New High Energy Gradient Concentration Cathode Material

K. Amine (PI)

G. Koenig, I. Belharouak, Y. K. Sun

Argonne National Laboratory

DOE merit review

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Project ID: ES016

Overview

Timeline

- Start - October 1st, 2008.
- Finish - September 30, 2014.
- 50% Completed

Barriers

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

Budget

- Total project funding
  - DOE share: 900K
  - FY11: 300K
  - FY10: 300K
  - FY09: 300K

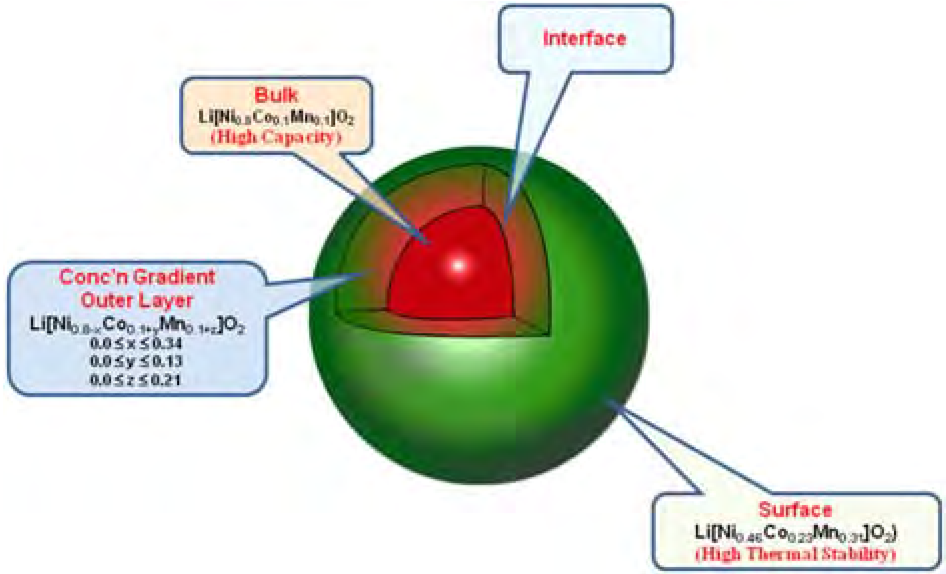
Partners

- Hanyang University
- ECPRO,
- TODA

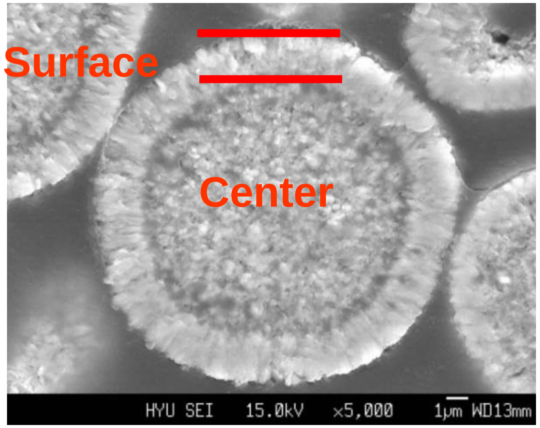
Objectives of the work

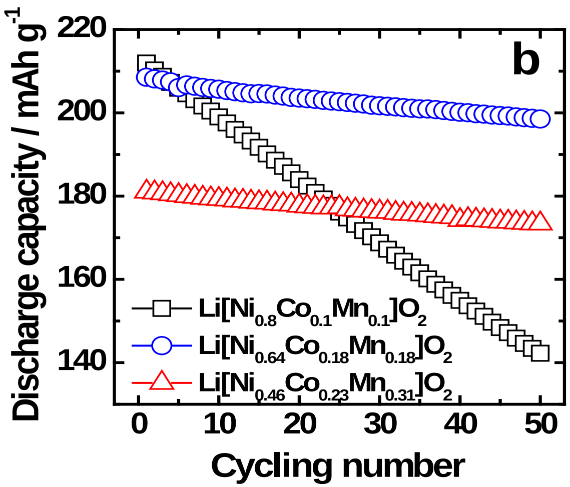
- Develop a new high energy cathode material for PHEV applications that provides:
  - Over 200mAh/g capacity
  - Good rate capability
  - Excellent cycle and calendar life
  - Good abuse tolerance

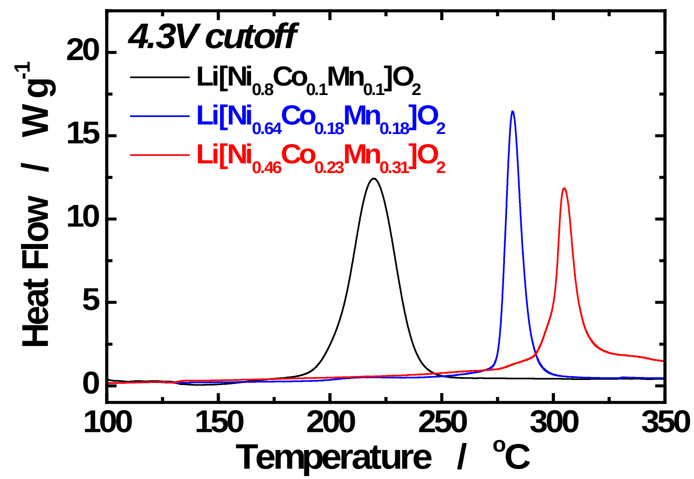
Approach



$Ni_{0.8}Co_{0.2}$ Core $Ni_{0.5}Mn_{0.5}$ Shell



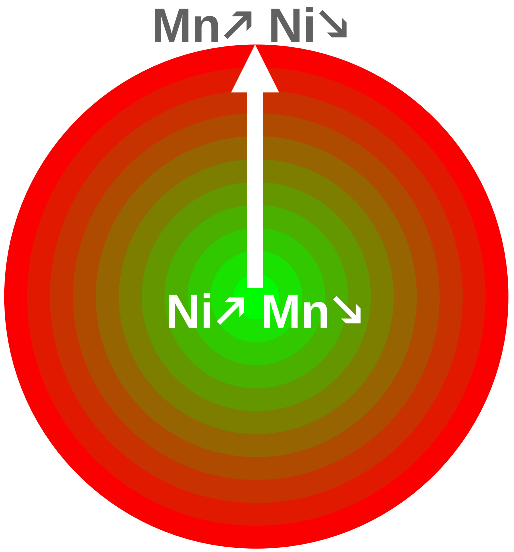




Previous research has demonstrated a core enriched in Ni for high capacity and a shell enriched in Mn for improved safety and cycle life.

Approach (Continued)

- Develop general synthetic method to tailor the internal composition gradient in cathode particles.
- Deposit a gradual composition gradient throughout particles to suppress stress during lithium intercalation and diffusion.
- Further enrich materials in Mn at the surface to enhance stability and safety.



