Coatings for Cathode and Separator

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2018 DOE Vehicle Technologies Program Annual Merit Review

Project ID #: bat364

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Overview

Timeline

- Start data: September 2016
- End date: September 2021
- Percent complete: 40%

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 2017: $10M
- Funding for FY 2018: $10M

Partners

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

Relevance

- **Overall Objectives**
  - Develop mixed conductor surface coating for Ni-rich NMC materials to largely improve their interfacial and cycling stability, while maintaining good rate capability
  - 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 300 cycles
  - Demonstrate separator coating to achieve 80% capacity retention after 100 cycles in high loading Li/NMC811 cells (4 mAh/cm^2)

- **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

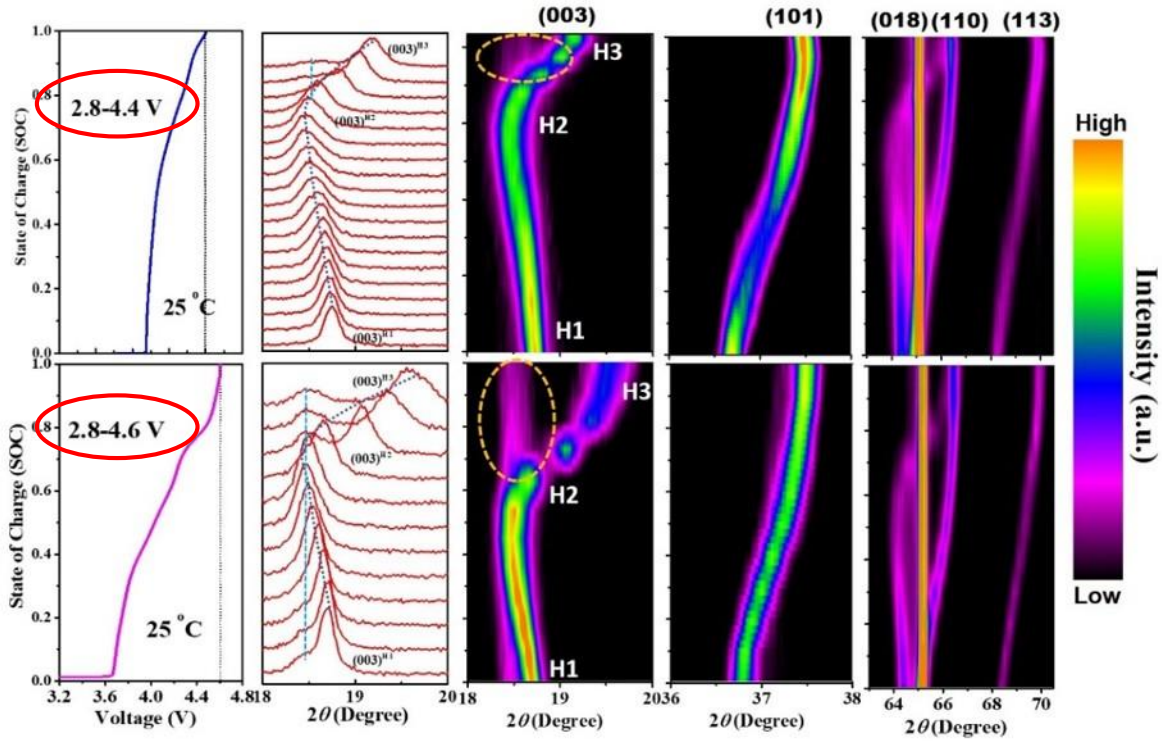
Data	Milestones	Status
March 2018	Develop coating for NMC811 materials, which can retain 80% of original capacity (~200 mAh/g between 2.8-4.4 V) after 200 cycles in coin cells	Complete
September 2018	Develop coating for NMC811 materials, which can retain 80% of original capacity (~230 mAh/g at 2.8-4.6 V) after 200 cycles in coin cells;	Complete
September 2018	Develop separator coating to achieve 80% capacity retention after 100 cycles in high loading Li/NMC811 cells (4 mAh/cm^2)	Complete
September 2019	Demonstrate coating for NMC811 materials, which can retain 80% of original capacity (~230 mAh/g at 2.8-4.6 V) after 200 cycles in coin cells with > 2 mAh/cm2 loading	On track
September 2019	Demonstrate separator coating to achieve 80% capacity retention after 200 cycles in high loading Li/NMC811 cells (4 mAh/cm^2)	On track

Approach/Strategy

- Utilize atomic layer deposition to uniformly coat thin-layer (several nanometers) Li-ion conductors or mixed 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 Accomplishment

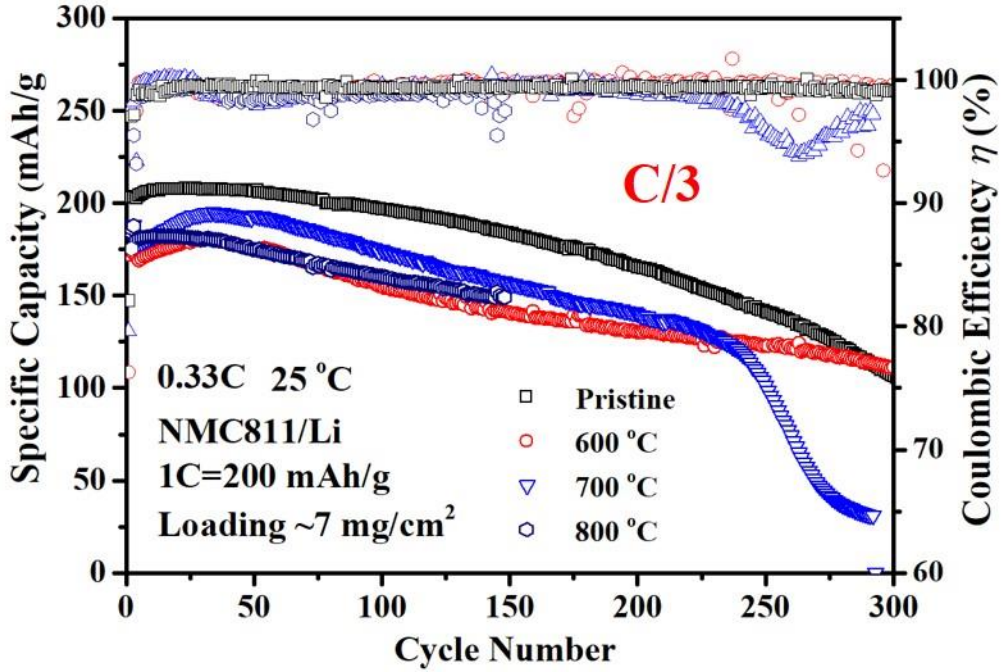
In Situ X-Ray Diffraction



- For 811, at high voltages (> 4.3 V): structural instability could lead to capacity fading and cell failure.
- Similar results in $LiNi_{0.94}Co_{0.06}O_2$, collaboration with UT Manthiram group, manuscript submitted (benefit of Al-doping)

