Advanced Nanostructured Cathode Materials for NASA Applications

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Outline

Part I:

- Layered-Spinel Composite Electrode: xLi_2MnO_3-(1-x) $LiMn_{1.5}Ni_{0.5}O_4$
- Structural and Electrochemical Analysis

Part II:

- Layered-Layered Composite Electrode:

  xLi_2MnO_3 - (1-x)$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$
- Phase & Microstructure Analysis
- Electrochemical Performance
- Discussion

Development of Cathode Materials

Objective

- Develop high energy density lithium-ion battery electrodes with reliable cycle, rate and high safety performance appropriate for NASA's exploratory applications.

Technical Approach

- Materials composition and design based on composite electrode
- Synthesis of composite electrodes:
  - I. xLi_2MnO_3 - (1-x) $Li(Ni,Co,Mn)_{0.33}O_2$
  - II. xLi_2MnO_3 - (1-x) $LiMn_{1.5}Ni_{0.5}O_4$
- Microstructure (particle size, morphology, degree of crystallinity, metal-ion ordering) and electrochemical characterization
- Determine optimum processing conditions for achieving maximum energy density and cathode stability.

Composite Electrodes

Why Composite Electrode?

- Bi-functional electrode: Provide high capacity through 2D layer structure and high rate capability by 3D spinel structure
- Prevent oxygen loss during charge
- Enhance cathode stability through the spinel-layered or layered-layered integrated composite structure

Material of Choice:

- Inexpensive and safe cathode material: Mn-based electrode
- High O_2 retention relative to Ni/Co based electrodes *(J. Dahn et al., Solid state ionics 69, 1994)*
- Stabilize the layered/spinel structure with Li_2MnO_3 (*Johnson et al., Electrochem. Commun, 6, 2004 and also Lu et al. J. Electrochem 149, 2002*)

PART I:

Layered – Spinel Structure

Funding provided by

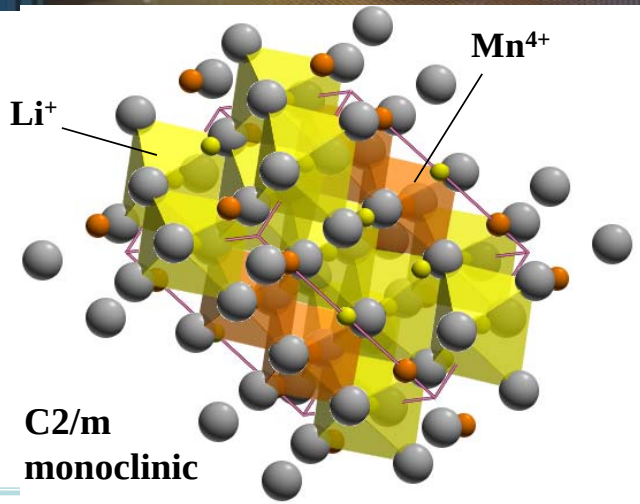
Phase I NASA STTR

Contract NNX09CF57P

Layered – Spinel Structure

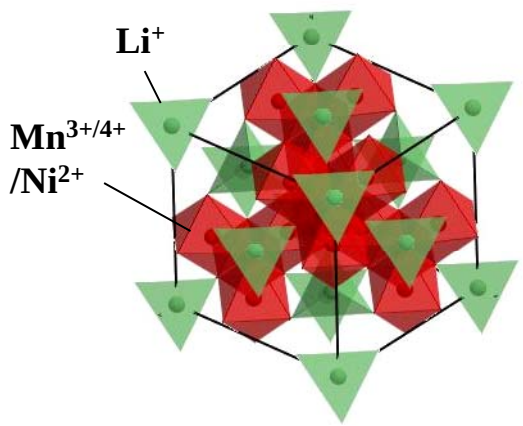
$Li[Li_{1/3}Mn_{2/3}]O_2$ (Layer):

- Li-rich layered structure
- Layers of Li only, mixed layers of 2/3Mn and 1/3Li and pure oxygen layer
- Oxygen layers separating the Li layer and Mixed layer (Li & Mn)
- Superlattice ordering of Li and Mn

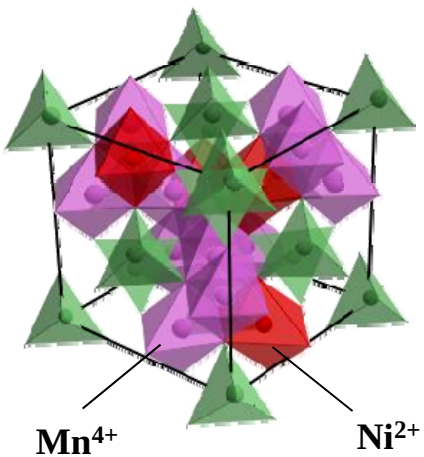


$Li[Mn_{1.5}Ni_{0.5}]O_4$ (Spinel):

- Two SG of $P4_332$ (ordered) and Fd-3m (disordered)
- Cubic structure (3D)
- 120-130 mAh/g
- Large capacity at 4.7 V



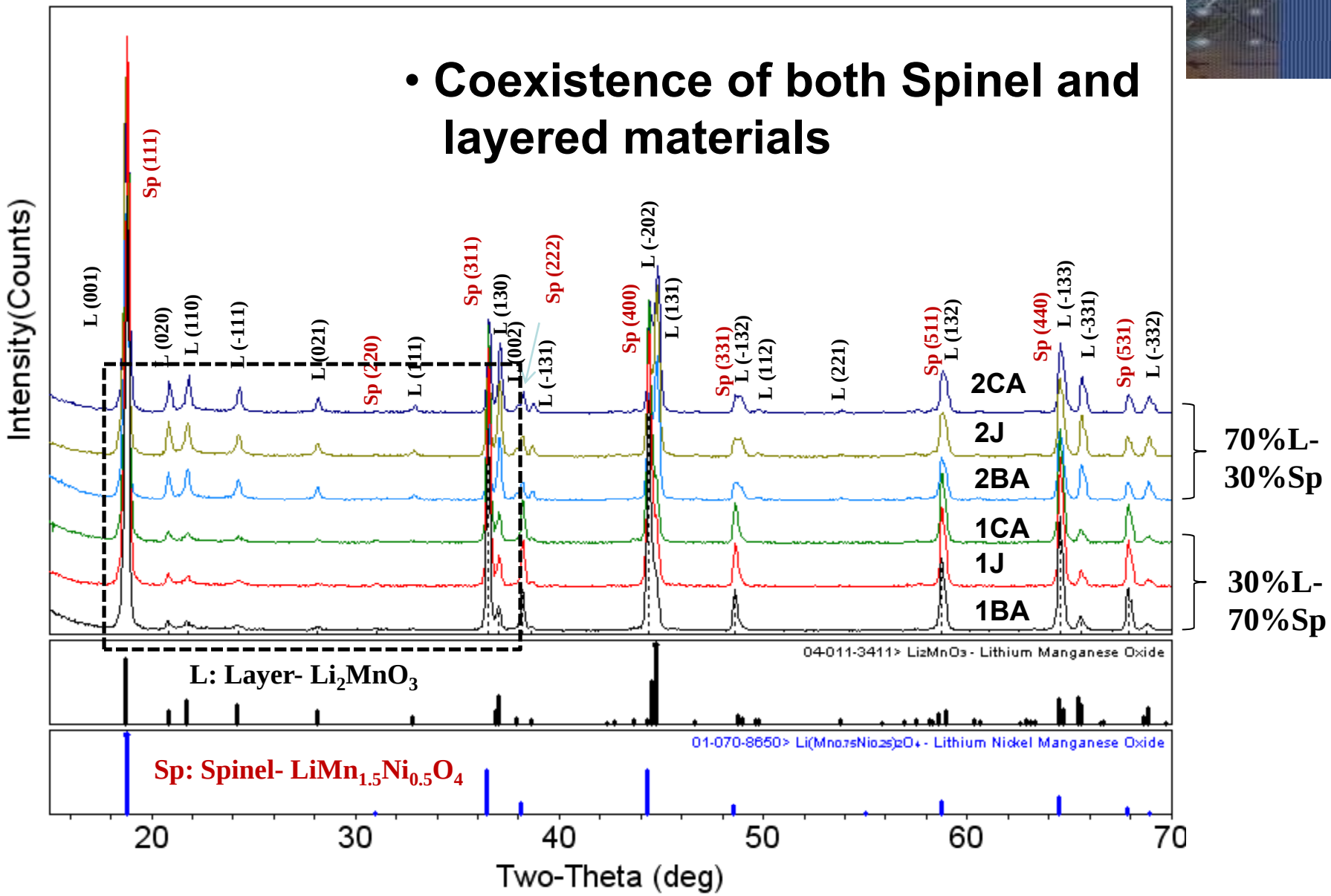
- **Fd-3m**: Randomly mixed metal ions at 16d site of octahedrons.



