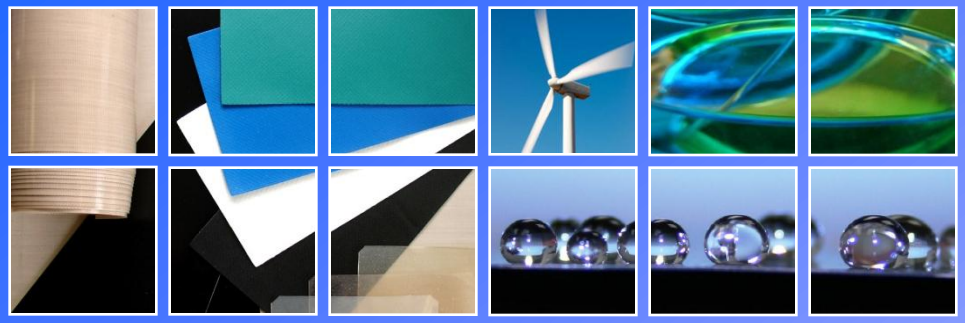

2010 NASA
Aerospace
Battery Workshop
November 16-18

Improvements in Energy Density and Stability of Advanced Cathode Materials for NASA's Applications

Presented by:

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Acknowledgments

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- Dr. Nathalie Pereira & Prof. Glenn Amatucci

Outline

- Choice of Cathode & HED Cathode
- Synthesis & Characterization
  - Structural & Electrochemical
- Particle Morphology & Energy Density
- Rate Capability & Stability
- Summary & Conclusion

Development of Cathode Materials

Objective:

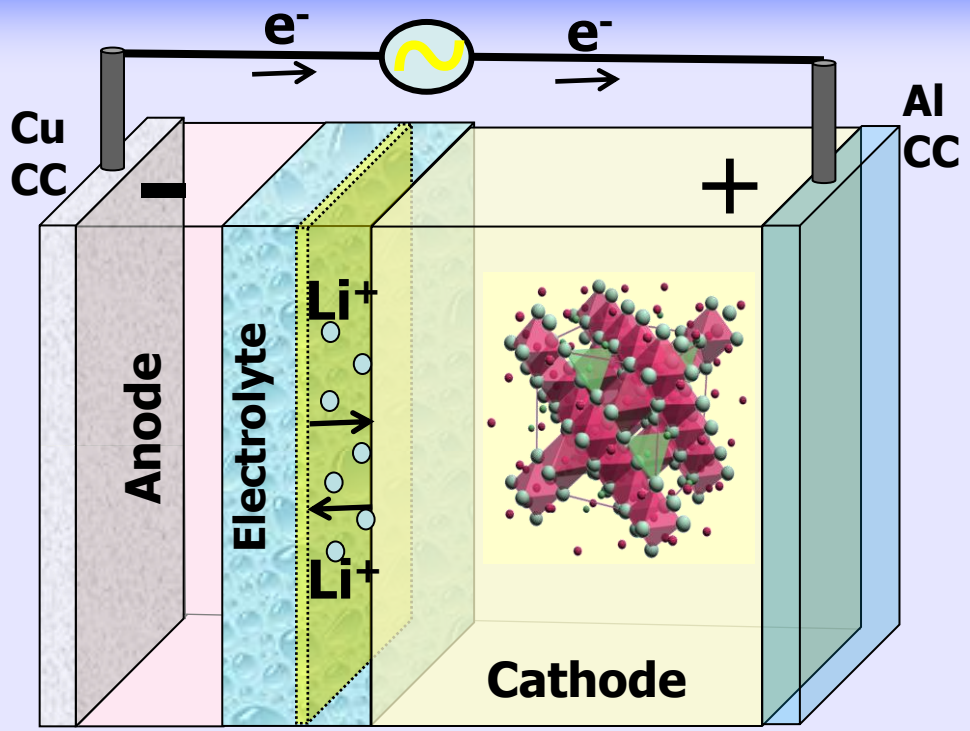
- Develop high energy density cathode material with reliable cycle life, rate & safety performance appropriate for NASA's explanatory applications.

Approaches:

- ❑ **Crystal structure → composite electrode**
  - Materials design & synthesis based on the composition of: $(1-x)Li_2MnO_3 - xLi(Ni,Co,Mn)_{0.33}O_2$ $(x = 0.5)$
  - Structural & electrochemical characterization
  - Determine optimum conditions to achieve max. energy density
- ❑ **Surface Modification**
- ❑ **Tailoring particle characteristics → bulk compaction**

Li-ion Battery

- **Cathode:**
  LFP, LMNO, NCA,
  HED-LMNC, LCO,…
- **Anode:**
  C, LTO, Alloys (Si, Sn,…)
- **Electrolyte:**
  Li-salt + Organic Carbonates & Esters
- **Separator:**
  Micro porous polymeric film/nonwoven fabrics



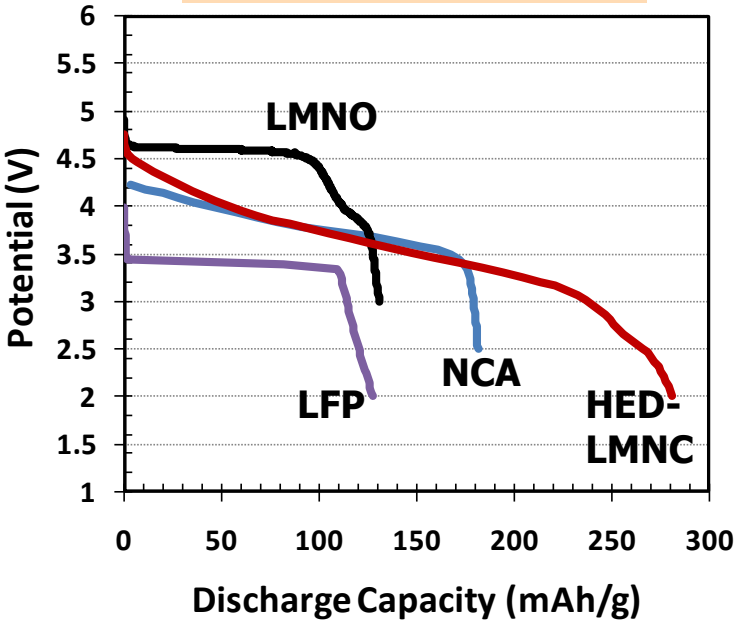
- **Structure & Chemistry** →Li-ion intercalation capacity
- **Chemical Bond → Structural stability** → Cycle life
- **Conductivity (ionic/electronic)**→Capacity & Rate

❑ **Particle characteristics will affect all aspects**

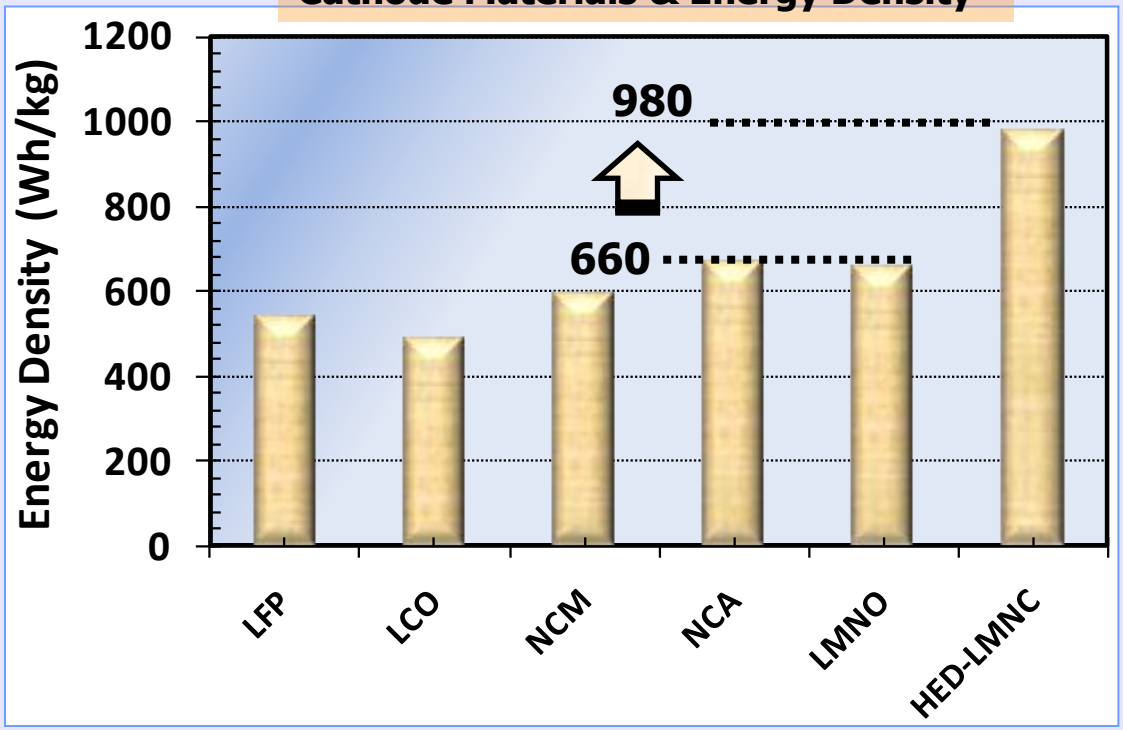
Energy Density & Choice of Cathode

- Major source of Energy Density is determined by Cathode
- Why HED-LMNC as a Cathode?

