



# Article Green Synthesis of Hierarchically Porous Carbon Derived from Coal Tar Pitch for Enhanced Lithium Storage

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**Abstract:** Coal tar pitch (CTP) is a high-quality raw material for producing functional carbon materials owing to its high carbon yield and high degree of condensation. The rational structure regulation of CTP-derived carbon materials is paramount for their special application. Herein, a green template strategy is proposed to fabricate hierarchically porous carbon (HPC) and employ it as the anode material for lithium-ion batteries. It can be demonstrated that the mass ratio of the template (KHCO<sub>3</sub>) and carbon source (CTP) significantly influences the microstructure and electrochemical performances of HPC. HPC-3 synthesized by a mass ratio of 3:1 shows a coral-like lamellar nanostructure with high specific surface area, developed nanopores, and ample defects, enabling fast and high-flux lithium storage. Thus, the HPC-3 electrode achieves an excellent rate capacity of 219 mAh g<sup>-1</sup> at 10 A g<sup>-1</sup> and maintains a high discharge capacity of 660 mAh g<sup>-1</sup> after 1400 cycles at 1 A g<sup>-1</sup>. This work takes a step towards the high-value-added and green utilization of CTP and offers a promising solution for the sustainable production of advanced carbon electrode materials.

**Keywords:** lithium-ion batteries; anode materials; coal tar pitch; carbon materials; green template method

## 1. Introduction

A profound global energy transformation is in progress because of the gradual depletion and environmental issues of traditional fossil energy sources. The burgeoning development of renewable energy has massively accelerated the need for electrochemical energy storage (EES) technologies, which play considerable and indispensable roles in eliminating the intermittent and regional limitations of renewable energy. Among various EES technologies, the rechargeable battery has been considered the most successful technology because of its environmental friendliness, cost-effectiveness, and application flexibility [1,2]. Lithium-ion batteries (LIBs) have achieved a leap-forward development in the portable electronics market over the past few decades, with a rapid spread to the markets of electric vehicles and even stationary energy storage systems [3,4]. The LIBs have numerous merits, including high energy density, low self-discharge, and long lifespan. In order to meet the current demand for power supplies, there is still a need to pursue higher performance indicators for LIBs, including improved energy density, prolonged lifespan, high power output, high safety, and low cost. These are all intimately correlative to the properties of electrode materials [5,6].

Graphite, as the dominant anode material for commercial LIBs, is far from satisfactory. It exhibits a low theoretical capacity of 372 mAh  $g^{-1}$ , and the intercalation of lithium into a graphite host suffers from a sluggish diffusion-controlled process, leading to a limited rate capability. In addition, because of the low average de-/lithiation potential, metallic lithium dendritic is prone to be precipitated on the anode surface, which will result in the degradation of battery performances and some safety issues [7,8]. Therefore, more efforts



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). should be devoted to exploring desirable anode materials. It has been widely demonstrated that a variety of carbon nanomaterials, such as graphene [9–11], carbon nanotubes [12–15], porous carbon [16,17], and heteroatom-doped carbon [18–21], can effectively improve the specific capacity, rate capability, and cycling stability of LIBs. In particular, two-dimensional (2D) porous carbon nanomaterials featuring a high specific surface area and developed pore structure are very favorable for shortening the transport distance of lithium ions and accelerating the interfacial kinetics, thus holding great potential as fast-charging electrode materials [22–24].

The choice of raw materials and synthesis methods is vital to modulating the microstructure and the relevant electrochemical performances of carbon anode materials. Coal tar pitch (CTP) is a bulk by-product of the coal coking process and has relatively limited applications, mainly as road and building materials, which suffer from low added value and waste of resources. Regarding the molecule level, CTP mainly consists of a polycyclic aromatic nucleus and alkyl side chains [25]. The CTP molecules can be easily rearranged into carbon through "bottom-up" chemical means. Therefore, it is an attractive way to motivate the high value-added utilization of CTP as a carbon precursor, which has the advantages of high carbon yield, low cost, and abundant resources [26,27]. Currently, the commonly used methods for preparing CTP-derived carbon encompass template methods [28–30] and chemical activation methods [31–33]. For example, He and his co-workers proposed a strategy of the nano-ZnO template coupled with KOH activation to prepare CTP-derived three-dimensional interconnected graphene nanocapsules [29]. Xing et al. developed porous graphitic carbons from CTP using CaCO3 nanoparticles as a template and activating agent [30]. Yang et al. first introduced oxygen functional groups into CTP to induce the crosslinking and condensation between oxidized CTP molecules and then carried out the carbonization–KOH activation process to obtain oxygen-rich hierarchical porous carbons [32]. Although substantial research has been performed, the preparation methods usually involve tedious preparation procedures and toxic or corrosive reagents. From a sustainable development perspective, developing facile, green, and controllable routes to CTP-derived porous carbon is long-sought-after.

