Novel Composite Cathode Structures

Christopher S. Johnson
Chemical Sciences and Engineering Division
Argonne National Laboratory

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Project ID: ES115

Overview

Timeline

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

  - new project

Budget

- Total project funding

  - 100% DOE
- FY11: $300K
- FY12: $400K

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead P.I. – C. S. Johnson
- Collaborators (Argonne):

  - S.-H. Kang, D. Kim, J. Vaughey, M. Slater (all of CSE)

  - M. Balasubramanian, N. Karan (Advanced Photon Source (all of Argonne))

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

Relevance

- New cathode materials are required to improve the energy density of Li-ion cells for transportation technologies.
- The cathode system in this project directly addresses the barriers to PHEVs and longer term EVs, which are low-energy density, low-power, high-cost and abuse tolerance limitations.
- This system represents a fresh approach to cathodes, and may be a possible next gen. cathode material for Li-ion battery technology.
- In this work, we are studying new novel cathode systems that are based on stable Mn(IV)-based layered transition metal oxides.

Objectives

Design and develop novel high capacity and high-energy cathode materials that are **low cost, with high-thermal stability** for PHEVs

- The implementation of layered transition metal oxides to Li batteries is well established, but this work is a fresh synthetic approach to new cathodes.
- Demonstrate the viability of the new synthesis route to Novel Cathode Composite Structures
  - Initiate optimizing synthetic conditions to produce material with the most favorable properties, such as surface area, tap density, phase purity, cost and safety
- Perform both physical property and electrochemical property measurements
  - Cycle the material in Li half cells and show at least 40 cycles above 200 mAh/g
  - Conduct power rate tests and demonstrate a capacity of 200 mAh/g at C/1 rate
  - Evaluate the phase type of the material using microscopy methods
  - Measure the phase purity by XRD after multiple cycles to evaluate stability

Milestones of FY11

- Synthesis of P2 precursors with variable Na/Li ratios – done
  - Precursor stoichiometries synthesized varied from $Na_{0.3}Li_{0.9}(Ni_{1/4}Mn_{3/4})O_{\delta}$ to $Na_{1.1}Li_{0.2}(Ni_{1/4}Mn_{3/4})O_{\delta}$
- Initial work/study on Li for Na ion exchange synthesis to make novel cathode materials - done
  - Materials have a typical composition: $Li_{1.09}Na_{0.02}Ni_{0.21}Mn_{0.62}O_2$
- Preliminary cell cycling of Li half cells – done
  - Baseline cycling (4.8 to 2.0 V)
  - Rate tests
- Characterization Work – used as a guide to optimize materials and understand underlying materials chemistry – on-going
  - X-ray Diffraction studies–initiated
  - XANES study - continuing
  - Microscopy studies on P2 precursor and ion-exchanged product – continuing
    - Field Emission Scanning electron Microscopy
    - Electron diffraction
    - Transmission electron microscopy
- Evaluation of cathode materials thermal stability – initiated
- Modeling/calculations of cathode-anode material balance, cost and performance parameters - initiated

Approach

- ***This approach is new***. It is the implementation of a rationally designed cathode technology that utilizes high-capacity (high energy) and high-power materials in a ***Li-Ion*** cell configuration. Materials formed by this process are made via an ion-exchange method and the product is written 'IE-LNMO' which stands for ion-exchanged lithium nickel manganese oxide.

•Synthesize, characterize, and develop new cathode materials that exploit the difference in sodium versus lithium cation radii and their respective coordination properties.

•Proposed cathodes will be derived from layered sodium transition metal oxide precursors that contain modest amounts of lithium in the transition metal (TM) layer.

•The sodium in the precursor materials is then ion-exchanged with lithium to form layered composite oxide cathodes for lithium batteries.

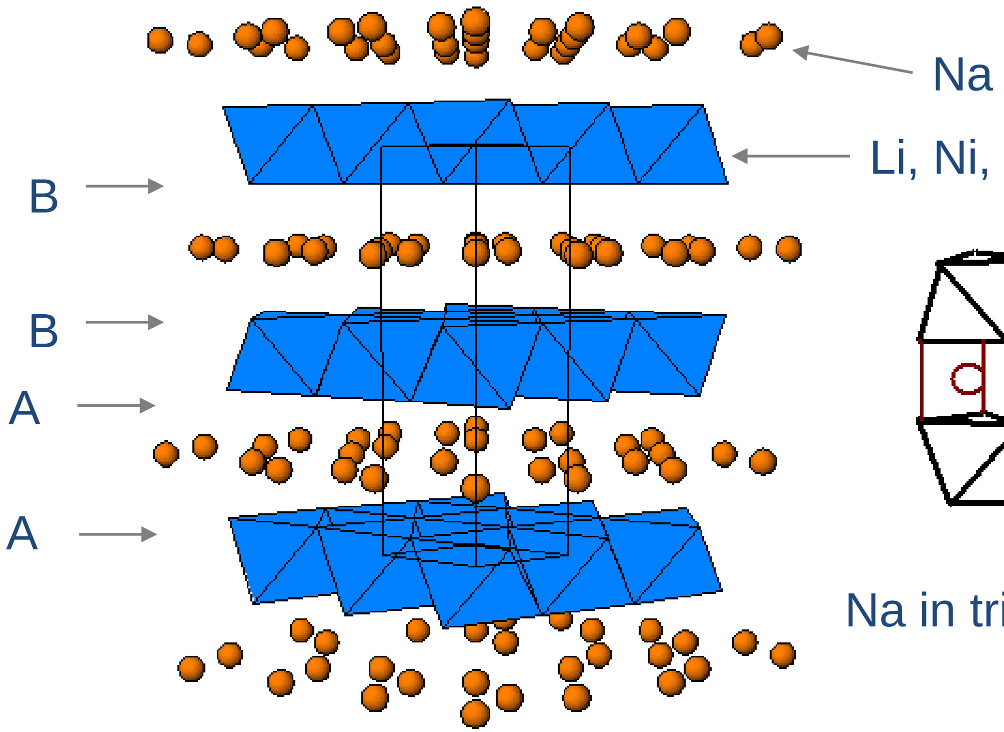
- We will focus on electrode materials that contain redox active Ni, and low cost Mn

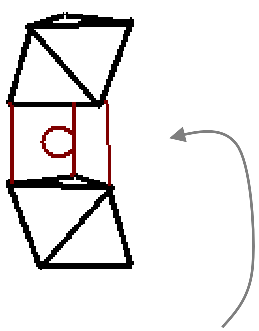
Synthesis Scheme

STEP 1

$$0.4Na_2CO_3 + 0.1Li_2CO_3 + Ni_{0.25}Mn_{0.75}CO_3 \xrightarrow{800 - 900\ ^oC} Na_{0.8}Li_{0.2}(Ni_{0.25}Mn_{0.75})O_\beta + 1.5\ CO_2$$

