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Bulk-phase and interface stability strategies of manganese oxide cathodes for aqueous Zn-MnO_x batteries

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The cyclic stability of the MnO_x cathodes for rechargeable zinc ion batteries have substantial obstacles due to Mn³⁺ disproportionation produces Mn²⁺ caused by Jahn Teller lattice distortion effect in the process of Zn²⁺ inter/deintercalation. This mini review summarized bulk-phase and interface stability strategies of manganese oxide cathodes for aqueous Zn-MnO_x batteries from the regulation of bulk electronic state of manganese oxide improves its structural stability and the formation of beneficial SEI layer at the interface of electrolyte. It provides theoretical support for the design of manganese oxide cathode materials for aqueous zinc ion batteries with high stability.

KEYWORDS

MnO_x, stability, cathode, interface, zinc ion battery

Introduction

Human society has been seeking new energy storage equipment with higher performance (such as higher energy density, power density and long life), low cost and high security to alleviate outstanding environmental problems and severe energy situation (Pomerantseva et al., 2019; Chen et al., 2021; Zheng et al., 2021). At present, lithium-ion batteries are widely used in mobile devices because of their high energy/power density and long life (Manthiram, 2020; Chen et al., 2022). However, with the increasing demand for large-scale energy storage such as electric vehicles and smart grid energy storage systems, as well as the high price of lithium resources and security, other high-performance and low-cost energy storage devices are needed to supplement (Jia et al., 2020; Zhong et al., 2020; Zhou et al., 2020). In recent years, batteries based on other monovalent metal ions (Na⁺, K⁺) and multivalent metal ions (Ca²⁺, Mg²⁺, Zn²⁺, Al³⁺, etc.) have attracted extensive attention due to their rich content and low cost (Li et al., 2020; Pan et al., 2021; Zhou and Guo, 2021). The aqueous zinc ion batteries used zinc metal as the anode material, which has many advantages, such as high theoretical specific capacity (820 mAh g⁻¹), low oxidation-reduction potential of Zn²⁺/Zn(-0.76 V relative to SHE), which endows the aqueous zinc ion battery with the intrinsic characteristics of environmental friendliness, low cost and high safety (Cui et al., 2022). Especially, zinc ion battery as a kind of

multivalent ion batteries, its energy density tends to increase due to the presence of high-capacity multivalent metals as the anode (Selvakumaran et al., 2019). The volumetric energy density of zinc ion battery is as high as 5851 mAh cm⁻³ higher than Li⁺ (2061 mAh cm⁻³), Mg²⁺ (3834 mAh cm⁻³), Ca²⁺ (2072 mAh cm⁻³) (Chen et al., 2019). This makes the aqueous rechargeable zinc ion battery one of the most promising electrochemical energy storage devices.

