Supporting Information

Design guideline for a high-performance hard carbon anode on sodium ion batteries

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Supplementary Methods

Preparation of the PHC series and microstructure-tuned PHC samples. Five grams of waste PET bottle, which was washed with ethanol and distilled water several times, was cut into small pieces of 3 cm \times 5 cm². The PET chips were then thermally treated at different temperatures—280, 320, 350, and 380 °C—for 30 min under an air flow rate of 100 mL min⁻¹ in a tubular furnace. The resulting samples were moved into a graphite furnace, and heated under Ar atmosphere, from room temperature to 1200, 1600, 2000, 2400, and 2800 °C. Different heating rates, specifically 5, 3, and 2 °C min⁻¹, were applied for the temperature ranges, room temperature to 1600 °C, 1600–2400 °C, and 2400–2800 °C, respectively. The asprepared PHC-series samples were washed several times using ethanol and distilled water and stored in a vacuum oven at 30 c. In addition, O280-2400 was mixed with potassium hydroxide (O280-2400 to KOH weight ratios of 10, 30, and 50 wt%) in a mortar, and the mixture was then heated in a tubular furnace at 800 °C for 2 h. Heating rate of 5 °C min⁻¹ and an Ar flow of 150 mL min⁻¹ were applied for the activation process. The products, activated hard carbon, were washed with distilled water and ethanol several times, and stored in a vacuum oven at 30 °C min⁻¹.

Characterizations. The morphologies of the samples were characterized using TEM (JEM2100F, JEOL, Japan) and field-emission scanning electron microscopy (FE-SEM; S-4300SE, Hitachi, Japan). Raman spectroscopy was conducted using a Renishaw InVia Raman microscope (Renishaw, U.K.) equipped with a laser with a wavelength of 514 nm, 0.15 mW output, of 1200 groove/mm grating. The spot size of the laser was focused through a 100X optical lens and the exposure time was set to 10 s. In the Raman spectra analysis, the L_a (lateral size of a polyhexagonal carbon plane was calculated from the intensity ratio of *D* to *G* bands,

 I_D/I_G . For cases wherein L_a exceeds 2 nm, the Tuinstra and Koenig equation, $I_D/I_G = (\lambda)/L_a$, was employed, and the constant $C(\lambda)$ was set at 4.4 for a 514 nm laser wavelength. When L_a is less than 2 nm, the Ferrari and Robertson relationship, $I_D/I_G = C'(\lambda)/L_a^2$, was utilized. The wavelength-dependent pre-factor C' (λ) was determined as C' (λ) = $C_0 + \lambda C_1$, where C_0 equals -12.6 nm and C1 is 0.033.38 XRD (Rigaku, DMAX 2500) was performed using a Cu-Ka radiation ($\lambda = 1.54$ Å) at 40 kV and 100 mA with a 2 θ range of 5°–60°. For the XRD analysis, a copper K α radiation source (wavelength $\lambda = 0.154$ nm) was employed within a 2 θ range of 5°–60° at 100 mA and 40 kV. The Scherrer formula, $L_c = K\lambda/\beta\cos\theta$, was applied to determine the crystallite thickness along the c-axis (L_c) , with K representing the shape factor (typically 0.9), λ denoting the X-ray source wavelength for Cu Ka (1.54 Å), β signifying the full width at half maximum in radians, and θ indicating the diffracted angle.³⁸ Specific surface areas of the samples were characterized through an analysis of the nitrogen adsorption and desorption isotherms at 77 K (ASAP2020, Micromeritics, USA). Surface properties of the samples were measured via X-ray photoelectron spectroscopy (XPS; PHI 5700 ESCA, Chanhassen, USA) using monochromatic Al-Ka radiation. Particle densities were recorded on an AccuPyc1330 analyzer using Helium as analysis gas. The SAXS data were collected using Lab-SAXS (Rigaku, NANOPIX) with Cu-Ka radiation at a sample to detector distance of 330 mm (qrange: $0.02 - 0.5 \text{ Å}^{-1}$) All the SAXS data reduction and model fitting was processed using Nika/Irena packages. Silver behenate (AgBe) was used to calibrated the q-space of SAXS data. The molecular weights of the pristine PET and oxidized samples were analyzed using gel permeation chromatography (Tosoh EcoSEC HLC-8420 GPC). The column temperature was maintained at 40 °C, and the flow rate was at 0.3 mL min⁻¹. 1-1-1-3-3-3-hexafluoro-2-propanol with 0.01 N sodium trifluoroacetate was delivered as the elution solvent. The molecular weights were calibrated using polymethyl methacrylate standards.

