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Supporting Information

Robust Cross-Linked $Na_3V_2O_{1.6}(PO_4)_2F_{1.4}$@rGO&MWCNTs as High-Performance Cathode for Aqueous Zinc-Ion Batteries

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Material characterization

The Rigaku SmartLab diffractometer was employed to record the X-ray diffraction (XRD) patterns of the samples. Scanning electron microscopy (SEM, JEOL-6300F) was utilized to investigate the morphologies of the samples. Raman spectroscopy was acquired using LabRAM HR evolution. X-ray photoelectron spectroscopy (XPS) analysis was conducted using Thermo Fisher Escalab 250Xi. Thermogravimetric (TG) analysis was conducted using a TGA 4000 instrument in air with a heating rate of 5 °C min^{-1}.

Electrochemical measurements

The electrode slurry was composed of the active material, super P, and polyvinylidene fluoride (PVDF) in a mass ratio of 7:2:1, using N-methyl-2-pyrrolidone (NMP) as the solvent. The slurry was uniformly coated onto a stainless steel mesh with

a diameter of 12 mm and vacuum-dried at 60 °C for 12 h, resulting in electrodes with an active material mass loading of approximately 2 mg cm^{-2}. The specific capacity was calculated using the total mass of N3VOPF@rGO&MWCNTs or N3VOPF@rGO. The cell was assembled in ambient air, with glass fiber as the separator, zinc foil as the anode, and an aqueous solution containing 2 M zinc triflate ($Zn(CF_3SO_3)_2$) and 4 M lithium triflate ($LiCF_3SO_3$) as the electrolyte. Soft-pack battery was fabricated by stacking positive electrode (3.2×3.5 cm^2) with approximately 12 mg active material, glass fiber separator (4.2×4.8 cm^2), and zinc foil anode (3.4×3.7 cm^2) within aluminum-plastic film pouches (5.0×6.0 cm^2). The electrolyte was injected into the soft-pack battery, followed by air evacuation and heat sealing. The galvanostatic charge/discharge (GCD) tests were conducted using the Neware battery testing system (CT-4008 T). Cyclic voltammetry (CV) profiles were obtained using an electrochemical workstation (CHI 760E) within a voltage range of 0.4–1.9 V. Electrochemical impedance spectroscopy (EIS) data were collected employing an electrochemical workstation (CHI 660E) across a frequency range of 0.01–10^5 Hz.

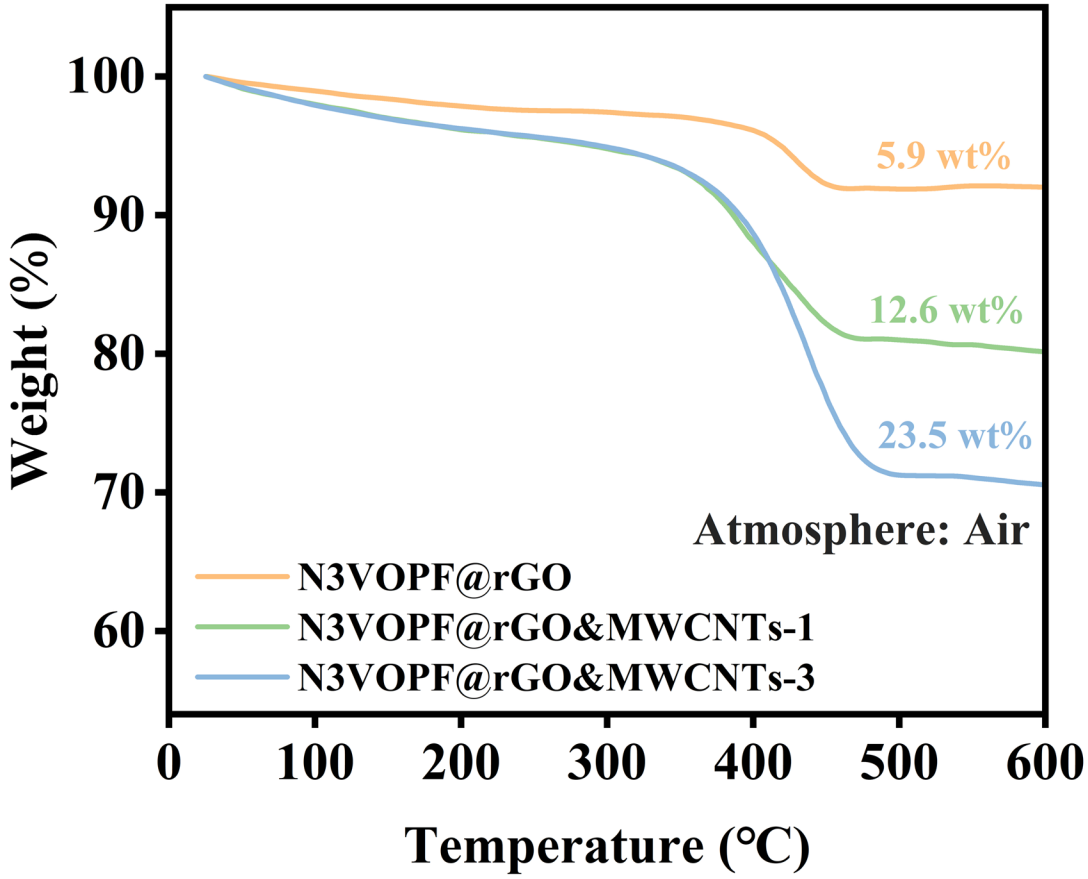

Fig. S1 TG curves in the air atmosphere.

