High-Performance, Low-Cobalt Cathode Materials for Lithium-Ion Batteries

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Project ID: bat413

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Overview

Timeline

- Project start date: Oct. 1, 2018
- Project end date: Dec. 31, 2021
- Percent complete: 35%

Budget

- Total project funding
  - DOE share: $1,952,017
  - Contractor share: $488,005
- Funding for FY 2019
  - DOE share: $680,347
  - Contractor share: $170,887
- Funding for FY 2020
  - DOE share: $680,263
  - Contractor share: $170,066

Barriers

- Synthesis of low cobalt cathode materials
- Stability of the materials
  - Interfacial stability against electrolyte;
  - Structural stability (H2-H3, Li/Ni mixing);
  - Stability at high-voltage conditions
- Pouch cell fabrication

Partners

- Project lead: PSU
- Interactions/collaborations: PNNL, ORNL

Relevance

Objective

- Development of stabilized NCM cathode materials with low Co content (namely $LiNi_xCo_yMn_{1-x-y}O_2$, $y \leq 0.04$), which realizes low Co loading (below 50 mg Wh^{-1}), and high energy density (240 Wh/kg) of battery cells with long cycle life (80% retention in 1000 cycles)
- Deep understandings of atomic and electronic level correlation of structure and chemistry of material with battery performance using advanced electron microscopy and spectroscopy.

Impacts

- This project will study and deliver high-performance low-Co NCM cathode materials, which can potentially decrease cost of cathode materials, especially reduce dependence on the strategic resource of cobalt, promote increased adoption of EVs, and make the LIBs sustainable for EV application.
- The structure-performance relationship of low-Co NCM cathodes will be investigated elaborately for the development of advanced cathode materials.

Approach

- Surface coating and infusion to mitigate solid-liquid reaction and enhance structural integrity

  (e.g., LFP coated NCM811 and Al_2O_3 coated $LiNi_{0.92}Co_{0.055}Mn_{0.025}O_2$)
- Transition metal cation composition optimization for enhanced lattice stability

  (e.g., Mo-doped $LiNi_{0.5-x/2}Mn_{0.5-x/2}Mo_xO_2$)
- Atomic-scale advanced characterization to envisage new designing principle

  (e.g., HAADF-STEM and ABF-STEM with EDS and EELS analysis)
- Pouch cell fabrication

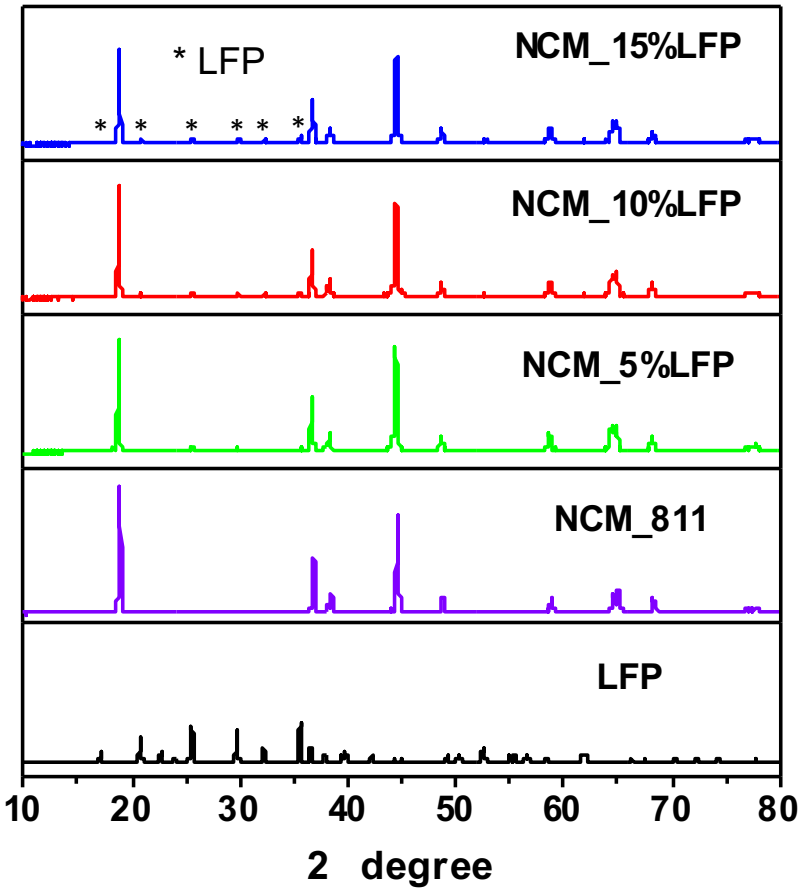
FY20 Milestones:

- Optimal synthesis of surface-protected/cation-doped low-Co cathode materials with high capacity and cycling stability.

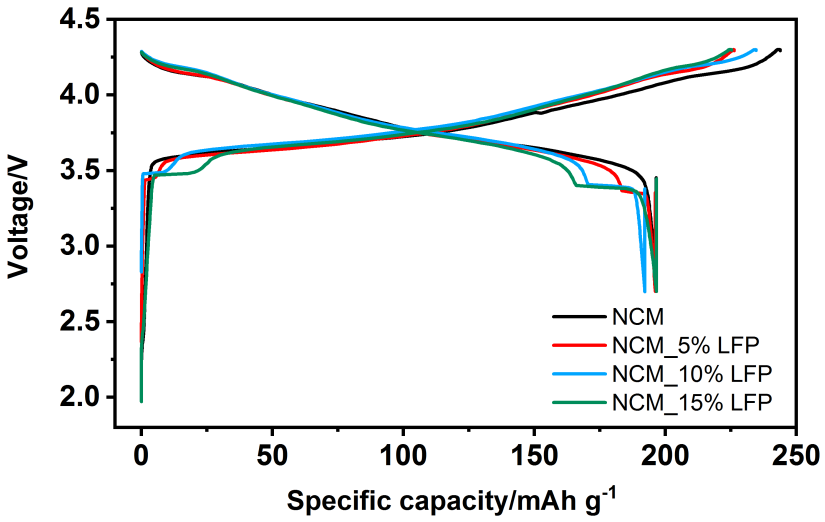
FY21 Milestones:

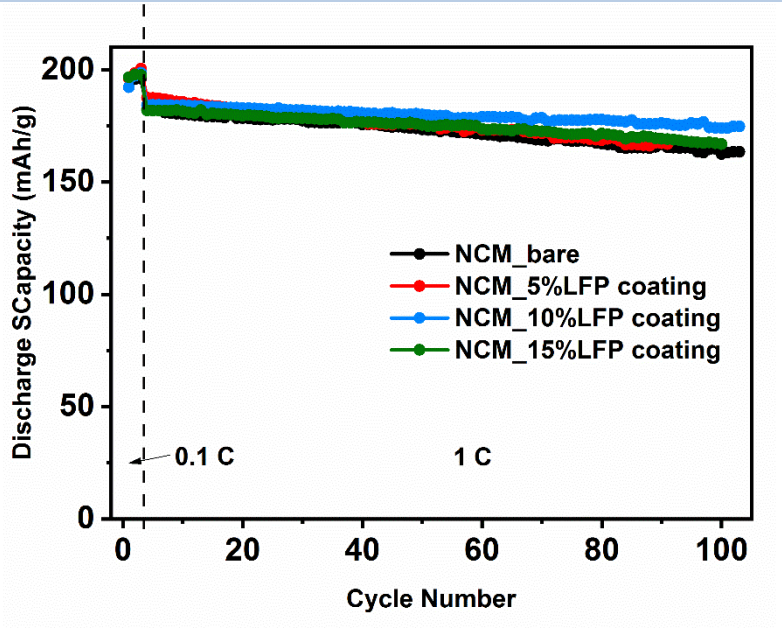
- Material scale-up and pouch cell fabrication.

Technical Accomplishments and Progress: LFP-coated NCM811



LFP is detected in the coated materials.

