Electrochemically induced cationic defect in MnO intercalation cathode for aqueous zinc-ion battery

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A B S T R A C T

The Mn dissolution is a key issue in the application of high-energy-density manganese-based materials, but the use of Mn dissolution to unlock the electrochemical activity of electrode materials is rarely achieved. Here, an in-situ electrochemical approach has been developed for the activation of MnO by inducing Mn-defect, wherein the Mn defects are formed through a charge process that converts the MnO with poor electrochemical activities towards Zn2+ into high electrochemically active cathode for aqueous zinc-ion batteries (ZIBs). More importantly, this cathode exhibits an insertion/extraction mechanism without structural collapse during storage/release of Zn2+. The as-designed Zn/MnO battery delivers a high energy density of 383.88 Wh kg⁻¹ at a power density of 135.6 W kg⁻¹. The results demonstrate that the Mn-defect MnO would be a promising cathode for aqueous ZIBs, which is expected to be used in commercial large-scale energy storage. This work may pave the way for the possibility of using defect chemistry to introduce novel properties in electrode materials for high-performance aqueous ZIBs.

1. Introduction

As alternative battery chemistry to lithium-ion batteries, rechargeable aqueous zinc-ion batteries (ZIBs) have attracted more attention due to their high safety, low cost, higher ionic conductivity [1–4], as well as the merit of Zn anode in terms of high theoretical capacity (820 mA h g⁻¹), cheap, low redox potential (−0.76 V vs. standard hydrogen electrode), and excellent stability in water [1,5–7]. Manganese-based materials are the promising cathode materials for aqueous ZIBs because of their high-energy-density, however thermal instabilities and the dissolution of Mn, which leads to capacity fading and may lead to structural collapse [8,9]. Researchers have tried various methods to inhibit the dissolution of Mn, but the utilization of the manganese dissolution to create cation defects for breakthrough performances is rarely achieved [10].

Due to the strong electrostatic interactions between the host lattice and multivalent ions, the intercalation chemistry process of multivalent ions is typically impeded by this intrinsic limitation. Recently, cationic vacancies have received much attention for multivalent metal-ion batteries, because they can attenuate the electrostatic interaction and facilitate the ions insertion from the host [11–13]. Koketsu et al. demonstrated that titanium-vacancy engineering in TiO₂ greatly improved its electrochemical activities towards Mg²⁺ and Al³⁺, due to vacancies weaken the electrostatic interactions between the multivalent ions and the titanium-vacancy TiO₂ host [11]. Cation-deficient technology is also verified to be a peculiar merit for aqueous ZIBs, in which Chen's work reported a Mn-deficient spinel ZnMn₂O₄ cathode [14]. It indicated that introducing abundant Mn vacancies in spinel ZnMn₂O₄ effectively facilitates the diffusion of Zn²⁺ ions within the spinel framework [14], while the perfect spinel is unfit for Zn²⁺ insertion due to the high electrostatic barrier [15]. So far, the cationic vacancies can be induced by aliovalent cation substitution [11], anion substitution [16], or pH-controlled method [17], etc. However, the introduction of defects via the electrochemically charging process has not been reported yet.

Herein, we report an electrochemically in-situ induced Mn-defect
MnO (Mn\(_{0.61}\square_{0.39}\)O, □ refers to Mn defect) for the first time, wherein the Mn defects were formed through a charge process that converts the MnO with poor electrochemical activities towards Zn\(^{2+}\) into high electrochemically active cathode for aqueous ZIBs. The density functional theory (DFT) calculation also indicated that the pristine MnO is unable to be imbedded by Zn\(^{2+}\) ions, while the presence of Mn defects enhances the conductivity of MnO and provides enough inserted channels and available active sites for insertion of Zn\(^{2+}\) ions. More importantly, the Mn\(_{0.61}\square_{0.39}\)O cathode exhibited an insertion/extraction mechanism without structural collapse during storage/release of Zn\(^{2+}\). The as-designed Zn/Mn\(_{0.61}\square_{0.39}\)O battery delivered a high energy density of 383.88 Wh kg\(^{-1}\) at a power density of 135.6 W kg\(^{-1}\). The results demonstrated that the Mn\(_{0.61}\square_{0.39}\)O would be a promising cathode for aqueous ZIBs, which are expected to be used in commercial large-scale energy storage.

