

Intercalation and Conversion Reactions of Nanosized #- MnO Cathode in the Secondary Zn/MnO Alkaline Battery

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3 ABSTRACT
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7 This work reports rechargeable Zn/ β -MnO₂ alkaline batteries as promising stationary energy
8 storage. Unlike commercial alkaline batteries with poor cyclic performance, the nanosized β -
9 MnO₂ cathode in the mixture of LiOH and KOH electrolyte enables rechargeable reactions with
10 high capacity. To unveil the underlying reaction mechanisms of nanosized β -MnO₂, we combine
11 thermodynamic frameworks with experimental characterization including electrochemistry, X-
12 ray diffraction, and X-ray photoelectron spectroscopy. The results demonstrate a series of proton
13 intercalation reaction (β -MnO₂ \rightarrow γ -MnOOH) and two-phase conversion reactions (γ -MnOOH
14 \rightarrow Mn(OH)₂ \rightarrow λ -MnO₂) during the first cycle, and Li and H co-intercalation in the host
15 structure of λ -MnO₂ spinel during the hundredth cycle. It is remarkable that the addition of Bi₂O₃
16 in the nanosized β -MnO₂ cathode exhibits the outstanding capacity. After one hundred
17 discharging, the battery demonstrates a capacity of 316 mAh g⁻¹. Our findings can serve in the
18 tailored cathode design in high capacity and rechargeable Zn/ β -MnO₂ alkaline batteries.
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INTRODUCTION

Ever since Lewis Urry invented a primary Zn/MnO₂ alkaline battery back in the late 1950's, it has been widely adopted as an energy source for low-power electronics. Recently, the Zn/MnO₂ aqueous battery is gaining attention as a rechargeable energy storage for smart grid technology.¹⁻

³ Compared to a Li-ion battery, a Zn/MnO₂ aqueous battery has several advantages such as low material cost, better safety, and non-toxicity. To illustrate, the current rechargeable Zn/MnO₂ aqueous battery technology costs under \$90 per kWh,² whereas the cost for Li-ion batteries are unlikely to fall below \$200 per kWh.³ In addition, Zn/MnO₂ aqueous battery operates with water-based electrolytes, furnishing a higher degree of safety making them an attractive option for grid-scale usage in residential homes and dense urban areas.

MnO₂ exists in multiple crystallographic structures including α -, β -, γ -, δ -, λ -, and R-MnO₂. These MnO₂ polymorphs are defined by different connection of the basic structural unit, MnO₆ octahedron, and various types of tunnels within the crystal structure.⁴⁻⁵ Electrochemical reactions vary in Zn/MnO₂ aqueous batteries dependent on the phase of MnO₂ and electrolyte used, however, the most common discharge mechanism of MnO₂ involves a homogeneous reaction and followed by a heterogeneous reaction.⁶⁻⁸ Once the discharge initiates, protons intercalate into tunnels of MnO₂ through the homogeneous reaction without Mn-O bond breakage, however the bonds begin to break in the heterogeneous reaction as the discharge proceeds further leading to eventual deformation of the lattice. During the homogeneous reaction, the voltage changes rapidly, however the heterogeneous reaction manifests the voltage plateaus due to two-phase reactions.

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3 Recently, many studies have reported the development of rechargeable Zn/MnO₂ aqueous
4 batteries which utilize mild acidic electrolytes.⁹⁻¹¹ Lee et al. describe that a Zn/ α -MnO₂ system in
5 ZnSO₄ electrolyte involves Zn/Zn²⁺ redox at the anode and α -MnO₂/Mn²⁺ at the cathode. An
6 additional reversible phase of Zn₄(OH)₆(SO₄) \cdot 5H₂O (zinc hydroxide sulfate) precipitates on the
7 cathode's surface due to Zn²⁺ and SO₄²⁻ in an aqueous electrolyte.¹⁰ Pan et al. report that the
8 rechargeability of Zn/ α -MnO₂ aqueous battery is significantly improved by adding MnSO₄ salt in
9 the ZnSO₄ electrolyte.¹¹ They describe the same redox reactions proposed by Lee et al. with an
10 undefined hydration number for the zinc hydroxide sulfate. However, the addition of the MnSO₄
11 salt in the electrolyte suppresses the dissolution of Mn²⁺ and enables longevity of over 5000
12 cycles.
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27 In addition to the acidic solutions, the basic solutions have been investigated to understand the
28 rechargeability of Zn/MnO₂ aqueous batteries. Gallaway et al. probed the phase transformation
29 of the cathode/anode in a commercial alkaline 'AA' cell.¹² They observed ZnMn₂O₄ (hetaerolite)
30 forming in the cathode, implying that it is a side product of the chemical reaction between
31 MnOOH and Zn(OH)₄²⁻. The Zn(OH)₄²⁻ (zincate ion) is generated from Zn(OH)₄²⁻/Zn redox at
32 the Zn anode which then migrates to the cathode where MnOOH is formed after MnO₂ is
33 reduced. The ZnMn₂O₄ phase produced is electrochemically inactive phase and degrades the
34 cycle performance of Zn/MnO₂ aqueous batteries. Turney et al. reported that the formation of
35 Zn(OH)₄²⁻ is favorable at the Zn anode where OH⁻ species are concentrated inducing the
36 production of ZnMn₂O₄.³ In another study, Hertzberg et al. found that the combination of LiOH
37 and KOH as electrolytes in a Bi species incorporated Zn/ β -MnO₂ alkaline battery improved the
38 rechargeability demonstrating a reversible single-electron reaction for 60 cycles.¹³ They
39 proposed that a reversible reaction occurs during the cycling between the reduced phases
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(Mn(OH)₂ and LiMn₂O₄) and the oxidized phase (δ-MnO₂). This reaction mechanism, however, is contentious due to δ-MnO₂ being measured solely during the first charged state and not in any of the subsequent cycles.

Optimizing the utilization of two electrons in MnO₂ is an essential for high-energy stationary storage. Many studies have demonstrated that the capacity increases using nanostructured materials.^{5, 14-15} Chen et al. reported that nanosized γ-MnO₂ shows almost two-times higher discharge capacity than bulk γ-MnO₂.¹⁴ They suggested that broad surface area in nano-scale MnO₂ enlarges contact between MnO₂ active materials and an electrolyte which lowers internal resistance and facilitates proton diffusion. In order to utilize large capacity and improve the reversibility of reactions in alkaline solutions, we synthesized nanoscale β-MnO₂ and assembled the Zn/β-MnO₂ alkaline battery with the LiOH and KOH electrolytes. The discharge capacity shows 225 mAh g⁻¹ at the hundredth cycle, which is higher than the capacity of the battery made of commercial β-MnO₂ by 113 mAh g⁻¹. Furthermore, we studied the phase transformation of nanosized β-MnO₂ in Zn/β-MnO₂ alkaline battery. The result indicates that the proton intercalation reaction is followed by two-phase conversion reactions at the first cycle, however, a different reaction mechanism is observed at the hundredth cycle. Li and H co-inserted λ-MnO₂ spinel and λ-MnO₂ spinel are formed at the hundredth discharged and charged state, respectively. Lastly, we incorporated β-MnO₂ cathode with 4% mole fraction of Bi₂O₃ to enhance the electrochemical performance. The discharge capacity is 316 mAh g⁻¹ at the hundredth cycle. Bi₂O₃ additive reacts with Zn(OH)₄²⁻, which alleviates the capacity loss driven by the formation of irreversible ZnMn₂O₄.

