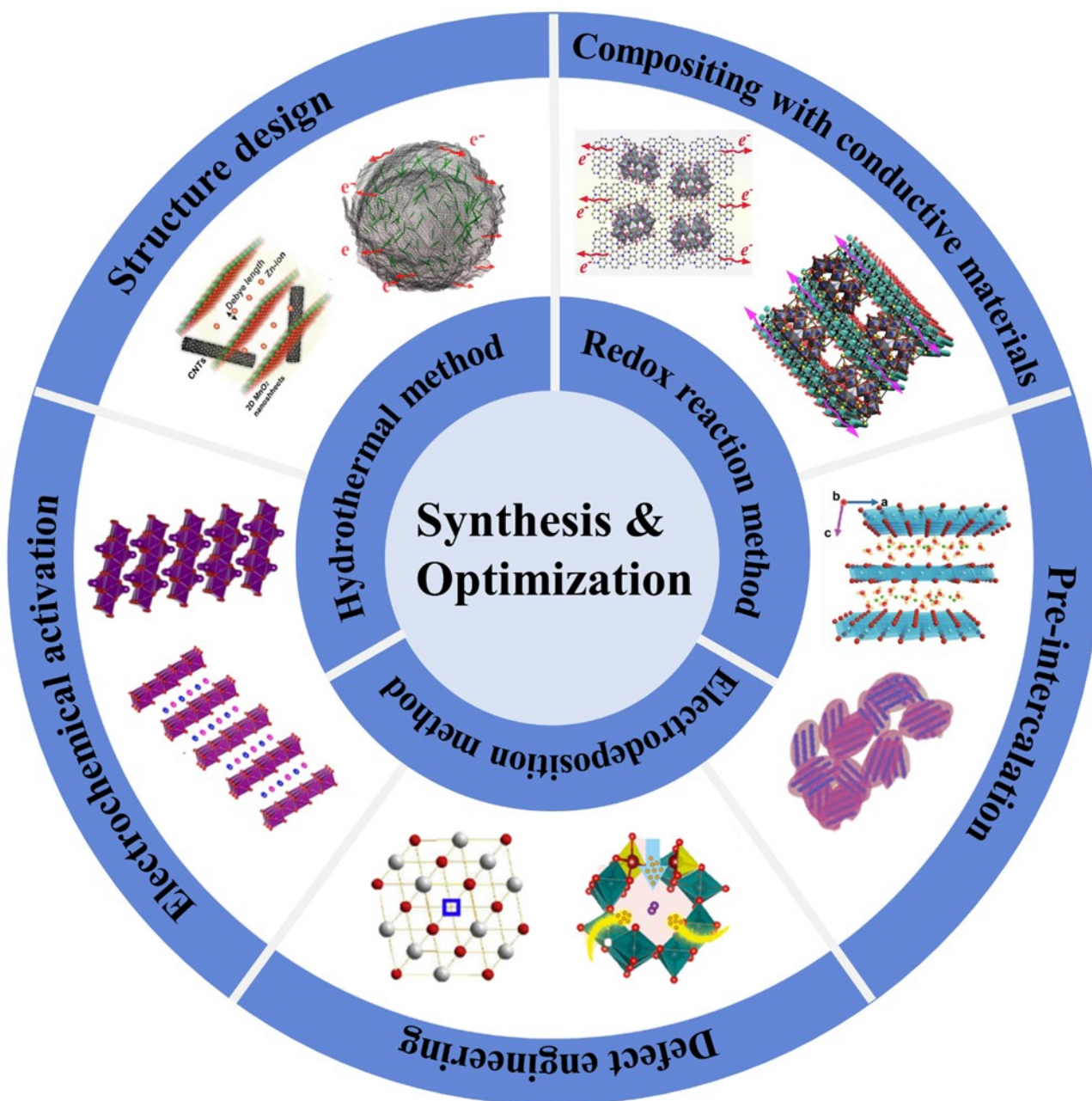


# Synthesis and Performance Optimization of Manganese-based Cathode Materials for Zinc-Ion Batteries

Song Wang,<sup>[a]</sup> Zhiyuan Sang,<sup>\*[a]</sup> Xinqi Zhao,<sup>[a]</sup> Jingdong Guo,<sup>[a]</sup> Hao Chen,<sup>[a]</sup> and De'an Yang<sup>\*[a]</sup>



Owing to the low cost, high specific capacity and high safety, zinc-ion batteries (ZIBs) have great advantages in replacing lithium-ion batteries to meet future demand for energy storage. Manganese-based cathode materials, benefiting from the abundant reserves, non-toxic, acceptable capacity and long cycle stability, have been widely developed and applied to develop high performance ZIBs. Unfortunately, poor conductivity,  $\text{Mn}^{2+}$  dissolution and unstable structure hinder it to achieve an ideal electrochemical performance. Thus, an overview of the cathodic performance optimization strategies and the synthesis

is provided. Firstly, the synthesis methods and their influence on the morphology and structure are summarized. Secondly, various strategies of performance optimization, including structure design, compositing with conductive materials, pre-intercalation, defect engineering and electrochemical activation, are categorized and analyzed in detail. Lastly, perspectives on the subsequent performance optimization are proposed. It is expected that this review will be beneficial to future scientific research on tailoring manganese-based cathode materials for ZIBs.

## 1. Introduction

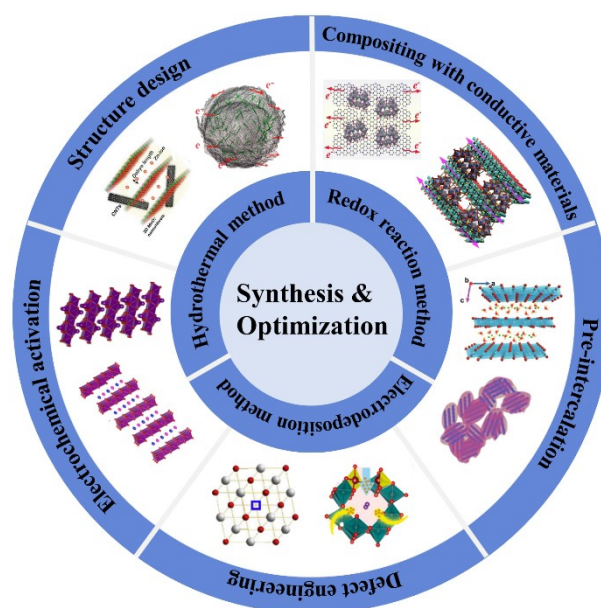
With the continuous consumption of fossil energy and the intensification of environmental pollution problems, the development of clean, renewable and sustainable energy (such as wind energy, solar energy) is imperative.<sup>[1–3]</sup> In order to solve the problems of intermittent and instability of sustainable energy, various energy storage systems have been developed and utilized. Among them, rechargeable batteries with the advantages of low cost, long cycle life, high efficiency and environmental friendliness are considered to be the most feasible options,<sup>[4–6]</sup> including lithium-ion battery,<sup>[7–10]</sup> sodium-ion battery,<sup>[11–14]</sup> potassium-ion battery,<sup>[15–18]</sup> lithium-air battery,<sup>[19–22]</sup> and so on.

However, the shortage of metal resources has greatly increased the cost of batteries, and the side reactions of organic electrolytes and their flammable and explosive characteristics have increased the safety risks.<sup>[23–26]</sup> In recent years, zinc-ion batteries (ZIBs) are expected to be their substitute, due to the following advantages.<sup>[27–31]</sup> (1) Abundant storage of zinc in nature, which greatly reduces the cost of ZIBs. (2) Safety and stability, (3) high theoretical capacity of metal zinc ( $820 \text{ mAh g}^{-1}$  or  $5854 \text{ mAh cm}^{-3}$ ) and energy density, (4) low redox potential of zinc ( $-0.763 \text{ V}$  vs. a standard hydrogen electrode [SHE]), which allows the batteries to work in aqueous electrolytes. Therefore, it is crucial for high-performance cathode materials to match the zinc anode of ZIBs.<sup>[27,30,32–35]</sup>

Commonly, the cathode materials are focused on manganese-based compounds, vanadium-based compounds,<sup>[36–40]</sup> prussian blue analogue,<sup>[41–43]</sup> organic materials,<sup>[44–47]</sup> etc. Due to high theoretical specific capacity ( $\sim 308 \text{ mAh g}^{-1}$ ) and working voltage ( $\sim 1.4 \text{ V}$ ), manganese-based cathode materials deliver great competitiveness in the cathode materials of ZIBs. There are still controversies about the energy storage mechanism of manganese-based cathode materials, mainly including:  $\text{Zn}^{2+}$  insertion/extraction,  $\text{H}^+/\text{Zn}^{2+}$  co-insertion/extraction, chemical conversion reaction, and so on.<sup>[34,35]</sup> Unfortunately, many challenges still exist in obtaining high-performance manga-

nese-based cathode materials for ZIBs, as follows: (1) Poor conductivity: it leads to the slow electron transfer kinetics, thus limiting the rate performance of manganese-based cathode. (2) Unstable structure: they suffer from structural damage and large volume change during the repetitive insertion/extraction of ions. (3)  $\text{Mn}^{2+}$  dissolution:  $\text{Mn}^{2+}$  can be dissolved in aqueous electrolyte, which may cause the collapse of host structure, thus lead to a capacity fading. These disadvantages seriously affect the actual specific capacity, rate performance and cycle performance.<sup>[32–34,48]</sup>

In this review, we focus on the strategies of performance optimization as well including the synthesis methods of manganese-based cathode materials. First, the synthesis methods and their relationship among the preparation-structure-performance are summarized. Second, various strategies of performance optimization are categorized by dividing into five parts: structure design, compositing with conductive materials, pre-intercalation, defect engineering and electrochemical activation (Figure 1). Finally, we make conclusions and perspectives on obtaining high-performance manganese-based cathode



**Figure 1.** Synthesis methods and strategies of performance optimization for manganese-based cathode materials in ZIBs.

[a] S. Wang, Dr. Z. Sang, X. Zhao, J. Guo, H. Chen, Prof. Dr. D'a. Yang  
School of Materials Science and Engineering  
Tianjin University  
Tianjin, China  
E-mail: sangzhiyuan@tju.edu.cn  
dayang@tju.edu.cn

materials. On the whole, we hope this review could shed light on the future scientific research on ZIBs.

## 2. Synthesis of Manganese-based Cathode Materials

For the manganese-based cathode materials, the synthesis methods and synthesis conditions often play a critical role on determining the morphology, structure, and then affect the electrochemical performances. Up to now, several different strategies have been developed to prepare manganese-based cathode materials of ZIBs with various sizes, morphologies (particles, rods, sheets, flowers, etc.), and structures (porous, hollow, etc.), mainly including hydrothermal method, other redox reaction method, electrodeposition method, etc.

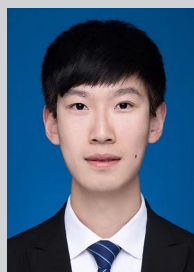
### 2.1. Redox Reaction Method

#### 2.1.1. Hydrothermal Method

Owing to the different connected ways of the basic structural unit  $[\text{MnO}_6]$  octahedra, the  $\text{MnO}_2$  possesses various crystal structure, including  $\alpha$ ,  $\beta$ ,  $\lambda$ ,  $\delta$ ,  $\gamma$ , R and todorokite-type (Figure 2a).<sup>[49]</sup> Among them,  $\alpha$ - $\text{MnO}_2$  has large  $[2 \times 2]$  tunnels of  $\sim 4.6$  Å for accommodating  $\text{Zn}^{2+}$  insertion without structural collapse,  $\beta$ - $\text{MnO}_2$  exhibits a better cycling stability benefiting

from the 3D tunnel structures, and  $\delta$ - $\text{MnO}_2$  with a typical layered structure delivers a layer spacing of 7 Å for ion diffusion. Notably, hydrothermal method is a feasible strategy for the controlled synthesis of different crystal forms of  $\text{MnO}_2$ .

Alfaruqi et al. synthesized highly crystalline  $\alpha$ - $\text{MnO}_2$  nano-rods by reducing  $\text{KMnO}_4$  with  $\text{H}_2\text{SO}_4$  at  $140^\circ\text{C}$  for 8 h.<sup>[50]</sup> The  $[2 \times 2]$  tunnels of the  $\alpha$ - $\text{MnO}_2$  structure could withstand the expansion/contraction caused by repeated insertion/extraction of  $\text{Zn}^{2+}$  (Figure 2b). Similarly, Zhao et al. synthesized  $\alpha$ - $\text{MnO}_2$  through the hydrothermal method, and demonstrated the promoting mechanism of Grotthuss proton transport in  $[2 \times 2]$  tunnels of  $\alpha$ - $\text{MnO}_2$ .<sup>[51]</sup> The O ion on the wall of  $[2 \times 2]$  tunnels accepts two  $\text{H}^+$  after the facile transfer of  $\text{H}^+$  via hydrogen bonds. The energy barrier of this Grotthuss proton transport mechanism is significantly lower than that of direct hopping mechanism, which could accelerate the  $\text{H}^+$  diffusion in the tunnels of  $\alpha$ - $\text{MnO}_2$ . (Figure 2c) Therefore, the  $\alpha$ - $\text{MnO}_2$  prepared by hydrothermal method with a typical  $[2 \times 2]$  tunnel structure, shows the fast ion diffusion, and then exhibits an excellent rate performance. Zhang et al. prepared  $\beta$ - $\text{MnO}_2$  through a simple hydrothermal reaction at  $140^\circ\text{C}$  for 12 h.<sup>[52]</sup> In initial discharge, the  $\beta$ - $\text{MnO}_2$  transforms into the  $\text{Zn}_x\text{MnO}_2 \cdot n\text{H}_2\text{O}$  with a layered structure for  $\text{Zn}^{2+}$  insertion/extraction (Figure 2d), and the  $\text{Zn}/\beta$ - $\text{MnO}_2$  battery shows a long-term cycling stability with 94% capacity retention over 2000 cycles at a high current density of 6.5 C (Figure 2e). Liao et al. synthesized  $\beta$ - $\text{MnO}_2$  with a preferred crystal orientation through the hydrothermal reaction between  $\text{MnSO}_4$  and APS at  $140^\circ\text{C}$  for 8 h, which delivers an enhanced electrochemical performance.<sup>[53]</sup> In addition, Guo



Song Wang received his bachelor's degree in the Department of Materials Science and Engineering, Tianjin University in 2019. He is currently a M.D candidate in the Department of Materials Science and Engineering at Tianjin University. His research focuses on the cathode materials of zinc-ion battery.



Zhiyuan Sang received his Ph.D. degree from the School of Materials Science and Engineering in Tianjin University in 2020, and then worked as an assistant research fellow. His research focuses on nanomaterials for energy storage and conversion, including metal-ion batteries and electrocatalysis.



Xinqi Zhao is currently a Ph.D candidate in the Department of Materials Science and Engineering at Tianjin University. She received her bachelor's degree in Chemical Materials and Engineering from Guizhou University in 2018. Her research focuses on development of functional materials for high performance zinc-ion batteries and lithium-sulfur batteries.



Jingdong Guo is currently pursuing his Ph.D. degree in the Department of Materials Science and Engineering at Tianjin University. He received his bachelor's degree in the Department of Materials Science and Engineering at University of Jinan in 2015. His research focuses on development of vanadium based oxide for high performance zinc-ion battery.

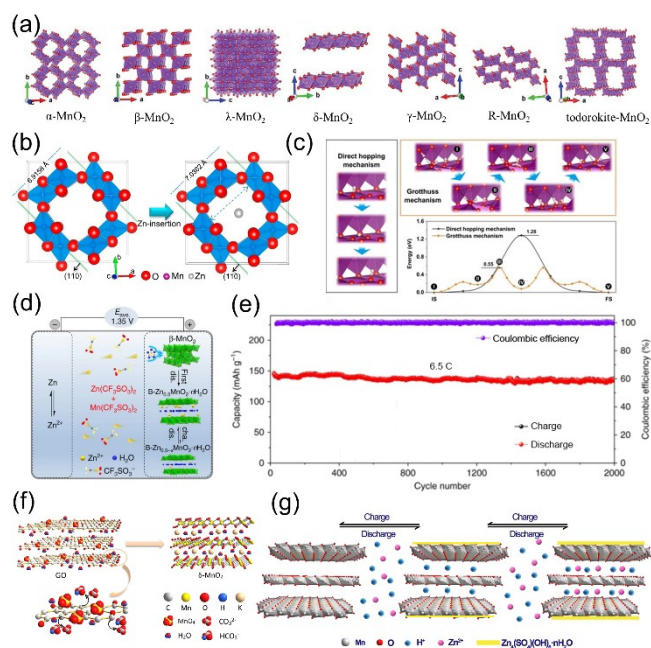


Hao Chen is currently a M.D candidate in the Department of Materials Science and Engineering at Tianjin University. He received his bachelor's degree in the Department of Materials Science and Engineering at Tianjin University in 2020. His research focuses on development of functional materials for high performance zinc-ion battery.



De'an Yang received his Ph.D. degree under the supervision of Prof. Tingxian Xu at School of Materials Science and Engineering, Tianjin University. He is currently a Prof. at Tianjin University. His research focuses on functional ceramics.



