

## *Supporting Information*

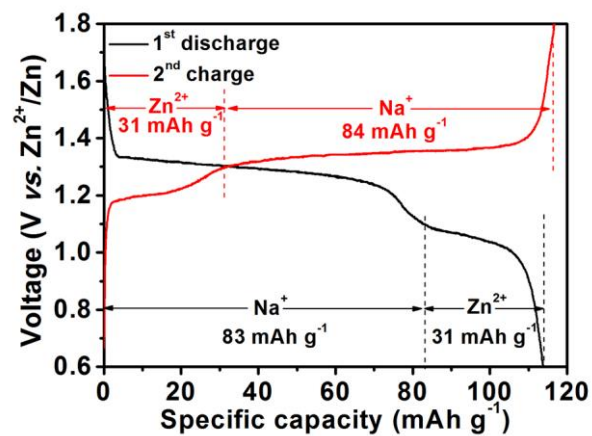
### **Aqueous Zn//Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>//Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> Batteries with Simultaneous Zn<sup>2+</sup>/Na<sup>+</sup> Intercalation/De-intercalation**

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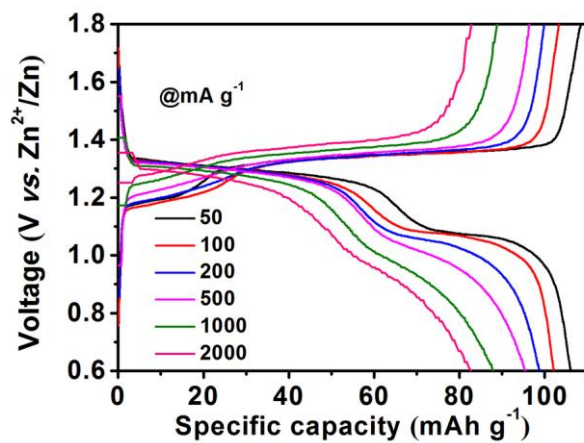
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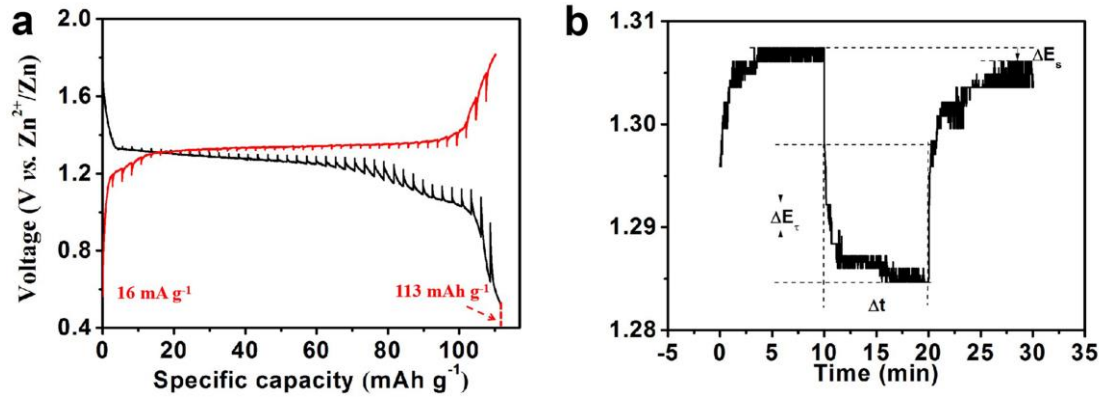
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**Fig. S1.** The capacity contributions from  $\text{Zn}^{2+}/\text{Na}^{+}$  intercalation/de-intercalation at  $50 \text{ mA g}^{-1}$ .



**Fig. S2.** Charge/discharge curves of NVP@rGO at different current densities.

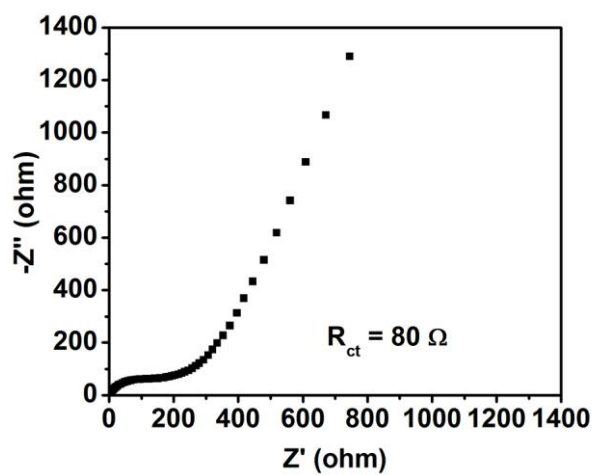


**Fig. S3.** The GITT test for NVP@rGO microspheres at a current density of 16 mA g<sup>-1</sup> in a charge/discharge process.

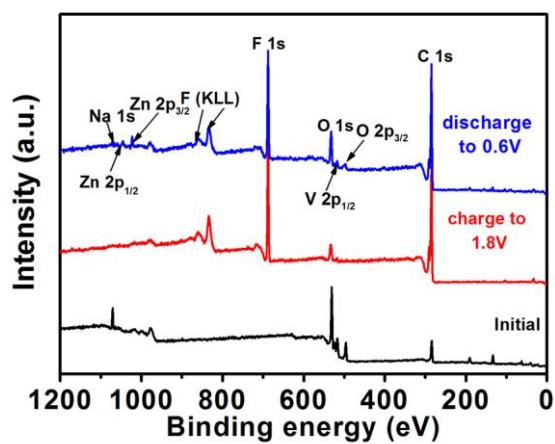
On the basis of Fick's second law, the diffusion coefficient of Na<sup>+</sup> and Zn<sup>2+</sup> could be calculated using the equation below

$$D = \frac{4}{\pi} \left( \frac{m_a V_M}{M_a S} \right)^2 \left( \frac{\Delta E_s}{\tau \left( \frac{dE_\tau}{d\sqrt{\tau}} \right)} \right)^2$$

