Engineering of High energy cathode material

K. Amine (PI)

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DOE merit review

June 7th to 11th , 2010

Project ID, ES015

Overview

Timeline

- Start - October 1st, 2008.
- Finish - September 30, 2014.
- **40% complete**

Barriers

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

Budget

- Total project funding
  - DOE share: $600K
    FY10: 300K
    FY09: 300K

Partners

- Interactions/ collaborations:
  H. Deng, H. Wu , I. Belharouak, A. Abouimrane (ANL)
- *Y.K. Sun (hanyang University)*
- *X.Q. Yang (BNL), Toda.,BASF, ,ECPRO*
- 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
- High packing density (2.2~2.4g/cc)
- 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 rate capability for PHEV applications

✓Optimize synthesis process to obtain high packing density

✓Explore surface modification to enable high rate and long cycle life at high voltage (4.6V)

FY 2010 plans & schedule

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

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

✓Improve the rate capability of the material (in progress)

✓Investigate the nano-coating of the material with AlF_3 to reduce the initial interfacial impedance and stabilize the cathode interface in order to improve the cycle life at elevated temperature (in progress)

FY 2010 plans & schedule

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

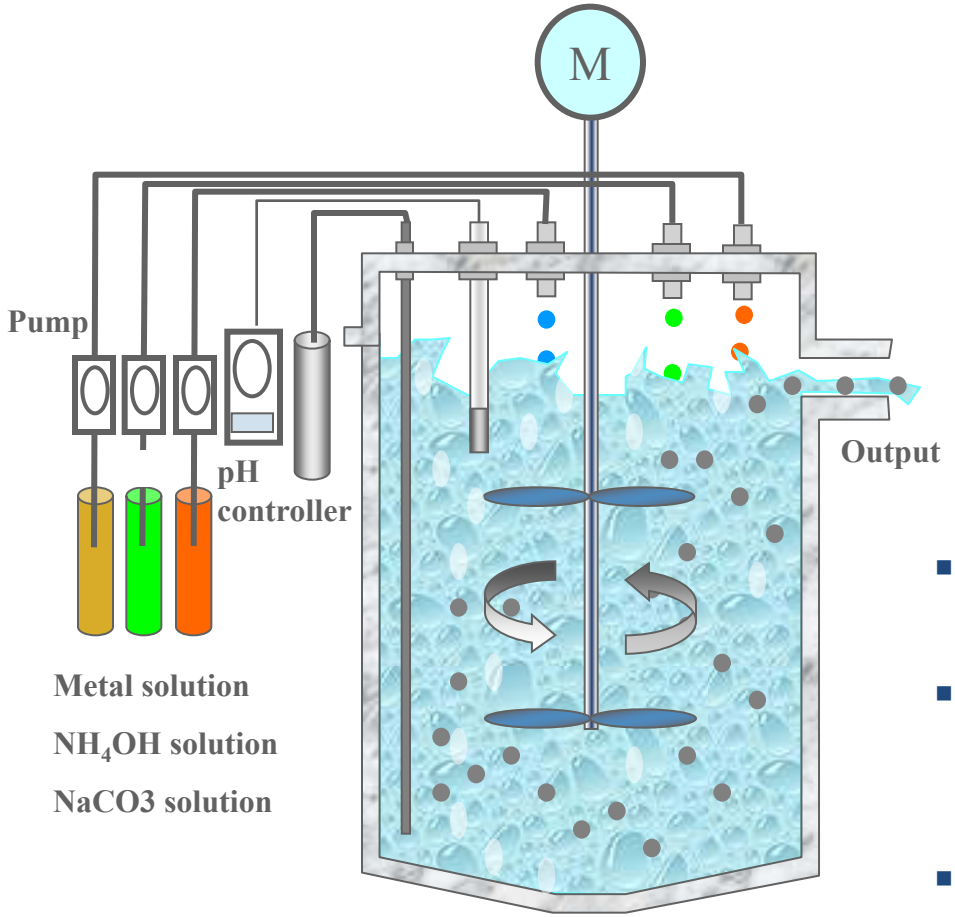
✓investigate the effect of making 3 micron secondary particle and 50 nm secondary particle that are distributed in dense configuration(limited pores) on the rate capability of the material (completed)

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

Recent accomplishments and progress

- developed a carbonate based co-precipitation process that provide spherical particle morphology.
- optimized the carbonate based co-precipitation process and composition to obtain high packing density cathode materials with high reproducibility.
- Optimize the composition to obtain reproducible and highly pure materials
- Validate the improvement of rate and cycling stability at high temperature using AlF_3 surface nano-coating
- Developed a new surface modification on high cathode material that result a significant improvement in power capability of the material

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

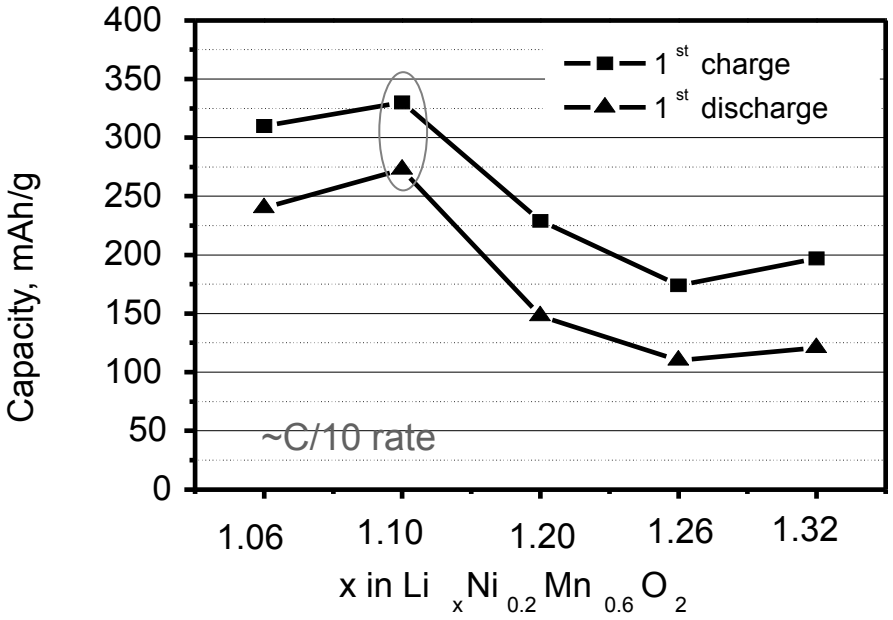


Key parameters:

- 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

Effect of lithium concentration on electrochemical performance of $Li_{1+x}Ni_{0.25}Mn_{0.75}O_{2.25+x/2}$