Technical Accomplishment

Sol-Gel Coating $LiAlO_2$ on NMC811

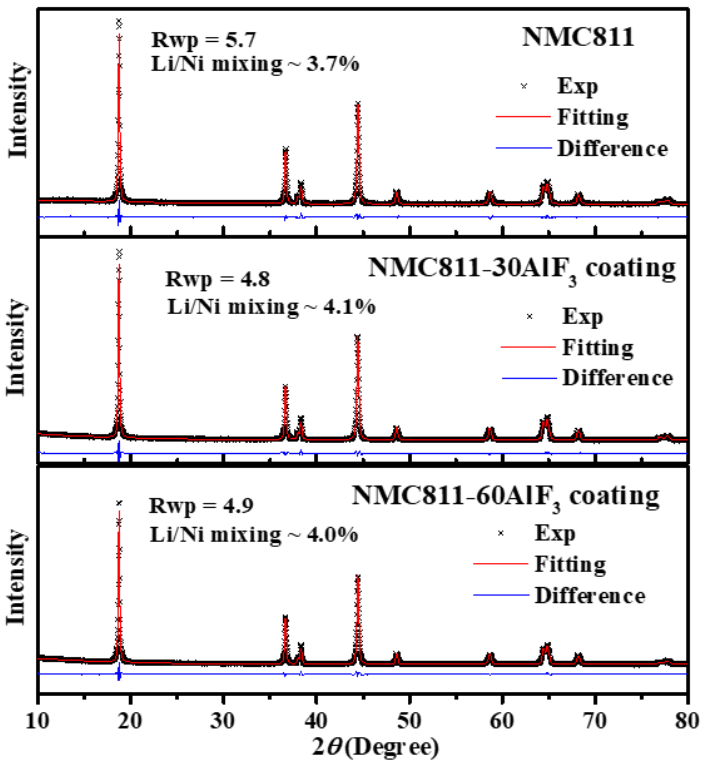


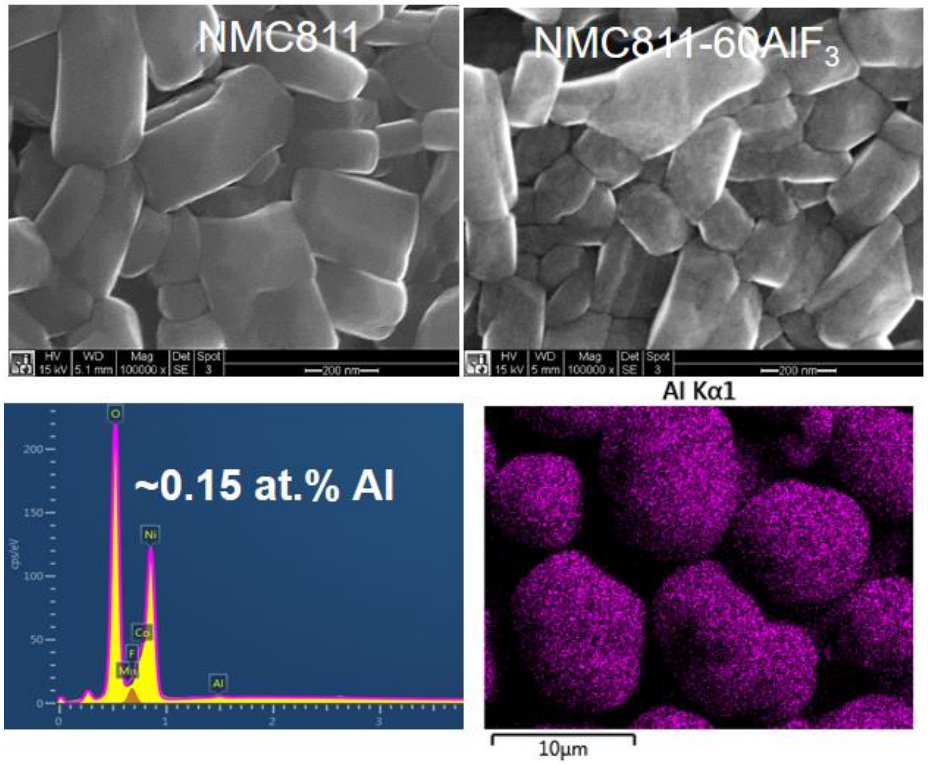
Li||NMC811, 1M $LiPF_6$ in EC:EMC (3:7 wt./wt.)+2 wt.% VC

- Coating rapidly increases cell polarization – capacity fading
- **High surface reactivity of NMC811 -** with moisture and CO_2, form inert hydroxides and carbonates – increase cell impedance and fast capacity fade **-** ***Roland Jung et al. JES, 165 A132 (2018)***
- Sol-gel coating doesn't improve the cycling stability of NMC811

Technical Accomplishment

ALD coating AlF_3 on NMC811

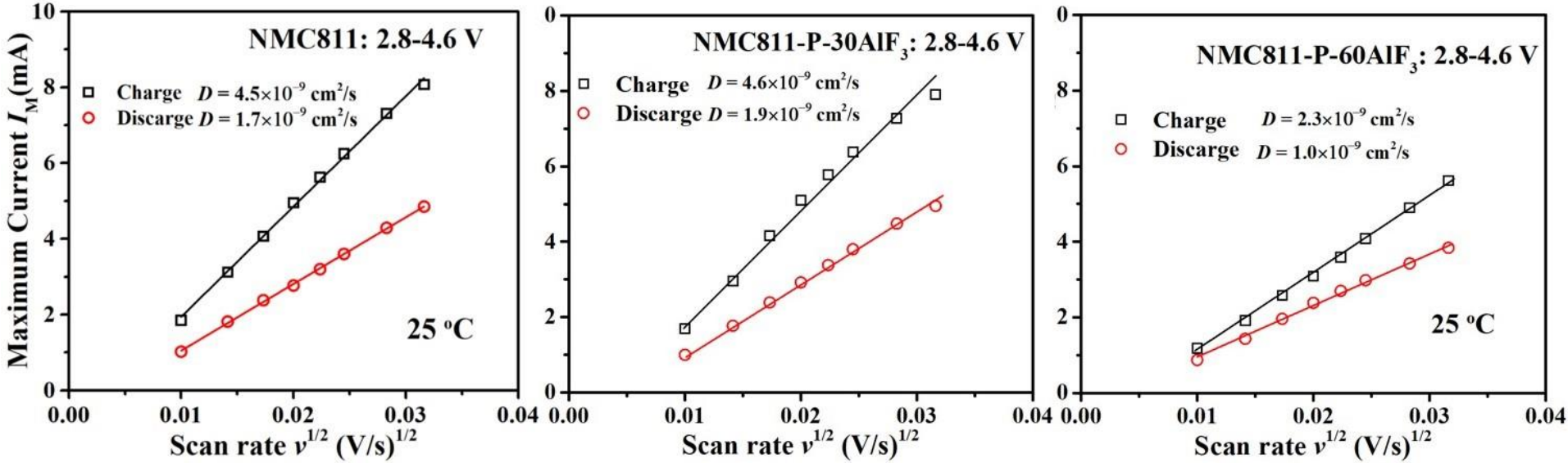




- ❑ **Phase & structure maintained**
- ❑ **Uniform AlF_3 coating**

Technical Accomplishment

ALD coating AlF_3 on NMC811



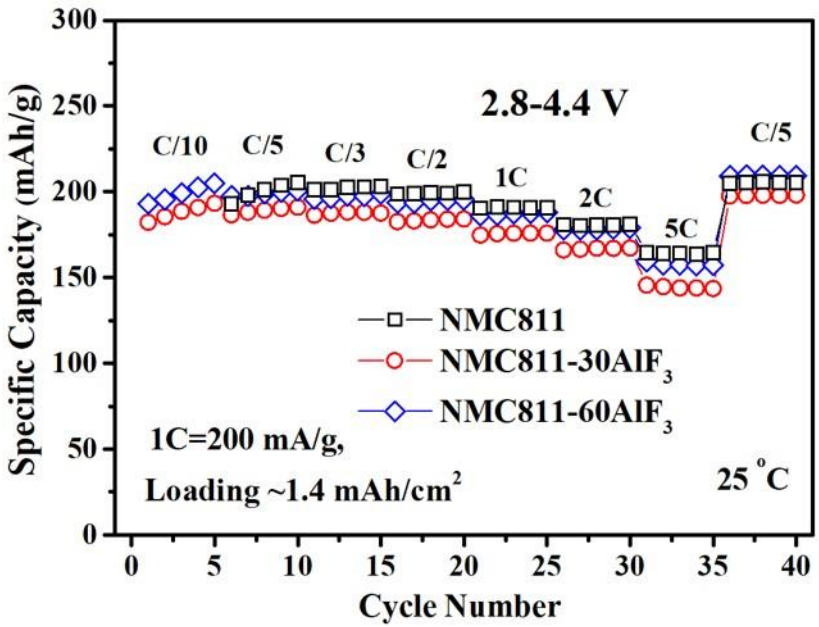
Samples	Diffusivity D_C (cm^2/s)	Diffusivity D_{DC} (cm^2/s)
NMC811	4.5×10^{-9}	1.7×10^{-9}
P-30AlF_3	**4.6×10^{-9}**	**1.9×10^{-9}**
P-60AlF_3	2.3×10^{-9}	1.0×10^{-9}