This work successfully fabricated hierarchically porous carbon (HPC) using CTP as the carbon precursor and KHCO<sub>3</sub> as the template. The KHCO<sub>3</sub> template is not only responsible for the formation of hierarchical pores but also induces the construction of coral-like lamellar structures. Notably, the KHCO<sub>3</sub> template and its derivatives can be removed by mild water washing, complying with the green and sustainable design concept. Furthermore, we systematically investigated the regulation laws of the template and CTP mass ratio on the HPC microstructure and the structure–performance relationship of HPC anode materials. It was found that the HPC material synthesized via a mass ratio of 3:1 (HPC-3) shows comprehensive advantages, including a well-designed coral-like framework, high specific surface area, a hierarchically porous structure, and a high disorder and defect degree. When used as the anode material for LIBs, HPC-3 exhibits a high rate capability (219 mAh g<sup>-1</sup> at 10 A g<sup>-1</sup>) and a good cycling performance (660 mAh g<sup>-1</sup> after 1400 cycles at 1 A g<sup>-1</sup>).

#### 2. Experimental

## 2.1. Chemicals

CTP with a softening point of 85 °C, 2–3 wt.% of quinoline insolubles, and 15 wt.% of toluene insolubles was purchased from Ansteel Co., Ltd. (Liaoning, China). KHCO<sub>3</sub> (purity  $\geq$  99.5%) and N-methylpyrrolidone (NMP, purity  $\geq$  99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetylene carbon black (purity  $\geq$  99.5%) and polypropylene separator (PP, Celgard 2500) were purchased from Aowei Technology Co., Ltd. (Shanghai, China). Polyvinylidene fluoride (PVDF, purity  $\geq$  98%) was purchased from Sigma–Aldrich (Burlington, Massachusetts, USA). Copper foil with a thickness of ~9  $\mu$ m was purchased from Hefei Kejing Co., Ltd. (Hefei, China). Lithium foil (purity  $\geq$  99.9%) from China Energy Lithium Co., Ltd. (Tianjin, China). The electrolyte

containing 1M LiPF<sub>6</sub> dissolved in an equal volume mixture of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate with 2 wt% of fluoroethylene carbonate additive was purchased from DoDo Chem.

#### 2.2. Synthesis of HPC

The HPC materials were fabricated from CTP via a KHCO<sub>3</sub> template method. In detail, CTP and KHCO<sub>3</sub> were evenly mixed via grinding in a mass ratio of 2:1, 3:1, and 4:1, respectively. The obtained mixture was then heated to 800 °C with a heating rate of 5 °C min<sup>-1</sup> and held for 2 h under a N<sub>2</sub> atmosphere. After cooling to room temperature, the carbonized product was washed with deionized water, filtrated, and dried in a vacuum oven at 60 °C for 24 h. The resulting sample was denoted as HPC-X, where X represents the mass ratio of KHCO<sub>3</sub> to CTP (X = 2, 3, and 4).

#### 2.3. Material Characterizations

The micromorphology was investigated via a scanning electron microscope (SEM, Regulus8200, Hitachi, Tokyo, Japan) and transmission electron microscope (TEM, JEM-2100F, JEOL Ltd., Tokyo, Japan). The crystalline structure was measured via X-ray diffraction (XRD, X' Pert Pro MPD system, PANalytical, Alemlo, Netherland). Raman spectra were obtained on a LabRAM HR Evolution Raman spectrometer. N<sub>2</sub> adsorption and desorption measurements were performed on an ASAP 2020 PLUS instrument to measure the surface area and pore structure. The surface chemical composition was detected via X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALab220i-XL, Thermo Fisher Scientific, Waltham, MA, USA).

