Engineering of High energy cathode material

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Project ID, ES-015

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Overview

Timeline

- Start - October 1st, 2008.
- Finish - September 30, 2014.
- 55%

Barriers

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

Budget

Total project funding: 900K

FY11: 300K
FY10: 300K
FY09: 300K

Partners

- Interactions/ collaborations:
  Y.K. Sun (hanyang University)
- *X.Q. Yang (BNL), Toda.,BASF, ,ECPRO*

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 2011 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)

✓Further optimize the composition for reproducibility & easy scale up. (ongoing)

✓Scale up materials to Kg batch for initial cell build (completed)

✓Improve the rate capability of the material. (ongoing)

FY 2011 plans & schedule

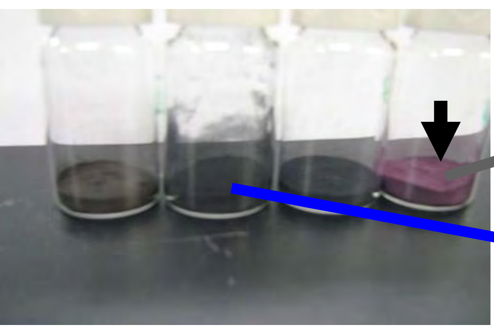
✓Investigate the nano-coating of the material with metal oxide or fluoride to reduce the initial interfacial impedance and stabilize the cathode interface in order to improve the cycle life at elevated temperature (ongoing)

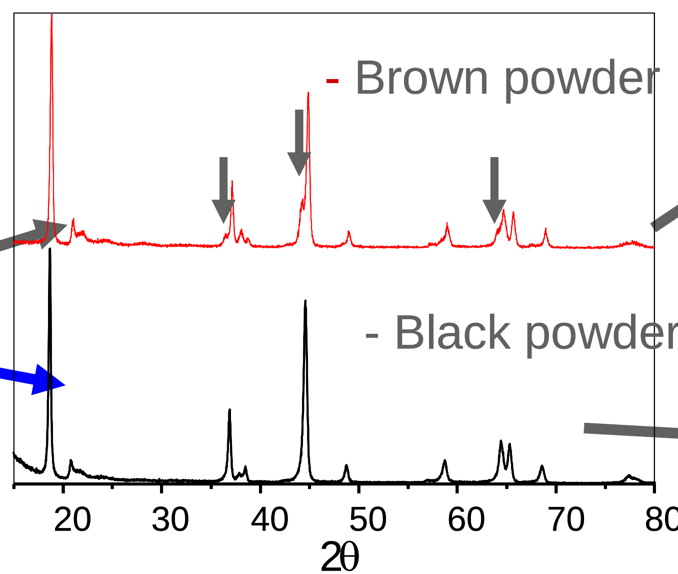
✓Investigate new ways of coating oxides with carbon to improve conductivity of the material and thus rate capability (ongoing)

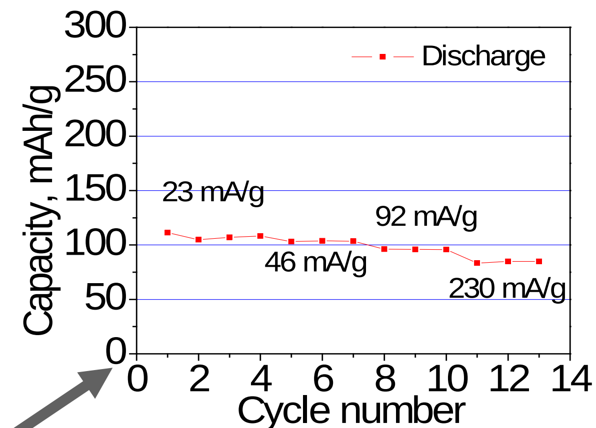
Recent accomplishments and progress

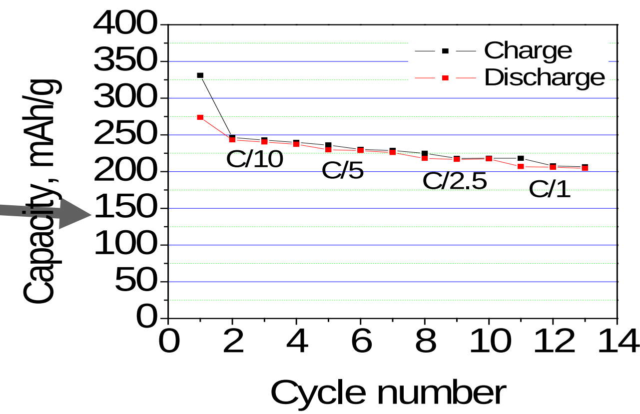
- Developed a new Co-free composition based on Argonne's high energy composite layered cathode $xLi_2MnO_3 \bullet (1-x)LiNiO_2$.
- Optimized the carbonate based co-precipitation process and composition to obtain high packing density with very high reproducibility.
- Validate the improvement of rate and cycling stability at high temperature using Al_2O_3 coating by ALD process.
- Developed a new carbon coating process on high cathode material that an improvement in performance of the material .

The performance of high energy composite cathode (HEM) with Low ratio of Ni is very sensitivity to the ratio of lithium in the structure $Li_{1+x}Ni_{0.25}Mn_{0.75}O_{2.25+x/2}$



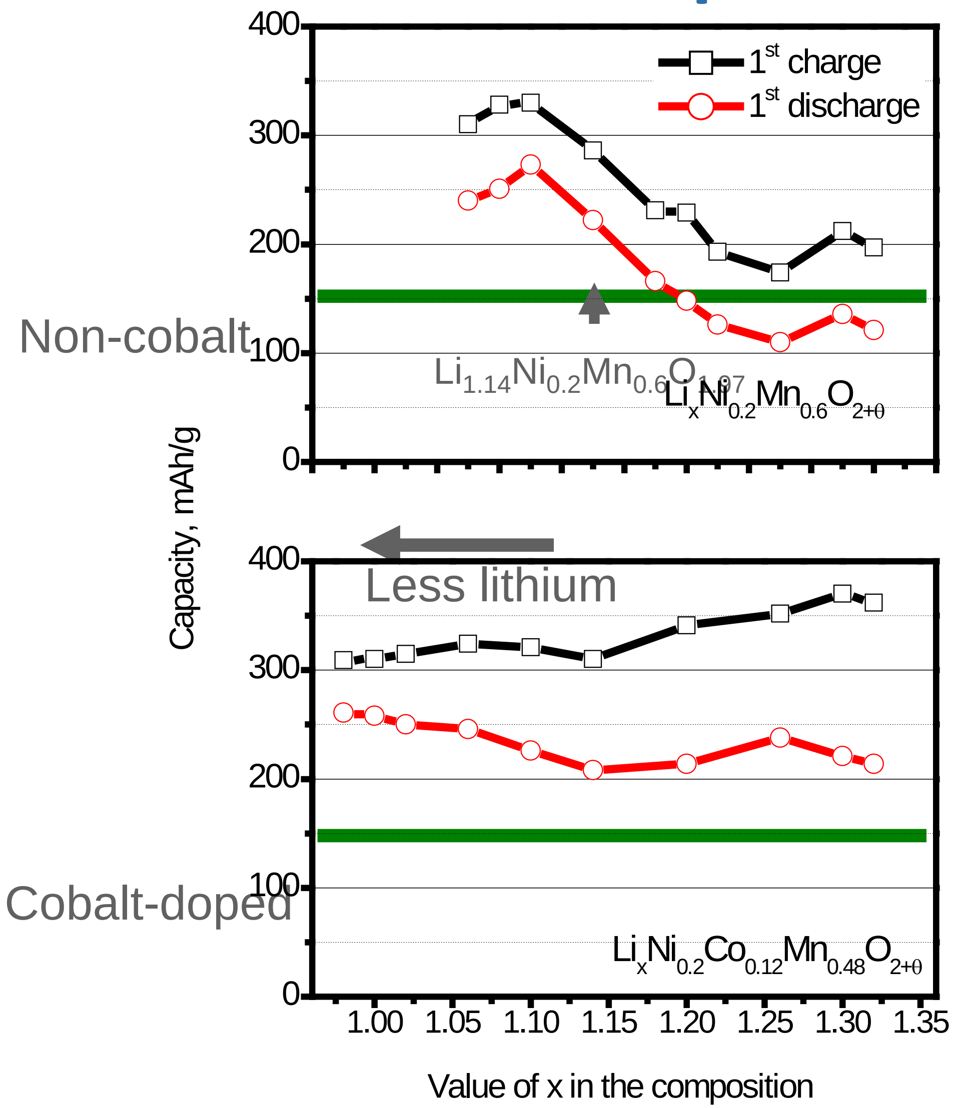






- Two materials with the same composition ($Li_{1.10}Ni_{0.2}Mn_{0.6}O_{1.95}$) and the same process of preparation shows different colors and different rates and cycling performance (difficult to reproduce Co-free and low Ni ratio -high energy composite material)

