Electronic Supplementary Information

$Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$: A stable and high-voltage cathode material for aqueous sodium-ion batteries with high energy density

*P. Ramesh Kumar‡, Young Hwa Jung‡, Chek Hai Lim, and Do Kyung Kim**

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea
E-mail: dkkim@kaist.ac.kr

Experimental Section

Preparation of the $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT composites

Initially, we prepared the $[V(PO_3)_3]_n$/MWCNT composite using a solid state reaction with stoichiometric amounts of V_2O_5, $NH_4H_2PO_4$, and multi-walled carbon nanotubes (MWCNTs: GM65 (diameter of 10- 15 nm), Iljin Nanotech Co. Ltd., S. Korea) which act as a reducing agent. This mixture was annealed twice under N_2 atmosphere at 300 and 850 °C. Second, $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT composite samples were prepared under mild hydrothermal conditions by reacting NaF and $[V(PO_3)_3]_n$/MWCNT in a 3.3:1 molar ratio. The reaction mixture was sealed in a polytetrafluoroethylene (PTFE)-lined steel pressure vessel, which was maintained at 170 °C for 72 h. This MWCNT prevents the complete oxidation from V^{3+} to V^{4+} in an aqueous medium. All of the chemicals were used without any further purification. The formation of the $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT composite can be explained according to the following reactions:

$$0.5\,V_2O_5 + 3\,NH_4H_2PO_4 + MWCNT \rightarrow [(VPO_3)_3]_n/MWCNT + 3\,NH_3 + CO + 4.5\,H_2O \quad (1)$$

$$4[(VPO_3)_3]_n/MWCNT + 6\,NaF + 22x\,O_2 + 44x\,H_2O \rightarrow 2Na_3V_2O_{2x}(PO_4)_2F_{3-2x} + 4xHF + 8H_3PO_4 \quad (2)$$

Preparation of the $NaTi_2(PO_4)_3$-C composites

First, titanium butoxide ($Ti[O(CH_2)_3CH_3]_4$) was hydrolyzed by ethanol and an NH_4OH solution, the obtained white precipitate (TiO_2) was centrifuged and washed with deionized (DI)

water several times. Then, a stoichiometric amount of sodium acetate (CH_3COONa) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) was added to a solution containing the TiO_2 precipitate. The mixture was allowed to dry at 60 ~ 70 °C, collected and ground in an agate mortar. Then, the powder was placed in an alumina boat and heated at 650 °C for 5 h in air. In the second step for carbon coating, the as-synthesized $NaTi_2(PO_4)_3$ was mixed and sonicated with 20 wt.% sucrose in DI water and dried at 60 ~ 70 °C. The final $NaTi_2(PO_4)_3$-C composite was obtained by heat treatment of the mixture at 800 °C for 12 h under an argon gas flow in a tube furnace.

Characterization

The final phase of the $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT composite was confirmed by synchrotron radiation powder X-ray diffraction (SPXRD) data collected at room temperature from the 9B HRPD beamline of the Pohang Accelerator Laboratory (PAL) in Korea at a wavelength of λ = 1.4640 Å. The diffraction patterns were acquired over an angular range of 10 ° ≤ 2θ ≤ 130 ° at a step width of 0.01 ° using a six multi-detector system. Full pattern matching of the SPXRD patterns was conducted using the GSAS[S1] program with the EXPGUI.[S2] The XRD patterns of the $NaTi_2(PO_4)_3$-C composite were obtained using an X-ray diffractometer (Rigaku D/Max-2500) with a Cu X-ray (λ = 1.5418 Å) at room temperature. The particle size and morphology were characterized using a field emission scanning electron microscope (FE-SEM Hitachi S-4800, Japan). The Raman spectra of the powders were recorded at RT on a HR 800 Raman spectrophotometer (Jobin Yvon- Horiba, France) using monochromatic a He-Ne laser (633 nm) operating at 20 mW. Elemental analysis (EA) was carried out using a Thermo Scientific Flash 2000 Series element analyzer. ^{23}Na NMR spectra were recorded on Bruker Advance 400 MHz spectrometer at room temperature.

