

High-performance coal-based hard carbons for sodium-ion storage enabled by Joule-heated rapid pyrolysis

Xuelel Gong^{1,a}, Yongxu Liu^{1,b}, Junwei Han^{1,2,c}, and Linjie Zhi^{1,2,d}

¹ School of Materials Science and Engineering, China University of Petroleum (East China), 266580, China;

² Research Center on Advanced Chemical Engineering and Energy Materials, China University of Petroleum (East China), 266580, China.

^a S21140020@upc.edu.cn, ^b liuyongxu@upc.edu.cn, ^c jwhan@upc.edu.cn, ^d zhilj@upc.edu.cn

Abstract. Hard carbon materials are potentially used in sodium-ion battery anodes, yet their structure is complex and not easy to control. In this paper, a Joule-heated rapid pyrolysis is proposed for the preparation of hard carbon. The selected highly volatile bituminous coal-based hard carbon is affected by the Joule-heated explosion, where a large number of volatile components are instantly released, which reorganizes the microstructure of hard carbon, increases the layer spacing of carbon microcrystals, and obtains an expanded structure. This coal-based hard carbon exhibits high sodium ion storage capacity (274 mAh g⁻¹), high ICE (80%), and remarkable cycling stability with 80% capacity retention for more than 1000 cycles. In addition, the coal-based hard carbon anode showed good capacity retention (40%) at an extremely low temperature (-40°C).

Keywords: Joule heat; sodium ion battery; coal-based hard carbon.

1. Introduction

Rapid development of new energy industries has created an urgent need for low-cost, scalable energy storage solutions. However, the high energy storage costs and limited availability of lithium resources make it challenging to apply lithium-ion batteries on a large scale [1]. Sodium-ion batteries operate similarly to lithium-ion batteries, offering high safety performance and a wide temperature range [2]. This makes them a promising option for use in energy storage with a large scale.

The intensive production of sodium-ion batteries places a demand on the anode materials, which has become a significant growth point for the capacity of sodium-ion batteries. Nevertheless, the ionic radius of sodium ions is much larger than that of lithium ions ((1.02 Å for Na⁺ versus 0.76 Å for Li⁺) [3], and the inability of conventional graphite anode to form a stable intercalation compound with sodium ions poses a challenge to the exploration of anode materials with high sodium storage capacity and rapid ion diffusion [4]. At present, the sodium-ion battery mainly adopts hard carbon with complex microstructure as anode material, which is primarily composed of many "graphite-like" microcrystals with sequential layered structure of disordered stacking, forming a short-range approximate order but long-range disordered structure [5]. However, the actual structure of hard carbon is much more complex, resulting in a complicated and unclear sodium storage mechanism that differs from the models describing the corresponding structure-property relationships, leading to much controversy [6]. Currently, the "adsorption-intercalation-filling" mechanism can describe most hard carbons' sodium ion storage behavior [7]. The hard carbon storing Na⁺ mainly based on graphite-like microcrystalline ordered phases and disordered phase structures such as defects and pores, where the ordered phase structures have good electrical conductivity and few side reactions, but the intercalation reaction capacity is low, and the kinetics is poor. The adsorption and filling sodium storage behavior of disordered phases can contribute high capacity and reaction kinetics, but with many side reactions and conductivity disruption of hard carbon. Therefore, regulating the microstructure of hard carbon is crucial for producing hard carbon anode materials with both high capacity and high cyclic stability. A deep understanding of the

relationship between microstructure, Na⁺ storage mechanism and electrochemical performance is also significant [8].

