Supporting Information

Na₃V₂(PO₄)₂F₃-SWCNT: A High Voltage Cathode for Non-aqueous and Aqueous Sodium-ion Batteries

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Fig. S1 (a) XRD pattern, and (b) the SEM image of pure Na₃V₂(PO₄)₂F₃.



Fig. S2 The SEM images of Na₃V₂(PO₄)₂F₃-SWCNT-1 (a, b), Na₃V₂(PO₄)₂F₃-SWCNT-2 (c, d),and Na₃V₂(PO₄)₂F₃-SWCNT-3 (e, f).



Fig. S3 N₂ adsorption and desorption isotherm of Na₃V₂(PO₄)₂F₃-SWCNT-2. (inset: pore-size distribution curves).



Fig. S4 Charge/discharge curves at 64 mA $g^{\mbox{-}1}$ of SWCNT electrode in non-aqueous electrolyte.



Fig. S5 The cycle performance of $Na_3V_2(PO_4)_2F_3$ -SWCNT-2 electrode in 17 m $NaClO_4$ aq..



Fig. S6 XRD spectra for pristine Na₃V₂(PO₄)₂F₃-SWCNT-2 electrode before cycle (green line) and Na₃V₂(PO₄)₂F₃-SWCNT-2 electrode



Fig. S7 SEM images for (a) pristine Na₃V₂(PO₄)₂F₃-SWCNT-2 electrode before cycle, (b) Na₃V₂(PO₄)₂F₃-SWCNT-2 electrode after 60 cycles at 1 C in 17 m NaClO₄ aq..

Fig. S6⁺ shows the XRD patterns of pristine $Na_3V_2(PO_4)_2F_3$ -SWCNT-2 electrode before cycle and $Na_3V_2(PO_4)_2F_3$ -SWCNT-2 electrode after 60 cycles. The results show that some main characteristic peaks (16.02 °, 16.52 °, 27.76 °, 28.68 °, 39.76 °, 49.75 °) weaken after 60 cycles, resulting from the structure degradation and/or the formation of amorphous crystal. Meanwhile, SEM results demonstrate that compared with the regular morphology of pristine $Na_3V_2(PO_4)_2F_3$ -SWCNT (Fig. S7a⁺), the cuboids crack into particles after 60 cycles (Fig. S7b⁺). These phenomena suggests the degradation of $Na_3V_2(PO_4)_2F_3$ -SWCNT-2.



Fig. S8 XPS spectra of (a) V 2P_{3/2} of the Na₃V₂(PO₄)₂F₃-SWCNT electrode, (b) Ti 2P_{3/2} of the NaTi₂(PO₄)₃-MWCNT electrode at different charge-discharge stages in 17 m NaClO₄ aq..

Fig. S8a illustrates the change of vanadium valence state. Compared with the V³⁺ signal (517.01 eV) at the pristine state, V⁴⁺ signal (518 eV) appears at the fully charged of 1.2 V. (Fig. 4b) After discharged to 0.2 V, the binding energy value changes from 518 eV for V⁴⁺ to 517.03 eV for V³⁺, indicating the conversion of V³⁺ \leftrightarrow V⁴⁺ during the cycling.^{1,2} Note that the appearence of V³⁺ is due to the incomplete reaction. In order to avoid water decomposition, cut-off voltage should be set to no more than 1.2 V, which causes the incomplete reaction. For anode, as shown in Fig. S8b, the peaks at 459.2 and 464.94 eV are assigned to Ti 2p_{3/2} and Ti 2p_{1/2} of Ti⁴⁺ at the pristine state.^{3,4} When the electrode is discharged to -0.9 V, the binding energy of the two peaks shift to lower positions of 457.7 and 463.25 eV, indicating that the valence state of the Ti is Ti³⁺.⁴ After charged to -0.5 V, the binding energy value changes from 457.7 eV for Ti³⁺ to 459.1 eV for Ti⁴⁺, suggesting the high conversion of Ti³⁺ \leftrightarrow Ti⁴⁺ during the cycling. The XPS results reveal that there exists reversible transformation between V³⁺ \leftrightarrow V⁴⁺ for cathode and Ti³⁺ \leftrightarrow Ti⁴⁺ for anode during the charge–discharge process.



Fig. S9 (a) *Ex situ* XRD spectra collected for $Na_3V_2(PO_4)_2F_3$ -SWCNT in 17 m NaClO₄ aq., (b) The corresponding galvanostatic charge/discharge curves of 1st cycle under 1C rate between 0.2-1.2 V. (c-f) Partial enlargement images of *ex situ* XRD profiles (The black, blue, red, purple and green lines in Fig. S9a and Fig. S9c-f are corresponding to the state of Fig. S9b, respectively).



Fig. S10 (a) XRD patterns (inset: crystal structure), (b) SEM images, (c) HRTEM image (the inset is the SAED pattern), (d) TG curve, (e) CV tested at 1 mV s⁻¹ and (f) charge/discharge curves at 1 C (1 C = 133 mA g⁻¹) (inset: the corresponding cyclic performance) of NaTi₂(PO₄)₃-MWCNT.

As displayed in Fig. S10a-b, the as-prepared NaTi₂(PO₄)₃-MWCNT microblocks appeare as well defined NASICON structure (JCPDS 84-2009) with aggregated particles of 2-10 μ m. The clear lattice planes in HRTEM (Fig. S10c) indicates high crystallinity of the NaTi₂(PO₄)₃-MWCNT, and the lattice spacing of 3.656 Å can agree well with the d spacing of (113) of the NaTi₂(PO₄)₃-MWCNT. The corresponding SAED pattern can be indexed to the (113), (211), and (400) planes, which are attributed to the NaTi₂(PO₄)₃-MWCNT composite. TG curve (Fig. S10d) suggests that the carbon contents is 7.5 wt%. In addition, we also examined the electrochemical performance of NaTi₂(PO₄)₃-MWCNT in 17 m NaClO₄ aq.. CV profile in Fig. S10e is a pair of symmetrical redox peaks, which are located at -0.74 V/-0.68 V vs. Ag/AgCl, indicating a reversible insertion/extraction reaction of Na⁺ in NaTi₂(PO₄)₃ lattice (NaTi₂(PO₄)₃ + 2Na⁺ + 2e⁻ \leftrightarrow Na₃Ti₂(PO₄)₃). Furthermore, the redox reaction potential is much larger than the potential of H₂ evolution, water decomposition can be avoided completely. Fig. S10f shows the charge/discharge profiles of the NaTi₂(PO₄)₃-MWCNT anode at 1 C (1 C = 133 mAh g⁻¹). It deliveres a high charge capacity of 125 mAh g⁻¹, and a best cycle stability. What's more, the charge/discharge curves are with very long and flat plateau, suggesting an electrochemical reversibility and rapid kinetics for Na⁺ in the NaTi₂(PO₄)₃ anode.



Fig. S11 (a) Charge/discharge curves at 128 mA g $^{-1}$ of SWCNT electrode in 17 m NaClO₄ aq.



Fig. S12 Nyquist plots of Na₃V₂(PO₄)₂F₃-SWCNT//NaTi₂(PO₄)₃-MWCNT aqueous full-cell in 17 m NaClO₄ aq..

Notes and references

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