Electrochemical testing

The electrochemical studies of the as-synthesized $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT composite were conducted in CR2032 coin cells. The composite electrode was prepared by mixing 80 wt. %

of the active materials with 10 wt. % Super P carbon black and 10 wt. % polyvinylidene fluoride (PVDF) binders in a N-methylpyrrolidone (NMP) solvent. For the nonaqueous electrolytes tests, the obtained slurry was coated on Al foil and cut into circular electrodes with diameter of 12 mm. Sodium metal was used as an anode, and 1 M $NaClO_4$ in propylene carbonate (PC) with 2 vol.% of fluoroethylene carbonate was used as the electrolytes. The coin cells were assembled in an argon-filled dry glove box using a borosilicate glass-fiber separator (Whatman GF/D). For the half-cell tests in an aqueous solution, the slurry was coated on stainless steel (SUS) foil or carbon paper (Toray, TGP-H-090) that was 1 cm x 1 cm in size. The counter electrode was a large piece of carbon paper, and the reference electrode was a saturated calomel electrode (SCE) in a beaker cell. The Zn foil (thickness 0.25 mm, 99.9 %, Aldrich) or the $NaTi_2(PO_4)_3$-C composite on the carbon paper was used as the anode for testing Na-ion aqueous full-cells. The cathode loading and area for the $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT composite were ~1 mg and 1 cm^{-2}, respectively, and the anode loading and area for the $NaTi_2(PO_4)_3$-C composite were ~0.9 mg and 1.54 cm^{-2}, respectively. The electrolyte for all of the aqueous cells was a 10 M $NaClO_4$ aqueous solution with 2 vol.% of vinylene carbonate (Aldrich). The cyclic voltammetry and galvanostatic cycling of the Na-ion aqueous full-cells were measured using a potentiostat VMP3 (Biologic, France). The Na coin half-cells were galvanostatically cycled between 2.5 V and 4.5 V using an automatic battery cycler WBCS3000 (Wonatech, Korea). The Zn//$Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT aqueous full-cell was tested from 1.0 V to 2.0 V at a rate of 1 C, and the $NaTi_2(PO_4)_3$-C//$Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT aqueous full-cell was cycled from 1.0 V to 1.8 V at a rate of 10 C based on the cathode weight. The C-rate in all of the aqueous cell tests was calculated using 1 C to be 65 mA g^{-1}.

References

[S1] A. C. Larson and R. B. Von Dreele, General Structure Analysis System (GSAS); Report LAUR 86-748, Los Alamos National Laboratory, New Mexico, USA, **2000**.

[S2] B. H. Toby, *J. Appl. Cryst.*, **2001**, 34, 210.

