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Llanos, Princess Stephanie; Ahaliabadeh, Zahra; Miikkulainen, Ville; Kong, Xiangze; Obrezkov, Filipp; Lahtinen, Jouko; Yao, Lide; Jiang, Hua; Lassi, Ulla; Kallio, Tanja Structural and interfacial stability of a coated Ni-rich layered oxide cathode at high-voltage operation

Published in: Materials Today Energy

DOI: 10.1016/j.mtener.2025.101862

Published: 01/06/2025

Document Version Publisher's PDF, also known as Version of record

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Please cite the original version: Llanos, P. S., Ahaliabadeh, Z., Miikkulainen, V., Kong, X., Obrezkov, F., Lahtinen, J., Yao, L., Jiang, H., Lassi, U., & Kallio, T. (2025). Structural and interfacial stability of a coated Ni-rich layered oxide cathode at high-voltage operation. Materials Today Energy, 50, Article 101862. https://doi.org/10.1016/j.mtener.2025.101862

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Contents lists available at ScienceDirect





Materials Today Energy

journal homepage: www.journals.elsevier.com/materials-today-energy/

Structural and interfacial stability of a coated Ni-rich layered oxide cathode at high-voltage operation

Princess Stephanie Llanos^a, Zahra Ahaliabadeh^{a,1}, Ville Miikkulainen^a, Xiangze Kong^a, Filipp Obrezkov^a, Jouko Lahtinen^b, Lide Yao^c, Hua Jiang^c, Ulla Lassi^d, Tanja Kallio^{a,*}

^a Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, Espoo, 02150, Finland

^b Department of Applied Physics, School of Science, Aalto University, Espoo, 02150, Finland

^c OtaNano-Nanomicroscopy Center, Aalto University, Espoo, 02150, Finland

^d Research Unit of Sustainable Chemistry, University of Oulu, Oulu, 90570, Finland

ARTICLE INFO

Keywords: Ni-rich NMC High-voltage cycling Operando X-ray diffraction Operando dilatometry Interfacial stabilization Coating W-modification

ABSTRACT

By increasing the cutoff potential of Ni-rich layered oxide cathodes, specifically LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NMC811), Li-ion batteries (LIBs) can deliver higher energy densities; a desirable performance trait in electric vehicle battery systems. However, this strategy compromises the structural and interfacial stability of NMC811, leading to a shorter operational lifetime. In this work, $Li_xW_yO_z$ (LWO) coating is formed on the surface of a NMC811 active material to address the instability issues. LWO-NMC811 reports an improved cycling stability compared with an uncoated NMC811 at a high-voltage operation of 3.0–4.6 V. Operando X-ray diffraction and operando dilatometry are combined with ex-situ characterization techniques to elucidate the degradation mechanisms that occur in the cathode material from initial cycling to after 100 charge-discharge cycles. The multiscale analyses show that LWO-NMC811 experiences a suppressed H2 \rightarrow H3 contraction at the high state-of-charge, which results in lesser particle cracking and electrode thickness change. The LWO coating also diminishes the parasitic side reactions and supports the agile movement of Li⁺ at the electrode-electrolyte interface. Overall, this work demonstrates an inter-mapping of the complex deterioration processes that occur during high-voltage cycling of Ni-rich NMC, which is useful in optimizing electrode design to achieve high performance LIBs.

1. Introduction

The electrification of passenger vehicles is a key action plan to reduce global CO_2 emissions from road transport, a sector that accounts for more than 70% of emissions from the transportation industry [1]. To entice vehicle owners to switch to electromobility, electric vehicles (EVs) should deliver comparable driving range with internal combustion engine vehicles, at an affordable cost. Thus, lithium-ion batteries (LIBs), which are among the most expensive components in today's EVs, should achieve higher energy density to enable farther driving distance on a single charge [2]. A general approach to meet the higher energy output requirement is through the improvement of energy density at the electrode material level. In recent years, the layered lithium nickel manganese cobalt oxide (LiNi_xCo_yMn_{1-x-y}O₂, NMC) has been the cathode material of choice for LIBs in EVs due to its high capacity and high nominal voltage [1–3].

Several studies on NMC have demonstrated that the increase in Ni content ($x \ge 0.6$) and cutoff potential (≥ 4.3 V vs Li/Li⁺) can effectively enhance the capacity and energy density output [4–6]. Moreover, the minimal utilization of Co reduces the overall cost and dependence on the critical raw material in battery systems [2]. However, these strategies give rise to structural and interfacial instability of the Ni-rich layered oxide material which can lead to drastic capacity fade as the cycling progresses [7,8]. The poor electrochemical performance stems from a number of degradation mechanisms such as electrolyte decomposition, non-uniform cathode-electrolyte interface (CEI) formation and growth, surface reconstruction, and particle cracking [4–6,9–11]. The compromised cycling stability challenges the commercial viability of Ni-rich NMCs in EV operation. Hence, numerous studies on Ni-rich NMC-based LIBs are motivated by the need to stabilize the cycling performance in an extended voltage range [2,3].

The development of a protective coating on the surface of an

https://doi.org/10.1016/j.mtener.2025.101862

Received 13 December 2024; Received in revised form 12 March 2025; Accepted 13 March 2025 Available online 14 March 2025 2468-6069/© 2025 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

^{*} Corresponding author.

E-mail address: tanja.kallio@aalto.fi (T. Kallio).

¹ Current address: Beneq, Espoo, 02200, Finland.

electrode has been recognized as an effective approach in improving the cycling stability of LIBs [8]. The choice of a Li⁺ conductive coating material is favored because it enables higher Li⁺ mobility during cycling, in addition to serving as a shielding layer against deleterious side reactions [7]. Recent studies have highlighted the advantages of utilizing lithium tungsten oxide (Li_xW_vO_z, LWO) as a coating material for NMC cathodes such as NMC111 [12], NMC532 [13], NMC622 [14, 15], NMC811 [16-18], NMC955 [19,20], LiNi_{0.83}Co_{0.12}Mn_{0.05}O₂ [21], LiNi_{0.83}Co_{0.07}Mn_{0.1}O₂ [22], and Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂ [23]. Some of these studies have demonstrated the effectiveness of LWO in enhancing the cyclability of Ni-rich NMCs at a high-voltage operation. For instance, at 2.8-4.6 V, Fu et al. [14] and Wu et al. [16] reported better cycling stability for LWO-coated NMC622 and LWO-coated NMC811, respectively, compared to the uncoated NMCs. It should be noted that much of the existing literature on LWO-modified NMCs report the enhanced electrochemical performance but provide limited analysis on the mechanism of improvement.

