Project ID: bat413

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

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06/25/2021

Overview

Timeline

- Project start date: Oct. 1, 2018
- Project end date: Dec. 31, 2021
- Percent complete: 70%

Budget

- Total project funding
  - DOE share: $1,952,017
  - Contractor share: $488,005
- Funding for FY 2021
  - DOE share: $591,407
  - Contractor share: $147,852

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 assembly

Partners

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

Relevance

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.

Objective

- Low-cobalt $LiNi_{0.92}Co_{0.055}Mn_{0.025}O_2$ (NCM92): Ti doping
- Low-cobalt NCM92: MoO_3 and Sb_2O_3 coating
- Low-cobalt NCM92: $LiPO_3$ coating

Approach

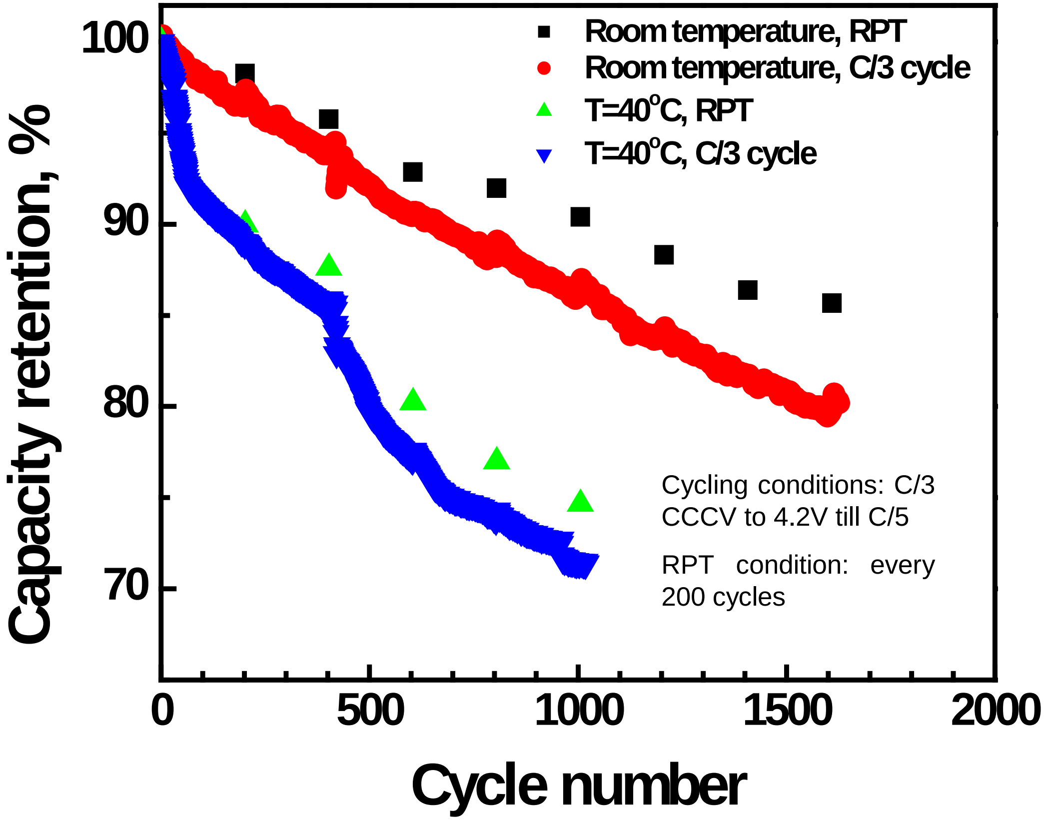
- Transition metal cation composition optimization for enhanced lattice stability (Example: Ti-doped NCM92)
- Surface coating and infusion to mitigate solid-liquid reaction and enhance structural integrity (Example: $LiPO_3/MoO_3/Sb_2O_3$-coated NCM92)
- Atomic-scale advanced characterization to envisage new designing principle (HAADF-STEM with EDS analysis)

FY21 Milestones:

- Scale up of the cation-doped low-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 thirty 2.5 Ah pouch cell with the developed low-Co cathode and graphite anode with over 240 Wh kg^{-1} and about a 80% capacity retention over 1000 cycles.

