

用于钠离子电池的热解氢化无烟煤负极材料

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摘 要: 无烟煤成本低廉, 在储能领域具有较大应用潜力, 但原始无烟煤作为钠离子电池负极材料可逆容量太低。在不同温度下对无烟煤进行煅烧处理。结果显示, 无烟煤 1 300 °C 热解产物(A-1300)具有最高可逆总量, 在 20 mA/g 电流密度下容量为 307 mA·h/g, 但其倍率性能不佳, 500 mA/g 时 A-1300 的容量仅为 105 mA·h/g。通过氢化-热解两步策略不仅能降低热解温度, 也可显著改善其倍率性能。结果表明: 氢化后的无烟煤更易石墨化, 900 °C 热解产物(H300-3-900)在 500 mA/g 电流密度下循环 500 圈后的容量可达 113 mA·h/g, 表现出优异的倍率性能, 而且低温制备更易商业化。

关键词: 氢化; 无烟煤; 钠离子电池; 负极

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Pyrolyzed Hydrogenated Anthracite as Anode Materials for Sodium-ion Batteries

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Abstract: Anthracite has a great application potential in energy storage because of its low cost, but the reversible capacity of raw anthracite as an anode material for the sodium-ion battery is rather low. In this paper, anthracite was pyrolyzed at different temperatures. The results show that the reversible capacity of anthracite pyrolyzed at 1 300 °C (A-1300) is 307 mA·h/g at 20 mA/g, which is the maximum value among the pyrolyzed anthracites. However, the reversible capacity of A-1300 at 500 mA/g is only 105 mA·h/g, exhibiting an inferior rate performance. The two-step strategy *via* hydrogenation and pyrolysis can decrease the pyrolyzed temperature and improve the rate performance. Hydrogenated anthracite turns into an easy-graphitized precursor. The reversible capacity of hydrogenated anthracite pyrolyzed at 900 °C (H300-3-900) can retain 113 mA·h/g at 500 mA/g after 500 cycles, exhibiting a superior rate performance and an easier commercial production at a lower temperature.

Keywords: hydrogenation; anthracite; sodium-ion battery; anode

1 Introduction

Energy storage technology is one of important means to meet the large-scale access of renewable energy, and a basis for the realization of the energy internet in the future. Among various energy storage technologies, electrochemical energy storage is a promising one, which is suitable for some occasions

with rapid response and high-power requirement, which cannot be restricted by the construction period and location^[1-3]. As a main electrochemical energy storage method, lithium-ion battery (LIB) was commercialized in 1991. However, some work focused on the development of alternative technologies at the end of the 2 000 s due to the uneven worldwide distribution of lithium reserves and resources.

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Sodium-ion battery (SIB) with the similar working principle and components like LIB has many advantages, such as abundant resource, low cost, and safety performance, making it promising in the field of large-scale energy storage^[4]. Surprisingly, graphite as the most excellent anode material for commercial LIB with easy obtainment, good conductivity, and high electrochemical performance^[2] is difficult for Na^+ insertion/extraction^[5–6], indicating that graphite is not adaptive for SIB and promoting to search for other carbon materials^[7–11].

In general, carbon anodes were prepared *via* pyrolyzing various precursors, such as carbohydrates, biomass wastes, and polymers^[12–14], all of which could promote the insertion/extraction of Na^+ . Among these carbons, anthracite anode with economy and high carbon yield could be produced through direct pyrolysis, and the capacity was $222 \text{ mA} \cdot \text{h/g}$ (at 30 mA/g)^[15]. If anthracite with a superior electrochemical performance could be developed, it would be able to be further commercialized for SIB, particularly for power-oriented applications.

It is demonstrated that the microstructures of the final carbon materials after pyrolysis, which are usually separated into graphitizing carbon and non-graphitizing carbon, depend on the nature of the precursors^[16]. The presence of oxygen or the shortage of hydrogen in the precursors will form a strongly cross-linked non-graphitizing carbon^[17]. The excessive hydrogen can lead to graphitizing carbons^[18–20]. Hu *et al.* verified that the oxygen-based functional groups could be introduced into carbon materials *via* pre-oxidation^[21] and *in-situ* $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solidification strategy^[22], thus achieving a highly disordered structure and preventing the graphitization. The results obtained indicate that changing the content of oxygen or hydrogen in the precursors is one of effective approaches to change the characteristics of carbon materials.

In this paper, anthracite was modified by an effective two-step strategy of hydrogenation and pyrolysis to obtain a high-performance SIB. The pyrolyzed hydrogenated-anthracite was synthesized through heating anthracite under 7% H_2/Ar flow and pyrolyzing at high temperatures. In addition, the electrochemical performances of pyrolyzed hydrogenated-anthracite as carbon anodes for SIB were also investigated.

2 Experimental

2.1 Sample preparation

Anthracite (A) was pyrolyzed at different temperatures (*i.e.*, 700°C , $1\,100^\circ\text{C}$, $1\,300^\circ\text{C}$, $1\,500^\circ\text{C}$, and $1\,900^\circ\text{C}$) for 2 h in a high-temperature graphitization furnace under Ar flow, respectively. The pyrolyzed products were pyrolyzed anthracites, denoting as A-X (X defines the pyrolyzed temperature).

