Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

of

“Synthesizing higher-capacity hard-carbons from cellulose for Na- and K-ion batteries”

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Experimental details

Hard carbon was synthesized via two-step heat-treatment of pre-heating and carbonization steps. Precursors were prepared by pre-heating 5 grams white powder of reagent-grade glucose (Kanto Chemical Co., Inc.), maltose (Nacalai Tesque), cellulose derived from cotton linter (Sigma-Aldrich Inc.), glycogen (Nacalai Tesque), and amylopectin (MP Biomedicals, Inc.) at 180 ^oC for 12 h at a heating rate of 5 ^oC min^{-1} with an electric muffle furnace (F-120-SP, Toyo Glass Machinery Co., Ltd.). Precursors derived from cellulose were prepared by heating cellulose powder in air at different temperatures of 180, 275, 300, and 350 ^oC for 12 h. The condition and apparatus for pre-heating are very important to have reproducible results of hard carbons, especially, for demonstrating high-capacity electrode materials.

The precursors were further carbonized with a tube furnace at 1300 ^oC for 1 h in Ar stream at a flow rate of 500 mL min^{-1}. Before reaching to the targeted temperature, temperature was raised at heating rates of 5 ^oC min^{-1} from room temperature to 250 ^oC, 1 ^oC min^{-1} from 250 to 450 ^oC, and 5 ^oC min^{-1} from 450 to 1300 ^oC [1]. In case of cellulose precursors, carbonization was carried at different temperatures of 700 - 1500 ^oC for 1 h at heating rates of 5^oC min^{-1} from room temperature to 250 ^oC, 1 ^oC min^{-1} from 250 to 450 ^oC, and 5 ^oC min^{-1} from 450 ^oC to the targeted temperature in Ar at a flow rate of 500 mL min$^{-1.}$.

X-ray diffraction (XRD) patterns were collected by using Multiflex (Rigaku Co.) with Cu Kα radiation at 40 kV and 30 mA at a scan rate of 2.0^o min^{-1}. Small angle X-ray scattering (SAXS) patterns were collected with UltimaIV and NANO-viewer (Rigaku Co.) with Cu Kα at 40 kV and 40 mA, for which a borosilicate glass capillary and a planer holder were used, respectively. N_2 adsorption/desorption measurement was carried out at 77 K in BET method with BELSORP-mini II (MicrotracBEL Co.) to estimate specific surface area. Prior to the measurements, the samples were heated at 200 ^oC for 3 h under vacuum. Thermogravimetry (TG)-differential thermal analysis (DTA) was carried with DTG-60 (Shimadzu Co.) in air at 5 ^oC min^{-1} heating.

For electrochemical test, hard carbon powder was mixed with sodium polyacrylate (Kishida Chemical) as a binder at a weight ratio of 95:5 with deionized water. The resulting slurry was uniformly pasted onto Cu for Li cell and Al foils for Na and K cells and dried at 80 ^oC in air and then at 150^oC under vacuum. Hard carbon electrodes with acetylene black (Strem Chemicals) and sodium polyacrylate were prepared at a weight ratio of 85:10:5 only for rate-capability tests. R2032-type coin cells were assembled in an Ar-filled glove box. Lithium metal (Honjo Chemical), sodium metal (Kanto Chemical), and potassium metal (Sigma-Aldrich) were used as a counter electrode. Electrolyte solutions used were 1.0 mol dm^{-3} $LiPF_6$ ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1 v/v) (Kishida Chemical), 1.0 mol dm^{-3} $NaPF_6$ propylene carbonate (PC) (Kishida Chemical), and 1.0 mol dm^{-3} $KN(SO_2F)_2$ (KFSA, Solvionic SA) EC:diethyl carbonate (DEC) (1:1 v/v) (Kishida Chemical) for Li, Na, and K cells, respectively. A glass fiber filter was used as a separator. Galvanostatic charge/discharge tests were performed in the voltage range of 0.002 - 2 V referring to Li, Na, or K electrodes at a current rate of 25 mA g^{-1} at approximately 25^oC. During the electroreduction process, constant voltage at 0.002 V for 8 h was applied after the galvanostatic reduction to minimize influence of polarization of the counter electrodes.

1) Xing, W.; Xue, J. S.; Dahn, J. R., *Journal of the Electrochemical Society* **1996,** *143* (10), 3046-3052.

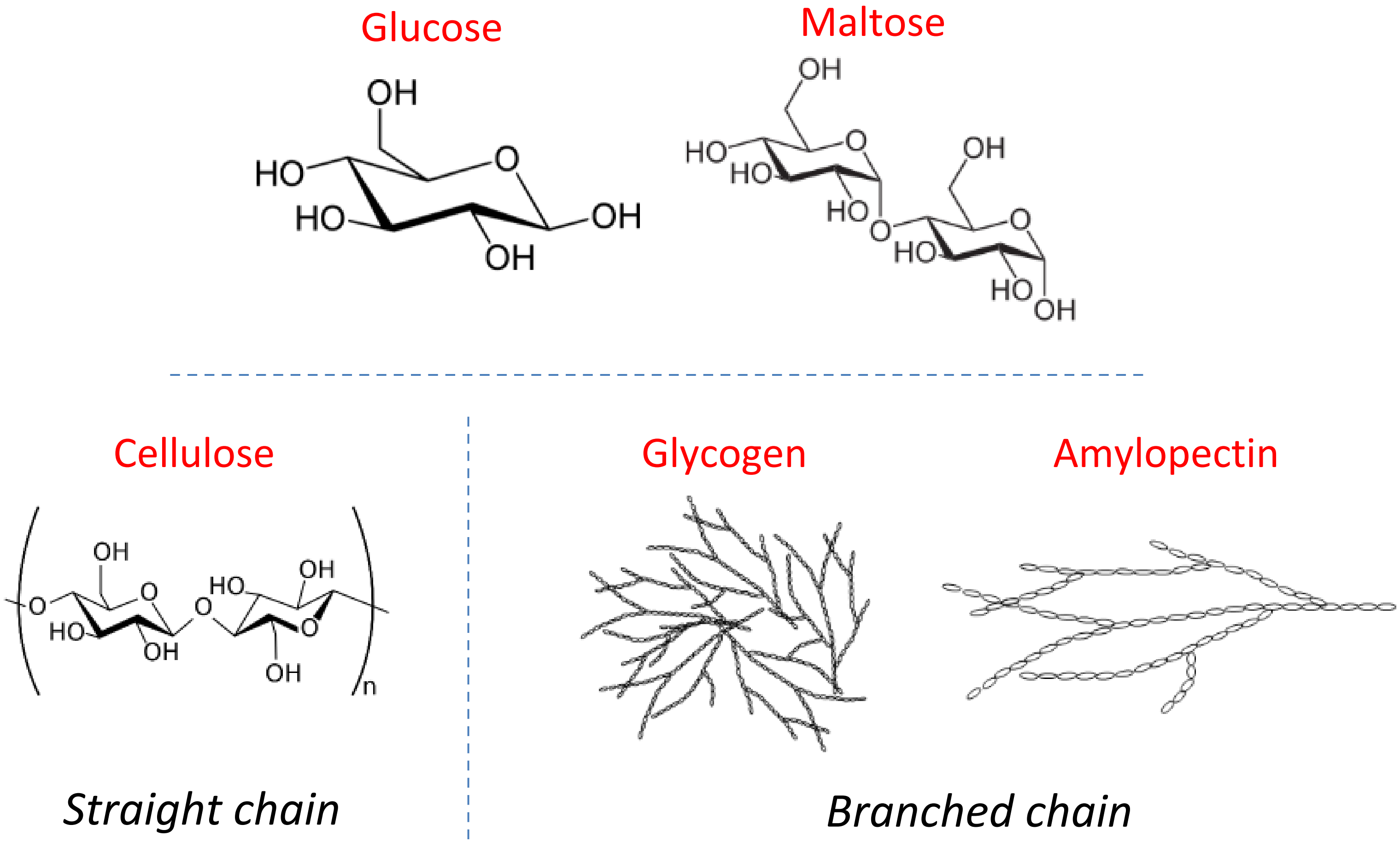


Figure S1. Molecular structures of raw saccharide materials used for HC synthesis.