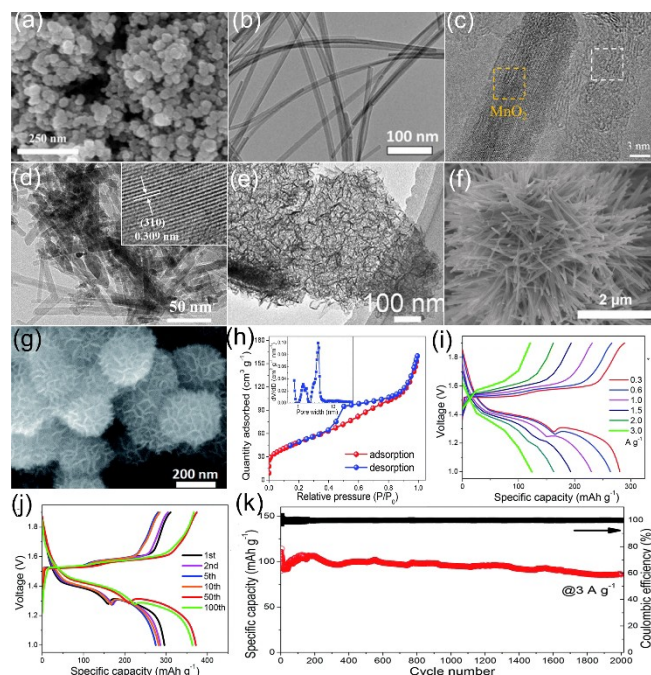


**Figure 2.** a) Various crystal structures of  $\text{MnO}_2$ . Adapted with permission from Ref. [49]. Copyright (2019) Royal Society of Chemistry. b) Schematic illustration of  $\text{Zn}^{2+}$  insertion into the tunnel of  $\alpha\text{-MnO}_2$ . Adapted with permission from Ref. [50]. Copyright (2015) Elsevier S. A. c)  $\text{H}^+$  ion migration pathway and corresponding energy barriers of direct hopping mechanism and Grotthuss proton transport mechanism in  $[2 \times 2]$  tunnels of  $\alpha\text{-MnO}_2$ . Adapted with permission from Ref. [51]. Copyright (2020) Wiley-VCH. d) Schematic illustration of  $\text{Zn}/\beta\text{-MnO}_2$  battery. e) Cycle performance of  $\text{Zn}/\beta\text{-MnO}_2$  battery. Adapted with permission from Ref. [52]. Copyright (2017) Springer Nature. f) Illustration of the formation of  $\delta\text{-MnO}_2$ . g) Schematic illustration of charge-discharge process with ions insertion/extraction. Adapted with permission from Ref. [54]. Copyright (2019) Elsevier.

et al. prepared ultrathin  $\delta\text{-MnO}_2$  nanosheets using graphene oxide (GO) as the reductant and self-sacrificing template (Figure 2f).<sup>[54]</sup> The stable layered structure could allow the  $\text{H}^+$  and  $\text{Zn}^{2+}$  co-insertion/extraction (Figure 2g), which makes an explanation for the discharge capacity of  $133 \text{ mAh g}^{-1}$  after 100 cycles at  $0.1 \text{ A g}^{-1}$ . Recently, we also synthesized  $\delta\text{-MnO}_2$  through the direct hydrothermal of  $\text{KMnO}_4$  at  $160^\circ\text{C}$  for 12 h.<sup>[55]</sup>

$\alpha$ ,  $\beta$ ,  $\delta\text{-MnO}_2$  with the typical tunnel structure or layered structure are the main form of  $\text{MnO}_2$ -based cathode in ZIBs. In contrast, limited by the specific capacity, there are fewer reports of other crystal types, such as  $\lambda\text{-MnO}_2$ ,<sup>[56]</sup>  $\gamma\text{-MnO}_2$ ,<sup>[57]</sup> etc. In short, diverse crystal types lead to the differences in electrochemical performance and energy storage mechanism. Hydrothermal method can synthesize different crystal forms of  $\text{MnO}_2$  by adjusting specific parameters, which provides a reference for the preparation of  $\text{MnO}_2$  with the specific crystal forms.

In addition, hydrothermal method has been widely used to synthesize nano-sized materials with various sizes and different morphologies. Figure 3(a–g) lists the different morphologies of  $\text{MnO}_2$ , including nanoparticles,<sup>[58]</sup> nanowires,<sup>[59]</sup> nanorods,<sup>[60]</sup> nanofibers,<sup>[61]</sup> nanoflakes,<sup>[62]</sup> urchin-like microspheres with nanorods,<sup>[63]</sup> and nanospheres,<sup>[64]</sup> which were prepared through hydrothermal methods by changing the synthesis parameters (raw materials, temperature, time, etc.). First, these nano-sized



**Figure 3.** Different morphologies of  $\text{MnO}_2$ : a) nanoparticles. Adapted with permission from Ref. [58]. Copyright (2017) Elsevier. b) Nanowires. Adapted with permission from Ref. [59]. Copyright (2020) American Chemical Society. c) Nanorods. Adapted with permission from Ref. [60]. Copyright (2020) Elsevier. d) Nanofibers. Adapted with permission from Ref. [61]. Copyright (2019) Elsevier. e) Nanoflakes. Adapted with permission from Ref. [62]. Copyright (2020) Elsevier. f) Urchin-like microspheres with nanorods. Adapted with permission from Ref. [63]. Copyright (2020) Springer. g) Nanospheres. h) Nitrogen adsorption-desorption isotherms and pore-size distributions (inset) of the  $\text{MnO}_2$  nanospheres. i) GCD curves at different current densities of  $0.3$  to  $3.0 \text{ A g}^{-1}$ . j) GCD curves of different cycles at  $0.3 \text{ A g}^{-1}$ . k) Cycle performance at  $3 \text{ A g}^{-1}$  of  $\text{MnO}_2$  nanospheres cathode. Adapted with permission from Ref. [64]. Copyright (2019) Royal Society of Chemistry.

and porous structures greatly provide sufficient active sites for energy storage. Second, these structures shorten the ion/electron transmission path, accelerating the kinetics process. Finally, they provide the enough room to tailor the volume changes during the repeated  $\text{Zn}^{2+}$  insertion/extraction, ensuring the stability of the structures. For instance, the  $\text{MnO}_2$  nanospheres deliver a large specific surface area ( $178 \text{ m}^2 \text{ g}^{-1}$ ) and a total pore volume of  $0.25 \text{ cm}^3 \text{ g}^{-1}$  (Figure 3h).<sup>[64]</sup> Therefore, the battery achieves a high reversible capacity of  $275 \text{ mAh g}^{-1}$  at  $0.3 \text{ A g}^{-1}$ , a high retained capacity of  $121 \text{ mAh g}^{-1}$  at  $3 \text{ A g}^{-1}$  (Figure 3i), and an excellent cycle stability at the current density of  $0.3$  and  $3 \text{ A g}^{-1}$  (Figure 3k).

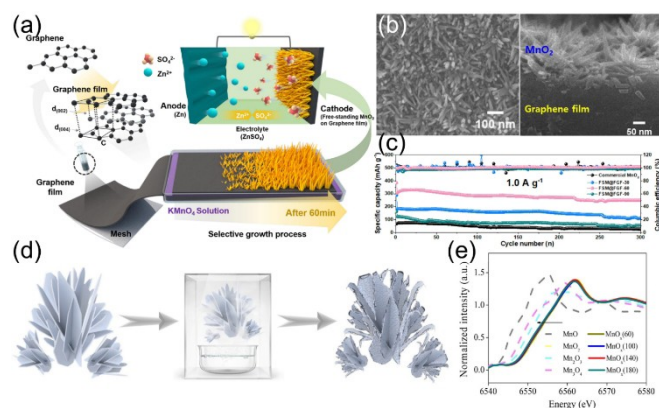
Besides  $\text{MnO}_2$ , hydrothermal method is also a convenient way to synthesize other manganese-based compounds, including  $\text{MnO}$ ,<sup>[65]</sup>  $\text{Mn}_3\text{O}_4$ ,<sup>[66,67]</sup>  $\text{ZnMn}_2\text{O}_4$ ,<sup>[68,69]</sup> etc. For instance, Zhu et al. putted  $\text{KMnO}_4$  in the hydrothermal reaction at  $140^\circ\text{C}$  to synthesize  $\text{Mn}_3\text{O}_4$ .<sup>[66]</sup> Reaction time of 24 h leads to a compact and uniform  $\text{Mn}_3\text{O}_4$  nanoflowers composed of ultrathin nanosheets. And the  $\text{Mn}_3\text{O}_4$  cathode delivers a high specific capacity of  $296 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  and there is no capacity fading after 500 cycles at  $0.5 \text{ A g}^{-1}$ .

In summary, hydrothermal synthesis is an efficient method to prepare various manganese-based nanocomposites with different sizes, morphologies and crystal structure. And the nano-sized manganese-based cathode materials share the advantages of fast transfer of ions and electrons as well as the sufficient contact area with the electrolyte, which will greatly improve the electrochemical performance in ZIBs.

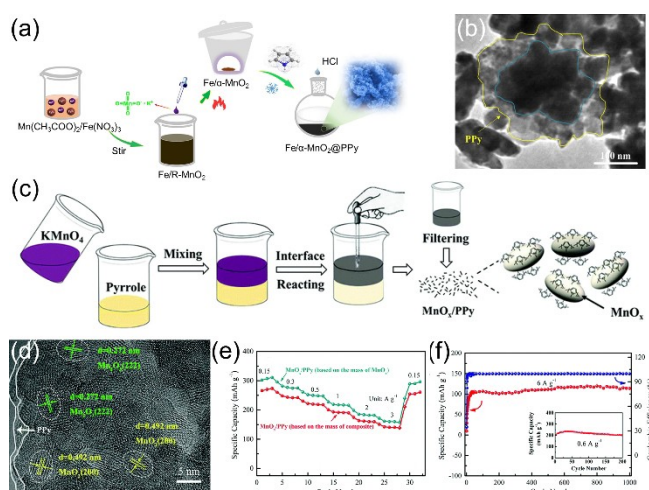
### 2.1.2. Other Redox Reaction Method

Manganese itself has different valence states ( $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ , and  $\text{Mn}^{7+}$ ), which provides the possibility of preparing different manganese-based compounds by redox reaction. As shown in Figure 4(a), Lee et al. used the reduction reaction of  $\text{KMnO}_4$  to grow  $\text{MnO}_2$  on the surface of flexible graphene film (FSM@FGF).<sup>[70]</sup> After reacting at  $80^\circ\text{C}$  for 60 min, the  $\text{MnO}_2$  needles with the size of 101.3–118.1 nm are well anchored on the FGF surface (Figure 4b). The free-standing FSM@FGF-60 cathode delivers the fast  $\text{Zn}^{2+}$  diffusion and electron transfer, leading to a high capacity of  $301.0 \text{ mAh g}^{-1}$  at  $1 \text{ A g}^{-1}$  and a capacity retention of 82.7% after 300 cycles (Figure 4c). As shown in Figure 4(d), Zang et al. prepared  $\text{MnO}_x$  by limitedly reducing  $\text{MnO}_2$  with hydrazine vapor.<sup>[71]</sup> The valence state of Mn decreases with the increase of the amount of hydrazine hydrate (Figure 4e). Compared to  $\text{MnO}_2$ ,  $\text{MnO}_x$  with a lower valence state of Mn shows the more rapid transfer of charges and the superior structural stability. Unlike this, Lu et al. directly synthesized  $\text{MnO}_2$  nanosheets through the redox process of  $\text{Mn}^{2+}$  using hydrogen peroxide as the oxidizing agent.<sup>[72]</sup> The  $\text{MnO}_2$  nanosheets have a typical layered structure with a lot of wrinkles, which provide a large number of active sites for  $\text{Zn}^{2+}$  insertion.

Additionally, redox reaction method is also helpful for synthesizing transition metals-doped  $\text{MnO}_2$  samples. Xu et al. added  $\text{KMnO}_4$  to the mixed solution of  $\text{Mn}(\text{CH}_3\text{COO})_2$  and  $\text{Fe}(\text{NO}_3)_3$  to obtain Fe-doped  $\text{MnO}_2$  (Figure 5a).<sup>[73]</sup> The process is achieved by stirring and annealing, and the prepared Fe-doped



**Figure 4.** a) Schematic diagram of the synthesis of FSM@FGF, b) SEM of FSM@FGF-60, c) cycle performance of FSM@FGF at  $1.0 \text{ A g}^{-1}$ . Adapted with permission from Ref. [70]. Copyright (2021) Elsevier. d) Schematic reaction of synthesizing  $\text{MnO}_x$ , e) Mn K-edge XANES spectra of  $\text{MnO}_x$ . Adapted with permission from Ref. [71]. Copyright (2021) Elsevier.



**Figure 5.** a) Preparation schematic diagram of Fe/ $\alpha$ - $\text{MnO}_2$ @PPy, b) TEM images of Fe/ $\alpha$ - $\text{MnO}_2$ @PPy. Adapted with permission from Ref. [73]. Copyright (2021) Elsevier. c) Schematic illustration of  $\text{MnO}_x$ @PPy, d) SEM image of  $\text{MnO}_x$ @PPy, e) rate performance and f) cycle performance of  $\text{MnO}_x$ @PPy. Adapted with permission from Ref. [76]. Copyright (2020) Royal Society of Chemistry.

$\text{MnO}_2$  presents the morphology of nanoparticles without other impurities (Figure 5b). Similarly, Alfuruqi et al. prepared V-doped  $\text{MnO}_2$  spheres by introducing  $\text{V}_2\text{O}_5$  into the precursor solution of  $\text{KMnO}_4$  and  $\text{Mn}(\text{CH}_3\text{COO})_2$ .<sup>[74]</sup> The entire synthesis process is carried out at ambient temperature.

Also, redox reaction method has the unique advantages in the preparation of manganese-based composite materials.<sup>[75]</sup> Li et al. synthesized  $\text{MnO}_x$ @PPy composites through organic/inorganic interface redox reaction using pyrrole and  $\text{KMnO}_4$  as the precursor (Figure 5c).<sup>[76]</sup> The chemical polymerization of pyrrole and the reduction of  $\text{MnO}_4^-$  occurred simultaneously, facilitating the formation of  $\text{MnO}_x$ @PPy. As shown in Figure 5(d), the synthesized  $\text{MnO}_x$  nanoparticles possessed a typical size of 11 nm covered by PPy nanolayers. The cathode suggests a high specific capacity of  $159.9 \text{ mAh g}^{-1}$  (based on the mass of  $\text{MnO}_x$ ) at  $3 \text{ A g}^{-1}$  (Figure 5e) and remains a capacity of  $113.7 \text{ mAh g}^{-1}$  after 1000 cycles at an extremely high current density of  $6 \text{ A g}^{-1}$  (Figure 5f).

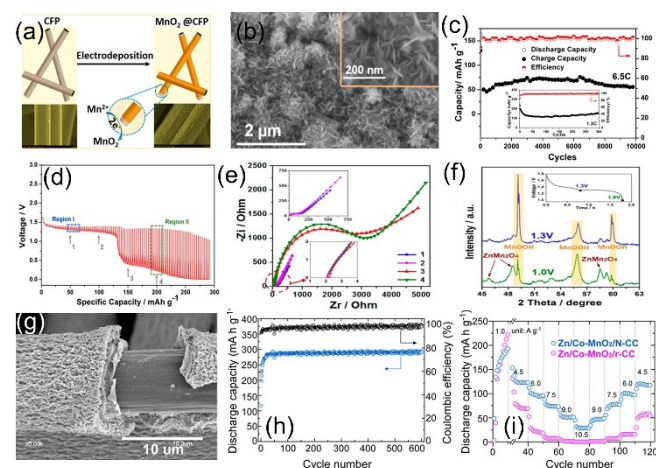
### 2.2. Electrodeposition Method

Electrodeposition works by depositing solvated ionic species onto a conductive substrate by applying an external potential or current. This method has the following characteristics: (1) Excellent conductivity: The conductive substrates are carbon materials in most cases, which can effectively improve the overall conductivity of cathode materials. (2) Porous structure: The interconnected nanostructures of manganese-based compounds form a highly porous structure. (3) Self-supporting (binder-free): The manganese-based compounds can be deposited on the conductive substrates, which is directly used as the cathode without any additives (such as binder).



