Surface Coating for High-Energy Cathode

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2020 DOE Vehicle Technologies Program Annual Merit Review

Project ID #: bat364

Overview

Timeline

- **Start data: September 2016**
- **End date: September 2021**
- **Percent complete: 75%**

Barriers

- **Barriers addressed**
  - **Cycle life of NMC811 at high voltages**
  - **The use of Li metal anode for high energy density**

Budget

- **Total project funding: $50M**
  - **DOE share 100%**
- **Funding for FY 2018: $10M**
- **Funding for FY 2019: $10M**

Partners

- **Project lead: University of Washington**
- **Interactions/Collaborations: Pacific Northwest National Laboratory, University of Texas at Austin, Binghamton University**

Relevance

- **Overall Objectives**
  - Develop surface coating for Ni-rich NMC materials to largely improve their interfacial and cycling stability
  - Develop separator coating with Li-ion conductor to improve the Coulombic efficiency and cycling stability of Li metal anode

- **Objectives this period**
  - Demonstrate coating for NMC 811 to achieve 80% capacity retention after at least 200 cycles but with reduced polarization, in coin cells
  - Demonstrate separator coating for capacity retention improvement in Li/NMC811 pouch cells

- **Impact**
  - Coatings for cathode and separator are critical for the Battery500 Consortium team to triple the specific energy (to 500 Wh/kg) relative to today's battery technology and achieve 1,000 charge/discharge cycles

Milestones

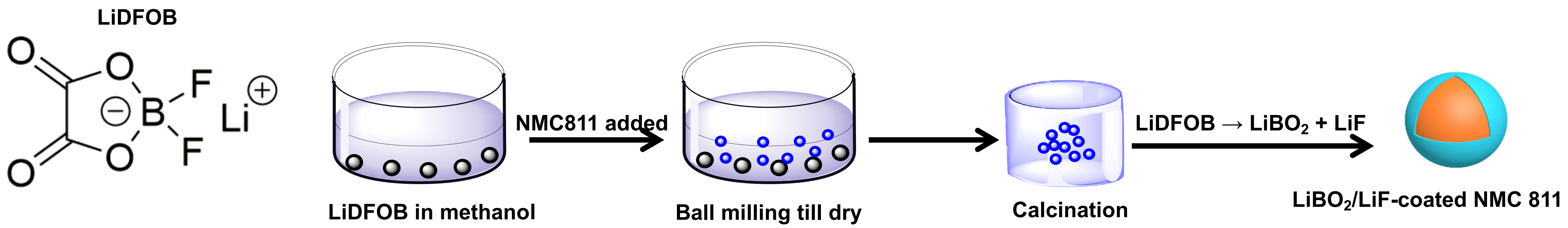
Data	Milestones	Status	Go/no-go
12/31/2019	Select an effective approach for coating NMC cathode materials and improve cathode stability for Battery500.	Complete	
03/31/2020	Evaluate and implement separator coatings in single-layered pouch cells with the PNNL electrolyte.	Complete	
06/30/2020	Investigate and separate electrolyte consumption from Li and cathode reactions.	On track	
09/30/2020	Complete the moving boundary model for lithium-metal batteries.	On track	

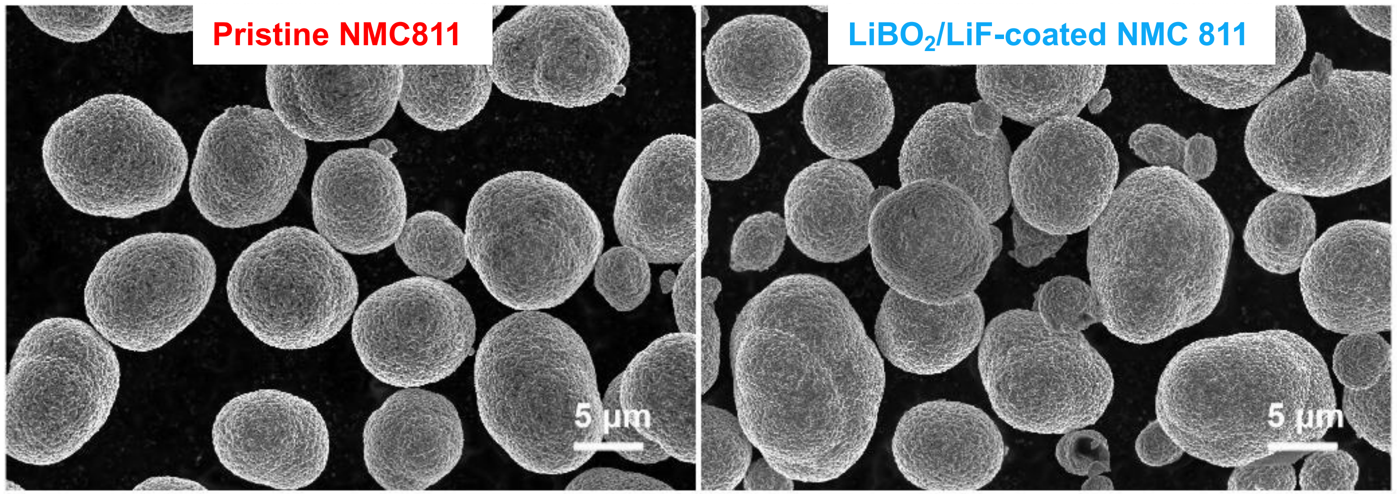
Approach/Strategy

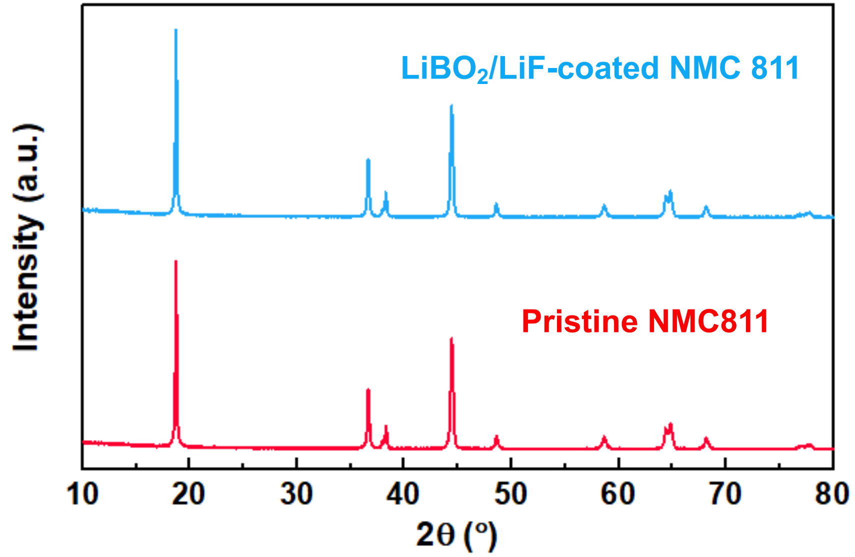
- Utilize a simple wet-chemical method to coat thin-layer (several nanometers) Li-ion conductors on the Ni-rich NMCs to separate direct cathode/electrolyte contact, ensuring good cycling stability and rate capability.
- Surface coating of commercial separators with Li-ion conductors that can mitigate the Li/electrolyte reactions and improve the cycling stability of Li metal anode.
- Utilize a Li metal anode combined with a compatible electrolyte, and a nickel-rich NMC to achieve cell level energy density larger than 350 Wh/kg.

Technical Accomplishments

$LiBO_2$/LiF (1.3 mol%) coating on NMC811



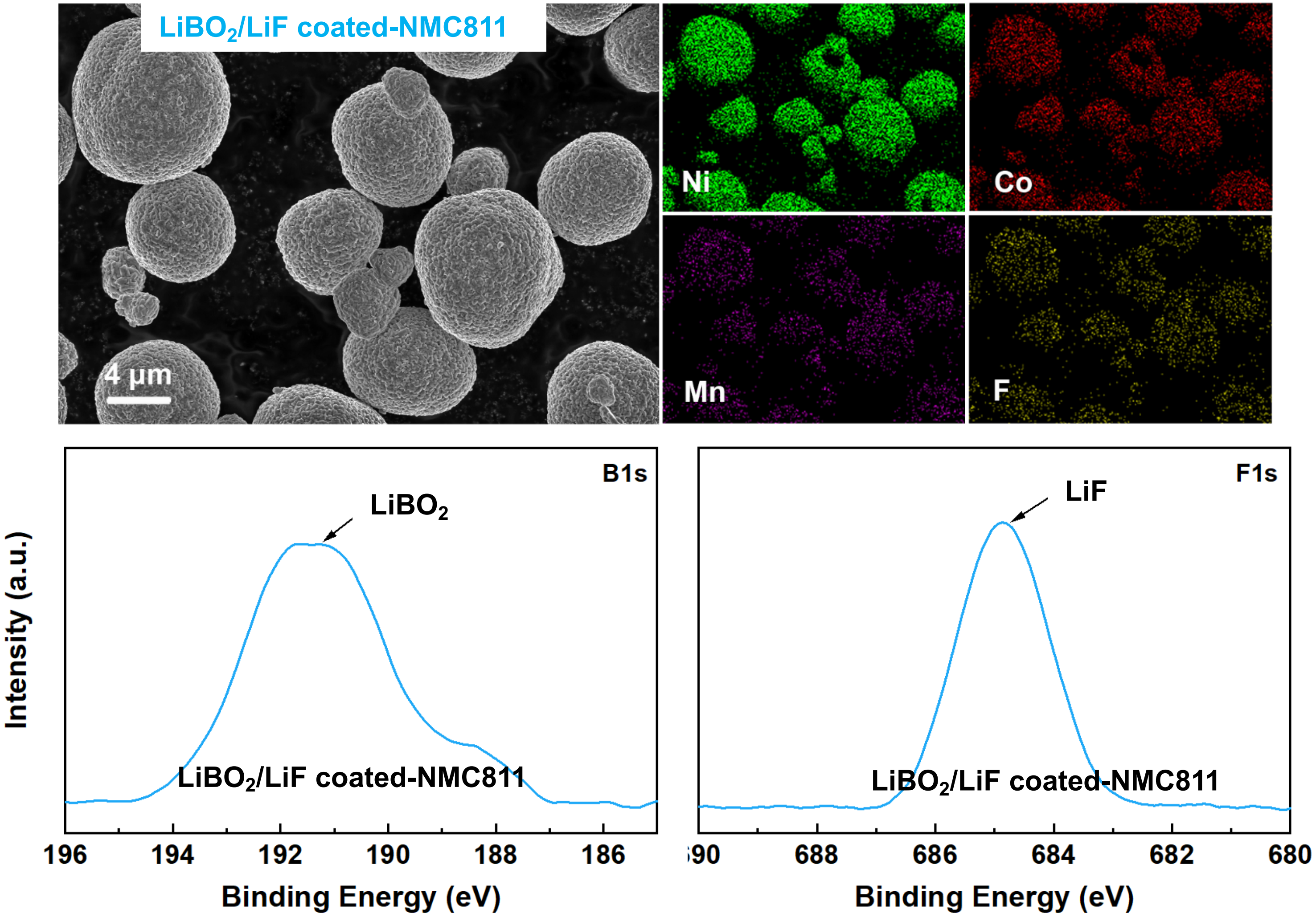




- The $LiBO_2$/LiF-coated NMC811 retain the original morphology and crystal structure.

