Supporting Information for

Lignin molecular sieving engineering enables high-plateau-capacity hard carbon anodes for sodium-ion batteries

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Supporting Experimental Section

1. Experimental

1.1 Materials

Pine lignin was purchased from Zhejiang Jiefa Technology Co., LTD. Ethanol was procured from Macklin, China. Acetone was acquired from Aladdin, China. Ethanol-dissolved lignin (EL), acetone-dissolved lignin (AL), and the residual lignin (RL) were extracted from pine lignin.

Lignin fractionation procedure：

Pour the dried 20g pine lignin (PL) into a 1000 mL blue-capped bottle and place a rotor. ①Add 500mL ethanol (99.7%) and stir for 12h. After stirring, the solution is filtered to obtain filtrate and filter residue, distillation filtrate by rotary evaporator removes ethanol to produce ethanol-dissolved lignin (EL). Repeat step ① for the remaining filter residue.

Dry the filter residue in ① pour it into a 1000 mL blue-capped bottle and place a rotor. ②Add 500mL acetone (99.5%) and stir for 12h. After stirring, the solution is filtered to obtain filtrate and filter residue, distillation filtrate by rotary evaporator removes acetone to produce acetone-dissolved lignin (AL). Repeat step ② for the remaining filter residue.

The remaining filter residue is dried to obtain residual lignin (RL).

Weigh the mass of EL, AL, and RL and calculate the yield as shown in Table S1.

1.2 Synthesis of hard carbons

The pine lignin (PL) and its graded lignin (EL, AL, and RL) in graphite boats were

put in a tube furnace and purged with nitrogen at a flowing rate of 80 cm^3 min^{-1} for 30 min. The corresponding hard carbons were obtained after carbonization of the as-prepared lignin in nitrogen at 1300 °C for 6 h (heating ramping rate: 5 °C min^{-1}). Then the hard carbon materials were mechanically ground into powders.

1.3 Materials characterization

The structural information of lignin was obtained from a Superconducting NMR spectrometer (AVANCE III HD 600 MHz, Bruker, Switzerland). The polar functional groups of lignin were determined by phosphorus spectrum conducted on a Superconducting NMR spectrometer (JNM-ECZ500R/S1 500MHz, JEOL Ltd., Japan). Gel Permeation Chromatography (Waters1515, Waters, USA) was conducted to determine the molecular weight of lignin. The high-temperature synchronous thermal analyzer (STA409PC, NETZSCH, Germany) was used to measure the mass loss during lignin pyrolysis, the specific experimental parameters are as follows, the lignin samples were heated up to 800 °C at a constant heating rate of 10 °C min^{-1} in purified nitrogen (99.99%) with a flow rate of 80 mL min^{-1}, and the weight was kept at ~5 mg. The scanning electron microscope (SEM) (SU8220, Hitachi, Japan) and transmission electron microscope (TEM) (Talos F200S, FEI Thermo, Chech) were used to capture the morphological characteristics of the samples. The structural parameters of the hard carbon materials were collected on a micro-Raman spectrometer (LabRAM HR Evolution, HORIBA Jobin Yvon, France) using a 532 nm and an X-ray Powder diffractometer (D8-ADVANCE, Bruker, Germany) with a Cu Kα radiation (λ=0.1541 nm). The parameters for open pores were acquired on an adsorption/desorption analyzer

(ASAP2460, Micromeritics, USA). N_2 adsorption/desorption isotherms at 77 K were measured within the range of relative pressures of 10^{-3} to 0.998. The small-angle X-ray scattering was performed on a small-angle scatterometer (Xenocs Xeuss, France), and the scattering vector range was $0.001\sim0.45\text{Å}^{-1}$.

Quantitative ^{31}P NMR spectra analysis：

(1)　sample preparation

①　The lignin sample is dried under vacuum at 80°C for 12 h.

②　Solvent A configuration: Pyridine-d5 and Chloroform-d are configured into solvent A according to the volume ratio of 1.6:1。

③　Internal standard liquid configuration: 0.018g (m_1) cyclohexanol is weighed as the internal standard and put into 4 mL small glass bottles; Then 0.005 g (m_2) of relaxant Chromium(III) acetylacetonate is added, and 1 mL(m_3) of solvent A is added。

④　Sample solution configuration: Weigh 0.03 g (mL) lignin sample, put it into 4 mL glass bottle, add rotor and 0.1 mL (m) internal standard solution; Then add 0.5mL A liquid and shake well, stir overnight, add 0.1mL phosphating agent, shake well and load into the NMR tube for sample delivery.

