Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Constructing Consistent Pore Microstructure of Bacterial Cellulose-Derived Cathode and Anode for Constructing High Energy Density Sodium-Ion Capacitor

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Experimental Section

1. Chemicals and Materials

Bacterial cellulose (BC) was purchased from *Hainan Yide Food Industry Co., Ltd., China*. 2, 2, 6, 6-tetramethylpiperidine-1-oxyl radical (TEMPO) was obtained from *Sigma-Aldrich*. Sodium hypochlorite (NaClO), sodium bromide (NaBr), ethanol, sodium hydroxide (NaOH), hydrochloric acid (HCl), and potassium hydroxide (KOH) were purchased from *Lanzhou Zhongke Kate Equipment Distribution Co., Ltd*. All the chemicals used in experiments were of analytic grade and without further purification.

2. Preparation of BC-Carbon Cathode

The gel-like BC pellicles were cut into small pieces, and pulped by a mechanical stirring and freeze drying for preparation of the precursor, which was then immersed into KOH solution, stirred for 24 h, and dried at 80 °C for another 24 h. After that, the mixture was pre-heated at 200 °C for 1 h under Ar atmosphere with a heating rate of 2 °C min^{-1}, and then heated to 800 °C for 2 h with a heating rate of 5 °C min^{-1}. After cooling down to the room temperature, the obtained sample was washed using HCl solution and deionized water until the pH value reached 7, then dried in an oven at 60 °C for 12 h to obtain BC-carbon (denoted as BCC). In addition, BCCs activated with different BC to KOH mass ratios of 1: 1, 1: 2, and 1: 3 (*wt*: *wt*) were prepared via the same procedure. For convenience, the obtained carbon sample activated with the BC to KOH mass ratio of 1: 2 was denoted as BCC. And the other samples activated by mass ratios of 1: 1, and 1: 3 were denoted as BCC-1, and BCC-3, respectively.

3. Preparation of MBC-Carbon Anode

The modified BC (MBC) was fabricated by TEMPO oxidation method[1]. The freeze-drying BC (1 g) were dispersed into deionized water (100 mL) including TEMPO (0.016 g) and NaBr (0.1 g) under gentle stirring to prepare BC slurry. Then, 12 % NaClO solution (5 mmol) was added to the BC slurry at room temperature. The pH of the BC slurry was adjusted to about 10 by adding 0.5 M NaOH solution. After 90 min, some ethanol was added into the solution to obtain MBC solution. Finally, MBC solution was washed with deionized water for several times and freeze drying for preparation of the MBC-carbon precursor. MBC was heat-treated at 1, 000 °C for 2 h in a tube furnace under Ar atmosphere with a heating rate of 2 °C min^{-1}. After cooling down to the room temperature, MBC based carbon was obtained and denoted as MBCC.

4 Characterizations

The microstructures and morphologies of all the samples were characterized by field emission scanning electron microscopy (FESEM, JSM 6701F), transmission electron microscopy (TEM, JEOL 2100FEG), powder X-ray diffraction (XRD, Rigaku D/MAX 2400 diffractometer) and Raman spectrum (Horiba Jobin Yvon HR Evolution). The nitrogen adsorption-desorption isotherm measurements were performed on an ASAP 2020 volumetric adsorption analyzer (Micromeritics) at 77 K.

5 Electrochemical Performance Tests

Fabrication of BCC Cathode: The BCC cathode was prepared by uniformly mixing BCC (80 *wt*%), conductive carbon (10 *wt*%), and polytetrafluoroethylene (PTFE, 10 *wt*%) with absolute ethyl alcohol. The obtained slurry was coated onto an Al foil and then dried at 150 °C for 12 h under vacuum. The loading

density was set as 1.0 mg cm^{-2}.

Fabrication of MBCC Anode: The MBCC anode was prepared by mixing MBCC, acetylene black, and polyvinylidenefluoride (PVDF) in a mass ratio of 8: 1: 1 (*wt*: *wt*: *wt*) and being homogenized in a N-methyl-2-pyrrolidinone (NMP); and then the slurry was coated on a copper foil as the working electrode. The as-coated anode electrode was dried at 110 °C for 12 h in vacuum. The loading mass of the active material was about 1.0 mg cm^{-2}.