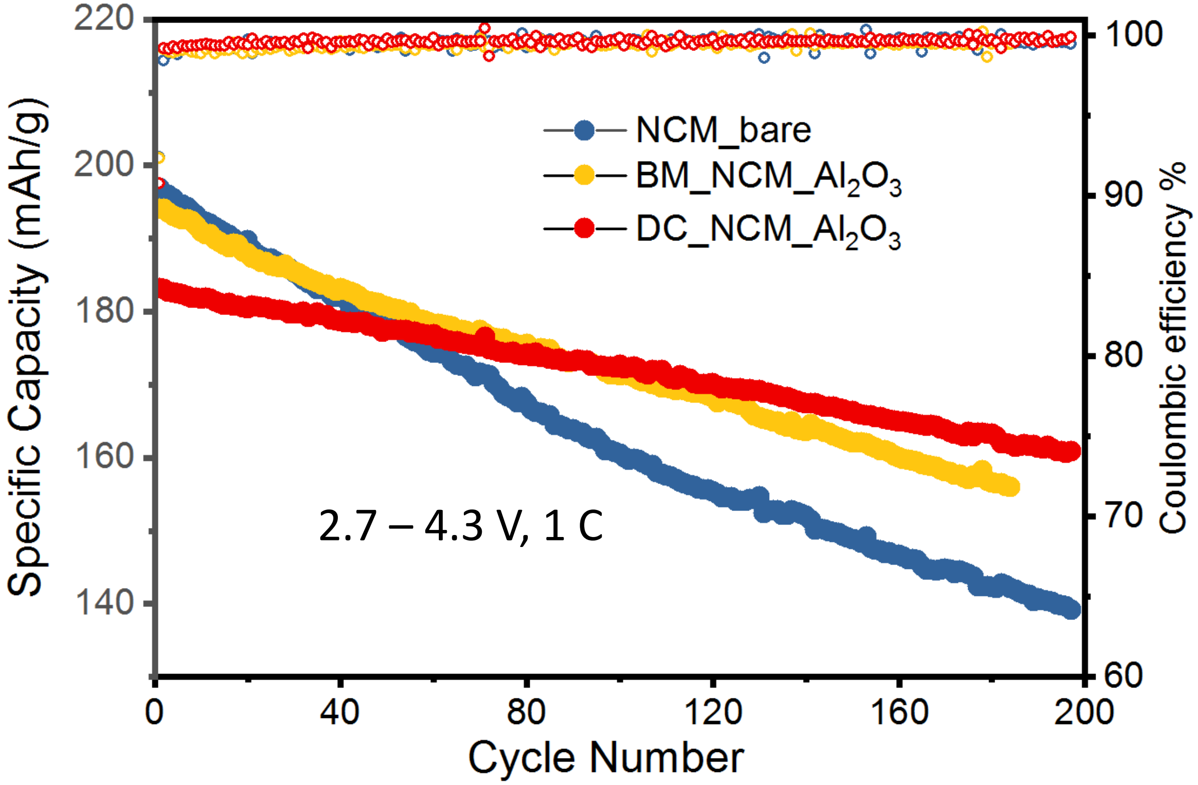
Previous Accomplishments

2.5 Ah Graphite/LFP coated NCM811 pouch cell



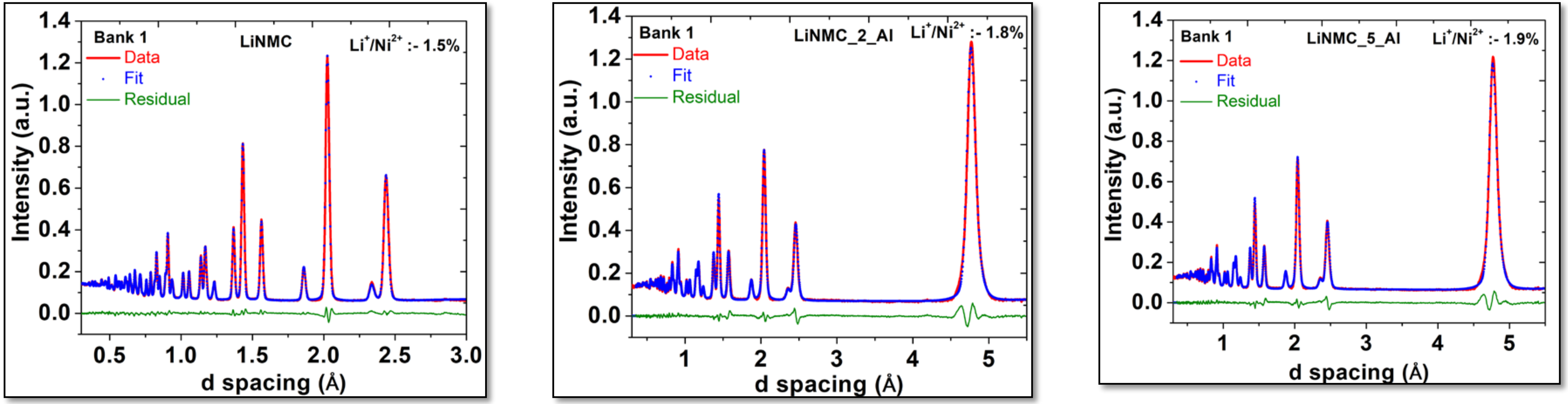
85.7% capacity retentions after 1609 cycles at RT, 74.7% capacity retentions after 1006 cycles at 40°C (RPT condition)

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



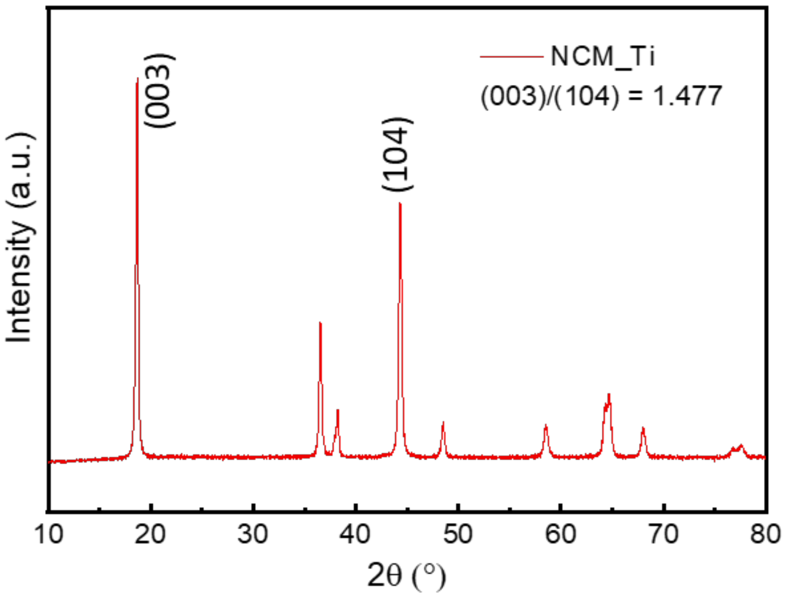
BM_NCM: ball milling DC_NCM: dry coating

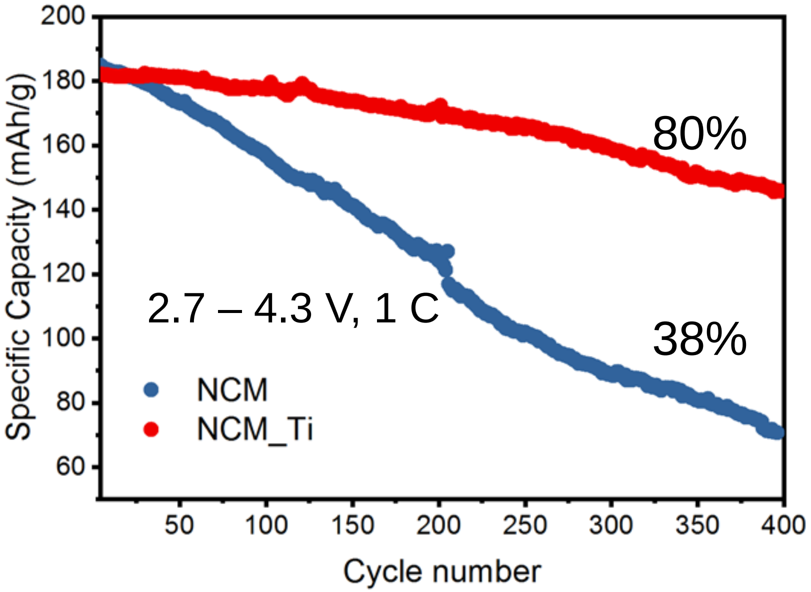
Technical Accomplishments and Progress: Neutron Diffraction Characterization

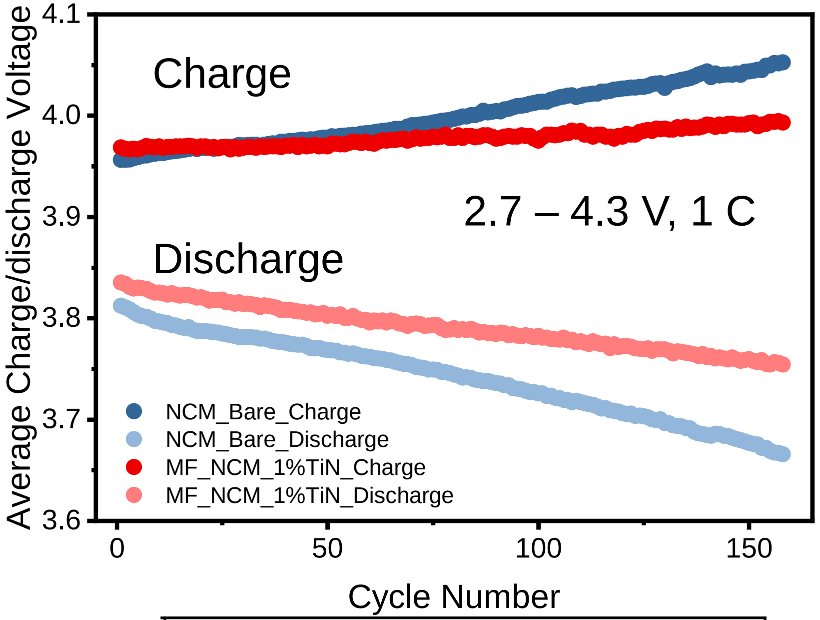


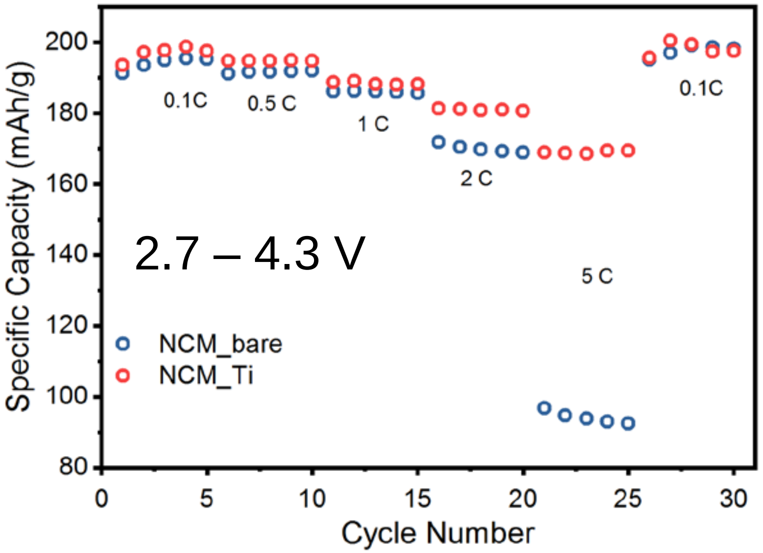
- Neutron diffraction data for all the cathode materials revealed that these compositional variants had good phase purity with conventional layered structure.
- The refinements indicated minimal (~1.5%) Li^{+}/Ni^{2+} anti-site defect for the pristine and slight increase in pair antisite defect ~2% was observed in the NCM with Al.