In ZIBs, electrodeposited manganese-based compounds have a nanocrystalline structure, usually in the form of interconnected nanosheets.<sup>[30,77]</sup> Sun et al. deposited  $\text{MnO}_2$  on the surface of the carbon fiber paper (CFP) through a potential-static method (Figure 6a).<sup>[78]</sup> The  $\text{MnO}_2$  is composed of the interconnected nanoflakes and forms a highly porous structure (Figure 6b). On the one hand,  $\text{MnO}_2$  nanoflakes provide abundant electrode/electrolyte contact interfaces and active sites for energy storage. On the other hand, the morphology of nanoflakes reduces the ions diffusion path and the porous structure allow the volume changes during ions insertion/extraction. As a result, the battery displays a specific discharge capacity of  $260 \text{ mAh g}^{-1}$  at  $1.3 \text{ C}$  and an excellent cycle stability over 10000 cycles at  $6.5 \text{ C}$  (Figure 6c). And the reaction mechanism of  $\text{H}^+$  and  $\text{Zn}^{2+}$  co-insertion/extraction is investigated by galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS). Specifically, due to the much smaller size of  $\text{H}^+$  and  $\text{Zn}^{2+}$ , the insertion of  $\text{Zn}^{2+}$  happens after the  $\text{H}^+$ -insertion. (Figure 6d, e) The ex-situ XRD patterns at different states also confirm this. (Figure 6f) Notably,  $\text{MnO}_2$  prepared by electrodeposition method is mostly the delta phase, which delivers the typical  $\text{H}^+$  and  $\text{Zn}^{2+}$  co-insertion/extraction and shows a fast reaction kinetics

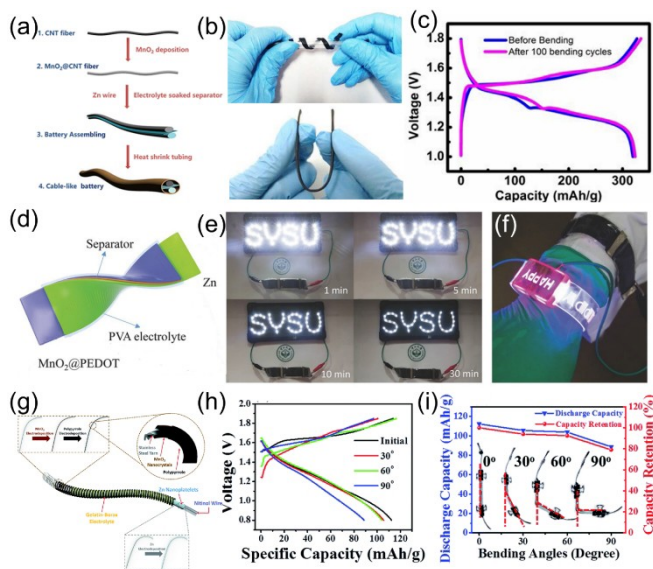
Electrodeposition method is also a simple method to obtain the metals-doped manganese-based cathode materials. Kataoka et al. added  $\text{CoSO}_4$  to the electrolyte to prepare cobalt-doped layered  $\text{MnO}_2$ .<sup>[79]</sup> Affected by cobalt doping, Co- $\text{MnO}_2$  shows a pleated morphology, suggesting an increased surface area (Figure 6g). Benefiting from N-doped carbon cloth substrate and Co-doped  $\text{MnO}_2$ , the Zn/Co- $\text{MnO}_2$ /N-CC generates a discharge capacity of  $280 \text{ mAh g}^{-1}$  at  $1.2 \text{ Ag}^{-1}$  after 600 cycles and a remained capacity of  $30 \text{ mAh g}^{-1}$  at an extremely high current density of  $10.5 \text{ Ag}^{-1}$  (Figure 6h, i). To shorten the



**Figure 6.** a) Schematic illustration of synthesis process  $\text{MnO}_2$ @CFP, b) SEM image of  $\text{MnO}_2$ @CFP, c) cycle performance of  $\text{MnO}_2$ @CFP cathode, d) GITT profiles, e) nyquist plots at different depth of discharge, f) ex-situ XRD patterns at depth of discharge at  $1.3 \text{ V}$  and  $1.0 \text{ V}$  of the  $\text{MnO}_2$ @CFP cathode. Adapted with permission from Ref. [78]. Copyright (2017) American Chemical Society. g) SEM images of Co- $\text{MnO}_2$  films, h) cycle performance and i) rate performance of Zn/Co- $\text{MnO}_2$ /N-CC battery. Adapted with permission from Ref. [79]. Copyright (2020) American Chemical Society.

synthesis time, Dhiman et al. adopted a novel pulse electrodeposition method to prepare  $\text{Mn}_3\text{O}_4$  onto carbon paper at a current of  $4.7 \text{ mA}$  with a  $0.25 \text{ s}$  ON cycle and a  $0.5 \text{ s}$  OFF cycle for a total of 2400 cycles.<sup>[80]</sup> The pulse electrodeposition method exhibits huge advantages on controlling the thickness of the deposited products, thus the obtained  $\text{Mn}_3\text{O}_4$  nanosheets is only  $1\text{--}2 \mu\text{m}$ , greatly shortening the ion/electron transmission path and the battery delivers a discharge capacity of  $143 \text{ mAh g}^{-1}$  at  $2.4 \text{ Ag}^{-1}$ .

In addition, the electrodeposition method commonly adopted to prepare flexible electrodes, which is expected to meet the needs of flexible energy storage devices. Wang et al. prepared a  $\text{MnO}_2$ @CNT fiber-like cathode by electrodeposition method (Figure 7a).<sup>[81]</sup> When it was assembled into a cable-type flexible battery, the battery could be twisted or bent without sacrificing the electrochemical performance, even after 100 bending cycles (Figure 7b, c). Zeng et al. synthesized  $\text{MnO}_2$ @PEDOT cathode through the electrodeposition method and assembled a flexible quasi-solid-state rechargeable Zn- $\text{MnO}_2$  battery (Figure 7d).<sup>[82]</sup> Due to the flexible cathode, the battery could work under the bending conditions (Figure 7e) and be applied to the flexible and wearable electronics (Figure 7f). Wang et al. electrodeposited PPy-coated  $\text{MnO}_2$  onto stainless steel (SS) yarn (Figure 7g),<sup>[83]</sup> and the assembled wire-shaped battery displays the excellent mechanical flexibility, which could be bent to different angles without reducing electrochemical performance (Figure 7h, i).



**Figure 7.** a) Schematic of preparation process of Zn- $\text{MnO}_2$  cable battery, b) flexibility of the Zn- $\text{MnO}_2$  cable battery, c) GCD curves before and after 100 bending cycles. Adapted with permission from Ref. [81]. Copyright (2018) American Chemical Society. d) Schematic illustration of flexible Zn- $\text{MnO}_2$ @PEDOT battery, e) photographs of light-emitting diodes and f) a watch powered by Zn- $\text{MnO}_2$ @PEDOT batteries. Adapted with permission from Ref. [82]. Copyright (2017) Wiley-VCH. g) Schematic diagram of Zn@NT- $\text{MnO}_2$ /PPy@SS wire-shaped battery, h) GCD curves and i) discharge capacity of the bent wire-shaped battery at different angles. Adapted with permission from Ref. [83]. Copyright (2018) Royal Society of Chemistry.

To sum up, different methods will affect the structure (tunnel structure, layered structure, etc.) of manganese-based cathode materials, which in turn affects the ion-transfer mechanism and electrochemical performance. Also, the synthesis methods often play a crucial role on deciding the morphology and structure. Briefly, As a typical redox reaction method, hydrothermal method helps to control the crystal form, morphology, and structure of manganese-based cathode materials. And redox reaction methods are the viable option to achieve the doping. Electrodeposition method has the significant advantages in self-supporting and flexible electrodes. Different methods will affect the structure (tunnel structure, layered structure, etc.) of manganese-based cathode materials, which in turn affects the ion-transfer mechanism and electrochemical performance. Besides the above methods, sol-gel method,<sup>[84]</sup> microemulsion method,<sup>[85,86]</sup> molten salt method,<sup>[87]</sup> thermal decomposition method,<sup>[88]</sup> co-precipitation method,<sup>[89]</sup> etc. have also been reported. These methods provide guidance for the synthesis of high-performance manganese-based cathode materials with different crystal forms, morphologies and structures, which are detailly listed in Table 1.

### 3. Strategies of Performance Optimization

#### 3.1. Structure Design

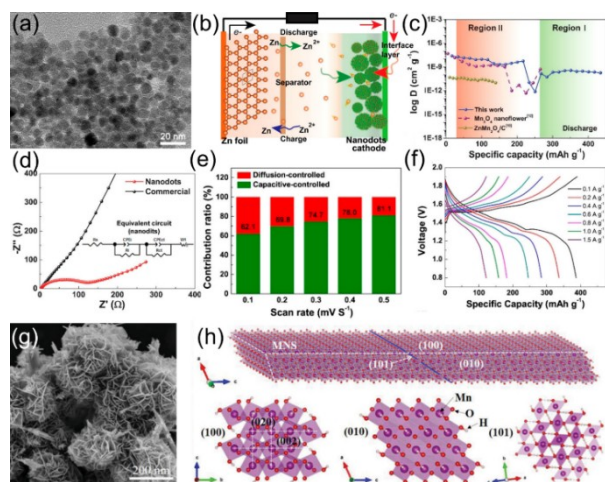
##### 3.1.1. 0D–3D Nanostructure

According to dimensions, manganese-based cathode materials can be divided into four categories: (1) 0D: Nanoparticles; (2) 1D: Nanowires, nanotubes and nanorods; (3) 2D: Nanosheets and nanoplates; (4) 3D: Assembled structures such as nanospheres and nanoflowers. Due to the size effect, nanostructures are preferred in the performance optimization of manganese-based cathode materials. They have the following advantages: (1) High electrode/electrolyte contact area, providing a large number of active sites for energy storage and promoting the ion diffusion at interfaces. (2) Short transmission path for ions and electrons, improving the electrochemical kinetic process. (3) Better adapt to the volume change of ions insertion/extraction, improving the cycle stability.

Benefiting from the large specific surface area and short diffusion distance, nano-structured manganese-based cathode materials often suggest high reversible capacities and excellent rate performances. Jiang et al. prepared the  $\text{Mn}_3\text{O}_4$  nanodots with an average size of 6.0 nm (Figure 8a), through refluxing and solvothermal treatment.<sup>[90]</sup> Due to the size effect of nanodots, when tested as cathode for ZIBs (Figure 8b), the  $\text{Mn}_3\text{O}_4$  cathode possesses a large  $\text{Zn}^{2+}$  diffusion coefficient of  $2.4 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  (Figure 8c) and a rather low charge transfer resistance (Figure 8d). In addition, the capacity contribution

**Table 1.** Synthesis methods of various manganese-based cathode materials.

| Synthesis methods            | Manganese-based cathode material                          | Morphology                         | Size                                   | Capacity [mAh g <sup>-1</sup> ]/current density [A g <sup>-1</sup> ] | Ref. |
|------------------------------|---|------------------------------------|--|--|------|
| hydrothermal method          | $\alpha\text{-MnO}_2$                                     | nanorods                           | 20 nm in width, 200 nm in length       | 233/0.083  | [50] |
| hydrothermal method          | $\beta\text{-MnO}_2$                                      | nanorods                           | 150 nm in diameter                     | 258/0.2  | [52] |
| hydrothermal method          | $\delta\text{-MnO}_2$                                     | nanosheets                         | 2–4 nm in thickness                    | 133/0.1  | [54] |
| hydrothermal method          | $\alpha\text{-MnO}_2\text{@C}$                            | nanoparticles                      | 20 nm in size                          | 272/0.066  | [58] |
| hydrothermal method          | D-MnO <sub>2</sub>  | nanowires                          | 10 nm in diameter                      | 290/0.3  | [59] |
| hydrothermal method          | $\Gamma\text{-MnO}_2\text{@graphene}$                     | nanorods                           | 10–20 nm in diameter                   | 301/0.5  | [60] |
| hydrothermal method          | $\alpha\text{-MnO}_2\text{@CNT}$                          | nanofibers                         | 8 nm in diameter                       | 296/0.2  | [61] |
| hydrothermal method          | N-CNS@MnO <sub>2</sub>                                    | nanoflakes                         | 200–300 nm in thickness                | 303.7/0.2  | [62] |
| hydrothermal method          | $\alpha\text{-MnO}_2$                                     | urchin microspheres with nanowires | 4–10 $\mu\text{m}$ in diameter         | 308/0.1  | [63] |
| hydrothermal method          | $\alpha\text{-MnO}_2$                                     | nanospheres                        | 200 nm in diameter                     | 275/0.3  | [64] |
| other redox reaction method  | FSM@FGF   | needle-shaped particles            | 103.7–110.2 nm in size                 | 440/0.1  | [70] |
| other redox reaction method  | $\text{MnO}_x$  | nanoflowers                        | 150 nm in diameter                     | 487.6/0.2  | [71] |
| other redox reaction method  | $\text{Fe/MnO}_2\text{@PPy}$                              | nanoparticles                      | 30–80 nm in size                       | 270/0.1  | [73] |
| other redox reaction method  | V-doped MnO <sub>2</sub>                                  | spherical particles                | 50 nm in diameter                      | 266/0.066  | [74] |
| other redox reaction method  | $\text{MnO}_x\text{/PPy}$                                 | nanoparticles                      | 11 nm in size                          | 302/0.15   | [76] |
| electrodeposition method     | $\text{MnO}_2\text{@CFP}$                                 | nanoflakes                         | 10 nm in thickness                     | 290/0.1  | [78] |
| electrodeposition method     | Co-doped MnO <sub>2</sub>                                 | thin film                          | –                                      | 288/0.3  | [79] |
| electrodeposition method     | $\text{Mn}_3\text{O}_4$                                   | flake-like islands                 | 1–2 $\mu\text{m}$ in thickness         | 328/0.3  | [80] |
| electrodeposition method     | $\text{MnO}_2\text{@CNT}$                                 | fibers                             | 100–120 $\mu\text{m}$ in length        | 322/0.1  | [81] |
| electrodeposition method     | $\text{MnO}_2\text{@PEDOT}$                               | film                               | –                                      | 366.6/0.74   | [82] |
| electrodeposition method     | PPy coated MnO <sub>2</sub>                               | nanocrystallites                   | 20 nm in crystal size                  | 143.2/0.3  | [83] |
| sol-gel method               | $\text{K}_{0.41}\text{MnO}_2 \cdot 0.5\text{H}_2\text{O}$ | nanosheets                         | 50 nm in thickness                     | 425/0.175  | [84] |
| microemulsion method         | $\alpha\text{-MnO}_2$                                     | nanorods                           | 12 nm in diameter                      | 210/0.5  | [85] |
| molten salt method           | $\text{MnO}_2/\text{Mn}_2\text{O}_3$                      | nanobelts/nanoparticles            | –                                      | 322.1/0.2  | [87] |
| thermal decomposition method | $\delta\text{-MnO}_2$                                     | flake-like particles               | 200 nm in diameter                     | 252/0.083  | [88] |
| co-precipitation method      | $\alpha\text{-MnO}_2$                                     | nanorods                           | 10 nm in diameter, 50–120 nm in length | 665/0.1  | [89] |

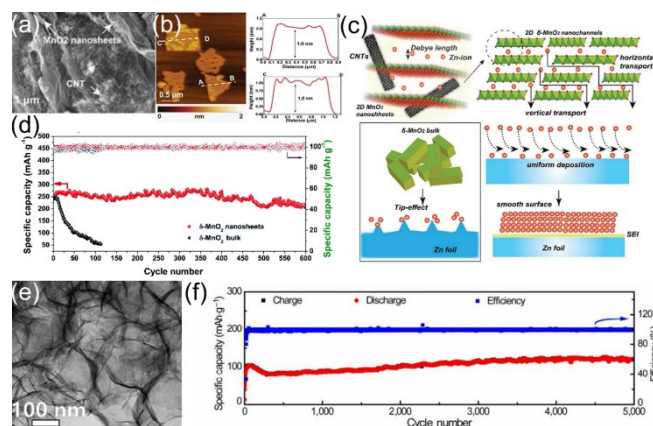


**Figure 8.** a) TEM image of  $\text{Mn}_3\text{O}_4$  nanodots, b) schematic representation of  $\text{Zn}^{2+}$  transport in Zn- $\text{Mn}_3\text{O}_4$  battery, c)  $\text{Zn}^{2+}$  diffusion coefficient, d) EIS of Zn- $\text{Mn}_3\text{O}_4$  battery, e) Contribution ratio of capacities at different scan rates, f) GCD curves at different current densities. Adapted with permission from Ref. [90]. Copyright (2019) American Chemical Society. g) SEM image of  $\text{MnO}_2$  nanosheets, h) schematic illustration of  $\text{MnO}_2$  polyhedral models. Adapted with permission from Ref. [91]. Copyright (2019) Wiley-VCH.

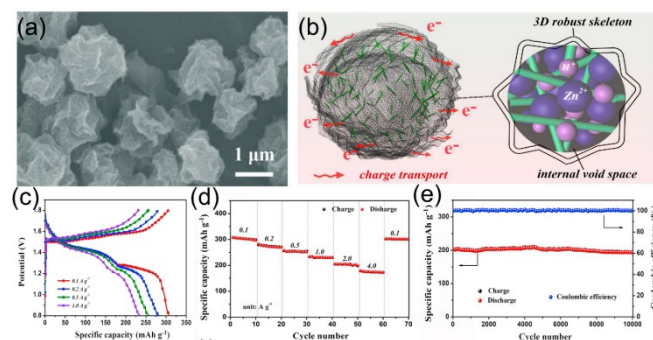
mainly comes from the capacitive process (Figure 8e), which is favorable for the fast kinetics. As a result, the cathode achieves a high capacity of  $386.7 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  and a superior rate performance of  $121.6 \text{ mAh g}^{-1}$  at  $1.5 \text{ A g}^{-1}$  (Figure 8f). Zhao et al. synthesized  $\text{MnO}_2$  nanosheets through one-step hydrothermal method (Figure 8g).<sup>[91]</sup> The  $\text{MnO}_2$  nanosheets with a surface area of  $120 \text{ m}^2 \text{ g}^{-1}$  and a thickness of  $2.5 \text{ nm}$ , not only provides the sufficient active sites, but also shorten the ion transmission path. In particular, the (100) plane of  $\text{MnO}_2$  presents large exposed areas of  $1 \times 1$  tunnel for the transmission of  $\text{H}^+$  and  $\text{Zn}^{2+}$  (Figure 8h), thus endowing a super rate performance of  $115.1 \text{ mAh g}^{-1}$  at a high current rate of  $10 \text{ C}$ .

Besides promoting the ion/electron transfer kinetics, nanostructures also have unique advantages in cycle stability. Wang et al. prepared single-atomic layer  $\text{MnO}_2$  nanosheets with a thickness of  $1 \text{ nm}$  (Figure 9a, b) through the exfoliation process.<sup>[92]</sup> Compared with the tip-effect caused by sharp corners and irregular morphology of bulk  $\text{MnO}_2$ , the smooth surface formed by the  $\text{MnO}_2$  nanosheets could significantly reduce the concentration gradient in the electrolyte and promote the uniform stripping/plating (Figure 9c), thus endowing a superior cycle stability over 600 cycles (Figure 9d). Ren et al. also constructed the inverse opal  $\text{MnO}_2$  ultrathin nanosheets (IO- $\text{MnO}_2$ ) with the thickness of approximately  $1 \text{ nm}$  (Figure 9e).<sup>[93]</sup> In  $\text{MnO}_2$  inverse opal structure, the hollow parts encompassed by nanosheets adapt to the volume expansion of ion insertion and avoid structural collapse. As a result, the IO- $\text{MnO}_2$  cathode could keep a capacity of  $121 \text{ mAh g}^{-1}$  even after 5000 long-term cycles at  $2 \text{ A g}^{-1}$  (Figure 9f).

