



Synergistic bulk-interface modification enables exceptional electrochemical performance of high-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode

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ABSTRACT

The high-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode holds great potential for lithium-ion batteries with high energy density. However, its practical implementation is impeded by bulk structural degradation and severe parasitic reactions. To simultaneously address these challenges, a synergistic bulk-interface strategy is proposed, combining Al (aluminium) interstitial doping in the bulk phase with a SmNiO_3 (SNO) coating at the interface. Al^{3+} incorporation into lattice interstitial sites stabilizes the crystal structure and suppresses detrimental phase transitions. The SNO coating serves as a protective shield, mitigates parasitic reactions, and impedes transition metal (Mn) dissolution. Electrochemical tests confirm the enhanced performance of the synergistic bulk-interface LNMO, which maintains 77.1 % of initial capacity after 1500 cycles at 1C and enables a stable run of LNMO// $\text{Li}_4\text{Ti}_5\text{O}_{12}$ full battery. Comprehensive characterizations confirm successful Al interstitial doping into the lattice, uniform SNO coating, and suppressed performance degradation of battery. This work highlights the effectiveness of synergistic bulk-interface engineering in stabilizing high-voltage cathodes, providing valuable insights for future failure mechanism study and modification strategies.

1. Introduction

With the rapid consumption of non-renewable energy sources, alleviating energy shortages and developing renewable energy have become increasingly urgent. In renewable energy, LIBs are central due to their cost-efficiency, high energy density, and low energy consumption [1–7]. Spinel-type $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) represents emerges as a viable cobalt-free electrode candidate offering an elevated operational voltage of 4.7 V vs. Li^+/Li . This voltage substantially exceeds those of commercial cathode materials including LiCoO_2 (3.9 V), layered $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (~3.6 V), and olivine-type LiFePO_4 (3.5 V) [8,9]. Furthermore, LNMO demonstrates 20–30 % higher energy density compared to conventional LiCoO_2 and LiFePO_4 [10,11]. These combined attributes

position LNMO as a high-energy-density cathode candidate for advanced LIBs. Despite its advantageous high redox potential, however, the practical implementation of LNMO faces significant challenges, with poor cycling stability constituting the primary bottleneck to commercialization [12–15].

The degradation of LNMO's cycling performance stems from several intrinsic material challenges. Firstly, LNMO undergoes an inherent two-phase transition during charge/discharge processes. This structural evolution compromises its intrinsic stability, directly contributing to cycling performance decay [16]. Secondly, transition metal manganese (Mn) ions readily dissolve from the lattice and migrate into the electrolyte during cycling. This Mn dissolution not only induces collapse of the spinel structure but also significantly increases charge transfer

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resistance, severely degrading overall cell performance [17]. Finally, the Jahn-Teller effect within the Mn—O framework induces structural distortion in the cathode material, further accelerating structural degradation during prolonged cycling [18].

To address the aforementioned issues, multiple engineered approaches have been devised to address the cycling instability of LNMO. Among these, elemental doping has been widely adopted due to its operational simplicity and high efficacy [19,20]. Cation dopants occupy specific lattice sites, effectively suppressing the detrimental irreversible two-phase reaction. For instance, Piao et al. introduced Al^{3+} into the octahedral (16c) sites of LNMO [21]. The incorporated Al ions act as structural pillars within the lattice, mitigating transition metal dissolution. Similarly, Liang et al. doped Mg into octahedral (16c) and tetrahedral (8a) sites within the $\text{Fd}\bar{3}\text{m}$ lattice [22]. Dual-site doping suppressed the two-phase reaction and enhanced LNMO stability. Furthermore, simultaneous modification of specific (16c) and (16d) sites using Sb as a dopant successfully suppressed two-phase reaction, thereby markedly suppressing Mn dissolution from the LNMO structure [23]. HAN et al. employed a coprecipitation method to introduce Cu^{2+} into interstitial sites, thereby suppressing the phase separation behavior of LNMO and enhancing its structural stability [24]. Collectively, these studies demonstrate that cationic doping at targeted site (16c) effectively inhibits the irreversible two-phase reaction during deep delithiation. Complementary to doping, surface coating technology has proven highly effective in stabilizing the spinel surface structure [25]. The coating physically separates the cathode from the electrolyte, thereby reducing HF attack, which arises from electrolyte decomposition under high voltage and accelerates the dissolution of transition metals [26]. Sm_2O_3 emerges as an exceptional coating material due to its superior resistance to acid/base corrosion and favorable Li^+ ion transport kinetics. As demonstrated by Wang et al., a uniform Sm_2O_3 coating applied via a sol-gel method substantially reduced parasitic side reactions and suppressed transition metal dissolution [27].

In this work, we demonstrate an effective strategy to simultaneously suppress the detrimental two-phase reaction and Mn dissolution under high-voltage conditions (Fig. 1). The co-modification of LNMO with bulk Al doping and surface SmNiO_3 coating (termed LNMO-AS) is accomplished via a single-step high-temperature solid-state synthesis

approach. Density functional theory (DFT) calculations reveal that synergistic bulk-interface modification substantially improves the stability of LNMO. In situ XRD results confirm that the modified material demonstrates a distinct solid-solution reaction behavior, effectively mitigating the deleterious two-phase transformation. Following the synergistic bulk-interface modification, the LNMO-AS cathode delivers substantially enhanced electrochemical performance.

2. Results and discussion

2.1. Synthesis and structures of LNMO-AS

LNMO-AS samples (Fig. 2a) were prepared by solid-phase reaction. Fig. 2b shows the XRD patterns of the LNMO and LNMO-AS. All peaks are indexed to the cubic spinel phase ($\text{Fd}\bar{3}\text{m}$) [28]. Fig. 2c and d show higher-angle shifts for both the (111) and (400) diffraction peaks in LNMO-AS, which is due to successful Sm^{3+} incorporation into the LNMO surface structure [29]. Since the Sm—O binding energy is higher than Mn—O, trace amounts of Sm^{3+} penetrate into the surface lattice, causing the valence change of manganese (from Mn^{3+} to Mn^{4+}).

