

Development of Cobalt-Free Cathodes for Lithium-Ion Batteries

by
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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

Section 1 and 2 were partially adapted from the following published review manuscripts that I co-authored:

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T. Or and S. Gourley contributed equally to the work, conducting the literature survey and preparing the manuscript. Dr. Z. Chen designed the scope and revised the manuscript. All authors reviewed and approved the final version of the manuscript.

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L. Qian, T. Or, and Dr. Y. Zheng contributed equally to the work, conducting the literature survey and preparing the manuscript. M. Li, D. Karim, A. Cui, M. Ahmed, Dr. H.W. Park, Dr. Z, Zhang, Dr. A. Yu, Dr. Z. Chen, and Dr. K. Amine helped revise the manuscript. All authors reviewed and approved the final version of the manuscript.

Section 4 consists of a submitted research manuscript that I co-authored:

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T. Or conducted the study and wrote the manuscript. L. Qian assisted with data acquisition. Dr. H.W. Park and Dr. K. Kaliyappan helped design the study. Dr. A. Yu and Dr. Z. Chen supervised the project. All authors reviewed and approved the final version of the manuscript.

Section 5 consists of work in progress intended for publication:

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T. Or conducted the study and wrote the manuscript. L. Qian and Dr. D. Luo assisted with data acquisition. Dr. H.W. Park helped design the study. Dr. A. Yu and Dr. Z. Chen supervised the project.

Abstract

Lithium-ion batteries (LIBs) are the dominant energy storage technology for mobile devices and plug-in electric vehicles due to their unmatched combination of energy density, power output, and cycle stability. A coveted goal in their development is the expansion of energy density, which is currently bottlenecked by the charge storage capacity of the cathode material. Moreover, the ramp-up and projected growth of LIB production raises concerns over the availability and cost of raw resources, particularly on the reliance of cobalt in the cathode material. To suit these requirements, layered structure $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC, $x + y + z = 1$) class materials are the most commercially relevant, with ongoing efforts to increase the Ni to Co ratio. Although Ni-rich NMC cathodes ($x \geq 0.8$) can achieve higher energy densities, their applicability is limited due to the poor cycle life and safety. Thus, it is critical to develop strategies to address these problems. In general, the performance of electrode materials can be modified by 1) altering the particle morphology, 2) applying a surface coating, 3) applying a transition metal dopant, and 4) modifying the electrolyte composition to suppress deleterious electrode-electrolyte side reactions, all of which were explored in this work. The electrochemical performance of single crystal $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ (SC-NMC811) electrodes was enhanced by coatings applied with atomic layer deposition (ALD). The performance of various coating materials (Al_2O_3 , alucone, TiO_2 , and titanicone) was thoroughly compared and their mechanisms were analyzed. As the coating was applied on the fabricated electrode, it was observed to be localized on the electrode surface. Thus, it was concluded that the ALD-applied coatings primarily act by accelerating the decomposition of LiPF_6 , coating the cathode with fluoride and phosphate species that passivate its surface. The coatings were most effective at improving cycle stability at low currents, where capacity degradation is dominated by active material loss from

HF corrosion. At elevated currents, kinetic factors dictate capacity degradation, which minimized the impact of the ALD-applied coatings. Preliminary investigation was also conducted on the relationship between coatings and electrolyte additives, which share many mechanisms. In subsequent work, Zr and Ce-based coatings were formed on SC-NMC811 particles by sintering. Consequently, doping within the particle bulk can also occur. The coating thickness and extent of doping were optimized in order to delineate the various improvement mechanisms. Doping was found to improve cycle stability at elevated currents, likely due to its improvement of Li^+ diffusion kinetics and suppression of lattice volume evolution. However, the thickness of the coating should be minimized, particularly when cycling at elevated currents, due to the rapid build-up of surface impedance. Finally, SC-NMC811 was cycled with a passivating high concentration LiFSI-based electrolyte, with its cycle stability further enhanced by incorporating coatings. Under this unconventional electrolyte system, the passivation mechanism of the coatings was proposed.

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List of Abbreviations

ALD – Atomic layer deposition

BE – Binding Energy

C_{dl} – Double-layer capacitance (EIS parameter)

CEI – Cathode-electrolyte interface

CPE – Constant phase element (EIS parameter)

DOD – Depth of discharge

DMC – Dimethyl carbonate

DME – Dimethoxyethane

EC – Ethylene carbonate

EMC – Ethyl methyl carbonate

EDX – Energy dispersive x-ray spectroscopy

EIS – Electrochemical impedance spectroscopy

EV – Electric vehicle

FEC – Fluoroethylene carbonate

HCE – High concentration electrolyte

HOMO – Highest occupied molecular orbital

LHCE – Localized high concentration electrolyte

LIB – Lithium-ion battery

LUMO – Lowest unoccupied molecular orbital

mA g⁻¹ – Milliamp per gram

mAh g⁻¹ – Milliamp hours per gram

LCO – LiCoO₂ LIB cathode

LFP – LiFePO_4 LIB cathode

LiFSI – Lithium bis(fluorosulfonyl)imide

LMO – LiMn_2O_4 LIB cathode

MLD – Molecular layer deposition

NCA – LIB cathode of form $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$

nm – Nanometer

NMC – LIB cathode of form $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$

PC – Polycrystalline

R_{ct} – Charge-transfer resistance (EIS parameter)

R_{f} – Resistance of Li^+ diffusion through a surface film

R_{s} – Bulk series resistance (EIS parameter)

SC – Single crystal

SEI – Solid-electrolyte interface

SEM – Scanning electron microscopy

SOC – State of charge

TEM – Transmission electron microscopy

TGA – Thermogravimetric analysis

TM – Transition metal

TMO – Transition metal oxide

USGS – United States Geological Survey

V – Voltage

VC – Vinylene carbonate

Wh kg^{-1} – Watt hours per kilogram

W kg⁻¹ – Watts per kilogram

XAS – X-ray absorption spectroscopy

XPS – X-ray photoelectron spectroscopy

XRD – X-ray diffraction

Z_w – Warburg element (EIS parameter)

List of Symbols

$^{\circ}\text{C}$ – Degrees Celsius

$\text{\AA}$ – Angstrom

μm – Micrometer

Z' – Real resistance (EIS)

Z'' – Imaginary resistance (EIS)

Ω – Ohm

F – Farad

eV – Electron volt

d – Lattice interlayer distance

λ – Wavelength

θ – Angle

1. Motivation

The growing demand for energy globally necessitates technological advancements in clean energy storage. Current energy generation relies on fossil fuels, which are inherently finite, limited in geographic distribution, and release greenhouse gases into the atmosphere during conversion. Although renewable energy sources (*e.g.*, wind, solar, and geothermal) can supplement the demand, their energy output is intermittent and thus requires energy storage solutions to generate an uninterrupted power supply system. Lithium-ion batteries (LIBs) are currently the dominant energy storage technology for mobile devices (cell phones, laptops, wireless earphones, *etc.*) and plug-in electric vehicles (EVs) due to their unmatched combination of energy density (150-250 Wh kg⁻¹, normalized by device mass), power density (>300 W kg⁻¹), and cycle stability (~2000 cycles).¹ Currently, demand for LIBs is correlated with the recent and skyrocketing growth of the EV market (**Figure 1A**). This sales growth is driven by government incentives, such as subsidies, rebates, tax breaks, and implementation of charging stations. In addition, expanded EV driving ranges and lower costs due to steady improvements in LIB technology and manufacturing are critical factors.

The International Energy Agency (IEA) estimates that the number of EV sales globally exceeded 10 million in 2022, and is projected to reach 45 million in 2030.² This projection is more optimistic than ones conducted by the IEA in previous years.³ Avicenne Energy estimated that EVs dominated the energy output of LIBs in 2017, more than doubling the usage from portable electronics (**Figure 1C**).⁴ This is projected to further increase (+31.6%) by 2025. The global expansion of LIB production capacity is projected by Benchmark Mineral Intelligence to balloon from ~290 GWh in 2018 to ~1700 GWh in 2028.⁵

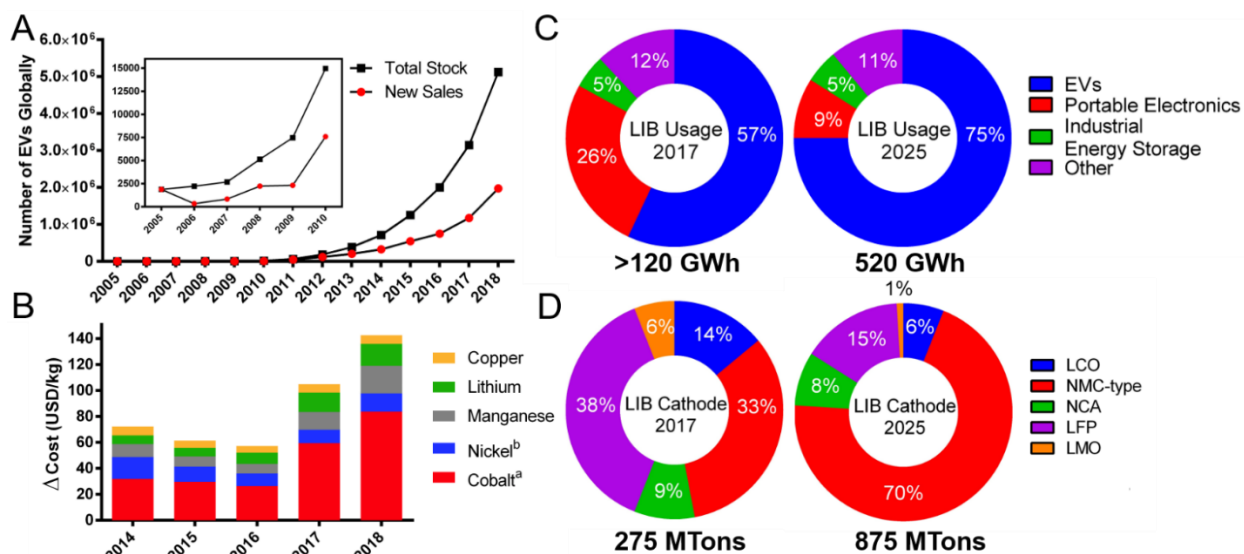


Figure 1. A) Global new EV sales to date B) Price (represented in bar size) of valuable metals used in LIBs in 2018 from the U.S. Geological Survey. Projection of LIB market share based on C) application and D) cathode composition. Projection assumes that Tesla, Inc. remains the only major EV manufacture to adopt NCA cells in 2025. Reprinted with permission from Wiley 2020.⁶

1.1. Sustainability of LIB Production

Naturally, the ramp-up and projected growth of LIB production raises concerns over the availability of raw resources. LIB technology for consumer EVs is currently dominated by two main cathode compositions, layered $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$, $x + y < 0.2$ (NCA-type) and $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, $x + y + z = 1$ (NMC-type).⁷ Due to the degree of commercialization and production of these materials worldwide, it is expected that they will remain the primary cathode chemistries for LIBs over the next decade (**Figure 1D**). Approximately 50-80% of the production cost of LIBs is associated with materials, with up to 50% of this ascribed to the cathode active material.^{8,9} As LIB manufacturing costs have substantially decreased due to economies of scale, transitions toward larger cell formats, and maturity in battery pack production techniques, the material input cost will become more prevalent.^{10,11} Constraints in the

supply of raw materials can lead to severe price fluctuations and make LIBs unreasonable for large-scale applications, bringing the momentum and optimism of the EV market to a halt.

Among the raw resources required for LIB production, concerns have been raised over the supply chains of lithium and cobalt, which are closely linked with battery production. While the exact quantity of recoverable global lithium reserves is difficult to determine, most projections concur that they are sufficient to meet long-term projected demands (up to 2100).^{12,13} However, concerns exist over the uneven geographic distribution of the reserves and whether production can meet high demands for lithium by 2050, which could lead to price spikes.^{14,15} On the other hand, reports have indicated that limited cobalt supply could occur as early as 2030.¹⁶

As seen in **Figure 2A** and **2B**, cobalt is by far the most valuable metal used in LIBs. In 2010, ~25% of all cobalt produced was used in secondary batteries (LIBs and minor quantity in Ni-MH batteries), which grew to 30% in 2017 and is expected to expand to 53% by 2025.¹⁷ Moreover, cobalt continues to be an important component in catalysts, integrated circuits, semiconductors, magnetic recording devices, and various high-strength alloys. However, cobalt is scarce and expensive to process, as it is mostly derived from low-concentration by-products of nickel and copper mining. Cobalt is considered a critical resource as ~60% of the worldwide mine production in 2018 originated from copper-cobalt ores in the Democratic Republic of the Congo (DRC), where geopolitical instability and unethical working conditions (*e.g.*, child labor and hazardous exposure) are well documented and could lead to halting of cobalt exports.^{18,19} This was apparent in 1978 where civil conflict generated a drastic price spike known as the Cobalt Crisis (**Figure 2A**). Moreover, China has dominance over the cobalt supply chain as the world largest producer, supplier, and consumer (**Figure 2C**). China has heavily invested and acquired foreign cobalt mining operations primarily in the DRC since 2000, which has reduced their net

import reliance of raw cobalt from 97% to 68%.²⁰ Considering that China itself may experience cobalt supply deficits by 2030 unless efficient recycling targets are achieved,²¹ China's cobalt production will likely be prioritized for domestic battery manufacturers. Continued global reliance on cobalt may lead to competition for raw materials and ensuing conflicts similar to the rare earth metals trade dispute in 2010. These factors have generated interest into developing cobalt-free energy storage technologies.²² Risk of a disruption to the cobalt supply chain and the economic importance of the material have caused it to be included on both the 2017 European Union's list of Critical Raw Materials (CRM) as well as the 2018 United States Federal Registrar's list of critical minerals vital to the Nation's security and economic prosperity.²³

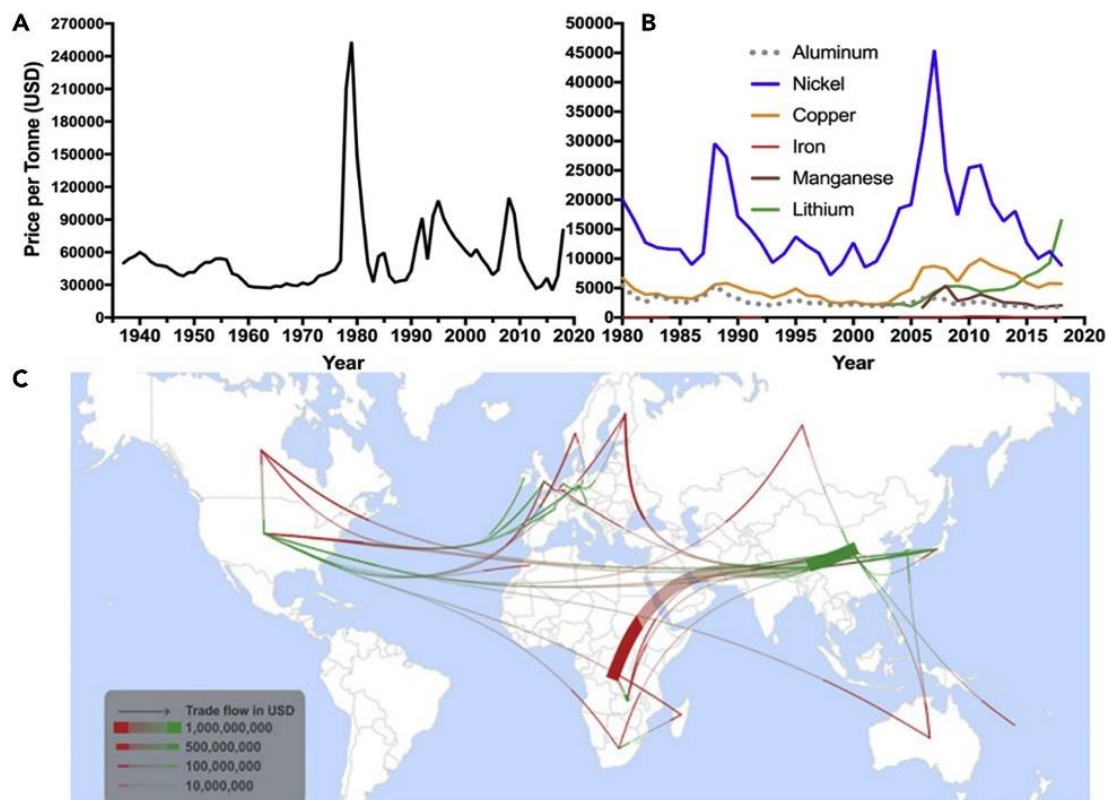


Figure 2. A) Historical inflation-adjusted commodity price of cobalt. B) Commodity price of other common metals used in LIBs. C) Trade flow of raw and processed cobalt. Reprinted with permission from Elsevier, 2020.²⁴

Additionally, the supply-demand balance of the resource should be considered. As mentioned, the growth in cobalt demand is dependent on the electrification of the automotive industry but is anticipated to be between 7-13% per year, bringing the total to around 390,000 tonnes in 2030. A report from Dias *et al.*¹⁶ describes a scenario where the demand will outpace the supply by 8000 tonnes in 2020 and upwards of 175,000 tonnes by 2030. This deficit risks disruption of the supply chain and threatens a rapid increase in the commodity price of raw cobalt. A second scenario was modeled for the surplus/deficit of cobalt affected by substitution (*i.e.*, the use of low-Co and Co-free chemistries in LIBs) which still indicated a deficit of 64,000 tonnes by 2030. LIB metal recycling is another important consideration when examining the supply and demand balance of cobalt as it can assist with the previously noted constraints surrounding the resource. However, owing to the continuous expansions in battery production (**Figure 1A**), production is expected to substantially outweigh the amount of end-of-life battery materials entering the waste stream over the foreseeable future. Furthermore, LIB recycling activities are concentrated in China, whereas infrastructure elsewhere consists of select private facilities focused on recovering high-value cobalt.²⁵ Although the recycling of end-of-life LiCoO₂ batteries in portable electronics is highly feasible and profitable, these are significant technical challenges and decreased financial motivation exist in recycling mixed-metal LIBs in EVs that will dominate the waste stream over the next decades.⁶ Furthermore, the dismantling of cells from EV battery packs is currently not economically feasible. Although the concept of repurposing end-of-life battery packs (~80% capacity retained) toward stationary energy storage has been proposed, it is not well developed.²⁶ Worldwide realization of LIB recycling will require legislation and political pressure, likely in the form of economic incentives (*e.g.*, refundable deposits with LIB purchases), public education, landfill disposal regulations, and defined responsibilities on the

collection and disposal of LIBs for consumers, retailers, and EV and battery manufacturers. Taken together, it is evident that cobalt-free cathodes are required for sustainable long-term applications of LIBs.

1.2. Thesis Organization

This thesis comprises seven sections. **Section 1** discusses the importance of reducing the reliance of cobalt in LIB manufacturing. **Section 2** introduces the reader to the general operating mechanism of LIBs and the currently available cobalt free and low-cobalt cathode materials. Ni-rich layered oxide cathode materials are discussed in detail, particularly their degradation mechanisms. Strategies to improve the performance of Ni-rich cathodes are then reviewed, which includes the synthesis of single crystal particles, the application of a surface coating, doping the lattice with certain transition metals, and developing novel electrolyte compositions. An emphasis is placed on discussing surface coatings, which is the central focus of the research. **Section 3** discusses the theory and rationale of the characterization, testing, and fabrication techniques used in this work. **Section 4** investigates the improvement in performance of a Ni-rich cathode coated by atomic layer deposition. Using conventional additive-free LIB electrolyte, the performance of four different coating materials was thoroughly compared and the mechanisms are discussed. This work reveals that the coatings primarily act by modifying chemical reactions at the electrode-electrolyte interface. Thus, the relationship between coatings and electrolyte additives is also discussed. **Section 5** investigates the mechanisms by which metal oxide coatings behave during battery operation in more detail in an attempt to delineate the impact of the surface coating versus transition metal doping mechanisms. ZrO_2 and CeO_2 coating materials were sintered on Ni-rich cathode particles at different quantities and temperatures to modify the coating thickness and degree of doping. The effects on performance were thoroughly

compared and analyzed. **Section 6** introduces a high-concentration electrolyte composition with excellent compatibility with Ni-rich cathodes. To further improve performance, the most promising coatings identified in the prior sections are paired with this electrolyte. The mechanism of the coating in the presence of this electrolyte is proposed. Finally, the conclusions, outstanding questions, and future research directions with respect to these projects are discussed in **Section 7**.

2. Background

2.1. LIB Operating Mechanism

Figure 3 below depicts the major components and operating mechanism of a conventional LIB cell. The negative and positive electrode correspond to the anode and cathode respectively during discharge and are conventionally designated this way. The separator typically comprises porous poly(ethylene)/poly(propylene) membrane, which is an electrically insulating material that prevents an electrical short-circuit due to electronic contact between the electrodes, but is porous to allow Li^+ transport. The electrolyte is typically lithium hexafluorophosphate (LiPF_6) dissolved in a mixture of ethylene carbonate and either dimethyl carbonate, diethyl carbonate, or ethyl methyl carbonate. This organic solvent is chosen due to its compatibility with graphite-based anode materials and high electrochemical stability, allowing the battery to operate at a higher voltage range. The operating principle relies on the intercalation and de-intercalation of Li^+ between the electrodes, where Li^+ can be reversibly inserted and removed from the host network. During charge, the positive electrode serves as a ‘source’ of lithium ions. A power source is applied to the battery in order to oxidize the transition metal oxide, resulting in the release of Li^+ into the electrolyte (*i.e.*, de-intercalation or de-lithiation) and simultaneously releasing an equimolar number of electrons into the external circuit. The electron combines with a Li^+ intercalated/inserted at the graphite-based negative electrode. During discharge, the reverse reaction occurs spontaneously, where electrons and Li^+ are simultaneously released from the negative electrode, and the electrons released can be used to power a load. A variety of different cathode materials are commercially available, with the most common being lithium cobalt oxide (LiCoO_2), lithium iron phosphate (LiFePO_4), lithium manganese oxide (LiMn_2O_4), NMC ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$), and NCA ($\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$). The various LIBs are referenced according to the

cathode composition, as the cathode dictates the battery capacity and energy density, while the anode is always a graphite-based material. LiCoO_2 was the first cathode material commercialized in LIBs by Sony in 1991. Due to the high cost of Co as established in **Section 1**, the other cathode materials are currently more prominent. Different materials have advantages and trade-offs with respect to energy density, power capabilities, cost, toxicity, safety, and stability.

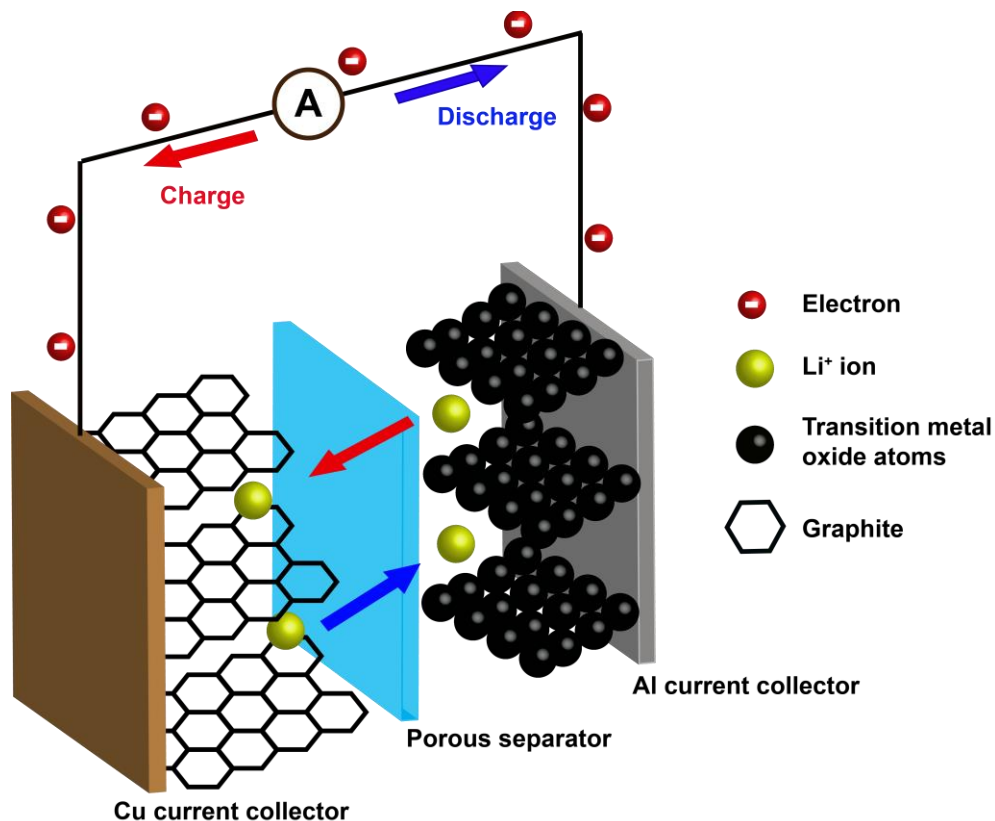
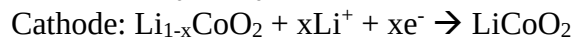
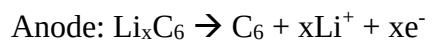


Figure 3. Components and operating mechanism of a lithium-ion battery. Reprinted with permission from Wiley, 2020.⁶



$$0 < x < 0.5^*$$

*For LiCoO_2 , over-extraction leads to severe phase changes and cobalt dissolution from the generation of Co^{4+}

2.2. Commercialized Cobalt-Free Cathodes

The following sections discuss the cobalt-free cathode materials that are currently commercially produced in LIBs. In brief, they have inherent limitations with respect to energy density and/or stability.

2.2.1. LiFePO₄

The olivine LiFePO₄ cathode has generated significant interest due to its cheap and abundant composition, and high thermal stability and safety associated with strong Fe-P-O bonds. This restricts the evolution of O₂ at high temperatures and limits thermal runaway. However, the main bottleneck toward application in EVs is the high cost relative to its energy density.²⁷ Although LiFePO₄ is known to have high electrochemical stability over a ~100% depth of discharge and a flat charge/discharge profile, thus allowing the practical capacity to approach the theoretical one, the low energy density is attributed to the low nominal voltage (3.3 V vs graphite anode) and poor packing/tapped density (g cm⁻³) of LiFePO₄ particles.²⁸ The poor packing density is because LiFePO₄ must be synthesized as carbon-coated nanoparticles.^{29,30} Synthesizing this morphology is necessary as LiFePO₄ displays poor intrinsic electronic and ionic conductivity. The poor electronic conductivity is due to the localized positions of Fe²⁺ and Fe³⁺ (LiFePO₄/FePO₄). Li⁺ can only diffuse in 1D along the *b*-axis formed by edge-shared LiO₆ octahedra. The nanoparticle morphology improves electrical conductivity by improving interparticle contact and also reducing the electron transport path and tunneling barrier between the particle surface and core. Meanwhile, the conductive carbon coating (permeable to Li⁺) ensures electrical percolation. The nanoparticle morphology also reduces the solid-state diffusion path for Li⁺.

The lower energy density of LiFePO₄ compared to other cathode materials limits the driving range of EVs, and thus it has achieved limited penetration in Western markets. Furthermore,

although the material composition of LiFePO_4 is cheap, costs associated with the complexity of the synthesis procedure tends to be high. The electrochemical performance of LiFePO_4 is highly sensitive to the preparation method, requiring rigorous control of morphology, particle size distribution, coating homogeneity, and reagent purity while ensuring that Fe^{2+} is not oxidized to Fe^{3+} for performance consistencies.^{31,32} Lowered costs of LiFePO_4 through maturity and economies of scale will expand its applicability.

Recently, interest in LiFePO_4 even for EV applications has resurged, due to its cobalt and nickel-free composition and potentially low cost. In China, it has been adopted by major EV manufacturers, such as the BYD Company and the Wanxiang Group Corporation. Most electric buses (~99% of the global stock concentrated in China) utilize LFP batteries.³³ Tesla Motors also announced in 2021 that it will implement LiFePO_4 for EVs with a lower driving range. Thus, LiFePO_4 will likely be prevalent in applications where cost, safety, and stability is more critical than the energy density.³⁴

2.2.2. LiMn_2O_4

Spinel LiMn_2O_4 , comprising a 1:1 mixture of Mn^{3+} and Mn^{4+} (denoted $\text{Mn}^{+3.5}$), is known for its high rate performance due to the 3D solid-state diffusion pathways for Li^+ . Its high average voltage (~4 V vs Li/Li^+) also enables high power output. It is worth mentioning that layered LiMnO_2 is unstable after electrochemical cycling and transforms into the spinel structure.

Although the high power output of LiMn_2O_4 makes it ideal for application such as power tools, its main setback is the low practical capacity and cycle stability. This is caused by the presence of Mn^{3+} , which due to its electronic configuration ($t_{2g}^3-e_g^1$) can induce Jahn-Teller distortion.³⁵ The Jahn-Teller distortion of Mn^{3+} can cause lattice changes from the cubic to tetragonal phase,

which increases the resistance for Li^+ diffusion. The distortion is more pronounced when discharging at high rates as Li^+ is more concentrated at the surface of the LiMn_2O_4 particles, which leads to more pronounced distortion and causes particle cracking and disconnection.³⁶ Moreover, Mn^{3+} is unstable and generates soluble Mn^{2+} based on the disproportionation reaction: $2\text{Mn}^{3+}(\text{solid}) \rightarrow \text{Mn}^{4+}(\text{solid}) + \text{Mn}^{2+}(\text{solution})$. Suppression of Jahn-Teller distortion has commonly been addressed by partially substituting Mn with other cations to reduce the amount Mn^{3+} ,^{37–39} while various coatings and particle morphologies have been explored to suppress the dissolution of Mn.⁴⁰ Ultimately, the poor reliability of LMO limits it toward niche applications.

2.3. Ni-Rich Layered Oxide Cathodes

In contrast to the previously discussed materials, layered oxide-type cathodes typically possess the highest combination of energy density, cycle stability, and rate performance. Thus, they are the most promising to reach the high energy and lifetime requirements expected for EVs. The general lattice structure is shown in **Figure 4**, where the oxygen lattice forms a cubic close packed structure while Li and transition metals (TMs) occupy the octahedral 3b and 3a Wyckoff sites, respectively. At a macroscale, the structure is comprised of alternating transition metal oxide (TMO) and Li slabs/layers. The distance between TMO slabs is known as the interlayer space.

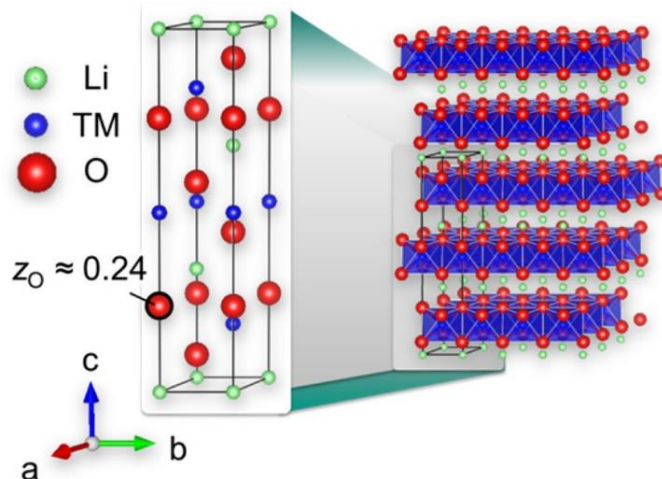


Figure 4. Unit cell and lattice structure of layered-type cathodes. Reprinted with permission from the American Chemical Society, 2017.⁴¹

The $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC-type) cathodes are the most established and commercially relevant series of layered oxide cathodes. Ni-rich layered oxides are typically associated with $x \geq 0.8$. In this solid blend, Mn^{4+} is electrochemically inactive and assists with thermal and electrochemical stability, while Co^{3+} contributes to the intrinsic electronic conductivity and suppresses cation site exchange between Ni^{2+} and Li^+ .^{42,43} Ni exists as either Ni^{2+} or Ni^{3+} in the pristine material, where capacity primarily comes from the $\text{Ni}^{2+} \rightleftharpoons \text{Ni}^{3+} \rightleftharpoons \text{Ni}^{4+}$ redox with some contribution from $\text{Co}^{3+} \rightleftharpoons \text{Co}^{4+}$ at higher voltages. A higher Ni/Mn^{4+} ratio in $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ increases the average valence of Ni based on charge balance, resulting in more reliance on the $\text{Ni}^{3+} \rightleftharpoons \text{Ni}^{4+}$ redox, which is more favorable compared to the $\text{Ni}^{2+} \rightleftharpoons \text{Ni}^{3+}$ redox. Thus, a higher capacity and energy density can be achieved at the same upper cut-off voltage as shown in **Figure 5**. A 4.3 V vs Li/Li^+ upper cut-off voltage is most commonly used in research studies and the reference point for the discussion below. At the same time, the amount of cobalt in the material is reduced. $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111, $\sim 160 \text{ mAh g}^{-1}$, 20.4 wt% Co) was the first reported and commercialized NMC-type material, and is well established for its safety and reliability.^{44,45} In an effort to increase energy density, $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622, $\sim 180 \text{ mAh g}^{-1}$, 12.2 wt%

Co) was developed, and this composition or small deviations from this are widely commercialized and currently employed in EVs. $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811, $\sim 200 \text{ mAh g}^{-1}$, 6.1 wt% Co) and even higher Ni compositions are under development in both academic and commercial settings, although their poor cycle stability and safety remain problematic.⁴³ Similarly, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) is a ‘low cobalt’ (9.2 wt% Co) cathode composition known to display a similar energy density to NMC811, although with better cycle retention but poorer thermal stability.

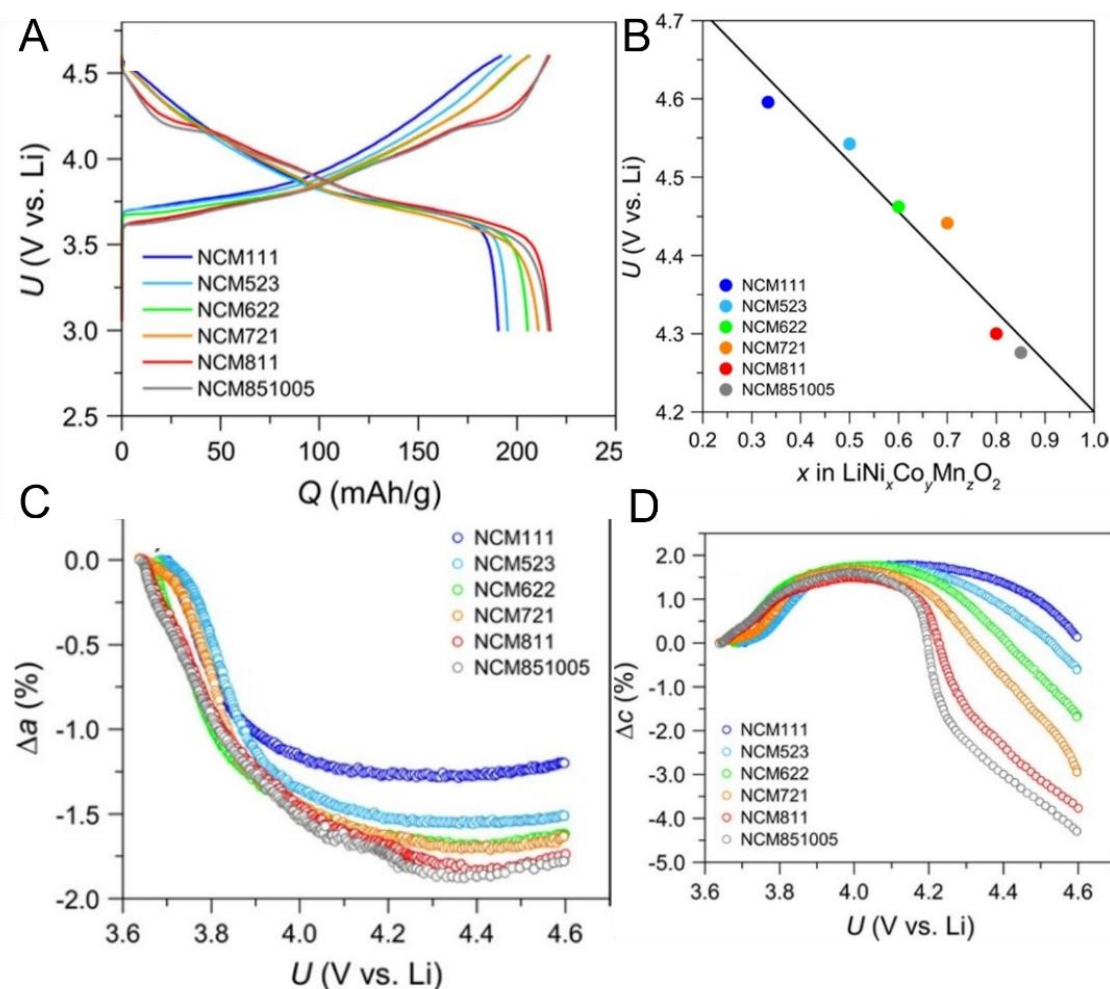


Figure 5. A) Initial discharge capacity of various NMC compositions cycled between 3 – 4.6 V vs Li/Li^+ . B) Cut-off voltage of various NMC compositions required to reach an energy density of 750 Wh kg^{-1} . C) Relative changes in the a -axis and D) c -axis lattice parameter as a function of cell voltage for various NMC compositions. Reprinted with permission from the American Chemical Society, 2017.⁴¹

NMC811 demonstrates poor cycle and thermal stability compared to NMC622 and NMC111 due to its increased moisture sensitivity, $\text{Li}^+/\text{Ni}^{2+}$ cation mixing, electrolyte side reactions, and phase transitions toward spinel and rock-salt structures along with gas evolution (O_2 , CO , and CO_2) at elevated temperatures and voltages.^{43,46} The issue with $\text{Li}^+/\text{Ni}^{2+}$ cation mixing occurs in the synthesis of nickel-rich cathodes, as the formation of Ni^{3+} ($t_{2g}^6 e_g^1$) is unfavorable due to the unpaired e_g electron.⁴⁷ The Ni^{2+} (0.69 Å) which is formed instead has a similar ionic radius to Li^+ (0.76 Å), and thus these two cations can undergo site exchange. The oxidation of Ni^{2+} present in the Li slab is known to generate poor charge-discharge cycle reversibility, since this causes local contraction of the interlayer distance, impeding Li^+ diffusion. As Ni^{2+} is also generated during cycling, a high initial amount of Ni^{2+} in the Li slab is believed to accelerate further $\text{Li}^+/\text{Ni}^{2+}$ mixing and structural degradation. To suppress Ni^{2+} formation during synthesis, a stoichiometric excess of Li precursor is often added. These residual species aggregate on the particle surface and react with moisture/ CO_2 , forming $\text{LiOH}/\text{Li}_2\text{CO}_3$ species, which can react with the electrolyte and increase the cell impedance.

Recent work has demonstrated that most of the degradation mechanisms of NMC811 during electrochemical cycling can be ascribed to its high capacity (Li utilization), rather than problems associated with Ni.⁴⁸ Several phase changes are observed in NMC811 upon de-lithiation: a hexagonal to monoclinic ($\text{H1} \rightarrow \text{M}$) transition at ~ 3.8 V vs Li/Li^+ , the $\text{M} \rightarrow \text{H2}$ transition at ~ 4 V vs Li/Li^+ , and the $\text{H2} \rightarrow \text{H3}$ transition at ~ 4.2 V vs Li/Li^+ . During the $\text{H1} \rightarrow \text{M}$ and $\text{M} \rightarrow \text{H2}$ phase transitions, the c -axis lattice parameter expands due to the loss of charge-screening Li^+ , resulting in increased repulsion between anionic oxygen in neighbouring TMO layers that widen the interlayer space (**Figure 5D**).⁴⁹ The $\text{H2} \rightarrow \text{H3}$ phase change is relatively unique to Ni-rich layered cathodes and responsible for a $\sim 5\%$ contraction of the c -axis lattice parameter and an

increased covalency of TM-O bonds. This is likely caused by loss of electron density of the lattice oxygen, which decreases the anionic charge density and relieves the interlayer repulsion. Throughout de-lithiation, the a -axis shrinks (**Figure 5C**), which reflects a shortened TM-TM distance, likely due to the increased oxidation state of Ni.⁴⁹ As changes in the c and a -axis dimensions behave quite differently, this causes the anisotropy of the lattice volume change.

This resulting volume change can lead to mechanical failure from particle cracking/pulverization (see **Section 2.4.1**). Clearly, Ni-rich NMC cathodes experience more severe lattice volume changes (**Figure 5D**). It has been hypothesized that a high nickel content is responsible for the H2 $\rightarrow$ H3 transition, potentially due to the transfer of electrons from lattice oxygen to nickel atoms at high voltages.⁵⁰ However, Li *et al.*⁴⁸ recently demonstrated that this phase transition is universal for $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ materials and evolution of the c -axis parameter is dictated by the degree of de-lithiation (**Figure 6B**). The H2 $\rightarrow$ H3 phase transition is not typically observed for NMC111 and NMC622 because they must be charged to voltages ≥ 4.6 and ≥ 4.5 V vs Li/Li⁺ respectively, which is impractical due to electrochemical oxidation of the electrolyte (**Figure 6A**). Thus, the H2 $\rightarrow$ H3 phase transition occurs due to thermodynamic instability of the highly de-lithiated lattice structure.

The H2 $\rightarrow$ H3 phase transition is also associated with O₂ gas evolution, driven by the oxidation of lattice oxygen atoms at high voltages. O₂ release is surface-initiated and is accompanied with phase changes from the layered (MO₂) $\rightarrow$ spinel (M₃O₄) $\rightarrow$ rock salt (MO) phase on the particle surface (**Figure 6C and 6D**). This surface-reconstructed layer has been shown to grow in thickness over extensive cycling, resulting in a build-up of cell impedance. Jung *et al.*⁵¹ suggested that oxygen release occurs due to thermodynamic instability of the layered structure at high degrees of de-lithiation, and that oxygen release is surface-initiated due to kinetic hindrance

of oxygen anion transport throughout the bulk. This is supported by the fact that bulk oxygen release and phase changes (toward spinel/rock salt) occur at elevated temperatures and delithiated states.⁵² Furthermore, based on thorough gas analysis measurements, they observed that oxygen evolution closely coincided with the release of CO and CO₂ gas, which are oxidation products of the carbonate-based electrolyte. Thus, they suggested that the released oxygen was in a reactive singlet state, which oxidizes the carbonate electrolyte, and that this mechanism is far more prevalent than the direct electrochemical oxidation of the electrolyte. These findings indicate that the primary failure mechanisms of nickel-rich cathodes are associated with their high achievable depth of discharge (DOD, *i.e.*, Li utilization) and ensuing H2 → H3 phase transition. While this explanation/model is both comprehensive and compelling, it is not universally accepted. For instance, it is also widely believed that at high voltages, Ni⁴⁺ directly oxidizes the electrolyte solvent, which forms Ni²⁺, leading to Li⁺/Ni²⁺ mixing and the formation of a surface Ni-O rock salt phase. Oxygen release ensues from this phase transition.

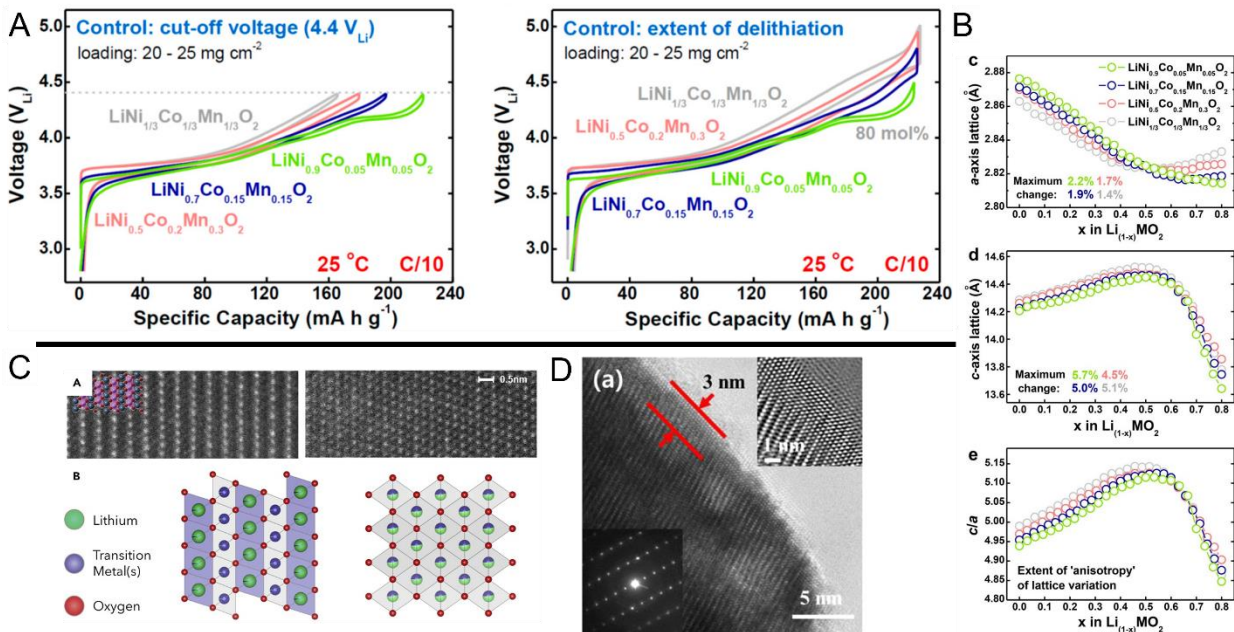


Figure 6. A) Comparison of various NMC-type cathodes under the same voltage range (left) and specific capacity (right). B) Comparison of lattice parameters and volumes of various NMC-type cathodes normalized by specific capacity (proportional to Li content). Reprinted with permission from the American Chemical Society, 2019.⁴⁸ C) Comparison of layered (left) and rock salt (right) structures. Reprinted with permission from Elsevier, 2020.²⁴ D) HR-TEM image showcasing rock salt surface layer on cycled NMC811 particle. Reprinted with permission from the American Chemical Society, 2017.⁵³

While stable cycling of NMC811 can be achieved by restricting the upper cut-off voltage to ~ 4 V vs Li/Li^+ , this severely impacts its energy density for practical applications. Thus, it is critical to develop strategies to address these failure mechanisms.

2.4. Modification of Ni-Rich Layered Oxide Cathodes

At the material level, the three general modification strategies to tailor performance involve 1) morphology control (*e.g.*, generation of nanocomposites, nanostructures, or polycrystalline vs. single-crystalline particles), 2) application of a surface coating, and 3) introduction of lattice dopants that improve the structural stability and/or enhance the conductivity. This section

reviews the application of these strategies to Ni-rich layered oxide materials with an emphasis on surface coatings.

2.4.1. Single Crystal Ni-Rich Cathodes

Ni-rich layered oxide cathodes are conventionally synthesized as 10-15 μm -size aggregates of 100 – 300 nm size primary particles. This ‘polycrystalline’ morphology is a product of the co-precipitated mixed-metal $\text{Ni}_x\text{Mn}_y\text{Co}_z(\text{OH})_2$ precursor, which can be produced at large scales (**Figure 7A**). The large size of the secondary particles enables a high particle tapped density, which closely correlates with the achievable volumetric energy density of compacted electrodes. However, a key degradation mechanism of polycrystalline particles is interparticle fracture at the grain boundaries over extended cycling due to anisotropic volume changes of the randomly oriented aggregated primary nanoparticles (**Figure 7C**). As discussed previously, this is primarily induced by the $\text{H2} \rightarrow \text{H3}$ phase transition. High current charge/discharge can also elevate anisotropic volume changes, as this results in a heterogeneous lattice structure with Li-rich and Li-poor phases.⁵⁴ Furthermore, fractures can form when the electrode is calendared at excessively high pressures.⁵⁵ These fractures expose fresh surfaces, leading to additional side-reactions with the electrolyte at high voltages, oxygen release, surface reconstruction, etc. that generate impedance growth and irreversible consumption of Li^+ as discussed previously. They can also lead to particle disintegration from the electrode and rapid performance decay.

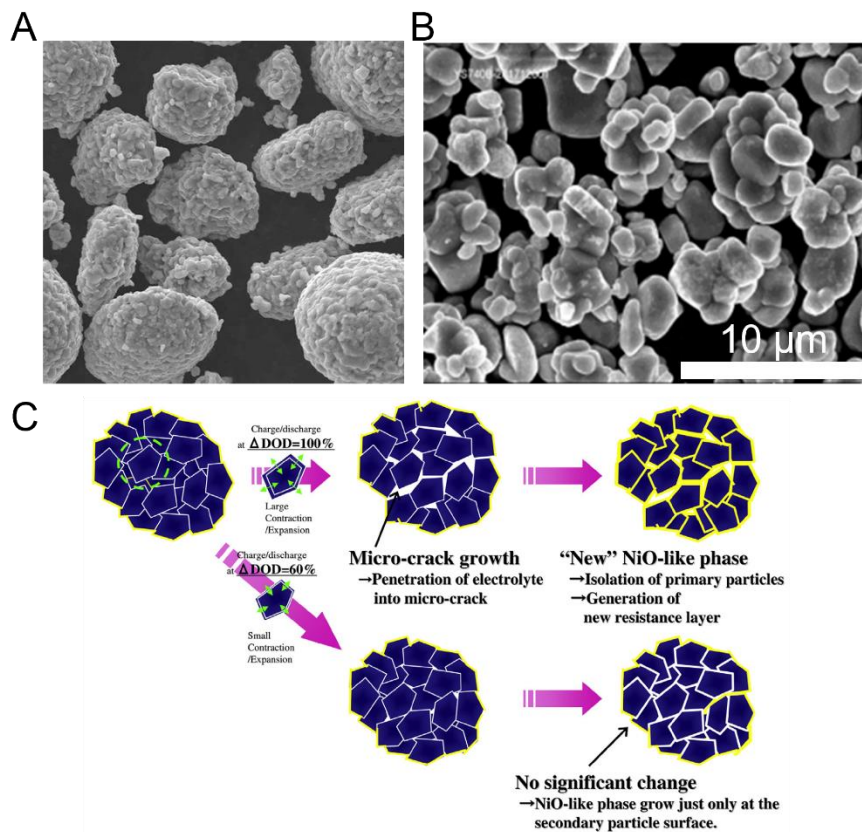


Figure 7. A) Polycrystalline and B) single crystal particle morphology. C) Schematic of particle cracking in Ni-rich cathode materials during charge/discharge with depth of discharge (DOD) at 60% and 100%. Reprinted with permission from Elsevier, 2014.⁶²

A promising approach to address these problems is to synthesize nickel-rich cathodes as micron-sized single crystal particles (**Figure 7B**). Compared to polycrystalline particles, single crystal particles have a uniform crystallographic orientation and the minimal number of grain boundaries can thus mitigate particle cracking and side reactions with the electrolyte.^{56,57} This property was observed by Li *et al.*⁵⁷ who showed that single crystal $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC532) had superior capacity retention over the polycrystalline variants with similar particle size when prepared in NMC532/artificial graphite full cells with selected electrolytes. Negligible gas evolution was also observed in the single crystal material after holding at high voltages ($\geq 4.4\text{V}$) for 300 h, showing that larger grain size and lower specific surface area of the particles decreased the amount of oxidation of electrolyte species on the particle surface.