Layered precursor



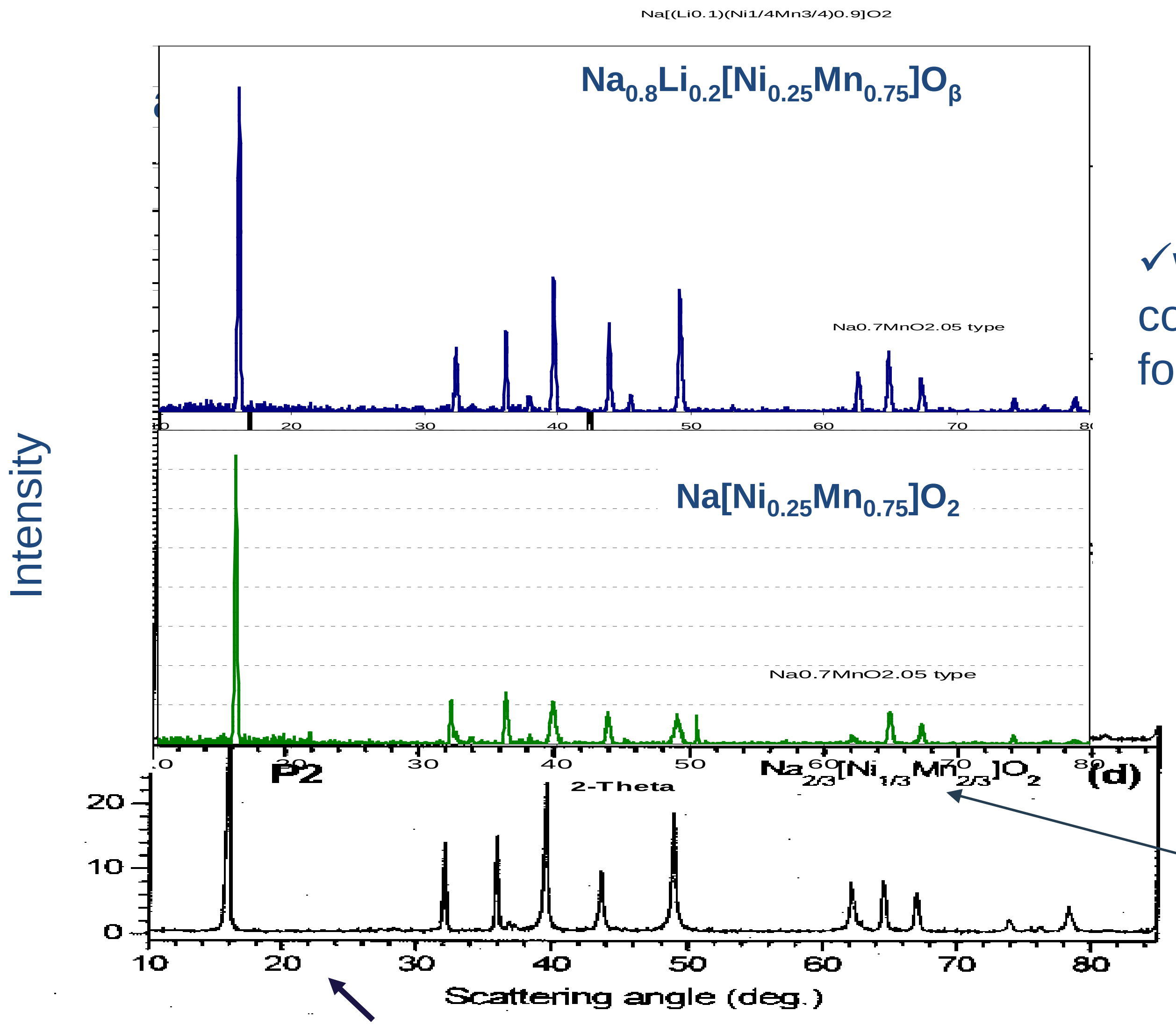


Na – **1.02 Å**
Li – **0.76 Å**
Ni^{2+} - 0.69 Å
Mn^{4+} - 0.53 Å

Na in trigonal prismatic coordination

JCPDS 27-0751 $Na_{0.7}MnO_{2.05}$ type

XRD results



✓wide range of compositions available for this structure type

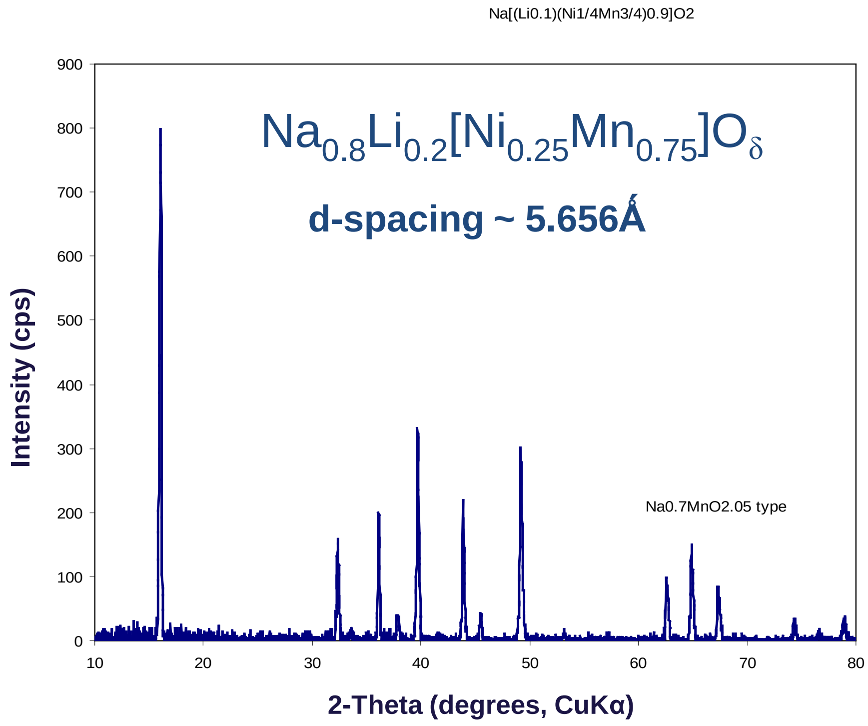
$Na_{0.67}[Ni_{0.33}Mn_{0.67}]O_2$ (no Li present)

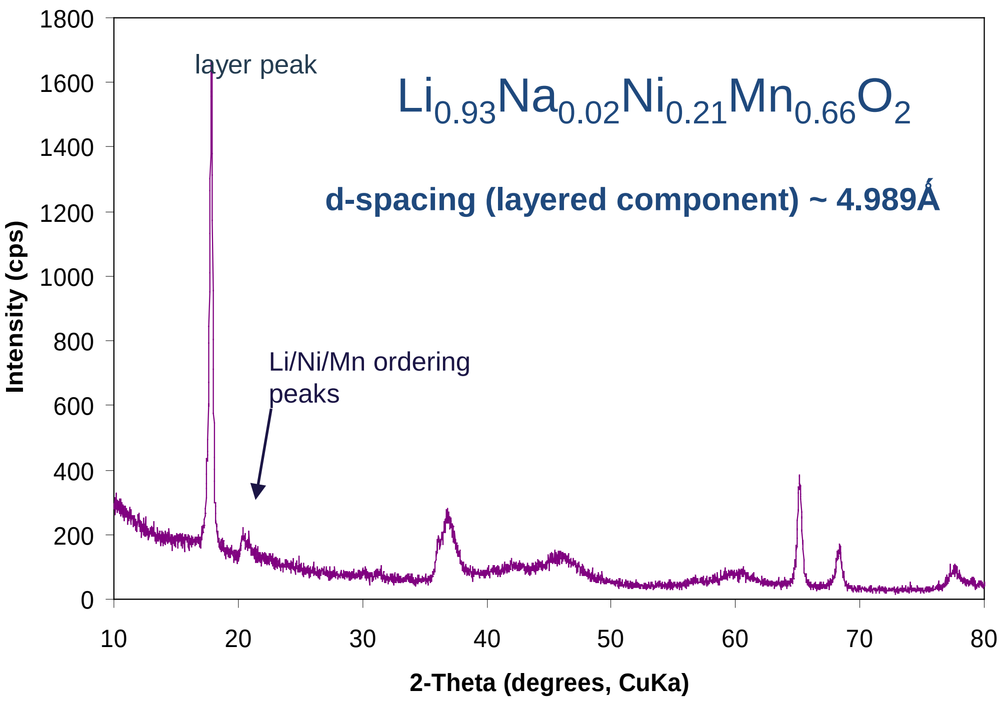
Paulsen and Dahn JES, 2000

STEP 2

$Na_{0.8}Li_{0.2}[Ni_{0.25}Mn_{0.75}]O_{\beta}$ —excess LiBr (refluxing hexanol) (4-5h)→

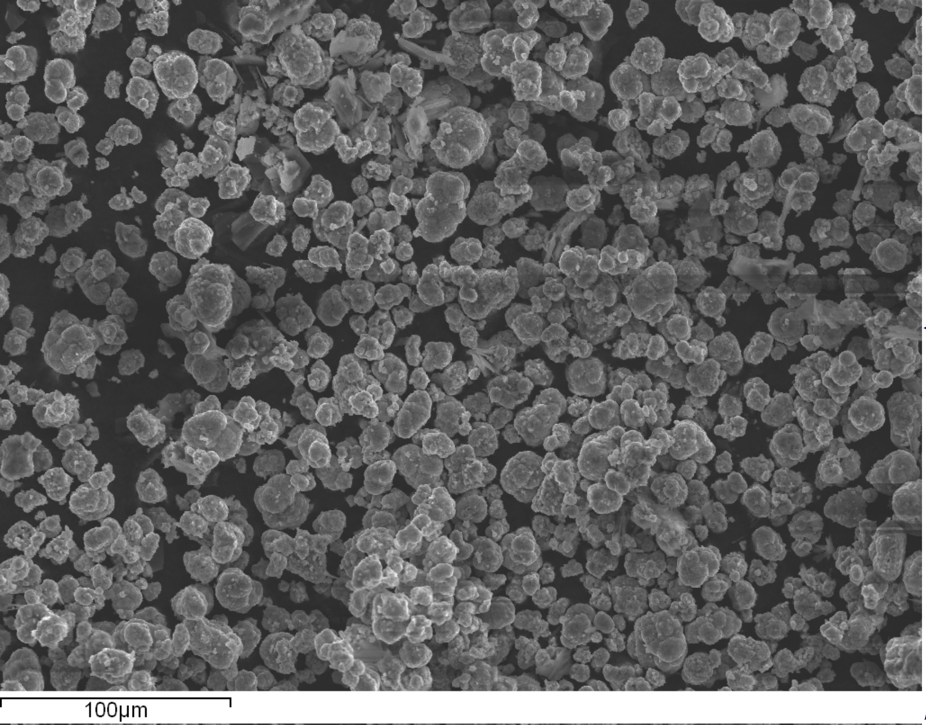
ion exchange product + x NaBr





- ✓ layering shrinks
- ✓ ordering peaks present
- ✓ peaks generally broad
- ✓ from ICP; Ni and Mn remain in material & Mn/Ni = 3