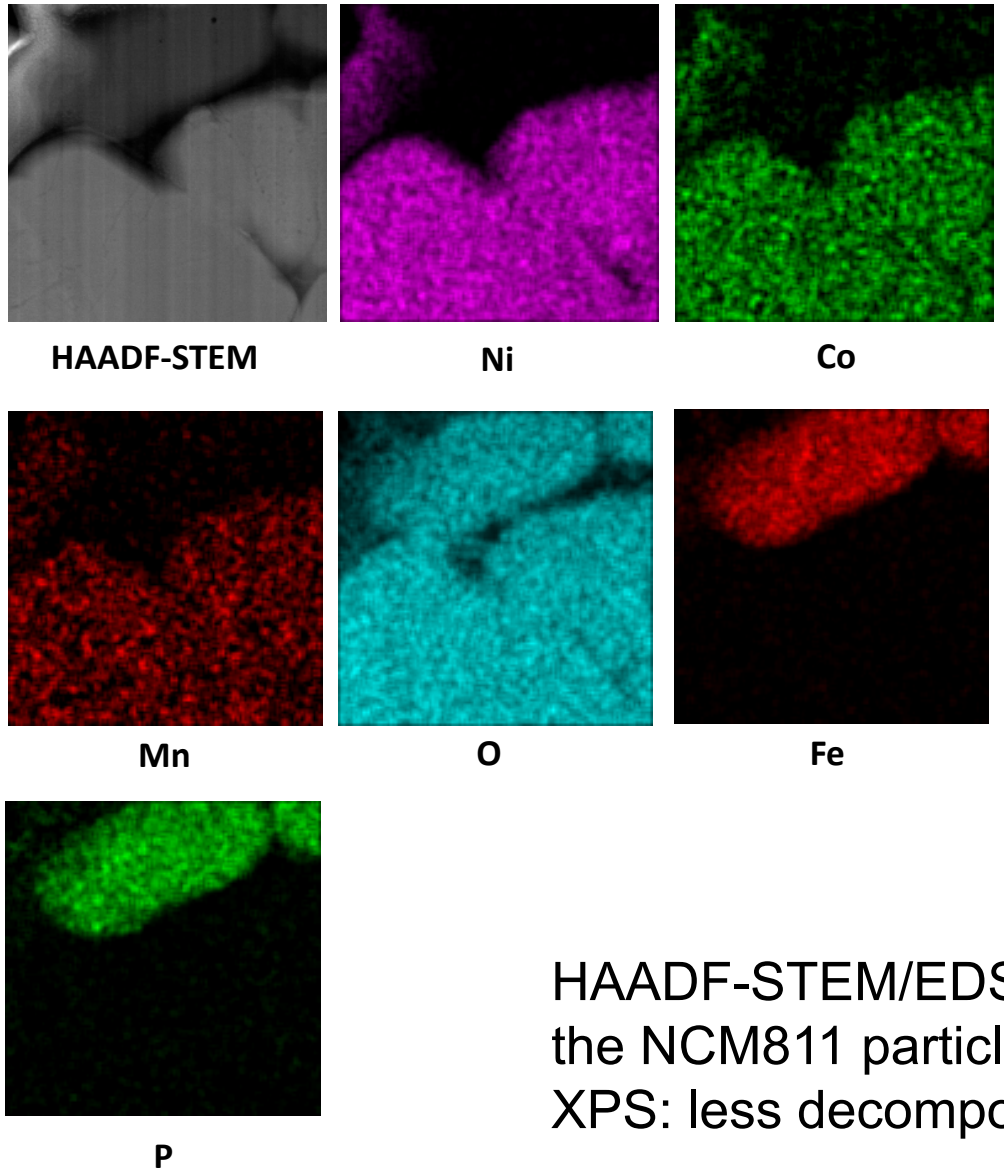




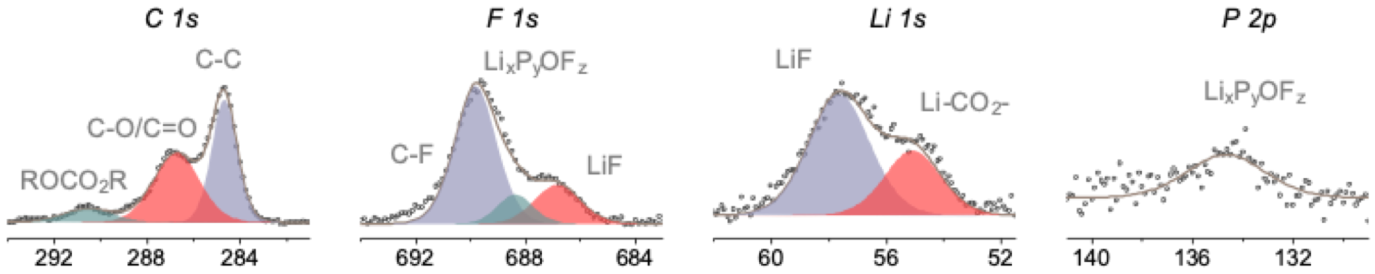
LFP	1st dis. specific cap. (0.1 C)	4th dis. specific cap. (1 C)	Cap. retention (%)
0	197	182	90%, 100 cyc
5%	196	188	90%, 100 cyc
10%	192	184	95%, 100 cyc
15%	197	182	92%, 97 cyc

10% LFP coated material shows the best EC performance.

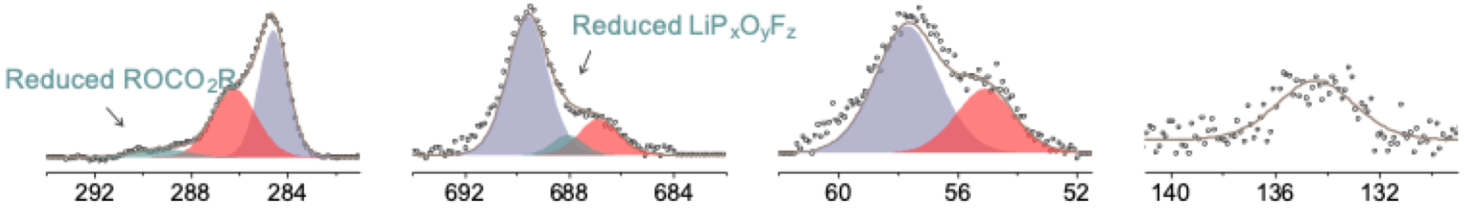
Technical Accomplishments and Progress: LFP-coated NCM811



SEI of bare NCM811 after 20 cycles



SEI of NCM811 10% LFP after 20 cycles



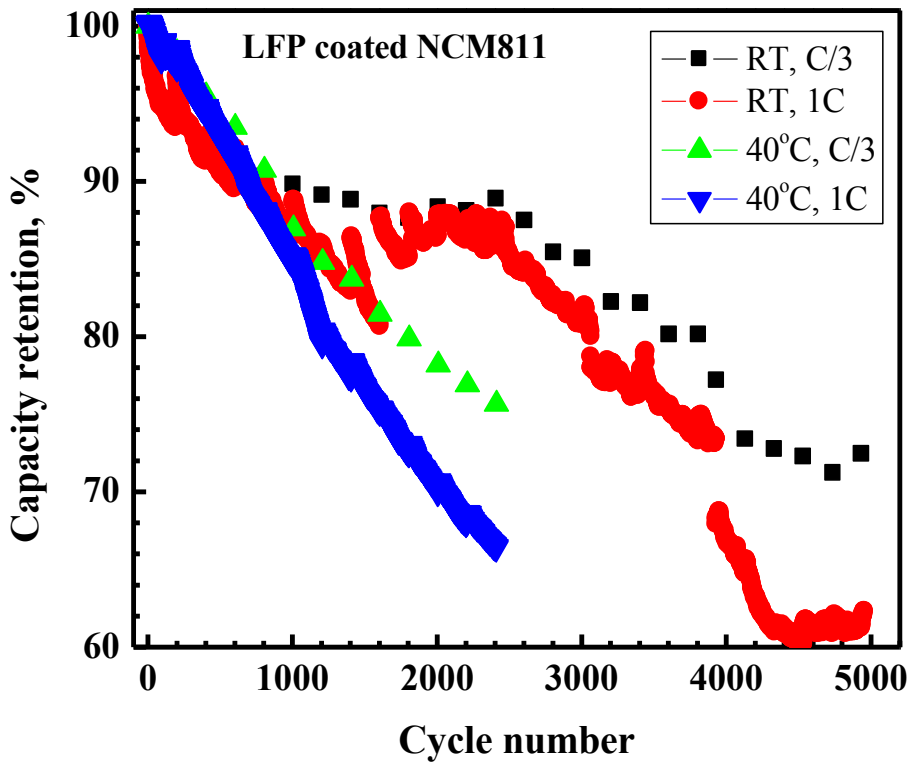
HAADF-STEM/EDS mapping: LFP nanoparticles are successfully coated onto the NCM811 particle

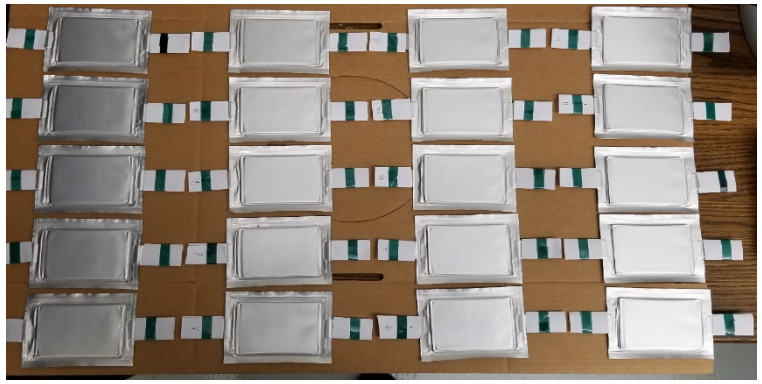
XPS: less decomposition products upon cycling for LFP coated sample

Technical Accomplishments and Progress: LFP-coated NCM811

1C CCCV to 4.2V till C/5

RPT condition every 200 cycles: C/3 CCCV to 4.2V till C/20





Cell number	Capacity (Ah)	Cell number	Capacity (Ah)
1	2.466	11	2.464
2	2.468	12	2.468
3	2.464	13	2.469
4	2.473	14	2.464
5	2.460	15	2.475
6	2.463	16	2.462
7	2.465	17	2.468
8	2.466	18	2.467
9	2.469	19	2.463
10	2.478	20	2.472

LFP-coated NCM811/Graphite 2.5Ah pouch cell

Capacity retention @RT, C/3:

72.4% after 4941 cycles

Pouch cells of ~2.5 Ah delivered to Idaho Natl Lab

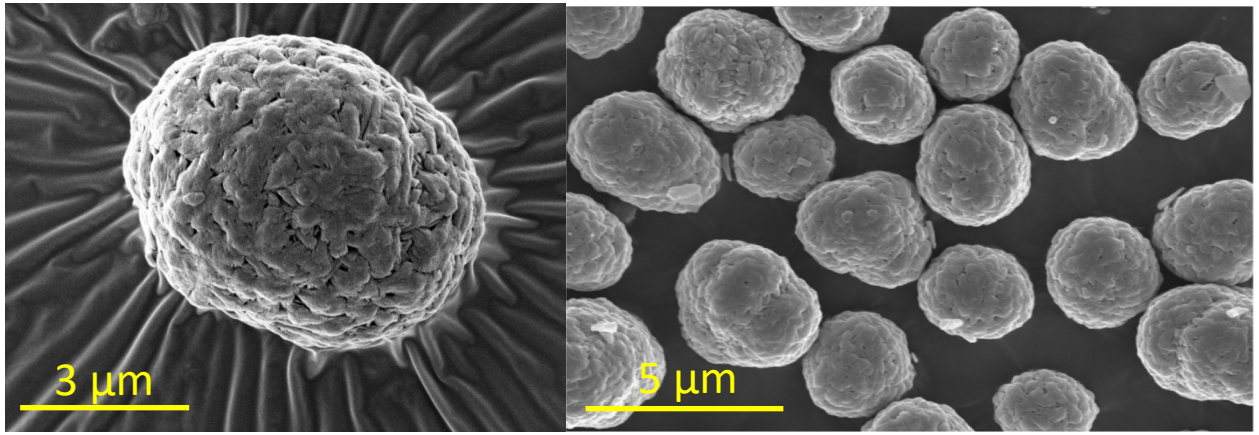
Cathode: LFP-coated (10wt%) NCM811; 17.5 mg/cm^2

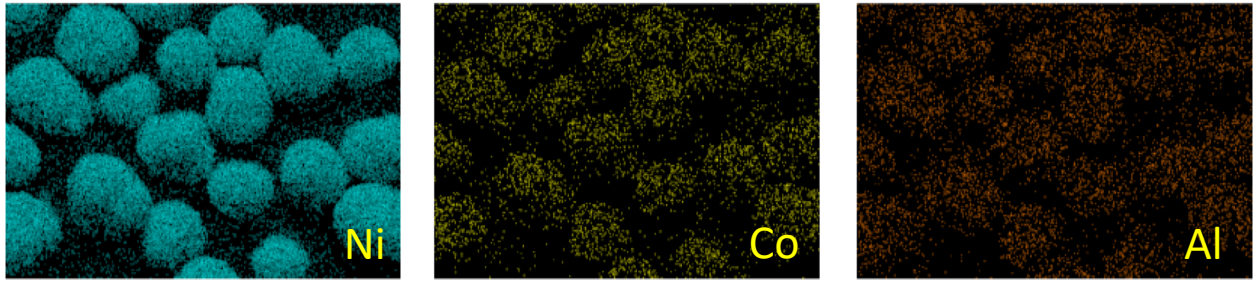
Anode: Gr with NPR=1.1

Technical Accomplishments and Progress : Al_2O_3 coated $LiNi_{0.92}Co_{0.055}Mn_{0.025}O_2$