High-temperature carbonization usually produces a hard carbon anode using carbon sources such as biomass [9], polymer resin [10], and coals [11]. Among them, biomass-based hard carbon usually selects coconut shells, starch, fruit shells, bamboo, etc., as precursor raw materials, a wide range of material sources. Yet, its carbon recovery rate is generally about 14%, far from meeting the output demand of sodium ion anode. Polymer resin-based hard carbon mainly chooses phenolic epoxy resin as a raw precursor. The product consistency is high, but the cost is high, and industrialization is difficult. Coal-based hard carbon mainly uses coal as precursor raw materials, of which coal-based materials are rich in reserves, low cost, and high residual carbon rate, and are one of the ideal precursors for hard carbon anode. The low cost and component diversity of coal make it a good choice for developing high-performance anode materials for Na⁺ storage [12]. The difficulty is solving the quality control problems of different batches of coal materials and improving the materials' consistency. It can be said that hard carbon anode derived from coals is one of the key route for future sodium-ion battery anode. Regarding sodium ion storage mechanism, polymer resin-based and biomass-based hard carbon materials lack aromatic structures and are mainly dominated by disordered phases after high-temperature carbonization. Although they have a high sodium storage capacity, sodium ion intercalation's excessive irreversible side reactions lead to low first Coulombic efficiency. Compared with the above two carbon sources, the anthracite coal material combines the advantages of low cost and high residual carbon [11], but it has too many aromatic units, and the microcrystalline structure is dominated by ordered phases after carbonization, resulting in low capacity, poor multiplication, and poor practical performance. When comparing coals with different degrees of coalification, bituminous coal, which is intermediate between lignite and anthracite, has more aromatic units and more side chain structures, which offers the possibility of producing carbon microcrystals with tunable.

A recently developed Joule-thermal rapid heating method achieves instantaneous heating and rapid cooling of materials by applying a high voltage and current between two electrodes to instantly reach a high target reaction temperature (3000°C) at a high rate of temperature rise (100-200°C/s). The Joule-heated rapid heating method achieves lower energy consumption than conventional kiln heating due to its ultra-short processing time, making the material synthesis process more efficient, using only 0.12% of the energy consumed by conventional kiln heating methods [13]. Currently, Joule rapid heating technology has been reported in plastic depolymerization [14], graphene preparation [13], high entropy alloy catalyst preparation [15], phase change material preparation [16], and precious metal extraction [17]. Compared with the high-temperature, long-time orderly carbonization process, rapid heating using Joule heat is expected to achieve rapid pyrolysis of highly volatile bituminous coal, reduce the degree of structural ordering and realize the anode of hard carbon sodium-ion batteries that takes into account both high capacity and high ICE. In addition, Joule heating method plays a vital role in removing metal impurities from hard carbon materials, which is expected to solve the problem of quality control of different batches of carbon materials and achieve low-cost production of hard carbon materials with high consistency.

Here we report a method for rapid pyrolytic carbonization of highly volatile bituminous coals by fast heating using Joule heat. Coal-based hard carbon with an expanded interlayer structure was produced by the instantaneous release of a large amount of volatile matter from bituminous coal due to the high heating rate. As a result, pore reorganization and layer spacing increase are achieved. This expanded structure coal-based hard carbon structure facilitates the storage and transport of Na⁺ ions, with a high sodium-ion storage capacity (274 mAh g⁻¹) and high ICE (80%), together with good cyclic stability with 80% capacity retention for over 1000 cycles. In addition, the coal-based hard carbon anode exhibits good capacity retention (40%) at an extremely low temperature (-40 °C). The proposed rapid pyrolysis strategy provides an effective way to enable efficient and low-cost anode materials for sodium ion batteries.

2. Experimental section

2.1 Materials preparation

The hard carbon with coal precursor was prepared by a two-step method using acid mixing to remove impurities and instantaneous heating with Joule heat. Firstly, 4 g lithium fluoride powder was put into 9 mol/L-1 hydrochloric acid and mixed and stirred for 30 min to produce a mixed HCl/HF acid solution in situ, and then 4 g of coal powder was added and acid washed at 35 °C for 6 h, then rinsed using water, and dried overnight. Afterwards, the coal powder was added to a graphite tube, and a high voltage current (30 V, Joule heat) was applied to the electrodes at both ends to remove impurities. After that, the pretreated coal powder was added to a graphite tube, and a high voltage current (30 V, 150 A) was applied to the electrodes at both ends, and the powdered material was heated up to 1200 °C in 10 seconds using the Joule heat effect, and then cooled rapidly to obtain the coal-based hard carbon material. The experimental samples described were bituminous coal, and the comparison samples were lignite and anthracite, both prepared by the same means.

2.2 Characterizations

SEM (Regulus8100, Japan) was used to observe the coal morphology. Raman spectra of the carbon materials were tested using a high-resolution micro-Raman spectroscopy system(HORIBA HR Evolution, French). The carbonation behavior of the coal-based precursors was analyzed using the TGA (NETZSCH STA 449F3, German) in N₂ atmosphere. The hard carbon phase structure was characterized by XRD (SHIMADZU XRD-7000, Japan). N₂ adsorption/desorption isotherms were conducted on Mack Tristar II 3020, USA. TEM was conducted using Field Emission STEM (Thermo Scientific Talos F200X, USA).