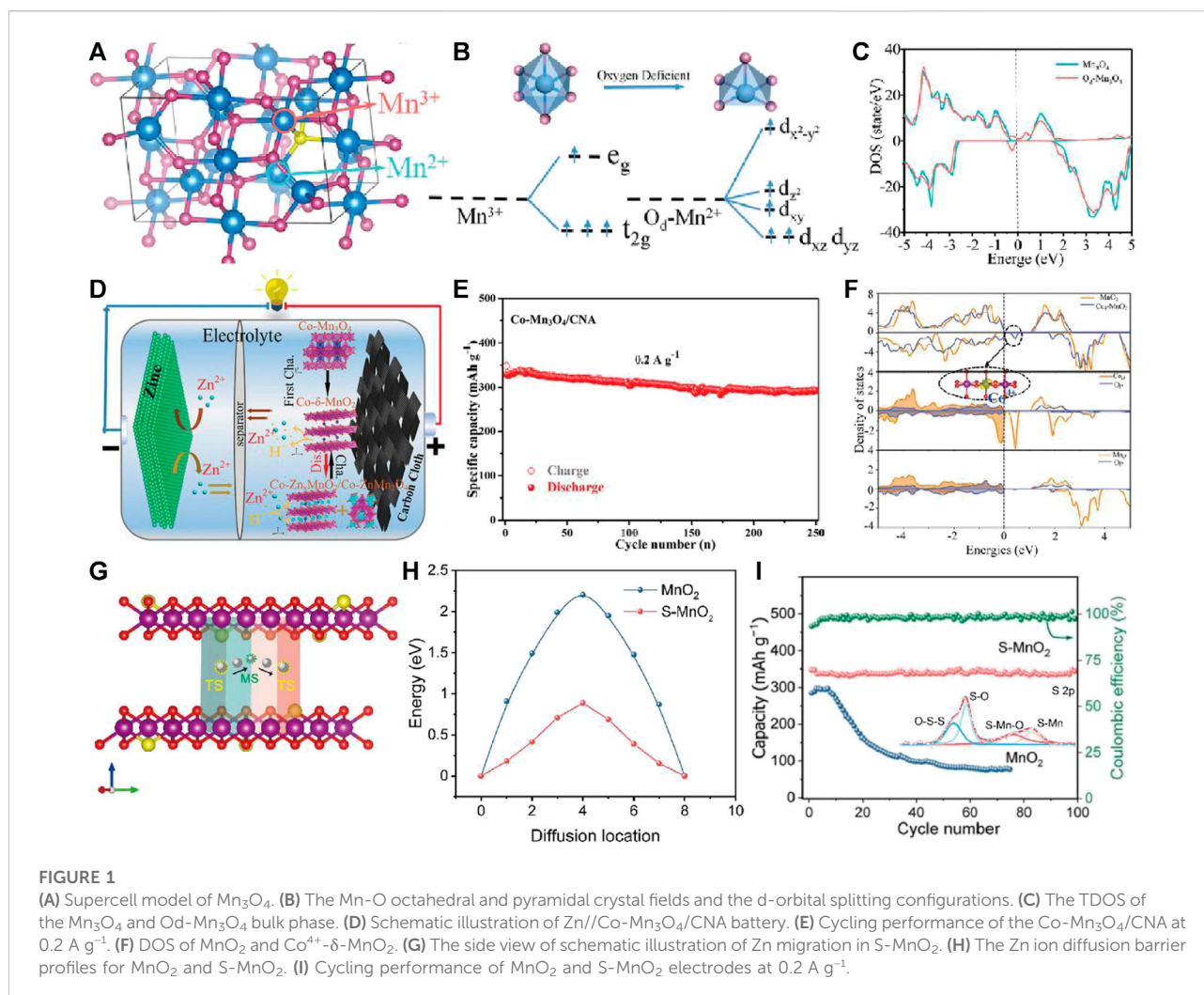
Because zinc metal anode has many advantages, the development of aqueous rechargeable zinc ion battery is largely limited by the cathode materials (Xia et al., 2018; Liu et al., 2019). At present, manganese based materials (MnO₂, Mn₃O₄, MnO, etc.) (Tang et al., 2019; Zhu et al., 2020), vanadium based materials (V₂O₅, VO₂, Zn_{0.25}V₂O₅, etc.) (Wan and Niu, 2019; Boruah et al., 2021; Wang et al., 2022) and Prussian blue (Ming et al., 2019) have been studied as cathode materials for aqueous Zn ion batteries. Among them, manganese oxides (MnO_x) have many advantages, such as high operating voltage (~1.35 V), high theoretical specific capacity (based on single electron reaction ~308 mAh g⁻¹), multiple valence states of manganese, low cost, etc., making MnO_x considered as one of the most potential cathode materials for aqueous rechargeable zinc ion batteries (Wang et al., 2020; Li et al., 2022; Zhang et al., 2022). These outstanding advantages make MnO_x, including α-, β-, γ-, λ-, δ- MnO₂, MnO, Mn₃O₄ and other structures are sought after. In 2015, S. H. Oh reported that α-MnO₂ (2 × 2 channels) showed a specific capacity of 195 mAh g⁻¹ at 10 mA g⁻¹ and maintained 70% after 30 cycles (Lee et al., 2015). Although MnO_x cathode materials show considerable specific capacity, they face the problem of rapid degradation of cycle stability. In order to solve this problem, Y.Y. Xia and Y.G. Wang inserted polyaniline into layered MnO₂, which improved the stability of the structure and improved the cycle stability (Huang et al., 2018). J. Zhou and S.Q. Liang grew Mn₃O₄ *in situ* on stainless steel mesh, and the structure maintained 500 cycles at 500 mA g⁻¹ (Zhu et al., 2018). These measures can help to improve the battery stability, but there are still substantial obstacles to the application of MnO_x based rechargeable zinc ion battery cathode materials (Ming et al., 2019): 1) Mn³⁺ disproportionation produces Mn²⁺ caused by Jahn Teller (J-T) lattice distortion effect in the process of Zn²⁺ inter/deintercalation, which will directly lead to the decline of MnO_x cycle stability. 2) The wide band gap of MnO_x leads to low conductivity, which results in its unsatisfactory rate capability.