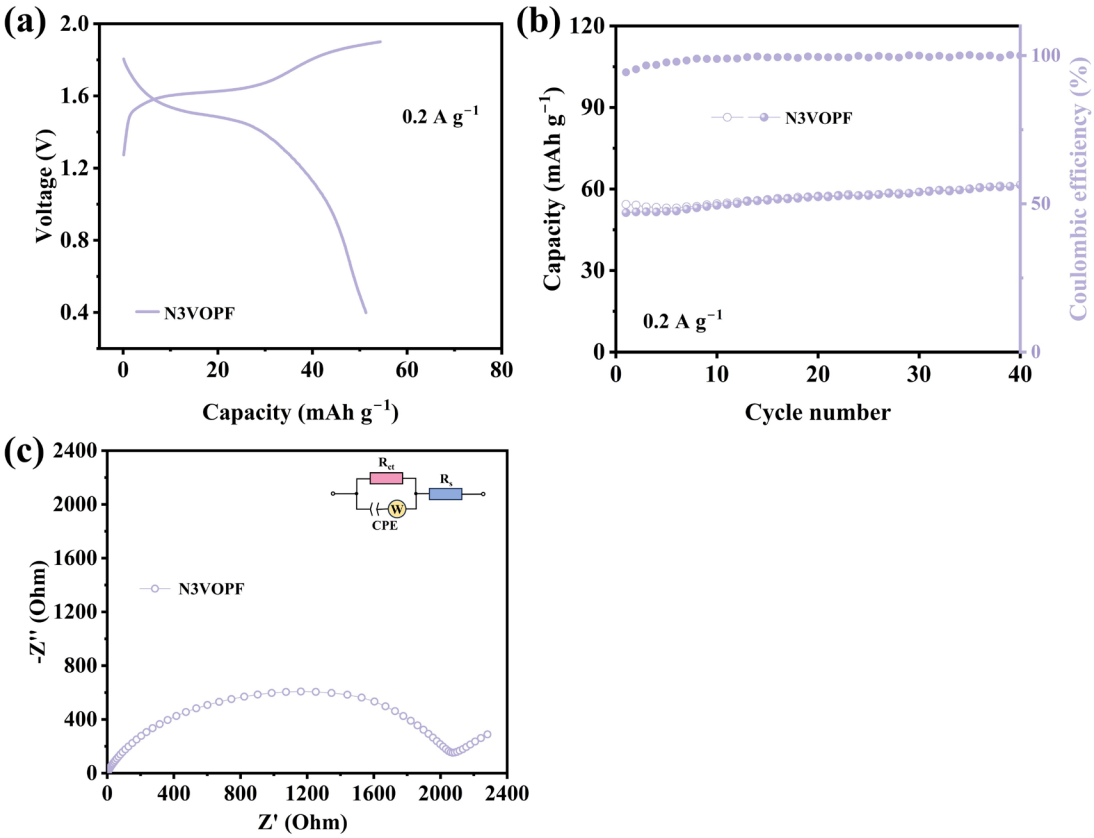

Fig. S2 (a) GCD profile of N3VOPF at 0.2 A g^{-1}. (b) Cycling performance of N3VOPF at 0.2 A g^{-1}. (c) Nyquist plot of N3VOPF.

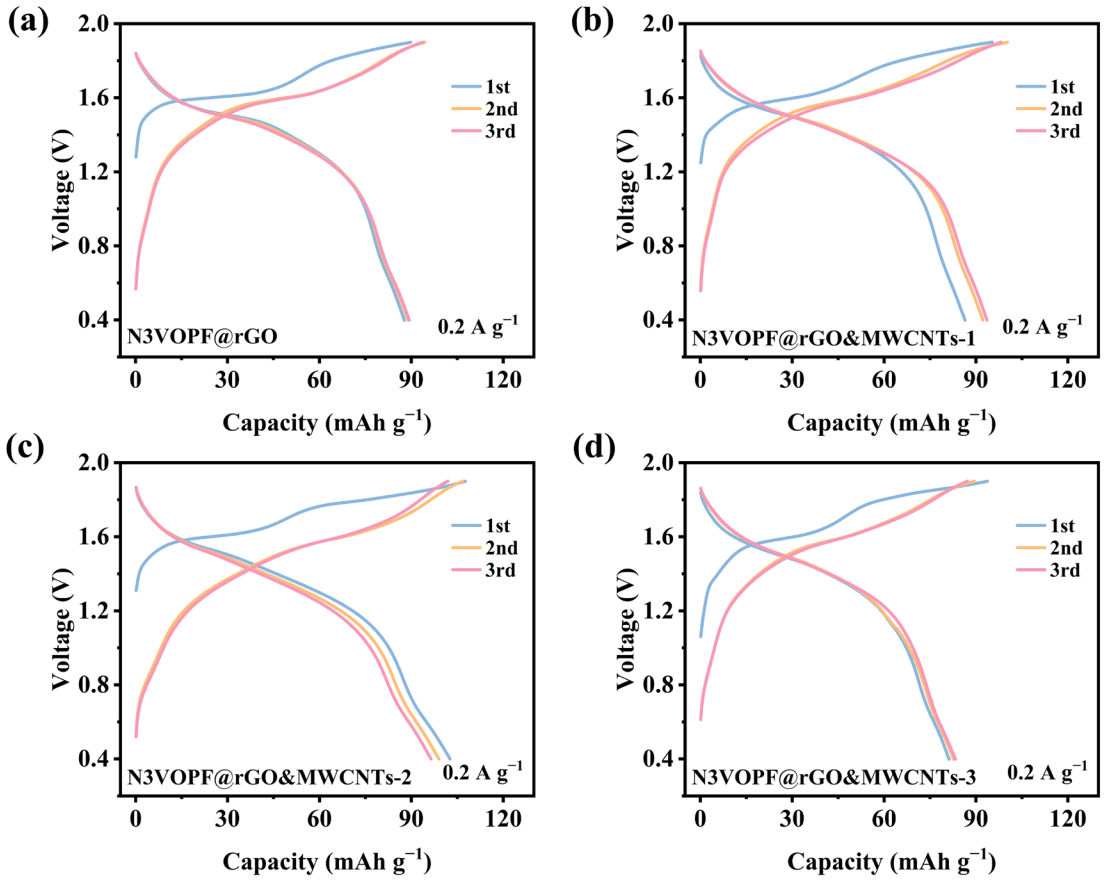

Fig. S3 Initial GCD profiles of (a) N3VOPF@rGO, (b) N3VOPF@rGO&MWCNTs-1, (c) N3VOPF@rGO&MWCNTs-2, and (d) N3VOPF@rGO&MWCNTs-3 at 0.2 A g^{-1}.

