Supporting Information

A Distinctive Edge-graphited Hard Carbon for Advanced Sodium-ion Batteries

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Experimental Section

Materials synthesis

The *Camellia semiserrata* shells (CSshell) were initially cleansed using deionized water and subsequently subjected to drying in a vacuum oven at 80 °C for a duration of 2000 min. The dried shells were then cut into species with a razor blade. Subsequently, the treated samples were then introduced into a tube furnace (OTF-1200X, Hefei Kejing Material Technology Co., Ltd) protected by an argon atmosphere, with the temperature gradually increasing at a rate of 3 °C/min from 25 to 1000, 1100 and 1200 °C, respectively. These three steps were carried out in three carbonization steps, during which they were held for 2 h at the time of rising to the target temperature, and then cooled down naturally. After collecting the hard carbon material after carbonization, it was washed with 1M hydrochloric acid while stirring on a magnetic stirrer for 12 h. Subsequently, the material underwent multiple rinses with deionized water until neutralization was achieved, after which it was dried in a vacuum oven at 80 ℃ for 12 hours. Commercial hard carbon mixed graphite material preparation: Commercial hard carbon and graphite are mixed together at a mass ratio of 10:1, and the required powder sample is then obtained by ball milling for 12 hours through a ball mill.

Electrochemical Measurements

The dried sample is the active substance material, which is used to prepare the anode material for sodium-ion batteries. The carbon material, super P and binder (CMC: SBR=6:4) were mixed into a slurry in the mass ratio of 7:2:1 and mixed with a small amount of deionized water and then placed in a magnetic stirrer for 3 h. The resulting slurry was then evenly applied onto a copper collector at 80 °C within a vacuum drying oven and left to dry for a duration of 12 hours.

The half-cell configuration consisted of a sodium metal counter electrode, a hard carbon electrode sheet as the working electrode (0.71-1.06 mg/cm^{-2}), GF/D glass fiber as the separator, and 1 M $NaPF_6$ diethylene glycol dimethyl ether as the electrolyte. The voltage range was set at 0.001-2.5 V. The full cell was assembled by using commercial $NaFe_{1/3}Ni_{1/3}Mn_{1/3}O_2$ (NFM, Dongguan Koluder Experimental Equipment Technology Co., Ltd.) as the cathode. The cathode material was prepared by mixing NFM, acetylene black and polyvinylidene fluoride (PVDF) into a slurry in the ratio of 8:1:1 by mass, and then a small amount of NMP was added to fully grind the slurry, and then the slurry was uniformly coated on the aluminum collector in a vacuum drying oven at 80 °C, and dried for 12 h, with the voltage range of the full cell set at 1.5-4.0 V. The N/P ratio of the full battery is ~1.08. 200 microliters of electrolyte were used during the assembly of the full cell.

The charge/discharge test of button cell batteries is carried out using a battery test system (Lanhe). Cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) were executed using an electrochemical workstation (CHI660e, Chenhua). The *in-situ* electrochemical impedance spectroscopy (EIS) test (Zahner, zennuim xc, Germany) conducted over a frequency range of 100 kHz to 0.1 Hz, with a voltage range from 0.001 V to 2.5 V; specifically, an impedance measurement is performed at 0.1 V, and the charge and discharge current density is set at 100 mA/g. Galvano-static intermittent titration technique (GITT) was performed on a battery test system with a current density of 50 mA g^{-1} and a current pulse time of 10 min, with a relaxation period of 60 minutes.

Morphological and structural characterizations

The structural characteristics of the acquired samples were assessed through X-ray diffraction (XRD) analysis using a D8 ADVANCE instrument. The operating voltage is 40 kV (λ = 0.154 nm), the operating current is 40 mA, the radiation source is Cu Kα. The detailed crystal structure of the material was analyzed using a high-resolution transmission electron microscope (HRTEM, Thermo Fisher TF20, JEM-F200). The morphology and microstructure of the samples were investigated through field emission scanning electron microscopy (SEM) with a Hitachi Regulus 8100 instrument. Simultaneous thermal analysis measurements (TG-DSC, TAQ600) were performed from room temperature to 1200 °C in Ar atmosphere at a heating rate of 10 °C/min. The SAXS (Xenocs Xeuss 2.0) sample test pattern was utilized a test scattering vector range of 2480 mm. The specific surface area, gas adsorption, and porosity of the samples were analyzed using the BET method with a Micromeritics ASAP 2460 instrument, employing nitrogen as the adsorbed gas. The degassing temperature was 200 °C, and the degassing time was 6 hours. The prepared hard carbon powder was mixed with dried potassium bromide according to a certain mass ratio, and then filled into the table ting molds after thorough grinding and mixing in a mortar, and then kept under a pressure of about 8 T cm^{-2} size for 1 min to get a translucent sheet sample. The laser wavelength of 532 nm was chosen for Raman spectroscopy (Raman, LabRAM Soleil) testing. The X-ray photoelectron spectrometer employed was a Thermo Scientific Nexsa model from the United States.

Density Functional Theory (DFT) Calculations

The theoretical calculation model is constructed, which is divided into edge graphitized layer and inner disordered layer. The edge structure is constructed by graphite standard model, and its morphology is composed of neatly structured graphene sheets stacked at the same spacing. The internal disordered layer is modeled on randomly stacked graphene sheets to represent the disordered structure of hard carbon materials.