In this mini review, the stability and rate capability improvement strategies of manganese oxide cathode materials are proposed from two perspectives: 1) The electronic state structure of MnO_x is regulated through defect engineering (O/Mn vacancy and transition metal doping), which can improve its structural stability, band gap and electrochemical activity, to inhibit Mn dissolution caused by J-T effect, accelerate ion/electron conduction, and improve

cycle stability and rate capability. 2) The interfacial reaction kinetics of MnO_x cathode and electrolyte are optimized enriching with electrolyte additives, which can be inhibit the dissolution of Mn in the process of MnO_x zinc storage and accelerate the diffusion kinetics of ion interface, so as to effectively improve the cycle stability and specific capacity. This review provides theoretical support for the design of manganese oxide cathode materials for aqueous zinc ion batteries with high stability.

Bulk-phase regulation

By changing the electronic state structure of t_{2g}³e_gⁿ1 with high spin of Mn³⁺ and substituting transition metal elements for Mn³⁺, the structural stability of MnO_x cathode material is improved to suppress the J-T effect, so as to improve its cycle stability, which has been deeply studied in the application of lithium/sodium ion batteries (Li et al., 2009; Xiao et al., 2018). Defect engineering (such as vacancy and doping) can improve the structural stability of MnO_x, inhibit Mn³⁺ disproportionation caused by J-T effect, and improve the cycle stability of MnO_x zinc storage process (H Zheng et al., 2022; Ji et al., 2022). At present, part of the work has carried out defect engineering research on manganese-based cathode materials for aqueous zinc ion batteries. In 2019, J. M. Xue pointed out that the Gibbs free energy of Zn²⁺ adsorption in the vicinity of O vacancy can be reduced to thermoneutral value (≈0.05 eV) by introduction of O vacancy in MnO₂ lattice, which suggested that Zn²⁺ adsorption/desorption process on oxygen-deficient MnO₂ is more reversible (Xiong et al., 2019). L. Q. Mai Doped Ti by surface gradient α-MnO₂ produces electron compensated O vacancy, which accelerates the migration rate of ions/electrons, thus improving the diffusion coefficient of Zn²⁺/H⁺ in Ti-MnO₂ (Lian et al., 2019). However, it mainly focuses on improving the electron/ion transfer rate to improve its performance, and less attention is paid to the influence of defect states on the electronic structure of Mn³⁺ and the improvement of the structural stability of MnO_x to inhibit J-T from improving its zinc storage cycle stability. H. Wang and H. Z. Wan introduced O vacancy into Mn-O octahedron of Mn₃O₄ to improve the electronic structure of Mn₃O₄, thus improving the cycle stability (Figures 1A–C) (Tan et al., 2020). At the same time, they have effectively improved the structural stability of Mn₃O₄ and realized high cycle stability by replacing Mn with Co²⁺ (Figures 1D–F) (Ji et al., 2021). The sulfur doped MnO₂ (S-MnO₂) nanosheets have been found to be high-performance cathodes for zinc ion batteries (Figures 1G–I). The doped S atoms in O sites with lower electronegativity can improve its bulk conductivity, reduce the electrostatic interaction with Zn²⁺, and accelerate the reaction kinetics to improve cycle stability