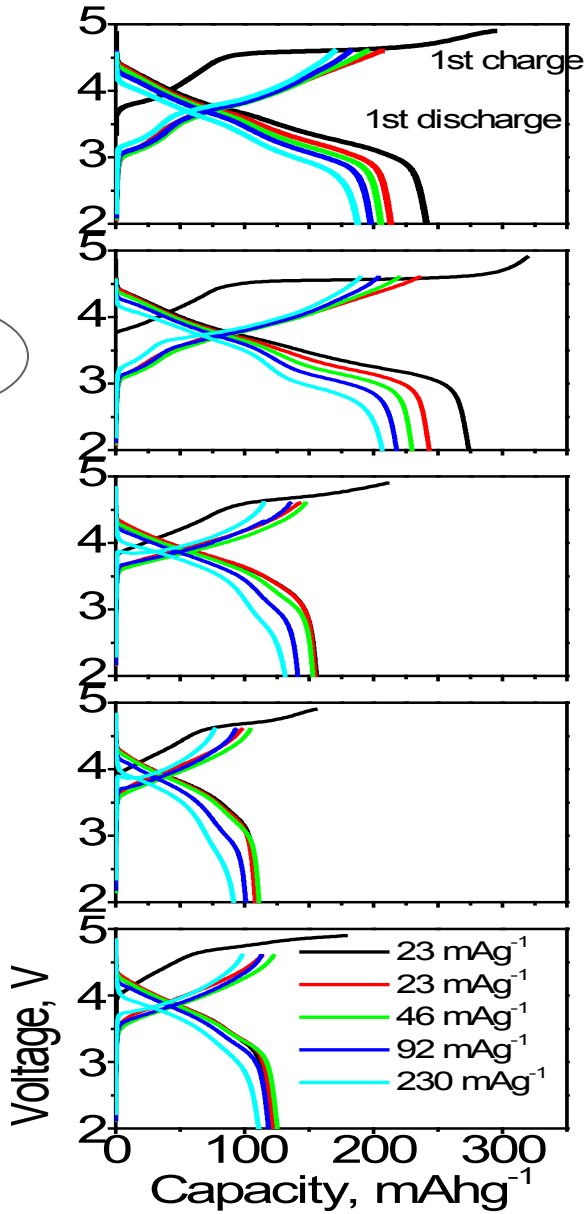
x=1.06

X=1.10

X=1.20

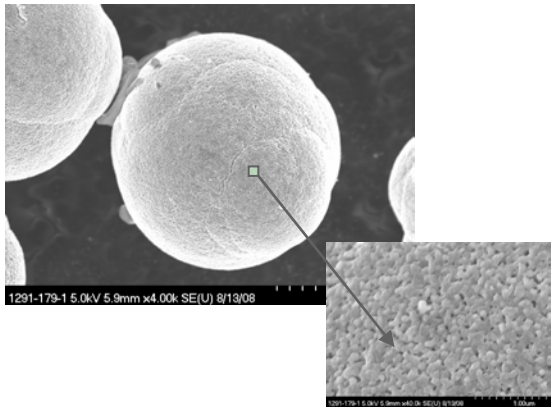
X=1.26

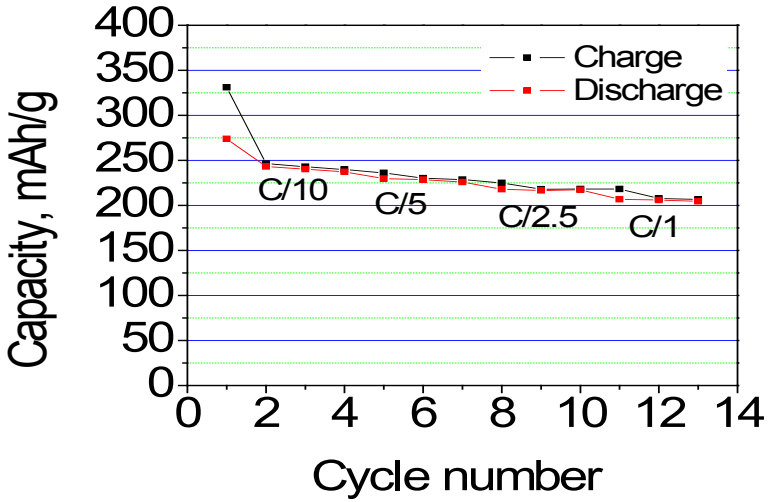
X=1. 32

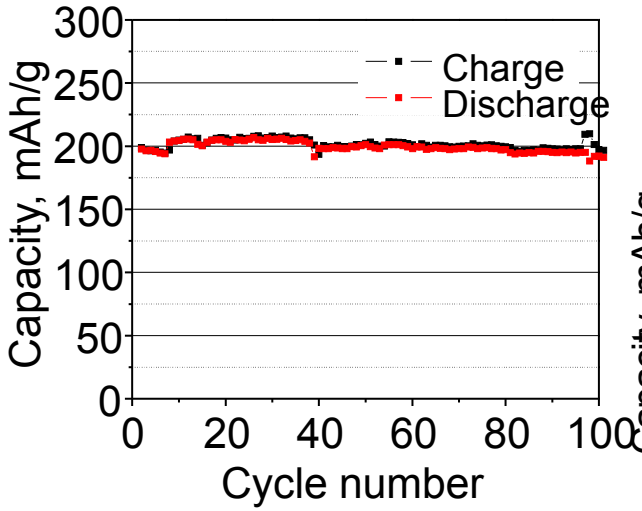


- $Li_{1.10}Ni_{0.2}Mn_{0.6}O_{1.95}$ showed highest capacity and better rate capability

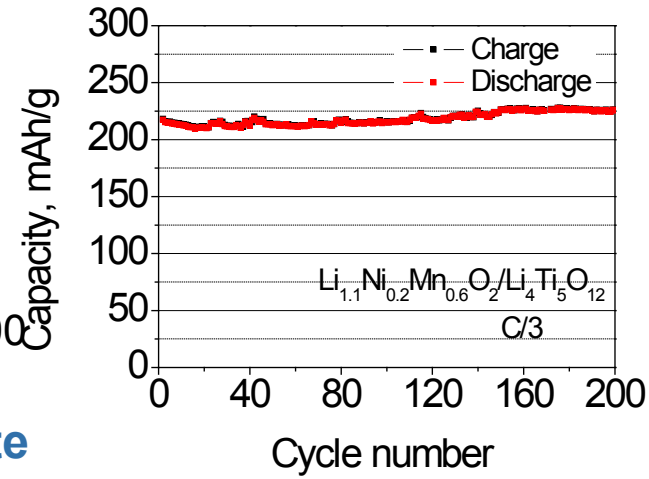
$Li_{1.10}Ni_{0.2}Mn_{0.6}O_{1.95}$ was initially selected as the optimum composition for high energy applications