However, the key limitation of single crystal particles is the low tapped density of the cathode powder, as the overall particle sizes are smaller (2 – 5 μm) and thus generate more interparticle friction. Powder tapped density directly correlates with the achievable volumetric energy density of the fabricated electrode. Furthermore, as the primary particle size is large with uniform crystallographic orientation, this increases the solid-state diffusion length of Li^+ and diminishes the rate/kinetic performance. It has been demonstrated that solid-state lattice diffusion of Li^+ is much slower compared to diffusion across grain boundaries.⁵⁸ Thus, despite their aggregation, the nanometer-sized primary particles in polycrystalline samples enables a high rate performance. The kinetic hindrance of single crystalline particles is reflected by a loss of discharge capacity in the low-voltage region ($\sim 3.4 - 3.6$ V vs Li/Li^+).⁵⁸ However, it should be noted that intragranular cracks can also form within single crystal particles at high DODs.⁵⁹ This occurs from lattice strain due to the formation of Li-rich and Li-poor domains within a particle, resulting in mismatched volumes.

Single crystal particles can be synthesized from the same $\text{Ni}_x\text{Mn}_y\text{Co}_z(\text{OH})_2$ precursor used for polycrystalline particles. ‘Lithiation’ is conducted by forming a solid-state reaction (750 – 900 $^\circ\text{C}$) with LiOH or Li_2CO_3 under oxidizing conditions to yield $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$. The sintering is often performed under flowing oxygen atmosphere to ensure that Ni is in the Ni^{3+} state. This is important as Ni^{2+} (0.69 Å) has a similar ionic radius to Li^+ (0.76 Å), which can cause site exchange or cation mixing. As discussed, oxidation of Ni^{2+} in the Li layer causes a local contraction of the interslab distance, resulting in first-cycle irreversible capacity loss. To avoid $\text{Ni}^{2+}/\text{Li}^+$ intermixing, it is also important to add a stoichiometric excess (typically 5 – 10 mol%) of Li precursors for the sintering process. This is because some Li is lost during sintering, and this deficiency will promote the migration of Ni into the Li layer.

In general, the single crystal morphology can be generated using higher Li/TM ratios (stoichiometric excess of Li) and elevated sintering temperatures.⁶⁰ The excess Li species can generate a flux-type environment to assist crystal growth. The mechanism is related to Ostwald ripening in molten salts: during sintering, the small crystals dissolve into the liquid flux and subsequently redeposit on larger crystals, where the flux generates an accelerated shuttle effect for mass transfer during calcination, forming highly crystalline and large-size oxide particles at lower temperatures than typically required.^{56,61} A separate inorganic flux reagent (*e.g.*, NaCl or KCl) can also be added, which can alleviate the elevated temperature and Li/TM ratio requirement.⁵⁶

2.4.2. Coatings for Ni-Rich Layered Oxide Cathodes

Applying a surface coating is a universal approach to improving the performance of existing electrode materials. In general, coatings are divided into three broad classifications:

- 1) redox-inactive metal coatings (**Figure 8A**), which include metal oxides, metal phosphates, metal fluorides, etc. These are relatively wide bandgap materials that are intended to increase the activation energy of side reactions between the electrode and electrolyte at elevated voltages and temperatures, and stabilize the solid/cathode electrolyte interphase (SEI/CEI) layer impedance. However, since they can potentially impede Li^+ and electron transport, it is critical to optimize the choice of material and coating thickness. In addition, they can serve as a physical barrier to suppress active material dissolution, oxygen evolution, and harmful reactions with moisture or air. Metal coatings can also help protect the electrode from mechanical degradation. Polymer coatings that are electronically insulative but ionically conductive can achieve a similar effect, although fewer candidate materials are available.

- 2) conductive carbon coatings (**Figure 8B**), which include graphene-based structures, carbon black, and conductive (conjugated) polymers (*e.g.*, polypyrrole). These help generate a percolated electronically conducting network on the surface of the particles. A uniform carbon coating is more effective at enhancing percolation compared to the conductive carbon additive in the composite electrode, which can only form point contacts with the active particles.⁶³ Thus, the coating can reduce the amount of conductive additive required.⁶⁴
- 3) core-shell structures (**Figure 8C**), where both the core and shell material are redox-active. Typically, the core material exhibits high capacity and low stability, while the shell material has lower capacity while demonstrating improved structural, interfacial, and thermal stability. The core-shell structure can produce an intermediate in performance between the core and shell material alone. To eliminate the potential mismatch in properties (*e.g.*, degree of volume change) between the core and shell material, concentration-gradient core-shell structures (**Figure 8D**) have been developed for layered mixed-metal oxides. The concentration of the redox active metal linearly increases from the surface to the center of the particle.

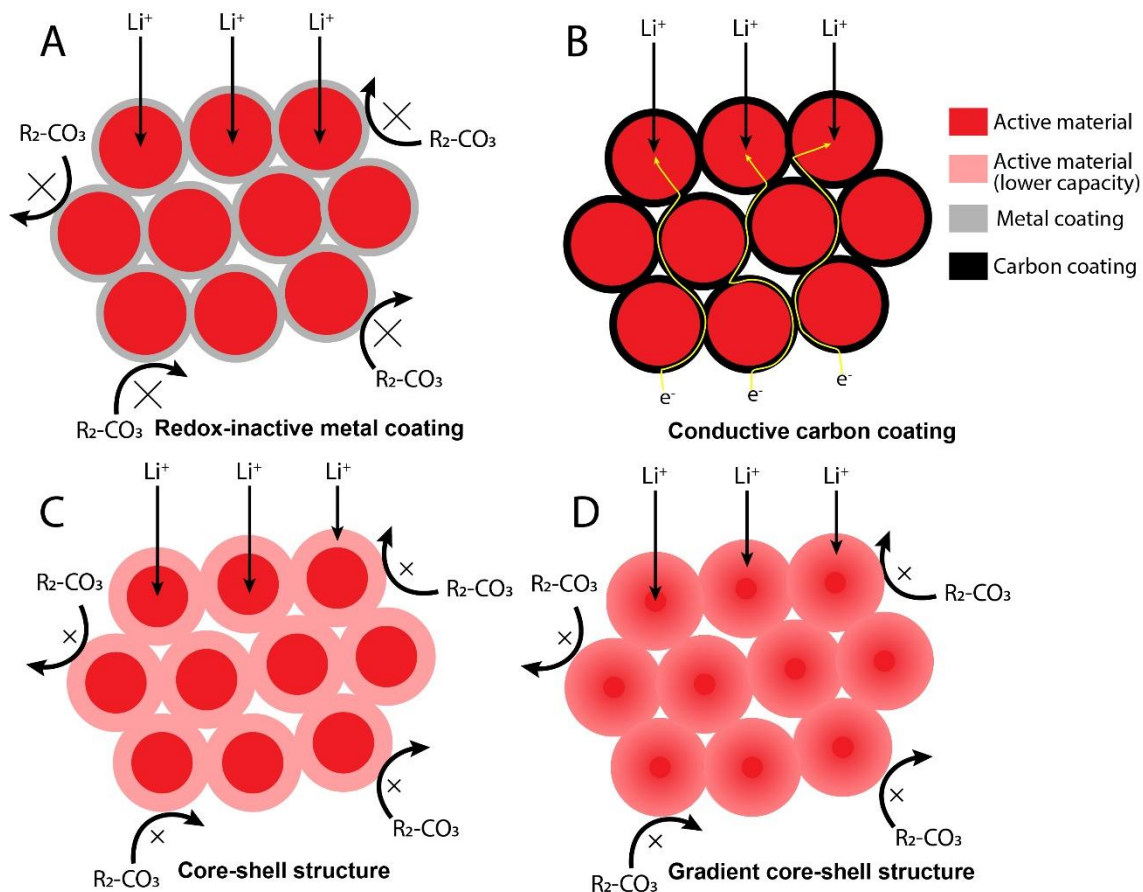


Figure 8. General classification of coatings. Reprinted with permission from Springer Nature, 2022.⁶⁵

In general, coatings should be stable over the desired voltage range, have sufficient Li^+ permeability, bind sufficiently to the active particles, and display the required mechanical robustness to accommodate potential volume changes of the active particles during Li^+ (de)insertion. The most common approaches to apply coatings to electrode active materials include:

- 1) mechanical mixing of the pre-prepared active material with coating precursors, followed by heat treatment to generate the coating (**Figure 9A**). While this approach is simple and scalable, the coatings tend to be nonuniform with incomplete surface coverage.⁶⁶ This is not

ideal for coatings intended to protect the active material from side-reactions with the electrolyte.

- 2) solution casting to improve coating conformality, where the active material powder and coating precursors are uniformly dispersed in an appropriate solvent, followed by solvent evaporation and sintering (**Figure 9B**). This approach can potentially raise scale-up concerns due to the large consumption of solvent. For active materials and coating precursors that have poor compatibility in a particular solvent, surface modification, surfactant, or polymer grafts may be used to improve dispersion. Nanoparticles coated by solution casting are often sterically stabilized in solution with a surfactant or polymer graft due to their tendency to aggregate.
- 3) *in situ* synthesis, where the coating is applied simultaneously during the synthesis of the active material. For instance, carbon precursors can be added to the sol-gel or hydrothermal reaction mixture, and subsequent sintering crystallizes the active material and forms the conductive carbon coating (**Figure 9C**). The carbon coating and active material can also be synthesized through a one-step solid-state route (**Figure 9D**).
- 4) application of ultrathin and conformal coatings via atomic layer deposition (ALD). ALD is a thin film deposition technique that has garnered interest over the past decade. It involves a self-controlled binary reaction sequence where two precursors are sequentially pulsed and react with the surface of a substrate (**Figure 9E**). It can achieve atomic-scale thickness control (~ 0.1 nm) with high conformality, although the film growth is slow, and the technique has not been adapted for large-scale applications. With this approach, the coating can be applied either on the active particles or on the fabricated electrode (including the binder and conductive additive).

5) chemical vapor deposition (CVD), which typically involves the pyrolysis of gaseous carbon precursors over the active particles to form a carbon coating.

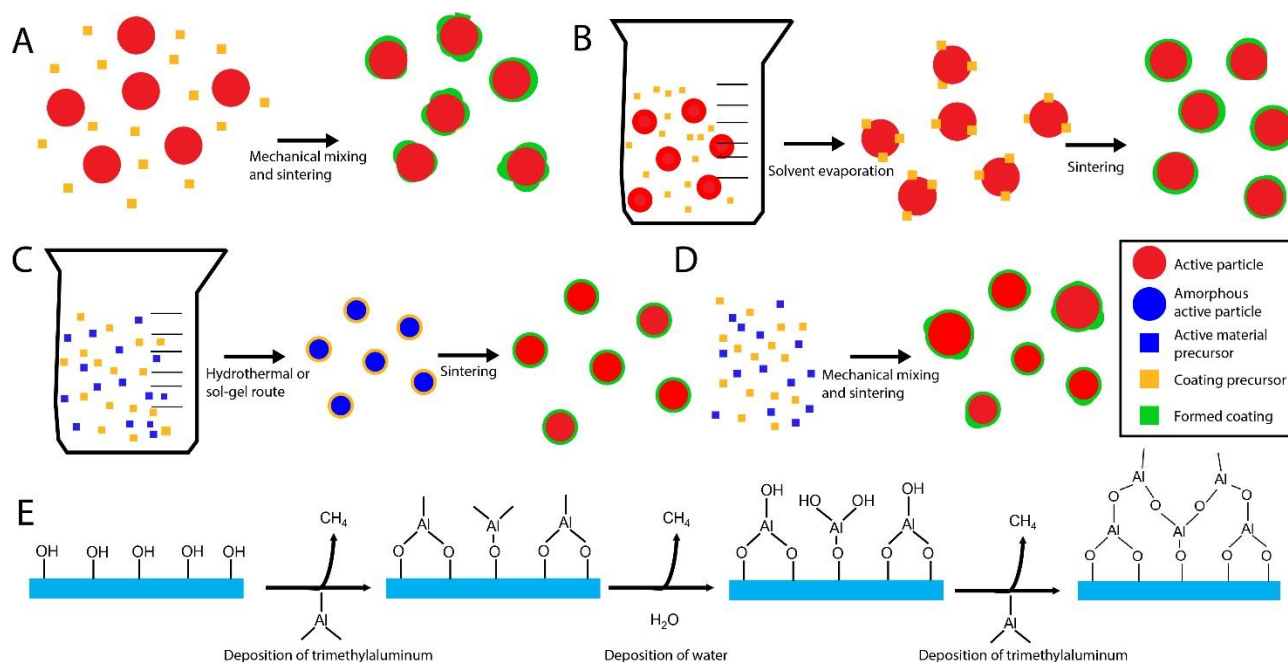


Figure 9. Common approaches to apply coatings. A) Mechanical mixing of active particles and coating precursors, forming a nonuniform coating after sintering. B) Solution casting approach to deposit coating. C) *In-situ* application of coating in solution synthesis of active material. D) *In situ* application of coating in solid-state synthesis. E) Mechanism of Al_2O_3 coating by ALD (1.5 cycles) using trimethylaluminum and water as precursors. Coating can be applied on the active particles or on the fabricated electrode. Reprinted with permission from Springer Nature, 2022.⁶⁵

2.4.2.1. Redox-Inactive Metal Coatings

Redox-inactive metal coatings (metal oxides, metal phosphates, metal fluorides, *etc.*) have been extensively explored to extend the lifetime of layered TMO structures cycled at high cut-off voltages. The earliest work on metal coatings to stabilize layered TMOs focused on expanding the cycling voltage window (capacity utilization) of $\text{Li}_{1-x}\text{CoO}_2$ (LCO), which has a stability window from $x = 0 - 0.5$, where structural transition from the hexagonal to monoclinic phase occurs at $x > 0.5$ (4.1 – 4.2 V vs Li/Li^+). Cho *et al.*⁶⁷ applied an Al_2O_3 coating on LCO for the

first time using a wet chemistry approach, and continued their investigation by comparing the effects of ZrO₂, Al₂O₃, TiO₂, and B₂O₃ coatings.⁶⁸ These coatings enhanced the cycle stability over a wider voltage range (2.75 – 4.4 V vs Li/Li⁺), enabling extended capacity utilization. They observed that the coating suppressed the *c*-axis lattice expansion upon Li⁺ extraction, and thus reasoned that the coating physically constrained the high-voltage transition from the hexagonal to monoclinic phase. The strong performance of ZrO₂ over the other materials was ascribed to its high fracture toughness. However, this explanation was disputed by Chen and Dahn^{69,70} due to the unlikeliness of a thin coating being able to supply the required stress on the LCO particles to resist phase transitions, and also found no differences in *c*-axis expansion between the pristine and coated samples. They instead proposed that the coatings mainly suppressed impedance growth on the surface of LiCoO₂. The impedance growth was linked with the use of LiPF₆ electrolyte.

Currently, the established benefits of metal coatings for cathodes involve one or more of the following effects:

- 1) They provide a physical barrier to mitigate the dissolution of active material and release of gaseous species. Active material dissolution is particularly concerning for cathodes reliant on the Mn³⁺/Mn⁴⁺ redox for charge compensation, as Mn³⁺ is Jahn-Teller active and undergoes disproportionation to form soluble Mn²⁺. Dissolved Mn²⁺ can diffuse and deposit onto the anode or cathode, which further throttles the cycle stability, especially in full cells.^{71–73} For other transition metals, dissolution is typically associated with HF corrosion. HF can be generated when LiPF₆ reacts with (unavoidable) trace quantities of water in the electrolyte according to **Equation 1**:



Moreover, coatings can improve the stability of active particles under ambient conditions by suppressing surface oxidation and formation of LiOH and Li₂CO₃ species on the surface, which contribute to interfacial impedance. These residual species also evolve gaseous products during cycling by electrochemical oxidation and reactions with the electrolyte, which presents safety concerns.^{74,75}

Optimizing the coating conformality and thickness is critical for this application. Sufficient coating material should be applied to ensure complete surface coverage, but coatings that are too thick can impede Li⁺ and electron transport, resulting in poor electrochemical performance. To help address this problem, Li⁺-conductive coatings have been employed. As discussed above, ALD can also be used to apply nanometer-thick coatings with high conformality.

2) On a related note, metal coatings can suppress impedance growth by surface modification of the active particles. Coatings can reduce electrolyte decomposition by masking side-reactions between the nucleophilic oxide groups in the TMO layers and the electrophilic alkyl carbonates in the electrolyte solvent. This mitigates the continuous build-up of the CEI layer and also the side-reactions that lead to the release of gaseous products.⁷⁶ Suppression of electrolyte oxidation at the cathode interface is critical for commercial cells with graphite anode, as the oxidized products can deposit on the anode surface. Excessive build-up on the anode surface results in rapid capacity decay by hindering Li⁺ transport, which is known as ‘rollover failure’.

Although the mechanism is unclear, coatings have been shown to mitigate lattice oxygen release at high cut-off voltages and temperatures, which is accompanied with phase changes (layered → spinel and rock salt structure) at the surface (*i.e.*, surface reconstruction/degradation) that can propagate through the bulk, subsequently increasing cell

impedance.^{77–79} It has been suggested that oxygen release is surface-initiated due to the poor kinetics of oxygen/oxide diffusion through the bulk cathode particles.^{51,52} Thus, an applied coating can potentially mitigate oxygen release by kinetic hindrance. Another explanation is the occurrence of metal doping (see below) on the particle surface, which can generate a structurally stable surface layer.⁸⁰ These coatings must be electrochemically inactive (stable valence state), electronically insulating, and insoluble, while also sufficiently ionically conductive. In this sense, they can be thought of as an artificial CEI layer. Metal oxide coatings (*e.g.*, Al₂O₃) can also serve as a Lewis base and quench HF according to:



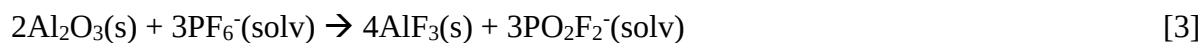
This ‘HF scavenging’ effect is considered highly significant for the stability of LIB cathodes due to the reliance on LiPF₆ salt and subsequent HF generation.⁸¹ This effect modifies the composition and properties of the CEI layer. The reaction depicted in **Equation 2** indicates water formation and suggests subsequent regeneration of HF and attack of Al₂O₃. This has led to explorations in applying metal fluoride coatings directly, which are resistant to HF corrosion and thus may provide improved long-term stability.^{82,83}

The exact relationship between the CEI composition and its stability based on the coating applied is unclear. CEI composition is often studied by *ex-situ* X-ray photoelectron spectroscopy (XPS) on cycled electrodes. The deposition of LiF on the electrode surface is generally correlated with HF generation in the electrolyte, as it is a product in **Equation 1**. This explains why in many studies, coated electrodes that can undergo HF scavenging according to **Equation 2** appear to have a lower amount of LiF in the CEI compared to uncoated counterparts.^{84,85} However, some studies have shown the opposite trend.^{86,87} LiF species are inherently insulating and contribute to

the impedance of the CEI/SEI layer,⁸⁸ but they are also known to improve its structural stability.⁸⁹

Regardless, due to the HF scavenging effect, cycled coated electrodes generally show a higher amount of fluoride species in the CEI layer, although the exact composition of the species is uncertain.^{86,87,90–92} Lu *et al.*⁸⁴ suggested that AlPO₄ and Al₂O₃ coatings promote the formation of metal fluorides, oxyfluorides, and PF_x(OH)_y species, which can help produce a stable and protective CEI layer that reduces further impedance growth over extended cycling. This appears similar to the mechanism of fluorinated electrolyte additives that undergo reductive decomposition at the anode and introduce fluoride species (including LiF) that help produce a stable and compact solid-electrolyte interphase (SEI) film, significantly improving cycle stability. Although the nature of the CEI layer is less studied, these additives can also be oxidized at the cathode at sufficiently high cut-off voltages and modify and stabilize the surface film.⁹³ The electronegative fluoride species can enhance network formation and aggregation of organic salts, which improves the mechanical strength and suppresses the dissolution of SEI/CEI layer components into the electrolyte.^{89,94}

Recently, Hall *et al.*⁹⁵ proposed an additional mechanism for Al₂O₃ coatings, indicating that they could react with the PF₆[−] counterion as shown in **Equation 3**:



PO₂F₂[−] is a known electrolyte additive that increases the fluoride content in both the CEI and SEI layer and controls impedance growth, thus extending the cycle life.^{96,97} These findings indicate that modification of the CEI/SEI layer composition is a significant mechanism of action for metal coatings and should be studied in more detail. In general, the mechanisms and chemical pathways responsible for the formation/modification of the SEI/CEI film and their relation to cell

performance are poorly understood. The discussion above suggests some overlap in mechanisms with electrolyte additives. For instance, vinylene carbonate is a commonly used electrolyte additive that is known to reduce electrolyte oxidation at the cathode surface. Preferential oxidation of this additive results in a radical polymerization that forms a stable film at the CEI.

3) Mechanical protection against electrode cracking, exfoliation, and disintegration.

As discussed previously, anisotropic volume changes from high-voltage phase transitions can generate interparticle stress in polycrystalline particles, generating cracks between particles. This opens channels for electrolyte penetration, resulting in increased electrolyte side reactions, and can also lead to particle disintegration, resulting in rapid capacity fading.^{98,99} In general, metal coatings are known to suppress particle cracking, pulverization, and exfoliation in LIB cathodes, although the exact mechanism is unclear. For instance, it is unclear whether the coating itself provides mechanical reinforcement, or if the effect primarily occurs through modification of the CEI composition and suppressing the side reactions that lead to surface-initiated cracking.⁸⁷

2.4.2.2. Conductive Carbon Coatings

Conductive carbon coatings are typically applied by mechanical mixing of the active material with a carbon source followed by pyrolysis.¹⁰⁰ High temperature pyrolysis (700 – 900 °C) under inert atmosphere is often required to limit oxidative decomposition and generate a uniform and highly conductive coating.^{63,101} This condition is optimal for the formation of polyanionic structures as the transition metals are at a low valence state. However, for layered TMOs that require an air/oxygen sintering environment for synthesis, as is the case for most mixed-metal cathodes, pyrolysis under such a reductive environment can alter the desired valence state of transition metals and also the lattice structure.¹⁰² In LIB work, some early attempts on $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ involved low-temperature (300 – 600 °C) and/or brief pyrolysis (< 2 h) often

with precursors like glucose, sucrose, and citric acid generating amorphous carbon coatings with short-ordered sp^2 and sp^3 coordination, which resulted in small improvements in rate capability and cycle stability.^{103–108} We believe this approach is incompatible with Ni-rich cathodes, due to its increased tendency to form Ni^{2+} , especially on the particle surface. However, some select work demonstrating this for NMC622 has been reported. Chen *et al.*¹⁰⁸ formed an N-doped carbon coating on NMC622 by ball milling the powder with melamine, followed by calcination in air. Optimized rate performance was achieved using a 5 wt% melamine coating and calcination at 650 °C for 1 h. Shim *et al.*¹⁰⁹ coated NMC622 with reduced graphene oxide (rGO) by first treating the active powder surface with 3-aminopropyltriethoxysilane to improve adhesion with GO. The treated active powder was then mixed with a pre-prepared GO solution, and following filtration, the GO was reduced at 300 °C under H_2 atmosphere for 4 h. The low temperature was chosen to limit potential reduction/degradation of the NMC622 surface. These strategies led to considerable improvements in capacity retention at elevated currents. Exposing $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ to these reductive environments did not appear to degrade its surface or rate performance.

Alternative, conductive coatings can be applied by coating the active particles with inherently conductive polymers or nanomaterials. He *et al.*⁵⁸ enhanced the rate performance of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ by coating it with 0.5 wt% graphene quantum dots (GQDs, 5 nm size). The GQDs were synthesized separately and deposited on $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ powder using a simple solution casting approach. Sun *et al.*¹¹⁰ coated $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ with polyphenylene, which led to enhanced kinetics and improved electrochemical performance at -20 °C. $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ particles were contacted with benzenediazonium tetrafluoroborate ($C_6H_5N_2^+BF_4^-$), with the intention of reducing $C_6H_5N_2^+BF_4^-$ to form an aryl radical, which

initiates polymerization. Ju *et al.*¹¹¹ coated $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ with PEDOT-*block*-PEG (0.78 wt%) simply by stirring the cathode powder and polymer in N-methyl-2-pyrrolidone solvent at 60 °C for 4 h, followed by drying and filtration. Supposedly, the PEG moiety enabled the polymer to adsorb to the active particles and enhanced Li^+ transport, while the PEDOT moiety contributed to the electronic conductivity. Recently, Gan *et al.*¹¹² uniformly coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ with polyacrylonitrile (PANI) by first treating the particle surface with PVP. PVP served to anchor PANI onto the $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ surface.

2.4.2.3. Core-Shell Structures

The concept of an electrochemically active core-shell structure was introduced and developed by Y.K. Sun and K. Amine with the aim of stabilizing Ni-rich LIB cathodes.^{113–117} In their preliminary work, Sun and Amine¹¹⁶ deposited a $\text{Ni}_{0.5}\text{Mn}_{0.5}(\text{OH})_2$ shell (1 – 1.5 μm thick) on a $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$ core (12–13 μm) by sequential coprecipitation. Following lithiation, the synthesized active material displayed two phases and can be represented as $\text{Li}[(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})_{0.8}-(\text{Ni}_{0.5}\text{Mn}_{0.5})_{0.2}]\text{O}_2$. The $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ shell material is known for its high thermal stability, low structural evolution, and interfacial stability, while the high capacity is attributed to the Ni-rich core. The core-shell electrode demonstrated an intermediate initial discharge capacity between the core and shell material along with a substantially improved cycle stability compared to the core material. To mitigate the mismatch in volume evolution and electrochemical properties between the core and shell material, which can generate a barrier for Li^+ diffusion at the interface, Sun and Amine¹¹⁷ subsequently introduced a gradient core-shell structure. The $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$ core was coated with a gradient Mn-rich Ni-Mn-Co coprecipitate. Lithiation and sintering allowed for diffusion of metals between the core and shell, generating a bulk average composition of $\text{LiNi}_{0.68}\text{Co}_{0.18}\text{Mn}_{0.18}\text{O}_2$ with a linear increase in the Mn

concentration and a decrease in Ni from the core to the shell. The gradient core-shell material demonstrated a considerably improved thermal stability compared to conventionally synthesized $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$.

2.4.3. Transition Metal Doping of Nickel-Rich Cathodes

In general, doping/substitution strategy can modulate the inherent electronic, ionic, and structural properties of the active material. For layered cathodes, substitution (2 – 10 mol%) of redox-active metals with inactive metals has been extensively explored as it can enhance cycle stability by suppressing high-voltage phase transitions. The dopant can also enhance rate performance by enlarging the *d*-spacing of the Li layer and by suppressing transitions to kinetically unfavorable phases. The substitution of a redox-active metal with an inactive dopant (Mg^{2+} , Al^{3+} , Ti^{4+} , Mn^{4+} , Zr^{4+} , *etc.*) lowers the initial discharge capacity (IDC) but improves the cycle stability. Redox-active dopants (Co^{3+} , Fe^{3+} , Ni^{2+} , Cu^{2+} , *etc.*) can also improve cycle stability without as much sacrifice in IDC, although are generally not as effective stabilizers. The typically discussed stabilizing mechanism(s) of action of redox-inactive dopants are as follows: 1) an inherent ‘pinning effect’, where MO_6 octahedra centered with inactive ions have negligible structural distortion,^{118,119} 2) greater TM-O bond strength for certain dopants than Ni-O, which structural distortion,¹²⁰ 3) suppression of high-voltage phase transitions (*i.e.*, $\text{H2} \rightarrow \text{H3}$) by retaining Li in the structure at high voltages or by serving as ‘pillar ions’. Certain dopants such as Mg^{2+} (0.72 Å) with similar ionic radius to Li^+ (0.76 Å) can enter the Li slab, and at high SOC serve as stable ‘pillar ions’ that suppress the severe lattice collapse during the $\text{H2} \rightarrow \text{H3}$ transition,¹²¹ and 4) modulation of the average valency of redox-active metals. Nickel-rich compounds such as $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ can be regarded as doped derivatives of the LiNiO_2 parent compound. Thus,

recent efforts have focused on exploring various transition-metal blends such as $\text{LiNi}_{0.89}\text{Mn}_{0.05}\text{Co}_{0.05}\text{Al}_{0.01}\text{O}_2$,¹²² $\text{LiNi}_{0.94}\text{Co}_{0.04}\text{Zn}_{0.02}\text{O}_2$,¹²³ and $\text{Li}_{0.98}\text{Mg}_{0.02}\text{Ni}_{0.94}\text{Co}_{0.06}\text{O}_2$,¹²¹ etc.

Cobalt as a substituent has traditionally been deemed critical to suppressing $\text{Li}^+/\text{Ni}^{2+}$ cation mixing and the H2 $\rightarrow$ H3 phase transition. In a recent study, Li *et al.*¹²⁴ questioned the conventional role of cobalt in Ni-rich layered oxides by systematically investigating the thermal and electrochemical contributions of a wide range of dopants in the $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (M= Al, Co, Mg, Mn, $x=0.05, 0.1$) system. The authors prepared hydroxide precursors by coprecipitation method that were then mixed with LiOH in a ratio of Li/TM ~ 1.02 . After heat treatment at 485 °C for 3 h, the powders were ground to homogenize any areas of excess LiOH. Finally, the powders were heated in two stages, first to 485 °C for 2 h followed by 700 °C (for $x=0.05$) or 735 °C (for $x=0.10$) for 20 h under oxygen flow. For samples synthesized with this method, it was found that increasing the Mn substituent content led to a greater number of Ni ions migrating to the Li layer ($\text{Ni}_{\text{Li}} \sim 6\%$ for $x=0.05$, $\text{Ni}_{\text{Li}} \sim 8\%$ for $x=0.10$) due to the formation of more Ni^{2+} compensating for Mn^{4+} in the structure. However, Al-, Mg-, and Co-doped samples all displayed $\text{Ni}_{\text{Li}} \leq 2\%$ for doping content up to $x=0.10$, similar to the amount found in modern NCA, indicating that Co is not required to eliminate cation mixing when Mn is not included in the system. Furthermore, substituent models were built within the formalism of density functional theory (DFT) to correlate structural changes to electrochemical performance of each sample. It was found that in $\text{LiNi}_{1-x}\text{Mg}_x\text{O}_2$ (LNO-Mg), Mg substitution causes Li atoms to occupy vertex sharing sites within the layer, thereby locking in two Li atoms for each Mg atom in the interlayer. This has the effect of reducing reversible capacity in the cathode as well as minimizing lattice oxide repulsion that is the cause of unwanted phase transitions. $\text{LiNi}_{1-x}\text{Al}_x\text{O}_2$ (LNO-Al) exhibited preference toward a random distribution of Al within the Ni-layer and

contributed to the reduction in ordering in the Li layer, again reducing presence of unwanted phase transitions. This was also indicated by *in-situ* XRD on the samples as a function of Li content, as no variation in unit-cell volume change was observed between the doped samples. Complete removal of Li is known to cause the unit-cell contraction due to the formation of the H3 phase; however, this phase was only observed in the pristine LNO sample. This further suggests that Co does not provide any noticeable benefit over other metal substituents in the structural stabilization of LNO during cycling. As anticipated, LNO-Mg displayed slightly reduced initial discharge capacity (~5%) but the highest capacity retention of all samples when cycled between 3.0-4.3V at C/5 rate. Initial discharge capacity and cycling performance of LNO-Al was similar to traditional NCA, showing that Co substitution in the system is not required. This work provides a promising path toward the development of cobalt-free LIBs.

2.5. Electrolyte Modification for Nickel-Rich Layered Oxide Cathodes

In an operating cell, the suppression of deleterious side reactions between the active material and electrolyte is equally, if not more important, than addressing inherent instabilities of the material. Often, these issues are closely correlated. For instance, as discussed in **Section 2.3**, the oxygen released from the lattice of layered Ni-rich layered oxide cathodes as a consequence of its instability at high SOC is believed to be in a reactive singlet state, which oxidizes the electrolyte. It is also believed that side reactions with the electrolyte catalyze the release of oxygen. This can occur from surface Ni^{4+} directly oxidizing the electrolyte, forming Ni^{2+} , which may induce phase changes and oxygen release. Another potential mechanism involves the direct transfer of electrons from the surface lattice oxygen to the solvent molecules. Furthermore, as discussed in **Section 2.4.2.1.**, HF generated in the electrolyte is the primary cause of active material loss via corrosion.

Rather than modifying the active material to suppress these side reactions, the electrolyte composition can be tuned to 1) reduce the likelihood of side reactions and 2) form a CEI/SEI layer with desirable properties – good kinetics and strong electrochemical and mechanical stability. A passivating CEI/SEI layer behaves in a similar manner to a surface coating. Thus, coatings are sometimes referred to as ‘artificial CEI/SEI layers’.¹²⁵

Electrolyte modification strategies have historically been focused on stabilizing anode materials and their interface with the electrolyte. In commercial LIBs, the SEI layer on graphite often dictates the kinetics and cycle stability of the cell. Thus, battery manufacturers and electrolyte suppliers have all developed proprietary combinations of electrolyte additives to improve cell performance. In the literature, significant effort has been devoted to stabilizing high-capacity anode materials, such as Li metal and Si. These materials experience uncontrolled side reactions when paired with the conventional LIB electrolyte, thus requiring extensive electrolyte engineering. Fortunately, many of these developed strategies are also known to benefit high capacity and voltage cathodes, including Ni-rich layered oxides.

2.5.1. Electrolyte additives

Electrolyte additive compounds typically comprise no more than 5 wt% or vol% of the conventional LIB electrolyte – LiPF₆ in carbonate-based solvent. The classical mechanism of additives involves their sacrificial decomposition, forming insoluble products that passivate the cathode and/or anode-electrolyte interface. Cathode passivation agents are expected to have a highest occupied molecular orbital (HOMO) energy level higher than other electrolyte components, resulting in its preferential oxidation and formation of a passivating CEI layer. However, some additive compounds expected to have a high oxidative stability (*e.g.*, highly fluorinated compounds, sulfone compounds, etc.) are also known to passivate the CEI layer.¹²⁶

This indicates that the chemical mechanisms of many additives are complicated and not well understood. Some electrolyte additives are also known to react/scavenge/neutralize H_2O or HF in the electrolyte, thus reducing the occurrence of active material loss.¹²⁷ Due to the poor understanding of electrolyte additive mechanisms, identifying promising additive materials and combinations is typically conducted by trial and error in both academic and industrial settings. Results are also highly dependent on the testing configuration. For instance, ‘half cells’ that employ Li metal as the counter-electrode/anode may generate significant side reactions between the Li metal and the additive. Thus, a large amount of additive is required to passivate the cathode. However, when paired with a graphite anode, an excess amount of additive will substantially increase cell impedance.¹²⁸

2.5.2. Solid State Electrolytes

The development of solid state electrolytes (SSEs) is theoretically a ‘holy grail’ approach to fabricating safe and long-lasting high energy density lithium-based batteries. Ideally, SSEs with high chemical/electrochemical stability and high shear modulus can stabilize both the anode (typically Li metal) and cathode (typically Ni-rich layered oxide). However, this goal has not been realized in the literature. As seen from the discussion below, the formation of surface coatings is also an important strategy to improve the performance of solid state batteries. Moreover, SSEs are currently plagued with additional challenges including cost, processability, and poor kinetics from both Li^+ transport through the SSE and interfacial charge transfer barriers.^{129,130}

Sulfide based SSEs (*e.g.*, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) possess competitive ionic conductivities even when compared to the liquid electrolyte batteries; however, they suffer from strong interfacial reactions between the electrodes and the SSE, inherently limiting their stability.¹³¹ When paired

with a Ni-rich layered oxide cathode, oxidative side reactions at the interface occur, forming inactive phases (*e.g.*, Li_2S) that increase cell impedance.¹³² Furthermore, a reconstructed rock salt phase forms on the surface of the cathode, similar to that observed in liquid electrolytes.¹³³ As such, cycle stability can be improved by implementing a passivating cathode coating (*e.g.*, Al_2O_3 , LiNbO_3 , Li_3PO_4 , etc.).^{133,134}

On the other hand, other SSEs such as Li_3InCl_6 exhibit limited side reactions at the cathode-SSE interface.¹³⁵ However, the high volume changes exhibited by Ni-rich layered oxides during the H2/H3 phase transition can disrupt the interparticle contacts between the SSE and cathode, increasing charge transfer resistance and quenching the cycle stability.¹³⁵ The interparticle disconnections can be mitigated by applying pressure to the cell stack while cycling (> 10 MPa), although this approach is impractical. Another approach is to coat the cathode with a flexible Li^+ conductive buffer layer to maintain interparticle contact within the composite cathode, in order to ensure good cycling performance at practical stack pressures.

2.5.3. High Concentration Electrolytes

Compared to SSEs, developing high-concentration electrolytes (HCEs) is a more practical approach to mitigating side reactions at the cathode-electrolyte interface. HCEs employ a near-equivalent molar ratio of salt to solvent, forming a unique solvation structure as depicted in **Figure 10**.¹³⁶ Lithium bis(fluorosulfonyl)imide (LiFSI) is commonly used as the salt due to its high solubility in dimethyl carbonate (DMC) or dimethoxyethane (DME). A conventional electrolyte comprises ~ 1 M salt in solvent, with strong separation of the cation and ion (**Figure 10A**). However, HCEs form contact ion pairs and cation-ion aggregates (**Figure 10B**). Consequently, in an electrochemical cell, this shifts the lowest unoccupied molecular orbital (LUMO) from the solvent to the salt. Thus, the salt is preferentially reduced at the anode,

forming inorganic-rich SEI layers. Utilizing LiFSI salt, the CEI/SEI layer is rich with N, S, and F-species, which substantially improves interfacial passivation, especially for Li metal or Si anodes.^{137–139} Moreover, the HOMO energy level of the solvent coordinated to the salt is decreased, improving its oxidative stability. Consequently, DME solvent, which normally decomposes > 3.8 V vs Li/Li⁺, can be cycled at high cut-off voltages >4.5 vs Li/Li⁺ in HCEs. This is significant as DME has excellent chemical stability against Li metal compared to carbonate-based solvents. Another positive outcome of the use of HCEs is that the Al current collector is passivated from corrosion at high voltages, eliminating the need for LiPF₆. This is possibly because the Al corrosion products have poor solubility in the HCEs.¹⁴⁰

However, the main drawback of HCEs is their high viscosity, which is not ideal for battery manufacturing, as it will significantly extend wetting times of the separators and electrodes of high-capacity cells. Thus, localized HCEs (LHCEs) introduce a diluent (typically a hydrofluoroether), which is miscible with the solvent but does not dissociate the contact ion pairs and salt-solvent clusters, thus preserving the solvation structure (**Figure 10C**).¹³⁶ The diluent can lower the salt concentration from ~ 5 M to $1.2 - 1.5$ M.¹³⁸ Thus, LHCEs can be substantially less costly than HCEs depending on the diluent chosen. Tuning the ratio of salt, solvent, and diluent can affect cell performance, although this has not been fully examined. For instance, the ionic conductivity of the LHCE can be optimized by adjusting the salt concentration and viscosity.¹⁴¹ While the diluent is theoretically an inert component, recent work has suggested that it also decomposes and potentially enhances the stability of the CEI/SEI layers.¹⁴²

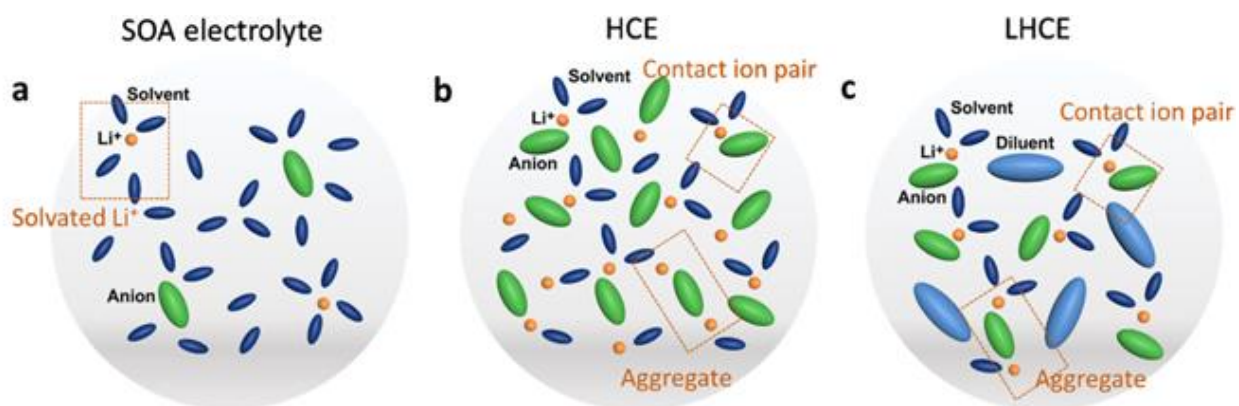


Figure 10. Solvation structure of A) state of the art (SOA) or conventional electrolyte for LIBs B) HCE, and C) LHCE. Reprinted with permission from IOPscience, 2021.¹³⁶

3. Methods

This section discusses the theory and rationale of the fabrication and characterization techniques used in **Sections 4 – 6**.

3.1. Electrode Fabrication

For lab-scale testing, the battery is fabricated using CR2032 coin cells comprised of the cathode, anode, polypropylene membrane separator, and LiPF_6 electrolyte dissolved in a carbonate-based electrolyte. Common electrolyte solvent compositions include 1:1:1 ethylene carbonate (EC): dimethyl carbonate (DMC): diethyl carbonate (DEC) and 3:7 EC: ethyl methyl carbonate (EMC) by volume.¹⁴³ EC is required to dissolve LiPF_6 . The addition of DMC lowers the viscosity of the solvent, resulting in improved kinetic performance of the battery. It is thus desirable for low-temperature battery operation. On the other hand, DEC has a higher viscosity and higher boiling point, minimizing electrolyte volatilization at elevated temperatures. Thus, a blend of DMC and DEC is often employed to produce a balance between stability and performance, which can also be accomplished using EMC.

To assess the performance of the cathode specifically, a ‘half-cell’ is typically constructed where lithium metal serves as both the counter and reference electrode. In this configuration, low-capacity ($< 2 \text{ mAh cm}^{-2}$) cathodes are paired with thick Li metal ($\sim 500 \text{ }\mu\text{m}$) to ensure minimal degradation or influence of the Li metal. While half-cells can generate highly reproducible data, they do not accurately reflect the practical performance in a full cell (*i.e.*, using graphite as the anode).¹⁴⁴ This is because lithium metal serves as an ‘infinite’ reservoir of Li^+ from lithium plating and stripping during the charge and discharge cycles, respectively. In full cells, which have a finite source of Li^+ from the electrolyte and cathode, irreversible consumption of Li^+ due

to side-reactions at the electrolyte-electrolyte interface is a key capacity degradation mechanism. Furthermore, electrolyte oxidation at the cathode-electrolyte failure can produce degradation products that deposit on the anode. Excessive build-up of these degradation products on the anode will result in sudden cell degradation after a certain number of cycles, which is known as rollover failure.¹⁴⁵ On the other hand, in half-cell configuration, electrolyte oxidation typically results in gradual capacity decline over cell cycling due to impedance build-up on the interface.¹⁴⁶

3.2. Battery Fabrication

Electrodes fabricated in both academic and industrial settings involve mixing a slurry comprised of the active material, conductive carbon additive, and polymeric binder in N-methyl-2-pyrrolidone (NMP) or aqueous solvent. NMP processing is typically employed for layered cathodes due to concerns over moisture stability as discussed in **Section 2.3**.¹⁴⁷ Here, the conductive additive is either carbon black or carbon nanotubes (CNTs), while the binder is polyvinylidene fluoride (PVDF). CNTs have more recently generated interest as the conductive additive, as their high aspect ratio makes them efficient at promoting electronic percolation.¹⁴⁸ However, CNTs tend to agglomerate due to strong van der Waals interactions and require additional surfactants to aid dispersion. The slurry is coated on a metal foil current collector, followed by drying and the application of pressure on the electrodes (calendaring). Optimization of this process is a major focus in industrial research and development – the mass loading (gravimetric and volumetric density) of active materials in the electrode needs to be as high as possible to maximize the overall energy density of the device. Furthermore, it is important to minimize processing time and consumption of materials without sacrificing battery performance.¹⁴⁹

Electrodes fabricated for academic studies typically comprise 80 wt% active material (dry mass), 10 wt% conductive additive, and 10 wt% binder casted at low active material areal loading density ($< 5 \text{ mg cm}^{-2}$). This configuration generally ensures that electrode processing does not hinder the electrochemical performance of the active material. These electrodes can also be processed under various conditions (*i.e.*, degree of slurry mixing and subsequent calendaring). However, industrially-produced electrodes comprise approximately 96 wt% active material, 2 wt% conductive additive, and 2 wt% binder at $> 10 \text{ mg cm}^{-2}$ active material areal loading density.¹⁵⁰

However, when fabricating electrodes at high active material loadings, the optimization of the slurry mixing and electrode calendaring process is critical to the ensuing electrochemical performance. Optimal slurry mixing is required to prevent the agglomeration of active particles and the conductive additive, which can severely affect the electronic conductivity of the electrode.¹⁴⁹ Mixing is typically conducted by forming hydrodynamic shear stresses or ball milling. While ball milling is more effective at breaking up agglomerates, this can cause structural degradation of the active particles (*e.g.*, cracking) and conductive additive (*e.g.*, scission of CNTs). Work has also demonstrated that a multi-step mixing processes can improve the electrode performance. For instance, pre-mixing the active particles with conductive additive, prior to adding the binder, can enhance the electronic conductivity.¹⁵¹ After the slurry is cast on the current collector and dried, electrode calendaring is required to improve the contact between the active particles, conductive additive, and binder. Electrodes with insufficient pressure applied exhibit poor rate performance and low cycle retention at elevated currents due to particle disintegration.¹⁵² The electrode may also delaminate from the current collector. However,

excessive pressure applied on the electrode generates insufficient porosity for electrolyte penetration and can also crack/damage the active particles.

3.3. Physical Characterization Techniques

3.3.1. X-Ray Diffraction

X-ray diffraction (XRD) is a fundamental technique to determine the identity of crystal lattices. The technique relies on the scattering of incident X-ray photons on the crystal atom's electrons. Most scattered photons disappear through destructive interference. However, evenly-spaced lattice planes (ordered atoms) can induce constructive interference of diffracted photons at certain angles to produce an intense signal that can be detected. The constructive interference is characterized by Bragg's law: $2d\sin\theta = n\lambda$, where d is the interlayer space between lattice planes, θ is the incident photon angle, and n is an integer. Diffraction peaks correspond to a lattice plane, which are represented by the Miller indices (h, k, l). The Miller indices are *derived* based on the three Cartesian coordinate intercepts of a lattice plane in a unit cell.

In battery research, XRD is critical toward assessing the phase purity and success of synthesized cathodes. For instance, all hexagonal ($R\bar{3}m$ space group) layered structures should display identical diffraction patterns with some variations in peak position. The exact lattice parameters (a and c) can be determined from the diffraction peak positions by curve-fitting, a technique known as Rietveld refinement. The c and a parameters correlate with the Li-O and TM-O bond lengths, respectively. The unit cell volume can be calculated based on $V = a^2c\sin(\pi/3)$. In LIB cathode research, XRD is often used to assess the degree of intermixing between Li^+ and other transition metal ions (often $\text{Li}^+/\text{Ni}^{2+}$) in layered cathodes, which can lead to low reversible capacity. This is done by measuring the intensity ratio of the (003) and (104) diffraction peaks as

well as the c/a lattice ratio. An intensity ratio of the $(003)/(104)$ peaks of < 1.2 implies a notable degree of cation mixing. *In situ* XRD is often used to monitor the evolution of the crystal lattice over electrochemical cycling – for instance, in layered cathodes, downshift of the (003) peak can be observed which is associated with interlayer space (d) expansion along the c -axis upon Li^+ extraction. After extended high-voltage cycling, conversion from the $R\bar{3}m$ phase to the $Fm\bar{3}m$ cubic rock-salt phase could be observed due to oxygen evolution.

XRD is also typically used to demonstrate evidence of metal doping – introducing a large-size dopant can expand the c -axis lattice parameter compared to the pristine material. However, XRD does not provide detailed information on atomic arrangement and local environments, as it only reveals the average atomic ordering.

3.3.2. Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy

Scanning electron microscopy (SEM) relies on the interaction between a focused beam of electrons bombarded on a sample surface, which can generate high-resolution images due to the small wavelength of the illumination source. Emissions from the sample-electron interactions are detected, with the most important involving secondary electrons, backscattered electrons, and characteristic X-rays. Secondary electrons are produced when the electron bombardment causes ionization of loosely-bound electrons (3 – 5 eV) on the sample surface.¹⁵³ This signal is primarily utilized to generate an image of the sample morphology. The detection of secondary electrons can provide an image of surface topology as electrons obstructed from reaching the detector will appear as a darker spot on the image. Backscattered electrons originate from the incident electron beam that collides with atomic nuclei on the sample and scatter at high energies (> 50 eV). Thus, larger atoms will generate more scattering and a higher signal intensity. Images produced using

backscattered electrons can produce excellent contrast between different elements. Finally, incident electrons can collide and eject inner shell electrons of the sample, resulting in relaxation of outer shell electrons to fill the hole. The relaxation energy loss is balanced by the emission of an X-ray photon of equivalent energy. As different elements produce characteristic X-ray emissions, this can be used to identify and quantify the relative ratio of certain elements. This microanalytical technique is known as energy-dispersive X-ray spectroscopy (EDX).

