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Oxygen Defects in $\beta$-MnO$_2$ Enabling High-Performance Rechargeable Aqueous Zinc/Manganese Dioxide Battery

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SUMMARY

Rechargeable aqueous Zn/manganese dioxide (Zn/MnO$_2$) batteries are attractive energy storage technology owing to their merits of low cost, high safety, and environmental friendliness. However, the $\beta$-MnO$_2$ cathode is still plagued by the sluggish ion insertion kinetics due to the relatively narrow tunneled pathway. Furthermore, the energy storage mechanism is under debate as well. Here, $\beta$-MnO$_2$ cathode with enhanced ion insertion kinetics is introduced by the efficient oxygen defect engineering strategy. Density functional theory computations show that the $\beta$-MnO$_2$ host structure is more likely for H$^+$ insertion rather than Zn$^{2+}$, and the introduction of oxygen defects will facilitate the insertion of H$^+$ into $\beta$-MnO$_2$. This theoretical conjecture is confirmed by the capacity of 302 mA h g$^{-1}$ and capacity retention of 94% after 300 cycles in the assembled aqueous Zn/$\beta$-MnO$_2$ cell. These results highlight the potentials of defect engineering as a strategy of improving the electrochemical performance of $\beta$-MnO$_2$ in aqueous rechargeable batteries.

INTRODUCTION

Among the various electrochemical energy storage devices, lithium-ion batteries have dominated the commercial rechargeable battery market because of their high energy density and excellent cycling stability (Wang et al., 2019a; Yin et al., 2018; Zhou et al., 2018a). However, the high cost of lithium source and the safety issue associated with flammable organic electrolyte limited their applications in large-scale energy storage systems (Fang et al., 2018a; Tan et al., 2019; Wang et al., 2019b). In this regard, there is urgent demand for alternative advanced rechargeable battery technologies. Aqueous rechargeable metal-ion batteries have become promising choice because of their high safety, low cost, and high ionic conductivity compared with the organic cells (Kundu et al., 2016; Wang et al., 2012). Some aqueous rechargeable batteries based on the insertion/extraction of Na$^+$ (Liu et al., 2014; Bin et al., 2018), K$^+$ (Su et al., 2016), Mg$^{2+}$ (Chen et al., 2017), Al$^{3+}$ (Liu et al., 2012), and Zn$^{2+}$ (Dai et al., 2018; Xu et al., 2012; Li et al., 2018; Zhang et al., 2015a) have already been investigated. Rechargeable aqueous zinc-ion batteries (ZIBs) have particularly attracted much attention because of the abundance of Zn and some impressive attributes of Zn anode that include high theoretical specific capacity (819 mA h g$^{-1}$) and low redox potential (∼0.76 V versus standard hydrogen electrode) (Fang et al., 2018b; Liu et al., 2019a; Song et al., 2018; Wan et al., 2018; Yang et al., 2018; Zhang et al., 2016a).

MnO$_2$ has been a promising cathode material since the primary alkaline Zn/MnO$_2$ batteries were introduced in the 1860s due to its abundance, cost-effectiveness, and eco-friendliness (Xu et al., 2012; Zhang et al., 2016a; Minakshi et al., 2004; Biswal et al., 2015; Sundaram et al., 2016). However, the formation of unwanted irreversible by-products like Mn(OH)$_2$ or Mn$_2$O$_3$ on the cathode side and Zn(OH)$_2$ or ZnO on anode side leads to poor coulombic efficiency and severe capacity fading in the alkaline Zn/MnO$_2$ systems (Boden et al., 1967; McBreen, 1975; Hertzberg et al., 2016). In an attempt to improve the performance of Zn/MnO$_2$ cells, mild acidic ZnSO$_4$-based electrolyte has recently been used, and the strategy resulted in great improvement (Xu et al., 2012; Zhang et al.; Zhao et al., 2018). Up to now, various types of MnO$_2$ (like α-MnO$_2$, γ-MnO$_2$ or δ-MnO$_2$, etc.) with different polymorphs have displayed satisfactory electrochemical performances in ZIBs due to their appreciable tunneled or layered structure (Alfaruqi et al., 2015a, 2015b; Huang et al., 2018a; Ko et al., 2018; Sun et al., 2017), and their polyhedral representations are shown in Figures S1A–S1C. $\beta$-MnO$_2$, a technologically important material for energy storage, has already been widely used in lithium-ion batteries and supercapacitors (Jiao and Bruce, 2007; Zhu et al., 2018). However,
its narrow tunnel size and the strong electrostatic interaction between $\beta$-MnO$_2$ host cathode and guest ions result in sluggish ion insertion kinetics (Wang et al., 2018; Islam et al., 2017). Although modifying MnO$_2$ with different polymorphs, hybridizing with conducting materials, or enlarging the interlayer spacing seems an available approach to improve the electrochemical performances (Huang et al., 2018b; Vatsalarani et al., 2005), defects engineering can be considered as another approach for enhancing the electrochemical performance of Zn/$\beta$-MnO$_2$ batteries. Defect engineering could imbue the metal oxide with some unusual physicochemical properties (Dawson et al., 2015; Liu et al., 2019b; Zeng et al., 2018). Among the various defect types, oxygen vacancy (VO) is one kind of effective technique for modifying surface chemistry (Liu et al., 2019b; Zhao et al., 2019). First, VO enables the charge and ion transport process by changing the electronic structure, resulting in improved ion insertion kinetics. Second, VO facilitates phase transition by modifying the thermodynamics on the electrode surface (Zhang et al., 2016b; Zou et al., 2019).

