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Ultra-Low-Strain Calcium and Magnesium Ion Storage Enabled by Tunnel-Structured MoO₃ Positive Electrode

Reona Iimura^{1,2}  | M. D. Hashan C. Peiris³  | Takashi Yabu²  | Toshihiko Mandai⁴  | Ruijie Zhu²  | Akira Nasu²  | Saneyuki Ohno¹  | Masaki Matsui²  | Itaru Honma¹  | Manuel Smeu^{3,5}  | Hiroaki Kobayashi² 

¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan | ²Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan | ³Materials Science and Engineering, Binghamton University, Binghamton, New York, USA | ⁴Research Center For Energy and Environmental Materials, National Institute for Materials Science (NIMS), Tsukuba, Japan | ⁵Department of Physics, Binghamton University, Binghamton, New York, USA

Correspondence: Reona Iimura (reona.iimura.r5@dc.tohoku.ac.jp) | Hiroaki Kobayashi (kobahi@g.ecc.u-tokyo.ac.jp)

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ABSTRACT

Rechargeable divalent batteries employing Ca or Mg metal negative electrodes have attracted considerable interest due to their low cost and potentially high energy density. However, the development of high-energy Ca and Mg batteries remains limited by the lack of oxide positive electrodes capable of reversibly accommodating divalent ions at room temperature. Here, we demonstrate a new positive electrode material, a nano-sized hexagonal tunnel-structured MoO₃ (nano-*h*-MoO₃), as a structurally robust host for both Ca²⁺ and Mg²⁺ storage, exhibiting markedly improved reversibility and capacities. Comprehensive structural analyses, supported by computational modeling, reveal a unique charge–discharge mechanism in which divalent-ion (de)insertion occurs through reversible modulation of host metal–oxygen bond lengths while retaining an intact host framework, resulting in minimal lattice expansion (<2%). This structurally resilient tunnel-oxide design provides a promising pathway for developing high-energy, practical divalent metal battery systems.

1 | Introduction

Rechargeable batteries represented by lithium-ion batteries support today's portable electronics and electric vehicles owing to their high energy densities, long cycle life, and mature manufacturing ecosystem [1]. However, the accelerating electrification of transport and stationary storage is straining supplies of rare metals due to cost volatility and sustainability concerns. These pressures have intensified interest in “earth-abundant” or “cost-effective” elements that can detach future energy storage from supply-chain risk while maintaining strict safety standards.

Nonaqueous divalent metal batteries that employ Ca or Mg metal negative electrode are promising candidates owing to the abundance of these elements and their high volumetric and gravimetric capacity [2–5]. In addition, under appropriate interface design between the negative electrode and electrolyte, Ca and Mg metal exhibit reduced dendrite formation compared with lithium metal, pointing to a compelling route to safer, high-energy storage [6, 7]. Yet the realization of practical rechargeable Ca or Mg batteries remains fundamentally limited. This is not only by the scarcity of electrolytes that enable reversible metal deposition/stripping at room temperature, but also the lack of promising positive electrode materials. In particular, no materials have been

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able to reversibly host divalent cations at room temperature while simultaneously achieving high capacity and high operating voltage. To date, the most reliable host structures for room-temperature operation have been a small subset of chalcogenides, notably chain-type VS_4 and chevreel-phase Mo_6S_8 [8, 9]. While these phases accommodate $\text{Ca}^{2+}/\text{Mg}^{2+}$ with comparatively fast kinetics, their average discharge voltages are low (e.g., $\text{Ca}||\text{VS}_4 \sim 1.7$ V, $\text{Mg}||\text{Mo}_6\text{S}_8 \sim 1.0$ V), thereby constraining the achievable energy density. Pushing the potential upward toward values competitive with state-of-the-art positive electrodes of lithium-ion batteries requires oxide materials that enable higher redox operation [10, 11].

Designing oxide hosts for divalent-ion intercalation, however, presents significant challenges for room-temperature operation. The high charge density of divalent ions such as Mg^{2+} results in strong electrostatic interactions with the anionic framework, leading to sluggish solid-state diffusion and reduced accessible capacity [12, 13]. Additionally, accumulated divalent ions at surface or defect sites induce phase transformations or conversion reactions, and ultimately accelerate capacity fade [14, 15]. To mitigate these issues, many studies have explored elevated-temperature operation (up to $\sim 150^\circ\text{C}$). According to a survey of more than 220 reports on oxide positive electrodes for Mg batteries [11], most studies that provide evidence of Mg^{2+} intercalation reactions operated above room temperature to enhance the divalent-ion mobility in the solid state. The median capacity improved from 59 to 106 mAh g^{-1} under these conditions. In particular, $\alpha\text{-MnO}_2$ (150°C) [16], ZnMnO_3 (150°C) [17], and MgCrMnO_4 (95°C) [18] electrodes exhibited reversible capacities of approximately 100, 120, and 110 mAh g^{-1} , respectively. Although these elevated-temperature approaches achieved some improvement in capacity and reversibility, they remain impractical for most applications due to the lack of suitable electrolytes and cell components for high-temperature operation.

In recent research on oxide materials for room-temperature operation, particle downsizing has emerged as an effective strategy to enhance electrochemical performance by shortening cation diffusion pathways [12, 19]. In particular, our studies have focused on $\alpha\text{-MnO}_2$, a promising host identified through DFT calculations [20] and 150°C operation test [16] as both a Ca and Mg battery host, respectively. By employing an alcohol-solution process, we successfully synthesized ultrasmall $\alpha\text{-MnO}_2$ nanoparticles (<10 nm) with a low aspect ratio ($c/a \approx 2$) [21]. This nanostructured material exhibited markedly improved utilization of the positive electrode compared with conventional counterparts. However, despite improved utilization in both Ca and Mg battery systems, its reversibility remained limited due to irreversible phase transitions, either into a highly distorted tunneled structure or into a stable rock salt phase, indicating that divalent ions tend to be trapped within the tunnel framework and progressively reduce accessible capacity. These findings highlight that the design of a structurally robust host framework is essential to achieving long-life oxide-type electrodes.

To demonstrate the necessity of a robust framework for divalent-ion insertion, we suggest a new positive-electrode material, a hexagonal tunnel-structured MoO_3 ($h\text{-MoO}_3$), which is geometrically predisposed to accommodate structural relaxation [22]. In both Ca and Mg battery systems, the nanosized $h\text{-MoO}_3$

(nano- $h\text{-MoO}_3$) positive electrode exhibited superior capacity and remarkable structural reversibility, enabling reversible divalent cation insertion with no phase transitions and minimal lattice distortion, supported by computational approaches. In particular, a Mg battery employing a fluorinated-alkoxyborate electrolyte [23], which offers superior compatibility with the Mg negative electrode, delivered excellent cyclability, retaining stable performance for 100 cycles.

2 | Results and Discussion

2.1 | Synthesis and Characterization of $h\text{-MoO}_3$

Molybdenum trioxide (MoO_3) exists in three main structural polymorphs: the thermodynamically stable orthorhombic phase ($\alpha\text{-MoO}_3$), which has a layered structure; the metastable monoclinic phase ($\beta\text{-MoO}_3$), composed of MoO_6 octahedral units forming a 1×1 tunnel structure; and the metastable hexagonal phase ($h\text{-MoO}_3$), which features a 1D tunnel framework. In $h\text{-MoO}_3$, the tunnels run along the c -axis and are surrounded by 12 MoO_6 octahedra (Figure 1a). The octahedra are corner-shared along the a direction, while edge-sharing occurs along the c direction, establishing a robust 1D tunnel network. Additionally, the tunnel size of $h\text{-MoO}_3$ is sufficiently large to accommodate cations of various ionic radii, and the nano $h\text{-MoO}_3$ synthesized in this study is therefore expected to facilitate reversible insertion and de-insertion of both monovalent and divalent cations at room temperature.