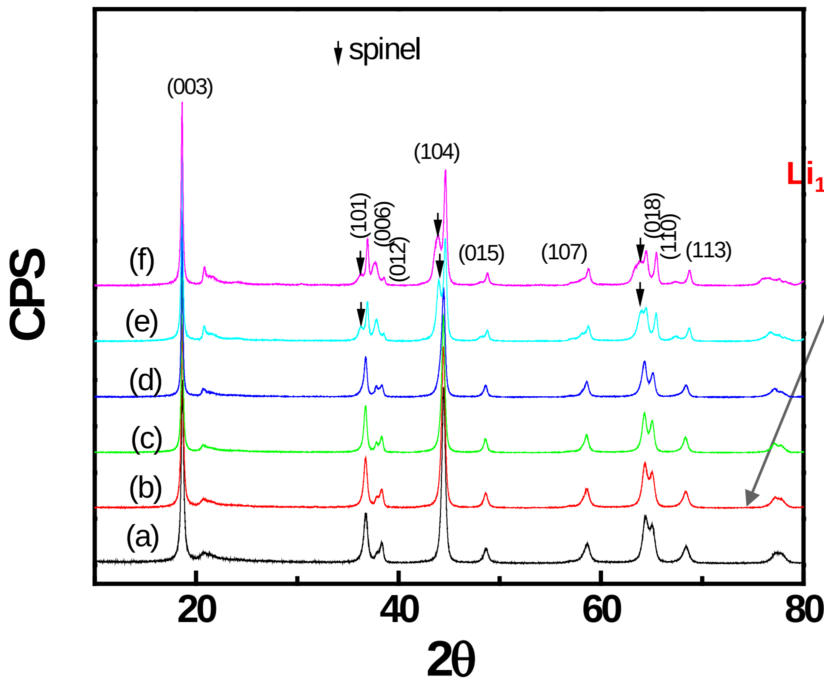
Co- Doped High Energy Cathode shows Better Reproducibility



Capacity is sensitive to lithium concentration.

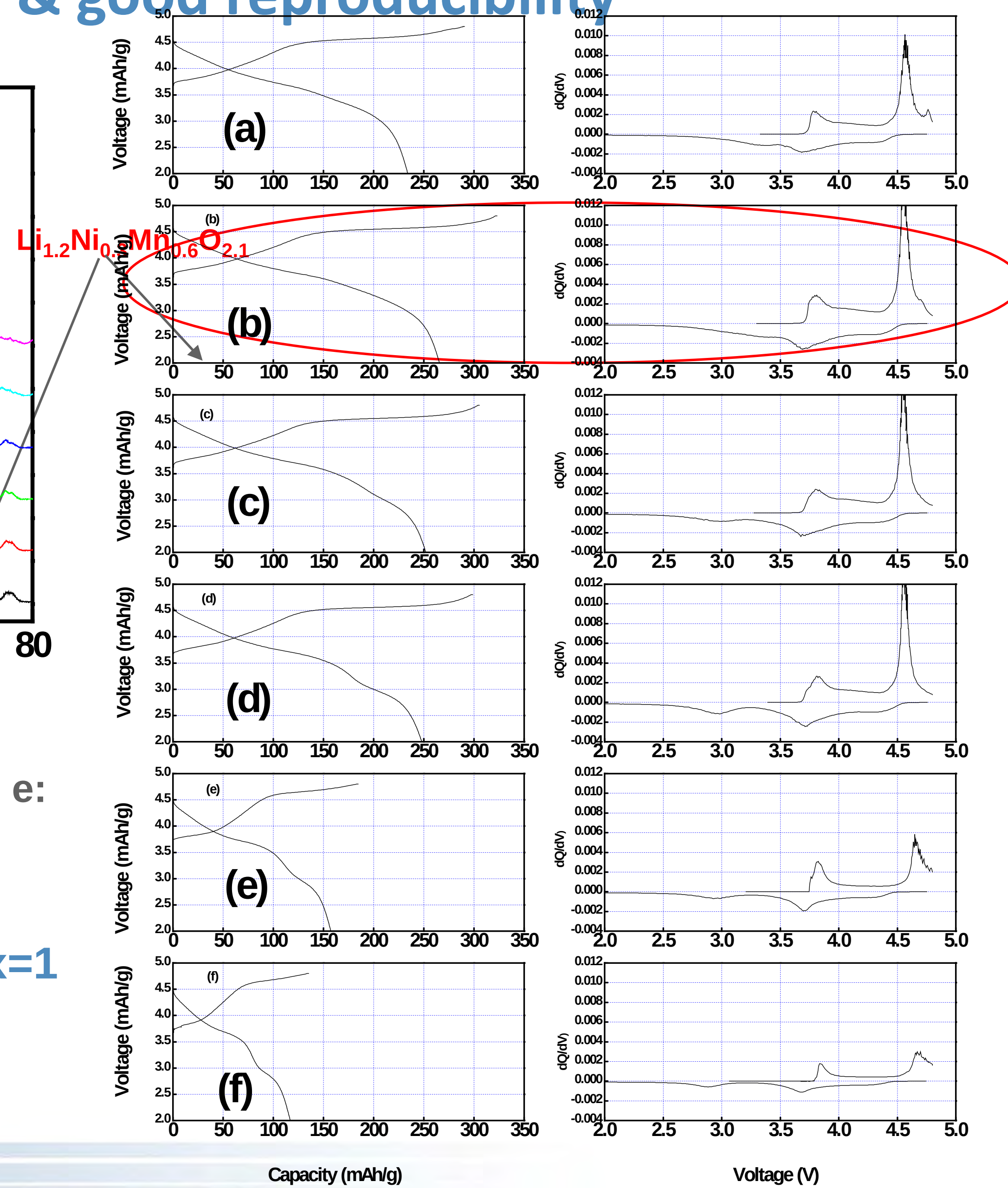
Capacity is Less sensitive to lithium concentration.

