

Electronic supplementary information

Na-site coordination environment regulation of Mn-based phosphate cathode for sodium ion batteries with elevated working voltage and energy density

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Experimental

Synthesis of Materials

Synthesis of NKMVP@C/CNT-x: The NKMVP@C/CNT-x ($x=0.1, 0.2, 0.3$) were prepared by a facile CNT-assisted sol-gel method. Citric acid monohydrate ($\geq 99.5\%$, Sinopharm), NH_4VO_3 ($\geq 99.0\%$, Sinopharm), $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ($\geq 99.0\%$, Sinopharm), $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ($\geq 98.0\%$, Sinopharm), NaCH_3COO ($\geq 99.0\%$, Sinopharm) and KNO_3 ($\geq 99.0\%$, Sinopharm) were used as precursor materials. Hydroxylated CNTs were obtained from Chengdu Organic Chemicals Co., Ltd., China. For better dispersion in aqueous phase, Hydroxylated CNTs were added into ethylene glycol under ultrasonic treatment for about 20 min. First, 0.4245 g of citric acid and 0.1182 g of NH_4VO_3 were dissolved in 10 mL of deionized water. Then, stoichiometric amounts of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, NaCH_3COO , KNO_3 and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ were added to the above solution. The dispersed hydroxylated CNT solution was added into the above solution and was constantly magnetic stirred at $80\text{ }^\circ\text{C}$ for 3 h and then dried at $80\text{ }^\circ\text{C}$ for 5 h in an oven. Final, the resulting powder was calcined at $350\text{ }^\circ\text{C}$ for 4 h and sintered at $750\text{ }^\circ\text{C}$ for 8 h under Ar atmosphere at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ to obtain black powder (marked as NKMVP@C/CNT-x, $x=0.1, 0.2$, and 0.3 , corresponding to the chemical formula $\text{Na}_{4-x}\text{K}_x\text{MnV}(\text{PO}_4)_3$).

Synthesis of control samples: For comparison, various control samples were also prepared with the same synthesis method except the use of K dopant or CNTs. Carbon coated $\text{Na}_4\text{MnV}(\text{PO}_4)_3$ (NMVP@C) was synthesis by the above synthesis strategy without K doping and CNT. Carbon coated $\text{Na}_4\text{VMn}(\text{PO}_4)_3$ with K doping (NKMVP@C) was prepared by the same above method with only K doping. Carbon coated $\text{Na}_4\text{VMn}(\text{PO}_4)_3$ with introducing CNT network (NMVP@C/CNT) was synthesized by the same synthesis method without K doping.

Material characterization

The structure information of the samples was probed by X-ray diffraction (XRD) using the Rigaku MiniFlex600 device. Thermogravimetric analysis (TGA) was conducted with a TG/DTA 6300 to determine the carbon content of all samples. The chemical components and bonds of the synthetic materials were determined by X-ray photoelectron spectroscopy (XPS, AXIS Supra, English) equipped with Al $\text{K}\alpha$ radiation, and the peak position of the binding energy was calibrated at 284.8 eV with reference to the C 1s peak. The element (Na, K, Mn, and V) compositions of prepared samples were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 5100). Raman spectra measurements of the samples were conducted on a WITec alpha 300 R Raman spectrometer with a laser power of 10 mW . The micromorphology, the EDAX, and microstructures of the samples were examined

using a scanning electron microscope (SEM, MIRA4 LMH, TESCAN) and a transmission electron microscope (TEM, Tecnai F20, FEI).

Electrochemical measurement

To fabricate working electrode, the mixed slurry was prepared by mixing active materials, super P Li and poly-vinylidene fluoride (PVDF) in the solvent of N-methyl-2-pyrrolidinone (NMP) with a weight ratio of 7:2:1, and was coated on the Al foil and then dried at 80 °C for overnight in a vacuum. After drying, it was cut into discs with 1.2 cm diameter. The loading mass of active materials of the electrodes was around 1.5 mg cm⁻². The electrochemical properties were evaluated with 2032 coin cells assembled in an argon-filled glove box (Super 1220/750, Mikrouna, shanghai, China) where both moisture and oxygen levels were kept below 1 ppm. Sodium metal was used as the counter electrode, 1 M NaClO₄ in propylene carbonate (PC) with 5 vol% fluoroethylene carbonate (FEC) was employed as electrolyte and glass fiber (GF/D) (Whatman) was used as separator. The galvanostatic charge and discharge tests were carried out on a battery testing system (BTS4008, Neware, Shenzhen, China) between 2.5 and 3.8 V (vs. Na⁺/Na) at various current densities (1 C=110 mA g⁻¹) at room temperature (25 °C). Cyclic voltammetry (CV) tests were carried out on an electrochemical workstation (CS 2350, Corrtest, Wuhan, China) at room temperature.

