New High Energy Gradient Concentration Cathode Material

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DOE merit review

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Project ID# ES016

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Overview

Timeline

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

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

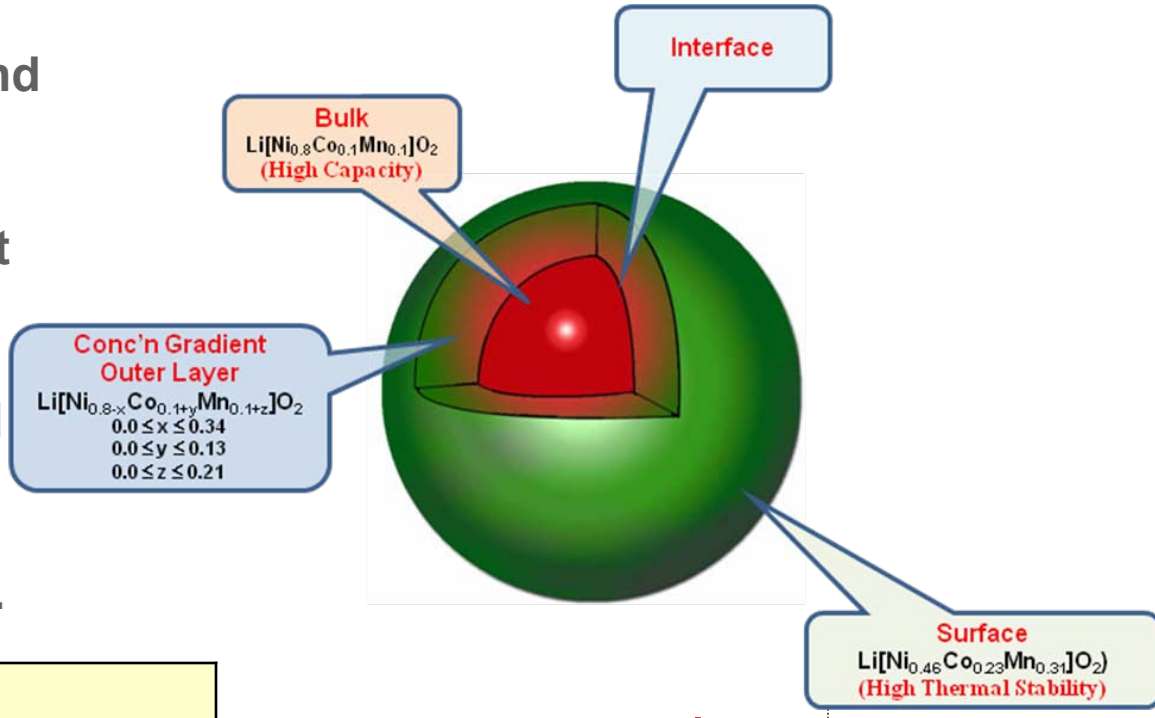
- Interactions/ collaborations:
  Prof. Y.K. Sun (Hanyang University)
  ECPRO, TODA, BASF, BNL
- Project lead: Khalil Amine

Objectives of the work

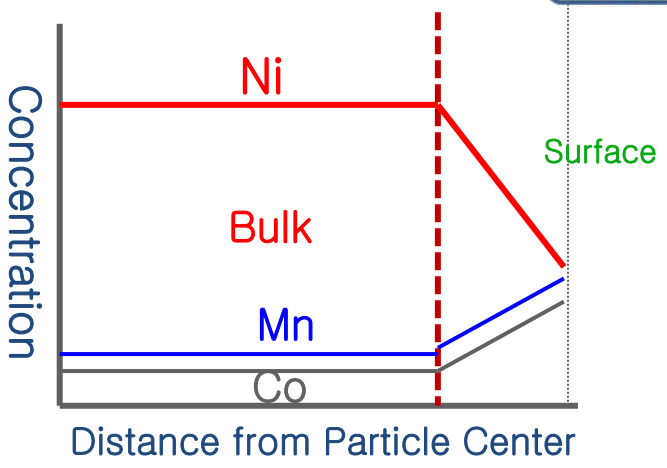
- Develop a new high energy cathode material for 40 miles PHEV applications that provides:
  - Over 200mAh/g capacity
  - Good rate capability
  - Excellent cycle and calendar life
  - Good abuse tolerance

Approaches

Develop a novel high-capacity and safe cathode material, in which each particle consists of bulk material $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$, that provide over 200mAh/g capacity, surrounded by a concentration-gradient outer layer where nickel ions are gradually replaced with manganese ions to provide outstanding cycle life and safety.



Effect of the metal	
Ni	High capacity, Poor thermal stability & cycling
Co	Structural Stability and conductivity
Mn	Excellent thermal stability & cycling, Low capacity



Approaches

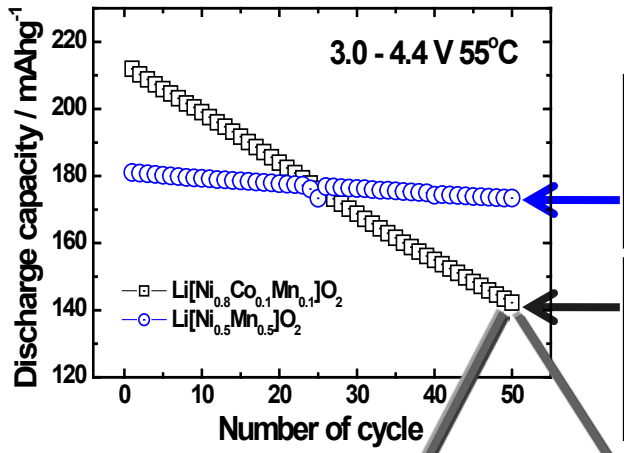
Core: $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$

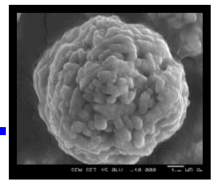
High capacity : ~ 200 mAh/g (3.0 - 4.3 V)