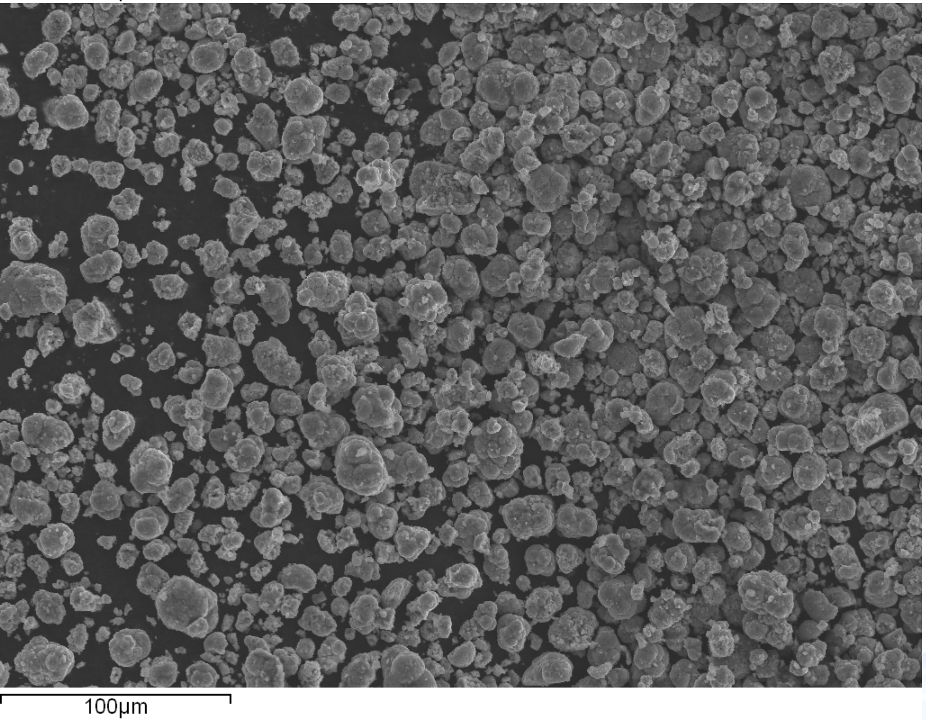
SEM results

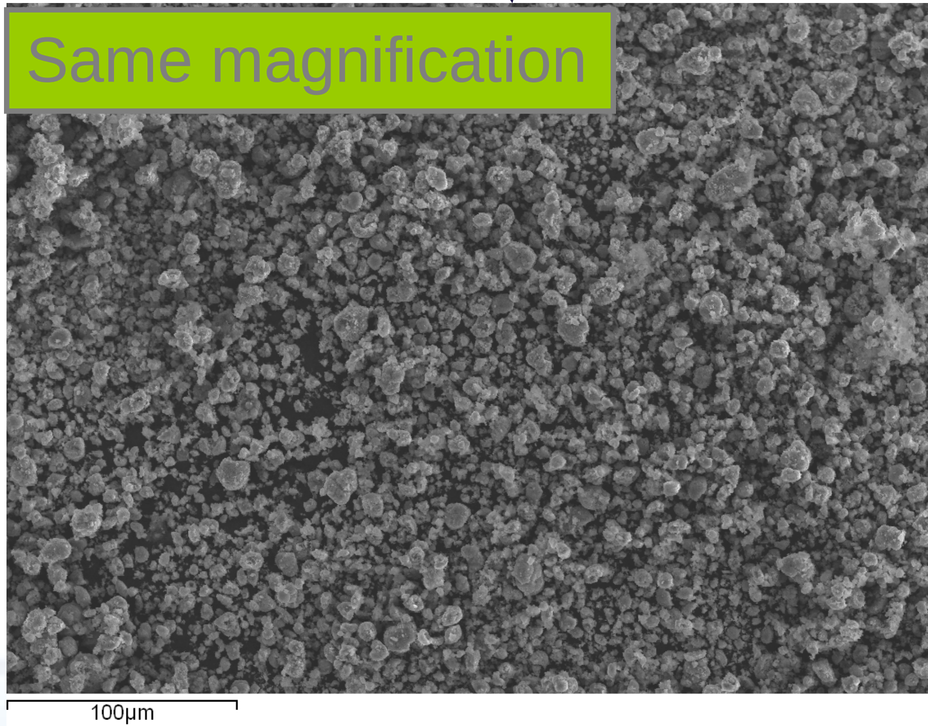


Na/Li precursor

4 h Li ion-exchange treatment

24 h Li ion-exchange treatment

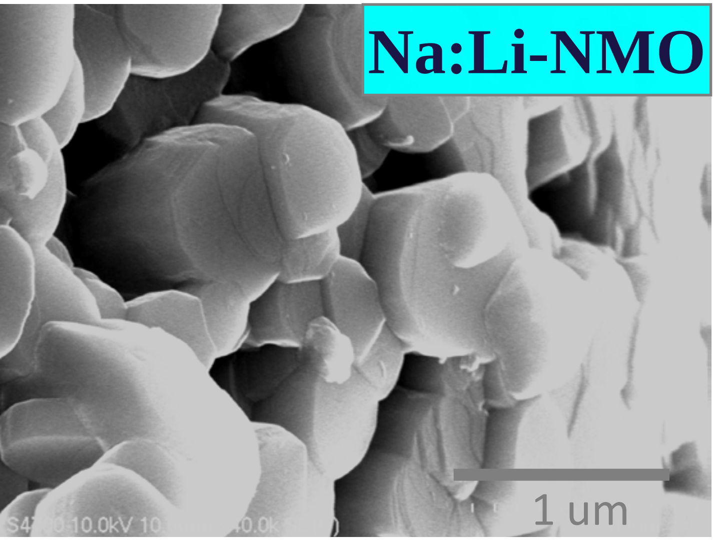




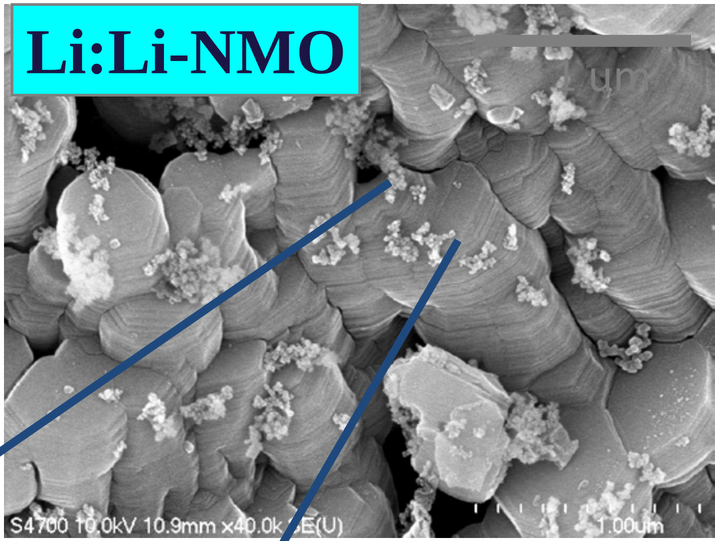
FESEM results

Na/Li-precursor

IE-LNMO

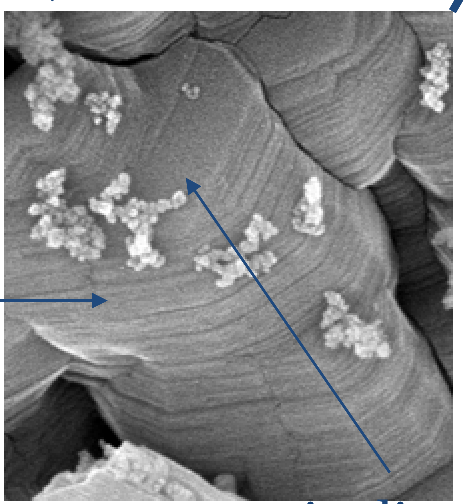


ion-exchange
Li for Na



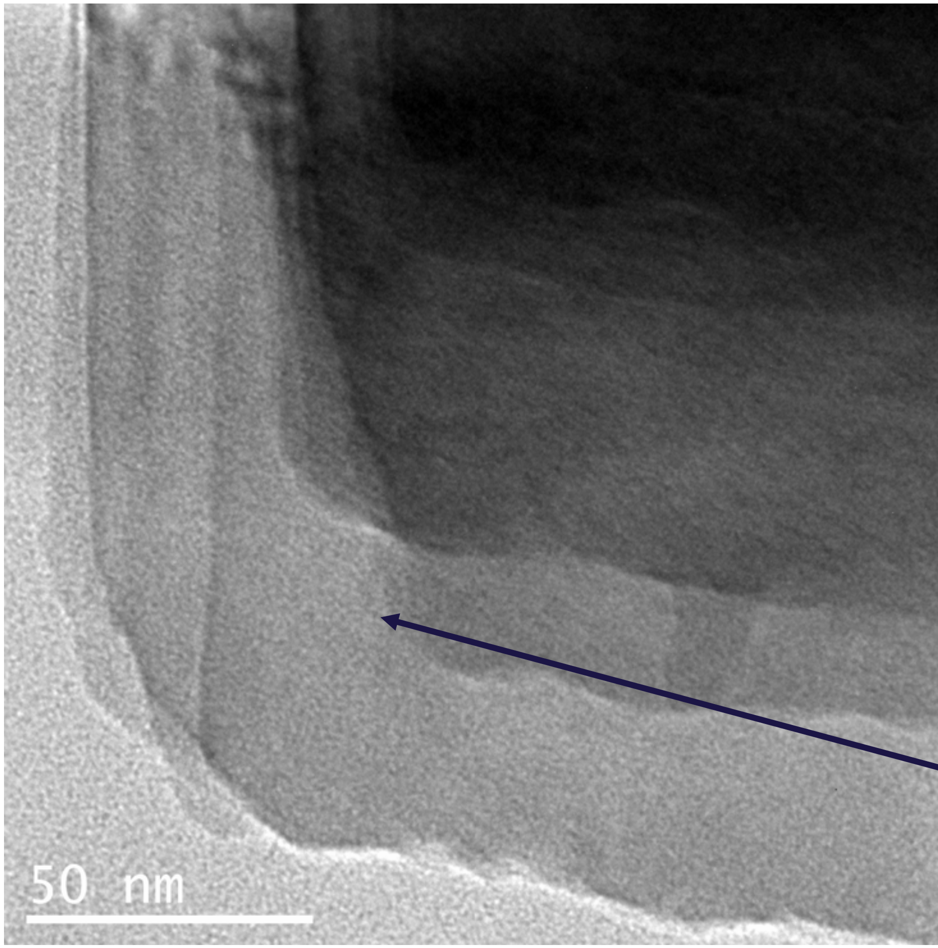
Particle is 'sliced' along the c-axis direction during ion-exchange reation (i.e. the layering direction)