3.3.3. X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is closely related to EDX that was discussed in **Section 3.3.2**. The technique relies on the complete transfer of energy from an X-ray photon (penetration depth of ~ 100 nm) to an inner shell electron, resulting in ionization. The kinetic energy (and quantity) of electrons is measured by a detector, and thus the electron binding energy can be calculated based on the fundamental equation for the photoelectric effect. XPS can be used to determine the valence state and bonding hybridization of atoms, as these events influence the electron energy levels. In general, the binding energy increases with a rise in valence state and bond ionicity. A notable exception is the binding energy of the Co $2p_{3/2}$ orbital, which displays binding energies of Co^0 (778.2 eV) < Co^{3+} (779.6 eV) < Co^{2+} (780.5). This is caused by electronic rearrangement (final state) effects after the ejection of photoelectrons to minimize its energy, such as the coupling of unpaired valence electrons with the inner-shell hole.

In this work, XPS is used to detect the presence of an applied coating layer on the active material. Potential interactions with the active material are also examined. For instance, the application of a sintered metal coating can also generate surface-level doping/substitution effects with the active material. XPS is also used to determine the composition of the CEI layer of

coated electrodes after electrochemical cycling. For instance, coatings that can quench HF typically demonstrate an elevated quantity of fluoride-containing species.^{86,87,90–92}

3.4. Electrochemical Characterization

3.4.1. Battery Performance Testing

The standard battery testing protocol involves charging and discharging the battery at a constant current (galvanostatic cycling) with specified cut-off voltages. This reflects the practical operation of a battery. The voltage response is recorded as a function of charge/discharge time, which is directly proportional to the specific capacity (mAh g^{-1}). Energy and capacity values are normalized relative to the mass of the electrode active material (*i.e.*, excluding the binder and conductive additive). The key parameters that dictate the battery performance (specific capacity and cycle retention) are the upper and lower voltage cut-offs and the charge/discharge current (rate). The current is often reported as a specific value (mA g^{-1}) or defined by the C-rate. By definition, a rate of 1 C indicates that it takes one hour to charge/discharge the battery at a rated capacity while 2 C indicates that 0.5 h is required. Practically, the C-rate is often defined based on a material's theoretical or practical capacity over a certain voltage range – for instance, NMC811 typically demonstrates a capacity of 200 mAh g^{-1} when cycled between 2 – 4.3 V vs Li/Li⁺, which corresponds to 200 mA g^{-1} at 1 C and 400 mA g^{-1} at 2 C.

At higher charge/discharge rates, the specific capacity retained decreases due to resistances within a cell, which will polarize the voltage output. In a rate performance test, the cell is progressively cycled at higher currents to determine the capacity retention. A favorable rate performance is generally an indication of good electronic and ionic conductivity of the cathode. For a cycle stability test, the cell is galvanostatically cycled at a constant current. In general, the cycle stability may improve at higher currents, as the depth of discharge is lowered due to

voltage polarization. The cell is also subjected to less time at high voltages, limiting electrolyte decomposition. However, for cathodes that experience high volume changes, higher discharge currents will concentrate Li^+ at the cathode-electrolyte interface, producing anisotropic volume changes that could lead to particle cracking and disconnection.

3.4.2. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a fundamental technique to delineate resistances within an electrochemical cell. The simplest equivalent circuit model of an electrochemical cell is based on the Randles circuit (**Figure 11A**). R_s refers to the bulk series resistance of the cell, which is primarily dictated by the electrolyte resistance along with other Ohmic contacts. C_{dl} refers to the electrical double layer at the electrode-electrolyte interface, which can be modelled by a capacitor or constant phase element (CPE). The most critical parameter is the charge-transfer resistance (R_{ct}), which describes the interfacial reaction between Li^+ and the electrodes. There are three sequential steps to the intercalation of Li^+ : 1) solvation/desolvation of Li^+ , 2) diffusion of Li^+ through the SEI/CEI layer and potential surface coatings, and 3) Faradic charge transfer upon intercalation. The first two processes are typically rate limiting and define the bulk of R_{ct} . Thus, the R_{ct} is often used in battery testing to monitor the stability and build-up of the SEI/CEI layer over various cycles. The third step is notable when lattice phase changes suppress Li^+ kinetics, and thus increases in R_{ct} is sometimes used to imply phase changes, especially when the battery is operated at high voltages. After these processes, Li^+ diffuses within the electrode lattice, which is associated with the Warburg element (Z_w).

Potentiostatic impedance measurements work by applying an AC potential over a range of frequencies and measuring the current response. This can delineate circuit elements due to their

relationship with impedance – for instance, the impedance of a capacitor is inversely proportional to the AC frequency while the impedance of a resistor is independent of frequency. Thus, at high frequencies the R_s element can be isolated. Analysis is conducted using the Nyquist plot output– the x-intercept at high frequency is R_s , the width of the complete semicircle is the R_{ct} , and the slope of the 45° incline at low frequency corresponds to Z_w (**Figure 11B**). The exact values are determined using a nonlinear least squares curve fitting program. In typical circumstances, two overlapped semicircles or one asymmetric semicircle is observed. In this scenario, the high-frequency semicircle is denoted R_{sei} and associated with Li^+ diffusion through the SEI layer and other surface film, while the mid-frequency semicircle is denoted R_{ct} and is generally proportional to the solid-state diffusivity of Li^+ in the electrodes. Z_w typically corresponds to bulk Li^+ diffusion in the electrode, which occurs over a larger time scale.

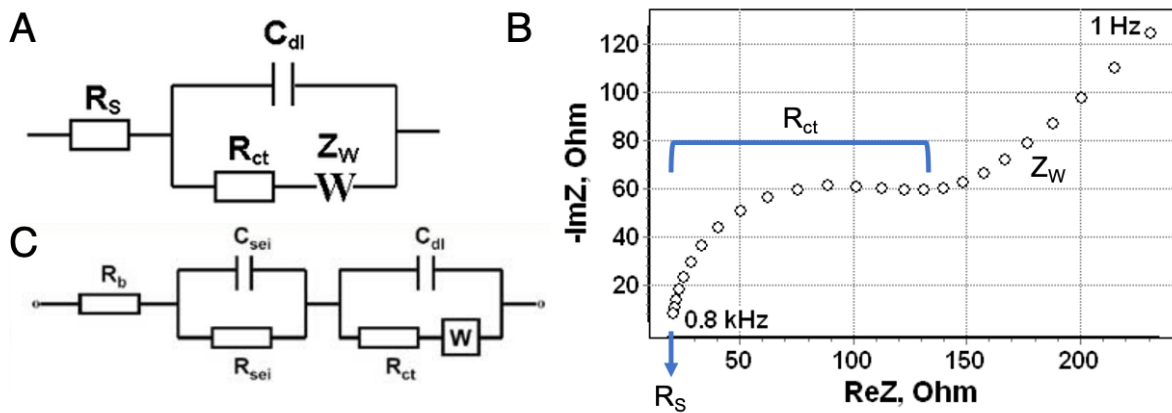


Figure 11. EIS analysis of a LIB cell. A) Randles circuit model for an electrochemical cell. B) Nyquist plot based on Randles circuit. C) Typical equivalent circuit model for LIB cells. Reprinted with permission from Elsevier, 2004.¹⁵⁴

In this work, the impedance of the coin cells is measured using a two-electrode setup (cathode and lithium foil). While this setup is simple, the impedance measured also accounts for the

reaction at the lithium metal counter electrode, which can generate some variability between cells as the lithium metal can have an unstable SEI film. However, for Ni-rich layered oxide cathodes, the CEI film tends to dictate cell impedance. Nevertheless, a more precise measurement involves a three-electrode setup, where a separate lithium metal reference electrode is used that does not participate in the reaction.

4. Analysis of ALD-Applied Coatings on Ni-Rich Cathodes for Lithium-Ion Batteries

4.1. Introduction

Increasing the energy density of lithium-ion batteries (LIBs) is a central focus in both academic and commercial research. The U.S. Department of Energy has set a goal of developing 500 Wh kg⁻¹ LIBs by 2030, which can only be achieved by developing and pairing high energy density cathode and anode (*e.g.*, Li metal, silicon, anode-free configuration, etc.) materials.¹⁵⁵ Among the candidates of cathode materials, Ni-rich layered transition metal oxide cathodes (typically LiNi_xMn_yCo_{1-x-y}O₂ or LiNi_xCo_yAl_{1-x-y}O₂, $x \geq 0.8$) have gained substantial interest due to their promising combination of energy density, cycle stability, and kinetic performance. Compared to established lower-Ni cathode compositions (*e.g.*, LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂), Ni-rich cathodes can achieve higher capacities or Li⁺ extraction/insertion when using the same upper cut-off voltage. Furthermore, they reduce or eliminate the reliance on cobalt, which is expensive, has a monopolistic supply chain, and is extracted by unethical mining procedures.^{6,24,43}

However, the higher achievable depth of discharge (DOD) of these materials leads to a diminished cycle stability, due to the increased expansion/contraction of the lattice resulting in inter and intra-particle fractures, increased reactivity with the electrolyte, poor thermal stability, and the formation of a resistive spinel or rock salt surface phase, which is accompanied with oxygen evolution. Thus, cell impedance grows rapidly over extended cycling. Although these issues have been well documented, the exact mechanisms remain unclear. For instance, the enhanced reactivity of Ni-rich cathodes with the electrolyte can be ascribed to lattice instability at low lithiation states, resulting in the release of reactive singlet oxygen which oxidizes the electrolyte solvent.⁵¹ This oxygen evolution is surface-initiated as the diffusion of lattice oxygen

is kinetically unfavorable, and a spinel or rock salt surface phase forms in accordance with the TM to O ratio. Another common explanation is that Ni^{4+} formed at high state-of-charge (SOC) directly oxidizes the electrolyte and is reduced to Ni^{2+} , which is accompanied by surface reconstruction and oxygen release.

Nevertheless, it is critical to develop strategies to improve the cycle stability of Ni-rich layered cathodes. In general, modification of active materials to improve performance typically involve one or more of the following: 1) modification of the particle morphology, 2) application of a surface coating, and 3) doping/substitution of redox-active transition metals with inactive metals (*e.g.*, Al^{3+} , Mg^{2+} , Zr^{4+} , etc.). The first two modification strategies are of interest in this work. Nickel-rich layered cathodes synthesized as 1 – 5 micron size single crystal (SC) particles have recently demonstrated promise in addressing these failure mechanisms.^{60,156–159} Conventional polycrystalline (PC) particles are typically 10 – 15 μm size secondary particles comprised of nanometer-sized primary particle aggregates at random crystallographic orientation. This morphology allows for optimal rate performance and particle compaction density in the electrode (*i.e.*, volumetric energy density). However, volume changes from (de)lithiation can generate fractures and voids within the secondary particle, exposing fresh surfaces that generate more cycle-degrading side reactions. On the other hand, SC particles do not undergo interparticle fracture, which can reduce the degree of electrolyte reactivity, transition metal dissolution, and surface reconstruction. However, their longer (micron vs nm) Li^+ diffusion paths results in diminished rate performances.

Applying a surface coating on the active particles is one of the most common approaches to improve cycle stability. In general, stability-enhancing coatings are electronically insulating but ionically conductive, where their most commonly cited mechanisms include: 1) providing a

kinetic barrier against electrochemical oxidation of the electrolyte (*i.e.*, electron transfer), 2) providing a physical barrier to suppress TM dissolution, oxygen evolution, and/or deleterious chemical reactions with the electrolyte, and 3) quenching/scavenging corrosive HF generated in the electrolyte (typically for ceramic coatings).⁶⁵ HF is generated in the electrolyte as a by-product of the decomposition of LiPF₆ in the presence of protic species. While it plays an important role in the passivation of the Al current collector, HF corrosion is known to be the primary cause of TM dissolution.^{81,160,161} Besides quenching the capacity due to cathode active material loss, the dissolved TMs can deposit on react with the anode surface, which is known as chemical ‘cross talk’. With graphite anodes, the TMs can irreversibly consume the limited Li reservoir. Li dendrites are also known to grow from these localized TM deposits on the anode, leading to micro-short circuits.^{162,163}

Despite their strong track record in improving performance, the specific mechanisms associated with cathode coatings remain unclear. Moreover, there have been limited attempts at comparing the performance and mechanisms of different coating materials applied by the same method.¹⁶⁴ Thus, in this work, the effect of four coating materials (Al₂O₃, alucone, TiO₂, and titanicone) applied on SC LiNi_{0.83}Mn_{0.06}Co_{0.11}O₂ electrodes was systematically compared and characterized. Atomic/molecular layer deposition (ALD/MLD) was chosen as the coating method as it can be conducted at low temperature (< 200 °C). In contrast, the conventional method of forming metal oxide coatings involves mixing the active material with the coating precursor, followed by sintering. Depending on the conditions, this process can result in doping/substitution of the coating TM into the active material lattice, which can also generate performance enhancing effects. Thus, it is difficult to delineate the impact and mechanism of the coating versus TM doping. On the other hand, performance enhancements from ALD/MLD modification can be

ascribed to the coating itself. ALD/MLD is also well established in its ability to generate highly conformal and ultrathin coatings with thickness control down to ~ 0.1 nm/cycle, allowing for consistent comparisons among different coating materials. Finally, preliminary work was conducted to study the effects of combining the coatings with a stability-enhancing electrolyte additive (fluoroethylene carbonate).

4.2. Materials and Methods

4.2.1. Electrode and Cell Fabrication

Pristine SC and PC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ powder was obtained as samples from XTC New Energy Materials Co., LTD (Xiamen, China) and used for electrode fabrication without further treatment. The powder was stored in an argon-filled glovebox while electrode fabrication was conducted in ambient conditions (RH $\sim 30\%$) with a maximum exposure of ~ 3 h.

The electrode was fabricated by mixing a slurry (solid content of 50 wt%) comprised of 90 wt% active material, 7 wt% poly(vinylidene fluoride) (PVDF, $M_w \sim 534,000$ Da, Sigma-Aldrich, Oakville, Canada), and 3 wt% carbon black (Super-P, AME Energy Co., Limited, Shenzhen, China) in 1-methyl-2-pyrrolidinone (anhydrous, Sigma-Aldrich). The slurry was mixed with a planetary mixer (THINKY AR-100, Tokyo, Japan) for 20 min., cast on a 20 μm -thick aluminum foil, dried at 120 $^\circ\text{C}$ for 1 h in a convection oven, subsequently calendared with a roll press, and stored under vacuum overnight at 80 $^\circ\text{C}$. Electrode calendaring was conducted at the maximum pressure equipped by the roll press (Xiamen TMAX Battery Equipments, Fujian, China). The porosity of the electrode was calculated using inherent densities of 4.95 g cm^{-3} , 1.95 g cm^{-3} , and 1.78 g cm^{-3} for NMC811, Super-P, and PVDF, respectively.

4.2.2. Electrochemical Characterization

12 mm diameter electrode discs were punched with an active material loading of $7 \pm 1 \text{ mg cm}^{-2}$. The electrochemical performance of the electrodes was assessed by assembling CR2032 coin cells in an argon-filled glove box using a pure lithium disc (14 mm diameter, 0.45 mm thick) as the counter electrode, a polyethylene/polypropylene separator (Celgard 2325, Charlotte, NC, USA), and an electrolyte comprised of 1 M LiPF_6 dissolved in 1:1 ethylene carbonate: dimethylcarbonate (Sigma-Aldrich) by volume. The modified electrolyte contained 5 vol% fluoroethylene carbonate (FEC, BASF, Germany). Constant current charge-discharge studies were carried out at ambient temperature using a CT2001A LANDt battery testing system (Wuhan, China) between 2.75 – 4.4 V vs Li/Li^+ at various C-rates. The C-rate is defined based on $200 \text{ mA g}^{-1} = 1 \text{ C}$. Cycle stability tests were conducted at ambient temperature while rate performance tests were conducted at 30 °C. Potentiostatic electrochemical impedance spectroscopy (EIS) measurements (Gamry Instruments, Warminster, PA, USA) were conducted from 1 MHz to 100 mHz with a 10 mV AC amplitude.

4.2.3. ALD Coating

The fabricated electrodes were coated in an ALD reactor (Thermal Gemstar 6XT, Arradance, MA, USA) using nitrogen as the purge and venting gas, a manifold temperature of 115 °C, and a purge time of 21 ms. Al_2O_3 and TiO_2 were coated with a reactor temperature of 175 °C using water as the oxidizer and trimethylaluminum (TMA) and TiCl_4 as the respective precursors (Strem Chemicals, MA, USA). TiCl_4 was preheated to 70 °C to increase its vapor pressure. Alucone and titanicone were coated with a reactor temperature of 120 °C using ethylene glycol as the oxidizer instead. Ethylene glycol was preheated to 90 °C. All electrodes were coated with 5 ALD cycles, which was demonstrated in our previous work to be the optimal thickness.¹⁶⁵ The

nominal thickness on an unobstructed substrate is < 1 nm. After the coating, the electrodes were stored under vacuum at 80 °C overnight prior to coin cell fabrication.

4.2.4. Physical Characterization

The phase purity of the active material was assessed using powder X-ray diffraction (XRDMiniflex 600, Rigaku, Japan) with Cu $K\alpha$ radiation ($\lambda = 1.5406$ nm) using a scan rate of 1 °/min and step size 0.02°. The morphology of the particles was observed using scanning electron microscopy (SEM, LEO Zeiss 1550, Switzerland) using a 20 kV acceleration voltage and a working distance between 8 – 9 mm. In order to observe the coating, high resolution transmission electron microscopy (HR-TEM, JEOL JEM 2010) was used to image the surface of cathode particles coated with 50 ALD cycles. X-ray photoelectron spectroscopy (XPS, Thermo Scientific Theta Probe, Waltham, MA, USA) was conducted using Al $K\alpha$ radiation. The binding energies reported are referenced to graphitic carbon at 284.8 eV.

For *ex-situ* characterization, all cells were cycled five times between 2.75 – 4.4 V vs Li/Li⁺ at 0.1 C under constant current constant voltage (CC-CV, 0.01 mA current cut-off) conditions, and subsequently charged to 4.4 V. Within two hours (OCV $\sim$ 4.35 V), the cells were disassembled in the glovebox with special care to avoid short-circuiting the cells. The cathode was rinsed in DMC and dried under vacuum. For XPS measurements, the cathodes were stored in argon-filled containers and transferred to the XPS chamber with minimal ambient air exposure. For X-ray absorption (XAS, Canadian Light Source, Saskatoon, Canada) measurements, cathodes were sealed using polyimide tape.

4.3. Results and Discussion

The SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particles used in this study were 1 – 3 μm size with high phase purity and low soluble base content (**Figure 12**).

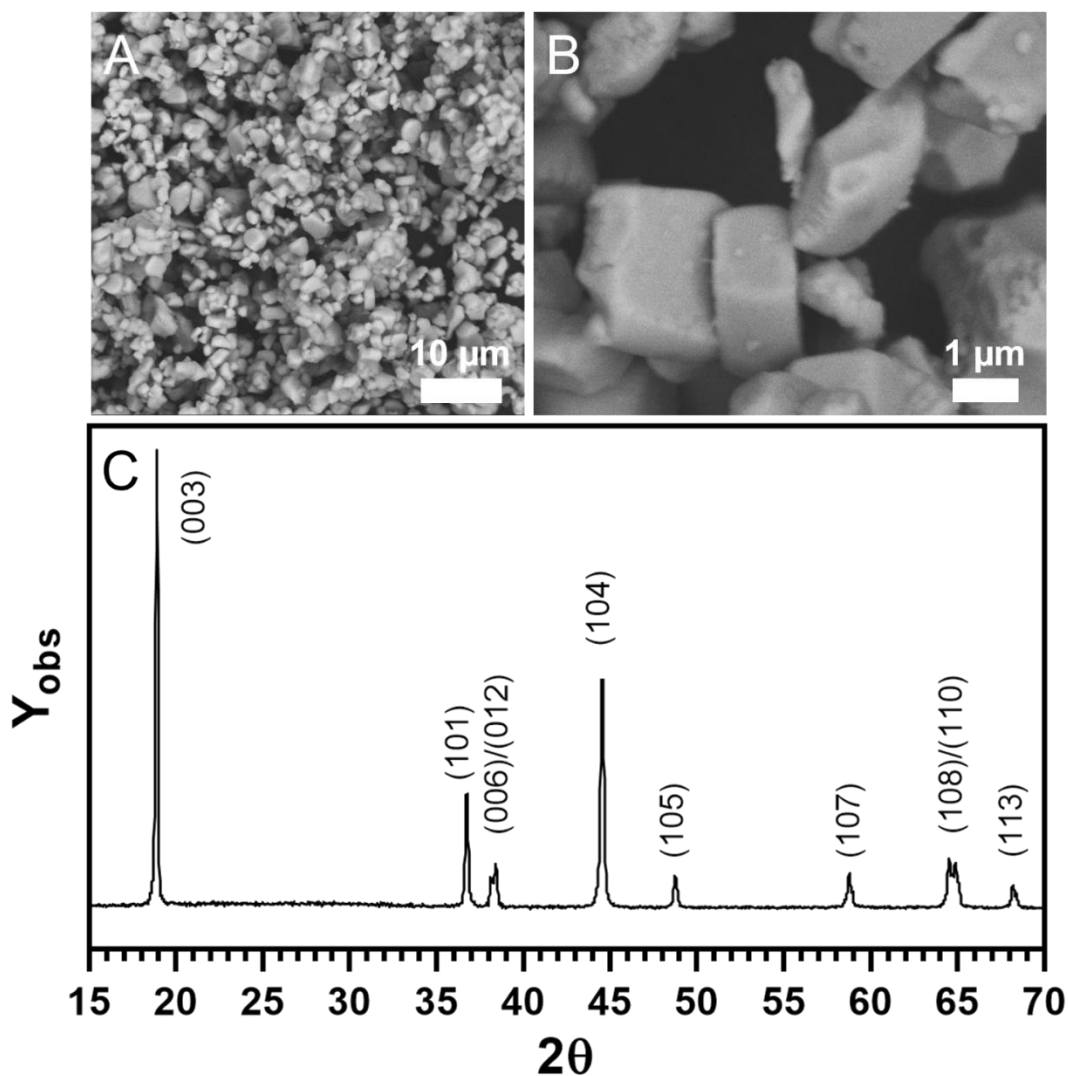


Figure 12. A and B) SEM images of SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particles. C) XRD diffraction of SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particles.

Figure 13 confirms that when cycled between 2.75 – 4.4 V vs Li/Li^+ at 0.1 C, SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ demonstrate an improved cycle stability compared to their PC analogue supplied by the same manufacturer. Further enhancement of the cycle stability was subsequently explored by applying coatings using ALD.

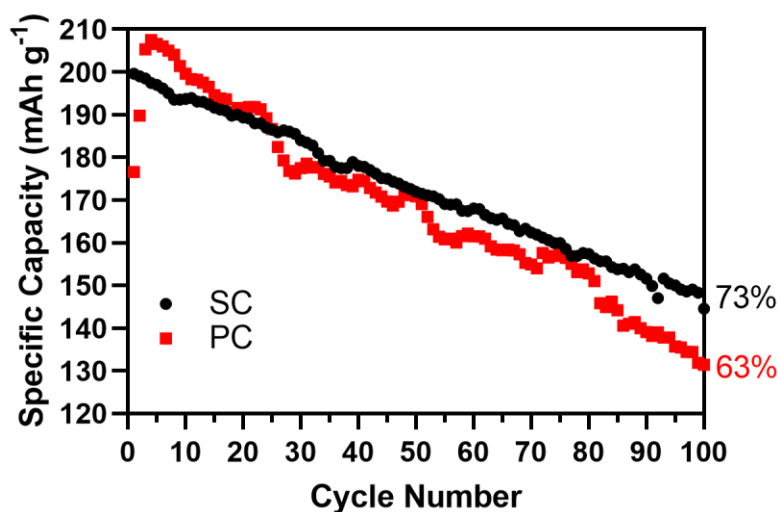


Figure 13. Cycle stability comparison of SC and PC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ tested at 2.75 – 4.4 V vs Li/Li^+ and 0.1 C.

Our previous work showed that the approximate ALD coating thickness observed using HR-TEM was 1.6 to 1.8 Å/cycle for alucone and Al_2O_3 .¹⁶⁶ As shown in **Figure 14**, this thickness range was similar for TiO_2 and titanicone.

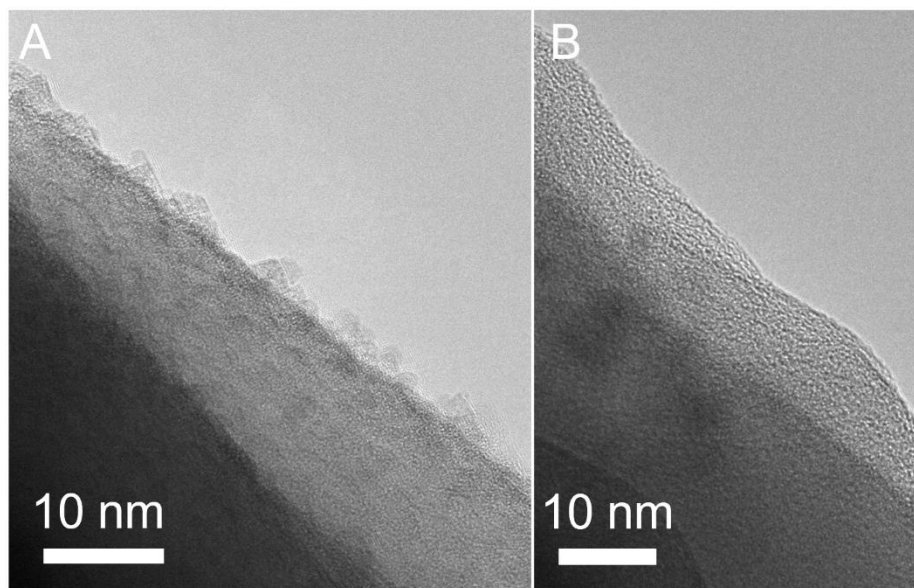


Figure 14. HR-TEM images of SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particle surface coated with 50 cycles of A) titanicone and B) TiO_2 .

4.3.1. Analysis of Coating Penetration within Electrode

ALD coatings can be applied either on the active material particles or the fabricated electrode. Prior work suggests that the latter method produces better performance, as the conductive additive and binder in the electrode is also coated. Electrolyte decomposition and side reactions also occur on the surface of these components, which the coating can potentially suppress.¹⁶⁷ Furthermore, coating the active particles with an insulating film can disrupt the electronic contact with the conductive additive in the electrode, thus severely affecting kinetic performance.¹⁶⁸ As discussed earlier, coatings are known to improve cycle stability by providing a physically or kinetically hindering barrier against oxygen release, transition metal dissolution, and deleterious side reactions with the electrolyte. For this mechanism to be valid, it is critical for the coating to cover all exposed surfaces of the active material. However, when the coating is applied on the fabricated electrode, it is unclear whether the gaseous ALD precursors can adequately penetrate relatively dense electrode film and reach all of the active particles. Although numerous reports have repeatedly shown improved cycle retention from ALD-applied coatings on fabricated electrodes, analysis on the coating penetration within the electrode typically is not conducted.

Gas transport of the ALD precursors in porous materials is diffusion-limited, and thus the coating may be localized on the outer regions of the electrode.¹⁶⁹ While ALD has been used to uniformly coat 3D porous materials/scaffolds, this is typically conducted on low-density materials such as aerogels and fiber mats.^{170–172} Denser films containing mesopores and micropores are known to have limited permeability to ALD precursors, although this is also affected by deposition conditions such as the pulse time and temperature.¹⁷³ Precursor penetration is expected to be particularly challenging for commercially produced calendared electrodes that typically are much thicker than lab-made electrodes and have low porosities (<

30% for cathodes). Thus, in our work the performance of coated electrodes was first compared by applying ALD before (B) and after (A) calendaring the electrodes. Calendaring reduced the average electrode porosity from ~73% (~70 μm thick excluding current collector) to ~48% (~36 μm thick).

It was thought that applying the coating prior to calendaring could improve the penetration of ALD precursors into the higher-porosity electrode and thus improve the cell cycle retention. This was assessed using surface-sensitive XPS scans of the coated electrode surface as shown in **Figure 15**.

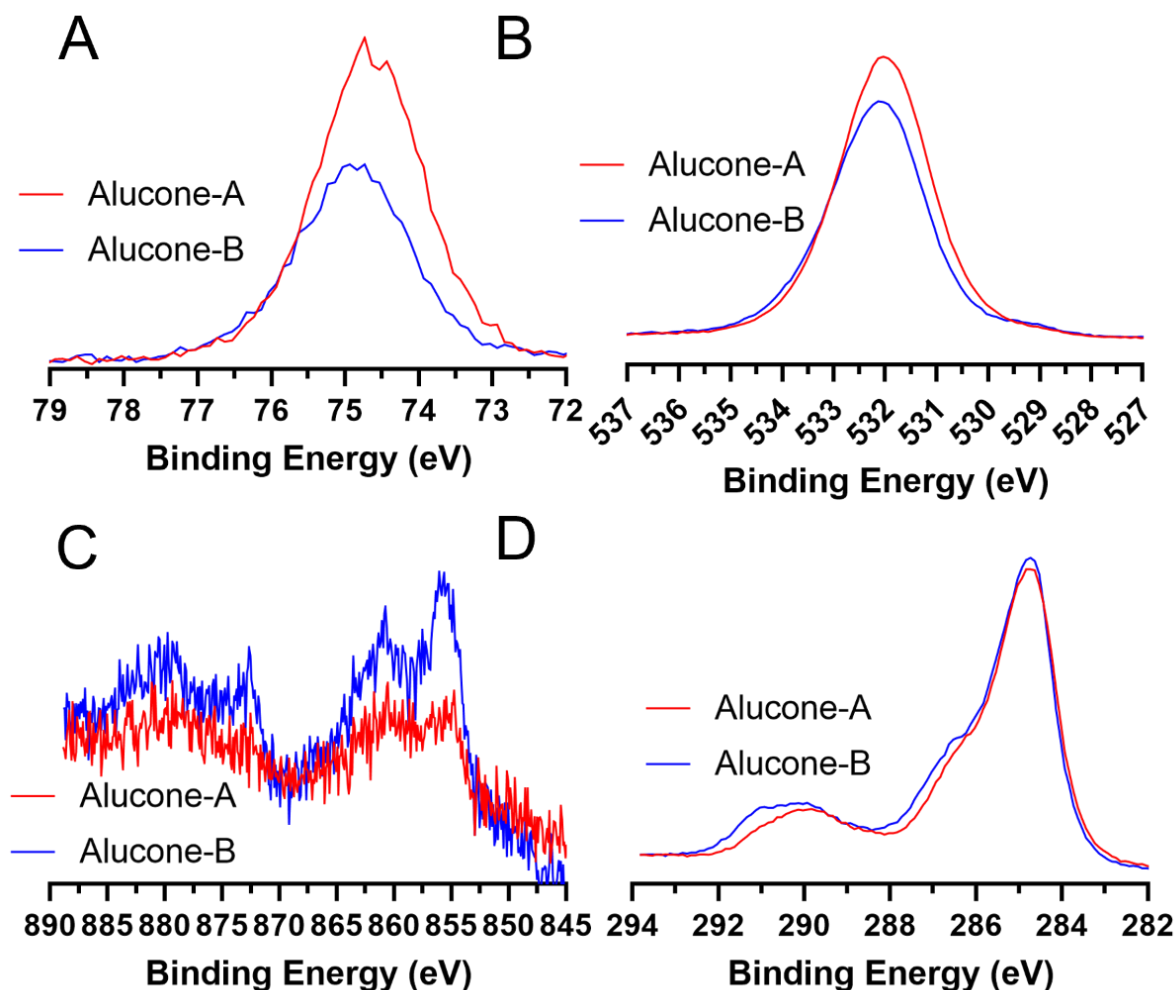


Figure 15. A) Al 2p, B) O 1s, C) Ni 2p, and D) C 1s XPS scans of electrode coated with 5 ALD cycles before (blue) and after (red) calendaring.

Alucone deposited after (denoted Alucone-A) calendaring displayed a higher intensity of the Al 2p and O 1s spectra compared to the electrode coated before calendaring (Alucone-B). Furthermore, the intensities of the Ni 2p and C 1s (particularly at B.E.s corresponding to PVDF) of Alucone-A are suppressed. Due to the limited penetration depth of XPS (< 10 nm), this implies that a higher amount of alucone is detected on the surface of the electrode, covering the pristine electrode components. Furthermore, **Figure 16** displays the depth profiling XPS scans (Al 2p, Ni 2p, O 1s, and C 1s) of the Alucone-A and Alucone-B coated electrodes etched using monatomic Ar^+ sputtering.

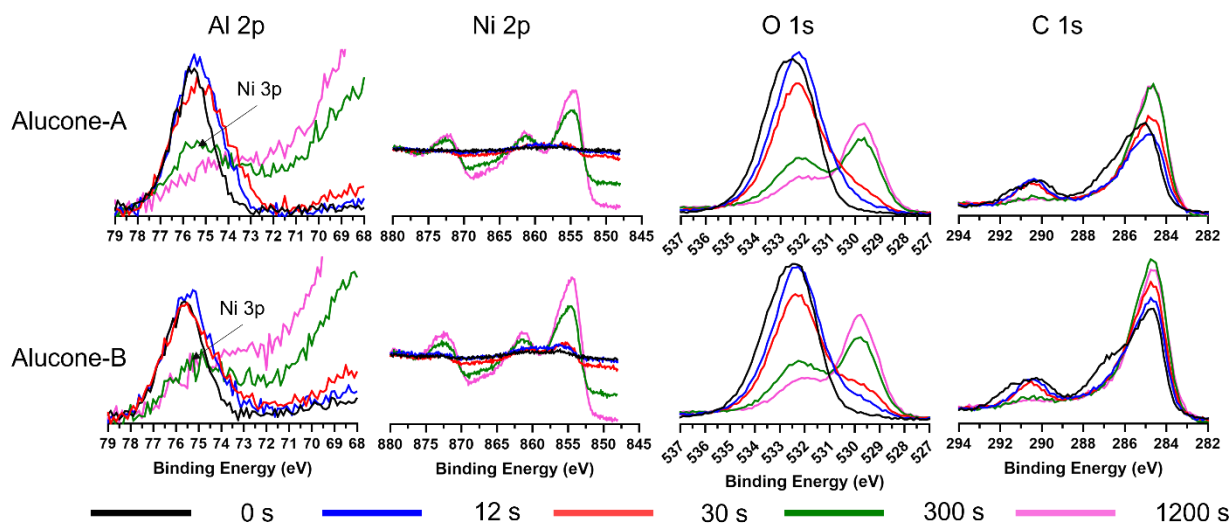


Figure 16. XPS scans of alucone-coated electrode with monatomic Ar^+ etching (4 keV, 2.7 μA). For each element, the plotted intensities are non-normalized with consistent y-axis scaling.

The Al 2p signal of Alucone-A is initially more intense, and within the first 30 s of etching, the peak area shows some decay, whereas the peak area of Alucone-B remains unchanged, confirming that the coating is more localized on the electrode surface. After 300 s of etching, both samples show significant attenuation of the Al 2p peak area. Here, the Al 2p signal overlaps with a growing Ni 3p signal. It appears that an organic surface layer of the electrode (binder and

conductive additive) is etched, exposing the active particles, which is confirmed by the drastically intensified signals of Ni 2p and O 1s NMC lattice oxygen (~529.5 eV). However, when comparing the peak intensities of the pristine (uncoated, **Figure 17**) and coated sample at the Al 2p / Ni 3p region, it appears a small amount of Al is present in both samples even after 1200 s of etching.

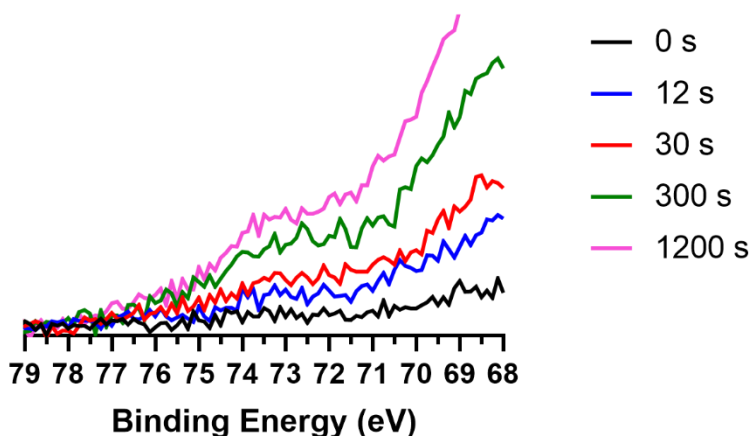


Figure 17. XPS scans of pristine electrode with monatomic Ar^+ etching (4 keV, 2.7 μA) at the Al 2p and Ni 3p region.

Although the degree of Al penetration cannot be quantified from this data, the results confirm that the coating penetration is more pronounced for Alucone-B than Alucone-A. However, in both cases, the coating was clearly concentrated on the electrode surface, as depicted in **Figure 18C**. It is unlikely that the entire depth of the electrode was coated. It is worth mentioning that the coating could not be detected by EDX due to the low quantity of Al/Ti present. Thus, a spatial mapping of the coating within the electrode cross section could not be generated.

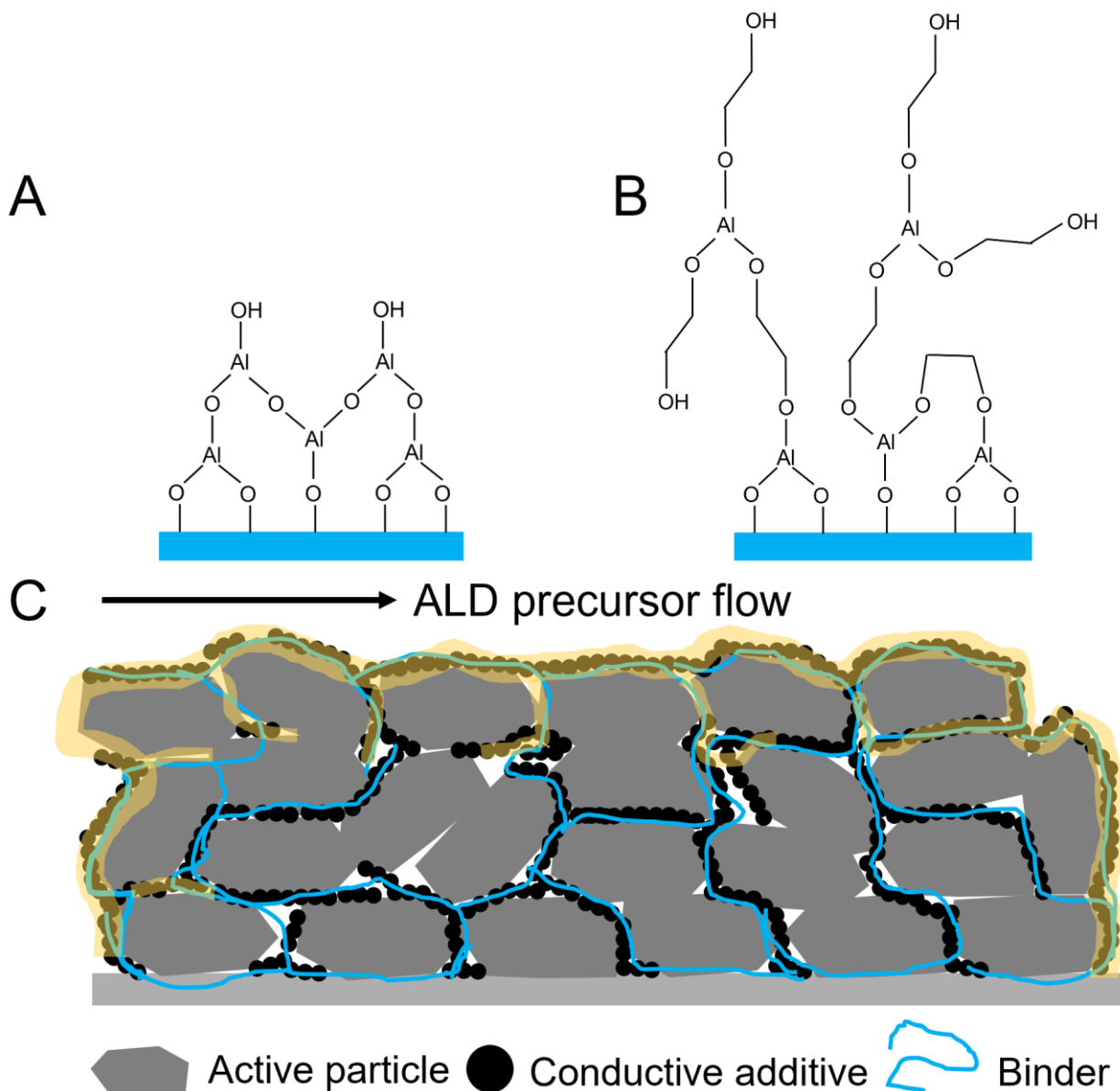


Figure 18. Structure of Al_2O_3 (A) and alucone (B) coating after two ALD cycles. Various plausible structures are depicted for the alucone coating. C) Depiction of localized ALD-applied coating on the electrode surface regions. Highlighted regions represent the coating penetration and thickness.

Figures 19 and 20 compare the cycling performance and coulombic efficiency (C.E.) at 0.1 C of each coating material when ALD is applied before and after calendaring. All electrodes coated prior to calendaring displayed a higher C.E., particularly during the initial cycles, which suggests that they are more effective in suppressing cathode-electrolyte side reactions. The increase in

C.E. is more notable in the metal oxide coatings, likely because they are more electronically insulating and dense. Both coating application methods improved the discharge capacity retention compared to the pristine sample. However, in all cases, applying the coating after calendaring resulted in a slightly improved capacity retention after 100 cycles. This indicates that the improved penetration of the coating within the electrode does not enhance cycle performance. Thus, in this particular case the coatings do not primarily act by providing a physically or kinetically hindering barrier against electrolyte side reactions.

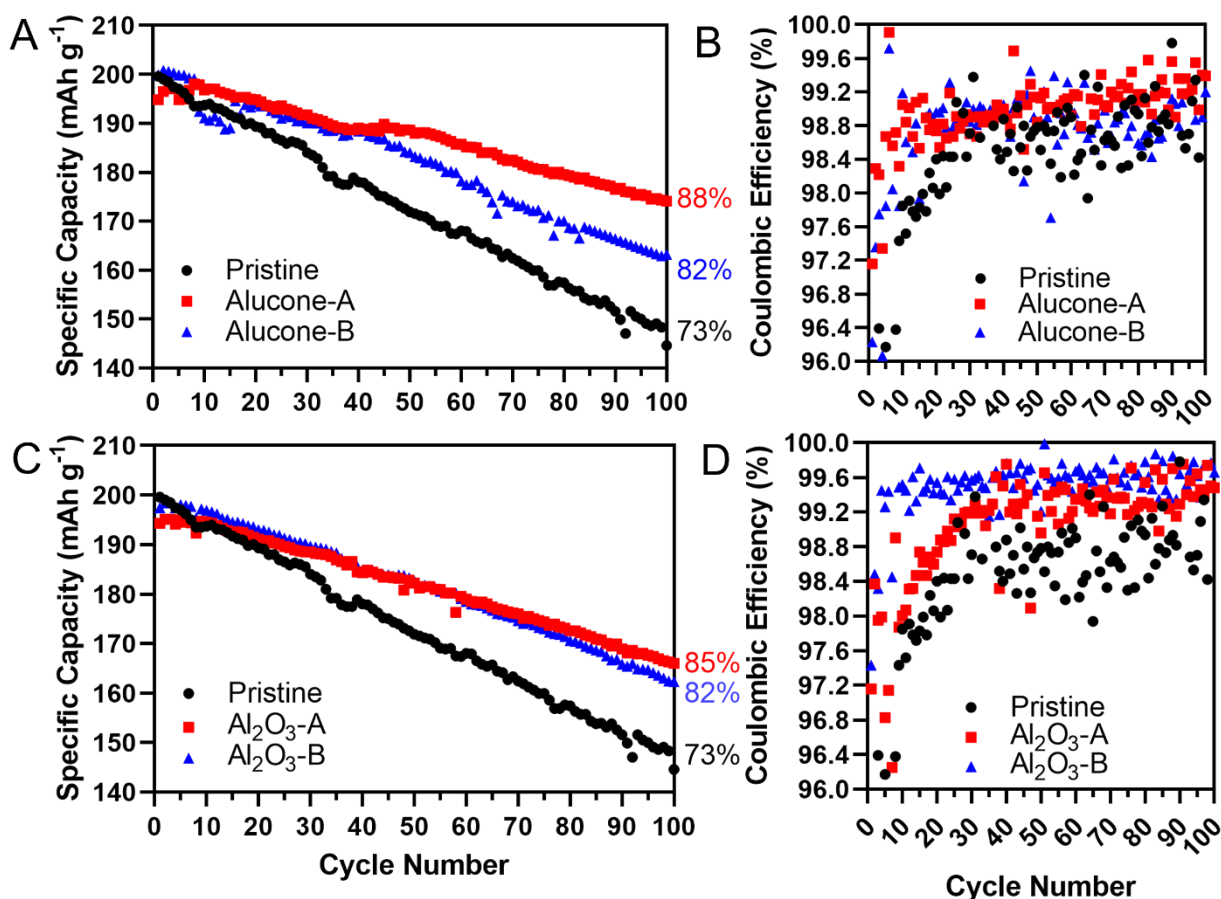


Figure 19. Comparison of capacity retention (A and C) and C.E. (B and D) of Al-based coating applied before (-B) or after (-A) calendaring the electrode. All cells cycled at 2.75 – 4.4 V vs Li/Li⁺ and 0.1 C.

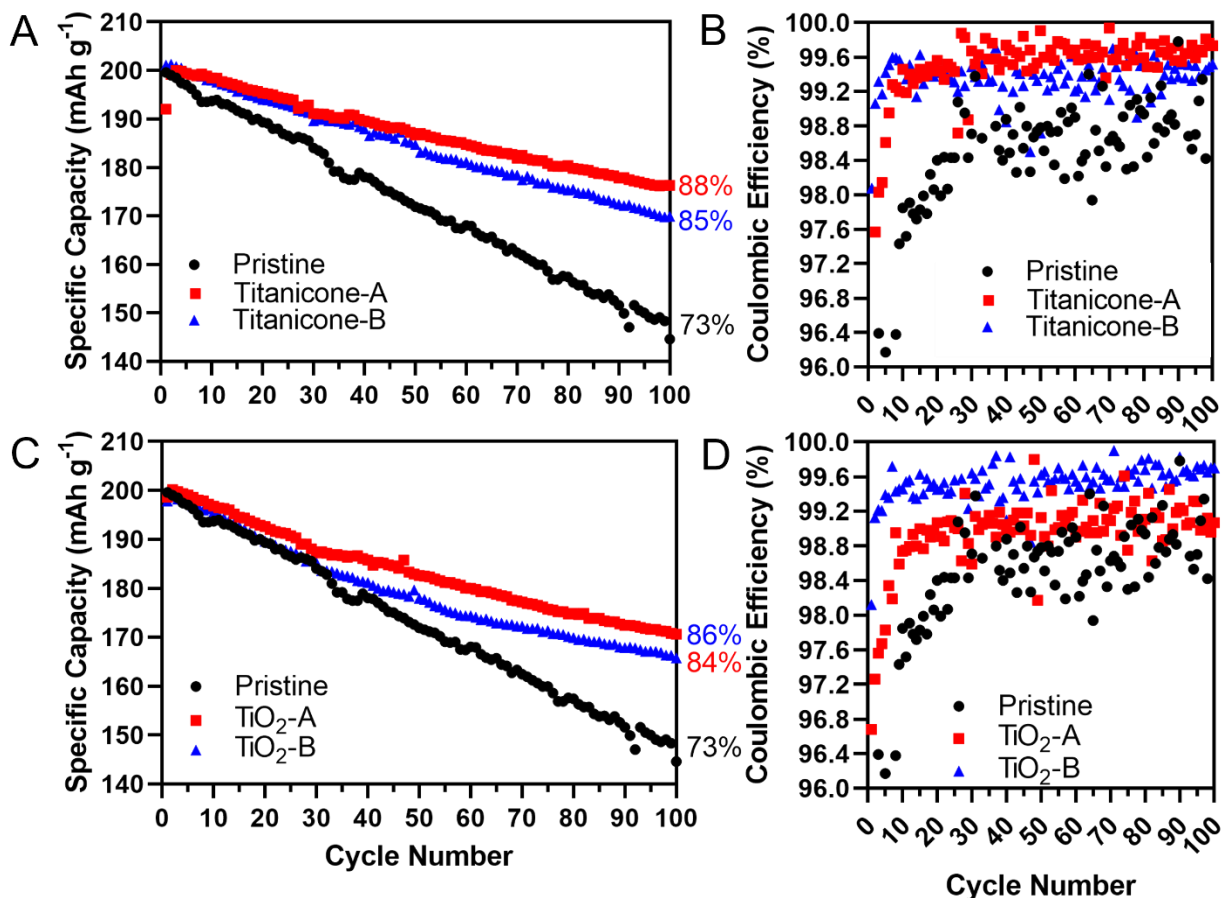


Figure 20. Comparison of capacity retention (A and C) and C.E. (B and D) of Ti-based coating applied before (-B) or after (-A) calendaring the electrode. All cells cycled at 2.75 – 4.4 V vs Li/Li⁺ and 0.1 C.

Figures 21 and 22 compare the rate performance of the discussed electrodes. In all coatings except for titaniconc, applying the coating before calendaring resulted in a lower kinetic performance. For all samples, capacity loss at increasing currents correlates with a lower average discharge voltage (**Figure 21B** and **22B**), which is indicative of cell impedance.¹⁷⁴ As the coating materials applied are inherently electronically and ionically insulating, this confirms that the coating applied before calendaring encapsulates more active particles within the electrode. The coating could also disrupt electronic contacts between the active particles and conductive additive. The loss of kinetic performance was also more pronounced in the metal oxide coatings (*i.e.*, Al₂O₃-B and TiO₂-B) compared to the metalcone analogues. This is likely because the

metalcone coatings are inherently more electronically conductive and expected to have approximately half the density of the metal oxide coatings (~ 1.5 vs ~ 3 g cm $^{-3}$),^{175,176} which is favorable for Li $^{+}$ permeation.¹⁷⁷ To illustrate this, **Figure 18A** and **18B** showcase the difference in chemical structures of Al $_2$ O $_3$ and alucone. In the following sections, the comparisons among different coating materials are conducted with the ALD coating applied *after* calendaring the electrode.

