Phase Engineering of Mo-V Oxides for Zinc-Ion Batteries

Gan Qu  
Shenzhen University

Chuntian Qiu  
Shenzhen University

Jun Wang  
Shenzhen University

Jiewen Tan  
South China University of Technology

Shuangfeng Jia  
Wuhan University  https://orcid.org/0000-0001-8199-5115

Zheshehng Chen  
Synchrotron SOLEIL

Jean-Pascal Rueff  
Synchrotron SOLEIL  https://orcid.org/0000-0003-3594-918X

Guangyuan Zheng  
Department of Chemical and Biomolecular Engineering, National University of Singapore  
https://orcid.org/0000-0003-0286-5908

Chenliang Su  
Shenzhen University  https://orcid.org/0000-0002-8453-1938

Bingbing Tian (✉️ tianbb2011@szu.edu.cn)  
Shenzhen University  https://orcid.org/0000-0003-1508-6217

Article

Keywords: Zn2+ Host Materials, Open Framework, Tunnel Structures, Diffusion Kinetics, Cathode Design

DOI: https://doi.org/10.21203/rs.3.rs-94180/v1

License: Creative Commons Attribution 4.0 International License. Read Full License
Abstract

With the ever-increasing demands of grid-scale energy storage, aqueous zinc-ion batteries (ZIBs) have garnered increasing attention around the world. However, limited Zn2+ host materials have hindered the commercialization of ZIBs. Hence, Mo-V oxides with different phase structures (orth-, tri-, and tetra-MoVO) were precisely constructed to develop phase-dependent Mo-V oxide cathodes for Zn2+ storage in ZIBs. The open frameworks and varied tunnel structures formed a favorable alternative for achieving suitable Zn2+ diffusion kinetics. With optimized phase engineering, a high specific capacity of approximately 400 mAh g\(^{-1}\) and the excellent cyclic stability of 1000 cycles were achieved with orth-MoVO as the cathode. The large amount of six- and seven-member rings in the orth-MoVO phase, which allow for alternative Zn2+ insertion, played a vital role in hosting Zn2+ ions reversibly. The proposed phase engineering strategy provides a new approach toward cathode design in ZIBs.

Introduction

Nowadays, the energy crisis and environmental pollution are the most critical global problems.\(^{1-5}\) Although numerous clean and renewable energy sources have been successfully investigated, these energy sources are severely limited by time and space.\(^{6-11}\) Therefore, an efficient large-scale energy storage system is necessitated.\(^{12-16}\) Aqueous zinc-ion batteries (ZIBs) are ideal candidates, owing to their low-cost and environmental efficiency.\(^{17-20}\) Zinc is abundant on earth, and Zn metal is easy to exploit, transfer, and store.\(^{21,22}\) Additionally, it exhibits high theoretical capacities of 819 mAh g\(^{-1}\) and 5851 mA h mL\(^{-1}\).\(^{23-26}\) The redox potential for Zn/Zn\(^{2+}\) is as low as −0.76 V versus the standard hydrogen electrode, when the overpotential for the hydrogen evolution reaction is very high.\(^{27-30}\) The two-electron transfer reaction renders high energy density feasible for ZIBs.\(^{31-34}\) Moreover, the neutral electrolyte provides high conductivity, alleviates the zinc loss, and eliminates the environmental impact. Regardless of these advantages, developing suitable cathodes in ZIBs is still an enormous challenge.\(^{35-39}\) In fact, most cathode materials often undergo a structural collapse and severe degradation.\(^{37,40}\) Therefore, innovations with regard to new cathode materials with high-energy density, which are capable of preventing structural collapse and degradation, are urgently needed.\(^{41}\) Mo-V-based oxides with a solid open framework, tunable phase, tunnel structures, and improved conductivity owing to the intervalence electron transfer between Mo and V, are potential candidates for Zn\(^{2+}\) storage in ZIBs.\(^{42,43}\)

Phase engineering is a promising strategy for structural modulation in developing advanced cathode materials.\(^{44}\) The crystal phase with a defined arrangement and organization of atoms and/or building blocks significantly influences the physical and chemical properties.\(^{45}\) Thus, subtle structural changes may generate different properties. For instance, the conductivities and structural stability are closely associated with the atomic arrangements.\(^{46}\) The organization of building blocks dictates the thermodynamic and kinetic processes, when the adsorption and activation of reactant molecules significantly depend on the atomic configurations. These phase engineering guidelines contribute toward
the designing and synthesizing of the desired phase-dependent cathodes for ZIBs. Moreover, successful phase engineering approaches may allow the further investigation of the charge/discharge mechanism and structure-activity relationship for fine-tuning the electrochemical performance of ZIBs.