FY 2011 Plans & Schedule

- Develop a model to predetermine the gradient in concentration in particles produced in the coprecipitation process (Sep 2011)
- Develop a process for precursors with a gradient in transition metal composition that was enriched in manganese (Sep. 2011)
- Demonstrate in a proof-of-principle experiment that precursors could be synthesized with predetermined compositional profiles (Sep. 2011)
- Demonstrate high capacity in final materials produced using the gradient precursors (Sep. 2011)
- Demonstrate that a tailored relative transition metal composition at the surfaces of gradient particles influences safety and cycle life (Sep. 2011)

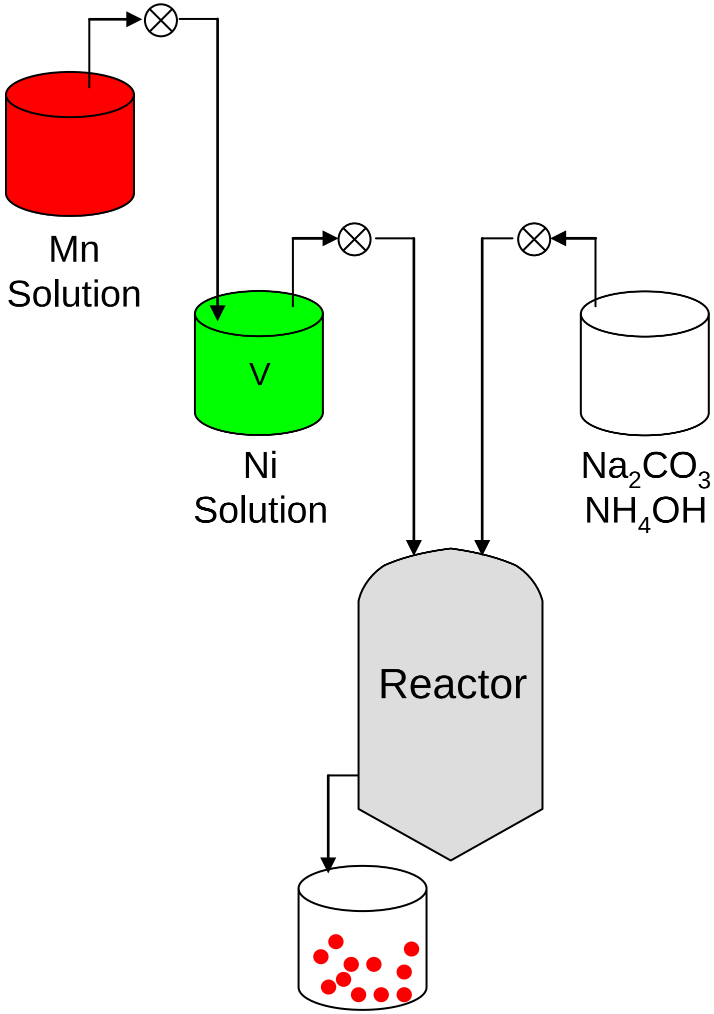
Recent Accomplishments and Progress

- Was able to develop a co-precipitation process with a predetermined relative transition metal compositional profile for synthesis of high energy gradient concentration precursors and cathode materials.

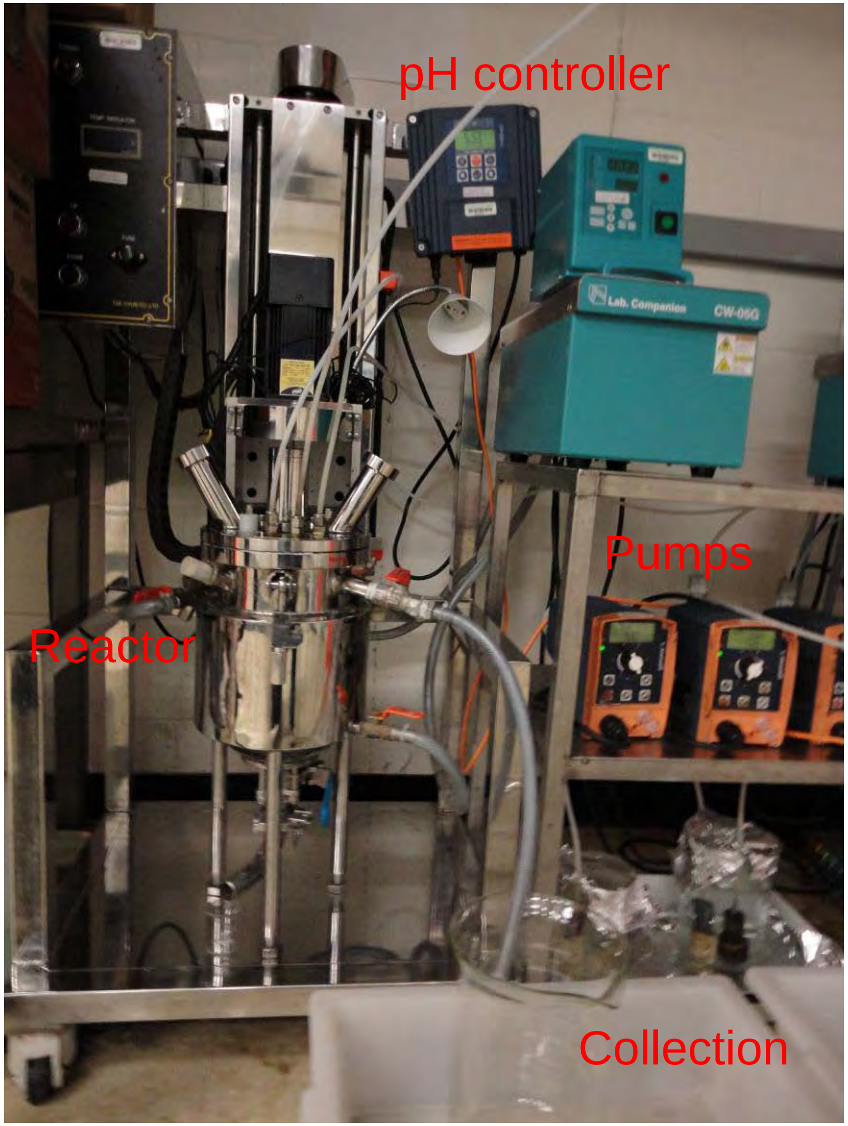
- Was able to characterize the material and demonstrate that both the precursor and lithiated final material had a gradient in relative transition metal concentration at the individual particle level.

- Was able to demonstrate that gradient concentration cathode materials safety and cycle life were dependent on the detailed compositional profile.

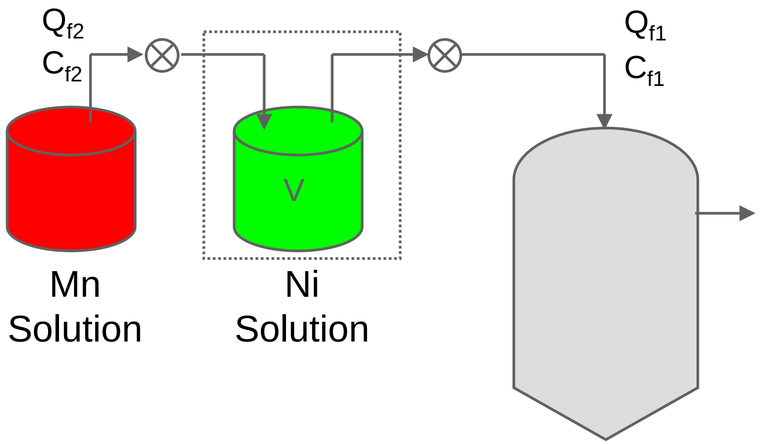
Synthesis of Precursor via CSTR Coprecipitation