The structural and interfacial evolution experienced by a Ni-rich NMC cathode during cycling occur in multiple length scales including crystallographic, particle, and electrode levels [23]. Due to the complex interplay of the aforementioned cycling-induced degradation mechanisms at each of these levels, the use of operando techniques to pinpoint the root cause of capacity fading is immensely desirable. Operando measurements can provide high temporal resolution of the dynamic behavior of Ni-rich NMC during real time charging and discharging operations [24]. In particular, operando X-ray diffraction (XRD) allows the investigation of the crystallographic changes that transpire during the deintercalation and intercalation of Li⁺ in the active material structure [25]. However, in a recent review by Morley et al. [24], it was reported that only 16% of eighty studies related to battery active materials that were published in 2020-2023 performed operando XRD measurements. The percentage of studies that performed operando XRD analysis after a prolonged cycling period was not specified. The review highlights the need to analyze the relationship between crystallographic structure and electrochemical performance, particularly for modified NMCs. Operando electrochemical dilatometry is also gaining recognition as a valuable technique in designing battery systems [26,27]. Unlike operando XRD that provides information on a crystallographic level, operando dilatometry can measure the macrosocpic dilation and contraction at the electrode level during cycling. Such information is useful in optimizing the electrode and battery pack design, and assessing the safety level of swelling in cells [25-29]. In addition, as LIB development moves toward thicker electrode with low conducting agent and binder content, the electrode dilation and contraction can be more distinct [23].

In this work, we systematically investigate the cycling stability of LWO-coated NMC811 at an extended working voltage of 3.0-4.6 V via a combination of operando XRD, operando dilatometry, and ex-situ techniques. To date, the use of operando XRD to examine a LWObased coating on NMC has only been performed in the studies of Liu et al. [19] and Zhang et al. [22] wherein the crystallographic structure changes of a single-crystalline NMC were observed at a cutoff voltage of 4.5 V and 4.3 V, respectively. Meanwhile, operando dilatometry has been employed to observe the electrode dilation in modified NMCs including a LixTivOz-coated NMC622, carbon nanotube-blended NMC622, and TiO₂-titanium terephthalate coated-NMC811 at 3.0-4.4 V [30-33]. To our knowledge, there is no current work that reports the multiscale degradation mechanism of a coated Ni-rich NMC cathode cycled at a high cutoff voltage of 4.6 V. Based on the promising findings on existing work related to LWO-coated NMCs and the knowledge gap in inter-mapping failure modes, the aim of this work is to acquire in-depth understanding of the cumulative effect of structural and interfacial changes at different length scales to the overall cycling performance. Since a satisfactory cycling stability is a vital requirement in high energy density LIBs, the main findings of this study can elucidate the role of surface coatings in circumventing rapid capacity decline and help

develop more advanced coating strategies to improve electrode design.

2. Materials and methods

2.1. Active material synthesis

Bare NMC811 active material was prepared by calcining laboratory grade $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$ precursor (University of Oulu) and 5% excess LiOH (Sigma-Aldrich, 98%) in a tube furnace set at 800°C in O_2 for 12 h. The $Li_xW_yO_z$ -coated NMC811 (LWO-NMC811) was prepared in the same method with the addition of 0.1 mol% WO₃ (Sigma-Aldrich, 99.9%). The samples were placed in a tightly sealed container and transferred to a desiccator to minimize exposure to ambient air.

2.2. Active material characterization

Different structural and chemical characterization techniques were employed to investigate the structural and chemical differences between the active material samples. The particle morphology was evaluated using a scanning electron microscope (SEM, JEOL, JIB-4700F) with an operating voltage of 5 kV. Using the energy dispersive X-ray spectroscopy (EDS) detector connected to the SEM, the elemental distribution is acquired. The cross-sectional transmission electron microscopy (TEM) specimens were prepared by using focused ion beam technique on a multi-beam system with Ga ion source. Prior to milling, a 1.5 µm Pt protective layer was deposited on the surface of the desired particle to avoid beam damage during milling. Ga ion beam energy/probe current were applied with 30 kV/10 nA and 5 kV/30 pA for coarse and fine millings, respectively. The TEM analysis of the LWO- coated NMC811 was carried out using a double aberration-corrected microscope (JEOL, JEM-2200FS) with an integrated EDS detector for analyzing the elemental composition. The surface chemistry was studied using an Xray photoelectron spectrometer (XPS, Kratox Axis Ultra) with a monochromatic Al Ka X-ray source. High-resolution scans were obtained using 20 eV pass energy with 0.1 eV energy step. The resulting spectra were calibrated using the C-C signal at 284.8 eV. X-ray diffraction (XRD, PANalytical X'Pert Pro Alpha 1) data were measured using Cu K- α radiation (operated at 45 kV and 40 mA) in a 2θ range of 10–70°. The refinement of powder XRD data was carried out using GSAS II.

2.3. Electrode preparation and coin cell assembly

To prepare the positive electrodes, the synthesized active material (95 wt%), carbon black (3 wt%, Timcal Super 65), and polyvinylidene fluoride binder (2 wt%, Solvay 5130) are dispersed in N-methyl-2-pyrrolidone solvent (Alfa Aesar) using a dispergator (Dispermat) to form a homogeneous slurry. The slurry was then coated onto an aluminum foil (MTI) and dried in an oven (Memmert UNB 100) at 80°C for 4 h. Afterwards, the printed electrodes were cut into disks with average loading of ${\sim}10$ mg cm $^{-2}.$ The electrodes were calendared and then dried at 80 $^{\circ}C$ for at least 12 h under vacuum prior to being transferred to an Ar-filled glovebox (Jacomex, <1 ppm of H₂O and O₂). CR2016 cells (Hohsen) were assembled with the bare NMC811 or LWO-NMC811 as the cathode, lithium metal foil (MSE Supplies) as the anode, and glass fiber (Whatman GF/A) as separator soaked in 200 µL of 1 M LiPF₆ in 1:1 (v/v %) ethylene carbonate and dimethyl carbonate (Sigma-Aldrich) solution as electrolyte. Three-electrode cells (EL-CELL, ECC-ref) were assembled with lithium-metal foil as the counter and reference electrode. The cells were subjected to different electrochemical studies after 24 h rest.

