Energy Storage Using Sodium-ion Batteries (SIB)

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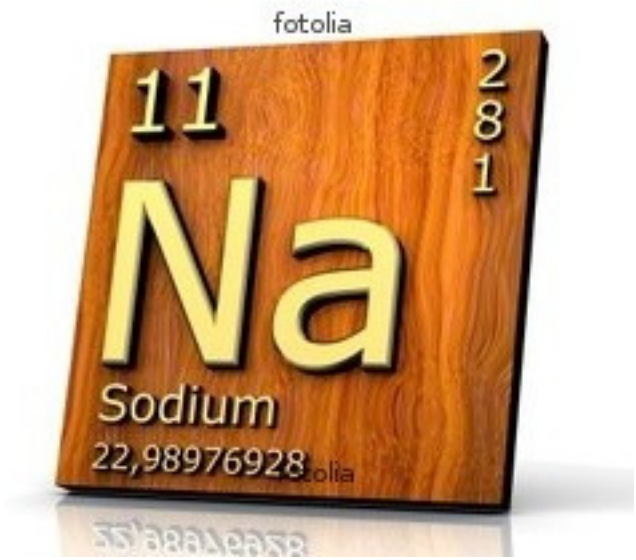


Chemical Sciences and Engineering Division
Argonne National Laboratory U.S.A.

Beyond Li-ion Batteries VIII Conference
Oak Ridge National Laboratory TN, 2-4 June 2015

Why Na-ion batteries?

- Revisit the system -> leverage knowledge from Li-ion
  - Room for big improvements and understanding in Na are possible
  - Motivating factor-> **nice potential for low-cost**
  - **May provide a quasi-backup technology to Li-ion or drop-in replacement**

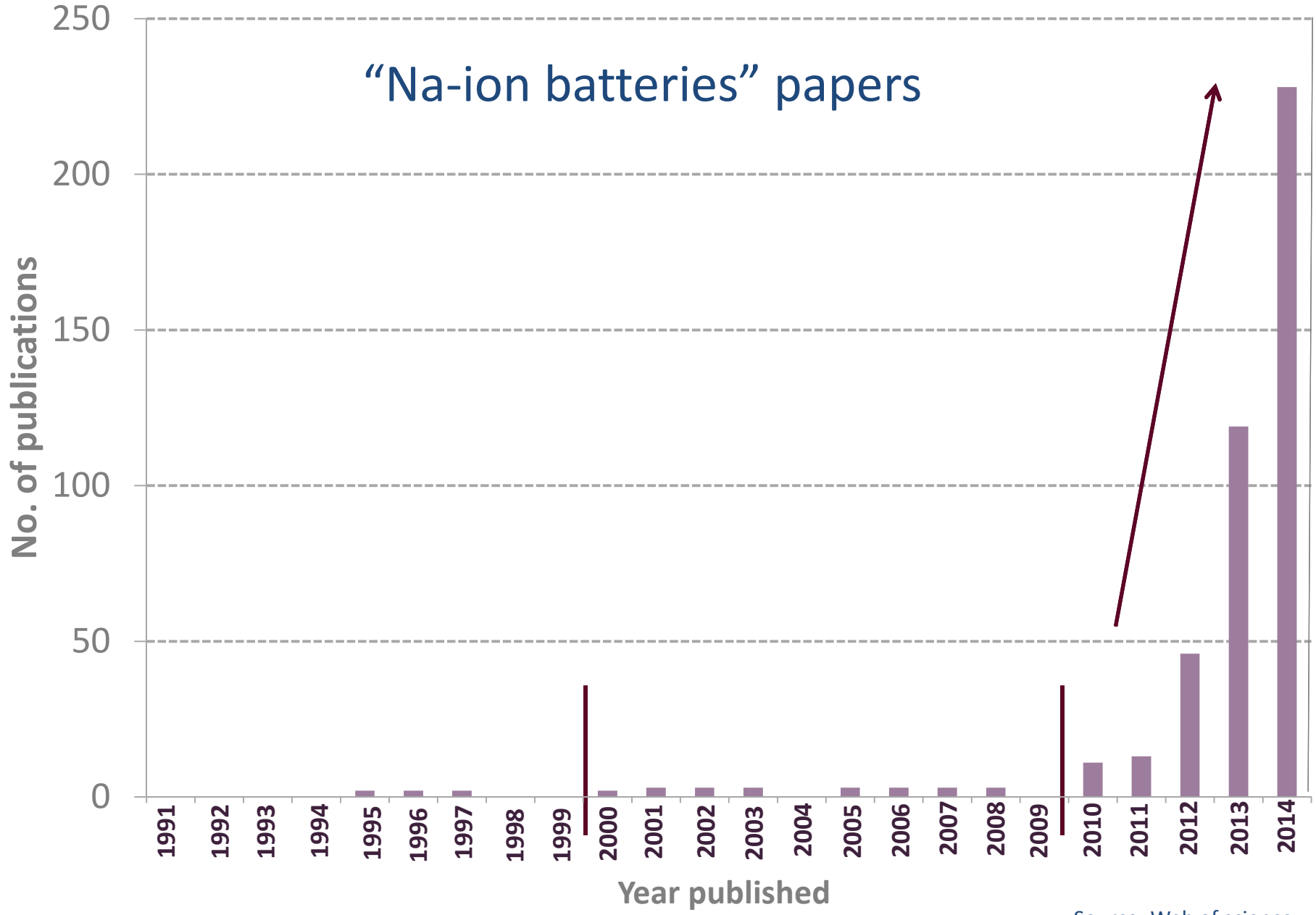
Al current collectors
Many known Na inorganic compounds
Lower voltage – longer stability
Solid-state electrolytes - proven

Lithium & Sodium - specifications

Li	Na	Categories
0.7 Å	1.0 Å	Cation radii
~ 7 g/mol	~ 23 g/mol	Molecular weight
0 V	-0.3 V	E^0 (vs. Li/Li^+)
$5000/ton	$150/ton[×]	Cost - carbonates
3829 mAh/g	1165 mAh/g	Capacity (mAh/g) - metal
Octahedral and tetrahedral	Octahedral and prismatic	Coordination preference

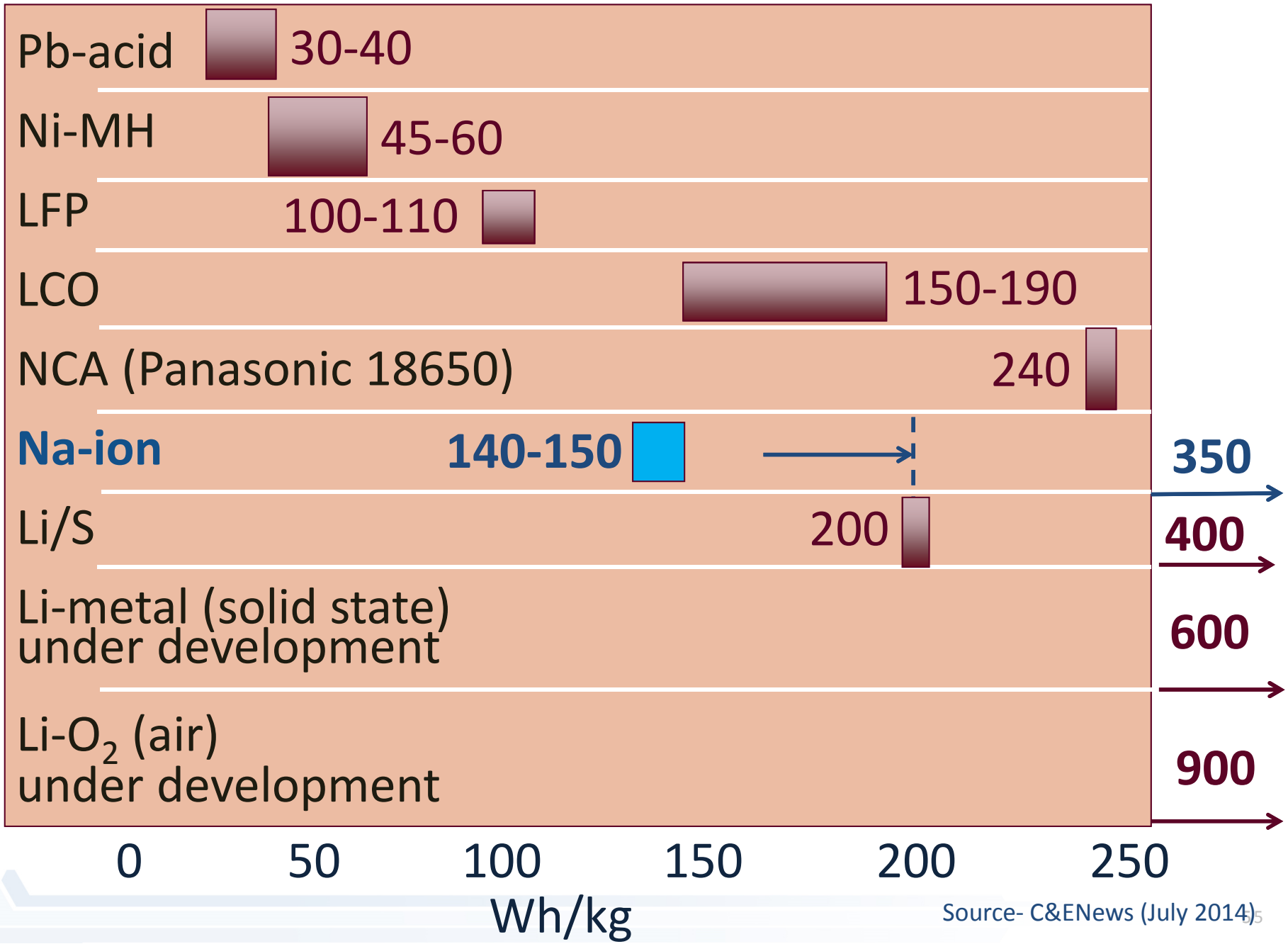
* ~ 2% seawater is Na

[×] http://minerals.usgs.gov/minerals/pubs/commodity/lithium/mcs-2011-sodaa.pdf



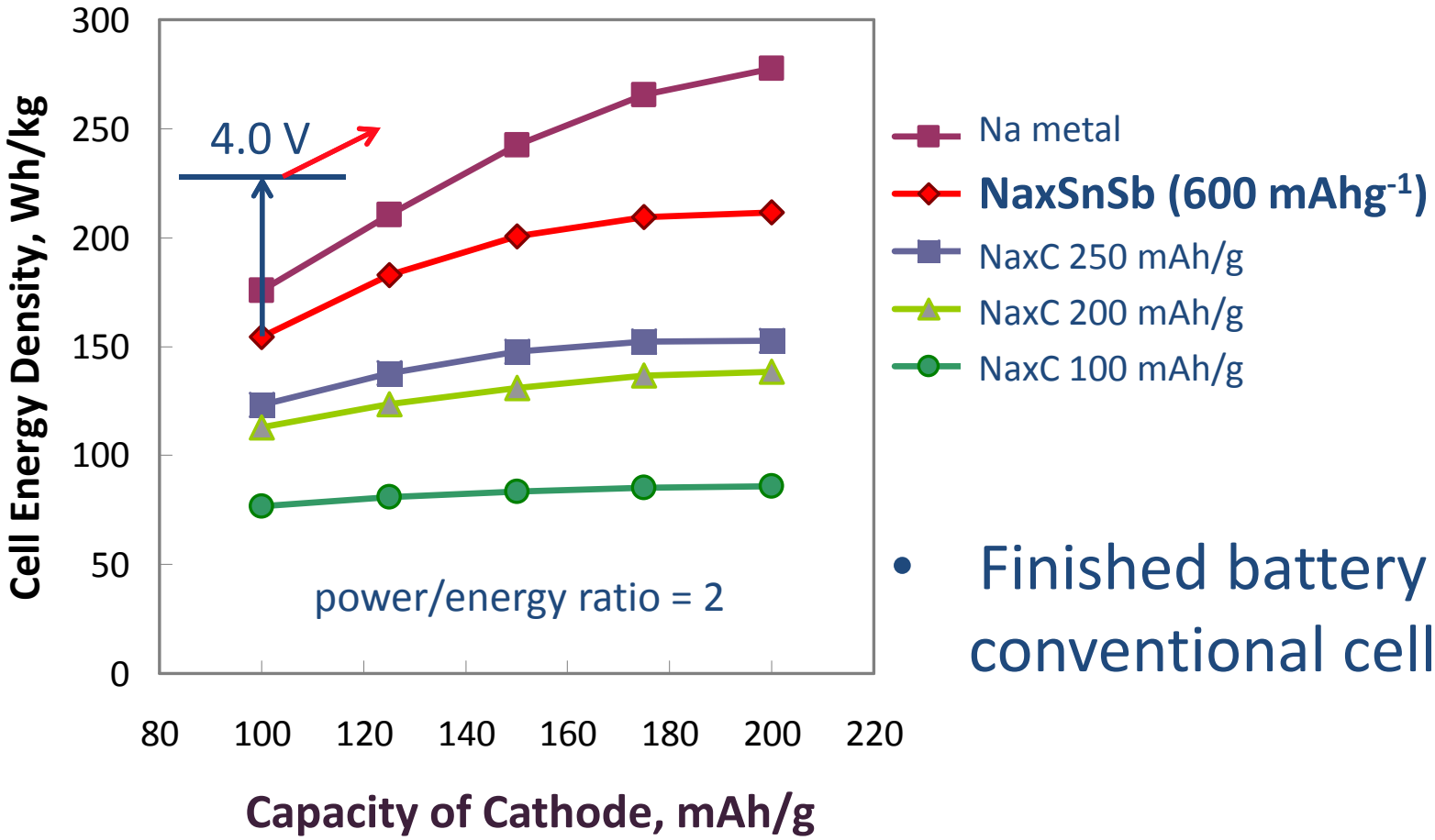
Source- Web of science

Energy densities of battery technologies



Source- C&ENews (July 2014)

