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: 75%

Barriers

- Low energy density
- Cost
- Cycle life

Budget

- Total project funding
  - DOE 100%
- Funding received in FY14

  $ 304K
- Funding for FY15

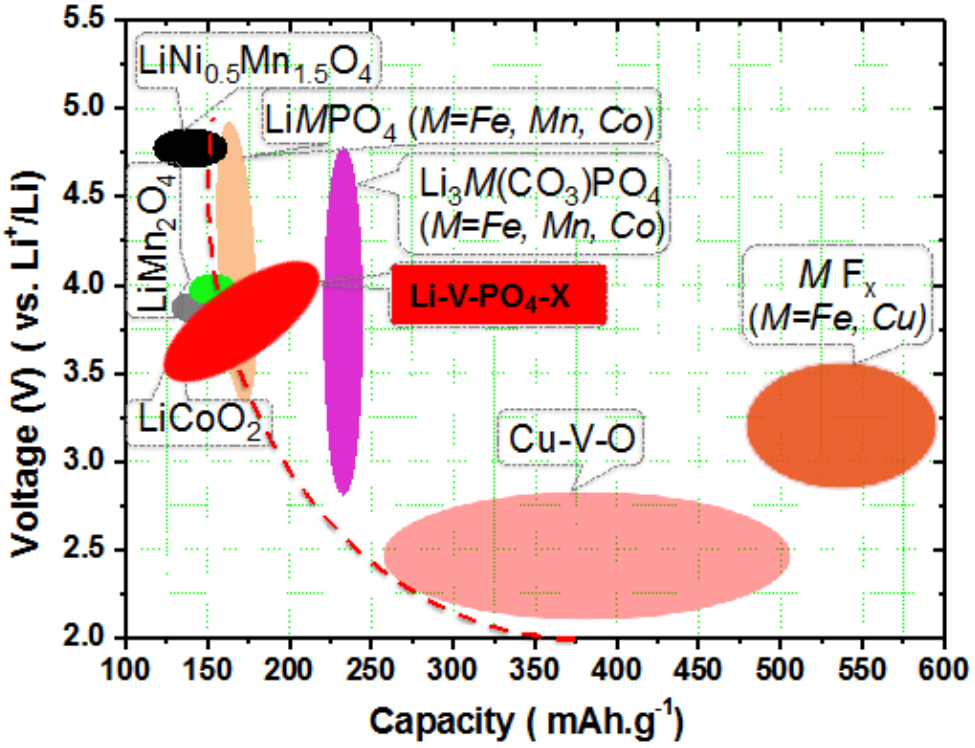
  $ 304 K

Partners

- Interactions/collaborations
  - Brookhaven National Lab
  - Lawrence Berkeley National Lab
  - Oak Ridge National Lab
  - Stony Brook University
  - 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 FY14/15 was focused on developing polyanionic cathodes (*Li-V-PO_4-X*)

- *multi-valent redox (V)*
- *high voltage (PO_4)*
- *open/stable framework (➔ high Li^+ mobility)*

➢ High energy/power density

** small effort on Cu-V-O and Cu-Fe-F cathodes of extremely high-capacity.*

Milestones

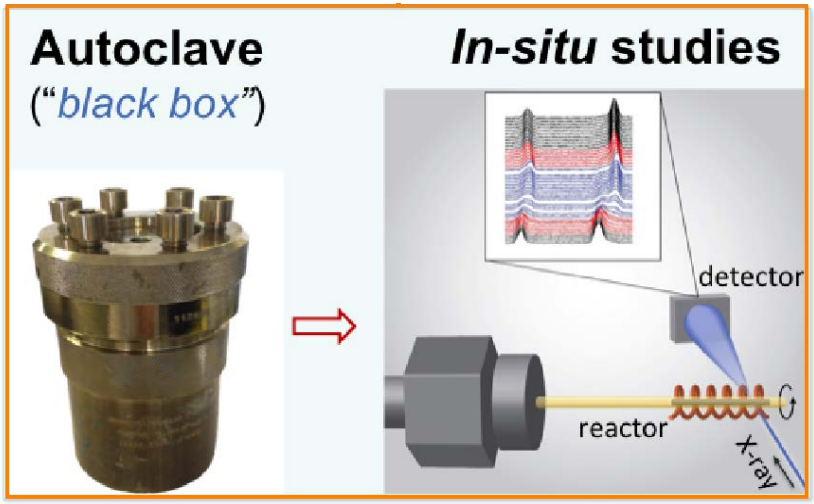
Time	Description (*status*)
Mar 14	Develop synthesis procedures to prepare Li-V-PO_4 cathodes (*complete*)
May 14	Optimize the synthesis and characterize the structural and electrochemical properties of 2nd class of Cu-V-O cathode (*complete*)
Sept 14	Develop synthesis procedures to prepare Li-V-PO_4-X cathodes, and electrochemically characterize at least one Li-V-PO_4-X compound (*complete*)
Dec 14	Determine the reaction pathways and phase evolution during hydrothermal ion exchange synthesis of Li(Na)VPO_5F_x cathodes *via in-situ* studies (*complete*)
Mar 15	Optimize ion exchange synthesis for preparing Li(Na)VPO_5F_x with maximized Li content, and characterize its structural and electrochemical properties (*complete*)

Approaches

Electrochemical performance of cathodes is often limited by the phases, stoichiometry and morphology of the active materials.

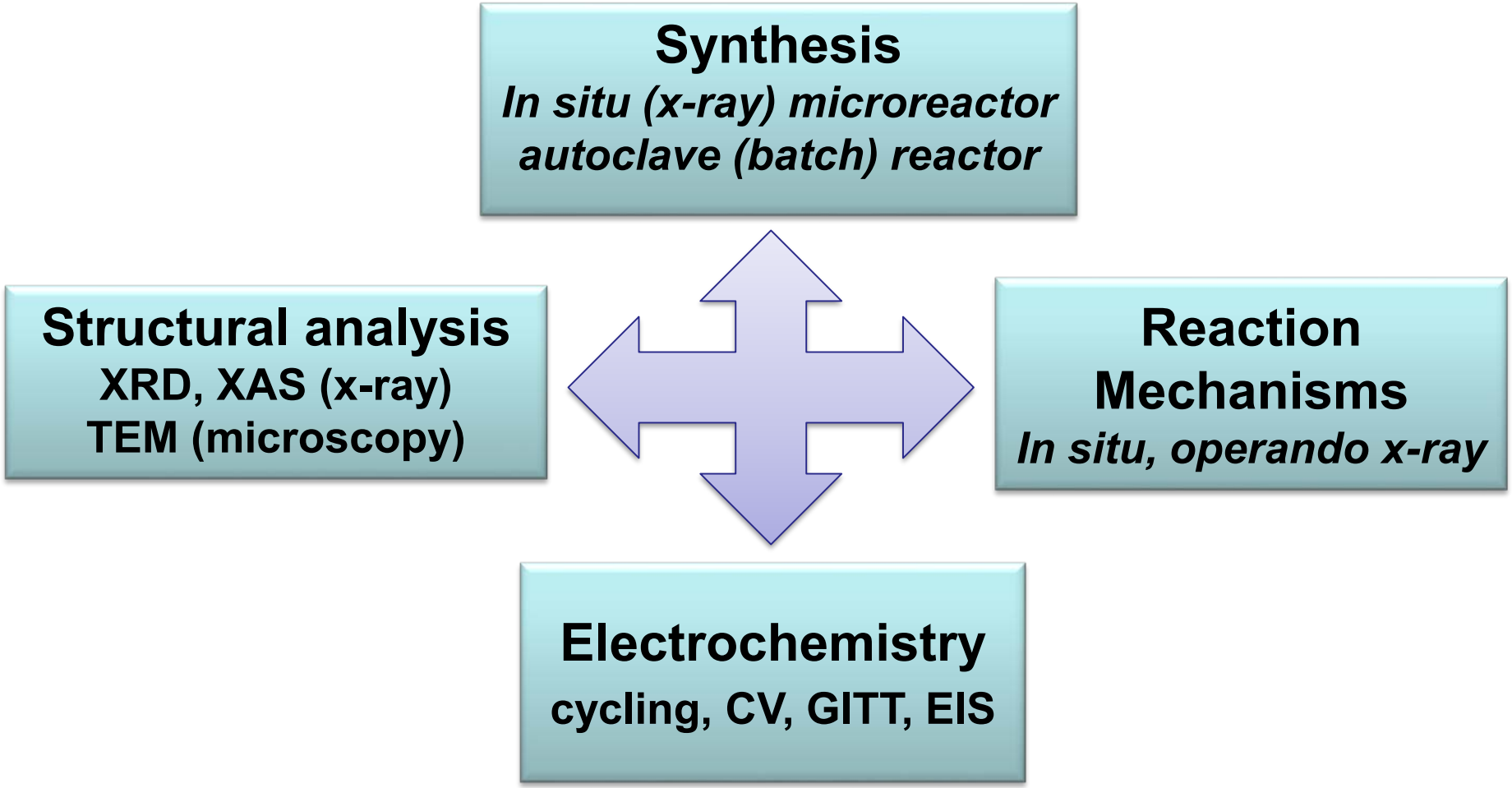
Cathode performance can be advanced by

- **synthesis of phase-pure materials**
- **control of stoichiometry, morphology**



We have developed tools and techniques for *in-situ*, *real time* studies of synthesis reactions that provide deep insights into synthesis reaction pathways.

