In-situ Solvothermal Synthesis of Novel High-Capacity Cathodes

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ES #183

Overview

Timeline

- Project start: Oct., 2015
- Project end: Oct., 2018
- Percent complete: 15%

Budget

- Total project funding
  - DOE 100%
- Funding received in FY 2015
  - 350K
- Funding for FY 2016
  - 350K

Barriers

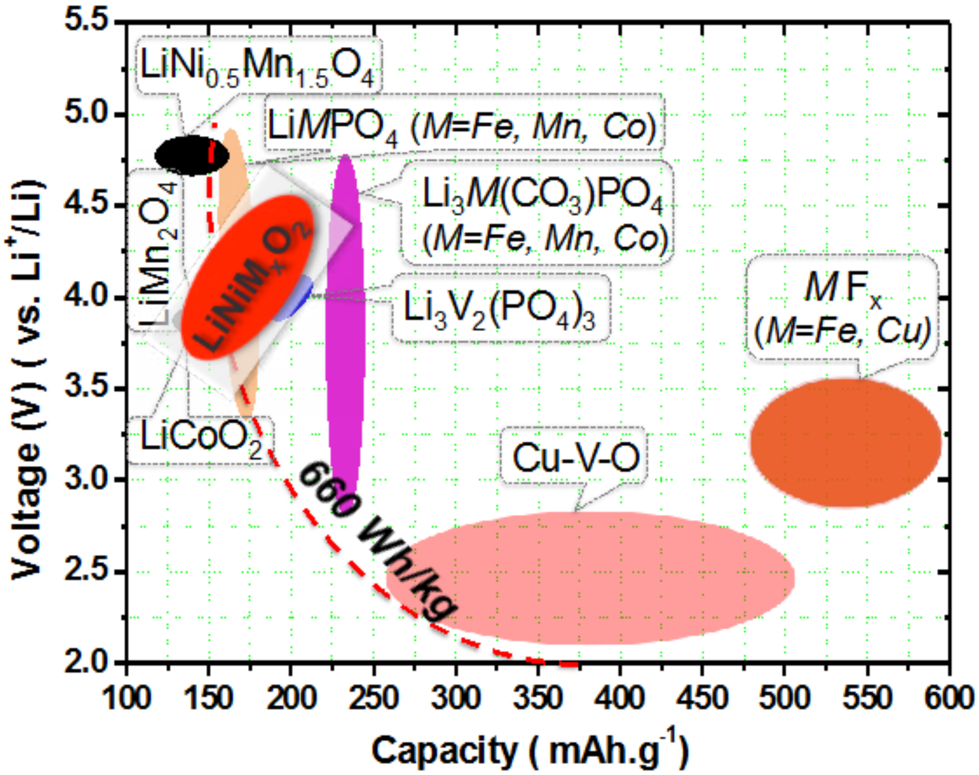
- Barriers addressed
  - Low energy density
  - Cost
  - Cycle life

Partners

- Interactions/ collaborations
  - Lawrence Berkeley National Lab
  - Oak Ridge National Lab
  - Argonne National Lab
  - Stony Brook University
  - University of Texas at Austin
- Project lead
  - Brookhaven National Lab

Relevance and 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 FY16 is focused on developing Ni-rich layered oxides

- $LiNiM_xO_2$ (M=Co, Mn, …)

with synthetic control of the phase, stoichiometry and morphology.

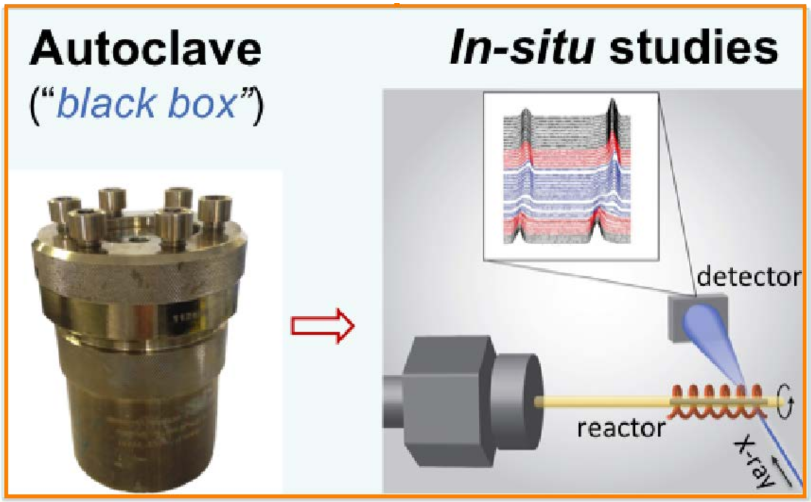
(**Some cathodes with target energy density (>660 Wh/kg) are given on the right side of the red dashed plot*)

Approaches

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

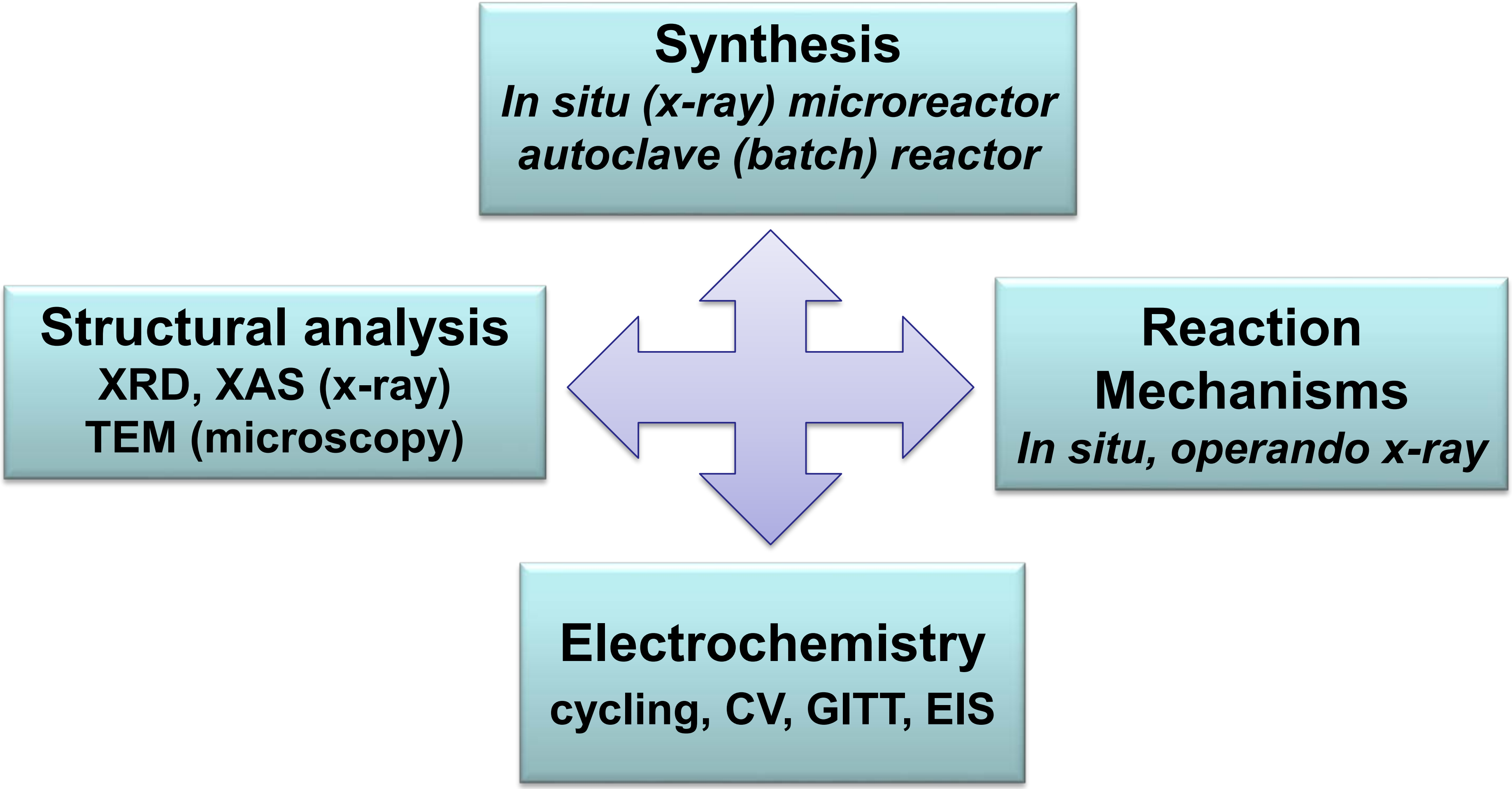
Cathode performance can be advanced by

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



- We have developed tools and techniques for *in-situ*, *real time* studies of synthesis reactions under real conditions, enabling us to identify the reaction pathways of making electrode materials of desired phases and properties.

