Constructing Safe and Durable High-Voltage P2 Layered Cathodes for Sodium Ion Batteries Enabled by Molecular Layer Deposition of Alucone

Karthikeyan Kaliyappan, Tyler Or, Ya-Ping Deng, Yongfeng Hu, Zhengyu Bai, and Zhongwei Chen*

Sodium ion batteries are a promising next-generation energy storage device for large-scale applications. However, the high voltage P2–O2 phase transition (>4.25 V vs Na/Na⁺) and metal dissolution of P2 layered cathodes into the electrolyte result in severe capacity fading, which is a major setback to fabricate high energy devices. Hence, it is essential to design an appropriate strategy to enhance interfacial behaviors to obtain safe and stable high voltage sodium ion batteries. Herein, an ultrathin alucone layer deposited through molecular layer deposition (MLD) is employed to stabilize the structure of a P2-type layered cathode cycled at a high cut-off voltage (>4.45 V) for the first time. The alucone coated P2-type Na₀.₆₆Mₐ₀.₉M₈₀.₁O₂ (NMM) cathode exhibits an 86% capacity retention after 100 cycles between 2 and 4.5 V at 1 C, demonstrating substantial improvement compared to pristine (65%) and Al₂O₃-coated (71%) NMM cathodes. Furthermore, the mechanically robust and conductive nature of the organometallic thin film enhances the rate capability relative to the pristine NMM electrode. This work reveals that the MLD of alucone on cathodes is a promising approach to improve the cycle stability of sodium ion batteries at high cut-off voltages.

1. Introduction

The world’s current energy demand has propelled a shift from fossil fuels to renewable energy sources, which are intermittent and thus require efficient energy storage technologies.[1] High performance and low cost batteries are also in high demand due to the rising popularity of plug-in electric vehicles. Lithium ion batteries (LIBs) are currently the most popularity secondary energy storage device, but the rising cost of raw lithium has driven a search for alternative battery technologies.[2] Sodium ion batteries (SIBs) are an attractive replacement because their operating mechanism is similar to LIBs and thus the knowledge from extensive LIB research can be applied to SIBs. Most importantly, sodium is much cheaper and more abundant compared to lithium. However, sodium has a large ionic radius (1.03 Å) and slightly lower redox potential (−2.71 V vs standard hydrogen electrode, SHE)) compared to lithium (0.79 Å and −3.0 V vs SHE).[3] This causes SIBs to have slower diffusion kinetics and lower energy densities than their lithium counterparts, so countermeasures must be developed to mitigate these drawbacks.[1,2]

Recently, numerous works had been reported to develop stable electrode materials for SIBs including the design of nanostructured cathodes and new material phases.[2,3] The former enables faster sodium ion diffusion while the latter opens a new channel to construct SIBs with advanced materials. Nanostructured pyrophosphates, Na₉V₃(PO₄)₄, Na₉V₃(PO₄)₂O₂F, and polymer-based cathodes have exhibited excellent sodium ion storage performances.[3–7] In our previous work, we synthesized NaMnBO₃ as a new polyanionic cathode for stable cycling performances, they possess low capacities and poor stable cyclic performances, they possess low capacities and poor rate performances, making them inappropriate for commercial applications. On the other hand, layered transition metal oxides (TMOs) have garnered much attentions due to their higher capacity, ease of synthesis, and similar chemistry with established LIB cathodes. TMO cathode materials can be divided into two main categories, O3 and P2, depending on the number of packing layers within each unit cell and whether the ion is located in an octahedral (O) or prismatic (P) environment.[8] P2-type structures are stable in sodium-deficient compounds (when x < 0.7 in NaₙMO₃) since the absence of ions creates vacancies, increasing repulsion between oxygens in adjacent slabs and leading to a larger interlayer spacing, which allows for faster sodium ion diffusion.[13] P2-type cathodes also tend to have a higher discharge capacity and reduced slab gliding compared to O3-type cathodes.[3] Materials such as P2-NaMO₂ (M = Fe, Cr,
Atomic layer deposition (ALD) can be used to create a homogeneous defect-free ultrathin coating of metal oxides on an electrode and this strategy has been used to improve the performance of LIBs. Various metal oxide coatings including Al₂O₃, TiO₂, ZrO₂, and SnO₂ deposited by ALD on LIB electrodes have resulted in improved cycling stability. Specifically, an ultrathin ALD coating of Al₂O₃ can increase the cathode’s cyclability while ZrO₂ improves rate capability due to its higher conductivity. Lately, solid-state electrolyte layers enabled via ALD on LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathodes have demonstrated improvements in the high-voltage performance of LIBs. Other examples of ALD metal oxide coatings include SnO₂ on graphene and TiO on Li[NiₓTi₁−ₓ]O₂ for improved LIB anodes. The application of ALD coating to SIB electrodes has only recently garnered attention. The first example was reported by Han et al. in 2013 on a tin SIB anode. Their work exhibited the ability of ALD-deposited Al₂O₃ to significantly stabilize the tin nanoparticles during the large volume changes occurring throughout charge and discharge cycling. Later, Kaliyappan et al. coated Al₂O₃ on Na₂/3[MnₓNi₁−ₓ]O₂ to stabilize the SIB cathode and continued their investigation by coating ZrO₂ and TiO₂ as well.

