Electronic Supplementary Information for

Symmetric Full Cell Assembled by Self-supporting $Na_3V_2(PO_4)_3$ Bipolar Electrodes for Superior Sodium Energy Storage

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Experimental Section

Synthesis of $Na_3V_2(PO_4)_3$/carbon elastic foam: A given amount of NaH_2PO_4 (0.115 g, 99%, Alfa Aesar), NH_4VO_3 (0.078 g, 99%, Alfa Aesar), oxalic acid (0.168 g, 99%, Alfa Aesar) and sucrose (0.1 g, 99%, Alfa Aesar) was dissolved in 40 mL deionized water to form a clear green solution. Then the solution was totally absorbed by a piece of melamine foam (5 cm × 3 cm × 3 cm). Afterwards, this melamine foam was transferred to oven for 12 h at 80 °C and the NVP foam precursor was obtained. The NVP foam precursor was first sintered at 350 °C for 4 h and then annealed at 700 °C for 4 h in Ar/H_2 (95%:5%) with the heating rate of 5 °C min^{-1}. Finally, the NVP/ECF was achieved. In contrast, sucrose are replaced by blank (without sucrose), hexadecyl trimethyl ammonium bromide (CTAB) and polyvinyl pyrrolidone (PVP) respectively to prepare NVP/ECF under the same condition and the digital picture are shown in Figure S1.

Electrochemical Measurements for SIB: The electrochemical test of NVP/ECF self-supporting electrode in half cell were carried out using CR2032 coin-type cells,

consisting of a NVP/ECF self-supporting electrode and sodium metal anode separated by a glass fiber. The cell were assembled in a glove box filled with dried argon gas. For full cell assembly, the NVP/ECF self-supporting electrodes (0.7 cm × 0.7 cm) was used as cathode and NVP/ECF self-supporting electrodes (1 × 1 cm) was used as anode, these two electrodes were separated by a piece of glass fiber under vacuum. Polyethylene film was used as a transparent packaging substance. The electrolyte was a mixture of ethylene carbonate and dimethyl carbonate 1:1 (w/w) containing 1 M $NaClO_4$ and 5 wt% flouroethylene carbonate additive.

CV and charge/discharge measurements were carried out on a CHI660D electrochemistry workstation and Land Battery Measurement System at room temperature. In half cell system, the electrochemical test was conducted at various current densities in different voltage ranges (2.5 V ~ 4.0 V for cathode test and 1.2 V ~ 2.5 V for anode test). CV studies were carried out between 1.2 and 4 V at 0.5 mV s^{-1}. In full cell system, the electrochemical test was conducted at various current densities in the voltage range of 1.0 V ~ 2.5 V. CV studies were carried out between 1.0 and 2.5 V at 0.2 mV s^{-1}, 0.5 mV s^{-1} and 1 mV s^{-1}.

Characterizations: HRTEM micrographs were obtained with a Philips Tecnai F20 FEG-TEM (The USA) operated at 200 kV. Raman spectrum of powder samples were recorded on LabRAM HR Raman microscope with a laser excitation wavelength of 532 nm. The X-ray diffraction XRD patterns were obtained using a Rigaku D/MAX-RB with monochromatized Cu Kα radiation (λ=1.5418 Å) in the 2θ ranging from 10° to 60°. X-ray photoelectron spectra (XPS) were conducted using a PHI

Quantera SXM instrument equipped with an Al X-ray excitation source (1486.6 eV). Binding energies (BEs) are referenced to the C1s of carbon contaminants at 284.6 eV. All samples were prepared by depositing a thin layer of products onto a cleaned Si wafer and drying at room temperature.