In this study, Mo-V oxides with diverse phase structures (orth-, tri-, and tetra-MoVO) were obtained, which comprised corner-sharing \([\text{MO}_6]\) octahedra and pentagonal \([\text{(M)}\text{M}_5\text{O}_{27}]\) to construct three-, four-, five-, six-, and seven-member rings. The open framework and varied phase structures were favorable to the \(\text{Zn}^{2+}\) diffusion kinetics. Consequently, high specific capacity (400 mAh g\(^{-1}\)) and excellent cyclic stability of 1000 cycles were achieved with orth-MoVO as the cathode. The \(\text{Zn}^{2+}\) insertion/extraction process was analysed in detail to elucidate the energy storage mechanism. Compared with tri- and tetra-MoVO, a large amount of six- and seven-member rings in orth-MoVO plays a vital role in hosting the \(\text{Zn}^{2+}\) reversibly.

Both Mo and V form various polyoxometalates, which may have acted as the building blocks of supramolecular compounds and constituted mixed polyoxometalates, thus resulting in a stabilized molecular architecture and exhibiting unique physical and chemical properties. The phases and bulk frameworks could be tuned by controlling the arrangement and organization of the Mo- and V-blocks. Thus, the modified metal-oxygen bond, pore size, and affinity in the molecules may have contributed toward achieving versatile performance. Therefore, it is possible to employ and engineer Mo-V oxides to reversibly host \(\text{Zn}^{2+}\) by adjusting the building blocks and designing suitable phase and tunnel structures.

**Results And Discussion**

By regulating the building units, a series of defined phases (orth-, tri-, and tetra-MoVO) could be fabricated and applied in ZIBs. Those Mo-V oxides consisted of the pentagonal polyoxomolybdate \([\text{Mo}_6\text{O}_{21}]\) with a central \(\text{MO}_7\) \((\text{M}=\text{Mo, V})\) pentagonal bipyramidal unit and edge-sharing \(\text{MO}_6\) octahedral. The existed various continuous channels in the [001] direction could give a positive effect on the \(\text{Zn}^{2+}\) diffusion (insets of Figure 1a, 1d, and 1g). The variable tunnel structures endowed the open channel frameworks for the three oxides, and resulted in varied diffusion kinetics of \(\text{Zn}^{2+}\). Compared with the tri-MoVO phase, orth-MoVO structure possesses more six- and seven-member rings in the [001] direction, while the tetra-MoVO only comprised four- and five-member rings. Power X-ray diffraction (XRD) patterns were employed to characterize the crystalline structure (Figure 1a, 1d, and 1g), in agreement with previously reported data. The well-defined XRD patterns indicate high crystallinity. The high-resolution transmission electron microscopy (HR-TEM) images in Figure 1b, 1e, and 1h show the lattice space of the three samples, and the morphological and elemental features are shown in Figure 1c, 1f, and 1i. The TEM images of the three samples show a 1D rod-like shape, with a diameter of approximately 200 nm. Moreover, the crystallographic growth occurred along the [001] direction. The elemental dispersion spectroscopy (EDS) mappings reveal that the distributions of the Mo, V, and O elements are completely consistent with the TEM images of the three samples. As shown in Figure S1, the ultra-visible-near infrared (UV-vis-NIR) diffuse reflectance spectra of the orth-, tri-, and tetra-MoVO exhibit an apparent
absorption in the visible light region, owing to the electron transfer between Mo and V. The unique band structure indicates improved conductivity, which is favorable to the electrochemical process.

To estimate the Zn$^{2+}$ storage ability of the as-prepared Mo-V oxides, the CR2016-type cell was assembled with Mo-V oxides as cathodes and Zn foil discs as anodes. The electrolyte was 2 M of aqueous Zn(CF$_3$SO$_3$)$_2$ solution. Figure 2 shows the cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) curves of the orth-, tri-, and tetra-MoVO cathodes. Obviously, the orth-MoVO exhibited a Zn$^{2+}$ insertion potential of approximately 0.55 V and a multistep extraction potential of approximately 0.55, 0.7, and 0.8 V (Figure 2a and 2d). In the subsequent 2$^{nd}$ and 3$^{rd}$ cycles, the Zn$^{2+}$ insertion processes became facile and the CV curves exhibited good reversible properties. In Figure 2b, the tri-MoVO exhibited similar CV as the orth-MoVO and an additional Zn$^{2+}$ insertion potential at 0.3 V. However, the tetra-MoVO exhibited one pair of redox peaks (Figure 2c), which suffered from severe irreversibility in the subsequent 2$^{nd}$ and 3$^{rd}$ cycles. As shown in Figure 2d-f, the orth-MoVO had a specific capacity of approximately 400 mAh g$^{-1}$ at 0.1 A g$^{-1}$ owing to the large amount of six- and seven-member ring tunnels, while the tri- and tetra-MoVO delivered less than 200 mAh g$^{-1}$. Additionally, the specific capacity of the orth-MoVO was approximately without attenuation during the first three cycles. Hence, the four- and five-member ring tunnels of the tetra-MoVO contribute toward slow diffusion kinetics, which lead to a lower specific capacity. The poor reversibility of the tetra-MoVO was caused by the large charge repulsion force of Zn$^{2+}$ and the narrow tunnels. Thus, the orth-MoVO is a more suitable cathode for ZIBs. The galvanostatic intermittent titration technique (GITT) measurements shows that the Zn$^{2+}$ diffusion coefficient for the orth-MoVO range from $10^{-8}$ to $10^{-9}$ cm$^2$ s$^{-1}$ order of magnitude, revealing the fast ion migration.