### 2.4. Electrochemical Measurements

The HPC-X powder, conductive additives (acetylene carbon black), and binder (PVDF) were mixed in an appropriate amount of NMP solvent in a mass ratio of 8:1:1. The slurry was then cast onto the copper foil and dried at 80 °C for 12 h. After cutting, an electrode sheet with a diameter of 12 mm was obtained. The mass loading of the active material was about 0.6 mg cm<sup>-2</sup>. The electrochemical performances were measured in a half-cell configuration. CR2032 coin-type cells were assembled in an argon-filled glovebox (Etelux Lab2000, Etelux, Beijing, China, H<sub>2</sub>O < 0.1 ppm and O<sub>2</sub> < 0.1 ppm). The as-fabricated HPC electrode sheet was used as the working electrode, lithium foil was used as the reference electrode and counter electrode, and the PP separator was the electron battier between the two electrodes. A total of 40  $\mu$ L of electrolyte was added dropwise to the HPC and lithium electrode sides, respectively. The galvanostatic charge–discharge (GCD) tests were performed on the Land CT2001A battery test instrument in the voltage range of 0.0–3.0 V. The cyclic voltammetry (CV) measurement at various scan rates and electrochemical impedance spectroscopy (EIS, 100 kHz–10 mHz) were conducted on the CHI760D electrochemical workstation.

#### 3. Results and Discussion

The low-cost and green synthesis strategy of HPC is schematically shown in Figure 1. CTP was used as the carbon precursor, and KHCO<sub>3</sub> functioned as the template and activation agent. It can be observed from the SEM images (Figure S1) that the original CTP shows a blocky morphology with a scaly surface, indicating that it is a promising precursor for lamellar carbon nanomaterials. During the heat treatment of the mixture of CTP and KHCO<sub>3</sub>, KHCO<sub>3</sub> was first decomposed into  $K_2CO_3$ , which is responsible for forming the coral-like laminar structure. Then,  $K_2CO_3$  would be further decomposed and reacted with carbon atoms, resulting in gas release and the formation of micropores and mesopores [34]. Finally, the residual  $K_2CO_3$  and other K-containing species were removed via facile water washing, avoiding the use of toxic or corrosive reagents.



Figure 1. Schematic illustration of the synthesis procedure of HPC.

The mass ratio of KHCO<sub>3</sub> and CTP significantly affects the microstructure of HPC. As shown in the SEM images of HPC-3 (Figure 2a,b), it presents a coral-like skeleton formed via the oriented arrangement of two-dimensional carbon lamella, which is conducive to exposing more surface accessible for electrolyte and shortening the diffusion path of lithium ions. The EDS elemental mapping and the EDS spectrum of the HPC-3 sample are shown in Figure S2. It can be found that the C element is dominant in HPC-3, while the content of the K element is negligible at only 0.02 at%, indicative of the successful removal of K-related compounds in the carbon material. It can be further observed from the TEM image (Figure 2c) that there are many nanopores on the surface of lamellar HPC-3, which is beneficial for the transport of electrolytes and the adsorption of lithium ions. The high-resolution TEM (HR-TEM) image (Figure 2d) shows ordered lattice fringes in short range with a lattice spacing of 0.38 nm, which is much larger than that of graphite (0.34 nm). The defect-rich microcrystalline structure and the expanded lattice spacing are favorable for lithium ions' adsorption and intercalation/deintercalation, thus contributing to high lithium storage capacity [35–37]. For comparison, the micromorphology of HPC-2 and HPC-4 was also observed via SEM characterization (Figure S3). As seen from Figure S3a and b, HPC-2 displays irregular blocky accumulations, indicating that the dosage of KHCO<sub>3</sub> is insufficient to effectively regulate the microstructure of CTP-derived carbon. In the case of excessive KHCO<sub>3</sub> (Figure S3c,d), the coral-like skeleton of HPC-4 is disrupted and collapsed owing to the severe etching of the carbon matrix via K-containing activators. With this information in mind, it can be demonstrated that an appropriate mass ratio of a template to carbon precursor is essential to rationally control the micromorphology and microstructure of carbon materials.