Theoretical Calculation Section

All the first-principles spin-polarized calculations were performed by using the Vienna ab initio simulation package (VASP).^[1] The ion-electron interactions were described by the projector augmented wave method.^[2] The electron exchange-correlation energy was treated within the generalized gradient approximation (GGA), using the functional of Perdew-Burke-Ernzerhof (PBE). The energy cutoff of the plane wave was set to 400 eV and the Brillouin zone was sampled with a 5 * 5 * 1 Monkhorst-Pack k-point grid.^[3] The convergence criterion for the residual force and energy was set to 0.05 eV/Å and 10⁻⁶ eV, respectively, during the structure relaxation. In the calculation of sodium ions diffusion, we used the CINEB method to get the ion diffusion barrier.^[4] The projected crystal orbital Hamilton population (pCOHP) was carried out to deal with the nature of bonding between two atoms.^[5] What needs illustration is that the formation energy of K doped NaMnV(PO₃)₄ calculated as follows:

$$E_f = E_{NKMVP} - E_{NMVP} - \mu_K + \mu_{Na} \quad (\text{Equation S1})$$

where E_{NKMVP} and E_{NMVP} is the total energy for the system of K doped NaMnV(PO₃)₄ and pure NaMnV(PO₃)₄, whereas μ_K and μ_{Na} represent the chemical

potentials of K atom and Na atom, respectively. The voltage during the charge/discharge process is defined by

$$V = \frac{E(\text{Na}_{x_2}\text{K}_y\text{MVP}) - E(\text{Na}_{x_1}\text{K}_y\text{MVP}) - (x_2 - x_1)E(\text{Na})}{(x_2 - x_1)e} \quad (\text{Equation S2})$$

where $E(\text{Na}_{x_2}\text{K}_y\text{MVP})$, $E(\text{Na}_{x_1}\text{K}_y\text{MVP})$, and $E(\text{Na})$ represent the total energies (in eV unit) of $\text{Na}_{x_2}\text{K}_y\text{MnV}(\text{PO}_4)_3$, $\text{Na}_{x_1}\text{K}_y\text{MnV}(\text{PO}_4)_3$, and an Na atom in Na bulk, respectively. $2e$ in the denominator stands for the total charge transfer during the redox process.

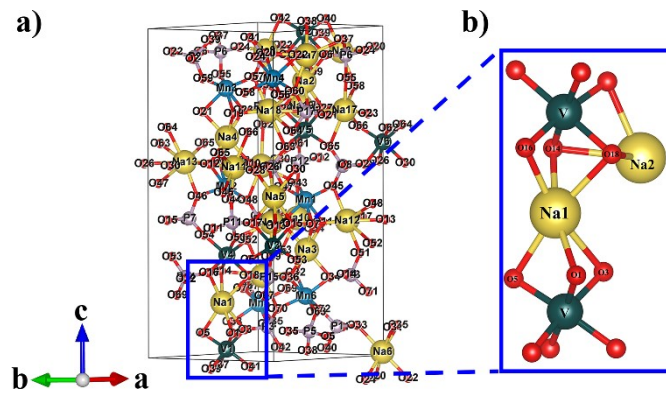


Figure S1. (a) Crystal structure of NMVP and (b) the enlarged crystal structure in the boxed area.