EXPERIMENTAL METHODS

β -MnO₂ synthesis. β -MnO₂ was synthesized by the multiple heating steps in order to confirm Mn⁴⁺, to remove NO_x gases completely and crystalize nanosized β -MnO₂. The thermal decomposition process begins with dissolving 10 g of Mn(NO₃)₂·4H₂O in 16 mL deionized (D.I.) water. The solution was stirred with a magnetic bar in a round-bottom flask while being heated in the silicon-oil bath to increase the reaction temperature to 140 °C. Once the temperature reached 140 °C, the reaction was held at that temperature until the initially clear solution developed a black color with high viscosity indicating the oxidation to the Mn⁴⁺ state. Then, the round flask was transferred to a preheated vacuum oven and kept at 125 °C overnight to facilitate complete drying of the MnO₂ product and to eliminate excess NO_x gases. The sample was removed from the vacuum oven after 12 h and transferred to a preheated box furnace heated to 125 °C. The temperature of the oven was programmed to increase up to 325 °C with a step of 5 °C/min, then to hold the temperature at 325 °C for 5 h to crystalize nanosized β -MnO₂. After natural cooling, the solid sample was ground with a mortar and a pestle to turn it into fine powder.

Electrochemical characterization. The working electrode is composed of the β -MnO₂ active material (synthesized β -MnO₂, commercial β -MnO₂, or synthesized β -MnO₂ with 4 % mole fraction of Bi₂O₃), carbon black Super-P, and polytetrafluoroethylene (PTFE) with a 60:30:10

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3 weight ratio. The typical mass loading of β -MnO₂ is 11.4 mg cm⁻². The electrode was implanted
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5 onto a Ni foam current collector and pressed using a hydraulic press with a pressure of eight
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7 tons. The pressed electrode was then covered with one layer of polyvinylidene chloride, two
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9 layers of nonwoven separator (FS 22145 from Freudenberg LLC) and a Zn plate counter
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11 electrode. They were sandwiched between two acrylic plates, which were held together tightly
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13 with screws. After an assembly, the battery was immersed in a 20 mL beaker with 10.5 mL of 1
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15 M KOH and 3 M LiOH electrolyte. This molar ratio of 1 : 3 = KOH : LiOH was optimized for
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17 alkaline batteries in previous report.¹³ Parafilm was used to seal the beaker. All batteries in this
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19 study were tested at C/10 current rate for the first cycle and C/5 for the following cycles.
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21 Considering the rate capability tests for synthesized β -MnO₂ with/without Bi₂O₃, the
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23 discharge/charge process was carried out over the course 20 cycles for each stage except for the
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25 last stage (9 cycles). Constant current rates were calculated using the theoretical two-electron
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27 capacity of MnO₂ which is 616 mAh g⁻¹. The voltage range used is 0.50 < V < 1.80. The constant
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29 voltage of 1.80 V was applied at the end of constant current charging until the current decreased
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31 to 10% of the current rate. The batteries were cycled using an Arbin battery cycler at room
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33 temperature. In addition, the electrochemical stability window of electrolyte was measured using
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35 a Solartron 1260 Impedance Analyzer. The linear sweep voltammetry was taken on Ni foam
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37 electrodes compared against Hg/HgO reference electrode in 1M KOH and 3M LiOH electrolyte
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39 at a scan rate of 1 mV/s.

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42 **In house X-ray diffraction (XRD).** The in-house XRD samples were synthesized and
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44 commercial β -MnO₂ powder, and cycled β -MnO₂ electrodes. Cycled electrodes were collected at
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46 1.25 V, 1.05 V, 0.50 V and 1.80 V during the first cycle of synthesized β -MnO₂ in Zn/ β -MnO₂
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48 alkaline batteries. The collected electrodes were washed with running D.I. water and soaked in
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3 the D.I. water overnight. After washing, the electrodes were dried in 60 °C for 3 hours in the
4 oven. All the XRD data were collected at an ambient temperature on a Bruker D8 Advance
5 diffractometer at 40 kV, 40 mA for Cu K α ($\lambda = 1.5418 \text{ \AA}$), with a scan speed of 5 s per step, a
6 step size of 0.02° in 2θ , and a 2θ range of $10\text{--}80^\circ$.
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12 **Synchrotron X-ray diffraction (SXR).** Cycled electrodes of synthesized $\beta\text{-MnO}_2$ collected at
13 the hundredth discharge/charged state were selected for SXR analysis. The cycled electrodes
14 were washed with running D.I. water and soaked in the D.I. water overnight. After washing,
15 electrodes were dried at 60 °C for 3 hours in the oven. SXR spectra were acquired at the
16 Advanced Photon Source (APS) at Argonne National Laboratory (ANL) on beamline 11-BM ($\lambda =$
17 0.4145 \AA). The beamline uses a sagittal focused X-ray beam with a high precision diffractometer
18 circle and perfect Si(111) crystal analyzer detection for high sensitivity and resolution. SXR
19 spectra were plotted based on $\lambda = 1.5418 \text{ \AA}$ to compare with the in-house XRD spectra.
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31 **X-ray photoelectron spectroscopy (XPS).** XPS was performed using a Kratos AXIS Supra at
32 the Laboratory for Electron and X-ray Instrumentation. Cycled samples were prepared by
33 washing with running D.I. water and soaking the electrode in the D.I. water overnight, and
34 drying in 60 °C for 3 h in the oven. The XPS was operated using an Al anode source running at
35 15 kV. All XPS measurements were collected using a $300 \mu\text{m}$ by $700 \mu\text{m}$ spot size without using
36 a charge neutralizer during acquisition. A step size of 0.3eV was used for survey scan and 0.1 eV
37 was for high-resolution scans. All the spectra were calibrated with carbon $1s$ sp³ at 284.8 eV .
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47 **Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS).** The
48 SEM/EDS samples selected were synthesized and commercial $\beta\text{-MnO}_2$ powders, Bi_2O_3 and
49 immersed Bi_2O_3 powder in 6M Zn nitrate solution. The sample of immersed Bi_2O_3 powder was
50 prepared by washing with running D.I. water, soaking the powder in the D.I. water overnight,
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3 and drying in 60 °C for 3 h in the oven. All powder samples were loaded onto a SEM holder
4 using a carbon adhesive tape. The images were obtained using a 15 kV energy source using the
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6 FEI/Phillips XL30 ESEM.
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10 **Computational details.** First principles calculations were conducted based on spin-polarized
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12 GGA+ U ¹⁶⁻¹⁷ using the Perdew–Burke–Ernzerhof of exchange and correlation functionals.¹⁸ A
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14 plane-wave basis set and the projector-augmented wave (PAW) method¹⁹⁻²⁰ were used as
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16 parameterized in the Vienna *ab initio* simulation package (VASP).²¹ A gamma point mesh is
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18 performed with $7 \times 7 \times 7$ k -points for λ -MnO₂. All the atoms were fully relaxed to calculate the
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20 optimized structure with a cutoff energy of 1.3 times the maximum cutoff specified by the
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22 pseudopotentials on a plane-wave basis set. The scheme proposed by Persson et al²² was adopted
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24 in order to obtain an accurate standard Gibbs free energy of formation.
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31 RESULTS AND DISCUSSION