High energy cathode material (HEM) with 30% Ni shows excellent performance & good reproducibility



$Li_{1.2*x}Ni_{0.3}Mn_{0.6}O_{2.1}$

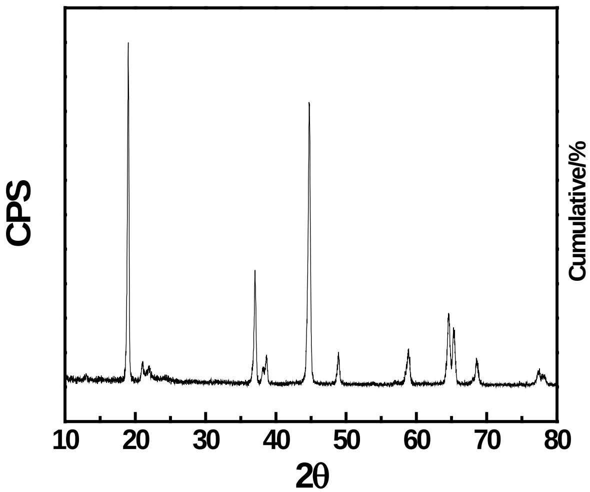
(a: x=1.03, b: x=1.0, c: x=0.97 d: x=0.94, e: x=0.91 f: x=0.88)

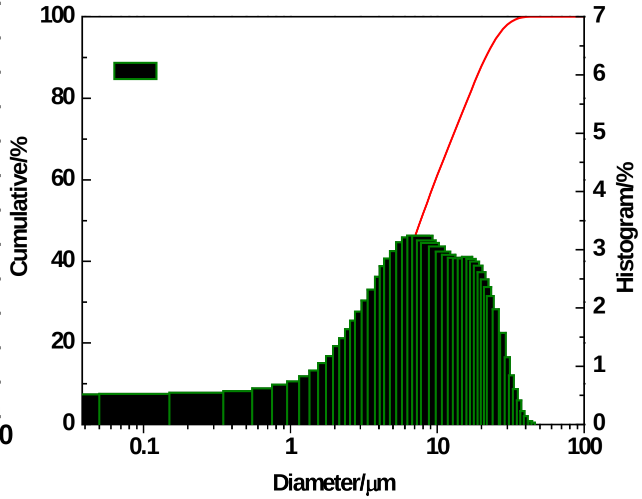


- High capacity was obtained with x=1

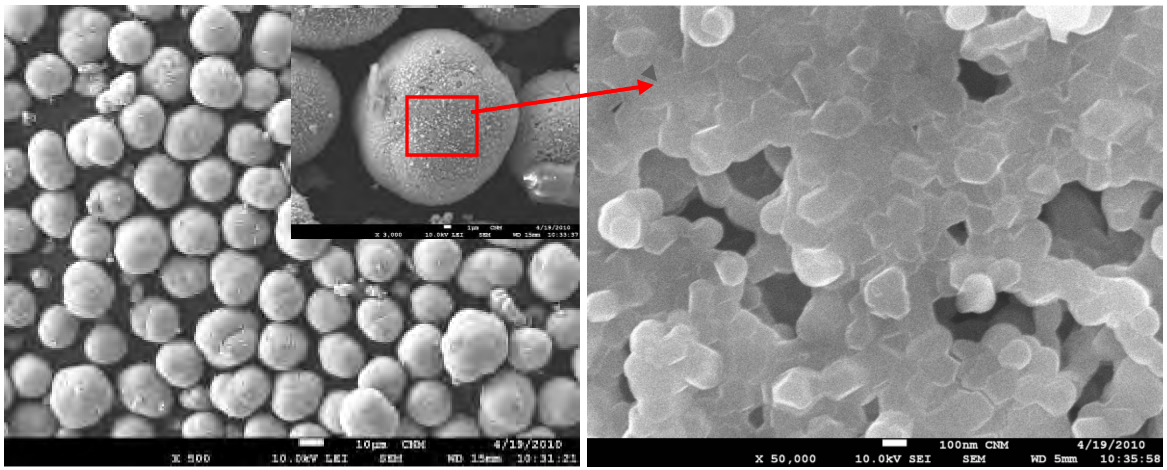
($Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$)

Structure & morphology of $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$





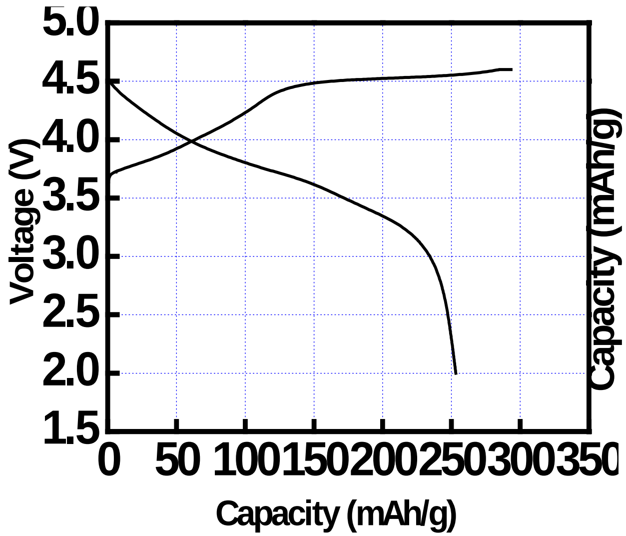
Target material	$Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$		
	element	Wt%	Mol ratio
ICP results	Li	8.52	1.23
	Ni	17.3	0.29
	Mn	32.6	0.59
	Li/(Ni+Mn)		1.38
impurity	Na	0.53	0.023
	S	0.15	0.0046
	Li1.23Ni0.29Mn0.59O2.1		

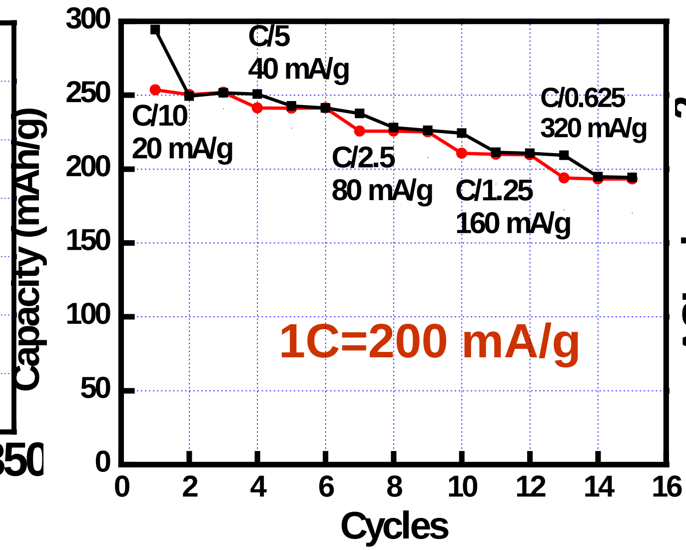


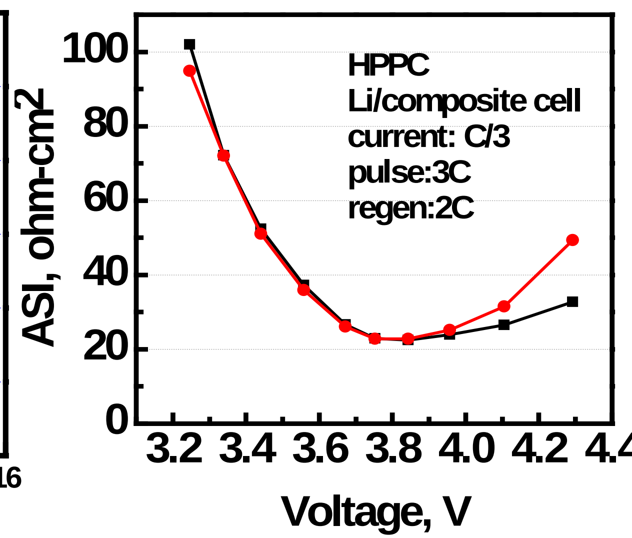
- Pure phase is obtained
- Uniform spherical & dense partic distribution
- Secondary particle: About 10 µm
- Primary particle: about 100 nm
- Average particle size: D50: 10 µm