Another debate on MnO$_2$ cathode is the energy storage mechanism (Li et al., 2019). The most prominent energy release or storage mechanism involves Zn$^{2+}$ insertion or extraction into or from the host materials during the electrochemical process (Alfaruqi et al., 2015b; Zhang et al., 2017). However, some cases demonstrate a Zn$^{2+}$ and H$^+$ co-insertion process (Sun et al., 2015), combination displacement/intercalation reaction (Shan et al., 2019a), or Zn-driven reduction displacement reaction (Shan et al., 2019b). Different insertion thermodynamics and kinetics of H$^+$ and Zn$^{2+}$ would contribute to the different reaction mechanisms, which results from the various polymorphs, particle sizes of the positive electrode, or electrolyte systems (Xiong et al., 2019). Remarkably, we proved the different kinetics of Zn$^{2+}$ and H$^+$ insertion into $\beta$-MnO$_2$ through density functional theory (DFT) calculations and experimental measurements. The results indicate that the energy required for H$^+$ to insert into and react with the nearest-neighboring O atoms in perfect $\beta$-MnO$_2$ is about 1.63 eV lower than that of Zn$^{2+}$ owing to the large ionic radius of Zn$^{2+}$ (Figures 1A–1F). Moreover, the binding energy of H$^+$ insertion into $\beta$-MnO$_2$ would be further reduced and a conversion reaction process would be speeded up by introducing oxygen defects (Figures 1G and S2).

Herein, we report a zinc/manganese dioxide aqueous system using $\beta$-MnO$_2$ with rich oxygen defects (noted as D-$\beta$-MnO$_2$) in ZnSO$_4$-based electrolyte. A conversion reaction mechanism between H$^+$ and MnO$_2$ is observed for the Zn/$\beta$-MnO$_2$ aqueous system by experimental and DFT calculation results. The D-$\beta$-MnO$_2$ cathode displayed a discharge capacity of 302 mA h g$^{-1}$ at 50 mA g$^{-1}$, a capacity retention of 94% after 300 cycles at 500 mA g$^{-1}$ and 78% retention for the commercial $\beta$-MnO$_2$. Furthermore, the D-$\beta$-MnO$_2$ electrode with a mass loading of 3.0 mg cm$^{-2}$ showed a maximum discharge capacity of 268 mA h g$^{-1}$ at 50 mA g$^{-1}$, and even at a high current density of 1,000 mA g$^{-1}$, it still delivered a capacity of 112 mA h g$^{-1}$. Interestingly, the electrode still displayed a high discharge capacity of 163 mA h g$^{-1}$ even at a higher mass loading of 4.0 mg cm$^{-2}$ of the active material.
The performance may not be much better than those of previously reported Zn/MnO₂ cells (Xiong et al., 2019; Zhang et al., 2017), but the presented results enlighten the potential application of oxygen-defected β-MnO₂ cathode in aqueous rechargeable batteries.

RESULTS AND DISCUSSION

Structure Identification and Characterization of β-MnO₂

Oxygen defects were introduced into β-MnO₂ through a successive calcination and reduction treatment; the detailed synthesis process is shown in Transparent Methods (Supplemental Information). Crystal structure analysis (Figure 2A) reveals that the D-β-MnO₂ compound possesses a tunneled structure interlinked with the basic structure unit of [MnO₆₋ₓ] octahedron by sharing corners. X-ray diffraction (XRD) patterns demonstrate that the as-prepared sample possesses similar crystalline phase as commercial β-MnO₂ (Figure 2B). The characteristic peaks suggest a high-purity property of the prepared tetragonal phase (JCPDS: 24-0735) with P42/mnm space group, which is expressed in Figure S3. Both the scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images (Figures 2C and 2D) confirm that the D-β-MnO₂ sample possesses one-dimensional homogeneous nanorod morphology. The nanorods are several micrometers in length and about 100 nm in width. The lattice distance of 0.24 nm corresponds to the (101) crystal plane of β-MnO₂ in high-resolution transmission electron microscopy (HR-TEM) image (Figure 2E). Moreover, energy-dispersive X-ray (EDX) elemental mapping images in Figure 2F suggest the homogeneous distribution of Mn and O elements in D-β-MnO₂.

To gain insights into the structural differences between commercial β-MnO₂ and D-β-MnO₂, TEM and HR-TEM were carried out. As displayed in Figures 3A and 3B, the commercial β-MnO₂ shows clear lattice fringes with lattice spacing of 0.31 nm assigned to (110) plane of perfect β-MnO₂, indicating that the commercial β-MnO₂ possesses nearly defect-free crystal structure. However, the D-β-MnO₂ sample exhibits a rough surface with various small pits, which may be created by the oxygen defects (Figures 2D and 3C). (Zhang et al., 2016b) Besides the pits (marked by the arrows in Figure 3C), slight lattice disorder and dislocations can also be observed at different sections in D-β-MnO₂ (Figures 3C and S4). Moreover, blurred sections in the HR-TEM image and the weak intensities of some continuous distributed Mn and O atoms marked by boxes in Figure 3D further confirm the rich defects in D-β-MnO₂ (Chen et al., 2019; Yao et al.)
In addition, the oxygen defects were further verified by the X-ray photoelectron spectroscopy (XPS) measurement and Raman spectra. As shown in Figure 3E, the peak at 529.5 eV for both samples is attributed to the lattice oxygen ubiquitously in oxide semiconductors. The peak centered at 531.2 eV is assigned to oxygen species beside the oxygen vacancies (Li and Su, 2019). The higher intensity and larger integrated area in D-β-MnO₂ than that in commercial β-MnO₂ confirm the existence of rich oxygen defects in D-β-MnO₂. It is also confirmed by the Mn 2p XPS spectra (Figure 3F), which showed stronger intensity of Mn³⁺ in D-β-MnO₂ than that in commercial β-MnO₂. Previous reports have clarified the linear relationship between the energy separation of Mn 3s peaks and the valence of Mn in oxides (Lei et al., 2016). The energy separation of 5.29 eV in D-β-MnO₂ is wider than that (4.55 eV) of commercial β-MnO₂ (Figure 3G), suggesting a lower average valence of Mn in D-β-MnO₂ (Cheng et al., 2013), which may be caused by the oxygen...
The Raman spectra of the two samples showed a Mn-O vibration peak centered at 649 cm\(^{-1}\) (Xia et al., 2017). However, compared with the commercial \(\beta\)-MnO\(_2\) sample, there is a reduction of the intensity of the Mn-O vibration peak in D-\(\beta\)-MnO\(_2\), indicating a decreased content of Mn-O bond caused by the oxygen defects (Figure S5). Also, the composition of D-\(\beta\)-MnO\(_2\) was analyzed by EDX, and the result indicates that the compositional ratio of Mn and O is 1:1.75. Herein, we define the amount of “Mn” as “1” and use it to calibrate the content of “O.” Therefore, the D-\(\beta\)-MnO\(_2\) could be expressed as MnO\(_{1.75}\) and the content of oxygen defects is about 12.5%, which is similar with that (11.2%) calculated according to the XPS result (Figures 3F and S6).

