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# Ultrasmall $\alpha$ -MnO<sub>2</sub> with Low Aspect Ratio: Applications to Electrochemical Multivalent-Ion Intercalation Hosts and Aerobic Oxidation Catalysts

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**Abstract:** Hollandite-type  $\alpha$ -MnO<sub>2</sub> exhibits exceptional promise in current industrial applications and in advancing next-generation green energy technologies, such as multivalent (Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Zn<sup>2+</sup>) ion battery cathodes and aerobic oxidation catalysts. Considering the slow diffusion of multivalent cations within  $\alpha$ -MnO<sub>2</sub> tunnels and the catalytic activity at edge surfaces, ultrasmall  $\alpha$ -MnO<sub>2</sub> particles with a lower aspect ratio are expected to unlock the full potential. In this study, ultrasmall  $\alpha$ -MnO<sub>2</sub> (<10 nm) with a low aspect ratio ( $c/a \sim 2$ ) is synthesized using a newly developed alcohol solution process. This material demonstrated exceptional performance across various multivalent battery systems, primarily due to the significantly reduced

cation diffusion distance. Notably, an ultrasmall  $\alpha$ -MnO<sub>2</sub>-graphene composite achieved high capacity with low overpotential when paired with an F-free electrolyte in Ca battery. Regarding aerobic oxidation catalysis, the nanosizing of  $\alpha$ -MnO<sub>2</sub> had a profound impact on aerobic oxidation catalysis. The increased efficiency of oxidative conversion reactions, such as the oxidation of 1-phenylethanol, was attributed to the greatly expanded active surface area of the catalyst. The versatile functionality of ultrasmall  $\alpha$ -MnO<sub>2</sub> underscores its potential to revolutionize energy storage and catalysis, offering broad applicability in next-generation green energy technologies.

## Introduction

Owing to its numerous advantages toward industrial use, manganese dioxides ( $\text{MnO}_2$ ) have attracted significant attention as promising functional materials.<sup>[1]</sup>  $\text{MnO}_2$  possesses a diverse range of crystalline structures with multiple valence states ( $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Mn}^{4+}$ ),<sup>[2]</sup> where  $\text{MnO}_6$  octahedral units are arranged in various configurations influenced by the presence of other cations and the thermodynamic conditions during crystallization.<sup>[3]</sup> This diversity results in a wide selection of crystal structures, including  $\alpha$  (hollandite),<sup>[4]</sup>  $\beta$  (pyrolusite),<sup>[5]</sup>  $R$  (ramsdellite),<sup>[6]</sup>  $\gamma$  (a mixture of  $\beta$  and  $R$ ),<sup>[7]</sup>  $\delta$  (birnessite),<sup>[8]</sup> and  $\lambda$  (defect spinel),<sup>[9]</sup> each possessing distinct physical and chemical properties. Among various crystal structures, the hollandite-type ( $\alpha$ -type) stands out as a commonly utilized high-performance material with versatile applications, such as cathode for energy storage,<sup>[10]</sup> aerobic oxidation catalysis,<sup>[11]</sup> sensing materials,<sup>[12]</sup> and absorbents.<sup>[13]</sup>

In the electrode applications,  $\alpha$ - $\text{MnO}_2$  has been deeply investigated as a cathode for monovalent cation intercalation host ( $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ).<sup>[10a, 14]</sup> However, the host structure tends to be distorted and collapsed after a large amount of cation insertion,<sup>[15]</sup> its application has been limited to the primary battery.<sup>[16]</sup> These days, the potential use of  $\alpha$ - $\text{MnO}_2$  cathode toward multivalent cation ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Zn}^{2+}$ ) battery systems, possessing cost-effectiveness and high-energy density, have been extensively investigated, since the amount of cations required is halved compared with the monovalent battery systems, enabling the reversibility of  $\alpha$ - $\text{MnO}_2$  cathode.<sup>[17]</sup> In addition, the redox cycling of  $\text{Mn}^{4+}/\text{Mn}^{3+}$  ions occurs at high voltage,<sup>[18]</sup> which can compensate for the disadvantage of lower reduction potential (Ca;  $-2.89$  V, Mg;  $-2.36$  V, and Zn;  $-0.763$  V) compared to Li.<sup>[19]</sup> Indeed, previous studies have indicated that  $\alpha$ -type materials are relatively suitable for cathode materials capable of reversible magnesium intercalation.<sup>[3d]</sup> Moreover, many researchers focus on zinc battery systems because of the superior performance in aqueous electrolytes,<sup>[20]</sup> demonstrating impressive capacity retention and high-rate capabilities.<sup>[21]</sup>

In the field of catalysis,  $\alpha$ - $\text{MnO}_2$  exhibits great potential as an eco-friendly aerobic oxidation catalyst in various oxidative functional group transformations<sup>[11, 22]</sup> because it can oxidize a variety of substrates by the Mars-van Krevelen mechanism, which directly utilizes its lattice oxygen, or by the one-electron transfer (SET) oxidation mechanism. This approach eliminates the demand for hazardous reagents and the generation of substantial quantities of inorganic by-products, thereby paving the way for environmentally responsible synthesis.

In both electrode and catalyst applications, a key to unlocking the full potential of  $\alpha$ - $\text{MnO}_2$  lies in nanoparticulation, but simply reducing particle size is not sufficient. Considering multivalent cations diffuse in the direction of the tunnel much slower than monovalent cations, and catalysts show high activity on the edge of tunnels, achieving a lower aspect ratio ( $c/a$ ), having low cation diffusion distance and many edge surfaces, holds considerable potential for enhancing material performance significantly. Moreover,  $\alpha$ - $\text{MnO}_2$  involves cations like  $\text{K}^+$ ,  $\text{NH}_4^+$ , and  $\text{Ag}^+$  to maintain the tunnel structure;<sup>[14b, 23]</sup> the type and the amount of introduced cations should affect the host capability. To harness

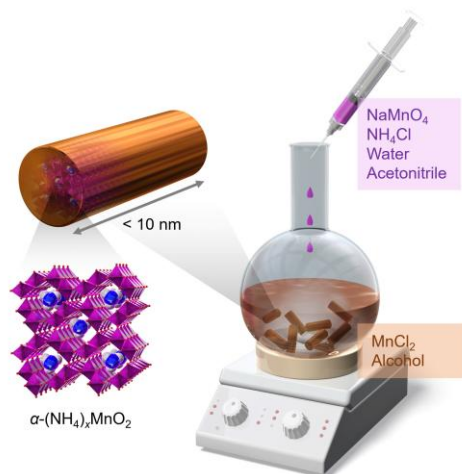
the full potential of  $\alpha$ - $\text{MnO}_2$  as an electrode material, a removable guest cation, *i.e.*,  $\text{NH}_4^+$  is the most promising choice. To date, numerous attempts have been made to achieve nanoparticulation of  $\alpha$ - $\text{MnO}_2$  through a wide range of metal-doping.<sup>[11a, 14b, 24]</sup> While their approaches have successfully led to an increase in the specific surface area, the doped metal is likely to enter the guest site of the tunnel structure and distort the structure significantly, which might compromise the host capability as the cathode. Therefore, nanoparticulation techniques without metal doping are required.

Typically,  $\alpha$ - $\text{MnO}_2$  is synthesized using a hydrothermal approach, which has a challenge toward nanoparticulation, since the dissolution and recrystallization of the nucleus easily occur during synthesis. Here, we have innovatively combined our extensively reported alcohol reduction method for Mn-based spinel/todorokite/buserite synthesis<sup>[25]</sup> and the conventional hydrothermal approach,<sup>[3a, 8a]</sup> enabling the nanoparticulation of  $\alpha$ - $\text{MnO}_2$ . Our developed alcohol solution process, devoid of any calcination steps, successfully produces ultrasmall  $\alpha$ - $\text{MnO}_2$  particles ( $<10$  nm) with a low aspect ratio ( $c/a \sim 2$ ). Thus obtained ultrasmall  $\alpha$ - $\text{MnO}_2$  shows a superior performance both in multivalent battery cathode and aerobic oxidation catalyst.

