

Electronic Supplementary Information

Boosting $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode stability by a concentrated aqueous electrolyte for high-voltage zinc batteries

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Experimental Section

Material: The $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanocomposite was synthesized by a hydrothermal-assisted sol-gel method. In a typical synthesis, 2 mmol V_2O_5 , 3 mmol Li_2CO_3 , and 6 mmol $\text{NH}_4\text{H}_2\text{PO}_4$ were dissolved into 35 mL distilled water. Then, 1.5 mmol ascorbic acid and 1.5 mL PEG-400 were added into the solution, which was stirred for 1 h. The mixed solution was loaded into a 50 mL Teflon-lined autoclave and maintained at 180 °C for 24 h. The resultant brown mixture was ultrasonically treated for 90 min to make a uniform dispersion, then it was heated on a hot plate at 80 °C to evaporate water and form a sol. The obtained sol was dried at 120 °C for 12 h. This precursor was thoroughly ground and pre-heated at 350 °C for 4 h, and then calcined at 750 °C for 6 h under Ar atmosphere. The aqueous electrolytes were prepared by adding 1 m $\text{Zn}(\text{OTf})_2$ into distilled water with different amounts of LiTFSI salt, i.e., 1 m $\text{Zn}(\text{OTf})_2$ in water with 0, 5 m, 10 m, and 15 m LiTFSI denoted as 1 m Zn, 1 m Zn + 5 m Li, 1 m Zn + 10 m Li, and 1 m Zn + 15 m Li, respectively (m, mol kg^{-1}).

Materials Characterization: SEM images were obtained on a field-emission scanning electron microscope (JEOL JSM-7500F). TEM images were taken on a Talos F200x G2 microscope, AEMC. TGA was measured by a Netzsch STA 449 F3 Jupiter analyzer with a heating rate 5 °C min^{-1} in air from room temperature to 600 °C. XRD patterns were characterized on a Bruker D8 ADVANCE (Cu $\text{K}\alpha$ radiation) at a scanning rate of 4° min^{-1} . Raman spectra of electrolyte systems were performed on a Horiba HR-Evolution Raman microscope. The UV-vis absorption spectra were measured by a Shimadzu UV-3600 spectrometer at room temperature. XPS spectra were recorded on a ESCALAB 250Xi spectrometer (ThermoFisher).

Electrochemical Measurements: Electrochemical performances were evaluated using CR2032 coin-type cells with LVP cathode, Zn foil anode, glass fiber separator, and different aqueous electrolytes (i.e., 1 m Zn, 1 m Zn + 5 m Li, 1 m Zn + 10 m Li, and 1 m Zn + 15 m Li electrolytes). The LVP electrode was fabricated by blending the active material, Super P carbon, and polyvinylidene fluoride in a weight ratio of 85:5:10 using N-methyl-2-pyrrolidone as solvent. The slurry was pasted onto Ti foil or stainless steel foil, and dried at 80 °C for 10 h under vacuum. The as-prepared electrodes were cut into round slices with a typical mass loading of $\sim 2 \text{ mg cm}^{-2}$. Charge/discharge of battery was tested on a LAND-CT2001A battery-testing instrument. Calculation of specific capacity and current density was based on the active cathode mass. EIS spectra, ionic conductivity tests, and CV profiles were performed on a CHI660E electrochemical work station. The frequency of EIS test ranged from 100 kHz to 100 mHz with the ac perturbation signal of 5 mV. The reversibility of Zn plating/stripping in different electrolytes was measured using Zn/Cu cells.

