# Supplementary Material

# Fabrication of a heterovalent dual-cation pre-embedded hydrated vanadium oxide cathode for high-performance zinc ion storage

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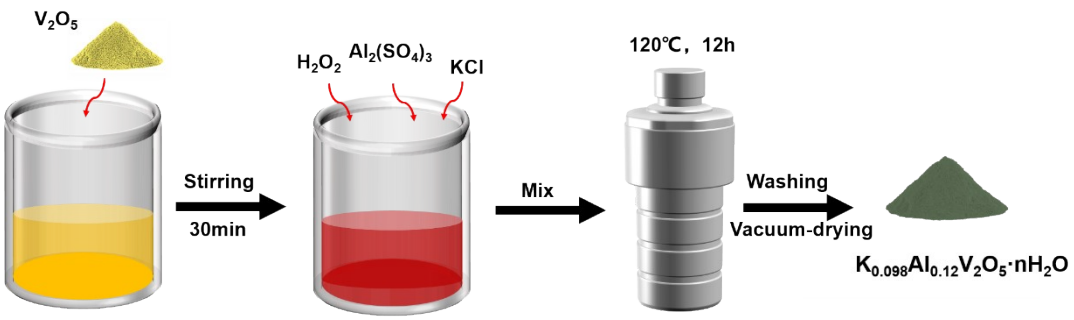


**Fig. S1.** Schematic illustration of preparation process of KAlVOH cathode material.

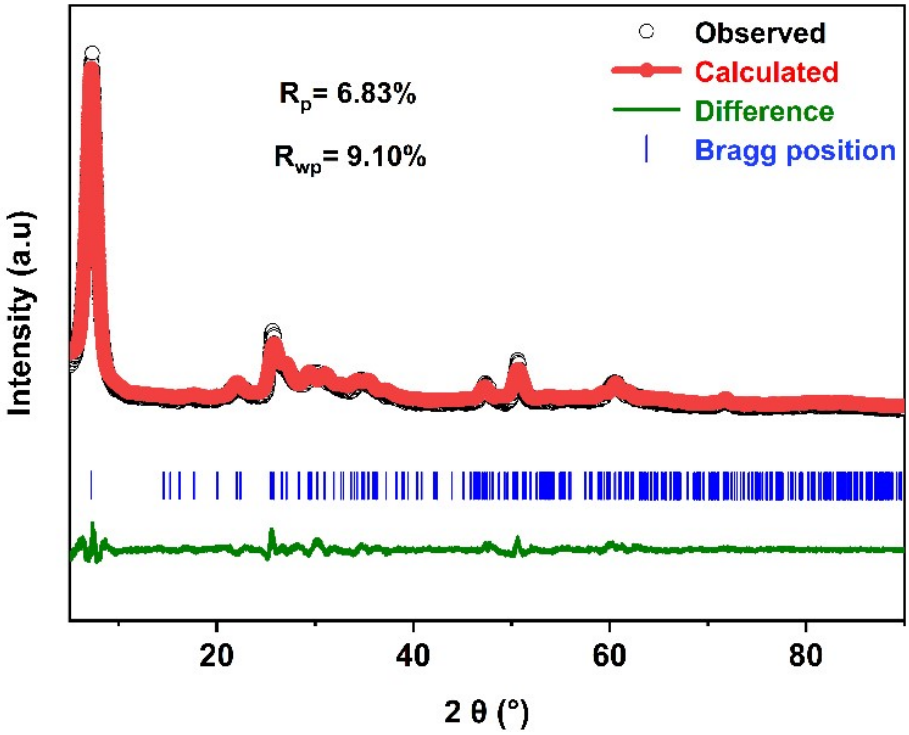


**Fig. S2.** The XRD Rietveld refinement patterns of KAlVOH.

**Table S1** The lattice parameters of KAlVOH.

| | ***a*** **(Å)** | ***b*** **(Å)** | ***c*** **(Å)** | ***α*** **(°)** | ***β*** **(°)** | ***γ*** **(°)** | ***V*** **(Å$^3$)** |
|---|---|---|---|---|---|---|---|
| **KAlVOH** | 11.57 | 3.60 | 12.09 | 90 | 96.25 | 90 | 500.67 |

| **Atom** | **Position** | **Occupancy** | **x** | **y** | **z** |
|---|---|---|---|---|---|
| **O1** | 4i | 0.907249 | 0.067908 | 0.000000 | 0.056304 |
| **V1** | 4i | 0.952933 | 0.573328 | 0.000000 | 0.149726 |
| **O5** | 4i | 1.000000 | 0.329173 | 0.000000 | 0.243342 |
| **O6** | 4i | 0.782890 | 0.105561 | 0.000000 | 0.473414 |
| **V2** | 4i | 0.820367 | 0.271684 | 0.000000 | 0.114128 |
| **O4** | 4i | 1.000000 | 0.571255 | 0.000000 | 0.298481 |
| **O2** | 4i | 0.960103 | 0.442318 | 0.000000 | 0.123395 |
| **O3** | 4i | 1.000000 | 0.744282 | 0.000000 | 0.001505 |
| **K** | 2c | 0.098000 | 0.000000 | 0.000000 | 0.500000 |
| **Al** | 2c | 0.120000 | 0.000000 | 0.000000 | 0.500000 |

**Table S2** Correlation between properties of the preintercalated M cations (size and electronegativity) and the interplanar spacing of $M_xV_2O_5{\cdot}nH_2O$ materials in this work [1-6].

| Preintercalated M cation | K/Al | Li | Na | K | Al |
|---|---|---|---|---|---|
| Ionic radius Å | - | 0.76 | 0.95 | 1.33 | 0.53 |
| Hydrated ion Radis Å | - | 3.82 | 3.58 | 3.31 | 4.8 |
| Interplanar spacing Å reported in this paper | **13.2** | 12.0 | 11.0 | 9.9 | 13.36 |
| Electronegativity of element (Pauling scale) | - | 1.0 | 0.93 | 0.82 | 1.61 |
| Electronegativity difference with O (3.44) | - | 2.44 | 2.51 | 2.62 | 1.83 |