(2)　Test conditions:

Model: AVANCE III HD400, manufacturer: Bruker, Switzerland. Recommended NMR Settings: Pulse Angle :30°; Scanning interval :10s; Signal acquisition :128 times; Width :400ppm; 01P:50ppm.

(3)　Calculation formula:

$$C = \frac{m_1}{179.17} \times 0.99 \times 1000 \times \frac{m}{m_1 + m_2 + m_3} \times \frac{A}{A_{IS} \times m_L}$$

Where C (nmol/g) is the functional group content, A is the peak area of the functional group, and A_{IS} is the peak area of the internal standard。

1.4 Electrochemical characterization

The electrodes were prepared by blade coating technique, i.e. casting the slurry containing 80 wt% hard carbon materials, 10 wt% polyvinylidene difluoride (PVDF, 99.5%, SOLVAY), and 10 wt% carbon black (XC-72R, CABOT) onto copper foil, which was then dried at 80 °C in a vacuum oven for 12h. The average mass loading of active materials was about 1 mg cm^{-2}. The electrochemical performance of the hard carbon material electrodes was evaluated in a coin half-cell, in which hard carbon material electrodes and sodium foil were used as working electrodes and counter electrodes, respectively. 1 mol L^{-1} NaPF$_6$ (99.5%, Canrd) in methoxymethane (DME, 99.95%, Canrd) was used as electrolyte. The galvanostatic charge/discharge (GCD) and galvanostatic intermittent titration technique (GITT) tests were conducted on the Neware Battery tester (Neware, China). The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on an electrochemical workstation (VMP3, Bio-Logic, France).

Supporting Tables

Table S1 Molecular weight and yield of pine lignin and extracted lignin

Sample	Mn (Da)	Mw (Da)	PDI	Yield (%)
PL	2266	13723	6.05	—
EL	2005	5540	2.76	7.0
AL	1933	10988	5.68	20.4
RL	2737	15931	5.81	72.6

Table S2 Deconvoluted band assignments of Raman spectra

Band	Raman shift (cm^{-1})	Corresponding structure
G	~1580	graphitic lattice
D(D1)	~1350	disordered graphitic lattice
D2	~1620	few-layer graphene
D3	~1500	amorphous structure
D4	~1200	sp^2-sp^3 hybrid structures or C–C/C=C stretching vibrations

Table S3 Simulated resistances of HC electrodes

Sample	Simulated resistances	
	R_s (ohm)	R_{ct} (ohm)
HC	3.78	20.80
HC-E	8.00	15.17
HC-A	4.27	31.45
HC-R	2.46	41.45

Supporting Figures
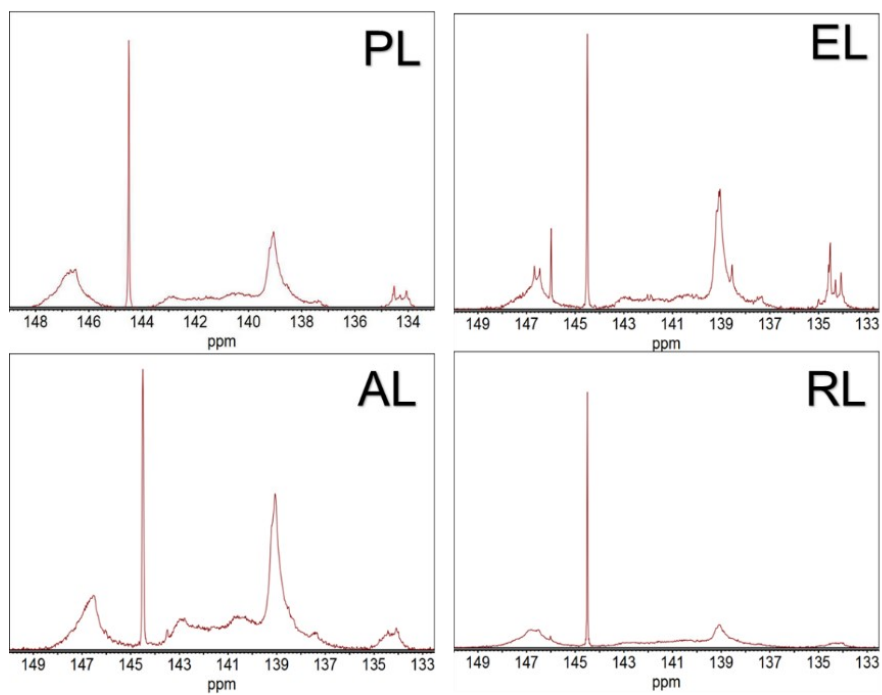
Figure S1 Quantitative ^{31}P NMR spectra of PL and extracted lignin.