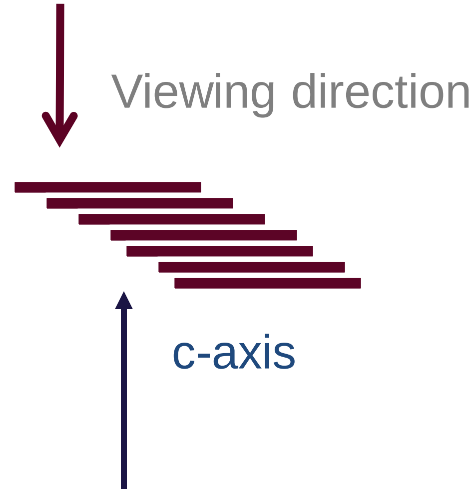
fast Li-insertion
on edge plane



c-axis direction

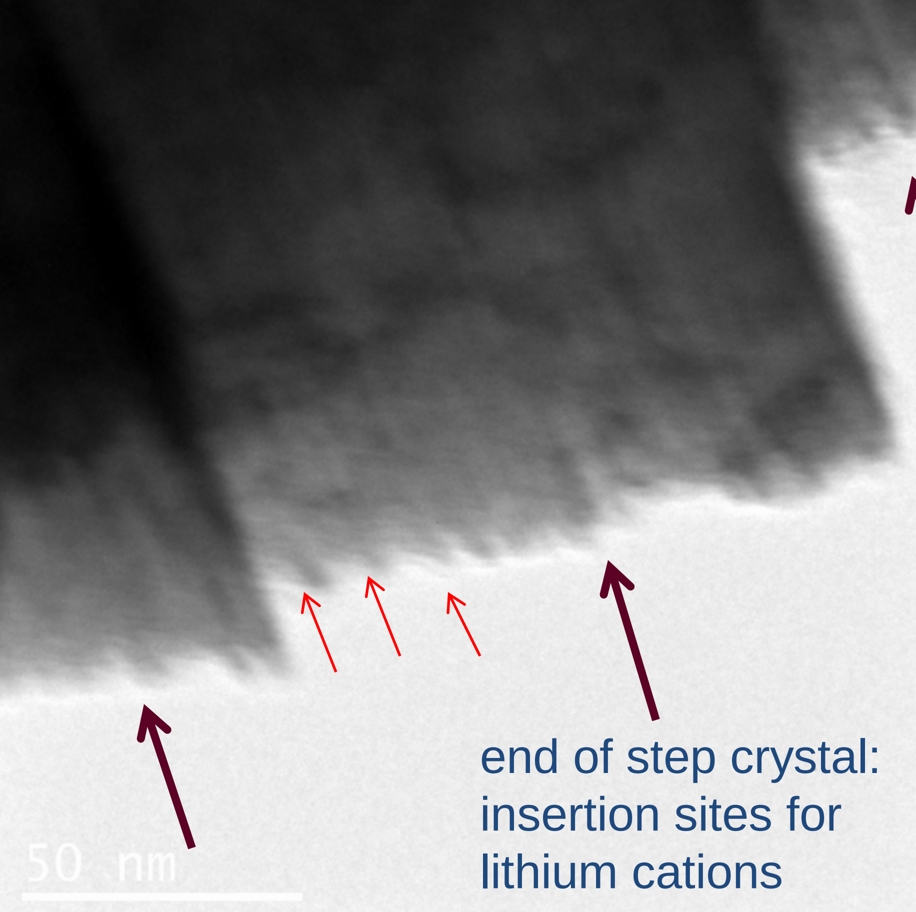
TEM results - I

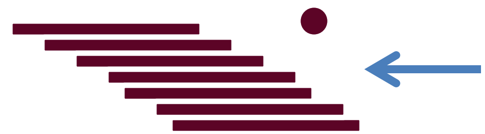


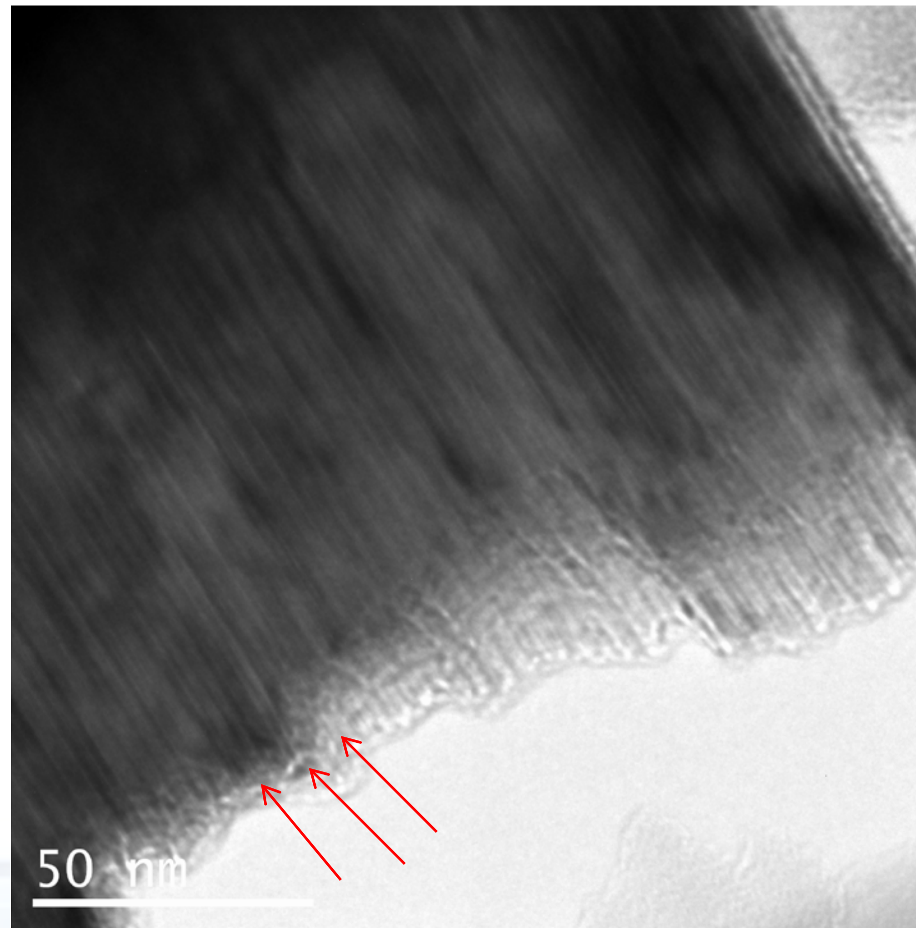


