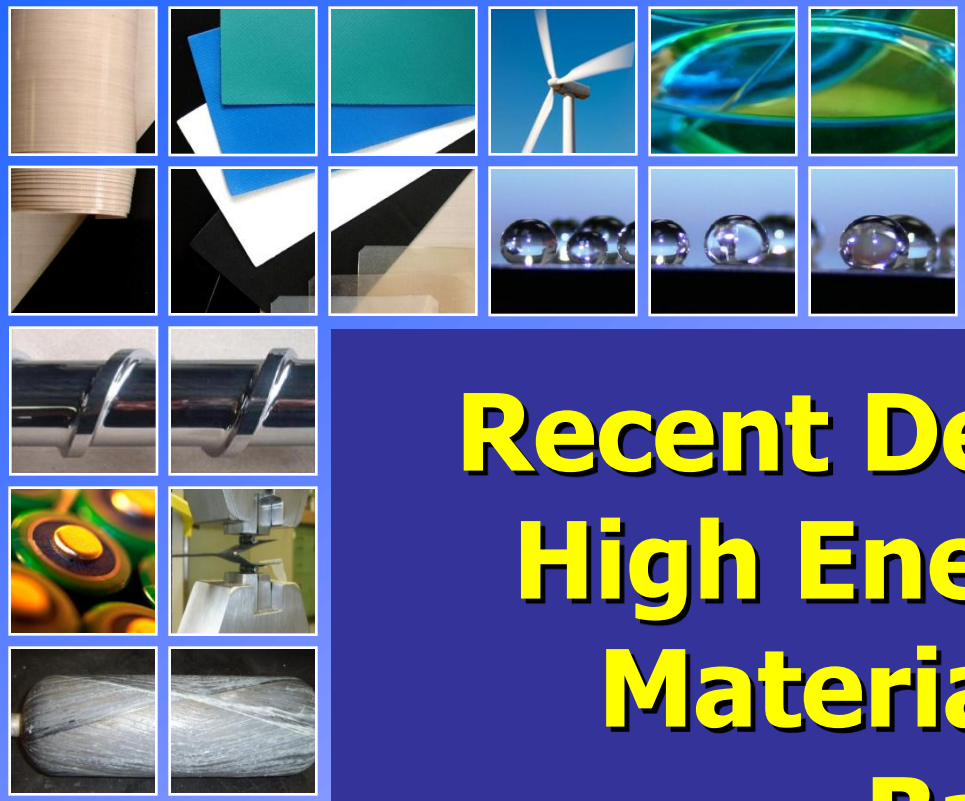
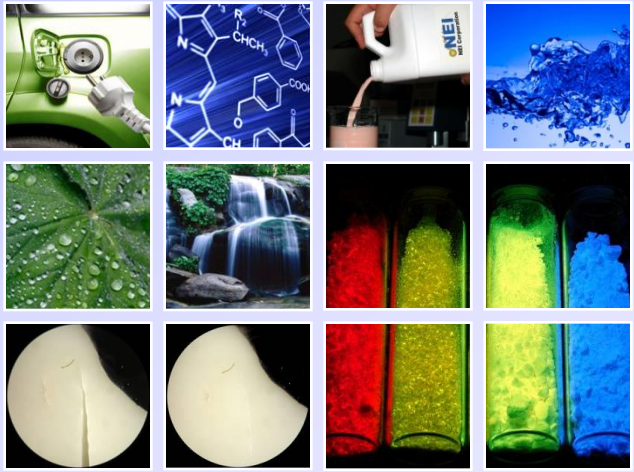


2011 NASA Aerospace Battery Workshop
Huntsville, AL
November 15-17

# Recent Developments in High Energy Electrode Materials for Li-ion Batteries

November 15, 2011

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# NASA STTR & SBIR Composite Cathode

## *(High Energy Density Cathode)*

# Development of Cathode Materials

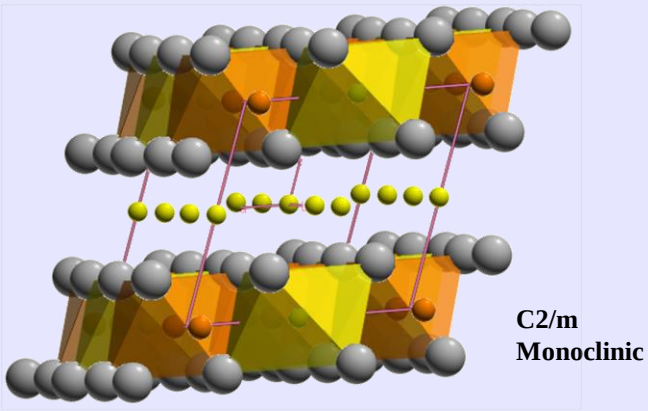
## Objective:

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

## Approaches:

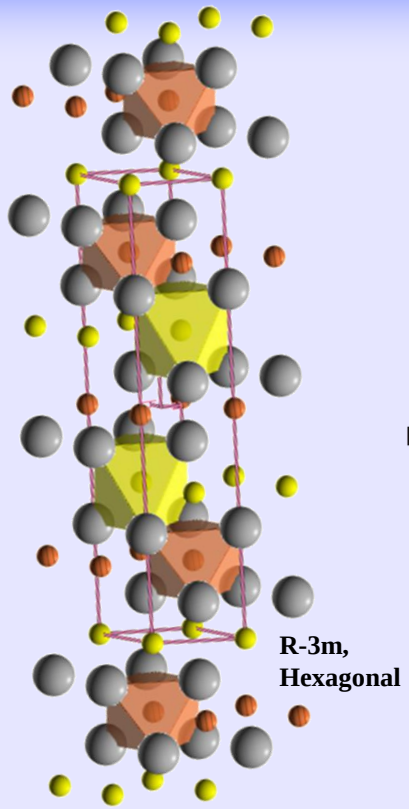
- ❑ **Crystal structure → composite electrode**
  - Binary, ternary or multi-component composite
  - Structural & electrochemical characterization
  - Determine optimum conditions to achieve max. energy & power densities
- ❑ **Tailoring particle characteristics → bulk compaction**
- ❑ **Structural and Surface Modifications**

# Composite Electrode



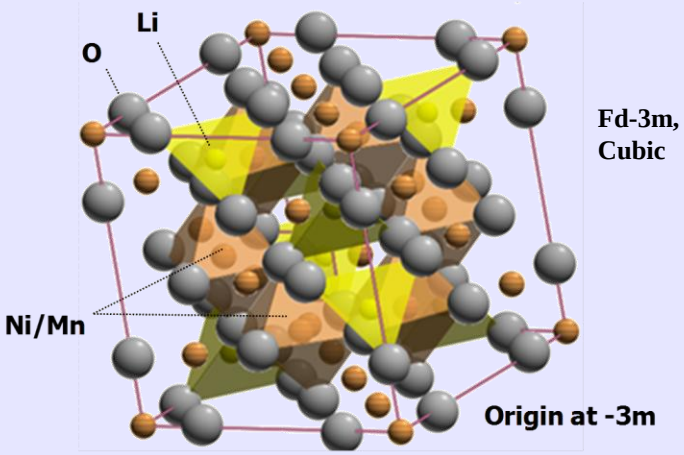

**$Li[Li_{1/3}Mn_{2/3}]O_2$ (Layered):**

- Li-rich layered structure
- Layers of Li only and mixed layers of 2/3Mn and 1/3Li
- 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




**$(Li)_{Tet.}[M{:}Ni, Mn]_{Oct.}O_4$**

**$Li[M{:}Ni, Mn]_2O_4$ (Spinel):**

- Li in tetra. & metal ions in Octa.
- 3D path for Li
- Possibility of integration w/ layered structures

