

Article

Bituminous Coal-Derived Carbon Anode: Molten Salt-Assisted Synthesis and Enhanced Performance in Sodium-Ion Battery

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Abstract

The high-efficiency and clean utilization of coal resources is a key strategy for new energy development, and converting coal into carbon materials offers a promising route to valorize bituminous coal. However, fabricating high-performance bituminous coal-derived carbon for sodium ion (Na⁺) insertion/extraction remains a major challenge, as it is difficult to regulate the carbon's microstructural properties to match Na⁺ storage demands. Herein, we propose a molten salt-assisted carbonization strategy to prepare bituminous coal-derived hard carbon (HC) for use as a sodium-ion battery (SIB) anode material, and we focus on regulating the structure of carbon. The results show that as-prepared HC exhibits significantly enhanced electrochemical performance for Na⁺ storage when the molar ratio of NaCl to KCl is 1:1. The optimized material achieves a reversible capacity of 366.7 mAh g⁻¹ at the current density of 100 mA g⁻¹ after 60 cycles and retains 99% of its initial capacity after 500 cycles at a current density of 1 A g⁻¹. The main finding is that the lattice spacing can be regulated by tuning the composition of the molten salt, and anode performance is enhanced remarkably by changes in the HC structure. This work provides a feasible strategy for designing and preparing a bituminous coal-derived carbon anode material for use in the energy storage field.

Keywords: bituminous coal; carbon anode; electrochemical performance; sodium-ion batteries



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1. Introduction

Lithium-ion batteries have been extensively studied and widely applied in the field of energy storage due to their high energy density, long-term stability, and high efficiency [1–4]. However, the scarcity of lithium resources poses a significant challenge to their sustainable utilization. More important, safety concerns associated with LIBs, particularly the formation of lithium dendrites during charge and discharge cycles, remain a critical issue, especially in electric vehicles [5,6]. These limitations have spurred the development of alternative battery technologies. In this context, sodium-ion batteries (SIBs) have garnered increasing attention owing to the abundant sources, lower costs, and enhanced safety [7]. While graphite is the dominant commercial anode material due to its stable electrochemical properties [8], its narrow interlayer spacing carbon is insufficient for reversible insertion and extraction of large-radius sodium ions [9].

Consequently, carbon materials such as soft carbon and hard carbon, which feature graphite-like or pseudo-graphite structures with larger interlayer spacing, abundant defects,

and porous architectures, have emerged as promising anode candidates for SIBs [10–12]. These structural characteristics provide expanded space for Na^+ intercalation, additional ion diffusion pathways, and numerous sites for Na^+ adsorption and storage [13]. The expanded interlayer spacing of hard carbon is particularly advantageous for ion insertion, thereby enhancing reversible capacity. For instance, Wang et al. prepared highly disordered carbons from pitch via a solvothermal and pre-oxidation strategy, and the as-obtained amorphous carbon had a high degree of disorder and large lattice spacing. As a result, it exhibited remarkably enhanced sodium storage ability [14]. Similarly, Zhou et al. improved the Na^+ storage capacity by adjusting the carbon surface [15]. Moreover, hard carbon is cost-effective and can be derived from diverse precursors, demonstrating significant application potential [16,17].

Beyond engineered carbon materials, in the quest for low-cost and sustainable precursors, there has been a move toward coal. The direct combustion of coal typically causes serious environmental pollution, necessitating its clean and highly efficient utilization. Coal consists of a three-dimensional cross-linked heterogeneous topological polymer and serves as an excellent precursor for carbon materials. Its intrinsic defects and micropores can be utilized as active sites and diffusion path in electrocatalysis [18–20]. Therefore, coal-derived materials (such as asphalt, lignite, and anthracite) are widely utilized as anode materials for various alkali metal secondary batteries. For example, graphite was prepared by using coal as raw material and it exhibited a higher specific capacity and superior cyclic lifespan for lithium-ion batteries [21]. Coal-based carbon fibers were prepared via electrospinning and used as a self-standing anode for a lithium-ion battery, and this carbon material showed outstanding electrochemical performance with a high reversible capacity [22].

Among various coal types, bituminous coal—a medium-metamorphosis coal between lignite and anthracite—is recognized as an abundant carbon source with good electrical conductivity, giving it wide application prospects for batteries. Zhu et al. prepared hard carbon used bituminous coal as a carbon precursor by pre-oxidation and carbonization, and this carbon anode material displayed a superior performance in sodium ion storage [23]. In another study, Wang et al. designed a molten salt-assisted strategy to regulate the microstructure of bituminous coal-based hard carbon, which was shown to accelerate Na^+ transport kinetic and facilitate sodium ion diffusion [24]. These findings indicate that molten salt-assisted preparation of hard carbon is a promising route. Moreover, the effects of molten salt on carbon structure derived from bituminous coal are critical for the development of a high-performance anode material for sodium batteries.