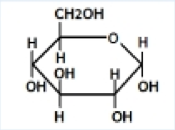
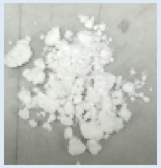
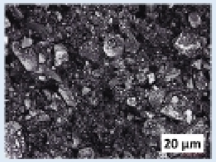
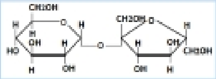
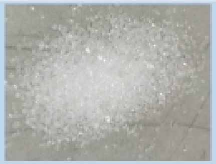
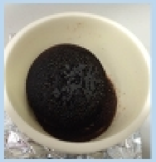
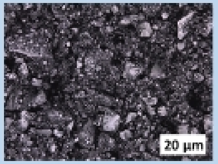
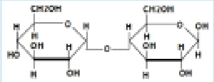
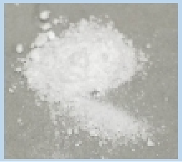
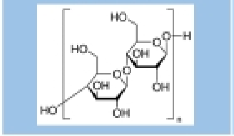
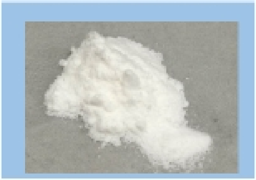
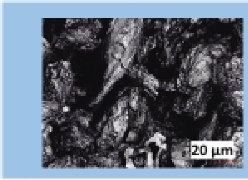
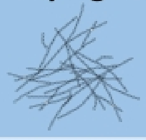
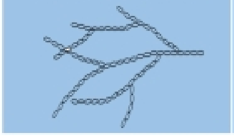
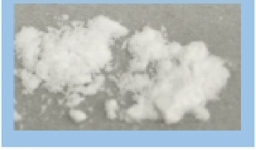
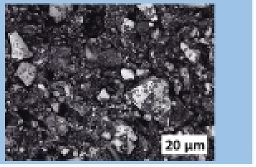
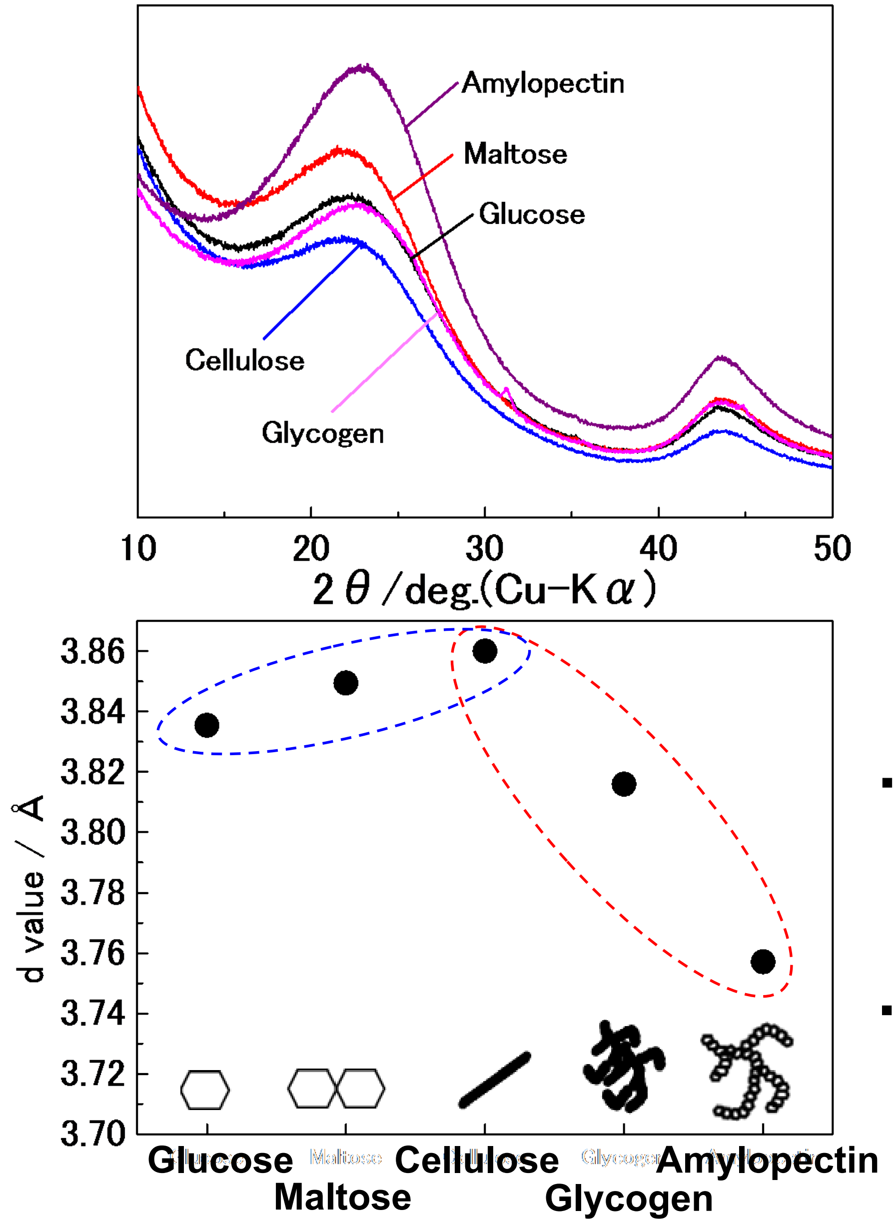
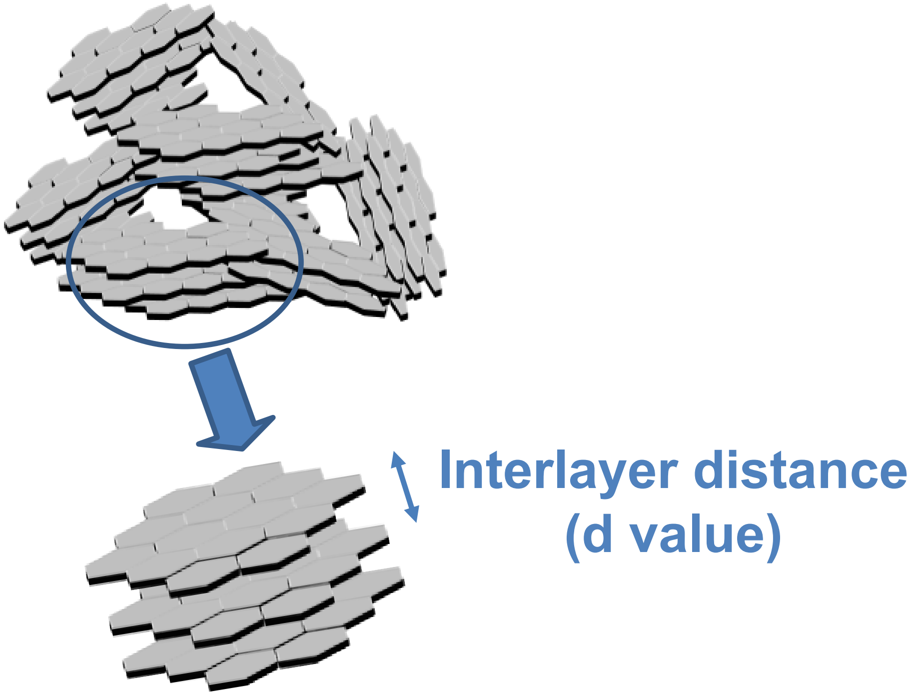
	Sample	Mw	Raw material	Precursor	Hard carbon
Mono-saccharide	Glucose 	180.2			
Di-saccharide	Sucrose 	342.3			
	Maltose 	342.3			
Poly-saccharide	Cellulose 	$1.0\times10^{5}\sim$ 1.0×10^{6}			
	Glycogen 	$1.0\times10^{6}\sim$ 1.0×10^{7}			
	Amylopectin 	$1.5\times10^{7}\sim$ 4.0×10^{7}			

Figure S2. Photos of raw powders of saccharides used in this study, precursors formed at 180°C, and hard carbons prepared at 1300°C.





- **Longer straight chain of poly saccharide**

  → ***Larger interlayer distance***

- **Many branches in the molecular**

  → ***Shorter interlayer distance***

Figure S3. XRD patterns and d values of the Bragg 002 peak of hard carbons prepared from various saccharides through the same heat treatment procedure.