The exact atomic ratio and electrochemical performances of the orth-MoVO was investigated in detail to clarify the Zn$^{2+}$ storage mechanism. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES), thermogrametric (TG) and in-situ XRD analysis revealed the molecular formula of the orth-MoVO can be defined as Mo$_{2.55}$VO$_{9.43}$ (Figure S2 and S3). The specific capacity gradually decreased from 400 mAh g$^{-1}$ at 0.1 A g$^{-1}$ to 170 mAh g$^{-1}$ at 2 A g$^{-1}$ (Figure 2g and 2h). And the orth-MoVO delivered a specific capacity of 347 mAh g$^{-1}$ at 0.1 A g$^{-1}$ after 100 cycles (Figure 2i). Additionally, the specific capacity reached 145 mAh g$^{-1}$ at 2 A g$^{-1}$ after 1000 cycles. However, the rate capabilities were quite poor for the tri- and tetra-MoVO, and both of them underwent severe capacity degradation at 0.1 A g$^{-1}$ (Figure S4). The discharge plot was divided into two parts for the GCD curves. One part was a platform at 0.65 V, while the other part was an inclined line from 0.55 V to 0.2 V. Figure S6 shows the GCD plots at 0.1 A g$^{-1}$ with Zn(CF$_3$SO$_3$)$_2$ dissolved in water and acetonitrile, respectively. The 1$^{st}$ discharge plot in water has a higher platform than that in acetonitrile, which indicates a more facile Zn$^{2+}$ diffusion process in water, compared with that in acetonitrile. The 2$^{nd}$ discharge plots in water and acetonitrile are similar, delivering the same specific capacity. This phenomenon indicates that water exerts a lubricant effect on the 1$^{st}$ Zn$^{2+}$ insertion process. However, the 2$^{nd}$ discharge plot illustrates that the extraction of Zn$^{2+}$ is
The residual Zn\textsuperscript{2+} may have acted as pillars for expanding and stabilizing the crystalline orth-MoVO structure, which facilitates the subsequent insertion process. In addition, the discharge plots for orth-MoVO rule out the intercalation of H\textsuperscript{+} in aqueous electrolyte.

In-situ XRD was carried out to clarify the crystal structure evolution of the orth-MoVO during the Zn\textsuperscript{2+} insertion/extraction process. Figure 3a shows the detailed pseudo-colouring XRD patterns evolution when the orth-MoVO undergoes a discharge/charge process (Figure S7). The XRD pattern of the prepared cathode is similar to that of the pristine orth-MoVO. During the Zn\textsuperscript{2+} insertion process, the diffraction peaks at 22.3° and 26.7° slightly moved toward a higher degree, while the peaks at 7.0°, 8.2°, 9.4°, 11.2°, 24.2°, 27.1°, 27.4°, 27.6°, 28.6°, and 29.6° shifted toward a lower degree. Moreover, the peaks at 27.4° and 27.6° merged together. The peaks at 7.0°, 8.2°, 9.4°, and 22.3° are attributed to the (020), (120), (210), and (001) crystal planes. These results indicate that the lattice space of (020) increases, while that of (001) decreases during the Zn\textsuperscript{2+} insertion process. During the Zn\textsuperscript{2+} extraction process, all peaks approximately revert to the pristine state, which indicates excellent reversibility of the phase structure. In-situ Fourier transfer infrared spectroscopy (FT-IR) was conducted (Figure S8). The peak at 901 cm\textsuperscript{-1} exhibited a red-shift while the peak at 937 cm\textsuperscript{-1} exhibited a blue shift during the Zn\textsuperscript{2+} insertion process. After the extraction of Zn\textsuperscript{2+}, the two peaks merged at 925 cm\textsuperscript{-1}. These two peaks are considered to have been induced by the V-O and Mo-O vibrations, which indicate that Zn\textsuperscript{2+} penetrates into the tunnels and coordinates with the O atoms. Additionally, a portion of Zn\textsuperscript{2+} remains in tunnels after the extraction process, and acts as pillars for stabilizing the orth-MoVO. The extended X-ray absorption fine structure (EXAFS) ensues, which indicates bond variations at different discharge/charge stages. Figure S9 shows the K-edge FFT function spectra of Mo, V, and Zn. After a full discharge/charge process, the first dominant peaks of Mo and V slightly increased, and there were approximately no changes for Zn.

