In-situ Solvothermal Synthesis of Novel High-Capacity Cathodes

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ES183

Overview

Timeline

- Project start date: April, 2012
- Project end date: April, 2016
- Percent complete: 50%

Barriers

- Low energy density
- Cost
- Cycle life

Budget

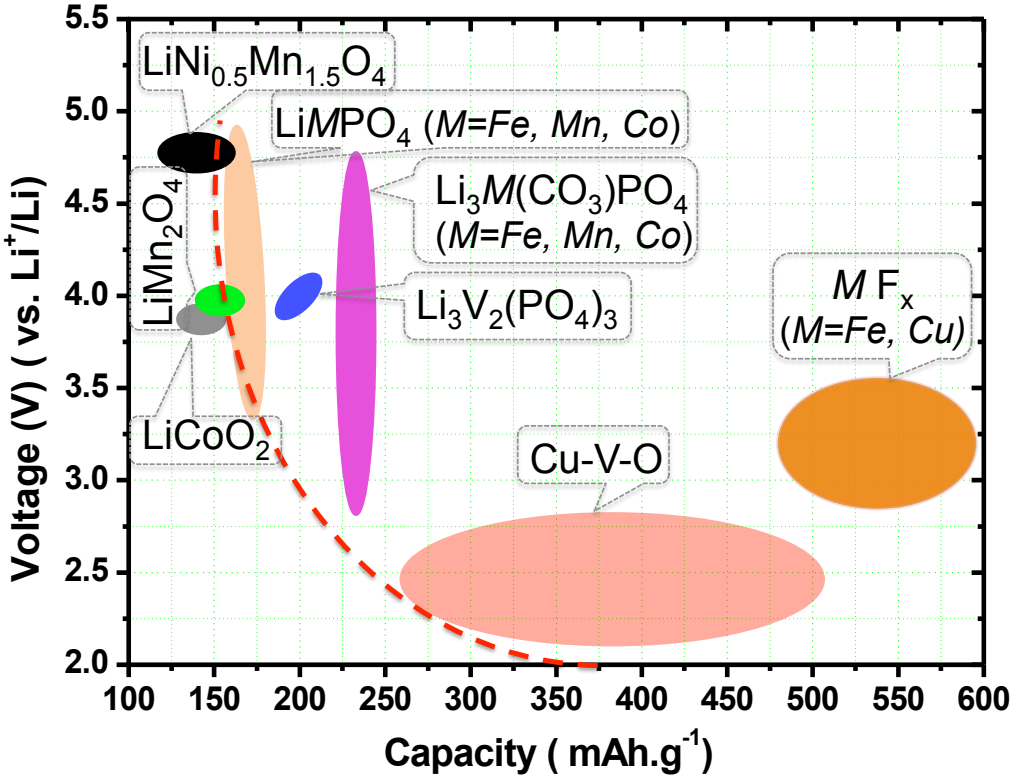
- Total project funding
  - DOE 100%
- Funding received in FY13
  $ 304K
- Funding for FY14
  $304 K

Partners

- Interactions/collaborations
  - Brookhaven National Lab
  - Stony Brook University
  - Lawrence Berkeley National Lab
  - University of Texas at Austin
  - Seoul Nat. U., Korea
  - HRL Laboratory
  - MIT
  - SUNY at Binghamton

Objectives

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



The effort in FY13/14 was focused on synthesis, and structural, electrochemical characterization of high-capacity cathodes, *including*

- two types of Cu-V-O compounds
- Li(Na)VPO_5F_x
- Li-V-PO_4
- Li-Fe-Mn-PO_4

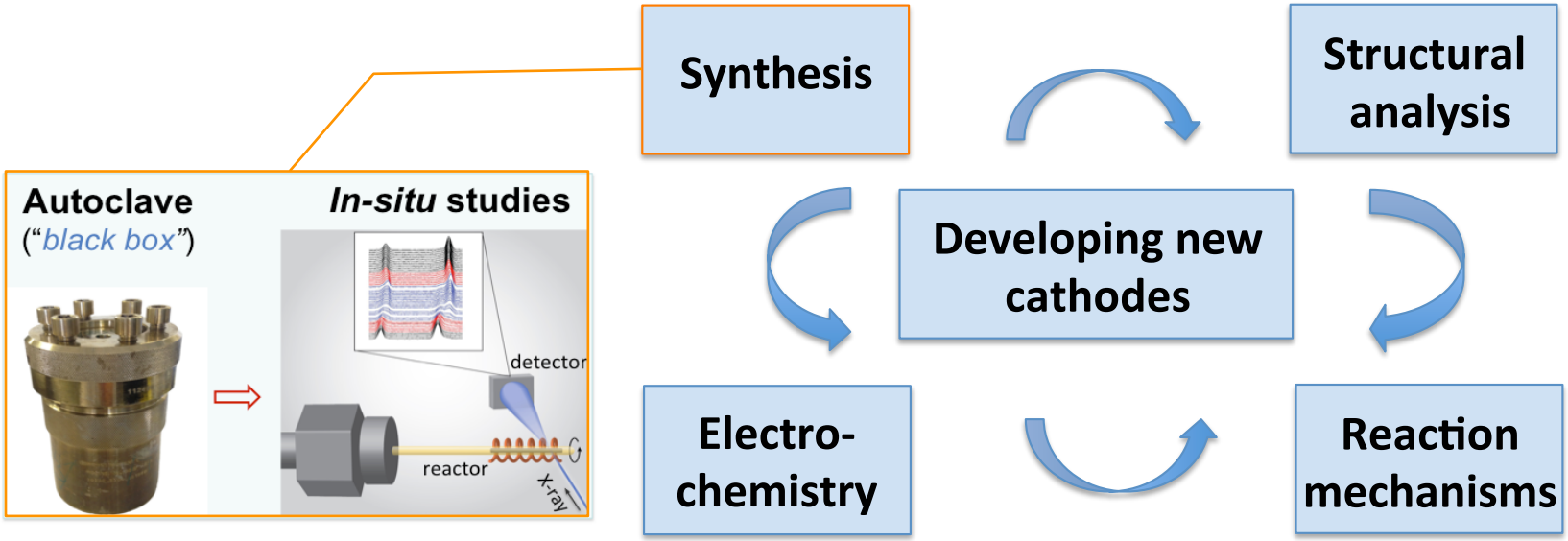
(**Some cathodes with target energy density (>660 Wh/kg) are given on the right side of the red dashed plot*)

Milestones

- Identify mechanism(s) responsible for poor cycling in ε-$Cu_xV_2O_5$ and identify a pathway for reducing capacity fade with cycling. (Mar. 13') *complete*
- Synthesize and electrochemically characterize at least one other Cu-V-O compound using hydrothermal/solvothermal. (May. 13) *complete*
- Determine the feasibility of using hydrothermal ion exchange reactions to prepare polyanion cathodes. (Sept. 13) *complete*
- Complete the structural and electrochemical characterization of ε-$Cu_xV_2O_5$ cathodes. (Dec. 13) *complete*
- Develop synthesis procedures to prepare Li-V-PO_4 cathodes. (Mar. 14) *complete*
- Optimize the synthesis and characterize the structural and electrochemical properties of 2nd class of Cu-V-O cathode. (Jun-14) *on going*

Approach

Developing new cathodes *via* synthesis, along with structure-property evaluation and diagnostics.



