# Ion-Exchanged Derived Cathodes (IE-LL-NCM) for High Energy Density LIBs

## (with Farasis Energy Inc. IC3P as lead: ES213)

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**Project ID: ES257**

# Overview

## Timeline

- Start: October 1, 2013
- End:   Sept. 30, 2015
- Percent complete: 80+%

## Budget

- 276K/2 yr.

## Barriers

- Calendar/cycle life of lithium-ion cells being developed for PHEV and EV batteries that meet or exceed DOE/USABC goals

## Partners

- Farasis Energy Inc.
- LBNL

# Relevance

- **New cathode materials are required to improve the energy density of Li-ion cells for transportation technologies.**

  – LMR-NMC class of layered compounds : Best known cathode option to date

  – However, voltage fade (VF) in LMR-NMC causes unacceptable energy loss

  – Need to solve structural and electrochemical performance problems

  – Explore new syntheses routes towards VF-free cathode materials

  – Focus on changing stacking sequence in c-axis direction for layered oxide materials
    - Remove O3 -> move to O2 stacking (no spinel change during cycling theoretically possible)

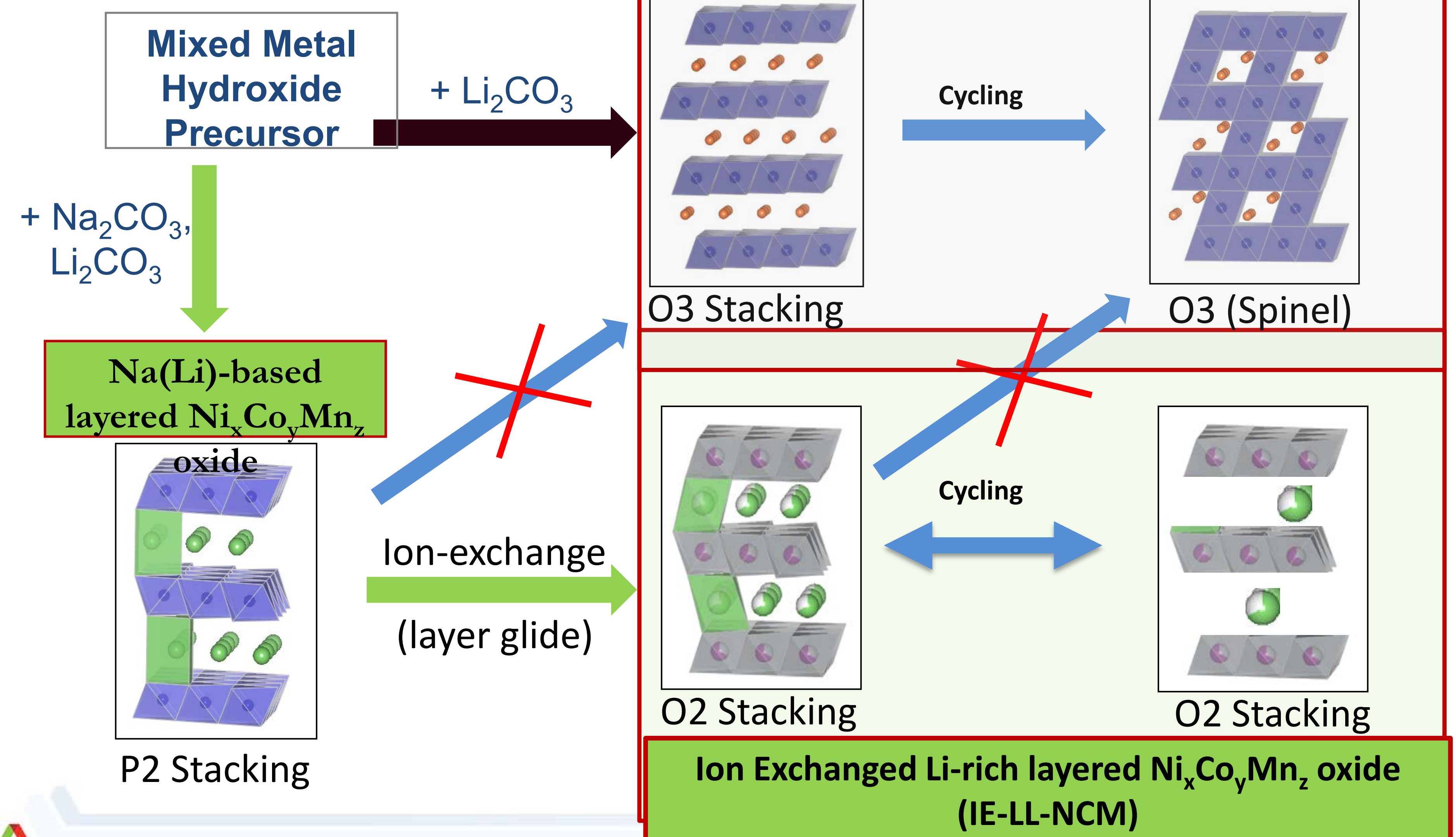
# Approach

Concepts explored:

- Develop new routes to synthesize high-energy cathode materials
  - This work: Ion-exchanged cathode materials*
- Use stacking faulted cathode material* that is:
  - Stacking faults guided by ion-exchange chemistry of Na-types
  - Li-rich (high-capacity)
  - Structurally 'flexible' – stacking faults/sliding of layers which will adjust naturally to Li-content as it cycles
    - No bulk phase transitions expected
    - No deleterious movement of TM cations expected; no spinel formation
    - High-rate capability possible – again stacking faults allow fast insertion of Li cations
    - High Mn content -possible good thermal stability, less expensive
- Use new synthesis and advanced characterization methods to examine material
- Test material as cathodes and use VF protocol developed @ Argonne
- Compare to baseline cathode materials (Toda HE5050 : $0.5Li_2MnO_3 \bullet 0.5Li[Ni_{0.375}Mn_{0.375}Co_{0.25}]O_2$); $Ni_{0.15}Mn_{0.55}Co_{0.1}$
- Work with **Farasis Energy Inc.** to develop full cell chemistry with *new cathode

# Ion-Exchange Synthesis of Layered-Layered NCM

Possible impact of ion-exchange route on structure of high energy materials.



# Milestones of FY'15

- Baseline with Toda HE5050 — Completed
- Synthesis — On-going
  - Ni-Mn-Co composition variance — Completed
  - Na/Li composition variance — Completed
  - Post heat-treatment — Completed
  - Ion-exchange conditions variants — On-going
- Characterization — On-going
  - Electrochemical — On-going
  - Structural — On-going
- Technology transfer to Farasis — Completed

# Synthesis flow Example

Precursor: $(Mn_{0.656}Ni_{0.219}Co_{0.125})(OH)_2$

↓ +Li & Na mixed salts (fired in air)

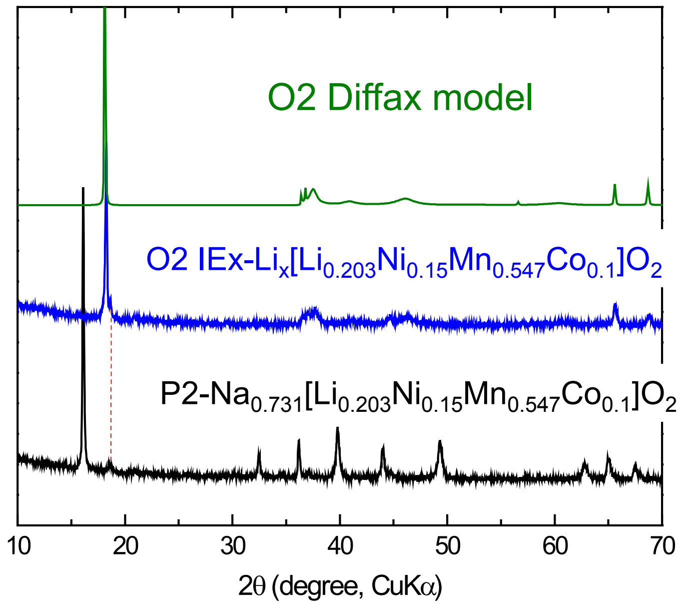
Parent: $Li_{1.0}Na_{0.2}(Mn_{0.656}Ni_{0.219}Co_{0.125})O_{2+\delta}$

↓ - 0.2 Na, + xLi (ion-exchange process; IEx)

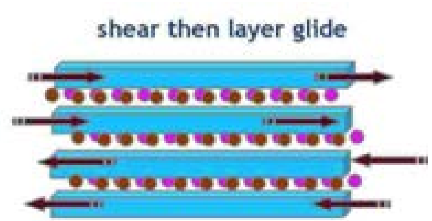
Product: $Li_{1+x}(Mn_{0.656}Ni_{0.219}Co_{0.125})O_{2+\delta}$

# Ion-Exchange Synthesis of Layered-Layered NCM (with Toda HE5050 TM composition ratio)

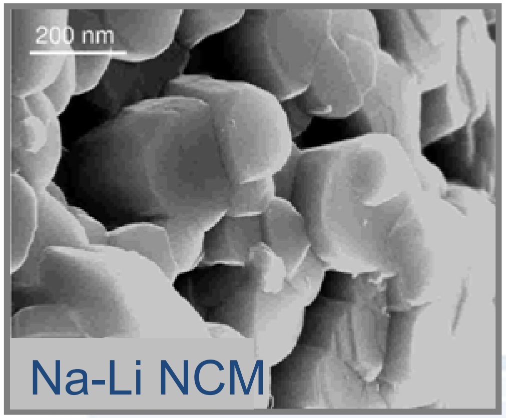
- X-ray diffraction indicates good layering order but significant disorder in other crystallographic directions suggesting presence of stacking faults.