Before calcination

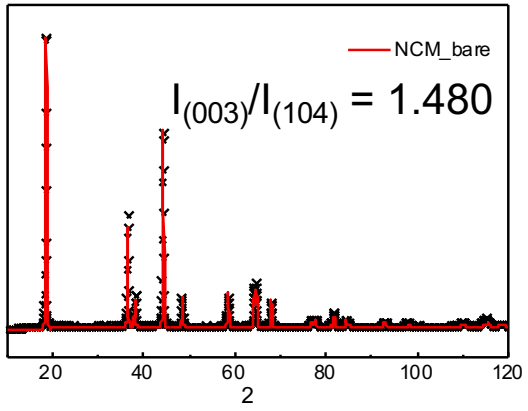
Al_2O_3 coated $LiNi_{0.92}Co_{0.055}Mn_{0.025}O_2$ precursors



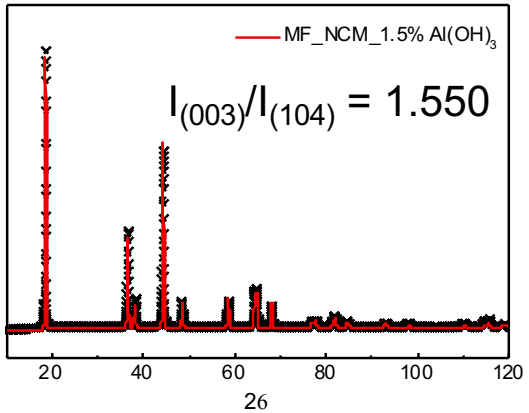


After calcination

NCM bare



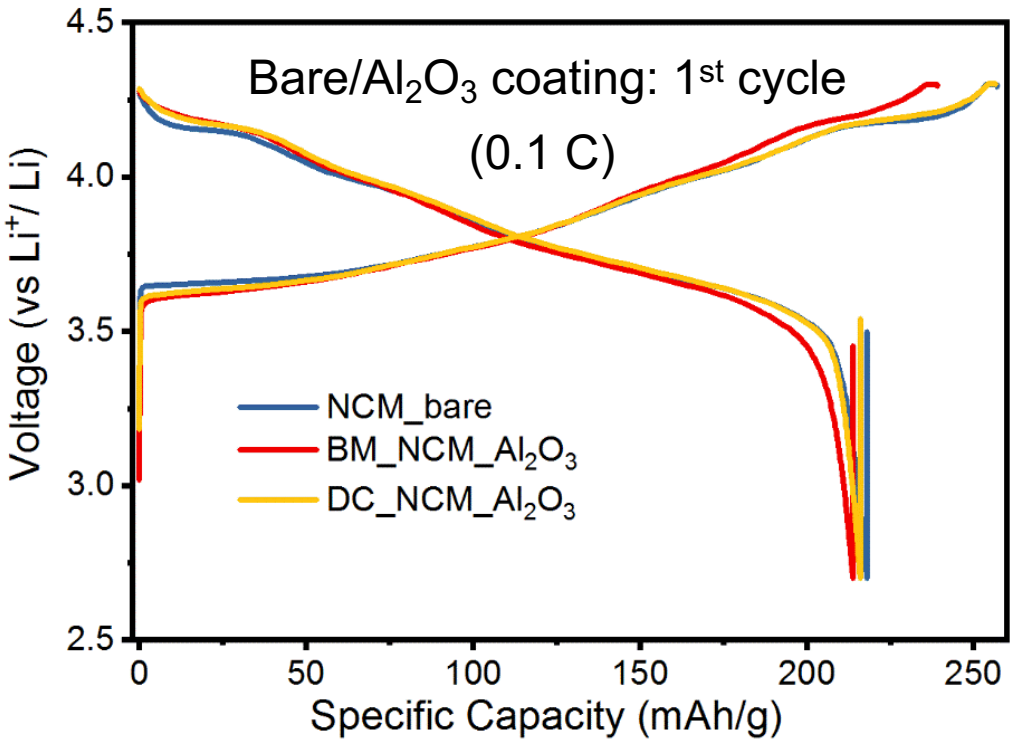
1% Al_2O_3 coated



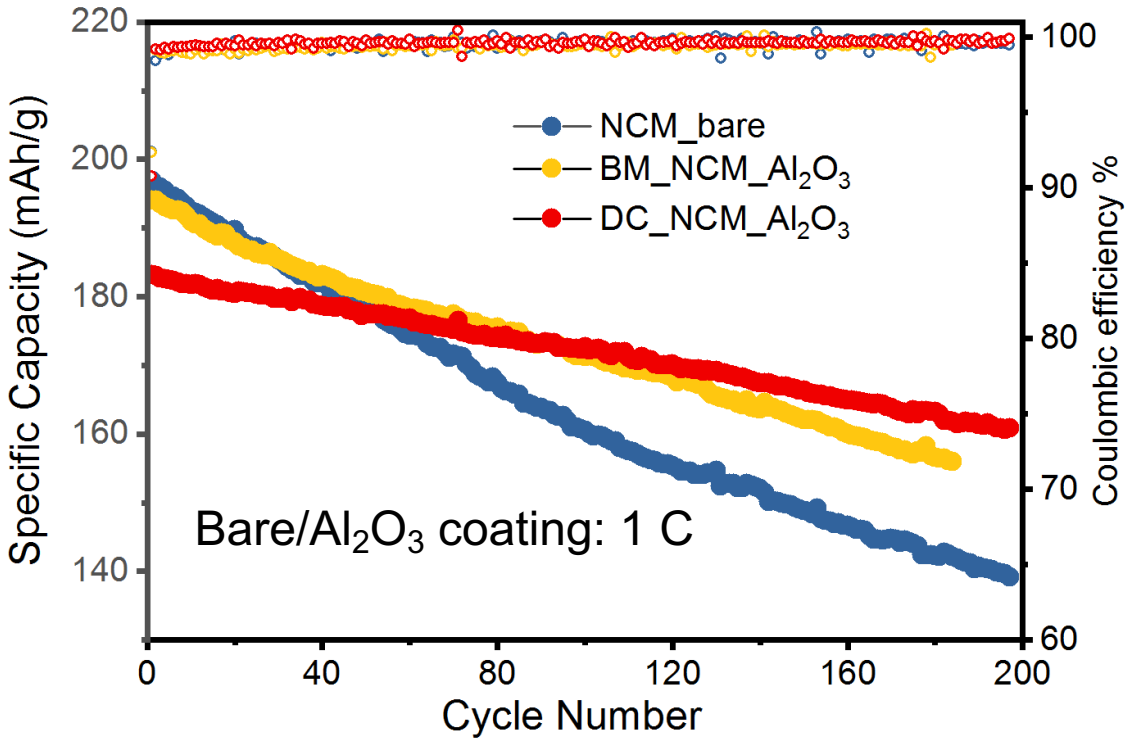
Sample Name	S (MO_2)	I (LiO_2)	Li Occupancy (Li Layer)	Ni Occupancy (Li Layer)
NCM_Bare	2.6771	2.0698	0.9389	0.0611
NCM_1% Al_2O_3	2.6960	2.0471	0.9484	0.0516

Al_2O_3 is successfully coated onto the surface of the NCM precursor, which can suppress Li/Ni mixing.

Technical Accomplishments and Progress : Al_2O_3 coated $LiNi_{0.92}Co_{0.055}Mn_{0.025}O_2$



DC_NCM_Al_2O_3: 88% over 200 cycles



BM_NCM: ball milling DC_NCM: dry coating

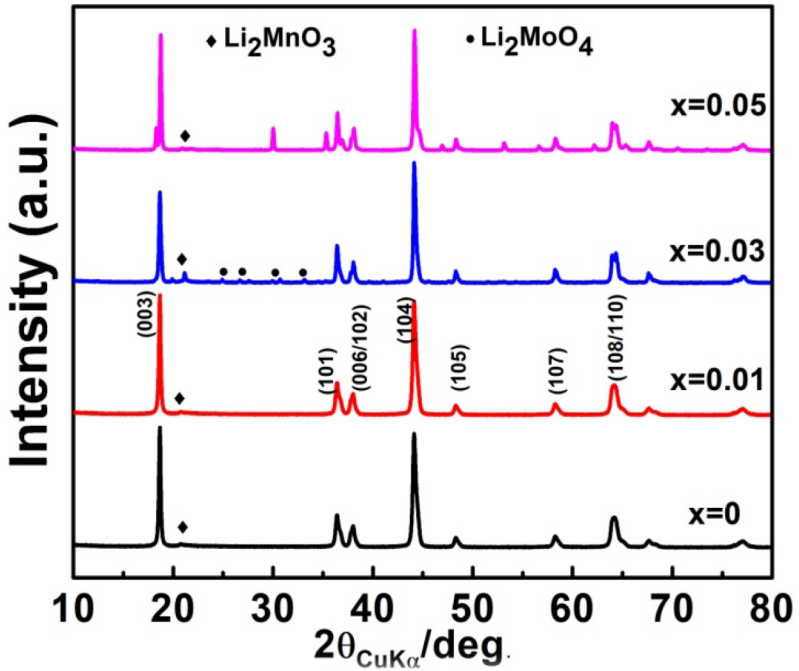
Voltage range: 2.7 – 4.3 V

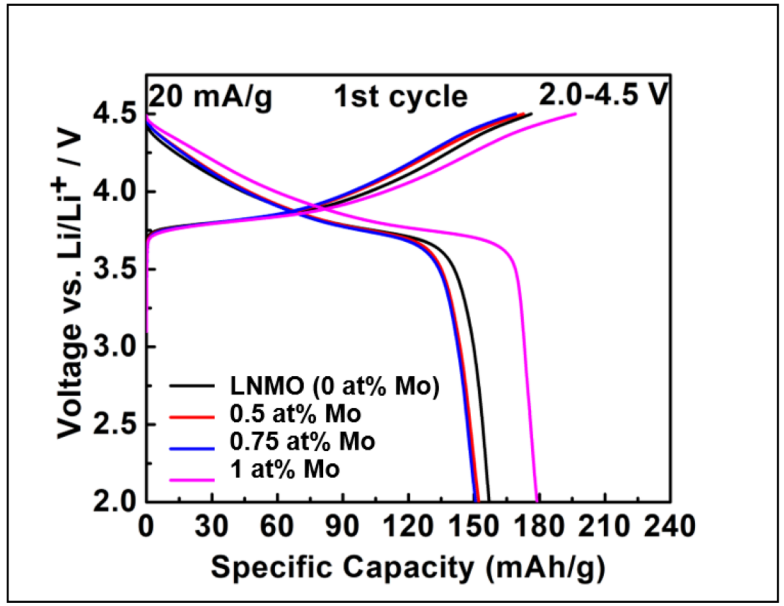
Current density: 0.1 C for the first 3 cycles, then 1 C

