New High Energy Gradient Concentration Cathode Material

K. Amine (PI)

G. M. Koenig Z. Chen; I. Belharouak, Y. K. Sun

Argonne National Laboratory

DOE merit review

May 14-18 , 2012

Project ID: ES016

Overview

Timeline

- Start - October 1st, 2008.
- Finish - September 30, 2014.
- 70% Completed

Barriers

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

Budget

- Total project funding
  - DOE share: 1200K
  - FY12: 300K
  - FY11: 300K
  - FY10: 300K
  - FY09: 300K

Partners

- Hanyang University
- ECPRO,
- Y. Ren (ANL-APS)

Objectives of the work

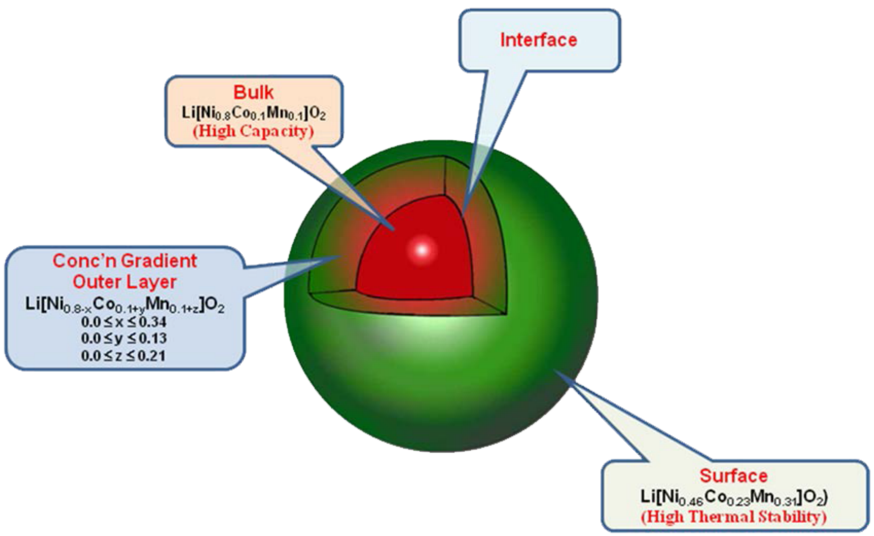
- Develop a new high energy cathode material for PHEV applications that provides:
  - Over 200mAh/g capacity
  - Good rate capability
  - Excellent cycle and calendar life
  - Good abuse tolerance

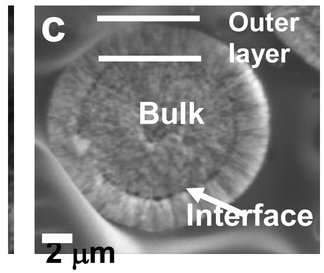
Approach

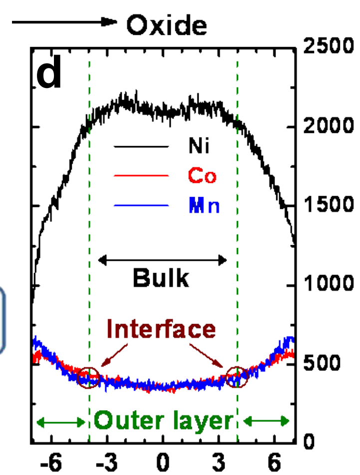
Use a Core-shell approach with gradient concentration (GCM):

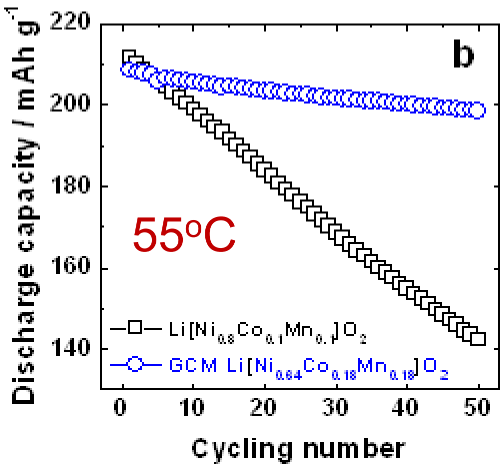
- a core enriched in Ni for high capacity

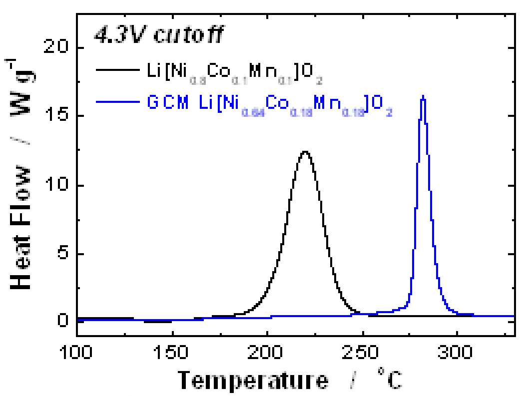
- a shell with gradient concentration enriched in Mn for improved safety and cycle life.











Approach (Continued)

- Develop a general synthetic method to tailor the gradient composition in cathode particles.
- Deposit a gradual composition gradient throughout particles (full gradient) to suppress stress during lithium intercalation and diffusion.
- Further enrich materials in Mn at the outer shell of the particle to enhance   cell stability and safety.

FY 2012 Plans & Schedule

- Use the model developed last year to predetermine the gradient concentration in each particles produced in the co-precipitation process (Sep 2012)
- Develop a batch process for precursors with a gradient in transition metal composition that have different manganese ratio in the outer shell layer of the particles (on going)
- Optimize the process to obtain full gradient materials (on going)
- Demonstrate high capacity in final materials produced using the full gradient precursors (March 2012)
- Demonstrate the benefit of full gradient on cycle life and safety (March 2012)
- Scale up the full gradient material to 1kg level and confirm its benefit to performance and safety in full cell system (on going)