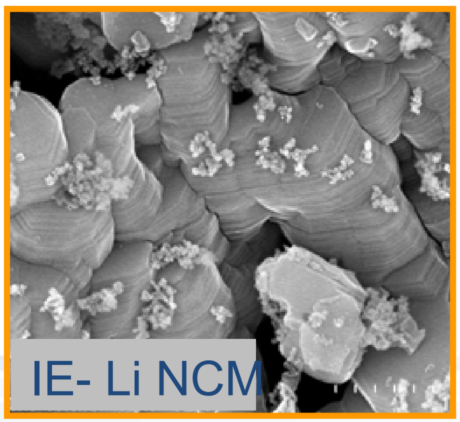


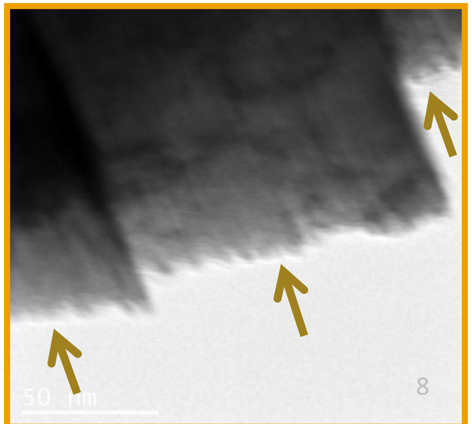

- Faults in shear order of crystal lattice during ion exchange
- Still strongly layered
- Local c-axis disorder
- DIFFAX modeling: O2 layer stacking is best fit



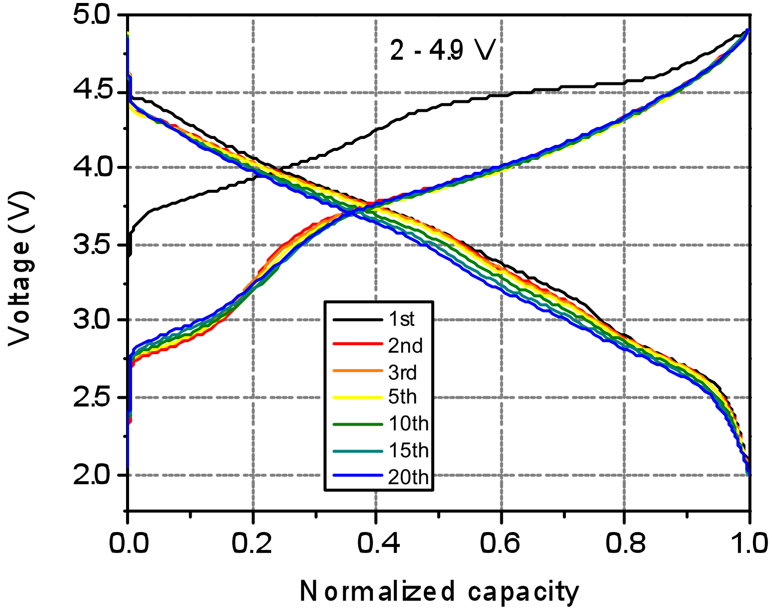


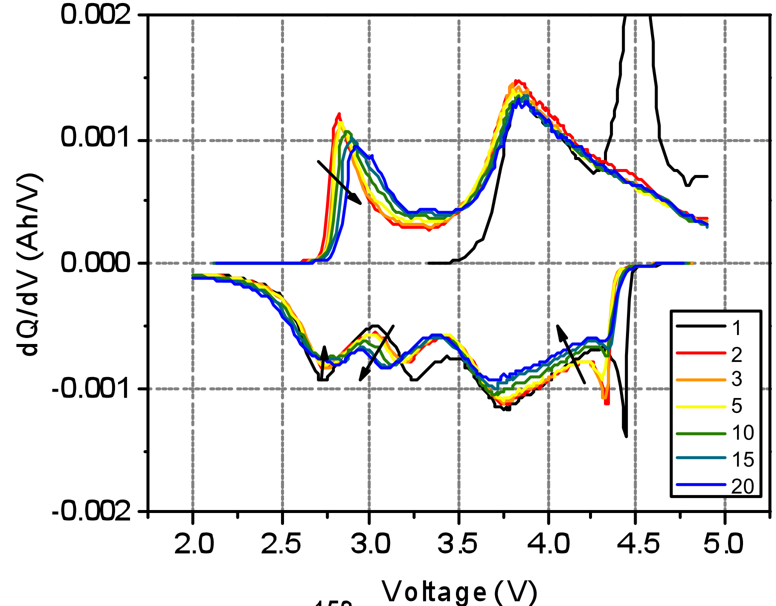


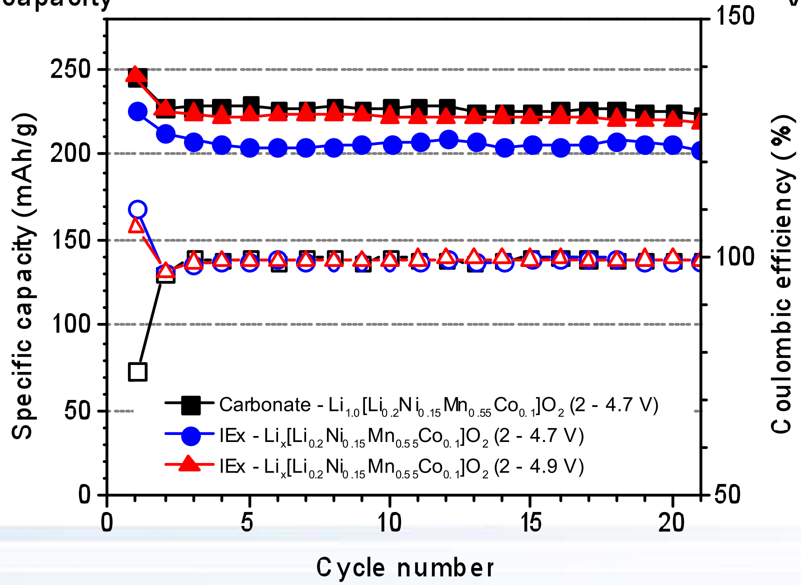



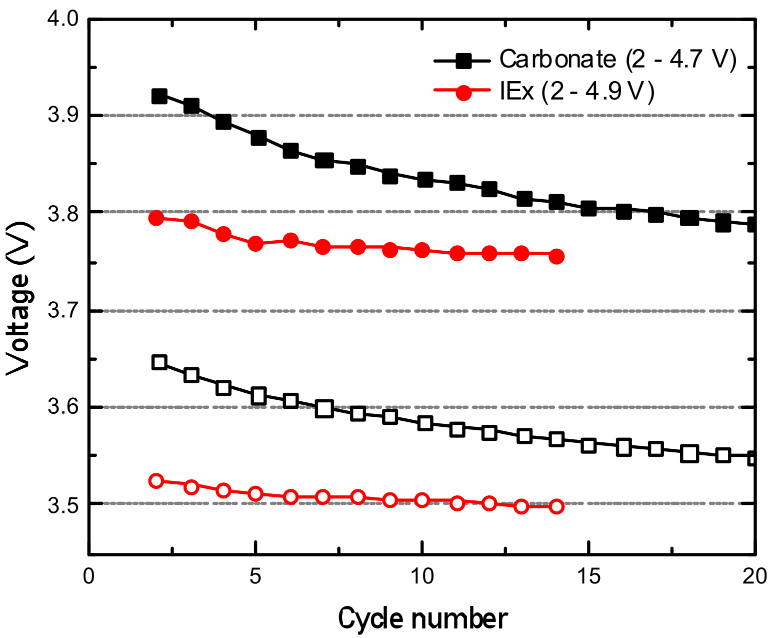
# $Li_x[Li_{0.2}Ni_{0.15}Mn_{0.55}Co_{0.1}]O_{2-d}$ IEx derived cathode material (Toda HE5050 composition)