Figure S1 shows the schematic illustration of the synthesis process for $h\text{-MoO}_3$ and nano- $h\text{-MoO}_3$. Commercial $\alpha\text{-MoO}_3$ and NH_4Cl were first dissolved in an H_2O_2 aqueous solution, transferred to an autoclave, and heated at 150°C to obtain $h\text{-MoO}_3$. The product was then ball-milled using ZrO_2 balls at 600 rpm, yielding the blueish nano- $h\text{-MoO}_3$.

Figure 1b shows the X-ray diffraction (XRD) patterns and Rietveld refinement results of $h\text{-MoO}_3$ and nano- $h\text{-MoO}_3$, the latter obtained by ball-milling of the as-synthesized $h\text{-MoO}_3$. The as-prepared $h\text{-MoO}_3$ exhibited high crystallinity and a single phase, which was indexed to the monoclinic structure with the $P6_3/m$ space group. CHN elemental analysis and thermogravimetric (TG) analyses (Figure S2), corrected for 2 wt.% absorbed water, confirmed the presence of nitrogen with an N/Mo ratio of 0.140. This nitrogen is reasonably attributed to NH_4^+ ions accommodated within the hexagonal tunnels, and the measured content agrees well with previously reported values [22]. In contrast, ball-milling yields broader diffraction peaks with reduced intensities in the XRD patterns of nano- $h\text{-MoO}_3$, while no additional phases were observed, indicating that particle downsizing occurred without structural decomposition. The reduced crystallite size estimated using the Halder–Wagner equation based on Rietveld refinement further supports the successful reduction in grain size (Table S1). Notably, the N/Mo ratio decreased to 0.118 after ball-milling. According to a previous study [24], the decrease in NH_4^+ content is attributable to partial decomposition of tunnel NH_4^+ species during ball-milling, where NH_3 is released by the heat and mechanical impact generated during milling, and residual proton species are likely left in the tunnel framework. In this study, these proton species were not directly quantified; however, the decrease

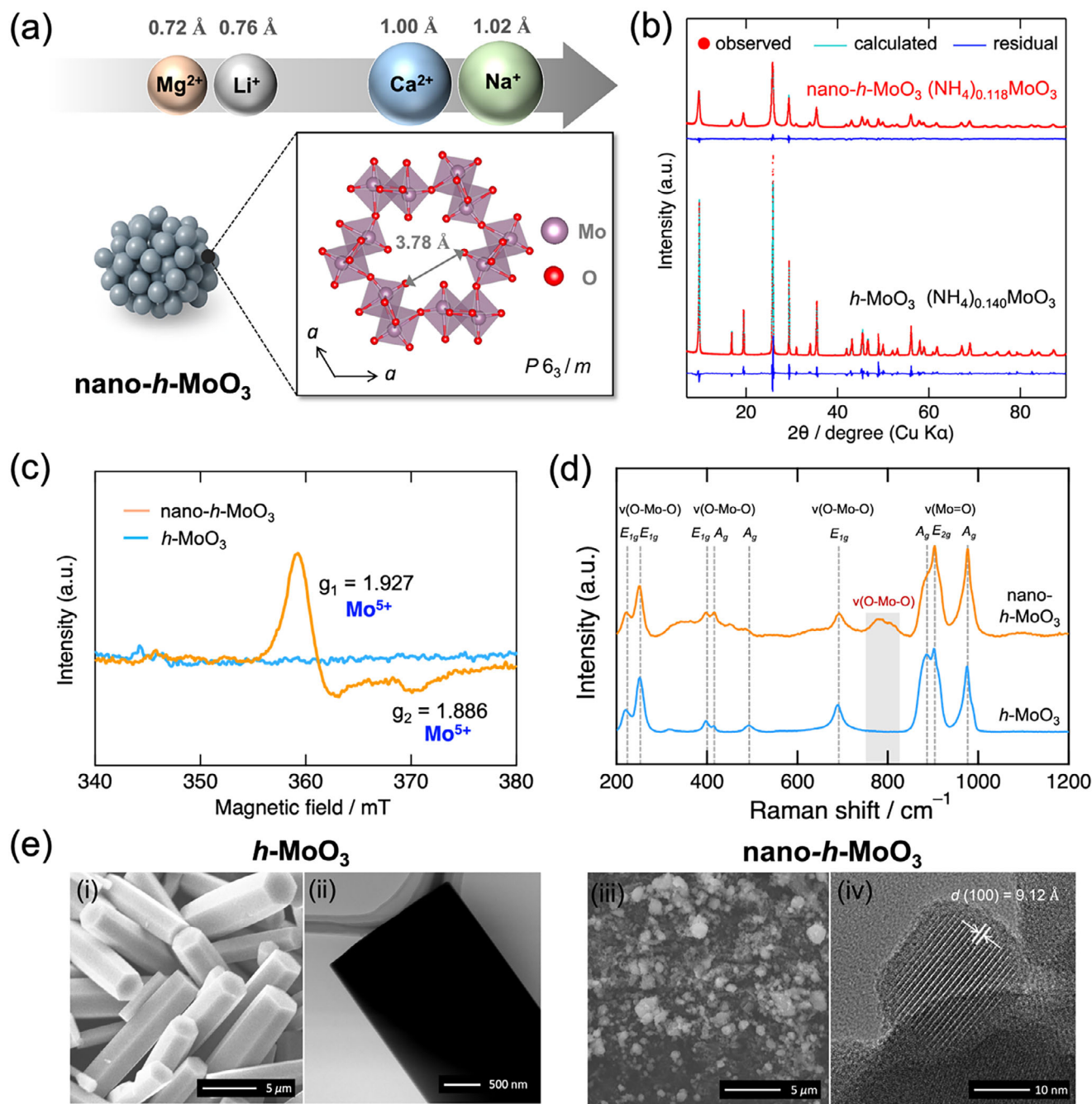


FIGURE 1 | (a) The crystal structure of $h\text{-MoO}_3$ and ionic radius of each guest cation, (b) XRD patterns with fitting curves by Rietveld refinement, (c) EPR spectra, (d) Raman spectra, (e) SEM images of (i) $h\text{-MoO}_3$ and (iii) $\text{nano-}h\text{-MoO}_3$, HR-TEM images of (ii) $h\text{-MoO}_3$ and (iv) $\text{nano-}h\text{-MoO}_3$.

in the N/Mo ratio from 0.140 to 0.118 suggests an upper-limit amount of approximately 0.022 per Mo, assuming one residual proton remains for each released NH_3 molecule. As shown in Figure S2, the lowered phase-transition temperature from $h\text{-MoO}_3$ to layered $\alpha\text{-MoO}_3$ [25] was also observed in the $\text{nano-}h\text{-MoO}_3$. This decrease is attributed to a reduction in NH_4^+ content, which serves as a structural pillar stabilizing the hexagonal tunnel framework. Therefore, the reduction in NH_4^+ concentration weakens the structural integrity of the tunnel, facilitating easier phase transformation of $\text{nano-}h\text{-MoO}_3$ compared to $h\text{-MoO}_3$. In addition, the lattice volume of $\text{nano-}h\text{-MoO}_3$ increased by approximately 1% compared with $h\text{-MoO}_3$, while the average Mo—O

bond length became longer. This bond-length variation was also confirmed by pair distribution function (PDF) analysis. As shown in Figure S3, the Mo—O(1) distance, which is assigned to the Mo—isolated O, was longer in $\text{nano-}h\text{-MoO}_3$ than in $h\text{-MoO}_3$ [26]. This structural change can be mainly attributed to the difference in the NH_4^+ content in the tunnels. The smaller amount of NH_4^+ in $\text{nano-}h\text{-MoO}_3$ likely induces shrinkage of the isolated-O hexagonal area, resulting in elongation of the Mo—O(1) distance. To investigate the Mo valence state before and after ball-milling, electron spin resonance (EPR) measurements were performed (Figure 1c). $h\text{-MoO}_3$ exhibited no detectable signal, whereas $\text{nano-}h\text{-MoO}_3$ displayed two distinct peaks at $g = 1.927$ and 1.886 ,