Recent Accomplishments and Progress

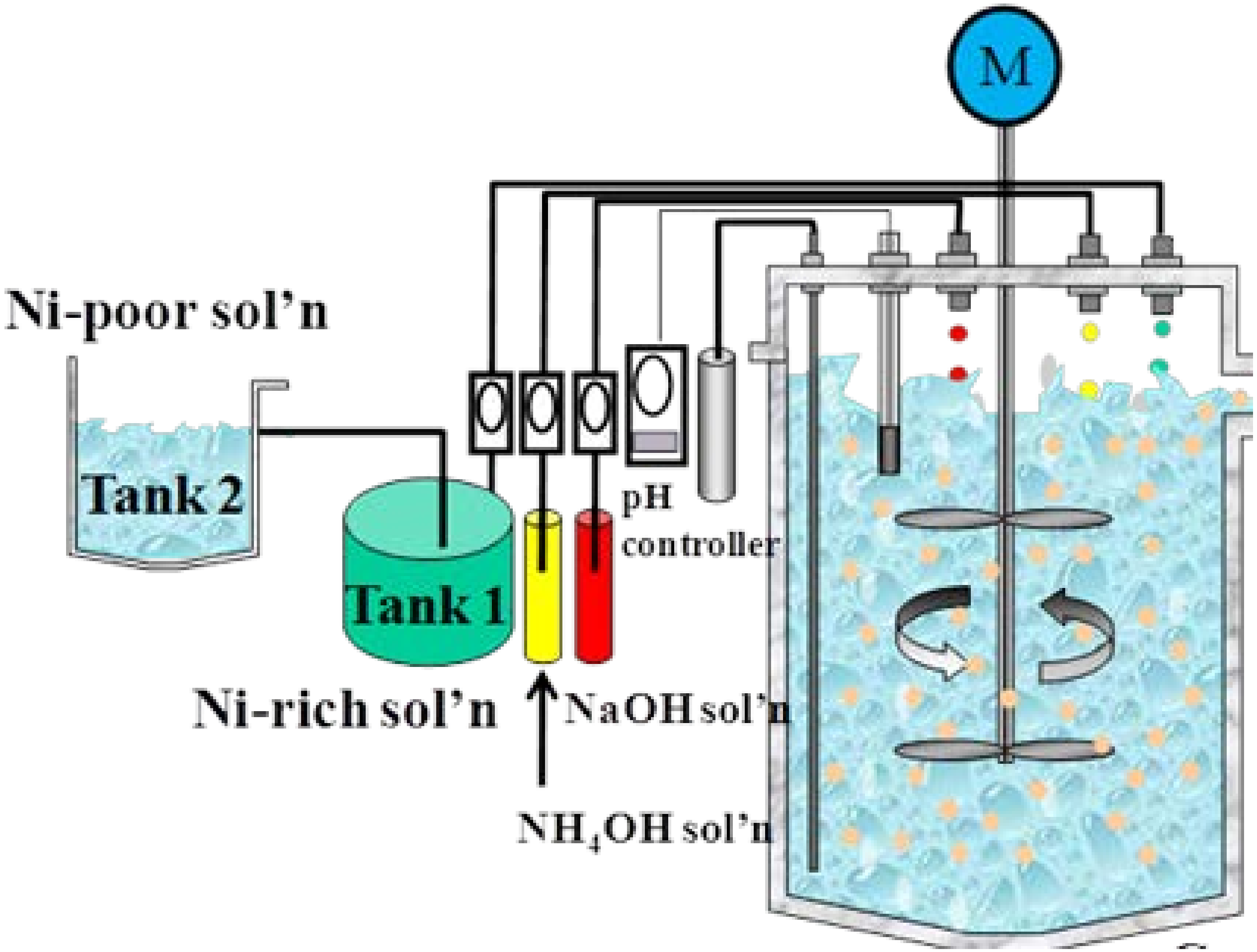
- Were able to make several core shell gradient with 80~90% Ni on bulk (increase energy) and different Mn concentration at the outer layer of the particle.

- Were able to make high capacity full gradient material using a batch process

- Were able to demonstrate the benefit of the full gradient on cycle performance and aging

- Were able to demonstrate the benefit of the full gradient cathode on safety

Synthesis of gradient Precursor via CSTR Co-precipitation using Batch Process



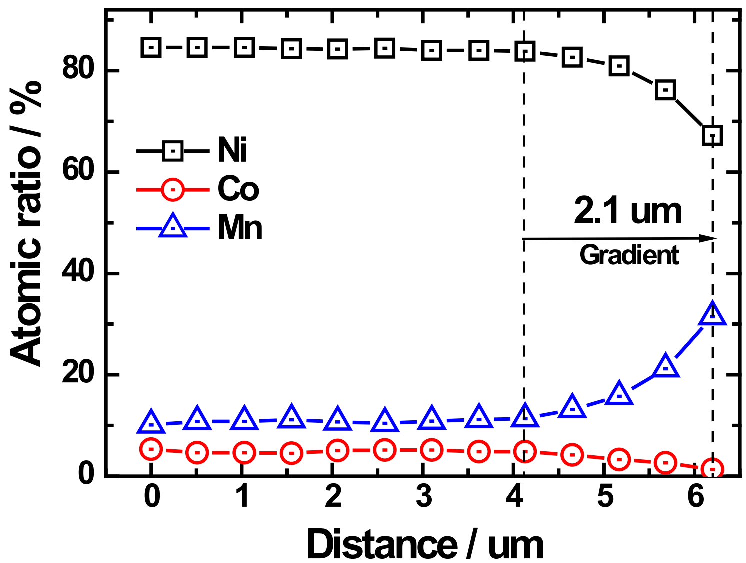
Effect of Mn content in the surface of particle on the performance of the core–shell structured gradient cathode

Core : Common $Li[Ni_{0.85}Co_{0.05}Mn_{0.1}]O_2$

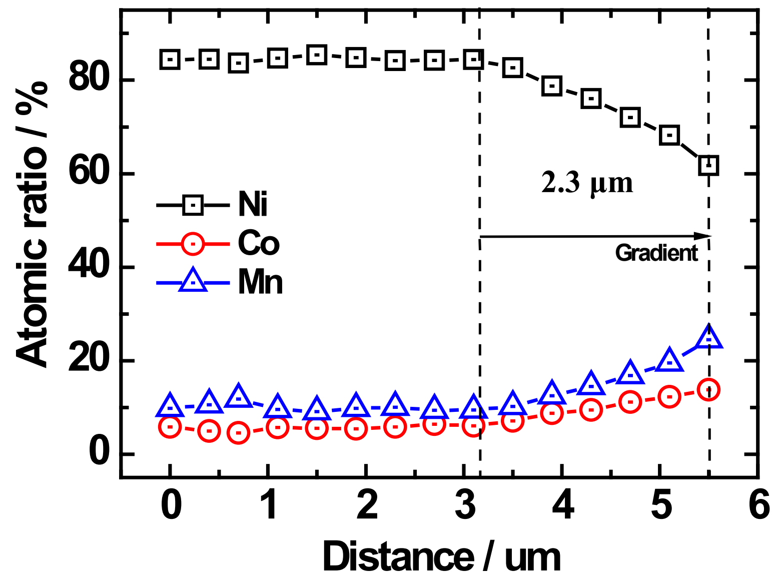
Shell: $Li[Ni_{0.67}Co_{0.1}Mn_{0.32}]O_2$: CSCG A
average composition: $Li[Ni_{0.82}Co_{0.04}Mn_{0.14}]O_2$

Shell: $Li[Ni_{0.62}Co_{0.14}Mn_{0.24}]O_2$: CSCG B
average composition: $Li[Ni_{0.81}Co_{0.06}Mn_{0.13}]O_2$