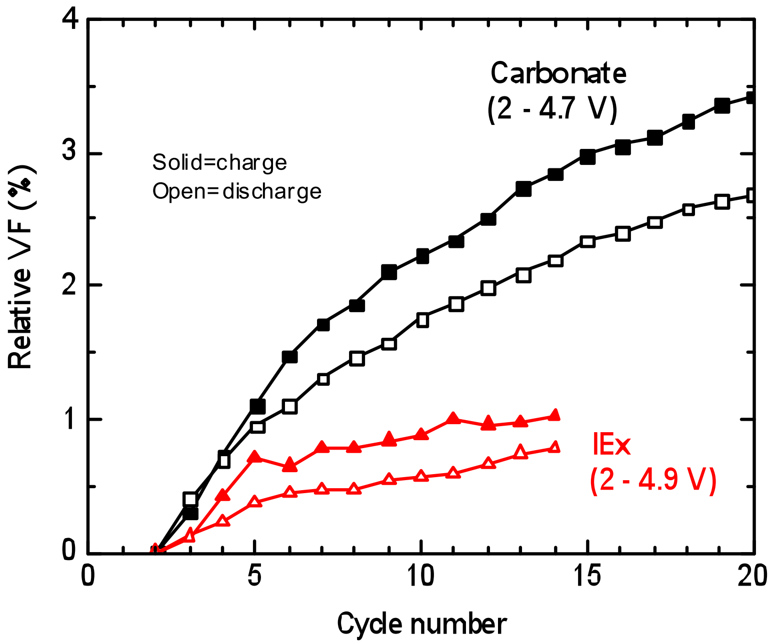


# $Li_x[Li_{0.2}Ni_{0.15}Mn_{0.55}Co_{0.1}]O_{2-d}$ IEx VF result




- Lower operating voltage, but less VF with IEx materials

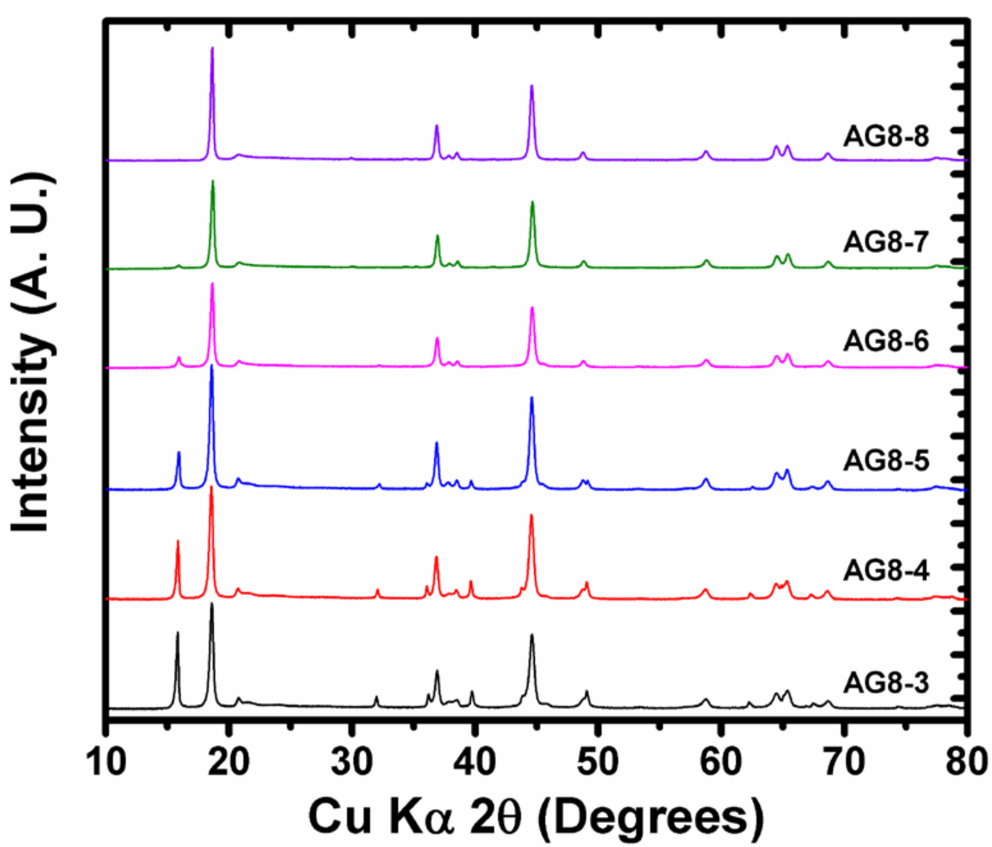
# $Li_xNa_{0.2}(Mn,Ni,Co)O_{2+d}$ : Exploration of mixed metals effect - hydroxide precursors: Na poor, Li rich

| Precursor | Mn | Ni | Co |
|---|---|---|---|
| AG7 | 0.45 | 0.15 | 0.4 |
| AG6 | 0.6 | 0.2 | 0.2 |
| AG8 | 0.656 | 0.219 | 0.125 |
| AG10 | 0.656 | 0.125 | 0.219 |

| Precursor | Li | Na |
|---|---|---|
| AGx-1 | 0.8 | 0.2 |
| AGx-2 | 0.9 | 0.2 |
| AGx-3 | 1.0 | 0.2 |

- Precursors are co-precipitated hydroxides

# AG8 XRD before ion-exchange



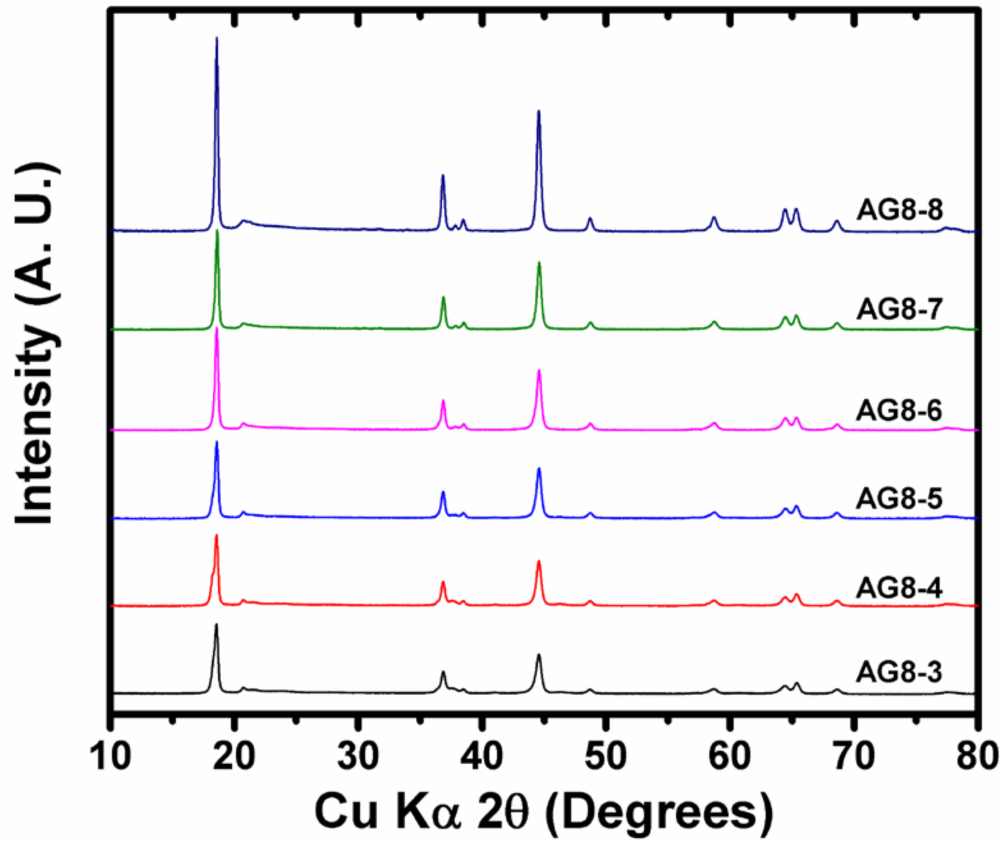

Decided to force more Li in structure

| Precursor | Li | Na |
|---|---|---|
| AG8-3 | 1.0 | 0.2 |
| AG8-4 | 1.1 | 0.2 |
| AG8-5 | 1.2 | 0.2 |
| AG8-6 | 1.3 | 0.2 |
| AG8-7 | 1.4 | 0.2 |
| AG8-8 | 1.5 | 0.2 |

single phase – sweet spot

- Material is composed of three phases (P2 and P3-type $Na_xMnO_2$, $Li_2MnO_3$, and LNMC)
- Sodium phase peaks decrease with increasing Li content, as expected and are completely gone when Li = 1.5 (Li/Mn+Ni+Co = 1.5)
- No carbonate peaks found in XRD

