Supporting Information

Superior Na-Storage Performance of Molten-State-Blending Synthesized Monoclinic $NaVPO_4F$ Nanoplates for Na-Ion Batteries

Moxiang Ling[a,b] Fan Li[a,b],Hongming Yi[a,b], , Xianfeng Li[a,c], Guangjin Hou[a], Qiong Zheng[a*], Huamin Zhang[a,c*]

a. Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China,

b. University of Chinese Academy of Sciences, Beijing 100039, China.

c. Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Dalian 116023, China.

**E-mail:* zhanghm@dicp.ac.cn, zhengqiong@dicp.ac.cn.

Experimental Section

Synthesis of $NaVPO_4F$@C: The $NaVPO_4F$@C samples were prepared by a two-step molten method. NaF and VPO_4 with a stoichiometric ratio of 1:1 were first put into a high temperature muffle furnace at 1000 ºC for 1 hour to react and obtain green intermediate precursor. Then the sucrose powder as the carbon source and reductant was added into the intermediate precursor during ball milling process. Then the mixture was ball-milled by planetary ball milling (ND-7, Nanjing, China) for 24 h at 480 rpm to obtain the precursor. The precursor was dried under vacuum conditions at 130 ºC for 12 h. Finally, the dried precursor was ground and sintered for 5 h at 350 ºC (to expel H_2O) and then calcined for 8 h at 750 ºC in Ar atmosphere to yield the final product

$NaVPO_4F@C$ composite. $NaVPO_4F@3.13$ wt% C, $NaVPO_4F@9.66$ wt% C, $NaVPO_4F@14.6$ wt% C can be obtained by incorporating different contents of sucrose powder during the ball milling procedure.

Material characterization: X-ray powder diffraction patterns (XRD) were obtained with a 2θ range of 10° to 60° using an X-ray powder diffractometer (D8 ADVANCE ECO; RIGAKU, Japan) with monochromatic Cu-Kα radiation at 40 kV and 40 mA and scan rate of 10° min^{-1}. In situ XRD measurement were carried out with a PAN analytical Empyrean diffractometer using Cu Kα radiation at a 2θ range of 10-60° at first, and then the characteristic peaks in the range of 28.5° to 30°, 31.5° to 33.5° and 35° to 37° were selected to explore the Na storage mechanism of the NVPF during the charge/discharge.

The Fourier transform infrared (FT-IR) absorption spectra measured by a JASCO FTIR 4100 spectrometer was used to determine the bonding nature of the samples. Each spectrum was recorded at the average rate of 48 scans with a resolution of 4 cm^{-1} collected from 500 to 1500 cm^{-1} in reflection mode. In situ diffuse reflectance IR spectroscopic (DRIFTS) was measured by Nicolet iS50 Fourier transforms infrared spectrometer. The DRIFTS was performed in the temperature from 25 °C to 300 °C at a heating rate of 5 °C min^{-1}. The morphology of the as-prepared $NaVPO_4F@C$ samples was characterized by a field-emission scanning electron microscope (FESEM, JSM-7000F; JEOL, Japan) and a high resolution transmission electron microscope (TEM, JEM-2100).

The carbon contents of the $NaVPO_4F@C$ samples were detected by a carbon sulfur analyzer (CS230C). Micro-Raman spectra were obtained from an LabRAM HR800 Raman microspectrometer (France) at a laser power of 0.8 mW in the range of 1250-1800 cm^{-1}.

The specific surface area and pore size distribution were measured using a Nova 2200e Brunauer-Emmett-Teller (BET) surface area analyser (Quantachrome, USA). The specific surface area was calculated by the BET method from the N_2 isotherm adsorption/desorption curve. The pore size distribution was obtained by BJH method from the isotherm adsorption/desorption curve as well.