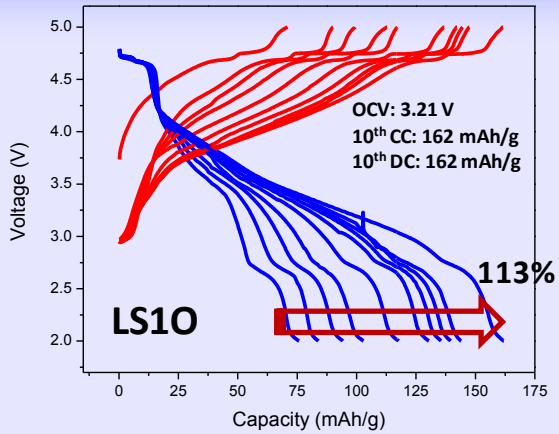
# Composite Cathode

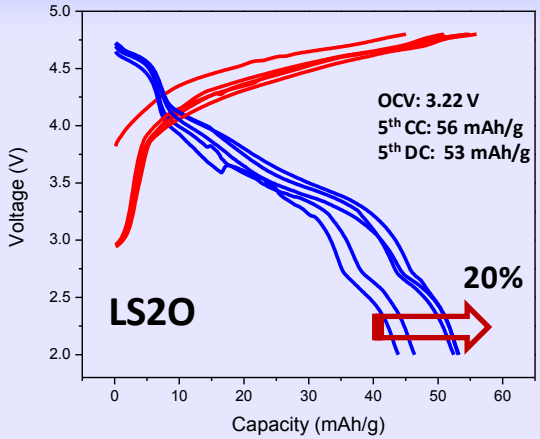
- **Spinel-Layered Composites (STTR)**
  - Layered-rich composite
  - Spinel-rich composite

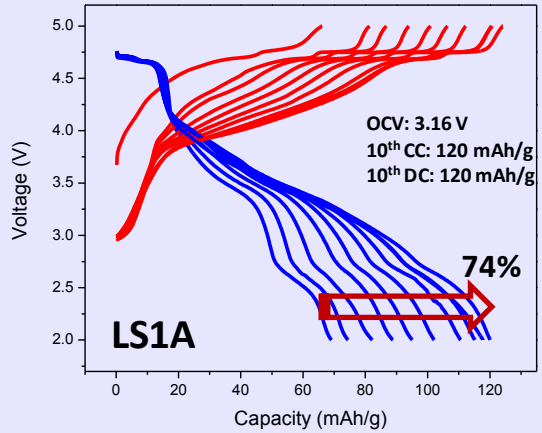
- **Layered-Layered Composites (SBIR)**
  - Effect of % $Li_2MnO_3$
  - Effect of dopants
  - Full cell energy & power performance

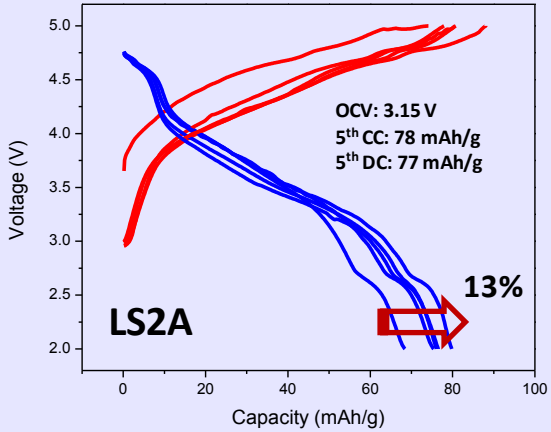
# Layered-rich Composite

## Layered-Spinel Composites



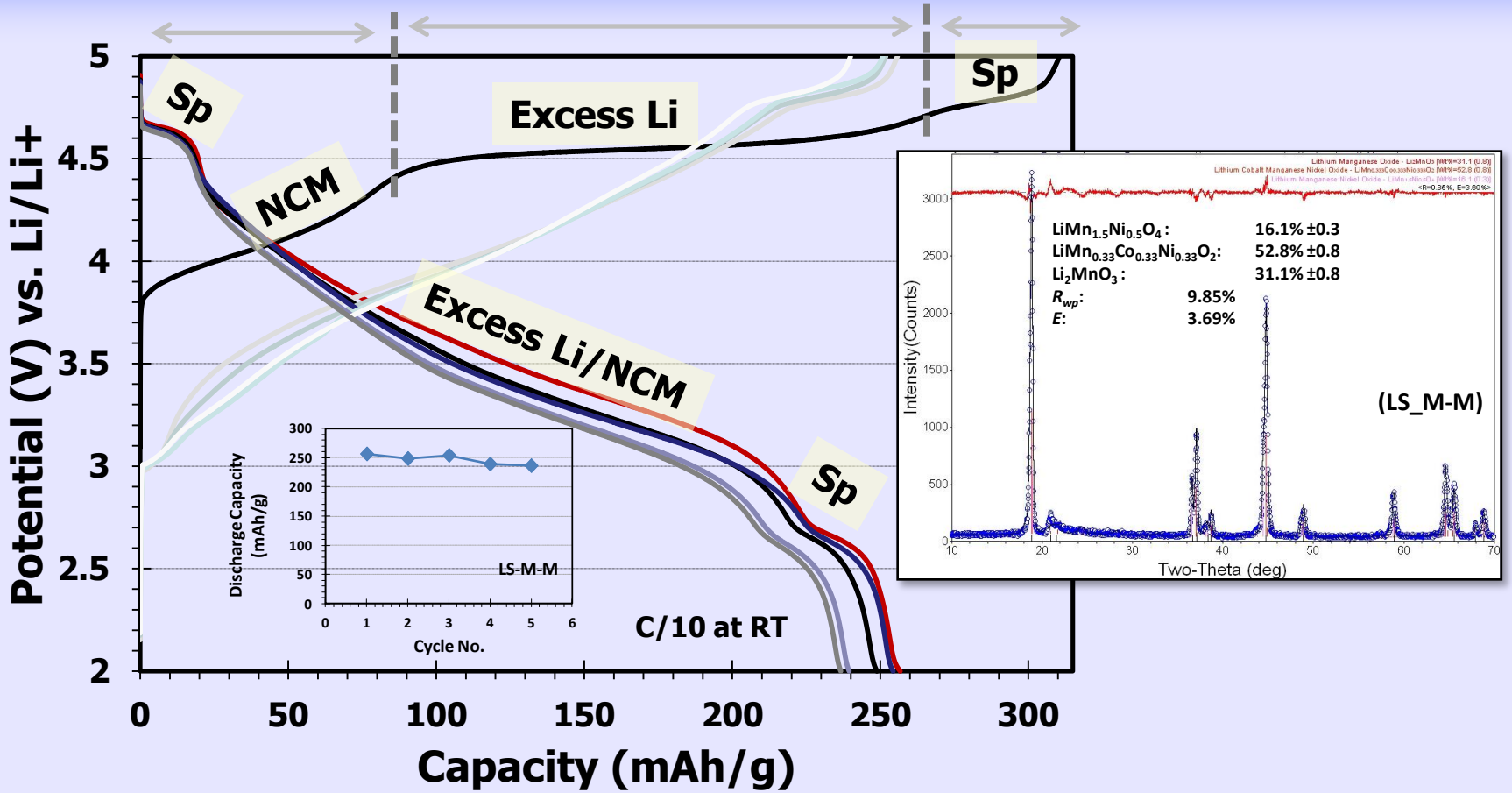




- **Electrochemical activation of excess Li component**
- **Signature of both layered & spinel phases**