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



Synthesis

In situ (x-ray) microreactor

autoclave (batch) reactor

Structural analysis

XRD, XAS (x-ray)

TEM (microscopy)

Reaction Mechanisms

In situ, operando x-ray

Electrochemistry

cycling, CV, GITT, EIS

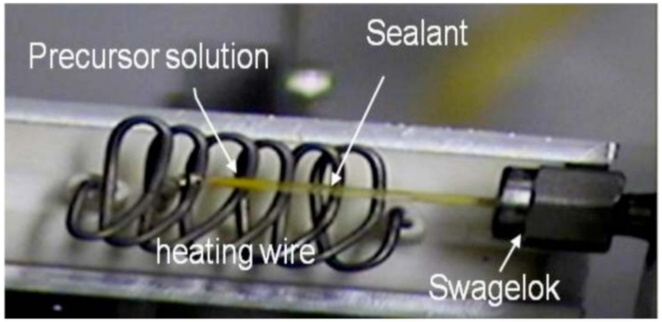
- Enabled by *on-site* resources and facilities at BNL, along with *in-house* developed *in-situ* capabilities (**see the backup slides*)

Technique development: *in-situ* reactors

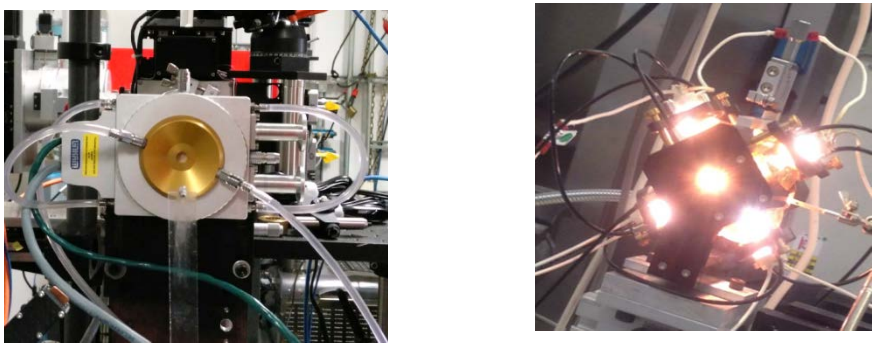
Time-resolved XRD enables synthetic control of the structure and properties of cathode materials

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

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



“In-situ” reactor for hydrothermal, solvothermal synthesis



Linkam TS1500, Quadrupole Lamp furnaces for solid-state reactions

Micro Reactors cover broad synthesis space

- All major synthesis techniques
- Wide range of temperature and pressure

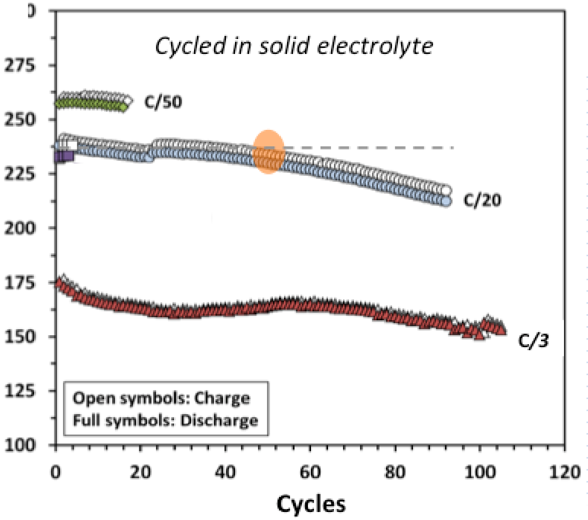
Milestones

Time	**Description (*status*)**
Dec. 01, 2015	Develop synthesis procedures for preparing Ni-Co-Mn layered oxides(*complete*)
Mach 01, 2015	Identify the impact of synthesis conditions on the reaction kinetics and pathways towards forming layered Ni-Co-Mn oxides *via* in-situ studies (*complete*)
June 01, 2016	Develop new capabilities for monitoring synthesis parameters (*P, T, PH values*) in real time during solvothermal synthesis of cathode materials (*on schedule*)
Sept. 01, 2016	Identify synthetic approaches for stabilizing the layered structure of Ni-Mn-Co cathodes (*on schedule*)

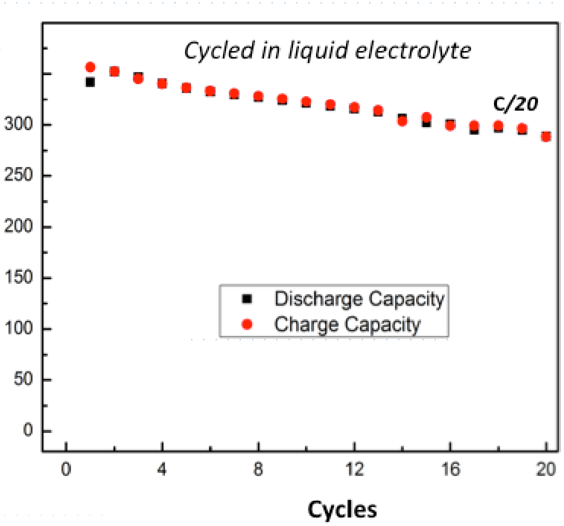
Summary of the Previous Accomplishments

- Complete *in-situ* studies of solvothermal, ion-exchange and solid state reactions for preparing polyanionic cathodes, vanadates and fluorites:
  - $Li_3V_2(PO_4)_3$ nanocrystals of high power density
  - $Li(Na)PO_5F$ of optimized Li content and electrochemical properties
  - Cu-V-O cathodes of high capacity and good cycling stability in the polymer electrolyte (*a, b*)
  - $CuFe_xF_2$ with enabled Cu redox for high energy density (*c*)

(a)



(b)