### Application for Zn-Ion Battery and Electrochemical Performance of \(\beta\)-MnO\(_2\)

To investigate the effects of oxygen defects on the electrochemical performances, CR2016 (the diameter of the positive shell is 20 mm and the height is 1.6 mm) cells were assembled using \(\beta\)-MnO\(_2\) cathode, Zn foil anode, ZnSO\(_4\)-based aqueous electrolyte, and glass fiber separator. The cyclic voltammetry (CV) curves tested at 0.2 mV s\(^{-1}\) are shown in Figures 4A and S7. The almost overlapped profiles after the gradual activation of the two initial cycles indicate good reversibility of the cell (Figure S7). Moreover, the polarization potentials (0.21 V, 0.31 V) of D-\(\beta\)-MnO\(_2\) electrode are lower than those (0.23 V, 0.40 V) of commercial \(\beta\)-MnO\(_2\) at the first (1.6/1.40) and second (1.56/1.25) redox pairs (Figure 4A). In addition, CV curves at 0.1 and 0.3 mV s\(^{-1}\) were tested (Figure S8), which showed similar profiles, and both the CV curves showed higher peak current response and smaller polarization potential of D-\(\beta\)-MnO\(_2\) electrode than that of commercial \(\beta\)-MnO\(_2\) electrode, demonstrating a higher reaction activity of D-\(\beta\)-MnO\(_2\). The discharge capacity can be observed through galvanostatic charge/discharge (GCD) profiles shown in Figure 4B. It shows a high discharge capacity of 302 mA h g\(^{-1}\) of D-\(\beta\)-MnO\(_2\), which is much higher than that of commercial \(\beta\)-MnO\(_2\).

The enhanced performance of D-\(\beta\)-MnO\(_2\) could be attributed to the introduction of oxygen defects, which increased ion absorption sites and opened up extra ion insertion channels, resulting in higher reaction activity and higher capacity (Fang et al., 2019). Nevertheless, the delivered capacity of D-\(\beta\)-MnO\(_2\) electrode in this work was a bit lower than that reported by Minakshi’s work (Minakshi, 2008), which may be due to the different crystal structures or energy storage mechanisms in the two distinct systems, but it surpassed that of some reported cathode materials, which can be seen in Table S1. Furthermore, the energy and power densities also surpassed those of many reported materials, like ZnMn\(_{1.86}\)O\(_4\) (Zhang et al., 2016a), NaV\(_2\)O\(_5\)·1.5H\(_2\)O (Wan et al., 2018), V\(_2\)O\(_5\)-nH\(_2\)O/rGO (Yan et al., 2018), Li\(_x\)V\(_2\)O\(_5\)·nH\(_2\)O (Yang et al., 2018), and so on, as shown in the Ragone plot (Figure 4C). In addition, the Zn/D-\(\beta\)-MnO\(_2\) battery was also assembled by using porous Zn anode instead of Zn foil to study the effect of porosity on the discharge capacity (Minakshi and Ionescu, 2010; Minakshi et al., 2010). The result, however, did not show significant improvement in discharge capacity (Figure S9).

The positive effects of oxygen defects on cyclability have already been proved in LIBs and sodium-ion batteries (Yao et al., 2018). However, the relevant researches on ZIBs are seldom reported. As shown in Figure 4D, commercial \(\beta\)-MnO\(_2\) electrode delivers a discharge capacity of 182 mA h g\(^{-1}\) after 50 cycles at 100 mA g\(^{-1}\). In contrast, there is still a high discharge capacity of 276 mA h g\(^{-1}\) for the Zn/D-\(\beta\)-MnO\(_2\) cell. Furthermore, the Zn/D-\(\beta\)-MnO\(_2\) battery delivers high capacity retention of 94% at 500 mA g\(^{-1}\) after 300 cycles, which is higher than that (78%) of commercial \(\beta\)-MnO\(_2\)-based cells (Figure 4F). In addition, the positive effect of the introduction of oxygen defects is also reflected by the improved electrical conductivity, as shown by electrochemical impedance spectroscopy (EIS, Figure S10 and Table S2). It shows a smaller charge-transfer resistance (\(R_{ct}\), 257 \(\Omega\) at the initial state, 46 \(\Omega\) after 10 cycles) of the D-\(\beta\)-MnO\(_2\) electrode compared with commercial MnO\(_2\) electrode (\(R_{ct}\), 610 \(\Omega\) at the initial state, 178 \(\Omega\) after 10 cycles), manifesting enhanced electrical conductivity after the introduction of oxygen defects (Barmi and Minakshi, 2016).

