



MgF₂ surface loading stabilizes the interfacial chemical environment of O3-Type NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ cathodes for sodium-ion batteries

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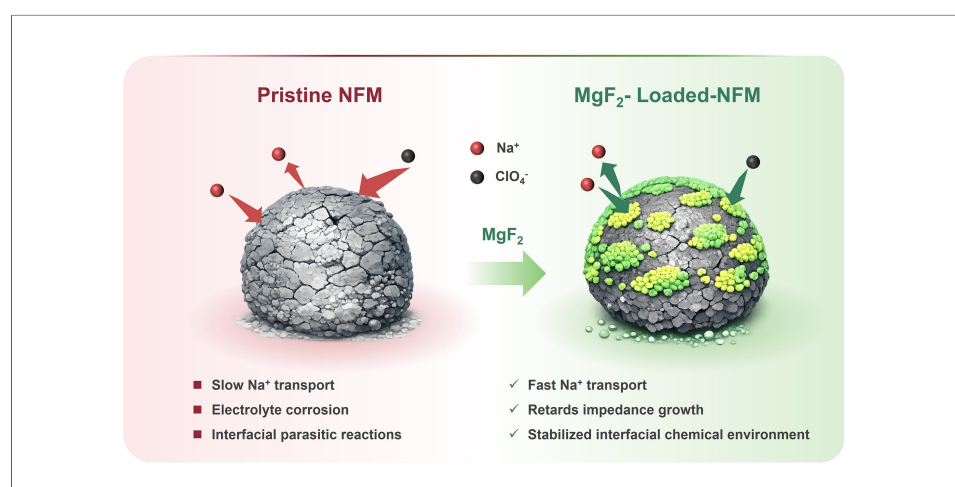
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Abstract

O3-Na_{1/3}Fe_{1/3}Mn_{1/3}O₂ (NFM) has drawn considerable attention as a cathode material for sodium-ion batteries, but its practical application is restricted by interfacial parasitic reactions, continuous impedance growth, and phase-transition-associated structural instability. Here, a MgF₂ surface layer is introduced onto NFM through a post-treatment surface-loading strategy to regulate the interfacial chemical environment of the cathode. The MgF₂ loading preserves the O3-type bulk framework and the dominant transition-metal valence states of NFM, while generating a non-uniform Mg/F-enriched surface layer. Among the investigated samples, NFM@1%MgF₂ exhibits the best overall electrochemical performance, delivering 103.01 mA h g⁻¹ after 100 cycles at 1C with a capacity retention of 85.65%, achieving 82.09 mA h g⁻¹ at 10C, and retaining 75.17% of its capacity after 300 cycles at 3C. Galvanostatic intermittent titration technique, electrochemical impedance spectroscopy, and post-cycling X-ray photoelectron spectroscopy collectively show that

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MgF₂ loading enhances apparent Na⁺ transport kinetics, suppresses interfacial side reactions, and retards impedance growth during cycling. Operando X-ray diffraction further reveals that MgF₂ does not alter the intrinsic O3-P3-O3 transition sequence of NFM but markedly mitigates the associated structural response. In addition, an NFM@1%MgF₂||hard carbon full cell exhibits 85.43% capacity retention after 100 cycles at 1C. These results establish MgF₂ surface loading as an effective route for interfacial stabilization in O3-type NFM cathodes and suggest a generalizable strategy for regulating interfacial chemistry in sodium-ion battery cathode materials.

INTRODUCTION

With the rapid development of large-scale energy storage technologies, sodium-ion batteries have attracted extensive attention as promising alternatives to lithium-ion batteries owing to their abundant resource availability, low cost, and partial compatibility with existing lithium-ion battery manufacturing infrastructure^[1-4]. Among the cathode candidates developed for sodium-ion batteries, layered transition-metal oxides remain a major research focus because of their relatively high operating voltages, high capacities, and mature synthesis routes^[5-11]. However, the larger ionic radius of Na⁺ and the distinctive interfacial chemistry of sodium-ion systems make these materials more susceptible to complex structural evolution, interfacial instability, and accumulated side reactions during Na⁺ extraction/insertion, thereby limiting their electrochemical performance^[12-14]. O3-type NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ (NFM) has been extensively explored owing to its simple composition, low cost, and comparatively high capacity. Previous studies have shown that NFM can deliver a reversible capacity of approximately 130 mA h g⁻¹ within 2.0-4.0 V and typically undergoes a relatively direct O3-P3-O3 structural evolution, making it a representative O3-type layered oxide cathode^[15-17]. Nevertheless, NFM still suffers from several coupled issues. On the one hand, it is sensitive to air and moisture, which can induce Na⁺ loss and the formation of surface residuals such as Na₂CO₃^[18,19]. On the other hand, the degradation of NFM is governed not by a single failure mode but by the interplay among bulk phase evolution, near-surface structural damage, and interfacial parasitic reactions. Repeated phase-transition-associated stress can progressively disrupt particle integrity, expose fresh reactive surfaces, and continuously alter the chemistry of the cathode electrolyte interphase (CEI), thereby accelerating impedance growth and capacity decay^[20-22].

Accordingly, various modification strategies have been developed, including elemental doping, surface coating, interfacial reconstruction, and electrolyte regulation^[23-27]. For the NFM system, NaTi₂(PO₄)₃ coatings^[28], Na₂MoO₄ reactive wetting layers^[29], composite surface modifications, and electrode-level regulation have all been shown to reduce polarization, retard interfacial degradation, and improve cycling stability and rate capability to varying extents^[30-32]. These studies indicate that improving the electrochemical performance of NFM cannot rely solely on bulk structural regulation; simultaneous stabilization of the particle surface and the cathode/electrolyte interface is also required. In recent years, fluoride-related strategies have attracted increasing attention. Reported studies have shown that fluorinated interfacial engineering can promote the formation of a robust NaF-rich CEI, suppress continuous electrolyte decomposition, reduce the accumulation of surface by-products, and alleviate structural perturbations during cycling, thereby enhancing both structural integrity and interfacial stability of layered oxide cathodes^[33-37]. Among reported fluoride-related strategies, AlF₃ and LaF₃ coatings mainly serve as protective fluoride layers to mitigate interfacial side reactions and electrolyte corrosion, while eutectic fluoride salts provide multicomponent fluorinated surface modification. In contrast, direct fluorination or F-doping usually involves lattice-level regulation through partial O/F substitution, which may influence Na⁺ diffusion

channels, phase evolution, and migration barriers^[35,38–41]. Compared with these strategies, the role of MgF_2 , a chemically stable metal fluoride, in O3-type NFM remains insufficiently understood. Previous studies have demonstrated that MgF_2 coatings can stabilize the cathode/electrolyte interface^[42,43], mitigate side reactions^[44,45], and suppress impedance growth^[42,45]. However, for NFM, which simultaneously suffers from air sensitivity, interfacial instability, and phase-transition-induced stress, whether MgF_2 surface loading can regulate the interfacial environment and further mitigate structural perturbation and impedance growth still requires systematic clarification.

