
- Project end date: April, 2016
- Percent complete: 25%

Budget

- Total project funding
  - DOE 100%
- Funding received in FY12
  $ 304K
- Funding for FY13
  $350 K

Barriers

- Low energy density
- Cost
- Cycle life

Partners

- Interactions/collaborations
  - **HRL Laboratory**
  - Stony Brook University
  - Brookhaven National Lab
  - Lawrence Berkeley National Lab
  - University of Texas at Austin
  - SUNY at Binghamton
  - Cambridge University
- Project lead - Brookhaven Nat. Lab.

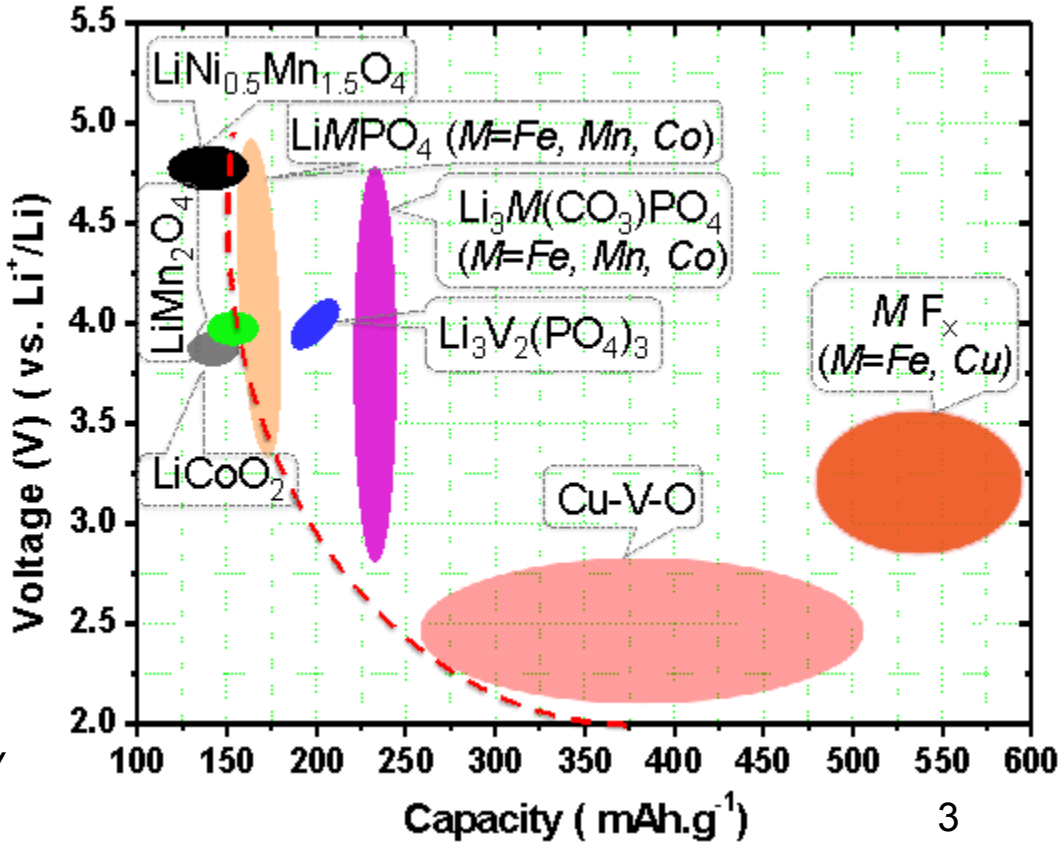
Objectives

Develop *low-cost* cathode materials with *energy density >660 Wh/kg* and electrochemical properties (cycle life, power density, safety) consistent with USABC goals.

Initial effort (FY12/13) was focused on high-energy Cu-V-O cathodes*:*

- Synthesize $Cu_{0.95}V_2O_5$ and other Cu-V-O compounds
- Optimize synthesis using *in-situ* methods
- Characterize structural and electrochemical properties
- Identify mechanisms that limit cycling stability via *in-operando* studies

(**Some cathodes with target energy density are given on the right side of the plot*)



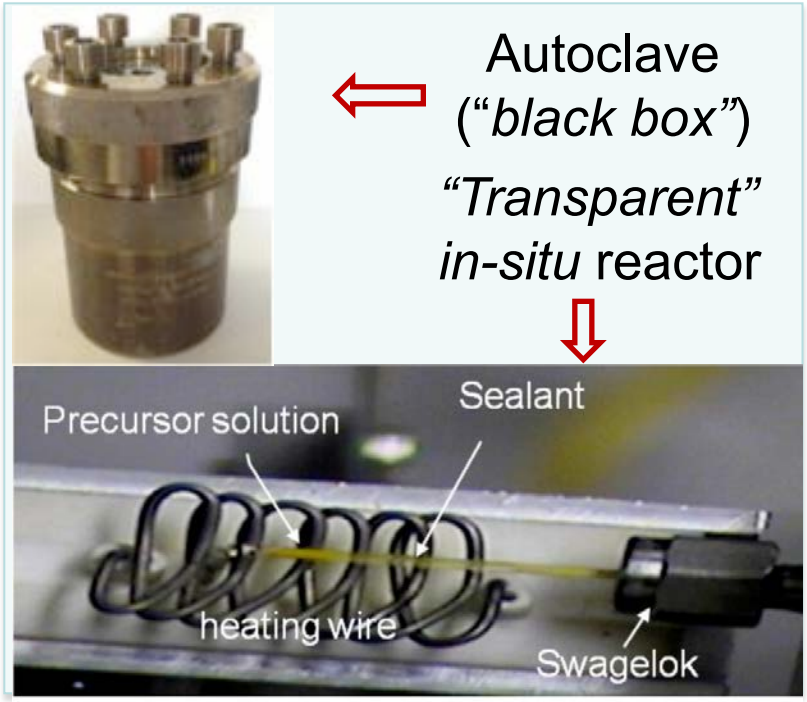
Milestones

- Complete design and construction of second-generation capillary reactor capable of accommodating higher pressures and temperatures. (April 12') *complete*
- Develop a procedure for the synthesis of $Cu_{0.95}V_2O_5$. (Sep. 12') *complete*
- Complete preliminary characterization of synthesis reaction(s) of $Cu_{0.95}V_2O_5$ using the *in situ* capillary reactor. (Sep. 12') *complete*
- Determine optimal procedure for $Cu_{0.95}V_2O_5$. synthesis (Jan. 13') *complete*
- Identify mechanism(s) responsible for poor cycling in $Cu_{0.95}V_2O_5$ and identify a pathway for reducing capacity fade with cycling. (Mar. 13') *on-schedule*

Approach

In-situ synthesis Controlled synthesis of phase-pure materials of desirable stoichiometry, morphology

- ***time-resolved* XRD**
  - direct quantitative identification of structure/phases during synthesis
- **specialized *in-situ* reactors**
  - wide-range temperature/pressure
  - wide applicability: hydrothermal, solvothermal, ion exchange, and solid-state reactions…