***In-situ* synthesis** Controlled synthesis of materials of desired phases and properties, *using*

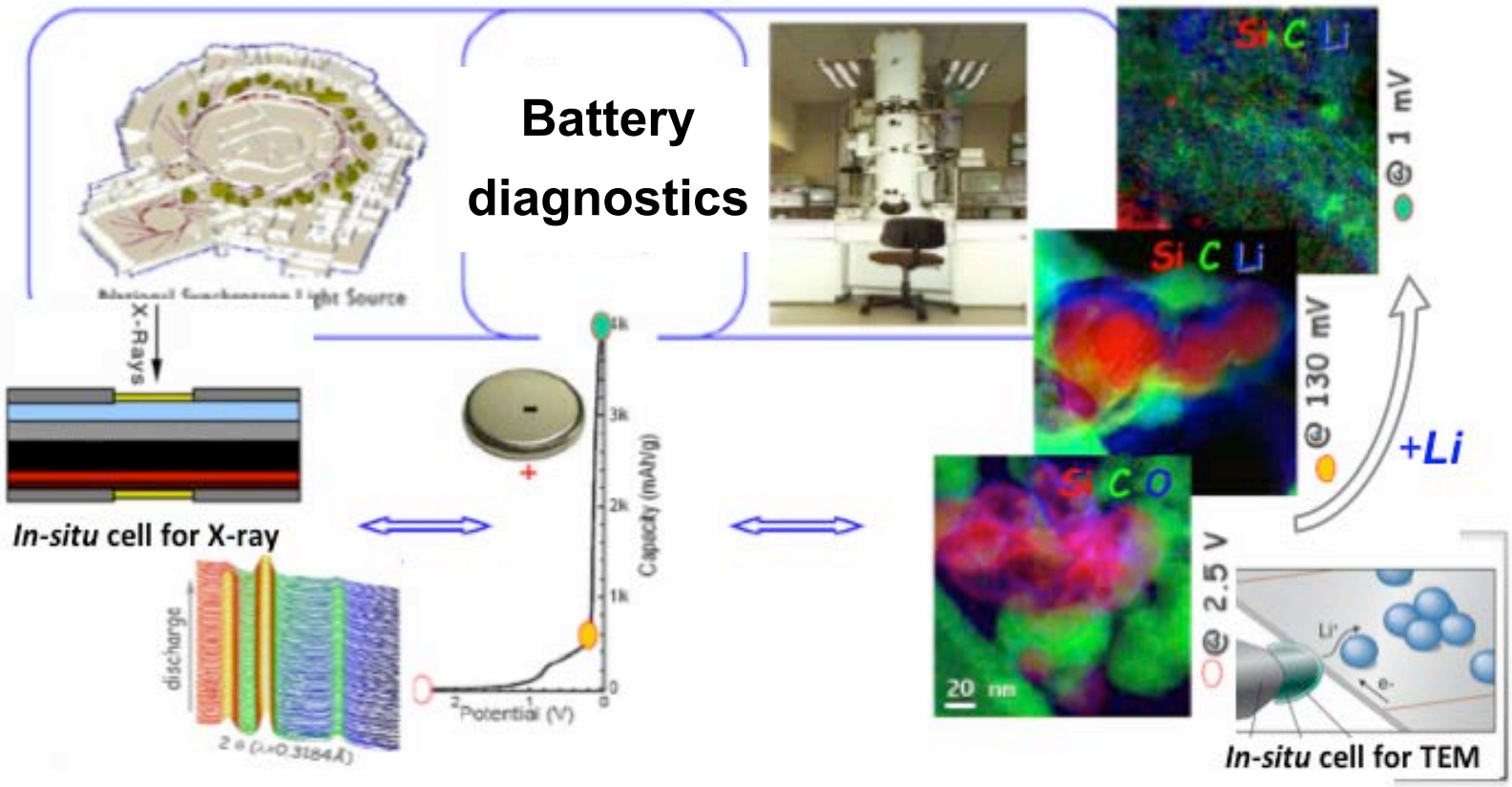
- specialized *in-situ* reactors suitable for variety of synthesis reactions
- *time-resolved* XRD for quantitative identification of structure/phases during synthesis

Technique development Explore structural evolution of intermediates and reaction pathways during synthesis under real working conditions, aiming to

- build up 'phase diagrams' in the space of working conditions (*i.e.* temperature, pressure…)
- develop ability to 'dial in' desired phases and material properties
- optimize synthesis of new cathodes
- provide insight for structure prediction (*potential synergy with theory)*

Approach (*cont'd*)

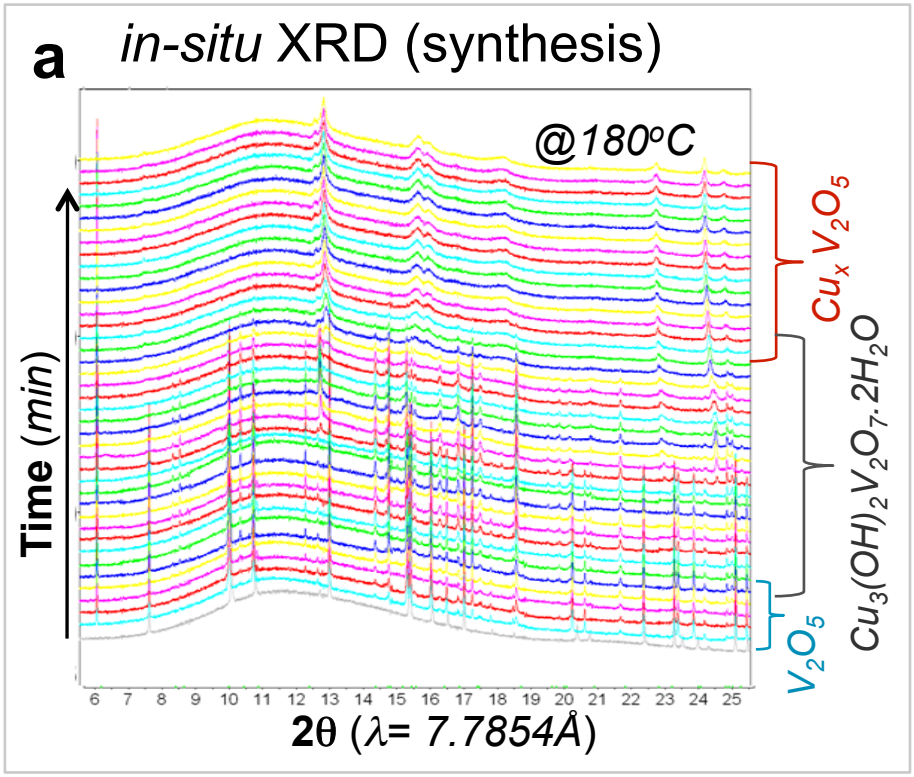
Diagnostics *via on-site* resources and *in-house* developed capabilities

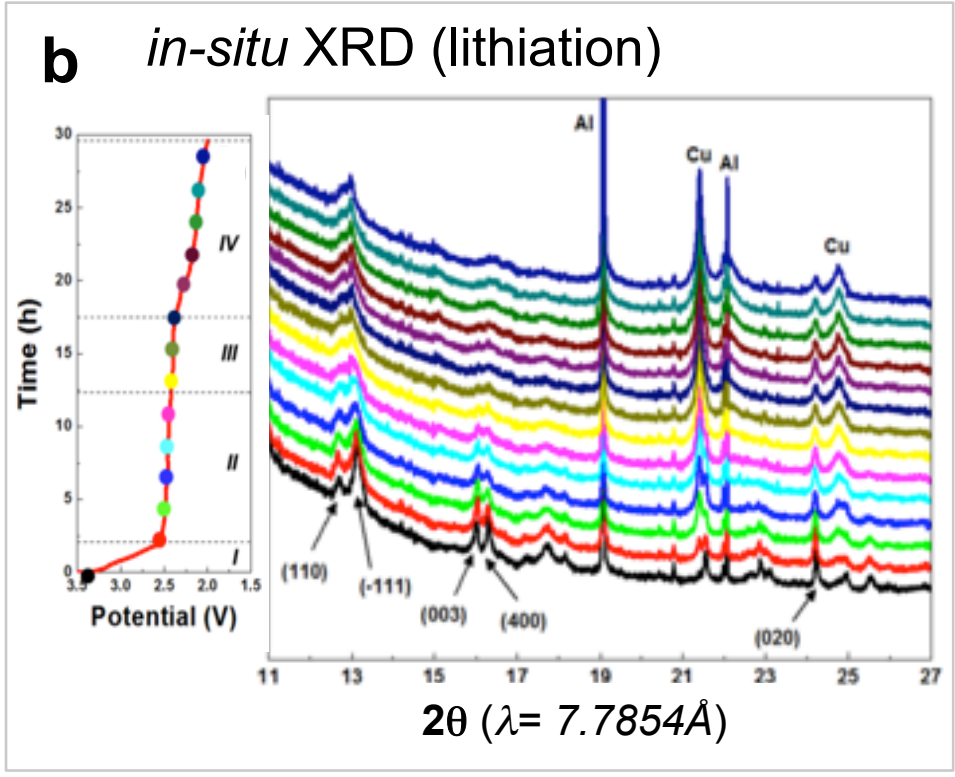


Synchrotron x-ray	**Electrochemistry**	***TEM-EELS***
studies of Li reaction, charge transfer @ electrode level.	↔ (*Functionality*)	tracking Li transport, reactions *@single-particle level*.

*__Ref.__: F. Wang et al., *Adv. Energy Mater.* 3 (2013) 1324; *Nat. Comm.,* 3 (2012)120.