which are unique peaks to Mo^{5+} species [27]. Importantly, no signal corresponding to oxygen vacancies (typically observed near $g \approx 2.0$) was detected, indicating that the oxygen framework remained unchanged upon nanoparticulation. To further investigate the Mo state, both Mo 3d X-ray photoelectron spectroscopy (XPS) and Mo K-edge X-ray absorption fine structure (XAFS) analyses, as shown in Figure S4, were conducted. In nano- $h\text{-MoO}_3$, new spectral features corresponding to Mo^{5+} appeared in the XPS spectra (Mo^{6+} : $3d_{5/2} = 232.8$ eV, $3d_{3/2} = 236.02$ eV, Mo^{5+} : $3d_{5/2} = 231.7$ eV, $3d_{3/2} = 234.5$ eV) [28, 29] and the XAFS absorption edge exhibited a slightly lower-energy shift. These changes were relatively minor, as XPS analysis with the semi-quantitative fitting revealed that only about 3% of Mo^{6+} was reduced to Mo^{5+} . Raman spectroscopy (Figure 1d) was employed to probe the vibrational modes of the tunnel framework. Most of the observed peaks, assigned to Mo—O—Mo and terminal Mo=O vibrations, were consistent with previously reported results [30, 31] and remained unchanged before and after nanoparticulation of $h\text{-MoO}_3$. However, additional peaks appeared in the spectrum of nano- $h\text{-MoO}_3$ at around 800 cm^{-1} . These new features are attributed to O—Mo—O vibrational modes that are characteristic of the layered $\alpha\text{-MoO}_3$ structure [32]. The emergence of these modes is likely related to the reduced amount of NH_4^+ ions in nano- $h\text{-MoO}_3$; with fewer NH_4^+ ions occupying the tunnels, the in-plane O—Mo—O vibrations toward the tunnel might become activated [33]. Figure 1e(i, iii) and (ii, iv) present the scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) images, respectively. $h\text{-MoO}_3$ exhibited well-defined hexagonal prismatic crystals with lengths of up to $\sim 30\text{ }\mu\text{m}$, consisting of single primary particles from the HR-TEM image (Figure 1e(ii)). In contrast, nano- $h\text{-MoO}_3$ showed markedly reduced particle sizes in the range of $0.5\text{--}2\text{ }\mu\text{m}$. HR-TEM observation of nano- $h\text{-MoO}_3$ (Figure 1e(iv)) further revealed that these particles were composed of aggregated, nearly spherical primary crystallites with an average size of $\sim 30\text{ nm}$. In addition, clear lattice fringes with a spacing of $9.12\text{ }\text{\AA}$ were observed, corresponding to the (100) plane identified in the XRD patterns. Table S2 summarizes the specific surface area values obtained from Brunauer–Emmett–Teller (BET) measurements. $h\text{-MoO}_3$ exhibited a very low specific surface area ($<1\text{ m}^2\text{ g}^{-1}$), whereas nano- $h\text{-MoO}_3$ showed a markedly higher specific surface area of $75\text{ m}^2\text{ g}^{-1}$. This substantial increase is primarily attributable to the nanoparticulation of $h\text{-MoO}_3$, which effectively reduces particle size and increases the exposed active surface area.

2.2 | Electrochemical Performance of $h\text{-MoO}_3$ Positive Electrode in Ca and Mg Battery Cells

For the electrochemical evaluation of Ca and Mg battery cells with nano- $h\text{-MoO}_3$ positive electrode, discharge-charge cycling tests were conducted, highlighting the markedly enhanced capacity and reversibility. The tests were performed using coin-type cells composed of a Ca or Mg foil negative electrode and the electrolyte of $0.3\text{ mol dm}^{-3}\text{ Ca}[\text{B}(\text{hfp})_4]_2$ in monoglyme (G1) or $0.3\text{ mol dm}^{-3}\text{ Mg}[\text{B}(\text{hfp})_4]_2$ in diglyme (G2) (hfp: hexafluoroisopropoxyl). Figure S5 presents the voltage profiles of Ca and Mg battery cells employing $h\text{-MoO}_3$ positive electrode. The Ca and Mg battery cells delivered discharge capacities of 40 and 52 mAh g^{-1} , respectively, which are significantly lower than the theoretical capacity of 372 mAh g^{-1} ($\text{MoO}_3 + \text{M}^{2+} + 2\text{e}^- \rightarrow \text{MMoO}_3$, M : Ca

or Mg). This limited capacity can be attributed to the restricted electrochemically active surface area, as $h\text{-MoO}_3$ consists of micron-sized, well-ordered particles. This morphology is evident in the SEM image of the electrode (Figure S6a), where the white regions correspond to $h\text{-MoO}_3$ particles and the surrounding black regions to acetylene black. In contrast, Ca and Mg battery cells employing nano- $h\text{-MoO}_3$ positive electrode exhibited markedly enhanced capacities, as shown in Figure 2a,b. This improvement is attributed not only to the significantly increased electrochemically active surface area but also to the shortened solid-state diffusion length, both of which result from particle size reduction at the secondary particle level (Figure 1e(iii) and Figure S6b) and, more importantly, at the primary crystallite level (Figure 1e(iv)).

In the Ca battery cell with the nano- $h\text{-MoO}_3$ positive electrode (Figure 2a), the initial discharge capacity reached $\sim 195\text{ mAh g}^{-1}$. However, significant capacity fade occurred, with the discharge capacity decreasing to $\sim 70\text{ mAh g}^{-1}$ by the fifth cycle. This rapid degradation is primarily attributed to the formation of passivation layers (e.g., CaF_2 and CaO) on the negative electrode during cycling, as widely reported in previous studies [34–36]. These insulating layers strongly hinder Ca stripping/plating, leading to large overpotential and severe capacity loss in the full cell, particularly during charging. The corresponding dQ/dV plots up to the second cycle revealed discharge peaks at $\sim 1.8\text{ V}$ and charge peaks at $\sim 3.5\text{ V}$.

On the other hand, the Mg battery cell delivered an initial discharge capacity of $\sim 130\text{ mAh g}^{-1}$, which is lower than Ca battery cell (Figure 2b). Although the first charge capacity was lower than the discharge capacity, both discharge and charge capacities gradually increased upon cycling, with the coulombic efficiency approaching nearly 100% after several cycles. Notably, the voltage profiles retained their overall shape even after repeated cycling. The corresponding dQ/dV plots revealed discharge peaks at $\sim 1.1\text{ V}$ and charge peaks at $\sim 3.0\text{ V}$, with negligible peak shifts during cycling, indicating that the electrochemical reactions were highly reversible.

To summarize the electrochemical performance of both batteries, the Mg battery cell exhibited markedly higher reversibility, primarily owing to the excellent interfacial compatibility between the electrolyte and the Mg metal electrode. In contrast, the Ca battery cell showed higher capacity (195 mAh g^{-1} , compared with 130 mAh g^{-1} for the Mg battery cell), implying that Ca^{2+} exhibits higher mobility than Mg^{2+} inside nano- $h\text{-MoO}_3$ structure.

