Supporting Informations

Aluminium vanadate with unsaturated coordinated V centers and oxygen vacancies: surface migration and partial phase transformation mechanism in high performance zinc-ion battery

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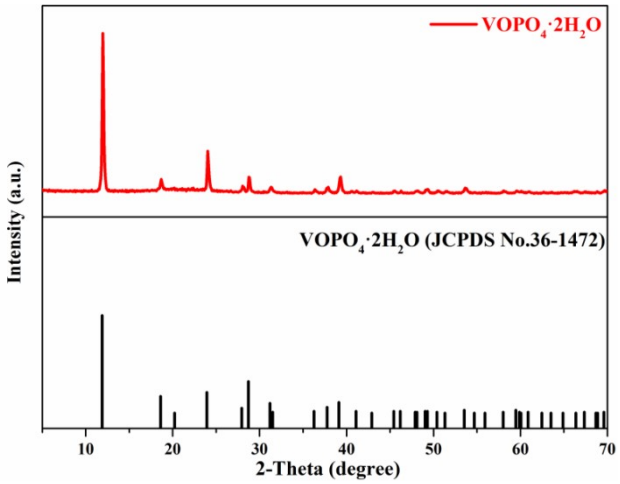
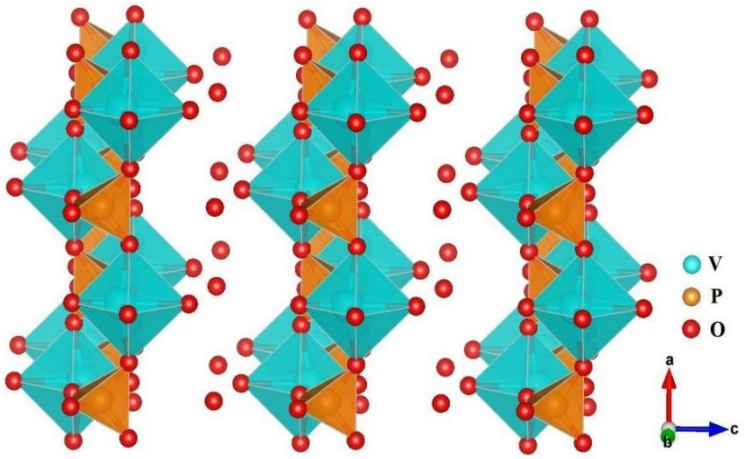
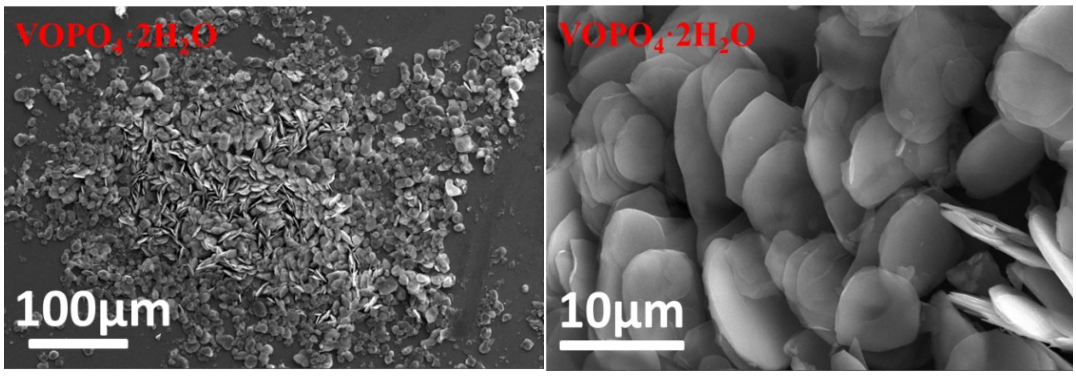
(a)



(b)



(c) **(d)**



(e)

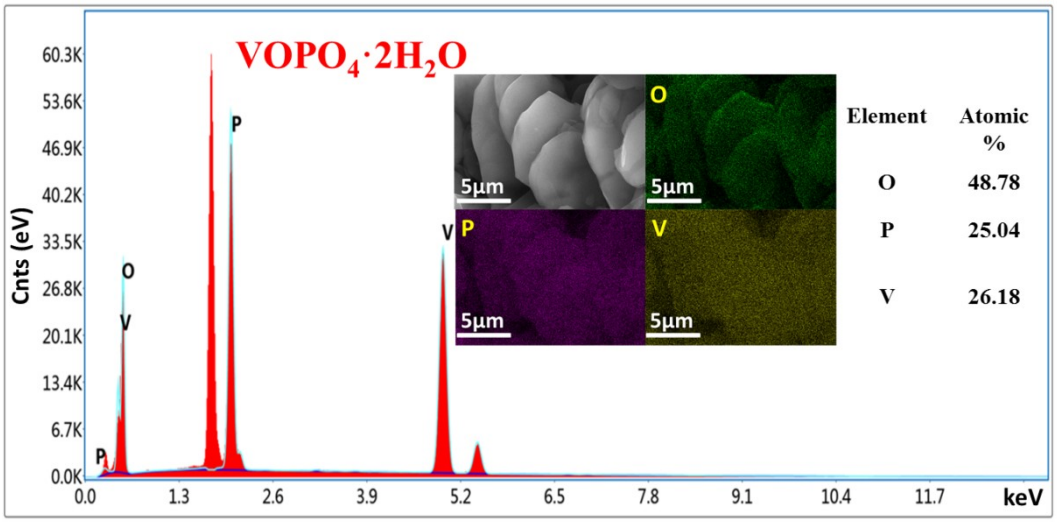


Fig. S1(**a**) XRD pattern of $VOPO_4 \cdot 2H_2O$ and the standard profile. (**b**) 2D layer in $VOPO_4 \cdot 2H_2O$ built by $\{PO_4\}$ tetrahedra and $\{VO_6\}$ octahedra (H omitted for clarity); (**c, d**) SEM imagesand (**e**) EDS as well as elemental mappings of $VOPO_4 \cdot 2H_2O$.

Table S1 The lattice parameters for AlVO and CaVO.

	a (Å)	*b* (Å)	*c* (Å)	*α*(°)	*β* (°)	*γ* (°)	*V* (Å^3)
AlVO	11.723 (5)	3.669 (4)	15.498(4)	90	88.377(7)	90	666.33 (8)
CaVO	11.899 (5)	3.649 (1)	14.041(8)	90	82.703(2)	90	604.68 (3)

Table S2 Selected bond lengths (Å) in AlVO and CaVO.

AlVO				CaVO			
V_a-O1	2.089	V_b-O1#1	1.926	V_a-O1	2.062	V_b-O1#1	1.930
V_a-O2	1.875	V_b-O1#2	1.926	V_a-O2	1.886	V_b-O1#2	1.930
V_a-O3#1	2.120	V_b-O2	1.699	V_a-O3#1	2.052	V_b-O2	1.738
V_a-O3#2	2.120	V_b-O3	2.361	V_a-O3#2	2.052	V_b-O3	2.424

V_a-O4	2.137	V_b-O8	2.731	V_a-O5	1.829	V_b-O4	1.955
Al-O5	2.230	V_b-O8#3	2.731	Ca-O6	2.236		
Al-O6	2.400						

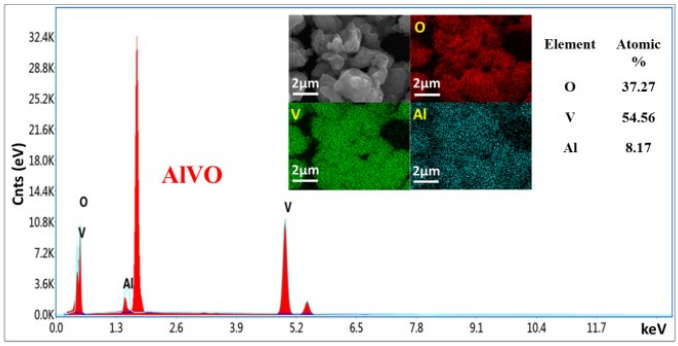
Symmetry transformations used to generate equivalent atoms:

#1 x+1/2, y+1/2, z #2 x+1/2, y-1/2, z #3 x, y-1, z

Table S3 The contents of Al/V in AlVO and Ca/V in CaVO.

Sample	Element	μg ml^{-1}	μmol ml^{-1}
AlVO	Al	3.567	0.1324
	V	78.82	1.5473
CaVO	Ca	8.960	0.2236
	V	99.94	1.9619

(a)



(b)

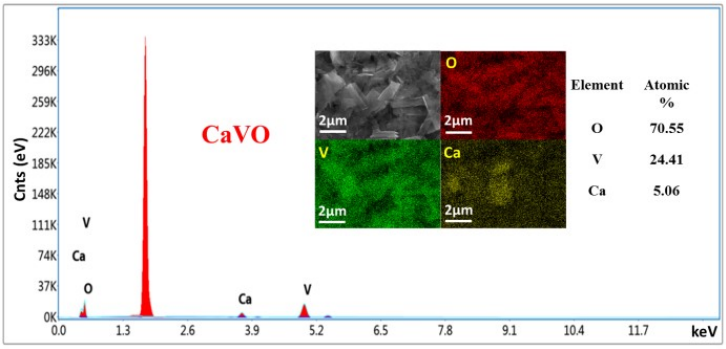


Fig. S2 EDS as well as elemental mappings (inset) of (**a**) AlVO and (**b**) CaVO.