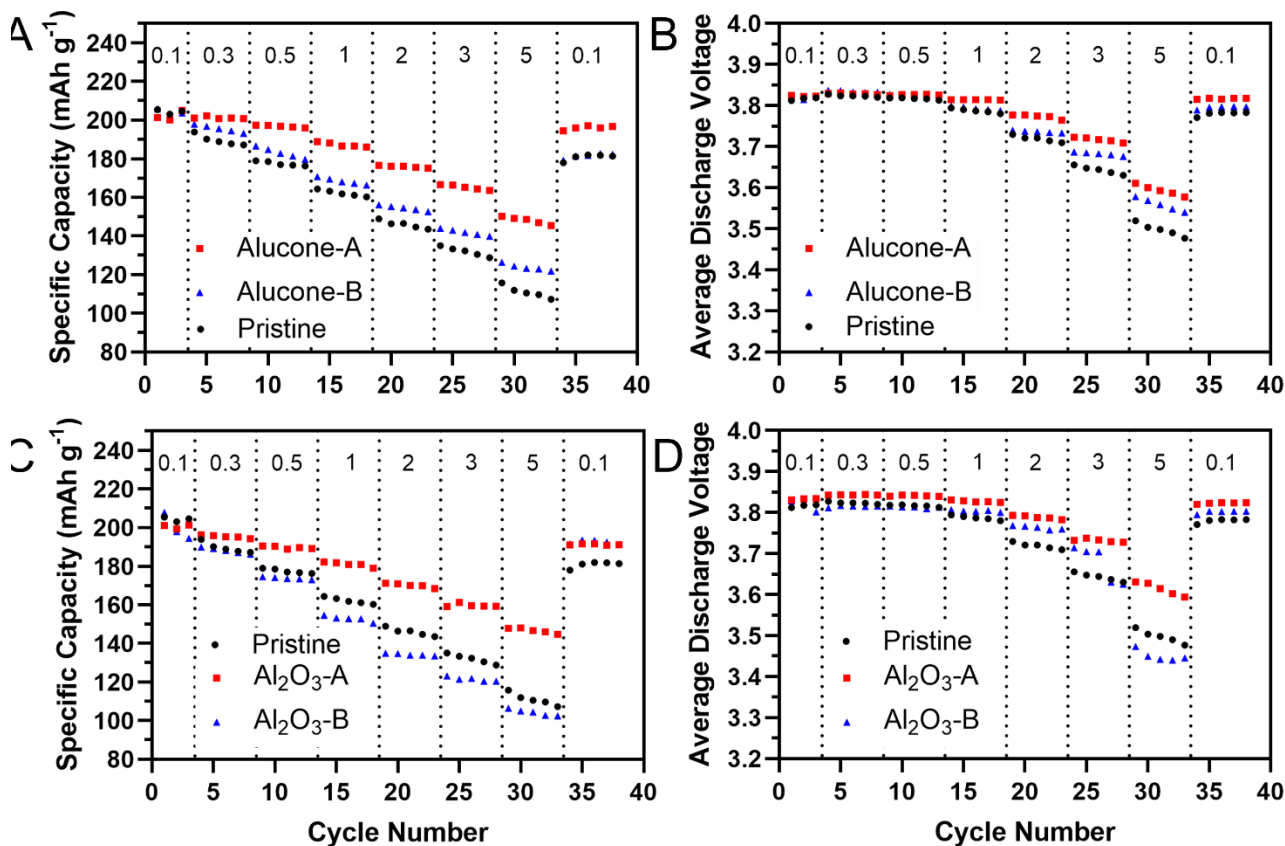


Figure 21. Comparison of rate performance of Al-based coating applied before (-B) or after (-A) calendaring the electrode. All cells cycled at 0.1 C charge and 0.1 to 5 C discharge at 2.75 – 4.4 V vs Li/Li $^{+}$.

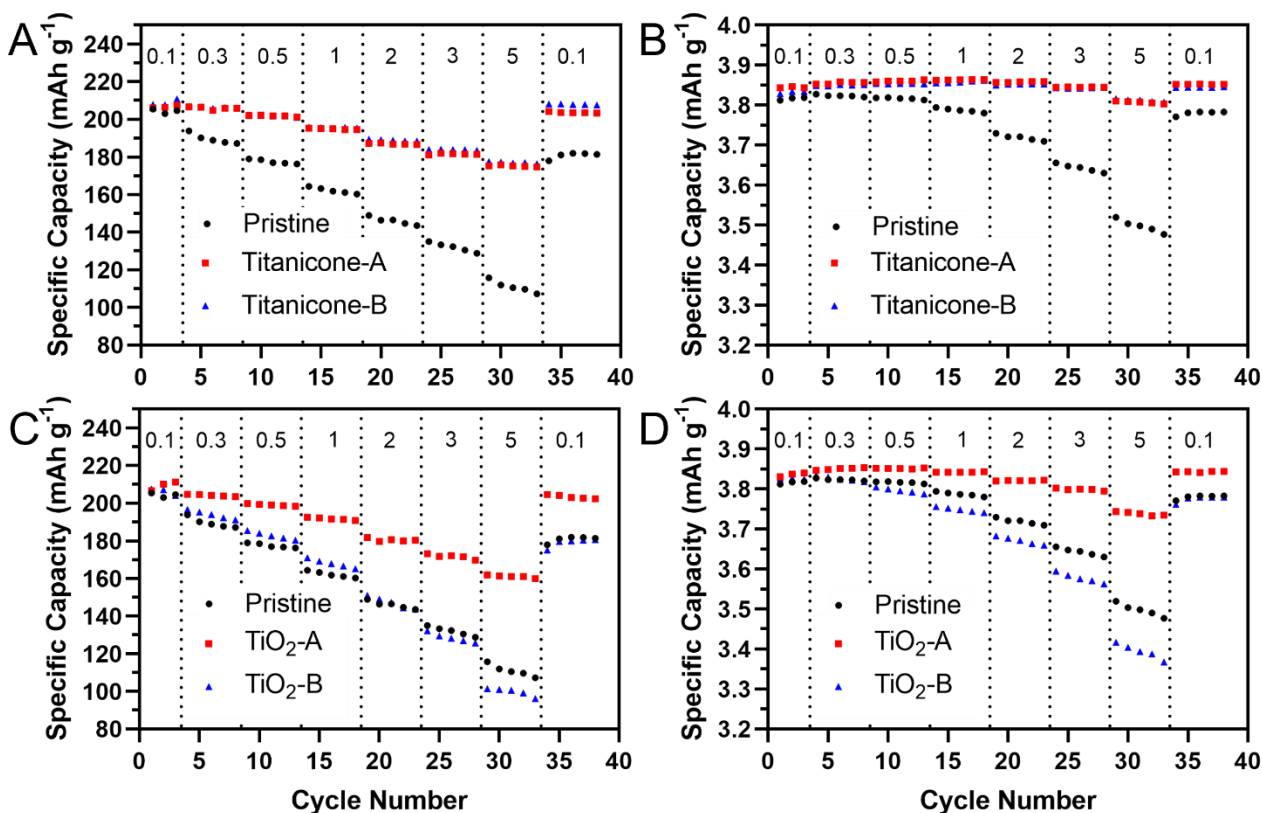


Figure 22. Comparison of rate performance of Ti-based coating applied before (-B) or after (-A) calendaring the electrode. All cells cycled at 0.1 C charge and 0.1 to 5 C discharge at 2.75 – 4.4 V vs Li/Li⁺.

4.3.2. Electrochemical Performance Comparison of Coatings

Under low current (0.1 C) cycling conditions at 2.75 – 4.4 V vs Li/Li⁺, cycle stability is dictated by thermodynamic factors, as the lithiation state of the active particles is expected to be mostly homogeneous. Furthermore, the cathode endures more time at elevated voltages and low lithiation states, which stresses key degradation mechanisms – electrolyte decomposition, oxygen release, surface reconstruction, and dissolution of transition metals.

As shown in **Figure 23** and **Table 1**, all coated electrodes show an improvement in discharge capacity retention after 100 cycles compared to the pristine (+12-15% increase). It is worth

noting that the initial discharge capacity of all samples was similar (195 – 200 mAh g⁻¹), as the DOD strongly correlates with the degradation of NMC/NCA-type layered cathodes, even more so than the voltage range.⁴⁸

Table 1. Comparison of discharge capacity and average discharge voltage retention after 100 cycles at 2.75 – 4.4 V vs Li/Li⁺.

Sample	Discharge Capacity Retention (0.1 C)	Average Discharge Voltage Retention (0.1 C)	Discharge Capacity Retention (C/3)	Average Discharge Voltage Retention (C/3)	Discharge Capacity Retention (0.1 C → C/3)
Pristine	73%	98.1%	82%	96.7%	87%
Alucone	88%	99.3%	86%	99.5%	91%
Al ₂ O ₃	85%	97.6%	82%	96.5%	83%
Titanicone	88%	99.4%	85%	98.8%	87%
TiO ₂	87%	99.3%	84%	99.1%	95%
Pristine + FEC	79%	98.2%	80%	98.6%	92%
Alucone + FEC	90%	99.5%	94%	99.1%	91%

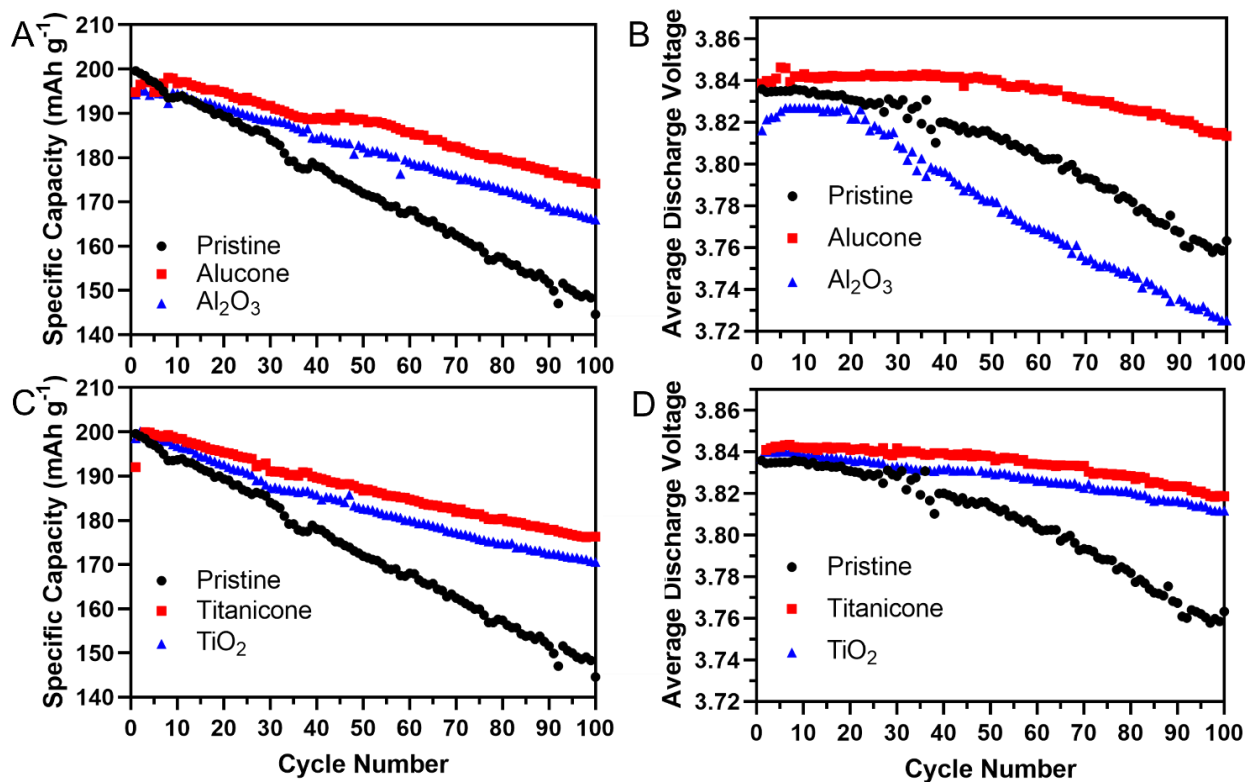


Figure 23. Cycle retention (A and C) and average discharge voltage (B and D) of pristine and coated electrodes cycled from 2.75 – 4.4 V vs Li/Li⁺ at 0.1 C.

Interestingly, despite the denser and more electronically insulating nature of the metal oxide coatings, which should help suppress electrolyte decomposition, the metalcone coatings exhibited the strongest capacity retention. With the exception of Al₂O₃, the coatings also preserve the average discharge voltage, which corresponds to a suppressed impedance growth. For Ni-rich cathodes cycled at low current, impedance growth is dictated by 1) formation and growth of a Ni²⁺-O type rock salt surface layer with slower Li⁺ diffusion kinetics and 2) build-up of the cathode-electrolyte interface (CEI) layer derived from electrolyte decomposition, where the impedance is dictated by its thickness and chemical composition. In the case of Al₂O₃, the capacity retention is improved despite displaying a higher impedance growth compared to the pristine electrode, which suggests that the coating primarily functions by suppressing active material loss. To further analyze changes in capacity and polarization over cycling, **Figure 24**

displays the dQ/dV vs V curves of each sample at cycle 1, 25, 50, and 100. All samples show a series of sharp peaks corresponding to phase transitions, with the most notable being the H2/H3 phase transition at ~ 4.2 V vs Li/Li⁺. This phase transition is responsible for a $\sim 5\%$ contraction of the c -axis lattice parameter and an increased covalency of the TM-O bonds.⁴⁹ It occurs due to the thermodynamic instability of the layered lattice structure at low lithiation state, and is accompanied by oxygen release, surface reconstruction, and electrolyte decomposition. Thus, most of the degradation mechanisms associated with Ni-rich cathodes can be traced to this phase transition.⁵¹

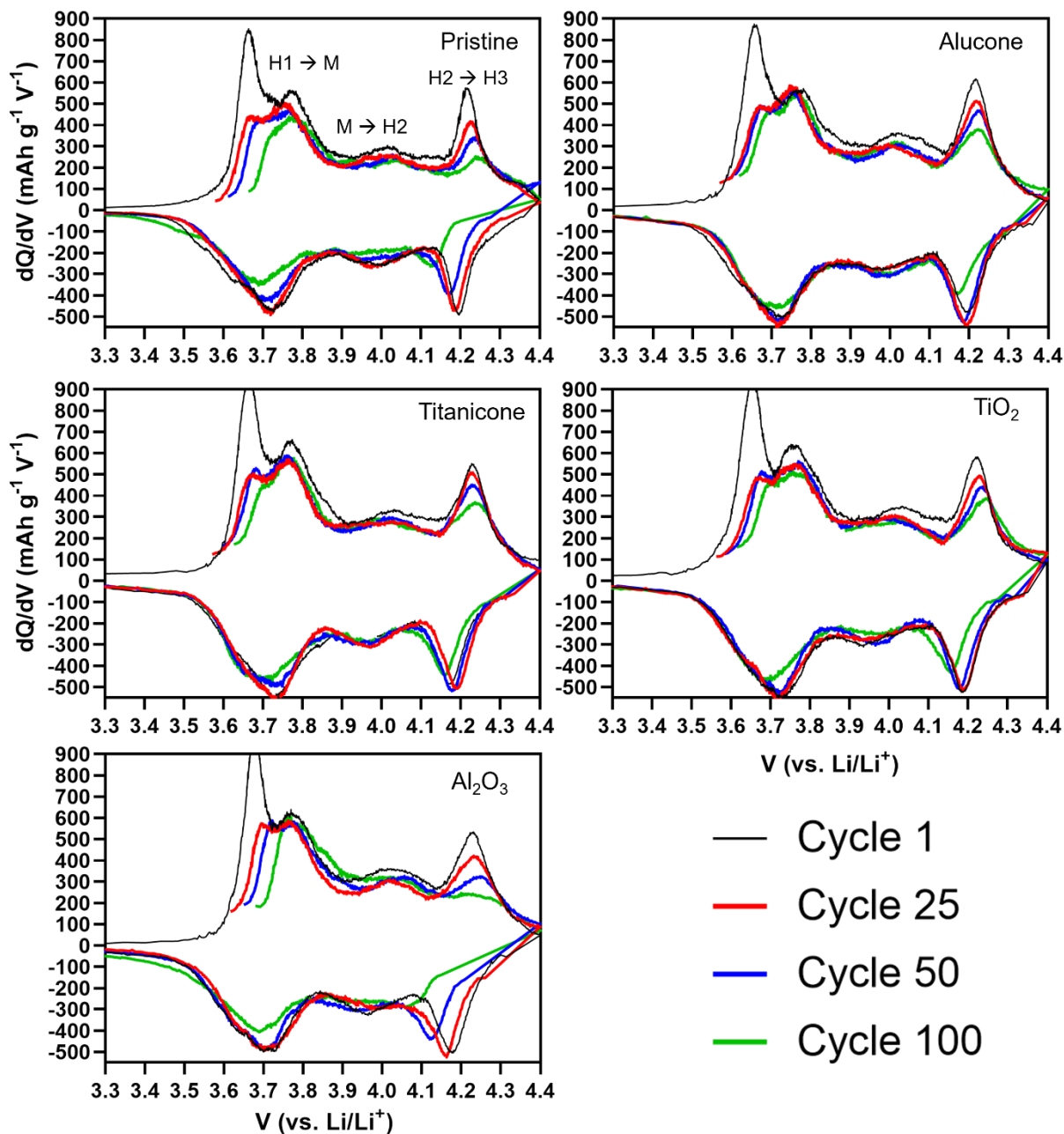


Figure 24. dQ/dV curves of pristine and coated electrodes cycled from 2.75 – 4.4 V vs Li/Li⁺ at 0.1 C.

Among all samples, increased peak polarization and loss of peak intensity as a function of the cycle number is most notable at low and high SOC, which is largely due to kinetic hindrance.¹⁷⁸

At low SOC, Li⁺ diffusion is hindered by electrostatic repulsion among Li⁺ and the limited number of divacancies available, forcing Li⁺ to migrate through tetrahedral sites to octahedral

sites, which has a high energy barrier.¹⁷⁹ At high SOC (>75%), Li diffusion kinetics in Ni-rich cathodes is greatly hindered due to lattice volume contraction, the increased valence state of Ni, ‘fatigue degradation’ due to the mismatch of lattice constants between the H3 phase and rock salt surface,¹⁸⁰ and potential dislocations within the crystal structure (*i.e.*, intragranular cracks).¹⁸¹ Decay of peak area (*i.e.*, capacity) can also be caused by active material loss or degradation.

Figure 24 shows that besides Al₂O₃, all coated samples preserved their peak positions (*i.e.*, polarization) and peak areas with continued cycling. This implies that the coatings maintained the Li⁺ diffusion kinetics, the reversibility of the phase transitions, and suppressed active material loss. Interestingly, the Al₂O₃-coated sample shows a faster decay and elevated polarization of the H2/H3 phase transition peak even when compared to the pristine sample. **Figure 25** also displays the charge-discharge voltage profiles of each sample after 100 cycles.

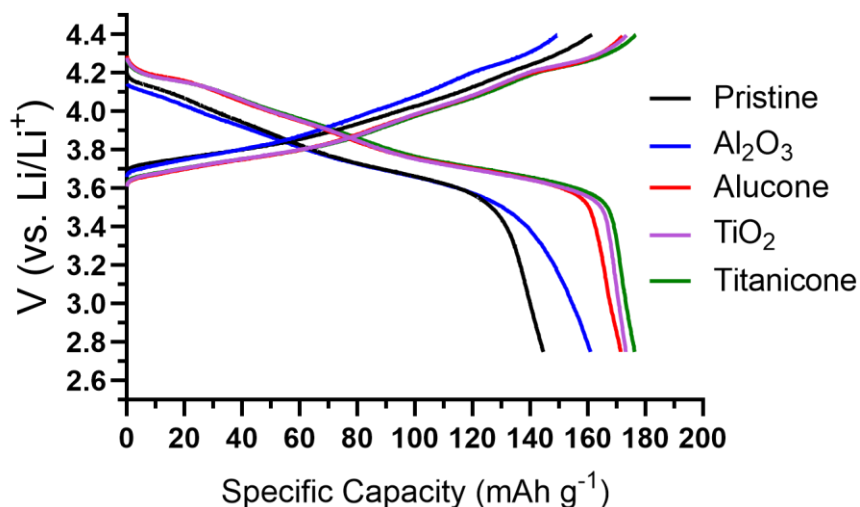


Figure 25. Charge-discharge curves of pristine and coated samples after 100 cycles at 0.1 C.

Typically, the voltage drops rapidly below ~ 3.6 V vs Li/Li^+ during discharge, forming a near-vertical line. However, the Al_2O_3 -coated sample shows a distinctly oblique line, which is indicative of a high Li^+ insertion barrier, particularly at low SOC. One potential explanation for this observation is that the CEI layer produced from Al_2O_3 modification is ineffective at suppressing oxygen release, increasing the thickness of the rock salt Ni-O layer at higher cycle numbers. However, this explanation is inconsistent given that 1) it does not explain why the polarization and decay of the H2/H3 phase transition peak is worse than the pristine sample, 2) a thicker rock salt layer should result in poor capacity retention from inactive Ni and increase the polarization at all SOC, and 3) its mechanism of action is expected to be similar to alucone (see XPS discussion below), which has a positive effect on the H2/H3 peak retention.

Instead, the kinetic limitations originating from the electronically and ionically insulating Al_2O_3 coating itself may act synergistically with other kinetic barriers (discussed earlier) to impede Li^+ transport, particularly at low and high SOC. Thus, at high SOC, Li^+ extraction and the occurrence of the H2/H3 phase transition are kinetically suppressed. At low SOC, the Al_2O_3 sample shows the strongest peak polarization during charge at the H1/M phase transition due to the compounded Li^+ diffusion barriers. As discussed, **Figure 25** also shows obvious polarization during discharge at low SOC. However, at other potentials with lower kinetic hindrance, the curve area and peak positions are mostly unaltered over the 100 cycles, similar to the other coated samples. This implies that despite the kinetic losses, the Al_2O_3 coating is still highly effective at suppressing active material loss, substantially improving the capacity retention relative to the pristine material. The kinetic hindrance of the H2/H3 phase transition explains the slightly inferior capacity retention of the Al_2O_3 -coated electrodes compared to other samples, as presented in **Figure 23** and **Table 1**.

Figure 26 presents the cycling performance at an elevated current of $C/3$. Three initial cycles were conducted at $0.1\ C$ to stabilize the CEI/SEI layers, and after every 25 cycles at $C/3$ the capacity was recorded at $0.1\ C$. For the pristine sample, capacity retention when cycling at $C/3$ was improved compared to $0.1\ C$ (Table 1). **Figure 27** shows that the C.E. is higher when cycling at $C/3$ compared to $0.1\ C$, particularly during the initial cycles, confirming that cathode-electrolyte side reactions are suppressed due to a shorter duration at elevated voltages. However, the retention of the average discharge voltage is lower when cycling at $C/3$. A considerable amount of capacity is recovered when the current is lowered to $0.1\ C$, indicating that active material loss is not the dominant degradation mechanism. With the exception of Al_2O_3 , the coated samples typically displayed a small improvement in capacity retention at $C/3$ compared to the pristine sample after 100 cycles (+2-4%, **Table 1**). The difference in capacity between the pristine and coated samples was more prominent after 200 cycles (**Figure 26A** and **26C**). Interestingly, for the coated samples, capacity retention was poorer when cycling at $C/3$ versus $0.1\ C$ after 100 cycles. This suggests that the coatings are most effective at suppressing active material loss/degradation rather than kinetic losses. Moreover, as shown in **Figure 26**, the trend in capacity decay mostly correlates with the attenuation of the average discharge voltage for all samples tested, which further indicates that kinetic factors (impedance growth) play a large role in capacity degradation at an elevated current.

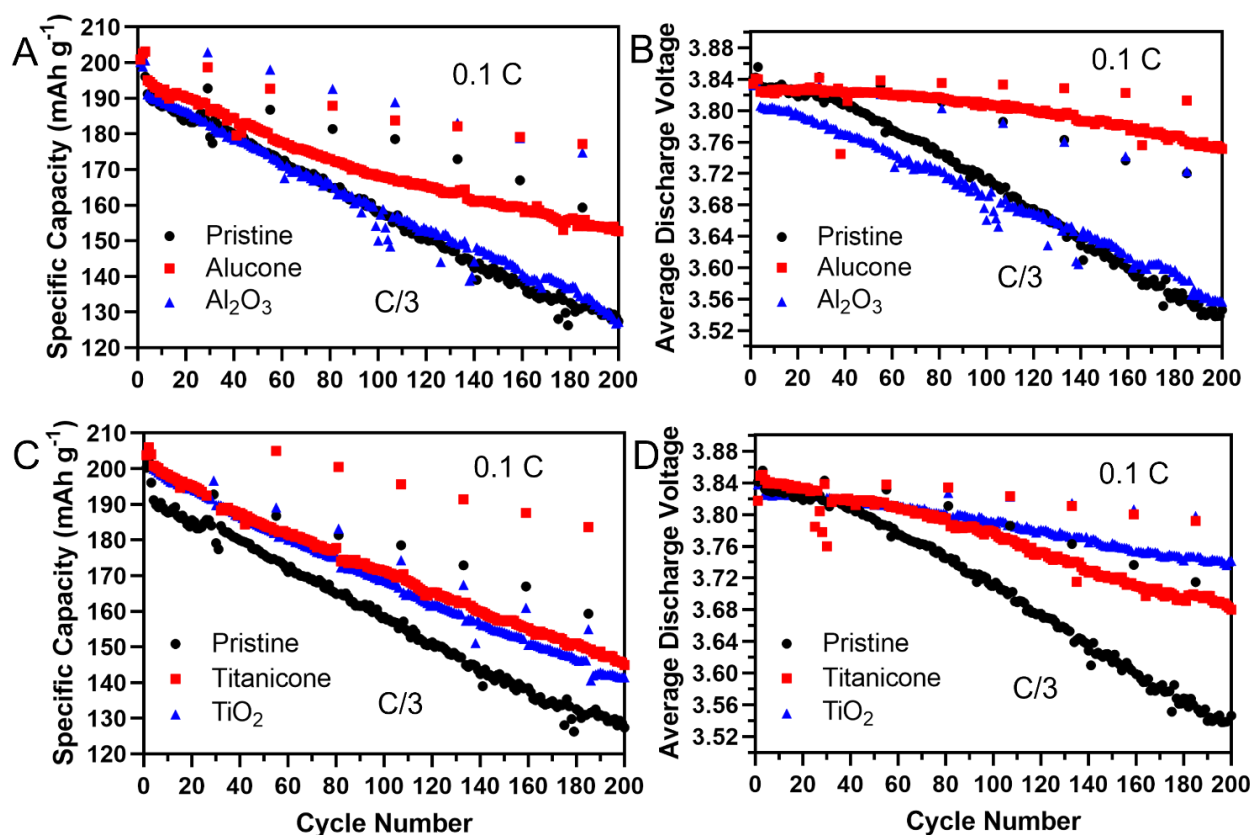


Figure 26. Capacity retention (A and C) and average discharge voltage (B and D) of pristine and coated electrodes cycled from 2.75 – 4.4 V vs Li/Li^+ at C/3.

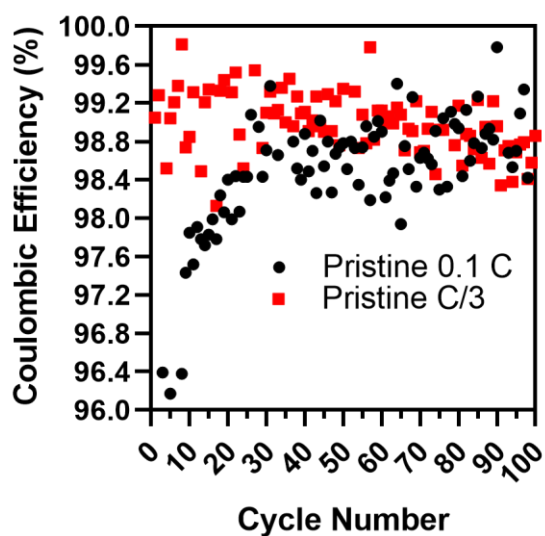


Figure 27. Comparison of C.E. of pristine electrode cycled at 0.1 C and C/3 between 2.75 – 4.4 V vs Li/Li^+ .

As shown in the dQ/dV curves (**Figure 28**), peak polarization over the first 100 cycles for the pristine sample is clearly more severe when cycling at $C/3$ compared to $0.1 C$. After 100 cycles, the area of the peaks associated with the $H2 \rightarrow H3$ phase transitions has completely decayed. The Al_2O_3 -coated samples appear to show evidence of active material retention based on preservation of the peak areas at lower SOC. However, polarization growth is more severe relative to the pristine sample. On the other hand, the alucone-coated sample appeared to suppress polarization, active material loss, and decay of the $H2 \rightarrow H3$ peaks even after 100 cycles. This rise in polarization is likely associated with the formation of intragranular particle cracks. At elevated discharge currents, lithiation is inhomogeneous and concentrated on the surface of the cathode particles. The resulting mismatch in lattice parameters generates strain within the particle, leading to cracks forming which can disrupt Li^+ diffusion channels. The coatings applied in this work are unlikely to suppress this occurrence.

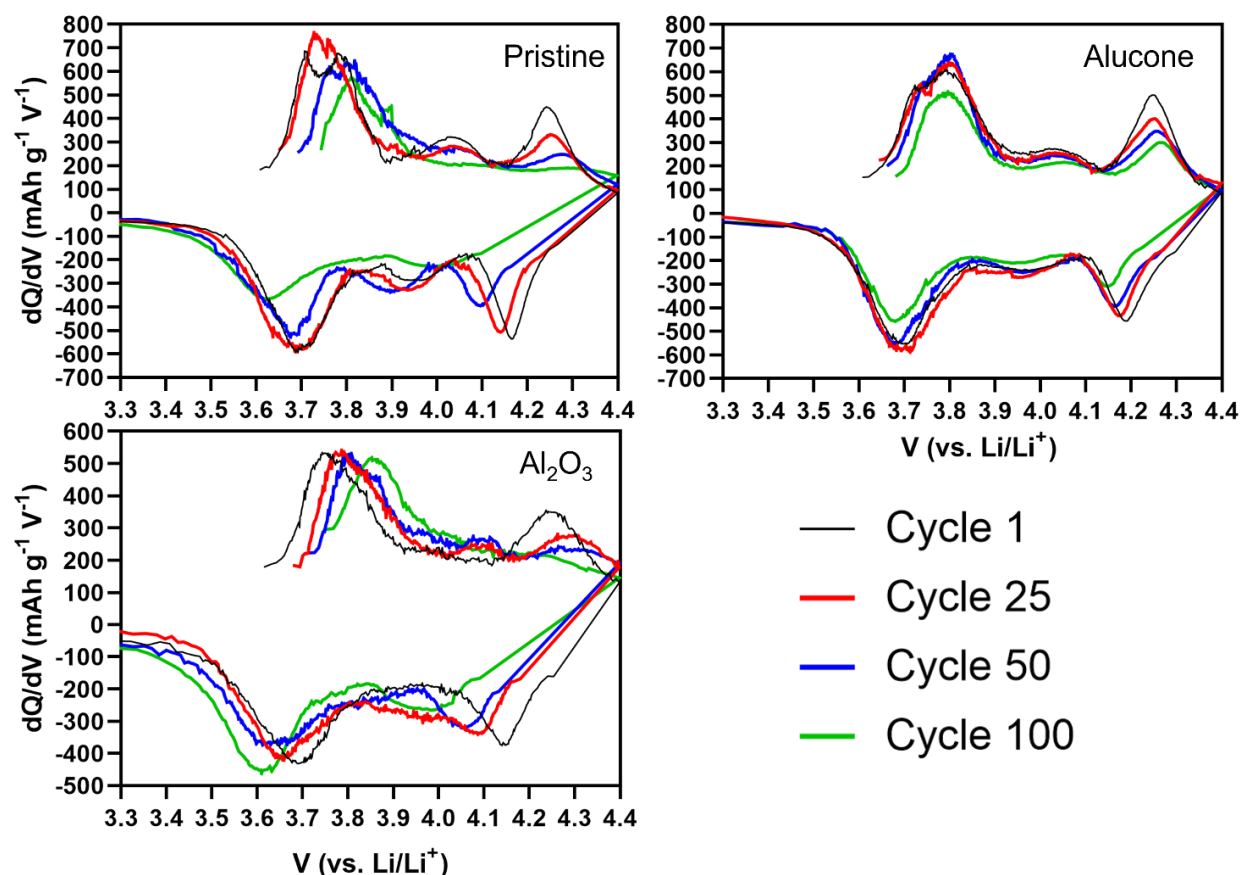


Figure 28. dQ/dV curves of cells cycled at C/3 and 2.75 – 4.4 V vs Li/Li⁺.

The analysis of cycle performance at various currents suggests that the coatings are most effective at suppressing active material loss. The most well studied mechanism of active material loss is transition metal dissolution driven by HF corrosion. HF is known to be generated from the reaction of LiPF₆ with trace moisture in the electrode or electrolyte in accordance with **Equation 1**:



This chemical reaction is independent of voltage. However, it is also known that substantial quantities of HF are generated at high voltages. A proposed mechanism suggests that lattice oxygen or evolved singlet oxygen dehydrogenates EC at high voltages, forming protic species on the surface of the cathode. These species subsequently react with LiPF₆, forming HF as a by-

product.¹⁸² Thus, the coatings play a prominent role in enhancing cycle stability at 0.1 C, as the cathode is exposed to lengthy durations at high voltages.

Figure 29 compares the rate performance of the pristine and coated electrodes from 0.1 C to 5 C. In general, the discharge capacity correlates closely with the average discharge voltage, with the metalcone coatings showing better kinetics than their metal oxide counterparts. This is likely because the metalcone coatings are more permeable to Li^+ diffusion as discussed previously. Interestingly, all coatings considerably improve the rate performance. In the case of the Al_2O_3 -coated electrode, this suggests that the initial CEI layer formed is passivating with low impedance compared to the pristine sample. However, as shown in **Figure 23** and **26**, the impedance grows considerably with extensive cycling. The Ti-coated electrodes show stronger kinetic performance compared to the Al-coated samples. In particular, the titanicone sample shows exceptional performance, retaining 85% and 99% of its discharge capacity and average discharge voltage respectively, when the current is ramped from 0.1 C to 5 C. This improvement in rate performance is in agreement with other work assessing TiO_2 -coated cathodes.^{183–185}

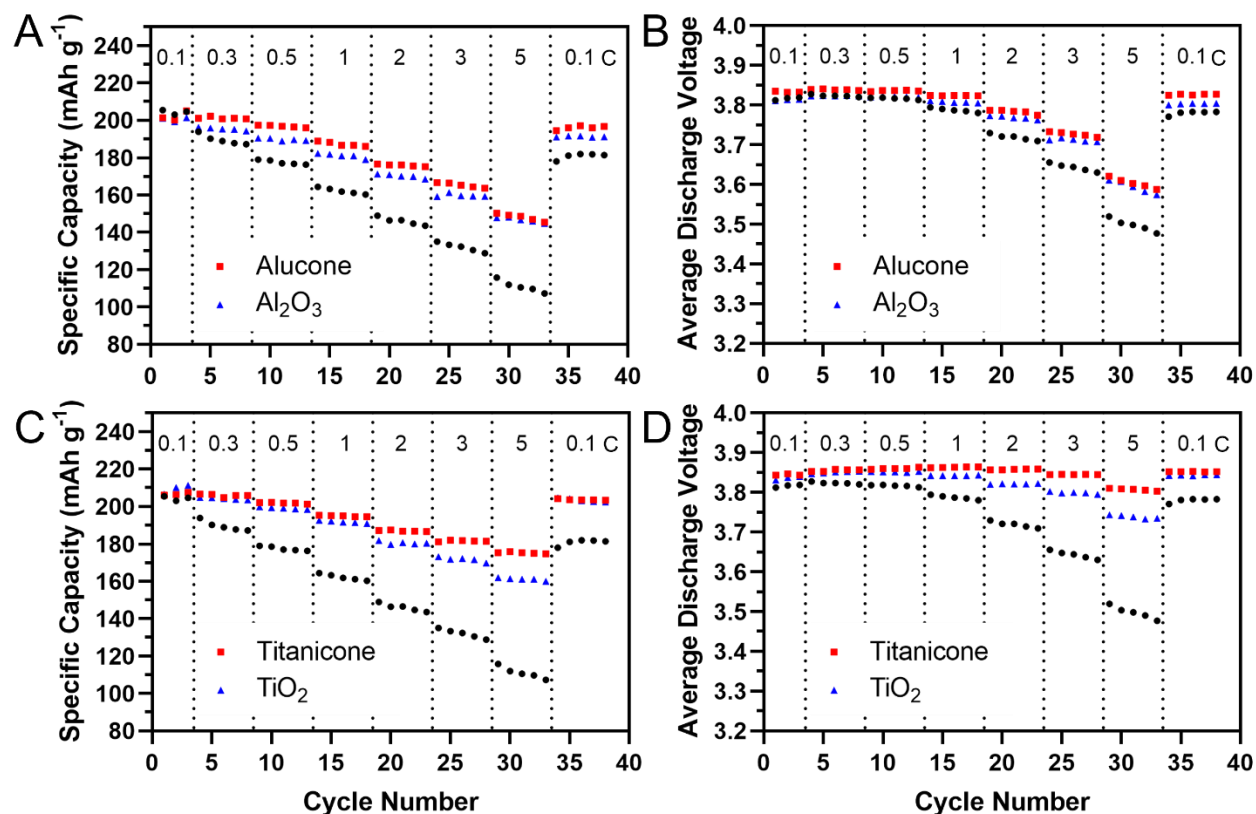


Figure 29. All cells cycled at 0.1 C charge and 0.1 to 5 C discharge at 2.75 – 4.4 V vs Li/Li⁺.

EIS analysis was conducted after five cycles at 0.1 C and compared at low (~ 3.5 V vs Li/Li⁺) and high (~ 4.35 V vs Li/Li⁺) SOC. **Figure 30** displays the equivalent circuit used for curve fitting, which reveals a high-frequency semicircle that corresponds to Li⁺ diffusion resistance through a surface film (R_{sf}) and a medium-frequency semicircle for charge transfer resistance (R_{ct}) on the active material surface. The fitted values for the circuit are listed in **Table 2**. Among all samples, the R_{ct} is lower at high SOC as Li⁺ insertion is more facile at low lithiation state. The Al₂O₃-coated electrode reveals a distinctly elevated R_{sf} , which confirms that the dense coating inhibits Li⁺ transport. On the other hand, the other coated samples display similar R_{sf} values while also lowering the R_{ct} relative to the pristine sample. This indicates that the coatings are Li⁺-permeable and can potentially also reduce surface reconstruction, which aids Li⁺ transport.

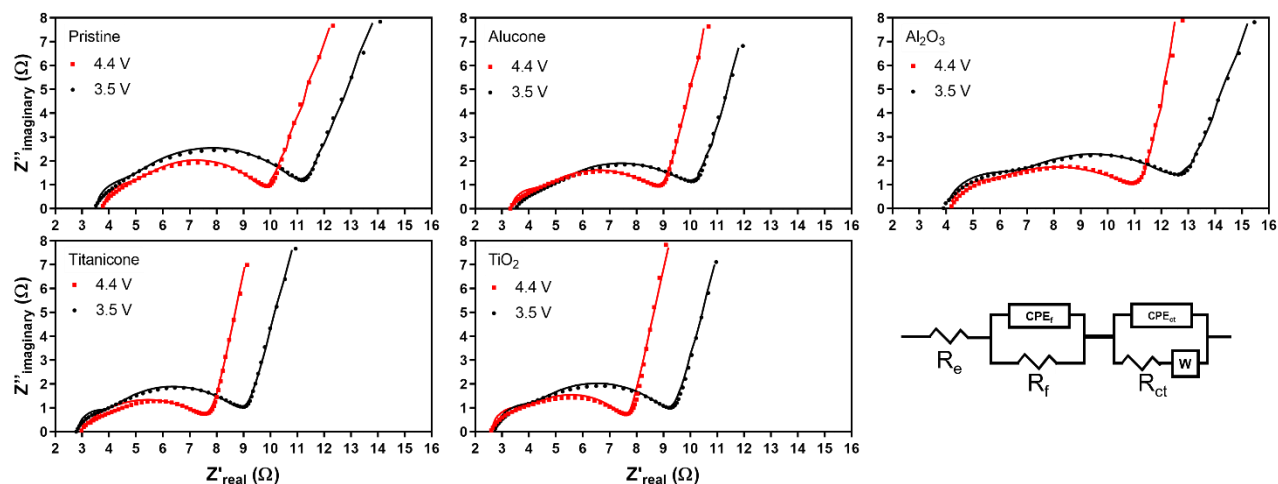


Figure 30. EIS curves of coated samples after five cycles at 0.1 C. Solid line represents the fitted curve based on the depicted equivalent circuit model.

Table 2. EIS curve fitting results.

Sample	Voltage (vs Li/Li ⁺)	R _{sf}	R _{ct}
Pristine	3.5	0.9	6.8
Pristine	4.35	0.9	5.1
Al ₂ O ₃	3.5	2.2	6.7
Al ₂ O ₃	4.35	1.8	5.8
Alucone	3.5	0.8	6.0
Alucone	4.35	0.7	5.0
TiO ₂	3.5	0.9	5.7
TiO ₂	4.35	0.9	4.2
Titanicone	3.5	0.7	5.5
Titanicone	4.35	0.6	5.0

4.3.3. Ex-Situ XPS Analysis of Cycled Electrodes

To analyze the chemical composition of the CEI layer, XPS was conducted on the cathode surface. Each sample was cycled five times between 2.75 – 4.4 V vs Li/Li⁺ under CC-CV conditions. The cathode was then recovered from the disassembled cell and analyzed at a high SOC (~4.35 V vs Li/Li⁺). This was done in order to avoid capturing chemical species that originate from Li metal ‘cross talk’. Recent work has shown that chemical species formed on the

highly reactive Li metal can dissolve into the electrolyte and deposit on the cathode during discharge.^{186–188}

Figures 31 and 32 show the peak-deconvoluted XPS spectra of key elements (C, O, F, and P) that comprise the CEI layer. For each element, the intensity is non-normalized and plotted with consistent y-axis scaling, and thus the peak areas correlate with their relative quantity. **Table 3 and 4** list the respective binding energies and relative quantity of the deconvoluted species. The notable peak assignments for the uncycled pristine (uncoated) sample include the $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ lattice oxygen (O 1s, ~529.4 eV) and PVDF (F 1s, ~688 eV; C 1s at ~286 eV and ~290.8 eV corresponding to $-\text{CH}_2-$ and $-\text{CF}_2-$ of PVDF respectively).¹⁸⁹ The other O 1s peaks are associated with surface groups of carbon black in the electrode. After cycling the pristine electrode, the CEI layer coats the electrode surface, suppressing the peak areas for the underlying $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ lattice oxygen and PVDF. Thus, the relative peak areas of these species can be used to qualitatively assess the thickness of the CEI layer. Inorganic species derived from the decomposition of LiPF_6 are present in the CEI layer – the F 1s spectra is deconvoluted with peaks assigned to LiF (~685 eV) and $\text{Li}_x\text{PF}_y\text{O}_z$ (~687 eV) species. The signal at ~685 eV may also include M-F such as NiF_2 / NiO_xF_y , which is a product of HF corrosion.⁹² It is worth mentioning that several reports indicate that at high voltage, fluoride species can be “leached” from the CEI layer and migrate to the anode.^{186–188} However, this is expected to occur at > 4.5 V vs Li/Li^+ and thus should not be significant in this work. The P 2p spectra is deconvoluted with two peaks corresponding to $\text{Li}_x\text{PF}_y\text{O}_z$ species, with the lower B.E. peak assigned to Li_3PO_4 or fluorophosphates with a lower degree of fluorination. Although organic species derived from the decomposition of the EC/DMC solvent are expected to comprise the CEI layer, the overall intensity of the C 1s spectra is lower when compared to the uncycled

electrode, likely because it is dictated by the underlying carbon black and PVDF electrode components. However, the increased intensity of the O 1s speak assigned to C-O/O-C=O species likely corresponds to poly(ethylene carbonate/oxide)-type species in the CEI layer.

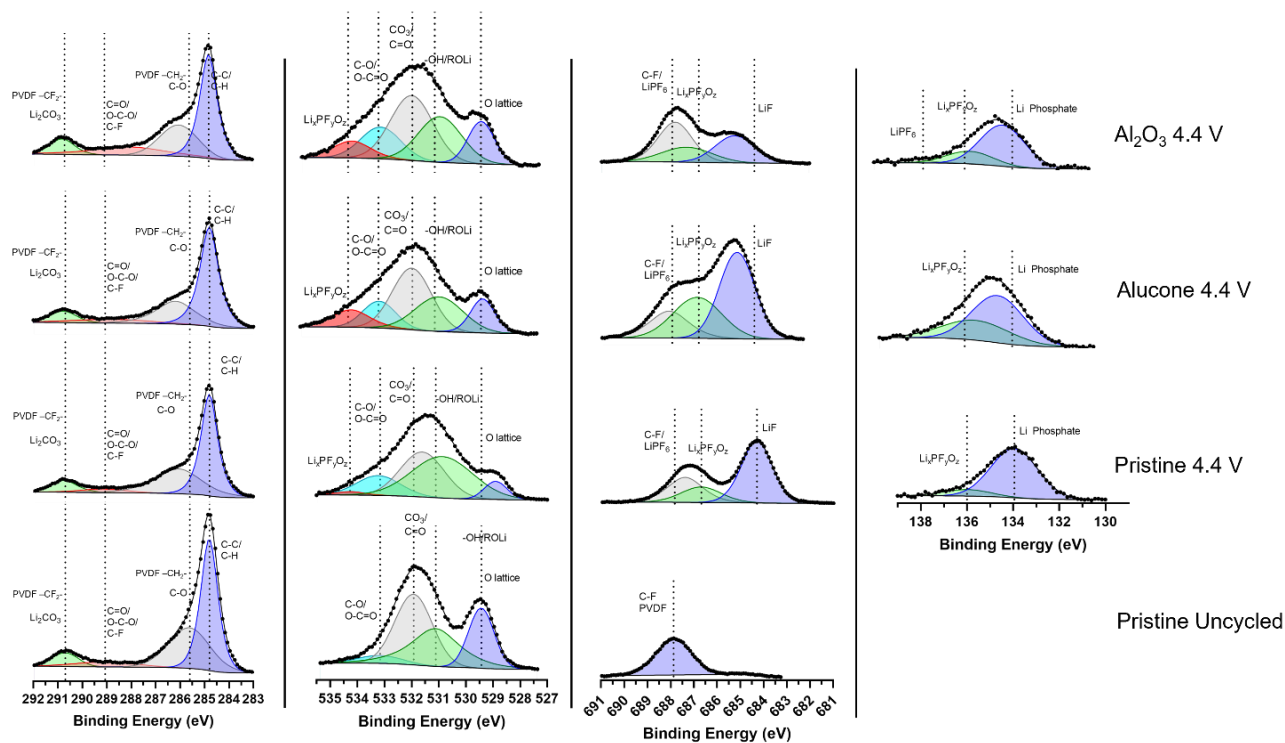


Figure 31. C 1s, O 1s, F 1s, and P 2p (left to right) *ex-situ* XPS spectra comparison of pristine and Al₂O₃/alucone-coated electrodes. For each element, the plotted intensities are non-normalized.

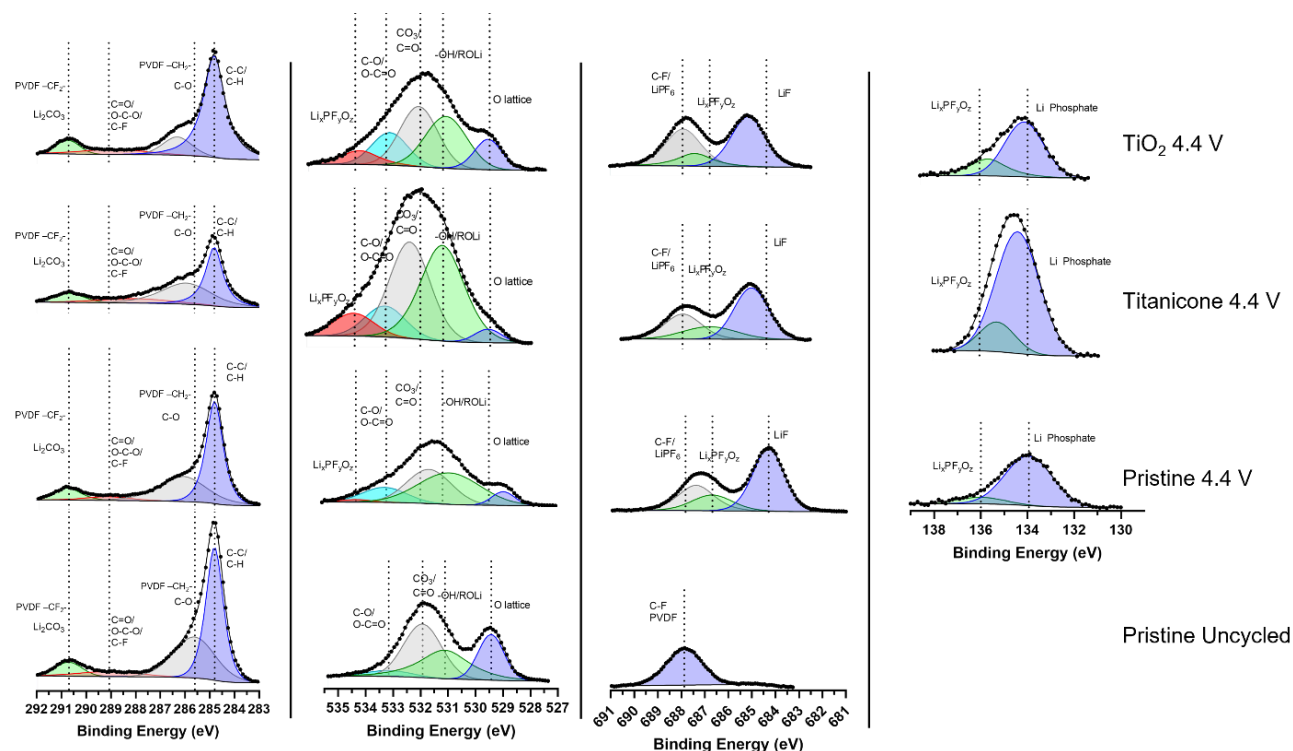


Figure 32. C 1s, O 1s, F 1s, and P 2p (left to right) *ex-situ* XPS spectra comparison of pristine and TiO₂/titanicene-coated electrodes. For each element, the plotted intensities are non-normalized.

