Oxygen-Deficient β-MnO₂@Graphene Oxide Cathode for High-Rate and Long-Life Aqueous Zinc Ion Batteries

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HIGHLIGHTS

• The concurrent application of vacancy enrichment and surface coating in β-MnO₂ electrode can both improve the intercalation kinetics and inhibit the Mn dissolution.

• The oxygen-deficient β-MnO₂@graphene oxide electrode delivers a reversible capacity of 129.6 mAh g⁻¹ after 2000 cycles at 4C, outperforming the state-of-the-art MnO₂-based cathodes.

• The excellent performance is rooted in the strong binding of graphene oxide on defective β-MnO₂ and the regulated structural evolution into the ZnₓMn₂O₄ phase.

ABSTRACT Recent years have witnessed a booming interest in grid-scale electrochemical energy storage, where much attention has been paid to the aqueous zinc ion batteries (AZIBs). Among various cathode materials for AZIBs, manganese oxides have risen to prominence due to their high energy density and low cost. However, sluggish reaction kinetics and poor cycling stability dictate against their practical application. Herein, we demonstrate the combined use of defect engineering and interfacial optimization that can simultaneously promote rate capability and cycling stability of MnO₂ cathodes. β-MnO₂ with abundant oxygen vacancies (V₀) and graphene oxide (GO) wrapping is synthesized, in which V₀ in the bulk accelerate the charge/discharge kinetics while GO on the surfaces inhibits the Mn dissolution. This electrode shows a sustained reversible capacity of ~129.6 mAh g⁻¹ even after 2000 cycles at a current rate of 4C, outperforming the state-of-the-art MnO₂-based cathodes. The superior performance can be rationalized by the direct interaction between surface V₀ and the GO coating layer, as well as the regulation of structural evolution of β-MnO₂ during cycling. The combinatorial design scheme in this work offers a practical pathway for obtaining high-rate and long-life cathodes for AZIBs.

KEYWORDS Manganese oxides; Oxygen defects; Surface optimization; Aqueous zinc battery

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1 Introduction

The worldwide transition from fossil fuels to sustainable energy sources has spawned a rising demand for more reliable and low-cost batteries in the field of large-scale energy storage [1], where safety and economic issues are more of a concern than energy density. Rechargeable aqueous zinc ion batteries (AZIBs) [2], because of their non-flammability, cost effectiveness, environmental benignity, and abundant sources, offer a promising alternative to the lithium-ion battery technology in stationary grid-connected applications. Currently, the performance of AZIBs is largely limited by available cathode materials, of which renowned examples include manganese oxides [3], vanadium oxides [4], Prussian blue analogs [5, 6], and organic species [7]. Among them, polymorphs of MnO₂ have captured particular attention due to their outstanding theoretical capacity and a preferable theoretical voltage versus Zn anode [8–12]. However, the development of MnO₂ cathodes has been impeded by scientific challenges related to the kinetic limitations and capacity fading, which can be ascribed to the sluggish Zn²⁺ diffusion in the cathode [13] and the irreversible phase transformation [14], respectively. To realize high-rate and long-life AZIBs, it is therefore required to formulate new design strategies for MnO₂-based cathode materials.

Toward this goal, researchers have adopted various technologies, including pre-intercalation engineering [15], defect engineering [16, 17], interfacial optimization [18, 19], and metal-doping [20], etc. Especially, the incorporation of oxygen vacancies (V₀) is an effective route to improve the rate performance of MnO₂ electrodes. Previous studies have suggested that electronic conductivity can be enhanced in the presence of V₀ [21, 22] and that the under-coordinated Mn ions will potentially afford facile transport pathways for ionic charge carriers [23–26]. It is worth mentioning that a recent study of β-MnO₂ cathode has revealed the massive proton insertion triggered by the introduction of V₀ into the bulk lattice [27]. These promising aspects enabled by oxygen deficiency may, however, be tarnished by a higher susceptibility to Mn dissolution, which is likely to incure phase transitions. In this regard, surface coating (SC) can be leveraged to inhibit the Mn ions diffusing into the electrolyte. For pristine MnO₂ cathodes, the benefits of SC have already been demonstrated in several reports with carbon-based coating materials ranging from graphene [28, 29] to polymers [30, 31]. Yet, the pertinent combination of V₀ and SC has not been explored in AZIB cathodes up to date, despite its fascinating potential to promote rate capability and cycling stability at the same time. Moreover, how such coatings interact with MnO₂ is rarely discussed, thus depriving researchers of a rational understanding of the role played by SC.