NEI Cathode Materials



Cathode Materials & Energy Density



NEI's Composite Cathode

	Delivery Date
Gen 0:	
NEI-D →	June 16, 2009
Gen 1:	
V2CA-I →	November 23, 2009
Gen 2 :	
V2CA-II →	August 23, 2010
Gen 3 :	
51R→	August 23, 2010

Composite Electrodes

Reported by:

- Dr. Thackeray et al., ANL (*Johnson et al., Electrochem. Comm. 6, 2004)*
- Prof. J. Dahn et al., Dalhousie U. *(Lu et al. J. Electrochem 149, 2002)*

Composite Electrode:

- **Electrode with dual functionality:**

  2D layer → high capacity & 2nd 2D layer → structural stability

- **Structural stability→ Prevent oxygen loss during charge**
- **Enhance cathode stability; Integrated structure**

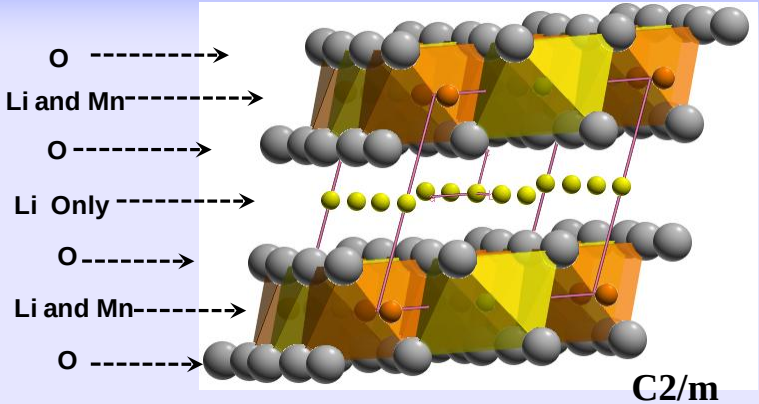
Material of Choice:

- **Inexpensive & safe cathode material: Mn-based electrode**
- **High O_2 retention relative to Ni/Co electrodes**
- **Stabilize the composite structure with Li_2MnO_3**

Composite Electrode

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

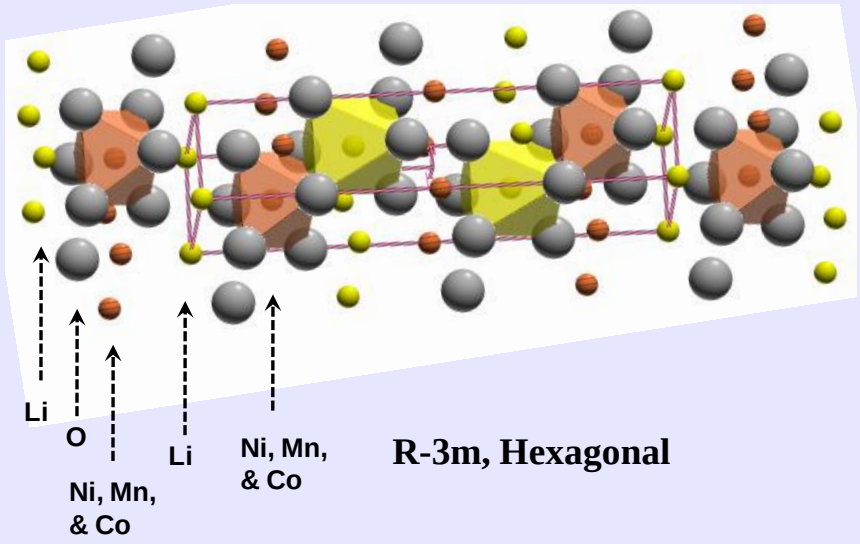
- Li-rich layered structure
- Layers of Li only, mixed layers of 2/3Mn and 1/3Li and pure oxygen layer
- Oxygen layers separating the Li layer and Mixed layer (Li & Mn)
- Superlattice ordering of Li and Mn



C2/m monoclinic

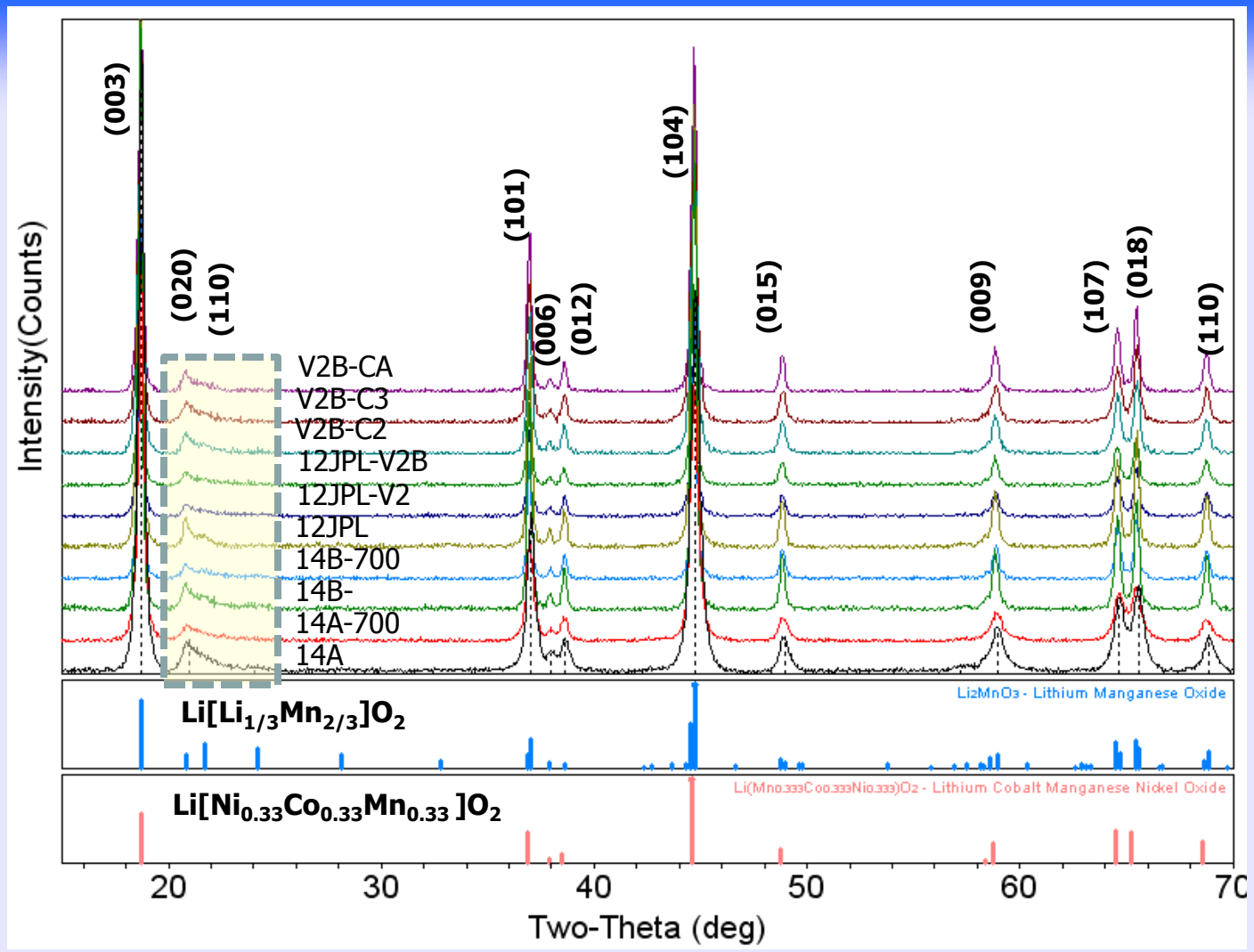
$Li[Mn_{0.33}Ni_{0.33}Co_{0.33}]O_2$ (Layered):

