Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information (ESI)

Effects of low doping on the improvement of cathode materials $Na_{3+x}V_{2-x}M_x(PO_4)_3$ ($M = Co^{2+}, Cu^{2+}$; $x = 0.01-0.05$) for SIBs

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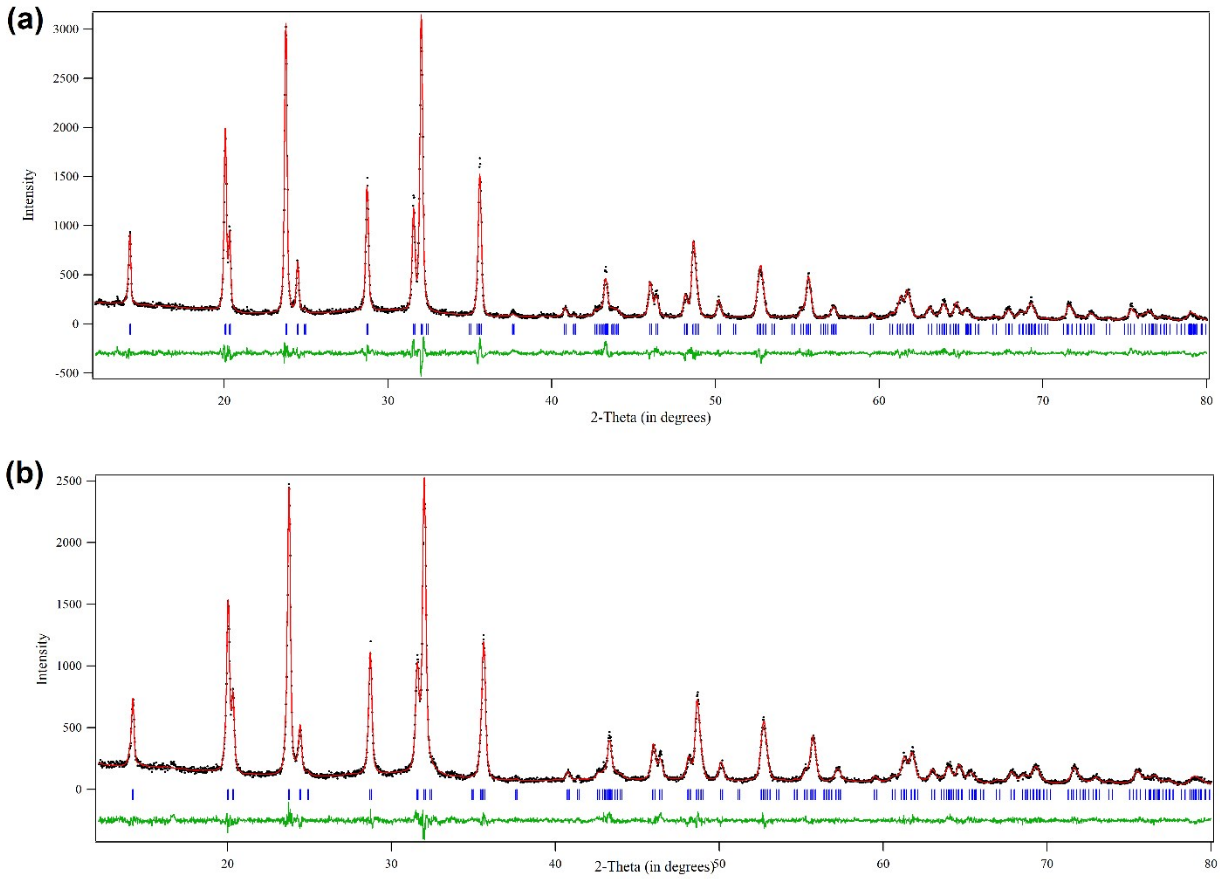

Figure S1. XRD Rietveld refinement for (a) $Na_{3.01}V_{1.99}Co_{0.01}(PO_4)_3/C$ and (b) $Na_{3.01}V_{1.99}Cu_{0.01}(PO_4)_3/C$ (circle signs (black) correspond to observed data; the solid line (red) is the calculated profile; tick marks (blue) represent the positions of allowed reflection; difference curve (green) on the same scale is plotted at the bottom of the pattern).