2. Experimental

2.1. Synthesis of carbon-coated MnO nanoparticle

Two steps were conducted to synthesize MnO nanoparticles. The precursors were synthesized via a simple precipitation route. Firstly, 2 mmol of Mn(NO\(_3\))\(_2\) and 1.3 g of 2-methylimidazole (Hmim) were dissolved in 40 ml deionized water, respectively, and following 30 min magnetic stirring at room temperature. Then the Mn(NO\(_3\))\(_2\) solution was poured into the Hmim solution quickly. The precursor solution was then kept at room temperature for 4 h with continuous stirring. The obtained brown precipitates were washed several times with deionized water and absolute ethanol and dried in air overnight at 60°C. Secondly, the precursors were collected and thermally treated at 500°C under an Ar flow for 2 h with a heating rate of 2°C min\(^{-1}\) to obtain carbon-coated MnO nanoparticles. For comparison, the carbon-free MnO was also prepared at the same experimental conditions, except prepared precursors were treated in the muffle furnace at 450°C for 60 min to remove carbon.

2.2. Synthesis of MnO sphere

In a typical synthesis, 1 mmol KMnO\(_4\) and 5 ml alcohol was dissolved in 35 ml deionized water. Then the above solution was transferred into a 50 ml Teflon-lined stainless steel autoclave. The hydrothermal reaction heated at 160°C for 24 h. After cooling, the precursors was washed several times with deionized water and absolute ethanol and dried in air overnight at 60°C. Then, the precursors were collected and thermally treated at 500°C under an Ar/H\(_2\) flow for 2 h with a heating rate of 2°C min\(^{-1}\).

2.3. Materials characterization

The XRD patterns were obtained by using a Rigaku D/MAX-2500 diffractometer (Cu Ka, λ = 0.15405 nm). X-ray photoelectron spectroscopy (XPS) spectra were performed on an ESCALAB 250XI X-ray photoelectron spectrometer (Thermo Fisher). The morphological features were observed with field-emission scanning electron microscopy (FEI Quanta FEG250) and field-emission transmission electron microscope (FEI Titan G2 60–300).

3. Results and discussion

As shown in in Fig. 1a, the X-ray diffraction (XRD) spectrum unveils that all the characteristic diffraction peaks match well with the face-centered cubic MnO phase (space group Fm-3m, PDF#75-0626) and its crystal structure is shown in inset of Fig. 1a. So far, most of the manganese-based oxides such as MnO\(_2\) with different crystallographic polymorphs (e.g. α, β, γ, etc.), α-Mn\(_2\)O\(_3\) and Mn\(_3\)O\(_4\) (Fig. S1 in ESI) have been explored as cathodes for aqueous ZIBs [18–21], but the MnO has not been reported yet, which is expected to exhibit good performance as a cathode for aqueous ZIBs. We further identify its chemical compositions by X-ray photoelectron spectroscopy (XPS) (Fig. S2 in ESI), which exhibits a spin-energy separation of 6.0 eV for the Mn 3s doublet (Fig. 1b),

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Fig. 1. Material characterization of MnO nanoparticles. (a) XRD pattern, inset showing the crystal structure of MnO; (b) Mn 3s region of the XPS spectra; (c) Raman spectrum; (d) SEM; (e) TEM; (f) HRTEM image, inset showing the corresponding SAED pattern; (g) TEM-EDX element mapping images.
indicating the Mn in the electrode has a charge state of ~2 [22,23]. Raman spectrum of MnO exhibits three notable Raman shifts (Fig. 1c): Mn–O vibration (626 cm⁻¹), the D band (1366 cm⁻¹) and the G band (1587 cm⁻¹) [24], indicating that the existence of carbon in MnO. The Raman peak at 626 cm⁻¹ is attributed to the symmetric Mn–O stretching in the MnO₆ slab. Its position remains throughout the charge and discharge processes. The Scanning electron microscopy (SEM) (Fig. 1d) and transmission electron microscopy (TEM) (Fig. 1e) images display a nanoparticle morphology of MnO with average size of 50 nm. A typical interplanar spacing of 0.26 nm corresponds to (111) plane of MnO phase. The corresponding energy-dispersive X-ray spectrometry (EDX) elemental mappings (Fig. 1f) display a uniform distribution of Mn, O, and C elements in MnO, further confirming the existence of carbon. The carbon coating may improve the conductivity of MnO nanoparticles, and it also may help to protect the stability of the MnO structure.

