Engineering of High energy cathode material

K. Amine (PI)
H. Wu, I. Belharouak, Y.K. Sun

Argonne National Laboratory

DOE merit review
May 14-18 , 2012

Project ID, ES-015

Overview

Timeline

- Start - October 1st, 2008.
- Finish - September 30, 2014.
- 65%

Barriers

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

Budget

- Total project funding:1200K
  - DOE share:
  - 2012: 300K
  - FY11: 300K
  - FY10: 300K
  - FY09: 300K

Partners

- Interactions/ collaborations:
- *X.Q. Yang (BNL)*
- *Kang Xu (ARL)*
- *Jun Liu (PNNL)*
- *Toda*
- *BASF*
- *ECPRO*

Objectives of the work

Enable the Argonne high energy composite layered cathode $xLi_2MnO_3 \bullet (1-x)LiNiO_2$ (LMR-NMC) for 40 miles PHEV

- Capacity of over 250mAh/g
- High packing density
- 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 and electrolyte additive to enable high rate and long cycle life at high voltage (4.6 V) and high temperature and mitigate voltage drop.

FY 2012 plans & schedule

✓ Further optimize the process to improve the physical properties of the material and prevent cracking of particles after calendaring. (ongoing)

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

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

✓Improve the rate performance and reduce the voltage fade at deep depth of discharge (ongoing)

✓Investigate the effect of high voltage electrolyte additives to stabilize the cathode material at 4.6 V. (ongoing)

✓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)

Recent accomplishments and progress

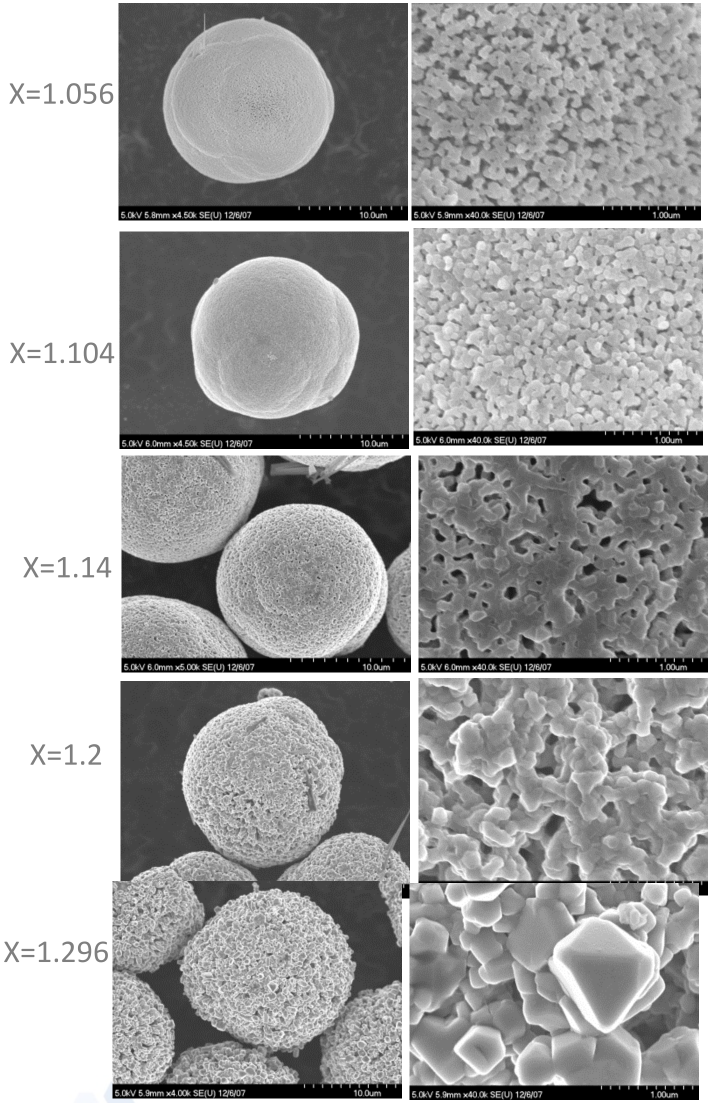
- Provided detail process to ANL scale up facility for scaling up the LMR-NMC ($Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$) (Kg batch level was scaled up by ANL scale up facility).

- Optimized the hydroxide co-precipitation process to improve the physical properties of the cathode material and prevent particle cracking during electrode calendaring .

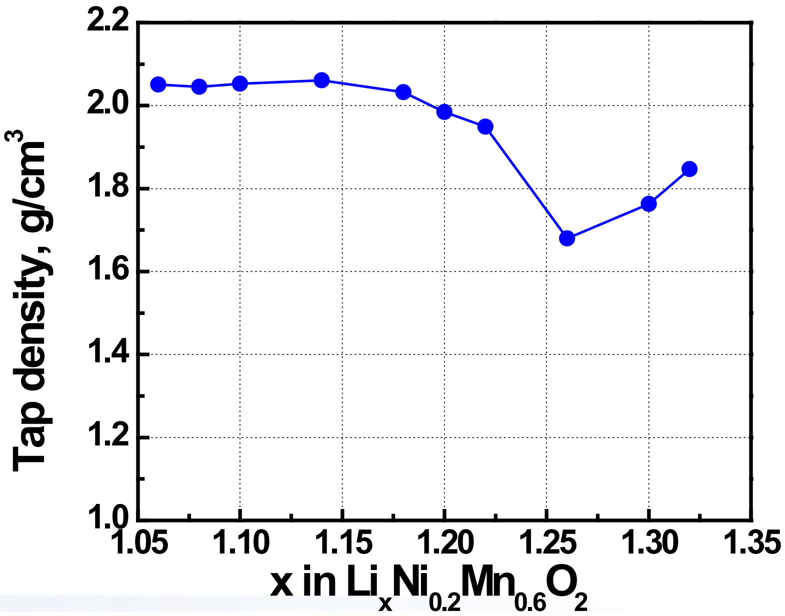
- Validated the improvement of rate and cycling stability at high temperature using dry AlF_3 coating process.

- Validated the reduction in voltage fade using AlF_3 coating

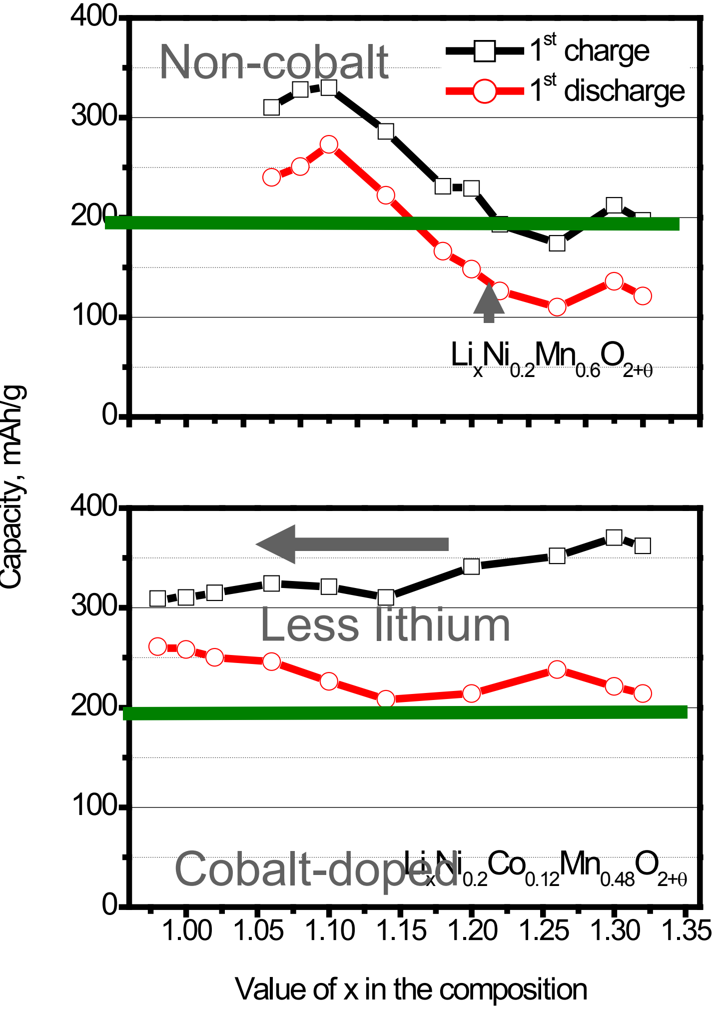
Lesson learned: Role of Excess Lithium in LMR-NMC morphology ($Li_xNi_{0.2}Mn_{0.6}O_2$)



Excess lithium in LMR-NMC controls the porosity and the size of the primary particle and thus the material tap density

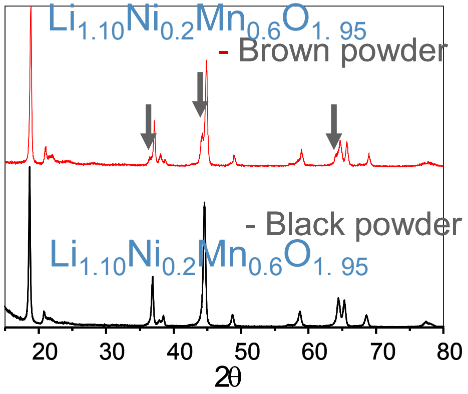


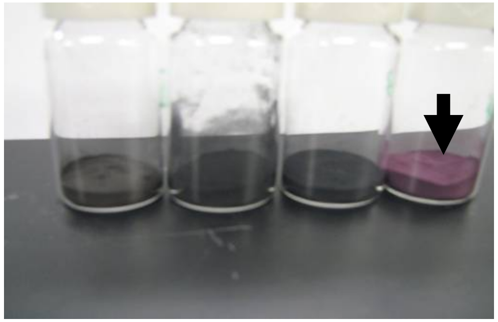
Lesson learned: Co- Doping in LMR-NMC shows better reproducibility

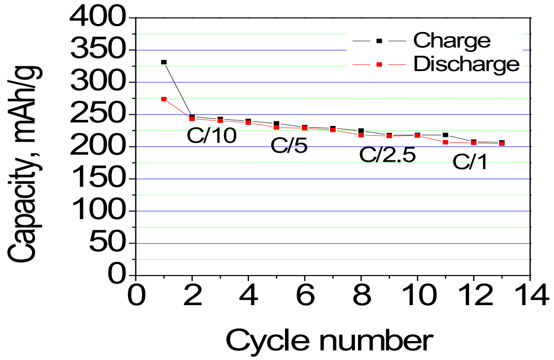


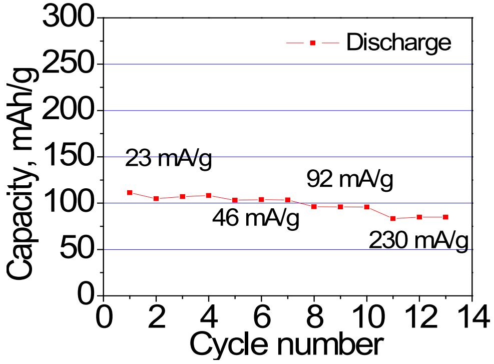
Capacity is Less sensitive to lithium concentration with Co doping.