# Layered-rich Composite

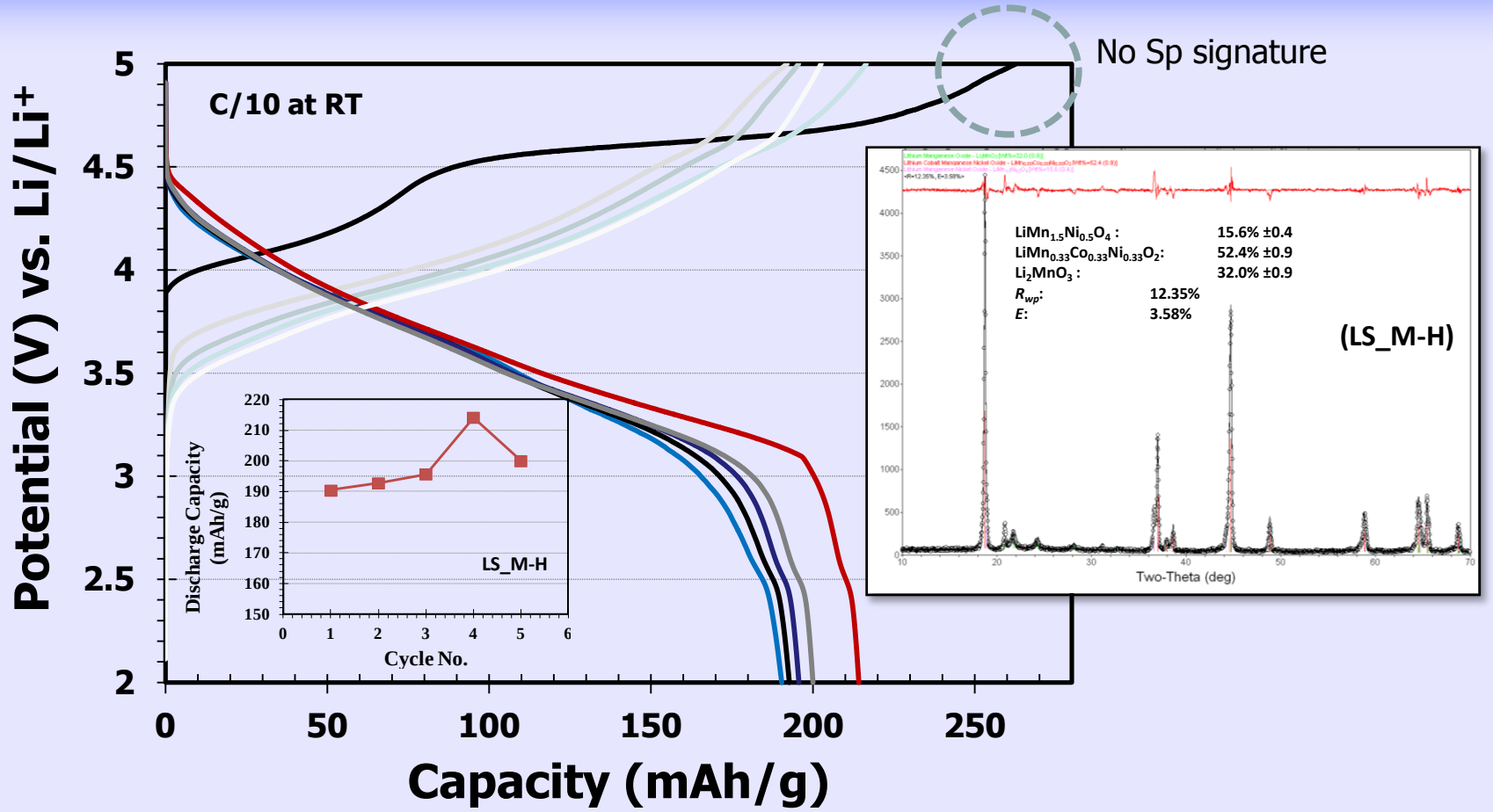
## Layered-Spinel (LS_M-M)




- Initial discharge capacity of 256.6 mAh/g
- 1st cycle I.L.: 17.2%

# Layered-rich Composite

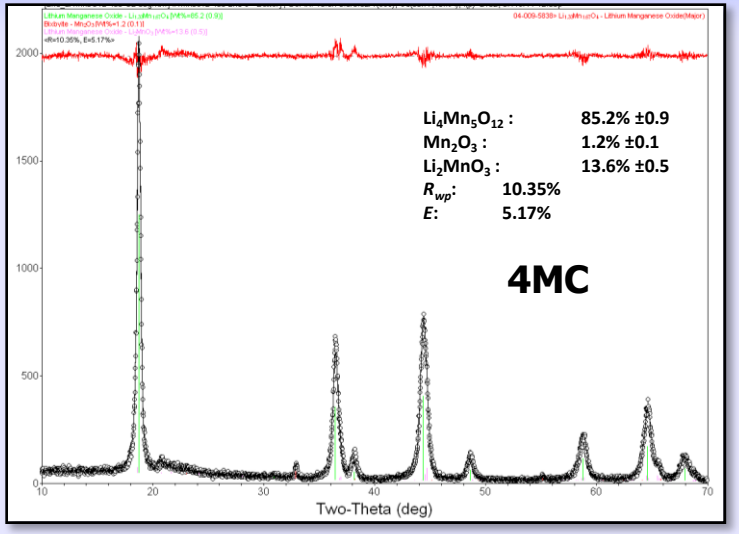
## Layered-Spinel (LS_M-H)