Table 3. Binding energies derived from XPS peak fitting.

C 1s Sample	C-C/C-H	C-O/PVDF	C=O/O-C-O/C-F	Li ₂ CO ₃ /PVDF	
Pristine	284.8	285.6	289.1	290.7	
Pristine 4.4 V	284.8	286.1	289.1	290.7	
Pristine FEC 4.4 V	284.8	286	289.2	290.8	
Alucone-A 4.4 V	284.8	286.2	288.8	290.7	
Alucone-B 4.4 V	284.8	286	289.4	290.8	
Alucone FEC 4.4 V	284.8	286.2	289.2	290.7	
Al ₂ O ₃ 4.4 V	284.8	286	288.1	290.8	
TiO ₂ 4.4 V	284.8	286.3	288.8	290.7	
Titanicone 4.4 V	284.8	285.9	288.0	290.7	
O 1s Sample	O Lattice	-OH/ROLi	CO ₃ /C=O	C-O/O-C=O	Li _x PF _y O _z
Pristine	529.4	531.1	531.9	533.2	--
Pristine 4.4 V	529.0	531.0	531.7	533.2	534.3
Pristine FEC 4.4 V	529.3	530.8	532.0	533.2	534.2
Alucone-A 4.4 V	529.4	530.9	531.9	533.1	534.2

Alucone-B 4.4 V	529.4	531.0	532.0	533.2	534.1
Alucone FEC 4.4 V	529.2	531.0	532.0	533.1	534.0
Al ₂ O ₃ 4.4 V	529.4	530.9	531.9	533.1	534.1
TiO ₂ 4.4 V	529.5	531.0	532.0	533.0	534.1
Titanicone 4.4 V	529.5	531.1	532.3	533.2	534.3
F 1s Sample	LiF/M-F	Li _x PF _y O _z	C-F/LiPF ₆		
Pristine	--	--	687.9		
Pristine 4.4 V	684.4	686.9	687.5		
Pristine FEC 4.4 V	684.9	686.9	687.9		
Alucone-A 4.4 V	685.1	686.8	688.0		
Alucone-B 4.4 V	685.0	686.7	688.1		
Alucone FEC 4.4 V	684.8	685.9	687.7		
Al ₂ O ₃ 4.4 V	685.1	687.2	687.7		
TiO ₂ 4.4 V	685.1	687.2	687.8		
Titanicone 4.4 V	685	686.7	687.9		
P 2p Sample	Li Phosphate	Li _x PF _y O _z	LiPF ₆		
Pristine	--	--	--		
Pristine 4.4 V	134.1	136.1	--		
Pristine FEC 4.4 V	134.2	135.7	137.8		
Alucone-A 4.4 V	134.5	135.5	--		
Alucone-B 4.4 V	134.5	136.2	137.6		
Alucone FEC 4.4 V	134.4	135.5	137.7		
Al ₂ O ₃ 4.4 V	134.4	135.8	138.1		
TiO ₂ 4.4 V	134.1	135.6	--		
Titanicone 4.4 V	134.3	135.3	--		

Table 4. Relative composition of deconvoluted species derived from XPS peak areas.

C 1s Sample	C-C/C-H	C-O/PVDF	C=O/O-C-O/C-F	Li ₂ CO ₃ /PVDF
Pristine	51.1%	35.1%	6.3%	7.5%
Pristine 4.4 V	52.5%	33.8%	5.0%	9.1%
Pristine FEC 4.4 V	48.8%	35.4%	8.2%	7.6%
Alucone-A 4.4 V	57.1%	26.2%	8.1%	8.5%
Alucone-B 4.4 V	47.0%	39.7%	8.2%	5.1%
Alucone FEC 4.4 V	60.7%	29.7%	6.2%	3.4%
Al ₂ O ₃ 4.4 V	47.8%	27.9%	15.1%	9.2%
TiO ₂ 4.4 V	70.0%	13.6%	8.4%	8.0%
Titanicone 4.4 V	42.0%	37.7%	10.9%	9.4%

O 1s Sample	O Lattice	-OH/ROLi	CO ₃ /C=O	C-O/O-C=O	Li _x PF _y O _z
Pristine	23.4%	31.1%	40.2%	5.3%	--
Pristine 4.4 V	6.9%	43.2%	33.3%	14.7%	1.8%
Pristine FEC 4.4 V	6.4%	21.1%	39.0%	23.3%	10.2%
Alucone-A 4.4 V	13.1%	25.4%	37.2%	13.6%	10.7%
Alucone-B 4.4 V	2.4%	21.7%	47.0%	20.0%	8.8%
Alucone FEC 4.4 V	1.2%	15.9%	49.7%	19.8%	13.3%
Al ₂ O ₃ 4.4 V	14.4%	25.4%	35.4%	16.3%	8.5%
TiO ₂ 4.4 V	12.3%	30.7%	32.3%	16.7%	7.9%
Titanicone 4.4 V	3.4%	39.9%	36.7%	11.5%	8.6%
F 1s Sample	LiF/M-F	Li _x PF _y O _z	C-F/LiPF ₆		
Pristine	--	--	100%		
Pristine 4.4 V	55.5%	18.0%	26.4%		
Pristine FEC 4.4 V	62.5%	23.7%	13.8%		
Alucone-A 4.4 V	49.8%	32.3%	17.9%		
Alucone-B 4.4 V	60.5%	35.2%	4.3%		
Alucone FEC 4.4 V	52.1%	37.4%	10.5%		
Al ₂ O ₃ 4.4 V	33.4%	23.2%	43.4%		
TiO ₂ 4.4 V	48.5%	13.7%	37.8%		
Titanicone 4.4 V	52.0%	20.0%	28.0%		
P 2p Sample	Li Phosphate	Li _x PF _y O _z	LiPF ₆		
Pristine	--	--	--		
Pristine 4.4 V	88.2%	11.8%	--		
Pristine FEC 4.4 V	47.6%	49.1%	4.3%		
Alucone-A 4.4 V	64.0%	36.0%	--		
Alucone-B 4.4 V	82.0%	13.5%	4.5%		
Alucone FEC 4.4 V	46.2%	47.2%	6.6%		
Al ₂ O ₃ 4.4 V	71.8%	23.0%	5.2%		
TiO ₂ 4.4 V	75.0%	25.0%	--		
Titanicone 4.4 V	83.3%	16.7%	--		

In the alucone-coated cycled electrode, the most notable distinctions compared to the cycled pristine sample are 1) the thinner CEI layer as inferred by the larger peak areas of the LiNi_{0.83}Mn_{0.06}Co_{0.11}O₂ lattice oxygen and PVDF and 2) the larger quantity of fluoride species (LiF/M-F and Li_xPF_yO_z) in the CEI layer. In the literature, analysis of the CEI layer composition has produced conflicting conclusions, particularly on the presence and role of fluoride species. In

some studies, a stability-enhancing cathode coating or electrolyte additive was employed, and the authors observed a decreased quantity of fluoride species (LiF and $\text{Li}_x\text{PF}_y\text{O}_z$) in the CEI layer compared to the pristine sample after electrochemical cycling. As these species originate from the decomposition of LiPF_6 , with HF generated as a by-product, the authors concluded that the cathode coating or electrolyte additive improves cycle stability by suppressing deleterious electrode-electrolyte side reactions.^{190–192} However, these fluoride and (fluoro)phosphate species are also known to enhance the stability of CEI/SEI layers.¹⁶⁴ Their electronically insulating nature and high electrochemical stability allow them to passivate electrodes from further side reactions. Moreover, recent work has suggested that phosphate and fluorophosphate species in the CEI layer can chelate with transition metals, forming insoluble complexes (*e.g.*, NiPO_3F), which can suppress their dissolution into their electrolyte.^{193–195} LiF in particular is also well known to mechanically reinforce the CEI/SEI layers, particularly for Li metal and silicon anodes, which undergo large volume changes during electrochemical cycling. Thus, LiF is likely an important component of the CEI layer for Ni-rich cathodes, as volume changes (~12%) are notable during the H2 $\rightarrow$ H3 phase transition.⁴⁸ On the other hand, LiF is known to increase interfacial impedance as it is ionically insulating.

Further complicating the discussion is that ceramic coatings are known to react with fluorides. Ceramic coatings (*e.g.*, Al_2O_3) are well known to serve as ‘HF scavengers’ in accordance with

Equation 2:



The alucone analogue of this reaction is depicted below in **Equation 3:**



In our work, the formation of Al-F in both the alucone and Al_2O_3 coating is confirmed from the Al 2p XPS spectra (**Figure 33**). Based on the binding energies (**Table 5**), the Al-F exists as an aluminum oxyfluoride rather than AlF_3 , which is expected as the cell was cycled only five times.⁹² As protic species like water and ethylene glycol (E.G.) are produced, they can rapidly react with LiPF_6 , re-generating HF.^{182,196} Assuming that the coating uniformly covers the active material, AlF_3 is inert to HF corrosion and can suppress further active material loss. However, as discussed earlier the ALD-applied electrode coating does not reach all active particles as depicted in **Figure 18C**. Thus, HF scavenging alone does not explain the improved cycle retention generated by the coating (**Table 1**).

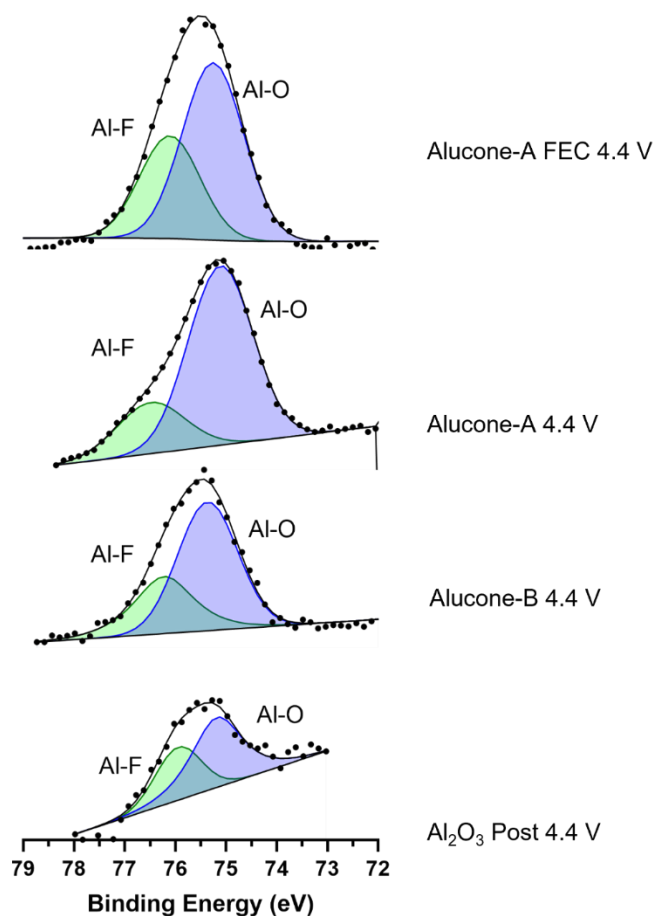


Figure 33. Al 2p XPS spectra of cycled Al_2O_3 and alucone-coated electrodes. Intensities are non-normalized and shifted vertically for clarity.

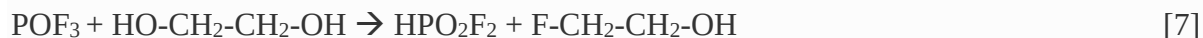
Table 5. XPS binding energies and relative composition of Al 2p on cycled electrodes.

Al 2p Sample	Al ₂ O ₃ /TiO ₂	Al-F/Ti-F	Al-F to Al-O / Ti-F to Ti-O Intensity Ratio
Alucone-A 4.4 V	75.1	76.5	0.23
Alucone-B 4.4 V	75.4	76.2	0.33
Al ₂ O ₃ 4.4 V	75.2	75.9	0.38
Alucone FEC 4.4 V	75.3	76.2	0.34
Titanicone 4.4 V	459.5	460.2	0.34

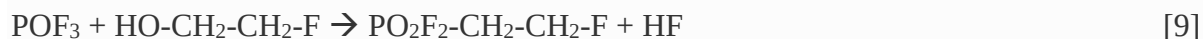
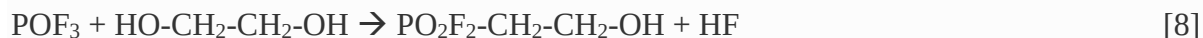
Recent work has suggested that ceramic coatings can catalyze the decomposition of LiPF₆ to form PO₂F₂⁻ as shown in **Equation 4**, which is a known electrolyte additive that increases the fluoride content in both the CEI and SEI layers and controls impedance growth, thus extending the cycle life.⁹⁵



This reaction should also occur with alucone, according to the equations portrayed below. It first begins with the production of E.G. as shown in **Equation 3**. The evolved E.G. can subsequently react with LiPF₆/PF₅:



The HF by-product (**Equation 6**) can react again with the alucone coating, generating more E.G. to propagate the reaction.¹⁹⁷ Besides HPO₂F₂, it should be noted that other potential reactions and products include:



$\text{PO}_2\text{F}_2\text{-CH}_2\text{-CH}_2\text{-F}$ can subsequently react with EC to form oligoethylene oxide capped with fluorophosphate and alkyl fluoride end groups ($\text{PO}_2\text{F}_2\text{-(CH}_2\text{-CH}_2\text{-O)}_n\text{-CH}_2\text{-CH}_2\text{-F}$).¹⁹⁶

As discussed, **Figure 23 – 28** show low impedance growth for the alucone-coated sample, which implies that the insulative LiF and fluorophosphate species do not continuously accumulate in the CEI layer with extended electrochemical cycling. Overall, the results suggest that the alucone coating acts by accelerating the formation of these fluoride species, which protect and reinforce the CEI layer against additional side reactions, oxygen release, and transition metal dissolution at an earlier onset.

With brief discussion, **Figure 34** compares the chemical composition of the cycled Alucone-A and Alucone-B coated electrode. **Figure 33** corresponds with **Figure 15**, where the Al 2p intensity of Alucone-B is diminished compared to that of Alucone-A as the coating is thinner on the upper electrode surface due to the increased penetration of the ALD precursors. In both cases, the quantity of fluoride species is elevated relative to that in the pristine sample. The CEI layer of Alucone-B is thicker with an increased presence of decomposition products from the carbonate solvent (O 1s C=O/O-C=O/C-O species) while also containing a lower amount of fluoride species compared to Alucone-A. This is likely because the coating on the Alucone-B electrode surface is thinner, which reduces the apparent passivation effect of the coating as detected by surface-sensitive XPS scans.

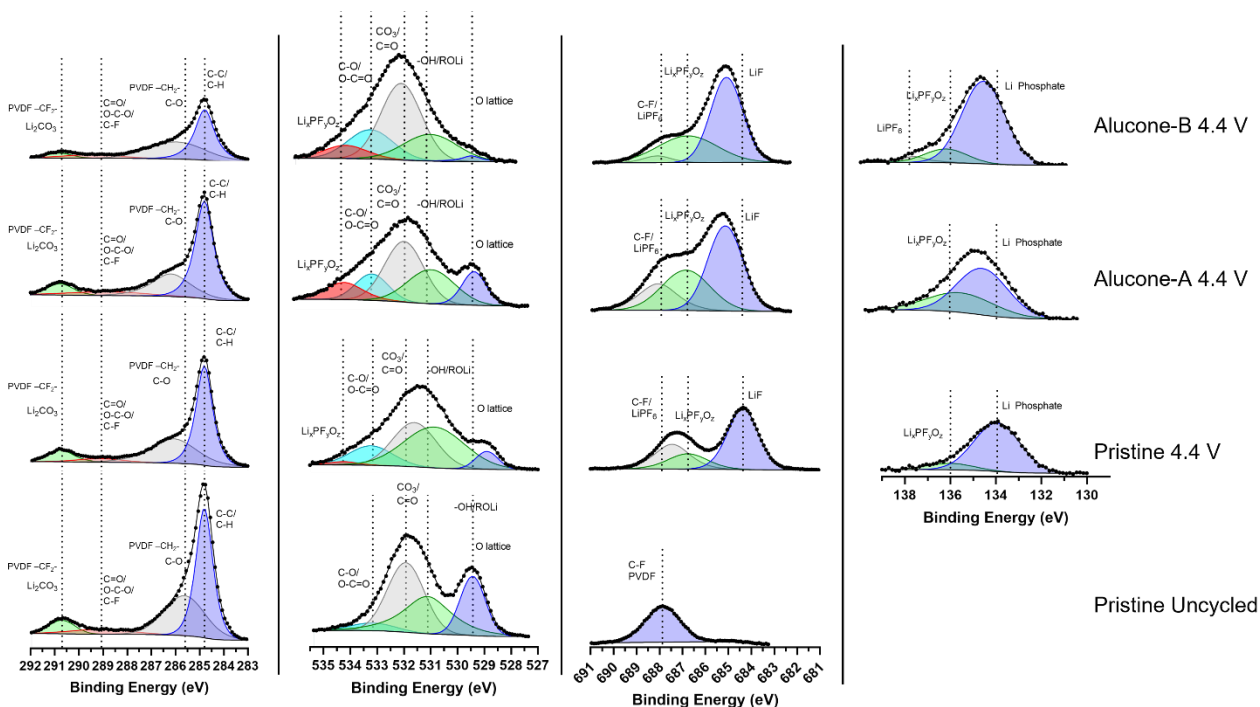


Figure 34. C 1s, O 1s, F 1s, and P 2p (left to right) *ex-situ* XPS spectra comparison of pristine and alucone-coated electrodes. For each element, the plotted intensities are non-normalized.

As shown in **Figure 33**, the peak intensity of the Al 2p spectra for the Al_2O_3 -coated electrode is lower compared to alucone, implying that the coating on the surface is thinner. This is likely because ALD for the metal oxide coatings was conducted at a higher temperature (175 vs 120 °C), which improves the diffusion and electrode penetration of the ALD precursors. However, as discussed earlier, the coating is unlikely to penetrate the entire electrode and these *ex-situ* XPS results only capture the upper surface layer of the electrode where the coating is localized. Compared to alucone, the cycled Al_2O_3 -coated electrode shows a thinner CEI layer, indicating that it is more effective at suppressing side reactions with the electrolyte due to its electronically and ionically insulating nature. Its higher density than alucone also makes it more effective at preventing direct contact between the electrode (surface) and electrolyte (**Figure 18**). However, due to the localized coating, this effect is not believed to occur throughout the entire electrode. Interestingly, the electrode surface shows a low quantity of inorganic LiF, $\text{Li}_x\text{PF}_y\text{O}_z$, and

phosphate species even when compared to the pristine sample. Similar to alucone, a reaction between Al_2O_3 and PF_6^-/F^- is expected, which should increase the quantity of fluoride species in the CEI layer, beginning with **Equation 2** and continuing with **Equations 10-11** below:



Figure 33 also confirms the formation of Al-F among Al_2O_3 . We propose that the Al_2O_3 coating has poorer kinetics for these reactions compared to alucone due to its high density, which hinders the accessibility of available Al^{3+} Lewis acid sites for fluorination, as depicted in **Figure 18**. The build-up of LiF and $\text{Li}_x\text{PF}_y\text{O}_z$ species was not evident as the CEI layer was analyzed after only five charge-discharge cycles. As LiF is well known to increase the impedance of the CEI, the low quantity of LiF detected here may explain the good initial kinetic performance of the Al_2O_3 -coated electrode shown in **Figure 29**. However, build-up of LiF species in combination with the insulating properties of the Al_2O_3 coating may explain the rapid impedance growth over increasing cycles as shown in **Figures 23** and **26**. Another key distinction with the alucone sample is that a much lower quantity of Li^+ is detected in the Al_2O_3 coating and CEI layer (**Figure 35**). This may imply poor permeability and saturation of Li^+ in Al_2O_3 . A low quantity of Li^+ in the CEI layer is associated with increased ohmic resistance and hindered Li^+ transport under an electric field.¹⁹⁸ In contrast, the low-density and polar ethylene oxide moieties of the alucone coating can promote Li^+ transport. These polar groups can promote Li^+ diffusion paths and assist with de-solvation during the Li^+ insertion process.¹⁹⁸

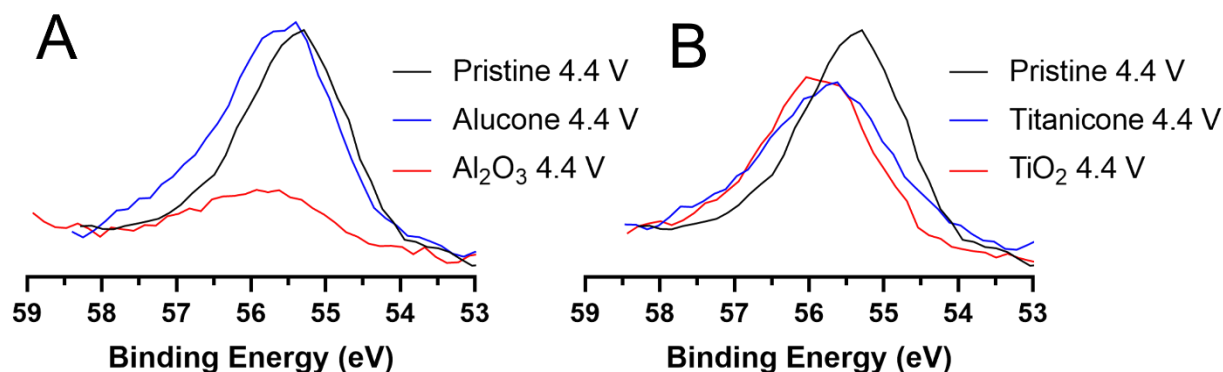


Figure 35. Comparison of Li 1s XPS peak areas for cycled pristine and coated electrode.

As shown in the Ti 2p spectra (**Figure 36**), the titanicone coating is substantially thicker and thus more localized on the electrode surface compared to TiO_2 . Based on the vapor pressure curve of the TiCl_4 ALD precursor used in both samples, the difference in deposition temperature (120 vs. 175 °C) used likely makes a substantial impact on the diffusion kinetics and electrode penetration. Similar to Al_2O_3 , the TiO_2 -coated electrode has a thinner CEI layer than with titanicone, likely due to its suppressed reactivity with the electrolyte. However, the TiO_2 -modified CEI layer is slightly thicker compared to Al_2O_3 , which is expected as Al_2O_3 is a higher band gap insulator and known to be more effective at suppressing solvent decomposition.¹⁹⁹ Interestingly, in both TiO_2 and titanicone, the fluoride content and profile (LiF to $\text{Li}_x\text{PF}_y\text{O}_z$ ratio, **Table 6**) are similar to that in the cycled pristine sample. One notable distinction is that the titanicone-coated sample contains a large amount of phosphate species (Li_3PO_4 or low-fluorine $\text{Li}_x\text{PF}_y\text{O}_z$) in the CEI layer.

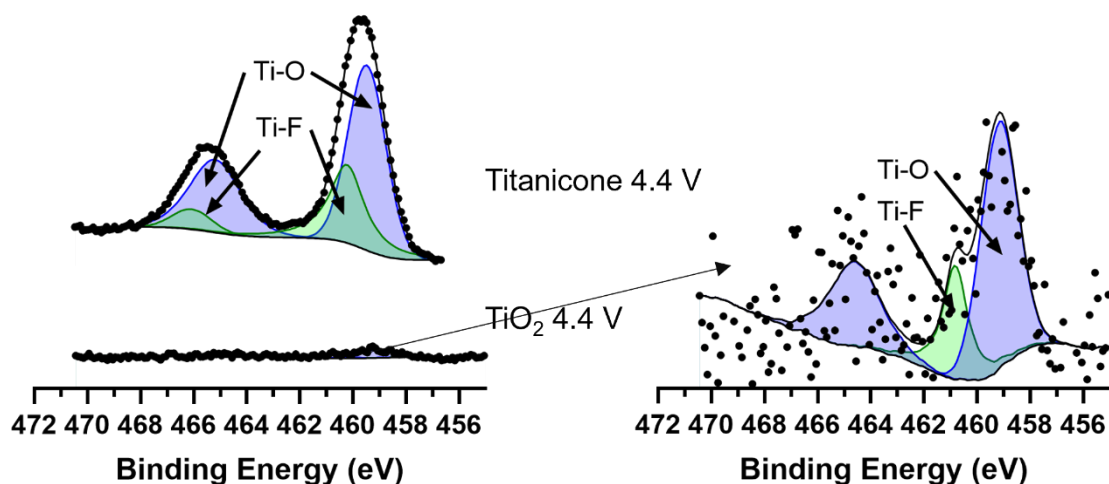


Figure 36. Ti 2p XPS spectra of cycled TiO_2 and titaniconce-coated electrodes. Intensities of the left plot are non-normalized and shifted vertically for clarity.

Table 6. Relative composition of fluoride species in the CEI layer based on XPS. Composition adjusted to exclude C-F from PVDF.

F 1s Relative Composition (Adjusted)	LiF/M-F	$\text{Li}_x\text{PF}_y\text{O}_z$
Pristine 4.4 V	75%	25%
Alucone-A 4.4 V	61%	39%
Alucone-B 4.4 V	63%	37%
Al_2O_3 4.4 V	58%	42%
Titaniconce 4.4 V	72%	28%
TiO_2 4.4 V	78%	22%
Pristine FEC 4.4 V	73%	27%
Alucone FEC 4.4 V	58%	42%

TiO_2 /titaniconce is expected to undergo similar reactions with F^-/PF_6^- as does Al_2O_3 /alucone (depicted in **Equations 2 – 11**). The Ti 2p spectra **Figure 36** confirms the formation of Ti-F (titanium oxyfluoride) species in both the TiO_2 and titaniconce coating.²⁰⁰ Moreover, Ti^{4+} has a higher Lewis acidity than Al^{3+} due to its higher formal charge, which implies enhanced reactivity with F^- .²⁰¹ However, the small quantity of LiF and $\text{Li}_x\text{PF}_y\text{O}_z$ detected, particularly for the surface

localized titanicone-coated sample, may imply they have poor adsorption or compatibility. On the other hand, phosphate species are known to adsorb strongly and bind to the surface of TiO_2 through inner sphere complexes.²⁰² It is emphasized that the XPS results capture the composition of the upper electrode surface, where the coating is localized. Given that the cycle performance of the Ti-coated electrodes is similar to the Al-based coatings (**Table 1**), LiF and $\text{Li}_x\text{PF}_y\text{O}_z$ are believed to be prevalent throughout the electrode to help passivate and reinforce the CEI layer. Another potential explanation is that TiO_2 is known to have a higher Brønsted acidity compared to Al_2O_3 , and thus it naturally has a lower amount of surface hydroxyl groups.²⁰³ These surface hydroxyl groups can react directly with $\text{LiPF}_6/\text{PF}_5$ to form LiF and $\text{Li}_x\text{PF}_y\text{O}_z$ as depicted in **Equation 6**. Thus, decomposition of LiPF_6 on the Ti-based coatings may be slower compared to Al. The isoelectric point (intrinsic surface charge) of TiO_2 is known to be similar to Ni-rich cathodes, which may explain the similar fluoride profiles among the pristine, TiO_2 , and titanicone-coated samples.²⁰³ Nevertheless, the prevalence of ionically conductive Li_3PO_4 ($\sim 10^{-6}$ S/m) and relatively low quantity of insulative fluoride species in the CEI layer likely explain the excellent rate performance of Ti-based coatings as depicted in **Figure 29**. Li_3PO_4 is an established cathode coating material that is known to enhance rate performance.^{204,205} Furthermore, a large quantity of Li is detected in the CEI and coating layer of both TiO_2 and titanicone, which may imply excellent Li^+ permeability.

Figure 37 shows the *ex-situ* XAS spectra of Ni for the pristine and coated samples. The electrodes were tested and prepared under the same conditions as analyzed by XPS. However, no distinctions in binding energies among the cycled pristine and coated samples are observed, because the binding energy is a bulk-average of the Ni valence state throughout the entire electrode. While differences in Ni valence state are expected on the particle surface due to

surface reconstruction (Ni^{2+} -O phase), this phase has a nanometer scale thickness, and thus comprises a negligible portion of the bulk Ni. These results simply confirm that the electrodes are analyzed at an identical SOC.

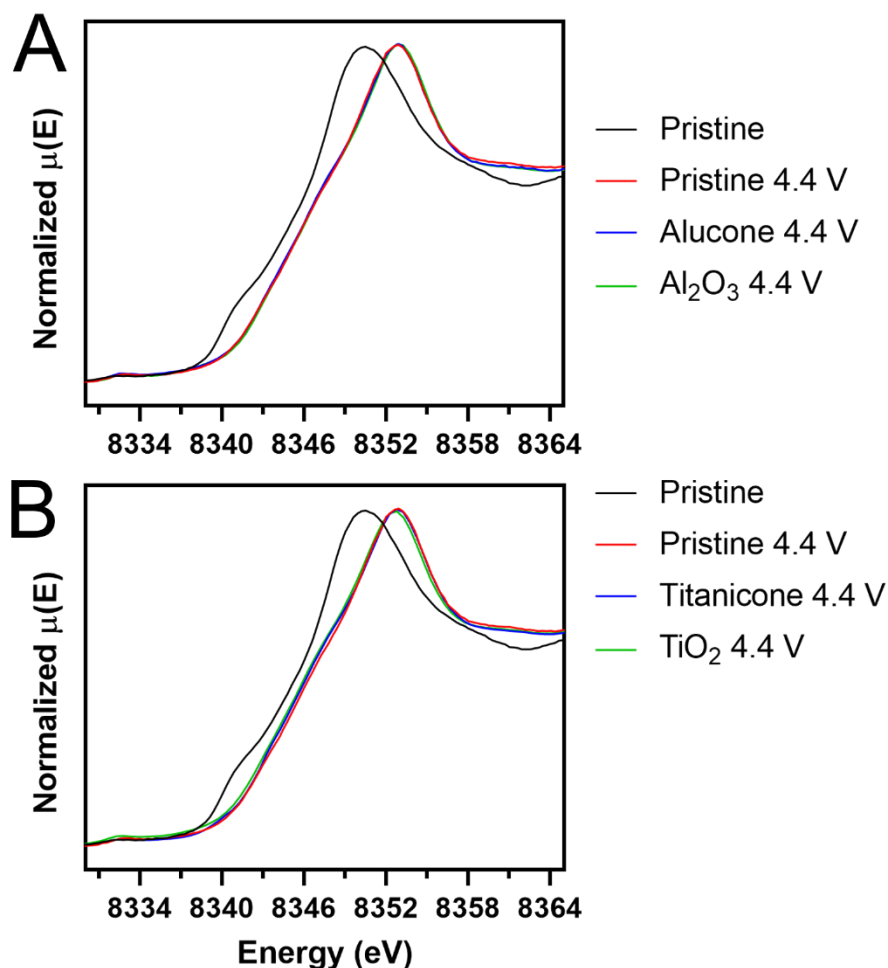


Figure 37. *Ex-situ* normalized XAS spectra comparison of A) Al-based electrode coatings and B) Ti-based electrode coatings.

4.3.4. Coatings and Electrolyte Additives

The body of results indicate that the coatings primarily act by reacting with the electrolyte, producing by-products that modify the composition of the CEI layer. Thus, the coating material does need to thoroughly cover all surfaces of the active particle. To further illustrate this, a TiO_2

‘coating’ was applied by mixing nanoparticles (~50 nm average size, 1 wt%) either in the cathode slurry during electrode fabrication or into the electrolyte as a suspension. **Figure 38** shows the cycle performance at 0.1 C, with both methods showing a substantial improvement in capacity retention, similar to the ALD-applied coating. Although these nanoparticles do not form a tight coating on the particle surface, it is believed that their close proximity to the cathode particles is beneficial to ensure that HF generated at elevated voltages reacts with the coating rather than corroding the active transition metals. The results shown in **Figure 38** also raises questions about side reactions with F^-/PF_6^- occurring in ceramic-coated separator materials. Although not used in this work, these separators are conventionally used in commercial LIBs due to their high resistance to thermal shrinkage. However, limited work that demonstrates their potential role in improving cycle stability has been reported.¹⁹⁷

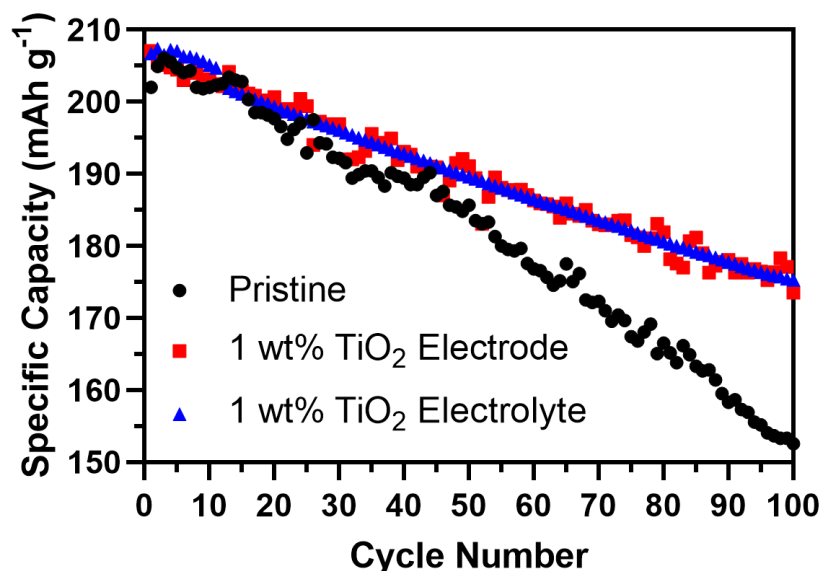


Figure 38. Comparison of capacity retention at 0.1 C and 2.75 – 4.4 V vs Li/Li⁺. TiO₂ nanoparticles (~50 nm, rutile, 1 wt%) were added either to the cathode slurry or electrolyte.

The key stability-enhancing mechanism observed in metal oxide and metalcone coatings appears to overlap with electrolyte additives, which preferentially decompose during cycling and help

form a passivating CEI/SEI layer. Thus, preliminary work was conducted to assess whether electrolyte additives could work synergistically with ALD-applied coatings to improve cycle stability. Fluoroethylene carbonate (FEC) was chosen as a representative electrolyte additive as it is commonly used in research work and known to form a compact and inorganic LiF-rich CEI and SEI layer.^{206,207} As this is similar to the results observed in the alucone-coated electrode, these two modification strategies were combined and analyzed. The modified electrolyte contained 5 vol% FEC – this amount was chosen as a large portion of the additive is expected to be consumed on the Li metal counter electrode.

Figure 39 shows that when cycled at 0.1 C, the incorporation of FEC additive alone yielded minor improvements in both the discharge capacity and average discharge voltage retention when compared to the conventional electrolyte. The improvement is largest beyond 50 charge-discharge cycles. However, this stability is still poor relative to the alucone-coated electrode cycled with conventional electrolyte. Interestingly, the FEC-modified electrolyte coupled with the alucone-coated electrode yields the best capacity retention by a small margin.

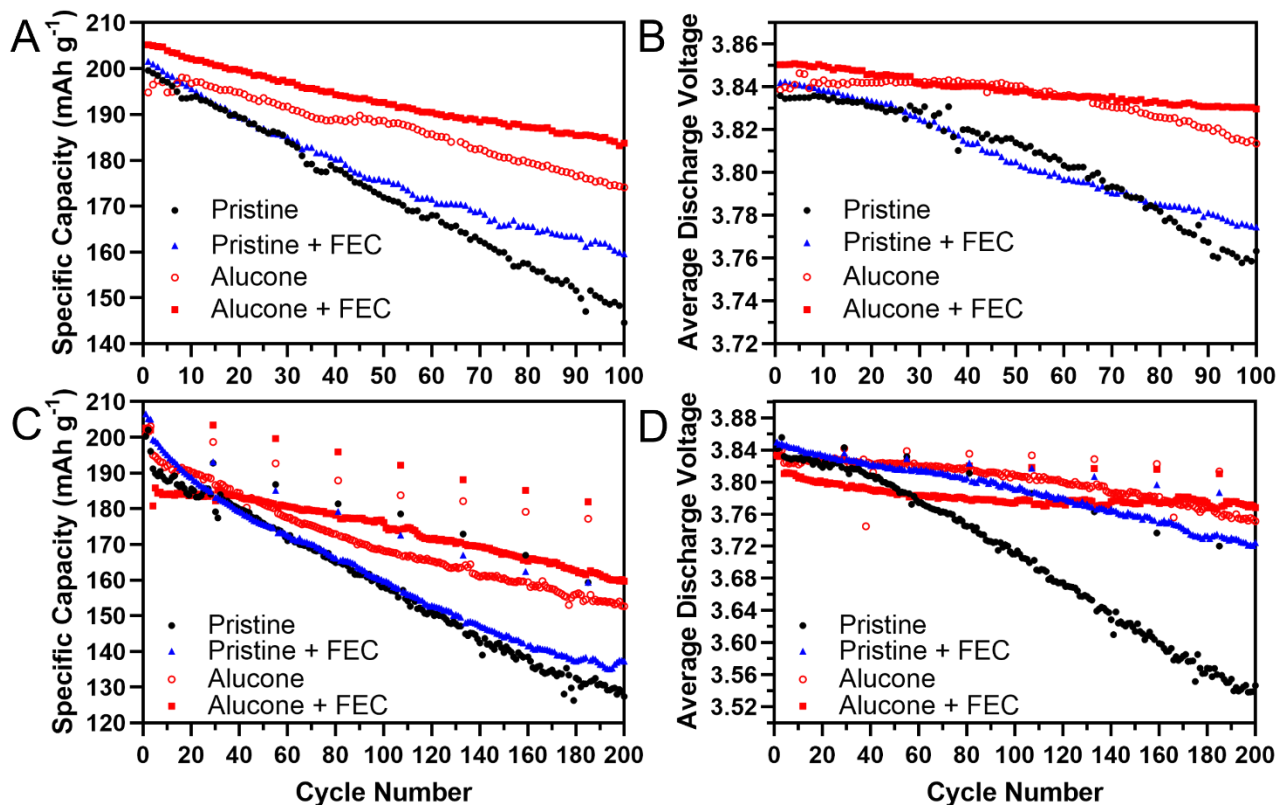


Figure 39. Capacity retention (A and C) and average discharge voltage (B and D) of pristine, FEC-modified, and alucone-coated electrodes cycled from 2.75 – 4.4 V vs Li/Li⁺ at 0.1 C (A and B) C/3 (C and D).

As shown in the dQ/dV curves (**Figure 40**), the alucone and FEC co-modified cell exhibits the lowest polarization and decay of the H2 → H3 phase transition peaks. Similar trends are observed when cycling at C/3. Modification by FEC alone produces little to no improvement in cycle retention in comparison to the pristine sample. However, retention of the average discharge voltage is substantially improved. The dQ/dV curves (**Figure 41**) show that FEC modification suppresses peak polarization and decay of the H2 → H3 peak intensities. However, similar to the pristine sample, severe capacity decay is observed after 100 cycles with the loss of peak area/intensity at all SOC. This decay is indicative of active material loss. The FEC and alucone co-modified cell exhibits outstanding preservation of peak shift and area at all SOC. In summary, the following conclusions are derived from the data: 1) FEC alone is capable of

suppressing impedance growth particularly at elevated currents, but minimally effective at preventing active material loss, 2) alucone alone is more effective than FEC at suppressing impedance growth at both 0.1 C and C/3, and 3) the combination of FEC with alucone produces the best results in suppressing both active material loss and impedance growth.

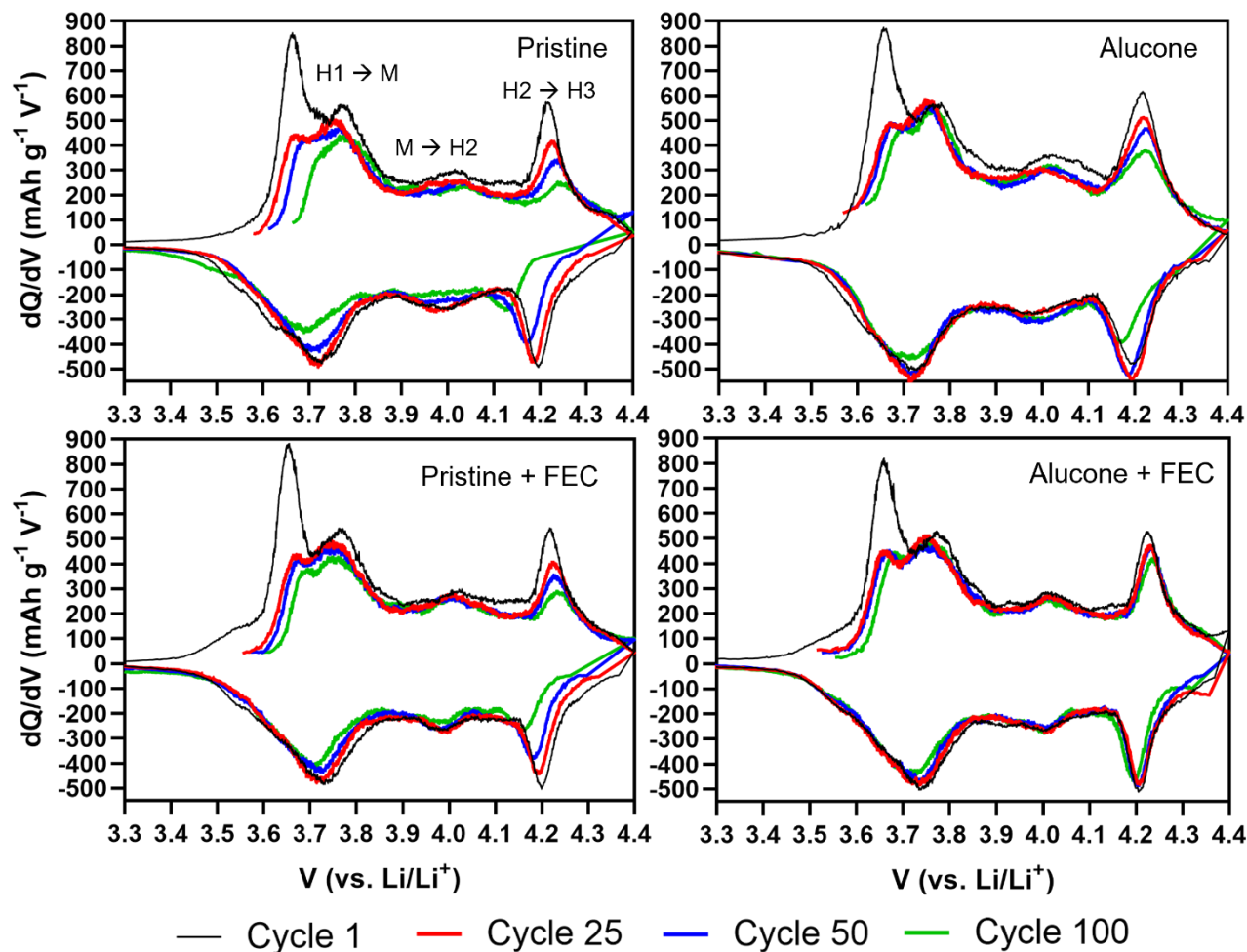


Figure 40. dQ/dV curves of cells cycled at 0.1 C and 2.75 – 4.4 V vs Li/Li⁺.

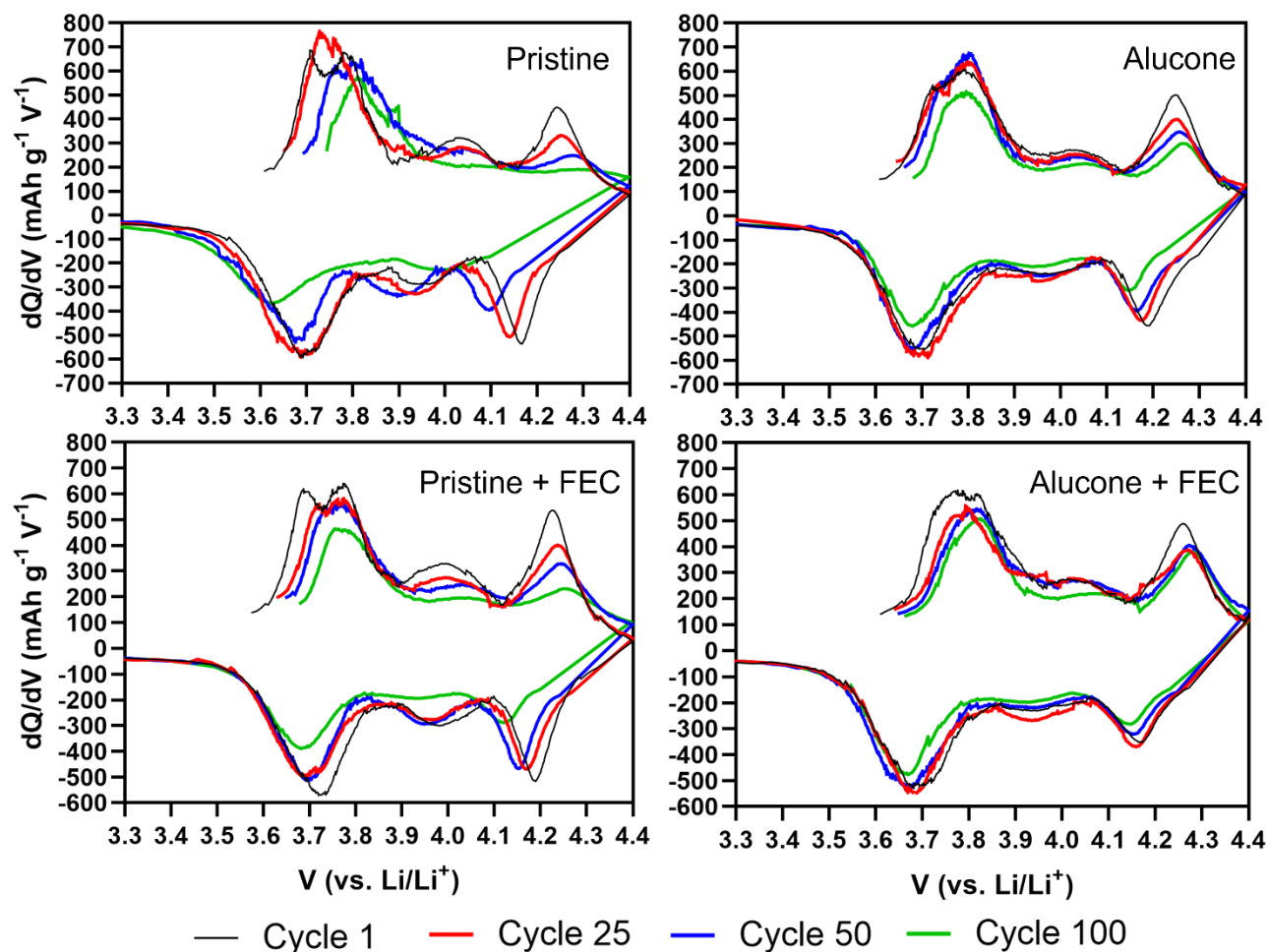


Figure 41. dQ/dV curves of cells cycled at C/3 and 2.75 – 4.4 V vs Li/Li⁺.

XPS analysis was conducted in the same manner previously described in order to study the chemical composition of the CEI layer (**Figure 42**). In comparison to the pristine sample, the FEC-modified CEI layer was thicker and contained a larger quantity of fluoride species, particularly LiF. FEC is expected to decompose *via* dehydrofluorination, forming HF and vinylene carbonate (VC) which further react at the electrode interfaces.²⁰⁷ The increased quantity of C-O/O=C=O species as revealed in the O 1s spectra likely indicates the presence of poly(vinylene carbonate) or polycarbonate species produced from VC, also a well known electrolyte additive that should aid in CEI passivation. LiF is likely produced from the reaction

of HF with Li^+ . It is also acknowledged that LiF may originate from the Li metal counter electrode through chemical ‘cross talk’. HF can react with the Li metal surface to form LiF, which can then dissolve into the electrolyte re-deposit on the cathode surface, as has been recently shown.¹⁸⁶ Although HF forms LiF that helps passivate the CEI layer, it can also corrode and dissolve the active material. This may explain why the cycle performance data show that FEC is mostly ineffective at suppressing active material loss.

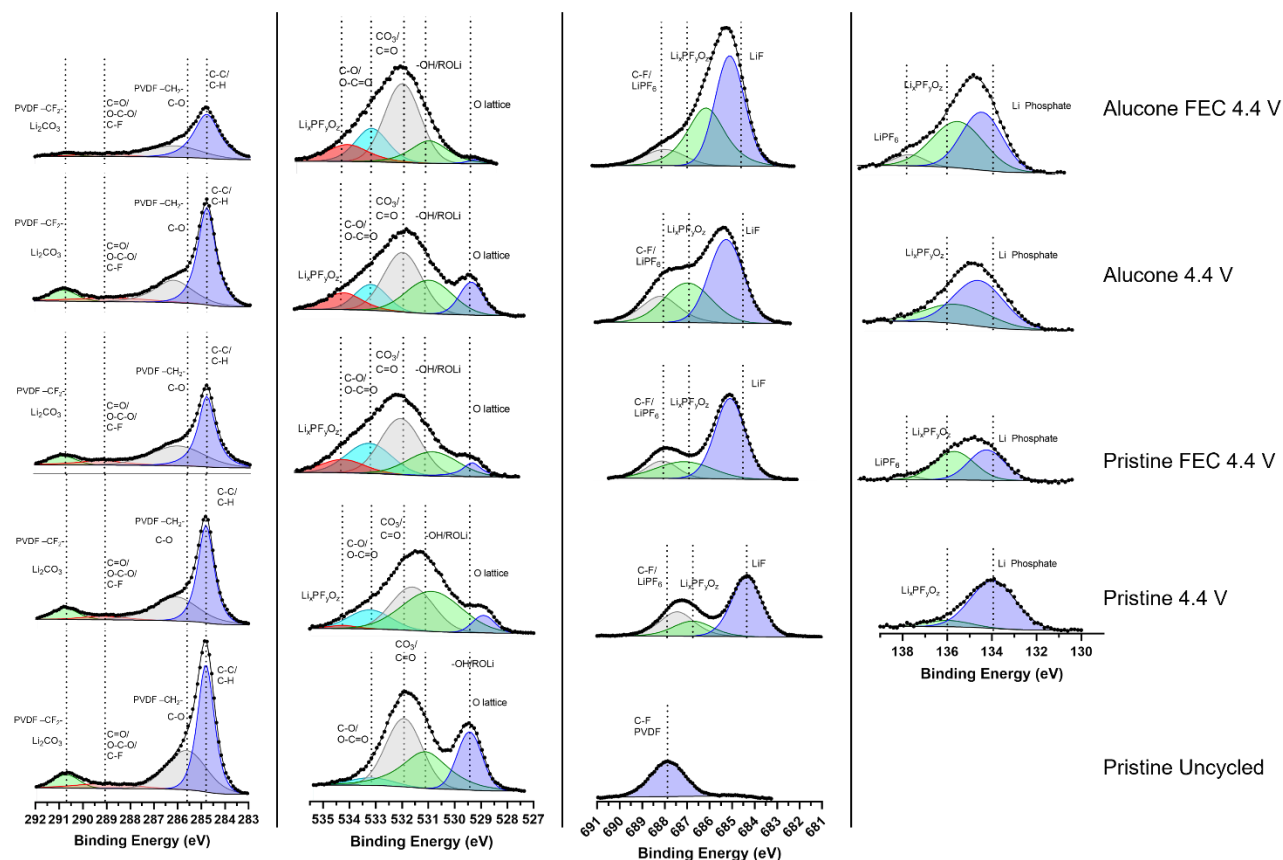


Figure 42. C 1s, O 1s, F 1s, and P 2p (left to right) *ex-situ* XPS spectra comparison of pristine, FEC-modified, and alucone-coated. For each element, the plotted intensities are non-normalized.