EPMA of lithiated oxide

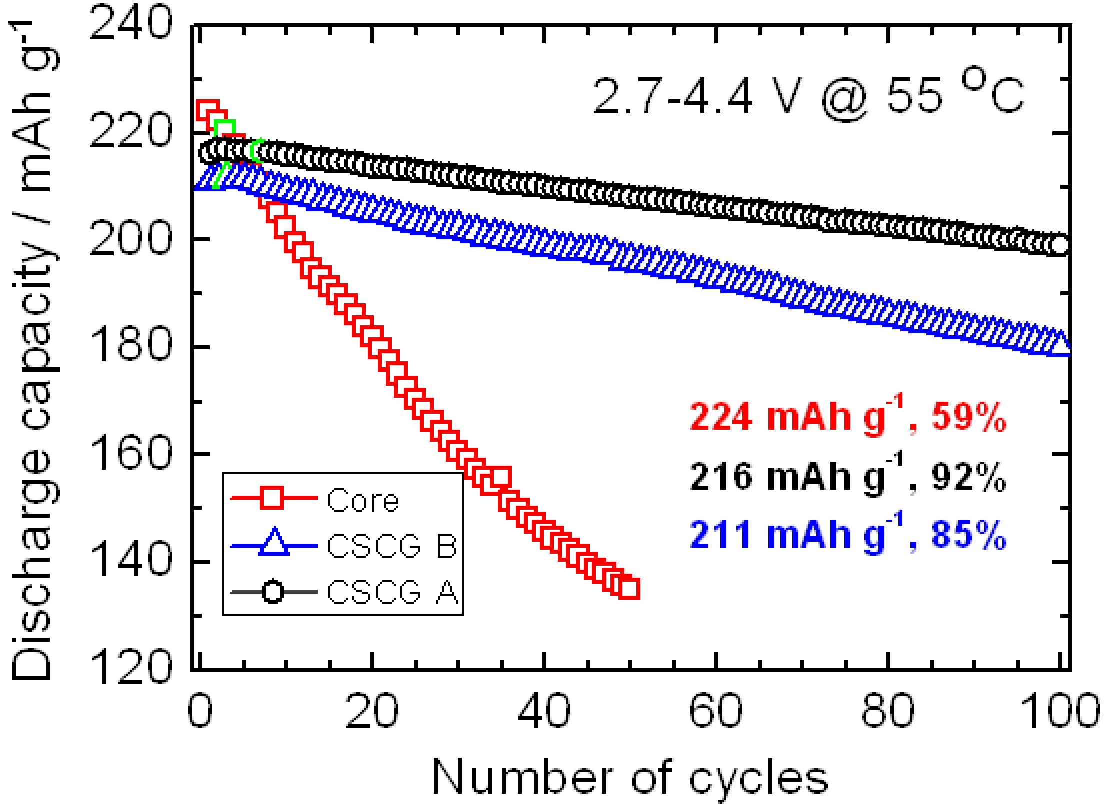


CSCG A (more Mn at the outer shell layer)



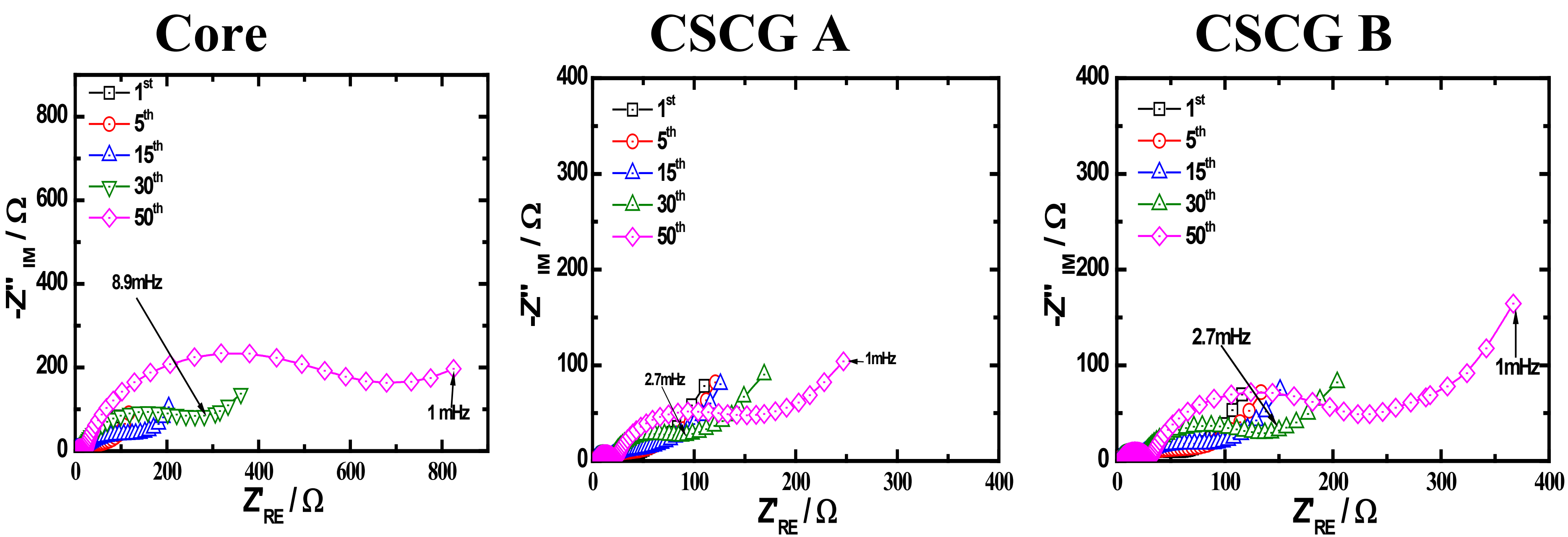
CSCG B(less Mn at the outer shell layer)

Effect of Mn content on the surface of the particle on the cycling performance at 55°C



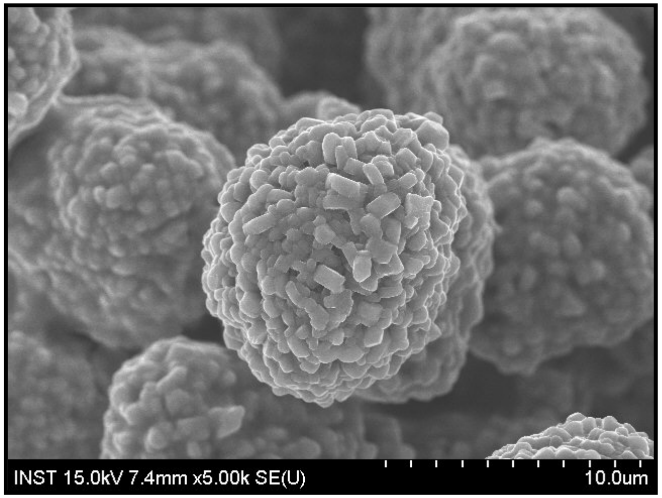
Gradient cathode that has the highest Mn content on the outer shell of the particle (CSCG A) shows better cycling performance than the one with less Mn content on the outer shell of the particles (thought the later has thicker shell thickness).

