Argonne NATIONAL LABORATORY

... for a brighter future

Engineering of High energy cathode material

K. Amine, H. Deng, H. Wu and I. Belharouak

Argonne National Laboratory

May 19th, 2009

Project ID: esp_09_amine

U.S. Department of Energy

UChicago Argonne LLC

Office of Science U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

Overview

Timeline

- Start - October 1st, 2008.
- Finish - September 30, 2009.
- 60%

Barriers

- Barriers addressed
  - Very high energy
  - Long calendar and cycle life
  - Excellent abuse tolerance

Budget

- Total project funding
  - DOE share: $200K

Partners

- Interactions/ collaborations: *H. Deng, H. Wu and I. Belharouak*
- Project lead: Khalil Amine

Objectives of the work

Enable the Argonne high energy composite layered cathode $xLi_2MnO_3 \bullet (1-x)LiNiO_2$ for 40 miles PHEV

- Capacity of over 250mAh/g
- Good rate capability
- Excellent cycle and calendar life
- Excellent abuse tolerance

Approaches for developing high energy cathode material

✓Optimize suitable composition and engineer the material to improve its packing density and rate capability for PHEV applications

✓Explore surface protection to enable high capacity and long cycle life at high voltage (4.5V)

FY 2009 plans & schedule

✓Develop a process that lead to very dense material to increase the electrode density and therefore the electrode capacity. (Sep 2009)

✓Investigate ways of obtaining spherical particle with high homogeneity (Sept 2009)

✓Investigating the nano-coating of the material with metal fluoride , phosphate and oxide to reduce the initial interfacial impedance and stabilize the cathode interface in order to improve the cycle life at elevated temperature (2010)

FY 2009 plans & schedule

✓Improve the rate capability. Our target is to increase the rate capability from C/10 to 1C ~ 2C. (2010)

✓investigate the effect of making 3 micron secondary particle and 50 nm secondary particle that are distributed in dense configuration(limited pores) on the rate capability of the material (Sept 2009)

✓investigate new ways of coating oxides with carbon to improve conductivity of the material (2010)

Recent accomplishments and progress

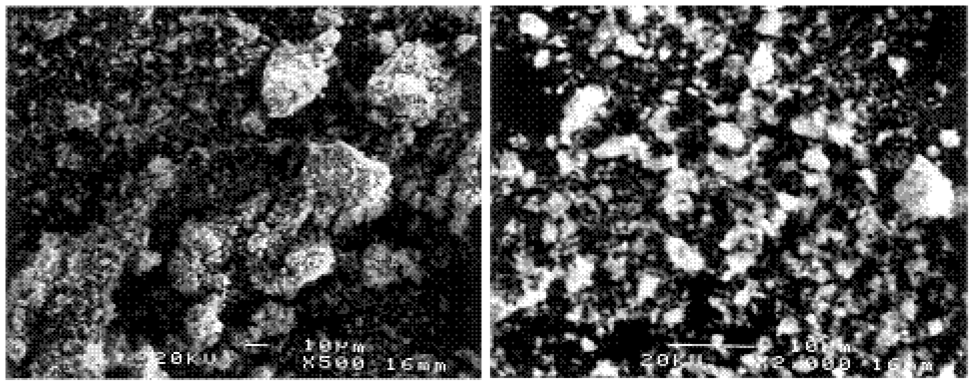
- developed a carbonate based co-precipitation process that provide spherical particle morphology.

- optimized the carbonate based co-precipitation process to obtain high packing density cathode materials.

- optimized composition that provide high energy, high packing density and 1c rate capability.