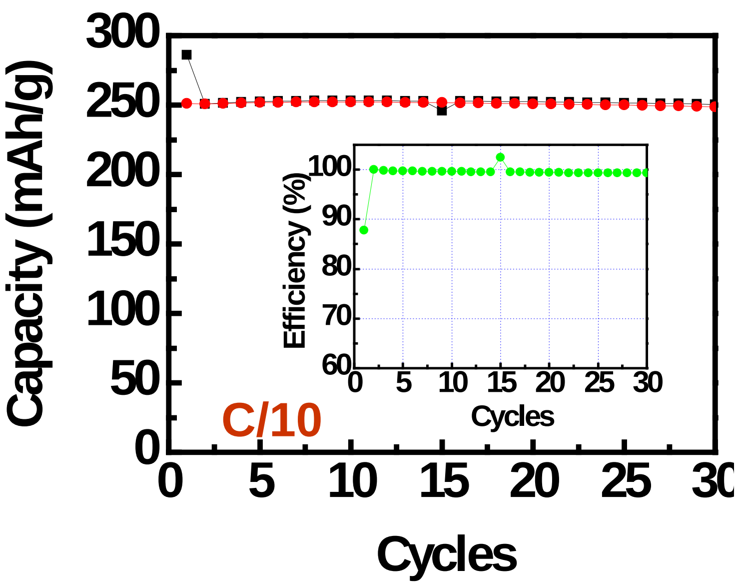
Co-Free high energy cathode material was prepared successfully with high reproducibility

Electrochemical Performance of $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$





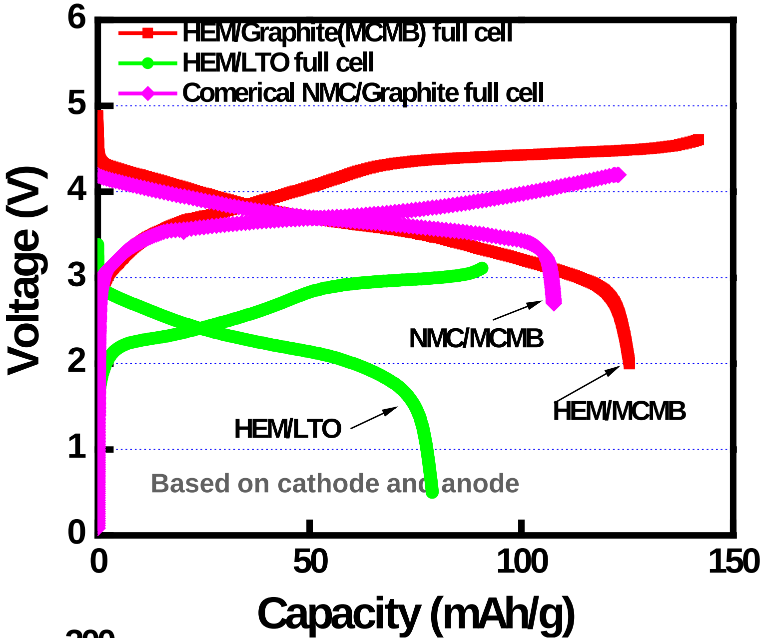


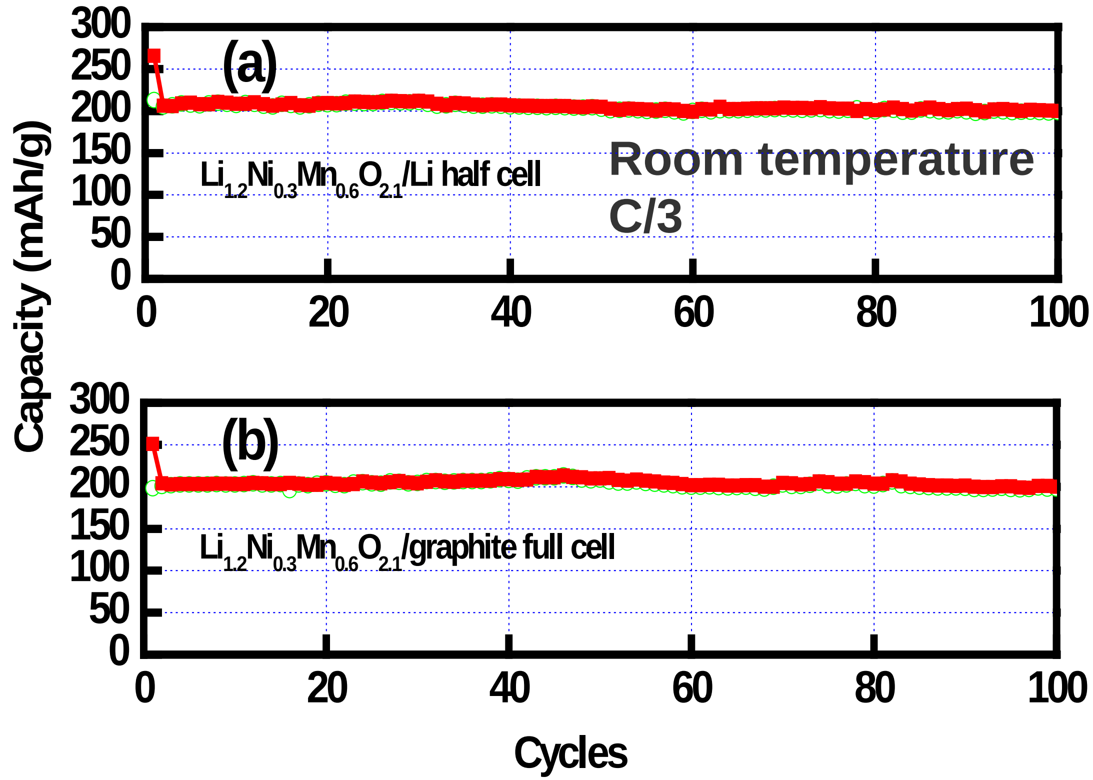


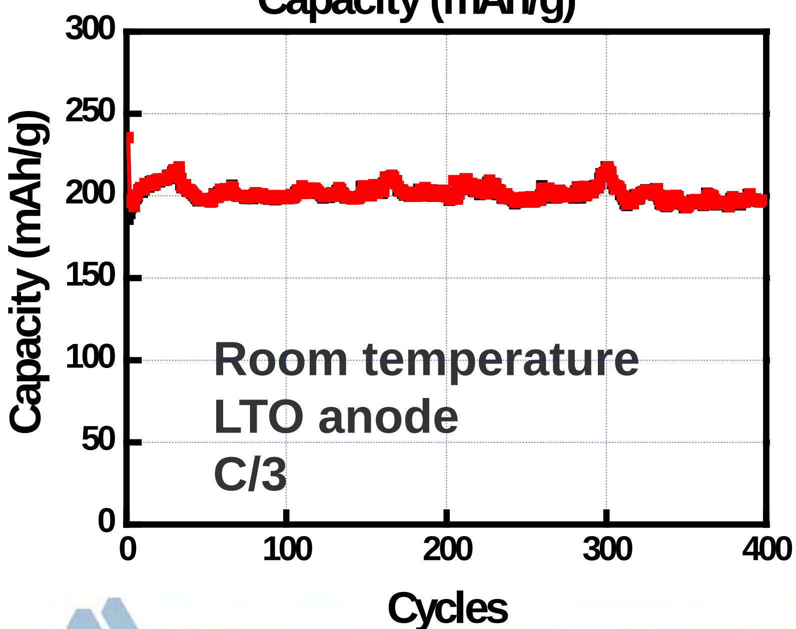
	Char. Cap.	Dischar. Cap.	Effic.	Mean voltage
C/10	294	253	86.0%	3.7

- High first charge/discharge efficiency
- High capacity
- Good rate capacity
- Low ASI value
- Good cycle performance