Capacity is sensitive to lithium concentration.



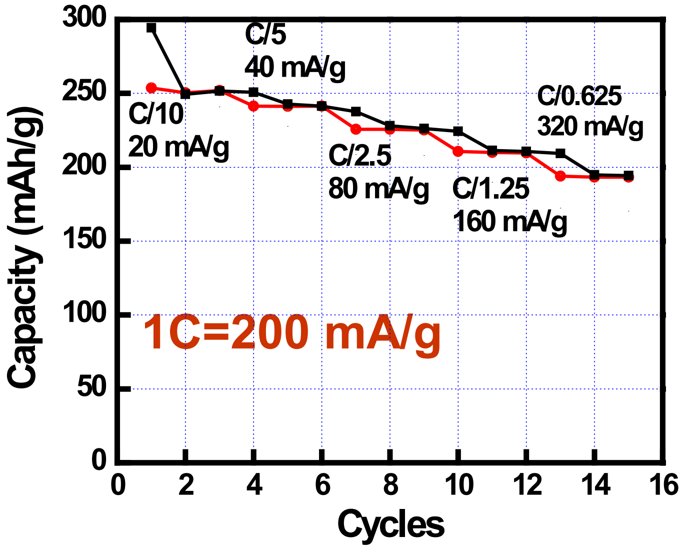


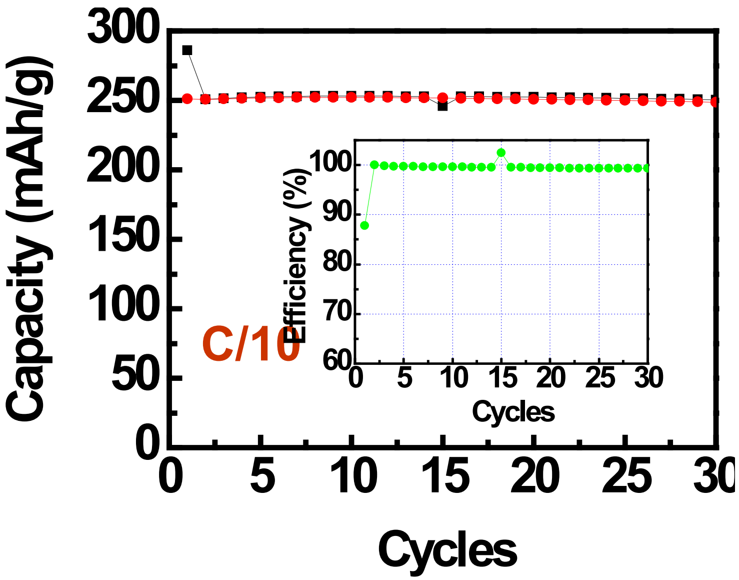


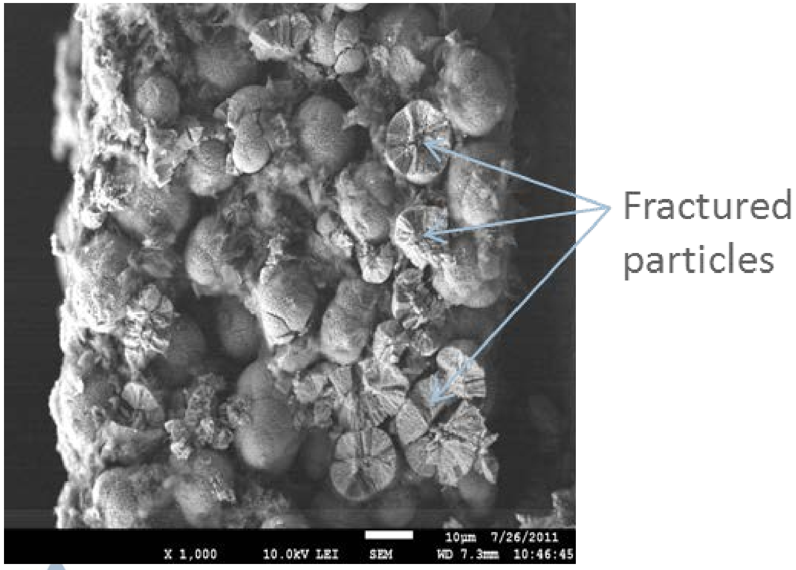


- **Two materials with the same composition ($Li_{1.10}Ni_{0.2}Mn_{0.6}O_{1.95}$) and the same process of preparation shows different colors and different rates and cycling performance (difficult to reproduce Co-free with low Ni/Mn ratio in LMR-NMC material)**

Lesson learned: optimizing Ni/Mn ratio to high level ($Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$) can lead to high reproducibility





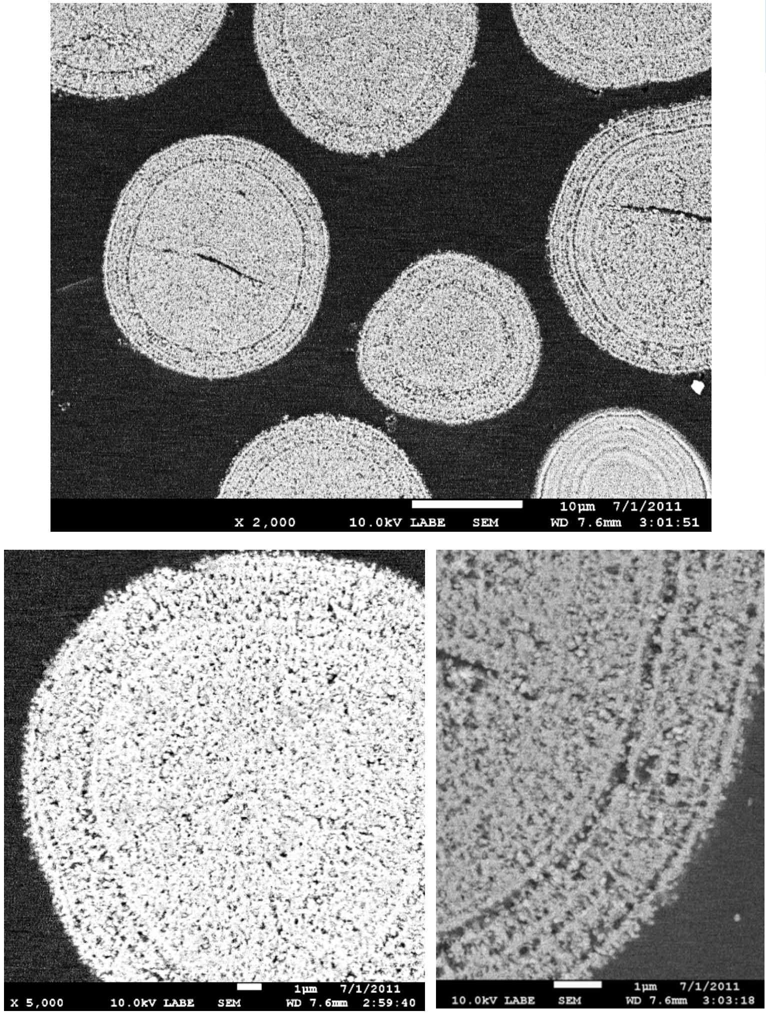


- Optimum composition that provide good performance and high reproducibility during scale up : ($Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$)

- Material made with carbonate process tends to crack during calendaring

Carbonate process yield high porosity inside the particle

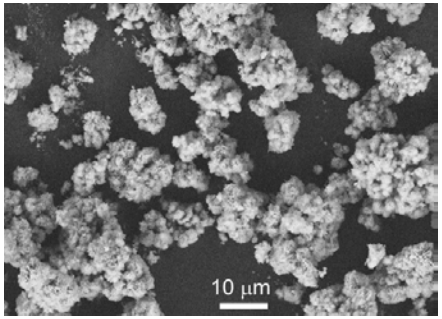
BET	$Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$ Carbonate process
Surface area	5.5 m^2/g
Average pore size	14 nm
Pore volume	3.766e-02 cc/g
Porosity (particle level, calculated)	16.5%



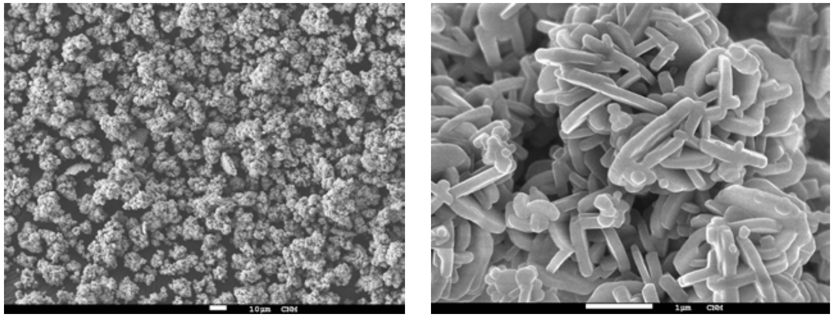
Cross-section SEM images of $Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$