Develop new cathodes *via* synthesis, structural, electrochemical analysis and mechanistic studies:



- Enabled by *on-site* resources and facilities at BNL, along with *in-house* developed *in-situ* capabilities (**see the backup slides*)

Technique development: *in-situ* reactors

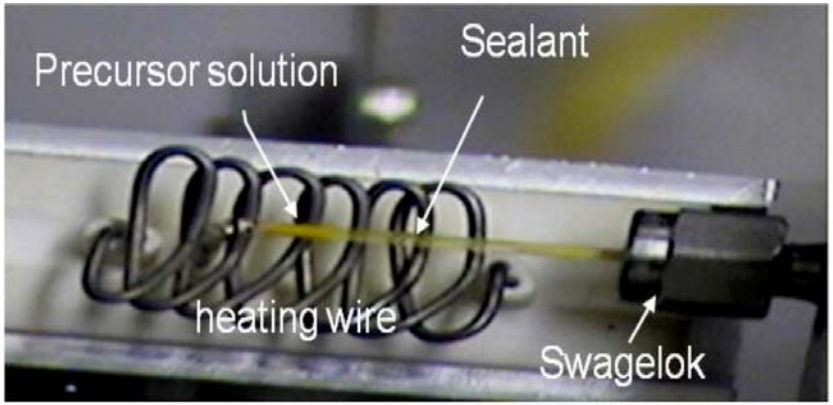
Time-resolved XRD enables synthetic control of the structure and properties of cathode materials

- determine intermediates and reaction pathway
- 'dial in' desired phases and material properties
- build up 'phase diagrams' in the composition space

Micro-reactors and time resolved synchrotron X-ray techniques were developed for controlled synthesis

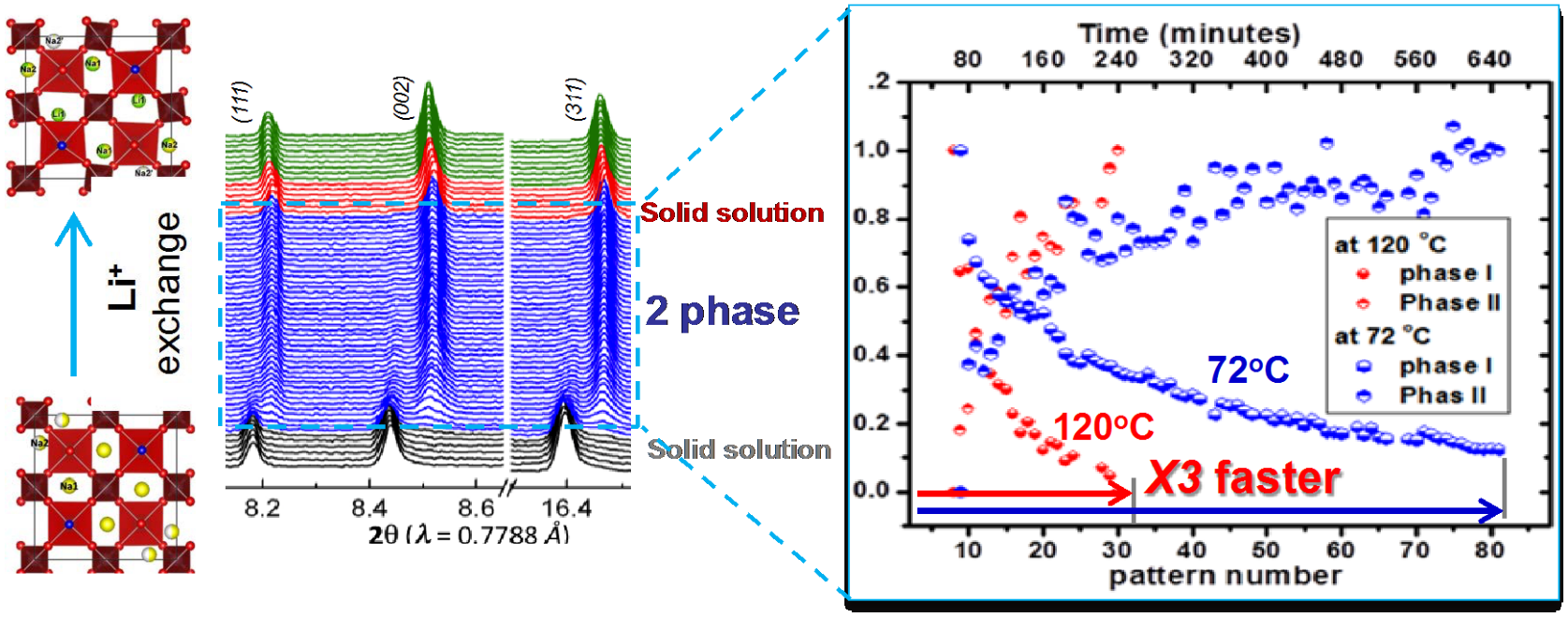
Micro Reactors cover broad synthesis space

- All major synthesis techniques
- Wide temperature and pressure



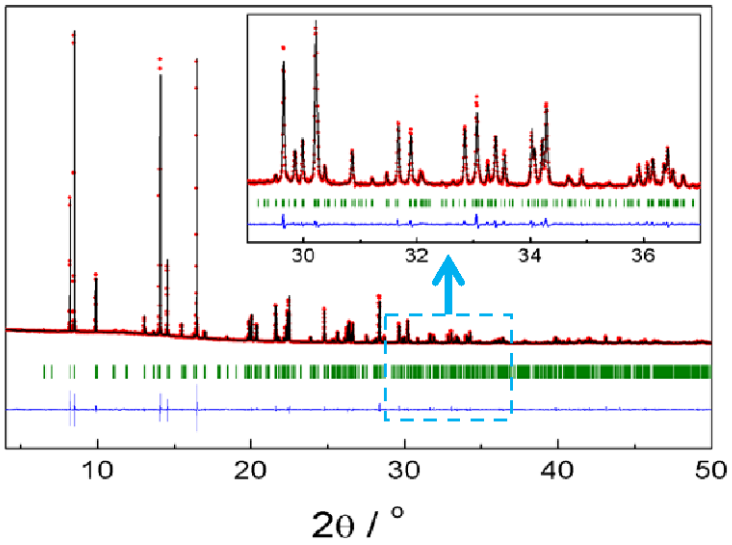
X-ray *"in-situ"* reactor

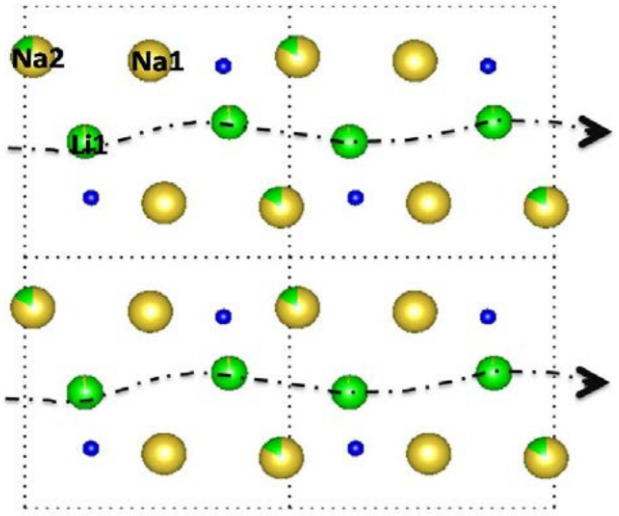
Ion-exchange synthesis of $Li(Na)VPO_5F_x$