Impedance growth during cycling of core material CSCGA and CSCGB



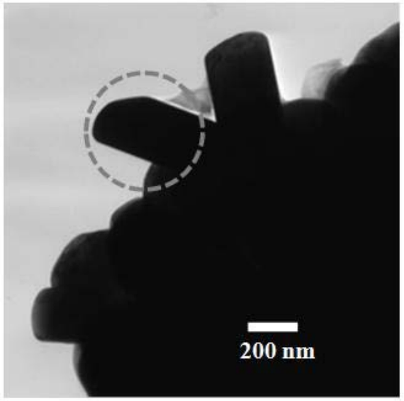
(CSCG A) with shorter shell thickness but high Mn content at the outer shell layer of the particle shows less impedance growth during cycling at 55^{o}C.

SEM, TEM and Electron Diffraction of pristine and cycled core material

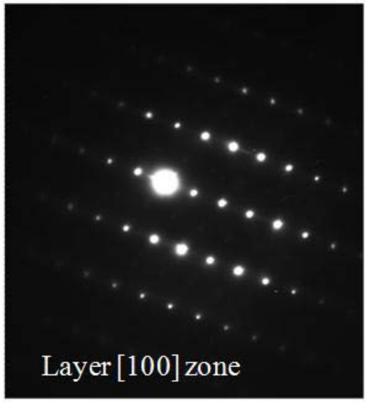


Pristine

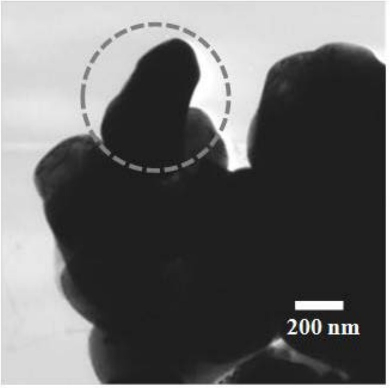
After cycling, the core structure is transformed to spinel phase



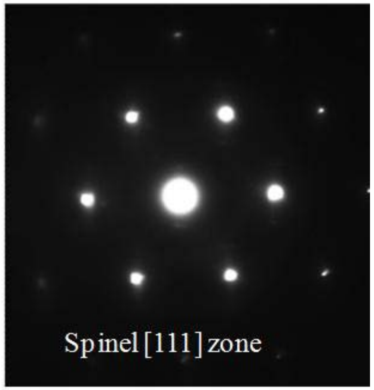
TEM of pristine Core



Electron diffraction of pristine core showing layered phase

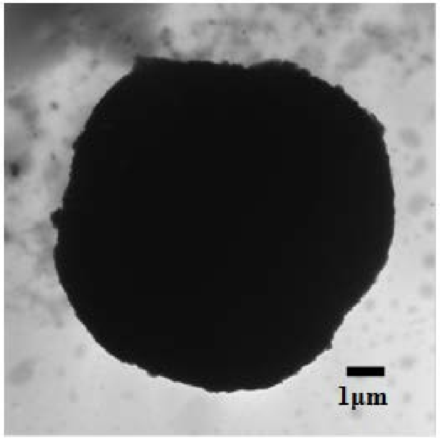


TEM of cycled Core

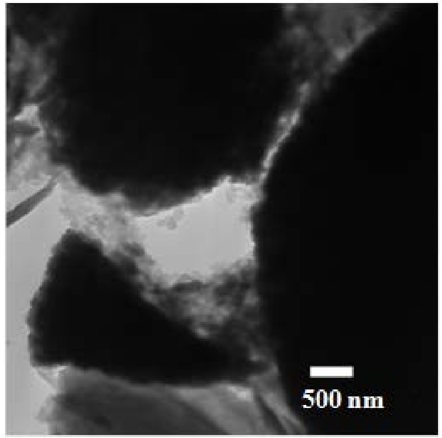


Electron diffraction of cycled core showing spinel phase

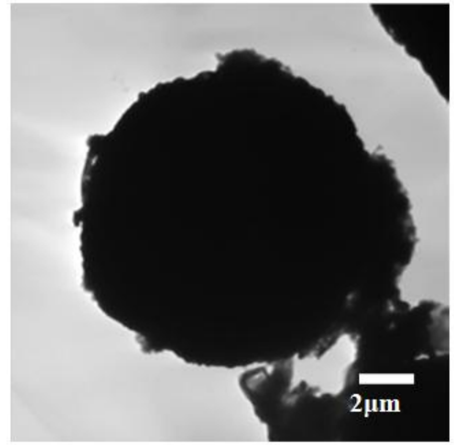
SEM, TEM and Electron Diffraction of pristine and cycled CSCG A and CSCG-B electrodes