Reactor Setup



Prediction of Transition Metal Concentration Gradient



$$\frac{d(C_{f1}V)}{dt} = Q_{f2}C_{f2} - Q_{f1}C_{f1} \qquad \frac{d(C_{f1}V)}{dt} = C_{f1}\frac{dV}{dt} + V\frac{dC_{f1}}{dt}$$

$$\frac{dV}{dt} = Q_{f2} - Q_{f1} \qquad V = V_i + (Q_{f2} - Q_{f1})t$$

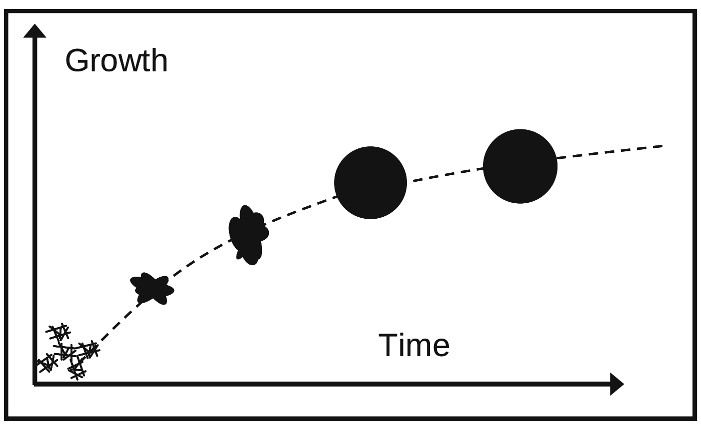
$$\frac{dC_{f1}}{dt} = \frac{Q_{f2}C_{f2} - Q_{f2}C_{f1}}{V_i + (Q_{f2} - Q_{f1})t}$$

Set Values: Q_{f2}, C_{f2}, Q_{f1}, V_i

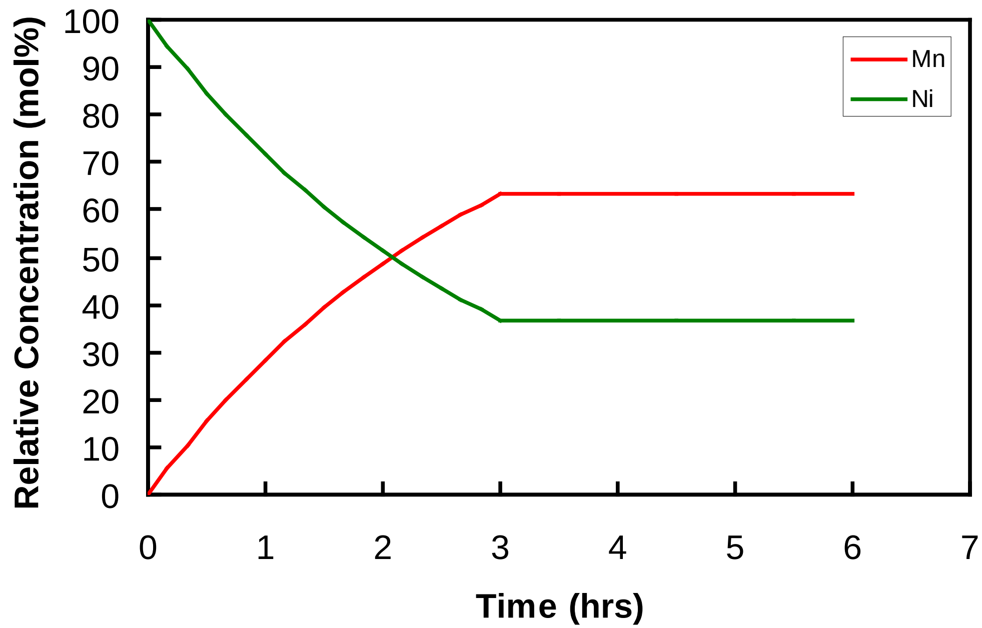
At t=0, $C_{f1}=C_{f1i}$

Solve for C_{f1} (feed to reactor) as a function of time

The concentration profile of the transition metal feed to the reactor was calculated by assuming that the feed (Ni Solution) was well-mixed.