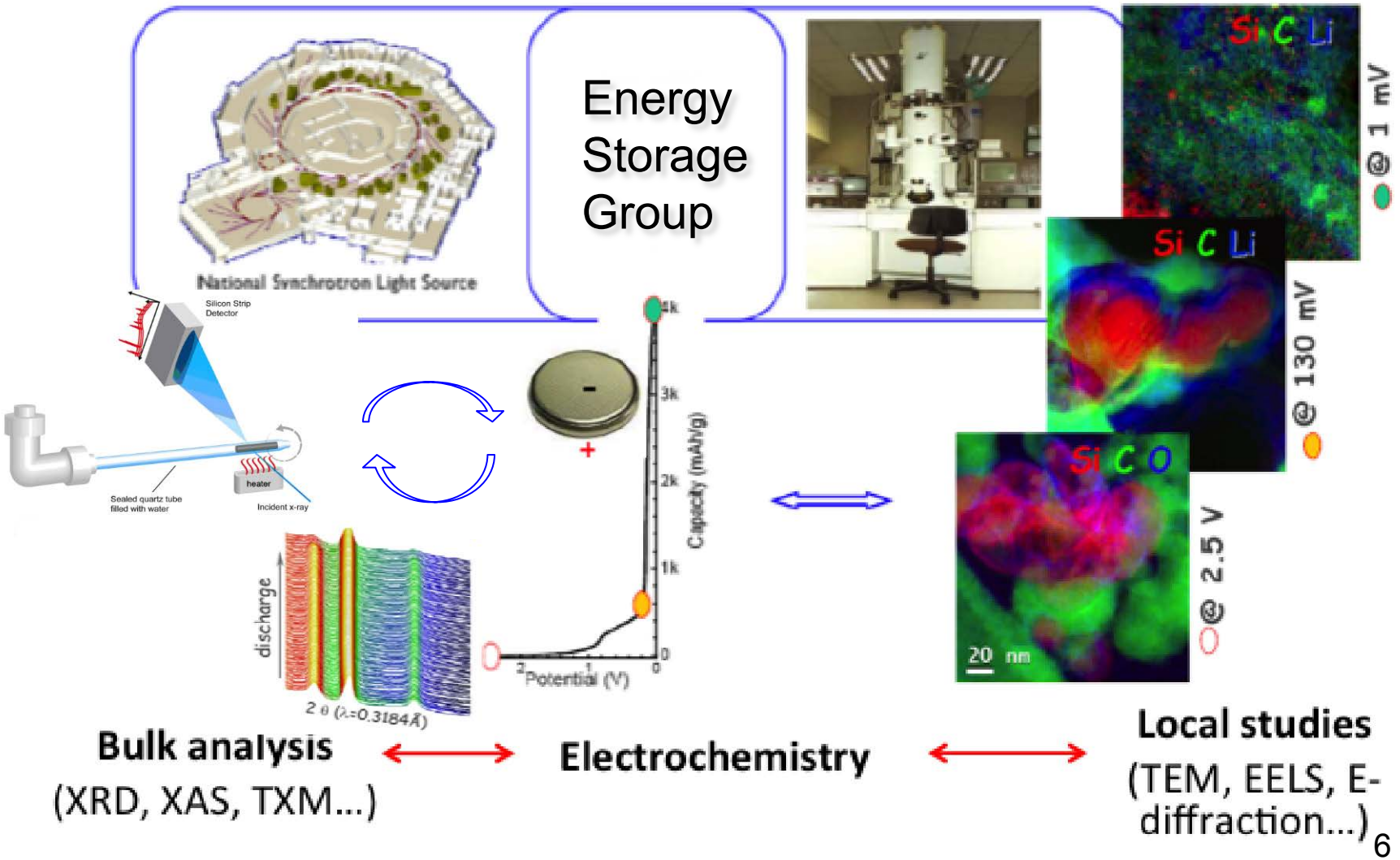


Technique development Explore reaction pathways and structural evolution of intermediates in real working conditions

- develop ability to 'dial in' desired phases and material properties;
- optimize synthesis conditions;
- provide insight for structure prediction (*potential synergy with theory)*.

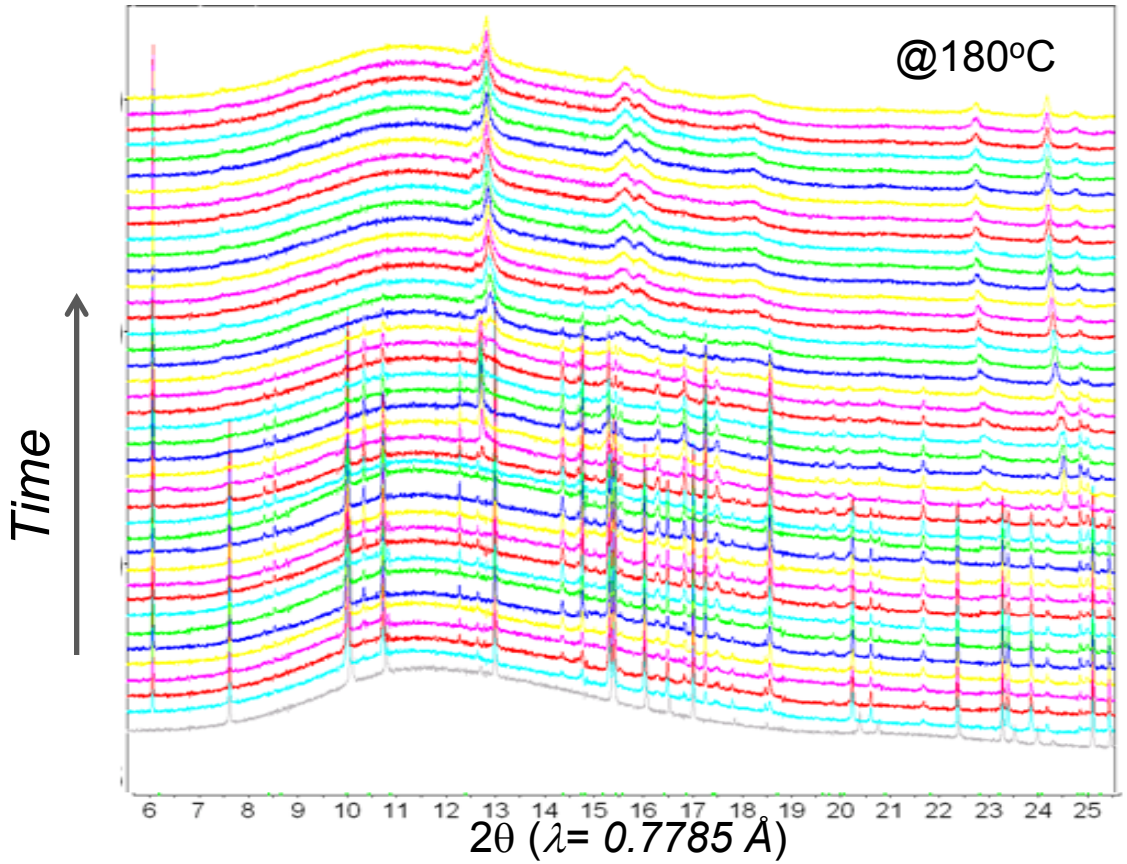
Approach (*cont'd*)

- *In-situ* synthesis, synergy with diagnostics using *on-site* resources and *in-house* developed capabilities

