Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Local Structure and Ions Storage Properties of Vanadate Cathode Materials Regulated by the Pre-Alkalization

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Supplementary Figures:

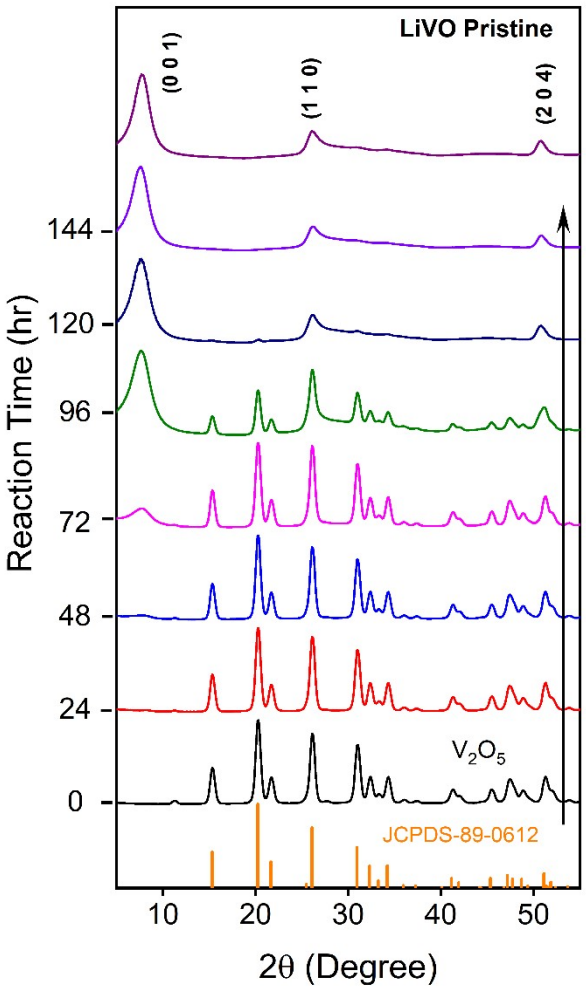

Figure S1. Lithiation of V_2O_5 bulk material using 0.5 M Li_2SO_4 solution at room temperature.