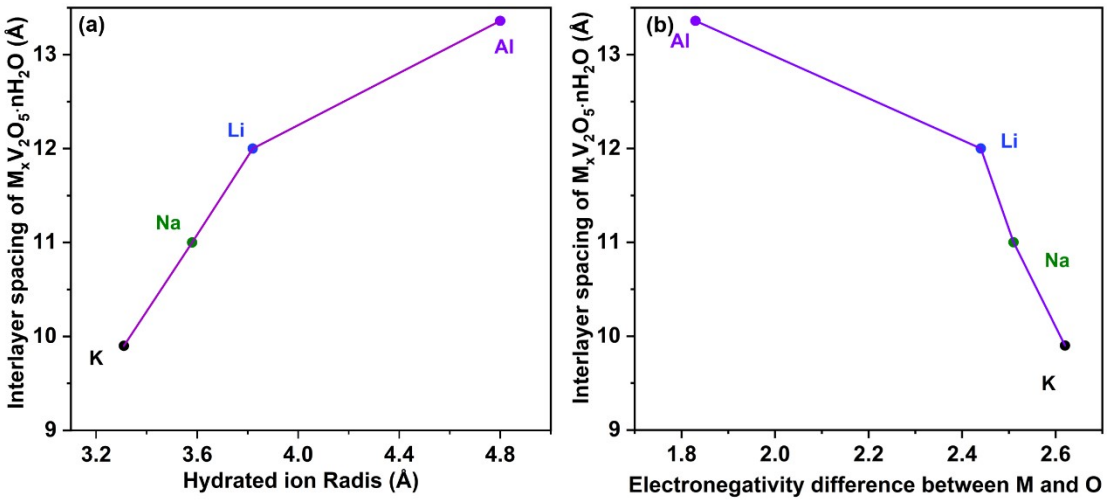


**Fig. S3.** The relationship between interlayer spacing of $M_xV_2O_5{\cdot}nH_2O$ (reported in this paper) with respect to the (a) radius of the hydrated M cation and (b) electronegativity difference between M and oxygen.