Electrochemical characterization. The electrochemical properties of the PHC series, A10, A30 and A50 were characterized using CR2032-type coin cells and a WonAtech automatic battery cycler (wbcs3000Le32 4, WonAtech, South Korea). For the half-cell tests, coin cells were assembled in a glovebox filled with argon gas using the samples as the working electrode and sodium foil as both the reference and counter electrodes. NaPF₆ (1 M; Sigma-Aldrich, 98%) was dissolved in a solution of ethylene carbonate (EC) and diethyl carbonate (DEC) mixture (1:1, v/v). A glass microfiber filter (GF/F, Whatman, UK) was used as a separator. The working electrodes were prepared by a slurry method using the PHCs active materials, conductive carbon (>99%, Alfa Aesar, USA), and polyvinylidene fluoride binder (M_w: 534,000, Sigma-Aldrich, USA) at a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone. The resulting slurries were applied uniformly to Cu foil (99.8%, Welcos, South Korea) substrates, which were dried at 80 °C for 1 h and roll pressed. The working electrodes were prepared by mechanically producing samples with a diameter of 1/2 in, wherein the active material loading density was approximately 2 mg cm⁻². Galvanostatic discharge and charge tests were conducted at a current density of 25 mA g⁻¹ in the voltage range of 0.001–2.0 V (Na⁺/Na). EIS was conducted at room temperature in the frequency range of 1 MHz to 50 Hz using an impedance analyzer (ZIVE SP1, WonAtech, South Korea). In situ XRD analysis was performed using a handmade coin-cell configuration. The charge and discharge processes were conducted in constant-current mode at a current rate of 25 mA g⁻¹ over a voltage range of 0.001–2.0 V. In situ XRD measurement was conducted on the 3D beamline at the Pohang Accelerator Laboratory (PAL) using synchrotron radiation ($\lambda = 0.68824$ Å). In situ Raman analysis was conducted in constant-current mode with a cover glass-assisted 2032 type handmade coin-cell to prevent air during the discharge and charge processes. The in situ volume expansion of the half-cells was measured using an HS Swell Analysis cell configuration and MGS USB gauge monitor software (Magnescale, Welcos, South Korea).

Sequential sodiation–lithiation tests. Sodium half-cells were constructed using O280-2400 or A30 as the working electrode, sodium foil as the counter/reference electrode, and a glass microfilter separator. These components were assembled using a sodium-based electrolyte (1 M NaPF₆ in EC/DEC). The sodium half-cells were galvanostatically pre-cycled at a current density of 25 mA g⁻¹ over a voltage range of 0.001–2.0 V vs Na⁺/Na. Subsequently, the samples were sodiated at 0.001 V. The fully sodiated O280-2400 or A30 working electrode was then extracted from the sodium half-cells and re-assembled with a lithium foil counter/reference electrode, a new separator (glass microfiber filter), and a lithium-based electrolyte (1 M LiPF₆ in EC/DEC) under an argon atmosphere. The fully sodiated electrodes were sequentially lithiated in lithium half-cells over a voltage window of 0.34–0.01 V and delithiated up to 2.0 V vs. Li⁺/Li.

Supplementary Texts

Supplementary Text 1. Transmuting macromolecular structure of a waste PET precursor A waste PET bottle was chopped into small slices of a few centimeters in lateral size and then thermally treated at different temperatures of 280, 320, 350 and 380 °C (hereafter called as O280, O320, O350, and O380, respectively), which are ranged between melting point and thermal decomposition temperature, for 30 min under air atmosphere in a lab-scale tube furnace. The oxidation process is the key to controlling the local microstructure of carbon in the resulting hard carbon materials. As the oxidation temperature increases, the numberaverage molecular weight (M_n) of the PET backbone gradually decreases (Fig. S1 and Table S1). With the reduction of molecular weight, the polydispersity index (PDI, bare PET bottle: 2.96) is also decreased by 2.72 and 2.28 for O280 and O320, respectively. This indicates that the polymer main chains were degraded by oxidation reactions. The Gel Permeation Chromatography (GPC) data for O280 and O320 showed that the main peak position gradually shifted with increasing oxidation temperature (Fig. S1). Note that the PDI values are surge increased in the higher oxidation temperature of 350 and 380 °C by 4.12 and 6.98, respectively (Table S1). The large change in the average molecular weight with the oxidation temperature supports this tendency. As shown in the GPC data, the main peaks of O350 and O380 were split into two, of which the small peak corresponded to the original PET molecules and the higher peak originated from the newly formed small molecules (Fig. S1). These results indicate that, in the higher oxidation temperature of \geq 350 °C, decomposition of the PET molecules asymmetrically happens, where smaller molecules are more reactive in the high-temperature, leading to the large separated molecular weight distribution. To confirm the change in chemical structure during the oxidation process, infrared (IR) spectroscopy was conducted on the oxidized PET series samples (Fig. S2).35 The IR spectra of all the oxidized PET samples showed similar profiles, indicating that the primary bonding nature of PET did not change