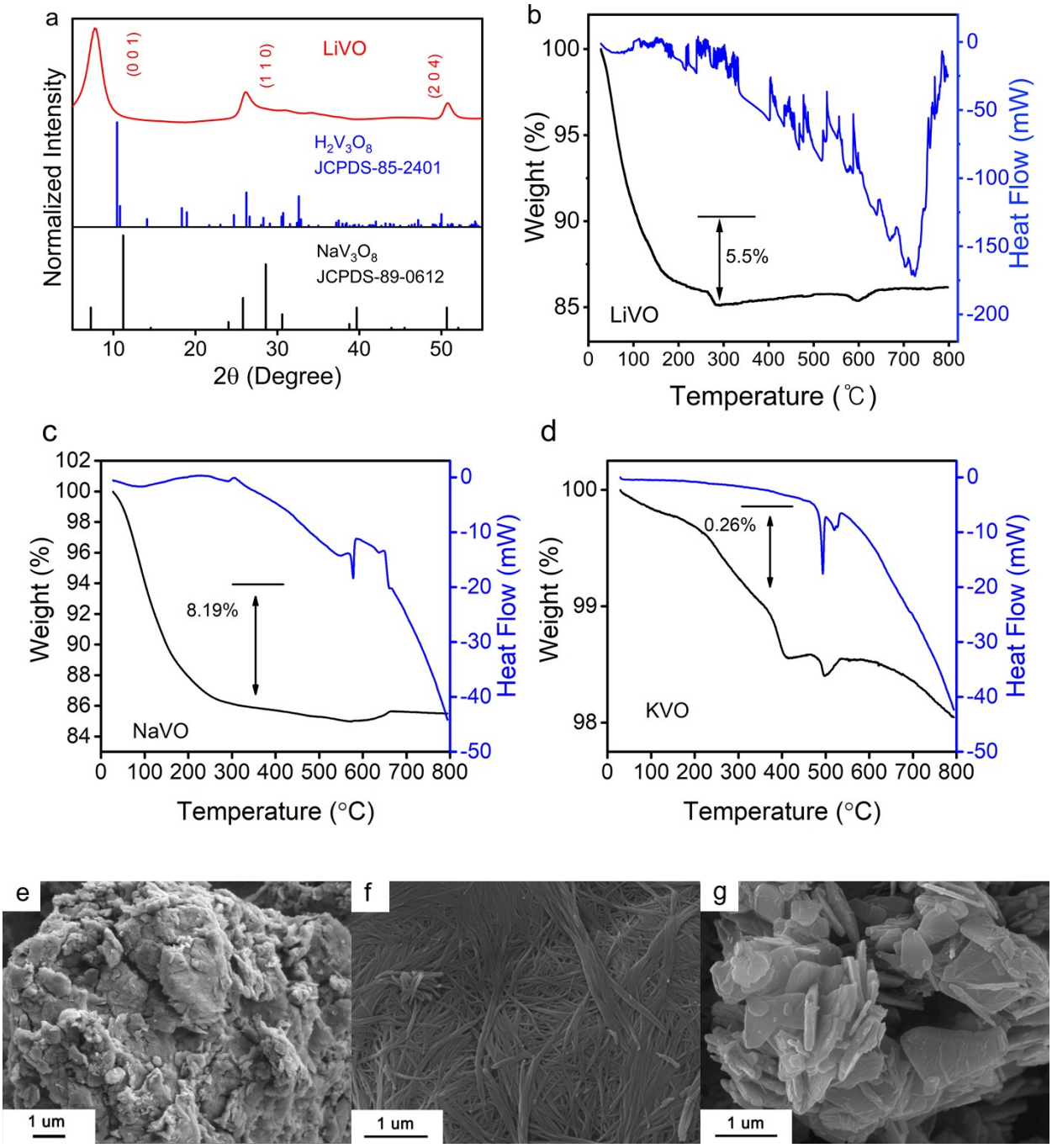

Figure S2. (a) LiVO compared to standards; TGA and DSC data of (b) LiVO, (c) NaVO, and (d) KVO; SEM images of (e) LiVO, (f) NaVO, and (g) KVO.