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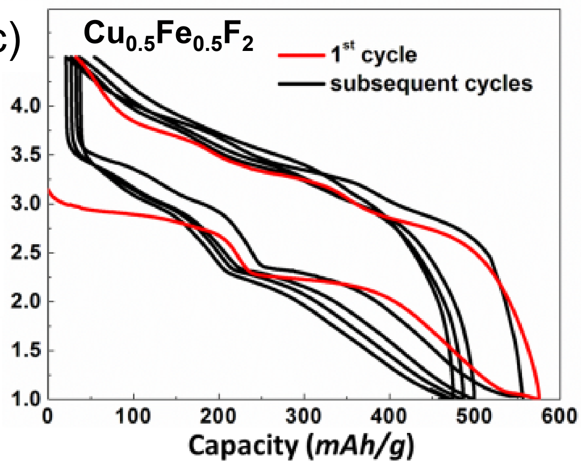
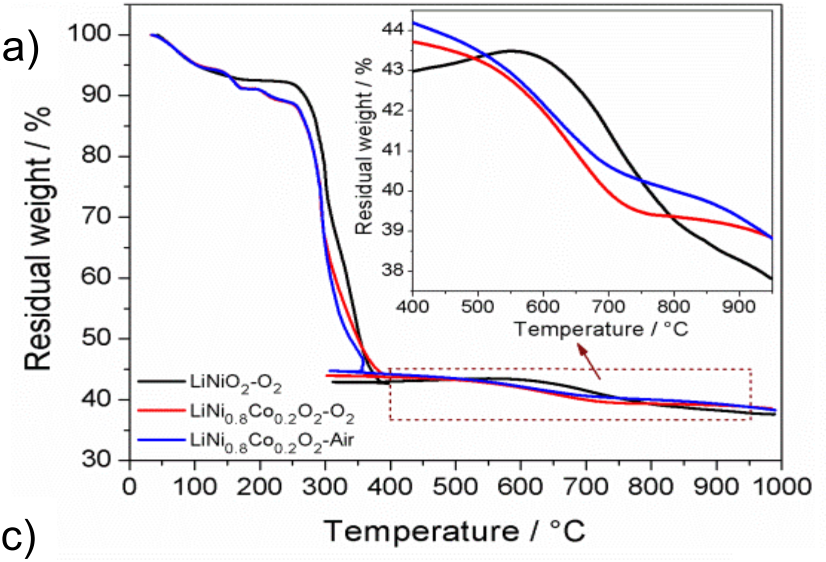


*(*see more details in the backup slides)*

Technical accomplishments Developed procedures for synthetic control of the phases and cationic ordering in $LiNiCo_xO_2$

(a)



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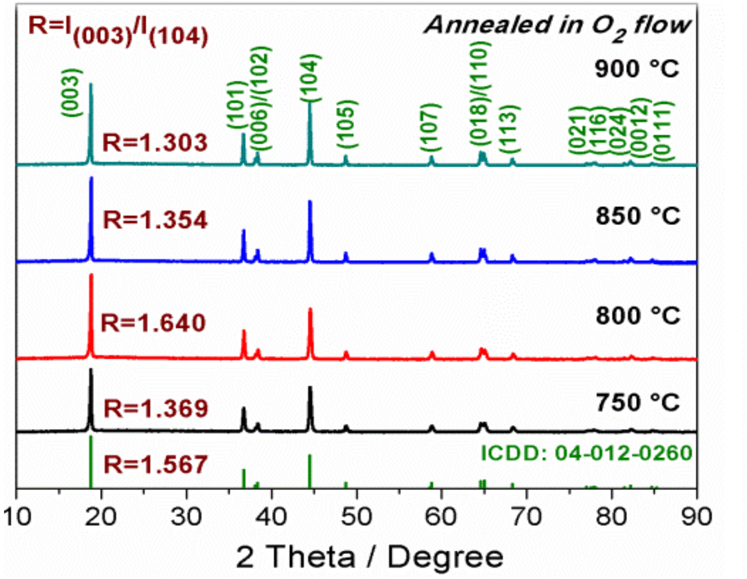
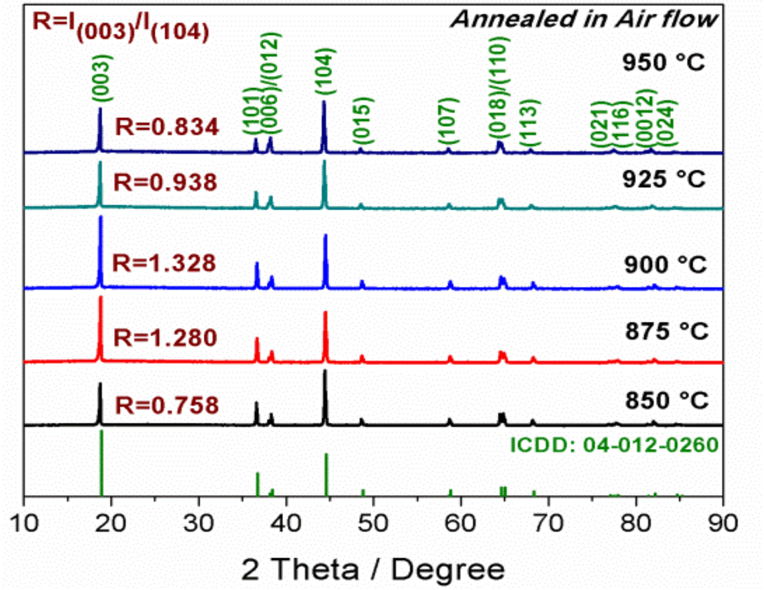


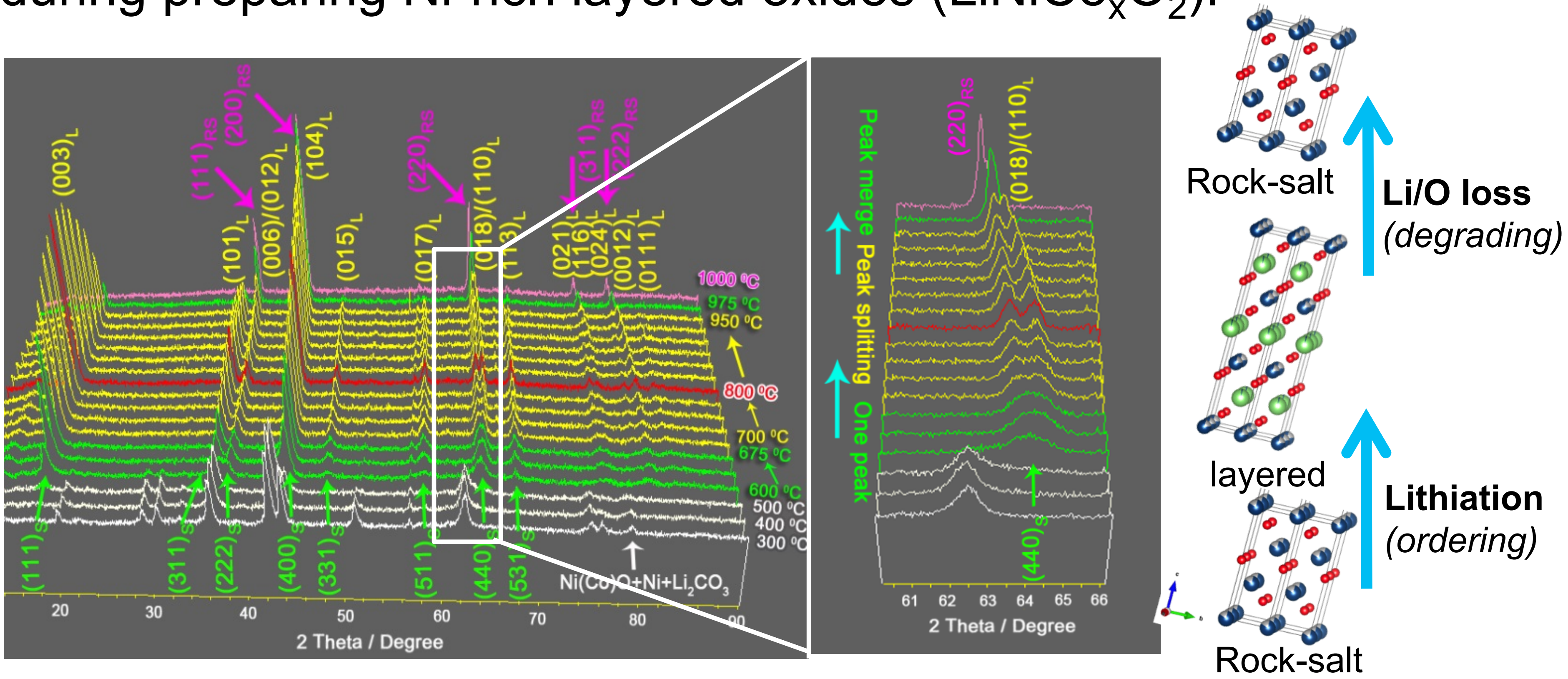
(c)



