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Supporting information

Building Highly Stable and Industrialized $NaVPO_4F/C$ as Bipolar Electrodes for High-rate Symmetric Rechargeable Sodium-ion Full Batteries

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Experimental Section

Material Synthesis

$NaVPO_4F/C$ composites were prepared with a two-step solid state carbon thermal reduction method. All the chemicals were of reagent grade including V_2O_5, $NH_4H_2PO_4$, NaF and $C_6H_{12}O_6$ (99.9% purity). Firstly, the VPO_4 intermediate precursor was synthesized by V_2O_5, $NH_4H_2PO_4$ and $C_6H_{12}O_6$ with a molar ratio of 3:6:1($3V_2O_5 + 6NH_4H_2PO_4 + C_6H_{12}O_6 = 6VPO_4 + 6NH_3 + 15H_2O + 6CO$, 20% mass excess of glucose was introduced over the stoichiometric ratio to ensure the complete vanadium reduction from V^{5+} to V^{3+}). The mixture were thoroughly ground and mixed by automatic grinder, and uniform powder was compressed at 10 MPa by hydraulic press. The mixture was calcinated in an Ar-atmosphere tube furnace at 800 ^{o}C for 6 h. Secondly, $NaVPO_4F/C$ composites was prepared by VPO_4, NaF and $C_6H_{12}O_6$ ($NaF + VPO_4 = NaVPO_4F$, VPO_4 and NaF with a molar ratio of 1:1). The $C_6H_{12}O_6$ amount control the carbon contents in the final products. Then, the mixtures of VPO_4, NaF and $C_6H_{12}O_6$ were calcinated under argon at 700 ^{o}C for 5 h, and achieve the black final products as electrode material for sodium-ion batteries.

Material Characterization

The structure and morphology of samples were measured by powder X-ray diffraction (XRD, Rigaku MiniFlex600, Cu Kα radiation, λ=1.54056 Å), field-emission scanning electron microscopy (SEM, JEOL JSM-7500F, 5 kV), and transmission electron microscopy (TEM, Philips Tecnai FEI, 200 kV). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, PerkinElmer Optima 8300) and Energy Dispersive X-ray Detector (EDX, JEOL JSM-7500F) were used to analyze composition of the materials. Specific surface areas of the resultant products were investigated by nitrogen adsorption–desorption measurements using a NOVA 2200e analyzer. The thermal behavior of the samples was investigated by TG-DTA (SETARAM S60). The electronic states of electrodes were investigated by XPS (PHI 5000 Versa Probe).

Electrochemical Measurement

The electrochemical performance was measured using a two electrode coin-type cell (CR2032) and assembled in an argon-filled glove box. For preparing the working electrodes, a mixture of the samples, Super P, and polyvinylidene fluoride (PVdF) binder at a weight ratio of 7:2:1 were dispersed in N-methyl-2-pyrrolidinone (NMP) solvent and ground thoroughly to form a slurry. Then, the slurry was pasted on pure Cu and Al current collectors and dried at 80 ^{o}C for 12 h as anode and cathode, respectively. The loading density is about 1.5 mg/cm^2 in this study. For the half-cell, sodium metal (99.99%) were used as the counter electrodes. The glass fibers were used as separators. The electrolyte was 1 mol L^{-1} $NaPF_6$ in ethylene carbon (EC)-dimethyl carbonate (DMC) (1:2 w/w) solution with 0.7 mmol fluoroethylene carbonate (FEC). For the symmetric full cell, the $NaVPO_4F$/C composites on Cu and Al current collectors as anode and cathode, respectively. Galvanostatic tests were run under different current densities between cut off voltages of 0.01-2.50 V and 2.50-4.00 V (*vs.* Na^+/Na) on a CT2001A cell test instrument (LAND Electronic Co.) at room temperature. Cyclic voltammetry (CV) of cells and electrolytes and electrochemical impedance spectroscopy (EIS) were measured on a Bio-Logic VSP-300 electrochemical work station.