$Li_{1.10}Ni_{0.2}Mn_{0.6}O_{1.95}$/Graphite

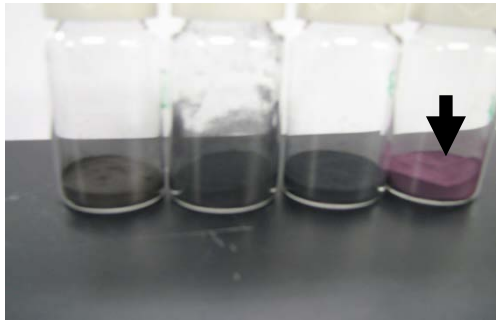


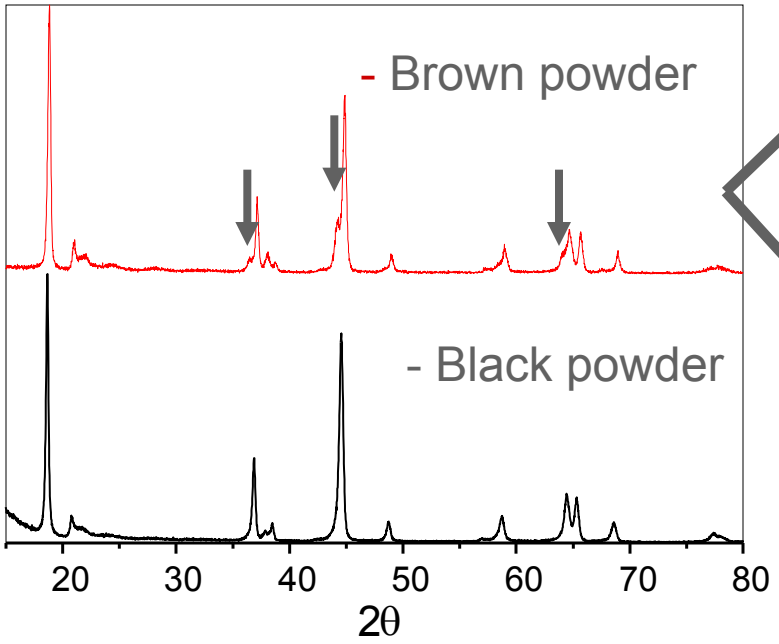
$Li_{1.10}Ni_{0.2}Mn_{0.6}O_{1.95}$/LTO

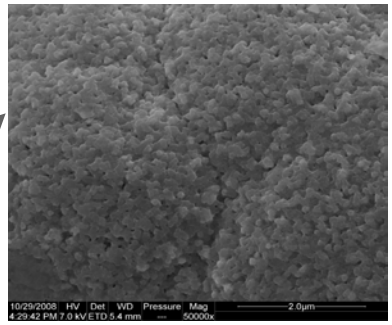
- Spherical morphology for easy processing
- high tab density (2.1g/cc) that can increase the loading of the material in the electrode
- Nano-primary that facilitate fast lithium diffusion and improve the rate capability
- High rate capability 200 mAh/g at 1 C rate
- good cycle life

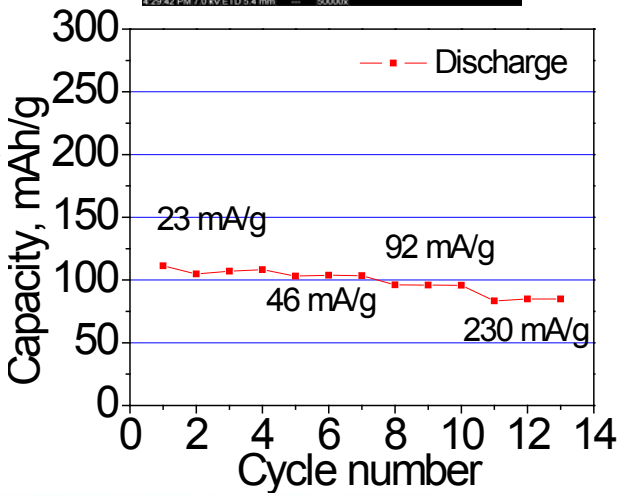
Issues of Reproducibility during Material Scale Up with Industry

- Difficulty to consistently reproduce the good performance of Co free cathode when scaling up the material to over 1Kg
- For the same composition, different powder colors were observed and in same cases high ratio of Li_2MnO_3 separate phase was observed