The DFT calculation in this work utilized the Vienna ab initio simulation software package. Specifically, the optimization and evaluation of the structure and electronic properties were conducted employing the projector–augmented plane–wave method. The Perdew–Burke–Ernzerhof functional was employed to describe the exchange–correlation energy within a generalized gradient approximation framework. A kinetic energy cutoff of 450 eV was applied for the plane wave. The geometric structure was fully optimized until the force on each atom and the energy reached values below 0.03 eV/Å and 1×10^{-4}/cell, respectively. A Brillouin zone with a 2 × 2 × 1 k–point grid was used to optimize the geometric structure and density of states (DOS). The Na^{+} absorption energy (ΔEa) was determined through the following calculation method:

$$\Delta E_a = E_T - E_{Na} - E_G$$

where E_T, E_{Na}, and E_G are the energies of the carbon models after Na adsorption, isolated Na atoms, and the energies of carbon models before Na adsorption, respectively.

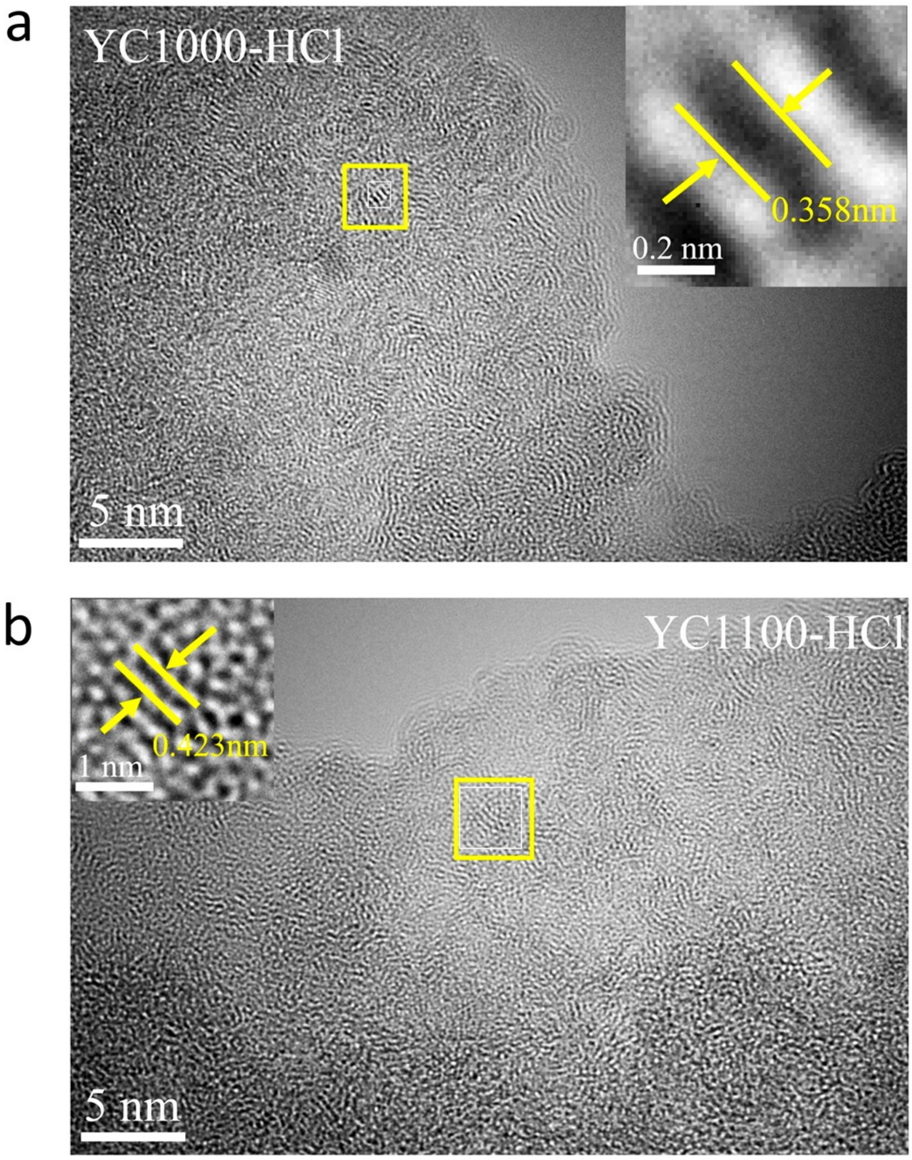

Fig. S1. HRTEM images of the (a) YC1000-HCl and (b) YC1100-HCl hard carbon samples.