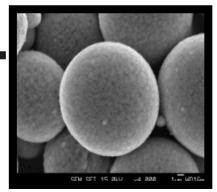
Poor cycling performance at 55°C

Swelling at 90 °C

Poor safety characteristics

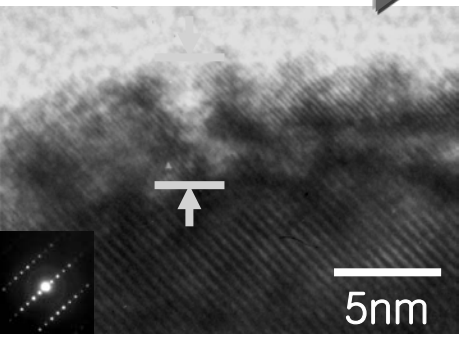


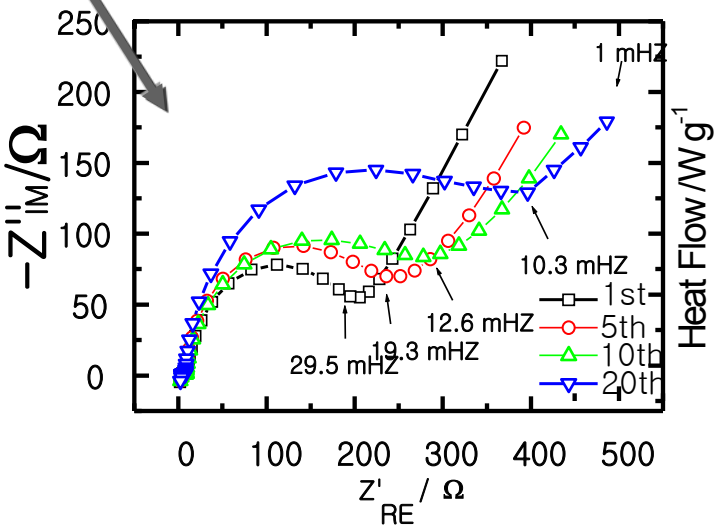


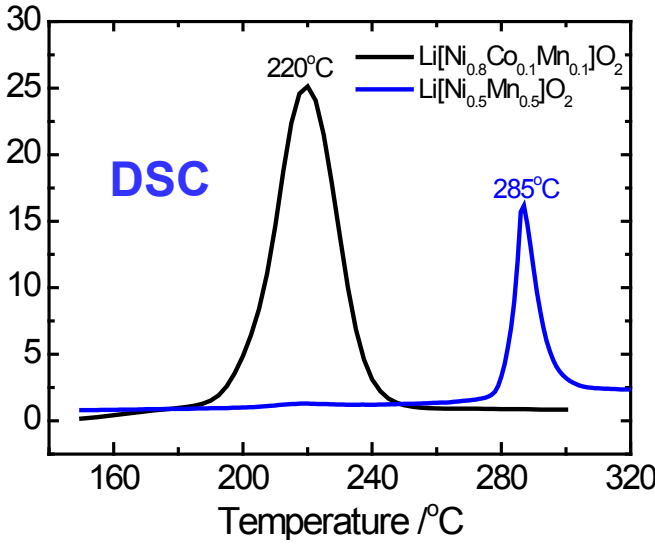


Shell : $LiNi_{0.5}Mn_{0.5}O_2$

1. **Stable cycling performance owing to stable Mn^{4+}**
2. **Thermally stable as high as 280 ℃ (~4.5 V)**
3. **Relatively lower capacity : 150 mAh/g**
4. **Poor rate capability**







FY 2009~ 2010 Millstones

- Optimize the process that provide a Ni-Mn-Co- hydroxide precursors having gradient concentration (ongoing)
- Proof of concept of high energy concentration gradient cathode material in small quantities (completed)
- Demonstrate the high capacity of concentration gradient material (completed)
- Demonstrate the good cycle life of the high capacity gradient concentration (on going)
- Demonstrate the improvement in the safety characteristics using DSC of the gradient concentration material (ongoing)

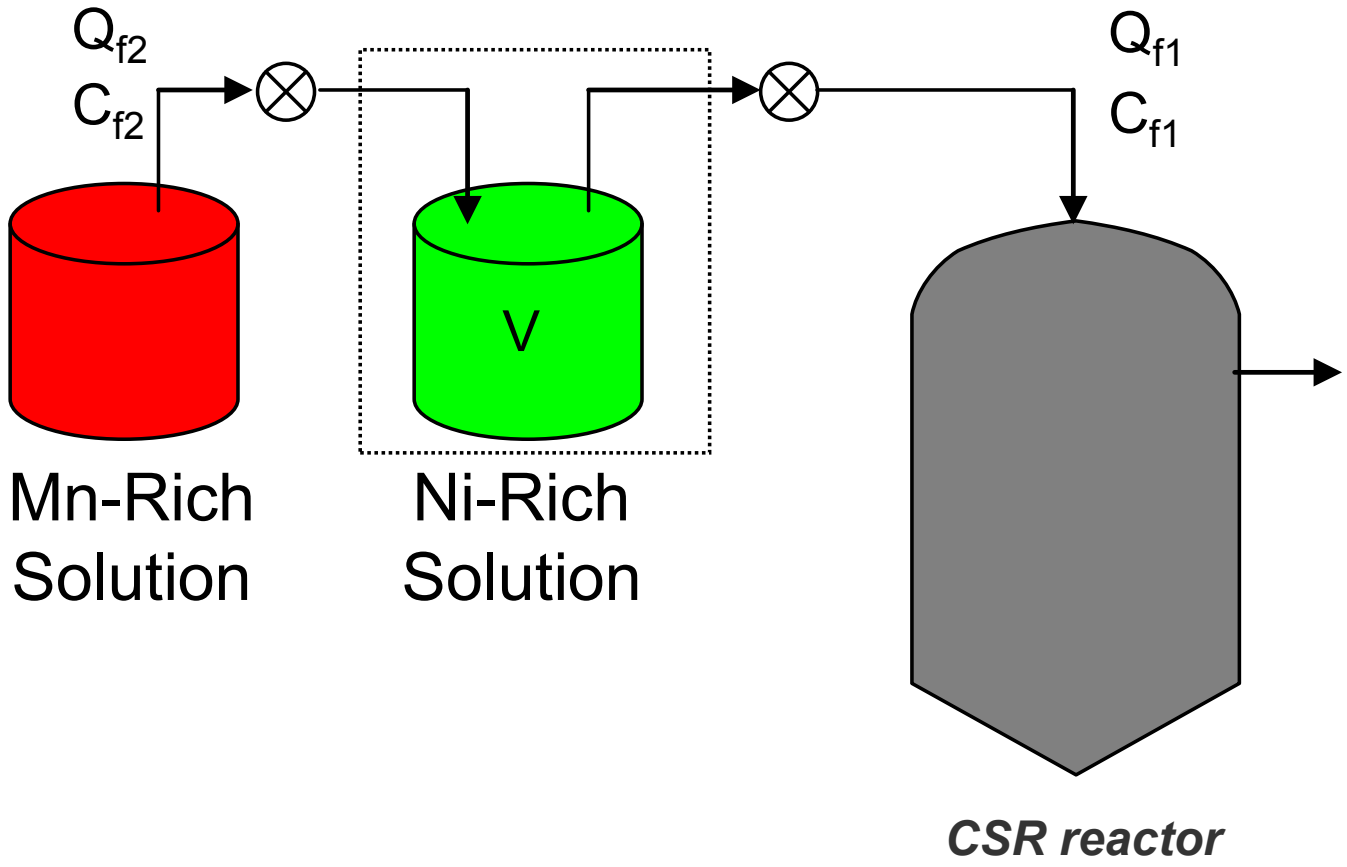
Recent Accomplishments and Progress

- **Developed a co-precipitation process that provide small quantities of a high energy gradient concentration precursor and cathode materials.**

- **Characterized the material and demonstrated that the material have a gradient concentration with changing concentration of Ni, Mn and Co within each particle.**

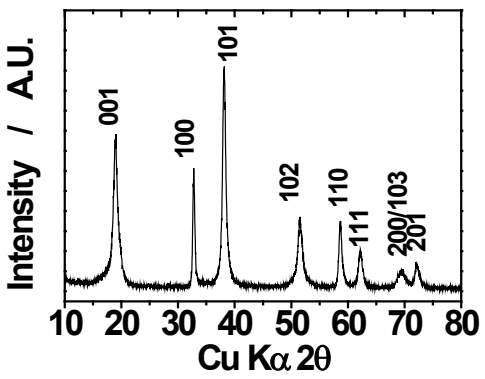
- **Demonstrated that the gradient concentration cathode material provides high capacity, good cycle life and excellent abuse tolerance in a small laboratory cells.**