Energy Density* range of Na-ion (3.0 V; pouch cell) BatPaC# (ANL model) for storage applications



- Finished battery module: conventional cell design

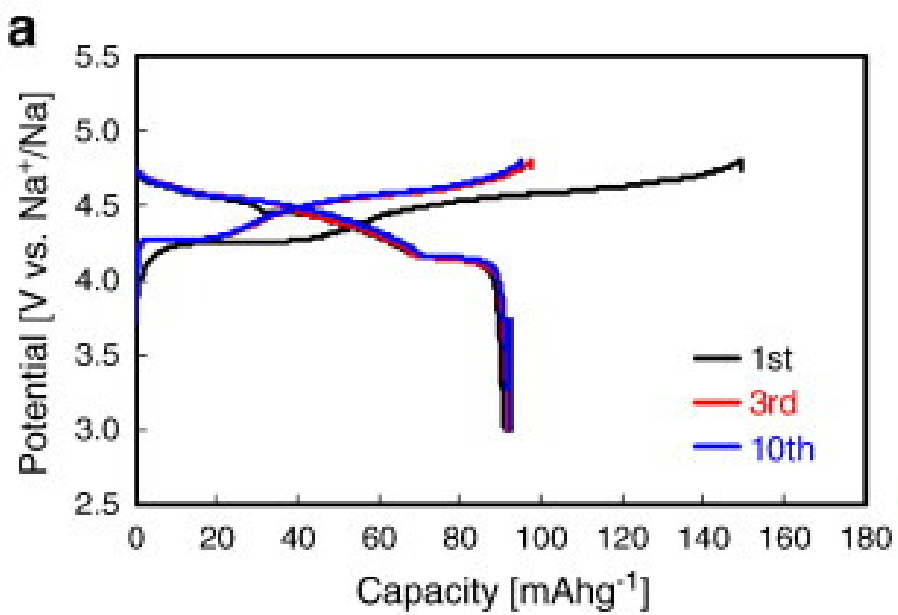
*Energy density model : quite cell voltage dependent (4.0 V; ~30-40% ↑)◊

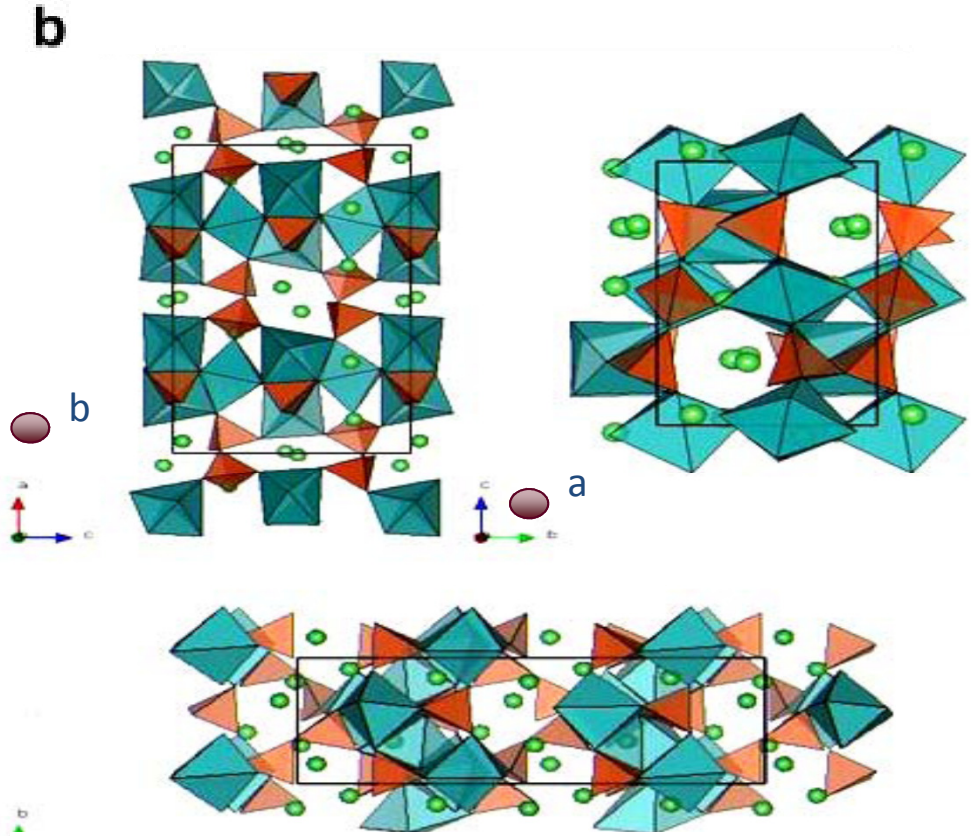
- http://www.cse.anl.gov/batpac/index.html

◊ Eroglu et al., *J. Power Sources*, **267**, 14 (2014)

4.4 V class Na-ion battery cathode

$Na/Na_4Co_{2.4}Mn_{0.3}Ni_{0.3}(PO_4)_2P_2O_7$

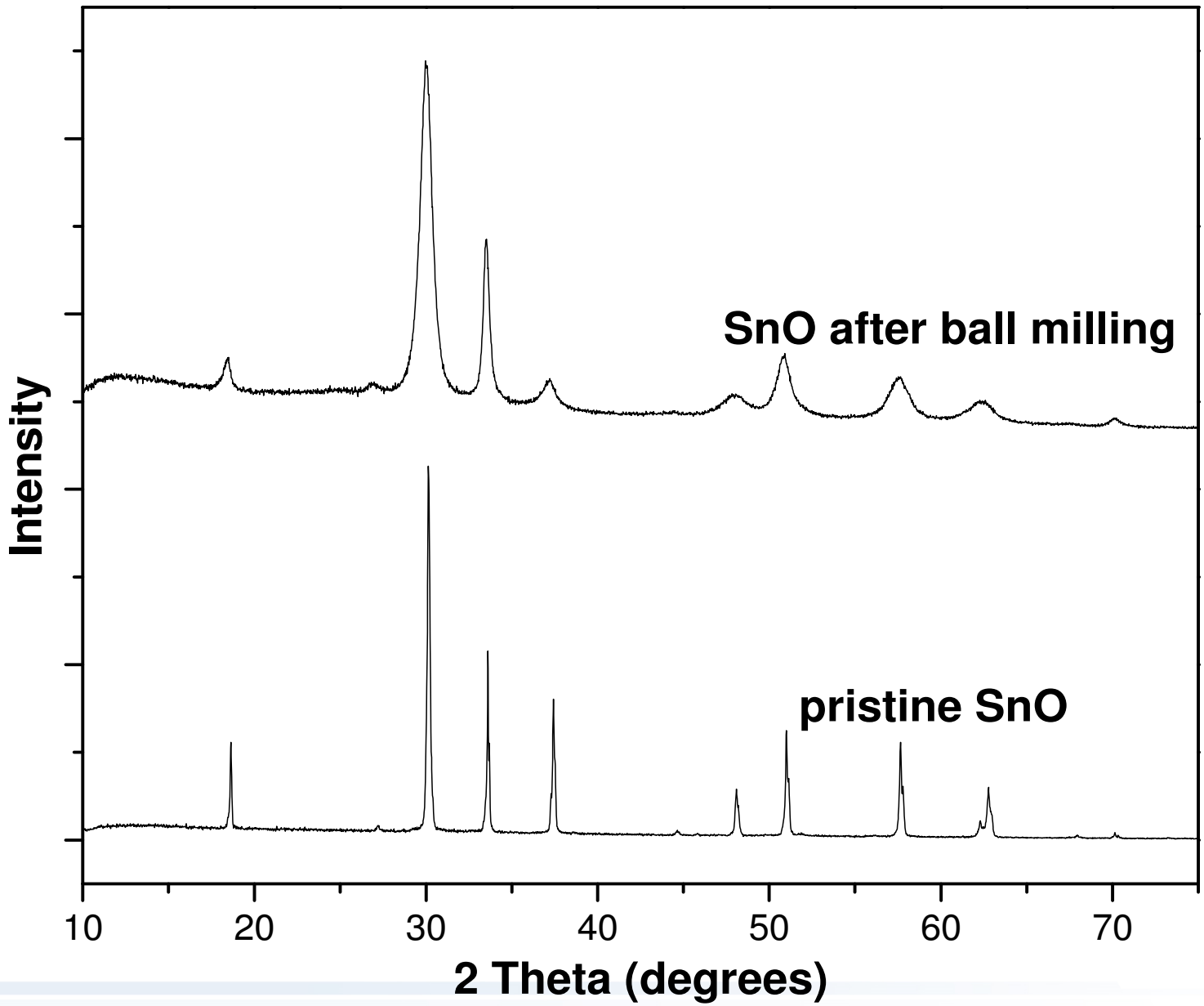




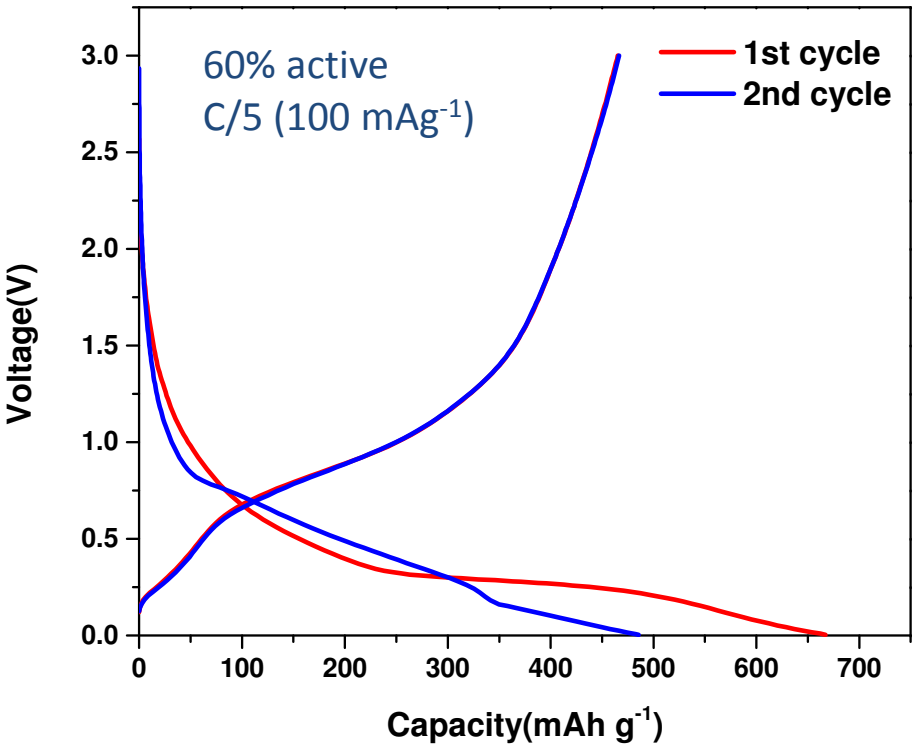
<u>Argonne BatPaC Model</u> - ED -> 275 – 300 $Whkg^{-1}$ (Na_xSnSb anode)