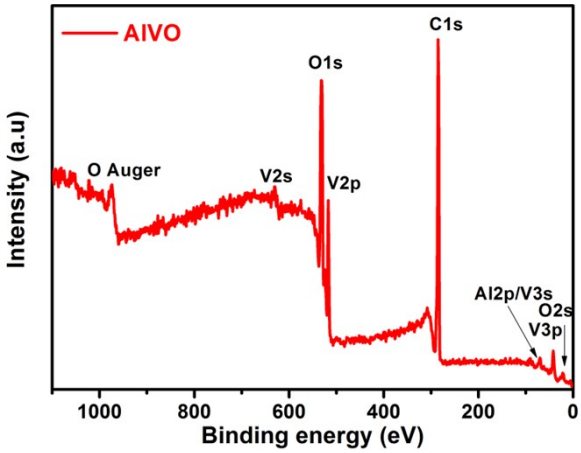


Fig. S3 The full XPS of AlVO

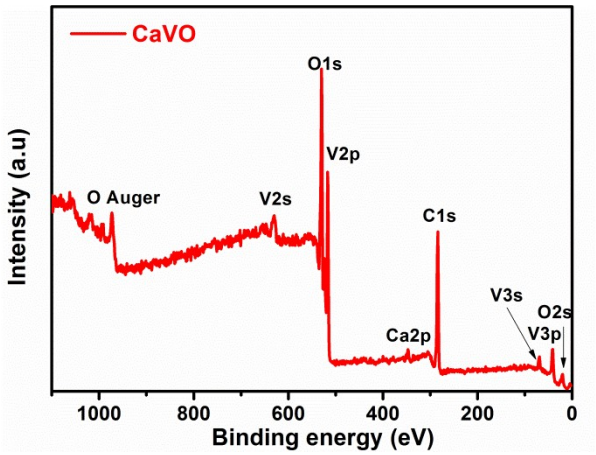


Fig. S4 The full XPS of CaVO.

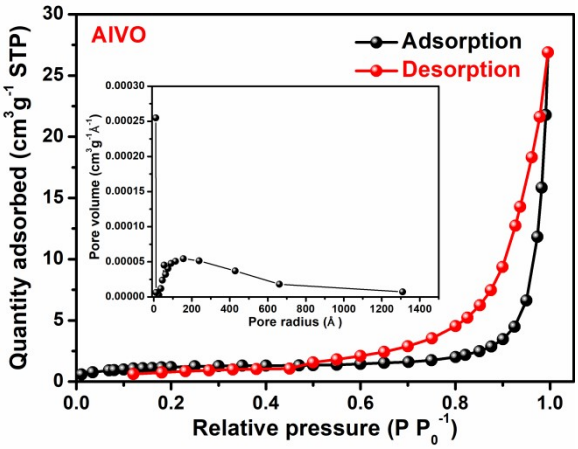


Fig. S5 Nitrogen adsorption/desorption isotherms and pore-size distributions (inset) of AlVO.

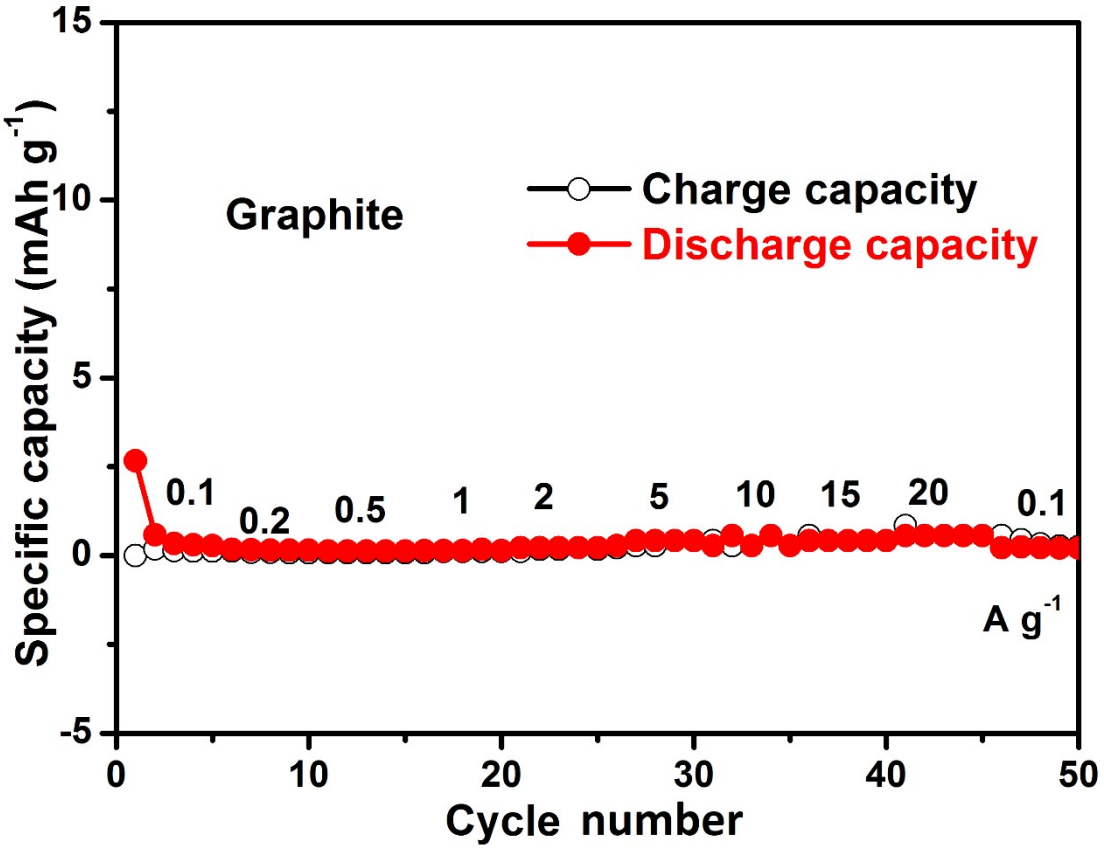


Fig. S6 Rate capability of the bare cathode.

Table S4 Comparison of the electrochemical performances of V_2O_5-based compounds

Cathode	Electrolyte	Voltage window (V)	Cycle number /n	Capacity /Retention@Current	Ref.
$Al_{0.17}V_2O_5(H_2O)_2 \cdot H_2O$	3 M $Zn(CF_3SO_3)_2$	0.2-1.8	2000	306 mAh g^{-1}/90.5 % (5.0 A g^{-1})	This work
$Mn_xV_2O_5 \cdot nH2O$	3 M $ZnSO_4$	0.2-1.6	2000	260 mAh g^{-1}/92 % (4.0 A g^{-1})	1
$Zn_{0.25}V_2O_5$	1 M $ZnSO_4$	0.5-1.4	1000	262 mAh g^{-1}/80 % (2.4 A g^{-1})	2

$Mg_{0.34}V_2O_5$ ·$0.84H_2O$	3 M $Zn(CF_3SO_3)_2$	0.1-1.8	2000	80 mAh g^{-1}/97 % (5 A g^{-1})	3
$H_2V_3O_8$	3 M $Zn(CF_3SO_3)_2$	0.2-1.6	1000	113 mAh g^{-1}/94 % (5.0 A g^{-1})	4
$Ca_{0.25}V_2O_5$	1 M $ZnSO_4$	0.6-1.6	5000	72 mAh g^{-1}/64 % (5.76 A g^{-1})	5
V_3O_7·H2O	1 M $ZnSO_4$	0.4-1.1	200	270 mAh g^{-1}/80 % (3.0 A g^{-1})	6
$V_{10}O_{24}$·$12H_2O$	3 M $Zn(CF_3SO_3)_2$	0.7-1.7	3000	80 mAh g^{-1}/80.1 % (2.0 A g^{-1})	7
NaV_3O_8·$1.5H_2O$	1 M $ZnSO_4$/ 1 M Na_2SO_4	0.3-1.25	1000	165 mAh g^{-1}/82 % (4.0 A g^{-1})	8
$(NH_4)_2V_{10}O_{25}$ ·$8H_2O$	3 M $Zn(CF_3SO_3)_2$	0.7-1.7	5000	123 mAh g^{-1}/90.1 % (5.0 A g^{-1})	9
$VOPO_4$	21 M LiTFSI+ 1 M $Zn(CF_3SO_3)_2$	0.7-2.1	1000	50 mAh g^{-1}/93 % (5.0 A g^{-1})	10

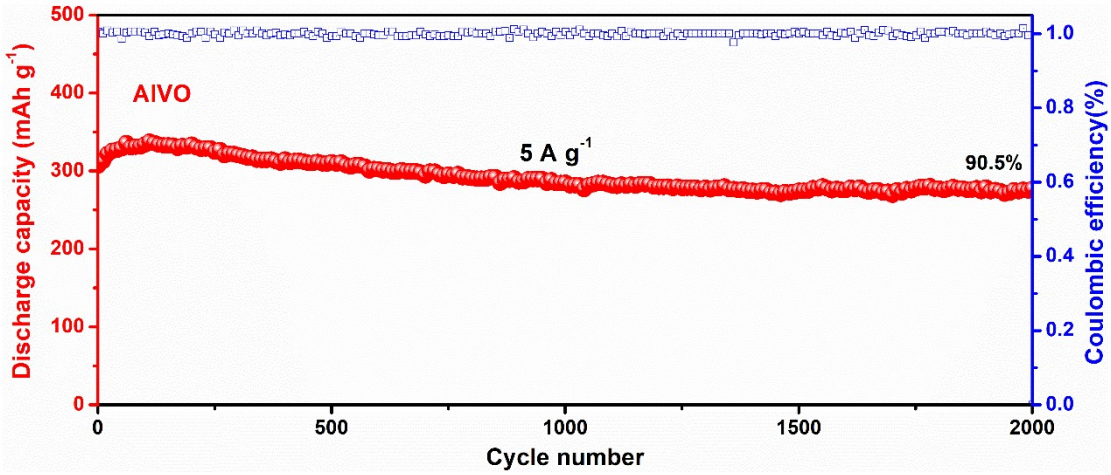


Fig. S7 Cycling performance of AlVO at 5 A g^{-1} for 2000 GCD cycles.

