Supplementary Materials

Fast-Charging 2D Phosphate Cathode via Green Exfoliation: Low Steric Hindrance and Efficient Na⁺ Transport

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Experiment Details

Synthesis of VOPO₄ precursor

The VOPO₄ sample was prepared by liquid phase method with the mixture of V_2O_5 , $H_2C_2O_4$ ·2H₂O, NH₄H₂PO₄, in stoichiometric ratio. In a typical synthesis process, V_2O_5 , $H_2C_2O_4$ ·2H₂O, NH₄H₂PO₄ were added into appropriate deionized water under stirring at 70 °C for 3 h. Then, it was further dried at 120 °C for 12 h to get a solid precursor. Finally, the precursor was sintered at 750 °C for 8 h in Air atmosphere to yield the final product VOPO₄.

Synthesis of NVPOF:

The NVPOF sample was prepared by a wet ball-milling method the mixture of VOPO₄, NaF, Na₂CO₃ in stoichiometric ratio. In a typical synthesis process, VOPO₄, NaF, Na₂CO₃ and an appropriate amount of absolute ethanol were added into an agate mortar. Then the agate mortar with the mixture and milling balls (weight ratio of 1:20 or 1-30) was sent to a planetary ball-milling machine and ball-milled at 500 rpm for 20 h. Then it was further dried at 80 °C for 12 h to get a solid precursor. Finally, the precursor was sintered at 750 °C for 1.5 h in Ar atmosphere to yield the final product NVPOF.

Synthesis of 2D-NVPOF sample

The NVPOF material was mixed with a certain amount of deionized water, and stirred for 4 h in an oil bath of 80 °C. Finally, the NVPOF products could be easily collected after washing the precipitation with distilled water and ethanol several times, and then drying in a vacuum at 80 °C.

Preparation of the HC anode

Preparation procedures for the hard carbon (HC): The raw materials were obtained from waste shells of commercially available sunflower seeds. Then, the preprocessed powder was obtained *via* high-energy ball mill and then mixed with chitosan (1:1 by weight ratio) in deionized water containing acetic acid. Following by a freeze-drying process, the mixture precursor was put into a corundum porcelain boat and heated to 1300 °C for 4 hours under an argon atmosphere in tube furnace. After cooling to ambient temperature, the as-prepared products were ground and washed with dilute HCl solution and distilled water. Finally, black sample was obtained after vacuum filtration.

Materials characterization

Crystalline phase analyses were evaluated by the X-ray diffraction (XRD) patterns, which were collected on a Rigaku SmartLab X-ray diffractometer (Cu-K α radiation, $\lambda = 1.5418$ Å, current: 30 mA, voltage: 40 kV) in the scan range (2 θ) of 5° - 80°. The particle size and morphology of the materials were investigated by using the scanning electron microscopy (SEM, Hitachi SU 8000). XPS measurements were performed using a VG MultiLab 2000 system with a monochromatic Al K α X-ray source (Thermo VG Scientific). A transmission electron microscope (TEM, JEQL-2100F) was used to capture the morphology of NVPOF and 2D-NVPOF materials.

Electrochemical measurements

The working electrodes were made by coating a slurry containing 70 wt % active material (NVPOF and 2D-NVPOF), 20 wt% carbon black and 10 wt% carboxymethylcellulose (CMC) on an aluminum foil, followed by a drying process under vacuum at about 60 °C overnight and transferred to a glove box under an Ar atmosphere before the cell assembly. The electrolyte was 1 mol L⁻¹ NaClO₄ in propylene carbonate (PC) with 5 vol % fluoroethylene carbonate (FEC). Glass fiber membranes were employed as the separator, and metallic sodium was used as both counter and reference electrodes in the half cells, HC electrode was used as counter electrode in the full cells. Before assembling the full cell, we pre-sodiated the hard carbon (HC) anode. Specifically, drop 100 μ L of electrolyte on the surface of the sodium metal is in complete contact with the HC anode), keeping this state for 3-7h to complete the pre-sodiation of HC. The galvanostatic charge-discharge (GCD) measurements were conducted on the battery testing systems (Neware) in the potential

window of 2.0-4.3 V versus Na⁺/Na at different rates. Cyclic voltammetry (CV) was performed on an electrochemical analyzer (CH Instruments, Model 660E) at varied scan rates and galvanostatic intermittent titration technique (GITT, Arbin battery tester) were used to study the electrode kinetics via calculating the apparent Na⁺ diffusion coefficients.

Full cells were fabricated in the glove box by coupling the NVPOF and 2D-NVPOF cathode with HC anode, and their electrochemical properties were tested on the battery testing systems in the voltage window of 1.2-4.2V Specific capacities of full cells were calculated according to the mass of cathode materials. In order to match the cathode/anode capacity, there is a slight excess capacity of anode compared with cathode, and the mass ratio of HC to NVPOF and 2D-NVPOF was about 1:2.1. Prior to the fabrication of full cells, pre-sodiation for the HC anodes was performed to activate the material and stabilize the electrode surface.