significantly with the thermal oxidation process despite the chain session. XPS C 1s spectra showed a relative intensity change of C-O to other bonds (Fig. S3a), where the relative C-O bond intensity slightly increased with the oxidation temperature by 350 °C, and accordingly, the oxygen content increased slightly (Fig. S3a and Table S1).³⁶ A similar trend was observed in the XPS O 1s spectra (Fig. S3b). Considering the previously reported studies exhibiting the thermal oxidation/degradation mechanism of PET, the increasing oxygen content is because of the increase in oxygen termination groups with main chain cleavage.³⁷ However, O380 shows a large reduction in oxygen content, particularly on the C-O bond (Fig. S3), which suggests that decarboxylation reactions progressed considerably as secondary thermal processes.³⁷ The reaction produces a broad range of cyclic oligomers and aromatic compounds, which cannot be detected in the IR spectra and XPS data owing to their similar molecular structure to PET. An optical image of an oxidized PET solution (1 wt%) dissolved in 1,1,1,3,3,3-hexafluoro-2propanol (HFIP) show a gradual color change with the oxidation temperature from tranperant to dark brown color close to black (Fig. S4). The oxidized PET solutes were fully dissolved in the solvent, indicating that macromolecules formed by a cross-linking reaction between intermolecules were slightly generated, which is also supported by the GPC results. Additionally, the microstructures of the bare and thermally oxidized PET samples were characterized using XRD. The amorphous structure of the bare PET crystallizes during the oxidization process at $280 \sim 350$ °C, where no distinctive microstructural differences were observed in the oxidized PET samples (Fig. S5). In contrast, a significant change in microstructure occured due to a further increase in the oxidation temperature to 380 °C. The O380 shows a very broad peak at around 22°, which is markedly different from those of other samples, which exhibit several sharp peaks indicative of PET crystallites. This result may be attributed to a broader range of molecular weight distribution. Hence, the PET backbones were gradually degraded with increasing thermal oxidation temperature, and the molecular weights

and PDI were significantly changed. In the subsequent carbonization process, thermal oxidation significantly affected the local carbon microstructures of the resulting PHCs.

The carbonization behavior of the oxidized PET samples at different temperatures was characterized by thermogravimetric analysis (TGA) as a heating rate of 5 °C min⁻¹ under a nitrogen flow of 200 ml min⁻¹, as shown in Fig. S6. The TGA curves, however, show almost same curves, where thermal decomposition occur at ~380 °C, and approximately 17% to the initial weight remained for O280, O320, and O350, whereas a higher yield of approximately 20% was rettained for O380. This could be because some molecules of O380 are already decomposed during the oxidation process, because the oxidation temperature is the starting point for thermal degradation. This can be confirmed by the oxidation yield; O380 has a lower oxidation yield of ~93% to others (98.1%–99.5%) (Table S1). In contrast to the characterless TGA curves, the differential scanning calorimetry (DSC) profiles show a noticeable change (Fig. S6). The DSC curves of bare PET, O280, O320, and O350 show a melting peak at 250 °C, whereas that of O380 did not show the meting peak. This indicates that O380 lost its crystallographic character of PET in the thermal oxidation process. The large number of small molecules produced in the thermal oxidation process can mitigate the intra-and intermolecular interactions of the PET molecules, hampering their crystallization. In addition, the second higher endothermic peaks are observed above 400 °C for all the samples, where them of O350 and O380 are split into two parts. This may be because smaller molecules are thermally degraded at lower temperatures. Immediately before the second endothermic peaks were exhibited, a broad exothermic slope was observed in the DSC curves of bare PET and O280, although rapid weight loss was initiated at this temperature. The presence of an exothermic slope in the high-temperature region with weight loss can be interpreted as a stronger exothermic reaction than endothermic reaction. As the endothermic reaction became dominant,

the exothermic slope disappeared in the DSC curve of O320, and strong endothermic peaks were observed for O350 and O380. In the case of O350 and O380, the thermal decomposition of CO or CO_2 mainly occurs because of the lower intermolecular interaction, where the remaining aromatic rings can be fused into poly aromatic structures. In contrast, bare PET and O280 were mainly cross-linked before thermal decomposition, and the aromatization reaction was relatively compact. These differences in thermal decomposition behavior result in highly different carbon microstructures in the resulting PHCs.

