

High-performance cathode for aqueous zinc-ion batteries: a novel lithium vanadate heterojunction with excellent mixed lithium-ion and electron conduction derived from decavanadate-type polyoxometalate

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Table S2 Comparison of the value of $D_{\text{Zn}^{2+}}$ between **LiVO** and other vanadium-based cathode materials.

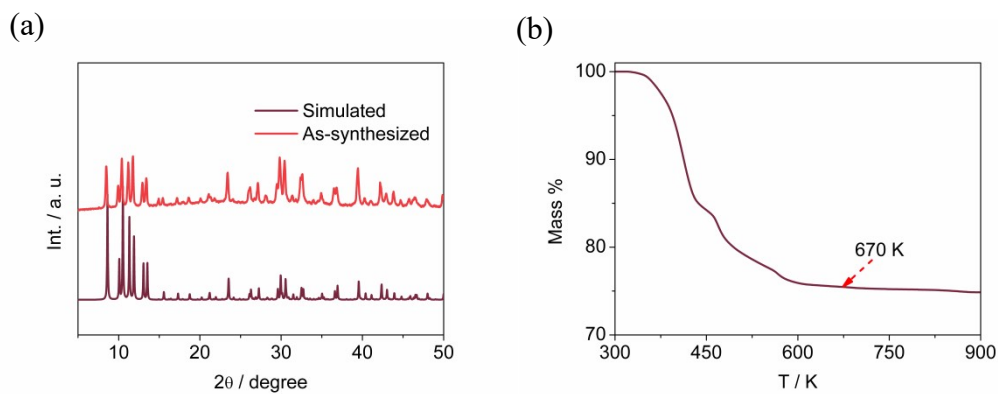


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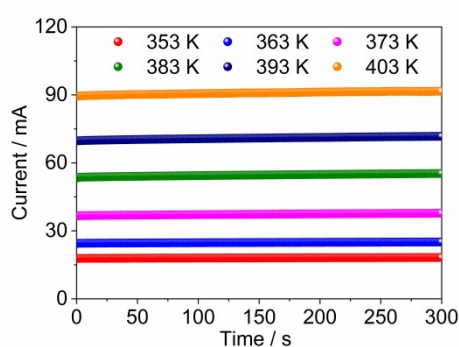


