In-situ growing amorphous vanadium oxide nanospheres on carbon cloth as free-standing cathodes toward high performance aqueous zinc-ion batteries

Xuguang Han[a, b],† Yan Zhang[a],* † Mengmeng Liu[a], Yifei Sun[a], Wenshan Gou[a], Zhao Xu[a] and Chang Ming Li[b]*

[a] *Institute of Advanced Cross-field Science, College of Life Sciences, Qingdao University, Qingdao 11065, P. R. China.*

[b] *Institute of Materials Science and Devices, School of Materials Science and Engineering, Suzhou University of Science and Technology, Suzhou 215011, P.R. China.*

† Xuguang Han and Yan Zhang contributed equally to this work.

* Corresponding authors: ecmli@swu.edu.cn; yzhang_iacs@qdu.edu.cn

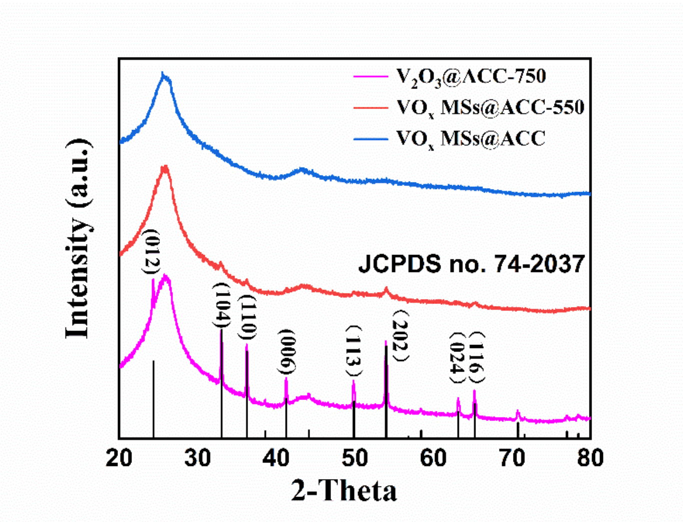

Figure S1. XRD patterns of the VO_x compounds were obtained at different calcination temperatures (350 °C, 550 °C, 750 °C).

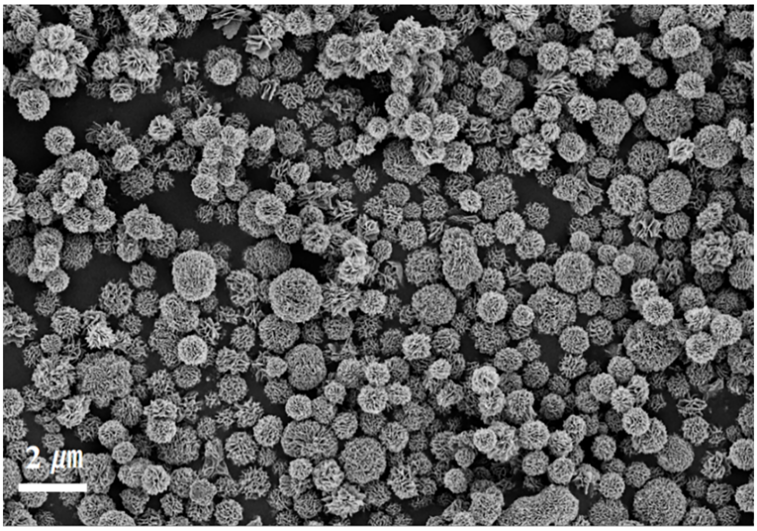

Figure S2. SEM image of the powder VO_x MSs.

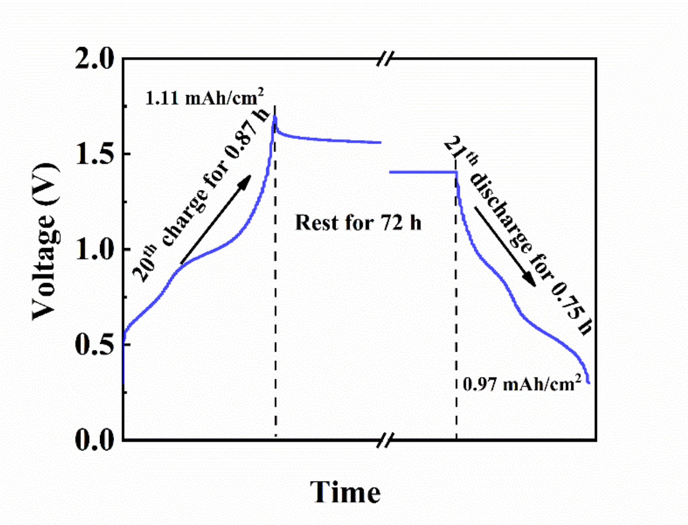

Figure S3. Self-discharge performance of VO_x MSs@ACC electrodes.