Herein, a non-uniform MgF_2 layer was introduced onto the surface of NFM through a post-treatment process. By combining structural characterization, surface chemical analysis, electrochemical evaluation, kinetic analysis, operando X-ray diffraction (XRD), and full-cell validation, the effects of MgF_2 on the interfacial chemistry and structural evolution of NFM were systematically investigated. The results reveal that an appropriate MgF_2 loading amount preserves the O3-type bulk framework while stabilizing the interfacial chemical environment, retarding impedance growth, and mitigating the phase-transition-associated structural response. This work therefore identifies MgF_2 surface loading as a viable strategy for interfacial stabilization in O3-type NFM cathodes and provides a useful design basis for surface-regulated layered oxide cathodes for sodium-ion batteries.

EXPERIMENTAL

Materials synthesis

NFM was prepared through a citric-acid-assisted sol-gel route followed by high-temperature calcination. Stoichiometric amounts of CH_3COONa , $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were first weighed and dissolved in deionized water to form a mixed metal-salt solution. All reagents were purchased from Macklin and used without further purification. The obtained solution was magnetically stirred (S82-8, Shanghai Zhiwei Electric Appliance Co., Ltd., China) at 400–500 rpm for approximately 30 min, during which the pH was approximately 3. Separately, anhydrous citric acid was dissolved in deionized water at a molar amount equal to 1.5 times the total amount of metal ions, and the solution was stirred at 400–500 rpm for approximately 30 min. The pH of the citric acid solution was approximately 1. Subsequently, the citric acid solution was slowly introduced into the metal salt solution under continuous stirring to obtain a homogeneous precursor solution. The precursor solution was then heated at 80 °C under stirring until a wet gel was formed, followed by drying in a vacuum oven (DZF-6213, Shanghai Yiheng Scientific Instrument Co., Ltd., China) to obtain a dry gel. The collected dry gel was calcined in air using a high-temperature muffle furnace (KSL-1200X-J, Hefei Kejing Materials Technology Co., Ltd., China) via a two-step heat-treatment process. Specifically, the dry gel was first heated to 500 °C at a heating rate of 3–5 °C min^{−1} and held at this temperature for 6 h. It was then further calcined at 900 °C for 12 h. For the MgF_2 -loaded samples, an appropriate amount of MgF_2 was added to the as-prepared NFM powder according to the designed mass fraction. The mixture was ball-milled at 400 rpm for 2 h using a planetary ball mill (QM-3SP04, Nanda Instrument Co., Ltd., China) in a sealed milling jar under an argon-protected atmosphere, with a ball-to-powder mass ratio of 10:1. The obtained mixture was then calcined at 500 °C for 6 h using a heating rate of 3–5 °C min^{−1}. After natural cooling to room temperature, the resulting products were immediately transferred into an argon-filled glove box for storage. The obtained samples are denoted as NFM@x MgF_2 , where x = 0.5%, 1%, 2%, 4%, and 10%.

Characterization

The elemental ratios were determined by inductively coupled plasma optical emission spectroscopy (ICPOES 730, Agilent, USA). Crystal structures were examined by powder XRD (Malvern Panalytical, Empyrean, Netherlands) using Cu K α radiation with a wavelength of 1.5405 Å. Data were collected over a 2 θ range of 10° to 90° at a voltage of 40 kV and a current of 30 mA. Operando XRD measurements were performed over a

scanning range of 10° to 70°. Morphological observations were carried out using scanning electron microscopy (SEM) (TESCAN, LYRA3 GMU, Czech Republic). Transmission electron microscopy (TEM) (Thermo Fisher Scientific, Talos F200X G2, USA) was further used to examine the microstructure and elemental distribution. Surface chemical states were analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, ESCALAB Xi+, USA), and spectral fitting was performed using Avantage software.

Electrochemical measurements

For half-cell tests, the cathode slurry was prepared by mixing the active material, carbon black, and polyvinylidene fluoride (PVDF) at a mass ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP). The slurry was uniformly cast onto aluminum foil and subsequently vacuum-dried at 120 °C for 10 h to yield the working electrodes, with an active material loading of approximately 2–3 mg cm⁻². The electrolyte consisted of 1 M NaClO₄ dissolved in an ethylene carbonate/propylene carbonate (1:1 by volume) mixture, supplemented with 5% fluoroethylene carbonate. Sodium metal was used as the negative electrode, and GF/D glass fiber (Whatman) was used as the separator. CR2032 coin cells were assembled in an argon-filled glove box. Galvanostatic charge-discharge (GCD) measurements were performed on a LAND CT2001A (China) battery testing system at 25 °C over the 2.0–4.0 V range. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed on an Autolab (PGSTAT302N, Switzerland) electrochemical workstation. The impedance spectra were collected over a frequency range of 0.01 Hz–1 MHz. Galvanostatic intermittent titration technique (GITT) measurements were conducted at 0.1C, corresponding to 13 mA g⁻¹, with a 10 min current pulse followed by a 2 h relaxation period. For the full cells, the anode slurry was prepared by mixing hard carbon, carbon black, and PVDF at a mass ratio of 9:1:1 in NMP. The slurry was uniformly cast onto aluminum foil and subsequently vacuum-dried at 90 °C for 10 h. Before full-cell assembly, the hard carbon anode was pre-sodiated by direct contact with metallic sodium. The N/P ratio, based on reversible capacity, was controlled at 1.05.

RESULTS AND DISCUSSION

Materials characterization

To determine the elemental composition, inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted on the powder samples, and the results are summarized in [Supplementary Table 1](#). No Mg signal was detected in pristine NFM. By contrast, the Mg atomic fractions in NFM@0.5%MgF₂ and NFM@1%MgF₂ were measured to be 0.0039 and 0.0078, respectively. The latter value is approximately twice the former, which is consistent with the designed loading gradient and confirms that Mg was successfully introduced in a controllable manner. In contrast, the atomic ratios of Ni, Fe, and Mn remained close to one-third, with only slight fluctuations, indicating that the introduction of MgF₂ did not cause any significant deviation in the transition-metal stoichiometry of the NFM host. Under the processing conditions used in this work, the introduced Mg mainly contributes to surface-related components rather than inducing an observable bulk compositional reconstruction. The structural characteristics were examined by XRD. [Figure 1A](#) displays the XRD patterns of pristine NFM and MgF₂-loaded samples with different loading amounts. The major diffraction peaks of all samples are located at nearly identical positions and can be indexed to a typical O3-type α-NaFeO₂ layered structure with an $R\bar{3}m$ space group^[46,47]. No obvious impurity phase is observed, indicating that MgF₂ loading does not damage the bulk crystal framework of NFM. Moreover, no clear systematic peak shift is observed among the differently loaded samples, suggesting that MgF₂ treatment does not induce significant bulk structural changes within the detection limit of XRD. Such a result is important because it implies that the effect of MgF₂ is likely exerted primarily at or near the particle surface, rather than through substantial modification of the host layered framework. To verify the structural features and thermal stability of MgF₂ itself, the XRD patterns of MgF₂ before and after calcination are compared in [Figure 1B](#). Both diffraction patterns match well with the standard card (PDF No. 72-1150),

indicating that MgF_2 retains a stable crystal structure under the calcination conditions used in this work. This point is also relevant for interpreting the subsequent modification results because the structural integrity of MgF_2 after thermal treatment supports its function as a persistent surface-associated component rather than a transient precursor. Furthermore, distinct diffraction peaks attributable to MgF_2 can be clearly identified in the highly loaded control sample $\text{NFM@10\%MgF}_2$ [Figure 1C], confirming that MgF_2 can be directly detected by XRD at sufficiently high loading levels. Therefore, the absence of obvious MgF_2 peaks in the low-loading samples should not be interpreted as evidence for the absence of MgF_2 . Instead, it is more reasonably attributed to the low content of the coating phase, its high surface dispersion, and its limited local crystallinity, all of which make its signal difficult to resolve by conventional powder XRD.