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



R-3m, Hexagonal

Layered-Layered Composite



1:1 layer to layer ratio

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

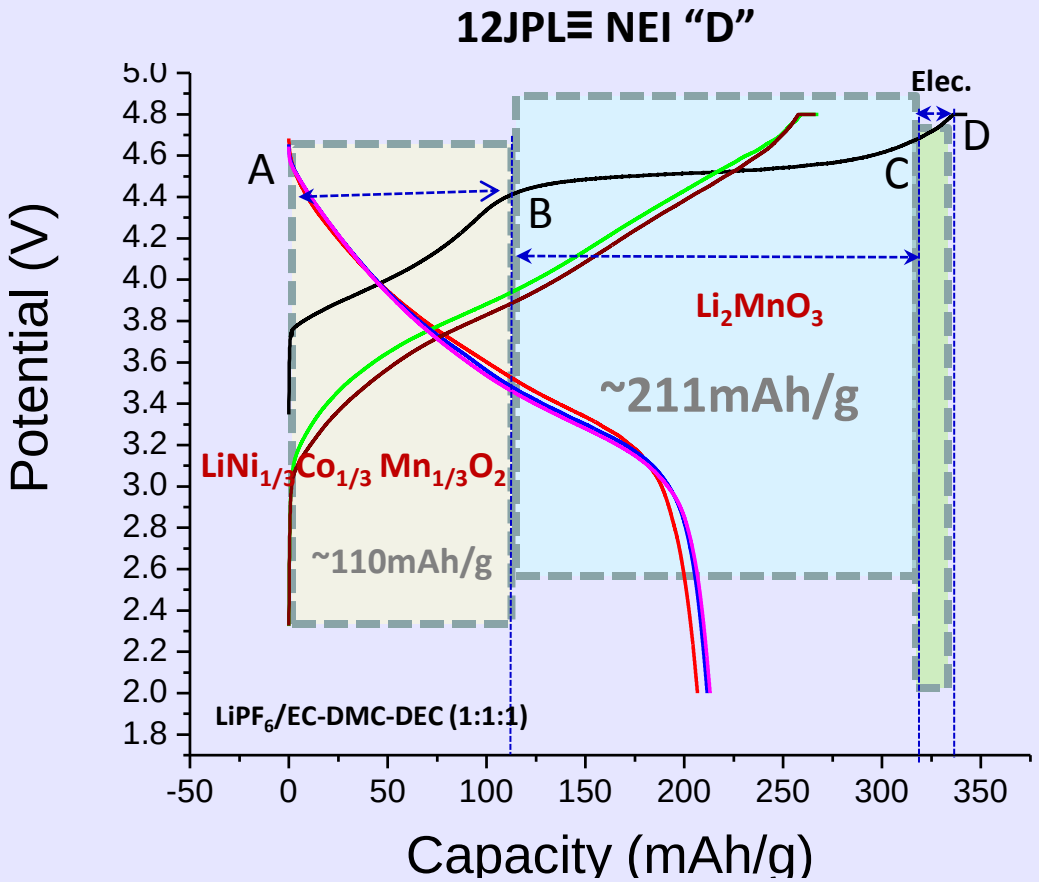
Capacity Contribution in Composite Electrode

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

1st Charge:

Three different processes:

- One reversible
- One partially reversible
- One irreversible

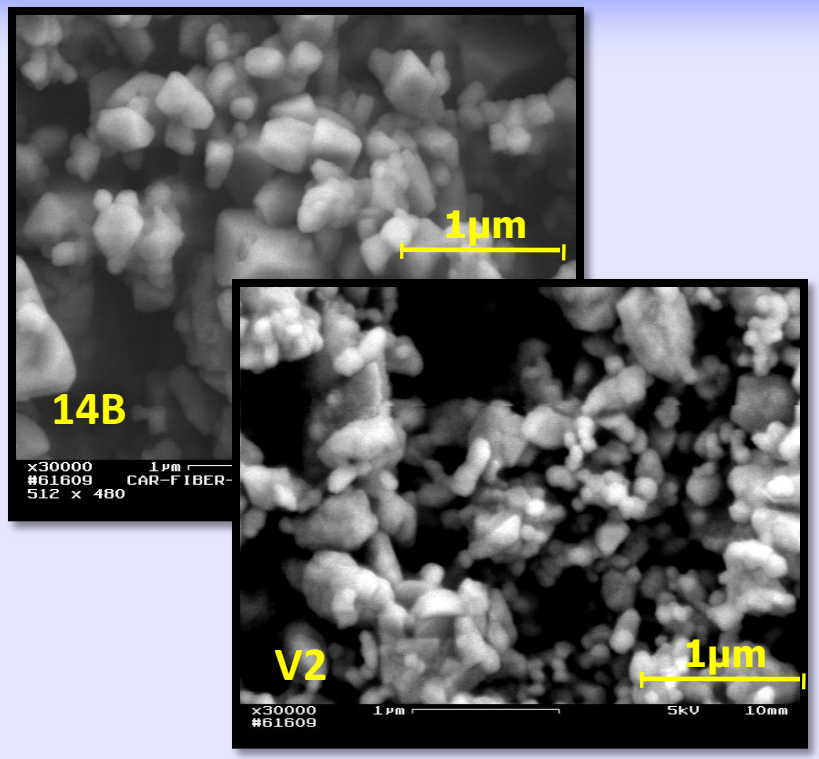


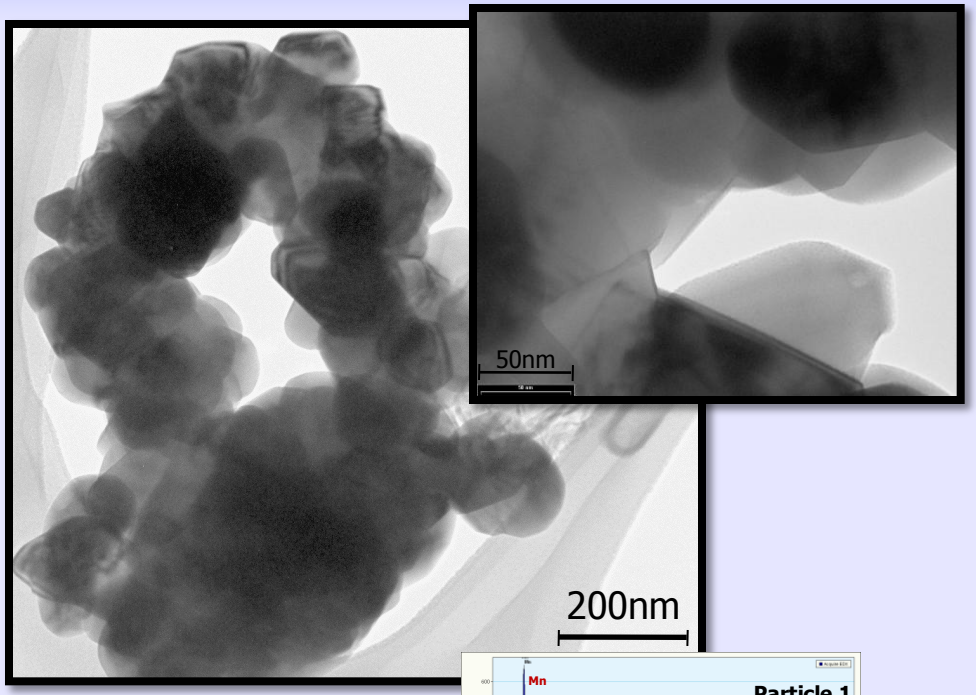
1st cycle: $Li_2Mn^{IV}O_3 \rightarrow Li_2O + MnO_2$ (C)

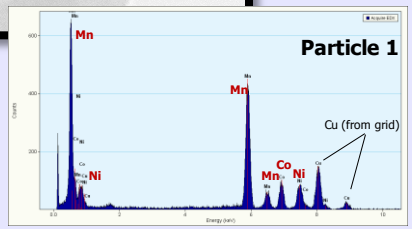
$Li^+ + MnO_2 \rightarrow Li_{1-x}Mn^{III}O_3$ (D)

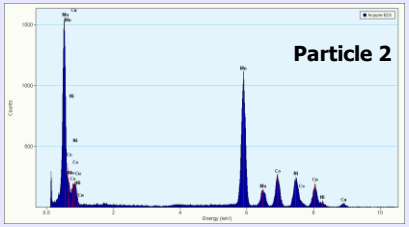
(Johnson et al., Elect. Comm., 9 2007)