To quantify the amount of divalent-ion insertion and de-insertion and to clarify the reaction mechanism of nano- $h\text{-MoO}_3$ electrodes in Ca and Mg battery cells, inductively coupled plasma optical emission spectrometry (ICP-OES), SEM-EDX, and TEM-EDX analyses (Table S3 and Figure S7) were conducted. These elemental analyses confirmed that the large amounts of Ca^{2+} and Mg^{2+} insertion and de-insertion. However, the quantified values were smaller than those estimated from the electrochemical charge-discharge profiles, suggesting the presence of side reactions that contribute to the measured capacities. According to previous studies, side reactions frequently occur and can substantially affect the measured capacity, particularly prominent in Mg battery systems paired with oxide-type positive electrodes. A

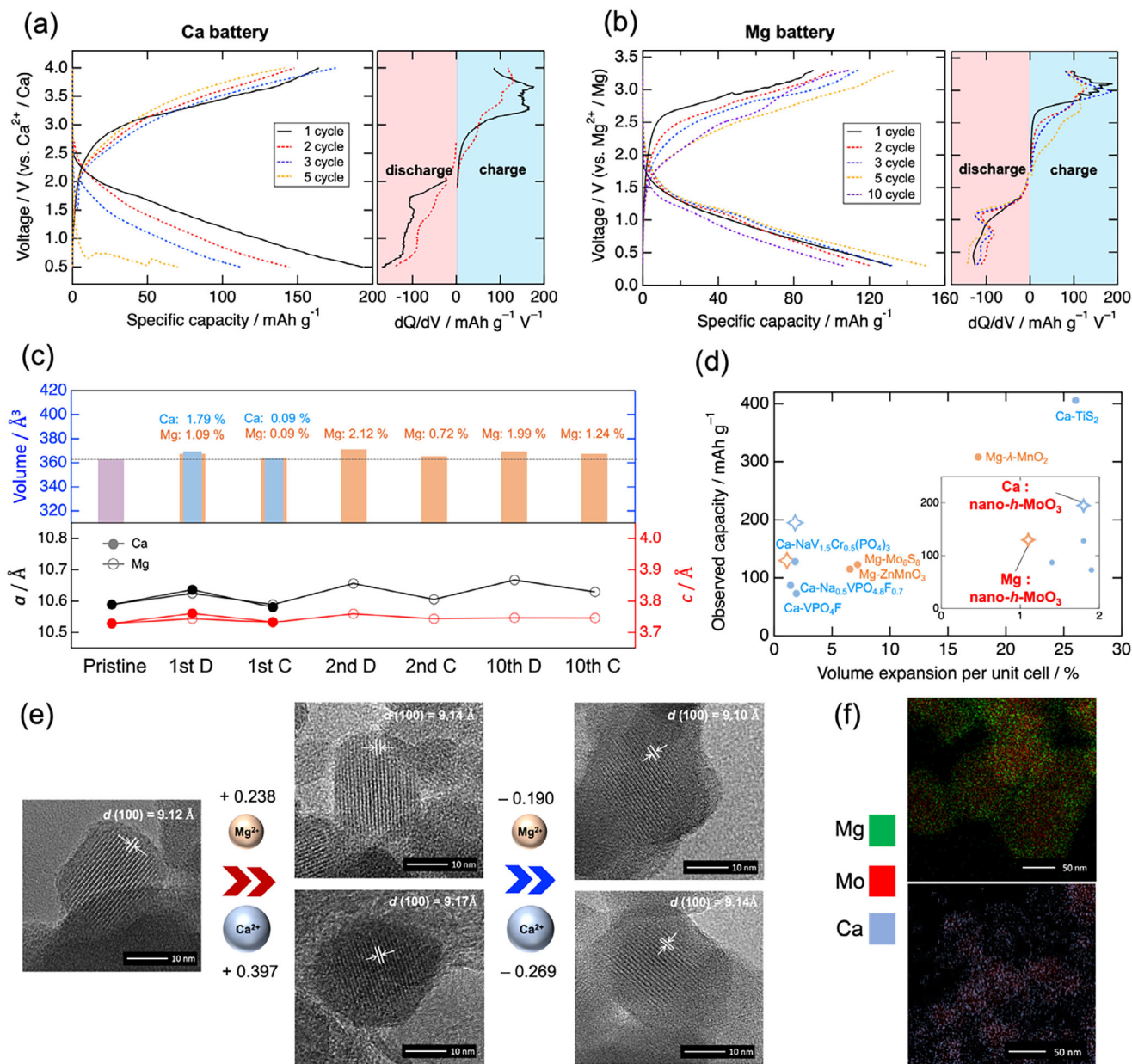


FIGURE 2 | Voltage profiles and corresponding dQ/dV plots of nano-*h*-MoO₃ positive electrode in (a) Ca battery cell (electrolyte water content is 200 ppm) and (b) Mg battery cell (electrolyte water content is 20 ppm) at 0.1 C rate (37 mA g⁻¹), (c) Lattice parameter and volume changes of nano-*h*-MoO₃ during cycling in Ca and Mg cells calculated by Rietveld refinement, (d) Volume expansion rate of nano-*h*-MoO₃ in Ca and Mg battery cells (e) HR-TEM images of nano-*h*-MoO₃ after discharge/charge in Ca and Mg battery cells. The colored arrows indicate the electrochemical states (red: discharge, blue: charge), and the numbers denote the corresponding amounts of inserted/de-inserted ions in each state. (f) TEM-EDX analysis of discharged nano-*h*-MoO₃ from Ca and Mg battery cells.

plausible explanation involves contributions from H⁺ insertion [37] and the formation of a cathode–electrolyte interface (CEI) [38, 39]. In the case of H⁺ insertion, protons may originate from trace H₂O inherently present in the electrolyte or may be generated via either decomposition on the Mg negative electrode [40]. Note that the residual H⁺ species originally present in the tunnels may, in principle, be electrochemically de-inserted. However, their amount is limited to approximately 0.022 per Mo, corresponding to only ~4 mA h g⁻¹, and therefore they are unlikely to be the main source of the side-reaction-related capacity. Additional factors may also contribute to side reactions, including corrosion of the current collector [37] and dissolution

of active materials into the electrolyte [41], both of which are strongly influenced by the water content in the electrolyte.

Figure S8 presents the cycling performance of the cell. The nano-*h*-MoO₃ electrode exhibited excellent cyclability, maintaining a stable capacity of 73 mA h g⁻¹ for up to 100 cycles. This capacity retention is remarkable when compared with other Mg battery cells employing the same non-corrosive [B(hfip)₄]⁻-based electrolyte but different oxide-type positive electrodes, which generally show much lower cycle life—for example, ~20 cycles for nano tunnel-type MnO₂ (hollandite or romanechite) [42], ~10 cycles for nano Cu–Mn spinel oxide [19], and ~10 cycles

for amorphous Mg–Li–Ti–Mo oxide [43]. However, similar to the preceding works, capacity fade and a gradual decrease in coulombic efficiency were also observed here.

To explore the origin of this capacity fade in the Mg battery cell with a nano-*h*-MoO₃ positive electrode and support the estimated side reaction, the water content in the electrolyte was intentionally increased from 20 to 200 ppm. Figure S9a shows the voltage profile of the Mg battery cell with the nano-*h*-MoO₃ electrode using an electrolyte containing 200 ppm water. In the first cycle, both the discharge and charge capacities were higher than those obtained with an electrolyte containing 20 ppm water. However, upon further cycling, the operating discharge and charge voltages gradually shifted to a lower position, and the coulombic efficiency dramatically decreased significantly due to an excess of charge capacity relative to discharge capacity. Figure S9b compares the Mg/Mo ratios determined by elemental analysis with those calculated from electrochemical capacities. With the 200 ppm H₂O-electrolyte, the fraction of Mg contributing to the measured capacity was dramatically reduced, indicating that a large portion of the capacity arose from side reactions. XRD analysis of the nano-*h*-MoO₃ electrodes after 10 cycles (Figure S9c) revealed that the diffraction peaks corresponding to the *h*-MoO₃ phase had almost completely disappeared when cycled with the 200 ppm water-containing electrolyte. In contrast, for the cell with 20 ppm water, the *h*-MoO₃ phase was still evident after 10 cycles, although with weaker peak intensities compared to the pristine state. Furthermore, SEM–EDX analysis of the GF/C separator on the positive electrode side (Figure S9d) revealed the homogeneous distributions of Mo along with Mg and F elements, where Mg and F are supposed to be from Mg[B(hfip)₄]₂ salt, after 10 cycles in the 200 ppm water-containing electrolyte. These analyses strongly confirmed the dissolution of *h*-MoO₃ into the electrolyte. This dissolution of MoO₃ leads to the loss of the higher-potential, reversible Mg²⁺ insertion reaction. The dissolved Mo species subsequently acts as a redox shuttle, promoting irreversible decomposition, dissolution, and precipitation reactions that occur predominantly at low potentials and induce significant polarization. As a result, the charge–discharge profiles progressively shift toward lower voltages, as observed in Figure S9a. This side-reaction mechanism can also account for the capacity fade observed in Mg battery cells even when the electrolyte contains as little as 20 ppm water (Figure S8).