2.4. Electrochemical studies

The cells were studied by galvanostatic charge-discharge tests (Land Cycler) at 1C (200 mA g⁻¹) within the voltage range 3.0–4.6 V. Rate capability tests were performed by constant-current charging at 0.2C, followed by constant voltage charging at 4.6 V with a 0.03C current

limit. Discharging was then conducted at different C-rates from 0.1C to 5C. Formation cycles were initially conducted for one cycle at 0.03C and three cycles at 0.1C from 3.0 to 4.3 V. Cyclic voltammetry (CV), electrochemical impedance spectrosocpy (EIS), and galvanostatic intermittent titration technique (GITT) were conducted in three-electrode cells at the same voltage window using a Biologic potentiostat (MPG-205). CV data were obtained using a sweep rate of 0.02 mV s^{-1} after the formation cycles and 100th charge and discharge cycles at 1C. The impedance tests were carried out at 3.9 V over 100 kHz and 10 mHz frequency range after the 25th, 50th, and 100th cycles at 1C. Spectral fitting was done using a Zview software. GITT experiment was performed by applying current pulses at 0.05C for 30 min, followed by a 2 h rest period. The measurements were performed after formation cycles and after 100 charge-discharge cycles at 1C. The computation of Li⁺ mobility is shown in the Supporting Information.

2.5. Operando measurements

Operando XRD was performed using an ECC-Opto-Std (EL-CELL) test cell with a Be window for X-ray transmission. XRD (PANalytical X'Pert Pro MPD Powder) patterns were continuously recorded every 16 min using a Cu target X-ray source while the cell is charging and discharging at 0.1C from 3.0 to 4.6 V using an Ivium Vertex Potentiostat. The collected XRD data was refined by GSAS II to determine the lattice parameters a (a = b), c, and unit cell volume. The electrode dilation during initial cycling was measured at 0.1C within 3.0–4.6 V by an ECD-3-nano (EL-CELL) cell inside a climatic chamber (Weiss Technik, VC3 4018) at 20°C. A similar cell assembly is described in detail in the work of Hamed et al. [32]. The formation cycles were performed at 0.03C and 0.1C rates for one and three cycles, respectively, at 3.0–4.3 V.

2.6. Electrode characterization

Fresh and cycled electrodes were characterized to investigate the changes in the morphology, microstructure, and surface chemistry after long term cycling. Cross-section SEM images were acquired using the same equipment. Before imaging, the samples were exposed to milling by broad ion beam (BIB, JEOL, IB-19520CCP) using a cryo cross section polisher with Ar ion source. TEM lamella of a cycled electrode was prepared using the same procedure as the active material lamella. JEOL JEM-2800 microscope was used to acquire the cross-sectional TEM image. For XPS, similar measurement parameters as the active material were employed.

3. Results and discussion

3.1. Characterization of the cathode active material

The SEM images of the synthesized bare NMC811 and LWO-NMC811 active materials show quasi-spherical secondary particles with average diameter of ~10–11 μ m, which are comprised of densely packed nanosized primary particles, as shown in Figs. S1a–b. The images reveal that the coating has no visible impact on the morphology of the bulk material. Due to Li being a very light element and the low concentration of WO₃ precursor utilized, an accurate quantification of Li and W via SEM-EDS is not possible. Nevertheless, the elemental mapping in Fig. S1c shows a homogeneous distribution of Ni, Mn, Co, and O even after the coating process.

To perform a more detailed observation of the coating layer, crosssectional high-resolution (HR-TEM) images of the synthesized LWO-NMC811 active material are acquired. Fig. 1a and b, which are taken from different regions in the sample, exhibit a distinct coating layer in between the bulk NMC811 and the deposited Pt during specimen



Fig. 1. (a–b) Cross-sectional HR-TEM image of the bulk NMC811 and coating interface taken at different regions; high-resolution XPS spectra of (c) O 1s, (d) Li 1s and W 4f; and (e) XRD patterns of the bare NMC811 and LWO-NMC811 active material.

preparation. On the other hand, the cross-section HR-TEM image of the bare NMC811 (Fig. S1d) shows a direct attachment of bulk NMC811 and Pt. The corresponding Fast Fourier Transform (FFT) analysis of the LWO-NMC811 (Figs. S2a–2b) confirms the amorphous structure of the coating, displaying a diffused halo ring in the coating region [15]. The non-uniform coating thickness, varying from 8 to 20 nm, is attributed to the solid state synthesis process employed, which is known to encounter challenges in controlling thickness and uniformity of coatings developed on cathode materials [7,12]. Nonetheless, the results show that the resulting surface coating has a good coverage on the NMC811 active material. The W peak in the EDS spectrum in Fig. S3 further confirms the presence of the coating on the surface. Due to the nanoscale thickness of the coating layer, the EDS mapping boundary extends into the bulk NMC811, resulting in the detection of peaks corresponding to the transition metals (TMs).

XPS was carried out to differentiate the surface chemistry of the coated active material from the bare. For the LWO-NMC811 sample, the shoulder in the O 1s spectrum (Fig. 1c) at ~530.5 eV indicates formation of a tungsten-oxide based compound [34]. The presence of tungsten on the surface of LWO-NMC811 is corroborated by the broad peak in the binding energy (BE) range of W 4f (Fig. 1d), whereas the bare NMC811 sample indicates only background noise. The presence of tungsten on the surface suppresses the intensity of the lattice oxygen peak at ~529.4 eV in Fig. 1c and Li 1s and Mn 3p signals in Fig. 1d [12,22,35]. This is also observed in the comparison of Ni 2p, Mn 2p, and Co 2p spectra in Fig. S4, wherein the peaks for LWO-NMC811 have lower intensities, indicating

that the layer with Ni, Mn, and Co are found beneath the surface coating layer. The broad Li 1s spectra also confirm the presence of surface impurities, such as Li₂CO₃, due to exposure to air during transport [16,35, 36]. By comparing the intensity of the peaks in the XPS data obtained, the ratio between the elements in each sample were determined and listed in Table S1.