- **$P4_332$**: Mn^{4+} at 12d & Ni^{2+} at 4a sites of octahedral.

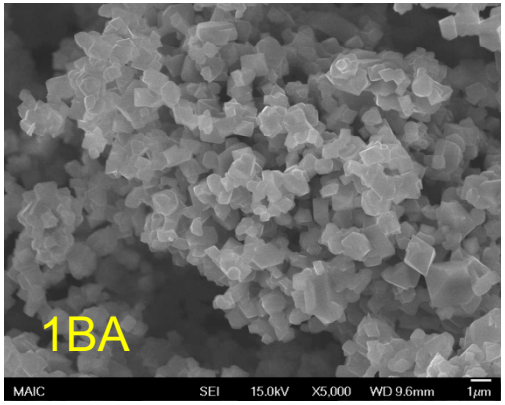
Layered – Spinel Structure

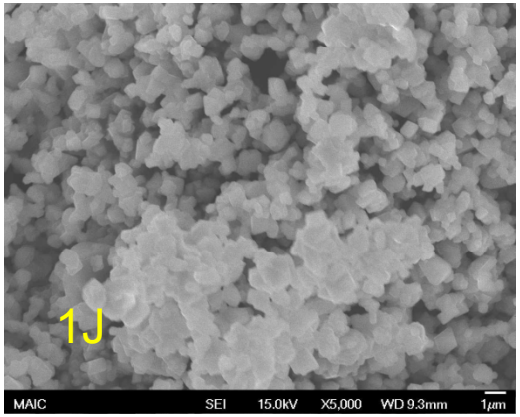
- Coexistence of both Spinel and layered materials

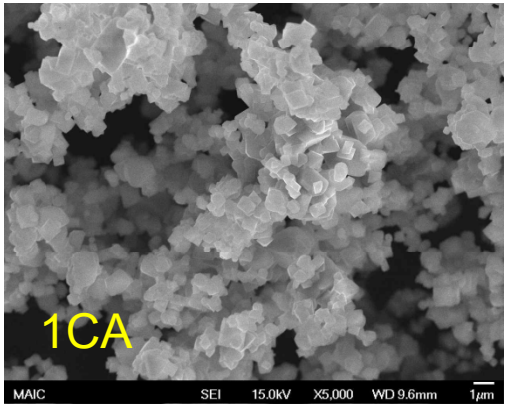


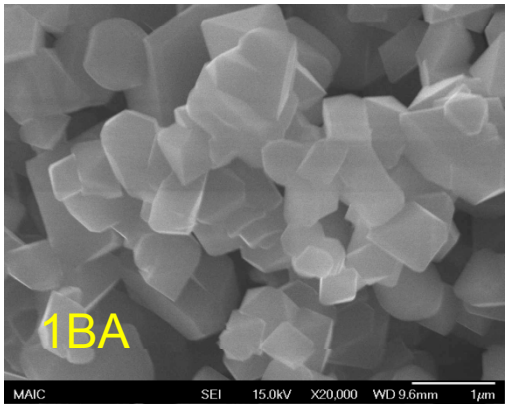
SEM: 30%Layered-70%Spinel

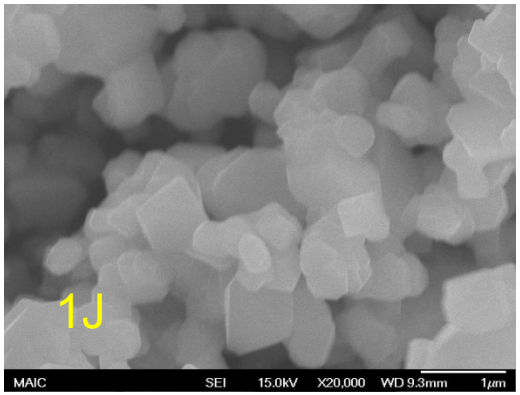
- **Three different processing conditions:**

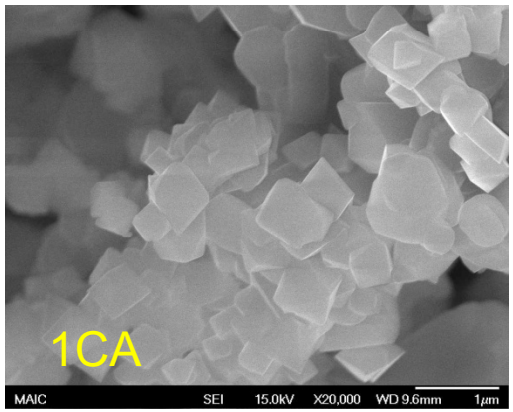












- **Well crystallized spinel-layered particles**
- **Uniform particle size distribution with particle size of 0.6-0.8 μm.**

30%Layered-70%Spinel

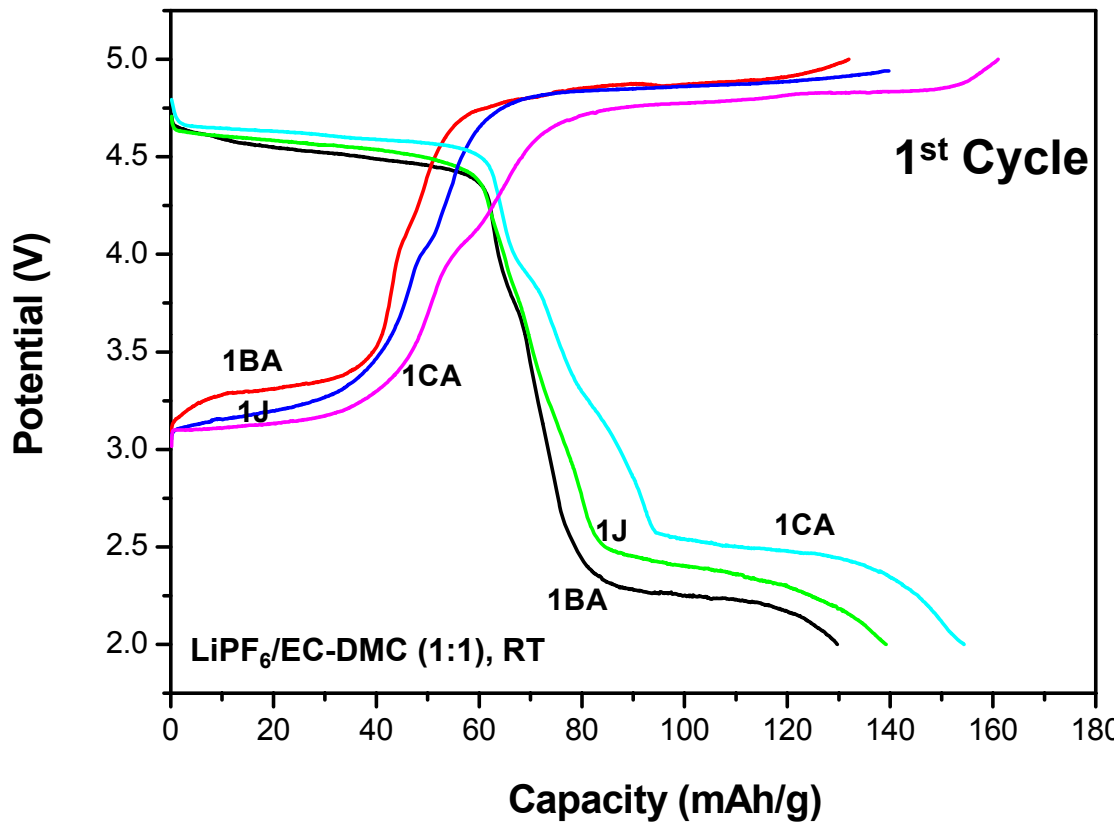
Capacity contribution:

At 1st Charge:

- 4-4.1V: Mn^{3+}- Mn^{4+}
- 4.4-4.6V: Layered activation range
- 4.7-4.9V: Spinel ($Ni^{2+} \rightarrow Ni^{4+}$)

1st Discharge:

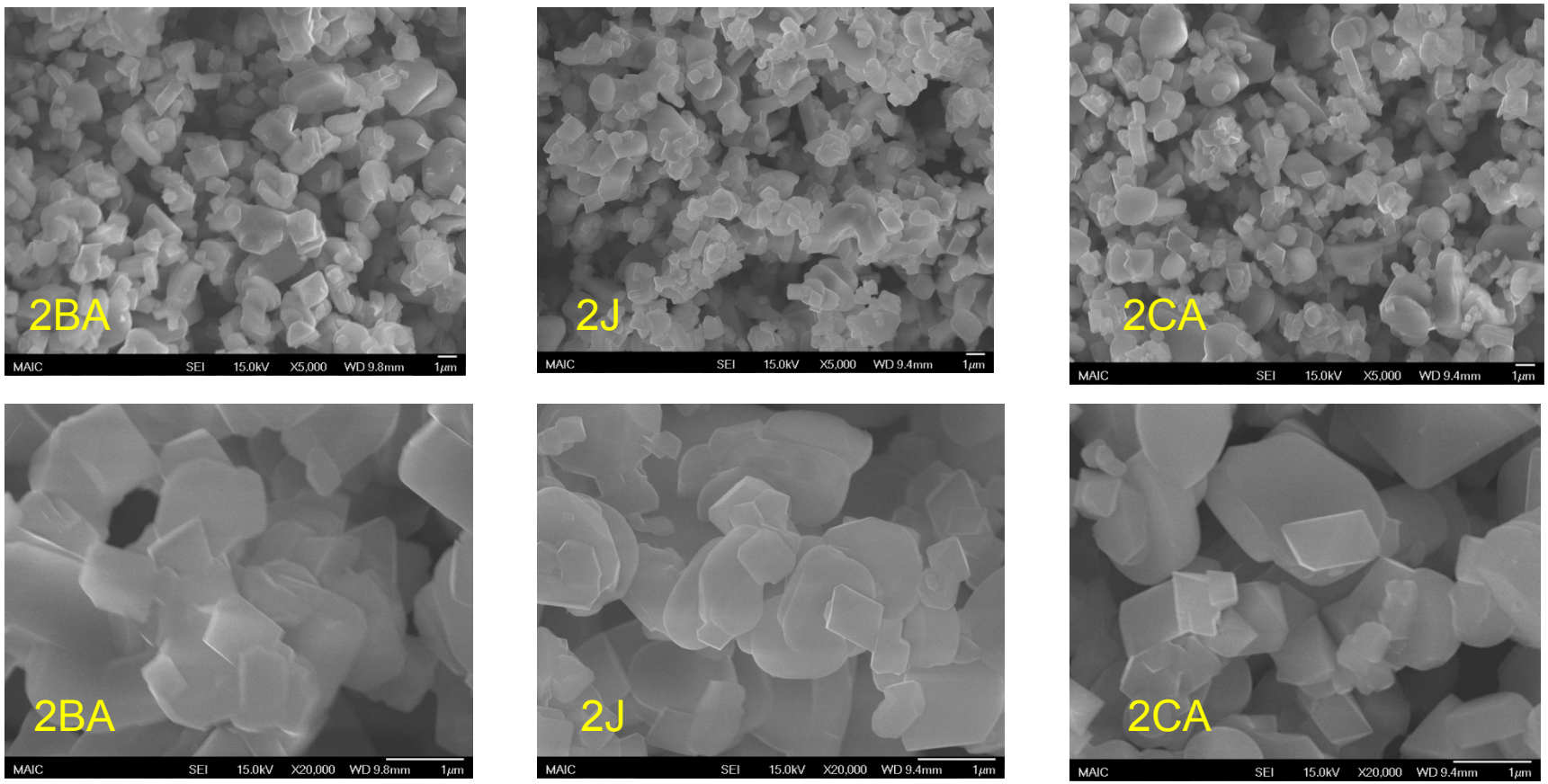
- 3-2.5V : layered
- 2.5: Spinel



- Confirmed coexistence of layered and spinel structures from voltage profile
- Higher capacity in 1CA due to more activation of layered component (3-2.5V region).

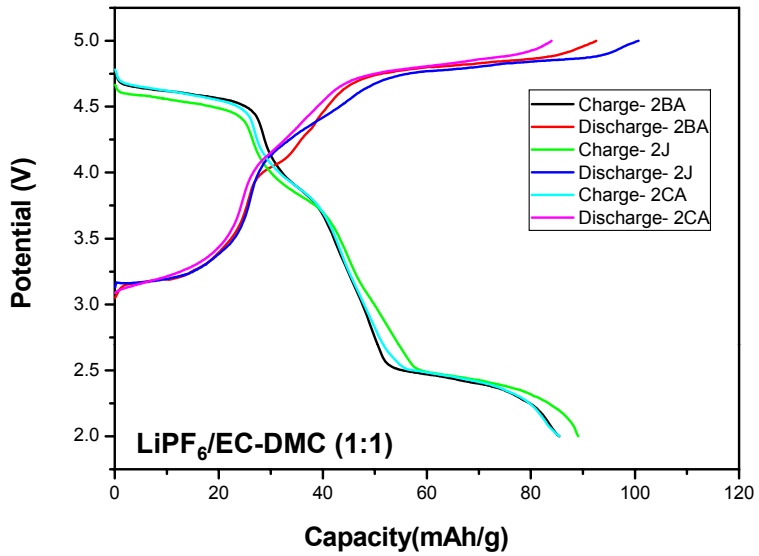
SEM: 70%Layered-30%Spinel

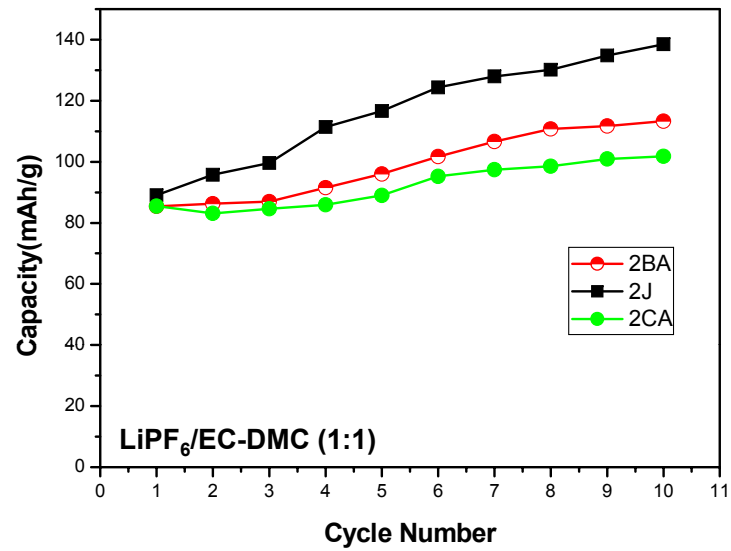
- **Three different processing conditions:**



- **Two different particle morphologies; Octahedral type, and irregular particle shape**
- **Octahedral particles ≤1 μm but irregular particles ≥ 1μm**

70%Layered-30%Spinel

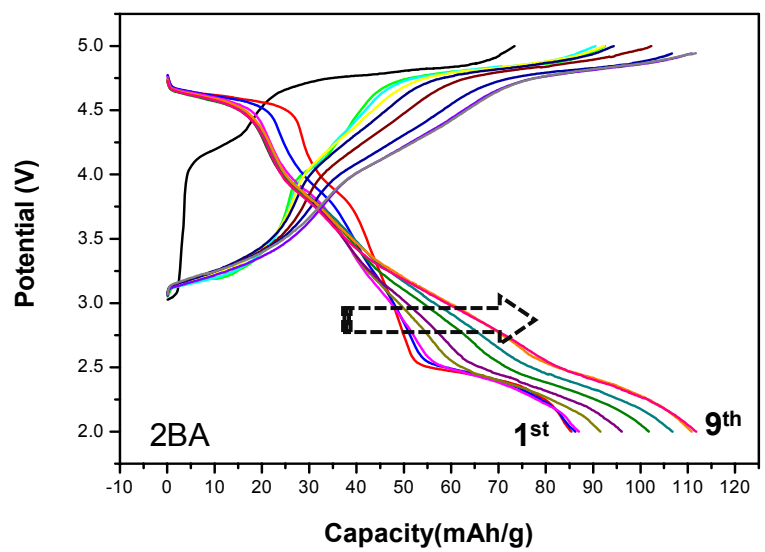




- In initial cycles: Less capacity contribution from Spinel and Layered →Low initial capacity
- Electrochemical activation of Li_2MnO_3 in subsequent cycles:
  - Charge: ~4.4- 4.6V
  - Discharge: 3-2.5V
- 3V capacity increase: 26%
- 2.5V capacity increase: 53%

At 1st cycle: $Li_2Mn^{IV}O_3 \rightarrow Li_2O + MnO_2$ (C)

$Li^+ + MnO_2 \rightarrow Li_{1-x}Mn^{III}O_3$ (D)



PART II:

Layered – Layered Structure

Funding provided by

Phase I NASA NRA Program

Contract NNC09CA07C

Layered – Layered Structure

$Li[Li_{1/3}Mn_{2/3}]O_2$ (Layered):