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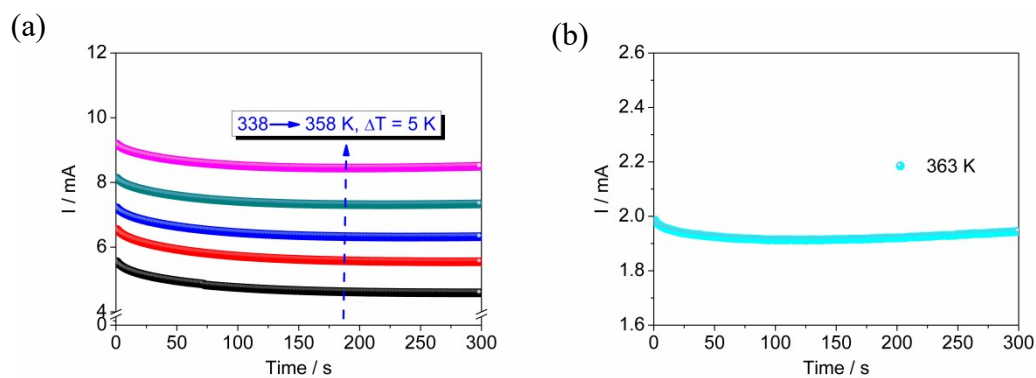
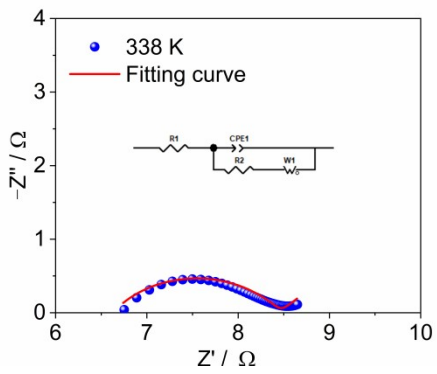
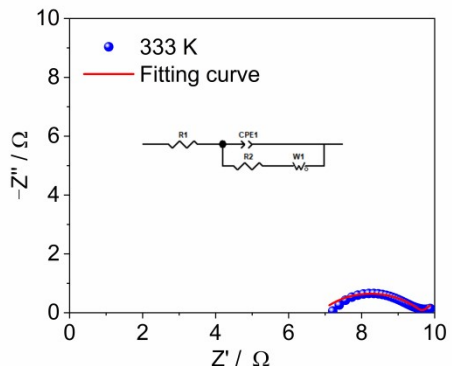
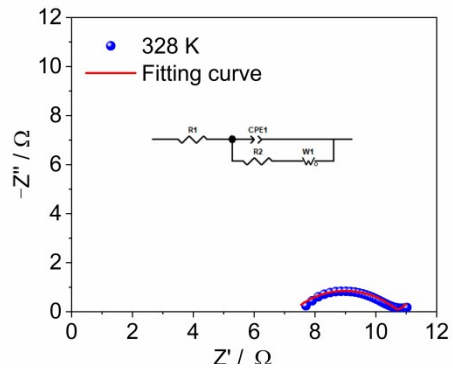
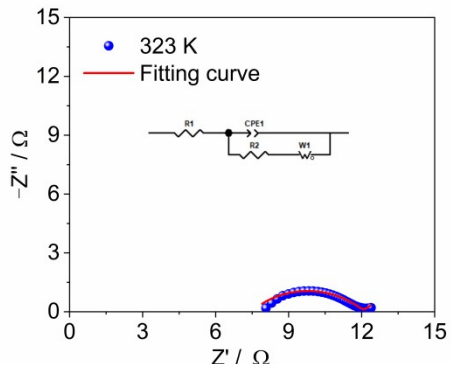
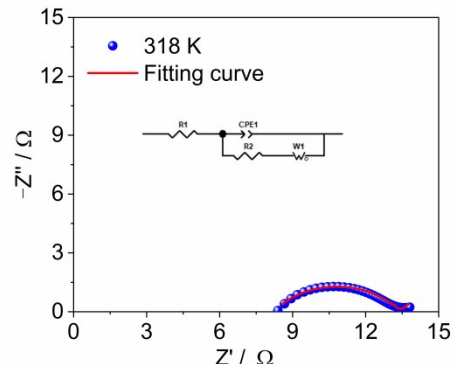
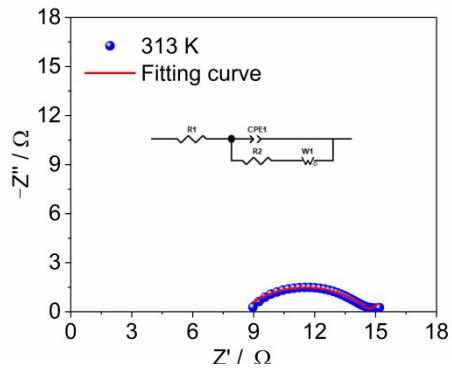
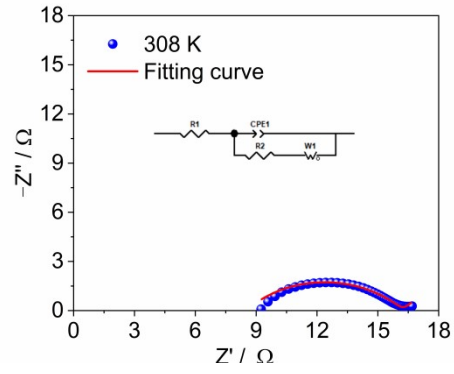
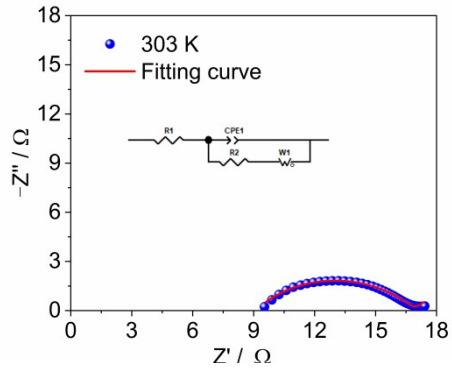