Similar to ALD, molecular layer deposition (MLD) can deposit ultrathin polymer or organometallic coatings while retaining precise control on coating thickness and conformality. MLD has been used to increase the mechanical stability and combat the huge volume expansion of electrodes during the charge–discharge (C–D) cycles. One class of polymer–metal coatings known as metalcones consist of metal oxides and short organic molecules and have gained attention for battery applications. An alucone coating, made by alternating reactions between trimethylaluminum and short organic diols such as ethylene glycol or glycerol, has been shown to be effective at preventing the shuttle effect caused by the dissolution of polysulfides in Li–S batteries. Other groups have studied the effect of alucone on silicon electrodes for LIBs and have similarly verified alucone’s ability to protect electrodes and improve the cycle life of Li–S batteries. Alucone has a distinct advantage over alumina, namely that it is less dense, allowing better ion diffusion, and is also more flexible and soft, thus improving its stabilizing effect on high-volume-change materials. It is also more electrically conductive than alumina due to its carbon linkers.

Although MLD has already been utilized to enhance the stability of electrode materials in various energy storage applications, coating of metalcones on SIB cathodes by MLD has not yet been explored. Herein, we demonstrate a method to enhance the electrochemical stability of SIBs at high cut-off voltage (>4.45 V) by MLD coating of alucone directly on P₂ type cathodes for the first time. In previous work, we have also optimized the composition of NaₓMn₁₋ₓMgO₂ and found that values of x = 0.66 and y = 0.10 maximize cell performance, but this optimization is not included in the scope of this work. It has been demonstrated that Mg doping into the P₂-type material NaₓMnO₂ smooths the electrochemical profiles, enhances ion conduction, and decreases capacity fading. Clément et al. studied NaₓMn₁₋ₓMgO₂ variants but cycled the cells up to only 4.0 V. It is essential to study the high voltage performance of these ecofriendly NaₓMn₁₋ₓMgO₂ materials beyond 4.4 V to adopt them for commercial applications. In our work, the alucone-coated NMM (Alu-NMM) exhibits prolonged cycle retention compared to pristine NMM and Al₂O₃-coated NMM (Al-NMM) electrodes.
2. Results and Discussion