- **Porosity inside the particle when using carbonate process: 16.5%**
- **High porosity inside particles is responsible for particle cracking during electrode calendaring**
- **Use hydroxide process to mitigate particle cracking**

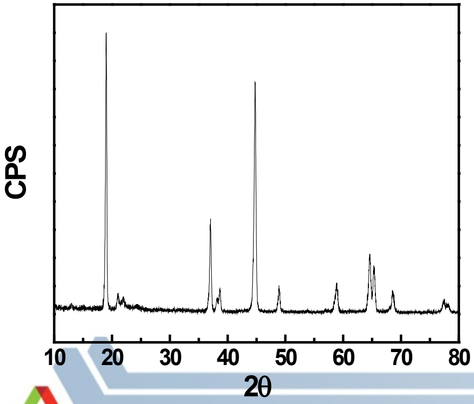
SEM & XRD of HEM prepared by hydroxide process



SEM of the hydroxide precursor $Mn_{2/3}Ni_{1/3}(OH)_2$



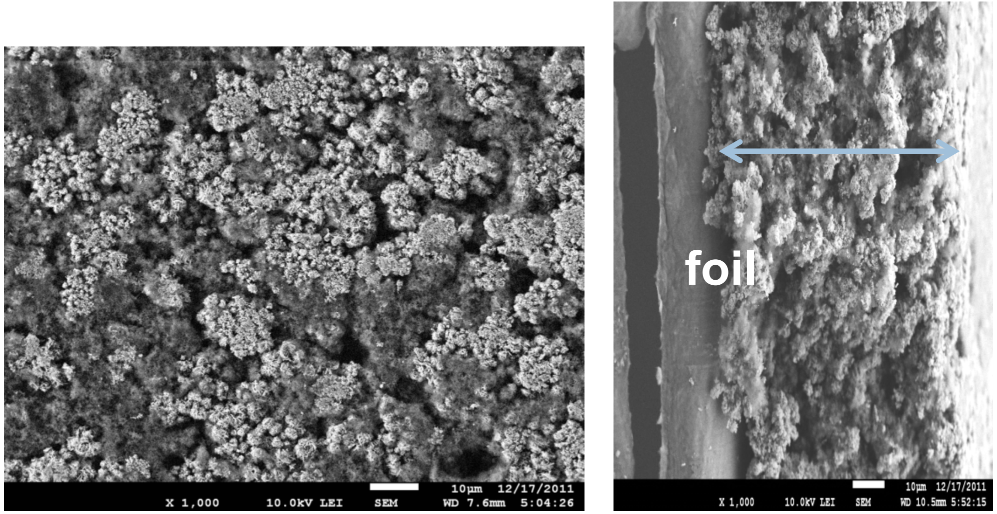
SEM of $Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$



XRD pattern of $Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$ from $Mn_{2/3}Ni_{1/3}(OH)_2$ precursor.

1. **$Mn_{2/3}Ni_{1/3}(OH)_2$ was synthesized by a hydroxide co-precipitation process.**
2. **$Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$ was prepared from $Mn_{2/3}Ni_{1/3}(OH)_2$ and Li_2CO_3.**
3. **SEM shows uniform 10 µm particles with 50 nm primary particles**
4. **XRD shows typical profile of LRM-NMC**

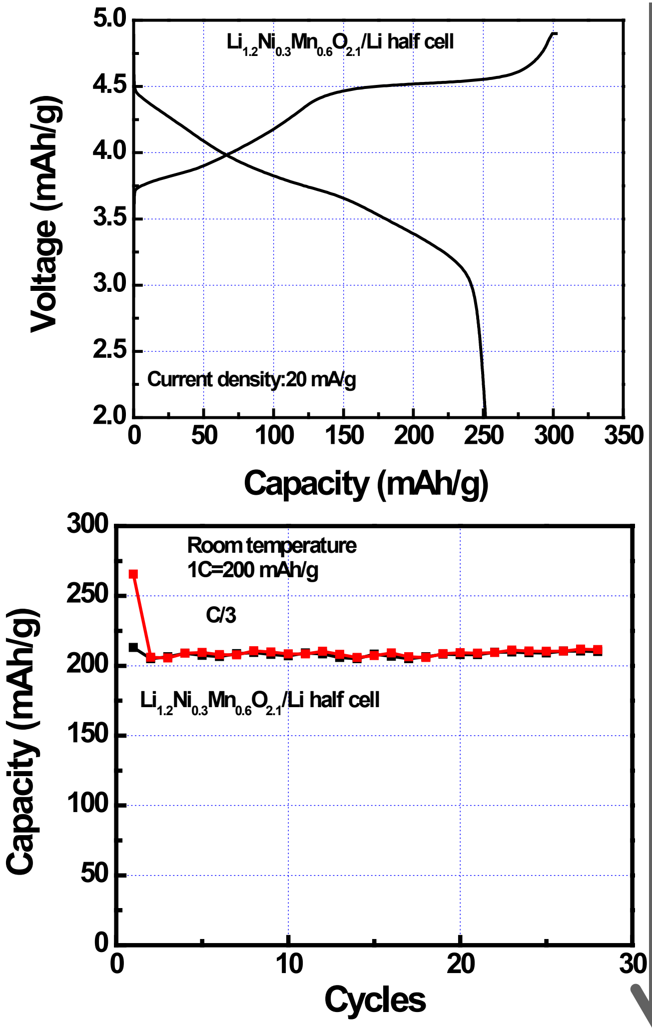
No Particle cracking was observed from material prepared by hydroxide process



BET	$Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$ From hydroxide precursor
Surface area	3.862 m^2/g
Average pore size	8 nm
Pore volume	1.582e-02 cc/g
Porosity (particle level, calculated)	6.6%

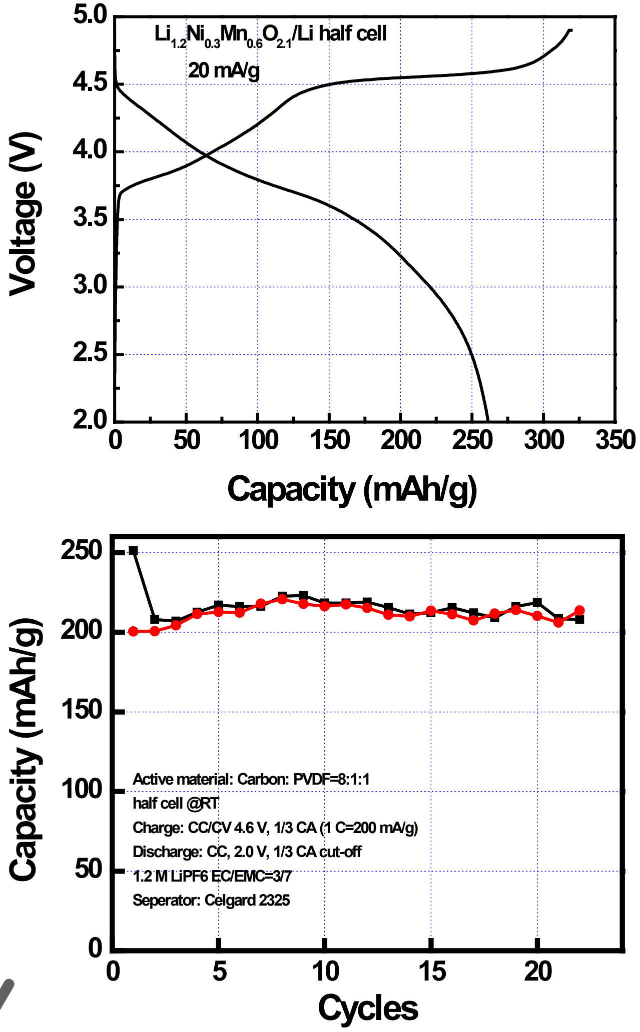
1. Porosity of particle made from hydroxide is : 6.6%
2. Material made by hydroxide process shows much lower surface area than the one made by carbonate
3. Electrode after calendaring shows no particle cracking

Comparison of electrochemical performance of cathodes made by carbonate & hydroxide process



$Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$

Hydroxide process

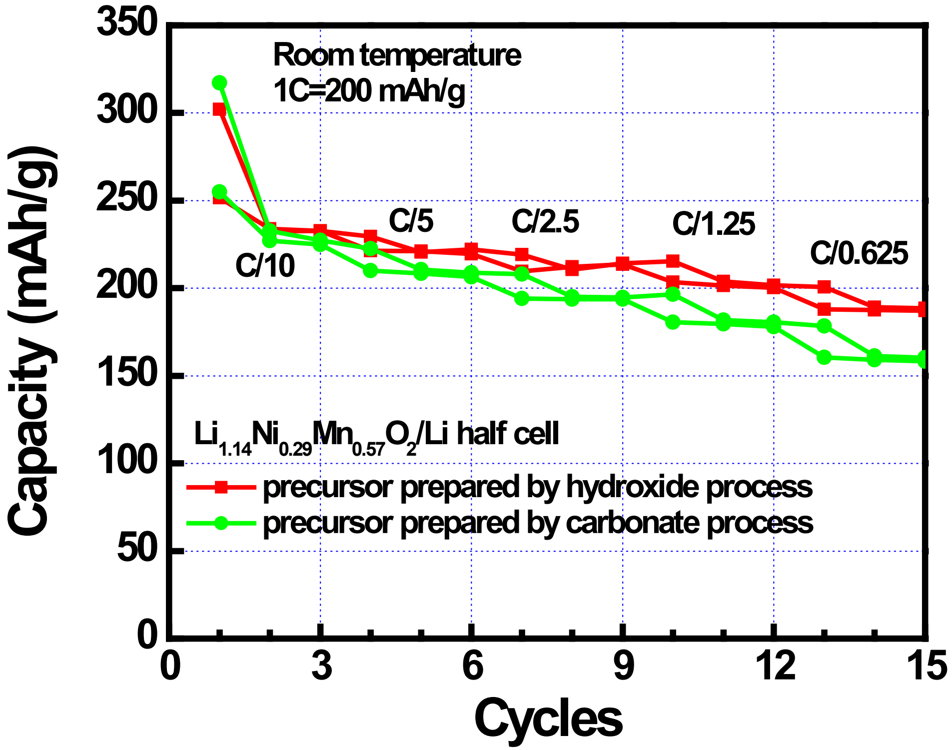


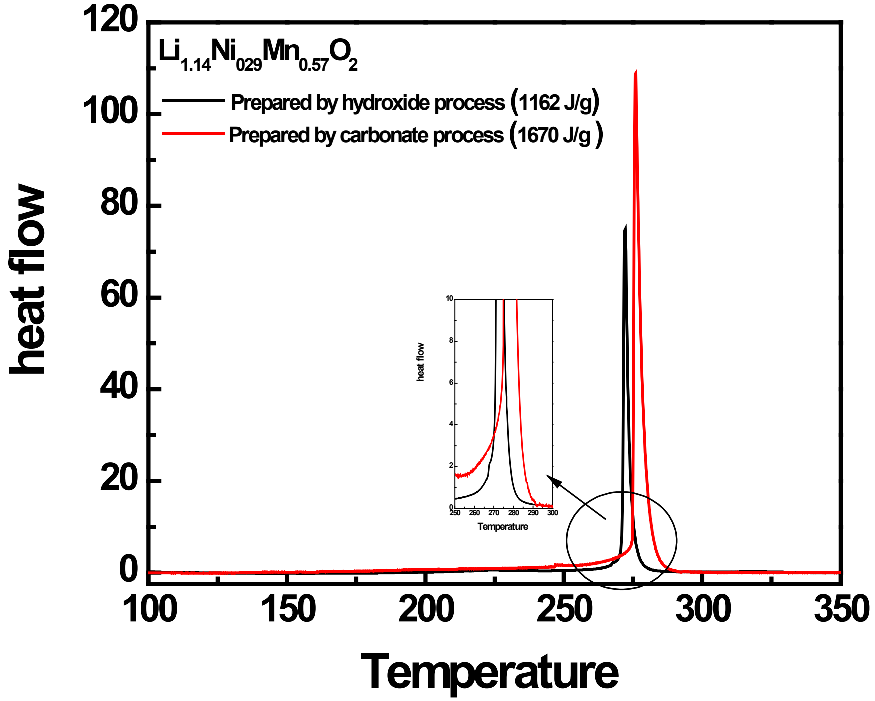
$Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$

Carbonate process

1. **Both samples have high capacity of 250 mAh/g at C/10.**
2. **Both samples have good cycle performance at C/3 at room temperature.**

Comparison of rate & safety performance of cathodes made by carbonate & hydroxide processes

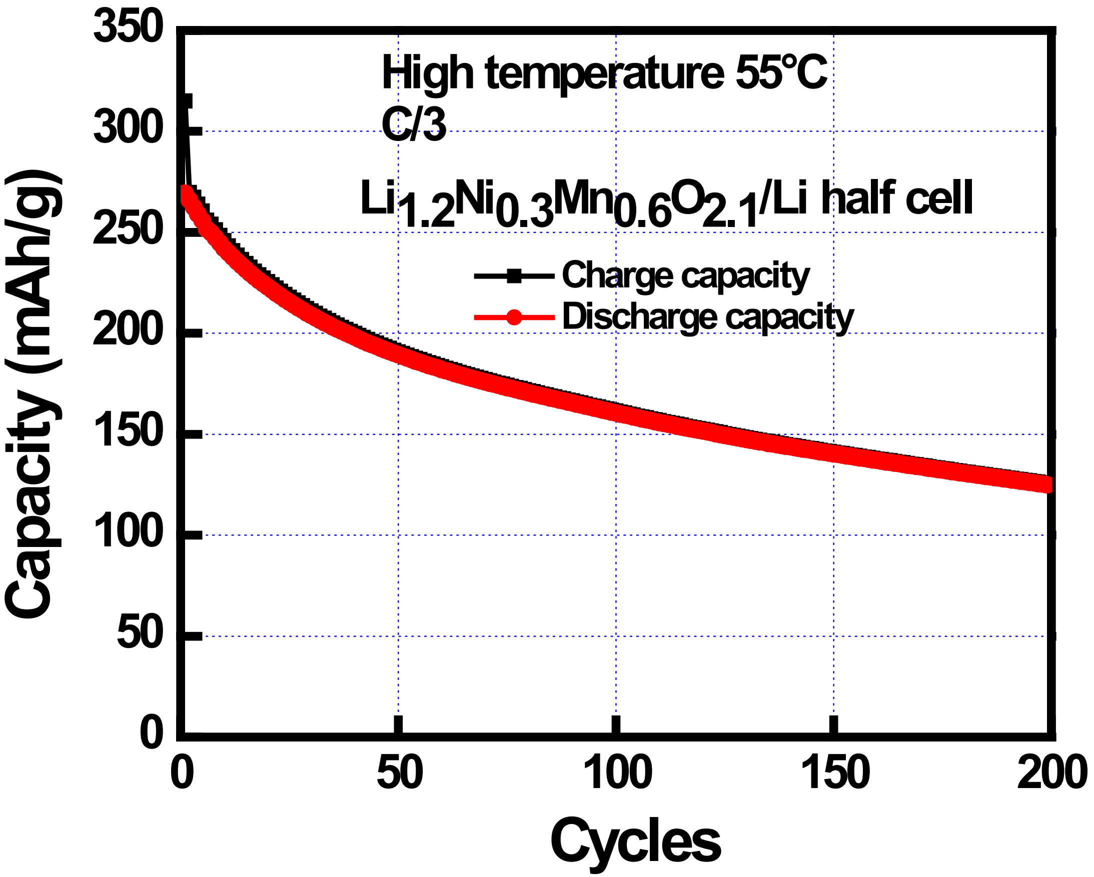




1. **Sample made from hydroxide precursor shows better rate performance than that from carbonate precursor.**

2. **Heat generated from charged electrode made from hydroxide process is lower than the one made from carbonate process (low surface area)**

Performance of LMR-NMC at high temperature



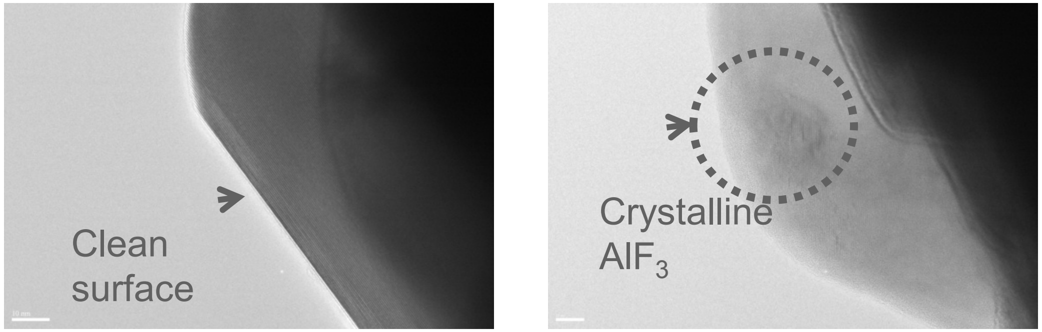
At high temperature, the capacity of the cell based on Co free LMR-NMC material fade during cycling

Coating LMR-NMC material with AlF_3 using a novel dry process

AlF_3 nano-powder preparation Using co-precipitation

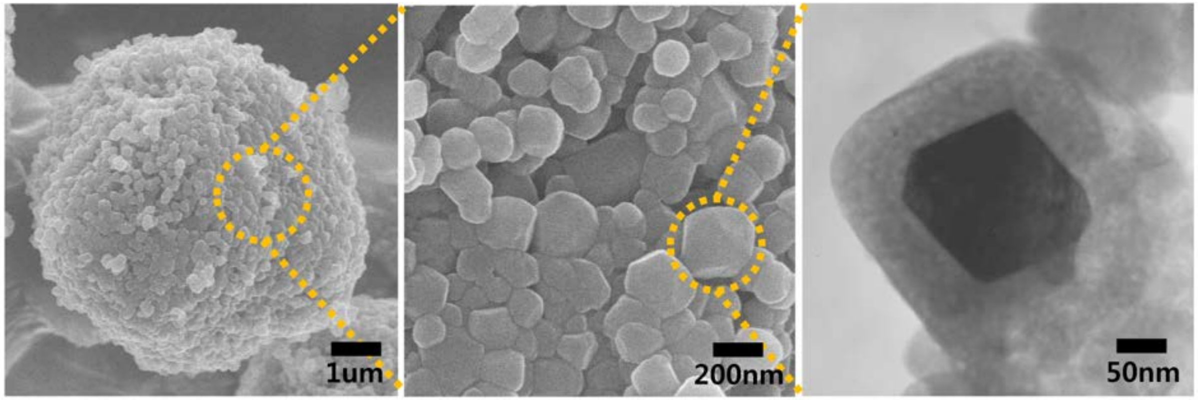
Dry coating of nano-AlF_3 on LRM-NMC

SEM of LMR-NMC ($Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$) material coated with AlF_3