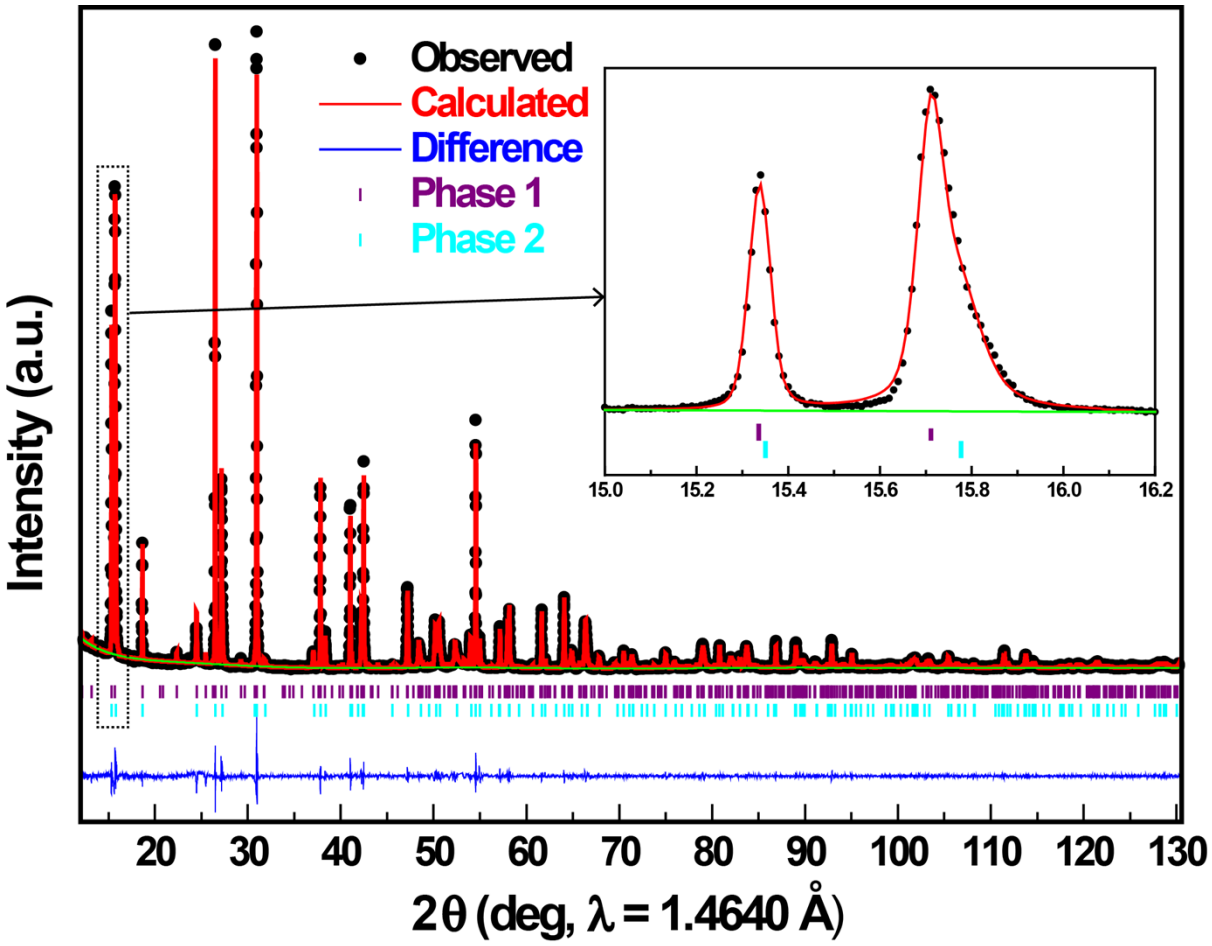

Figure S1. The magnified synchrotron XRD pattern of the $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT composite.