Supplementary Text 2. Microstructure analysis of the PHC series samples

The XRD patterns and Raman spectra revealed microstructural differences in the PHC series of samples (Fig. S7 and S8). In the PHCs prepared at relatively low heating temperature of ≤2,000 °C, their XRD patterns show highly broad graphite (002) peaks regardless of oxidation temperatures, whereas a sharp graphite (002) peaks occur in the samples prepared at 2400 °C and the sharp peaks are significantly increased in the 2800 °C-treated samples (Fig. S6). Effects of the oxidation temperatures are clearly observed in the 2400 and 2800 °C-treated samples, where the graphite (002) peaks are more intensified and narrower with increasing oxidation temperatures. Gradual improvements in the graphite (002) peak intensity and sharpness indicated that the graphitic layers became more ordered and developed. The growth of the graphitic structures accompanies densification of the graphene layers, reducing d-spacing of the graphitic lattices from 3.99 to 3.37 Å (Fig. 1a and Table S2).³⁸ In particular, the presence of sharp graphite (002) peaks for 2400 and 2800 °C-treated samples mean that long-range ordered graphitic structures with more densified lattice spacing of ≤ 3.4 Å are developed in their bulk microstructures. According to Scherrer equation, thicknesses of the graphitic layers (L_c) are calculated as 0.97–33.67 nm (Table S2).³⁸ A clear growth of L_c values is observed in the samples prepared at higher heating temperatures of \geq 2400 °C, where the L_c values become higher with increasing oxidation temperatures.

The Raman spectra of all the PHC-series samples showed the signature D and G bands of sp^2 -structured carbon materials (Fig. S8). The D band originates from a range of coupled vibrational modes from various carbon defect structures, whereas the G band is induced by the primary Raman-active mode of highly ordered graphenic domains. In the 1200 °C-treated samples, the D and G bands are fused each other, indicating most of the ordered graphenic building blocks are mixed with defective carbon structures without clear phase separation. HR- TEM images of the 1200°C-treated sample reveal the highly disordered carbon microstructure (Fig. S9–S12). The *D* and *G* band fusion is considerably mitigated in the Raman spectra of 1600 °C-treated samples, and those of \geq 2000 °C-treated samples exhibit clearly separated bands (Fig. S8). HR-TEM images of the 1600, 2000, 2400, and 2800 °C-treated samples confirm the microstructural transition with increasing heating temperatures, where the sp²-structured polyhexagonal carbon domains are more developed and gradually grown in size (Fig. S9–S12). The *D* to *G* band intensity ratio (I_D/I_G) indicated the size of the ordered graphene domain (L_a). The L_a values gradually increased with increasing heating temperature, where a higher oxidation temperature led to higher L_a values in samples with the same heating temperature (Table S2). In particular, the S380-2800 sample exhibited a significantly high L_a value of ~53 nm.

Supplementary Text 3. Calibration to mass-specific scattering cross-seciton

All the collected scattering profiles were calibrated to the mass-specific scattering crosssection, $I^{cm^2g^{-1}}$ by the method previously reported.^{39,40} Firstly, the as-collected SAXS profiles were calibrated to the volumetric scattering cross-section, I_s^{cm-1} , using standard glassy carbon (NIST SRM 3600, SN: A37) as a reference sample (Fig. S13). Then, $I_s^{cm^{-1}}$ was converted to mass-specific scattering cross-section, $I_s^{cm^2g^{-1}}$, by normalization with effective desnity of sample, ρ_{eff} ,

$$I_{s}^{cm^{2}g^{-1}}(q) = \frac{I_{s}^{cm^{-1}}(q)}{\rho_{eff}}$$

 $\rho_{\rm eff}$ is calculated using the following equation:

$$\rho_{eff} = -\frac{\ln T_s}{\mu/\rho \cdot d_s}$$

where T_s is the transmission of sample, μ/ρ is the X-ray mass attenuation coefficient of the sample, and d_s is the thickness of sample. The μ/ρ for the sample (carbon) was collected from the NIST database.

Supplementary Text 4. Pore structures analysized by SAXS

The pore size distribution and specific pore volume (unit: cm³ g⁻¹) were calculated by model fitting of the mass-specific scattering cross-section, $I_s^{cm^2g^{-1}}$ of each sample. Model fitting for full-range (0.02 – 0.5 Å⁻¹) profile, I_{calc} was obtained by taking a sum of surface scattering, $I_{surface}$ and pore scattering, I_{pore} and background, BKG. The $I_{surface}$ is scattering from micrometer scale grains, and in the range of our measurement (q_{min} : 0.02 Å⁻¹), only appear the porod's slope as q^{-4} From the surface. For the case of I_{pore} (shoulder at approximately 0.1 Å⁻¹), we assumed that the average morphology of the micropores is an isotropic sphere. Therefore, the mass-specific cross-sections of all samples were modeled using the spherical form factor with a log-normal size distribution. BKG was fixed at 0.01 cm² g⁻¹. Hence, the total calculated intensity I_{calc} can be expressed as

$$I_{\text{calc}} = I_{\text{surface}} + I_{\text{pore}} + \text{BKG}.$$

The calculations yielded a log-normal pore radius distribution for the samples, including the mean radius, r and standard deviations of the radius distribution (Table S3 and Fig. S14 and S15). SAXS data reduction and model fitting were performed using the NIKA/Irena package.⁴¹

