Novel Composite Cathode Structures

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Project ID: ES115

Overview

Timeline

- Start date: FY11
- End date: FY14
- Percent complete:

  - ongoing

Budget

- Total project funding

  - 100% DOE
- FY12: $500K
- FY13: $400K

Barriers

- Low energy density
- Rate capability (power)
- Cost
- Abuse tolerance limitations

Partners

- P.I. – C. S. Johnson
- Collaborators :

  - M. Slater, S. Rood, E. Lee (CSE Argonne)

  - M. Balasubramanian, N. Karan (APS Argonne)

  -Ray Osborn, Steven Rosenkranz (MSD Argonne)

  -Robert Winarski (CNM Argonne)

  - S. Hackney (Michigan Technological University (MTU))

Relevance

- New cathodes are needed to improve the performance of Li-ion batteries for transportation applications.
- This cathode discovery project directly addresses the barriers to advanced Li-ion battery powered PHEVs, which are low-energy density, low-power, high-cost and abuse tolerance limitations.
- New synthesis methods and approaches are needed in order to pursue and make novel composites and materials with improved properties over existing materials and their respective cathodes.

Objectives

Design and develop novel high capacity , high-energy, high-power cathode materials that are **low cost** for advanced Li-ion PHEVs.

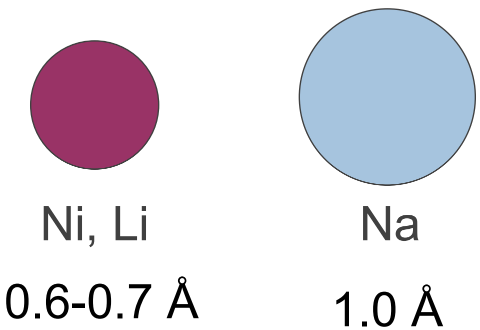
- Demonstrate the **viability of a new synthesis route** for making novel high-performance cathode materials.
- Understand these **novel materials' properties** through characterization methods.
- Make batteries and **test their electrochemical performance**.

Milestones of FY'12

- Initial work & evaluation of Li ion exchange synthesis conditions– on-going
  - *Numerous ion-exchange reaction conditions explored.*
    - *Powder is suspended in polar solvent (alcohol or water) under reflux*
  - *Typical cathode composition: $Li_{\underline{1.04-1.09}}Na_{0.02}Ni_{0.21}Mn_{0.63}O_2$.*
    - *Li/Ni+Mn= 1.24; Mn/Ni ratio of three is unchanged; Ni(II) and Mn(IV) by XANES*
- Survey of cell cycling in Li half cells – done
  - *Baseline cycling (C/15; 2 to 4.8 V); > 240 $mAhg^{-1}$*
  - *Rate tests; select materials demonstrate high rate: 1.5 Ag^{-1} and show specific capacity of 150 $mAhg^{-1}$.*
- Characterization work ; used as a guide to optimize materials and understand underlying materials chemistry – on-going
  - *X-ray diffraction and scattering studies–continuing*
  - *Electron microscopy studies on Na precursor and Li ion-exchanged product – continuing*

Approach

Ni and Mn-containing composite cathode materials in this task are synthesized via a **lithium ion-exchange reaction** from a precursor layered Na-containing oxide. These ion-exchanged lithium nickel manganese oxide products then serve as Li intercalation battery cathodes.



Ionic radii mismatch of Ni and Li versus Na negates site disorder in precursor materials

Ion exchange process: **$Na(Li)MO_2 \rightarrow Li(Li)MO_2$**

Incorporate extra Li into layered sodium precursor before ion-exchange, in order to gain capacity in product.

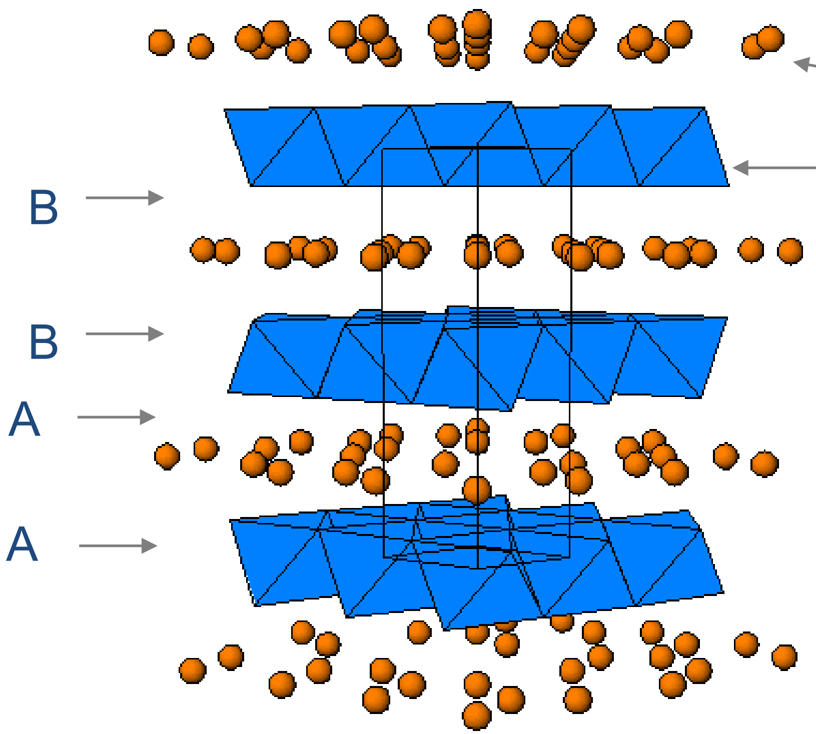
Note the precursor is Na+Li=1.2, Na+Li/Ni+Mn=1.2 & Mn/Ni=3

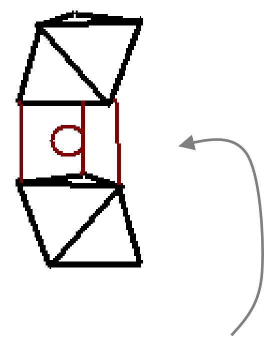
Layered Na transition metal oxide precursor synthesis