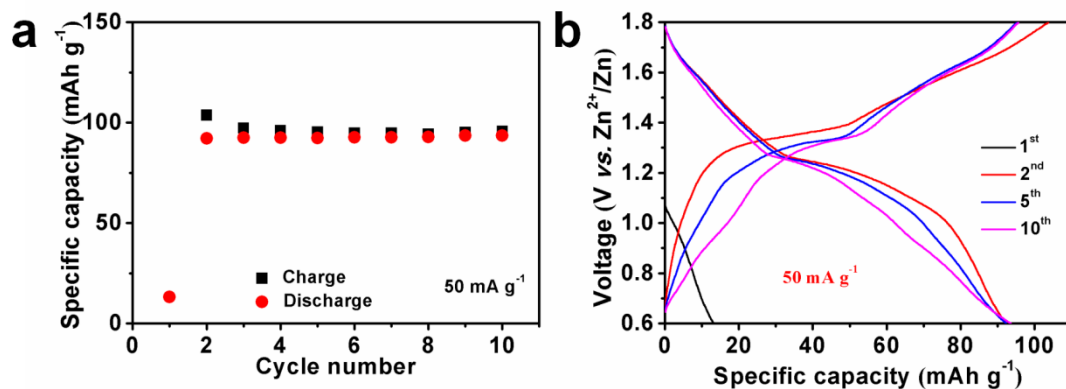
where  $m_a$  and  $M_a$  are the mass and the molecular weight.  $V_M$  is the molar volume of the compound.  $S$  represents the active surface area.  $\tau$  is the time period of the current pulse.  $dE_\tau/d(\tau^{1/2})$  is the derivative of the voltage change during the current pulse with respect to the charge or discharge time  $\tau$ .  $\Delta E_\tau$  is the total change of cell voltage during a constant current pulse, and  $\Delta E_s$  is the change of the steady-state voltage at the end of the relaxation period over a single galvanic static titration.



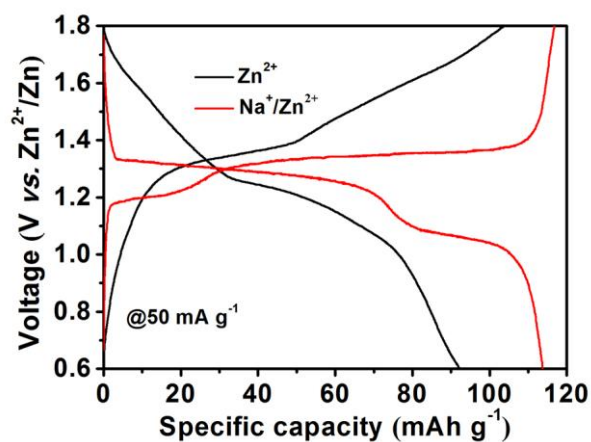
**Fig. S4.** Nyquist plots of NVP@rGO.



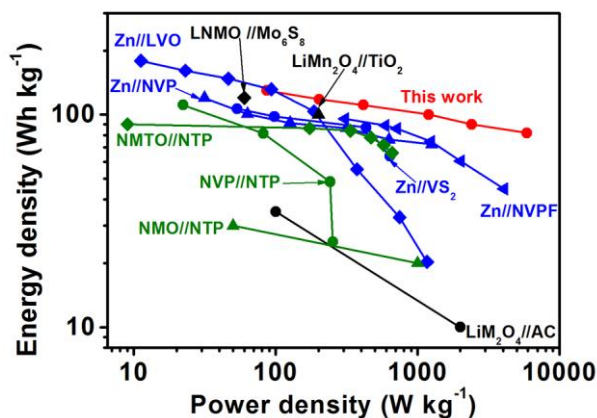
**Fig. S5.** XPS survey spectra of the electrodes obtained at different states (original, charged, and discharged states). The fluorine comes from the PVDF binder.



**Fig. S6.** Cycling performance (a) and charge/discharge curves (b) of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3@\text{rGO}$  (prepared by charging NVP@rGO to 1.8 V and then washed with deionized water).



**Fig. S7.** Charge/discharge curves of NVP@rGO and  $\text{Na}_x\text{V}_2(\text{PO}_4)_3@\text{rGO}$  (prepared by charging NVP@rGO to 1.8 V and then washed with deionized water).



**Fig. S8.** Ragone plot comparing the electrochemical performance of the Zn//Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>//Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> battery with other recently reported aqueous metal-ion batteries. The black dots represent data from aqueous Li-ion batteries of LiMn<sub>2</sub>O<sub>4</sub>//TiO<sub>2</sub>,<sup>[1,2]</sup> LiMn<sub>2</sub>O<sub>4</sub>//AC,<sup>[3]</sup> LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>2</sub>//Mo<sub>6</sub>S<sub>8</sub>;<sup>[4]</sup> the green dots represent data from aqueous Na-ion batteries of Na<sub>0.66</sub>[Mn<sub>0.66</sub>Ti<sub>0.34</sub>]O<sub>2</sub>//NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C,<sup>[5]</sup> NaMnO<sub>2</sub>//NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>,<sup>[6]</sup> Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>//NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>;<sup>[7]</sup> the blue dots represent data from aqueous Zn-ion batteries of Zn//LiV<sub>3</sub>O<sub>8</sub>,<sup>[8]</sup> Zn//Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>,<sup>[9]</sup> Zn//VS<sub>2</sub>,<sup>[10]</sup> Zn//Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub>.<sup>[11]</sup>

## References

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