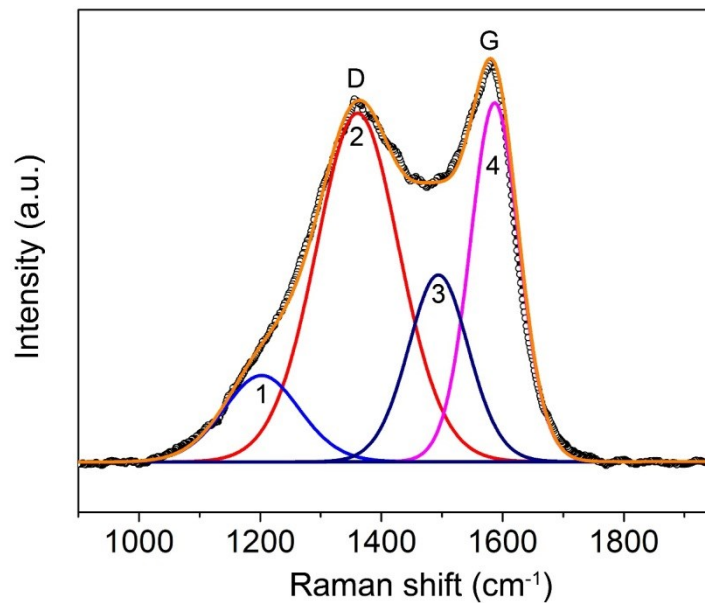


Fig. S1 Raman spectrum of the LVP/C nanocomposite. The two broad peaks of carbon can be deconvoluted into four peaks (labeled peaks 1–4). The peaks at around 1361 (peak 2) and 1592 (peak 4) cm⁻¹ are ascribed to the sp²-type carbon, while the others at around 1203 (peak 1) and 1498 (peak 3) cm⁻¹ are related to the sp³-type carbon. The integrated area ratio of sp³ to sp² is 0.35, suggesting that the carbon content has a high electronic conductivity.^{1,2}

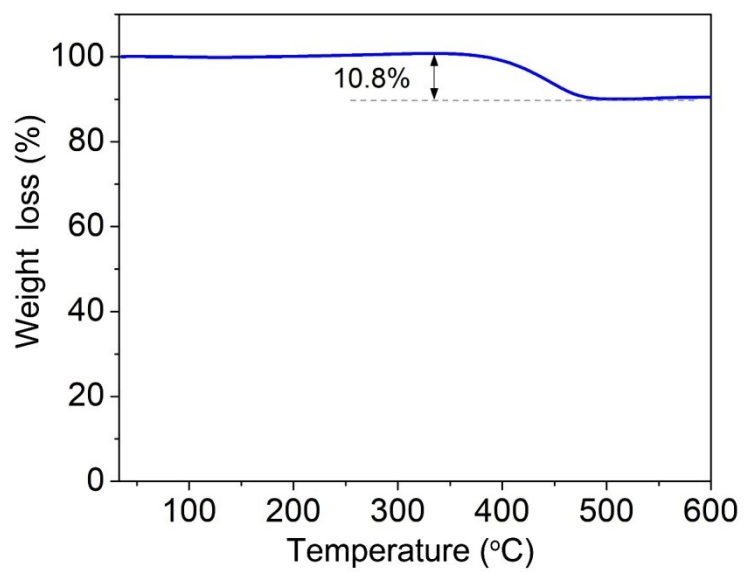


Fig. S2 Thermogravimetric (TG) curve of the as-prepared LVP/C composite with a heating rate $5^{\circ}\text{C min}^{-1}$ in air. Based on the TG result, the carbon content is $\sim 10.8\%$ in this composite.

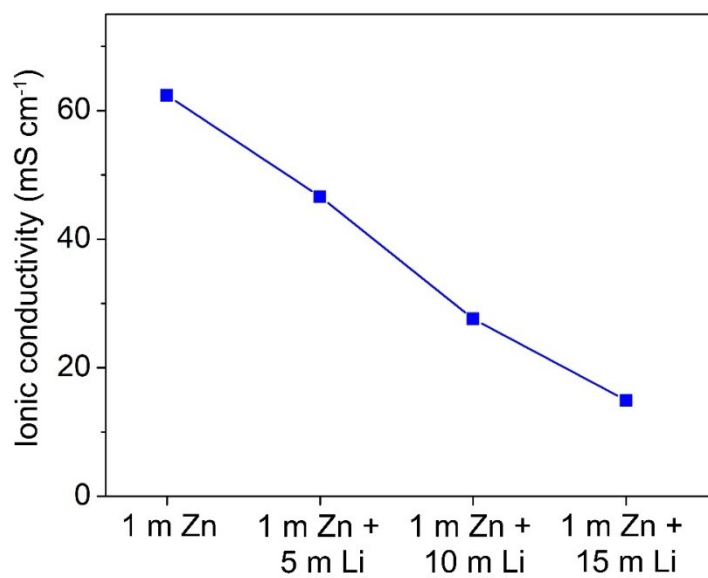


Fig. S3 Ionic conductivities of 1 m Zn, 1 m Zn + 5 m Li, 1 m Zn + 10 m Li, and 1 m Zn + 15 m Li electrolytes.

