

Supporting Information

The Energy Storage Behavior of a Phosphate-Based Cathode Material in Rechargeable Zinc Batteries

Cuicui Li,^a Wanlong Wu,^a Hua-Yu Shi,^a Zengming Qin,^a Duo Yang,^a Xianpeng Yang,^a Yu Song,^a Di Guo,^a Xiao-Xia Liu^{a,b} and Xiaoqi Sun^{*a}

^a Department of Chemistry, Northeastern University, Shenyang, 110819, China

^b Key Laboratory of Data Analytics and Optimization for Smart Industry (Northeastern University), Ministry of Education, Shenyang, 110819, China

*Corresponding author

Email: sunxiaoqi@mail.neu.edu.cn

Experimental Section

Synthesis of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{rGO}$ composite: The $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{rGO}$ composite was obtained using a previously reported method ¹. Typically, oxalic acid and V_2O_5 (3:1 molar ratio) were dissolved in deionized water under magnetic stir at 70 °C. After a clear blue solution was formed, the stoichiometric $\text{NH}_4\text{H}_2\text{PO}_4$ and Li_2CO_3 were added to the solution. The GO suspension was also added. The mixture was stirred and sonicated, followed by drying in an oven at 100 °C to form a gel. The gel was heated at 350 °C for 4 h under argon, and the obtained product was ground. The powder was then pressed into pellets and sintered at 750 °C for 6 h under argon.

Material characterization: X-ray diffraction (XRD) patterns of the samples were measured using a PANalytical Empyrean diffractometer with Cu $\text{K}\alpha$ radiation. The morphology and elemental contents were obtained using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) detector (HITACHI SU8010, Japan). The carbon content was obtained with a carbon sulfur analyzer (CS-200), and the weight percentage of rGO was 9.19%.

Electrochemical measurement: The cathodes were prepared by mixing $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{rGO}$ with super P and polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP), drop casting on carbon paper substrate and drying at 60 °C in air then under vacuum. The diameter of the electrodes is 12 mm, and the area is 1.13 cm^2 . The mass loading of active material is around 2.0 mg cm^{-2} or 2.3 mg per electrode. The 1 m $\text{Zn}(\text{ClO}_4)_2/\text{H}_2\text{O}$ electrolyte was prepared by dissolving desired amount of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in water, while 1 m $\text{Zn}(\text{ClO}_4)_2/\text{ACN}-11\%\text{H}_2\text{O}$ was obtained by dissolving desired amount of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile. The water content in the latter was confirmed to be 10.85% using a Mettler Toledo DL31 Karl Fischer Coulometer. To prepare the $\text{Zn}(\text{ClO}_4)_2/\text{ACN}-3\%\text{H}_2\text{O}$ electrolyte, the $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was dried at 100 °C under vacuum and dissolved in acetonitrile. The water content was measured to be 2.7%. The cathode, electrolyte, zinc foil anode and filter paper separators were assembled in CR2032-type coin cells in air. For the test in Li ion cells, FePO_4 was obtained by electrochemical delithiation of LiFePO_4 . The FePO_4 electrode was prepared by mixing

FePO₄ with super P and polyvinylidene fluoride (PVDF) with a weight ratio of 7:2:1 in N-methyl-2-pyrrolidone (NMP). The obtained slurry was drop casted onto carbon paper and dried at 60 °C in vacuum. The mass loading of FePO₄ was more than four times of Li₃V₂(PO₄)₃. Galvanostatic charge/discharge tests were performed with a Land CT2001A battery cycler. Electrochemical impedance spectroscopy (EIS) was obtained in T-shaped PFA Swagelok 3-electrode cells with Zn as the counter and reference electrodes on the Bio-logic VMP3 potentiostat/galvanostat. The measurements were carried out in 3-electrodes to ensure the precise control of potential.

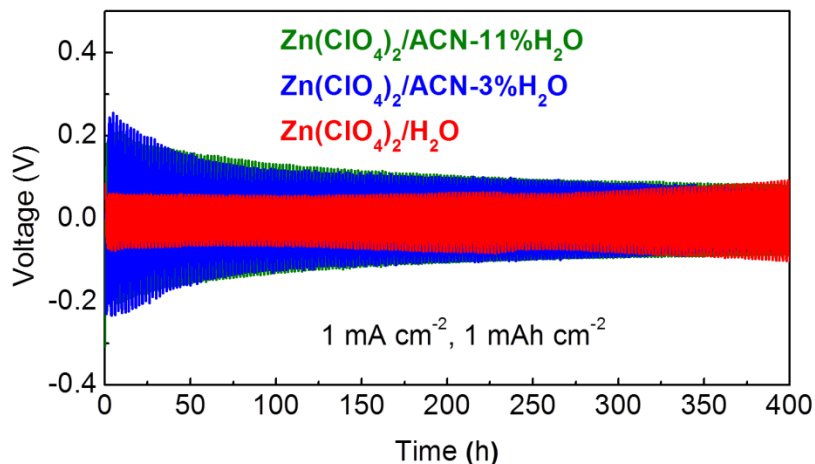


Figure S1. Zn plating/stripping tests in symmetric cells.