As for the promising large-scale energy storage devices, the rechargeable Zn/MnO\(_2\) batteries not only need to provide high energy density and long cycling stability with a low active material loading but also need to ameliorate the cell-fabrication parameters to reach a stable electrochemical performance with a sufficient amount of MnO\(_2\) active material. Therefore, the Zn/D-\(\beta\)-MnO\(_2\) batteries were tested with active material loadings of about 3.0 and 4.0 mg cm\(^{-2}\), respectively. Figure 4E shows the rate performances of the battery with the D-\(\beta\)-MnO\(_2\) loading about 3.0 mg cm\(^{-2}\). It is interesting to observe that the maximum discharge capacity of 268 mA h g\(^{-1}\) can be achieved at 50 mA g\(^{-1}\), even though the current density increased to 1,000 mA g\(^{-1}\), the battery could still deliver a capacity of 112 mA h g\(^{-1}\). Furthermore, the
Zn/D-β-MnO₂ batteries show high capacity retention of 82% compared with the maximum discharge capacity after 100 cycles at 100 mA g⁻¹ (Figure 4G). Similarly, the batteries still display a discharge capacity of 163 mA h g⁻¹ with a higher active material loading of 4.0 mg cm⁻² (Figures S11A and S11B). It is to be noted that the electrodes with high mass loading exhibit almost the same open circuit voltage as the electrode at low mass loading. However, they showed an increased polarization potential of 0.27 V for
D-β-MnO₂ electrode at a mass loading of 3.0 mg cm⁻² and 0.30 V for the D-β-MnO₂ electrode at 4.0 mg cm⁻² in the initial cycle (Figure S12), which are higher than that of D-β-MnO₂ electrode (0.22 V) at a mass loading of 1.3 mg cm⁻². The increased polarization potentials may be due to the increased charge transfer and ion diffusion resistance. In addition, the commercial β-MnO₂ electrodes at mass loadings of 3.0 and 4.0 mg cm⁻² were also tested, and relatively lower discharge capacity was observed (Figures S13A–S13D).

As discussed before, DFT calculations have revealed that the introduction of oxygen defects would reduce the energy barrier for H⁺ insertion. To confirm the fast rate of H⁺ ion insertion kinetics in D-β-MnO₂ (H⁺ is the main charge carrier in this work, which will be discussed in following section), the CV curves of the D-β-MnO₂ sample were tested from 0.2 to 1.0 mV s⁻¹ (Figure 4H). The relationship between the CV current and the scan rate obey the power law \( i = a v^b \), where \( i \) refers to current, \( v \) refers to the scan rate, and \( a \) and \( b \) are adjustable parameters (Yan et al., 2018). In general, the \( b \) value is in the range of 0.5–1.0 (He et al., 2017). As for the D-β-MnO₂ sample, the \( b \) value calculated by the slopes of the redox peaks of peak 1 and peak 2, are 0.69 and 0.90, respectively (Figure 4I), demonstrating a favored capacitive kinetics in D-β-MnO₂ sample (Yao et al., 2019). In addition, the capacitive contributions of the above-mentioned different electrochemical processes can be calculated by the equation \( i = k_1 v + k_2 v^{1/2} \), where \( i \) refers to current response, \( k_1 \) represents capacitive contribution, and \( k_2 v^{1/2} \) represents ion-diffusion contribution. As a result, at 0.2 mV s⁻¹, 55% of the capacity is determined to be capacitive for D-β-MnO₂. With the increase of scan rates, the percentage of capacitive contribution increases to 56.9%, 60.1%, 61.2%, and 62.3% at scan rates of 0.4, 0.6, 0.8, and 1.0 mV s⁻¹, respectively, indicating that the capacitive contribution holds the main position in the total capacity.

Galvanostatic intermittently titration technique was adopted to investigate the diffusion coefficients of H⁺ in β-MnO₂ electrodes because the diffusion coefficient is another parameter to evaluate the reaction kinetics (Figure S14). (Fang et al., 2019) The calculated diffusion coefficient value (1.35 × 10⁻¹¹ cm² s⁻¹) of D-β-MnO₂ electrode at second discharge plateaus is much higher than that (1.73 × 10⁻¹² cm² s⁻¹) of commercial β-MnO₂ electrode, which is even higher than that of Li⁺ in β-MnO₂ electrode (Wang et al., 2016). It further proved that the introduction of oxygen defects would improve the ion insertion kinetics. The reason for the fast H⁺ insertion kinetics during the charge/discharge process could be explained by Figure 5A (the H⁺ diffusion along [001] direction in ab plane). As shown in the diagram, the abundant oxygen defects opened up the [MnO₆] polyhedron walls, resulting in extra ion channels in the distorted [MnO₆] units, which would be beneficial for the insertion of guest ions into the electrode (Fang et al., 2019).