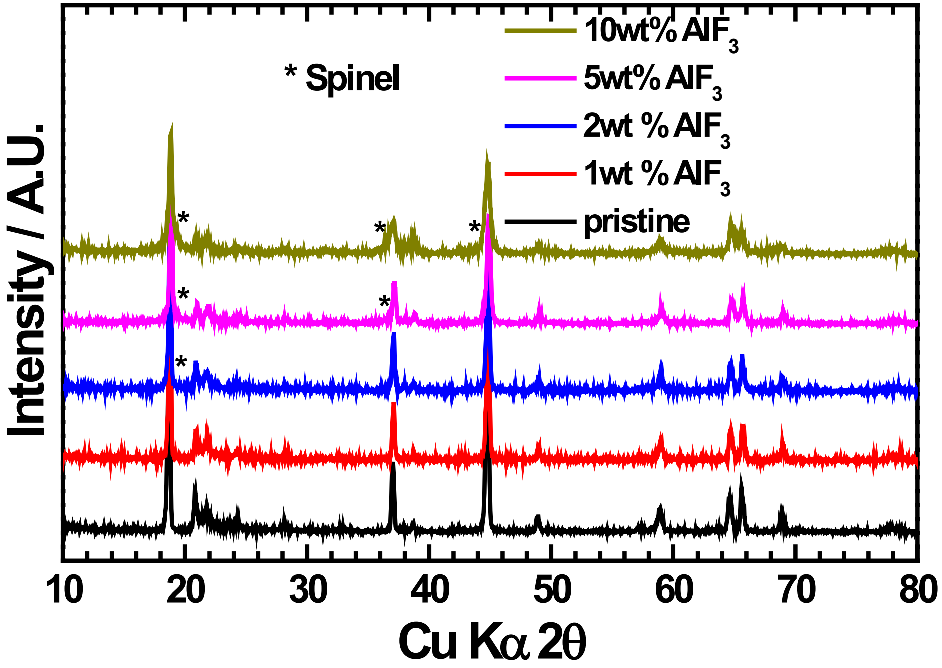
None **coated** AlF_3 **coated**

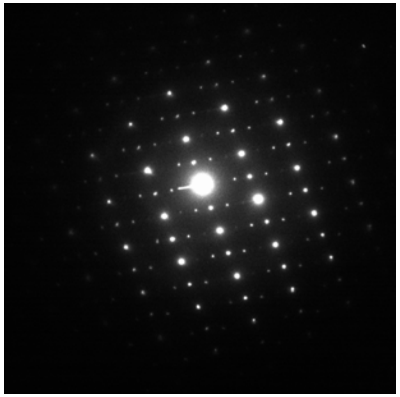
2 wt.% AlF_3-coated LMR-NMC (10nm coating thickness).



10 wt.% AlF_3-coated LMR-NMC (over 60nm coating thickness).

X-ray diffraction and bright-field TEM images of $Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$ and different AlF_3-coated $Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$.



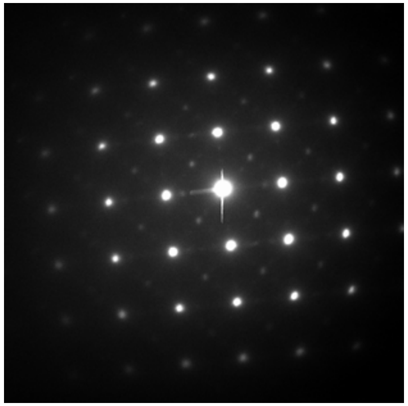


Pristine

Layered phase

5% AlF_3

Mixed phases)

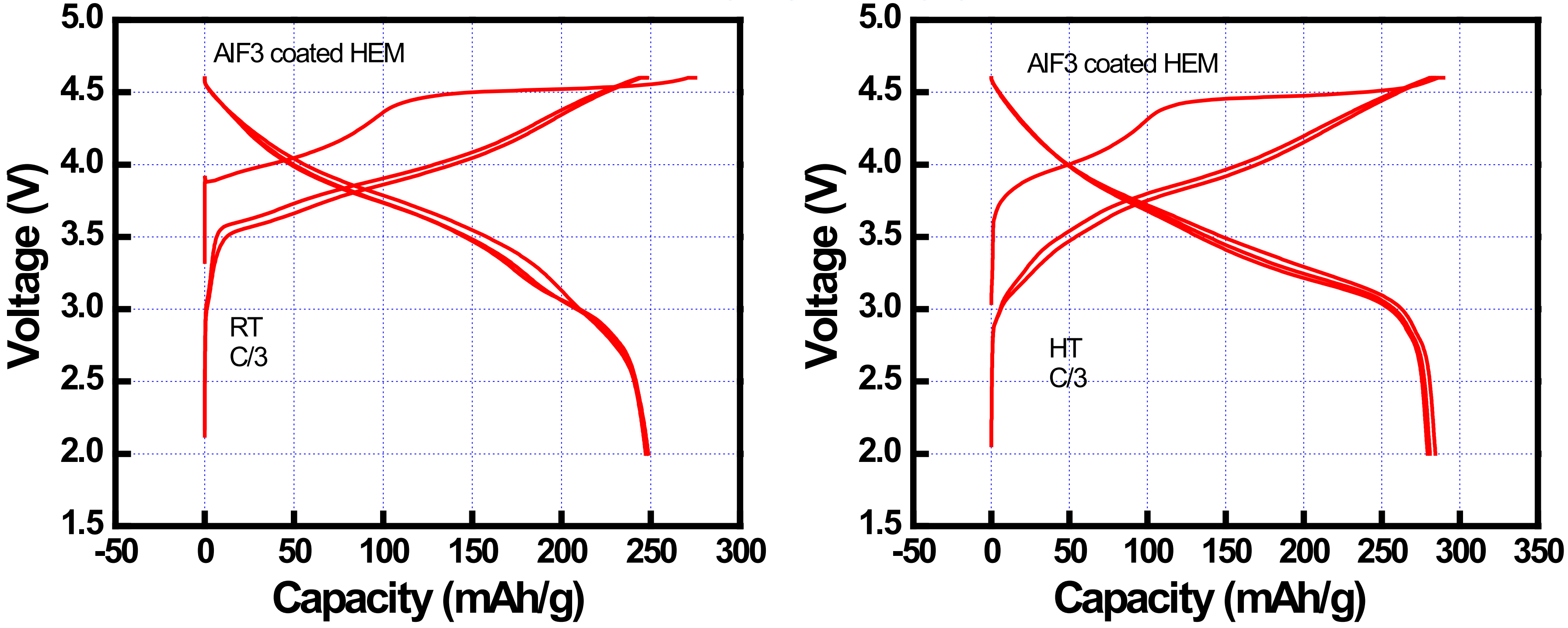


10% AlF_3

Spinel phase

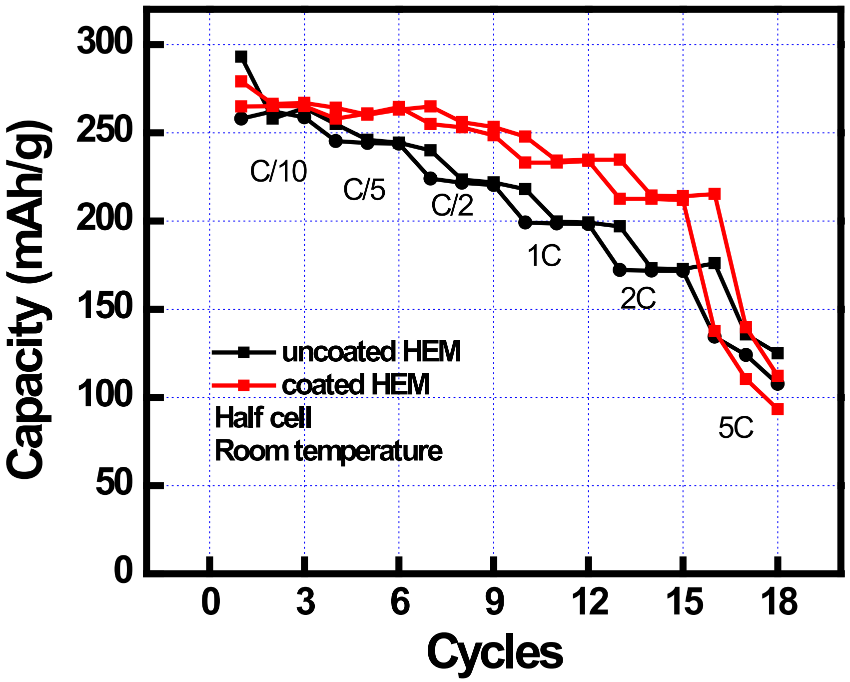
High coating ratio of AlF_3 on LMR-NMC result in structural change from layered to a spinel phase (optimum coating is less than 2wt%)

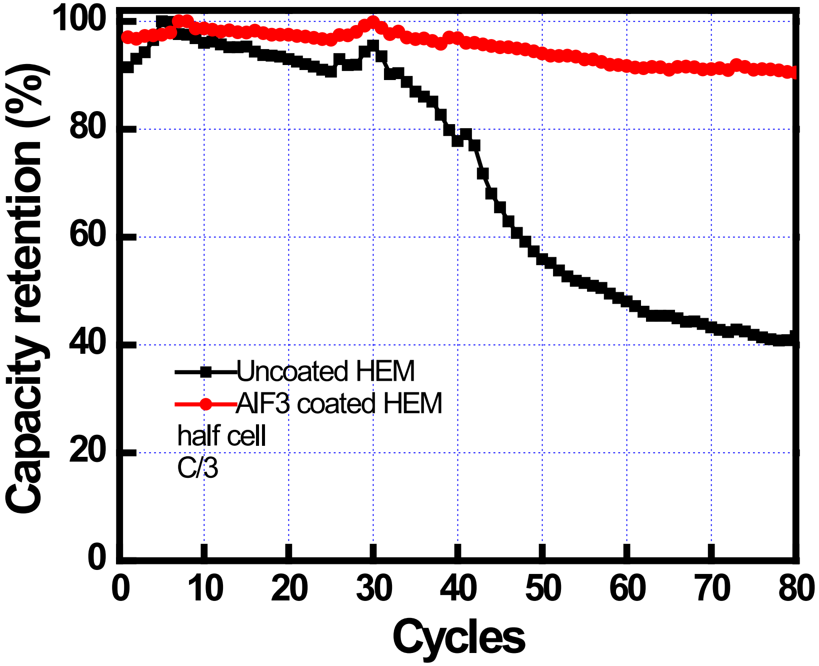
Charge & Discharge of 2wt% AlF_3 coated $Li_{1.14}Ni_{0.29}Mn_{0.57}O_2$



C/3	1st charge	1st discharge	Efficiency
RT	275	248	90%
HT	289	284	98%

Rate capability and cycle life at 55°C of LMR-NMC material with and without AlF_3 Coating