# AG8 XRD after ion-exchange



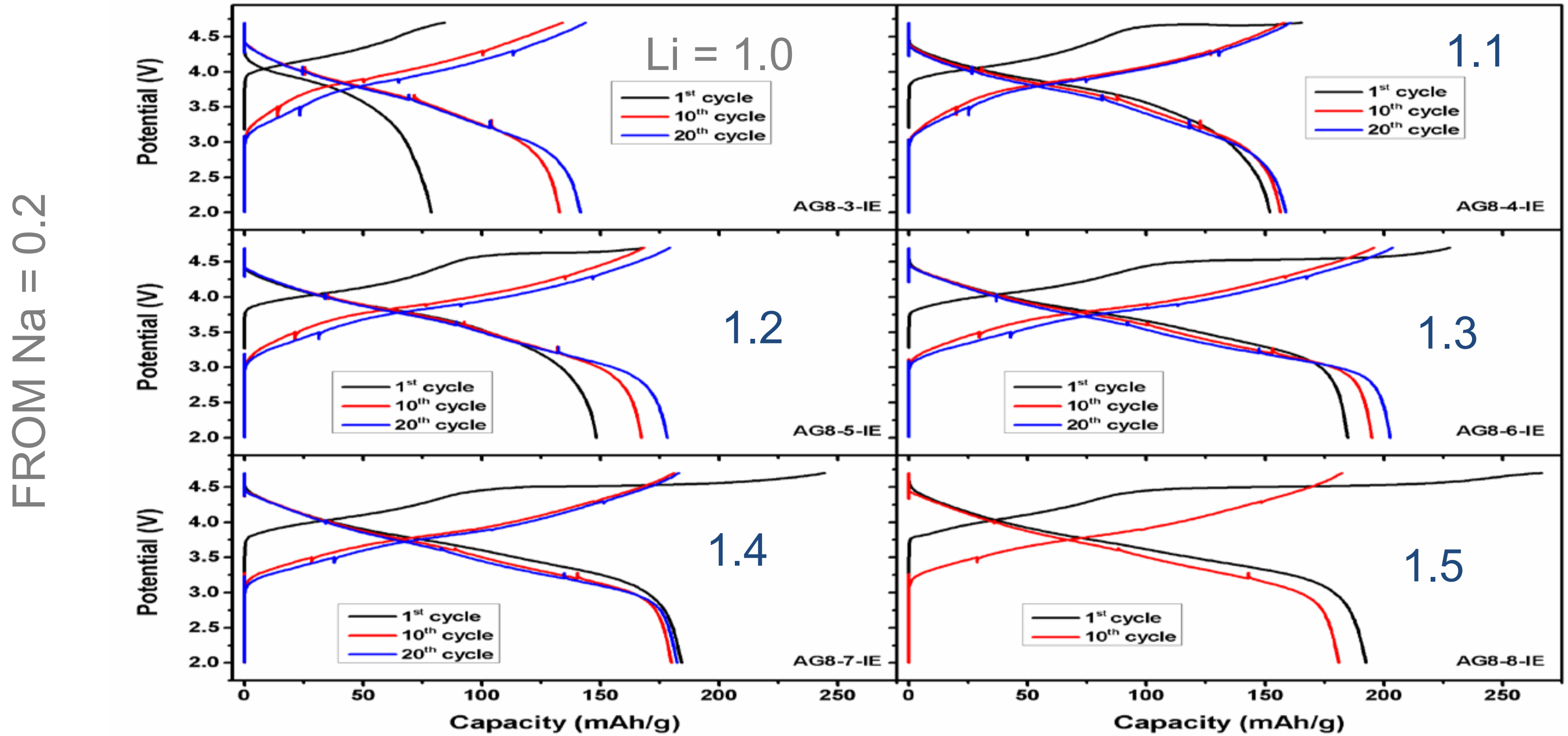

| Precursor | Li | Na |
|---|---|---|
| AG8-3 | 1.0 | 0.2 |
| AG8-4 | 1.1 | 0.2 |
| AG8-5 | 1.2 | 0.2 |
| AG8-6 | 1.3 | 0.2 |
| AG8-7 | 1.4 | 0.2 |
| AG8-8 | 1.5 | 0.2 |

- Ion-exchange using LiBr and hexanol for 24 h w/ nice crystallinity
- Sodium phase peaks disappear
- All peaks after ion-exchange appear to be associated with layered-layered material (i.e. LMR-NMC)

# Composition after ion-exchange

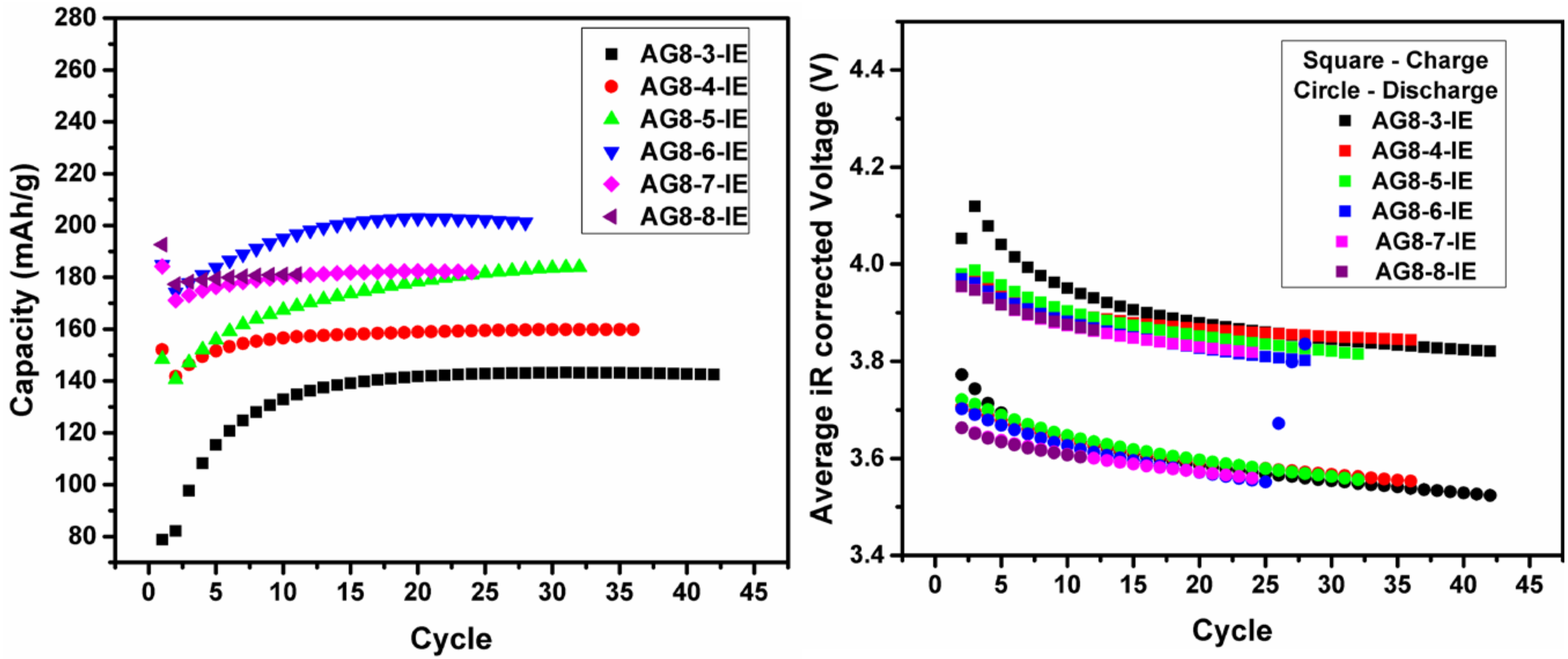
| Sample | Composition | Two-component notation | Oxidation State in NMC | | |
|---|---|---|---|---|---|
| | | | Mn | Ni | Co |
| AG8-3 | $Li_{1.2}Mn_{0.656}Ni_{0.219}Co_{0.125}O_x$ | $0.2Li_2MnO_3$ * $0.8LiMn_{0.57}Ni_{0.27}Co_{0.16}O_2$ | 3.47+ | 2+ | 3+ |
| AG8-4 | $Li_{1.3}Mn_{0.656}Ni_{0.219}Co_{0.125}O_x$ | $0.3Li_2MnO_3$ * $0.7LiMn_{0.51}Ni_{0.31}Co_{0.18}O_2$ | 3.61+ | 2+ | 3+ |
| AG8-5 | $Li_{1.4}Mn_{0.656}Ni_{0.219}Co_{0.125}O_x$ | $0.4Li_2MnO_3$ * $0.6LiMn_{0.43}Ni_{0.36}Co_{0.21}O_2$ | 3.84+ | 2+ | 3+ |
| AG8-6 | $Li_{1.5}Mn_{0.656}Ni_{0.219}Co_{0.125}O_x$ | $0.5Li_2MnO_3$ * $0.5LiMn_{0.31}Ni_{0.44}Co_{0.25}O_2$ | 4+ | 2.30+ | 3+ |
| AG8-7 | $Li_{1.6}Mn_{0.656}Ni_{0.219}Co_{0.125}O_x$ | $0.6Li_2MnO_3$ * $0.4LiMn_{0.14}Ni_{0.55}Co_{0.31}O_2$ | 4+ | 2.75+ | 3+ |
| AG8-8 | $Li_{1.7}Mn_{0.656}Ni_{0.219}Co_{0.125}O_x$ | $0.656Li_2MnO_3$ * $0.344LiNi_{0.64}Co_{0.36}O_2$ | N/A | 3+ | 3+ |