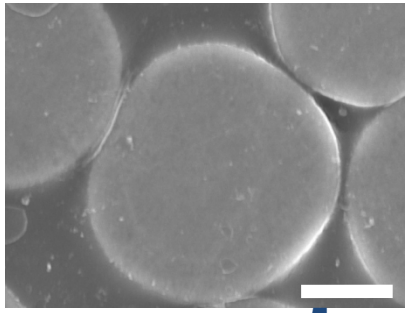
Experimental set up for making gradient concentration material (GCM)

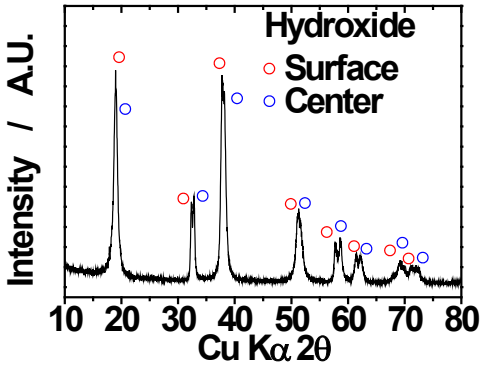


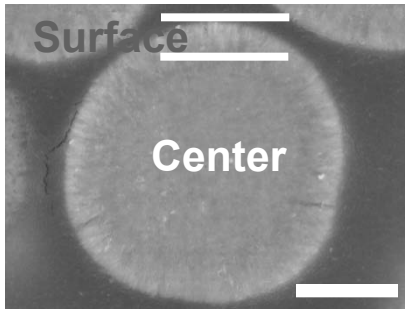
Process is continuous and scalable

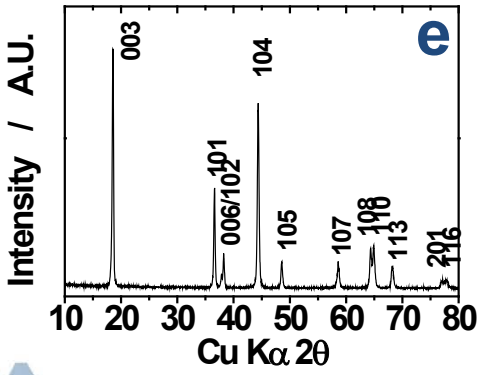
XRD & SEM images of GCM particle during synthesis

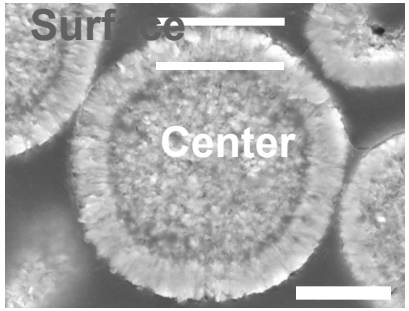












Step I

Formation of $[Ni_{0.8}Co_{0.1}Mn_{0.1}](OH)_2$

Step II

Pumping Ni-Co-Mn (0.08:0.46:0.46) aqueous solution into Ni-Co-Mn(0.8:0.1:0.1) aqueous solution reservoir, then continuous feeding the mixed solution to a reactor until the concentration of mixed solution reaches Ni-Co-Mn (0.4:0.3:0.3)

Step III

Formation of $[Ni_{0.64}Co_{0.18}Mn_{0.18}](OH)_2$ with concentration gradient of Ni, Co, and Mn contents

Outer surface : $[Ni_{0.4}Co_{0.3}Mn_{0.3}](OH)_2$

Step IV

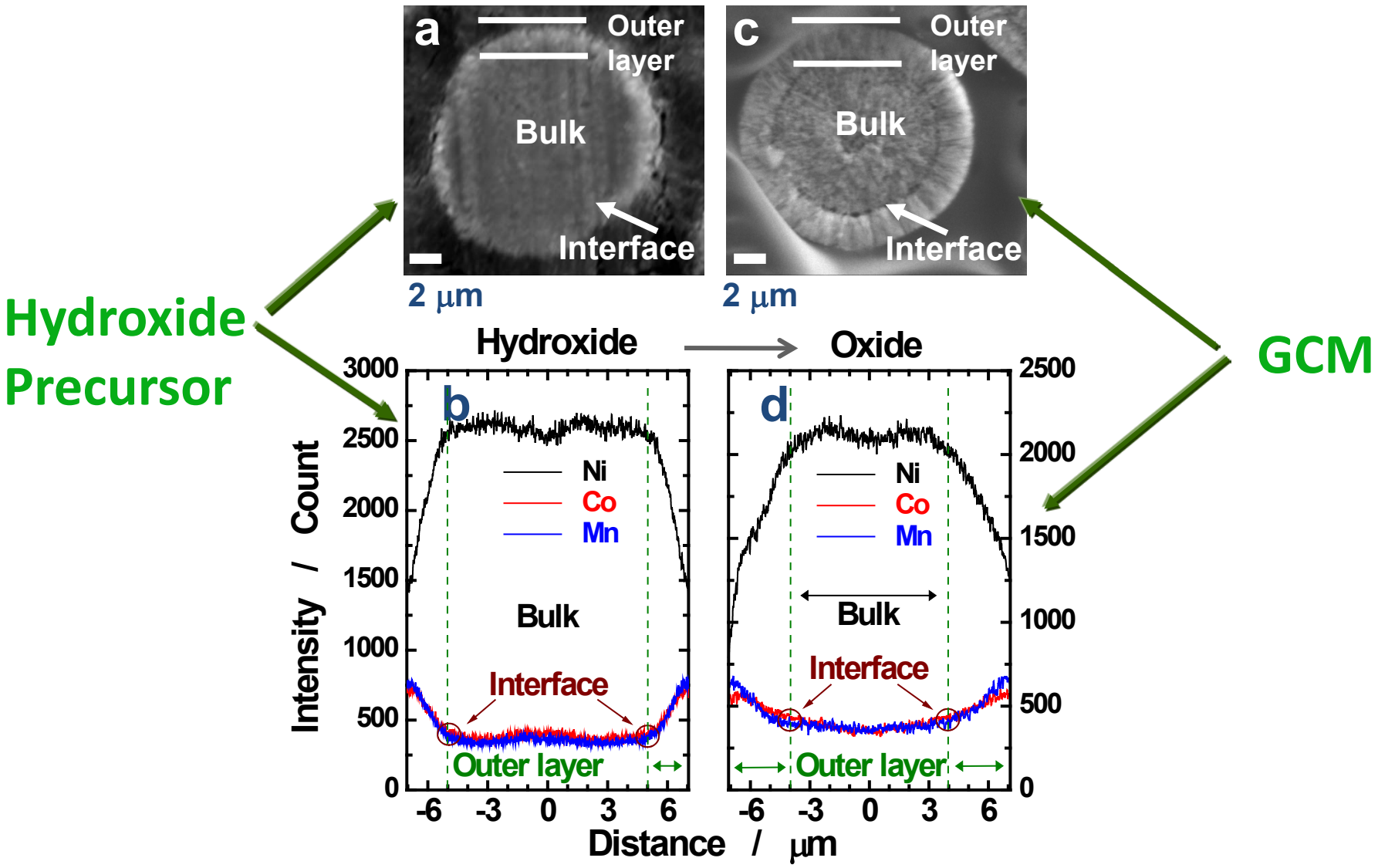
Incorporation of Li at high temperature (~750°C in air)