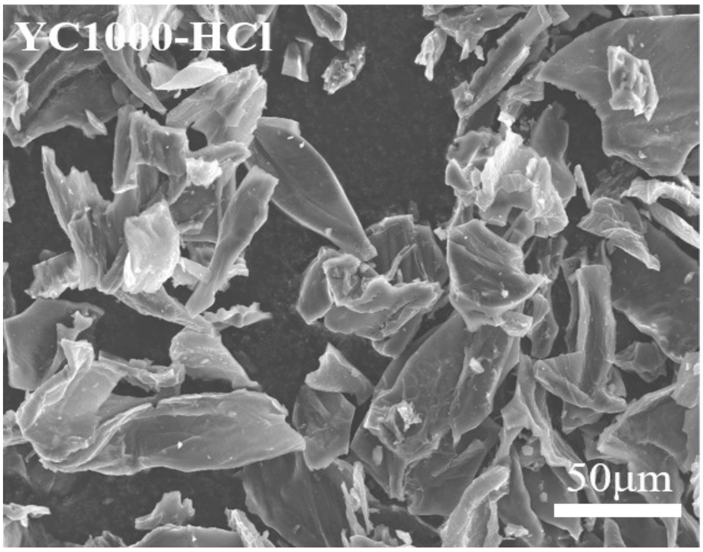

Fig. S2. Scanning electron microscope (SEM) image of the YC1000-HCl

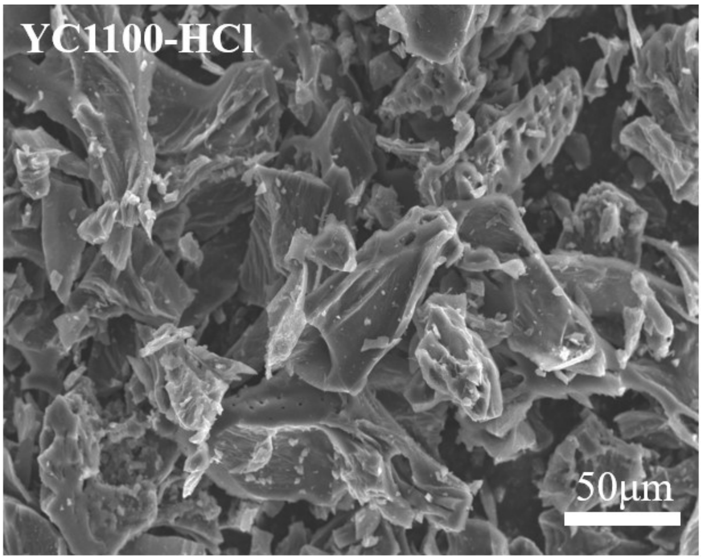

Fig. S3. SEM image of the YC1200-HCl.

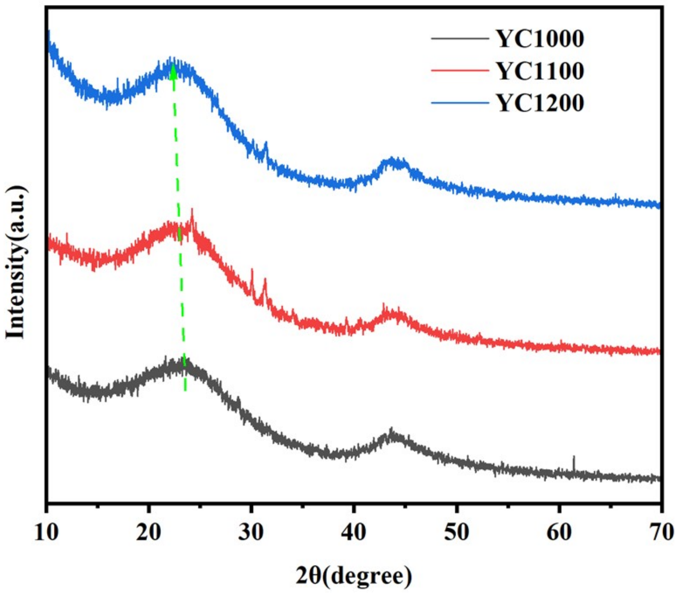

Fig. S4. XRD Patterns of the YC1000, YC1100 and YC1200 samples.

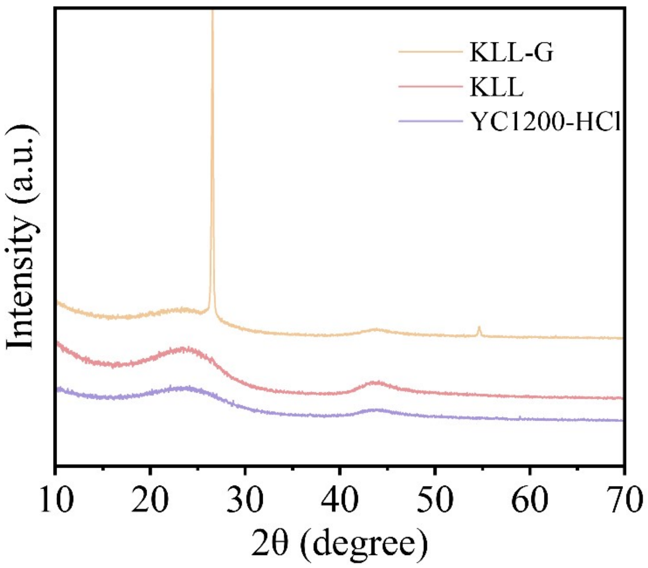

Fig. S5. XRD patterns of different samples

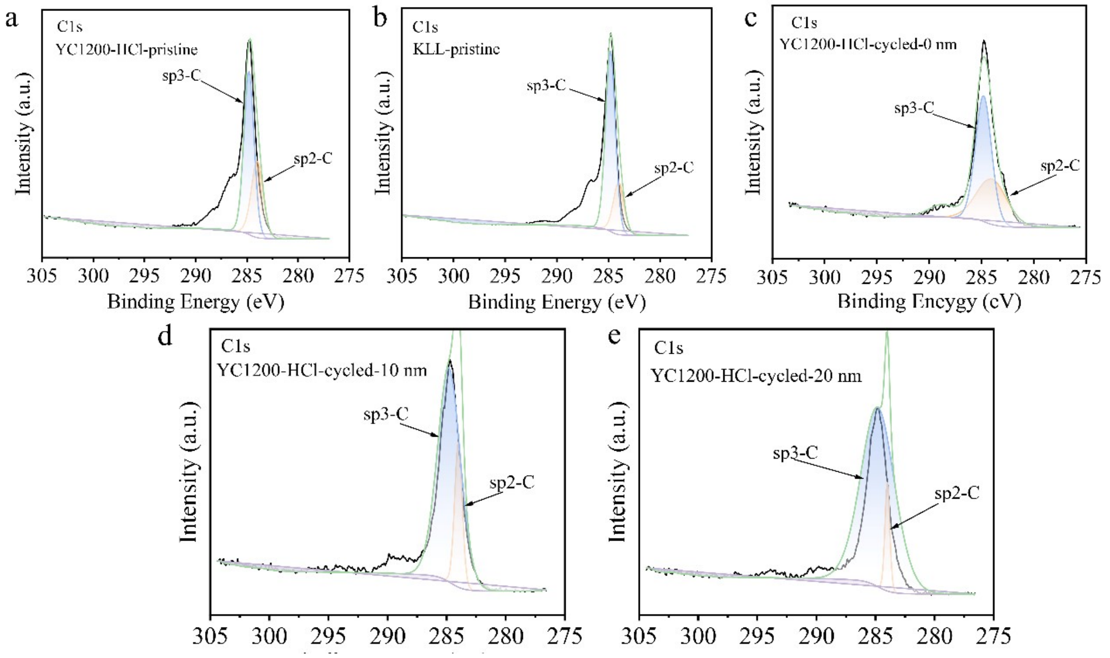

Fig. S6. (a) C1s of the YC1200-HCl electrode at the stage of pristine; (b) C1s of the KLL electrode at the stage of pristine; (c) C1s on the surface of the electrode after ten cycles in the YC1200-HCl electrode; (d) C1s spectrum of the YC1200-HCl electrode etched at 10 nm; (e) C1s spectrum of YC1200-HCl etched at 20 nm.