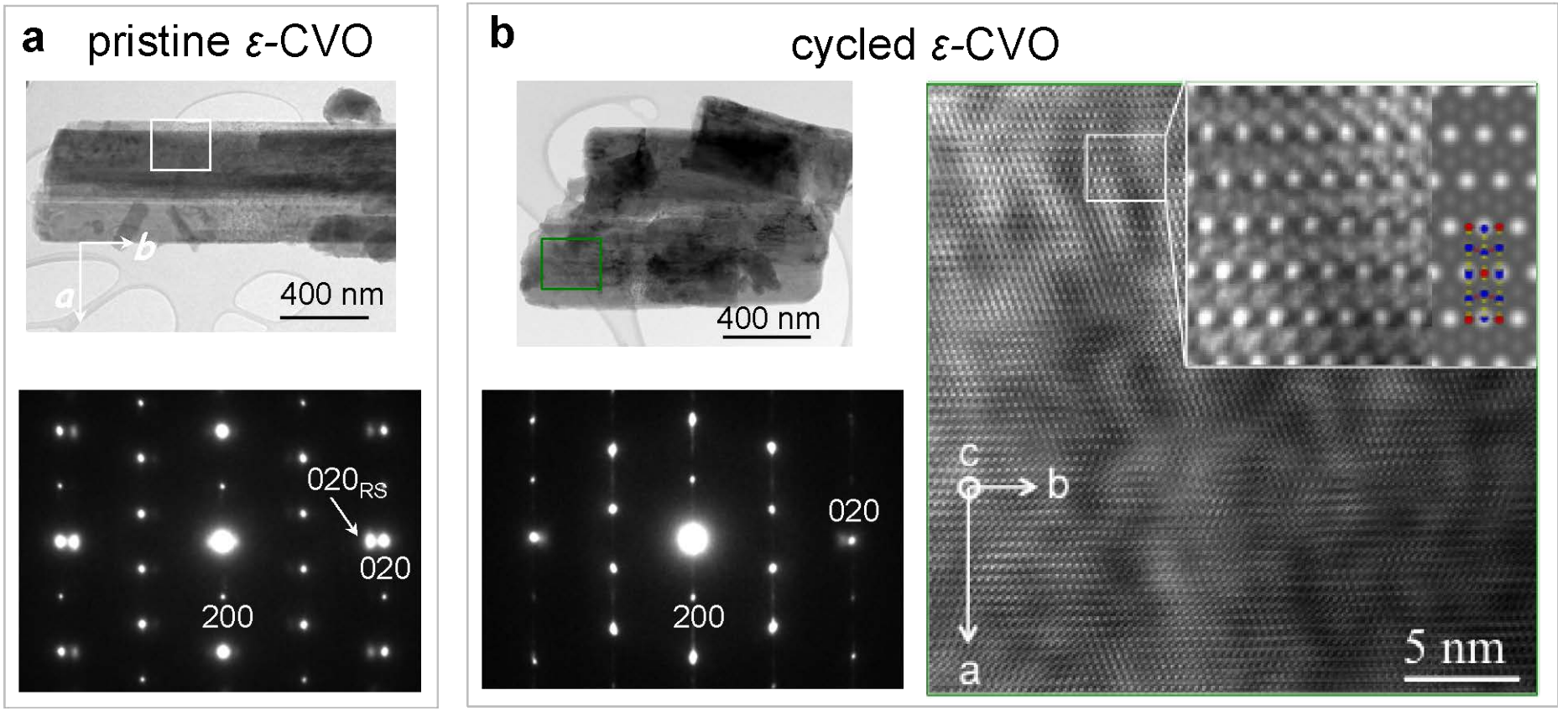
ε-$Cu_xV_2O_5$ (ε-CVO) cathodes: *in situ* studies





- *In-situ* XRD techniques were developed for studying synthesis reactions, and thereby optimizing procedures in preparing *ε*-CVO cathodes (*Fig. a*);
- *In-situ* XRD *was also applied for* studies of lithium reactions in *ε*-CVO cathodes, to identify possible limitations to their cycling stability (*Fig. b*).

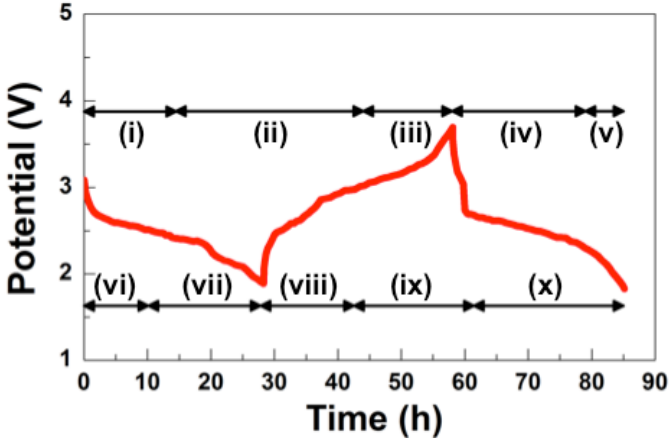
Local structural re-organization in ε-CVO after cycling



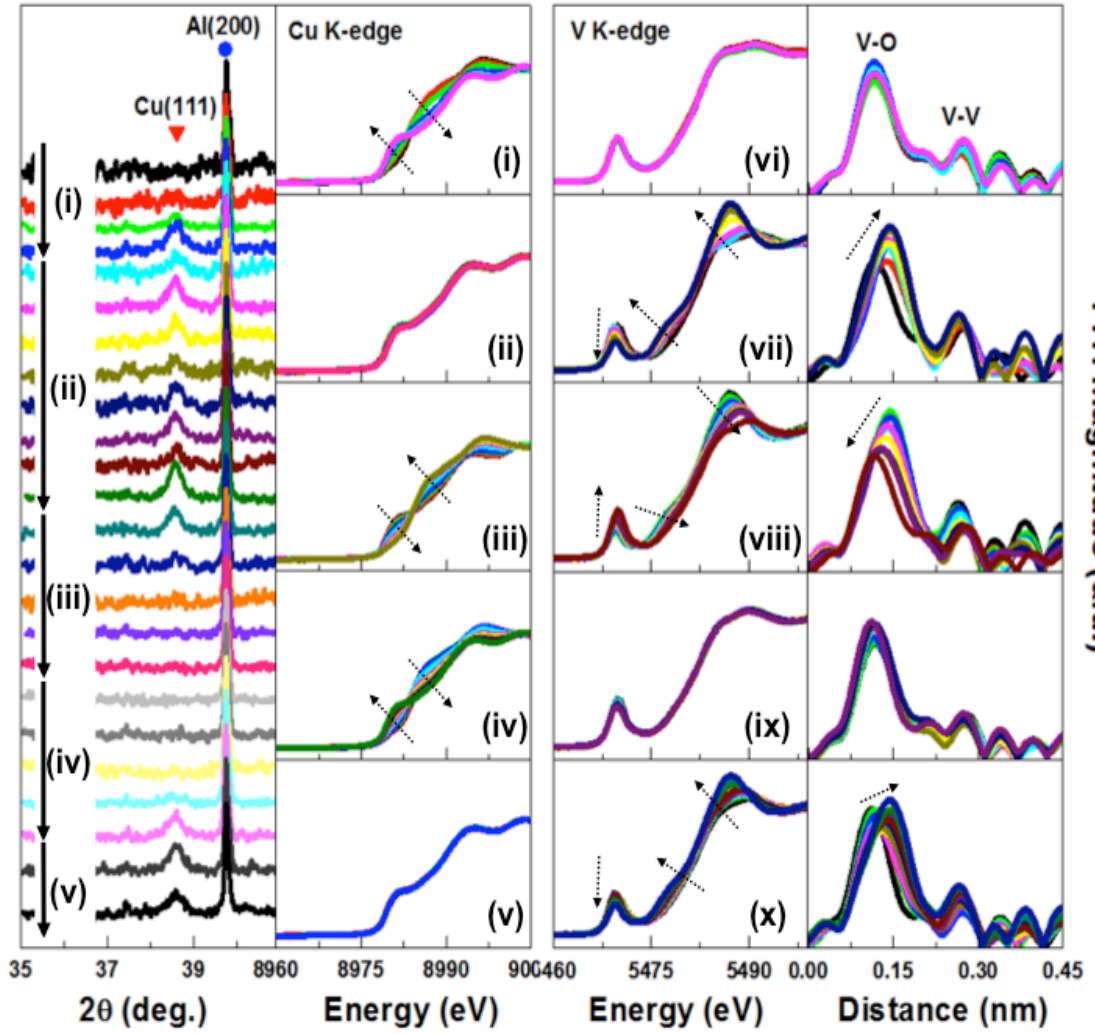
- Pristine ε-CVO: single-crystalline rods, coated with rock-salt (*Fig. a*);
- Cycled ε-CVO: retained rod shape, but with new local ordering (*Fig. b*)
  - nano-sized “mosaic”-like domains across the particles
  - structural distortion/expansion for facile Li and Cu ions (de)insertion