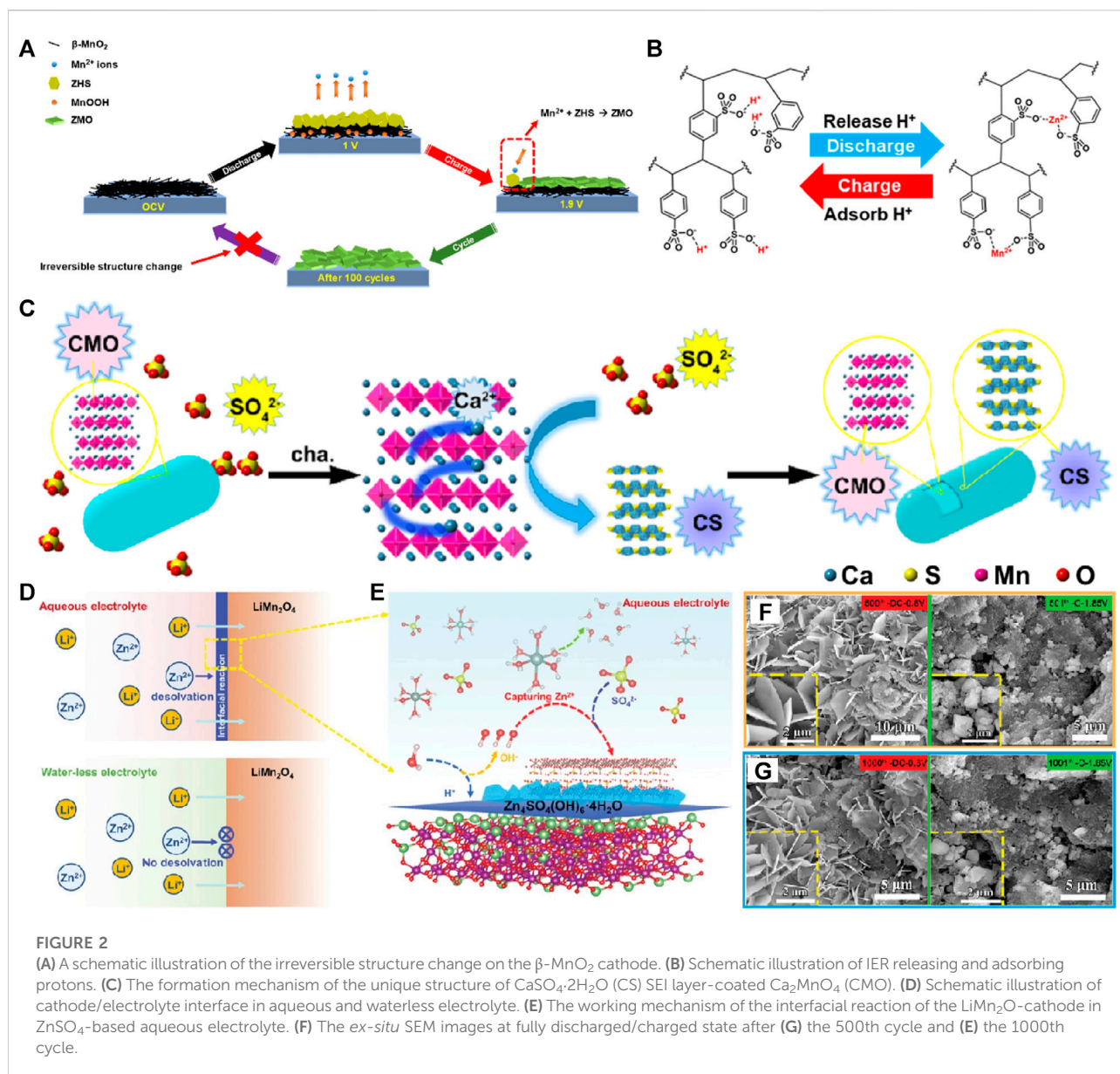
(Zhao et al., 2022). The MnO_x cathode can be modified by defect engineering (O/Mn vacancy or transition metal element doping, etc.) to improve structural stability, inhibit Mn dissolution, and effectively improve cycle stability. This has important theoretical significance for the commercialization of manganese based zinc ion batteries.

Electrode/electrolyte interface optimization

The electrode/electrolyte interface reaction process plays a key role in the performance of electrochemical energy storage devices. The different types of electrodes to optimize the electrode/electrolyte interface reaction dynamics using advanced electrolyte and new electrolyte additives can maximize the performance of aqueous zinc ion batteries (Wang et al., 2018; Xu et al., 2019). In 2016, J. Liu added Mn^{2+} into 2 M ZnSO_4 electrolyte to improve the Mn^{2+}

dissolution chemical potential of $\alpha\text{-MnO}_2$ electrode material in the process of zinc storage, which can effectively inhibit the J-T effect and improves cycle stability of $\alpha\text{-MnO}_2$ /Zn battery (Pan et al., 2016). P. Chen etc (Wu et al., 2022) reported that the by-product of $\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot x\text{H}_2\text{O}$ (ZHS) from pH fluctuation can react with Mn^{2+} during charge process at over 1.55 V to form a lowly crystallized $(\text{Zn,Mn})_2\text{Mn}_5\text{O}_{12} \cdot 4\text{H}_2\text{O}$ (ZMO), which severely hinders the capacity of MnO_2 cathode rapid fading (Figures 2A,B). The introduction of ion exchange resin (IER) can adjust the proton distribution in the electrolyte and eliminate the above adverse ZHS, so as to effectively inhibit the formation of ZMO, to improve cycle stability of MnO_2 as cathode of Zn/ MnO_2 battery. Although some studies have shown that electrolyte optimization can improve the cycle stability of MnO_x cathode materials, it is difficult to ensure that the cycle stability is improved without loss of specific capacity and rate performance.