Step V

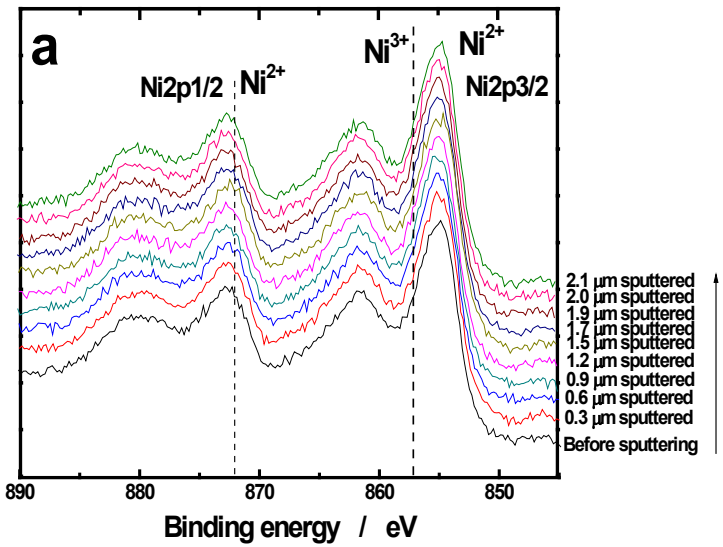
Formation of $Li[Ni_{0.64}Co_{0.18}Mn_{0.18}]O_2$ with concentration gradient of Ni, Co, and Mn contents

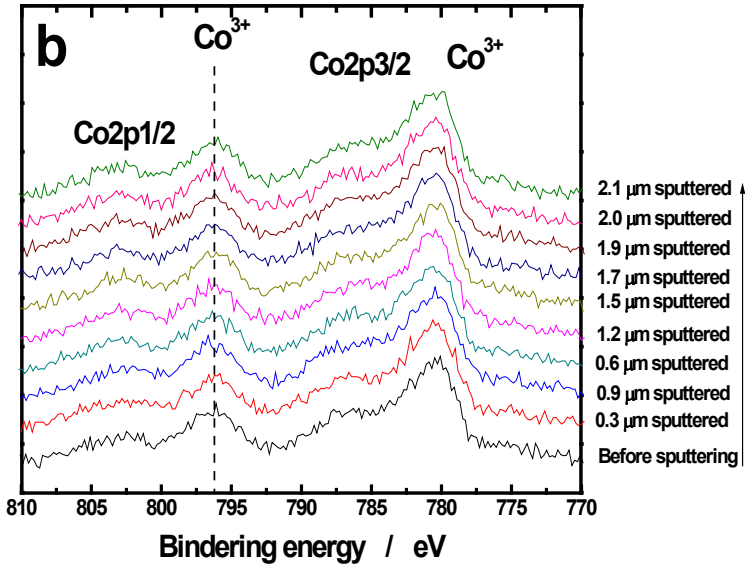
GCM

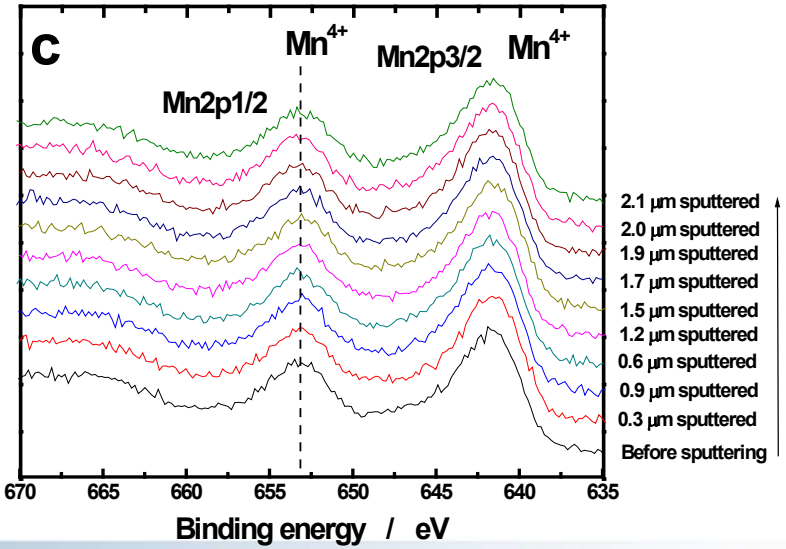
SEM & EPMA images of GCM (Hydroxide, Oxide)