X-ray photoelectron spectroscopy (XPS) was performed to further demonstrate the changes of Mo, V, and C during the discharge/charge process (Figure S10). This XPS results indicated that CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{-} underwent an insertion/extraction process along with the Zn\textsuperscript{2+} ions, which is consistent with the EDS results presented in Figure S11. The XPS and EDS analysis further revealed that the Zn\textsuperscript{2+} extraction process was not completely reversible in the first cycle. The TEM image of the orth-MoVO morphology under 0.2 V (Figure S12b) shows a precipitation layer on the surface. This precipitation layer decomposed during the charging process (Figure S12c). As shown in Figure S13, the voltage of the orth-MoVO cathode remained stable below 0.25 V after the discharge process. However, the voltage sharply jumped to about 0.6 V after dipping in HCl, which may be induced by the dissolution of the precipitation layer.

Subsequently, HR-TEM was employed to track the structural transfer of the orth-MoVO during the GCD process. The HR-TEM image of the orth-MoVO in Figure 3b and the corresponding FFT pattern in the [100]
zone axis reveal a crystalline structure, which is in agreement with the results of scanning transmission electron microscopy (STEM, Figure S14). After discharged to 0.2 V, the insertion of Zn$^{2+}$ resulted in crystalline transformation (Figure 3c). The lattice space of (001) decreased from 0.408 to 0.371 nm, while the lattice space of (020) increased from 1.27 to 1.39 nm. This phenomenon is in agreement with the in-situ XRD analysis results. The angle between (010) and (001) became 77.23° (Figure 3c), then returned to 88.8° after charging to 1.6 V (Figure 3d). Additionally, the lattice spaces of (001) and (020) underwent reversible changes during the charging process. Figure S15 shows the Rietveld-refined XRD of the orth-MoVO at 0.2 V and the corresponding atomic structure in the [001] direction. It is proposed that Zn$^{2+}$ inserted into the six- and seven-member rings of the orth-MoVO. The Zn$^{2+}$ storage mechanism is illustrated in Figure 3e according to the abovementioned results. In the discharge process, Zn$^{2+}$ and CF$_3$SO$_3$ entered into the orth-MoVO tunnels. Then, part of Zn$^{2+}$ and CF$_3$SO$_3$- remained in the tunnels to stabilize the orth-MoVO after the 1st charge process. Thereafter, the Zn$^{2+}$ ions can insert and extract reversibly from the orth-MoVO in the subsequent GCD processes.

With consideration to the most favorable path of Zn$^{2+}$ diffusion, the possible adsorption sites on the oxygen atoms of MoO$_6$ and/or VO$_6$ in seven-, six- and five-member MO$_6$ units were considered. The density functional theory (DFT) calculation was carried out to theoretically evaluate the adsorption properties of Zn$^{2+}$. The formation energies of Zn$^{2+}$ ion embedded into the three investigated systems are employed. The porous channel consisting of heptagonal and hexagonal MO$_6$ clusters (channel) were selected for the orth- and tri-MoVO, while pentagonal channel for tetra-MoVO, with the consideration to the most favorable path of Zn$^{2+}$ diffusion. Additionally, different possible adsorption sites on the oxygen atoms around the porous channel were considered, and the one with strongest adsorption was chosen as the most stable adsorption site. According to the calculation results in Figure 4a and S16, the Zn atoms is prone to entering the hepta-member channel with two Zn$^{2+}$ simultaneously in, which is consistent with the experimental estimations. The 11 diffusion pathways were considered to give the optimal model of Zn$^{2+}$ diffusion. In Figure 4b, Zn$^{2+}$ tends to alternately enter the hepta- and hexa-member channels of orth-MoVO, both of which allow for 2 Zn$^{2+}$ insertions. The system becomes unstable if the third Zn$^{2+}$ entered the hepta- and hexa-member channel. Consistent with the Figure S13, about one third of discharge capacity is ascribed to the 4 Zn$^{2+}$ insertion process, whereas the other two thirds discharge capacity is obtained from the precipitation reaction on the surface of the orth-MoVO. Figure 4c and S17 show the optimal atomic model after accommodating Zn$^{2+}$ for orth-MoVO. However, the situation is different for tri-MoVO. In Figure S18 and S19, the system is unstable for Zn$^{2+}$ insertion in hepta- or hexa-member channels. As shown in Figure S20, the only possible channel to accommodate Zn$^{2+}$ is the penta-member channel in tetra-MoVO. Considering the channel density and the structural stability, the orth-MoVO exhibits the maximal capacity accommodation and highest kinetic properties for ZIBs.

Conclusions
In summary, a series of Mo-V oxides with diverse phase structures were precisely constructed. The obtained orth-, tri-, and tetra-MoVO were composed of various tunnels, which provided alternative paths for Zn$^{2+}$ diffusion as cathodes in the ZIBs. Consequently, the orth-MoVO phase achieved the highest specific capacity and best cyclic stability. The structural and elemental evolutions are also discussed in detail. According to the analyses, the outstanding Zn$^{2+}$ storage ability is attributed to the numerous six- and seven-member ring tunnels in the orth-MoVO phase. Additionally, the orthorhombic phase structure provides a stable framework for the alternative zinc insertion process, which results in a superior cyclic stability. Both the phase and tunnel structures are responsible for the outstanding electrochemical behaviors. In conclusion, the proposed phase engineering strategy provides a new approach for designing cathodes that can be effectively incorporated in ZIBs.