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34 **The influence of a particle size.** The powder of synthesized and commercial β -MnO₂ are
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36 measured by in-house X-ray diffractometer as shown in figure 1(a). The peak broadenings are
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38 observed in synthesized β -MnO₂, however, the peak positions match the reference β -MnO₂. The
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40 XPS result confirms Mn 3s multiplet splitting with $\Delta E = 4.62$ eV in figure 1(b); this value agrees
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42 well with $\Delta E = 4.65$ eV found in commercial β -MnO₂ (Alfa Aesar) as shown in figure S1.²³ The
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44 SEM image shows agglomerated secondary particles from the synthesized β -MnO₂ (the red color
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46 box) and chunky particles with small parasites from the commercial β -MnO₂ (the orange color
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48 box) in figure 1(c). In the synthesized β -MnO₂ the primary particle is in a size range of less than
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51 50 nm. The Brunauer–Emmett–Teller (BET) surface analysis conducted with the nitrogen
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53 sorption isotherms at -196 °C by Autosorb - iQ (Quantachrome) indicates ~21 times larger
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3 surface area for the synthesized β -MnO₂ than the commercial β -MnO₂ in (figure S2). The cyclic
4 performance of Zn/ β -MnO₂ alkaline batteries is tested in 1 M KOH and 3 M LiOH containing
5 electrolyte as shown in figure 1(d). The first discharge capacity of synthesized β -MnO₂ is 574
6 mAh g⁻¹ (approximately 93% of the MnO₂'s theoretical capacity of 616 mAh g⁻¹). The
7 commercial β -MnO₂ produces 464 mAh g⁻¹ during the first discharge (approximately 75% of the
8 theoretical capacity). The discharge capacity of synthesized β -MnO₂ at the hundredth cycle is
9 225 mAh g⁻¹, which is higher than that of commercial β -MnO₂, 112 mAh g⁻¹. The coulombic
10 efficiency (CE) defined by the percentage of charge capacity over discharge capacity is less than
11 100 %. This is due to the different amount of additional capacity produced by H₂ and O₂ gases,
12 which are generated within the battery's operating voltage (figure S3). The gases are released
13 from the customized beaker cell and its configuration is demonstrated in the experimental.
14 Another factor affecting the CE is the size of β -MnO₂. We estimate that bulk β -MnO₂ materials,
15 which have relatively small surface-area-to-volume ratio do not promote the formation of
16 irreversible ZnMn₂O₄ phase, resulting in relatively higher CE than the synthesized β -MnO₂
17 nanomaterials. In case of synthesized β -MnO₂ nanomaterials, it improves the specific capacity
18 during cycles, however it promotes the formation of ZnMn₂O₄ phase at the same time due to its
19 large surface-area-to-volume ratio.
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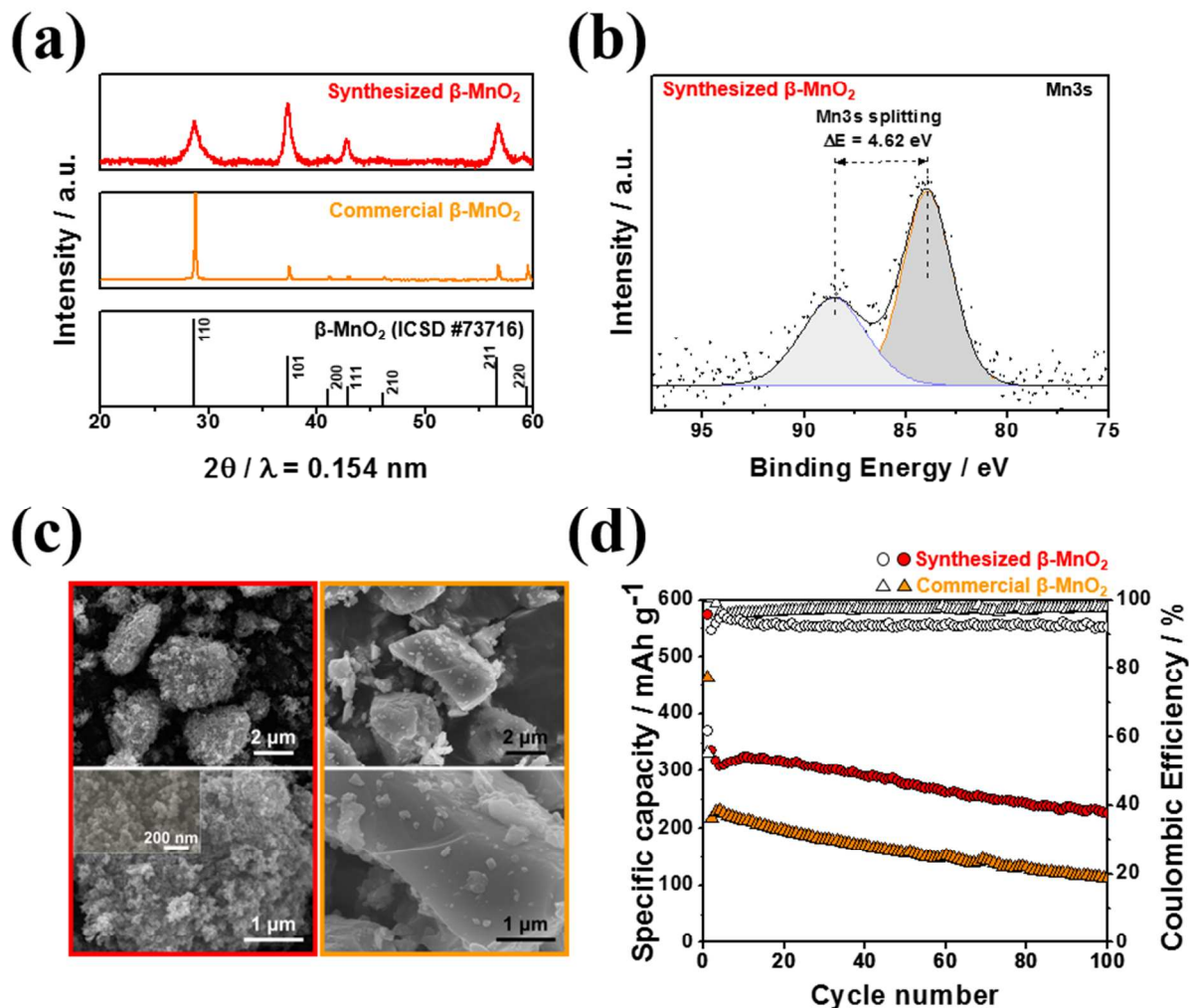


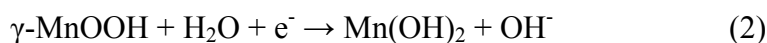
Figure 1. (a) In-house XRD patterns for synthesized and commercial β -MnO₂ (Alfa Aesar); (b) Mn 3s splitting in the XPS result of synthesized β -MnO₂; (c) SEM images for synthesized (red box) and commercial β -MnO₂ (orange box); (d) Cyclic performance for synthesized β -MnO₂ and commercial β -MnO₂ at C/10 current rate for the first cycle and C/5 for the following cycles.

The gap between the discharge capacities from two batteries is most likely due to the difference between particle sizes of the active materials. The nanoscale β -MnO₂ particles have broader electrochemical surface area than the bulk β -MnO₂ particles, which increases the effective contact points with the electrolyte, lowering internal resistance and shortening diffusion

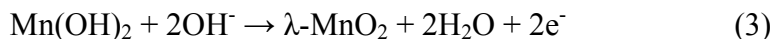
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3 pathways.^{5, 15} In addition, insufficiently coordinated surface atoms of the synthesized β -MnO₂
4 nanoparticles are expected to facilitate chemical adsorptions from aqueous solutions and undergo
5 electrochemical reactions. Han et al. reported the effect of the nanosized particle on an
6 adsorption energy of chemicals in aqueous media.²⁴ It shows that the adsorption energy of
7 chemicals on the surface of a nanoparticle is stronger than that on the surface of a bulk material.
8 Nanoparticles hold a high ratio of undercoordinated surface atoms to coordinated atoms, thus
9 their chemisorption is greater than that of the bulk materials. The nanosized β -MnO₂ case are
10 expected to undergo facile electrochemical reactions once H₂O adsorption from aqueous
11 electrolytes has occurred. The reaction mechanism of synthesized β -MnO₂ will be discussed
12 further in this study. Another factor to consider regarding surface chemisorption is the cohesive
13 energy per atom of a nanoparticle.²⁵ Constituent atoms in a nanoparticle are bound together with
14 weak cohesive energy, which is a less stable formation than a bulk material. Thus nanoparticles
15 in aqueous media are likely to bind with nearby molecules for stabilization, which in turn
16 stimulates electrochemical reactions.
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39 **The reaction mechanism of nanosized β -MnO₂ during the first cycle.** *Ex situ* in-house XRD
40 patterns are measured for synthesized β -MnO₂ cathodes during the first cycle of Zn/ β -MnO₂
41 alkaline batteries (figure 2). The reaction mechanism of synthesized β -MnO₂ nanomaterial is
42 proposed as follows:
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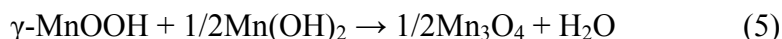
49 Electrochemical reaction (the first discharge):
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Electrochemical reaction (the first charge):