## Results and Discussion

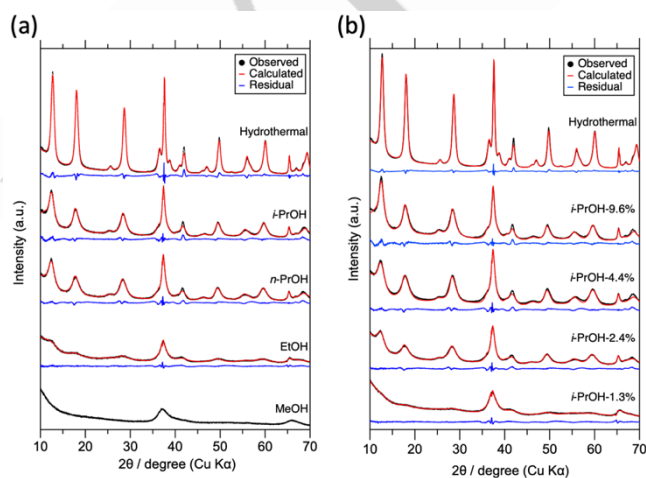
### Synthesis and Characterization of Ultrasmall $\alpha$ - $\text{MnO}_2$

Figure 1 illustrates the alcohol solution process of ultrasmall  $\alpha$ - $\text{MnO}_2$  synthesis. In the process, alcohol is just a solvent that suppresses the dissolution and recrystallization of oxides, and  $\alpha$ - $\text{MnO}_2$  is synthesized by the redox reaction of  $\text{Mn}^{7+}$  (permanganate  $\text{MnO}_4^-$ ) and  $\text{Mn}^{2+}$  in primary ( $n$ -PrOH, EtOH, or MeOH; PrOH: propanol, EtOH: ethanol, MeOH: methanol) or secondary ( $i$ -PrOH) alcohol solution. Note that  $\text{NaMnO}_4$  was used as a permanganate salt in this work instead of the generally used  $\text{KMnO}_4$ , since  $\text{NaMnO}_4$  has higher solubility in an organic solvent compared to  $\text{KMnO}_4$ .<sup>[26]</sup> Additionally, sodium-containing manganese oxides usually form a layered structure;<sup>[8a]</sup> they serve as precursors for various tunnel-type manganese oxides containing  $\alpha$ - $\text{MnO}_2$ .<sup>[3a]</sup> On the other hand, the permanganate should react with alcohol rapidly. Therefore,  $\text{NaMnO}_4$  was dissolved in acetonitrile (stable against oxidation) to prepare a precursor solution. In the precursor solution, water and  $\text{NH}_4\text{Cl}$  were added for nucleation of  $\alpha$ - $\text{MnO}_2$ . This precursor solution was then added dropwise to an alcohol solution containing  $\text{MnCl}_2$ . A brown precipitate promptly formed, followed by refluxing for an hour to obtain ultrasmall  $\alpha$ - $\text{MnO}_2$ .



**Figure 1.** Schematic illustration of ultrasmall  $\alpha$ -MnO<sub>2</sub> synthesis.

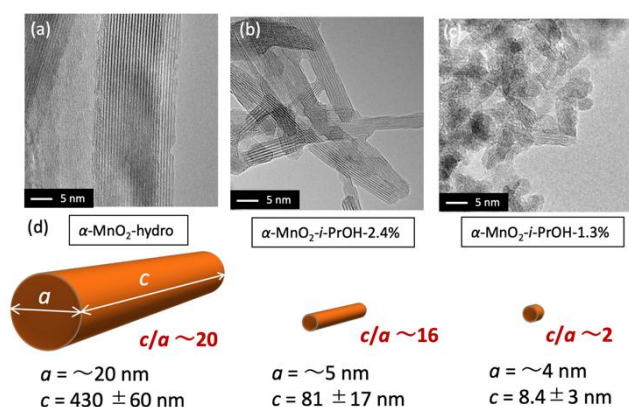
**Figure 2a** shows X-ray diffraction (XRD) patterns of  $\alpha$ -MnO<sub>2</sub> synthesized via the hydrothermal process ( $\alpha$ -MnO<sub>2</sub>-hydro) and the alcohol solution process with different alcohol solvents ( $\alpha$ -MnO<sub>2</sub>-*i*-PrOH,  $\alpha$ -MnO<sub>2</sub>-*n*-PrOH,  $\alpha$ -MnO<sub>2</sub>-EtOH, and  $\alpha$ -MnO<sub>2</sub>-MeOH). All the XRD patterns, except  $\alpha$ -MnO<sub>2</sub>-MeOH, well-matched the single-phase of tetragonal  $\alpha$ -MnO<sub>2</sub> with the  $I4/m$  space group through Rietveld refinements (Table S1). Compared with XRD patterns of  $\alpha$ -MnO<sub>2</sub>-hydro,  $\alpha$ -MnO<sub>2</sub> synthesized via the alcohol solution process presented markedly broad XRD patterns, suggesting the formation of nanoparticles. The variation in particle size can be attributed to variations in the dielectric constant of the alcohol solvent, as well as disparities in reflux temperatures. For instance, comparing  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH to  $\alpha$ -MnO<sub>2</sub>-EtOH having a similar reflux temperature, EtOH has the higher polarity, strengthening the hydrogen bonds with the permanganate anion. Consequently, this lowers the activation energy required for  $\alpha$ -MnO<sub>2</sub> nucleation, favoring nucleation over the growth of larger  $\alpha$ -MnO<sub>2</sub> particles. This is in line with a previous report on  $\delta$ -MnO<sub>2</sub> nanoparticle formation.<sup>[27]</sup>



**Figure 2.**  $\alpha$ -MnO<sub>2</sub> XRD patterns with fitting curves by Rietveld refinement with differences of (a) alcohol solvent and (b) differences of water content in *i*-PrOH reaction solution.

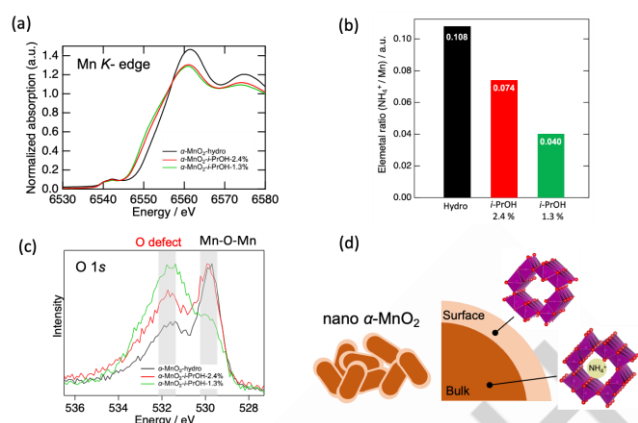
**Figure 2b** displays the XRD pattern of  $\alpha$ -MnO<sub>2</sub>, illustrating the influence of varying water contents in the synthesis process. Samples were labeled as  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH- $x$  ( $x$  is the volume ratio of H<sub>2</sub>O/(*i*-PrOH+H<sub>2</sub>O)) to clarify the amount of H<sub>2</sub>O in the reaction solution. As well as Figure 2a, all the XRD patterns well-matched the single-phase of tetragonal  $\alpha$ -MnO<sub>2</sub> through Rietveld refinements (Table S1). Moreover, the selected area electron diffraction (SAED) analysis of  $\alpha$ -MnO<sub>2</sub>-hydro,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4%, and  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% shown in Figures S1a-S1c reveals the diffraction rings correlating to the obtained XRD pattern, supporting the formation of  $\alpha$ -MnO<sub>2</sub>. To further investigate the crystalline phase of the  $\alpha$ -MnO<sub>2</sub>, a pair distribution function (PDF) analysis using X-ray total scattering data (Figure S2) was conducted. The total correlation function  $T(r)$  of the  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% and  $\alpha$ -MnO<sub>2</sub>-EtOH clearly shows both edge-shared and corner-shared Mn-Mn peaks. However,  $\alpha$ -MnO<sub>2</sub>-MeOH exhibits a weak and broad peak of edge-shared Mn-Mn, suggesting the existence of both tunnel and layered phases.