**Declarations**

**ACKNOWLEDGMENTS**

The authors acknowledge the ……

**DECLARATION OF INTRESTS**

The authors declare no competing interests.

**References**

1. Yufit, V., Tariq, F., Eastwood, D.S., Biton, M., Wu, B., Lee, P.D. and Brandon, N.P. Operando Visualization and Multi-Scale Tomography Studies of Dendrite Formation and Dissolution in Zinc Batteries. *Joule* **3**, 485-502 (2018).

2. Song, M., Tan, H., Chao, D. and Fan, H.J. Recent Advances in Zn-ion Batteries. *Adv. Funct. Mater.* **28**, 1802564 (2018).

3. Parker, J.F., Ko, J.S., Rolison, D.R. and Long, J.W. Translating Materials-Level Performance into Device-Relevant Metrics for Zinc-Based Batteries. *Joule* **2**, 2519-2527 (2018).

4. Zhang, N., Cheng, F., Liu, Y., Zhao, Q., Lei, K., Chen, C., Liu, X. and Chen, J. Cation-Deficient Spinel ZnMn$_2$O$_4$ Cathode in Zn(CF$_3$SO$_3$)$_2$ Electrolyte for Rechargeable Aqueous Zn-ion Battery. *J. Am. Chem. Soc.* **138**, 12894-12901 (2016).

5. Pan, H., Shao, Y., Yan, P., Cheng, Y., Han, K.S., Nie, Z., Wang, C., Yang, J., Li, X., Bhattacharya, P., et al. Reversible Aqueous Zinc/Manganese Oxide Energy Storage from Conversion Reactions. *Nat. Energy* **1**, 16039 (2016).

6. Fang, G., Zhou, J., Pan, A. and Liang, S. Recent Advances in Aqueous Zinc-Ion Batteries. *ACS Energy Lett.* **3**, 2480-2501 (2018).

7. Chao, D., Zhu, C., Song, M., Liang, P., Zhang, X., Tiep, N.H., Zhao, H., Wang, J., Wang, R., Zhang, H., et al. A High-Rate and Stable Quasi-Solid-State Zinc-Ion Battery with Novel 2D Layered Zinc
Orthovanadate Array. *Adv. Mater.* **30**, 1803181 (2018).

8. Cai, Y., Liu, F., Luo, Z., Fang, G., Zhou, J., Pan, A. and Liang, S. Pilotaxitic Na$_{1.1}$V$_3$O$_{7.9}$ Nanoribbons/Graphene as High-Performance Sodium Ion Battery and Aqueous Zinc Ion Battery Cathode. *Energy Storage Mater.* **13**, 168-174 (2018).

9. Zhu, K., Wu, T. and Huang, K. A High Capacity Bilayer Cathode for Aqueous Zn-Ion Batteries. *ACS Nano* **13**, 14447-14458 (2019).

10. Yang, Y., Tang, Y., Fang, G., Shan, L., Guo, J., Zhang, W., Wang, C., Wang, L., Zhou, J. and Liang, S. Li$^+$ Intercalated V$_2$O$_5$·nH$_2$O with Enlarged Layer Spacing and Fast Ion Diffusion as an Aqueous Zinc-Ion Battery Cathode. *Energy Environ. Sci.* **11**, 3157-3162 (2018).

11. Xu, X., Xiong, F., Meng, J., Wang, X., Niu, C., An, Q. and Mai, L. Vanadium-Based Nanomaterials: A Promising Family for Emerging Metal-Ion Batteries. *Adv. Funct. Mater.* **30**, 1904398 (2020).

12. Zhong, W., Huang, J., Liang, S., Liu, J., Li, Y., Cai, G.-M., Jiang, Y. and Liu, J. New Prelithiated V$_2$O$_5$ Superstructure for Lithium-ion Batteries with Long Cycle Life and High Power. *ACS Energy Lett.* **5**, 31-38 (2020).

13. Liu, Y., Li, Q., Ma, K., Yang, G. and Wang, C. Graphene Oxide Wrapped CuV$_2$O$_6$ Nanobelts as High-Capacity and Long-Life Cathode Materials of Aqueous Zinc-Ion Batteries. *ACS Nano* **13**, 12081-12089 (2019).

14. Nam, K.W., Park, S.S., dos Reis, R., Dravid, V.P., Kim, H., Mirkin, C.A. and Stoddart, J.F. Conductive 2D Metal-Organic Framework for High-Performance Cathodes in Aqueous Rechargeable Zinc Batteries. *Nat. Commun.* **10**, 4948 (2019).

15. Xing, Z., Wang, S., Yu, A. and Chen, Z. Aqueous Intercalation-Type Electrode Materials for Grid-Level Energy Storage: Beyond the Limits of Lithium and Sodium. *Nano Energy* **50**, 229-244 (2018).