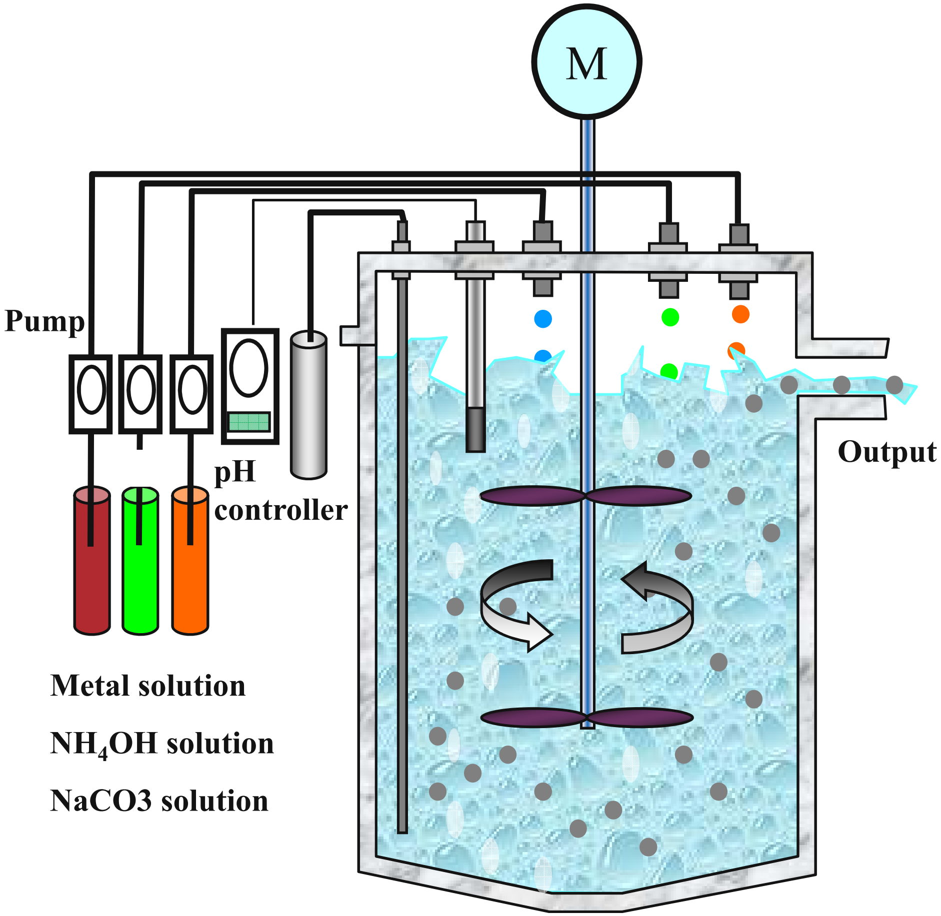
Use of the sol-gel process leads to highly porous and low packing density material

SEM of material prepared by sol-gel



- ❖ Density of the material using sol-gel process is very low (0.8g/cc) theoretical value is 4.6g/cc (density of conventional cathode in lithium ion batteries is: 2.4g/cc)
- ❖ Need to develop alternative process to make spherical and high packing density composite cathode material to take full advantage of its very capacity

ANL Advanced Continuous Process for Making Ni,Co,Mn- Precursors used to Prepare Composite Cathode Material

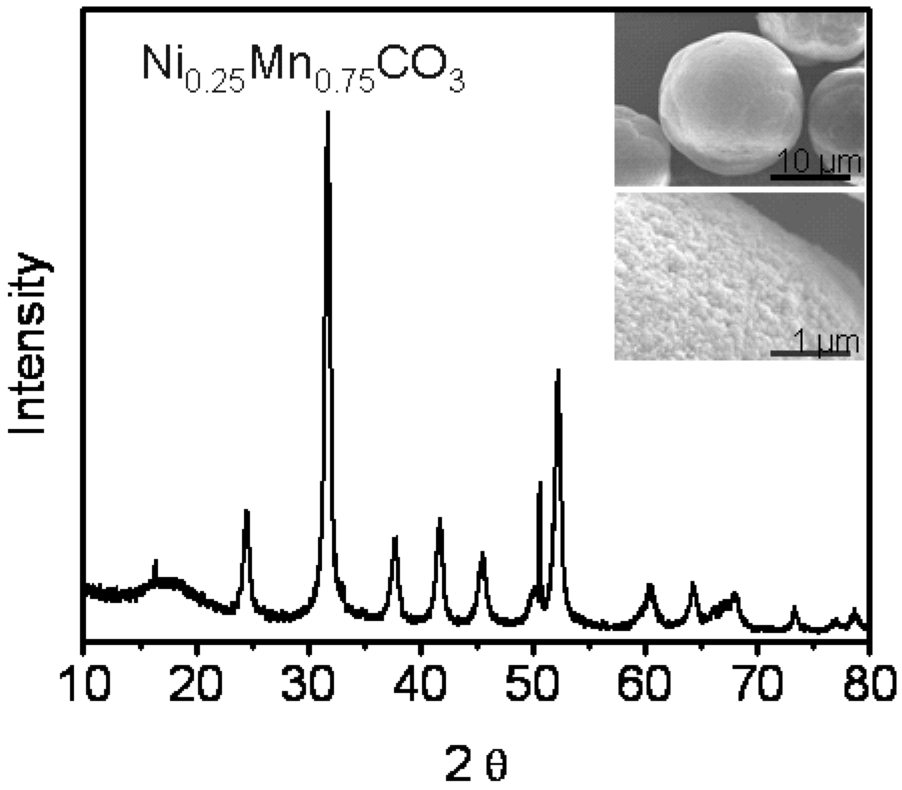


Key parameters:

- **Temperature**
- **pH**
- **Stirring speed**
- **Concentration of metal solution**

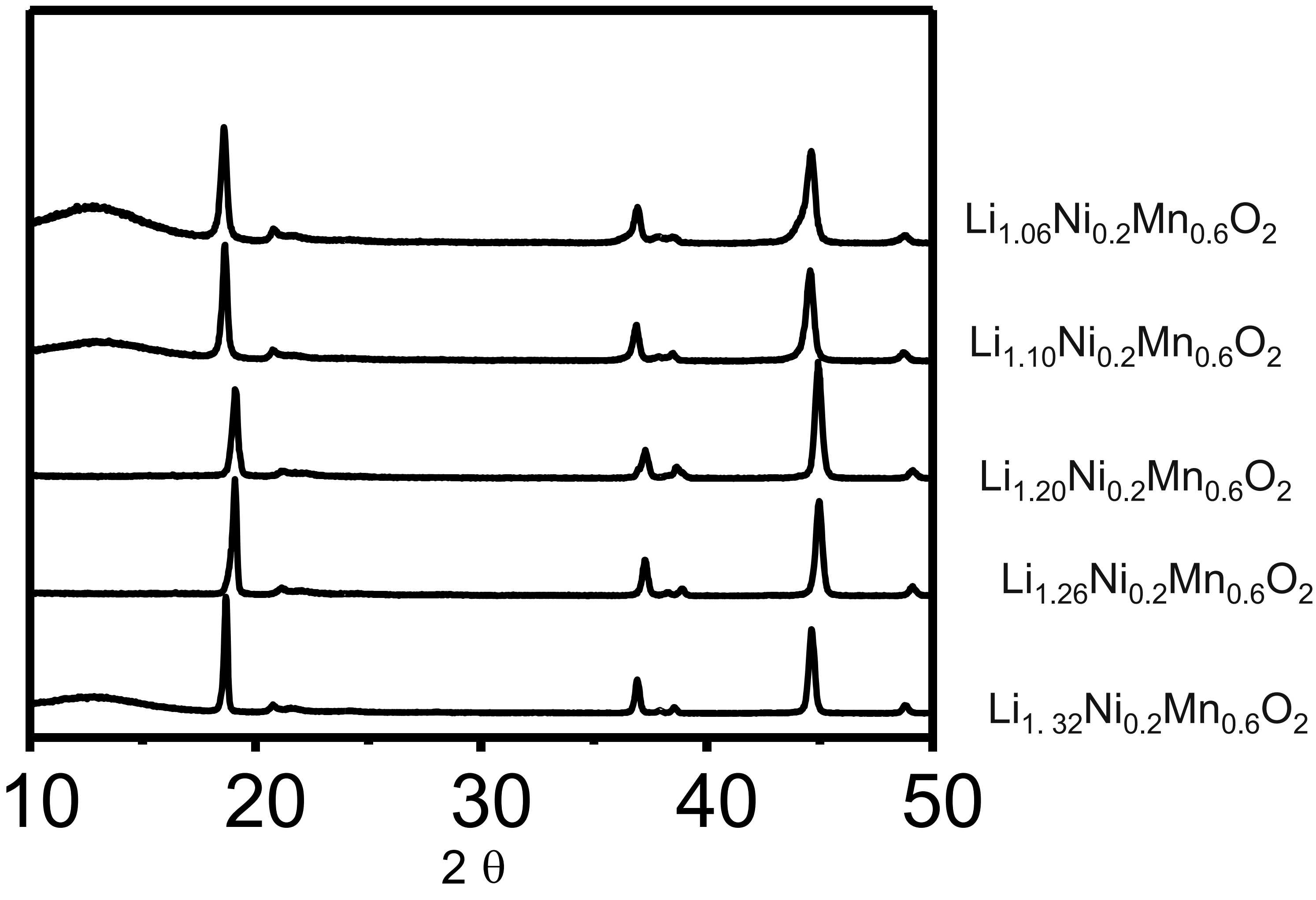
- Co-precipitation process using carbonate process
- continuous process where carbonate precursor is obtained continuously as long as metal solution are fed in the reactor
- Low cost process that leads to highly homogeneous materials

X-ray Diffraction and SEM of Ni,Mn-Carbonate Precursor used to Prepare Composite Cathode Material