2.3 Electrochemical measurements

The active materials were subjected to 2032 coin half-cell assembly and the electrochemical properties were measured. First, we mixed the active material, conductive additives of carbon black and hydroxymethylcellulose (CMC) into a slurry and their mass ratio is 8:1:1. Second, the obtained slurry was coated on a Cu foil and dried at 80°C in a vacuum condition. Third, we prepared an electrode sheets with a diameter of 14 mm. The button cell was assembled using a hard carbon electrode as the working electrode and sodium metal as the counter electrode..The button cell 2023 was assembled with the hard carbon as working electrode, Na metal foil as the counter electrode, a glass microfibre filter as the separator, 1 M NaPF₆ in EC:DEC=1:1 vol% as the electrolyte. The electrochemical performance of this assembled half cell was tested in a potential range of 0.01-3V.

3. Results and discussion

By selecting bituminous coal, which has a carbon content between lignite and anthracite, as the object of study, Fig. 1a shows the flow chart of the preparation of bituminous coal-based hard carbon, which was prepared by a two-step method using mixed acid pre-treatment and Joule heating. In this process, the bituminous coal powder is pre-treated by adding mixed acid HCl/HF to remove the oxide impurities such as silica-aluminium-calcium from the coal powder. The acid-mixed pre-treated bituminous coal powder is placed in the Joule heating device for rapid heating. This step aims to use the high heating rate to remove the metal impurities in the coal powder. The second is to use the high-temperature shock impact to accelerate the volatilization of the gas inside the particles, activate the pore remodeling of the formed carbon, increase the layer spacing of carbon microcrystals, and achieve the expanded structure of the coal-based hard carbon preparation. Figures 1b-d show the scanning electron microscope (SEM) images of bituminous coal particles, bituminous coal mixed acid pre-treated particles, and Joule-heated bituminous coal particles. Bituminous coal powder particles can be found in the SEM after the removal of impurities by the mixed acid. They present micron-sized lamellar morphology. The morphological characteristics are

in accordance with the formation of the law of coal deposition. The morphology is further fragmented into smaller lamellar particles by the rapid thermal impact of Joule heat. Figure 1e-f shows the Raman spectra of bituminous coal particles, mixed acid pre-treated bituminous coal particles, and Joule-heated bituminous coal particles. After rapid pyrolysis treatment, the ID/IG of the carbon material increases from 0.65 to 0.91, and the defect density in the hard carbon increases significantly. In sodium-ion battery applications, this favors Li^+ conduction and cycling efficiency.