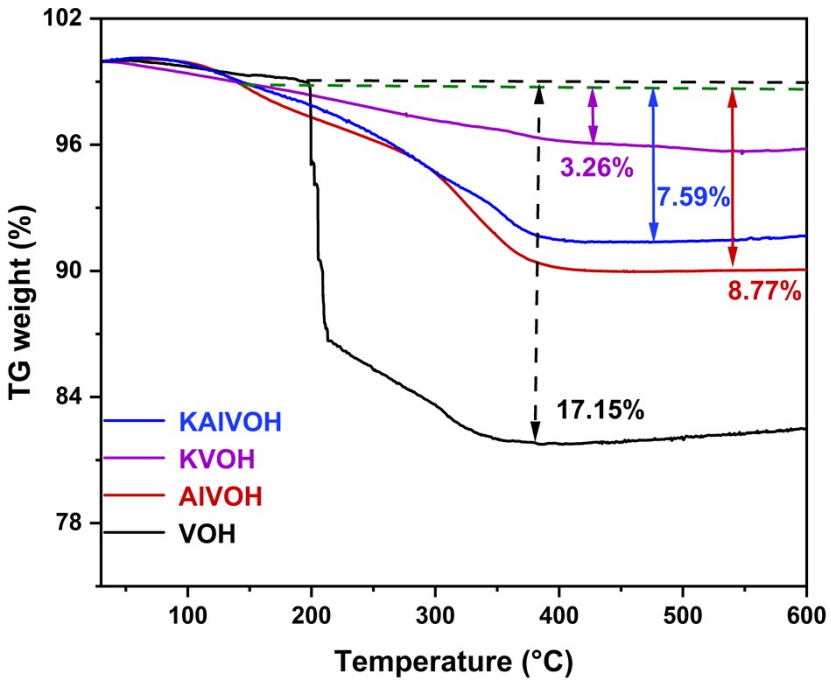


**Fig. S4.** TG curves of KAlVOH, KVOH, AlVOH and VOH materials.

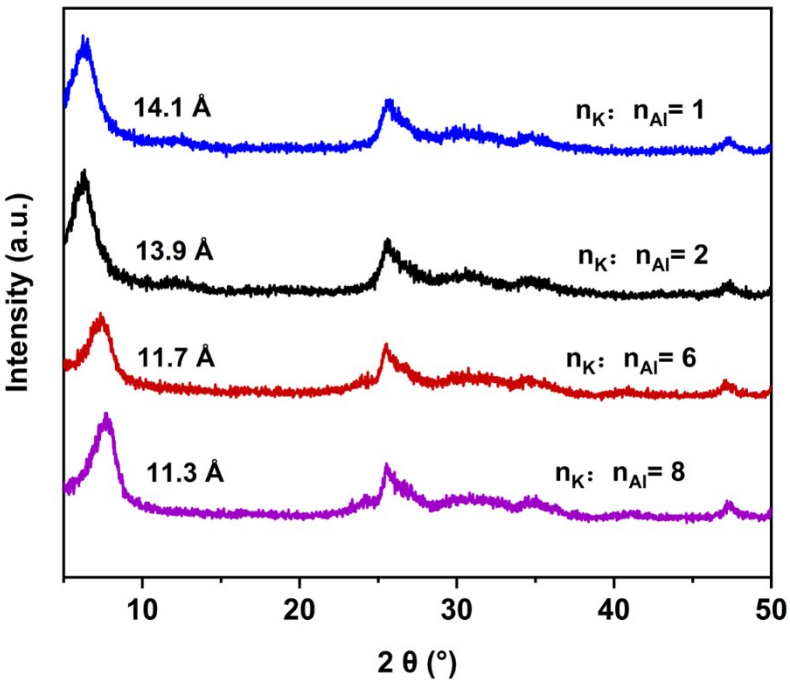


**Fig. S5.** XRD patterns of KAlVOH with various $K^{+}/Al^{3+}$ molar ratios of 1, 2, 6 and 8.

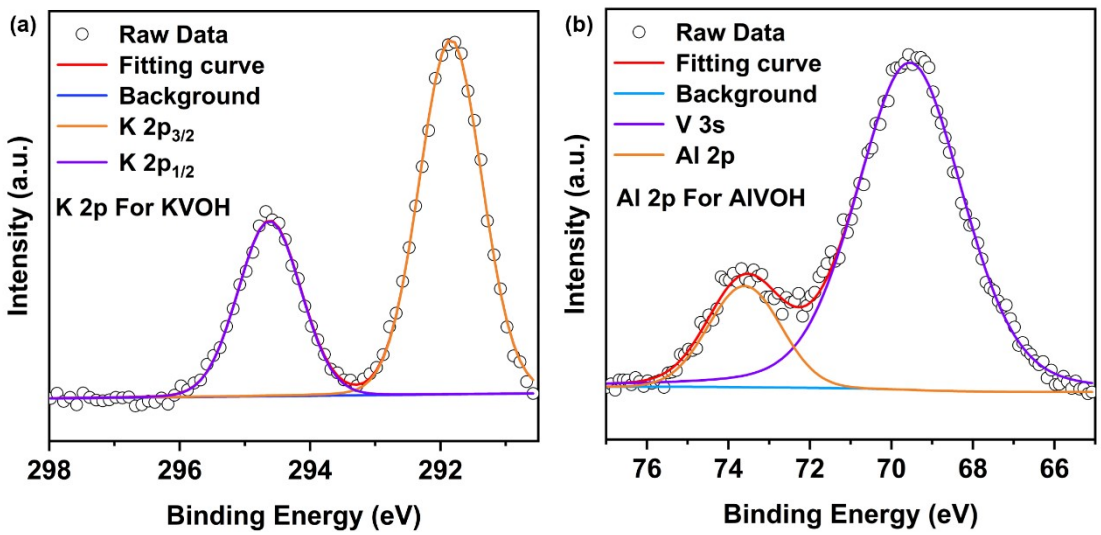


**Fig. S6.** High-resolution XPS spectra of (a) K 2p for KVOH material and (b) Al 2p for AlVOH material.

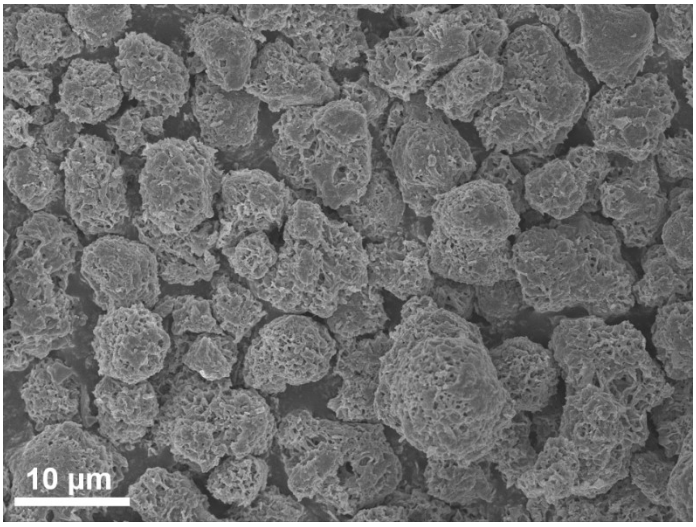


**Fig. S7.** Low-magnification SEM image of KAlVOH material.

**Table S3** Atomic ratio of K, Al and V in KAlVOH by ICP analysis.

| Element | ratio |
|---|---|
| K : Al : V | 0.098 : 0.12 : 2 |

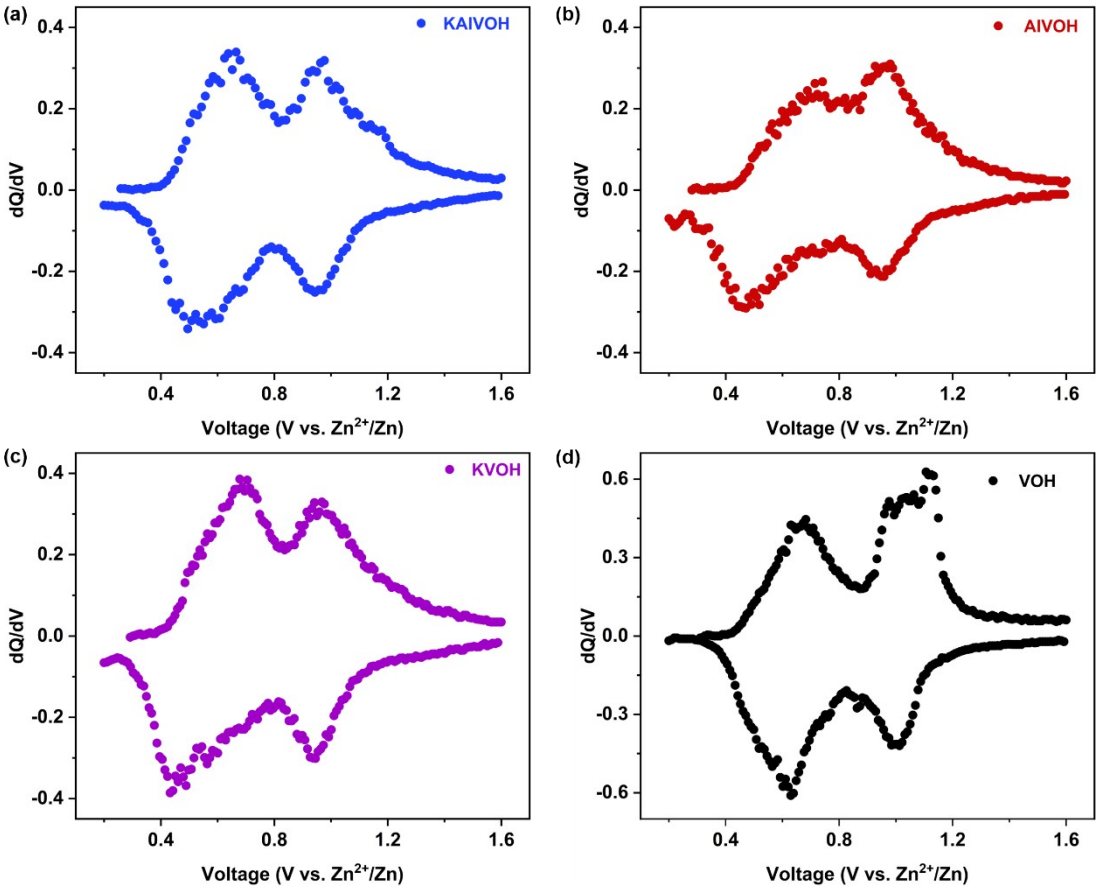


**Fig. S8.** The differential capacity curves of (a) KAlVOH, (b) AlVOH, (c) KVOH, (d) VOH cathode materials at 0.05 A $g^{-1}$.