- Li-rich layered structure
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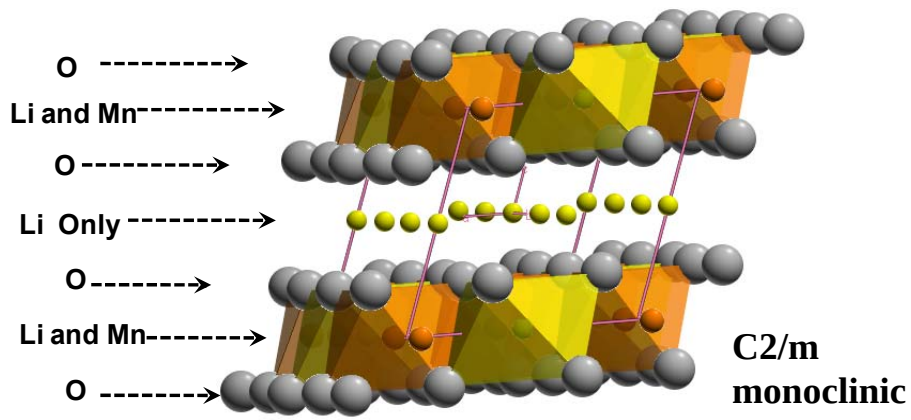
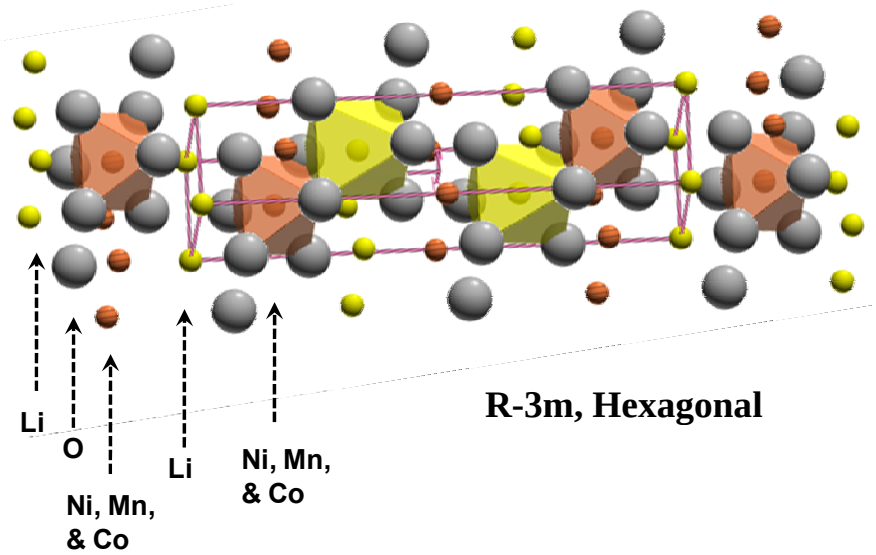
- Oxygen layers separating the Li layer and Mixed layer (Li & Mn)
- Superlattice ordering of Li and Mn

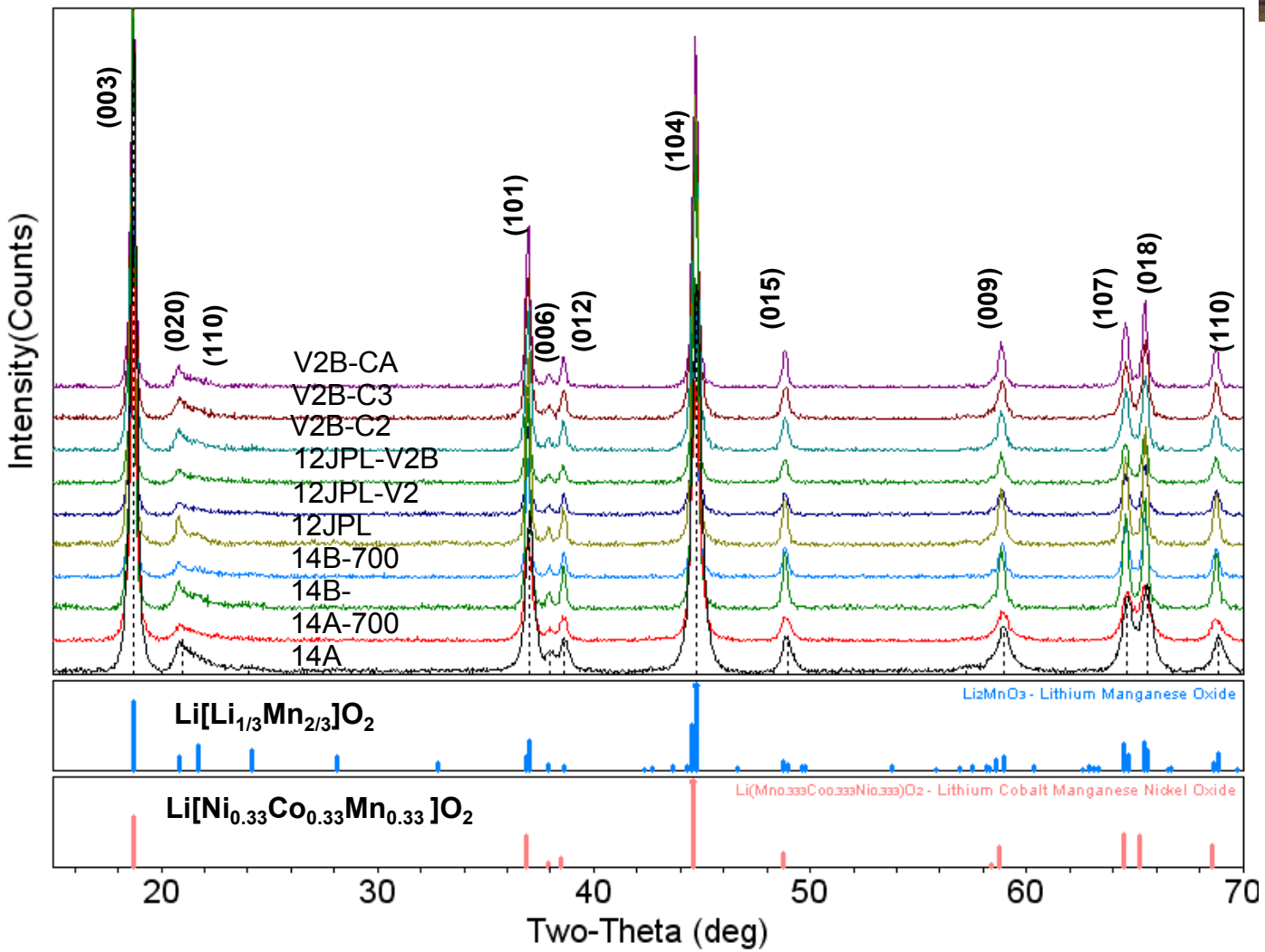


$Li[Mn_{0.33}Ni_{0.33}Co_{0.33}]O_2$ (Layered):

- Similar to Li_2MnO_3 but no Li in transition metal layer
- Capacity of 180-220 mAh/g



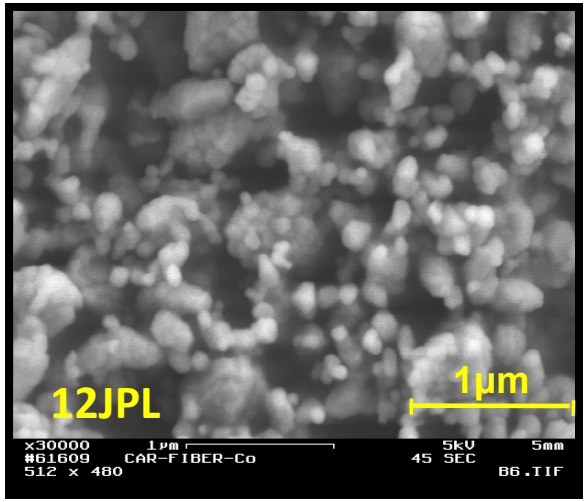
Layered – Layered Structure

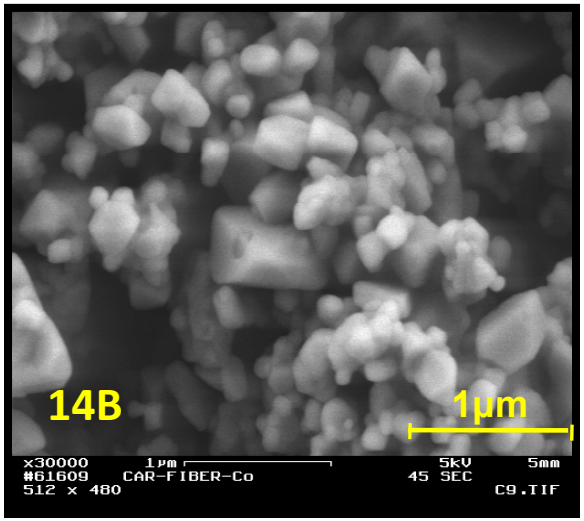


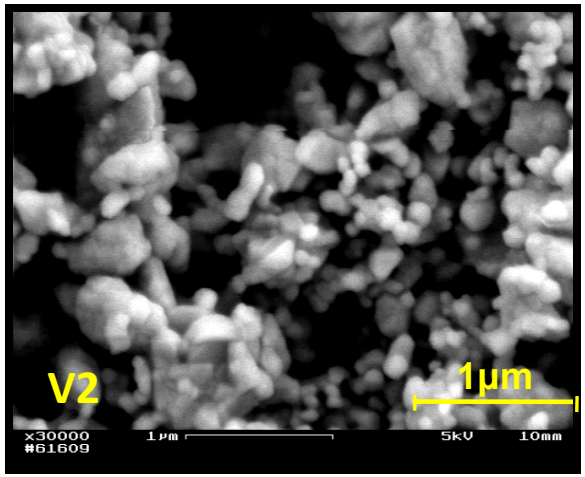
1:1 layer to layer ratio

- **Formation of ordered layer Li_2MnO_4 (superlattice Li and Mn) and randomly ordered transition metal ions $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$.**