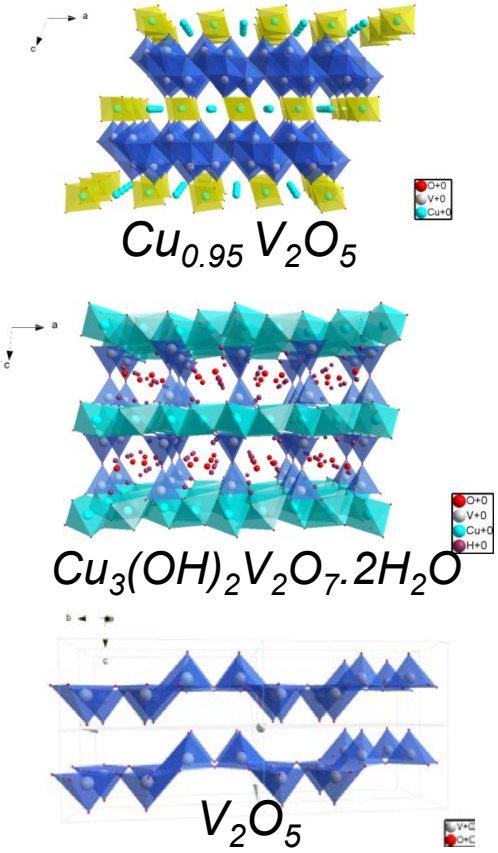


Optimization of synthesis via *in-situ* method

$V_2O_5 + Cu(NO_3)_2 \cdot 3H_2O + reducing\text{-}agent \rightarrow Cu_xV_2O_5$



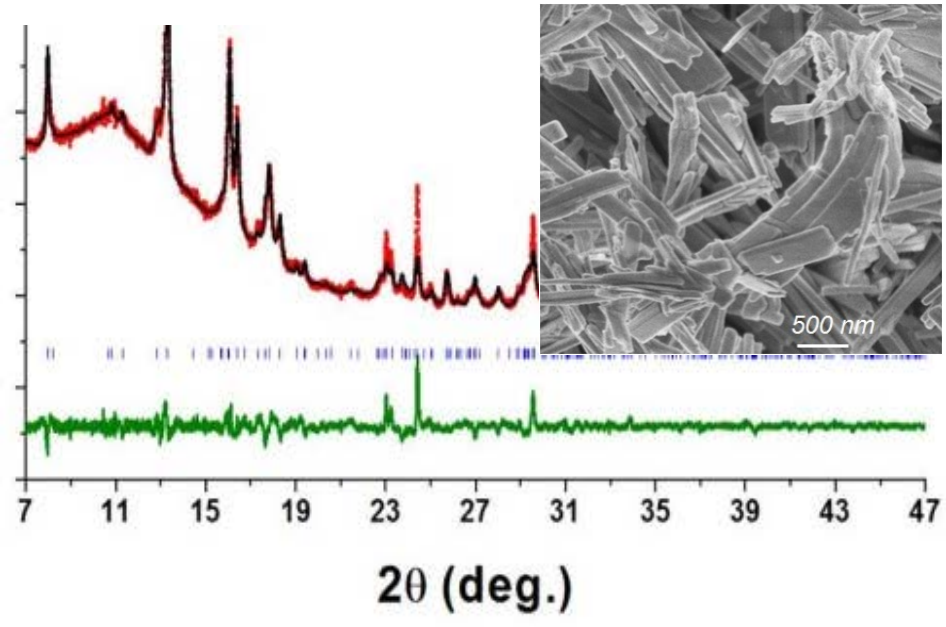
precursor intermediate final



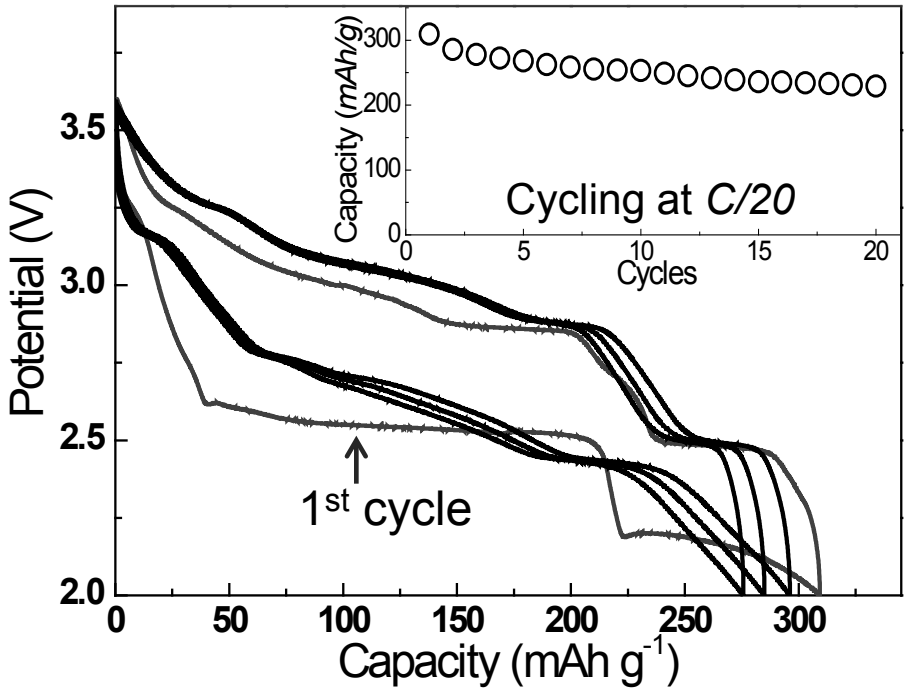
- Determined reaction path and intermediate phases:
  - decoded synthesis reaction mechanisms;
  - developed optimal procedures for synthesis of desired phases.*

(**See backup slides for hydrothermal synthesis of a different phase*)

Synthesis and characterization of ε-$Cu_{0.95}V_2O_5$



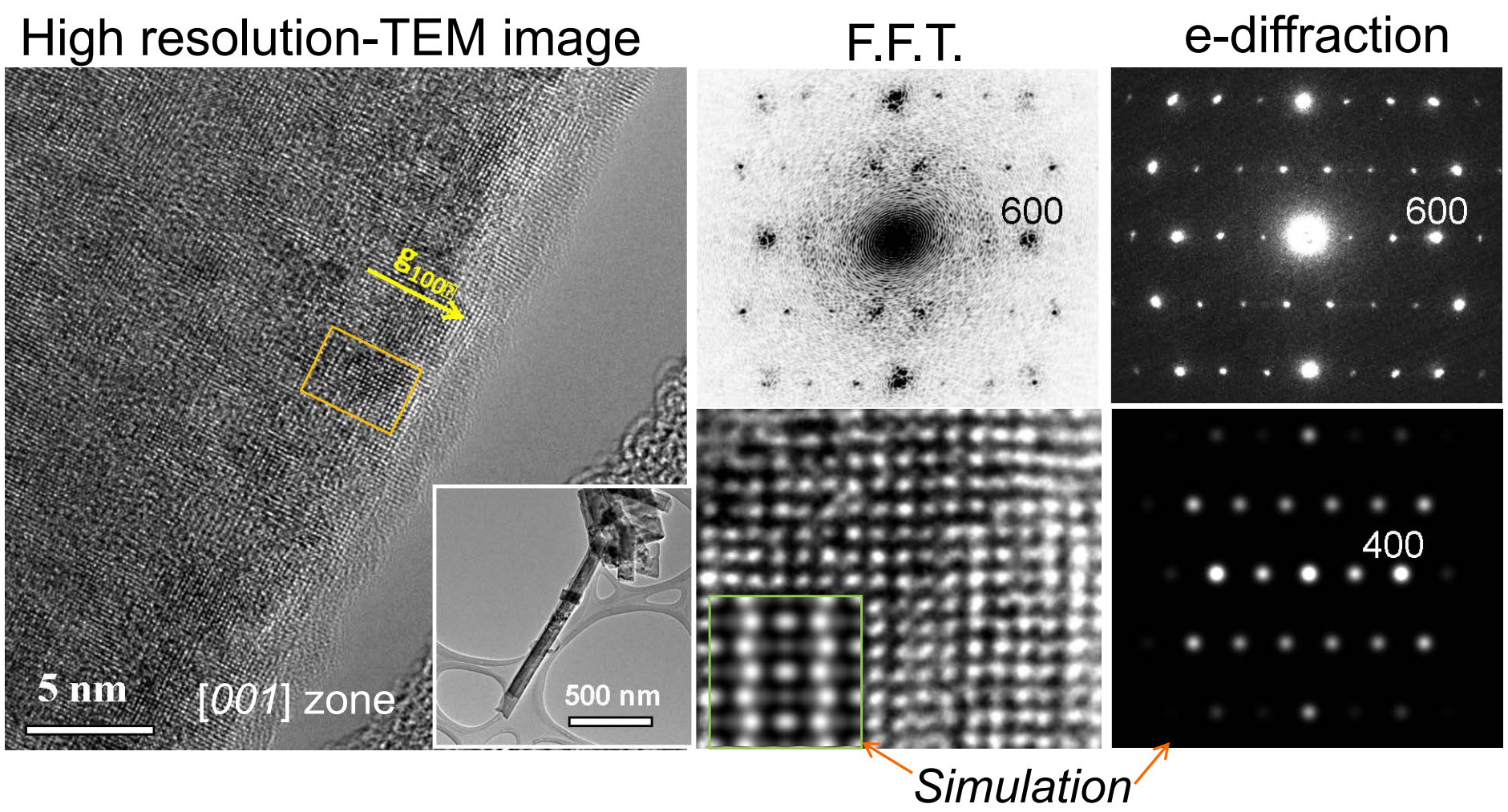
2θ (λ= 0.7785Å)



- Determined structure of ε-$Cu_{0.95}V_2O_5$ (ε-CVO)
  - high degree of purity and crystallinity
  - rod-like morphology: *1-2 μm* long, *~100 nm* thick
- Demonstrated excellent electrochemical performance

- high capacity (~300 mAh/g)
- reasonable cycling stability (between 3.6 - 2 V)
- *but abrupt* change of the voltage profile after 1st cycle

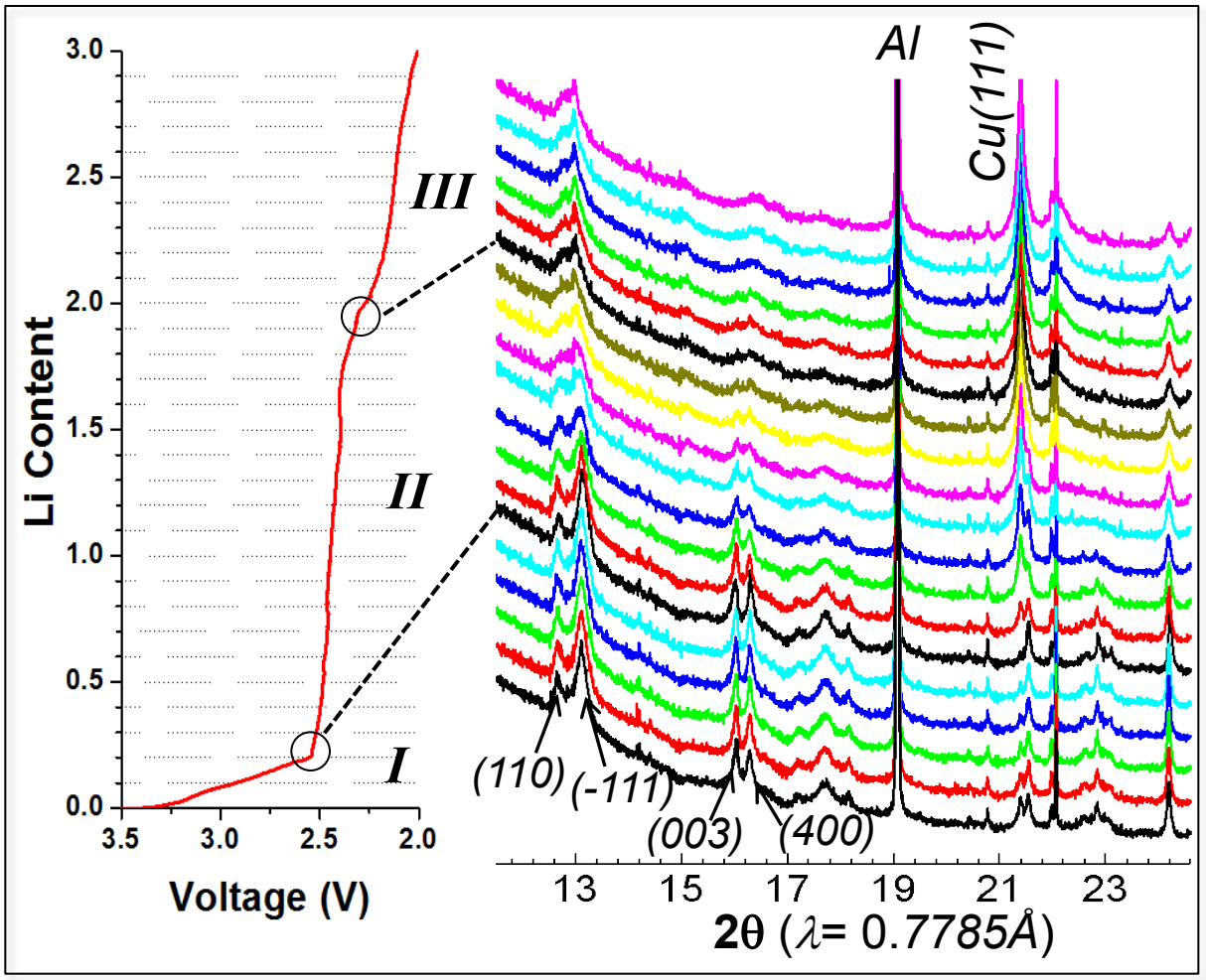
Local structural ordering of ε-$Cu_{0.95}V_2O_5$