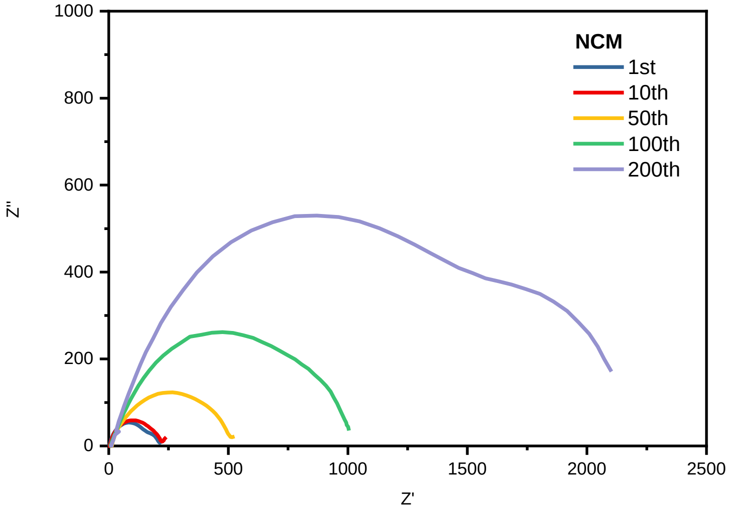
Technical Accomplishments and Progress: Ti-doped NCM92

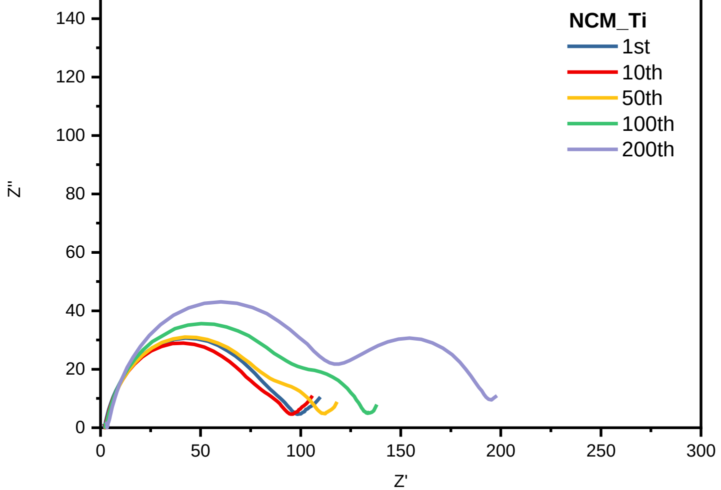








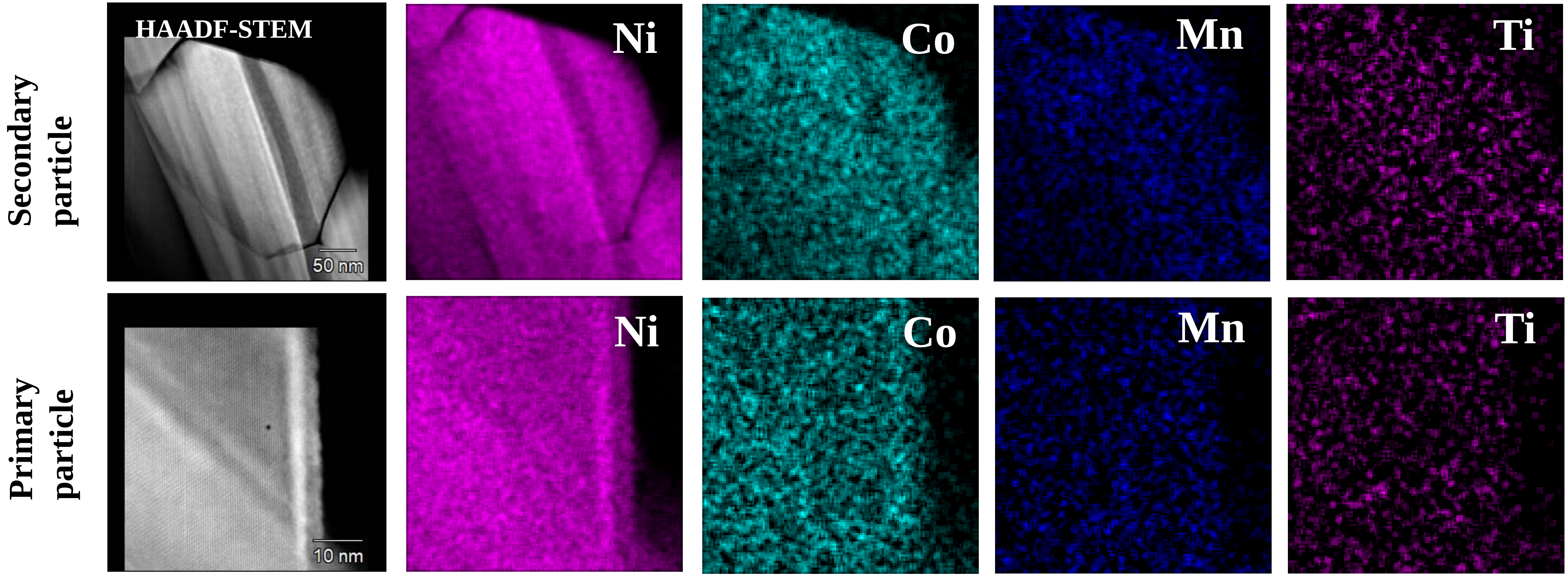




Ti-doped NCM92 shows excellent cyclability and rate performance.

Technical Accomplishments and Progress: Ti-doped NCM92

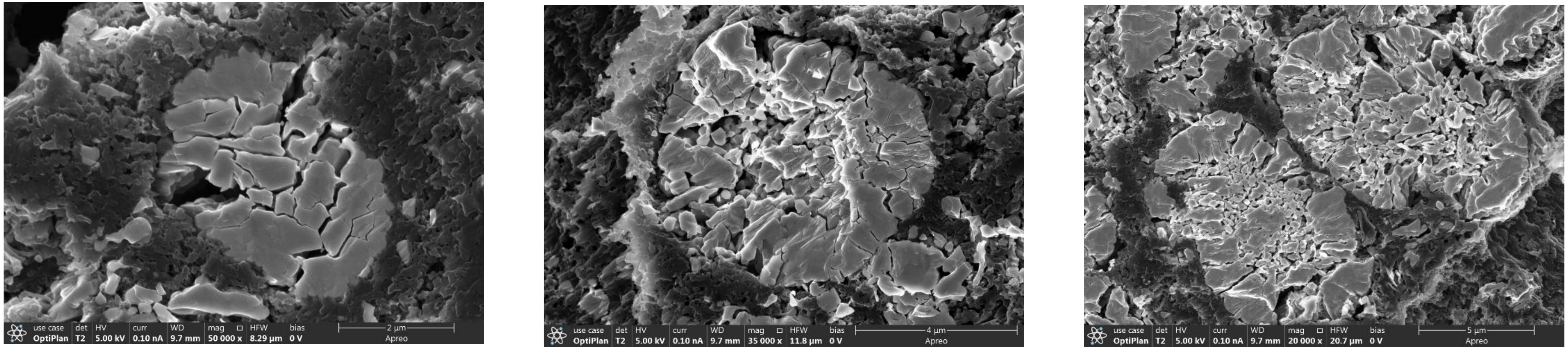
HAADF-STEM with Elemental Distribution of Pristine NCM_Ti