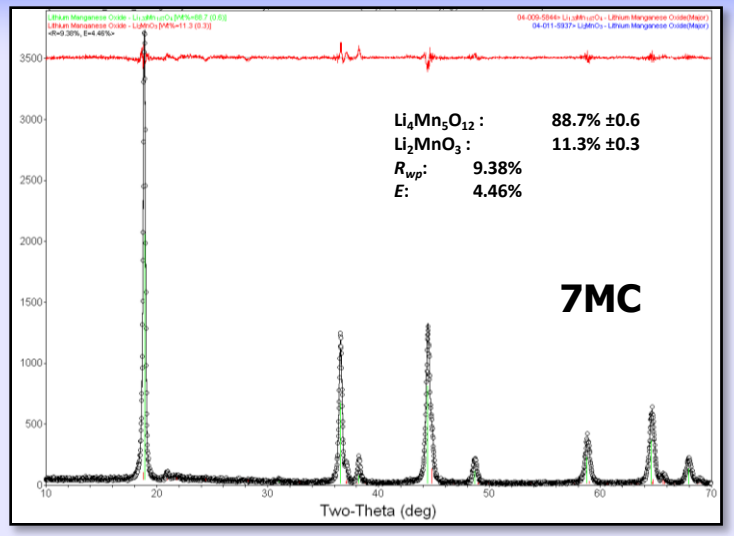


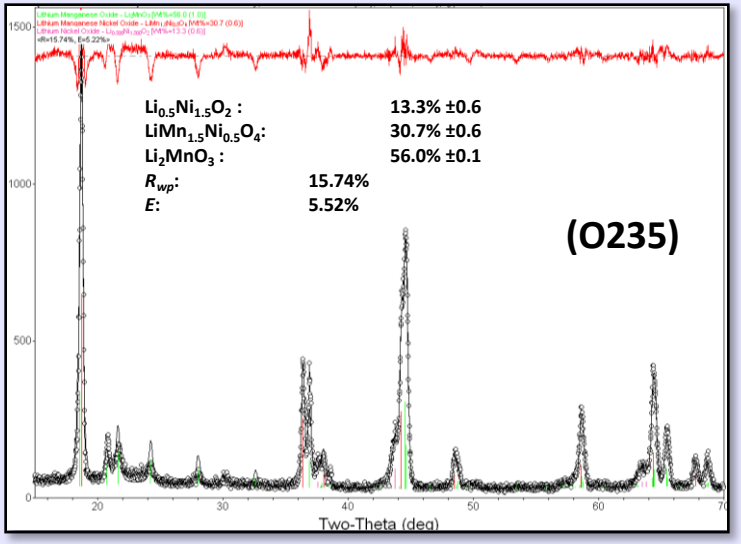

- **Spinel phase activates upon cycling**
- **Growth of discharge capacity**

# Layered-Spinel Composite

## Spinel-rich vs. Layered-rich



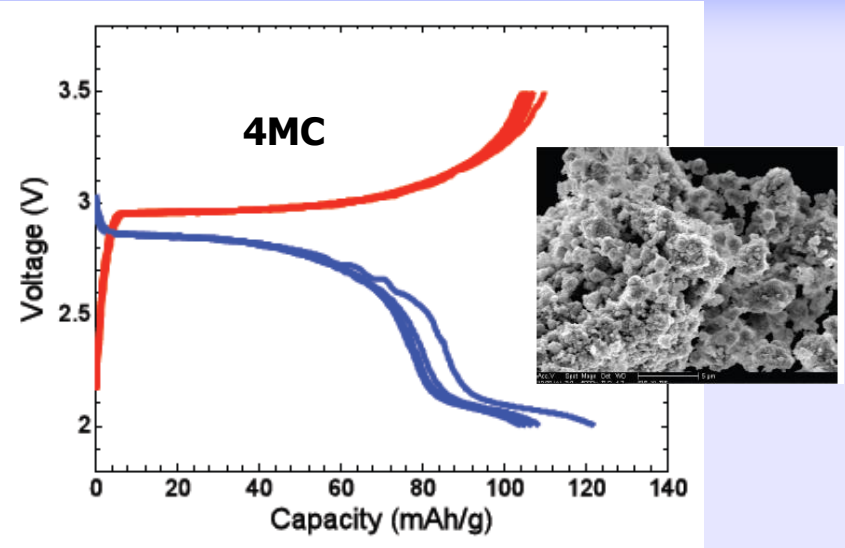



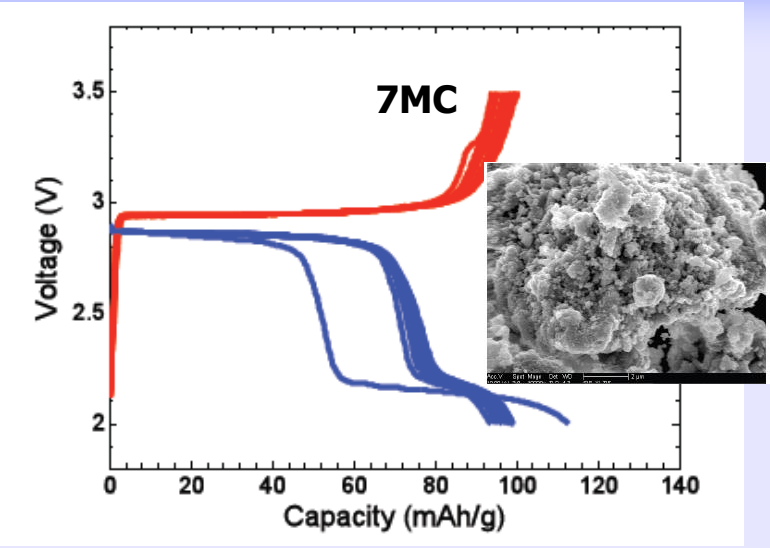




- 4MC & 7MC: Spinel rich
- O235: layered rich composite
- Co-existance of layered & spinel phases
- Diminishing the supperlattice ordering in spinel-rich composites

# Layered-Spinel Composite

## Spinel-rich composite

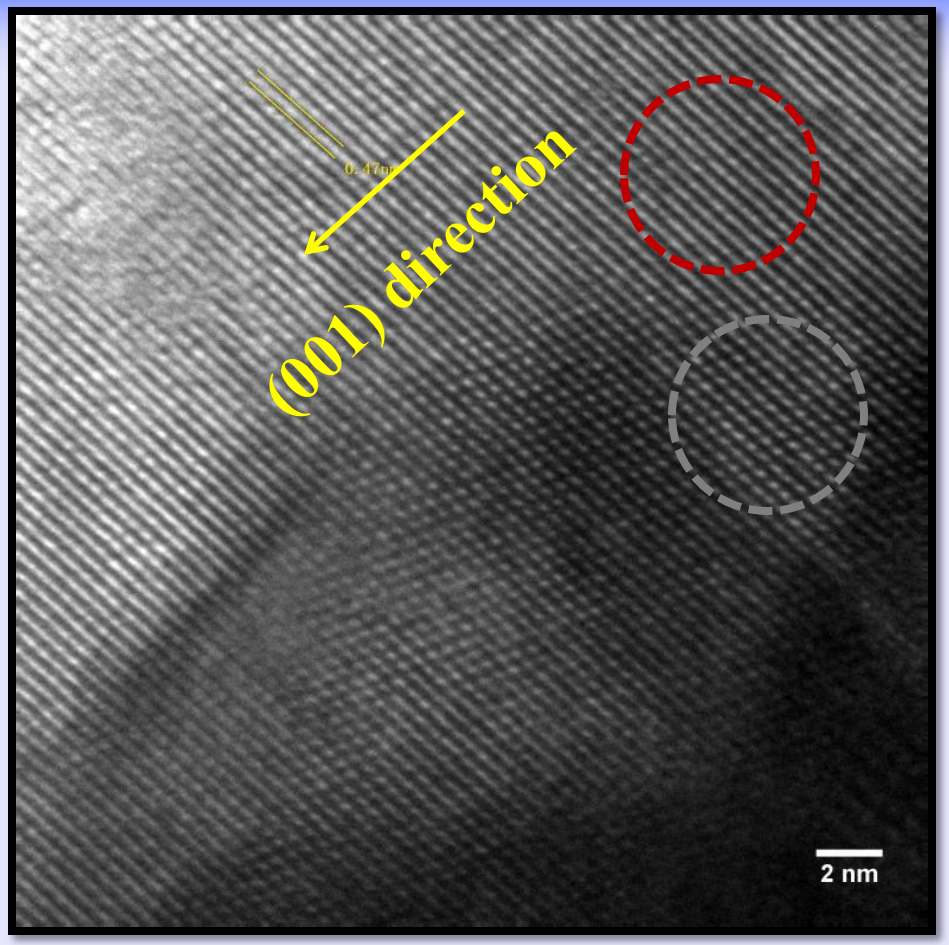



- **Small potential windows of 3.5V-2.0V activates ONLY the Spinel component**
- **Higher activation potential delivers the 230-250mAh/g but is not reversible**
- **Possibility of large strain develops during the activation of excess Li**
- **May require integration of structure by second layered system (incorporation of NCM)**