**Reaction Mechanism of Aqueous Zn/β-MnO₂ Cell**

An understanding of the prevailing electrochemical reaction mechanism of a cell is important. Here, ex situ tests like Fourier transform infrared (FTIR) spectroscopy, XRD, XPS, and TEM were carried out to study the structural evolutions of D-β-MnO₂ during the electrochemical process. The selected states in the first and second cycles were marked in Figure 5B. It is interesting to discover that the strong XRD diffraction peaks (Figure 5C) corresponding to Zn₄SO₄(OH)₆·xH₂O in the discharge process dominate the XRD patterns of other phases, such as, β-MnO₂ and MnOOH. Subsequently, these signals disappear after charging to 1.8 V. Apart from the XRD, FTIR spectroscopy is another powerful technique to characterize the materials. The FTIR spectra (Figure 5D) were obtained in the range from 400 to 2,000 cm⁻⁻; they are marked by the labels A–L corresponding to Figure 5B. The absorption peaks at 600 and 1,120 cm⁻¹ during the discharge process are ascribed to Zn-O bond and SO₄²⁻ in Zn₄SO₄(OH)₆·xH₂O (Wan et al., 2018). However, the intensity of the two peaks weakened and completely disappeared at the fully charged state. The XRD and FTIR results collaboratively demonstrate the reversible formation and disappearance of Zn₄SO₄(OH)₆·xH₂O in the electrochemical process. Moreover, SEM images were used to further investigate the structure evolutions (Figure 5E). Flake-like solids were observed clearly in the fully discharged stage, which may be the Zn₄SO₄(OH)₆·xH₂O compounds. They disappeared later, and an interconnected porous layer is observed after charging. It is to be noted that the commercial β-MnO₂ electrode undergoes the same reaction behavior and structural evolutions during the discharge and charge processes (Figures S16 and S17).

In the Zn/D-β-MnO₂ cells, the water solvent in electrolytically decomposed into OH⁻ and H⁺, with a large amount of OH⁻ ions reacting with ZnSO₄ forming Zn₄SO₄(OH)₆·xH₂O. To reach a neutral charge system, the H⁺ ions move into the host structure and react with MnO₂ electrode, forming MnOOH during the discharge process (Pan et al., 2016). In addition, the reversible formation and disappearance of
Zn₄SO₄(OH)₆ₓH₂O and MnOOH also demonstrates the good reversibility of this Zn/β-MnO₂ system. It can also be supported by the XRD pattern of the MnO₂ cathode after 50 cycles (Figure S18), which revealed the same peaks with the pristine electrode. To further prove the H⁺ insertion mechanism, high-resolution XPS of O 1s and Mn 2p at different states and ¹H nuclear magnetic resonance (NMR) study were conducted (Figures 6 and S19). The high-resolution XPS spectra of O element (Figures 6A–6C) indicate that there are almost no -OH (532.8 eV) and Mn-O-H (531.5 eV) (Jabeen et al., 2016; Zhang et al., 2015b) signals in the initial state. However, the two signals appeared at discharged state accompanied by decreased intensities at charged state. It is to be noted that the –OH signal may come from the Zn₄SO₄(OH)₆ₓH₂O, and the Mn-O-H signal, from MnOOH. The Mn 2p XPS spectra shows increased contents of Mn³⁺ and Mn²⁺ at the fully discharged state compared with the initial state. Reversibly, they decreased after charging to 1.8 V. Furthermore, the ¹H NMR study also confirms the formation of Zn₄SO₄(OH)₆ₓH₂O and the change of magnetic susceptibility of the electrode at the discharged state. All the results confirmed that the Zn₄SO₄(OH)₆ₓH₂O and MnOOH formed in discharged state and decomposed in charged state, which is consistent with the XRD and FTIR results.

As suggested by the above-mentioned results, the energy storage mechanism involves H⁺ insertion, but whether or not Zn²⁺ ions have participated in the energy storage process was studied by TEM images at the fully discharged state. Figure 5E presents a kind of flake-like solid that is Zn₄SO₄(OH)₆ₓH₂O compound, as supported by EDX mappings (Figure 5G), which reveals intense signals of Zn and S. However, the Mn and O elements are mainly distributed on the nanorod. This observation supports the fact that Zn²⁺ ions have not participated in the energy storage process. Moreover, HR-TEM images (Figure 5F) of the nanorod exhibit two kinds of lattice fringes, which match well with MnO₂ and MnOOH phases. The corresponding selected area electron diffraction (SAED) patterns also confirm the formation of MnOOH on the surface of MnO₂ electrode.

In addition, the conversion reaction mechanism was proved by assembling the Zn/D-β-MnO₂ cell using organic electrolyte containing Zn²⁺. The limited discharge capacity further indicates that the energy storage in this Zn/D-β-MnO₂ system is from the conversion reaction between H⁺ and MnO₂ (note: Zn can reversibly strip/plate in this organic electrolyte as reported in other literature, Pan et al., 2016; Figure S20).
All the aforementioned results indicate a conversion mechanism in this Zn/MnO₂ cell, and the electrochemical reaction equation is listed in the Supplemental Information, which is similar to the literature reported by Liu’s group (Pan et al., 2016). However, the limitation of our experimental condition may make it hard to unveil the veil of the energy storage mechanism deeply. More experimental data or advanced characterization techniques would be needed to understand the reaction mechanism in the future.

Conclusion

In summary, we have investigated the Zn/β-MnO₂ aqueous battery chemistry, in terms of its energy storage mechanism and the performance improvement strategy by introducing oxygen defects. The introduction of abundant oxygen defects into the β-MnO₂ reduces the binding energy of H⁺ insertion into β-MnO₂. In addition, the energy storage mechanism is demonstrated as a conversion reaction process between H⁺ and MnO₂. It is interesting to find that the D-β-MnO₂ electrode displays a discharge capacity of 302 mA h g⁻¹ at 50 mA g⁻¹ and 114 mA h g⁻¹ even at 2,000 mA g⁻¹ and a capacity retention of 94% after 300 cycles at 500 mA g⁻¹. Such Zn/D-β-MnO₂ cells will pave way for advanced large-scale energy storage applications.