Example:

$$0.5Na_2CO_3 + \boxed{0.1Li_2CO_3} + Ni_{0.25}Mn_{0.75}CO_3 + \delta O_2 \xrightarrow{\text{800 - 900 °C, air}} Na_{1.0}Li_{0.2}Ni_{0.25}Mn_{0.75}O_y + 2.2\ CO_2$$

Layered precursor crystal structure (P2 type)



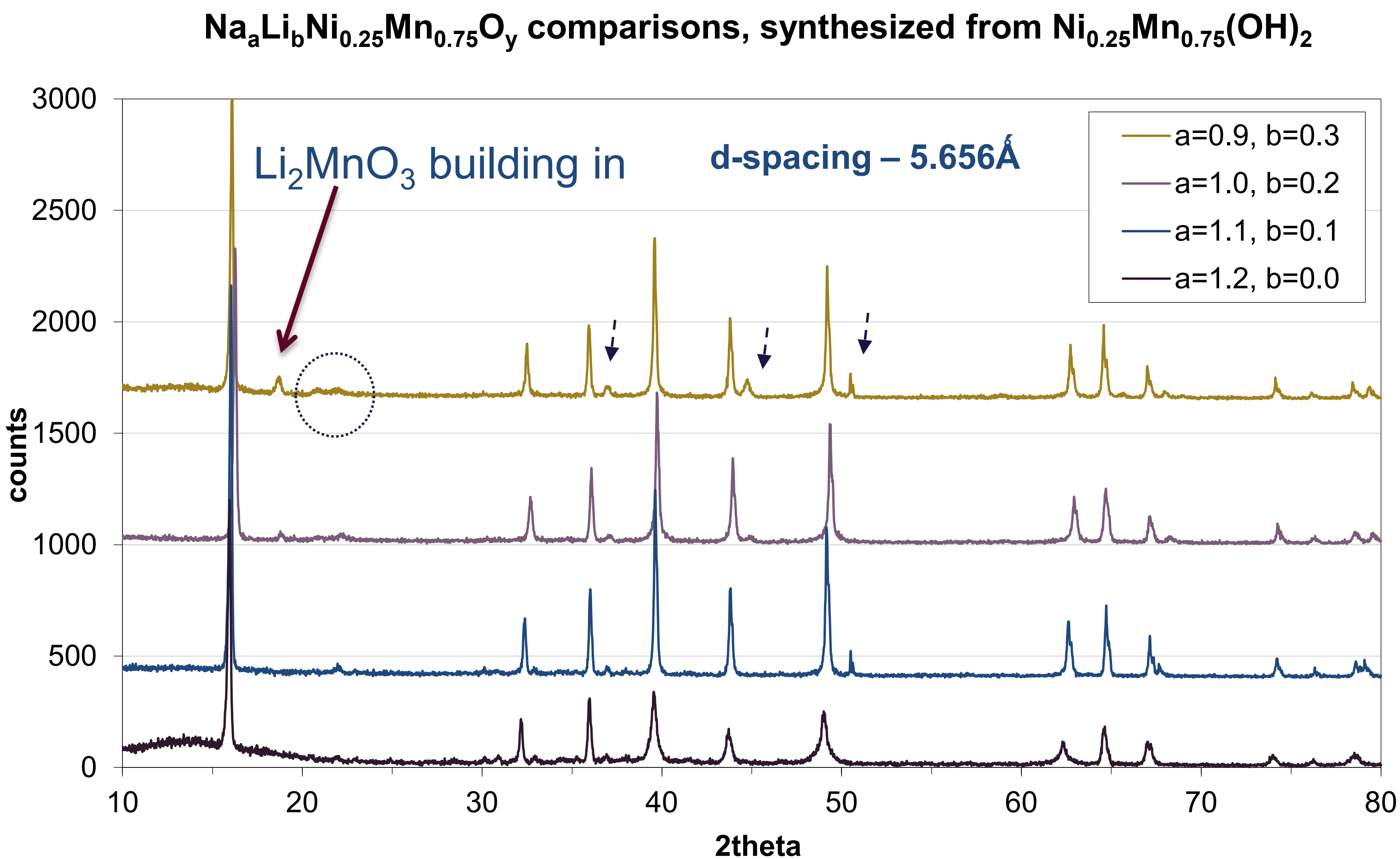


Na in trigonal prismatic coordination

Na – **1.02 Å**
Li – **0.74 Å**
Ni^{2+} - 0.69 Å
Mn^{4+} - 0.53 Å

- Large Na cation radii size negates Ni site disorder.

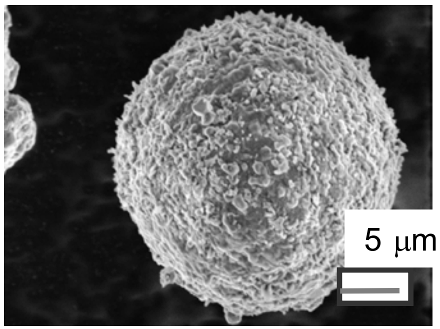
XRD of a series of Na precursors

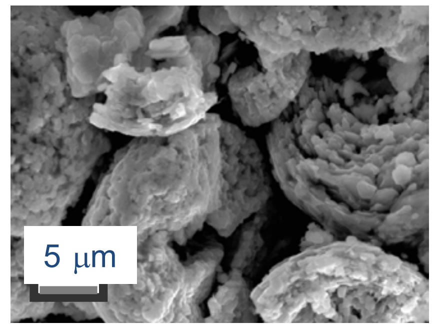


- Li (80-90%) is incorporated in the Na major phase.
- Li_2MnO_3 minor phase in precursor confirmed by Li-6 NMR.