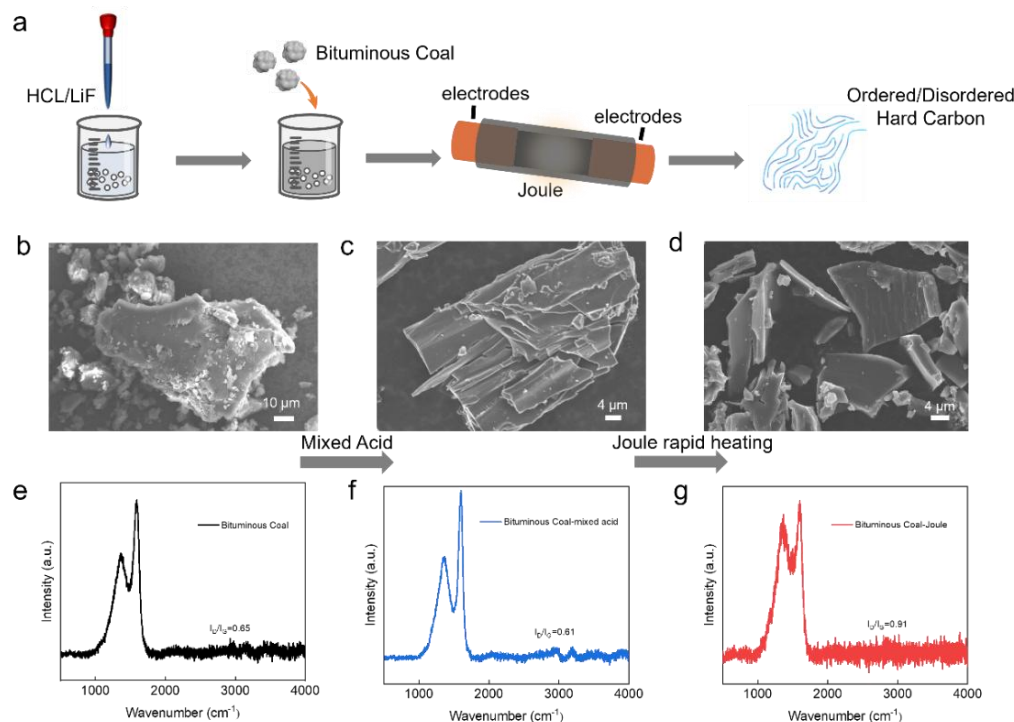


Figure 1 a Process for the preparation of hard coal from bituminous coal. b-d SEM images of bituminous coal particles, mixed acid pre-treated bituminous coal particles, and Joule-heated bituminous coal particles. e-f Raman spectral of bituminous coal particles, mixed acid pre-treated bituminous coal particles, and Joule-heated bituminous coal particles.

Figures 2a-c show the thermogravimetric analyzer (TGA) curves of the residual carbon content of coal dust for three different coal chemistry levels, where the residual carbon content after mixed acid pretreatment is, in order, lignite (49.05%), bituminous coal (54.11%) and anthracite (78.18%). In addition, by comparing the residual carbon rate before and after the mixed acid pretreatment, it can be found that the mixed acid can effectively remove the oxide impurities such as silica, silicon, aluminium, calcium and other oxide impurities in the coal powder.

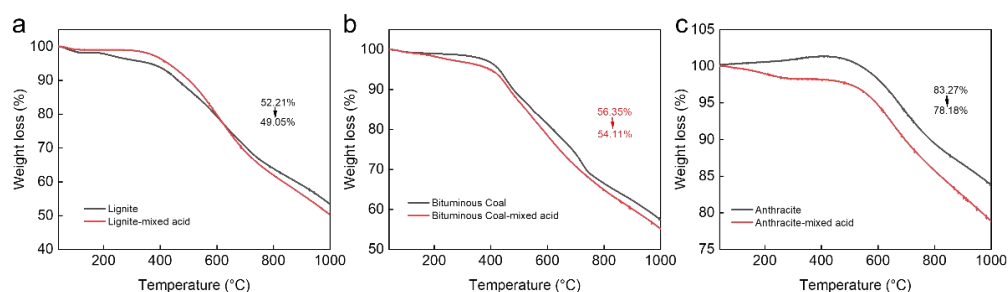


Figure 2 TGA curves for three coals of a lignite b bituminous, and c anthracite coals.

The X-ray diffraction (XRD) spectra in Figure 3a, b of bituminous coal before and after mixed acid pretreatment. After the mixed acid pre-treatment, the XRD impurity peaks were obviously reduced and according to the spectral analysis, the main residual impurities were FeS_2 and a small amount of LiF . In addition, the hard carbon (002) peak 2θ is shifted to the left from 24.88° to 23.54° and the layer spacing is increased after the bituminous coal powder is intercalated with an excess of LiF . As shown in Figure 3c,d, comparing the XRD diagrams of coal-based hard carbon with

conventional heat treatment (1200 °C, 2h) and Joule-heated rapid heating treatment (1200 °C, 10s), it can be seen that the Joule-heated rapid heating treatment has a significant effect on the removal of metal impurities. In addition, the peak 2θ of hard carbon (002) shifted from 23.54° to 23.27° after conventional heat treatment (1200 °C, 2h) with little change in layer spacing, but after Joule-heated rapid heating treatment (1200 °C, 10 s), the peak 2θ of hard carbon (002) shifted from 23.54° to 21.6°. The spacing calculated by the Bragg equation $2d \sin \theta = n\lambda$, where $n=1$ and $\lambda=1.54056$, increases from 3.78 nm to 4.11 nm. It confirms that rapid pyrolysis means widening the carbon microcrystalline layer spacing and obtaining expanded interlayer structures.