In this work, we report the combinatorial use of defect engineering and interfacial optimization to boost the electrochemical performance of β-MnO₂ cathode. Electrode with excessive V₀ and graphene oxide (GO) wrapping is directly synthesized via a simple hydrothermal reaction. V₀ plays the vital role in facilitating the transfer of electrons and protons, while GO coating suppresses the dissolution of Mn ions. As a consequence, the oxygen-deficient β-MnO₂@graphene oxide architecture exhibits high capacity, superior charge/discharge rates, and excellent cycle stability. Our work highlights that the tight binding of GO to the surfaces of β-MnO₂ via the interaction with V₀ acts in synergy with the regulated formation of spinel ZnₓMn₂O₄ to guarantee the structural integrity of the electrode during long-term cycling.

2 Experimental Section

2.1 Synthesis of β-MnO₂@GO Nanorods

The β-MnO₂@GO nanorod was synthesized via a typical hydrothermal method. 30 mL 0.6 M MnSO₄, 2 mL 0.5 M H₂SO₄, and 4 mL 1 mg mL⁻¹ GO dispersed aqueous solutions were mixed and continuously stirred for 30 min. 30 mL 0.1 M KMnO₄ was then added into the resultant solution dropwise, after which the solution was stirred at room temperature for another 30 min and then loaded into a 100 mL Teflon-lined autoclave and maintained at 120 °C for 12 h. Finally, the obtained products were collected by the filter and were washed with deionized water and absolute ethyl alcohol for three times, respectively, and then dried at 80 °C for 12 h. The β-MnO₂ counterpart was synthesized with the same method without adding GO.

2.2 Materials Characterization

The prepared materials were characterized by X-ray diffraction (XRD, Bruker D8 ADVANCE) with Cu Kα radiation. Scanning electron microscopy (SEM, ZEISS SUPRA55) and
transmission electron microscopy (TEM, JEM-3200FS) were
employed to investigate the micromorphology and micro-
structure. The thermogravimetric analysis (TGA) data were
recorded in O2 atmosphere using a 10 °C min⁻¹ heating rate
from 30 to 700 °C. X-ray photoelectron spectroscopy (XPS,
ESCALAB 250Xi) was used to conduct the element com-
position and electronic structure analysis, in company with the
energy-dispersive spectroscopy (EDS, Oxford X-Max 20)
and Fourier transform infrared spectroscopy (FTIR). Elec-
tron paramagnetic resonance (EPR, Bruker A300-10/12) was
performed to characterize the unpaired electron.

2.3 Electrochemical Tests

Electrochemical performance was tested in CR2032-type
coin cells which were assembled in air condition. The work-
ing cathodes were fabricated by blending active materials,
acetylene black (AB) and polyvinylidene fluoride (PVDF) in
a weight ratio of 7:2:1 with N-methyl-2-pyrrolidone (NMP)
used as a solvent to form a viscous slurry and coat onto
Ti foil. The areal active loading for both the β-MnO2 and
β-MnO2@GO is about ~ 2 mg cm⁻². The as-prepared elec-
trodes were dried in vacuum oven of about 110 °C for 24 h.
Zinc foil in 10 mm and glass fiber membrane in 16 mm were
used as the anode and separator, respectively. The electrolyte
contained 3 M ZnSO4 and 0.2 M MnSO4 in aqueous solu-
tion. The LAND-CT2001A battery-testing instrument was
conducted for cycle and rate test with assembled cells. EIS
was performed on a Chi 660e electrochemical workstation
with frequency range from 100 kHz to 0.1 Hz.

2.4 First Principles Calculations

Density functional theory (DFT) calculations were carried
out using projected augmented wave pseudopotentials and
the generalized gradient approximation in the form of the
Perdew–Burke–Ernzerhof exchange–correlation functional
modified for solids (PBEsol), as embedded in Vienna ab ini-
tio simulation package (VASP). The van der Waals interac-
tions were treated using Grimme’s correction (DFT-D3). To
deal with the localization of d electrons on Mn ions, Hub-
bard-corrected PBEsol+U(+J) functional was employed.
More details are given in the Supporting Information.