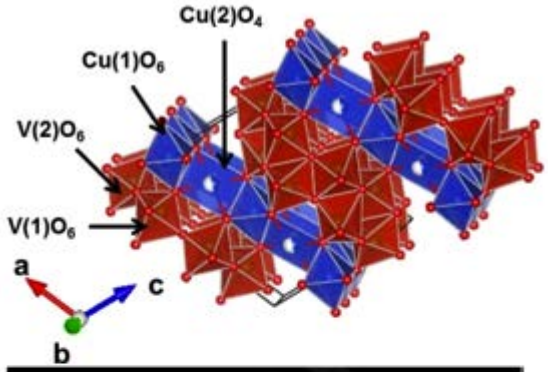


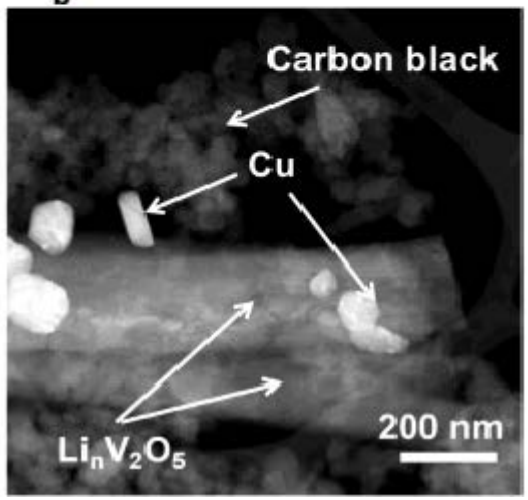
- Single-crystalline, surface layer ~5 nm (rock-salt structure);
- Found different structural ordering and stoichiometry than literature*

*(*Ref.: Rozier, et al., J. Solid State Chem. 182, 1481, 2009)*

Structural change upon lithiation (ε-$Cu_{0.95}V_2O_5$)



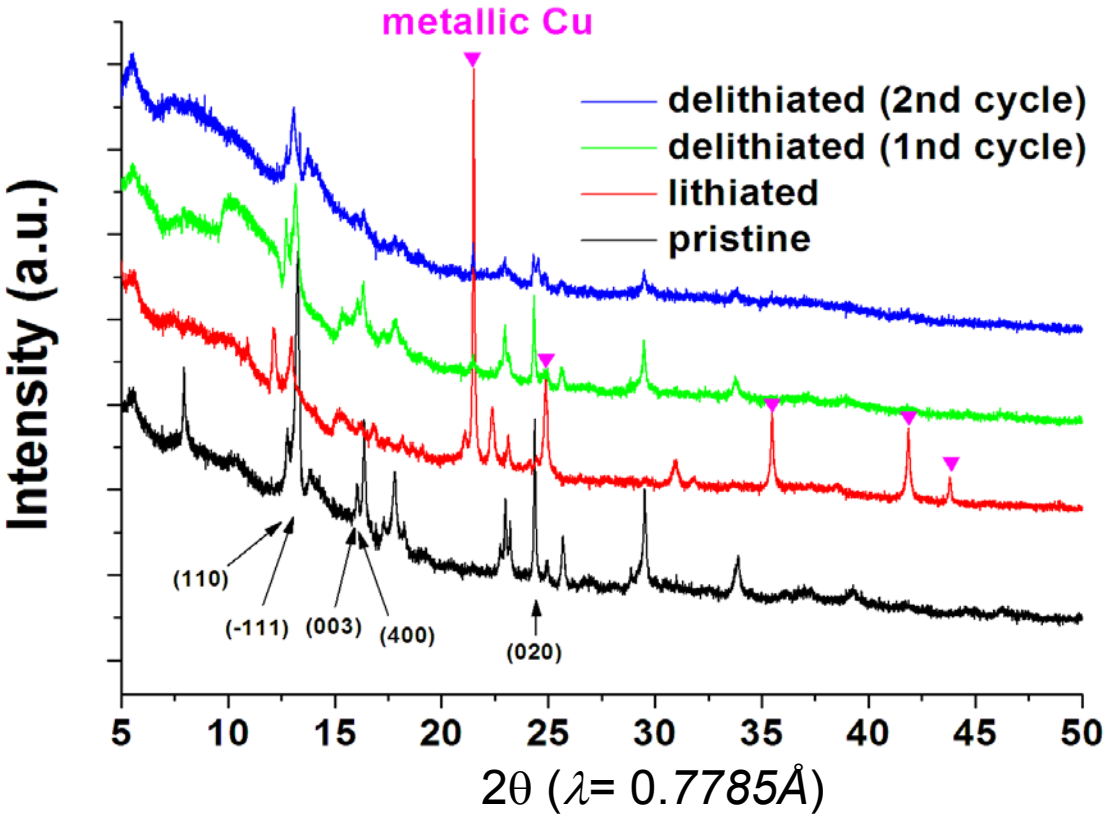


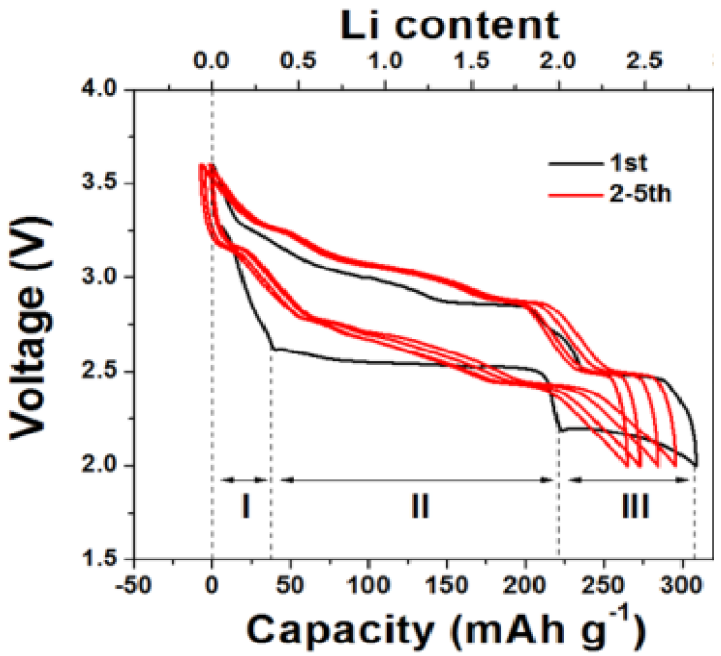


Formation of large Cu particles on the surface of CVO rods with lithiation

- Found loss of long-range ordering (i.e. periodic V_2O_5 stacking) with Cu extrusion (*disappearing of (*003*) in Stage *II*).