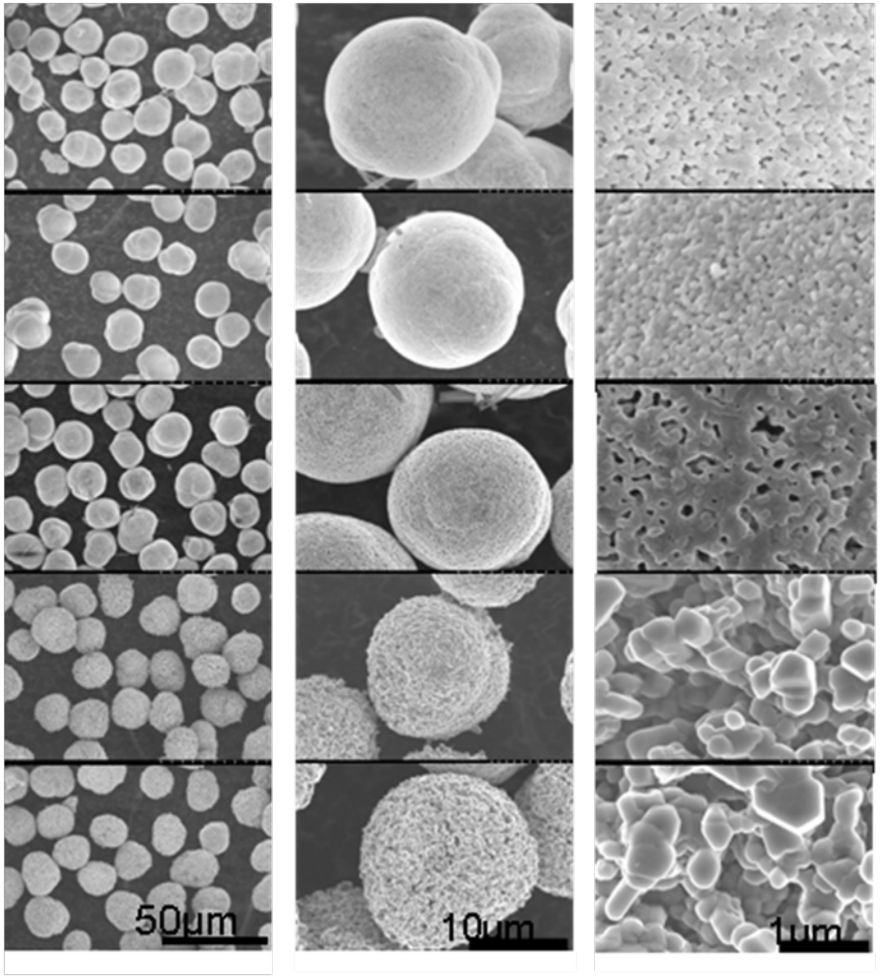
- New carbonate process led to pure Ni,Mn-carbonate precursor with spherical and dense particles
- Precursor particle morphology is reflected in the final composite cathode after lithiation and calcination
- Morphology of the final composite cathode can be optimized by optimizing the morphology of the precursor

X-ray Diffraction shows Pure Phases Regardless of Li Excess Concentration



Morphology of the particles changes with lithium excess content

- Materials with 6 to 10% excess lithium shows highly packed nano-primary particles
- Nano primary particle could help improve rate capability of the material by reducing the lithium diffusion pathway
- High amount of excess lithium leads to porous material with large primary particles