3 Results and Discussion

3.1 Material Characterization

XRD patterns of the prepared β-MnO2 and β-MnO2@GO
are shown in Fig. 1a, which match very well with the
standard β-MnO2 (tetragonal, space group of P42/mmm,
PDF #42-0735). This result indicates that GO wrapping
does not alter the crystal structure of the β-MnO2. SEM
results show the nanorod morphologies of β-MnO2 and
β-MnO2@GO with several micrometers in length and
200–300 nm in width (Fig. S1). The high-resolution TEM
(HRTEM) confirms the adhesion of GO to the surfaces of
β-MnO2 (Fig. 1b). Two lattice fringes of (101) and (110)
planes are observed for β-MnO2@GO (Fig. 1c), with
interlayer spacing values of ~ 2.40 and ~ 3.13 Å, respec-
tively, consistent with the XRD results in Fig. 1a. Similar
lattice fringe results are also observed for β-MnO2 (Fig.
S2). There exist some ambiguous areas in β-MnO2@GO,
which can be ascribed to the formation of a large number
of defects.

EDS, FTIR, and XPS further justify the successful
wrapping of GO (Fig. 1b) in the β-MnO2@GO sample. Figure 1d reveals the uniform distributions of Mn, O, and
trace amount of C elements. Comparison of FTIR results
in Fig. 1e demonstrates the characteristic peaks of C-O
(~ 1432 cm⁻¹) and C=C (~ 1576 cm⁻¹) [32] in β-MnO2@GO.
Three clear peaks located at ~ 284.8, ~ 286.0, and ~ 288.8 eV in XPS C 1s spectrum of β-MnO2@GO
(Fig. 1f) indicate the existence of C–C/C=C, C–O, and
O–C=O bonds, respectively.

The formation of VO can be implied by the XPS O 1s
spectra (Fig. 1g), where the characteristic peak of VO
(~ 531.2 eV) in β-MnO2@GO is substantially higher than
that in β-MnO2. EPR spectra (Fig. S3) showing an appar-
ent symmetrical signal at g = 2.0 also suggest the high con-
centration of VO [33]. The TGA curves of β-MnO2 and
β-MnO2@GO in O2-containing atmosphere are shown in
Fig. 1h. In the temperature range of 200–600 °C, the TGA
curve of β-MnO2@GO rises, indicating the filling of VO
by oxygen, in contrast to the β-MnO2 sample where the
mass change is negligible. Here, we cannot rule out the
possibility of GO decomposition, which will contribute
to mass loss. Due to the formation of more VO, Mn ions in
β-MnO2@GO show lower valence than those in β-MnO2,
as revealed by Mn 3s spectra in Fig. S4. Such a remarkable increase in V₀ concentration is associated with both the low average oxidation state of Mn (+2.7) in the reactant solution, and the deoxygenation of GO during hydrothermal process, which will develop a strong tendency to extract the surface O ions of the as-produced β-MnO₂ so as to compensate the abundant dangling bonds on the reduced GO. The functional groups on GO may also accelerate the formation of β-MnO₂, in which case the fast kinetics will potentially give rise to offset from the equilibrium state, for example, in the form of bulk V₀. This scenario is similar to the cases of TiO₂@GO [34] and other MnO₂@GO electrodes in previous report, where the generation of V₀ in the transition metal oxides can be triggered during their hydrothermal growth in the presence of GO [35–37].