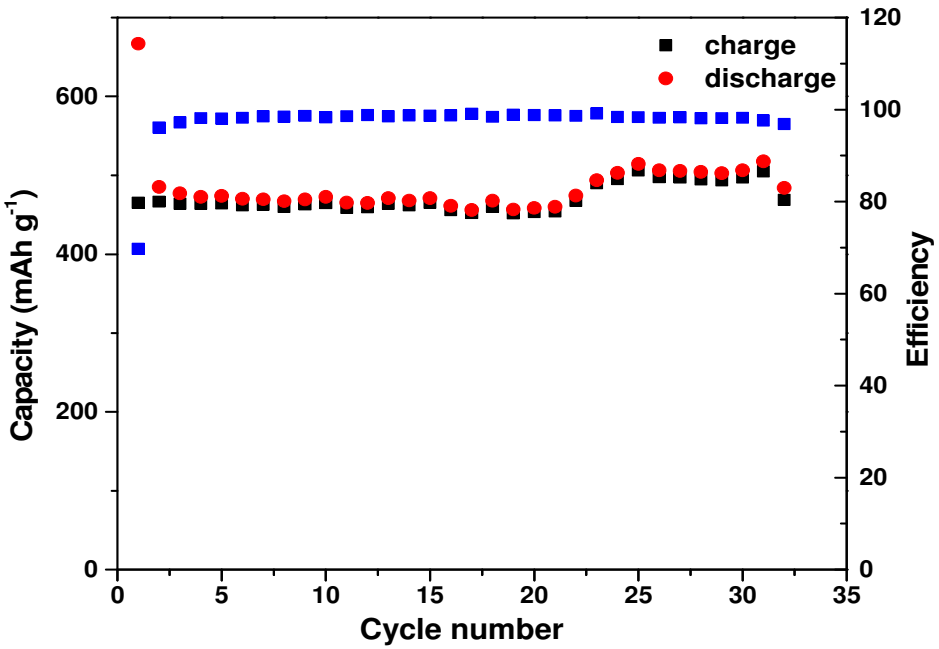
Nose et al., *Electrochem. Commun*, **34**, 266 (2013)

SnO_C nanocomposite anode material

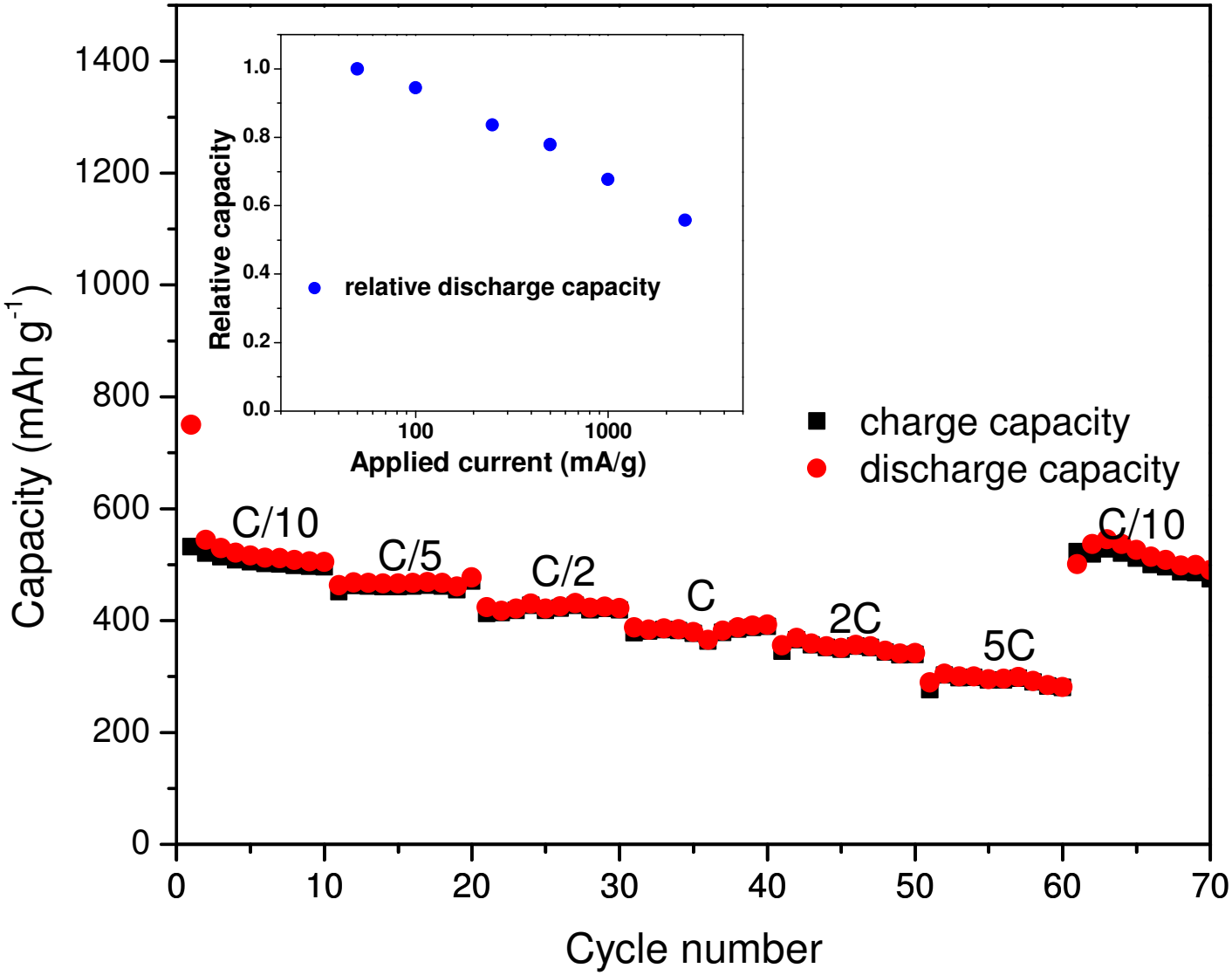


SnO_C conversion anode (~740 mAhg^{-1})



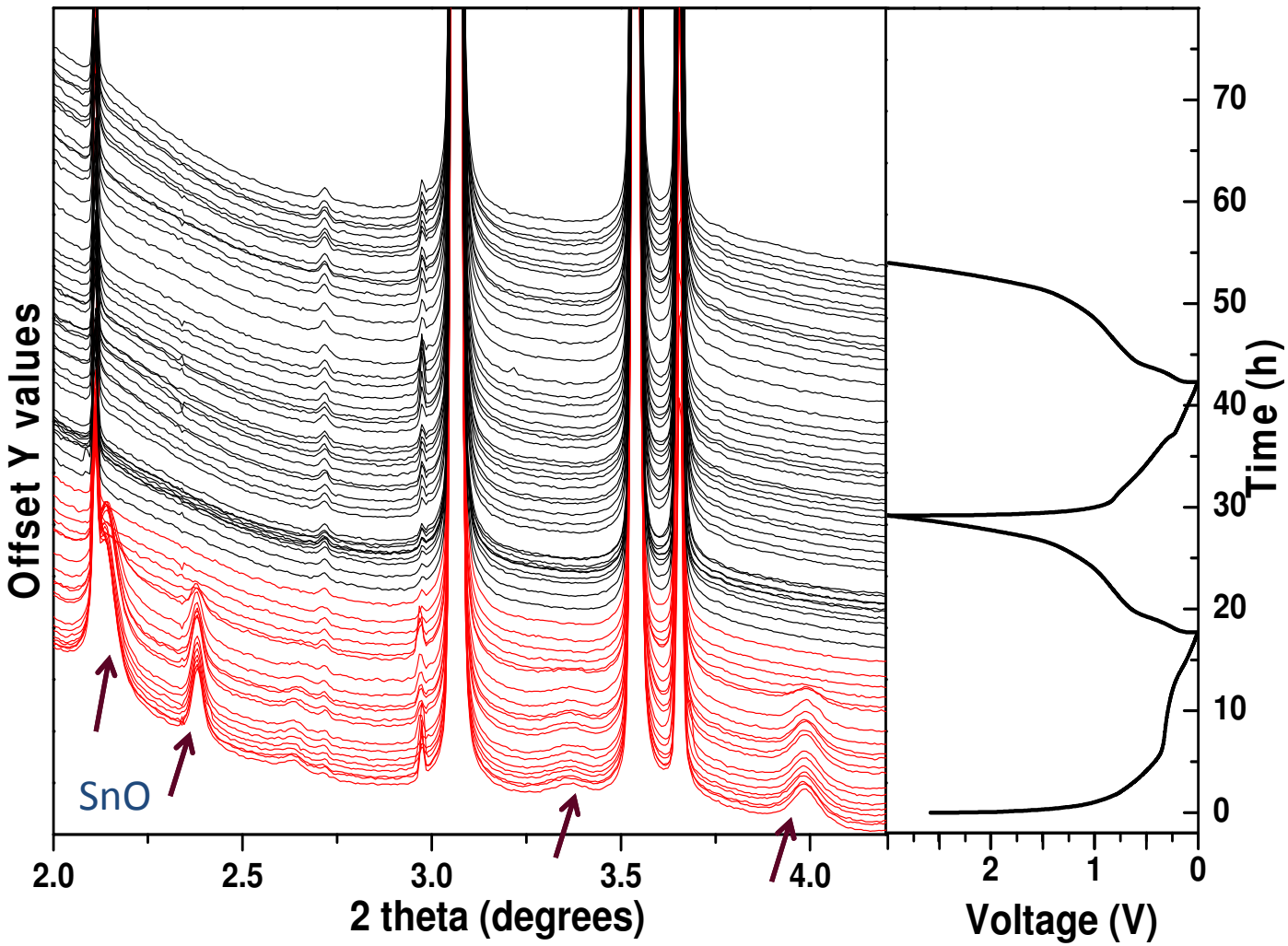


SnO_C cell rate



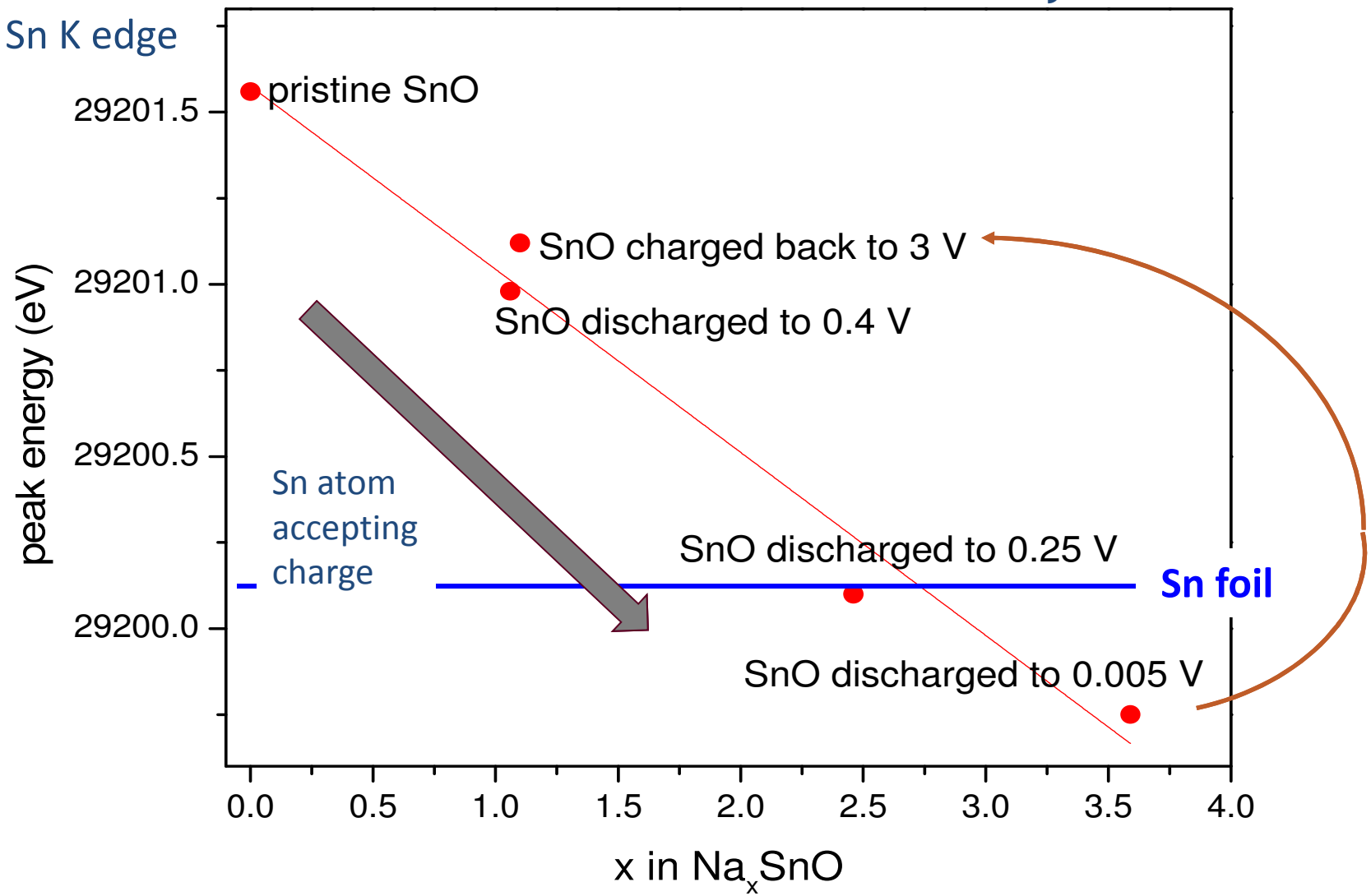
- Dual amorphous buffer – carbon & sodia matrix

