Supplementary Information (SI) for Nanoscale.

Supporting Information

Fabrication of pitch-derived hard carbon via bromination-assisted pyrolysis strategy for sodium-ion batteries

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Material characterization

The morphology and microstructure of the brominated pitch-based hard carbon materials were observed by field emission transmission electron microscopy (TEM, JEM-F200) and field emission scanning electron microscopy (SEM, MAIA3 LMH). The porosity and specific surface area properties of the prepared samples were characterized using the Micrometrics ASAP 2460 N_2 adsorption-desorption tester at 77 K. X-ray diffraction (XRD, SHIMADZU 6100) with Cu-K alpha radiation was used to characterize the crystal structure and parameters of hard carbon materials. The DXR 2xi Raman spectrometer with a 532 nm Argon ion laser to determine the defect structure of samples. X-ray photoelectron spectroscopy (XPS) analysis was performed using ESCALAB 250Xi to measure the elemental composition and surface chemical properties of the samples.

Electrochemical test details

The electrochemical properties of samples were tested in a CR2016 coin cell. For the preparation of the working electrodes, the obtained hard carbon was mixed with carbon black and SA in a mass ratio of 8:1:1 and then coating the slurry on a copper foil. The slurry was vacuum-dried at 80°C for 12 hours and left to cool to room temperature. The mass loading was approximately 1 mg cm^{-2}. Coin cells were mounted in a glove box under an argon atmosphere (Mikrouna, $H_2O< 0.1$ ppm, $O_2 < 0.1$ ppm), Na disc was used as counter-electrode, and glass fiber was used as separators by adding a certain amount of electrolyte. The Galvanostatic charge-discharge (GCD) and galvanostatic intermittent titration technique (GITT) measurements were made using the Land 2001A battery test system at 0.001-2.6 V. Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were performed on the Biologic VMP3 electrochemical workstation.

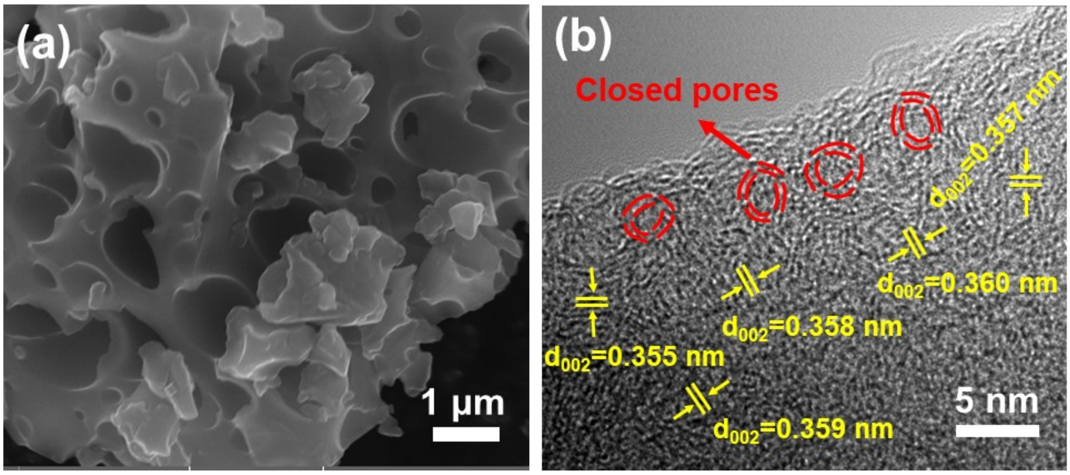

Fig. S1 SEM (a) and HR-TEM (b) images of the BHC-1500.