- Thin coating does not change diffusivity

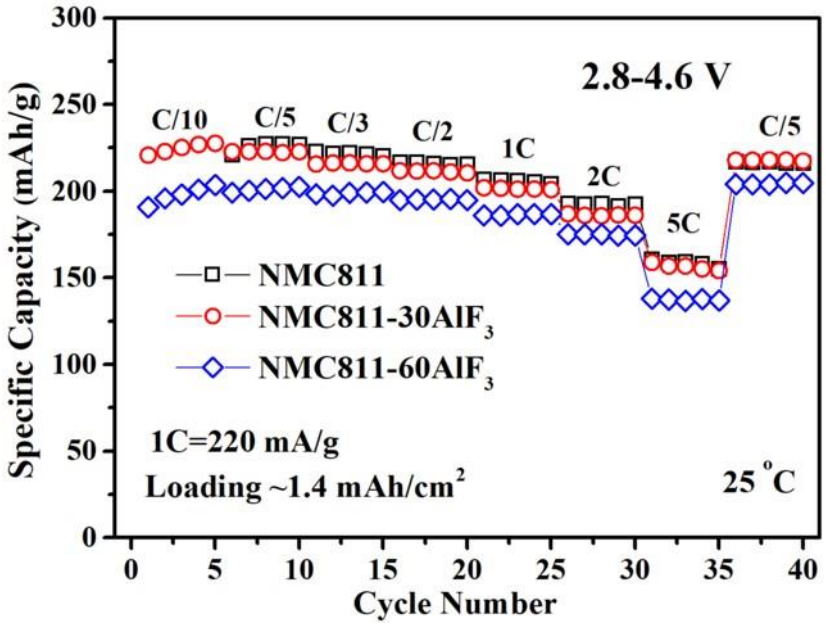
Technical Accomplishment

ALD coating AlF_3 on NMC811

2.8-4.4 V



2.8-4.6 V

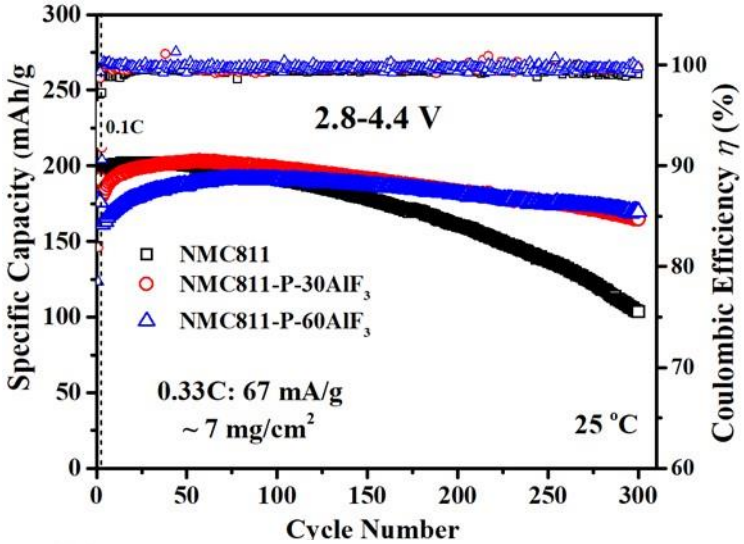


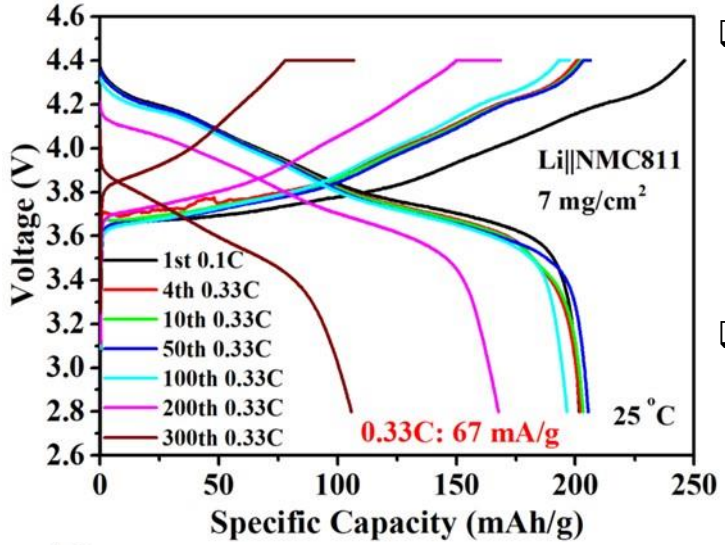
- **NMC811:** excellent rate capability due to high ionic and electronic conductivity
- **AlF_3 coating slightly deteriorates the rate performance, especially for the thick coating**

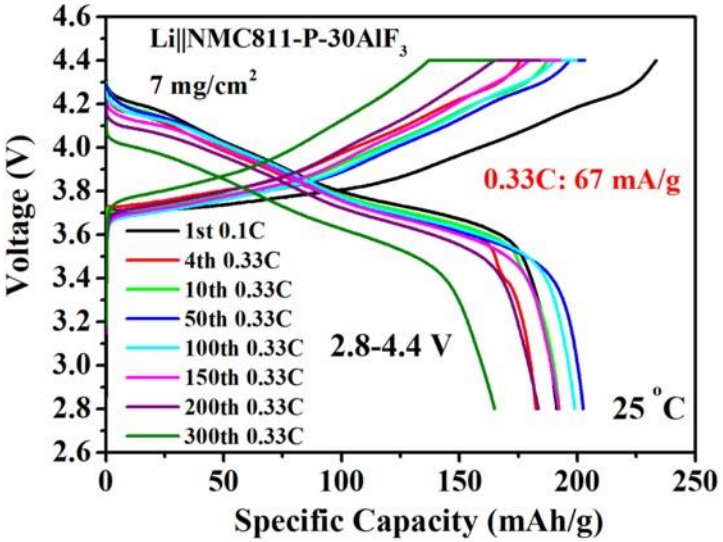
Technical Accomplishment

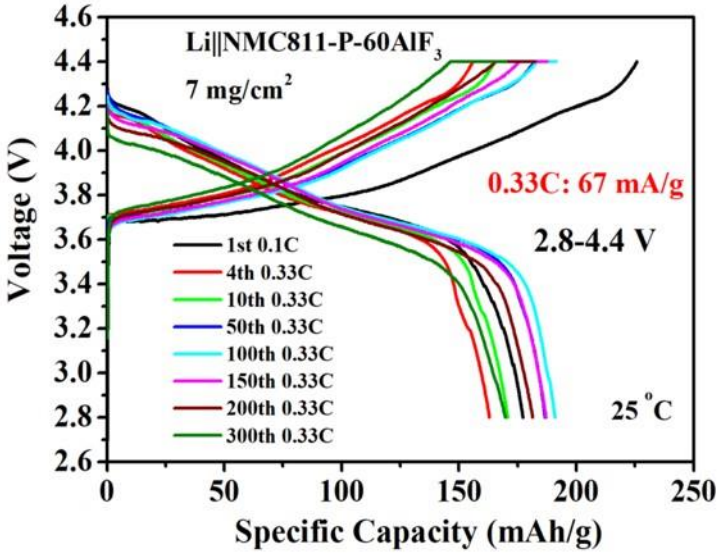
ALD coating AlF_3 on NMC811

2.8-4.4 V







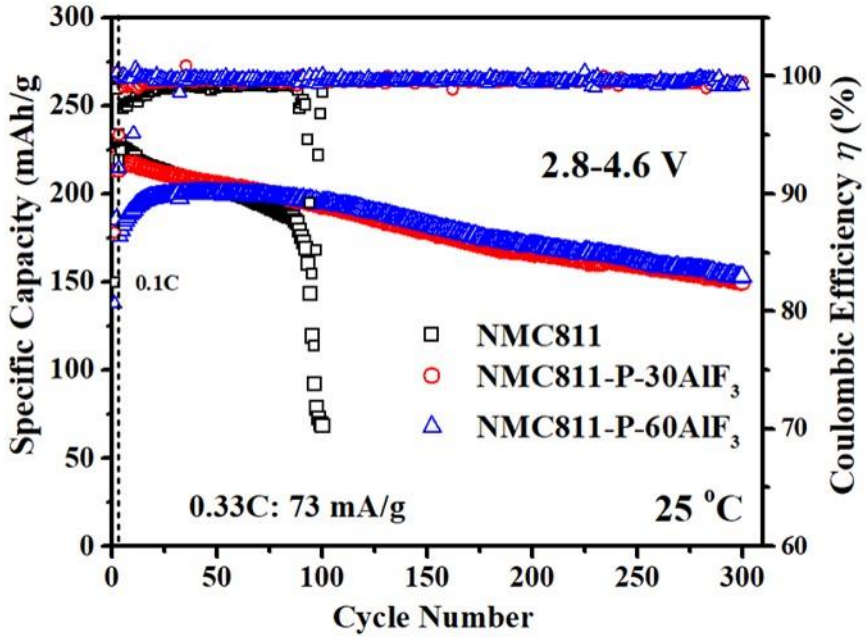


- AlF_3 Coated samples: low initial capacity and capacity activation – electrolyte wetting, lithiation of the coating layer
- AlF_3 coating largely improves capacity retention: **80% capacity retention** (vs. **55%** for the uncoated) after 300 cycles
- ALD Coating alleviates polarization growth: improved the interfacial stability of NMC811 – physical separation of 811/electrolytes