Structural degradation with cycling



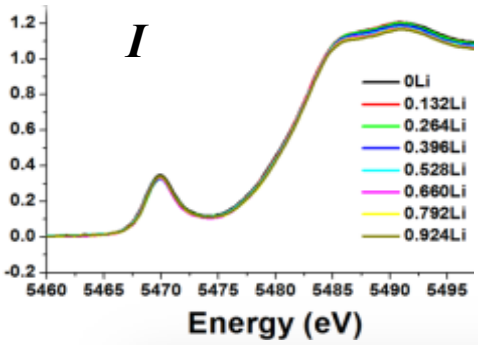


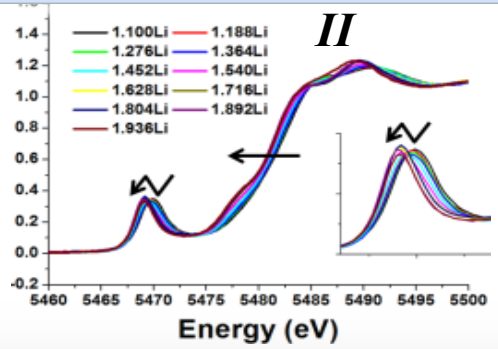
- Direct correlation of structural changes with voltage profile
  - "multiple plateaus" in the 1st cycle;
  - sloppy curves in the following cycles.
- Structural degradation and residual Cu may explain gradual capacity decay with cycling.*

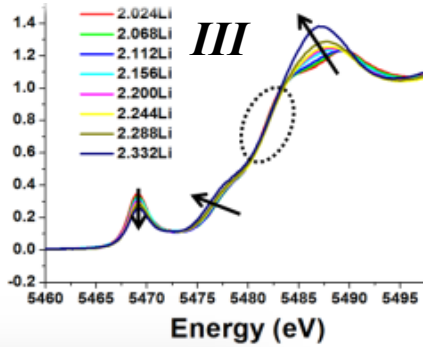
*(*See backup slide showing the residual Cu with cycling)*

Redox of V and Cu in ε-$Cu_{0.95}V_2O_5$ (*in-situ* XAS)

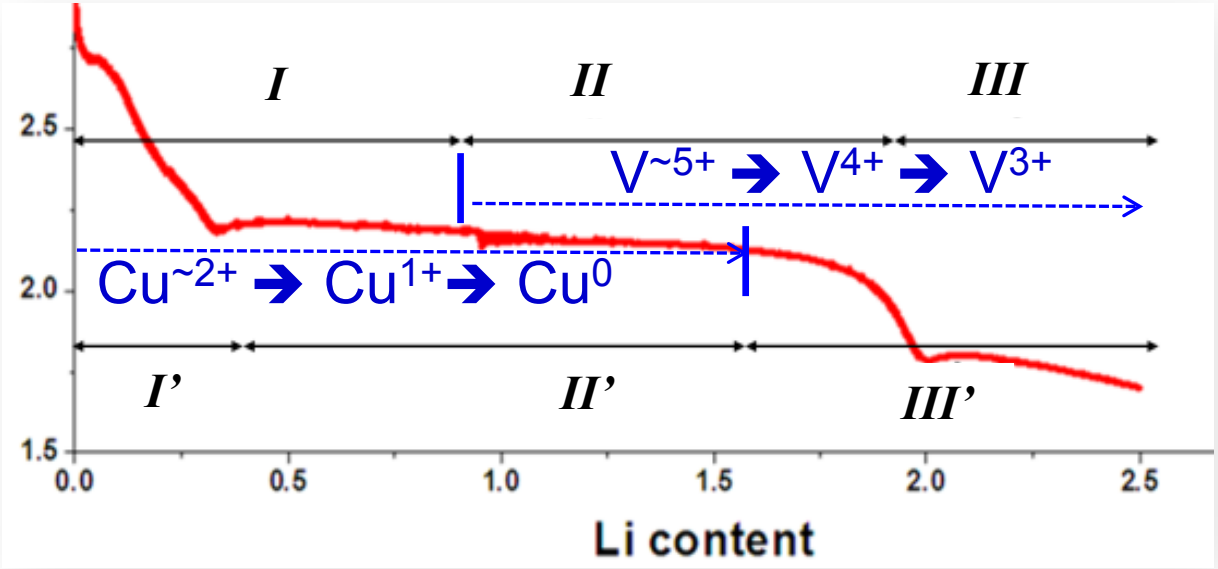
XANES:
V K-edge



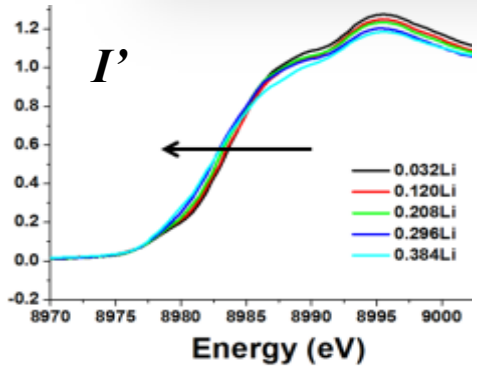


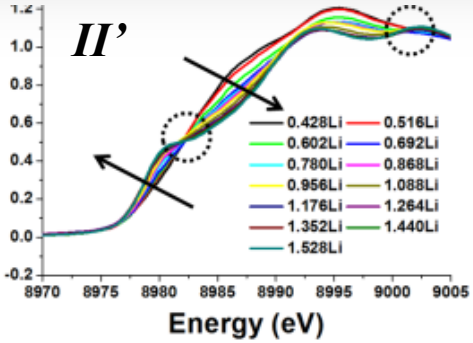


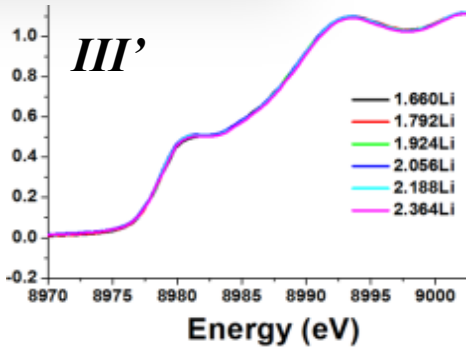
Voltage
profile



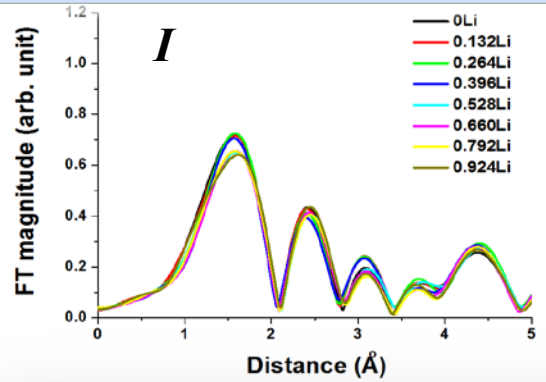
XANES:
Cu K-edge

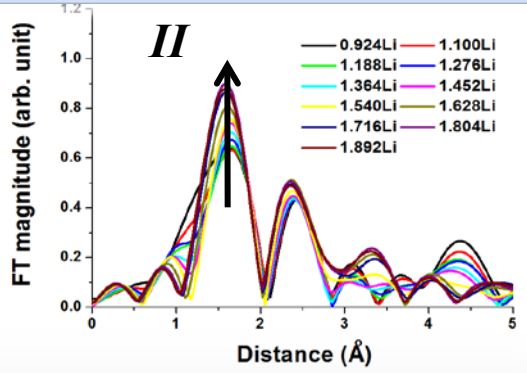


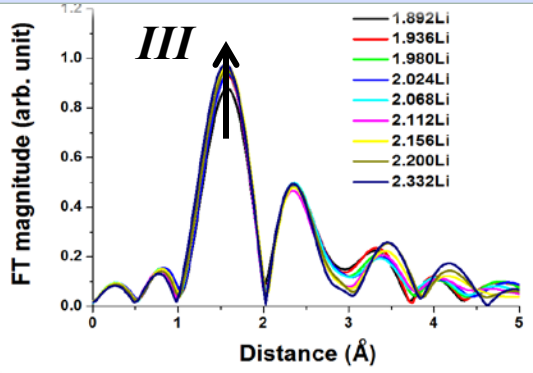


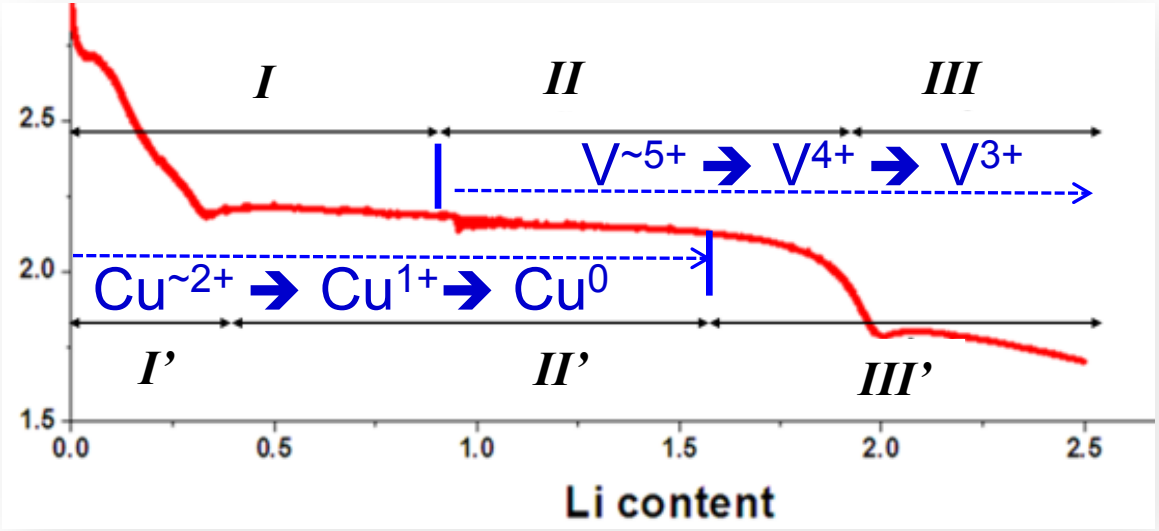


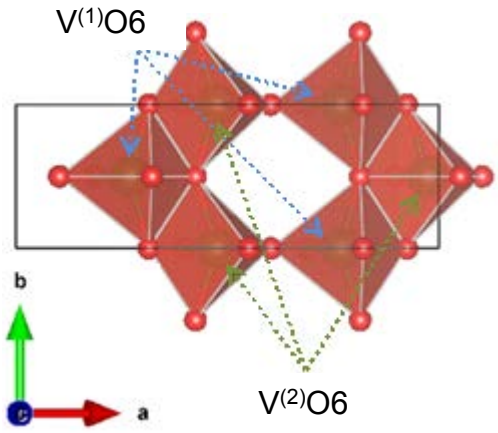
Local structural re-ordering(*in-situ* XAS: EXAFS)