In this study, bituminous coal was employed as a precursor to prepare hard carbon materials through a simple acid-washing process combined with molten salt assistance. The excellent electrochemical performance of the as-prepared materials is attributed to the effective modulation of the carbon structure induced by molten salt. This study provides a simple strategy for preparing a high-performance and low-cost carbon anode for sodium-ion batteries.

2. Experimental Section

2.1. Synthesis of Carbon Materials

2.1.1. Pre-Treatment of Raw Materials

The bituminous coal (BC) used in this study was obtained by Coal Co., Ltd. (Taiyuan, China). A 150–200 mesh BC was selected. First, BC was mixed with 6 mol L^{-1} HCl at room temperature for 10 h, followed by filtration and washing treatment until the pH was 7. Afterward, it was dried in a vacuum oven at 60°C for 6 h. The same procedure was repeated using 5 mol L^{-1} HF to obtain raw materials. The industrial analysis and elemental composition of the acid-washed bituminous coal precursor are shown in Table S1.

2.1.2. Preparation of Molten Salt

Next, 37 g KCl and 29 g NaCl were added to 100 mL of deionized water and agitated intensely for 30 min to form a saturated solution. Under magnetic stirring, ethanol was added drop-by-drop to the saturated solution till the recrystallization of KCl and NaCl. The resulting crystal was then subjected to suction filtration and dried at 50 °C for 10 h. The powder as obtained by recrystallization was further ball-milled to obtain uniform and fine crystal particles.

2.1.3. Synthesis of Hard Carbon

Hard carbon was prepared using pre-treated bituminous coal (BC) as a carbon source by the molten salt-assisted method (Figure S1). A typical preparation process is as follows: 1 g BC is dissolved in 50 mL of N-methylpyrrolidone (NMP) and is stirred for 1 h, and after that, 15 g NaCl-KCl mixtures with different molar ratios (1:0, 0:1, 1:1, 1:2, and 2:1) are added to the above solution, and it is stirred continuously at room temperature for 1 h. After NMP is evaporated at 70 °C, the mixture is dried at 60 °C for 12 h. The as-obtained gray powder is heated to 900 °C under an Ar atmosphere for 3 h. After natural cooling, the sample is washed and filtered to remove residual salts. The yield of hard carbon (HC) is about 65% to 75%.

The as-obtained hard carbon assisted with NaCl, KCl, and mixed salt are named as HC-N, HC-K, and HC-NK11, HC-NK12, and HC-NK21 in terms of the different ratios of salts, respectively. For comparison, the hard carbon prepared using BC and uBC (untreated BC) as a carbon source without molten salt assistance is labeled as HC and uHC, respectively.

2.2. Characterization

The structures of bituminous coal-based carbon materials were characterized by X-ray diffraction (XRD, Rigaku SmartLab, Tokyo, Japan) and Raman spectrometer (Renishaw-inVia, Gloucestershire, UK). The morphology and elemental distribution were analyzed by scanning electron microscopy (SEM, TescanMIRA3LMH, Brno, Czech Republic), and transmission electron microscopy (TEM, JEOL 2100F, Tokyo, Japan). The pore structure was analyzed by isothermal N₂ adsorption/desorption. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Waltham, MA, USA) was conducted on an ESCAL ab 250Xi with Al K_α radiation, calibrated against carbon at 284.8 eV.

2.3. Preparation and Performance

Bituminous coal-based carbon, acetylene black (Super-P), and polyvinylidene fluoride (PVDF) were ground with a mass ratio of 7:2:1. An appropriate amount of N-methyl pyrrolidone (NMP) was added to form a slurry that was covered by copper foil, then it was dried at 60 °C and vacuumed for 24 h to evaporate the solvent. After that, the copper foil was taken out and cut into small disks with a diameter of 15 mm to serve as the working electrode. A sodium sheet was used as the counter electrode, and a glass-fiber membrane (Whatman GF/C) was used as a separator. The electrolyte was prepared by dissolving 1 mol L⁻¹ NaPF₆ in a 1:1:1 (volume ratio) mixture of ethyl carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC), followed by adding 5% fluoroethylene carbonate (FEC). The sodium ion half-cell was assembled in an argon glove box using a CR2032 button cell case, with H₂O and O₂ levels maintained below 0.1 ppm. The LAND CT2001A battery testing system was used to test the cycling performance, rate performance, and galvanostatic charge-discharge curve (GCD) of the battery. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using the CHI660e electrochemical workstation. The potential range was set at 0.001–3 V

(vs Na^+/Na). CV was tested at scan rates ranging from 0.2 to 1.2 mV s^{-1} , while EIS was conducted in a frequency domain of 0.01 Hz to 100 kHz with an amplitude of 10 mV.