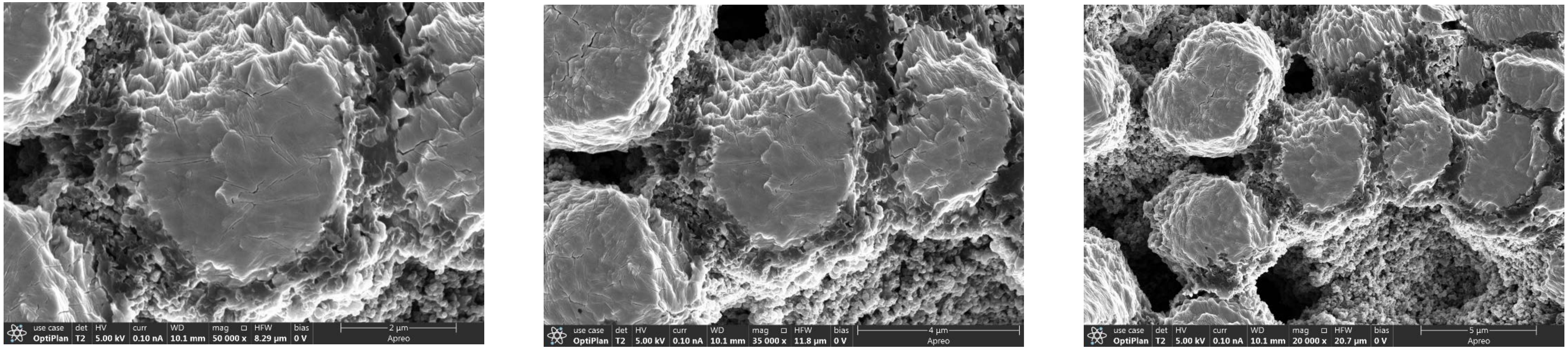
Ti is uniformly distributed at both secondary and primary particle level.

Technical Accomplishments and Progress: Ti-doped NCM92

NCM_bare after 200 cycles (@charged 4.3 V state)

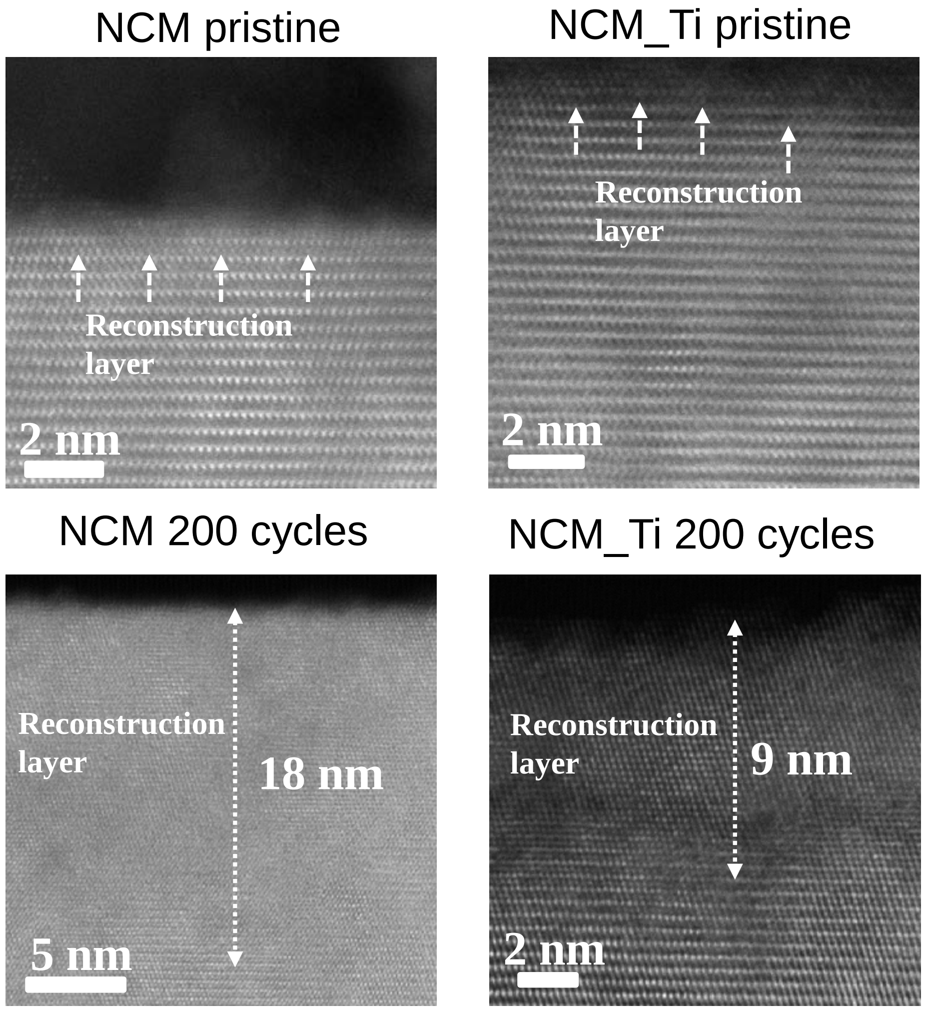


NCM_Ti after 200 cycles (@charged 4.3 V state)

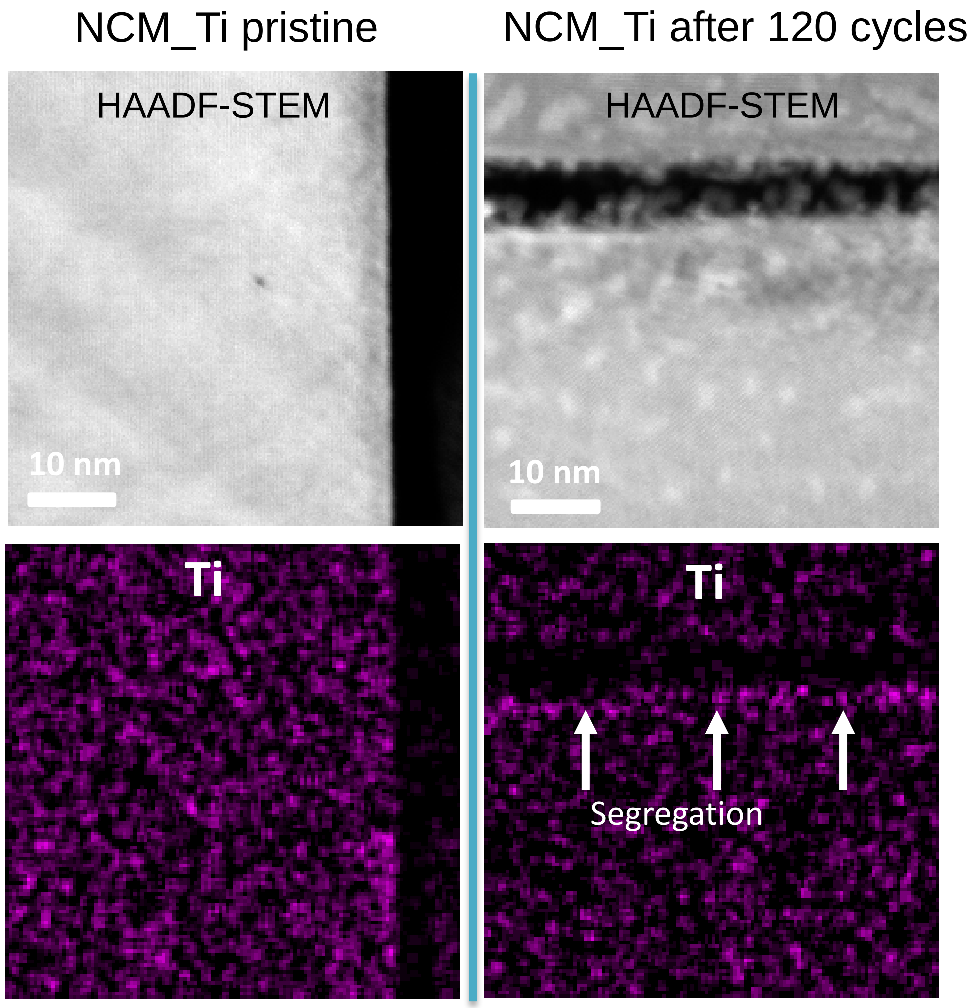


Ti doping can prevent the crack formation and particle destruction.