The Rietveld refinement of the pristine and surface-modified NMM materials are illustrated in Figure 1a and their corresponding structural parameters are presented in Table 1. The refinement of pristine NMM in Figure 1a exhibits the peaks of a typical P2 type layered hexagonal structure with a P63/mmc space group, which corresponds with other reports.[9,16,20,44,57] The diffraction shows high intensity peaks with no impurity phases, confirming the formation of highly crystalline and pure NMM from the modified Pechini synthesis. Furthermore, peaks associated with the coating materials (alucone/Al₂O₃) were not detected in the X-ray diffraction (XRD) patterns in Figure 1a because of the ultrathin and amorphous nature of the coating layers. The cell parameters such as \( a \), \( c \), and cell volumes of the pristine, Al₂O₃, and alucone coated NMM materials are also calculated from the XRD patterns and shown in Table 1. The lattice parameters of all samples are almost identical, indicating that the surface modification by ALD or MLD does not affect the structure of the parent NMM materials. In addition, the large intensity ratio between \( I_{002}/I_{104}\) peaks (≈1.95) for all samples is an ideal indication of low cation mixing between alkali and other metal ions in the NMM sample.[20,58] Fractional cation mixing and high crystallinity of cathode materials are crucial parameters to deliver good structural stability during the electrochemical cycling process.

The scanning electron microscope (SEM) image of NMM is presented in Figure 1b, demonstrating the formation of sub-micrometer-sized particles with uniform size distribution. It can be observed from Figure 1b that the average size of the NMM particles was about 650 nm with smooth edges. It is well known that the surface morphology plays a vital role on electronic and ionic migration.[16–18,44] As nanostructured materials with uniform size distribution significantly reduce the pathway for Na-ion migration, good electrochemical performance is expected from the NMM powders.[15,16] However, after 50 cycles of ALD and MLD coatings, the surface of the NMM particles became rough, as shown in Figure 1c,d, respectively. The subatomic level mixing of Na, Mn, and Mg in NMM powder and the existence of the coating materials on the surface of NMM were analyzed by energy-dispersive X-ray spectroscopy (EDX) and the mappings are presented in Figures S1 and S3 of the Materials.

![Image](https://example.com/image.png)

**Table 1.** Lattice parameter and fitting factor of NMM, Al-NMM, and Alu-NMM particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( a [\text{Å}] )</th>
<th>( c [\text{Å}] )</th>
<th>Cell volume [Å³]</th>
<th>Fitting factor ( R_p ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NNM</td>
<td>2.725</td>
<td>11.324</td>
<td>77.427</td>
<td>5.25</td>
</tr>
<tr>
<td>Al-NMM</td>
<td>2.731</td>
<td>11.337</td>
<td>77.436</td>
<td>5.35</td>
</tr>
<tr>
<td>Alu-NMM</td>
<td>2.721</td>
<td>11.321</td>
<td>77.433</td>
<td>4.29</td>
</tr>
</tbody>
</table>
Supporting Information. Figure S1 of the Supporting Information illustrates the similar intensities of Mn, Mg, and Na-ions in NNM powders, indicating the molecular-level mixing of the starting materials. Figures S2 and S3 of the Supporting Information also confirmed the presence of Al ions on the surface of the NMM powder. In addition, the C mapping in Figure S3 of the Supporting Information further reveal the successful deposition of polymer–metal hybrid coatings (alucone) on the NMM surface.

In order to observe the thickness of the coating layers on the surface of the NMM powder, high-resolution transmission electron microscopy (HR-TEM) images are displayed in Figure 1e,f. Since thinner coatings increase the difficulty of accurate measurement using TEM, these samples were coated with 50 ALD or MLD cycles for calculating the thickness deposited per cycle, which corresponds to ~1.8 and ~1.6 Å per cycle for Al₂O₃ and alucone, respectively, which is in accordance with other reports.\[16,18,44,47,49,50\] From the TEM images, it can be inferred that the electrodes fabricated in half-cells for electrochemical testing coated with 5 cycles of ALD or MLD have a thickness of ~0.9 nm for Al₂O₃ and ~0.8 nm for alucone. The TEM images on the 50-cycle samples also confirm the ultrathin uniform coating thickness expected from ALD and MLD. This uniformity is vital for preventing reactions between the active material and the electrolyte, as uneven or hole-riddled coatings would make the electrode susceptible to electrolyte attack.\[40,59\]