Figure S2 Digital photos of lignin-derived hard carbon materials.
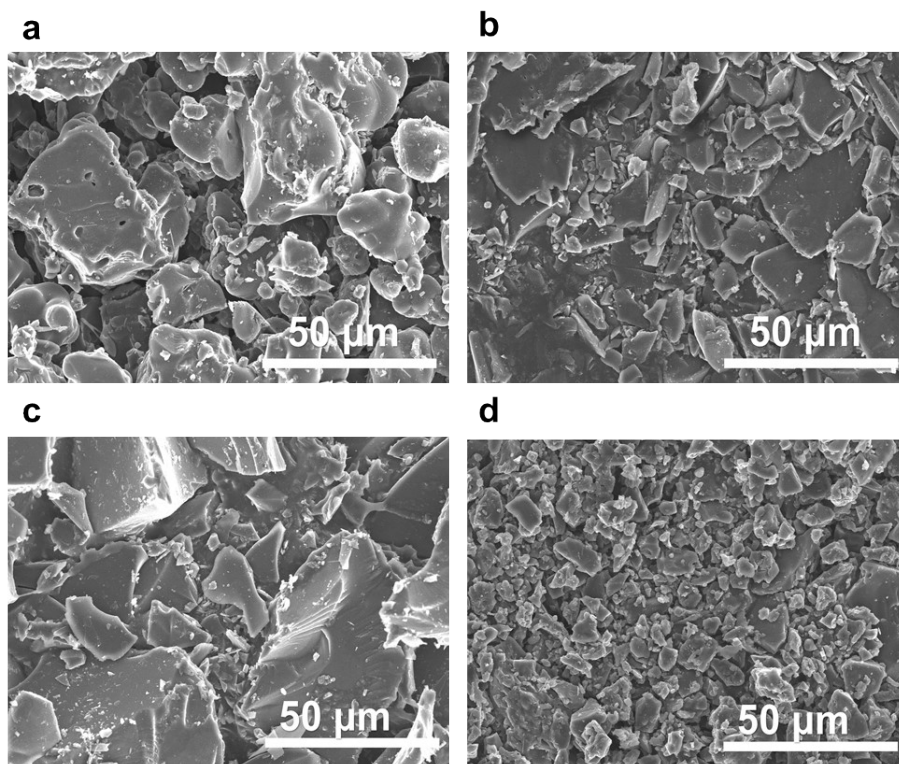
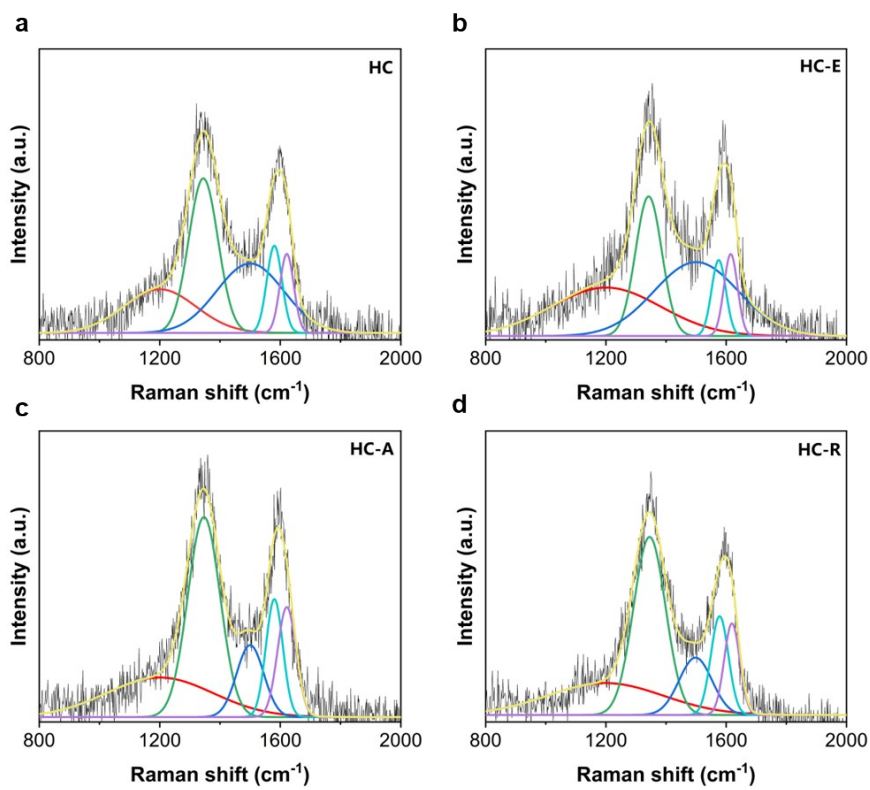
Figure S3 SEM images of (a) HC; (b) HC-E; (c) HC-A; (d) HC-R.