Chemical reaction:



To further validate the reaction mechanism characterized by *ex situ* in-house XRD patterns, the theoretical reaction voltage (E) for each electrochemical reaction proposed in Eq. (1-4) is calculated by applying the Nernst equation as follows:

$$E = E^\circ + 2.303 \frac{RT}{F} \log \text{pOH} - (-1.119) \text{ V vs. Zn(OH)}_4^{2-} | \text{Zn} \quad (6)$$

where E° is the standard reduction potential (table S1) which is obtained by the standard Gibbs free energy of formation (table S2); R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$); T is the room temperature (298.15 K); F is the Faraday constant (96485 C mol^{-1}); pOH is the concentration of hydroxide. The theoretical value of pOH = -0.6 (pH = 14.6) is used since the electrolyte consists of 1 M KOH and 3 M LiOH, where 4 M OH^- exists in total. In alkaline media, the Zn anode has a redox couple with Zn(OH)_4^{2-} .^{12, 26} The theoretical reaction voltage is therefore measured with respect to the standard reduction potential of $\text{Zn(OH)}_4^{2-} | \text{Zn}$ (1.119 V vs. SHE).²⁷ The ideal voltage curve of a Zn/ β - MnO_2 alkaline battery fabricated with synthesized β - MnO_2 nanomaterial is presented in figure 2(b). The theoretical voltage profile (dotted line) matches well with the experimental voltage profile, which will be discussed in detail.

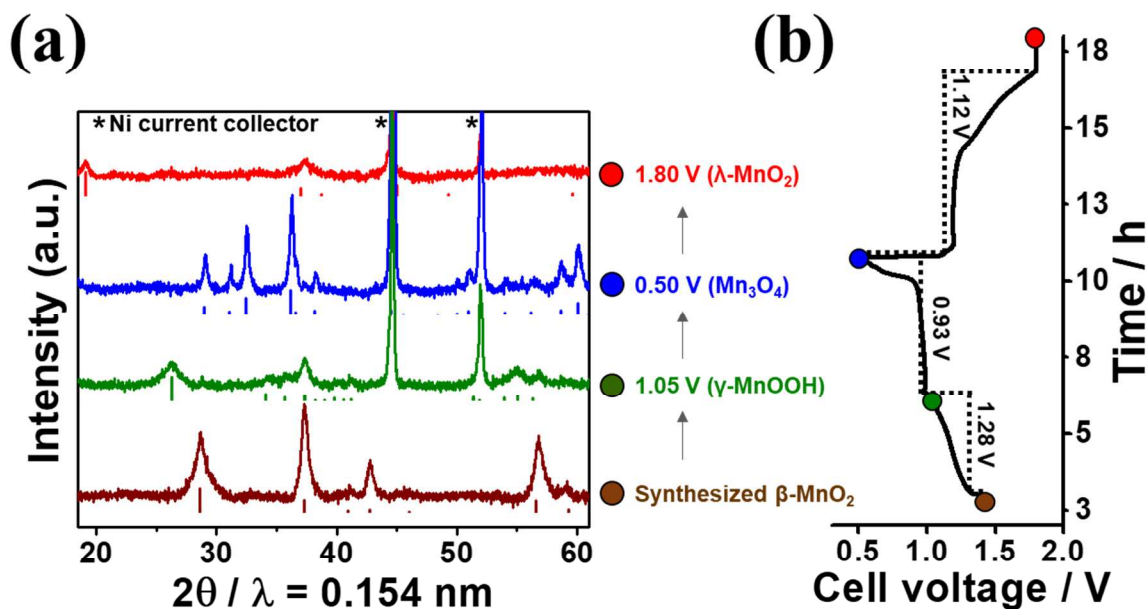


Figure 2. (a) *Ex situ* in-house XRD patterns for synthesized β -MnO₂ nanomaterial and its intermediate phases during the first cycle. The vertical line presents XRD patterns from ICSD database (β -MnO₂: #73716, γ -MnOOH: #84949, Mn₃O₄: #643199, and λ -MnO₂: #193445). Detailed XRD patterns are shown in figure S4. (b) The voltage profile for the first discharge/charge of a Zn/ β -MnO₂ alkaline battery at C/10 current rate. The colored circles represent points that synthesized β -MnO₂ nanomaterial and cycled β -MnO₂ cathode samples are collected. The dotted line indicates the theoretical voltage profile at pH=14.6.

As mentioned above, XRD analysis shown in figure 2(a) indicates that the synthesized powder is β -MnO₂. β -MnO₂ has a tetragonal crystal lattice where Mn-O octahedrons are connected in a corner-sharing and an edge-sharing configurations as shown in figure 3. Void tunnels and Mn-O octahedrons are positioned 1 x 1. Upon the initiation of the first discharge, protons originating from H₂O molecules adsorbed on the surface of nanosized β -MnO₂ intercalate into the void tunnels and form γ -MnOOH at the end of the first-electron reaction (Eq. (1)). The XRD pattern