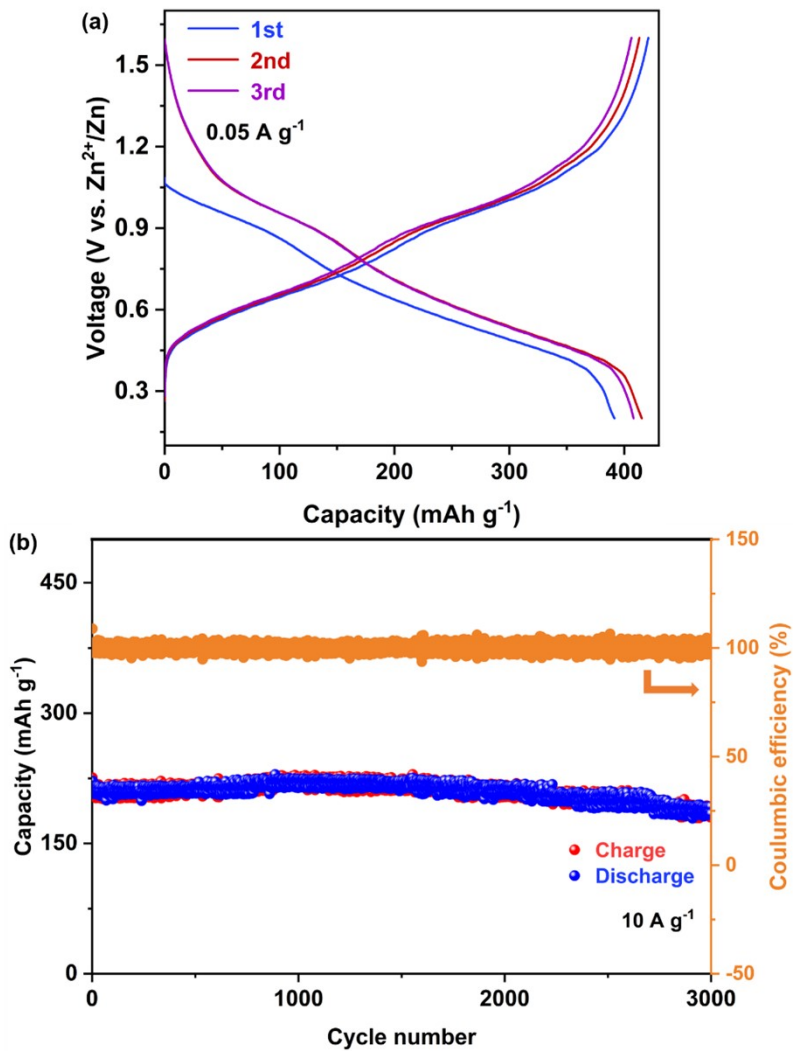


**Fig. S9.** Electrochemical properties of KAlVOH cathode material: (a) voltage profiles at 0.05 A $g^{-1}$ in the initial three cycles; (b) Cycling performance at 10 A $g^{-1}$.

**Table S4** Performance comparison of selected V-based cathode materials of ZIBs.

| **Materials** | **Specific capacity / mAh $g^{-1}$ (Current density: A $g^{-1}$)** | **Cycle numbers (Current density: A $g^{-1}$)** | **Capacity retention** | **Ref.** |
|---|---|---|---|---|
| CaVOH/rGO | 409 (0.05) | 2000 (4) | 90% | 4 |
| $H_{11}Al_2V_6O_{23}\cdot_2$@graphene | 305.4 (1) | 900 (5) | 94% | 5 |
| $Na_{0.33}V_2O_5$ | 367.1 (0.1) | 1000 (5) | 93% | 7 |
| KVO NBs | 361 (0.2) | 2000 (5) | 90.3% | 8 |
| $NaCa_{0.6}V_6O_{16}\cdot 3H_2O$ | 347 (0.1) | 2000 (2) | 94% | 9 |
| LPVO | 377 (0.1) | 800 (5) | 94% | 10 |
| KMgVOH | 423 (0.1) | 2000 (4) | 72% | 11 |
| Na-$V_2O_5$ | 306 (0.1) | 1000 (2) | 83.4% | 12 |
| KAlVOH | 424 (0.05) | 3000 (5) | 96% | **This work** |