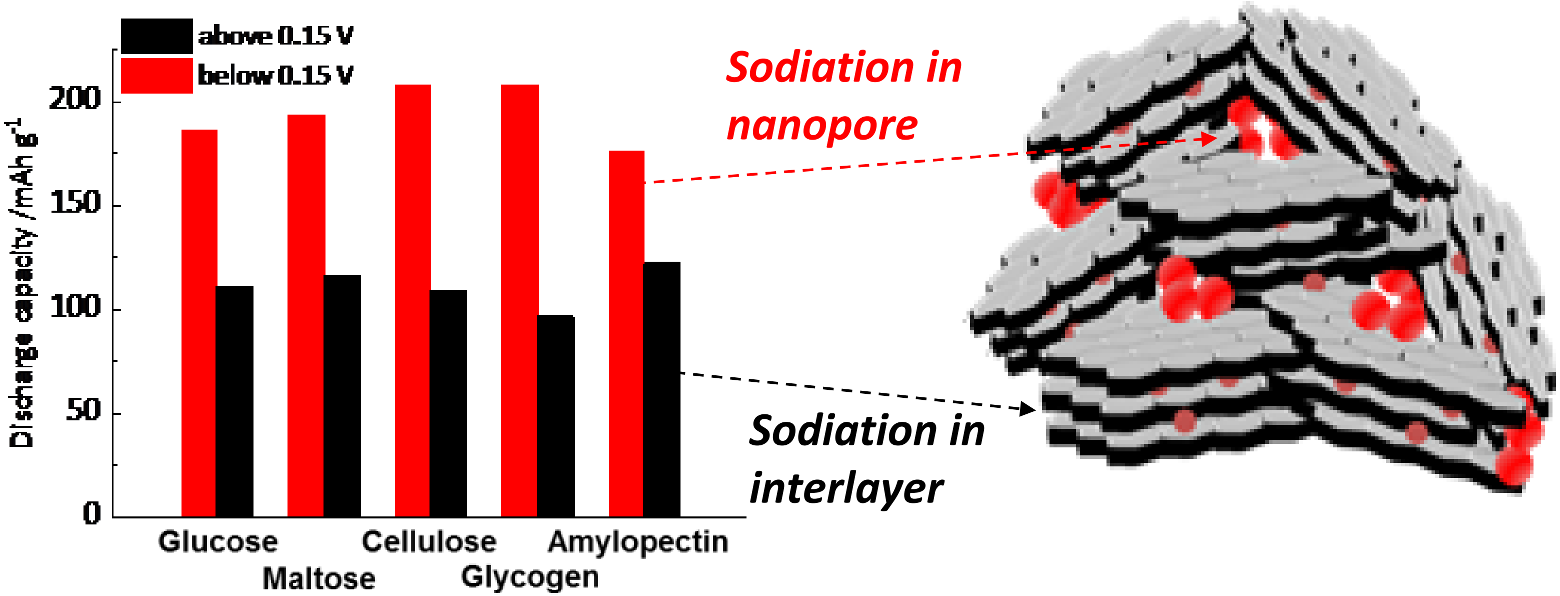


Figure S4. Reversible capacities divided at 0.15 V to find variation trends of the low-voltage plateau and high-voltage slope corresponding Na insertion into nanopore and interlayer, respectively, of hard carbons prepared from five saccharides.

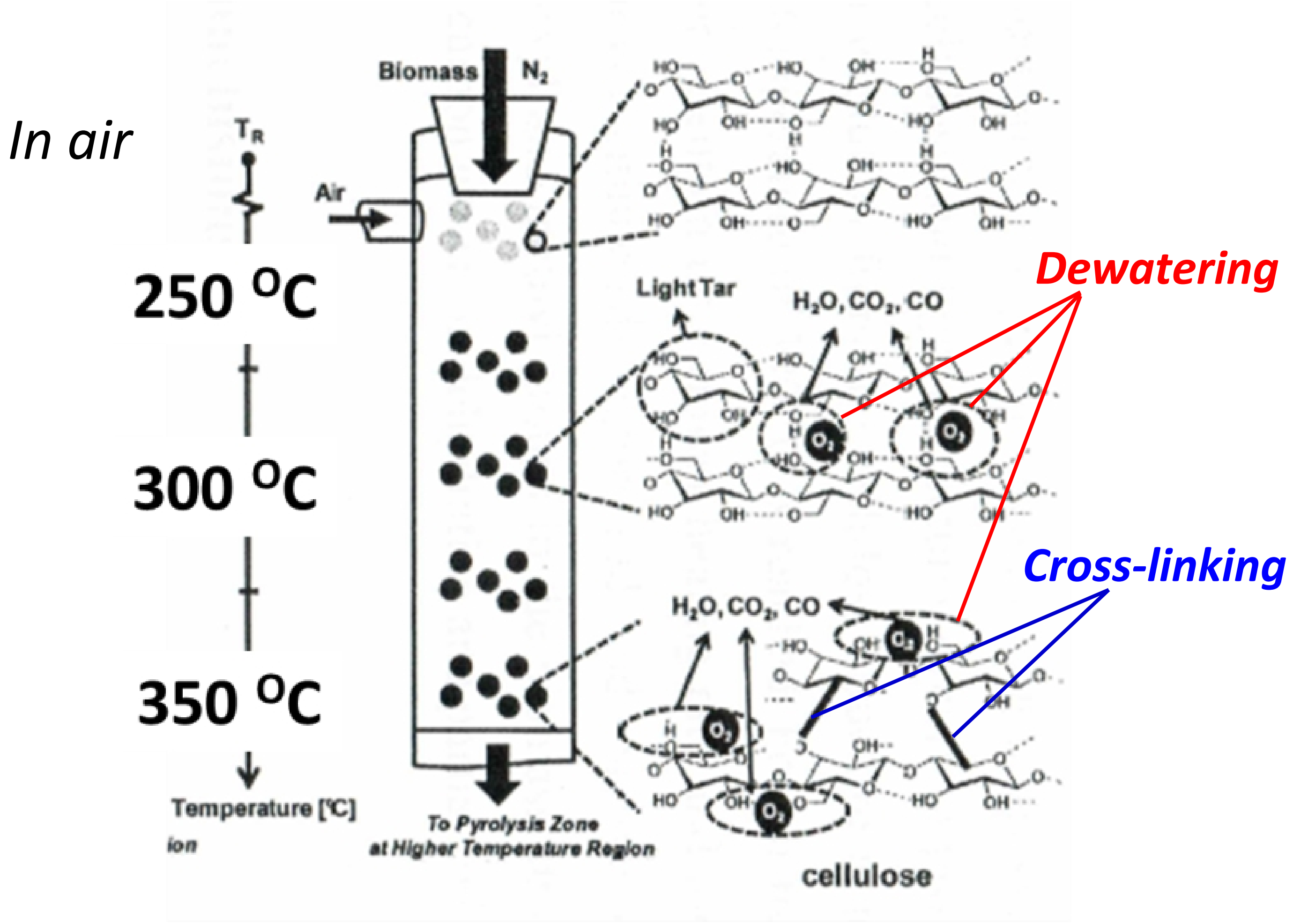


Figure S5. Thermal decomposition of cellulose, from a literature, W. Chariwat, Doctoral thesis, Kyoto University (2010). The decomposition of dewatering and crosslinking at temperature up to 350^{o}C should affect the micro structure of hard carbon.

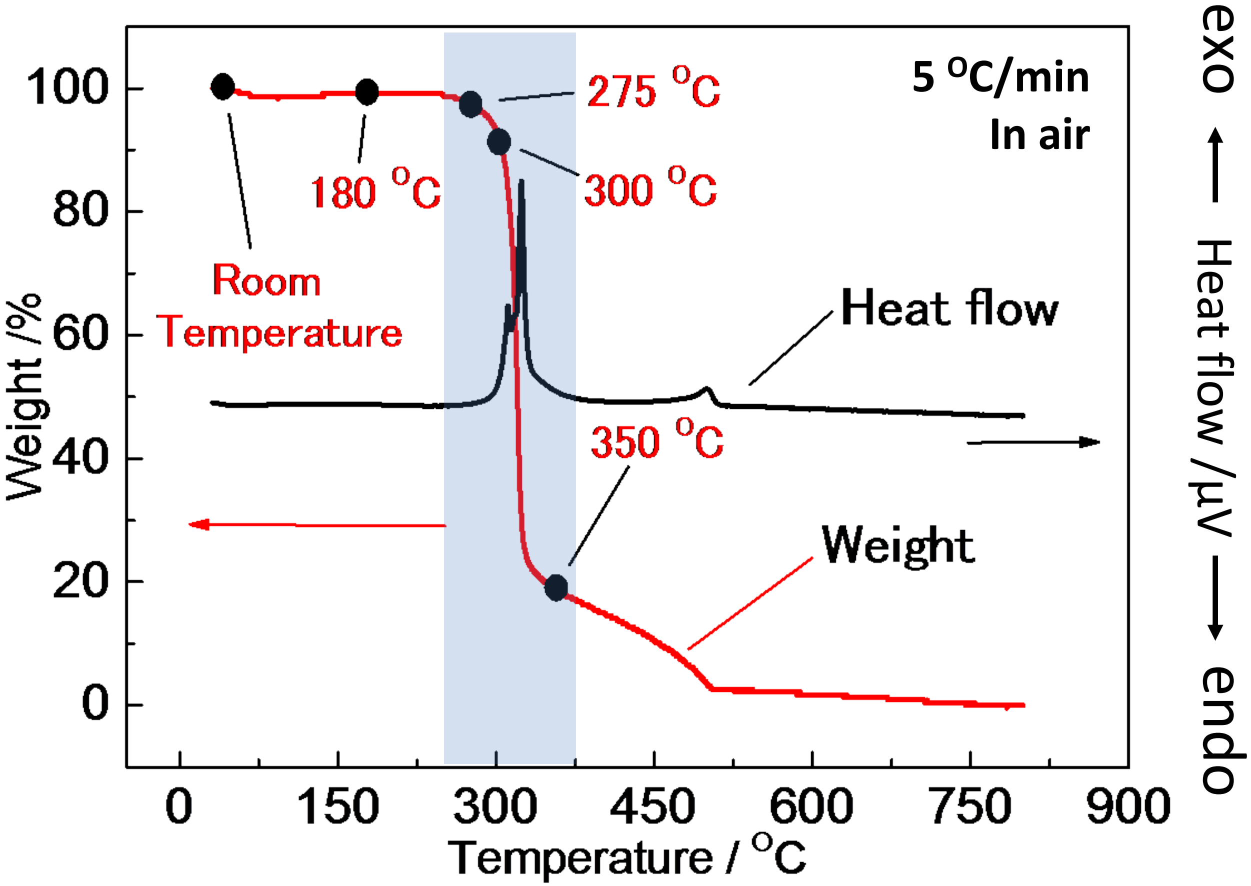


Figure S6. TG curve of cellulose powder measured in air. Large weight loss and exothermic peak were observed around 300 ^{o}C.