Table S1.

Structural parameters obtained from XRD Rietveld refinement of samples $Na_{3.01}V_{1.99}Co_{0.01}(PO_4)_3$/C and $Na_{3.01}V_{1.99}Cu_{0.01}(PO_4)_3$/C (space group *R-3c*, Z = 6, occupancy of V/M sites was fixed in the refinement based on nominal chemical composition, bond distances are in Å, U_{iso} are Å^2).

	$Na_{3.01}V_{1.99}Co_{0.01}(PO_4)_3$	$Na_{3.01}V_{1.99}Cu_{0.01}(PO_4)_3$
Na1 in 6*b*		
x y z	1/3 2/3 1/6	1/3 2/3 1/6
U_{iso}	0.120(10)	0.105(10)
occupancy	0.87(3)	0.98(3)
Na2 in 18*e*		
x y z	2/3 0.9657(10) 1/12	2/3 0.9672(10) 1/12
U_{iso}	0.050(5)	0.054(5)
occupancy	0.696(10)	0.667(9)
V/M in 12*c*		
x y z	1/3 2/3 0.01941(12)	1/3 2/3 0.01915(12)
U_{iso}	0.0053(10)	0.0082(10)
occupancy	0.99/0.01	0.99/0.01
P in 18*e*		
x y z	-0.0437(4) 1/3 1/12	-0.0446(4) 1/3 1/12
U_{iso}	0.0066(13)	0.0132(13)
occupancy	1	1
O1 in 36*f*		
x y z	0.1393(5) 0.5006(6) 0.0773(3)	0.1414(5) 0.4997(6) 0.0780(3)
U_{iso}	0.0052(17)	0.0082(16)
occupancy	1	1
O2 in 36*f*		
x y z	0.5454(8) 0.8484(6) -0.0264(2)	0.5433(8) 0.8479(6) -0.0267(2)
U_{iso}	0.022(2)	0.020(2)
occupancy	1	1
Bond distance		
V–O	3 x 2.0007 3 x 2.0264	3 x 1.9887 3 x 2.0326
P–O	1.4993 1.4994 2 x 1.5387	1.4944 1.4945 2 x 1.5472
Na1–O	3 x 2.5117 3 x 2.5118	3 x 2.4951 3 x 2.4952
Na2–O	2 x 2.3489 2 x 2.4753 2.6089 2.6090 2 x 2.8377 2 x 3.2559	2 x 2.3643 2 x 2.4601 2.6239 2.6240 2 x 2.8331 2 x 3.2287
R_p/R_{wp}	7.69/10.17	6.77/9.02

Table S2.

Crystal lattice parameters for $Na_{3+x}V_{2-x}M^{II}_x(PO_4)_3/C$ ($M^{II} = Co^{2+}, Cu^{2+}$; x = 0−0.05).

Samples	Lattice constant, Å		
	a	*c*	*V*
$Na_3V_2(PO_4)_3$	8.7173(5)	21.7873(14)	1433.83(14)
$Na_{3.01}V_{1.99}Co_{0.01}(PO_4)_3$	8.7276(3)	21.7992(7)	1437.99(8)
$Na_{3.03}V_{1.97}Co_{0.03}(PO_4)_3$	8.7172(5)	21.7856(15)	1433.69(15)
$Na_{3.05}V_{1.95}Co_{0.05}(PO_4)_3$	8.7209(2)	21.7928(7)	1435.36(7)
$Na_{3.01}V_{1.99}Cu_{0.01}(PO_4)_3$	8.7167(3)	21.8218(9)	1435.89(10)
$Na_{3.03}V_{1.97}Cu_{0.03}(PO_4)_3$	8.7211(4)	21.7929(12)	1435.44(12)
$Na_{3.05}V_{1.95}Cu_{0.05}(PO_4)_3$	8.7205(5)	21.7964(16)	1435.47(16)

Table S3.