Na||SnO_C *operando* HEXRD



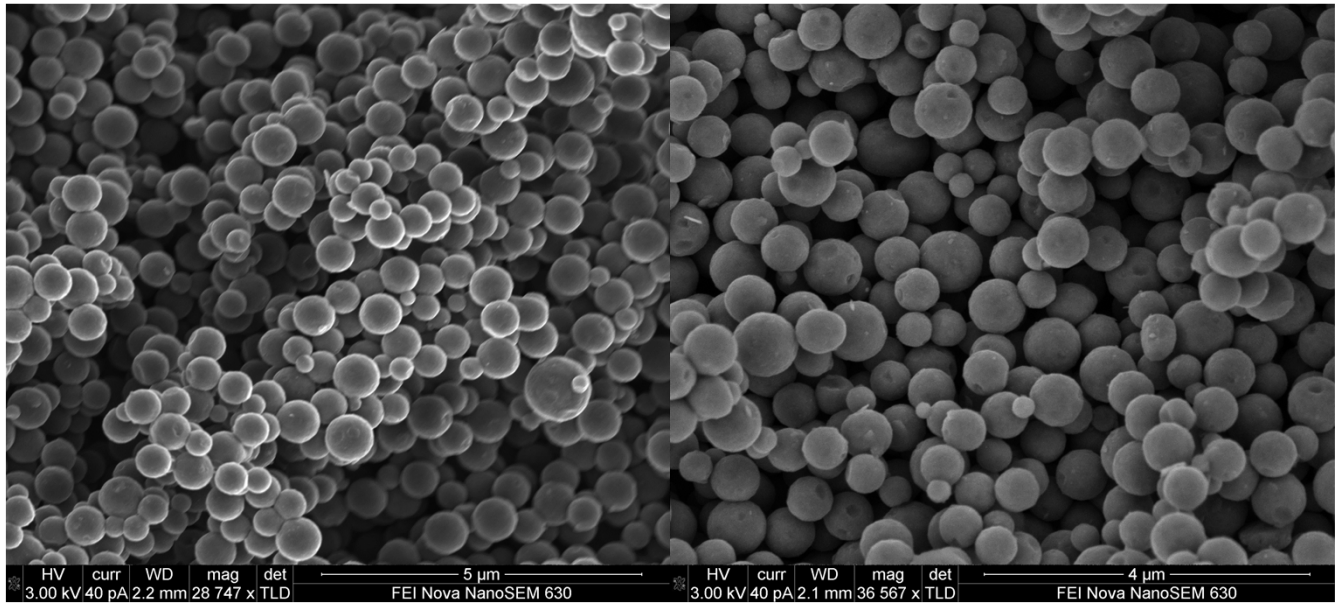
- SnO decomposes to amorphous phase

XANES result of cycled Na_ySnO_C



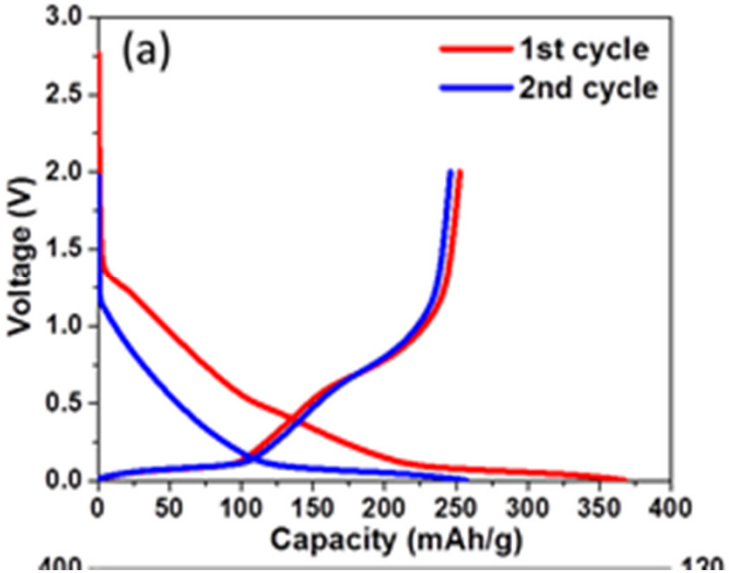
- Amorphous intermetallic formed with Sn as Zintl anion

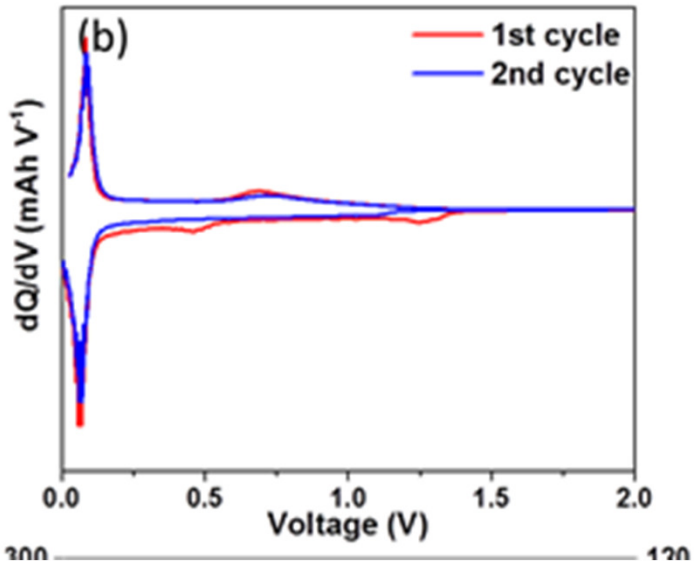
Spherical hard carbon

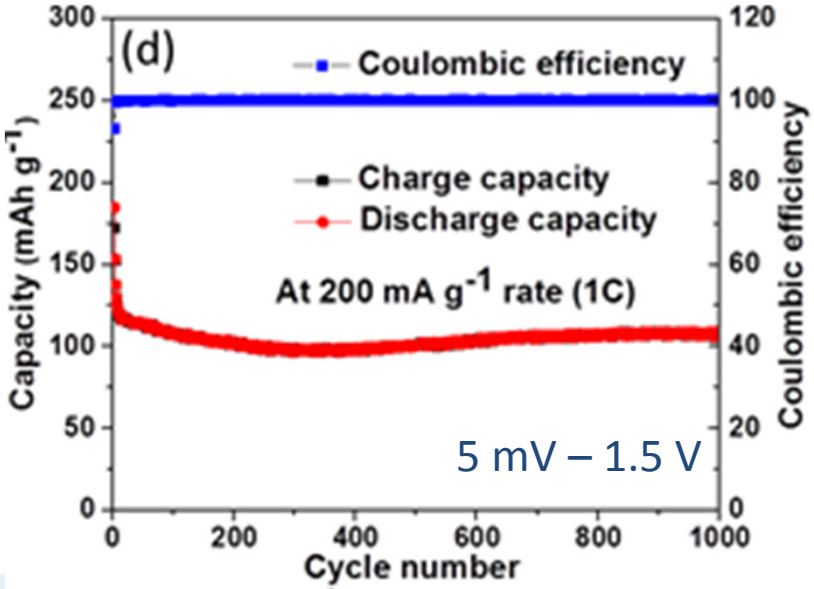


- polymer precursor pyrolysis method
- 0.2 to 0.6 micron spheres
- graphene sheets interlayer distance is 0.4 nm
- I(D)/I(G) ratio is 1.04
- BET is 480 $m^2\ g^{-1}$
- Cumulative pore volume is 0.164 $cm^3\ g^{-1}$

Hard carbon electrochemical performance

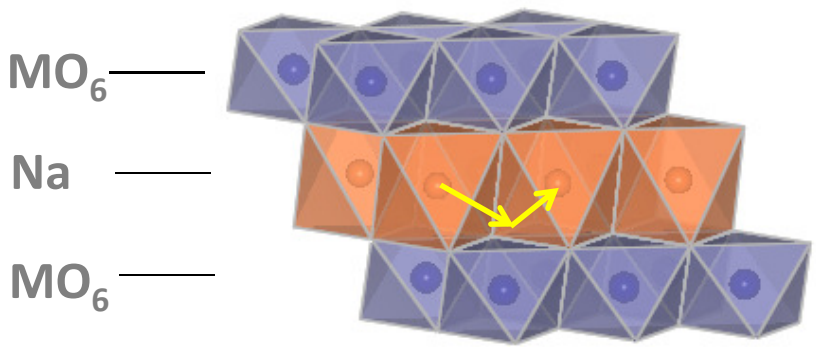






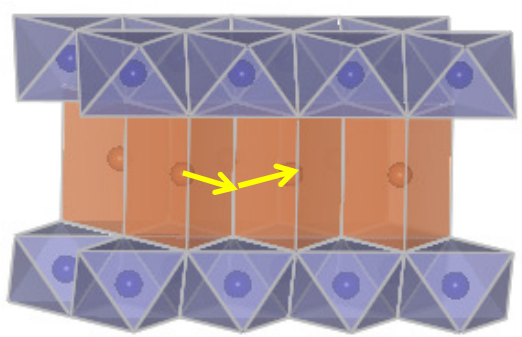
- superior cycling stability observed
- ^{23}Na NMR analysis in progress

Na diffusion in O- vs. P-type layered compounds



Octahedral

Diffusion thru face-sharing tetrahedral sites → High energy barrier

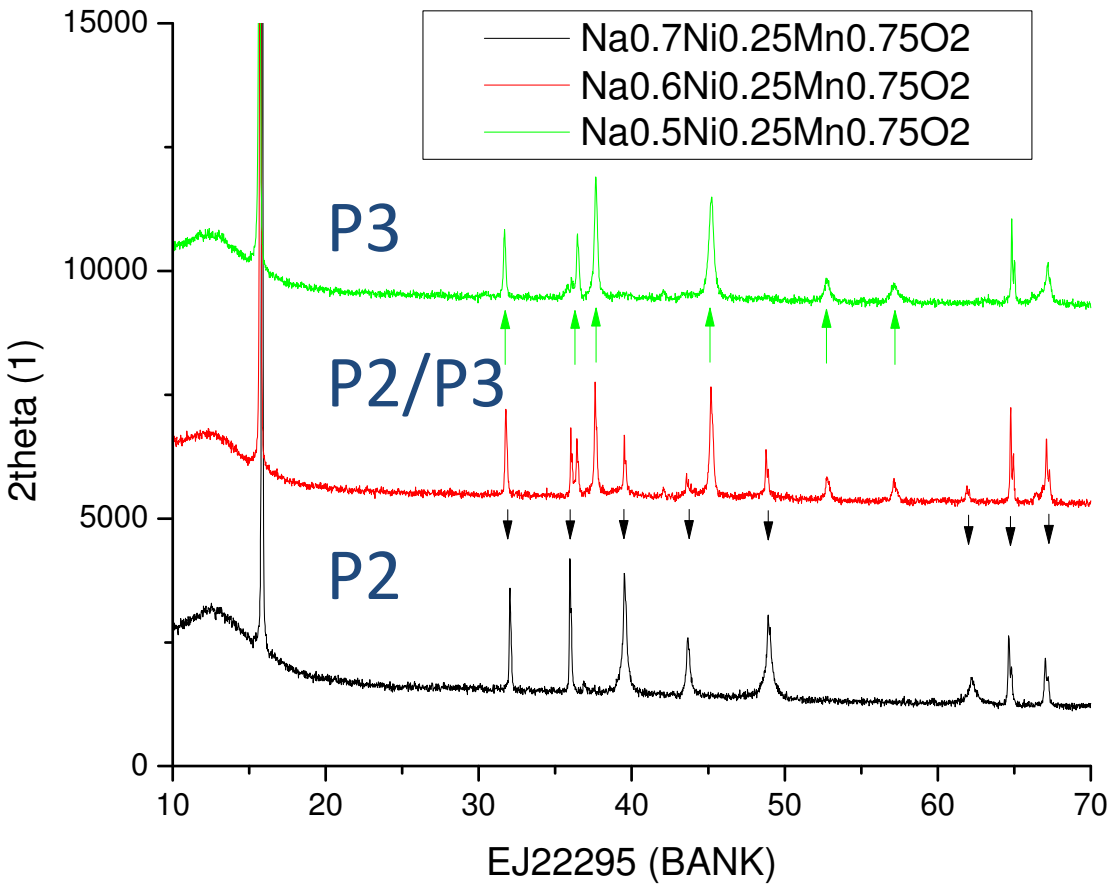


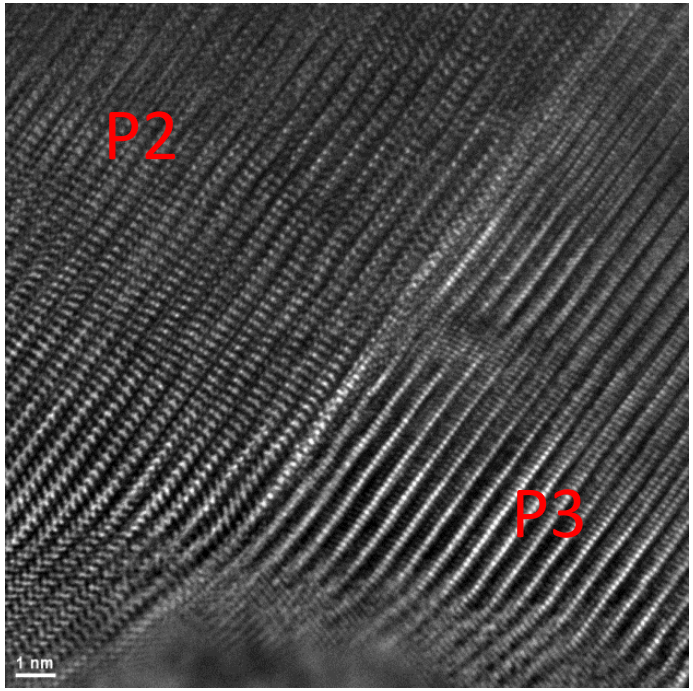
Prismatic

Diffusion thru face-sharing another trigonal prismatic sites → Low energy barrier