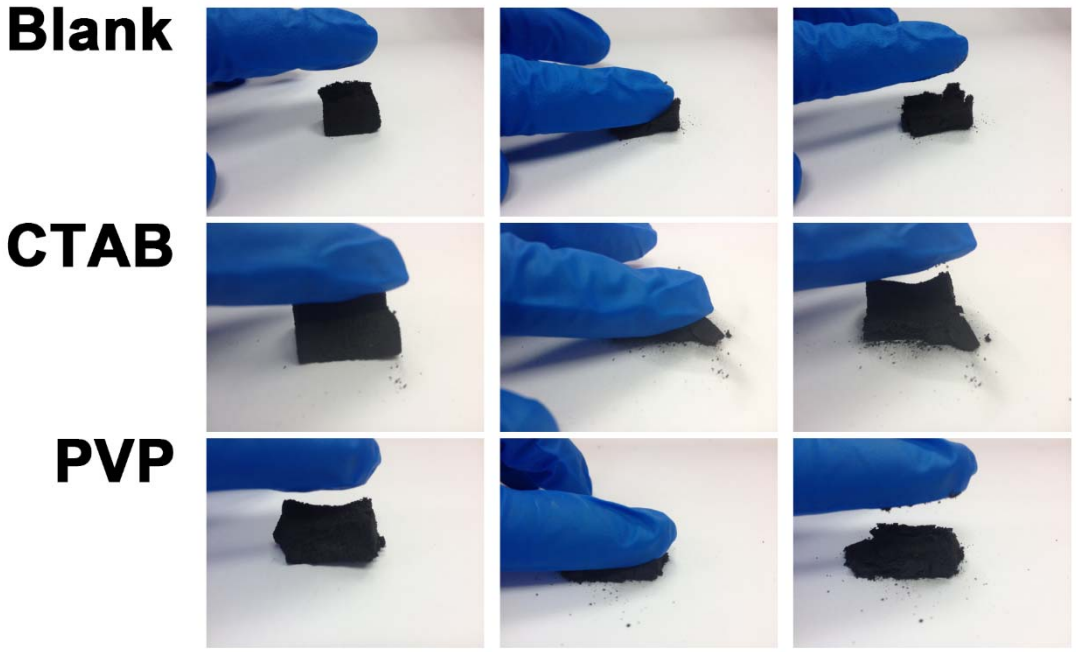

Figure S1. Digital picture of the NVP/CF samples prepared under other conditions.