Theoretical ratios of Na, V, M^{II}, and P in M^{II}-NVP for various doping mechanisms.

Chemical composition	Molar ratio Na/V
$Na_3V_2(PO_4)_3$ (pure)	**1.5**
Doping of the V1 site with the simultaneous addition of sodium for Na sites	
$Na_{3.01}V_{1.99}M^{II}_{0.01}(PO_4)_3$	**1.513**
$Na_{3.03}V_{1.97}M^{II}_{0.03}(PO_4)_3$	**1.538**
$Na_{3.05}V_{1.95}M^{II}_{0.05}(PO_4)_3$	**1.564**
Doping of the Na1 site and the extraction of sodium from the Na sites	
$Na_{2.98}M^{II}_{0.01}V_2(PO_4)_3$	**1.49**
$Na_{2.94}M^{II}_{0.03}V_2(PO_4)_3$	**1.47**
$Na_{2.9}M^{II}_{0.05}V_2(PO_4)_3$	**1.45**
Doping of the V1 site during the formation of heterovalent pair M^{2+} + V^{4+} (provides for a partial valence change in vanadium)	
$Na_3V_{1.99}M^{II}_{0.01}(PO_4)_3$	**1.508**
$Na_3V_{1.97}M^{II}_{0.03}(PO_4)_3$	**1.523**
$Na_3V_{1.95}M^{II}_{0.05}(PO_4)_3$	**1.538**

Table S4.

ICP results for Co^{2+} doped $Na_3V_2(PO_4)_3$ samples.

Sample	Found molar fraction for NVP				Molar ratio Na/V
	Na	V	Co	P	
NVP (pure)	3.0301	2.1061	0	3.0703	**1.4387**
Co1-NVP	3.0105	1.9906	0.0098	3.1415	**1.5124**
Co5-NVP	3.0506	1.9465	0.0493	3.0762	**1.5672**