3.2 Electrochemical Performance

Coin-type cells are assembled with Zn plate as anode and aqueous 3 M ZnSO₄ + 0.2 M MnSO₄ as electrolyte. The role of the pre-added Mn²⁺ in the electrolyte is to suppress the Mn²⁺ dissolution upon discharge processes, and the optimized Mn²⁺ concentration in electrolyte is ~0.2 M (Fig. S5). Figure 2a compares the rate performance of the β-MnO₂ and β-MnO₂@GO electrodes. It can be seen that both electrodes show similar capacity activation process in the initial eight cycles at a current of 0.1C (1C = 308 mA g⁻¹), indicating that GO wrapping shows little influence on the capacity delivery of β-MnO₂ at low current rates. After eight cycles, the discharge capacity of β-MnO₂@GO is stabilized at ~322.6 mAh g⁻¹. Figure 2b shows the galvanostatic charge/discharge (GCD) curves of the β-MnO₂ and β-MnO₂@GO electrodes at a current of 0.1C in the second cycle, indicating that GO wrapping can induce an elevated discharge platform, i.e., a smaller polarization. Figures 2c and S6 show the GCD curves of the β-MnO₂@GO and β-MnO₂ electrodes at various current rates, respectively. The discharge capacities of β-MnO₂@GO are ~312.4, ~290.9, ~259.6, ~211.7, ~158.6, ~132.5, ~106.8, and ~94.9 mAh g⁻¹ at current rates of 0.25, 0.5, 1, 2, 4, 6, 8, and 10C, respectively, which are much higher than those of β-MnO₂.

Figure 2d, e provides the cycling performances of β-MnO₂ and β-MnO₂@GO electrodes at current rates of 1C and 4C.
respectively. It can be seen that the cycling performances follow the similar trend: The discharge capacity is activated in the initial cycles and then continuously reduces in the subsequent cycles. This kind of capacity variation is similar to other manganese oxide electrodes in previous reports [38, 39], and the initial capacity activation process can be attributed to the bulk-nanocrystalline evolution during cycling. For β-MnO₂@GO, at a current rate of 1C, the discharge capacity first increases to ~278.6 mAh g⁻¹ in 50 cycles and then reduces slowly to ~236.6 mAh g⁻¹ in 200 cycles. Furthermore, at a current rate of 4C, the discharge capacity first increases to ~166.9 mAh g⁻¹ in 220 cycles and then reduces slowly to ~129.6 mAh g⁻¹ in 2000 cycles, with nearly no capacity fading as compared with the initial discharge capacity (~106.7 mAh g⁻¹). The capacity, rate, and cycling performances of β-MnO₂@GO are among the best reported
manganese oxides (Table S1). Therefore, the combination of V0 and GO wrapping on β-MnO2 not only enhances the charge/discharge kinetics for superior rate performances, but also improves the cycling stability of the electrode.

3.3 Charge Storage Mechanism

Insights into the charge storage mechanism is highly significant to understand the enhanced electrochemical performances of β-MnO2@GO. Herein, XRD, SEM, TEM, and XPS are comprehensively applied to reveal the charge storage mechanism and the correlated structural evolution of β-MnO2@GO upon cycles. Figure 3a shows the GCD curves of β-MnO2@GO electrode in the initial two cycles (at current rate of 0.1C), with the correlated XRD patterns at selected states (from point #A to #J) given in Fig. 3b. It can be seen that the (110), (101), (211) peaks of β-MnO2@GO located at 28.62°, 37.28°, 56.60° shift negligibly upon discharge/charge processes. After discharge (i.e., at point #B in the first cycle, and point #H in the second cycle), two diffraction peaks at 16.35° and 33.95° emerge, corresponding well to the monoclinic MnOOH (orthorhombic, Pnma (62), PDF #88-0648), a typical product of proton conversion in MnO2 [40, 41]. Meanwhile, zinc sulfate hydroxide hydrate by-product (Zn6(OH)6·ZnSO4·xH2O, abbreviated as “ZSH,” PDF #44-0673) is generated upon discharge, featuring a set of strong diffraction peaks located at 8.12°, 15.08°, 21.56°, and 24.57°, which is a critical evidence for proton intercalation into the lattice framework of MnO2 [20]. The presence of ZSH on the electrode can be further confirmed by the morphology evolutions of β-MnO2@GO electrodes, (Figs. 3c, S7), and the detailed analysis for the morphology evolutions is shown in Supporting Information.