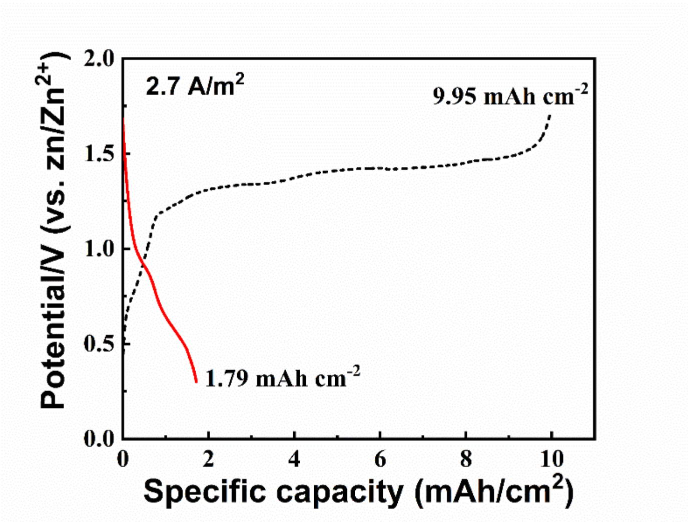

Figure S4. The galvanostatic discharge/charge profiles of the VO_x MSs@ACC at 2.7 A m^{-2} of the 1st cycle.

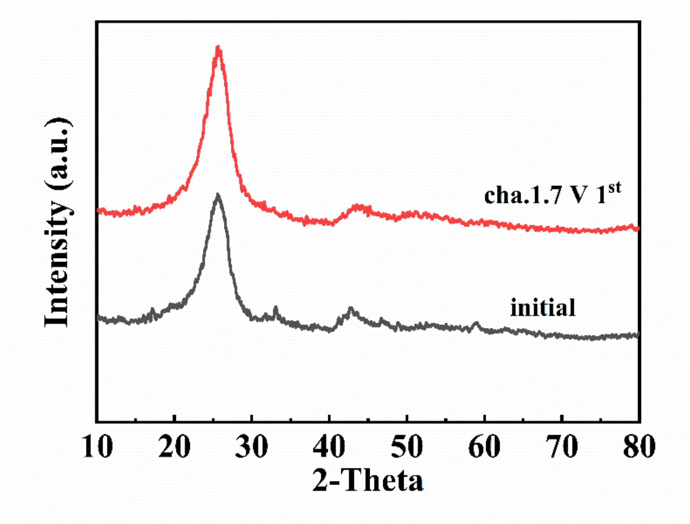

Figure S5. XRD patterns of VO_x MSs@ACC electrode at the pristine state and after the 1st charge process.

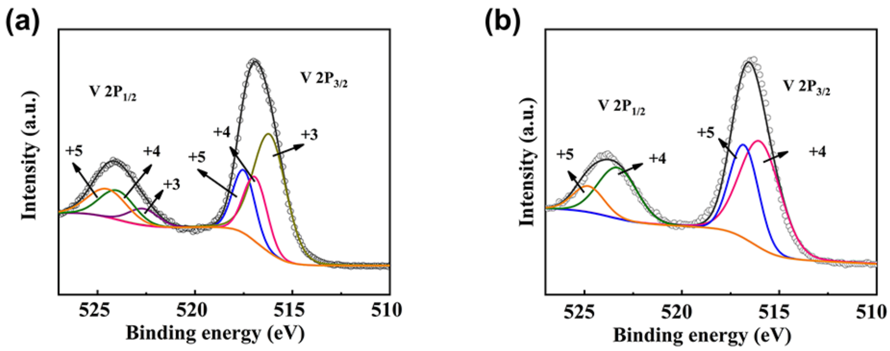

Figure S6. V 2p XPS spectra of VO_x MSs@ACC electrode at pristine state (a) and after the 1st charge process (b).