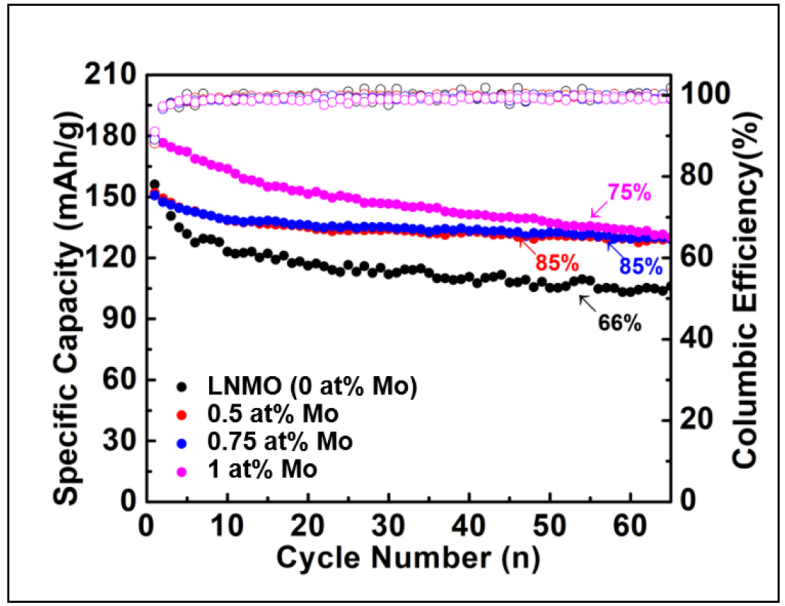
Al_2O_3 coating can improve the cycling stability of $LiNi_{0.92}Co_{0.055}Mn_{0.025}O_2$

Technical Accomplishments and Progress: $LiNi_{0.5-x/2}Mn_{0.5-x/2}Mo_xO_2$

$LiNi_{0.5-x/2}Mn_{0.5-x/2}Mo_xO_2$ (LNMMO)







For x = 0.01, Mo is successfully into the lattice.

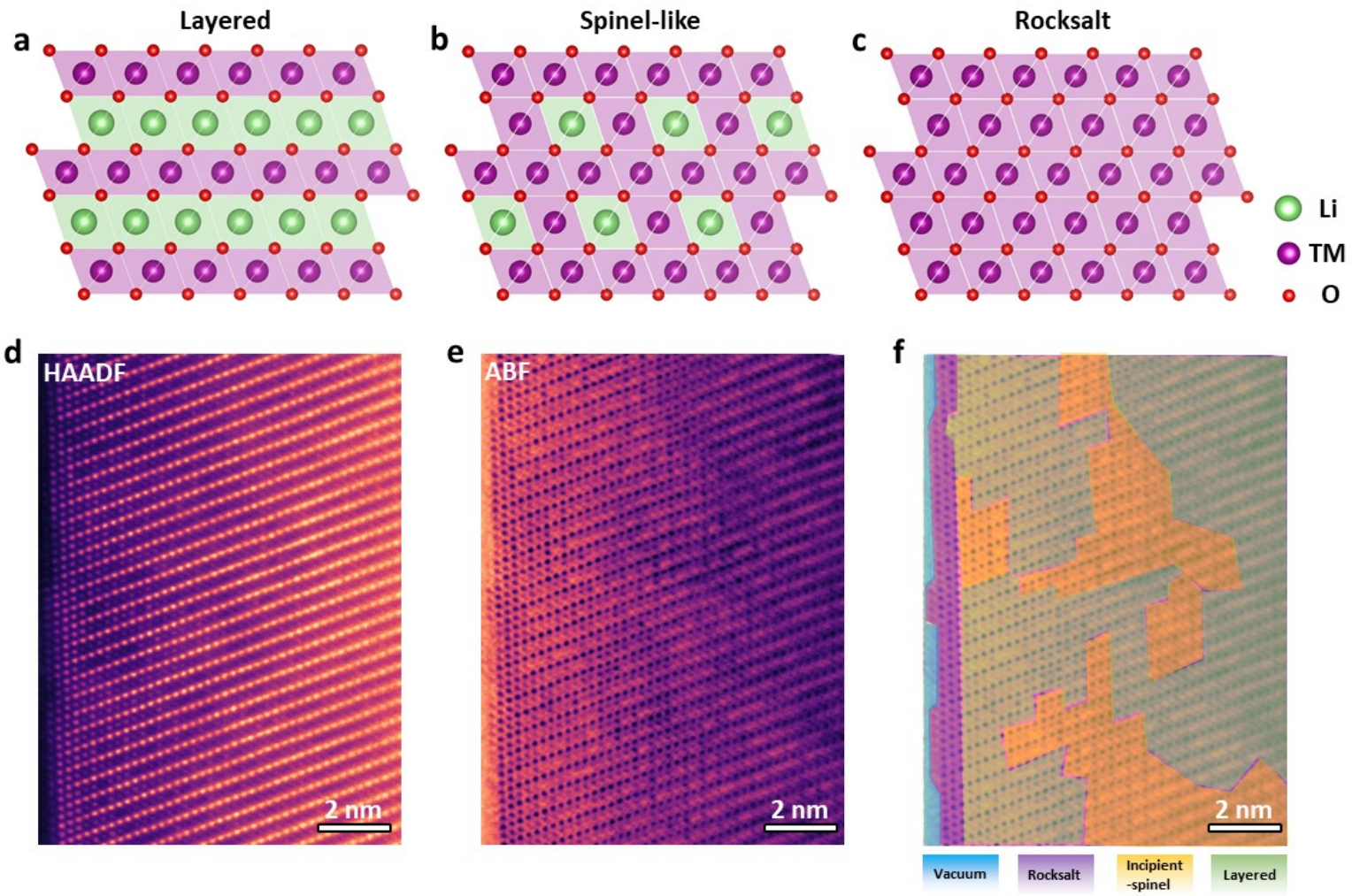
For x > 0.01, Li_2MoO_4 impurities can be observed.

After Mo doping, the capacity retention for all the materials is improved.

x = 0.01 shows the best EC performance, which is selected for further measurements.

Technical Accomplishments and Progress: $LiNi_{0.5-x/2}Mn_{0.5-x/2}Mo_xO_2$

Pristine Mo-doped material



All layered in subsurface

Layered with spinel in subsurface

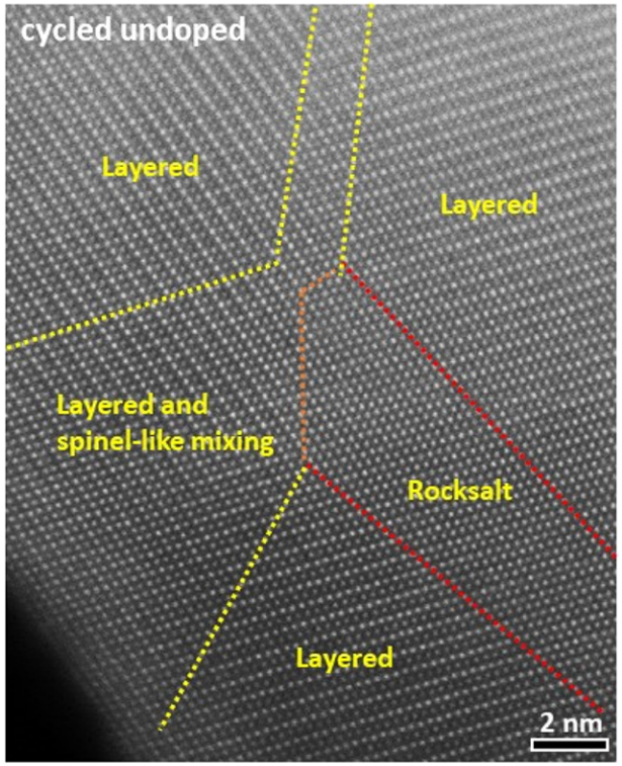
Schematic of **Fig. e**

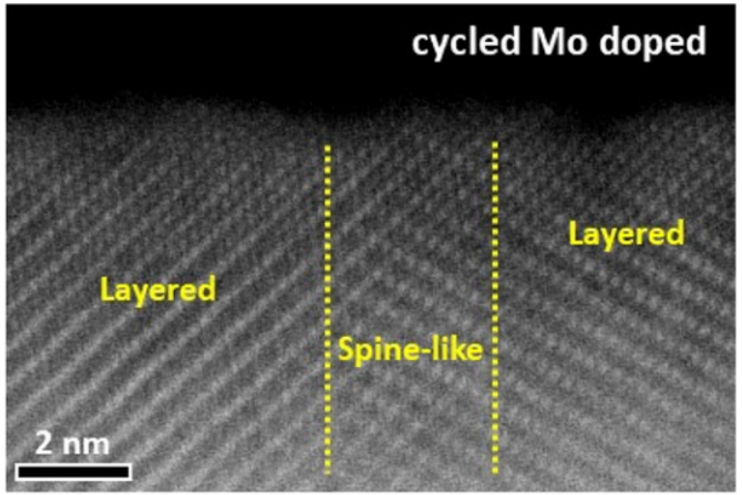
Spinel-like structures are only evident in the ABF image, but nearly invisible in the HAADF image.

An "incipient-spinel" status is considered to exist in the Mo-doped pristine material, which only involve a small number of TM migration.

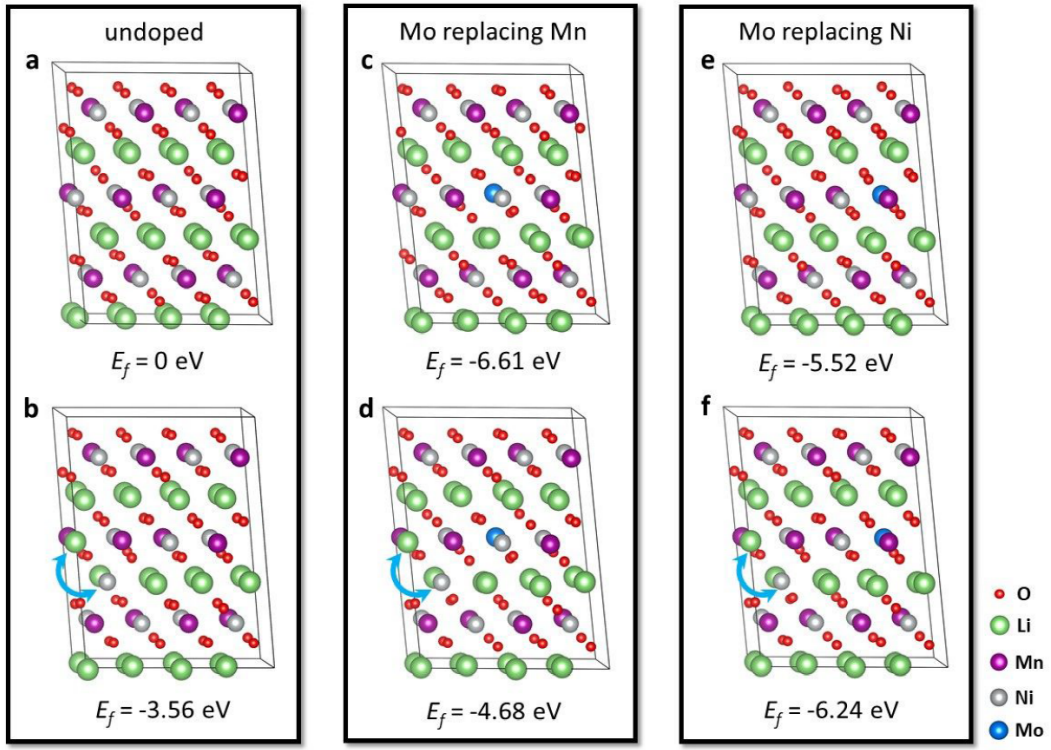
Technical Accomplishments and Progress: $LiNi_{0.5-x/2}Mn_{0.5-x/2}Mo_xO_2$