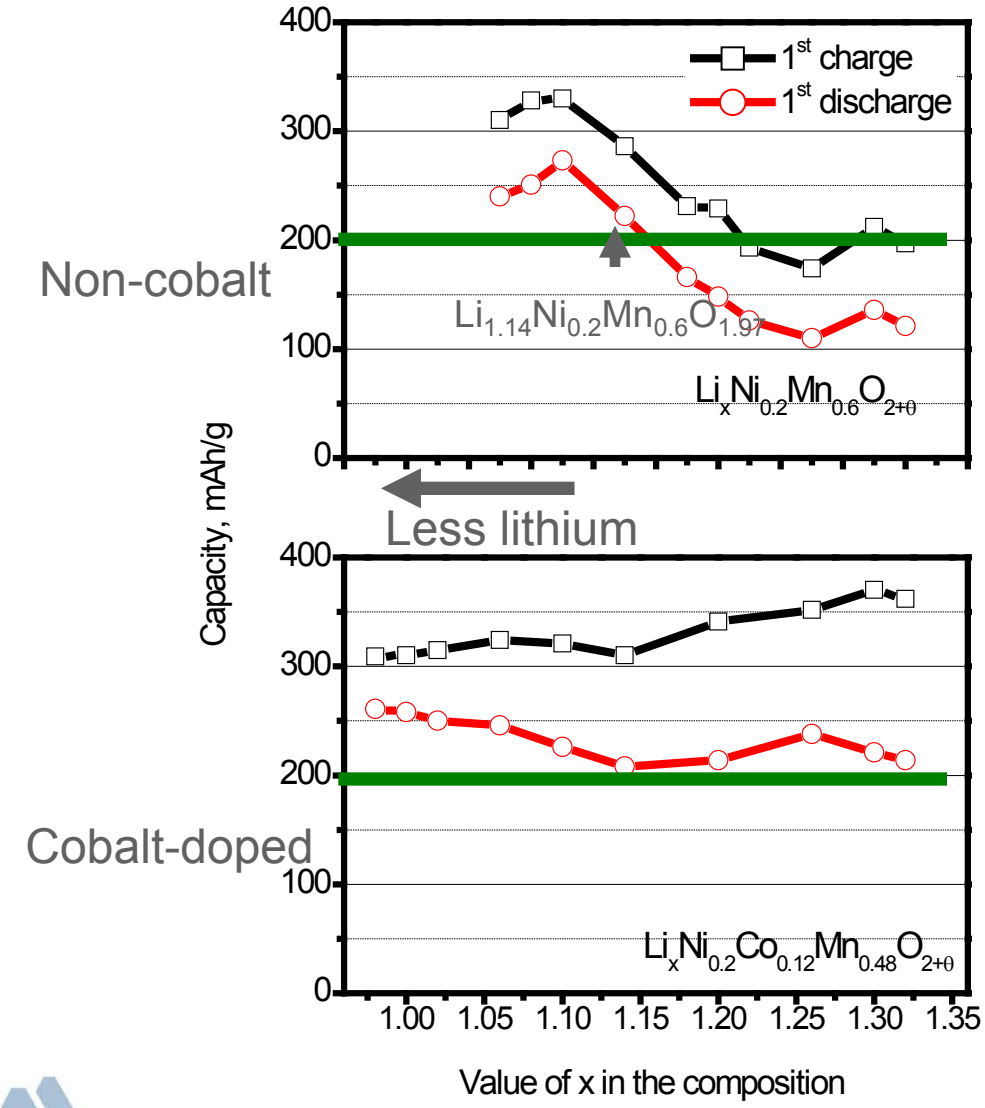








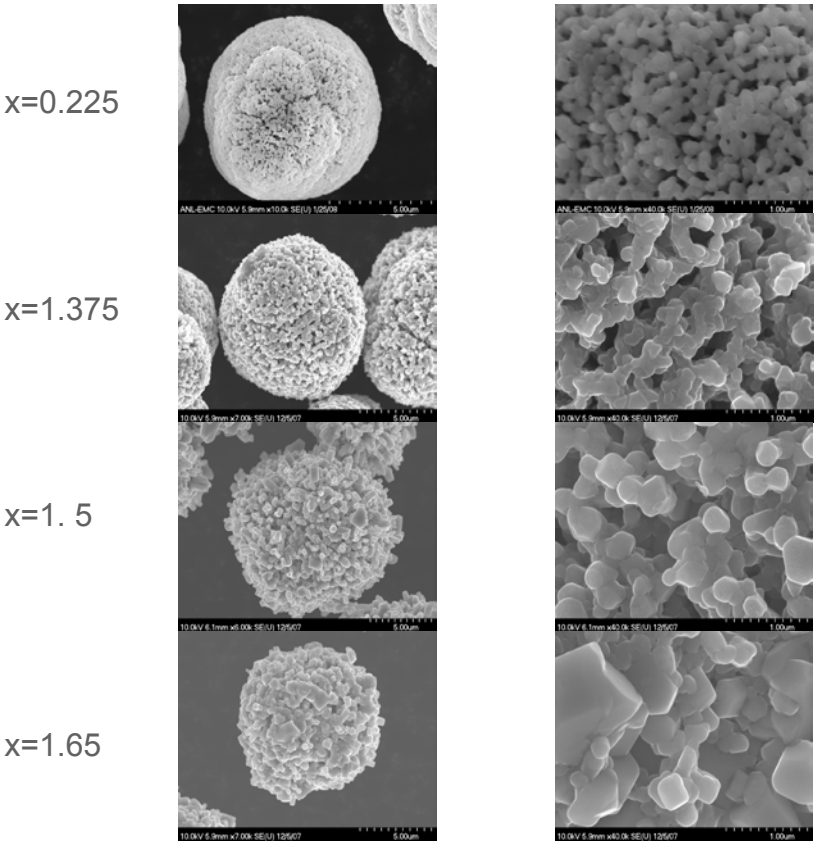
Co- Doped High Energy Cathode shows Better Reproducibility



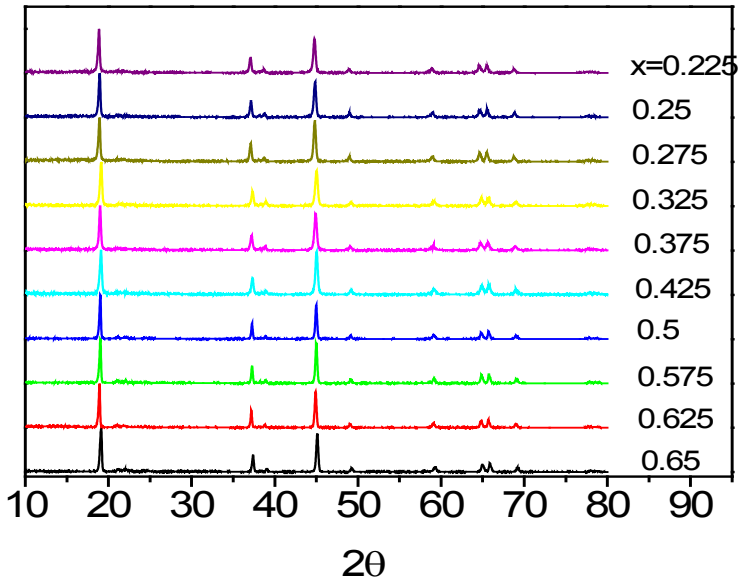
Capacity is sensitive to lithium concentration.

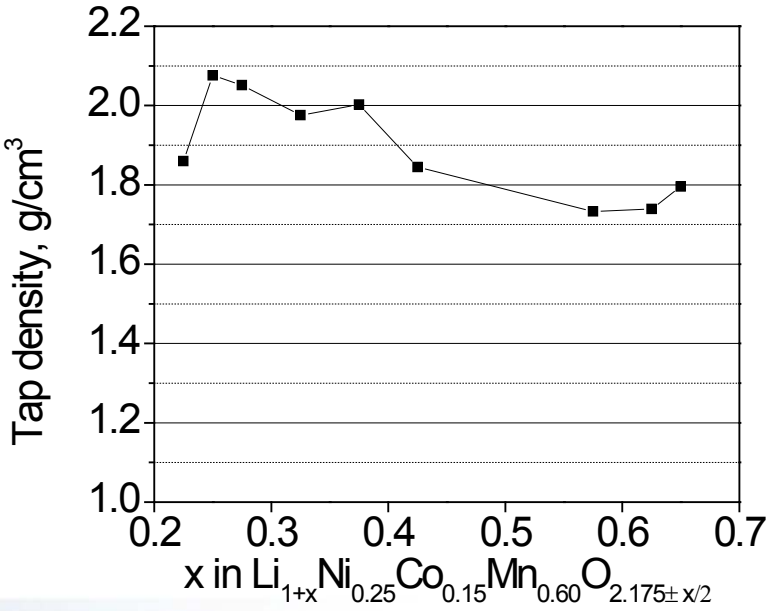
Capacity is Less sensitive to lithium concentration.

Optimization of Co-doped High Energy Cathode



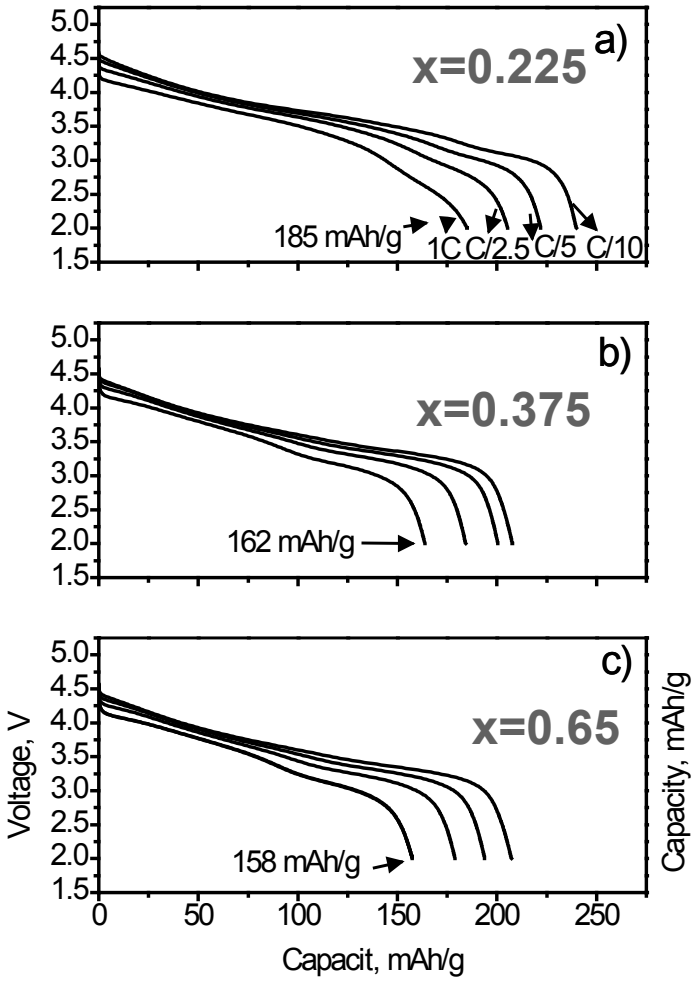
$Li_{(1+x)}Ni_{0.25}Co_{0.15}Mn_{0.6}O_{(2.175+x/2)}$
(x = 0.225-0.65)