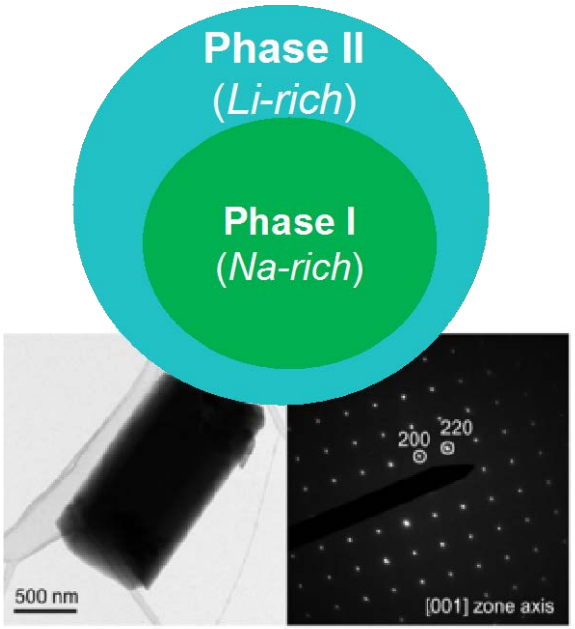


- Established *in-situ* techniques for probing ion exchange;
- Determined multiple phase transformations/reaction kinetics
  - 2-phase transformation *(tetragonal ➔ orthorhombic)* can be a rate-limiting step, and highly impacted by temperature;
- Determined thermodynamic aspects of exchange *(backup sides).*

Structural aspects of limiting Na^+/Li^+ ion exchange



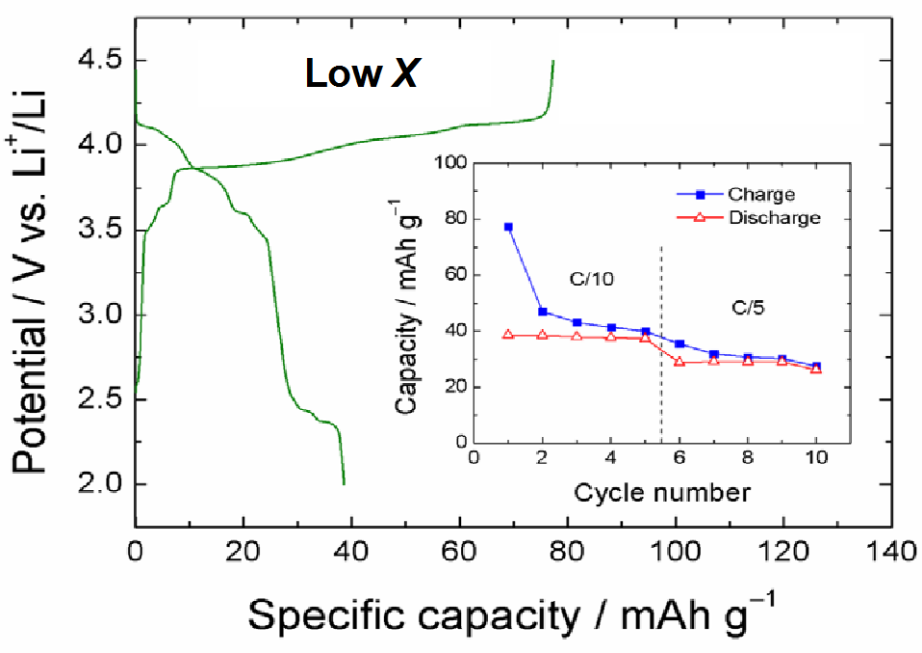


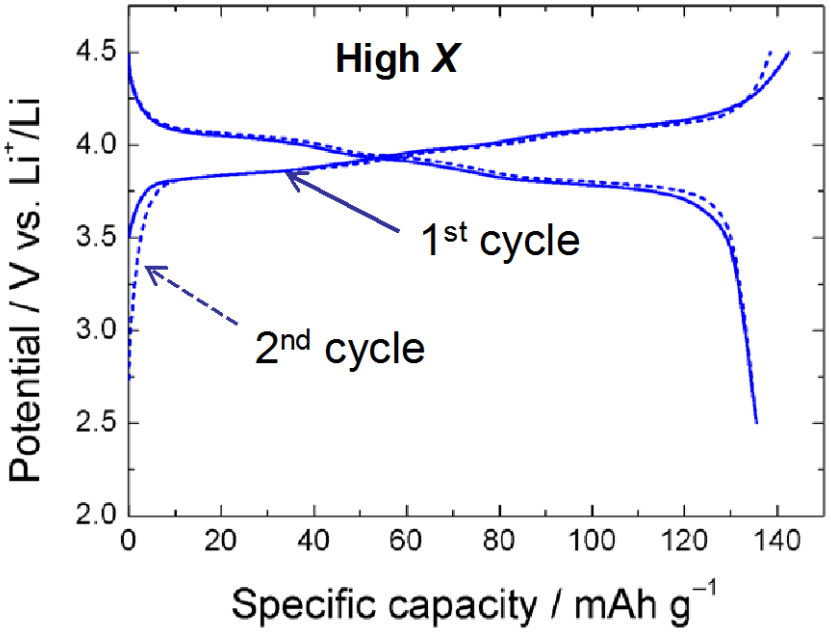


- <u>Quantitative structure analysis</u> by synchrotron X-ray and neutron diffraction, coupled with *refinement*
  - Identified Na^+/Li^+/vacancy ordering
- Single-particle TEM imaging/diffraction
  - *local* phase distribution

➢ shed light on the *thermodynamics* and *kinetics* of ion exchange in $Li(Na)VPO_5F_x$.

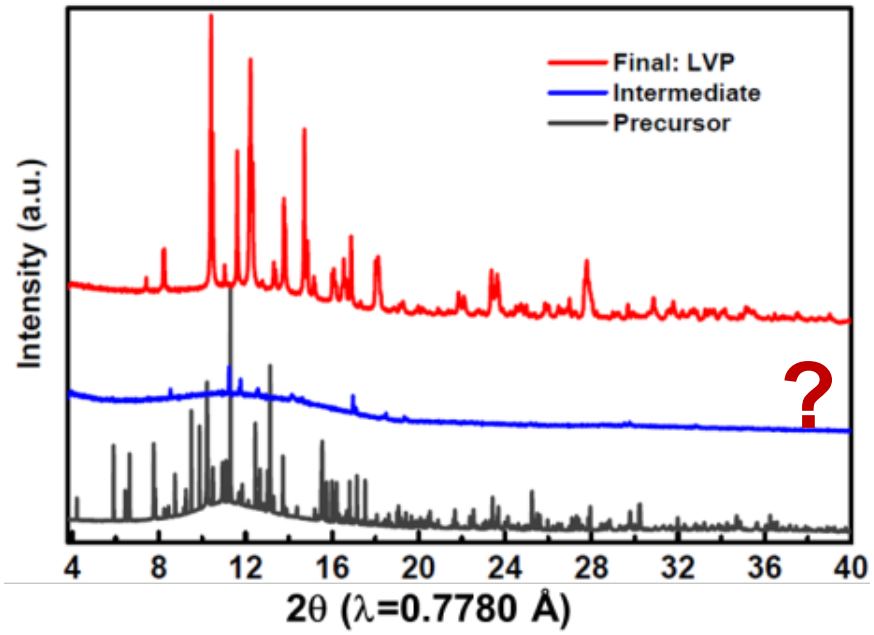
Optimized synthesis of $Li_xNa_{1.5-x}VPO_5F_{0.5}$