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3 of γ -MnOOH is obtained during the first discharge at 1.05 V (figure 2). γ -MnOOH is a
4 monoclinic crystal lattice where the original 1 x 1 void tunnels in β -MnO₂ are occupied with
5 protons, resulting in a distortion in the lattice (figure 3). The XRD spectrum acquired at 1.25 V
6 during the early stage of proton intercalation at the first discharge shows the overall peak
7 intensity of β -MnO₂ decreasing, yet the phase still holds the tetragonal crystal lattice (figure
8 S4(b)). The crystal lattice gets increasingly distorted as the proton concentration increases and
9 the structure becomes monoclinic at the end of the first-electron reaction at 1.05 V (figure 2(a)
10 and figure 3). Kordesch et al. proposed that the first-electron reaction of MnO₂ in a Zn/MnO₂
11 alkaline battery is a solid-solution intercalation reaction.²⁸ This reaction is a homogeneous step
12 because Mn-O bonding in the host MnO₂ is retained during proton intercalation. The theoretical
13 voltage for the β -MnO₂ | γ -MnOOH redox couple averages 1.28 V upon proton intercalation,
14 which is located within the experimental voltage curve of the first-electron reaction (figure 2(b)).
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31 In addition the XRD results indicate Mn₃O₄ species at the end of first discharge (0.50 V) in
32 figure 2(a). Mn₃O₄ has the tetrahedral crystal lattice where corner-sharing Mn-O tetrahedrons
33 and edge-sharing Mn-O octahedrons are interconnected (figure 3). It is noted that Mn₃O₄ is
34 unlikely to reduce from γ -MnOOH by electrochemical reaction because Mn₃O₄ has incorporating
35 two Mn³⁺ and only one Mn²⁺, which would indicate the involvement of only 1/3 electron. The
36 first discharge is a two-electron reaction as its experimental capacity is 574 mAh g⁻¹, which is
37 approximately 93% of theoretical capacity of MnO₂'s two electrons. Therefore Mn²⁺ species
38 should be formed at the end of the first discharge. It has been reported that MnOOH is reduced to
39 Mn(OH)₂ by a two-phase conversion reaction (Eq. (2))²⁹⁻³⁰ and Mn₃O₄ is formed by a parallel
40 chemical reaction (Eq. (5))^{12, 30} in the alkaline batteries. Mn(OH)₂ has the trigonal crystal lattice
41 where the layer of edge-sharing M-O octahedrons and the layer of the proton are aligned along
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3 the c-axis as shown in figure 3. Mn_3O_4 is generated by the chemical reaction between MnOOH
4 and $\text{Mn}(\text{OH})_2$ while the $\beta\text{-MnO}_2$ reduces to $\text{Mn}(\text{OH})_2$ electrochemically. We estimate this
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6 chemical reaction proceeds further while collecting the XRD sample for a cathode by *ex situ*
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8 methods. Additional Mn_3O_4 begins to form after the electrochemical test stopped at the end of
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10 first discharge (0.50 V) and its amount increases extensively until the *ex situ* sample is collected.
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14 Donne et al. demonstrated that the formation of Mn_3O_4 is a kinetically limited reaction.²⁹ They
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16 measured Mn_3O_4 when experiments were tested over the extended time duration. Hertzberg et
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18 al., however, did not detect the Mn_3O_4 but $\text{Mn}(\text{OH})_2$ while conducting *in situ* X-ray
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20 diffractometer.¹³ Mn_3O_4 formation is alleviated in the relatively short-time frame between
21
22 stopping the electrochemical reaction and measuring its XRD spectra. It is noted that the
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24 theoretical voltage of $\gamma\text{-MnOOH} \mid \text{Mn}(\text{OH})_2$ redox couple demonstrates the formation of
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26 $\text{Mn}(\text{OH})_2$ during the first discharge. The voltage is 0.93 V, which corresponds well with the
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28 experimental voltage plateau during the second-electron reaction (figure 2(b)).
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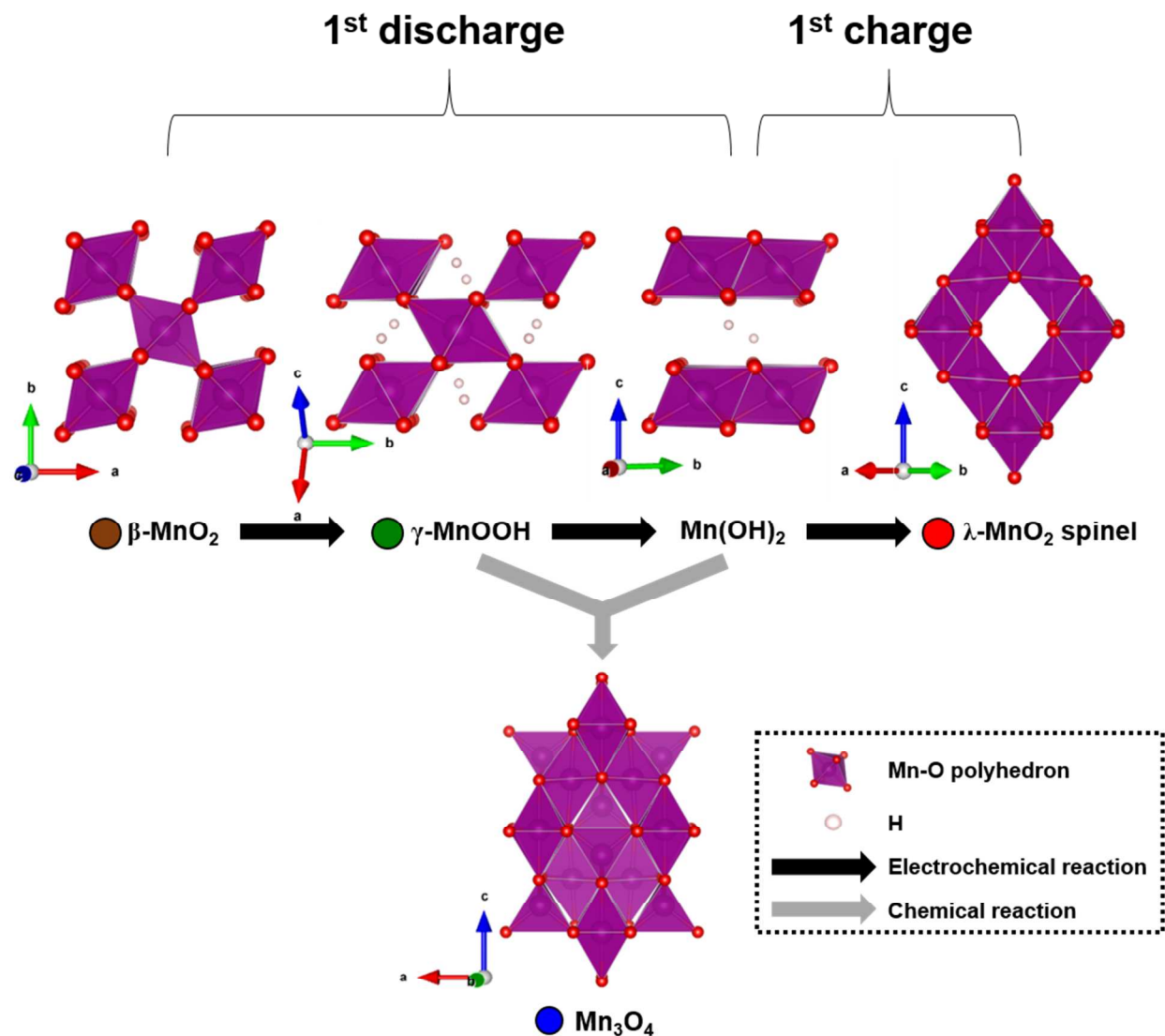


Figure 3. Schematic illustration of the electrochemical reaction mechanism of nanosized β - MnO_2 during the first cycle.

At the end of the first charge, λ - MnO_2 is measured (figure 2(a)) as a result of Mn(OH)_2 oxidation (Eq. (3)). λ - MnO_2 is a spinel phase with the cubic crystal lattice where M-O octahedrons are interconnected in an edge-sharing manner creating a 3D network of 1 x 1 void channel (figure 3). The XRD pattern of the cell at 1.80 V has a peak at $\sim 19.1^\circ$, which corresponds to the (111) plane of λ - MnO_2 (figure S5(b)). This peak is the characteristic Bragg diffraction found in the λ - MnO_2

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3 phase exclusively among the MnO_2 polymorphs (figure S5(a)). It is important to note that the
4 XRD pattern at 1.80 V is weak and broadened. We attribute this phenomenon to the formation of
5 nano-structured λ - MnO_2 particles, which are less than ~ 50 nm (figure S6). In very
6 small particles, a large fraction of the atoms are located on the surface region, which undergo the
7 structural relaxation for thermodynamic stability. Relaxed atoms are distorted from the original
8 atomic positions of the crystal lattice, which could lead to the low intensity and peak broadening
9 in the XRD pattern. Gallaway et al. reported that the irreversible ZnMn_2O_4 phase can be
10 generated during the operation of primary alkaline batteries.¹² In our study, however, the XRD
11 pattern at the first charged state does not indicate ZnMn_2O_4 phase (figure S4(e)). Also, no Zn 2p
12 signal is found from XPS at the first charged state (figure S7(a)). We estimate that the formation
13 of ZnMn_2O_4 is dependent on the rate of reaction. It is reported that ZnMn_2O_4 is not formed at
14 fast C-rate, but generated at slow C-rate during the first discharge.¹²