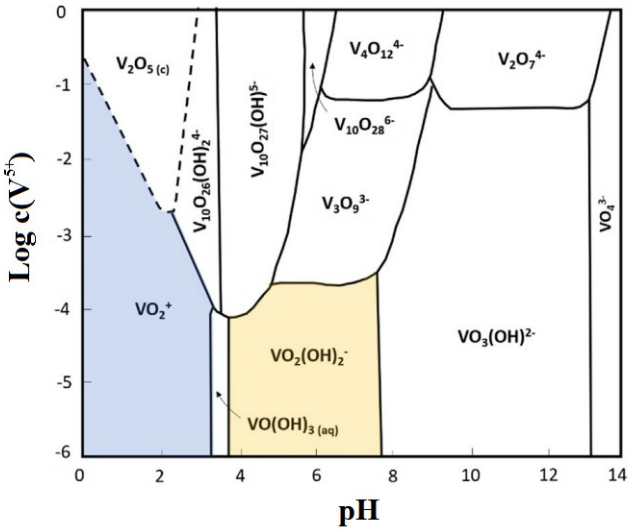
Table S5 The values for the parameters in the simulated equivalent circuit for AlVO and CaVO.

	R_s (Ω cm^{-2})	R_{ct} (Ω cm^{-2})	CPE	R_1(Ω cm^{-2})
AlVO	2.9	7.9	8.8E-5	6.1
CaVO	2.9	8.7	1.6E-4	11.4

(a) **(b)** **(c)**

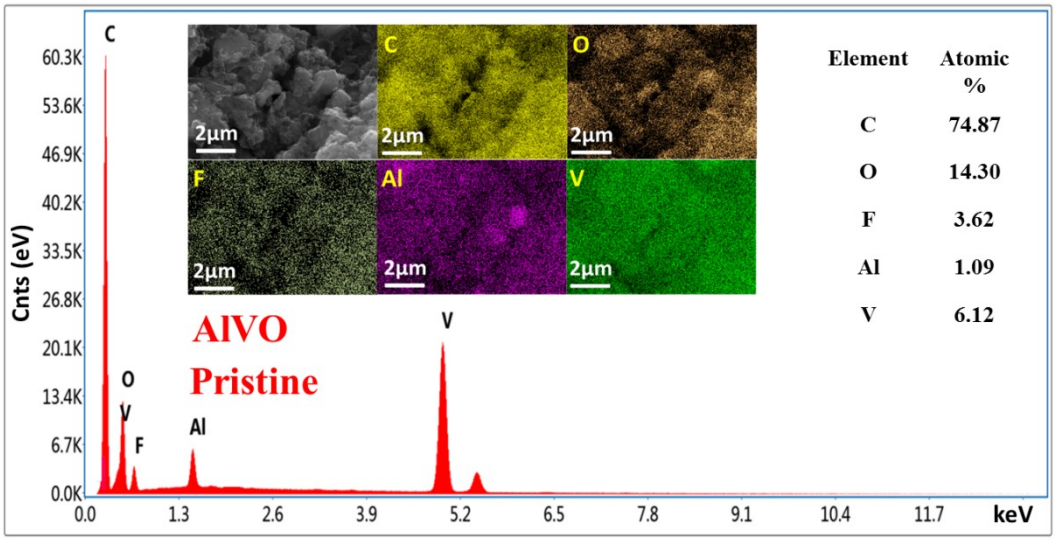
pH = 3.73 **pH=3.96** **pH=3.77**

Fig. S8 The images of the electrolyte solution at different states: (**a**) initial solution; (**b**) 1st discharge to 0.2 V; (**c**) 1st charge to 1.8 V.

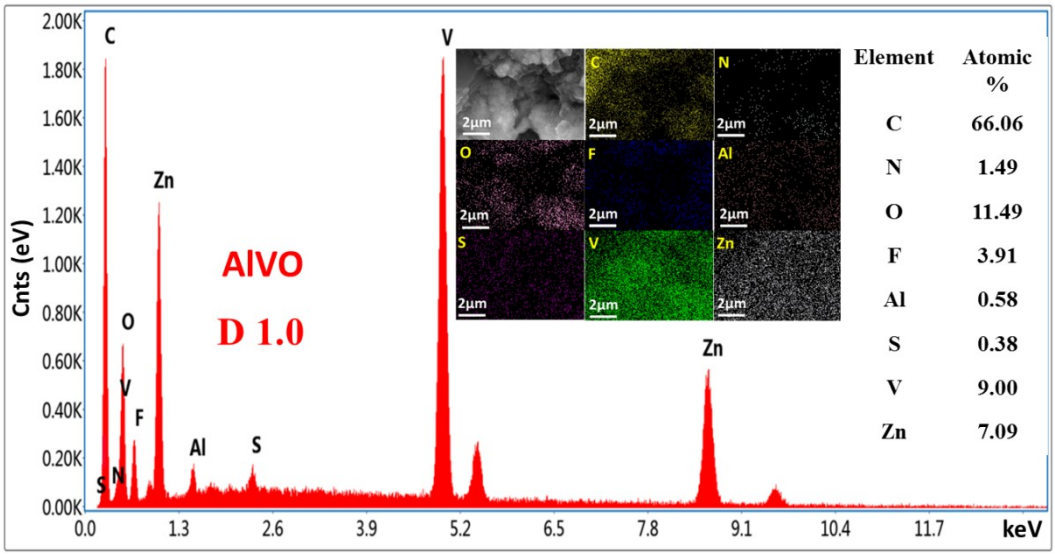


Scheme S1 The pH-logc(V^{5+}) diagram in V_2O_5-H_2O system. [11]

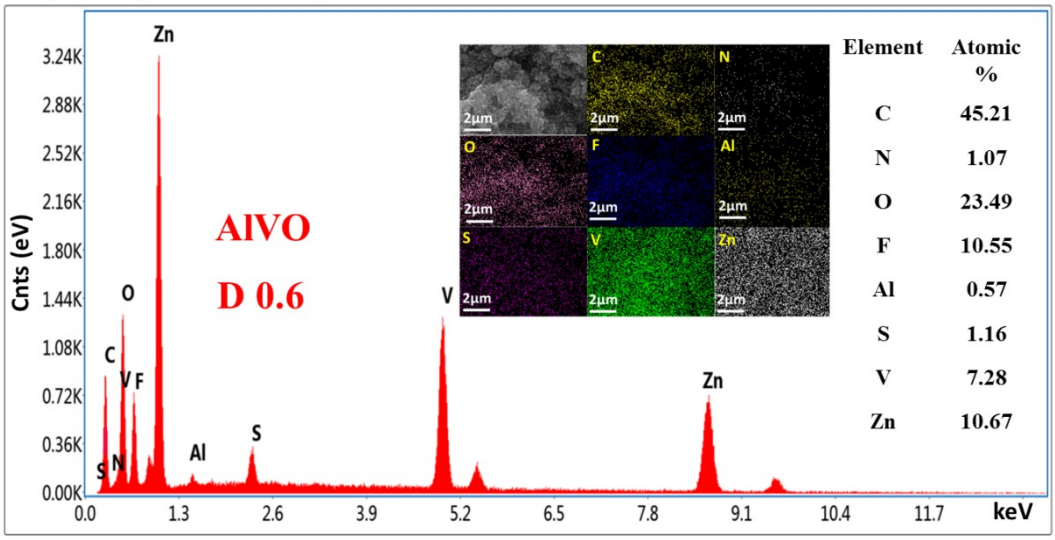
(a)



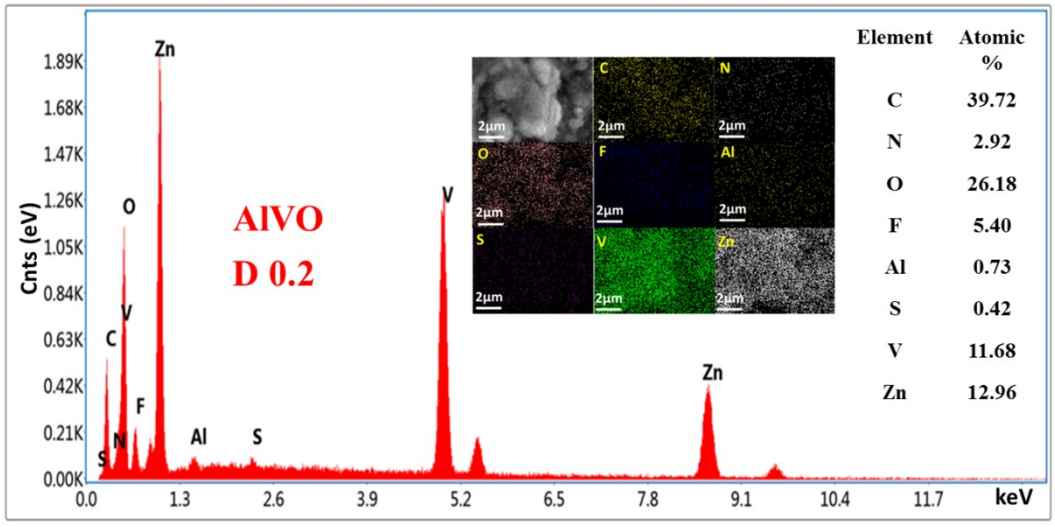
(b)