As the water content decreases, the XRD patterns become broader (Figure 2b), indicating the downsizing of nanoparticles, also supported by the Rietveld refinement (Table S1). A large specific surface area (SSA) of more than 150 m<sup>2</sup> g<sup>-1</sup> supports the nanoparticulation (Table S2); the SSA of hydrothermally synthesized  $\alpha$ -MnO<sub>2</sub> is typically 70~100 m<sup>2</sup> g<sup>-1</sup>.<sup>[23a]</sup> **Figure 3** presents high-resolution transmission electron microscopy (HR-TEM) images of  $\alpha$ -MnO<sub>2</sub>-hydro,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4%, and  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%. The low-magnified images are shown in Figure S1c-S1i. In all the samples, clear lattice fringes were observed with evenly spaced intervals, indicating the formation of  $\alpha$ -MnO<sub>2</sub> crystals. Additionally, primary particles of  $\alpha$ -MnO<sub>2</sub> synthesized through the alcohol solution process underwent significant nanoparticulation, as summarized in Figure 3d. By adjusting the water content in the reaction solution, not only the particle size but also the aspect ratio ( $c/a$ ) changed significantly. Interestingly,  $\alpha$ -MnO<sub>2</sub>-EtOH exhibited a needle-like particle morphology with a longer  $c$ -axis direction and a larger aspect ratio shown in Figure S3, though it shows a similar XRD pattern shape and lattice constants to  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%. This discrepancy may derive from the amount of water. During the crystallization process from amorphous manganese oxide to  $\alpha$ -MnO<sub>2</sub> and subsequent crystal growth along the  $c$ -axis direction, the presence of an adequate amount of water is crucial. Although the high dielectric constant of EtOH contributes to an overall reduction in the particle size, the presence of sufficient water in the reaction solution may have promoted crystal growth along the  $c$ -axis direction. From the above discussions, the mechanism of this nanoparticulation can derive from the reduced amount of water in the reaction solution; the crystal growth of  $\alpha$ -MnO<sub>2</sub> via the dissolution/recrystallization process is successfully suppressed.



**Figure 3.** HR-TEM images of (a)  $\alpha$ -MnO<sub>2</sub>-hydro, (b)  $\alpha$ -MnO<sub>2</sub>-i-PrOH-2.4%, (c)  $\alpha$ -MnO<sub>2</sub>-i-PrOH-1.3%. (d) Summary of  $a$  and  $c$  axis length for each  $\alpha$ -MnO<sub>2</sub> particle.

In addition to the crystallite size, the lattice constants also changed as shown in Figure S4 and Table S1. The lattice constants  $a$  and  $c$  increase as the particles become nanoparticles; the trend in  $c$  has a threshold of crystallite size. This is possibly due to the increase in the surface region of the particles, which have O defect regions and lower valence of Mn. The lower valence of Mn forces lattice expansion compared to the bulk, leading to an increase in the bulk lattice parameters. **Figure 4a**, Figure S5 and S6 display the Mn valence state of  $\alpha$ -MnO<sub>2</sub> as determined by X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) analyses, respectively. As the particle size decreases, the Mn valence state decreases as well, evinced by both the Mn  $K$ -edge X-ray absorption near edge structure (XANES) and the Mn  $2p$  XPS spectra, as evinced by lower energy shifts. **Figure 4b** shows the relative amount of NH<sub>4</sub><sup>+</sup> cation in the tunnel of  $\alpha$ -MnO<sub>2</sub>, estimated from CHN and inductively coupled plasma atomic emission spectroscopy (ICP-AES) elemental analyses. The NH<sub>4</sub><sup>+</sup>/Mn ratio of 0.108 for  $\alpha$ -MnO<sub>2</sub>-hydro aligns with previous research findings.<sup>[10c, 28]</sup> As the particle size decreases, the NH<sub>4</sub><sup>+</sup>/Mn ratio decreases. These results imply that despite the reduced NH<sub>4</sub><sup>+</sup> content inside the tunnel, the Mn valence state becomes smaller, suggesting the formation of oxygen vacancies. The O 1s XPS spectra (**Figure 4c**) show larger peaks (around 532 eV) for  $\alpha$ -MnO<sub>2</sub>-i-PrOH-2.4% and -1.3% compared to  $\alpha$ -MnO<sub>2</sub>-hydro, supporting the presence of oxygen defects. In addition, EPR spectra of  $\alpha$ -MnO<sub>2</sub>-i-PrOH-1.3% (Figure S7) confirm the presence of oxygen defect since the single width ( $\Delta B$ ) has a positive correlation with the amount of oxygen defect<sup>[29]</sup>. These findings are summarized in **Figure 4d**. Ultrasmall  $\alpha$ -MnO<sub>2</sub> exhibits a large surface area, which is associated with oxygen vacancies, lower NH<sub>4</sub><sup>+</sup> content, and a lower Mn valence state.



**Figure 4.** (a) Mn  $K$ -edge XANES spectra. (b) NH<sub>4</sub><sup>+</sup>/Mn ratio calculated by CHN and ICP-AES elemental analyses. (c) O 1s XPS spectra. (d) Illustration of Nanosized  $\alpha$ -MnO<sub>2</sub> surface and bulk.

Furthermore, highly porous  $\alpha$ -MnO<sub>2</sub> nanoparticles are obtained using tetrabutyl ammonium (TBA) permanganate salt instead of NaMnO<sub>4</sub>, as shown in Figure S6. Such organic ammonium cations are introduced into a layered MnO<sub>2</sub> precursor to form mesoporous structures.<sup>[30]</sup> Both  $\alpha$ -MnO<sub>2</sub>-i-PrOH-2.4% and -1.3% synthesized using TBAMnO<sub>4</sub> exhibited broader XRD patterns and smaller primary particles according to TEM images compared to those synthesized with NaMnO<sub>4</sub>. Notably,  $\alpha$ -MnO<sub>2</sub>-i-PrOH-2.4% synthesized with TBAMnO<sub>4</sub> (Figure S8c) has a smaller aspect ratio particle compared to that synthesized with NaMnO<sub>4</sub> (Figure 3b). The SSAs of  $\alpha$ -MnO<sub>2</sub>-i-PrOH-1.3% is 263 m<sup>2</sup> g<sup>-1</sup>, a larger value synthesized from NaMnO<sub>4</sub>.