The electrochemical Zn²⁺ ion storage performance of MnO cathode electrode was evaluated. Unlike other manganese oxides with high open-circuit voltages, the galvanostatic discharge-charge (GDC) and cyclic voltammetry (CV) tests show that MnO has no reduction peaks in the initial discharge process (Fig. S3 in ESI). It is different from the electrochemical behavior of other manganese oxides, for example, the first discharge process of MnO₂ has an obvious platform at about 1 V [10]. This phenomenon may be due to the small channels for insertion of Zn²⁺ ions, thus leads to low electrochemical activity of Mn (II) in MnO, which is also confirmed by the DFT calculation discussed later. Interestingly, the obvious oxidation platforms or peaks are observed in subsequent charging process. To reveal the reason accounting for this phenomenon, the Zn/Mn concentration ratio in electrolyte was measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) technology (Note: 2 M ZnSO₄ was used for this experiment). It is obvious that the value of Zn/Mn ratio in the electrolyte solution increased after initial charge process (Fig. 2a), suggesting the electrochemical extraction of Mn²⁺ from MnO host, which will induce Mn defects. XPS analysis were used to analyze the valence state. In Fig. 2b, the Mn 3s multistate splitting distance is reduced after initial charging, indicating the oxidation state of Mn increased [25]. We attribute this phenomenon to the extraction of Mn²⁺ from MnO host into the electrolyte during charging to form Mn defects.

To further confirm the Mn defects in the charged electrode, the HRTEM images and Rietveld analysis of the XRD patterns were conducted. The HRTEM image (Fig. 2c) suggests that the basic structure of MnO at fully charged state is clearly resolved. An obvious interplanar spacing of 0.26 nm corresponds to (111) plane of MnO phase. The magnified images (1, 2 and 3) directly show that Mn columns in some areas become weak or missing, indicating the Mn defects (marked with dotted circles) in MnO after full charged state. The amounts of Mn defects were further determined by the Rietveld analysis of the XRD patterns. As displayed in Table S1 in ESI, the atomic occupancies of Mn and O in MnO at initial state are 0.97 and 1, respectively. In the fully charged state, the structure of MnO has no obvious change (Fig. 2d), but the atomic occupancy of Mn and O are 0.61 and 0.99, respectively. It means that the amount of Mn-defects in per mole MnO is 0.39 mol. Therefore, the chemical formula could be described as Mn₀.₆₁O₀.₉₉, which is further confirmed by the calculation of the extracted Mn²⁺ ions in the initial charge process. The formation of Mn defects rises the average valence of Mn in MnO, which is converted to be electrochemically active cathode in the subsequent cycles to enable the storage of Zn²⁺. The Mn defects and Mn–O grid distortion may unlock the electrochemical activity of MnO framework. It should be noted that we for the first time proposed the formation of cation defects in the electrode material during the charging process, which converts the poor electrochemical active cathode towards Zn²⁺ into high electrochemically active cathode. Moreover, these Mn defects will provide facile pathways with reduced energy barriers for Zn²⁺ migration [17], thus facilitates the Zn²⁺ ions to be inserted/extracted from the MnO host.
Fig. 3a displays that the initial charge CV curve is quite different from that in subsequent charge process. A strong anodic peak at 1.55 V accompanied by a weak shoulder peak in the initial charge process may be ascribed to the extraction of Mn$^{2+}$ from the host material [26,27], while the two anodic peaks located at around 1.57 and 1.60 V in subsequent cycles are possibly due to the stepwise egress of Zn$^{2+}$. In cathodic scans, two distinct peaks are observed at around 1.39 and 1.25 V, which is due to the intercalation of Zn$^{2+}$ accompanied by the change of Mn valence state, which will be discussed later. Fig. S4a in ESI shows the high-rate capability of MnO electrodes with specific capacities ranging from 300 mA h g$^{-1}$ at 0.1 A g$^{-1}$ to 105 mA h g$^{-1}$ at 2 A g$^{-1}$. In addition, a discharge capacity of 283.1 mA h g$^{-1}$ is well preserved after 50 cycles at the current density of 100 mA g$^{-1}$ (Fig. S4b in ESI). The Zn/Mn concentration ratio in electrolyte after several cycles was also measured by ICP-OES technology (Fig. S5 in ESI). It is obvious that the proportion of Mn element in the electrolyte does not increase significantly during the subsequent cycles compared to that after first charge process, indicating the Mn dissolution tends to balance. This is probably because the Mn$^{2+}$ ions in the electrolyte suppress significant continuous Mn$^{2+}$ dissolution. Therefore, the electrode material remains approximately stable during the cycle. The Zn/Mn$_{0.61}$O$_{0.39}$O successfully lit the LED light (Fig. S6 in ESI). Ragone plots show the corresponding energy density of 356.86 Wh kg$^{-1}$ (135.6 Wh kg$^{-1}$) to 144.92 Wh kg$^{-1}$ (2760 Wh kg$^{-1}$) for Zn/Mn$_{0.61}$O$_{0.39}$O battery. Other previous reported cathode materials for aqueous ZIBs were also listed in Fig. 3b. Although the energy densities of partial cathode materials surpass that of Mn$_{0.61}$O$_{0.39}$O, the energy density of Mn$_{0.61}$O$_{0.39}$O is maintained at a high level, which is higher than that of the reported $\alpha$-MnO$_2$ [26,28,29], $\beta$-MnO$_2$ [10,30], ZnMn$_2$O$_4$ [14], Mn$_3$O$_4$ [20], $V_2$O$_5$:nH$_2$O [31], V$_2$O$_5$ [32], VO$_2$ [33], Na$_2$V$_6$O$_{16}$:3H$_2$O [5], Zn$_{0.25}$V$_2$O$_5$:nH$_2$O [1], Na$_3$V$_2$(PO$_4$)$_2$F$_3$ [34], MgMn$_2$O$_4$ [27] and so on. The comparison of electrochemical performances between Mn$_{0.61}$O$_{0.39}$O and previously reported manganese-based compounds in terms of cycles performance (cycles number, current density, capacity retention), discharge capacity, and rates capability were listed in Table S2 in ESI.