Three-electrode testing system: Three electrode testing system was constructed by BCC electrode as a working electrode, a platinum electrode as a counter electrode, and a saturated calomel (SCE) electrode as a reference electrode in 2 M KOH electrolyte. The BCC electrode was prepared by mixing active material (80 *wt*%), conductive carbon (10 *wt*%), and PTFE (10 *wt*%) in absolute ethyl alcohol. The obtained slurry was coated onto the nickel foams under the pressure of 10 MPa and dried at 60 °C for 12 h in a vacuum oven. The loading density was set as 1.0 mg cm^{-2}.

Fabrication of Half-cell: The electrode fabricated as mentioned above was assembled into a coin cell (CR2032) in an argon-filled glovebox using 1 M $NaClO_4$ in a mixture of ethylene carbonate (EC) and propylene carbonate (PC) (1: 1, *V*: *V*) as the electrolyte. A sodium foil was used as the counter electrode and Whatman GF/D glass fibers as separator.

Fabrication of SIC Device: SIC was assembled in coin cells using the preactivated MBCC anode and BCC cathode in the same electrolyte and separator. The anode was cycled for 10 cycles in a half-cell versus Na/Na^+ under 0.1 A g^{-1} before assembly into a SIC device.

Electrochemical Performance Measurement: All electrochemical measurements were carried out at room temperature. Cyclic voltammetry (CV), galvanostatic charging-discharging (GCD), and electrochemical impedance spectroscopy (EIS) were performed on the electrochemical workstations (*Chenhua*, CHI660D; PGSTAT 302N, Metrohm). Cycle-life tests for SIC were employed on Land CT2001A (*Land Electronic Co.)*. In SIC tests, all specific capacities were calculated based on the total mass of both anode and cathode active materials. The energy and power densities of SICs were calculated based on GCD measurements by the following equations:

$$C = i/[(\Delta V/\Delta t) \times m] \quad (1)$$

$$E = C\left(V_{max}^{\ 2} - V_{min}^{\ 2}\right)/2 \times 3.6 \quad (2)$$

$$P = E \times 3600/t \quad (3)$$

Where *i* is charging/discharging current (A), *t* is discharging time (s), *m* indicates the total mass of the active materials in both anode and cathode (g), V_{max} and V_{min} are the initial and final discharging voltages (V), ΔV represents the voltage change after a full discharging, *C* is specific capacitance (F g^{-1}), *E* is energy density (W h kg^{-1}), and *P* is power density (W kg^{-1}).