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16 Also, we investigated the formation of possible Ni hydroxide phases including β - NiOOH as a
17 result of Ni oxidation (figure S8), however their XRD patterns were not aligned with the XRD
18 pattern at the first charged state (1.80 V). Considering the λ - MnO_2 , the theoretical voltage of
19 $\text{Mn}(\text{OH})_2 \mid \lambda\text{-MnO}_2$ redox couple (1.12 V) supports its formation, which is approximately the
20 experimental voltage plateau during the first charge shown in figure 2(b). The first charge
21 capacity is 353 mAh g^{-1} , which is 57 % of the theoretical capacity for the two-electron reaction.
22 We ascribe the capacity loss to any unreacted $\text{Mn}(\text{OH})_2$ which dissolves in the electrolyte as OH^-
23 coordinated-complex ions or $[\text{Mn}(\text{OH})_{n+2}]^{n-}$,³¹ because Mn^{2+} in $\text{Mn}(\text{OH})_2$ is soluble in highly
24 concentrated basic solution. It is interesting that Mn_3O_4 which is generated during the first
25 discharge is not measured at 1.80 V because it is also oxidized to λ - MnO_2 (Eq. (4)). Mn_3O_4 has
26 poor electrical conductivity (10^8 ohm \cdot cm) which hinders electrochemical reactions in Zn/ MnO_2

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3 alkaline batteries.¹² However, Mn_3O_4 converts into $\lambda\text{-MnO}_2$ in this study and we attribute it to
4 the particle size of Mn_3O_4 . We think that our synthesized active materials remain as nanoscale
5 particles during phase transformations, which compensates for the intrinsic high resistivity of
6 Mn_3O_4 and facilitates electrochemical reactions. Compared to bulky Mn_3O_4 , nanoscale Mn_3O_4
7 has advantages in terms of large electrode/electrolyte interface for electrochemical reactions,
8 superior conductivity through its ability to embed into carbon networks, and short electron/ion
9 transport distance.³² Recently, nano-sized Mn_3O_4 has been reported on for displaying high
10 reversible capacity and enhanced CE as an anode material in Li-ion batteries.³²⁻³⁴ The theoretical
11 redox potential of $\text{Mn}_3\text{O}_4 \mid \lambda\text{-MnO}_2$ is calculated as 1.28 V, which is also close to the
12 experimental voltage plateau observed during the charge (figure 2(b)).
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30 **The reaction mechanism at the hundredth cycle.** The *ex situ* SXRD pattern is measured at the
31 hundredth discharged/charged state of the synthesized $\beta\text{-MnO}_2$ cathode in the $\text{Zn}/\beta\text{-MnO}_2$
32 alkaline battery (figure 4(a,c)). It is interesting to note that the ZnMn_2O_4 phase is found, which
33 was not formed during first cycle. This phase exists in both discharged/charged states because of
34 its irreversibility in alkaline solutions. A Li and H co-inserted $\lambda\text{-MnO}_2$ spinel is also formed at
35 the hundredth discharged state as shown in figure 4(a). The 111 and 311 peaks from the
36 reference Li and H co-inserted $\lambda\text{-MnO}_2$ spinel align with the peaks from *ex situ* SXRD. The
37 presence of Li is confirmed at the hundredth discharge state by XPS spectra with a signal in the
38 Li 1s region shown in figure 4(b), which supports the formation of Li contained phase. We
39 investigated other lithiated $\lambda\text{-MnO}_2$ spinel phases as the function of Li concentration to see if
40 their XRD patterns match the *ex situ* SXRD pattern at the hundredth discharged state. However,
41 there are no other phases that demonstrate as good a match as shown in figure S9. As the lithium
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3 concentration in the λ -MnO₂ spinel increases, the peak positions of XRD shift to low diffraction
4 angle (2θ) values. These values do not correspond to the *ex situ* SXRD pattern at the hundredth
5 discharged state. It should be noted that the specific stoichiometry of the Li and H co-inserted λ -
6 MnO₂ spinel is not defined quantitatively, however, we anticipate the Li and H co-inserted λ -
7 MnO₂ spinel is generated based on our *ex situ* SXRD and XPS.
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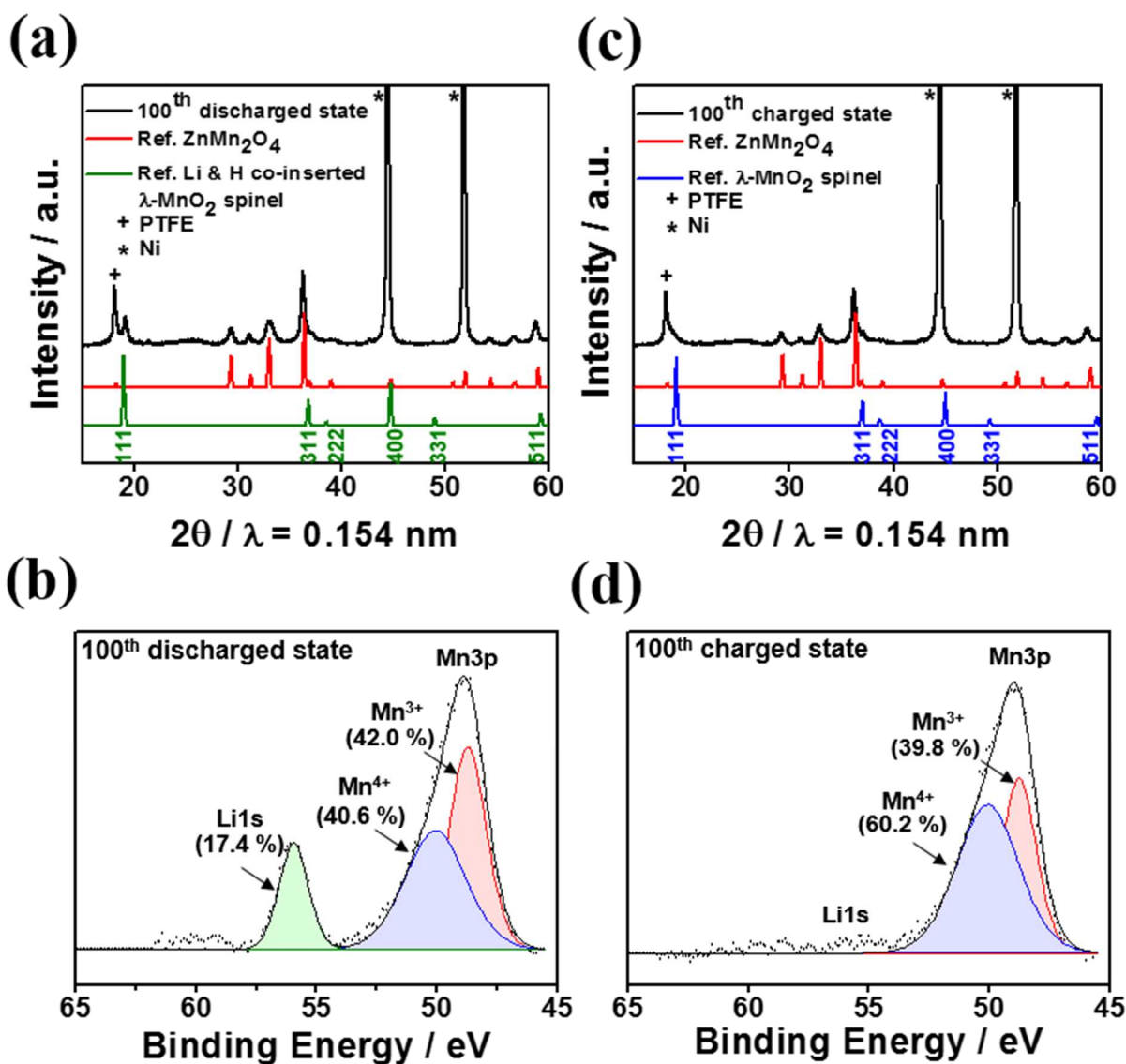
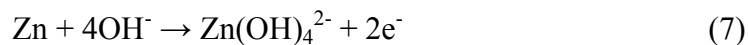


Figure 4. (a) *Ex situ* SXR D pattern from the cathode at the hundredth discharged state, the reference ZnMn_2O_4 (ICSD #15305) and the reference Li & H co-inserted $\lambda\text{-MnO}_2$ spinel (ICSD #85606); (b) XPS spectra for Li 1s and Mn 3p region from the cathode at the hundredth discharged state; (c) *Ex situ* SXR D pattern from the cathode at the hundredth charged state, the reference ZnMn_2O_4 (ICSD #15305) and the reference $\lambda\text{-MnO}_2$ spinel (ICSD #193445); (d) XPS spectra for Li 1s and Mn 3p region from the cathode at the hundredth charged state.