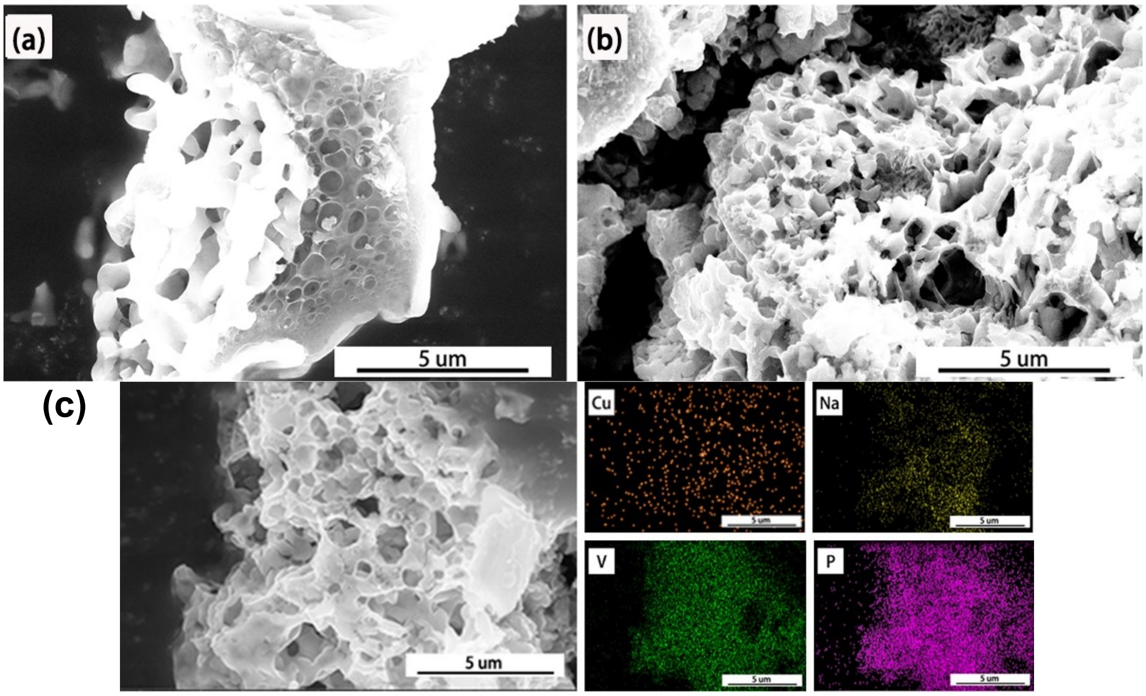

Figure S2. (a) SEM image of $Na_{3.03}V_{1.97}Co_{0.03}(PO_4)_3/C$; (b) SEM image of $Na_{3.05}V_{1.95}Co_{0.05}(PO_4)_3/C$; (c) SEM image and element mapping of $Na_{3.01}V_{1.99}Cu_{0.01}(PO_4)_3/C$.

Table S5.

The cycling performance of $Na_{3+x}V_{2-x}M^{II}_x(PO_4)_3/C$ (M^{II} = Co, Cu) compounds at 0.5C in a potential range of 2.5–4.0 V, mAh/g (capacity retention is indicated in %).

Sample	**Number of cycles**	
	1	**100**
NVP/C	93	88 (94.1%)
Co1-NVP/C	116	107 (92.2%)
Co3-NVP/C	108	103 (95.3%)
Co5-NVP/C	106	95 (88.9%)
Cu1-NVP/C	102	95 (93.4%)
Cu3-NVP/C	114	100 (87.7%)
Cu5-NVP/C	101	89 (87.9%)

Table S6.

The cycling performance of $Na_{3+x}V_{2-x}M^{II}_x(PO_4)_3/C$ (M^{II} = Co, Cu) compounds at 10C in a potential range of 2.5–4.0 V, mAh/g (capacity retention is indicated in %).

Sample	**Number of cycles**			
	1	**100**	**500**	**1000**
NVP/C	756	74 (97.4 %)	73 (95.8 %)	71 (93.3 %)
Co1-NVP/C	106	101 (94.8 %)	95 (89.3 %)	88 (83.2 %)
Co3-NVP/C	97	95 (97.0 %)	86 (88.6 %)	78 (80.3 %)
Co5-NVP/C	85	79 (92.0 %)	71 (83.5 %)	66 (77.4 %)
Cu1-NVP/C	89	88 (98.1 %)	84 (93.7 %)	83 (93.1 %)
Cu3-NVP/C	92	86 (93.8 %)	78 (84.6 %)	72 (78.8 %)
Cu5-NVP/C	83	80.3 (96.9 %)	74 (89.9 %)	69 (82.6 %)

