

## Supporting Information

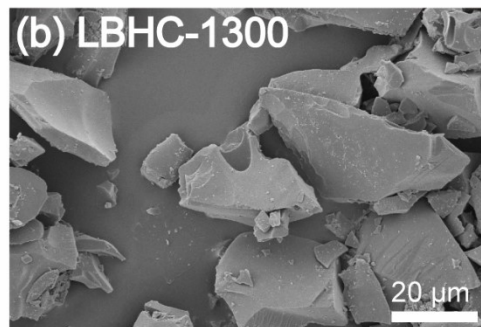
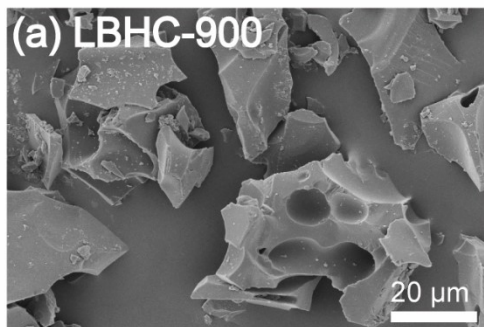
# **Biomass-derived highly graphitized hard carbon *via* tandem carbonization-graphitization for high-performance sodium-ion batteries**

Tianqi Cao, Guanyu Zhang, Zengjian Guo, Jiarui Zhu, Ge Kong, Xuesong Zhang\*, Lujia Han.

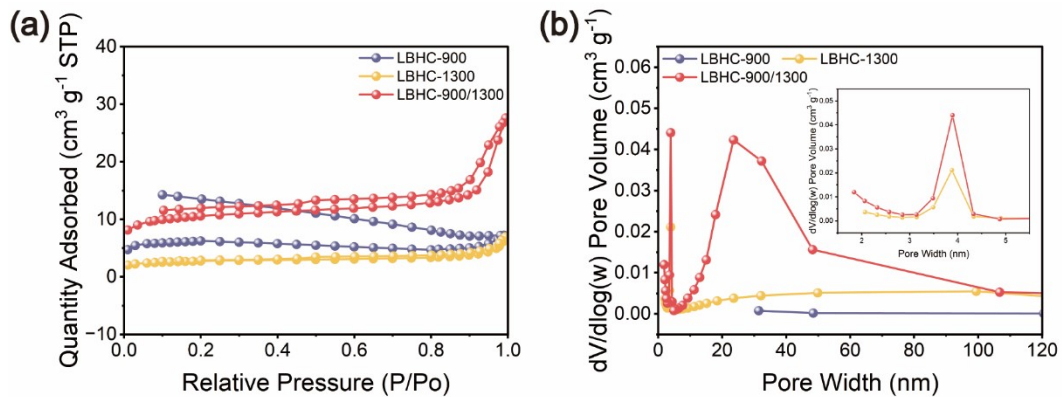
*Engineering Laboratory for AgroBiomass Recycling & Valorizing, College of Engineering, China*

*Agricultural University, Beijing 100083, China*

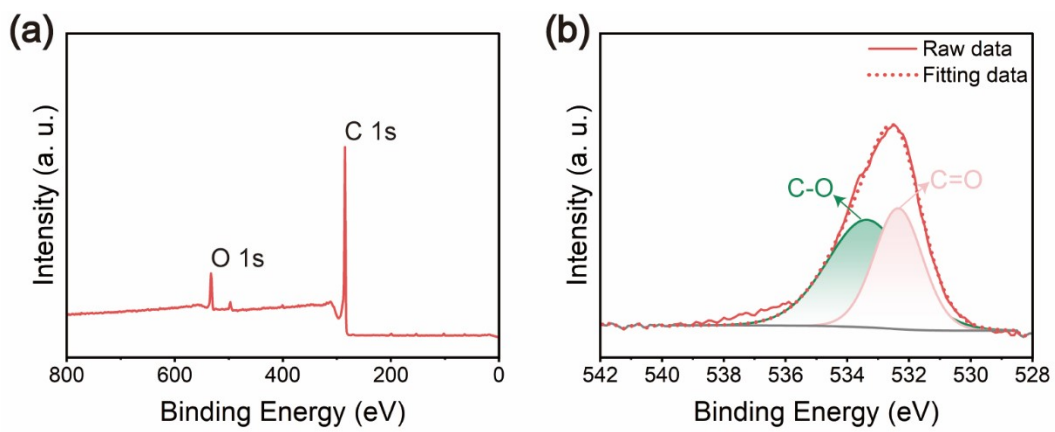
*\*Corresponding author, E-mail: [xs Zhang@cau.edu.cn](mailto:xs Zhang@cau.edu.cn)*