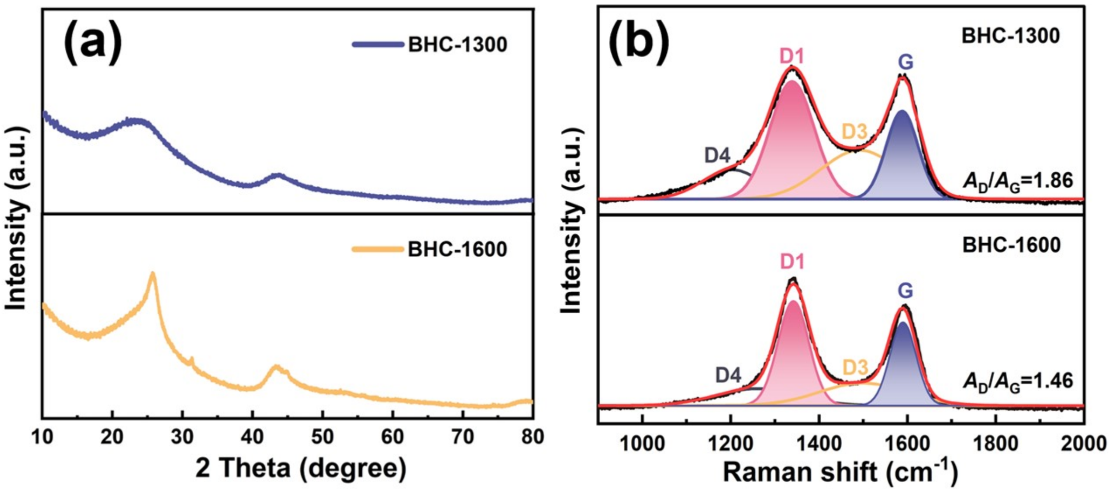

Fig. S2 (a) XRD patterns and (b) Raman spectra of the BHC-1300 and BHC-1600.

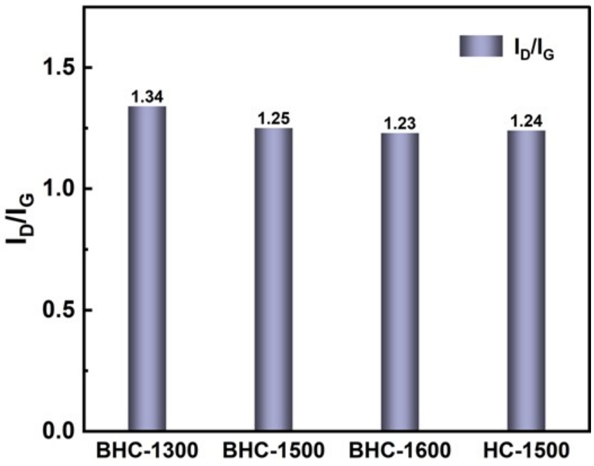

Fig. S3 I_D/I_G values of BHC-1300, BHC-1500, BHC-1600, and HC-1500 samples.