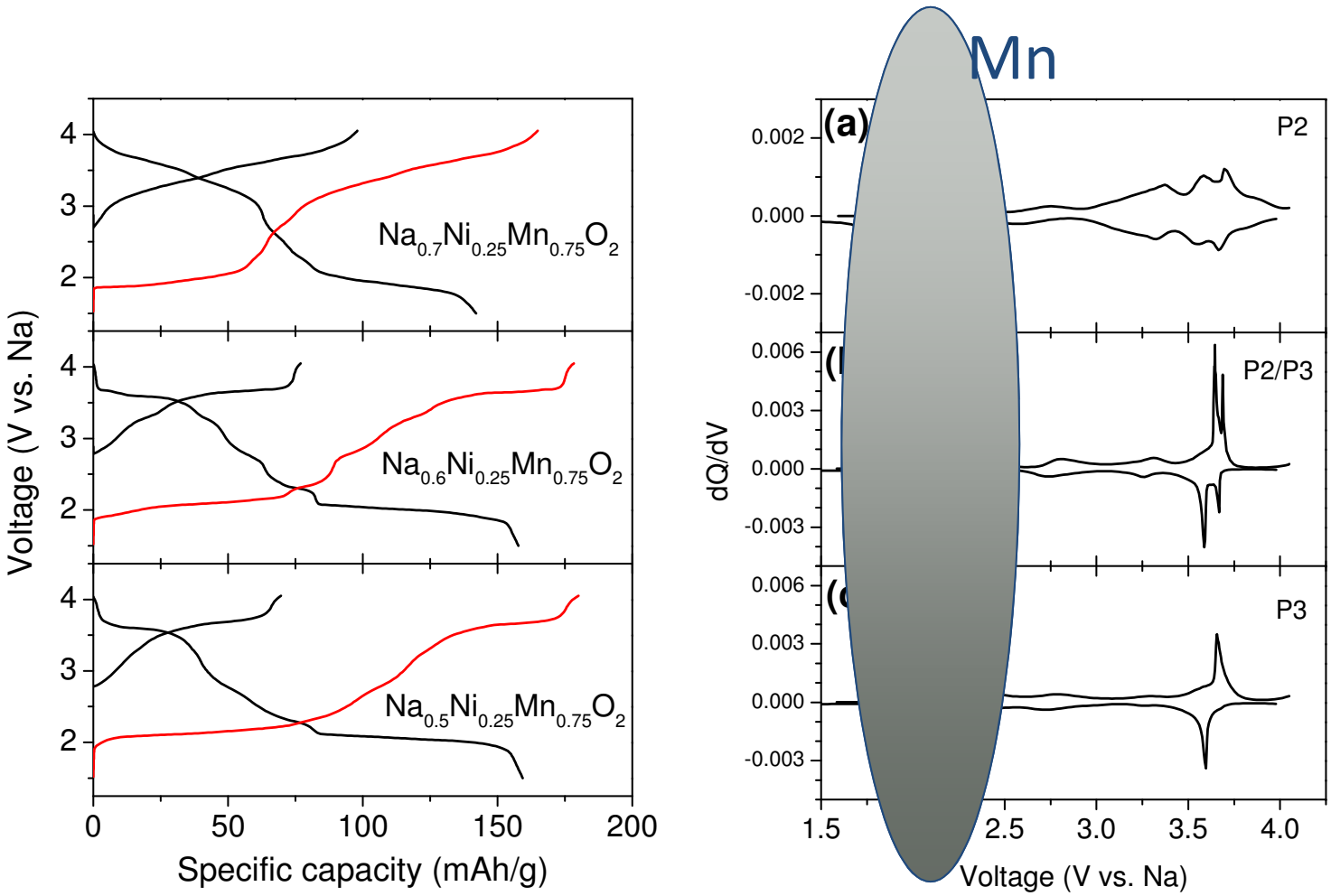
- P2 – less Na than O3 structure in as-prepared state
  - Na/M < 1

P3, P2/P3, and P2 Na TM layered oxide materials: $Na_xNi_{0.25}Mn_{0.75}O_2$





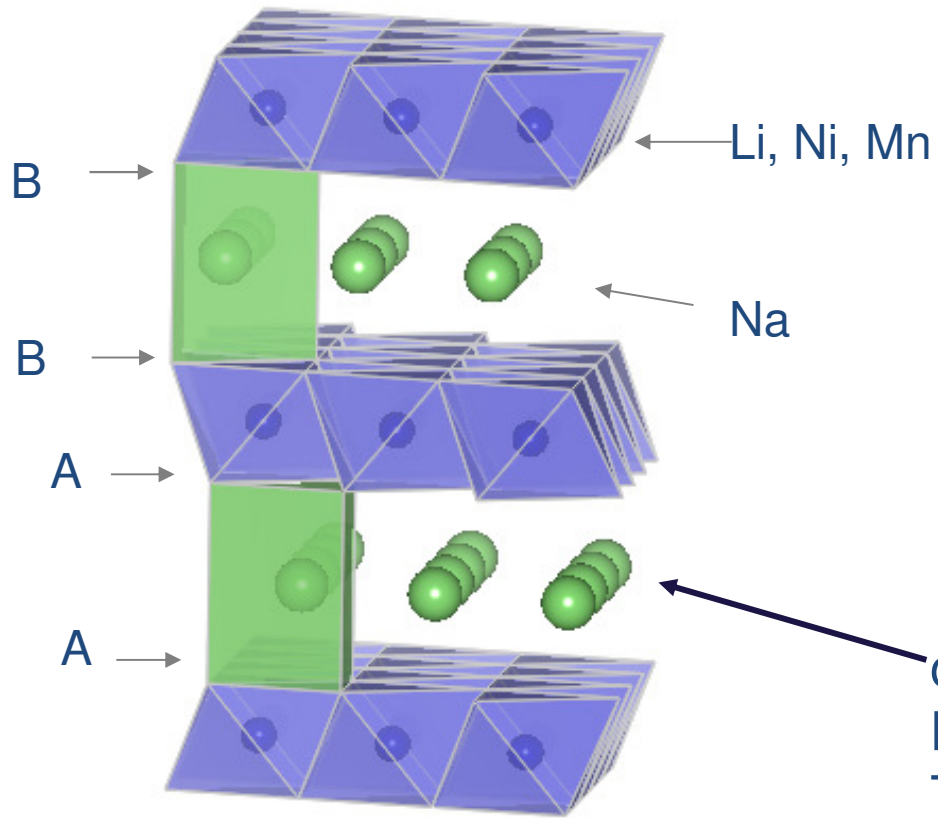
Electrochemical Na-(de)intercalation



- Weak charge ordering
- Mn redox occurring

Structure schematic: $Na_{1.0}Li_{0.2}Ni_{0.25}Mn_{0.75}O_y$

$Na_{0.85}Li_{0.17}Ni^{II}_{0.21}Mn^{IV}_{0.64}O_2$



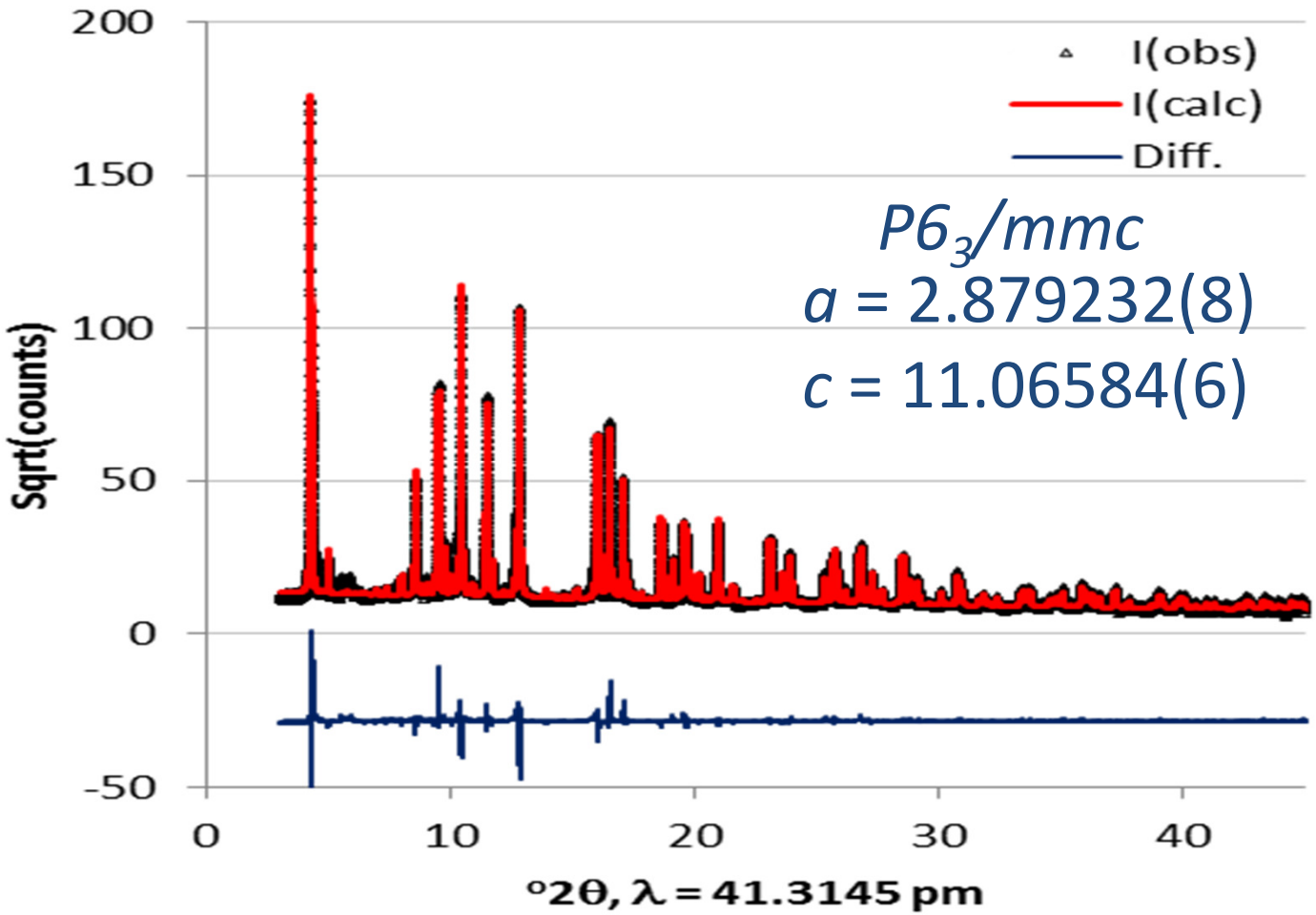
Na – **1.02 Å**
Li – **0.76 Å**
Ni^{2+} - 0.69 Å
Mn^{4+} - 0.53 Å

cycle Na into and out of host
Li reversibly moves inside host
TM<->Na layer (O_h/T_d) *