# Charge-Discharge curves - 1st, 10th, and 20th cycles - (IEx material tested in Li half cell - VF protocol)



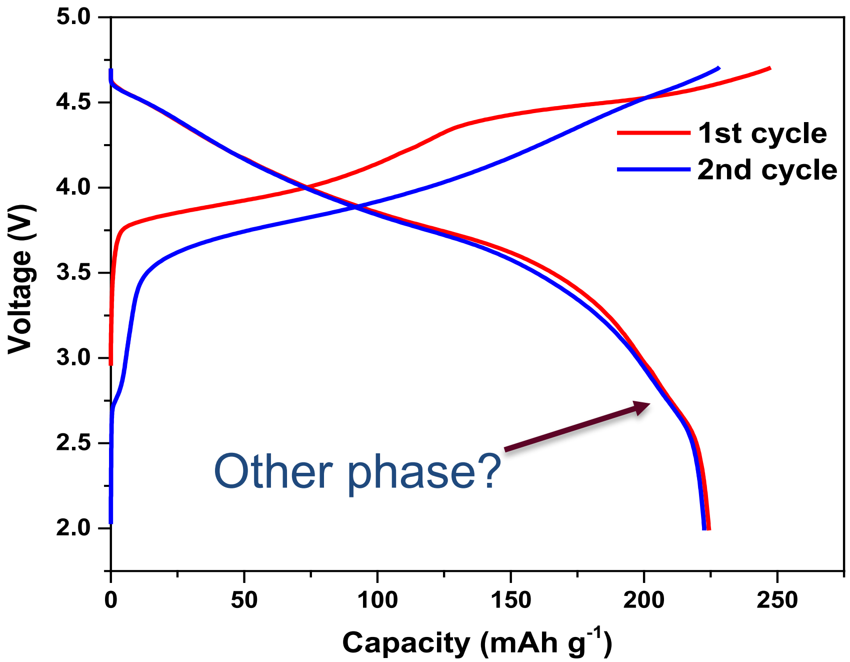

- First cycle capacity increases with lithium content in material
- Further activation of some materials in subsequent cycles increases capacity
- In samples with highest lithium content (AG8-7 and AG8-8) the capacity slightly decreases with subsequent cycling

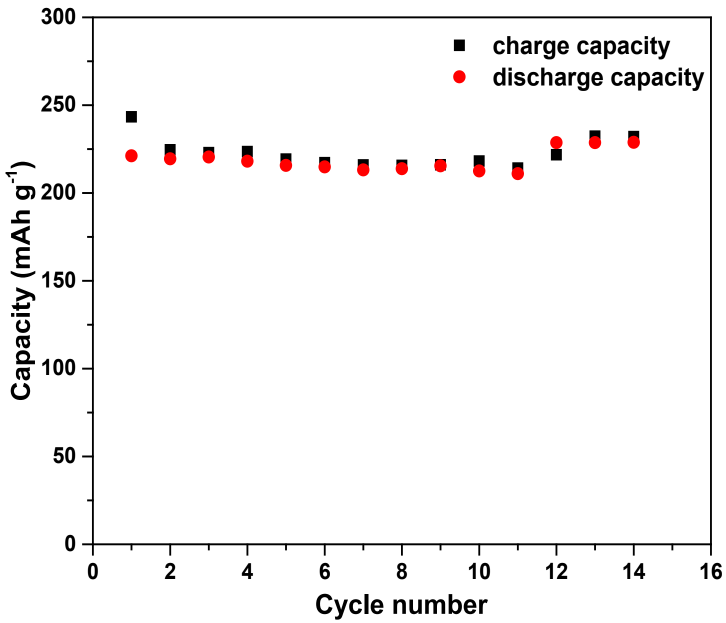
# Cycling behavior - (IEx material tested in Li half cell - VF protocol)




- Low capacities
- Initial voltage fade rate decreases for first 10 – 15 cycles
- Average voltage generally decreases with increasing lithium content
- Amp-hour and Watt-hour efficiencies improve with increasing lithium content in starting material

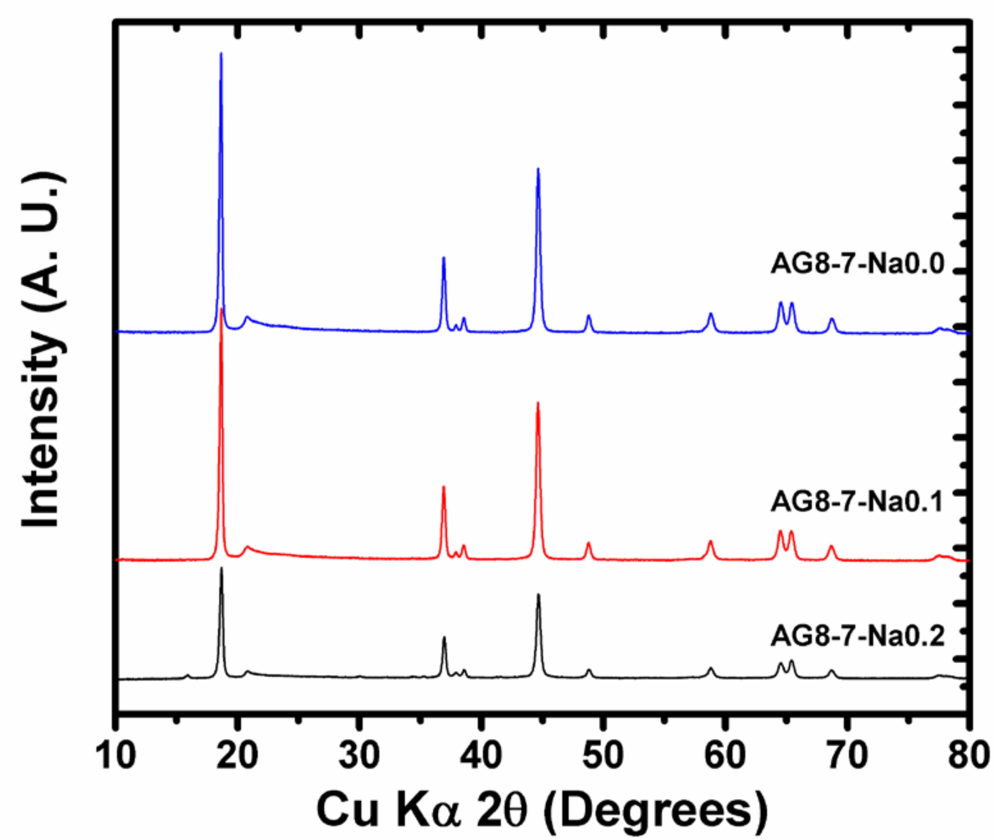
# Repeat synthesis run: IEx AG8-3; voltage profile