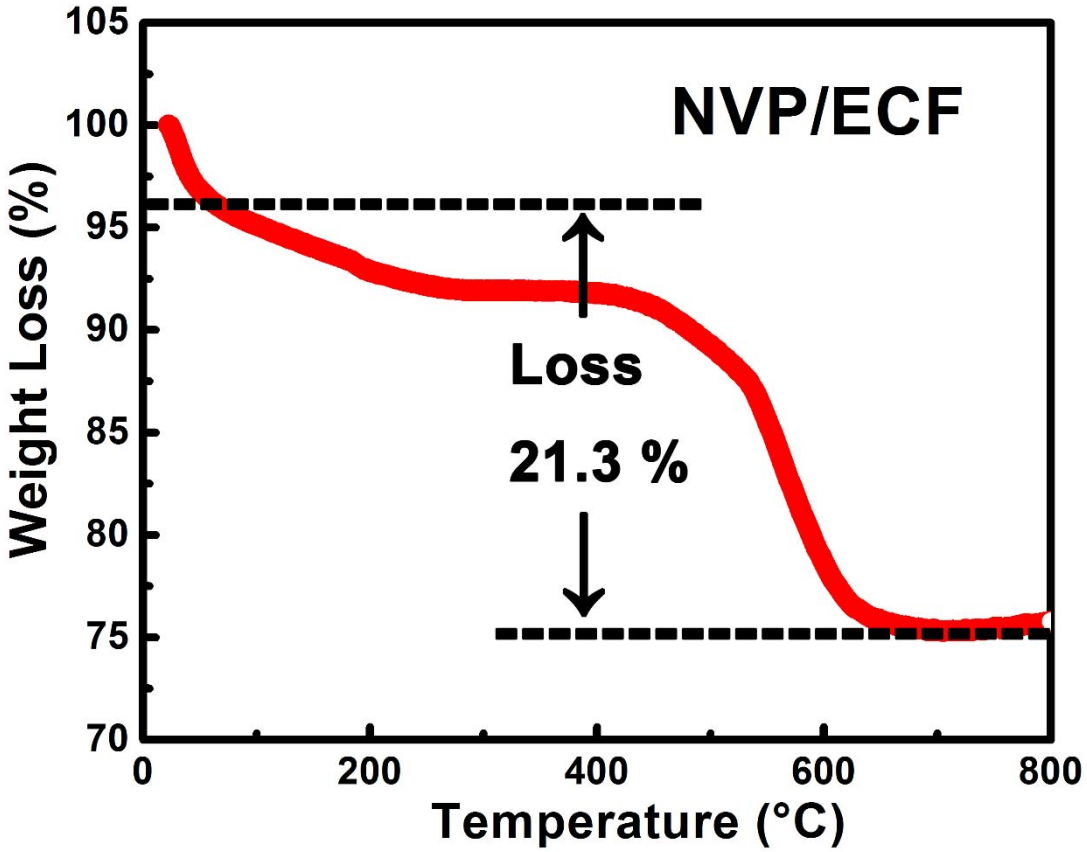

Figure S2. TG curve of the NVP/ECF sample in air atmosphere.

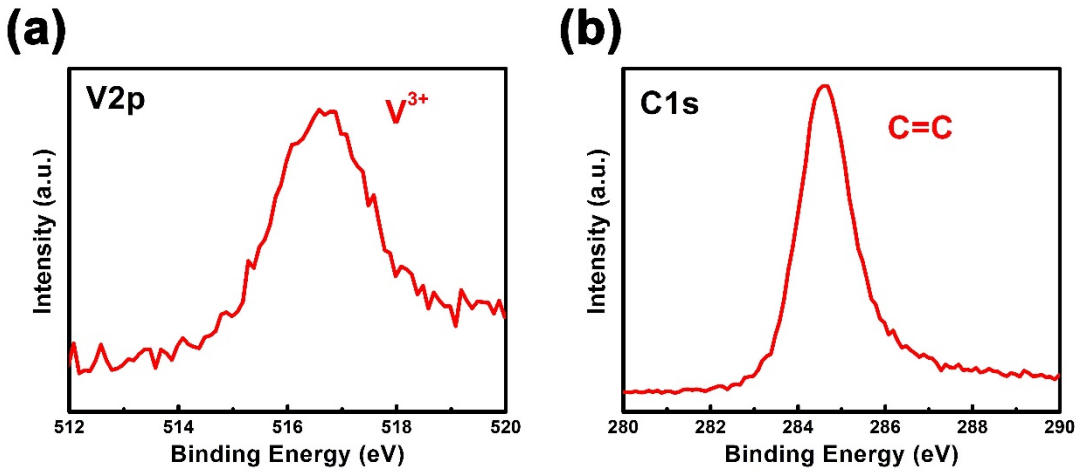

Figure S3. XPS spectra of V2p (a) and C1s (b) for the NVP/ECF sample.

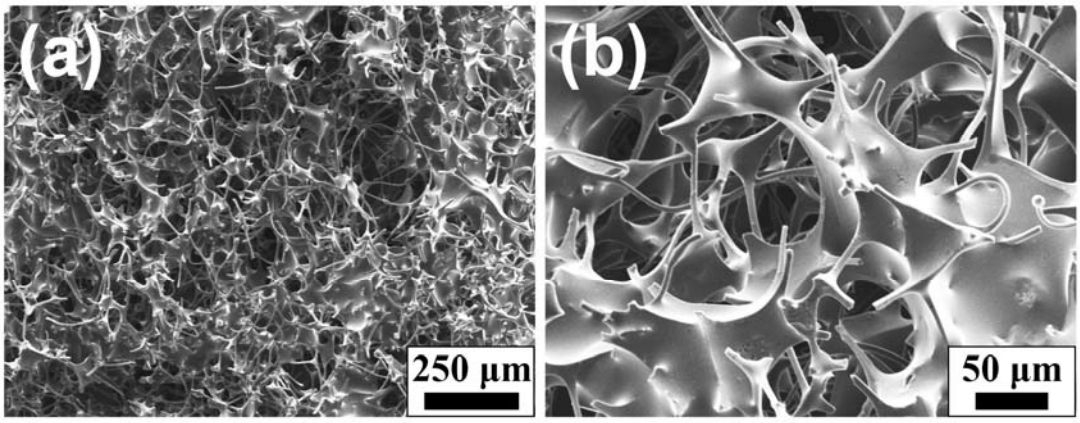

Figure S4. SEM images of NVP/melamine foam precursor.