X-ray photoelectron spectroscopy (XPS) traces in Figure S4 of the Supporting Information were collected to further verify the presence of coatings on the NMM powders. Figure S4a of the Supporting Information depicts a peak at ~74.4 eV corresponding to Al 2p from the Al₂O₃ and alucone coatings, respectively. Generally, the Al–O bonds are typically identified at 74.4 eV and the slight shift toward high band energy noted in the peak position for Alu-NMM sample indicates the presence of higher oxidized form such as Al–O–C.\[60\] The core-level C 1s of Alu-NMM sample in Figure S4b of the Supporting Information clearly exhibits the presence of functional groups over the NMM surface. In the core-level C 1s spectra, the sp² C–C binding energy is centered around 284.8 eV, and the existence of peaks at 286.3 and 288.4 eV correspond to carbonyl (C=O) and carboxyl (O=C=O–OH) groups, respectively.\[61\] Compared to the inorganic coating layers (Al₂O₃ in this case), the presence of C–C and C–O bonds in alucone would provide necessary toughness and flexibility to the cathode surface, which assists significantly in improving cycling stability, columbic efficiency (CE) and rate performance of parent NMM materials.\[62,63\]

This unique nature of the alucone film not only offers ample room for the volume change observed above 4.3 V cycling due to the P2–O2 phase changes but also effectively protects the cathode surface from collapse by inherent stress and strain during the high current rate cycling and from the metal dissolution by acidic electrolyte attack.\[16,44\]

In order to understand the impact of Mg doping in the Na₀.₅₋ₓMnO₂ (NM) structure, the differential capacity versus voltage plot of the second cycle recorded at 1 C rate in 1 M NaClO₄ dissolved in EC:DEC (1:1 v:v) electrolyte is given in Figure 2a. It has been reported that layered NaₓMnO₂ (x = 0.5 to 0.66) exhibits complex C–D curves and severe capacity decay due to charge ordering and structural transitions caused by the Jahn–Teller distortion of Mn⁺⁺ ions.\[55,64,65\] However, the incorporation of Mg into Mn lattice results in smoother C–D curves as shown in Figure 2a, along with high reversible capacity and enhanced Na-ion conduction.\[55,65\] It is apparent from Figure 2a that the redox peak that corresponds to the Na-ion/vacancy ordering transitions at 3.5/3.7 V disappears, which confirms that the Mg doping has altered the electrochemical profile of the parent materials.\[55,65\] The Na-ion/vacancy ordering phenomenon has detrimental effect toward the cycle retention of Mn-based P2 layered cathode materials as the Na ion is large and results in strong Na⁺–Na⁺ in-plane repulsions during C–D studies at high voltages.\[18\] This phase transition and Na-ion/vacancy ordering upon Na removal from the NaₓMnO₂ structure significantly reduces the Na-ion diffusion coefficient and transport and thereby decreases the cycling stability.\[65,66\] Most importantly, the Jahn–Teller distortion of Mn⁺⁺ ions and the Na-ion/vacancy ordering modify the Na-ion conduction by affecting the activation energy barrier of adjacent Na-ion sites.\[67\] It is worth mentioning here that the absence of extended voltage plateau at 3.5 V in Figure 2a during the charge process clearly demonstrates that the phase transformation between P2 to OP4 is successfully eliminated after Mg doping as reported elsewhere.\[18,47,59\] Moreover, a clear peak shift is observed in Figure 2a at the end of the discharge corresponding well with the previous reports, which mainly results from the difference in reaction mechanisms after the Mg doping.\[59\]