Figure 1D–G show SEM images of pristine NFM and MgF_2 -loaded samples with different loading amounts. Pristine NFM mainly consists of irregular block-like or platelet-like primary particles aggregated into micron-sized secondary particles. After MgF_2 treatment, $\text{NFM@0.5\%MgF}_2$, $\text{NFM@1\%MgF}_2$, and $\text{NFM@2\%MgF}_2$ retain similar particle morphologies and size distributions, with no obvious particle fracture, abnormal grain growth, or significant size broadening. These results indicate that MgF_2 loading does not alter the overall morphology of the NFM powder at the micrometer scale^[27]. Therefore, the subsequent electrochemical performance differences are more likely associated with surface and interfacial regulation rather than macroscopic particle-size or morphology effects.

TEM reveals differences in surface microstructure before and after modification. As shown in Figure 1H, pristine NFM exhibits a relatively clean and smooth particle edge without an obvious additional outer layer. In contrast, an additional surface layer with a contrast distinct from that of the bulk can be observed at the particle edge of the modified sample [Figure 1I], indicating the formation of a discernible surface layer after the loading treatment. The thickness of this layer varies considerably across locations, with a minimum of about 4 nm and a local maximum of approximately 32 nm, suggesting that it is not a continuous and uniform dense coating film but rather a non-uniform surface layer enriched with Mg/F species. The non-uniform Mg/F-enriched surface layer can be understood as a surface configuration that balances interfacial protection and Na^+ transport. MgF_2 is chemically stable and can protect the cathode surface from electrolyte attack and resistive surface-film growth, but it is not an intrinsically fast ionic/electronic conductor^[42,48,49]. Therefore, an excessively thick and fully dense MgF_2 layer may hinder Na^+ transfer across the cathode/electrolyte interface^[50,51]. In this work, the locally thicker MgF_2 -rich regions may help passivate highly reactive surface sites and suppress parasitic interfacial reactions, while thinner or less-covered regions may shorten Na^+ transport pathways and avoid forming a fully dense, transport-blocking shell. This protection-transport balance is consistent with the optimized electrochemical performance of $\text{NFM@1\%MgF}_2$. Energy-dispersive X-ray spectroscopy (EDS) mapping was further performed to examine the elemental distribution [Supplementary Figure 1, Figure 1J]. For pristine NFM, Na, Ni, Fe, Mn, and O are homogeneously distributed throughout the particle region, indicating the uniform composition of the NFM host. For the MgF_2 -loaded sample, Mg and F signals are clearly detected, while Na, Ni, Fe, Mn, and O remain uniformly distributed overall, and the Mg and F signals show good spatial correspondence. Together with the additional surface layer observed by TEM, these results confirm that the introduced Mg and F are closely associated with the surface-loaded layer, demonstrating the successful introduction of MgF_2 onto the surface of NFM particles in terms of elemental composition, microstructure, and spatial distribution. In addition, SEM images show that the MgF_2 powder consists of irregular particles of approximately 100–500 nm [Supplementary Figure 2]. Since MgF_2 has a high melting point, the Mg/F-enriched surface layer is not formed by melting at 500 °C but mainly through ball-milling-assisted dispersion and subsequent low-temperature interfacial anchoring^[42,48,49].

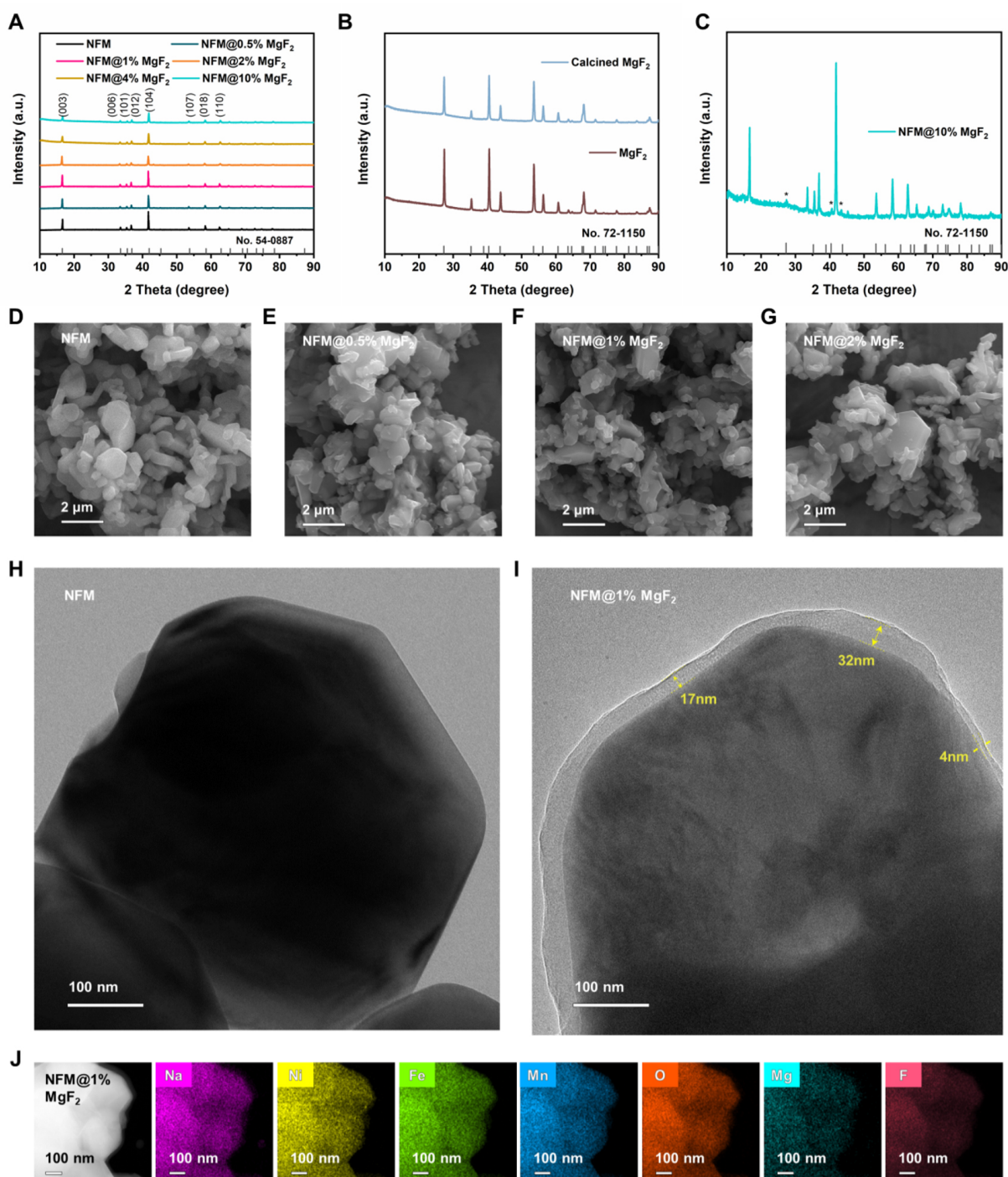


Figure 1. Morphological and structural characterization of the prepared samples. (A) Powder XRD patterns of pristine NFM and MgF₂-loaded at different loading amounts, (B) XRD patterns of MgF₂ before and after calcination, (C) XRD patterns of NFM@10%MgF₂ sample. (D-G) SEM images of pristine NFM, NFM@0.5%MgF₂, NFM@1%MgF₂, and NFM@2%MgF₂. (H and I) TEM images of pristine NFM and NFM@1%MgF₂. (J) HAADF-STEM image of NFM@1%MgF₂ and the corresponding elemental mapping results.