3. Results and Discussion

Figure 1a illustrates the synthesis procedure for bituminous coal-based hard carbon. Initially, bituminous coal and salt were mixed in solution, followed by solvent evaporation and drying to obtain a solid powder. This powder was subsequently subjected to high-temperature heat treatment, leading to the formation of hard carbon. The structures of bituminous coal-derived hard carbon were characterized by XRD, as shown in Figure 1. The pre-treated carbon (CH) exhibits two characteristic diffraction peaks of carbon without any impurity peaks (Figure 1b), whereas the untreated carbon (uHC) shows additional impurity peaks, confirming the effective removal of impurities after acid treatment. Figure 1c presents the XRD patterns of different hard carbon materials synthesized via the molten salt-assisted method. All samples display two characteristic peaks at approximately 25° and 43° , corresponding to the (002) and (100) crystal planes of carbon, respectively [6]. The peak intensities of HC-N and HC-NK11—synthesized with NaCl and a mixed NaCl/KCl molten salt, respectively—are higher than that of HC-K. Moreover, the (002) peaks of the molten salt-assisted samples shift slightly to lower angles, suggesting an expansion of the carbon lattice. The results demonstrate that molten salt treatment can regulate the lattice spacings of HC materials, and the lattice spacings of HC-N, HC-K, and HC-NK11 are 0.362, 0.360, and 0.377, respectively (Table S2), indicating that the mixed molten salts of NaCl and KCl play a key role in changing the carbon structure, leading to a significant increase in interlayer spacing.

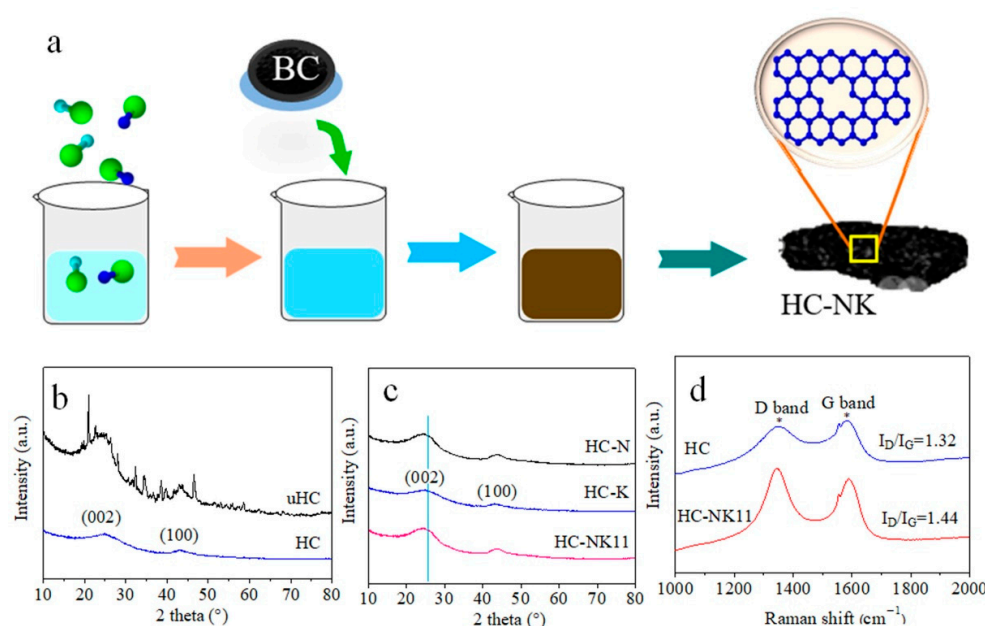


Figure 1. (a) Synthetic scheme of hard carbon (HC) from bituminous coal assisted with molten salt. XRD patterns of HC materials (b) prepared with treated and untreated BC and (c) with salt assistance. (d) Raman spectra of HC and HC-NK.