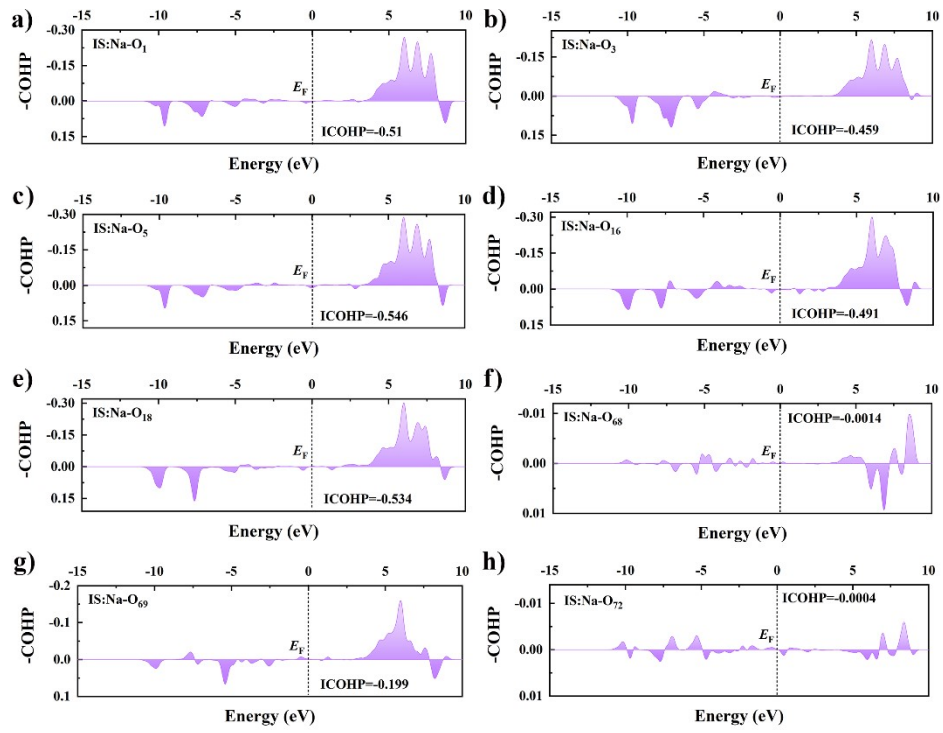


Figure S2. ICOHP curves of NMVP in initial states.

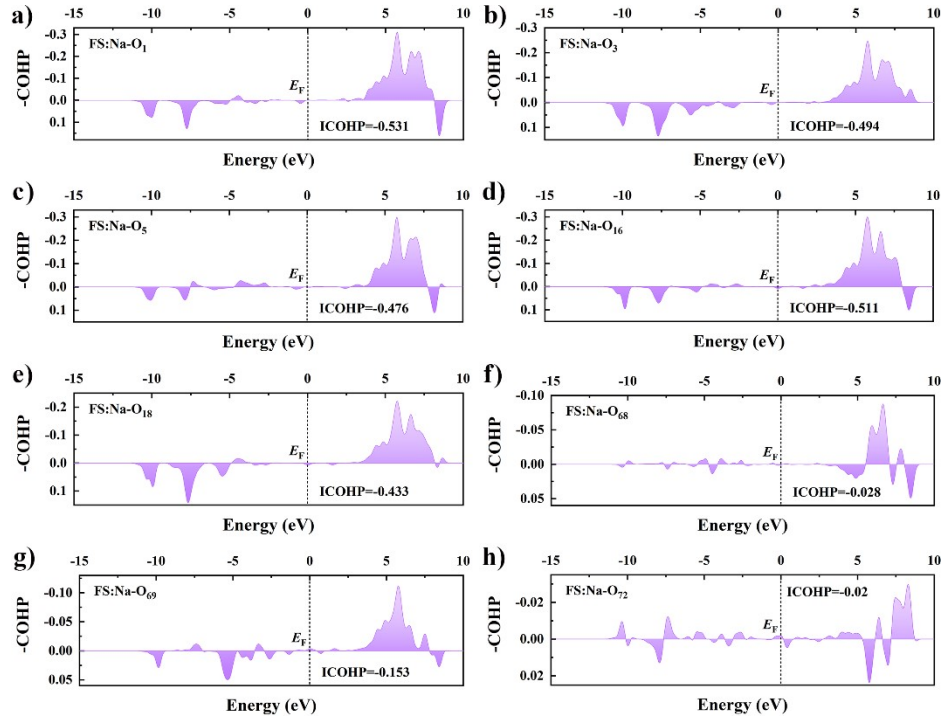


Figure S3. ICOHP curves of NMVP in final states.