Fig. 3. (a) CV curves at 0.1 mV s$^{-1}$; (b) Comparison of the Ragone plot (based on the weight of cathode material only) of the Mn$_{0.61}$O$_{0.39}$O with other previous cathode materials for aqueous ZIBs; (c) Long-term cycling performance at 1000 mA g$^{-1}$ of carbon coated and carbon free MnO nanoparticles; (d) The corresponding plots of log (peak current) vs. log (scan rate) at each peak in CV curves; (e) Charge transfer contribution from diffusion-controlled capacity and capacitance for initial and after 300th cycles.
The electrochemical performance of Mn$_{0.61}$□$_{0.39}$O is maintained at a high level among the previous reported cathode. However, it should be noted that the Mn$_{0.61}$□$_{0.39}$O is still far from practical applications, more efforts should be devoted to enhance their performances, such as the rate capability.

Fig. 3c indicates the long-term cycling performance of MnO cathode with a high reversible capacity of 116 mA h g$^{-1}$ at 1 A g$^{-1}$ after 1500 cycles. The carbon-free MnO nanoparticles were also prepared (Fig. S7 in ESI†), which showed continuously capacity fading. For Mn$_{0.61}$□$_{0.39}$O, the capacity decreases in the initial stage, then stabilize and increase in the following cycles. In fact, the rapid decline of specific capacity in initial stage is a common phenomenon occurred in many aqueous ZIBs cathodes [3,27]. From Rietveld XRD analysis (Fig. S8 and Table S1 in ESI†), Zn atomic occupancy rates is 0.07 at the 2nd charge state. The decline of specific capacity in initial stage may be due to that a few inserted Zn$^{2+}$ ions cannot be extracted from the lattice of electrode during the following charge process because of the strong electrostatic interaction between Zn$^{2+}$ and lattice host, resulting in the irreversible capacity. To reveal the increase of capacity in the following cycles, CV measurements of the initial and after 300th cycles with the continuous increase of the scan rates from 0.1 to 1.0 mV s$^{-1}$ were tested (Fig. S12 in ESI†). The slope values ($b$ values) of peaks 1 and 2 are calculated to be close to 0.5 in the initial state, indicating mainly diffusion-controlled kinetics (Fig. 3d). After 300 cycles, the slope values of peaks 1 and 2 are calculated to 0.84 and 0.91, respectively, indicating partially capacitive-controlled kinetics. The calculated ratios of capacitive contribution to total capacities for the initial and 300th cycles were 35.75% and 63.09% in 0.4 mV s$^{-1}$, respectively (Fig. 3e). The results indicate that the interfacial storage ability improves after cycling due to the electrochemical activation, which may be responsible for the increased capacity during the following cycles [35].