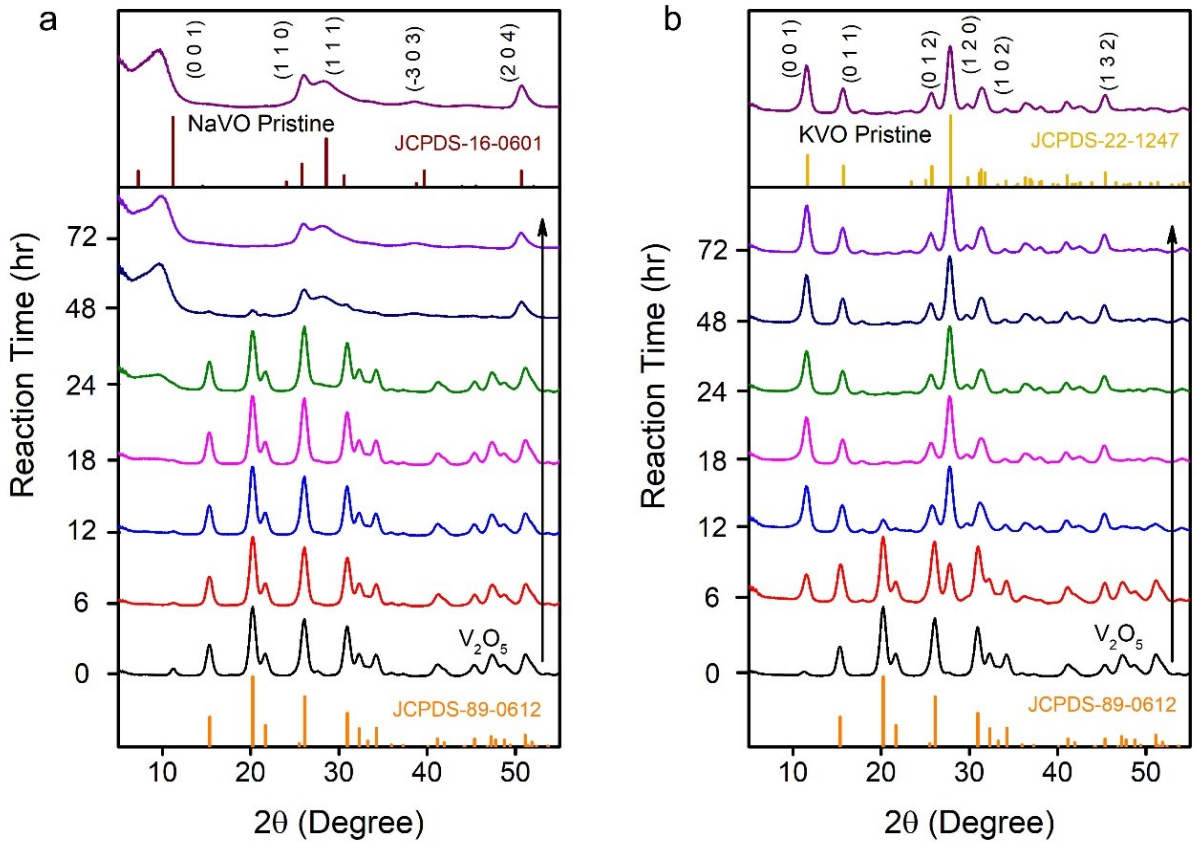

Figure S3. (a) Pre-sodiation using 0.5 M Na_2SO_4 and (b) pre-potassiation using 0.5 M K_2SO_4 solution of V_2O_5 bulk material at room temperature.

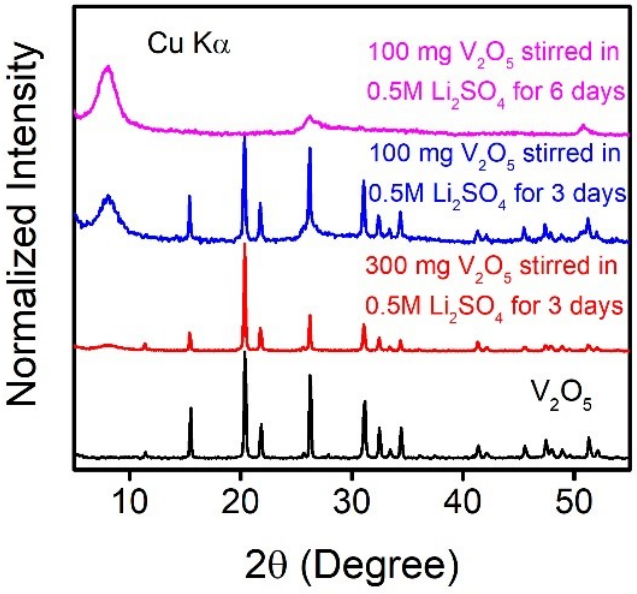

Figure S4. V_2O_5 was stirred in 0.5 M Li_2SO_4 for the various duration of time and various amounts of added V_2O_5. The NaVO and KVO are obtained by stirring 300 mg of V_2O_5 in 0.5 M Na_2SO_4 or K_2SO_4 solution for three days.

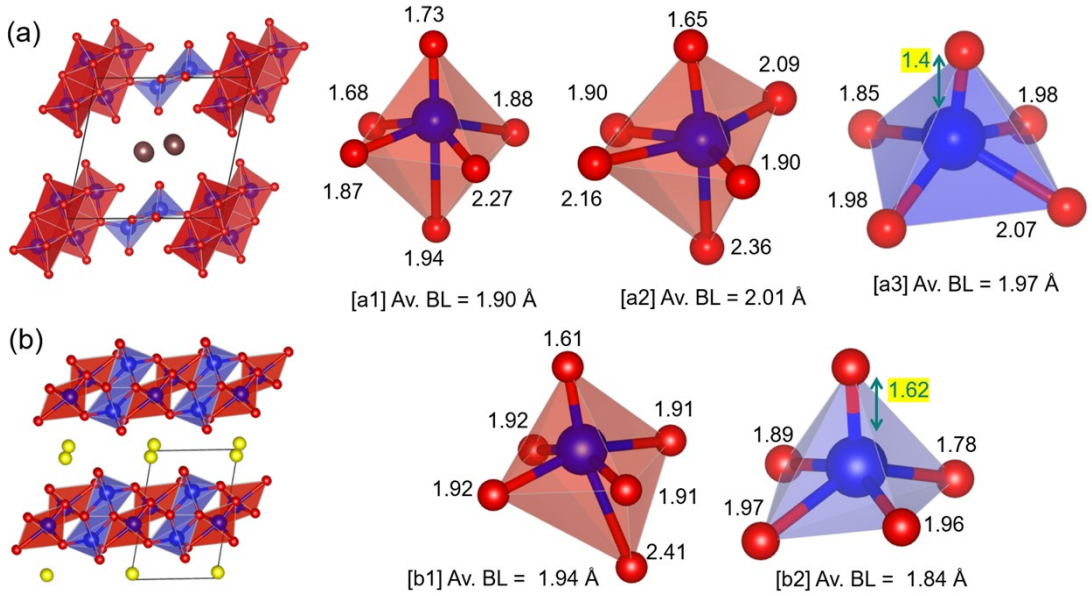

Figure S5. Crystal structures and building polyhedral units of (a) NaVO with [a1, 2] VO_6 octahedral and [a3] VO_5 bipyramid units; (b) KVO with [b1] VO_6 and [b2] bipyramid building units. (VO_5 pyramid in blue and VO_6 octahedral in red, green: Li, blue: V, red: O).