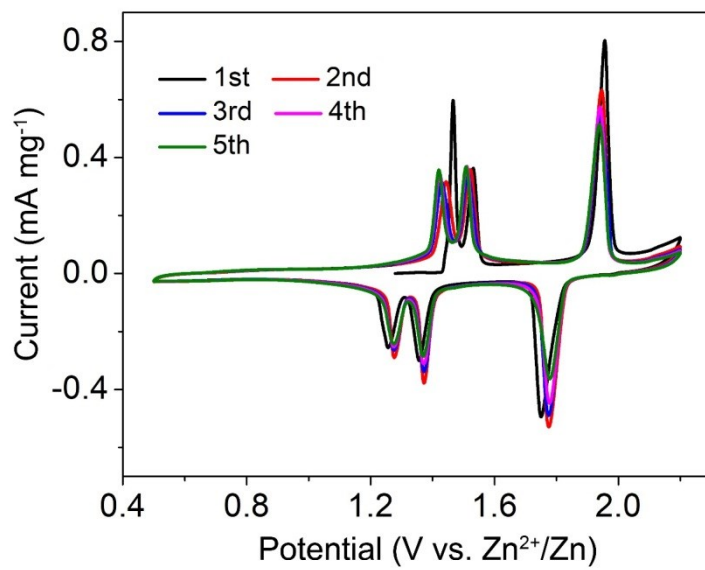


Fig. S4 CV profiles of the LVP cathode in 1 m Zn + 10 m Li electrolyte at 0.2 mV s⁻¹.

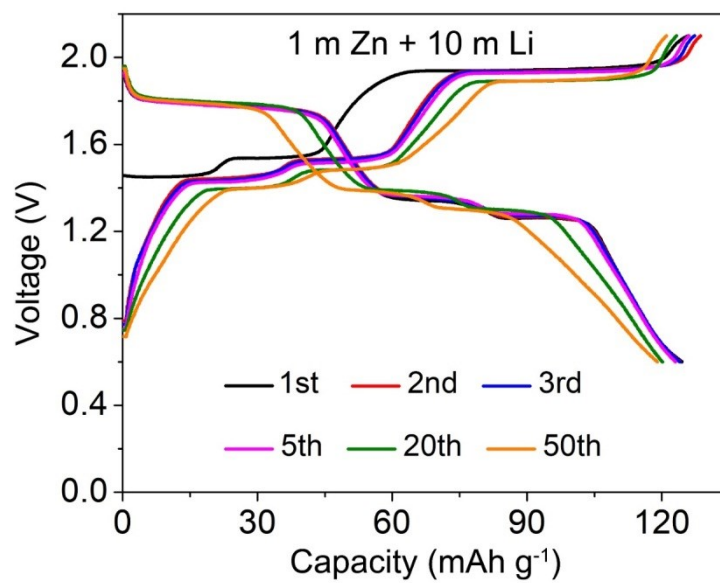


Fig. S5 Charge/discharge profiles of the LVP cathode in 1 m Zn + 10 m Li electrolyte at 200 mA g⁻¹.

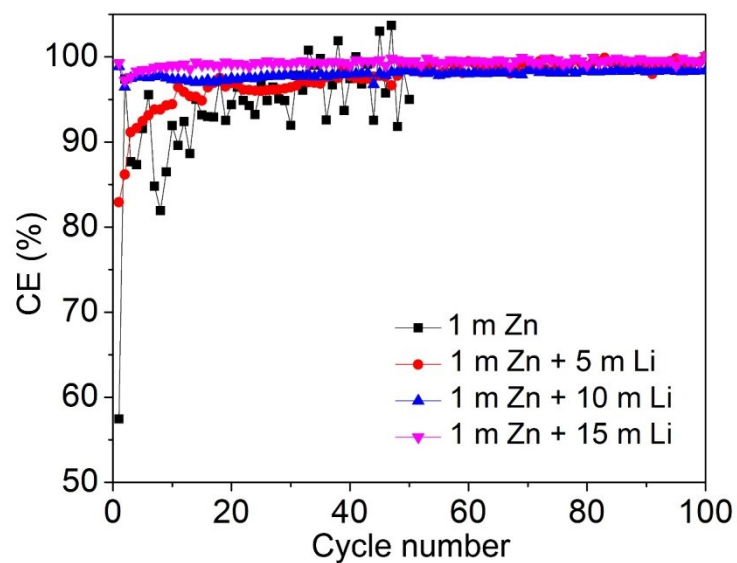


Fig. S6 Coulombic efficiencies of LVP cathodes in 1 m Zn + 15 m Li, 1 m Zn + 10 m Li, 1 m Zn + 5 m Li, and 1 m Zn electrolytes at 200 mA g⁻¹.