Supplementary Text 5. Effects of chemical activation on hard carbon microstructures

The chemical activation mechanism with potassium hydroxide progresses in two steps: steambased carbon etching and carbon etching with metallic potassium. During the etching process, defective carbon structures can be primarily removed as CO or CO₂, increasing the relative ratio of ordered graphene domains and the relative G band intensity.⁴⁵ The subsequent chemical etching process produces metallic potassium in the higher activation temperature of \geq 700 °C, which can be intercalated into the ordered graphitic lattices.⁴⁶ The potassium-intercalated graphitic layers are highly expanded over >5Å, which makes the internal graphitic domains active for the carbon etching process. Controlling the contents of activation agent plays an important role in the microstructural tuning. In a relatively mild chemical activation process with a lower activation agent content, the relative G band intensity can be increased by removing defective carbon structures. However, the local graphitic ordering cannot be affected by this process, maintaining the original 2D band intensity. In contrast, a strong chemical activation process with more activation agents can attack the ordered domains. As a result, dense graphitic structures can be damaged by strong carbon etching and metallic potassium intercalation/removal processes, loosening them. Moreover, strong chemical etching can increase the closed pore volume ratio by removing internal carbon components, which can significantly enhance the SPC factor.

Supplementary Text 6. Materials properties of the A10, A30, and A50

The XRD pattern of O280-2400 reveals a sharp shoulder in the broad graphite (002) peak (Fig. S21). This indicates complex carbon microstructures composed of well-ordered graphite-like domains and disordered graphitic structures. The shoulder peak intensified after a relatively mild chemical activation process with a lower KOH content of 10 wt%, indicating that the disordered graphitic structures were mainly removed by the chemical activation. In contrast, a further increase in the activation agent content affected the ordered domains and the disordered area, leading to a large reduction in shoulder peak intensities. Hence, hard carbon microstructures can be tuned by controlling the activation agent content. Local changes in the hard carbon microstructures were also confirmed by Raman spectroscopy (Fig. S22). In Raman spectra nomalized by *G* band, the relative 2*D* band intensity is highly decreased after chemical activation, and thereby, the I_{2D}/I_G value (0.76) of the O280-2400 is decreased by 0.48, 0.45, and 0.54 for A10, A30, and A50, respectively. The reduction in the I_{2D}/I_G value indicated an increase in the SPC factor (Fig. 3e). The FE-TEM images support the microstructural changes in O280-2400 with a controlled chemical activation process (Fig. S23). The detailed microstructural properties are shown in Table S5.

The morphologies of A10, A30, and A50 were similar to those of O280-2400 in the FE-SEM images (Fig. S24). However, the more magnified FE-SEM images revealed several nanosized pores on the surface of the hard carbon particles. The nitrogen adsorption and desorption isotherms also support the increase in the specific surface area with chemical activation (Fig. S25 and Table S5). The specific surface areas of A10, A30, and A50 increased by approximately 2-, 5, and 14 times compared to those of O280-2400. More importantly, the closed pore volume ratios of the A10, A30, and A50 are increased from 36% for the O280-2400 to 38, 41, and 43%, respectively, and the major closed pore size are decreased to approximately 1 nm (Fig. S26–S28 and Table S6 and Table S7).

Supplementary Text 7. Reversibility of nanopore-filling sodiation cycles

To ascertain the pore volume ratio of the A30 sample post-cycling, ex situ SEM and TEM analyses were performed. The ex situ SEM images show that the hard carbon particles were fully enveloped by SEI layers and byproducts (Fig. S32a). Conversely, the ex situ TEM images indicate that the disordered graphitic structures remain unchanged from their initial state (Fig. S32b).

To further elucidate structural changes in the pores, ex situ SAXS measurements were conducted. As depicted in Fig. S32c, the shoulder near 0.1 Å⁻¹, indicative of micropore scattering, exhibited no significant alterations before and after cycling, affirming the preservation of micropores throughout the cycling process. The diminished intensity of surface scattering observed in the low-q region (< 0.5 Å⁻¹) post-cycling is primarily attributed to the SEI layers and byproducts formation on the macroscopic surface, as identified via SEM in Fig. S32a. This effect stems from the decreased scattering length density contrast ($\Delta \rho_e$) between the carbon matrix and the external surface. The squared contrast value directly correlates with the scattering intensity (i.e. $I \propto \Delta \rho_e^2$), influenced by SEI formation. Initially, the surface scattering intensity is dictated by $\Delta \rho_e$ between the carbon matrix and air ($\Delta \rho_e = \rho_{carbon} - \rho_{air}$). Post-cycling, the pertinent $\Delta \rho_e$ is between the carbon and the SEI layer ($\Delta \rho_e = \rho_{carbon} - \rho_{SEI}$).