X-ray photoelectron spectroscopic data of GCM

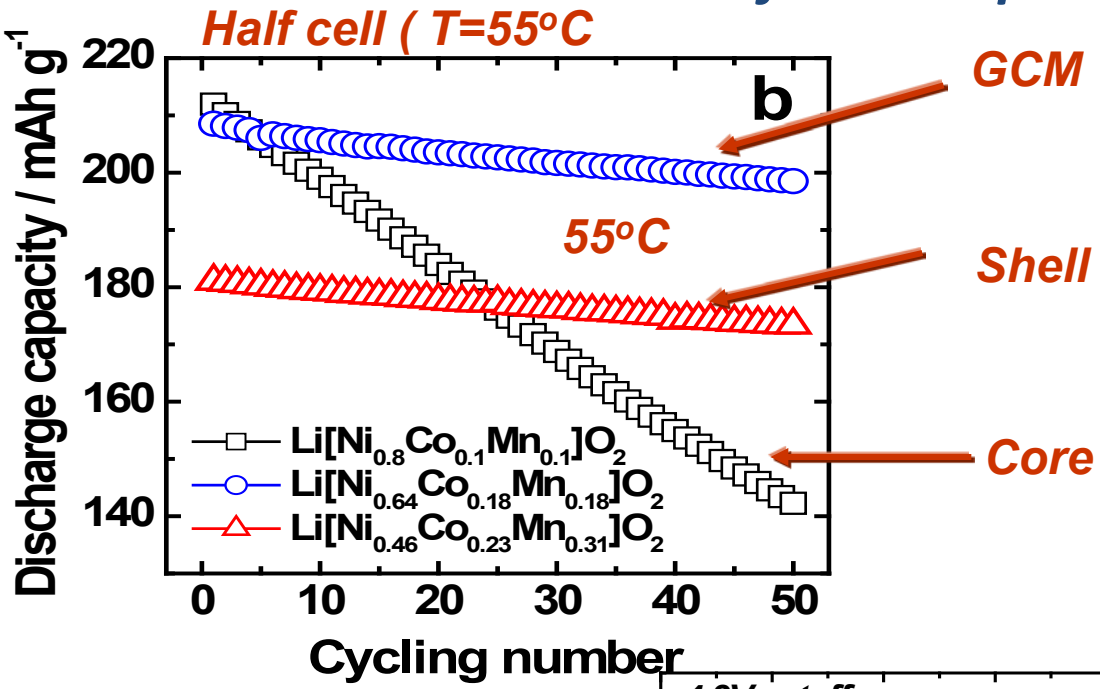


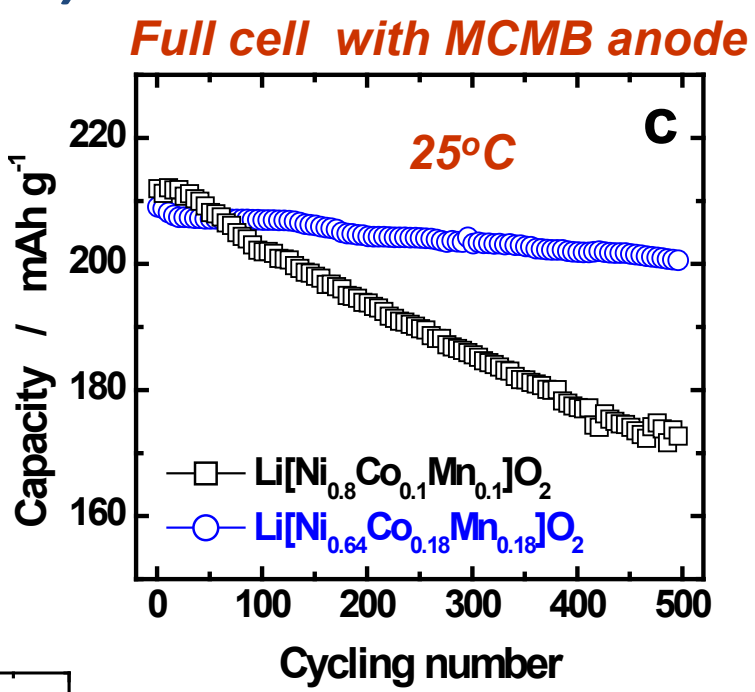


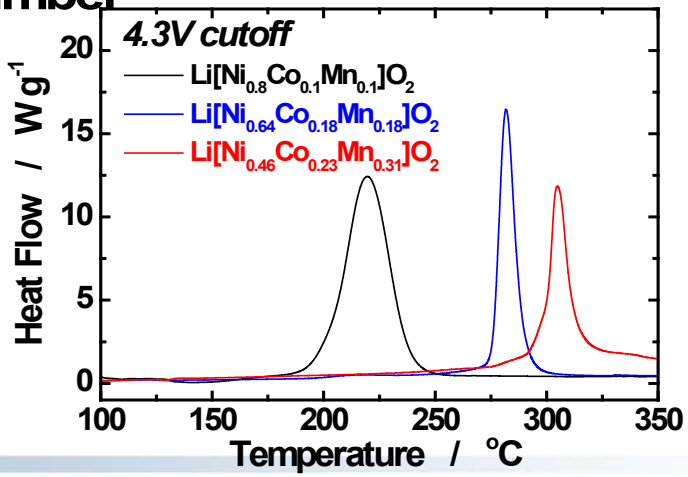


Ni : 2+
Co : 3+
Mn: 4+

Comparison of performance of GCM ($LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$) $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (Core composition) and $LiNi_{0.46}Co_{0.23}Mn_{0.31}O_2$ (outer surface composition)



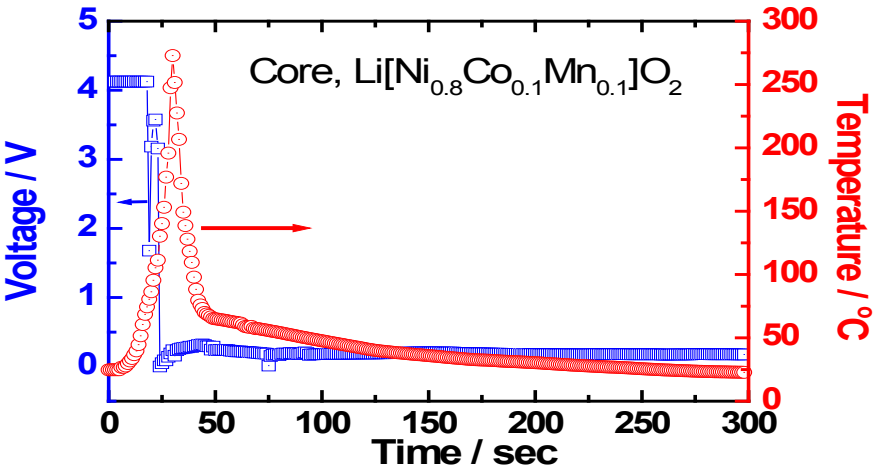


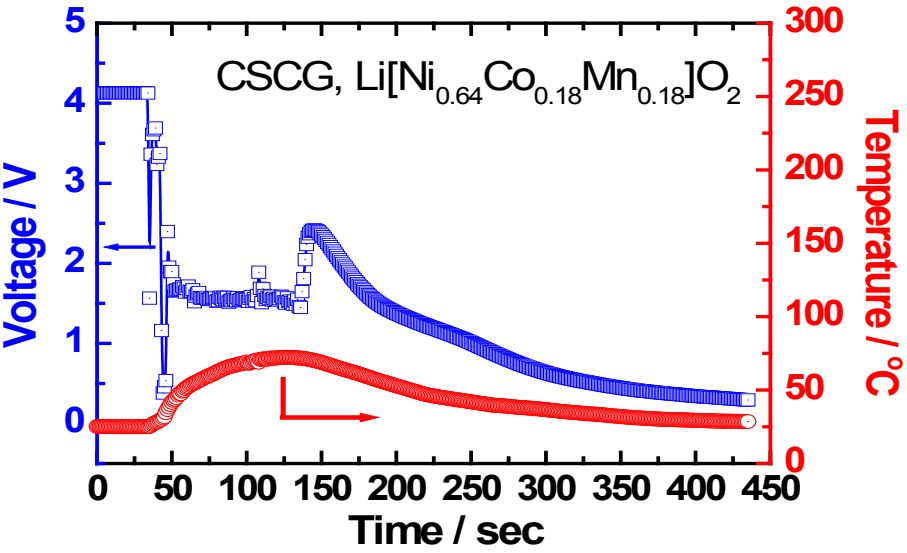


DSC of charged GCM, Core and shell materials

Thermal Stability of GCM (Nail Penetration on 100mAh cell)

Temperature and Voltage response





Core/MCMB cell After test (thermal runaway)

GCM/MCMB cell After test (thermal runaway)

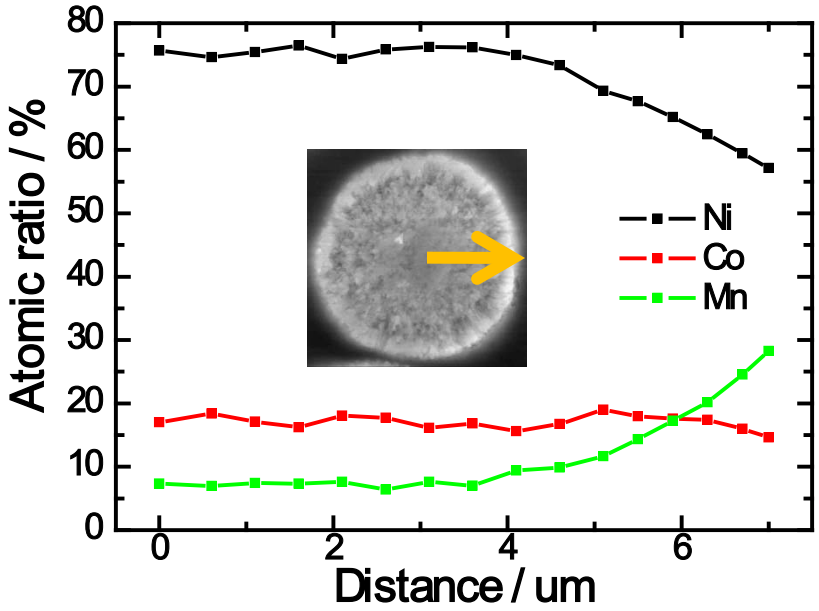
Cell with GCM shows excellent safety performance than cell with Core material

GCM having lower Ni content in the Core

How the material perform if we change the Ni concentration in the Core?