HAADF-STEM of cycled undoped and Mo-doped materials





DFT calculations

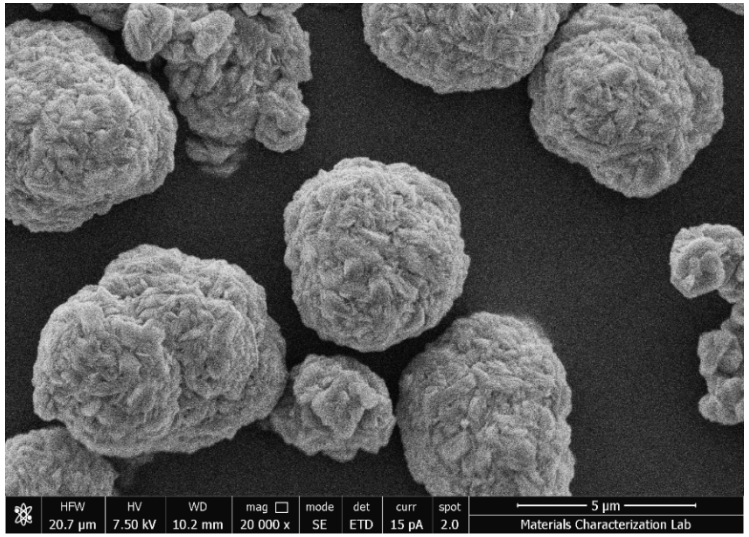


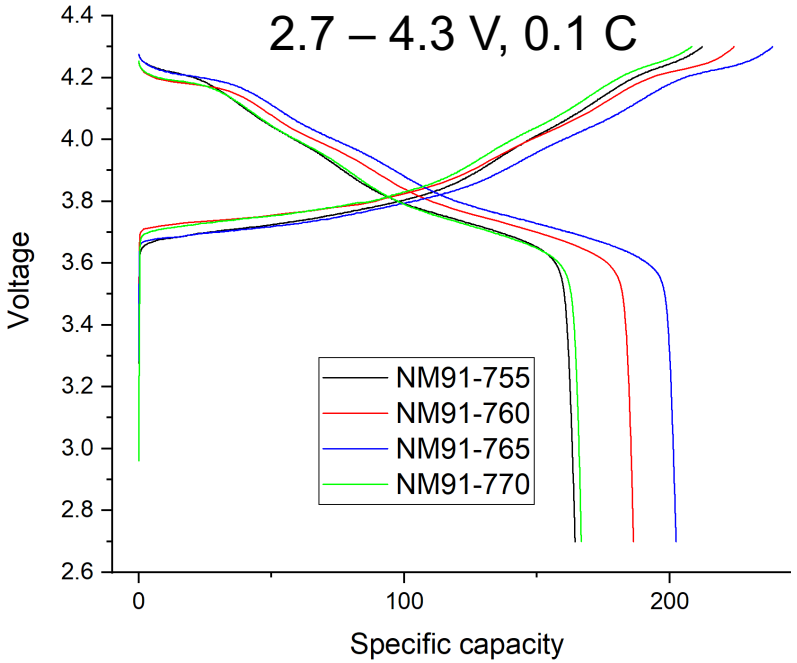
Mo-doping can mitigate cation mixing and suppress the formation of rocksalt structure upon cycling, and thus help keep good structural stability.

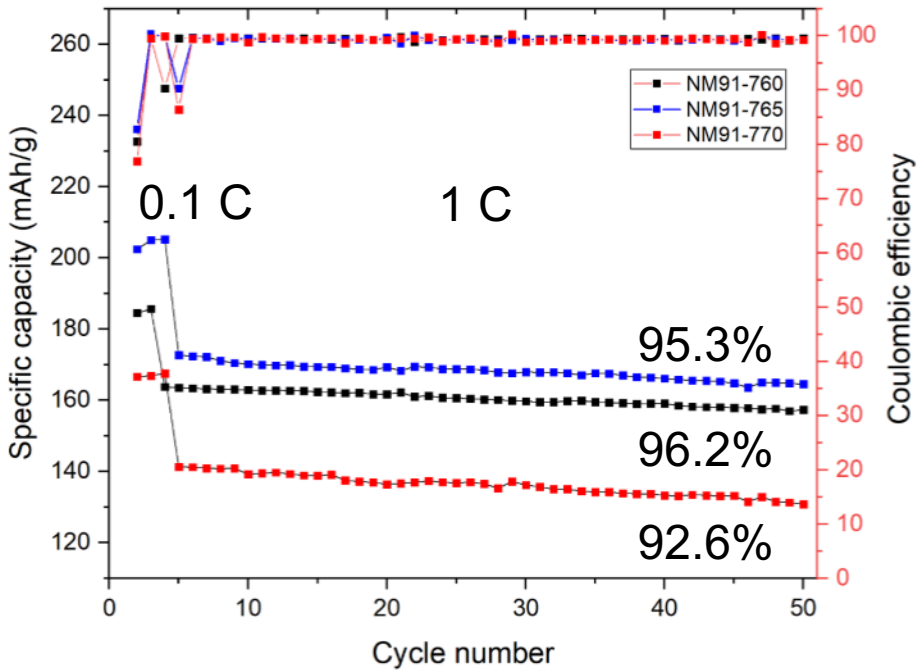
1) Mo doping can alleviate cation mixing
2) Mo prefer to occupy more at the Mn sites

Technical Accomplishments and Progress: Co-free $LiNi_{0.9}Mn_{0.1}O_2$

$LiNi_{0.9}Mn_{0.1}O_2$ (NM91)







	$I_{(003)}/I_{(104)}$	1st discharge capacity (mAh/g)	1st cycle CE
NM91-755	0.937	164.4	76.4
NM91-760	0.989	186.4	79.9
NM91-765	1.011	202.4	82.8
NM91-770	0.972	166.7	76.9

Synthesis: $Ni_{0.9}Mn_{0.1}(OH)_2 + LiOH{\cdot}H_2O$

480°C 5 h, then various temperatures for 15 h

The minimum Li/Ni mixing, higher capacity and capacity retention are achieved by the optimization of synthesis condition (e.g., temperature and Li excess amount)

Collaboration and Coordination with Other Institutions

- Pennsylvania State University (Shanhai Ge)
  - Materials synthesis, cell design, fabrication, and testing.
- Oak Ridge National Lab (Ethan Self, Devendrasinh Darbar)
  - Synthesis optimization, Mo-doping modification
- Pacific Northwest National Lab (Linze Li)
  - TEM (HRTEM, EDS, HAADF-STEM, ABM-STEM) characterization

Proposed Future Research

FY20:

- Al_2O_3 coated $LiNi_{0.92}Co_{0.055}Mn_{0.025}O_2$: further characterization and analysis for observing Li/Ni mixing and phase transition before/after long-term cycling
- Co-free $LiNi_{0.9}Mn_{0.1}O_2$: optimization of coating and doping process to further improve rate and cycling performance.
- Demonstrate surface-protected cation-optimized low-cobalt cathode (Co loading < 50 mg Wh^{-1}) with a capacity of ~ 190 mAh g^{-1} and over 92% capacity retention in 100 cycles under C/3 discharge rate.

FY21:

- Scale up of the cation-doped low/no-Co cathode material (Co loading < 50 mg Wh^{-1}, with a capacity of ~ 190 mAh g^{-1} and 92% capacity retention in 100 cycles).
- Deliver 2.5 Ah pouch cells with the developed low-Co cathode and graphite anode with over 240 Wh kg^{-1} and about a 80% capacity retention over 1000 cycles.

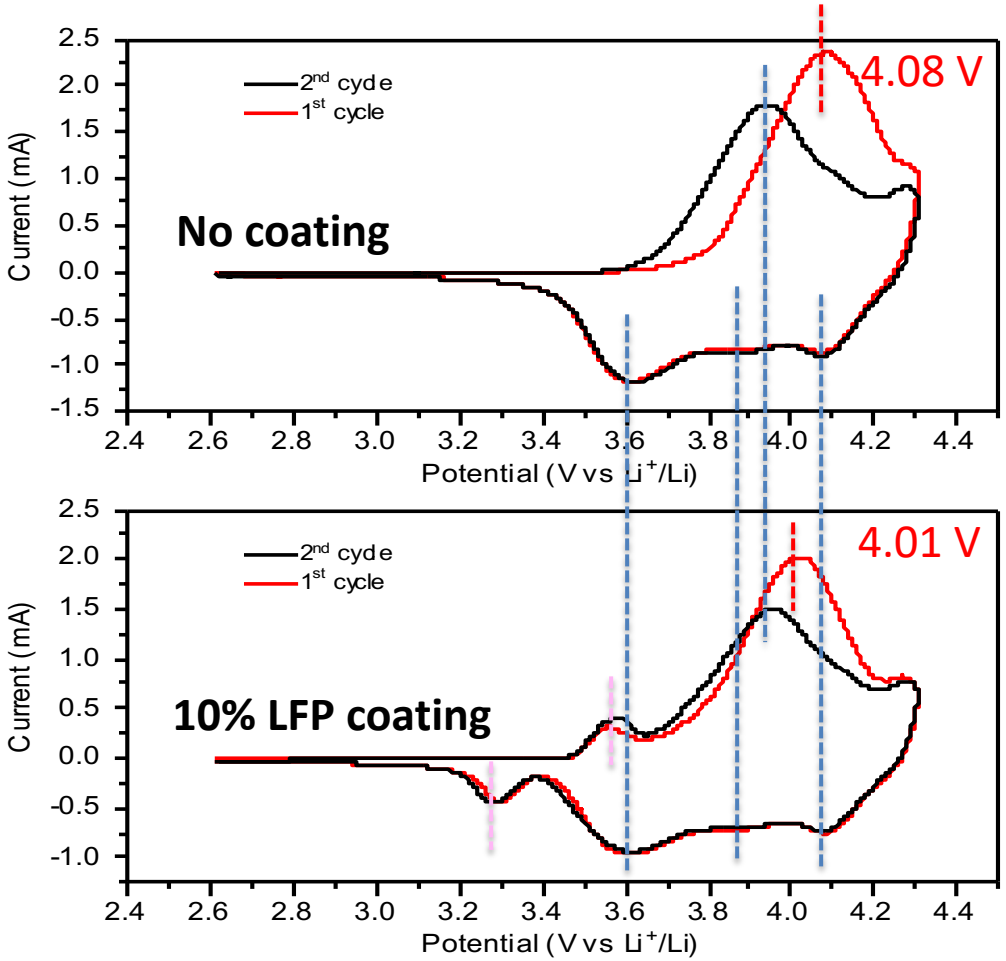
Any proposed future work is subject to change based on funding levels.