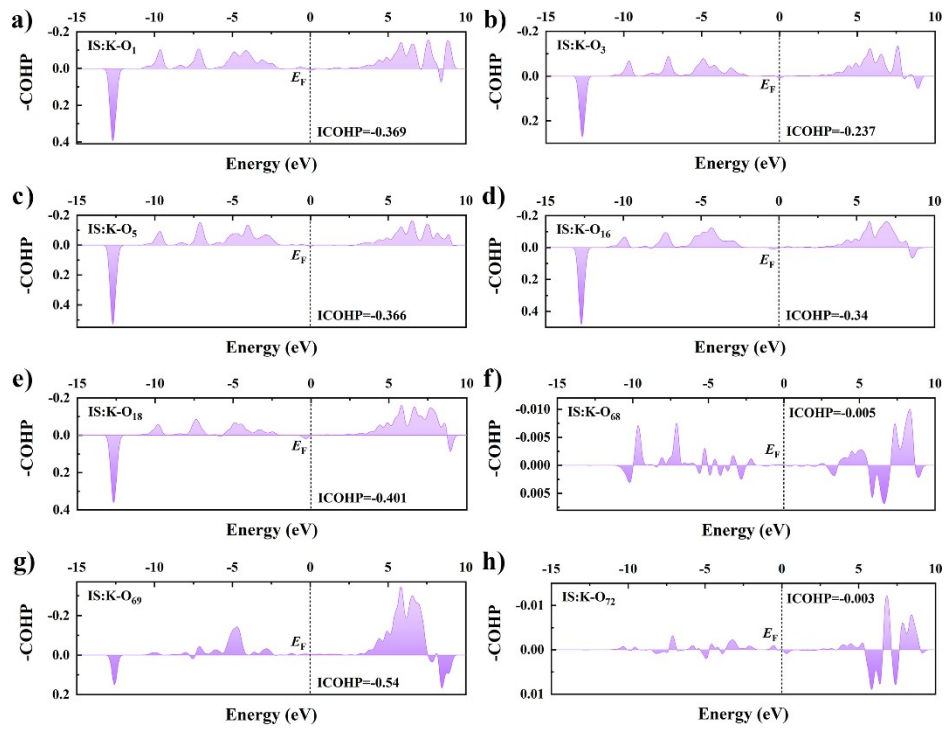


Figure S4. ICOHP curves of NKMVP in initial states.

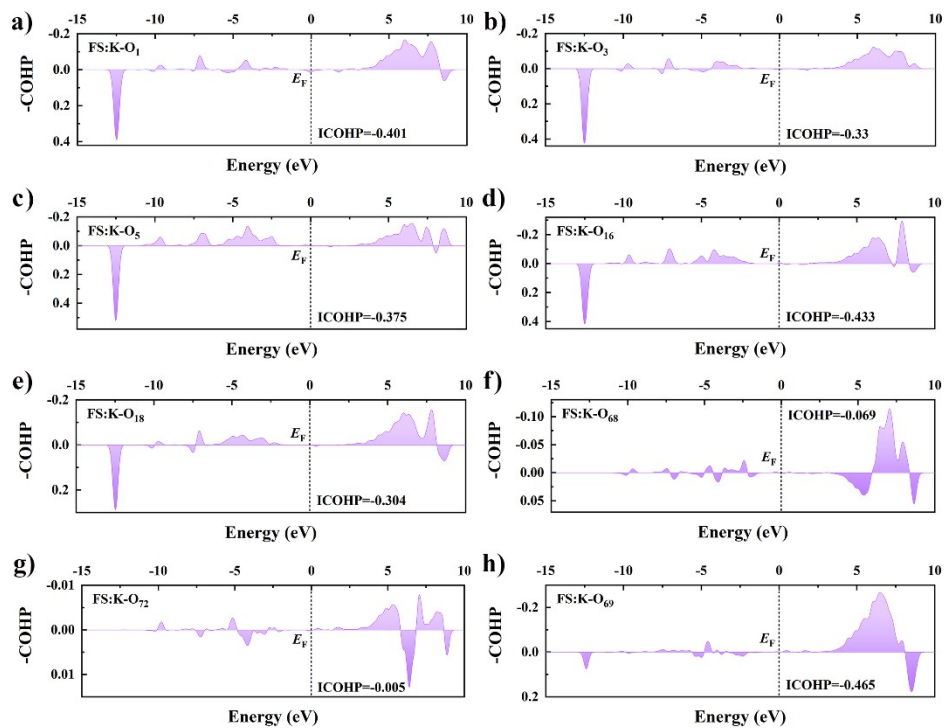


Figure S5. ICOHP curves of NKMVP in final states.