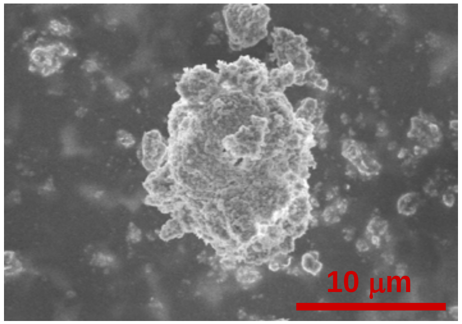


Predicted Concentration Profile

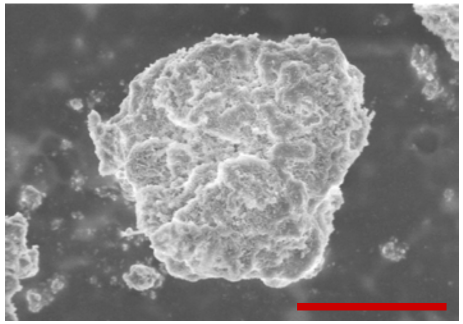


Precursor Particle Morphology During Coprecipitation

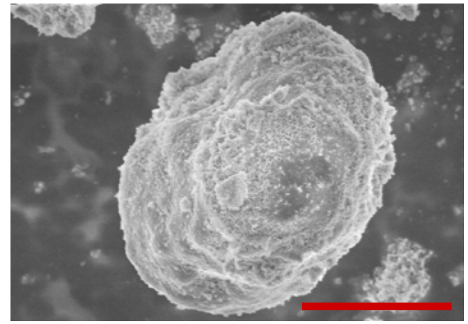
Hour 0-1



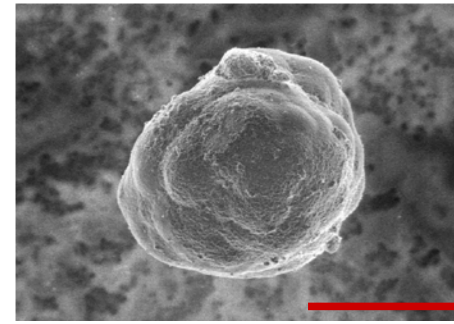
Hour 1-2



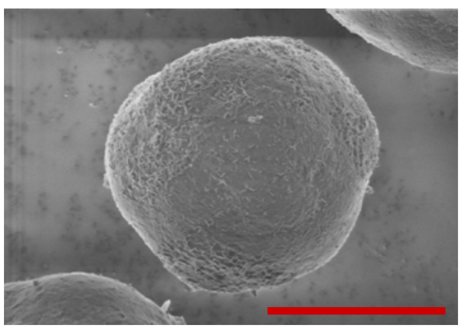
Hour 2-3



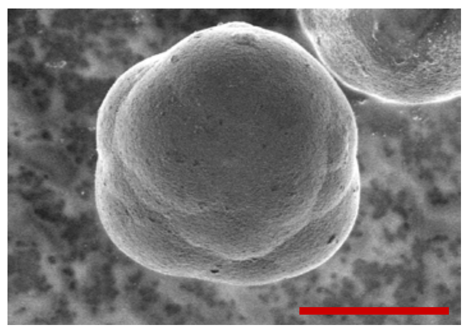
Hour 3-4



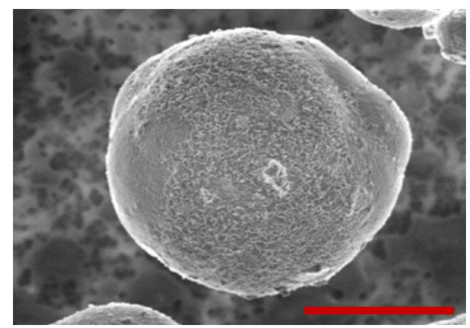
Hour 4-5



Hour 5-6

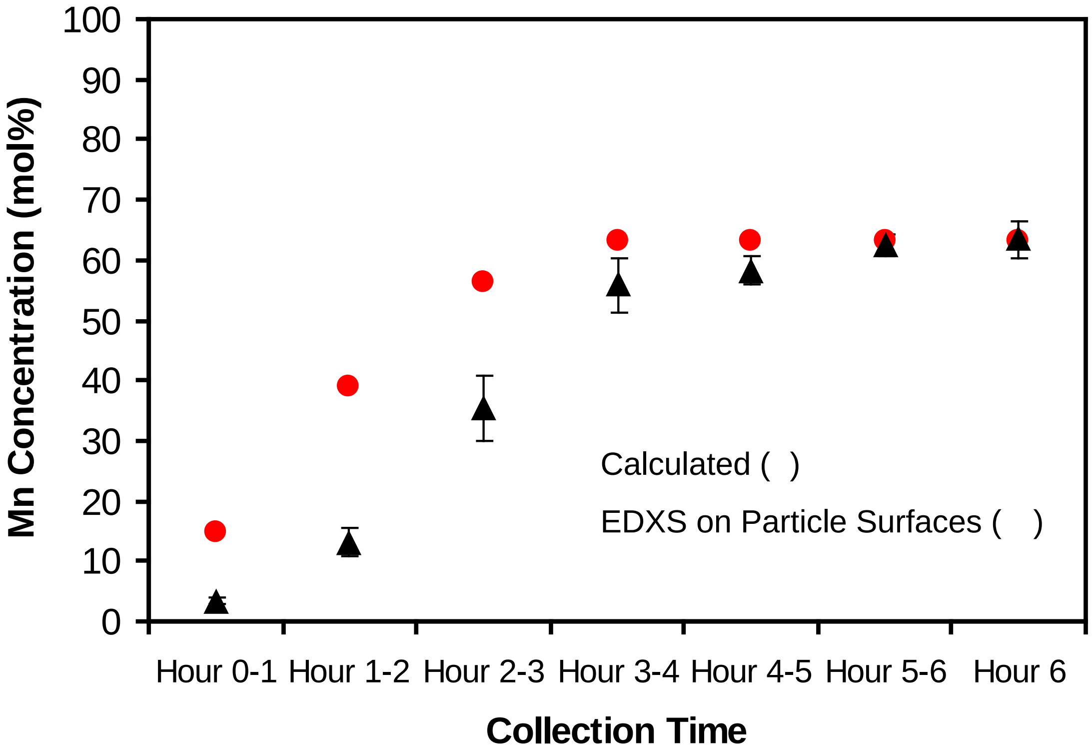


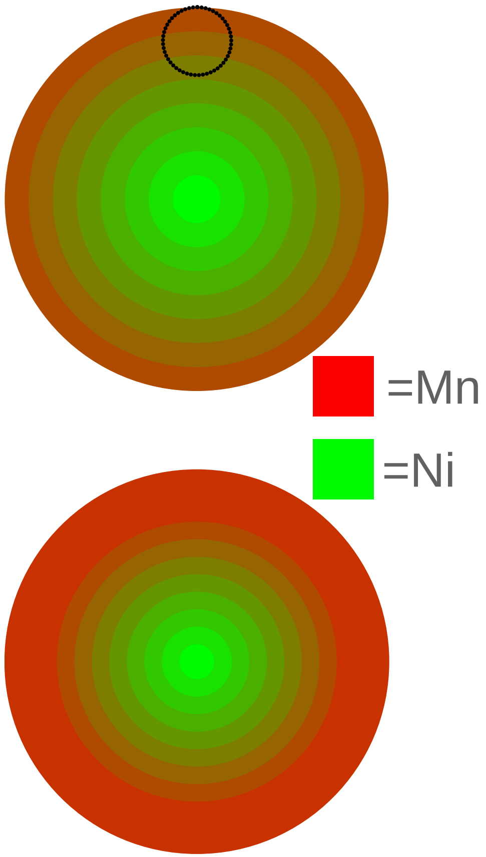
Hour 6



Particles became more spherical and less rough as time increased

Precursor Relative Transition Metal Surface Composition



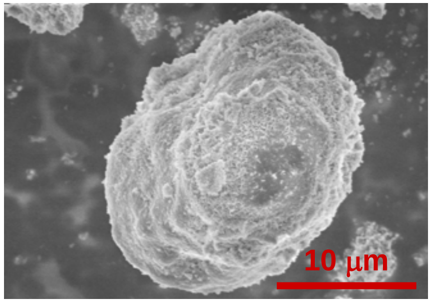


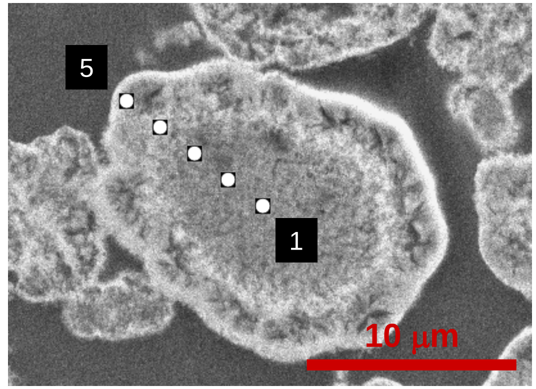
Measured concentrations showed good agreement with calculated concentrations late in the process.

Measured concentrations were lean in Mn compared to calculations early in the process, possibly due to contributions from the interaction volume below the surface.