High structural reversibility in ε-CVO with cycling

a. cycling profile of ε-CVO



b. *In-situ* XRD patterns (left), XANES, EXAFS

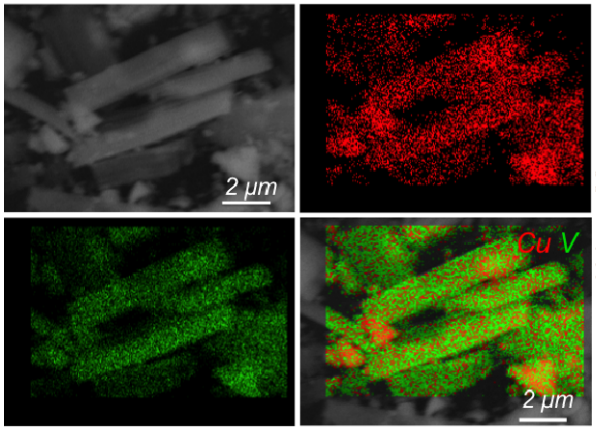


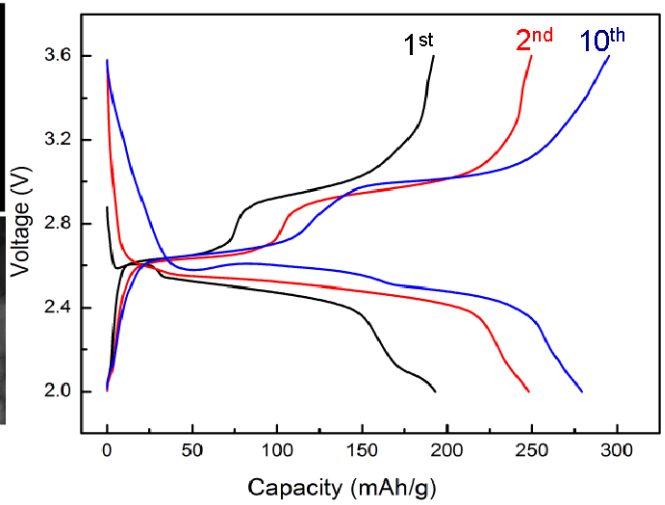
Complete information on structural/chemical evolution of ε-CVO with cycling was obtained *via* simultaneous *in-situ* XRD/XAS, indicating:

- reversible Cu, V redox
- stabilized local structure (*e.g.* retaining VO_6 octahedra)

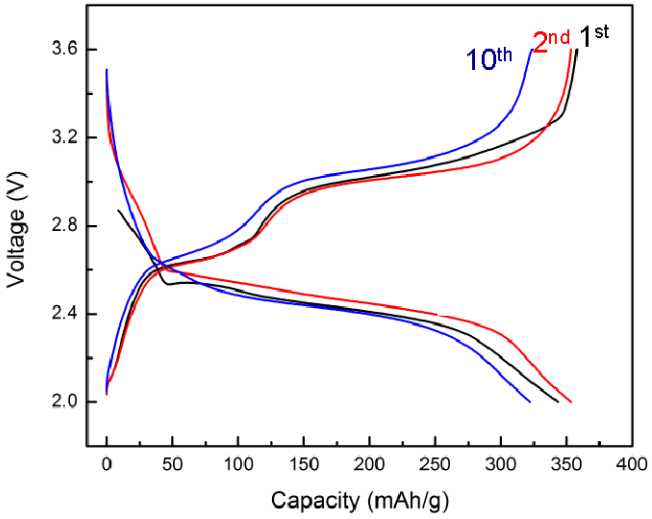
New α-CuVO cathodes

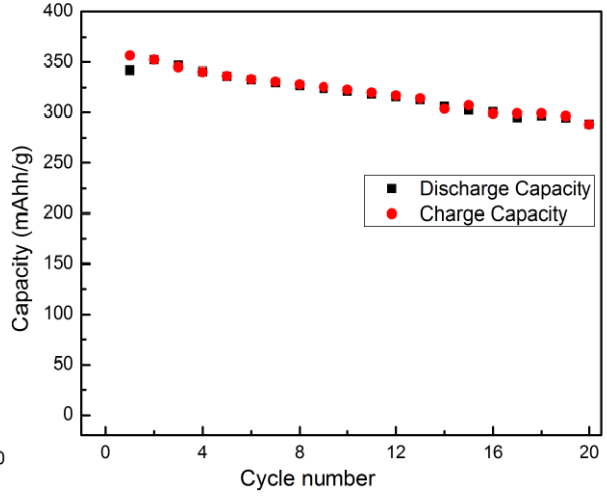
a. SEM/EDX and voltage profiles for α-CVO *via* hydrothermal reaction





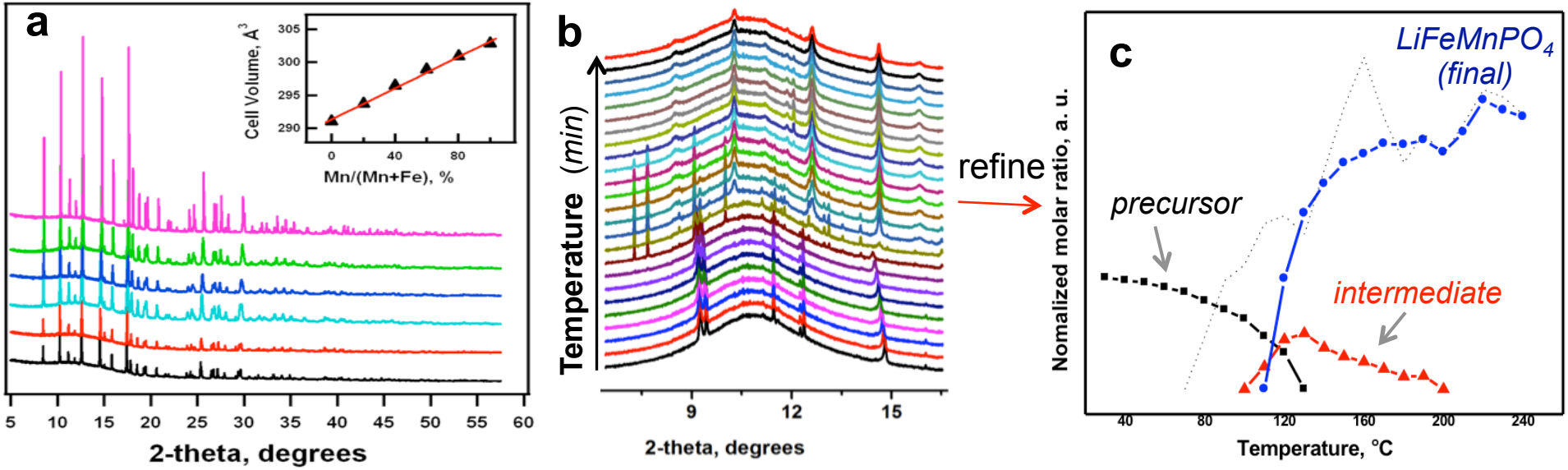
b. Voltage profiles and cycling for α-CVO *via* solid state reaction (*after size reduction*)