In addition, the adverse effects of zinc hydroxysulfate by-products produced at the electrode/electrolyte interface of Mn



based cathode materials in the process of $\text{Zn}^{2+}/\text{H}^+$ co-insertion have not attracted much attention. The interface of the MnOx electrode/electrolyte form a layer of zinc hydroxysulfate favorable SEI film from adverse factors by adjusting electrolyte environment, which can inhibit the dissolution of Mn^{2+} , and effectively improve the cycle stability and the specific capacity and rate performance at the same time. J. Zhou found in the research of $\text{Ca}_2\text{MnO}_4/\text{Zn}$ battery containing $(\text{Zn}^{2+} + \text{Mn}^{2+})\text{SO}_4^{2-}$ electrolyte that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ -SEI film formed on the surface of Ca_2MnO_4 cathode material, which effectively inhibited the dissolution of Mn during charge and discharge, and significantly improved the stability of the battery compared with the

battery containing only CH_3COO electrolyte (Figure 2C) (Shan et al., 2019). G.Z. Fang and S.Q. Liang put forward the relationship between the desolvation of Zn^{2+} from $[\text{Zn}(\text{OH})_2]^{2+}$ -solvation shell and the electrolyte/electrode interfacial reaction to form $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ phase (Figures 2D–G). The Zn// MnO_2 battery based on electrolyte optimization displayed the cycling stability of over 2000 cycles (Zhang et al., 2020). Thus, the process dynamics of the interface between cathode and electrolyte can be optimized by adjusting the electrolyte additives to match the manganese removal cathode materials, and the cycle stability can be effectively improved.

Conclusion and perspectives

This work summarizes the bulk-phase and interface stability strategies of manganese oxide cathodes for aqueous Zn-MnO₂ batteries. On the one hand, defect engineering regulated MnO_x cathode can improve its structural stability and conductivity to improve cycle stability and rate capability. On the other hand, the interfacial reaction kinetics of MnO_x cathode and electrolyte are optimized enriching with electrolyte additives can inhibit the dissolution of Mn and accelerate the diffusion kinetics of ion interface to effectively improve the cycle stability and specific capacity.

Although a lot of research work has been done on the optimization and modification of the cycle stability of MnO_x cathode materials, the research on the regulation of bulk electronic states and the mechanism of interface adaptation is not deep and systematic, and the cycle stability that meets the commercial application has not been completely solved. To further improve the overall performance of MnO_x cathode in aqueous solution system, we put forward the following anticipations: 1) To explore the best synthetic means and defect types of bulk electronic state regulation of manganese oxide, and systematically study the internal mechanism of bulk electronic state regulation; 2) The Zn²⁺ solvation structure was optimized by adding polar molecules or other additives into the electrolyte to improve the interface structure of manganese oxide and electrolyte. 3) Seeking an electrolyte adaptation system for *in-situ* construction of favorable SEI film on the surface of MnO_x cathode, and establish a theoretical system of interface optimization; 4) Study the influence of parameters such as cathode and anode matching, electrolyte proportion and adaptation on device performance, and carry out a comprehensive evaluation of key performance such as energy

density, power density and cycle stability of aqueous MnO_x/Zn battery.

Author contributions

GY was responsible for text editing and article composing. HW were responsible for article review and revision.