The FEC and alucone co-modified electrode reveals a thicker CEI layer with a substantially larger quantity of fluoride species. We propose that the HF generated from the dehydrofluorination of FEC reacts with the alucone coating, initiating the reaction sequences

depicted in **Equations 2 and 4 – 6**. As the HF can react with alucone, this also reduces its likelihood of corroding the active material. Subsequently, LiF and $\text{Li}_x\text{PF}_y\text{O}_z$ species are rapidly produced that help passivate the cathode surface against further HF corrosion. The Al 2p spectra (**Figure 33**), shows that a larger proportion of Al is fluorinated when FEC is employed, supporting this proposed mechanism.

4.4. Conclusions

This work aims to explore the mechanisms of ALD coatings applied on fabricated electrodes and compare the effects of different coating materials (Al_2O_3 , alucone, TiO_2 , and titanicone). The performance of electrodes was first compared when the coating was applied before or after calendaring the electrode, which could affect the penetration of coating precursors within the electrode. However, both cases showed minor differences in cycle retention, and XPS analysis suggests that the coating does not penetrate the entire electrode but is instead localized on the surface regions. Thus, the coating primarily acts by reacting with the electrolyte and modifying the composition of the CEI layer, similar to that of an electrolyte additive. This was confirmed by introducing TiO_2 nanoparticles into the electrode slurry or into the electrolyte as a suspension. Despite their poor coverage of the active particle surfaces, both methods led to an improvement in cycle stability. Metal oxide coatings, particularly Al_2O_3 , displayed poorer kinetic performance compared to their metalcone analogues due to their inherently insulating nature. On the other hand, the low-density ethylene oxide units in metalcones promoted Li^+ transport. The metalcones also displayed improved capacity retention compared to the metal oxides. All coating materials were highly effective at enhancing capacity retention when cycled at high cut-off voltage and low current, primarily due to the suppression of active material loss induced by HF corrosion. However, the coatings were not as effective at suppressing kinetic losses induced at higher

currents. XPS analysis reveals that the coatings react with HF, triggering the early onset formation of LiF and $\text{Li}_x\text{PF}_y\text{O}_z$ species, which help passivate the CEI layer. Although metal oxide coatings are inherently more effective at suppressing solvent decomposition, the metalcone coatings react rapidly with F^-/PF_6^- , enabling earlier passivation of the CEI layer.

5. Controlled Simultaneous Coating and Doping of ZrO_2 and CeO_2 on Ni-Rich Cathodes for Lithium Batteries

5.1. Introduction

Ni-rich layered oxide cathodes (typically $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ or $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$, $x \geq 0.8$) are among the most promising lithium-ion battery (LIB) materials under development for commercial applications. Compared to their lower-Ni counterparts such as $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$, Ni-rich cathodes can achieve higher capacities (Li^+ extraction/insertion) when cycled at the same upper cut-off voltage. Thus, their implementation can expand the energy density of LIBs, which is a highly desired yet elusive goal. Furthermore, Ni-rich cathodes comprise a lower quantity of cobalt, which is a critical raw material with a monopolistic and unethical supply chain.^{6,24} Thus, the elimination of cobalt in batteries is a long-term strategic goal set by many government agencies worldwide.

However, Ni-rich cathodes are currently unsuitable for commercial applications due to their poor cycle life, safety, and ambient storage.²⁰⁸ Ni-rich cathodes primarily contain Ni^{3+} based on charge balance, which is thermodynamically less stable than Ni^{2+} . Excess Ni^{2+} formed during the material synthesis can exchange sites with Li^+ due to their similar ionic radius (0.69 and 0.76 Å respectively). Electrochemical cycling of Ni^{2+} in the Li slab results in lattice distortion and irreversible capacity loss. Additionally, at low lithiation state or high state of charge (SOC), the layered lattice structure is unstable and undergoes an $\text{H2} \rightarrow \text{H3}$ phase transition. This phase transition is accompanied with a rapid contraction (~5%) of the *c*-axis lattice parameter and release of oxygen from the lattice surface.⁴⁸ This loss of oxygen alters the surface structure, forming a spinel and subsequently an inactive Ni-O rock salt phase that substantially hinders Li^+

transport. The growth in thickness of this layer greatly influences the cell impedance. Furthermore, the released oxygen is known to be a reactive singlet state, which readily oxidizes the electrolyte, forming poly(ethylene carbonate)-type products on the cathode-electrolyte interface (CEI) layer that augment cell impedance.⁵¹ The large volume changes ($\sim 12\%$) during the $H2 \rightarrow H3$ phase transition also presents a problem for conventional polycrystalline particles, which are 10-15 μm size secondary particles composed of 100-400 nm size nanoparticle agglomerates. At high SOC, the particles contract, forming voids or interparticle cracks between primary particles, which exposes fresh surfaces to the electrolyte, generating deleterious side reactions.^{53,209} With extensive cycling, severe crack propagation can lead to electrical isolation of active material. Finally, Ni-rich cathode materials exhibit poor ambient stability, reacting with moisture and CO_2 to form LiOH and Li_2CO_3 on the particle surface.²¹⁰ These polar species can induce agglomeration of the polyvinylidene fluoride (PVDF) binder during slurry mixing. Furthermore, they can react with the LiPF_6 electrolyte, forming HF by-product, which is well known to induce active material loss by corrosion. Thus, electrode fabrication should ideally be conducted under very low humidity conditions, which considerably increases processing costs.

Active material modification to enhance electrochemical performance is often conducted through the following: altering the particle morphology, applying a surface coating, and doping the lattice with inactive transition metals (TMs).⁶⁵ Regarding the first approach, the use of Ni-rich cathodes synthesized as 1 – 5 μm size single crystal (SC) particles can eliminate the intergranular crack issue exhibited in PC particles, thus improving cycle life.⁵⁷ However, SC particles exhibit poorer kinetic performance dependent on the particle size, due to the longer Li^+ diffusion paths. SC particles are still known to develop intragranular cracks at elevated voltages – these can occur due to heterogeneous lithiation states developed within the particle, which can generate stress from

lattice size mismatches.^{211,212} This tends to occur during electrochemical cycling at elevated currents. Furthermore, the use of SC particles cannot eliminate the continuous surface degradation. Thus, further developments are urgently required.

The application of surface coatings and TM dopants is known to enhance cycle stability through a variety of mechanisms, including the kinetic hindrance of electrode-electrolyte side reactions and oxygen release, alleviating phase transitions, suppressing HF corrosion, etc. Metal oxide coatings are typically applied on layered oxide cathodes due to their compatible synthesis conditions (oxidative sintering), wide band gap, Li^+ permeability, and HF scavenging properties. Recently, it was established that a simultaneous coating and doping co-modification can be achieved by mixing the active material with a metal oxide coating precursor, followed by high-temperature sintering to form the coating. Certain cations (*e.g.*, Zr^{4+} , Al^{3+} , Mg^{2+} , Nb^{5+} etc.) can dope into the lattice structure, and the degree of dopant penetration within the bulk particle can be controlled by the sintering temperature.²¹³ Thus, a beneficial coating and doping co-modification is generated. However, this raises questions on the stability-enhancing contributions provided by either the coating or doping process. For instance, it has been suggested that the doping effect is more beneficial to cycle stability than the surface coating.²¹⁴ Thus, the coating and doping conditions should be controlled, optimized, and studied in detail.

Furthermore, although many different coating materials have shown promise in improving the cycle performance of Ni-rich cathodes, the exact mechanisms by which this occurs remain unclear. Limited work that systematically compares the effects of different coating materials has been reported. In this work, ZrO_2 and CeO_2 coatings on SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ were systematically characterized and assessed at various amounts (wt%) and sintering temperatures (300 vs 500 °C under oxygen). These parameters altered the coating thickness and extent of bulk

doping. The electrochemical performance of the lithiated analogues, Li_2ZrO_2 and Li_2CeO_3 , was also assessed with the idea that their Li^+ conductive property could alleviate the coating charge transfer barrier.

5.2. Materials and Methods

5.2.1. Coating/Doping Application

SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ powder was obtained as samples from XTC New Energy Materials Co., LTD (Xiamen, China). For Zr-based coatings, zirconium butoxide (80 wt% in 1-butanol, Sigma-Aldrich, Oakville, Canada) and lithium ethoxide (95%, Sigma-Aldrich) were used as the Zr and Li source, respectively. For Ce-based coatings, cerium(III) nitrate hexahydrate (99%, Sigma-Aldrich) and lithium nitrate (99%, Sigma-Aldrich) were used as the Ce and Li source, respectively. A coating batch consisted of 3 g of active material in 50 mL of anhydrous ethanol. The appropriate amount of coating precursor and stoichiometric Li was calculated and added to the suspension based on the nominally formed coating material (wt% of ZrO_2 , Li_2ZrO_3 , CeO_2 , or Li_2CeO_3) on the active material. The mixture was agitated in an ultrasonic bath sonicator for 10 min. to dissolve the coating precursor, and the ethanol was subsequently evaporated while stirring at 70 °C. The coated powder was collected and sintered in a tube furnace (Lindberg, ThermoFisher Scientific, Mississauga, Canada) at 300 or 500 °C (10 °C/min ramp rate) for 6 h under flowing pure oxygen. Sintering under pure oxygen was conducted in order to avoid the formation of Li_2CO_3 or LiOH for the Li-containing coatings.

5.2.2. Electrode and Cell Fabrication

The pristine and modified $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ powders were stored in an argon-filled glovebox while electrode fabrication was conducted in ambient conditions (RH ~30%) with a maximum exposure of ~3 h. The electrode was fabricated by mixing a slurry (solid content of 50

wt%) comprised of 90 wt% active material, 7 wt% poly(vinylidene fluoride) (PVDF, $M_w \sim 534,000$ Da, Sigma-Aldrich, Oakville, Canada), and 3 wt% carbon black (Super-P, AME Energy Co., Limited, Shenzhen, China) in 1-methyl-2-pyrrolidinone (anhydrous, Sigma-Aldrich). The slurry was mixed with a planetary mixer (THINKY AR-100, Tokyo, Japan) for 20 min., cast on a 20 μm -thick aluminum foil, dried at 120 $^{\circ}\text{C}$ for 1 h in a convection oven, subsequently calendared with a roll press, and stored under vacuum overnight at 80 $^{\circ}\text{C}$. Electrode calendaring was conducted at the maximum pressure provided by the roll press (Xiamen TMAX Battery Equipments, Fujian, China). The calculated porosity of the electrode was $\sim 48\%$ after calendaring.

5.2.3. Electrochemical Characterization

12 mm diameter electrode discs were punched with an active material loading of $7 \pm 1 \text{ mg cm}^{-2}$. The electrochemical performance of the electrodes was assessed by assembling CR2032 coin cells in an argon-filled glove box using a pure lithium disc (14 mm diameter, 0.45 mm thick) as the counter electrode, a polyethylene/polypropylene separator (Celgard 2325, Charlotte, NC, USA), and an electrolyte comprised of 1 M LiPF_6 dissolved in 1:1 ethylene carbonate: dimethylcarbonate (EC:DMC, Sigma-Aldrich) by volume. Constant current charge-discharge studies were carried out at ambient temperature using a CT2001A LANDt battery testing system (Wuhan, China) between 2.75 – 4.4 V vs Li/Li^+ at various C-rates. The C-rate is defined based on $200 \text{ mA g}^{-1} = 1 \text{ C}$. Cycle stability tests were conducted at ambient temperature while rate performance tests were conducted at 30 $^{\circ}\text{C}$. Potentiostatic electrochemical impedance spectroscopy (EIS) measurements (Gamry Instruments, Warminster, PA, USA) were conducted from 1 MHz to 100 mHz with an AC amplitude of 10 mV.

5.2.4. Physical Characterization

The crystal structure of the pristine and coated active material was assessed using powder X-ray diffraction (XRDMiniflex 600, Rigaku, Japan) with Cu K α radiation ($\lambda = 1.5406$ nm) at a scan rate of 1 °/min and step size 0.02°. The morphology of the particles was observed by scanning electron microscopy (SEM, LEO Zeiss 1550, Switzerland) using a 20 kV acceleration voltage and a working distance between 8 – 9 mm. The morphology and thickness of the coating were characterized using high resolution transmission electron microscopy (HR-TEM, JEOL JEM 2010, Japan). X-ray photoelectron spectroscopy (XPS, Thermo Scientific Theta Probe, Waltham, MA, USA) was conducted using Al K α radiation. The binding energies reported are referenced to graphitic carbon at 284.8 eV.

For *ex-situ* characterization, all cells were cycled five times between 2.75 – 4.4 V vs Li/Li⁺ at 0.1 C under constant current constant voltage (CC-CV, 0.01 mA current cut-off) conditions, and subsequently charged to 4.4 V. Within two hours (OCV $\sim$ 4.35 V), the cells were disassembled in an argon-filled glovebox with special care to avoid short-circuiting the cells. The cathode was rinsed in DMC and dried under vacuum. For XPS measurements, the cathodes were stored in argon-filled containers and transferred to the XPS chamber with minimal ambient air exposure. For X-ray absorption (XAS, Canadian Light Source, Saskatoon, Canada) measurements, cathodes were sealed using polyimide tape.

5.3. Results and Discussion

5.3.1. Physical Characterization of Coated Cathodes

The thickness of the coating and penetration of the dopant was controlled by varying the coating amount (1 or 1.5 wt%) and sintering temperature (300 or 500 °C under pure oxygen). Sintering

at 700 °C was found to cause agglomeration of the SC particles as shown in **Figure 43**, and thus was not explored further in this study.

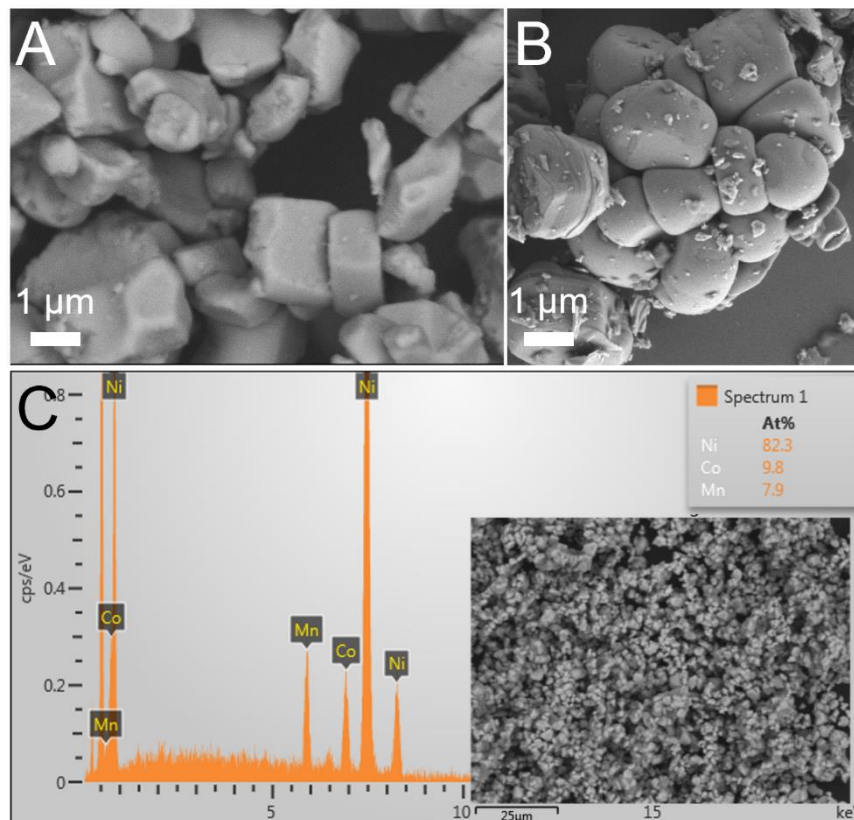


Figure 43. SEM-EDX characterization. A) Pristine particles B) Agglomerate from 1 wt% ZrO₂-700 °C treatment. C) EDX derived composition of pristine particles.

Based on the ionic radius of the dopants (Zr⁴⁺ 0.79 Å and Ce⁴⁺ 0.97 Å) and cathode metals (Li⁺ 0.76 Å, Ni²⁺ 0.69 Å, Ni³⁺ 0.56 Å, Co³⁺ 0.55 Å, and Mn⁴⁺ 0.53 Å), Zr⁴⁺ is expected to substitute into Li and Ni sites whereas Ce⁴⁺ doping is likely more thermodynamically unfavorable.^{213,215} In order to assess evidence of bulk doping, **Figure 44** presents the XRD patterns of the (003) and (101) planes to assess for changes in the lattice parameters. The pristine and ZrO₂-coated cathode sintered at 300 °C show a symmetric (003) diffraction peak centered at 18.7 deg (**Figure 44A**). However, the ZrO₂-coated material sintered at 500 °C show a slightly downshifted and asymmetric fronting peak. This indicates that the *c*-axis of the hexagonal lattice has increased,

likely because Zr^{4+} has entered the Li slab. The asymmetric peak suggests that the occurrence of gradient doping, with Zr more prevalent near the surface of the particle. Meanwhile, the (101) diffraction peak (**Figure 44B**) is identical for all samples, indicating that the a -axis is unaltered. All CeO_2 modified samples show no distinctions for the (003) (**Figure 44C**) and (101) (**Figure 44D**) diffraction peaks, confirming that Ce^{4+} is unable to dope the lattice bulk due to its large size. This is in contrast with past reports on Ce doping in layered oxide cathodes, likely because of the low sintering temperatures and ‘top-down’ doping employed in this work.^{216–218} However, doping may occur on the particle surface at a nanometer scale. **Figure 45** presents the full XRD range for the active material. Under the employed scan rate of 1 °/min, diffraction peaks ascribed to the ZrO_2 coating were not observed in all samples, which corresponds with past studies.²¹³ However, for the CeO_2 coating sintered at 500 °C, peaks are observed for its face centered cubic structure ($Fm\bar{3}m$ space group), indicating its high crystallinity.²¹⁹ On the other hand, the CeO_2 coating sintered at 300 °C is amorphous.

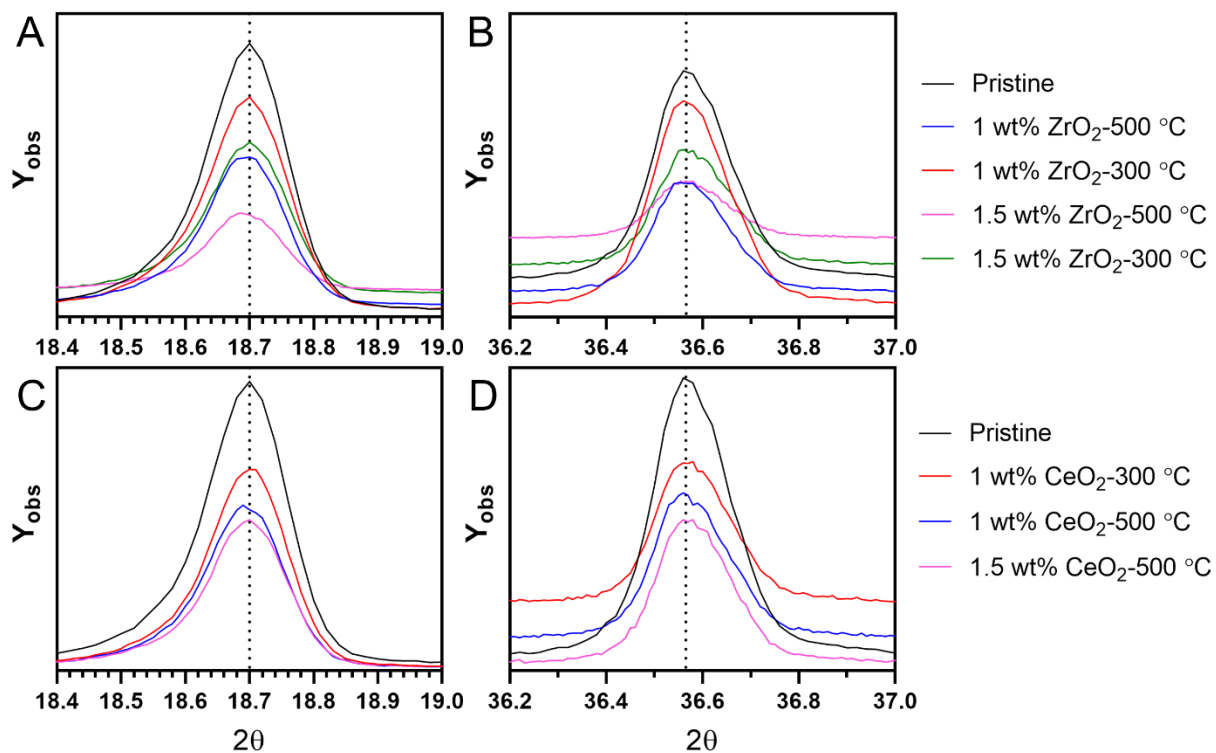


Figure 44. XRD peaks of ZrO_2 (A and B) and CeO_2 (C and D) coated/doped samples at (003) (A and C) and (101) (B and D) planes.

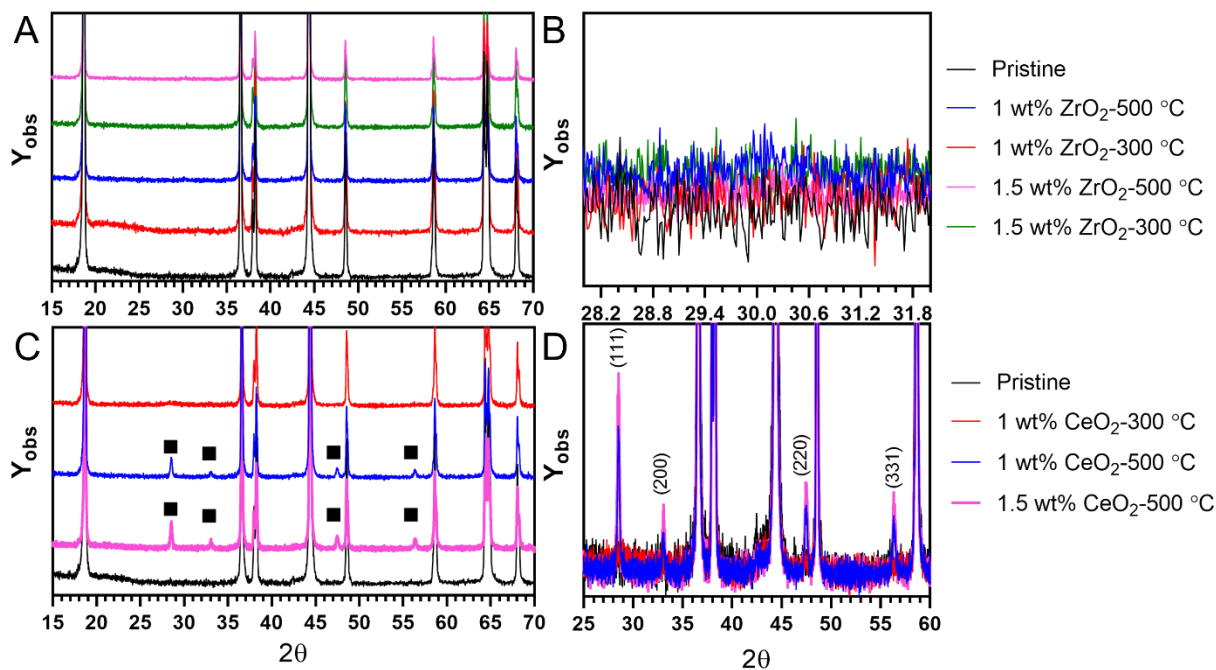


Figure 45. XRD patterns of ZrO_2 (A and B) and CeO_2 (C and D) coated/doped samples using a scan rate of 1 deg/min. Labelled peaks in panel C and D are assigned to CeO_2 .

The morphology of the coatings was assessed using TEM (**Figure 46**). The 1 wt% ZrO₂-500 °C applied coating shows good coverage of the particle surface (**Figure 46B**). However, the coating thickness is non-uniform, with smoother regions of ~20 nm thickness and up to ~100 nm size agglomerates. As expected, increasing the coating amount (1.5 wt%, **Figure 46C**) increased the coating thickness and non-uniform appearance, showing agglomerates up to ~200 nm in size. Meanwhile, the 1 wt% ZrO₂-300 °C coating shows a smoother appearance with an estimated average thickness of ~100 nm. This considerable increase in thickness compared to 1 wt% ZrO₂-500 °C is likely because Zr does not dope into the particle and thus accumulates on the surface. With the coatings observed under HR-TEM (**Figure 47A and 47B**), ZrO₂ sintered at 500 °C shows more crystalline domains compared to at 300 °C. Finally, the 1.5 wt% ZrO₂-300 °C coating has a relatively smooth appearance with a further elevated thickness (~200 nm average). On the other hand, the 1 wt% CeO₂-500 °C coating shows a unique morphology, with a thick coating (~100 nm) in addition to ~20 nm-size nanoparticles scattered over the surface. HR-TEM shows that the nanoparticles are highly crystalline (**Figure 47C**), which contributes to their observed XRD signal in **Figure 45**. As Ce⁴⁺ is unable to dope into the lattice, it accumulates and crystallizes on the particle surface.

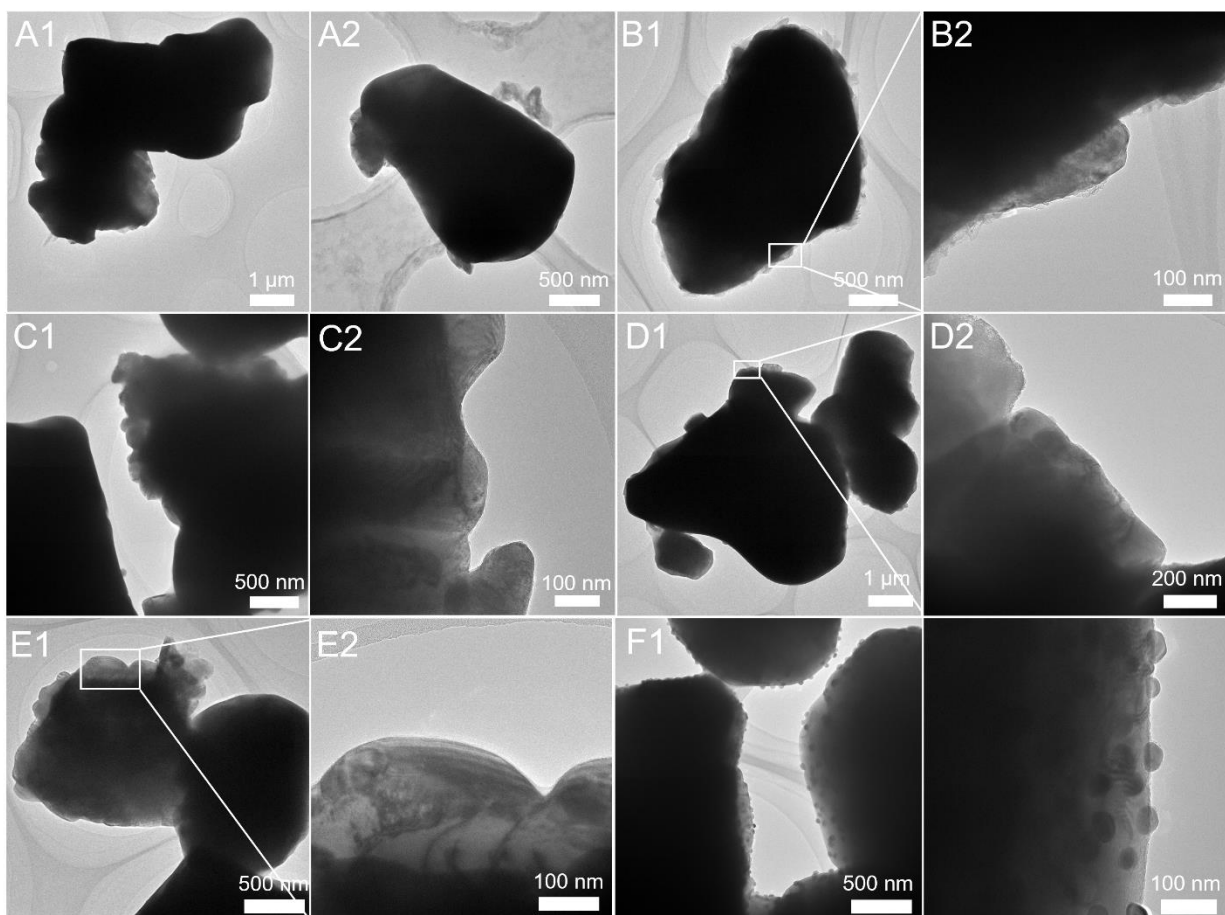


Figure 46. TEM images of coating on SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particle(s). A) Pristine particle. B) 1 wt% ZrO_2 -500 °C, C) 1.5 wt% ZrO_2 -500 °C D) 1 wt% ZrO_2 -300 °C, E) 1.5 wt% ZrO_2 -300 °C, and F) 1 wt% CeO_2 -500 °C treated particle.

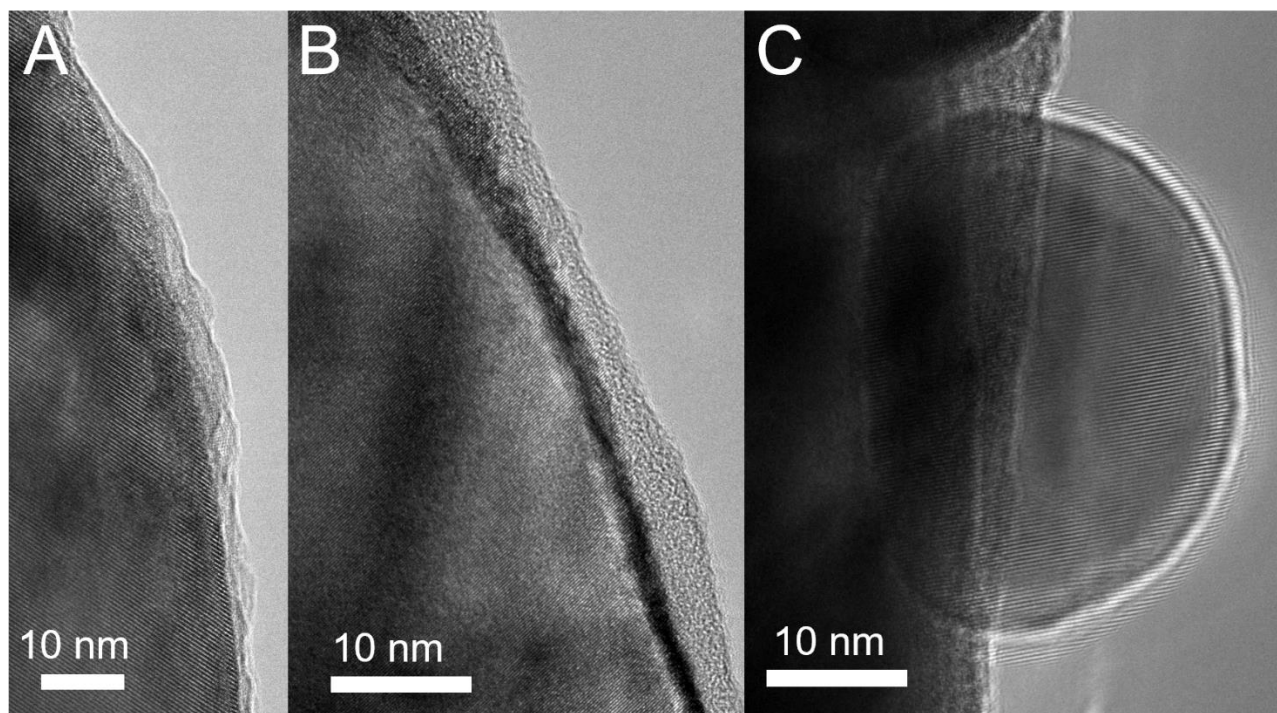


Figure 47. HR-TEM images of A) 1 wt% ZrO₂-500 °C, B) 1 wt% ZrO₂-300 °C and C) 1 wt% CeO₂-500 °C.

Figure 48 and **Figure 49** display the fitted Ni 2p and Zr/Ce 3d XPS spectra respectively of the pristine and coated particles. The key results are also summarized in **Table 7**. For all ZrO₂-treated samples, the Zr 3d_{5/2} peak is symmetric and centered at 182.0 eV, which is characteristic of pure Zr⁴⁺. All CeO₂-treated samples show complex peak spitting, where the six characteristic peaks are indicative of pure Ce⁴⁺. The calculated Zr or Ce to Ni atomic ratio (**Table 7**) do not correspond with the expected and observed coating thickness. This is likely because the coatings are very heterogeneous as displayed in **Figure 46**, and thus the results are affected by the limited sample size. One notable observation is that the samples that exhibit Zr⁴⁺ doping (*i.e.*, 1 and 1.5 wt% ZrO₂-500 °C) contain a larger proportion of Ni²⁺ on the particle surface (**Figure 48** and **Table 7**). Two possible explanations for this include: 1) Zr⁴⁺ substitutes for Ni²⁺, bringing bulk Ni²⁺ to the particle surface and²¹³ 2) high-valence Zr⁴⁺ substitution induces Ni²⁺ formation based

on charge balance.²²⁰ Meanwhile, the ZrO₂-coated samples sintered at 300 °C and all CeO₂-coated samples exhibit similar Ni²⁺ proportions as in the pristine sample.

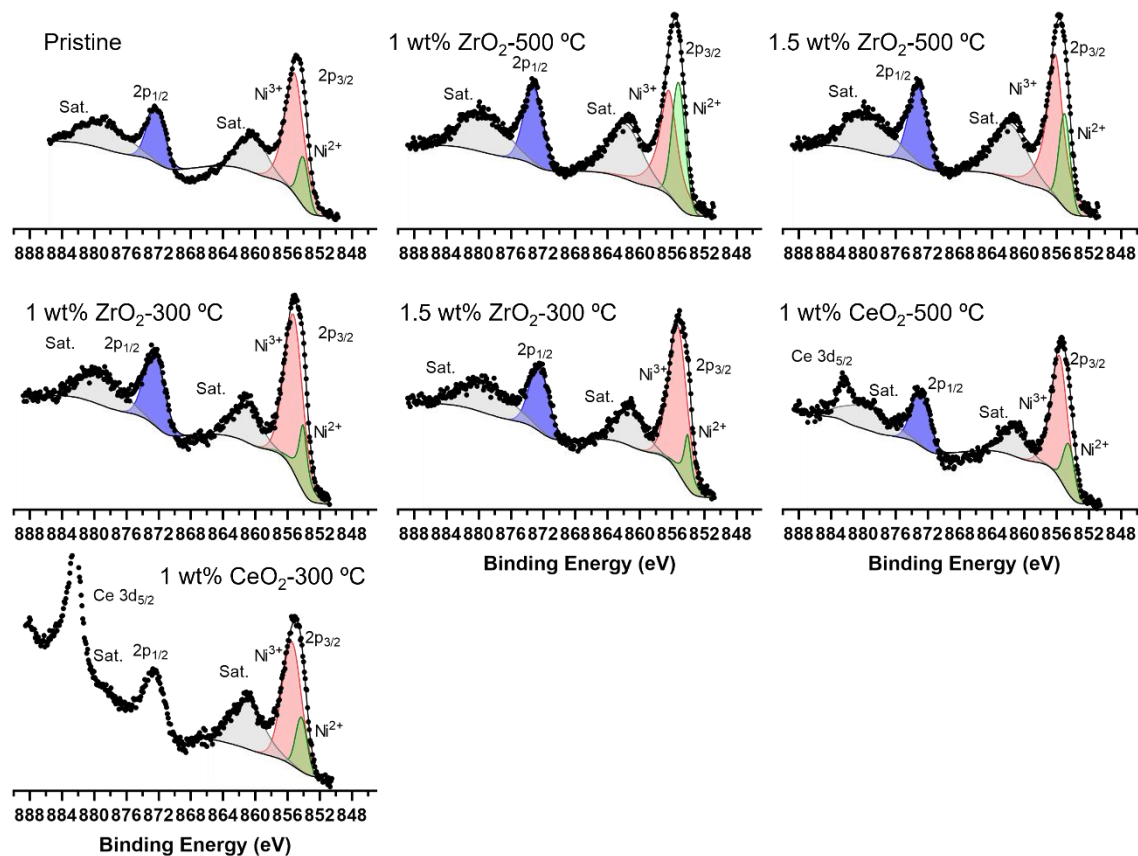


Figure 48. Non-normalized Ni 2p XPS spectra of pristine and coated/doped particles.

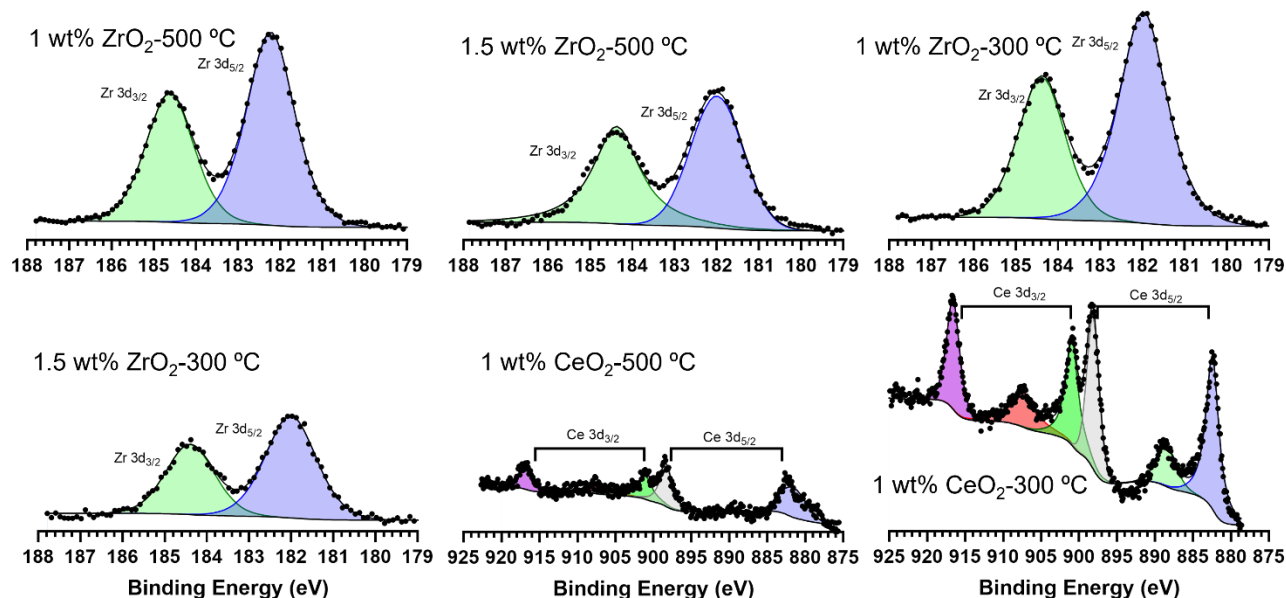


Figure 49. Non-normalized Zr or Ce 3d spectra of coated/doped particles.

Table 7. XPS peak fitting results from **Figure 48** and **Figure 49**.

Sample	Ni ²⁺ 2p _{3/2} B.E.	Ni ³⁺ 2p _{3/2} B.E.	Zr or Ce 3d _{5/2} B.E.	Zr or Ce 3d _{3/2} B.E.	Zr or Ce / Ni atomic ratio	Ni ²⁺ /Ni atomic ratio
Pristine	854.0	855.1	--	--	--	0.18
1 wt% ZrO ₂ -500	854.0	855.1	182.0	184.4	0.4	0.42
1.5 wt% ZrO ₂ - 500	854.0	855.1	182.0	184.4	0.27	0.31
1 wt% ZrO ₂ -300	854.0	855.2	182.0	184.4	0.45	0.21
1.5 wt% ZrO ₂ - 300	854.0	855.2	182.0	184.4	0.28	0.17
1 wt% CeO ₂ -500	854.0	855.1	881.7, 889.6, 898.3	901.1, 907.4, 916.8	0.29	0.20
1 wt% CeO ₂ -300	854.0	855.2	882.4, 888.5, 898.2	900.9, 907.4, 916.1	0.49	0.20

5.3.2. Electrochemical Performance of Zr-Based Coatings

The stability of the cathode is first assessed at a low current of 0.1 C cycling between 2.75 – 4.4 V vs Li/Li⁺. Under these conditions, the lithiation state within each particle should be mostly homogeneous, which should suppress the formation of intragranular cracks. However, the

cathode is subjected to a high depth of discharge, in particular extended durations at high voltages and low lithiation states. This accentuates capacity degradation from oxygen release, surface reconstruction, and electrolyte decomposition. Moreover, a large amount of HF is known to be generated at high voltages, potentially as a consequence of the oxidative dehydrogenation of EC solvent, which induces active material loss by corrosion.¹⁸² As presented in **Figure 50A** and **Table 8**, all ZrO₂-based coatings tested show an improvement in discharge capacity retention relative to the pristine sample, with the 1 wt% ZrO₂-500 °C sample showing optimal performance. This treatment also markedly preserved the average discharge voltage (**Figure 50B**), which correlates with a suppressed growth in cathode impedance.

Table 8. Comparison of discharge capacity and average discharge voltage retention after 100 cycles at 2.75 – 4.4 V vs Li/Li⁺.

Coating Material	Wt%	Sintering Temperature	Discharge Capacity Retention (0.1 C)	Average Discharge Voltage Retention (0.1 C)	Discharge Capacity Retention (C/3)	Average Discharge Voltage Retention (C/3)	Discharge Capacity Retention (0.1 C → C/3)
Pristine	N/A	N/A	75%	98.0%	82%	97.8%	87%
ZrO ₂	1	300	88%	99.3%	81%	97.6%	89%
ZrO ₂	1	500	93%	99.4%	90%	98.6%	90%
ZrO ₂	1.5	300	79%	96.8%	79%	97.3%	85%
ZrO ₂	1.5	500	89%	99.2%	91%	98.9%	92%
Li ₂ ZrO ₃	0.5	300	89%	98.9%	84%	98.3%	89%
Li ₂ ZrO ₃	0.5	500	90%	99.5%	85%	98.9%	89%
Li ₂ ZrO ₃	1	300	85%	98.2%	84%	98.7%	85%
Li ₂ ZrO ₃	1	500	91%	99.4%	90%	99.0%	92%
Li ₂ ZrO ₃	1.5	300	71%	96.6%	69%	95.0%	79%
Li ₂ ZrO ₃	1.5	500	76%	97.4%	73%	97.2%	82%
CeO ₂	0.5	300	32%	81.9%	--	--	--
CeO ₂	0.5	500	81%	98.2%	86%	99.2%	90%
CeO ₂	1	300	23%	81.1%	--	--	--
CeO ₂	1	500	92%	99.8%	89%	99.6%	90%
CeO ₂	1.5	500	64%	96.1%	74%	96.2%	84%
Li ₂ CeO ₃	0.5	500	85%	99.1%	81%	98.5%	88%
Li ₂ CeO ₃	1	500	86%	99.1%	72%	96.6%	83%
Li ₂ CeO ₃	1.5	500	69%	97.6%	72%	96.8%	83%

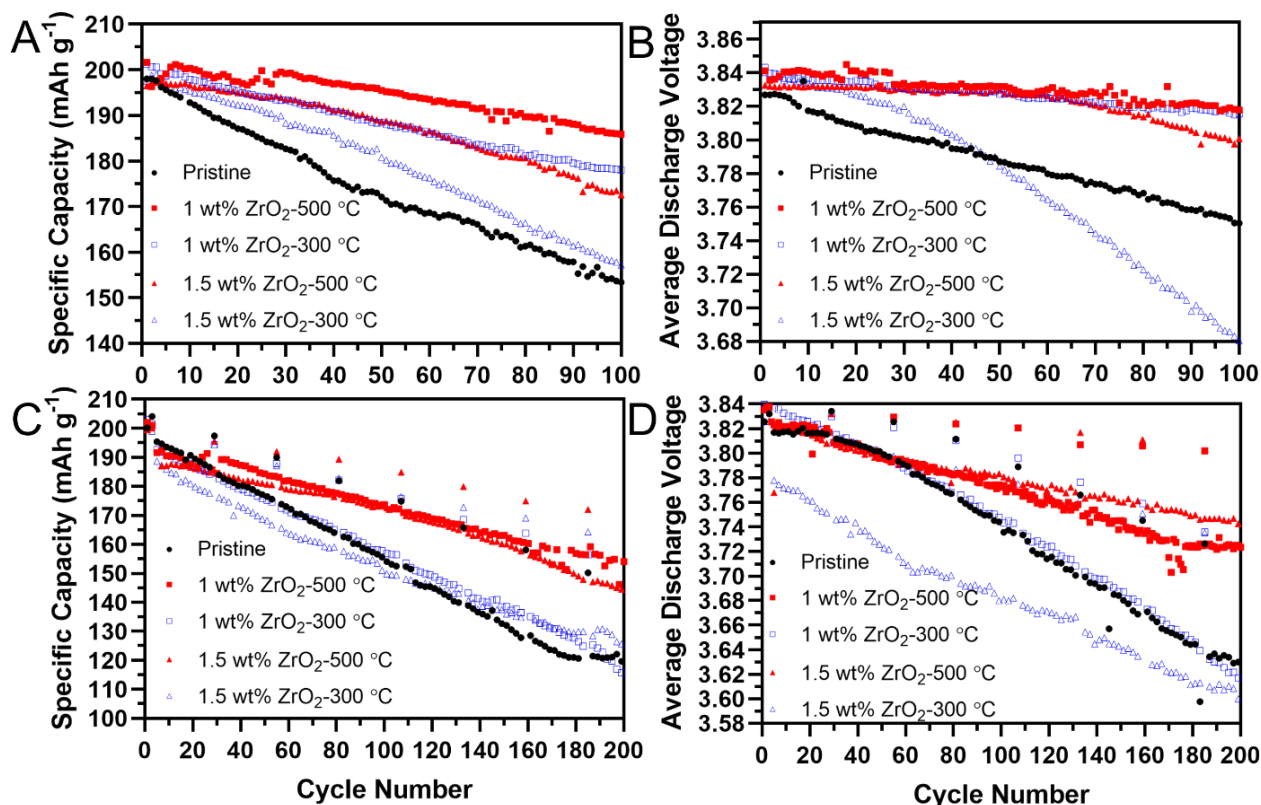


Figure 50. Capacity retention (A and C) and average discharge voltage (B and D) of pristine and ZrO_2 -treated SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particles cycled from 2.75 – 4.4 V vs Li/Li^+ at 0.1 C (A and B) C/3 (C and D).

Cathode impedance is dictated by 1) the thickness of the reconstructed spinel or rock salt surface layer and 2) the thickness and composition of the CEI layer comprised of decomposed electrolyte products. These effects may be correlated as the released oxygen is known to be a reactive singlet state, which readily oxidizes the electrolyte.⁵¹ As established earlier, the 1 wt% ZrO_2 -500 °C sample exhibits a simultaneous coating and doping effect. The ZrO_2 coating can kinetically suppress oxidative side reactions with the electrolyte due to its electronically insulating nature. It also serves as a physical barrier against direct contact between the active material and electrolyte. This physical barrier can potentially also suppress oxygen evolution from the lattice, as this process is known to be kinetically unfavorable and surface initiated.⁵¹ Meanwhile, Zr^{4+} doping can suppress oxygen release based on several potential mechanisms: 1) Zr^{4+} is confirmed

to be present into the Li layer based on the enlarged *c*-axis lattice parameter (**Figure 44A**). Thus, Zr⁴⁺ can serve as pillar ions that suppress the sudden contraction of the *c*-axis during the H2 → H3 phase transitions.^{220,221} 2) Redox-inactive TM dopants are known to increase the activation energy barrier of neighboring Ni migrating into the Li layer.²²² 3) The Zr-O bond strength is theoretically stronger than Ni-O.²²³

Besides impedance growth, active material loss from HF corrosion is the primary cause of capacity degradation. The ZrO₂ coating can suppress active material loss by HF scavenging according to **Equation 1** below:



Although water is produced as a by-product, which can decompose LiPF₆ and re-generate HF, ZrF₄ is inert to HF corrosion and can protect the active material. In comparison, the 1.5 wt% ZrO₂-500 °C sample also exhibits an improvement in capacity and average discharge voltage retention relative to the pristine particles. However, it was not as effective as the 1 wt% sample, likely due to the increased impedance growth as a consequence of the increased coating thickness. Interestingly, the 1 wt% ZrO₂-300 °C sample displayed nearly identical performance characteristics (capacity retention and polarization growth) to the 1.5 wt% ZrO₂-500 °C sample. This indicates that under these testing conditions, the surface coating itself can address most of the failure mechanisms of SC LiNi_{0.83}Mn_{0.06}Co_{0.11}O₂. However, the 1.5 wt% ZrO₂-300 °C sample displayed high initial and growth of impedance over cycling, even when compared to the pristine sample, due to the high charge transfer barrier of its excessively thick coating. Interestingly, this coating displayed a slightly improved capacity retention compared to the pristine sample, which implies that it is still effective at suppressing active material loss.