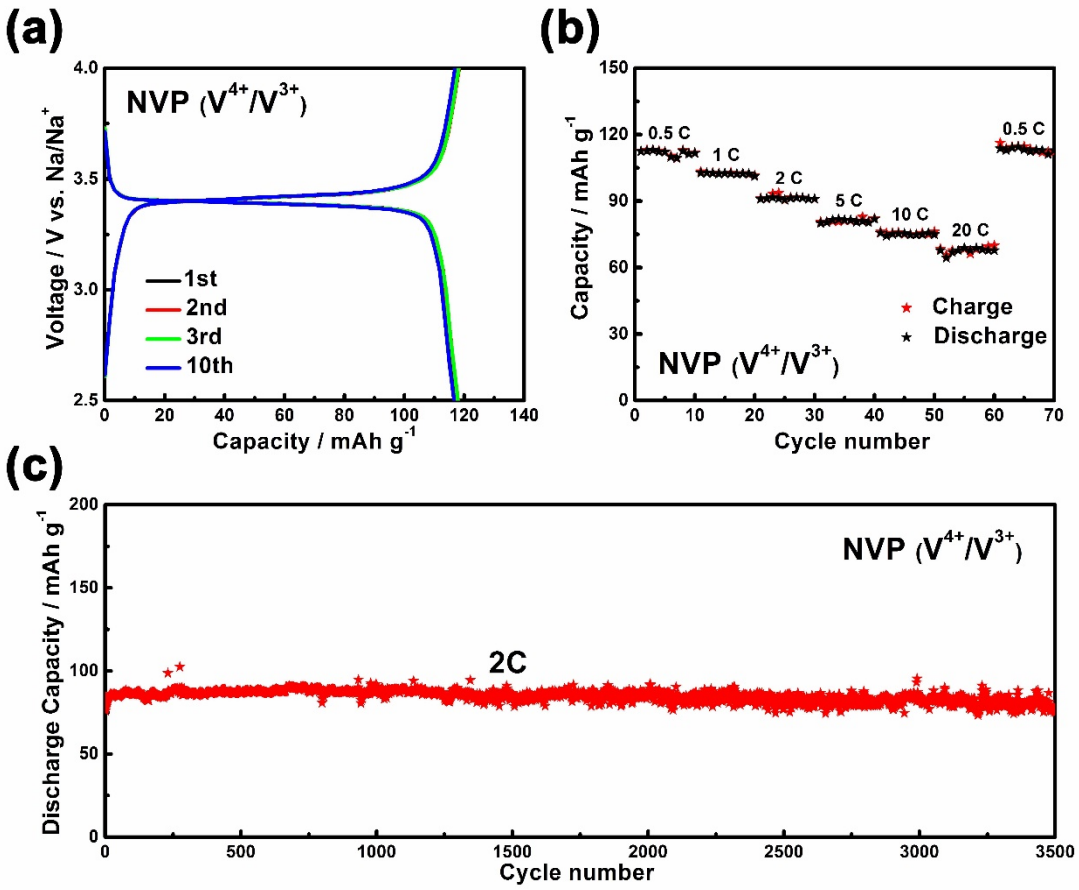

Figure S5. Electrochemical performance of NVP/ECF self-supporting electrode as cathode material for half cell test in a voltage range from 2.5 to 4.0 V. (a) Charge/discharge curves cycling at 0.5 C, (b) Rate performance, (c) Cyclic properties at 2 C throughout 3500 cycles.