1 T. Zhang, J. Lang, L. Y. Liu, L. Liu, H. Li, Y. Gu, X. Yan, X. Ding, *Chin. Chem. Lett.*, 2017, **28**, 2212-2218.

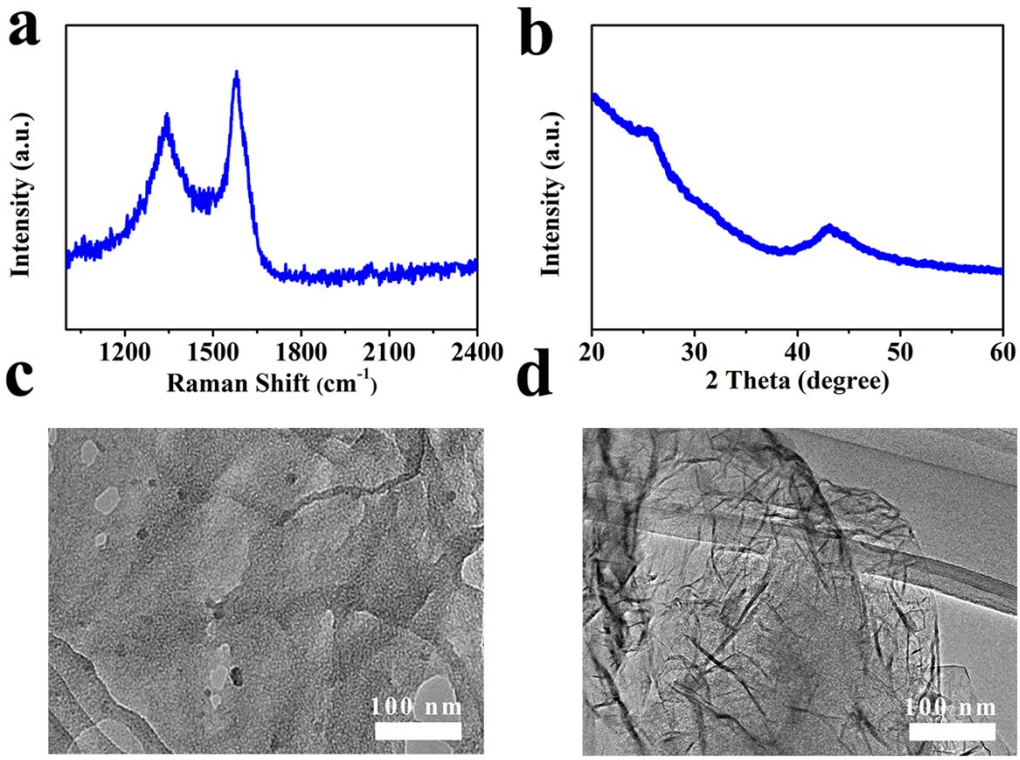

Figure S1 *(a) Raman pattern, and (b) XRD pattern for BCC cathode; TEM images for (c) MBCC and (d) BCC*

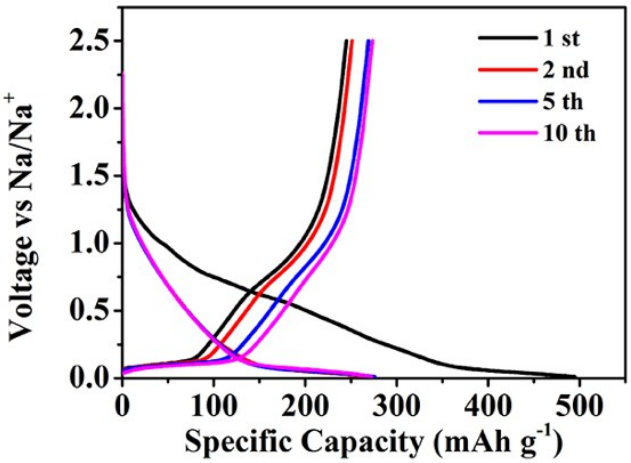

Figure S2 *Galvanostatic 1st, 2nd, 5th and 10th discharge/charge profiles of MBCC at a current rate of 0.05 A* g^{-1} *in a voltage range of 0.01 - 2.5 V.*

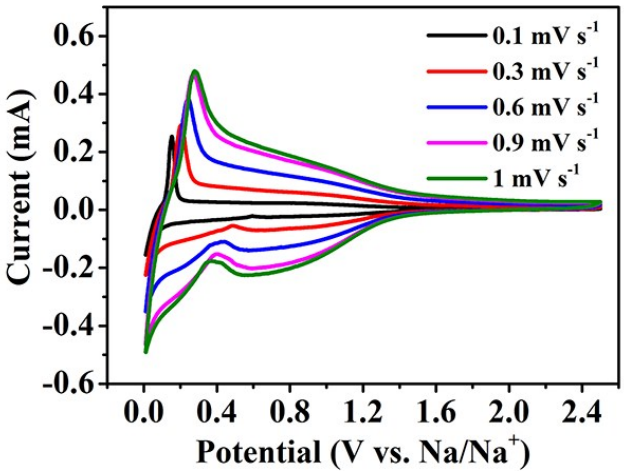

Figure S3 *CV curves at different scan rates from 0.1 to 1 mV s^{-1} for MBCC anode*