XRD patterns of the active materials, shown in Fig. 1e, exhibit similar peaks indexed to the layered α -NaFeO₂ with the R-3m space group. The well-ordered layered structure is confirmed by the clear separation between the (006)/(102) and (018)/(110) peaks, and corroborates the SEM findings that the bulk structure is preserved after the addition of the LWO coating. The $I_{(003)}/I_{(104)}$ ratio obtained for bare NMC811 and LWO-NMC811 are 1.67 and 1.70, respectively. Both samples have values higher than 1.2, which means that there is low degree of Li⁺ and Ni²⁺ mixing in the structure [17]. No peak related to any tungsten oxide feature can be detected, which is due to the amorphous structure and nanosized thickness of the LWO coating, as demonstrated by the TEM analysis. The Rietveld refinement results for powder XRD measurements, shown in Table S2, reveal no significant difference in the lattice parameters between the bare and coated NMC811 [13,17,20,22]. The results suggest that the tungsten ions do not diffuse into the bulk structure, but rather remain as part of the surface coating [20,22]. This observation is further supported by the lack of clear W signal in the cross-sectional TEM-EDS analysis of the bulk region of the coated sample (Fig. S5). Overall, the structural and chemical characterization confirm the successful formation of a LixWvOz-based coating on the surface of the



Fig. 2. Electrochemical performance of bare NMC811 and LWO-NMC811 tested at 3.0–4.6 V. Comparison of (a,b) specific discharge capacity and mean discharge voltage over 100 cycles at 1C; (c) specific energy density at the active material level for the 1st, 25th, 50th, and 100th cycles; and (d) evolution of the specific discharge capacity during rate capability test for three cycles at 0.1C–5C.

NMC811 active material. Similar results were reported by previous studies on layered oxide cathode materials coated with LWO [12,16–18, 20,22].

3.2. Cycling stability

In this study, a moderately high loading (~ 2.0 mAh cm⁻²) of NMC811 is utilized at the positive electrode. Aside from its direct influence on the energy density and cost of the battery, a higher areal capacity allows electrochemical studies close to practical applications [37]. To investigate the effect of coating in protecting NMC811 at high-voltage operation, the cycling stability and rate capability of the bare NMC811 and LWO-NMC811 electrodes were compared at 3.0-4.6 V. Fig. 2a presents the specific discharge capacity over 100 cycles at 1C. Both samples have comparable initial discharge capacities at 186 mAh g⁻¹ and 184 mAh g⁻¹ for bare NMC811 and LWO-NMC811, respectively. Despite the added layer to the Li⁺ diffusion pathway created by the coating, there is no significant reduction to the initial discharge capacity since LWO has good Li⁺ conductivity [12,20,22]. By the end of 100 cycles, LWO-NMC811 maintains a specific discharge capacity of 156 mAh g^{-1} , which corresponds to 15% capacity loss. On the other hand, bare NMC811 underwent worse capacity decline to 149 mAh g⁻ resulting to a higher capacity loss of 20%. As the cycling progresses, bare NMC811 experiences a higher increase in overpotential, resulting to a bigger shift in the voltage profile (Fig. S6). Accordingly, the mean discharge voltage curve in Fig. 2b shows a steep voltage loss for bare NMC811, while LWO-NMC811 exhibits a gradual decline as a result of slower polarization growth. Both samples started at \sim 3.85 V but by the end of cycling, the bare NMC811 and LWO-NMC811 reported a discharge voltage of 3.55 V and 3.63 V, respectively. The smaller voltage fade resulted to a higher retention of specific energy density at the active material level for LWO-NMC811 (563 Wh kg⁻¹) compared with bare NMC811 (528 Wh kg⁻¹), as shown in Fig. 2c.

Fig. 2d compares the specific discharge capacities at different current densities (0.1C–5C). Generally, the discharge capacities of both samples decrease as the C-rate increases, due to the incomplete utilization of active material during rapid Li⁺ movement. At 0.1C, bare NMC811 and LWO-NMC811 exhibit comparable discharge capacities of 213 mAh g⁻¹ and 214 mAh g⁻¹, respectively. However, the higher discharge capacity of LWO-NMC811 becomes more apparent as the C-rate increases, albeit with minimal difference. In particular, at 5C, the discharge capacity is 172 mAh g⁻¹ for LWO-NMC811 and 170 mAh g⁻¹ for bare NMC811. Liu et al. [19] reported a similar trend in rate performance for a LWO-modified single-crystal NMC955, with a more evident enhancement at higher C-rates, which may be attributed to the lower mass loading and coating thickness used, compared to this study [37,38]. When the C-rate is reverted back to 0.2C, LWO-NMC811 has a higher capacity retention at 96.4% compared with bare NMC811 at 95.8%. The results demonstrate that the LWO coating has no detrimental effect to the rate performance of the bulk material. The ease of Li⁺ transport in the coated material even at high C-rates (2C and 5C) validates the effective Li⁺ conductivity of LWO. In summary, the electrochemical results show that LWO-NMC811 has superior cycling stability than bare NMC811 during high-voltage operation at 3.0-4.6 V.

3.3. Structural and interfacial evolution during cycling

To have an in-depth understanding of the mechanism of



Fig. 3. Cyclic voltammetry curves at 0.02 mV s^{-1} scan rate for (a) bare NMC811 and (b) LWO-NMC811 measured after the initial formation cycles and after 100 cycles at 1C; charging profile and contour plots showing (003) and (101) 2Theta regions of XRD patterns for (c,e) bare NMC811 and (d,f) LWO-NMC811, acquired during the 1st and 101th cycle at 0.1C. The scale bars shown are consistent for all contour plots.