- VO6 octahedra: largely distorted in pristine, little change in early Li insertion
  - become highly symmetric with Cu extrusion/further lithium intercalation*
- Li reaction process: solid solution with $Cu^{2+/1+}$ reduction (***I'***) ➔ displacement ($Cu^{1+/0}$; ***II'***) ➔ further Li intercalation leading to $V^{5+/4+/3+}$ reduction (***II, III***).

*(*See backup slide for reference XAS spectra and V-O bond distances)*

Collaborations

- HRL Lab (*J. Graetz**)
  - Synthesis and characterization of high-capacity cathode materials
- Brookhaven National Lab (*J. Bai, Y. Zhu*)
  - Development of *in-situ* reactors and synchrotron techniques;
  - Advanced TEM imaging and spectroscopy of cathodes
- Stony Brook University (*P. Khalifah*, *X. Wang*(*shared student*))
  - Synthesis of novel high-capacity cathodes
- Lawrence Berkeley National Lab (*J. Cabana**)
  - *In-situ* synthesis of new mixed-anion cathodes.
- University of Texas at Austin (*A. Manthiram**)
  - Synchrotron X-ray characterization of high-capacity polyanion cathodes.
- *NECCES* EFRC at Stony Brook University
  - *In-situ* TEM, NMR, magnetization characterization.

* *PIs in the BATT program*.

Future work in FY13/FY14

- Continue the investigation of Cu-V-O cathodes
  - synthesize and characterize other high-capacity Cu-V-O phases;
  - identify mechanisms responsible for cycling stability of electrodes using newly developed *simultaneous in-situ* XRD/XAS method;
  - improve electrode performance by tailoring particle morphology through the control of reaction conditions (precursor, reducing agent, temperature, time, etc.).
- Develop new high-capacity cathodes
  - prepare and *in-situ* characterize olivine-type cathodes ($Li(MnFe)PO_4$, $Li_3V_2(PO_4)_3$, …);
  - determine the feasibility of solvothemral and/or ion exchange synthesis of lithium metal carbonophosphates ($Li_3M(CO_3)(PO_4)$), carbonofluorosulfates ($Li_3M(CO_3)SO_4F$);
  - prepare polyanion and other types of lithium materials *via* ion-exchange from earth-abundant Na compounds.
- Develop new *in-situ* synthesis methods *via* collaboration with BATT community.

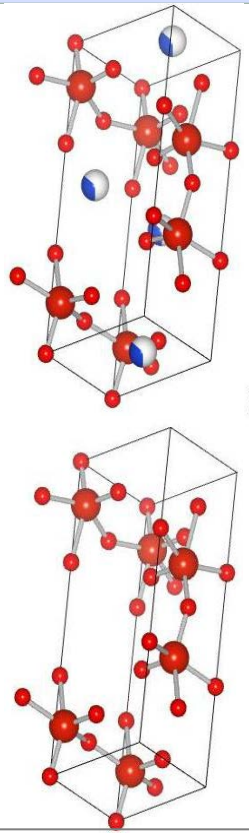
Summary

- **Synthesis Technique Development**
  - *Developed in-situ* reactors, *time resolved* XRD techniques specialized for hydrothermal, solvothermal, ion exchange, solid reaction synthesis*
    - *key for understanding synthesis reaction mechanism and thereby optimizing synthesis conditions to obtain desired phases and material properties*
- **High-Capacity Cathodes Development**
  - Synthesized high-quality ε-$Cu_{0.95}V_2O_5$ materials after optimization of reaction conditions (precursors, reducing agents, temperature);
  - Conducted detailed electrochemical and structural characterization of as-synthesized and (de)lithiated ε-$Cu_{0.95}V_2O_5$ materials.
- **Cycling Stability Investigation**
  - Determined Li reaction process and possible mechanisms responsible for poor cycling stability of ε-$Cu_{0.95}V_2O_5$ *via in-situ* XRD and XAS studies.
- **Collaboration**
  - Established collaborations both within BATT and with external partners on technique development, synthesis, and characterization.

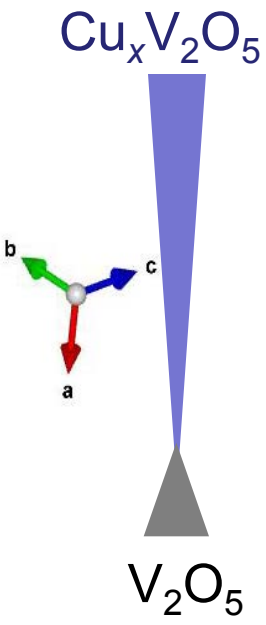
**See backup slides for results of in-situ ion exchange, solvothermal synthesis*

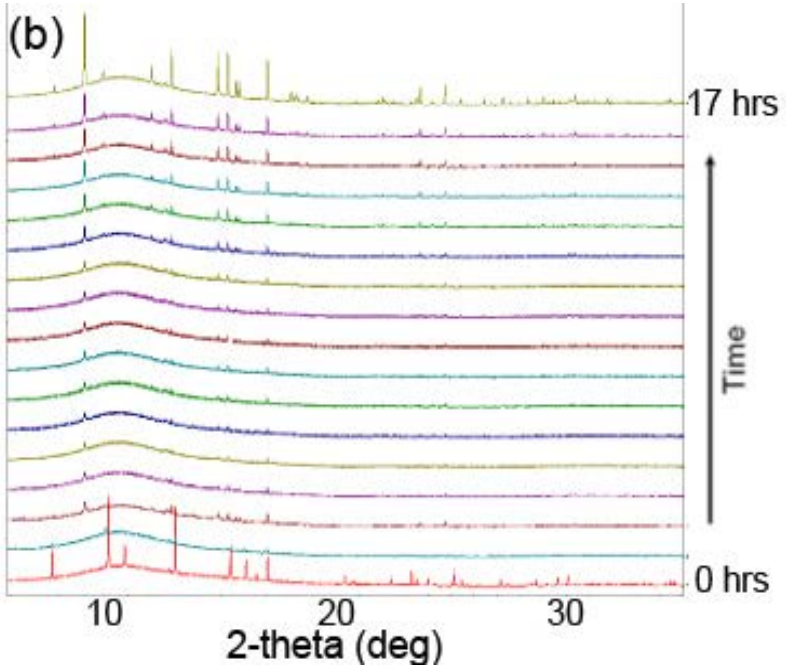
Technical Back-Up Slides

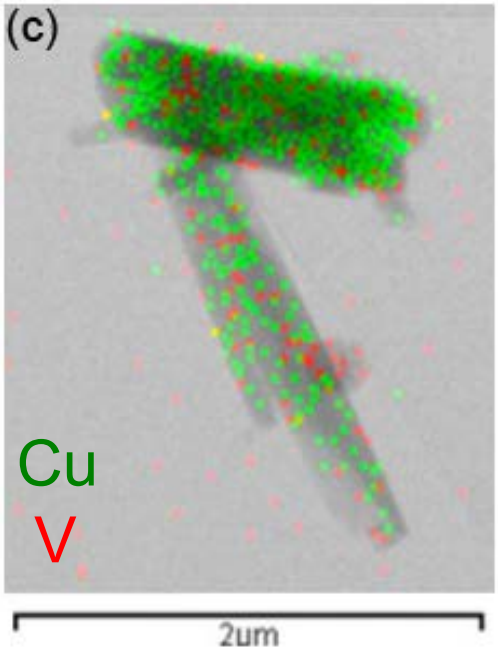
In-situ synthesis of $Cu_{0.36}V_2O_5$



$$V_2O_5 + Cu(NO_3)_2 \cdot 3H_2O + reducing\text{-}agent \xrightarrow{180^oC} Cu_xV_2O_5$$