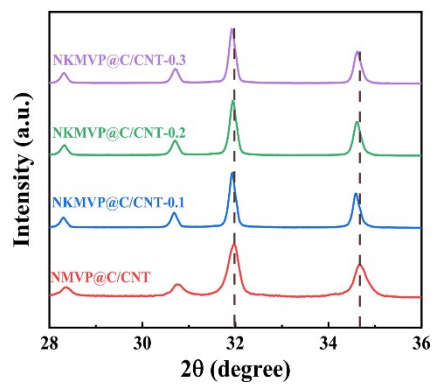


Figure S6. The enlarged XRD patterns between 28 and 36° corresponding to Figure 2a.

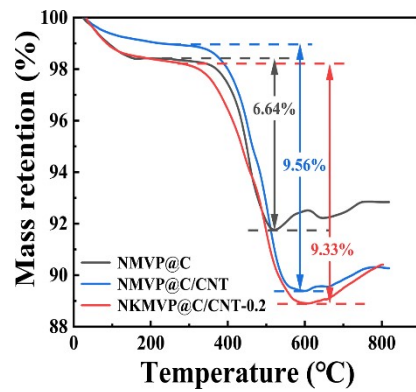


Figure S7. TG curves of the NMVP@C, NMVP@C/CNT and NKMVP@C/CNT-0.2.

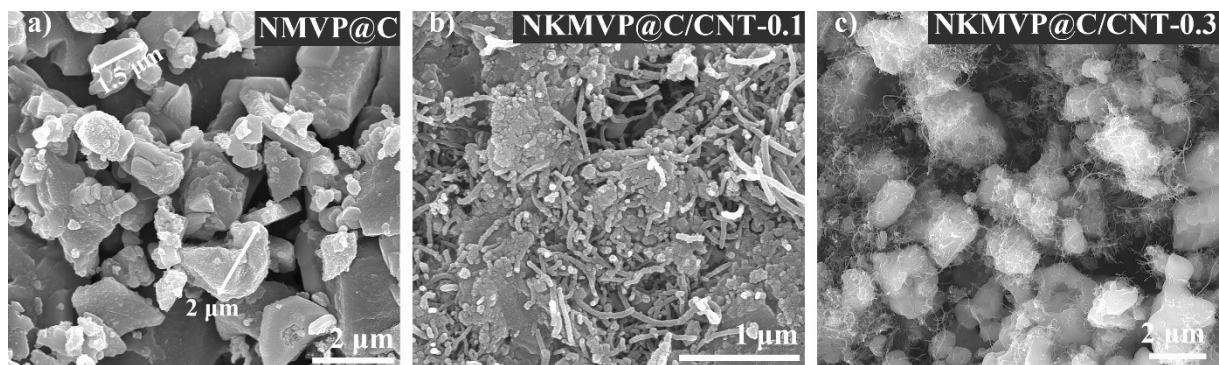


Figure S8. SEM images of (a) NMVP@C, (b) NKMVP@C/CNT-0.1, (c) NKMVP@C/CNT-0.3.

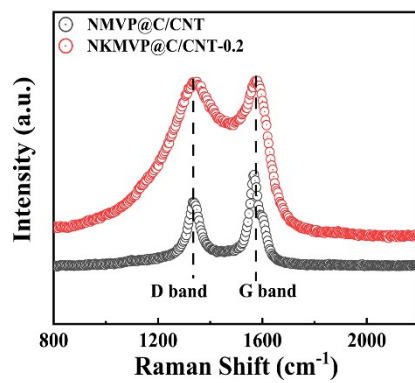


Figure S9. Raman spectra of the obtained NMVP@C/CNT and NKMVP@C/CNT-0.2.