Summary

- 10% LFP-coated NCM811 exhibits excellent cyclability. The pouch cell with graphite anode shows a capacity retention of 72.4% over 4941 cycles.
- Al_2O_3 coated $LiNi_{0.92}Co_{0.055}Mn_{0.025}O_2$ materials shows better cycling performance than uncoated NCM92, and the mechanisms need to be further analyzed.
- Mo-doped Co-free material $LiNi_{0.45}Mn_{0.45}Mo_{0.1}O_2$ (LNMMO) shows greater structural stability compared with the undoped material, and Mo-doping is proved to be beneficial for suppressing cation mixing and rocksalt structure generation.
- Spherical $Ni_{0.9}Mn_{0.1}(OH)_2$ precursor is obtained for NM91 synthesis, and the final product NM91 shows a stable cycling.

Technical Back-up Slides

Technical Accomplishments and Progress: LFP coated NCM811



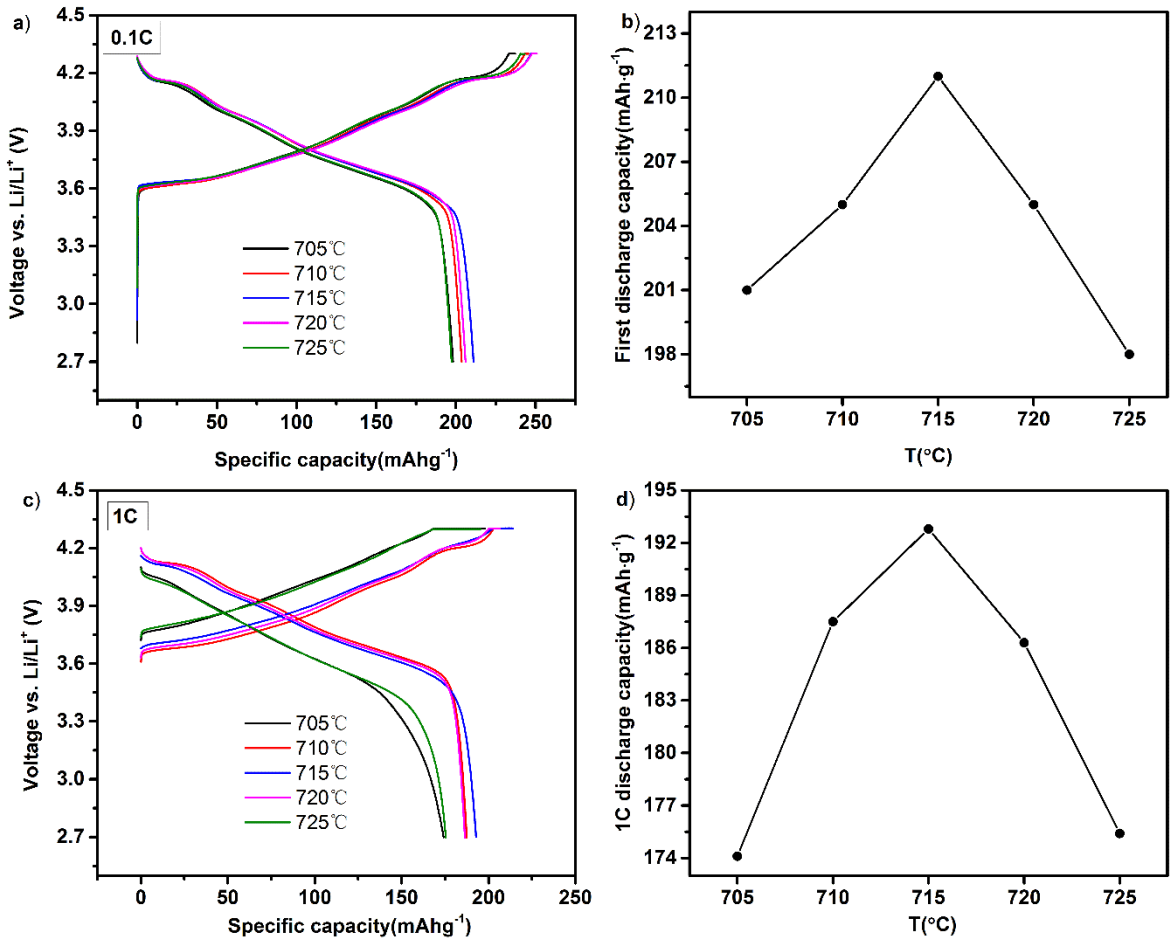
First cycle NCM oxidation

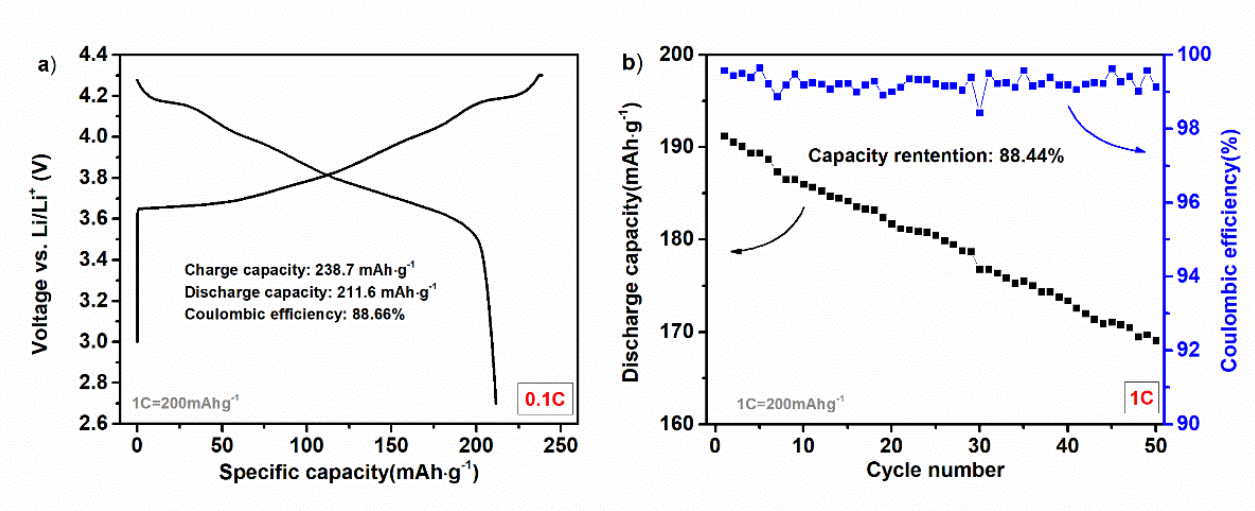
Subsequent NCM redox

LFP redox

CV: lowered oxidation potential after LFP coating for the 1st cycle - a more stable interface

Technical Accomplishments and Progress: Al_2O_3 coated $LiNi_{0.92}Co_{0.055}Mn_{0.025}O_2$





Synthesis: $NCM(OH)_2$+LiOH·H2O (Li 5% excess), 480°C 5 h, then 715°C 15 h

211 mAh g^{-1} at 0.1 C, 192 mAh g^{-1} at 1 C, 88% after 50 cycles

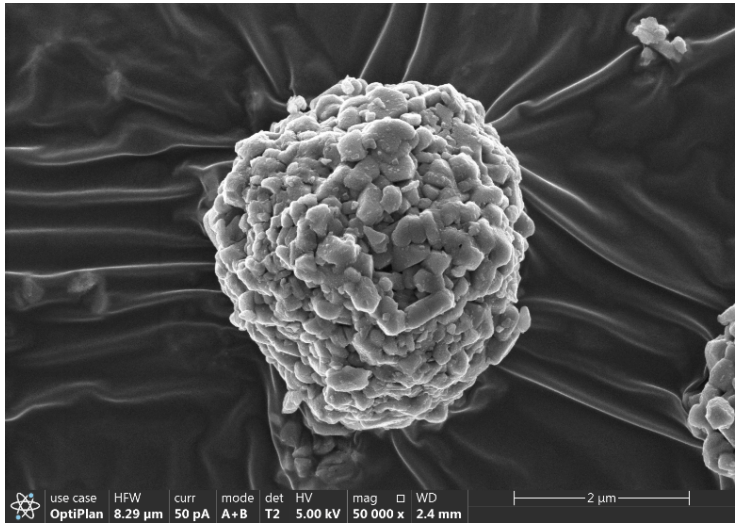
715 °C is chosen as synthesis temperature.

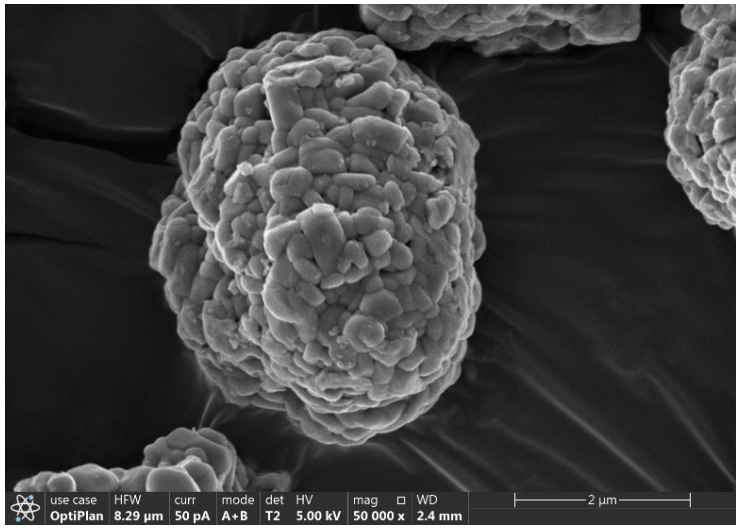
Technical Accomplishments and Progress: Al_2O_3 coated $LiNi_{0.92}Co_{0.055}Mn_{0.025}O_2$