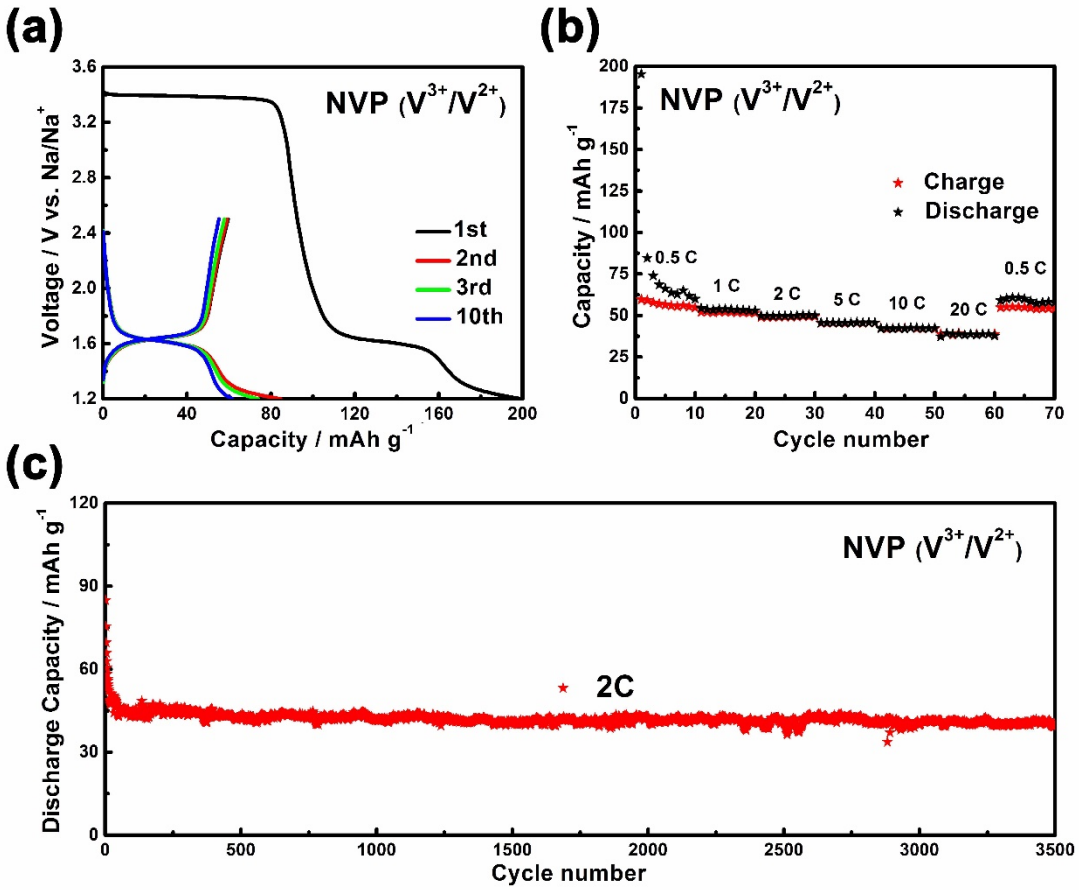

Figure S6. Electrochemical performance of NVP/ECF self-supporting electrode as anode material for half cell test in a voltage range from 1.0 to 2.5 V. (a) Charge/discharge curves cycling at 0.5 C, (b) Rate performance, (c) Cyclic properties at 2 C throughout 3500 cycles.