To further elucidate the surface chemical composition and valence states after MgF₂ loading, XPS measurements were carried out on NFM and NFM@1%MgF₂. As shown in the XPS survey spectra in [Supplementary Figure 3](#), NFM@1%MgF₂ retains the intrinsic signals of Na 1s, Ni 2p, Fe 2p, Mn 2p, and O 1s, while additional Mg 1s, F 1s, and Mg Auger peaks appear, which are absent in pristine NFM. This result confirms the successful introduction of Mg- and F-containing species onto the sample surface. Combined

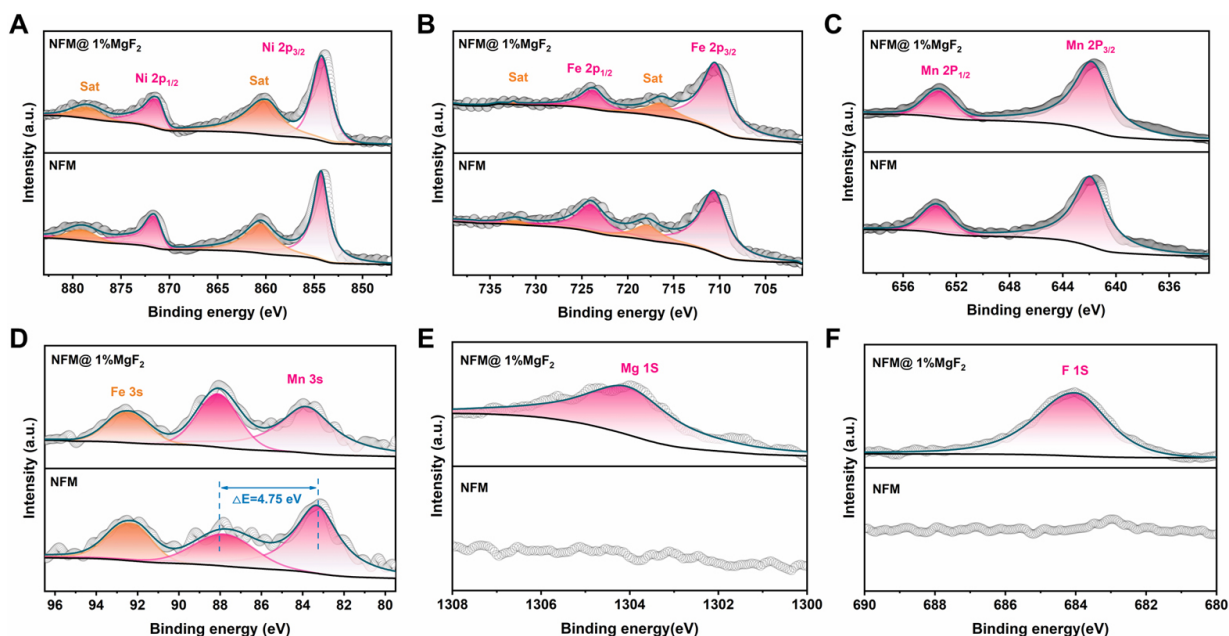


Figure 2. High-resolution XPS spectra of pristine NFM and NFM@1%MgF₂. (A) Ni 2p, (B) Fe 2p, (C) Mn 2p, (D) Mn 3s, (E) Mg 1s and (F) F 1s.

with the aforementioned XRD, ICP, and TEM results, the introduction of MgF₂ can thus be understood primarily as the formation of a Mg/F-enriched surface layer rather than a significant bulk compositional reconstruction. At the same time, the persistence of clear matrix-element signals suggests that the fluorinated layer is not an excessively thick and fully continuous dense shell. Rather, it remains a relatively thin and non-uniform surface-loaded layer. High-resolution XPS spectra [Figure 2] further reveal that MgF₂ loading does not induce an obvious change in the dominant surface valence states of the transition metals in NFM. The Ni 2p, Fe 2p, and Mn 2p spectra show nearly identical peak positions and satellite features before and after modification. The splitting energy of Mn 3s is about 4.75 eV, indicating that Mn remains mainly in the Mn⁴⁺ state. Therefore, the surface of NFM@1%MgF₂ still shows dominant Ni²⁺/Fe³⁺/Mn⁴⁺ surface states, suggesting that MgF₂ does not significantly alter the intrinsic redox-active centers of NFM^[47,52,53]. In contrast, the newly emerged Mg 1s and F 1s signals in NFM@1%MgF₂ provide direct chemical evidence for the surface modification. Specifically, the F 1s peak at approximately 684.05 eV and the Mg 1s peak at approximately 1,304.15 eV can be assigned to Mg/F-containing fluoride species, confirming the formation of a Mg/F-enriched surface layer on NFM@1%MgF₂^[44,45]. On this basis, the role of MgF₂ in the present system is more reasonably understood as the regulation of the surface chemical environment rather than the modification of the bulk framework or intrinsic transition-metal redox chemistry. This distinction is critical for the subsequent mechanistic discussion because it confines the major function of MgF₂ to the surface/interface region, where the key electrochemical instability of O3-type NFM is expected to originate.

Overall, the ICP-OES, XRD, SEM, TEM, EDS, and XPS results demonstrate that MgF₂ does not significantly alter the bulk stoichiometry or the O3-type layered framework of NFM, but instead leads to the formation of a Mg/F-enriched surface layer with locally non-uniform thickness. This structural feature provides a direct basis for understanding the subsequent interfacial and electrochemical behavior. In the present system, the non-uniformity of the MgF₂ surface layer should not be regarded as an imperfection. Instead, it is likely to be functionally beneficial. A non-uniform and discontinuous surface-loaded layer may preferentially protect highly reactive surface sites while avoiding the severe Na⁺ transport penalty commonly associated with overly thick and continuous coatings. This structure-property relationship is consistent with the central idea of this

work, namely that proper regulation of the cathode interfacial chemical environment can improve electrochemical stability without sacrificing the intrinsic structural advantages of the O3-type cathode.