The calculate $\Delta \rho_e$ values are as follows:

Before cycling:
$$\Delta \rho_e = \rho_{carbon} - \rho_{air} = 1.7 \times 10^{-5} \text{ Å}^2 - 0 \text{ Å}^2 = 1.7 \times 10^{-5} \text{ Å}^2$$

After cycling: $\Delta \rho_e = \rho_{carbon} - \rho_{SEI(Na2CO3)} = 1.7 \times 10^{-5} \text{ Å}^2 - 2.1 \times 10^{-5} \text{ Å}^2 = 0.4 \times 10^{-5} \text{ Å}^2$

This reduction in $\Delta \rho_e$ accounts for the observed decrease in surface scattering intensity postcycling. Model fitting for pore scattering at 0.1 Å⁻¹ was executed, affirming that the micropore distribution for the samples before and after cycling is essentially equivalent (Fig. S32d). The use of arbitrary units for the y-axis in the volume distribution arises from the challenge of accurate mass calibration, as measurements for both conditions were performed in the electrode slurry form, encompassing additional components such as binders and additives. Thus, only a relative comparison of the volume distributions was conducted between the samples.

Supplementary Figures



Fig. S1. GPC data of the pristine and thermally oxidized PET samples.



Fig. S2. FT-IR spectra of the pristine and thermally oxidized PET samples.



Fig. S3. Deconvoluted XPS (a) C 1s and (b) O 1s spectra of the pristine and thermally oxidized PET samples.



Fig. S4. Opitical images of the pristine and thermally oxidized PET samples dissolved in 1,1,1,3,3,3,-hexafluoro-2-propanol (HFIP) solvent as 1 wt%.



Fig. S5. XRD patterns of the pristine and thermally oxidized PET samples.



Fig. S6. TGA and DSC curves of the pristine and thermally oxidized PET sampels under N_2 atmosphere.



Fig. S7. XRD patterns of the (a) O280-, (b) O320-, (c) O350-, and (d) O380-based PHC samples prepared at different heating temperatures from 1200 to 2800 °C.



Fig. S8. Raman spectra of the (a) O280-, (b) O320-, (c) O350-, and (d) O380-based PHC samples prepared at different heating temperatures from 1200 to 2800 °C.



Fig. S9. FE-TEM images of the (a) O280-1200, (b) O280-1600, (c) O280-2000, (d) O280-2400, and O280-2800.



Fig. S10. FE-TEM images of the (a) O320-1200, (b) O320-1600, (c) O320-2000, (d) O320-2400, and O320-2800.



Fig. S11. FE-TEM images of the (a) O350-1200, (b) O350-1600, (c) O350-2000, (d) O350-2400, and O350-2800.



Fig. S12. FE-TEM images of the (a) O380-1200, (b) O380-1600, (c) O380-2000, (d) O380-2400, and O380-2800.



Fig. S13. Mass-specific X-ray scattering cross-section profile from SAXS data of the PHC-series samples: (a) O280, (b) O320, (c) O350, and (d) O380.



Fig. S14. Model fitting results for mass-specific X-ray scattering cross-section from SAXS data of the PHC-series samples: (a) O280, (b) O320, (c) O350, and (d) O380.



Fig. S15. Volume distributions of pores analyzed from mass-specific X-ray scattering crosssection of the (a) O280-, (b) O320-, (c) O350-, and (d) O380-based PHC samples prepared at different heating temperatures from 1200 to 2800 °C.



Fig. S16. Galvanostatic sodiaion/desodiation profiles of the (a) O280-, (b) O320-, (c) O350-, and (d) O380-based PHC samples prepared at different heating temperatures from 1200 to 2800 °C over a voltage window of 0.001–2.0 V vs. Na⁺/Na at a current density of 25 mA g⁻¹ in an operating temperature of 25 °C.



Fig. S17. Galvanostatic sodiaion/desodiation profiles of the (a) O280-, (b) O320-, (c) O350-, and (d) O380-based PHC samples prepared at different heating temperatures from 1200 to 2800 °C over a voltage window of 0.001-2.0 V vs. Na⁺/Na at a current density of 25 mA g⁻¹ in an operating temperature of 60 °C.



Fig. S18. Interrelation plots showing several structure parameter vs. SPC relationships of the PHC-series sampels: (a) L_a , (b) L_c , (c) d-spacing, (d) Particle density, (e) Pore volume ratio, and (f) Pore diameter.