- **TG measurements** (*a*): determined the temperature window (750-900°C) for obtaining stable layered structure.
- **Ex-situ XRD** (*b, c*): indicated the high sensitivity of structural ordering to the synthesis conditions (calcination temperature, time, gas environment)

(➔ in-situ XRD tracking structural ordering)

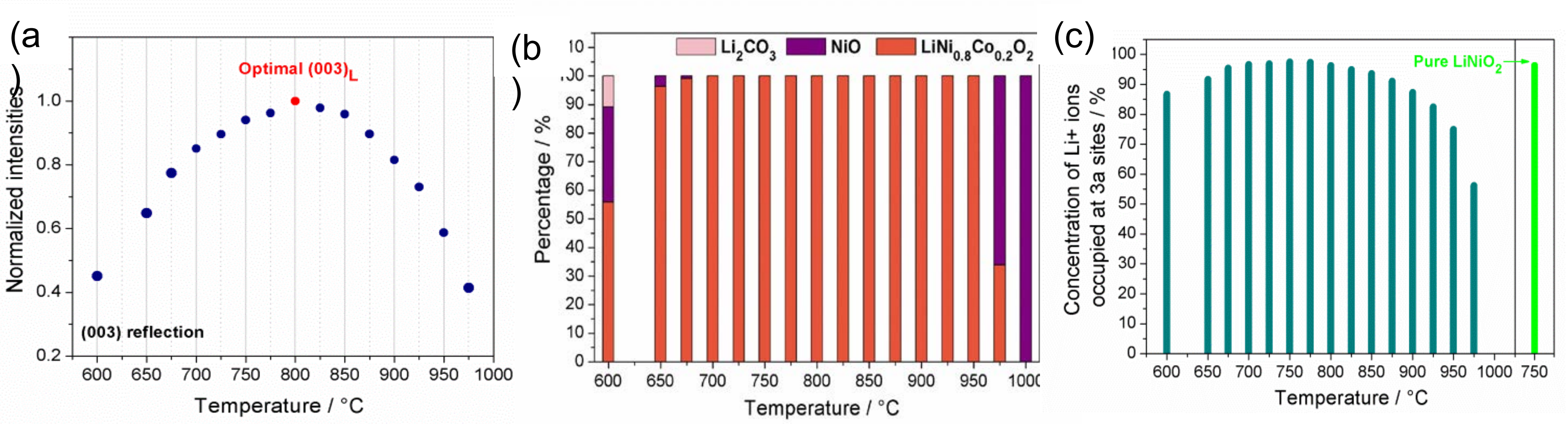
In-situ temperature-resolved XRD for tracking cationic ordering during preparing Ni-rich layered oxides ($LiNiCo_xO_2$):

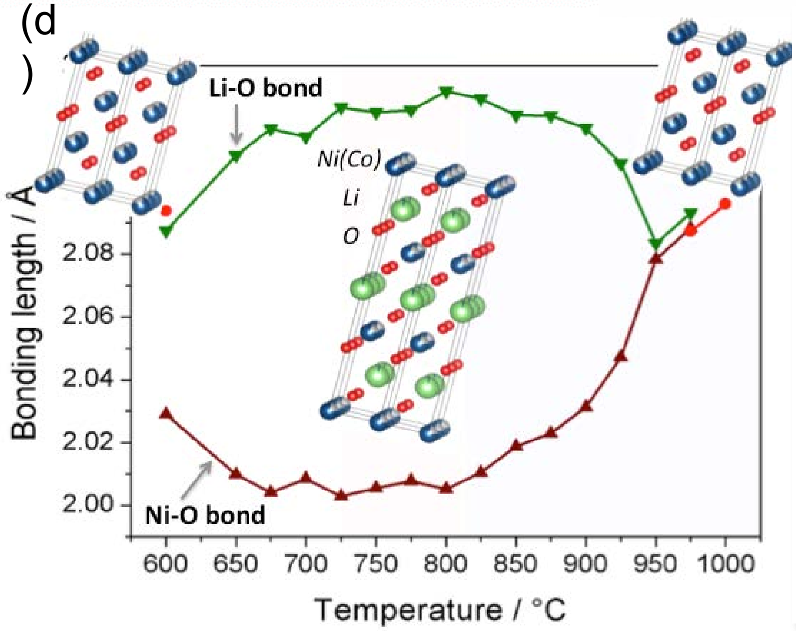


- Direct transformation from rock-salt to the layered structure at ~ 600°C (lower than that during synthesis of $LiNiO_2$; see the backup);
- Highly ordered layered structure is formed at ~ 800°C, and sustained in high temperatures, up to 950°C.

➔ Structural ordering/stabilization by Co substitution (revealed *in-situ*)

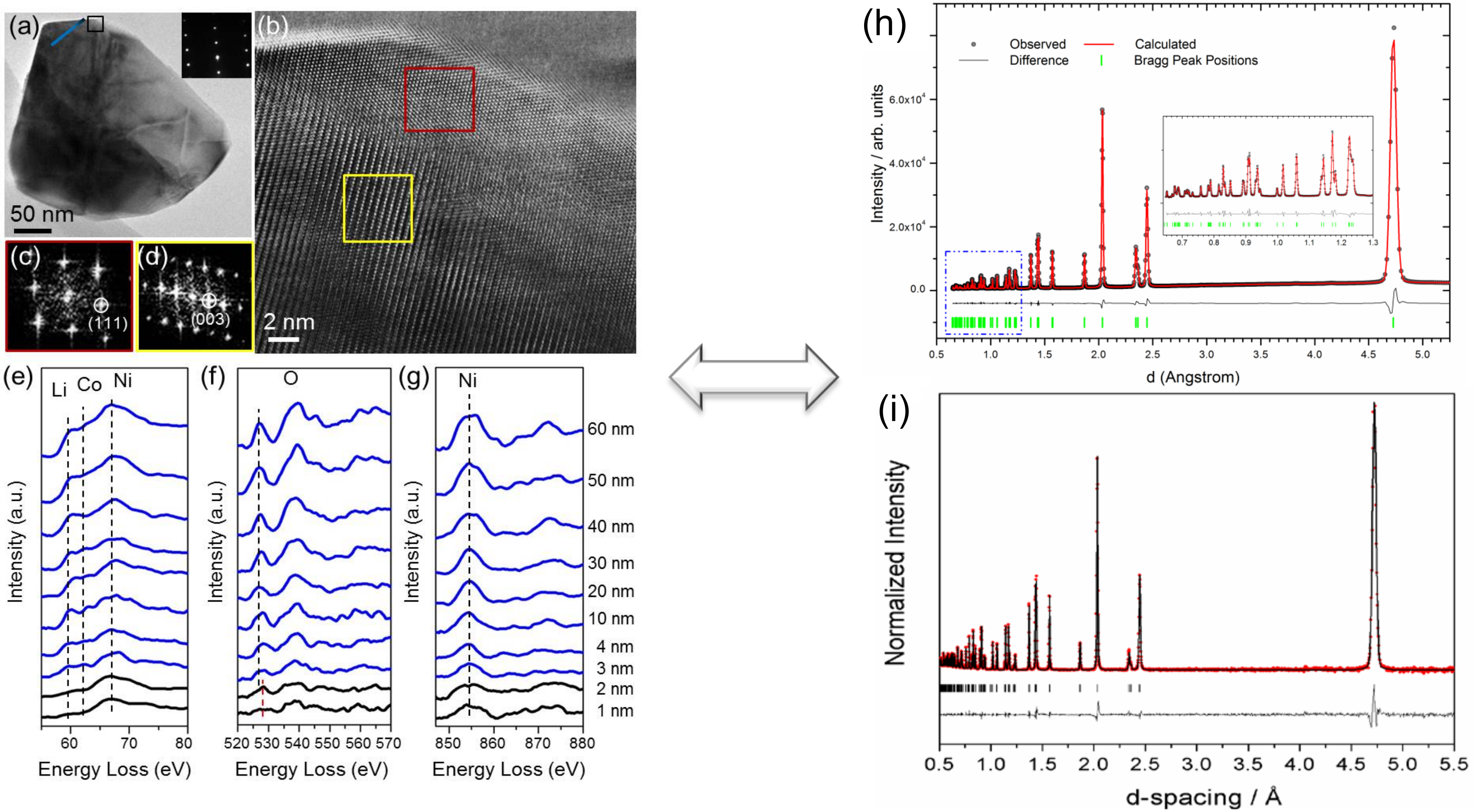
Local cationic ordering in $Li_xNi_{0.8}Co_{0.2}O_2$ was revealed by refinement of the XRD data from *in-situ* meaurements