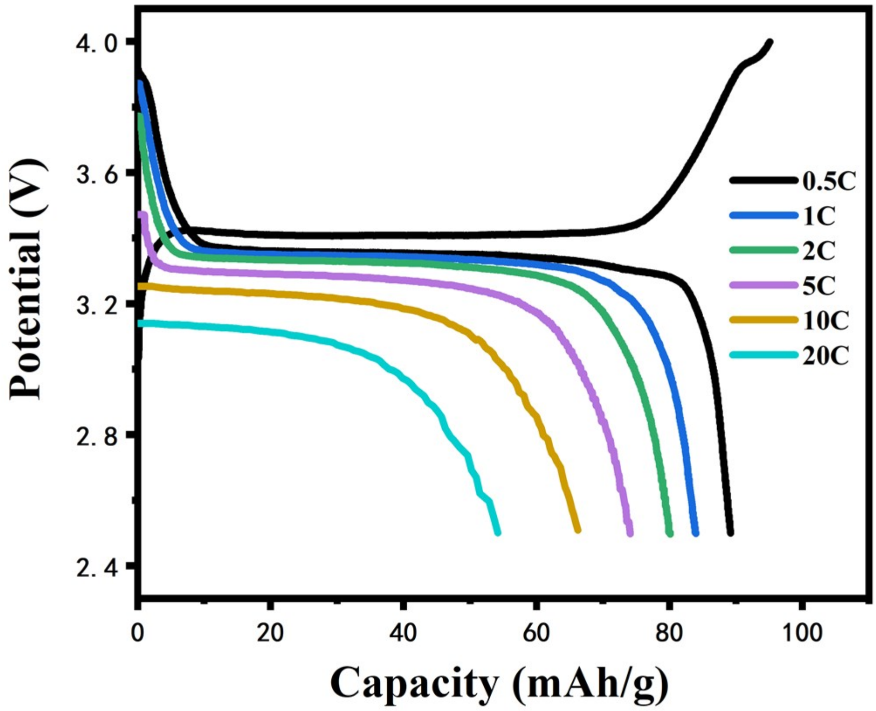

Figure S3. Charging-discharging profiles of NVP/C at different rates.