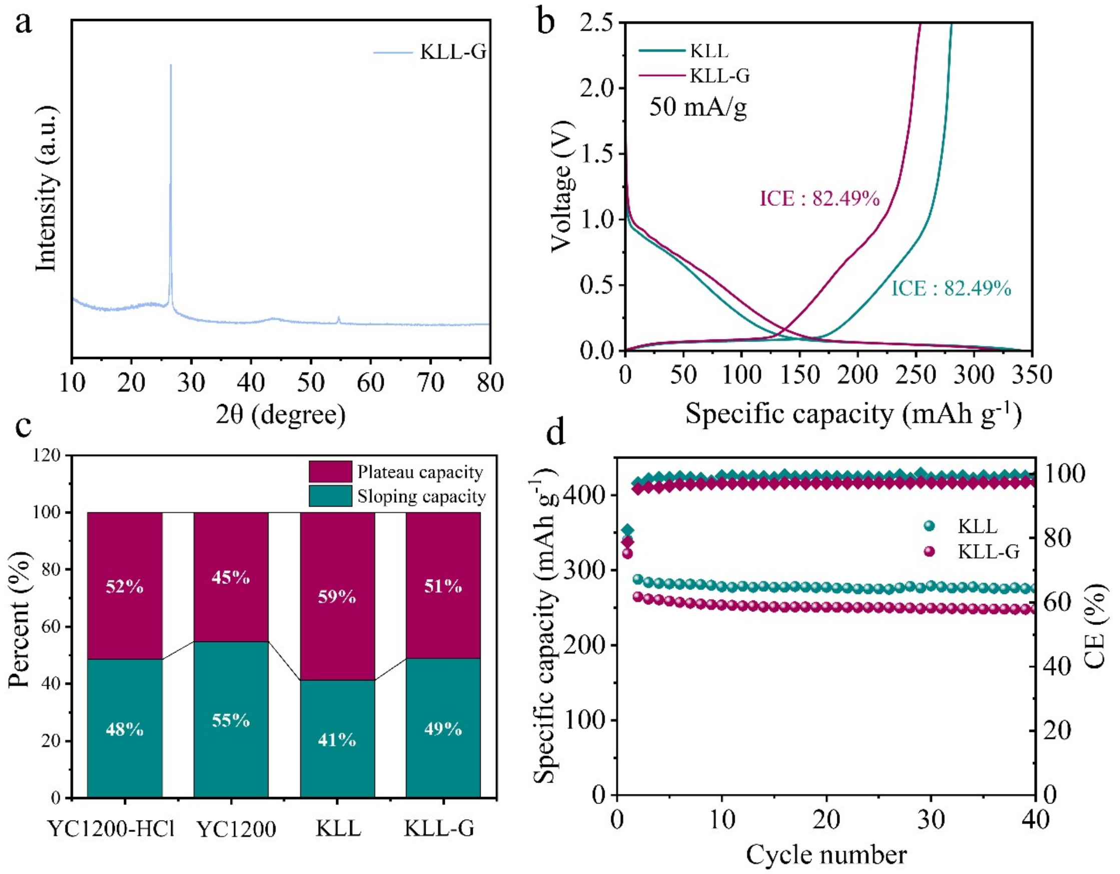

Fig. S7. (a) XRD with Commercial hard carbon hybrid graphite; (b) Charge and discharge curves of commercial hard carbon and mixed graphite samples at 50 mA/g current density; (c) Contribution ratios of the slope capacity and plateau capacity in the second discharge process of the four different electrodes; (d) Cycling performances of the KLL and KLL-G electrodes

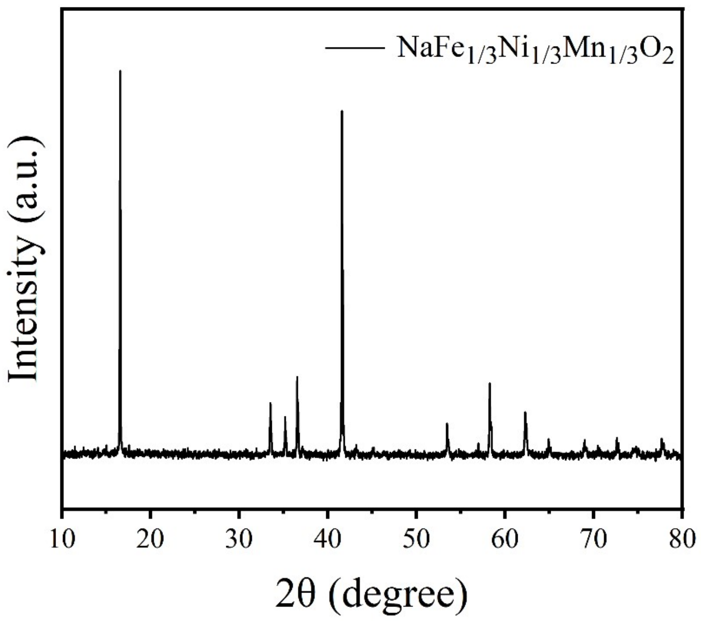

Fig. S8. XRD pattern of the $NaFe_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode materials.