Morphology & Metal Ion Distribution





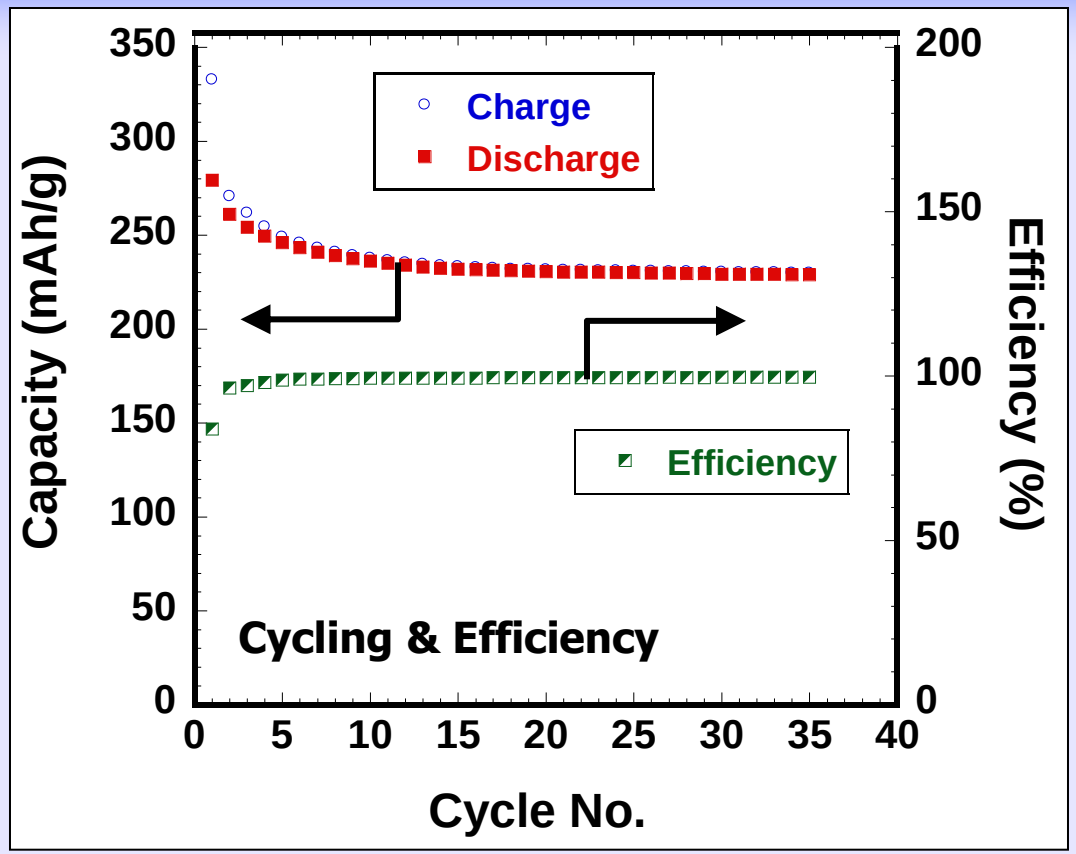




- Surface area: 4.00 – 5.2 m^2/g
- Particle sizes:
  - 50-100nm →220-280 mAh/g
  - 200-600nm → 198 mAh/g

NEI HED-LMNC

Cycling



Highlights:

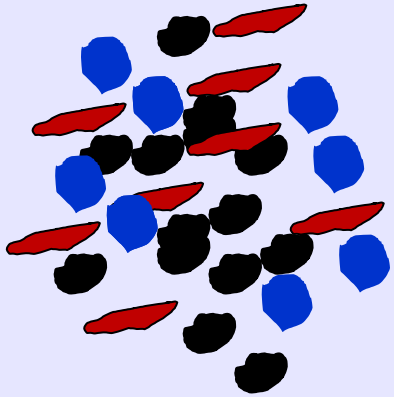
- High discharge capacity & relatively reliable cycle life
- Nearly 100% columbic efficiency

Tap Density and Particle Morphology

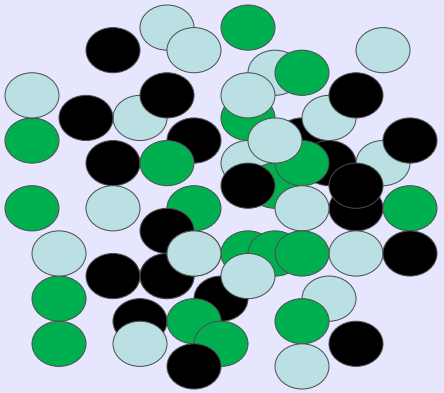
Important factors affecting Tap Density:

- Particle Morphology
- Particle size and size distribution

Particulate morphology:



- Irregular particle with anisotropic morphology
- Less packing and hence lower tap density

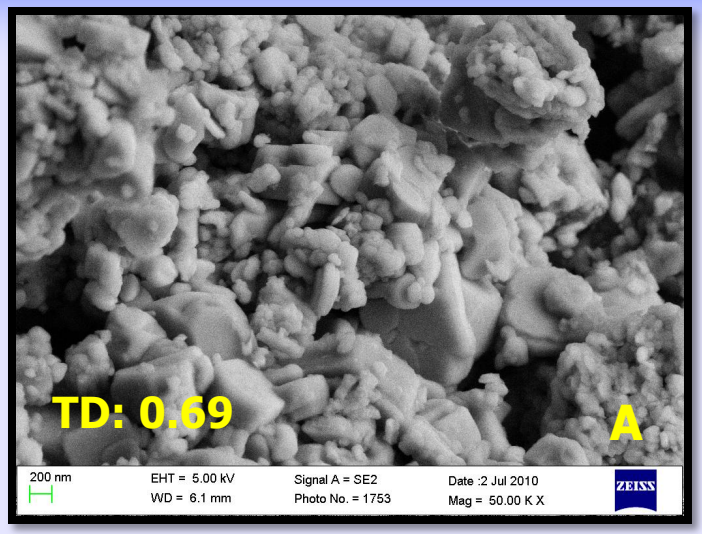


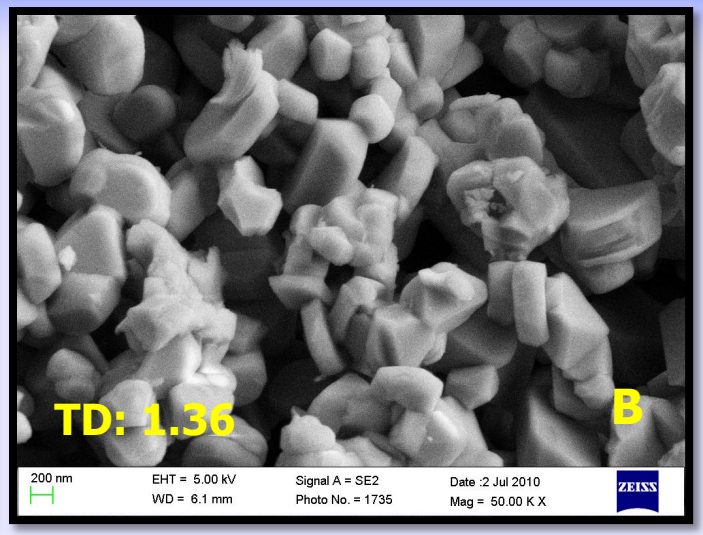
- Spherical particle morphology
- High packing density → high tap density

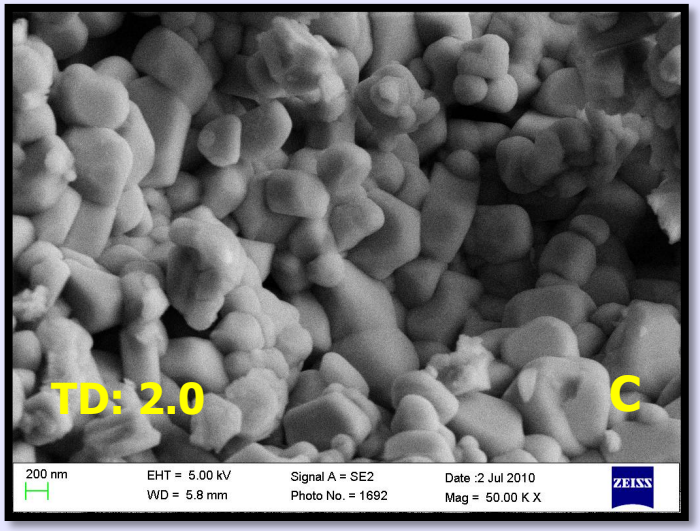
Microstructural modifications → Tap density increase