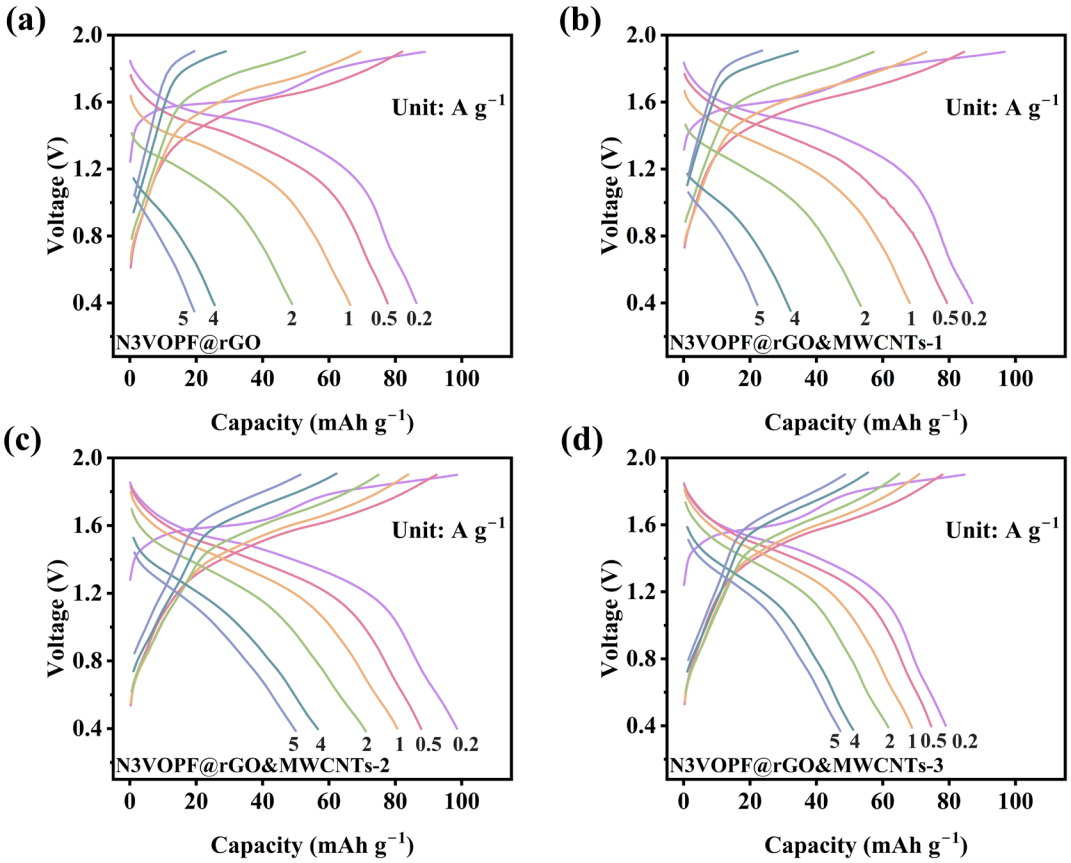

Fig. S4 GCD profiles of (a) N3VOPF@rGO, (b) N3VOPF@rGO&MWCNTs-1, (c) N3VOPF@rGO&MWCNTs-2, and (d) N3VOPF@rGO&MWCNTs-3 at different current densities from 0.2 to 5 A g^{-1}.

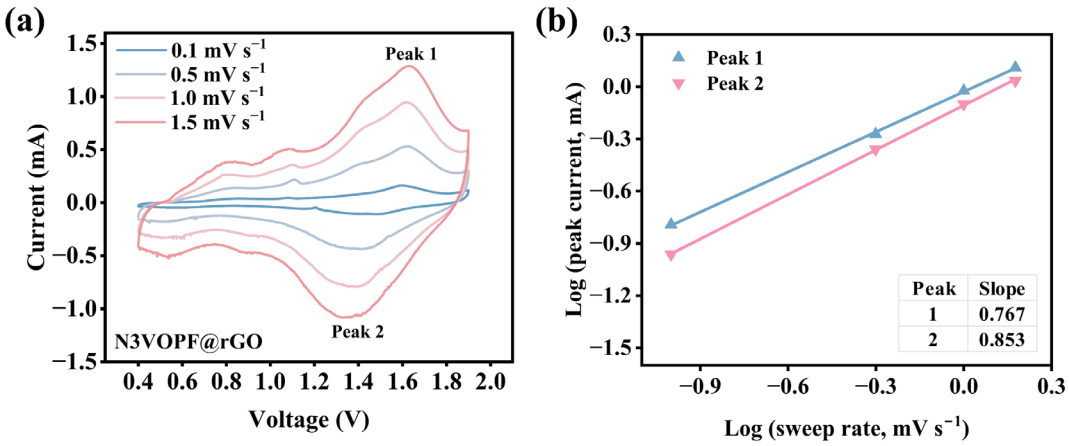

Fig. S5 (a) CV curves at different scan rates for N3VOPF@rGO electrode.

(b) Linear relationship between Log (i) and Log (v).

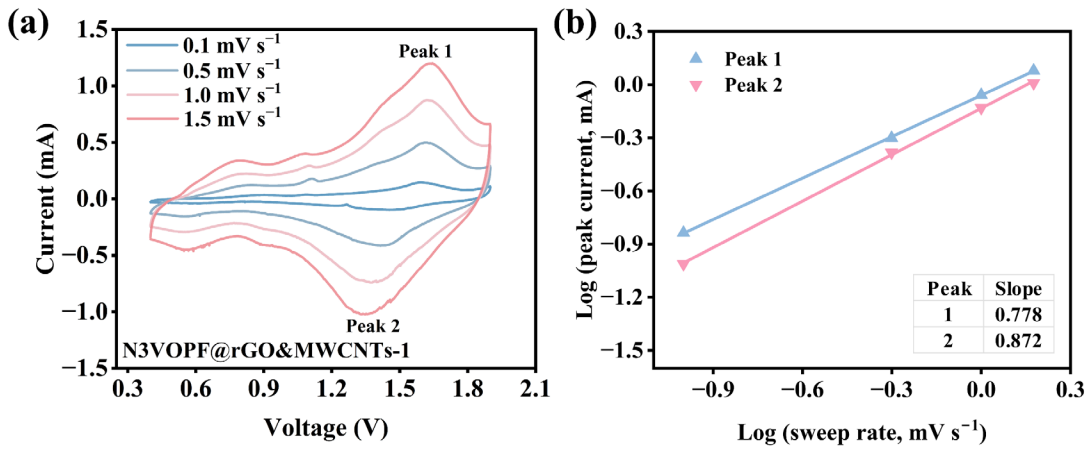

Fig. S6 (a) CV curves at different scan rates for N3VOPF@rGO&MWCNTs-1 electrode. (b) Linear relationship between Log (i) and Log (v).