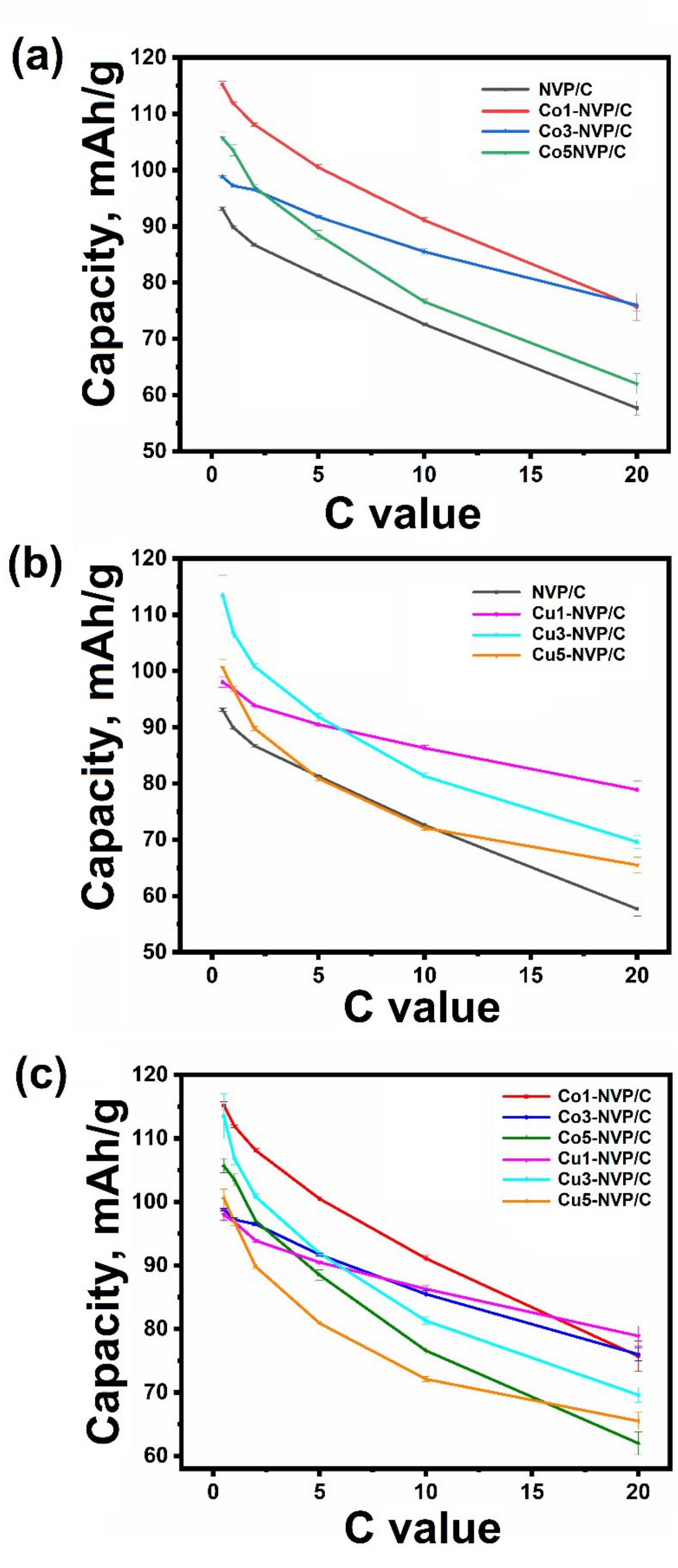

Figure S4. Changing the capacity of electrodes with different doping at different rates: (a) Co^{2+}-doped and pure NVP (b) Cu^{2+}-doped and pure NVP (c) comparison of Co^{2+} and Cu^{2+}-doped samples.

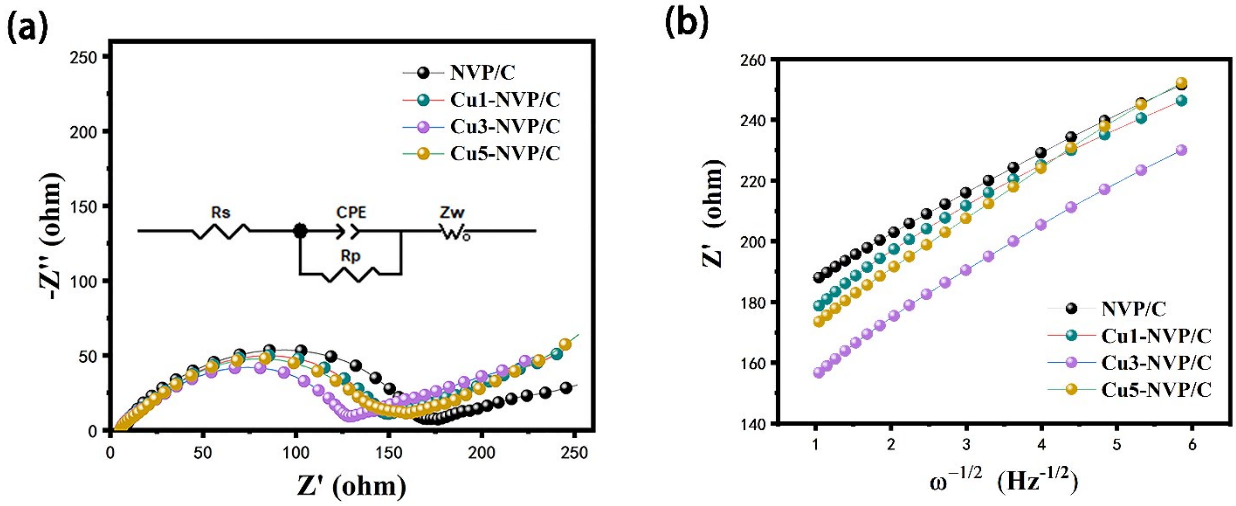

Figure S5. (a) Nyquist plots of $Na_{3+x}V_{2-x}Cu_x(PO_4)_3/C$ (x=0−0.05) after 100 cycles at 0.5 C (inset - the equivalent electrical circuit for the EIS); (b) Zwre and $\omega^{-1/2}$ relationship.

Table S7.

Kinetic parameters of $Na_{3+x}V_{2-x}M^{II}_x(PO_4)_3/C$ (M^{II} = Co, Cu; x = 0−0.05) obtained from equivalent circuit fitting.