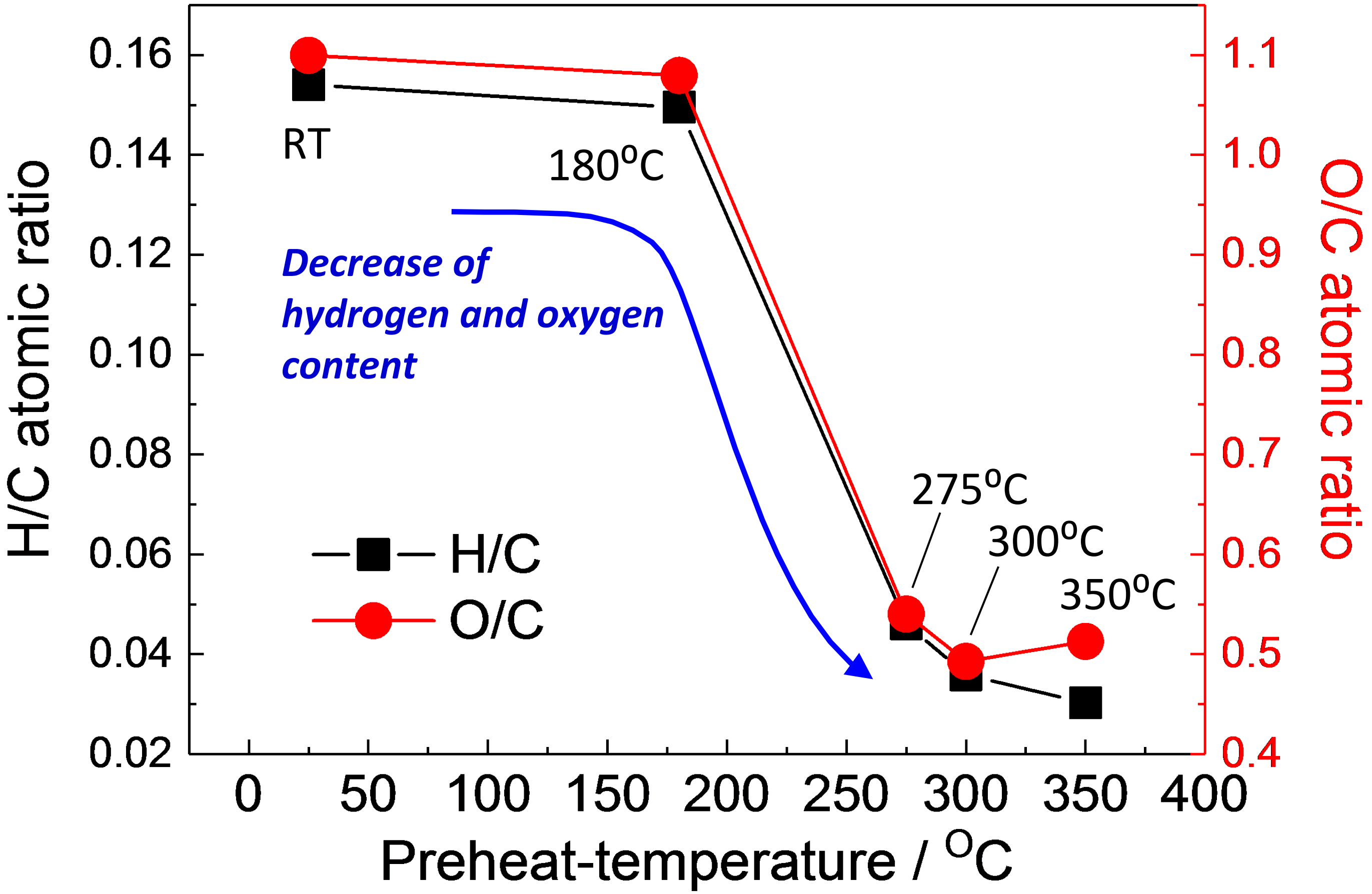
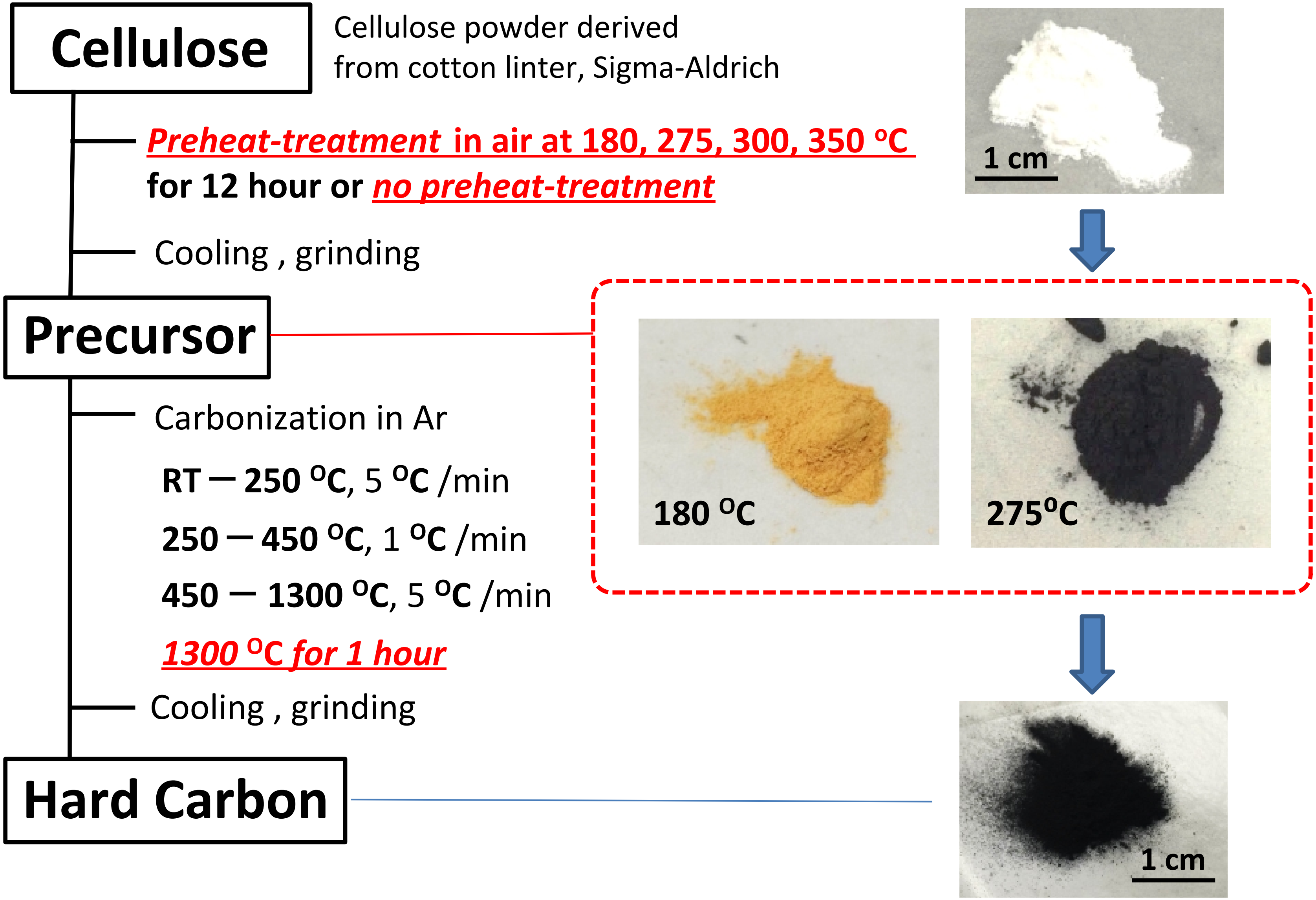


Figure S7. Elemental analysis results of H/C and O/C atomic ratio of hard carbon precursors of the preheat-treated cellulose . Heat-treatment in air results in decrease of oxygen and hydrogen content, which proved dewatering and cross-linkage in the precursors.