Cycling Performance of $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$

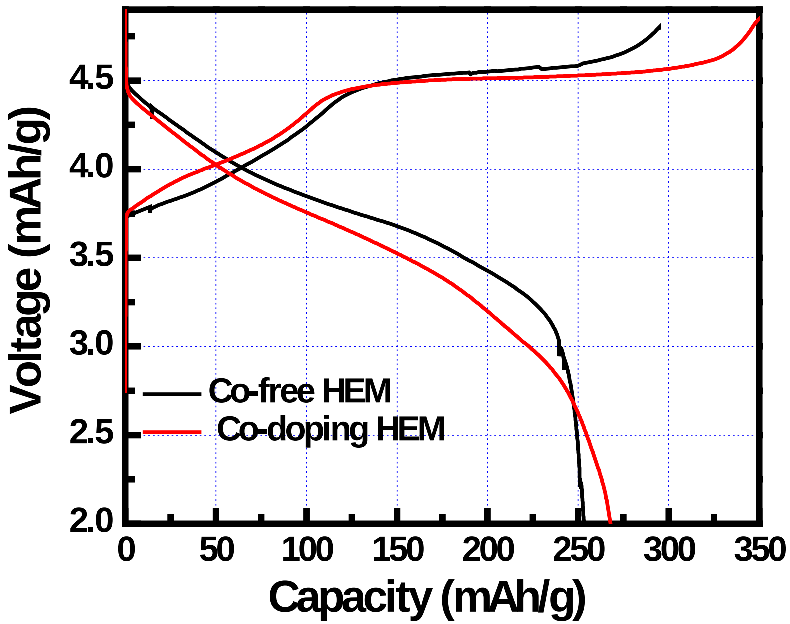


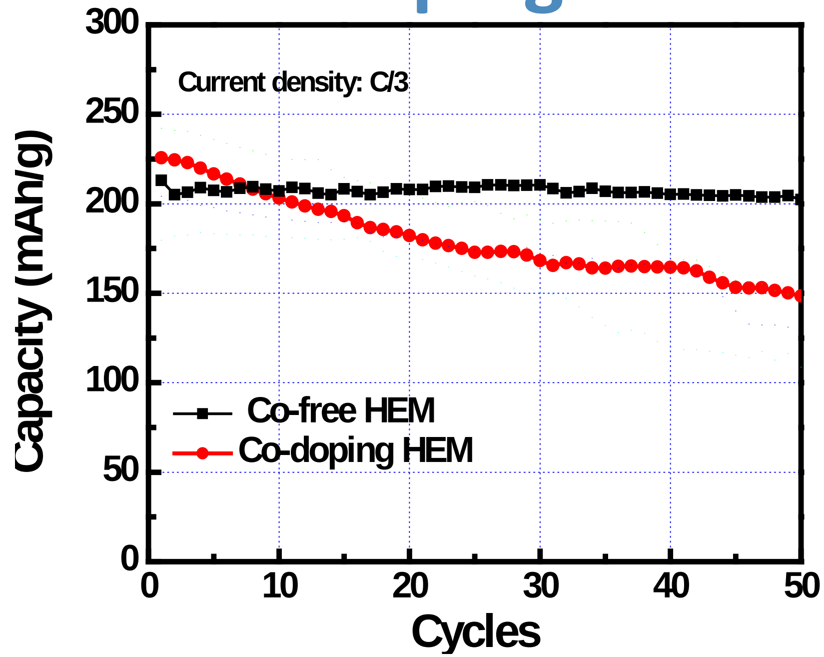




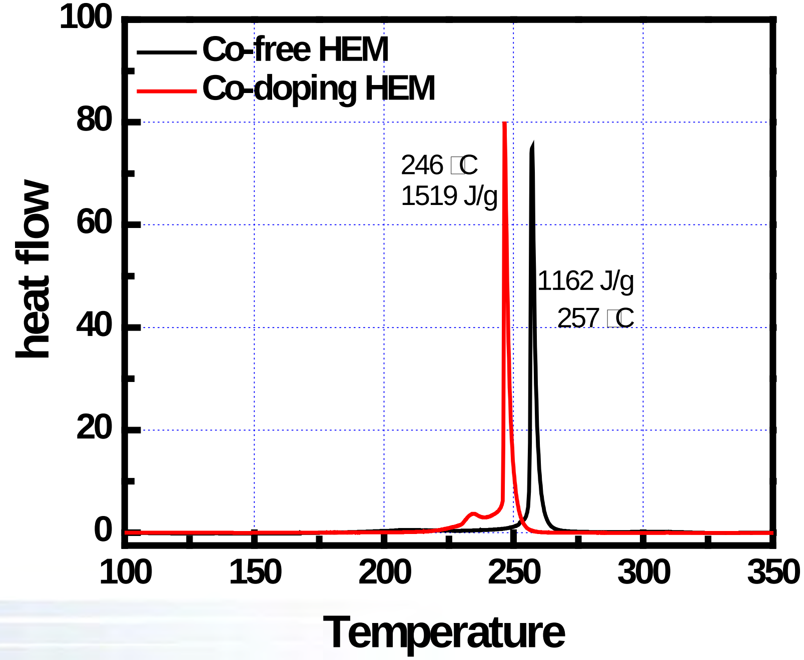
- High rate capability over 200 mAh/g at 1/3 C rate
- good cycle life using Li metal, and graphite as anode
- Excellent cycle life using LTO as anode

Comparison of Co-free and Co-doping HEM





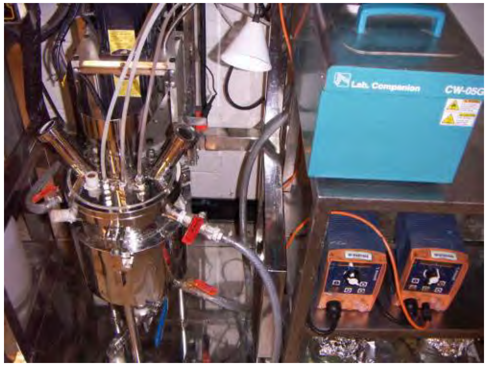
C/10	Cap.	Aver. Volt.	Effic.
$Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$	253	3.70	86.0%
$Li_{1.2}Ni_{0.175}Co_{0.1}Mn_{0.525}O_2$	267	3.60	76.5%

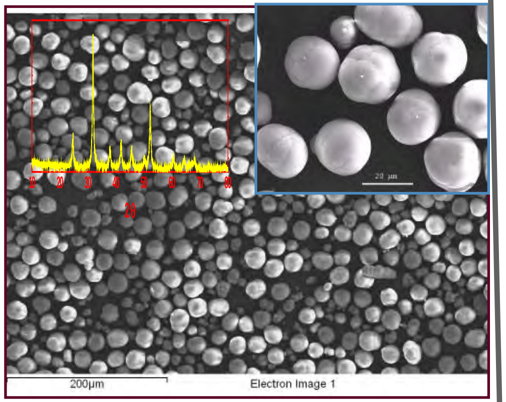


- **Co-free HEM shows stable cycle life and better thermal stability than Co-doped HEM**

$Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ material was scaled up to Kg level with High reproducibility

Precursor scale-up process





4 L Continuous stirred-tank reactor

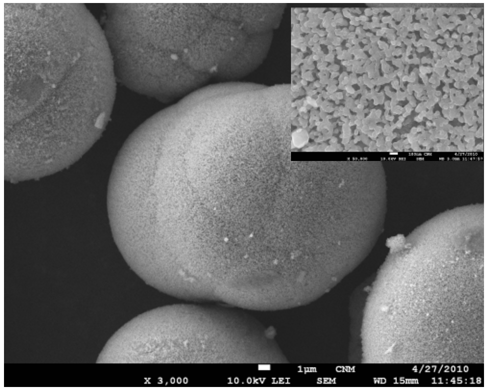
100 gram/hour of precursor can be obtained
Precursor preparation is a continuous process
The amount is determined by the time