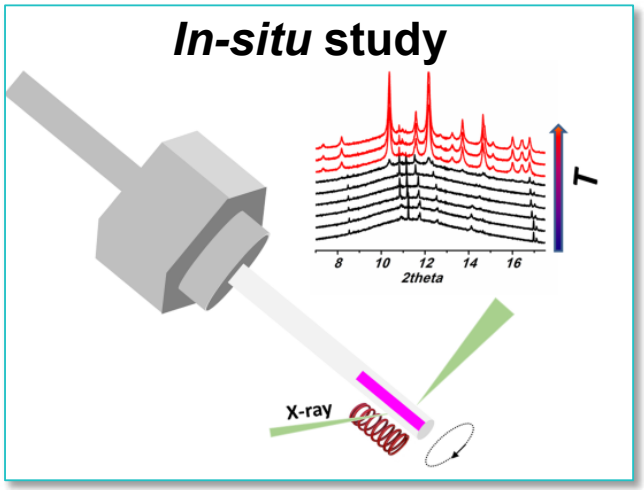


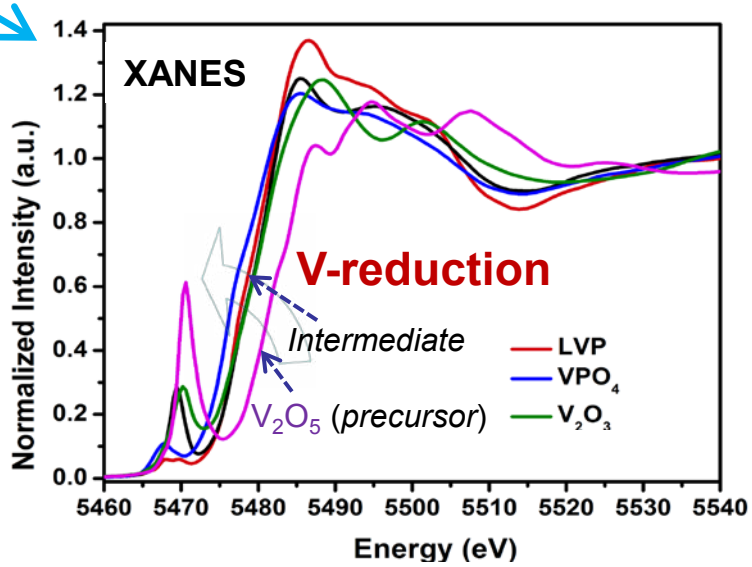


- Determined dependence of exchange process on the synthesis parameters *(temperature, Na/Li ratio, LiBr concentration…);*
- Optimized the synthesis procedures to obtain the $Li_xNa_{1.5-x}VPO_5F_{0.5}$ of high Li capacity and cyclability
  - ➢ *via maximizing Li content in the exchanged phase*

Structure tracking-aided synthesis of Li-V-PO_4

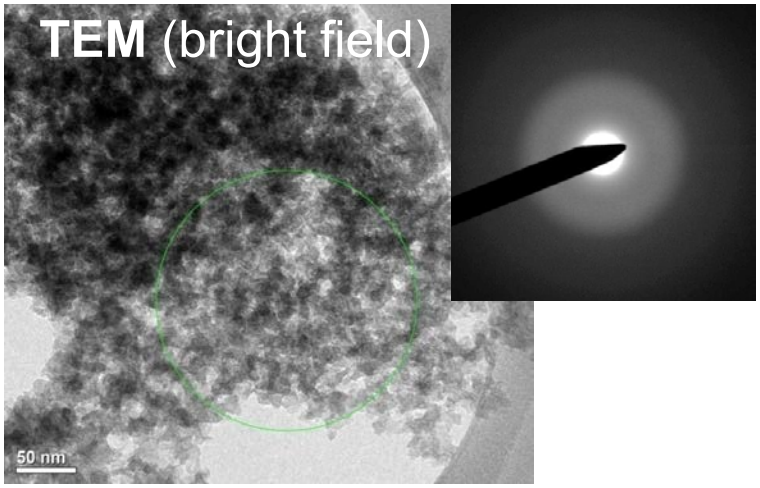




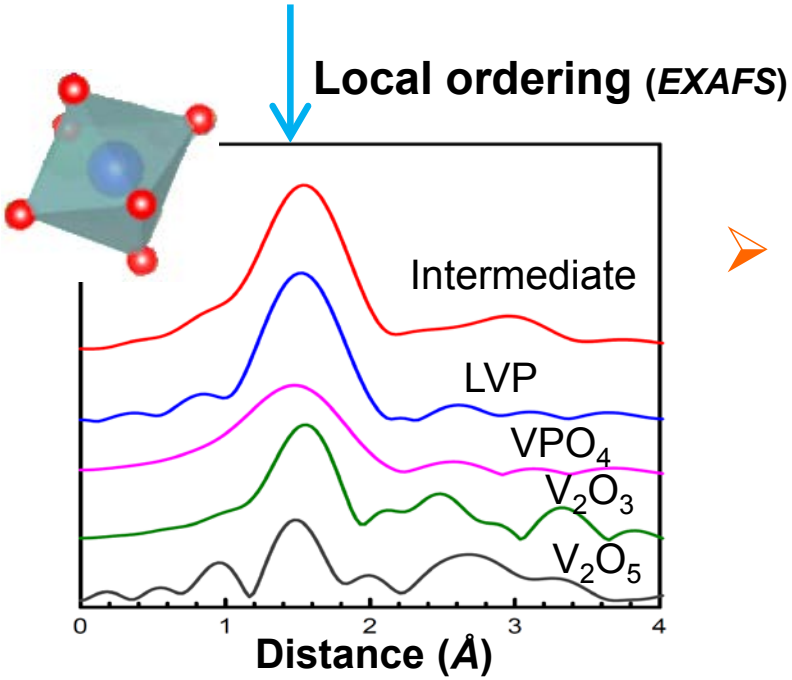


- Developed structure tracking-aided synthesis approach for obtaining $Li_3V_2(PO_4)_3$ (LVP) nanocrystals
  *(*solvothermal step: amorphous intermediate but with V reduction)*

Local structural reorganization of the intermediate:

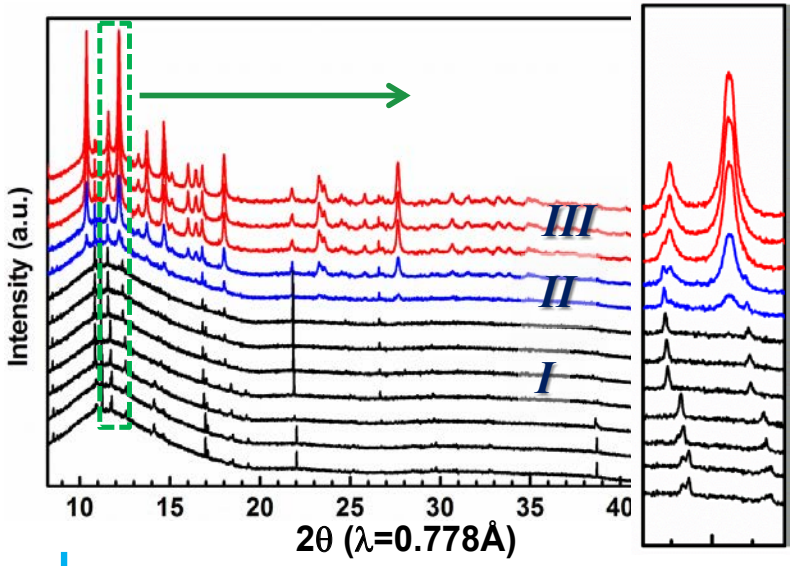


- Solvothermal treatment leads to *disordered*, *highly-mixed* phases (at *nm* scale).