In recent years, 3D assembly structures based on nanostructures have also been reported.<sup>[61,64,94–96]</sup> For example, Shi et al. synthesized a 3D micro-flowers-like structure of  $\text{MnO}_2$  nanowires (Figure 10a) through spray drying technology.<sup>[95]</sup> The



**Figure 9.** a) SEM image and b) AFM image of  $\text{MnO}_2$  nanosheets, c) schematic illustration of  $\text{Zn}^{2+}$  transport process in  $\text{MnO}_2$  nanosheets and  $\delta\text{-MnO}_2$  bulk, d) cycle performance of  $\text{MnO}_2$  nanosheets and  $\delta\text{-MnO}_2$  bulk cathode at  $0.1 \text{ A g}^{-1}$ . Adapted with permission from Ref. [92]. Copyright (2019) Royal Society of Chemistry. e) TEM image of IO- $\text{MnO}_2$ , f) cycle performance of IO- $\text{MnO}_2$  cathode at  $2 \text{ A g}^{-1}$ . Adapted with permission from Ref. [93]. Copyright (2019) Springer.



**Figure 10.** a) SEM image of 3D micro-flowers-like  $\text{MnO}_2$ , b) schematic diagram of 3D micro-flowers-like structure confined  $\text{MnO}_2$  nanowires. c) GCD curves at different current densities, d) rate performance and e) cycle performance at  $2 \text{ A g}^{-1}$  of 3D micro-flowers-like  $\text{MnO}_2$  cathode. Adapted with permission from Ref. [73]. Copyright (2020) Elsevier.

3D structure provides abundant reaction sites, convenient ion/electron diffusion channels and enough room to alleviate the volume expansion (Figure 10b). Thus, the battery delivers a high capacity of  $306.8 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  (Figure 10c) and a superior rate capacity of  $180.2 \text{ mAh g}^{-1}$  at  $4 \text{ A g}^{-1}$  (Figure 10d). What's more, an ultralong-cycle stability of  $\sim 97.5\%$  retention even after 10000 cycles is achieved (Figure 10e).

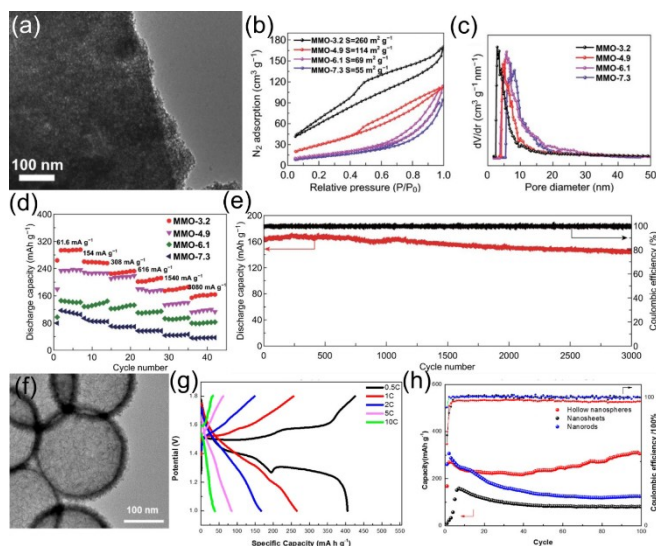
There is no doubt that nanostructures have unique advantages in the performance optimization of manganese-based cathode materials due to the typical size effect. Based on the characteristics of the nanostructures, such as high specific surface, fine electron/ion transport channels, etc. the reasonable nanostructure or assembly structures design is a feasible strategy for performance optimization.



### 3.1.2. Porous and Hollow Structure

The porous or hollow structure provides more active sites for energy storage and channels for ion diffusion. At the same time, the pores alleviate the volume change caused by repeated ion insertion/extraction, which is beneficial to the structural stability. Up to now, porous or hollow structure has been widely applied to improve the electrochemical performance of manganese-based cathode materials in ZIBs.<sup>[66,97–102]</sup> Feng et al. prepared mesoporous  $\text{Mn}_2\text{O}_3$  (MMO) with controllable pore size and large specific surface areas.<sup>[97]</sup> For the MMO with pore size of 3.2 nm (MMO-3.2), it shows the morphology of nanoparticles with a diameter of 5 nm (Figure 11a) and the specific surface area is  $260 \text{ m}^2 \text{ g}^{-1}$  (Figure 11b, c). The porous structure exposes a large number of active sites and alleviates the volume expansion of  $\text{Zn}^{2+}$  insertion. Benefiting from this, the mesoporous MMO-3.2 cathode delivers a high capacity of  $292 \text{ mAh g}^{-1}$  at  $0.2 \text{ A g}^{-1}$ , an excellent rate performance ( $162 \text{ mAh g}^{-1}$  retains at  $3.08 \text{ A g}^{-1}$ ) and cycle stability over 3000 cycles at  $3.08 \text{ A g}^{-1}$  (Figure 11d, e).

The hollow structure can be regarded as a special porous structure. Guo et al. prepared the hollow  $\text{MnO}_2$  nanospheres with a specific surface area of  $200 \text{ m}^2 \text{ g}^{-1}$ .<sup>[98]</sup> The hollow  $\text{MnO}_2$  shell is around 15 nm thick (Figure 11f), which extremely shorten the  $\text{Zn}^{2+}$  diffusion path, and avoid structural collapse caused by volume expansion during the ion insertion. Therefore, the hollow  $\text{MnO}_2$  cathode suggests a high specific capacity up to  $405 \text{ mAh g}^{-1}$  at  $0.5 \text{ C}$  (Figure 11g) and the discharge capacity is stabilized at  $305 \text{ mAh g}^{-1}$  after 100 cycles at  $1 \text{ C}$  (Figure 11h).



**Figure 11.** a) TEM image of MMO-3.2, b) nitrogen sorption isotherms and c) pore-size distribution curves of MMO, d) rate performance and e) cycle performance at  $3.08 \text{ A g}^{-1}$  MMO cathode. Adapted with permission from Ref. [97]. Copyright (2020) Springer. (f) TEM image of hollow  $\text{MnO}_2$  nanospheres, (g) GCD curves at different current densities, (h) cycle performance of hollow  $\text{MnO}_2$  cathode. Adapted with permission from Ref. [98]. Copyright (2018) The authors.

To summarize, the structures affect the specific surface area, ion/electronic diffusion distance, etc. directly, which in turn affect the specific capacity, rate performance and cycle stability of manganese-based cathode. Anyway, Reasonable structure design is a viable option to further improve the performance of manganese-based cathode in ZIBs.

### 3.2. Compositing with Conductive Materials

Structure design is difficult to solve the problem of poor conductivity of the manganese-based cathode materials, and the structural stability of the materials still needs to be improved. Compositing with conductive materials (carbon materials, conductive polymers, etc.) is a commonly used strategy to improve the conductivity and structural stability.

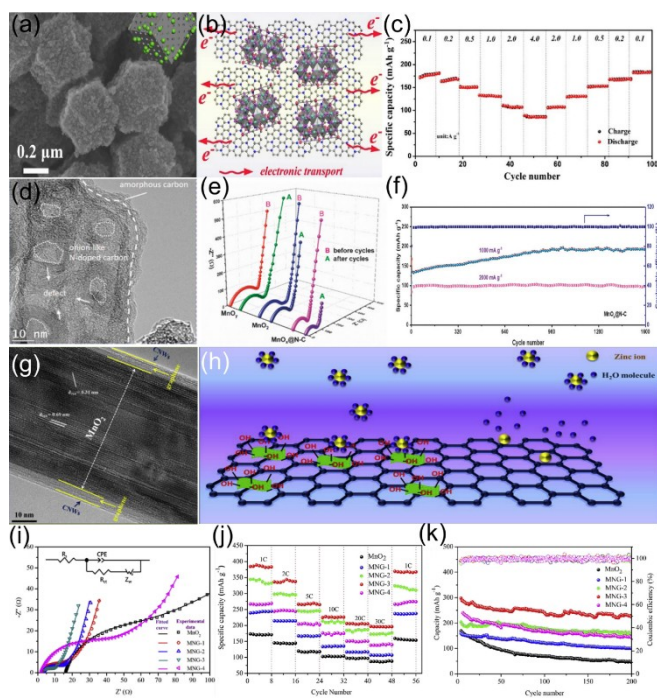
#### 3.2.1. Inorganic Carbon Materials

In recent years, various studies have reported the application of carbon materials in manganese-based cathode materials.<sup>[61,62,65,68,99,103–107]</sup> Carbon materials with high conductivity, including porous carbon, graphene, etc., are widely used in composite materials, which can serve as substrate, network, coating, and so on. The carbon materials play a vital role in the electron/ion transport and structural stability of manganese-based cathode materials. With the development of different types and sizes of carbon materials, they have shown great potential in manganese-based cathode materials.

Carbon materials are good substrates for in-situ growth of manganese-based compounds. Yang et al. prepared  $\text{ZnMn}_2\text{O}_4$  nanoparticles anchored on the porous carbon polyhedrons (ZMO@PCPs) (Figure 12a).<sup>[68]</sup> The porous carbon as the substrate, acts as the “highways” for electronic transmission (Figure 12b), thus leading to the fast electron transfer kinetics. Therefore, the MO@PCPs cathode delivers a prominent rate capacity of  $88.7 \text{ mAh g}^{-1}$  at  $4 \text{ A g}^{-1}$  (Figure 12c).

Carbon network with excellent mechanical stability not only accelerates the electron transmission, but also guarantees the structural stability due to its porous structure. Fu et al. prepared onion-like N-doped carbon composited with  $\text{MnO}_x$  nanorods ( $\text{MnO}_x$ @N-C) (Figure 12d),<sup>[99]</sup> in which the carbon conductive network would significantly reduce the charge transfer resistance (Figure 12e), improving the overall conductivity. In addition, the porous structure of the carbon network adapts to the volume expansion of ions insertion. As a result, the battery delivers a superior rate performance of  $100 \text{ mAh g}^{-1}$  at  $2 \text{ A g}^{-1}$  and a long-term cycle performance up to 1600 cycles at the current densities of 1 and  $2 \text{ A g}^{-1}$  (Figure 12f).

Coating is an important form of carbon materials in composite materials. The carbon coating promotes electron/ion transfer, and plays a key role in inhibiting the dissolution of  $\text{Mn}^{2+}$ . Wu et al. obtained  $\alpha\text{-MnO}_2$ /graphene scrolls by uniformly coating graphene scrolls on  $\text{MnO}_2$  nanowires.<sup>[107]</sup> The graphene coating effectively alleviated the dissolution of  $\text{Mn}^{2+}$ , which greatly increased the structural stability during cycling. There-

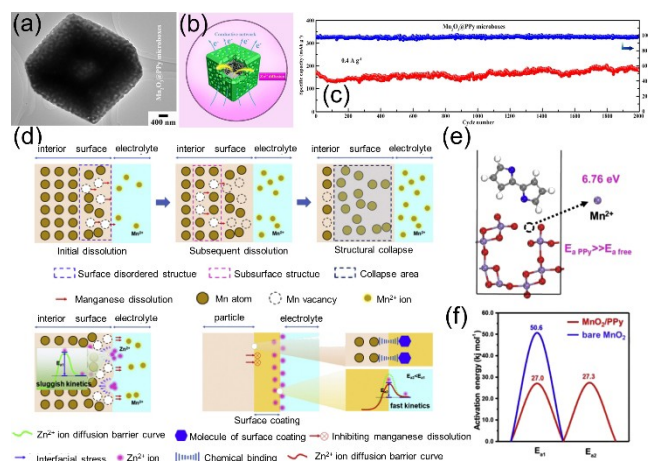


**Figure 12.** a) SEM image of ZMO@PCPs, b) schematic diagram of electronic transport in ZMO@PCPs, c) rate performance of ZMO@PCPs cathode. Adapted with permission from Ref. [68]. Copyright (2020) Elsevier. d) TEM image of MnO<sub>2</sub>@N-C composite, e) EIS and f) cycle performance of MnO<sub>2</sub>@N-C cathode at 1 and 2 Ag<sup>-1</sup>. Adapted with permission from Ref. [99]. Copyright (2018) Wiley-VCH. g) HRTEM image of MNG, h) schematic diagram of hydrated Zn<sup>2+</sup> desolvation at MNG surface, i) EIS of MNG cathode, j) rate performance and k) cycle performance at 5 C of MNG cathode. Adapted with permission from Ref. [103]. Copyright (2020) Elsevier.

fore, the battery exhibited a long-term cycling stability (94% retention after 3000 cycles). Zhang et al. prepared MnO<sub>2</sub>-based composites by coating hydrophobic graphene and amphiphilic cellulose nano-whiskers (MNG) (Figure 12g).<sup>[103]</sup> As shown in Figure 12(h), proper hydrophobicity of graphene greatly forces hydrated Zn<sup>2+</sup> desolvation, facilitating Zn<sup>2+</sup> insertion into host materials, which promotes the Zn<sup>2+</sup> transportation and avoid the structural collapse caused by the insertion of a large number of hydrated Zn<sup>2+</sup>. Combined with the excellent conductivity of graphene and cellulose nanowhiskers (Figure 12i), the MNG cathode achieves a superior rate capacity of 196 mAh g<sup>-1</sup> at an extremely high current density of 20 C and an excellent cycle stability (Figure 12j, k).

### 3.2.2. Conductive Polymers

Conductive polymers have the advantages of easy synthesis, low cost, and good conductivity. Currently, reports of conductive polymers compound with manganese-based materials mainly focus on the polypyrrole (PPy).<sup>[76,108,109]</sup> Liu et al. developed a 3D PPy-encapsulated Mn<sub>2</sub>O<sub>3</sub> composite, in which the PPy not only formed a conductive network for fast electron transport but also act as a coating preventing structural damage (Figure 13a, b).<sup>[108]</sup> The crystal structure had no



**Figure 13.** a) TEM of Mn<sub>2</sub>O<sub>3</sub>@PPy microbox, b) schematic diagram of Mn<sub>2</sub>O<sub>3</sub>@PPy cathode, c) Ex-situ XRD patterns of Mn<sub>2</sub>O<sub>3</sub>@PPy. Adapted with permission from Ref. [108]. Copyright (2019) American Chemical Society. d) Schematic diagram of the problems and proposed ideal model of manganese-based cathode materials, e) energy barrier to remove Mn atom, f) activation energy of charge transfer process of bare MnO<sub>2</sub> and MnO<sub>2</sub>/PPy. Adapted with permission from Ref. [110]. Copyright (2020) Elsevier.

significant variation during charge and discharge, thus the battery suggests a high-rate performance and long-term stability (no capacity decay over 2000 cycles) (Figure 13c).

Recently, Huang et al. further pointed out that PPy coating has advantages on preventing the dissolution of Mn<sup>2+</sup> and improving the sluggish interfacial kinetics.<sup>[110]</sup> As shown in Figure 13(d), structural damage of MnO<sub>2</sub> can be attributed to the dissolution of surface atoms and a series of chain reactions and the high diffusion barrier caused by electrostatic repulsion will slow down the sluggish interfacial kinetics. When PPy is introduced as a coating, the Mn atom on the surface will bond with the N atom in PPy to form a strongly Mn–N bonding. This greatly increases the energy barrier to remove manganese atoms ( $E_{a, \text{free}} = 0.26 \text{ eV}$ ) (Figure 13e), which is effective to prevent the dissolution problems. The PPy coating reduces the energy barrier for the charge transfer process, thus achieving the fast reaction kinetics (Figure 13f).

Other conductive polymers such as polyaniline (PANI) and polyacrylic acid (PAA) have also been reported. Mao et al. used PANI as a coating for the composite aerogel of MnO<sub>2</sub>/rGO.<sup>[111]</sup> The PANI coating not only provides excellent conductivity, but also effectively inhibits the dissolution of Mn<sup>2+</sup>. Recently, Zhang et al. reported a freestanding MnO<sub>2</sub>/CNT/PAA cathode for ZIBs,<sup>[112]</sup> in which PAA plays a unique advantage on achieving excellent mechanical and electrical properties.

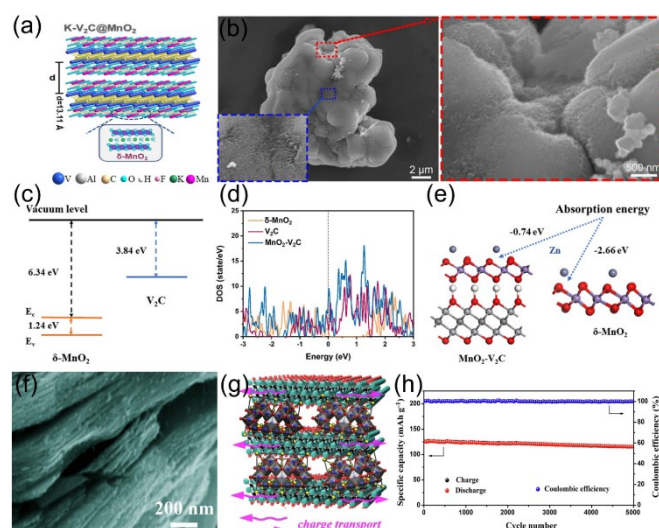
### 3.2.3. Others

Besides carbon materials and conductive polymers, layered MXene, owing to the typical accordion structure with large interlayer spacing, large specific surface area, excellent electrical conductivity and structural stability, is also composited with manganese-based compounds.