Figure S10(i, ii) shows the *ex situ* XRD patterns of nano-*h*-MoO₃ electrodes after discharge and charge in Ca and Mg battery cells. No apparent peak shifts or phase transformations were observed in either system, indicating that nano-*h*-MoO₃ remains electrochemically stable over a wide potential window. To further investigate subtle structural changes, Rietveld refinement was performed on the nano-*h*-MoO₃ electrodes before and after cycling (Figure 2c). During the first discharge in both battery systems, the lattice constants *a* and *c* exhibited slight increases, resulting in only minor lattice volume expansions (Ca battery: 1.79%; Mg battery: 1.09%). These small expansions can be attributed to the reduction of Mo⁶⁺ to Mo⁵⁺, which is consistent with the Mo *K*-edge XANES negative shifts shown in Figure S11a, b. Notably, the lattice expansion was more pronounced in the Ca battery cells than in the Mg battery cells, primarily because larger Ca insertion induced a greater extent of Mo⁶⁺ reduction to

Mo⁵⁺. In addition, ion-specific local structural changes associated with Ca²⁺ and Mg²⁺ insertion, which will be discussed in detail later, also contribute to this difference. Upon the first charge, the lattice parameters nearly returned to their pristine values, demonstrating the high structural robustness of nano-*h*-MoO₃. These ultra-low-strain Ca²⁺ and Mg²⁺ insertion properties of nano-*h*-MoO₃ are particularly remarkable, especially considering its role as a host material for high charge-density carriers such as Mg²⁺. Compared with other reported divalent-ion insertion materials summarized in Figure 2d (experimental data) and Table S4 (experimental and computational data), nano-*h*-MoO₃ exhibits a favorable combination of relatively high reversible capacity and exceptionally small lattice volume change. Although higher capacities in many reported materials are often accompanied by larger structural expansion, nano-*h*-MoO₃ deviates from this general trend, highlighting the robust nature of the *h*-MoO₃ tunnel framework.

For instance, the volume change of Ca insertion is even smaller than that of typical polyanion-type positive electrodes, which are well known for their structural robustness. Furthermore, nano-*h*-MoO₃ demonstrates only ~1–2% volume expansion even after 10 cycles in Mg battery cells, highlighting its superior structural stability compared to conventional divalent-ion electrode materials. Consistent with this behavior, no apparent phase changes of nano-*h*-MoO₃ were observed in either system from HR-TEM observation (Figure 2e). The lattice fringes corresponding to the (100) plane remained almost unchanged after discharge and charge, with only a slight expansion detected upon discharge. Furthermore, TEM-EDX mapping (Figure 2f) revealed that Mg and Ca were distributed almost homogeneously within the primary particles of the discharged electrodes. Note that Mg was not uniformly distributed to the particle center because its smaller overall insertion amount compared to Ca, which resulted in partially unreacted regions. Furthermore, Figure S12 presents the cyclic voltammetry (CV) curves of the Mg battery two-electrode cell, providing additional evidence for the Mg intercalation reaction. As shown in Figure S12b, the well-defined cathodic and anodic peaks originate predominantly from diffusion-controlled processes, with minimal contribution from (pseudo)capacitive behavior. With increasing sweep rate, the (pseudo)capacitive contribution becomes more pronounced (Figure S12c). In contrast, at lower sweep rates, the electrochemical response is dominated by diffusion-controlled reactions, indicating that Mg²⁺ storage in nano-*h*-MoO₃ primarily proceeds via solid-state intercalation rather than surface-controlled processes. Taken together, the absence of significant lattice disruption and the uniform distribution of inserted ions demonstrate that nano-*h*-MoO₃ undergoes a stable intercalation-type reaction, rather than a conversion or surface-captive mechanism.

To clarify the origin of the ultra-low-strain intercalation behavior of Ca²⁺ and Mg²⁺, it is necessary to identify their insertion sites and diffusion pathways within the *h*-MoO₃ framework. However, the large hexagonal tunnels and the complexity of divalent cation coordination environments make purely experimental determination impractical. Therefore, in the following section, we employ density functional theory (DFT) combined with nudged elastic band (NEB) calculations to predict the stable insertion sites and diffusion pathways of Ca²⁺ and Mg²⁺, providing mechanistic insight into their distinct intercalation behaviors.