particles' planes are sheared at the unit-cell level – smooth plates are formed

TEM results - II

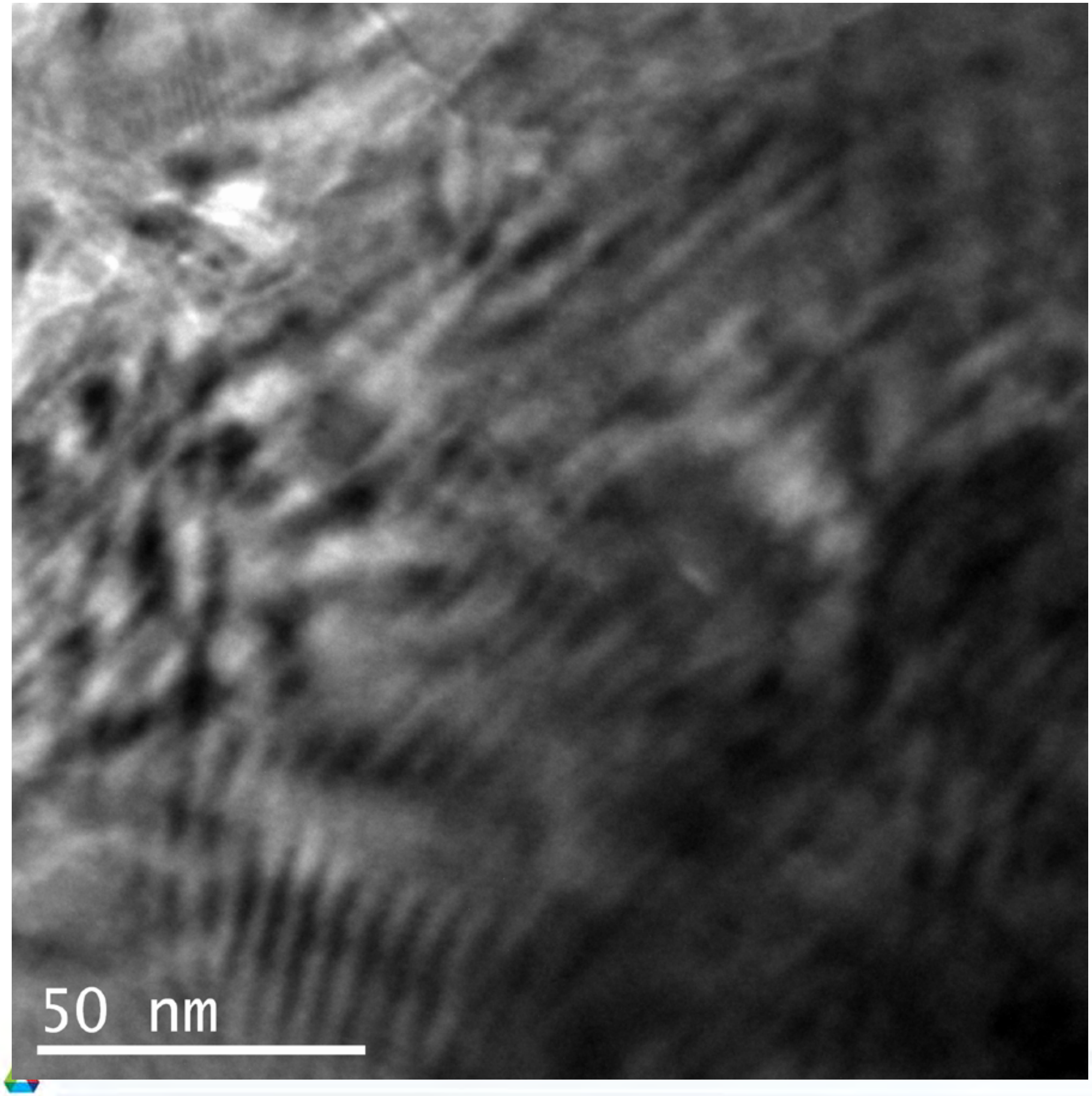




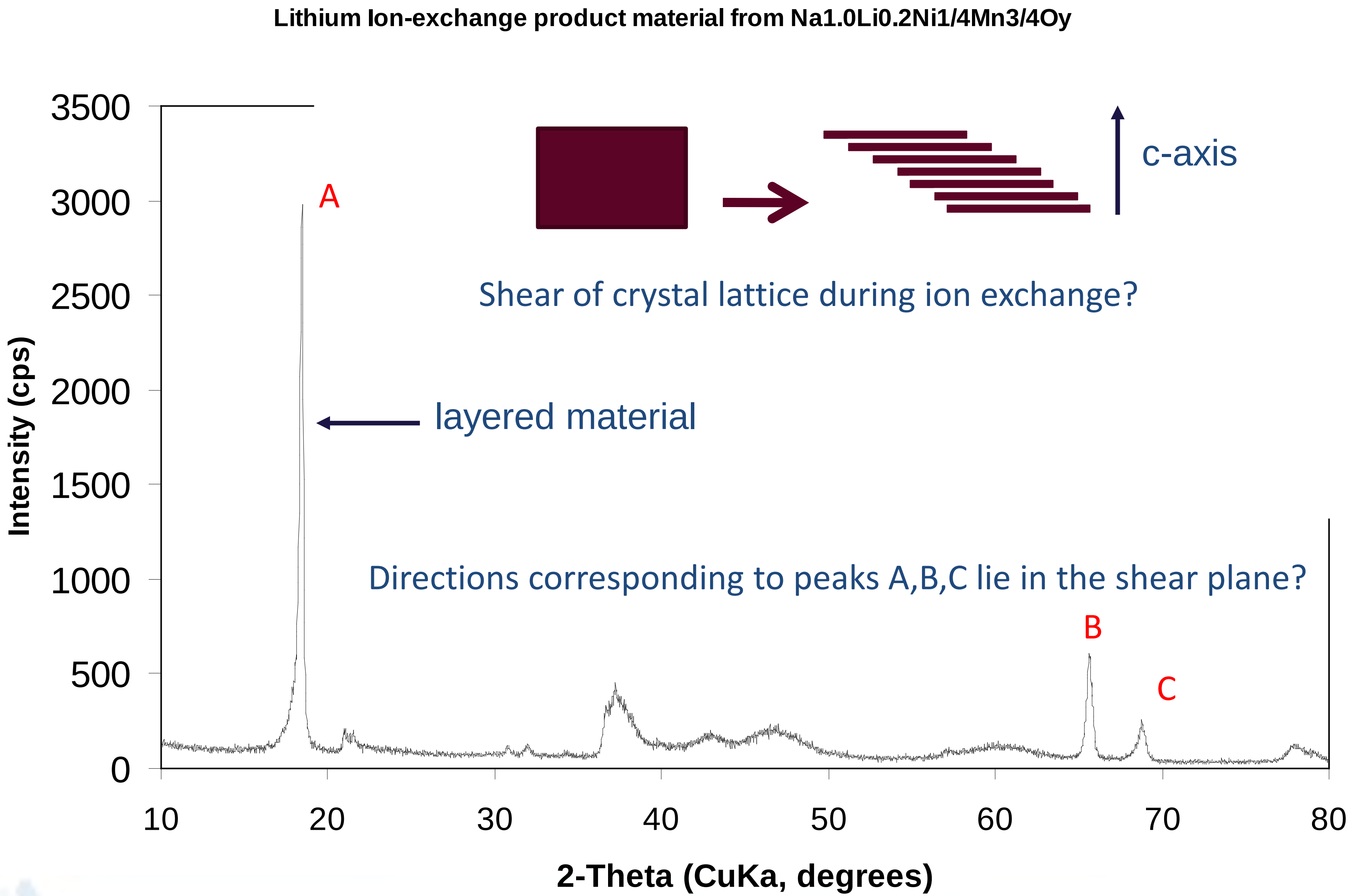


•Ion-exchange occurs perpendicular to the c-axis direction;