- Repeatability (composition variance) hard to control in ion-exchange process
- High capacities are obtainable from this chemistry

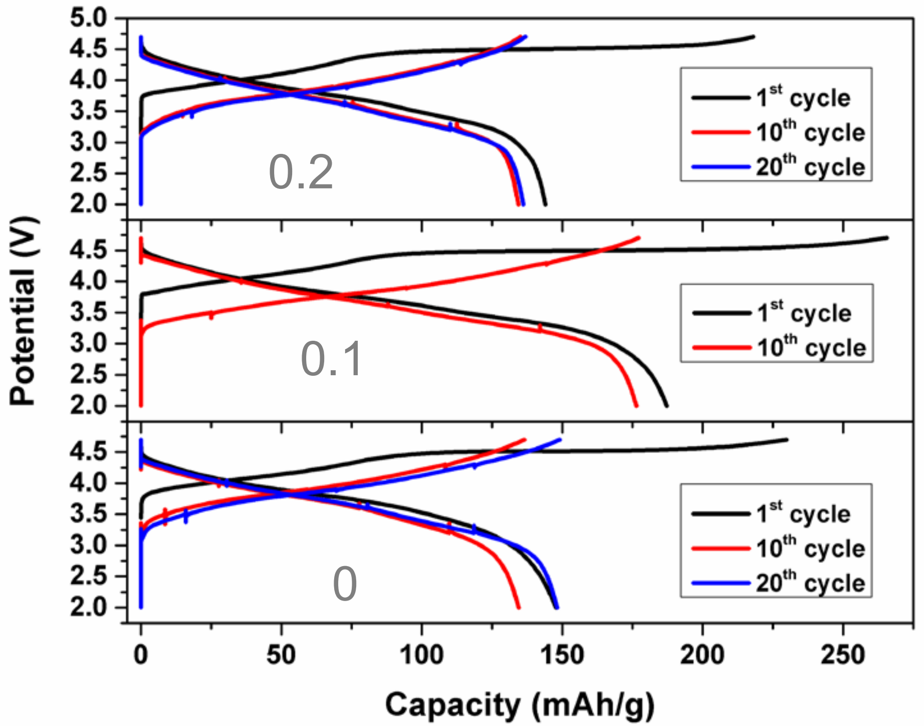
# AG8 XRD after ion-exchange

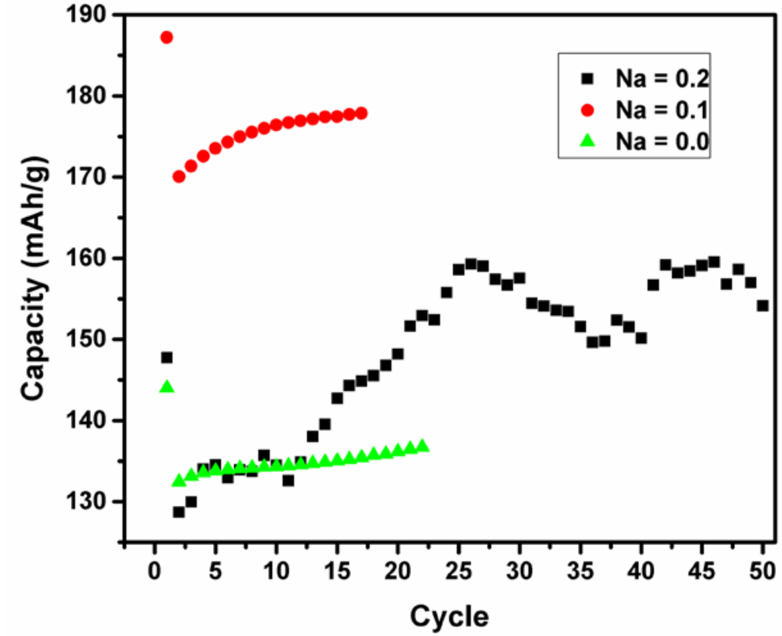



| Precursor | Li | Na | 003/020 peak ratio |
|---|---|---|---|
| AG8-7-Na0.0 | 1.4 | 0.0 | 0.40 |
| AG8-7-Na0.1 | 1.5 | 0.1 | 0.19 |
| AG8-7-Na0.2 | 1.6 | 0.2 | 0.29 |

- Ion-exchange using LiBr in hexanol and heating for 24 h
- Sodium phase peaks disappear
- All peaks after ion-exchange appear to be associated with layered-layered material (i.e. LMR-NMC)

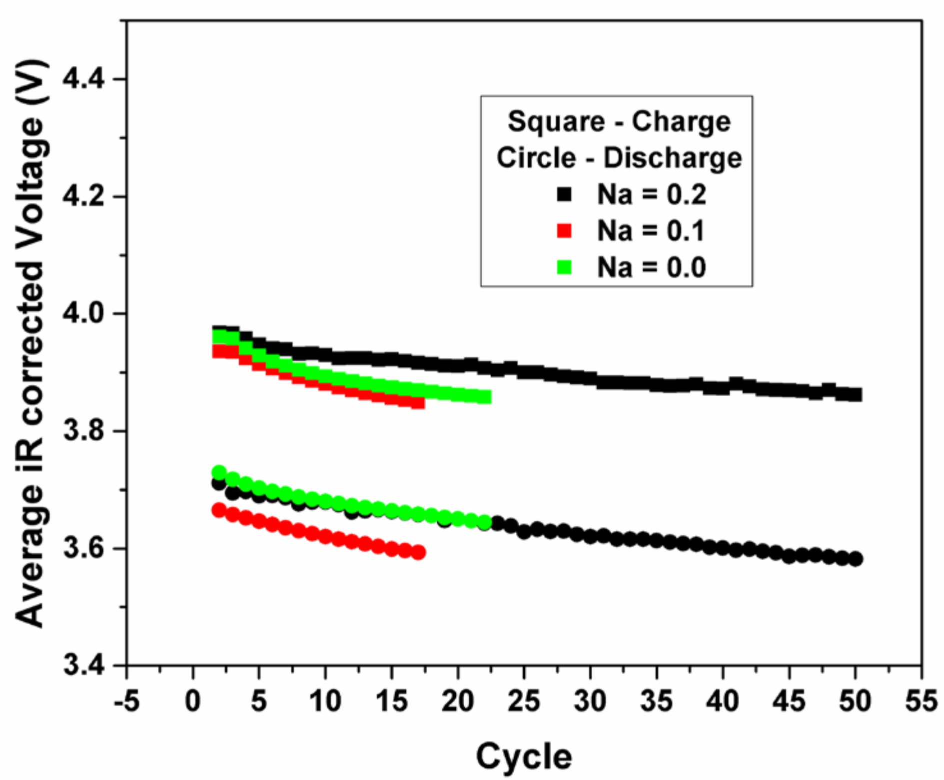
# Cycling behavior – Na effect (IE material – VF protocol)



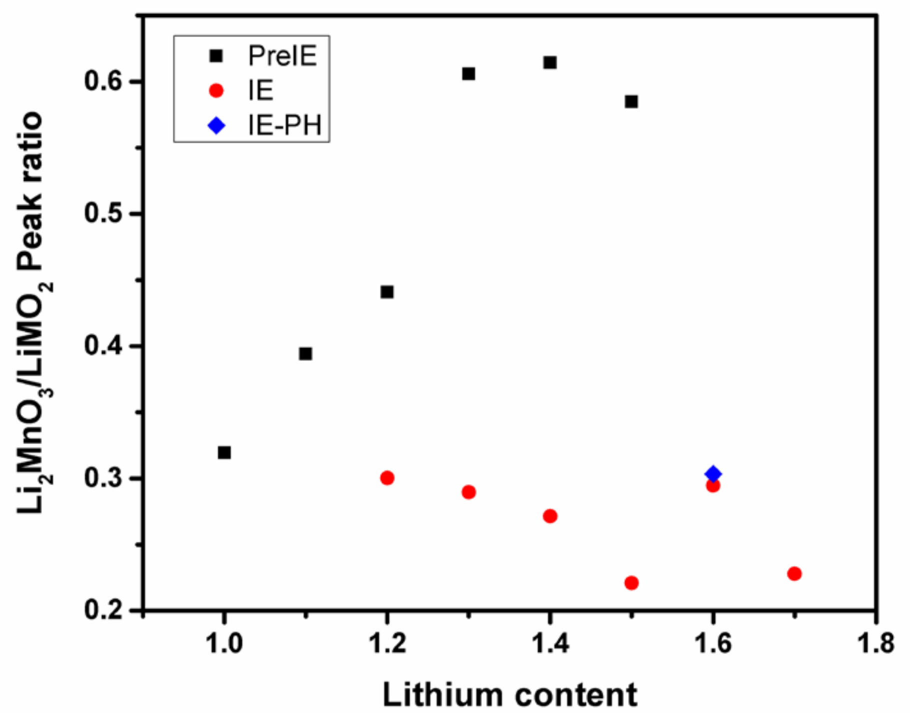

- No obvious trend in capacity was found based on initial Na content
- Initial Li content more dominant