16. Wang, L., Huang, K.-W., Chen, J. and Zheng, J. Ultralong Cycle Stability of Aqueous Zinc-Ion Batteries with Zinc Vanadium Oxide Cathodes. *Sci. Adv.* **5**, eaax4279 (2019).

17. Ma, L., Chen, S., Long, C., Li, X., Zhao, Y., Liu, Z., Huang, Z., Dong, B., Zapien, J.A. and Zhi, C. Achieving High-Voltage and High-Capacity Aqueous Rechargeable Zinc Ion Battery by Incorporating Two-Species Redox Reaction. *Adv. Energy Mater.* **9**, 1902446 (2019).

18. Xia, C., Guo, J., Li, P., Zhang, X. and Alshareef, H.N. Highly Stable Aqueous Zinc-Ion Storage Using a Layered Calcium Vanadium Oxide Bronze Cathode. *Angew. Chem. Int. Ed.* **57**, 3943-3948 (2018).

19. Xia, C., Guo, J., Lei, Y., Liang, H., Zhao, C. and Alshareef, H.N. Rechargeable Aqueous Zinc-Ion Battery Based on Porous Framework Zinc Pyrovanadate Intercalation Cathode. *Adv. Mater.* **30**, 1705580 (2018).

20. Hu, P., Zou, Z., Sun, X., Wang, D., Ma, J., Kong, Q., Xiao, D., Gu, L., Zhou, X., Zhao, J., et al. Uncovering the Potential of M1-Site-Activated NASICON Cathodes for Zn-Ion Batteries. *Adv. Mater.* **32**, 1907526 (2020).

21. Kim, S.J., Tang, C.R., Singh, G., Housel, L.M., Yang, S., Takeuchi, K.J., Marschilok, A.C., Takeuchi, E.S. and Zhu, Y. New Insights into the Reaction Mechanism of Sodium Vanadate for an Aqueous Zn Ion
Battery. *Chem. Mater.* **32**, 2053-2060 (2020).

22. Zheng, J., Liu, C., Tian, M., Jia, X., Jahrmann, E.P., Seidler, G.T., Zhang, S., Liu, Y., Zhang, Y., Meng, C., et al. Fast and Reversible Zinc Ion Intercalation in Al-Ion Modified Hydrated Vanadate. *Nano Energy* **70**, 104519 (2020).

23. Li, Y., Wang, S., Dong, Y., Yang, Y., Zhang, Z. and Tang, Z. Glass-Ceramic-Like Vanadate Cathodes for High-Rate Lithium-Ion Batteries. *Adv. Energy Mater.* **10**, 1903411 (2020).

24. Liu, Y., Li, C., Xu, J., Ou, M., Fang, C., Sun, S., Qiu, Y., Peng, J., Lu, G., Li, Q., et al. Electroactivation-Induced Spinel ZnV$_2$O$_4$ as a High-Performance Cathode Material for Aqueous Zinc-Ion Battery. *Nano Energy* **67**, 104211 (2020).

25. Yang, X.-G., Liu, T., Gao, Y., Ge, S., Leng, Y., Wang, D. and Wang, C.-Y. Asymmetric Temperature Modulation for Extreme Fast Charging of Lithium-Ion Batteries. *Joule* **3**, 3002-3019 (2019).

26. Shi, H.-Y. and Sun, X. Interlayer Engineering of Layered Cathode Materials for Advanced Zn Storage. *Chem* **6**, 817-819 (2020).

27. Soundharrajan, V., Sambandam, B., Kim, S., Alfaruqi, M.H., Putro, D.Y., Jo, J., Kim, S., Mathew, V., Sun, Y.-K. and Kim, J. Na$_2$V$_6$O$_{16}·3$H$_2$O Barnesite Nanorod: An Open Door to Display a Stable and High Energy for Aqueous Rechargeable Zn-Ion Batteries as Cathodes. *Nano Lett.* **18**, 2402-2410 (2018).

28. Tang, B., Shan, L., Liang, S. and Zhou, J. Issues and Opportunities Facing Aqueous Zinc-Ion Batteries. *Energy Environ. Sci.* **12**, 3288-3304 (2019).

29. Liao, M., Wang, J., Ye, L., Sun, H., Wen, Y., Wang, C., Sun, X., Wang, B. and Peng, H. Extraction of Oxygen Anions from Vanadium Oxide Making Deeply Cyclable Aqueous Zinc Ion Battery. *Angew. Chem. Ed. Int.* **59**, 2273-2278 (2019).

30. Javed, M.S., Lei, H., Wang, Z., Liu, B.-t., Cai, X. and Mai, W. 2D V$_2$O$_5$ Nanosheets as a Binder-Free High-Energy Cathode for Ultrafast Aqueous and Flexible Zn-Ion Batteries. *Nano Energy* **70**, 104573 (2020).

31. Konarov, A., Voronina, N., Jo, J.H., Bakenov, Z., Sun, Y.-K. and Myung, S.-T. Present and Future Perspective on Electrode Materials for Rechargeable Zinc-Ion Batteries. *ACS Energy Lett.* **3**, 2620-2640 (2018).