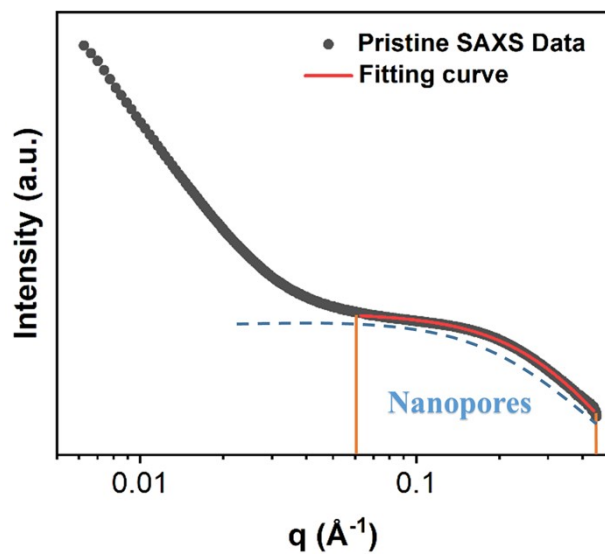**Figure S4** Raman spectra of (a) HC, (b) HC-E, (c) HC-A, (d) HC-R.

Figure S5 SAXS profile and fitting curve in the range of 0.06~0.45 Å^{-1}
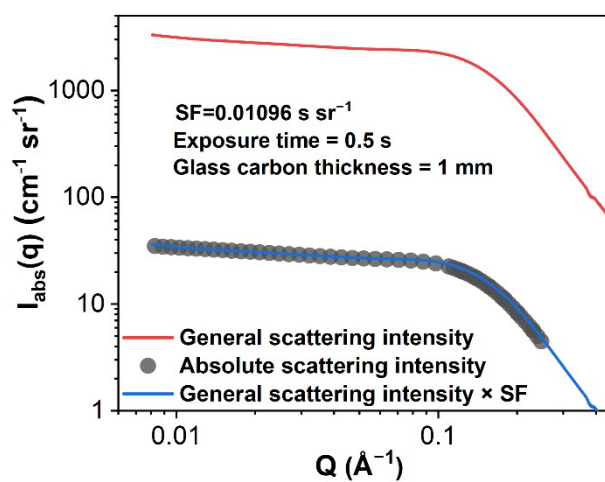

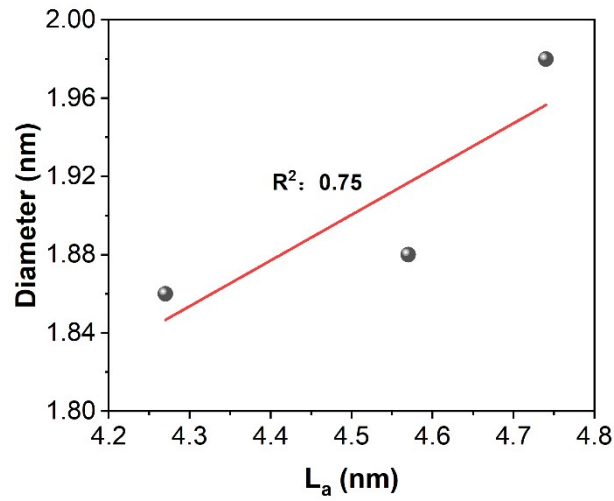**Figure S6** Scattering profiles of glass carbon and their linear fits. SF is 0.01096 s sr^{-1}.