$Li_{1.06}Ni_{0.2}Mn_{0.6}O_2$

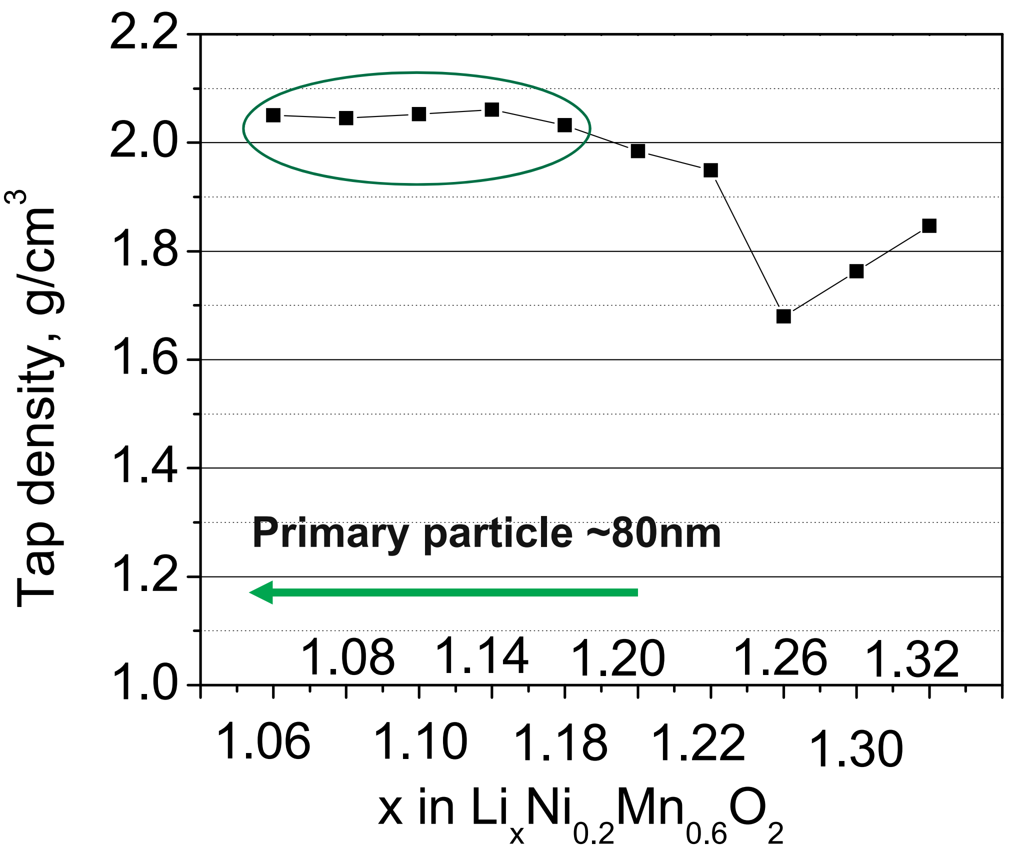
$Li_{1.10}Ni_{0.2}Mn_{0.6}O_2$

$Li_{1.20}Ni_{0.2}Mn_{0.6}O_2$

$Li_{1.26}Ni_{0.2}Mn_{0.6}O_2$

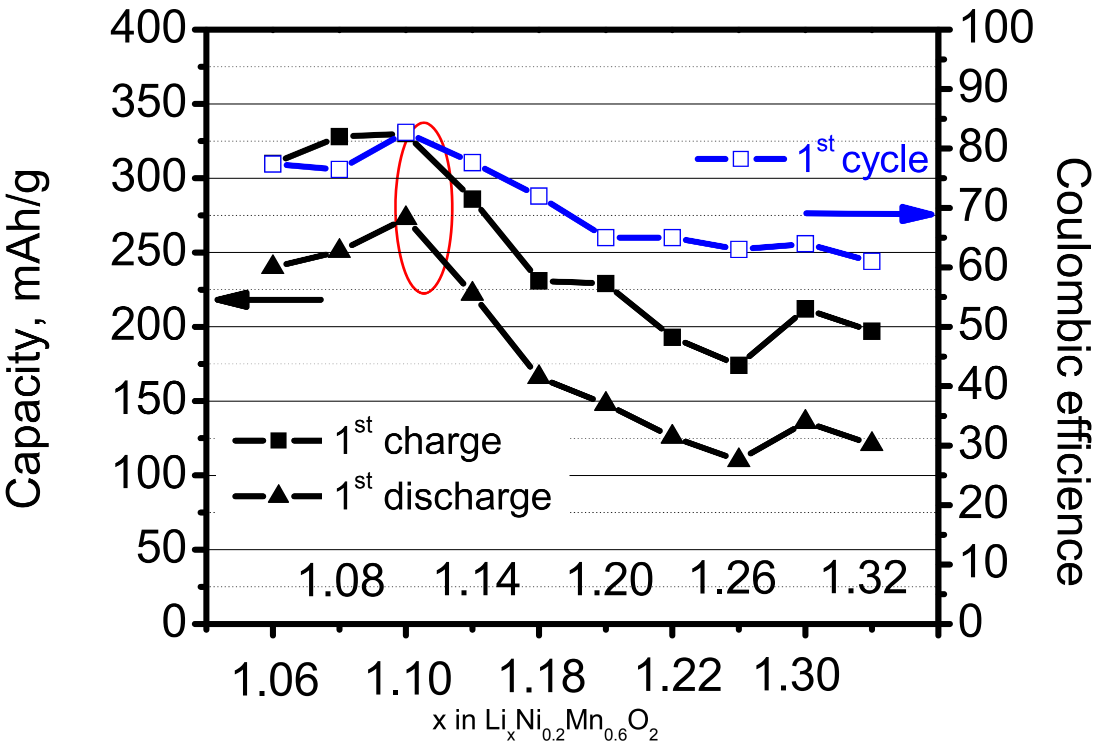
$Li_{1.32}Ni_{0.2}Mn_{0.6}O_2$

Materials with Highly Packed Nano-Primary Particles Exhibit High Packing Density



Material with excess lithium between 5% ~15% shows high packing densities that can lead to high electrode energy density (Packing density is around 2.05g/cm^3)