### Electrochemical Multivalent-Ion Intercalation Hosts

Ultrasmall  $\alpha$ -MnO<sub>2</sub> ( $\alpha$ -MnO<sub>2</sub>-i-PrOH-2.4% and -1.3%) exhibits superior cathode performances to hydrothermally synthesized  $\alpha$ -MnO<sub>2</sub> ( $\alpha$ -MnO<sub>2</sub>-hydro) in multivalent (Zn, Mg, and Ca) battery full-cells (**Figure 5**), indicating that nanoparticulation of the active material reduces multivalent ion diffusion distance, thereby enhancing cathode performance without being hindered by the sluggish diffusion of multivalent ion. Aqueous Zn-battery, using a 1.0 M ZnSO<sub>4</sub> + 0.05 M MnSO<sub>4</sub> electrolyte, is more easily cyclable compared with nonaqueous batteries. Even at the 50th cycle (Figure 5a),  $\alpha$ -MnO<sub>2</sub>-i-PrOH-2.4% achieved the discharge capacity of more than one electron reaction (308 mA h g<sup>-1</sup>) with a clear discharge plateau at around 1.3 V attributable to Zn<sup>2+</sup> intercalation,<sup>[20a]</sup> significantly improved compared with  $\alpha$ -MnO<sub>2</sub>-hydro. Note that the cathode performance of  $\alpha$ -MnO<sub>2</sub>-i-PrOH-1.3% was lower than  $\alpha$ -MnO<sub>2</sub>-i-PrOH-2.4%, despite its smaller particle size. It is probably due to a strong particle aggregation, especially occurring in ultrasmall nanoparticles.<sup>[31]</sup> Such aggregation increases the resistance of multivalent ion migration between particles as the interfacial resistance of  $\alpha$ -MnO<sub>2</sub>-i-PrOH-1.3% is large as shown in EIS spectra in Figure S9, resulting in inferior cathode properties, which is also a similar trend with nanosized-LiCoO<sub>2</sub> for Li-ion battery case<sup>[32]</sup>. Therefore,  $\alpha$ -MnO<sub>2</sub> with smaller particle size

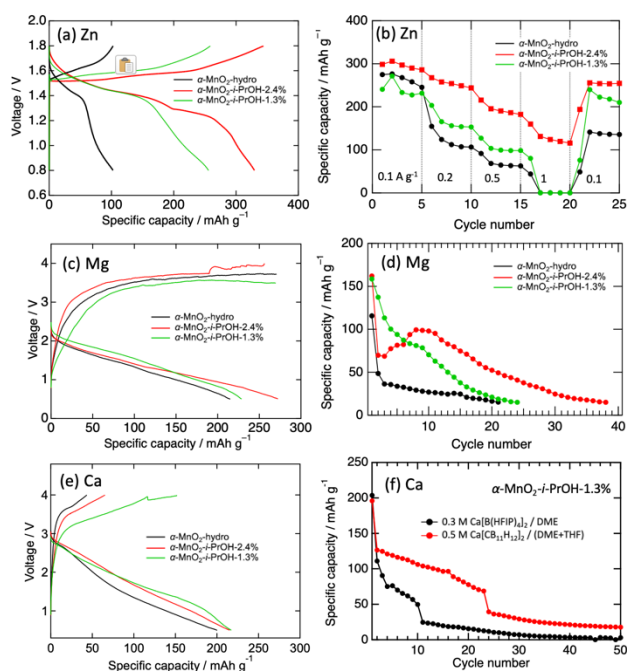
without severe aggregation is suitable for multivalent ion battery cathodes as illustrated Figure S10.  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4% holds a higher capacity compared with previous works<sup>[33] [34]</sup> and a high-capacity retention rate of around 100 cycles (Figure S11), while  $\alpha$ -MnO<sub>2</sub>-hydro and  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% exhibit capacity degradation. Furthermore, as Figure 5b shows,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4% exhibits superior rate performance; even at 1 A g<sup>-1</sup>, it exhibits a reversible capacity of around 150 mAh g<sup>-1</sup>. In addition, the nanosizing effect positively influences the liquid-solid reaction involving dissolved Mn<sup>2+</sup>, as reported in a previous study<sup>[35]</sup>. After discharge, Mn<sup>2+</sup> readily dissolves into the electrolyte and returns to the  $\alpha$ -MnO<sub>2</sub> core during charging, accompanied by the formation of ZnMn<sub>2</sub>O<sub>4</sub> on the core surface. This indicates that the cathodic performance, driven by H<sup>+</sup> and Zn<sup>2+</sup> co-intercalation as well as the liquid-solid reaction involving dissolved Mn<sup>2+</sup>, is strongly dependent on the size of the  $\alpha$ -MnO<sub>2</sub> core.

In nonaqueous Mg-battery, nanosized  $\alpha$ -MnO<sub>2</sub> also exhibits higher discharge capacity and cyclability (Figures 5c, 5d and Figure S12), indicating that nanoparticulation of the active material reduces Mg<sup>2+</sup> diffusion distance, thereby enhancing cathode performance without being hindered by the sluggish diffusion rate of Mg<sup>2+</sup>. Moreover, galvanostatic intermittent titration technique (GITT) measurements (Figure S13) exhibit that  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4% has the smallest overvoltage at discharge.

To evaluate the impact of oxygen defects on charge/discharge performance, EPR spectra of  $\alpha$ -MnO<sub>2</sub> were measured before and after annealing at 300°C. The annealed sample of  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% exhibited a greater  $\Delta B$  in the EPR spectra, indicating an increased amount of oxygen defects (Figure S14a). This observation aligns with the previous report<sup>[36]</sup>. When comparing the voltage profiles of  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4%, which demonstrated the best cathodic performance, with its annealed counterpart, the cathodic performance significantly deteriorated after annealing. The annealed sample showed a lower operating voltage and reduced discharge capacity, attributed to a higher concentration of oxygen defects. These defects impair the structural stability required for Mg-ion insertion, reducing structural tolerance. We estimate that the increased oxygen defects accelerate the phase transition from the hollandite structure to the halite phase, resulting in diminished capacity and a lower operating voltage. Note that there is no significant change in its specific surface area before and after annealing; annealed  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4% possess 122 m<sup>2</sup> g<sup>-1</sup>. Despite optimizing  $\alpha$ -MnO<sub>2</sub> particle size, controlling aggregation and changing the amount of oxygen defect, degradation occurred during cycling. According to the recent DFT calculations, the insertion of Mg ions into  $\alpha$ -MnO<sub>2</sub> distorts the tunnel structure from square to rhombus.<sup>[37]</sup> Consistently, *ex-situ* XRD measurements of  $\alpha$ -MnO<sub>2</sub>-hydro, exhibiting the most severe cycle degradation, revealed a broadening of the 310-plane peak after discharge, failing to revert to its pristine state (Figure S15). This observation suggests the entrapment of Mg<sup>2+</sup> ions within the tunnel structure, impeding their deintercalation during charging, consequently leading to capacity degradation. Thus, even with optimized particle conditions as in  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4%, complete deintercalation of Mg ions remains a challenge.

For nonaqueous Ca-battery cell tests as shown in Figure 5e,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4% and -1.3% demonstrate superior cathodic performance, as well as the Mg-battery cell, primarily due to the reduction in the diffusion distance of Ca<sup>2+</sup>. On the contrary to the Mg and Zn-battery cases,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% exhibits a larger charge capacity, suggesting that nanoparticulation may contribute rather to charge performance, specifically in Ca<sup>2+</sup> deintercalation. Furthermore, upon comparing the voltage profiles at 10 mA g<sup>-1</sup> and 100 mA g<sup>-1</sup>, there appears to be no significant deviation in capacity and polarization between discharge and charge (Figure S16), implying that Ca<sup>2+</sup> undergo intercalation and deintercalation more rapidly than Mg<sup>2+</sup>, possibly due to differences in their charge density.

Concerning the cyclability of  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% in the Ca-battery system, assessing its cathode performance with Ca[B(HFIP)<sub>4</sub>]<sub>2</sub> electrolyte presents challenges due to the formation of a CaF<sub>2</sub> passivation layer on Ca metal,<sup>[38]</sup> resulting in substantial cycle degradation. To address this issue, a Ca full-cell test using Ca[CB<sub>11</sub>H<sub>12</sub>]<sub>2</sub> electrolyte was conducted; a fluorine-free electrolyte having high anodic stability (> 4 V vs. Ca<sup>2+</sup>/Ca).<sup>[39]</sup> As shown in Figure 5f and Figure S17, Ca[CB<sub>11</sub>H<sub>12</sub>]<sub>2</sub> electrolyte notably enhances the cyclability of the cathode compared with Ca[B(HFIP)<sub>4</sub>]<sub>2</sub> electrolyte, suggesting that most cycle degradation stems from anodic issues and  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% was found to be superior host material for Ca-battery. Note that the coulombic efficiency of Ca[CB<sub>11</sub>H<sub>12</sub>]<sub>2</sub> electrolyte is around 84 % and the passivation layer, which is mainly CaH<sub>2</sub>, is gradually formed. This is the main reason for capacity degradation shown Figure 5f. In addition, the coulombic efficiency in the first cycle was far from ideal even with using an F-free electrolyte. Figure S18 presents the XRD patterns of  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% after discharge and charge. Even though DFT calculation expect no structural distortion for Ca<sup>2+</sup> insertion, the 310 peak shifted to a lower angle, indicating its structural change and Ca ions were trapped within the structure. Then, this causes low coulombic efficiency in the first cycle and the charge capacity is significantly dependent on the particle size, suggesting that the short migration path facilitate the Ca ion de-insertion.