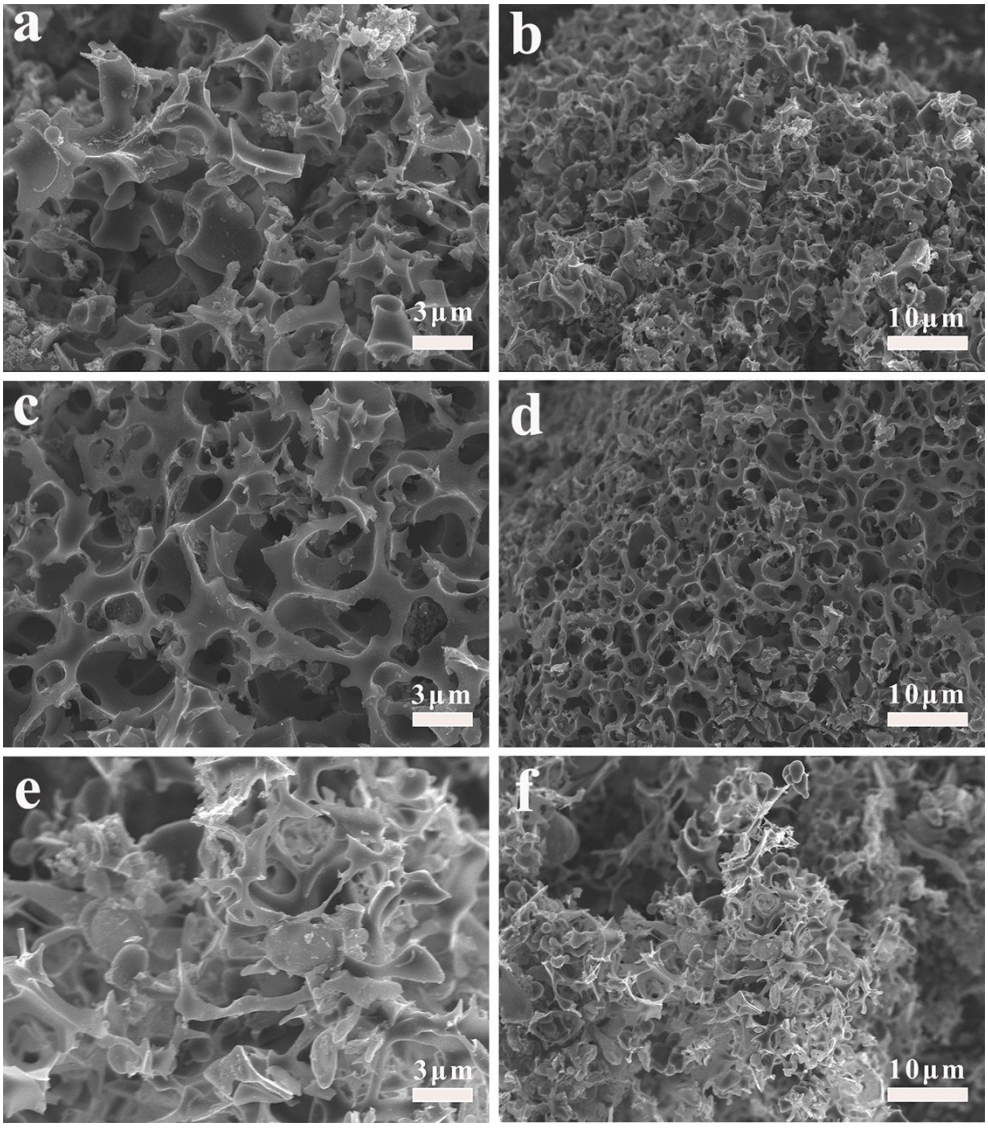

Figure S4 *SEM images for BCC electrodes: the mass ratio of BC and KOH were changed from (a) 1:1 (b) 1:2 to (c) 1:3*

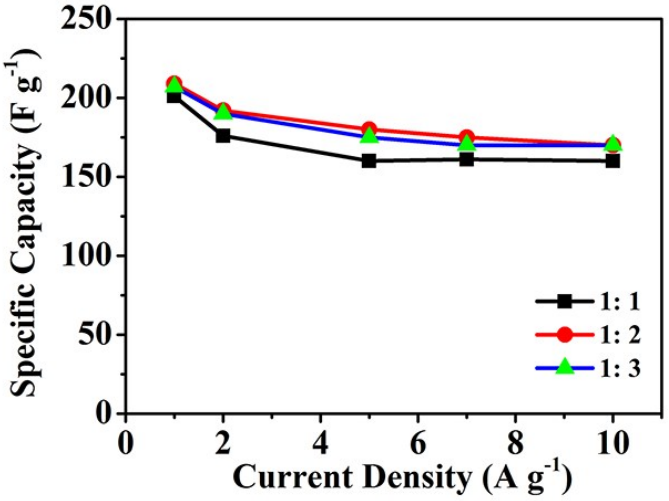

Figure S5 *The specific capacity of BCC electrode at different current densities in 2 M KOH*