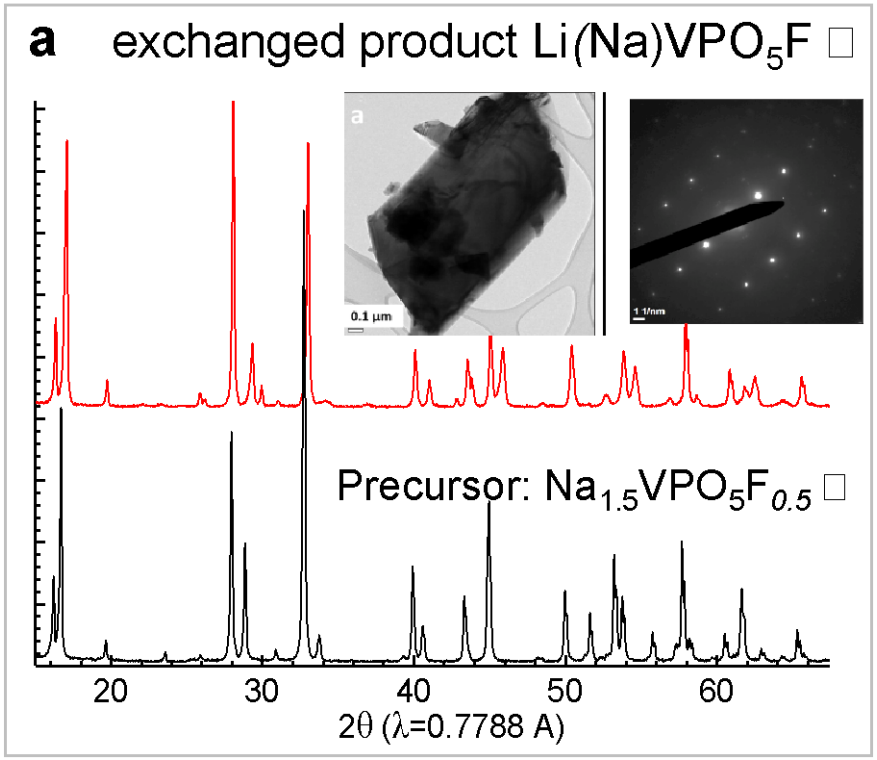
- Developed procedures for synthesis of α-CuVO compounds with identified new structure using both hydrothermal (*Fig. a*) and solid state reactions (*Fig. b*);
- Measured high capacity, up to 350 mAh/g and reasonable cycling stability between 2.0-3.6V;
- Obtained even higher capacity, >500 mAh/g but poor cycling stability between 2.0-4.5 V (*backup slides*).

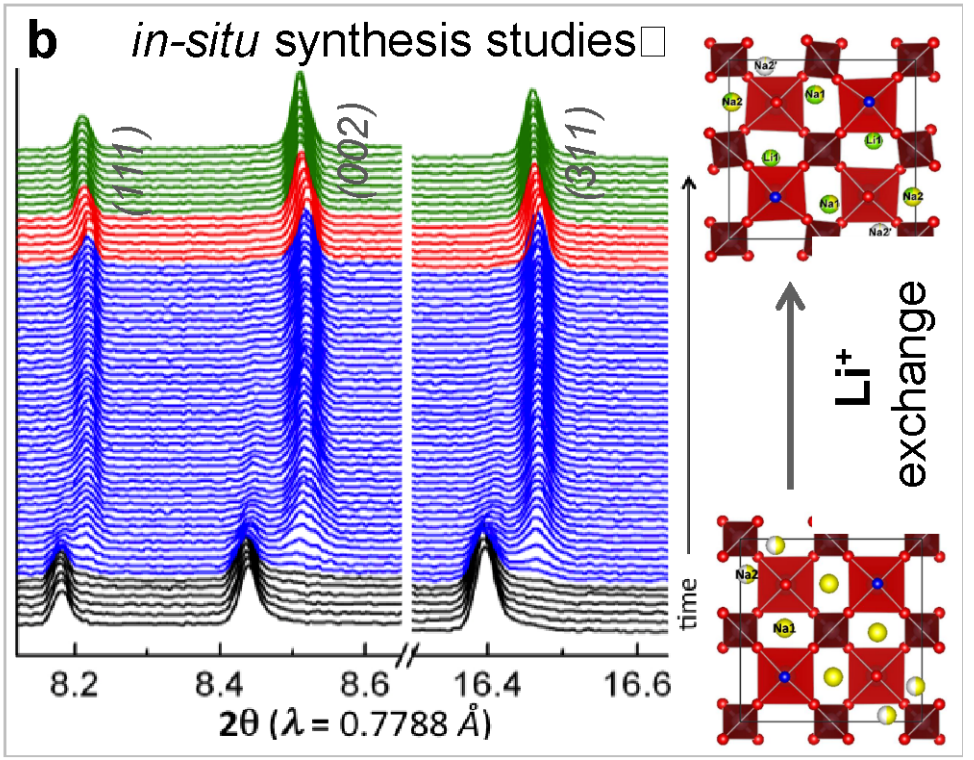
$LiFeMnPO_4$: *in-situ* solvothermal synthesis



- Developed procedures for solvothermal synthesis of $LiFe_xMn_{1-x}PO_4$ series (*Fig. a*);
- *In situ* synthesis studies and structure refinement (*Fig. b, c*)
  - identified intermediates and reaction pathway
  - determined reaction mechanisms and important role of ethylene glycol (EG) in incorporating Fe and Mn into the same lattice in the solid solution

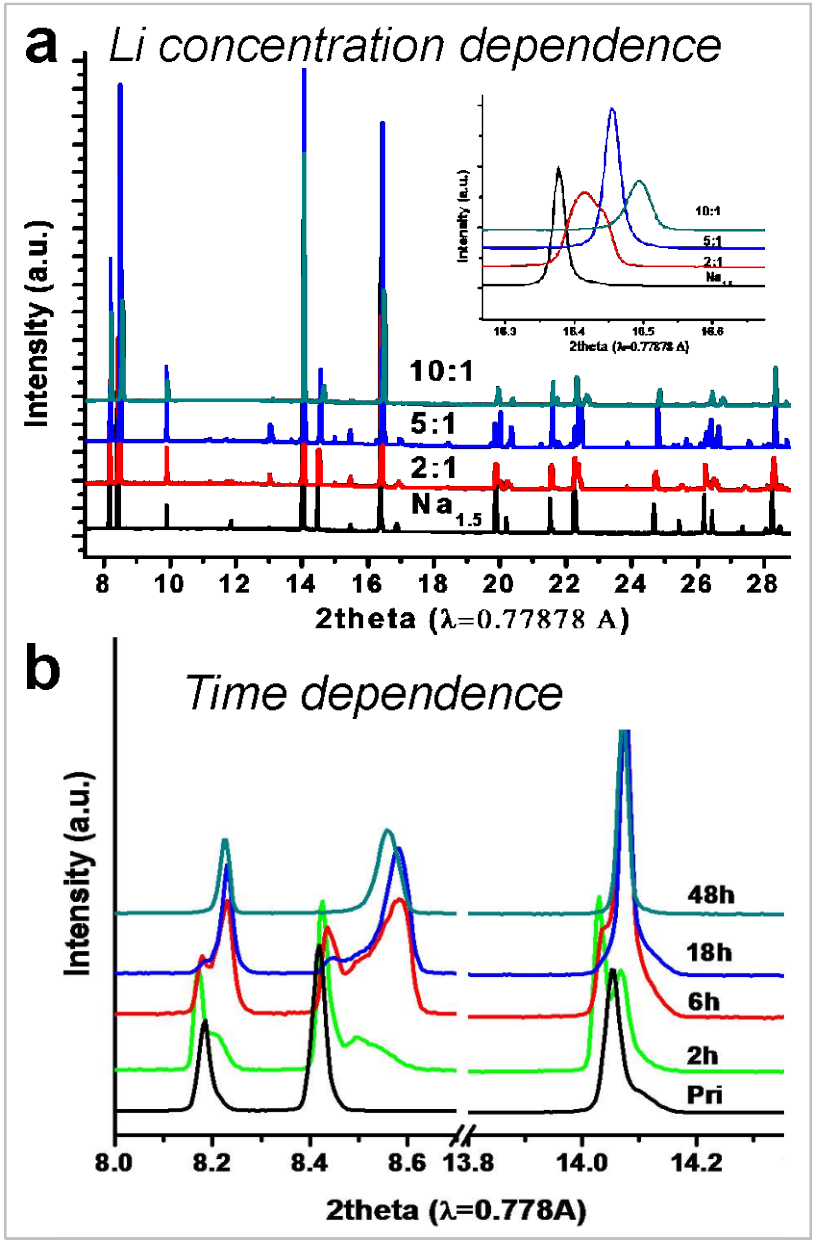
Li(Na)VPO_5F cathodes: *in-situ* synthesis