Raman spectroscopy was further employed to investigate the graphitization degree and structural disorder of hard carbon materials prepared with and without molten salt assistance (Figure 1d). Both HC-NK11 and HC samples exhibit characteristic D and G bands at around 1350 cm^{-1} and 1580 cm^{-1} , respectively. A notable difference, however, lies in the intensity and width of these peaks, suggesting distinct graphitization and disorder characteristics between HC-NK11 and HC. Specifically, the $I_{\text{D}}/I_{\text{G}}$ ratio of HC-NK11 is

significantly larger than that of HC, indicating a higher degree of structural disorder and more defect sites in the molten salt-assisted sample. Combined with the XRD results, these findings confirm that molten salt treatment effectively modulates the structural disorder of bituminous coal-derived hard carbon.

SEM was employed to examine the morphologies of the recrystallized salts and the as-prepared carbon materials (Figure 2). The treated NaCl and KCl samples consist of uniformly sized microparticles (Figure 2a,b). Figure 2c–f present the morphology and structure of the bituminous coal-based hard carbons. The hard carbon (HC) prepared directly from bituminous coal exhibits a densely stacked structure composed of nanoparticles (Figure 2c). A similar morphology is observed in samples prepared with the addition of NaCl or KCl alone (Figure 2d,e). In contrast, HC-NK11 consists of uniformly sized nanoparticles with a looser particle arrangement (Figure 2f). This morphological difference can be attributed to the role of molten salts in inducing thermal decomposition, activation, and microstructural rearrangement during carbonization. Notably, the distinct morphology of HC-NK11 is due to the lower melting point of the mixed NaCl/KCl molten salt, which promotes carbon nucleation [25]. The mixed-salt system increases entropy and lattice disorder, thereby reducing the temperature required for hard carbon formation [26].

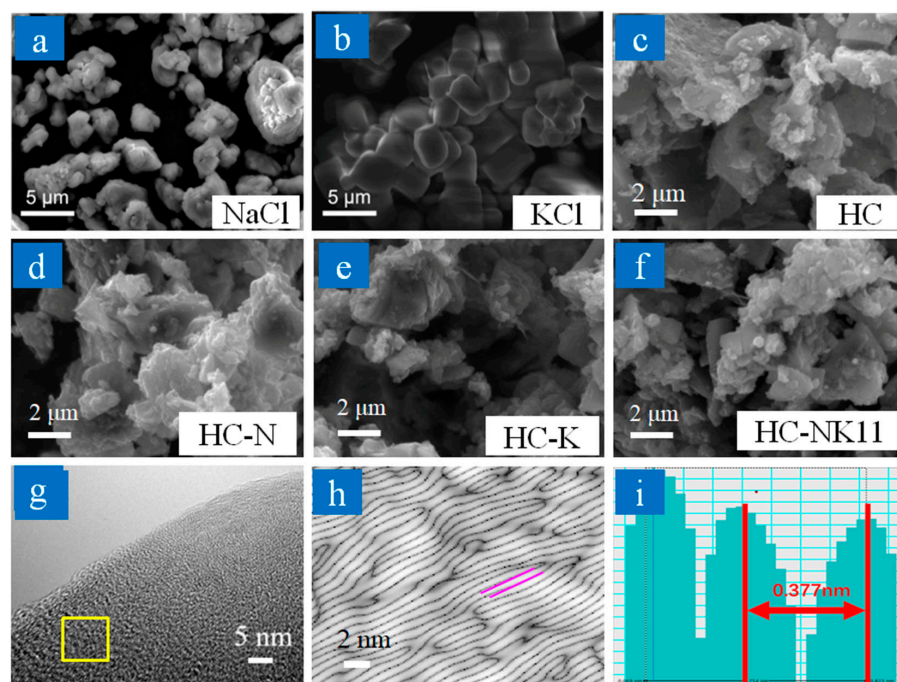


Figure 2. SEM images of (a) NaCl and (b) KCl after recrystallization. SEM image of bituminous coal-based carbon: (c) HC, (d) HC-N, (e) HC-K, and (f) HC-NK11. (g,h) HRTEM images (yellow rectangle area is magnified in (h), and pink double lines represent interlayer spacing) and (i) line profiles of IFFT of HC-NK11.

The fine structure of HC-NK11 was examined by TEM, with a high-resolution image revealing its carbon microstructure (Figure 2g). A local region marked by the yellow rectangle was enlarged and is displayed in Figure 2h. The lattice fringes were analyzed by measuring the inter-peak distance in the corresponding FFT pattern (Figure 2i), revealing a lattice spacing of approximately 0.377 nm, which is consistent with the XRD results. These findings confirm that molten salt treatment effectively enlarges the interlayer spacing of the hard carbon material.