- Quantitative analysis was made to the structural evolutions *in real time condition*: (*a*) layer ordering, (*b*) phase concentration, (*c*) Li occupancy, (*d*) bond length;
  - details in structural ordering
  - stabilizing layered structure by Co-substitution
- Optimal conditions were determined for synthesis of stoichiometric $LiNi_{0.8}Co_{0.2}O_2$ with low cationic disordering.

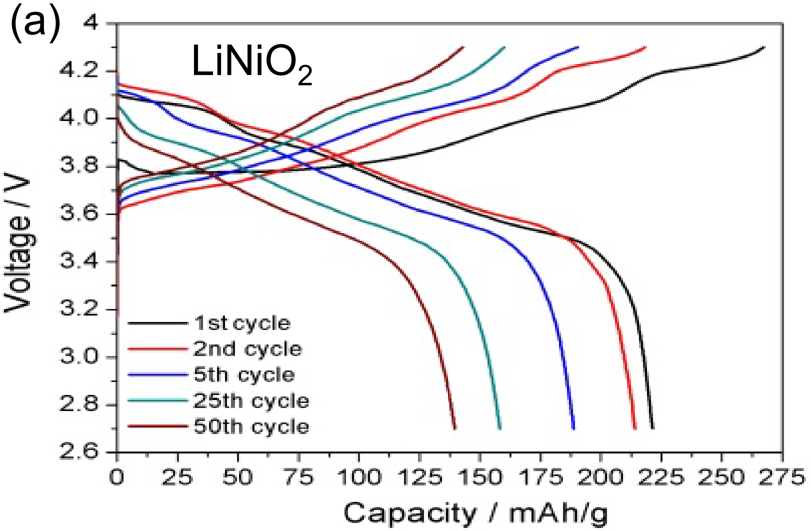
Highly ordered Ni-rich layered oxides were synthesized using the optimal synthesis conditions (being identified via in-situ studies)



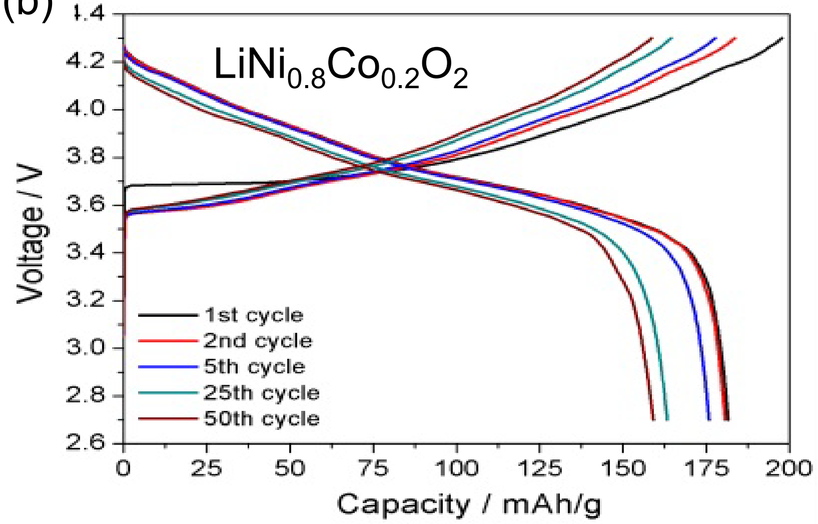
- **(S)TEM-EELS** (*a-g*): thin surface layer of rock-salt (~ 2 nm);
- Synchrotron X-ray & neutron diffraction(*h, i*): highly ordered $LiNi_{0.8}Co_{0.2}O_2$, with low anti-site defects (1.5% Ni^{2+} on Li^+ sites)

Electrochemical performance of the optimized Ni-rich layered oxides ($LiNi_{0.8}Co_{0.2}O_2$ *vs* $LiNiO_2$)

(a)



(b)