Calculation detail

The calculations were carried out using density functional theory with the PBE form of generalized gradient approximation functional (GGA).¹ The Vienna ab-initio simulation package (VASP) was employed.^{2 3 4 5}The plane wave energy cutoff was set as 400 eV. The Fermi scheme was employed for electron occupancy with an energy smearing of 0.1 eV. The first Brillouin zone was sampled in the Monkhorst–Pack grid.⁶ The $3\times3\times3$ and $3\times3\times1$ k-point mesh for the bulk and surface calculations, respectively. The energy (converged to 1.0×10^{-6} eV/atom) and force (converged to 0.03eV/Å) were set as the convergence criterion for geometry optimization. The spin polarization was considered in all calculation. For structural optimization of bulk phase, the lattice and all the atoms will be relaxed to local the energy minimum state. For slab optimization, the lattices in the x-y plane will be relaxed and the one in the z direction will be fixed, while the atom in the bottom layer will be fixed to model the bulk phase.

The transition state (TS) structures and the reaction pathways were located using the climbing image nudged elastic band (CI-NEB) method.⁷ The minimum energy

pathway was optimized using the force-based conjugate-gradient method until the maximum force was less than 0.03 eV/Å. A semiempirical DFT-D3 force-field approach is employed in our calculations to describe the van der Waals (vdW) interaction.⁸⁹



Figure S1. XRD of NVPOF and 2D-NVPOF materials.



Figure S2. SEM images of NVPOF and 2D-NVPOF; (a) NVPOF; (b) 2D-NVPOF.



Figure S3. Survey XPS full spectrum of (a) NVPOF and (b) 2D-NVPOF.



Figure S4. High-resolution XPS spectra of NVPOF and 2D-NVPOF for the orbital peaks of Na 1s, and V 2p.

Figure S5. High-resolution XPS spectra of NVPOF and 2D-NVPOF for the orbital peaks of P 2p and O 1s.

Figure S6. Rate capability and the corresponding GCD curves from 0.1 to 20 C.

Figure S7. The GCD curves of 2D-NVPF and NVPOF half-cells at different cycles at 2C charge 0.2C discharge.

Figure S8. The GCD curves of 2D-NVPF and NVPOF half-cells at different cycles at 5 C charge 0.5 C discharge.

Figure S9. Studies of Na-storage properties (a) Rate capability from 0.1 C to 20 C; (b) Cycle stabilities at 0.5C.

Figure S10. Studies of 2D-NVPOF for Na-storage properties at -25 °C; (a) Rate capability from 0.1 C to 20C; (b) Cycle stabilities at 0.5C.

Figure S11. Studies of 2D-NVPOF for Na-storage properties at 50 °C; (a) Rate capability from 0.1 C to 20C; (b) Cycle stabilities at 0.5C.

Figure S12. Electrochemical performance of HC anode. (a) GCD curves for 3 cycles at 30 mA h/g. (b) Rate capability.

Figure S13. CV curves at various scan rates from 0.1 to 1.0 mV s⁻¹ and (b) the linear fitting for the relationship between i_p and $v^{1/2}$ from the CV profiles of NVPOF.

CV curves were recorded in a potential window of 2.0-4.3 V versus Na⁺/Na at various scan rates from 0.1 to 1.0 mV s⁻¹. In the CV curves, the $D_{app,Na}$ values were calculated according to the following Randles-Sevcik equation:¹⁰

$$i_p = 2.69 \times 10^5 n^{3/2} A D_{app,Na} v^{1/2} C_0 v^{1/2}$$

where i_p is the peak current density, n is the electron-transfer number per molecule formula during the redox reaction (n = 2 for the present NVPOF), A is the surface area of the electrode, C_0 is the concentration of Na ions in the electrode (7.7 mmol cm⁻³), and v is the scan rate.

Figure S15. One single GITT profile of NVPOF in the (a) charge and (c) discharge processes. The corresponding linearly fitting behavior for the *E* versus $\tau^{1/2}$ in the (b) charge and (d) discharge GITT titration.

Figure S16. One single GITT profile of 2D-NVPOF in the (a) charge and (c) discharge processes. The corresponding linearly fitting behavior for the *E* versus $\tau^{1/2}$ in the (b) charge and (d) discharge GITT titration.

Calculation process for the $D_{app,Na}$ values through GITT tests. The $D_{app,Na}$ values can be calculated according to the following equation:¹¹

$$D_{app,Na} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_{\tau}} \right)^2 \left(\tau \ll L^2 / D \right)$$

where $m_{\rm B}$, $M_{\rm B}$, and $V_{\rm M}$ are the mass, molecular weight, and molar volume of the NVPF material, respectively; τ is the time for an applied galvanostatic current; S is the active surface of the electrode; L is the average radius of the material particles; and ΔEs and $\Delta E\tau$ are the quasi-equilibrium potential and the change of cell voltage E during the current pulse, respectively.

Figure S17. Electronic conductivity comparison between NVPOF and 2D-NVPOF.

samples	a(=b) / Å	c / Å	Volume /Å3
NVPOF	6.368	10.638	431.39
2D-NVPOF	6.372	10.63	431.39

Table S1. The refined crystallographic data of 2D-NVPOF obtained from XRD Rietveld refinements.

Atom	Туре	Wyckof f	X / a	Y / b	Z / c	Occupancy
Na (1)	Na	8 h	-0.26480	0.26480	0.00000	0.510
Na (2)	Na	161	-0.36800	-2.1300	0.0000	0.122
O (1)	Ο	16 n	0.30829	0.0000	0.16410	1.000
O (2)	Ο	4 e	0.0000	0.0000	0.35320	1.000
V	V	4 e	0.0000	0.0000	0.20007	1.000
Р	Р	4 d	0.5000	0.0000	0.2500	1.000
F	F	2 a	0.0000	0.0000	0.0000	1.000

Table S2. Refined structural parameters of the unsubstituted 2D-NVPOF.

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