Li^+/Na^+ ion-exchange reaction

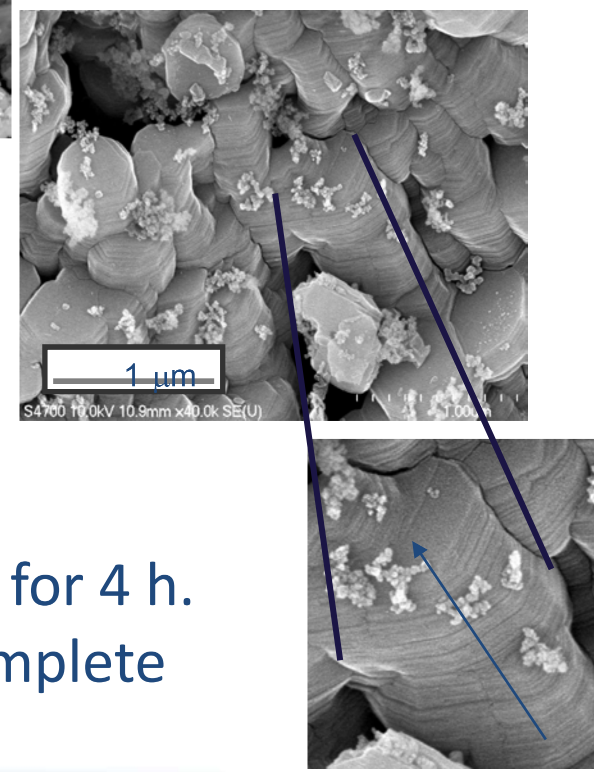
$Na_{1.0}Li_{0.2}Ni_{0.25}Mn_{0.75}O_y \xrightarrow[\text{polar solvent}]{\text{LiBr}} \boxed{\mathbf{Li_{1.05}Na_{0.02}Ni_{0.21}Mn_{0.63}O_2}} \xrightarrow{\Delta}$ HT-$Li_{1.05}Na_{0.02}Ni_{0.21}Mn_{0.63}O_2$