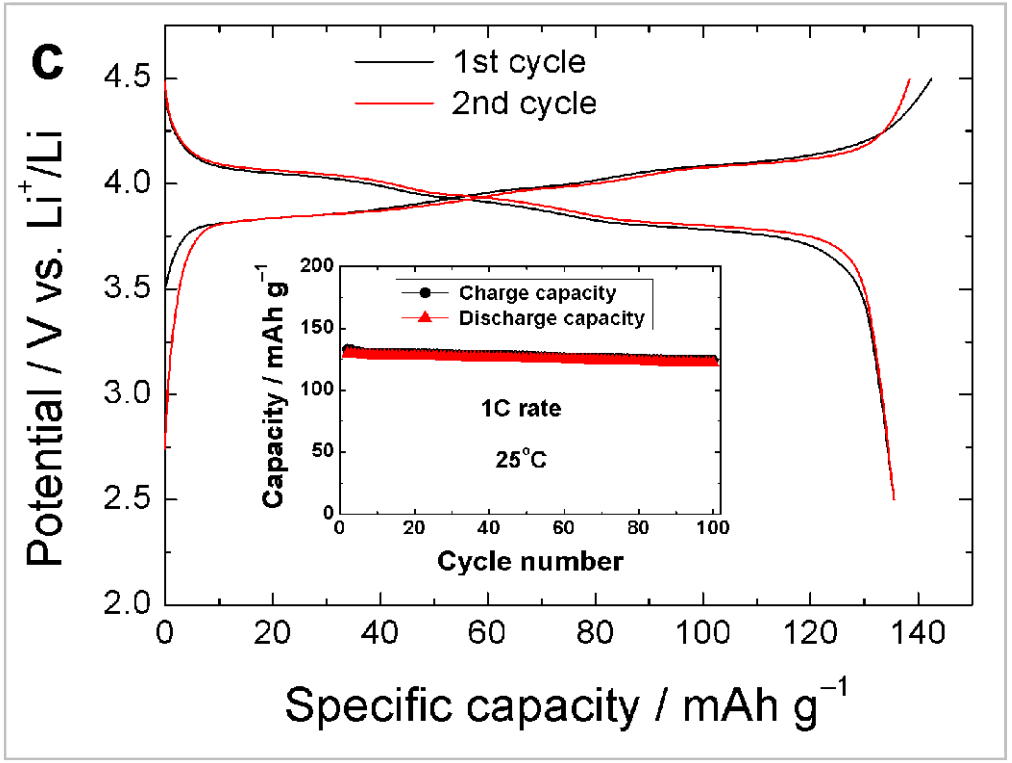




- Synthesis of *um*-sized, single crystalline Li(Na) VPO_5F *via* hydrothermal ion-exchange (*Fig. a*);
- *In-situ* studies of ion exchange process (*Fig. b*).
  - observed complicated phase transformation process
  - identified structures and phases of intermediates and final product
  - determined ion exchange pathway

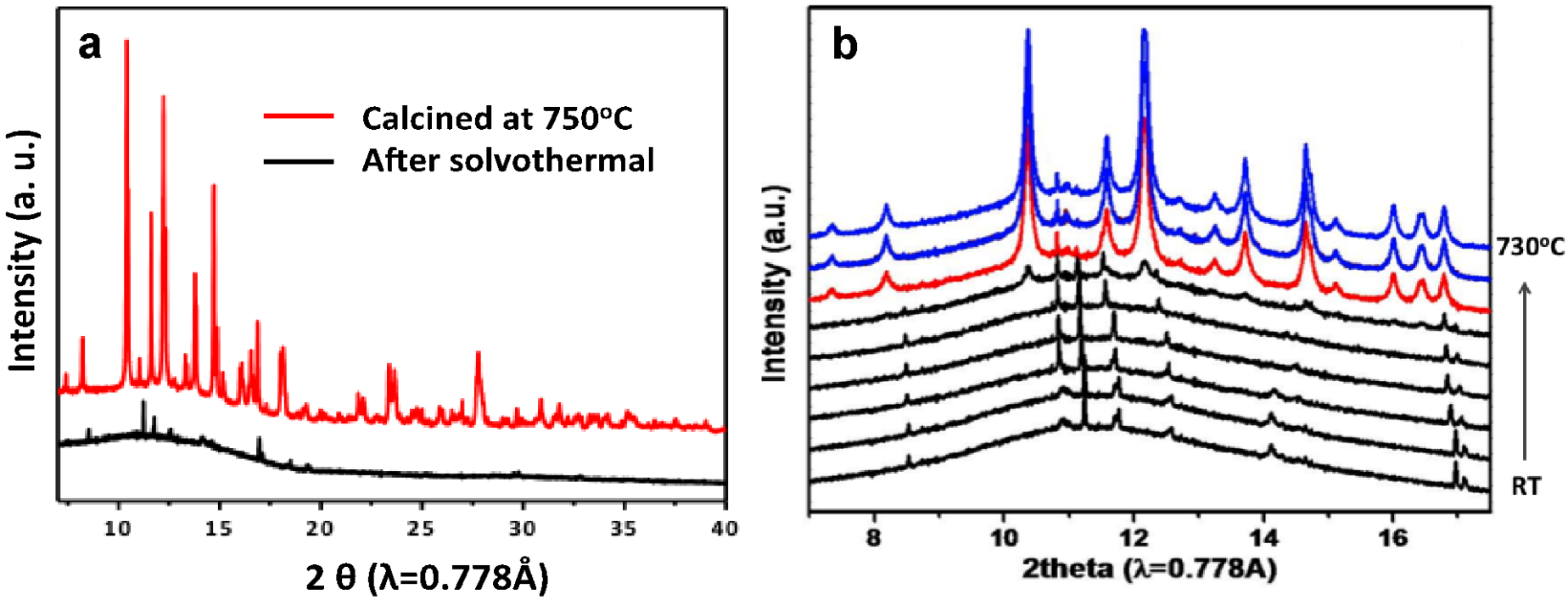
Optimized ion-exchange synthesis of Li(Na)VPO_5F





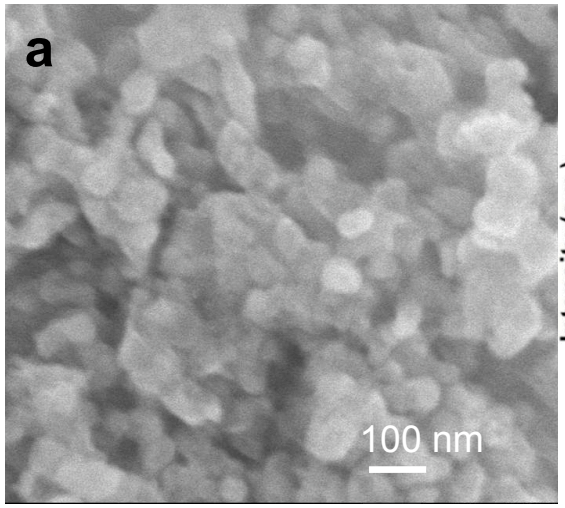
- Determined time, temperature dependence of Li exchange contents (*Fig. a, b*);
- Optimized ion exchange conditions for synthesis of Li(Na)VPO_5F with excellent electrochemical properties (*Fig. c*).

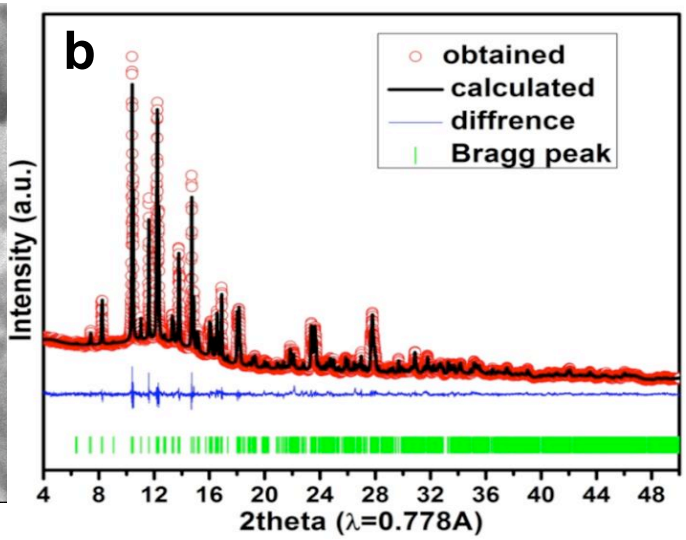
Li-V-PO_4(-X) cathodes: synthesis reactions