To further analyze the structure of hard carbon (HC and HC-NK11), and its composition and surface chemical state, N₂ adsorption–desorption analyses were performed.

Adsorption–desorption isotherms of HC and HC-NK11 display a type IV hysteresis loop (Figure 3a,b), which suggests the presence of mesopore structures. The molten salt treatment enriches the mesoporous structure, resulting in a high specific surface area of $15.2 \text{ m}^2 \text{ g}^{-1}$, which is higher than that of $13.1 \text{ m}^2 \text{ g}^{-1}$ for the HC material. Based on the BJH calculations, the pore volume is about $0.28 \text{ cm}^3 \text{ g}^{-1}$, and the average pore size of HC-NK11 obtained by the molten salt treatment is about 2 nm, which is larger than that of HC (inset in Figure 3a,b). These mesopores can act as fast diffusion channels for sodium ions, not only reducing the diffusion distance of sodium ions but also providing a charge regulation region to enhance the specific capacity. This structure can contribute to the sodium storage performance of HC-NK11 [27]. The chemical state and composition of HC-NK11 was analyzed by XPS technology. The XPS survey reveals that two prominent peaks at 284.5 eV and 531.7 eV are ascribed to C 1s and O 1s (Figure 3c), indicating the surface composition of the carbon material. The high-resolution C 1s spectrum in Figure 3d exhibits two fitted peaks, which is ascribed to the C-C bond (284.5 eV) and C-O bond (286 eV) [28]. The O 1s spectrum (Figure 3e) shows one peak at 531.7 eV, which is assigned to the C-O bond [29]. The N 1s spectrum can be deconvoluted into two weak peaks that belong to pyrrole-N (400.4 eV) and graphitic-N (401.1 eV), which may contribute to the sodium storage performance. No peaks of Na or K were detected in the XPS analysis, which can be attributed to the fact that the soluble Na and K salts were removed by water washing.

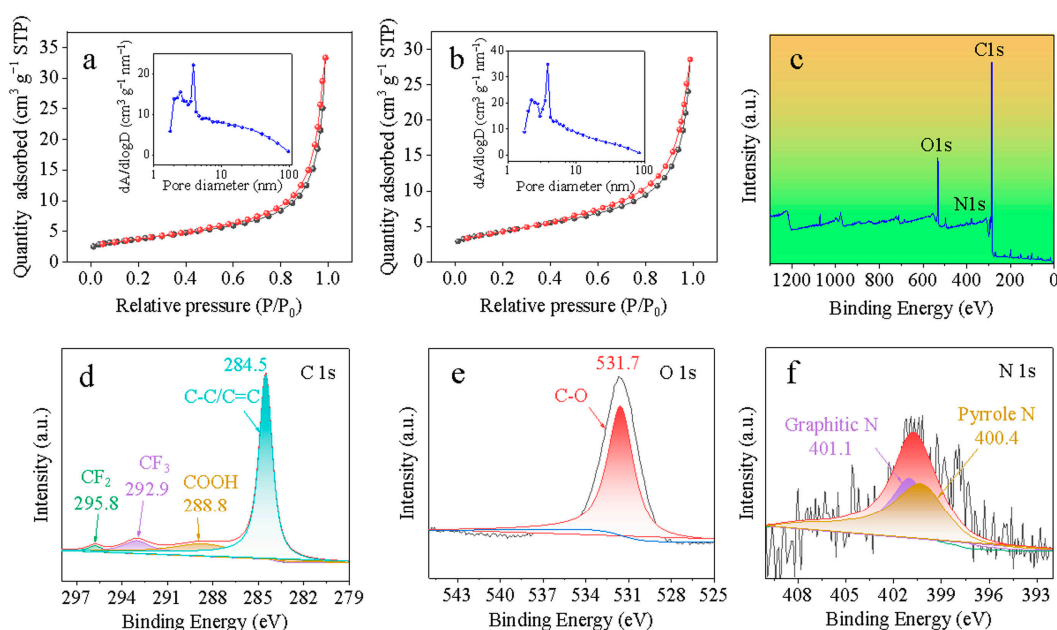


Figure 3. N_2 adsorption/desorption curves of (a) HC and (b) HC-NK11 (inset: pore size distribution (blue line). Black is adsorption, red is desorption). (c) XPS survey spectrum of HC-NK11, (d) C 1s, (e) O 1s, and (f) N 1s high-resolution spectra (different colors represent XPS peaks in (d–f)).