Electrochemical measurements

The effect of MgF_2 surface loading on the electrochemical properties was evaluated at 25 °C within 2.0–4.0 V. [Figure 3A](#) and [B](#), [Supplementary Figure 4](#) display the GCD profiles of NFM, NFM@0.5% MgF_2 , NFM@1% MgF_2 , and NFM@2% MgF_2 during the first two cycles at 0.1C. All samples exhibit similar charge-discharge profiles, indicating that MgF_2 loading does not alter the fundamental Na-storage reaction characteristics of NFM. The increased initial Coulombic efficiency (ICE) with higher MgF_2 loading can be attributed to the suppression of initial irreversible interfacial reactions^[42,54]. During the first charge/discharge process, electrolyte oxidation, cathode surface-film formation, parasitic reactions at highly reactive surface sites, and irreversible surface/structural reconstruction may consume part of the charge capacity, thereby lowering the ICE. However, with increasing MgF_2 loading, the initial discharge capacity decreases from 141.03 mA h g⁻¹ for NFM to 137.13, 130.48, and 125.87 mA h g⁻¹ for NFM@0.5% MgF_2 , NFM@1% MgF_2 , and NFM@2% MgF_2 , respectively. This decrease is partly attributed to the reduced proportion of electrochemically active material caused by the introduction of electrochemically inactive MgF_2 , but it also reflects the influence of MgF_2 on the initial interfacial reactions and electrochemical activation behavior. Notably, the voltage hysteresis around the ~3.0 V plateau is slightly alleviated in the modified samples, suggesting that surface MgF_2 plays a role in regulating interfacial polarization and voltage decay. This point is consistent with the expectation that a fluorinated surface layer can modify the local cathode-electrolyte interaction and thereby regulate the electrochemical response of the electrode even when the bulk structure remains unchanged. In this sense, the electrochemical effect of MgF_2 is better interpreted as an interfacial phenomenon before obvious structural differences emerge. Although the initial low-rate capacity is partially sacrificed, MgF_2 loading significantly improves the cycling stability of the material. As shown in [Figure 3C](#), after 100 cycles at 1C, the capacity retentions of NFM, NFM@0.5% MgF_2 , NFM@1% MgF_2 , and NFM@2% MgF_2 are 65.87%, 80.65%, 85.65%, and 74.69%, respectively. In particular, NFM@1% MgF_2 still delivers a reversible capacity of 103.01 mA h g⁻¹ after 100 cycles, which is higher than that of pristine NFM (84.53 mA h g⁻¹).

To further analyze polarization and electrochemical reversibility during the initial cycling stage, CV measurements were performed on NFM and NFM@1% MgF_2 at a scan rate of 0.1 mV s⁻¹ for the first five cycles [[Figure 3D](#) and [E](#)]. In the first cycle, pristine NFM exhibits a main pair of redox peaks at around 3.106/2.664 V, which can be mainly assigned to the $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox couple, while the weak peak or shoulder near 4.0 V can be attributed to the onset of $\text{Ni}^{3+}/\text{Ni}^{4+}$ and $\text{Fe}^{3+}/\text{Fe}^{4+}$ oxidation at higher potentials^[17,55]. Compared with pristine NFM, NFM@1% MgF_2 shows oxidation/reduction peak positions at 3.058/2.661 V, with the peak separation decreasing from 0.442 to 0.397 V, indicating reduced electrochemical polarization after MgF_2 loading. In addition, the CV curves of NFM@1% MgF_2 exhibit a higher degree of overlap in subsequent cycles. This feature suggests improved reaction reversibility and less pronounced polarization evolution during early cycling. Such behavior further supports the idea that MgF_2 mainly acts by stabilizing the local interfacial environment, thereby allowing the layered host to operate in a more reversible manner.

The rate performance of all samples was further evaluated over the range of 0.1–10C. As shown in [Figure 3F](#), although the capacities of all samples decrease to varying extents with increasing current density, NFM@1% MgF_2 consistently exhibits the best high-rate response. At 10C, the discharge capacities of NFM, NFM@0.5% MgF_2 , NFM@1% MgF_2 , and NFM@2% MgF_2 are 33.02, 72.11, 82.09, and 51.61 mA h g⁻¹, respectively. Relative to the capacity at 0.1C, the capacity retention of NFM@1% MgF_2 at 10C reaches 61.78%, which is higher than that of pristine NFM (24.47%). The corresponding GCD curves at different rates shown in [Figure 3G–J](#) reveal that NFM@1% MgF_2 maintains relatively distinct voltage plateaus and lower