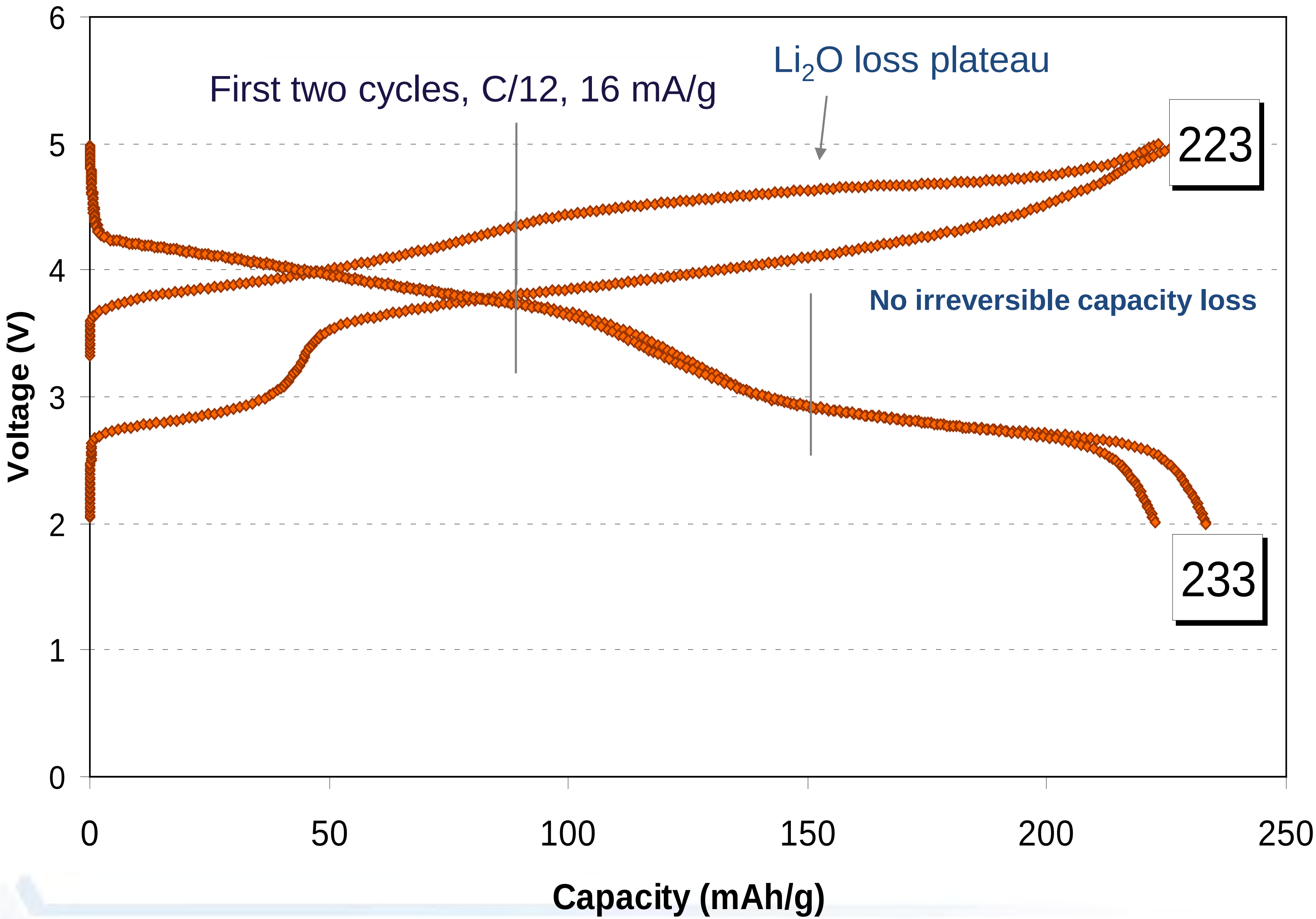
TEM results - III



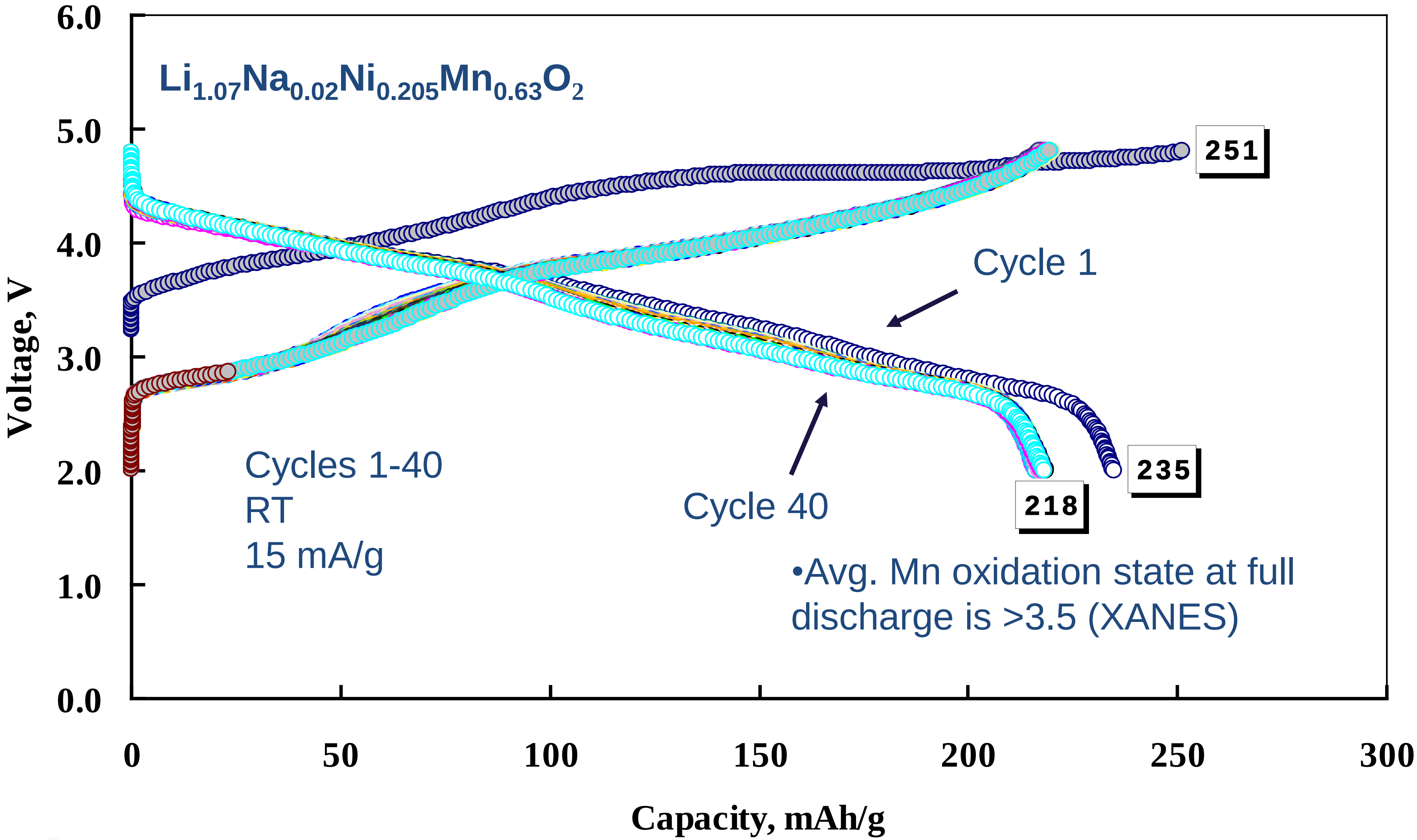
Plausible mechanism of ion-exchange



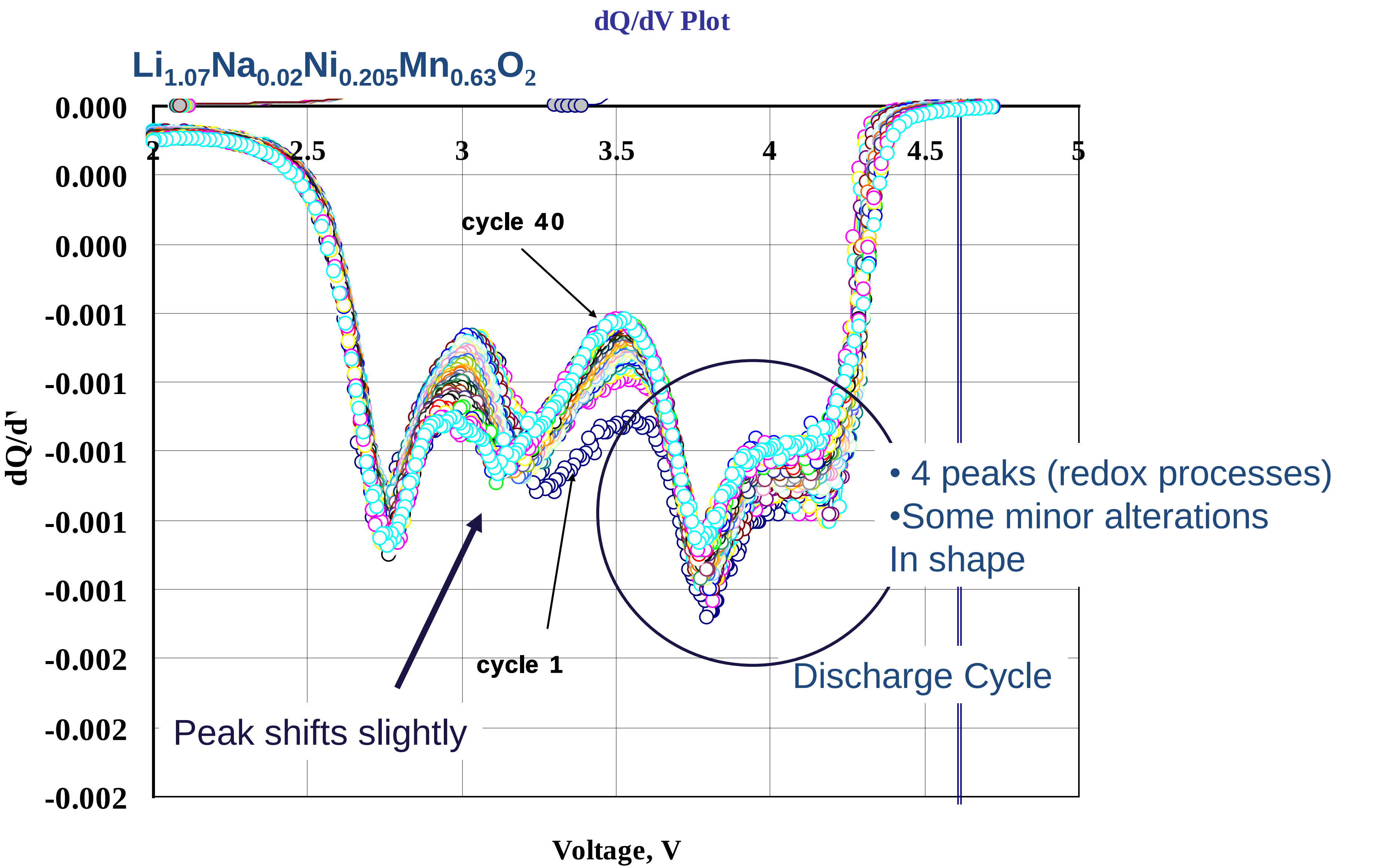
Voltage profile - IE-LNMO ($Li_{0.93}Na_{0.02}Ni_{0.21}Mn_{0.66}O_2$)



