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Supplementary Information

Hollandite-type Al-doped VO_{1.52}(OH)_{0.77} as a zinc ion insertion host material

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S-Figure 1. HR-TEM images of (a) bare $VO_{1.52}(OH)_{0.77}$, (b) $V_{0.95}Al_{0.05}O_{1.52}(OH)_{0.77}$ and (c) $V_{0.91}Al_{0.09}O_{1.52}(OH)_{0.77}$.



S-Figure 2. (a) The XRD pattern of x = 0.15 and 0.19 in $V_{1-x}Al_xO_{1.52}(OH)_{0.77}$ powder. (b) First discharge-charge curves of x = 0.15 and 0.19 in $V_{1-x}Al_xO_{1.52}(OH)_{0.77}$.



S-Figure 3. (a) Continuous cycles of the disassembled / reassembled $V_{0.95}Al_{0.05}O_{1.52}(OH)_{0.77}$ electrode after 1 cycle. The cycle performance was measured at 15 mA g⁻¹ in a Zn cell with an operation range 0.2 – 1.13V by using 1M Zn(SO)₄ electrolyte. (b) EDX mapping data of disassembled / reassembled $V_{0.95}Al_{0.05}O_{1.52}(OH)_{0.77}$ electrode after 1 cycle.



S-Figure 4. (a) The XRD pattern of bare $VO_{1.52}(OH)_{0.77}$ electrode discharged to 0.2 V in the first cycle. The matched peaks by red line are from the discharged product of $VO_{1.52}(OH)_{0.77}$ electrode. Also, the blue x is stainless steel mesh current collector. (b) The XRD patterns of Zn anodes from bare $VO_{1.52}(OH)_{0.77}$ for Zn/VO_{1.52}(OH)_{0.77} batteries after cycling process. The purple x is Zinc metal and the closed red circles indicate the Zn₄SO₄(OH)₆·xH₂O compounds.



S-Figure 5. Scheme of the phase transition from tetragonal $VO_{1.52}(OH)_{0.77}$ to hexagonal $Zn_3V_2O_7(OH)_2 \cdot 2H_2O$ after cycling.



S-Figure 6. Rietveld refinement result of XRD pattern for the extensively cycled $V_{0.95}Al_{0.05}O_{1.52}(OH)_{0.77}$ electrode.



S-Figure 7. Continuous cycles of (a) bare $VO_{1.52}(OH)_{0.77}$ electrode, (b) $V_{0.95}Al_{0.05}O_{1.52}(OH)_{0.77}$ electrode and (c) $V_{0.91}Al_{0.09}O_{1.52}(OH)_{0.77}$ electrode. The cycle performance was measured at 15 mA g⁻¹ in a Li cell with an operation range 1.5 - 3.7V by using 1M LiPF₆ electrolyte.



S-Figure 8. Continuous discharge and charge curves of (a) bare $VO_{1.52}(OH)_{0.77}$ and (b) $V_{0.95}Al_{0.05}O_{1.52}(OH)_{0.77}$. The cycle performance was measured at 15 mA g⁻¹ in a Zn cell with an operation range 0.2 - 1.13V by using 1M Zn(NO₃)₂ electrolyte.

		Lattice	Lattice parameter	
		a-axis / Å	c-axis / Å	
	Fresh electrode	10.4010(2)	2.9910(1)	
VO _{1.52} (OH) _{0.77}	After discharge	10.4540(2)	3.0097(1)	
	After charge	10.4228(1)	2.9985(1)	
V _{0.95} Al _{0.05} O _{1.52} (OH) _{0.77}	Fresh electrode	10.3615(1)	2.9533(1)	
	After discharge	10.4026(2)	2.9621(1)	
	After charge	10.3694(1)	2.9561(1)	

Table S1. The variation in the measured lattice parameters of $VO_{1.52}(OH)_{0.77}$ and $V_{0.95}Al_{0.05}O_{1.52}(OH)_{0.77}$.

Formula Crystal syste Space gr	em oup	VO _{1.52} (OH) _{0.77} electrode after cycle Tetragonal I4 / m				
Atom	Site	х	У	Z	g	B/Å
V	8h	0.1410(2)	0.6592(2)	0	1	1.18
O1	8h	0.3483(8)	0.9676(6)	0	1	0.99
O2	8h	0.3432(8)	0.7171(6)	0	1	0.99
O3	4e	0	0	0.2236(4)	0.58	0.99
Η	8h	0.4987(1)	0.4110(1)	0	0.74(2)	0.99
Zn	8h	0.4987(1)	0.4110(1)	0	0.03(2)	0.99
	R _{wp} /9	6			15.1	

Table S2. The rietveld refinement result of $VO_{1.52}(OH)_{0.77}$ electrode after cycle