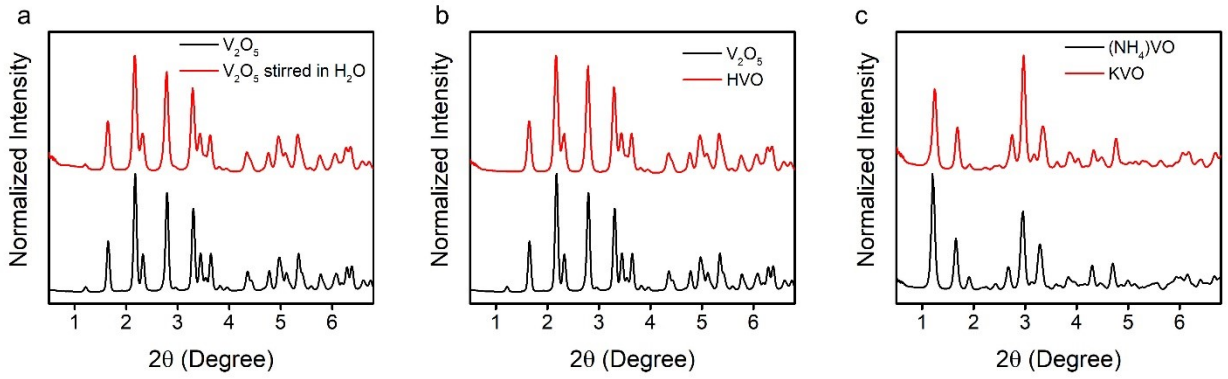

Figure S6. After stirring in different solutions, we obtained the final V2O5, HVO, and (NH4)VO products. (a) V_2O_5 bulk stirred in water as a control sample; (b) V_2O_5 stirred in 0.5 M H_2SO_4; (c) V_2O_5 stirred in 0.5 M $(NH_4)_2SO_4$ compared to that obtained in K_2SO_4 solution.

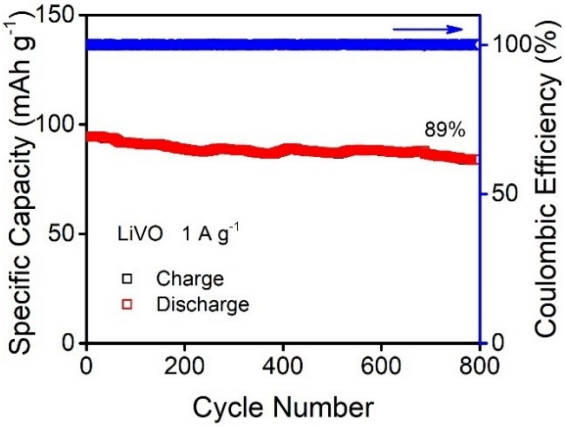

Figure S7. Long-term cycling performance of LiVO at a current density of 1 A g^{-1} for 800 cycles.