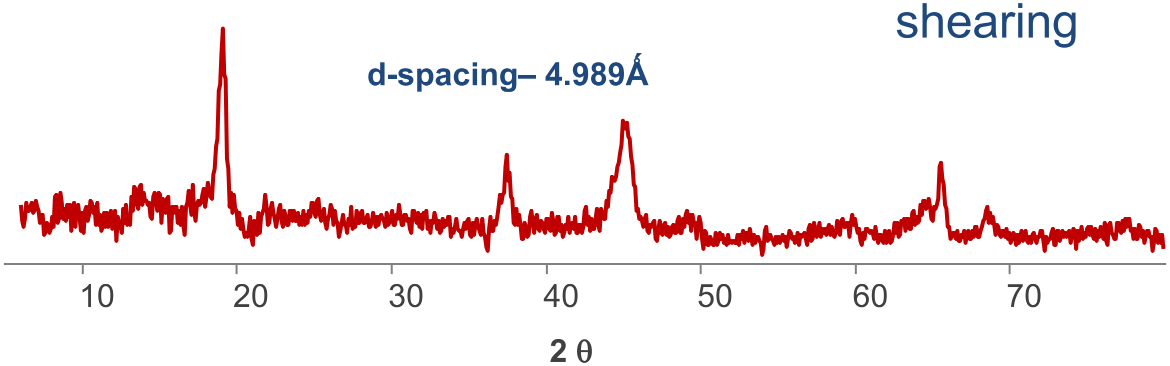


shearing

stacking layer faults

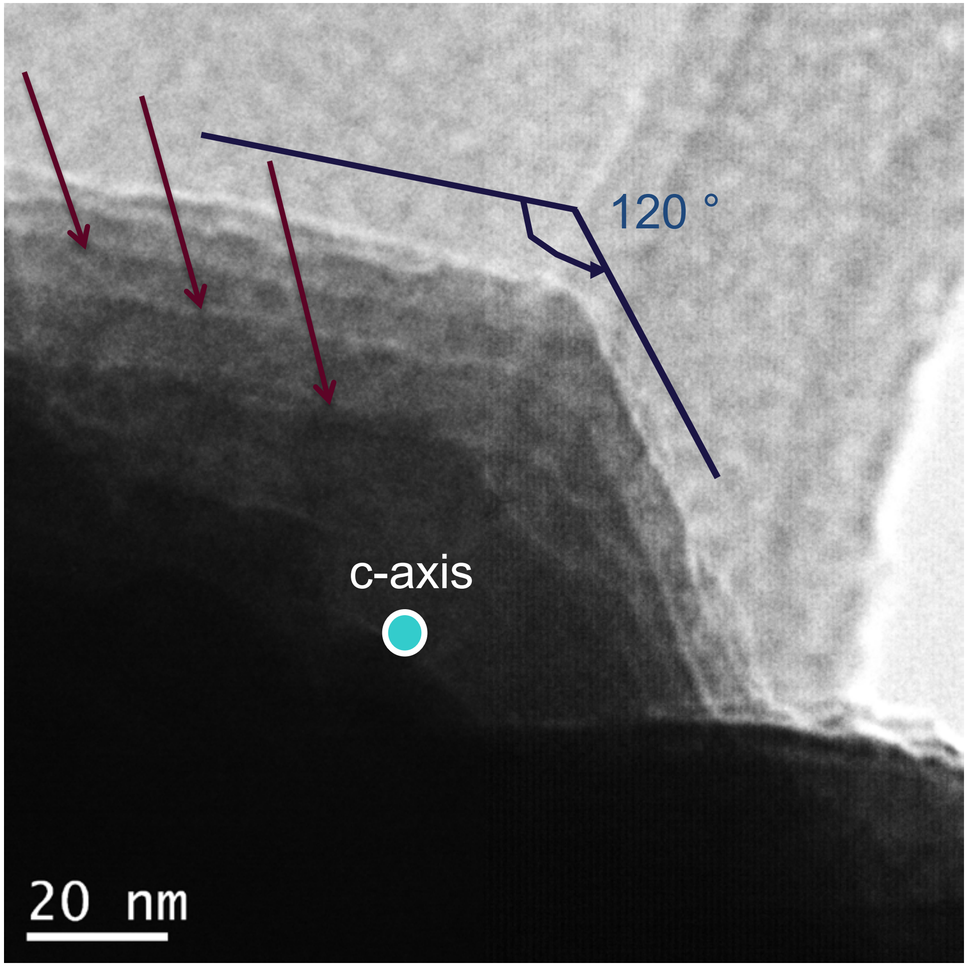


c-axis direction

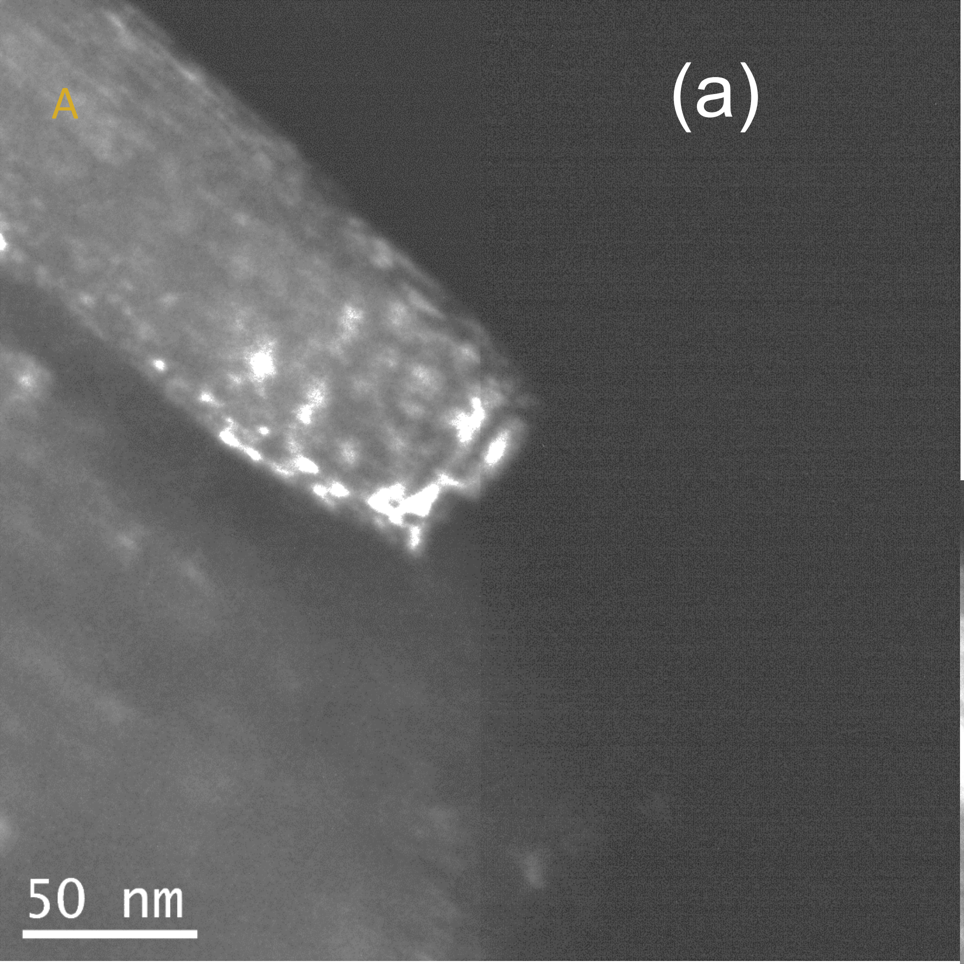


- Ion-exchange is effected by heating at reflux for 4 h.
- Equilibrium favors $LiMO_y$ as seen by near complete replacement of Na with a mild excess of Li.

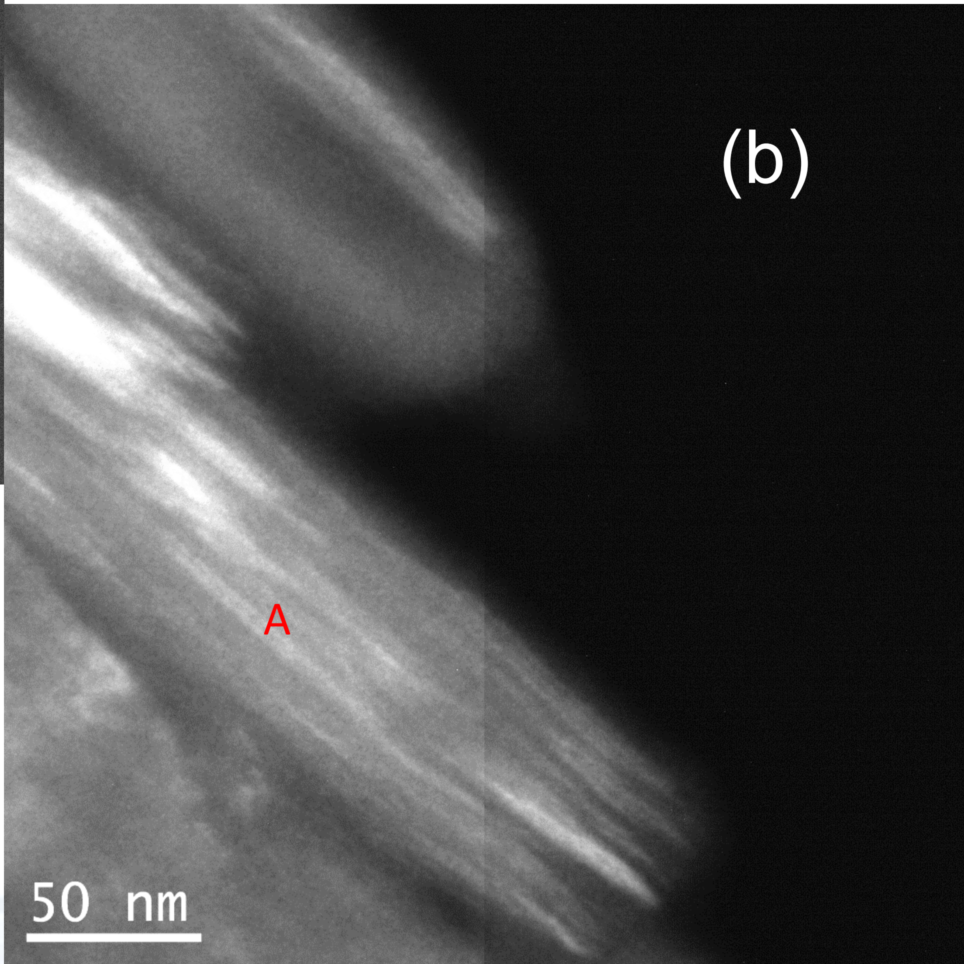
TEM shows layered stacking faults and edge defects



- Exposed crystal platelets maintain hexagonal symmetry & can provide fast pathways for Li diffusion.