Zhu et al. prepared K-V<sub>2</sub>C@MnO<sub>2</sub> with MnO<sub>2</sub> nanosheets formed on the V<sub>2</sub>CT<sub>x</sub> MXene surface (Figure 14a, b).<sup>[113]</sup> Due to the lower electron affinity of V<sub>2</sub>C (3.84 eV), the electrons tend to transfer into the conduction band of MnO<sub>2</sub>, increasing the density of states of MnO<sub>2</sub> near the Fermi level, which significantly increase the electronic conductivity of K-V<sub>2</sub>C@MnO<sub>2</sub> (Figure 14c, d). In addition, the lower Gibbs free energy of Zn<sup>2+</sup> adsorption of K-V<sub>2</sub>C@MnO<sub>2</sub> (−0.74 eV) delivers the fast ion transport kinetics and high reversibility of ion adsorption/desorption (Figure 14e), resulting in high rate

capacity of 87.7 mAh g<sup>−1</sup> at 15 Ag<sup>−1</sup>. Luo et al. created a nanoscale parallel circuitry based on manganese decorated MXene (MnO<sub>x</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>).<sup>[114]</sup> Layered MXene provided a parallel circuitry for fast ion transport, and the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> stacks improve the electron conductivity. Thus, the MnO<sub>x</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> possess a high rate performance of 130 mAh g<sub>(Mn)</sub><sup>−1</sup> at an extremely high current density 30 Ag<sub>(Mn)</sub><sup>−1</sup>.

Shi et al. synthesized a 3D assembly of MXene-stabilized ZnMn<sub>2</sub>O<sub>4</sub> through hydrothermal method.<sup>[69]</sup> The ZnMn<sub>2</sub>O<sub>4</sub> nanoparticles are evenly anchored on the MXene without obvious aggregation (Figure 14f). The MXene effectively inhibits the structural degradation and side reaction of ZnMn<sub>2</sub>O<sub>4</sub> (Figure 14g), which is contributed to the long cycle performance of 92.4% retention after 5000 cycles at 1 Ag<sup>−1</sup> (Figure 14h). They also prepared 3D Ti-MXene@MnO<sub>2</sub> microflowers for the cathode in ZIBs.<sup>[115]</sup> The 3D microflower structure with a robust skeleton could prevent the structural collapse during cycling and avoid the direct contact between MnO<sub>2</sub> nanoparticles and electrolyte, which greatly inhibits the dissolution of Mn<sup>2+</sup>. As a result, the cathode delivers an outstanding cycle stability over 2000 cycles. Manganese-based composite materials are shown in Table 2.



**Figure 14.** a) Schematic illustration of K-V<sub>2</sub>C@MnO<sub>2</sub>, b) SEM image of K-V<sub>2</sub>C@MnO<sub>2</sub>, c) band edge positions of  $\delta$ -MnO<sub>2</sub> and V<sub>2</sub>C, d) DOS calculations of  $\delta$ -MnO<sub>2</sub>, V<sub>2</sub>C, and MnO<sub>2</sub>-V<sub>2</sub>C, e) Absorption energies of Zn<sup>2+</sup> on the surfaces of  $\delta$ -MnO<sub>2</sub> and MnO<sub>2</sub>-V<sub>2</sub>C. Adapted with permission from Ref. [108]. Copyright (2021) American Chemical Society. f) SEM image of ZnMn<sub>2</sub>O<sub>4</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, g) schematic illustration of MXene-stabilized ZnMn<sub>2</sub>O<sub>4</sub>, h) cycle performance at 1 Ag<sup>−1</sup> of ZnMn<sub>2</sub>O<sub>4</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> cathode. Adapted with permission from Ref. [110]. Copyright (2020) Elsevier.

### 3.3. Pre-Intercalation

The incorporation of conductive agents shares advantages on improving the conductivity and preventing the Mn<sup>2+</sup> dissolution of manganese-based cathode materials, while suggesting little effect on the manganese-based compound itself. Pre-intercalated crystal water, ions and molecules in the manganese-based compound, will expand the interlayer spacing, reducing the diffusion resistance of ions and serve as “structural pillar”, stabilizing the structure of the manganese-based compound during repeated Zn<sup>2+</sup> insertion/extraction.

**Table 2.** Electrochemical properties of manganese-based cathode materials composited with conductive materials.

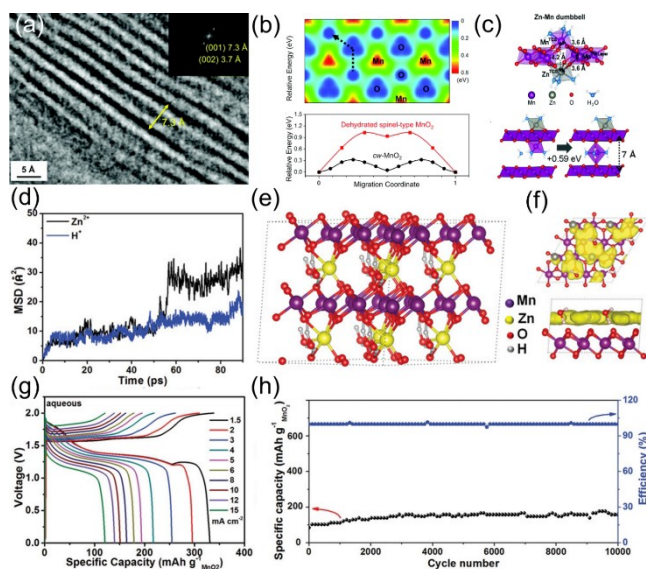
| Cathode   | Anode         | Electrolyte                                      | Voltage [V] | Maximum capacity [mAh g <sup>−1</sup> ]/current density [Ag <sup>−1</sup> ] | Rate performance: capacity [mAh g <sup>−1</sup> ]/current density [Ag <sup>−1</sup> ] | Retention/cycles/current density [Ag <sup>−1</sup> ] | Ref.  |
|---|---------------|--|-------------|---|---|--|-------|
| ZnMn <sub>2</sub> O <sub>4</sub> @porous carbon                 | Zn plate      | 1 M ZnSO <sub>4</sub> + 0.05 M MnSO <sub>4</sub> | 0.8–1.8     | 176.8/100   | 88.7/4  | 90.3%/2000/1000                                      | [68]  |
| MnO <sub>x</sub> @N-doped carbon                                | Zn foil       | 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub>  | 0.8–1.8     | 385/0.1   | 100/2   | ~100%/1600/2   | [99]  |
| cellulose/graphene/MnO <sub>2</sub>                             | Zn foil       | 2 M ZnSO <sub>4</sub> + 0.2 M MnSO <sub>4</sub>  | 0.8–1.9     | 384/0.3   | 196/9   | 52.68%/5000/6  | [103] |
| Mn <sub>2</sub> O <sub>3</sub> @C/CNT fibers                    | Zn/CNT fibers | 2 M ZnSO <sub>4</sub> + 0.5 M MnSO <sub>4</sub>  | 1.0–1.8     | 253.1/0.5   | 147.5/5   | 79.6%/3000/5   | [104] |
| MnO <sub>2</sub> @N-doped hollow carbon spheres                 | Zn foil       | 3 M ZnSO <sub>4</sub> + 0.15 M MnSO <sub>4</sub> | 1.0–1.85    | 349/0.1   | 100/2   | 78.7%/2000/2   | [105] |
| ZnMn <sub>2</sub> O <sub>4</sub> /N-doped graphene              | Zn foil       | 1 M ZnSO <sub>4</sub> + 0.05 M MnSO <sub>4</sub> | 0.8–1.8     | 221/0.1   | 75/2  | 97.4%/2500/1   | [106] |
| MnO <sub>2</sub> /graphene scrolls                              | Zn foil       | 2 M ZnSO <sub>4</sub> + 0.2 M MnSO <sub>4</sub>  | 0.8–1.8     | 362.2/0.3   | 145.3/3   | 94%/3000/3   | [107] |
| Mn <sub>2</sub> O <sub>3</sub> @PPy                             | Zn foil       | 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub>  | 1.0–1.8     | 255/0.1   | 75.6/2  | ~100%/2000/0.4                                       | [108] |
| MnO <sub>x</sub> /PPy   | Zn foil       | 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub>  | 1.0–1.8     | 408/0.3   | 67/3  | 78%/2800/1.5   | [109] |
| MnO <sub>2</sub> /PPy   | Zn foil       | 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub>  | 0.8–1.8     | 256/0.1   | 90/1.5  | 100%/500/1   | [110] |
| MnO <sub>2</sub> /rGO/PANI                                      | Zn foil       | 2 M ZnSO <sub>4</sub>                            | 0.8–1.8     | 241.1/0.1   | 111.7/1   | 82.7%/600/1  | [111] |
| MnO <sub>2</sub> /CNT/PAA                                       | Zn foil       | 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub>  | 1.0–1.9     | 302/0.3   | 103/3   | 82%/1000/1.5   | [112] |
| K-V <sub>2</sub> C@MnO <sub>2</sub>                             | Zn sheet      | 2 M ZnSO <sub>4</sub> + 0.25 M MnSO <sub>4</sub> | 0.8–1.8     | 316.3/0.3   | 87.7/15   | ~100%/10000/10                                       | [113] |
| MnO <sub>x</sub> @Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> | Zn foil       | 2 M ZnSO <sub>4</sub> + 0.2 M MnSO <sub>4</sub>  | 0.8–1.8     | 270/0.1   | 130/30  | ~100%/400/5  | [114] |
| Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> @MnO <sub>2</sub> | Zn foil       | 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub>  | 0.8–1.8     | 301.2/0.1   | 202.2/2   | 90.6%/2000/0.5                                       | [115] |



## 3.3.1. Crystal Water

Pre-intercalated crystal water in manganese-based compound can effectively expand the interlayer spacing and weaken the electrostatic interaction between  $\text{Zn}^{2+}$  and  $[\text{MnO}_6]$  skeleton, which is beneficial to the  $\text{Zn}^{2+}$  diffusion. Nam et al. prepared a crystal water pre-inserted  $\text{MnO}_2$  layered structure (cw- $\text{MnO}_2$ ), which possesses a larger interlayer spacing of 7.3 Å than that of pure  $\text{MnO}_2$  (7.0 Å) (Figure 15a).<sup>[116]</sup> One the one hand, the cw- $\text{MnO}_2$  delivers a lower energy barrier of Zn migration of 0.25 eV, much lower than the migration energy of  $\text{Zn}^{2+}$  in  $\text{MnO}_2$  (1.03 eV) (Figure 15b), which suggests the fast  $\text{Zn}^{2+}$  diffusion. One the other hand, in cw- $\text{MnO}_2$ , the escaped  $\text{Mn}^{2+}$  is difficult to form the freely movable  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ , but exists in the form of stable Zn–Mn dumbbell structure (Figure 15c), thereby effectively inhibiting the dissolution of  $\text{Mn}^{2+}$ . Therefore, the cw- $\text{MnO}_2$  cathode exhibits an excellent rate capacity of  $150.0 \text{ mAh g}^{-1}$  at  $3 \text{ Ag}^{-1}$  and long cycle stability with 75.3% retention after 200 cycles.

Jiang et al. further predicted the transport behavior of  $\text{Zn}^{2+}$  and  $\text{H}^+$  in crystal water pre-inserted  $\text{MnO}_2$  through the ab initio molecular dynamics (AIMD) simulation.<sup>[117]</sup> Driven by  $\text{H}_2\text{O}$  molecules, the  $\text{Zn}^{2+}$  and  $\text{H}^+$  could co-exist stably and transmit smoothly between the layers of  $\text{MnO}_2$  without damaging the layered structure (Figure 15d–f), which makes an explanation for the improved rate performance and long cycle stability up to 10000 cycles (Figure 15g, h).

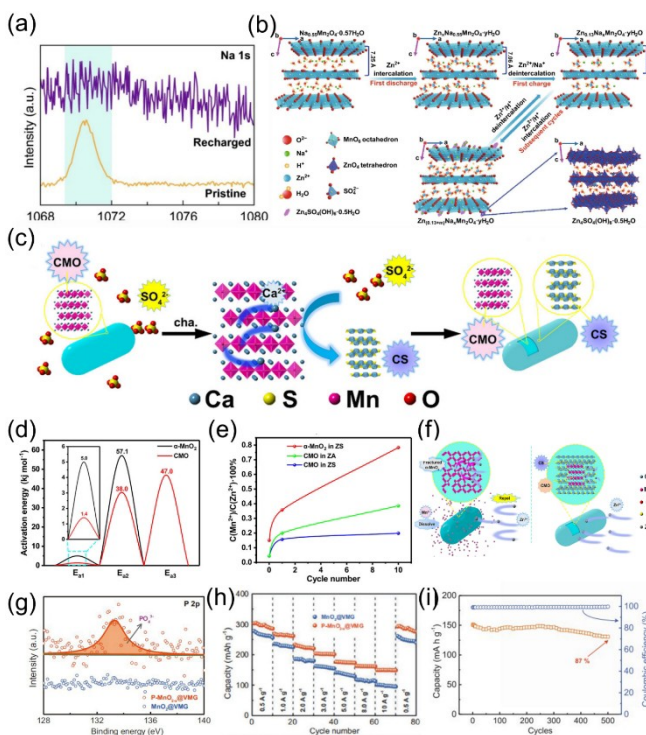


**Figure 15.** a) HRTEM of cw- $\text{MnO}_2$ , b) the migration pathway and barriers of  $\text{Zn}^{2+}$  in cw- $\text{MnO}_2$ , c) schematic diagram of Zn–Mn dumbbell structure and complexation behavior of Mn-octahedra. Adapted with permission from Ref. [117]. Copyright (2019) Royal Society of Chemistry. d) Mean square displacements of  $\text{Zn}^{2+}$  and  $\text{H}^+$  in  $\text{MnO}_2$ , e) schematic diagram of  $\text{Zn}^{2+}$  and  $\text{H}^+$  intercalated structure, f) diffusion trajectories of  $\text{Zn}^{2+}$  and  $\text{H}^+$ , g) GCD curves at different current densities, h) cycle performance at  $5 \text{ mA cm}^{-2}$ . Adapted with permission from Ref. [117]. Copyright (2020) Wiley-VCH.

## 3.3.2. Ions

Pre-intercalated ions in the manganese-based compound not only adjusts the interlayer spacing to accelerate ion transfer, but also plays a supporting role for improving the structural stability of the manganese-based cathode materials. Zhai et al. prepared layered  $\text{Na}_{0.55}\text{Mn}_2\text{O}_4 \cdot 0.57\text{H}_2\text{O}$  with  $\text{Na}^+/\text{H}_2\text{O}$  co-intercalated  $\text{MnO}_2$ .<sup>[118]</sup> As shown in Figure 16a, b, during the first cycle,  $\text{Na}^+$  acts as the pillar for  $\text{Zn}^{2+}$  insertion upon discharge progress. And then, the  $\text{Zn}^{2+}$  replaces part of  $\text{Na}^+$  to stabilize the interlayers during the following discharge/charge process. Therefore, the cathode shows an excellent rate and cycle performance with a high capacity of  $201.6 \text{ mAh g}^{-1}$  at  $0.5 \text{ Ag}^{-1}$  after 400 cycles.

Guo et al. prepared a  $\text{Ca}_2\text{MnO}_4$  (CMO) cathode with  $\text{Ca}^{2+}$  pre-intercalated into  $\text{MnO}_2$ .<sup>[119]</sup> In the first charging process, the pre-intercalated  $\text{Ca}^{2+}$  releases from the CMO and forms a single-component  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (CS) solid electrolyte interface (SEI) film on the surface of CMO (Figure 16c).  $\text{Ca}^{2+}$  pre-intercalation could improve ion/electron kinetics and stable structure of  $\text{MnO}_2$ , and the CS SEI film further reduces the interface activation energy (Figure 16d), promoting the insertion/extraction of  $\text{Zn}^{2+}$  and inhibits the dissolution of  $\text{Mn}^{2+}$ ,



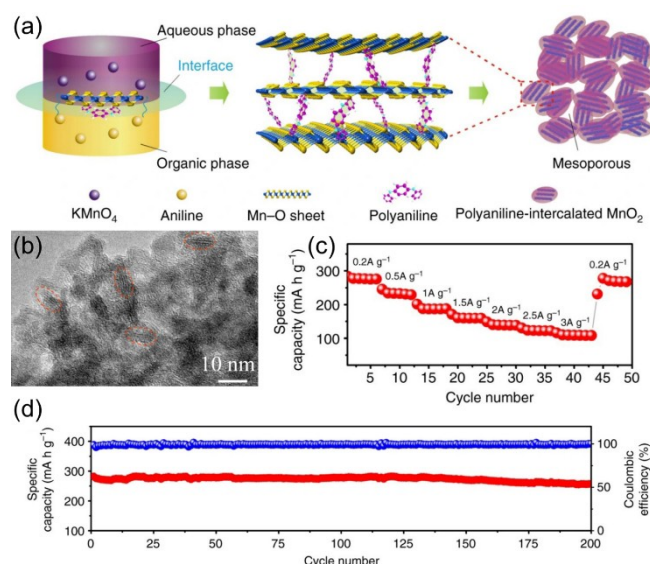
**Figure 16.** a) XPS Na 1s spectra at different statuses of  $\text{Na}_{0.55}\text{Mn}_2\text{O}_4 \cdot 0.57\text{H}_2\text{O}$ , b) schematic illustration in discharge/charge processes of  $\text{Na}_{0.55}\text{Mn}_2\text{O}_4 \cdot 0.57\text{H}_2\text{O}$  cathode. Adapted with permission from Ref. [118]. Copyright (2020) Springer. c) Formation mechanism of CS SEI film, d) activation energy curve of  $\text{MnO}_2$  and CMO, e) manganese dissolution rate of  $\text{MnO}_2$  and CMO, f) schematic diagram of reaction mechanism of  $\text{MnO}_2$  and CMO cathode. Adapted with permission from Ref. [119]. Copyright (2019) American Chemical Society. g) XPS P 2p spectra of  $\text{MnO}_2$ @VMG and  $\text{P-MnO}_{2-x}$ @VMG, (h) rate performance and (i) cycle performance at  $5 \text{ Ag}^{-1}$  of  $\text{P-MnO}_{2-x}$ @VMG cathode. Adapted with permission from Ref. [121]. Copyright (2020) Wiley-VCH.

improving the structural stability of CMO (Figure 16e, f). As a result, the CMO cathode achieves a specific capacity of  $100 \text{ mAh g}^{-1}$  at  $1 \text{ A g}^{-1}$  and there is no obvious capacity fading after 1000 cycles. Similarly, Sun et al. prepared  $\text{Ca}^{2+}$  and  $\text{H}_2\text{O}$  as pillars pre-inserted layered  $\delta\text{-MnO}_2$ ,<sup>[120]</sup> noted as  $\text{Ca}_{0.28}\text{MnO}_2 \cdot 0.5\text{H}_2\text{O}$ , which possess a capacity of  $100.9 \text{ mAh g}^{-1}$  at  $3.5 \text{ A g}^{-1}$  even after 5000 cycles.