enhancement implemented by the LWO coating, the structural and interfacial evolution of the cathode during high-voltage operation have been evaluated. CV curves of bare NMC811 (Fig. 3a) and LWO-NMC811 (Fig. 3b) display three pairs of oxidation and reduction peaks between 3.0 and 4.6 V [16,22,38]. The absence of additional redox peaks related to LWO demonstrates its electrochemical stability at the specified voltage window, even during the formation cycles as shown in Fig. S7. In the anodic scan following the initial formation cycles, it can be seen that both samples undergo the H2 \rightarrow H3 transition at \sim 4.26 V, a phase change that has been identified as a major cause of structural failure in Ni-rich layered oxide cathode materials due to the drastic anisotropic changes it introduces into the lattice structure during cycling [39]. Consequently, after 100 charge-discharge cycles at 1C, the samples exhibit lower redox peak intensities, with the most prominent reduction observed at the H2↔H3 region. Increase in polarization is also observed in the shift of the oxidation and reduction peaks to higher and lower potentials, respectively [14]. The evident peak fading in the H2 \rightarrow H3 region of bare NMC811 exhibits its poor structural stability after being subjected to cyclic lattice expansion and contraction, as further discussed in the operando XRD results. In contrast, the clearer H2→H3 peak in LWO-NMC811 demonstrates the superior reversibility of the coated sample [16,18,19]. These CV findings validate the benefit of using LWO as a coating to improve electrochemical performance, consistent with the higher capacity retention reported by LWO-NMC811 in Fig. 2a. The NMC811 active material sustains continuous crystallographic changes during the delithiation and lithiation processes [24]. To examine the mechanism of structural damage caused by employing a high cutoff potential, operando XRD measurements were carried out during cycling at 3.0-4.6 V. In view of the reversibility of the phase changes as shown in CV, the following discussion is limited to the delithiation process. Fig. 3c-f illustrate the charging profile and the contour plot of particular crystallographic planes obtained from the operando XRD patterns measured during the 1st and 101th charging cycles at 0.1C. The shift of the (003) peak between 18 and 20° and the (101) peak between 36 and 38° reflect the lattice changes along the *c*-axis and *a*-axis, respectively [39]. During delithiation, (003) behaves in a dynamic manner while (101) follows a single trend, in agreement with previous operando XRD studies on Ni-rich layered oxide-based materials [22,33,39-41].

As shown in Fig. 3c and d, when Li⁺ extraction from the NMC structure starts during charging, (003) moves towards lower 2θ angles. The expansion along the c-axis is due to the increasing electrostatic repulsion between oxygen anions in the neighboring layers, which are suddenly exposed to each other upon Li⁺ removal [6,39,42,43]. The expansion continues until ~3.96 V, then the peak slowly shifts to higher angles indicating the onset of the H2 phase. When the delithiation proceeds above \sim 4.20 V, a drastic contraction of the c-axis ensues, denoting the H2 \rightarrow H3 transition [44]. By the end of charging, the (003) peak for the bare NMC811 and LWO-NMC811 have shifted by ${\sim}0.85^\circ$ and $\sim 0.55^{\circ}$, respectively (marked by vertical dotted lines). Using X-ray absorption spectroscopy and density functional theory calculations, Kondrakov et al. [6] reported a reduced electron density between adjacent oxygen layers as the cause of substantial shrinkage at high state-of-charge (SOC). The charge removal from oxygen results in oxygen evolution which induces the collapse of the layered crystalline structure, as evidenced by the broader peaks (lower intensity based on the colormap) in the H2 \rightarrow H3 region [4,6]. Meanwhile, (101) only demonstrates a shift towards higher 2θ angles from the start to the end of the charging cycle, implying a continuous contraction of the *a*-axis. As Li⁺ is removed, TM ions are oxidized in order to compensate for charge loss. Consequently, the TM-O layer along the *a*-axis shrinks due to the smaller ionic radii of oxidized species [4,6,39,42,43]. Bare NMC811 (Fig. 3c) and LWO-NMC811 (Fig. 3d) exhibit similar behaviors for (003) and (101) during the initial charging cycle. As expected, weaker peak intensities are observed at the 101th charging cycle (Fig. 3e and f), indicative of the damaging impact of the cycling on lattice structure changes [45]. However, the lower peak intensity in Fig. 3e, especially at

the H2 \rightarrow H3 region of (003), shows that the bare NMC811 suffers more lattice distortion compared with its counterpart, LWO-NMC811 in Fig. 3f. These findings corroborate the CV analysis, demonstrating a strong correlation between electrochemical stability and crystallographic changes along the *c*-axis.

A review by Yin et al. [10] outlined the existence of the H2 \leftrightarrow H3 transition to be limited to Ni-rich layered oxides operated at a high cutoff potential (above 4.2 V vs Li/Li⁺), which becomes more severe when either Ni content or cutoff potential is increased [5,9]. To quantify the degree of crystallographic changes sustained by the active material, refinement of the operando XRD patterns was performed. Fig. 4a–f show the refinement results for lattice parameters *c* and *a*, and unit cell volume as a function of potential. At the 1st charging cycle, the samples undergo similar degree of variation along the *c*-axis until the start of the H3 phase at ~4.20 V. Afterwards, the trends start to diverge, with bare NMC811 experiencing higher contraction compared to LWO-NMC811. By the end of charging, the maximum Δc values reported are 4.9% (0.70 Å) and 3.6% (0.52 Å) for bare NMC811 and LWO-NMC811, respectively. On the other hand, the changes along the *a*-axis are comparable for both samples, with maximum Δa at 1.7–1.8%.

Based on these trends, the changes in the unit cell volume are highly anisotropic [42], as shown in Fig. 4c. Since the lattice parameter *a* appears to be stable from 4.2 V, it can be inferred that the unit cell volume follows the evolution of the lattice parameter *c* at higher SOC and H2 \rightarrow H3 is identified to have a significant influence on the structural stability of the lattice. As a result, bare NMC811 reports a higher maximum Δ V of 6.8% compared with LWO-NMC811 of 5.3%.

The variation of the lattice parameters and unit cell volume at the 101th charging cycle are shown in Fig. 4d-f. Except for an apparent polarization growth, the changes for bare NMC811 are minimal. However, LWO-NMC811 reports an increase in Δc , and hence ΔV , by 0.9% and 1.1%, respectively; mainly due to a higher contraction during H2→H3 transition after 100 cycles. A per cycle operando XRD measurement can provide the definite stage at which higher contraction starts to occur. Nevertheless, the refinement data are still comparable to bare NMC811 even after 100 cycles. The operando XRD results reveal that the suppressed *c*-axis shrinkage during the H2 \rightarrow H3 transition in the initial cycling stages plays a critical role in enhancing the structural stability of LWO-NMC811. As previously discussed, the presence of H2→H3 is unavoidable in Ni-rich layered oxide materials cycled at a higher voltage range. However, a closer look at the 4.4–4.6 V charging window reveals a minimal and almost negligible structural changes to both bare NMC811 and LWO-NMC811 before and after long term cycling. Since the majority of detrimental contraction occurs at the early stages of H3 (i.e. \leq 4.4 V) as shown in Fig. 4c, this study shows that the additional extraction of Li⁺ does not cause further lattice collapse.