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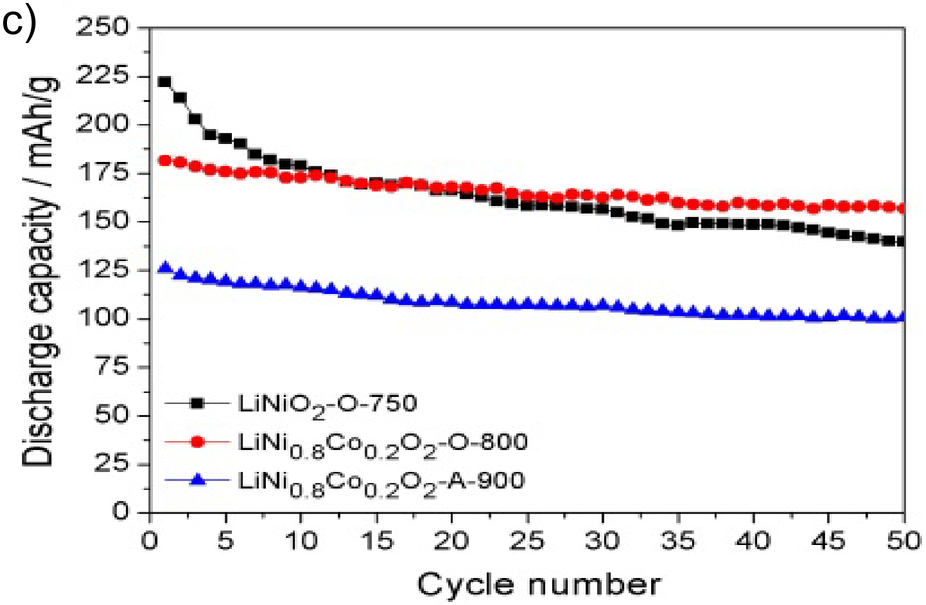
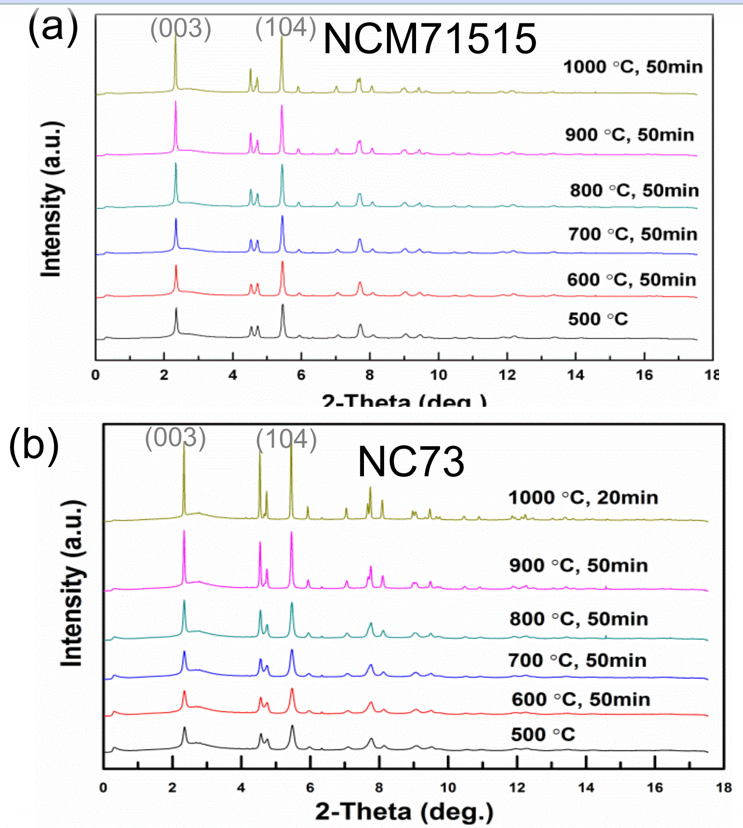
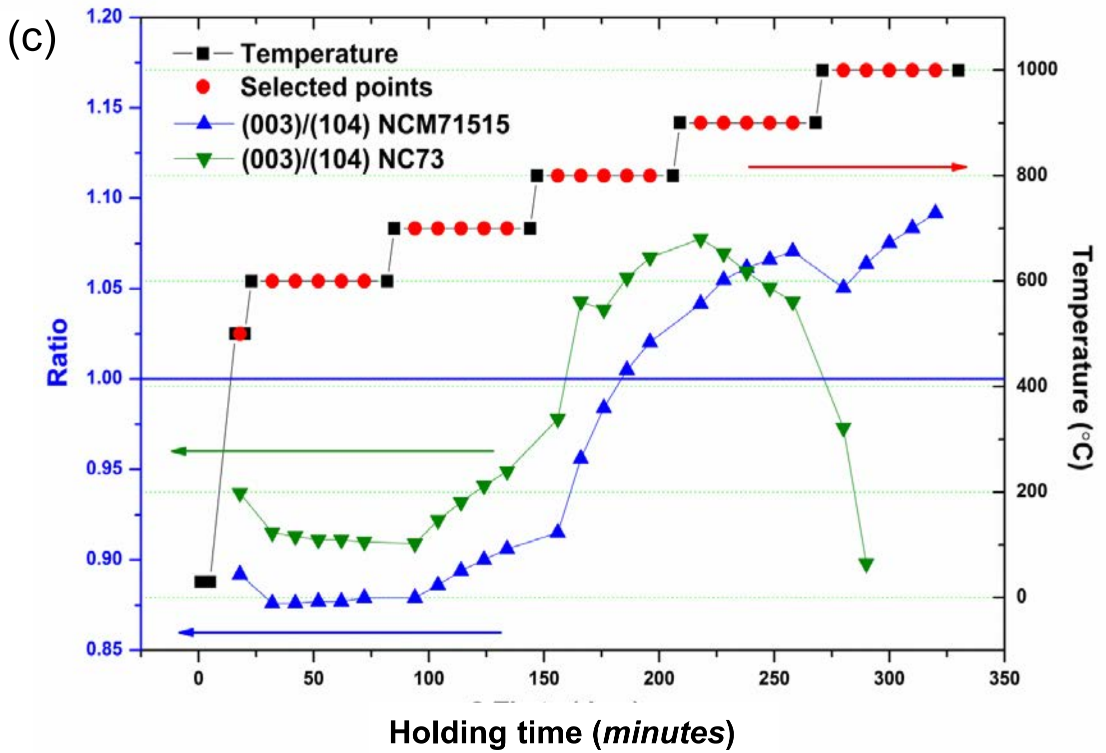


- Enhanced electrochemical performance in optimized $LiNi_{0.8}Co_{0.2}O_2$ (compared to $LiNiO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ synthesized in the air)
  - initial capacity: 180 mAh/g
  - 85% retention after 50 cycles

➔ **Importance of synthetic control of cationic ordering & electrochemical properties, *via in-situ* studies.**

Technical accomplishments Determined structural ordering in $LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2$(NCM71515)/$LiNi_{0.7}Co_{0.3}O_2$(NC73) *vs* temperature

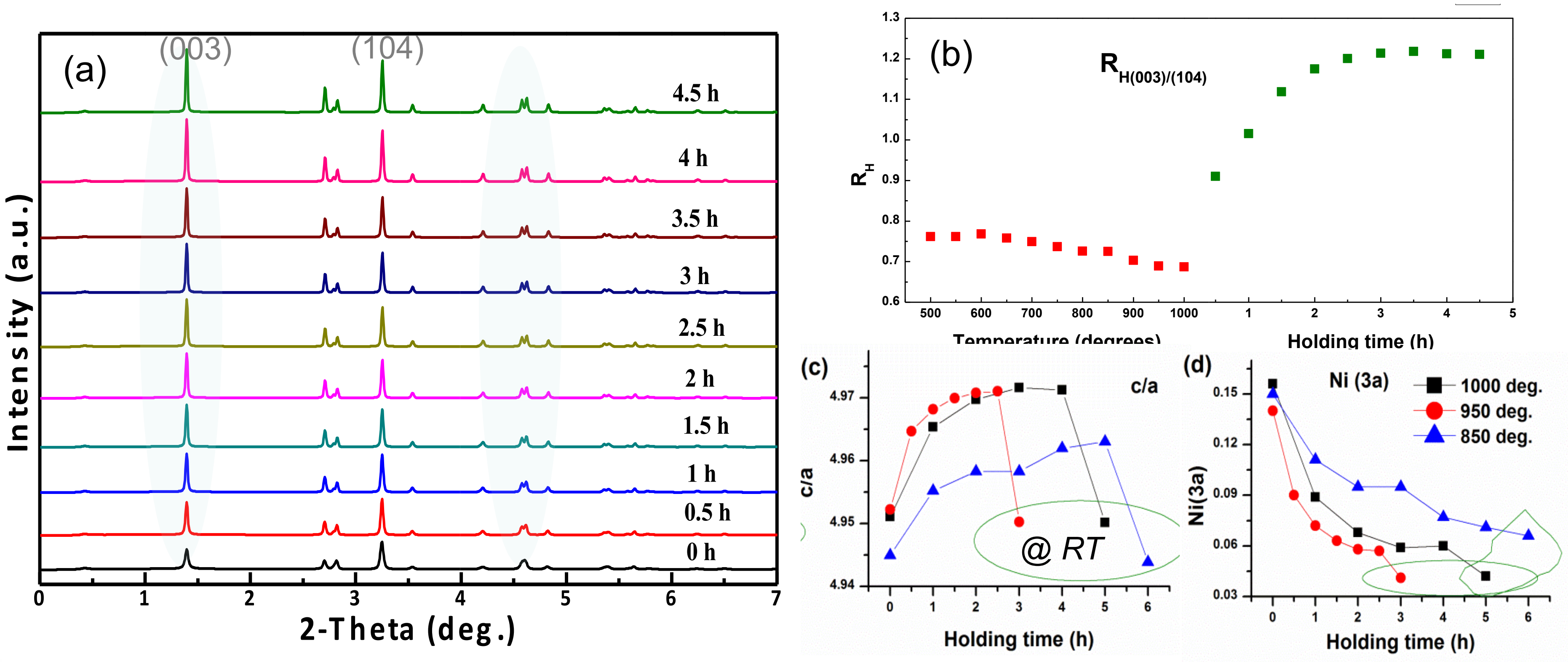




(Courtesy: Zonghai Chen (ANL) for NCM71515 precursor)