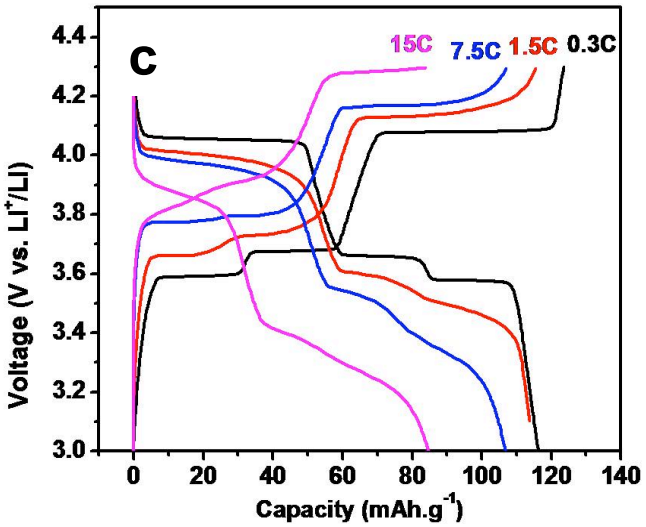


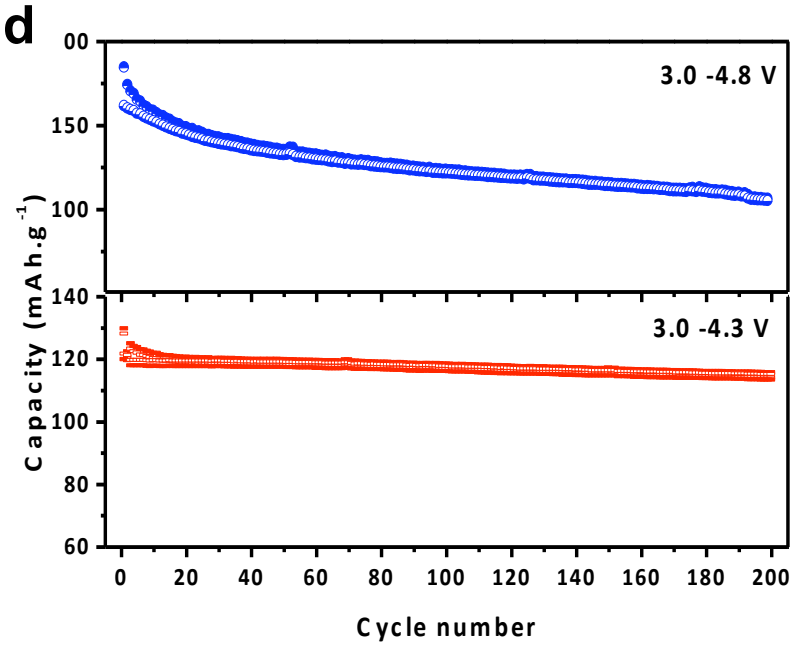
- Developed solvothermal-assisted synthesis of $Li_3V_2(PO_4)_3$ (*Fig. a*)
  - 2-step process, solvothermal followed with calcination
- Determined synthesis reactions *(Fig. b)*
  - *In-situ* XRD, combined with TEM, XANES and EXAFS of V K-edge for measuring the structural evolution and chemical changes
  - Importance of solvothermal process, in reduction of V and formation of an intermediate with local ordering similar to final $Li_3V_2(PO_4)_3$ phase

Structural and electrochemical properties









- Synthesized $Li_3V_2(PO_4)_3$ (*Fig. a, b*)
  - nano-sized, carbon-coated particles;
  - high phase purity.
- Measured reasonable electrochemical properties (*Fig. c, d*)
  - good cycling stability in narrow voltage range (3.0-4.2 V)
  - Higher capacity but poor cycling stability in wide voltage range (3.0-4.8 V).

Collaborations

- Brookhaven National Lab (*J. Bai, L. Wu, Y. Zhu*)
  - Development of *in-situ* reactors and synchrotron techniques;
  - Advanced TEM imaging and spectroscopy of cathodes
- Stony Brook University (*P. Khalifah*)
  - Synthesis of novel Cu-V-O based high-capacity cathodes
- Seoul Nat. U., Korea (*K. Kang*)
  - Synthesis of new high-capacity cathodes
- University of Texas at Austin (*A. Manthiram*)
  - Synchrotron X-ray characterization of high-capacity polyanion cathodes.
- Lawrence Berkeley National Lab (*N. Balsara*)
  - Test of Cu-V-O cathodes in solid batteries
- MIT (*G. Ceder*)
  - *In-situ* synthesis and characterization of high-capacity cathode materials
- HRL Lab (*J. Graetz*)
  - Synthesis and characterization of high-capacity cathode materials
- SUNY, Binghamton (*S. Whittingham*)
  - Synthesis and Synchrotron characterization of high-capacity cathode materials
- *NECCES* EFRC at Stony Brook University
  - *In-situ* TEM, NMR, magnetization characterization.

* We also participate in the Si focus group, collaborating with Brett Lucht (U. Rhode Island), Shirley Meng (UCSD), Gao Liu (LBNL) on studying degradation mechanisms of Si anodes.

Future work in FY14/FY15

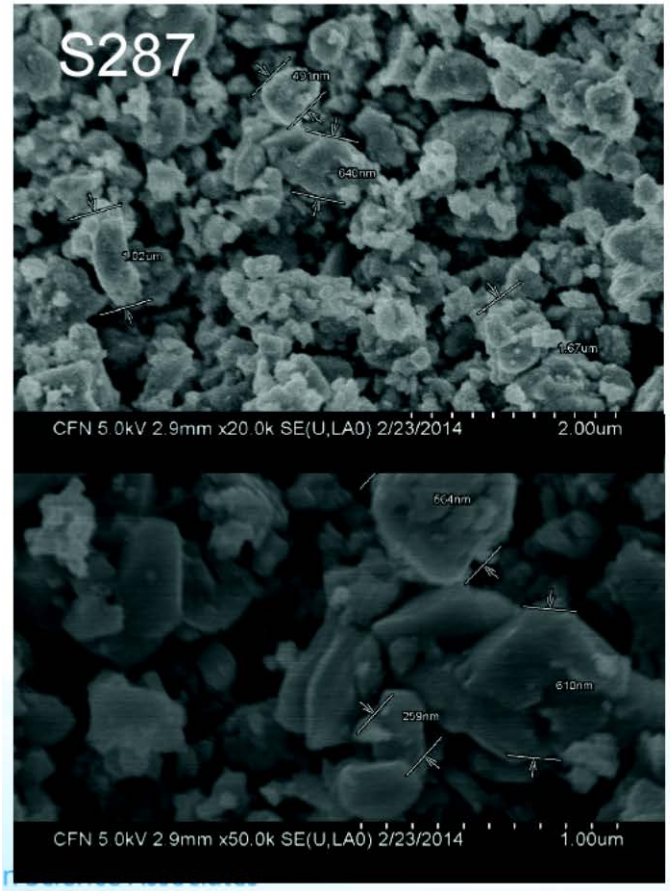
- Continue the investigation of Li(Na)VPO_5F_x cathodes
  - explore the phase diagram in the space of temperature and Li concentration, *via in-situ* ion-exchange studies
  - optimize synthesis to maximize the Li capacity
  - Measure structural and electrochemical properties
- Develop new polyanion-type cathodes
  - optimize synthesis of Li-V-PO_4 cathodes
  - synthesize ternary and quaternary lithium vanadium phosphates, Li-V-PO_4(-X)
- Continue the investigation of new α-CuVO cathodes
  - complete structural and electrochemical characterization
  - test electrochemical performance of α-CuVO in polymer electrolyte, in collaboration with Balsara group at Lawrence Berkeley National Lab
- Continue to develop advanced diagnostic techniques for studies of synthesis reactions during preparation of cathode materials and lithium reactions in electrodes.