Li⁺ deintercalation and intercalation produce volumetric changes in the individual lattice structure, and consequently, to the active material particles [24]. To compare the impact of the crystallographic changes on a microparticle level, SEM was employed to investigate the surface and cross-section morphology before and after prolonged cycling. Fresh bare NMC811 (Fig. 5a) and LWO-NMC811 (Fig. 5b) electrodes display densely packed primary particles which form the spherical secondary particle. There is no substantial particle deformation that can be observed even after the calendaring process. However, after 100 charge-discharge cycles at 1C, bare NMC811 (Fig. 5c) exhibits multiple intergranular cracking and particle fragmentation. In contrast, cycled LWO-NMC811 (Fig. 5d) maintains the secondary particle morphology and compact cross-sectional structure, with only fine hairline microcracks observed in the cross-section. The cross-sectional HR-TEM image of the cycled LWO-NMC811 sample (Fig. S8) shows that the coating layer remains intact on the surface of the NMC811 even after prolonged cycling.

The extent of particle cracking and damage in the cycled samples agrees with the trend of crystallographic changes reported in the operando XRD results. The severe cracking of the bare NMC811 particles can



Fig. 4. Variation of (a,d) *c*-axis and (b,e) *a*-axis lattice parameters, and (c,f) unit cell volume of bare NMC811 and LWO-NMC811 during the 1st and 101th charging processes.



Fig. 5. Surface and cross-sectional SEM images of the fresh and cycled (a,c) bare NMC811 and (b,d) LWO-NMC811 electrodes; Nyquist plot of (e) bare NMC811 and (f) LWO-NMC811, and (g) impedance spectra fitting results for R_{CT} at 25th, 50th, and 100th cycles.

be mainly attributed to the more drastic H2 \rightarrow H3 contraction [4,9,22, 39]. The abrupt lattice volume changes lead to the accumulation of mechanical strain in the lattice structures of neighboring particles, which can eventually lead to crack formation [9,10,23,35,41,45]. Moreover, when cracks start to propagate, the degree of damage can be exacerbated by inhomogenous Li⁺ movement across the primary and secondary particles, leading to particle pulverization [42]. The less severe H2 \rightarrow H3 contraction of LWO-NMC811 during the initial stages of cycling has lessened the strain build up in the lattice structure, thereby suppressing the formation and propagation of cracks and stabilizing the structure during extended periods of cycling. Due to the minimal changes observed in the operando XRD at 4.6 V, it can be assumed that extending the cutoff potential beyond the onset of the H2 \rightarrow H3 transition does not have a deleterious impact on a structural stability point of view.

In addition to the influence on structural stability, the presence of cracks and fragmented particles can also result in poor ionic and electronic conductivity within the composite electrode material [5]. The newly formed gaps in between the primary particles can extend into the secondary particle surface and create a pathway for electrolyte to spread into the interior structure and create new sites for harmful side reactions between the electrode and electrolyte. The emergence of these new CEI sites increases the overall cell impedance, causing further capacity fading [17,39]. The impedance evolution in bare NMC811 and LWO-NMC811 are shown in the Nyquist plots in Fig. 5e and Fig. 5f, respectively. The plots are composed of three semicircles related to (from higher to lower frequencies) interfacial resistance (R_{CEI}), grain boundary resistance (R_{GB}), and charge transfer resistance (R_{CT}), and a sloping line reflecting the Li⁺ diffusion through the bulk material [16, 20,33,40]. Noticeably, R_{CT} contributes the largest portion in the impedance values for both samples. The impedance spectra were fitted based on the equivalent circuit in Fig. S9 and the R_{CT} values are plotted in Fig. 5g. LWO-NMC811 reports a gradual growth of R_{CT} from 1.2 Ω after 25 cycles to 7.4 Ω after 100 cycles. Meanwhile, bare NMC811 demonstrates a significant R_{CT} increase from 4.4 Ω to 25.9 Ω at the same cycling periods. By the end of 100 cycles, the charge transfer impedance for bare NMC811 is almost 4 times higher than LWO-NMC811.

The continuous increase of R_{CT} reveals the dynamic changes that occur at the electrode-electrolyte interface as the cycling progresses. These changes include the non-uniform formation and growth of CEI and the emergence of a rock-salt phase, both of which emanate from the reaction between the Ni-rich cathode and the electrolyte at a high cutoff potential [39]. Several recent studies have reported that these interfacial phenomena occur due to the release of lattice oxygen from layered oxide materials at high degrees of delithiation [11,46]. Using operando emission spectroscopy, Wandt et al. [46] verified the release of reactive singlet oxygen (¹O₂) from NMC811 at 4.55 V. ¹O₂ attacks the electrolyte, resulting to its decomposition on the cathode surface and the simultaneous release of CO2 and CO gases. If unreacted, the lattice oxygen leaves the structure as O₂ gas instead [11,46]. Regardless of the reaction route, the release of lattice oxygen results in the formation of an oxygen-depleted rock-salt phase. The growth of this layer is restricted to the cathode surface due to the slow diffusion of oxygen anions in the bulk structure at ambient conditions [4,6,11,46].

It can be inferred that the sluggish kinetics of bare NMC811 stems from a thicker CEI and rock-salt phase formation on the surface of the cathode after an extended cycling at a high cutoff potential [36,38,39]. These additional interfacial structures combined with particle cracking increase the overall impedance by creating additional barriers for and slowing down the motion of charge transfer due to their poor ionic conductivities [4,5,18,35]. The gradual impedance increase for LWO-NMC811 has been enabled by the presence of LWO on the cathode surface. The coating can impede the release of reactive oxygen from the bulk structure and physically separate the cathode from the electrolyte, thereby inhibiting unwanted side reactions and irreversible phase transitions [11,14]. To validate the efficiency of the LWO coating in suppressing side reactions during cycling, the surface composition of the cycled bare NMC811 and LWO-NMC811 electrodes have been characterized by XPS analysis.