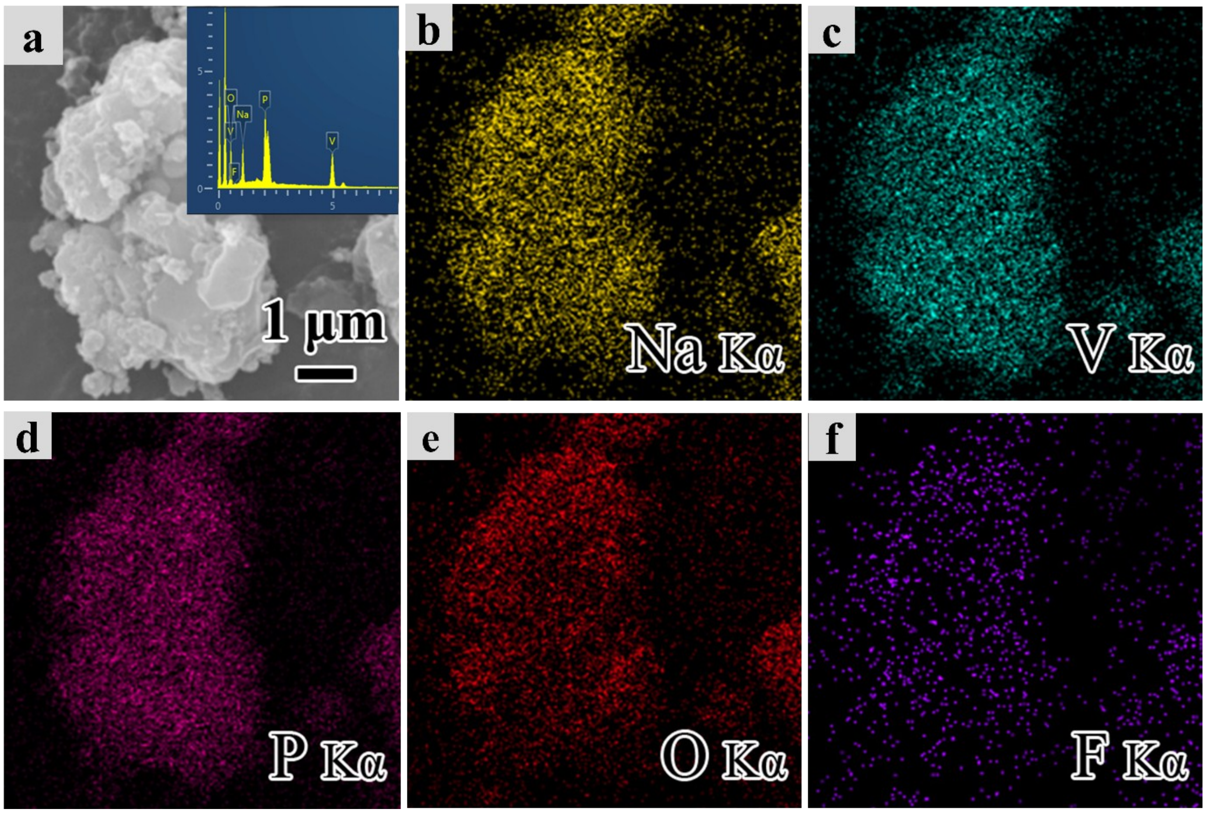

Fig. S1 SEM image and the corresponding EDX-mapping images of $NaVPO_4F/C$.