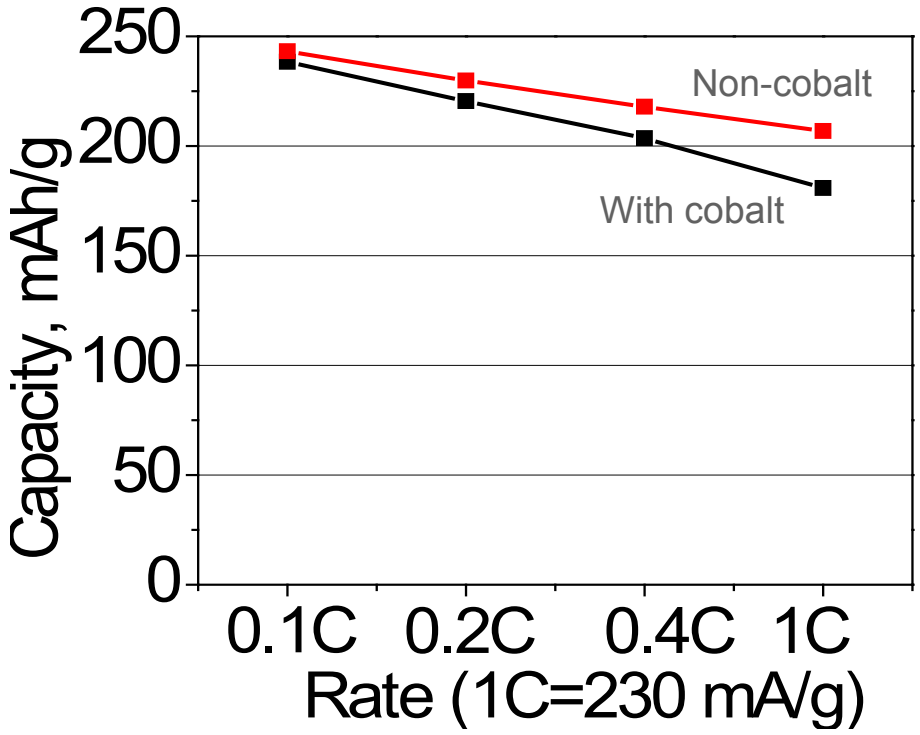




primary particle size depend on lithium content in the material

Electrochemical Performance of Co-doped High Energy Cathode

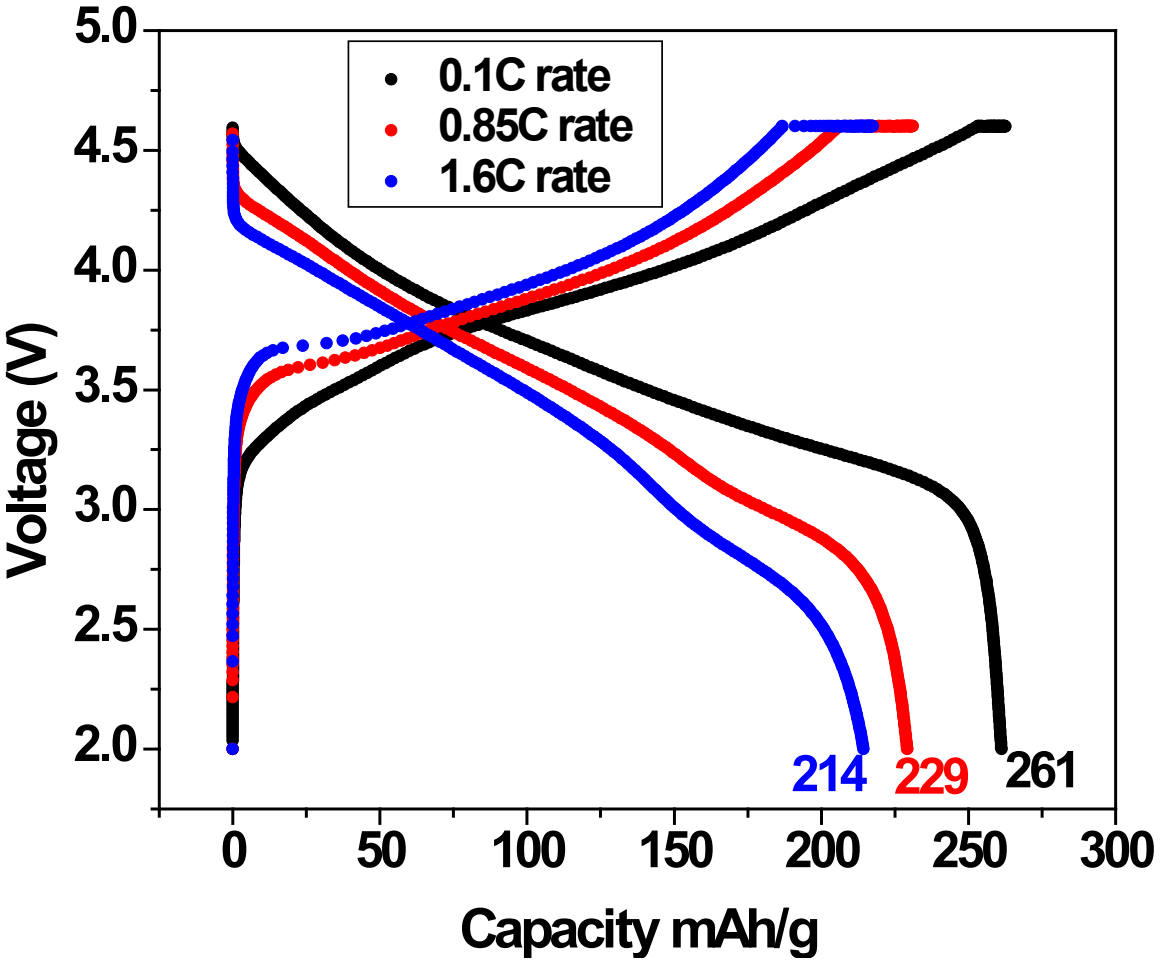




Cobalt-doped materials showed slightly lower rate compared to the best non doped material