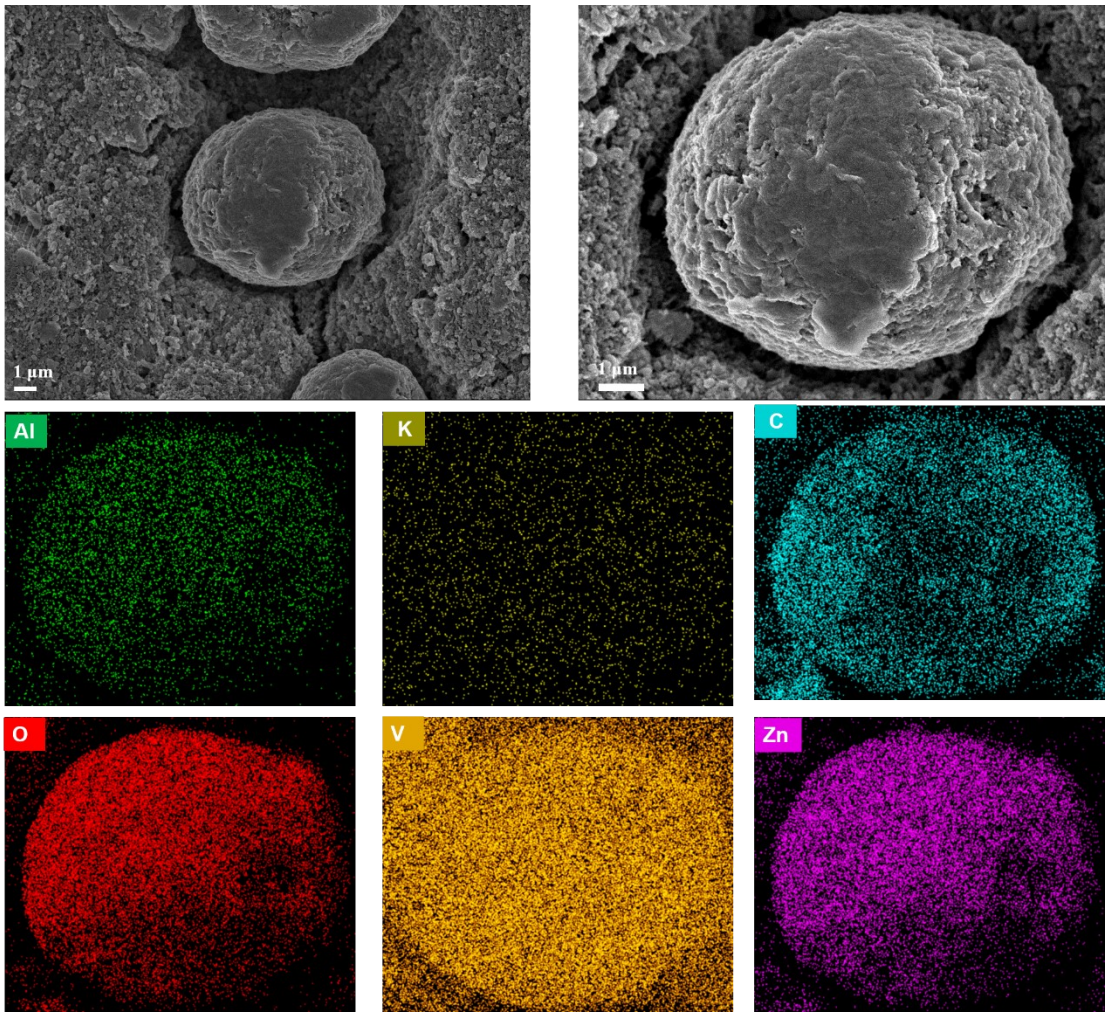


**Fig. S10.** SEM and EDS element mapping images of KAlVOH cathode material after 3000 cycles.

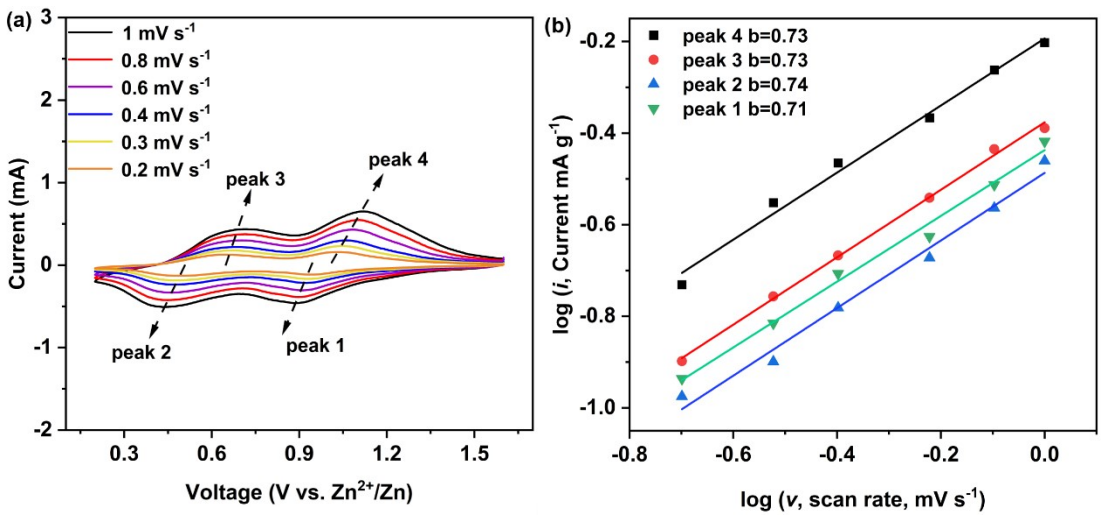


**Fig. S11.** (a) CV curves at various sweep rates and (b) the relationship between peak currents and sweep rates of the VOH cathode.

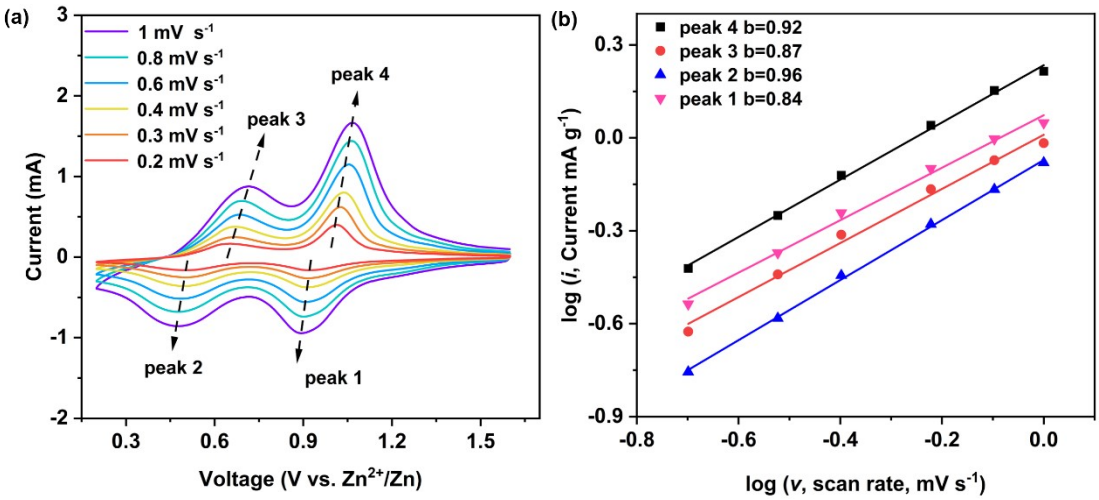


**Fig. S12.** (a) CV curves at various sweep rates and (b) the relationship between peak currents and sweep rates of the AlVOH cathode.