Cellulose

Cellulose powder derived from cotton linter, Sigma-Aldrich

Preheat-treatment in air at 180, 275, 300, 350 °C for 12 hour or *no preheat-treatment*

Cooling , grinding

Precursor

Carbonization in Ar

RT — 250 °C, 5 **°C** /min

250 — 450 °C, 1 **°C** /min

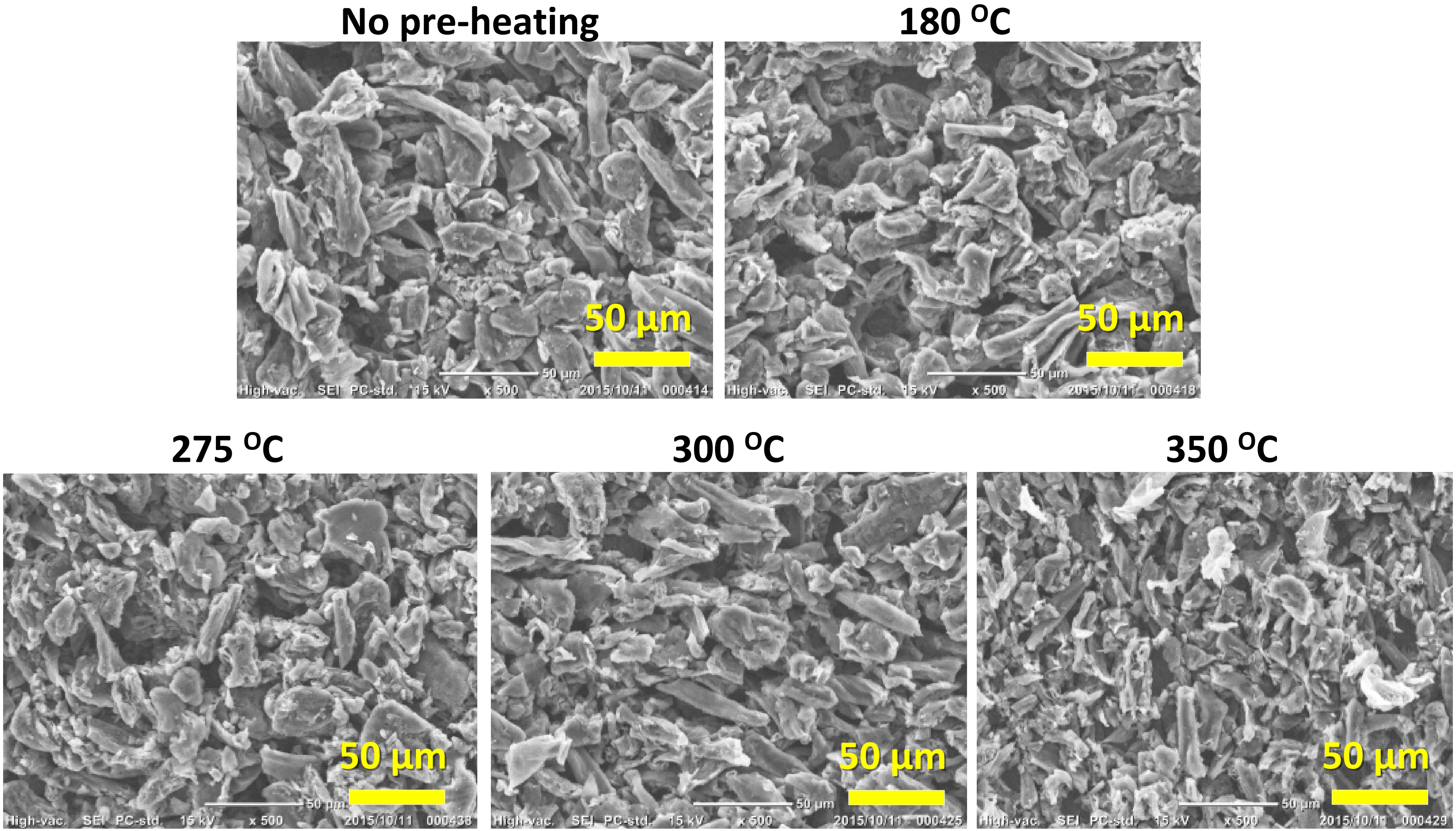
450 — 1300 °C, 5 **°C** /min

1300 °C for 1 hour

Cooling , grinding

Hard Carbon

Figure S8 Synthesis process of hard carbon from cellulose with photos of corresponding product powders.



No pre-heating

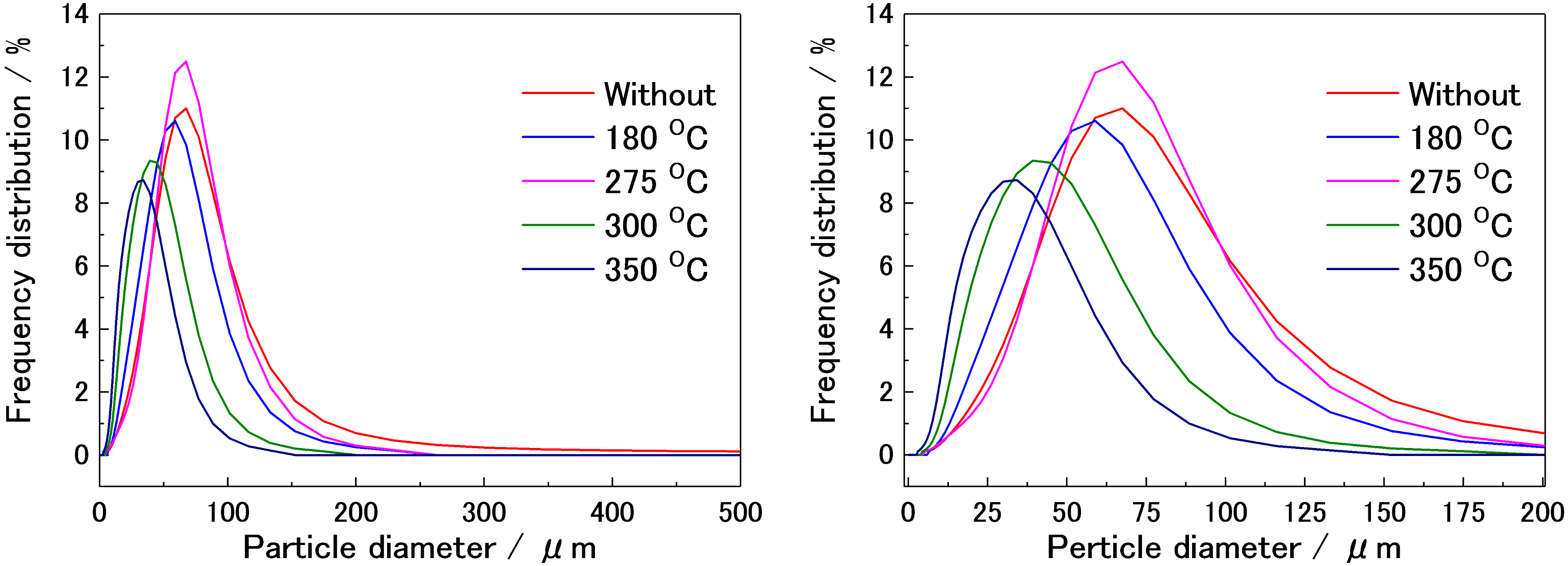
180 °C

275 °C

300 °C

350 °C

Figure S9. SEM images of hard carbons prepared by carbonization of precursors at 1300°C of different temperature of preheat-treatment.



Treat at ~275 ^{O}C ⟶ 50 ~ 70 µm

Treat at 300 ~ 350 ^{O}C ⟶ 25~50 µm

Figure S10. Particle size distribution of hard carbons prepared by carbonization of precursors at 1300^{o}C of different temperature of preheat-treatment. The data shows the decrease in particle size with elevating the temperature of pretreatment.