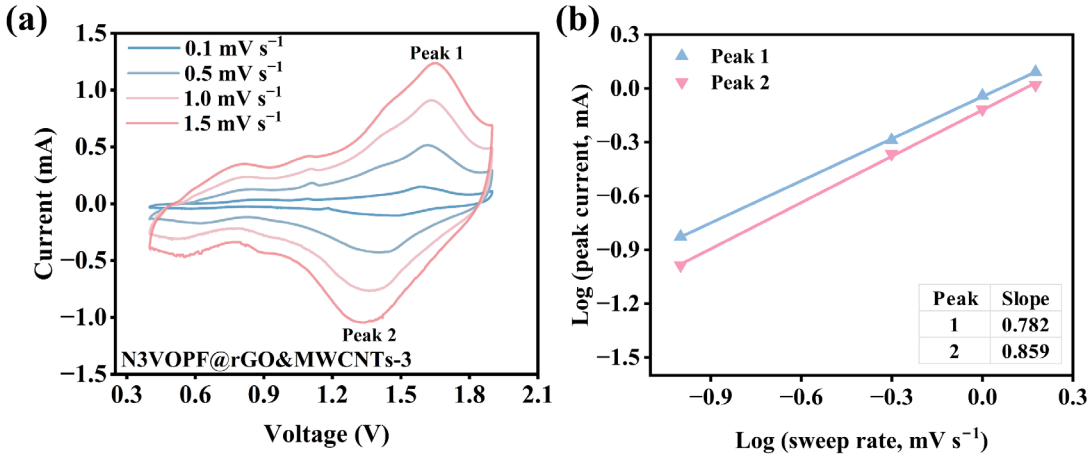

Fig. S7 (a) CV curves at different scan rates for N3VOPF@rGO&MWCNTs-3 electrode. (b) Linear relationship between Log (i) and Log (v).

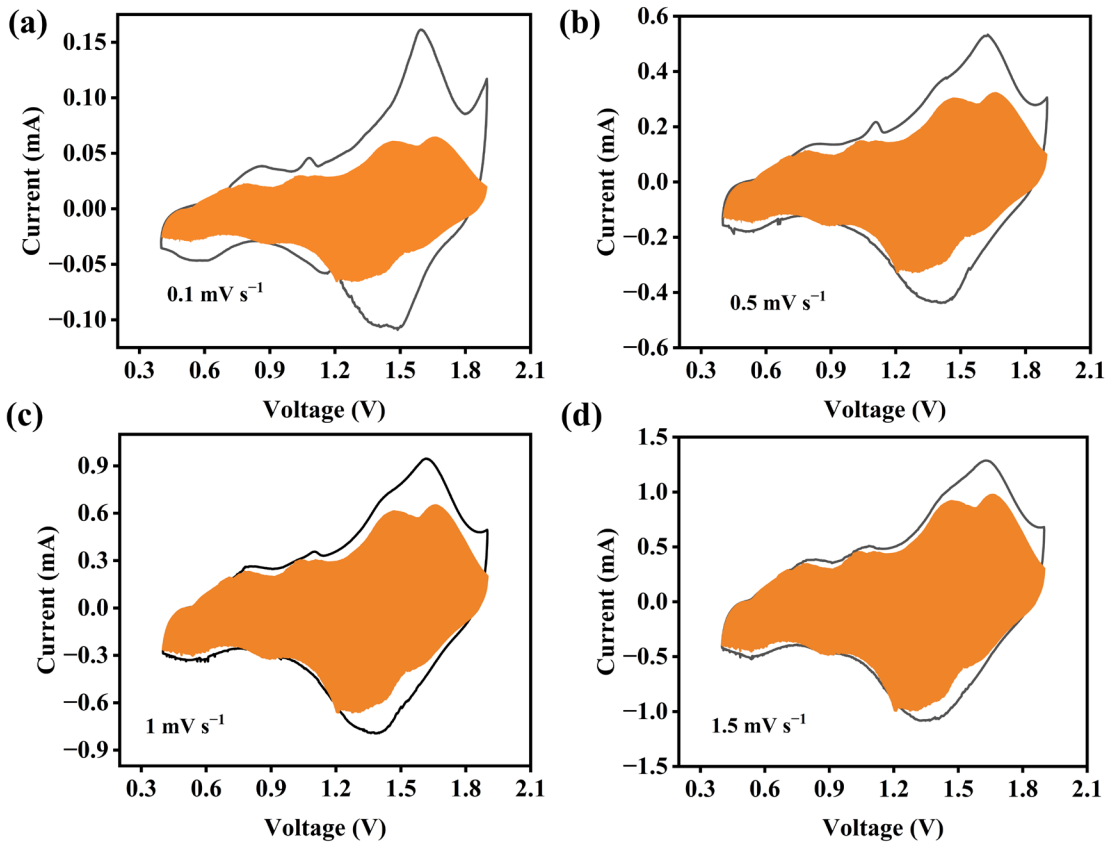

Fig. S8 The capacitive controlled portion at different scan rates for N3VOPF@rGO electrode.