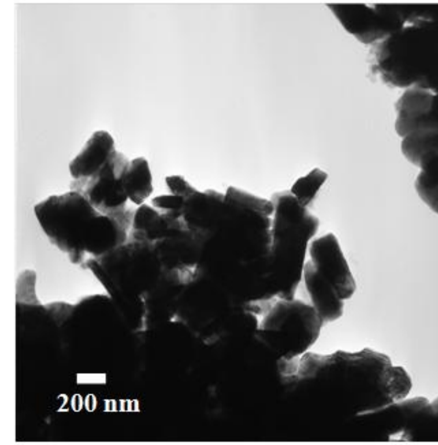
e. CSCG A



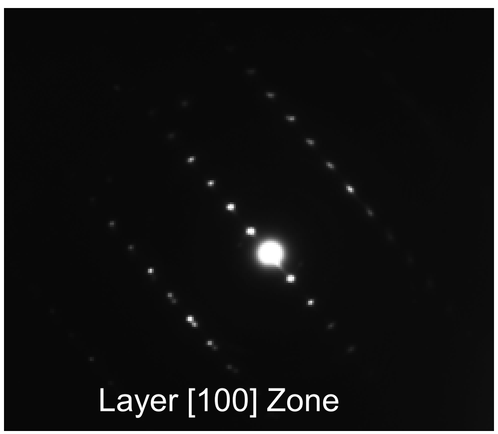
f. CSCG A

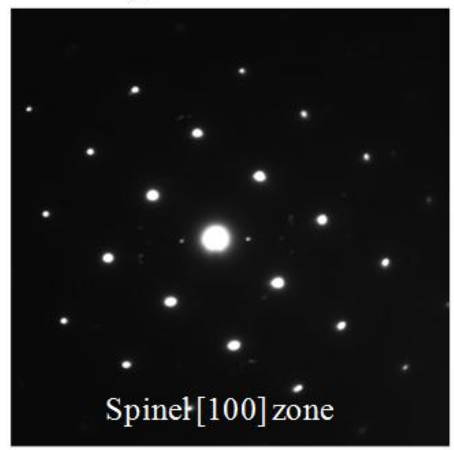


g. CSCG B



h. CSCG B

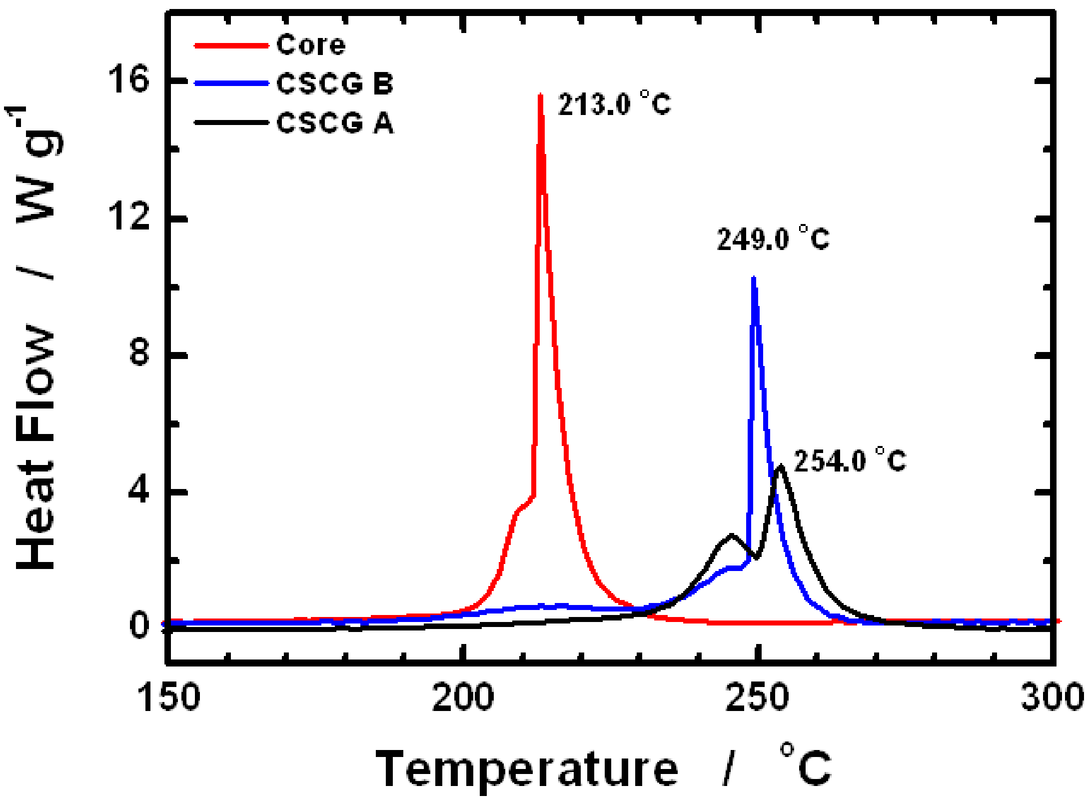




i. CSCG B

Electron Diffraction shows that CSCG-B with less Mn at the particle surface transform to the spinel after cycling while CSCG-A with High Mn content at the surface remain layered.

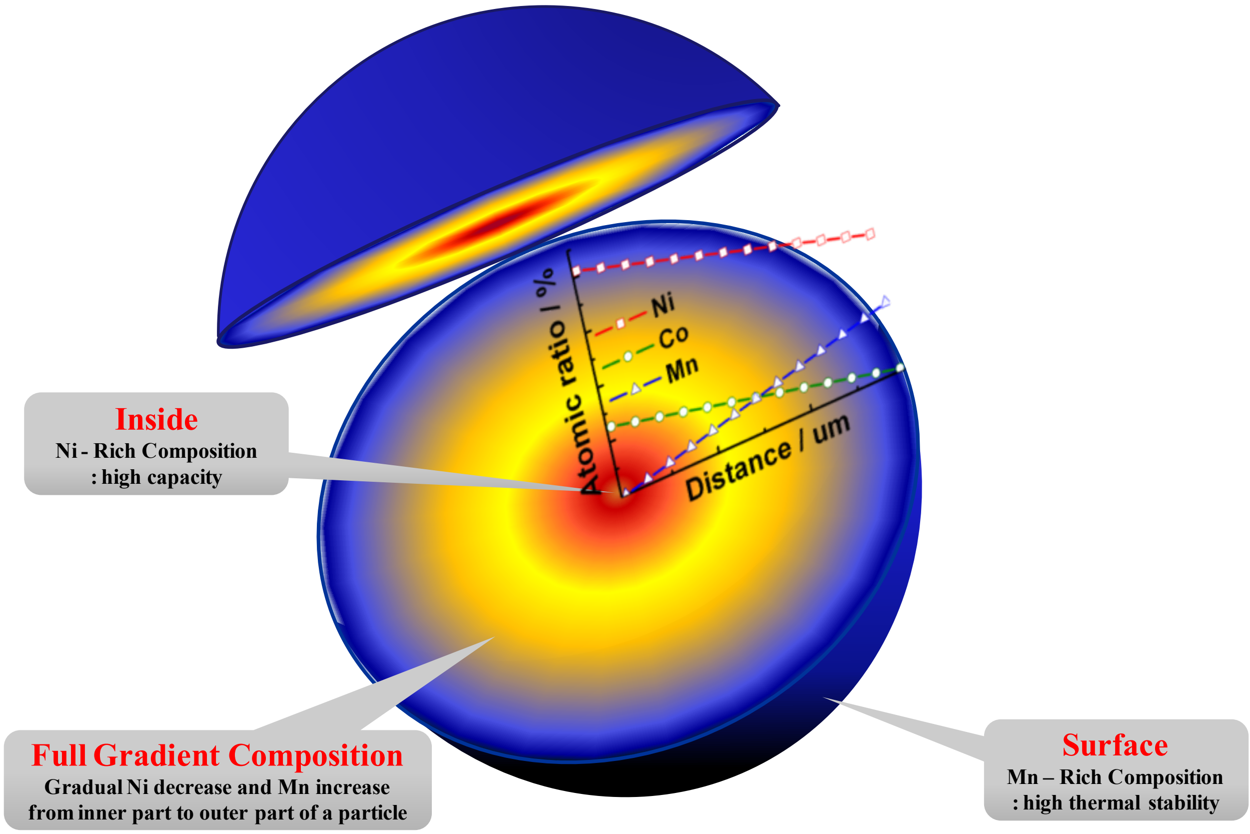
DSC of core, CSCGA and CSCGB gradient materials charged to 4.4V in the presence of 1.2M$LiPF_6$/EC:EMC(3:7)