- *In-situ* XRD was applied to track synthetic reactions and structural ordering during preparing NCM71515 and NC73
  - obtained highly ordered structure under optimal conditions (with/without Mn)
  - similar trend of structural ordering at low temperature, but much different at high temperatures (> 800°C) ➔ *impact of Mn on Li^+/Ni^{2+} exchange*

Kinetic aspects of structural ordering in NCM71515



- Structural evolution of NCM71515 with time/temperature was determined *by in-situ* XRD and refinements, which sheds light on:
  - Thermodynamic and kinetic of structural ordering
  - Optimizing synthesis conditions (*temperature, holding time*) to minimize the cationic disordering (i.e. Li^+/Ni^{2+} mixing)

➔ **kinetic control of the structural ordering and electrochemical properties.**

Response to the Reviewers

Reviewers were positive regarding the approaches and project progress, but expressed concerns regarding the low energy density of the cathode materials ($Li(Na)VPO_5F$, $Li_3V_2(PO_4)_3$)

--*"not much improvement in the energy densities compared to the conventional cathode materials".*

"*displayed high capacities, but only at low potentials".*

There are also some helpful suggestions from reviewers, for example:

-- "focusing more on *materials that can offer improved energy densities compared to the conventional cathodes to take advantage of this method"*

-- "urged this project continue to identify and screen new cathode materials that have the potential to provide higher specific energies compared to state-of-the-art cathode materials"

In response to reviewer comments, we concluded efforts on $Li(Na)VPO_5F$, $Li_3V_2(PO_4)_3$. In FY16, the efforts were focused on $LiNiM_xO2$ *layered oxides and other cathodes of high capacity*

Collaborations

- Brookhaven National Lab (P. Looney, *L. Wu, D. Su, Y. Zhu*)
  - *Techniques/capabilities for synthesis and characterization of new cathodes*
  - *Advanced TEM imaging and spectroscopy of cathodes*
- Argonne National Lab (*Z. Chen, Y. Ren, K. Amine*)
  - *Precursors for preparing Ni-rich layered oxides*
  - *In-situ synthesis and characterization of Ni-rich layered cathodes*
- Lawrence Berkeley National Lab (G. Ceder, *N. Balsara, W. Tong*)
  - Theoretical prediction of the phases/ordering in Ni-rich layered cathodes
  - Synthesis and characterization of cathode materials
- Oak Ridge National (*J. Nanda, A. Huq*)
  - *Neutron/synchrotron characterization of Ni-rich layered cathodes*
- Xiamen U. (*Y. Yang*)
  - *Surface treatment and characterization of layered cathodes for working at high voltages*
  - *Develop high-voltage polyanionic cathodes*
- Alfred U. (S. Misture)
  - *In-situ synthesis and characterization of Ni-rich layered cathodes*
- Stony Brook U. (*P. Khalifah*)
  - *Synthesis of new high-capacity cathodes*
- Seoul Nat. U. (*K. Kang*)
  - *Synthesis of new high-capacity cathodes*
- U. Texas at Austin (*A. Manthiram*)
  - *Synchrotron X-ray characterization of high-capacity polyanionic cathodes*

Remaining Challenges and Barriers

- In general, designing and synthesizing new cathode materials with the desired phases and properties has proven difficult, due to the complexity of the reactions involved in chemical synthesis. The synthesis of Ni-rich layered oxides is more challenging:
    - The cationic disordering (Li^+/Ni^{2+} mixing) is one critical issue (among many others), leading to reduced capacity and poor cycling performance of the electrodes that prevents its wide use in commercial batteries.
    - An added challenge in preparing Ni-rich layered oxides is due to the high sensitivity of the phases, stoichiometry and morphology to the synthesis conditions: co-precipitation pH value, lithium content, sintering temperature/ atmosphere, heating/cooling rates.
    - Additional challenges come from surface rock-salt layer in the as-synthesized materials, and further degradation (with Li/O loss) upon exposure to the electrolyte and cycling (particularly at high voltages), leading to low cycling stability.

Future work

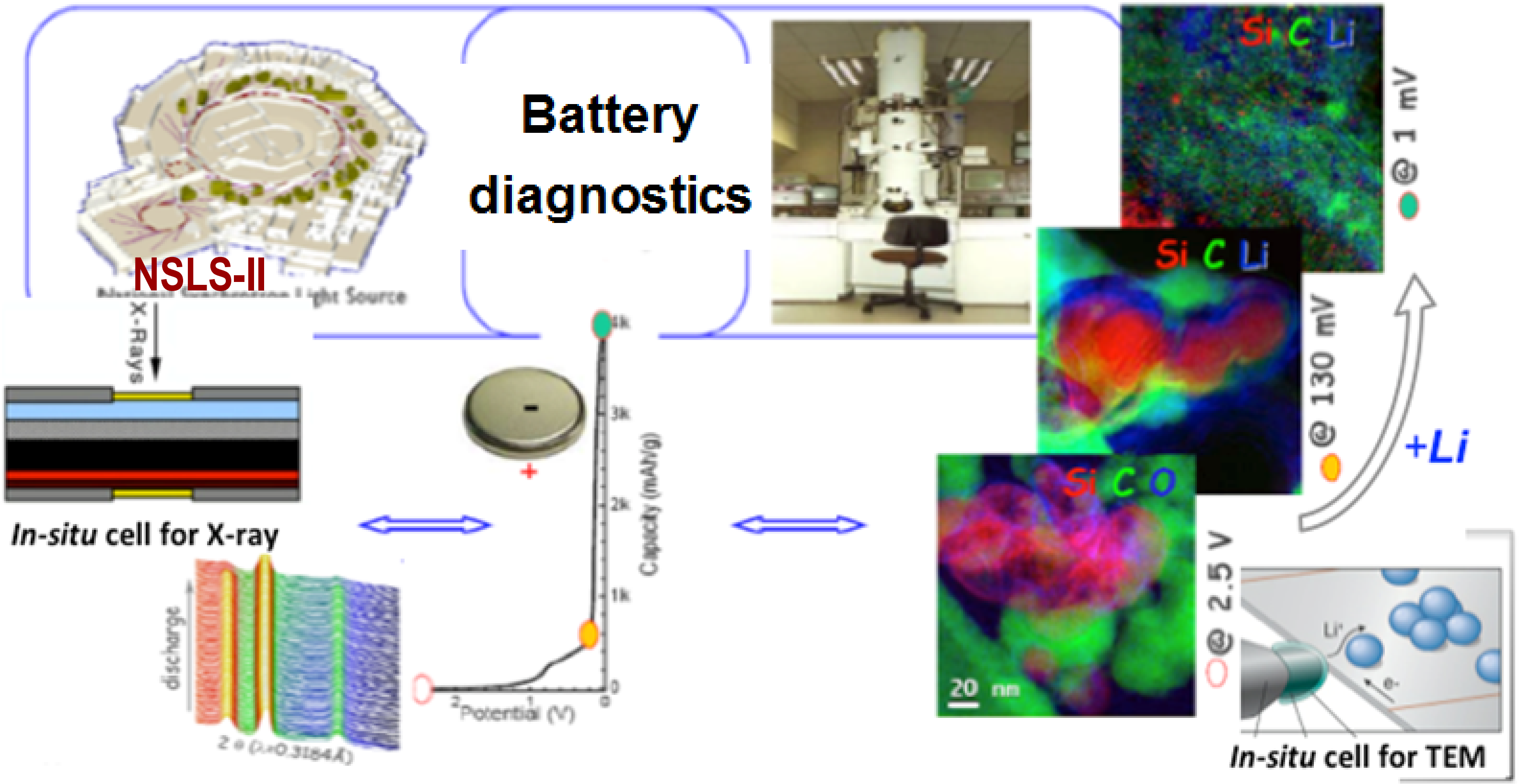
- Develop procedures for *in-situ* synthetic control of the structural ordering in NCM71515, combined with *ex-situ* characterization
  - measure phase evolution during synthesis using TGA analysis
  - determine thermodynamic and kinetic factors governing the reaction pathway/cationic ordering via *in-situ* neutron/synchrotron diffraction
  - measure local chemical/structural ordering by STEM-EELS
- Develop new approaches for synthesizing layered oxides with good control of the structure/phases
  - high structural ordering in the bulk
  - minimized surface rock-salt phase
- Develop new techniques/capabilities for preparing NCM cathodes
  - *in-situ* solvothermal synthesis with real time monitoring synthesis parameters (P, T, PH values)
  - Structure and morphology control via solvothermal and other methods
- Apply the developed approaches and techniques to NCM (of different Ni content) and other high-capacity cathodes, via collaboration within BMR & beyond.