Furthermore, as illustrated in Fig. S1, the Raman spectroscopic profile of the samples shows characteristic peaks at 636 cm^{-1} and 496 cm^{-1} , respectively, which are characteristic of Mn—O and Ni—O [30]. Notably, no significant peak splitting was observed in the $570\text{--}620\text{ cm}^{-1}$ range [31]. This suggests that the bulk-phase interface modification treatment exerted no substantial impact on the structural features of the samples. All specimens retained the $\text{Fd}\bar{3}\text{m}$ space group structure.

Fig. 2e and f present XRD refinement results for LNMO and LNMO-AS. The R_{wp} values for all samples were below 6 %. All samples possessed a disordered cubic spinel phase ($\text{Fd}\bar{3}\text{m}$), with Mn/Ni cations occupying the 16d sites, Al ions occupied the 16c sites, and Li and O ions occupying the 8a and 32e sites, respectively (Fig. S2). The refinement results clearly show that the lattice constant decreased from $8.17568\text{ \AA}$ to $8.17093\text{ \AA}$ (Table S1), indicating the contraction of the crystal cell volume after modification. LNMO-AS exhibits two phases: $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (PDF#80–2162) and SmNiO_3 (PDF#80–1948) [32]. The secondary peaks observed at 23.2° , 23.5° , 26° , 33.2° , and 33.5° between the (111) and (311) peaks in the XRD pattern of LNMO-AS correspond to

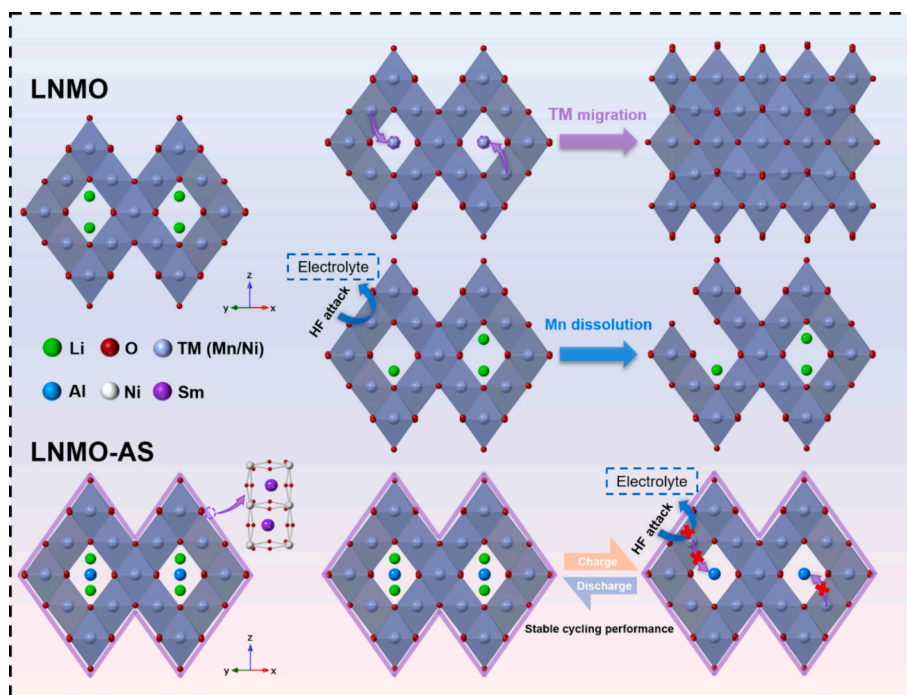


Fig. 1. Illustrative diagram of the principle of synergistic bulk-interface modification of LNMO to inhibit harmful two-phase reactions and Mn dissolution.