Technical Accomplishments

Evidence of $LiBO_2$/LiF coating on NMC811



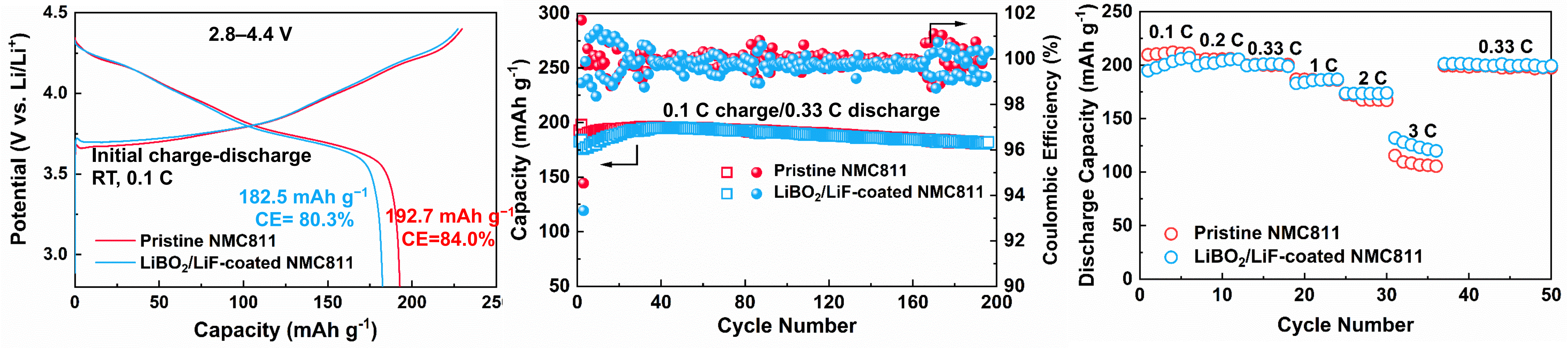
- Fluorine is uniformly distributed on the cathode in the form of Li–F.
- $LiBO_2$ exists on NMC811.

S.H.Garofalini et al., Appl. Surf. Sci., 1994, 81, 331
Daniel Brandell et al., J. Mater. Chem. A, 2014, 2, 7256

Technical Accomplishments

Electrochemical performance of $LiBO_2$/LiF-coated NMC811

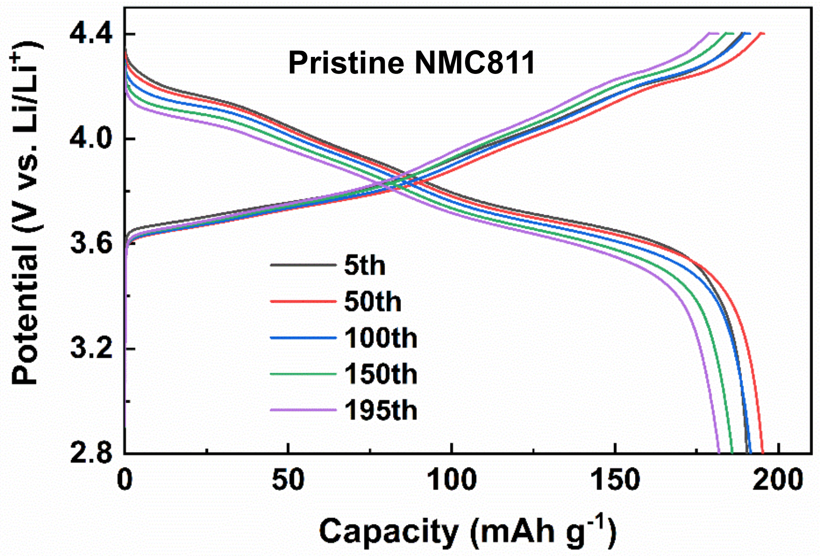
~4 mAh cm^{-2} | 1.0 M $LiPF_6$ in EC-EMC (3:7 wt.%) + 2.0 wt% VC

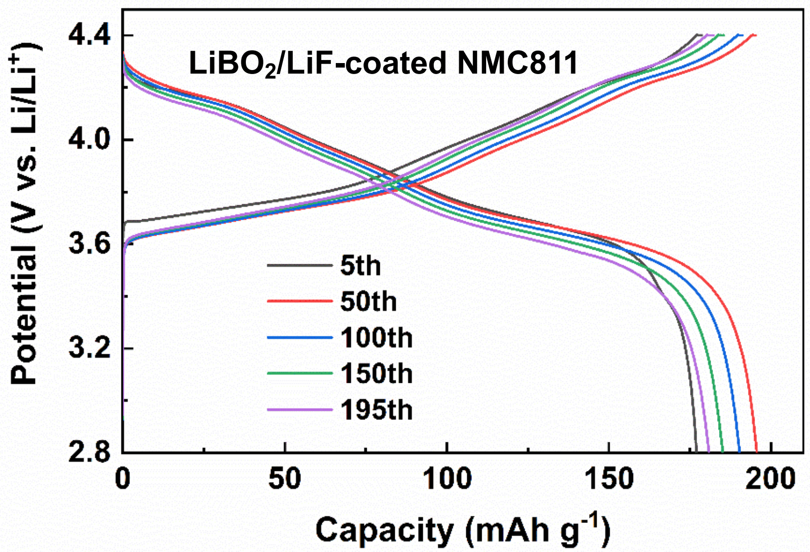


- $LiBO_2$/LiF-coated NMC811 has lower initial discharge capacity and initial Coulombic efficiency, because of the low electronic conductivity and electrochemical inactivity of $LiBO_2$/LiF.
- $LiBO_2$/LiF-coated NMC811 shows longer activation process to reach the highest capacity (195 mAh g^{-1}), which is similar with that of pristine NMC811.
- $LiBO_2$/LiF-coated NMC811 shows higher rate capability at 3 C.