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Conflict of interest

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References

- Boruah, B. D., Mathieson, A., Park, S. K., Zhang, X., Wen, B., Tan, L. F., et al. (2021). Vanadium dioxide cathodes for high-rate photo-rechargeable zinc-ion batteries. *Adv. Energy Mat.* 11, 2100115. doi:10.1002/aenm.202100115
- Chen, L. N., An, Q. Y., and Mai, L. Q. (2019). Recent advances and prospects of cathode materials for rechargeable aqueous zinc-ion batteries. *Adv. Mat. Interfaces* 6, 1900387. doi:10.1002/admi.201900387
- Chen, M. Z., Liu, Y. F., Zhang, Y. Y., Xing, G. C., and Tang, Y. X. (2022). Lithium-rich sulfide/selenide cathodes for next-generation lithium-ion batteries: Challenges and perspectives. *Chem. Commun.* 58, 3591–3600. doi:10.1039/d2cc00477a
- Chen, M. Z., Zhang, Y. Y., Xing, G. C., Chou, S. L., and Tang, Y. X. (2021). Electrochemical energy storage devices working in extreme conditions. *Energy Environ. Sci.* 14, 3323–3351. doi:10.1039/d1ee00271f
- Cui, H. L., Ma, L. T., Huang, Z. D., Chen, Z., and Zhi, C. Y. (2022). Organic materials-based cathode for zinc ion battery. *SmartMat* 3, 1. doi:10.1002/smm2.1110
- H Zheng, Z., Yang, G. C., Yao, J., Li, J. Y., Zheng, J. J., Wu, Z. A., et al. (2022). High-valence molybdenum promoted proton migration and inhibited dissolution for long-life aqueous Zn-MnO₂ batteries. *Appl. Surf. Sci.* 592, 153335. doi:10.1016/j.apsusc.2022.153335
- Huang, J. H., Wang, Z., Hou, M. Y., Dong, X. L., Liu, Y., Wang, Y. G., et al. (2018). Polyaniline-intercalated manganese dioxide nanolayers as a high-performance cathode material for an aqueous zinc-ion battery. *Nat. Commun.* 9, 2906. doi:10.1038/s41467-018-04949-4
- Ji, J., Wan, H. Z., Zhang, B., Wang, C., Gan, Y., Tan, Q. Y., et al. (2021). Co^{2+/3+/4+}-Regulated electron state of Mn-O for superb aqueous zinc-manganese oxide batteries. *Adv. Energy Mat.* 11 (6), 2003203. doi:10.1002/aenm.202003203
- Ji, J., Yao, J., Xu, Y. C., Wan, H. Z., Zhang, B., Lv, L., et al. (2022). Promoting proton migration kinetics by Ni²⁺ regulating enables improved aqueous Zn-MnO₂ batteries. Zhengzhou, China: Energy & Environmental Materials. doi:10.1002/eem2.12340
- Jia, X. X., Liu, C. F., Neale, Z. G., Yang, J. H., and Cao, G. Z. (2020). Active materials for aqueous zinc ion batteries: Synthesis, crystal structure, morphology, and electrochemistry. *Chem. Rev.* 120 (15), 7795–7866. doi:10.1021/acs.chemrev.9b00628
- Lee, B., Lee, H. R., Kim, H., Chung, K. Y., Cho, B. W., and Oh, S. H. (2015). Elucidating the intercalation mechanism of zinc ions into α-MnO₂ for rechargeable zinc batteries. *Chem. Commun.* 51, 9265–9268. doi:10.1039/c5cc02585k
- Li, M., Lu, J., Ji, X. L., Li, Y. G., Shao, Y. Y., Chen, Z. W., et al. (2020). Design strategies for nonaqueous multivalent-ion and monovalent-ion battery anodes. *Nat. Rev. Mat.* 5, 276–294. doi:10.1038/s41578-019-0166-4
- Li, S. Y., Yu, D. X., Liu, L. N., Yao, S. Y., Wang, X. Q., Jin, X., et al. (2022). *In-situ* electrochemical induced artificial solid electrolyte interphase for MnO@C