Technical Accomplishment

ALD coating AlF_3 on NMC811

2.8-4.6 V

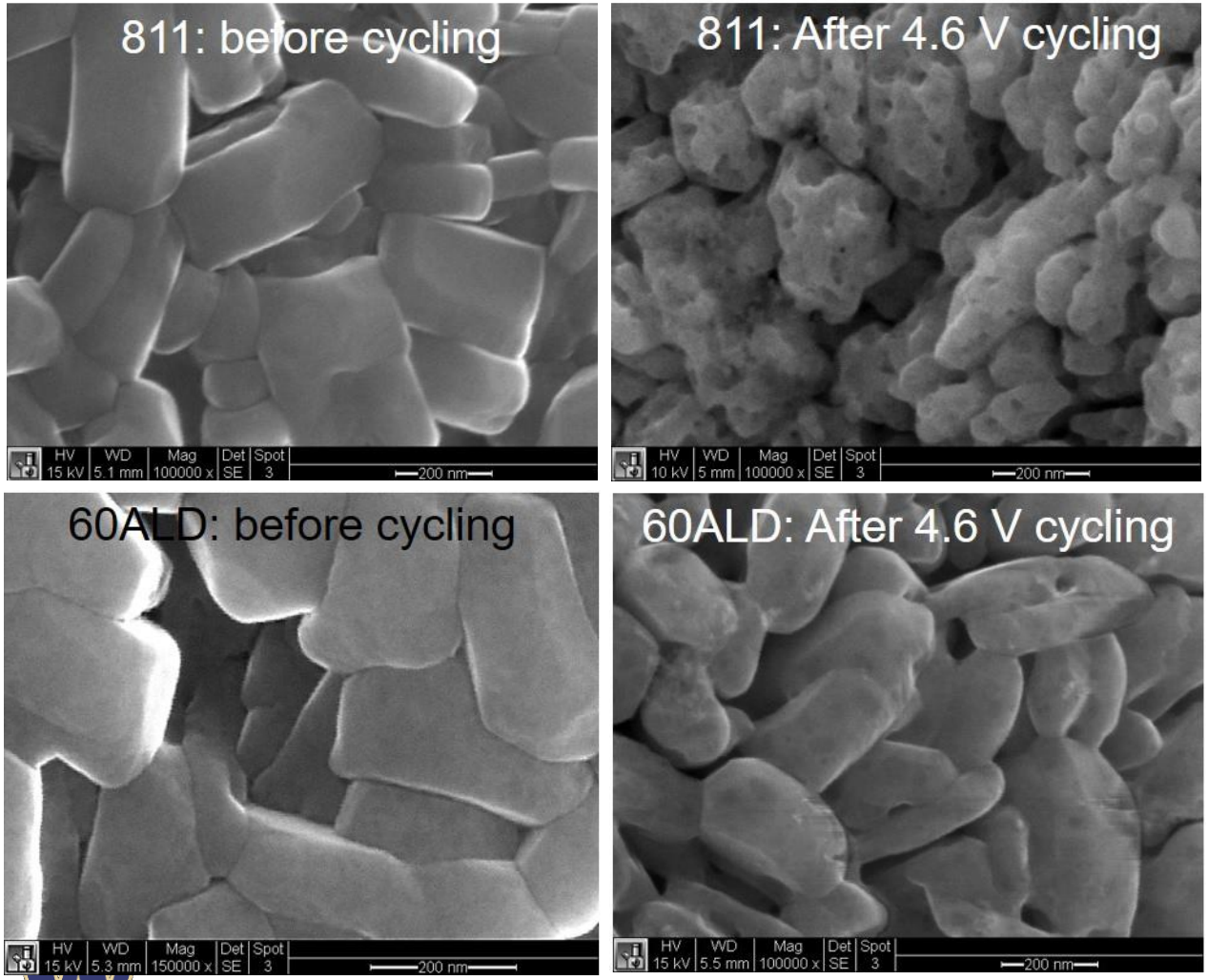


- NMC811: high capacity of ~225 mAh/g at 4.6 V but rapid fading, and **fail suddenly after 100 cycles**
- Coated samples: low initial capacity and capacity activation; much better capacity retention ($60AlF_3$: retain **~80% capacity** after 300 cycles)
- Coating largely mitigates overpotential growth

Technical Accomplishment

ALD coating AlF_3 on NMC811

***Postmortem:* 2.8-4.6 V, C/3, 100 cycles**

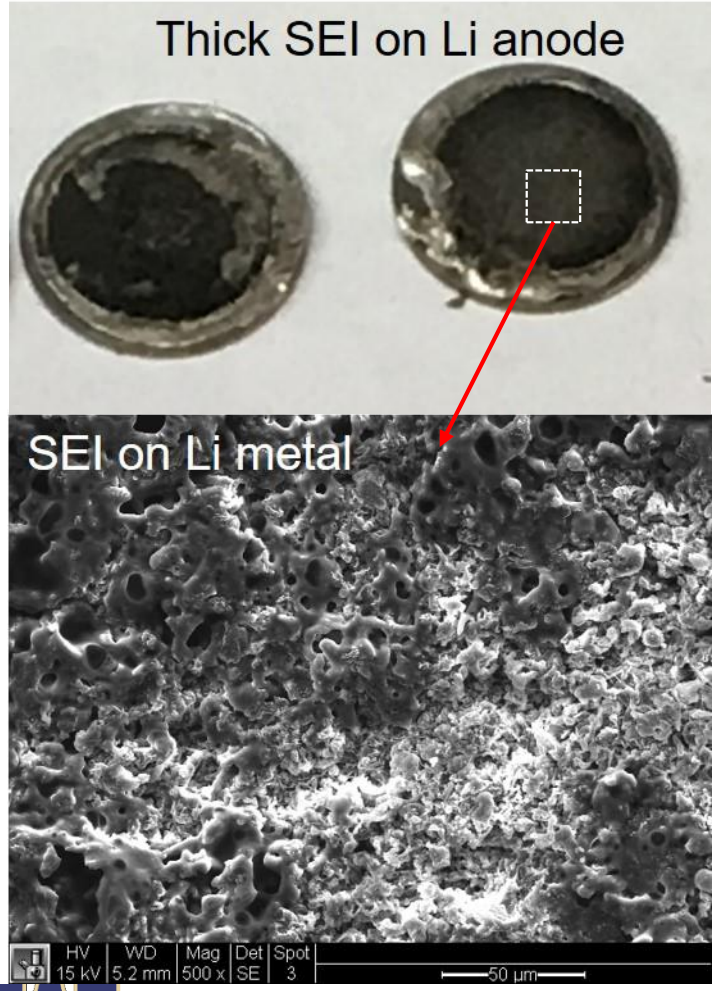


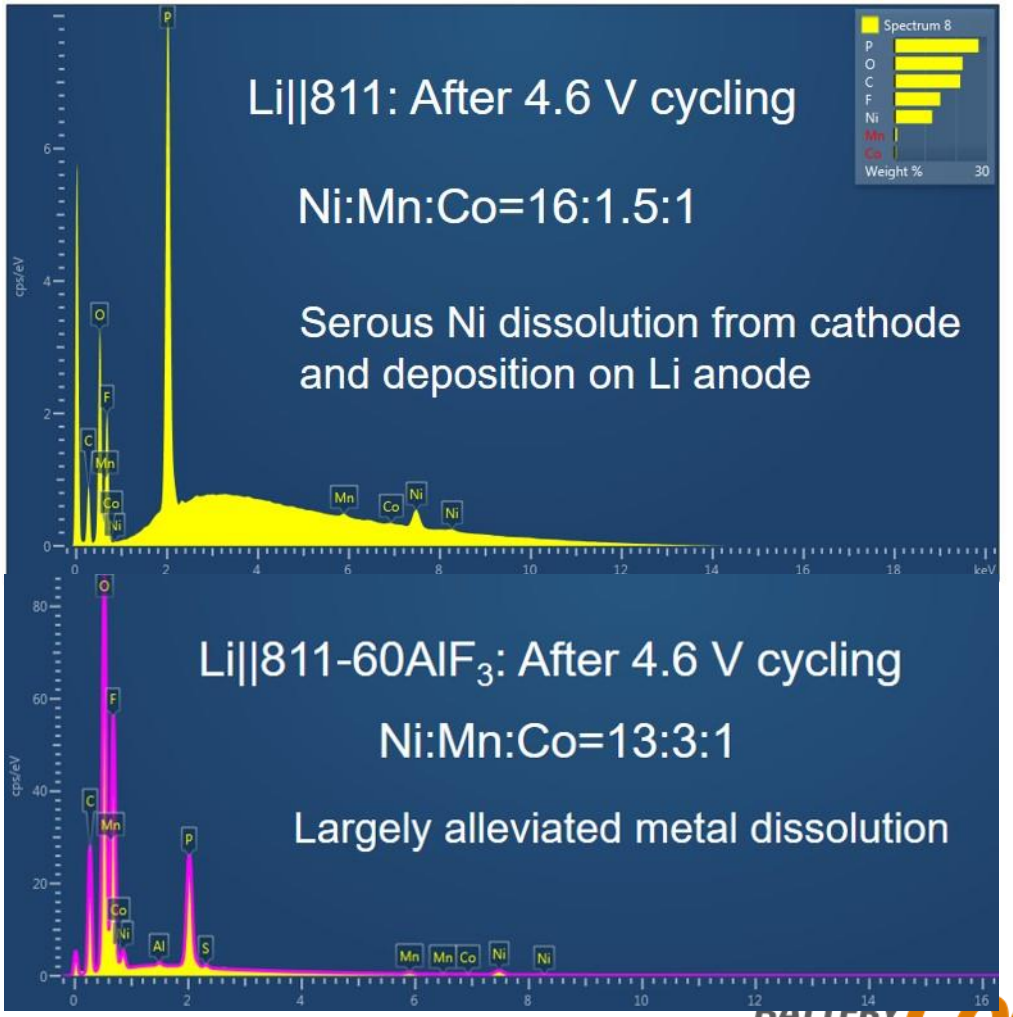
- The particle integrity is well maintained for both un-coated and AlF_3-coated sample.
- NMC811: serious **particle corrosion and metal dissolution** on the surface
- AlF_3 coating reduces metal dissolution – alleviated **electrode/electrolyte reactions** at high voltages

Technical Accomplishment

ALD coating AlF_3 on NMC811

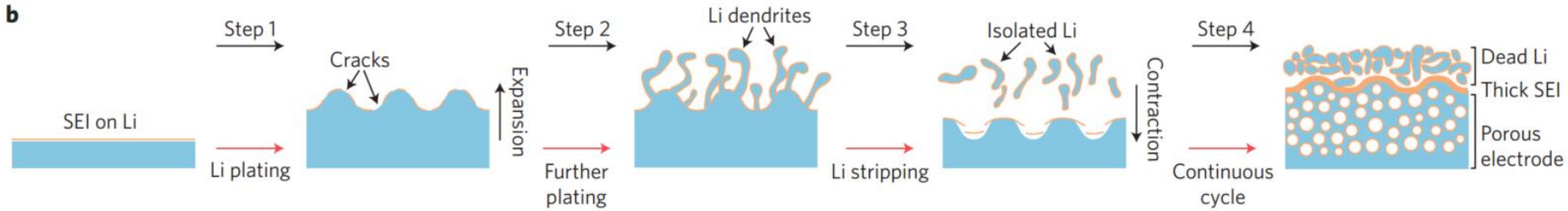
***Postmortem:* 2.8-4.6 V, C/3 ~0.5 mA/cm^2** Li metal after 100 cycles





Technical Accomplishment

Separator Coating with Li-ion Conductors



D. Lin, Y. Liu, and Y. Cui, Nat Nanotech. ***12****, 194 (2017)*

- ***Li Metal* Challenges**

  At high current densities (e.g., > **0.5 mA/cm^2**) non-uniform Li deposition, infinite volume change, and Li-electrolyte reactions -> **consuming Li (including forming dead Li), electrolyte dry-up** and **Li dendrites**

- **Solutions**
  - Minimize direct Li/electrolytes contact – form stable SEI or mitigate electrolyte/Li reactivity
  - Electrolyte engineering (concentration or additives), Li surface engineering, etc.