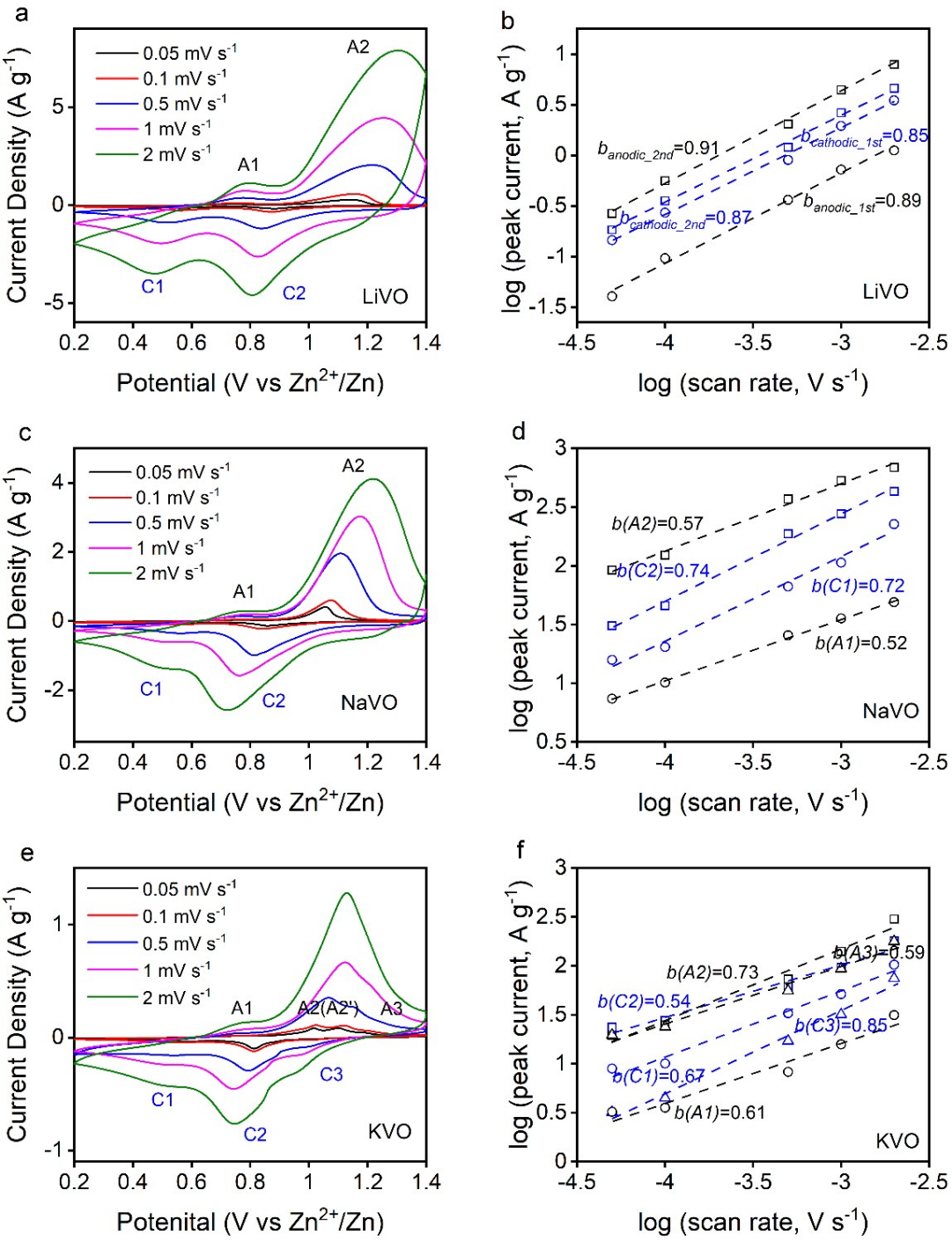

Figure S8. (a, c, e) CVs of LiVO, NaVO, and KVO at scan rates from 0.05 mV s^{-1} to 2 mV s^{-1}; (b, d, f) Kinetics analysis with b-values of LiVO, NaVO, and KVO. C1 and A1 are the first redox peaks of cathodic and anodic scan (empty circles), and C2 and A2 are the second ones (open squares).