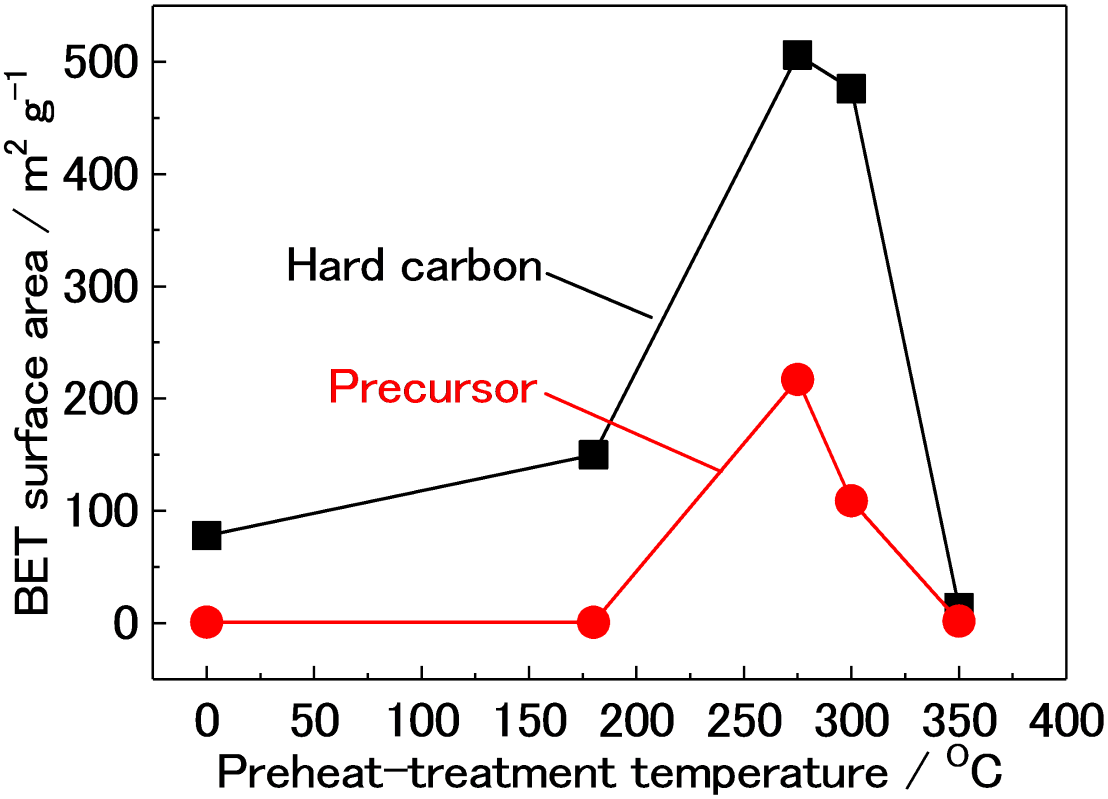
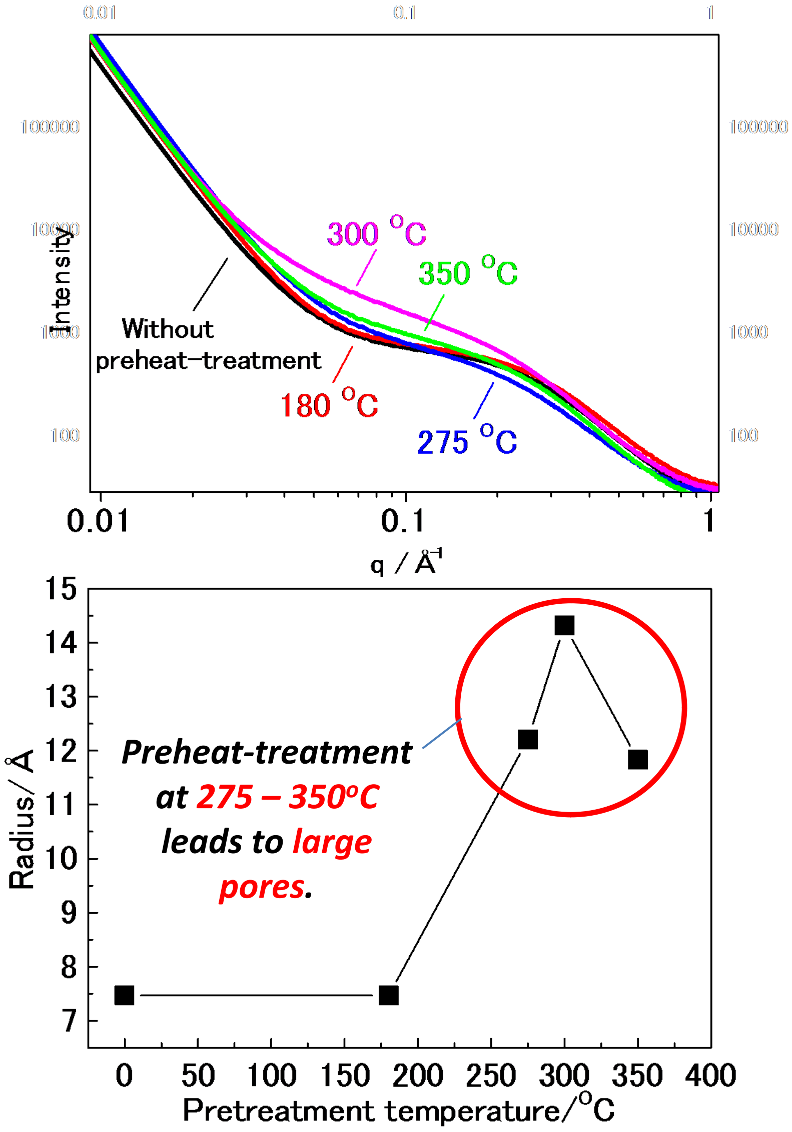


Figure S11. Variation of BET surface area of precursors and 1300°C-carbonized HCs as a function of pretreatment temperature.



Preheat-treatment at 275 – 350°C leads to large pores.

A model used for SAXS analysis

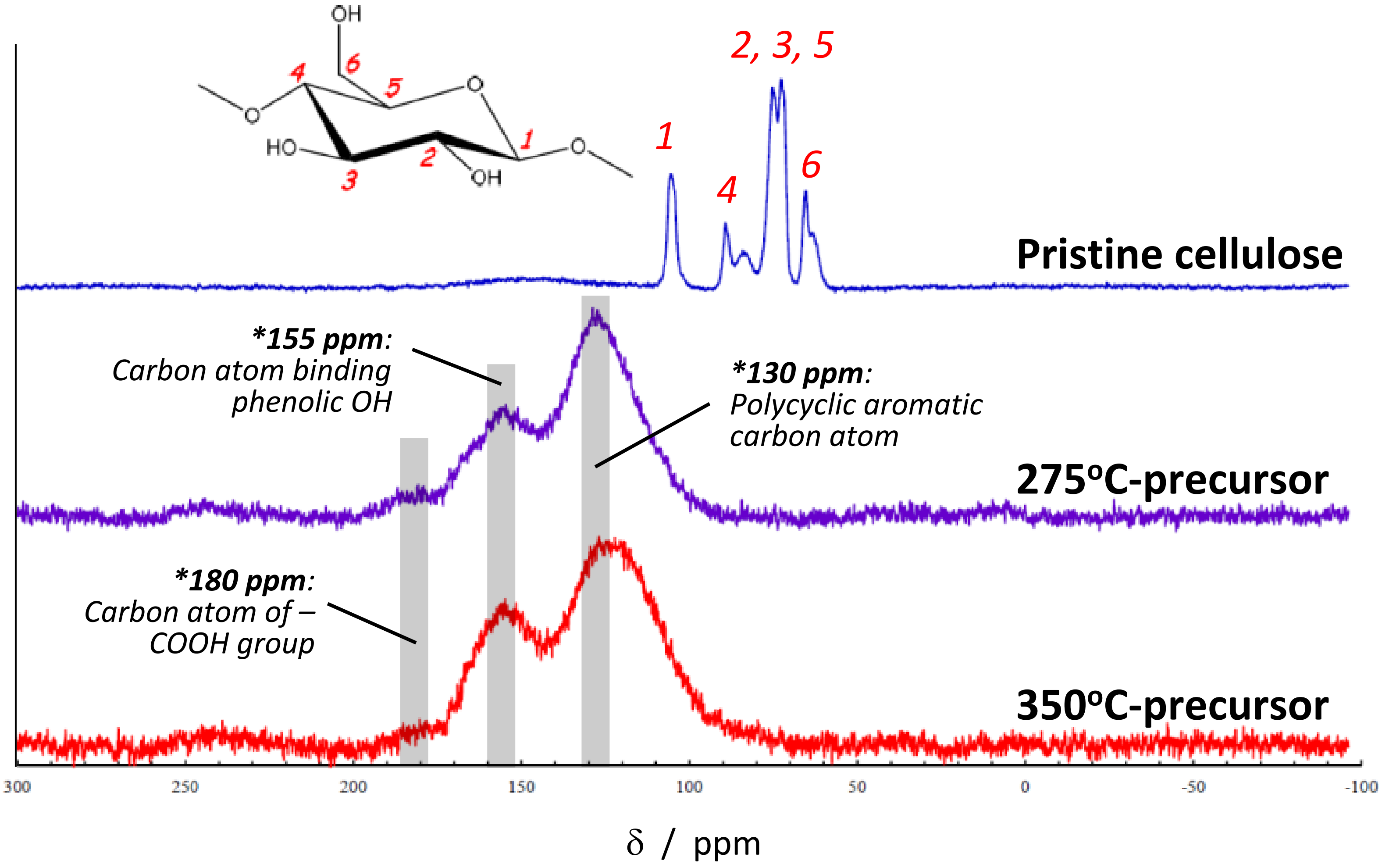
$$I(q) = \rho^2 I_{0K}\left[\frac{A}{q^n} + \frac{C_{mi}}{\left(1+b^2q^2\right)^2}\right]$$

$$R = \sqrt{10}b$$

q : the wave vector
A : proportional to the surface area of large mesopores
n : the fitting constant (n=4)
ρ^2 : the squared electron density of graphite
C_{mi} : proportional to the volume of micropores in the sample
b : the Debye autocorrelation length of the micropores
R : radius of micropores

Ref.) M.J. McDonald, J.R. Dahn *et al.*, *Carbon*, **68**, 452 (2014)

Figure S12. SAXS patterns and micropore's radii of hard carbons. A model used for pore size calculation is shown from the literature.