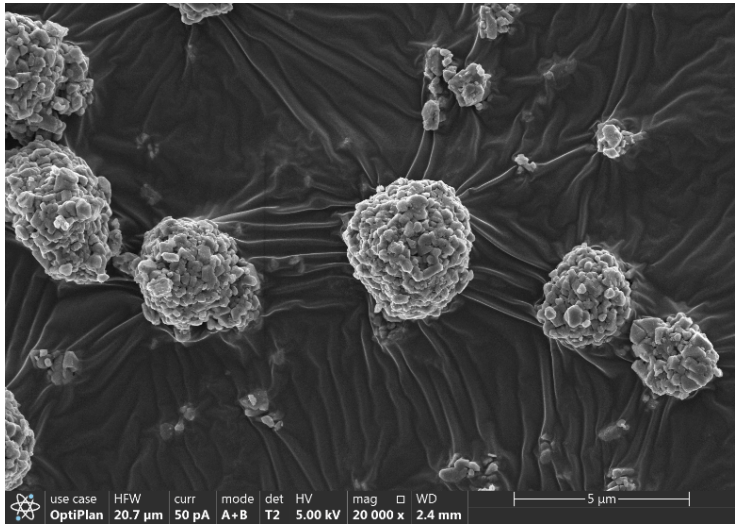
After calcination

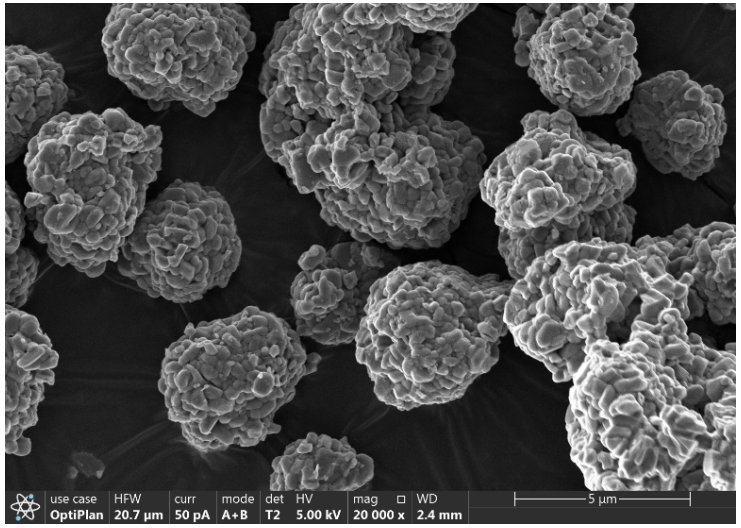
NCM bare

1% Al_2O_3 coated



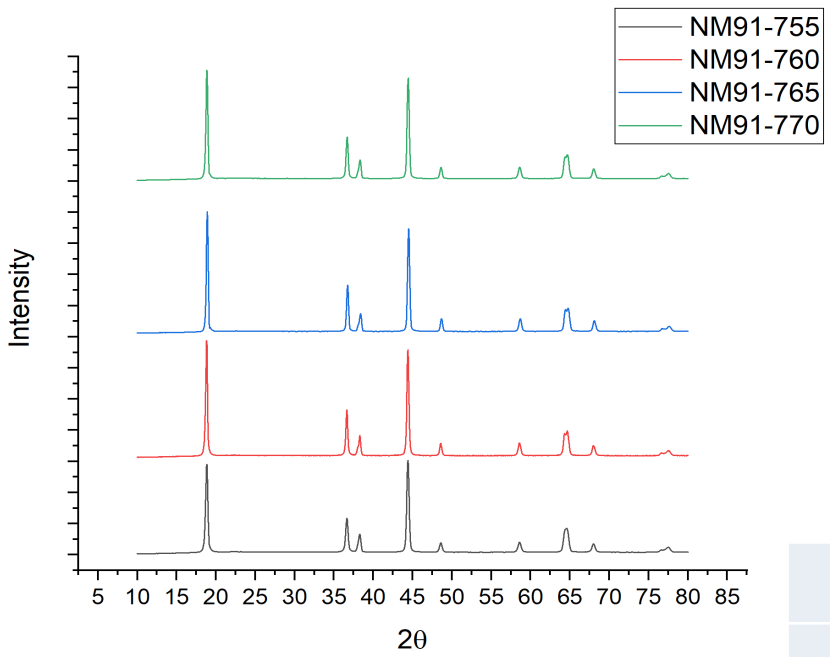




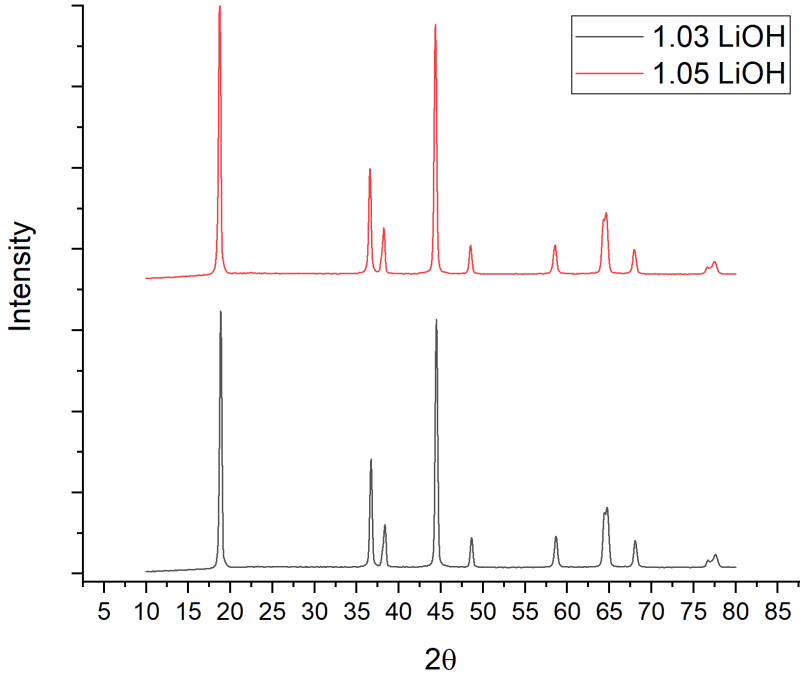


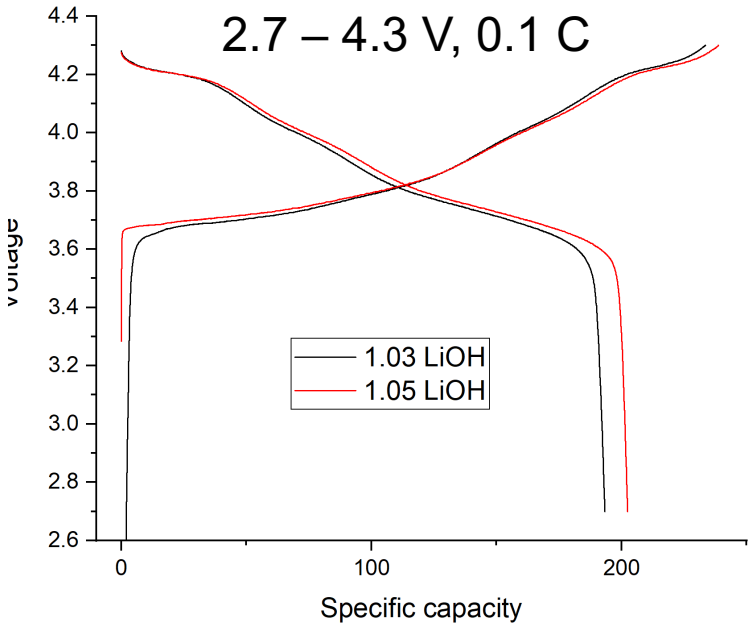
Technical Accomplishments and Progress: Co-free $LiNi_{0.9}Mn_{0.1}O_2$

Temperature optimization



Li excess amount optimization



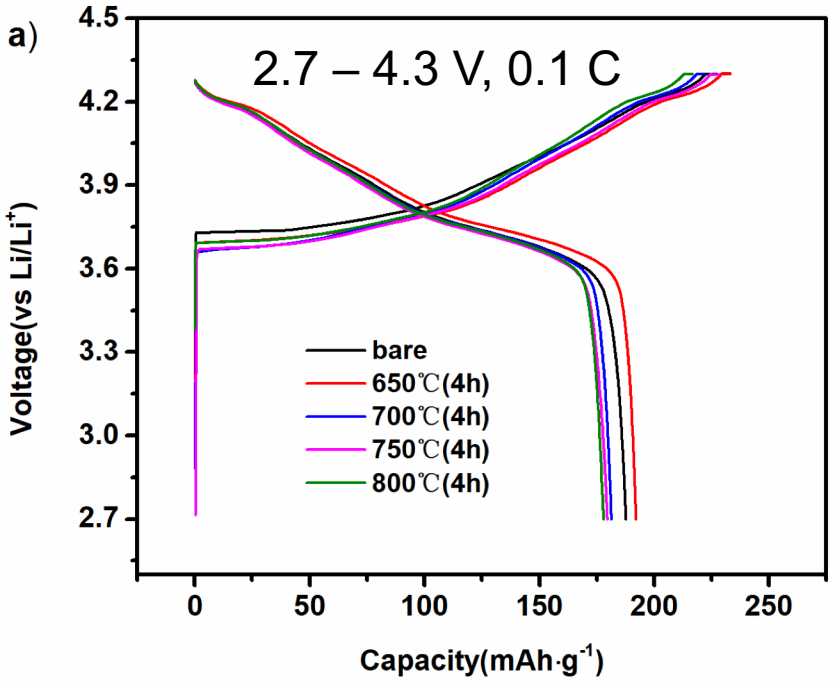


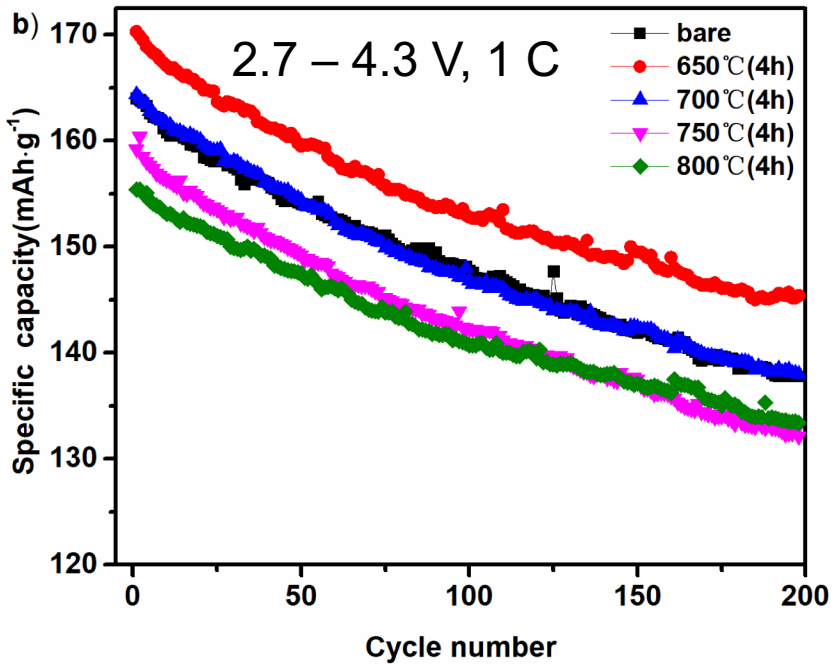
NM91-765	a	c	I(003/104)	1st charge	1st discharge	1st cycle CE
1.03 LiOH	2.878	14.142	0.970	237.6	193.3	81.3
1.05 LiOH	2.876	14.166	1.011	244.5	202.4	82.8

The 5% Li excess sample delivers higher specific capacity.

