Supporting Information

Synthesis of hard carbon samples

Hard carbon samples were synthesized from Zn gluconate hydrate ($Zn(C_6H_{11}O_7)_2$ xH_2O, purity of >98.0 wt.% by titrimetry, water content of ≤13.0 wt.%, Tokyo Chemical Industry Co. Ltd.) as both ZnO and carbon sources. The precursors were then preheated at 600 °C for 2 h at the heating rate of 10 °C min^{-1} under an argon stream and naturally cooled to room temperature. The preheated precursors were crushed and ground with an agate mortar and pestle and then soaked into 1.0 mol dm^{-3} HCl solution. Thus obtained suspension was ultrasonically treated for 1 h, filtrated, and the residue precursor powder was washed with deionized water and then dried at 80 °C under vacuum according to our previous report. Finally, hard carbon samples were obtained by post-heating the precursor at 1500 or 1600 °C for 100 min at the heating rate of 2 °C min-1 under an argon stream and naturally cooled to room temperature.

Electrode synthesis

With a mass ratio of 8:1:1, hard carbon powder, polyacrylate (PAA), and carbon black were mixed in deionized water to form a homogeneous slurry, which was uniformly cast on the Cu foil (9 μm thickness) as the work electrode. The electrode film was first dried at 60 °C for 1h and then dried at 80 °C under vacuum for one night before being punching out into disk of 11 mm diameter (mass of active material is approximately 1.21 mg/cm^2). The obtained electrodes were further dried in a vacuum oven at 80 °C for 2 h to completely remove residual water.

Electrochemical characterization

2032-type coin cells were assembled inside the glovebox with metallic Na foil as a counter/reference electrode. A glass microfiber filters (Whatman GF/D) was used as separator and was soaked with a 200 μL electrolyte consisting of 1 M $NaPF_6$ in diethylene glycol dimethyl.

The constant-current charge/discharge test of the half-cell was performed on LAND CT2001A battery testing system with a voltage range of 0.01-2 V and sodium metal as the counter electrode. Specifical capacity (mAh g^{-1}) was calculated based on the mass of hard carbon in the composite electrode.

Material characterization

X-ray diffraction (XRD) data of preheated precursors and hard carbon samples were collected with an X-ray diffractometer (SmartLab, Rigaku Corp.) in Bragg-Brentano geometry with a Ni-filtered Cu Kα radiation and a 1D silicon strip detector (D/tex Ultra 250, Rigaku Corp.). Morphologies of the samples and MgO distribution in the preheated precursors were observed with a scanning electron microscope (SEM, JCM-6000, JEOL Ltd.) equipped with an energy dispersive X-ray spectrometer (EDS) at an acceleration voltage of 15 kV and a transmission electron microscope (TEM, JEM-2100F, JEOL Ltd.) equipped with EDS (JED-2300T, JEOL Ltd.) at an acceleration voltage of 200 kV. Specific surface area of the samples was analyzed via N_2 gas adsorption-desorption technique at 77 K with BELSORP-mini II (MicrotracBEL Corp.) and by Brunauer–Emmett–Teller (BET) method. Prior to the adsorptiondesorption measurement, the samples were heat-treated at 300 °C for 5 h under vacuum to remove moisture trapped in the surface pores. Apparent densities of hard carbon samples were measured via helium gas pycnometry with the BELPycno density analyzer (MicrotracBEL Corp.) and via n-butanol displacement pycnometry with a specific gravity bottle (Shibata Scientific Technology Ltd.) based on Japanese Industrial Standard (JIS) R7212:1995 as

reported in the literatures.

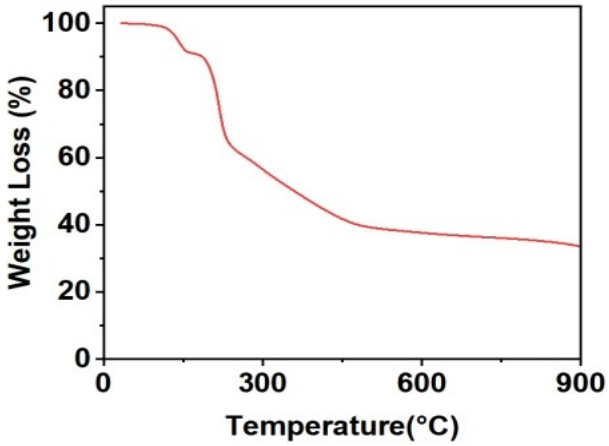

Fig.S1 TG of the Zn gluconate hydrate

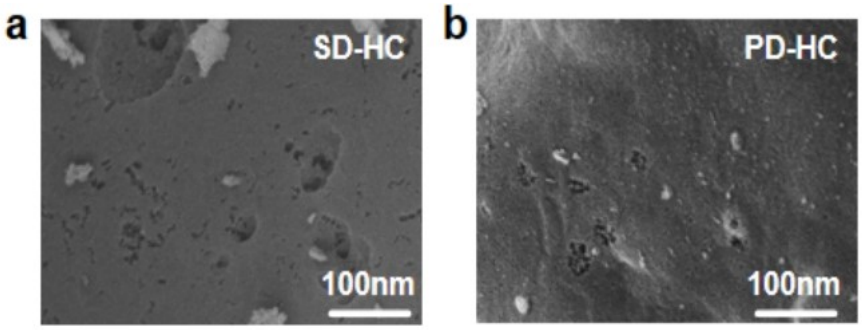

Fig.S2 SEM images of (a) SD-HC, (b) PD-HC samples.