***155 ppm**: Carbon atom binding phenolic OH*

***130 ppm**: Polycyclic aromatic carbon atom*

***180 ppm**: Carbon atom of –COOH group*

Figure S13. Solid-state ^{13}C cross-polarization (CP) magic angle spinning (MAS) nuclear magnetic resonance (NMR) (CP/MAS NMR) spectra for pristine and heat-treated cellulose precursors at 275 and 350 . Contact time 2 ms.

*Ref.) S. Suganuma et al., *J. Am. Chem. Soc.* **2008**, *130*, 12787-12793 and related references therein.

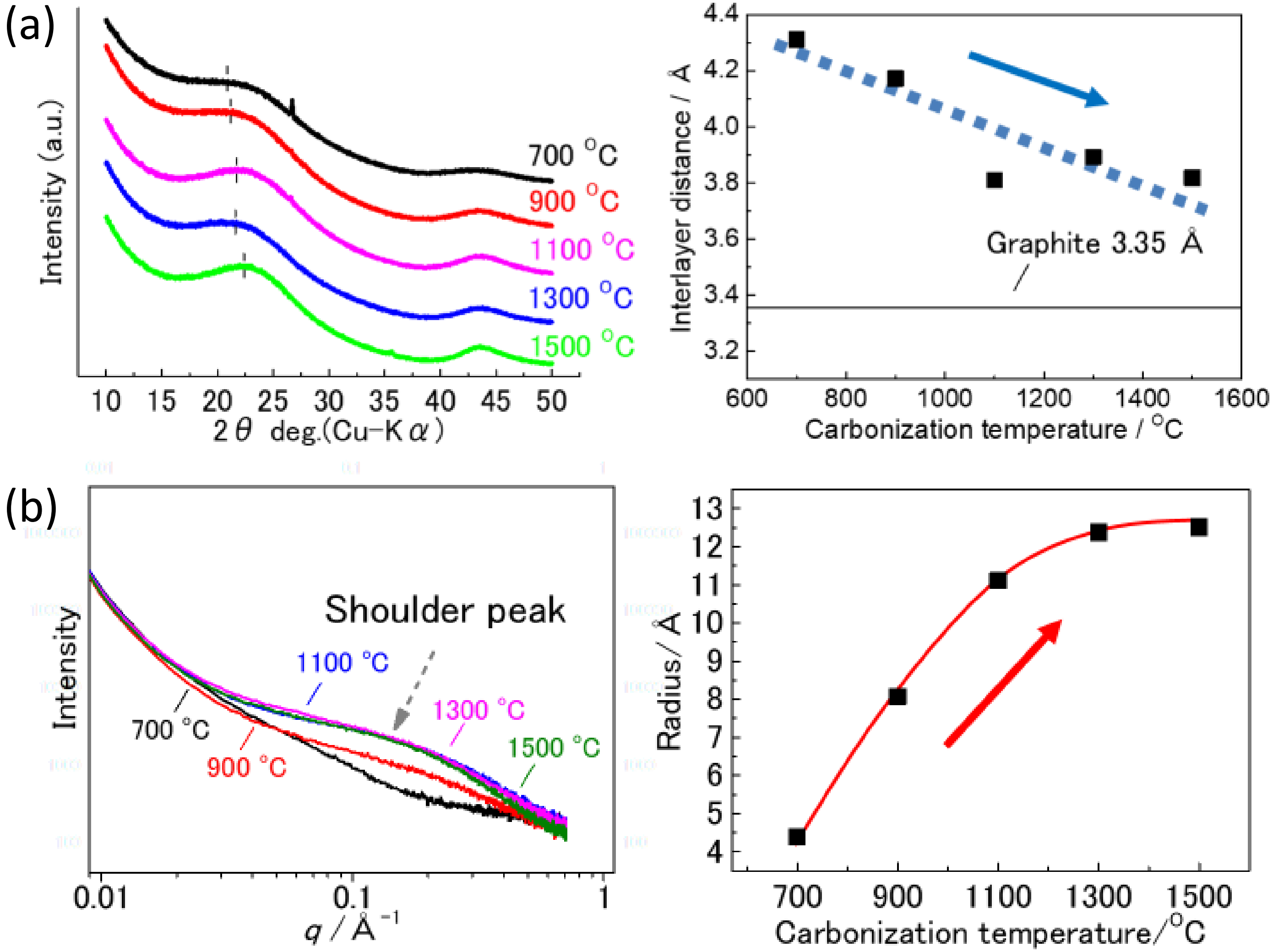
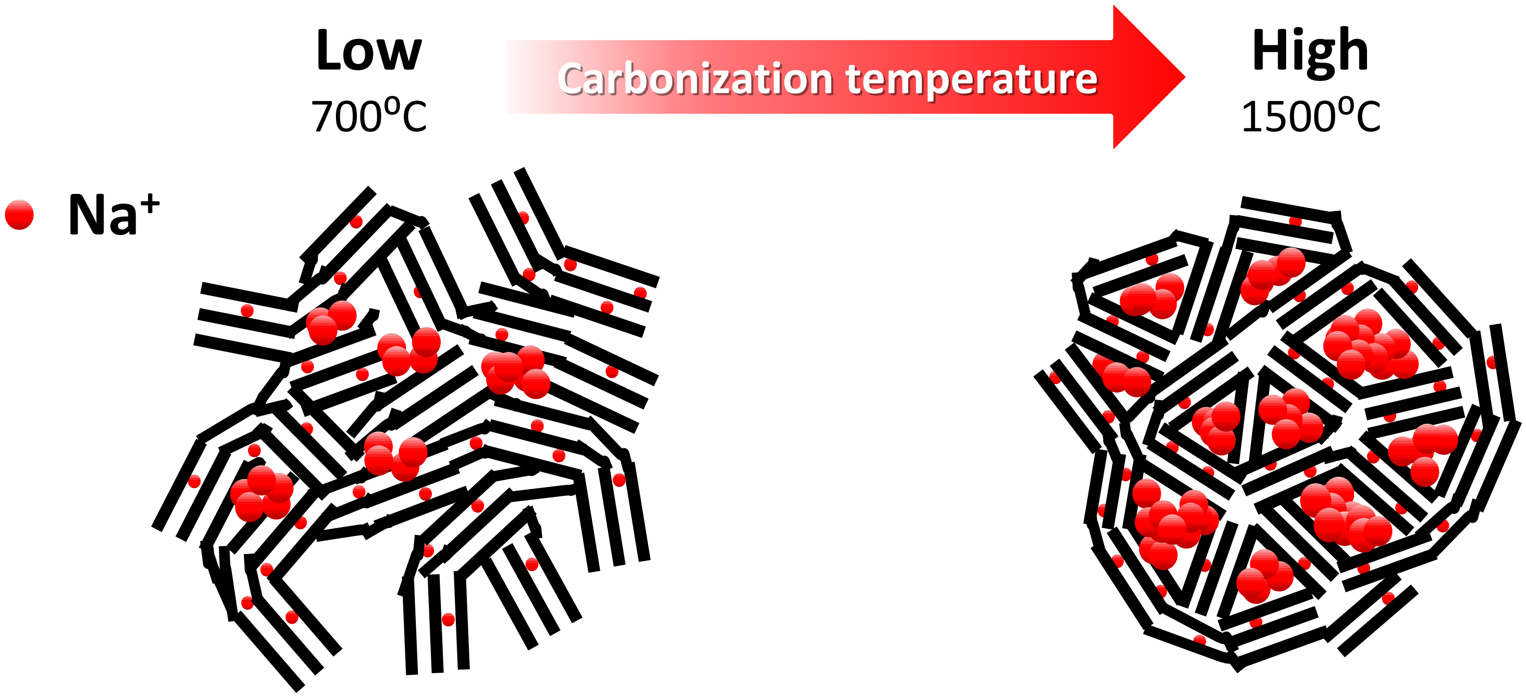
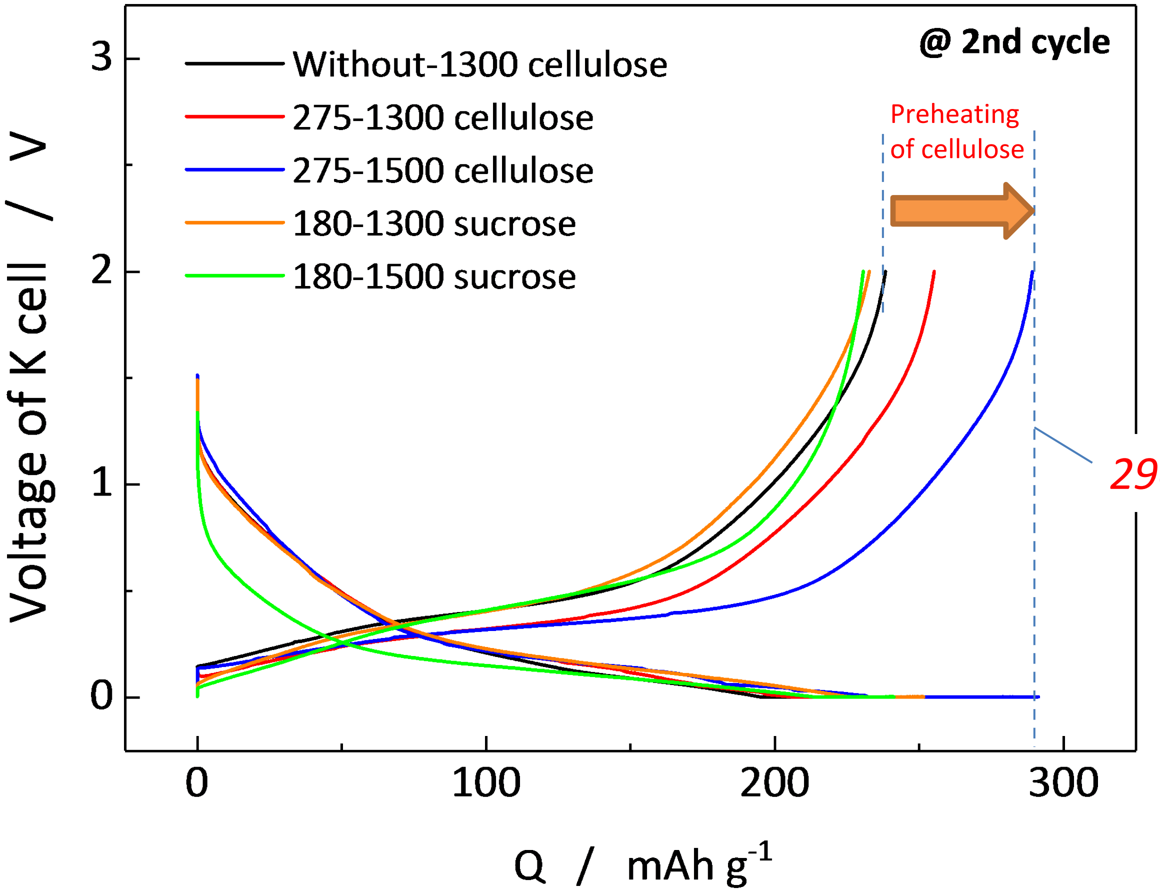