P2 structure

D. Kim et al., *Adv. Energy Mater.* **1**, 333 (2011)
*J. Xu, S. Meng et al., *Chem. Mater.* (2013)

Rietveld refinement (HEXRD): $Na_{0.85}Li_{0.17}Ni_{0.21}Mn_{0.64}O_2$



- Superstructure peaks (Li/Ni(II)/Mn(IV) motif)
- Slight Li_2MnO_3 impurity

N. Karan, M. Slater et al., *J. Electrochem. Soc,* **161**, A1107 (2014)

Changes During Cycling

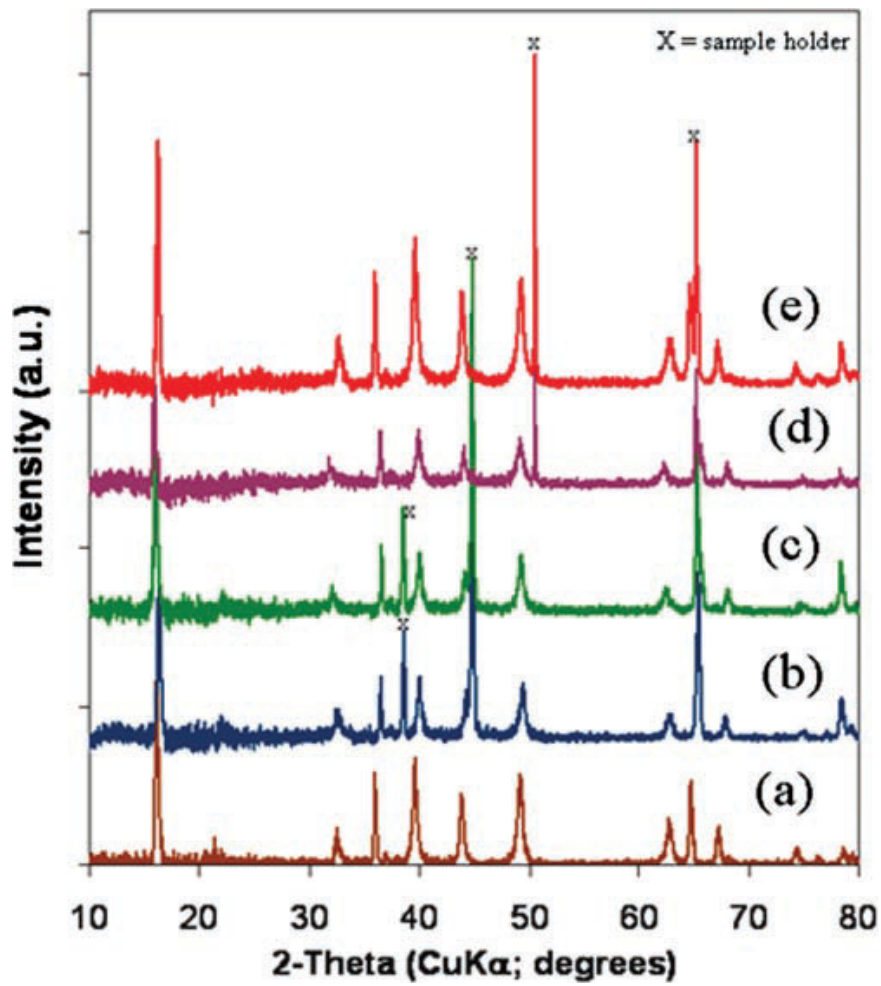
As prepared:

$Na_{1.08}Li_{0.22}Ni_{0.25}Mn_{0.75}O_y$

Charged to 4.2 V:

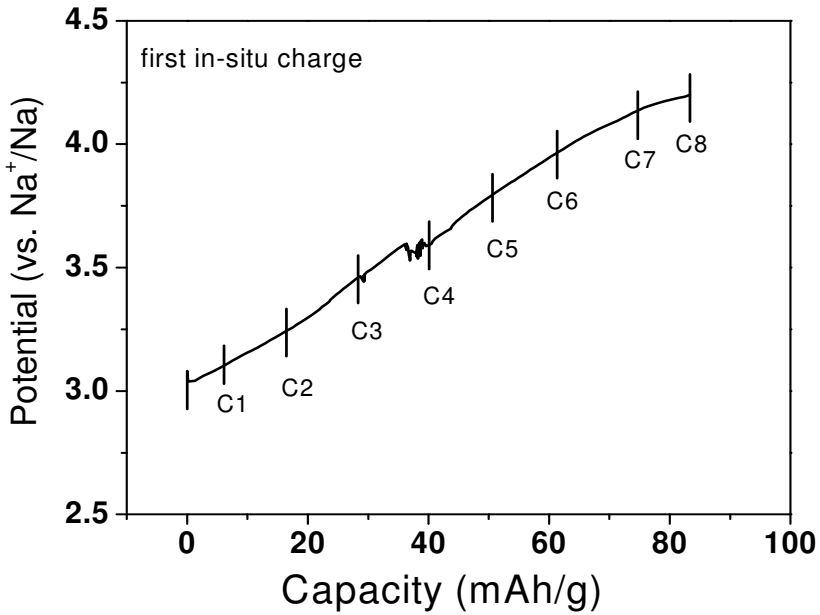
$Na_{0.54}Li_{0.19}Ni_{0.23}Mn_{0.75}O_y$

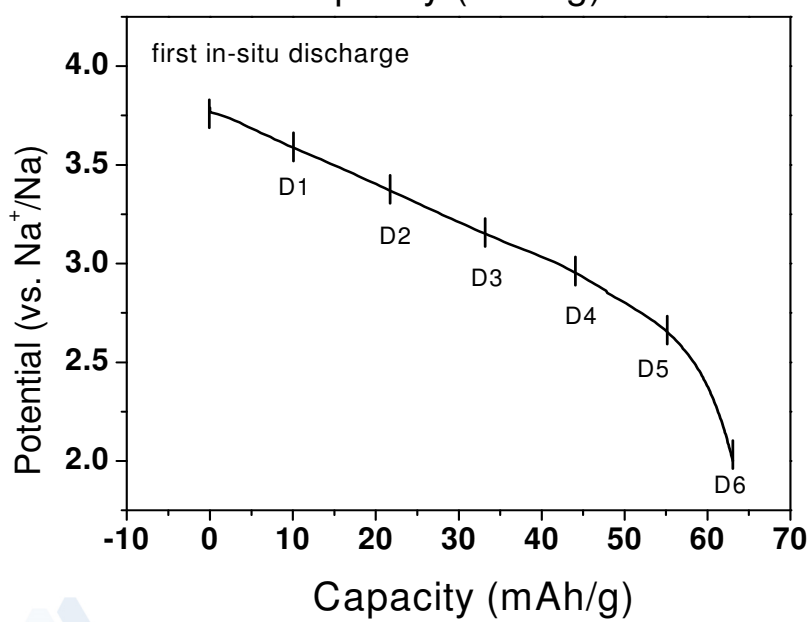
- Unit-cell volume contracts by 0.6% on charging to 4.2 V



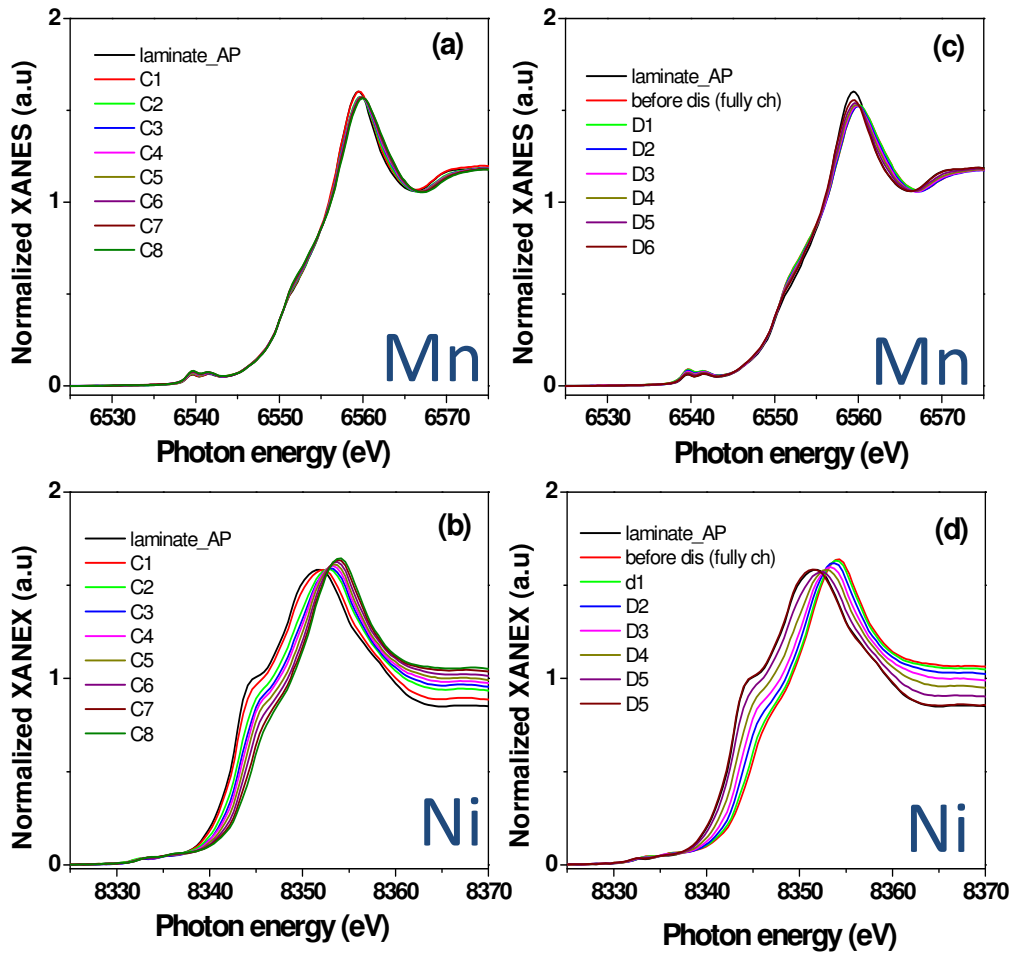
Kim, et al., Adv. Energy Mat., 2011

Operando X-ray Absorption (XAS) $Na/Na_{0.85}Li_{0.17}Ni_{0.21}Mn_{0.64}O_2$ cell operation