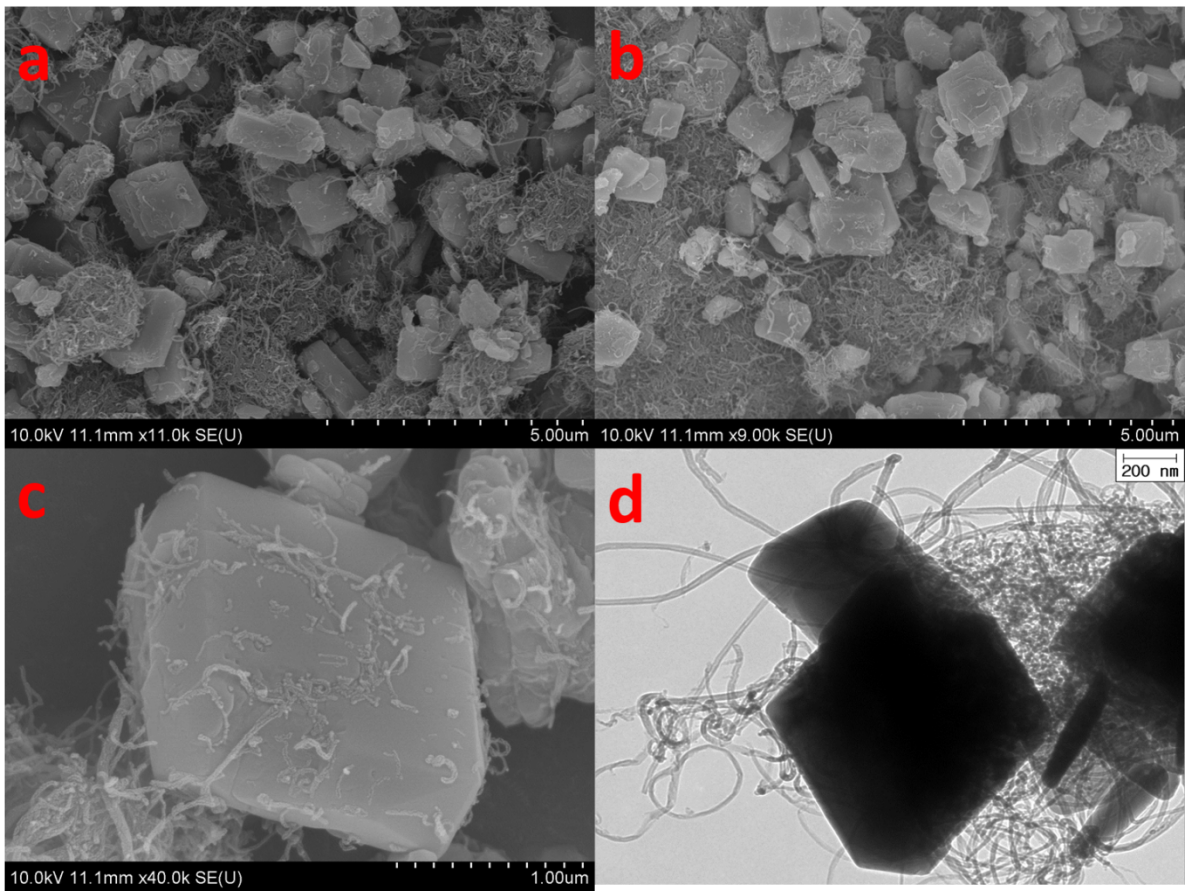

Figure S2. (a-c) SEM images at different magnifications and (d) a TEM image of the $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT composite.

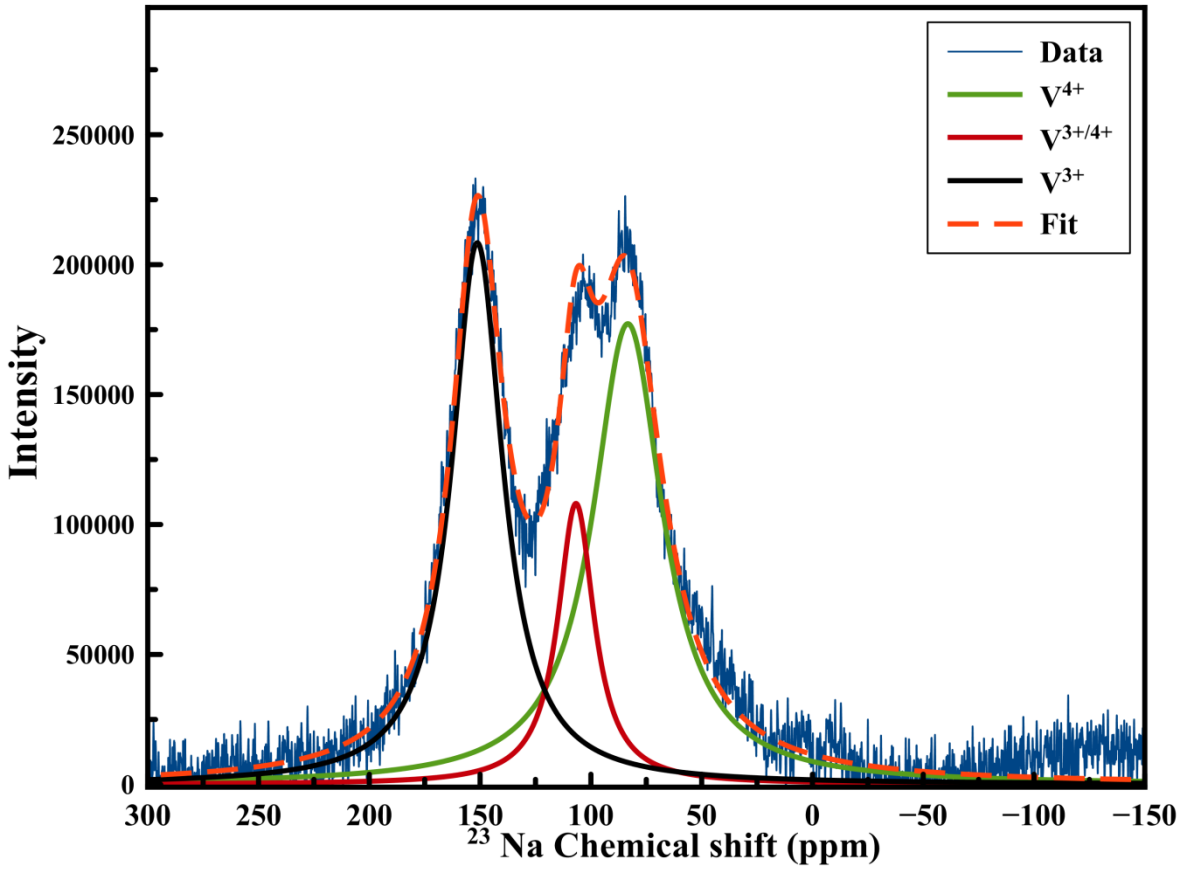

Figure S3. ^{23}Na solid-state NMR spectrum and fitting result for the $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT composite.