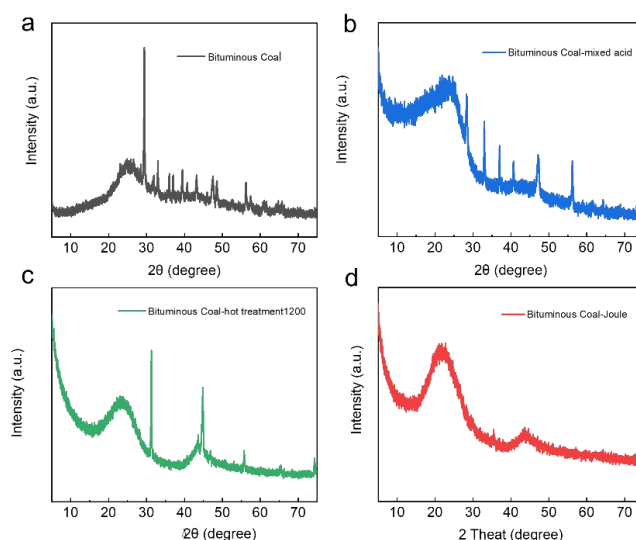


Figure 3 x-ray diffraction (XRD) patterns of bituminous coals with different treatments. a bituminous coal. b mixed acid pre-treated bituminous coal. c Conventional heat treatment (1200 °C 2h). d Joule rapid heat treatment (1200 °C 10s).

Figure 4a shows the optical photographs of bituminous coal powder after conventional heat treatment (1200 °C, 2 h) and Figure 4b shows the optical photographs of bituminous coal powder after Joule heat treatment (1200 °C, 2 h). From the comparison, it can be seen that the carbon particles of bituminous coal with higher volatile matter undergo pyrolytic cross-linking and form fluffy lumps after Joule heat treatment. Figure 4c, d shows the transmission scanning electron microscope image TEM of the bituminous coal after Joule heat treatment, it can be found that the hard carbon powder after Joule heat rapid heating treatment has a typical hard carbon microcrystalline phase structure, which is conducive to the storage and transport of sodium ions.

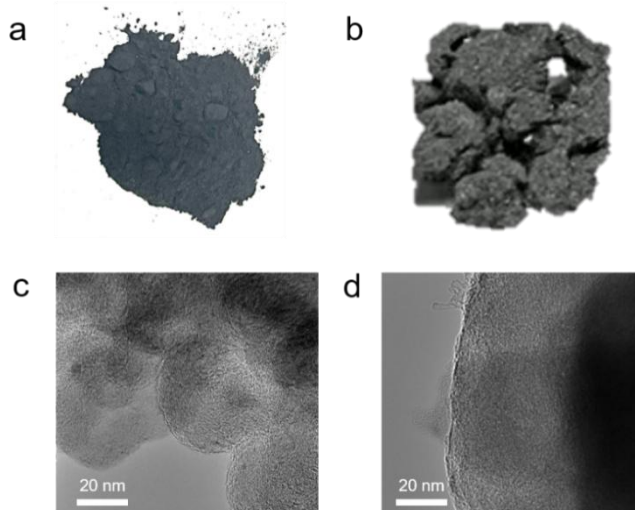


Figure 4 a Optical photographs of conventional heat-treated (1200 °C, 2h) bituminous coal powder. b Optical photographs of joule-heated (1200 °C, 2h) bituminous coal powder. c-d Transmission electron microscope (TEM) of Joule rapid heat-treated bituminous coal powder.

To further characterize the large amount of volatile matter released on the pore structure of coal-based hard carbon after the rapid impact of bituminous coal by Joule heat. Fig. 5 shows that the pore size of bituminous coal powder without Joule heat treatment is mainly distributed around 3.4 nm, and the calculated BET-specific surface area value is 3 m²/g. After Joule heat treatment, the pore size is primarily distributed around 3.768 nm, and the calculated BET-specific surface area value is 11 m²/g. It has been demonstrated that rapid pyrolysis releases volatile components from the particles, increase the specific surface area (SSA) and pore size of hard carbon, but this is still controlled at a deficient level to avoid the increase of electrolyte side reactions.