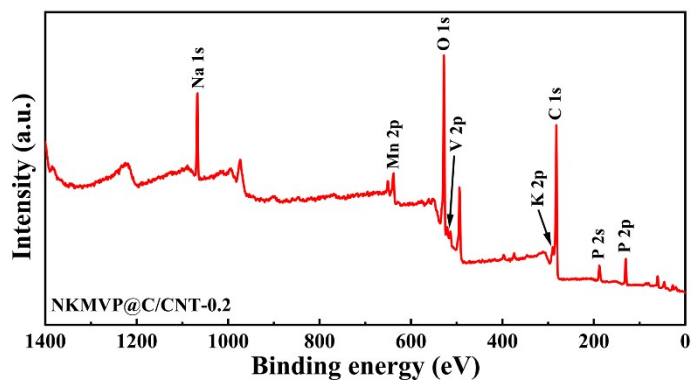


Figure S10. The full XPS spectrum of NKMVP@C/CNT-0.2.

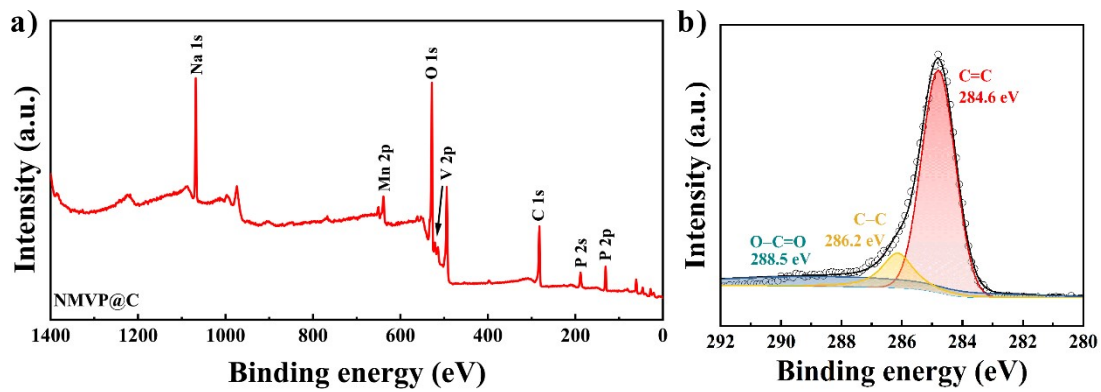


Figure S11. (a) The full XPS spectrum of NMVP@C, high-resolution XPS spectra of (b) C 1s.

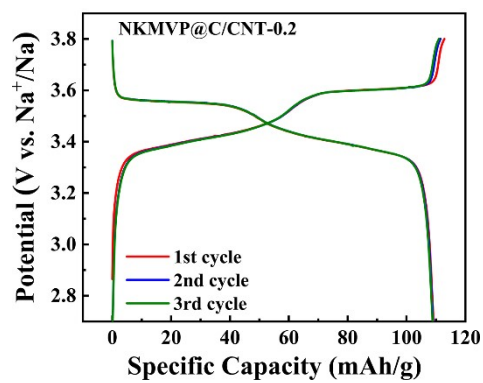


Figure S12. The galvanostatic charge-discharge profiles of the initial three cycles for NKMVP@C/CNT-0.2 electrode at 0.1 C.

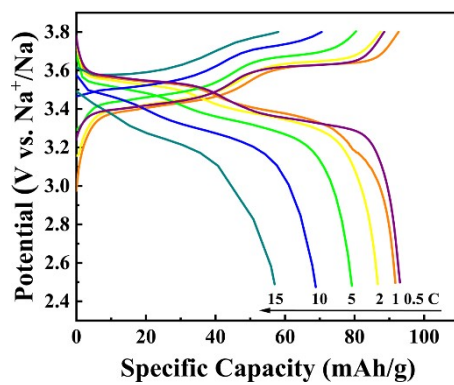


Figure S13. The charge and discharge profiles of the NKMVP@C/CNT-0.2 electrode at different current rates.

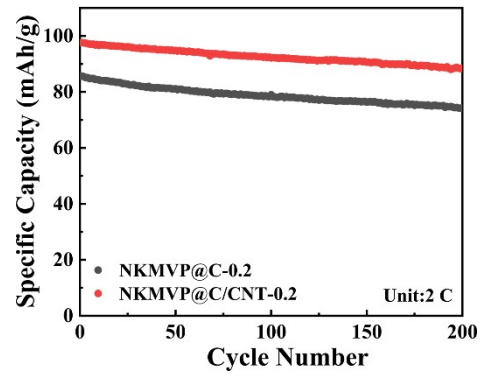


Figure S14. Cycle performance of NKMVP@C-0.2 and NKMVP@C/CNT-0.2 at 2C.