Technical Accomplishments and Progress: Ti-doped NCM92

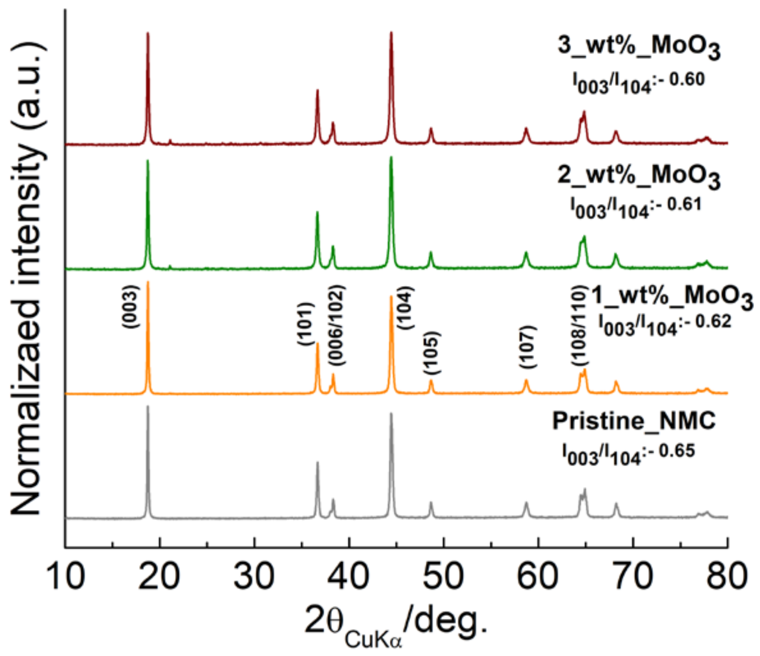


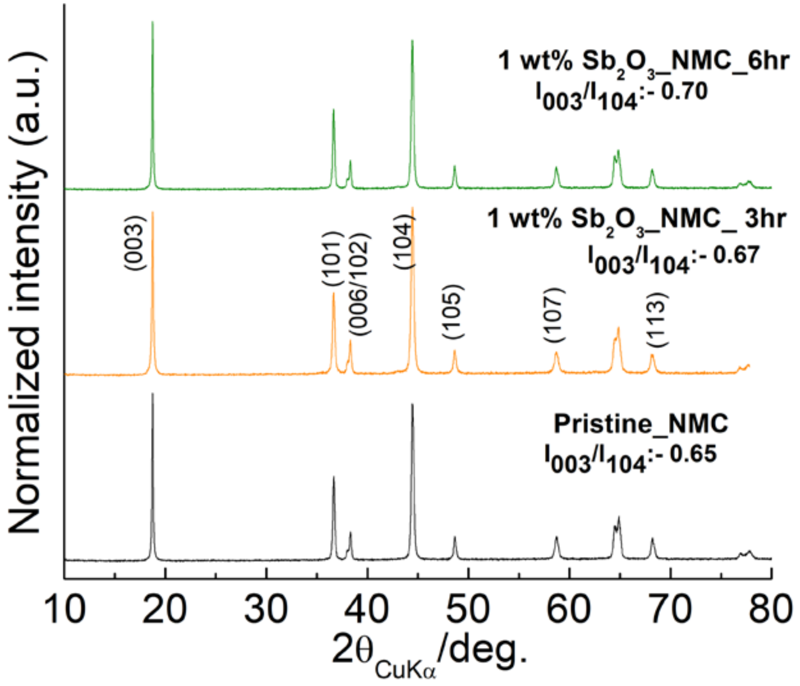
Ti doping leads to the apparent mitigation of the surface reconstruction layer thickness

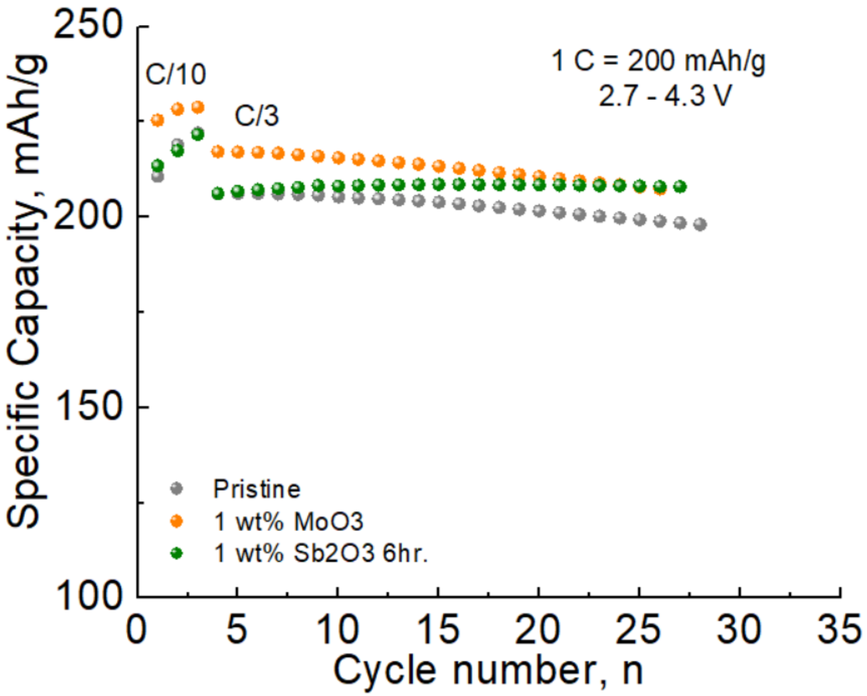


Ti shows uniform distribution in the lattice, and Ti surface segregation can be noticed occasionally

Technical Accomplishments and Progress: MoO_3/Sb_2O_3-coated NCM92

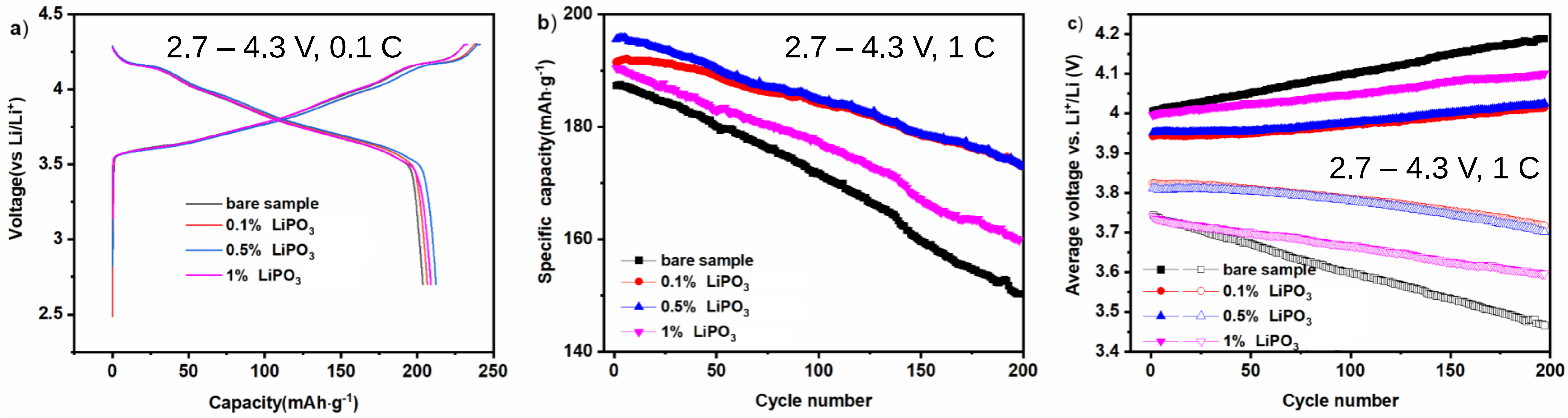






- NCM92 cathodes were coated with 1-3 wt.% MoO_3 and 1 wt.% Sb_2O_3 using a co-precipitation + solid-state synthesis route.
- 1 wt.% MoO_3 coated NCM92 shows initial higher capacity but poor capacity retention whereas 1 wt.% Sb_2O_3 coated NCM92 gives excellent capacity retention.