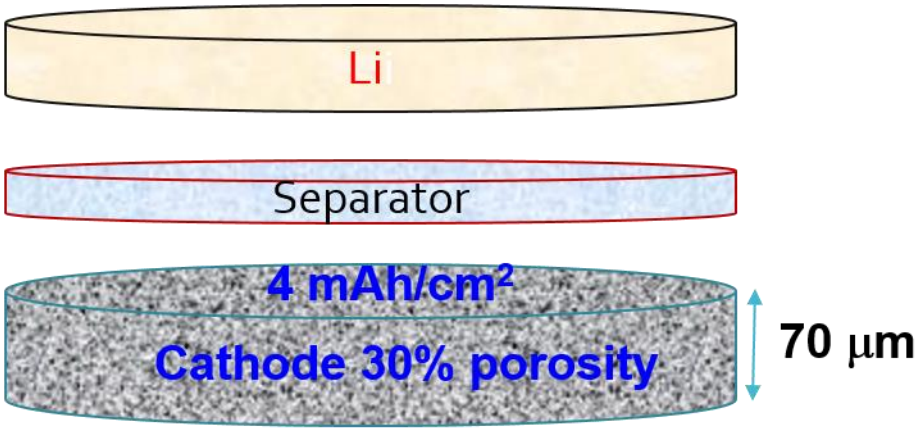
- ***Separator Coating with Li-ion Conductors***
  - Reduce the Li/electrolyte contact
  - Improve wettability,
  - Improve the mechanical properties – such as puncture resistance, thermal shrinkage resistance, and thus improve safety
  - Form SEI ?

Technical Accomplishment

Separator Coating with Li-ion Conductors

Electrolytes in Liquid Cell

- Electrolyte up-taking by cathode with 30% porosity is ~**2.11 μL/cm²**
- Electrolyte up-taking by 25 μm thick separator (Celgard 2500) with 39% porosity is ~ **0.98 μL/cm²**
- Therefore, the total amount for completely wetting cathode and separator is ~ **3.1 μL/cm²**, corresponding to ~ **0.77 μL/mAh**



NMC811: 200 mAh/g, 20 mg/cm², 92 wt.% active material loading

- PNNL's 300-350 Wh/kg porch cell design: lean electrolyte amount is ~ 3.1g/Ah, corresponding to ~ **2.58 μL/mAh** - enough electrolytes to react with Li metal - **consume Li** and in-turn **dry the electrolyte**

Technical Accomplishment

Separator Coating with Li-ion Conductors

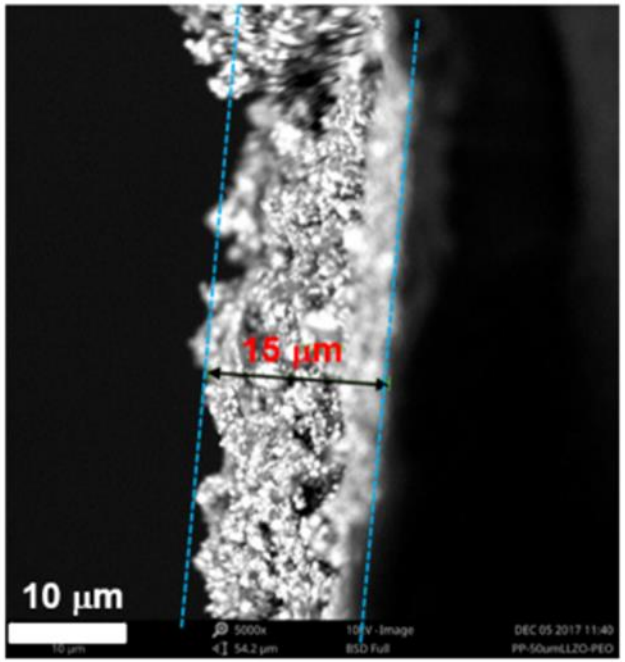
Interface Thermodynamics in Solid State Batteries

Prior collaboration with PNNL (submitted to *Energy & Environmental Science*)

- **Stable LLZO** – Li dendrites penetrating through via defects and grain boundaries
- **Unstable LATP** – reaction products self-terminating Li dendrites

Technical Accomplishment

Separator Coating with Li-ion Conductors

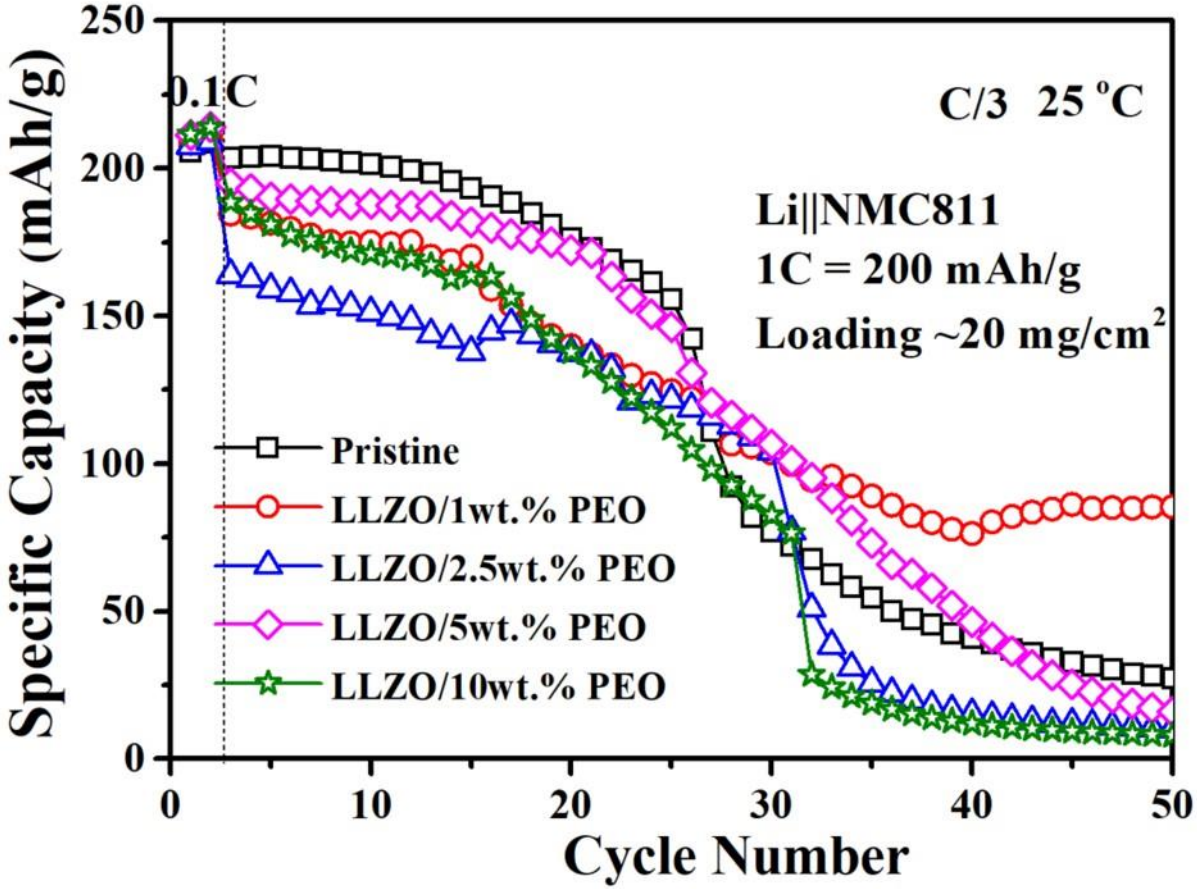


- High ionic conductivity of LLZO ~**10^{-3} S/cm** at 25 ^{o}C, made by our solid state reaction method
- **5-10wt.%PEO:** LLZO particles embedded in the PEO matrix, **flat and uniform** surface ~ 15 µm