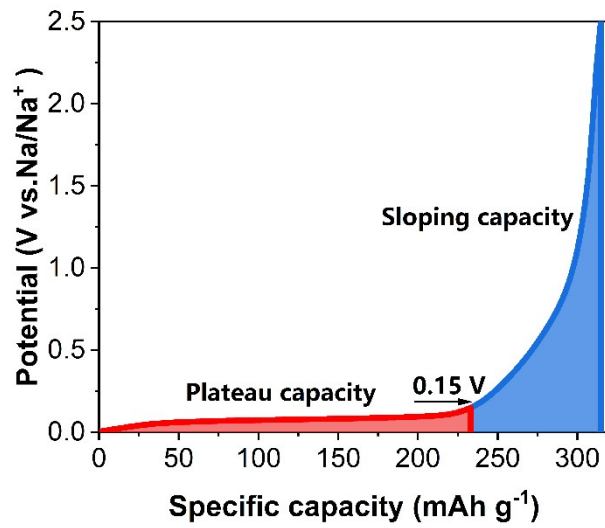**Figure S7** The relationship of L_a and the diameter of the closed pore.

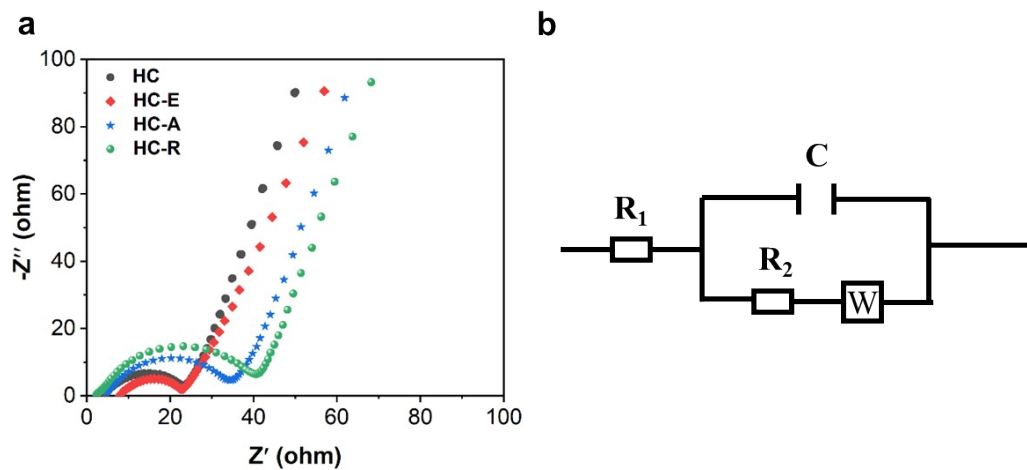**Figure S8** The composition of sloping capacity and plateau capacities.