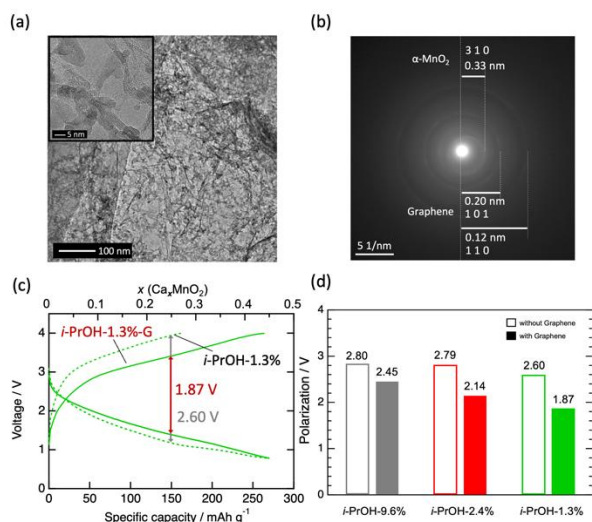


**Figure 5.** (a) 50th-cycled voltage profile of Zn-battery cell at a current density of 100 mA g<sup>-1</sup>. (b) Rate capability of Zn-battery cell. (c) 1st voltage profile of Mg-battery cell at a current density of 10 mA g<sup>-1</sup>. (d) Discharge capacity of Mg-battery cell during cycles at a current density of 100 mA g<sup>-1</sup>. (e) 1st voltage profile of Ca-battery cell at a current density of 10 mA g<sup>-1</sup>. (f) Discharge capacity of Ca-battery cell with different electrolytes during cycles at a current density of 100 mA g<sup>-1</sup>.

In charge-discharge reactions using organic electrolytes such as Ca- and Mg-battery, in addition to cation insertion reactions, side reactions such as electrolyte reductive decomposition reactions<sup>[40]</sup> and O<sup>2-</sup> desorption<sup>[41]</sup> are likely to occur, hence the contribution ratio of cation insertion to capacity is important. Scanning electron microscopy (SEM)-energy dispersive X-ray spectroscopy (EDX) analyses were applied to quantify the cation insertion levels. Figure S19 presents the ratio of Mg<sup>2+</sup> and Ca<sup>2+</sup> intercalation reaction per whole discharge reaction. Concerning Mg<sup>2+</sup> intercalation ability,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4% exhibits the highest Mg<sup>2+</sup> contribution of 78% to discharge capacity; more than 20% of side reactions occur. In particular, only 60% of capacity is contributed by Mg<sup>2+</sup> insertion in the case of  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%. In contrast, Ca<sup>2+</sup> intercalation rather proceeds in all  $\alpha$ -MnO<sub>2</sub> cathodes. Particularly noteworthy is  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%, showing a remarkable 91% cation contribution to capacity. Moreover,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% shows excellent selectivity in both Ca<sup>2+</sup> intercalation and de-intercalation reactions. As displayed in Table S3, almost all charging capacity stems from Ca<sup>2+</sup> de-intercalation, highlighting the superior performance of nanosized  $\alpha$ -MnO<sub>2</sub> as a host material for Ca<sup>2+</sup> at room temperature compared to Mg<sup>2+</sup>. This host performance owes not only to the low charge density of Ca<sup>2+</sup> and facile diffusion through its solid phase but also to previous DFT calculations<sup>[42]</sup> indicating that Ca<sup>2+</sup> insertions cause minimal distortion to the tunnel

structure of  $\alpha$ -MnO<sub>2</sub>. Additionally, as shown in Figure S20, Mn K-edge XANES analysis, tracing the redox reactions of Mn during the intercalation and deintercalation of Ca ions, indicates semi-reversible redox processes, consistent with the observed voltage profile in the first cycle. Notably, compared with spectra of other samples,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% possess the highest Mn re-oxidation ability.

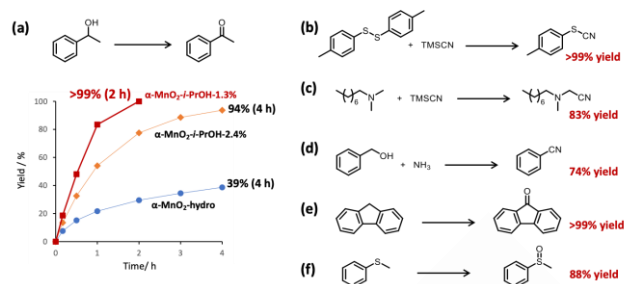
As discussed above,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% exhibits excellent properties as a Ca-battery cathode. However, there is still potential for further performance improvement. As shown in the TEM images (Figures 3c and S1f), the primary particles are strongly aggregated. Additionally, electrochemical impedance spectroscopy (EIS) data presented in Figure S21 indicated a large cathodic interfacial resistance for  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%. This aggregation thereby causing the lack of conductivity likely contributes to the reduced performance. To address this issue, we aimed to suppress particle aggregation by compositing nanoparticles with some porous dispersant materials. Since the alcohol solution process is a wet process, the composite is easily obtained by mixing dispersant into the solution. Here we selected conductive graphene nanosheets. **Figure 6a** displays HR-TEM images of the  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%-graphene composite, denoted as  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%-G. The primary  $\alpha$ -MnO<sub>2</sub> nanoparticles were homogeneously dispersed on the graphene sheet, and particle aggregation was scarcely observed. The SAED patterns (**Figure 6b**) and XRD patterns (Figure S22) show diffraction rings corresponding to the XRD patterns, confirming the crystalline phases of  $\alpha$ -MnO<sub>2</sub> and graphene. Regarding its cathodic performance in Ca-battery tests (**Figure 6c**),  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%-G exhibited significantly superior charge-discharge performance, especially in the charge curve. The polarization at 150 mA h g<sup>-1</sup> was reduced from 2.60 V to 1.87 V, achieving the fully reversible charge. When comparing the polarization of nanosized  $\alpha$ -MnO<sub>2</sub>-graphene composite cathodes with different particle sizes and aspect ratios, the most significant reduction in polarization was observed with the  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% cathode (**Figure 6d**). This implies that the graphene composite is a highly effective method for fully utilizing the strongly aggregated nanoparticles as cathodes. As shown in Figure S23, its capacity degradation at first few cycles was significantly suppressed by compositing with graphene.



**Figure 6.** (a) HR-TEM images and (b) SAED patterns of  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%-G. (c) Voltage profiles of Ca-battery cell at a current density of 100 mA g<sup>-1</sup> and (d) polarizations at the point of 150 mAh g<sup>-1</sup>.