# TEM (Spinel-rich Composite)

## Layered-Spinel – 4MC

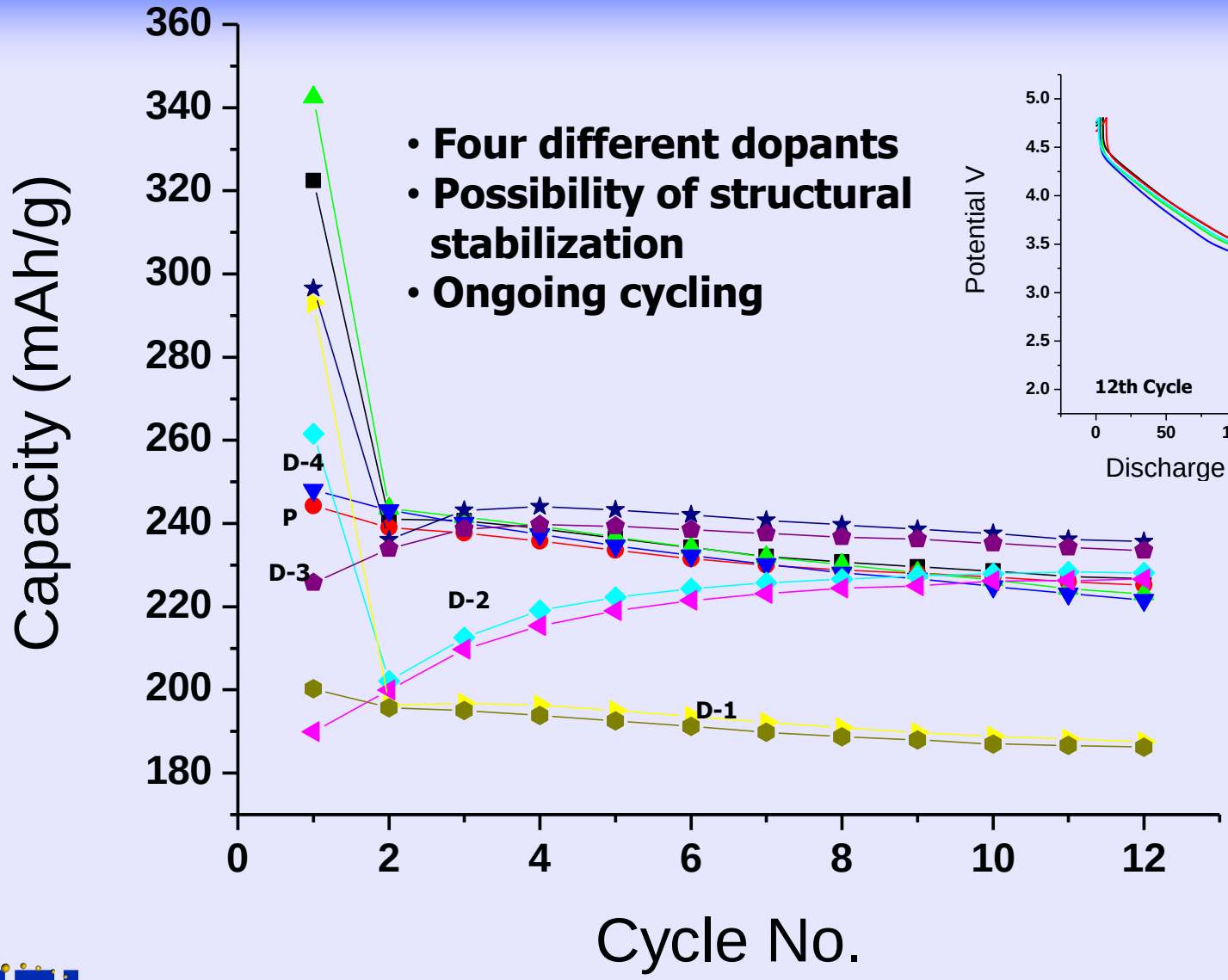


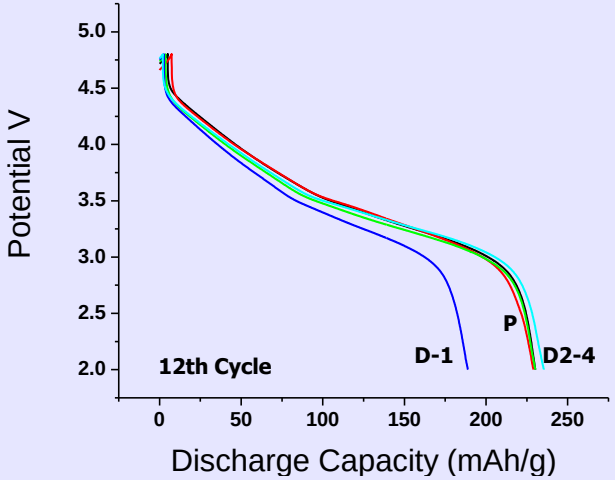

- d-spacing of 4.7A (003) plane
- Suggesting the integration of spinel & layered systems in one monolithic nano-particle

# Layered-Layered Composite

## Dopant Effect

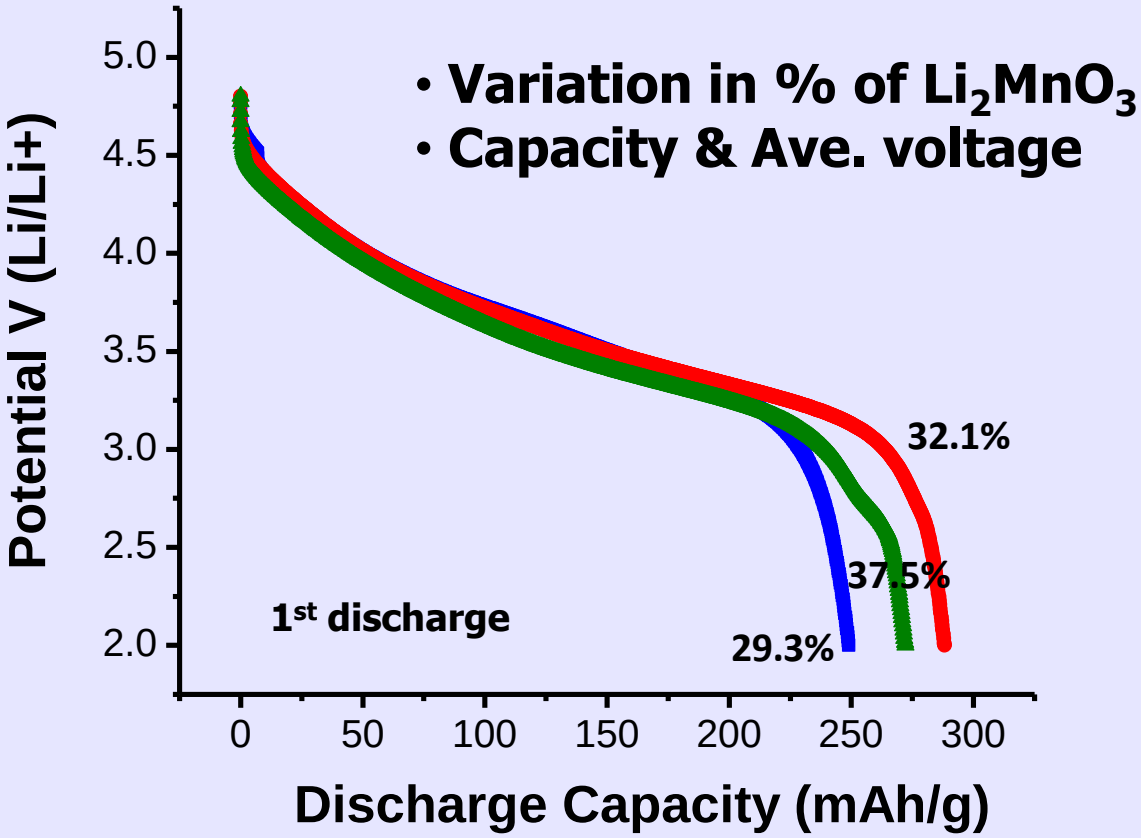
- Four different dopants
- Possibility of structural stabilization
- Ongoing cycling