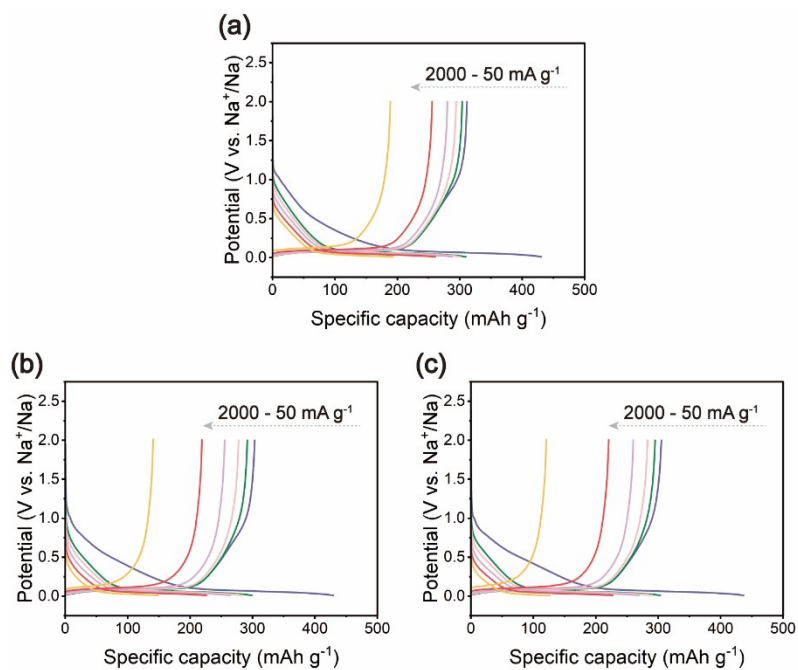
**Figure S1.** SEM image of (a) LBHC-900, and (b) LBHC-1300.



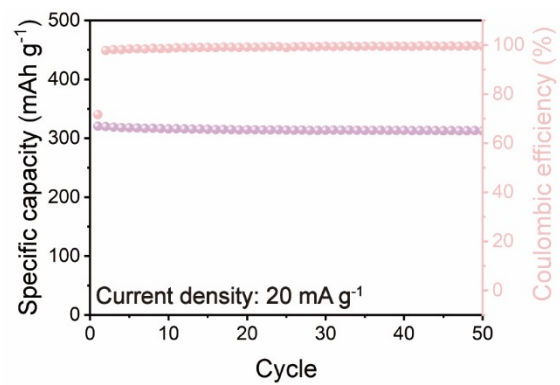
**Figure S2.** (a) N<sub>2</sub> sorption-desorption isotherms, (b) pore size distribution of lignin-based hard carbon materials.



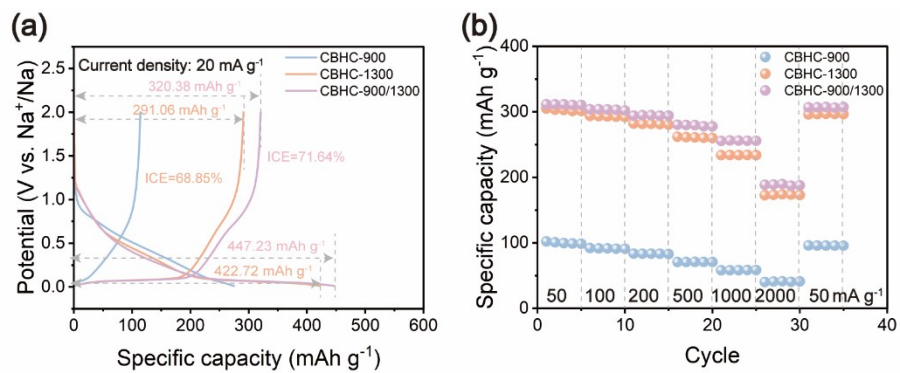
**Figure S3.** (a) Full survey, and (b) High-resolution O 1s XPS spectra of LBHC.



