Supporting Information for

A High Capacity Ammonium Vanadate Cathode for Zinc-ion Battery

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Supplementary Figures and Table



Fig. S1 Schematics of possible diffusion pathways for Zinc ion diffusion in monoclinic $NH_4V_4O_{10}$ viewed along the [100] (black arrows), [010] (blue arrow) and [001] (red arrow) direction. Orange and black balls indicate NH_4^+ ions and the most energetically

favorable location for Zn^{2+} intercalation, respectively. The VO layers are represented by red polyhedrons.



Fig. S2 The full XPS spectrum (a), and high-resolution XPS spectra of O (b) and N (c) species.



Fig. S3 TEM images of the 3D-NVO sample at different magnifications



Fig. S4 (a-c) SEM and (d) TEM images of the sample prepared by conventional autoclave hydrothermal method at reaction time of 2 h (a), 6 h (b) and 12 h (c and d). Inset in (d) is the corresponding XRD pattern obtained at 12 h, which can be assigned to a pure monoclinic structure of $NH_4V_4O_{10}$ (JCPDS Card No. 31-0075).



Fig. S5 Schematic illustration of the difference between microwave and conventional heating. In conventional heating system, there is a temperature gradient from the outside to the inner core.



Fig. S6 Galvanostatic discharge and charge profiles of the 3D-NVO cathode at different current densities



Fig. S7 Galvanostatic discharge and charge profiles of the 3D-NVO cathode during different cycles at 10 Ag^{-1}



Fig. S8 Cycling performance of the NVO nanobelts obtained from the traditional hydrothermal method at 10 A g^{-1}



Fig. S9 Plots of log(i) vs. log(v) based on anodic and cathodic peaks in Fig. 3f



Fig. S10 The XRD pattern of the 3D-NVO cathode after 100 cycles at 10 A g^{-1}

Cathode materials	Reversible capacity	Rate	Number of	Capacity
	[mAh g ⁻¹]	[mA g ⁻¹]	cycles	retention
This work	107	100	50	000/
(3D-NH ₄ V ₄ O ₁₀)	480	100	20	98%0
α-MnO ₂ [S1]	233	83	50	63%
δ-MnO ₂ [S2]	225	83	100	50%
Mn ₃ O ₄ [S3]	195	200	70	67%
ZnMn ₂ O ₄ [S4]	106	100	300	59%
VO ₂ [S5]	357	100	50	99%
VS ₂ [S6]	138	200	200	80%
V ₂ O ₅ [S7]	215	100	160	95%
V ₂ O ₅ ·nH ₂ O [S8]	196	14.4	120	87%
H ₂ V ₃ O ₈ @Graphene [S9]	360	300	150	93%
LiV ₃ O ₈ [S10]	185	133	65	78%
Na _{0.33} V ₂ O ₅ [S11]	276	200	100	91%
$Zn_2V_2O_7$ [S12]	210	300	200	94%
Zn ₃ V ₂ O ₇ (OH) ₂ ·2H ₂ O [S13]	149	200	300	68%
Na ₂ V ₆ O ₁₆ ·1.63H ₂ O [S14]	296	100	100	78%
Na _{1.1} V ₃ O _{7.9} @rGO [S15]	200	50	30	87%
V _{1-x} Al _x O _{1.52} (OH) _{0.77} [S16]	156	15	50	68%
Na ₃ V ₂ (PO ₄) ₃ @C [S17]	97	50	100	74%

Table S1 A comparison of the reversible capacity of our 3D-NH4V4O10 cathode topreviously reported superior ZIB cathodes

Supplementary References

- [S1] M.H. Alfaruqi, J. Gim, S. Kim, J. Song, J. Jo, S. Kim, V. Mathew, J. Kim, Enhanced reversible divalent zinc storage in a structurally stable alpha-MnO₂ nanorod electrode. J. Power Sources 288, 320-327 (2015). https://doi.org/10.1016/j.jpowsour.2015.04.140
- [S2] M.H. Alfaruqi, J. Gim, S. Kim, J. Song, P. Duong Tung et al., A layered delta-MnO₂ nanoflake cathode with high zinc-storage capacities for eco-friendly battery applications. Electrochem. Commun. 60, 121-125 (2015). https://doi.org/10.1016/j.elecom.2015.08.019
- [S3] J. Hao, J. Mou, J. Zhang, L. Dong, W. Liu, C. Xu, F. Kang, Electrochemically induced spinel-layered phase transition of Mn₃O₄ in high performance neutral aqueous rechargeable zinc battery. Electrochim. Acta 259, 170-178 (2018). https://doi.org/10.1016/j.electacta.2017.10.166
- [S4] X. Wu, Y. Xiang, Q. Peng, X. Wu, Y. Li et al., Green-low-cost rechargeable

aqueous zinc-ion batteries using hollow porous spinel ZnMn₂O₄ as the cathode material. J. Mater. Chem. A **5**, 17990-17997 (2017). https://doi.org/10.1039/C7TA00100B