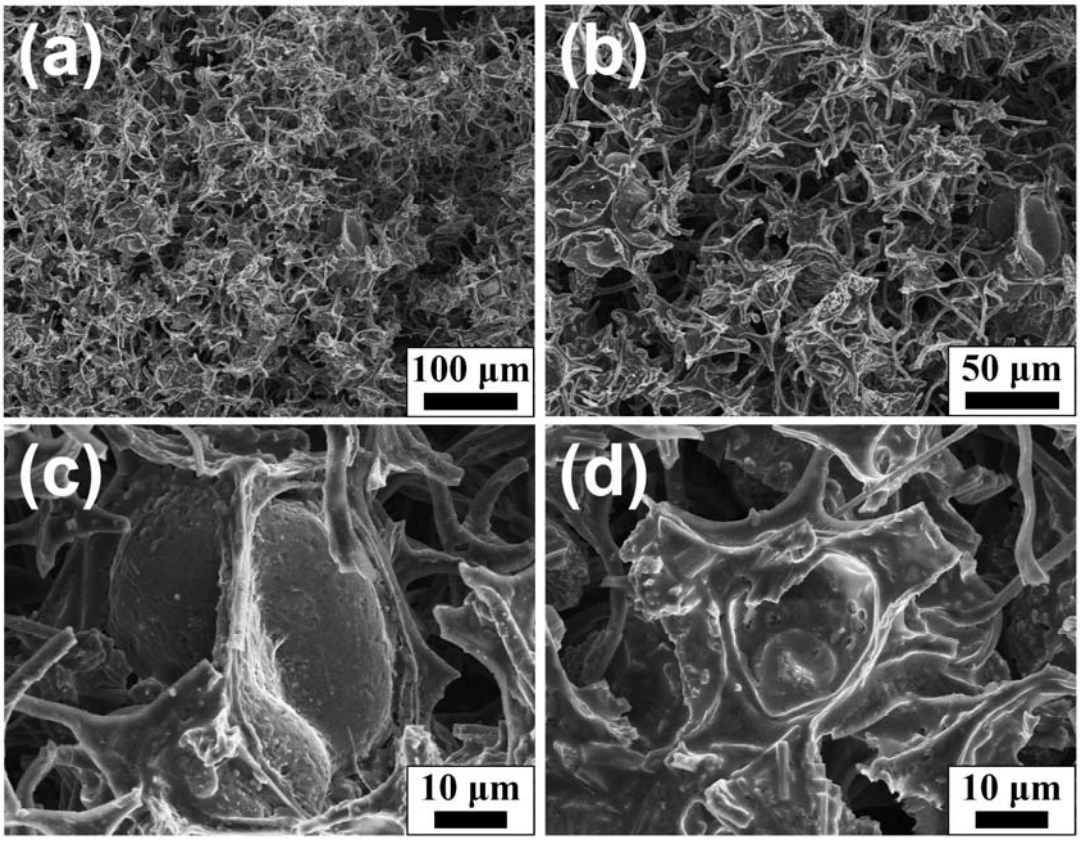

Figure S7. SEM images of NVP/ECF cathode after 280 cycles at 2 C.