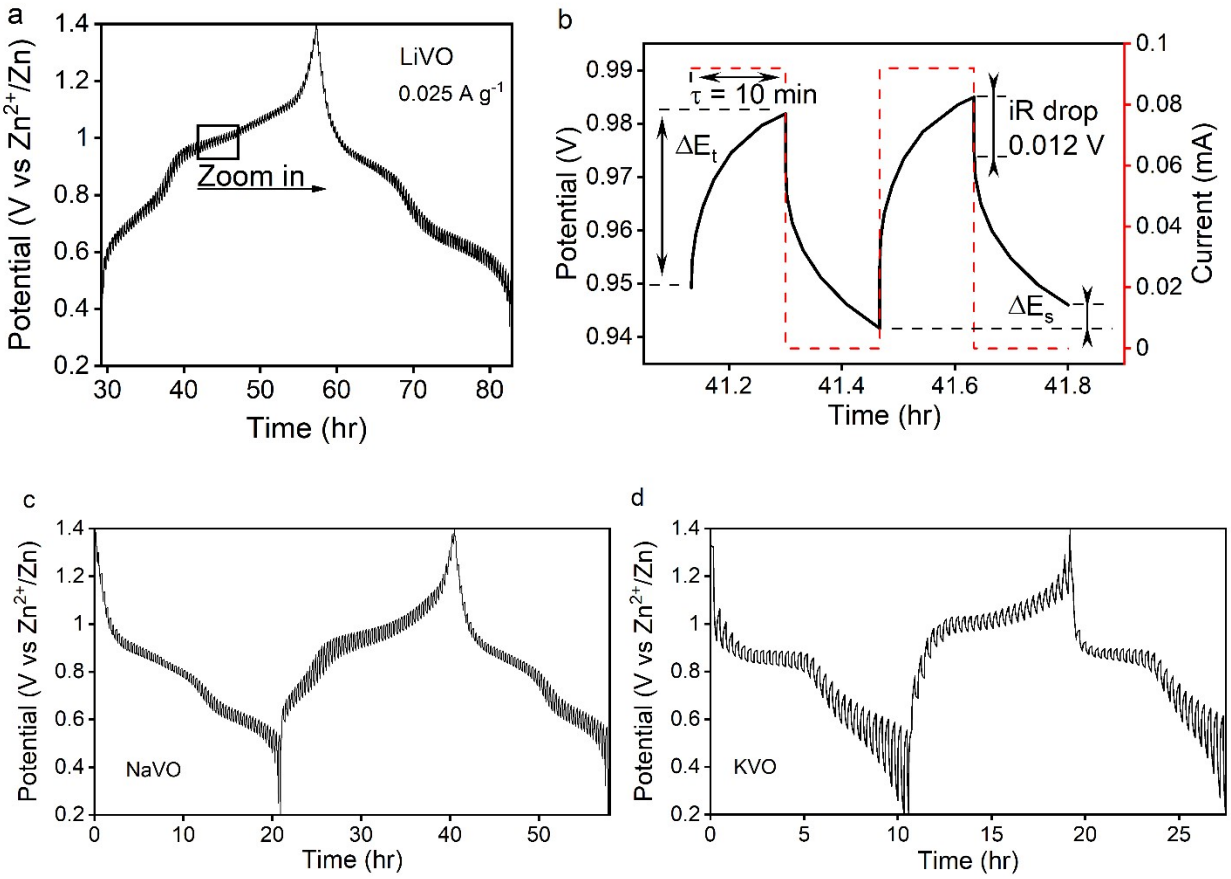

Figure S9. GITT test of (a) LiVO with (b) zoom-in potential curve with values, (c) NaVO and (c) KVO at a current density of 0.025 A g^{-1}.