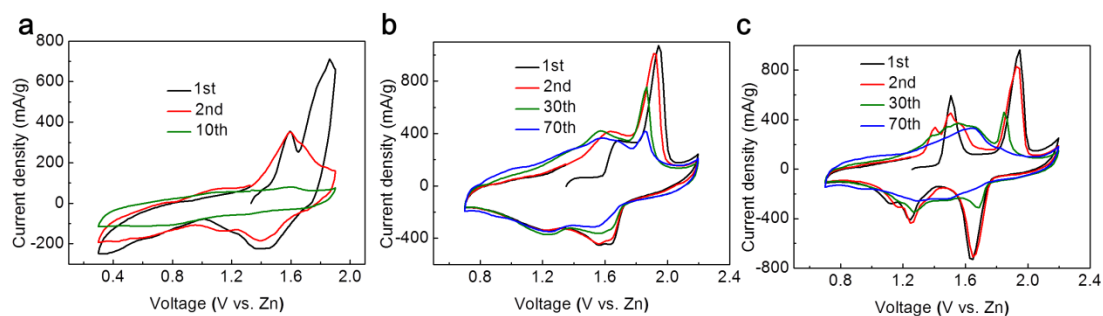


Figure S2. Cyclic voltammograms of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ at 0.5 mV s^{-1} in the electrolytes of (a) $\text{Zn}(\text{ClO}_4)_2/\text{H}_2\text{O}$, (b) $\text{Zn}(\text{ClO}_4)_2/\text{ACN}-3\%\text{H}_2\text{O}$, (c) $\text{Zn}(\text{ClO}_4)_2/\text{ACN}-11\%\text{H}_2\text{O}$.

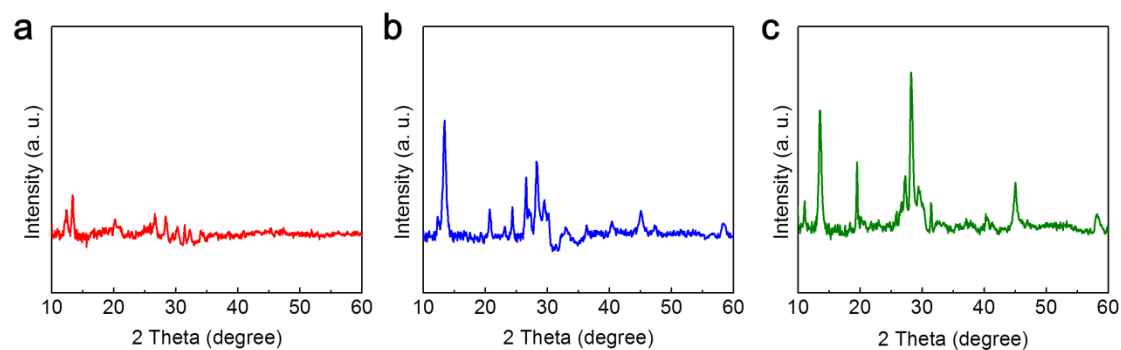


Figure S3. XRD of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ electrode after running at 2C for 200 cycles in (a) $\text{Zn}(\text{ClO}_4)_2/\text{H}_2\text{O}$, (b) $\text{Zn}(\text{ClO}_4)_2/\text{ACN}-3\%\text{H}_2\text{O}$ and (c) $\text{Zn}(\text{ClO}_4)_2/\text{ACN}-11\%\text{H}_2\text{O}$ electrolytes.