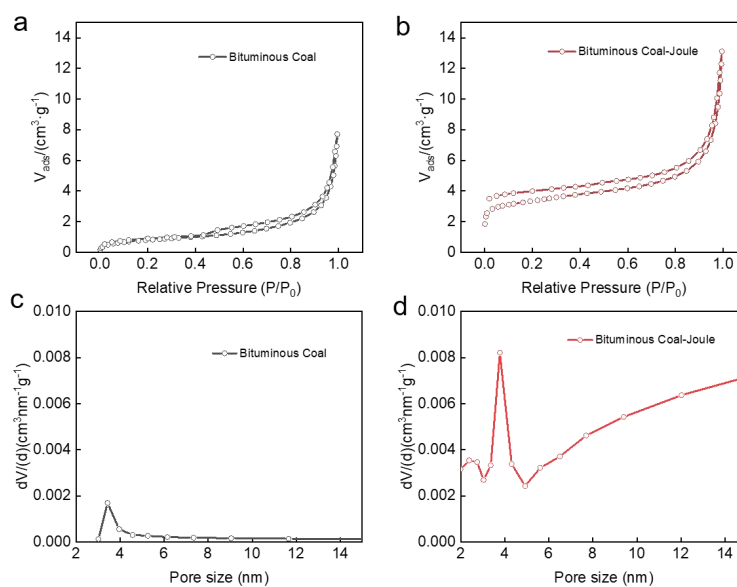


Figure 5 The N₂ adsorption/desorption isotherms and the corresponding pore size distribution. a,c Bituminous Coal and b,d Joule Rapid Heat Treatment of Bituminous Coal.

Bituminous coal-based hard carbon was subjected to sodium-ion half-cell assembly to investigate the electrochemical performance. Consequently, the coal-based sodium-ion hard carbon anode delivered high capacity of 274 mAh g⁻¹, high first Coulombic efficiency (80%) and excellent rate performance, and excellent long 1000 cycle performance operated at a current density of 300 mA g⁻¹. In addition, the hard carbon anode based on bituminous coal afforded a capacity of 113 mAh g⁻¹ in an extremely low-temperature environment (-40%), with 40% retention compared to room temperature.

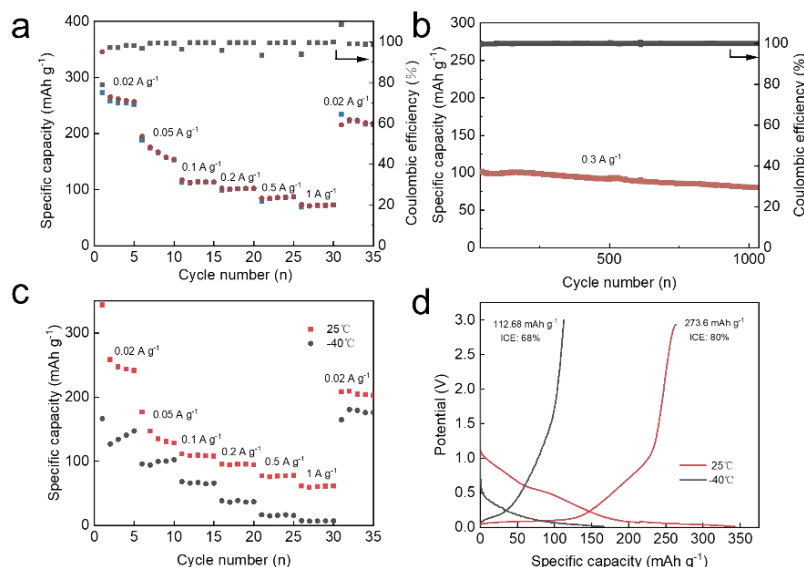


Figure 6 a Rate performance. b Cycle performance of half-cell at 300 mA g⁻¹. c Rate performance at different temperatures. d Constant current charge/discharge curves at different temperatures.

4. Summary

In this work, we report a method for rapid pyrolytic carbonization of highly volatile bituminous coals by fast heating using Joule heat. Coal-based hard carbon with an expanded interlayer structure was produced by the instantaneous release of a large amount of volatile matter from bituminous coal due to the high heating rate. As a result, pore reorganization and layer spacing increase are achieved. This expanded structure coal-based hard carbon structure facilitates the storage and transport of Na-ions, with a high sodium-ion storage capacity (274 mAh g⁻¹) and high ICE (80%), together with good cyclic stability with 80% capacity retention for over 1000 cycles. In addition, the coal-based hard carbon anode exhibits good capacity retention (40%) at an extremely low temperature (-40 °C). The proposed rapid pyrolysis strategy provides an effective way to enable efficient and low-cost anode materials for sodium ion batteries.

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