### Aerobic Oxidation Catalysis

In general, it is known that the catalytic activity increases with decreasing the SSA of manganese oxides, but there is no detailed discussion on how the aspect ratio of  $\alpha$ -MnO<sub>2</sub> affects the catalytic performance for the oxidation reactions. Firstly, the catalytic activities of three manganese oxide catalysts prepared in this study,  $\alpha$ -MnO<sub>2</sub>-hydro,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4%, and  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%, were compared for the oxidation of 1-phenylethanol (secondary alcohol) to acetophenone using O<sub>2</sub> as a model reaction. **Figure 7a** shows the reaction profiles, where the order of the catalytic activities was  $\alpha$ -MnO<sub>2</sub>-hydro <  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4% <  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%. In all cases, the reactions proceeded selectively, and no byproducts other than acetophenone were detected. The initial reaction rates determined at less than 10% 1-phenylethanol conversion were 1.25 mM min<sup>-1</sup>, at 2.21 mM min<sup>-1</sup>, and 3.05 mM min<sup>-1</sup> for  $\alpha$ -MnO<sub>2</sub>-hydro,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4%, and  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%, respectively, and the relationship between initial reaction rates and the SSAs was found to be a nearly first order (Table S2). This means that the oxidation of 1-phenylethanol by  $\alpha$ -MnO<sub>2</sub> (in other words, the reduction of  $\alpha$ -MnO<sub>2</sub>) can be considered to depend simply on just their SSA, without regard to the aspect ratios. However, comparing the reaction profiles of  $\alpha$ -MnO<sub>2</sub>-hydro and  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%, for example, a clear difference can be observed in the latter half of the reaction that cannot be explained by the difference in their SSAs alone. This result is considered to be due to the fact that more *c* planes are exposed in the case of  $\alpha$ -MnO<sub>2</sub> with a low aspect ratio (*c/a*), where electron transfer from the reduced manganese species to O<sub>2</sub> proceeds smoothly to complete the catalytic cycle. Based on these results, designing  $\alpha$ -MnO<sub>2</sub> with a small SSA and small aspect ratio (*c/a*) is a very effective strategy for oxidation reactions of this type of substrate.



**Figure 7.**  $\alpha$ -MnO<sub>2</sub>-catalyzed aerobic oxidations of (a) 1-phenylethanol, (b) benzyl alcohol, (c) di-*p*-tolyl disulfide, (d) *N,N*-dimethyl octylamine, (e) fluorene, and (f) thioanisole. Reaction conditions were described in the experimental section. For the reactions (b)-(f),  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% was used as a catalyst. In reactions (b), (c), and (f), benzamide (25% yield), methylene cyanated product (11% yield), and methyl phenyl sulfone (5% yield) formed as byproducts, respectively.

Finally, the substrate scope of ultrasmall  $\alpha$ -MnO<sub>2</sub> catalysts to various oxidation reactions was investigated. With ultrasmall  $\alpha$ -MnO<sub>2</sub> catalysts, the selective oxidation of not only secondary alcohols but also primary alcohols to aldehydes proceeded efficiently. The reaction of benzyl alcohol with  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% as a catalyst in the presence of NH<sub>3</sub> gave benzonitrile in 74% yield for 30 min (**Figure 7b**); this reaction consists of oxidation of benzyl alcohol to benzaldehyde, the reaction of benzaldehyde with NH<sub>3</sub> to form an aldimine, followed by the oxidation to the corresponding nitrile. In this case, benzamide was also formed in 25% by nitrile hydration.<sup>[43]</sup> When the reaction of benzyl alcohol with  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-2.4% (otherwise conditions were the same) was carried out for 1 h, the selectivity switch occurred to afford benzamide in 93% yield.  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% was also extremely effective for reactions originating from SET oxidation (**Figures 7c** and **7d**). In the reaction of a disulfide, a thiol and target thiocyanate were first formed by the nucleophilic addition of CN<sup>-</sup> to the disulfide substrate, but  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% showed extremely high catalytic activity for thiol homocoupling via SET oxidation, resulting in selective production of the thiocyanate product (Figure 7c). The  $\alpha$ -methyl-selective oxidative cyanation was achieved through the  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3%-mediated SET/deprotonation/SET sequence followed by the nucleophilic addition of CN<sup>-</sup> (Figure 7d). Moreover,  $\alpha$ -MnO<sub>2</sub>-*i*-PrOH-1.3% was effective for the oxygenation reactions of various substrates such as alkylarenes (**Figure 7e**) and sulfides (**Figure 7f**).

### Conclusion

Ultrasmall  $\alpha$ -MnO<sub>2</sub> (<10 nm) with a low aspect ratio (*c/a* ~2) was, for the first time, successfully synthesized using an alcohol solution process, without any metal doping. Its potential as a host material for multivalent ion (Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Zn<sup>2+</sup>) battery cathodes and as an aerobic oxidation catalyst was fully demonstrated. In the realm of battery application, ultrasmall  $\alpha$ -MnO<sub>2</sub> demonstrates superior cathodic performance compared to

conventional-sized counterparts in all the battery systems, primarily due to the significant reduction in cation diffusion distance within the solid structure. In particular, ultrasmall  $\alpha$ -MnO<sub>2</sub> homogeneously dispersed onto graphene nanosheets was found to be a promising cathode material for Ca-battery. Regarding aerobic oxidation catalysis, the impact of nanosizing is profound, leading to a substantial increase in the efficiency of oxidative conversion reactions of various molecules, such as 1-phenylethanol oxidation, attributable to the vastly expanded active surface area of the catalyst. Thus, the ultrasmall  $\alpha$ -MnO<sub>2</sub> has made a significant impact not only in the field of batteries but also in catalysis. It can be anticipated that this material will not only find applications in next-generation green energy technologies but also set new standards for technologies across various industrial sectors.

Main Text Paragraph.

## Supporting Information

The authors have cited additional references within the Supporting Information. [44] [45] [46] [47] [48] [49]

## CRedit Authorship Contribution

Conceptualization: H.K.; Methodology: H.K.; Formal Analysis: R.I. (lead), H.K.; Investigation: R.I. (synthesis, Mg and Zn battery), S.K. (synthesis, Ca battery), T.Y. (Zn battery), S.T. (Zn battery), K.Y. (catalyst), N.K. (PDF); Resources: T.M. (Mg electrolyte), K.K. (Ca electrolyte); Writing – Original Draft: R.I.; Writing – Review & Editing: H.K. (lead), K.Y., T.M., K.K., N.K., Z.Z.-K., S.O., Y.I., M.M., M.F., I.H., T.I.; Supervision: Z.Z.-K., S.O., Y.I., M.M., M.F., I.H., T.I.; Project Administration: H.K.; Funding Acquisition: H.K.

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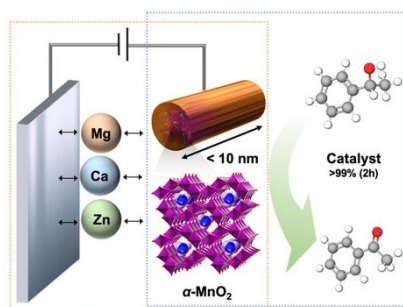
**Keywords:** Manganese oxide • nanoparticle • cathode • catalyst

- [1] R. Yang, Y. Fan, R. Ye, Y. Tang, X. Cao, Z. Yin, Z. Zeng, *Adv. Mater.* **2021**, 33, 2004862.  
 [2] I. Kruk, P. Zajdel, W. van Beek, I. Bakaimi, A. Lappas, C. Stock, M. A. Green, *J. Am. Chem. Soc.* **2011**, 133, 13950.  
 [3] a) Q. Feng, H. Kanoh, K. Ooi, *J. Mater. Chem.* **1999**, 9, 319; b) C. Sun, Y. Zhang, S. Song, D. Xue, *J. Appl. Cryst.* **2013**, 46, 1128; c) D. M. Robinson, Y. B. Go, M. Mui, G. Gardner, Z. Zhang, D. Mastrogianni, E. Garfunkel, J. Li, M. Greenblatt, G. C. Dismukes,