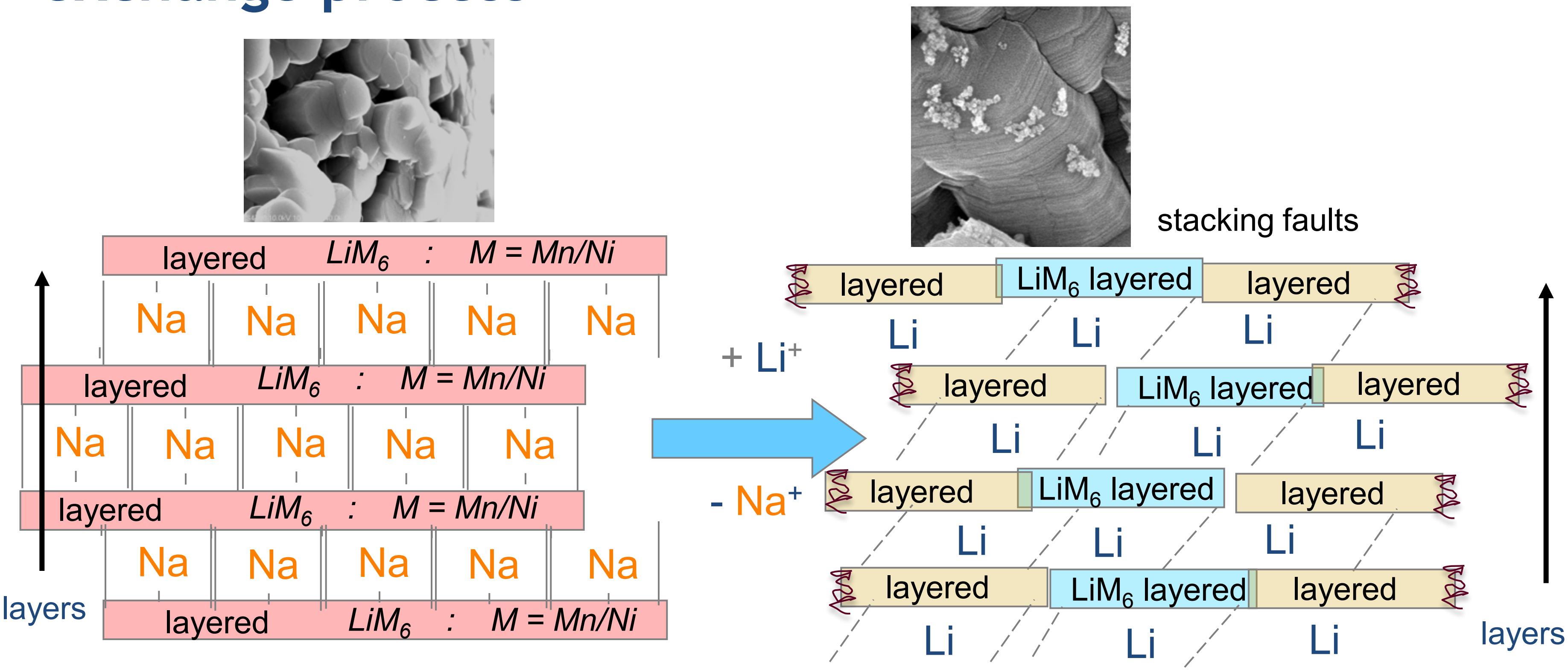


TEM of crystal plates



- Direct observation of crystal surface defects (a) and non-ideal layered crystallites (b)