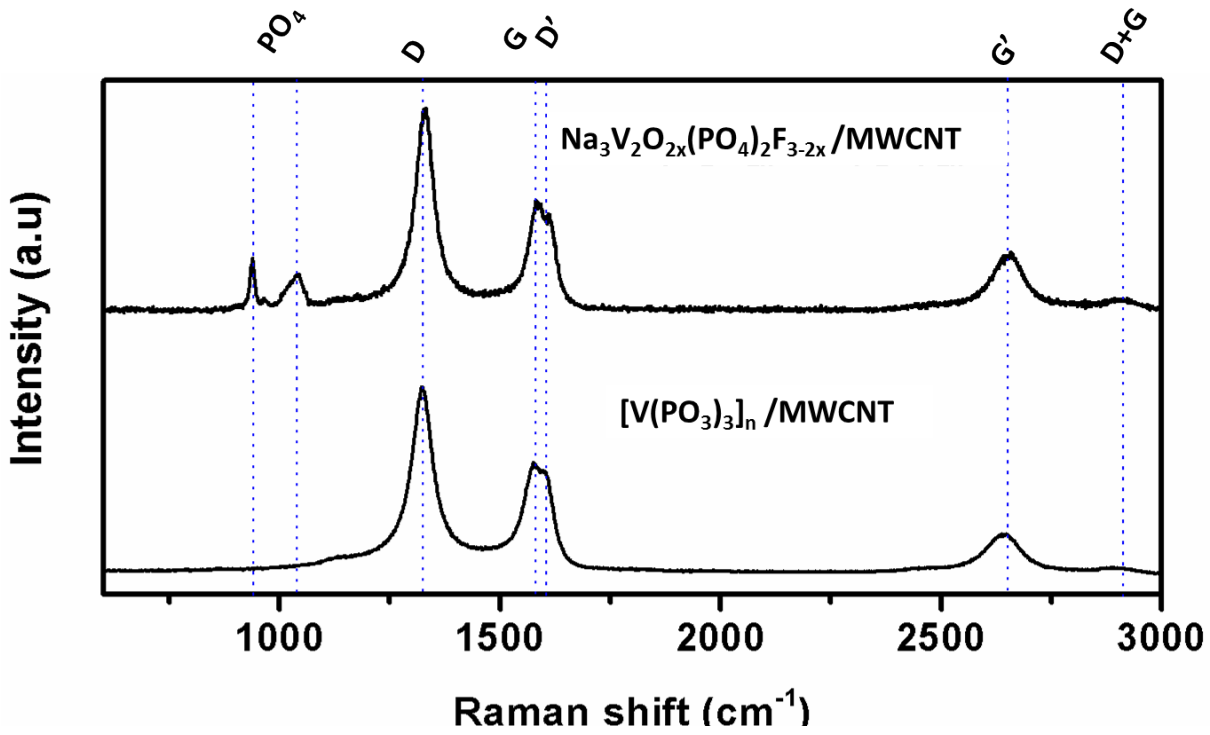

Figure S4. Raman spectra of the $[V(PO_3)_3]_n$/MWCNT and the $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ /MWCNT composite.