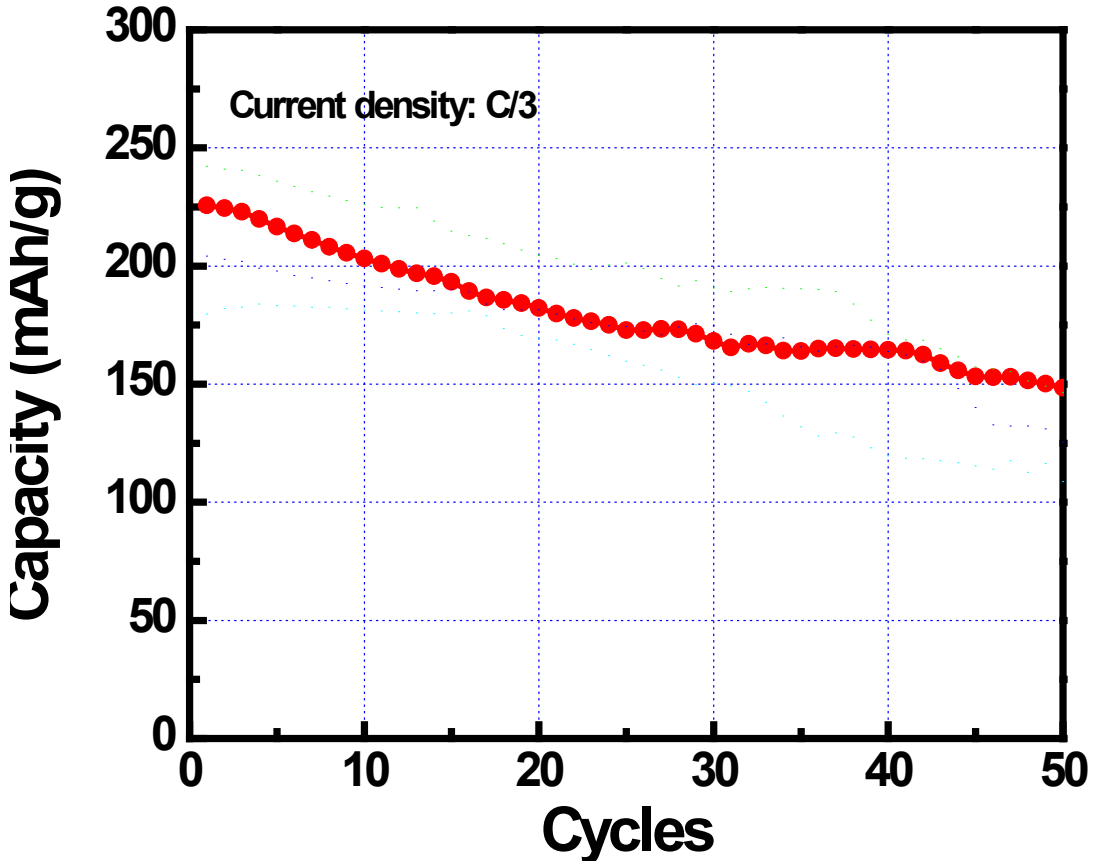
$Li_{(1+x)}Ni_{0.25}Co_{0.15}Mn_{0.6}O_{(2.175+x/2)}$
(x = 0.225-0.65)

Surface Modification of Co-doped high energy cathode Can Significantly Improve the Rate of the Material



Patent is in the process of being filed.

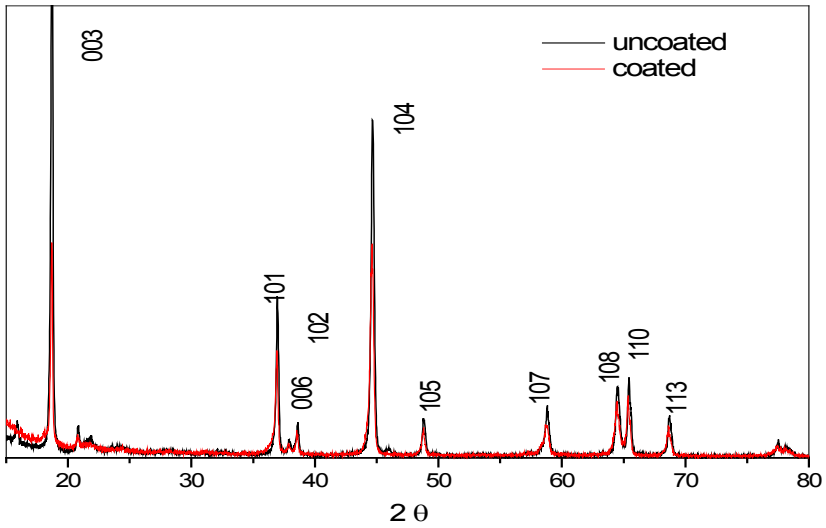
Cycling Performance of Co-doped High Energy Cathode *vs.* Li/Li^+

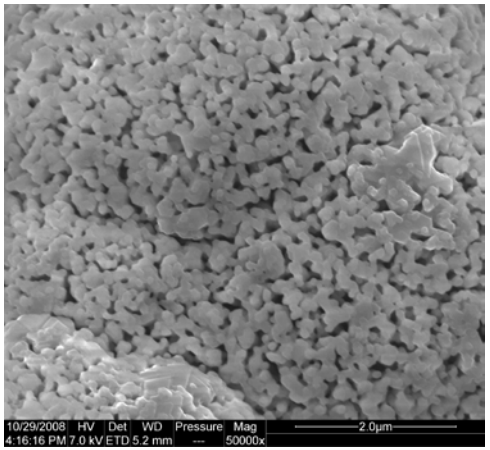


With Co-doping, the capacity of the cell fade during cycling

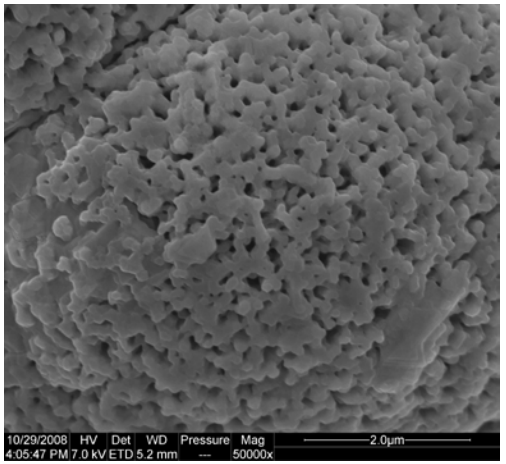
AlF_3 Coated Co-doped High Energy Cathode

Coating the cathode with nano-AlF_3 film can stabilize the interface and prevent surface reaction at high voltage and high temperature operation