Apart from cations, anion ( $\text{PO}_4^{3-}$ ) was also pre-intercalated into  $\text{MnO}_2$  (Figure 16g).<sup>[121]</sup> The pre-intercalated  $\text{PO}_4^{3-}$  expands the interlayer spacing from 0.68 to 0.70 nm, accelerating the  $\text{Zn}^{2+}$  diffusion. Under the synergistic effect of vertical multilayer graphene arrays and oxygen defects, the cathode delivers an impressive high-rate capacity ( $150.1 \text{ mAh g}^{-1}$  at  $10 \text{ A g}^{-1}$ ), and excellent cycle performance (91.3 % retention after 1000 cycles) (Figure 16h, i).

### 3.3.3. Molecules

Apart from cations/anions, polymer molecules, such as PANI, PPy, etc., are also adopted to pre-intercalated into the  $\text{MnO}_2$  for an excellent electrochemical performance. Huang et al. prepared polyaniline (PANI)-intercalated  $\text{MnO}_2$  through an inorganic/organic interface reaction (Figure 17a).<sup>[122]</sup> The intercalated PANI molecules not only enlarge the interlayer space of  $\text{MnO}_2$  (Figure 17b), improving ion diffusion kinetics, but also strengthen the layered structure, avoiding the phase change and structural collapse during ion insertion/extraction. Based on the co-insertion/ extraction mechanism of  $\text{H}^+$  and  $\text{Zn}^{2+}$ , the battery achieved a high capacity of  $110 \text{ mAh g}^{-1}$  at  $3 \text{ A g}^{-1}$  and a cycle stability of 200 cycles (Figure 17c, d).



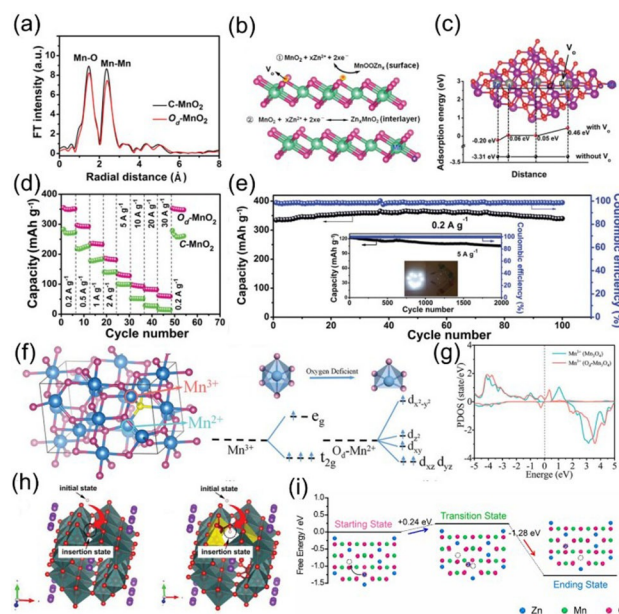
**Figure 17.** a) Schematic illustration of PANI-intercalated  $\text{MnO}_2$ , b) HETEM of PANI-intercalated  $\text{MnO}_2$ , c) rate performance and d) cycle performance at  $0.2 \text{ A g}^{-1}$  of PANI-intercalated  $\text{MnO}_2$  cathode. Adapted with permission from Ref. [122]. Copyright (2018) Springer Nature.

## 3.4. Defect Engineering

Fragile crystal structure and strong ion insertion barrier by electrostatic repulsion between  $\text{Zn}^{2+}$  and manganese-based compounds severely limit the electrochemical performance. Defect engineering is expected to modify the crystal structure, and then reduce the ion insertion barrier.<sup>[123–125]</sup> The defect engineering strategies for manganese-based cathode materials mainly focus on oxygen vacancy, cation vacancy and cationic doping.

### 3.4.1. Oxygen Vacancy

Oxygen vacancy can not only change the thermodynamics of the electrode surface, increase the active sites, but also adjust the electronic structure to promote the transfer of electrons and ions. Xiong et al. prepared oxygen-deficient  $\text{MnO}_2$  as the cathode material for ZIBs (Figure 18a).<sup>[126]</sup> As shown in Figure 18(b, c), due to the oxygen vacancy, the Gibbs free energies of  $\text{Zn}^{2+}$  adsorption near the vacancies are close to thermoneutral values (0.05 eV), which indicates that the adsorbed  $\text{Zn}^{2+}$  are easier to desorb, and then the once-occupied active surface areas could be accessible for the next  $\text{Zn}^{2+}$  adsorption. The high reversibility of  $\text{Zn}^{2+}$  adsorption/desorption results that oxygen-deficient  $\text{MnO}_2$  cathode displays a high specific



**Figure 18.** a)  $k^3$ -weighted Fourier transform of the extended X-ray absorption fine structure data of  $\text{O}_\delta\text{-MnO}_2$  and  $\text{C-MnO}_2$ , b) mechanisms of  $\text{O}_\delta\text{-MnO}_2$  for  $\text{Zn}^{2+}$  storage, c)  $\text{Zn}^{2+}$  adsorption energies of  $\text{O}_\delta\text{-MnO}_2$  and  $\text{C-MnO}_2$ , d) rate performance and e) cycle performance at  $0.2 \text{ A g}^{-1}$  and  $5 \text{ A g}^{-1}$  of  $\text{O}_\delta\text{-MnO}_2$  cathode. Adapted with permission from Ref. [126]. Copyright (2019) Wiley-VCH. f) octahedral and pyramidal crystal fields and the d-orbital splitting configurations of  $\text{O}_\delta\text{-Mn}_2\text{O}_4$ , g) partial DOS of  $\text{Mn}^{3+}$  atom around the oxygen vacancy. Adapted with permission from Ref. [127]. Copyright (2020) Wiley-VCH. h)  $\text{H}^+$  storage path in ab-plane of perfect and oxygen-defect  $\text{MnO}_2$ . Adapted with permission from Ref. [128]. Copyright (2019) Wiley-VCH. i) energy profiles of the Zn diffusion in  $\text{O}_\delta\text{-ZnMn}_2\text{O}_4$ . Adapted with permission from Ref. [129]. Copyright (2019) Elsevier.



capacity of  $345 \text{ mAh g}^{-1}$  at  $0.2 \text{ Ag}^{-1}$ , a superior rate capacity at  $30 \text{ Ag}^{-1}$  and a capacity retention of 84% after 2000 cycles at  $5 \text{ Ag}^{-1}$  (Figure 18d, e).

Tan et al. explored the effect of oxygen vacancy on the electrical conductivity of  $\text{Mn}_3\text{O}_4$ .<sup>[127]</sup> After introducing oxygen vacancy, the octahedral crystal of  $\text{Mn}^{3+}$  changes to form a pyramidal crystal field, increasing the  $\text{Mn}^{3+}$  charge density (Figure 18f) and the bandgap changes to 0 eV (Figure 18g), thereby improving the conductivity. Fang et al. confirmed that oxygen vacancies are essential for the fast  $\text{H}^+$  diffusion through opening the  $[\text{MnO}_6]$  polyhedral wall and creating additional ion channels in the deformed  $[\text{MnO}_6]$  polyhedral (Figure 18h).<sup>[128]</sup> Zhang et al. also simulated the diffusion kinetics of  $\text{Zn}^{2+}$  in the  $\text{ZnMn}_2\text{O}_4$ .<sup>[129]</sup> The energy barrier of  $\text{Zn}^{2+}$  mobility near oxygen vacancy is 0.24 eV, much lower than that in perfect  $\text{ZnMn}_2\text{O}_4$  (0.39 eV) (Figure 18i), which indicates the rapid  $\text{Zn}^{2+}$  diffusion in oxygen-deficient  $\text{ZnMn}_2\text{O}_4$ . These all confirm that oxygen vacancy plays a vital role in promoting ion/electron transfer and stabilizing the crystal structure, leading to an excellent electrochemical performance of manganese-based cathode materials.

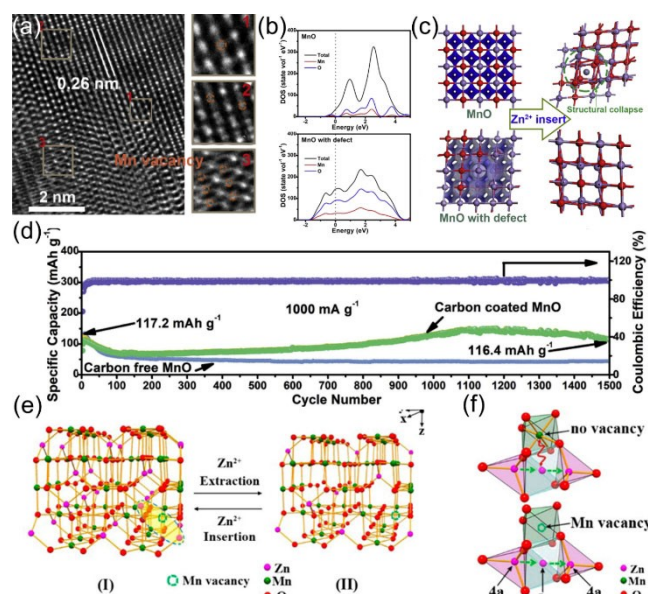
### 3.4.2. Cation Vacancy

Cation vacancy could weak the electrostatic interaction between the ions and the host lattice and then promote the insertion of ions into the host, which have been applied in various ion batteries.<sup>[130–133]</sup> In the field of ZIBs, Mn vacancy is the most common cation vacancies in manganese-based cathode materials. Zhu et al. prepared a  $\text{Mn}_{0.61}\square_{0.39}\text{O}$  ( $\square$  refers to Mn defect) cathode with Mn defects (Figure 19a) and analyzed the influence of Mn vacancy through DFT calculations.<sup>[134]</sup> On the one hand, Mn vacancy increases the charge density around the Fermi level (Figure 19b), improving the conductivity of MnO. On the other hand, Mn vacancy creates the large channels for  $\text{Zn}^{2+}$  insertion and available active sites for  $\text{Zn}^{2+}$  storage, effectively avoiding the structural collapse during the repeated insertion/extraction (Figure 19c). With the carbon coating, the  $\text{Mn}_{0.61}\square_{0.39}\text{O}$  cathode possess a high capacity of  $116 \text{ mAh g}^{-1}$  at  $1 \text{ Ag}^{-1}$  after 1500 cycles (Figure 19d).

In addition, Zhang et al. clarified the kinetics and mechanism of  $\text{Zn}^{2+}$  insertion/extraction in  $\text{ZnMn}_2\text{O}_4$  with Mn vacancy.<sup>[135]</sup> As shown in Figure 19(e, f), in perfect  $\text{ZnMn}_2\text{O}_4$ , the large electrostatic repulsion of Mn cations at octahedral sites strongly hindered the  $\text{Zn}^{2+}$  diffusion between adjacent tetrahedrons. While the Mn vacancy weakens this electrostatic barrier, resulting in the fast  $\text{Zn}^{2+}$  diffusion kinetics. Thus, the cation-defected  $\text{ZnMn}_2\text{O}_4$  exhibits a remarkable electrochemical performance.

### 3.4.3. Cation Doping

Cation doping into the manganese-based compounds to change the lattice spacing of the crystal structure, is also a



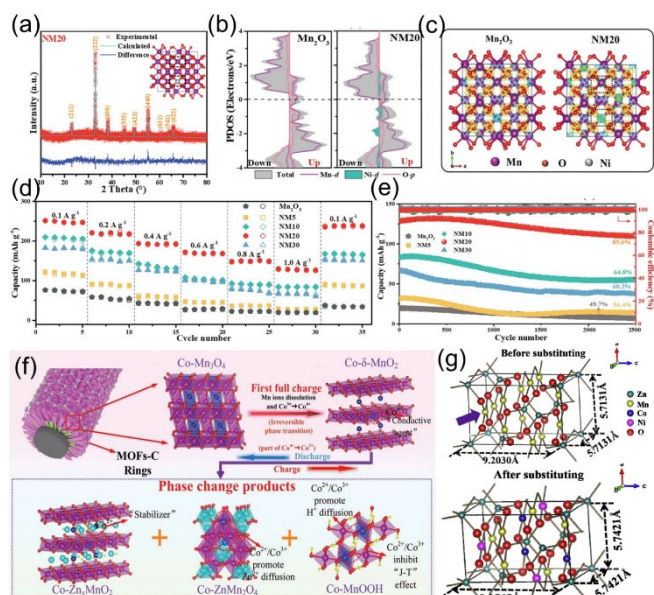
**Figure 19.** a) HRTEM image of  $\text{Mn}_{0.61}\square_{0.39}\text{O}$ , b) calculated density of states of MnO and  $\text{Mn}_{0.61}\square_{0.39}\text{O}$ , c) charge distribution and structures after  $\text{Zn}^{2+}$  insertion of MnO and  $\text{Mn}_{0.61}\square_{0.39}\text{O}$ , d) cycle performance at  $1 \text{ Ag}^{-1}$ . Adapted with permission from Ref. [134]. Copyright (2020) Elsevier. e) Schematic illustration of  $\text{Zn}^{2+}$  insertion/extraction in  $\text{ZnMn}_2\text{O}_4$  with Mn vacancy, f)  $\text{Zn}^{2+}$  diffusion pathway in  $\text{ZnMn}_2\text{O}_4$  without and with Mn vacancy. Adapted with permission from Ref. [135]. Copyright (2016) American Chemical Society.

feasible strategy to improve the energy storage performance. Zhang et al. prepared Ni-doped  $\text{Mn}_2\text{O}_3$  (NM20) with the atomic ratio of Ni and Mn in the precursor 1:20 (Figure 20a).<sup>[136]</sup> Ni doping increases the charge density around the Fermi level (Figure 20b), thereby increasing the electronic conductivity of NM20. In addition, in NM20, the extra electrons are accumulated around the Mn atoms adjacent to the doped Ni atoms (Figure 20c), generating the strong interaction between the Mn and O atoms, which greatly enhances the structural stability. As a result, NM20 cathode exhibits a discharge capacity of  $132 \text{ mAh g}^{-1}$  at  $1 \text{ Ag}^{-1}$  and a superior cycle stability of 85.6% retention over 2500 cycles (Figure 20d, e).

Ji et al. prepared a multi-valence cobalt-doped  $\text{Mn}_3\text{O}_4$ ,<sup>[137]</sup> in which the  $\text{Co}^{2+}$  doping acts as “structural pillar”, effectively improving the structural stability, the  $\text{Co}^{2+/3+}$  doping inhibits the Jahn-Teller effect and promotes ion diffusion, and the  $\text{Co}^{4+}$  increases the conductivity (Figure 20f).

Tao et al. reported a Ni and Co co-substituted  $\text{ZnMn}_2\text{O}_4$  as the cathode for ZIBs.<sup>[138]</sup> The Co and Ni replaced Mn in the octahedral sites (Figure 20g), which increases the lattice parameters and then promotes the  $\text{Zn}^{2+}$  diffusion. Moreover, the co-doping of Ni and Co also inhibits the Jahn-Teller distortion of  $\text{Mn}^{3+}$  and stabilizes the crystal structure. Benefit from this, the Ni and Co co-doped  $\text{ZnMn}_2\text{O}_4$  cathode shows a stable capacity of  $117.7 \text{ mAh g}^{-1}$  after 600 cycles at  $0.5 \text{ Ag}^{-1}$ .





