Electrochemical performance and reaction mechanism investigation of V$_2$O$_5$ positive electrode material for aqueous rechargeable zinc batteries

Qiang Fu$^a$, Jiaqi Wang$^a$, Angelina Sarapulova$^a$, Lihua Zhu$^a$, Alexander Missyul$^c$, Edmund Welter$^d$, Xianlin Luo$^a$, Ziming Ding$^{e,f}$, Michael Knapp$^a$, Helmut Ehrenberg$^{a,b}$, Sonia Dsoke$^{a,b}$

$^a$Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
$^b$Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Helmholtzstrasse 11, 89081 Ulm, Germany
$^c$CELLS-ALBA Synchrotron, E-08290 Cerdanyola del Valles, Barcelona, Spain
$^d$Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, D-22607 Hamburg, Germany
$^e$Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
$^f$Technische Universität Darmstadt, 64289 Darmstadt, Germany

Corresponding author: qiang.fu@kit.edu (Q. Fu)
Tel: 49-721 608-41445, Fax: 49-721 608-28521.
Figure S1 Discharge-charge profiles of V$_2$O$_5$ nanowires at 200 mA g$^{-1}$ in 1 M ZnSO$_4$
(b) 10th pattern of discharged V$_2$O$_5$
- Yobs
- Ycalc
- Difference
- Bragg

Intensity / a.u.
2 Theta / degree
Zn$_{0.15}$V$_2$O$_5$
Zn$_{3.8}$O$_5$$_2$V$_2$O$_2$$_2$H$_2$O

(c) 36th pattern, fully discharged V$_2$O$_5$
- Yobs
- Ycalc
- Difference
- Bragg

Intensity / a.u.
2 Theta / degree
1: Zn$_{0.84}$V$_2$O$_5$
2: Zn$_{3.8}$O$_5$$_2$V$_2$O$_2$$_2$H$_2$O
3: ZnSO$_4$Zn$_{5}$OH$_{5}$$_5$H$_2$O
Figure S2 Rietveld refinement based on the pattern of the pristine $V_2O_5$ (a), discharged state in the beginning of Region II with the capacity of 44 mAh g$^{-1}$ (10$^{th}$ pattern, 1.02 V) (b), first fully discharged $V_2O_5$ electrode at 0.3 V (36$^{th}$ pattern) (c), fully charged at 1.6 V(69$^{th}$ pattern) (d), and 2$^{nd}$ fully discharged $V_2O_5$ electrode at 0.3 V (97$^{th}$ pattern) (e)
Figure S3 In operando synchrotron diffraction of V$_2$O$_5$ during the first one and half cycles and the corresponding voltage profile at a current density of 50 mA g$^{-1}$
**Figure S4** Images of separator from the 1st discharged V$_2$O$_5$ at 0.3 V (a) and the 1st charged V$_2$O$_5$ at 1.6 V (b)

**Figure S5** Discharge-charge profiles of V$_2$O$_5$ in 1 M ZnSO$_4$ electrolyte for *in operando* XAS (50 mA g$^{-1}$)
Figure S6 STEM-HAADF EDX mapping of O (red), S (blue), V (magenta), and Zn (green) for the 1st discharged V$_2$O$_5$
| Samples            | Wavenumbers / cm\(^{-1}\) | assignments                                      |
|--------------------|----------------------------|--------------------------------------------------|
| Pristine and       | 994                        | V-O(1) stretching mode                           |
| charged V\(_2\)O\(_5\) | 700                        | V–O(2) stretching vibration                      |
|                    | 528                        | V–O(4) stretching vibration                      |
|                    | 484                        | V–O(3) bending vibration                         |
|                    | 405 and 284                | V-O(1) stretching and bending vibrations          |
|                    | 304                        | V–O(4) bending vibrations                        |
|                    | 197                        | δ(O2-V-O2)                                       |
|                    | 145                        | δ(O3-V-O2)                                       |
| Discharged         | 1129, 967, and 610         | \(v_3, v_1, v_4\) of SO₄²⁻ vibration in           |
| V\(_2\)O\(_5\)    | 876 and 450                | ZnSO\(_4\)Zn\(_3\)(OH)\(_n\)·nH\(_2\)O          |
|                    |                            | V-O and Zn-O vibration of Zn\(_x\)V\(_2\)O\(_5\) and |
|                    |                            | Zn\(_3\)(OH)\(_2\)V\(_2\)O\(_7\)·2H\(_2\)O      |
| Zn counter         | 440 and 566                | Zn-O vibration of Zn\(_{1+x}\)O on the surface   |
| electrode          |                            | of Zn                                            |
|                    | 1129, 967, and 398         | \(v_3, v_1, v_4\) of SO₄²⁻ vibration in the       |
|                    |                            | ZnSO\(_4\)Zn\(_3\)(OH)\(_n\)·nH\(_2\)O          |