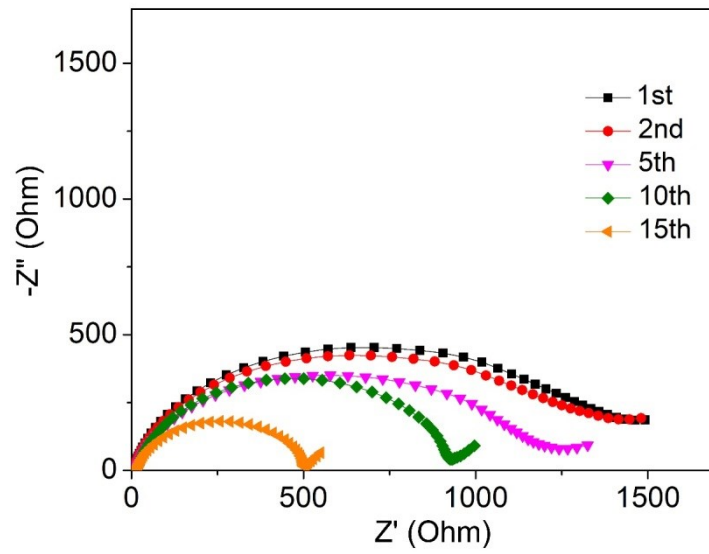


Fig. S7 EIS spectra of the LVP electrode in 1 m Zn + 15 m Li electrolyte at selected cycles.

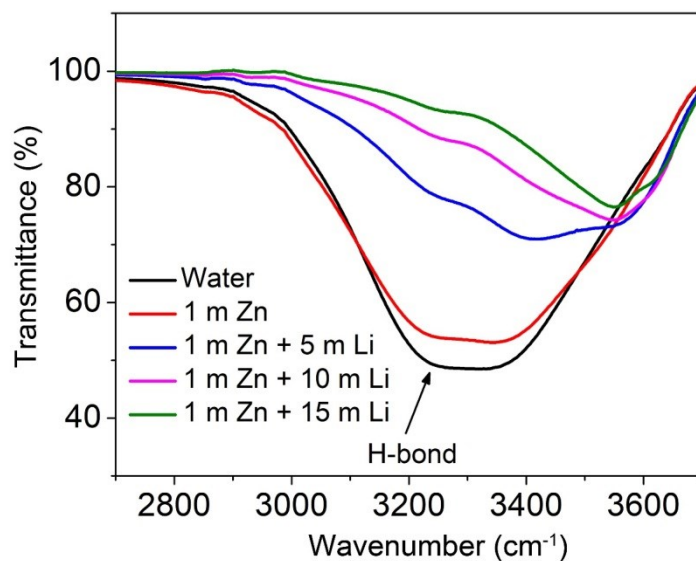


Fig. S8 FTIR spectra of 1 m Zn + 15 m Li, 1 m Zn + 10 m Li, 1 m Zn + 5 m Li, and 1 m Zn electrolytes. The peak located at $\sim 3240\text{ cm}^{-1}$ in 1 m Zn corresponds to the vibration of H_2O with strong H-bond, suggesting the aggregation of H_2O molecules.³ With the increase of Li-salt portion, this H_2O signal experiences blueshift and weaken, indicating the disruption of H_2O network connected by H-bonds.