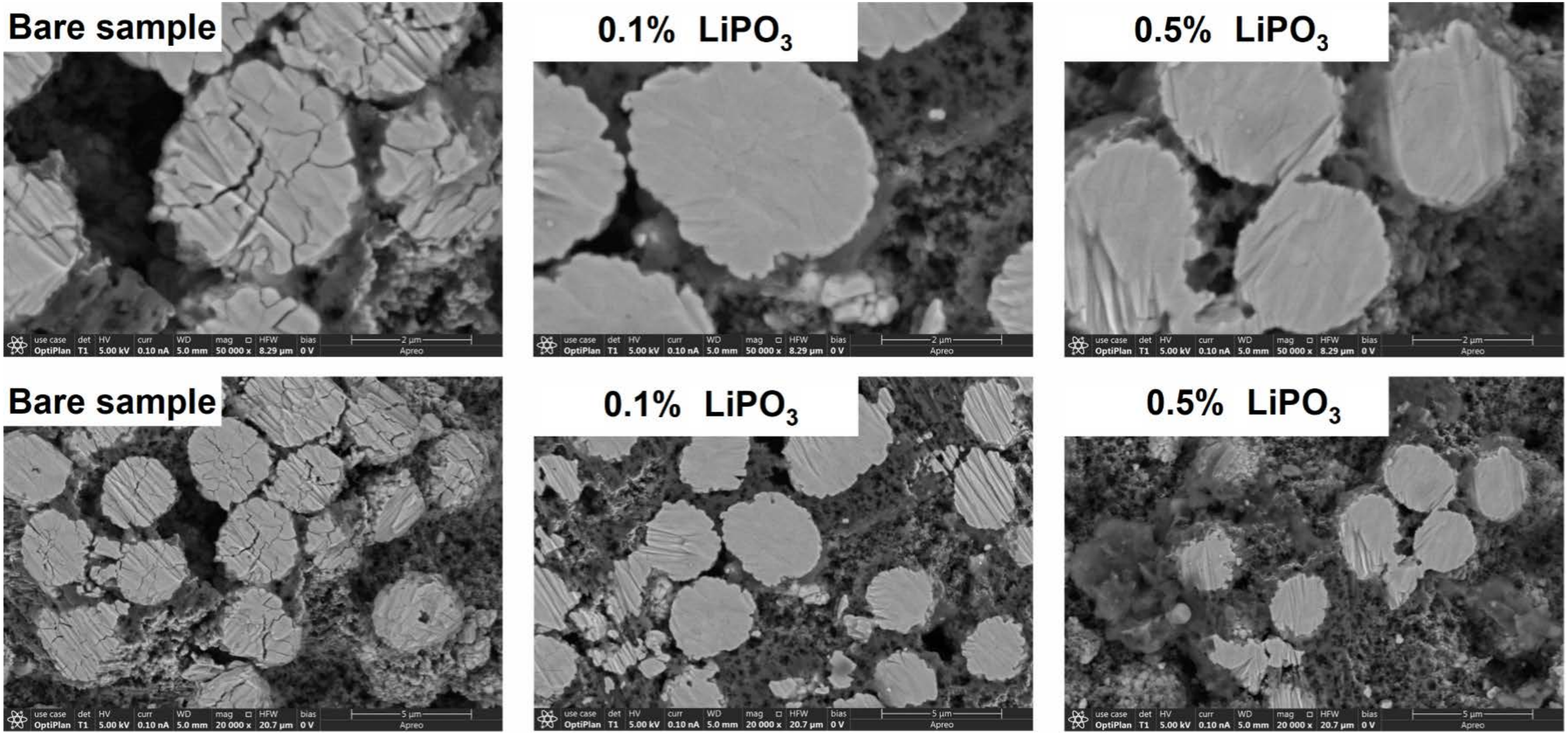
Technical Accomplishments and Progress: $LiPO_3$-coated NCM92



	1st char (mAh/g) (0.1 C)	1st dis (mAh/g) (0.1 C)	Initial CE(%)	1st dis (mAh/g) (1 C)	200th dis (mAh/g) (1 C)	Capacity retention after 200 cycles (%)	Capacity fade per cycle
Bare	233	204	88	187	150	80	0.187
0.1%	240	207	86	192	173	90	0.095
0.5%	241	212	88	196	173	88	0.115
1.0%	233	209	90	190	160	84	0.155

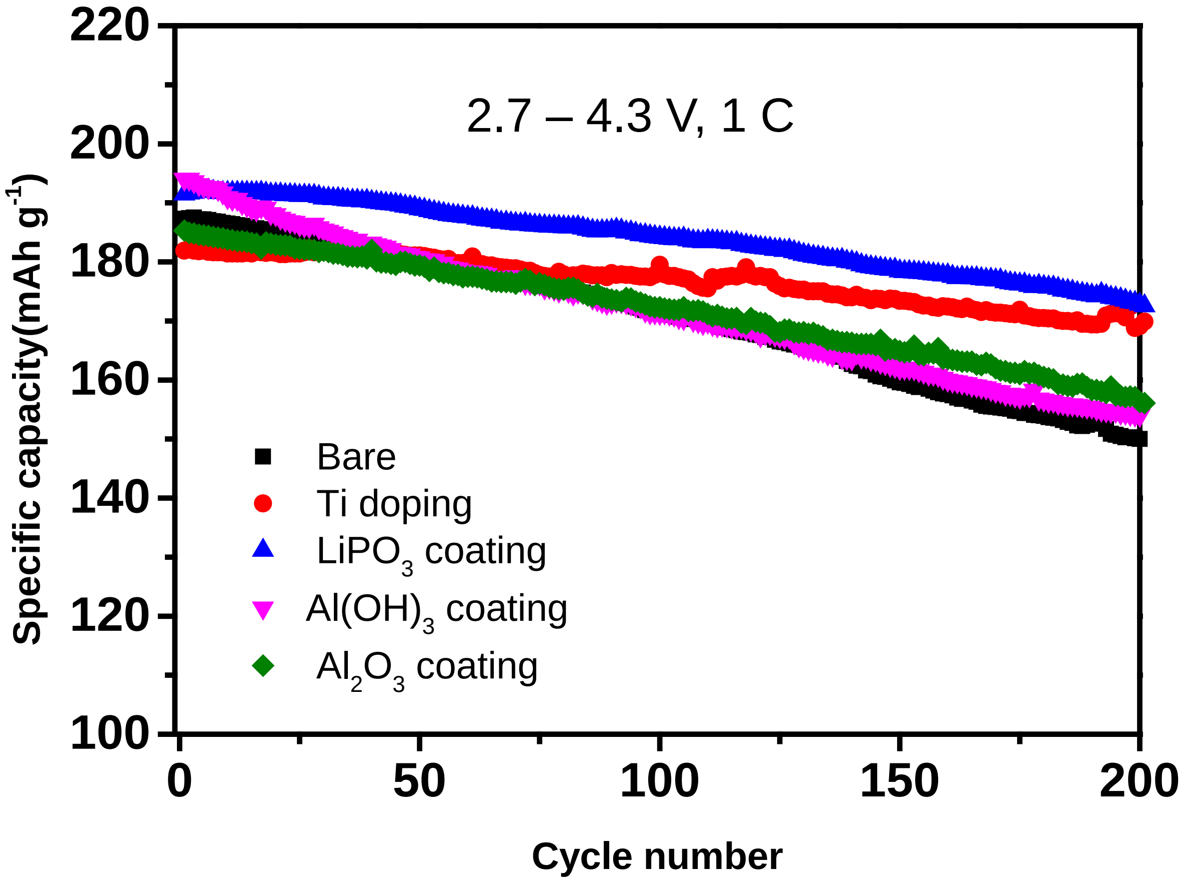
All the coated samples show improved initial specific capacity and cyclability. The 0.1% sample shows the highest capacity retention and the 0.5% sample shows the highest initial discharge capacity.