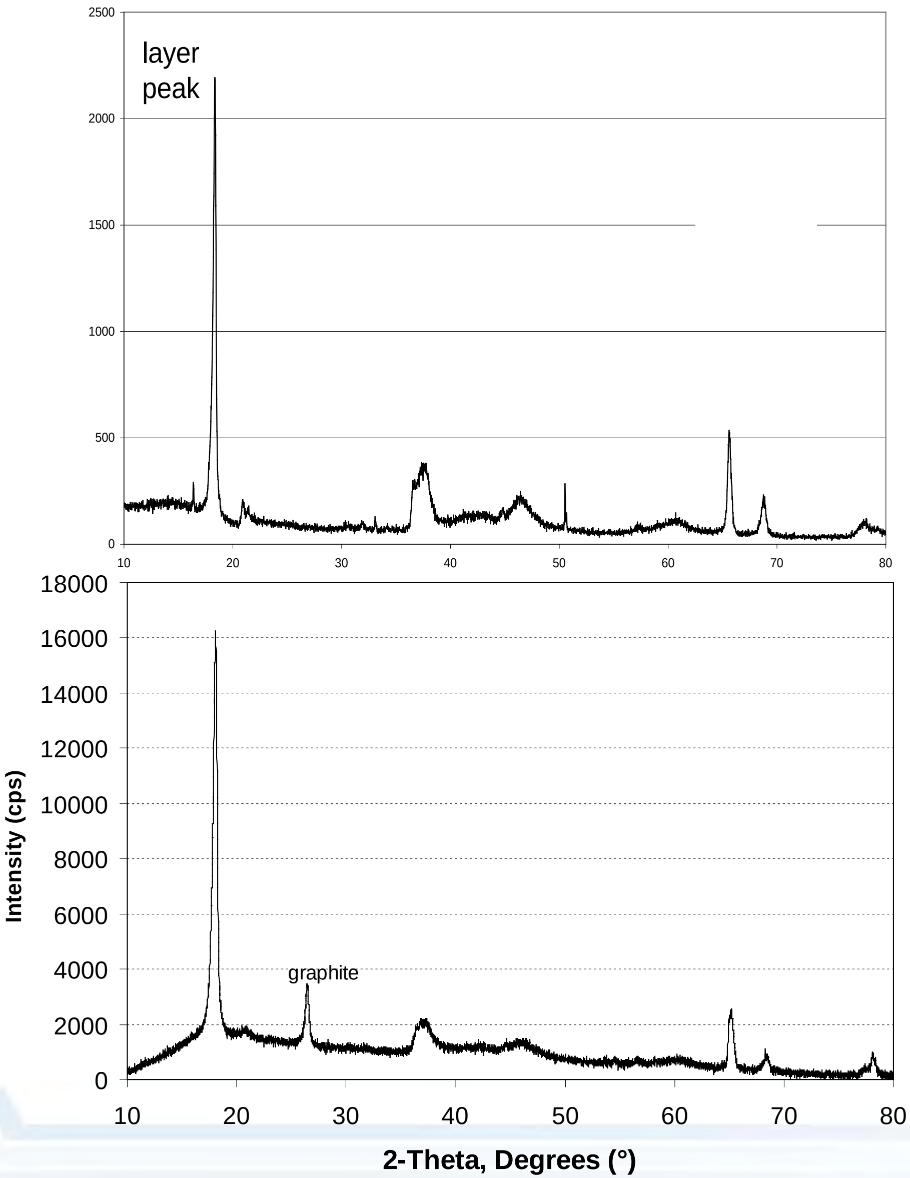
Voltage profile - IE-LNMO ; multiple cycles