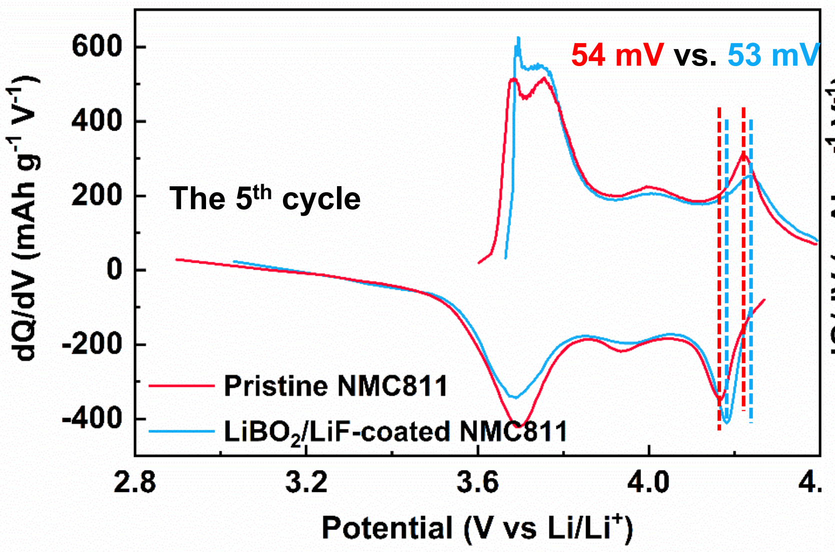
Technical Accomplishments

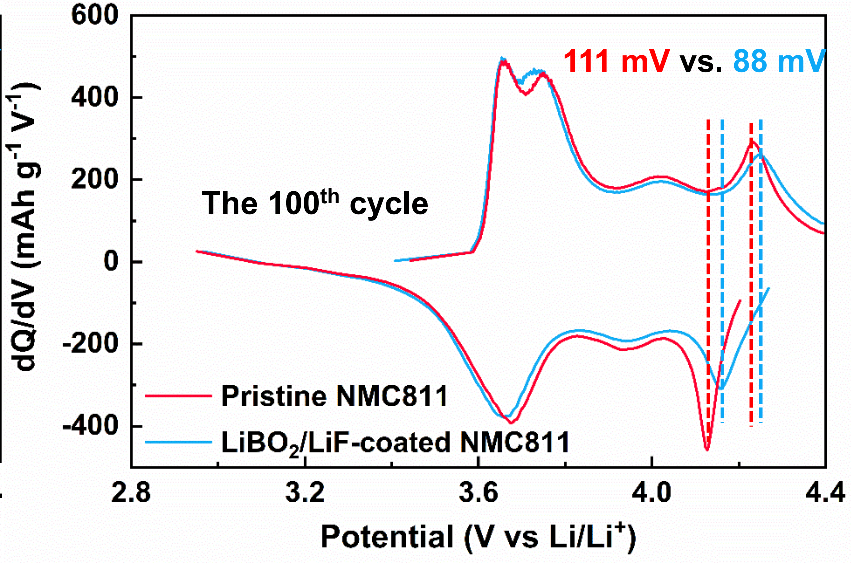
Polarization comparison

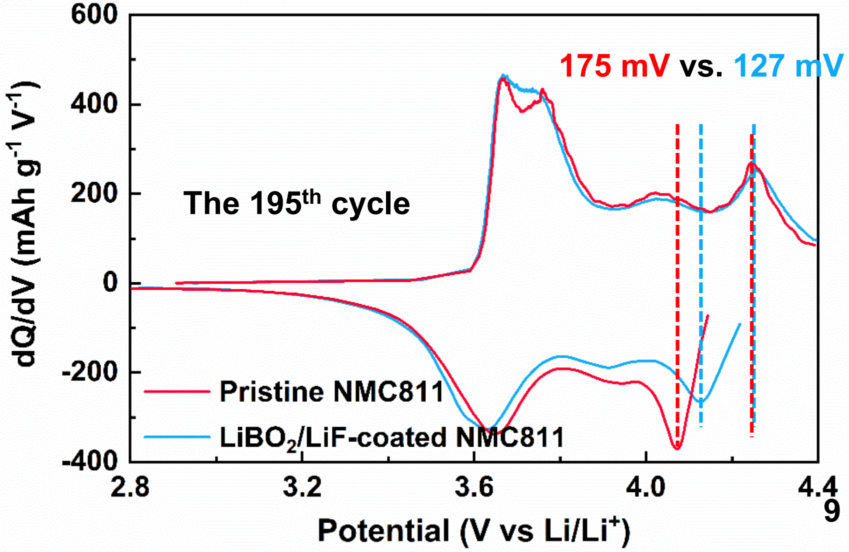




- $LiBO_2$/LiF coating on NMC811 helps to reduce polarization increase.





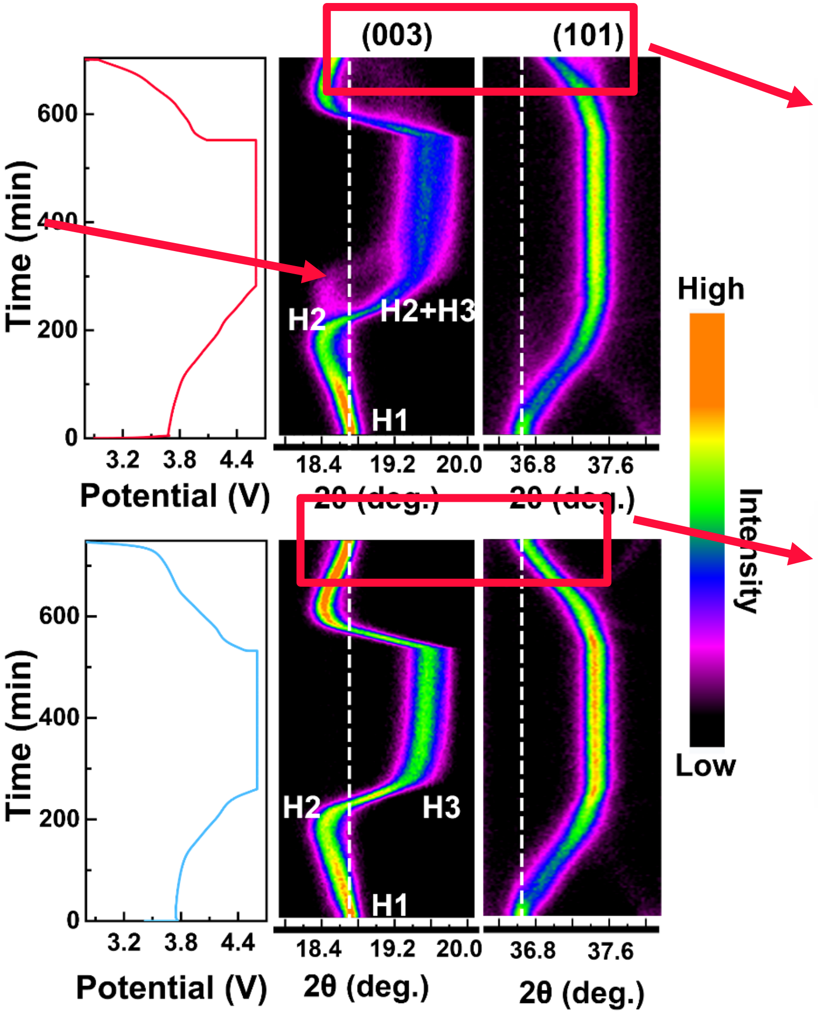


Technical Accomplishments

In-situ X-ray diffraction data

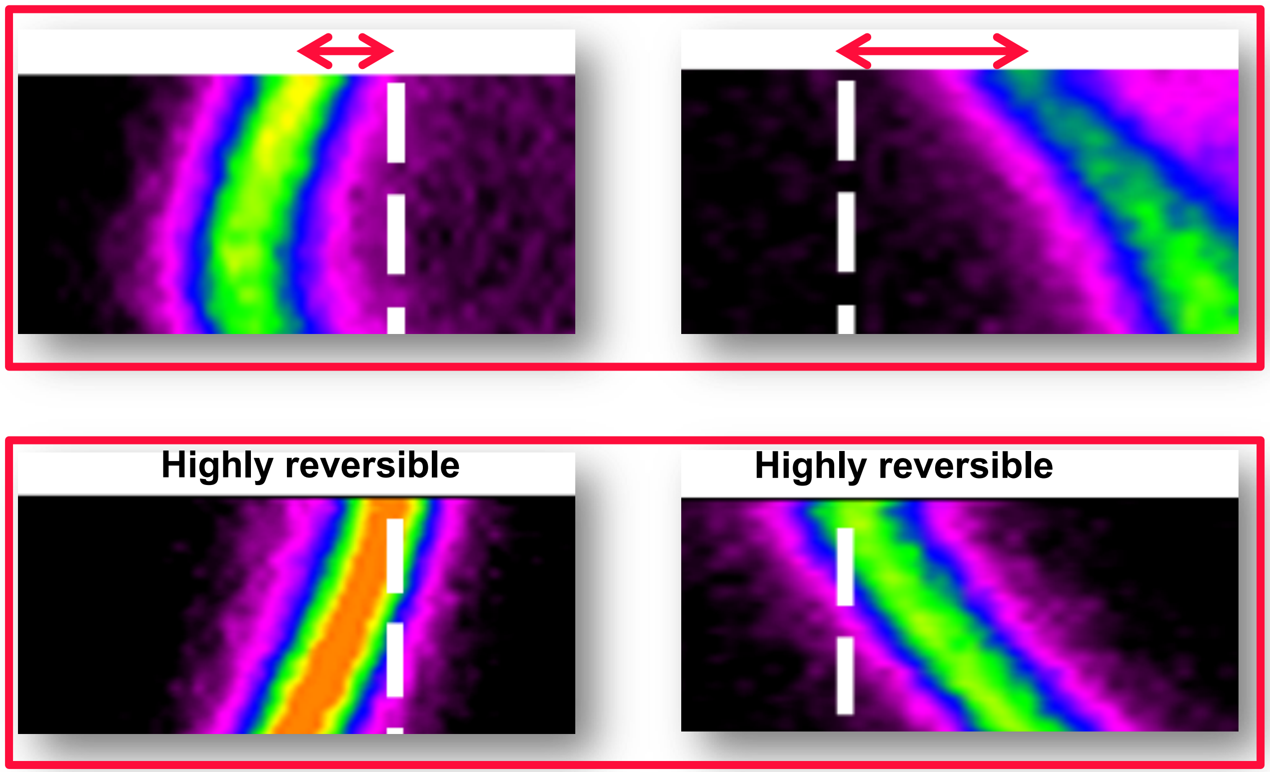
Undesired structural evolution

Pristine NMC811



$LiBO_2$/LiF-coated NMC811

Inferior reversibility of structural change

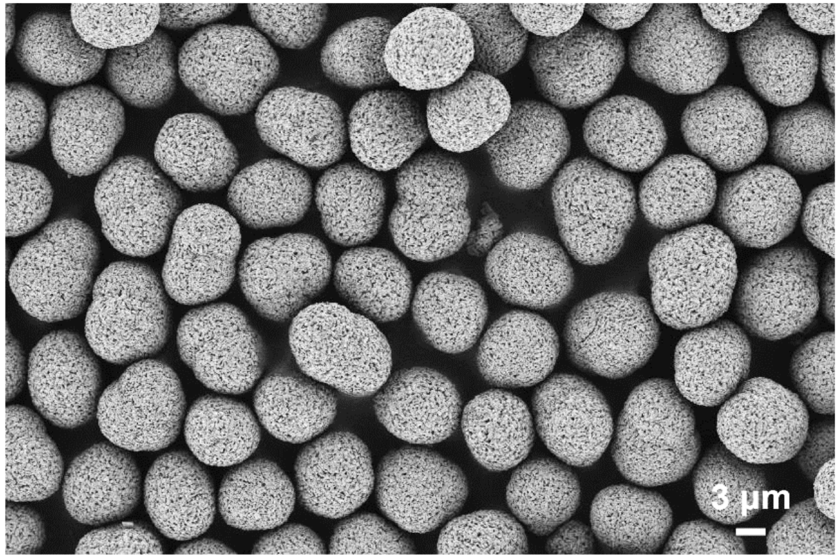


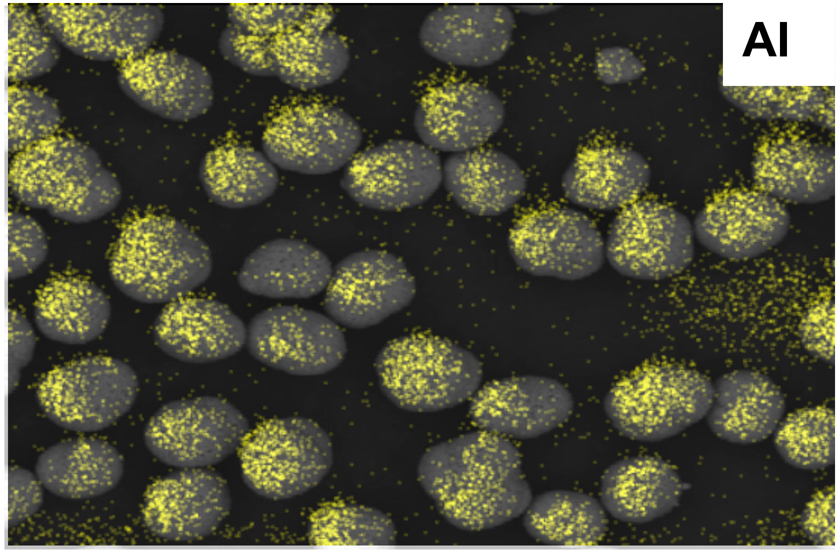
- $LiBO_2$/LiF coating can stabilize the crystal structures and suppress the phase transition even during high voltage cycle.