Technical Accomplishments and Progress: $LiPO_3$-coated NCM92



No cracks observed for 0.1% and 0.5% samples after 200 cycles

Technical Accomplishments and Progress: Comparison



Ti doping to NCM92 shows the best cycling performance after 200 cycles.

	Bare NCM92	Ti doping	$LiPO_3$ coating	$Al(OH)_3$ coating	Al_2O_3 coating	MoO_3/Sb_2O_3 coating
Capacity Retention of 200 cycles	80%	93%	90%	79%	87%	Under test

Responses to Previous Year Reviewers' Comments

Comment 1: The quality of the NCM materials needs to be improved.

Response 1: This year we have improved our material synthesis and modification, and now the electrochemical performance is much better. The capacity retention is up to 93% after 200 cycles. We believe that the new materials can fulfill the requirements of characterization, scale up and final cell delivery.

Comment 2: The reviewer found no consistent theme within the work but rather a mix of different approaches based on different material sets and development activities.

Response 2: Different approaches were conducted last year in order to find the best solution of obtaining low-cobalt materials with great electrochemical performance. We found that NCM92 is a proper candidate and this year all the works are based on NCM92.

Comment 3: Al_2O_3 is a common coating technology in the industry these days and is well known to provide some benefit and is widely available in commercial materials.

Response 3: Last year we have conducted Al coating/doping NCM materials and we have gained much experience and comprehension of low-cobalt NCM materials and corresponding optimization. This year we are focusing on different modifications of Ti doping, $LiPO_3$ coating and MoO_3/Sb_2O_3 coating to NCM materials, and the electrochemical performance is further improved.

Collaborations

- Pennsylvania State University (Chao-Yang Wang, Shanhai Ge)
  - Pouch cell testing
- Oak Ridge National Lab (Jagjit Nanda, Ethan Self, Devendrasinh Darbar)
  - Doping elements optimization and neutron scattering characterization
- Pacific Northwest National Lab (Chongmin Wang, Linze Li, Lianfeng Zou)
  - TEM (HRTEM, EDS, HAADF-STEM) characterization

Proposed future research

- Further optimize cation-doped low-Co cathode materials
- Analysis of $LiPO_3$ coating distribution
- Scale up of the optimized low-Co cathode materials
- 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

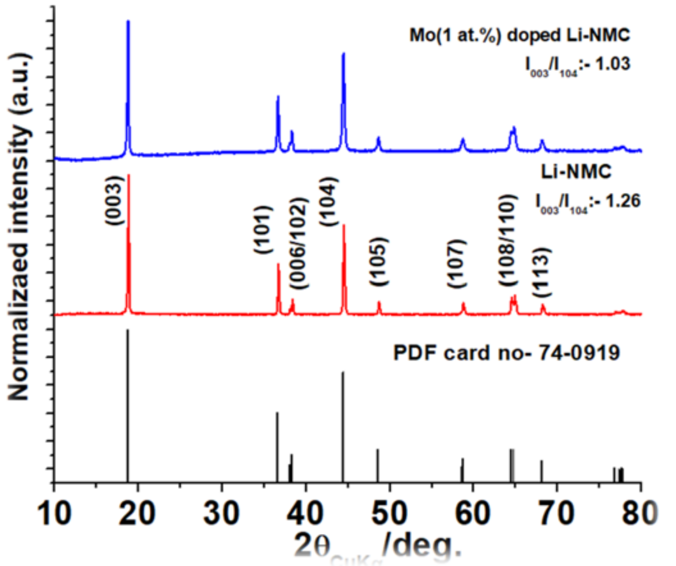
- Ti-doped NCM92 exhibits excellent capacity retention of 80% after 400 cycles in a half cell.
- Ti doping can prevent the crack formation and particle destruction, and suppress the growth of surface reconstruction layer.
- MoO_3 and Sb_2O_3 coating can improve the electrochemical performance of NCM92, and the mechanism needs to be further investigated.
- $LiPO_3$-coated NCM92 shows improved cyclability, and the structure and morphology of the material can be well preserved after 200 cycles.

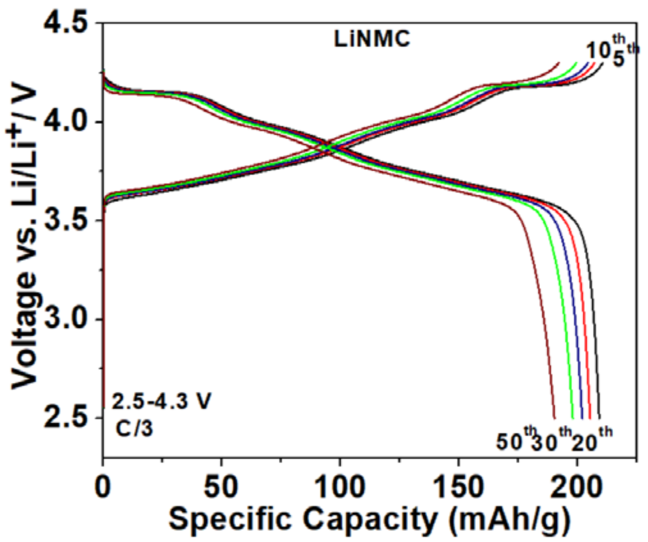
Acknowledgement

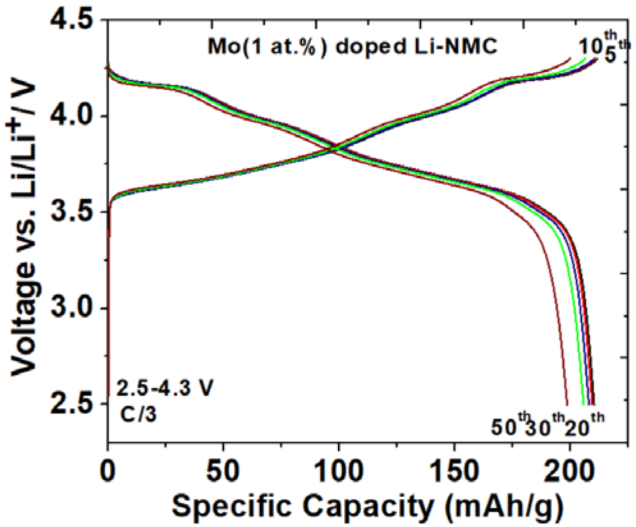
Support from David Howell and Pete Faguy at the US Department of Energy's Office of Vehicle Technologies is greatly appreciated.