Fig. S19. EIS profiles of the (a) O280-, (b) O320-, (c) O350-, and (d) O380-based PHC samples prepared at different heating temperatures from 1200 to 2800 °C.



Fig. S20. The SPC factor vs. CCU plots of the different types of hard carbon samples which were preapred at different heating temperatures of 2000, 2400, and 2800 °C.



Fig. S21. XRD patterns of the microstructure-tuned PHC samples which were fabricated from the O280-2400 by controlled activation process with different KOH ratio.



Fig. S22. (a) Raman spectra of the microstructure-tuned PHC samples which were fabricated from the O280-2400 by controlled activation process with different KOH ratio, and (b) their normalized comparison plots based on G band intensity.



Fig. S23. FE-TEM images of the (a) A10, (b) A30, (c) A50.



Fig. S24. FE-SEM images of the (a) A10, (b) A30, and (c) A50.



Fig. S25. (a) Nitrogen adsorption and desoprtion isotherm curves of the O280-2400, A10, A30, and A50, and (b) their pore size distribution data.



Fig. S26. Model fitting results for mass-specific X-ray scattering cross-section obtained from SAXS data of the microstructure-tuned PHC samples.



Fig. S27. (a) Mass-specific X-ray scattering cross-section profiles obtained from SAXS data of the O280-2400, A10, A30, and A50, and (b) their pore volume distributions.



Fig. S28. EIS profiles of the O280-2400, A10, A30, and A50.



Fig. S29. Galvanostatic lithiation/de-lithiation profiles of the (a) O280-2400 and (b) A30.



Fig. S30. Galvanostatic lithiation/de-lithiation profiles of the (a) O280-2400 and (b) A30 for 2nd, 5th, 8th and 10th cycles.



Fig. S31. (a) Galvanostatic sodiation/de-sodiation profiles of the A30, and (b) rate–cycling performances and reversibilities of the A10, A30, and A50.



Fig. S32. Ex situ (a) TEM and (b) SEM images of the A30 sample. (c) Ex-situ SAXS profiles of the A30 sample before and after cycling, and (d) their micropore volume distribution.

Supplementary Tables

| Sample | M _n | $M_{\rm w}$ | PDI | Oxidation yield (%) |
|--------------|----------------|-------------|------|---------------------|
| Pristine PET | 48,000 | 142,000 | 2.96 | |
| O280 | 39,640 | 107,820 | 2.72 | 99.5 |
| O320 | 22,000 | 50,160 | 2.28 | 98.1 |
| O350 | 20,800 | 85,696 | 4.12 | 96.0 |
| O380 | 11,980 | 83,620 | 6.98 | 93.0 |

Table S1. Molecular weight distribution of bare and oxidized PET samples obtained from gel-

permeation chromatography.

| Sample | d ₀₀₂ (Å) | L_a (nm) | $L_c(nm)$ |
|-----------|----------------------|------------|-----------|
| O280-1200 | 3.83 | 1.82 | 0.97 |
| O280-1600 | 3.78 | 1.90 | 1.08 |
| O280-2000 | 3.64 | 2.31 | 1.38 |
| O280-2400 | 3.40 | 2.50 | 3.21 |
| O280-2800 | 3.37 | 4.68 | 12.06 |
| O320-1200 | 3.91 | 1.94 | 1.05 |
| O320-1600 | 3.83 | 2.05 | 1.24 |
| O320-2000 | 3.65 | 2.21 | 1.43 |
| O320-2400 | 3.38 | 2.61 | 3.95 |
| O320-2800 | 3.37 | 5.43 | 18.49 |
| O350-1200 | 3.99 | 1.91 | 1.14 |
| O350-1600 | 3.86 | 2.10 | 1.22 |
| O350-2000 | 3.67 | 2.55 | 1.34 |
| O350-2400 | 3.39 | 3.21 | 3.28 |
| O350-2800 | 3.37 | 14.19 | 18.54 |
| O380-1200 | 3.94 | 2.07 | 1.07 |
| O380-1600 | 3.84 | 2.41 | 1.12 |
| O380-2000 | 3.65 | 2.78 | 1.40 |
| O380-2400 | 3.40 | 7.09 | 6.18 |
| O380-2800 | 3.37 | 53.01 | 33.67 |
| | | | |

Table S2. Textural properties for the graphitic microstructures of the PHC samples.