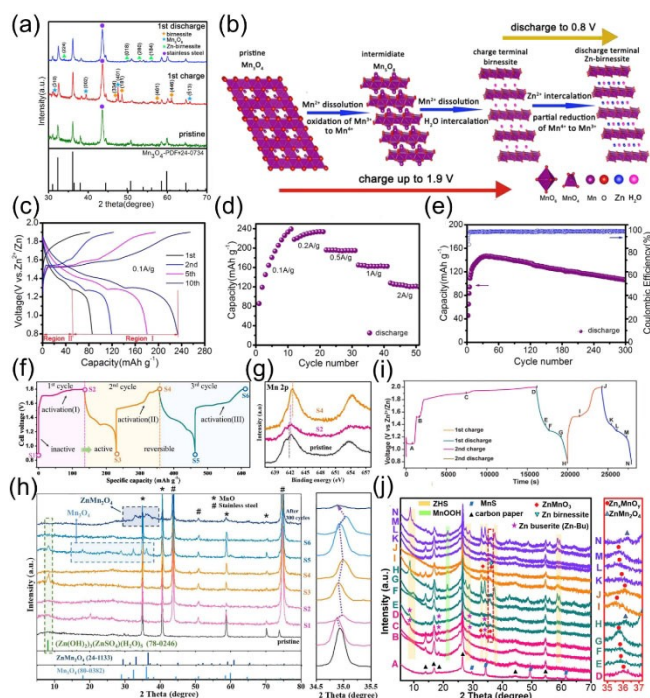
**Figure 20.** a) Rietveld refinement results of NM20, b) density of states of  $\text{Mn}_2\text{O}_3$  and NM20, c) electron density of  $\text{Mn}_2\text{O}_3$  and NM20, d) rate performance and e) cycle performance at  $1.0 \text{ A g}^{-1}$  of NM cathode. Adapted with permission from Ref. [136]. Copyright (2021) Wiley-VCH. f) Schematic illustration of the multi-valence cobalt-doped  $\text{Mn}_3\text{O}_4$ . Adapted with permission from Ref. [137]. Copyright (2021) Wiley-VCH. g) Crystal structure of  $\text{ZnMn}_2\text{O}_4$  with and without Ni co-doping. Adapted with permission from Ref. [138]. Copyright (2020) Elsevier.

### 3.5. Electrochemical Activation

The  $\text{ZnSO}_4$  or  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  aqueous solution is used as the electrolytes of ZIBs. Due to the weakly acidic, manganese-based cathode materials will slowly dissolve into electrolytes.<sup>[34]</sup> Adding  $\text{Mn}^{2+}$  to the electrolyte in advance not only changes the dissolution equilibrium of  $\text{Mn}^{2+}$ , inhibiting its dissolution, but also the  $\text{Mn}^{2+}$  in the electrolyte contributes to the capacity of the cathode materials.<sup>[139]</sup> This is mainly due to the fact that  $\text{Mn}^{2+}$  can be electro-oxidized into active  $\text{MnO}_2$ .<sup>[27,140]</sup> Inspired by this, manganese-based cathode materials without electrochemically active are expected to be activated via in situ electrochemical charging. Notably, the activation process is often accompanied by phase change and occurs in the initial cycles.

Hao et al. proposed electrochemically induced spinel-layered phase transition of  $\text{Mn}_3\text{O}_4$ .<sup>[67]</sup> As displayed in Figure 21(a, b), when charging up to 1.9 V, with the dissolution of  $\text{Mn}^{2+}$  and oxidation of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$ ,  $\text{Mn}_3\text{O}_4$  was oxidized to  $\text{Mn}_5\text{O}_8$  intermediate and further transformed into layered Zn-birnessite for  $\text{Zn}^{2+}$  insertion/extraction. As a result, the capacity of  $\text{Mn}_3\text{O}_4$  cathode gradually increases from 85.6 to  $239.2 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  (Figure 21c), and a superior rate and cycle performance is achieved (Figure 21d, e).

In principle, MnO with divalent manganese is electrochemically inactive, but it can also store  $\text{Zn}^{2+}$  after electrochemical activation. Li et al. analyzed the activation process of MnO through ex-situ XPS and XRD tests (Figure 21f–h).<sup>[141]</sup> With the dissolution of  $\text{Mn}^{2+}$ , the valence of Mn continues to rise in the



**Figure 21.** a) Ex-situ XRD of  $\text{Mn}_3\text{O}_4$  at first cycle, b) reaction pathway of  $\text{Mn}_3\text{O}_4$  in the first cycle, c) GCD curves of different cycles at  $0.1 \text{ A g}^{-1}$ , d) rate performance and e) cycling performance at  $0.5 \text{ A g}^{-1}$  of  $\text{Mn}_3\text{O}_4$  cathode. Adapted with permission from Ref. [67]. Copyright (2018) Elsevier. f) Discharge/charge profiles for the first 3 cycles of MnO cathode, g) ex-situ XPS and h) XRD of MnO. Adapted with permission from Ref. [141]. Copyright (2020) Elsevier. i) GCD curve of the first two cycles of MnS-EDO cathode, j) ex-situ XRD of MnS-EDO. Adapted with permission from Ref. [143]. Copyright (2020) Elsevier.

first 2 cycles, and the MnO changes to  $\text{Mn}_3\text{O}_4$  for  $\text{Zn}^{2+}$  and  $\text{H}^+$  insertion/extraction. Similarly, commercial MnO particles were oxidized to porous layered-type  $\text{MnO}_2$  nanosheets through the electrochemical activation,<sup>[142]</sup> which indicates that the originally inactive MnO could act as the cathode material of ZIBs directly, and exhibit an excellent electrochemical performance.

In addition, Chen et al. reported an electrochemically derived oxide (MnS-EDO) from MnS through in situ electrochemical activation (Figure 21i, j).<sup>[143]</sup> In the first charge, inactive MnS is completely transformed to Zn birnessite and  $\text{ZnMnO}_3$  for  $\text{Zn}^{2+}$  and  $\text{H}^+$  insertion/extraction. The MnS-EDO demonstrates a large number of active sites, high electrochemical reactivity, fast ion diffusion kinetics, and excellent structural stability, thus exhibiting an outstanding rate capability and long-term stability with a capacity of  $104 \text{ mAh g}^{-1}$  after 4000 cycles at  $3 \text{ A g}^{-1}$ .

## 4. Conclusion and Perspectives

Among the various cathode materials, manganese-based cathode materials with the unique advantages such as low cost, non-toxic, high specific capacity ( $308 \text{ mAh g}^{-1}$ ) and operating voltage ( $\sim 1.4 \text{ V}$ ), are very competitive for ZIBs compared with others.

Herein, first, various synthetic methods of manganese-based cathode materials are summarized, including hydrothermal method, electrodeposition method, redox reaction method, etc. Different methods affect the morphology and structure of manganese-based cathode materials and then affect the specific capacity, rate performance and cycle stability.

The inherent poor conductivity,  $\text{Mn}^{2+}$  dissolution and structural instability of manganese-based cathode materials make it difficult to reach the theoretical specific capacity. What's more, the rate performance and cycle performance are also unsatisfactory, which severely restricts its application. 5 performance optimization strategies are analyzed in detail, as follows:

- (1) Structure design: Nanostructures improve the specific surface area and ion diffusion, providing more active sites for energy storage and promoting the fast ion/electron kinetics, and the porous and hollow structures significantly alleviate the volume change, improving the structural stability.
  - (2) Compositing with conductive materials: The composite materials not only retain the high capacity of manganese itself, but also exert the excellent conductivity of another component.
  - (3) Pre-intercalation: It is able to expand the layer spacing, thereby promoting the ion insertion/extraction. Furthermore, the pre-intercalated crystal water, ions, and molecules act as "structural pillars" to avoid the structural collapse.
  - (4) Defect engineering: Defect engineering modifies the crystal structure, thus substantially improving the conductivity and structural stability and the introduction of defects provides more ion intercalation channels and active sites, which is beneficial to the fast electrochemical kinetic process.
  - (5) Electrochemical activation: The charging and discharging process itself is an electrochemical activation process. Especially, this strategy can activate the manganese-based compounds without electrochemical activity, such as  $\text{MnO}$ .
- At present, the above 5 strategies have been applied to optimize the performance of manganese-based cathode materials. Apart from them, the following strategies may be feasible to improve the performance:

- (1) Design of the heterostructure: The properties of heterostructure arise from the contributions of each component as well as from processes that occur at the interfaces between the components. Therefore, well-designed heterostructures may help improve the performance of manganese-based cathode materials.
- (2) Modification of surface or interface: It is noteworthy that with the charge transfer and ion diffusion, the structure of surface or interface will change, which has a great impact on the electrochemical properties. At present, coating can be regarded as a surface modification method. Other methods and modification mechanisms are worthy of consideration.

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** manganese-based cathode materials · performance optimization · synthesis · zinc-ion batteries

- [1] Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, *Chem. Rev.* **2011**, *111*, 3577.
- [2] S. Chu, A. Majumdar, *Nature* **2012**, *488*, 294.
- [3] S. Chu, Y. Cui, N. Liu, *Nat. Mater.* **2017**, *16*, 16.
- [4] B. Dunn, H. Kamath, J.-M. Tarascon, *Science* **2011**, *334*, 928.
- [5] X. Wang, X. Lu, B. Liu, D. Chen, Y. Tong, G. Shen, *Adv. Mater.* **2014**, *26*, 4763.
- [6] D. Larcher, J. M. Tarascon, *Nat. Chem.* **2015**, *7*, 19.
- [7] G. Zubi, R. Dufo-Lopez, M. Carvalho, G. Pasaoglu, *Renewable Sustainable Energy Rev.* **2018**, *89*, 292.
- [8] M. Li, J. Lu, Z. Chen, K. Amine, *Adv. Mater.* **2018**, *30*, 1800561.
- [9] G. Assat, J.-M. Tarascon, *Nat. Energy* **2018**, *3*, 373.
- [10] W. Lee, S. Muhammad, C. Sergey, H. Lee, J. Yoon, Y.-M. Kang, W.-S. Yoon, *Angew. Chem. Int. Ed.* **2020**, *59*, 2578.
- [11] T. Sun, Z.-J. Li, H.-G. Wang, D. Bao, F.-L. Meng, X.-B. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 10662.
- [12] L. Fan, X. Li, X. Song, N. Hu, D. Xiong, A. Koo, X. Sun, *ACS Appl. Mater. Interfaces* **2018**, *10*, 2637.
- [13] J. Liu, Y. Zhang, L. Zhang, F. Xie, A. Vasileff, S.-Z. Qiao, *Adv. Mater.* **2019**, *31*, 1901261.
- [14] T. Jin, Q. Han, L. Jiao, *Adv. Mater.* **2020**, *32*, 1806304.
- [15] J.-Y. Hwang, S.-T. Myung, Y.-K. Sun, *Adv. Funct. Mater.* **2018**, *28*, 1802938.
- [16] X. Wu, Y. Chen, Z. Xing, C. W. K. Lam, S.-S. Pang, W. Zhang, Z. Ju, *Adv. Energy Mater.* **2019**, *9*, 1900343.
- [17] J. Ding, H. Zhang, H. Zhou, J. Feng, X. Zheng, C. Zhong, E. Paek, W. Hu, D. Mitlin, *Adv. Mater.* **2019**, *31*, 1900429.
- [18] S. Chong, L. Sun, C. Shu, S. Guo, Y. Liu, W. Wang, H. K. Liu, *Nano Energy* **2019**, *63*, 103868.
- [19] X.-Y. Yang, J.-J. Xu, Z.-W. Chang, D. Bao, Y.-B. Yin, T. Liu, J.-M. Yan, D.-P. Liu, Y. Zhang, X.-B. Zhang, *Adv. Energy Mater.* **2018**, *8*, 1702242.
- [20] Q. Xiong, G. Huang, X.-B. Zhang, *Angew. Chem. Int. Ed.* **2020**, *59*, 19311–19319.
- [21] T. Liu, Y. Yu, X.-Y. Yang, J. Wang, X.-B. Zhang, *Small Structures* **2020**, *1*, 2000015.
- [22] K. Chen, G. Huang, X.-B. Zhang, *Chin. J. Chem.* **2021**, *39*, 32–42.
- [23] H. Li, L. Ma, C. Han, Z. Wang, Z. Liu, Z. Tang, C. Zhi, *Nano Energy* **2019**, *62*, 550.
- [24] N. Zhang, X. Chen, M. Yu, Z. Niu, F. Cheng, J. Chen, *Chem. Soc. Rev.* **2020**, *49*, 4203.
- [25] L. E. Blanc, D. Kundu, L. F. Nazar, *Joule* **2020**, *4*, 771–799.
- [26] K. Chen, D.-Y. Yang, G. Huang, X.-B. Zhang, *Acc. Chem. Res.* **2021**, *54*, 632–641.
- [27] Z. Yi, G. Chen, F. Hou, L. Wang, J. Liang, *Adv. Energy Mater.* **2021**, *11*, 2003065.
- [28] D. Selvakumaran, A. Pan, S. Liang, G. Cao, *J. Mater. Chem. A* **2019**, *7*, 18209.
- [29] S. Huang, J. Zhu, J. Tian, Z. Niu, *Chem. Eur. J.* **2019**, *25*, 14480.
- [30] C. Li, X. Zhang, W. He, G. Xu, R. Sun, *J. Power Sources* **2020**, *449*, 227596.
- [31] Y. Shi, Y. Chen, L. Shi, K. Wang, B. Wang, L. Li, Y. Ma, Y. Li, Z. Sun, W. Ali, S. Ding, *Small* **2020**, *16*, 2000730.
- [32] J. Ming, J. Guo, C. Xia, W. Wang, H. N. Alshareef, *Mat. Sci. Eng.* **2019**, *135*, 58.
- [33] X. Liu, J. Yi, K. Wu, Y. Jiang, Y. Liu, B. Zhao, W. Li, J. Zhang, *Nanotechnology* **2019**, *31*, 122001.
- [34] Y.-L. Zhao, Y.-H. Zhu, X.-B. Zhang, *InfoMat* **2020**, *2*, 237.
- [35] V. Mathew, B. Sambandam, S. Kim, S. Kim, S. Park, S. Lee, M. H. Alfaruqi, V. Soundharajan, S. Islam, D. Y. Putro, J. Y. Hwang, Y. K. Sun, J. Kim, *ACS Energy Lett.* **2020**, *5*, 2376.
- [36] Y. Yang, Y. Tang, S. Liang, Z. Wu, G. Fang, X. Cao, C. Wang, T. Lin, A. Pan, J. Zhou, *Nano Energy* **2019**, *61*, 617.
- [37] F. Liu, Z. Chen, G. Fang, Z. Wang, Y. Cai, B. Tang, J. Zhou, S. Liang, *Nano-Micro Lett.* **2019**, *11*, 25.