Summary

- **Relevance:** Develop low-cost, high energy density cathode with electrochemical properties consistent with USABC goals.
- **Approaches:** Tools and techniques were developed and applied for *in-situ* studies of synthesis reactions in preparing Ni-rich layered cathodes, enabling us to
  - identify reaction pathways/intermediates
  - quantify thermodynamic and kinetic parameters governing the reaction pathway and cationic ordering
- **Technical Accomplishments:** Synthesis procedures were developed for preparing Ni-rich layered cathodes, with control of the cationic ordering in:
  - $LiNiO_2$, $LiNiCo_xO_2$,$LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2$
- **Collaborative Research:** Established extensive collaborations within ABR and with external partners on development and utilization of advanced synchrotron x-ray, neutron diffraction, and TEM-EELS techniques in developing advanced cathodes.
- **Future work:** Continue our efforts on developing Ni-rich layered cathodes, with synthetic control of the structural/chemical ordering *via* in-situ studies.

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*)

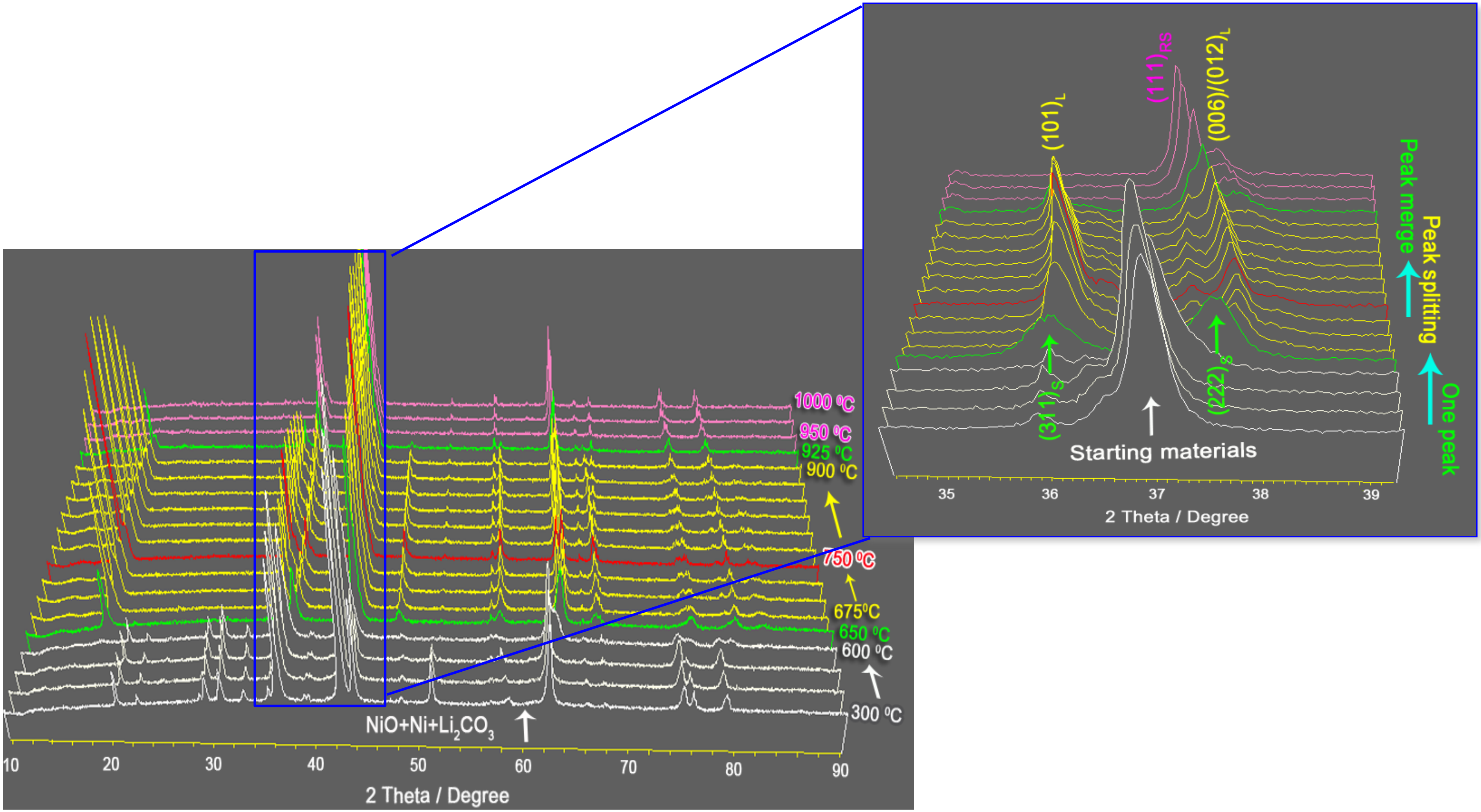
TEM-EELS
tracking Li transport, reactions *@single-particle level*.

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

Summary of the Previous Accomplishments

Materials	Synthesis	Method	Outcome
LFP, LMP and $LiMn_xFe_{1-x}PO_4$	Hydrothermal, Solvothermal with $C_2H_6O_2$	In situ Synchrotron x-ray diffraction, TEM	Anti-site defects handling, intermediate phase, reaction mechanism *J. Phys. Chem. Lett. 2011, 2, 1874 – 1878, J. Phys. Chem. C 2015, 119, 2266−2276*
Monoclinic $Li_3V_2(PO_4)_3$-- LVP (40 nm)	Solvothermal (230° C) followed by solid state annealing (730° C)	Synchrotron XRD, XAS, TEM, In situ XRD	Local structural ordering in the amorphous intermediate, crystal growth in annealing 120 mAh · g^{-1} initial capacity (3.0-4.3V), 95% capacity retention after 200 cycles.. *Chem. Mater. 2015, 27, 5712−5718*
$Li_xNa_{1.5-x}VOPO_4F_{0.5}$ x = 0.65 – 1.34	Ion-exchange from $Na_{1.5}VOPO_4F_{0.5}$	In situ Synchrotron XRD, Neutron Diffraction, TEM	Observed selective replacement of Na by Li, Phase transition at x = 0.5, a thermodynamically stable phase with partial Li-ion exchange. For x = 1.34, 145 mAh g^{-1} @ C/10, 580 Whk g^{-1}, 94% capacity retention for 100 cycles @ 1C. (to be submitted)
ε-$Cu_xV_2O_5$ and α-$Cu_xV_2O_5$	Hydrothermal and solid state reactions	In situ Synchrotron XRD, XAS, TXM, SEM/EDX,	High capacity, up to 350 mAh/g A patent was filed (2015). (to be submitted)
$CuFe_xF_2$	Mechanical ball-milling for obtaining solid-solution phase	In-situ XAS, XRD, TEM-EELS	High capacity, up to 500 mAh/g, and low hysteresis. Nat. Comm. *6: 6668 (2015); US patent, WO2015109181 A1.*

In-situ temperature-resolved XRD for tracking cationic ordering during preparing $LiNiO_2$



➔ *Real time* monitoring structural ordering/degradation W/ heating