The electrochemical impedance during cycles were also analyzed (Fig. 4a, Fig. S9 and Table S3 in ESI†). It is evident that the $R_{ct}$ value of the Mn$_{0.61}$□$_{0.39}$O electrode (105.3 Ω) is lower than that of MnO electrode (195.6 Ω), indicating that the induced Mn defects facilitates the diffusion of Zn$^{2+}$ ions. It shows that the $R_{ct}$ after 5 and 10 cycles are significantly higher than that of initial state, which may due to the trapped Zn$^{2+}$ ions in Mn$_{0.61}$□$_{0.39}$O as revealed by the Rietveld XRD results that leads to structural collapse.

Fig. 4. (a) Nyquist plots of the battery in different states, the inset shows the equivalent circuit model for the impedance spectra; (b) The discharge/charge curves in GITT measurement and corresponding diffusivity coefficient $D$ of Zn$^{2+}$ in discharge and charge processes; Calculated density of states (DOS) of (c) partial MnO and (d) partial MnO with Mn defect (Mn$_{0.61}$□$_{0.39}$O); (e) Charge distribution of MnO and Mn$_{0.61}$□$_{0.39}$O, and the structures after Zn$^{2+}$ insert (The green circle shows structural collapse). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
decline of specific capacity. And then, the $R_p$ values gradually decrease and stabilize to a balance from 100th cycle to 400th cycle, corresponding to the increase and stability of specific capacity. It is further revealed that the carbon coating can effectively protect the stability of the MnO structure. The Rietveld refinement of XRD analysis was carried out of carbon-coated and carbon-free MnO in different states, respectively (Fig. S8 in ESI†). The atomic occupancies of Mn are below 0.7 during cycling in carbon-coated MnO, suggesting the Mn defect can be well maintained upon charge-discharge processes. It was found that the cell parameters of carbon-free MnO changed more significantly, while the structure of carbon-coated MnO varied slightly (Fig. S10 in ESI†), suggesting the carbon coating could buffer the volume variation during $Zn^{2+}$ insertion/extraction. Moreover, carbon-coated MnO showed original structure even after 100 cycles, but the carbon-free MnO underwent a phase transformation accomplished by a new phase of $ZnMn_2O_4$ after 50 cycles (Fig. S11 in ESI†), further confirming that carbon-coated can stabilize the structure.