Interior Cross-Section SEM and EDXS

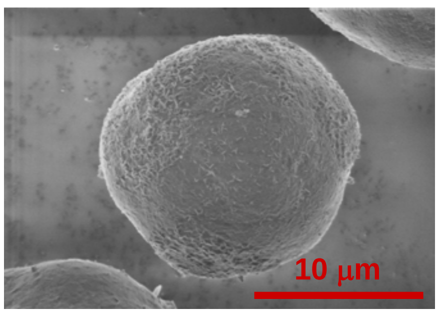
Hour 2-3

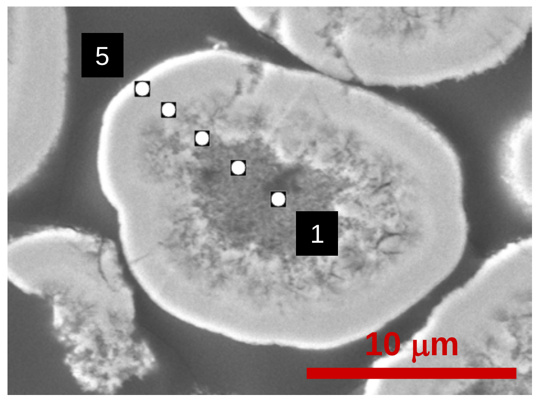




Point	%Mn
1	19.1
2	24.2
3	22.5
4	26.3
5	48.4

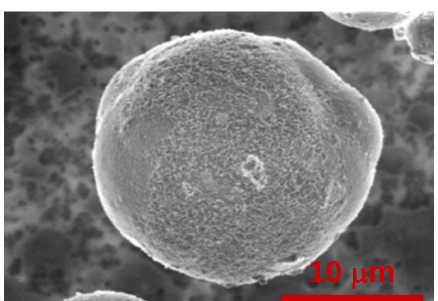
Hour 4-5

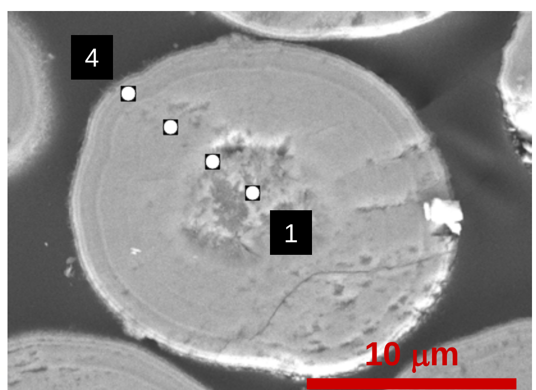




Point	%Mn
1	21.2
2	25.7
3	34.5
4	56.6
5	54.7

Hour 6

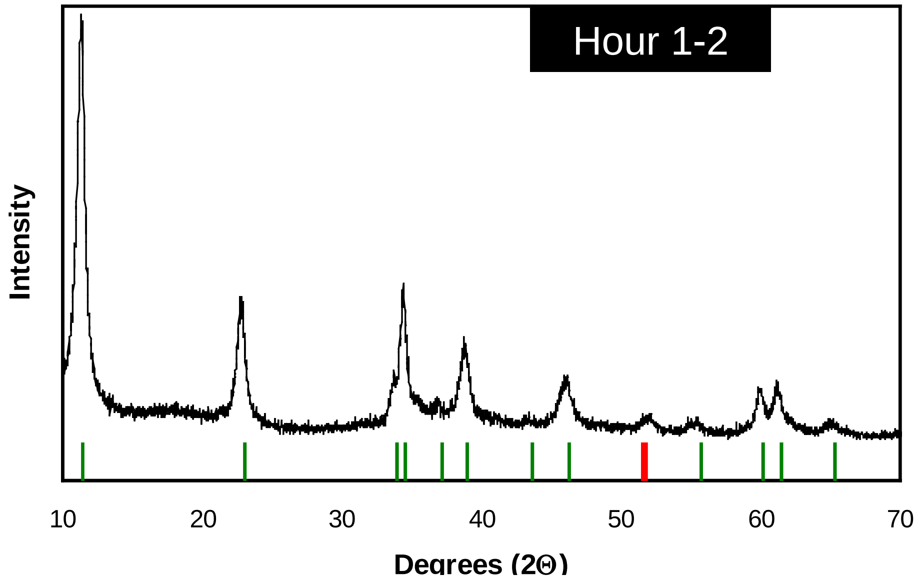


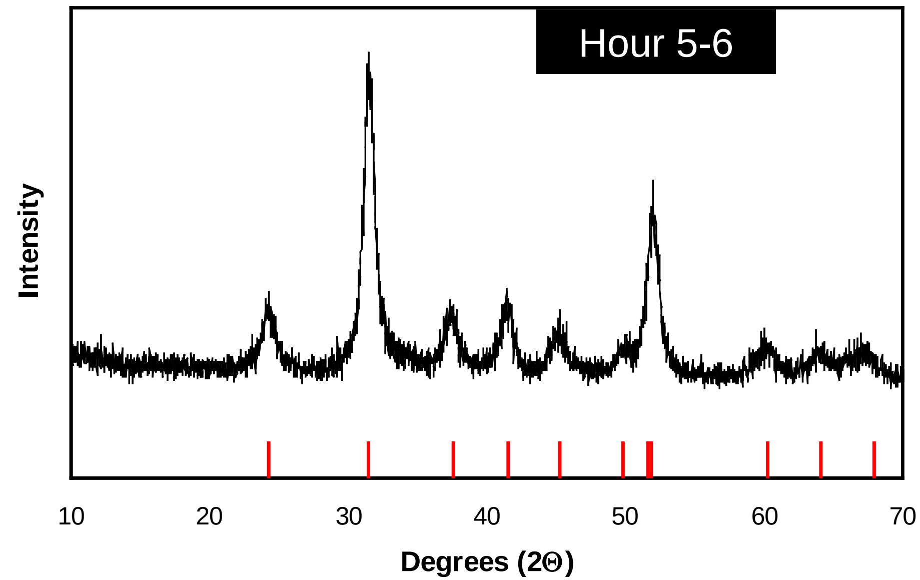


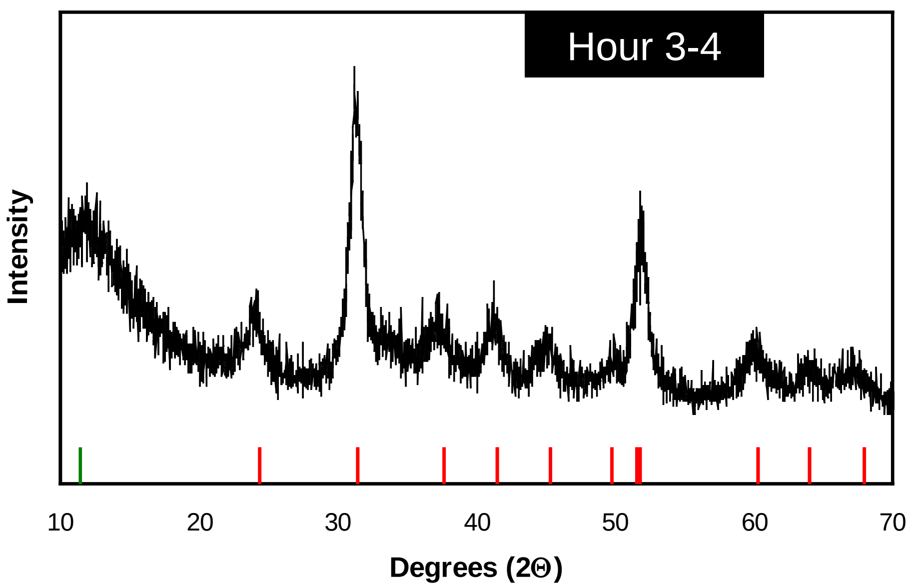
Point	%Mn
1	27.1
2	52.5
3	64.1
4	62.1

EDXS results confirm internal concentration gradient

XRD of Precursor Materials







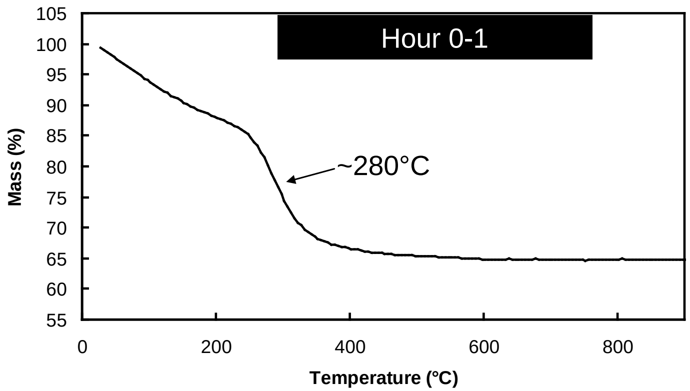
$Ni(OH)_2 \cdot (NiOOH)_{0.167}$

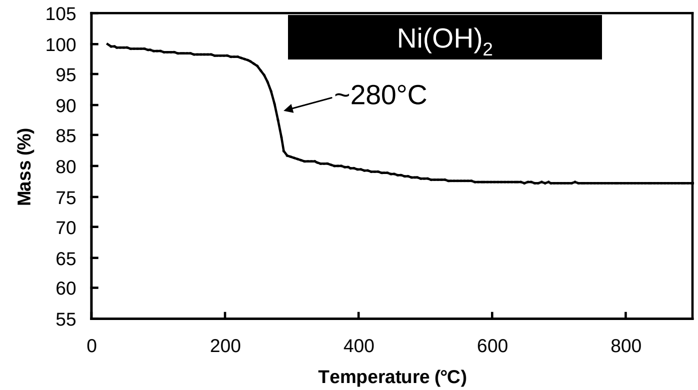
$MnCO_3$

Particles collected early in the process had primarily $Ni(OH)_2 \cdot (NiOOH)_{0.167}$–type features, while at the end of the process only $MnCO_3$-type features were distinguishable