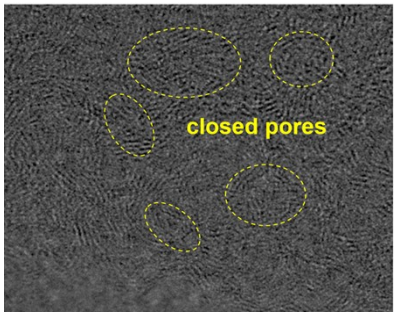

Fig.S3 High-magnification TEM image of PD-HC

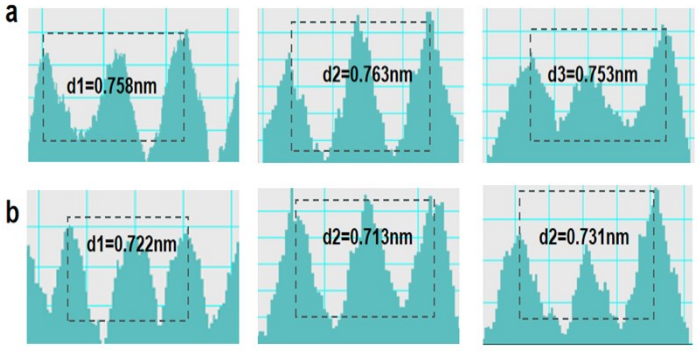

Fig.S4 TEM measured interlayer distances for a) SD-HC b) PD-HC

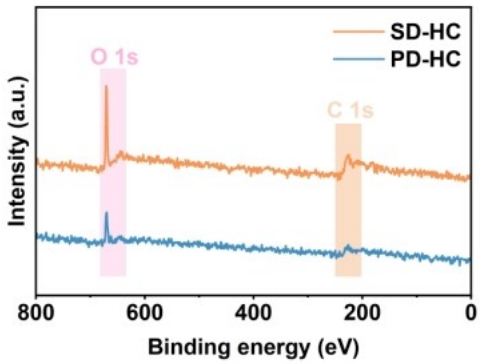

Fig.S5 XPS survey spectra of SD-HC and PD-HC samples.

Table S1. The Atomic percentage of SD-HC and PD-HC.

Elements	SD-HC	PD-HC
C	90.72%	96.81%
O	9.28%	3.19%

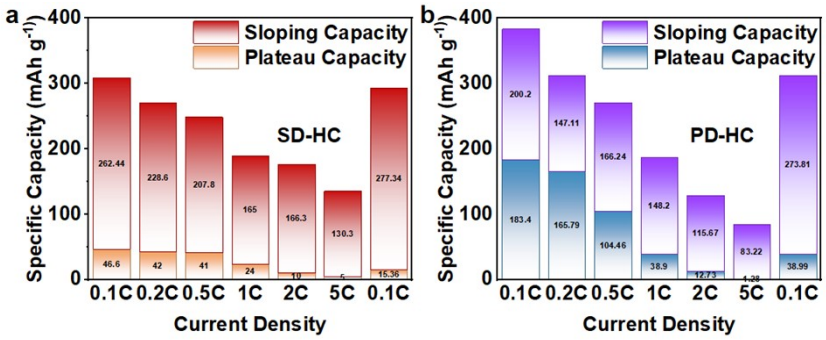

Fig.S6 Comparison of slope and plateau capacity contributions of SD-HC (a) and PD-HC (b) at different current densities.

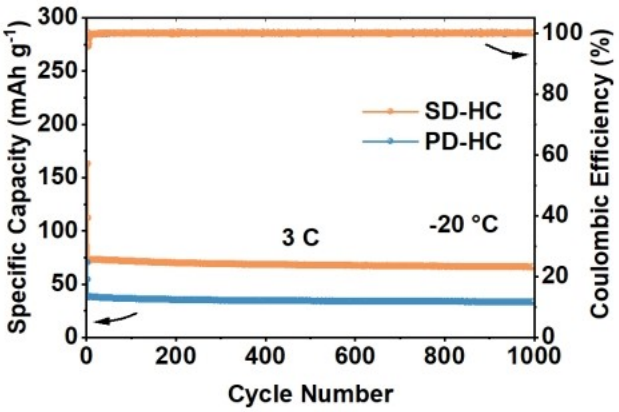

Fig.S7 The cycling stability of SD-HC and PD-HC at 3 C at -20 °C .

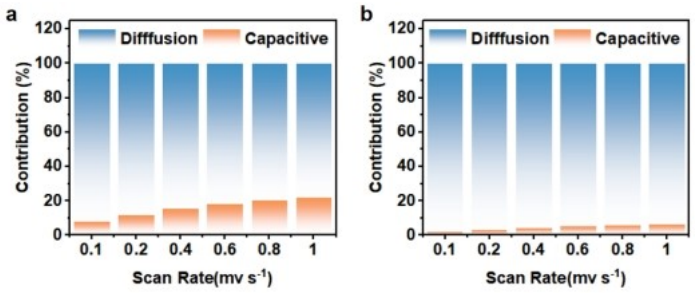

Fig.S8 The capacitive and diffusion contribution of SD-HC and PD-HC across varying scan rates

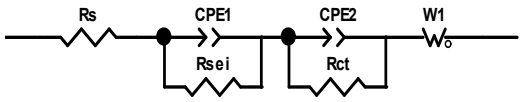

Fig.S9 The equivalent circuit model and fitting parameter(Rs represents the electrolyte and overall ohmic resistance. RSEI corresponds to the resistance of the solid electrolyte interphase (SEI) layer, while Rct denotes the charge-transfer resistance at the electrode–electrolyte interface. CPE1 and CPE2 are constant phase elements used to replace ideal capacitors, accounting for non-ideal capacitive behavior; CPE1 is typically coupled with RSEI to model the SEI film capacitance, whereas CPE2 is coupled with Rct to represent the double-layer capacitance. W denotes the Warburg impedance associated with Na^+ diffusion in the low-frequency region.)