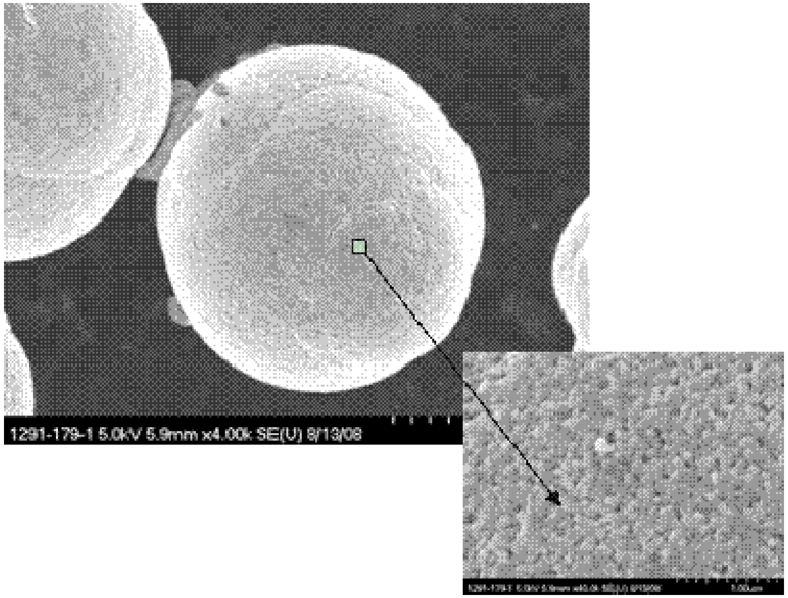
Effect of Excess Lithium on Discharge Capacity and First Cycle Columbic Efficiency

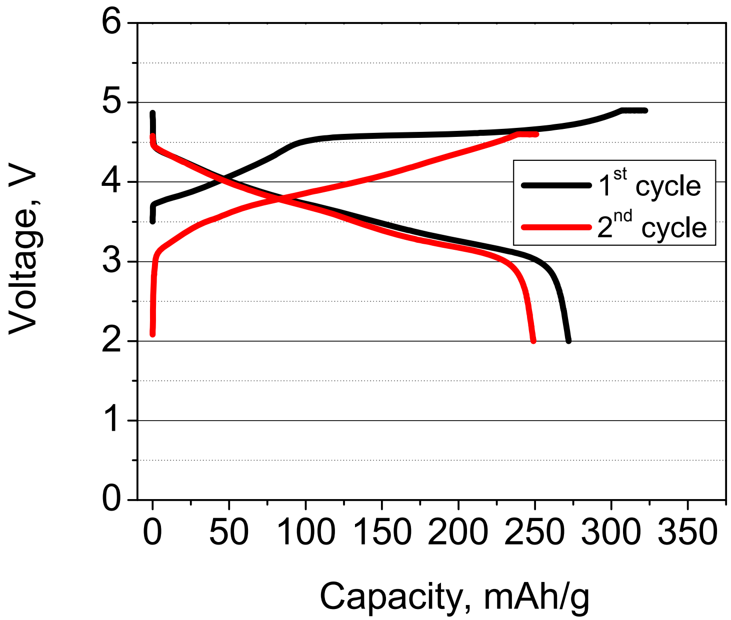


- Materials with 6 to 10% excess lithium not only shows high packing density, nano-primary particle that can offer good rate but also shows high charge and discharge capacity and high columbic efficiency