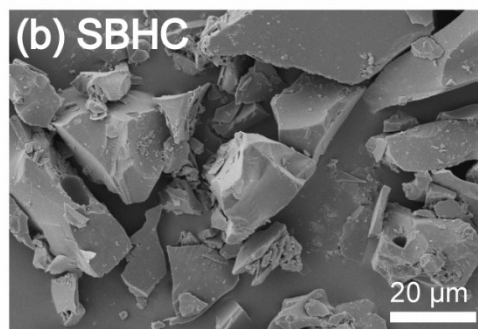
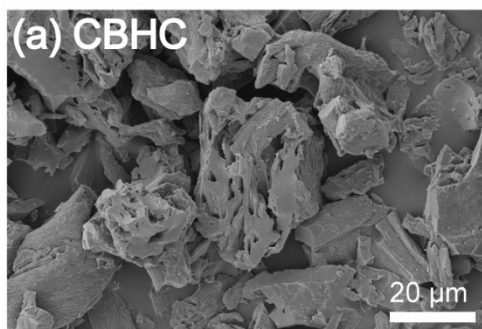
**Figure S4.** The GCD curves of (a) CBHC, (b) LBHC, and (c) SBHC at the current density increased from 50 to 2000 mA g<sup>-1</sup>.



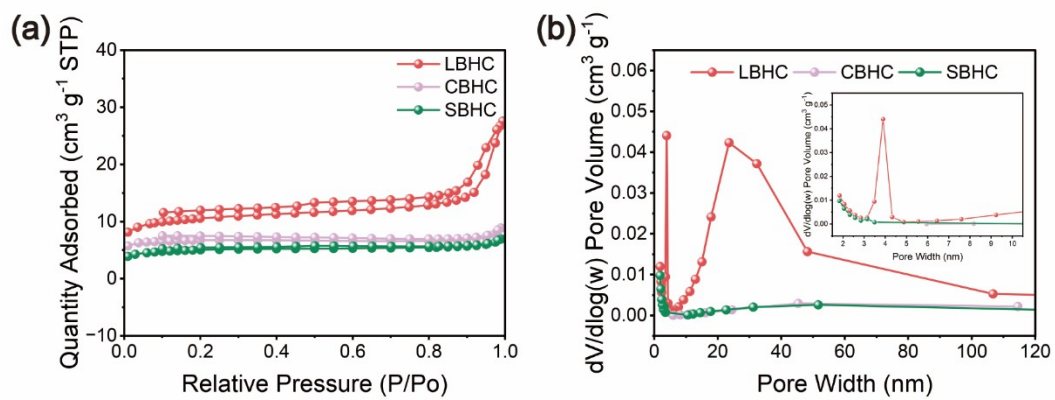
**Figure S5.** Cycling stability of CBHC at the current density of 20 mA g<sup>-1</sup>.



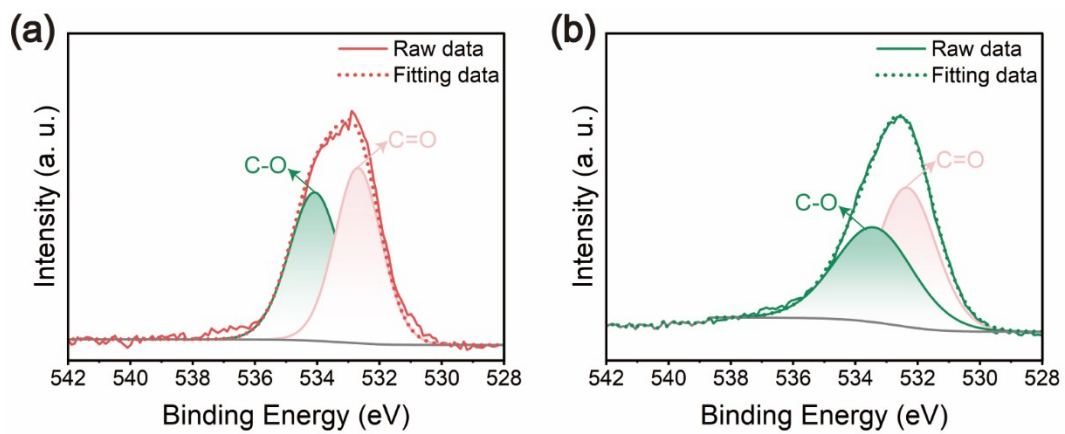
**Figure S6.** Electrochemical performance of CBHC in Na//HC half-cells; (a) initial charge and discharge curves of CBHC-900/1300 at  $20 \text{ mA g}^{-1}$ ; (b) rate performance