Limitations of the Study

The effects of oxygen vacancy were confirmed by electrochemical results, DFT, TEM, and XPS in this work. However, to further get the insight of the effects of oxygen vacancy, in situ characterization is still needed but is very challenging. In addition, the limitation of our experimental condition may make it hard to unveil the veil of the energy storage mechanism deeply. More experimental data or advanced characterization techniques would be needed to understand the reaction mechanism in the future.

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

Figure 6. High-Resolution O 1s and Mn 2p XPS Spectra for D-β-MnO₂
Electrodes at different states: (A-C) The O 1s XPS spectra at initial, discharged and charged states in the second cycle, respectively; (D-F) The Mn 2p XPS spectra at initial, discharged and charged states in the second cycle, respectively.
SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.100797.

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AUTHOR CONTRIBUTIONS

J.Z. and M.H. designed the project. M.H. wrote the manuscript. The experiments were carried out by M.H. and Z.Y. Y.W. carried out the DFT calculations. S.G. provided helpful suggestions on the DFT calculations. X.X., J.H., and S.L. helped to polish the manuscript. All the authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Oxygen Defects in $\beta$-MnO$_2$ Enabling High-Performance Rechargeable Aqueous Zinc/Manganese Dioxide Battery

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Supplemental Information
Table S1. A summary of the reported cathode materials for different Zn-ion battery systems, related to Figure 4.

| Cathode | Electrolyte | Capacity | Capacity retention | Reference |
|---------|-------------|----------|--------------------|-----------|
| α-MnO₂ | 2M ZnSO₄+0.1M MnSO₄ | 285 at 1/3 C | 92% after 5000 cycles at 5 C | Pan et al., 2016 |
| α-MnO₂ | 2M ZnSO₄+0.2M MnSO₄ | 301 at 100 mA g⁻¹ | 67% after 800 cycles at 7 A g⁻¹ | Wu et al., 2018 |
| δ-MnO₂ | 0.5M Zn(TFSI)₂ | 110 at 12.3 mA g⁻¹ | 48% after 125 cycles at 12.3 mA g⁻¹ | Han et al., 2017 |
| α-MnO₂ | 1M ZnSO₄ | 231 at 66 mA g⁻¹ | 45% after 75 cycles at 83 mA g⁻¹ | Alfaruqi et al., 2016 |
| α-MnO₂ | 1M ZnSO₄ | 233 at 83 mA g⁻¹ | 65% after 50 cycles at 83 mA g⁻¹ | Alfaruqi et al., 2015a |
| α-MnO₂ | 1M ZnSO₄+0.2M MnSO₄ | 345 at 0.2 A g⁻¹ | 80% after 2000 cycles at 5 A g⁻¹ | Xiong et al., 2019 |
| Na₀.₄₄Mn₂O₄·1.₅H₂O | 2M ZnSO₄+0.2M MnSO₄ | 278 at 1 C | Nearly 100% after 2000 cycles at 8 C. | Wang et al., 2019 |
| γ-MnO₂ | 1M ZnSO₄ | 285 at 0.05 mA cm⁻² | 37% after 40 cycles at 0.5 mA cm⁻² | Alfaruqi et al., 2015b |
| β-MnO₂ | 1M ZnSO₄ | 270 at 100 mA g⁻¹ | 75% after 200 cycles at 0.2 A g⁻¹. | Islam et al., 2017 |
| β-MnO₂ | 3M Zn(CF₃SO₃)₂+0.1M Mn(CF₃SO₃)₂ | 258 at 0.65C | 94% after 2000 cycles at 6.5 C | Zhang et al., 2017 |
| NaV₂O₅·1.5 | 1M ZnSO₄+1M NaSO₄ | 380 at 50 mA g⁻¹ | 82% after 1000 cycles at 4 A g⁻¹ | Wan et al., 2018 |
| Zn₀.₂₂V₂ | 1M ZnSO₄ | 282 at 1 C | 80% after 1000 cycles at 8 C | Kundu et al., 2016 |
| O₂·nH₂O | V₂O₅·nH₂O | 3M Zn(CF₃SO₃)₂ | 381 at 60 mA g⁻¹ | 71% after 900 cycles at 6 A g⁻¹ | Yan et al., 2018 |
| C-RZnHCF | 3M ZnSO₄ | 69.1 at 60 mA g⁻¹ | 93% after 100 cycles at 300 mA g⁻¹ | Zhang et al., 2015 |
| β-MnO₂ | 3M ZnSO₄+0.1M MnSO₄ | 302 at 50 mA g⁻¹ | 94% after 300 cycles at 500 mA g⁻¹ | This work |

S2
**Table S2.** The $R_s$ (the sum of electrolyte resistance and ohmic resistances of the cell components) and $R_{ct}$ (charge-transfer) resistance values of D-$\beta$-MnO$_2$ and commercial $\beta$-MnO$_2$ at different cycles, related to Figure 4.

| Sample               | $R_{ct}$ | $R_s$ |
|----------------------|----------|-------|
| D-$\beta$-MnO$_2$    |          |       |
| Initial              | 257      | 2.0   |
| 5$^{th}$ cycle       | 138      | 3.8   |
| 10$^{th}$ cycle      | 46       | 3.7   |
| Commercial $\beta$-MnO$_2$ |    |       |
| Initial              | 610      | 1.7   |
| 5$^{th}$ cycle       | 207      | 0.8   |
| 10$^{th}$ cycle      | 178      | 3.2   |
Table S3. The calculated bulk lattice parameters (Å) of $\beta$-MnO$_2$, compared with available experimental values. The calculated equilibrium lattice parameters are well consistent with the experimental data, related to Figure 1.

|         | This work | Other calculations (Wang et al., 2013) | Experimental (Bolzan et al., 1993) |
|---------|-----------|---------------------------------------|-----------------------------------|
| a=b(Å)  | 4.4713    | 4.473                                 | 4.4041                            |
| c(Å)    | 2.9362    | 2.957                                 | 2.8765                            |
Transparent Methods

Preparations of D-β-MnO₂ nanorods: In a typical experiment, 26 ml of Mn(NO₃)₂ solution (50% wt) was dissolved into distilled water (15 ml). Then, the mixed solution was ultrasoniced for 30 min and magnetically stirred for another 30 min at room temperature until a homogeneous pink solution was formed. Afterwards, the above solution was transferred into the autoclave (50 ml) and heated at 180°C for 10 h, obtaining black β-MnO₂ powder. Then the obtained powder was calcinated in muffle furnace at air atmosphere at 450 °C for 1 hour, followed by NaBH₄ (0.25 M) reduction for 50 minutes. Finally, the D-β-MnO₂ powder was obtained.