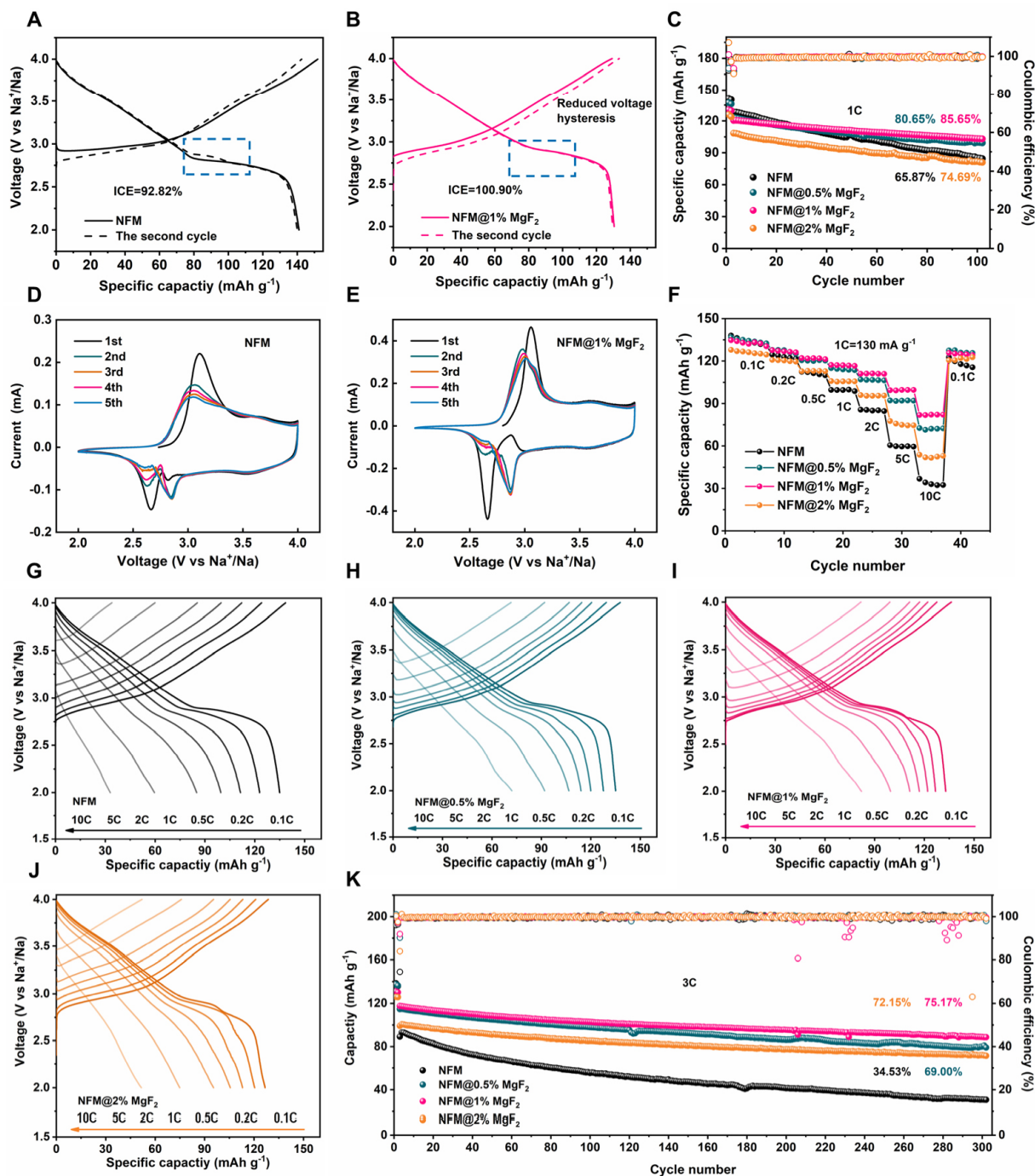


Figure 3. Electrochemical behaviors of pristine NFM and MgF_2 -loaded NFM electrodes measured between 2.0 and 4.0 V. (A and B) GCD profiles of pristine NFM and $\text{NFM}@1\%\text{MgF}_2$ of the initial two cycles of 0.1C, the second cycle is dashed line. The blue dashed lines indicate the alleviated voltage hysteresis. (C) Cycling performance of 1C. (D and E) CV curves of pristine NFM and $\text{NFM}@1\%\text{MgF}_2$ recorded during the 5 cycles at a scanning speed at 0.1 mV s^{-1} . (F) Rate capability from 0.1C to 10C. (G–J) GCD curves collected at 0.1–10C for the rate-performance test. (K) Long-cycling performance at 3C.

polarization even at high current densities. When the current density returns to 0.1C, its capacity nearly recovers to the initial value, indicating good reversibility under high-rate operation. The beneficial effect of MgF_2 loading is further demonstrated by long-term cycling at 3C [Figure 3K]. After two activation cycles at

0.1C, the cells were cycled at 3C, and the capacity retentions were calculated based on the first discharge capacity at 3C. After 300 cycles, the capacity retentions of NFM, NFM@0.5%MgF₂, NFM@1%MgF₂, and NFM@2%MgF₂ are 34.53%, 69.00%, 75.17%, and 72.15%, respectively. Notably, NFM@1%MgF₂ still maintains a reversible capacity of about 88.37 mA h g⁻¹ at the end of the test, much higher than that of pristine NFM (30.72 mA h g⁻¹). It is also worth noting that although the 2% sample shows long-term cycling retention comparable to that of the 1% sample, its initial discharge capacity and 10C rate capacity are both clearly lower than those of NFM@1%MgF₂. This suggests that although a higher loading amount provides stronger surface protection, it also introduces a more pronounced kinetic penalty. These results demonstrate that MgF₂ loading improves the durability of the NFM cathode under repeated cycling. The advantages of MgF₂ loading are further demonstrated by comparison with previously reported O3-type NFM cathodes in [Supplementary Table 2](#)^[28,29,47,56–58]. More importantly, these results reveal the existence of an optimal loading window. When the MgF₂ amount is too low, the surface protection remains insufficient to effectively suppress interfacial degradation. When the loading amount becomes too high, interfacial stabilization continues to improve, but additional transport and kinetic penalties emerge. Therefore, 1% MgF₂ achieves the best balance between interfacial stabilization and charge/ion transport.

Mechanistic investigation

To further clarify the influence of MgF₂ surface loading on reaction kinetics and interfacial evolution during cycling, GITT, EIS, and post-cycling XPS analyses were performed on NFM and NFM@1%MgF₂ electrodes. It should be noted that the Na⁺ diffusion coefficients derived from GITT reflect the apparent transport kinetics during charge and discharge. These values are influenced not only by bulk Na⁺ diffusion but also by interfacial film states and electrochemical polarization. Therefore, the present discussion focuses on the improvement of Na⁺ transport kinetics during operation rather than directly attributing the GITT results to a reduced intrinsic Na⁺ migration barrier in the pristine NFM lattice. As shown in [Figure 4A and B](#), the GITT profiles of NFM and NFM@1%MgF₂ are generally similar after 2 cycles, indicating comparable Na-storage pathways for the two samples. However, the corresponding diffusion coefficient distributions reveal that NFM@1%MgF₂ exhibits higher logD values over most of the charge/discharge range. The box plots in [Figure 4C](#) further show that, within 2.0–4.0 V during the first two cycles, the Na⁺ diffusion coefficient distribution of NFM@1%MgF₂ shifts toward higher values, with a higher median value than that of pristine NFM. After 100 cycles, as shown in [Figure 4D–F](#), the diffusion coefficients of both samples decrease to some extent. This decrease is expected because prolonged cycling generally leads to interfacial thickening, increased polarization, and structural degradation. Nevertheless, NFM@1%MgF₂ still maintains a higher range of diffusion coefficients and a higher median value. These results indicate that the kinetic advantage enabled by MgF₂ loading is not limited to the initial stage but persists after prolonged cycling. Such behavior suggests that the fluoride-induced interfacial stabilization exerts a lasting effect on the operating kinetics of NFM.

To validate the above conclusion from the perspective of interfacial impedance, EIS spectra of the electrodes after 2 and 100 cycles at open-circuit potential were fitted, and the results are shown in [Figure 4G and H](#), [Supplementary Table 3](#). In the equivalent circuit, R_s represents the solution/ohmic resistance, R_{sf} corresponds to the surface film resistance, R_{ct} is the charge-transfer resistance, and the low-frequency sloping line is associated with the Warburg diffusion process^[6,59]. After two activation cycles, the R_s values of NFM and NFM@1%MgF₂ are 6.345 and 5.252 Ω, respectively, indicating a negligible difference in bulk electrolyte resistance. At the same time, R_{ct} decreases dramatically from 1,016 Ω for NFM to 191.1 Ω for NFM@1%MgF₂, indicating much faster charge transfer at the electrode/electrolyte interface after MgF₂ loading. After 100 cycles, both samples exhibit obvious increases in surface-film-related impedance, indicating the gradual formation and thickening of the interfacial layer. Moreover, the R_{sf} and R_{ct} values of NFM@1%MgF₂ remain at 540.8 and 969.8 Ω, respectively, both of which are lower than those of pristine NFM, which reach 607.2