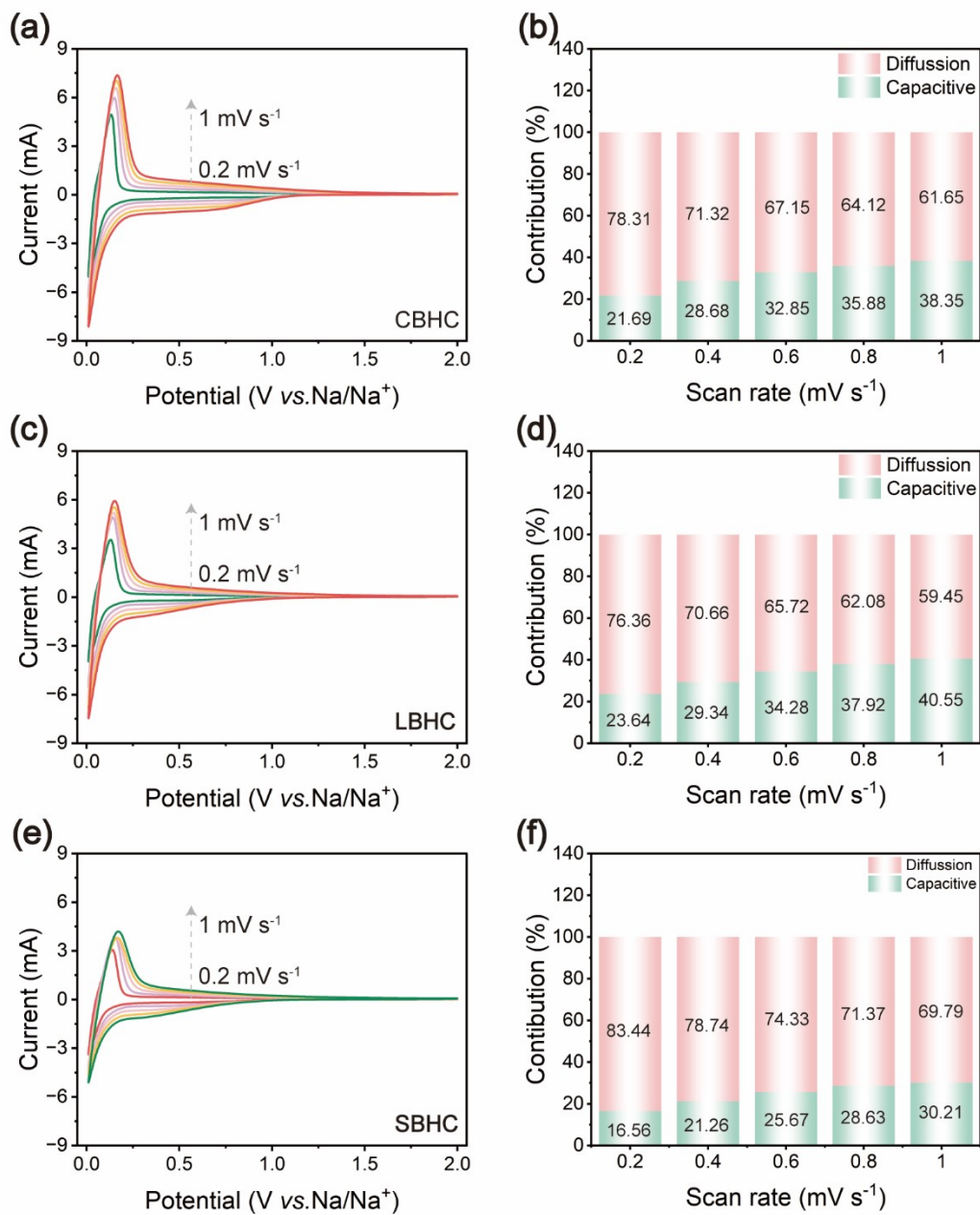
**Figure S7.** SEM image of (a) CBHC, and (b) SBHC.