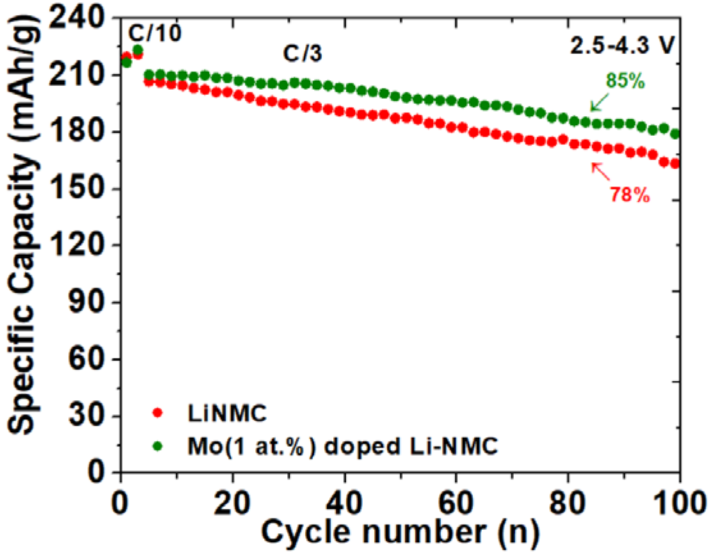
Technical Back-up Slides

Mo-doped NCM92





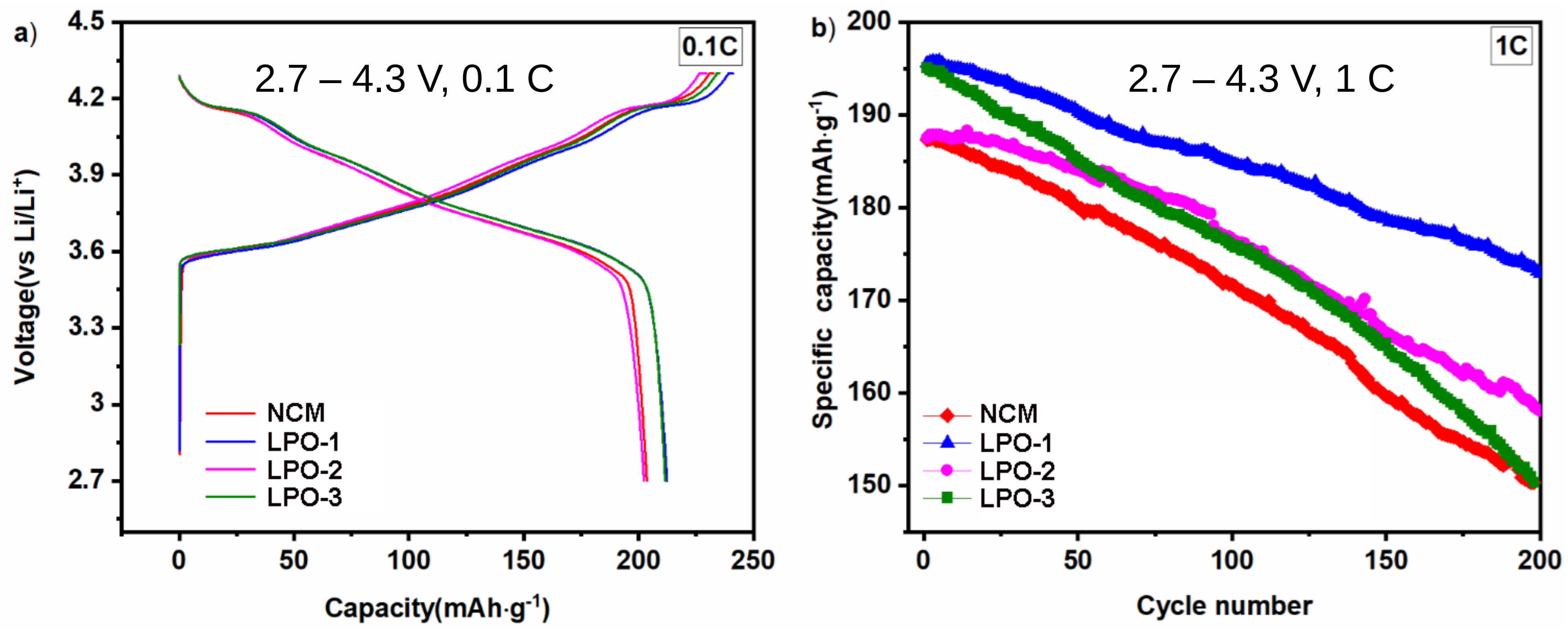




- Mo dopant has increased the Li^+/Ni^{2+} cation mixing, and this might be due to its higher valent state because it increase the unbalance in terms of charge neutrality, and this increase the amount of Ni^{2+} ion.
- Mo doping slightly increased the capacity and the cycling stability of Li-NMC cathodes.
- Mo doped cathode shows less degradation in terms of cyclability and no significant changes in charge discharge curves.

Technical Accomplishments and Progress: $LiPO_3$-coated NCM92

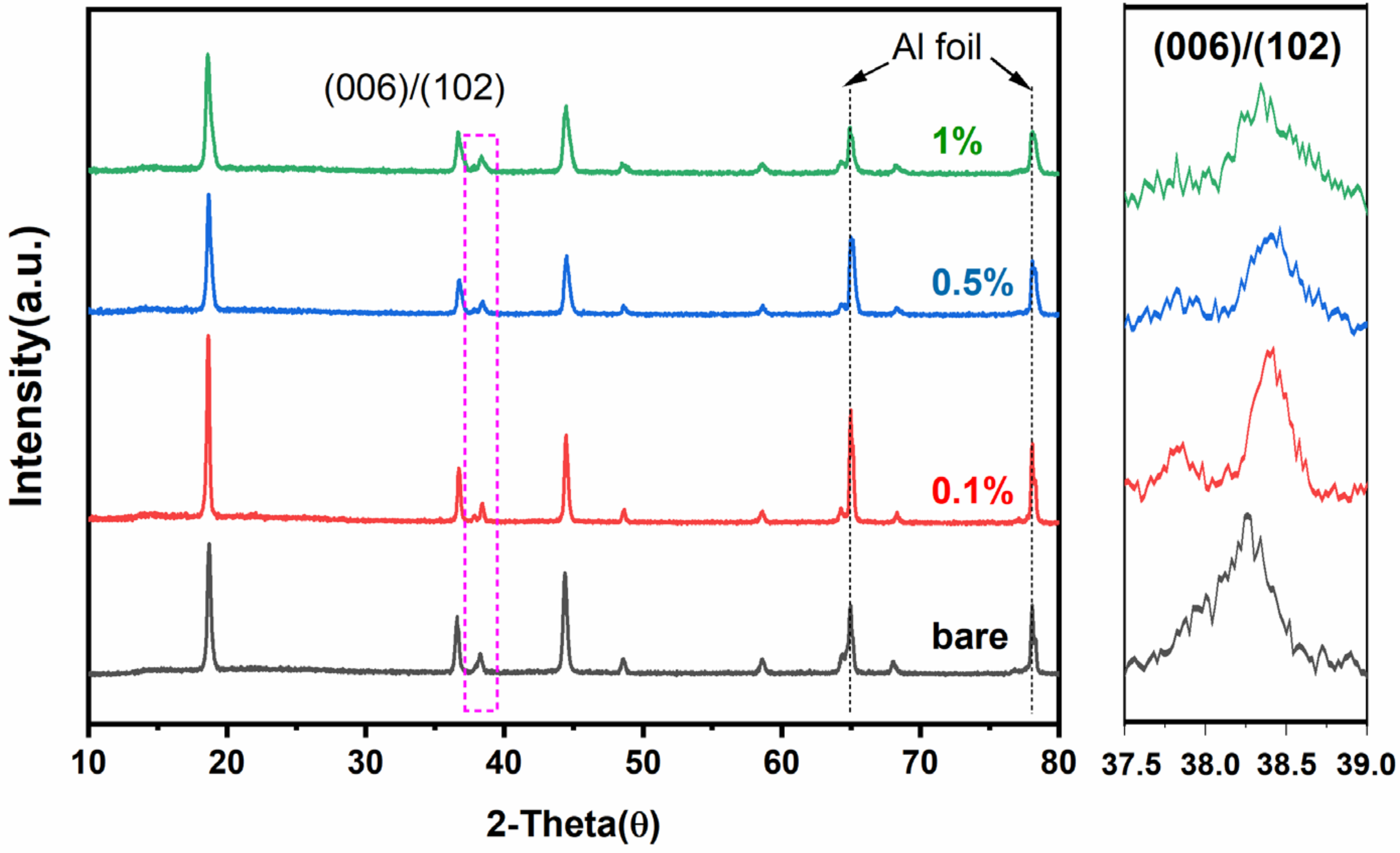
Coating material selection: different precursors, LPO-1, LPO-2 and LPO-3 (0.5% coating)



LPO-1 coating shows the highest initial specific discharge capacity and capacity retention.

Technical Accomplishments and Progress: $LiPO_3$-coated NCM92

XRD of electrodes of bare and coated cathode materials after 200 cycles



The 0.1% and 0.5% samples exhibit separate peaks (006) and (102) after 200 cycles, indicating a well-preserved layered structure.

Ti precursor selection