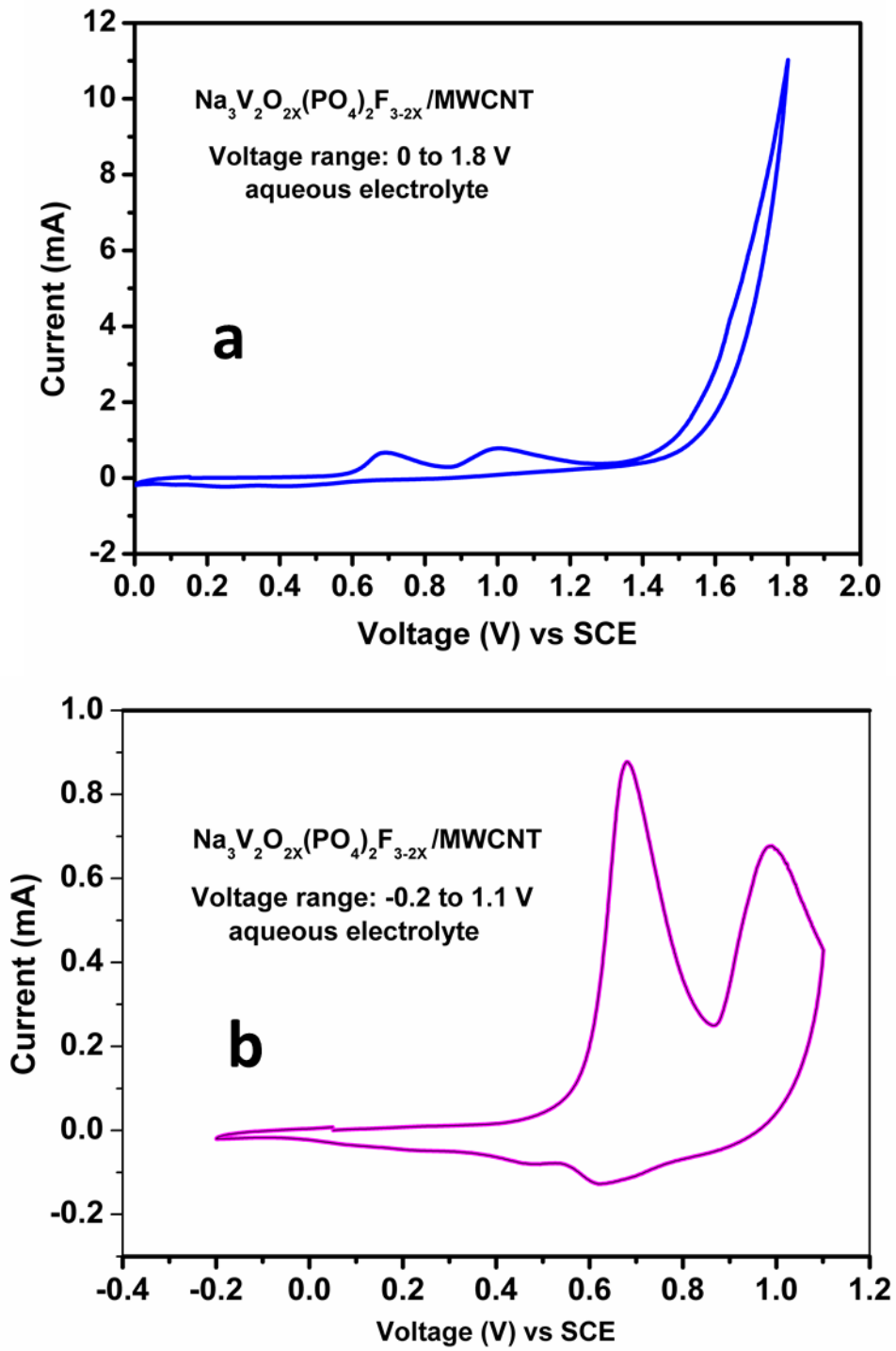

Figure S5. CV plots of the $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT composite in aqueous electrolytes with voltage ranges of (a) 0.0 ~ 1.8 V vs. SCE and (b) -0.2 ~ 1.1 V vs. SCE.