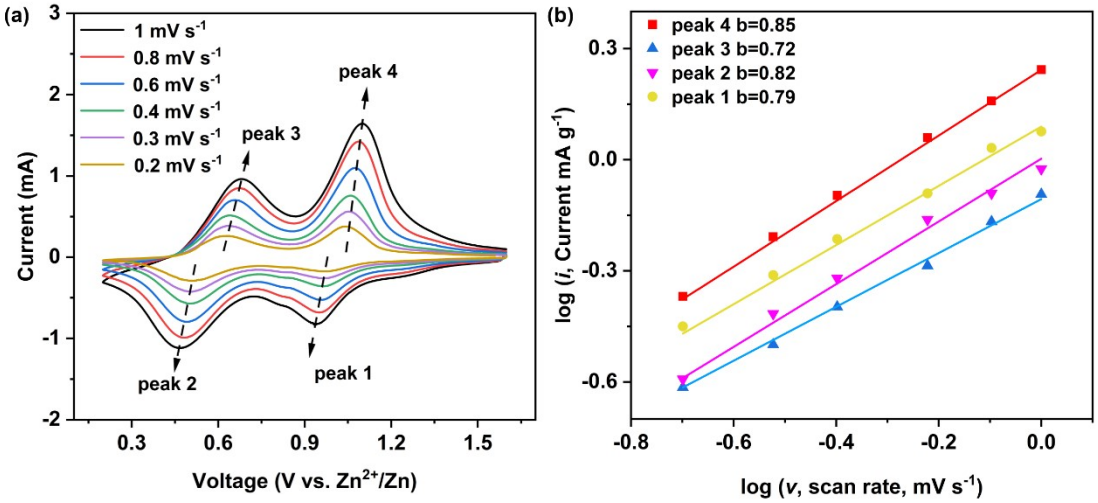


**Fig. S13.** (a) CV curves at various sweep rates and (b) the relationship between peak currents and sweep rates of the KVOH cathode.

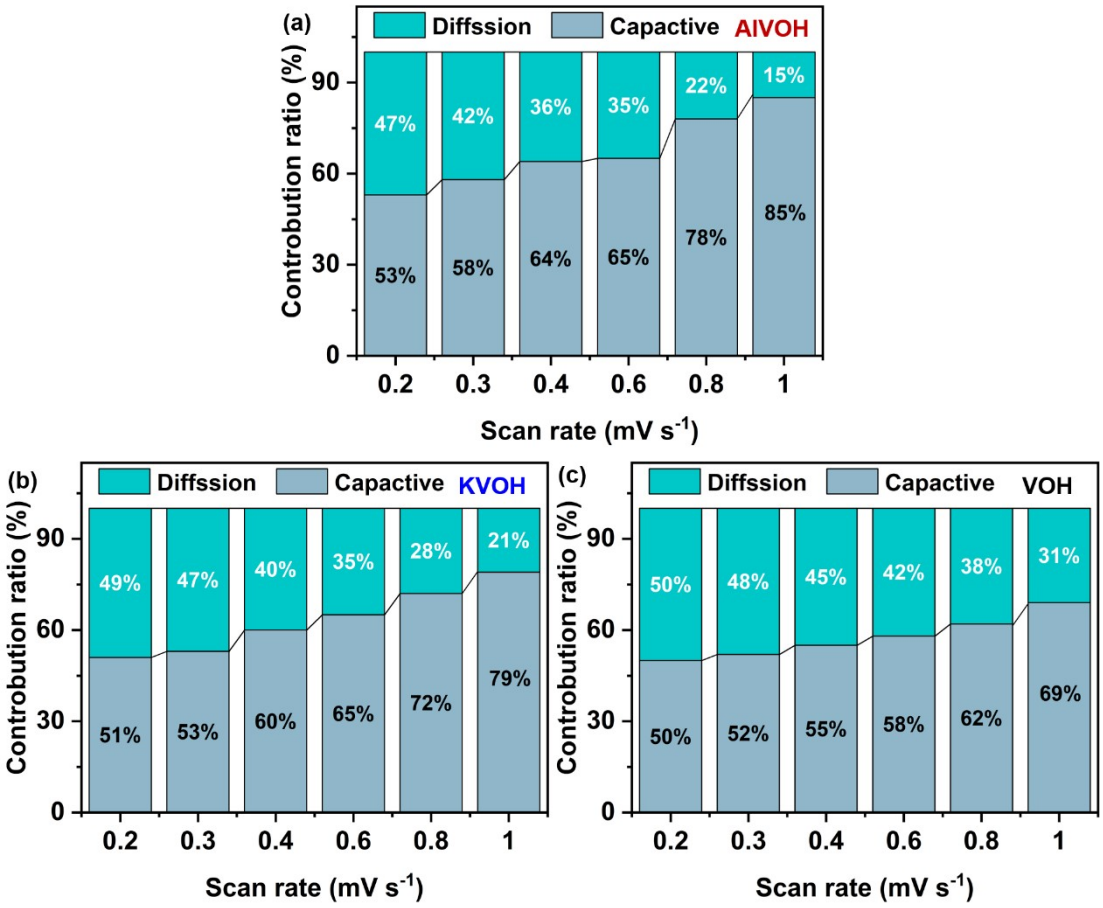


**Fig. S14.** Contribution ratios of capacity on capacitive contribution and diffusive contribution of the (a) AlVOH, (b) KVOH and (c) VOH cathode materials.

**Table S5** The fitting results of distinct resistance elements for VOH, KVOH, AlVOH and KAlVOH cathode materials.

| Material | $R_s$ (Ω) | $R_{ct}$ (Ω) |
|---|---|---|
| VOH | 2.814 | 760.9 |
| KVOH | 1.136 | 225.7 |
| AlVOH | 1.361 | 134.4 |
| KAlVOH | 0.77243 | 77.03 |

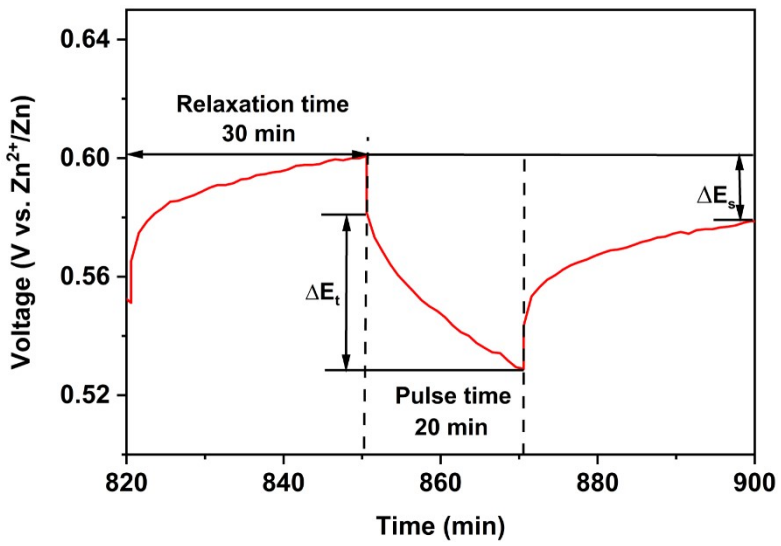


**Fig. S15.** Schematic illustration of a single step of the GITT during discharge process.

The GITT (Galvanostatic Intermittent Titration Technique) was used to thoroughly investigate the kinetics of solid-state diffusion in the electrode. The solid-state diffusion coefficient of zinc-ion was calculated using the following equation.

