Electronic Supplementary Material (ESI) for Energy & Environmental Science. This journal is © The Royal Society of Chemistry 2021

Electronic Supplementary Information

Principle in Interlayer-Spacing Regulation of Layered Vanadium Phosphates

for Superior Zinc-ion Batteries

Linfeng Hu*a,b, Zeyi Wu^b, Chengjie Lu^a, Fei Ye^a, Qiang Liu^a, Zhengming Sun^a

- a. School of Materials Science and Engineering, Southeast University, Nanjing, 211189, China
- b. Department of Materials Science, Fudan University, Shanghai 200433, China
 - * Address correspondence to: <u>linfenghu@seu.edu.cn</u>

Contents:

Fig. S1-Fig. S11



Fig. S1. Thermogravimetric analysis (TGA) curve of VOP and PA-VOP (16.5 Å), respectively. Moreover, thermo gravimetric analysis (TGA) result reflects a weight loss of 19.2 % before 150 °C of VOP, consistent with two H₂O contained per molecule in VOP, while the weight loss of 25.3 % of PA-VOP indicates 0.6 phenylamine per molecule in PA-VOP. In view of the primary loss before 600 °C, polymerization of the intercalated phenylamine is certainly Infinitesimal.



Fig. S2. SEM image of precursor VOP bulk.



Fig. S3. AFM image of VOP nanoplates precursor. Insert is a typical height curve of an individual

nanoplate.



Fig. S4. Typical TEM image, the cross-sectional HRTEM image and corresponding V, P, O, C, N element mapping of an individual PA-VOP sheet.



Fig. S5. XRD patterns of various PA-VOP samples synthesized under different temperature and solvent (2θ range: 4° - 13°).



Fig. S6. TGA curves of PA-VOP samples with different interlayer spacing, respectively.



Fig. S7. CV curves of the Zn / PA-VOP (16.5 Å) battery in initial three cycles.



Fig. S8. GCD curves of the Zn / PA-VOP (16.5 Å) battery in intial three cycles.



Fig. S9. CV curve of Zn / PA-VOP battery at the scan rate of 0.1 mV \cdot s⁻¹ using different electrolyte (aqueous and non-aqueous).



Fig. S10. *Ex-situ* XRD characterization and corresponding scheme of Zinc-ion storage mechanism in PA-VOP cathode.



Fig. S11. CV and GCD curves of Zn // PA battery at different scan rate and varied current density, respectively.



Fig. S12. Dependence between specific capacity, electronic conductivity and the interlayer spacing of various VOPO₄-based cathodes.

Fig. S13. (a)-(c) CV curves of VOP (7.4 Å), PA-VOP (14.8 Å phase) and PA-VOP (16.5 Å phase) cathode at different scan rate and (d)-(f) the corresponding dependence of logrithm of peak current density and scan rate, repectively.

Fig. S14. Cycling performance at 5.0 A·g⁻¹and coulombic efficiency of Zn / PA-VOP coin cells employing 2M Zn(CF₃SO₃)₂ and 2M ZnSO₄ aqueous solution as electrolyte, respectively. Compared to a capacity loss of 20.3 % in aqueous Zn(SO₄)₂ electrolyte, superior lifespan with less capacity decay (7.7%) was observed in Zn(CF₃SO₃)₂ electrolyte due to the better desolvation effect of bulky (CF₃SO₃)⁻ versus (SO₄)²⁻

Fig. S15. Nyquist plots of pure VOP (7.4 Å) and PA-VOP (16.5 Å) composited cathode after several cycles.