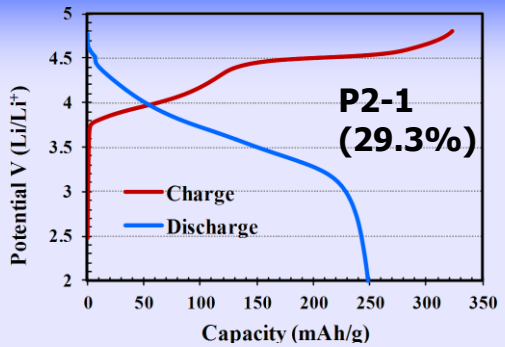


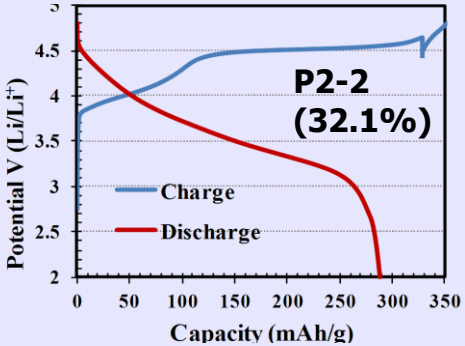



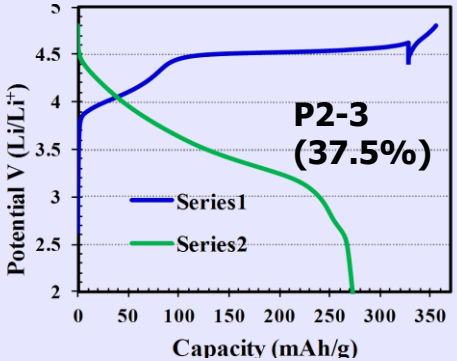
# Layered-Layered Composite

## Compositional Variation



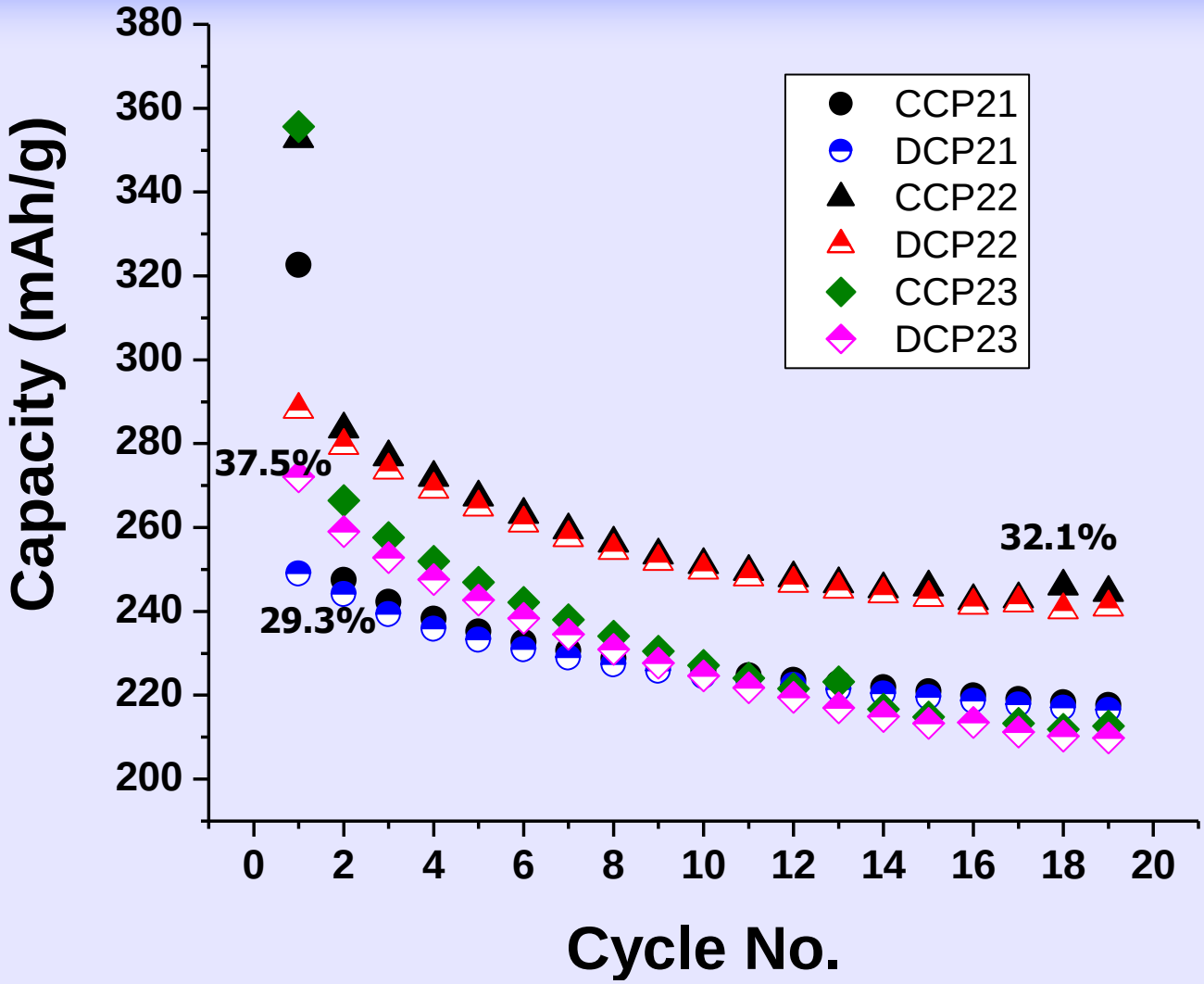