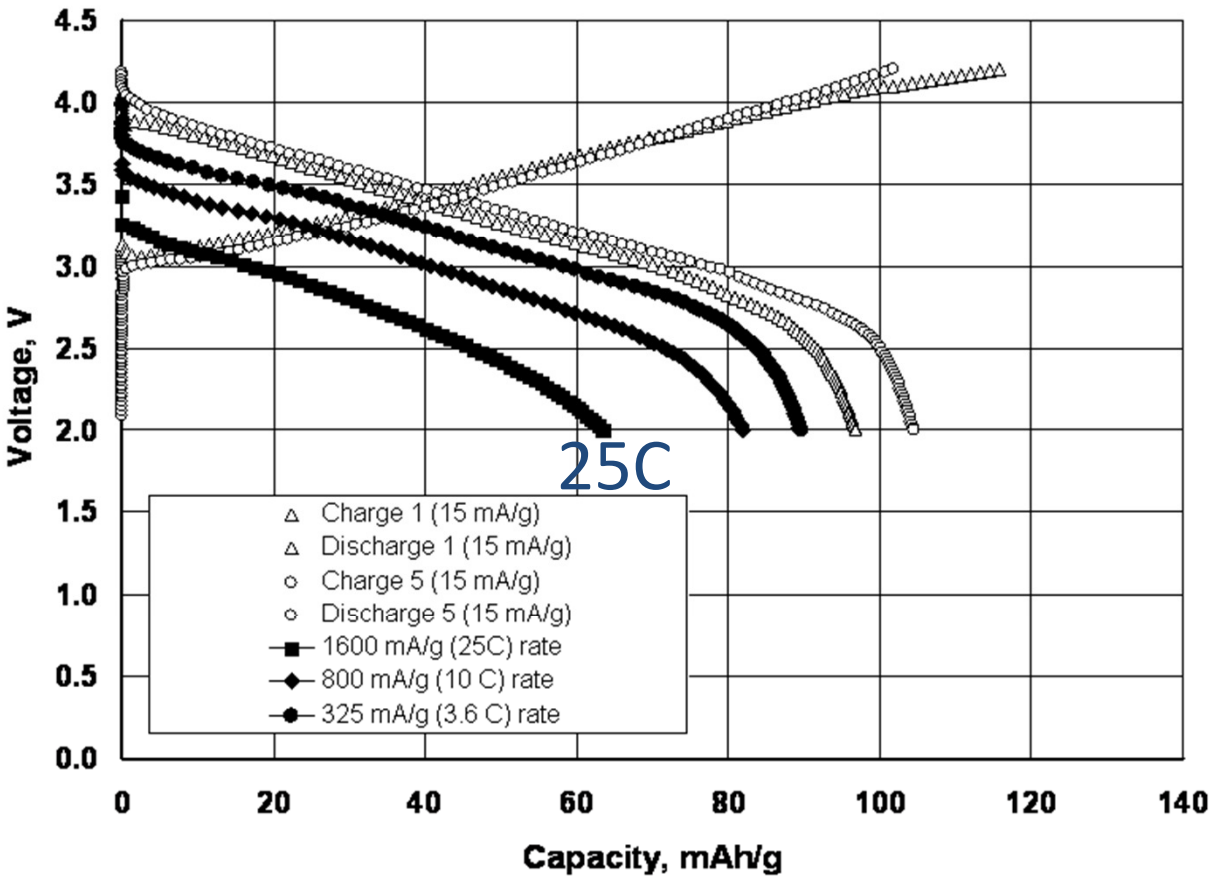
XANES



N. Karan, M. Slater et al., *J. Electrochem. Soc,* **161**, A1107 (2014)

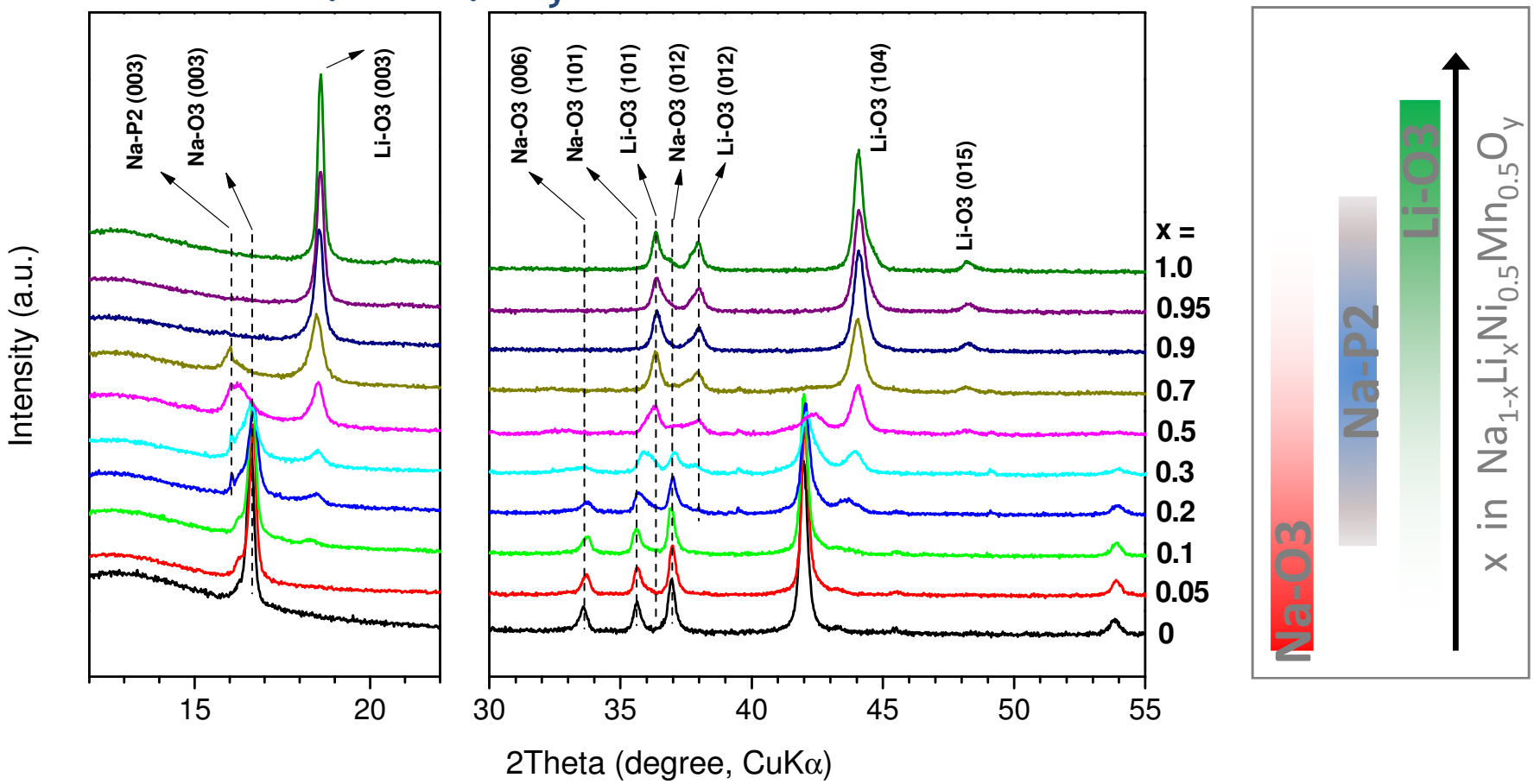
Cycling performance – $Na/Na_{0.85}Li_{0.17}Ni_{0.21}Mn_{0.64}O_2$ half cell

P2-Layered $Na_{0.85}Li_{0.17}Ni_{0.21}Mn_{0.64}O_2$



Kim, et al., Adv. Energy Mat., (2011)

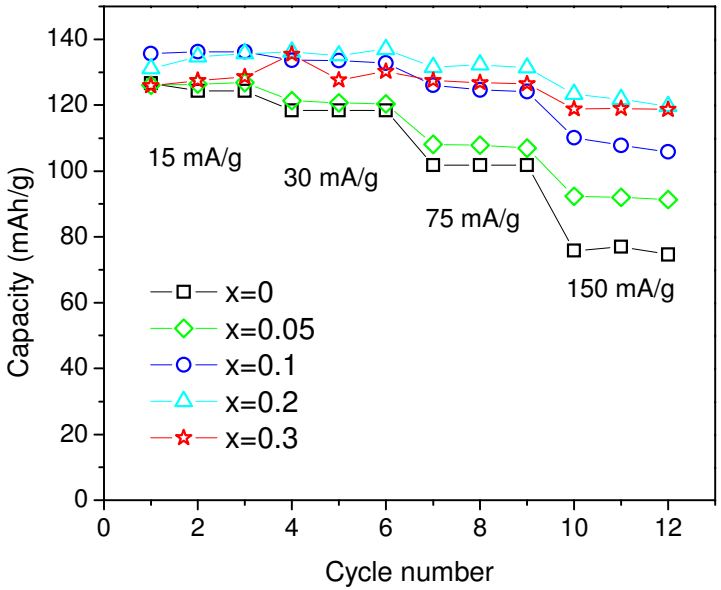
Capacity boost 25% Ni -> 50% content Ni using $Na_{1-x}Li_xNi_{0.5}Mn_{0.5}O_y$ (effect on phase distributions)

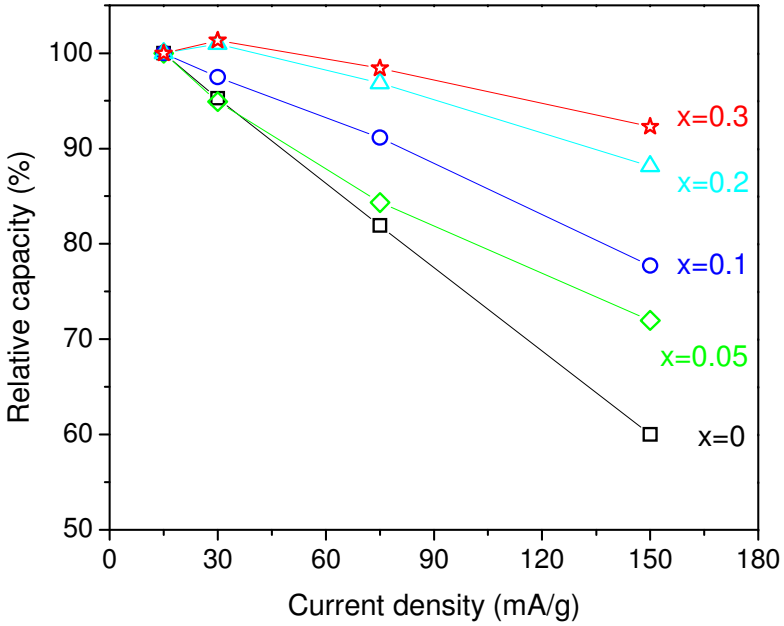


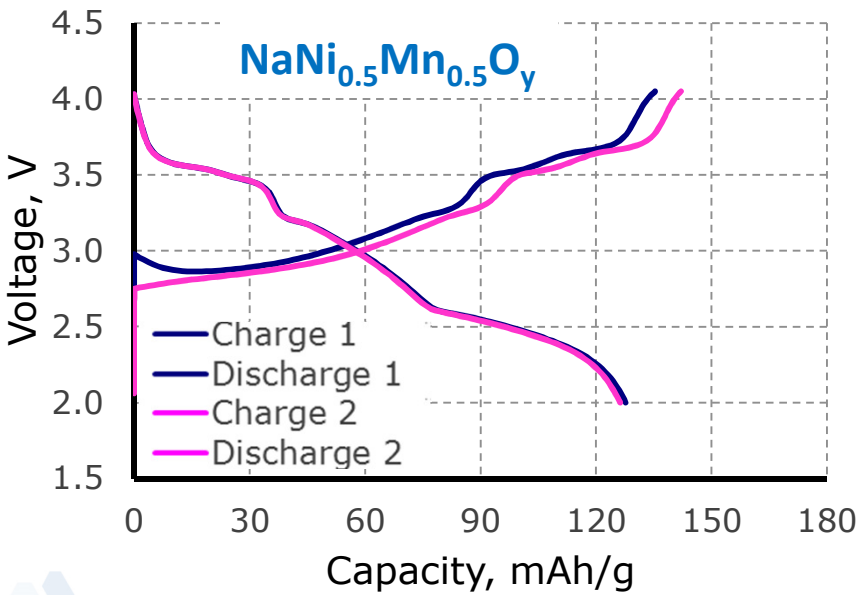
- Upon Li substitution, Na-O3 phase is gradually replaced by Na-P2 phase, and Na-P2 by Li-O3
- The presence of P2 structure, which normally forms at low Na/TM ratio, implies the possible formation of lithium rich layered phase and Ni-Mn ratio offset in the rest of Na phases.

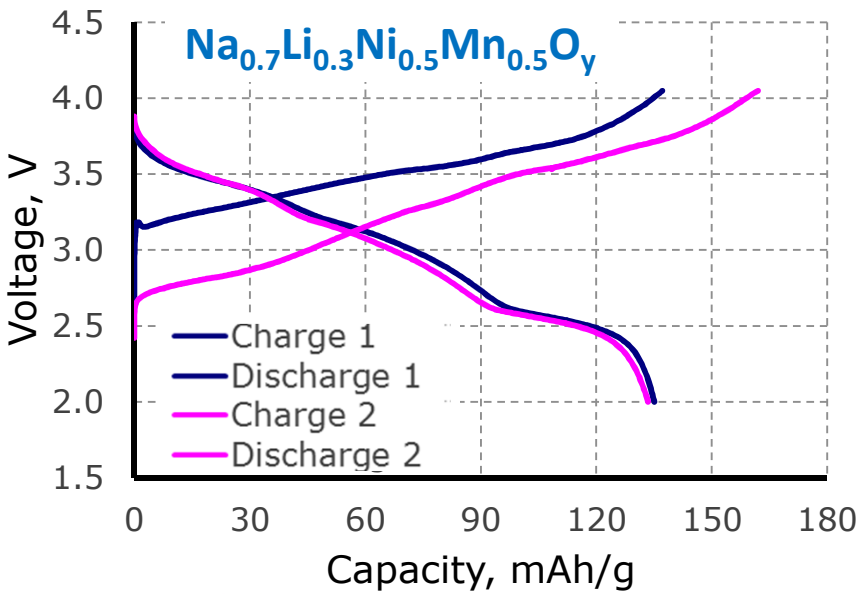
E. Lee et al., *Adv. Energy Mater.* (2014)