The cyclic voltammetry (CV) curves of the three cycles of HC-NK11 were measured at a scan rate of 0.2 mV s^{-1} using HC-NK11 as the negative electrode in a sodium-ion battery. A redox peak is observed in the range of 0 to 0.3 V (Figure 4a), corresponding to the insertion and extraction of Na^+ in the hard carbon material. A broad peak near 1.0 V is ascribed to the formation of a solid electrolyte interface (SEI) film on the negative electrode material during cycling, which results from the irreversible reaction of the electrolyte at the electrode solid–liquid interface. An appropriate SEI film can passivate the electrode surface, reducing further side reactions between the electrolyte and the electrode material, thereby enhancing the stability of the negative electrode material at high current densities [30]. The rate performance of the bituminous coal-based hard carbon materials was evaluated. The

rate performances of different hard carbon materials at various current densities (0.05, 0.1, 0.3, 0.5, 1, and 3 A g⁻¹) are shown in Figure 4b, along with the corresponding galvanostatic charge–discharge (GCD) curves of HC-NK11 (Figure 4c). Owing to its higher defect density and rich pore structure, the HC-NK11 material with mixed molten salt treatment exhibits a superior rate performance. A comparison of the rate performance of HC and HC-NK11 at different current densities demonstrates that the molten salt modification significantly enhances the electrochemical performance of sodium-ion storage, particularly at high current densities. Furthermore, cyclic tests were conducted to assess the long-term performance of these materials. The results reveal that dual molten salts (NaCl and KCl) are more efficient compared to a single molten salt. The sodium storage performance of hard carbon is significantly improved by changing the ratio of molten salts (Figure S2). HC-NK11 delivers an excellent reversible specific capacity of 366.7 mAh g⁻¹ at a current density of 100 mA g⁻¹ (Figure 4d). This outstanding performance results from the high porosity, structural disorder, and continuous framework of the as-prepared hard carbon material. Specifically, when the HC-NK11 electrode is tested at a high current density of 1 A g⁻¹, it demonstrates exceptional cycling stability (Figure 4e). After 500 cycles, the discharge capacity remains at 128.4 mAh g⁻¹, with a capacity retention rate of 99% and a Coulombic efficiency close to 100%. The morphology of the negative electrode material after cycling was characterized, and its SEM image is presented in Figure 4f. The structural integrity of HC-NK11 is well-maintained after 500 cycles, indicating excellent structural stability during repeated charge–discharge processes. This stability facilitates the rapid diffusion of electrolytes and the simultaneous activation of multiple active sites for Na⁺ adsorption, effectively mitigating volume expansion.

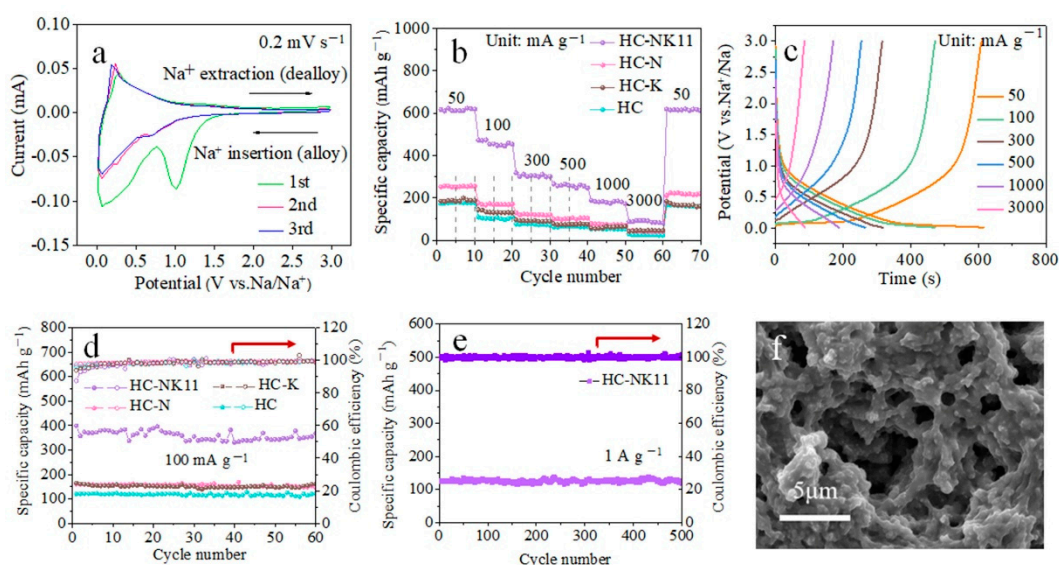


Figure 4. (a) CV curve of HC-NK11. (b) Rate performance of HC and HC-NK11 at different current densities and (c) galvanostatic discharge/charge profiles of HC-NK11. (d) Cycling performance of different HC materials. (e) Long cycling stability (red arrow toward coulombic efficiency shown as dark purple line) and (f) SEM image of HC-NK11 after 500 cycles.