CSCGA with high Mn content at the outer shell layer shows less heat generation

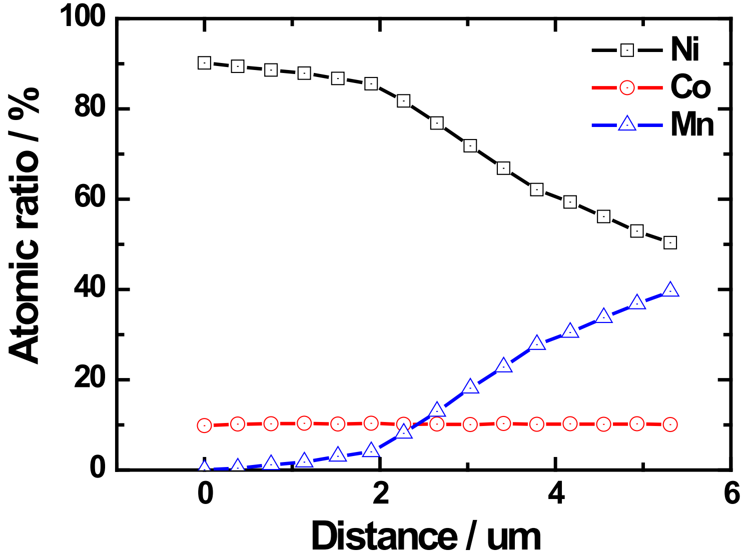
High Energy Full Gradient Concentration Materials (FGC) with average composition $LiNi_{0.6}Co_{0.10}Mn_{0.30}O_2$

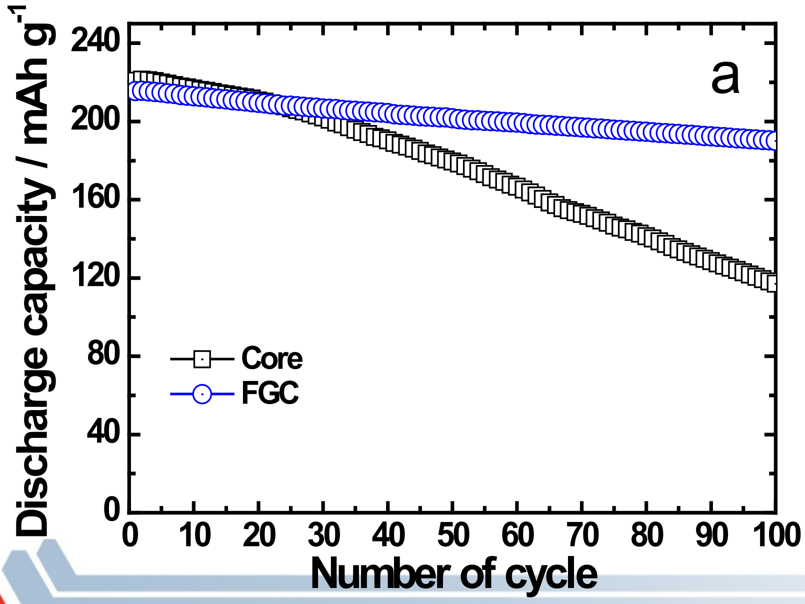
1. To further stabilize the material, we need to increase further the Mn content at the outer shell layer
2. Explore continuous full gradient to achieve goal

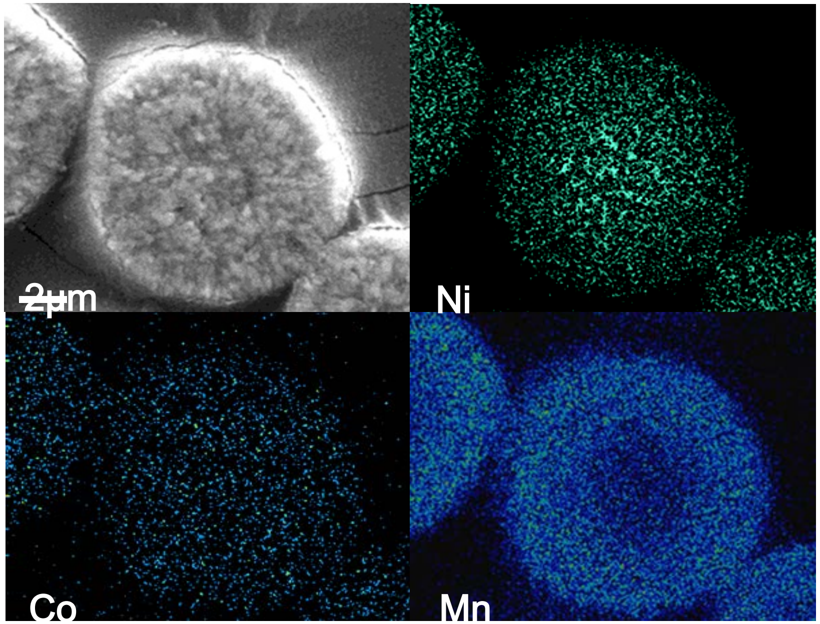


Schematic diagram of the full concentration gradient lithium transition metal oxide particle with the nickel concentration decreasing from the center toward outer layer and the concentration of manganese increasing accordingly.

High Energy Continuous Gradient Concentration materials (FGC) with composition $LiNi_{0.6}Co_{0.10}Mn_{0.30}O_2$