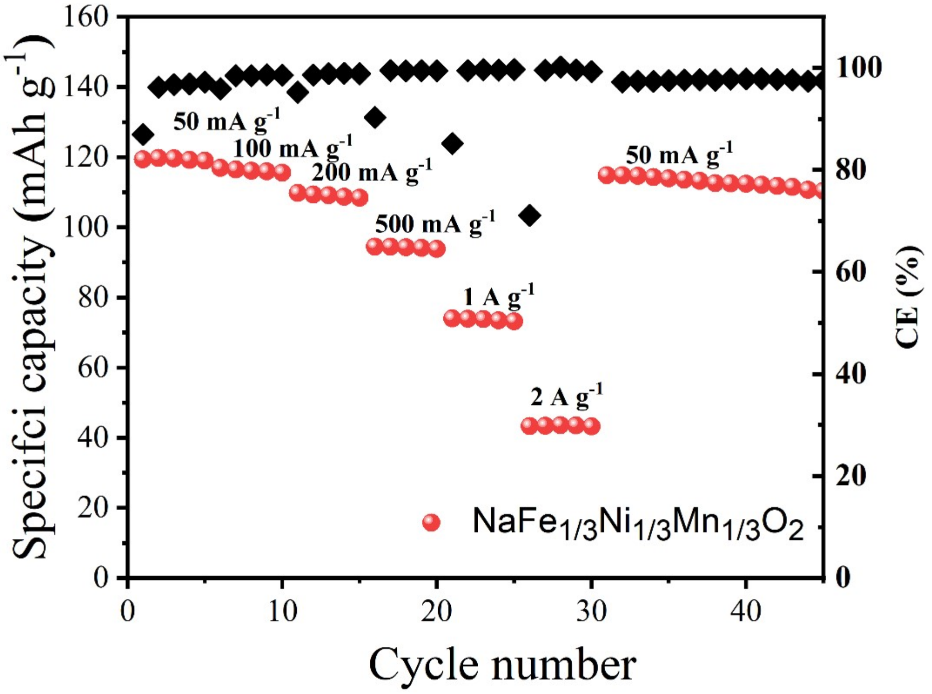

Fig. S9. Rate performances of the $NaFe_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode materials.

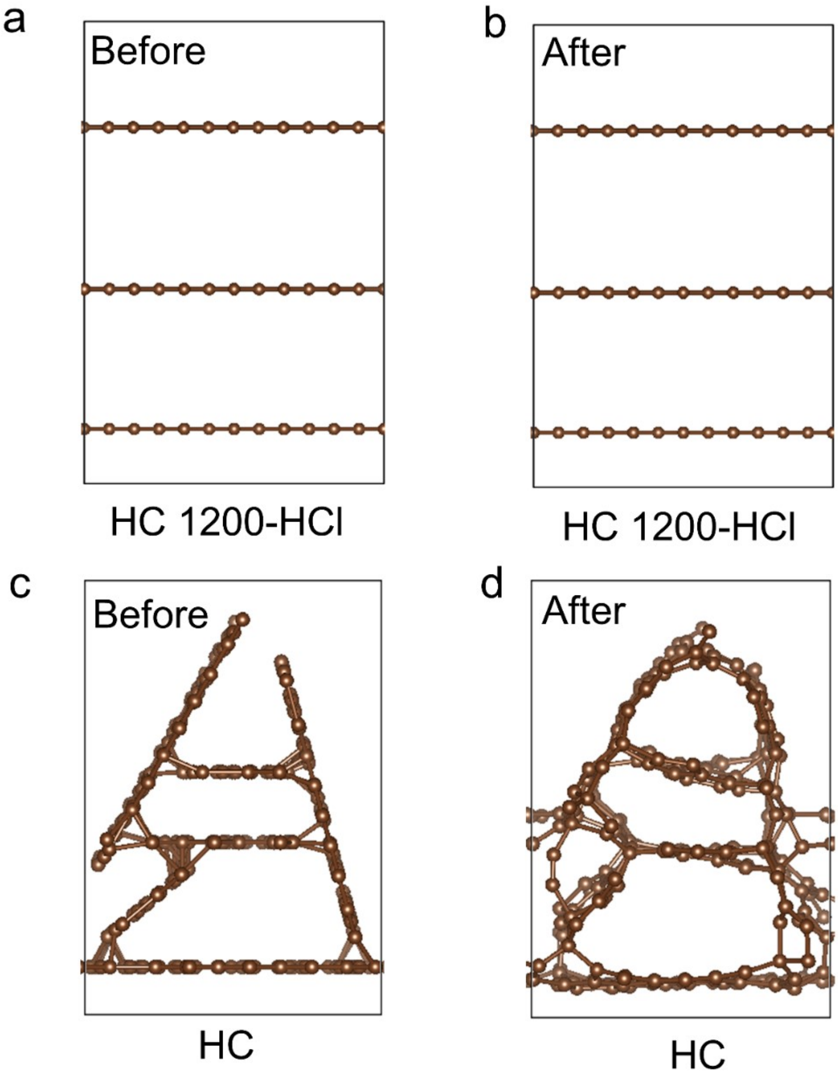

Fig. S10. Two models the hard carbon materials: HC1200-HCl (a) before optimization; (b) after optimization; common HC materials (c) before optimization; (d) after optimization.