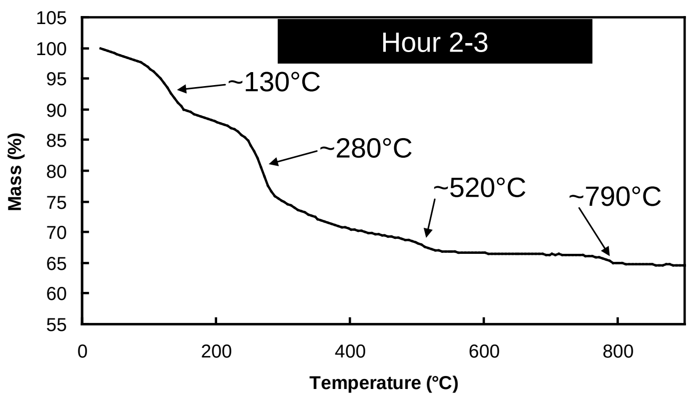
TGA of Precursor Materials

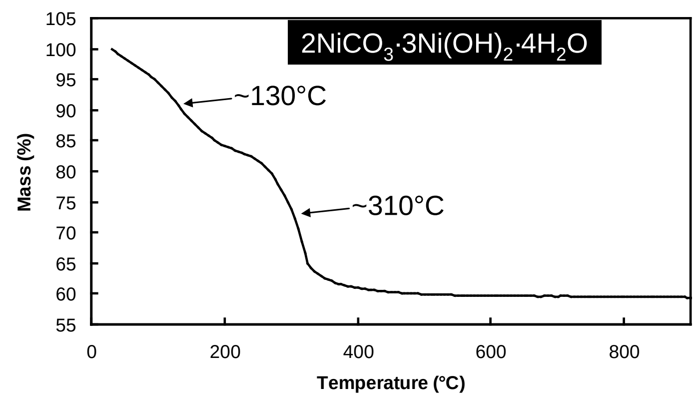
Mainly $Ni(OH)_2$-type decomposition early in the process



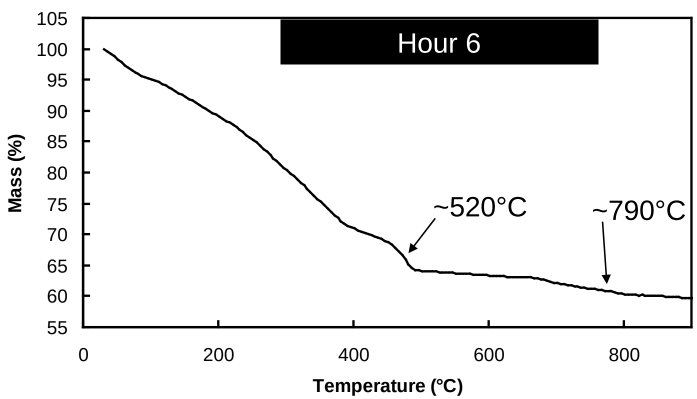


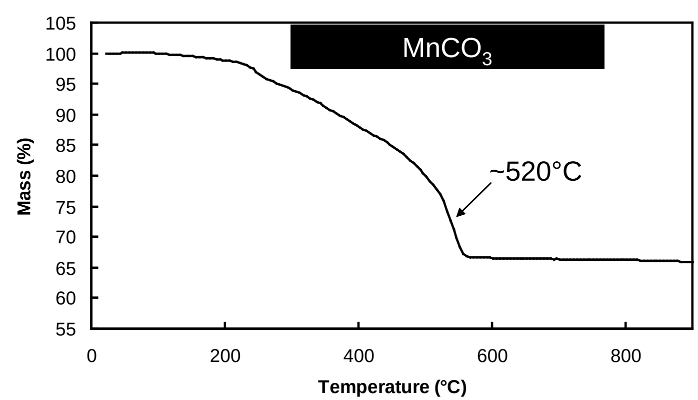
$NiMnO_3 + Mn_2O_3 \rightarrow NiMn_2O_4 + 0.5\ Mn_2O_3 + 0.25\ O_2$





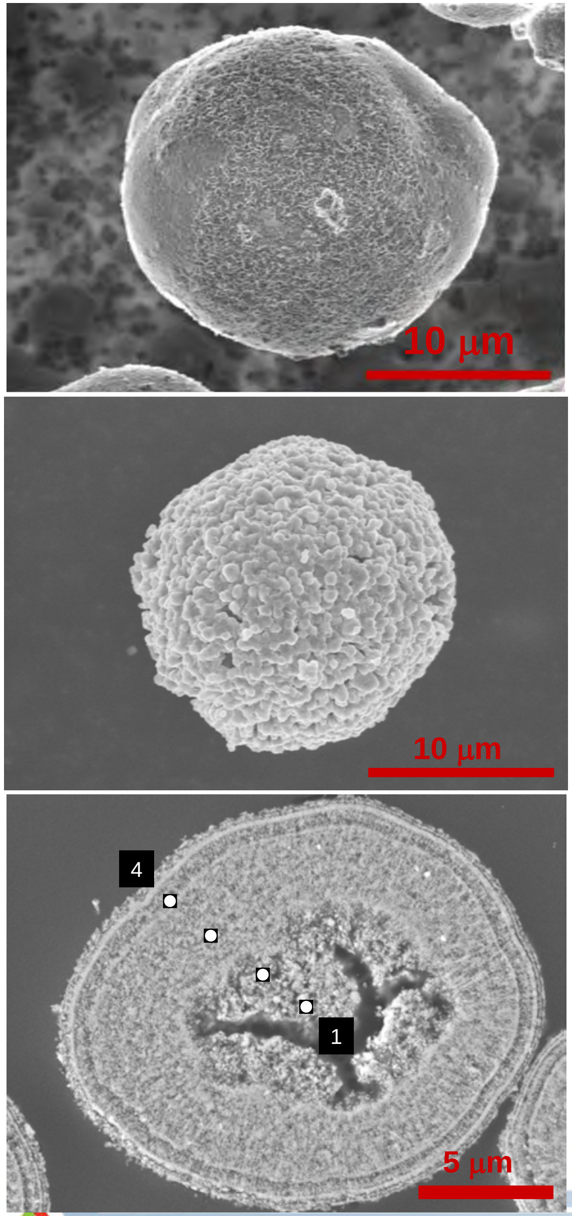
Increasingly $MnCO_3$-type decomposition at the end of the process

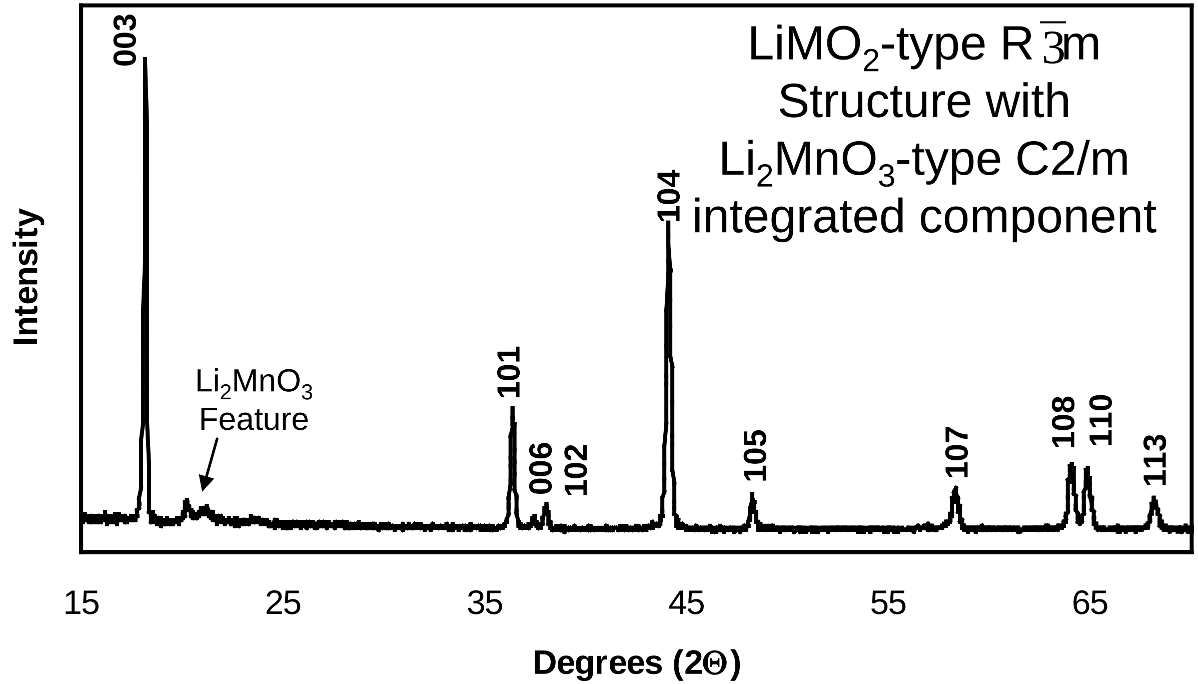




Lithiated Final Material ($Li_{1.2}(Mn_{0.62}Ni_{0.38})_{0.8}O_2$) Structure and Morphology