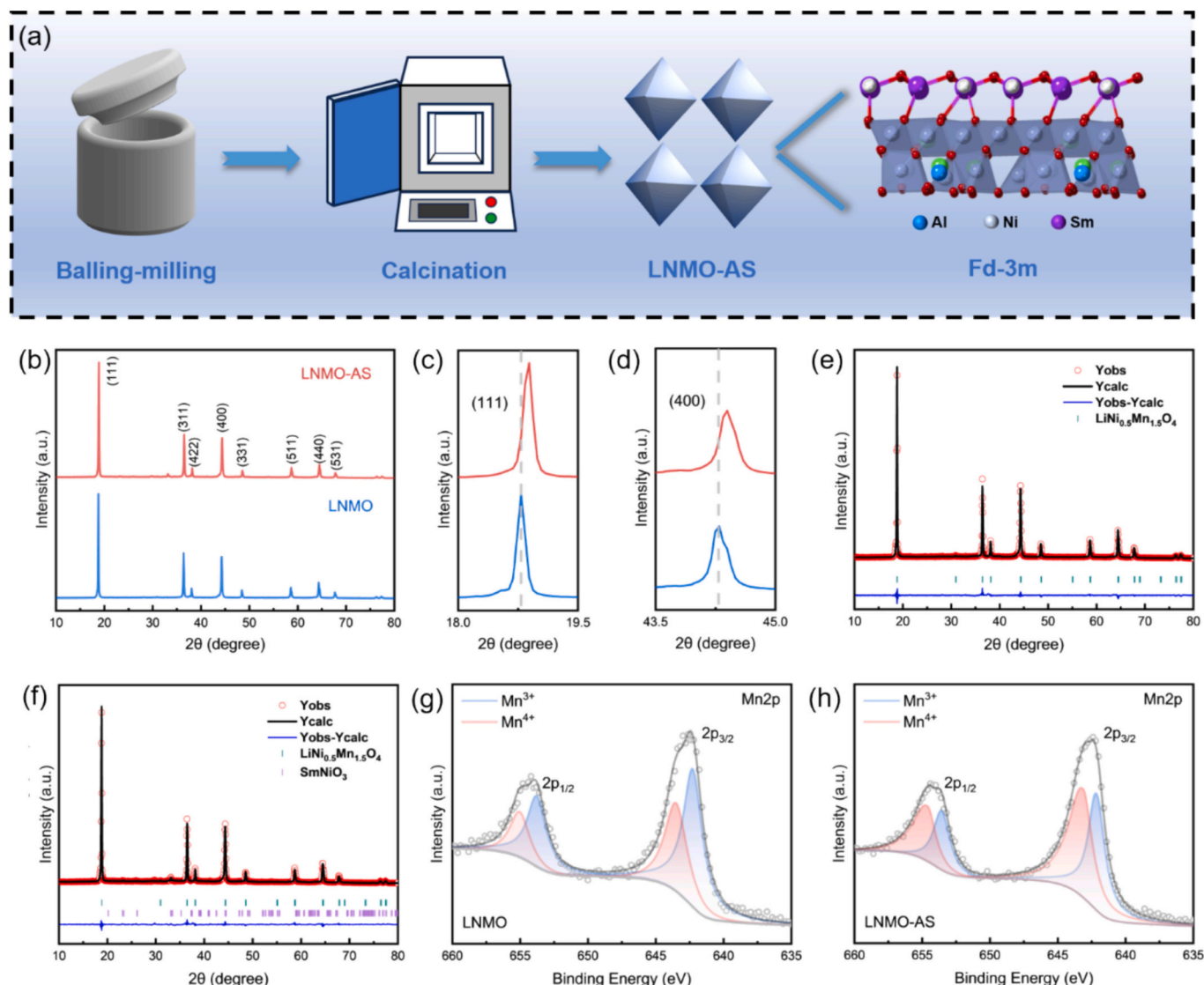


Fig. 2. (a) LNMO-AS synthesis schematic. (b) XRD patterns. (c and d) Magnified areas of peaks (111) and (400). (e and f) Refined XRD profiles of LNMO and LNMO-AS. (g and h) Mn 2p XPS spectra of LNMO and LNMO-AS.

the (110), (002), (111), (112), and (200) crystal planes of SmNiO_3 (space group: Pbnm), indicating the successful presence of the surface coating.

To reveal the chemical makeup and distribution of valence states in surface elements, X-ray photoelectron spectroscopy (XPS) analysis was performed on the samples. Fig. S3 presents full XPS spectrum, Al 2p and Sm 3d spectra of LNMO-AS are in Fig. S4a and b. The XPS spectra show that the binding energy of the Al 2p spectrum is 84.2 eV, while that of the Sm 3d spectrum is 1082.9 eV [33], confirming Al and Sm dopants on LNMO-AS surfaces. Fig. 2g and f display Mn 2p spectra for LNMO and LNMO-AS. Binding energies of 642.17 eV and 643.19 eV for Mn 2p_{3/2} confirm Mn^{3+} and Mn^{4+} coexistence in both samples [34]. Mn^{3+} and Mn^{4+} relative amounts were calculated from their XPS peak areas. Mn^{3+} and Mn^{4+} account for 63.81 % and 36.19 % in LNMO 63.81 % and 36.19 %, respectively, while in LNMO-AS they are 46.07 % and 54.93 %, respectively. This indicates an increase in Mn^{4+} content in LNMO-AS. A high Mn^{4+} content is essential for LNMO performance. Firstly, Mn^{4+} predominance (d^3 , Jahn-Teller inactive) minimizes Mn^{3+} (d^4 , Jahn-Teller active), eliminating Jahn-Teller-induced lattice distortion and structural degradation during cycling [35], thereby enhancing structural stability. Secondly, the small ionic radius of Mn^{4+} and high charge density strengthen Mn—O bonds, effectively maintaining spinel

structural integrity. Finally, low Mn^{3+} concentration suppresses its detrimental disproportionation ($2 \text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$) in electrolyte, preventing Mn^{2+} migration and capacity fade [36], thus improving cycle life.

2.2. Morphology and elemental distribution of LNMO-AS

Figs. 3a and S5 present the microstructures of LNMO-AS and LNMO, respectively, which were found to be similar, and the size of LNMO-AS is smaller compared to the LNMO. Fig. 3b shows the high-resolution transmission electron microscopy (TEM) image of LNMO-AS. It can be found that the surface is covered with about 10 nm thick coating interface. Fig. 3c shows the lattice spacing of 0.249 nm, consistent with the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (311) facet (PDF # 80-2162) [37], and Fig. 3d shows the lattice spacing of 0.264 nm of the coating in agreement with the SmNiO_3 (200) facet (PDF # 80-1948) [38]. The lattice fringe spacing is shown in Fig. S6. Selected-area electron diffraction (SAED) maps of LNMO-AS exhibits a perfect hexagonal array corresponding to the fundamental reflection (111) of the Fd3m spinel structure (Fig. 3e). Fig. 3f shows a STEM image showing the LNMO-AS along the [110] crystallographic direction in particle HAADF mode. The characteristic rhombic pattern of the spinel-type structure can be clearly observed,