Sample	R_s/Ω	R_p/Ω
NVP/C	7.104	150.03
Co1-NVP/C	6.942	85.12
Co3-NVP/C	5.6	92.3
Co5-NVP/C	5.243	101.6
Cu1-NVP/C	4.786	113
Cu3-NVP/C	4.72	110.3
Cu5-NVP/C	5.038	143.1

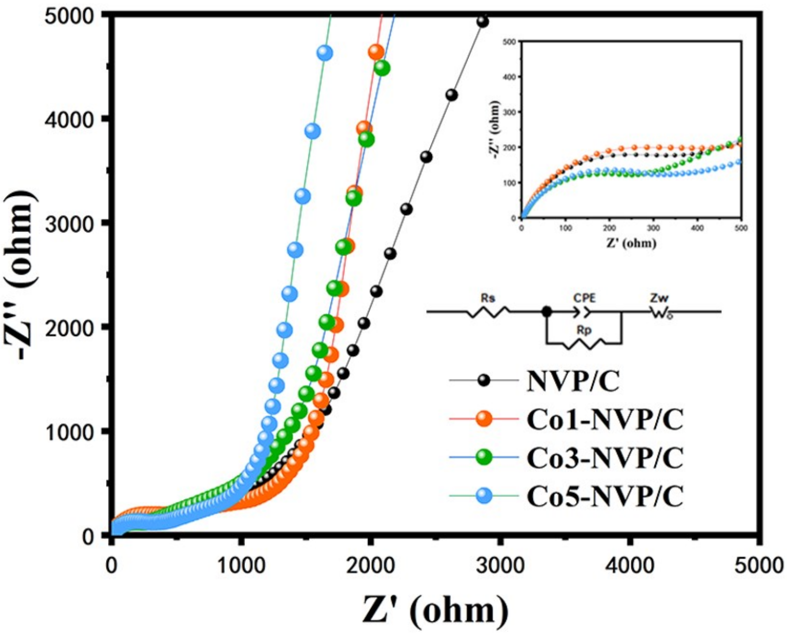

Figure S6. Nyquist plots of $Na_{3+x}V_{2-x}Co_x(PO_4)_3/C$ (x = 0−0.05) before testing, inset, the equivalent electrical circuit for the EIS.

Table S8.

Kinetic parameters of $Na_{3+x}V_{2-x}Co_x(PO_4)_3/C$ before testing obtained from equivalent circuit fitting.

Sample	R_s/Ω	R_p/Ω
NVP/C	4.218	430.6
Co1-NVP/C	3.648	390.5
Co3-NVP/C	3.945	371.0
Co5-NVP/C	3.385	300.2

Calculations of the diffusion coefficient (D_{Na+}) of sodium ions

To estimate the diffusion coefficient of sodium ions (D_{Na+}), the low-frequency region of the EIS spectra is used. The diffusion kinetics can be determined according to the following equations:

$$D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \quad \text{(S1)},$$

$$Z' = R_s + R_p + \sigma\omega^{-1/2} \quad \text{(S2)},$$

where R is the gas constant (8.314 J/molK), T stands for the absolute temperature (K), A is the contacting area of electrode with electrolyte (cm^2), n is the number of transferred electrons, F is the Faraday constant (96500 C/mol), C is the concentration of Na ions in the cathode electrode (3.47×10^{-3} mol/cm^{-3}), given the chemical composition of the active material, σ is the Warburg factor which can be calculated from Z'. The D_{Na+} can be calculated from equation (S1), σ is related to Z' through equation (S2), and its value can be determined from the slope of the line between Z' and $\omega^{-1/2}$.

Table S9.

Sodium diffusion coefficients of $Na_{3+x}V_{2-x}M^{II}_{x}(PO_4)_3/C$ (M^{II} = Co, Cu; x = 0−0.05).

Sample	D (cm^2/s)
NVP/C	5.05×10^{-11}
Co1-NVP/C	1.06×10^{-10}
Co3-NVP/C	2.86×10^{-11}
Co5-NVP/C	6.34×10^{-11}
Cu1-NVP/C	4.49×10^{-11}
Cu3-NVP/C	3.81×10^{-11}
Cu5-NVP/C	3.28×10^{-11}

Table S10.

A comparison of the electrochemical performance of prepared Co- and Cu-doped NVP/C with the similar M^{2+} or M^{3+}-doped NVP electrodes.