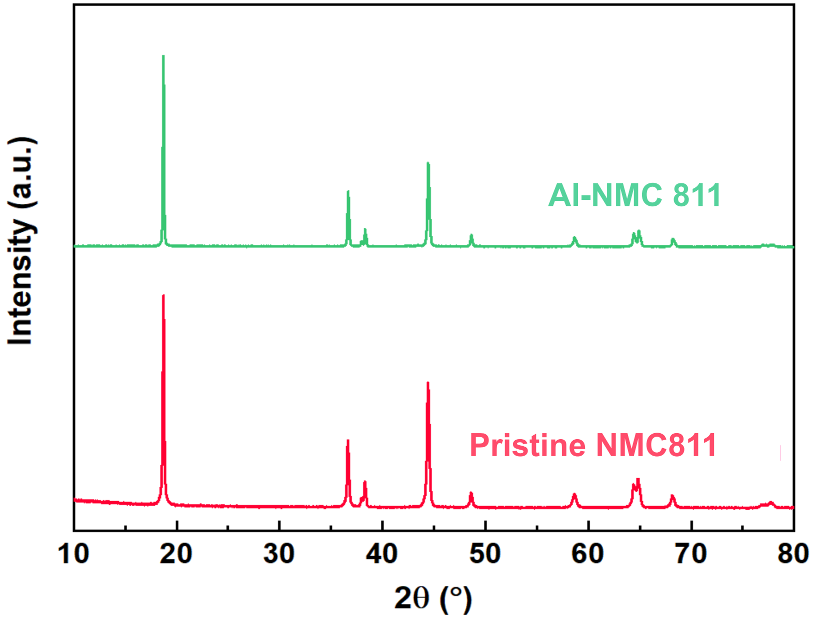
Technical Accomplishments

Evidence of Al doping (1 mol%) in NMC811

Al-NMC811 prepared by coprecipitation method





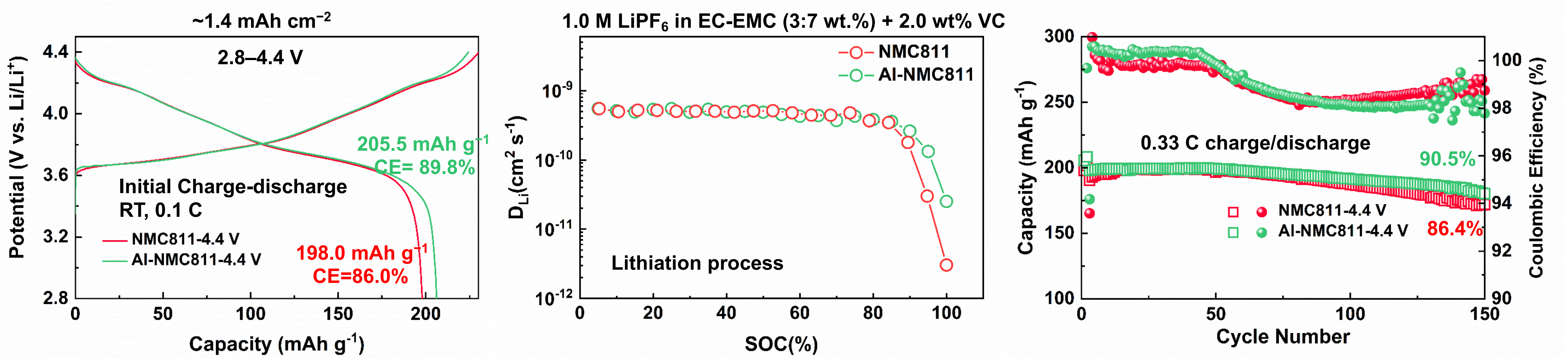


- The Al-doped NMC811 displays secondary spherical morphology with good crystallinity.
- Aluminum is uniformly distributed in the cathode.

Materials made by Y-K Sun's group at Hangyang Univ.

Technical Accomplishments

Electrochemical performance of Al-doped NMC811



- Al-NMC811 delivers higher initial capacity and Coulombic efficiency, which could be ascribed to the improved Li^+ kinetics.
- Al-NMC811 shows better cycling performance because of the enhanced bulk structural reversibility.

X. Xu et al., ACS Sustainable Chem. Eng. 2018, 6, 5653
A. Manthiram et al., Chem. Mater. 2018, 30, 3101
M. S. Whittingham et al., ACS Energy Lett. 2019, 4, 1902