Product scale-up process
Solid state reaction

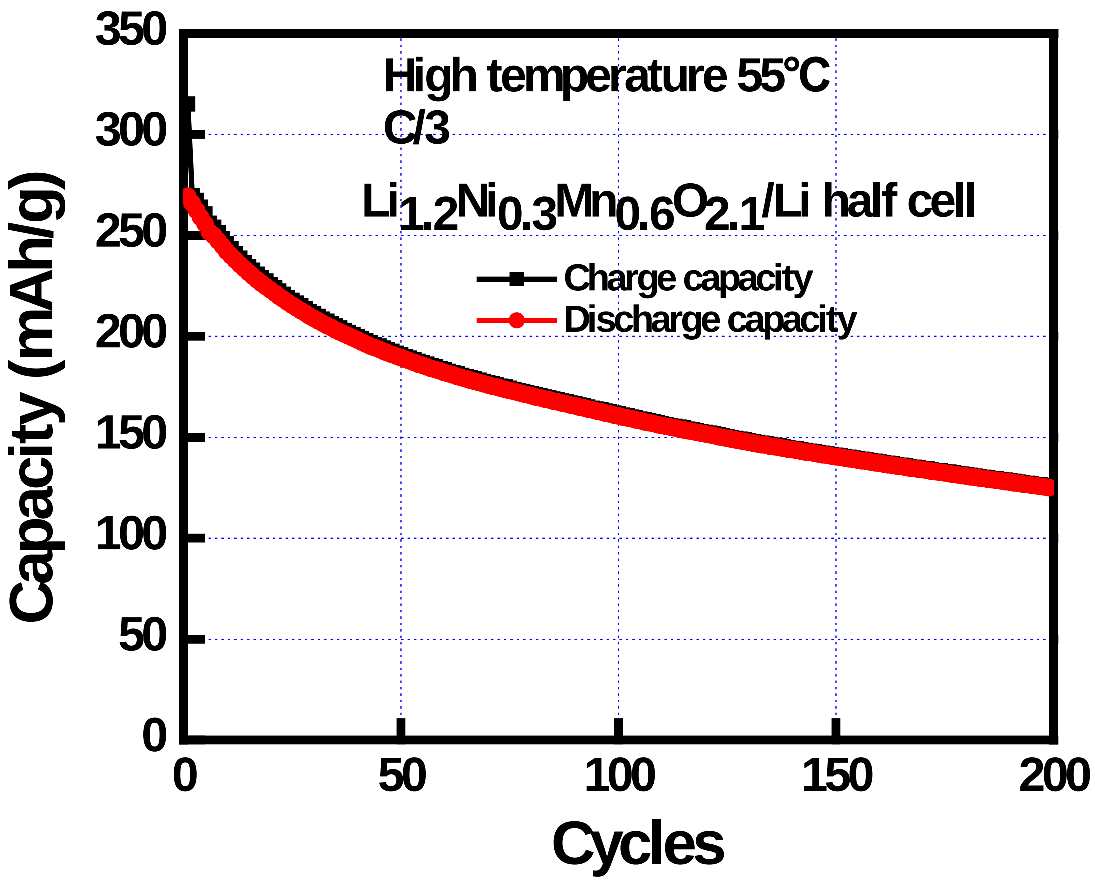
Scale up

5 gram

1 kilogram

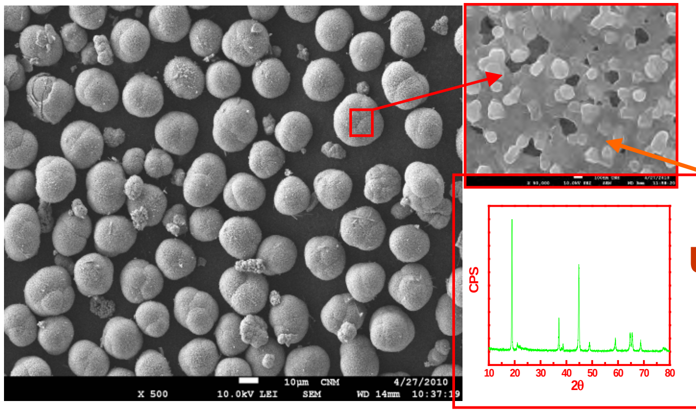


Electrochemical performance of Co-free HEM at HT

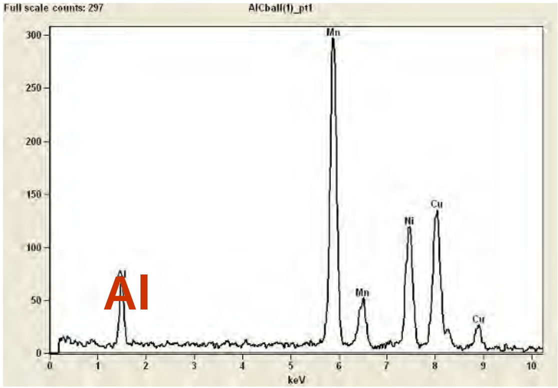


At high temperature, the capacity of the cell based on Co free HEM ($Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$) fade during cycling

Al_2O_3 coating on $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ particles by ALD