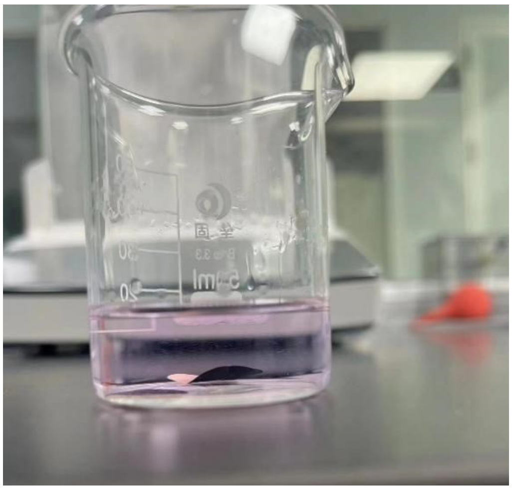

Fig. S11. Photographs of fully discharged YC1200-HCl electrodes with an ethanol solution containing 1% phenolphthalein.

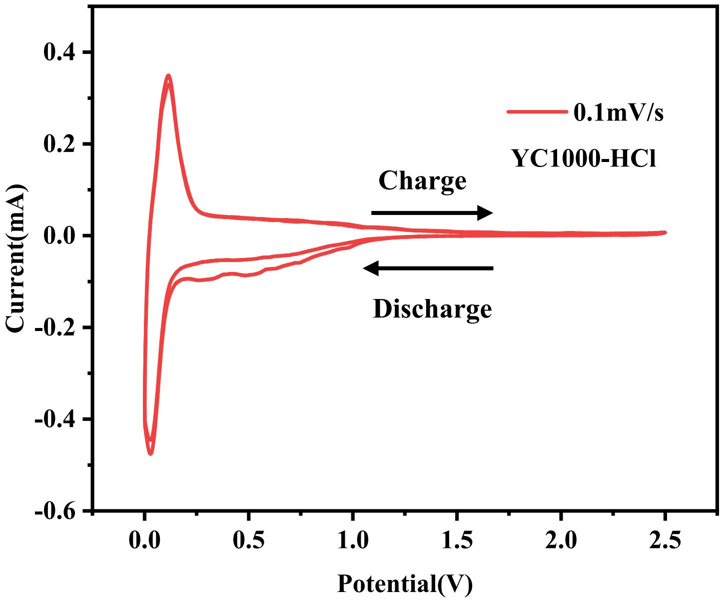

Fig. S12. CV cyclic voltammetry of the YC1000-HCl

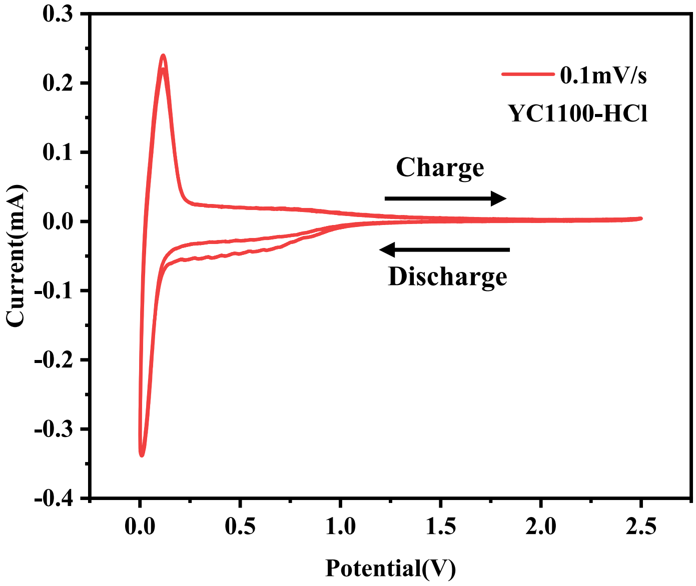

Fig. S13. CV curves of the YC1100-HCl

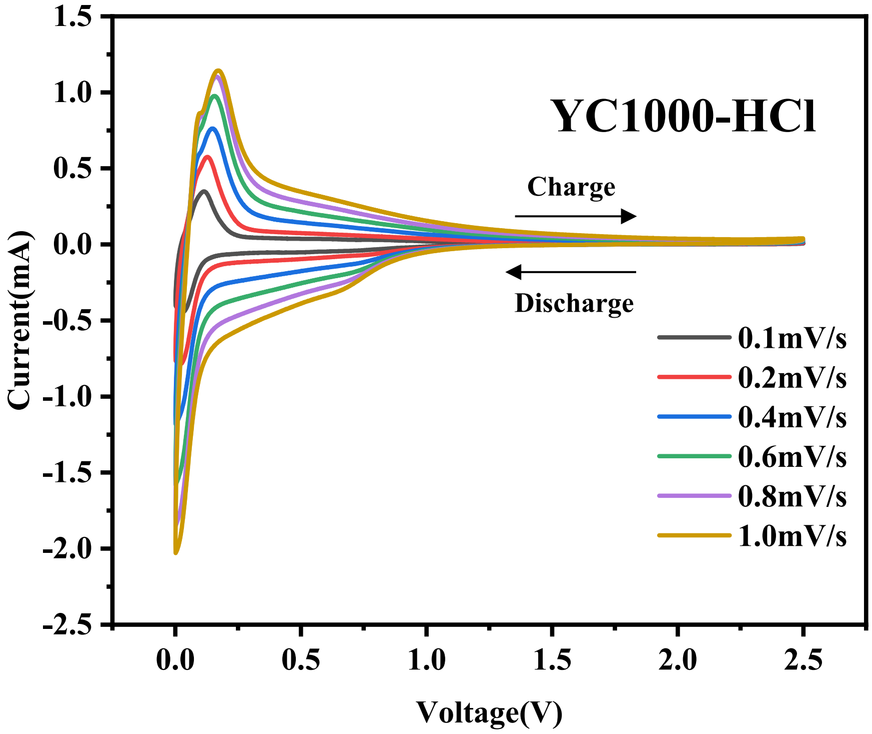

Fig. S14. CV curves of the YC1000-HCl at different scan rates.