Cycling rate: C/10

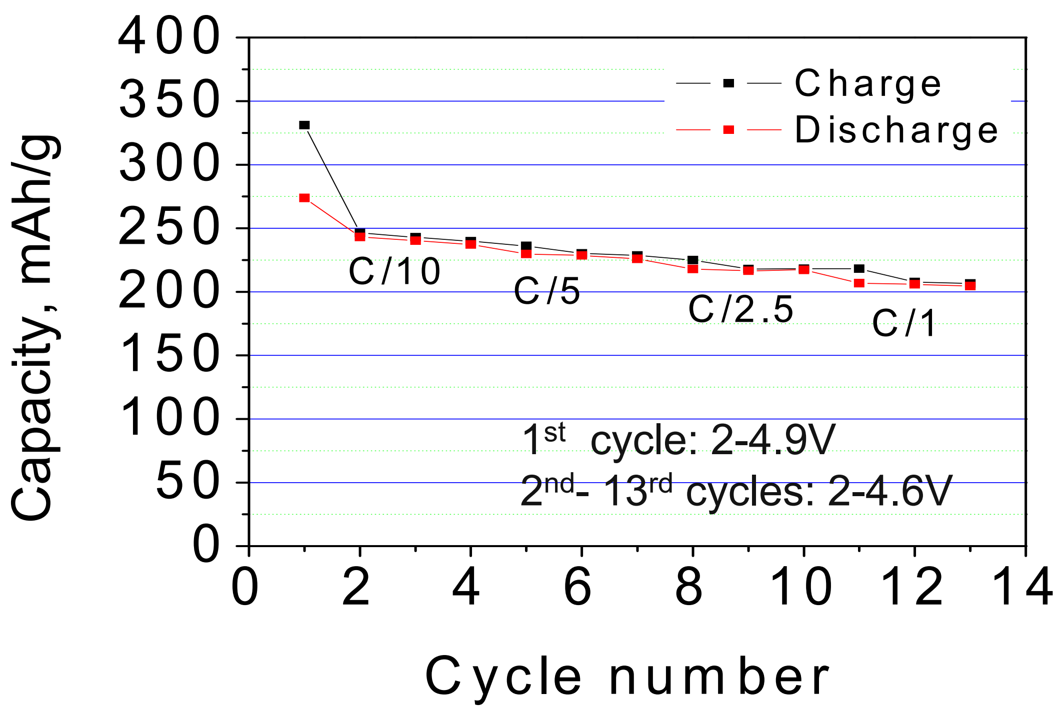
$Li_{1.10}Ni_{0.2}Mn_{0.6}O_2$ was Selected as the Optimum Composition for High Energy Applications





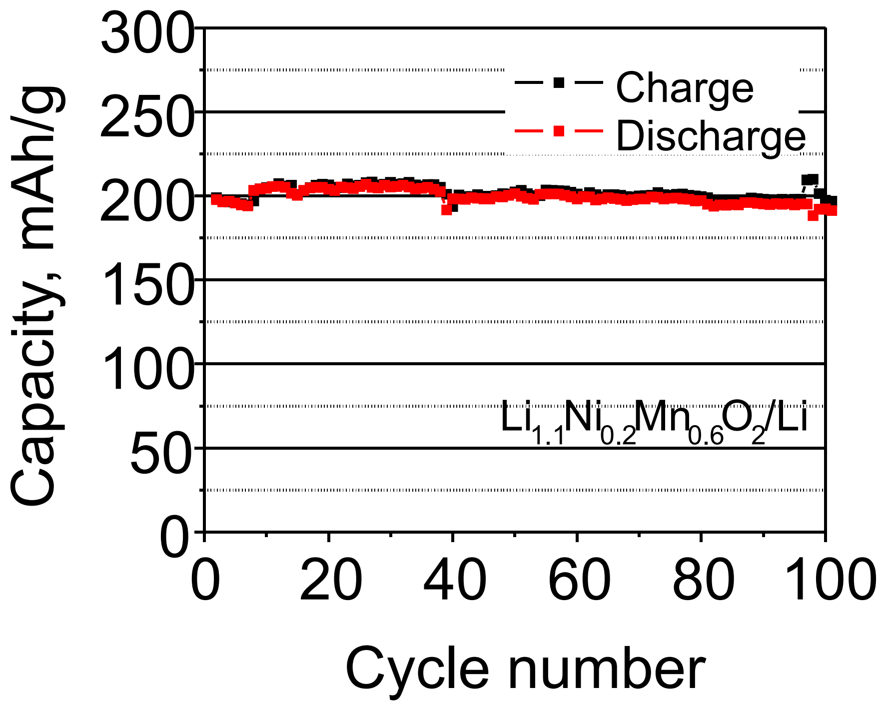
- Material exhibit:
  - Spherical morphology for easy processing
  - high tab density that can increase the loading of the material in the electrode
  - Nano-primary that facilitate fast lithium diffusion and improve the rate capability
  - High discharge capacity of 260mAh/g and high columbic efficiency over 80%

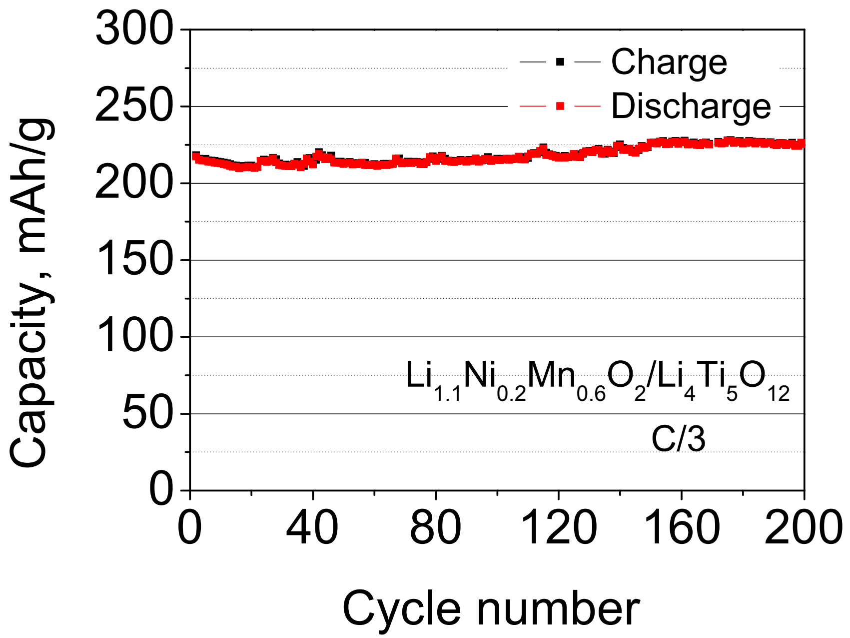
Rate Capability of $Li_{1.1}Ni_{0.2}Mn_{0.6}O_2$ Material