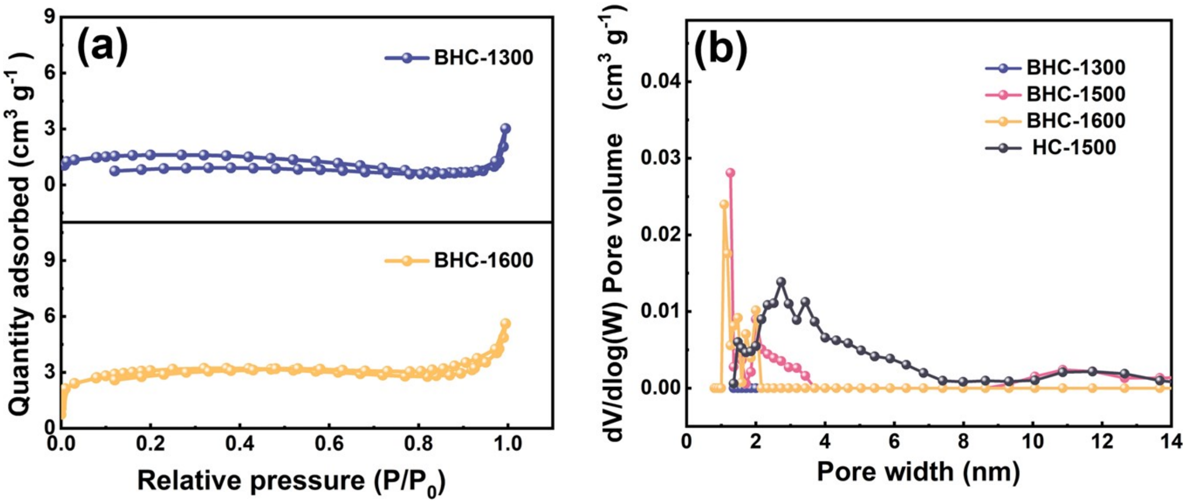

Fig. S4 (a) N_2 adsorption and desorption curves of BHC-1300 and BHC-1600. (b) Pore width distribution of BHC-1300, BHC-1500, BHC-1600, and HC-1500.

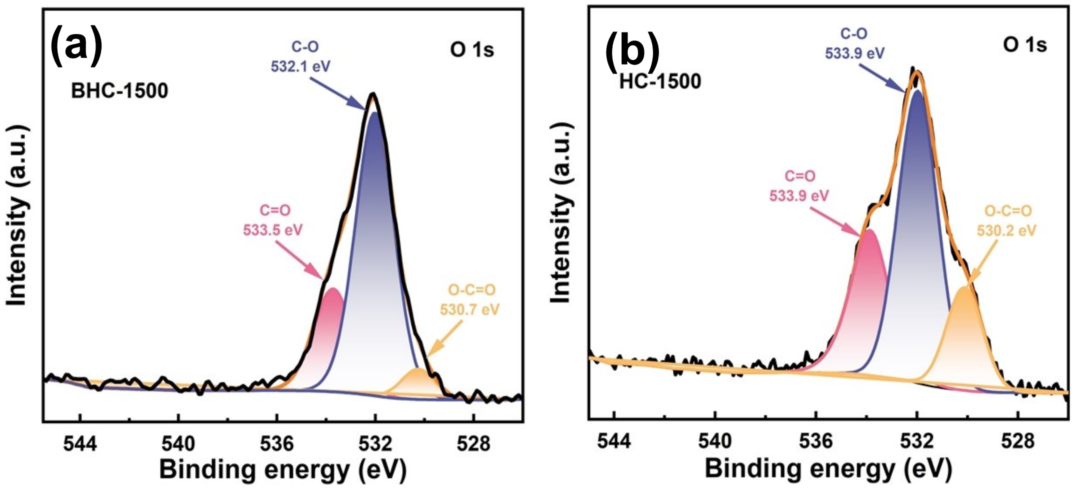

Fig. S5 High-resolution O 1s spectra of (a) BHC-1500 and (b) HC-1500.