Electrochemical tests: Firstly, the cathode electrodes were prepared by casting a slurry mixed with β-MnO₂ powder (70% wt), acetylene black (20% wt) and polyvinylidene fluoride (10% wt) onto the stainless steel wire mesh (SSWM, 400 orders) with the area of 1.13 cm². Then they were dried at 80 °C for 12 h in a vacuum atmosphere. The electrochemical performances of the MnO₂ electrodes were tested by assembling with the Zn foil anode (the purity greater than or equal to 99.9%, without using a reference electrode), glass fiber separator and 3 M ZnSO₄ electrolyte with 0.1 M MnSO₄ additives the CR2016 coin-type cells. Cyclic voltammetry measurements were conducted on an electrochemical workstation (CHI660E, CHI Instruments) between 0.8-1.8 V. Galvanostatic charge/discharge and cycling performance were carried on the LAND-2001A battery-testing system.

Material Characterizations: The morphology of MnO₂ powder was characterized on FEI Nova NanoSEM 230. The crystal phase was analysed through a X-ray powder diffraction mechanism (Rigaku D/Max-2500, Cu Kα radiation, λ = 1.54178 Å). The FTIR were tested on a BIORAD FTS 6000 FTIR. TEM, HR-TEM images, SAED patterns and EDX mappings were collected on Titan G2 60-300 machine. XPS were carried out on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) to identify the surface chemical composition and investigate the evolution of Mn valence.
Computation Details

All the calculations were carried out in the Vienna ab initio simulation package (VASP) (Kresse et al., 1996) with generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE) (Perdew et al., 1996) combined with projector augmented wave (PAW) (Kresse et al., 1999). PBE+U approaches are applied to describe the d states of Mn compound. The Hubbard U value of Mn atoms is taken as 4 eV based on our calculations and literatures. For bulk lattice optimizations, a cutoff energy of 500 eV and a Monk-horst pack k-point mesh 5*5*7 was adopted. The total energy convergence was set to less than $10^{-5}$ eV and the force on each atom was less than 0.02 eV/Å in both structural optimizations and the self-consistent calculations. All atom coordinates and lattice vectors are fully relaxed for each structure. A 2*2*2 $\beta$-MnO$_2$ supercell is applied with 16 Mn atoms and 32 O atoms. Spin-polarizations are included in all the calculations, and antiferromagnetic ordering is considered for $\beta$-MnO$_2$.

Formation energies ($E_f$) for the defects are considered as

$$E_f = E_{II} - E_I - \sum N_i \cdot \mu_i + q e_{VBM}$$

Here, $E_{II}$ and $E_I$ stand for the total energy of the supercell with or without concerned defects. $N_i$ stands for the numbers of atoms of type i that have been added to ($N_i > 0$) or removed from ($N_i < 0$) the supercell when defect is created, and $\mu_i$ represents the relevant chemical potentials of these atoms. $q$ is the valence state for the induced defect, and $e_{VBM}$ is the VBM of the host supercell. The chemical potential of O is taken as the energy of oxygen which refers to the O-rich condition, Zn and H are taken as the relevant bulk energy.
The reaction equation of the Zn/D-β-MnO₂ battery, related to Figure 5.

The positive electrode:

\[
\begin{align*}
    & \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \\
    & \text{MnO}_2 + \text{H}^+ + e^- \leftrightarrow \text{MnOOH} \\
    & \frac{1}{2} \text{Zn}^{2+} + \text{OH}^- + \frac{1}{6} \text{ZnSO}_4 + \frac{x}{6} \text{H}_2\text{O} \leftrightarrow \frac{1}{6} \text{ZnSO}_4[\text{Zn(OH)}_2]_3.x\text{H}_2\text{O}
\end{align*}
\]

The negative electrode:

\[
\frac{1}{2} \text{Zn} \leftrightarrow \frac{1}{2} \text{Zn}^{2+} + e^-
\]

Overall:

\[
\text{MnO}_2 + \frac{1}{2} \text{Zn} + \frac{x}{6} \text{H}_2\text{O} + \frac{1}{6} \text{ZnSO}_4 \leftrightarrow \text{MnOOH} + \frac{1}{6} \text{ZnSO}_4[\text{Zn(OH)}_2]_3.x\text{H}_2\text{O}
\]
**Figure S1.** a-c) Crystal structures of $\alpha$-MnO$_2$, $\gamma$-MnO$_2$ and $\delta$-MnO$_2$, related to Figure 2.

**Figure S2.** The calculated (a) TDOS and (b) PDOS of inserted H$^+$ and the NN-O in MnO$_2$ supercell with a (V$_O$+ H$^+$) as shown in Fig.1(f), related to Figure 1.
Figure S3. a) The front view, b) the side view, c) the top view of the apace group of P42/mnm, related to Figure 2.