Technical Accomplishment

Separator Coating with Li-ion Conductors

2.8-4.4 V, C/3, 4.0 mAh/cm^2, 75 μL electrolyte, 450 μm Li foil

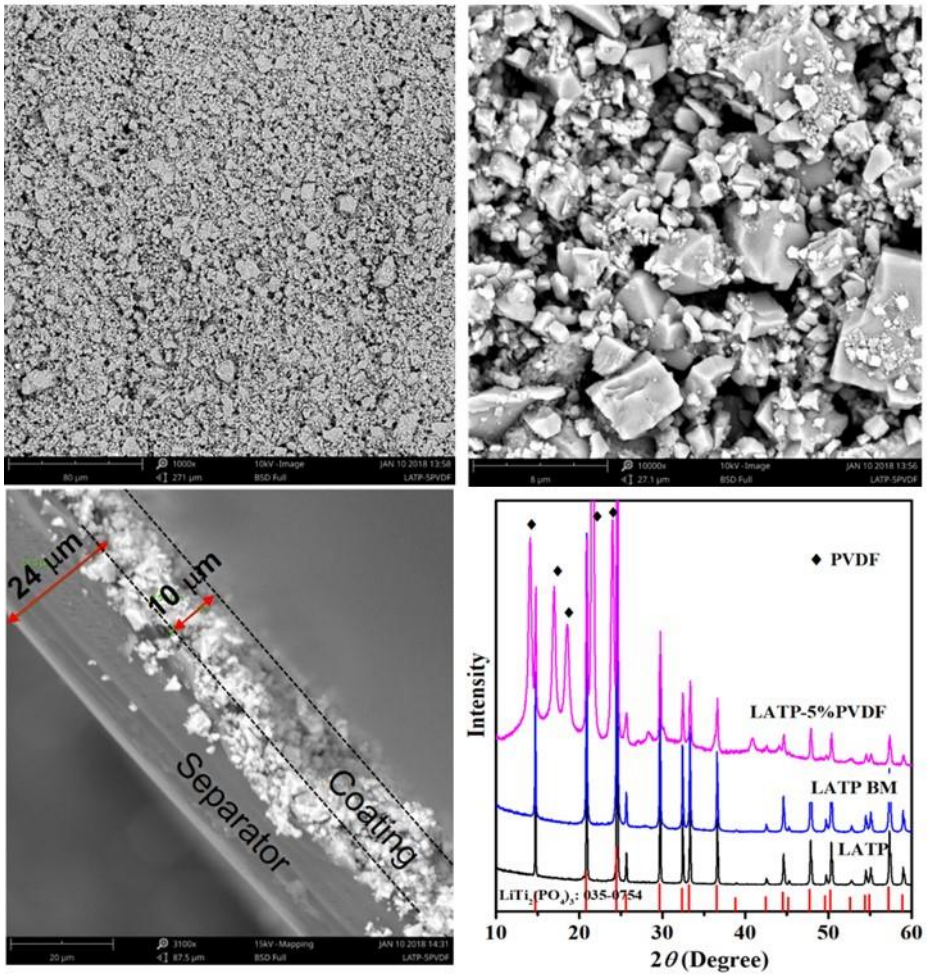


- Celgard 2500: the cell degrades at **#13** cycle, and fails after **25** cycles
- LLZO-coated 2500-the cells show same voltage profile at C/10, but much larger voltage polarizations at C/3
- LLZO coating doesn't improve the cycle stability of Li metal

Technical Accomplishment

Separator Coating with Li-ion Conductors

LATP/5wt.% PVDF coating on PP2500

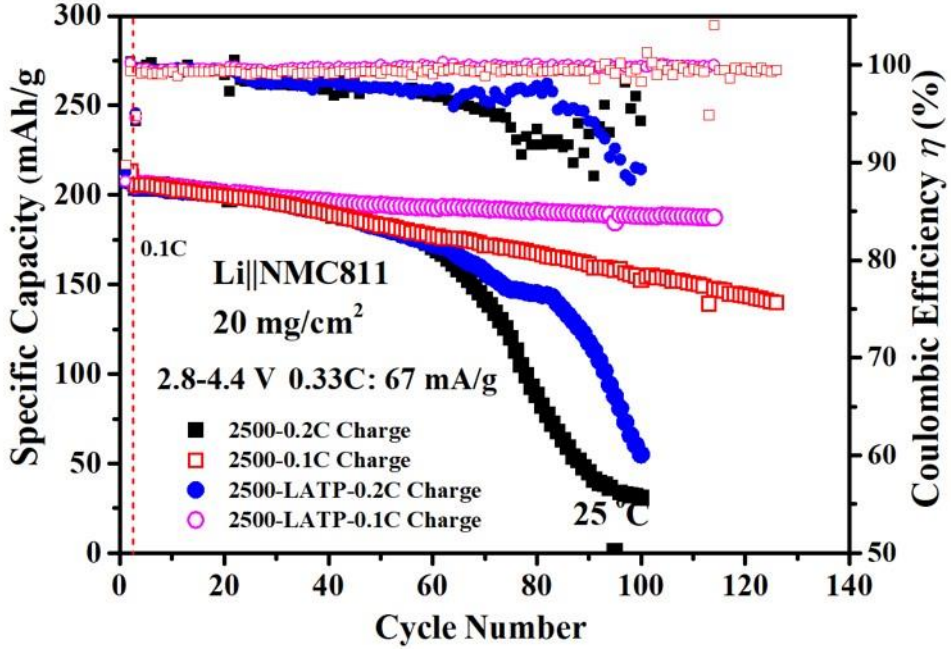


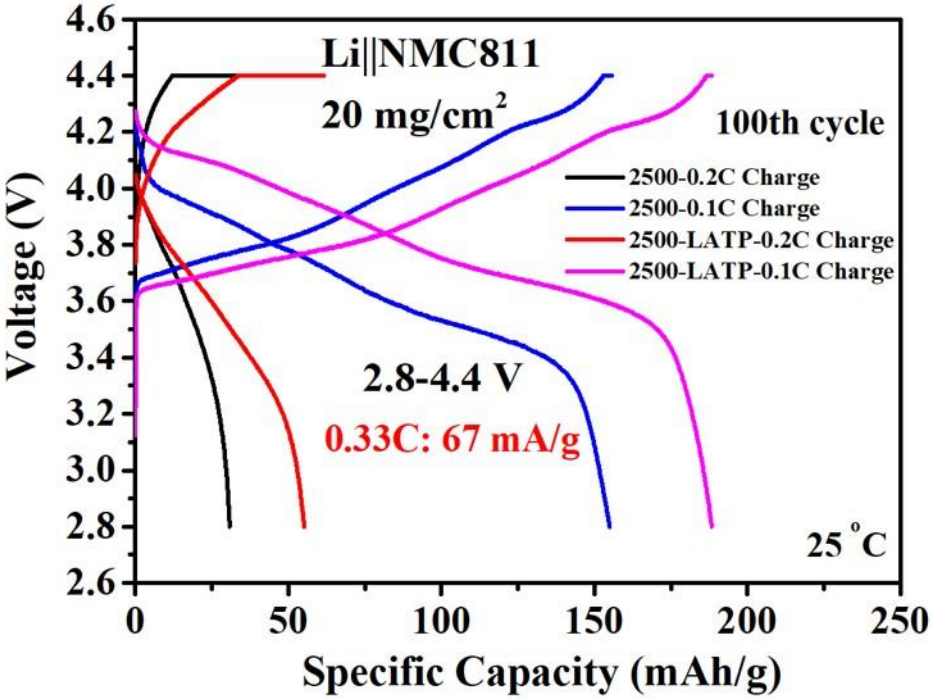
- Successful synthesis of single phase and high conducting LATP
- High ionic conductivity of LATP **~ 6×10^{-4} S/cm** at 25 ^{o}C
- **Coating:** 10 μm thick, well maintained LATP structure and phase

Technical Accomplishment

Separator Coating with Li-ion Conductors

The cells are still in cycling





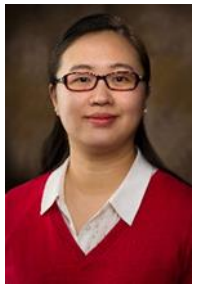
- **0.2 C charge 0.33C discharge**: both cells lose 16% capacity in initial 60 cycles, then experience an rapid capacity drop – electrolyte dry-up, Li metal anode dead.
- **0.1 C charge 0.33C discharge**: the cells with PP2500 loses **~32%** capacity after 125 cycles, while the cell with LATP-coated PP2500 retains **~ 91.5%** initial capacity after 115 cycles.
- Coating also decreases the overpotential

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
- General Motor: ALD coating of Ni-rich NMCs
- 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 4.5 volts.
- ALD coating of high-voltage stable, complex Li-ion conductors, such as $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP), and improve the electronic conductivity of the Li-ion conductors by proper doping
- Engineering the surface and grain boundary of Ni-rich NMCs to mitigate micro-crack formation and electrolyte penetration
- Controlling separator coating thickness down to 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

- **Complete on-going projects:** AlF_3 coating on NMC811 (TEM, cycling, microstructure analysis, full cell cycling for 2 mAh/cm^2 loading); LLZO and LATP coating on separator (particle size and binder ratio control, microstructure analysis, cycling, etc.)
- **ALD coating on NMC811**
  - ✓ Other stable coating material: $AlPO_4$
  - ✓ Li-ion conductors: LATP, Li_3NbO_4
  - ✓ Mix conductors: Mg-doped LATP, Zr-doped Li_3NbO_4
- **Separator coating**
  - ✓ Optimize the coating:
    - Coating thickness (< 5 μm) - by controlling the particle size (down to < 200 nm), setting blade gap, etc.
    - Binder ratio (PEO, PVDF, or others)
    - Particle size (< 200 nm)
    - Try other coating techniques: spin coating
    - Other Li-ion conductor coatings
  - ✓ Mechanical properties testing: *puncture resistance, tensile strength, thermal stability, flammability, etc.*

