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## Sodiophilic VN interlayer stabilizing Na metal anode

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## **Experimental Section**

**Preparation of the artificial Na/VN interlay:** The artificial interlayer was constructed via the roll-to-roll process. Typically, the VN powder (purchased from Zhejiang Yamei Nano Technology Co., Ltd. (Jiaxing, China) without further purification and processing) was spread onto the surface of fresh Na foil, followed by repeated mechanically rolling. The preparation was carried out in the glovebox filled with Ar gas (O<sub>2</sub> and H<sub>2</sub>O < 0.1 ppm).

**Materials characterization:** The morphologies and elements distribution of artificial VN interlayer were characterized by field emission scanning electron microscopy (SEM, JEOL, JSM-6360LA) and high-resolution transmission electron microscopy (HRTEM, Talos F200S). The phase structures of VN interlayer before and after cycling were investigated by X-ray diffraction (XRD, Bruker with a Cu K $\alpha$  radiation). And the chemical state of the artificial interlayer was analyzed via X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi).

Noting that the polyimide tape was used to seal the ample during the process of XRD test. Moreover, during the preparation process of Na/VN for HRTEM, the Na/VN was dispersed and ultrasound in diethyl carbonate (DEC) solution with Ar protection. For the materials characterization of FESEM, HRTEM and XPS, all the samples are sealed in a vessel with Ar protection to avoid the side reactions during transportation.

**Electrochemical characterization:** All electrochemical performances were measured in 2032 coin-type cells at room temperature. The electrolytes of symmetrical cells and full cells is 1.0 M NaClO<sub>4</sub> in EC: DEC = 1:1 (volume ratio) with 5% FEC as the additive. To standard the testing, the amount of electrolyte was 200 µL. The Whatman GF/D glass fiber was applied as the separator. And the Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NVP) cathode was fabricated by coating the slurry (a mixture of 80 wt% commercial NVP, 10 wt% CNT, and 10 wt% PVDF) on Al foil and then dried under vacuum at 60 °C overnight. The mass of NVP active material was about 3.0 mg cm<sup>-2</sup>. The electrochemical performance of all cells was tested on Neware testing system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS, 0.01-10<sup>5</sup> Hz) were obtained by CHI660 workstation.

**Computational methods:** The calculations of the adsorption energy of VN were performed using Vienna ab initio simulation package (VASP). Projector-augmented-wave (PAW) potentials were used to take into account the electron-ion interactions, while the electron exchange-correlation interactions were treated using generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof. A plane wave cutoff of 500 eV was used for all the calculations. All atomic positions and lattice vectors were fully optimized using a conjugate gradient algorithm to obtain the unstrained configuration. Atomic relaxation was performed until the change of total energy was less than 0.01 meV and all the forces on each atom were smaller than 0.01 eV/Å. For the Na adsorption, the supercell was as follows: VN 3 \* 3 \* 1. A vacuum space of 20 Å was placed to form a surface structure. The energy of an isolated Na atom was calculated in a large cubic cell of side length 20 Å. K-point samplings of  $7 \times 7 \times 1$  were used to calculate energies.



Fig. S1 The SEM image (a) and XRD pattern (b) of commercial VN powder.



Fig. S2 The optical images of (a) bare Na and (b) Na modified by VN.



**Fig. S3** SEM image of Na/VN and the corresponding elemental mapping images of V and N.



**Fig. S4** The cross-section SEM image of Na/VN electrode and the corresponding elemental mapping images of V, Na and N.



Fig. S5 The XRD patterns of Na/VN electrode and polyimide tape.



Fig. S6 HRTEM images of Na/VN electrode.



Fig. S7 The XPS spectra of (a) V 2p and (b) N 1s for Na/VN electrode.



**Fig. S8** The enlarge voltage profiles of symmetric cells with bare Na and Na/VN electrode at (a) 0-21 h, (b) 121-141 h and (c) 1049-1067 h.



**Fig. S9** The enlarge voltage profiles in Fig. 2b at (a) 0-21 h, (b) 111-127 h and (c) 665-677 h.



**Fig. S10** The SEM images of Na/VN electrode after plating different capacity of (a) 0.0, (b) 0.5 and (c) 1 mAh cm<sup>-2</sup> at current density of 0.5 mA cm<sup>-2</sup>. And (d) the SEM images of Na/VN electrode after stripping capacity of 1 mAh cm<sup>-2</sup>.



**Fig. S11** The SEM images of bare Na electrode after plating different capacity of (a) 0.0, (b) 0.5 and (c) 1 mAh cm<sup>-2</sup> at current density of 0.5 mA cm<sup>-2</sup>. And (d) the SEM images of bare Na electrode after stripping capacity of 1 mAh cm<sup>-2</sup>.



Fig. S12 The optical image of homemade transparent quartz symmetrical cells with Na/VN electrode after plating 120 min at a current density of 0.5 mA cm<sup>-2</sup>.



**Fig. S13** The optical images of bare Na and Na/VN electrodes. (a) The photograph of initial bare Na electrode and (b) after 10 cycles at 0.5 mA cm<sup>-2</sup> with 1 mAh cm<sup>-2</sup>. (c, d) the photograph of initial and after 10 cycles of Na/VN electrode, respectively.



Fig. S14 The SEM images of (a) bare Na and (b) Na/VN electrodes after 10 cycles at  $0.5 \text{ mA cm}^{-2}$  with 1 mAh cm<sup>-2</sup>.



Fig. S15 The XRD pattern of Na/VN electrode after 10 cycles at 0.5 mA cm<sup>-2</sup> with 1 mAh cm<sup>-2</sup>.



Fig. S16 The XPS spectra of (a) V 2p and (b) N 1s for symmetrical Na/VN cell after 10 cycles at 0.5 mA cm<sup>-2</sup> with 1 mAh cm<sup>-2</sup>.



**Fig. S17** The front view of Na<sup>+</sup> adsorptions at (a) bridge, (b) hollow, (c) top on N and (d) top on V sites of VN surface, respectively.



**Fig. S18** The top view of charge density differences of Na<sup>+</sup> on the surface of VN at (a) bridge, (b) hollow, (c) top on N and (d) top on V sites, respectively.



Fig. S19 The Tafel curves of Na/VN and bare Na symmetric cells.



Fig. S20 The Nyquist plots of (a) bare Na and (b) Na/VN symmetric cell at different temperatures.



**Fig. S21** (a) The corresponding charge-discharge curves of NVP||bare Na under rates ranging from 1 to 50 C. (b) The charge/discharge curves of NVP||Na/VN full cell during the 1st, 100th, 200th, 500th and 800th cycles. (c) EIS curves obtained after 100 cycles at 5 C.