Particle Size & Morphology







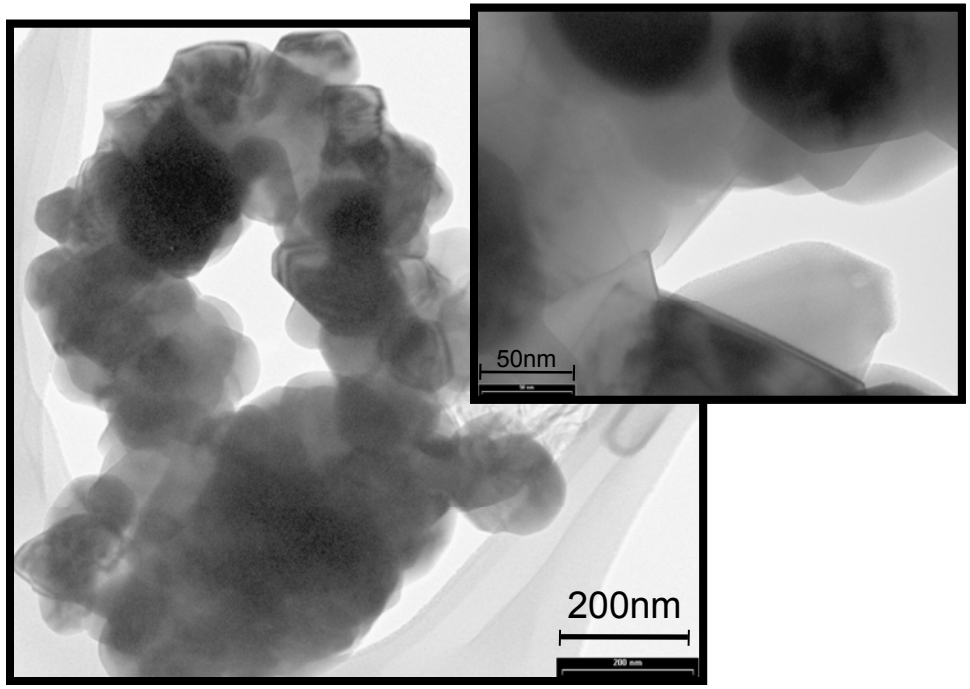
- Surface area of all samples in the range of 4.00 – 5.2 m^2/g (tap density: 0.6–0.7 g/cc)

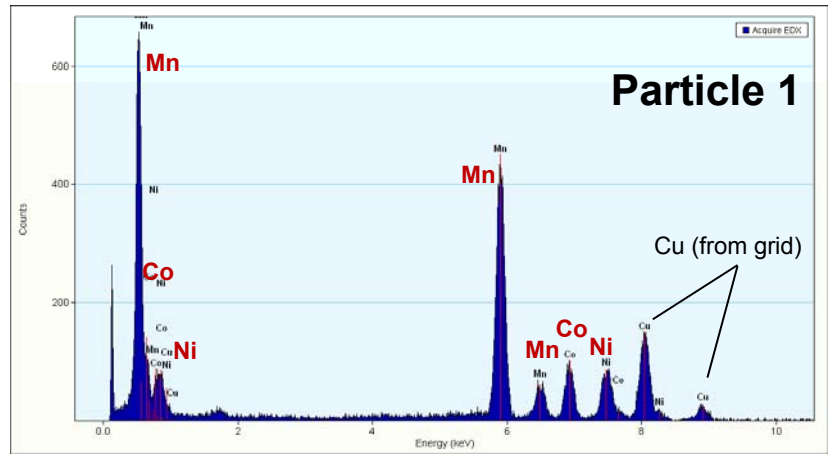
12JPL:
- Uniform nanometer particle (50-100nm); 220 mAh/g

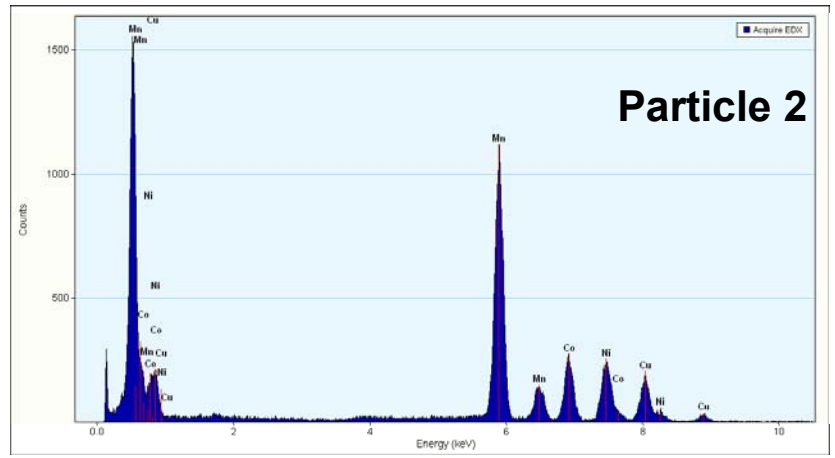
14B:
- Faceted particles (200-600nm); wider particle size distribution (198 mAh/g)

V2:
- Similar to 12 JPL in terms of particle size and morphology but higher initial discharge capacity (270 mAh/g)

TEM: Sample 12 JPL



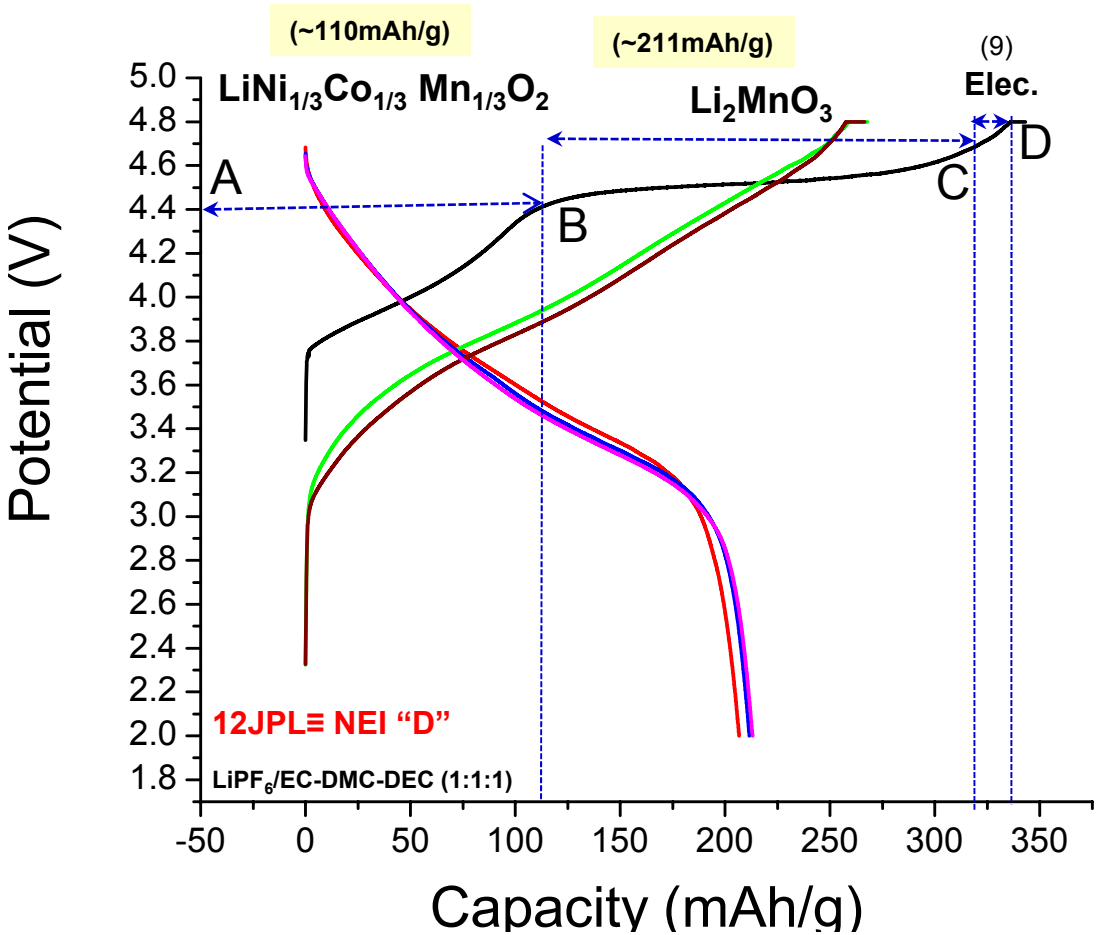




- **Spherical and uniform particles**
- **Uniform metal ion distribution**

Capacity Contribution in Composite Electrode

0.5 Li_2MnO_3 - 0.5 Li $(NiCoMn)_{1/3}O_2$



1st Charge Cap. Contributions:

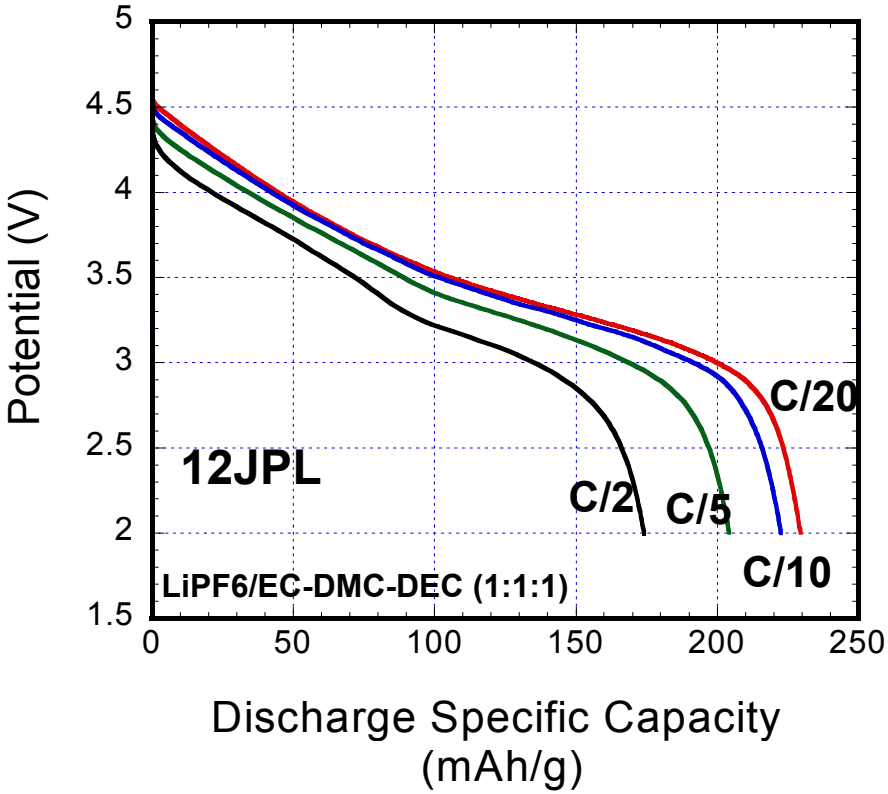
AB: ~110 mAh/g (up to 4.4V)
BC: ~211 mAh/g (4.4 – 4.6V)
CD: ~9 mAh/g Electrolyte (> 4.6 V)

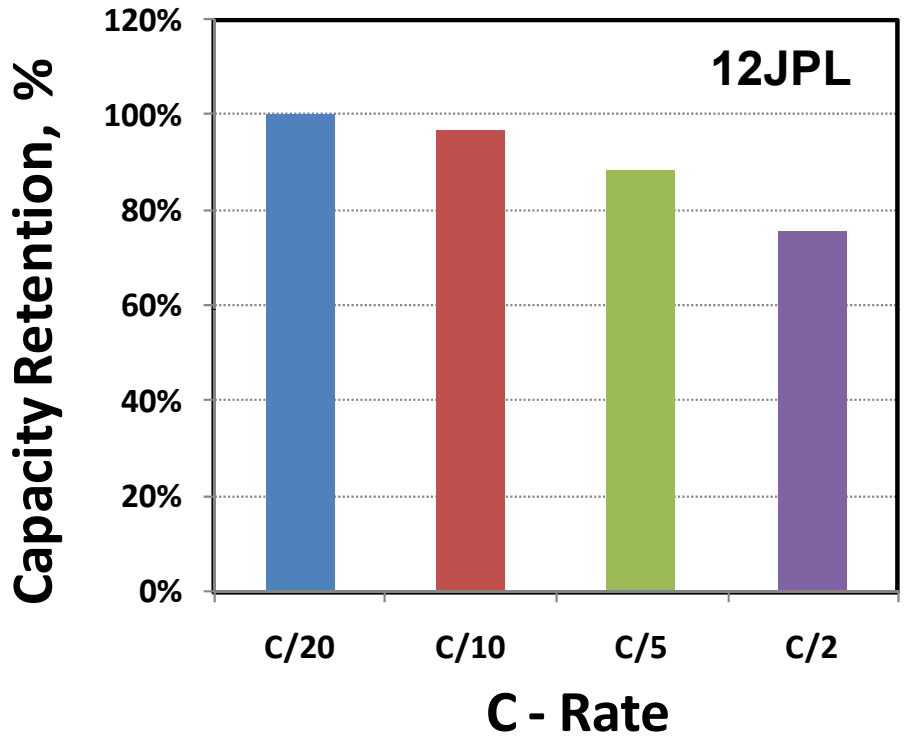
1st Discharge (calculated):

From $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: 110
Li_2MnO_3: 211 *1/2: 105.5
Total: 105.5 + 110= 215.5 mAh/g

1st cycle: $Li_2Mn^{IV}O_3 \rightarrow Li_2O + MnO_2$ (C)
$Li^+ + MnO_2 \rightarrow Li_{1-x}Mn^{III}O_3$ (D)