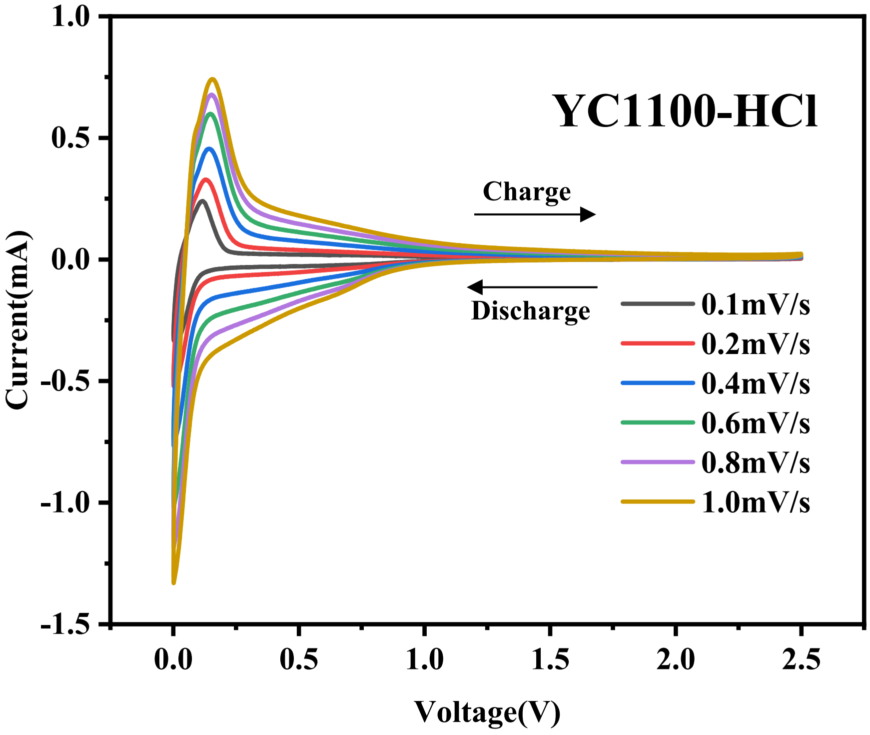

Fig. S15. CV curves of the YC1100-HCl at different scan rates

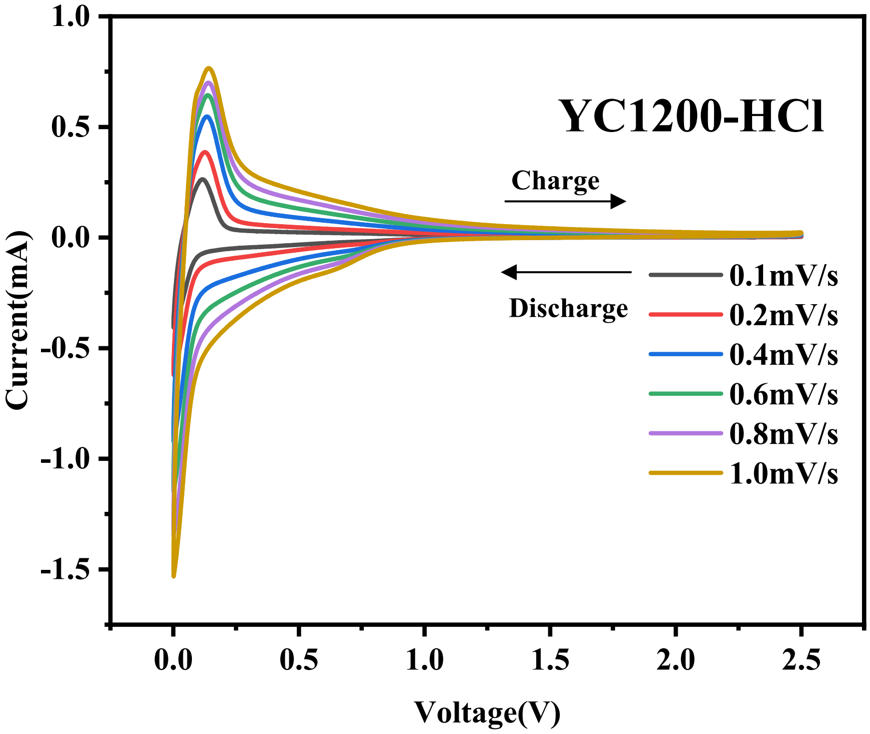

Fig. S16. CV curves of YC1200-HCl at different scan rates.

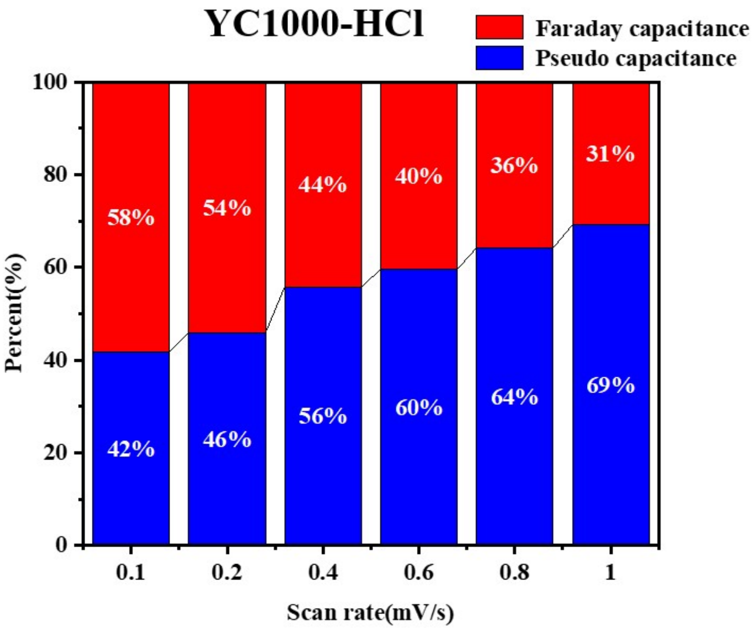

Fig. S17. YC1000-HCl pseudo capacitance and Faraday capacitance bar diagram.