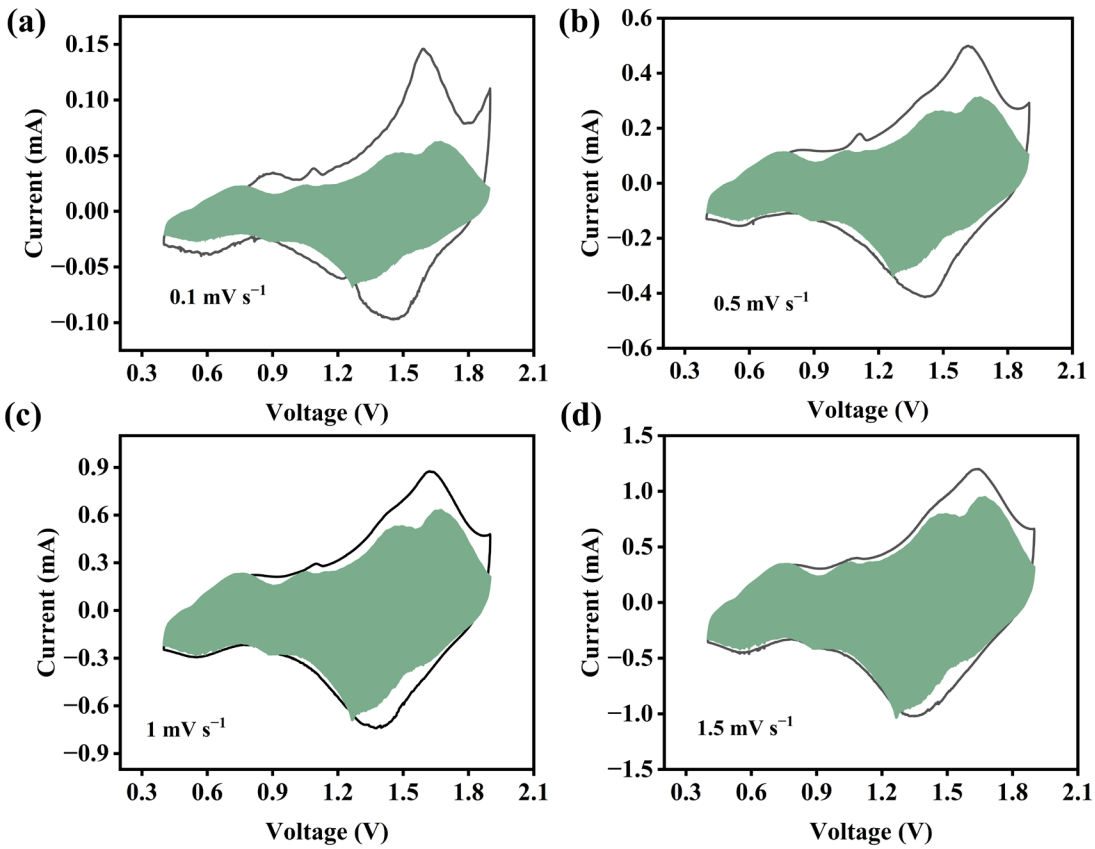

Fig. S9 The capacitive controlled portion at different scan rates for N3VOPF@rGO&MWCNTs-1 electrode.

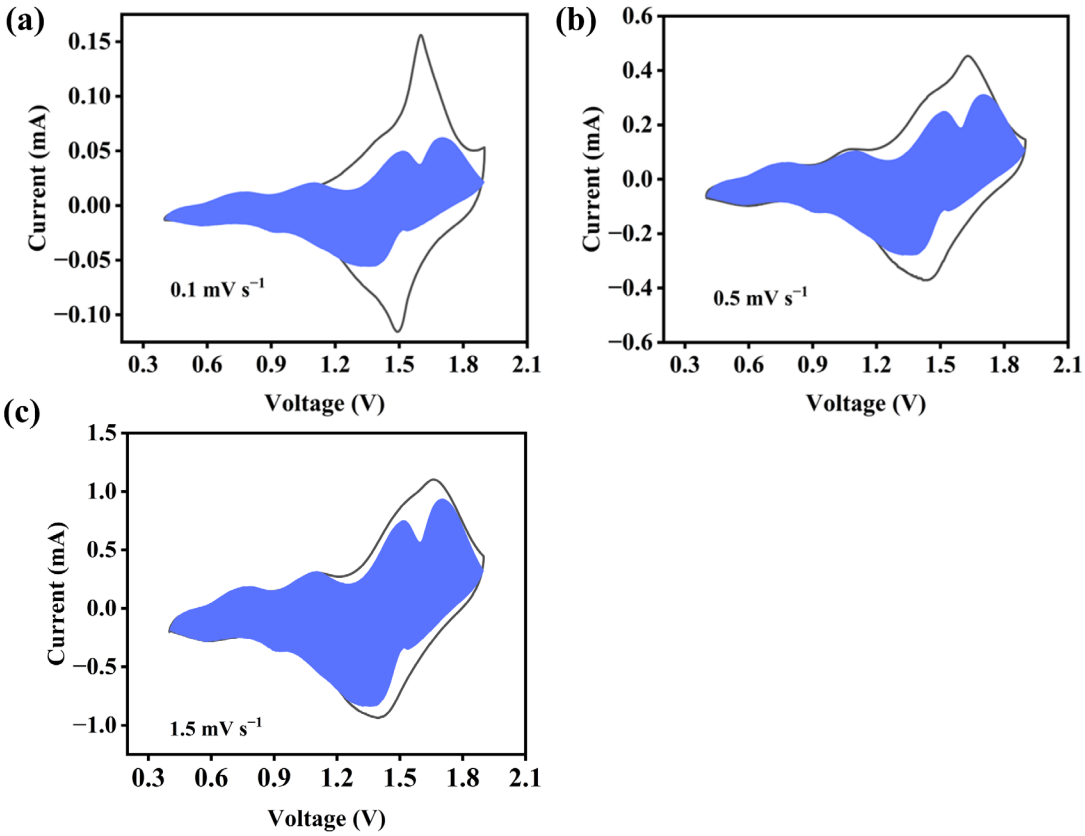

Fig. S10 The capacitive controlled portion at different scan rates for N3VOPF@rGO&MWCNTs-2 electrode.