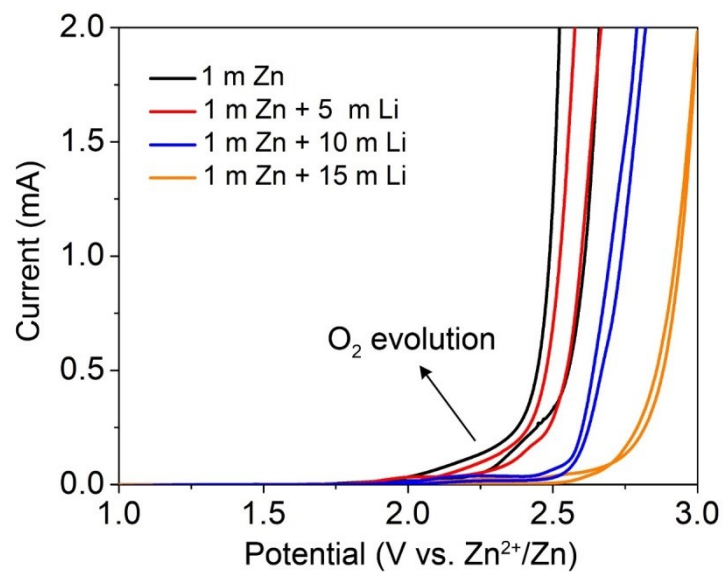


Fig. S9 CV profiles of 1 m Zn + 15 m Li, 1 m Zn + 10 m Li, 1 m Zn + 5 m Li, and 1 m Zn electrolytes at 1 mV s^{-1} between 1.0 and 3.0 V (vs. Zn^{2+}/Zn) in Zn/Ti cells. A much wider electrochemical window up to 2.7 V is characterized for the 1 m Zn + 15 m Li electrolyte, compared with those of the other counterparts, such as, 2.0 V for 1 m Zn, 2.2 V for 1 m Zn + 5 m Li, and 2.5 V for 1 m Zn + 10 m Li.

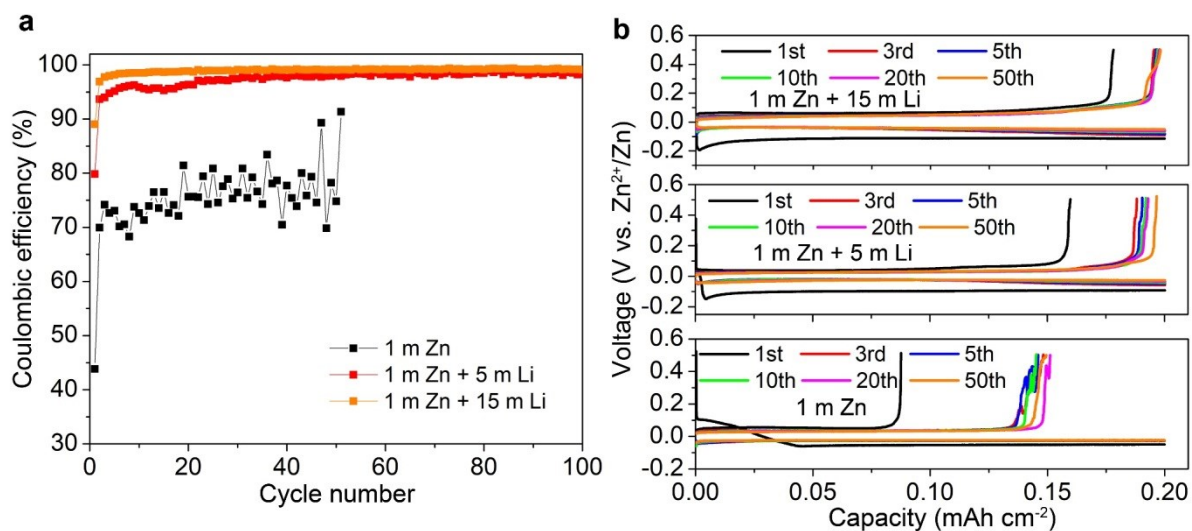


Fig. S10 (a) Coulombic efficiencies and (b) typical voltage profiles of Zn/Cu cells in 1 m Zn, 1 m Zn + 5 m Li, and 1 m Zn + 15 m Li electrolytes at 0.2 mA cm^{-2} with a plating capacity of 0.2 mAh cm^{-2} . The formulated 1 m Zn + 15 m Li electrolyte enables a good reversibility of Zn anode, showing a high initial CE of Zn^{2+} plating/stripping (89.1%) and a considerable average CE of 99.2% after 100 cycles, which significantly outperforms the 1 m Zn and 1 m Zn + 5 m Li systems.