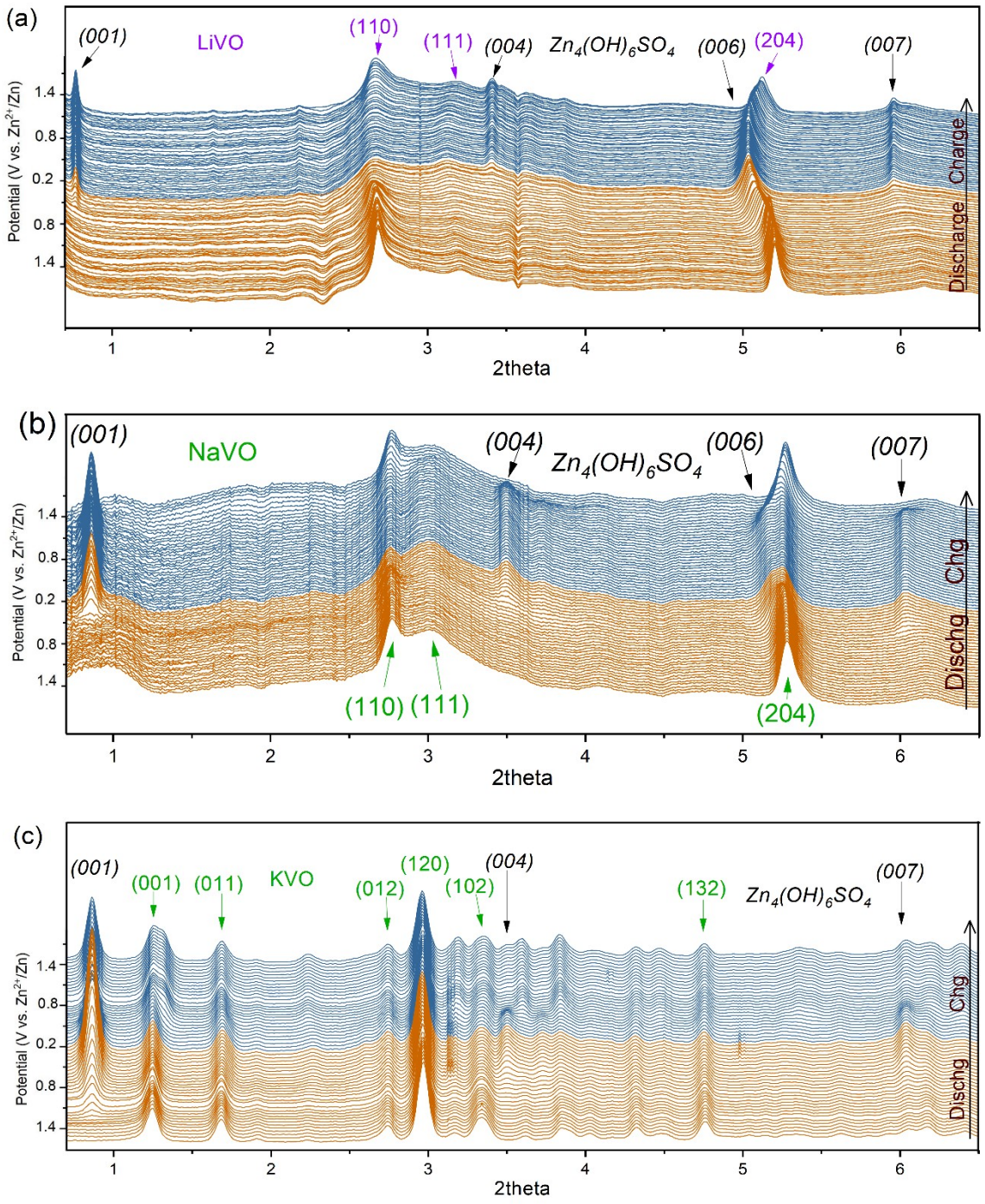

Figure S10. Contour plot of XRD patterns during a CV scan of (a) LiVO, (b) NaVO, and (c) KVO cathodes measured *in situ* Zn-cell (AVO peaks and $Zn_4(OH)_6SO_4{\cdot}4H_2O$ peaks are labeled while the latter one as *Italic*).

Supplementary Tables:

Table S1. Refined crystal structural parameters of LiVO material with X-ray PDF fitting with R_{wp}=36.8%. LiVO is expressed as $Li_x(H_y)V_3O_8 \cdot nH_2O$, where lithium and water amount is determined from EDXS and TGA measurements.

Refined crystal structural parameters of LiVO

Atom	Type	x	y	z	Occ.	Site	Uiso	U_{11}	U_{22}	U_{33}	U_{13}
V	V1	0.095	0.250	0.185	1.00	2a	0.17	0.194	0.013	0.340	0.201
V	V2	0.847	0.250	0.088	1.00	2a	0.04	0.062	0.031	0.014	0.025
V	V3	0.547	0.250	0.871	1.00	2a	0.13	0.105	0.020	0.275	0.118
Li	Li1	0.296	0.250	0.442	1.00	2a	0.02	0.004	0.022	0.045	0.008
O	O1	0.895	0.250	0.900	1.00	2a	0.03	0.005	0.006	0.064	0.001
O	O2	0.147	0.250	0.865	1.00	2a	0.16	0.073	0.052	0.331	0.084
O	O3	0.460	0.250	0.102	1.00	2a	0.03	0.007	0.013	0.065	0.004
O	O4	0.963	0.250	0.260	1.00	2a	0.04	0.051	0.017	0.053	0.052
O	O5	0.239	0.250	0.251	1.00	2a	0.03	0.007	0.053	0.025	0.007
O	O6	0.714	0.250	0.190	1.00	2a	0.04	0.003	0.064	0.038	0.008
O	O7	0.655	0.250	0.765	1.00	2a	0.03	0.015	0.038	0.038	0.004
O	O8	0.365	0.250	0.724	1.00	2a	0.08	0.027	0.019	0.196	0.051
O	O9	0.296	0.250	0.442	1.00	2a	0.02	0.004	0.022	0.045	0.008

Space group: P 21/m

a=12.453 b=3.642 c=8.664 (Å) α=90 β=95.257 γ=90 (°)

Table S2. Refined crystal structural parameters of NaVO material with X-ray PDF fitting with R_{wp}=27.9%. NaVO is expressed as $Na_{0.24}(H_{0.76})V_3O_8 \cdot 1.48H_2O$, where sodium and water amount is determined from EDXS and TGA measurements.