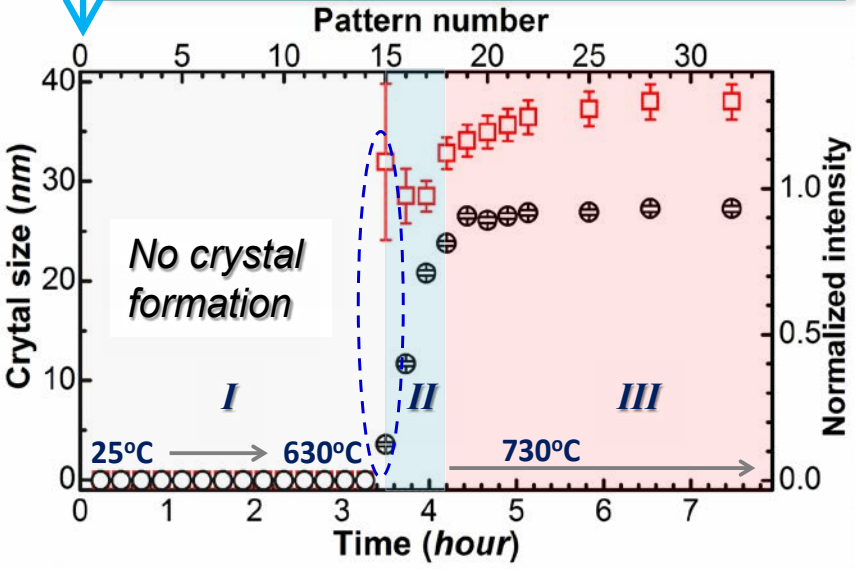


- Local structural re-organization of intermediate, with short-range ordering (*i.e.* VO_6 octehedra) resembling that of the final LVP phase.

Crystal growth monitored in *real time* during calcination



quantitative analysis (***via* refinement**)



***Time-resolved in-situ* XRD to get information about**

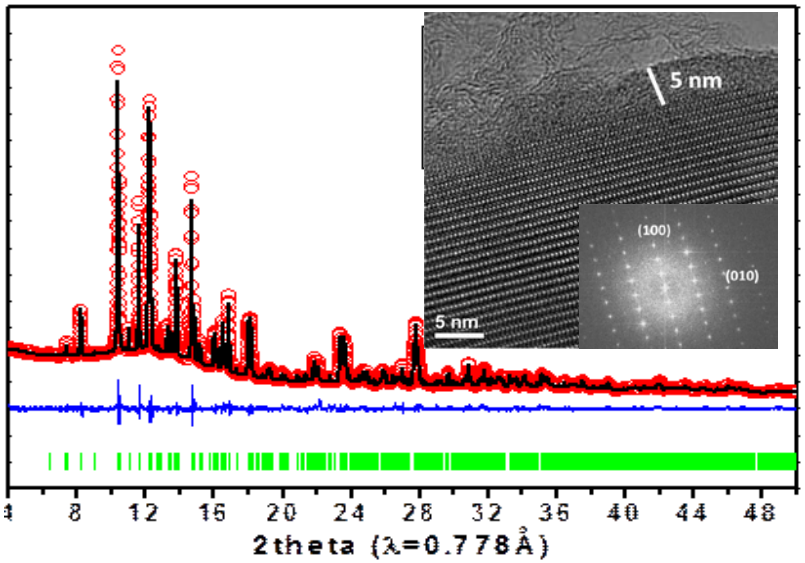
- *thermodynamics*
- *growth kinetics*

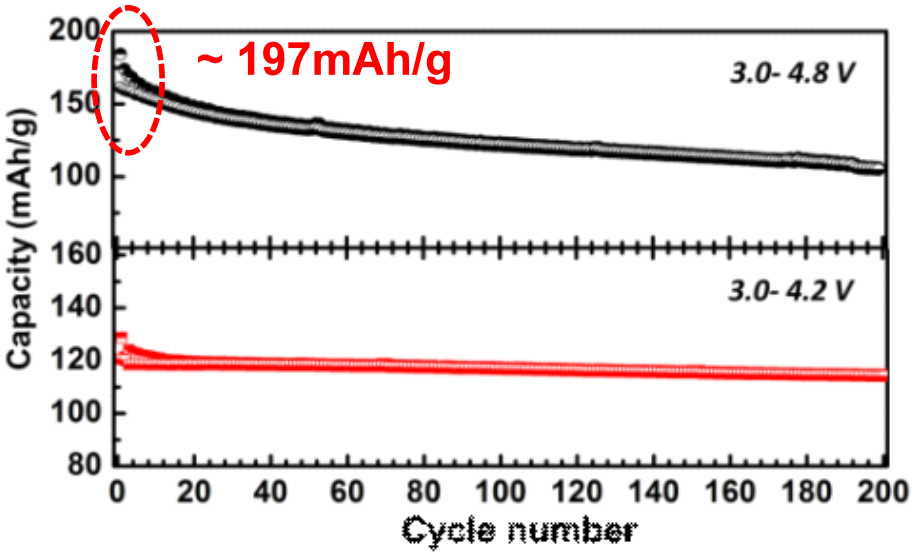
"Nanocrystallization" from amorphous intermediate

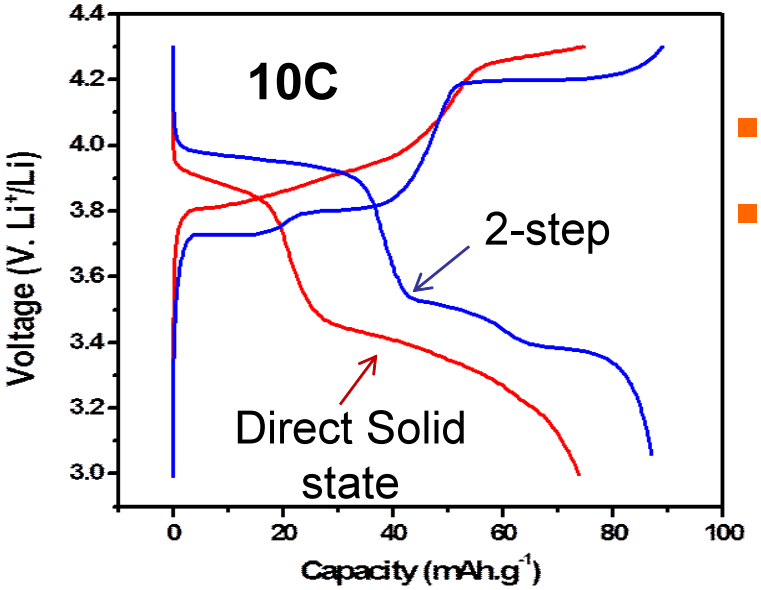
- quick formation of crystals within minutes *(*below* 730°C)

➢ *optimize conditions (i.e. time, temperature) for low cost.*

Synthesized LVP nanocrystals *via* 2-step protocol:

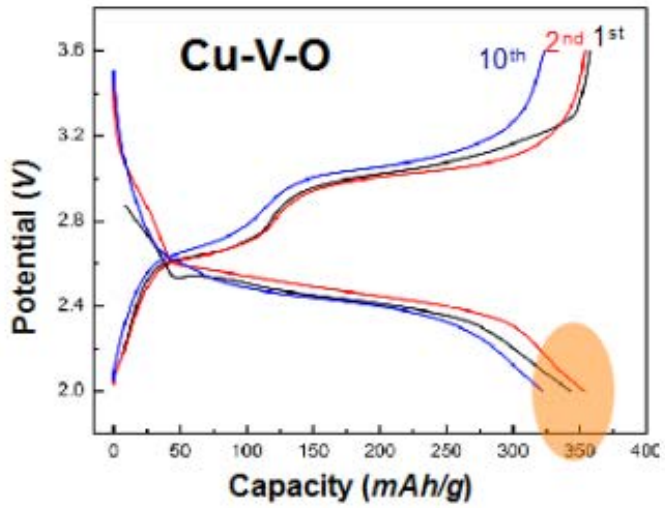


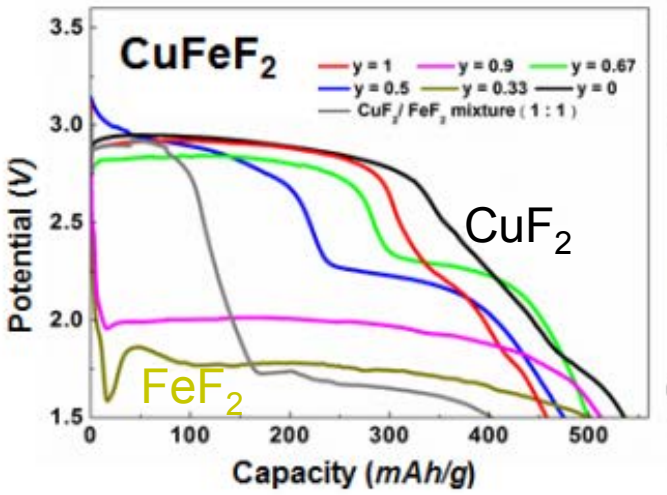


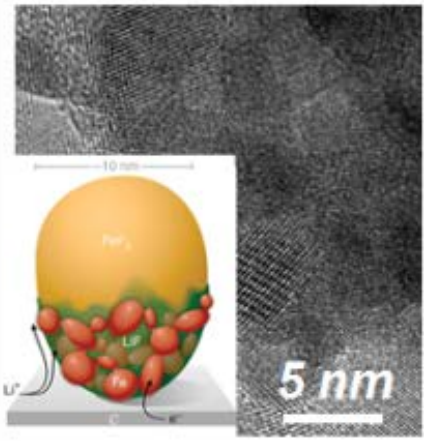


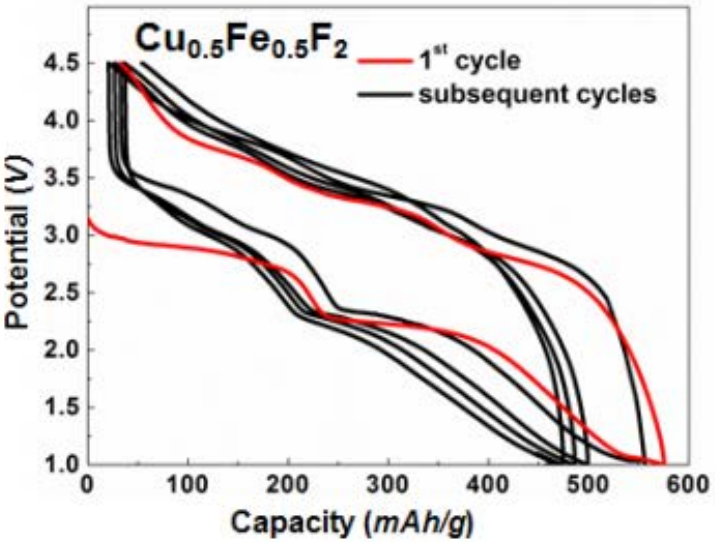
- **High phase purity (*monoclinic*)**
- **Single crystalline/small size**
  - achieve excellent cycling stability and rate capability *via synthetic control.*

New vanadates and fluorites as cathodes









(***Nat. Comm.*** *6: 6668 (2015)*)

Multiple e- reaction (MER) for achieving high capacity (**volumetric density* > *Li-S*)

- identified two MER cathode systems:
  - Cu-V-O (~*350 mAh/g*)
  - $Cu_xFe_{1-x}F_2$ (*500 mAh/g*)
- measured reasonable cyclability in liquid electrolyte (**and improvement in solid electrolyte*)

Response to the Reviewers

Comment: Reviewers expressed concerns regarding Cu-V-O based cathodes and Li-Fe-Mn-PO4 system: "--*Cu-V-O system is not new" and "Li-Fe-Mn-PO4 is sufficiently matured and has low specific energy*".

- Response: we have concluded our efforts on Cu-V-O and Li-Fe-Mn-PO4 systems, and focus on

  -- Li-V-PO_4-X type cathodes (e.g. Li(Na)VPO_5F, $Li_3V_2(PO_4)_3$)

Comment: "*the analysis for identifying structures and crystallinities during the synthesis process have not been fully explored*"

- Response: we have made efforts on

  -- in-depth structural analysis with refinement

  -- exploration of the phase diagram via in-situ studies

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
- **Lawrence Berkeley National Lab (*N. Balsara*)**
  - Tests of Cu-based cathodes in solid batteries
- **Oak Ridge National Lab (*J. Nanda*)**
  - Synthesis and characterization of new cathode materials
- **Stony Brook University (*P. Khalifah*)**
  - Synthesis of novel Cu-V-O based high-capacity cathodes
- **Seoul Nat. U. (*K. Kang*)**
  - Synthesis of new high-capacity cathodes
- **University of Texas at Austin (*A. Manthiram*)**
  - Synchrotron X-ray characterization of high-capacity polyanion cathodes.
- **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
- ***m2M* EFRC at Stony Brook University (E. Takeuchi)**
  - *In-situ* TEM studies of ionic transport at liquid-solid interfaces

Remaining Challenges and Barriers

- The reversible capacity of currently available Li-V-PO4-X compounds (*i.e.* $Li_3V_2(PO_4)_3$, Li(Na)$VOPO_4F$) is low. This requires developing new phases of V based phosphates, with a second anion group (X) being incorporated to enable > 1e redox reaction.
- The cycling stability of the Cu-containing fluorites and vanadates is low mostly due to the Cu dissolution, which may be largely mitigated or eliminated in solid batteries.
- New *in-situ* tools and techniques are needed to track the structural evolution of all the involved phases, including amorphous/disordered phases during synthesis.

Future work in FY15/FY16

- Develop new high-capacity Ni-Mn based oxides cathodes, by
  - exploring synthesis approaches of making new Ni-Mn based layered and/or spinel phases
  - *in-situ* studies of the synthesis reactions
  - electrochemical/structural characterization of the synthesized materials
- Continue the investigation of high-capacity polyanionic cathodes
  - complete the *in-situ* studies of ion-exchange mechanisms
  - build the phase diagram of Li(Na)VOPO4F in the space of temperature and Li concentration
  - improve the electrochemical properties of $Li_3V_2(PO_4)_3$ nanocrystals
  - search for new high-capacity Li-V-PO_4-X cathodes
- Explore new fluorites and vanadates for potential use as cathodes
  - develop synthesis procedures for making new compounds, *and*
  - evaluate the structural/electrochemical properties for their use as viable cathodes
- Develop new reactor design to enable high-throughput synthesis of phase-pure cathode materials

Summary

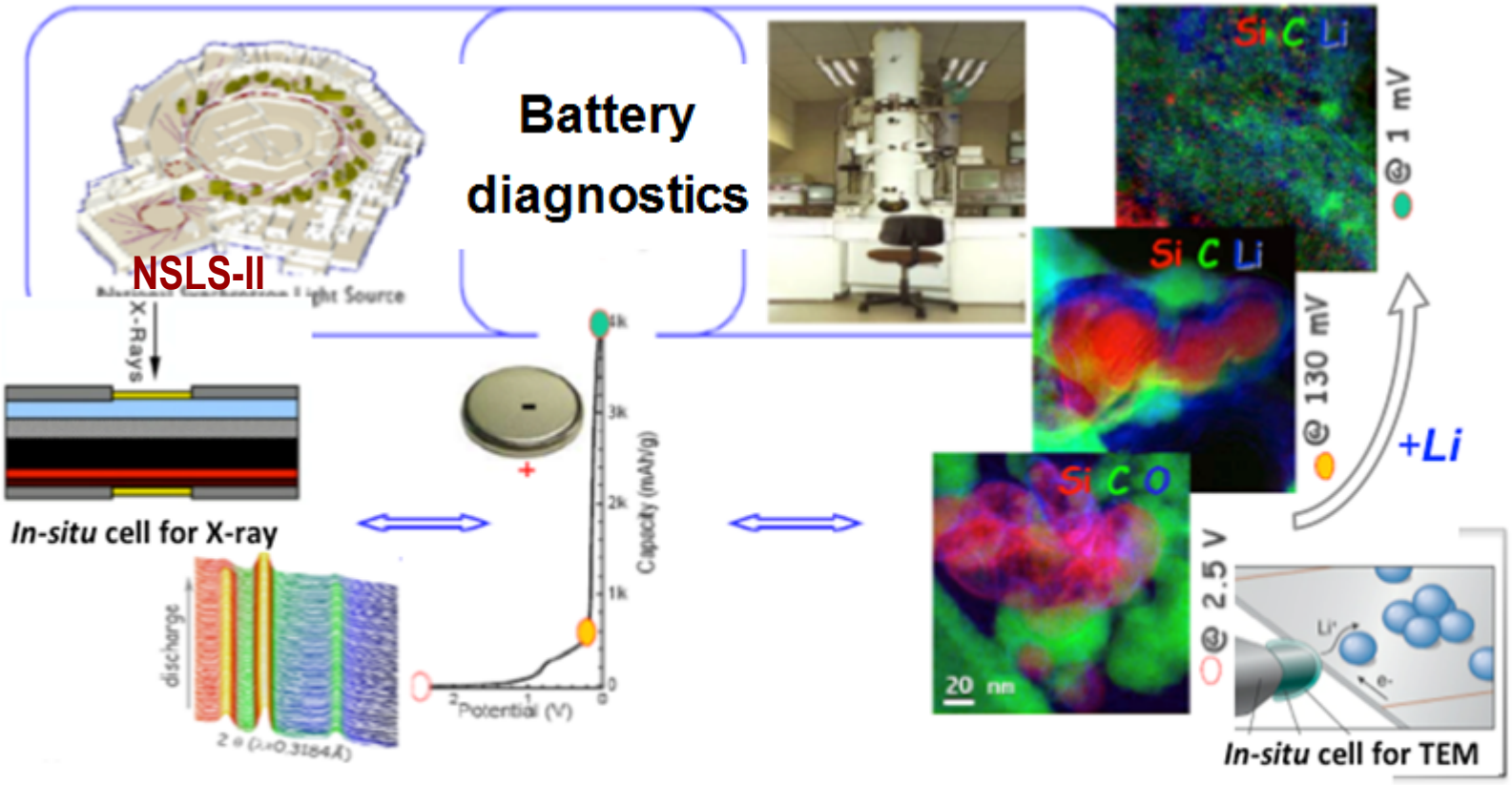
- **Approach** Developing new cathodes *via in-situ* synthesis, along with structure-property evaluation