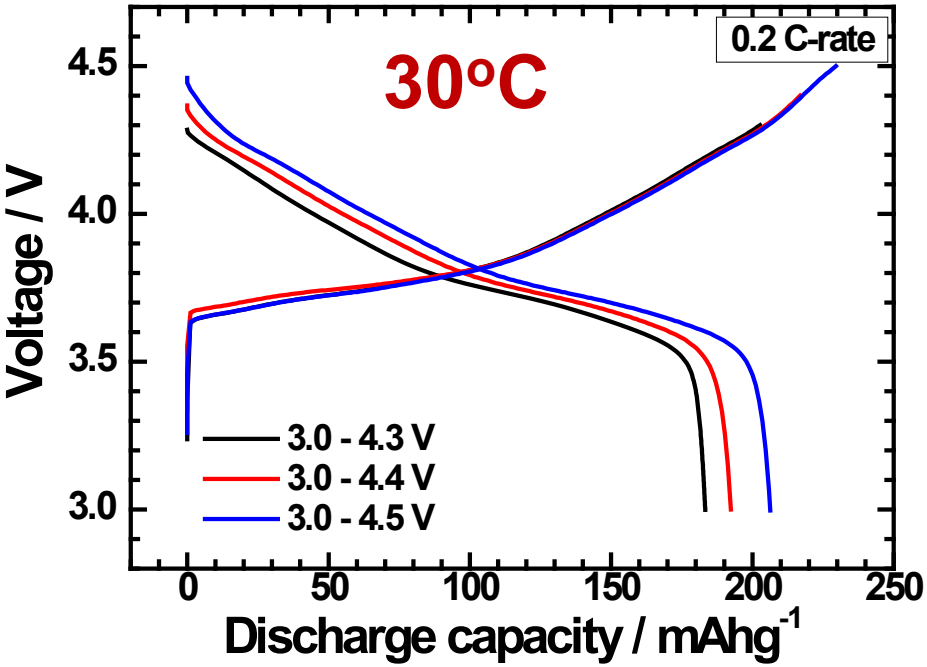
Bulk Composition = Li $[Ni_{0.70}Co_{0.12}Mn_{0.18}]O_2$

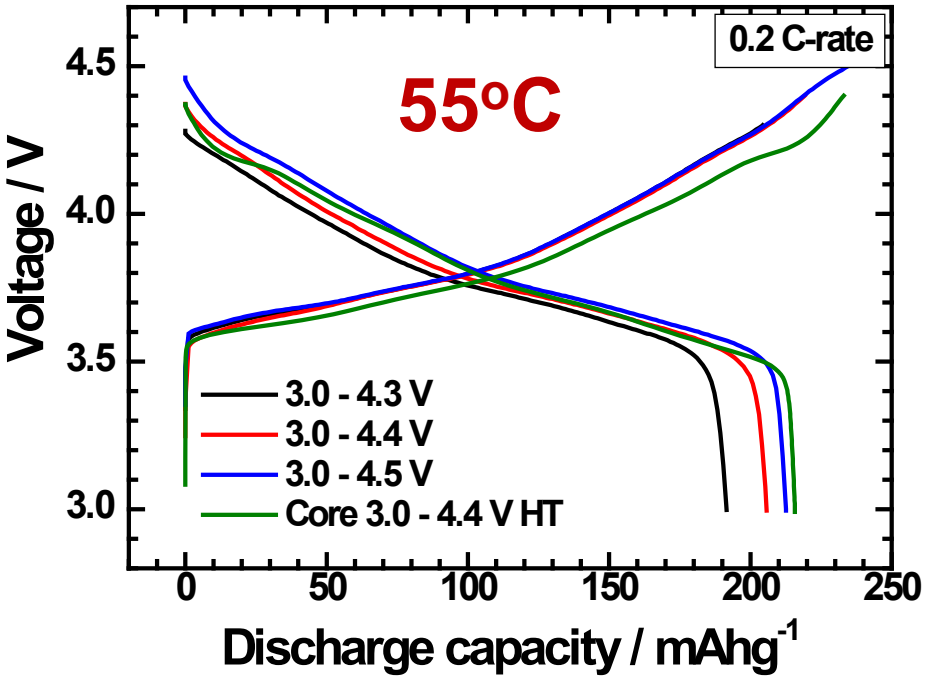
Shell Composition = $Li_{1+x}[Ni_{0.57}Co_{0.15}Mn_{0.28}]O_2$



EDAX compositional change from a cross-section of the Core-Shell

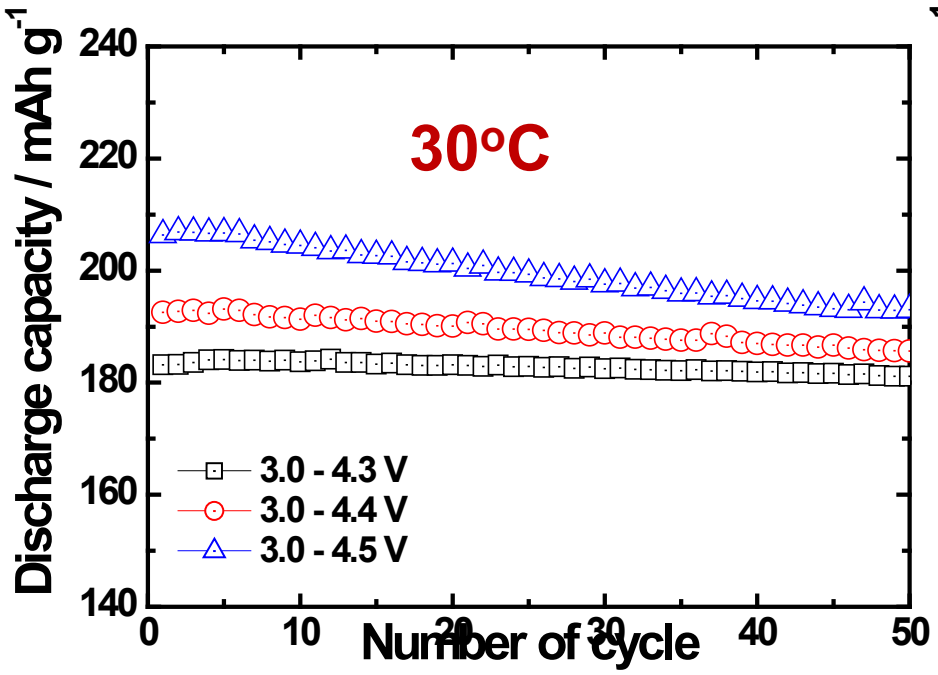
Initial Discharge Capacity of GCM at Different cut off Voltages