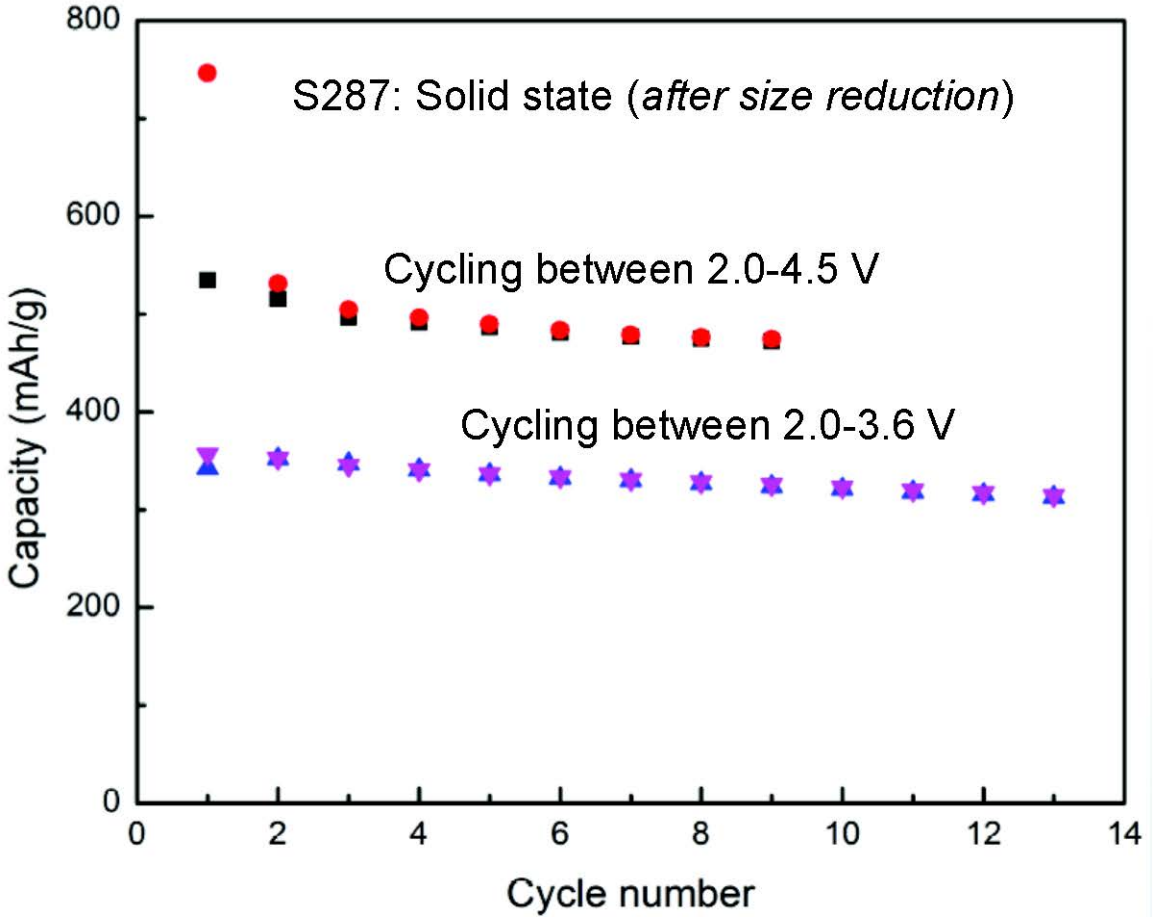
Summary

- **Relevance** Develop low-cost cathode materials with energy density and electrochemical properties (cycle life, power density, safety) consistent with USABC goals.
- **Approach** Developing new cathodes *via* synthesis, along with structure-property evaluation and diagnostics. Specialized *in-situ* reactors, *time resolved* XRD techniques were developed and utilized for studies of synthesis reactions and thereby optimizing procedures for making materials of desired phases and properties.
- **Technical Accomplishments** Synthesized Cu-V-O, Li-Fe-Mn-PO_4, Li-V-PO_4(-X) cathodes with optimized procedures, and made good progress in in-depth structural and electrochemical analysis of these compounds.
- **Collaborating Research** Established extensive collaborations within BATT and with external partners on development and utilization of advanced synchrotron x-ray and TEM techniques for studies of synthesis reactions during preparation of cathode materials and lithium reactions in electrodes.
- **Future work** Continue our efforts on synthesis and characterization of high-capacity cathodes, with an emphasis on polyanion-type materials.

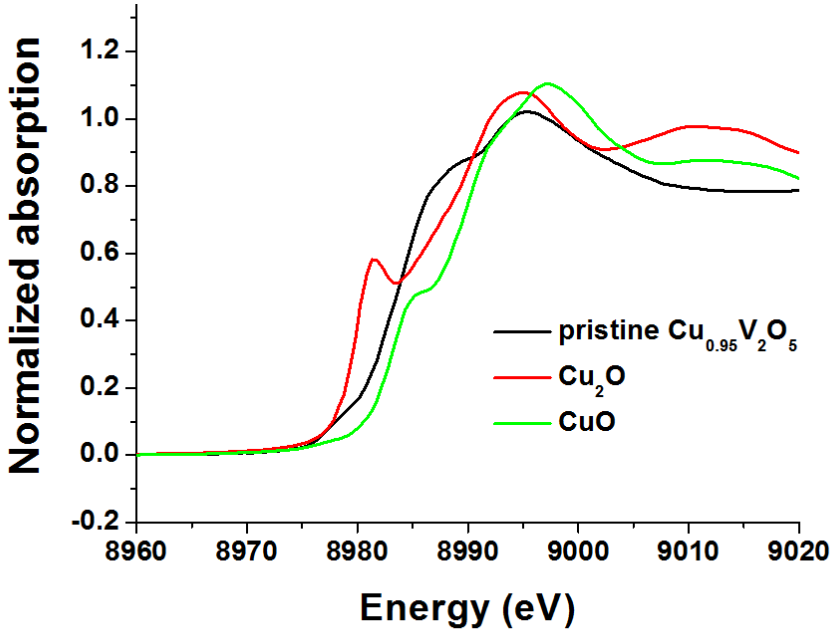
Technical Back-Up Slides

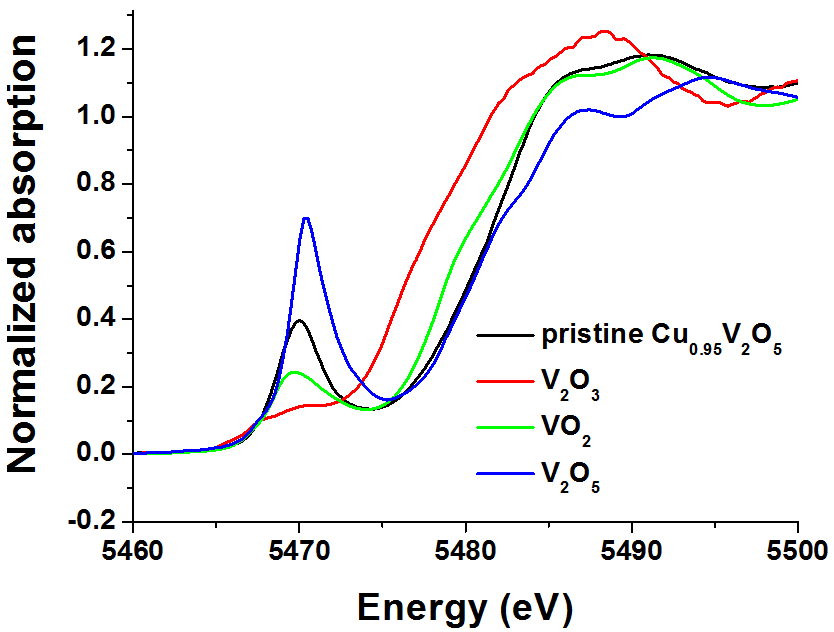
New Cu-V-O cathode: electrochemical performance

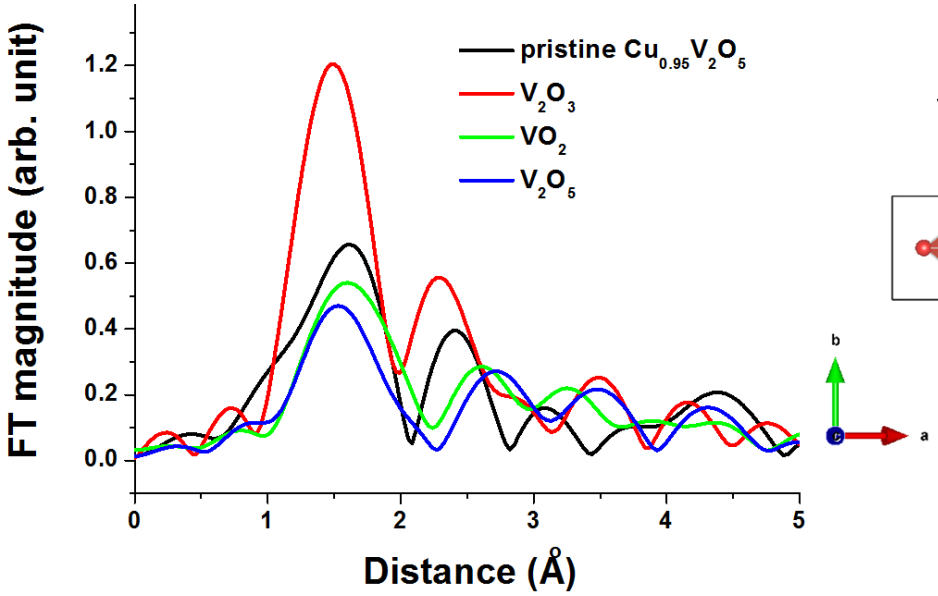


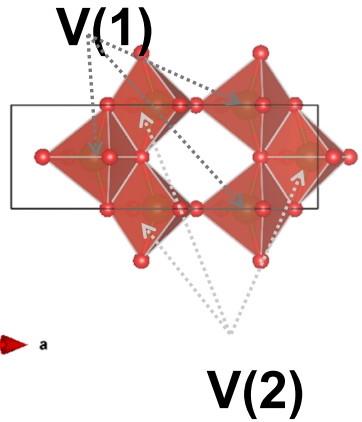


CuVO: reference XAS spectra









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