To understand the charge storage kinetics in the MnO host, the zinc diffusion coefficient was measured by using Galvanostatic Intermittent Titration Technique (GITT) [36]. As shown in Fig. 4b, the apparent chemical diffusion coefficients of MnO electrode are in the range of $10^{-13}$ to $10^{-9}$ cm$^2$s$^{-1}$, which are close to the previous reported Mn-defect $ZnMn_{0.61}O_{0.39}$ [14], and higher than that of manganese oxides, such as $\alpha$-MnO$_2$ [37,38], layered MnOOH$\cdot$H$_2$O and MnOOH [39, 40]. The corresponding EXAFS spectra in Fig. 5d show that the Mn interactions in MnO are similar to that of pristine MnO. The Mn L-edge near edge X-ray absorption fine structure (NEXAFS) profiles of Mn K-edge were recorded to determine the valence states of Mn. As shown in Fig. 5c, the primary peak position of Mn L-edge NEXAFS spectra shifted to higher energy after charging to 1.8 V, meaning that the main oxidation state of Mn may be from Mn$^{2+}$ to Mn$^{3+}$ and Mn$^{4+}$. Meanwhile, the peak position shifted toward lower energy by reduction of Mn$^{3+}$ to Mn$^{2+}$, which is further confirmed by XPS spectra. The NEXAFS and XPS analysis proved that the oxidation state of Mn increased by Mn defects occurred in fully charged state, the oxidation state of Mn decreases due to the insertion of $Zn^{2+}$ after discharged. The proportion of different oxidized states of manganese can be determined by the area of the fitting peaks of Mn L-edge NEXAFS spectra (Table S4 in ESI†). It exhibits that Mn$^{2+}$ accounts for 16.8%, Mn$^{3+}$ accounts for 74.3% and Mn$^{4+}$ accounts for 8.9% in Mn$0.61\Box0.39$O after charging. In addition, the extended X-ray absorption fine structure (EXAFS) profiles of Mn K-edge were recorded to determine the local structure and the coordination of Mn. Table S5 in ESI† displays the coordination number of Mn–Mn interaction in the fully charged state is substantially reduced to 7.9 in comparison with 9.7 for the initial MnO, which may be due to the existence of rich Mn defects in MnO. The corresponding EXAFS spectra in Fig. 5d show that the Mn–O and Mn–Mn peaks of MnO electrodes at different states have no significant deviation compared to that of standard MnO sample, suggesting the structure of MnO is stable during cycling.

To further prove the electrochemical reaction mechanism of MnO, the MnO spheres with radio of about 2 $\mu$m was successfully prepared (Figs. S16a and b in ESI†) and evaluated as cathode for aqueous ZIBs. The MnO spheres also exhibited electrochemical inactivity (Fig. S16c in ESI†), which is similar to the carbon-coated MnO nanoparticles. More importantly, the ex-situ XRD patterns of sphere-like MnO cathode also revealed that the carbon coating can effectively protect the stability of the MnO structure. The Rietveld refinement of XRD analysis was carried out of carbon-coated and carbon-free MnO in different states, respectively (Fig. S8 in ESI†). The atomic occupancies of Mn are below 0.7 during cycling in carbon-coated MnO, suggesting the Mn defect can be well maintained upon charge-discharge processes. It was found that the cell parameters of carbon-free MnO changed more significantly, while the structure of carbon-coated MnO varied slightly (Fig. S10 in ESI†), suggesting the carbon coating could buffer the volume variation during $Zn^{2+}$ insertion/extraction. Moreover, carbon-coated MnO showed original structure even after 100 cycles, but the carbon-free MnO underwent a phase transformation accomplished by a new phase of $ZnMn_2O_4$ after 50 cycles (Fig. S11 in ESI†), further confirming that carbon-coated can stabilize the structure.

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indicate no phase change with a stable structure. Based on the above discussions, we describe the energy storage mechanism of MnO as following (Fig. 5e):

\[
\begin{align*}
\text{MnO} & \rightarrow \text{Mn}^{0.61}\square_{0.39}\text{O} + 0.39 \text{Mn}^{2+} + 0.78 \text{e}^- \quad (1\text{st charge}); \\
\text{Mn}^{0.61}\square_{0.39}\text{O} + y\text{Zn}^{2+} + 2y\text{e}^- & \leftrightarrow \text{Zn}_y\text{Mn}^{0.61}\square_{0.39}\text{O} \quad (\text{further cycle}).
\end{align*}
\]

4. Conclusions

In conclusion, we firstly report an electrochemical approach that activate the MnO by inducing Mn-defect. The Mn_{0.61}\square_{0.39}O may provide more accessible channels for the diffusion of Zn^{2+} ions during charge/discharge process, leading to enhancement of cycling capability. Furthermore, the Mn_{0.61}\square_{0.39}O cathode exhibits an insertion/extraction mechanism without structural collapse during storage/release of Zn^{2+}. The Zn/Mn_{0.61}\square_{0.39}O battery can deliver a high energy density of 383.88 Wh kg\(^{-1}\) at a power density of 135.6 W kg\(^{-1}\), and long-term cycling performance with a high reversible capacity of 116 mA h g\(^{-1}\) at 1 A g\(^{-1}\) after 1500 cycles, which is expected to be used in commercial practical application. This work may provide a new strategy for designing high-performance electrode materials for aqueous ZIBs via defect engineering.

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Appendix A. Supplementary data

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