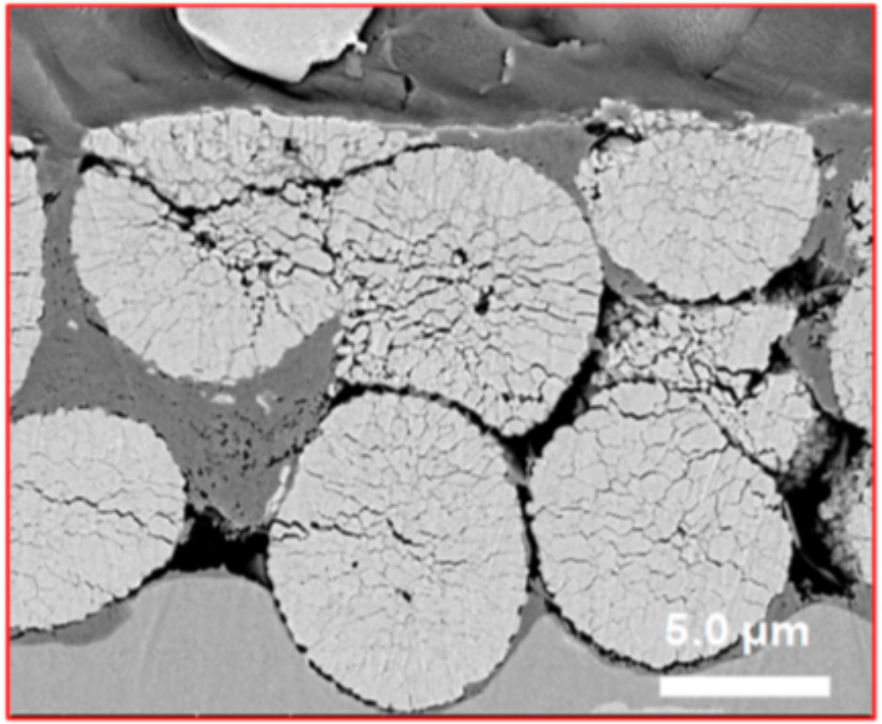
Technical Accomplishments

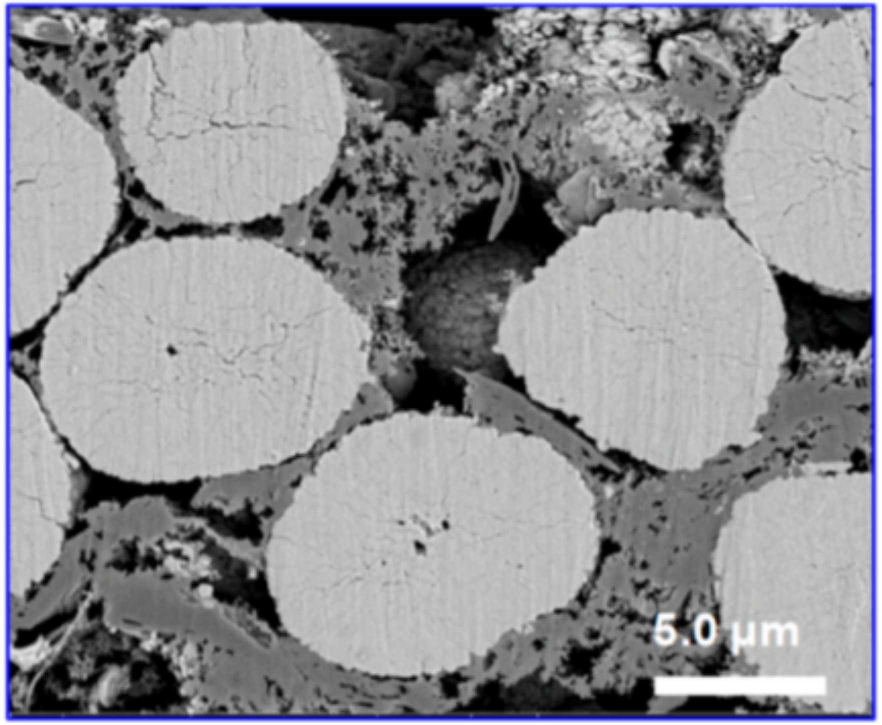
The Al doping effect - mechanical

Ni-Rich Cathode

Al-doped Ni-Rich Cathode

After 1000 cycles



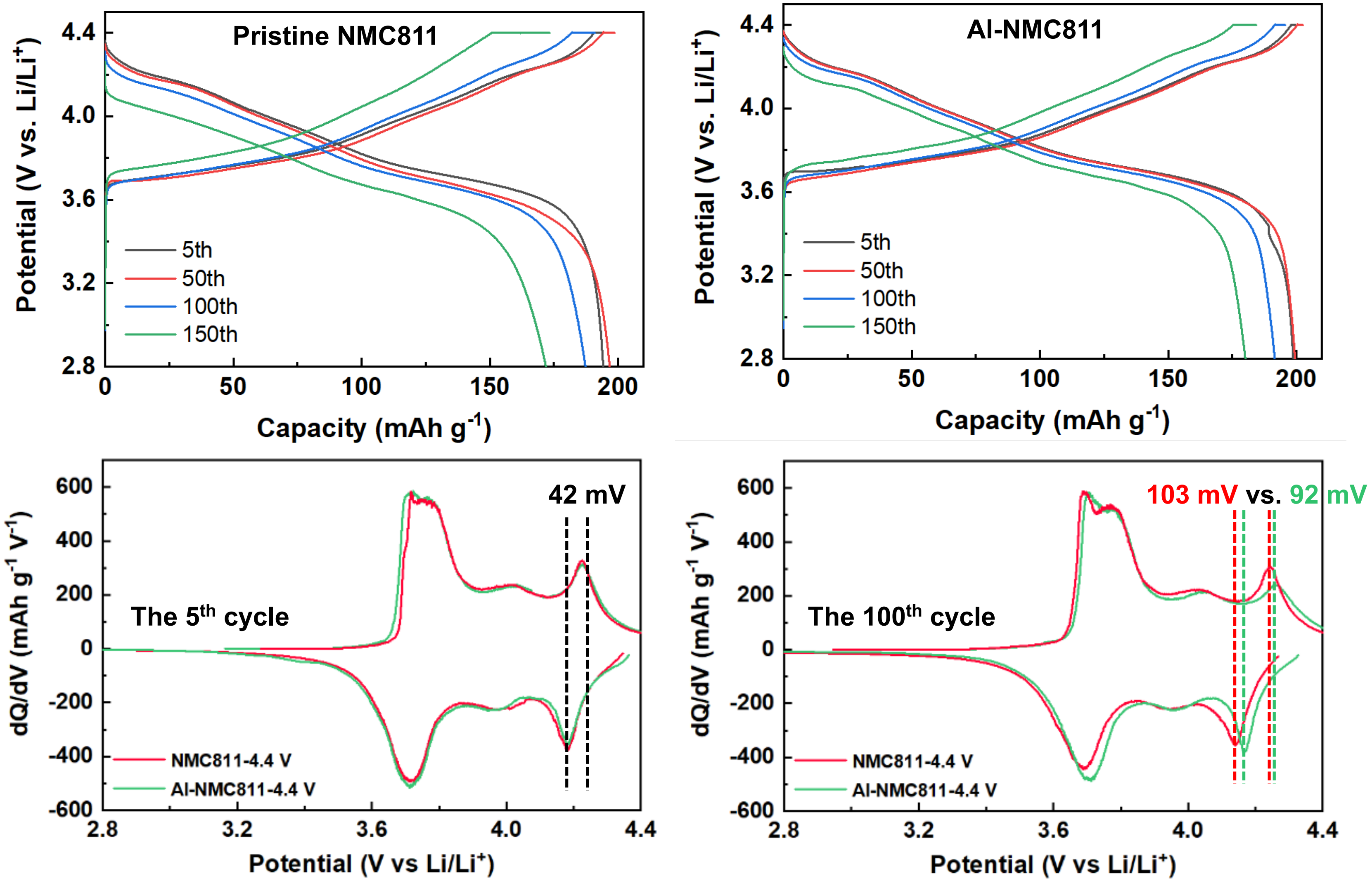


- Al doping enhances intrinsic mechanical strength of NMC and reduces its volume change during cycling, hence suppresses the microcrack nucleation and propagation, which is the key to ensure the long-term cycling stability.

Y.-K. Sun et al., ACS Energy Lett. 2019, 4, 576−582

Technical Accomplishments

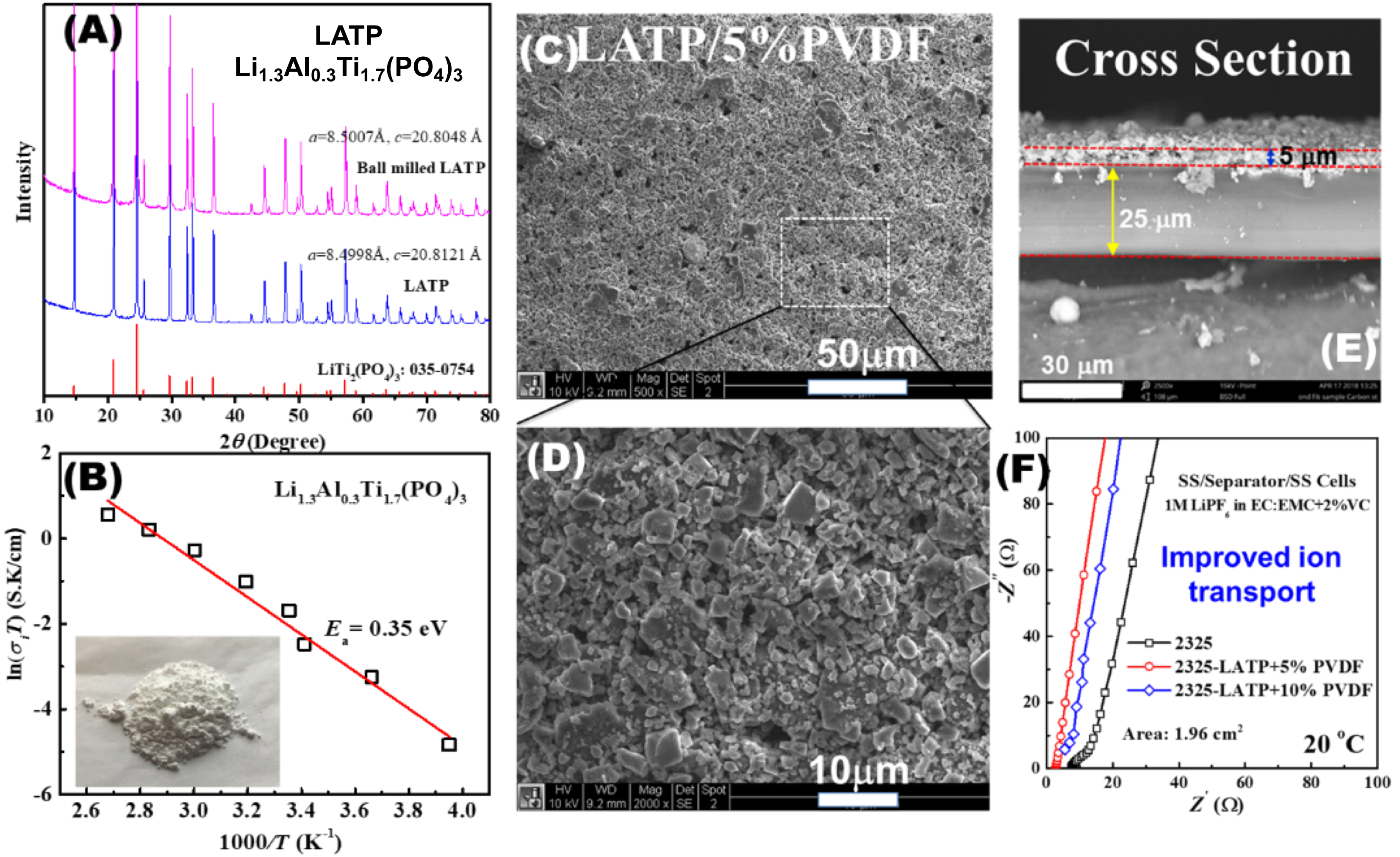
Polarization comparison



- Al doping in NMC811 helps to reduce polarization increase.