- nanocomposite enabling long-lived aqueous zinc-ion batteries. *Chem. Eng. J.* 430, 132673. doi:10.1016/j.ccej.2021.132673
- Li, X. F., Xu, Y. L., and Wang, C. L. (2009). Suppression of Jahn–Teller distortion of spinel LiMn_2O_4 cathode. *J. Alloys Compd.* 479, 310–313. doi:10.1016/j.jallcom.2008.12.081
- Lian, S. T., Sun, C. L., Xu, W. N., Huo, W. C., Luo, Y. Z., Zhao, K. N., et al. (2019). Built-in oriented electric field facilitating durable Zn– MnO_2 battery. *Nano Energy* 62, 79–84. doi:10.1016/j.nanoen.2019.04.038
- Liu, F., Chen, Z. X., Fang, G. Z., Wang, Z. Q., Cai, Y. S., Tang, B. Y., et al. (2019). V_2O_5 nanospheres with mixed vanadium valences as high electrochemically active aqueous zinc-ion battery cathode. *Nanomicro. Lett.* 11, 25. doi:10.1007/s40820-019-0256-2
- Manthiram, A. (2020). A reflection on lithium-ion battery cathode chemistry. *Nat. Commun.* 11, 1550. doi:10.1038/s41467-020-15355-0
- Ming, J., Guo, J., Xia, C., Wang, W. X., and Alshareef, H. N. (2019). Zinc-ion batteries: Materials, mechanisms, and applications. *Mater. Sci. Eng. R Rep.* 135, 58–84. doi:10.1016/j.mser.2018.10.002
- Pan, H. L., Shao, Y. Y., Yan, P. F., Cheng, Y. W., Han, K. S., Nie, Z. M., et al. (2016). Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. *Nat. Energy* 1, 16039. doi:10.1038/nenergy.2016.39
- Pan, Z. H., Liu, X. M., Yang, J., Li, X., Liu, Z. L., Loh, X. J., et al. (2021). Aqueous rechargeable multivalent metal-ion batteries: Advances and challenges. *Adv. Energy Mat.* 11, 2100608. doi:10.1002/aenm.202100608
- Pomerantseva, E., Bonaccorso, F., Feng, X. L., Cui, Y., and Gogotsi, Y. (2019). Energy storage: The future enabled by nanomaterials. *Science* 366, eaan8285. doi:10.1126/science.aan8285
- Selvakumaran, D., Pan, A. Q., Liang, S. Q., and Cao, G. Z. (2019). A review on recent developments and challenges of cathode materials for rechargeable aqueous Zn-ion batteries. *J. Mat. Chem. A* 7, 18209–18236. doi:10.1039/c9ta05053a
- Shan, G., Quan, L. S., Shan, Z. B., Zhao, F. G., Dan, M., and Jiang, Z. (2019). Cathode interfacial layer formation via *in situ* electrochemically charging in aqueous zinc-ion battery. *ACS Nano* 13, 13456–13464. doi:10.1021/acsnano.9b07042
- Tan, Q. Y., Li, X. T., Zhang, B., Chen, X., Tian, Y. W., Wan, H. Z., et al. (2020). Valence engineering via *in situ* carbon reduction on octahedron sites Mn_3O_4 for ultra-long cycle life aqueous Zn-ion battery. *Adv. Energy Mat.* 10 (38), 2001050. doi:10.1002/aenm.202001050
- Tang, B. Y., Shan, L. T., Liang, S. Q., and Zhou, J. (2019). Issues and opportunities facing aqueous zinc-ion batteries. *Energy Environ. Sci.* 12, 3288–3304. doi:10.1039/c9ee02526j
- Wan, F., and Niu, Z. Q. (2019). Design strategies for vanadium-based aqueous zinc-ion batteries. *Angew. Chem. Int. Ed. Engl.* 58, 16508–16517. doi:10.1002/ange.201903941
- Wang, F., Borodin, O., Gao, T., Fan, X. L., Sun, W., Han, F. D., et al. (2018). Highly reversible zinc metal anode for aqueous batteries. *Nat. Mat.* 17, 543–549. doi:10.1038/s41563-018-0063-z
- Wang, N. Z., Yang, G. C., Gan, Y., Wan, H. Z., Chen, X., Wang, C., et al. (2020). Contribution of cation addition to MnO_2 nanosheets on stable Co_3O_4 nanowires for aqueous zinc-ion battery. *Front. Chem.* 8, 793. doi:10.3389/fchem.2020.00793
- Wang, X., Zhang, Z. C., Huang, M., Feng, J. K., Xiong, S. L., and Xi, B. J. (2022). *In situ* electrochemically activated vanadium oxide cathode for advanced aqueous Zn-ion batteries. *Nano Lett.* 22, 119–127. doi:10.1021/acsnanolett.1c03409