32. He, P., Zhang, G., Liao, X., Yan, M., Xu, X., An, Q., Liu, J. and Mai, L. Sodium Ion Stabilized Vanadium Oxide Nanowire Cathode for High-Performance Zinc-Ion Batteries. *Adv. Energy Mater.* **8**, 1702463 (2018).

33. Guo, X., Fang, G., Zhang, W., Zhou, J., Shan, L., Wang, L., Wang, C., Lin, T., Tang, Y. and Liang, S. Mechanistic Insights of Zn$^{2+}$ Storage in Sodium Vanadates. *Adv. Energy Mater.* **8**, 1801819 (2018).

34. Wang, F., Hu, E., Sun, W., Gao, T., Ji, X., Fan, X., Han, F., Yang, X.-Q., Xu, K. and Wang, C. A Rechargeable Aqueous Zn$^{2+}$-Battery with High Power Density and a Long Cycle-Life. *Energy Environ. Sci.* **11**, 3168-3175 (2018).

35. Guo, S., Liang, S., Zhang, B., Fang, G., Ma, D. and Zhou, J. Cathode Interfacial Layer Formation via in Situ Electrochemically Charging in Aqueous Zinc-Ion Battery. *ACS Nano* **13**, 13456-13464 (2019).
36. Guo, J., Ming, J., Lei, Y., Zhang, W., Xia, C., Cui, Y. and Alshareef, H.N. Artificial Solid Electrolyte Interphase for Suppressing Surface Reactions and Cathode Dissolution in Aqueous Zinc Ion Batteries. *ACS Energy Lett.* **4**, 2776-2781 (2019).

37. Fang, G., Liang, S., Chen, Z., Cui, P., Zheng, X., Pan, A., Lu, B., Lu, X. and Zhou, J. Simultaneous Cationic and Anionic Redox Reactions Mechanism Enabling High-Rate Long-Life Aqueous Zinc-Ion Battery. *Adv. Funct. Mater.* **29**, 1905267 (2019).

38. Bin, D., Huo, W., Yuan, Y., Huang, J., Liu, Y., Zhang, Y., Dong, F., Wang, Y. and Xia, Y. Organic-Inorganic-Induced Polymer Intercalation into Layered Composites for Aqueous Zinc-Ion Battery. *Chem* **6**, 968-984 (2020).

39. Wang, X., Xi, B., Ma, X., Feng, Z., Jia, Y., Feng, J., Qian, Y. and Xiong, S. Boosting Zinc-Ion Storage Capability by Effectively Suppressing Vanadium Dissolution Based on Robust Layered Barium Vanadate. *Nano Lett.* **20**, 2899-2906 (2020).

40. Fu, Y., Wei, Q., Zhang, G., Wang, X., Zhang, J., Hu, Y., Wang, D., Zuin, L., Zhou, T., Wu, Y., et al. High-Performance Reversible Aqueous Zn-ion Battery Based on Porous MnO$_x$ Nanorods Coated by MOF-Derived N-Doped Carbon. *Adv. Energy Mater.* **8**, 1801445 (2018).

41. Wang, F., Hu, E., Sun, W., Gao, T., Ji, X., Fan, X., Han, F., Yang, X.-Q., Xu, K. and Wang, C. A Rechargeable Aqueous Zn$^{2+}$-Battery with High Power Density and a Long Cycle-Life. *Energy Environ. Sci.* **11**, 3168-3175 (2018).

42. Sadakane, M., Endo, K., Kodato, K., Ishikawa, S., Murayama, T. and Ueda, W. Assembly of a Pentagonal Polyoxomolybdate Building Block, [Mo$_6$O$_{21}$]$^6$–, into Crystalline MoV Oxides. *Eur. J. Inorg. Chem.* **2013**, 1731-1736 (2013).

43. Pyrz, W.D., Blom, D.A., Sadakane, M., Kodato, K., Ueda, W., Vogt, T. and Buttrey, D.J. Atomic-Level Imaging of Mo-V-O Complex Oxide Phase Intergrowth, Grain Boundaries, and Defects Using HAADF-STEM. *P. Natl. Acad. Sci.* **107**, 6152-6157 (2010).

44. Wang, P.-F., You, Y., Yin, Y.-X. and Guo, Y.-G. Layered Oxide Cathodes for Sodium-Ion Batteries: Phase Transition, Air Stability, and Performance. *Adv. Energy Mater.* **8**, 1701912 (2018).

45. Wang, P.-F., Yao, H.-R., Liu, X.-Y., Zhang, J.-N., Gu, L., Yu, X.-Q., Yin, Y.-X. and Guo, Y.-G. Ti-Substituted NaNi$_{0.5}$Mn$_{0.5-x}$Ti$_x$O$_2$ Cathodes with Reversible O3–P3 Phase Transition for High-Performance Sodium-Ion Batteries. *Adv. Mater.* **29**, 1700210 (2017).