Ex-situ ^{23}Na MAS NMR spectra was collected to investigate the sodiation/desodiation mechanism of the NVPF during the charge/discharge on a Bruker AVANCE III 600 MHz spectrometer equipped with a 3.2 mm HXY probe at the temperature of 298 K. The spinning rate was 22 kHz. ^{23}Na NMR spectra was acquired at a Larmor frequency of 158.7 MHz with a single pulse program. The 90° pulse length for ^{23}Na was 1.78 μs. The recycle delay was of 100 ms for all the experiments. All chemical shifts of ^{23}Na were referenced to 1.0 M NaCl aqueous solution.

Electrochemical measurements: The $NaVPO_4F@C$ cathodes were prepared by mixing 70 wt% active materials, 20 wt% Super P and 10 wt% PVDF (poly-vinylidene fluoride), with aluminum used as the current collector and the glass micro-fiber as the separator. A metallic sodium foil served as the anode electrode. The electrolyte comprised a 1.0 M $NaClO_4$ solution in ethylene carbonate/diethyl carbonate (1:1 by volume) and Fluoroethylene Carbonate (2 wt%).

Electrochemical characterization was carried out using CR2016 coin cells. The capacity of the cell was calculated with the mass of the pure $NaVPO_4F$ cathode. All of the cells were assembled in a glove box filled with argon gas and then submerged at room temperature for 12 h before measurements. Galvanostatic charge/discharge measurements were carried out in the voltage range of 2.0-4.5 V (vs Na^+/Na) by using the LAND 2100 cycler (Wuhan, China). Six state points including 1C (charge to 30 mA h g^{-1}), 2C (charge to 60 mA h g^{-1}), 3C (charge to 4.3 V), 4D (discharge 30 mA h g^{-1}) , 5D (discharge 60 mA h g^{-1}) and 6D (discharge to 2.0 V). during the charging and discharging process were selected to explore the sodiation/desodiation mechanism during the electrochemical cycling.

Cyclic voltammetry (CV) tests were performed from 2.5-4.3V vs. Na^+/Na at a scan rate of 0.5 mV s^{-1} by using a CHI electrochemical working station. Electrochemical impedance spectroscopy (EIS) spectra of the batteries were measured in a frequency range of 100 kHz to 0.1 Hz using a Solarton 1287 test system with perturbation amplitude of 10 mV under open circuit potential conditions.

Carbon source	**Active materials**	**Carbon content/%**	**BET surface area/m^2 g^{-1}**
Citric acid/ PEO	$Na_3V_2(PO_4)_3$	18	140
AC	$Na_3V_2(PO_4)_3$	8.46	25
CNT		8.37	12
graphite		8.54	4
graphene	$Na_3V_2(PO_4)_3$	10.1	95.9
PVP/ Citric acid	$NaVPO_4F$	4.93	35.24
Oxalic acid dihydrate	$NaVPO_4F$	5.0	11.7&13.7
sucrose	$NaVPO_4F$	3.13	64.85
		9.66	109.7
		14.6	139.4

Table S1. Comparison of specific surface area for some representative NASICON cathodes