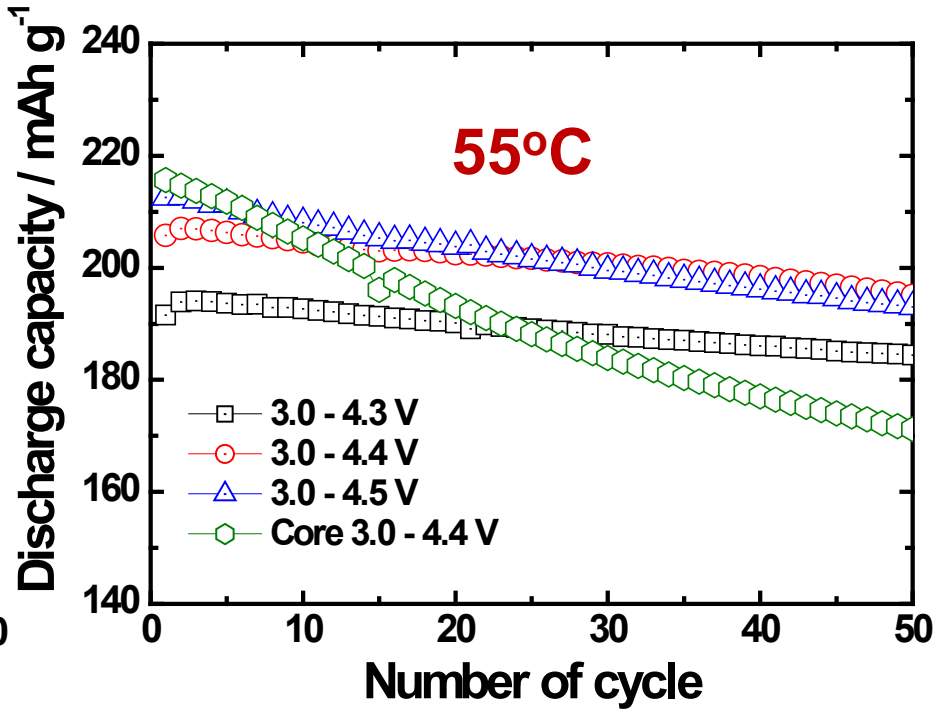




1st charge-discharge curves of the gradient cathode at different cut-off voltage 4.3, 4.4 and 4.5 V

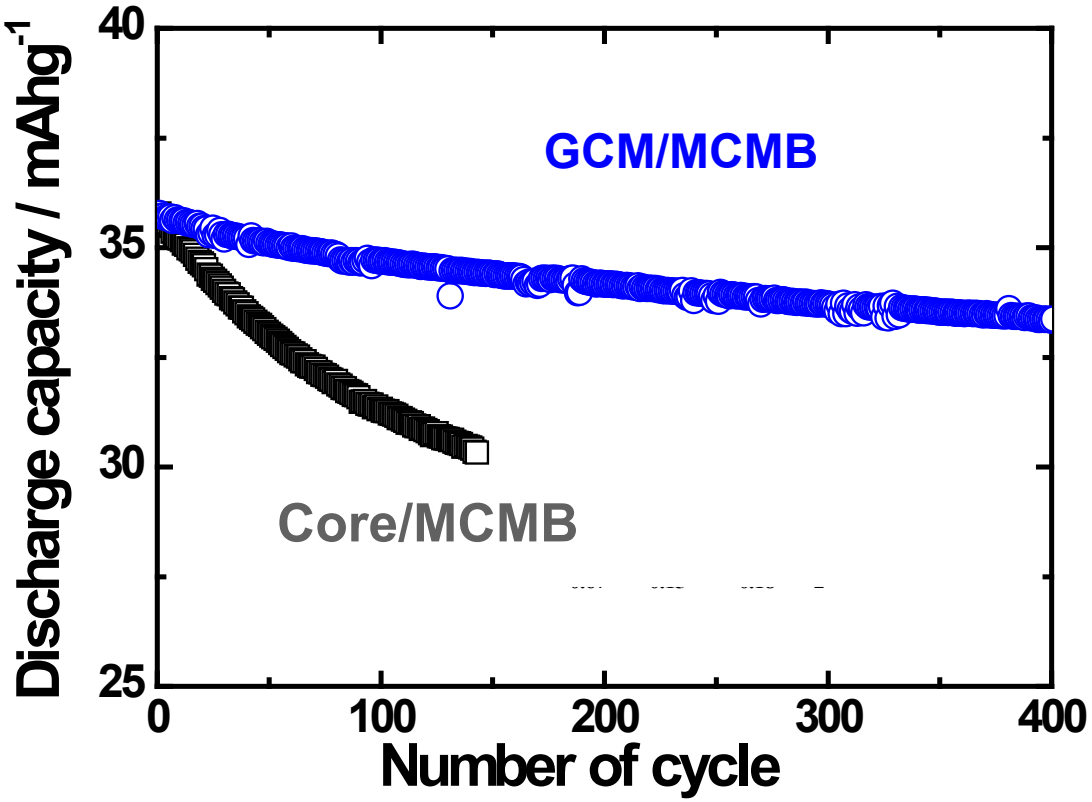
Cycling Performance of Gradient Cathode at Different cut off Voltages and Temperatures





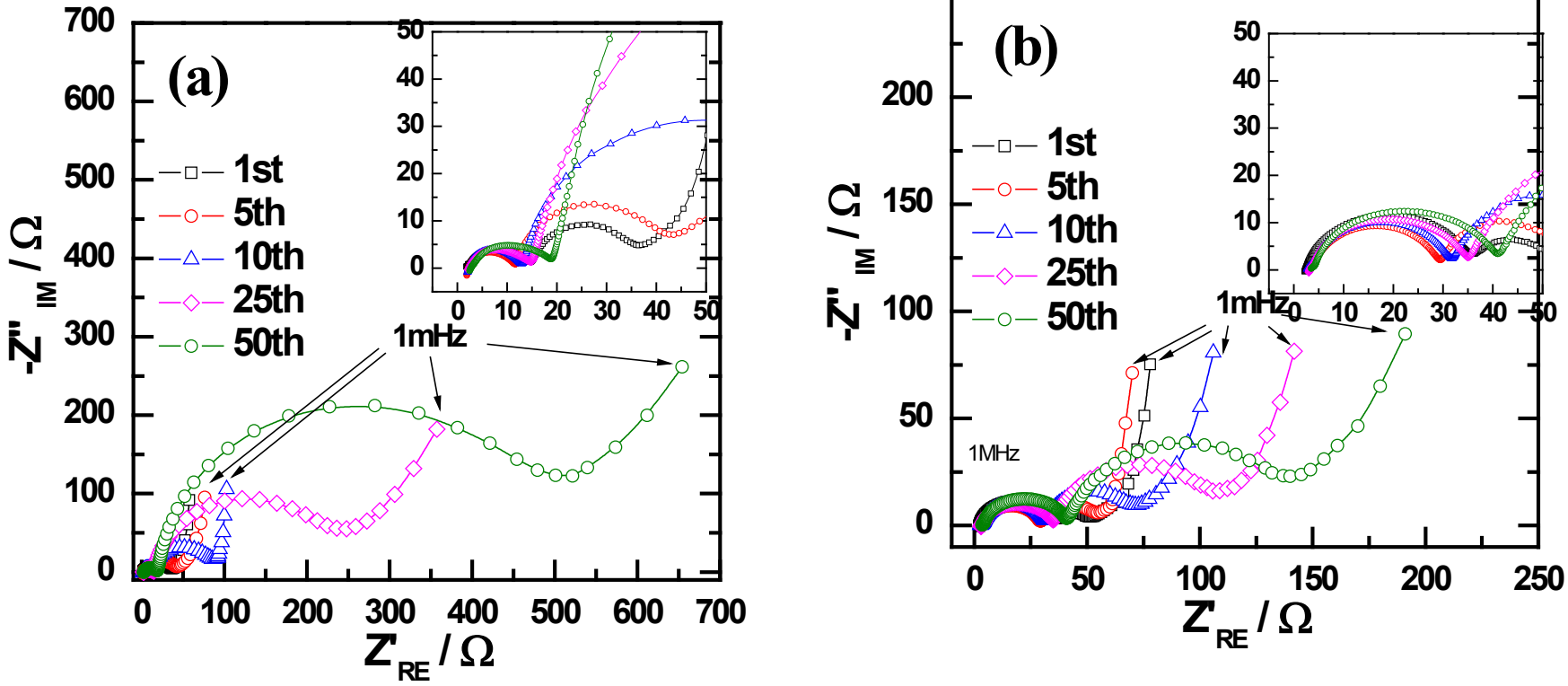
Capacity retention of the GCM with the various cut-off voltage 4.3, 4.4 and 4.5 V at 30°C and 55°C