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3 We estimate delithiated λ -MnO₂ spinel is formed at the hundredth charged state as shown in
4 figure 4(c). It is noted that the right side of asymmetrically broadened peak at $\sim 19.1^\circ$ in the
5 SXR pattern matches the (111) peak in the reference XRD pattern of λ -MnO₂ (figure S10).
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7 This asymmetric peak belongs to the convoluted peak from PTFE and λ -MnO₂. We believe this
8 phase is formed by the extraction of Li and H process during charging as shown in figure 5.
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10 There is no detection of Li in the Li 1s region from the XPS spectrum, which is evidence for the
11 formation of the delithiated spinel phase. In addition, the XPS spectrum for surface Mn species
12 can be used for qualitative understanding of elements' change. The increase in the ratio of Mn⁴⁺
13 species to Mn³⁺ species indicates delithiation upon charging as shown in figure 4(b, d).
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15 Assignments for Mn 3p of ~ 50 eV (Mn⁴⁺) and ~ 48.5 eV (Mn³⁺) were made based on the previous
16 reports.³⁵⁻³⁶ The ratio is approximately 1:1 at the hundredth discharge which increases to 3:2 at
17 the hundredth charge. Mn³⁺ is partially oxidized to Mn⁴⁺ when Li⁺ and H⁺ leave the cathode. We
18 demonstrate the voltage curve at the hundredth cycle combining with the voltage curve at the
19 first cycle for comparison in figure S11.
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36 We measure irreversible ZnMn₂O₄ from both the hundredth discharge/charge states in the *ex situ*
37 SXR pattern (figure 4(a, c)). In Zn/MnO₂ alkaline batteries, Zn(OH)₄²⁻ is formed during the
38 discharge reaction:²⁶
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47 Once Zn(OH)₄²⁻ is formed, it chemically reacts with MnOOH at the cathode:³⁷
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53 ZnMn₂O₄ has a tetrahedral crystal lattice where corner-sharing Zn-O tetrahedrons and edge-
54 sharing Mn-O octahedrons are interconnected (figure 5). Mn and Zn have 3+ and 2+ oxidation
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states, respectively. ZnMn_2O_4 is known to have higher resistivity than MnO_2 by six orders of magnitude, which causes a loss of conductivity in the cathode.¹² In this study, ZnMn_2O_4 is not found after the first cycle as shown in figure 2(a), however, it is seen in the hundredth cycle in both the discharged/charged states as shown in figure 4. The amount of ZnMn_2O_4 in the cathode increases as the cycle of Zn/ β - MnO_2 alkaline battery proceeds, which leads to capacity fading.

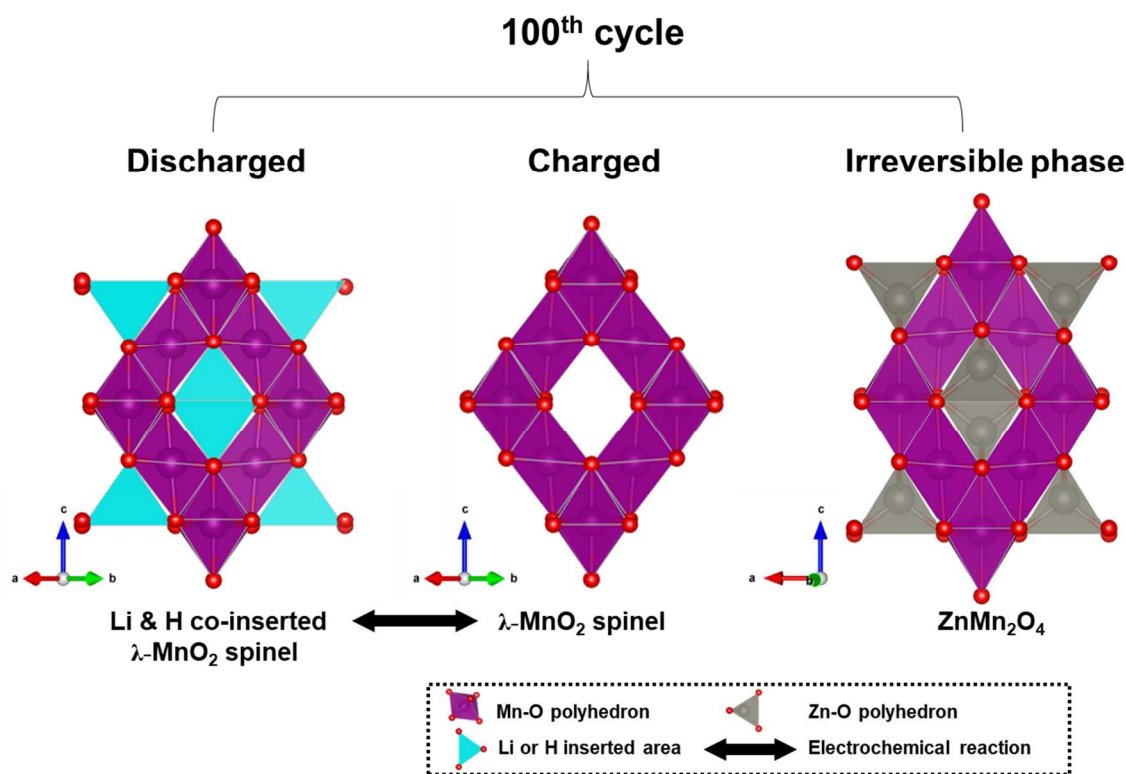


Figure 5. The reaction mechanism of β - MnO_2 during the hundredth cycle.

The effect of Bi_2O_3 additive. It has been reported that the addition of Bi^{3+} either chemically or physically to the MnO_2 cathode improves the cycling performance of Zn-based aqueous batteries.³⁸⁻⁴¹ Dzieciuch et al. reported that Bi_2O_3 in the MnO_2 cathode of alkaline batteries using KOH electrolytes inhibits ZnMn_2O_4 formation to some level.⁴⁰ In another study, Shin et al. found

