Supporting information

Trace Topological Doping Strategy and Deep Learning to Reveal High-rate Sodium Storage Regulation of Barium doping Na₃V₂(PO₄)₃

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Experimental procedure

Synthesis of barium doping Na₃V₂(PO₄)₃

All raw chemicals, including Na₂CO₃, V₂O₅, NH₄H₂PO₄, Ba(CH₃COO)₂ and citric acid were purchased from Aladdin reagent Corp without any purification. The synthesis of graphene oxide was identical as our previous report^[36]. Typically, 2 mmol V₂O₅ was firstly dispersed into 4 mmol citric acid solution (100 ml) at room temperature and maintained the mixture at 80°C water-bath condition with continuously magnetic stirring until obtaining a clear dark blue solution. Then, stoichiometric amounts of Na₂CO₃, NH₄H₂PO₄, and Ba(CH₃COO)₂ with an appropriate amount of glucose were added in series. Once the raw materials were completely dissolved into the solution, graphene oxide solution (2 mg ml⁻¹, 30 ml volume) was dropped into above mixture and stirring for another 30 min. When the color of solution changed to complete dark, extra water was evaporated until the formation of uniform wet-gel. Further drying the wet-gel at 120°C to get the dry gel, the precursor was heated at 350°C for 4 h in a program-controlled tube furnace under N₂ flow. After gridding the pre-heated precursor, the obtained brown powder was further sintered at 700°C for 10 h in N₂ atmosphere to get final products.

Materials characterizations

The crystal structure and phase purity of final products were characterized by X-ray diffraction pattern (XRD) by using Cu-K as irradiation source at ramp of 5°C min⁻¹. Surface morphology and inner architecture of products were observed on a scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Elemental valence of materials was detected by X-ray photoelectron spectrum (XPS) while the graphitization as well as disorder extent of materials were analyzed by Raman spectrum. Thermogravimetric analysis (TGA) plot of sample was recorded by using Diamond TG/DTA at a ramp rate of 5°C from room temperature to 700°C.

Electrochemical testing

Electrochemical properties of materials were conducted on slurry-based electrode by coin cells in argon filled glovebox, where 1 M NaClO₄ dissolved in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) with 5% fluoroethylene caronate (FEC) additive and sodium foil was used as both counter and reference electrode. The electrode slurry was prepared by mixing as-obtained active material, conductive carbon black and polyvinylidene fluoride (PVDF) in a mass ratio of 80:10:10 with adding appropriate amount of 1-methyl-2-pyrrolidinone (NMP) as dispersant. After magnetically mixing the slurry for 12 h, the uniform slurry was coated on aluminum (Al) foil by using a doctor blade with controlling the thickness of 50 um. Drying the slurry-coated Al foil in a vacuum oven at 120°C for 12 h and following press the dried electrode at 10 MPa for 60 seconds. Cutting the dried electrode into circle-shape plate with diameter of 12 mm and controlling the mass loading of NVBP on the shaped plate around 2.5 mg cm⁻². Once the assembling process finished, setting the coin cell at room temperature for 12 h before test to guarantee the full penetration of electrolyte into electrode. Galvanostatic charge/discharge (GCD) test was carried out to identify the electrochemical capacity of NVBP electrode in the potential range 2.5-4.3 V with varying C rate from 0.2C to 50C, in which 1C equals to the theoretical capacity of 117 mA g⁻¹. Cyclic voltammetry (CV) was characterized on a CHI-660E electrochemical workstation in the potential range 2.5-4.3 V at various scanning rates from 0.1, 0.2, 0.3, 0.4 and 0.5 mV s⁻¹. Electrochemical impedance spectrum (EIS) was recorded in the frequency range from 0.01 Hz to 100 KHz with an AC amplitude of 5 mV.

Data deep learning

DFT calculations: The first principles calculations were performed within the density functional theory (DFT) framework, using the generalized gradient approximation (GGA) exchange-correlation

functional by QUANTUM ESPRESSO package^[50]. The total energies were calculated by means of the projector-augmented-wave (PAW) method^[51, 52], with the cutoff kinetic energies for wave function and for charge density were set to 45 and 500 Ry, respectively. Perdew, Burke and Ernzerhof (PBE) form of the generalized gradient approximation (GGA) was adopted for the exchange-correlation energy^[42]. Brillouin zone were evaluated with the Monkhorst-Pack mesh of $12 \times 12 \times 12$. The atomic positions in all of the computational models were fully relaxed until reaching a convergence energy of 10^{-6} eV, where on-site Coulomb correction (GGA + U) was used to describe the localized electronic states and the effective Hubbard-U parameters for V and Ba were set to 3.0 and 6.2 eV, respectively.