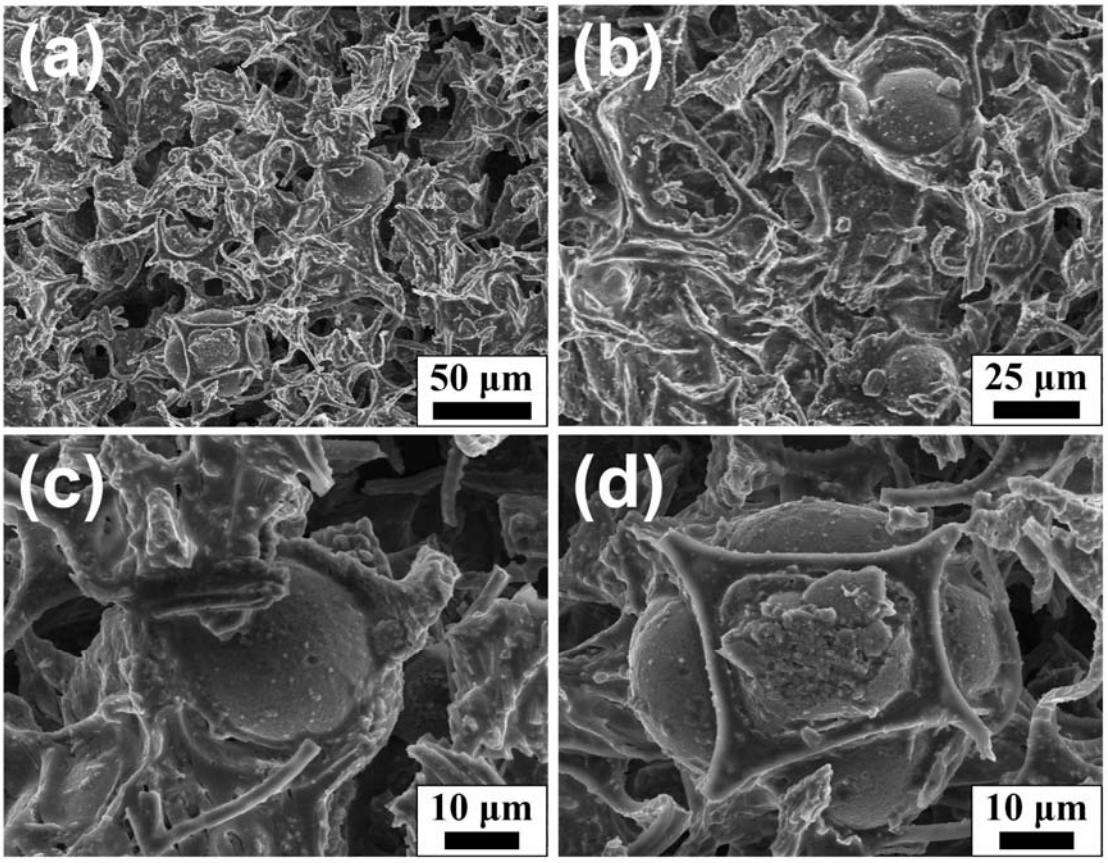

Figure S8. SEM images of NVP/ECF anode after 280 cycles at 2 C.

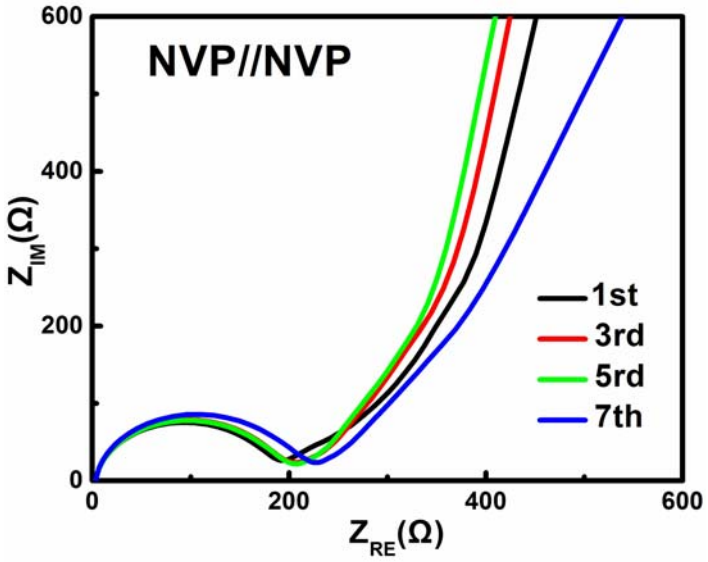

Figure R1. Electrochemical impedance spectroscopy (EIS) of the NVP//NVP full cell after 1st, 3rd, 5th and 7th charge/discharge process (current density = 0.5 C), respectively.

Table S1. Comparison of the present sodium symmetric full cell

Bipolar material	Self-supporting	Calculation based on	Rate performance of full cell		Cycling performance of full cell		Ref
			capacity (mAh/g)	maximum current density (C)	current density (C)	capacity retention (to 100th cycle)	
NVP/ECF self-supporting electrode	Yes	Total mass of the cathode	33.8	10	2	90.2%	Present work
		The mass of active material of the cathode	43				
NVP/AC	No	The mass of active material of the cathode	42.2	10	1	79.5%	Adv. Mater. 2014. 26, 3545-3553
$Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$	No	The mass of active material of the cathode	53	1	1	81%	Energy. Environ. Sci. 2015. 8,
$Na_{0.66}Ni_{0.17}Co_{0.17}Ti_{0.66}O_2$	No	The mass of active material of the cathode	92	2	5	95%	Angewandte Chemie 2015. 54,
$Na_{0.6}Cr_{0.6}Ti_{0.4}O_2$	No	The mass of active material of the cathode	58	12	1	75%	Nat Commun. 2015. 6