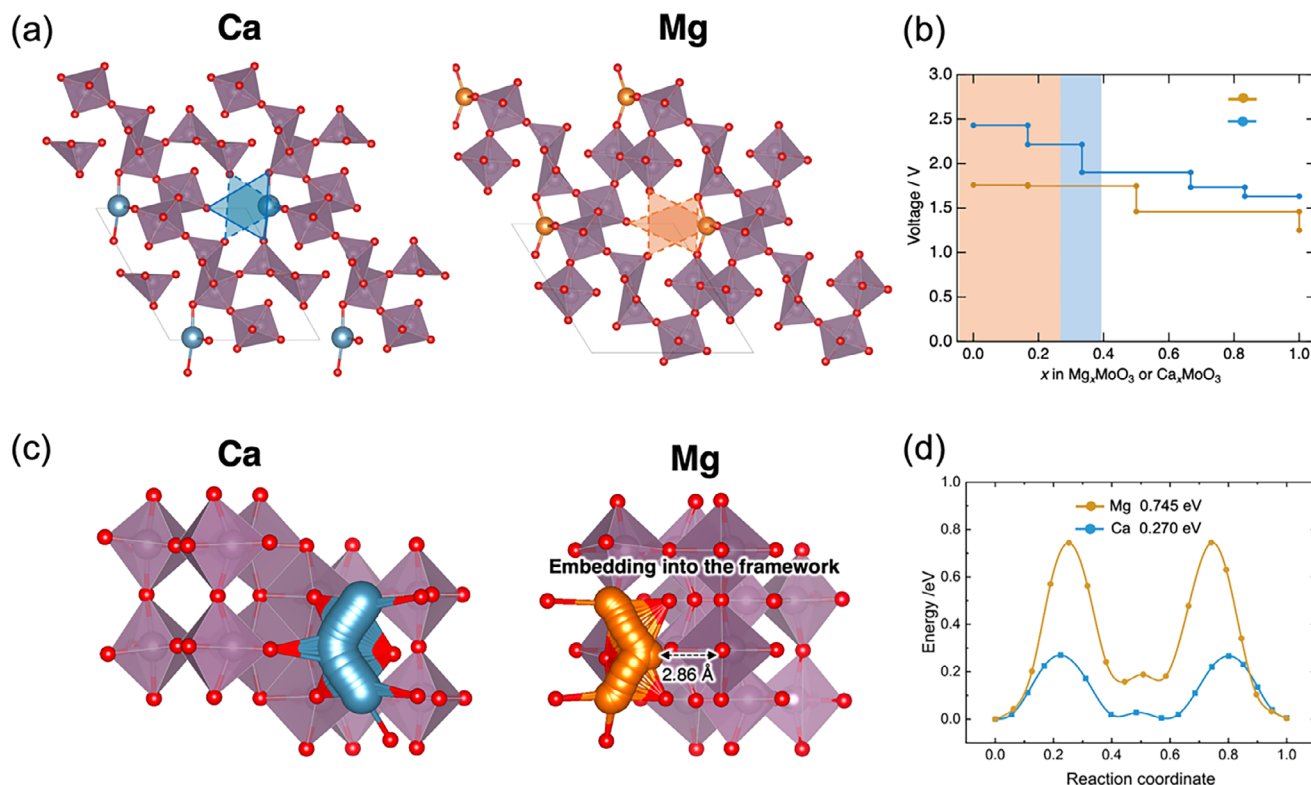


FIGURE 3 | (a) Stable Ca (left) and Mg (right) insertion sites in *h*-MoO₃ crystal, (b) Calculated voltage profile with the Ca/Mg insertion with the shaded region indicating the experimental range for cation insertion, (c) Diffusion pathway for the intercalant, Ca(left) and Mg(right) with the diffusing intercalant atoms superimposed into one structure to illustrate the diffusion path, (d) Energetics of intercalant diffusion calculated using NEB.

2.3 | Computational Prediction of Ca²⁺ and Mg²⁺ Diffusion in *h*-MoO₃

To predict the Mg and Ca diffusion pathways inside the tunnel of the *h*-MoO₃ structure, various potential insertion sites were examined to evaluate the stability of Ca/Mg insertion (Figures S13–S15). The inserted ions (*M*), Ca and Mg, were both found to stabilize by anchoring to four framework oxygen atoms at distances of 2.25–2.47 Å for Ca–O and 1.95–2.10 Å for Mg–O (Figure 3a). The inserted ion resides off-axis relative to the tunnel center, giving an asymmetric four-coordinated environment. Additionally, three energetically equivalent sites exist in the hexagonal tunnel framework, and another three equivalent sites on the next layer. Bond-valence analysis of the relaxed intercalated cell identifies *M* as M²⁺, yielding a mixed Mo valence, with two Mo⁵⁺ sites and the remaining Mo as Mo⁶⁺. This satisfies charge neutrality per M²⁺ and indicates that the two electrons introduced by Ca localize on nearby Mo centers. The shorter bond length of Mg–O compared to Ca–O results in the ability of the Mg²⁺ to embed deeper into the tunnel framework compared to Ca²⁺.

The theoretical voltage was calculated by progressively adding the intercalant atoms into the structurally relaxed *h*-MoO₃ system (Figure 3b).

The voltage can be obtained as,

$$V = - \frac{E_{\text{discharged}} - E_{\text{charged}}}{\eta}$$

where E_{charged} , $E_{\text{discharged}}$, and η refer total energy of the constituent battery components in the charged/discharged state and the number of electrons transferred, respectively [44]. Here, when inserted cations (*M*) are inserted.

$$V = - \frac{E_{M_{x+n}MoO_3} - E_{M_xMoO_3} - nE_M}{nZ}$$

where $E_{M_xMoO_3}$ and $E_{M_{x+n}MoO_3}$ are the energies of the charged and discharged positive electrodes, E_M is the energy per atom of the pure metal anode (Ca/Mg), and Z is the valency of the inserted cation (+2 for Ca and Mg), and n number of ions inserted [44]. To ensure conformity to thermodynamic principles, this equation can only be applied to those cation insertion concentrations residing on a convex hull of formation energies. Ca insertion into *h*-MoO₃ results in an initial voltage of 2.43 V, whereas it provides a much lower 1.76 V for Mg insertion. As more intercalant atoms are added, the voltage in Ca_xMoO₃ drops to 1.63 V, whereas Mg_xMoO₃ is driven to 1.25 V.

Then, the migration energy barriers for the inserted atoms were calculated to move through the tunnel structure of the *h*-MoO₃, as shown in Figure 3c. The Ca²⁺ diffuses as an off-axis ‘double hop’. In the initial lattice, the adjacent site Ca²⁺ is fourfold coordinated with O atoms. During migration, it stays close to the tunnel framework and moves along a shallow arc, successively breaking and forming Ca–O bonds with adjacent oxygens in two well-defined hops (Figure S16a). At the saddle point, the coordination decreases transiently to 3 weak O contacts, and Ca passes a local bottleneck defined by opposing O rows. Ca then re-establishes

four short Ca–O bonds at the neighboring wall adjacent site before repeating the second hop. The trajectory traced in Figure 3c corresponds to this wall-hugging path, and the calculated nudged elastic band (NEB) profile in Figure 3d gives a low barrier of about 0.270 eV for this hop, consistent with facile diffusion of Ca along the tunnels.

The Mg ion diffuses in a similar manner to Ca ion diffusion, with a migration barrier for a single hop of 0.745 eV, as shown in Figure 3d. Comparatively, the significant energy difference relative to Ca is attributed to the more inward embedding of the Mg ion into the contact oxygens in the intermediate layer due to the shorter Mg–O bond lengths (2.86 Å). The longer length of Ca–O seems to enable the Ca ions to glide along the wall of the tunnel more easily compared to Mg, which gets trapped (Figure 3c and Figure S16b). Therefore, Ca ion shows considerably easier diffusion enabled by the ability to glide more easily along the tunnel framework.

2.4 | Local and Tunnel Structural Changes in Nano-*h*-MoO₃ Induced by Ca²⁺ and Mg²⁺ Insertion

To elucidate the origin of the ultra-low-strain discharge/charge behavior of nano-*h*-MoO₃, it is crucial to identify the preferred insertion sites and diffusion pathways of Mg²⁺ and Ca²⁺ within the hexagonal tunnels, which were clarified by DFT and NEB calculations, and to correlate them with experimentally observed local structural changes. Here, we first employed Mo *K*-edge wavelet transform-extended X-ray absorption fine structure (WT-EXAFS), which is highly sensitive to local coordination and can capture subtle bond-length variations.

Figure 4a shows the WT-EXAFS maps of the pristine state, Ca-inserted state, and Mg-inserted state of nano-*h*-MoO₃. Based on the previous report [45, 46], the dotted lines were set to indicate the Mo–O correlation (from 1.1 to 1.7 Å) in the pristine state, and spectral peaks near ~3.0 Å correspond to closed Mo–Mo interactions (Figure 4a(i)). Upon Ca and Mg insertion, the strong spectral intensity of the Mo–O bond length around all *k* values (2–11 Å^{−1}) and 1.2 Å in the pristine state shifted toward the lower radial distance region, outside of the Mo–O correlation window in the pristine state (Figure 4a(ii,iii)). In particular, this change is clearer with Ca insertion, indicating a shortening of the Mo–O bond. In contrast, the Mg-inserted state exhibits noticeable intensity around ~1.8 Å at higher *k* values (~8 Å^{−1}), indicative of elongated Mo–O components. Moreover, new spectral peaks emerge at higher *k* values near ~2.0 Å, implying the formation of local Mo–Mg-associated coordination environments. Regarding Mo–Mo interactions, only Ca insertion results in a clear shift toward shorter radial distances, as shown in Figure 4a(ii), whereas no appreciable change is observed for the Mg-inserted state. Overall, the WT-EXAFS results indicate that Ca insertion predominantly induces contraction of both Mo–O and Mo–Mo distances, while Mg insertion leads to a mixed response characterized by partial Mo–O shortening accompanied by more prominent bond elongation, with minimal impact on Mo–Mo distances. Importantly, all observed radial-distance variations are highly reversible upon charging in both battery systems, as shown in Figure S17.