Technical Accomplishments

Separator Coating with LATP

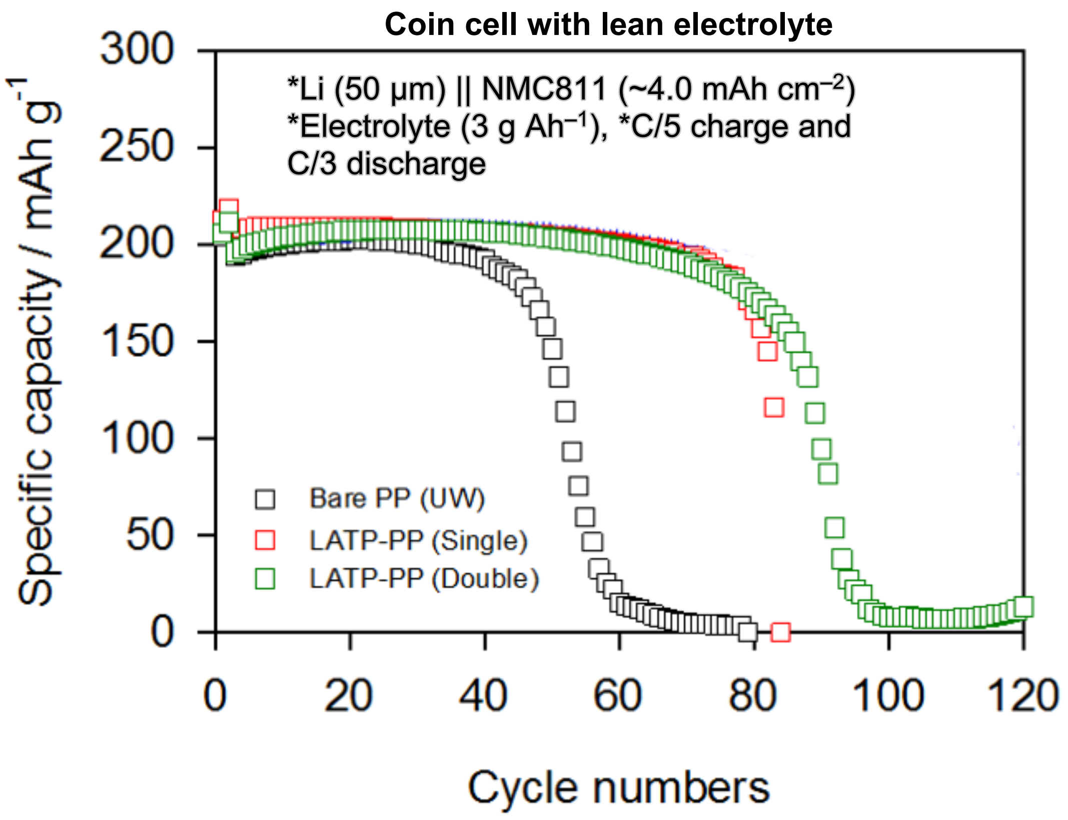


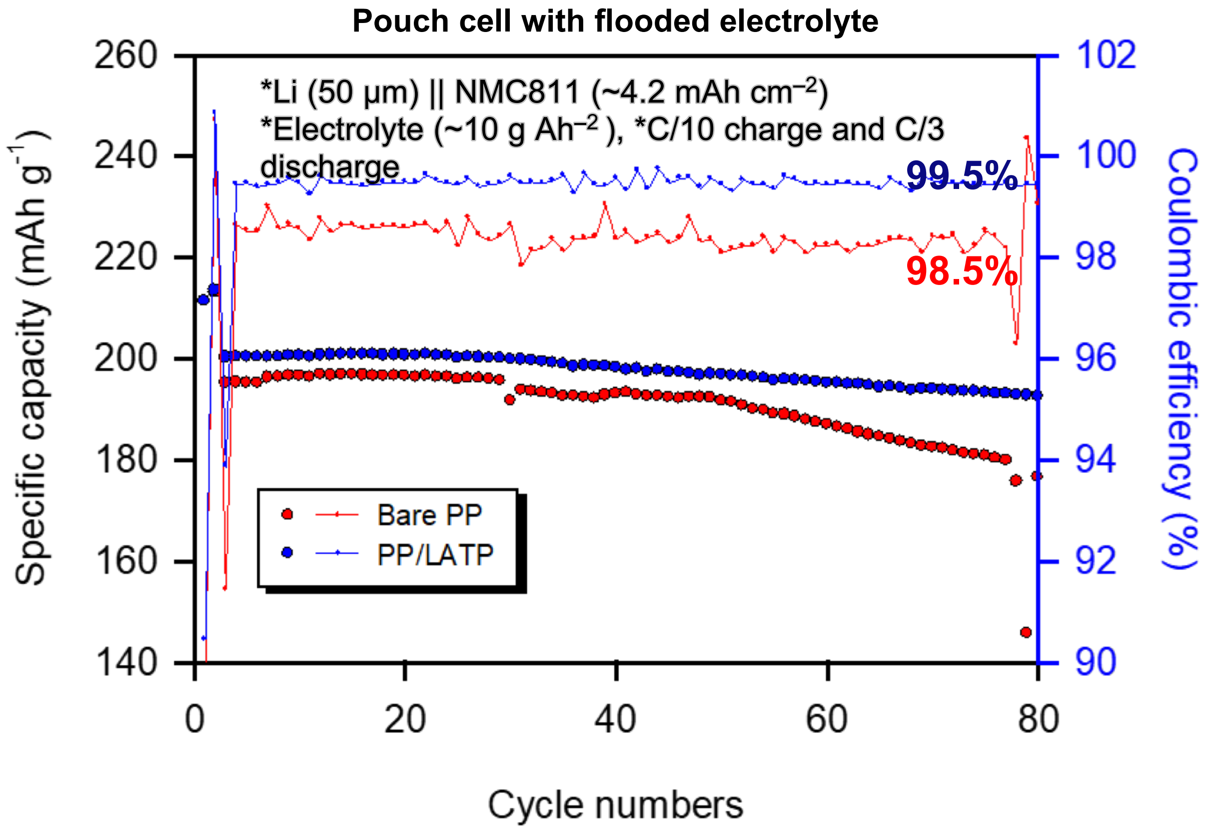
- Improve electrolyte wettability
- Reduce/eliminate Li dendrite formation
- Improve cycle stability

Patent Application filed on June 19, 2019

Technical Accomplishments

Coin and pouch cell Data





- The coin cell using LATP-coated PP separator shows better cycling performance than that of using bare PP.
- For the pouch cell, it shows a higher Coulombic efficiency and a higher capacity retention when using LATP-coated PP separator.

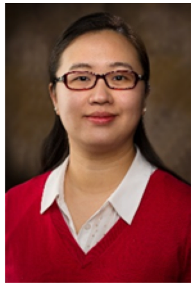
In collaboration with PNNL

Responses to Previous Year Reviewers' Comments

- The project did not present the results in last year's AMR

Partners/Collaborators

- PNNL: Separator coating and solid electrolyte modification in stabilizing Li metal anode



- UT Austin and Binghamton University: Ni-rich NMC synthesis and characterization, in-situ XRD

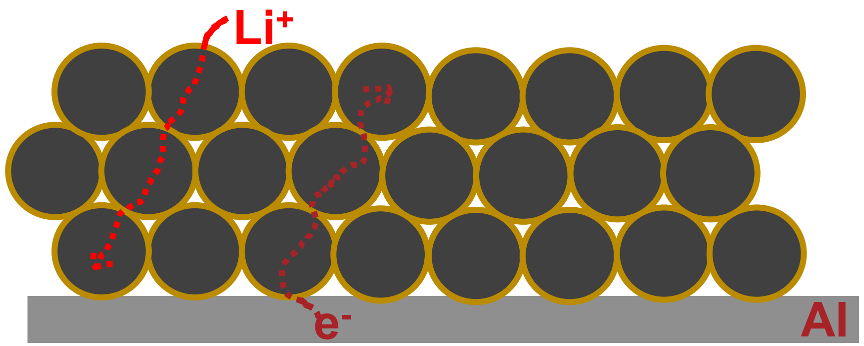
Remaining Challenges and Barriers

- Increasing structural and interfacial stability of Ni-rich NMCs while operating over at high voltages.
- ALD coating of high-voltage stable, complex Li-ion conductors, such as $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP).
- Optimal doping composition of Ni-rich NMCs to mitigate micro-crack formation and electrolyte consumption
- Controlling separator coating thickness less than 1 μm and improve its mechanical integrity with the separator
- Studying the electrolyte-coating-Li interactions and achieving dendrite free Li deposition with more than 99.9% Coulombic efficiency by modifying the separator coating and electrolyte

Proposed Future Research

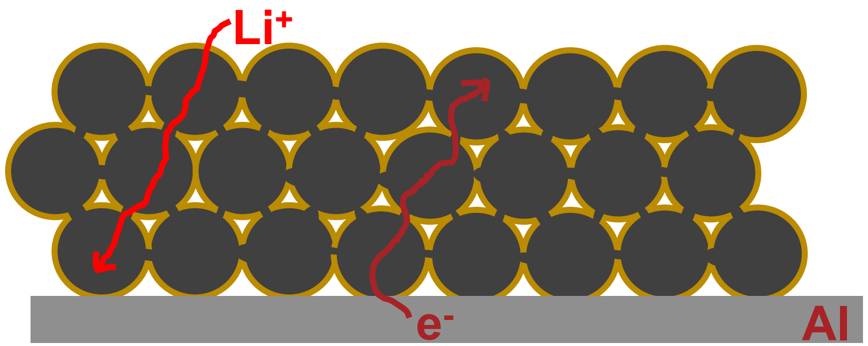
ALD coating on NMC811 electrodes

Coating on powder



Coating layer must be electronic and ionic conductor.