- [S5] J. Ding, Z. Du, L. Gu, B. Li, L. Wang, S. Wang, Y. Gong, S. Yang, Ultrafast Zn²⁺ intercalation and deintercalation in vanadium dioxide. Adv. Mater. **30**, 1800762 (2018). https://doi.org/10.1002/adma.201800762
- [S6] P. He, M. Yan, G. Zhang, R. Sun, L. Chen, Q. An, L. Mai, Layered VS₂ nanosheet-based aqueous zn ion battery cathode. Adv. Energy Mater. 7, 1601920 (2017). https://doi.org/10.1002/aenm.201601920
- [S7] P. Hu, M. Yan, T. Zhu, X. Wang, X. Wei et al., Zn/V₂O₅ aqueous hybrid-ion battery with high voltage platform and long cycle life. ACS Appl. Mater. Interfaces 9, 42717-42722 (2017). https://doi.org/10.1021/acsami.7b13110
- [S8] P. Senguttuvan, S.D. Han, S. Kim, A.L. Lipson, S. Tepavcevic et al., A high power rechargeable nonaqueous multivalent Zn/V₂O₅ battery. Adv. Energy Mater. 6, 1600826 (2016). https://doi.org/10.1002/aenm.201600826
- [S9] Q. Pang, C. Sun, Y. Yu, K. Zhao, Z. Zhang et al., H₂V₃O₈ nanowire/graphene electrodes for aqueous rechargeable zinc ion batteries with high rate capability and large capacity. Adv. Energy Mater. 8, 1800144 (2018). https://doi.org/10.1002/aenm.201800144
- [S10] M.H. Alfaruqi, V. Mathew, J. Song, S. Kim, S. Islam, Electrochemical zinc intercalation in lithium vanadium oxide: a high-capacity zinc-ion battery cathode. Chem. Mater. 29, 1684-1694 (2017). https://doi.org/10.1021/acs.chemmater.6b05092
- [S11] P. He, G. Zhang, X. Liao, M. Yan, X. Xu, Q. An, J. Liu, L. Mai, Sodium ion stabilized vanadium oxide nanowire cathode for high-performance zinc-ion batteries. Adv. Energy Mater. 8, 1702463 (2018). https://doi.org/10.1002/aenm.201702463
- [S12] B. Sambandam, V. Soundharrajan, S. Kim, M.H. Alfaruqi, J. Jo et al., Aqueous rechargeable zn-ion batteries: an imperishable and high-energy Zn₂V₂O₇ nanowire cathode through intercalation regulation. J. Mater. Chem. A 6, 3850-3856 (2018). https://doi.org/10.1039/C7TA11237H
- [S13] C. Xia, J. Guo, Y. Lei, H. Liang, C. Zhao, H.N. Alshareef, Rechargeable aqueous zinc-ion battery based on porous framework zinc pyrovanadate intercalation cathode. Adv. Mater. **30**, 1705580 (2018). https://doi.org/10.1002/adma.201705580

- [S14] P. Hu, T. Zhu, X. Wang, X. Wei, M. Yan, Highly durable Na₂V₆O₁₆·1.63H₂O nanowire cathode for aqueous zinc-ion battery. Nano Letters 18, 1758-1763 (2018). https://doi.org/10.1021/acs.nanolett.7b04889
- [S15] Y. Cai, F. Liu, Z. Luo, G. Fang, J. Zhou, A. Pan, S. Liang, Pilotaxitic Na_{1.1}V₃O_{7.9} nanoribbons/graphene as high-performance sodium ion battery and aqueous zinc ion battery cathode. Energy Storage Mater. **13**, 168-174 (2018). https://doi.org/10.1016/j.ensm.2018.01.009
- [S16] J.H. Jo, Y.K. Sun, S.T. Myung, Hollandite-type Al-doped VO_{1.52}(OH)_{0.77} as a zinc ion insertion host material. J. Mater. Chem. A 5, 8367-8375 (2017). https://doi.org/10.1039/C7TA01765K
- [S17] G. Li, Z. Yang, Y. Jiang, C. Jin, W. Huang, X. Ding, Y. Huang, Towards polyvalent ion batteries: a zinc-ion battery based on NASICON structured Na₃V₂(PO4)₃. Nano Energy 25, 211-217 (2016). https://doi.org/10.1016/j.nanoen.2016.04.051