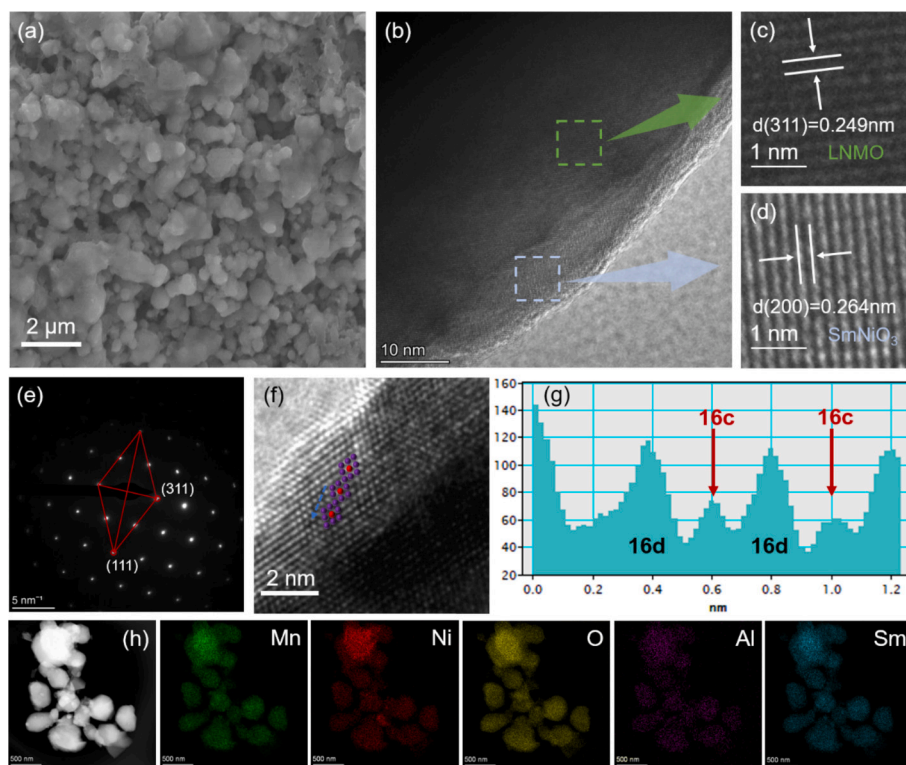


Fig. 3. (a) SEM image of LNMO-AS. (b–d) high-resolution TEM images of LNMO-AS. (e) SAED image of LNMO-AS particles. (f) HAADF STEM image of LNMO-AS particles. (g) line profile analysis along the blue line. (h) EDS elemental mapping of LNMO-AS.

where purple dots indicate TM in the 16d site and red dots indicate TM in the 16c site. The line contour map corresponding to the STEM (Fig. 3g) confirms the successful doping of Al in the interstitial octahedral 16c site [39]. In contrast, LNMO exhibits a normal spinel structure (Fig. S7). In addition, the energy dispersive (EDS) elemental distribution maps (Fig. 3h and Fig. S8) show that Mn, Ni, O, Al, and Sm are uniformly distributed in LNMO-AS. The EDS elemental mapping of LNMO is shown in Fig. S9. These results demonstrate that the LNMO-AS samples are spinel-type structures with Al octahedral 16 c site doping and SmNiO₃ coating.

2.3. Electrochemical performances of LNMO-AS

The corresponding charge/discharge curves of LNMO and LNMO-AS at 1C ($1C = 146 \text{ mAh g}^{-1}$) during the first and 1500th cycles at 3.5–4.9 V are presented in Fig. 4a. Charge/discharge plateaus appear at approximately 4.7 V ($\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$ redox reaction) and approximately 4.0 V ($\text{Mn}^{3+}/\text{Mn}^{4+}$ redox reaction). Although the $\text{Mn}^{3+}/\text{Mn}^{4+}$ reaction contributes to capacity, the soluble Mn^{2+} generated by the Mn^{3+} disproportionation reaction leads to manganese dissolution [40], thereby reducing cycle stability. Based on the calculation of the proportion of capacity at 4 V to the total discharge capacity, LNMO-AS exhibits reduced Mn^{3+} concentration (Table S2). These results demonstrate synergistic bulk-interface stabilization of LNMO spinel structure to prevent the formation of Mn^{3+} during cycling, thereby suppressing Mn dissolution. After 1500 cycles, the charge/discharge curves of LNMO-AS showed minimal changes, indicating that the voltage polarization was significantly reduced after modification.

Galvanostatic intermittent titration technique (GITT) measurements determined Li^+ diffusion coefficients (D_{Li}^+) for LNMO and LNMO-AS. Fig. 4b displays their half-cell charge/discharge GITT curves, while Fig. 4c demonstrates significantly enhanced D_{Li}^+ for LNMO-AS during both processes. This improvement is further supported by the linear relationship between peak current (i_p) and square root of scan rate ($v^{1/2}$)

in cyclic voltammetry (CV) tests at multiple scan rates (Fig. S10) further confirm that LNMO-AS has a faster lithium-ion diffusion rate. Concurrently, CV scans revealed that LNMO-AS exhibits reduced voltage polarization (Table S3). These results demonstrate that the synergistic bulk-interface modification significantly enhances the lithium-ion diffusion dynamics and significantly reduces voltage polarization [41].

Fig. S11 shows cycling performance curves for different Al contents and SNO layer thicknesses to determine the optimum configuration. Fig. 3a compares the 1C cycle stability of LNMO, LNMO-A (Al doping), LNMO-S (SNO-coating) and LNMO-AS. LNMO-AS delivers $112.8 \text{ mA h g}^{-1}$ initial discharge capacity compared to $112.2 \text{ mA h g}^{-1}$ for LNMO, $112.5 \text{ mA h g}^{-1}$ for LNMO-A, and $113.6 \text{ mA h g}^{-1}$ for LNMO-S. After 1500 cycles, LNMO-AS retains 77.1 % of its capacity, exhibiting the best capacity retention rate compared to other samples. Corresponding average discharge voltages are in Fig. S12. LNMO-AS has better voltage retention. Fig. S13 illustrates the cycling performance of LNMO-AS and LNMO under high load conditions at a 1C rate. The enhanced cycling stability originates from Al^{3+} interstitial doping, which enhances the structural stability, while the Sm-rich surface layer suppresses parasitic reactions [42]. Fig. S14 shows the cyclic performance of our work at 1C rate is compared with literature data. It can be observed that the LNMO-AS material in this study exhibits significantly enhanced cycling stability and discharge specific capacity.