Summary

Demonstrated progress on the project:

- ❑ Demonstrated that ALD coating of AlF_3 largely improves the interfacial and cycling stability of NMC811, especially at high voltages, by separating 811/electrolyte and mitigating metal dissolution, while the rate capability is largely retained
- ❑ Demonstrated that sol-gel coating using wet chemistry hardly improves the cycle stability of NMC811due to surface contamination and non-uniform coating
- ❑ Developed Li-ion conductor coated separators that can efficiently improve the cycling stability of Li metal anode
  - ✓ LATP coatings on commercial Celgard 2500 separator: in-situ form SEI and mitigate direct Li/electrolytes contact
  - ✓ LATP coated separators - work well in high loading Li/NMC811 cells (4 mAh/cm^2: stably cycle at C/3 and retain **~ 92%** initial capacity over 100 cycles
  - ✓ Further optimizing the coating and understanding the Li-LATP-electrolyte interactions will be pursued in the future

Acknowledgements

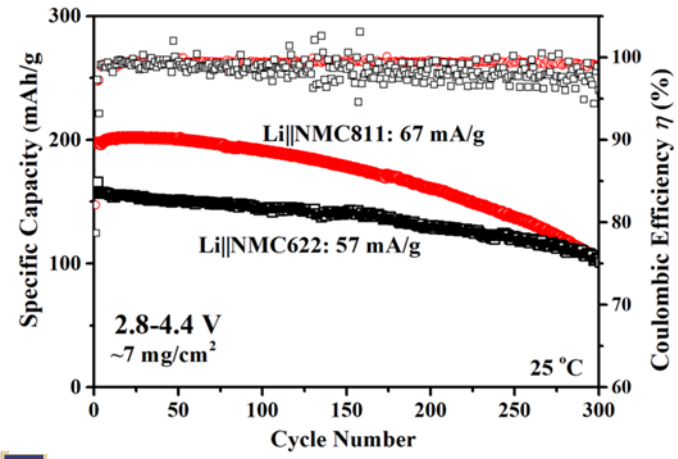
- Support from the DOE Vehicle Technologies Office Battery500 Consortium through Advanced Battery Materials Research Program
- PNNL – Jie Xiao and Jun Liu (separator coating, solid electrolytes)
- UT Austin and Binghamton University (materials characterization, in-situ XRD on high Ni cathode, coating, etc.)
- GM – Xingcheng Xiao (ALD)

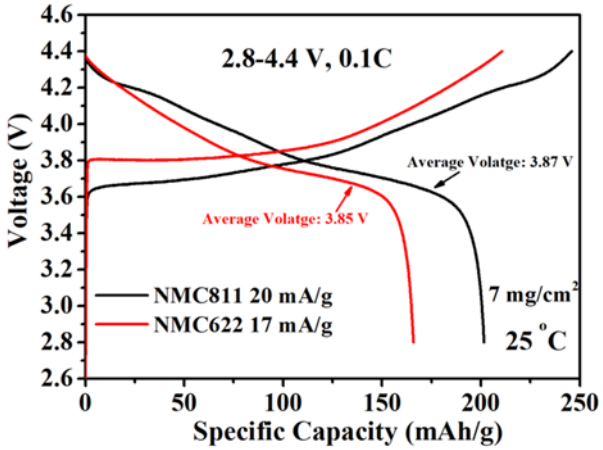
Technical Back-Up Slides

300 and 350 Wh/kg Design

	Parameters	Experimental Value
Cathode	Material	622
	1st dicharge capacity (mAh/g)	180
	Active material Loading	96%
	Coating weight (mg/cm^2 each side)	21.8
	Areal Capacity (mAh/cm^2 each side)	3.81
	Electrode press density (g/cm^3)	3.00
	Electrode Length (mm)	54
	Electrode width (mm)	36
	Electrode thickness(single side) (μm)	72
	Al foil thickness (μm)	12
	Layers	7
Anode	Cell Balance (N/P ratio)	2.6
	Electrode thickness(single side) (μm)	50
	Cu foil thickness (μm)	8
Electrolyte	Electrolyte/capacity (g/Ah)	3.1 g/Ah
	Weight (g)	3.33 g
Separator	Thickness (μm)	20
Packet Foil	Thickness (μm)	115
Cell	Voltage (V)	3.80 V
	Capacity (mAh)	1073 mAh
	Energy density (Wh/Kg)	300

	Parameters	Experimental Value
Cathode	Material	811
	1st dicharge capacity (mAh/g)	203
	Active material Loading	96%
	Total Coating weight (mg/cm^2 on each side)	20.8
	Areal Capacity (mAh/cm^2 each side)	4.19
	Electrode press density (g/cm^3)	3.2
	Electrode thickness (on each side) (μm)	66
	Al foil thickness (μm)	12
	Layers	10
Anode	Cell Balance (N/P ratio)	2.1
	Electrode thickness(on each side) (μm)	42 (Hydro Quebec Li)
	Cu Mesh thickness (μm)	9
Electrolyte	Electrolyte/capacity (g/Ah)	2.75
	Weight (g)	4.22
Separator	Thickness (μm)	20
Packet Foil	Thickness (μm)	88
Cell	Voltage (V)	3.65
	Capacity (mAh)	1565
	Energy density (Wh/Kg)	340





Our focus in the past quarters has been on NMC 811

Technical Back-Up Slides

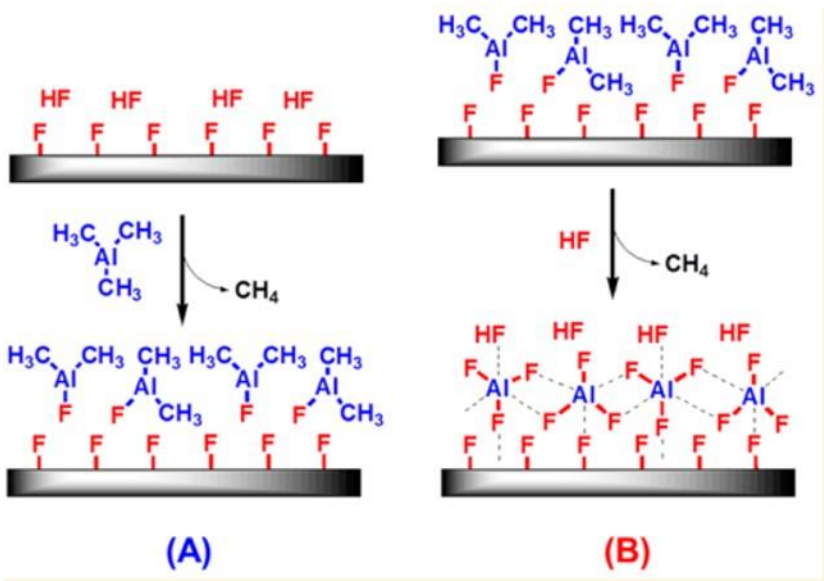
ALD Attributes:

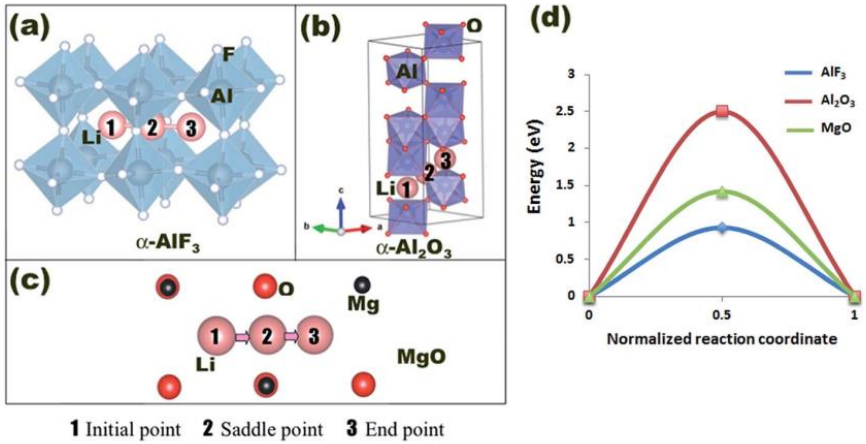
- ❑ Atomic scale thickness control
- ❑ Excellent conformity
- ❑ Uniformity over large and complex surface
- ❑ Control of coating composition
- ❑ Minimal contamination

Why AlF_3:

- ❑ Stable in electrolytes and against HF
- ❑ Good electrochemical stability
- ❑ Durable during cycling
- ❑ Refrain the phase transition
- ❑ Low Li^+ diffusion barrier

ALD AlF_3 Chemistry





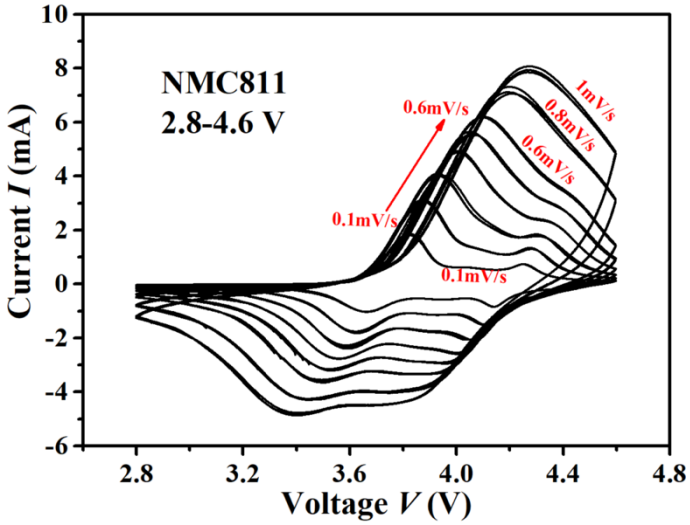
J. Mater. Chem. A (2015) **3**, 17248-17272