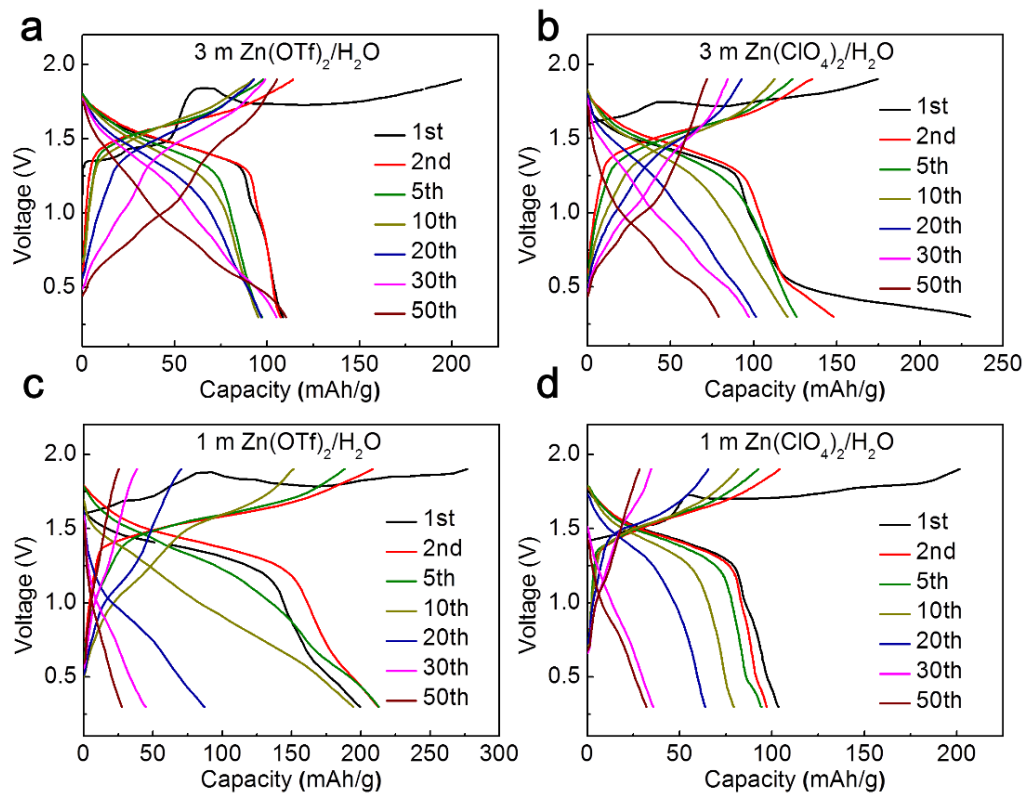


Figure S4. Voltage profiles of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ in (a) 3 m $\text{Zn}(\text{OTf})_2$, (b) 3 m $\text{Zn}(\text{ClO}_4)_2$, (c) 1 m $\text{Zn}(\text{OTf})_2$ and (d) 1 m $\text{Zn}(\text{ClO}_4)_2$ aqueous electrolytes at 2C during different cycles.

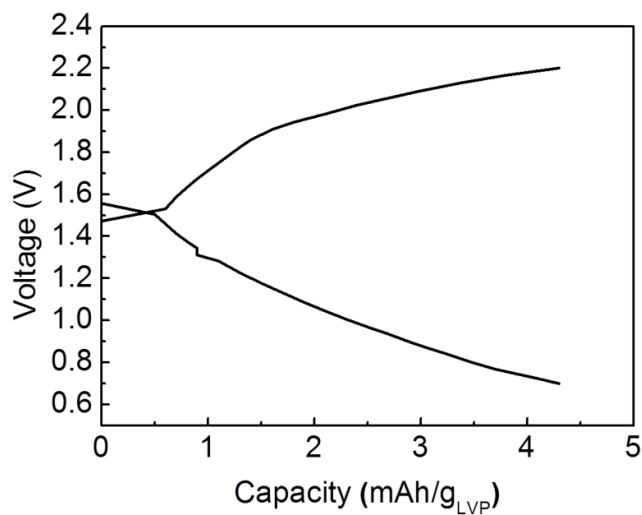


Figure S5. Voltage profile of bare carbon paper in the $\text{Zn}(\text{ClO}_4)_2/\text{ACN}-11\%\text{H}_2\text{O}$ electrolyte at 1C (mass based on the average loading of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$).

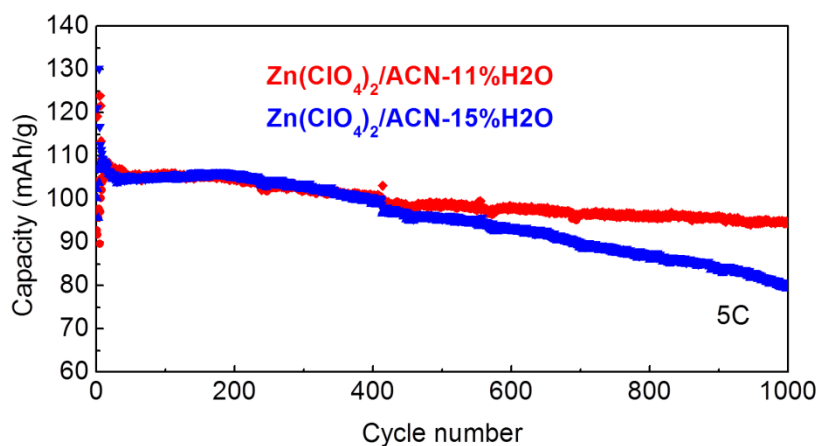


Figure S6. Cycling performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ in the $\text{Zn}(\text{ClO}_4)_2/\text{ACN}-11\%\text{H}_2\text{O}$ and $\text{Zn}(\text{ClO}_4)_2/\text{ACN}-15\%\text{H}_2\text{O}$ electrolytes at 5C.