Fig. 3e compares LNMO and LNMO-AS rate performance. LNMO-AS exhibits superior rate performance, delivering higher reversible capacities of 119.6, 112.9, and 94.7 mAh g^{-1} at 1, 2, and 5C, respectively, whereas LNMO yields 105.2, 96, and 45.5 mAh g^{-1} . This enhancement originates from conductivity improvement and reduced Li^+ diffusion barriers via bulk-interface modification, as verified by DFT below. As shown in Fig. 3f, after 1000 cycles at 10C, LNMO-AS retains a reversible capacity of 73.1 mAh g^{-1} , outperforming LNMO's 24.3 mAh g^{-1} , further highlighting the significant enhancement in rate performance achieved through synergistic bulk-interface modification.

To assess the practicality of the prepared LNMO-AS material, we

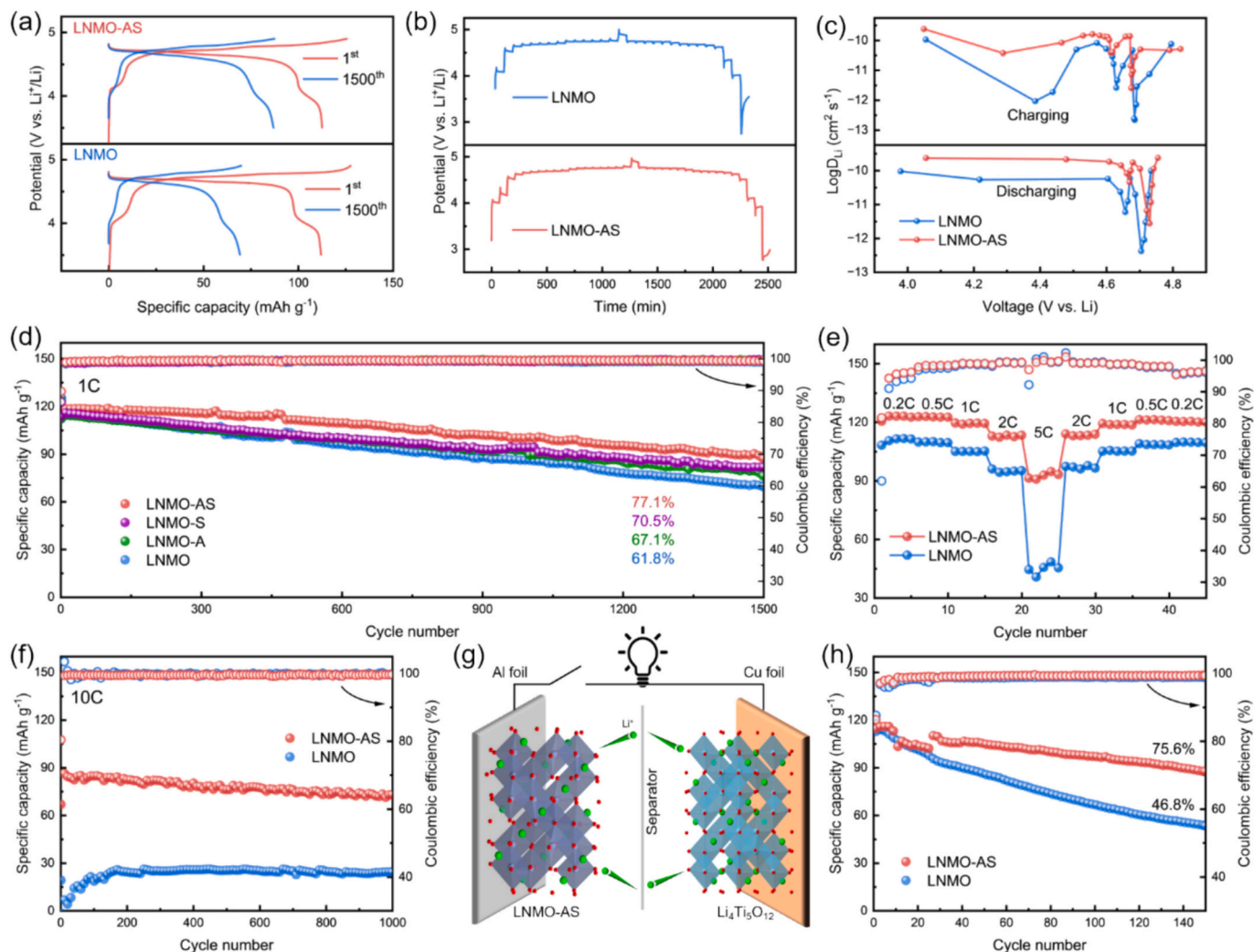


Fig. 4. (a) Initial and after 1500 cycles charge-discharge curves. (b) GITT response during charge/discharge processes. (c) Apparent DLi^+ derived from GITT. (d) Performance curves after 1500 cycles at 1C current density. (e) Rate performance. (f) Cycling performance at 10C. (g) Schematic diagram of the LNMO-AS//LTO full cell. (h) Cyclic performance curve of the LNMO-AS//LTO full cell at 1C.

assembled LNMO-AS// $Li_4Ti_5O_{12}$ (LTO) and LNMO//LTO full cells (Fig. 4g). The LNMO-AS//LTO full cell exhibited superior initial performance (114.5 mAh g^{-1} at 1C) compared with LNMO//LTO (112.8 mAh g^{-1}) in Fig. 4h, achieving 350 Wh/kg energy density. Additionally, the LNMO-AS//LTO full cell retained 75.6 % of its capacity after 150 cycles, significantly outperforming the 46.8 % of LNMO//LTO.