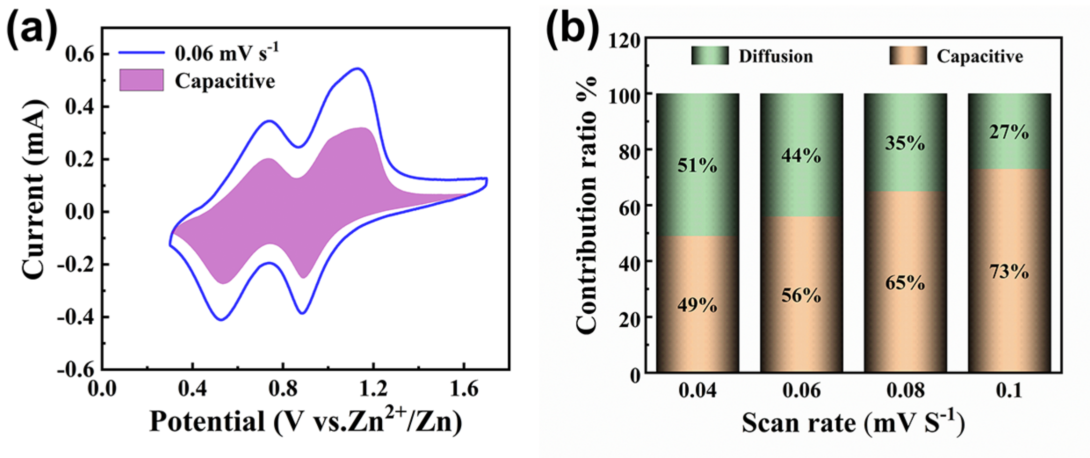

Figure S7. (a) CV profile with the capacitive contribution at 0.06 mV s^{-1}. (b) Capacitive-diffusion contributions at various sweep rates.

Table S1. ICP-MS results of vanadium content of electrodes immersed in electrolytes after 3 days in the inset.

Samples	**V content (mg L^{-1})**
VO_x MSs@ACC	8.09
the powder VO_x MSs	8.48

Table S2. Comparison of the electrochemical performance at a small current density with those of the reported vanadium-based cathodes for aqueous ZIBs.

Materials	**Cycling performance**	**Areal capacity (mAh cm^{-2})**	**Ref.**
$NH_4V_3O_8{\cdot}0.5H_2O$	85% after 120 cycles at 5.4 A m^{-2}	0.976	1
$Na_3V_2(PO4)_3$	80% after 100 cycles at 2.7 A m^{-2}	0.23	2
V_2O_x@V2CTx	81.6% after 200 cycles at 27 A m^{-2}	0.89	3
$(NH_4)_2V_{10}O_{25}{\cdot}8H_2O$	73.2% after 100 cycles at 2.7 A m^{-2}	1.06	4
$V_2O_5{\cdot}nH_2O$/rGO-PVA	28.5% after 100 cycles at 2.7 A m^{-2}	0.628	5
$Na_2V_6O_{16}{\cdot}1.63H_2O$	78% after 100 cycles at 2.7 A m^{-2}	0.79	6
VO_x MSs@ACC	82.3% after 100 cycles at 2.7 A m^{-2}	1.79	**This work**

Table S3. Comparison of the electrochemical performance in this work with those of the recently reported vanadium oxides-based cathodes for ZIBs.

Materials	**Collector**	**Areal capacity (mAh cm^{-2})**	**Cycling performance**	**Mass Loading (mg cm^{-2})**	**Ref.**
V_6O_{13}	carbon cloth	0.446 at 10 A m^{-2}	99% after 1000 cycles at 243 A m^{-2}	1.0	7
V_6O_{13}	carbon cloth	0.825 at 13.5 A m^{-2}	85.3% after 1000 cycles at 54 A m^{-2}	1.5	8
CaVOH@CC	carbon cloth	1.599 at 2.7 A m^{-2}	70% after 800 cycles at 27 A m^{-2}	~7.0	9
KNVO	stainless steel net	0.492 at 2.7 A m^{-2}	90% after 3000 cycles at 135 A m^{-2}	1.2	10
CuVOH@CC	carbon cloth	1.563 at 27 A m^{-2}	50% after 2000 cycles at 27 A m^{-2}	~7.0	11
VO_x MSs@ACC	carbon cloth	1.794 at 2.7 A m^{-2}	80% after 2500 cycles at 135 A m^{-2}	2.1	**This work**