Electrochemical performance of $Na_{1-x}Li_xNi_{0.5}Mn_{0.5}O_y$



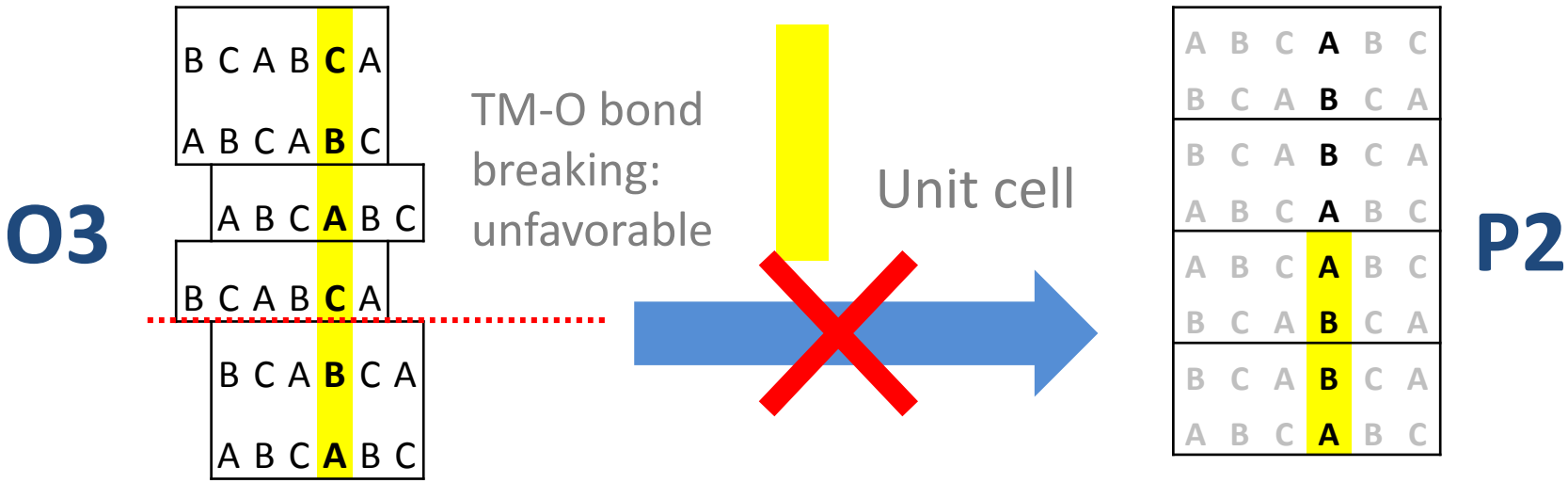






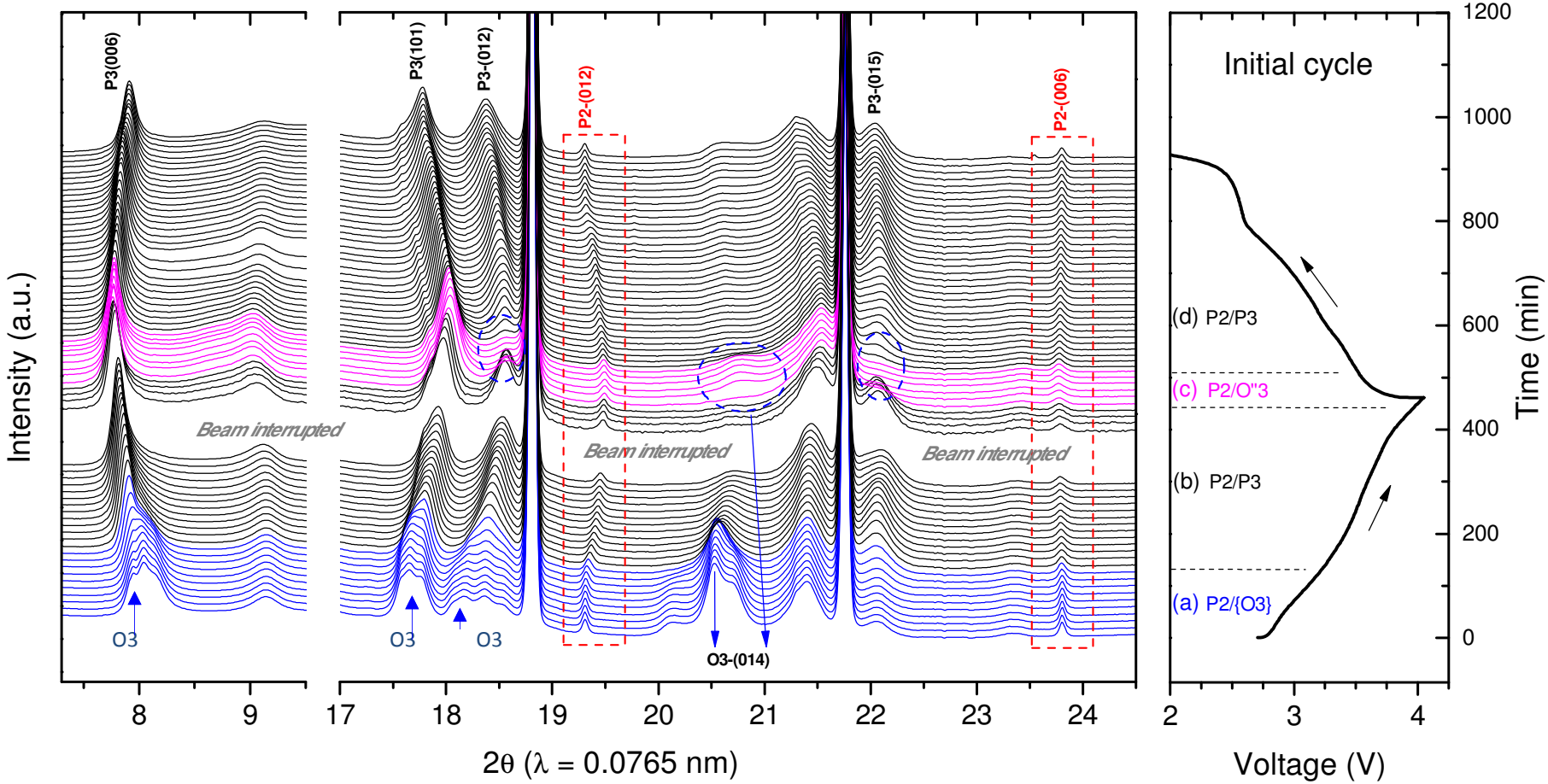
E. Lee et al., *Adv. Energy Mater.* (2014)

O3 to P2 conversion is unfavorable process

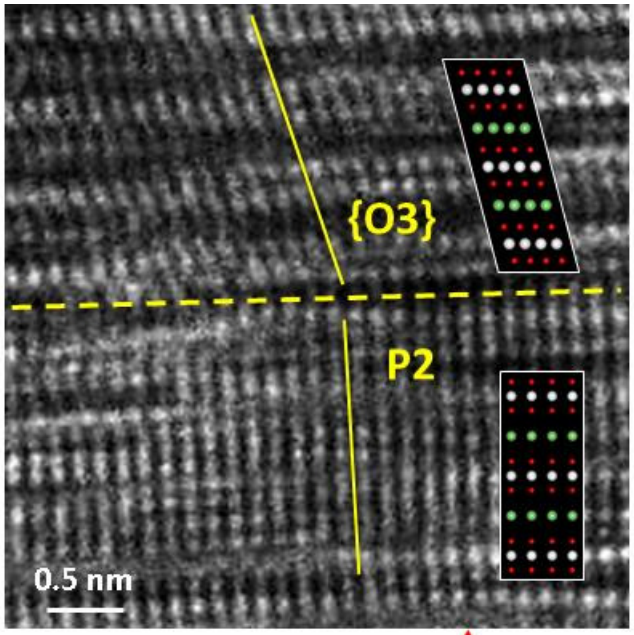


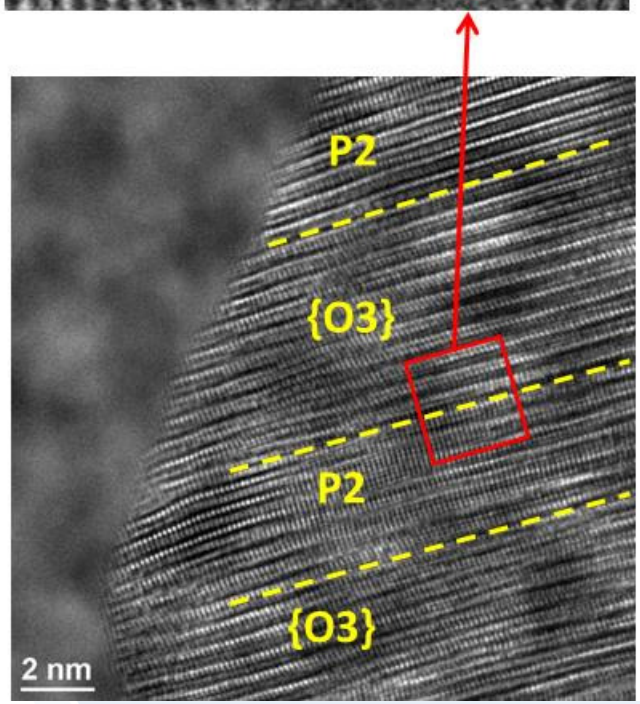
- Need to synthetically incorporate P2 in composite to improve echem performance

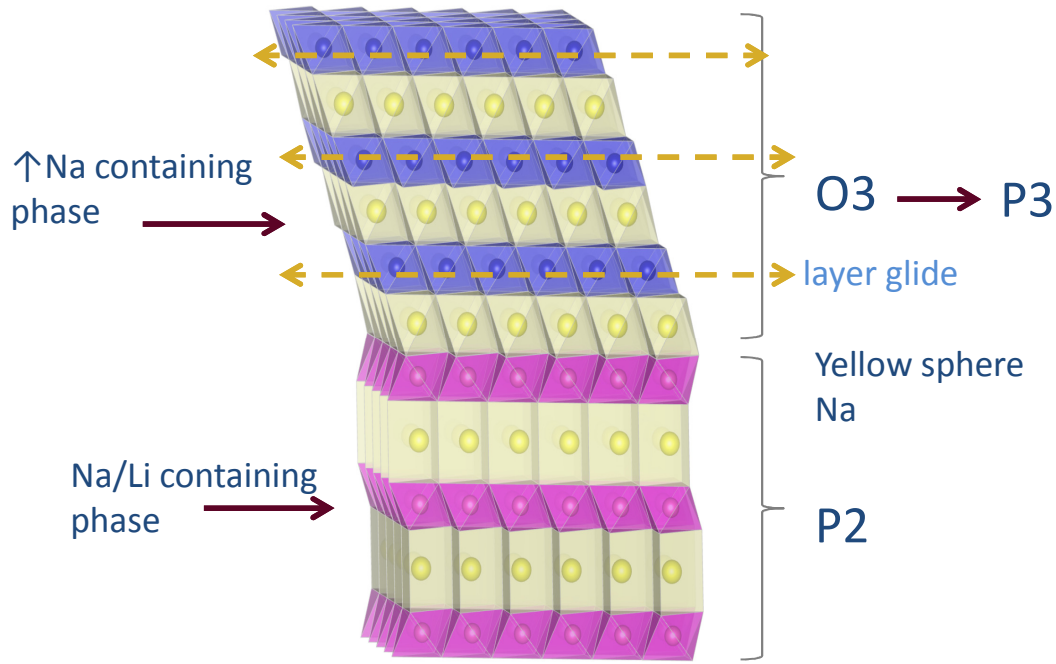
Operando synchrotron HEXRD of $Na_{0.7}Li_{0.3}Ni_{0.5}Mn_{0.5}O_y$



E. Lee et al., *Adv. Energy Mater.* (2014)







- O3/P2 Intergrowth (pristine)
- Li presence assists in P2 formation
- P3 formed from O3 (aligns w/P2)
- P2 phase remains and acts like a 'glue'

E. Lee et al., *Adv. Energy Mater.* (2014)

Thoughts, Summary and Conclusions

- Na-ion batteries are an <u>emerging energy storage technology</u>
- The battery work presented herein encompassed:
  - High-capacity SnO_C anodes
    - Amorphous intermetallics
  - Long-life Hard carbon anodes
    - 1000 cycles @ 1C rates
  - Bulk mixed-metal layered oxide cathodes
    - Li-containing systems
  - Flexible and inter-block stacking arrangements
    - P2 importance
- Energy density more tied to cell voltage
  - New materials needed
    - Anodes with lower voltages & high capacities
    - Raise cathode reaction voltage

Na-ion intermetallic alloy anodes and hard carbon:

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Maryam Peer[5]
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Na-ion layered transition metal oxides:

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Donghan Kim[1]
Sun-Ho Kang[1]
Michael Slater[1]
Jun Lu[1]
Dean Miller[3]
Jianguo Wen[3]
Naba Karan[2]
M. Balasubramanian[2]
Yang Ren[2]
Xiangyi Luo[2]
Xiaoyi Zhang[3]

Stephen Hackney[4]
Aaron DeWahl[4]

BatPaC

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[3]Electron Microscopy Center
[4]Michigan Technological University
[5]Penn State University

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