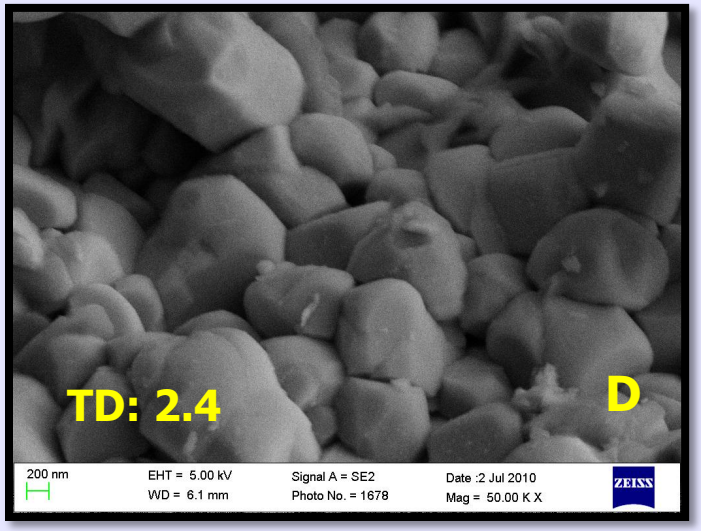
→ Increase in energy density

Change in Particle Morphology (SEM)

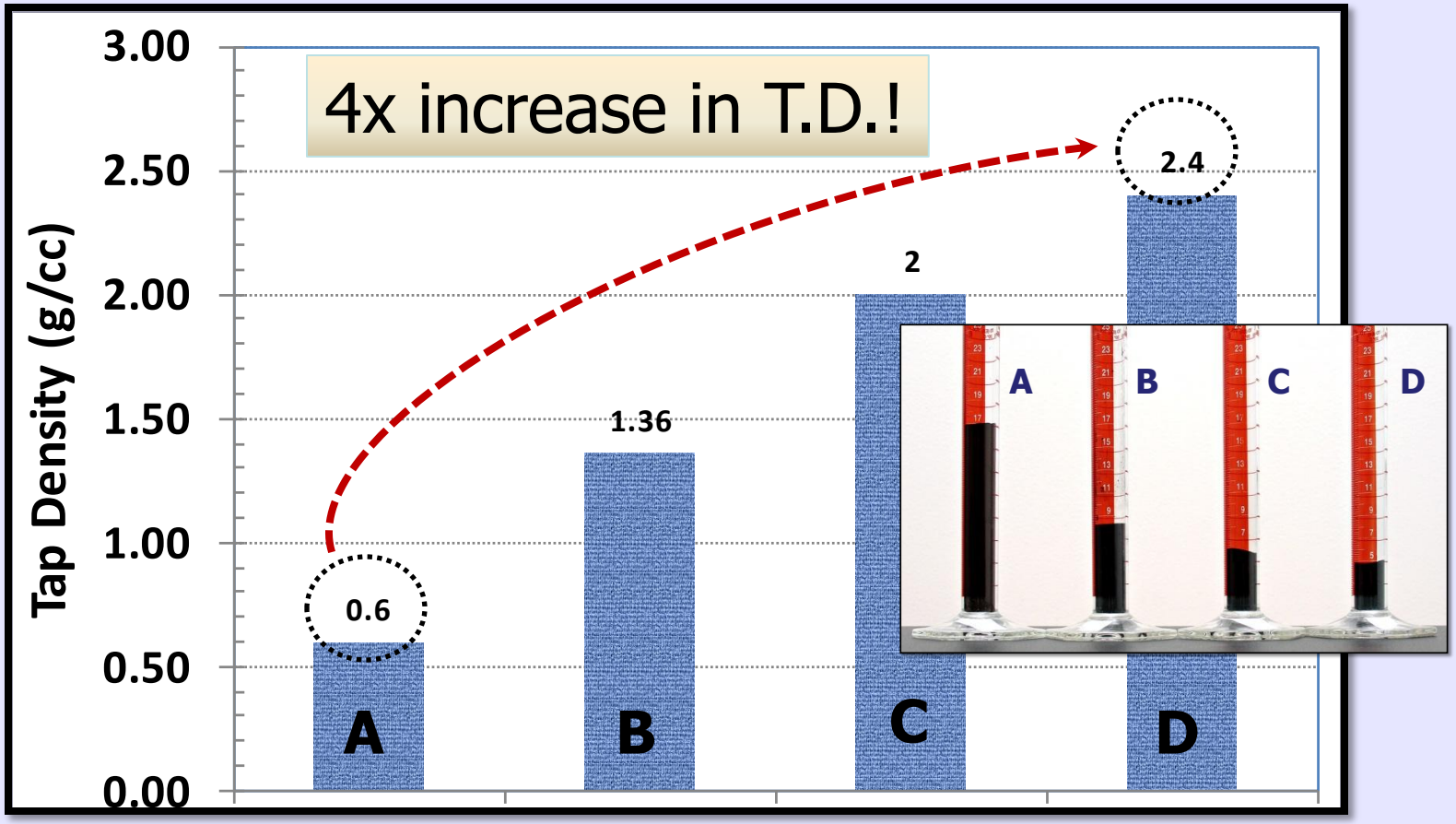








Trend of Improvement in Tap Density



- **Starting TD value: 0.6-0.7 g/cc**
- **Current TD: 2.0-2.4 g/cc**

Tap Density vs. Tape Loading

TD: 0.69 g/cc

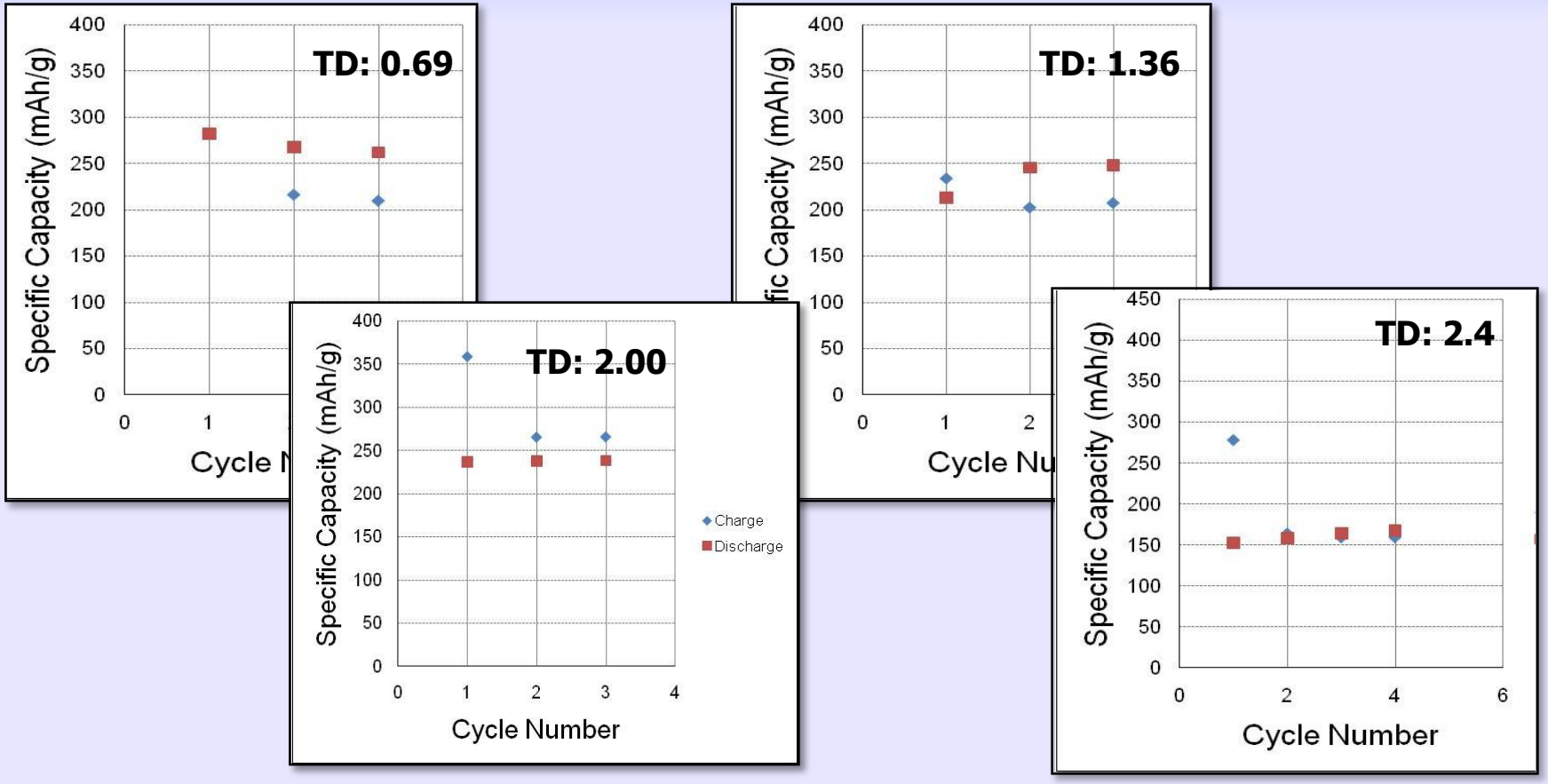
	thick. -micron	Std. Dev.	weight (Al foil+JPL)	weight-JPL	mg/cm^2	Vol.- cm3
1	44.3	±3	0.0266	0.0101	4.35	0.0103
2	44.6	±1.4	0.0268	0.0103	4.44	0.0103
3	45.7	±4.4	0.0277	0.0112	4.83	0.0106
4	40.8	±5.2	0.0259	0.0094	4.05	0.0094
5	37.1	±3.2	0.0249	0.0084	3.62	0.0086
Ave.	**42.5**		**0.02638**	**0.0099**	**4.26**	**Ave.**