- J. Am. Chem. Soc.* **2013**, 135, 3494; d) T. Hatakeyama, H. Li, N. L. Okamoto, K. Shimokawa, T. Kawaguchi, H. Tanimura, S. Imashuku, M. Fichtner, T. Ichitsubo, *Chem. Mater.* **2021**, 33, 6983; e) W. Zhao, S. J. B. Rubio, Y. Dang, S. L. Suib, *ACS ES&T Eng.* **2022**, 2, 20.  
 [4] a) J. Luo, H. T. Zhu, H. M. Fan, J. K. Liang, H. L. Shi, G. H. Rao, J. B. Li, Z. M. Du, Z. X. Shen, *J. Phys. Chem. C* **2008**, 112, 12594; b) Y. Yuan, A. Nie, G. M. Odegard, R. Xu, D. Zhou, S. Santhanagopalan, K. He, H. Asayesh-Ardakani, D. D. Meng, R. F. Klie, C. Johnson, J. Lu, R. Shahbazian-Yassar, *Nano Lett.* **2015**, 15, 2998.  
 [5] a) D. Zheng, S. Sun, W. Fan, H. Yu, C. Fan, G. Cao, Z. Yin, X. Song, *J. Phys. Chem. B* **2005**, 109, 16439; b) Y. Dong, H. Yang, K. He, S. Song, A. Zhang, *Appl. Catal. B* **2009**, 85, 155.  
 [6] a) M. M. Thackeray, M. H. Rossouw, R. J. Gummow, D. C. Liles, K. Pearce, A. De Kock, W. I. F. David, S. Hull, *Electrochim. Acta* **1993**, 38, 1259; b) P. K. Gupta, A. Bhandari, D. D. Meng, R. F. Klie, C. Johnson, J. Lu, R. Shahbazian-Yassar, *Nano Lett.* **2015**, 15, 2998.  
 [7] a) Y. Chabre, J. Pannetier, *Prog. Solid State Chem.* **1995**, 23, 1; b) S. Chou, F. Cheng, J. Chen, *J. Power Sources* **2006**, 162, 727.  
 [8] a) C. A. J. Appelo, D. Postma, *Geochim. Cosmochim. Acta* **1999**, 63, 3039; b) J. Zhou, L. Yu, M. Sun, S. Yang, F. Ye, J. He, Z. Hao, *Ind. Eng. Chem. Res.* **2013**, 52, 9586.  
 [9] a) J. C. Hunter, *J. Solid State Chem.* **1981**, 39, 142; b) J. E. Greedan, N. P. Raju, A. S. Wills, C. Morin, S. M. Shaw, J. N. Reimers, *Chem. Mater.* **1998**, 10, 3058.  
 [10] a) D. A. Tompsett, M. S. Islam, *Chem. Mater.* **2013**, 25, 2515; b) C. Ling, R. Zhang, F. Mizuno, *ACS Appl. Mater. Interfaces* **2016**, 8, 4508; c) L. M. Housel, L. Wang, A. Abraham, J. Huang, G. D. Renteros, C. D. Quilty, A. B. Brady, A. C. Marschilok, K. J. Takeuchi, E. S. Takeuchi, *Acc. Chem. Res.* **2018**, 51, 575; d) J. Fu, X. Luo, *RSC Adv.* **2020**, 10, 39895; e) X. Gao, H. Wu, W. Li, Y. Tian, Y. Zhang, H. Wu, L. Yang, G. Zou, H. Hou, X. Ji, *Small* **2020**, 16, 1905842.  
 [11] a) T. Uematsu, Y. Miyamoto, Y. Ogasawara, K. Suzuki, K. Yamaguchi, N. Mizuno, *Catal. Sci. Technol.* **2016**, 6, 222; b) E. Hayashi, Y. Yamaguchi, K. Kamata, N. Tsunoda, Y. Kumagai, F. Oba, M. Hara, *J. Am. Chem. Soc.* **2019**, 141, 890.  
 [12] a) A. Umar, A. A. Ibrahim, R. Kumar, H. Albargi, W. Zeng, M. A. M. Alhmami, M. A. Alsaiani, S. Baskoutas, *Mater. Lett.* **2021**, 286, 129232; b) C. Revathi, R. T. R. Kumar, *Electroanalysis* **2017**, 29, 1481.  
 [13] a) H. Li, L. Gui, Z. Gao, F. Ren, H. Zhang, R. Peng, *Nanotechnology* **2021**, 32, 215705; b) M. A. El-Ghobashy, I. A. Salem, W. M. El-Dahrawy, M. A. Salem, *J. Mol. Struct.* **2023**, 1272, 134118.  
 [14] a) L. I. Hill, R. Portal, A. Verbaere, D. Guyomard, *Electrochem. Solid-State Lett.* **2001**, 4, A180; b) J. Huang, A. S. Poyraz, S.-Y. Lee, L. Wu, Y. Zhu, A. C. Marschilok, K. J. Takeuchi, E. S. Takeuchi, *ACS Appl. Mater. Interfaces* **2017**, 9, 4333; c) X. Wang, F. Zhang, C. Xia, L. Cui, F. Yang, *J. Alloys Compd.* **2024**, 970, 172599.  
 [15] A. B. Brady, K. R. Tallman, E. S. Takeuchi, A. C. Marschilok, K. J. Takeuchi, P. Liu, *J. Phys. Chem. C* **2019**, 123, 25042.  
 [16] a) N. Tang, X. Tian, C. Yang, Z. Pi, Q. Han, *J. Phys. Chem. Solids* **2010**, 71, 258; b) Y. Sun, S. Wang, Y. Dai, X. Lei, *Functional Materials Letters* **2015**, 09, 1650005.  
 [17] a) R. Zhang, X. Yu, K.-W. Nam, C. Ling, T. S. Arthur, W. Song, A. M. Knapp, S. N. Ehrlich, X.-Q. Yang, M. Matsui, *Electrochem. Commun.* **2012**, 23, 110; b) B. Wu, G. Zhang, M. Yan, T. Xiong, P. He, L. He, X. Xu, L. Mai, *Small* **2018**, 14, 1703850; c) C. Zuo, F. Xiong, J. Wang, Y. An, L. Zhang, Q. An, *Adv. Funct. Mater.* **2022**, 32, 2202975; d) Y. Qi, H. Li, K. Shimokawa, X. Ye, T. Kawaguchi, T. Ichitsubo, *J. Phys. Chem. C* **2023**, 127, 21271; e) K. Shimokawa, T. Hatakeyama, H. Li, T. Ichitsubo, *Curr. Opin. Electrochem.* **2023**, 38, 101209.  
 [18] W. Zhang, H. Li, Z. Zhang, M. Xu, Y. Lai, S.-L. Chou, *Small* **2020**, 16, 2001524.  
 [19] Y. Tian, G. Zeng, A. Rutt, T. Shi, H. Kim, J. Wang, J. Koettgen, Y. Sun, B. Ouyang, T. Chen, Z. Lun, Z. Rong, K. Persson, G. Ceder, *Chem. Rev.* **2021**, 121, 1623.  
 [20] a) T. Le, N. Sadique, L. M. Housel, A. S. Poyraz, E. S. Takeuchi, K. J. Takeuchi, A. C. Marschilok, P. Liu, *ACS Appl. Mater. Interfaces* **2021**, 13, 59937; b) Q. Yang, Y. Chen, Y. Yang, T. Xu, Y. Lin, X. Zhang, J. Wang, Y.-N. Liu, Y. Li, *Ind. Eng. Chem. Res.* **2023**, 62, 16757.