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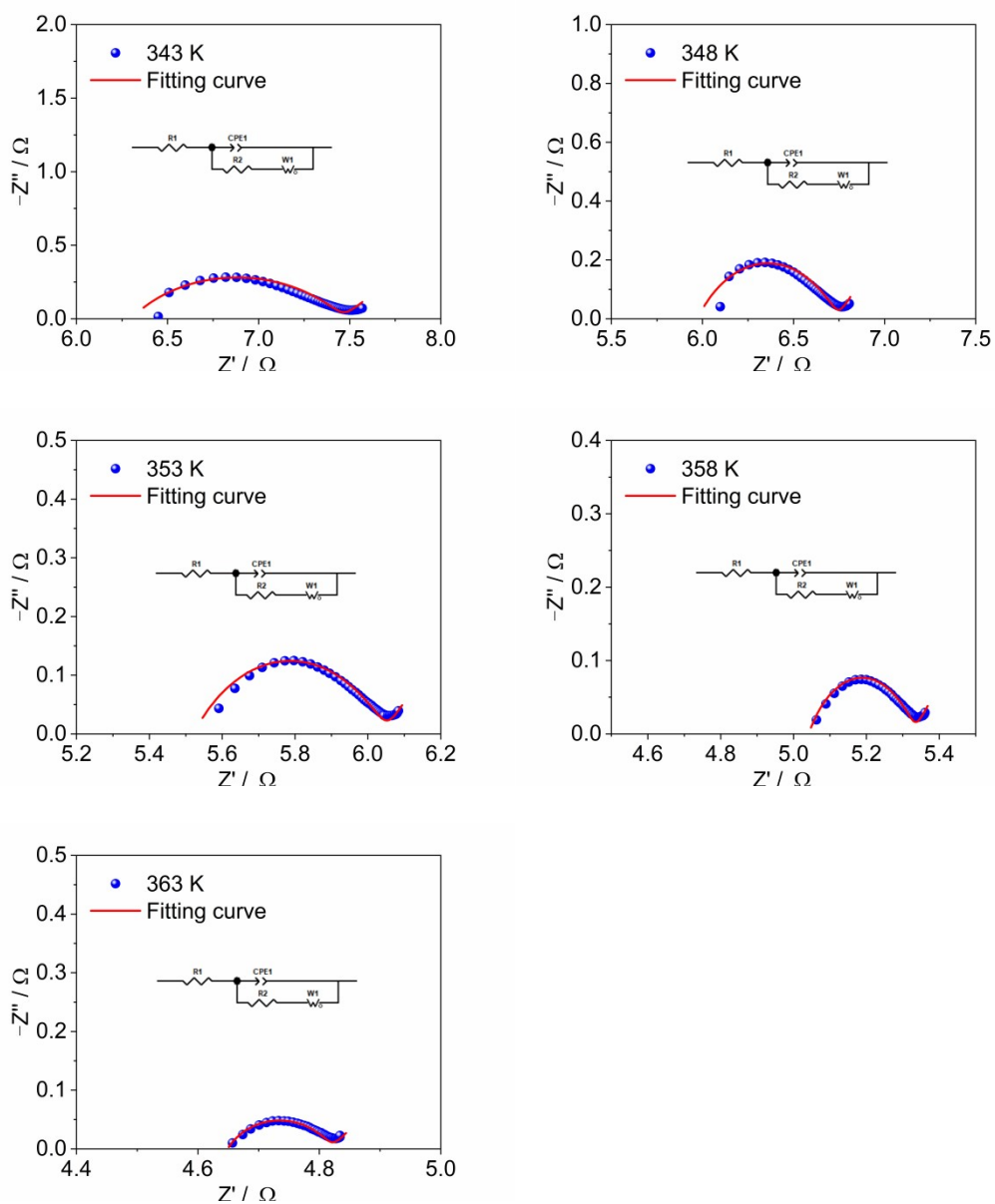


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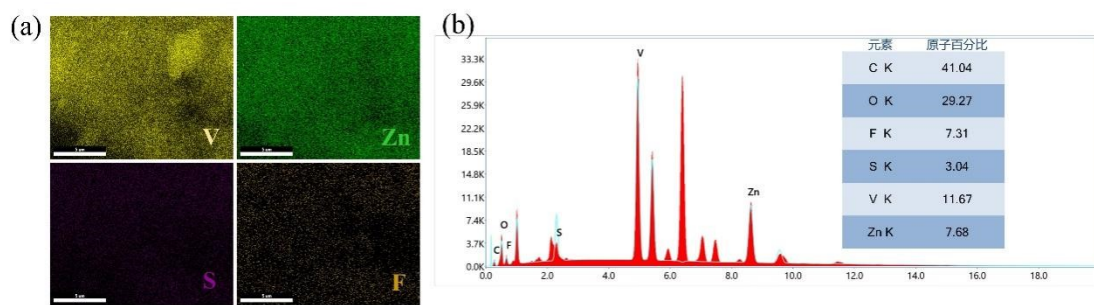