2.4. Phase structure evolution of LNMO-AS

In situ XRD tracked cycling-induced phase changes in LNMO and LNMO-AS [43]. Fig. 5a and b presents the in situ XRD patterns of LNMO and LNMO-AS. To better analyze peak displacement during cycling, specific diffraction peaks like (311) and (400) were selected. The pattern of XRD of LNMO shows an abrupt change of the peaks upon charging up to 4.75 V, indicating a phase transition to a fully delithiated phase through a two-phase reaction under high voltage (Fig. 5a) with abrupt (400) peak shift ($\Delta 2\theta = 1.1^\circ$) causing lattice strain and lattice dislocations, which impairs the structural stability of LNMO, resulting in energy dissipation and inferior cycling performance of the cell [44]. In contrast the LNMO-AS XRD profile maintains a smooth and uniform variation throughout the charging and discharging process, indicating a smooth transition from LNMO to $Ni_{0.5}Mn_{1.5}O_4$ during the occurrence of the solid solution reaction (Fig. 5b) Specifically, LNMO-AS maintains

solid-solution behavior through gradual shift ($\Delta 2\theta = 0.8^\circ$) reducing strain, thereby preventing strain accumulation at phase boundaries and mechanical cracking [45]. This indicates the successful implementation of the strategy of bulk phase doping with Al^{3+} to inhibit transition metal migration and thus stabilize the lattice structure.

2.5. Morphology and structure of LNMO-AS after cycling

Post-cycling SEM characterization shows (Fig. 5c and d) that microcracks appeared on the surface of the LNMO after 300 cycles (3.0–4.9 V, 1C, 25 °C), whereas the LNMO-AS remained intact in the particle structure. The cracks in the pristine samples originated from repeated lattice volume changes, interfacial side reactions, and accumulated mechanical stresses during high-pressure cycling. The synergistic bulk-Interface modification strategy suppresses cracks through a synergistic mechanism: Al interstitial doping buffers the lattice strain and significantly suppresses the grain volume fluctuation during the charge/discharge process, while the Sm-rich coating effectively prevents the microcrack extension by suppressing the side-reactions and utilizing its toughness to absorb/disperses the surface stresses. This synergistic bulk-interface reinforcement significantly improves the cyclic stress resistance, thus maintains the structural stability.