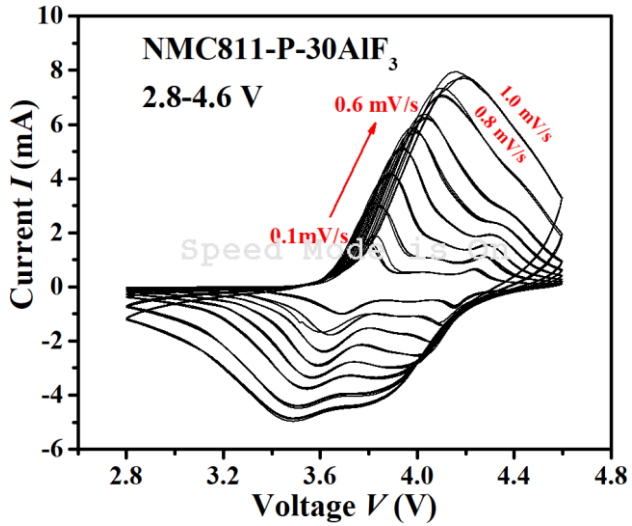
- ❑ ALD coating in a controlled environment, 0.15-0.19 nm/cycle for 30 & 60 ALD cycles ~ 5 nm or 10 nm thick

Technical Back-Up Slides

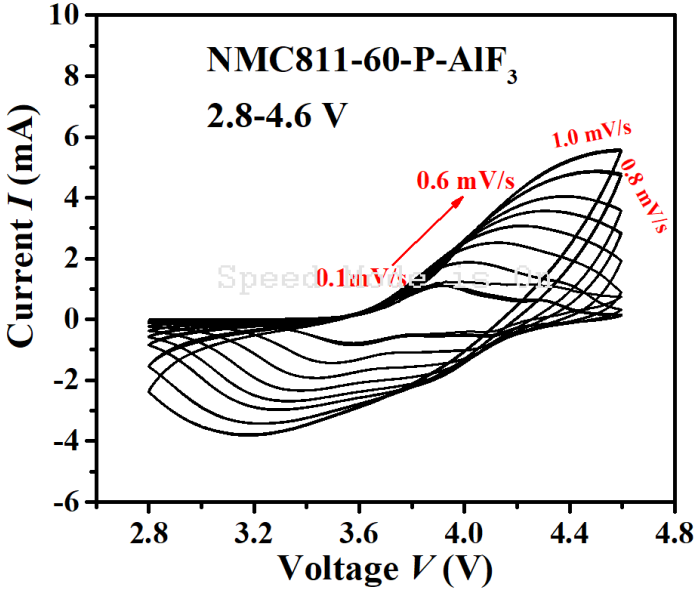
ALD coating AlF_3 on NMC811

Li||NMC811, 1M $LiPF_6$ in EC:EMC (3:7 wt./wt.)+2 wt.% VC





- **0.1-1.0 mV/s scan rate for 2.8-4.6 V**
- **3 cycles for each rate**
- **Loading 7 mg/cm^2 Tested at 25 ^{o}C**



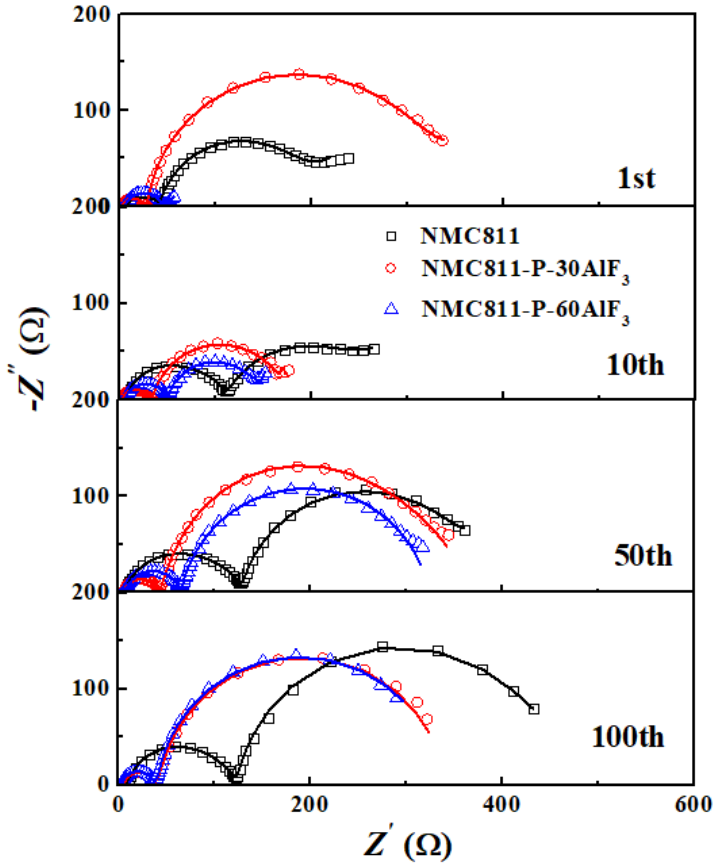
$$I_p = 2.69 \times 10^5 \times n^{3/2} \times A \times D^{1/2} \times \nu^{1/2} \times \Delta C$$

- **The H1-H2 transition peak was used to calculate the Li^+ diffusion coefficients: the electron transfer number n = 0.58 (~ 160 mAh/g), A = 1.27 cm^2, ΔC= 1.73×10^{22} cm^{-3} =0.0287 mol/cm^3**

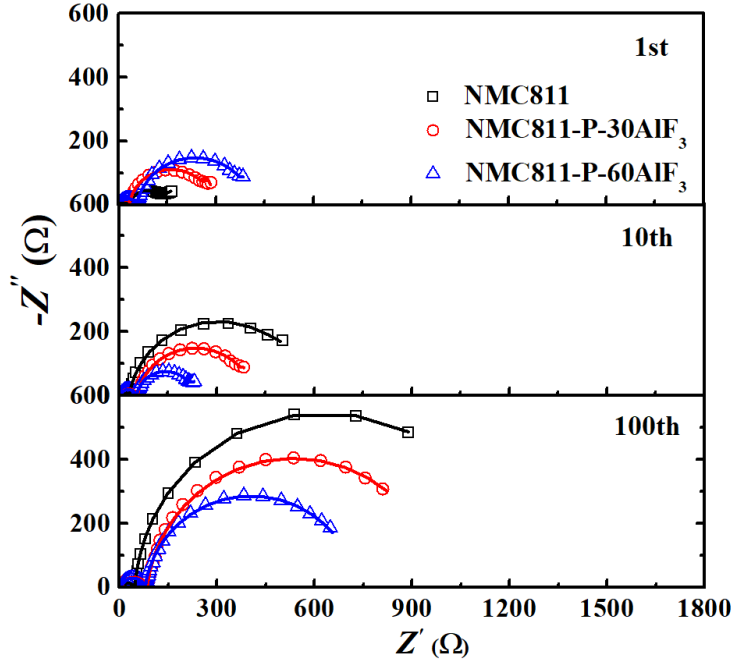
Technical Back-Up Slides

EIS of AlF3-coated NMC811

2.8-4.4 V



2.8-4.6 V



- 2.8-4.4 V: AlF_3 coating effectively alleviates impedance growth, including R_{SEI} and R_{ct}.
- 2.8-4.6 V: AlF_3 coating causes a high impedance initially but mitigates R_{ct} growth

Technical Back-Up Slides

Separator Coating with LLZO & LATP

DFT calculations

LLZO and Li

$Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$ and Li	
ΔG (eV)	Phase equilibria
2.69	Li_5GaO_2,ZrO_2,La_2O_3,Li_2O
2.38	$La_2Zr_2O_7$,$La_4Ga_2O_9$,Li_5GaO_2, La_2O_3,Li_2O
2.82	$La_2Zr_2O_7$,$La_4Ga_2O_9$,Li_2ZrO_3, ZrO_2,Zr_3O,La_2O_3,Li_2O
7.90	$La_2Zr_2O_7$,$La_3Ga_5O_{12}$,Li_5GaO_2, La_2O_3,Li_2O
7.74	$La_2Zr_2O_7$,$La_3Ga_5O_{12}$,Li_2ZrO_3, ZrO_2,Zr_3O,La_2O_3,Li_2O
7.28	La_2Zr_2O7,$La_3Ga_5O_{12}$,$Li_6Zr_2O_7$, Zr_3O,La_2O_3,Li_2O
8.34	$La_2Zr_2O_7$,$La_3Ga_5O_{12}$,Li_2ZrO_3, ZrO_2,Zr_3O,La_2O_3,Li_2O

$Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$ and Li

$$2Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3 + 3Li \rightarrow 3TiPO_4 + AlPO_4 + 2Li_3PO_4$$

ΔG= -5.227 eV