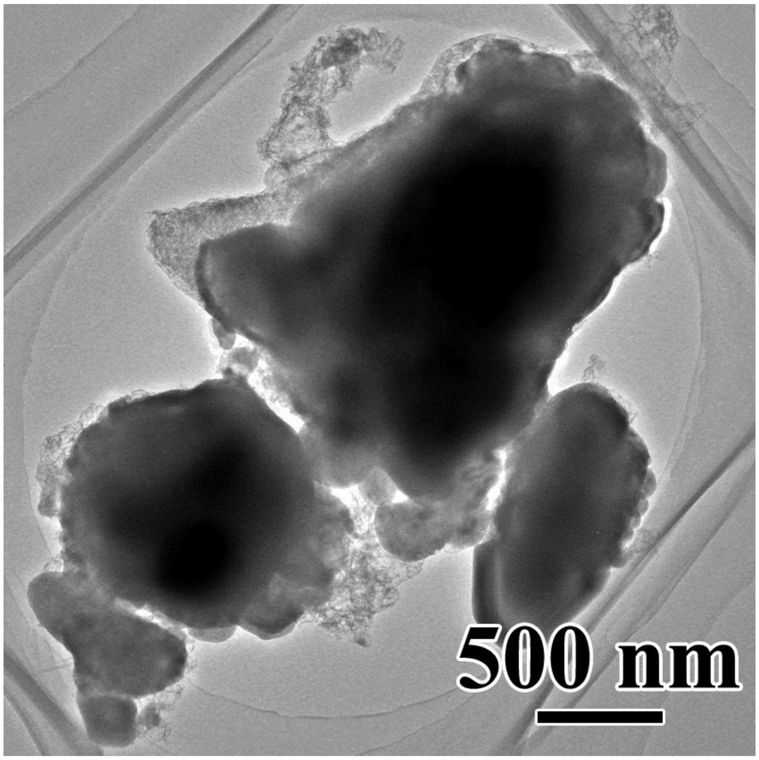

Fig. S2 TEM image of $NaVPO_4F/C$.

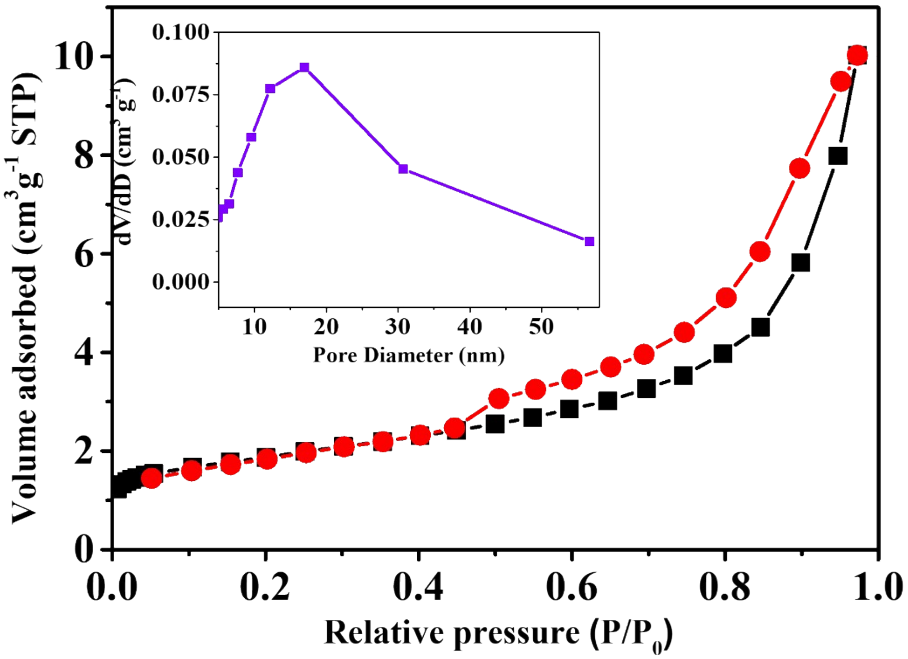

Fig. S3 Nitrogen adsorption and desorption isotherm of NaVPO$_4$F/C (black: nitrogen adsorption curve; red: nitrogen desorption curve).