To further analyze the electrochemical behavior of the coated/doped samples, **Figure 51** displays their corresponding dQ/dV vs V curves at cycle 2, 25, 50, and 100. All samples show a series of sharp peaks corresponding to phase transitions, with the most notable being the H2/H3 phase transition at ~ 4.2 V vs Li/Li^+ . As discussed earlier, this phase transition is responsible for a $\sim 5\%$ contraction of the c -axis lattice parameter and is linked with oxygen release from the lattice surface. Peak shift (polarization) is particularly noticeable at the H2/H3 phase transition, as Li diffusion is greatly hindered at this state due to lattice volume contraction, the increased valence state of Ni, ‘fatigue degradation’ due to the mismatch of lattice constants between the H3 phase and rock salt surface,¹⁸⁰ and potential dislocations within the crystal structure (*i.e.*, intragranular cracks).¹⁸¹ Moreover, the occurrence of this phase transition is kinetically hindered over extensive cycling as impedance accumulates, resulting in peak area decay. At other regions of the curve, loss of peak area (capacity) is likely dictated by active material loss. **Figure 51** shows that besides the 1.5 wt% ZrO_2 -300 °C sample, the coating/doping treatment markedly suppressed impedance growth and active material loss, and improved the reversibility of the H2/H3 phase transition.

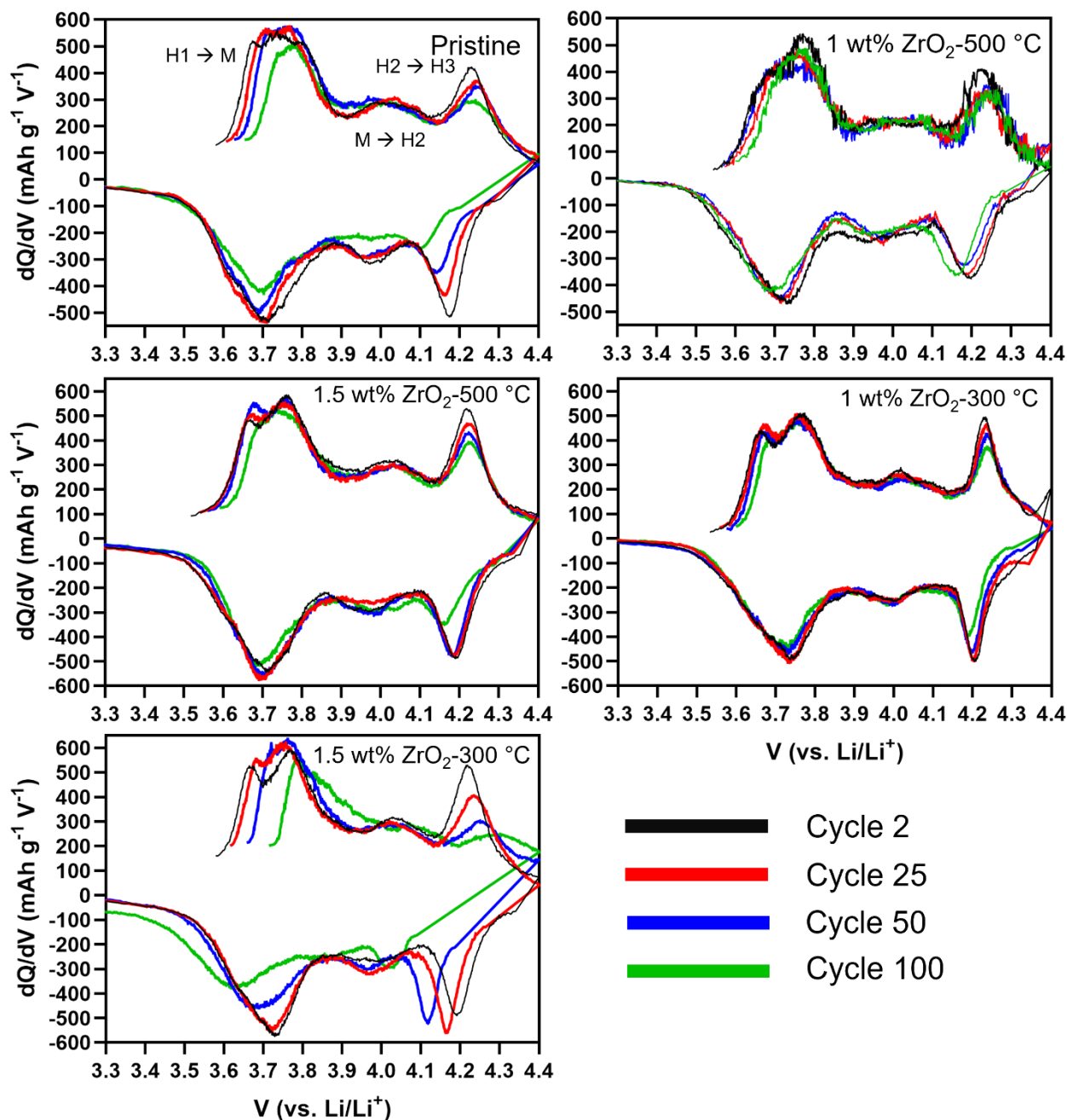


Figure 51. dQ/dV curves of pristine and ZrO₂-treated cells cycled at 0.1 C and 2.75 – 4.4 V vs Li/Li⁺.

The cycle performance behavior at an elevated current of C/3 (**Figure 50C**) reveals different trends. Here, three ‘formation’ cycles were conducted at 0.1 C to stabilize the CEI/SEI layers, and after every 25 cycles at C/3 the capacity was recorded at 0.1 C. For the pristine sample, capacity retention when cycling at C/3 is improved compared to 0.1 C (**Table 8**). However, the

average discharge voltage decays more rapidly (**Figure 50D**), indicating that impedance growth is more prevalent. Throughout the 200 cycles shown at C/3, an increasing amount of capacity is recovered when the current is lowered to 0.1 C (**Figure 50C**), confirming that active material loss is not the dominant degradation mechanism. This is likely because the cathode endures shorter durations at elevated voltages, which minimizes HF generation. The corresponding dQ/dV vs V curve shows rapid polarization growth and kinetic suppression of the H2/H3 phase transition, with its peaks hardly visible after 100 cycles. This growth in polarization is likely associated with the formation of intragranular particle cracks. At elevated charge/discharge currents, (de-)lithiation is inhomogeneous and concentrated on the surface of the cathode particles. The mismatch in lattice parameters generates stress within the particle, leading to cracks forming, which disrupt Li^+ diffusion channels and generate new surfaces that form harmful side reactions with the electrolyte.²²⁴ In this regard, the ZrO_2 coatings sintered at 300 °C do not improve the capacity or polarization retention at C/3, as a surface coating is theoretically unable to ameliorate intragranular cracking, assuming this occurrence is dictated by Li^+ diffusion barriers. The fresh surfaces subsequently generated are not passivated by the coating. The dQ/dV curves (**Figure 52**) show almost identical characteristics between the 1 wt% ZrO_2 -300 °C and pristine sample, while the 1.5 wt% ZrO_2 -300 °C sample exhibits more severe peak polarization and decay of the H2/H3 phase transition due to its thicker coating. Moreover, a thick and non-uniform coating (as seen in **Figure 46D** and **46E**) can exacerbate the inhomogeneous (de-)lithiation of the cathode, as Li^+ will preferentially diffuse through the thinner regions of the coating. Interestingly, beyond 100 cycles, the capacity recorded at 0.1 C is higher for the ZrO_2 coatings sintered at 300 °C, indicating that they remain effective at suppressing active material loss. On the other hand, the ZrO_2 coatings sintered at 500 °C exhibit a sizeable improvement in

capacity retention and polarization growth at C/3, likely due to the doping effect. As discussed previously, Zr^{4+} doped into the Li layer can alleviate the rapid contraction of the *c*-axis and improve Li^+ diffusion kinetics based on the pillar ion effect. Thus, it can suppress the occurrence of intragranular cracks.

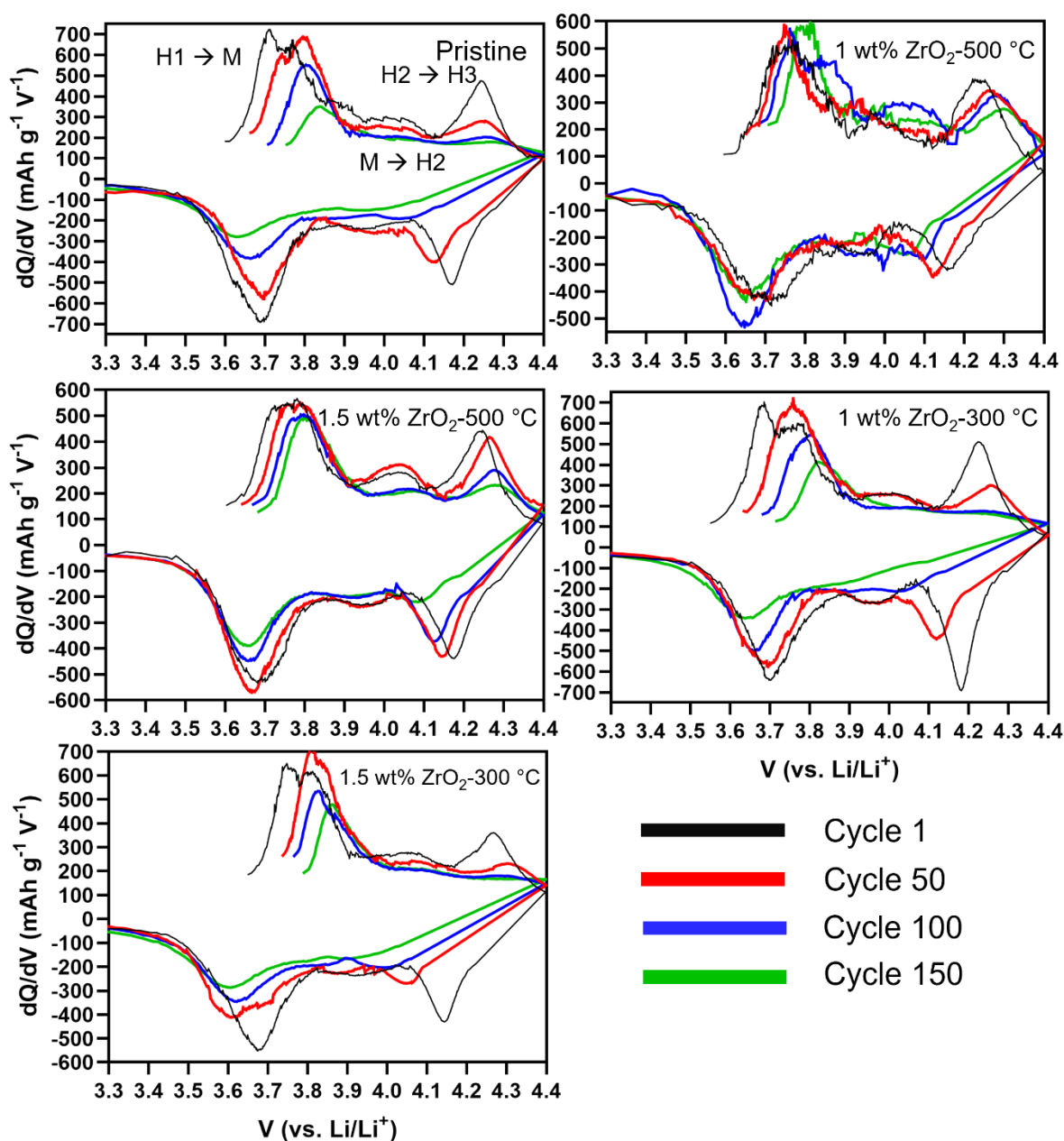


Figure 52. dQ/dV curves of pristine and ZrO₂-treated cells cycled at C/3 and 2.75 – 4.4 V vs Li/Li⁺.

The cycle performance of the lithiated analogue coating (Li_2ZrO_3) has also been assessed and presented in **Figure 53**. The coating was formed in an identical manner to ZrO_2 with the addition of the stoichiometric amount of Li precursor. Zr doping presumably also occurs when the coating is sintered at 500 °C. Due to its Li^+ conductive nature, it was thought that this could alleviate the inherent charge transfer barrier of the coating. Similar overall trends to that of ZrO_2 are observed with respect to modifying the coating amount sintering temperature, with the 1 wt% Li_2ZrO_3 -500 °C sample showing the best performance. However, Li_2ZrO_3 appears to generate a higher impedance – at 1.5 wt% (**Figure 54**), Li_2ZrO_3 sintered at both 300 and 500 °C show high initial and growth of impedance even when cycling at 0.1 C. Thus, a 0.5 wt% composition was assessed for comparison. This may imply that the Li_2ZrO_3 coating is thicker. Another consideration is that the ZrO_2 coating can react with and ‘clean’ the surface of contaminant and ever-present $\text{LiOH/Li}_2\text{CO}_3$ species on the pristine particle, partially forming Li_2ZrO_3 .²²⁵ Thus, the addition of stoichiometric Li to nominally form Li_2ZrO_3 can generate $\text{LiOH/Li}_2\text{CO}_3$ from the excess Li, increasing the cathode impedance.

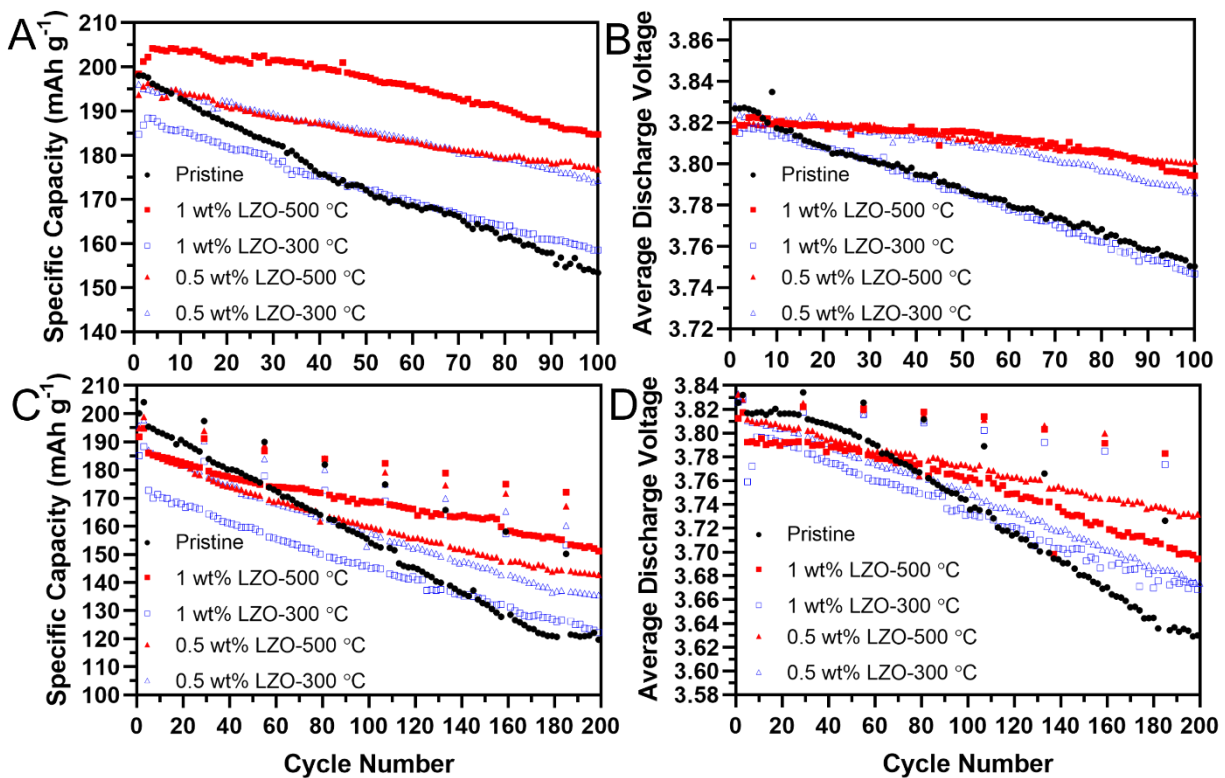


Figure 53. Capacity retention (A and C) and average discharge voltage (B and D) of pristine and Li₂ZrO₃ (LZO)-treated SC LiNi_{0.83}Mn_{0.06}Co_{0.11}O₂ particles cycled from 2.75 – 4.4 V vs Li/Li⁺ at 0.1 C (A and B) C/3 (C and D).

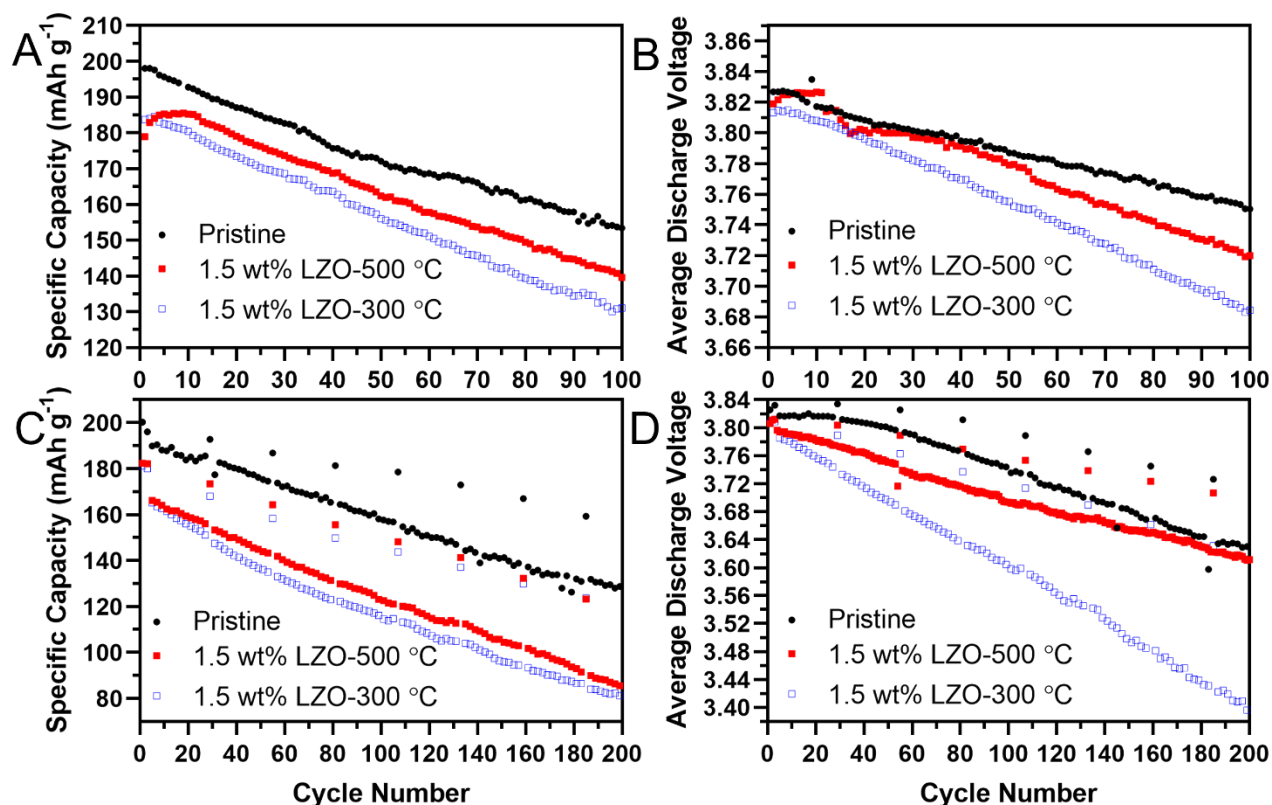


Figure 54. Capacity retention (A and C) and average discharge voltage (B and D) of pristine and 1.5 wt% Li_2ZrO_3 (LZO)-treated SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particles cycled from 2.75 – 4.4 V vs Li/Li^+ at 0.1 C (A and B) C/3 (C and D).

Figure 55 compares the rate performance of the above-discussed coating/doping treatments from 0.1 to 5 C. The change in average discharge voltage (**Figure 55B**) as a function of the C-rate matches the expected trends established in the previous results – coatings formed at higher wt% and/or at 300 °C generally exhibit higher voltage polarization. This is because these samples have thicker coatings and/or do not benefit from lattice doping. Specifically, the 1 and 1.5 wt% ZrO_2 -500 °C samples exhibit lower voltage polarization compared to the pristine cathode at all discharge currents tested, likely because the presence of Zr^{4+} can improve Li^+ diffusion in the lattice, particularly at high SOC. The 1 wt% ZrO_2 -300 °C coating displays higher voltage polarization than the pristine sample only from 0.1 to 2 C. This type of behavior is consistent with other reports on metal oxide cathode coatings. It is likely a consequence of competing

effects between the electronically and ionically insulating nature of the coating itself and the ability of the coating to passivate the CEI layer. Meanwhile, the 1.5 wt% ZrO_2 -300 °C sample exhibits higher voltage polarization at all currents due to the excessively thick coating. **Figure 55D** also confirms that the Li_2ZrO_3 does not show definitively improved kinetics compared to the ZrO_2 analogues. On the other hand, the trend in discharge capacity does not always align with the average discharge voltage. This is possibly due to the ability of the coating to preserve active material loss, particularly during the initial low-current cycles.

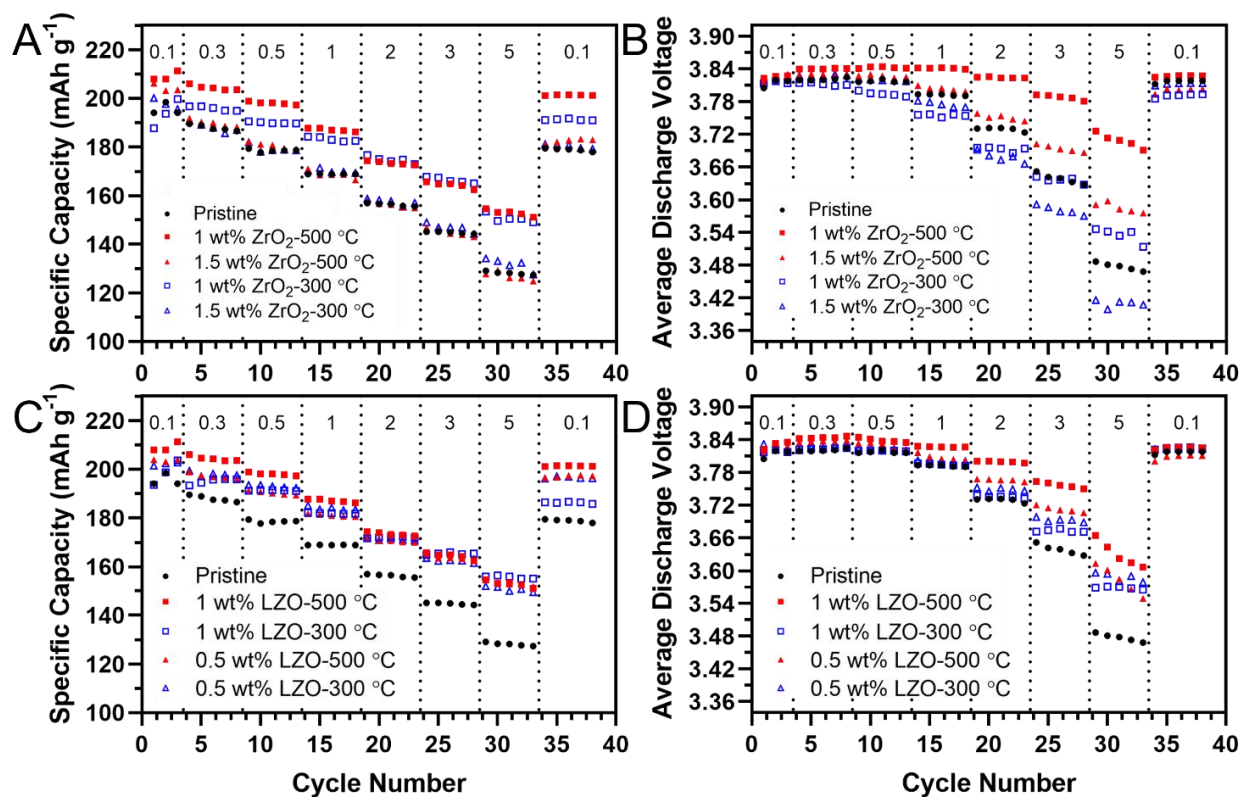


Figure 55. Comparison of rate performance of ZrO_2 (A and B) and Li_2ZrO_3 (LZO, C and D) coatings. All cells cycled at 0.1 C charge and 0.1 to 5 C discharge at 2.75 – 4.4 V vs Li/Li^+ .

5.3.3. Electrochemical Performance of Ce-Based Coatings

Ce-based coatings were tested under the same conditions as the Zr-based coatings. When sintered at 300 °C, the CeO_2 coating exhibits poor electrochemical performance regardless of the wt% used (**Figure 56**). This indicates that the amorphous coating formed at this temperature has

poor Li^+ conductivity. Thus, **Figure 57** compares the performance of CeO_2 coatings sintered at 500°C .

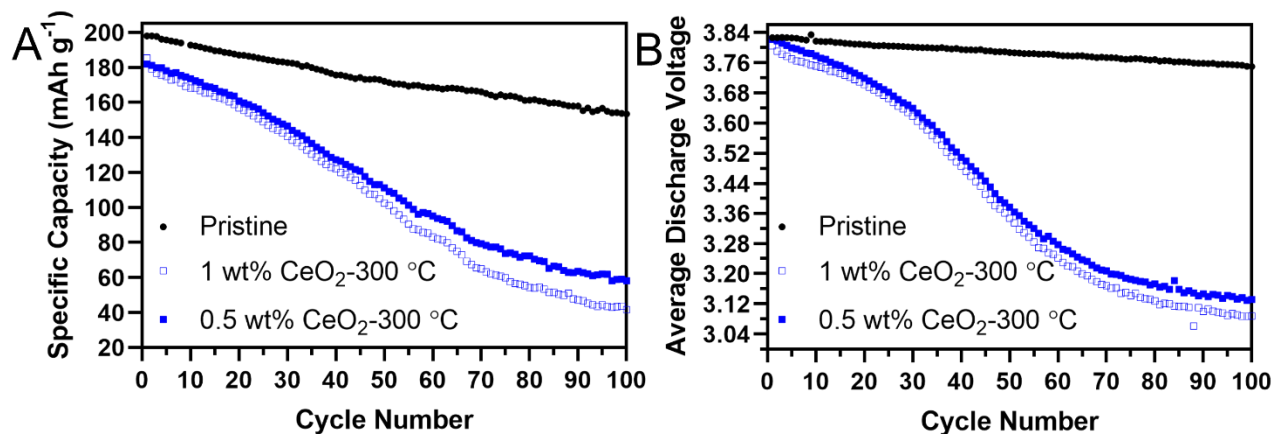


Figure 56. Capacity retention (A) and average discharge voltage (B) of pristine and CeO_2 -300 $^\circ\text{C}$ -treated SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particles cycled from 2.75 – 4.4 V vs Li/Li^+ at 0.1 C.

At both 0.1 C and C/3, the 1 wt% CeO_2 -500 $^\circ\text{C}$ sample displays exceptionally strong discharge capacity retention, nearly identical to the best performing 1 wt% ZrO_2 -500 $^\circ\text{C}$ sample. However, the retention of the average discharge voltage is even stronger at both currents. This result is quite remarkable given that Ce^{4+} does not dope into the bulk lattice. As the CeO_2 coating is relatively thick with high crystallinity, it can potentially reinforce the particles against intragranular cracks, which may explain the excellent stability and polarization when cycling at C/3. In comparison, at 0.5 wt%, the CeO_2 coating shows an improvement in cycle performance relative to the pristine sample, albeit not as effective compared to 1 wt%. This is likely because the coating amount is inadequate at covering all surfaces of the active material. In contrast, the 1.5 wt% CeO_2 coating shows poor capacity retention and high polarization due to the excessive coating thickness.

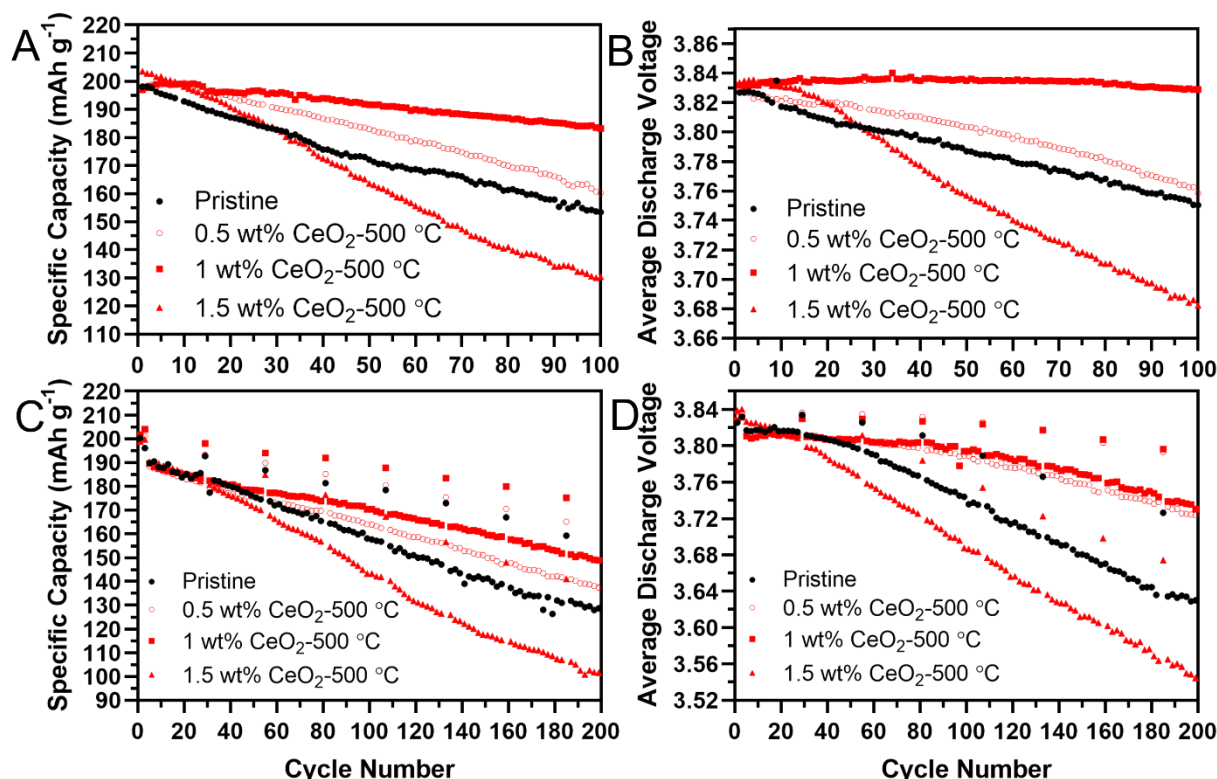


Figure 57. Capacity retention (A and C) and average discharge voltage (B and D) of pristine and CeO_2 -500 °C-treated SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particles cycled from 2.75 – 4.4 V vs Li/Li^+ at 0.1 C (A and B) C/3 (C and D).

Figure 58 and **59** show the corresponding dQ/dV vs V curves at 0.1 C and C/3 respectively.

Figure 58 confirms that the 1 wt% CeO_2 coating is highly effective at suppressing peak shift (polarization growth) at all SOCs, preventing active material loss, and improving the reversibility of the H2/H3 phase transition. At C/3, the 1 wt% CeO_2 -500 °C coating does not exhibit as strong reversibility of the H2/H3 phase transition compared to the ZrO_2 coated and doped samples, particularly within the first 50 cycles (**Figure 59**). This is likely because Zr^{4+} doping can improve Li^+ diffusion kinetics and alleviate lattice strain at this SOC as previously discussed. However, the occurrence of the H2/H3 phase transition is well maintained beyond 100 cycles. Moreover, at other SOCs, the peak positions are well maintained throughout the 150 cycles analyzed. The implications on the lack of Ce^{4+} doping in this work is unclear. On one hand, due to the large size of Ce^{4+} , doping into the Li layer will enlarge the interlayer space considerably,

which may enhance Li^+ diffusion.²²⁶ However, the large size of this ion may exacerbate distortion and deterioration of the lattice structure.²²⁷

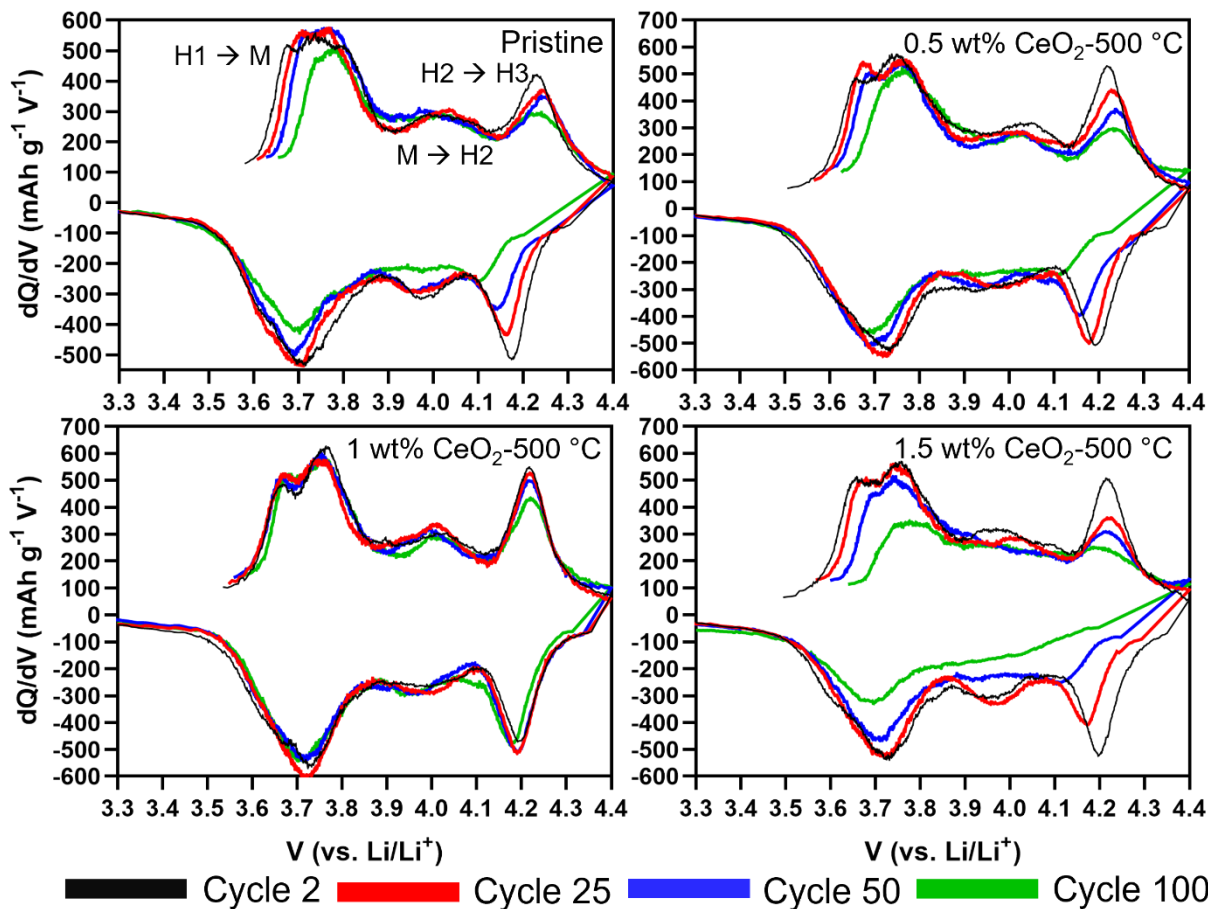


Figure 58. dQ/dV curves of pristine and CeO₂-500 °C-treated cells cycled at 0.1 and 2.75 – 4.4 V vs Li/Li⁺.

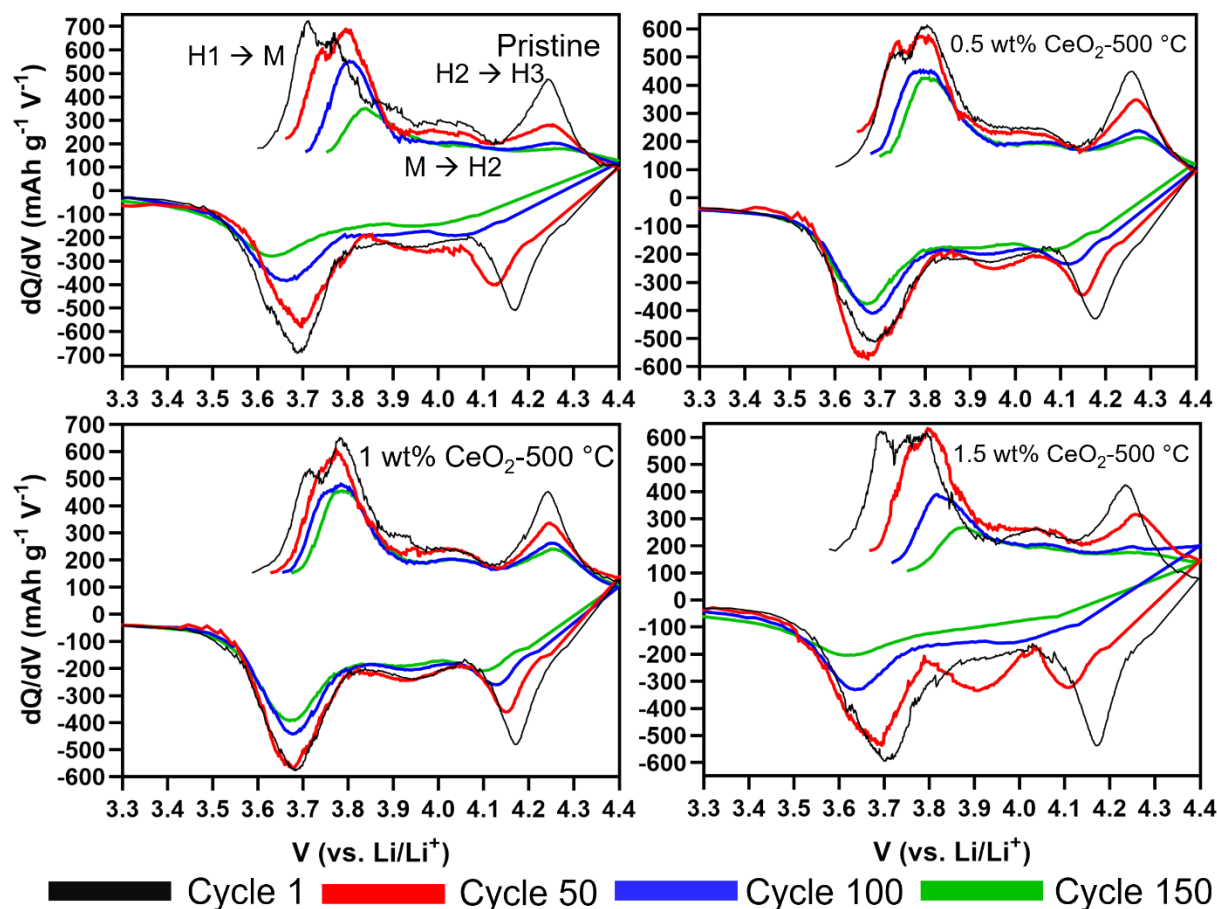


Figure 59. dQ/dV curves of pristine and CeO₂-500 °C-treated cells cycled at C/3 and 2.75 – 4.4 V vs Li/Li⁺.

Figure 60 shows the rate performance of the CeO₂-coated cathodes. In general, both the discharge capacity loss and voltage polarization at elevated currents increase as the coatings become thicker. In comparison, the 0.5 and 1 wt% CeO₂-500 °C coated samples exhibit very similar voltage polarization behavior to the 1 and 1.5 wt% ZrO₂-300 °C, respectively. Although the CeO₂ coatings are highly capable of suppressing impedance growth during cycling, the results suggest that they are not as inherently Li⁺ conductive as ZrO₂.

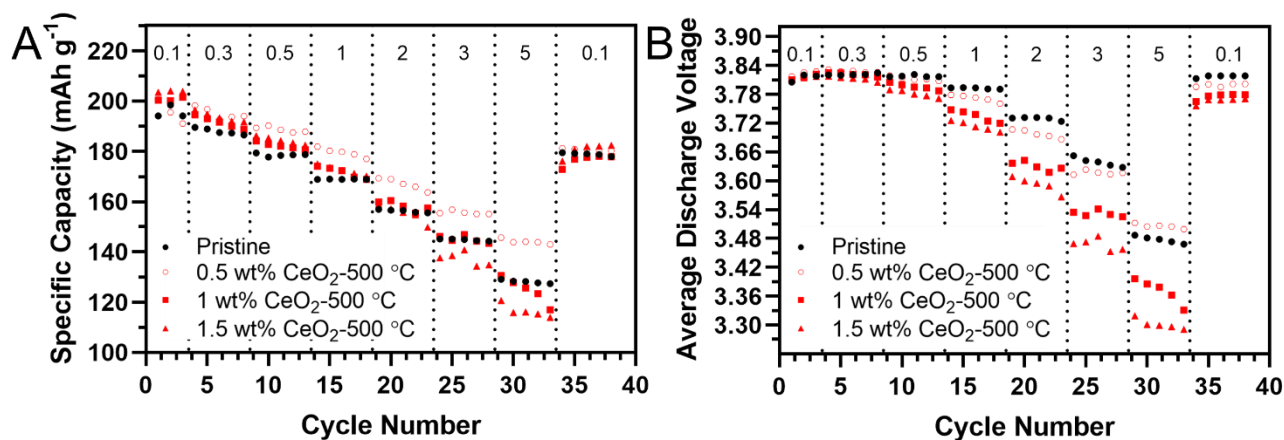


Figure 60. Comparison of rate performance of CeO₂-500 °C coatings. All cells cycled at 0.1 C charge and 0.1 to 5 C discharge at 2.75 – 4.4 V vs Li/Li⁺.

Finally, **Figure 61** displays the cycle performance of the lithiated analogues (Li₂CeO₃) sintered at 500 °C. Similar to the previously discussed Li₂ZrO₃ coating, Li₂CeO₃ exhibits higher impedance compared to their CeO₂ counterparts, with the 0.5 wt% Li₂CeO₃ coated sample showing the best overall performance (**Table 8**). The results indicate that the lithiated coatings do not provide an obvious improvement in cell performance.

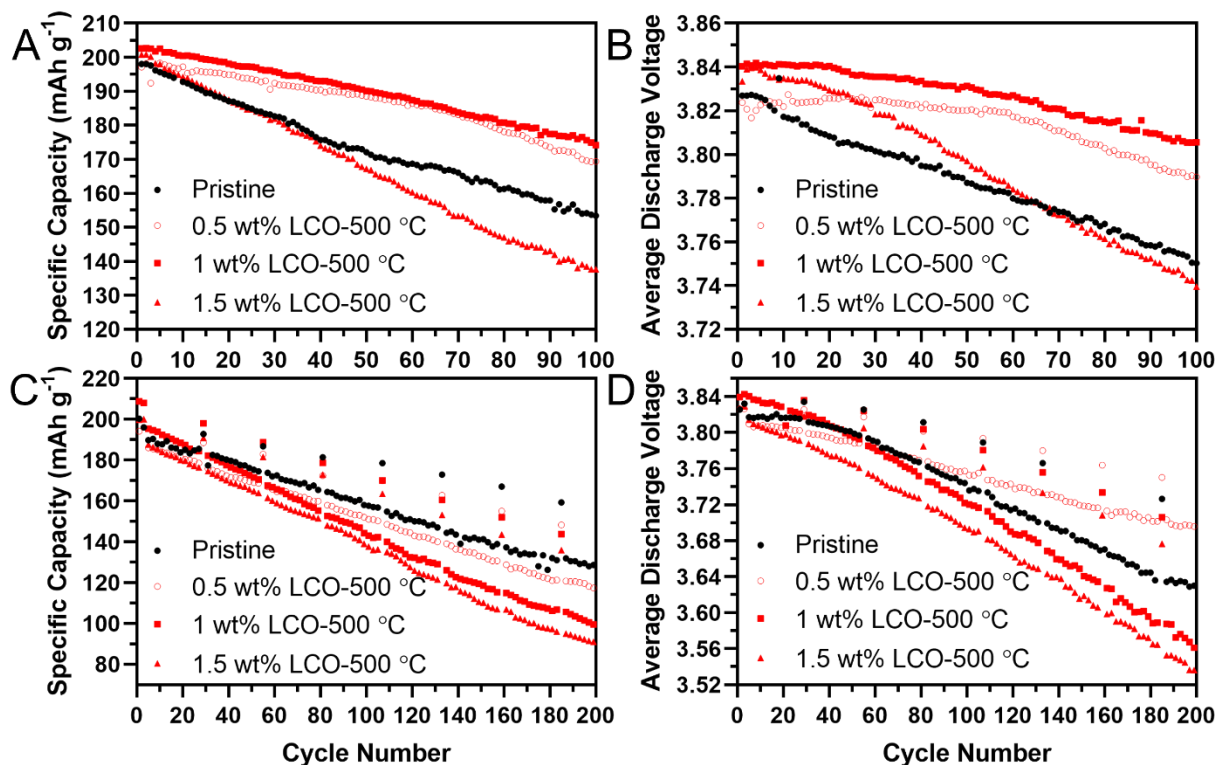


Figure 61. Capacity retention (A and C) and average discharge voltage (B and D) of pristine and Li_2CeO_3 (LCO)-500 °C-treated SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particles cycled from 2.75 – 4.4 V vs Li/Li^+ at 0.1 C (A and B) C/3 (C and D).

5.3.4. *Ex-situ* XPS Characterization of Cycled Electrodes

Representative coating samples (1 wt% ZrO_2 -500 °C, 1 wt% ZrO_2 -300 °C, and 1 wt% CeO_2 -500 °C) have been chosen for *ex-situ* XPS analysis to study and compare their CEI layer composition. Each sample was cycled five times between 2.75 – 4.4 V vs Li/Li^+ under CC-CV conditions. The cathode was then recovered from the disassembled cell and analyzed at a high SOC (~4.35 V vs Li/Li^+).

Figure 62 compares the peak-deconvoluted XPS spectra of key elements (C, O, F, and P) that comprise the early-formed CEI layer. For each element, the intensity is non-normalized and plotted with consistent y-axis scaling in order to compare their relative quantity among different samples. **Table 9** and **10** list the respective binding energies and relative quantity of the deconvoluted species.

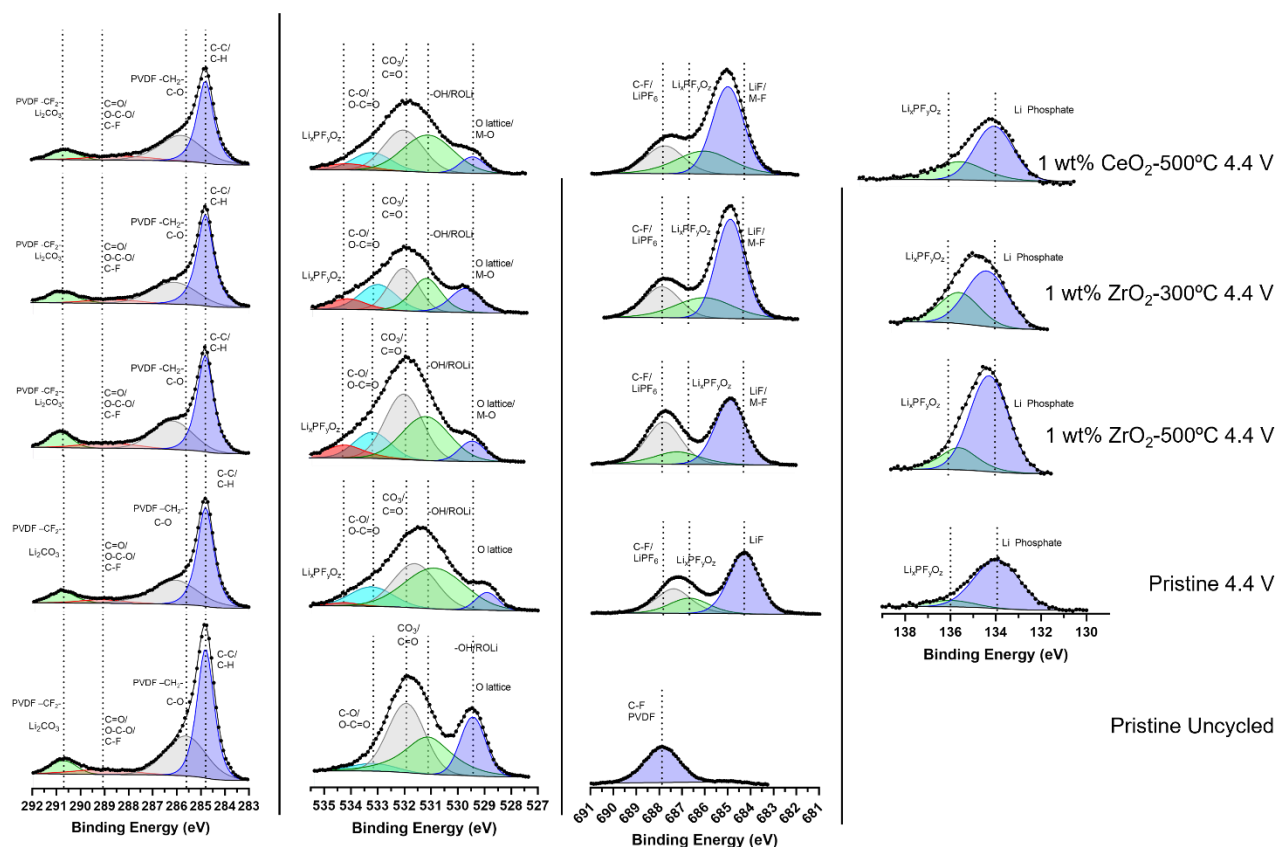


Figure 62. C 1s, O 1s, F 1s, and P 2p (left to right) *ex-situ* XPS spectra comparison of select samples. For each element, the plotted intensities are non-normalized.

Table 9. Binding energies derived from XPS peak fitting.