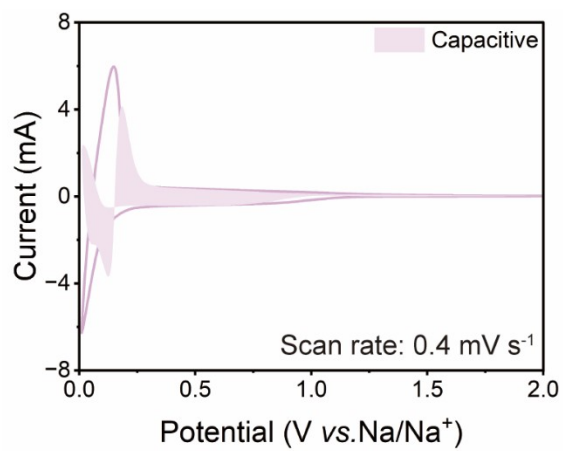
**Figure S8.** (a) N<sub>2</sub> sorption–desorption isotherms, (b) pore size distribution of biomass-based hard carbon materials.



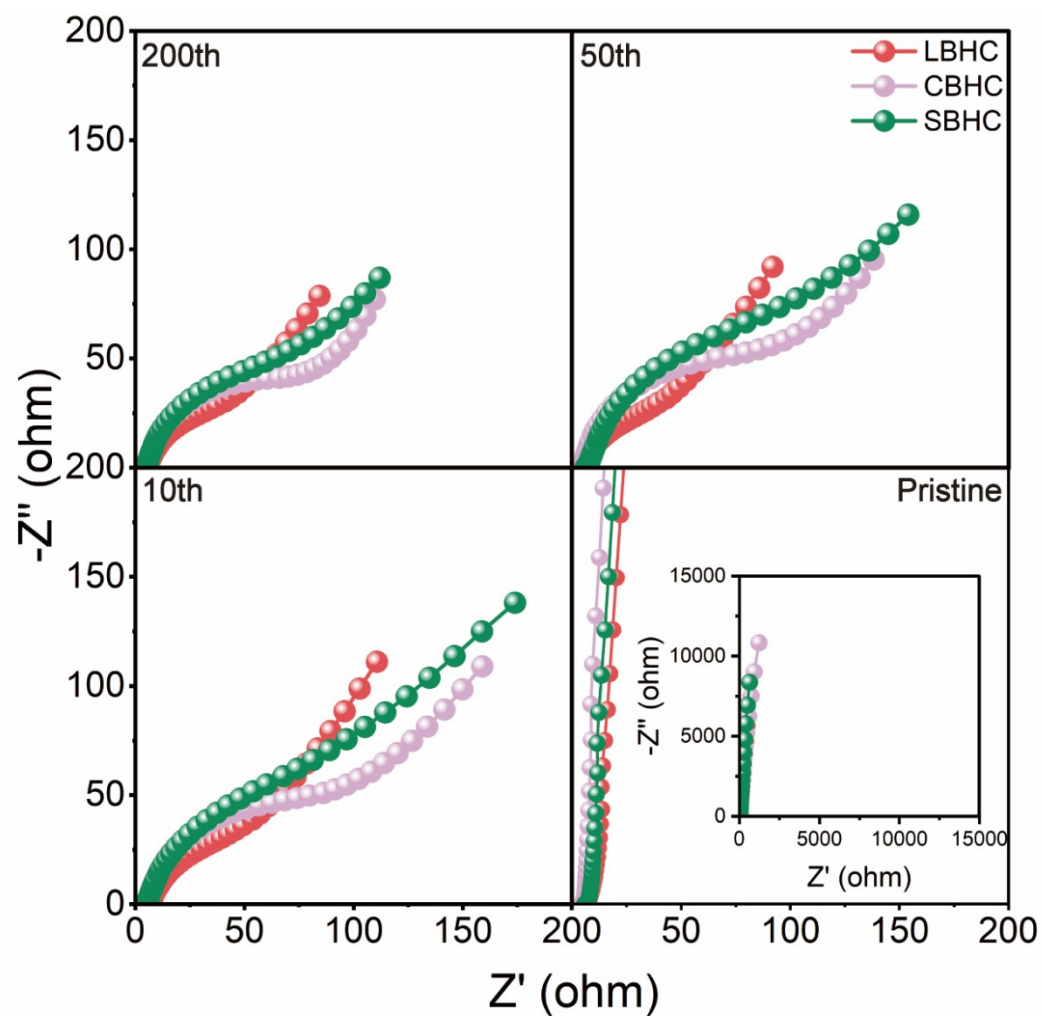
**Figure S9.** High-resolution O 1s XPS spectra of (a) CBHC and (b) SBHC.