Transformation and structural schematic of ion-exchange process

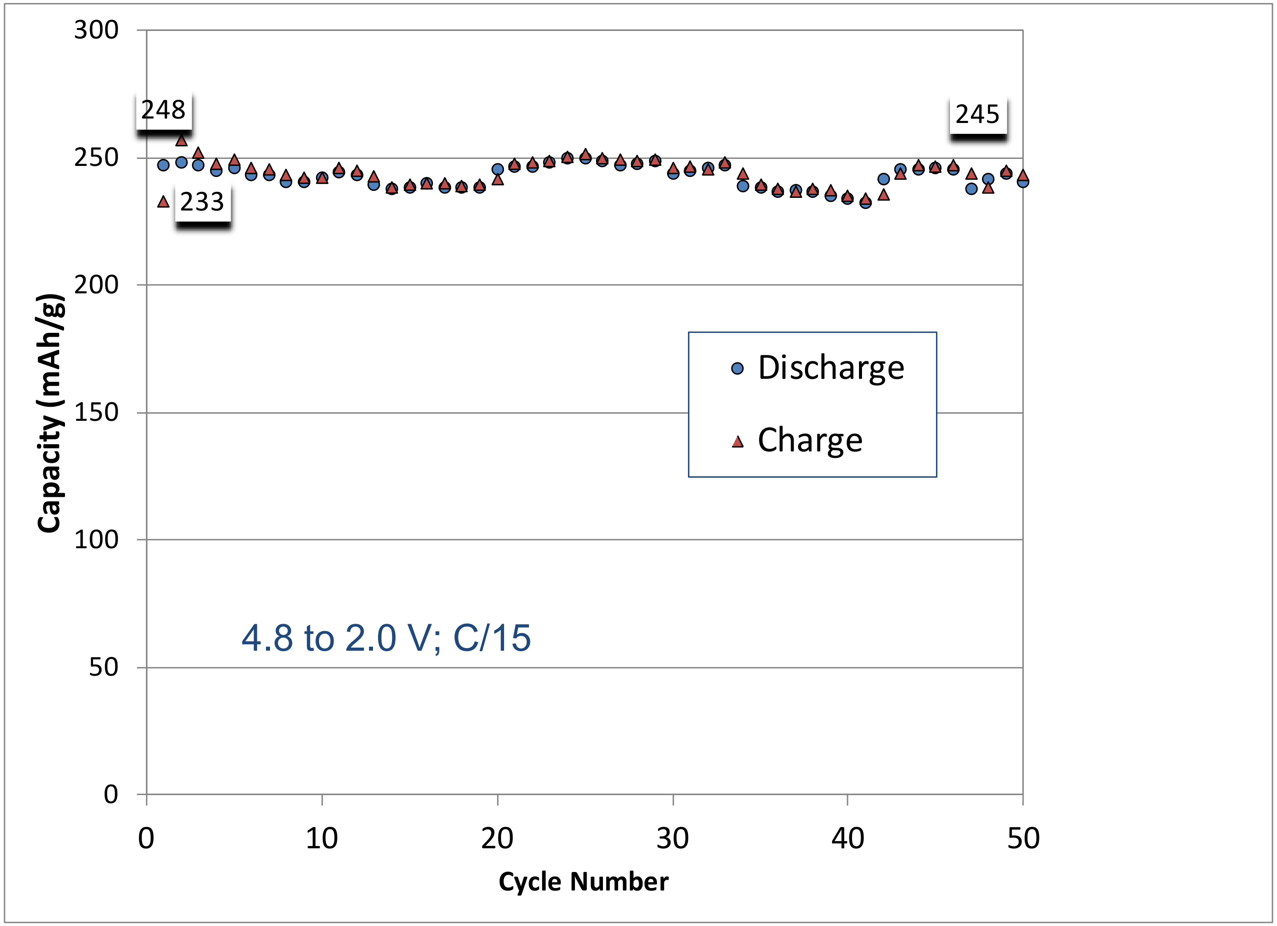


prismatic (P2-type)

composite

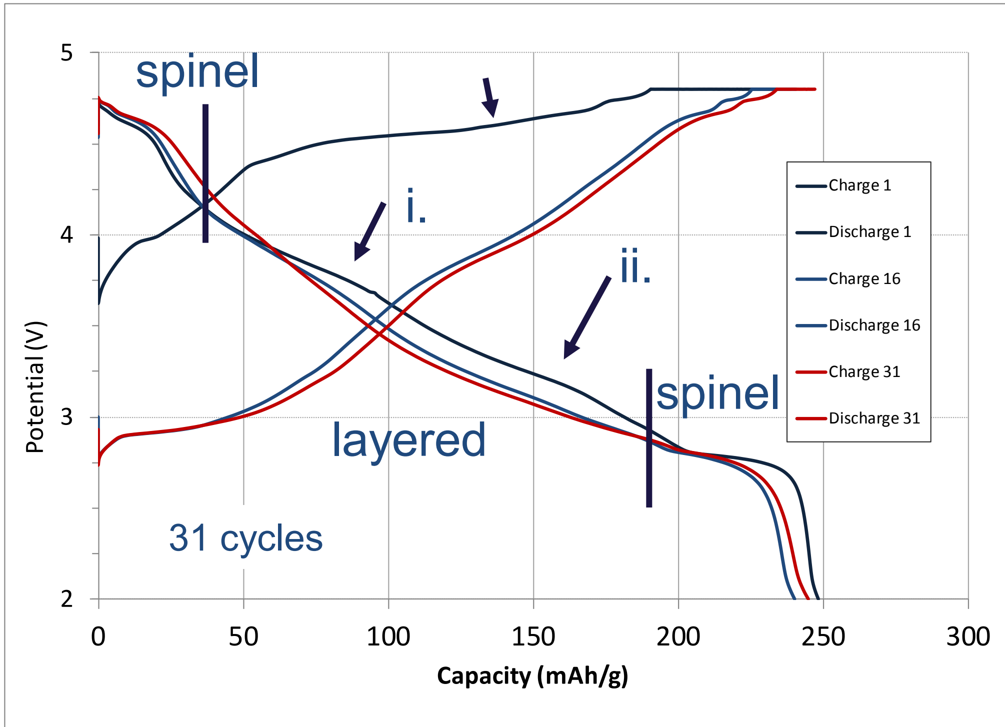
- Major Li-Ni-Mn atomic rearrangement in the layers must occur at grain boundaries of crystal platelets initiated from internal stress during IE from Na layered precursor.

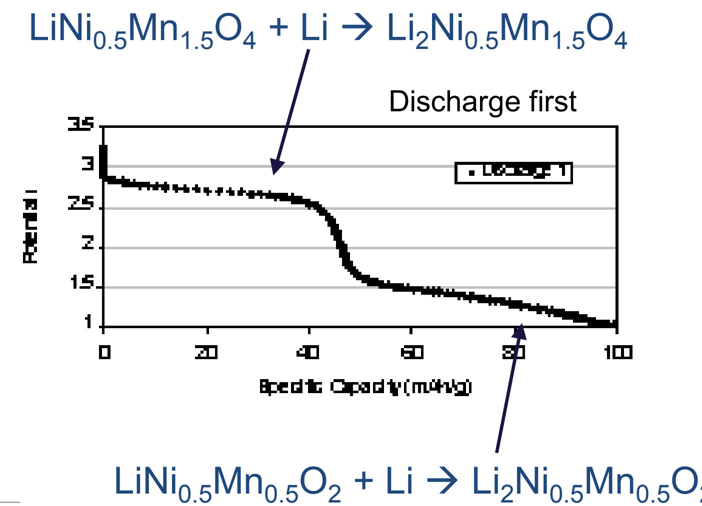
Stable high capacity observed over 50 cycles