Migration pathway of Na ions: We investigated diffusion of Na ion using the nudged elastic band (NEB) method as implemented in QUANTUM ESPRESSO code to calculate the activation barriers for a variety of possible diffusion hops, using 5 images between each meta-stable configuration. At each optimization step, the highest-energy image (HEI) is found. If this HEI is one of the two terminal points, then there is no climbing. If it is next to the fixed terminal point, then single climbing image (C1-NEB) is used for this step. Finally, if the HEI does not coincide with the fixed ends or their direct neighbors, then two climbing images (C2-NEB) algorithm is used for this step. Because the current HEI is determined at each step, the climbing images (and even the algorithm) can change from step to step. The post-processing including collection and analysis of obtained data were performed with Python package.

Tight binding model: We use Wannier90 package^[43] to map the ground-state wave functions onto a maximally localized Wannier functions (MLWFs) basis. With the basis of atomic orbitals (s orbital of Na atoms, dxz, dyz, dxy, $\frac{d_z^2}{z^2}$ and $\frac{d_x^2 - y^2}{x^2 - y^2}$ orbitals of V and Ba atoms, and px, py and pz orbitals of P and O atoms), we employ an adaptivek-mesh strategy to extract the matrices to build the real-space tightbinding matrix HTB:

$$H_{TB}(\vec{k}) = \sum_{ij} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} t_{ij}(\vec{R})$$
(1)

Where \vec{R} is the Bravais lattice vector, \vec{k} is the momentum and $t_{ij}(\vec{R})$ is the matrix element extracted from Wannier90 output file.

Topological analysis: As we got the TB Hamiltonian of NVP, we checked the effects on topology of this electrode materials as function of Ba-doping. If the lattice of material holds time reversal symmetry, inversion symmetry and chiral-symmetry, the low-energy Hamiltonian will satisfy:

$$\Upsilon H_{TB}(\vec{k})\Upsilon^{-1} = H_{TB}(-\vec{k}), \tag{1}$$

$$\hat{I}H_{TB}(-\vec{k})\hat{I}^{-1} = H_{TB}(\vec{k}), \qquad (2)$$

and

$$SH_{TB}(\vec{k})S^{-1} = -H_{TB}(\vec{k})$$
 (3)

respectively, where $\hat{T} = -i\sigma y^{\bigotimes I_n \times n}$ is the time reversal matrix promoting a spin flip with n being half of the dimension of H_{TB} , $\hat{I} = \sigma z^{\bigotimes I_n \times n}$ is the inversion operator, and $\hat{S} = I_n \times n^{\bigotimes} \sigma y$ is the chiral matrix promoting the chiral transformation.



Figure S1 TGA plot of NVBP-2 from room temperature (RT) to 700°C.



Figure S2. XPS spectra of barium before/after Na storage on $Na_3V_2(PO_4)_3$.



Figure S3. EIS spectrum of NVP and NVBP-2 electrode after 5C cycling test (Insert image shows

the equivalent circuit).



Figure. S4 Charge density distribution in (a) NVP and (b) NVBP-2, where the yellow and blue region represent electron accumulation and depletion, respectively, representing the iso-surface of charge density at isovalue of 0.001/a03. The vanadium site replaced by barium is indicated by the black arrow.

Ref	Materials	Rate capacity	Capacity Retention (%)
		(mAh g ⁻¹)	
This work	NVBP/C	69.2 at 50C	52.5 mAh g ⁻¹ after 2000 cycles at 50C
[1]	NVP/C	65 at 30C	70 mAh g ⁻¹ after 2000 cycles at 10C
[2]	Nb-doping NVP/C	69.9 at 50C	56.6 mAh g ⁻¹ after 1600 cycles at 50C
[3]	NVP/C	96 at 10C	82 mAh g ⁻¹ after 200 cycles at 1C
[4]	NVP/C micro-balls	52 at 50C	82 mAh g ⁻¹ at 100 cycles at 20C
[5]	K, Mg-doped NVP/C	109.4 at 10C	99.7 mAh g ⁻¹ after 100 cycles at 1C
[6]	Ga-doped NVP/C	80.6 at 50C	101.1 mAh g ⁻¹ after 1000 cycles at 1C
[7]	NVP/C	78 at 20C	86.7% after 600 cycles at 20C
[8]	Co-doing NVP/C	88.0 at 10C	83.2% after 1000 cycles at 10C
[9]	Zn-doing NVP/C	90.4 at 10C	89.6% after 400 cycles at 10C
[10]	Mo-doing NVP/C	90.0 at 10C	83.5% after 500 cycles at 10C
[11]	Mg-doing NVP/C	77.3 at 10C	80.3% after 1200 cycles at 10C
[12]	Fe-doing NVP/C	91.16 at 20C	88.7% after 100 cycles at 20C
[13]	W-doping NVP/C	92.6 at 50C	66.18% after 2000 cycles at 50C

Table S1 Comparison of electrochemical properties.

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