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3 that the zincate ion is deposited on Bi_2O_3 and prolongs the cycle life of Zn-based batteries.⁴¹ In
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5 order to study the effect of the Bi^{3+} compound on nanosized $\beta\text{-MnO}_2$ in the 1 M KOH and 3 M
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7 LiOH electrolyte, we physically mix Bi_2O_3 into the synthesized $\beta\text{-MnO}_2$ nanomaterial with 4%
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9 mole fraction and measure the performance of Zn/ $\beta\text{-MnO}_2$ alkaline battery. The discharge
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11 capacity measured is 316 mAh g^{-1} at the hundredth cycle (figure 6(a)). This indicates increased
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13 capacity compared to the commercial $\beta\text{-MnO}_2$ and synthesized $\beta\text{-MnO}_2$ nanomaterial (112 and
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15 225 mAh g^{-1} , respectively). The CE is less than 100 % due to the H_2 and O_2 gas evolution within
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17 the operating voltage window of a battery as was discussed earlier. Furthermore, the synthesized
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19 $\beta\text{-MnO}_2$ nanomaterial with Bi_2O_3 incorporated demonstrates improved specific capacity over a
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21 range of rates as shown in figure 6(b). This exhibits higher discharge capacity and better cycling
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23 stability than the synthesized $\beta\text{-MnO}_2$ without Bi_2O_3 . To be specific, the synthesized $\beta\text{-MnO}_2$
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25 with Bi_2O_3 has an average capacity of 506 mAh g^{-1} during the first stage and retains 86% of that
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27 initial capacity (434 mAh g^{-1}) at the last stage. Comparatively, the synthesized $\beta\text{-MnO}_2$ without
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29 Bi_2O_3 has an average capacity of 403 mAh g^{-1} at the first stage and 292 mAh g^{-1} at the last stage,
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31 indicating 72% recovery. In order to investigate the role of Bi_2O_3 in the rechargeable Zn/ MnO_2
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33 alkaline chemistry, Bi_2O_3 powder was immersed in the 6 M Zn nitrate solution. SEM images
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35 show that original disordered structures transform to relatively ordered structures with island
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37 meshes in a Zn^{2+} solution (figure S12). The EDS mapping for immersed Bi_2O_3 powder that was
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39 carefully cleansed and dried indicates the presence of Zn species on the surface of the Bi_2O_3
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41 (figure S13). These SEM and EDS analyses imply that Zn^{2+} reacts with the surface Bi_2O_3 . In
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43 addition, we took EDS of synthesized $\beta\text{-MnO}_2$ with and without Bi_2O_3 at the hundredth charged
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45 state as shown in figure S14. We find that the atomic percent of Zn out of Mn and Zn reduces
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47 from 11.71 % to 8.84 % in the synthesized $\beta\text{-MnO}_2$ with Bi_2O_3 , indicating Bi_2O_3 additive
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alleviates the formation of ZnMn_2O_4 . As was discussed for Zn/MnO_2 alkaline batteries, $\text{Zn}(\text{OH})_4^{2-}$ or potentially a combination of Zn^{2+} and OH^- in alkaline solution undergo chemical reactions with Mn species to produce an electrochemically irreversible phase consisting of ZnMn_2O_4 . Our results suggest that the formation of ZnMn_2O_4 can be alleviated through $\text{Zn}(\text{OH})_4^{2-}$ reactions with Bi_2O_3 which lessens the likelihood that Mn species will react with $\text{Zn}(\text{OH})_4^{2-}$.

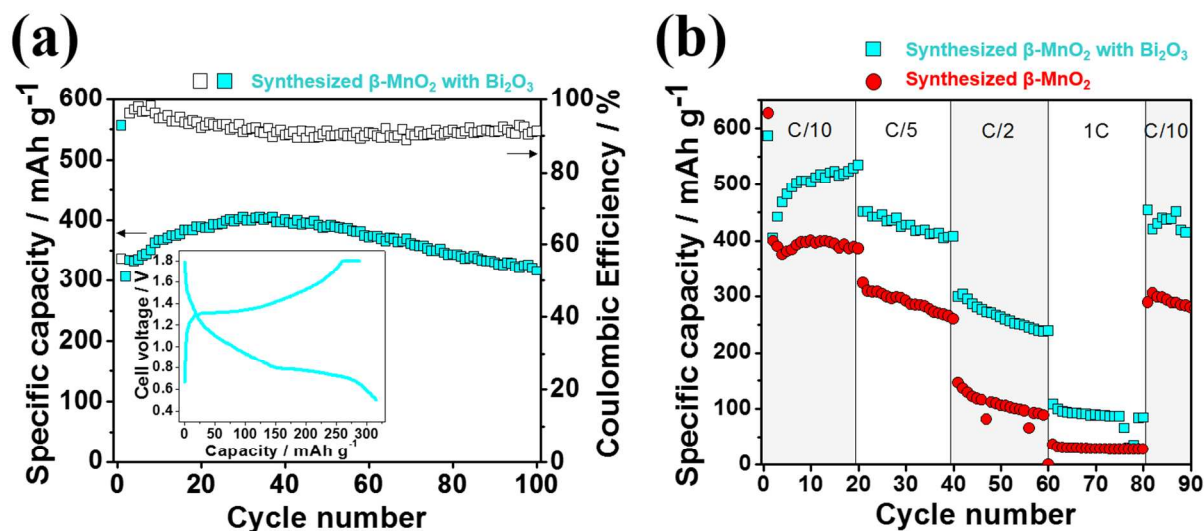


Figure 6. (a) Cyclic performance for the synthesized $\beta\text{-MnO}_2$ with Bi_2O_3 additive. The inset indicates the voltage curve at the hundredth cycle; (b) Rate capability test for the synthesized $\beta\text{-MnO}_2$ with and without the Bi_2O_3 additive are conducted with C/10, C/5, C/2, 1C, and C/10 in sequence.

CONCLUSIONS

This study has demonstrated that synthesized $\beta\text{-MnO}_2$ nanomaterials have high utility for rechargeable $\text{Zn}/\beta\text{-MnO}_2$ alkaline batteries. The nanosized $\beta\text{-MnO}_2$ cathode in the 1 M KOH and

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3 3 M LiOH mixed electrolyte shows higher rechargeable capacity compared to the bulky β -MnO₂
4 cathode's capacity. The β -MnO₂ nanomaterials have large surface area and strong surface-
5 chemisorption property to facilitate electrochemical reactions in alkaline solutions. In addition,
6 the phase transformation of synthesized β -MnO₂ nanomaterial involves proton intercalation
7 reactions followed by two-phase conversion reactions during the first cycle. At the hundredth
8 cycle, Li and H intercalate together into the host structure of λ -MnO₂ spinel. Additionally the
9 physical incorporation of Bi₂O₃ into synthesized β -MnO₂ nanomaterials shows an excellent
10 discharge capacity of 316 mAh g⁻¹ at the hundredth cycle. The findings of this study may provide
11 useful insights towards the development of rechargeable Zn/MnO₂ alkaline batteries in high-
12 energy and low-cost stationary energy storage.
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30 ASSOCIATED CONTENT

31 32 33 **Supporting Information**

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37 Standard reduction potentials, standard Gibbs free energy of formation, Mn 3s splitting in the
38 XPS result of commercial β -MnO₂, Nitrogen adsorption/desorption isotherm of the β -MnO₂ and
39 BET surface areas, the electrochemical stability window of 1M KOH and 3M LiOH electrolytes
40 on Ni foam electrodes, in-house XRD patterns for synthesized β -MnO₂ nanomaterial and its
41 intermediates during the first cycle, XRD patterns of MnO₂ polymorphs from the ICSD database,
42 and in-house XRD pattern for synthesized β -MnO₂ nanomaterial at the first charged state (1.80
43 V), the SEM image of MnO₂ cathode at the first charged state (1.80 V), the XPS spectra for Zn
44 2p region from the cathode at the first and the hundredth charged state, the XRD pattern
45 measured at the first charged state (1.80 V) and possible Ni hydroxides phases, XRD patterns of
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3 lithiated Mn oxide spinels from ICSD database and the SXRD pattern at the hundredth
4 discharge, the SXRD pattern measured at the hundredth charged state, the comparison of voltage
5 curves between the first and the hundredth cycle, SEM images of Bi_2O_3 and immersed Bi_2O_3 in
6 6M Zn nitrate solution with corresponding EDS mapping for Zn $K\alpha_1$ and Bi $M\alpha_1$, and SEM
7 images and the corresponding EDS of the hundredth charged state for MnO_2 cathode with and
8 without Bi_2O_3 (PDF)
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42 **Notes**

43
44 The authors declare no competing financial interest.
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