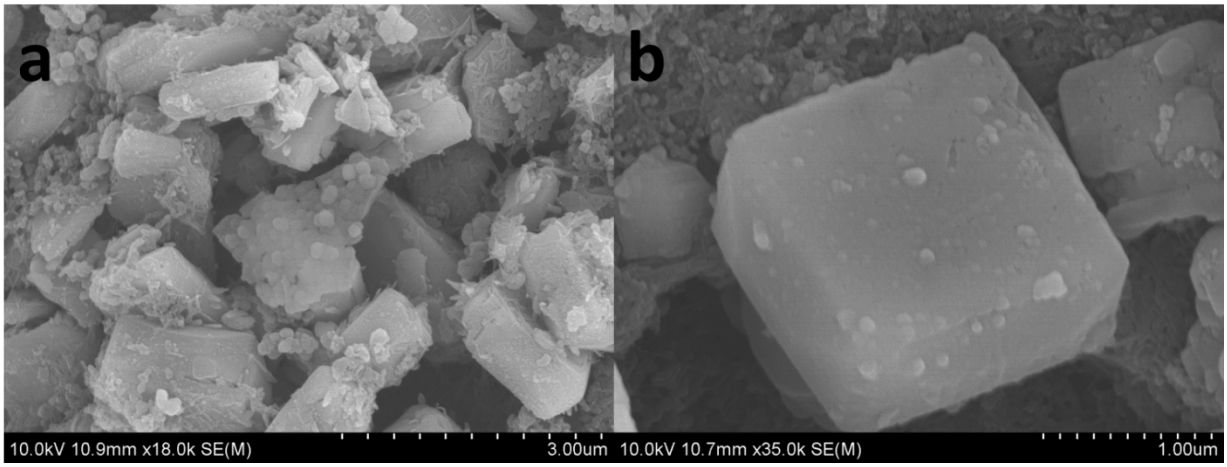

Figure S6. (a) and (b) SEM images of the $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT composite electrode after 1100 cycles in aqueous electrolytes.

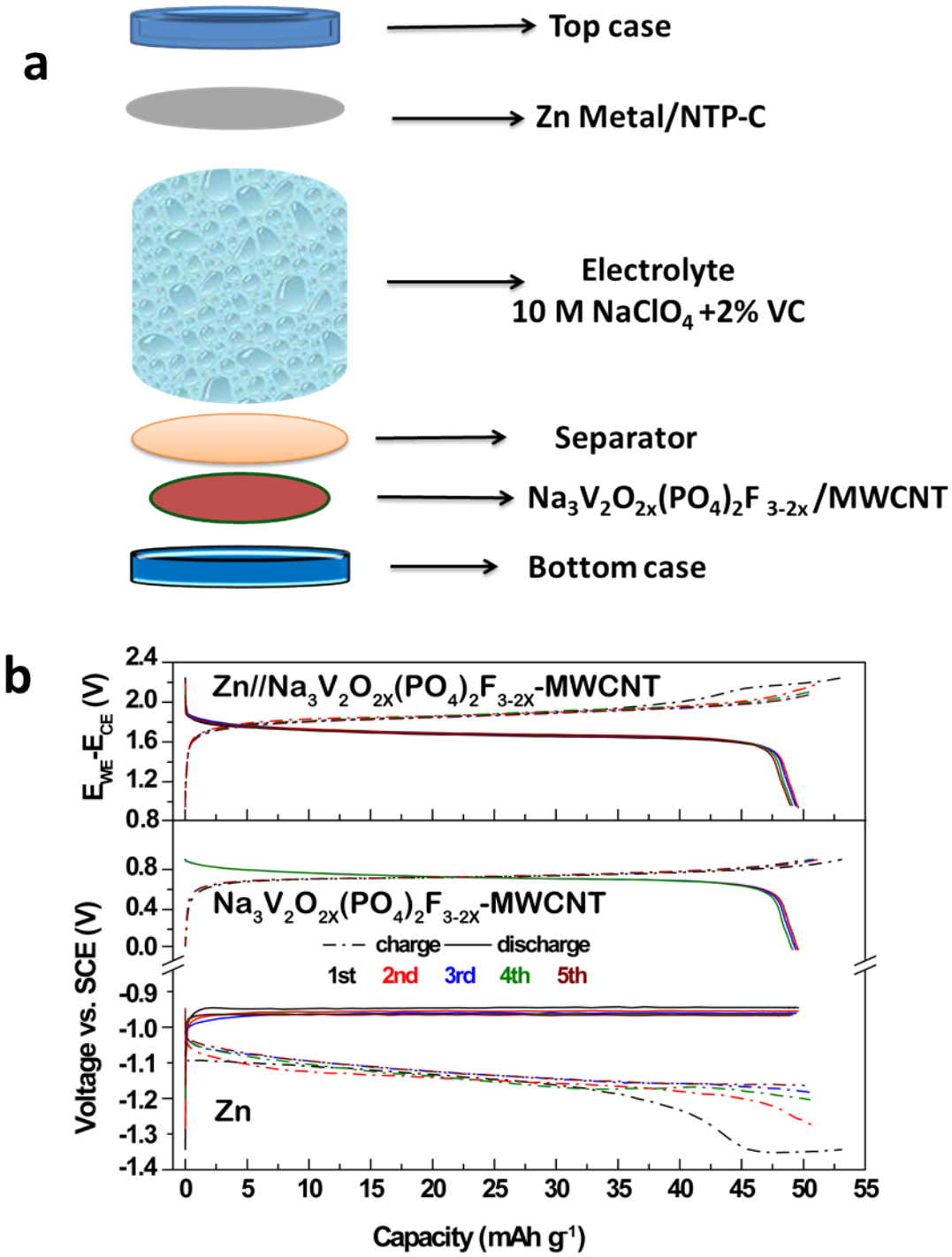

Figure S7. (a) Schematic representation of the Na-ion coin full-cell. (b) Galvanostatic voltage profiles of the Zn// $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT full-cells as well as a separate profile of the cathode ($Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$/MWCNT) and the anode (Zn metal).