Figure 2. (a,b) SEM images, (c) TEM image, and (d) HR-TEM image of HPC-3.

The structure and composition of HPC-X were further investigated via XRD, Raman spectra, nitrogen adsorption experiment, and XPS characterization. From the XRD patterns of three samples (Figure 3a), two broad and weak peaks located at ca. 24° and 43° can be recognized, corresponding to the characteristic peaks of (002) and (100) lattice planes of graphitic structure, respectively [27]. The spacing of (002) lattice planes of three samples can be determined based on the Bragg equation:

$$2d_{002}\sin\theta = n\lambda\tag{1}$$

where  $d_{002}$  refers to the lattice spacing (nm),  $\theta$  refers to the angle (°) between the incident X-ray and the (002) crystal plane, *n* refers to the diffraction order (*n* = 1), and  $\lambda$  refers to the wavenumber of incident X-ray ( $\lambda$  = 0.15406 nm). The calculated results are summarized in Table 1. The interlayer spacing of HPC-2, HPC-3, and HPC-4 is 0.378, 0.382, and 0.380 nm, respectively, suggesting that the KHCO<sub>3</sub> template can effectively regulate the microcrystalline arrangement structure of HPC-X, and thus modulate the intercalation and deintercalation behavior of lithium ions between graphite layers. Figure 3b displays the Raman spectra of three samples. The peak at ca. 1350 cm<sup>-1</sup> corresponds to the disorder-related D band, and the peak at ca. 1589 cm<sup>-1</sup> is assigned to the *sp*<sup>2</sup>-hybridized G band [38]. The strength ratio ( $I_D/I_G$ ) between the D and G bands is usually used to assess the degree of defect and disorder in carbon materials. As listed in Table 1, the  $I_D/I_G$  values of HCP-2, HPC-3, and HCP-4 are 0.91, 0.97, and 0.94, respectively, demonstrating that HCP-3 has more defects and thus can provide more adsorption sites for lithium ions.



**Figure 3.** (**a**) XRD patterns, (**b**) Raman spectra, (**c**) N<sub>2</sub> adsorption–desorption isotherms, (**d**) pore size distributions, and (**e**) XPS survey spectra of HPC-X. (**f**) High-resolution XPS spectra of O 1*s* in HPC-3.

Table 1. Structure parameters of HPC-X.

Samples	d <sub>002</sub> (nm)	I <sub>D</sub> /I <sub>G</sub>	${S_{ m BET}}^{(a)} ({ m m}^2~{ m g}^{-1})$	${S_{ m mic}}^{ m (b)}_{ m (m^2 g^{-1})}$	$V_{\rm t}~^{ m (c)}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{ m mic}^{ m (d)}$ (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>mic</sub> /V <sub>t</sub> <sup>(e)</sup> (%)
HPC-2	0.378	0.91	1048	877	0.56	0.43	76.8
HPC-3	0.382	0.97	1643	751	0.99	0.36	36.4
HPC-4	0.380	0.94	986	776	0.64	0.38	59.4

<sup>(a)</sup> total specific surface area; <sup>(b)</sup> micropore specific surface area; <sup>(c)</sup> total pore volume; <sup>(d)</sup> micropore volume; <sup>(e)</sup> micropore proportion.

The N<sub>2</sub> adsorption–desorption isotherms of HPC-X are shown in Figure 3c. As can be recognized from the Bruno–Emmett–Taylor and density functional theory model calculation