Raman spectroscopy further supports the distinct local responses to Ca and Mg insertion (Figure S18). No measurable shift in the Mo=O vibrational mode, corresponding to the Mo–O bond to the isolated oxygen atom located inside the hexagonal tunnel, was observed for Ca-inserted nano-*h*-MoO₃, whereas a distinct red shift appeared in the discharged state of Mg-inserted nano-*h*-MoO₃, indicating bond softening and elongation of the Mo–O bond within the tunnel, which is consistent with the presence of elongated Mo–O components suggested by WT-EXAFS in the Mg battery system. After charging, the peak position returns close to that of the pristine electrode, supporting the reversibility of the Mg-induced local distortion.

To quantitatively assign the bond-length changes suggested by the local-probe analyses and to connect them to specific structural motifs, Rietveld refinement was performed for nano-*h*-MoO₃ electrodes in the pristine, discharged, and charged states for both Ca and Mg battery systems. All XRD patterns of nano-*h*-MoO₃ in all the states were well-fitted (Table S5, S6 and Figure S19). These results support that both Ca²⁺ and Mg²⁺ are inserted at the predicted sites and that their insertion induces systematic changes in the Mo–O and Mo–Mo distances, consistent with the ion-dependent local structural variations observed in the WT-EXAFS spectra. Using the refined structural parameters, we investigated six distinct Mo–O bond lengths (bond 1–6) within the Mo–O polyhedral unit. In the nano-*h*-MoO₃ framework, these bonds are equivalent within the structural unit; however, they respond differently upon divalent-ion insertion. As shown in Figure 4b, bonds 1 and 2 (along the *c* axis) remain nearly unchanged after either Ca²⁺ or Mg²⁺ insertion. In contrast, bond 6, which is the Mo-isolated O bond (i.e., the oxygen atom located inside the tunnel), exhibits pronounced ion-dependent variation: it elongates upon Mg²⁺ insertion but shortens upon Ca²⁺ insertion. Given that the uncertainty in bond lengths obtained from Rietveld refinement is less than 0.02 Å, these changes are sufficiently large to be considered significant. These results indicate that divalent cations residing inside the tunnel strongly modulate the position of the isolated oxygen, thereby governing the local distortion mode of the MoO₆ polyhedral unit. To further confirm these trends, Mo–O bond lengths shorter than the shortest bond in the pristine state were classified as “short bonds,” whereas those longer than the longest pristine bond were classified as “long bonds,” following the same criteria used to define the dotted lines indicating the Mo–O correlation window in the WT-EXAFS spectra. Ca²⁺ insertion increased the number of bonds in the short-bond region, reducing the average Mo–O distance from 2.08 to 1.96 Å. In contrast, the Mo–O bond lengths became widely distributed across the short-to-long range, including 1/3 of the numbers in the “long bond” region, resulting in an increased average Mo–O distance from 2.08 to 2.21 Å. These Mo–O bond-length trends are in good agreement with those observed in the WT-EXAFS spectra and are found to be predominantly governed by changes in the Mo-isolated O bond. Figure 4c,d shows the Mo–M (M=Ca or Mg) and Mo–Mo bond lengths. The shortest Mo–Mg distances were smaller than the corresponding Mo–Ca distances. Additionally, only Ca²⁺ insertion caused a contraction of the nearest Mo–Mo distance, from 3.31 to 3.15 Å. This shorter length change was clearly observed in WT-EXAFS, while the Mo–Mo length was not changed with Mg insertion.

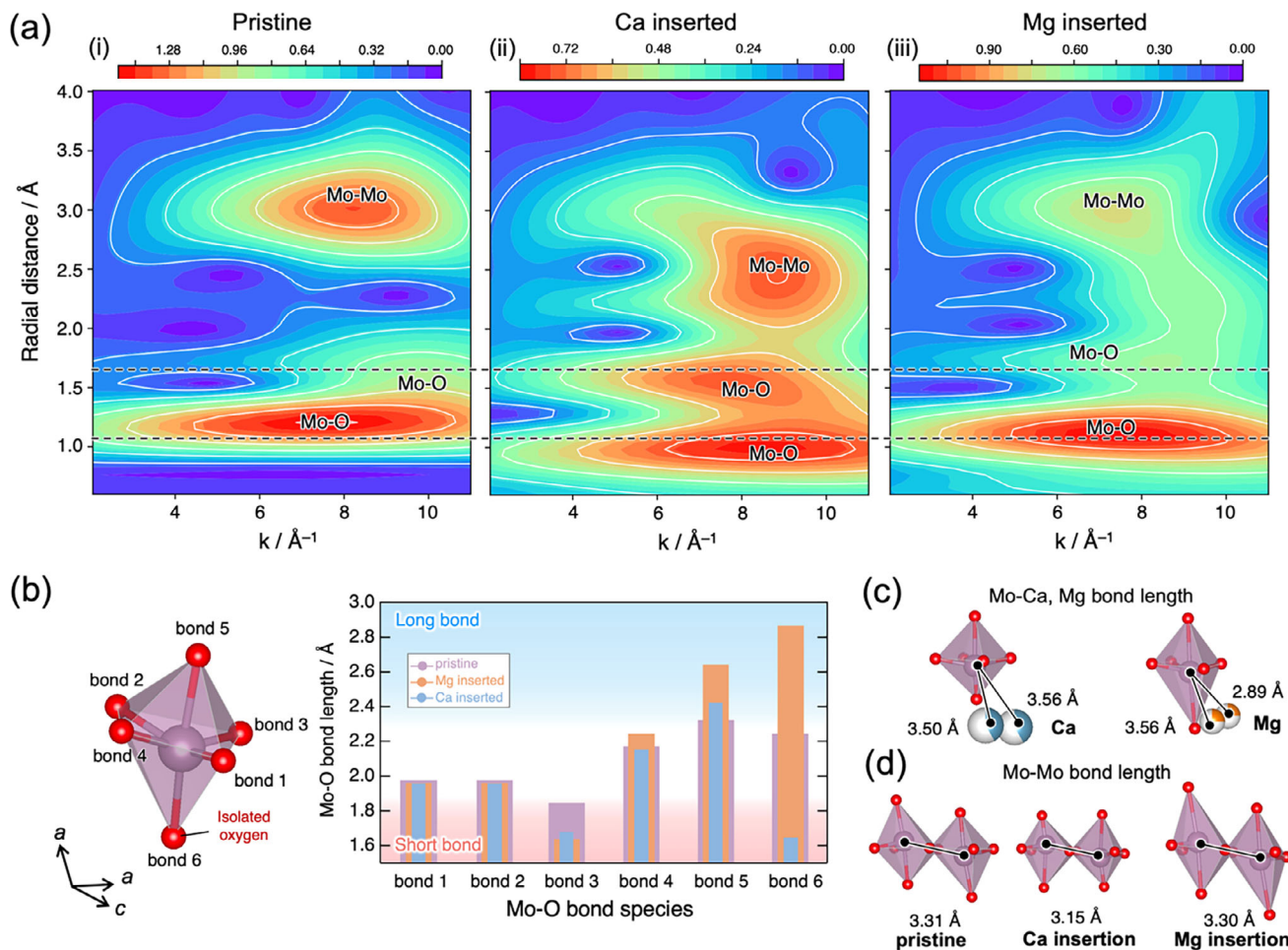


FIGURE 4 | (a) Mo K -edge k^3 -weighted WT-EXAFS of nano h - MoO_3 (i) pristine state, (ii) Mg inserted state, (iii) Ca inserted state. Local structural change of nano- h - MoO_3 by Rietveld refinement for Ca and Mg insertion (b) Mo–O bond length, (c) Mo–Ca, Mg bond length, (d) Shortest Mo–Mo bond length.