AlVO
D 1.0
Cnts (eV)
keV
C
V
Zn
O
F
Al
S
N
Element
Atomic %
C 66.06
N 1.49
O 11.49
F 3.91
Al 0.58
S 0.38
V 9.00
Zn 7.09

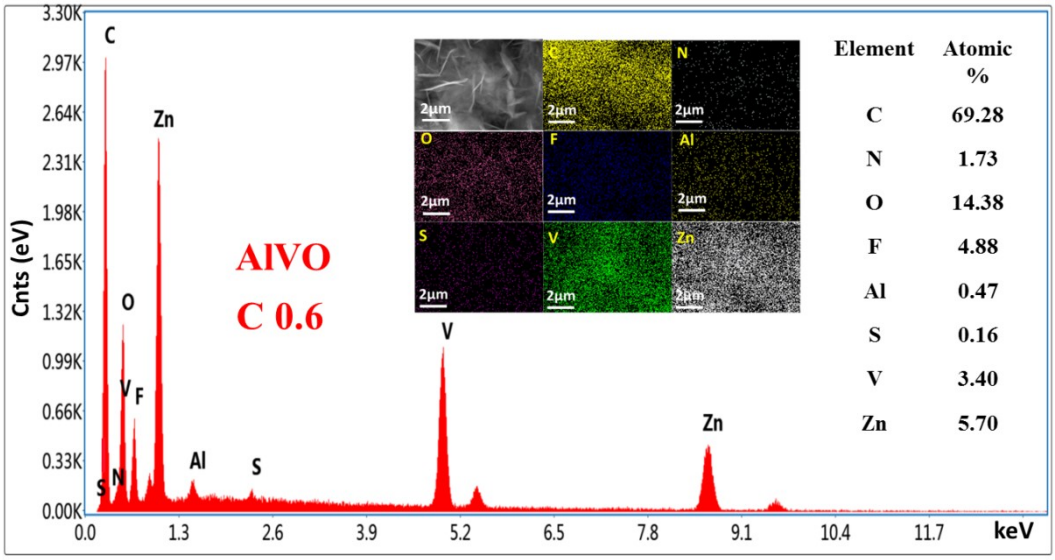
(c)


AlVO
D 0.6
Cnts (eV)
keV
Zn
O
C
V
F
Al
S
N
Element
Atomic %
C 45.21
N 1.07
O 23.49
F 10.55
Al 0.57
S 1.16
V 7.28
Zn 10.67

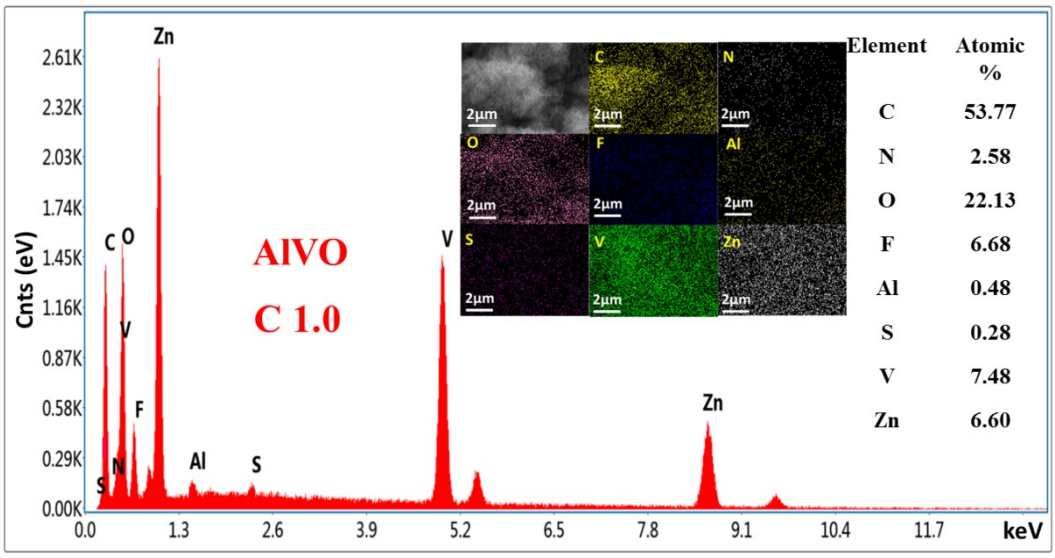
(d)


AlVO
D 0.2
Cnts (eV)
keV
Zn
O
V
C
F
Al
S
N
Element
Atomic %
C 39.72
N 2.92
O 26.18
F 5.40
Al 0.73
S 0.42
V 11.68
Zn 12.96

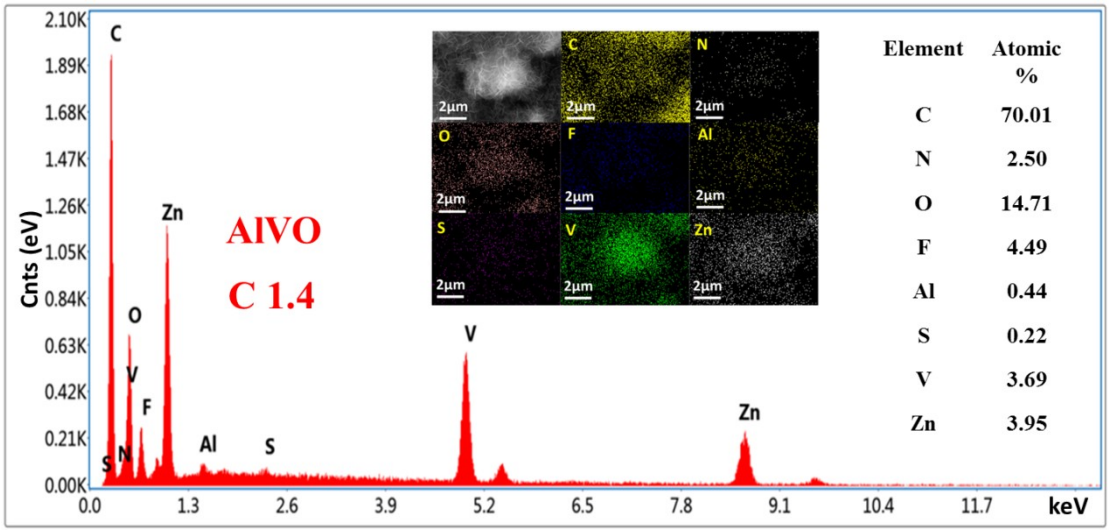
(e)


AlVO
C 0.6
Cnts (eV)
keV
Element
Atomic %
C 69.28
N 1.73
O 14.38
F 4.88
Al 0.47
S 0.16
V 3.40
Zn 5.70

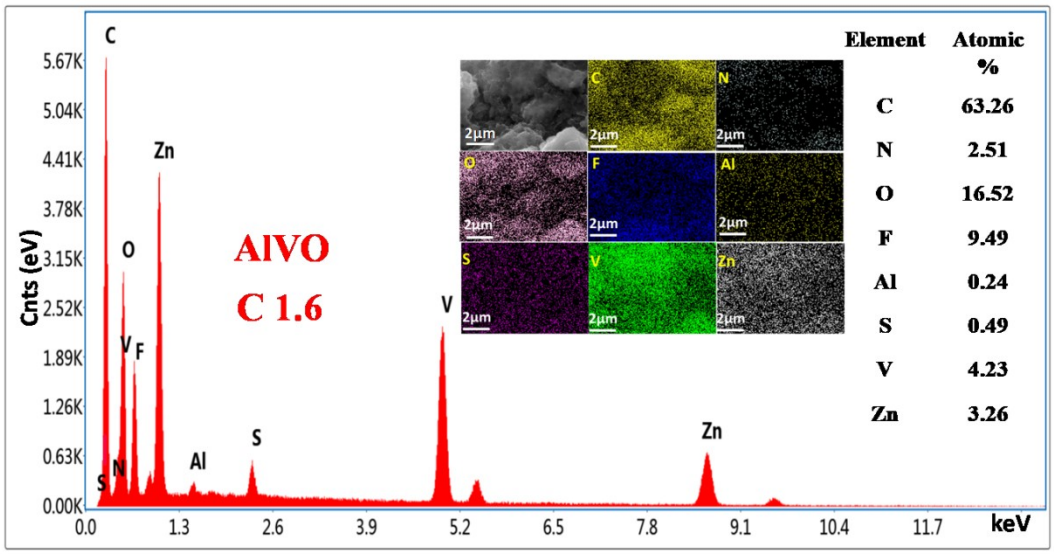
(**f**)


AlVO
C 1.0
Cnts (eV)
keV
Element
Atomic %
C 53.77
N 2.58
O 22.13
F 6.68
Al 0.48
S 0.28
V 7.48
Zn 6.60

(**g**)


AlVO
C 1.4
Cnts (eV)
keV
Element
Atomic %
C 70.01
N 2.50
O 14.71
F 4.49
Al 0.44
S 0.22
V 3.69
Zn 3.95

(**h**)



(i)