The C–D profile of NM and NMM conducted between 2 and 4.5 V at 1 C rate is presented in Figure 2b, in which the NMM electrode displays a smoother C–D curve than the NM electrode. It is noted from Figure 2b that the initial discharge capacity (IDC) of NMM (162 mA h g⁻¹) is lower than the parent NM materials (186 mA h g⁻¹). The decrease in IDC
This demonstrates that Mg doping suppresses the capacity decay and displays a retention of 46% after 100 cycles. On the other hand, the NM sample has severe capacity decay at the higher voltage region.\[55,65,66,68\] Nevertheless, the lower cyclic performance obtained at 1 C is the best reported value among P2-Na\(_0.66\)Mn\(_2\)O\(_4\)-Na\(_2\)O materials and other P2 layered materials.\[15,44,55,56,65,66,68\] The overall impact of different coatings has been inspected through the following main aspects: 1) difference in cell polarization, 2), initial CE, and 3) cycle life of the electrodes at different currents. Initially, the influence of surface modification is tested by electrochemical impedance spectroscopy (EIS) and its corresponding Nyquist plots are presented in Figure 3a. The Nyquist plots of the cells are similar in shape and are composed of two partially overlapped semicircles and an inclined line. The first semicircle at the high frequency region is associated with the Na-ion diffusion through the SEI layer and the other semicircle at the middle frequency region is correlated to the charge transfer resistance (R\(_{ct}\)), which measures the electrochemical reaction kinetics. The sloping line at the low frequency region represents the diffusion of Na-ions in the bulk electrode. According to the equivalent circuit inserted in Figure 3a, the impedance data are fitted, and the parameters are presented in Table 2. Based on the fitting data, the clear difference in both R\(_{ct}\) and R\(_s\) could be observed from the pristine and surface modified NMM electrodes. Especially, the R\(_s\) shows predominant difference in resistance values. The R\(_{ct}\) values of the NMM, Al\(_2\)O\(_3\)-NMM, and Alu-NMM electrodes are calculated to be about 391.38, 185.51, and 154.51 Ω, respectively. It is clear that the cell containing the Alu-NMM electrode has lower R\(_{ct}\) compared to NNM and Al\(_2\)O\(_3\)-NMM electrodes. Lowering the R\(_{ct}\) could effectively enhance the Na-ion diffusion toward the electrode and thus improve electrochemical performance.\[61\] In addition, the higher conductivity of alucone over Al\(_2\)O\(_3\) makes alucone an ideal coating material to construct high-performance SIB with a longer lifespan.\[34,69,70\]

The Na-ion diffusion coefficient (D\(_{Na}\)) of all electrodes were calculated based on the following equation\[71,72\]

\[
D = 1/2 [ R^2 T^2 / S \sigma F^2 C^2 \sigma^2 ] 
\]

where C is the electrolyte molar concentration (1 m), n is the number of electrons involved (n = 1), F is the Faraday constant (96 485 C mol\(^{-1}\)), S is the active surface area (1 cm\(^2\)), R is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), T is the absolute temperature (298.15 K), and \(\sigma\) represents the Warburg factor that is calculated from the slope of the Warburg line in the EIS spectra. The D\(_{Na}\) of 6.32 \(\times\) 10\(^{-13}\), 3.08 \(\times\) 10\(^{-13}\), and 2.67 \(\times\) 10\(^{-13}\) cm\(^2\) s\(^{-1}\) were calculated from Equation (1) for NMM, Al-NMM, and Alu-NMM electrodes, respectively. The Na-ion diffusion coefficient of Alu-NMM electrode is higher than the pristine and Al\(_2\)O\(_3\) coated NMM electrodes, resulting in improvements in the electrochemical performance.

The half-cell performance of pristine and surface modified NMM were tested against Na metal anode in 1 m NaClO\(_4\) electrolyte and the corresponding C–D plots are presented in Figure 3b. In spite of displaying identical C–D curves, the pristine and Al\(_2\)O\(_3\) coated NMM electrodes show extreme potential

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**Table 2.** Electrochemical impedance and C–D data of NMM, Al-NMM, and Alu-NMM electrode recorded at 1 C rate within 2–4.5 V.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>R(_{ct}) [Ω]</th>
<th>Initial discharge capacity [mA h g(^{-1})] at 1 C</th>
<th>Initial CE [%]</th>
<th>Discharge capacity after 100 cycles [mA h g(^{-1})] at 1 C</th>
<th>Capacity retention after 100 cycles [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NNM</td>
<td>391.38</td>
<td>162.9</td>
<td>85.2</td>
<td>106</td>
<td>65</td>
</tr>
<tr>
<td>Al-NMM</td>
<td>189.51</td>
<td>163.2</td>
<td>90.1</td>
<td>117</td>
<td>71</td>
</tr>
<tr>
<td>Alu-NMM</td>
<td>154.32</td>
<td>163.1</td>
<td>95.8</td>
<td>140</td>
<td>86</td>
</tr>
</tbody>
</table>