  -- new *in-situ* reactors, *time resolved* synchrotron techniques were developed and utilized for studies of synthesis reactions and have been applied for optimizing synthesis and discovering new cathodes.

- **Technical Accomplishments** Built on *in-situ* studies of solvothermal, ion-exchange and solid state reactions, we have developed low-temperature, cost-efficient procedures for making several interesting cathode materials:
  - $Li_3V_2(PO_4)_3$ nanocrystals of high power density
  - $Li(Na)PO_5F$ of maximized Li content and optimized electrochemical properties
  - Cu-V-O and $CuFeF_2$ cathodes of extremely high capacity
- **Collaborating Research** We have established extensive collaborations within BMR and with external partners on development and utilization of synchrotron X-ray and TEM techniques for studies of synthesis reactions in preparation of cathodes and electrochemical reactions in electrodes.
- **Future work** Continue our efforts on synthesis and characterization of new cathodes, with high capacity (> 200 mAh/g).

Technical Back-Up Slides

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



Synchrotron x-ray
studies of Li reaction, charge transfer @ electrode level.

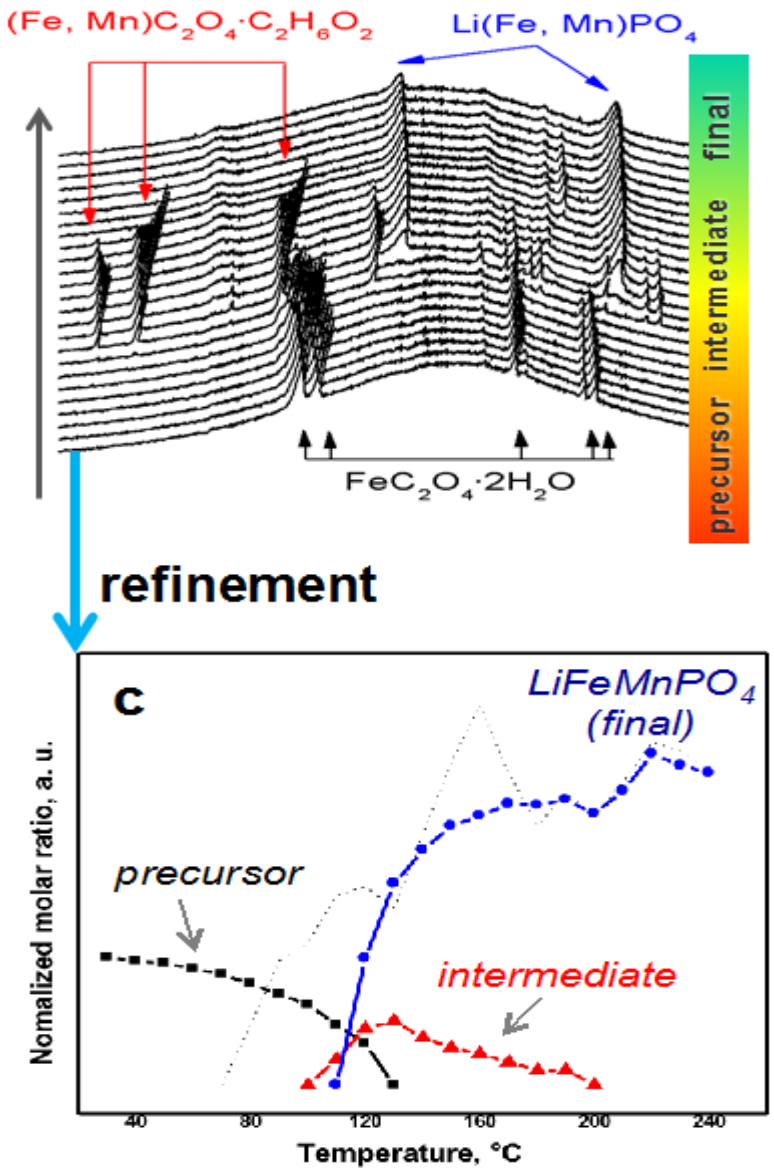
Electrochemistry

(*Functionality*)

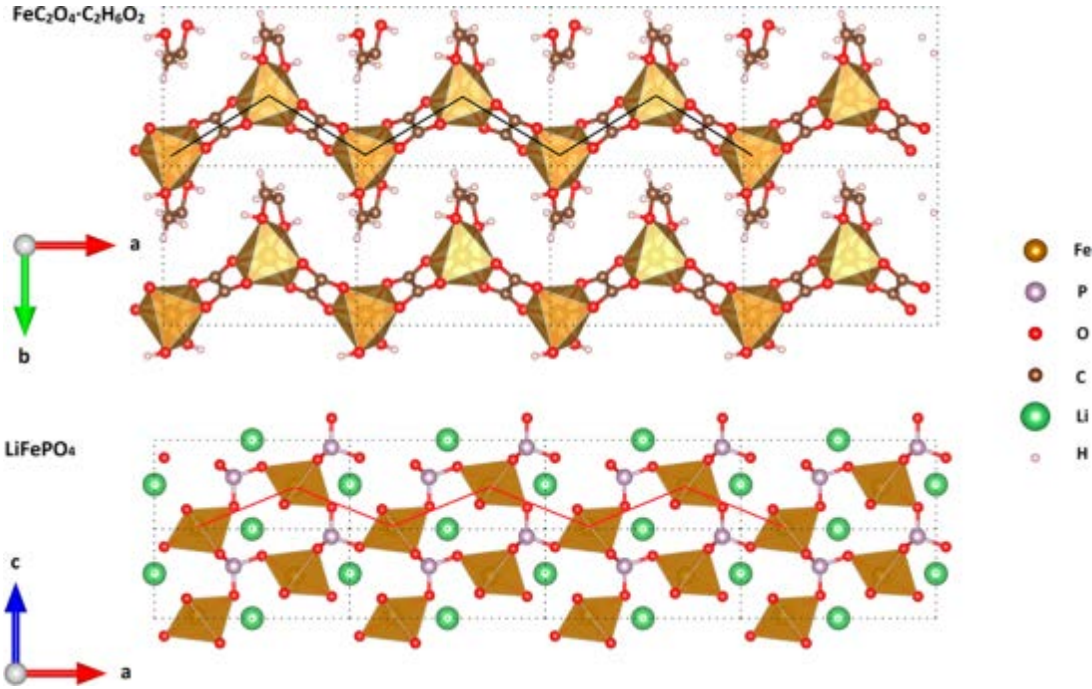
TEM-EELS
tracking Li transport, reactions *@single-particle level.*

*__Ref.__: F. Wang et al., *Adv. Energy Mater.* 3 (2013) 1324; *Nat. Comm.,* 3 (2012)120 & 6 (2015) 6668.