Technical Accomplishments and Progress: NCM811 secondary sintering

$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811)

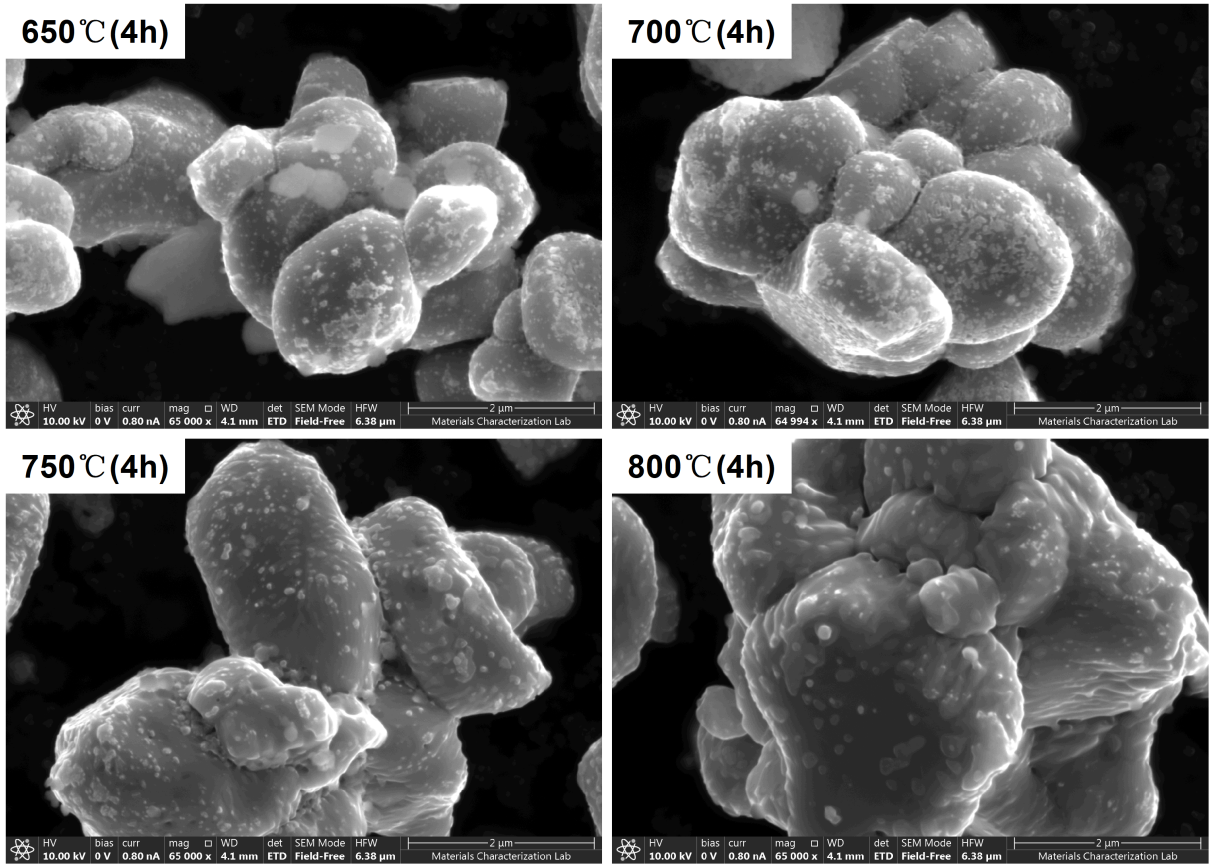


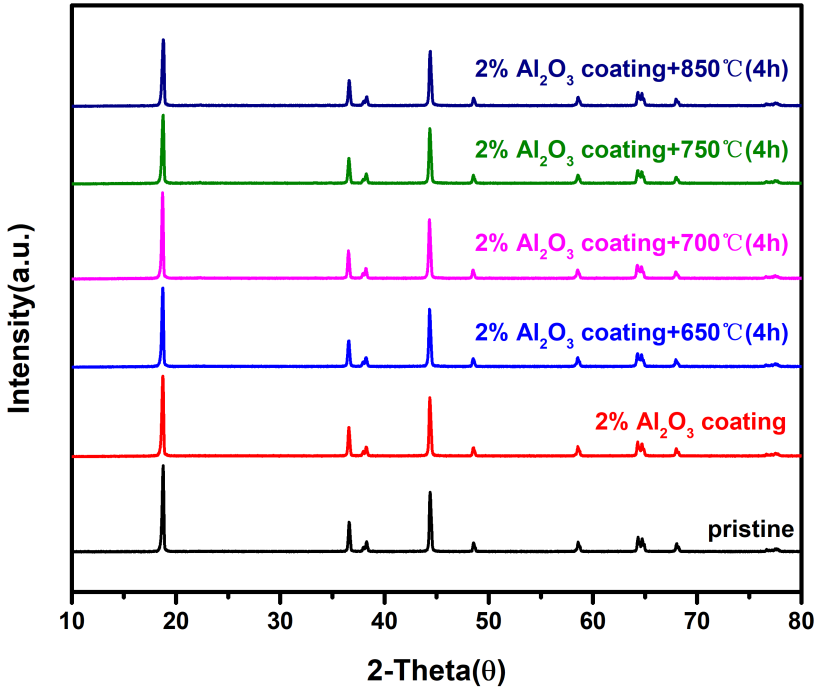


650 °C second sintering can improve the electrochemical performance, including both specific capacity and cyclability.

Sample	1st Cha(mAh g-1)	1st Dis(mAh g-1)	CE(%)	1st 1C Dis(mAh g-1)	Capacity retention over 200 cycles(%)
pristine	227.1	187.7	82.65	164.0	84.02
650C°	233.2	192.1	82.38	170.3	85.38
700C°	221.6	181.4	81.86	164.4	83.94
750C°	228.0	179.6	78.77	159.2	82.98
800C°	216.6	177.9	82.13	155.4	85.84

Technical Accomplishments and Progress: Al_2O_3 coating + secondary sintering

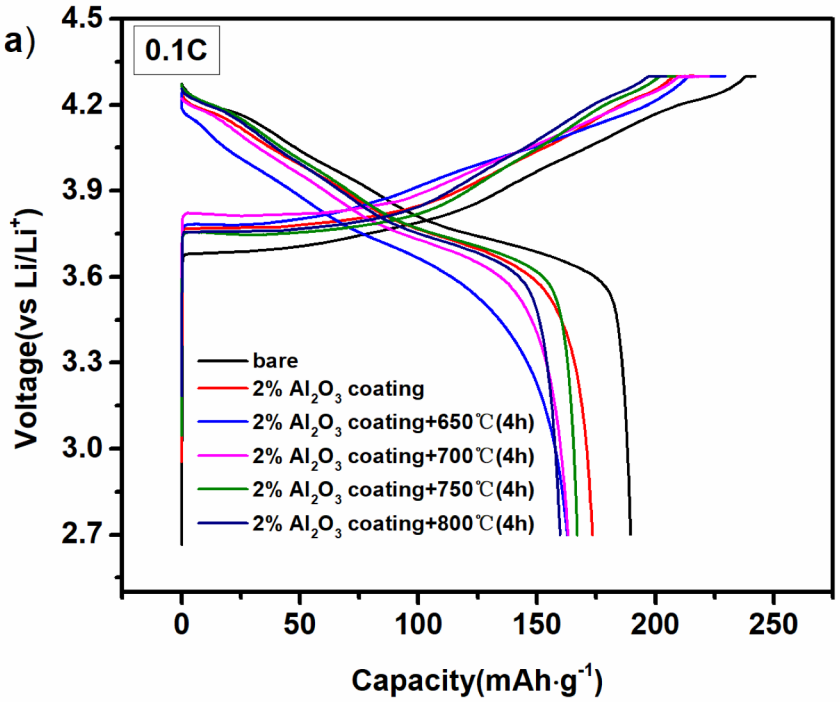


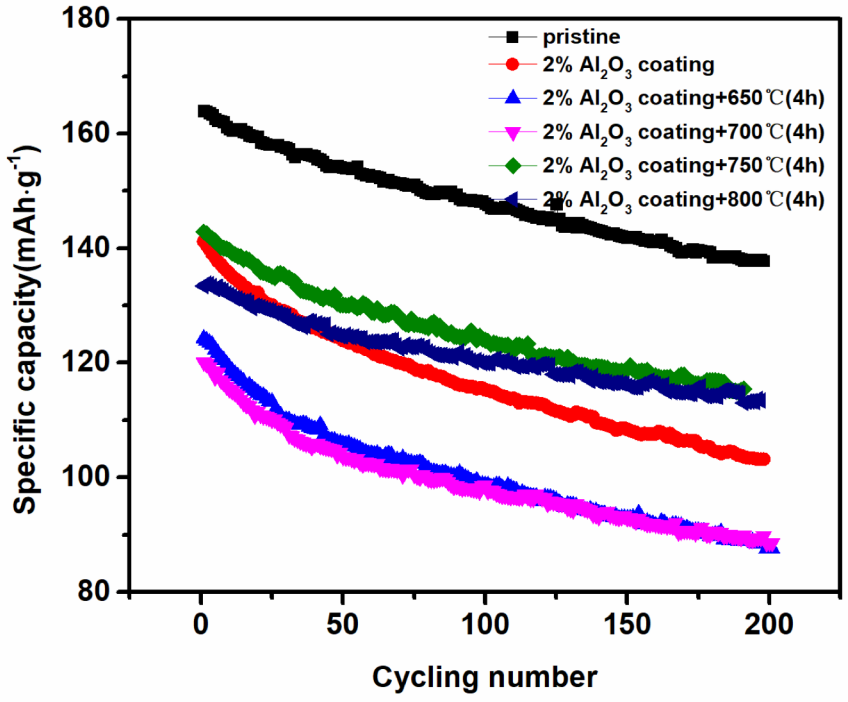


Sample	a(Å)	c(Å)	c/a	V(Å^3)
pristine	2.8810	14.2338	4.9406	102.31
2% Al_2O_3 coating	2.8816	14.2353	4.9400	102.37
2% Al_2O_3 coating+650℃(4h)	2.8821	14.2349	4.9391	102.40
2% Al_2O_3 coating+700℃(4h)	2.8821	14.2314	4.9379	102.37
2% Al_2O_3 coating+750℃(4h)	2.8822	14.2356	4.9391	102.41
2% Al_2O_3 coating+800℃(4h)	2.8826	14.2378	4.9392	102.46

Particle size: 2-3 μm
All materials show great layered structure.

Technical Accomplishments and Progress: Al_2O_3 coating + secondary sintering





Sample	1st Cha(mAh g^{-1})	1st Dis(mAh g^{-1})	CE(%)	1st 1C Dis(mAh g^{-1})	Capacity retention over 200 cycles(%)
pristine	242.0	189.5	78.31	164.0	84.02
coating	216.4	173.4	80.13	141.2	73.09
650℃	229.4	162.8	70.97	124.3	70.47
700℃	222.5	163.1	73.30	120.1	73.77
750℃	208.1	167.0	80.25	142.8	80.81
800℃	204.3	159.7	78.17	133.4	85.01