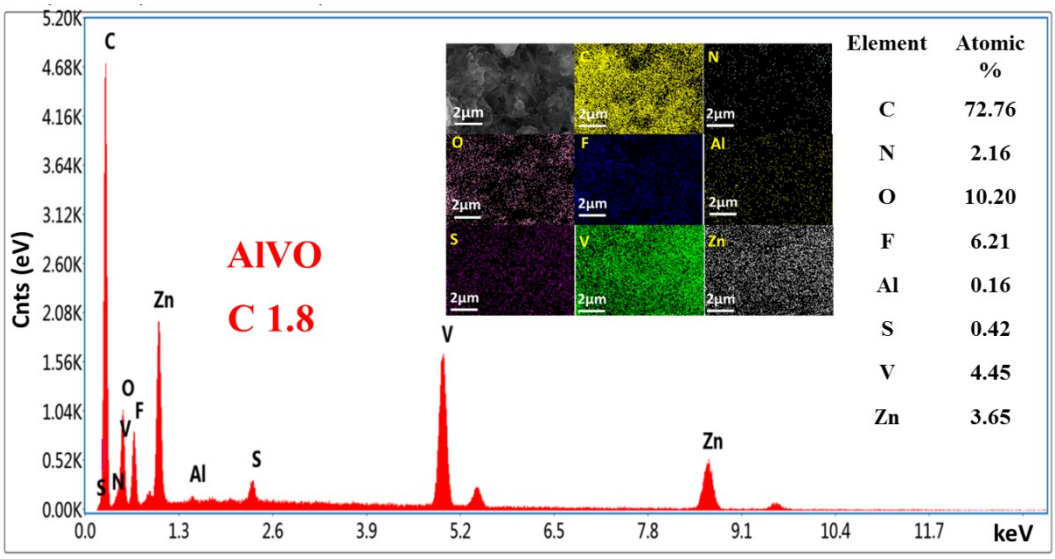


Fig. S9 EDS as well as elemental mappings of the AlVO electrode at different states in the first discharge/charge cycle: (**a**) pristine; (**b**) discharge to 1.0 V; (**c**) discharge to 0.6 V; (**d**) discharge to 0.2 V; (**e**) charge to 0.6 V; (**f**) charge to 1.0 V; (**g**) charge to 1.4 V, (**h**) charge to 1.6 V and (**i**) charge to 1.8 V.

Table S6 The contents of C, N, O, F, Al, S, V and Zn elements in the AlVO electrode at different states and their contents in the cycled AlVO as well as the cycled Zn anode.

Element (at. %)	C	N	O	F	Al	S	V	Zn
Pristine	74.87	/	14.30	3.62	1.09	/	6.12	/
Discharge to 1.0 V	66.06	1.49	11.49	3.91	0.58	0.38	9.00	7.09

Discharge to 0.6 V	45.21	1.07	23.49	10.55	0.57	1.16	7.28	10.67
Discharge to 0.2 V	39.72	2.92	26.18	5.40	0.73	0.42	11.68	12.96
Charge to 0.6 V	69.28	1.73	14.38	4.88	0.47	0.16	3.40	5.70
Charge to 1.0 V	53.77	2.58	22.13	6.68	0.48	0.28	7.48	6.60
Charge to 1.4 V	70.01	2.50	14.71	4.49	0.44	0.22	3.69	3.95
Charge to 1.6 V	63.26	2.51	16.52	9.49	0.24	0.49	4.23	3.26
Charge to 1.8 V	72.76	2.16	10.20	6.21	0.16	0.42	4.45	3.65
The cycled AlVO	32.57	/	13.13	5.74	0.51	9.75	9.67	28.17

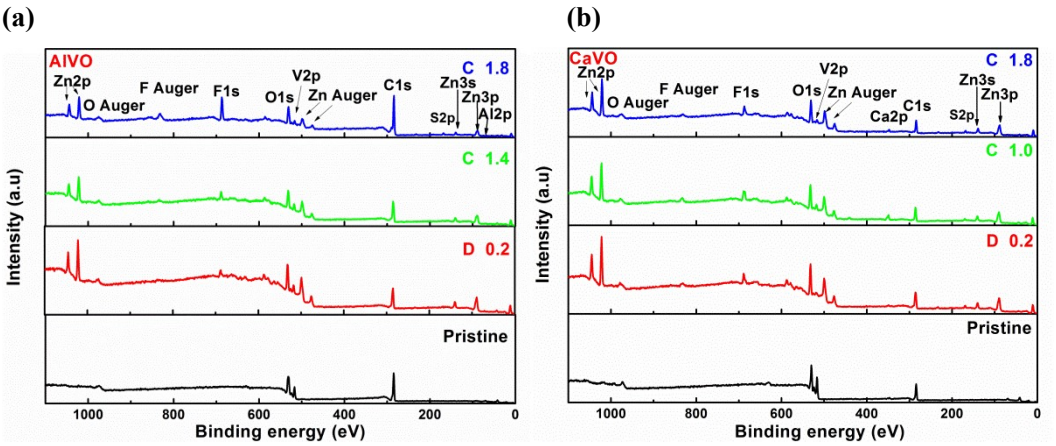


Fig. S10 *Ex situ* XPS spectra of the full region for the AlVO and CaVO electrodes at different states.

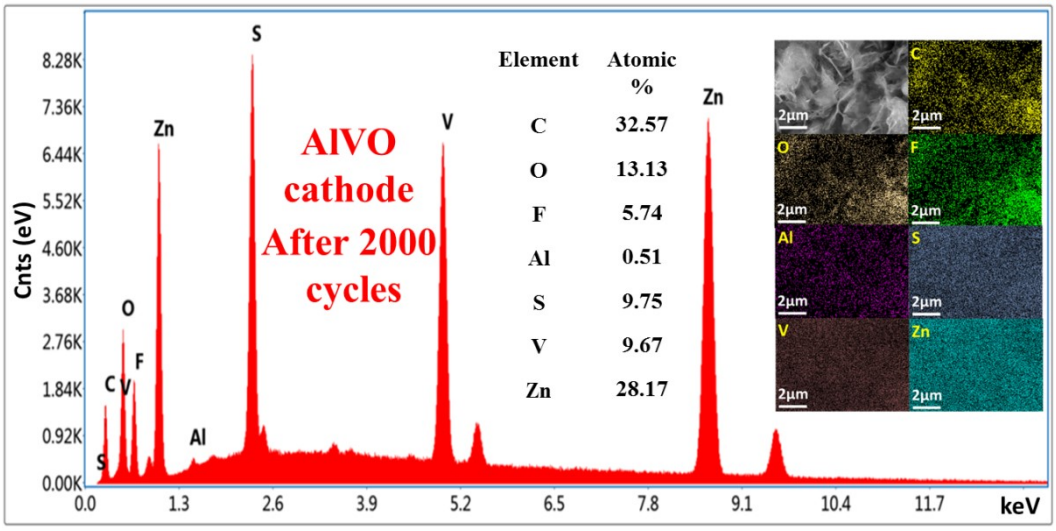


Fig. S11 EDS and elemental mappings of the AlVO cathode after 2000 GCD cycles at 5 A g^{-1}.

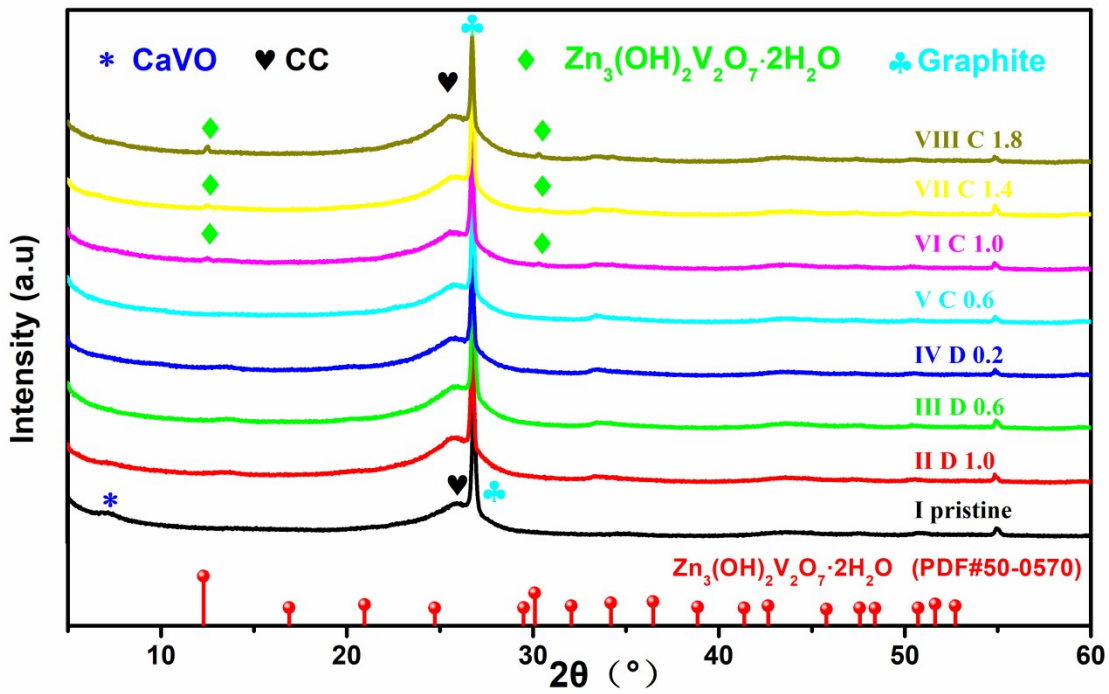
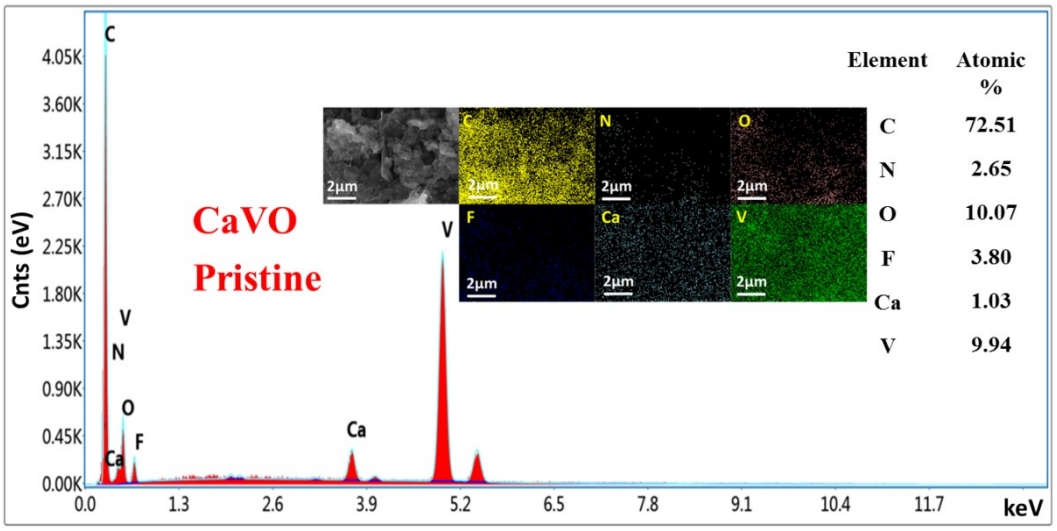
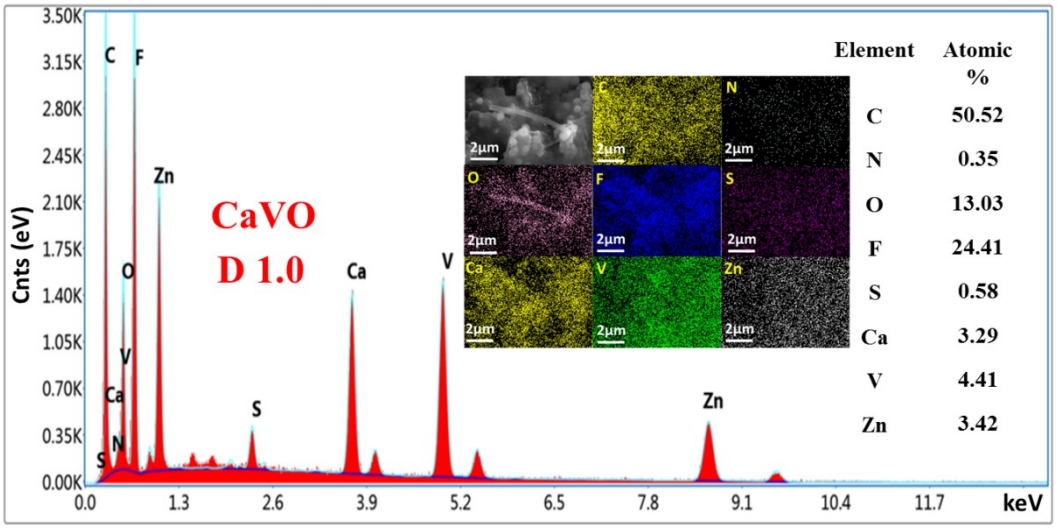