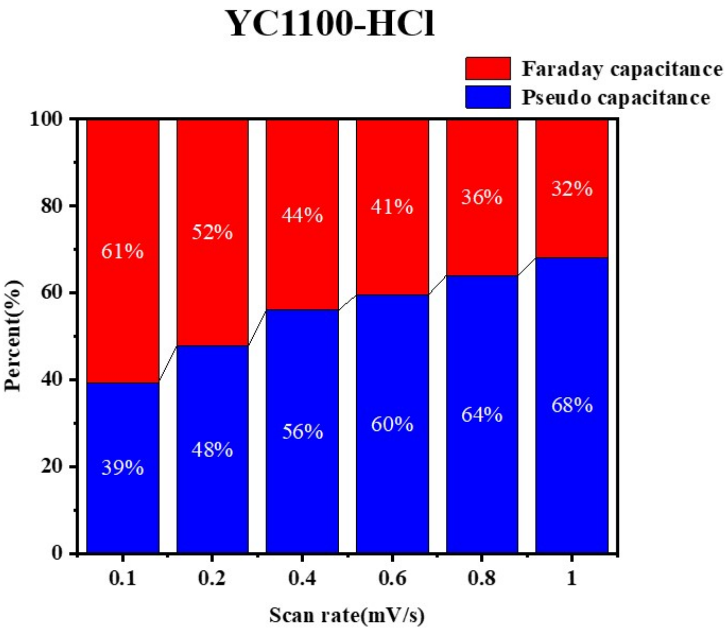

Fig. S18. YC1100-HCl pseudo capacitance and Faraday capacitance bar diagram.

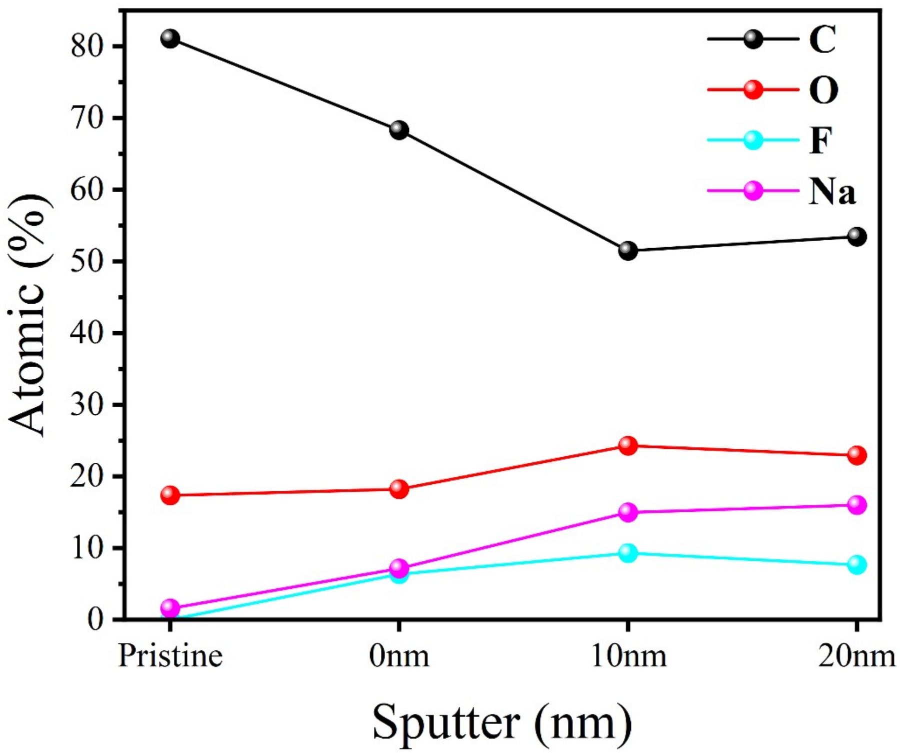

Fig. S19**.** the percentage of the atomic ratio with the depth etching increases.

Table S1 Ratio of sp2-C to sp3-C in different samples.

	sp2-C	sp3-C
KLL-pristine	24.14 %	75.86 %
YC1200-H-pristine	35.62 %	64.38 %
YC1200-H-cycle-0 nm	40.16 %	59.84 %
YC1200-H-cycle-10 nm	18.22 %	81.78 %
YC1200-H-cycle-20 nm	7.97 %	92.03 %

Table S2 The electrochemical performance comparation with previous

Reference	Specific capacity	ICE（%）
This Work	320 mAh^{-1} g	72.29
[34]	276 mAh^{-1} g	53.10
[35]	290 mAh^{-1} g	70.00
[36]	281 mAh^{-1} g	36.42
[37]	328 mAh^{-1} g	50.40
[38]	245 mAh^{-1} g	66.00
[39]	264 mAh^{-1} g	32.00
[40]	331 mAh^{-1} g	45.00
[41]	241 mAh^{-1} g	45.00
[42]	220 mAh^{-1} g	83.00
[43]	337 mAh^{-1} g	63.00
[44]	272 mAh^{-1} g	47.00
[45]	315 mAh^{-1} g	66.00
[45]	294 mAh^{-1} g	63.00
[45]	314 mAh^{-1} g	62.00

Table S3 Atomic ratio at different etching depths

Etching depth	Atomic %			
	C	O	F	Na
Pristine	81.08	17.35	0	1.57
0 nm	68.30	18.21	6.35	7.15
10 nm	51.47	24.26	9.29	14.97
20 nm	53.45	22.91	7.64	15.99