In Nyquist plots (Figure 5a), the small arc radius of HC-NK11 shows a smaller charge transfer resistance, implying that the molten salt benefits the formation of the microstructure. To investigate the Na⁺ storage behavior of HC-NK11, CV curves were recorded at scan rates ranging from 0.2 to 1.2 mV s⁻¹, as illustrated in Figure 5b. The oxidation peak

of the CV curve shifted to higher potentials with increasing scan rates. The relationship between the peak current (i) and the scan rate (v) can be expressed as Equation (1),

$$i(v) = av^b \quad (1)$$

where a is a constant, and b reflects the energy storage mechanism. When b equals 0.5, the charge storage is determined by ion diffusion processes. When b is 1.0, the charge storage is primarily attributed to surface capacitive behavior. If b is in the range of 0.5 and 1.0, the charge storage mechanism involves ion diffusion and surface capacitive behavior. Thus, b can be obtained from the linear relationship of Equation (2) [31],

$$\log i = b \log v + \log a \quad (2)$$

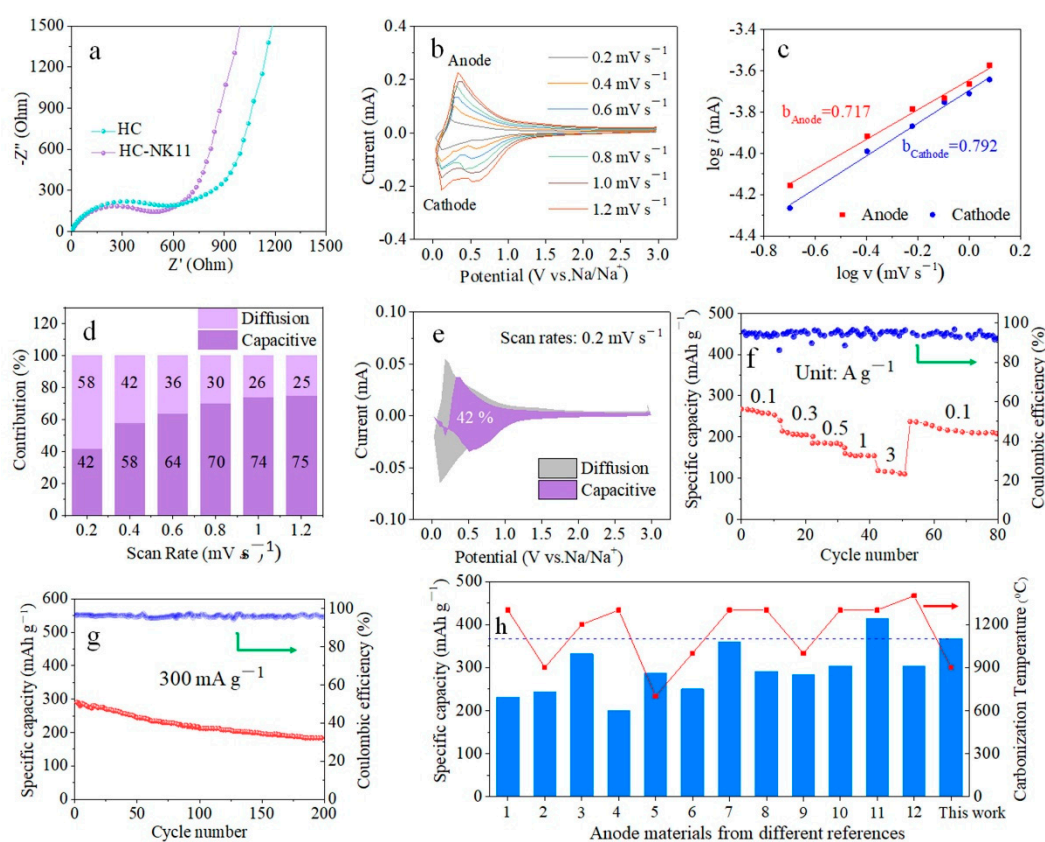


Figure 5. (a) Nyquist plots of HC and HC-NK11 electrodes. (b) CV curves of HC-NK11 at different scan rates. (c) Fitting lines of peak current vs. scan rate. (d) Pseudo capacity and diffusion ratio at different scan rates, and (e) pseudo capacity ratio of HC-NK11 at 0.2 mV s^{-1} . (f) Rate and (g) cycling performances of the full cell at different current densities (blue line is coulombic efficiency shown as green arrow, red line is specific capacity). (h) Comparisons of specific capacity of HC prepared at different temperatures (red line shows change in carbonation temperature. x-axis: 1—[32], 2—[33], 3—[34], 4—[35], 5—[36], 6—[37], 7—[38], 8—[39], 9—[40], 10—[24], 11—[41], 12—[42]).