Fig.S12 *Ex situ* XRD patternsof the CaVO electrode in the first discharge/charge cycle, including the states of the pristine sample (I), discharge to 1.0V (II), discharge to 0.6V (III), discharge to 0.2V (IV), charge to 0.6V (V), charge to 1.0V (VI), charge to 1.4 V (VII) and charge to 1.8 V (VIII).

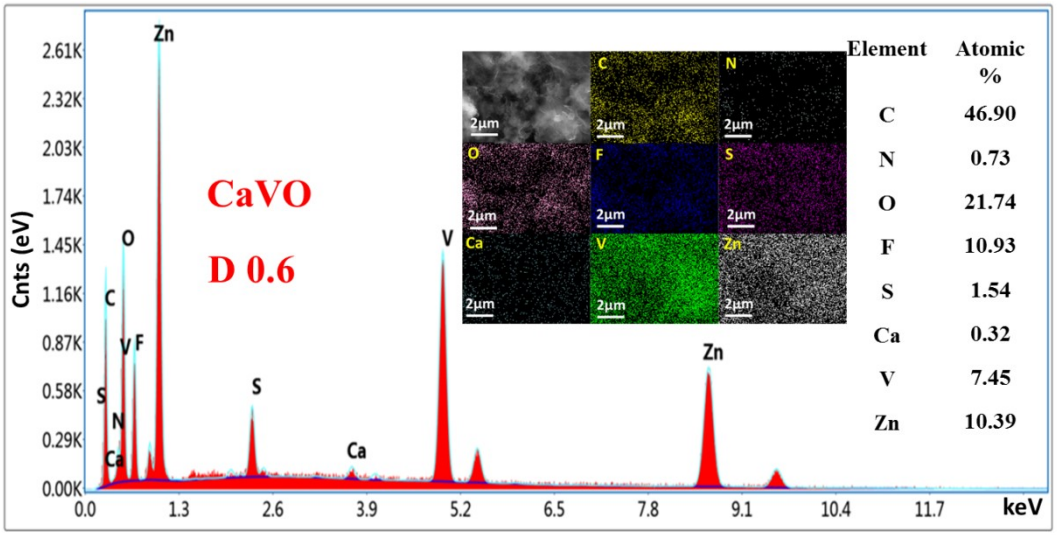
(**a**)


CaVO
Pristine
Cnts (eV)
keV
Element
Atomic %
C 72.51
N 2.65
O 10.07
F 3.80
Ca 1.03
V 9.94

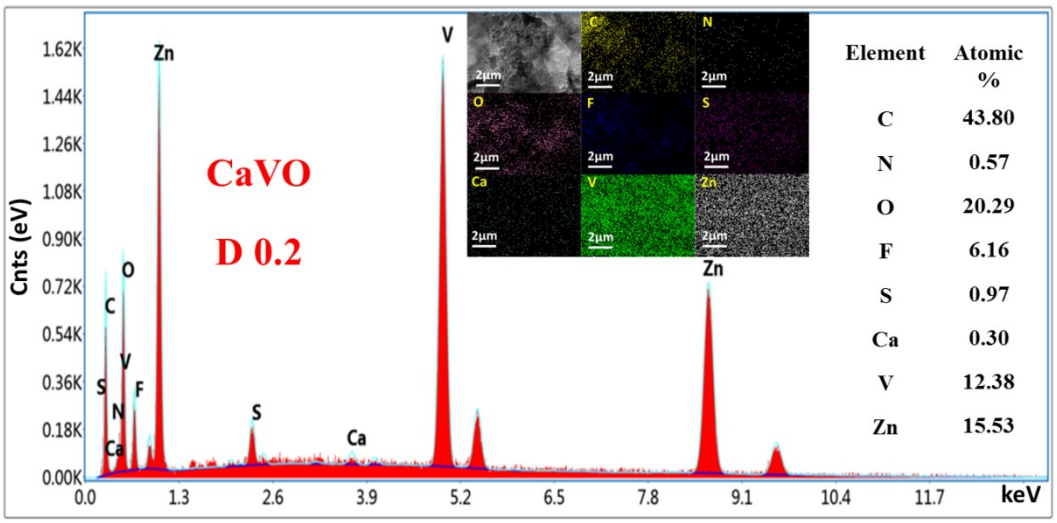
(**b**)


CaVO
D 1.0
Cnts (eV)
keV
Element
Atomic %
C 50.52
N 0.35
O 13.03
F 24.41
S 0.58
Ca 3.29
V 4.41
Zn 3.42

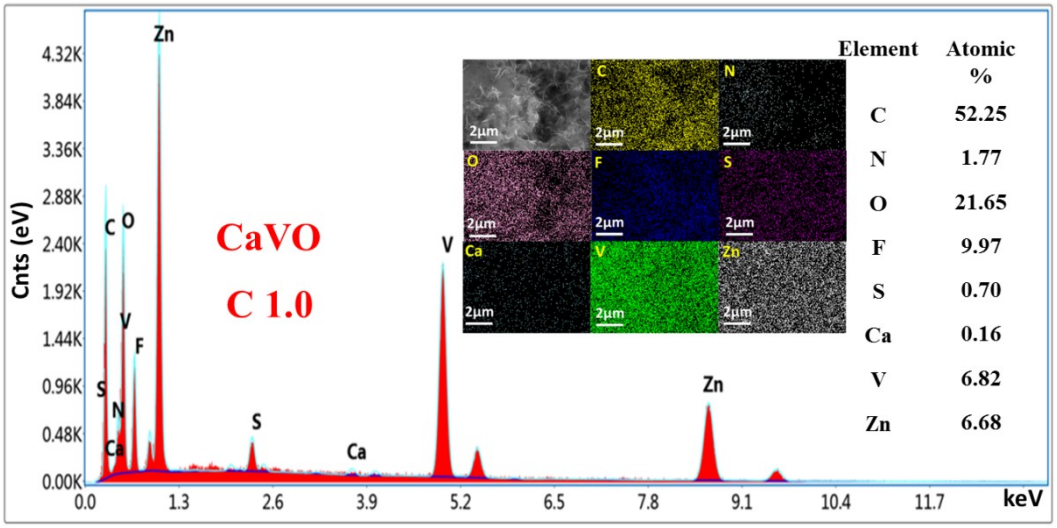
(**c**)


CaVO
D 0.6
Cnts (eV)
keV
Element
Atomic %
C 46.90
N 0.73
O 21.74
F 10.93
S 1.54
Ca 0.32
V 7.45
Zn 10.39