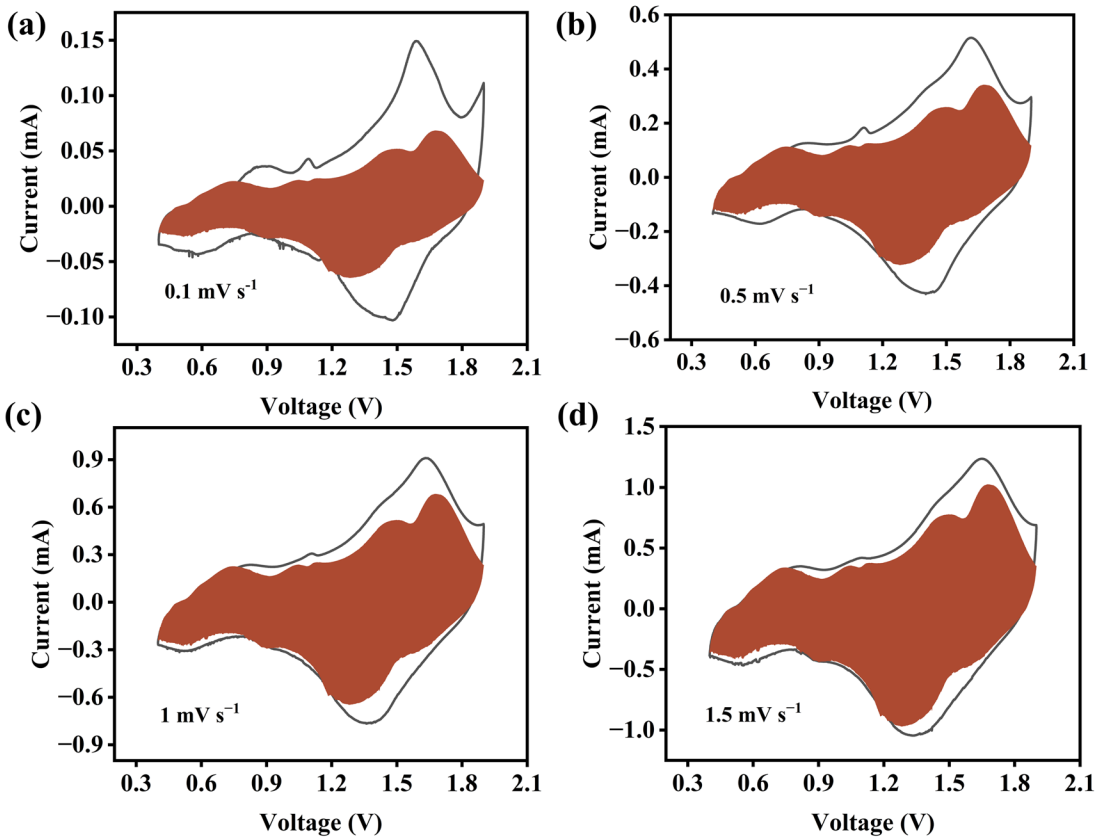

Fig. S11 The capacitive controlled portion at different scan rates for N3VOPF@rGO&MWCNTs-3 electrode.

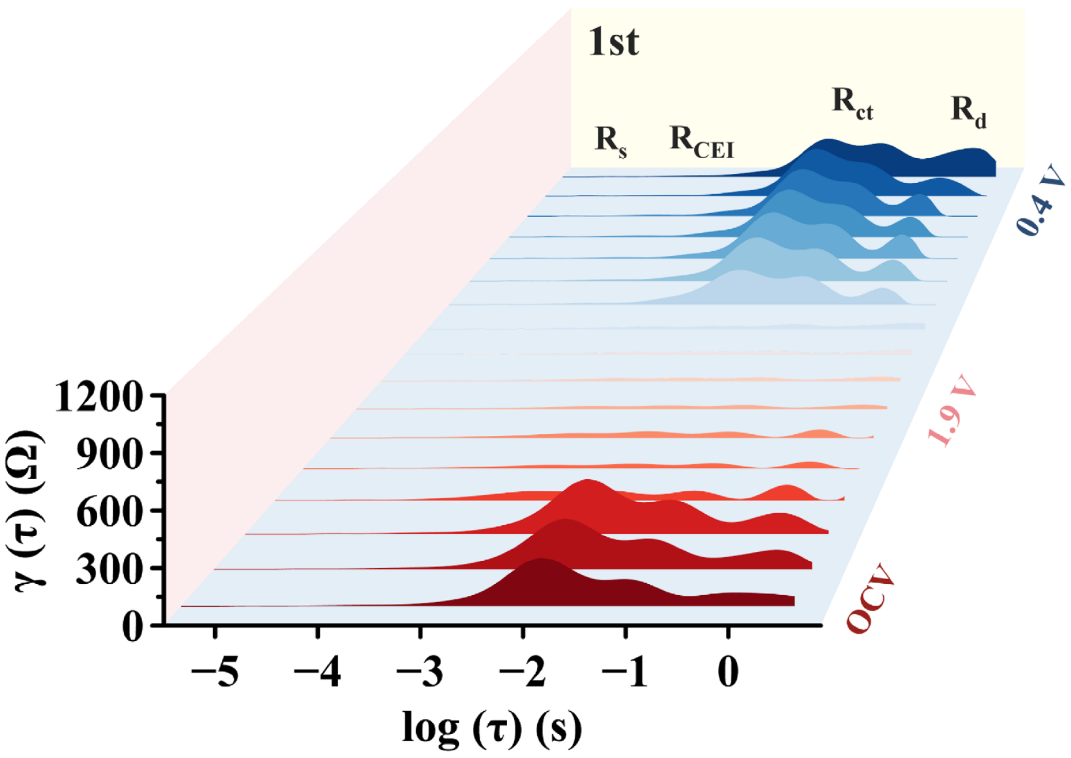

Fig. S12 DRT plots of N3VOPF@rGO&MWCNTs-2 for the first cycle.