Coating on electrode

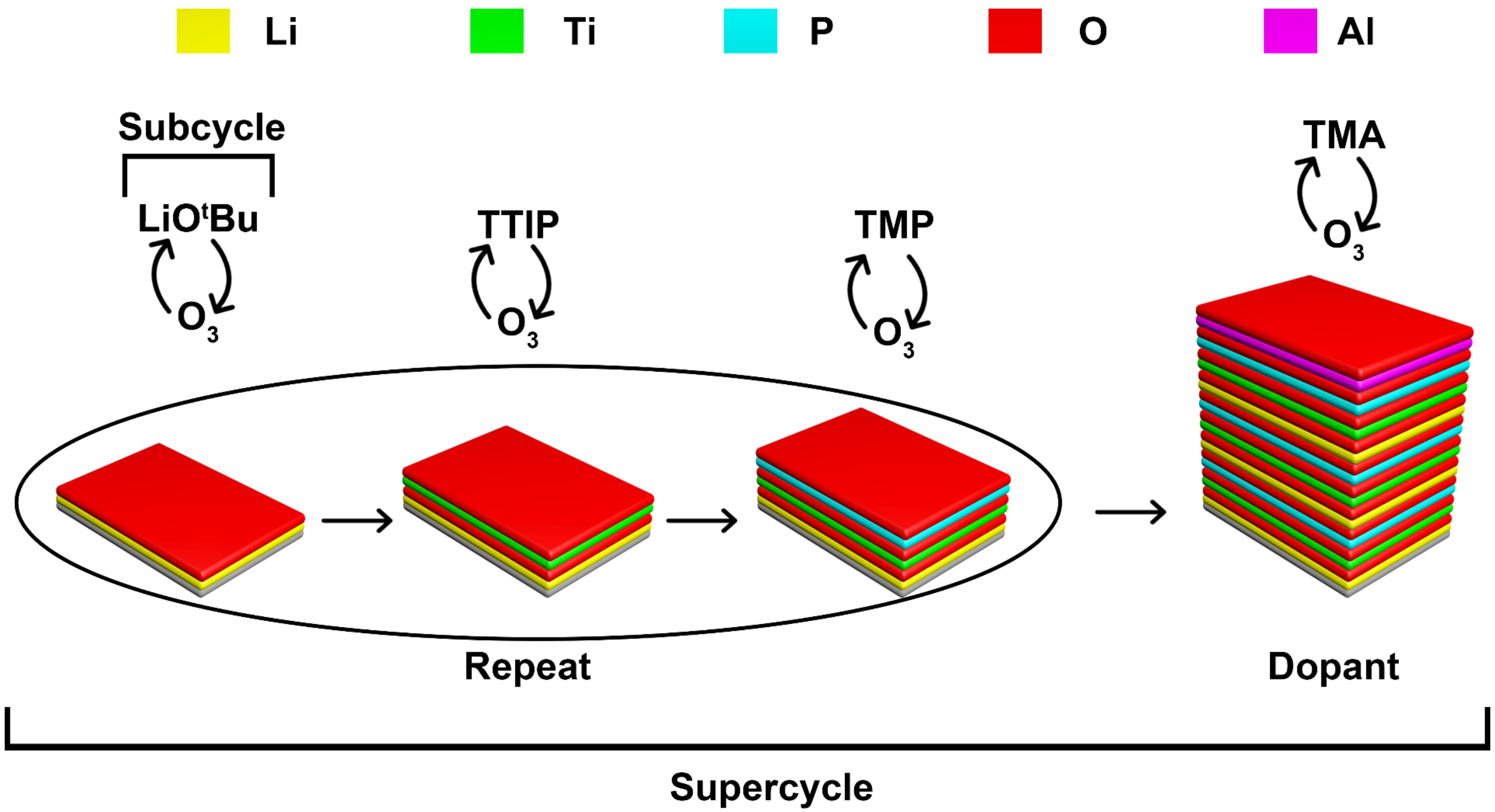


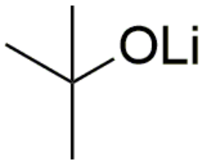
Coating layer could be solely ionic conductor.

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

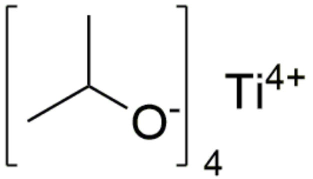
Proposed Future Research

ALD coating on NMC811 electrodes

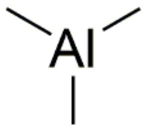




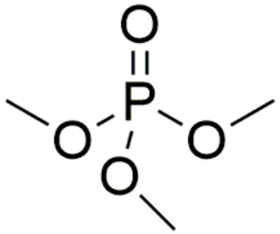
LiO^{t}Bu



TTIP



TMA



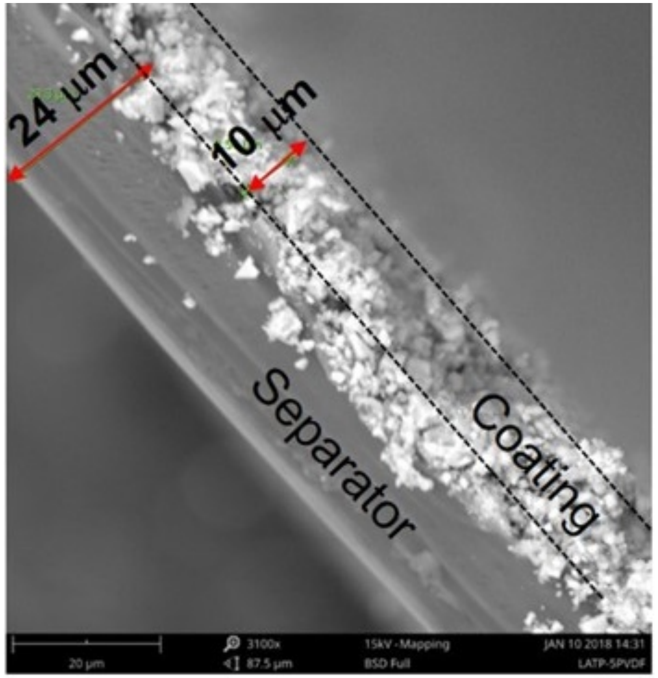
TMP

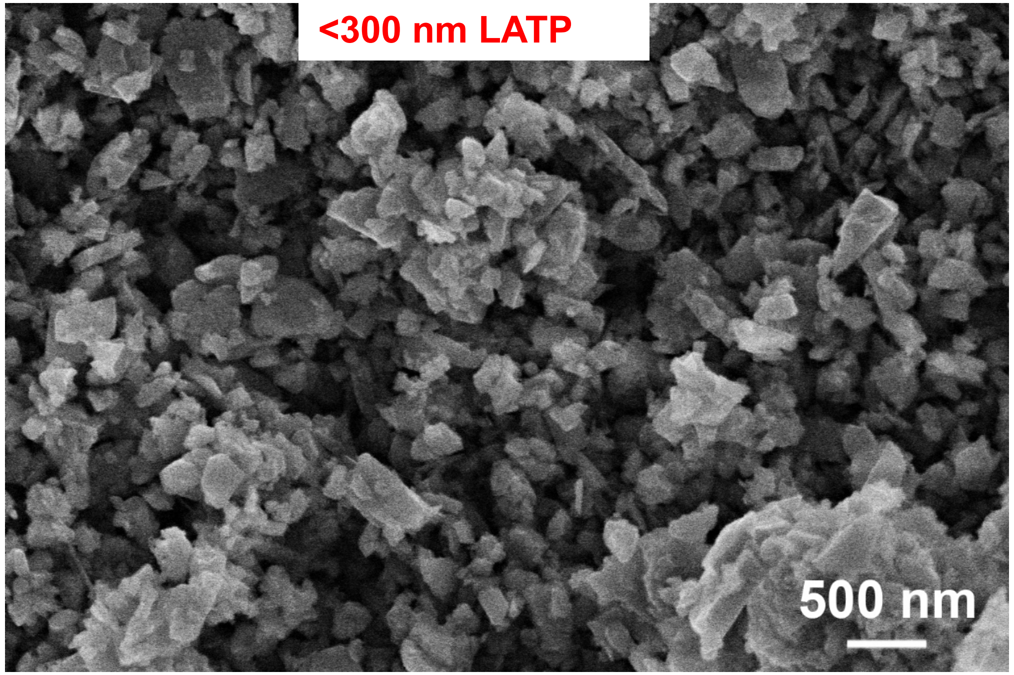
- $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP, ~10^{-3} S cm^{-1}) coating process by ALD

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

Proposed Future Research

Optimize the separator coating





- Reducing the thickness of separator coating by using nanosized LATP and other coating methods, e.g., spray coating.

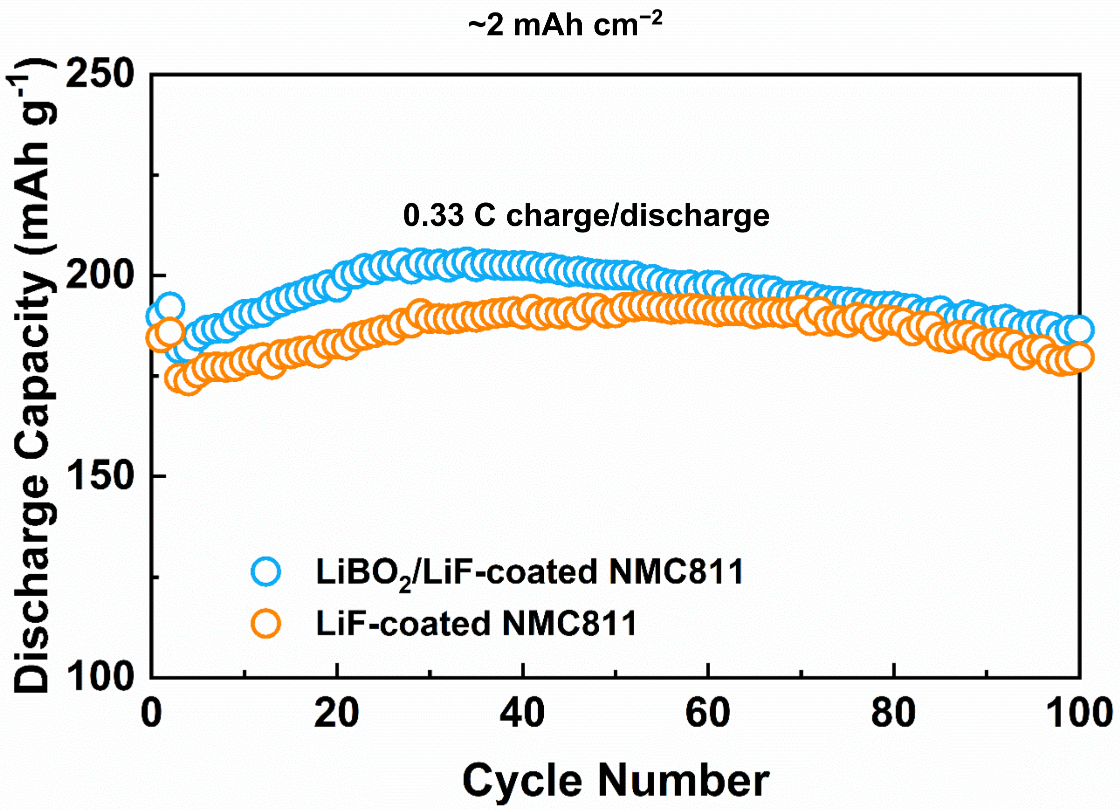
Any proposed future work is subject to change based on funding levels.

Summary

- $LiBO_2$/LiF coating on NMC811 shows similar discharge capacity but lower polarization with cycling, due to the high ionic conductivity of $LiBO_2$ and the superior anodic stability of LiF.
- Al doping in NMC811 exhibits excellent electrochemical performance, which could be attributed to the better kinetic property and structural stability.
- Benefit of LATP solid electrolyte coating on battery separator demonstrated in Li/811 pouch cells.