uncoated

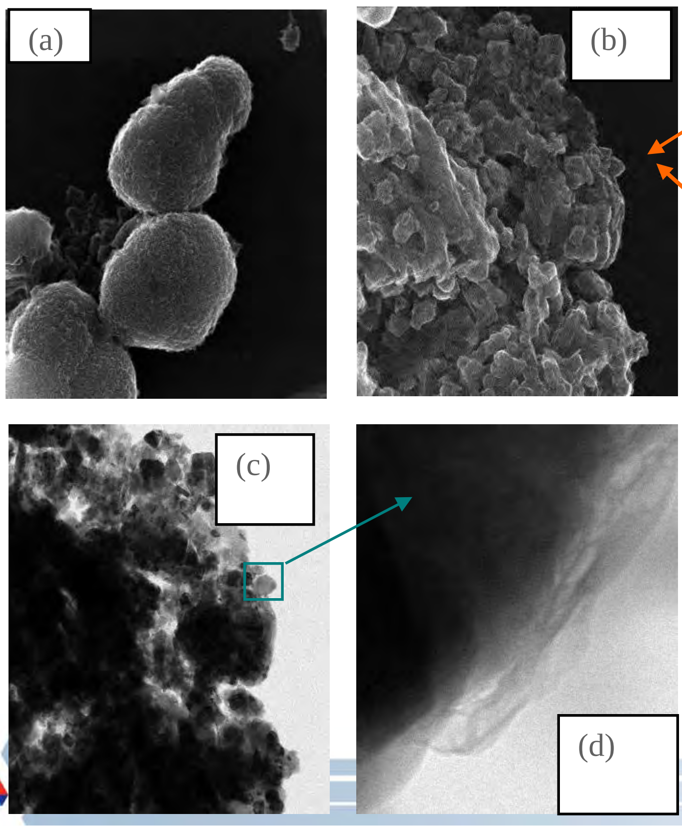


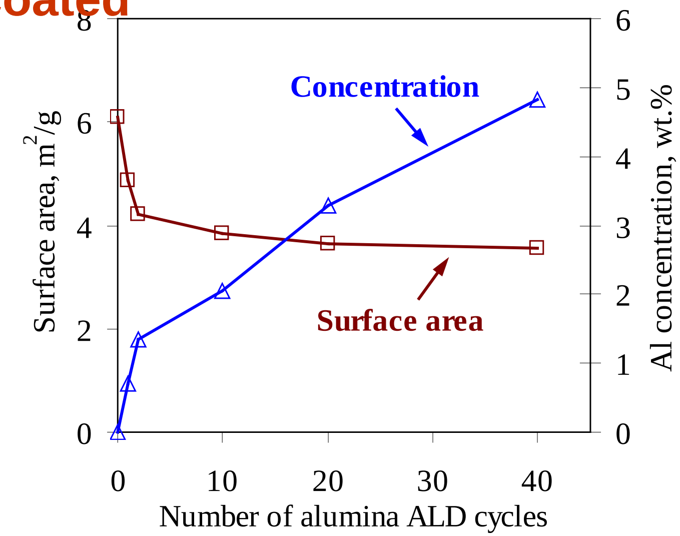
EDS

Al

SEM and EDS show Al_2O_3 coated on the surface of particles

Al_2O_3 coated

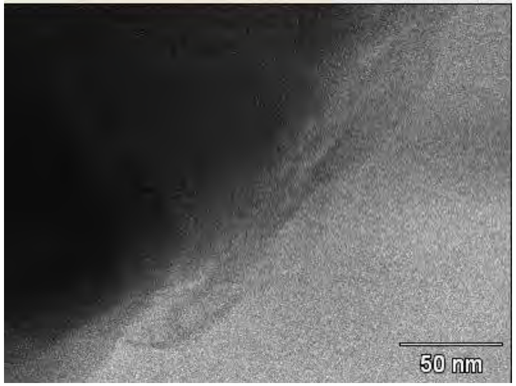




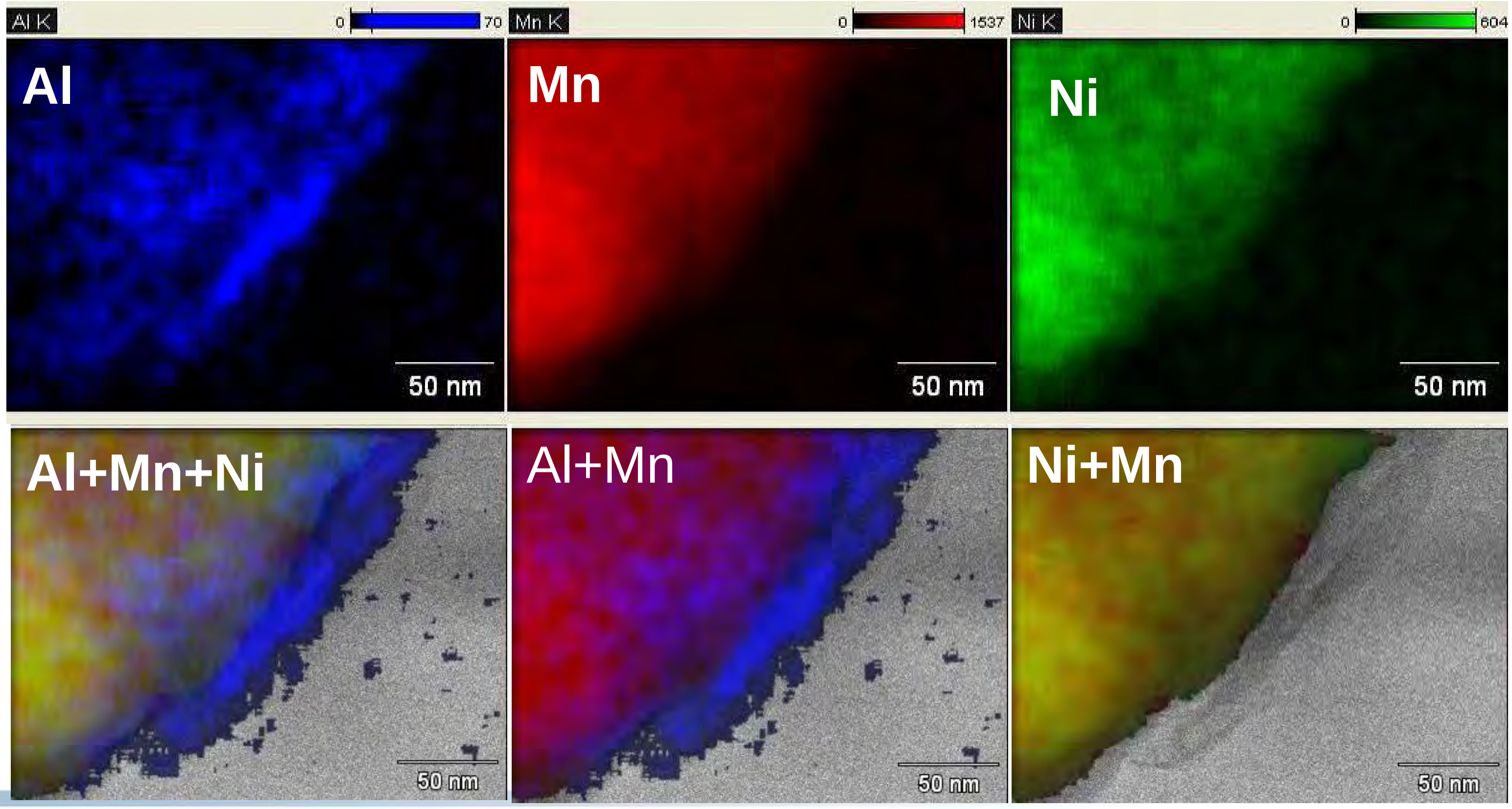
BET

Coated material shows low surface area compared to the non coated material

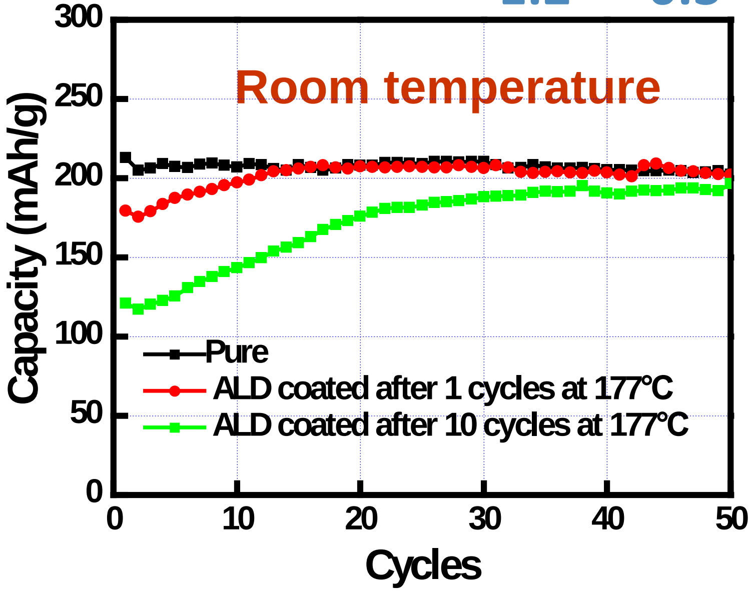
Al_2O_3 coating on $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ particles by ALD



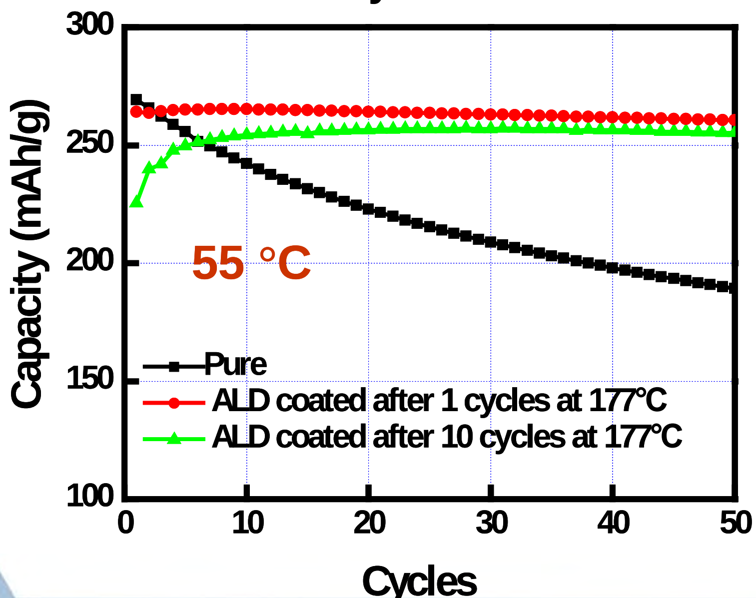
EDS mapping images of Al, Mn, Ni distribution
Al_2O_3 coating by ALD provide uniform coating layer with a thickness of 2 to 5 nm