- [21] K. Ma, Q. Li, C. Hong, G. Yang, C. Wang, *ACS Appl. Mater. Interfaces* **2021**, 13, 55208.
- [22] a)M. Koutani, E. Hayashi, K. Kamata, M. Hara, *J. Am. Chem. Soc.* **2022**, 144, 14090; b)K. Kamata, N. Kinoshita, M. Koutani, R. Aono, E. Hayashi, M. Hara, *Catal. Sci. Technol.* **2022**, 12, 6219.
- [23] a)J.-H. Moon, H. Munakata, K. Kajihara, K. Kanamura, *Electrochemistry* **2013**, 81, 2; b)G. Zhu, J. Zhu, W. Li, W. Yao, R. Zong, Y. Zhu, Q. Zhang, *Environ. Sci. Technol.* **2018**, 52, 8684.
- [24] a)Z. Hu, X. Xiao, C. Chen, T. Li, L. Huang, C. Zhang, J. Su, L. Miao, J. Jiang, Y. Zhang, J. Zhou, *Nano Energy* **2015**, 11, 226; b)S. Chen, S. Zhang, T. Wang, Z. Lei, M. Zhu, X. Dai, F. Liu, J. Li, H. Yin, *Mater. Chem. Phys.* **2018**, 208, 258; c)A. Khan, A. M. Toufiq, F. Tariq, Y. Khan, R. Hussain, N. Akhtar, S. u. Rahman, *Mater. Res. Express* **2019**, 6, 065043; d)M. Lübke, A. Sumboja, L. McCafferty, C. F. Armer, A. D. Handoko, Y. Du, K. McColl, F. Cora, D. Brett, Z. Liu, J. A. Darr, *ChemistrySelect* **2018**, 3, 2613; e)R. Cerc Korošec, P. Umek, A. Gloter, J. Padežnik Gomilšek, P. Bukovec, *Beilstein J. Nanotechnol.* **2017**, 8, 1032; f)S. M. Alharbi, M. A. Alkhalifah, B. Howchen, A. N. A. Rahmah, V. Celorrio, D. J. Fermin, *ACS Mater. Au* **2024**, 4, 74; g)X. Hu, J. Chen, S. Li, Y. Chen, W. Qu, Z. Ma, X. Tang, *J. Phys. Chem. C* **2020**, 124, 701.
- [25] a)H. Kobayashi, K. Yamaguchi, I. Honma, *RSC Adv.* **2019**, 9, 36434; b)Y. Sugawara, H. Kobayashi, I. Honma, T. Yamaguchi, *ACS Omega* **2020**, 5, 29388; c)R. Iimura, H. Watanabe, T. Mandai, I. Honma, H. Imai, H. Kobayashi, *ACS Applied Energy Materials* **2024**, 7, 5308.
- [26] A. Manthiram, J. Kim, S. Choi, *MRS Proc.* **1999**, 575, 9, 9.
- [27] S. Hong, S. Jin, Y. Deng, R. Garcia-Mendez, K.-i. Kim, N. Utomo, L. A. Archer, *ACS Energy Lett.* **2023**, 8, 1744.
- [28] C. S. Johnson, D. W. Dees, M. F. Mansuetto, M. M. Thackeray, D. R. Vissers, D. Argyriou, C. K. Loong, L. Christensen, *J. Power Sources* **1997**, 68, 570.
- [29] M. Kakazey, N. Ivanova, Y. Boldurev, S. Ivanov, G. Sokolsky, J. G. Gonzalez-Rodriguez, M. Vlasova, *J. Power Sources* **2003**, 114, 170.
- [30] J. Luo, S. L. Suib, *Chem. Commun.* **1997**, 1031.
- [31] H. Kobayashi, Y. Fukumi, H. Watanabe, R. Iimura, N. Nishimura, T. Mandai, Y. Tominaga, M. Nakayama, T. Ichitsubo, I. Honma, H. Imai, *ACS Nano* **2023**, 17, 3135.
- [32] M. Okubo, E. Hosono, J. Kim, M. Enomoto, N. Kojima, T. Kudo, H. Zhou, I. Honma, *J. Am. Chem. Soc.* **2007**, 129, 7444.
- [33] Y. Chen, Z. Li, B. Li, Z. Zhang, J. Wei, B. Wang, Y. Huang, *ACS Applied Energy Materials* **2023**, 6, 3329.
- [34] L. Wu, Z. Li, Y. Xiang, W. Dong, X. Qi, Z. Ling, Y. Xu, H. Wu, M. D. Levi, N. Shpigel, X. Zhang, *Small* **2024**, 20, 2404583.
- [35] S. J. Kim, D. Wu, N. Sadique, C. D. Quilty, L. Wu, A. C. Marschilok, K. J. Takeuchi, E. S. Takeuchi, Y. Zhu, *Small* **2020**, 16, 2005406.
- [36] T. Subramaniam, B. S. Krishnaveni, S. Devaraj, *Journal of Materials Science: Materials in Electronics* **2024**, 35, 1184.
- [37] C. Ling, R. Zhang, T. S. Arthur, F. Mizuno, *Chem. Mater.* **2015**, 27, 5799.
- [38] a)Z. Li, O. Fuhr, M. Fichtner, Z. Zhao-Karger, *Energy Environ. Sci.* **2019**, 12, 3496; b)Z. Li, B. P. Vinayan, T. Diemant, R. J. Behm, M. Fichtner, Z. Zhao-Karger, *Small* **2020**, 16, 2001806.
- [39] a)K. Kisu, S. Kim, T. Shinohara, K. Zhao, A. Züttel, S. Orimo, *Sci. Rep.* **2021**, 11, 7563; b)K. Kisu, R. Mohtadi, S. Orimo, *Adv. Sci.* **2023**, 10, 2301178.
- [40] a)R. Iimura, H. Kobayashi, I. Honma, *Electrochemistry* **2022**, 90, 067002; b)J. Han, S. Yagi, H. Takeuchi, M. Nakayama, T. Ichitsubo, *J. Phys. Chem. C* **2022**, 126, 19074; c)W. Zhou, C. Xu, B. Gao, M. Nakayama, S. Yagi, Y. Tateyama, *ACS Energy Lett.* **2023**, 8, 4113.
- [41] X. Ye, H. Li, T. Hatakeyama, H. Kobayashi, T. Mandai, N. L. Okamoto, T. Ichitsubo, *ACS Appl. Mater. Interfaces* **2022**, 14, 56685.
- [42] T. R. Juran, J. Young, M. Smeu, *J. Phys. Chem. C* **2018**, 122, 8788.
- [43] a)K. Yamaguchi, H. Kobayashi, T. Oishi, N. Mizuno, *Angew. Chem. Int. Ed.* **2012**, 51, 544; b)K. Yamaguchi, Y. Wang, H. Kobayashi, N. Mizuno, *Chem. Lett.* **2012**, 41, 574; c)K. Yamaguchi, H. Kobayashi, Y. Wang, T. Oishi, Y. Ogasawara, N. Mizuno, *Catal. Sci. Technol.* **2013**, 3, 318.
- [44] F. Izumi, K. Momma, *Solid State Phenomena* **2007**, 130, 15.
- [45] S. Kohara, M. Itou, K. Suzuya, Y. Inamura, Y. Sakurai, Y. Ohishi, M. Takata, *J. Phys. Condens. Matter* **2007**, 19, 506101.
- [46] D. A. Keen, *J. Appl. Cryst.* **2001**, 34, 172.
- [47] B. Ravel, M. Newville, *J. Synchrotron Rad.* **2005**, 12, 537.
- [48] T. Mandai, *ACS Appl. Mater. Interfaces* **2020**, 12, 39135.
- [49] A. Shyamsunder, L. E. Blanc, A. Assoud, L. F. Nazar, *ACS Energy Lett.* **2019**, 4, 2271.

## Entry for the Table of Contents



An ultrasmall  $\alpha$ - $\text{MnO}_2$  ( $<10 \text{ nm}$ ) with a low aspect ratio ( $c/a \sim 2$ ) is synthesized using an alcohol solution process. It exhibits superior performances in both multivalent-ion battery cathodes and aerobic oxidation catalysts. The versatile functionality of ultrasmall  $\alpha$ - $\text{MnO}_2$  underscores its potential to revolutionize energy storage and catalysis, offering broad applicability in next-generation green energy technologies.