| Sample | Mean Radius (Å) | Standard deviation |
|-----------|-----------------|--------------------|
| O280-1200 | 2.244 | 0.88 |
| O280-1600 | 4.536 | 0.55 |
| O280-2000 | 5.941 | 0.60 |
| O280-2400 | 16.564 | 0.46 |
| O280-2800 | 19.570 | 0.57 |
| O320-1200 | 2.669 | 0.47 |
| O320-1600 | 4.306 | 0.53 |
| O320-2000 | 8.013 | 0.57 |
| O320-2400 | 16.603 | 0.56 |
| O320-2800 | 20.232 | 0.61 |
| O350-1200 | 1.877 | 0.78 |
| O350-1600 | 6.424 | 0.54 |
| 0350-2000 | 6.925 | 0.60 |
| O350-2400 | 16.361 | 0.56 |
| O350-2800 | 19.506 | 0.60 |
| O380-1200 | 2.611 | 0.71 |
| O380-1600 | 5.513 | 0.51 |
| O380-2000 | 8.131 | 0.76 |
| O380-2400 | 16.562 | 0.53 |
| O380-2800 | 27.818 | 0.61 |
| | | |

 Table S3. Calculated pore sizes of the PHC samples.

| Sample | I_{2D}/I_G ratio | Pore volume ratio (%) | SPC factor | CCU at 25 °C (%) | CCU at 60 °C (%) |
|-----------|--------------------|--------------------------|------------|---------------------|---------------------|
| O280-1200 | 0.15 | 18 | 0.97 | 73.26 | 78.81 |
| O280-1600 | 0.15 | 26 | 0.96 | 74.10 | 80.18 |
| O280-2000 | 0.43 | 31 | 0.87 | 56.53 | 82.28 |
| O280-2400 | 0.76 | 36 | 0.73 | 42.01 | 45.69 |
| O280-2800 | 0.90 | 35 | 0.69 | 30.43 | 43.72 |
| O320-1200 | 0.13 | 11 | 0.99 | 83.61 | 87.74 |
| O320-1600 | 0.20 | 23 | 0.95 | 75.91 | 88.24 |
| O320-2000 | 0.36 | 29 | 0.9 | 74.13 | 98.16 |
| O320-2400 | 0.71 | 35 | 0.75 | 48.36 | 52.23 |
| O320-2800 | 0.85 | 31 | 0.74 | 40.32 | 43.10 |
| O350-1200 | 0.11 | 13 | 0.99 | 79.99 | 84.05 |
| O350-1600 | 0.18 | 22 | 0.96 | 82.48 | 91.26 |
| O350-2000 | 0.35 | 29 | 0.9 | 82.15 | 97.77 |
| O350-2400 | 0.70 | 35 | 0.76 | 47.62 | 48.47 |
| O350-2800 | 0.76 | 33 | 0.75 | 46.16 | 50.48 |
| O380-1200 | 0.10 | 14 | 0.99 | 87.25 | 94.53 |
| O380-1600 | 0.19 | 21 | 0.96 | 76.42 | 94.17 |
| O380-2000 | 0.18 | 32 | 0.94 | 87.20 | 94.24 |
| O380-2400 | 0.54 | 36 | 0.81 | 51.26 | 66.52 |
| O380-2800 | 0.55 | 33 | 0.82 | 54.23 | 67.96 |

Table S4. I_{2D}/I_G ratio, pore volume ratio, SPC factor and CCU of the PHC samples.

| - | Sample | $d_{002}(A)$ | $L_a(nm)$ | L_c (nm) | $S_{BET}(m^2 g^{-1})$ |
|---|-----------|--------------|-----------|------------|-----------------------|
| _ | O280-2400 | 3.40 | 2.50 | 3.21 | 1.15 |
| | A10 | 3.38 | 5.56 | 4.70 | 2.31 |
| | A30 | 3.43 | 4.41 | 3.10 | 6.50 |
| | A50 | 3.43 | 3.94 | 2.80 | 16.28 |

Table S5. Textural properties for graphitic microstructures of the O280-2400, A10, A30, andA50.

| Sample | Mean Radius (Å) | Standard deviation |
|-----------|-----------------|--------------------|
| O280-2400 | 16.564 | 0.46 |
| A10 | 8.362 | 0.77 |
| A30 | 7.256 | 0.73 |
| A50 | 9.497 | 0.77 |

Table S6. Calculated pore sizes of the O280-2400, A10, A30, and A50.

| Sample | I_{2D}/I_G ratio | Pore volume ratio (%) | SPC factor | CCU at 60 °C (%) |
|-----------|--------------------|-----------------------|------------|------------------|
| O280-2400 | 0.76 | 36 | 0.73 | 45.69 |
| A10 | 0.48 | 38 | 0.82 | 74.72 |
| A30 | 0.45 | 41 | 0.82 | 83.89 |
| A50 | 0.54 | 43 | 0.77 | 57.85 |

Table S7. I_{2D}/I_G ratio, pore volume ratio, SPC factor and CCU of the O280-2400, A10, A30, and A50.