$$D_{zn^{2+}} = \frac{4}{\pi\tau}\left(\frac{n_M V_M}{S}\right)^2\left(\frac{\triangle E_s}{\triangle E_t}\right)^2$$

In this formula, $V_M$ ($cm^3$ $mol^{-1}$), $n_M$ (g $mol^{-1}$) are the molar volume and the molar mass of the VOH, KVOH, AlVOH, KAlVOH cathodes, respectively. And $\tau$ (s) is constant current pulse duration and S ($cm^{-2}$) is the contact area between electrolytes. In addition, Es is the steady-state voltage change measured by a single-step GITT, and Et is the voltage change over the duration of

one discharge/charge pulse, independent of the IR drop. As shown in Fig. S11, during the GITT test, discharge or charge the battery at a current rate of 50 mA $g^{-1}$ for 20 minutes, then leave the circuit open for 30 minutes to allow the battery to relax to equilibrium.

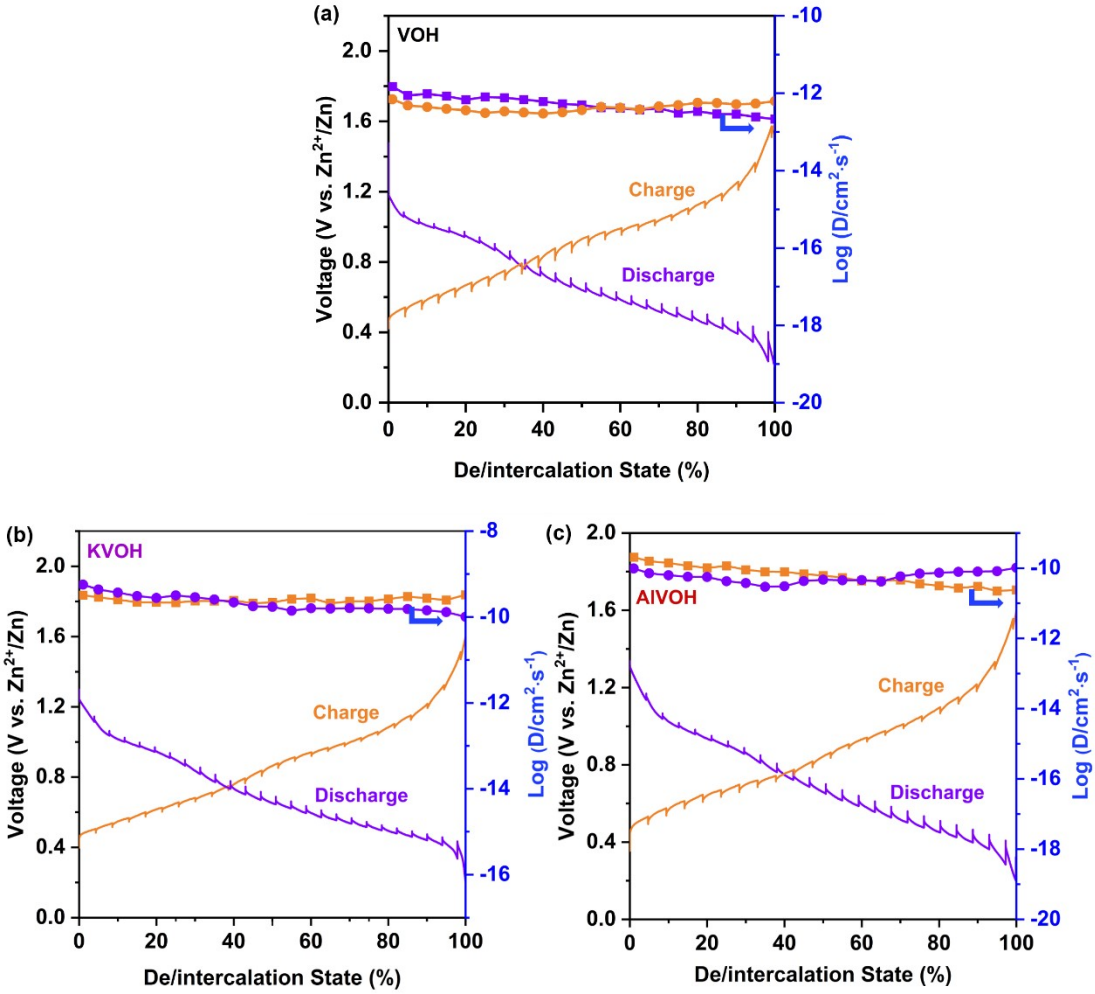


**Fig. S16.** Galvanostatic intermittent titration technique (GITT) curves at the current density of 0.05 A $g^{-1}$ and the corresponding $Zn^{2+}$ diffusion coefficients of the (a) VOH, (b) KVOH and (c) AlVOH cathode materials.