As reported previously, for β-MnO2, protons rather than Zn2+ ions tend to intercalate into the [1 × 1] tunnel framework, owing to the large ion radius and high charge density of the divalent Zn2+ ions [24]. Hence, the charge storage in β-MnO2@GO is likely to be dominated by the proton intercalation/conversion reactions. When the amount of intercalated proton in surface area exceeds a threshold, it converts to the orthorhombic MnOOH, which explains the co-existence of diffraction patterns of MnOOH (surface area) and protonated β-H2MnO2 (internal area) phases [27] upon discharge in Fig. 3b. Furthermore, some weak peaks locating at 32.97° and 58.70° are observed upon discharge in the second cycle, which is indexed to the ZnMn2O4 phase (hetaerolite, 141/amd, PDF No. 24-1133) [3, 42]. HRTEM is also applied to reveal the lattice structures of β-H2MnO2, MnOOH, and ZnMn2O4 phases in the discharged electrode, as shown in Fig. 3d–g. The nanorod morphology of β-MnO2@GO maintains well upon discharge. We note that the internal part (region I) remains the pristine crystal lattice of β-MnO2 (Fig. 3e), while the surface parts (i.e., in region II and III) show a different scenario. The magnified HRTEM images and the correlated diffraction patterns in region II and III (Fig. 3f, g) show the lattice fringes corresponding to (200) plane of MnOOH and (103) plane of ZnMn2O4, respectively. The detailed analyses of diffraction patterns from regions I to III are illustrated in Fig. S8.

The proton storage behavior in β-MnO2@GO can be further confirmed by XPS analyses. Before the XPS tests, the ZSH on electrode is removed by dilute acid to eliminate the influence of by-products. Figure 3h shows the evolution of O 1s spectra in initial two cycles, where the peaks near 531.9 eV (referred to Mn–O–H bonds on [MnO6] octahedron units) increase upon discharge and decrease upon charge, which is correlated with the regular variation in Mn valence (Fig. S9). Accompanying with the proton insertion/extraction processes, the inevitable Mn3+ disproportionation occurs upon discharge. As a consequence, some Mn2+ ions dissolve and migrate into the electrolyte, resulting in Mn vacancies on the surface of β-MnO2. In the subsequent discharge process, Zn2+ ions can easily insert into the defective structure and give rise to the transformation into ZnxMn2O4 (x < 1) spinel phase in the surface region.

Figure 3i shows the evolution of Zn 2p spectra in the initial two cycles. It can be seen that the Zn 2p peaks become obvious starting from the second discharge process (since point #F), indicating that Zn2+ cannot insert into the lattice framework of β-MnO2 until there are some Mn vacancies generated after the first discharge process. The Zn2+ ions in Zn4Mn2O4 are largely unextractable, demonstrating a low reversibility of Zn2+ insertion/extraction. Similar charge storage behavior in β-MnO2 is also characterized in Figs. S10–S12. Moreover, after long-term cycles, the proton storage reactions still dominate the charge storage of β-MnO2@GO electrode (Figs. S13–S15, Tables S2, S3) despite such structural evolution. V0 and SC will significantly influence the proton storage behavior and Zn4Mn2O4 formation process, which will be discussed in the following part.
3.4 Superior Reaction Kinetics

As displayed in Fig. 2a, the boosted rate performance is mainly attributed to the incorporation of \( V_O \) in \( \beta\text{-MnO}_2@GO \). Figure 4a shows the calculated electron density of states of \( \beta\text{-MnO}_2 \) and \( \beta\text{-MnO}_2 + V_O \) by DFT calculations. The pristine \( \beta\text{-MnO}_2 \) has a bandgap of ~0.25 eV, while a lower value of ~0.12 eV is obtained after introducing a \( V_O \) in the supercell, indicating an enhanced electronic conductivity of \( \beta\text{-MnO}_2 + V_O \). Consistent with the above result, the \( \beta\text{-MnO}_2@GO \) electrode presents much lower charge transfer impedance of ~365.3 \( \Omega \) cm\(^2\) when compared with that of the
The β-MnO$_2$ electrode (~604.3 Ω cm$^2$). The galvanostatic intermittent titration technique (GITT) measurements are further applied to illustrate the proton insertion kinetics (Fig. 4c, d), and the detailed calculation processes of diffusion coefficients are illustrated in SI. The β-MnO$_2$@GO electrode shows average diffusion coefficients of ~1.13 × 10$^{-11}$ cm$^2$ s$^{-1}$ in region I (from 1.8 to 1.35 V) and ~4.00 × 10$^{-14}$ cm$^2$ s$^{-1}$ in region II (from 1.35 to 1.05 V), which are consistently higher than that of β-MnO$_2$ electrode (~4.25 × 10$^{-12}$ cm$^2$ s$^{-1}$ in region I and ~2.57 × 10$^{-14}$ cm$^2$ s$^{-1}$ in region II).