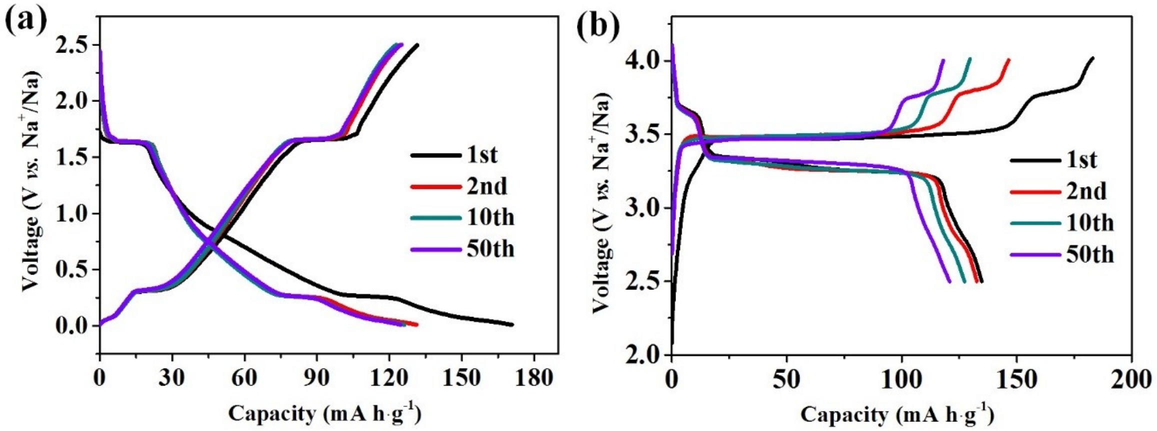

Fig. S4 Discharge/charge curves of $NaVPO_4F/C$ electrodes at 50 mA g^{-1} during the voltage of (a) 0.01-2.50 V and (b) 2.50-4.00 V.

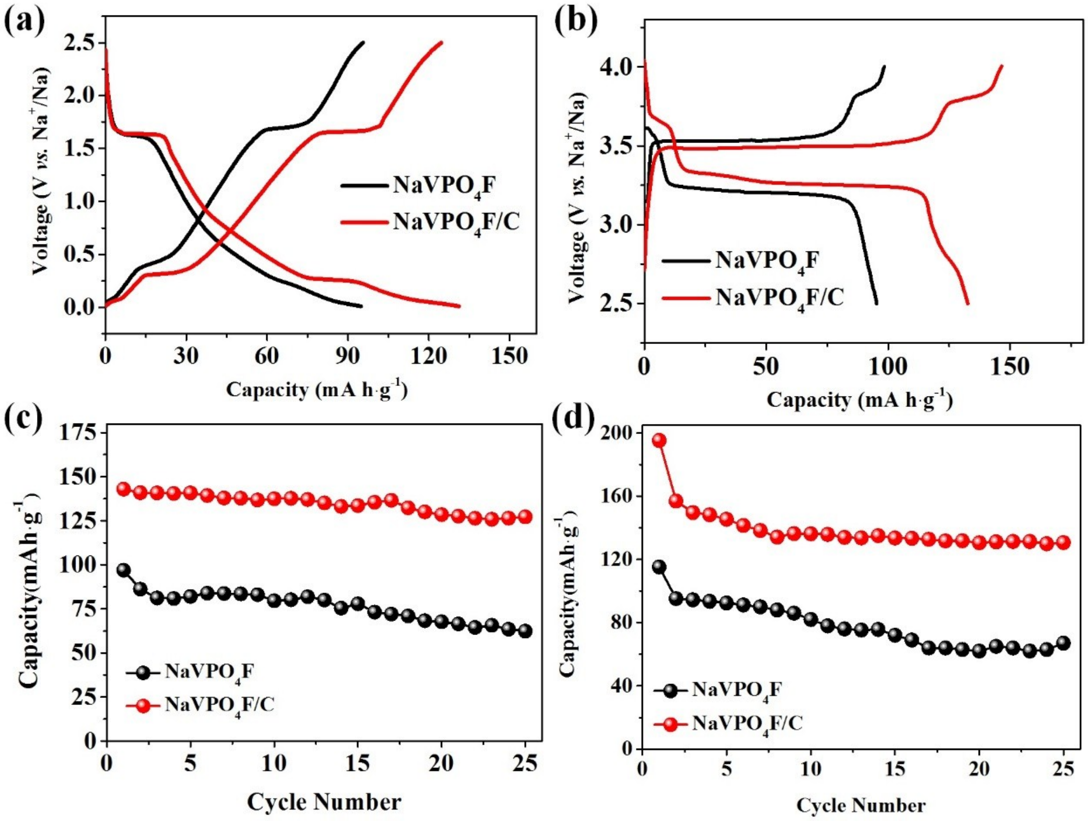

Fig. S5 Comparison of $NaVPO_4F$ and $NaVPO_4F/C$ electrode in their electrochemical performances (current density of 50 mA g^{-1}), discharge/charge curves as (a) anode and (b) cathode, and cycle performance as (c) anode and (d) cathode.