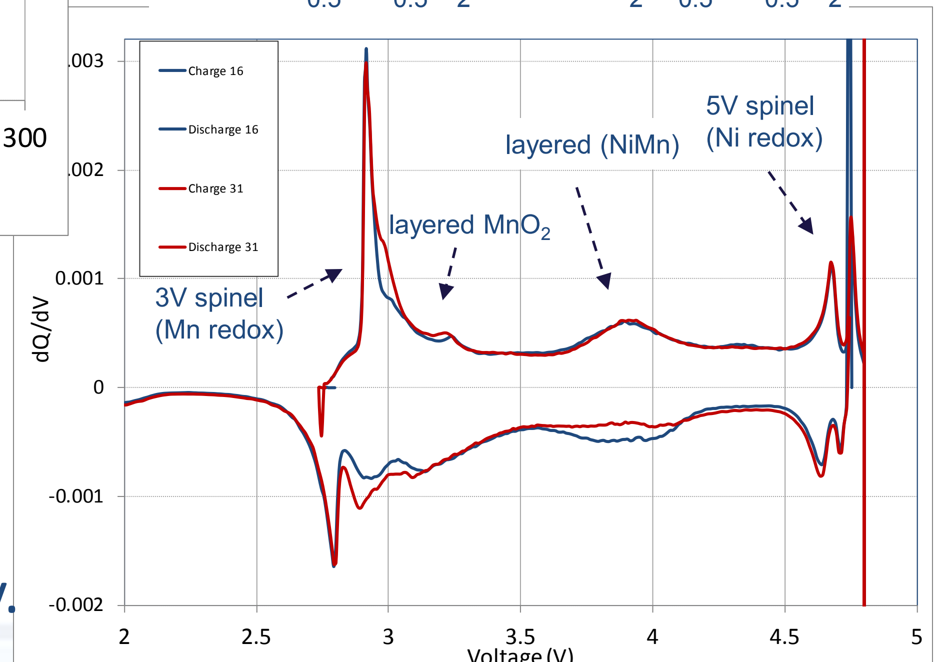


- A stable capacity of ~ 250 $mAhg^{-1}$ or 0.9Li/M is cycled.

$Li_{1.05}Na_{0.02}Ni_{0.21}Mn_{0.63}O_2$ layered composite contains chemically integrated $LiNi_{0.5}Mn_{1.5}O_4$ spinel component