C 1s Sample	C-C/C-H	C-O/PVDF	C=O/O-C-O/C-F	Li ₂ CO ₃ /PVDF	
Pristine	284.8	285.6	289.1	290.7	
Pristine 4.4 V	284.8	286.1	289.1	290.7	
1 wt% ZrO ₂ -500	284.8	286.2	288.8	290.8	
1 wt% ZrO ₂ -300	284.8	286.1	288.7	290.7	
1 wt% CeO ₂ -500	284.8	285.8	288.3	290.1	
O 1s Sample	O Lattice/M-O	-OH/ROLi	CO ₃ /C=O	C-O/O-C=O	Li _x PF _y O _z
Pristine	529.4	531.1	531.9	533.2	--
Pristine 4.4 V	529.0	531.0	531.7	533.2	534.3
1 wt% ZrO ₂ -500	529.4	531.2	532.0	533.2	534.2
1 wt% ZrO ₂ -300	529.7	531.2	532.0	533.0	534.1
1 wt% CeO ₂ -500	529.4	531.1	532.0	533.2	534.2
F 1s Sample	LiF/M-F	Li _x PF _y O _z	C-F/LiPF ₆		
Pristine	--	--	687.9		
Pristine 4.4 V	684.4	686.9	687.5		
1 wt% ZrO ₂ -500	684.9	687.2	688.0		
1 wt% ZrO ₂ -300	684.9	686.0	687.9		
1 wt% CeO ₂ -500	685.0	686.1	687.8		

P 2p Sample	Li Phosphate	Li _x PF _y O _z	LiPF ₆
Pristine	--	--	--
Pristine 4.4 V	134.1	136.1	--
1 wt% ZrO ₂ -500	134.2	135.5	--
1 wt% ZrO ₂ -300	134.3	135.5	137.6
1 wt% CeO ₂ -500	134.0	135.5	--

Table 10. Relative composition of deconvoluted species derived from XPS peak areas.

C 1s Sample	C-C/C-H	C-O/PVDF	C=O/O-C-O/C-F	Li ₂ CO ₃ / PVDF	
Pristine	51.1%	35.1%	6.3%	7.5%	
Pristine 4.4 V	52.5%	33.8%	5.0%	9.1%	
1 wt% ZrO ₂ -500	49.6%	32.1%	8.0%	10.3%	
1 wt% ZrO ₂ -300	53.5%	30.3%	5.8%	10.4%	
1 wt% CeO ₂ -500	48.4%	35.8%	7.8%	8.0%	
O 1s Sample	O Lattice/M-O	-OH/ROLi	CO ₃ /C=O	C-O/O- C=O	Li _x PF _y O _z
Pristine	23.4%	31.1%	40.2%	5.3%	--
Pristine 4.4 V	6.9%	43.2%	33.3%	14.7%	1.8%
1 wt% ZrO ₂ -500	7.9%	32.0%	37.3%	14.4%	8.4%
1 wt% ZrO ₂ -300	17.2%	23.3%	29.0%	21.4%	9.1%
1 wt% CeO ₂ -500	8.3%	38.7%	33.3%	14.1%	5.6%
F 1s Sample	LiF/M-F	Li _x PF _y O _z	C-F/LiPF ₆		
Pristine	--	--	100%		
Pristine 4.4 V	55.5%	18.0%	26.4%		
1 wt% ZrO ₂ -500	49.1%	14.3%	36.7%		
1 wt% ZrO ₂ -300	55.0%	23.5%	21.5%		
1 wt% CeO ₂ -500	53.7%	25.7%	20.6%		
P 2p Sample	Li Phosphate	Li _x PF _y O _z	LiPF ₆		
Pristine	--	--	--		
Pristine 4.4 V	88.2%	11.8%	--		
1 wt% ZrO ₂ -500	80.6%	19.4%	--		
1 wt% ZrO ₂ -300	64.8%	35.2%	--		
1 wt% CeO ₂ -500	68.5%	31.5%	--		

For the pristine (uncoated and uncycled) peak, the C 1s spectra comprises carbon black and the PVDF binder (~286 eV and ~290.8 eV corresponding to -CH₂- and -CF₂- of PVDF respectively).¹⁸⁹ The O 1s peak at ~529.4 is ascribed to M-O from the LiNi_{0.83}Mn_{0.06}Co_{0.11}O₂ lattice oxygen (O 1s, ~529.4 eV), with other peaks associated with surface groups of carbon

black in the electrode. In comparison, the cycled pristine electrode shows smaller areas for peaks assigned to PVDF and $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ lattice oxygen, because they are coated by the CEI layer formed from decomposed electrolyte species, and XPS has a low depth of analysis (<10 nm). Thus, the relative peak areas of these species can be used to qualitatively assess the thickness of the CEI layer. Fluoride and phosphate species derived from the decomposition of LiPF_6 are also detected on the surface. The F 1s spectra is deconvoluted with two additional peaks assigned to LiF (~685 eV) and $\text{Li}_x\text{PF}_y\text{O}_z$ (~687 eV) species. The P 2p spectra is deconvoluted with two peaks corresponding to $\text{Li}_x\text{PF}_y\text{O}_z$ species, with the lower B.E. peak assigned to Li_3PO_4 or fluorophosphates with a lower degree of fluorination. The CEI layer also comprises organic species from the decomposition of EC/DMC. However, this is difficult to delineate from carbon black or PVDF in the composite electrode based on the C 1s and O 1s spectra. Nevertheless, the increased intensity of the O 1s speak assigned to C-O/O-C=O species likely corresponds to poly(ethylene carbonate/oxide)-type species in the CEI layer.

For the coated samples, a notable distinction is the thinner CEI layer, based on the larger peak areas of the underlying M-O and PVDF signals compared to the cycled pristine sample. A thinner layer likely occurs due to the dense and electronically insulating nature of the coating, which can help suppress solvent decomposition. Moreover, the CEI layer of the coated samples exhibit a larger quantity of inorganic species (LiF, M-F, $\text{Li}_x\text{PF}_y\text{O}_z$, Li_3PO_4), which are known to be thinner and denser than organic constituents.

As discussed in **Section 4**, the formation of these species in the CEI layer is a consequence of the Lewis acid-base reaction between metal oxides and F^-/PF_6^- . It begins with the fluorination reaction consistent with the ‘HF scavenging’ mechanism depicted in **Equation 1** and **2** for Zr

and Ce, respectively. Among the coated samples, the 1 wt% ZrO₂-500 °C displays the lowest quantity of fluoride species, likely because the coating is thinner which lowers the reaction rate.



It should be noted that the F 1s peak at ~685 eV overlaps with Zr-F/Ce-F signals. The Zr 3d spectra (**Figure 63A**) confirms the formation of Zr-F species (ZrF₄ and/or Zr oxyfluorides). It is deconvoluted with three broad peaks centered at 182.4, 184.4, and 186.4 eV. The first peak is assigned to Zr-O 3d_{5/2} while the central peak comprises an overlap of Zr-O 3d_{3/2} and Zr-F 3d_{5/2}. The highest B.E. peak is assigned to Zr-F 3d_{3/2}. On the other hand, the identification of Ce-F from the Ce 3d spectra is more challenging due to the complex multiple splitting.²²⁸ As shown in (**Figure 63B**), the broader appearance of the Ce 3d_{5/2} peaks likely indicates the presence of Ce-F.

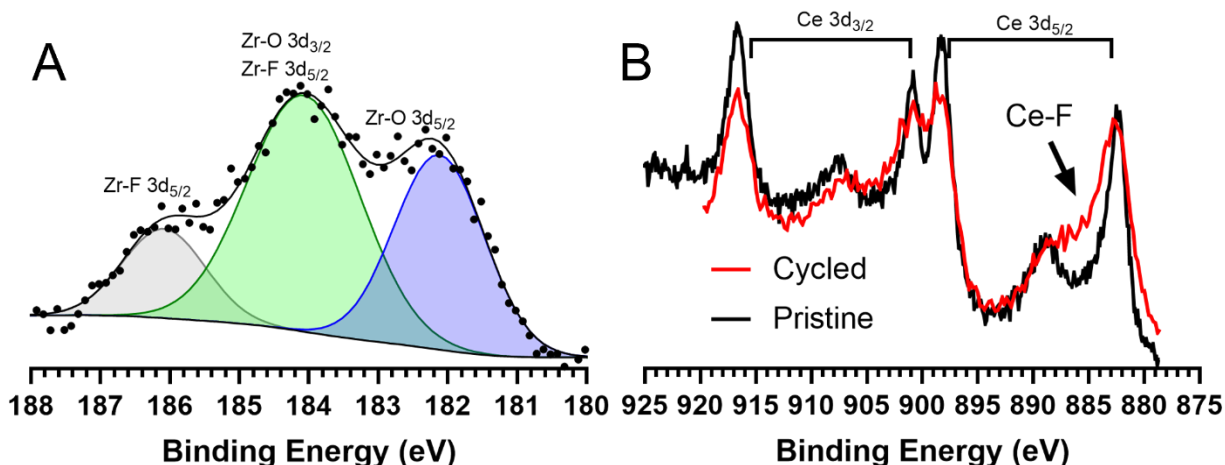


Figure 63. A) *Ex-situ* Zr 3d spectra from 1 wt% ZrO₂-500 °C sample. B) Comparison of pristine and *ex-situ* Ce 3d spectra from 1 wt% CeO₂-500 °C. Intensities are normalized for visual clarity.

The water released from these fluorination reactions can subsequently decompose LiPF₆, forming HPO₂F₂ as depicted in **Equations 3 – 5** below:





The HF by-product produced can repeatedly react with the metal oxide coating (**Equation 1** and **2**), propagating these reactions to produce more LiF and HPO₂F₂. Meanwhile, coverage of the active particle surfaces with the metal oxide or metal fluoride-generated coating minimizes Ni loss by HF corrosion. HPO₂F₂ can further decompose, forming LiF, Li_xPF_yO_z, and Li₃PO₄ species in the CEI layer, which corresponds with the XPS results. These fluoride and (fluoro)phosphate species are also known to enhance the stability of CEI/SEI layers, due to their electronically insulating nature and high electrochemical stability (up to ~4.5 V vs Li/Li⁺).¹⁶⁴. Moreover, recent work has suggested that phosphate and fluorophosphate species in the CEI layer can chelate with transition metals, forming insoluble complexes (*e.g.*, NiPO₃F), which can suppress their dissolution into their electrolyte.^{193–195} LiF in particular is also well known to mechanically reinforce the CEI/SEI layers.

While the electronically insulating coating itself should passivate the interface, particularly against electrochemical decomposition of solvent, the formation of these fluoride and phosphate species is still beneficial because they can passivate any uncoated regions of the active particles. The work in **Section 4** showed that metal oxide coatings still improve cycle stability (particularly at low currents) even without good coverage of active particles. In addition, they can passivate the surfaces of the PVDF and carbon black, where electrolyte decomposition is also known to occur. Finally, they can generate positive ‘cross talk’ effects, in which the fluoride and phosphate species diffuse toward the anode and help passivate the SEI layer. A fluoride-rich SEI layer is well known to be beneficial for high capacity and high volume change anode materials, such as Si and Li metal.

5.4. Conclusions

This work systematically characterized and compared the performance of ZrO_2 and CeO_2 coatings applied on SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particles by sintering. In all cases, the coating wt% must be carefully optimized to balance surface coverage and thickness. While all coatings were found to suppress HF-driven active material loss, excessively thick coatings display high cell impedance and growth over cycling. The ZrO_2 coating sintered at 500 °C under pure oxygen exhibited bulk doping as noted by the expansion in the lattice c -axis from XRD. The ZrO_2 coatings sintered at 300 °C were thicker with no apparent bulk doping. Consequently, under optimized conditions, both ZrO_2 -500 °C and ZrO_2 -300 °C treatments showed similar performance when cycling at 0.1 C, where capacity retention is dictated by active material loss. However, the contribution of Zr^{4+} doping was more significant when cycling at C/3, likely due to its ability to improve Li^+ diffusion kinetics and suppress volume evolution, thus ameliorating the formation of intragranular cracks and defects. Meanwhile, the CeO_2 coating sintered at 500 °C exhibited no bulk doping, forming a relatively thick and highly crystalline surface layer. Under optimized conditions, the CeO_2 coating exhibited similar cycle performance to ZrO_2 coating/doping at both 0.1 C and C/3. However, its kinetic performance was poorer. The high crystallinity of the coating can potentially reinforce the active particles against cracking. Finally, both ZrO_2 and CeO_2 coatings were found to react with HF, resulting in an increased quantity of fluoride and phosphate species in the CEI layer, which aids in its passivation. This work provides insight on the rational design and optimization of coatings for Ni-rich layered oxide cathodes.

6. Stabilization of Ni-Rich Cathodes with Novel Electrolyte Compositions

6.1. Introduction

Section 4 and **Section 5** focus on the use of surface coatings and TM dopants to enhance the kinetics and cycle retention of SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$. As discussed, a prominent mechanism of these coatings involves their reactivity with LiPF_6 , accelerating its decomposition to generate an inorganic-rich LiF and $\text{Li}_x\text{PF}_y\text{O}_z$ -rich CEI layer, which passivates the cathode surface against oxygen release and further side reactions with the electrolyte. An equally effective approach to achieving this effect is to modify the electrolyte composition in order to reduce the likelihood of cathode-electrolyte side reactions and/or generate a passivating CEI layer composition. **Section 4** describes a preliminary analysis incorporating an electrolyte additive (FEC) with the conventional electrolyte to further improve cycle performance. While the use of new electrolyte additives and their combinations can generate promising results, they ultimately do not resolve the inherent instabilities at the CEI. The aim is to develop next-generation electrolytes that exhibit drastically improved behavior.

The conventional LiPF_6 in carbonate-based solvent electrolyte has been suitable for commercially produced LIBs due to 1) compatibility with the graphite anode – certain solvents can co-intercalate (with Li^+) into the graphite interlayer, resulting in its exfoliation, 2) passivation of the Al current collector by generating an AlF_3 surface layer, which would otherwise corrode at $> 3.8 \text{ V vs Li/Li}^+$, 3) good ionic conductivity and rate performance, and 4) excellent stability for current energy density capabilities (up to $\sim 300 \text{ Wh kg}^{-1}$, normalized by cell mass). However, this electrolyte has poor stability at elevated voltages ($> 4.3 \text{ V vs Li/Li}^+$), generating a thick CEI layer with high impedance. This electrolyte also has extremely poor

compatibility with high capacity anode materials such as Li metal and Si. Thus, this electrolyte is not suitable for next-generation lithium-based batteries aiming for $> 350 \text{ Wh kg}^{-1}$ energy density.

High-concentration electrolytes (HCEs) have attracted significant research interest in the past five years. They consist of a near-equivalent molar ratio of salt to solvent, forming a unique solvation structure with minimal separation between the cation and ion.¹³⁶ Lithium bis(fluorosulfonyl)imide (LiFSI) is commonly used as the salt due to its high solubility in dimethyl carbonate (DMC) or dimethoxyethane (DME). Consequently, in an electrochemical cell, this shifts the lowest unoccupied molecular orbital (LUMO) from the solvent to the salt. Thus, the salt is preferentially reduced at the anode, forming inorganic-rich SEI layers. Moreover, the highest occupied molecular orbital (HOMO) energy level of the solvent coordinated to the salt is decreased, improving its oxidative stability. When utilizing LiFSI salt, the CEI/SEI layer is rich with inorganic N, S, and F-species, which substantially improves interfacial passivation.^{137–139} Unlike LiPF_6 , LiFSI is known to be stable against trace moisture in the electrolyte and is much less prone to HF release.²²⁹ Another positive outcome of HCEs is that the Al current collector is passivated from corrosion at high voltages, negating the need for LiPF_6 , possibly because the Al corrosion products have poor solubility in HCEs.¹⁴⁰

However, the main drawback of HCEs is their high viscosity, which is not ideal for battery manufacturing, as it will significantly extend wetting times of the separators and electrodes of high-capacity cells. Furthermore, LiFSI is currently far more expensive than LiPF_6 , although this is expected to change with more widespread adoption of LiFSI. Thus, localized HCEs (LHCEs) introduce a diluent (typically a highly fluorinated ether), which is miscible with the solvent but does not dissociate LiFSI, thus preserving the solvation structure.¹³⁶ The diluent can lower the salt concentration from $\sim 5 \text{ M}$ to $1.2 - 1.5 \text{ M}$.¹³⁸

In this section, the two most promising coating treatments on SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ from **Section 4** (alucone deposited on fabricated electrode by ALD) and **Section 5** (1 wt% ZrO_2 -500 °C sintering treatment) are paired with an LiFSI-based LHCE to assess whether cell performance can be further enhanced. Building on past work, the passivation mechanism of the coatings under this novel electrolyte composition is proposed.

6.2. Materials and Methods

The LHCE comprised LiFSI salt (99%, BenchChem, Austin, TX, USA), DME solvent (anhydrous, 99.5%, Sigma-Aldrich), and 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE, 99%, SynQuest Laboratories, Alachua, FL, USA) as the diluent mixed at a 1:1.2:3 molar ratio, respectively. The conventional additive-free electrolyte (1 M LiPF_6 in 3:7 EC:DMC by volume, BASF, Germany) is denoted as LP30. Materials were used as received. The electrode fabrication, application of coatings, coin cell assembly, and electrochemical cycling (2.75 – 4.4 V vs Li/Li^+) were conducted as described in **Section 4** and **5**. The only exception is the use of Al-clad CR2032 positive coin cell casings (MTI Corporation, Richmond, CA, USA) due to corrosion of the conventional stainless steel casing. The alucone coating was applied by ALD after calendaring the electrode.

6.3. Results and Discussion

6.3.1. Electrochemical Performance

Figure 64 compares the electrochemical performance of the pristine electrode cycled with the conventional LP30 electrolyte, the pristine electrode with the LHCE, and the coated electrodes paired with the LHCE. For the pristine electrodes cycled at 0.1 C, the LHCE drastically improves both the capacity retention and suppresses polarization growth relative to the LP30 electrolyte as expected (**Figure 64**). As discussed in **Sections 4** and **5**, capacity loss under the LP30 electrolyte

is largely driven by active material loss from HF corrosion, while polarization growth is dictated by oxygen release from the particle surface and the increasing CEI layer thickness.

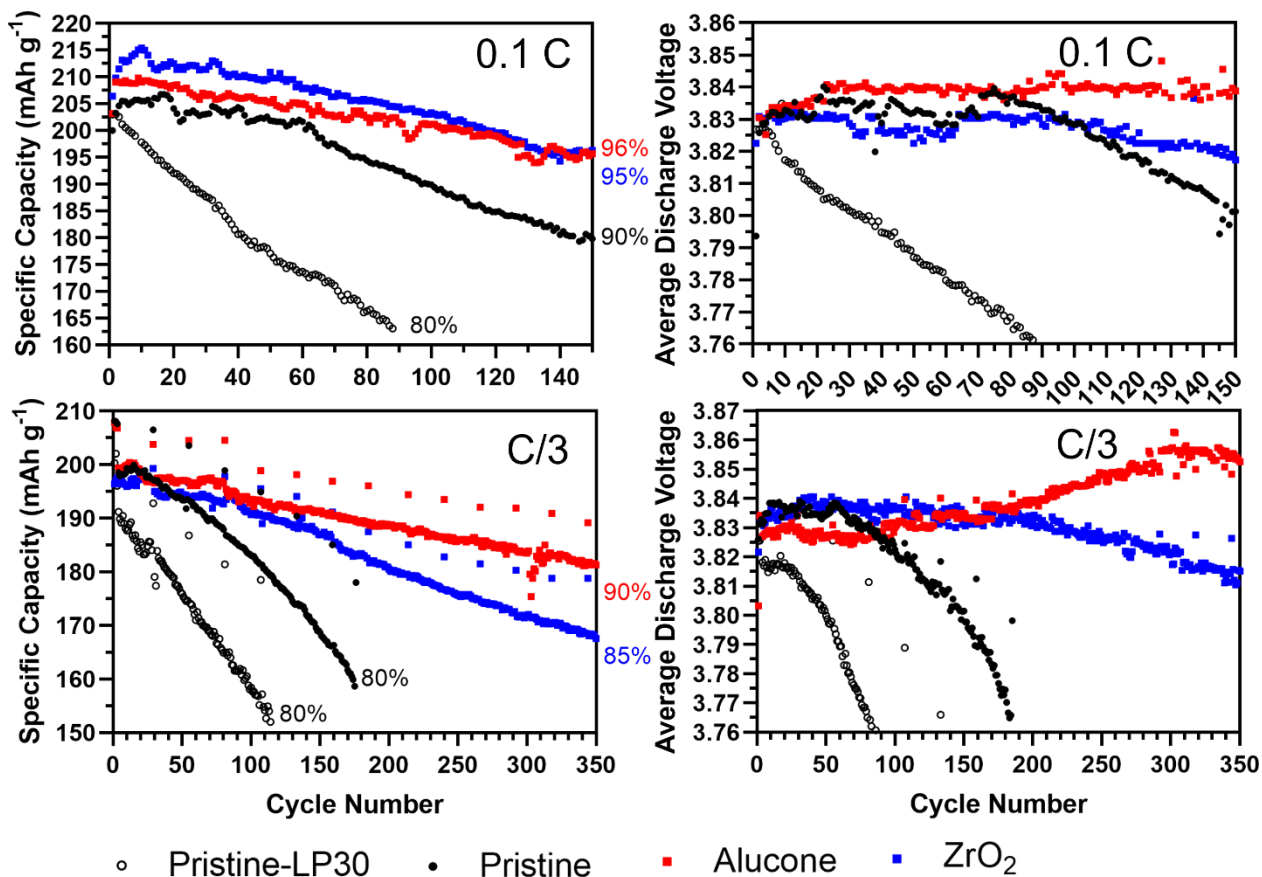


Figure 64. Capacity retention (A and C) and average discharge voltage (B and D) of pristine electrode in LP30 electrolyte (Pristine-LP30), and pristine, ZrO₂, and alucone-coated electrodes paired with the LHCE. Electrodes cycled from 2.75 – 4.4 V vs Li/Li⁺ at 0.1 C (A and B) C/3 (C and D).

As shown in the respective dQ/dV curves (**Figure 65**), the pristine electrode cycled with the LHCE shows noticeable peak polarization and area loss at the H2/H3 phase transition after 150 cycles. However, peaks at other SOCs are mostly unaffected. This implies that minimal active material loss occurs, likely because LiFSI does not generate HF upon decomposition. However, impedance buildup is noticeable, which kinetically suppresses the H2/H3 phase transition, despite the fact that both DME and TTE should be electrochemically stable under the voltage

range tested. This suggests that oxygen release and the subsequent formation of the high-impedance Ni^{2+} -O surface layer on the cathode continues to occur.

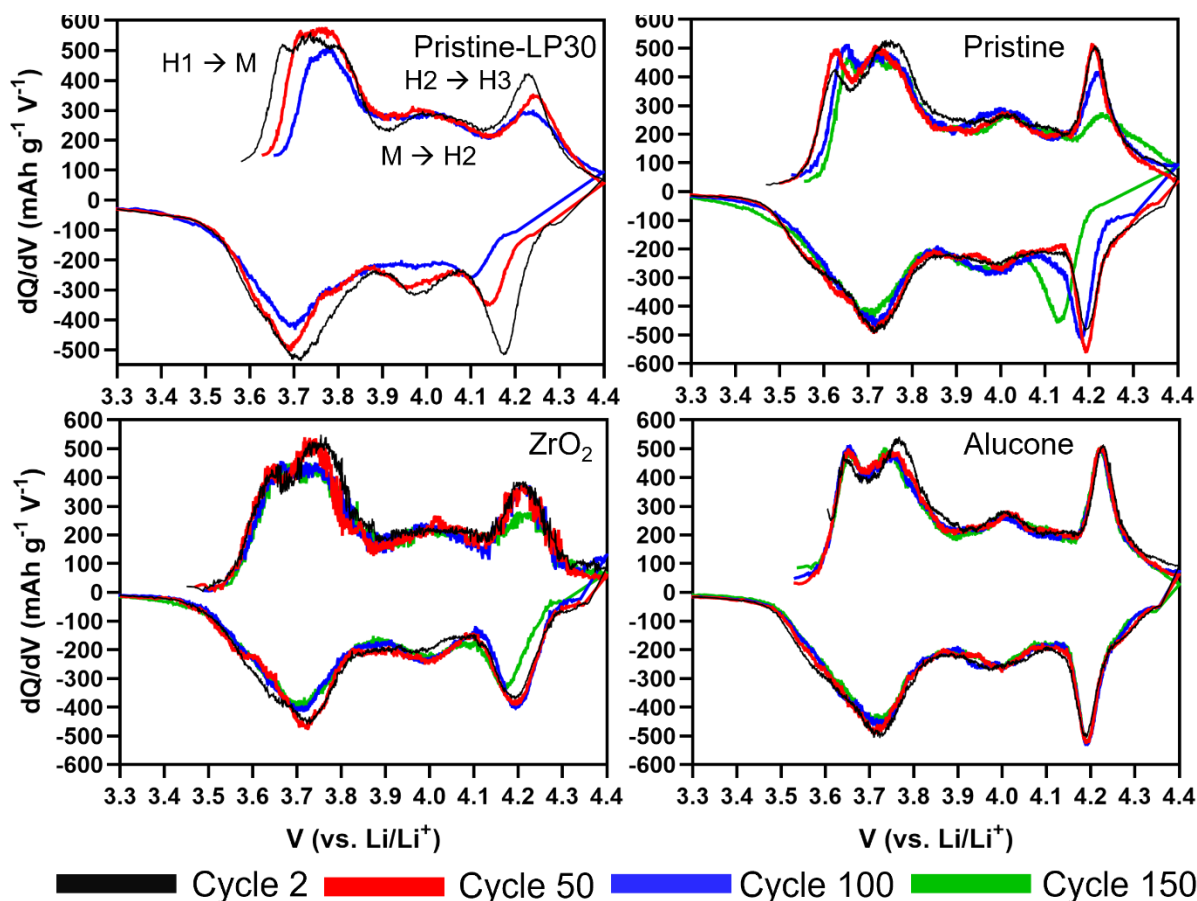


Figure 65. dQ/dV curves of pristine and coated cells cycled at 0.1 C and 2.75 – 4.4 V vs Li/Li⁺.

Both coatings paired with the LHCE show clear improvements in both capacity retention and suppressing impedance growth. The most notable improvement is preserving the reversibility and suppressing peak polarization of the H2/H3 phase transition. However, the alucone coating exhibits the best performance, with remarkable active material retention and stable impedance. It is worth noting that all samples cycled with the LHCE appear to exhibit ‘activation/formation cycling’, whereby the cell impedance decreases over the initial 10 cycles. This is likely due to side reactions (LiFSI decomposition) at the electrode-electrolyte interfaces, or the overcoming of

initial transport limitations within the electrolyte. Li^+ transport in the LHCE occurs by hopping within salt-solvent clusters and the diffusion of these clusters – these pathways likely stabilize during the initial cycles.

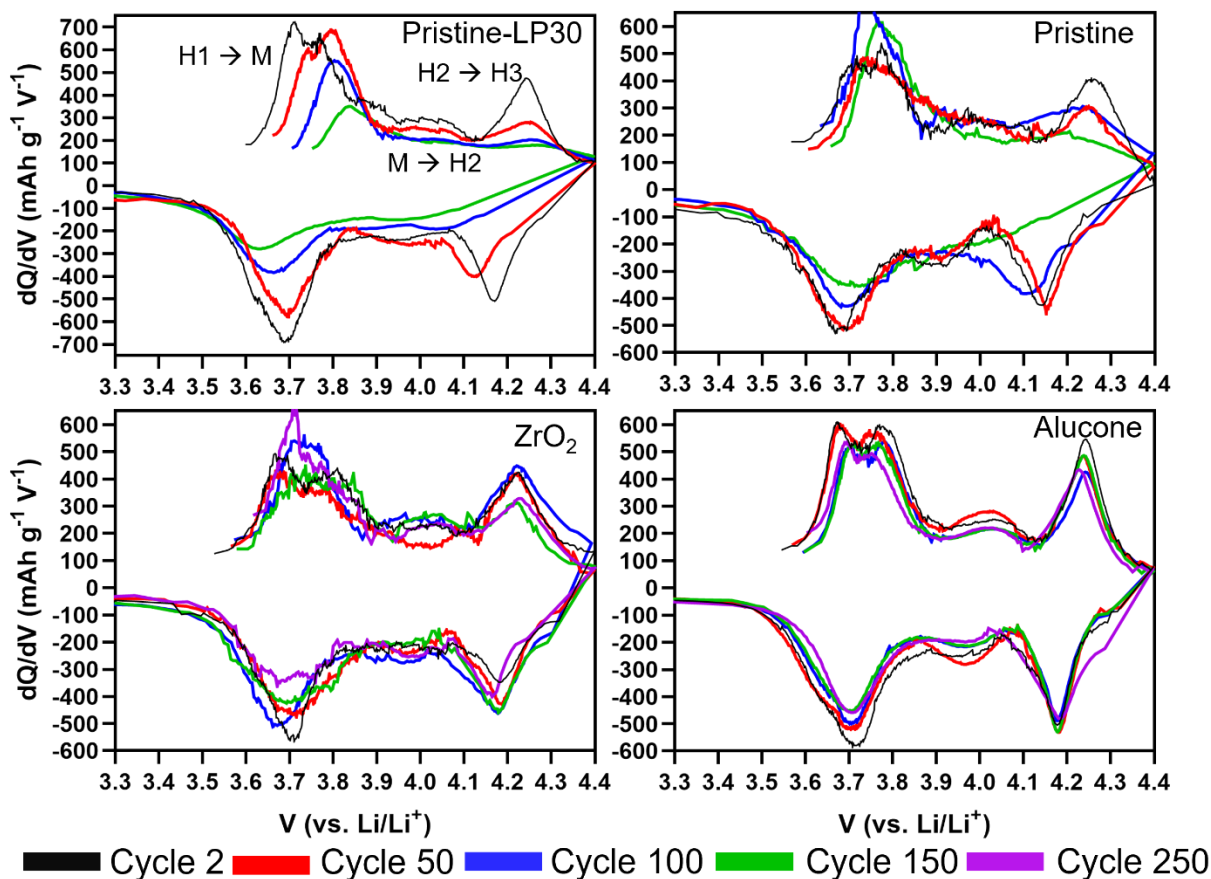


Figure 66. dQ/dV curves of pristine and coated cells cycled at C/3 and 2.75 – 4.4 V vs Li/Li⁺.

As shown in **Figure 64** and **Figure 66**, the same trends are noted when cycling at C/3. The strong performance of the alucone coating is more notable with extensive cycling. As shown in the dQ/dV curves, the alucone coating retains the peak positions and areas at the H2/H3 phase transition remarkably well, even after 250 cycles at C/3. However, some decay of peak area at other SOC is observed, which is ascribed active material loss. As a result, the average discharge voltage shows an increasing trend (**Figure 64D**).

This result is interesting and somewhat unexpected considering that the 1 wt% ZrO_2 -500 °C coating outperforms the alucone coating in LP30 electrolyte (**Figure 67**). As established in **Section 4** and **5**, both the alucone and ZrO_2 coating accelerate the decomposition of LiPF_6 , passivating the CEI layer with LiF and $\text{Li}_x\text{PF}_y\text{O}_z$ species. However, the 1 wt% ZrO_2 -500 °C treatment also exhibits Zr^{4+} doping, which can improve kinetics and alleviate inherent lattice instabilities at the H2/H3 phase transition, suppressing oxygen release and lattice volume changes. As the oxygen release occurs due to the instability of the lattice structure at low lithiation states (high SOC), this effect should be beneficial regardless of the electrolyte composition employed. Meanwhile, the alucone coating is localized on the upper surface of the electrode and does not cover all active particle surfaces, which implies that it reacts with the LHCE in a favorable manner, generating a passivating CEI layer. This likely occurs by accelerating the decomposition of LiFSI .

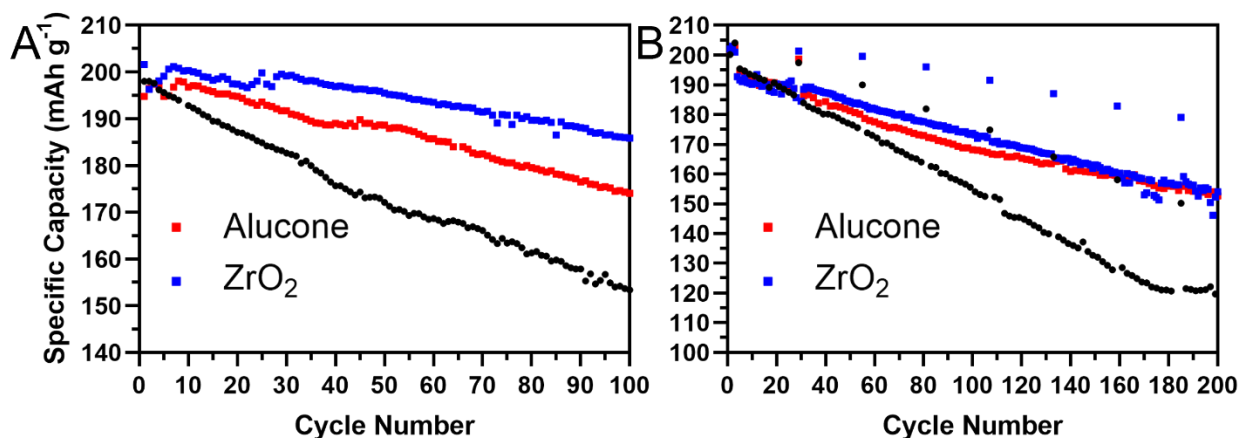
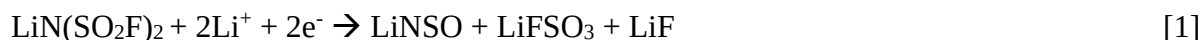


Figure 67. Cycle stability of alucone and ZrO_2 -coated electrodes in additive-free LP30 electrolyte at 2.75 – 4.4 V vs Li/Li^+ and A) 0.1 C and B) C/3.

6.3.2. Mechanism of LHCE and Coatings

In the literature, analysis of the CEI layer by XPS after cycling under a LiFSI-based HCE/LHCE reveals a large quantity of LiF, NSO_xF_y, and SO_xF_y species derived from the decomposition of LiFSI.^{141,142,230} These species help suppress the formation of the reconstructed surface layer universally observed in cycled Ni-rich layered oxide cathodes. However, the decomposition mechanism of LiFSI on the cathode surface remains uncertain. Based on thermodynamic calculations, the reductive decomposition of LiFSI on the Li metal counter-electrode/anode is known to occur based on **Equation 1**.



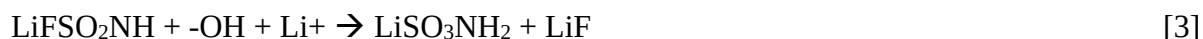
However, LiFSI does not undergo direct electrochemical oxidation. Thus, one potential explanation is that the LiF, NSO_xF_y, and SO_xF_y are formed on the anode surface, and subsequently deposited on the cathode through the chemical ‘cross talk’ phenomenon. However, this mechanism alone cannot explain the improved performance generated by the cathode coatings, particularly alucone.

We propose that similar to LiPF₆, LiFSI decomposes on the cathode surface by reacting with protic species. As depicted in **Equations 2 – 4**, S-N and S-F bonds can be cleaved by reacting with surface hydroxyl groups on the cathode. These mechanisms are consistent with past studies on the hydrolysis of LiFSI.^{231,232}

Cleavage of S-N bond:



Cleavage of S-F bonds:





In HCEs and LHCEs with LiFSI, these reactions are favored due to the close proximity between Li^+ and FSI^- . Thus, FSI^- is in close proximity to the hydroxyl groups on the cathode surface. For the pristine electrode, hydroxyl groups are present on the surface of $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particles. Similar to the mechanism observed in conventional LP30 electrolyte,¹⁸² reactive singlet oxygen released from the lattice at high voltage may dehydrogenate TTE or DME, forming more hydroxyl groups on the particle surface. The TTE is more likely to be decomposed due to its higher quantity in the electrolyte. This may explain observations in other work where TTE appears to ‘assist’ with the decomposition of LiFSI on the cathode surface.^{141,142,230}

On the other hand, metal oxide coatings naturally contain hydroxyl groups on their surface, thus accelerating the decomposition of LiFSI. The alucone coating is more effective than ZrO_2 as its surface is saturated with hydroxyl groups in accordance with the ALD deposition mechanism. Thus, a thicker layer of LiF, NSO_xF_y , and SO_xF_y species form on the cathode surface during the initial cycles, which helps suppress oxygen release and surface reconstruction.¹⁴² N, and S-containing species are known to be lithophilic, which helps alleviate the interfacial charge transfer barrier.²³³ Furthermore, the alucone coating itself imposes a lower kinetic barrier compared to the ZrO_2 coating. As established in **Section 4** the alucone coating does not disrupt electronic conductivity within the electrode and has low density, which facilitates Li^+ transport. This can partially explain the remarkable suppression of impedance growth. The body of results suggest that complete passivation of the CEI layer with LiF, NSO_xF_y , and SO_xF_y species is more effective and kinetically favorable than both the ZrO_2 coating and Zr^{4+} doping.

On a related note, this decomposition mechanism of LiFSI may explain the passivation of Al against corrosion in HCE/LHCEs at elevated voltages. Although the Al passivation mechanism

is not fully understood, one explanation involves the formation of a passivating LiF layer on the Al surface.²²⁹ The surface of Al comprises Al_2O_3 , with native hydroxyl groups that accelerate the decomposition of LiFSI to form the passivation layer. On the other hand, stainless steel contains low quantities of surface hydroxyl groups,²³⁴ and thus corrosion occurs from FSI⁻ etching the surface.¹⁴⁰ Thus, Al-coated CR2032 positive casings are required in order to electrochemically cycle LiFSI-based HCE/LHCEs (see **Materials and Methods**).

7. Conclusions and Perspectives

7.1. Conclusions

The application of a surface coating is among the most promising and fundamental approaches in improving the performance of existing electrode materials. This work examined various metal oxide and metalcone coating materials and application methods to enhance the performance of SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$. **Section 4** studies the effects of coatings applied on fabricated electrodes by ALD. Although this approach has been repeatedly demonstrated in the literature with strong electrochemical performances generated, the mechanism of the coating remains ambiguous. XPS characterization reveals that the coating remains localized on the outer regions of the electrode due to the limited penetration of the gaseous coating precursors. Despite this, the coatings improved the cycle stability of the cathode, particularly at low currents, where active material loss from HF corrosion is predominant. A marginally improved coating penetration was achieved by conducting ALD prior to compacting/calendaring the electrode. However, this did not noticeably improve the cycle performance of the cells. Among the four coating materials tested (Al_2O_3 , alucone, TiO_2 , and titanicone), Al_2O_3 exhibited the poorest performance due to its poor Li^+ permeability, resulting in rapid impedance growth. Due to the limited coating coverage of the active particles, the improvement in cycle performance cannot be ascribed to the passivating nature of the coating itself. Analysis of the chemical composition of the early-formed CEI layer reveals that the coatings accelerate the decomposition of LiPF_6 , forming a thin inorganic-rich CEI layer containing LiF , $\text{Li}_x\text{PF}_y\text{O}_z$, and Li_3PO_4 . This passivates the cathode surface from HF corrosion, electrolyte solvent decomposition, and lattice oxygen release, suppressing both active material loss and impedance growth. The results indicate that 1) metal oxide or metalcone coatings can behave in a similar manner to electrolyte additives and 2)

complete coverage of the active particle surface is not required. To support these conclusions, the cathode was loosely ‘coated’ with TiO_2 nanoparticles either by mixing them in the electrode slurry or adding them to the electrolyte as a suspension. Both cases also resulted in an improvement in cycle retention, due to the side reactions generated between TiO_2 and F^-/PF_6^- . Preliminary work was also conducted in analyzing the relationship between electrode coatings and electrolyte additives. The alucone coating was also paired with FEC electrolyte additive, which synergistically improved the cycle stability of the cathode. In this particular case, FEC helped further accelerate the decomposition of LiPF_6 , producing more LiF , $\text{Li}_x\text{PF}_y\text{O}_z$, and Li_3PO_4 species in the CEI layer.

Section 5 examines ZrO_2 and CeO_2 coatings applied directly to the SC $\text{LiNi}_{0.83}\text{Mn}_{0.06}\text{Co}_{0.11}\text{O}_2$ particles by sintering. The coating wt% was carefully optimized to balance surface coverage and thickness. While all coatings were found to suppress HF-driven active material loss, excessively thick coatings display high cell impedance and growth over cycling. The ZrO_2 coating sintered at 500 °C under pure oxygen exhibited bulk doping as noted by the expansion in the lattice c -axis from XRD. The ZrO_2 coatings sintered at 300 °C exhibited no apparent bulk doping and were consequently thicker. Under optimized wt%, both ZrO_2 -500 °C and ZrO_2 -300 °C treatments showed similar performance when cycling at 0.1 C, where capacity retention is dictated by active material loss. However, the impact of Zr^{4+} doping was more significant when cycling at C/3, likely due to its ability to improve Li^+ diffusion kinetics and suppress volume evolution particularly during the H2/H3 phase transition, thus ameliorating the formation of intragranular cracks and defects. Meanwhile, the CeO_2 coating sintered at 500 °C exhibited no bulk doping, forming a relatively thick and highly crystalline surface layer. When sintered at 300 °C, the CeO_2 coating was amorphous with very poor Li^+ permeability. Under optimized wt%, the CeO_2 -500 °C

coating exhibited similar cycle performance to ZrO_2 coating/doping at both 0.1 C and C/3. However, its kinetic performance was poorer. The high crystallinity of the coating can potentially reinforce the active particles against cracking. Finally, similar to **Section 4**, XPS analysis reveals that both the ZrO_2 and CeO_2 coatings can react with HF, resulting in an increased quantity of LiF , $\text{Li}_x\text{PF}_y\text{O}_z$, and Li_3PO_4 species in the CEI layer, which aids in its passivation. The lithiated analogues of the coatings (Li_2ZrO_3 and Li_2CeO_3) did not improve cycle retention or kinetic performance any further. This work provides insight on the rational design and optimization of coatings for Ni-rich layered oxide cathodes.

Comparing the results from **Section 4** and **Section 5**, the three best-performing coatings with respect to cycle performance at both 0.1 C and C/3 are ordered at 1 wt% ZrO_2 -500 °C > 1 wt% CeO_2 -500 °C > Alucone, although they were very similar. With respect to kinetic (rate) performance, these coatings are ordered at 1 wt% ZrO_2 -500 °C > Alucone > 1 wt% CeO_2 -500 °C. The excellent overall performance of alucone is remarkable given that the coating amount is miniscule (< 1 nm thickness). This indicates that alucone is highly efficient at accelerating the decomposition of LiPF_6 , likely because its surface is saturated with hydroxyl groups. Furthermore, the low density of alucone can sterically accelerate reactions with HF. The excellent Li^+ permeability of the alucone coating ensures that it does not contribute to impedance growth. Meanwhile, the 1 wt% ZrO_2 -500 °C sample combines the benefits from the surface coating and Zr^{4+} doping. The coating thickness is also optimized to minimize the Li^+ transport barrier. The similar overall performance between the alucone and 1 wt% ZrO_2 -500 °C samples suggests that the formation of a dense CEI layer with abundant LiF , $\text{Li}_x\text{PF}_y\text{O}_z$, and Li_3PO_4 species is the most significant mechanism toward enhancing cycle stability.

Finally, **Section 6** applies the alucone and 1 wt% ZrO₂-500 °C coatings with a new electrolyte composition – 1:1.2:3 molar ratio of LiFSI:DME:TTE. Similar to LiPF₆, the decomposition of LiFSI generates a dense CEI layer rich with LiF, NSO_xF_y, and SO_xF_y species, which is essential to passivating the SC LiNi_{0.83}Mn_{0.06}Co_{0.11}O₂ surface. However, unlike LiPF₆, the decomposition of LiFSI does not produce HF by-product, thus reducing active material loss. Furthermore, the NSO_xF_y and SO_xF_y species are also known to be lithophilic, which reduces impedance growth. Both coatings were found to improve cycle performance under this electrolyte composition, with the alucone coating showing by far the strongest performance. It was proposed that the coatings aided the decomposition of LiFSI based on its reaction with surface hydroxyl groups, cleaving the S-N and S-F bonds. Alucone was the most efficient at accelerating LiFSI decomposition, likely because its surface is saturated with hydroxyl groups. Furthermore, the alucone coating itself imposes a minimal kinetic barrier. On the other hand, the ZrO₂ coating likely contained a lower quantity of surface hydroxyl groups. While Zr⁴⁺ doping is expected to benefit the cathode stability and kinetics regardless of the electrolyte composition employed, it may be offset by impedance contributions from the ZrO₂ coating itself. The ZrO₂ coating is thicker and denser than alucone, which increases the Li⁺ diffusion barrier. Its thorough coverage of the active particles also disrupts electronic contacts with the conductive carbon black in the electrode.

7.2. Outstanding Questions and Proposed Future Work

1. *Transition toward cobalt-free cathodes*

This work explored various coatings and electrolyte additives to improve the performance of low cobalt SC LiNi_{0.83}Mn_{0.06}Co_{0.11}O₂. Ultimately, the goal is to develop high energy density cobalt-free cathodes, with obvious candidate materials being higher-Ni layered oxides such as LiNi_{0.95}Mg_{0.05}O₂, LiNi_{0.95}Mn_{0.05}O₂, LiNi_{0.95}Al_{0.05}O₂, etc. These materials are expected to display

a higher capacity output, although the degradation mechanisms are accentuated (oxygen release, surface reconstruction, moisture sensitivity, and particle cracking). As the mechanisms are identical, the strategies developed in this work to enhance cycle stability are directly applicable to cobalt-free layered oxide cathodes. However, it would require a combination of strategies to improve their viability.

2. Clarifying the role of fluorides, fluorophosphates, and phosphates in the CEI layer

Section 4 and **Section 5** emphasized that increasing the quantity of LiF, $\text{Li}_x\text{PF}_y\text{O}_z$, and Li_3PO_4 species in the CEI layer was a critical aspect of improving cycle stability. However, in other work where a cathode or electrolyte modification demonstrated improved cycle stability, a lower quantity of these species was found in the CEI layer. Thus, it can be inferred that the modification successfully suppressed side reactions between the cathode surface and LiPF_6 , simultaneously restricting the release of deleterious HF by-product. These conclusions appear to be contradictory.

We believe that the most critical factor in improving cycle stability is to prevent active material loss by HF corrosion. This can be achieved through various mechanisms. In our work, metal oxide and metalcone coatings react with HF, release protic species that accelerate the decomposition of LiPF_6 during the initial charge-discharge cycles. The coating also quenches the HF by-product generated, minimizing active material loss while propagating LiPF_6 decomposition. Eventually, the large quantity of LiF, $\text{Li}_x\text{PF}_y\text{O}_z$, and Li_3PO_4 in the CEI layer can suppress both HF corrosion and further generation of HF.

On the other hand, electronically insulating coatings that are chemically inert against HF (*e.g.*, metal fluorides, polyimide, etc.) will serve as their own passivation layer, suppressing both active material loss and decomposition of LiPF_6 . In this case, it is reasonable to expect the

coating to lower the quantity of LiF , $\text{Li}_x\text{PF}_y\text{O}_z$, and Li_3PO_4 found in the CEI layer. Alternatively, success with the use of stability-enhancing electrolyte additives which function by ‘scavenging’ H_2O or protic species in the electrolyte has been reported, which suppresses both the decomposition of LiPF_6 and generation of HF . These are all valid approaches of protecting the cathode from HF corrosion. At this time, it is difficult to comment on which approach is the most promising.

As discussions on the mechanisms of cathode coatings and electrolyte additives tend to be focused on the decomposition of LiPF_6 , it would be interesting to study their performance with an alternative salt such as LiBF_4 , which is more hydrolytically stable and thus less likely to liberate HF . This would aid in fundamental understanding of the mechanisms involved.

3. Chemical cross-talk effects and cathode coatings

The occurrence of chemical cross-talk in LIBs has been understood for the past decade. In fact, it is a key factor that limits the cycle life of commercial LIBs. However, cross-talk is more prevalent with Ni-rich layered oxide cathodes, due to their high reactivity with the electrolyte. Decomposed electrolyte products and dissolved transition metals originating from the cathode can diffuse through the electrolyte and deposit on the anode, disrupting the SEI layer. In the case of a graphite anode, this can quench the limited reservoir of Li^+ in the cells. With Li metal anodes, disrupting the homogeneity of the SEI layer can lead to dendrite growth, accelerating its degradation. Thus, the application of a cathode coating that suppresses side reactions with the electrolyte can also improve the stability of the anode material. In the case of metal oxide and metalcone coatings, the generated LiF , $\text{Li}_x\text{PF}_y\text{O}_z$, and Li_3PO_4 species can potentially also deposit on the anode and help passivate its surface. Moreover, coatings applied on anode materials can improve the cathode stability based on the same effect. The chemical cross-talk effect can be

studied by simultaneously analyzing the chemical composition and impedance of the CEI and SEI layer.

4. *Coatings and electrolyte additives*

Section 4 and **Section 5** assessed the performance of coatings in additive-free LiPF_6 in EC and DMC electrolyte. However, commercial LIBs implement a proprietary mixture of electrolyte additives to substantially enhance the lifetime of the cell. The impact of the coating may appear less significant when combined with promising electrolyte additives, as their mechanisms may overlap. **Section 4** found that the alucone coating synergistically improved performance when paired with one particular additive, FEC. The decomposition of FEC is believed to generate HF, which reacts with the coating and further accelerates the decomposition of LiPF_6 . However, other electrolyte additives may overlap in mechanisms with coatings. For instance, introducing LiPO_2F_2 as an electrolyte additive, which is a product of LiPF_6 decomposition, appears to accomplish the same function as metal oxide coatings. Although it is difficult to comment on whether utilizing the coating or electrolyte additive modification approach to improve the stability of Ni-rich layered oxide cathodes is more promising overall, it should be noted that the incorporation of electrolyte additives is far simpler and more scalable. Thus, it is critical to discover coating-additive combinations that act synergistically. However, the lack of understanding in the mechanisms of many (even established) electrolyte additives makes this difficult to predict.

5. *LiFSI decomposition mechanism*

Finally, the LiFSI decomposition mechanism proposed in **Section 6** should be verified. This can be done through *ex-situ* XPS analysis to compare the quantity of LiF , NSO_xF_y , and SO_xF_y species in the CEI layer. The performance of the coatings can also be compared to an

electronically insulating coating that lacks surface protic species (*e.g.*, AlF_3). Furthermore, the alucone coating can be applied on the stainless steel CR2032 positive casing, to assess whether it can passivate its surface against corrosion from LiFSI.

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