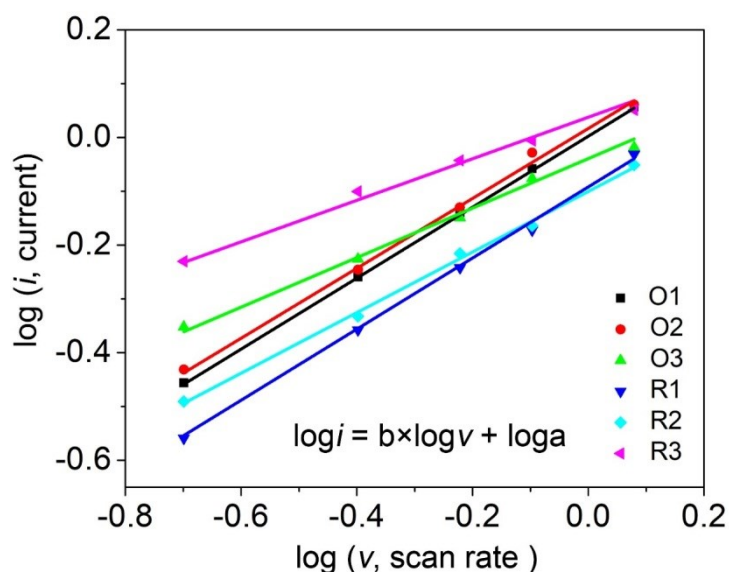


Fig. S11 $\log i$ versus $\log v$ plots according to the CV data at selected oxidation/reduction states. The peak current (i) and sweep rate (v) has a relation of $i = av^b$, in another type, $\log i = b \times \log v + \log a$, where a and b are adjustable parameters, and b is the slope of $\log i$ vs. $\log v$. If b value is close to 0.5, the charge/discharge process is dominated by ionic diffusion; when b value approaches to 1.0, the pseudocapacitance will govern the electrochemical process.^{4,5} By fitting the plots of $\log i$ vs. $\log v$, the b values of the O1, O2, O3, R1, R2, and R3 peaks are calculated to be 0.66, 0.65, 0.47, 0.66, 0.56, and 0.40 respectively. Moreover, the ratio of capacitive contribution can be determined by the equation of $i = k_1v + k_2v^{1/2}$, where k_1v and $k_2v^{1/2}$ refer to the capacitance and ionic diffusion contributions, respectively.^{6,7} The k_1 and k_2 values can be calculated based on the equation $iv^{-1/2} = k_1v^{1/2} + k_2$, by reading the peak currents (i) at the same potential from different sweep rates (v). Thus, the capacitive contribution was depicted in Fig. 3d by plotting the capacitance-dominated current (k_1v) vs. potential (V).

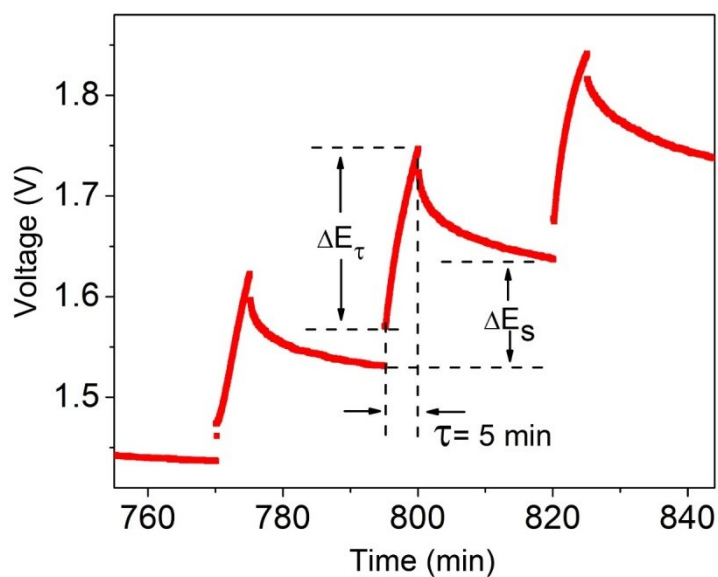


Fig. S12 Schematic illustration of selected steps from the GITT curve during charging.