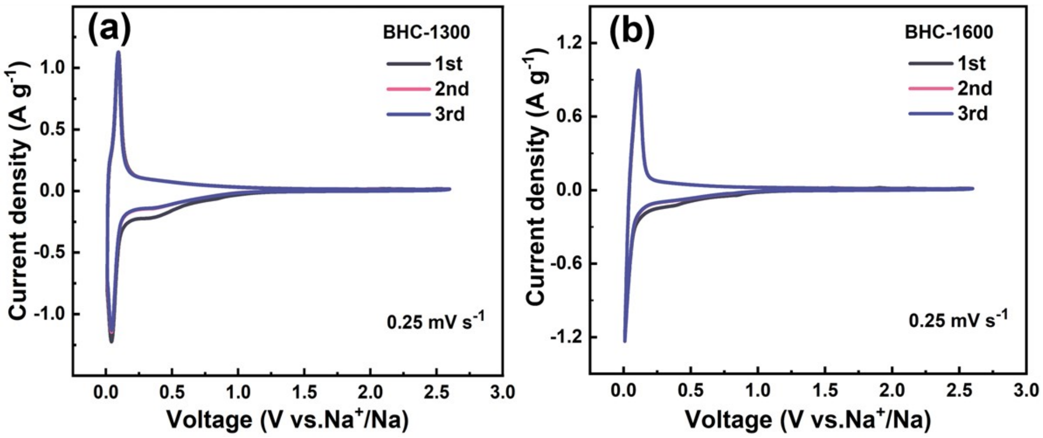

Fig. S6 CV curves of (a) BHC-1300 and (b) BHC-1500 at a scan rate of 0.25 mV s^{-1} in the initial three cycles.

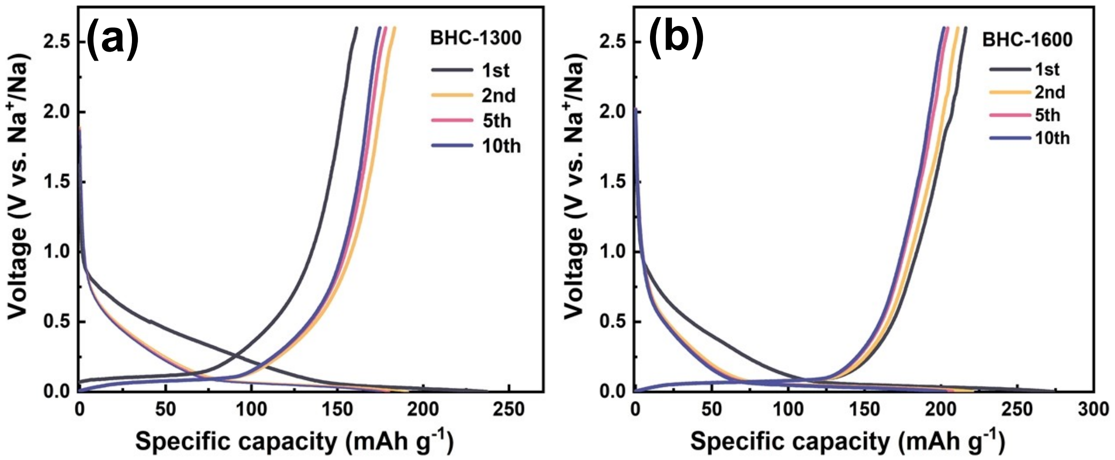

Fig. S7 GCD profiles in the first 10 cycles of (a) BHC-1300 and (b) BHC-1600 at a current density of 0.1 A g^{-1}.

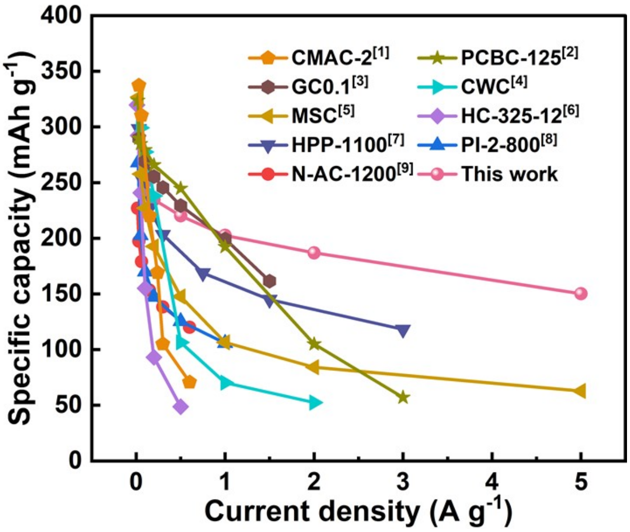

Fig. S8 Comparison of rate performance of pitch-derived hard carbon for sodium-ion batteries between this work and others reported in previous literature[1-9].