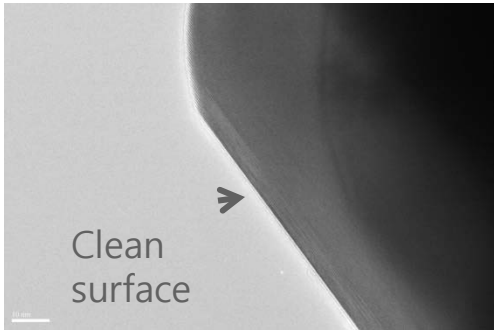




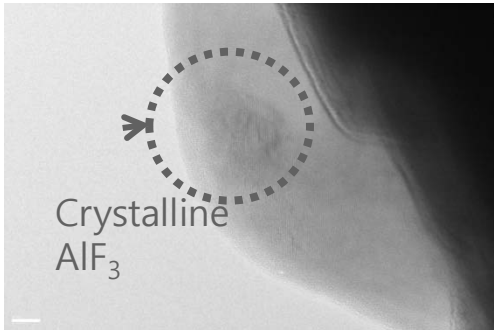
uncoated



2 wt.% AlF_3-coated

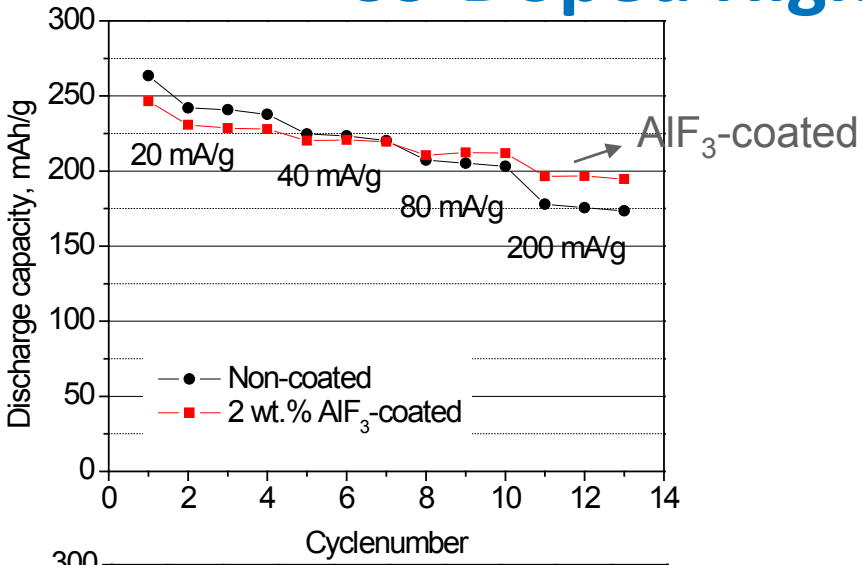


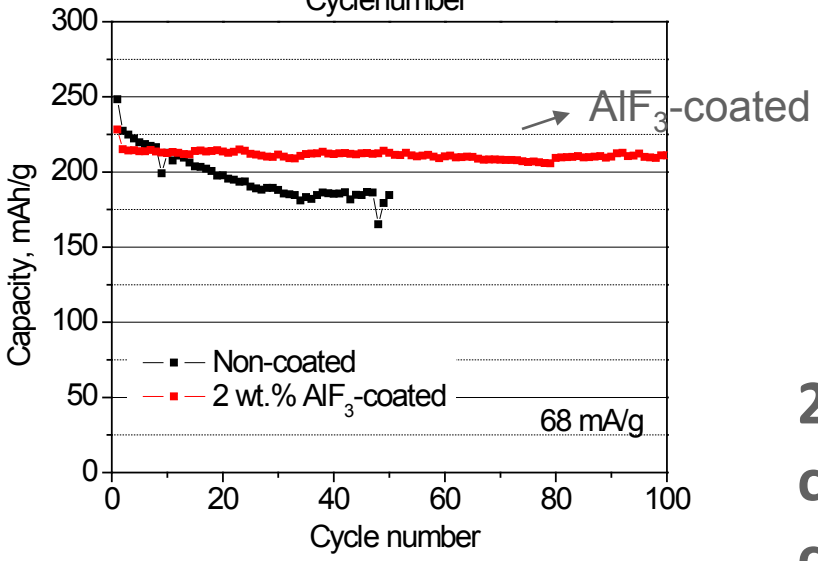
None **coated**

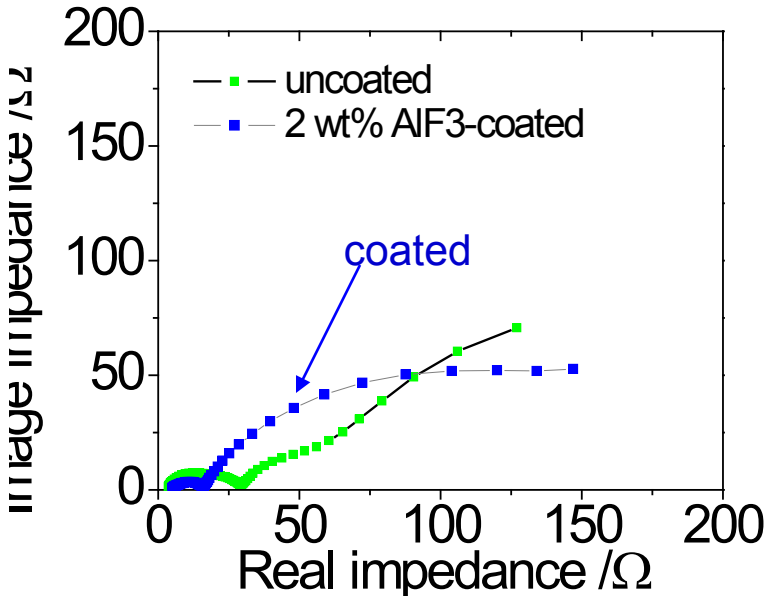


AlF_3 **coated**

Effect of AlF_3-Coating on Rate and Cycle Life of Co-Doped High Energy Cathode

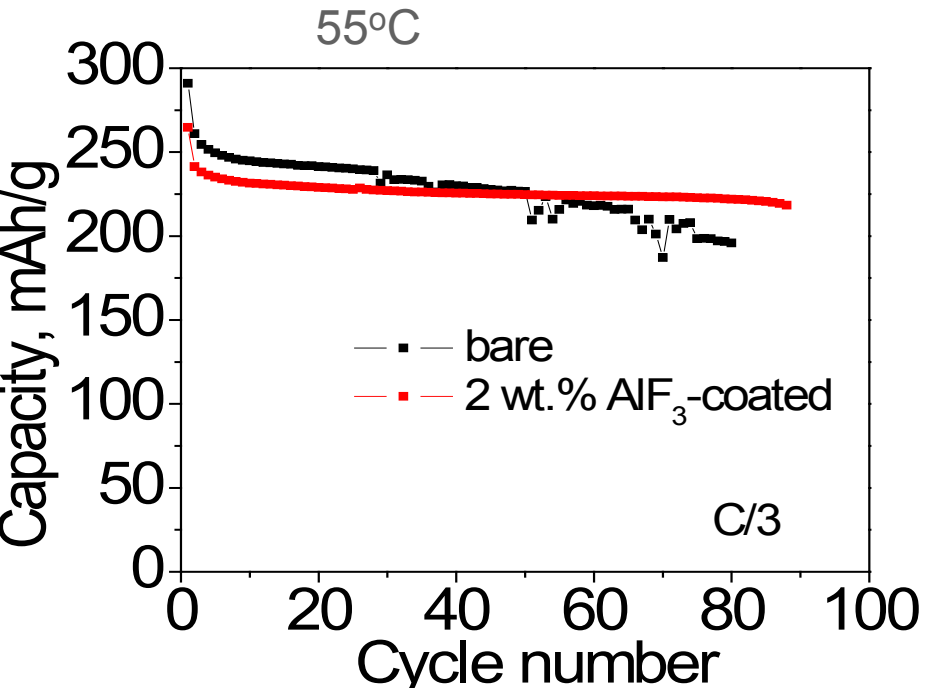


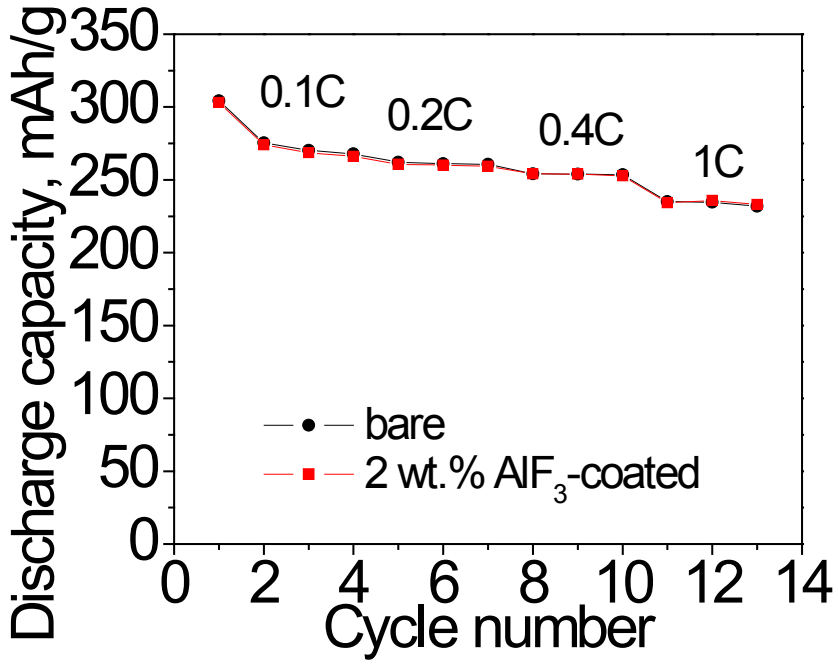




2 wt.% AlF_3 coating on cobalt-doped cathode improved the rate, and the cycling performance.

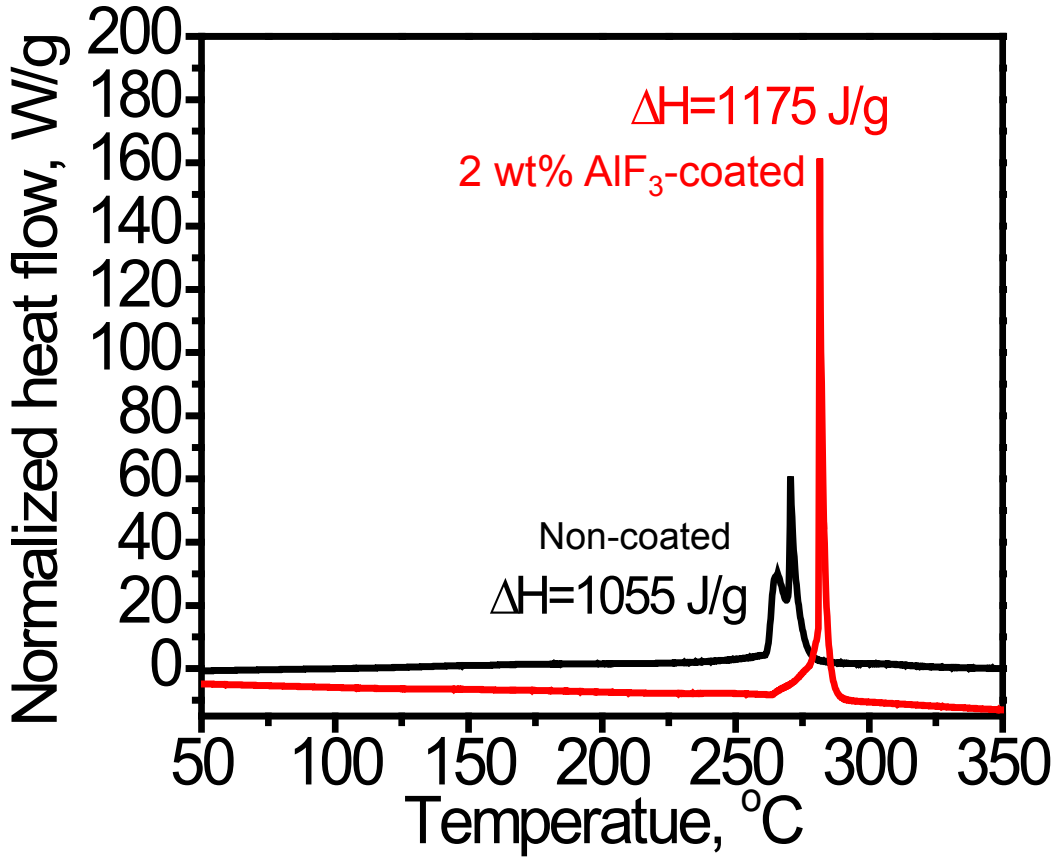
Effect of AlF_3-Coating on Rate and Cycle Life of Co-Doped High Energy Cathode at 55°C





2 wt.% AlF_3-coated $Li_{1.395}Ni_{0.1875}Co_{0.125}Mn_{0.6875}O_{2.4475}$ showed improved cycling performance at 55°C performance.

Effect of AlF_3-Coating on the Safety of High Energy Cathode



Summary

✓Continuous co-precipitation process based on carbonate precursors was developed. Resulting high energy composite cathode shows:

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

✓Lithium concentration on cathode material can influence the material morphology and performance

✓ Performance of none cobalt doped cathode is sensitive to lithium concentration (reproducibility issues)

✓Co-doped cathode is less sensitive to lithium concentration (reproducibility is good when scaling up the material)

✓ Surface modification of Co-doped cathode shows the highest power ever reported in this composite cathode material (215mAh.g at 1.6C rate)

✓AlF_3 coated Co-doped cathode shows excellent cycle life and improved power at 55^{o}C

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
✓Further optimize the composition by varying the Mn/Ni ratio to enable the Co-free composite material, Initial work shows some reproducibility
✓Explore further the surface modification of high energy cathode to improve the power capability
✓Explore new process for carbon coating of high energy cathodes.
✓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.
✓Work with Toda & BASF to scale up these high energy cathode for validation in 18650 cells

Collaborations

- ✓Hanyang University, South Korea
- ✓Brookhaven National Laboratory, USA (
- ✓Iwate University, Japan
- ✓Toda Corporation, USA & Japan
- ✓ECPRO Corporation, Korea
- ✓BASF, USA & Germany