Fig. 6 compares the high resolution XPS spectra of the electrodes before and after 100 cycles at 1C for F 1s and C 1s. Due to the unclear C-C signal measured from the cycled electrodes, it was necessary to recalibrate all the XPS spectra measured after cycling so that the C-F peak appears at the same BE (\sim 291 eV) as in the fresh samples. The results show that the CEI layer primarily consists of decomposition products from the electrolyte including the carbonate-based solvent and LiPF₆ salt [22,36]. The detailed mechanism of different electrolyte decomposition routes are summarized in the work of Heiskanen et al. [47] In the F 1s spectra, both fresh electrodes (Fig. 6a) show the C-F peak (~688.0 eV) attributed to the PVDF binder [35]. After cycling, the spectra (Fig. 6c) reveal that the bare NMC811 surface is predominantly made up of LiF and Li_xPF_vO_z [38,47]. Since LiF has low ionic conductivity, its accumulation can slow down the movement of Li^+ across the electrode-electrolyte interface, and result in the sharp increase of charge transfer impedance [14,22]. In contrast, the cycled LWO-NMC811 presents comparable intensities of the PVDF binder and LiF, demonstrating the effective inhibition of CEI growth by the coating [14]. These behaviors corroborate the charge transfer impedance trend exhibited in Fig. 5g. As shown in the C 1s spectra (Fig. 6b and d), the decomposition of the carbonate-based electrolyte solvent can be validated by the relative increase at the BE corresponding to C-O and to some extent C=O in the cycled samples [36]. Similar increase at the BE corresponding to C-O can be found in the O 1s spectra in Fig. S10. Since CEI is known to grow in a non-uniform manner, additional spots on the cycled bare NMC811 and LWO-NMC811 electrodes were subjected to XPS analysis. Fig. S11 confirms that more byproducts, especially LiF, can be detected on the bare NMC811 surface for both spots. Based on the EIS and XPS results, extending the working voltage to 4.6 V can critically impact the interfacial stability of Ni-rich cathode materials. However, electrolyte decomposition can be suppressed by the LWO coating, allowing facile charge transfer across the electrode-electrolyte interface even after a long period of cycling which results in better capacity retention for LWO-NMC811.

The enhancement of charge transfer at the electrode-electrolyte interface can also be ascribed to the choice of an ionically conductive LWO coating. Several studies engaged in improving the electrochemical performance of cathode materials via surface coatings have reported LWO as a good Li⁺ conductor [12,14,18,22,48]. In this study, the ease of Li⁺ movement during deintercalation and intercalation processes has been evaluated using GITT. The relative Li⁺ diffusivity kinetics of bare NMC811 and LWO-NMC811 are compared in terms of D_sS^2/V_m^2 as a function of potential. Märker et al. [43] and Li et al. [49] have reported the same parameters in evaluating Li⁺ mobility due to the difficulty in defining accurate values for the molar volume (V_m) and active surface area (S) of the composite electrode material. The equation used to obtain the Li⁺ mobility (D_sS^2/V_m^2) values are described in the Supporting Information.

The GITT results for the 1st and 101th charge and discharge cycles are plotted in Fig. 7a-d. The results show that the kinetics of Li⁺ mobility change at different states of charge and discharge, with both samples showing similar trend in variation during delithiation and lithiation. However, LWO-NMC811 reports higher D_sS²/V_m² values compared with bare NMC811. The faster Li⁺ kinetics in the coated sample at the 1st cycle can be ascribed to the relatively high ionic conductivity of LWO, which allows smoother Li⁺ transport between the electrode and electrolyte [12,14,18,22]. However, despite the increased Li⁺ mobility in the coated sample, the relatively high coating thickness (~8-20 nm) limits the substantial enhancement of rate performance, especially at high current densities (Fig. 2d). Additionally, the higher Li ⁺ mobility at the 101th cycle may be a result of lesser CEI growth and particle cracking in the LWO-NMC811 electrode, in contrast with bare NMC811 which suffered from severe particle cracking and thicker CEI formation. Such kinetic barriers challenge the complete Li⁺ insertion/extraction



Fig. 6. F 1s and C 1s XPS spectra for bare NMC811 and LWO-NMC811 electrodes: (a,b) before and (c,d) after 100 cycles at 1C.

into the structure and negatively affects the reversible capacity retention [5].

It can be observed that the variation in Li⁺ mobility of the samples during the initial delithiation process in Fig. 7a behaves in a similar trend as the evolution of lattice *c* parameter illustrated in Fig. 4a. At the early stages of delithiation, the sparse availability of Li vacancies coupled with the narrow Li slab space result to low Li⁺ mobility [40]. As more Li⁺ are removed from the lattice structure, additional vacancies are made available for Li⁺ hopping to occur, thereby increasing the $D_s S^2/V_m^2$ values. Moreover, the Li $^+$ migration barrier is reduced by the expansion of Li slab along the *c*-axis [43,49]. The Li⁺ mobility then stabilizes at the highest level until a drastic drop takes place above \sim 4.2 V. The lattice contraction that accompanies the H2 \rightarrow H3 phase transition slows down Li⁺ movement due to the collapse of the Li slab spacing and substantial structural rearrangement [40,43]. A similar trend in reverse order is observed in the lithiation process (Fig. 7c), except at the initial stage when the Li⁺ mobility is high due to ample number of Li vacancies available [40]. At the end of discharge, the Li⁺ mobility also drops as the slab spacing gets smaller and the structure is almost fully lithiated.