Electrochemical impedance spectroscopy (EIS) probed bulk-interface

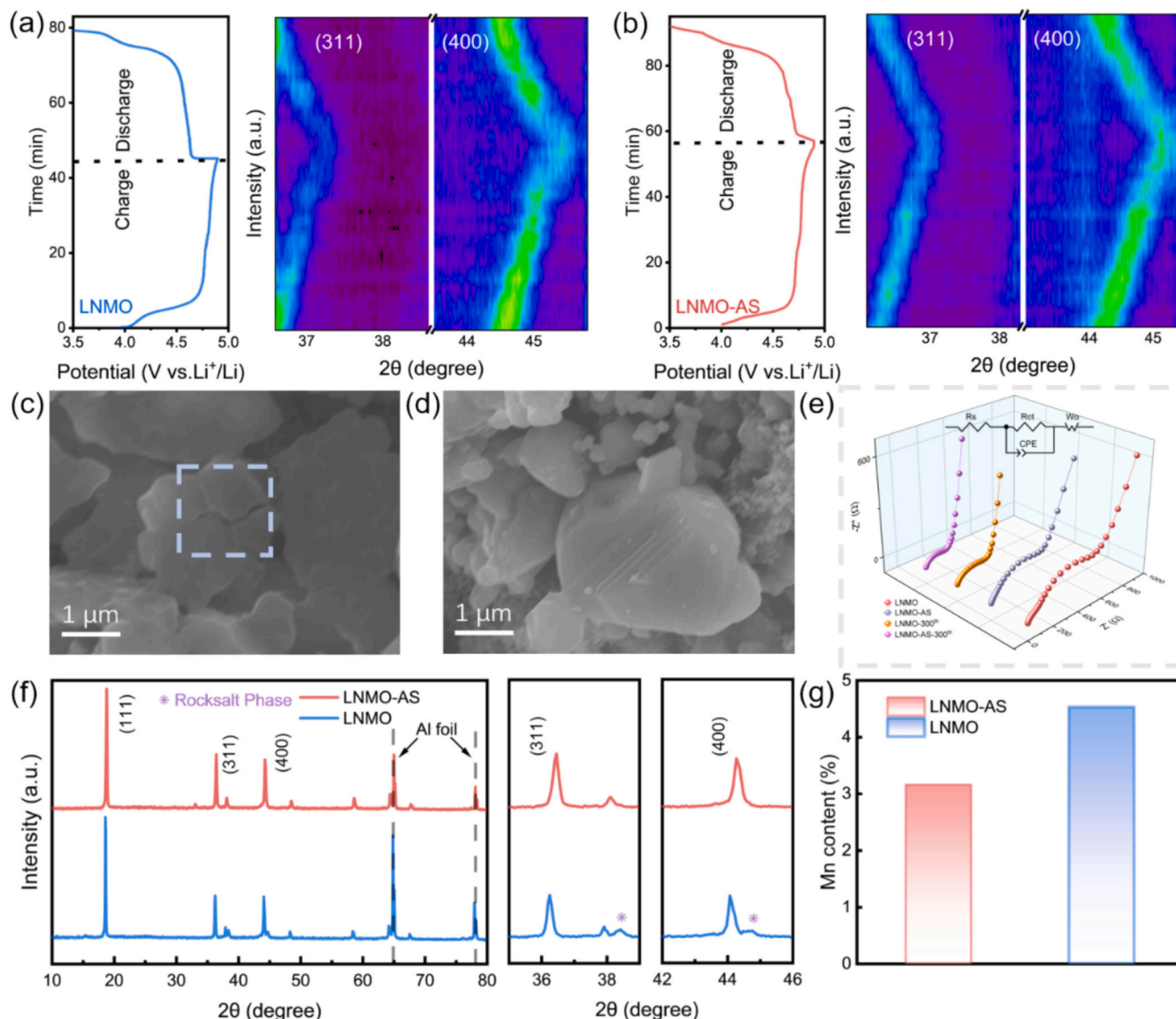


Fig. 5. (a and b) In situ XRD patterns at peaks (311) and (400) under the first cycle. (c and d) SEM images after 300 cycles at 1C. (e) EIS impedance plots before and after 300 cycles. (f) XRD profiles following 300 cycles. (g) Mn dissolution ratio on the lithium foils removed from the LNMO and LNMO-AS half-cells after 300 cycles.

co-modification effects on reaction kinetics. Fig. 5e shows the Nyquist plots of LNMO and LNMO-AS based on the equivalent circuit diagram after the first cycle and 300 cycles, where R_s and R_{ct} denote ohmic and electrode-electrolyte interfacial resistances respectively. Before the first cycle, the R_{ct} value of LNMO was 504.6 Ω , while that of LNMO-AS was lower at 368.2 Ω . After 300 cycles, LNMO-AS consistently exhibited a lower R_{ct} (138.7 Ω) compared to LNMO (222.4 Ω). EIS confirms notably diminished charge-transfer resistance for LNMO-AS. This is attributed to its surface-enriched Sm coating effectively inhibiting interfacial parasitic reactions under high voltage, thereby maintaining low interfacial impedance during cycling.

The XRD pattern of Fig. 5f after 300 cycles shows that the LNMO undergoes a phase transition triggered by the migration of transition metal ions, leading to the generation of a rocksalt phase [46]. In contrast, such structural transformations are significantly suppressed in the LNMO-AS sample, with its main phase characteristic peaks remaining intact and no obvious impurity peaks observed. This comparison indicates that LNMO-AS maintains excellent crystal structural stability even after 300 cycles. This stable crystal structure effectively suppresses cycle-induced phase transitions, thereby significantly

improving the long-term cycling performance. To investigate element dissolution behavior during cycling, the electrodes were disassembled after cycling, and the lithium foils were subjected to inductively coupled plasma (ICP) testing. The results (Fig. 5g and Fig. S15) show that the Mn dissolution ratio of LNMO-AS is only 3.16 %, significantly lower than the 4.53 % of LNMO. This indicates that the synergistic bulk-interface modification effectively inhibits parasitic reactions, thereby inhibiting Mn dissolution. In summary, the synergistic bulk-interface modification strategy provides an effective guarantee for the long-term cycling stability.

2.6. Theoretical analysis of stabilization mechanisms

The electrochemical performance of LNMO and LNMO-AS is intrinsically linked to the electronic properties. Consequently, DFT calculated total (TDOS) and projected (PDOS) density of states are shown in Fig. 6a–c. For Al-only doping (Fig. 6b), the TDOS near the Fermi level (E_f) slightly decreases relative to the pristine LNMO (Fig. 6a), indicating fewer charge carriers and a modest reduction in electric conductivity. Concurrently, the weakened contribution of Mn-3d and O-2p features