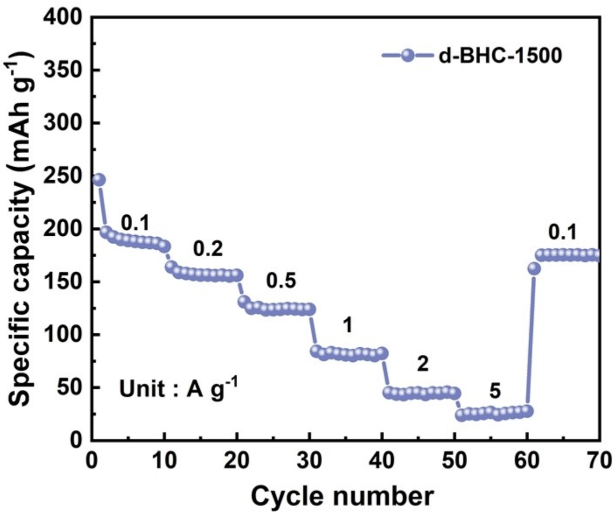

Fig. S9 Rate capability of the d-BHC-1500 at different current densities.

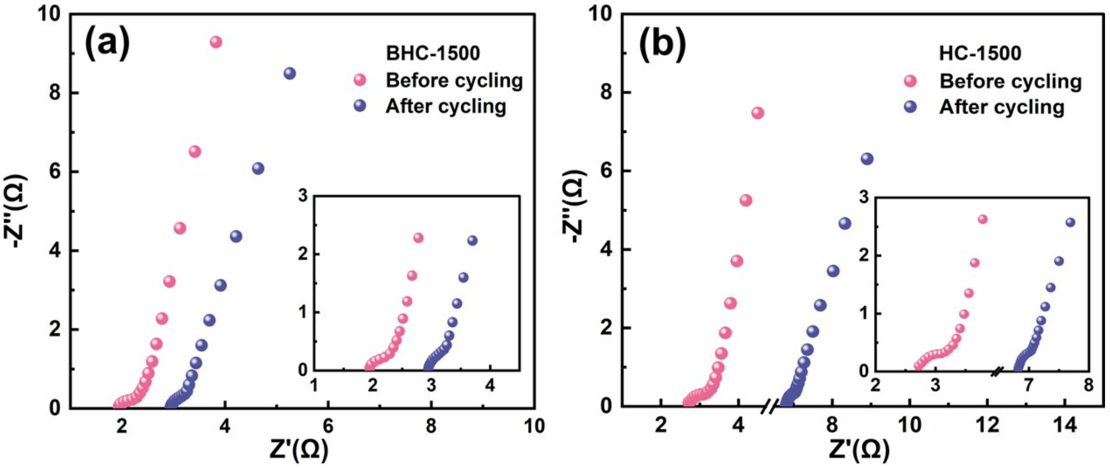

Fig. S10 EIS profiles of (a) BHC-1500 and (b) HC-1500 before and after long-term cycling (the inset is an enlarged view of the EIS).

Table S1 The calculated interlayer spacing of pitch-derived hard carbon materials based on (002) diffraction peak

Sample	2θ (°)	d_{002} (nm)
BHC-1300	23.150	0.384
BHC-1500	25.246	0.355
BHC-1600	25.723	0.346
HC-1500	25.554	0.348

Table S2 Textural properties of pitch-derived hard carbon materials

Sample	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
BHC-1300	6.00	0.0042
BHC-1500	16.35	0.0115
BHC-1600	11.18	0.0083
HC-1500	13.5	0.0111

Table S3 Surface elemental composition of BHC-1500 and HC-1500

Sample	C (at.%)	O (at.%)	Br (at.%)
BHC-1500	94.63	5.34	0.03
HC-1500	94.01	5.99	0

Table S4 The R_{ct} values of BHC-1500 and HC-1500 before and after long-term cycling

Sample	R_{ct} before cycling (Ω)	R_{ct} after cycling (Ω)
BHC-1500	0.234	0.438
HC-1500	0.296	0.518

Notes and references

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