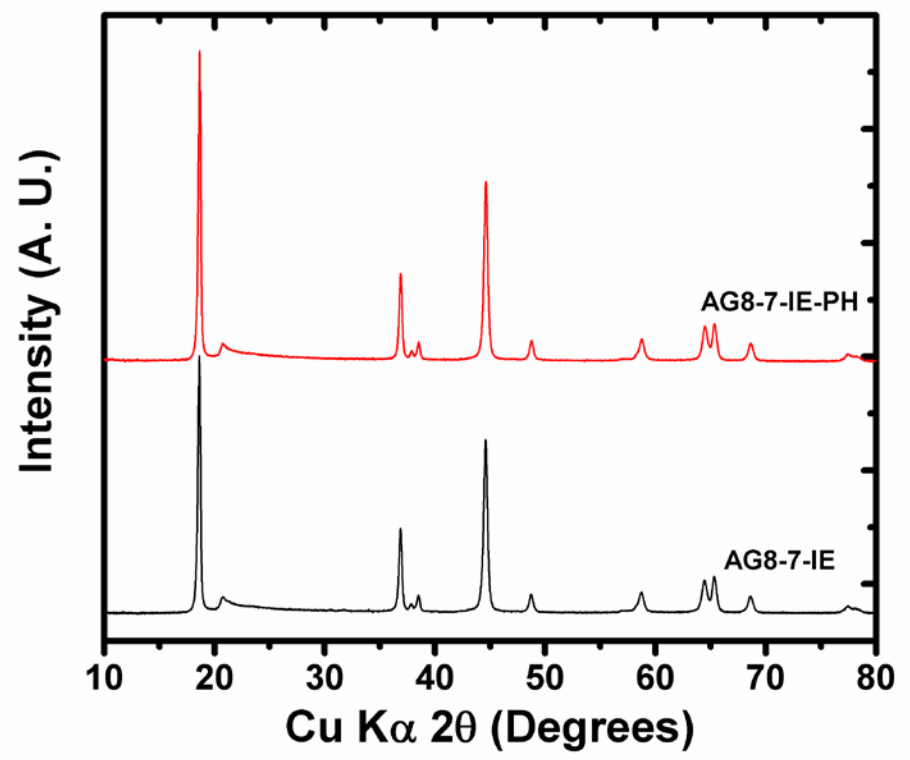
# iR Corrected Voltage – Na effect (IE material – VF protocol)




- Highest sodium content lead to higher average resistance during cycling
- Highest sodium content sample displayed lower charge voltage fade