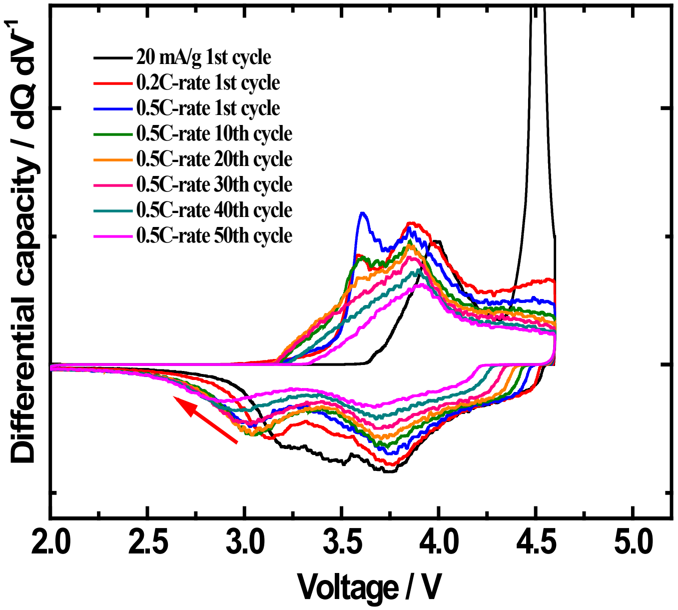


AlF_3 coating improves the rate capability of the high energy material

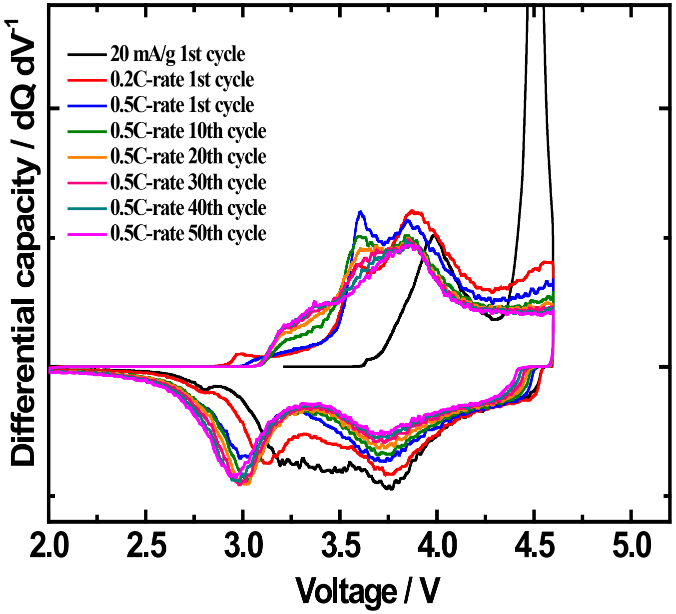
AlF_3 coating improves the cycle life of the high energy material at 55°C

Comparison of the dQ/dV vs. V curves of (a) Li/LMR-NMC and Li/AlF_3-coated LMR-NMC cells as a function of cycles at 30 ℃.

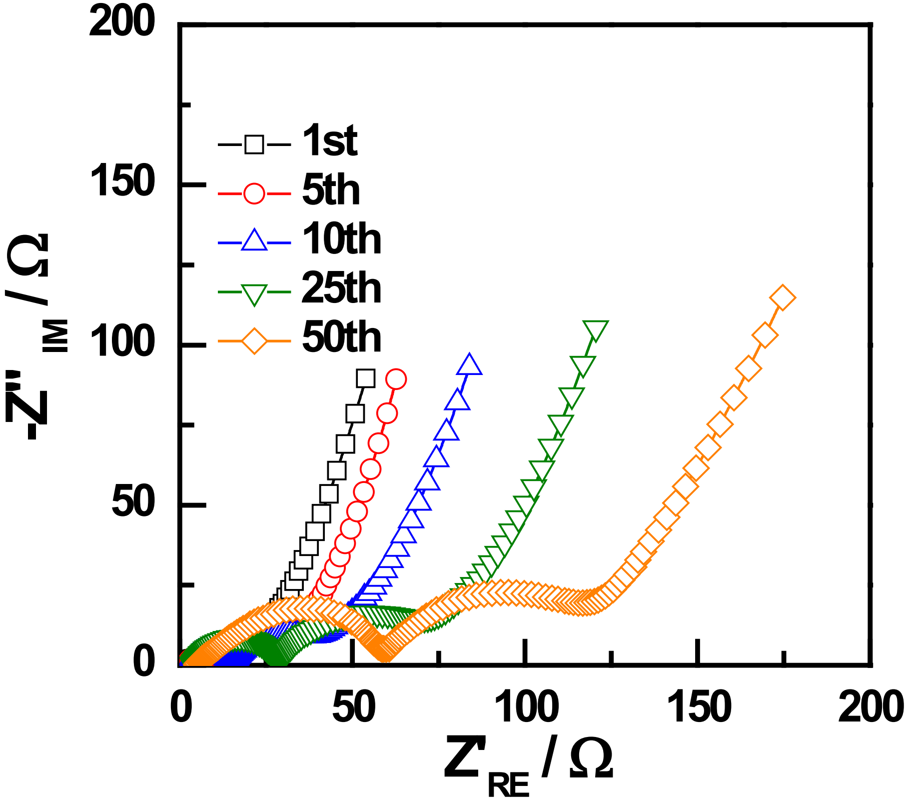
Li/LMR-NMC



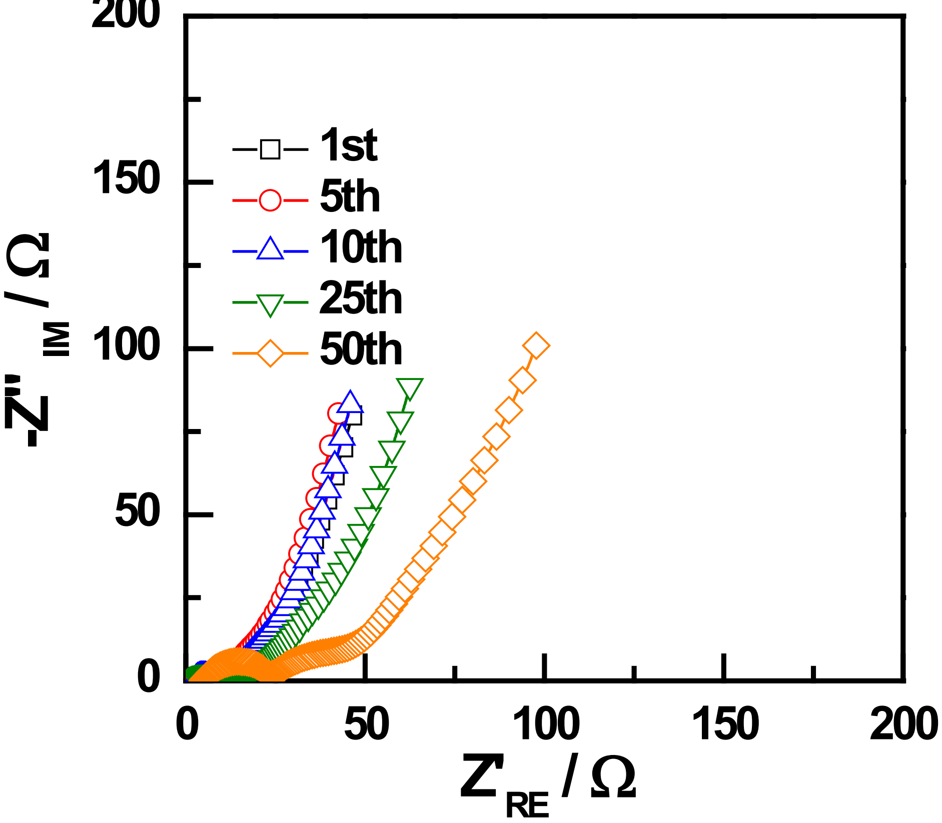
Li/AlF_3-coated LMR-NMC(2wt%)



Nyquist plots of pristine LMR-NMC and AlF_3-coated HEC (2wt%) at different cycles.