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Compounds	Specific capacity (mAh g ⁻¹)		Capacity retention (loss / cycle) (5 A g ⁻¹)	Ref.
	(0.1 A g ⁻¹)	(2 A g ⁻¹)		
LiV_3O_8	176 (0.1 A g ⁻¹)	153 (2 A g ⁻¹)	63.3% / 4000 (5 A g ⁻¹)	1
LiV_3O_8	350.2 (0.1 A g ⁻¹)	250 (2 A g ⁻¹)	15% / 4000 (5 A g ⁻¹)	2
LiV_3O_8	197 (0.1 A g ⁻¹)	74.3 (0.8 A g ⁻¹)	23.8% / 7000 (0.8 A g ⁻¹)	3
$\text{Li}_{0.45}\text{V}_2\text{O}_5 \cdot 0.89\text{H}_2\text{O}$	345 (0.3 A g ⁻¹)	248 (2 A g ⁻¹)	14% / 1000 (10 A g ⁻¹)	4
LiVO	374.9 (0.2 A g ⁻¹)	293.9 (3 A g ⁻¹)	7.2% / 2000 (3 A g ⁻¹)	This work

Table S2 Comparison of the value of $D_{\text{Zn}^{2+}}$ between **LiVO** and other vanadium-based cathode materials.

Cathode	The value of $D_{\text{Zn}^{2+}}$	Ref.
$\text{Zn}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$	10^{-12} – 10^{-11} cm ² s ⁻¹	5
$\text{O}_d\text{-VO}$	0.4×10^{-11} – 1.1×10^{-11} cm ² s ⁻¹	6
VO-300	2.278×10^{-16} – 2.77×10^{-11} cm ² s ⁻¹	7
$\text{Zn}_x\text{LiV}_3\text{O}_8$	10^{-14} – 10^{-10} cm ² s ⁻¹	8
$\text{Ba}_{1.2}\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$	10^{-12} – 10^{-9} cm ² s ⁻¹	9
LiVO	1.3×10^{-11} – 6.0×10^{-9} cm ² s ⁻¹	This work

References

References

- [1] Q. Pang, X. Yu, S. Zhang, W. He, S. Yang, Y. Fu, Y. Tian, M. Xing and X. Luo, High-Capacity and Long-Lifespan Aqueous $\text{LiV}_3\text{O}_8/\text{Zn}$ Battery Using Zn/Li Hybrid Electrolyte, *Nanomaterials*, 2021, **11**, 1429.

- [2] P. He, M. Yan, X. Liao, Y. Luo, L. Mai and C.-W. Nan, Reversible V^{3+}/V^{5+} Double Redox in Lithium Vanadium Oxide Cathode for Zinc Storage, *Energy Storage Mater.*, 2020, **29**, 113.
- [3] J. Pyun, H. Lee, H. Lee, H. Kwon, H. Lee, S.-T. Hong, W.-J. Lee, M. S. Chae, Unveiling the Charge Storage Mechanism of High-Performance LiV_3O_8 Cathode for Mn^{2+}/H^+ Hybrid Batteries, *Small*, 2025, **21**, 2504200.
- [4] Y. Tong, X. Li, S. Su, J. Li, J. Fang, B. Liang, J. Hou, M. Luo, Hydrated Lithium Ions Intercalated V_2O_5 with Dual-Ion Synergistic Insertion Mechanism for High-Performance Aqueous Zinc-Ion Batteries, *J. Colloid Interface Sci.*, 2022, **606**, 645.
- [5] M. Liao, J. Wang, L. Ye, H. Sun, Y. Wen, C. Wang, X. Sun, B. Wang and H. Peng, A Deep-Cycle Aqueous Zinc-ion Battery Containing an Oxygen-Deficient Vanadium Oxide Cathode, *Angew. Chem. Int. Ed.*, 2020, **59**, 2273–2278.
- [6] K. Hu, D. Jin, Y. Zhang, L. Ke, H. Shang, Y. Yan, H. Lin, K. Rui and J. Zhu, Metallic Vanadium Trioxide Intercalated with Phase Transformation for Advanced Aqueous Zinc-Ion Batteries, *J. Energy Chem.*, 2021, **61**, 594–601.
- [7] F. Liang, M. Chen, S. Zhang, Z. Zou, C. Ge, S. Jia, S. Le, F. Yu and J. Nong, Electrochemical Activation in Vanadium Oxide with Rich Oxygen Vacancies for High-Performance Aqueous Zinc-Ion Batteries, *ACS Sustainable Chem. Eng.*, 2024, **12**, 5117–5128.
- [8] P. He, M. Yan, X. Liao, Y. Luo, L. Mai and C.-W. Nan, Reversible V^{3+}/V^{5+} Double Redox in Lithium Vanadium Oxide Cathode for Zinc Storage, *Energy Storage Mater.*, 2020, **29**, 113–120.
- [9] X. Wang, B. Xi, X. Ma, Z. Feng, Y. Jia, J. Feng, Y. Qian and S. Xiong, Boosting Zinc-Ion Storage Capability by Effectively Suppressing Vanadium Dissolution Based on Robust Layered Barium Vanadate, *Nano Lett.*, 2020, **20**, 2899–2906.