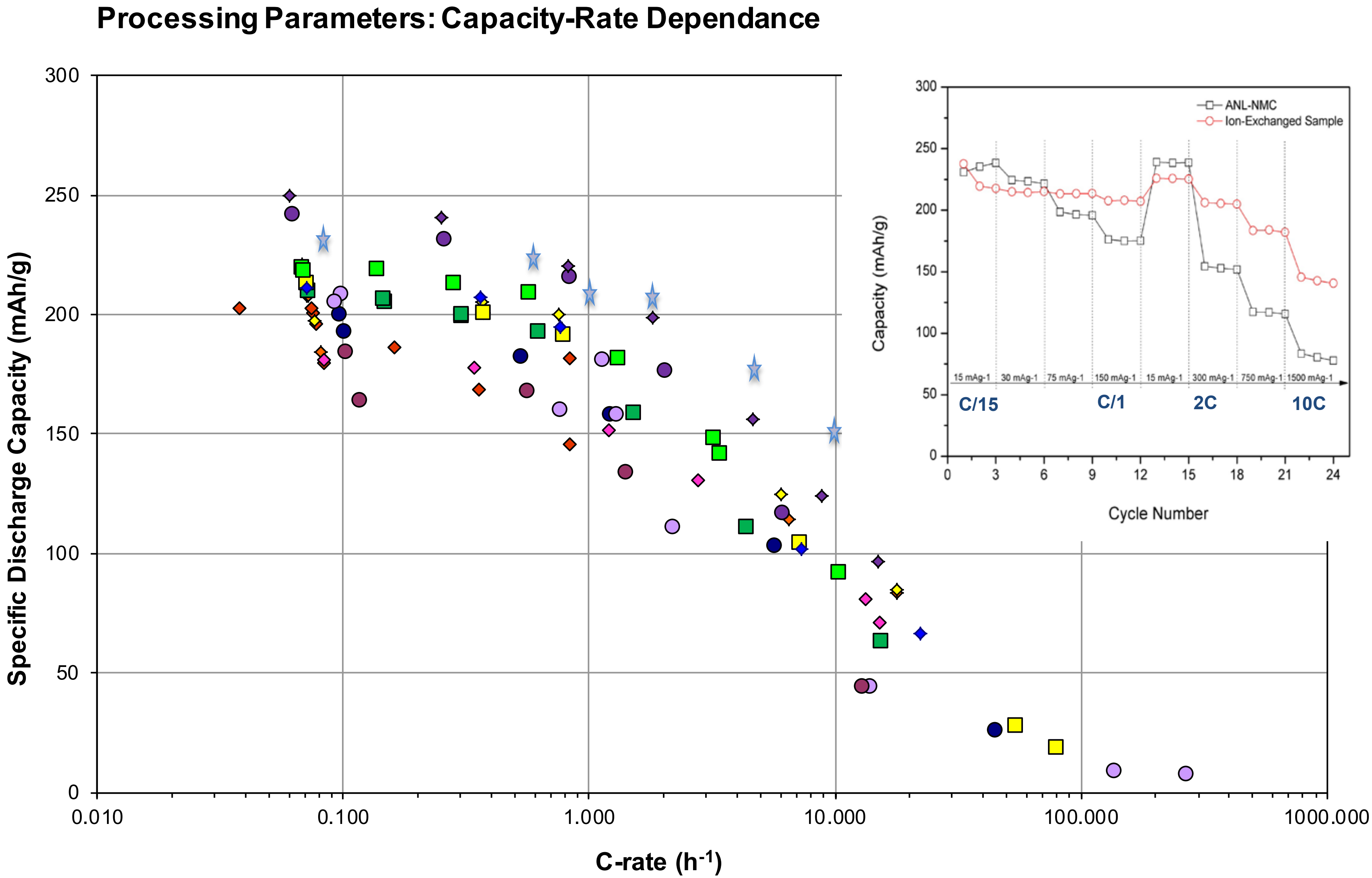






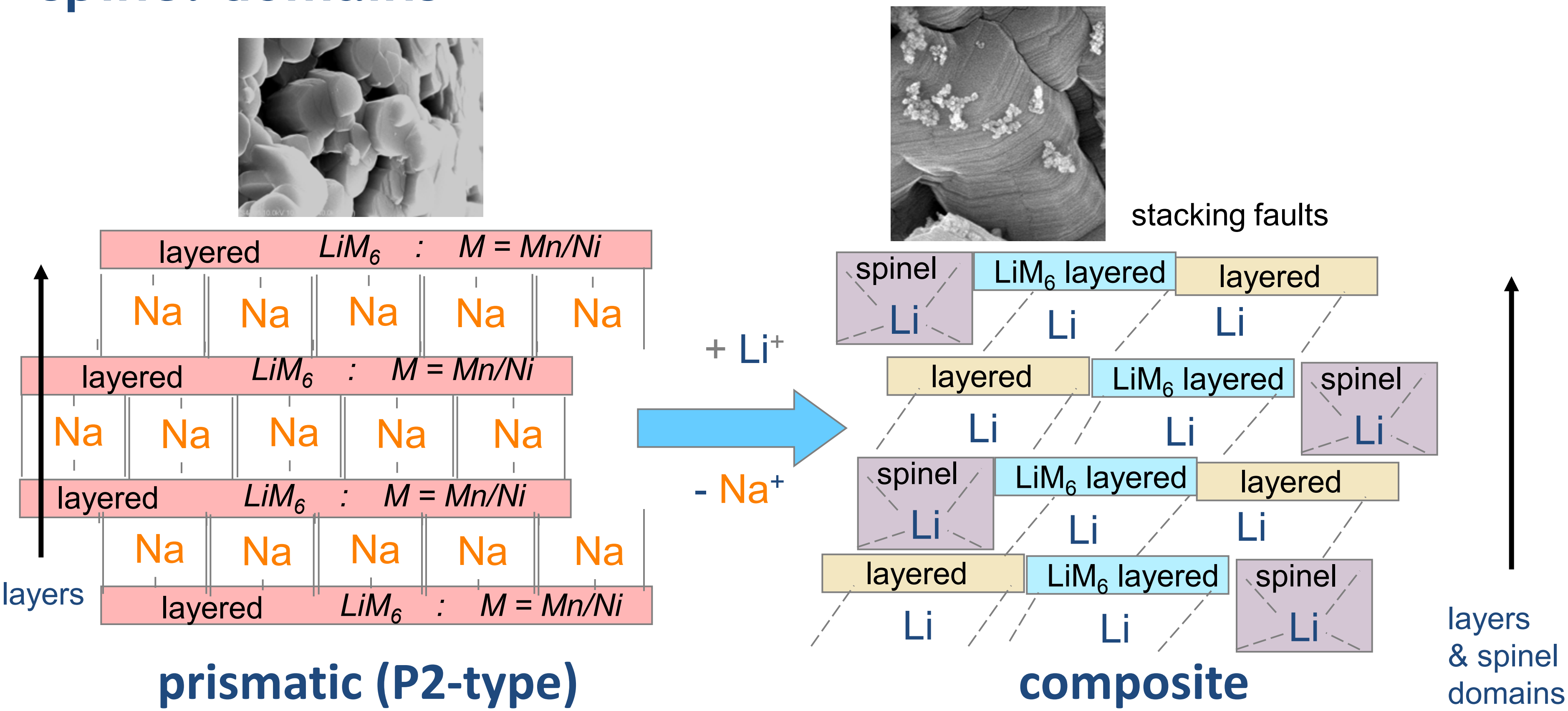
- 3 V process has sharp dQ/dV spinel peaks.
- Spinel component together with layered phases raises average voltage & increases energy density.

Cycling data summary for multiple samples



- IE synthesis route dictates different Li-Ni-Mn oxide composites & the resultant cathode cycling performance is quite variable.

Transformation and structural schematic showing spinel domains



- ‘layered (Li_2MnO_3)-layered ($LiNi_{0.5}Mn_{0.5}O_2$)-spinel ($LiNi_{0.5}Mn_{1.5}O_4$)’ composite is formed from IE reaction. Spinel forms under certain conditions when IE reaction is not too aggressive.

Collaborations

- **Partners:**
  - Academic partner – MTU sub-contract (Prof. Stephen Hackney)
    - Project titled "Transmisson Electron Microscopy (TEM) Characterization of Battery Materials"
  - Government Laboratory Partners -
    - ES028 ABR project – "Materials screening" (P.I. Dr. Wenquan Lu)
    - The Center of Nanoscale Materials (CNM) at Argonne is used to analyze materials.
      - Scientists: Dr. David Gozstola and Dr. Vic Maroni
    - The Advanced Photon Source (APS) at Argonne is used to analyze materials.
      - Scientists: Dr. Mali Balasubramanian, and N. Karan.

Future work

- Increase the energy density of Li ion-exchanged cathode materials

  -Optimize chemically integrated Ni-Mn spinel content

  -Adjust 'layered-layered' ratios

  -Increase average voltage and mitigate voltage fade
- Possible incorporate other elements such as Co, coatings, etc..
- Measure the thermal stability (DSC) of the charged material.
- Test a full cell with graphite or other appropriate anode.
- Advanced analytical methods and diagnostic tools will provide basic science knowledge on mechanism of IE process.
- Collaborations with other ABR teams will continue, and others will be initiated.

  -*Material screening (W.Lu), diagnostic analysis (new; D. Abraham), spectroscopy (new; Z.Chen)*

Summary & Conclusions

- Ion-exchange synthesis method has employed P2 Na/Li layered precursors as a route to make novel composite cathode structures with good electrochemical properties.
  - *Numerous (40) synthetic IE reaction combinations probed; all IE products, due to Na layered precursor show layered stacking faults, and pocked mark edges at surfaces of particles.*
  - *General capacities of 240 - 250 mAh/g (4.8 – 2.0 V) observed.*
  - *Favorable composites contain a Ni-Mn spinel (5 V) component, that raises the average voltage of the cathode.*
  - *Rate – variable; best materials ~ 150 mAh/g @ 10C rate; common is ~ 200 mAh/g @ 2C rate*
- Characterization
  - *XRD shows broad peaks; materials do not possess long-range order.*
  - *HRTEM on IE composite product indicate presence of layered and Li_2MnO_3 cubic domains.*
  - *6-Li solid state NMR confirms that Li resides in the TM layer.*
  - *XANES results show Ni(II) and Mn(IV) are present.*
- Li ion-exchange causes shearing of the crystal planes in the c-axis direction producing layers with stacking faults.
  - *Resultant crystal has small particle size, featuring layered crystal plates that have defects at the surface.*
  - *Creation of multiple entry points for Li may account for the high-power in the cathode.*