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polarization as presented in Figure 3b. On the other hand, the lower polarization of the cell containing Alu-NMM electrode is ascribed to the better conductive properties of the alucone coating layer, which agrees well with the results obtained from the EIS studies. The NMM, Al-NMM, and Alu-NMM electrodes delivered a similar discharge capacity of ≈163 mA h g⁻¹ at 1 C rate as presented in Table 2. However, the electrodes exhibit different CE at the first cycle. As shown in Table 2, the CE of NMM, Al-NMM, and Alu-NMM are calculated from C–D curves as 85.2%, 90.1%, and 95.8%, respectively. This clearly reveals that the irreversible insertion/extraction of Na⁺ to/from the NMM structure and the formation of the electrode–electrolyte interphase layer during the initial C–D cycle are successfully alleviated by the ultrathin encapsulation of coating materials.

Although all electrodes deliver a similar initial discharge capacity, obvious differences in capacity retention could be observed from Figure 3c. It is clear from Figure 3c that the pristine and Al₂O₃ coated NMM electrode show severe capacity fading during the initial cycles. Notably, about 15% of initial discharge capacity is lost after 10 C–D cycles. There are numerous reasons responsible for the capacity decay during the initial cycles including i) formation of electrode–electrolyte interfacial (EEI) layer by electrolyte decomposition, ii) active material dissolution into the electrolyte, iii) severe internal stress due to the larger Na-ion insertion/extraction, and iv) incorporation of solvated ions into the metal oxide matrix.⁴⁵,4⁶ After 100 cycles, the pristine NMM electrode exhibits a low capacity retention of 65% whereas the Al₂O₃-NMM electrode displays a 71% capacity retention. In contrast, the Alu-NMM retains 86% of its capacity after 100 cycles. The higher mechanical stability and conductive nature of the alucone coating layer compared to Al₂O₃ enhances the overall performance of the cell at high currents.⁴⁷,4⁹ In addition, the alucone coating is soft and more flexible than alumina layer, which provides a flexible buffer against the volume changes during the high current cycling process.⁴⁷,4⁹ It is worth mentioning here that the capacity and the cyclic stability obtained from Alu-NMM electrode between 2 and 4.5 V is one of the first ever reported values among P₂-type materials. Figure S5 of the Supporting Information reveals that the Alu-NMM electrode delivery ≈113 mA h g⁻¹ while pristine NMM retains only 66.5 mA h g⁻¹. In addition, when the current density is reverted to 1 C, almost 95% of the original capacity is retained, as illustrated in Figure 3d. Although the Al-NMM electrode shows improved rate performance compared to the pristine electrode, the Alu-NMM electrode delivered the best performance among all electrodes. Since long term cyclability of the SIBs at high currents is a crucial factor for energy demanding applications, the stability of the Alu-NMM electrode was evaluated at 10 C rate and the results are presented in Figure S7 of the Supporting Information. As seen from Figure S7 of the Supporting Information, the discharge capacity difference between the 1st and 300th cycles is small and corresponds to 84% retention. Moreover, the cell displays an average CE of ≈100%. The stability obtained at 10 C rate for the Alu-NMM electrode is among the best reported for a P₂-layered intercalation electrode.¹⁶,1⁸,4⁴,5⁵,5⁶,6⁵,6⁶,6⁸,7¹,7² The excellent cycling behavior of the Alu-NMM is attributed to the mechanically robust nature of the alucone coating and low cell resistance as confirmed from the EIS data in Figure 3a.