Refined crystal structural parameters of NaVO

Atom	Type	x	y	z	Occ.	Site	Uiso	U_{11}	U_{22}	U_{33}	U_{13}
V	V1	0.614	0.250	0.892	1.00	2e	0.12	0.118	0.010	0.173	0.097
V	V2	0.852	0.250	0.197	1.00	2e	0.03	0.019	0.008	0.054	0.024
V	V3	0.914	0.250	0.867	1.00	2e	0.02	0.023	0.005	0.026	0.014
Na	Na1	0.635	0.474	0.469	1.00	4f	0.01	0.013	0.013	0.013	0.003
Na	Na2	0.582	0.420	0.490	1.00	4f	0.02	0.020	0.020	0.020	0.004
O	O1	0.697	0.250	0.151	1.00	2e	0.03	0.078	0.011	0.003	0.015
O	O2	0.999	0.250	0.434	1.00	2e	0.11	0.177	0.008	0.190	0.155
O	O3	0.771	0.250	0.982	1.00	2e	0.02	0.026	0.013	0.042	0.032
O	O4	0.813	0.250	0.685	1.00	2e	0.06	0.120	0.004	0.071	0.063
O	O5	0.027	0.250	0.105	1.00	2e	0.12	0.325	0.000	0.079	0.173
O	O6	0.174	0.250	0.780	1.00	2e	0.29	0.705	0.024	0.052	0.185
O	O7	0.560	0.250	0.738	1.00	2e	0.05	0.004	0.069	0.057	0.009
O	O8	0.404	0.250	0.018	1.00	2e	0.10	0.012	0.010	0.259	0.051
O	O9	0.434	0.389	0.500	1.00	4f	0.02	0.023	0.023	0.023	0.005

Space group: P 21/m

a=10.214 b=3.602 c=9.312 (Å) α=90 β=100.369 γ=90 (°)

Table S3. Refined crystal structural parameters of KVO material with X-ray PDF fitting with R_{wp}=20.6%. KVO is expressed as $K_{0.9}(H_{0.1})V_3O_8 \cdot 0.04H_2O$, where potassium and water amount is determined from EDXS and TGA measurements.

Refined crystal structural parameters of KVO

Atom	Type	x	y	z	Occ.	Site	Uiso	U_{11}	U_{22}	U_{33}	U_{13}
V	V1	0.455	0.055	0.691	1.00	4f	0.01	0.007	0.010	0.012	0.004
V	V2	0.069	0.750	0.423	1.00	2e	0.01	0.005	0.008	0.008	0.001
K	K1	0.032	0.750	0.931	1.00	2e	0.04	0.049	0.013	0.040	0.028
O	O1	0.107	0.085	0.756	1.00	4f	0.01	0.010	0.023	0.011	0.004
O	O2	0.328	0.591	0.503	1.00	4f	0.02	0.011	0.043	0.014	0.001
O	O3	0.387	0.056	0.146	1.00	4f	0.02	0.048	0.014	0.003	0.005
O	O4	0.070	0.025	0.400	1.00	2e	0.01	0.012	0.007	0.009	0.009
O	O5	0.403	0.750	0.253	1.00	2e	0.02	0.029	0.017	0.010	0.016

Space group: P 21/m

a=4.985 b=8.388 c=7.675 (Å) α=90 β=97.043 γ=90 (°)

Table S4. Physical properties of monovalent ions.[1]

Ions	Ionic radius (pm)	Hydrated radius (pm)	Water number in shell	Hydration enthalpy (kJ mol^{-1})	Ionic mobility (ohm^{-1} cm^2 mol^{-1})
Li	76	340	5.2	-506	33.5
Na	102	276	3.5	-406	43.5
K	138	232	2.6	-330	64.5
NH_4	148	N.A.	2.4	N.A.	N.A.

Reference:

1. (a) Wang, Y.; Weinstock, I. A., Polyoxometalate-decorated nanoparticles. *Chemical Society Reviews* **2012,** *41* (22), 7479-7496; (b) Marcus, Y., Thermodynamics of solvation of ions. Part 5.—Gibbs free energy of hydration at 298.15 K. *Journal of the Chemical Society, Faraday Transactions* **1991,** *87* (18), 2995-2999; (c) Zhong, C.; Deng, Y.; Hu, W.; Qiao, J.; Zhang, L.; Zhang, J., A review of electrolyte materials and compositions for electrochemical supercapacitors. *Chemical Society Reviews* **2015,** *44* (21), 7484-7539.