46. Song, J., Zhu, C., Xu, B.Z., Fu, S., Engelhard, M.H., Ye, R., Du, D., Beckman, S.P. and Lin, Y. Bimetallic Cobalt-Based Phosphide Zeolitic Imidazolate Framework: CoP$_x$ Phase-Dependent Electrical Conductivity and Hydrogen Atom Adsorption Energy for Efficient Overall Water Splitting. *Adv. Energy Mater.* **7**, 1601555 (2017).

47. Gu, M., Belharouak, I., Zheng, J., Wu, H., Xiao, J., Genc, A., Amine, K., Thevuthasan, S., Baer, D.R., Zhang, J.-G., et al. Formation of the Spinel Phase in the Layered Composite Cathode Used in Li-Ion Batteries. *ACS Nano* **7**, 760-767 (2013).
48. Jiang, S., Zhou, W., Niu, Y., Zhu, Z. and Shao, Z. Phase Transition of a Cobalt-Free Perovskite as a High-Performance Cathode for Intermediate-Temperature Solid Oxide Fuel Cells. *ChemSusChem* **5**, 2023-2031 (2012).

49. Nishimura, S.-i., Natsui, R. and Yamada, A. Superstructure in the Metastable Intermediate-Phase Li$_2$/3FePO$_4$ Accelerating the Lithium Battery Cathode Reaction. *Angew. Chem. Int. Ed.* **54**, 8939-8942 (2015).

50. Zhao, D., Qin, J., Zheng, L. and Cao, M. Amorphous Vanadium Oxide/Molybdenum Oxide Hybrid with Three-Dimensional Ordered Hierarchically Porous Structure as a High-Performance Li-Ion Battery Anode. *Chem. Mater.* **28**, 4180-4190 (2016).

51. Qu, G., Zhao, L., Jia, S., Zheng, H., Li, L., Ma, W., Yang, W., Wang, H., Tang, Y. and Wang, J. In Situ Facile Bubble-Templated Fabrication of New-Type Urchin-Like (Li,Mo)-Doped Li$_x$(Mo$_{0.3}$V$_{0.7}$)$_2$O$_5$ for Zn$^{2+}$ Storage. *J. Mater. Chem. A* **5**, 18253-18260 (2017).

52. Qu, G., Wang, J., Liu, G., Tian, B., Su, C., Chen, Z., Rueff, J.-P. and Wang, Z. Vanadium Doping Enhanced Electrochemical Performance of Molybdenum Oxide in Lithium-Ion Batteries. *Adv. Funct. Mater.* **29**, 1805227 (2019).

53. Sadakane, M., Watanabe, N., Katou, T., Nodasaka, Y. and Ueda, W. Crystalline Mo$_3$VO$_x$ Mixed-Metal-Oxide Catalyst with Trigonal Symmetry. *Angew. Chem. Int. Ed.* **46**, 1493-1496 (2007).

54. Sadakane, M., Kodato, K., Kuranishi, T., Nodasaka, Y., Sugawara, K., Sakaguchi, N., Nagai, T., Matsu, Y. and Ueda, W. Molybdenum–Vanadium-Based Molecular Sieves with Microchannels of Seven-Membered Rings of Corner-Sharing Metal Oxide Octahedra. *Angew. Chem. Int. Ed.* **47**, 2493-2496 (2008).

55. Ishikawa, S. and Ueda, W. Microporous Crystalline Mo–V Mixed Oxides for Selective Oxidations. *Catal. Sci. Technol.* **6**, 617-629 (2016).

56. Pyrz, W.D., Blom, D.A., Sadakane, M., Kodato, K., Ueda, W., Vogt, T. and Buttrey, D.J. Atomic-Scale Investigation of Two-Component MoVO Complex Oxide Catalysts Using Aberration-Corrected High-Angle Annular Dark-Field Imaging. *Chem. Mater.* **22**, 2033-2040 (2010).

57. Huang, J., Wang, Z., Hou, M., Dong, X., Liu, Y., Wang, Y. and Xia, Y. Polyaniline-Intercalated Manganese Dioxide Nanolayers as a High-Performance Cathode Material for an Aqueous Zinc-Ion Battery. *Nat. Commun.* **9**, 2906 (2018).

58. Pyrz, W.D., Blom, D.A., Shiju, N.R., Guliants, V.V., Vogt, T. and Buttrey, D.J. Using Aberration-Corrected STEM Imaging to Explore Chemical and Structural Variations in the M1 Phase of the MoVNbTeO Oxidation Catalyst. *J. Phys. Chem. C* **112**, 10043-10049 (2008).

59. Yan, M., He, P., Chen, Y., Wang, S., Wei, Q., Zhao, K., Xu, X., An, Q., Shuang, Y., Shao, Y., et al. Water-Lubricated Intercalation in V$_2$O$_5$·nH$_2$O for High-Capacity and High-Rate Aqueous Rechargeable Zinc Batteries. *Adv. Mater.* **30**, 1703725 (2018).