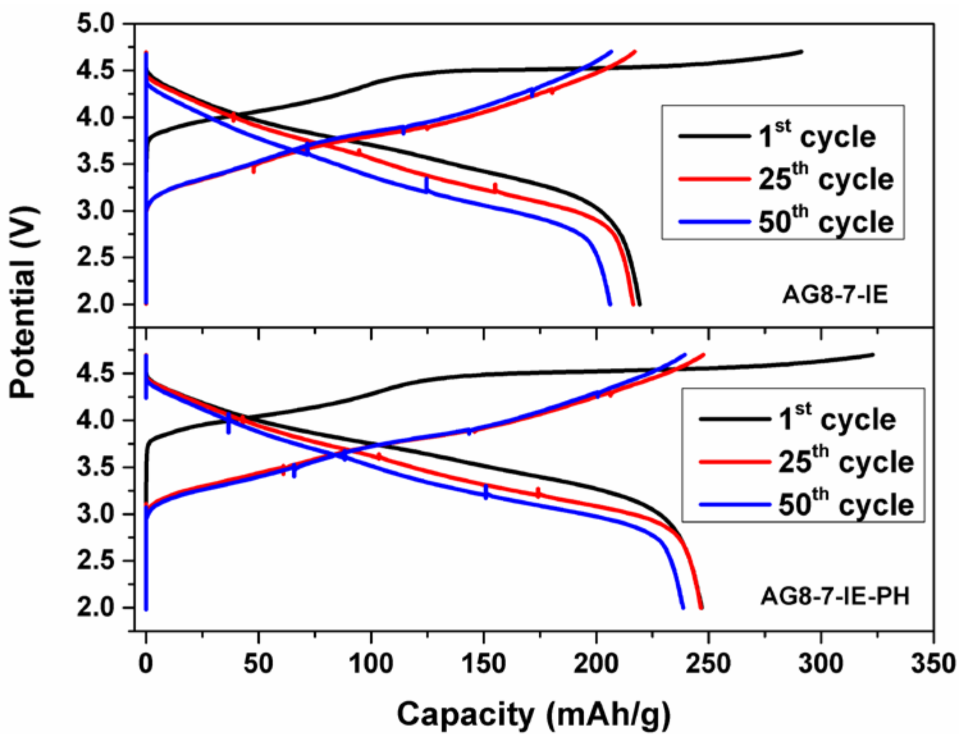
# AG8 XRD after ion-exchange

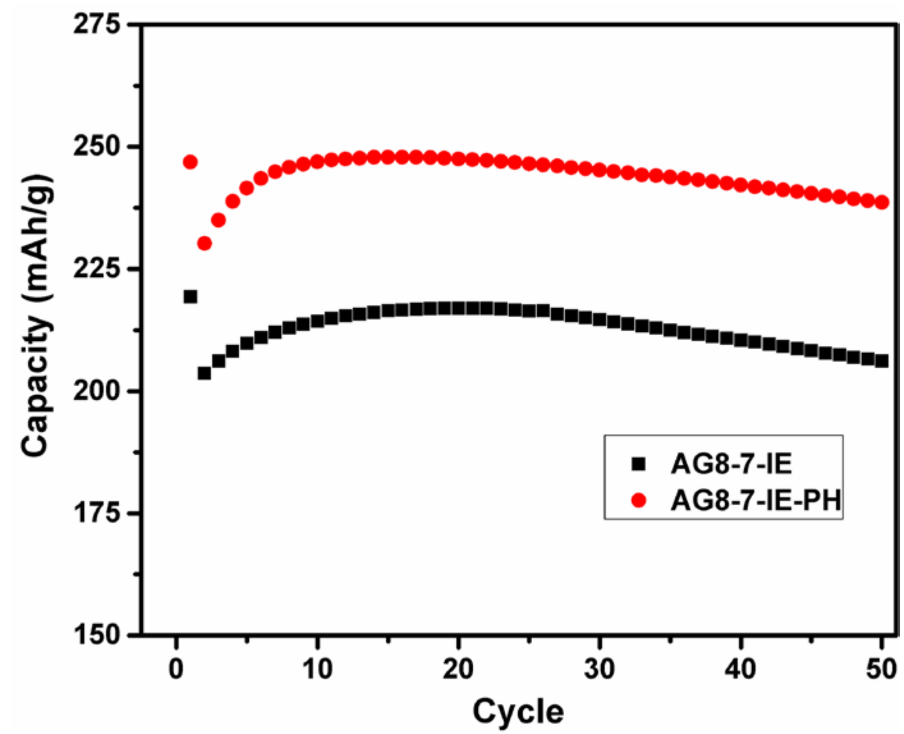



- Post heated sample does not show any significant structural changes

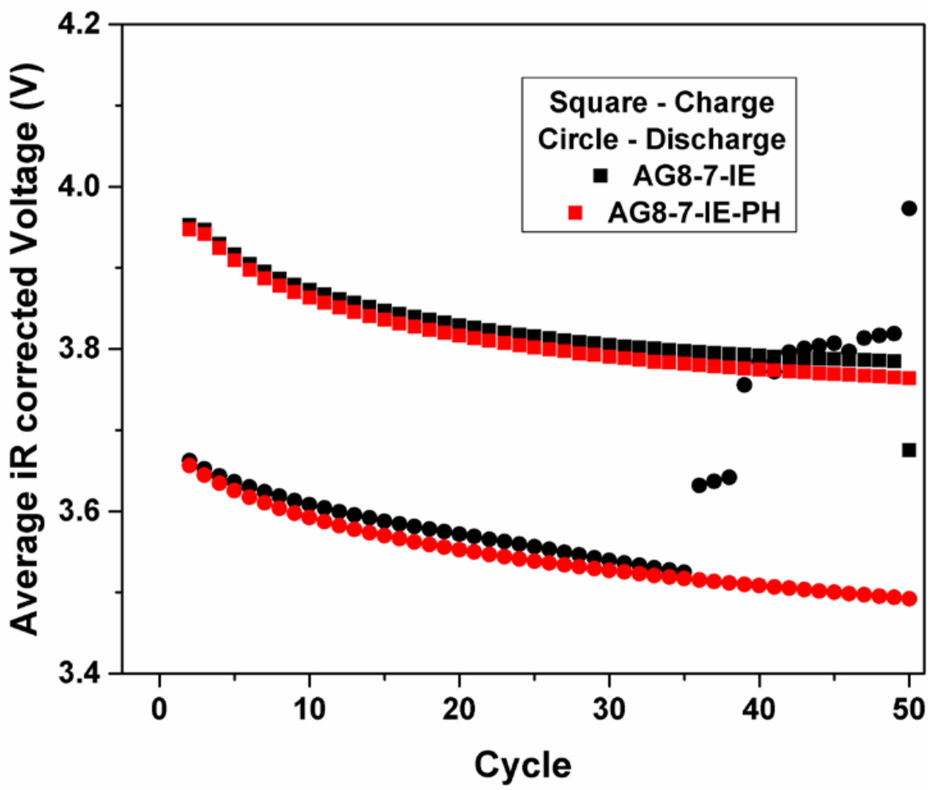
# Cycling behavior - Postheated AG8-7-IE (VF protocol)



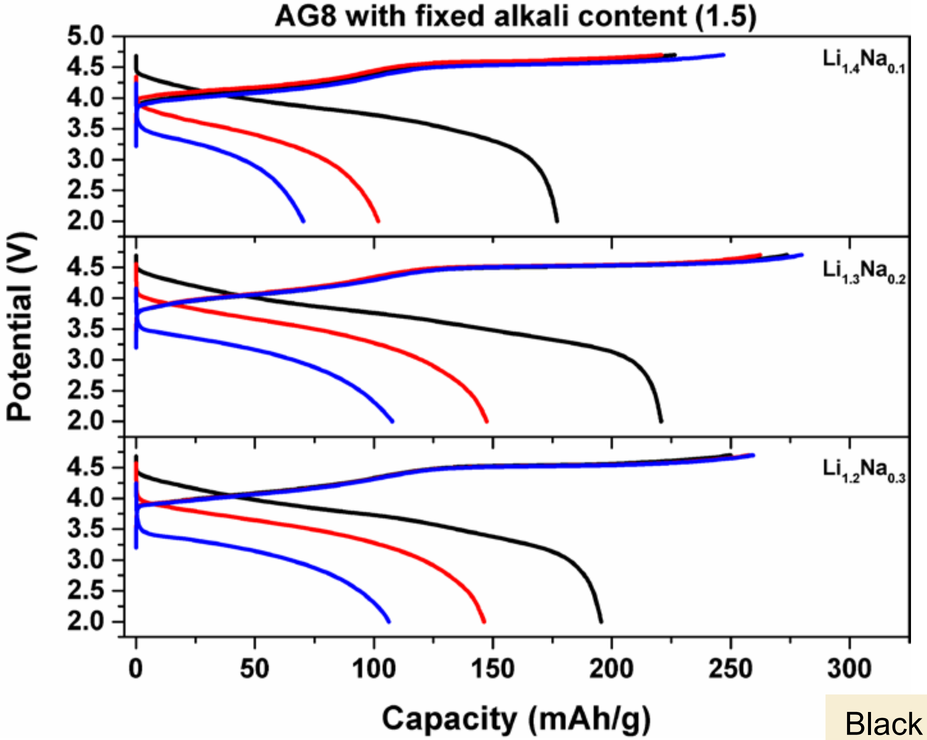

- Post heat treatment enables a 25 – 30 mAh/g increase in capacity for all cycles
- Capacity fade appears to be slightly less in post heated samples
- Both samples display similar voltage fade

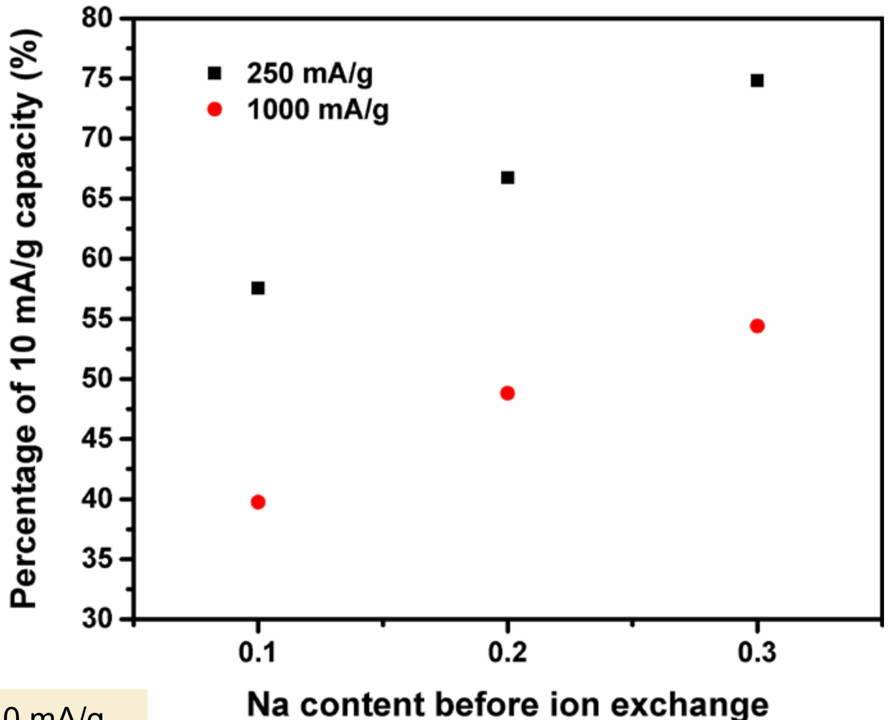
# Average Voltage and Resistance - Postheated AG8-7-IE (VF protocol)




- Voltage fade is slightly worse after post heat treatment
- Both samples decrease in resistance over the 10 – 15 cycles
- Post heated sample displays higher average resistance

# Cycling behavior – AG8 with different starting material Na+Li ratios




Black – 10 mA/g
Red – 250 mA/g
Blue – 1000 mA/g

- Rate capability of samples is improved when the starting material has more sodium content

# Summary

- Evaluation of various Mn, Ni, and Co compositions suggest that Mn-rich systems are best in making the Li O3 phase with Na P2 second phase
  - High Li, low Na not the right direction
  - Should use P2 High Na, Low Li in Pre-IEx layered phase
- For Mn-rich, more Li creates Na incorporation in Li O3 structure (pre IEx)
- Ion-exchange process: more crystalline materials from dilution factor in reaction
- Clean pre-IEx material makes better Ion Ex product in terms of echem
- Capped out with capacity about 200-205 mAh/g
  - Need to get to 250 mAh/g level

# Remaining Challenges and Barriers

- Work still exploratory at this juncture
- Can we find a new synthesis route not yet used that will stop voltage fade
- Must determine location of Li, TM cations in IEx-LL-NCM to direct syntheses going forward
  - Confirm no spinel phase formation upon cycling
- Synthesis:
  - Increase tap density
  - Streamline ion-exchange route
    - Can it be scaled?
- Improve high-power properties
  - Surface coatings

# Future Work

- Explore more Na-rich and Li poor P2 Pre-IEx materials
- Continue with mixed Ni, Mn, Co phases precursors – optimize
  - Move into Ni rich systems
- Continue exploration of post HT after IEx reaction
- More characterization to be done
  - Microscopy
  - X-ray absorption
- Continue **working with Farasis** on enabling these cathode materials for high-energy LIBs