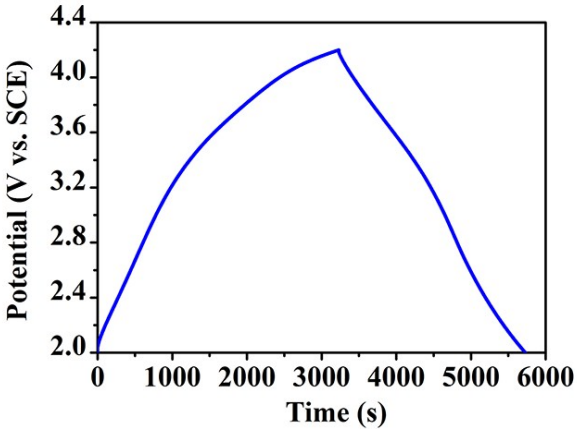

Figure S6 *GCD curves at 0.1 A* g^{-1}

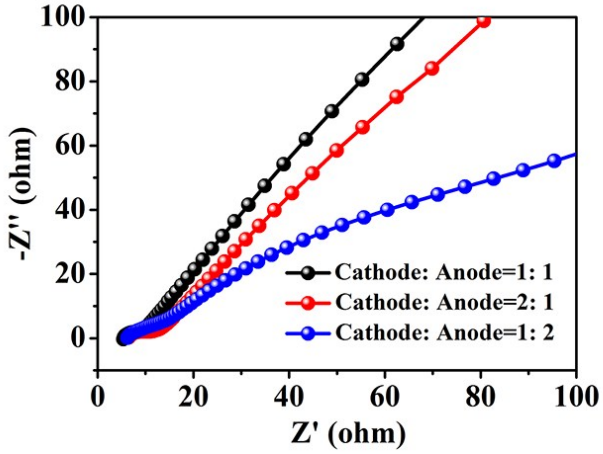

Figure S7 *Nyquist plots*

Table S1 *Equivalent electronic circuits used to simulate the EIS data*

Cathode||Anode	R_0 (Ω)	R_{ct} (Ω)	CPE1-T	CPE1-P
2: 1	6.69	4.24	4.00×10^{-5}	0.97
1: 1	5.71	2.43	9.25×10^{-7}	1.16
1: 2	5.87	2.86	0.55×10^{-5}	0.54

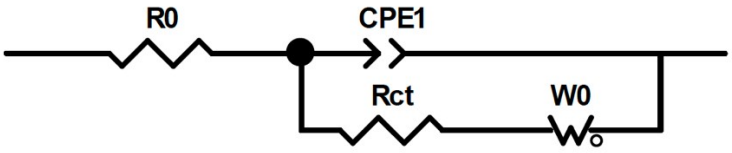

Figure S8 *The fitting electric equivalent circuit*

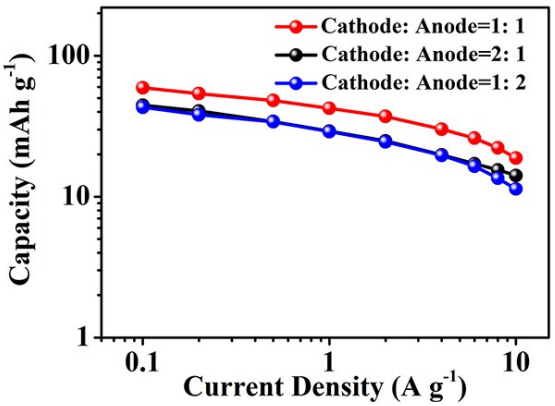

Figure S9 *Rate performance*

Table S2 *The capacity of SIC devices with different mass ratios of BCC to MBCC at various current densities*

Current density (A g^{-1})	Capacity with different mass ratio (BCC//MBCC) (mAh g^{-1})		
	1: 1	2: 1	1: 2
0.1	59.22	44.56	43.08
0.2	53.83	40.51	38.11
0.5	48.09	34.14	33.98
1	42.40	29.14	28.91
2	37.09	24.83	24.50
4	30.14	19.80	19.65
6	26.00	17.11	16.46
8	22.20	15.47	13.48
10	18.82	14.14	11.33