- Good rate capability (>80% capacity retention when rate increased from 0.1C to 1C rate).
- Capacity of the material at 1 C rate is 210mAh/g

Cycling Performance of $Li_{1.1}Ni_{0.2}Mn_{0.6}O_2$ Material

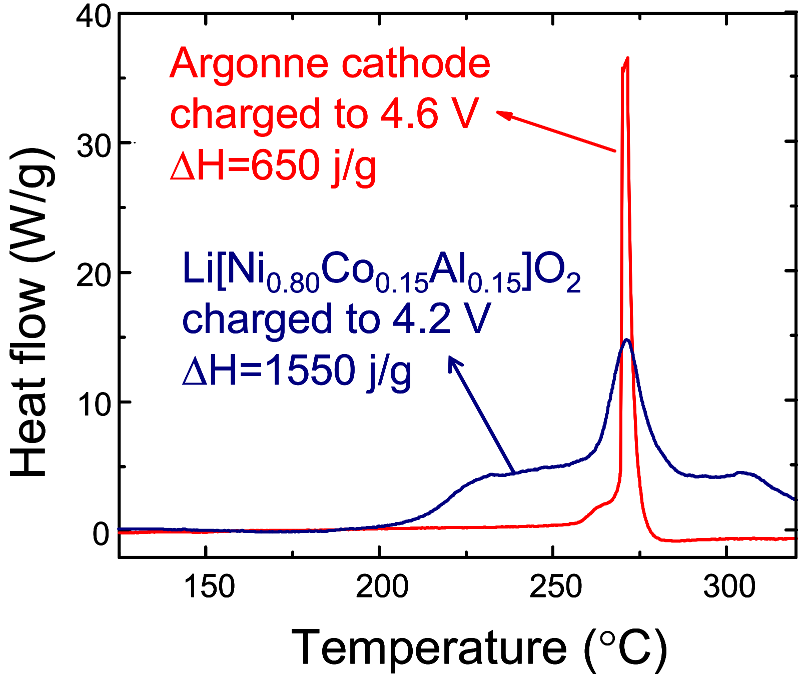




- Material shows good cycling performance at high rate both *vs.* Li and *vs.* $Li_4Ti_5O_{12}$ anode.

ANL Composite Electrode Shows Outstanding Safety Performance Even When Charged to 4.6V

Differential Scanning Calorimetry (DSC)



ANL composite cathode exhibit:

- **Much higher onset temperature**
- **Much less heat from exothermic reactions**
- **Much sharper peak shape**
- **All of these are attributed to low Ni-content (<20%) and Mn stabilizing effect.**

- **ANL composite cathode exhibits superior thermal stability than any other existing layered metal oxide even though charged to 4.6V**

Summary

✓Argonne developed a continuous co-precipitation process that provides:

- ✓Spherical particle morphology
- ✓Highly dense particles with packing densities of 2.1g/cc
- ✓Sharp particle distribution for uniform performance

✓Material composition was optimized to obtain very high energy of over 250mAh/g.

✓Engineering the composite cathode to obtain highly dense nano primary particles has led to:

- ✓reduction of lithium pathway diffusion
- ✓significant improvement in the rate capability with 210 mAh/g capacity at 1 hour charge and discharge rate.

✓Composite cathode shows outstanding safety characteristics even when charged to 4.6V

Future work

✓Further engineer the composite cathode to increase rate by optimizing the secondary and primary particles

✓Further optimize the co-precipitation process to increase packing density to 2.4g/cc

✓Investigate a new process of coating composite cathode with conductive materials to improve conductivity and rate.

✓Investigate the nano-coating of the material with metal fluoride , phosphate and oxide to reduce the initial interfacial impedance and stabilize the cathode interface in order to improve the cycle life at elevated temperature (2010)