Composition	Specific Capacity (mAh/g)	Cycle Number	C-rate	Capacity Retention (%)	Ref.
Co^{2+}-doped NVP					
$Na_{3.01}V_{1.99}Co_{0.01}(PO_4)_3$	**116**	**100**	**0.5C**	**92.2**	**This work**
	106	**1000**	**10C**	**83.3**	
$Na_{3.03}V_{1.97}Co_{0.03}(PO_4)_3$	**108**	**100**	**0.5C**	**95.3**	**This work**
	97	**1000**	**10C**	**80.3**	
$Na_{3.05}V_{1.95}Co_{0.05}(PO_4)_3$	**106**	**100**	**0.5C**	**88.9**	**This work**
	85	**1000**	**10C**	**77.4**	
$Na_{3.1}V_{1.9}Co_{0.1}(PO_4)_3$	111	100	1C	99	[49]
$Na_{3.5}V_{1.5}Co_{0.5}(PO_4)_3$	83	100	1C	97	[49]
Cu^{2+}-doped NVP					
$Na_{3.01}V_{1.99}Cu_{0.01}(PO_4)_3$	**102**	**100**	**0.5C**	**93.4**	**This work**
	89	**1000**	**10**	**83.2**	
$Na_{3.03}V_{1.97}Cu_{0.03}(PO_4)_3$	**114**	**100**	**0.5C**	**87.7**	**This work**
	92	**1000**	**10C**	**78.8**	
$Na_{3.05}V_{1.95}Cu_{0.05}(PO_4)_3$	**101**	**100**	**0.5C**	**87.9**	**This work**
	83	**1000**	**10C**	**82.6**	
Ni^{2+}-doped NVP					
$Na_{3.03}V_{1.97}Ni_{0.03}(PO_4)_3$	113.4	100	0.5C	90.5	[40]
	107.1	100	1C	95.5	
$Na_3V_{1.97}Ni_{0.03}(PO_4)_3$	98.1	50	5C	93.5	[52]
$Na_{3.1}V_{1.9}Ni_{0.1}(PO_4)_3$	109	100	1C	94.7	[49]
Mn^{2+}-doped NVP					
$Na_3V_{1.875}Mn_{0.025}(PO_4)_3$	89.2	100	10C	97.2	[38]
	86.7	100	15C	91.6	
$Na_3V_{1.9}Mn_{0.1}(PO_4)_3$	78	50	10C	90	[69]
$Na_3V_{1.8}Mn_{0.2}(PO_4)_3$	77.8	10.000	30C	82	[70]
$Na_3V_{1.7}Mn_{0.3}(PO_4)_3$	104	20	0.5C	-	[39]
	92	20	2C	-	
Mg^{2+}-doped NVP					
$Na_3V_{1.95}Mg_{0.05}(PO_4)_3$	86.2	50	20C	81	[36]
$Na_3V_{1.95}Mg_{0.05}(PO_4)_3$	102	108	1C	90.2	[37]
	96.7	180	10C	88.9	
$Na_3V_{1.93}Mg_{0.07}(PO_4)_3$	95	1000	10C	84.6	[51]
$Na_{3.1}V_{1.9}Mg_{0.1}(PO_4)_3$	113	100	1C	94	[49]
$Na_{3.5}V_{1.5}Mg_{0.5}(PO_4)_3$	100	100	1C	97	[49]
Al^{3+}-doped NVP					
$Na_3V_{1.98}Al_{0.02}(PO_4)_3$	95.8	50	0.6C	99.2	[42]
$Na_3V_{1.8}Al_{0.2}(PO_4)_3$	117.1	100	1C	95	[72]
Cr^{3+}-doped NVP					
$Na_3V_{1.92}Cr_{0.08}(PO_4)_3$	112.2	50	0.1C	97.2	[45]
$Na_3V_{1.9}Cr_{0.1}(PO_4)_3$	107	40	2C	99	[18]
La^{3+}-doped NVP					
$Na_3V_{1.99}La_{0.01}(PO_4)_3$	108.1	100	0.2C	97	[46]