One step solvothermal synthesis of $LiFeMnPO_4$

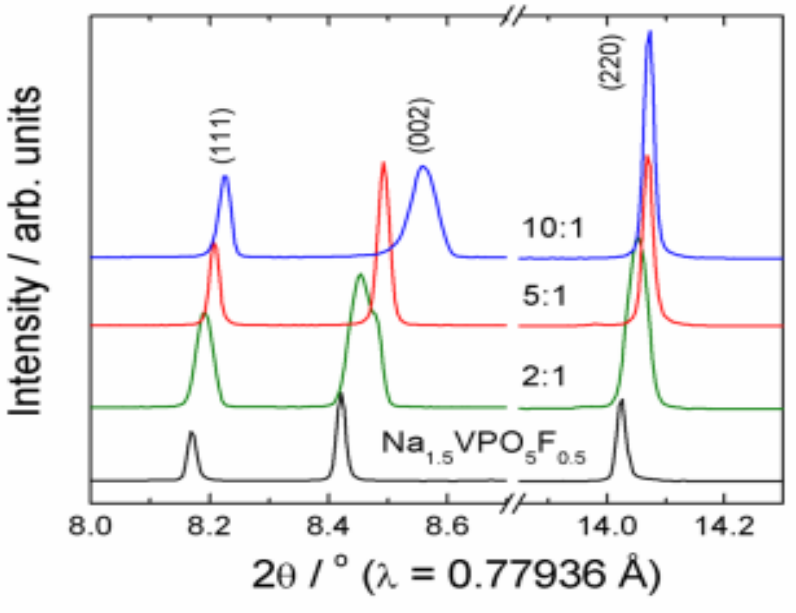


Interface-coupled dissolution re-precipitation mechanism:

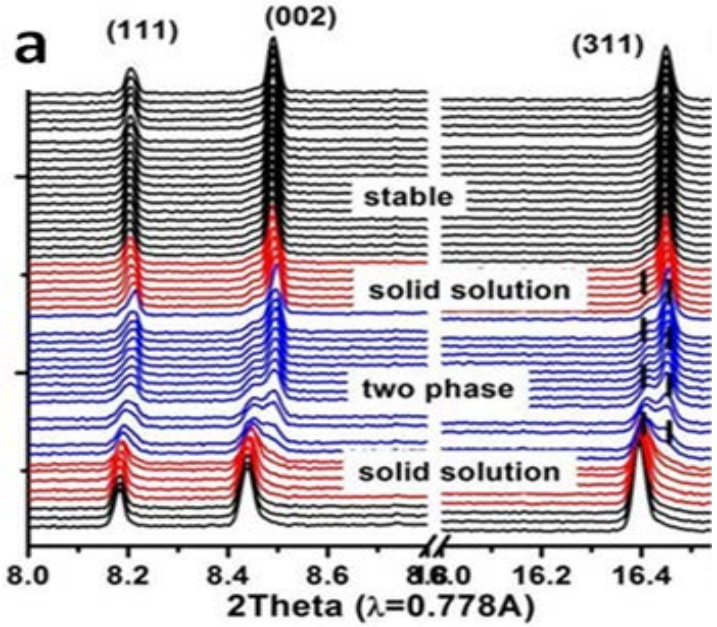


Study ion-exchange reactions

Ex-situ (fixed time, temp…)



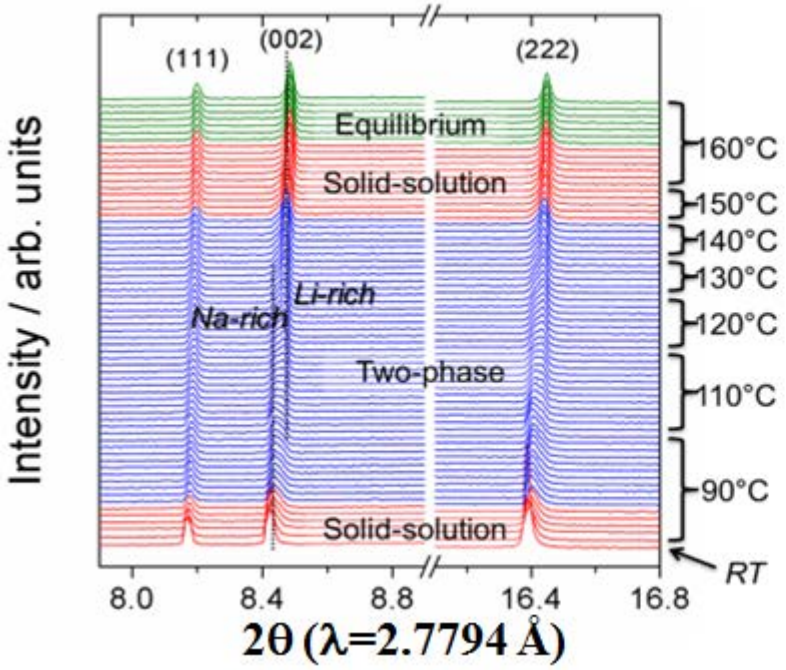
In -situ (time resolved)

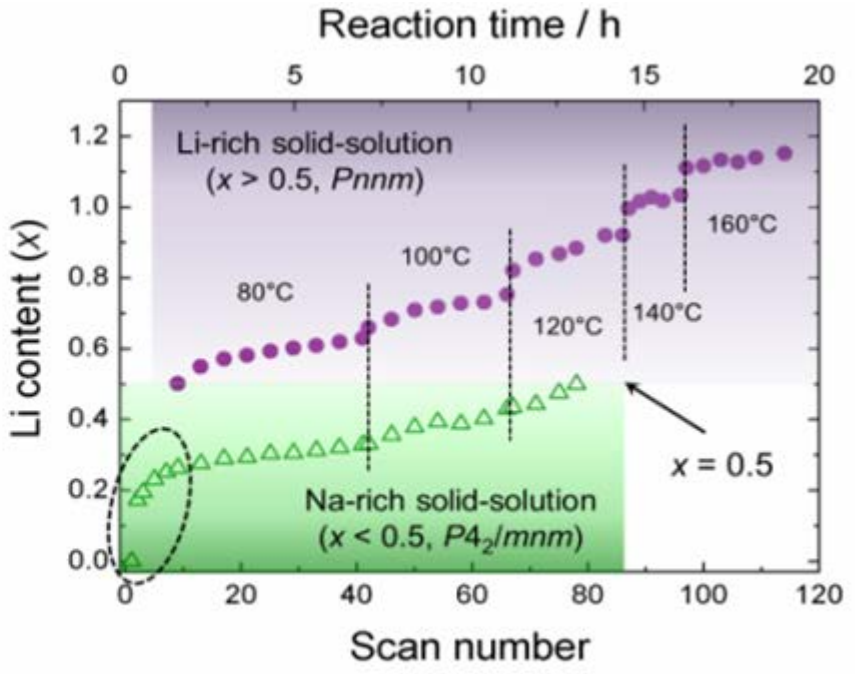


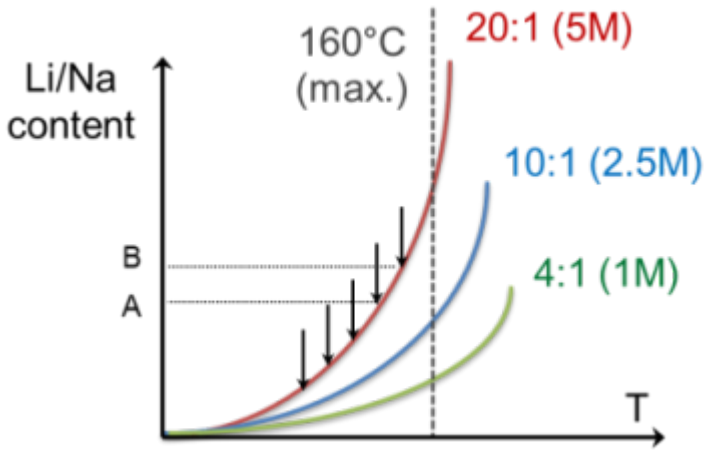
- *Ex-situ*: too many parameters to be evaluated, and no access to kinetic reaction pathway under *non-equilibrium* conditions
- *In-situ*: to catch intermediate steps and kinetics, elucidating intermediates and how temperature, pressure, time and precursor concentrations affect the *kinetic* reaction pathway.

Thermodynamics of ion-exchange/phase diagram

Temperature resolved in-situ XRD studies







- revealed phase transformation: *thermodynamics* and *kinetics*
- optimize the Li exchange and electrochemical properties

➔ build the phase diagram in the composition space