Rate Capability

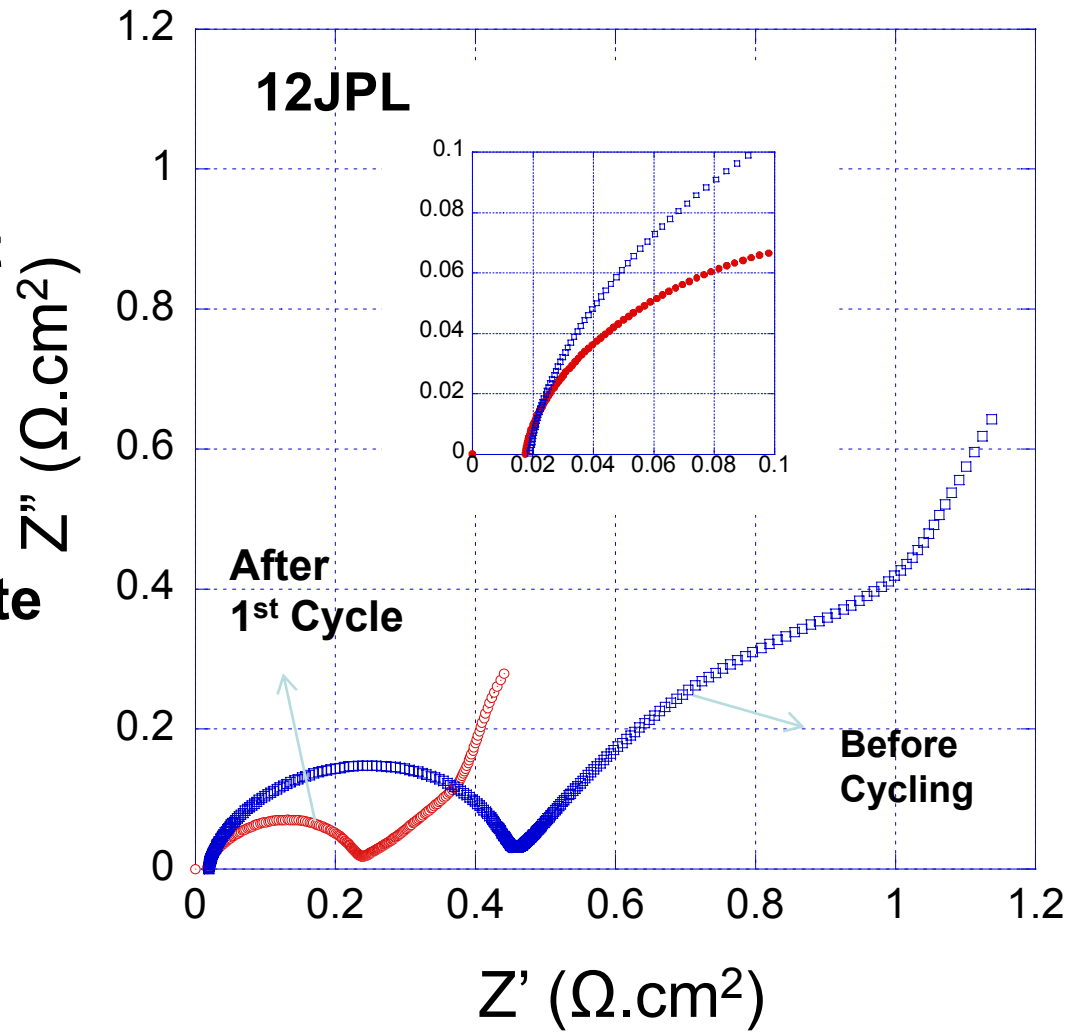




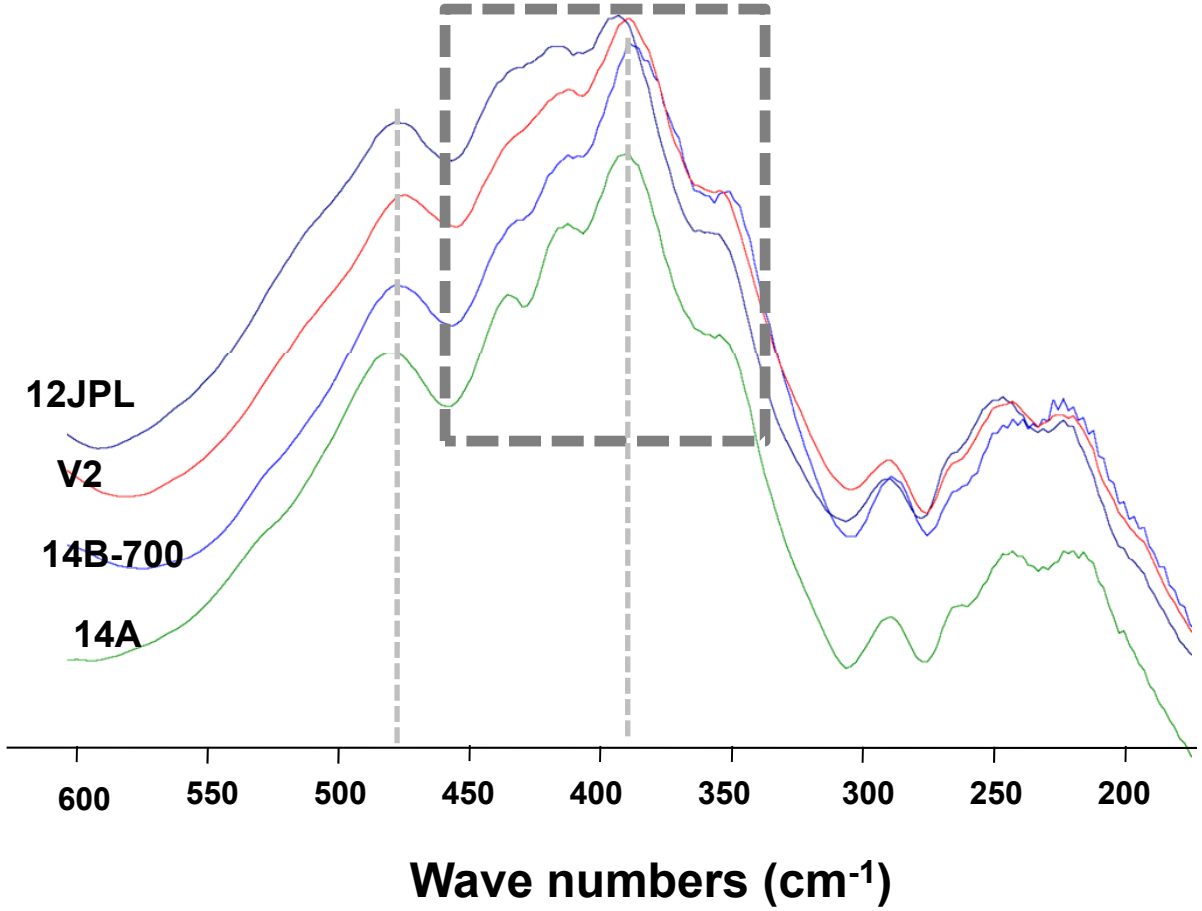
- **Good rate capability:**
  - **Only 3% capacity loss when the cycling rate doubled (from C/20 to C/10)**

Impedance Spectroscopy

- Cell impedance reduced by half after 1st cycle (not increased noticeably at subsequent cycles)
- Good transport property of formed Solid Electrolyte Interface (SEI) Layer.

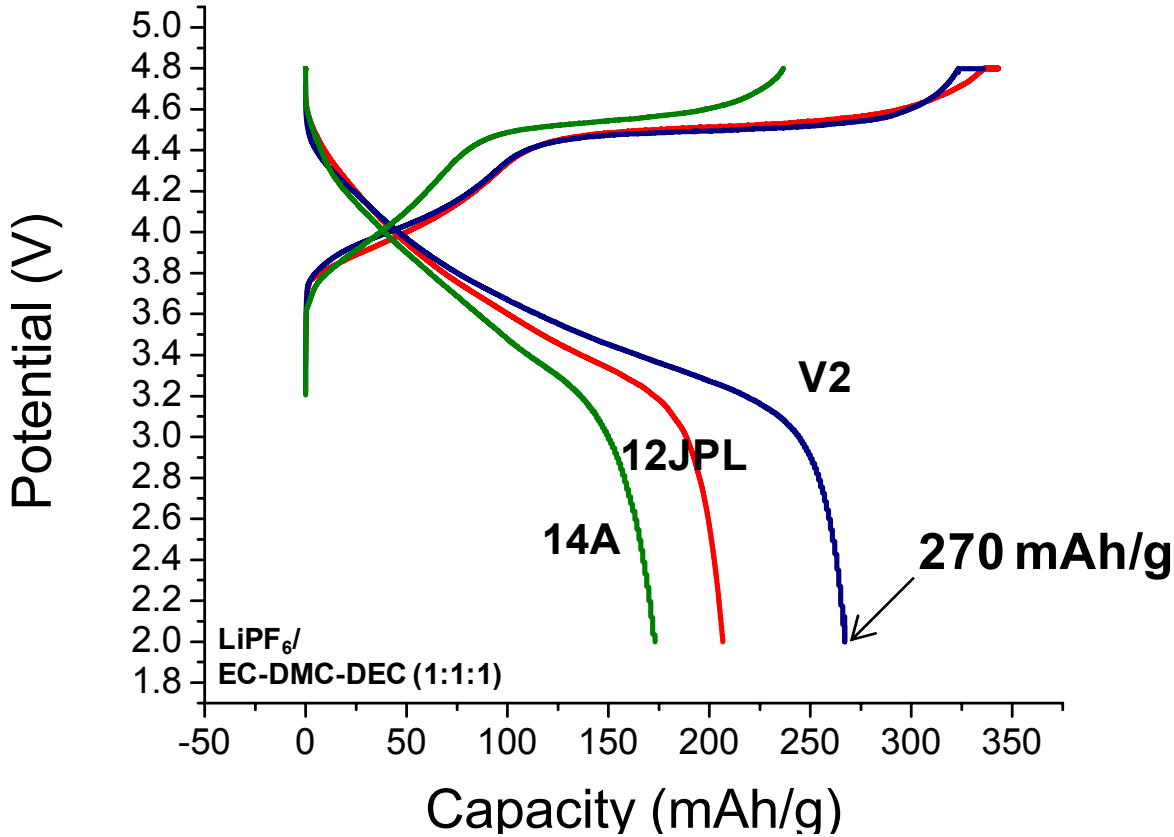


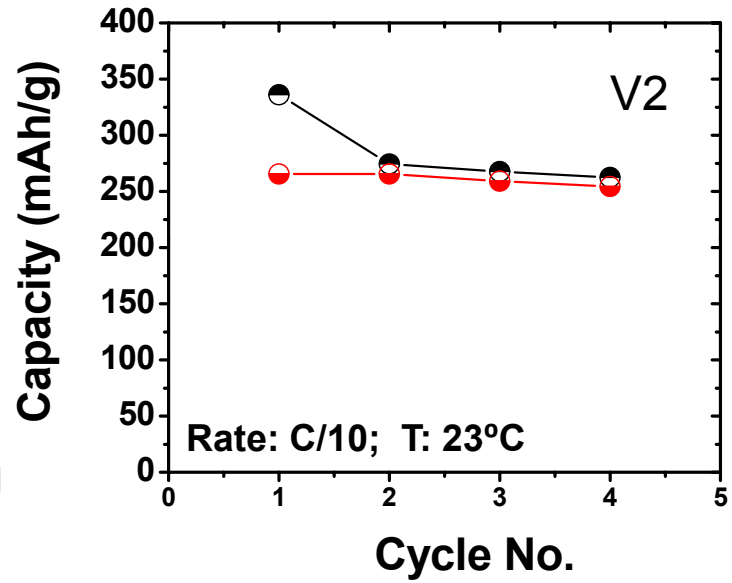
Far Infra Red Spectroscopy



- More vibration bands for 14A relative to V2 or 12JPL
- Loss of resolution in spectra: Partial loss of long-range order and have more random cation distribution