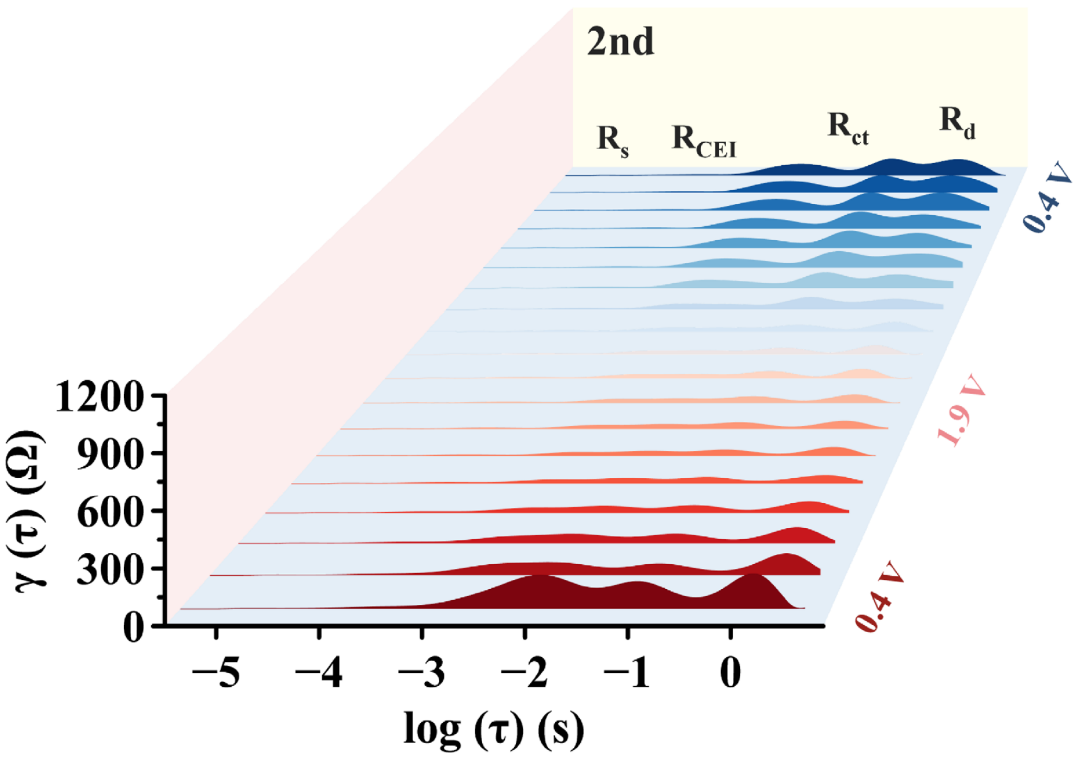

Fig. S13 DRT plots of N3VOPF@rGO&MWCNTs-2 for the second cycle.

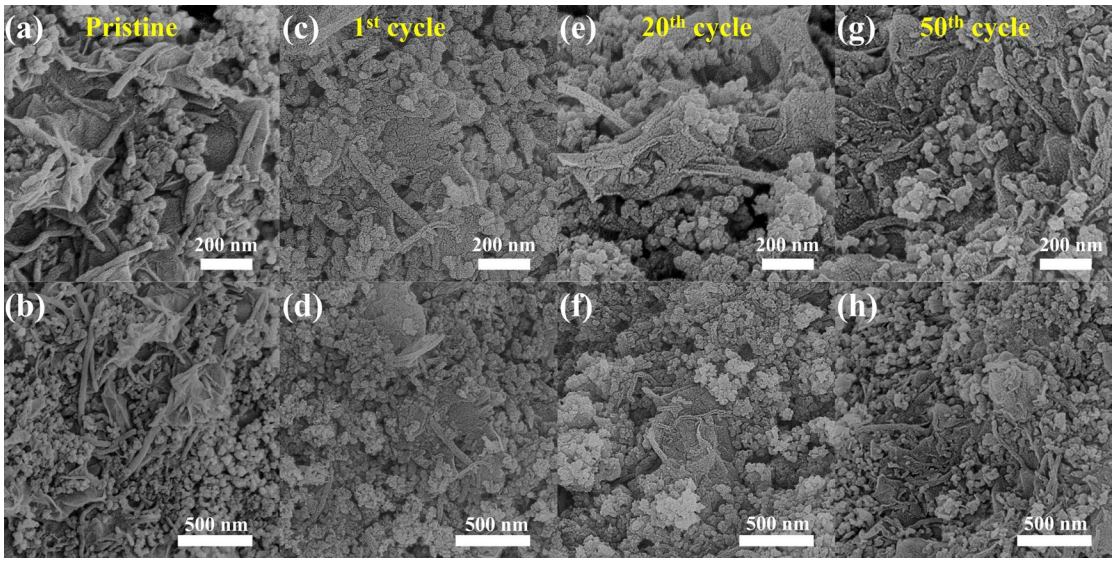

Fig. S14 SEM images of N3VOPF@rGO&MWCNTs-2 electrode cycled at 0.2 A g^{-1} for (a, b) pristine, (c, d) 1st cycle, (e, f) 20th cycle, and (g, h) 50th cycle states.

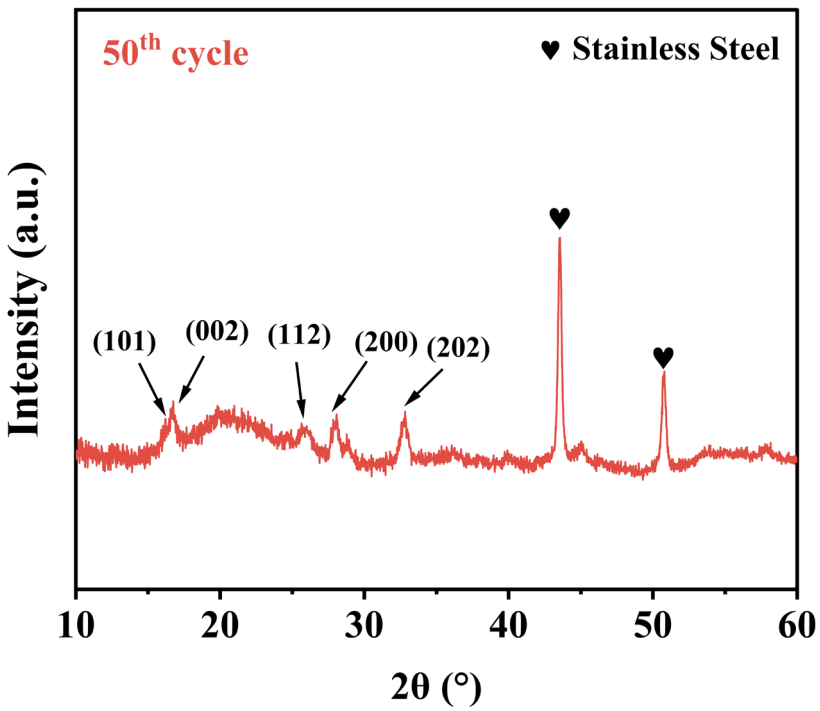

Fig. S15 XRD pattern of N3VOPF@rGO&MWCNTs-2 after 50 cycles.