The improvement that both coatings offer can be explained by their ability to stabilize the particles during the expansion/contraction that occurs during sodium insertion/deinsertion and to prevent unwanted interactions with the electrolyte, including dissolution of the active material and side reactions. However, the difference in performance between Al-NMM and Alu-NMM as shown in Figure 3 is likely due to the following reasons. First, an alucone coating is about half as dense as an Al₂O₃, which also explains faster Na-ion diffusion which is important for rate performance.⁴⁵,4⁶ Additionally, the alucone coating has a higher electronic conductivity compared to Al₂O₃, which also explains the rate performance in Figure 3d. Finally, since alucone is softer and more flexible than Al₂O₃, it is able to better accommodate the volume changes associated with sodiation/desodiation of the electrode as seen in the cycling performance in Figure 3c. It is clear from the above results that the alucone coating is robust against the electrolyte attack, flexible enough to accommodate deep Na-ion insertion/extraction and has high ionic conductivity for long-term Na-ion charge transfer processes.

To further investigate the impact of coatings, the EIS spectra of the half cells containing pristine and coated electrodes were recorded before and after 50 and 100 cycles and
the corresponding Nyquist plots and $R_{ct}$ versus cycle number are presented in Figure 4. As shown in Figure 4a, the EIS spectra of NMM cell is drastically changed during the C–D cycles whereas the surface-modified electrodes display small $R_{ct}$ changes values after 50 and 100 cycles. The $R_{ct}$ values of the pristine NMM electrode is dramatically increased from 391.98 to 864.8 Ω after 100 cycles, which is much higher than the value of 662.44 and 198.77 Ω obtained from Al-NMM and Alu-NMM electrodes, respectively, after 100 cycles. Although all the cells exhibit an increased value of $R_{ct}$ upon cycling, the trend in increasing $R_{ct}$ for the Alu-NMM electrode is by far the lowest among all electrodes tested. The Alu-NMM electrode exhibits the $R_{ct}$ of 145.32, 175.37, and 198.77 Ω during the initial, 50th and 100th cycles, respectively. It is evident from EIS studies that porous and less dense alucone protecting layer with carbon linkers in its structure has effectively enhanced the conductive nature of the NNM electrode, decreasing the cell resistance and consequently improving its stability.[37,38]

The changes in local structure around the Mn after 100 cycles at 1 C rate were examined using X-ray absorption fine structure (XAFS) studies and the corresponding Mn K-edge spectra of the NNM electrode samples along with standard NMM powders prior to cycling are presented in Figure 5. The XAFS spectrum exhibits an important pre-edge and main absorption spectra, which is labeled as A and B, respectively, in Figure 5a. The weak pre-edge (A) represents the degree of distortion in the octahedral whereas the main adsorption (B) indicates the dipole electrode movement from 1s core to the unoccupied 4p bound state.[12] The existence of this weak pre-edge (A) is associated with 3d–4p orbital mixing resulting from the noncentrosymmetric environment of the slightly distorted octahedral 3a site in the rhombohedral $R\bar{3}m$ space group.[14] Consequently, the degree of distortion in the octahedra and the oxidation state of the core atoms information can be attained from these pre-edge peaks.[12,14] Figure 5a illustrates the Mn K-edge spectra of pristine NNM and surface modified NNM electrode after 100 cycles at 1 C rate. As seen from Figure 5, the main Mn K-edge spectra of pristine NNM electrode after cycles exhibit clear positional shifts toward higher energy level compared to standard NMM and surface modified electrodes. These positional shifts of the NNM electrode demonstrates that the local environment of the Mn atom is rearranged after the cycling process.[14] By contrast, the surface modified NNM through ALD and MLD do not display any obvious shifts as shows in Figure 5, indicating that Mn in Al-NMM and Alu-NMM is stable even after cycles and that the Mn$^{3+/4+}$ redox couple is completely reversible.

The pre-edge peak (A) of various electrodes are presented in Figure 5b, in which the pre-edge intensity of NNM and Al-NMM have increased whereas the intensity height of Alu-NMM pre-edge peak does not change much compared to the standard NMM powders. The increase in pre-edge peak intensity is attributed to local structural distortion of the Mn-O6 octahedra due to the higher amount of Jahn–Teller active Mn$^{3+}$ ions.[14] The Mn K-edge clearly reveals the importance of surface modification by alucone to retain the structural integrity of NNM electrode by maintaining the valence state of Mn-ions during the C–D process, which enhances the cycling performance even at a high voltage cut-off. These results clearly demonstrate that MLD can be utilized as a promising technique to construct safe and durable high-performance next generation cathode materials for SIBs.
3. Conclusion