TD: 2.4 g/cc

	thick. -micron	Std. Dev.	weight (Al foil+JPL)	weight-JPL	mg/cm^2	Vol.- cm3
1	97.4	±3.1	0.039	0.0225	9.71	0.0226
2	86.4	±5	0.0371	0.0206	8.89	0.0200
3	84.5	±3.2	0.0386	0.0221	9.54	0.0196
4	94.9	±5.0	0.0388	0.0223	9.62	0.0220
5	88.7	±6.9	0.0371	0.0206	8.89	0.0205
Ave.	**90.38**		**0.03812**	**0.0216**	**9.33**	**Ave.**

- **Direct effect of loading through tap density**

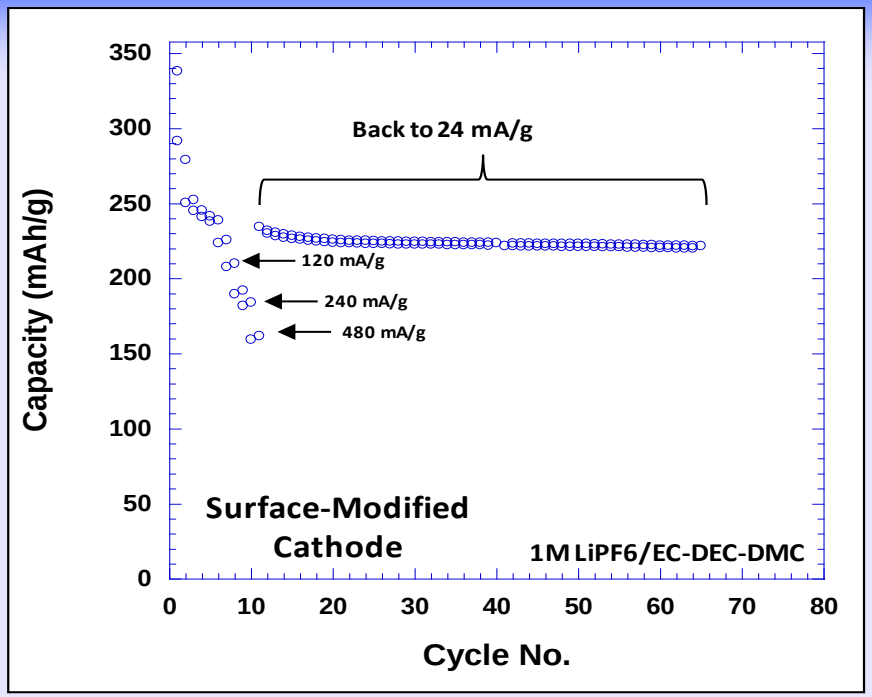
Electrochemical Performance

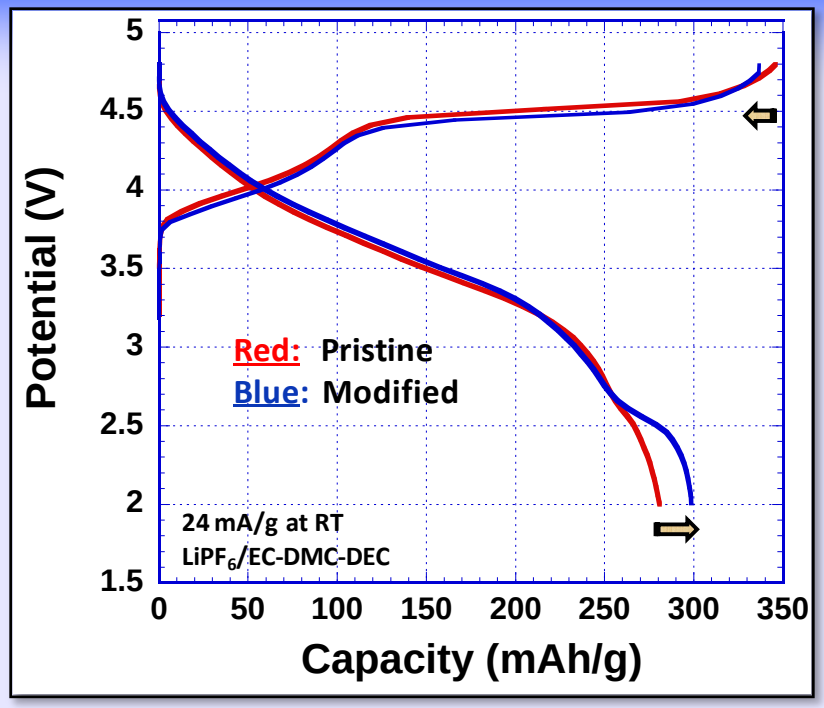


- **For TD: 1.36 and 2.00, capacity range 240-250mAh/g**

Electrochemical test performed by Dr. William West, JPL

NASA SBIR Phase I





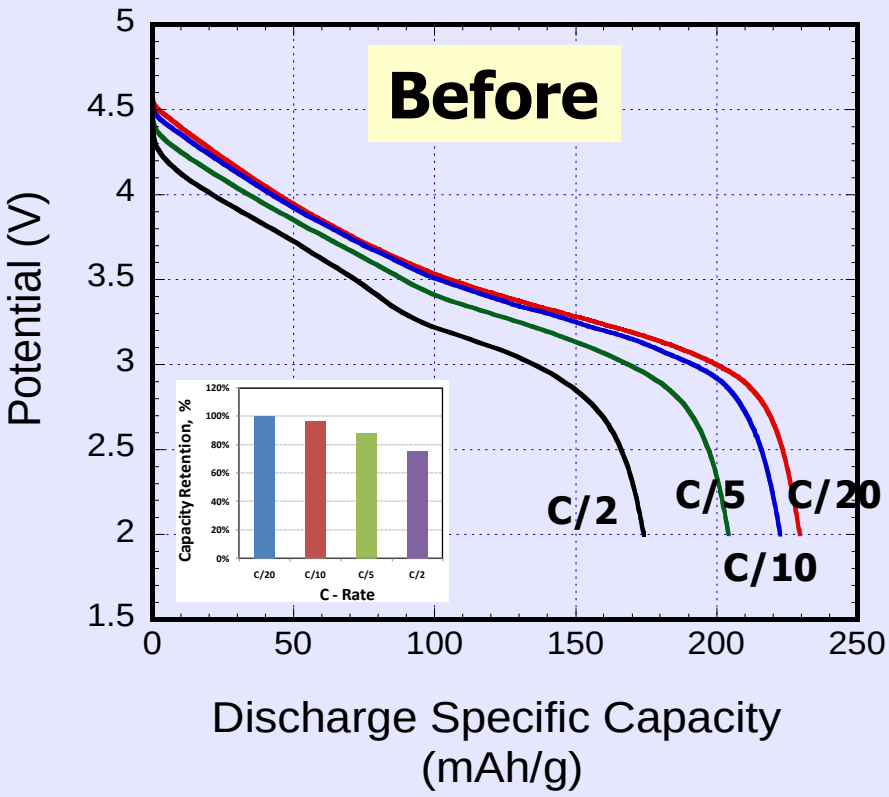
Further improvement in:

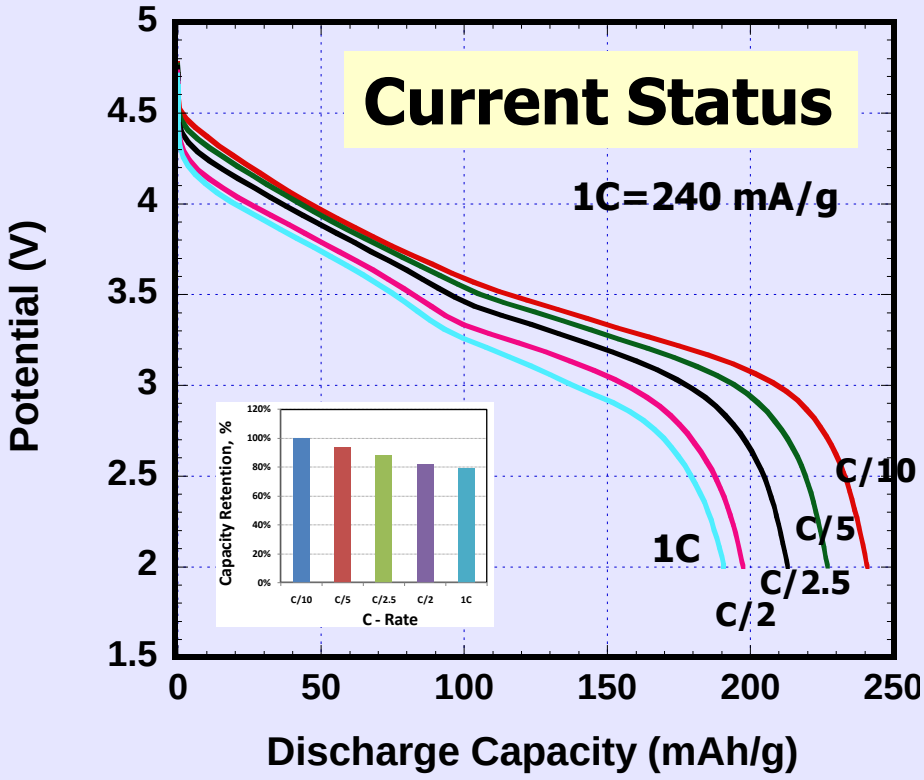
- Discharge capacity & Cycling stability
- Improve efficiency & decrease 1st cycle irreversible capacity loss (from 17% to 12%)

Electrochemical test performed at Rutgers University

Rate Capability

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

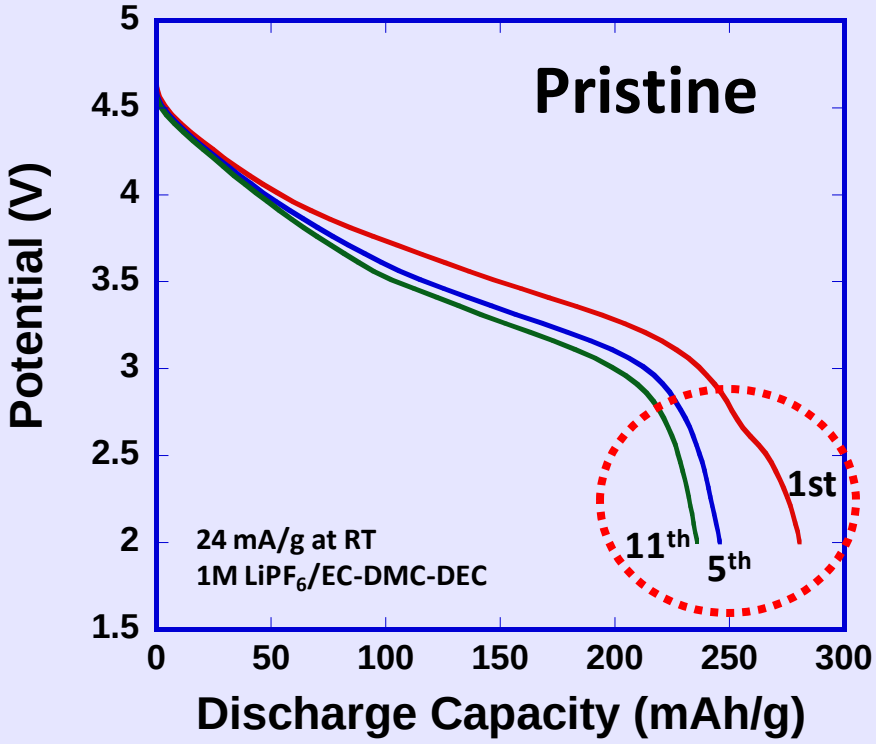


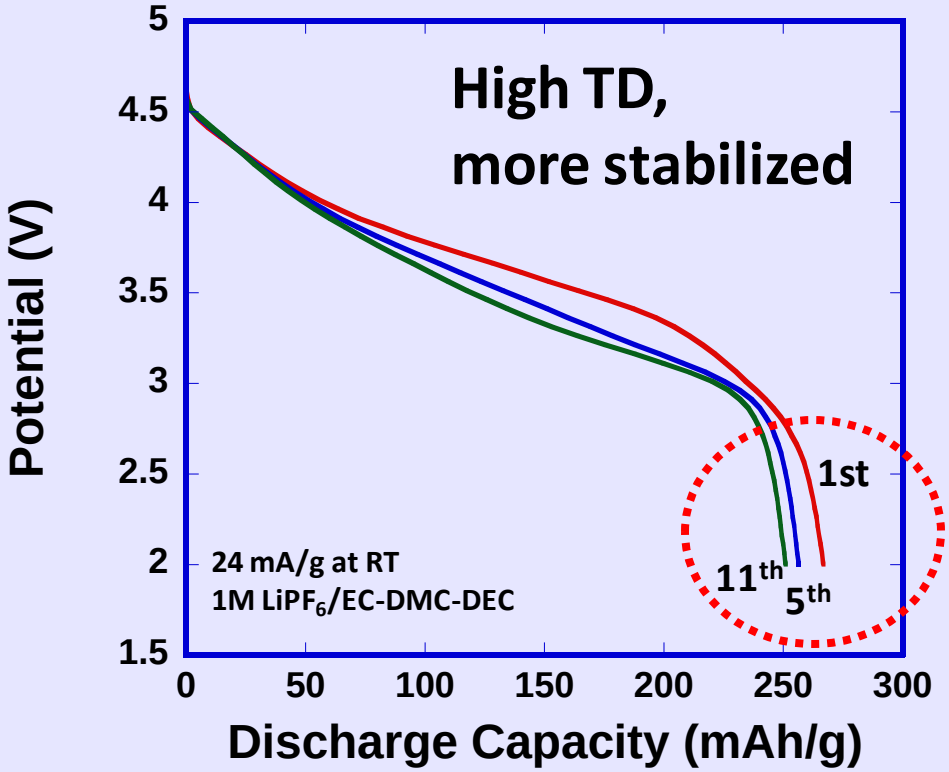


- **Approaching to 200 mAh/g capacity at 1C rate**

Cathode Stability

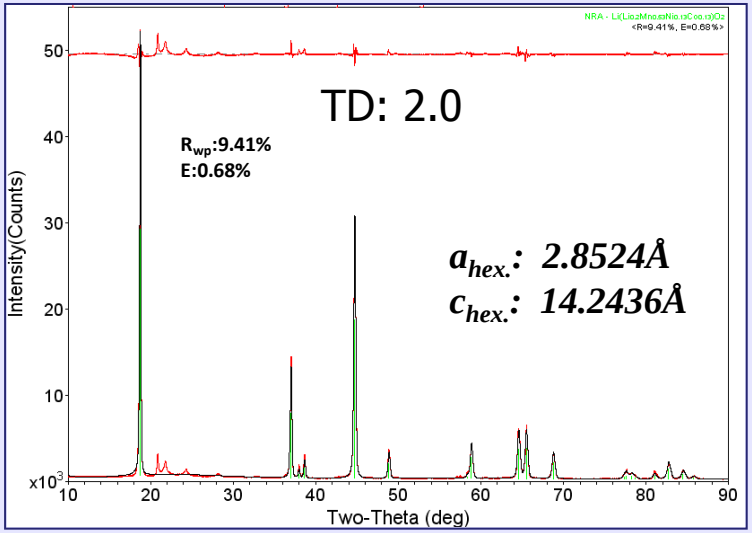
$0.5\ Li_2MnO_3\text{-}0.5Li(NiCoMn)_{1/3}O_2$

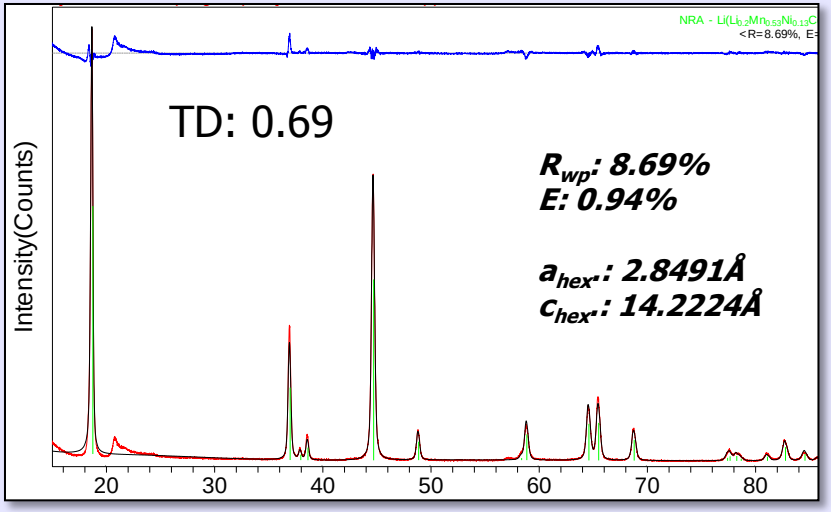




- **Improve in capacity retention (cathode's stability)**

Origin of Improved Stability
(Rietveld Analysis)