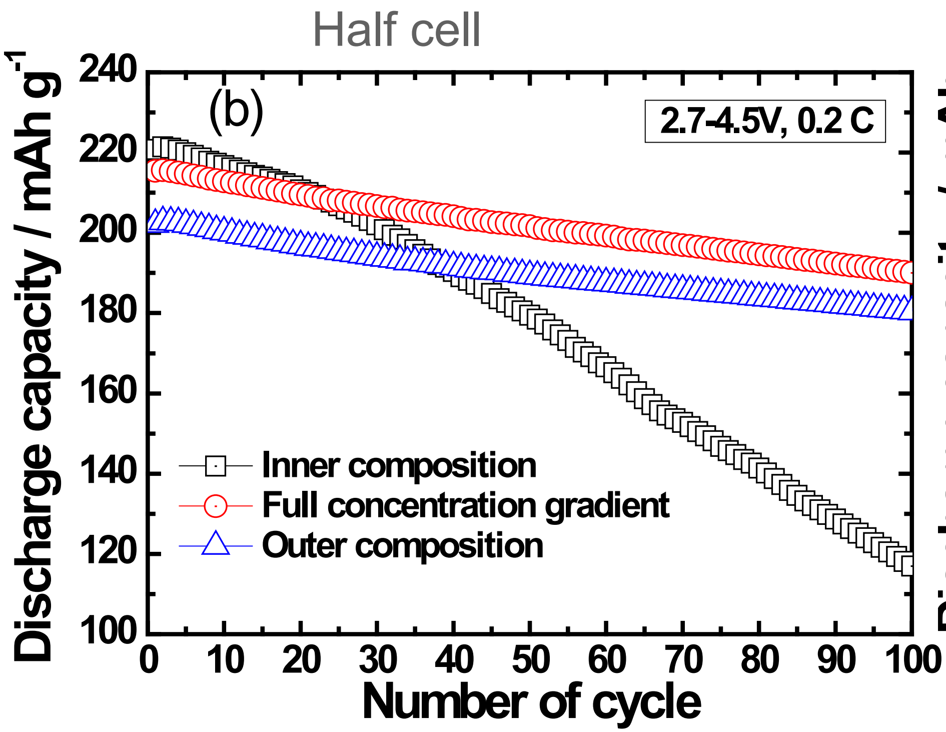


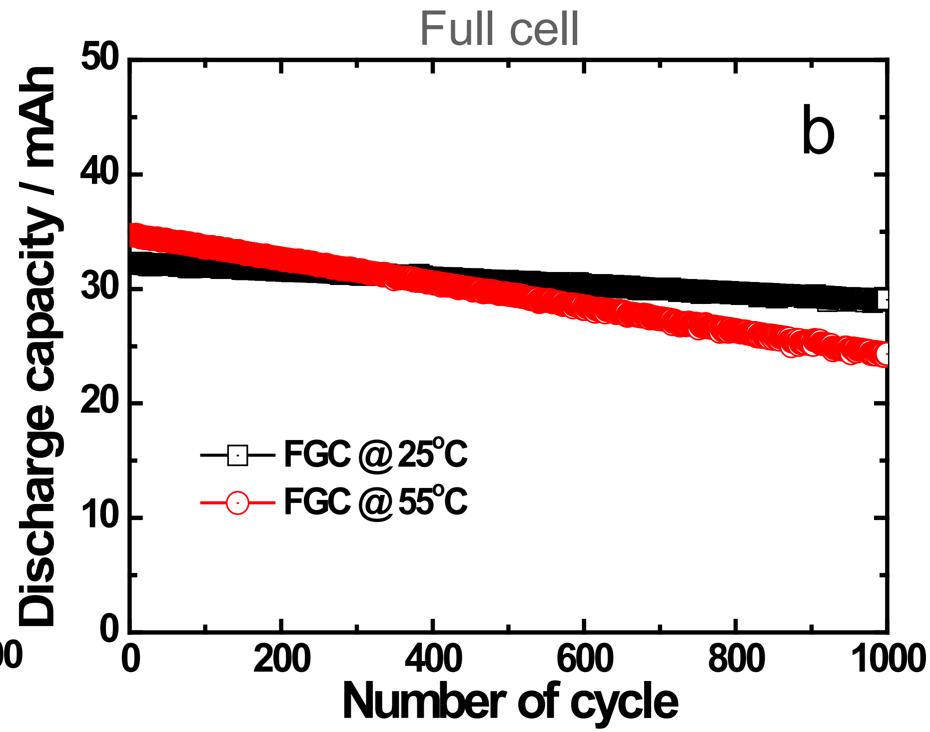




EDAX showing high concentration of Ni in the center of particle and high concentration of Mn in the outer layer of the particle

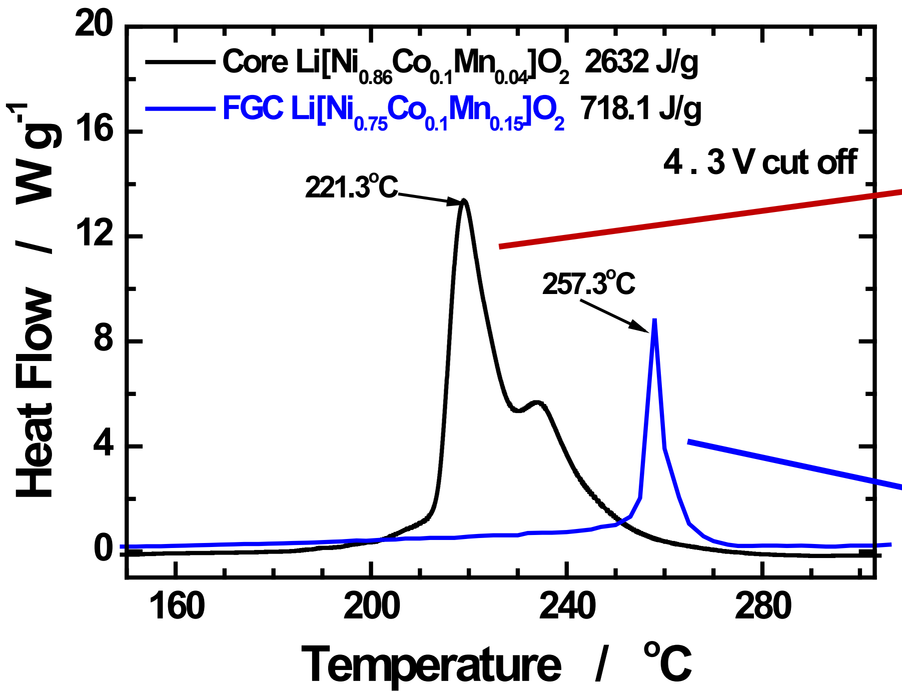
Half and Full Cell Cycling performance of High Energy Full Gradient materials (FGC) at 25 and 55°C





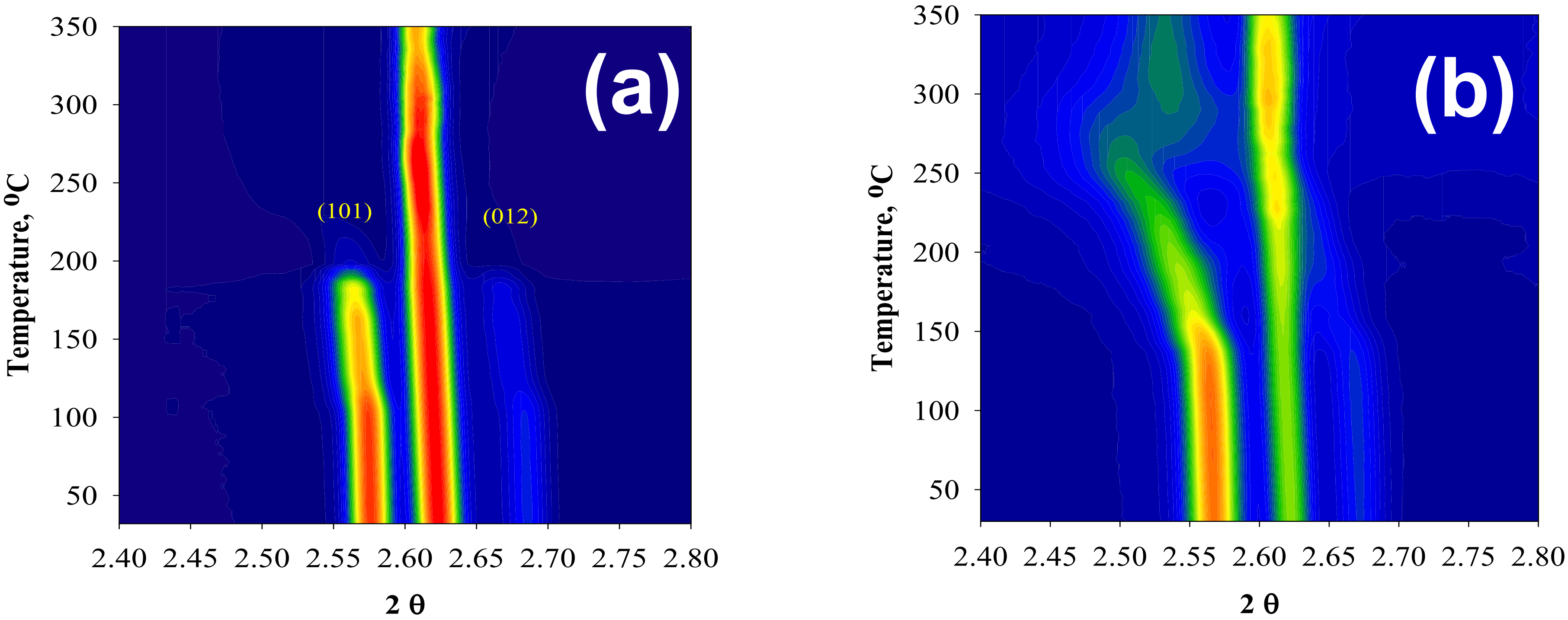
Full concentration gradient shows high capacity and very limited capacity fade after 1000 cycles at 55°C in a full cell, Electrolyte used is $LiPF_6$/EC:EMC with 1%VC