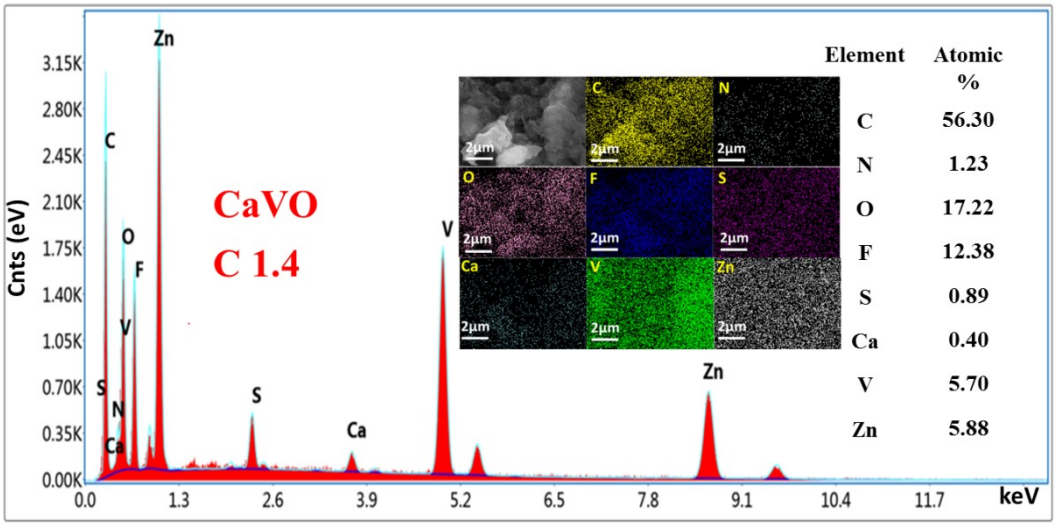
(**d**)


CaVO
D 0.2
Cnts (eV)
keV
Element
Atomic %
C 43.80
N 0.57
O 20.29
F 6.16
S 0.97
Ca 0.30
V 12.38
Zn 15.53

(e)


CaVO
C 1.0
Cnts (eV)
keV
Element
Atomic %
C 52.25
N 1.77
O 21.65
F 9.97
S 0.70
Ca 0.16
V 6.82
Zn 6.68

(f)


CaVO
C 1.4
Cnts (eV)
keV
Element
Atomic %
C 56.30
N 1.23
O 17.22
F 12.38
S 0.89
Ca 0.40
V 5.70
Zn 5.88

(g)

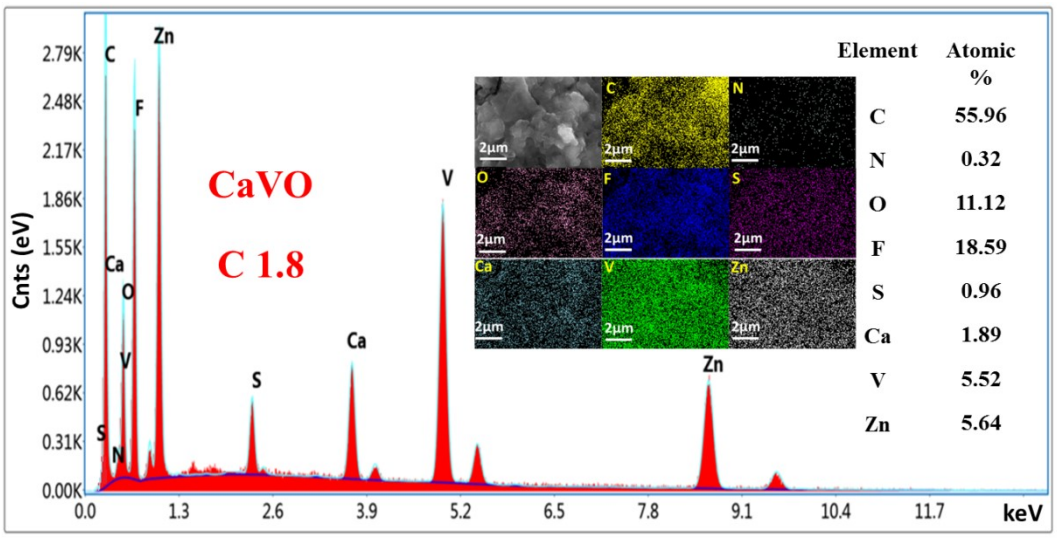
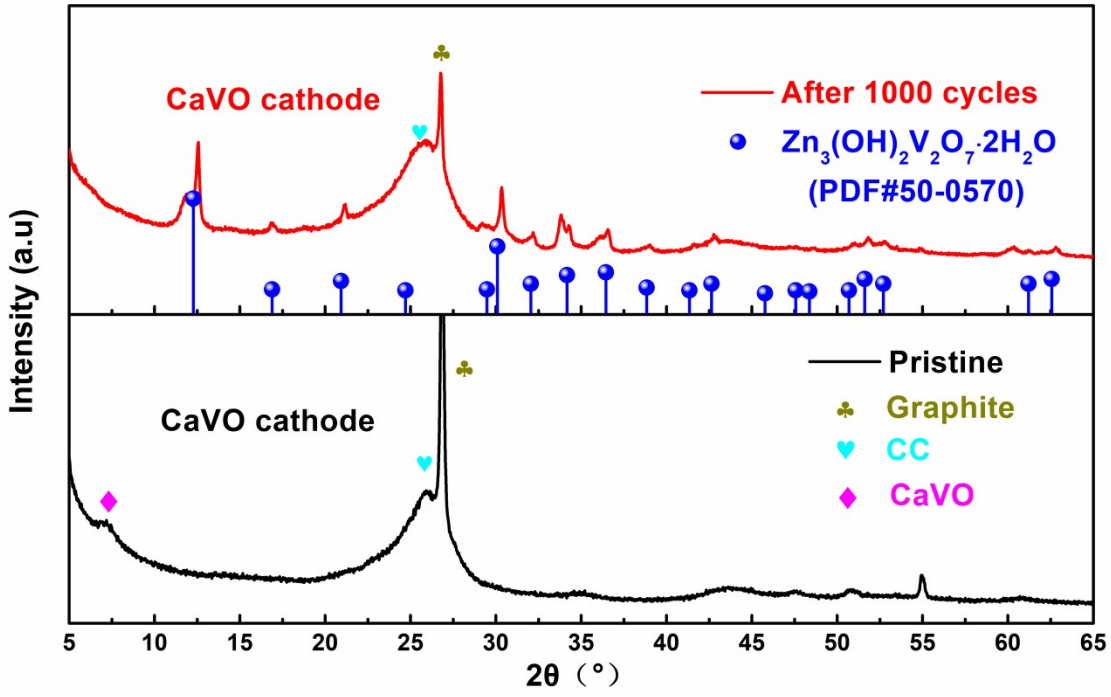


Fig. S13 EDS as well as elemental mappings of the CaVO electrode at different discharge/charge states in the first cycle: (**a**) pristine; (**b**) discharge to 1.0 V; (**c**) discharge to 0.6V; (**d**) discharge to 0.2V; (**e**) charge to 1.0V; (**f**) charge to 1.4 V and (**g**) charge to 1.8 V.

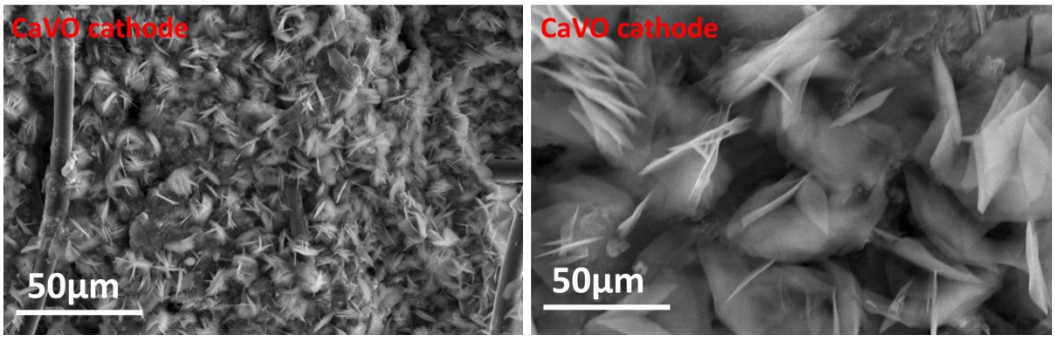
Table S7 The contents of C, N, O, F, Ca, S, V and Zn elements in the CaVO electrode at different states and their contents in the cycled CaVO as well as the cycledZn anode

Element (at. %)	C	N	O	F	S	Ca	V	Zn
Pristine	72.51	2.65	10.07	3.80	/	1.03	9.94	/
Discharge to 1.0 V	50.52	0.35	13.03	24.41	0.58	3.29	4.41	3.42
Discharge to 0.6 V	46.90	0.73	21.74	10.93	1.54	0.32	7.45	10.39
Discharge to 0.2 V	43.80	0.57	20.29	6.16	0.97	0.30	12.38	15.53
Charge to 1.0V	52.25	1.77	21.65	9.97	0.70	0.16	6.82	6.68
Charge to 1.4V	56.30	1.23	17.22	12.38	0.89	0.40	5.70	5.88
Charge to 1.8 V	55.96	0.32	11.12	18.59	0.96	1.89	5.52	5.64
The cycled CaVO	59.91	2.16	18.09	1.54	0.49	0.19	5.64	11.78

(a)



(b) (c)



(d)

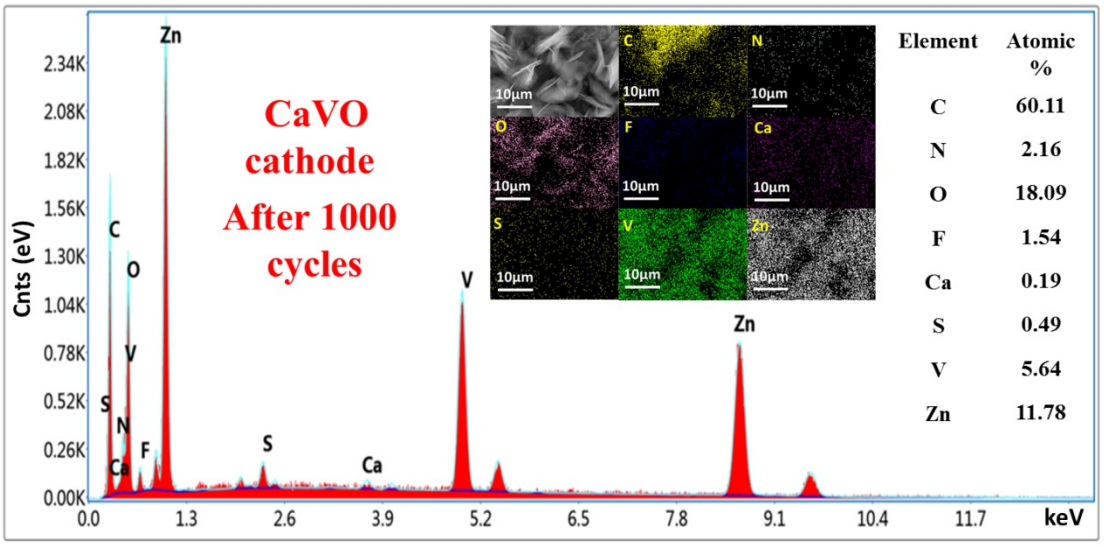


Fig. S14 (**a**) XRD pattern, (**b, c**) SEM images and (**d**) EDS as well as element mappings of the CaVO cathode after 1000 GCD cycles at 5 A g^{-1}.