After prolonged cycling at high cutoff potential, both samples experience a decrease in Li⁺ mobility. As shown in Fig. 7b, the GITT curves demonstrate negligible ($\leq 1e^{-12})\,D_sS^2/V_m^2$ values from $\sim\!\!4.2\!-\!4.6$ V. Interestingly, this potential window is consistent with the H2 $\rightarrow\!$ H3 region described in CV and operando XRD analyses, highlighting the substantial impact of this phase transition to the structural stability of the cathode material [5]. The GITT findings demonstrate a direct correlation between the Li⁺ mobility and crystal structure and underscores the importance of a stable layered structure to achieve faster Li⁺ kinetics

during the cycling process. Overall, the operando XRD and ex-situ SEM results after long-term cycling show that the repetitive extraction and insertion of Li⁺ can lead to structural changes at the crystallographic and particle level of the NMC811 cathode. Moreover, the XPS results highlight the importance of a stable cathode-electrolyte interface in achieving a superior electrochemical performance at high-voltage operation. The structural and interfacial changes that occur in the NMC811 active material at the crystallographic and particle level during cycling, result to macroscopic changes of the composite electrode [27]. To investigate the changes at the electrode level, operando electrochemical dilatometry was employed. Fig. 8a shows the thickness change in the bare NMC811 and LWO-NMC811 electrodes, during the first cycle delithiation and lithiation at 3.0-4.6 V (Fig. 8b). Since the electrode is composed of active material particles dispersed in conducting agent-binder matrix, the thickness difference recorded originates from different structural and morphological changes, including lattice expansion/contraction, CEI formation, and particle cracking [23,27,28]. The main drawback of dilatometry lies in the difficulty of separating which aspect contributes more to the thickness change [28]. However, the dilatometry curve during the initial charging seems to follow the evolution of the c parameter in Fig. 4a and d. A similar trend has also been reported by other electrochemical dilation studies on NMC811 [29, 33,50].

As Li⁺ deintercalation occurs, the electrode thickness increases as a result of lattice parameter *c* expansion [33]. The thickness reduction starts from \sim 4.2 V and continues until the end of charging, which strongly suggests a correlation with the H2 \rightarrow H3 phase transition. Similar to the operando XRD observations, the thickness change at this



Fig. 7. Li⁺ mobility as a function of potential calculated from GITT analysis of bare NMC811 and LWO-NMC811 during the 1st and 101th (a–b) delithiation, and (c–d) lithiation processes.

region is more drastic for bare NMC811 (1.34 μ m) compared with LWO-NMC811 (0.49 μ m). The maximum thickness variation during the entire initial cycling period is 4.3% for bare NMC811, compared to only 3.2% for LWO-NMC811.

Generally, a higher thickness change is unwanted as it signifies the more prominent occurrence of the undesirable reactions within the electrode, such as particle cracking [27]. Additionally, by the end of the lithiation process, bare NMC811 demonstrates a higher irreversible thickness change of 0.39 μ m compared with 0.34 μ m for LWO-NMC811. A minimal irreversible thickness change during cycling is desired as it lessens the pressure changes in the cell and aids in the optimization of battery packing design to extend cycle life [26,28,50]. The lower electrode thickness change demonstrated by the LWO-NMC811 exhibits the effectiveness of the coating in suppressing the mechanical strains in the NMC811 structure, leading to longer cycling lifetime.

The initial dilatometry results reveal that extending to 4.6 V still brings observable thickness change to the electrode material. For comparison, Pegel et al. [50] reported a maximum of 2.58% thickness change for a pristine NMC811 cycled between 3.0 and 4.3 V. Hamed et al. [32] reported 1.83% thickness change during delithiation of NMC622 up to 4.3 V. The difference in thickness variation is typically linked to electrode composition, electrolyte, and cell configuration [28]. The higher electrode thickness change in Fig. 8a can be attributed to the higher mass loading of the electrode and the elevated operating voltage [23,27]. Overall, the findings obtained show that at the early cycling stages, the mechanical strain at the crystallographic level of the active material directly influences the thickness change at the composite electrode [25]. The implementation of operando dilatomery after long

term cycling of the electrodes can provide more information as to how the electrodes behave when severe particle cracking and CEI formation are present, as shown in the SEM (Fig. 5c and d) and XPS (Fig. 6) results, respectively.

4. Conclusion

In this work, NMC811 was successfully coated with Li_xW_vO_z (LWO) to improve its high-voltage cycling stability. LWO-NMC811 delivered a capacity retention at 85% while bare NMC811 only reported 80% after 100 charge-discharge cycles (1C) at 3.0-4.6 V. A multiscale degradation mechanism analysis was performed by investigating the structural and interfacial behavior at the crystallographic level, particle level and electrode level. Operando XRD and operando dilatometry showed that the H2→H3 phase transition plays a critical role in dictating the electrochemical performance of the cathode material. This finding was corroborated with the Li⁺ mobility trend demonstrated in the GITT results. In summary, the LWO coating addresses the structural and interfacial instabilities of NMC811 based on the following: (1) suppressing severe volume changes during phase transition at high SOC to mitigate particle cracking, (2) shielding the bulk cathode material from the electrolyte to pair down the undesirable side reactions that lead to nonuniform cathode-electrolyte interface (CEI) growth, (3) facilitating the ease of Li⁺ diffusion during cycling. The key findings of this work highlight the advantage of combining ex-situ characterization with operando measurements to provide a more comprehensive investigation of the dynamic processes involved in the cell operation. In spite of the non-uniform thickness, the study shows that a good surface coating



Fig. 8. (a) Percentage of the electrode thickness change and (b) potential profile during the 1st charge-discharge cycle of bare NMC811 and LWO-NMC811.

coverage is achieved, consequently protecting the bulk NMC811 material and delivering better electrochemical performance compared to bare NMC811. Given the promising cycling stability of the LWO-NMC811 sample at high-voltage operation, it is recommended to develop the coating layer through an alternative approach that produces more uniform and controlled thickness, such as atomic layer deposition, to further enhance the rate performance of the cathode material.

CRediT authorship contribution statement

Princess Stephanie Llanos: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. Zahra Ahaliabadeh: Writing – review & editing, Conceptualization. Ville Miikkulainen: Writing – review & editing. Xiangze Kong: Writing – review & editing, Investigation, Formal analysis. Filipp Obrezkov: Writing – review & editing, Investigation. Jouko Lahtinen: Writing – review & editing, Investigation, Formal analysis. Lide Yao: Writing – review & editing, Investigation. Hua Jiang: Writing – review & editing, Investigation. Hua Jiang: Writing – review & editing, Investigation, Supervision, Project administration, Funding acquisition, Data curation, Conceptualization.

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.

Acknowledgements

This work was supported by Business Finland under the NextGenBat project (grant no. 211849). The provision of facilities and technical support by the Aalto University OtaNano- Nanomicroscopy Center and RawMatters Research Infrastructures (RAMI) are acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtener.2025.101862.

Data availability

Data will be made available on request.

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