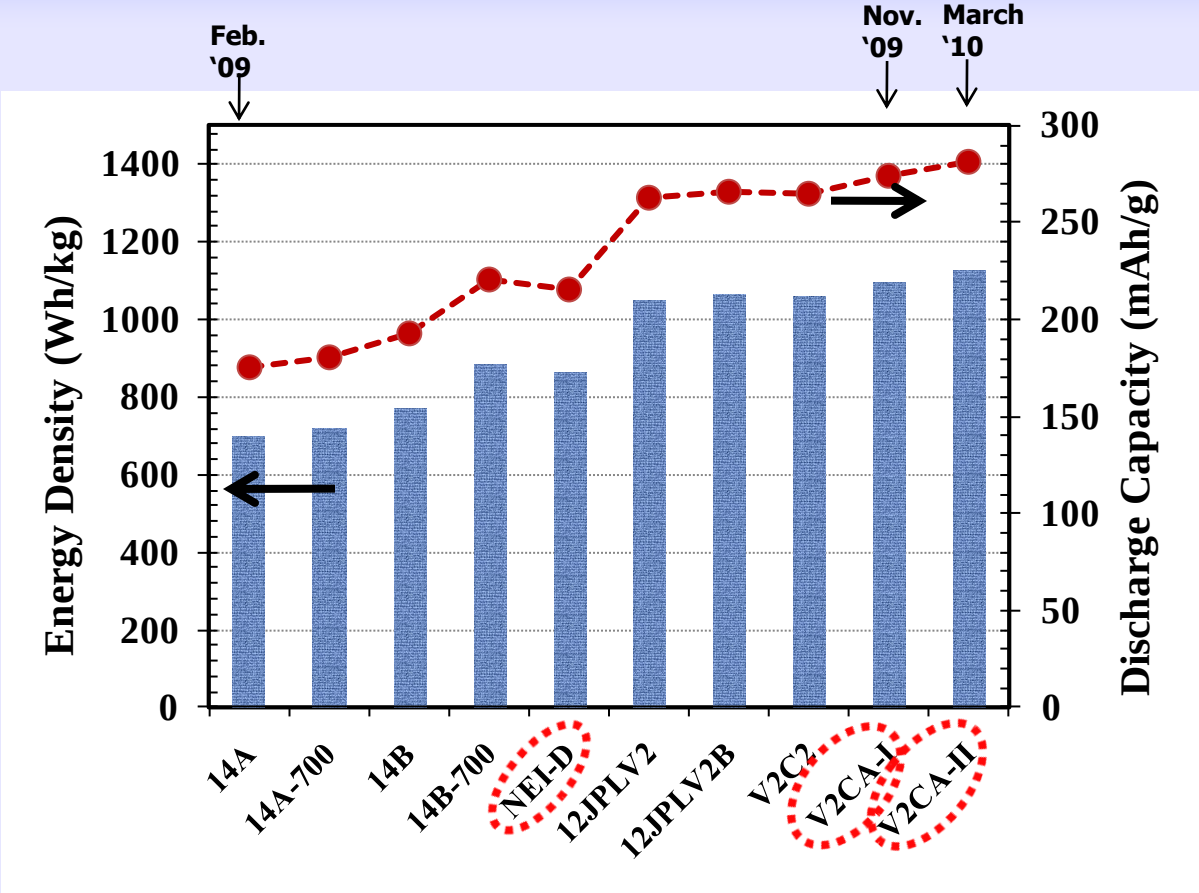


	Site	Occupancy	B	x	y	z
Li	3a	1.0004	0.67	0	0	0
Li	3b	0.2026	0.05	0	0	1/2
Ni	3b	0.1332	0.39	0	0	1/2
Co	3b	0.1332	0.4	0	0	1/2
Mn	3b	0.5332	0.48	0	0	1/2
O	6c	2	0.5	0	0	0.24

	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

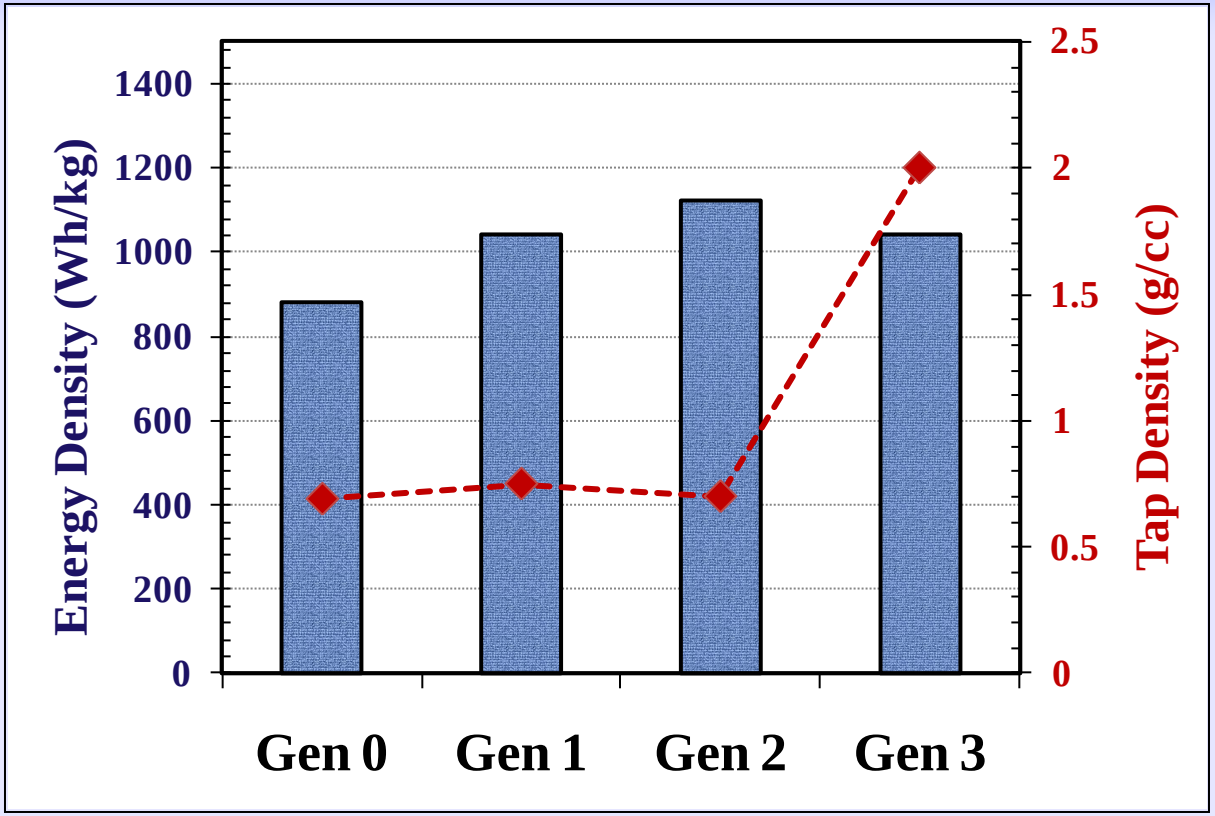
- **Occupancy values: very close to ideal model**
- **High compatibility of model & observed pattern**

Trend of Improvement in Energy Density



- **Continuation of improvement in discharge capacity & energy density**

Energy Density vs. Tap Density



Gen 3: Combination of high tap density & high energy density

Summary & Conclusions

- **Continuation of improvement in energy density**
- **Increase the initial TD (0.6g/cc) to commercial level of 2.0 – 2.4 g/cc**
- **Minimal impact on capacity due to higher tap density (up to 2.0 g/cc) while improving the cathode stability**
- **Higher stability: Crystal structure & SA**

What NEI Can Do!

- **Produce oxide-based cathode materials: tens of kilograms in our Somerset facility - expandable to tonnage level**

- **Produce material through a reproducible process**

- **In-house quality control capability**

(Please visit: http://www.neicorporation.com/Nanotech_Analytics_Brochure.pdf)