To capture the overall impact of local distortions in the MoO_6 polyhedral units on the tunnel framework, the O- and Mo-constituted hexagonal units and the corresponding Mo–O (Mo-isolated O) bond lengths were investigated through Rietveld refinement as illustrated in Figure 5a. As shown in Figure 5b, shortening of the Mo-isolated O bond upon Ca^{2+} occupation at the three equivalent insertion sites leads to expansion of the O-hexagonal area, which increases by 53.1%. In addition, the Mo-hexagonal framework expands slightly by 5.9%. This modest lattice expansion is attributed to the larger extent of Mo^{6+} reduction induced by Ca^{2+} insertion compared with Mg^{2+} , as supported by the XANES results (Figure S11). In contrast, Mg^{2+} insertion results in a distinctly different structural response. As shown in Figure 5c, the O-hexagonal area contracts by 46.5%, accompanied by elongation of the Mo-isolated O bond, while the Mo-hexagonal framework remains essentially unchanged.

This opposite behavior is possibly attributed to the larger ionic radius of Ca^{2+} (1.00 Å) compared to Mg^{2+} (0.72 Å), and to the DFT-predicted diffusion mode in which Ca^{2+} diffuses within the tunnel cavity rather than embedding into the framework as Mg^{2+} does, leading to expansion of the O-hexagonal tunnel (Figure S20).

After charging, the structural parameters largely returned to their pristine values, indicating reversible Ca^{2+} and Mg^{2+} insertion.

The Mg^{2+} and Ca^{2+} insertion sites predicted by DFT and NEB calculations show excellent agreement with the experimental observations, and multiple crystallographic analyses consistently validate the local structural evolution of nano- h - MoO_3 . To the best of our knowledge, no other divalent-ion insertion system has been reported in which reversible ion insertion and de-insertion proceed exclusively through modulation of host metal–oxygen bond lengths while preserving an intact Mo framework, as summarized in Figure 5d. In conventional zero-strain lithium- and sodium-ion insertion materials [47, 48], zero-strain is often achieved by incorporating rigid pillars or redox-inactive metal species into the framework to suppress lattice distortion induced by guest-ion insertion. In contrast, the divalent-ion insertion system in this study represents a fundamentally different strategy: lattice distortion is mitigated through dynamic and reversible adjustment of host metal–oxygen bond lengths rather than by static structural reinforcement. This highly unusual charge-discharge mechanism enables ultralow lattice distortion during cycling and represents an unprecedented approach to achieving structurally resilient oxide hosts for divalent metal batteries.

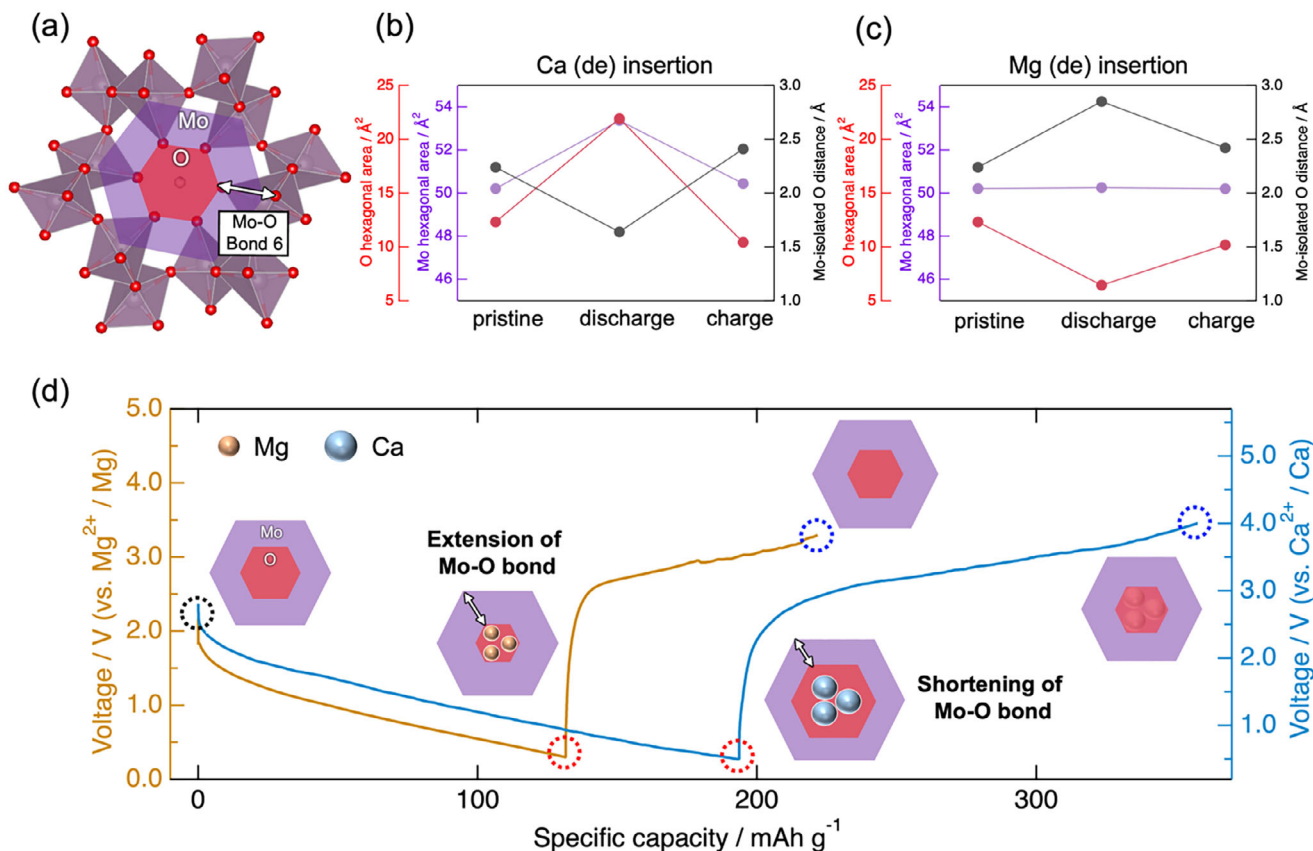


FIGURE 5 | (a) The crystal structure of nano-*h*-MoO₃ illustrating the Mo and O hexagonal tunnel frameworks and Mo-isolated O bond. Their changes of nano-*h*-MoO₃ by Rietveld refinement in (b) Ca and (c) Mg battery cell, (d) Summary of tunnel framework change of *h*-MoO₃ for both battery systems.

3 | Conclusion

In this study, we approached material design from the viewpoint of structural robustness, in addition to nanoparticulation of the oxide positive electrode, for room-temperature operation in divalent metal batteries. By focusing on *h*-MoO₃ with its geometrically stable hexagonal tunnel structure, we achieved reversible Ca and Mg insertion in full cells using nano-*h*-MoO₃ electrodes. In Mg battery systems, where the Mg metal electrode exhibits excellent stability, the nano-electrode delivered superior cyclability up to 100 cycles. Moreover, comprehensive structural analyses revealed minimal lattice distortion (<2% volume change) and a unique mode of local structural evolution during divalent-ion (de)insertion, both of which were further supported by computational modeling. This reversible modulation of Mo—O bond lengths while preserving an intact Mo-based framework represents a previously unreported insertion mechanism. Collectively, our findings highlight a new design principle for oxide-type positive electrodes, paving the way toward practical room-temperature divalent batteries.

ulation), M.S. (calculation); Resources: T.M. (Mg electrolyte), H.K. (Ca electrolyte); Writing – Original Draft: R.I.; Writing – Review & Editing: H.K. (lead), T.M., R.Z., S.O., M.P., T.Y., A.N., A.M., M.M., I.H., H.P., M.S.; Supervision: H.K., T.M., M.S., S.O., I.H.; Project Administration: R.I., H.K.; Funding Acquisition: R.I., H.K.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author Contributions

Conceptualization: R.I.; Methodology: R.I.; Formal Analysis: R.I. (lead), T.Y., H.K.; Investigation: R.I. (synthesis, Mg battery, Ca battery), H.P. (cal-

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Supporting Information

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