3.5 Enhanced Cycling Stability

As illustrated in Fig. 2d, e, the GO wrapping can dramatically enhance the cycling stability. In this part, the mechanism of such enhancement is comprehensively investigated. DFT calculations are applied to reveal the interaction between β-MnO$_2$ and GO. In the absence of an ether oxygen on GO, the graphene layer is weakly bound to the β-MnO$_2$ surfaces via van der Waals forces, with adsorption energies ranging from 0.21 to 0.44 eV (Fig. S16). Surface V$_O$ of β-MnO$_2$ cannot contribute to sufficiently strong interaction. However, when there exist surface V$_O$ and an ether oxygen in the vicinity, chemical bonding is established featuring Mn–O–C configuration, which pushes the adsorption energy to as high as 0.95–1.52 eV (Fig. 5a). It can be drawn that V$_O$ in β-MnO$_2$ and ether oxygen on GO work in synergy to achieve an intimate self-assembled wrapping of GO on β-MnO$_2$, which provides a direct physical barrier rendering the Mn ions tightly confined beneath the surfaces even at low valence states.

Figure 5b shows the structure evolution of the β-MnO$_2$ electrodes. During cycling, the characteristic peaks of β-MnO$_2$ at 28.7° and 37.5° decrease gradually and disappear after 50 cycles. Meanwhile, the characteristic peaks of ZnMn$_2$O$_4$ at 18.7° and 36.3° emerge and increase gradually.
upon cycling. These results indicate a progressive structure evolution from bulk β-MnO$_2$ to ZnMn$_2$O$_4$ spinel. Figure 5c, d shows the TEM/HRTTEM images and correlated diffraction pattern of the active material in β-MnO$_2$ after 200 cycles. We observe a severe degradation on the structural integrity of β-MnO$_2$, and the active material has completely converted into a bulk (or long-range-ordered) Zn$_x$Mn$_2$O$_4$ spinel (x = 1.000, from ICP result), as confirmed by the clear lattice fringe of (101) plane, as well as the apparent diffraction spots representing the (101), (211), and (312)
plane (diffraction pattern shown in the inset of Fig. 5d). The TEM EDS mapping in Fig. S17 further indicates the uniform distribution of Zn, O, and Mn elements, substantiating the generation of ZnMn$_2$O$_4$ spinel after long-term cycling.

For β-MnO$_2$@GO, the structural evolution is different from that of the β-MnO$_2$, as illustrated in Fig. 5e. The characteristic peaks of β-MnO$_2$@GO retain well after 100 cycles, demonstrating the beneficial effect of GO wrapping on stabilizing the pristine lattice framework. The relative intensities of the characteristic peaks of ZnMn$_2$O$_4$ in β-MnO$_2$@GO electrode are much lower than that in β-MnO$_2$ electrode, indicating that GO wrapping can effectively inhibit ZnMn$_2$O$_4$ accumulation upon long-term cycling. The nanorod morphology of β-MnO$_2$@GO is well preserved even after 200 cycles (Fig. 5f), showing an enhanced structural integrity. Figure 5g shows the HRTEM morphologies and correlated diffraction patterns of the active material, which shows vague lattice fringes referring to the (101) and (211) planes of ZnMn$_2$O$_4$ ($x=0.846$, from ICP result) spinel with lattice spacing of ~4.90 Å and ~2.48 Å, respectively. The correlated diffraction pattern shows two diffraction rings (inset in Fig. 5g), indicating the nanocrystalline (or short-term ordered) feature that favors proton intercalation/conversion reactions. EDS mapping results show a uniformly distributed Zn, O, and Mn elements in the active material of β-MnO$_2$@GO electrode after 200 cycles (Fig. S18), confirming the generation of nanocrystalline ZnMn$_2$O$_4$.