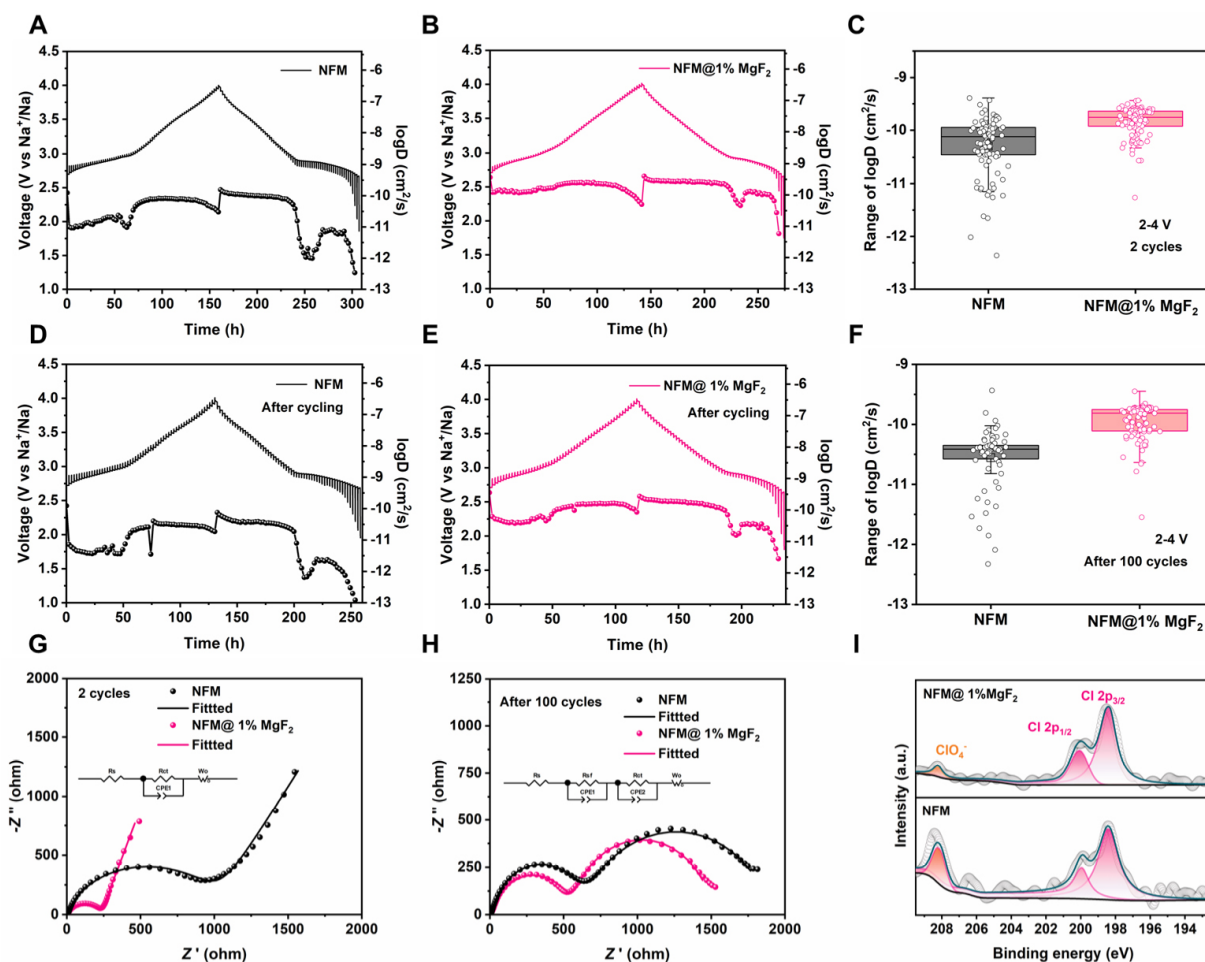


Figure 4. Electrochemical characterization and interfacial evolution of pristine NFM and NFM@1%MgF₂. (A and B) Representative GITT and calculated Na⁺ diffusion coefficients of pristine NFM and NFM@1%MgF₂ after 2 cycles. (C, F) Box plots of the logD values calculated from the corresponding GITT steps in (A and B) and (D and E), respectively. The scattered points represent individual logD values obtained from valid GITT steps within the corresponding representative GITT measurement, rather than from independent repeated experiments. The boxes indicate the 25–75th percentile range, the horizontal lines indicate the median values, the square symbols indicate the mean values, and the whiskers indicate the minimum–maximum range. The sample size *n* represents the number of valid GITT-derived logD values used for each box plot. (D and E) Representative GITT and calculated Na⁺ diffusion coefficients of pristine NFM and NFM@1%MgF₂ after 100 cycles. (G and H) Representative EIS spectrum together with the fitting results of pristine NFM and NFM@1%MgF₂ with the inset showing the equivalent circuit for fitting. (I) Cl 2p XPS spectra of cycled pristine NFM and NFM@1%MgF₂ after 100 cycles.

and 1,305 Ω. These results indicate that although MgF₂ cannot completely prevent impedance growth, it can effectively slow the growth rate and maintain lower interfacial reaction resistance and charge-transfer resistance after long-term cycling. Therefore, the role of MgF₂ is not to create a perfectly inert surface, which would be unrealistic under repeated electrochemical operation. Instead, its function is to regulate interfacial evolution so that the resistance increases more slowly and remains at a lower level. Such behavior is expected from an effective interfacial stabilization strategy. TEM images of the cycled NFM@1%MgF₂ [Supplementary Figure 5] show that the surface-loaded layer remains after cycling, with locally varied thicknesses of approximately 4–26 nm. The HAADF-STEM image and corresponding elemental mapping further show that Mg and F signals remain detectable after cycling, indicating the retention of Mg/F-containing species on the cycled electrode. Meanwhile, Na, O, C, and Cl signals are also observed, suggesting the coexistence of electrolyte-derived CEI components.

To further clarify the CEI chemistry after cycling, high-resolution F 1s, C 1s, O 1s, and Na 1s XPS spectra were collected for the cycled NFM and NFM@1%MgF₂ electrodes [Supplementary Figure 6]. In the F 1s spectra, cycled NFM shows both Na-F and C-F components, indicating the coexistence of inorganic fluoride species and fluorinated organic decomposition products. In contrast, NFM@1%MgF₂ is dominated by the Na-F/Mg-F-related inorganic fluoride component, while the C-F contribution is significantly weakened. The C 1s and O 1s spectra further show weakened C-F and O-C=O-related contributions after MgF₂ loading, suggesting suppressed accumulation of fluorinated organic species and modified carbonate/oxygenated surface chemistry. The Na 1s spectra mainly show broad Na-containing signals and are used as supporting evidence for Na-containing surface species. The Cl 2p XPS spectra after 100 cycles [Figure 4I] provide further evidence for the interfacial chemical evolution. Both samples exhibit Cl 2p doublets at about 198–200 eV^[60], together with ClO_x⁻-related signals in the higher binding-energy region^[60,61]. Compared with cycled NFM, NFM@1%MgF₂ shows clearly weakened high-binding-energy ClO_x⁻-related peaks and an overall lower Cl signal intensity. This result indicates that a smaller amount of electrolyte-derived chlorine-containing species accumulates on the cycled surface of the MgF₂-loaded sample. Combined with the lower R_{sf} and R_{ct} values, these XPS results suggest that MgF₂ loading suppresses continuous electrolyte side reactions at high potentials and mitigates the deposition of chlorine-containing decomposition or residual products on the cathode surface, thereby stabilizing the interfacial chemical environment. Overall, the GITT, EIS, and post-cycling XPS results demonstrate that the beneficial effect of MgF₂ on NFM is mainly manifested in interface-dominated kinetic optimization. Rather than reconstructing the intrinsic bulk diffusion mechanism of NFM, MgF₂ stabilizes the particle/electrolyte interface, suppresses side reactions, and retards impedance growth, thereby sustaining Na⁺ transport efficiency during cycling and ultimately supporting the improved rate capability and cycling stability observed above.