results (Table 1), with the increase of the mass ratio of KHCO3 and CTP, the specific surface area and pore volume of HPC-X first increase and then decrease, which is attributed to the fact that less template has limited effect on the modulation of lamellar morphology and pore structure. In contrast, excessive templates would severely etch the carbon matrix and cause the collapse of pores. HPC-3 has the highest specific surface area (1643 m<sup>2</sup>  $g^{-1}$ ) and pore volume (0.99 cm<sup>3</sup> g<sup>-1</sup>), which can increase the contact interface between the electrode and electrolyte and accelerate the mass transport. As demonstrated by the pore size distribution curves (Figure 3d) and pore structure parameters (Table 1), HCP-2 and HCP-4 are dominated by micropores, whereas HPC-3 possesses a hierarchical pore structure, and the mesopores with the pore size in the range of 2~5 nm are significantly increased, which is more favorable for the fast diffusion of electrolyte and lithium ions. The full XPS spectra (Figure 3e) confirm that all HPC-X samples mainly comprise C and O elements; the corresponding element contents are listed in Table S1. The trace amount of elemental N originated from the raw CTP. The C 1s and O 1s peaks of HPC-X were further fitted and analyzed. As shown in the high-resolution XPS spectra of C 1s in HPC-3 (Figure S4a), the peaks at 284.6, 285.4, 287.3, and 288.3 eV can be assigned to *sp*<sup>2</sup> C=C, C-O/C-N, C=O, and O=C-O bonding, respectively. The high-resolution XPS spectra of the O 1s peak in HPC-3 (Figure 3f) can be deconvoluted into four subpeaks: C=O (530.7 eV), O-C-O/C-OH (531.9 eV), -O-C=O (533.0 eV), and -COOH (534.2 eV) [39]. These surface functional groups can significantly increase HPC-X's wettability and accelerate electrolyte penetration and transport [40]. The analysis results for C 1s and O 1s peaks of HPC-2 and HPC-4 are similar to the above explanation (Figure S4b-e). All the characterization results fully reveal that the lamellar HPC-3 has comprehensive superiority, including ultrahigh specific surface area, abundant micropores and mesopores, as well as a high degree of disorder caused by lattice defects and O heteroatom doping, and thus is expected to achieve high and fast lithium storage.

The electrochemical performances of HPC-X were evaluated in a half-cell configuration. Figure 4a displays the CV curves of HPC-3 in the voltage range of 0.01–3 V at a scan rate of 0.2 mV s<sup>-1</sup>. Three obvious reduction peaks are present during the first discharge. The irreversible peaks at ca. 1.7 and 0.7 V can be ascribed to the formation of solid electrolyte interphase (SEI) film and the decomposition of electrolyte [41]. The reversible reduction peak at ca. 0.01 V accounts for the insertion of lithium ions into the graphite domain and nanopores. The CV curves almost overlap during the subsequent cycles, manifesting that the formed SEI film is stable. Figure 4b shows the GCD curves of HPC-3 in the initial three cycles at a current density of 0.1 A g<sup>-1</sup>. In accordance with the CV curves, a blurry high-discharge plateau is present in the initial discharge but disappears in the following cycles, which can be attributable to the formation of SEI film and irreversible side reactions [42].

The GCD curves maintain a good consistency during the subsequent cycles. The discharge curve can be divided into two regions: a slope region corresponding to the adsorption of lithium ions on the surface and defect sites of HPC-3 and a low-plateau region corresponding to the interlayer intercalation and nanopore filling of lithium ions. The charge curve corresponds to the reverse electrochemical process. The rate performances of HPC-X are shown in Figure 4c. At a low current density of 0.1 A  $g^{-1}$ , the initial discharge specific capacities of HPC-2, HPC-3, and HPC-4 anode materials are 541.8, 1066.8, and 522.5 mAh  $g^{-1}$ , respectively, and the corresponding initial coulombic efficiency (ICE) is 47.5%, 49.1%, and 47.0%, respectively. The low ICE is a common failing for carbon electrode materials and is closely related to the specific surface area, pore size, and surface functional groups [30,43]. Although the larger specific surface area of HPC-3 adversely affects the ICE, this effect is offset by fewer O-containing functional groups and wider pore size distribution. With the increase of current density, the discharge-specific capacities of all anode materials gradually decrease. Despite this, HPC-3 consistently affords significantly higher capacity. At a current density of 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 A  $g^{-1}$ , the dischargespecific capacities of HPC-3 are 792, 563, 415, 333, 258, and 219 mAh  $g^{-1}$ , respectively. In addition, most of the specific capacity can still be restored when the current density is