Overall, the combinatorial incorporation of VO and SC in β-MnO$_2$ could help in achieving better electrochemical performance on the following mechanistic aspects: (1) both VO and GO wrapping could facilitate electron transport; (2) intimate adhesion of GO on the defective surface could pose barrier to the dissolution of Mn ions; (3) combination of VO and GO wrapping can retard the Zn$_x$Mn$_2$O$_4$ accumulation and regulate the structural evolution.

4 Conclusions

In this work, the concurrent application of both defect engineering and interfacial optimization to a manganese oxide electrode for AZIBs is for the first time demonstrated. Oxygen vacancies are spontaneously introduced into β-MnO$_2$ during its synthesis in the presence of GO that eventually builds a coating layer on the active material. For the as-prepared oxygen-deficient β-MnO$_2$@GO cathode, the successful suppression of Mn dissolution during electrochemical cycling is made possible, along with an apparent enhancement in charge/discharge kinetics. This electrode delivers a capacity of ~129.6 mAh g$^{-1}$ even after 2000 cycles at a current rate of 4C, which is much superior than that of pristine β-MnO$_2$ electrode. The excellent cycle stability is rooted in the strong binding between the surface VO and ether oxygen on GO, as well as the regulated structural evolution into the nanocrystalline Zn$_x$Mn$_2$O$_4$ phase. The results in this work highlight the advantages of integrating multiple strategies in the design of AZIB electrodes via bottom-up synthetic approaches, which will cast light on the feasibility of AZIBs in meeting the high-rate and long-life requirements for large-scale energy storage applications.

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References

1. G. Fang, J. Zhou, S. Liang et al., Recent advances in aqueous zinc-ion batteries. ACS Energy Lett. 3(10), 2480–2501 (2018). https://doi.org/10.1021/acsenergylett.8b01426
2. L. Blanc, D. Kundu, L. Nazar, Scientific challenges for the implementation of Zn-ion batteries. Joule 4, 1–29 (2020). https://doi.org/10.1016/j.joule.2020.03.002
3. C. Xu, B. Li, H. Du, F. Kang, Energetic zinc ion chemistry: the rechargeable zinc ion battery. Angew. Chem. Int. Ed. 51(4), 933–935 (2012). https://doi.org/10.1002/anie.201106307
4. D. Kundu, B. Dams, V. Duffort, S. Vajargah, L. Nazar, A high-capacity and long-life aqueous rechargeable zinc battery using a metal oxide intercalation cathode. Nat. Energy 1(10), 16119 (2016). https://doi.org/10.1038/ENERGY.2016.119
12. N. Zhang, F. Cheng, Y. Liu, Q. Zhao, K. Lei et al., Activating C-coordinated iron of iron hexacyanoferrate for Zn hybrid-ion batteries with 10000-cycle lifespan and superior rate capability. Adv. Mater. 31(32), 1901521 (2019). https://doi.org/10.1002/adma.201901521

13. J. Huang, Z. Wang, M. Hou, X. Dong, Y. Liu et al., Poly-aniline-intercalated manganese dioxide nanolayers as a high-energy-density and high power density cathode material for aqueous rechargeable zinc-ion batteries. Nat. Commun. 8(1), 405 (2016). https://doi.org/10.1038/s41467-016-00467-x

14. N. Zhang, F. Cheng, Y. Liu, Q. Zhao, K. Lei et al., Cation-deficient spinel ZnMn₂O₄ cathode in Zn(CF₃SO₃)₂ electrolyte for rechargeable aqueous Zn-ion battery. J. Am. Chem. Soc. 138(39), 12894–12901 (2016). https://doi.org/10.1021/jacs.6b05958

15. T. Xiong, Z. Yu, H. Wu, Y. Du, Q.J. Chen et al., Defect engineering of oxygen-deficient manganese oxide to achieve high-performing aqueous zinc ion battery. Adv. Energy Mater. 9(14), 1803815 (2019). https://doi.org/10.1002/aenm.201803815

16. T. Xiong, Z. Yu, H. Wu, Y. Du, Q.J. Chen et al., Defect engineering of oxygen-deficient manganese oxide to achieve high-performing aqueous zinc ion battery. Adv. Energy Mater. 9(14), 1803815 (2019). https://doi.org/10.1002/aenm.201803815