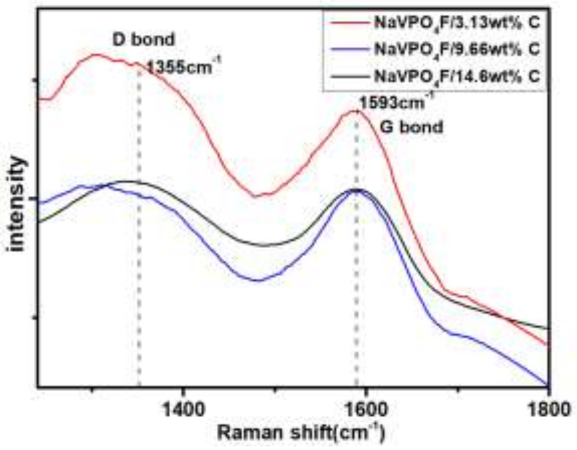

Fig. S1. Raman of $NaVPO_4F$@C samples

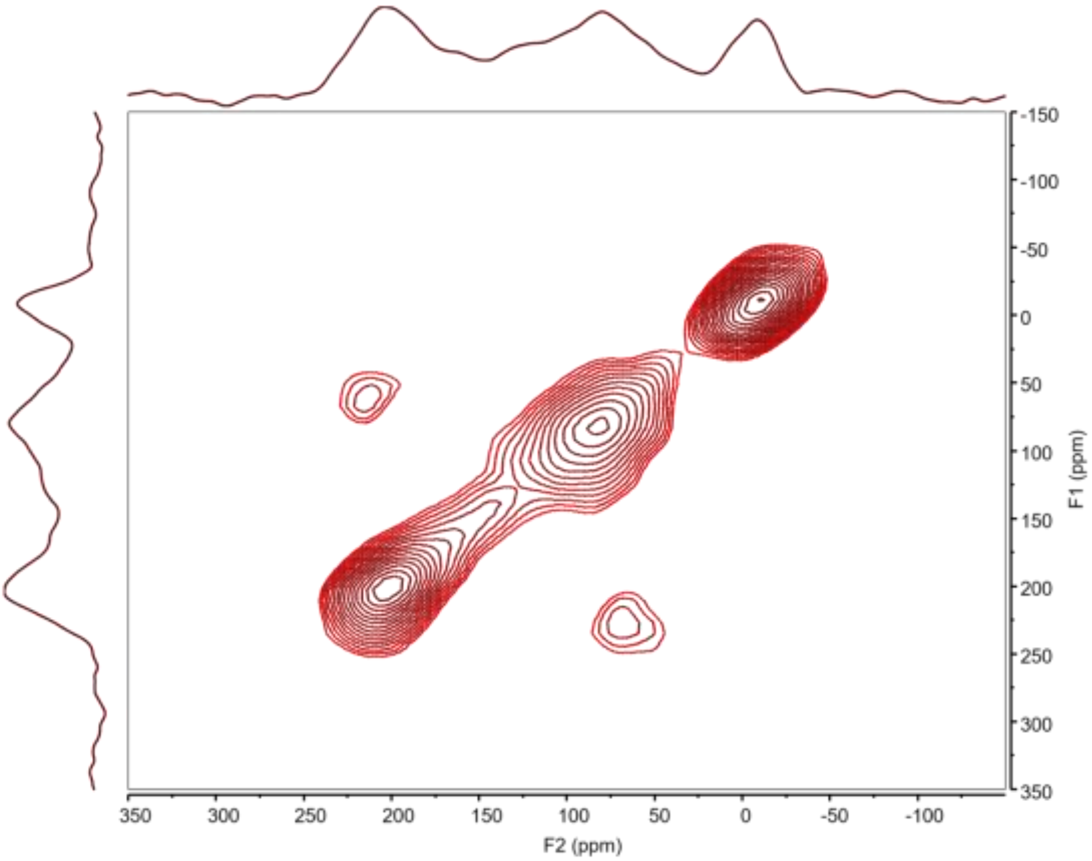

Fig. S2. 2D ^{23}Na EXSY spectrum of NaVPO$_4$F@C 3C with a mixing time of 0.1 ms

Electrochemical state	**Weight of NaVPO$_4$F@C(mg)**	**normalized coefficient**
As synthesized	4.60	1.00
1C	4.76	0.97
2C	4.53	1.02
3C	4.36	1.06
4D	4.47	1.03
5D	4.28	1.07
6D	3.90	1.18

Table S2. Weight normalization of NaVPO4F@C samples used in EX-situ NMR test.

Electrochemical state	**peak area (80ppm)**	**normalized area**	**Deintercalated Na$^+$ ratio**
As synthesized	3573860	776926	0.000
1C	3004284	631152	0.188
2C	1508371	332974	0.571

3C	444345.4	101914	0.869
4D	1378250	308333	0.603
5D	1911692	446657	0.425
6D	1761490	451664	0.418

Table S3. The area of the peak located at 80 ppm and the ratio of the deintercalated sodium ion.