- Wu, Y., Zhi, J., Han, M., Liu, Z. Y., Shi, Q. Y., Liu, Y., et al. (2022). Regulating proton distribution by ion exchange resin to achieve long lifespan aqueous Zn– MnO_2 battery. *Energy Storage Mater.* 51, 599–609. doi:10.1016/j.ensm.2022.07.009
- Xia, C., Guo, J., Lei, Y. J., Liang, H. F., Zhao, C., and Alshareef, H. N. (2018). Rechargeable aqueous zinc-ion battery based on porous framework zinc pyrovanadate intercalation cathode. *Adv. Mat.* 30, 1705580. doi:10.1002/adma.201705580
- Xiao, Y., Wang, P. F., Yin, Y. X., Zhu, Y. F., Yang, X., Zhang, X. D., et al. (2018). A layered-tunnel intergrowth structure for high-performance sodium-ion oxide cathode. *Adv. Energy Mat.* 8, 1800492. doi:10.1002/aenm.201800492
- Xiong, T., Yu, Z. G., Wu, H. J., Du, Y. H., Xie, Q. D., Chen, J. S., et al. (2019). Defect engineering of oxygen-deficient manganese oxide to achieve high-performing aqueous zinc ion battery. *Adv. Energy Mat.* 9, 1803815. doi:10.1002/aenm.201803815
- Xu, W. N., Zhao, K. N., Huo, W. C., Wang, Y. Z., Yao, G., Gu, X., et al. (2019). Diethyl ether as self-healing electrolyte additive enabled long-life rechargeable aqueous zinc ion batteries. *Nano Energy* 62, 275–281. doi:10.1016/j.nanoen.2019.05.042
- Zhang, L., Yang, S. H., Fu, W. Q., Cui, Y. W., Wang, J. Q., Zhao, D. G., et al. (2022). Plasma-induced $\epsilon\text{-MnO}_2$ based aqueous zinc-ion batteries and their dissolution-deposition mechanism. *J. Mater. Sci. Technol.* 127, 206–213. doi:10.1016/j.jmst.2022.03.028
- Zhang, T. S., Tang, Y., Fang, G. Z., Zhang, C. Y., Zhang, H. L., Guo, X., et al. (2020). Electrochemical activation of manganese-based cathode in aqueous zinc-ion electrolyte. *Adv. Funct. Mater.* 30, 2002711.
- Zhao, Y. J., Zhang, P. J., Liang, J. R., Xia, X. Y., Ren, L. T., Song, L., et al. (2022). Uncovering sulfur doping effect in MnO_2 nanosheets as an efficient cathode for aqueous zinc ion battery. *Energy Storage Mater.* 47, 424–433. doi:10.1016/j.ensm.2022.02.030
- Zheng, J., Bock, D. C., Tang, T., Zhao, Q., Yin, J., Tallman, K. R., et al. (2021). Regulating electrodeposition morphology in high-capacity aluminium and zinc battery anodes using interfacial metal-substrate bonding. *Nat. Energy* 6, 398–406. doi:10.1038/s41560-021-00797-7
- Zhong, C., Liu, B., Ding, J., Liu, X. R., Zhong, Y. W., Li, Y., et al. (2020). Decoupling electrolytes towards stable and high-energy rechargeable aqueous zinc–manganese dioxide batteries. *Nat. Energy* 5, 440–449. doi:10.1038/s41560-020-0584-y
- Zhou, J. H., and Guo, S. J. (2021). Carbon-based anode materials for potassium-ion batteries: From material, mechanism to performance. *SmartMat* 2, 176–201. doi:10.1002/smm2.1042
- Zhou, W. H., Zhu, D., He, J., Li, J. C., Chen, H., Chen, Y. G., et al. (2020). A scalable top-down strategy toward practical metrics of Ni–Zn aqueous batteries with total energy densities of 165 Wh kg^{-1} and 506 Wh L^{-1} . *Energy Environ. Sci.* 13 (11), 4157–4167. doi:10.1039/d0ee01221a
- Zhu, C. Y., Fang, G. Z., Liang, S. Q., Chen, Z. X., Wang, Z. Q., Ma, J. Y., et al. (2020). Electrochemically induced cationic defect in MnO intercalation cathode for aqueous zinc-ion battery. *Energy Storage Mater.* 24, 394–401. doi:10.1016/j.ensm.2019.07.030
- Zhu, C. Y., Fang, G. Z., Zhou, J., Guo, J. H., Wang, Z. Q., Wang, C., et al. (2018). Binder-free stainless steel/ Mn_3O_4 nanoflower composite: A high-activity aqueous zinc-ion battery cathode with high-capacity and long-cycle-life. *J. Mat. Chem. A Mat.* 6, 9677–9683. doi:10.1039/c8ta01198b