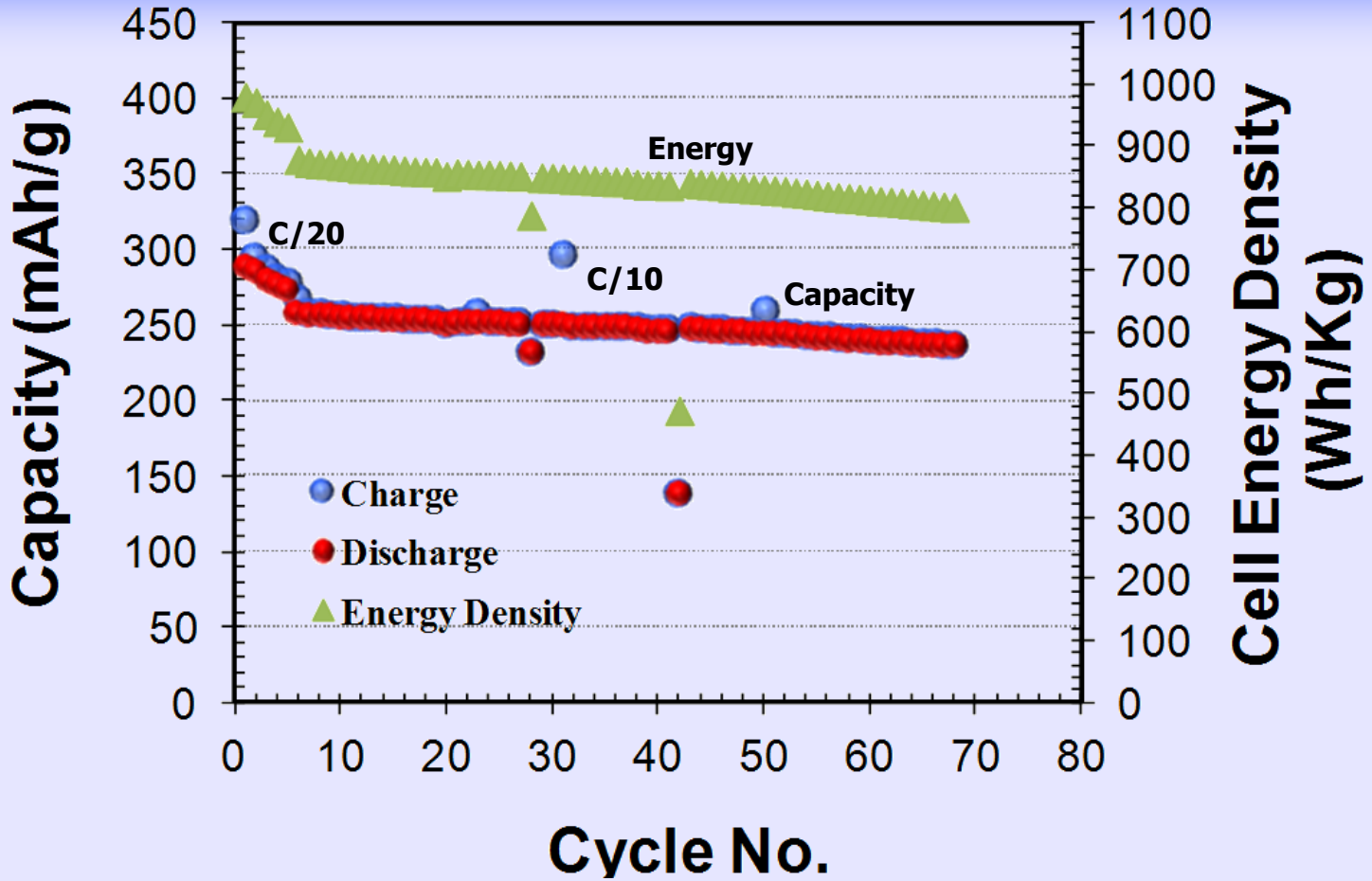



# Layered-Layered Composite

## Compositional Variation



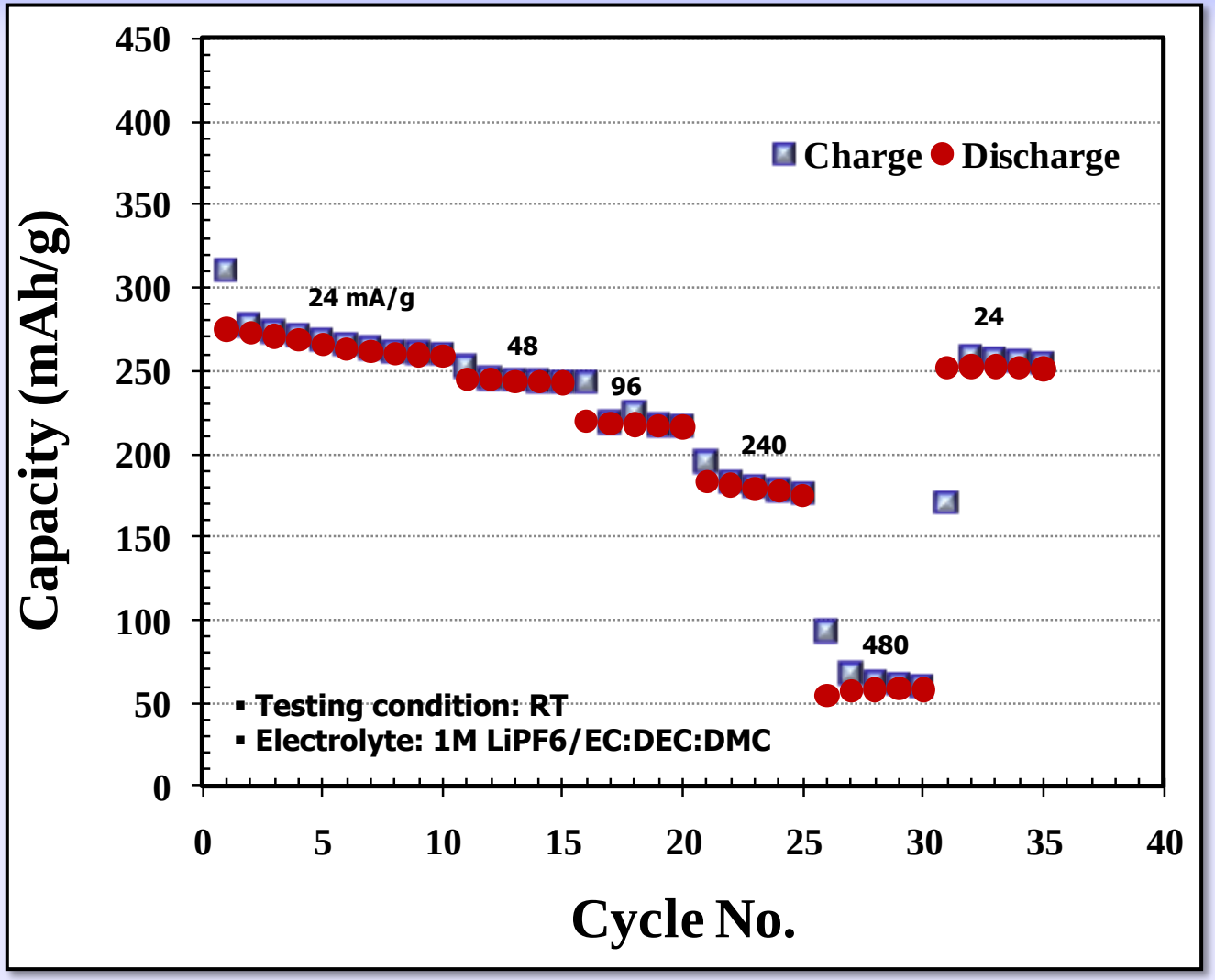
# Layered- Layered Composite




- **Discharge capacity of 240-250 mAh/g**
- **Cathode energy density of 800-1000 Wh/kg**