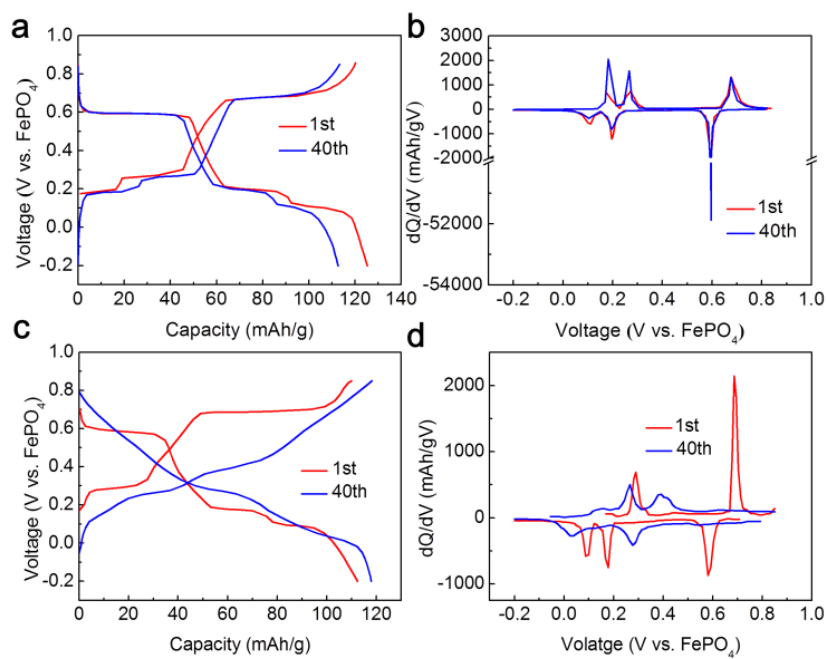


Figure S7. The charge/discharge and differential capacity curves of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ in the (a,b) $\text{LiClO}_4/\text{ACN}$ and (c,d) $\text{LiClO}_4/\text{ACN}-11\%\text{H}_2\text{O}$ electrolytes.

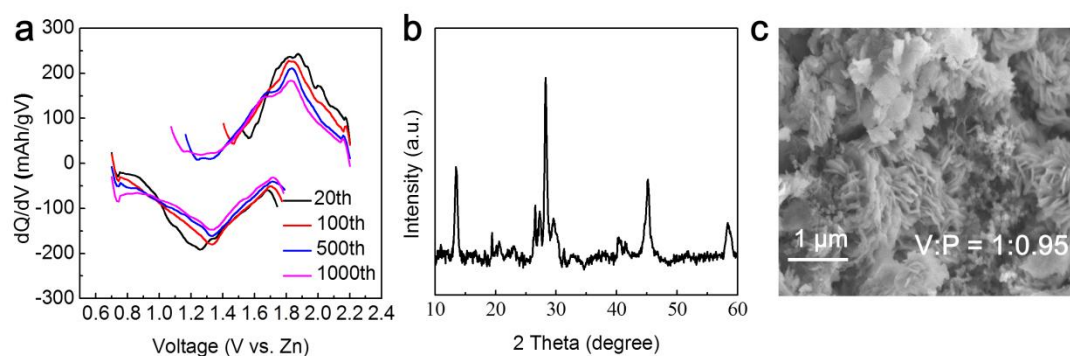


Figure S8. (a) The differential capacity curves of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ in zinc cells with the $\text{Zn}(\text{ClO}_4)_2/\text{ACN}-11\%\text{H}_2\text{O}$ electrolyte at 5C. (b) XRD pattern and (c) SEM image of the electrode after 1000 cycles.

Table S1. The EIS fitting results

Electrolyte	R_s (ohm)	R_{ct} (ohm)
$\text{Zn}(\text{ClO}_4)_2/\text{ACN}-11\%\text{H}_2\text{O}$	4.8	55.7
$\text{Zn}(\text{ClO}_4)_2/\text{ACN}-3\%\text{H}_2\text{O}$	6.9	201.5

Reference

- 1 M. J. Park, H. Yaghoobnejad Asl, S. Therese and A. Manthiram, *J. Mater. Chem. A*, 2019, **7**, 7159-7167.