Cycling Performance of Cells based on Core/MCMB and Gradient/MCMB at 1C rate



Specific discharge capacity *vs.* cycling number for the MCMB / Core and MCMB / GCM

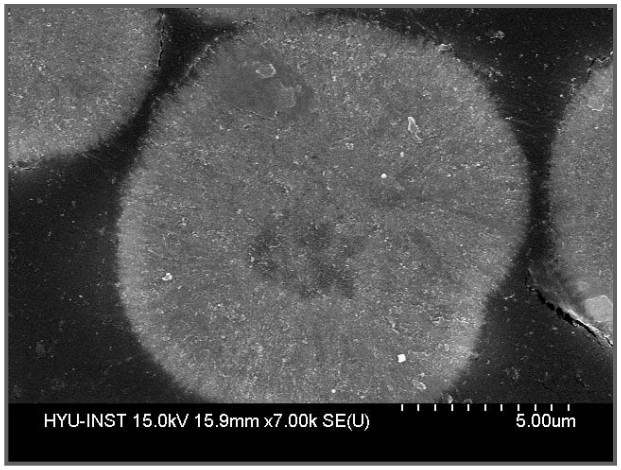
Ac Impedance of cells based on Core/Li and Gradient/Li at different cycles and 55°C



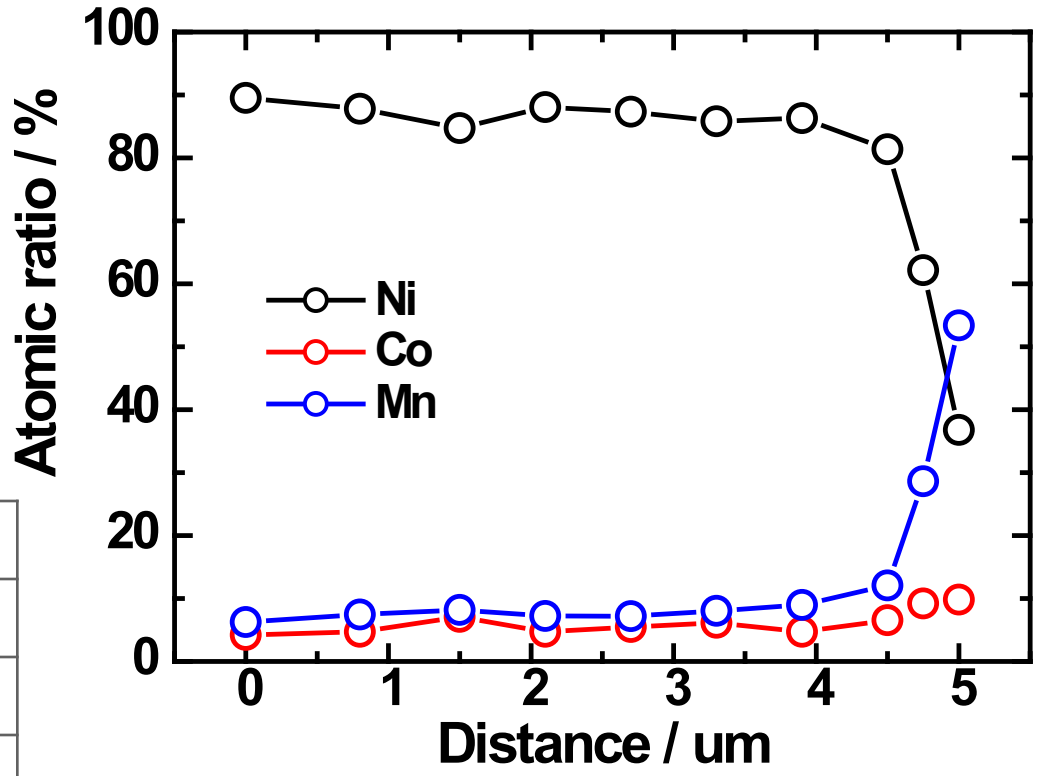
Nyquist plot of (a) the Li / Core, and (b) the Li / GCM at 1st, 5th10th, 25th 50th cycle at 55°C.

GCM having High Ni content in the Core

Increasing the Ni concentration in the Core can result in very high capacity (240mAh/g) at 4.4V



	Core	Shell	
Ni	89.53	36.79	52.74
Co	4.22	9.82	5.60
Mn	6.25	53.39	47.14



Recent result, testing is underway!!

Summary

•New gradient concentration cathode material with very high capacity was developed.

•Cross section SEM and EPMA shows that each particle of the material has a bulk composition rich Ni and outer layer composition rich in Mn.

•Gradient concentration material shows 209 mAh/g at 1 C rate when charged to 4.4V.

•Gradient concentration material shows excellent cycling performance at 55^{o}C, 4.4V and 1C rate.

• Safety performance of gradient concentration material is excellent when compared to the bulk material.

• Process optimization to control the concentration of the core and the shell is underway (was able to make 90% Ni rich bulk and 54% Mn rich outer layer shell) expect high capacity due to high Ni content.

Future work

- Tune the synthetic process to obtain highly pure gradient concentration material in 100~500g quantities to carry out extensive characterization and testing.

- Further optimize the composition of the outer layer of the gradient concentration to maximize the surface stability of the material

- Further optimize the thickness of the outer layer of the gradient concentration to a minimum possible to further increase capacity while maintaining good surface stability.

- Carry out calendar and cycle life test of optimum gradient concentration material.

- Carry out extensive safety test including ARC test and overcharge test.

- investigate the process of scaling up the optimum gradient concentration cathode material with an industrial partner (ECPRO) for potential use in the high energy cylindrical cells.

- Explore the effect of surface modification to improve life and safety further

Collaborators

- Y. K. Sun of Hanyang University (Sub Contractor, assist in the optimization of GCM)
- ECPRO Corp. (assist in the scale up of the GCM, and future 18650 cell fabrication using this high energy GCM)
- X.Q. Yang , BNL (collaborate in studing the structure of these new materials)
- EnerDel (testing in pouch cell the GCM for possible use in PHEV and EVs)