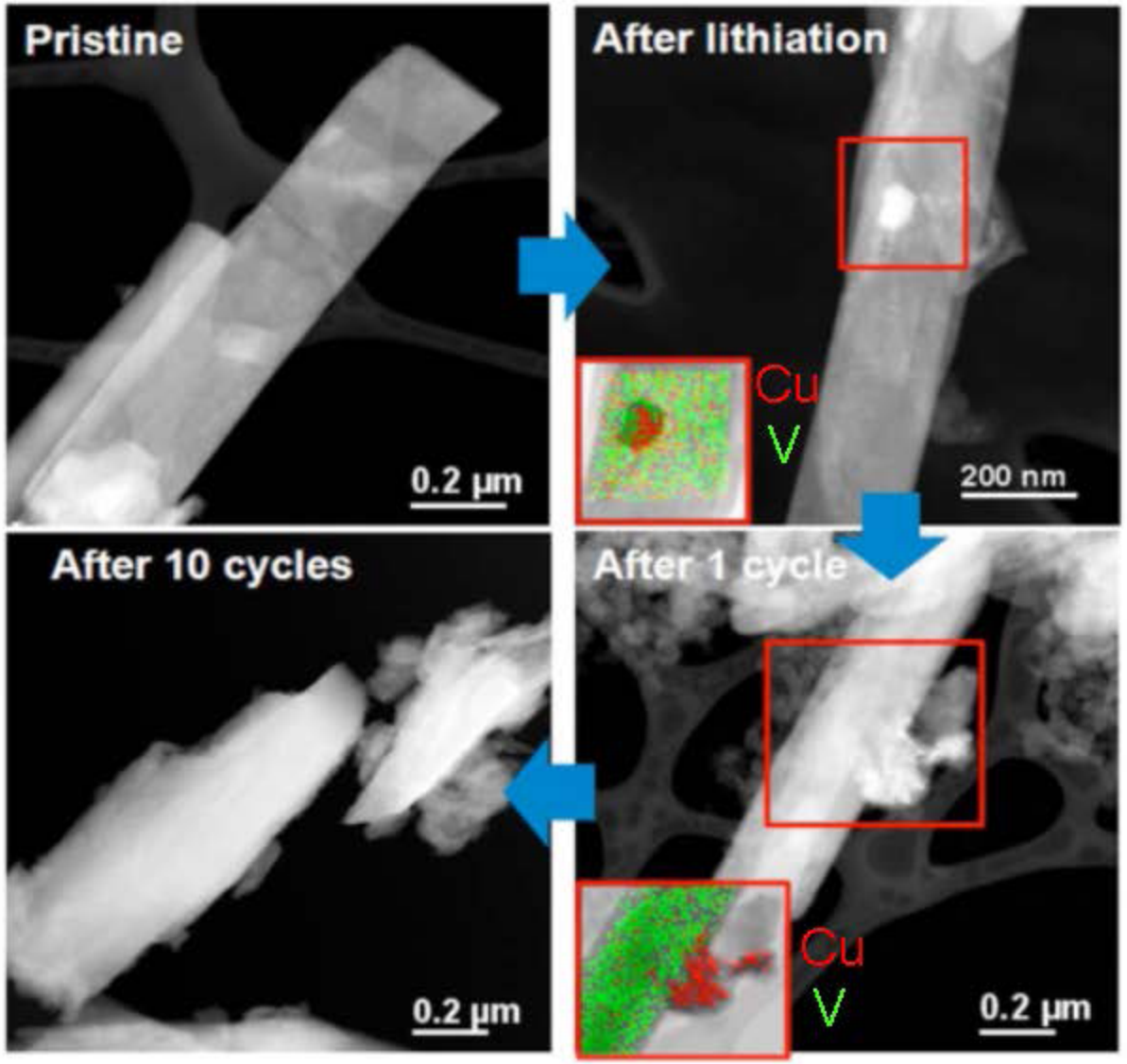




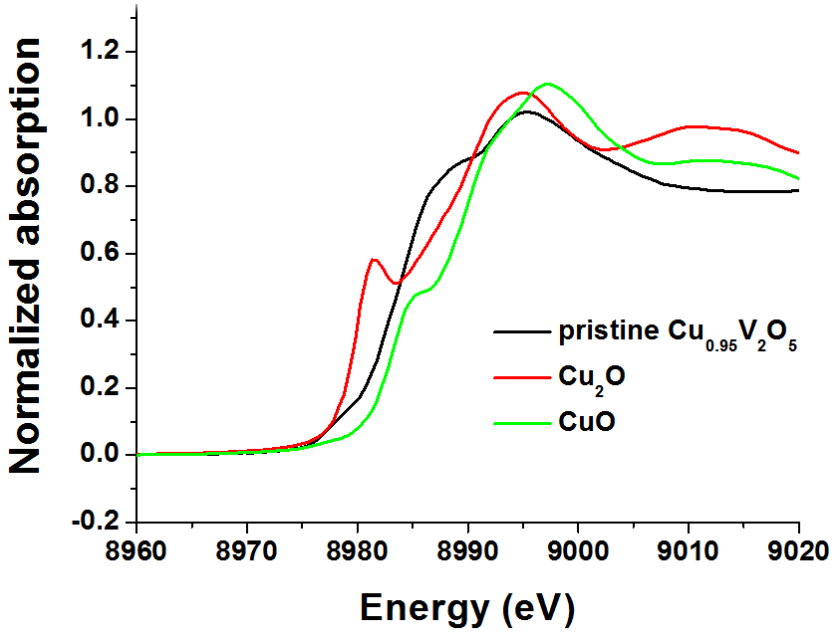


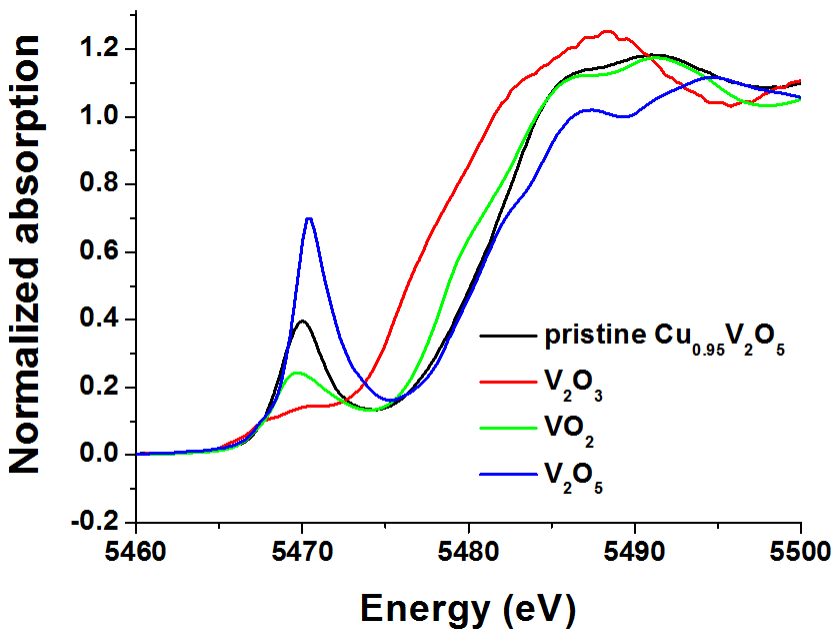
- In-situ synthesis of $Cu_xV_2O_5$ ($x \approx 0.36$) with an iso-structure to V_2O_5, (orthorhombic) and an volume expansion by ~9.93% (by refinement);
- Direct dissolution-recrystallization reaction process;
- As-synthesized $Cu_xV_2O_5$ ($x \approx 0.36$): a rod-like morphology and uniform Cu distribution across the rods (by STEM- EDS mapping).