DSC of core charged to 4.2V and Full Gradient Materials (FGC) charged to 4.5V



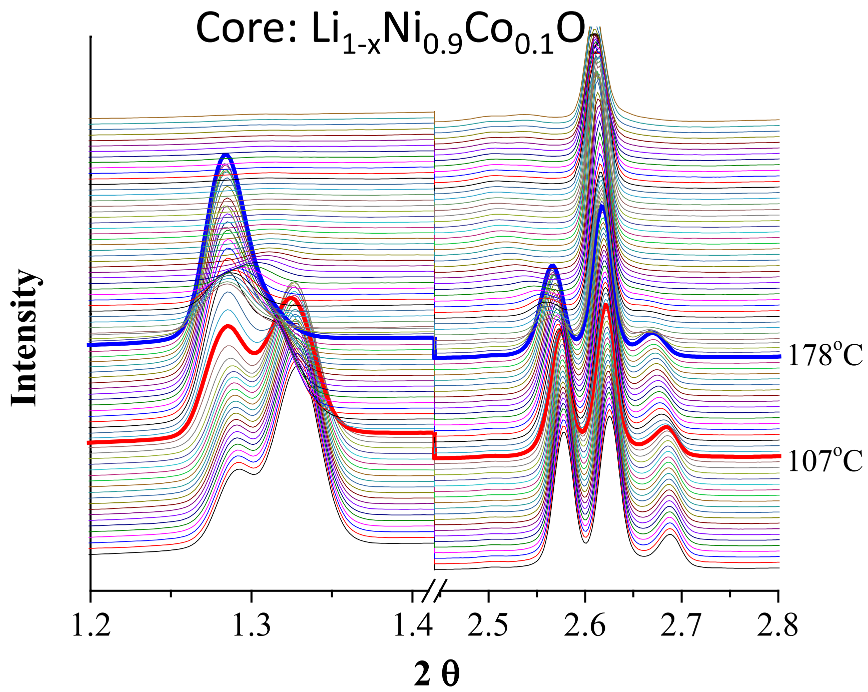
FGC material shows high onset temperature and 3 times lower heat flow than the core composition

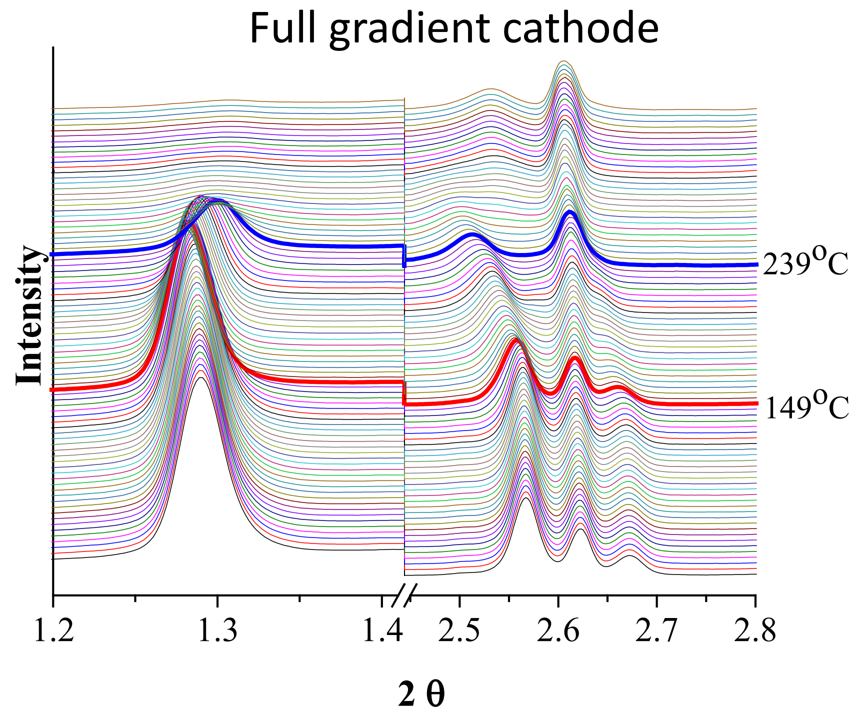
In situ high energy X-ray diffraction profile of delithiated Core and delithiated FGC material



Contour plots of in situ high energy X-ray diffraction profile of (a) delithiated core composition material [$Li_{1-x}(Ni_{0.86}Co_{0.10}Mn_{0.04})O_2$] and (b) delithiated FGC material during thermal ramping from room temperature to 375^{o}C with a scanning rate of 10^{o}C min^{-1}

Detail In situ high energy X-ray diffraction profile of delithiated Core and delithiated FGC material





1. Spinel phase appears at 25°C after cycling.
2. Reaction with the electrolyte take place at 178°C

1. Mostly layered phase after cycling and heating up to 150°C
2. Reaction with the electrolyte take place at 239°C

Summary

- Several core shell with gradient concentration cathode material with high Ni content in the core and different Mn content at the outer shell layer were prepared.

- Material with High Mn content in the outer shell layer (CSCGA) shows high capacity (220mAh/g), and High Tab density 2.4g/cc, with good cycle life and safety.

- Increasing Mn Content at the outer shell layer is more critical to the stability of the material than increasing the shell thickness.

- Full gradient concentration (FGC)material which can allow for increasing the Mn-content at the outer shell layer was prepared, characterized and tested.

- FGC material shows excellent cycling performance both at room and 55^{o}C with very limited capacity fade after 1000 cycles.

- The safety of the FGC material was outstanding and better than the core shell material with gradient concentration.

Future work

• Due to the re-scoping of the ABRT, this high energy cathode will be subject to a full proposal to further optimize develop, scale up and use it in a full system for PHEV and EVs

• Synthesize gradient materials with different surface compositions, as well as different gradient concentration slopes to determine the detailed effects of the composition profile on cathode capacity and stability.

• Tune the thickness of both the gradient and the Mn-rich shell to optimize material performance.

• Calendar and cycle life testing of new gradient materials.

• Extensive safety testing including ARC test and overcharge test.

• Scale up of optimum cathode material for full cell studies using Argonne scale up facility and with industrial partners.