

# Development of Advanced High-Energy Cathode Materials for Power Vest for Future Force Warriors

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## INTRODUCTION

Today's military personnel are equipped with many high-tech electronics, all of which need reliable mobile power sources. Because batteries are the most readily available and widely used mobile power sources, it is often said that battery power, rather than fire power, is rapidly becoming a major factor in military planning.

Currently, military personnel rely mostly on primary batteries (non-rechargeable). However, rechargeable lithium-ion batteries offer advantages in long-term cost saving, transportation, logistics, gravimetric and volumetric energy density, and are considered alternative or next-generation power sources for military equipment.

Funded by the U.S. Army CECOM (Communications-Electronics Command), this project was launched to develop a safe, low-cost, high-energy-density, and lightweight rechargeable Li-ion battery system as a power source for the Power Vest for Future Force Warriors.

## Lithium-Ion Batteries for Power Vest

In this project, the battery chemistry is developed by Argonne, and the battery pack by Quallion, LLC. More specifically, Argonne develops

- Cathode material with low cost, high energy density, and good thermal safety, and
- Polymer electrolyte with high Li-ion conductivity, non-flammability, and good electrochemical redox stability.

In general, performance requirements for military-grade portable power sources are much more demanding than for commercial ones.

Energy Density	Current conventional cell design	Target
Gravimetric	120 Wh/kg	200 ~ 250 Wh/kg
Volumetric	350 Wh/l	500 Wh/l

To meet the challenging target for gravimetric and volumetric energy density, a dense cathode material with capacity of at least 240 mAh/g is required.\*

\* Most commercial Li-ion batteries adopt LiCoO<sub>2</sub> as the cathode, whose practical capacity is only 140 mAh/g.

## Argonne's Approach

Our approach centers on the battery chemistry that is the basis for two U.S. patents for layered composite cathode materials.\*

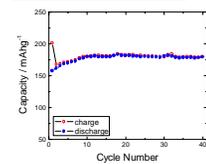
We selected xLi<sub>2</sub>MnO<sub>3</sub>(1-x)LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> with x=0.5 as the starting chemistry, based on our previous work.\*\* To meet the project's requirement for the cathode material, we adopted two approaches:

- Chemistry optimization (intrinsic property)
  - ✓ Cation and anion substitution with Co and F, respectively
  - ✓ Improvement of gravimetric energy density
- Morphology optimization (extrinsic property)
  - ✓ Development of dense, spherical metal precursor
  - ✓ Increase tap density (packing density) => increase of volumetric energy density

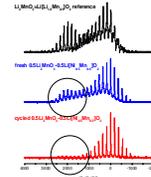
\*6,877,062 and 6,880,143, M. M. Thackeray, C. S. Johnson, K. Amine, and J. Kim  
 \*\*S.-H. Kang, Y.-K. Sun, K. Amine, *Electrochem. Solid-State Letters*, 6(9), A183, 2003.  
 S.-H. Kang, K. Amine, *J. Power Sources*, 124(2), 533, 2003.

## CHEMICAL COMPOSITION OPTIMIZATION

### 0.5Li<sub>2</sub>MnO<sub>3</sub>-0.5LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>

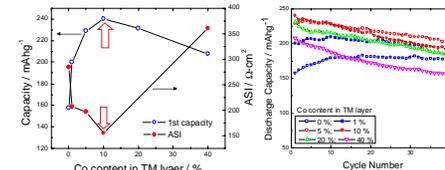


➢ The material showed higher capacity than theoretical value (126 mAh/g) based on Ni<sup>2+</sup>/Ni<sup>3+</sup> redox couple.



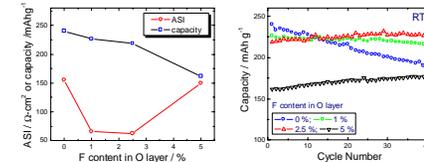
➢ The nuclear magnetic resonance spectra indicate that Li is extracted from the transition metal TM layer as well as from the Li layer.

### Cation substitution with Co



- Substitution of Ni/Mn with 10% Co exhibited the highest first discharge capacity and the lowest impedance.
- However, the cycleability was deteriorated by the Co-substitution.
- Fluorine substitution at the oxygen site was carried out for the material with 10% Co in the TM layer to improve cycling performance.

### Anion substitution with F



- Substitution of O with F
  - Further reduced the impedance,
  - Significantly improved the cycling performance, and
  - Decreased the first capacity.
- Based on capacity, impedance, and cycling performances, the chemical composition has been optimized as (in layered notation)



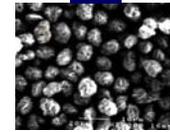
## MORPHOLOGY OPTIMIZATION

### □ Sol-gel vs. coprecipitation

- The sol-gel method produces very fine (not dense) powder and is not adequate for mass production of cathode materials.
- By carefully controlling experimental conditions, dense, spherical metal precursors can be produced by coprecipitation. The coprecipitation method can also be adopted in a production line if a properly designed CSTR (continuously stirred tank reactor) is used.

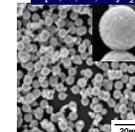
### Morphologies by various synthetic methods

#### ANLCC



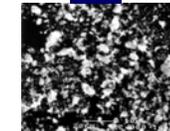
Prepared using coprecipitated (Ni,Co,Mn)-hydroxide

#### Li[Li,Ni,Co,Mn]O<sub>2</sub>



Prepared using coprecipitated (Ni,Co,Mn)-carbonate

#### ANLCC

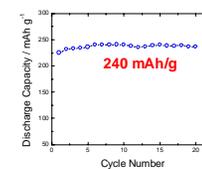


Prepared by the sol-gel method

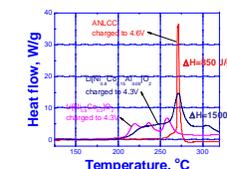
- By using coprecipitated transition metal precursors, dense, spherical cathode materials with very narrow size distribution could be synthesized.

- On the other hand, the cathode material prepared by sol-gel consists of very fine particles and their agglomerates.

### Cycling performance



### Thermal reactivity – DSC curves



- The ANLCC material prepared using the coprecipitated transition metal precursor showed a stable discharge capacity of 240 mAh/g, which meets our goal for the Power Vest project.

- The ANLCC material also exhibited much higher onset temperature and smaller heat generation than a Ni-based system in spite of the much higher charge voltage (4.6 V vs. 4.3 V).

## SUMMARY

Advanced cathode materials with high capacity and improved thermal safety have been successfully developed by

- Chemical composition optimization
  - Co substitution reduced impedance and increased initial capacity but deteriorated cycling performance.
  - F substitution further reduced impedance and significantly improved cycling performance.
- Particle morphology optimization
  - Dense, spherical cathode powder with narrow size distribution could be synthesized by using a coprecipitated transition metal precursor.

The cathode material optimized in chemical composition and particle morphology as well (ANLCC) met the targeted gravimetric energy density (240 mAh/g) and exhibited excellent thermal safety characteristics.