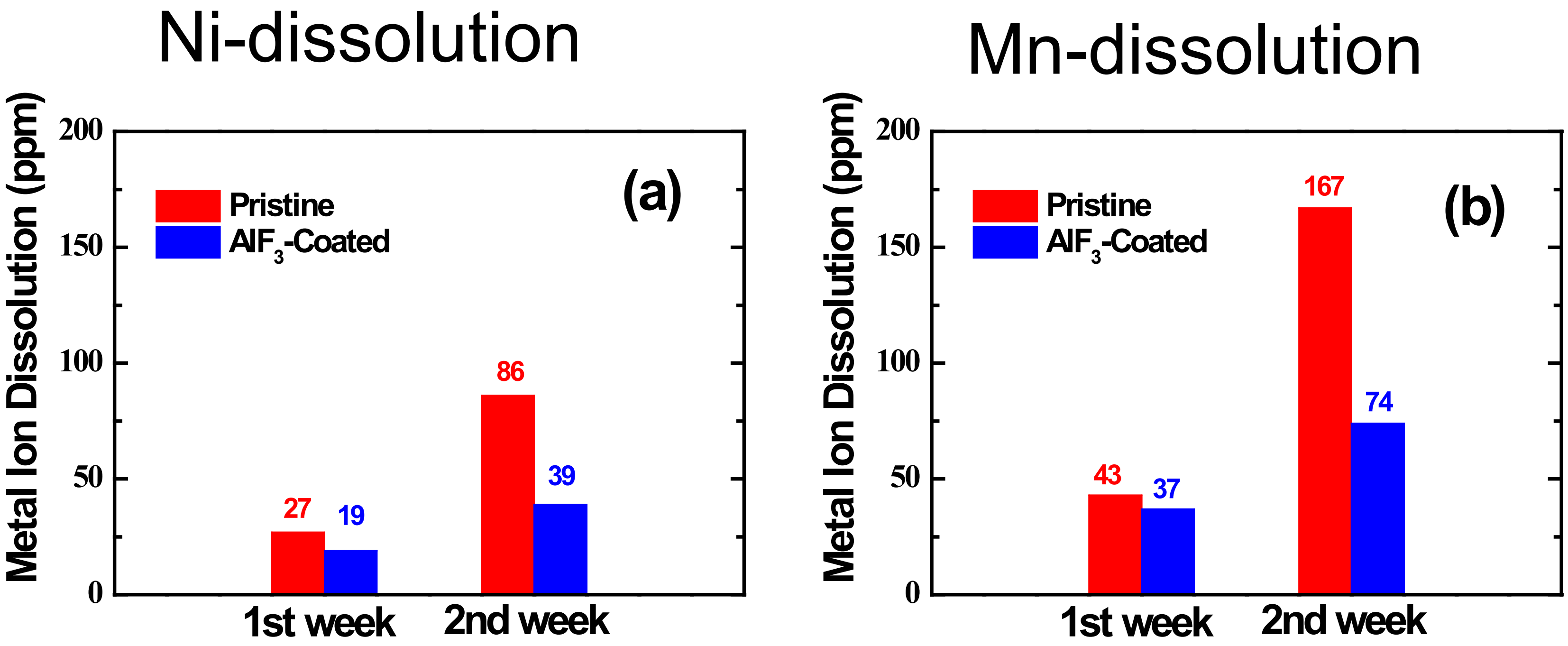


Li/LMR-NMC

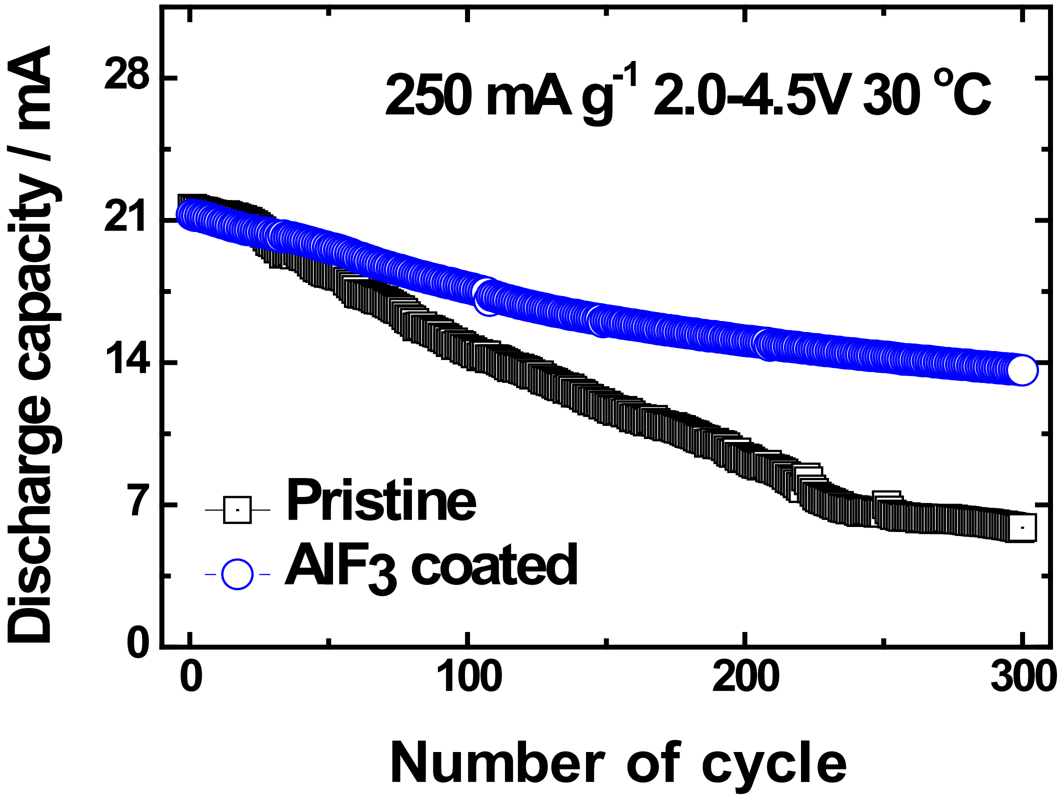


Li/AlF_3-coated LMR-NMC (2wt%)

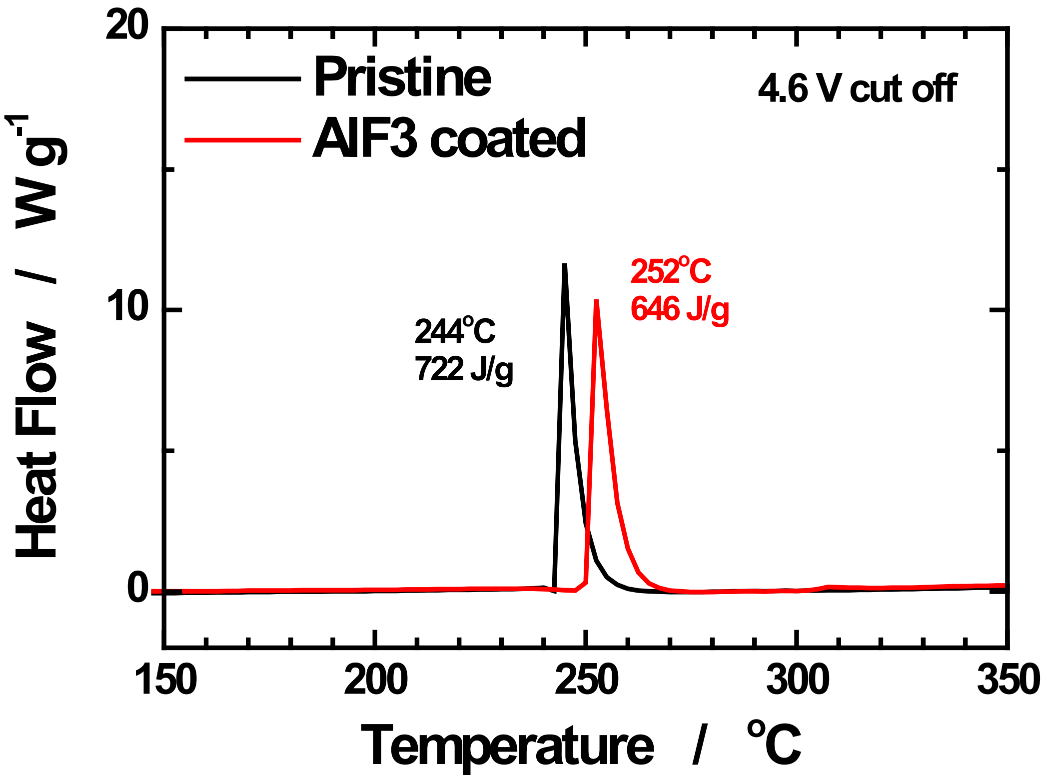
Metal (Ni, Mn) dissolution amount from pristine LMR-NMC electrode and 2wt% AlF$_3$ coated LMR-NMC electrode stored in electrolyte at 55^{o}C



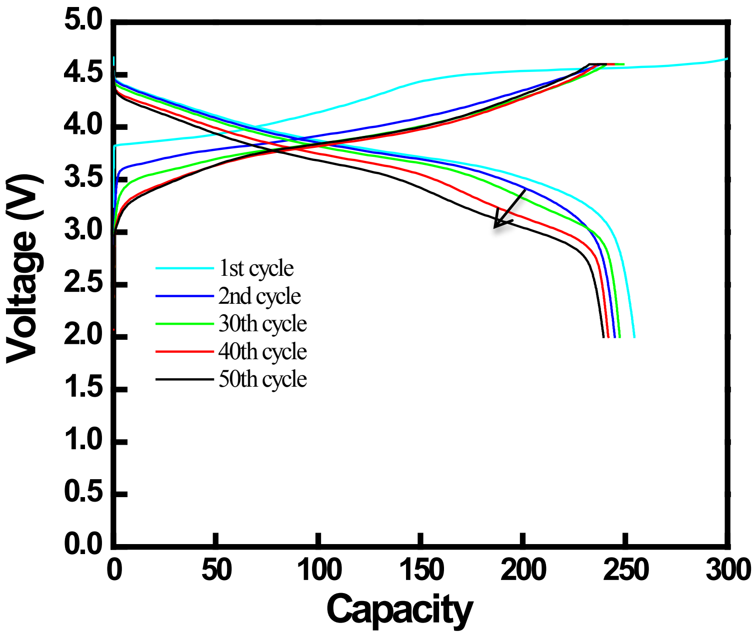
Cycling performance of carbon /LMR-NMC full cell with and without AlF_3 coating



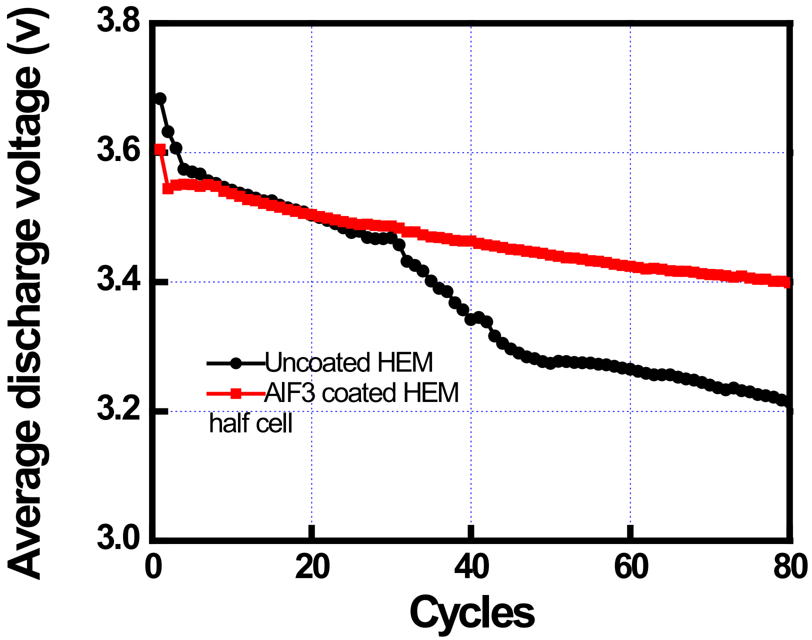
DSC of charged LMR-NMC (4.6V) with and without AlF_3 coating in the presence of $1.2MLiPF_6$/EC:EMC electrolyte