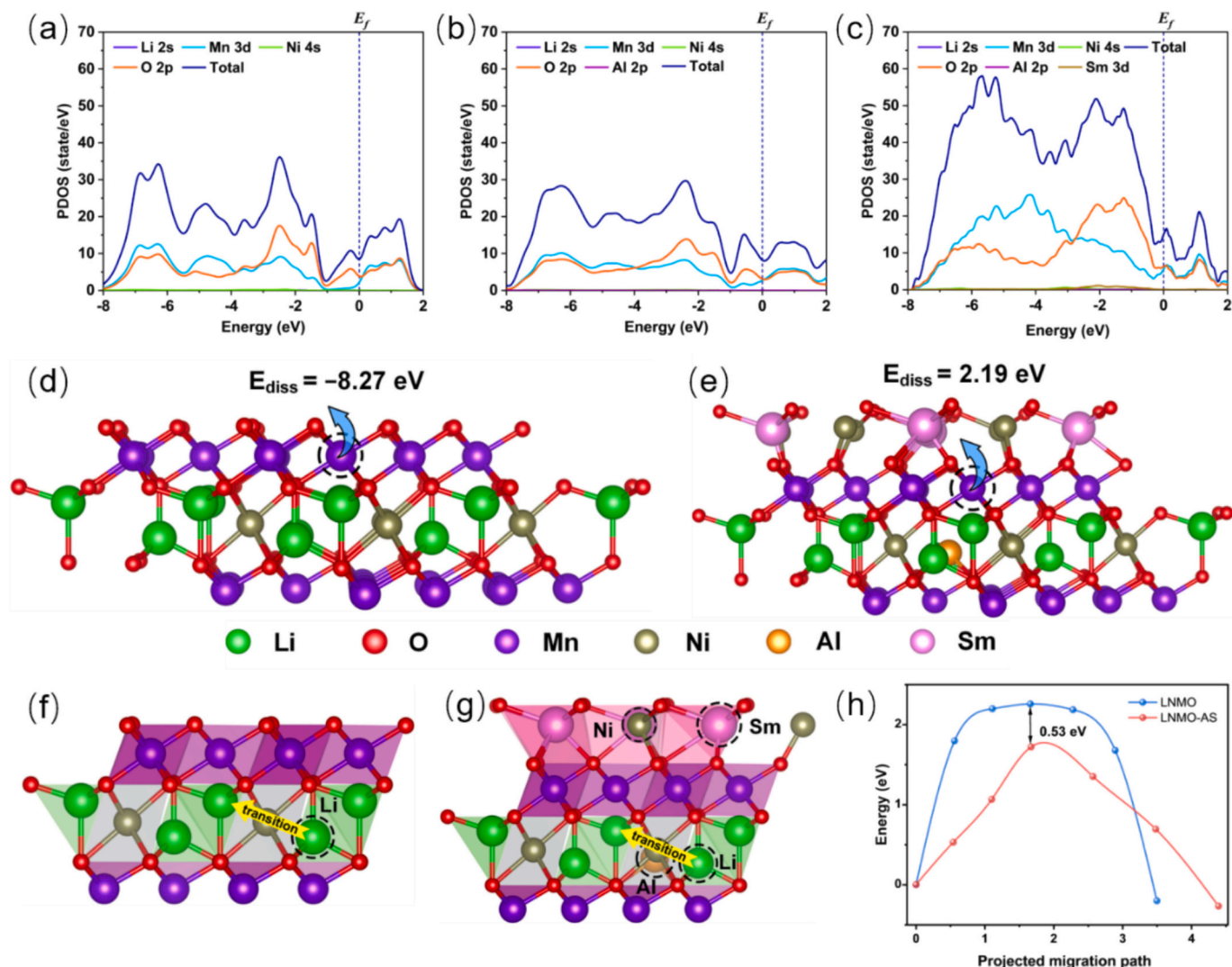


Fig. 6. (a–c) Total density of states and partial density of states diagrams of LNMO, Al-only doping, and LNMO-AS. (d and e) Schematic diagram of the Mn dissolution process in LNMO and LNMO-AS. (f and g) Structural models for Li^+ migration. (h) Li^+ diffusion energy barriers in LNMO and LNMO-AS.

indicate that the occupation of Mn–O antibonding states is reduced, thereby strengthening the interaction between Mn–O and stabilizing the electronic structure of Mn. Importantly, the synergistic bulk-interface modification in LNMO-AS will dramatically improve the DOS near the Fermi level (as presented in Fig. 6c), achieving stronger delocalization of charge carriers and superior electron transport, thereby strengthening the conductivity of the system. This facilitates efficient electron transfer [47]. The lower charge transfer impedance (EIS results) and smaller redox peak potential difference (CV results) of LNMO-AS directly confirm its excellent charge transport dynamics, this is consistent with the high conductivity density characteristics predicted by DFT.

Charge density difference diagram (Fig. S16) reveals dopant-induced electron accumulation near O atoms adjacent to Sm/Al and along Mn–O bonds, with depletion in interlayer voids and near Li. This signifies charge transfer into the Mn/Ni–O framework, strengthening TM–O hybridization. Due to the localized f-electrons of Sm, redistribution concentrates carrier states near E_f within the Mn–O network, enhancing transport channel connectivity. Furthermore, Al/Sm synergistic modification significantly increases the DOS near E_f , promoting carrier delocalization and improving electron transport.

To further reveal the inhibitory effect of the synergistic bulk-interface modification on the inhibition of Mn dissolution, we investigate and determine the Mn dissociation energies in LNMO and LNMO-AS

during cycling [48,49]. The detailed values were listed in Table S4. As shown in Fig. 6d and e, the Mn dissociation energies for LNMO and LNMO-AS are -8.27 eV and 2.19 eV, respectively. The substantially higher Mn dissociation energy in LNMO-AS indicates that synergistic bulk-interface modification makes Mn dissolution from the crystal lattice significantly more difficult. This conclusion is corroborated by the ICP measurements, which further confirm that the modification helps to preserve structural integrity and improve cycling performance. Furthermore, Fig. 6f and g illustrate the Li^+ migration pathway in LNMO and LNMO-AS. As shown in Fig. 6h, the corresponding diffusion energy barriers for Li^+ are 2.25 eV and 1.72 eV, respectively, which is consistent with the higher Li^+ diffusion rate measured by the GITT test. These together indicate that the synergistic modification not only suppresses Mn dissolution but also significantly enhances Li^+ diffusion kinetics [50].

3. Conclusion

In summary, we have successfully developed a synergistic bulk-interface modification for high-voltage LNMO, stabilizing the bulk structure via Al^{3+} occupancy of the 16c sites and optimizing the interface with a 10 nm-coating $SmNiO_3$ (SNO) synergistically suppresses structural degradation and interface failure. Specifically, Al^{3+}

occupation stabilizes the lattice framework, suppressing transition metal ion migration and mitigating harmful phase transformations. This enhances the intrinsic structural stability under high-voltage working condition. Concurrently, the SNO nanocoating isolates the cathode from electrolyte contact, thereby suppressing severe interfacial side reactions and effectively inhibiting Mn dissolution. The modified cathode material exhibits a working voltage of up to 4.7 V and matches LTO anodes to deliver an energy density of up to 350 Wh/kg, while demonstrating excellent cycling stability. Furthermore, the LNMO-AS maintains 89.1 mAh g⁻¹ at 10C, demonstrating superior rate performance. This research reveals that the synergistic bulk-interface modification is an effective approach to improve structural integrity and cycling stability in high-voltage spinel cathodes.

CRediT authorship contribution statement

Pei Wang: Writing – original draft. **Yusong Ding:** Software. **Han-cheng Ma:** Formal analysis. **Pu Cai:** Data curation. **Zibing Pi:** Investigation. **Ruixi Chen:** Methodology. **Wei Chen:** Supervision. **Qian Liu:** Writing – review & editing. **Wen Luo:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2025.170798>.

Data availability

Data will be made available on request.

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