- [38] C. Liu, Z. Neale, J. Zheng, X. Jia, J. Huang, M. Yan, M. Tian, M. Wang, J. Yang, G. Cao, *Energy Environ. Sci.* **2019**, *12*, 2273.
- [39] S. Liu, H. Zhu, B. Zhang, G. Li, H. Zhu, Y. Ren, H. Geng, Y. Yang, Q. Liu, C. C. Li, *Adv. Mater.* **2020**, 2001113.
- [40] Z. Cao, L. Wang, H. Zhang, X. Zhang, J. Liao, J. Dong, J. Shi, P. Zhuang, Y. Cao, M. Ye, J. Shen, P. M. Ajayan, *Adv. Funct. Mater.* **2020**, 2000472.
- [41] Y. Zhao, Y. Wang, Z. Zhao, J. Zhao, T. Xin, N. Wang, J. Liu, *Energy Storage Mater.* **2020**, 28, 64.
- [42] H. Yao, Q. Li, M. Zhang, Z. Tao, Y. Yang, *Chem. Eng. J.* **2020**, 392, 123653.
- [43] G. Kasiri, J. Glenneberg, A. B. Hashemi, R. Kun, F. La Mantia, *Energy Storage Mater.* **2019**, *19*, 360.
- [44] T. Xin, Y. Wang, N. Zhang, Y. Zhao, H. Li, Z. Zhang, J. Liu, *J. Mater. Chem. A* **2019**, *7*, 23076.
- [45] C. Han, H. Li, R. Shi, T. Zhang, J. Tong, J. Li, B. Li, *J. Mater. Chem. A* **2019**, *7*, 23378.
- [46] R. Cang, K. Ye, K. Zhu, J. Yan, J. Yin, K. Cheng, G. Wang, D. Cao, *J. Energy Chem.* **2020**, *45*, 52.
- [47] L. Ma, S. Chen, C. Long, X. Li, Y. Zhao, Z. Liu, Z. Huang, B. Dong, J. A. Zapien, C. Zhi, *Adv. Energy Mater.* **2019**, *9*, 1902446.
- [48] P. Yu, Y. Zeng, H. Zhang, M. Yu, Y. Tong, X. Lu, *Small* **2019**, *15*, 1804760.
- [49] B. Tang, L. Shan, S. Liang, J. Zhou, *Energy Environ. Sci.* **2019**, *12*, 3288.
- [50] M. H. Alfaruqi, J. Gim, S. Kim, J. Song, J. Jo, S. Kim, V. Mathew, J. Kim, *J. Power Sources* **2015**, *288*, 320.
- [51] Q.-H. Zhao, A.-Y. Song, W.-G. Zhao, R.-Z. Qin, S.-X. Ding, X. Chen, Y.-L. Song, L.-Y. Yang, H. Lin, S.-N. Li, F. Pan, *Angew. Chem. Int. Ed.* **2021**, *60*, 4169.
- [52] N. Zhang, F. Cheng, J. Liu, L. Wang, X. Long, X. Liu, F. Li, J. Chen, *Nat. Commun.* **2017**, *8*, 405.
- [53] X. Liao, C. Pan, Y. Pan, C. Yin, *J. Alloys Compd.* **2021**, *888*, 161619.
- [54] C. Guo, H. Liu, J. Li, Z. Hou, J. Liang, J. Zhou, Y. Zhu, Y. Qian, *Electrochim. Acta* **2019**, *304*, 370.
- [55] S. Wang, W. Ma, Z. Sang, F. Hou, W. Si, J. Guo, J. Liang, D.-A. Yang, *J. Energy Chem.* **2022**, *67*, 82.
- [56] N. Liu, K. Mohanapriya, J. Pan, Y. Hu, Y. Sun, X. Liu, *J. Electrochem. Soc.* **2020**, *167*, 040517.
- [57] B. Yang, X. Cao, S. Wang, N. Wang, C. Sun, *Electrochim. Acta* **2021**, 385, 138447.
- [58] S. Islam, M. H. Alfaruqi, J. Song, S. Kim, P. Duong Tung, J. Jo, S. Kim, V. Mathew, J. P. Baboo, Z. Xiu, J. Kim, *J. Energy Chem.* **2017**, *26*, 815.
- [59] J. Wang, J.-G. Wang, X. Qin, Y. Wang, Z. You, H. Liu, M. Shao, *ACS Appl. Mater. Interfaces* **2020**, *12*, 34949.
- [60] C. Wang, Y. Zeng, X. Xiao, S. Wu, G. Zhong, K. Xu, Z. Wei, W. Su, X. Lu, *J. Energy Chem.* **2020**, *43*, 182.
- [61] Y. Liu, X. Chi, Q. Han, Y. Du, J. Huang, Y. Liu, J. Yang, *J. Power Sources* **2019**, *443*, 227244.
- [62] Y. Zhang, S. Deng, Y. Li, B. Liu, G. Pan, Q. Liu, X. Wang, X. Xia, J. Tu, *Energy Storage Mater.* **2020**, *29*, 52.
- [63] Y. Wu, Y. Tao, X. Zhang, K. Zhang, S. Chen, Y. Liu, Y. Ding, M. Cai, X. Liu, S. Dai, *Sci. China Mater.* **2020**, *63*, 1196.
- [64] J. Wang, J.-G. Wang, H. Liu, C. Wei, F. Kang, *J. Mater. Chem. A* **2019**, *7*, 13727.
- [65] F. Tang, J. Gao, Q. Ruan, X. Wu, X. Wu, T. Zhang, Z. Liu, Y. Xiang, Z. He, X. Wu, *Electrochim. Acta* **2020**, *353*, 136570.
- [66] C. Zhu, G. Fang, J. Zhou, J. Guo, Z. Wang, C. Wang, J. Li, Y. Tang, S. Liang, *J. Mater. Chem. A* **2018**, *6*, 9677.
- [67] J. Hao, J. Mou, Q. Zhang, L. Dong, W. Liu, C. Xu, F. Kang, *Electrochim. Acta* **2018**, *259*, 170.
- [68] C. Yang, M. Han, H. Yan, F. Li, M. Shi, L. Zhao, *J. Power Sources* **2020**, *452*, 227826.
- [69] M. Shi, B. Wang, Y. Shen, J. Jiang, W. Zhu, Y. Su, M. Narayanasamy, S. Angaiah, C. Yan, Q. Peng, *Chem. Eng. J.* **2020**, *399*, 125627.
- [70] Y. Lee, J. Lee, G. An, *Chem. Eng. J.* **2021**, *414*, 128916.
- [71] X. Zang, L. Li, J. Meng, L. Liu, Y. Pan, Q. Shao, C. Ning, *J. Mater. Sci. Technol.* **2021**, *74*, 52.
- [72] K. Lu, B. Song, Y. Zhang, H. Ma, J. Zhang, *J. Mater. Chem. A* **2017**, *5*, 23628.
- [73] J. Xu, Q. Gao, Y. Xia, X. Lin, W. Liu, M. Ren, F. Kong, S. Wang, C. Lin, *J. Colloid Interface Sci.* **2021**, *598*, 419.
- [74] M. H. Alfaruqi, S. Islam, V. Mathew, J. Song, S. Kim, T. Duong Pham, J. Jo, S. Kim, J. P. Baboo, Z. Xiu, J. Kim, *Appl. Surf. Sci.* **2017**, *404*, 435.
- [75] B. Ding, P. Zheng, P. A. Ma, J. Lin, *Adv. Mater.* **2020**, *32*, 1905823.
- [76] Z. Li, Y. Huang, J. Zhang, S. Jin, S. Zhang, H. Zhou, *Nanoscale* **2020**, *12*, 4150.
- [77] X. Jia, C. Liu, Z. G. Neale, J. Yang, G. Cao, *Chem. Rev.* **2020**, *120*, 7795.
- [78] W. Sun, F. Wang, S. Hou, C. Yang, X. Fan, Z. Ma, T. Gao, F. Han, R. Hu, M. Zhu, C. Wang, *J. Am. Chem. Soc.* **2017**, *139*, 9775.
- [79] F. Kataoka, T. Ishida, K. Nagita, V. Kumbhar, K. Yamabuki, M. Nakayama, *ACS Appl. Energy Mater.* **2020**, *3*, 4720.
- [80] A. Dhiman, D. G. Ivey, *Batteries & Supercaps* **2020**, *3*, 293.
- [81] K. Wang, X. Zhang, J. Hang, X. Zhang, X. Sun, C. Li, W. Liu, Q. Li, Y. Ma, *ACS Appl. Mater. Interfaces* **2018**, *10*, 24573.
- [82] Y. Zeng, X. Zhang, Y. Meng, M. Yu, J. Yi, Y. Wu, X. Lu, Y. Tong, *Adv. Mater.* **2017**, *29*, 1700274.
- [83] Z. Wang, Z. Ruan, Z. Liu, Y. Wang, Z. Tang, H. Li, M. Zhu, T. F. Hung, J. Liu, Z. Shi, C. Zhi, *J. Mater. Chem. A* **2018**, *6*, 8549.
- [84] T. Sun, Q. Nian, S. Zheng, X. Yuan, Z. Tao, *J. Power Sources* **2020**, *478*, 228758.
- [85] C. Xu, B. Li, H. Du, F. Kang, *Angew. Chem. Int. Ed.* **2012**, *51*, 933.
- [86] C. Xu, S. W. Chiang, J. Ma, F. Kang, *J. Electrochem. Soc.* **2013**, *160*, A93.
- [87] A. Huang, W. Zhou, A. Wang, M. Chen, Q. Tian, J. Chen, *J. Energy Chem.* **2021**, *54*, 475.
- [88] M. H. Alfaruqi, J. Gim, S. Kim, J. Song, P. Duong Tung, J. Jo, Z. Xiu, V. Mathew, J. Kim, *Electrochem. Commun.* **2015**, *60*, 121.
- [89] D. Xu, B. Li, C. Wei, Y.-B. He, H. Du, X. Chu, X. Qin, Q.-H. Yang, F. Kang, *Electrochim. Acta* **2014**, *133*, 254.
- [90] L. Jiang, Z. Wu, Y. Wang, W. Tian, Z. Yi, C. Cai, Y. Jiang, L. Hu, *ACS Nano* **2019**, *13*, 10376.
- [91] Q. Zhao, X. Chen, Z. Wang, L. Yang, R. Qin, J. Yang, Y. Song, S. Ding, M. Weng, W. Huang, J. Liu, W. Zhao, G. Qian, K. Yang, Y. Cui, H. Chen, F. Pan, *Small* **2019**, *15*, 1904545.
- [92] Y. Wang, Z. Wu, L. Jiang, W. Tian, C. Zhang, C. Cai, L. Hu, *Nanoscale Adv.* **2019**, *1*, 4365.
- [93] H. Ren, J. Zhao, L. Yang, Q. Liang, S. Madhavi, Q. Yan, *Nano Res.* **2019**, *12*, 1347.
- [94] T. Zhao, G. Zhang, F. Zhou, S. Zhang, C. Deng, *Small* **2018**, *14*, 1802320.
- [95] M. Shi, P. Xiao, C. Yang, Y. Sheng, B. Wang, J. Jiang, L. Zhao, C. Yan, *J. Power Sources* **2020**, *463*, 228209.
- [96] S. Kim, J. Kim, D. B. Ahn, S. Lee, *Small* **2020**, *16*, 2002837.
- [97] D. Feng, T.-N. Gao, L. Zhang, B. Guo, S. Song, Z.-A. Qiao, S. Dai, *Nano-Micro Lett.* **2020**, *12*, 14.
- [98] X.-T. Guo, J.-M. Li, X. Jin, Y.-H. Han, Y. Lin, Z.-W. Lei, S.-Y. Wang, L.-J. Qin, S.-H. Jiao, R.-G. Cao, *Nanomaterials* **2018**, *8*, 301.
- [99] Y. Fu, Q. Wei, G. Zhang, X. Wang, J. Zhang, Y. Hu, D. Wang, L. Zuin, T. Zhou, Y. Wu, S. Sun, *Adv. Energy Mater.* **2018**, *8*, 1801445.
- [100] L. Chen, Z. Yang, H. Qin, X. Zeng, J. Meng, H. Chen, *Electrochim. Acta* **2019**, *317*, 155.
- [101] H. Moon, K.-H. Ha, Y. Park, J. Lee, M.-S. Kwon, J. Lim, M.-H. Lee, D.-H. Kim, J. H. Choi, J.-H. Choi, K. T. Lee, *Adv. Sci.* **2021**, *8*, 2003714.
- [102] X. Wu, Y. Xiang, Q. Peng, X. Wu, Y. Li, F. Tang, R. Song, Z. Liu, Z. He, X. Wu, *J. Mater. Chem. A* **2017**, *5*, 17990.
- [103] X. Zhang, J. Li, H. Ao, D. Liu, L. Shi, C. Wang, Y. Zhu, Y. Qian, *Energy Storage Mater.* **2020**, *30*, 337.
- [104] C. Liu, Q. Li, H. Sun, Z. Wang, W. Gong, S. Cong, Y. Yao, Z. Zhao, *J. Mater. Chem. A* **2020**, *8*, 24031.
- [105] L. Chen, Z. Yang, F. Cui, J. Meng, Y. Jiang, J. Long, X. Zeng, *Mater. Chem. Front.* **2020**, *4*, 213.
- [106] L. Chen, Z. Yang, H. Qin, X. Zeng, J. Meng, *J. Power Sources* **2019**, *425*, 162.
- [107] B. Wu, G. Zhang, M. Yan, T. Xiong, P. He, L. He, X. Xu, L. Mai, *Small* **2018**, *14*, 1703850.
- [108] Y. Liu, X. Zhou, R. Liu, X. Li, Y. Bai, H. Xiao, Y. Wang, G. Yuan, *ACS Appl. Mater. Interfaces* **2019**, *11*, 19191.
- [109] X. Zang, X. Wang, H. Liu, X. Ma, W. Wang, J. Ji, J. Chen, R. Li, M. Xue, *ACS Appl. Mater. Interfaces* **2020**, *12*, 9347.
- [110] J. Huang, X. Tang, K. Liu, G. Fang, Z. He, Z. Li, *Mater. Today* **2020**, *17*, 100475.
- [111] J. Mao, F. F. Wu, W.-H. Shi, W.-X. Liu, X.-L. Xu, G.-F. Cai, Y.-W. Li, X.-H. Cao, *Chin. J. Polym. Sci.* **2020**, *38*, 514.
- [112] J. Zhang, Y. Huang, Z. Li, C. Gao, S. Jin, S. Zhang, X. Wang, H. Zhou, *Nanotechnology* **2020**, *31*, 375401.
- [113] X. Zhu, Z. Cao, W. Wang, H. Li, J. Dong, S. Gao, D. Xu, L. Li, J. Shen, M. Ye, *ACS Nano* **2021**, *15*, 2971.
- [114] S. Luo, L. Xie, F. Han, W. Wei, Y. Huang, H. Zhang, M. Zhu, O. G. Schmidt, L. Wang, *Adv. Funct. Mater.* **2019**, *29*, 1901336.
- [115] M. Shi, B. Wang, C. Chen, J. Lang, C. Yan, X. Yan, *J. Mater. Chem. A* **2020**, *8*, 24635.



- [116] K. W. Nam, H. Kim, J. H. Choi, J. W. Choi, *Energy Environ. Sci.* **2019**, *12*, 1999.
- [117] Y. Jiang, D. Ba, Y. Li, J. Liu, *Adv. Sci.* **2020**, *7*, 1902795.
- [118] X.-Z. Zhai, J. Qu, S.-M. Hao, Y.-Q. Jing, W. Chang, J. Wang, W. Li, Y. Abdelkrim, H. Yuan, Z.-Z. Yu, *Nano-Micro Lett.* **2020**, *12*, 56.
- [119] S. Guo, S. Liang, B. Zhang, G. Fang, D. Ma, J. Zhou, *ACS Nano* **2019**, *13*, 13456.
- [120] T. Sun, Q. Nian, S. Zheng, J. Shi, Z. Tao, *Small* **2020**, *16*, 2000597.
- [121] Y. Zhang, S. Deng, G. Pan, H. Zhang, B. Liu, X.-L. Wang, X. Zheng, Q. Liu, X. Wang, X. Xia, J. Tu, *Small Methods* **2020**, 1900828.
- [122] J. Huang, Z. Wang, M. Hou, X. Dong, Y. Liu, Y. Wang, Y. Xia, *Nat. Commun.* **2018**, *9*, 1.
- [123] Y. Zhang, L. Tao, C. Xie, D. Wang, Y. Zou, R. Chen, Y. Wang, C. Jia, S. Wang, *Adv. Mater.* **2020**, *32*, 1905923.
- [124] J. Xie, X. Yang, Y. Xie, *Nanoscale* **2020**, *12*, 4283.
- [125] W. Xu, C. Sun, K. Zhao, X. Cheng, S. Rawal, Y. Xu, Y. Wang, *Energy Storage Mater.* **2019**, *16*, 527.
- [126] T. Xiong, Z. G. Yu, H. Wu, Y. Du, Q. Xie, J. Chen, Y.-W. Zhang, S. J. Pennycook, W. S. V. Lee, J. Xue, *Adv. Energy Mater.* **2019**, *9*, 1803815.
- [127] Q. Tan, X. Li, B. Zhang, X. Chen, Y. Tian, H. Wan, L. Zhang, L. Miao, C. Wang, Y. Gan, J. Jiang, Y. Wang, H. Wang, *Adv. Energy Mater.* **2020**, *10*, 2001050.
- [128] G. Fang, C. Zhu, M. Chen, J. Zhou, B. Tang, X. Cao, X. Zheng, A. Pan, S. Liang, *Adv. Funct. Mater.* **2019**, *29*, 1808375.
- [129] H. Zhang, J. Wang, Q. Liu, W. He, Z. Lai, X. Zhang, M. Yu, Y. Tong, X. Lu, *Energy Storage Mater.* **2019**, *21*, 154.
- [130] F. Lu, Q. Chen, S. Geng, M. Allix, H. Wu, Q. Huang, X. Kuang, *J. Mater. Chem. A* **2018**, *6*, 24232.
- [131] C. Sun, X. Tang, Z. Yin, D. Liu, Y.-J. Wang, G. Yang, A. Ignaszak, J. Zhang, *Nano Energy* **2020**, *68*, 104376.
- [132] L. Luo, K. Zhou, R. Lian, Y. Lu, Y. Zhen, J. Wang, S. Mathur, Z. Hong, *Nano Energy* **2020**, *72*, 104716.
- [133] T. Koketsu, J. Ma, B. J. Morgan, M. Body, C. Legein, P. Goddard, O. J. Borkiewicz, P. Strasser, D. Dambournet, *Energy Storage Mater.* **2020**, *25*, 154.
- [134] C. Zhu, G. Fang, S. Liang, Z. Chen, Z. Wang, J. Ma, H. Wang, B. Tang, X. Zheng, J. Zhou, *Energy Storage Mater.* **2020**, *24*, 394.
- [135] N. Zhang, F. Cheng, Y. Liu, Q. Zhao, K. Lei, C. Chen, X. Liu, J. Chen, *J. Am. Chem. Soc.* **2016**, *138*, 12894.
- [136] D. Zhang, J. Cao, X. Zhang, N. Insin, S. Wang, J. Han, Y. Zhao, J. Qin, Y. Huang, *Adv. Funct. Mater.* **2021**, 2009412.
- [137] J. Ji, H. Wan, B. Zhang, C. Wang, Y. Gan, Q. Tan, N. Wang, J. Yao, Z. Zheng, P. Liang, J. Zhang, H. Wang, L. Tao, Y. Wang, D. Chao, H. Wang, *Adv. Energy Mater.* **2021**, *11*, 2003203.
- [138] Y. Tao, Z. Li, L. Tang, X. Pu, T. Cao, D. Cheng, Q. Xu, H. Liu, Y. Wang, Y. Xia, *Electrochim. Acta* **2020**, *331*, 135296.
- [139] H. Pan, Y. Shao, P. Yan, Y. Cheng, K.-S. Han, Z. Nie, C. Wang, J. Yang, X. Li, P. Bhattacharya, K. T. Mueller, J. Liu, *Nat. Energy* **2016**, *1*, 16039.
- [140] M. Chamoun, W. R. Brant, C.-W. Tai, G. Karlsson, D. Noreus, *Energy Storage Mater.* **2018**, *15*, 351.
- [141] W. Li, X. Gao, Z. Chen, R. Guo, G. Zou, H. Hou, W. Deng, X. Ji, J. Zhao, *Chem. Eng. J.* **2020**, *402*, 125509.
- [142] J. Wang, J.-G. Wang, H. Liu, Z. You, C. Wei, F. Kang, *J. Power Sources* **2019**, *438*, 226951.
- [143] X. Chen, W. Li, Y. Xu, Z. Zeng, H. Tian, M. Velayutham, W. Shi, W. Li, C. Wang, D. Reed, V. V. Khramtsov, X. Li, X. Liu, *Nano Energy* **2020**, *75*, 104869.

---

Manuscript received: October 25, 2021

Revised manuscript received: November 18, 2021

Accepted manuscript online: December 1, 2021

Version of record online: December 2, 2021