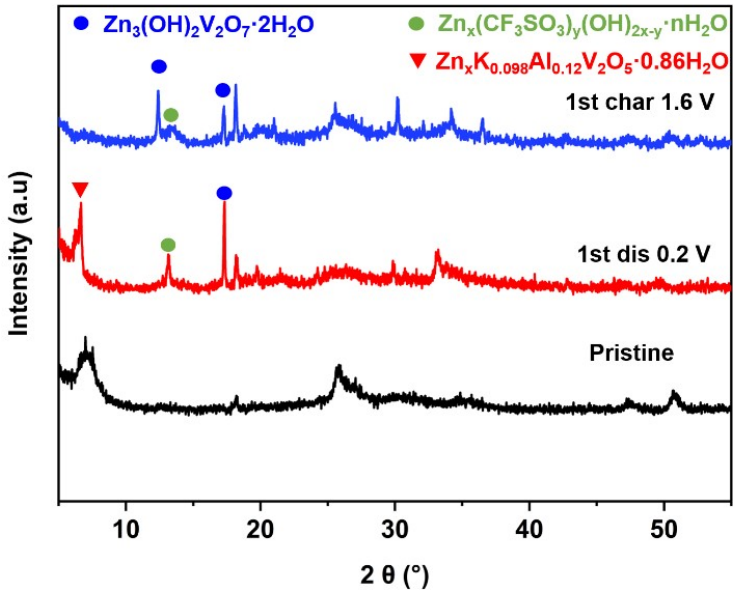


**Fig. S17.** The *ex situ* XRD patterns of KAlVOH cathode material at various states at 0.1 A·g$^{-1}$.

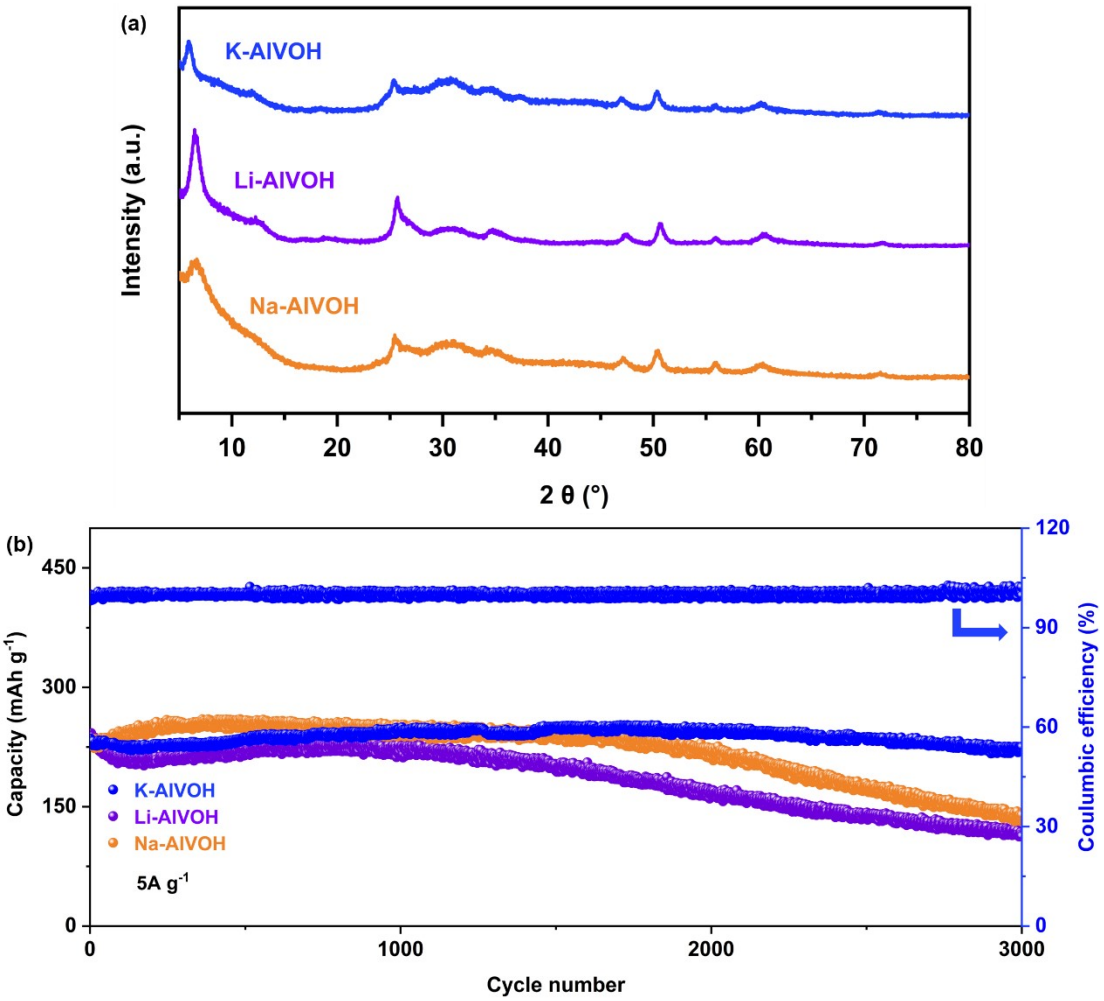


**Fig. S18.** (a) XRD patterns of KAlVOH, NaAlVOH, and LiAlVOH cathode materials and (b)

cycling performance of three cathode materials at 5 A $g^{-1}$.

## References


1. M. Tian, C. Liu, J. Zheng, X. Jia, E. P. Jahrman, G. T. Seidler, D. Long, M. Atif, M. Alsalhi and G. Cao, *Energy Storage Materials*, 2020, **29**, 9-16.
2. A. G. Volkov, S. Paula and D. W. Deamer, *Bioelectrochemistry and Bioenergetics*, 1997, **42**, 153-160.
3. H. Ma, H. Chen, Y. Hu, B. Yang, J. Feng, Y. Xu, Y. Sun, H. Cheng, C. Li, X. Yan and L. Qu, *Energy & Environmental Science*, 2022, **15**, 1131-1143.
4. W. He, C. Meng, Z. Ai, D. Xu, S. Liu, Y. Shao, Y. Wu and X. Hao, *Chemical Engineering Journal*, 2023, **454**, 140260.
5. W. Zhang, S. Liang, G. Fang, Y. Yang and J. Zhou, *Nano-Micro Letters*, 2019, **11**, 69.
6. X. Jia, R. Tian, C. Liu, J. Zheng, M. Tian and G. Cao, *Materials Today Energy*, 2022, **28**, 101063.
7. T. Hu, Z. Feng, Y. Zhang, Y. Liu, J. Sun, J. Zheng, H. Jiang, P. Wang, X. Dong and C. Meng, *Inorganic Chemistry Frontiers*, 2021, **8**, 79-89.
8. P. He, G. Zhang, X. Liao, M. Yan, X. Xu, Q. An, J. Liu and L. Mai, *Advanced Energy Materials*, 2018, **8**, 1702463.
9. K. Zhu, T. Wu and K. Huang, *Advanced Energy Materials*, 2019, **9**, 1901968.
10. W. He, Z. Fan, Z. Huang, X. Liu, J. Qian, M. Ni, P. Zhang, L. Hu and Z. Sun, *Journal of Materials Chemistry A*, 2022, **545**, 231920.
11. Z. Feng, Y. Zhang, J. Sun, Y. Liu, H. Jiang, M. Cui, T. Hu and C. Meng, *Chemical Engineering Journal*, 2022, **433**, 133795.
12. M. Liu, Z. Li and Y. Zhang, *Journal of The Electrochemical Society*, 2023, **170**, 110524.