References:

1. H. Jiang, Y. Zhang, Z. Pan, L. Xu, J. Zheng, Z. Gao, T. Hu, C. Meng and J. Wang, $NH_4V_3O_8\cdot0.5H_2O$ nanobelts with intercalated water molecules as a high performance zinc ion battery cathode, *Mater. Chem. Front*. 2020, **4**, 1434-1443.
2. J. S. Ko, P. P. Paul, G. Wan, N. Seitzman, R. H. DeBlock, B. S. Dunn, M. F. Toney and J. Nelson Weker, NASICON $Na_3V_2(PO_4)_3$ Enables Quasi-Two-Stage Na^+ and Zn^{2+} Intercalation for Multivalent Zinc Batteries, *Chem. Mater.*, 2020, **32**, 3028-3035.
3. R. Venkatkarthick, N. Rodthongkum, X. Zhang, S. Wang, P. Pattananuwat, Y. Zhao, R. Liu and J. Qin, Vanadium-Based Oxide on Two-Dimensional Vanadium Carbide MXene (V_2O_x@V_2CTx) as Cathode for Rechargeable Aqueous Zinc-Ion Batteries, *ACS Appl. Energy Mater.*, 2020, **3**, 4677-4689.
4. H. Jiang, Y. Zhang, Z. Pan, L. Xu, J. Zheng, Z. Gao, T. Hu and C. Meng, Facile hydrothermal synthesis and electrochemical properties of $(NH_4)_2V_{10}O_{25}\cdot8H_2O$ nanobelts for high-performance aqueous zinc ion batteries, *Electrochim. Acta*, 2020, **332**, 135506.
5. J. Sun, Y. Zhang, Y. Liu, H. Jiang, X. Dong, T. Hu and C. Meng, Hydrated vanadium pentoxide/reduced graphene oxide-polyvinyl alcohol $V_2O_5\cdot nH_2O$/rGO-PVA film as a binder-free electrode for solid-state Zn-ion batteries, *J. Colloid Interface Sci.*, 2021, **587**, 845-854.
6. P. Hu, T. Zhu, X. Wang, X. Wei, M. Yan, J. Li, W. Luo, W. Yang, W. Zhang, L. Zhou, Z. Zhou and L. Mai, Highly Durable $Na_2V_6O_{16}.1.63H_2O$ Nanowire Cathode for Aqueous Zinc-Ion Battery, *Nano Lett*., 2018, **18**, 1758-1763.
7. M. Tamilselvan, T. V. M. Sreekanth, K. Yoo and J. Kim, Binder-free coaxially grown V_6O_{13} nanobelts on carbon cloth as cathodes for highly reversible aqueous zinc ion batteries, Appl.

Surf. Sci., 2020, **529**, 147077.

8. P. He, J. Liu, X. Zhao, Z. Ding, P. Gao and L.-Z. Fan, A three-dimensional interconnected V_6O_{13} nest with a V^{5+}-rich state for ultrahigh Zn ion storage, J Mater. Chem. A, 2020, **8**, 10370-10376.
9. J. Ren, P. Hong, Y. Ran, B. Wang, T. Chen and Y. Wang, High-loading and high-performance zinc ion batteries enabled by electrochemical conversion of vanadium oxide cathodes, Electrochim. Acta, 2022, **415**, 140265.
10. T. Zhou, H. Xiao, L. Xie, Q. Han, X. Qiu, Y. Xiao, X. Yang, L. Zhu and X. Cao, Research on the electrochemical performance of polyoxovanadate material $K_4Na_2V_{10}O_{28}$ as a novel aqueous zinc-ion batteries cathode, Electrochim. Acta, 2022, **424**, 140621.
11. J. Ren, P. Hong, Y. Ran, Y. Chen, X. Xiao and Y. Wang, Binder-free three-dimensional interconnected $CuV_2O_5 \cdot nH_2O$ nests as cathodes for high-loading aqueous zinc-ion batteries, Inorg. Chem. Front., 2022, **9**, 792-804.