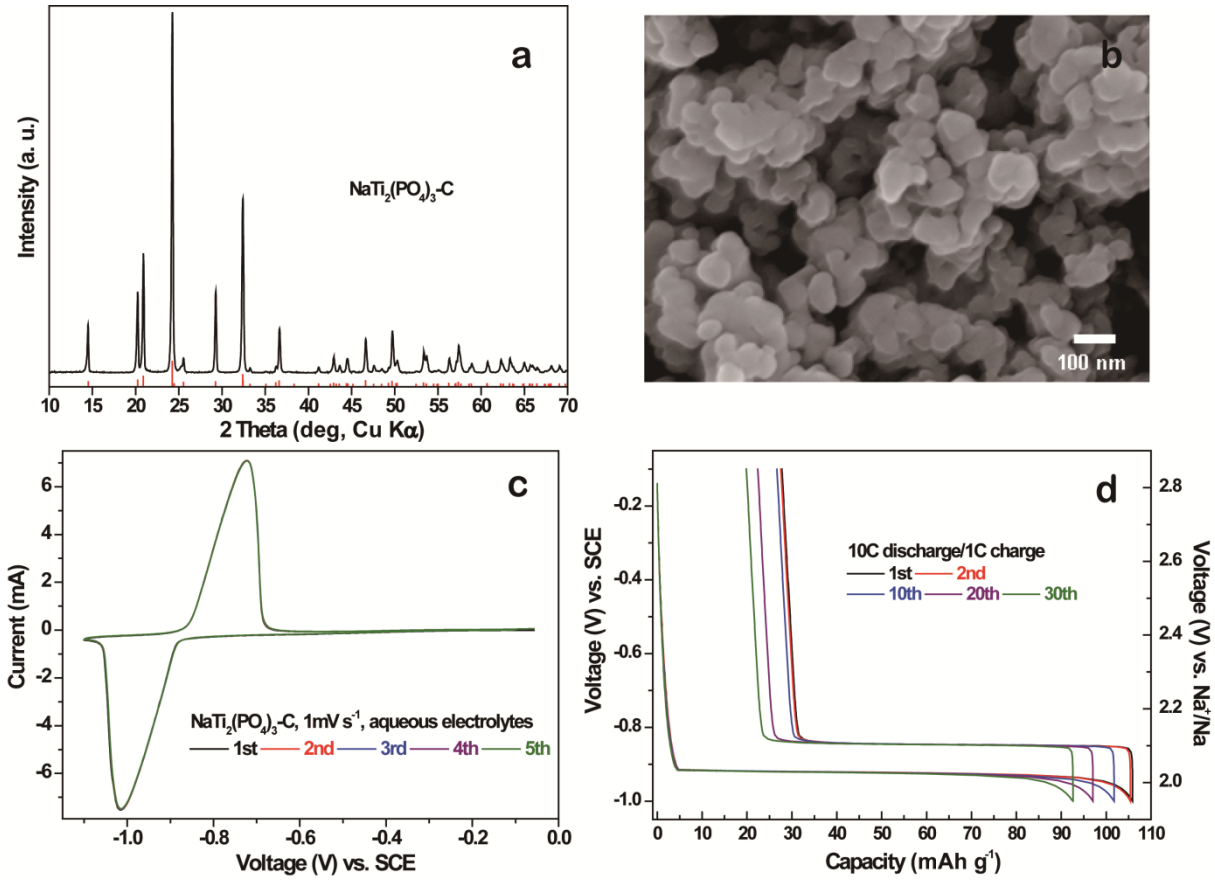

Figure S8. (a) XRD pattern and (b) SEM image of the $NaTi_2(PO_4)_3$-C composite. (c) CV curves and (d) galvanostatic cycling profiles of the $NaTi_2(PO_4)_3$-C composite in aqueous electrolytes.