We successfully demonstrate that the alucone coating of electrodes by MLD is a novel approach to construct safe and stable high voltage sodium ion batteries. Ultrathin alucone coated P2-type Na$_{0.66}$Mn$_{0.9}$Mg$_{0.1}$O$_2$ cathode displays stable cycle life at a high operating voltage (2–4.5 V) with 86% retention after 100 cycles, exhibiting substantially improved cycle performance compared to pristine (65%) and Al$_2$O$_3$-coated electrodes (71%). Both the alucone and Al$_2$O$_3$ coatings improve the capacity and rate performance in a half-cell configuration, but the alucone coating outperforms the Al$_2$O$_3$ coating. This can be attributed to alucone possessing a higher ionic conductivity, electronic conductivity, and flexibility compared to Al$_2$O$_3$. The impedance and XAS studies before and after extended cycling reveals that the alucone layer can maintain the local ionic structure and minimize the overall cell polarization, thus enabling superior electrochemical performance. Therefore, the introduction of organometallic coatings through MLD offers a new approach to develop conformal and ultrathin conductive coatings for next generation sodium ion batteries.

4. Experimental Section

Preparation of NMM: The synthesis of highly crystalline NMM particles was carried out using a modified Pechini method in which metal acetates, citric acid, and polyethylene glycol (PEG) were used as reagents. In typical synthesis, stochiometric amounts of sodium, manganese, and magnesium acetates were dissolved in 50 mL of distilled water in one beaker. In another beaker, 2.5 g of PEG and 5 g of citric acid were completely dissolved and mixed with the metal solution. Concentrated nitric acid was slowly added into the above solution until a clear solution was obtained. The solution mixture was stirred at 110 °C for 24 h to obtain a viscous gel precursor. The precursor was first decomposed at 400 °C for 4 h, then grounded to a fine powder, and finally calcined at 850 °C for 12 h in air. For performance comparisons, Na$_{0.66}$MnO$_2$ (NM) was also prepared using the same method described above without Mg.

ALD and MLD Coatings on NMM Electrodes: The electrodes for ALD and MLD coating were prepared in accordance with the prior work.[2,17,18]
The coating of ultrathin Al2O3 on NMM electrodes was done using an ALD reactor (Thermal GEMstar GTX, Arradance, LLC, USA) at 115 °C in which trimethylalumimum (TMA) and H2O were used as the precursor and oxidizer, respectively. The purging time for water and TMA was set to 21 ms. On the other hand, the MLD of alucone on NMM electrode was also performed at 100 °C by alternatively introducing TMA and ethylene glycol (EG). EG was set to 21 ms. On the other hand, the MLD of alucone on NMM powder for physical characterization. The Al2O3 and alucone coated NMM electrodes are denoted as Al-NMM and Alu-NMM, respectively. Scheme 1 demonstrates that one MLD cycle consists of two half reactions in which TMA and EG react to form an ultrathin inorganic–organic alucone layer (Al connected by –O–C2H4–O– link).

Physical and Electrochemical Characterizations: Power diffraction patterns of the prepared materials were examined using XRD (Miniflex 600, Rigaku, Japan) with Cu Krz radiation (λ = 1.5406 nm). The particle morphology of pristine and ALD and MLD-coated NNM powders were imaged using a field emission SEM (LEO Zeiss 1530, Switzerland) coupled with EDX. The coating thickness of the Al2O3 and alucone layer on NMM surface was measured by HR-TEM (JEOL 2010). Measurements were made on a 06ID superconducting wiggler sourced hard X-ray microanalysis beamline at the Canadian Light Source, Canada with a preprior—double crystal monochromator—postmirror configuration coupled with EDX. The coating thickness of the Al2O3 and alucone was measured by HR-TEM (JEOL 2010 FEG).

Keywords
Al2O3, alucone, atomic layer deposition, molecular layer deposition, sodium ion batteries

Keywords


Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.