Hour 6 Precursor



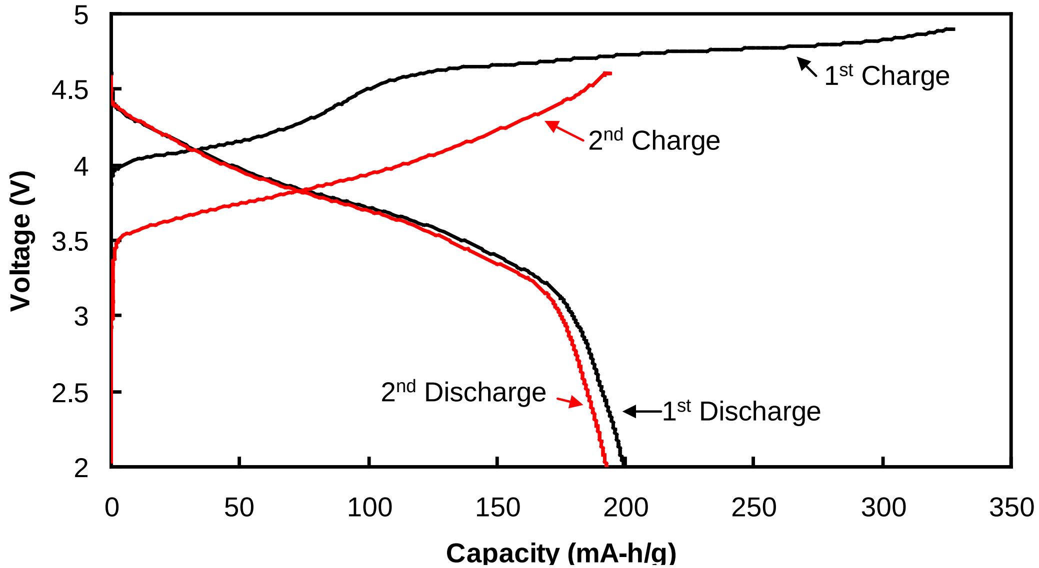


EDXS analysis

Point	%Mn
1	27.1
2	52.5
3	64.1
4	62.1

Concentration gradient is retained for the final lithiated cathode material.