The fitting results of the oxidation peaks from CV curves at different scan rates are presented in Figure 5c. The calculated b values are 0.717 and 0.792 for the anode and cathode, falling within the range of 0.5 to 1.0, indicating that the sodium storage capacity of HC-NK11 arises from a combination of capacitive and battery-like behavior. Additionally, the contributions of surface capacitance and diffusion can be quantitatively evaluated using the following equation:

$$i(v) = k_1 v + k_2 v^{1/2} \quad (3)$$

where k_1 and k_2 are constants, where k_1v represents the proportion of surface capacitance, and $k_2v^{1/2}$ represents the proportion of diffusion process [43]. The capacitance contribution rate of the material at scan rates ranging from 0.2 to 1.2 mV s⁻¹ was calculated using the specific formula, and the results are presented in Figure 5d. Specifically, the capacitance contribution of the material at 0.2 mV s⁻¹ is shown in Figure 5e. As the scan rate increases, the contribution ratio of capacitor charge to the total capacity increases from 42 to 75%.

The rate capability and cycling performance of the sodium-ion full battery were evaluated at current densities of 0.1, 0.3, 0.5, 1, and 3 A g⁻¹ (Figure 5f,g). In this cell, the cathode material was commercially available sodium vanadium phosphate (Na₃V₂(PO₄)₃, NVP). The full battery demonstrated a remarkable rate of performance, achieving a specific capacity of 115.30 mAh g⁻¹ even at the high current density of 3 A g⁻¹. This result confirms that the bituminous coal-based hard carbon maintains excellent electrochemical performance in practical full-cell applications. Furthermore, despite this inherent challenge, the full cell still exhibited outstanding cycling stability, maintaining a capacity retention rate of 62% after 200 cycles at a current density of 300 mA g⁻¹ (Figure 5g), which is lower than that in the half-cell test. The possible reason is that the sodium metal sheet as a cathode in the half-cell test provides a sufficient Na source, while sodium vanadium phosphate as a cathode in the full-cell test provides insufficient Na, leading to a decline in capacity retention. These superior performance characteristics primarily arise from the unique microstructure and enhanced conductivity of hard carbon. The synergistic effects of these structural advantages effectively mitigate structural degradation caused by volume expansion during charge/discharge processes. Comparisons of the Na⁺ storage performance of as-prepared HC with reported materials in the literature are displayed in Table S3 and Figure 5h, showing that this molten salt-assisted HC can be prepared under a lower carbonization temperature and demonstrating the superior performance of sodium ion storage compared to the reported results. This exceptional performance of as-prepared HC is ascribed to its intrinsic structural characteristics such as rich pores, a wide interlayer, and defect sites, which promote Na ion transport.

4. Conclusions

A promising, environmentally friendly, and cost-effective strategy is proposed for synthesizing bituminous coal-derived hard carbon materials for sodium-ion batteries. The as-prepared hard carbon, produced via a molten salt-assisted approach combined with high-temperature treatment of bituminous coal, exhibits expanded interlayer spacing and a defect-rich structure. When used as an anode material in sodium-ion batteries, this hard carbon demonstrates exceptional electrochemical performance, including remarkable cycling stability and excellent full-cell performance. Notably, the reversible specific capacity surpasses that of several reported counterparts. This outstanding capacity is attributed to the enlarged interlayer spacing and unique pore structure, which facilitate intimate contact between the hard carbon and the electrolyte, thereby significantly enhancing sodium-ion storage capacity and transport kinetics. This study offers a practical synthesis route for high-performance carbon materials, supporting the clean utilization of bituminous coal in sustainable energy storage applications.

Supplementary Materials: The supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/c11040082/s1>, Figure S1: Preparation flow; Figure S2: Cycling performance; Table S1: Compositions of hard carbon; Table S2: Calculation of lattice spacing by XRD results; Table S3: Comparisons of raw materials.

Author Contributions: Y.D., investigate, data curation, writing—original draft; J.W., supervision, project administration and writing—review and editing; P.L., analysis; Y.W., analysis; Y.Z., analysis; S.C., supervision, project administration, and writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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