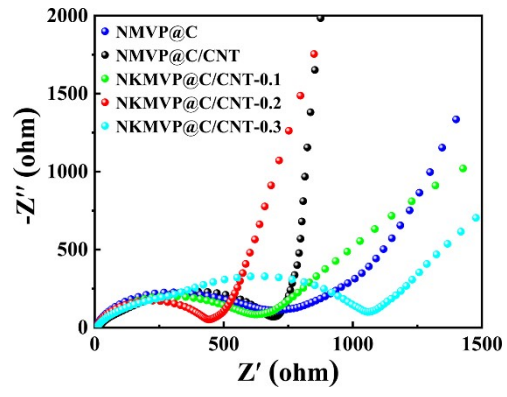


Figure S15. EIS plots of the electrodes.

Table S1. Detailed structural information of NKMVP@C/CNT-0.1 derived from Rietveld refinement.

Space group=R-3c		Rwp=6.48%		$\chi^2=2.96$	
a(Å)= 8.95941		c(Å)= 21.45927		V(Å ³)= 1491.780	
$\alpha(^{\circ})=90$		$\beta(^{\circ})=90$		$\gamma(^{\circ})=120$	
Atom	x	y	z	frac	mult
Na1	0.33330	0.66670	0.16670	0.779	6
Na2	0.66670	0.97362	0.08330	0.731	18
K1	0.33330	0.66670	0.16670	0.026	6
Mn	0.33330	0.66670	0.01773	0.500	12
V	0.33330	0.66670	0.01773	0.500	12
O1	0.15311	0.49961	0.08360	1.000	36
O2	0.54636	0.86171	- 0.02661	1.000	36
P1	- 0.03563	0.33330	0.08330	1.000	18

Table S2. Detailed structural information of NKMVP@C/CNT-0.2 derived from Rietveld refinement.

Space group=R-3c	Rwp=6.25%	$\chi^2=2.80$			
a(Å)= 8.95909	c(Å)= 21.46178	V(Å ³)= 1491.848			
$\alpha(^{\circ})=90$	$\beta(^{\circ})=90$	$\gamma(^{\circ})=120$			
Atom	x	y	z	frac	mult
Na1	0.33330	0.66670	0.16670	0.756	6
Na2	0.66670	0.97345	0.08330	0.731	18
K1	0.33330	0.66670	0.16670	0.049	6
Mn	0.33330	0.66670	0.01774	0.500	12
V	0.33330	0.66670	0.01774	0.500	12
O1	0.14982	0.49757	0.08415	1.000	36
O2	0.54634	0.86381	- 0.02618	1.000	36
P1	- 0.03568	0.33330	0.08330	1.000	18

Table S3. Detailed structural information of NKMVP@C/CNT-0.3 derived from Rietveld refinement.

Space group=R-3c	Rwp=6.46%	$\chi^2=2.86$			
a(Å)= 8.95300	c(Å)= 21.49921	V(Å ³)= 1492.417			
$\alpha(^{\circ})=90$	$\beta(^{\circ})=90$	$\gamma(^{\circ})=120$			
Atom	x	y	z	frac	mult
Na1	0.33330	0.66670	0.16670	0.733	6
Na2	0.66670	0.97274	0.08330	0.731	18
K1	0.33330	0.66670	0.16670	0.072	6
Mn	0.33330	0.66670	0.01795	0.500	12
V	0.33330	0.66670	0.01795	0.500	12
O1	0.15051	0.49748	0.08300	1.000	36
O2	0.54286	0.85907	- 0.02524	1.000	36
P1	- 0.03669	0.33330	0.08330	1.000	18

Table S4. ICP results of the as-prepared various NMVP samples.

Sample	Na	Mn	V	K
NMVP@C	3.75	1.00	1.00	0.00
NMVP@C/CNT	3.72	1.00	1.00	0.00
NKMVP@C/CNT-0.1	3.57	1.08	1.00	0.09
NKMVP@C/CNT-0.2	3.60	1.05	1.00	0.16
NKMVP@C/CNT-0.3	3.55	1.20	1.00	0.26

References

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