Technical Back-Up Slides

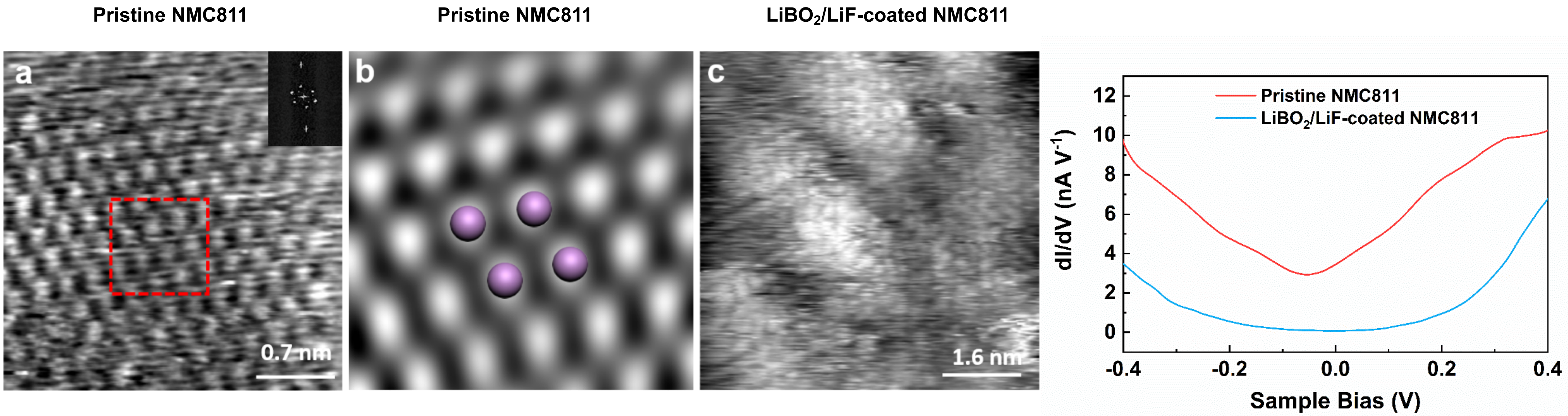
$LiBO_2$/LiF vs. LiF coating



- $LiBO_2$/LiF-coated NMC811 shows higher discharge capacities that that of LiF-coated NMC811, which could be due to the higher ionic conductivity of $LiBO_2$/LiF.

Technical Back-Up Slides

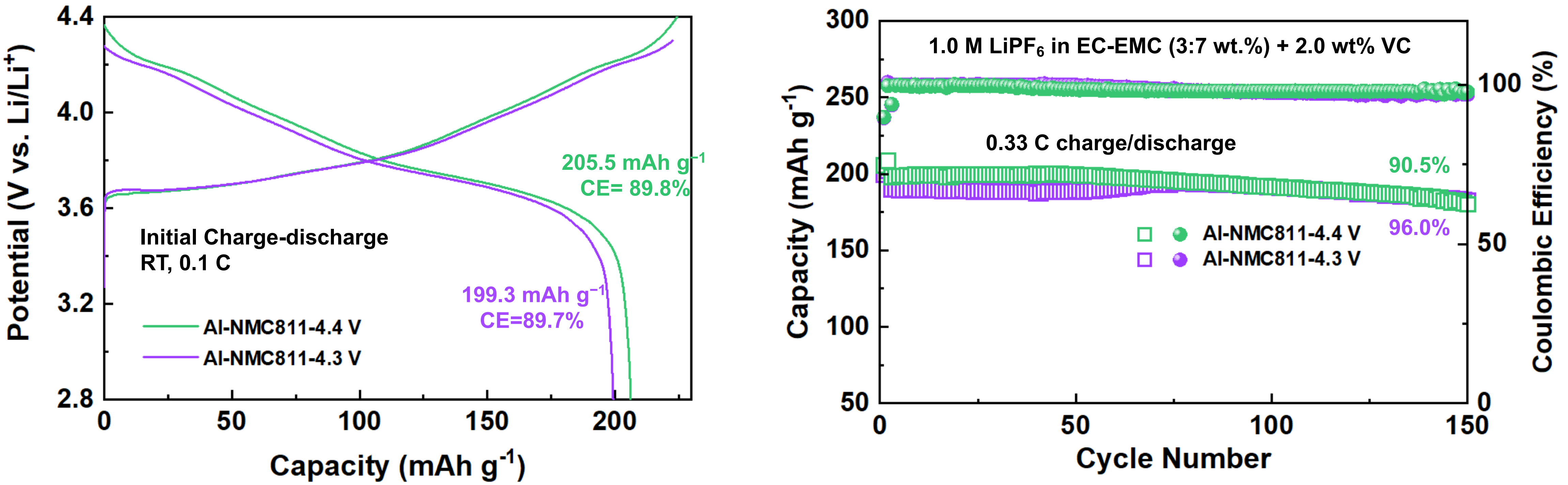
Evidence of successful surface coating



- STM images shows a coating layer for $LiBO_2$/LiF-coated NMC811.
- The $LiBO_2$/LiF-coated NMC811 exhibits larger bandgap because of its poor electronic conductivity, which is beneficial to reduce electrolyte decomposing on the cathode.

Technical Back-Up Slides

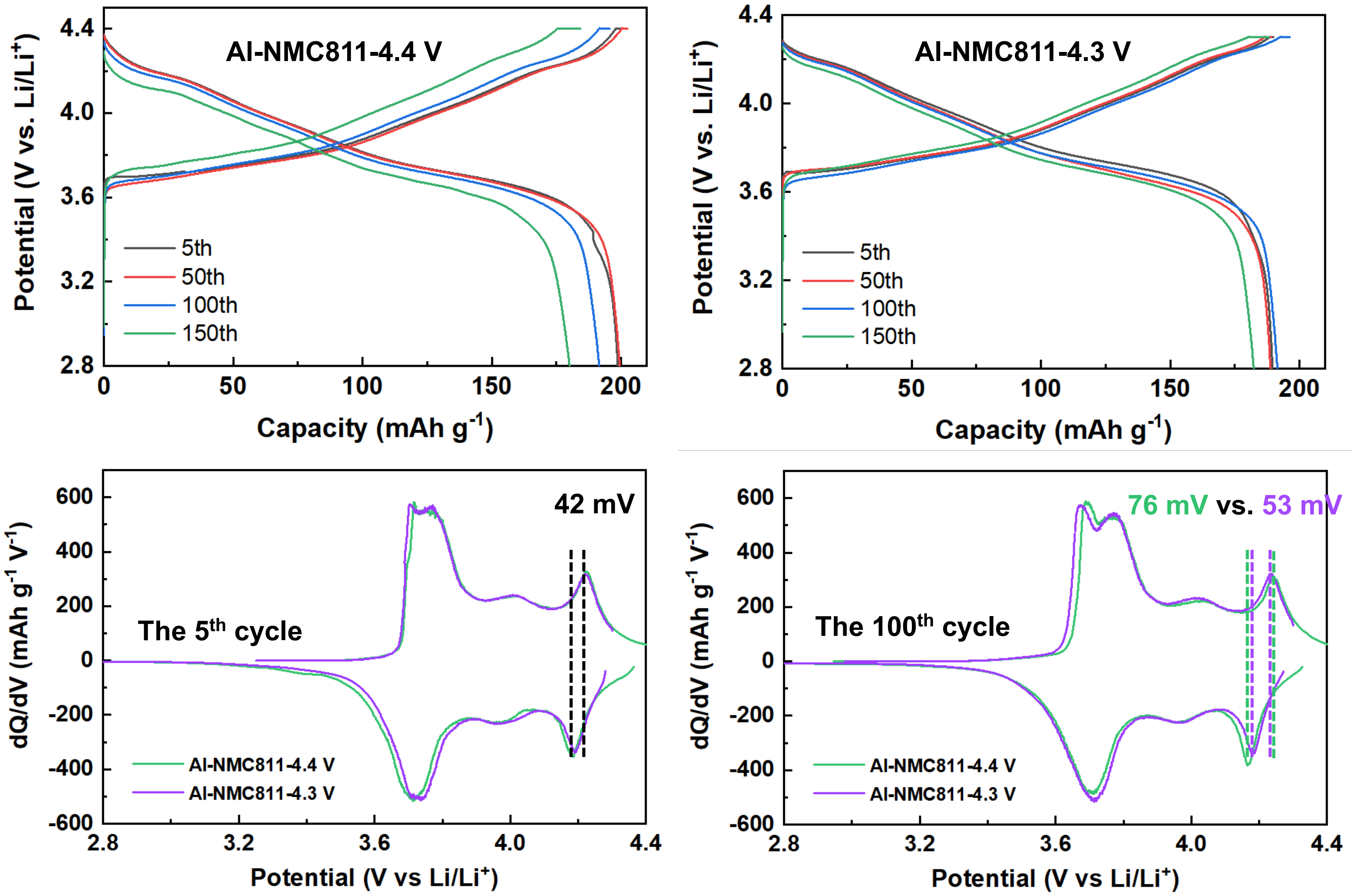
Charge to 4.3 V vs. 4.4 V



- Al-NMC811 Charged to 4.3 V has lower initial capacity but similar Coulombic efficiency.
- Al-NMC811 Charged to 4.3 V displays better cycle owing to the less volume change.
- Al-NMC811 charged to 4.3 V shows lower accumulate capacity for 150 cycles (28.0 Ah g^{-1} vs. 28.7 Ah g^{-1}).

Technical Back-Up Slides

Charge to 4.3 V vs. 4.4 V



- Al-NMC811 charged to 4.3 V presents less polarization with cycling.
- Higher cut-off voltage induces larger polarization, coating is more necessary for that charge to high potentials.

Technical Back-Up Slides

ALD/MLD system