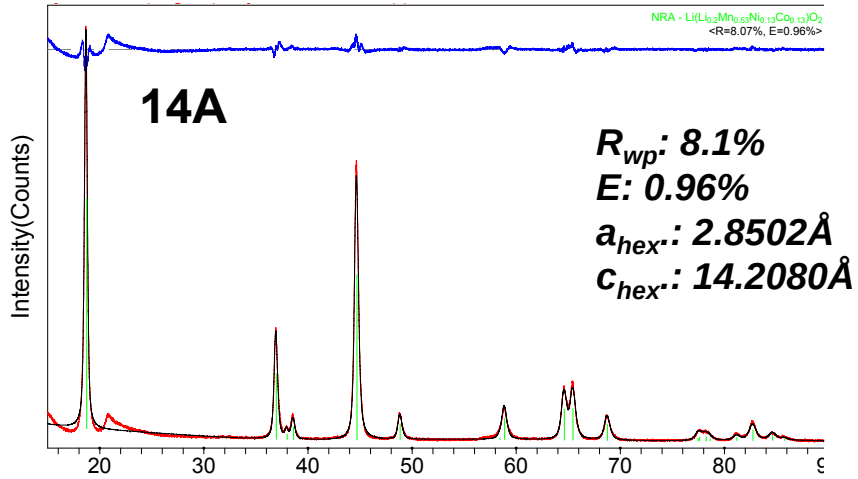
Electrochemical Performance



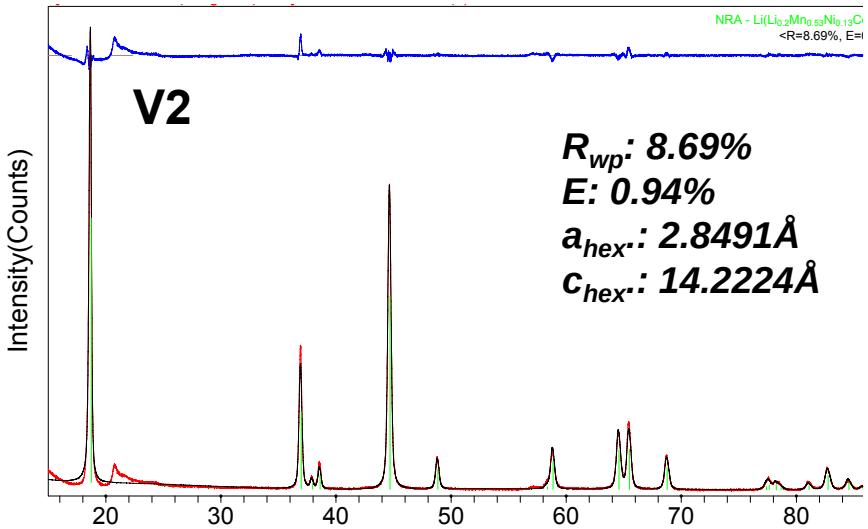


- Improvement in discharge capacity and efficiency in V2 batch
- Drastic decrease in irreversible capacity loss in V2 vs. 12JPL (17% vs. 35%)

Rietveld Analysis



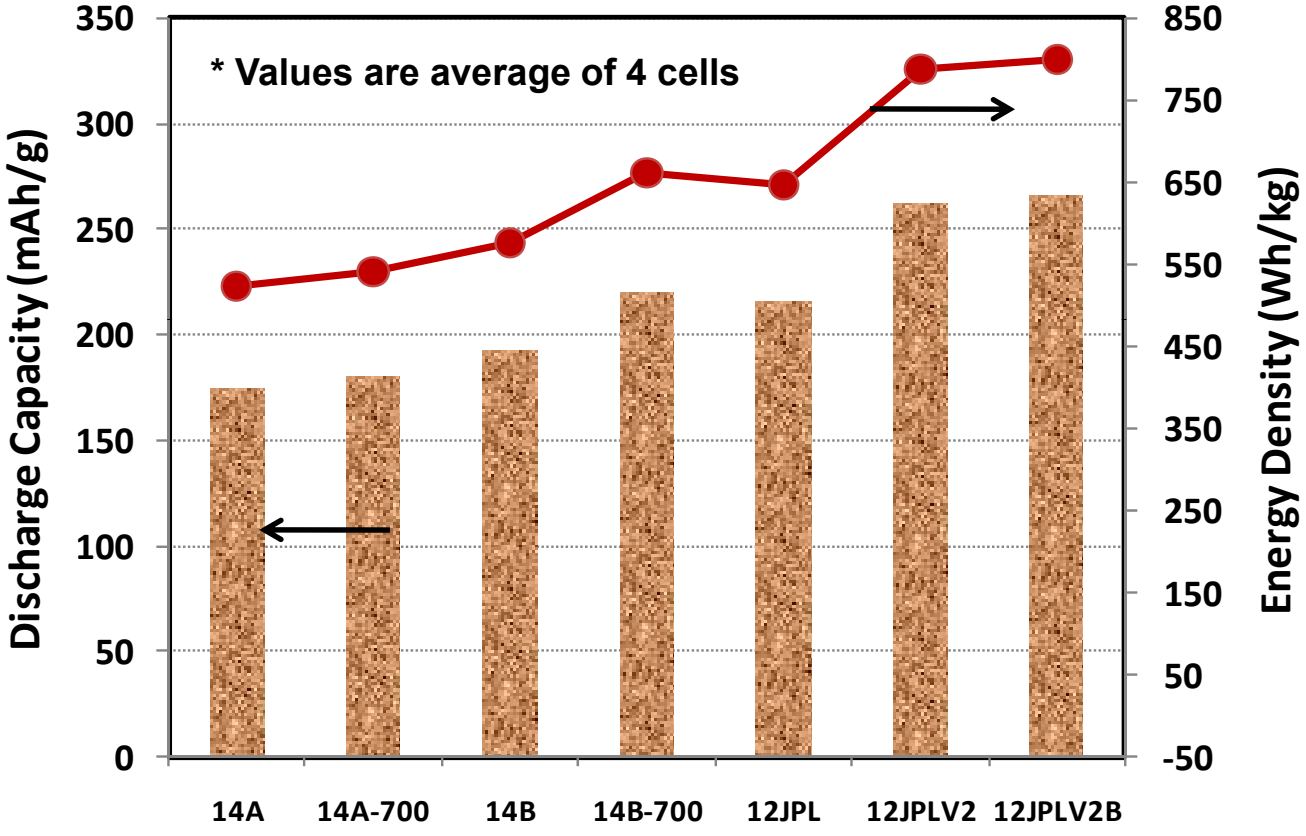
	Site	Occupancy	B	x	y	z
Li	3a	1.057	-0.595	0	0	0
Li	3b	0.2071	0.7639	0	0	1/2
Ni	3b	0.1333	-0.0170	0	0	1/2
Co	3b	0.1334	-0.2024	0	0	1/2
Mn	3b	0.5335	0.4407	0	0	1/2
O	6c	2	0.5	0	0	0.24



	Site	Occupancy	B	x	y	z
Li	3a	1.0025	0.1328	0	0	0
Li	3b	0.2014	-1.0387	0	0	1/2
Ni	3b	0.1331	0.208	0	0	1/2
Co	3b	0.13311	0.2035	0	0	1/2
Mn	3b	0.53312	0.43	0	0	1/2
O	6c	2	0.5	0	0	0.24

- **Negative thermal parameter in 3a site for 14A**
- **Mixing of metal ions in the 3a site of Li in 14A**
  (r_{Ni}^{2+}: 0.69Å, r_{Co}^{3+}: 0.71Å, and r_{Li}^{+}: 0.76Å)

Electrochemical Test



- 12JPL series (i.e. V2 and V2B) of samples demonstrated an average discharge capacity of 272 mAh/g with energy density of >800 Wh/kg

Summary

- Successfully synthesized and characterized two composite electrodes.

- Good transport properties of formed SEI layer reflected good electronic conductivity (*lower impedance*) and high Li-ion conductivity (*good rate capability*).

- Electrochemical activation of Li_2MnO_3 in both composite systems represents structural integration of this phase with the second layered/spinel component.

- NEI has capability for large scale synthesis, and can custom manufacture electrode materials for specialty needs.

NEI