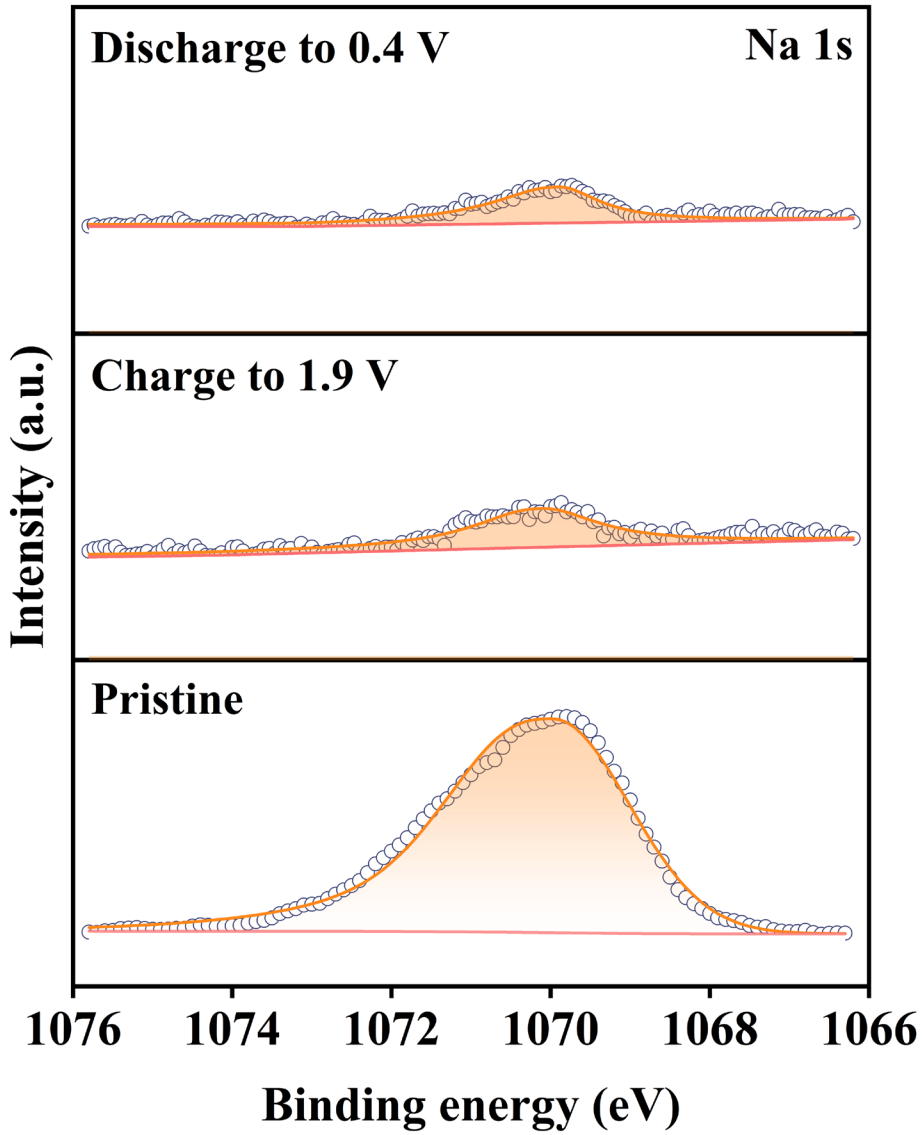

Fig. S16 XPS Na 1s spectra of N3VOPF@rGO&MWCNTs-2 at different states.

Table S1 Refined atomic occupancies in N3VOPF@rGO.

Space group: *I4/mmm*. a=b=6.389 Å, c=10.629 Å, V=433.874 Å^3

Name	x	y	z	Occ	Mult
O2	0.00000	0.00000	0.35350	0.125	4
Na2	-0.34893	-0.24529	0.00000	0.095	16
O1	0. 31194	0.00000	0.16349	0.500	16
P1	0.50000	0.00000	0.25000	0.125	4
V1	0.00000	0.00000	0.19832	0.125	4
Na1	-0.25038	-0.25038	0.00000	0.095	8
F1	0.00000	0.00000	0.00000	0.062	2

Table S2 Refined atomic occupancies in N3VOPF@rGO&MWCNTs-1.

Space group: *I4/mmm*. a=b=6.386 Å, c=10.636 Å, V=433.699 Å^3

Name	x	y	z	Occ	Mult
O2	0.00000	0.00000	0.35350	0.125	4
Na2	-0.34893	-0.24529	0.00000	0.095	16
O1	0. 31194	0.00000	0.16349	0.500	16
P1	0.50000	0.00000	0.25000	0.125	4
V1	0.00000	0.00000	0.19832	0.125	4
Na1	-0.25038	-0.25038	0.00000	0.095	8
F1	0.00000	0.00000	0.00000	0.062	2

Table S3 Refined atomic occupancies in N3VOPF@rGO&MWCNTs-2.

Space group: *I4/mmm*. a=b=6.384 Å, c=10.632 Å, V= 433.349 Å^3

Name	x	y	z	Occ	Mult
O2	0.00000	0.00000	0.35936	0.125	4
Na2	-0.33222	-0.25537	0.00000	0.095	16
O1	0.31009	0.00000	0.16569	0.500	16
P1	0.50000	0.00000	0.25000	0.125	4

V1	0.00000	0.00000	0.19730	0.125	4
Na1	-0.24461	-0.24461	0.00000	0.095	8
F1	0.00000	0.00000	0.00000	0.062	2

Table S4 Refined atomic occupancies in N3VOPF@rGO&MWCNTs-3.

Space group: *I4/mmm*. a=b= 6.386 Å, c= 10.647 Å, V= 434.251 Å^3

Name	x	y	z	Occ	Mult
O2	0.00000	0.00000	0.36036	0.125	4
Na2	-0.33360	-0.24741	0.00000	0.095	16
O1	0.31031	0.00000	0.16769	0.500	16
P1	0.50000	0.00000	0.25000	0.125	4
V1	0.00000	0.00000	0.19580	0.125	4
Na1	-0.25211	-0.25211	0.00000	0.095	8
F1	0.00000	0.00000	0.00000	0.062	2

Table S5 The charge transfer resistances and ion diffusion coefficients for as-prepared samples.

Sample ID	**R_{ct} (Ω)**	**Average D_{Zn}^{2+} (10^{-10} cm^2 s^{-1})**
N3VOPF@rGO	1849	2.79
N3VOPF@rGO&MWCNTs-1	1563	2.88
N3VOPF@rGO&MWCNTs-2	844	3.54
N3VOPF@rGO&MWCNTs-3	1014	2.15