To further understand the role of MgF₂ surface loading in structural evolution, operando XRD measurements were performed on NFM and NFM@1%MgF₂ during the first cycle at 0.1C within 2.0–4.0 V. As shown in Figure 5A and B, both samples display clear and reversible peak shifts during the initial charge/discharge process. The (003), (006), (101), and (102) reflections evolve synchronously with Na⁺ extraction and insertion, indicating that the two samples follow similar layered structural evolution pathways within this voltage window. According to the reported structural evolution behavior of NFM, this process can be assigned to the O3-P3-O3 phase transition^[22,62]. Notably, the MgF₂-modified sample exhibits a smaller peak shift amplitude. During the O3 → P3 transition, the (003) peak shift of NFM reaches approximately 1.05°, whereas that of NFM@1%MgF₂ is only 0.84°. This indicates that MgF₂ does not alter the fundamental phase-transition type of NFM but rather mitigates the phase-transition-associated structural response. A similar tendency is also observed for the (006), (101), and (102) reflections, all of which exhibit more moderate migration behavior in the MgF₂-loaded sample. The operando XRD results also bridge the structural and interfacial observations described above. Once the interfacial chemical environment becomes more stable, the host lattice can undergo the same intrinsic phase transition under less severe interfacial perturbation. Conversely, once the phase-transition-associated structural response is moderated, the probability of generating highly reactive fresh surfaces is reduced. In this sense, interfacial stabilization and structural stabilization are not independent. They reinforce each other and jointly contribute to the improved electrochemical stability of NFM@1%MgF₂.

To evaluate the practical applicability of this interfacial regulation strategy, full cells were assembled using hard carbon (HC) as the anode. First, the HC half-cell exhibits stable Na-storage behavior within 0.01–2.0 V, retaining 95.30% of its capacity after 100 cycles at 1C [Supplementary Figure 7], which confirms the good cycling stability of the employed HC anode and provides a reliable basis for subsequent full-cell evaluation. Based on this, the charge/discharge curves for the initial two cycles of the NFM@1%MgF₂||HC full cell within 1.5–4.0 V are shown in Figure 5C, demonstrating stable voltage profiles and good initial reversibility. More

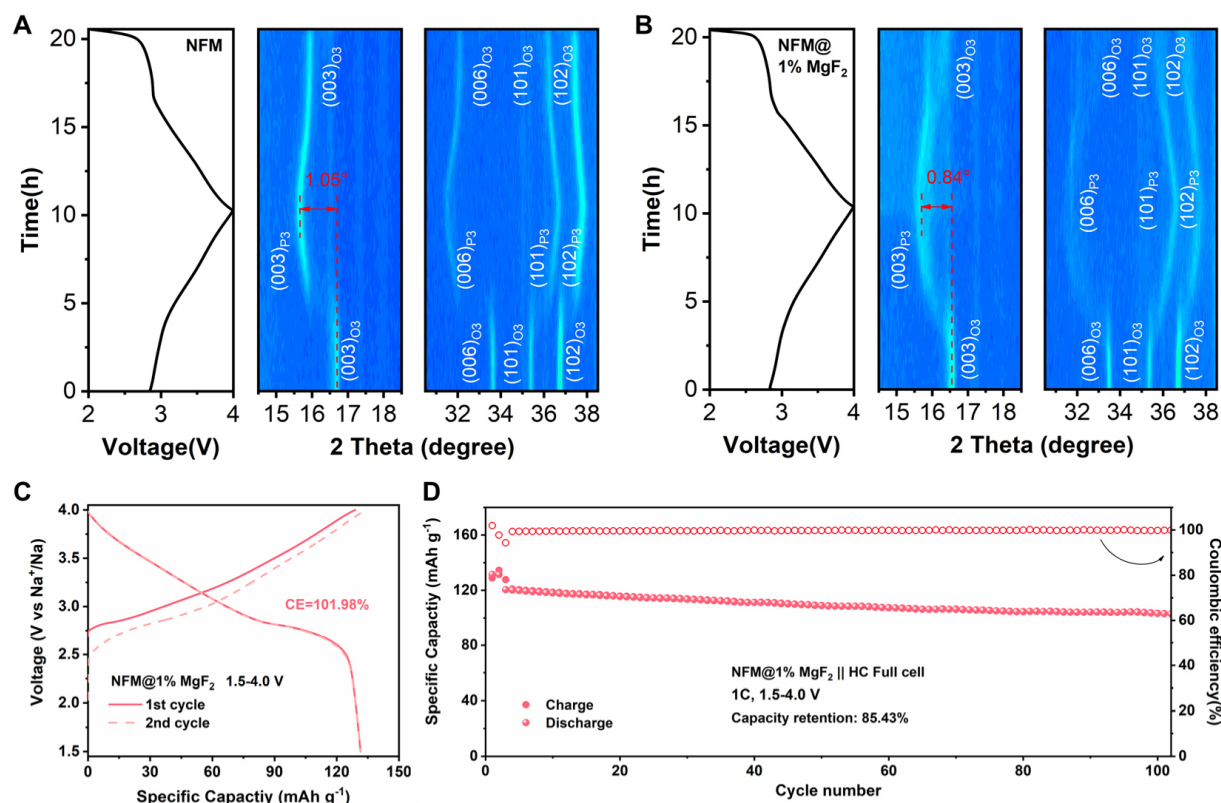


Figure 5. Operando XRD analysis of pristine NFM and NFM@1%MgF₂ during the initial charge-discharge process at 0.1C within 2.0–4.0 V, together with the electrochemical performance of the corresponding full cell. (A and B) Charge-discharge profiles and corresponding operando XRD patterns of the NFM and NFM@1%MgF₂ electrodes. (C) Initial two-cycle capacity-voltage profiles of the NFM@1%MgF₂||HC full cell at 0.1 C in the voltage range of 1.5–4.0 V. The specific capacity is calculated based on the mass of cathode materials. (D) Cycling performance of the NFM@1%MgF₂||HC full cell at 1C for 100 cycles.

importantly, after 100 cycles, the capacity retention of the NFM@1%MgF₂||HC full cell reaches 85.43% at 1C [Figure 5D], which is markedly superior to that of the pristine NFM||HC full cell (56.15%, Supplementary Figure 8). Overall, MgF₂ surface loading not only mitigates the structural evolution of NFM but also stabilizes the cathode interfacial chemical environment, ultimately improving cycling stability in the NFM||HC full cell. Therefore, the key value of MgF₂ surface loading does not lie in reconstructing the intrinsic phase-transition mechanism of NFM, but in alleviating phase-transition-induced stress through interfacial stabilization, maintaining structural reversibility, and improving the long-term operational stability of practical devices.

CONCLUSIONS

In summary, MgF₂ surface loading provides an effective means to stabilize the interfacial chemical environment of O3-type NFM cathodes. The introduced MgF₂ layer preserves the bulk O3 framework while forming a non-uniform Mg/F-enriched surface region. The optimized NFM@1%MgF₂ cathode exhibits improved cycling stability and rate capability, slower impedance growth, and a mitigated phase-transition-associated structural response. The improved performance in both half-cell and full-cell configurations indicates that the beneficial effect of MgF₂ mainly arises from interfacial stabilization. This work highlights fluoride surface loading as a viable strategy for stabilizing O3-type layered oxide cathodes for sodium-ion batteries.

DECLARATIONS

Authors' contributions

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All authors discussed the results and contributed to the final version of the paper.

Availability of data and materials

The original contributions presented in this study are included in the article/[Supplementary Material](#). Further inquiries can be directed to the corresponding author(s).

AI and AI-assisted tools Statement

During the preparation of this work, the AI tool ChatGPT image generation tool (OpenAI, version GPT-5.4, released 2026-03-05) was used solely to generate part of the particle elements in the Graphical Abstract. The tool did not influence the study design, data collection, analysis, interpretation, or the scientific content of the work. All authors take full responsibility for the accuracy, integrity, and final content of the manuscript.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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