The complete international symbol of P42/mnm is $P4_12_1\bar{2}m\bar{m}$, where $P$ represents simple grid, $4_1$ represents that “c” axis is the $4_1$ rotation axis, the first $m$ represents that the plane vertical to the c axis is specular plane, $2_1$ represents that the direction of “a” axis is the $2_1$ rotation axis, $n$ represents that the plane vertical to the “a” axis is diagonal slip plane and the slip direction is $\frac{a+b}{2}$, the “2” represents that the diagonal line of $\frac{a+b}{2}$ is the secondary axis, the second “m” represents the plane vertical to the diagonal line of $\frac{a+b}{2}$ is a specular plane.

Figure S4. HR-TEM image of D-β-MnO₂, related to Figure 3.
Figure S5. Raman spectra of D-β-MnO₂ and commercial β-MnO₂, related to Figure 3.

Figure S6. EDX of the D-β-MnO₂ sample, related to Figure 3.
Figure S7. CV curves of the initial 5 cycles at 0.2 mV s\(^{-1}\) of the D-\(\beta\)-MnO\(_2\) electrode, related to Figure 4.

The cathodic peaks centered at about 1.25 and 1.40 V were attributed to the insertion of \(\text{H}^+\) into the \(\beta\)-MnO\(_2\) host (\(\text{H}^+\) is the main charge carrier in this work), and the anodic peaks centered at 1.56 V with a shoulder at 1.61 V correspond to the extraction of \(\text{H}^+\) from \(\beta\)-MnO\(_2\) cathode, accompanying the evolution between Mn(IV) and Mn(III)/Mn(II) states.

Figure S8. CV curves at 0.1 and 0.3 mV s\(^{-1}\) of the D-\(\beta\)-MnO\(_2\) and commercial \(\beta\)-MnO\(_2\), related to Figure 4.
**Figure S9.** GCD profiles of the Zn/D-β-MnO$_2$ cell using the porous Zn and Zn foil anode, related to Figure 4.

**Figure S10.** The electrochemical impedance spectra of D-β-MnO$_2$ and commercial β-MnO$_2$ electrodes at different cycles, related to Figure 4.
**Figure S11.** Electrochemical performances of the Zn/D-β-MnO₂ batteries with a high mass loading of 4.0 mg cm⁻². a) Rate capacities; b) Cycling performances at 100 mA g⁻¹, related to Figure 4.

**Figure S12.** The GCD curves in the initial cycle of D-β-MnO₂ electrode with different mass loadings, related to Figure 4.
Figure S13. Electrochemical performances of the commercial β-MnO$_2$ electrodes with high mass loadings of 3.0 and 4.0 mg cm$^{-2}$. a, c) Rate capacities; b, d) Cycling performances at 500 mA g$^{-1}$, related to Figure 4.
Figure S14. GITT curves and the corresponding diffusion coefficients at different states of the H⁺ in D-β-MnO₂ and commercial β-MnO₂ electrodes, related to Figure 4.
Figure S15. The \textit{ex-situ} SEM images of D-\(\beta\)-MnO\(_2\) electrode. a, b) Initial state; c, e) 1\textsuperscript{st}, 2\textsuperscript{nd} fully discharged state; d, f) 1\textsuperscript{st}, 2\textsuperscript{nd} fully charged state, related to Figure 5.

Figure S16. a) GCD curves at 50 mA g\(^{-1}\) for the second cycle; b) The corresponding \textit{ex-situ} XRD patterns at selected states of commercial \(\beta\)-MnO\(_2\) electrode, related to Figure 5.
Figure S17. The ex-situ SEM images of commercial β-MnO$_2$ electrode. a, b) Initial state; c, d) Fully discharged state and e, f) fully charged state at the second cycle, related to Figure 5.

Figure S18. XRD patterns of the D-β-MnO$_2$ electrode at the initial and after 50 cycles state, related to Figure 5.
Figure S19. The solid state $^1$H NMR spectra. a), MnOOH; b) Zn$_4$SO$_4$(OH)$_6$$\cdot$$x$H$_2$O and c) MnO$_2$ electrode discharged to 0.8V, related to Figure 6.

The solid state $^1$H NMR spectra were carried out to further confirm the reaction mechanism. The peaks marked by the little square frame are spinning side bands in NMR spectrum. Two isotropic peaks centered at 10.3 and -1.6 ppm in Figure S19a are attributed to the resonance from MnOOH and the physical absorbed H$_2$O on the surface of MnOOH. (Pan et al., 2016) Figure S19b shows a sharp $^1$H signal at 5.3 ppm, which is resonated from the numerous hydroxyl groups and crystalliferous water in Zn$_4$SO$_4$(OH)$_6$$\cdot$$x$H$_2$O compound. (Paik et al., 2001) Remarkably, the D-β-MnO$_2$ electrode at discharged state (Figure S19c) shows a dominant peak at 2.1 ppm resonated from Zn$_4$SO$_4$(OH)$_6$$\cdot$$x$H$_2$O. The slight up shift is due to the difference of magnetic susceptibility between a composite electrode and Zn$_4$SO$_4$(OH)$_6$$\cdot$$x$H$_2$O compound, (Pan et al., 2016) which may be caused by the insertion of H$^+$. Additionally, the missing peak at 10 ppm from MnOOH is probably because the composite electrode is coated by quantities of Zn$_4$SO$_4$(OH)$_6$$\cdot$$x$H$_2$O, which limited the signal of MnOOH inside the composite electrode.
Figure S20. The comparison of discharge capacities of D-β-MnO₂ electrodes in organic (0.1 M Zn(Tf)₂/DMSO) and aqueous electrolyte (2nd cycle, current density of 0.05 A g⁻¹), related to Figure 5.
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