Table S8 Bader charges of all elements in AlVO and CaVO after the intercalation of Zn^{2+}, the data in parenthesis is the average Bader charge.

		Bader charge (electron)				
		Zn	V	O	Al	Ca
After Zn^{2+} intercalated into unit cell	Zn_xAlVO (A)	1.35 (1.35)	2.03 ~ 2.04 (2.03)	-1.25~ -0.12 (-0.86)	3.00 (3.00)	/
	Zn_xAlVO (B)	1.22 (1.22)	2.00 ~ 2.06 (2.03)	-1.04~ -0.07 (-0.85)	3.00 (3.00)	/
	Zn_xCaVO (I)	1.14 ~1.15 (1.15)	2.11 ~ 2.20 (2.15)	-1.12~ -0.65 (-0.89)	/	1.60 (1.60)
After Zn^{2+} intercalated on AlVO (001) surface	Zn_xAlVO (001) (A')	1.16	1.92 ~ 2.01 (1.97)	-1.14~ -0.96 (-1.05)	3.00 (3.00)	/
	Zn_xAlVO (001) (I')	1.18	1.92 ~ 2.01 (1.97)	-1.15~ -0.96 (-1.05)	3.00 (3.00)	/

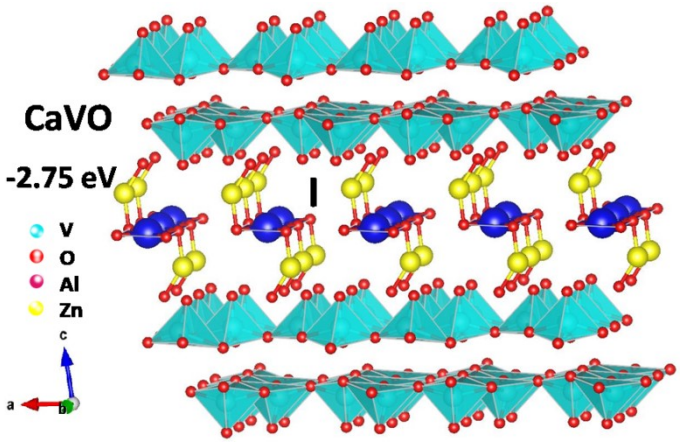


Fig. S15 The optimized configuration of the intercalated Zn^{2+} on site I in the channel of CaVO (H atoms omitted for clarity).

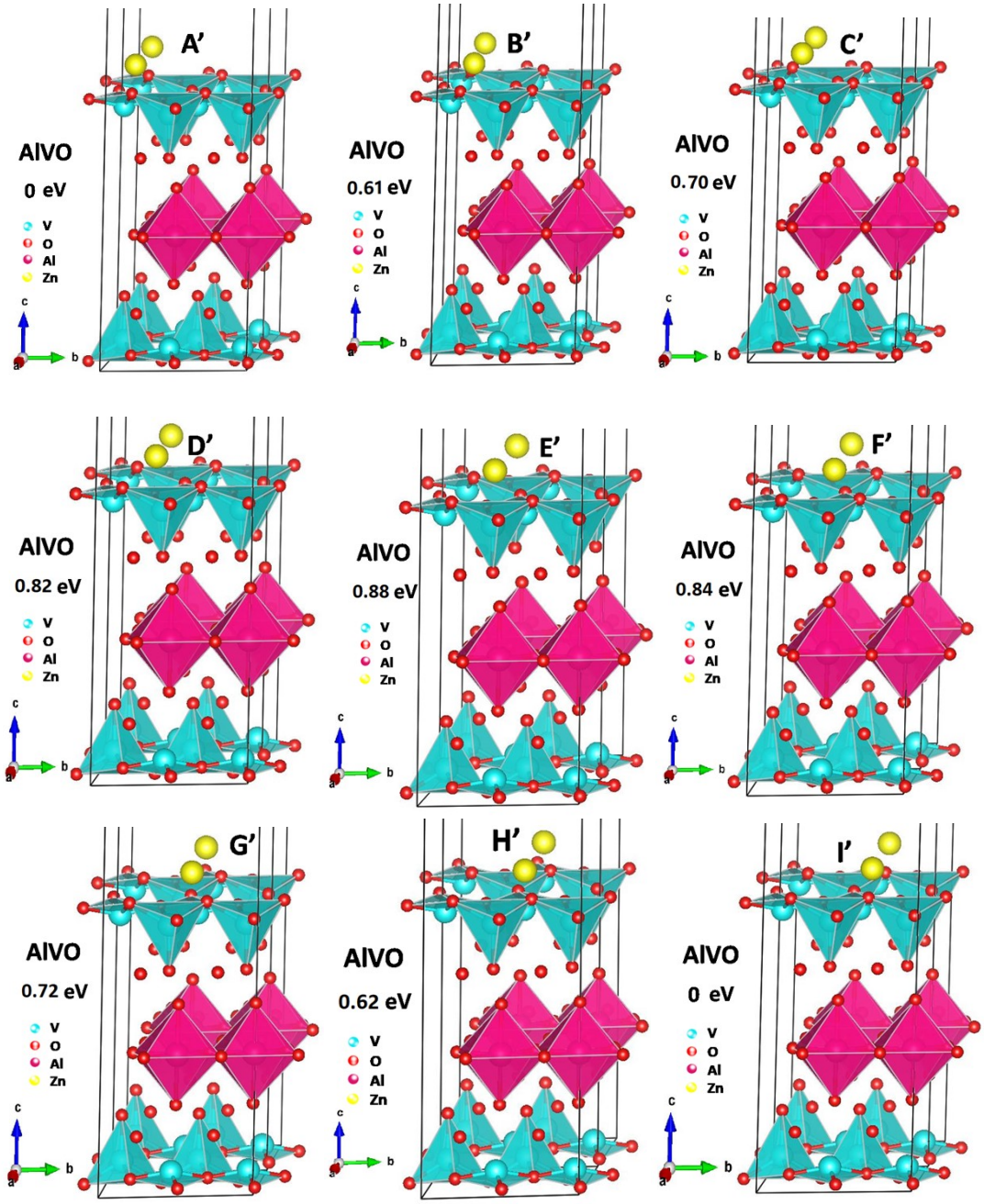


Fig. S16 The optimized configurations of Zn^{2+} migrated across sites A'-I' on the AlVO (001) surface (H atoms omitted for clarity).

References:

1. C. Liu, Z. Neale, J. Zheng, X. Jia, J. Huang, M. Yan, M. Tian, M. Wang, J. Yang and G. Cao, *Energy Environ. Sci.*, 2019, **12**, 2273-2285.
2. D. Kundu, B. D. A Da Ms, V. Duffort, S. H. Vajargah and L. F. Nazar, *Nat. Energy*, 2016, **1**, 16119.
3. F. Ming, H. Liang, Y. Lei, S. Kandambeth and H. N. Alshareef, *ACS Energy Lett.*, 2018, **3,** 2602-2609.
4. H. Pan, Y. Quan, X. Xu, M. Yan and L. Mai, *Small*, 2017, **13**, 1702551.
5. C. Xia, J. Guo, P. Li, X. Zhang and H. N. Alshareef, *Angew. Chem. Int. Ed.*, 2018, **3**, 3943-3948
6. N. J. Zhang, M.; Dong, Y.; Wang, Y.; Xu, J.; Liu, Y.; Jiao, L.; Cheng, F., *Adv. Funct. Mater.*, 2019, **29,**

1807331-1807339.

7. T. Wei, L. Qian, G. Yang and C. Wang, *Electrochim. Acta*, 2018, **287**, S0013468618318164.
8. Z. Xie, J. Lai, X. Zhu and Y. Wang, *ACS Appl. Energy Mater.*, 2018, **1,** 6401-6408.
9. T. Wei, Q. Li, G. Yang, C. Wang, *J. Mater. Chem. A*, 2018, **6***,* 8006-8012.
10. F. Wan, Y. Zhang, L. Zhang, D. Liu, C. Wang, L. Song, Z. Niu and J. Chen, *Angew. Chem. Int. Ed.*, 2019, **58**, 7062-7067.
11. K. Huang, Y. Lu, T. Zhu, W. Bergh and M. Stefik, *Angew. Chem. Int. Ed.,* 2020, **58**, 17004-17011.