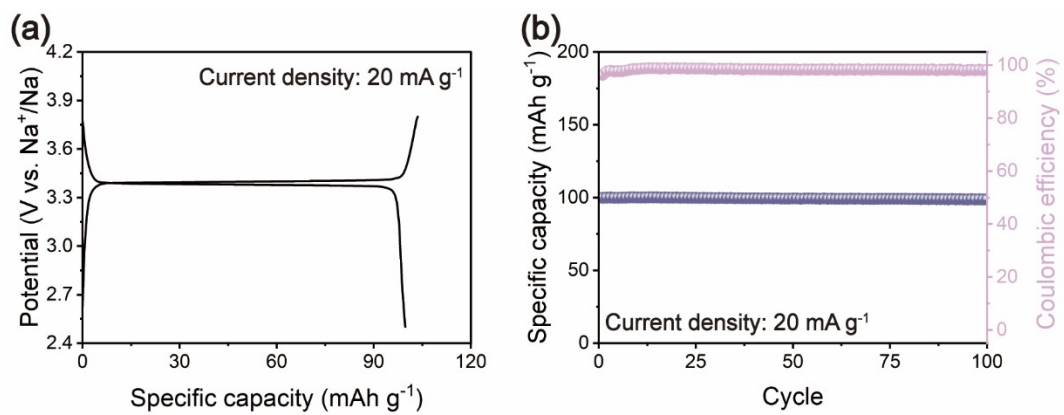
**Figure S10.** (a) cyclic voltammograms of CBHC at various scan rates; (b) the capacitive contribution of CBHC; (c) Cyclic voltammograms of LBHC at various scan rates; (d) The capacitive contribution of LBHC; (e) Cyclic voltammograms of SBHC at various scan rates; (f) The capacitive contribution of SBHC.



**Figure S11.** The capacitive contribution of CBHC at 0.4 mV s<sup>-1</sup>.



**Figure S12.** Nyquist plots of the EIS data for the biomass-based highly graphitization hard carbon materials before and after different cycles.



**Figure S13.** The electrochemical performance of NVP cathode in half-cell. (a) The GCD curves, and (b) Cycling stability of NVP cathode at 20 mA g<sup>-1</sup>.

**Table S1.** The rate performance for biomass-based hard carbon.

Current density (mA g <sup>-1</sup> )	Average specific capacity (mAh g <sup>-1</sup> )						
	50	100	200	500	1000	2000	50
Sample							
LBHC-90	247.37 (285.88)	233.98 (237.31)	220.17 (222.94)	199.98 (202.71)	174.40 (176.44)	122.55 (124.84)	241.60 (232.34)
LBHC-1300	301.69 (334.18)	289.69 (293.25)	276.08 (278.57)	246.91 (249.16)	197.66 (199.12)	101.46 (102.70)	292.63 (287.95)
LBHC-900/1300 (LBHC)	301.37 (331.16)	290.07 (293.19)	276.96 (279.30)	253.96 (256.38)	218.31 (220.04)	139.87 (141.52)	294.51 (288.24)
CBHC	311.01 (338.23)	303.30 (305.59)	294.44 (296.35)	279.03 (281.00)	255.94 (257.25)	188.47 (189.56)	306.94 (302.60)
SBHC	304.10 (335.10)	294.06 (297.14)	281.91 (284.40)	259.24 (261.58)	219.81 (221.32)	120.85 (122.01)	299.06 (293.11)