Effect of AlF_3 coating on reducing voltage drop of LMR-NMC material



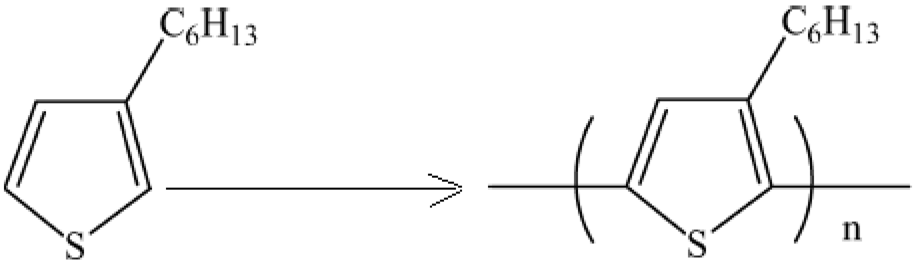
LMR-NMC material suffers from voltage drop at low State of Charge



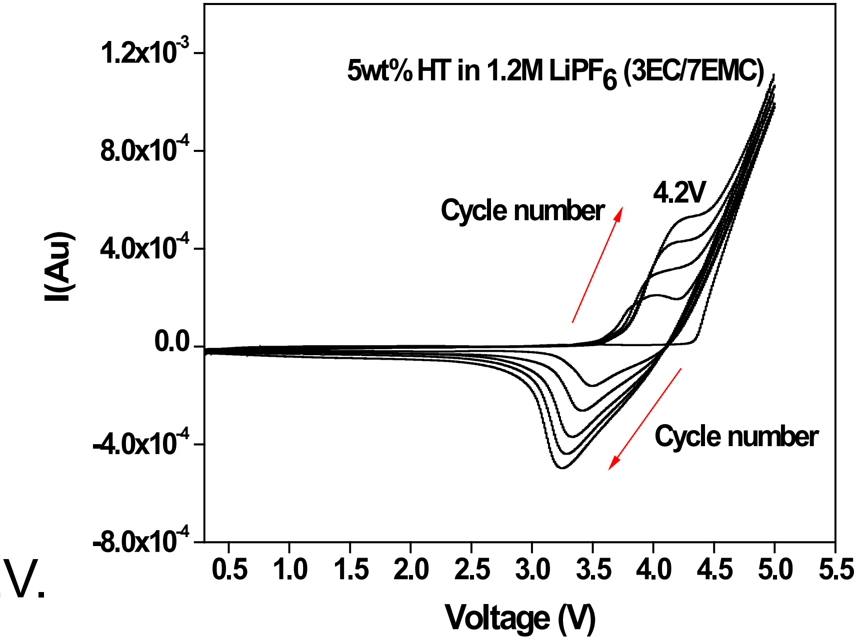
AlF_3 coating on LMR-NMC shows reduced voltage drop during cycling

Stabilizing LMR-NMC electrode using 3-Hexylthiophene additive

Gen 2 = 1.2$LiPF_6$ in 3EC/7EMC (w/w)



3-Hexylthiophene

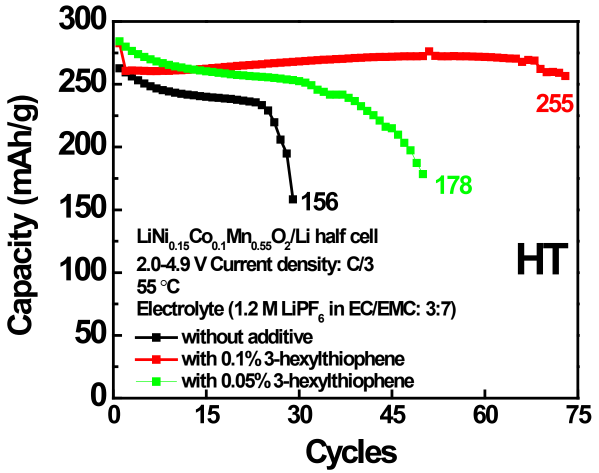


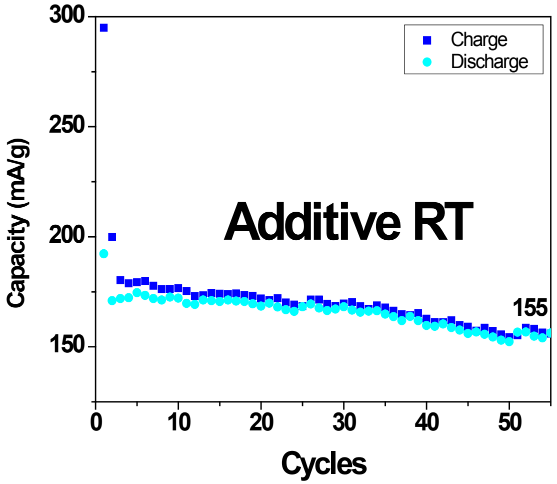
- An Oxidation (polymerization) peak at 4.2V.
- An Increase of the current is due to an increase of the conductivity.

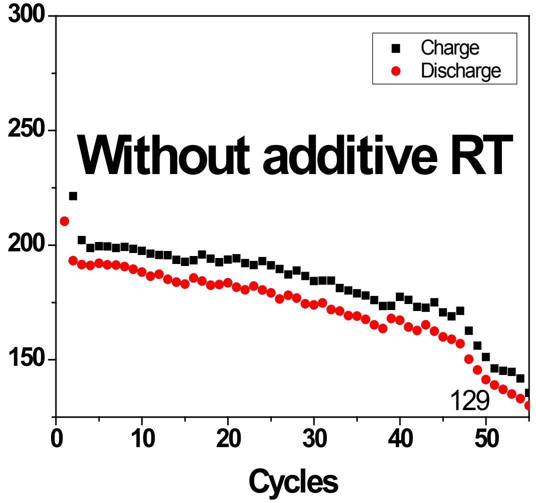
- No significant change in the ionic conductivity of the electrolyte when adding small % of 3HT

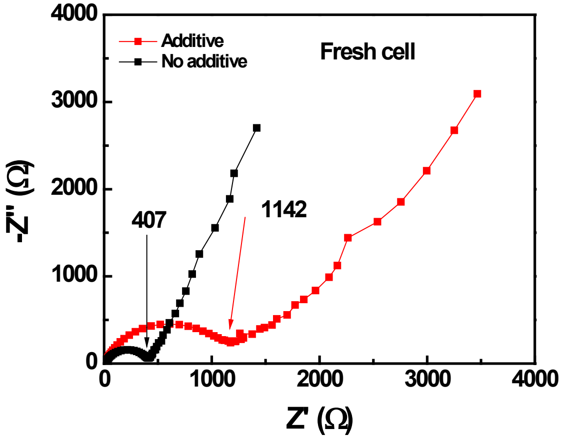
3HT amount	Conductivity (mS/cm)
Gen 2	8.96
0.05 wt%	9.01
0.1wt%	9.00
0.15wt%	8.81

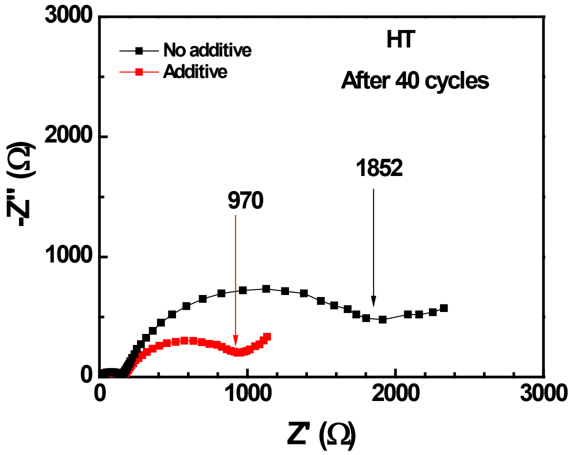
Effect of 3 -Hexylthiophen on the performance of LMR-NMC/Li half cell at 55°C

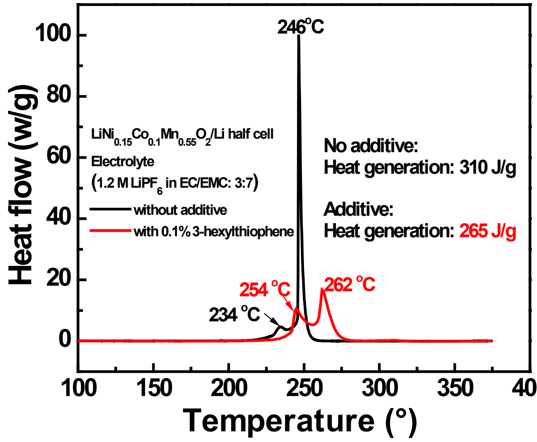












Summary

✓Lithium ratio in LMR-NMC material dictate the size and density of primary particles while high Ni/Mn ratio may be need to obtain high reproducibility when scaling up Co-free LMR-NMC

✓Carbonate process leads to high porosity inside particles and thus possible particle cracking during electrode calendaring

✓ Hydroxide process leads to low porosity inside particles and no particle cracking during electrode calendaring

✓Rate capability, cycle life and safety improved when using hydroxide process

✓AlF_3 coating using dry process improves the rate capability and the cycle life of LMR-NMC material at high temperature. It also reduces voltage drop during cycling

✓3-Hexylthiophen protect LMR-NMC electrode surface and provide similar benefit as AlF_3 coating

Future work

✓Continue to optimize the hydroxide process to obtain high tap density and spherical particles

✓Explore coating effect on material prepared by hydroxide process and investigate effect on performance and voltage drop

✓Explore other coating materials using gas solid phase reaction and investigate effect on performance and voltage drop

✓Investigate the combined effect of particle coating and additive on performance, safety and voltage drop.

Collaborations

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