Figure S9 (a) Nyquist plot of the 5th cycle, (b) The corresponding equivalent circuit of (de-)sodiation process of HC.
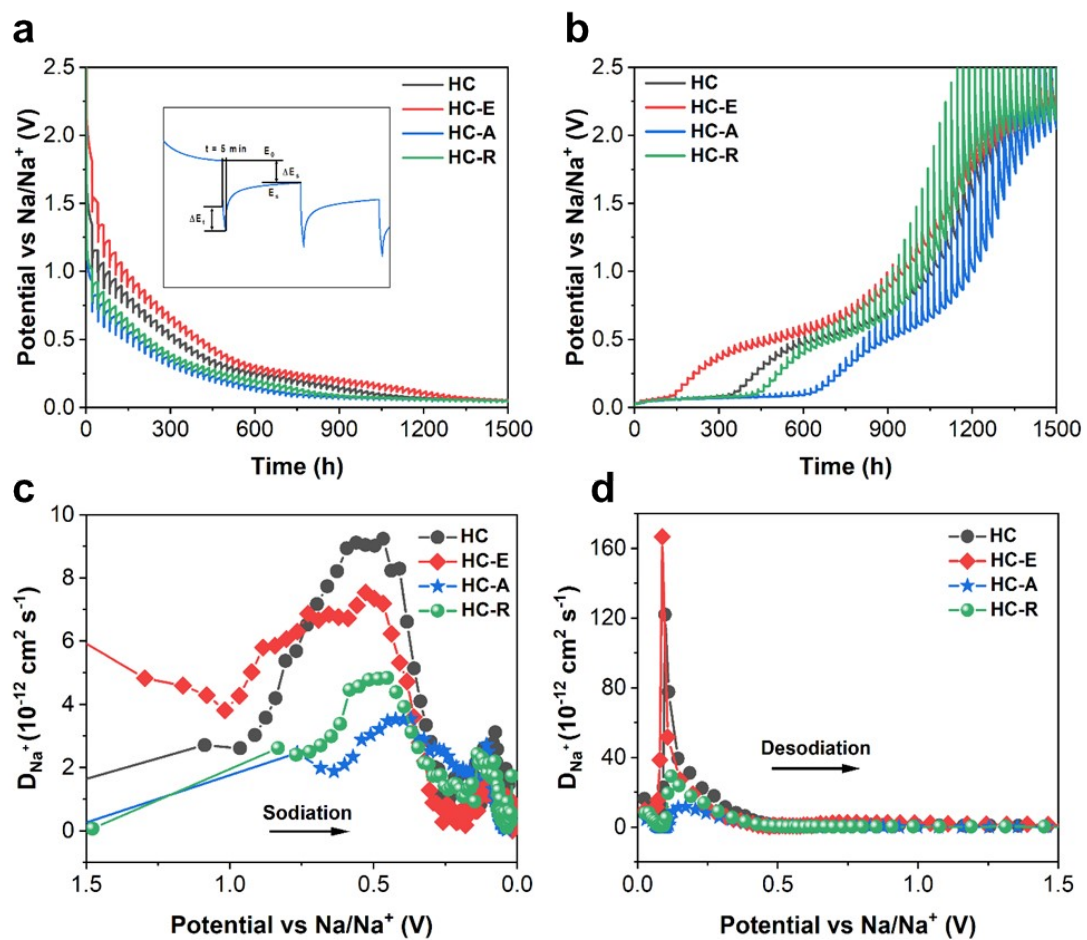
Figure S10 The GITT profiles of the (a) discharge and (b) charge process, Na^+-ion diffusion coefficients calculated from GITT profiles of hard carbons during (c) sodiation and (d) desodiation.
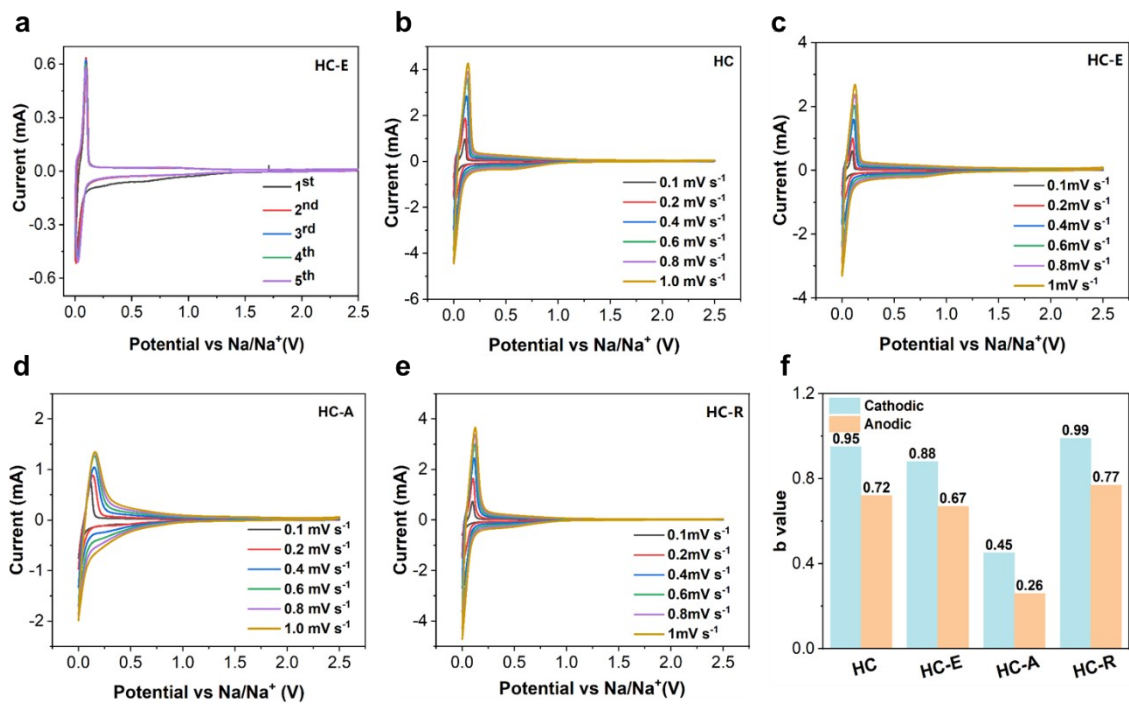
Figure S11 (a) CV profiles collected at 0.1 mV s⁻¹ and 0.001–2.5 V from HC-E, CV curves of

LDHC at various scan rates, (b) HC; (c) HC-E; (d) HC-A; (e)HC-R, (f) *b* values of LDHC.