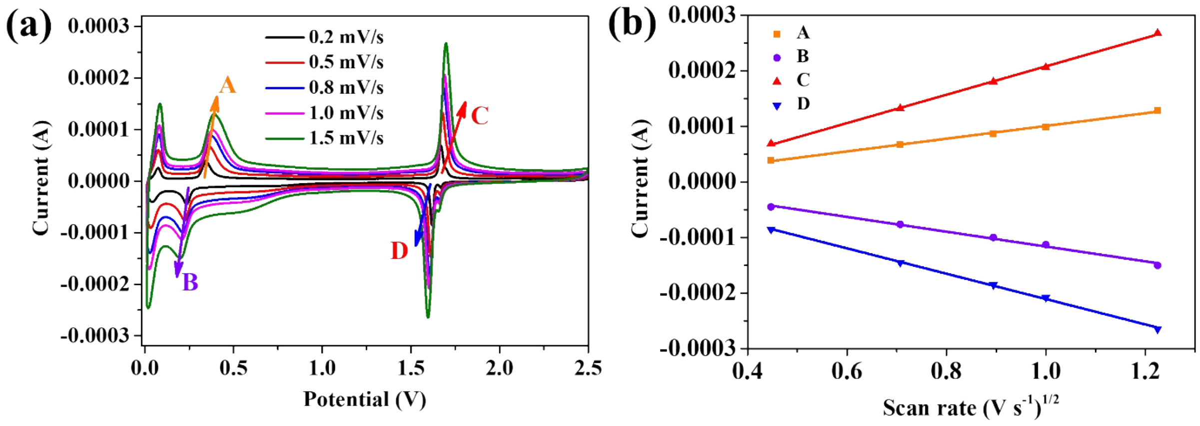

Fig. S6 (a) CV curves of $NaVPO_4F/C$ electrodes at different scan rates at voltage of 0.01-2.50 V. (b) The relationships between the peak current and scan rate.

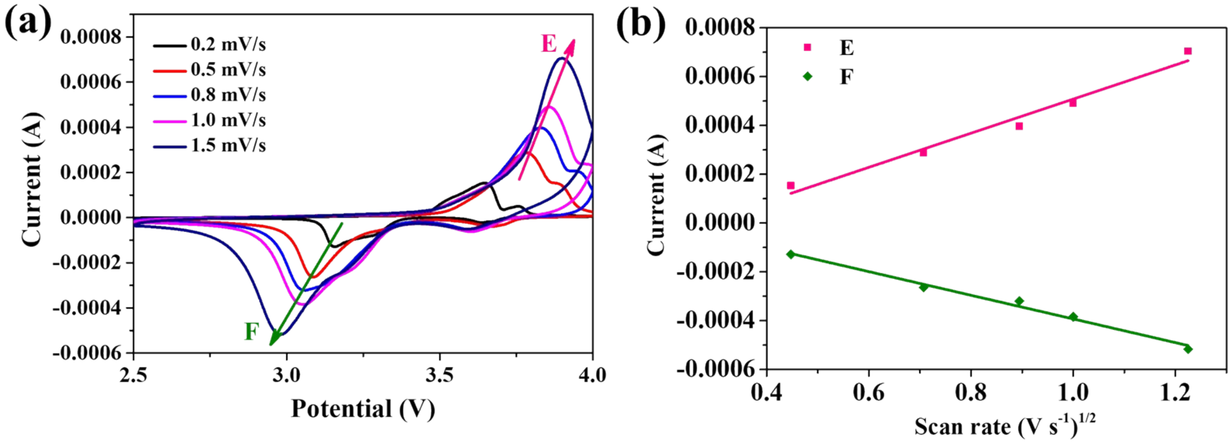

Fig. S7 (a) CV curves of $NaVPO_4F/C$ electrodes at different scan rates at voltage of 2.50-4.00 V. (b) The relationships between the peak current and scan rate.