**Table S2.** The comparisons regarding electrochemical performance of hard carbons in full-cells.

Material	Reversible capacity	Capacity retention	Energy density (Wh kg <sup>-1</sup> )	Powder density (W kg <sup>-1</sup> )	Electrolyte	Ref.
Conventional hard carbon//Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	-	-	109.3	-	1 M NaClO <sub>4</sub> in PC+ 5 vol% FEC	<sup>1</sup>
Carbon nanofiber//Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>			87.1	-		
reduced graphene oxide//Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>			87.2	-		
NDCS// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>			146.1	-		
NHC-0.8M-800//Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> O <sub>2</sub> F	116 mAh g <sup>-1</sup> at 50 mA g <sup>-1</sup>	86% (1000 cycles at 500 mA g <sup>-1</sup> )	301	123	1 M NaPF <sub>6</sub> in DME	<sup>2</sup>
HCMP-CO <sub>2</sub> // Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	61 mAh g <sup>-1</sup> at 600 mA g <sup>-1</sup>	80.9% (800 cycles at 200 mA g <sup>-1</sup> )	281	74	1 M NaPF <sub>6</sub> in DEGDME	<sup>3</sup>
SCHC1300// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	299 mAh g <sup>-1</sup> at 0.1C	86% (80 cycles at 0.5 C)	201	-	1 M NaPF <sub>6</sub> in DEGDME	<sup>4</sup>
CoHC// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>a</sup>	270mAh g <sup>-1</sup> at 5000 mA g <sup>-1</sup>	94% (150 cycles at 100 mA g <sup>-1</sup> )	255.2	19.68	1 M NaPF <sub>6</sub> in DEGDME	<sup>5</sup>
PAHC-1500// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>a</sup>	102.2 mAh g <sup>-1</sup> at 0.1 C (1C=117.6 mAh g <sup>-1</sup> )	-	242.1	28.1	1 M NaPF <sub>6</sub> in DEGDME	<sup>6</sup>
HC-1500// Na <sub>x</sub> TMO <sub>2</sub> <sup>a</sup>	300 mAh g <sup>-1</sup> at 20 mA g <sup>-1</sup>	-	243.4	-	1 M NaPF <sub>6</sub> in DEGDME	<sup>7</sup>
HC-150-09// Na <sub>4</sub> Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sup>b</sup>	277.25 mAh g <sup>-1</sup> at 0.1 C (1C=300 mAh g <sup>-1</sup> )	-	225.03	23.19	1 M NaPF <sub>6</sub> in DEGDME	<sup>8</sup>
HCA10// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>a</sup>	307.2 mAh g <sup>-1</sup> at 30 mA g <sup>-1</sup>	81.7% (300 cycles at 300 mA g <sup>-1</sup> )	309.4	-	1 M NaPF <sub>6</sub> in DME	<sup>9</sup>
PCHC-10// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	-	-	231.2	24.1	1 M NaClO <sub>4</sub> in EC: DEC = 1:1 vol % + 5 vol% FEC)	<sup>10</sup>
CSC// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>a</sup>	299 mAh g <sup>-1</sup> at 0.1C (1C=300 mA g <sup>-1</sup> )	89% (80 cycles at 0.5 C)	212	-	1 M NaPF <sub>6</sub> in DEGDME	<sup>11</sup>
TC10%// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>a</sup>	230 mAh g <sup>-1</sup> at 0.05C (1C=300 mA g <sup>-1</sup> )	89.2% (100 cycles at 0.05 C)	-	-	1 M NaPF <sub>6</sub> in EC: DEC = 1:1 vol %	<sup>12</sup>
RHHC-1300// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> F <sub>3</sub> /C <sup>a</sup>	258 mAh g <sup>-1</sup> at 25 mA g <sup>-1</sup>	-	185	-	1 M NaClO <sub>4</sub> in EC: DEC = 1:1 vol %	<sup>13</sup>
H300-1100// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>a</sup>	310.4 mAh g <sup>-1</sup> at 50 mA g <sup>-1</sup>	85.2% (55 cycles at 50 mA g <sup>-1</sup> )	243.1	-	1 M NaPF <sub>6</sub> in EC: DEC = 1:1 vol %	<sup>14</sup>
H-OLHC1300 °C// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	307.2 mAh g <sup>-1</sup> at 50 mA g <sup>-1</sup>	83.3% (200 cycles at	-	-	1 M NaPF <sub>6</sub> in DEGDME	<sup>15</sup>

		600 mA g <sup>-1</sup> )				
Zn-HC// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>a</sup>	524 mAh g <sup>-1</sup> at 50 mA g <sup>-1</sup>	86% (650 cycles at 2000 mA g <sup>-1</sup> )	323	-	1 M NaPF <sub>6</sub> in DEGDME	<sup>16</sup>
CBHC// Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	144.57 mAh g <sup>-1</sup> at 50mA g <sup>-1</sup>	99.05% (50 cycles at 200 mA g <sup>-1</sup> )	110.05	37.90	1 M NaPF <sub>6</sub> in DEGDME	This work

<sup>a</sup>: The reversible capacity calculated based on the mass of anode; <sup>b</sup>: The reversible capacity calculated based on the mass of cathode.

## References

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