back to 0.2 A  $g^{-1}$ , indicative of a high reversibility. By comparison with the GCD curves of HPC-X at different current densities (Figure S5a–c), it is apparent that the polarization phenomenon of HPC-2 and HPC-4 is more and more serious with the increase of current densities, but HPC-3 still retains good charge–discharge behavior even at high current densities, which is attributed to the fact that the aligned channels within the coral-like skeleton and the abundant nanopores on the lamella surface provide smooth routes for the fast transport of lithium ions. The cycling performances of HCP-X anode materials at a current density of 1 A  $g^{-1}$  are shown in Figure 4d. During the first few hundred cycles, the capacity of the HPC-X increases because more electrolyte ions gradually infiltrate into the meso- and micropores of the carbon materials [43], which can be revealed via the increase of capacity contribution at the low-plateau region with the cycling, as shown in the GCD curves during cycles (Figure S6). After 1400 cycles, the discharge-specific capacities of HPC-2, HPC-3, and HPC-4 are 239, 660, and 401 mAh g<sup>-1</sup>, respectively.



**Figure 4.** (a) CV curves at a scan rate of 0.2 mV s<sup>-1</sup> and (b) GCD profiles at a current density of 0.1 A g<sup>-1</sup> of HPC-3. (c) Rate performances, (d) cycling performances, and (e) EIS curves of HPC-2, HPC-3, and HPC-4.

The HCP-3 shows a higher capacity and better cycling performance, demonstrating that the well-developed porous network and a wealth of defects provide enough active sites for high-volume lithium storage. The capacity increase phenomenon is absent when the cell is discharged/charged at a low current density of 0.2 A  $g^{-1}$  (Figure S7). The capacity of HPC-3 gradually decreases in the first 10 cycles and remains relatively stable in subsequent cycles. The EIS curves of HPC-X are displayed in Figure 4e. There is a depressed semicircle in the high-to-medium frequency region and an inclined line in the low-frequency region, corresponding to the charge transfer resistance and the diffusion resistance of lithium ions, respectively [44,45]. In contrast with HPC-2 and HPC-4, HPC-3 shows a smaller semicircle and a smaller slope of the inclined line, indicative of faster electron and ion transport. These outstanding electrochemical performances of HPC-3 can be credited to its structure merits. On the one hand, the large specific surface area and expanded lattice distance shorten the transport route of electrolyte and lithium ions and accelerate the diffusion kinetics of lithium ions into graphite layers. On the other hand, the hierarchically microporous and mesoporous structure and abundant defects increase storage and adsorption sites for lithium ions. Furthermore, we compared the preparation strategy and cycling performance of HPC-3 with those of previously reported carbon anode materials. As listed in Table 2, HPC-3 shows overwhelming superiorities as the anode material for LIBs. The low cost, simplicity, and environmental friendliness of its preparation strategy and its marvelous cycling performance demonstrate great potential for large-scale application.

Anode Material	Precursor	Method	Cycling Performance	Ref.
HPC-3	CTP	KHCO <sub>3</sub> template	$1 \mathrm{A~g^{-1}}$ , 660 mAh $\mathrm{g^{-1}}$ after 1400 cycles	This work
N-doped porous carbon nanosheets	Eucalyptus leaves	KHCO <sub>3</sub> template	$0.5 \mathrm{A} \mathrm{g}^{-1}$ , 513 mAh $\mathrm{g}^{-1}$ after 500 cycles	[18]
Porous graphitic carbons	CTP	CaCO <sub>3</sub> template	$1 \text{ A g}^{-1}$ , 391 mAh g $^{-1}$ after 1000 cycles	[30]
Amorphous carbon	Semicoke	Direct pyrolysis	$1 \mathrm{~A~g}^{-1}$ , 210 mAh $\mathrm{g}^{-1}$ after 1000 cycles	[36]
Hierarchical porous carbon sheets	Soft pitch	Oyster shell template	$1~{\rm A~g^{-1}}$ , 451 mAh ${\rm g^{-1}}$ after 450 cycles	[41]
Carbon nanosheets	Soluble starch	Vermiculite template	$0.1 \mathrm{~A~g^{-1}}$ , 522 mAh g $^{-1}$ after 100 cycles	[46]
Nonporous graphite	Anthracite	MgO template /KOH activation	$0.5~{\rm A~g^{-1}}$ , 174 mAh ${\rm g^{-1}}$ after 1000 cycles	[47]
Mesoporous carbon	Spent asphalt	Fe <sub>2</sub> O <sub>3</sub> template	$0.2 \text{ A g}^{-1}$ , 565 mAh g $^{-1}$ after 80 cycles	[48]

Table 2. Comparison of the preparation strategy and cycling performance of carbon anode materials.