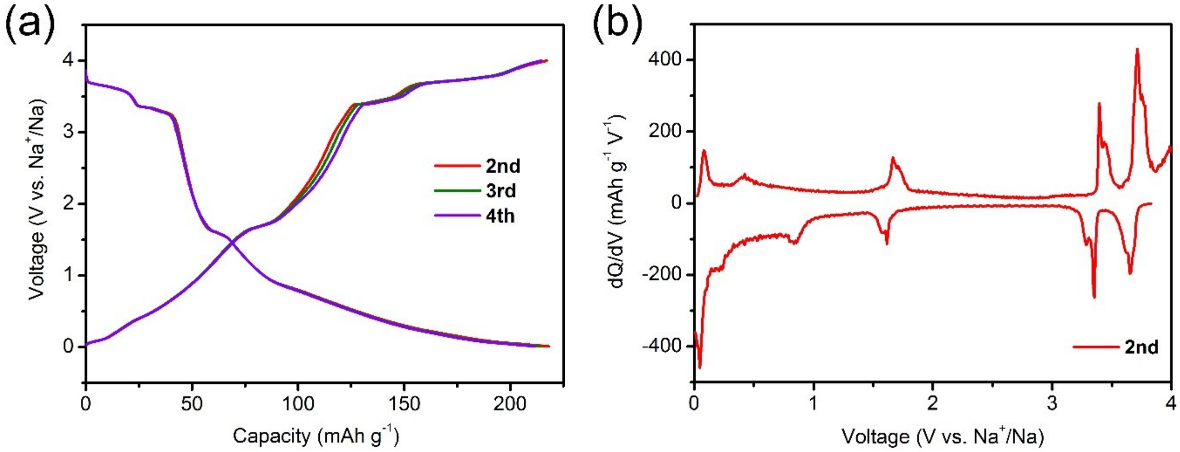

Fig. S8 (a) Discharge/charge curves of $NaVPO_4F/C$ electrodes at 50 mA g^{-1} at voltage of 0.01-4.00 V. (b) The corresponding differential capacity (dQ/dV) curve of the selected cycle.

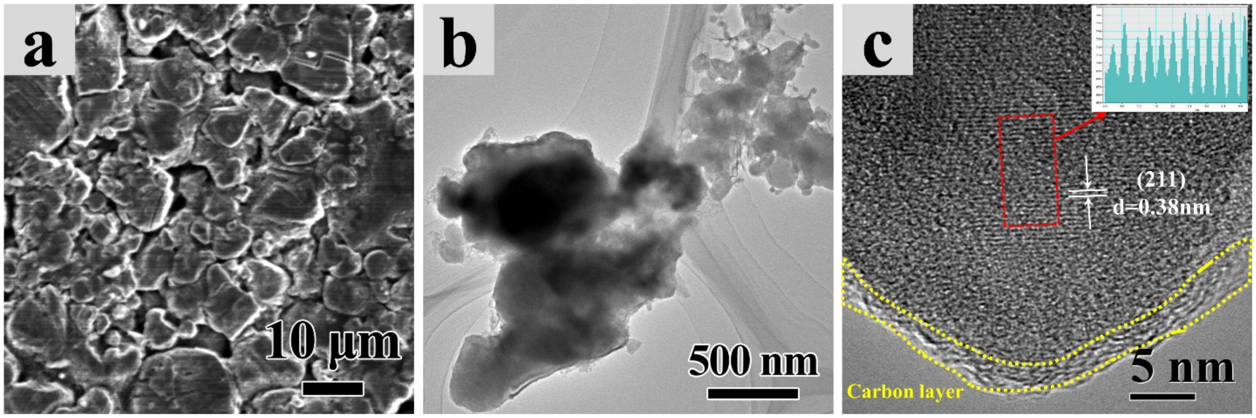

Fig. S9 (a) SEM, (b) TEM and (c) HRTEM images of $NaVPO_4F/C$ electrodes after 400 cycles at a current density of 50 mA g^{-1}.

Table S1. the ICP-AES results of $NaVPO_4F$ electrodes in symmetric SIFBs at full charged state as cthode and anode.

Element	Na	V	P
Cthode (ppm)	0.71	4.25	2.67
Anode (ppm)	4.85	6.63	4.19

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to determine composition of products. The $NaVPO_4F$ electrodes in symmetric SIFBs were measured at full charged state as cthode and anode, respectively. The cells were disassembled in the glovebox at pure Ar atmosphere. Electrodes were washed using DEC for 3 times to remove residual electrolyte. The active products were dissolved into solution, and the product solution was filtered to disgorge the carbon and impure precipitate. According to the ICP results, the mass ratio of Na, V, P elements in the cthode is 0.71: 4.25: 2.67, equal to the atomic ratio of 0.36: 1: 1. Thus, the product of cathode at full charged state should be $Na_{0.36}VPO_4F$. The mass ratio of Na, V, P elements in the anode is 4.85:6.63:4.16, equal to the atomic ratio of 1.61: 1: 1.02. Thus, the product of anode at full charged state should be $Na_{1.61}VPO_4F$.