Charge-Discharge of $Li/Li_{1.2}(Mn_{0.62}Ni_{0.38})_{0.8}O_2$ Cell



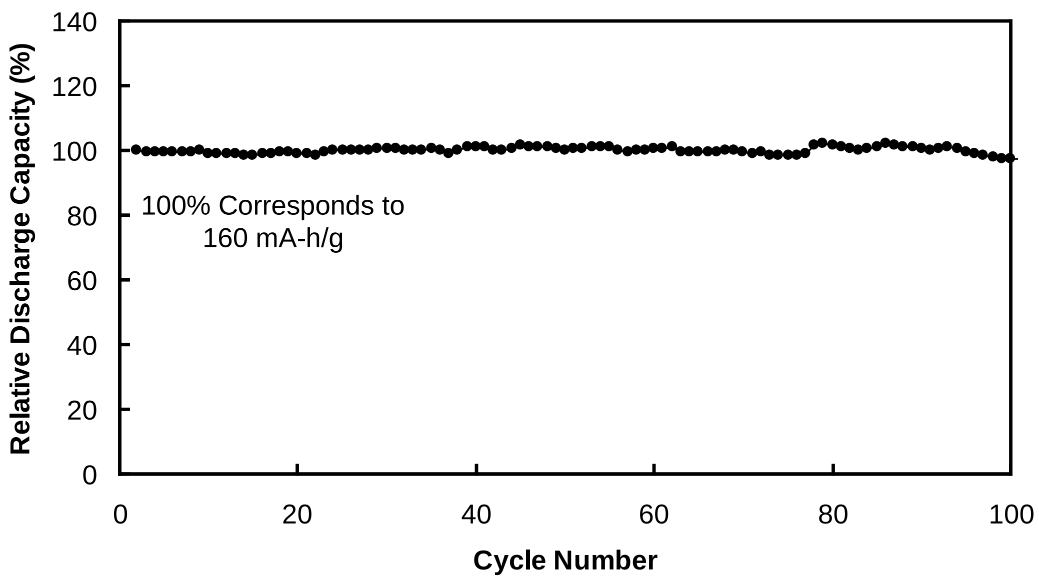
1st Charge-327 mAh/g

1st Discharge-199 mAh/g

2nd Charge-194 mAh/g

2nd Discharge-193 mAh/g

Profile consistent with Li-and Mn-enriched cathode material



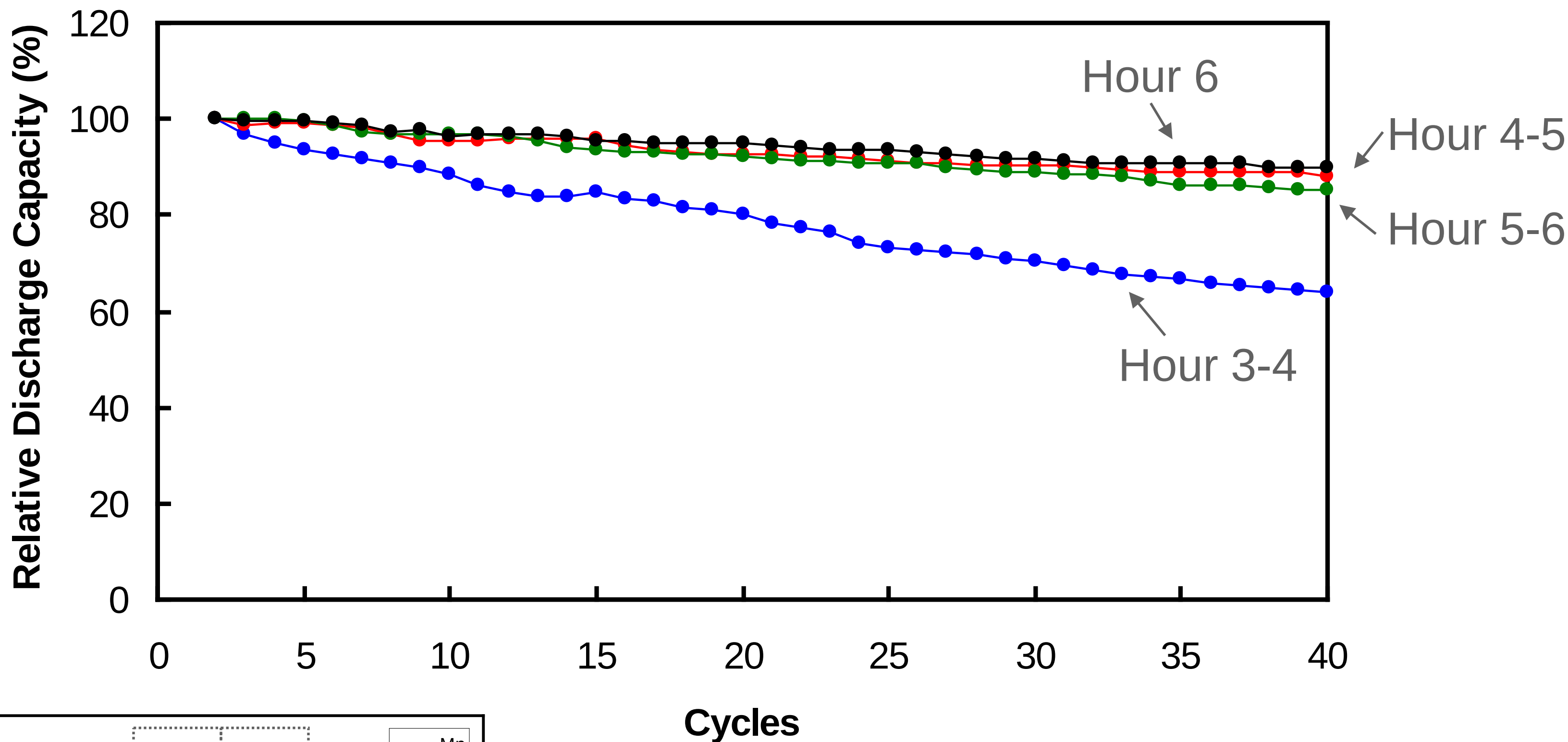
50 Cycles-100%

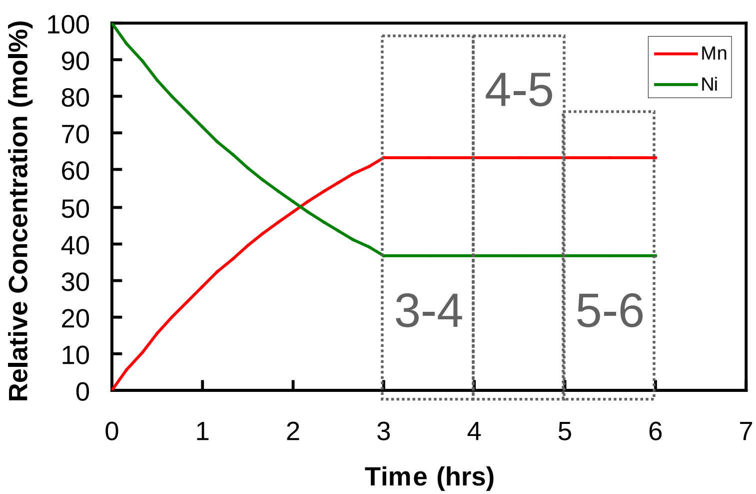
100 Cycles-97%

Rate-C/2 (100 mA/g)

2.0-4.6 V

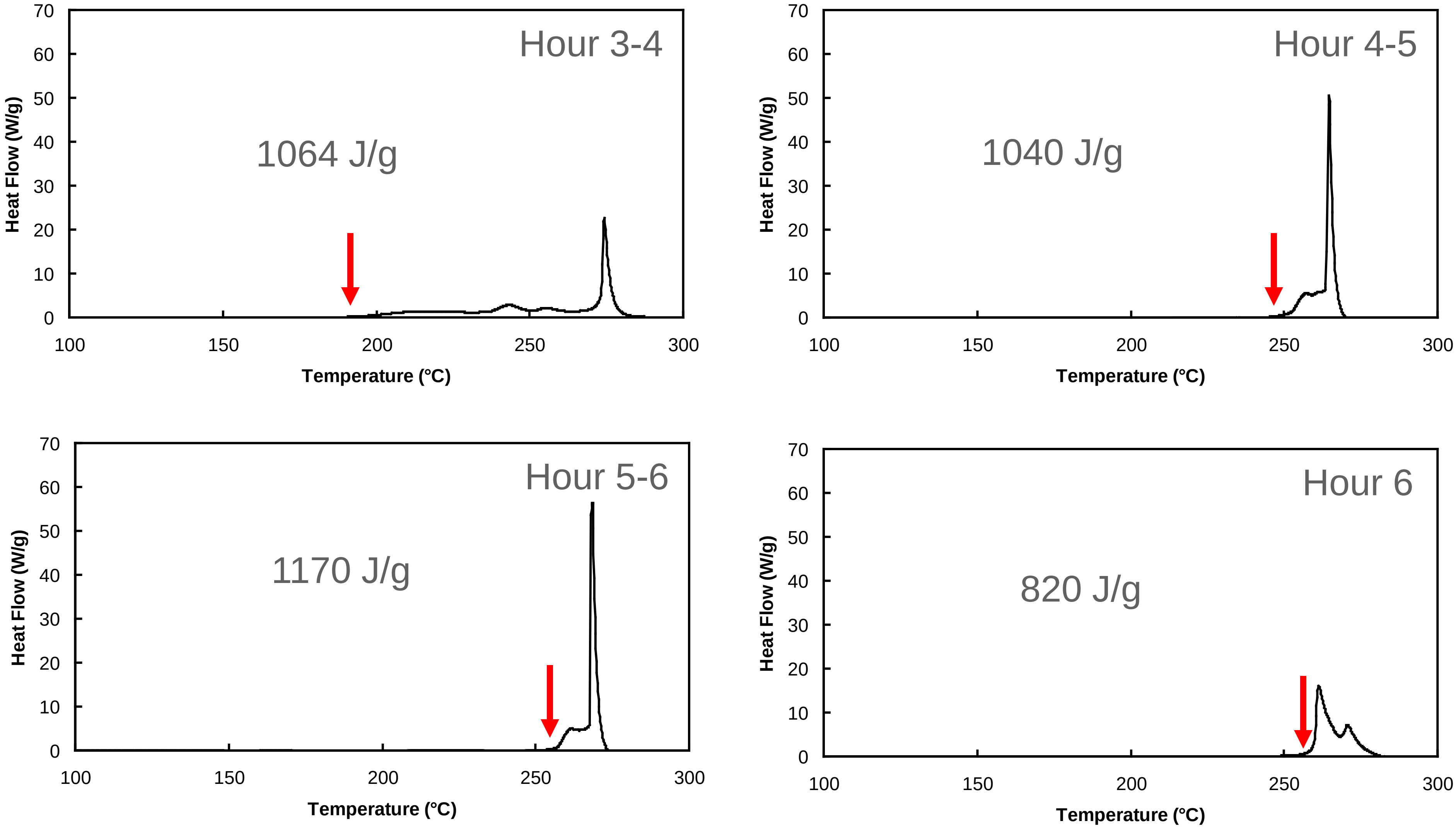
Capacity Fade of Gradient Materials





Materials made from precursors collected at later times (with greater relative surface manganese compositions and a thicker Mn-enriched shell) had better retention of capacity during cycling.

DSC on Gradient Materials



Manganese-enriched shell provides enhanced thermal stability

Summary

- New gradient concentration cathode material was developed with a continuous change in relative transition metal composition from the core to the surface.

- SEM, EDXS, XRD, and TGA confirmed the gradient in the synthesized precursor materials from Ni-enriched in the core to Mn-enriched near the surface.

- The compositional gradient was also confirmed to be retained after high temperature calcination with lithium.

- Gradient concentration final material shows 193 mAh/g capacity and good capacity retention during cycling.

- Safety and cycle life of gradient concentration materials are improved as the thickness of the Mn-enriched shell increases.

Future work

- Further refine model of coprecipitation process.

- Synthesize gradient materials with different overall and 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 larger battery cells.

- Investigate other nano-coatings (metal fluorides, oxides, and phosphates) on gradient materials to further enhance surface stability.