In order to gain a deep insight into the energy storage mechanism of HPC-3, its CV curves were tested within the potential range of 0.01-3 V at different scan rates. As depicted in Figure 5a, with the increase in scan rate, the cathodic peak and the anodic peak slightly shift toward low and high potential, respectively, indicating a small polarization. The relationship between peak current (i) and scan rate (v) is according to the following equation [49,50]: i

$$(v) = av^{o} \tag{2}$$

$$\log i(v) = \log a + b \log v \tag{3}$$

where *a* and *b* are adjustable constants. Generally, the charge storage mechanism is divided into the capacitive behavior with faster kinetics and the diffusion-controlled behavior with slower kinetics. If the *b* value is 0.5, the electrochemical process is controlled by the ionic diffusion, whereas if the *b* value is 1, the electrochemical process is controlled by surface capacitive behavior. In this regard, the charge storage mechanism can be qualitatively distinguished via linearly fitting log (i) versus log (v). It can be seen from Figure 5b that the values of b for the cathodic and anodic peaks are 0.87 and 0.74, respectively, indicating that the capacitive contribution is dominant. Such a high capacitive contribution can effectively improve the rate and cycling performances of LIBs [51,52].



Figure 5. (a) CV curves of HPC-3 at different scan rates. (b) Linear relationship between log (i) and  $\log(\nu)$ .

### 4. Conclusions

In summary, a simple, green, and cost-effective route is presented to synthesize CTPderived HPC anode materials for high-performance LIBs. The micromorphology and structure of HPC were effectively regulated by adjusting the mass ratio of the KHCO<sub>3</sub> template and CTP. The obtained HPC-3 presents a coral-like lamellar structure with a specific surface area as high as 1643 m<sup>2</sup> g<sup>-1</sup> and a pore volume up to 0.99 cm<sup>3</sup> g<sup>-1</sup>, which can effectively enlarge the contact interface between the electrode and electrolyte and propel the diffusion kinetics of lithium ions. There are also many structural defects induced

by the intrinsic lattice disorder and the introduction of O heteroatom in HPC-3, endowing sufficient space and active sites for lithium storage. As a result, the HPC-3 electrode achieves an excellent rate capacity of 219 mAh  $g^{-1}$  at 10 A  $g^{-1}$  and maintains a high reversible capacity of 660 mAh  $g^{-1}$  after 1400 cycles at 1 A  $g^{-1}$ . This work takes a step towards the high value-added and green utilization of coal tar pitch and provides a desirable candidate for advanced carbon anode materials.

**Supplementary Materials:** The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/batteries9090473/s1. Figure S1: SEM images of CTP; Figure S2: SEM image and the corresponding EDS elemental mapping of HPC-3. Figure S3: SEM images of HPC-2 and HPC-4; Figure S4: High-resolution XPS spectra of C 1*s* in HPC-2, HPC-3, and HPC-4 and O 1*s* in HPC-2 and HPC-4; Figure S5: GCD profiles of HPC-2, HPC-3, and HPC-4; Figure S6: GCD profiles of HPC-2, HPC-3, and HPC-4 during cycling; Figure S7: Cycling performance of HPC-3 at a current density of 0.2 A g<sup>-1</sup>; Table S1: Element contents and O element configuration in HPC-X.

**Author Contributions:** M.Z.: conceptualization, methodology, investigation, and writing—original draft. M.Q. and W.Y.: investigation and data curation. J.M. and Z.H.: writing—review and editing. M.W.: supervision and resources. All authors have read and agreed to the published version of the manuscript.

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