17. Y. Tian, X. Liu, L. Xu, D. Yuan, Y. Dou et al., Engineering crystallinity and oxygen vacancies of Co(II) oxide nanosheets for high performance and robust rechargeable Zn-air batteries. Adv. Funct. Mater. 31, 2101239 (2021). https://doi.org/10.1002/adfm.202101239
rechargeable aqueous Zn-MnO$_2$ battery. ACS Appl. Mater. Interfaces 12(32), 36072–36081 (2020). https://doi.org/10.1021/acsami.0c08579

31. J. Huang, X. Tang, K. Liu, G. Fang, Z. He et al., Interfacial chemical binding and improved kinetics assisting stable aqueous Zn–MnO$_2$ batteries. Mater. Today Energy 17, 100475 (2020). https://doi.org/10.1016/j.mtene.2020.100475

32. W. Chen, X. Feng, J. Chen, L. Yan, Power-output reduction of graphene oxide and a MnO$_2$-free Zn/GO primary cell. RSC Adv. 4(80), 42418–42423 (2014). https://doi.org/10.1016/j.c4ra.06354f

33. Y. Zhang, S. Deng, G. Pan, H. Zhang, B. Liu et al., Introducing oxygen defects into phosphate ions intercalated manganese dioxide. Small Methods 4(6), 1900828 (2020). https://doi.org/10.1002/smdt.201900828

34. M. Long, Y. Qin, C. Chen, X. Guo, B. Tan et al., Origin of visible light photoactivity of reduced graphene oxide/TiO$_2$ by in situ hydrothermal growth of undergrown TiO$_2$ with graphene oxide. J. Phys. Chem. C 117(23), 16734–16741 (2013). https://doi.org/10.1021/jp4058109

35. M. Sun, X. Dong, B. Lei, J. Li, P. Chen et al., Graphene oxide mediated Co-generation of C-doping and oxygen defects in Bi$_2$WO$_6$ nanosheets: a combined DRIFTS and DFT investigation. Nanoscale 11, 20562 (2019). https://doi.org/10.1039/C9NR06874K

36. M. Zhu, Y. Cai, S. Liu, M. Fang, X. Tan et al., K$_2$Ti$_6$O$_{13}$ hybridized graphene oxide: effective enhancement in photodegradation of RhB and photoreduction of U(VI). Environ. Pollut. 248, 448–455 (2019). https://doi.org/10.1016/j.envpol.2019.02.025

37. X. Lei, X. Li, Z. Ruan, T. Zhang, F. Pan et al., Adsorption–photocatalytic degradation of dye pollutant in water by graphite oxide grafted titanate nanotubes. J. Mol. Liq. 266, 122–131 (2018). https://doi.org/10.1016/j.molliq.2018.06.053

38. M. Liu, Q. Zhao, H. Liu, J. Yang, X. Chen et al., Tuning phase evolution of β-MnO$_2$ during microwave hydrothermal synthesis for high-performance aqueous Zn ion battery. Nano Energy 64, 103942 (2019). https://doi.org/10.1016/j.nanoen.2019.103942

39. Q. Zhao, X. Chen, Z. Wang, L. Yang, R. Qin et al., Unravelling H$^+$/Zn$^{2+}$ synergistic intercalation in a novel phase of manganese oxide for high-performance aqueous rechargeable battery. Small 15, 1904545 (2019). https://doi.org/10.1002/smll.201904545

40. N. Li, G. Li, C. Li, H. Yang, G. Qin et al., Bi-cation electrolyte for a 1.7 V aqueous Zn ion battery. ACS Appl. Mater. Interfaces 12(12), 13790–13796 (2020). https://doi.org/10.1021/acsami.9b20531

41. H. Pan, Y. Shao, Y. Chen, K. Han, Z. Nie et al., Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. Nat. Energy 1(5), 16039 (2016). https://doi.org/10.1038/ENERGY.2016.39

42. M. Chamoun, W. Brant, C. Tai, D. Noréus et al., Rechargeability of aqueous sulfate Zn/MnO$_2$ batteries enhanced by accessible Mn$^{2+}$ ions. Energy Storage Mater. 15, 351–360 (2018). https://doi.org/10.1016/j.ensm.2018.06.019