The cell was charged/discharged at a constant current flux (50 mA g^{-1}) for an interval of 5 min, and then relaxed for 20 min to make the voltage reach the equilibrium. The calculation

method is according to the following equation: $D = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B A} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2$, where τ is the duration

time of the current pulse, m_B is the mass of the active material, M_B is the molecular weight (g/mol), V_m is its molar volume (cm^3/mol), A is the total contacting area of electrode with electrolyte, ΔE_τ is the variation of the cell voltage, and ΔE_S is related to the change of steady-state voltage for the corresponding step. Accordingly, the ion diffusion coefficients of LVP electrode are in the range of 10^{-10} to $10^{-11} \text{ cm}^2 \text{ s}^{-1}$.

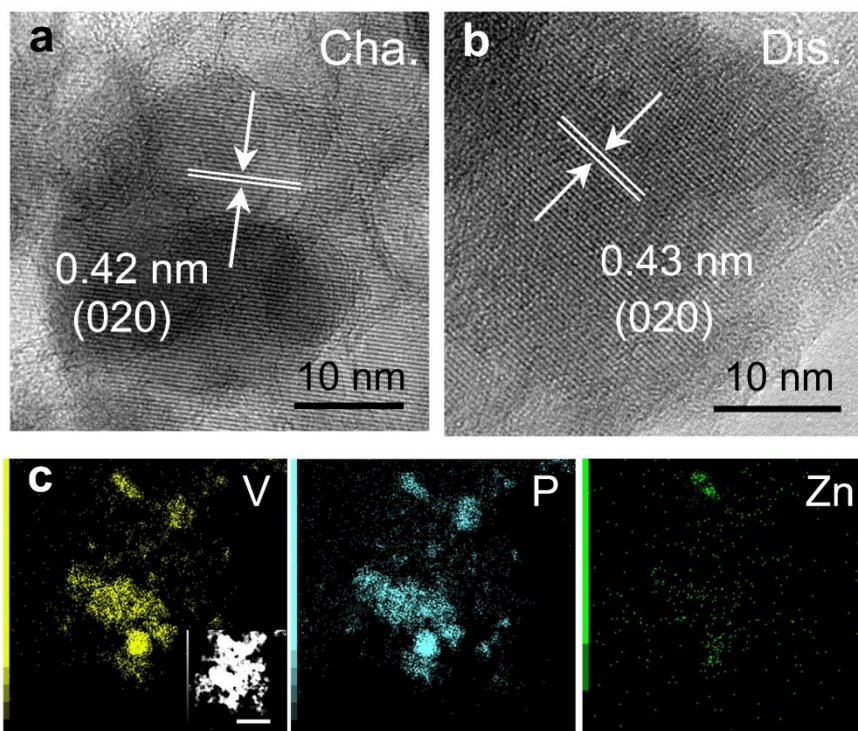


Fig. S13 HRTEM images of LVP cathodes at the (a) fully charged and (b) discharged states. (c) STEM image (inset) with the corresponding element mapping images of the fully discharged LVP electrode. The trace Zn mainly originates from the absorbed Zn^{2+} -salt on the electrode surface.

Supplementary References

1. Z. Zhu, S. Wang, J. Du, Q. Jin, T. Zhang, F. Cheng and J. Chen, *Nano Lett.*, 2014, **14**, 153.
2. W. Duan, Z. Hu, K. Zhang, F. Cheng, Z. Tao and J. Chen, *Nanoscale*, 2013, **5**, 6485.
3. F. Wang, O. Borodin, T. Gao, X. Fan, W. Sun, F. Han, A. Faraone, J. A. Dura, K. Xu and C. Wang, *Nat. Mater.*, 2018, **17**, 543.
4. T. Brezesinski, J. Wang, S. H. Tolbert and B. Dunn, *Nat. Mater.*, 2010, **9**, 146.
6. Y. Dong, S. Di, F. Zhang, X. Bian, Y. Wang, J. Xu, L. Wang, F. Cheng, and N. Zhang, *J. Mater. Chem. A*, 2020, **8**, 3252.
5. J. Wang, J. Polleux, J. Lim, and B. Dunn, *J. Phys. Chem. C* 2007, **111**, 14925.
7. N. Zhang, Y. Dong, M. Jia, X. Bian, Y. Wang, M. Qiu, J. Xu, Y. Liu, L. Jiao and F. Cheng, *ACS Energy Lett.*, 2018, **3**, 1366.