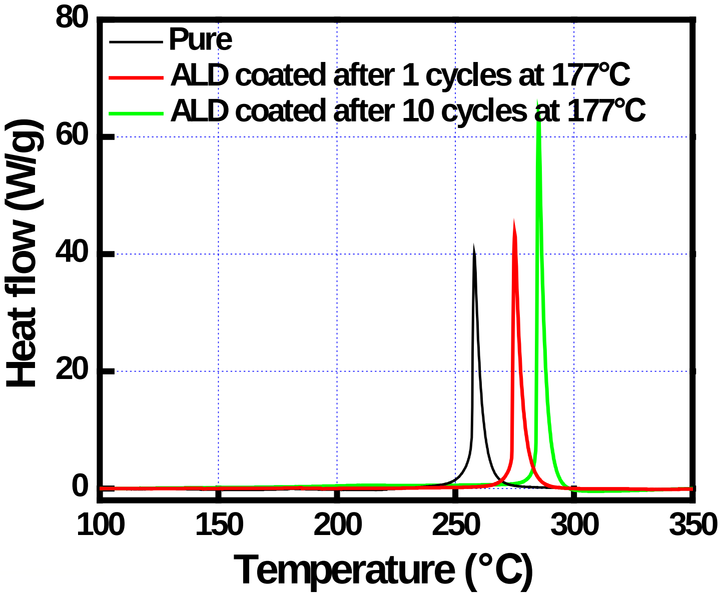


Effect of Al_2O_3-Coating on Cycle Life & safety of ($Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$) Cathode



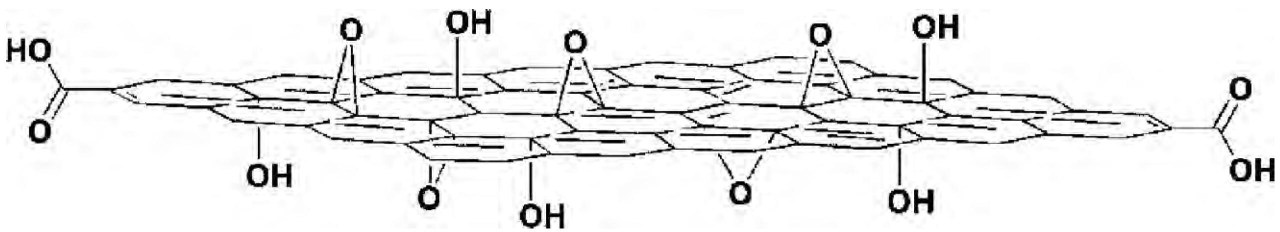
- Coated material shows improved cycling performance at high temperature
- Coated material shows improved abuse tolerance
- Material with thick coating (10 ALD cycles) shows the highest onset temperature by DSC





Carbon coating of Co- doped HEM using graphene

Graphene oxide can be easily dispersed in water.



Preparation:

- Co-doped HEM cathode material is added to a solution of Graphene oxide. The mixture is stirred for 2h and heated at 140ºC until the totality of water is removed. The mixture is then heated in the oven at 250ºC under Ar atmosphere or Ar/H_2 for 2 hours

Carbon coating using graphene

- **Co-doped HEM cathode material surface contains carbon.**

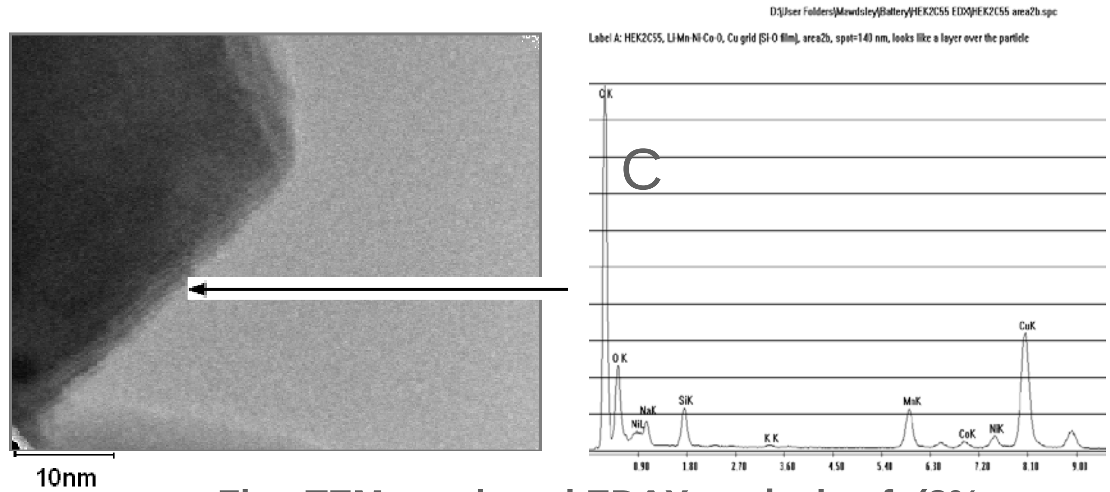


Fig. TEM graph and EDAX analysis of (2% graphene coated $Li_{1.2}Mn_{0.5}Ni_{0.176}Co_{0.1}O_2$

- 2% of the carbon coating is enough to reach higher capacity at high rate.
- The capacity is improved by approximately 15%.

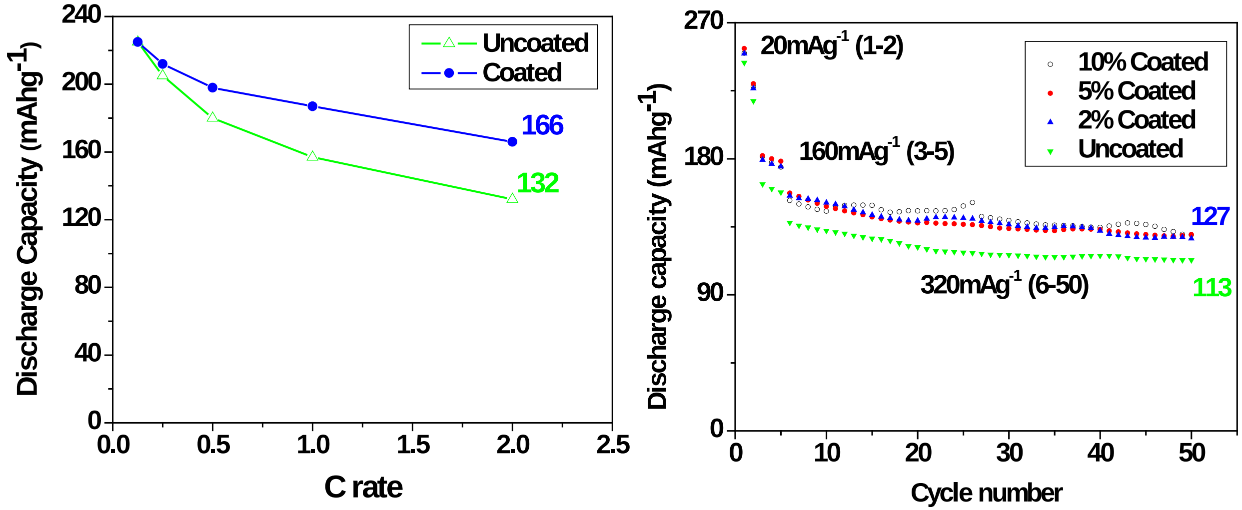


Fig. Rate capability and cycle performance

Summary

✓New $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ composition was found to provide good reproducibility during scale up. This material shows: .

- ✓ Spherical particle morphology
- ✓ Sharp particle distribution for uniform performance
- ✓ Pure structure with no impurities

✓ Performance of Co-free $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ cathode is excellent compared Co-doped HEM with good rate capability, good cycling performance and better safety

✓ Surface modification of HEM cathode with Al_2O_3 using ALD shows good cycle life at 55^{O}C and improved safety.

✓Graphene coating of the high capacity cathode material by using a water dispersed graphene oxide precursor is a new approach to improve further the electronic conductivity of HEM and protect its surface from electrolyte reactivity.

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 Lithium and Ni/Mn ratio to improve the capacity and performance
- ✓Explore further the surface modification of high energy cathode to improve further the power capability
- ✓Optimize the process of carbon coating on HEM to maximize the performance
- ✓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.
- ✓Investigate new ways f surface modification using solid gas phase process