Differential capacity plots- IE-LNMO



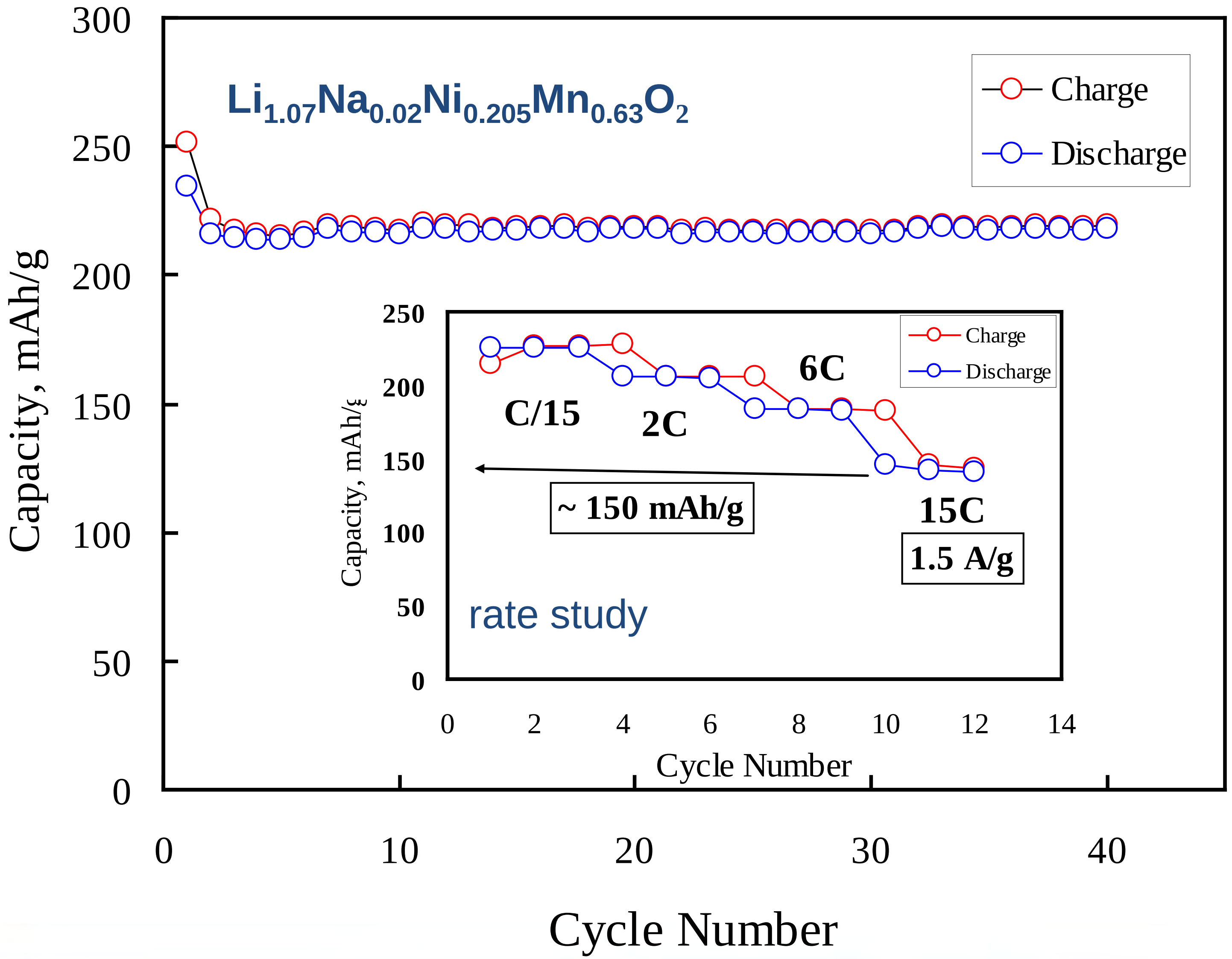
XRD result post-cycling for IE-LNMO



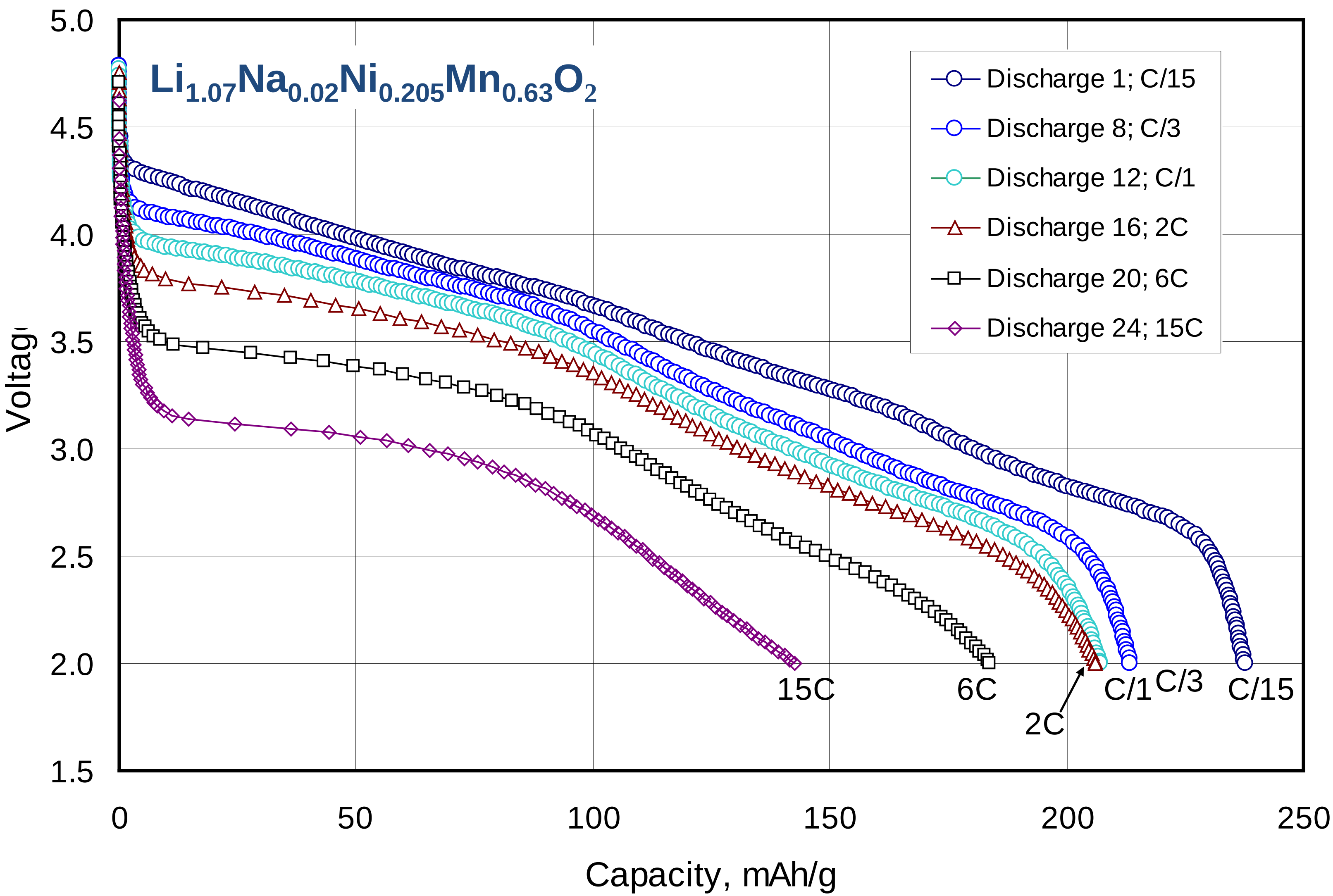
- ✓ strong layering peak
- ✓ ordering peaks less prominent
- ✓ other peaks maintained

after 50 cycles

Coin cell Cycling - Li Half cell

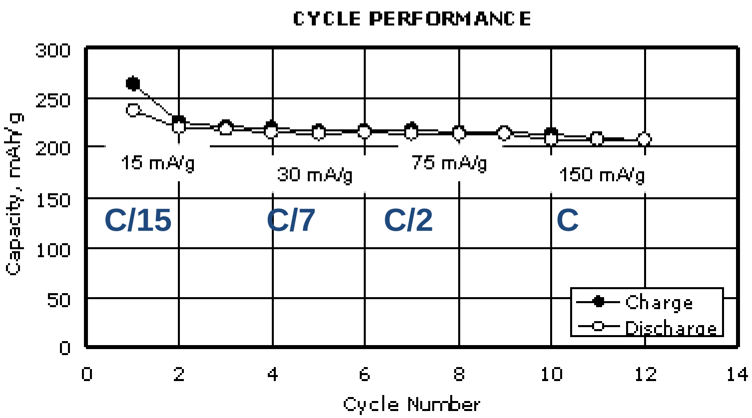


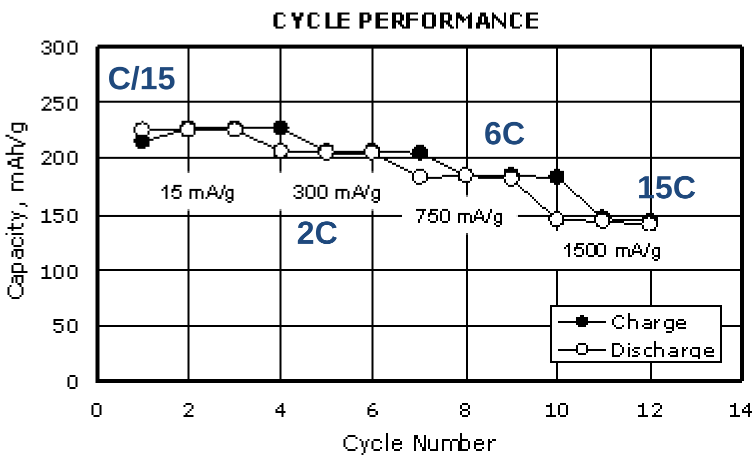
Discharge profiles - IE-LNMO rate studies



Rate Study Summary

$Li_{1.07}Na_{0.02}Ni_{0.205}Mn_{0.63}O_2$





Discharge rates

- ✓ 205 mAh/g @ C rate
- ✓ 200 mAh/g @ 2C rate
- ✓ 180 mAh/g @ 6C rate
- ✓ 150 mAh/g @ 15C rate

4.8 to 2.0 V
trickle charge @ 4.8 V

Johnson, et al.. Electrochem. Commun. 12 (2010) 1618

Collaborations

- **<u>Partners:</u>**
  - <u>Academic partner</u> – MTU sub-contract
    - Project titled “Transmisson Electron Microscopy (TEM) Characterization of Battery Materials”
  - <u>Government Laboratory Partners</u> -
    - ES022 ABR project – “Intermetallic electrodes” (P.I. Dr. Andy Jansen)
    - 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: Drs. Mali Balasubramanian, and N. Karan.

Future work

- Increase the energy density of cathode materials
  - Adjust Ni-Mn content; adjust Na/Li amount in P2 precursor
- Synthetically check the incorporation of other elements – namely Fe
- Put surface coatings on IE-LNMO and check performance
  - Evaluate long-term stability of charged cathode in electrolyte
  - Attempt to mitigate all changes in voltage profiles during cycling
- Measure the thermal stability of the material
- Test a full cell with graphite as anode
- Advanced analytical methods (SEM, TEM) and diagnostic tools @APS & CNM (Raman) will be used to characterize new materials and will provide basic science knowledge
  - Measure transport properties of new materials
- Collaborations with other ABR teams will continue, and will be initiated.
  - Intermetallic anode project (Jansen), material screening (Lu), diagnostic analysis (Abraham)

Summary & Conclusions

- Ion-exchange synthesis method utilized P2 Na/Li layered precursors as a route to make novel composite cathode structures with excellent electrochemical properties
  - 220 mAh/g (4.8 – 2.0 V)
  - <10% irreversible capacity and is tunable per system
  - Rate – 2C rate is 200 mAh/g, 15 C is 150 mAh/g
- Characterization
  - SEM and TEM indicate nanoscale morphology changes upon IE
  - XRD shows strong layering peak, and a cluster of peaks at about 20-23 °2-θindicative of possible Li/Ni/Mn ordering in the TM layer
- Mechanism of sodium removal for lithium causes shearing of the crystal planes in the c-axis direction producing layers with stacking faults
  - Resultant crystal has small particle size, featuring plates that are robust and layered
  - Creation of multiple entry points for Li giving rise to high-power