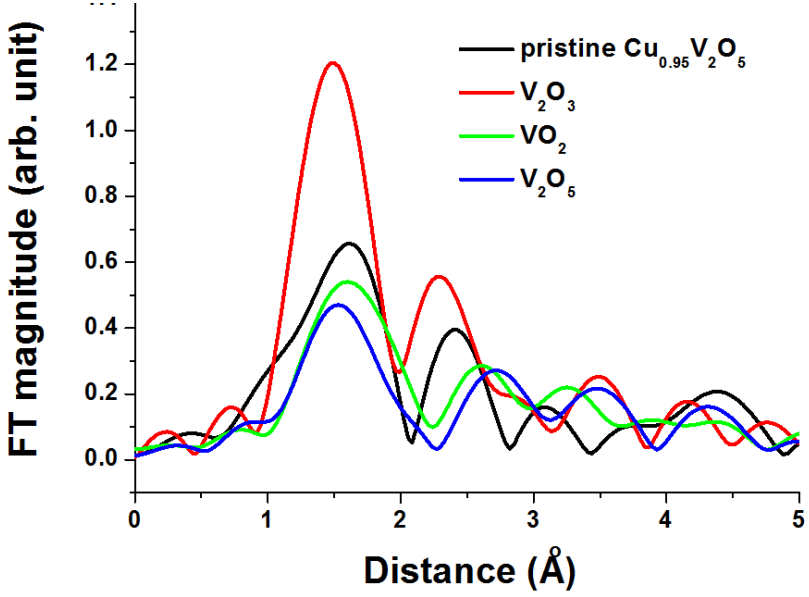
Residual Cu with cycling

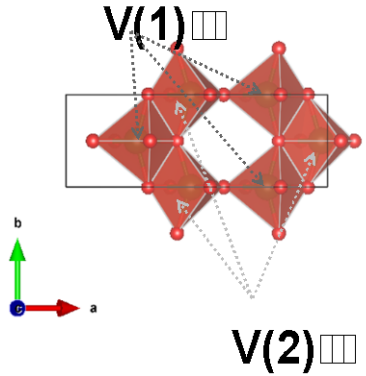


Reference XAS spectra and V-O bonds



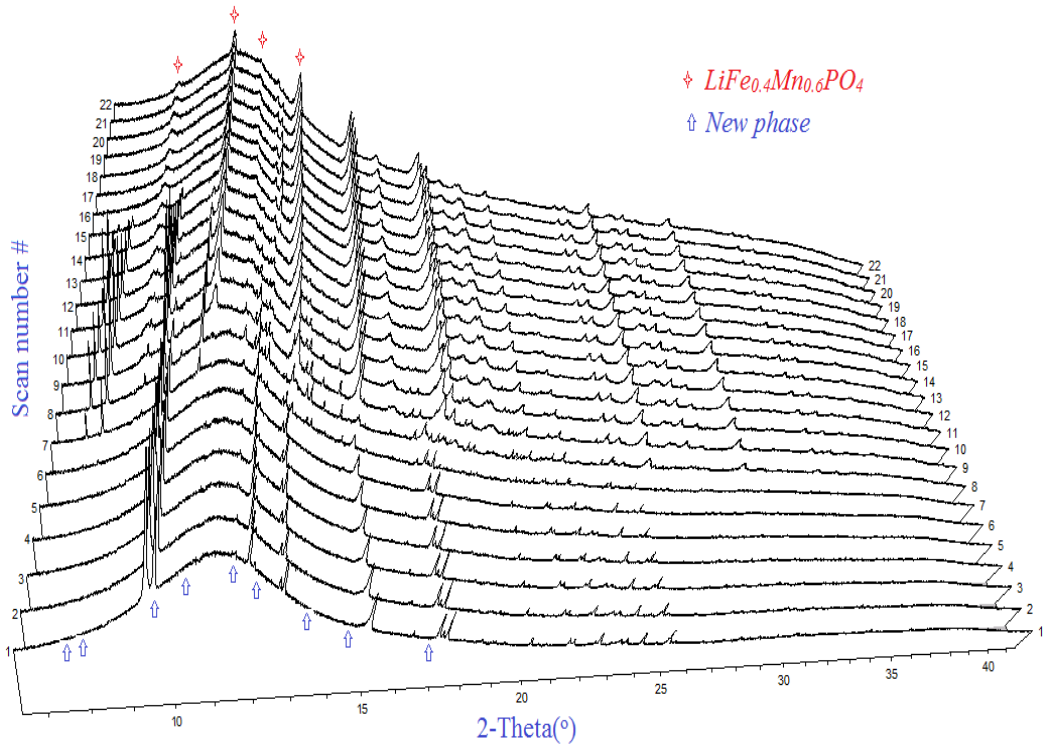


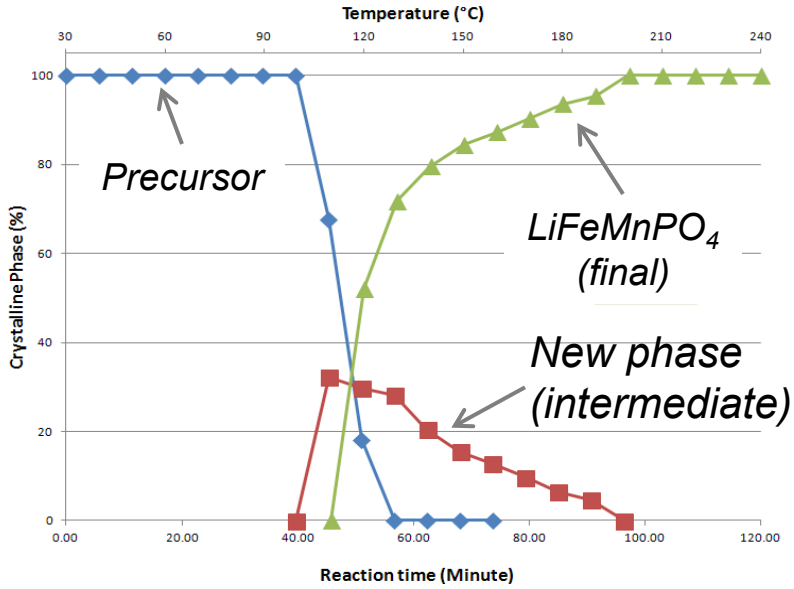




V(1)-O distance	V(2)-O distance
2.48651 Å	2.27843 Å
1.92084 Å	1.93599 Å
1.92084 Å	1.93599 Å
1.86345 Å	1.92276 Å
1.80197 Å	1.85527 Å
1.47617 Å	1.68412 Å

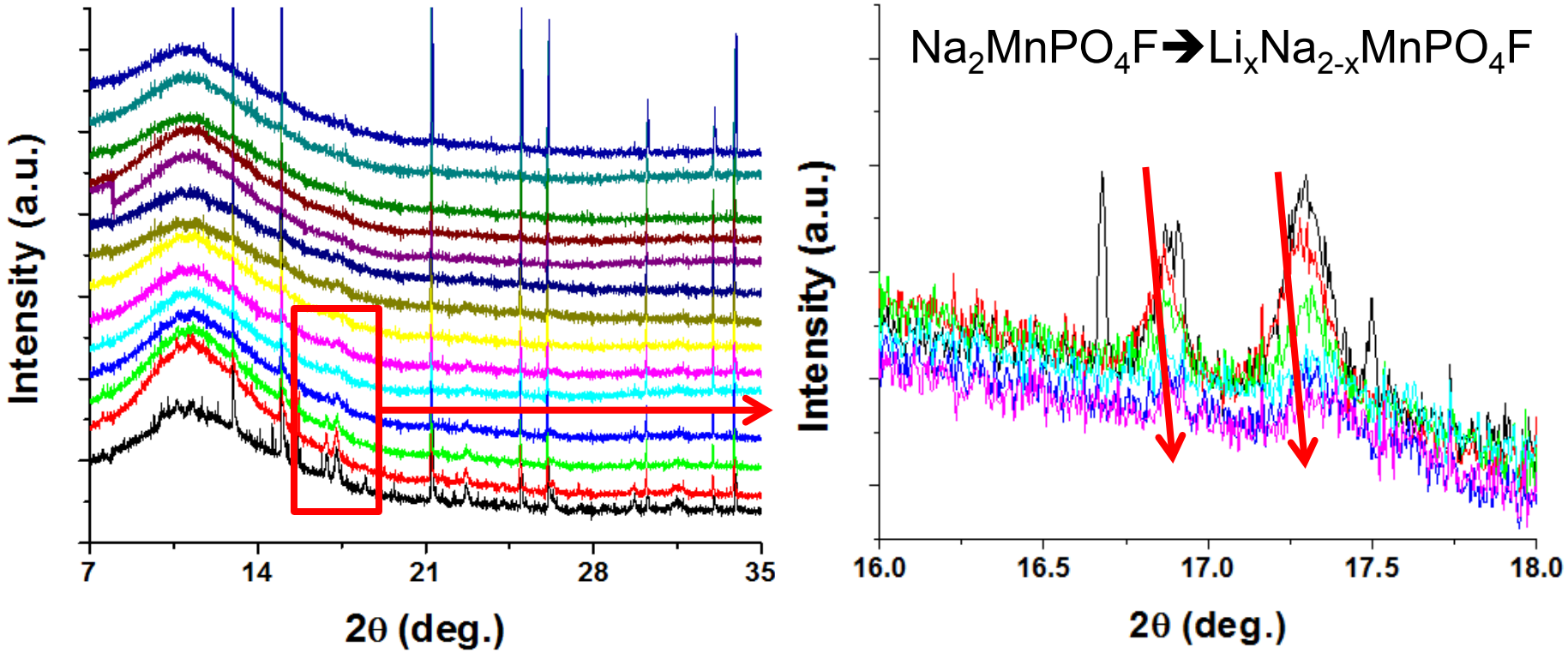
In-situ solvothermal synthesis of $LiFeMnPO_4$





- Succeeded in *in situ* synthesis of LiFePO4 and $LiFe_xMn_{1-x}PO_4$ solid solution using ethylene glycol (EG) as solvent;
- Identified reaction path way – forming an intermediate phase at ~100°C and transformation to $LiFe_{0.4}Mn_{0.6}PO_4$ at ~180°C;
- Determined reaction mechanism (* *to be published*).

In-situ ion exchange synthesis of $LiNaMnPO_4F$



- Formation of NaBr and higher-angle shift of Na_2MnPO_4F peaks indicate the Li/Na ion-exchange reaction;
- However, the crystallinity is too poor to make detailed analysis and higher crystalline samples are being prepared.