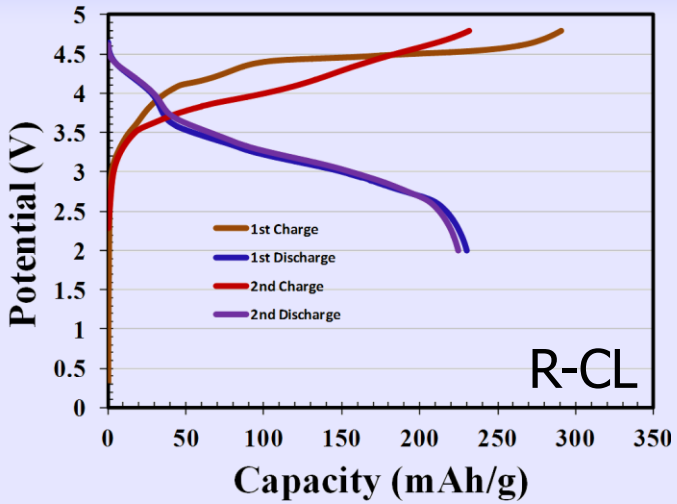
# Layered-Layered Composite

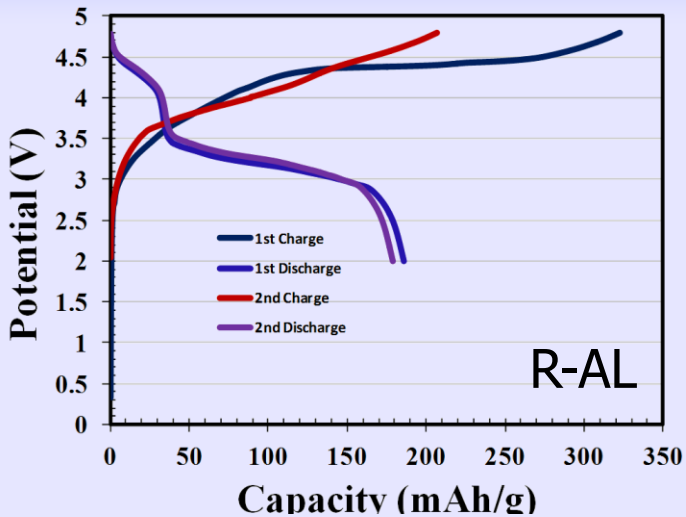
## Power Capability



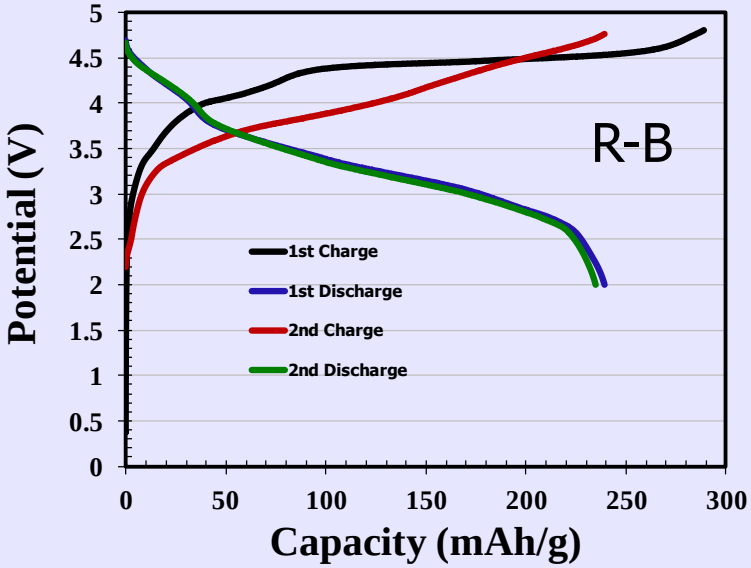
# Full Cell; Effect of Mass Ratios

## Layered-Layered Composite



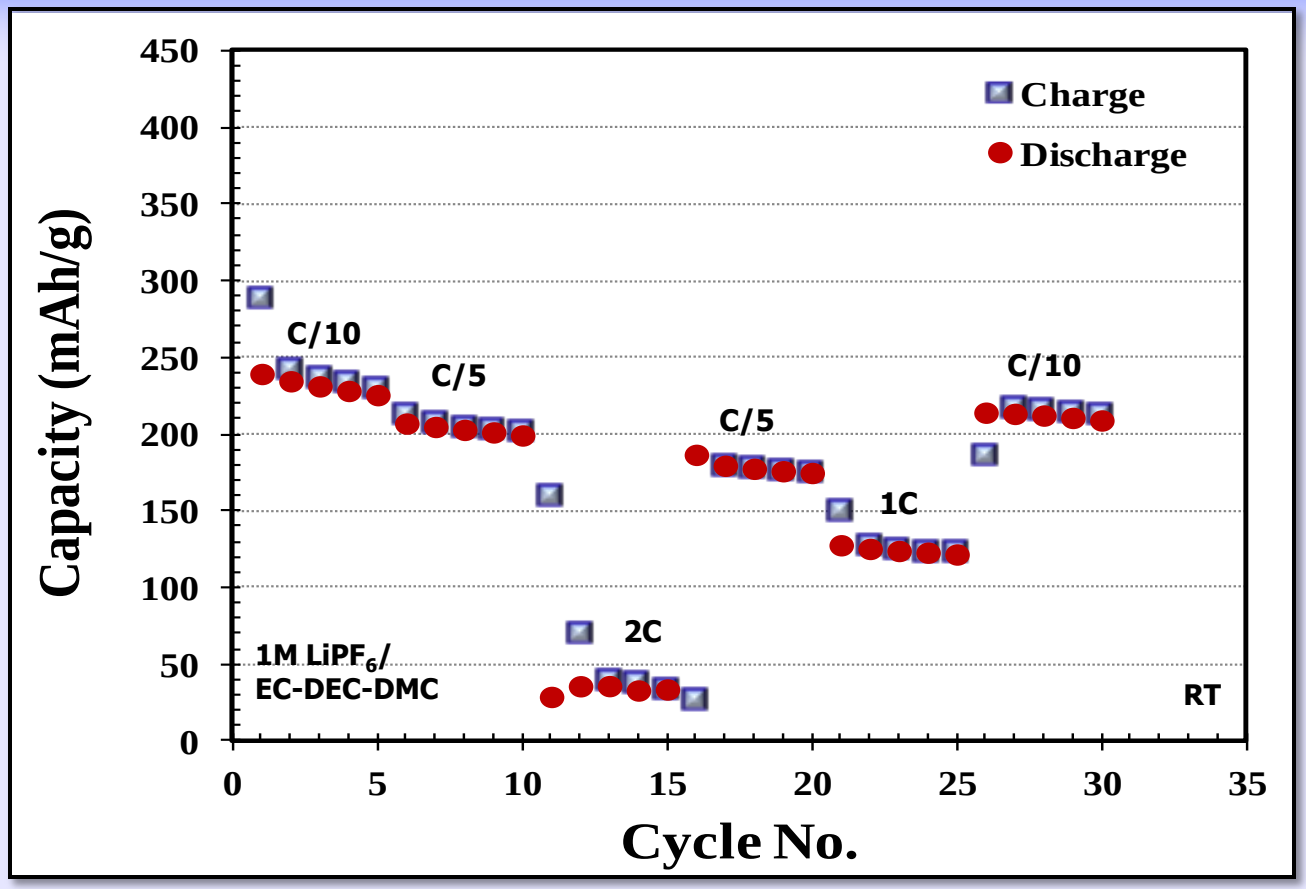

- **Cathode: 80%**
- **Anode (G):90%**




- **Right balance between C&A in R-B**

# Full Cell Performance

## Rate Capability; R-B




- Good Rate capability at C/5
- Almost full recovery after 2C and 1C rates

# Summary & Conclusions

- Promising performance of the composite cathodes in delivering high energy
- Power performance needs to be optimized; intrinsic modification may be a viable solution to increase ionic cond. (ongoing dopant study)

- Type of application defines the priority but search will continue to provide:
  - Higher energy and moderate power
  - High stability
  - Safe electrode material
  - Eco friendly or recyclable materials
  - High efficiency and
  - Low cost

# Collaborators

**NASA**
- Ms. Concha Reid, Glenn Research Center (GRC)
- Dr. William West and Dr. Bugga Ratnakumar, Jet Propulsion Lab (JPL)

**Lithium Battery Engineering LLC**
- Dr. Jim Manning

**Sandia National Laboratory**
- Dr. Ganesan Nagasubramanian ("Mani")

**Lawrence Berkeley National Laboratory**
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**Univ. of California, San Diego**
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**Energy Storage Research Group, Rutgers University**
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**Dept. of Materials Science & Engineering, Rutgers University**
- Dr. Jafar Al-Sharaab

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