Figure S14. (a) XRD and (b) SAXS results of hard carbons prepared from precursors prepared at 275 ^{o}C by carbonization at different temperature.



Opened ←	*Micropore structure*	→ **Closed**
Large ←	*Interlayer distance*	→ **Small**
Small ←	*Micropore size*	→ **Large**
Low ←	*Na storage capacity into pores*	→ **High**

Figure S15. Scheme of dependence of hard-carbon properties on carbonization temperature showing that reversible capacity of hard carbon sodium cell gradually increased with the raising carbonization temperature from 700 to 1500°C which correlates with structural evolution.



290 mAh/g

HC: **PANa** = 95 : 5
1 M KFSA EC:DEC (1:1)
@ 25 mA/g
CC-CV @ 0.002 V
Sucrose HC ; 5 h
Cellulose HC ; 8 h

Figure S16. Second potassiation and depotassiation curves of hard carbons prepared through 274°C- and 180°C-pretreatment of cellulose and sucrose, respectively, followed by 1300°C- or 1500°C-carbonization. Cellulose- and sucrose-derived hard carbons are tested at a current rate of 25 mA g^{-1} under CC-CV potassiation by applying 0.002 V for 8 and 5 h, respectively.

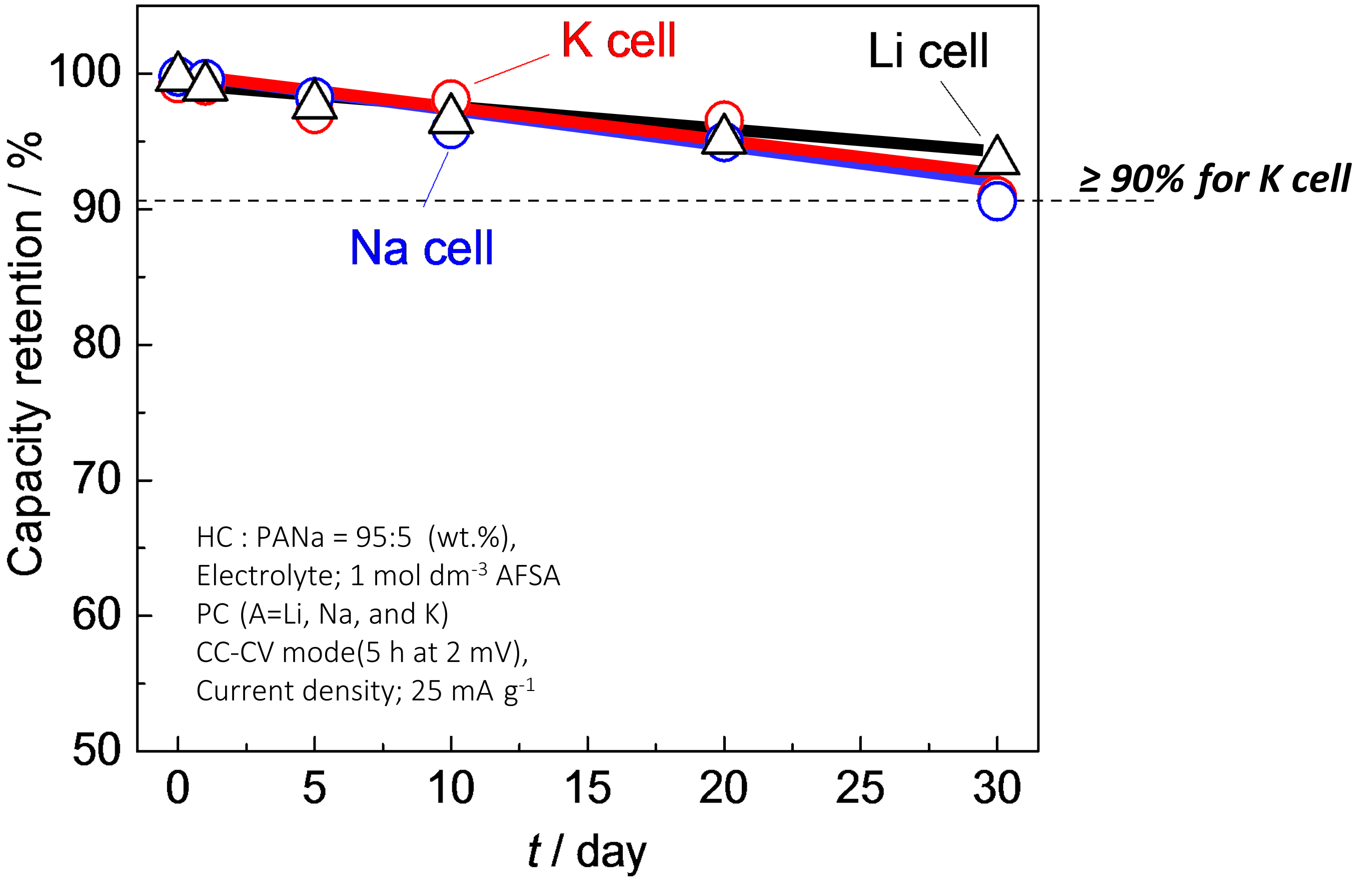


Figure S17. Capacity retention during storage of the hard-carbon electrodes after full insertion of potassium, sodium, and lithium at the tenth cycle, showing the self-discharge of negative electrode of K-ion battery will be comparable to the Li and Na cases.