Pyrolyzed hydrogenated-anthracite was synthesized through an effective two-step strategy of hydrogenation and pyrolysis. First, anthracite was heated in a tube

furnace under 7% H_2/Ar flow at 300°C for 3 h to receive a hydrogenated anthracite. Then, the hydrogenated-anthracite was pyrolyzed in a high-temperature graphitization furnace under Ar flow at different temperatures (*i.e.*, 700°C , 900°C , $1\,100^\circ\text{C}$, and $1\,300^\circ\text{C}$) for 2 h, respectively. The final samples were pyrolyzed hydrogenated-anthracites, named HM-N-X (H denotes the hydrogenation, M refers to the hydrogenation temperature, N is the hydrogenation time, and X is the pyrolyzed temperature).

2.2 Characterizations

The morphologies of the materials were determined by a model JEOL-F200 high-resolution transmission electron microscope (HRTEM, Jeol, Japan) and a selected area electron diffractometer (SAED, Jeol, Japan). The structures were characterized by a model Rigaku Ultima IV X-ray diffractometer (XRD, Rigaku, Japan). The Raman spectra were obtained on a model DXR Raman spectroscope (Thermo Scientific Co., USA). The surface element distributions were measured by a model AXIS Supra X-ray photoelectron spectroscope (XPS, Shimadzu, Japan). The thermal behaviors were determined on a model STA 449 F5 thermogravimeter and differential scanning calorimeter (TG–DSC, Netzsch, Germany).

2.3 Electrochemical measurement

The electrochemical properties were determined on a model CR2025 coin cells at ambient temperature. The working electrode was prepared *via* spreading homogeneous slurry onto a copper foil, which consisted of 80% active materials, 10% acetylene black, and 10% PVDF in N-methyl-2-pyrrolidone. The active material loading of the electrode was controlled as 0.8 mg/cm^2 . Sodium metal was used as a counter electrode, and glass fiber filters (GF/D) were used as a separator. The electrolyte was 1 mol/L NaClO_4 with 2% fluoroethylene carbonate (FEC) additive dissolved in a mixture of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate ($V(\text{EC}): V(\text{DMC}): V(\text{EMC}) = 1: 1: 1, \%$). The coin cells were assembled in an Ar-filled glovebox (Mikrouna, $V(\text{H}_2\text{O}) < 1 \times 10^{-7}$, $V(\text{O}_2) < 1 \times 10^{-7}$). The galvanostatic charge/discharge curves, rate performances, and cycling performances were obtained in a potential range of $3.00\text{--}0.01 \text{ V}$ (*vs.* Na^+/Na) on a model Land CT2001A battery tester. The results from galvanostatic intermittent titration technique (GITT) tests were obtained in a potential range of $2.60\text{--}0.02 \text{ V}$ (*vs.* Na^+/Na) on a Land CT2001A battery tester (Land, China). The cyclic voltammetry (CV) was conducted using a model CHI604E electrochemical workstation (CHI, China).

3 Results and discussion

3.1 Anthracite and its pyrolyzed products

Fig. 1 shows the XRD patterns and Raman spectra of anthracite and anthracites pyrolyzed at different temperatures. In Fig. 1(a), a broadened diffraction peak occurs at 25.3° and an almost invisible diffraction peak

appears at 42.6° , corresponding to the (002) and (100) planes, revealing that anthracite has a low graphitization degree^[15]. The value of $I_D/I_G \approx 3.16$ (see Table 1), which is calculated from the fitting area ratio of D and G bands in the Raman spectra (see Fig. 1(b)), indicates a high disorder degree of anthracite^[15]. Fig. 2 shows the HRTEM images of anthracite and anthracites pyrolyzed at different temperatures. In Fig. 2(a), anthracite only has the randomly oriented short carbon layers, and the SAED pattern is blurred, both indicating a poor crystallization of anthracite^[23]. Fig. 3 shows the electrochemical performances of anthracite and anthracites pyrolyzed at different temperatures. In Fig. 3(a), the initial coulomb efficiency (ICE, 16.9%) and initial reversible capacity ($112 \text{ mA}\cdot\text{h/g}$ at 20 mA/g) are not satisfactory. The results above indicate that raw anthracite is an amorphous carbon, which is not appropriate for SIB.

A simple pyrolyzed method was adopted to improve the electrochemical performances of anthracite. In

Fig. 1(a), anthracites pyrolyzed at different temperatures have diffraction peaks of (002) planes. The (002) peaks turn narrow and symmetrical, especially the sample A-1900, with increasing the pyrolyzed temperature, revealing a trend of graphitization. In Fig. 1(b), D and G bands both become sharp, and the value of I_D/I_G (see Table 1) gradually decreases when the pyrolyzed temperature increases, indicating a reduced disorder degree of pyrolyzed anthracite. In Fig. 2(b), the HRTEM image of the sample A-700 shows a disordered structure with randomly oriented short carbon layers. In Fig. 2(c) and Fig. 2(d), the samples A-1100 and A-1300 exhibit amorphous micron-sized crystallites with clearly defined carbon layers. In Fig. 2(e), a few small graphite ribbons occur in the HRTEM image as the pyrolyzed temperature increases to 1500°C . In Fig. 2(f), graphite ribbons grow longer with a further increase in the pyrolyzed temperature to 1900°C , indicating a graphite-like crystallite structure (see Fig. 1).

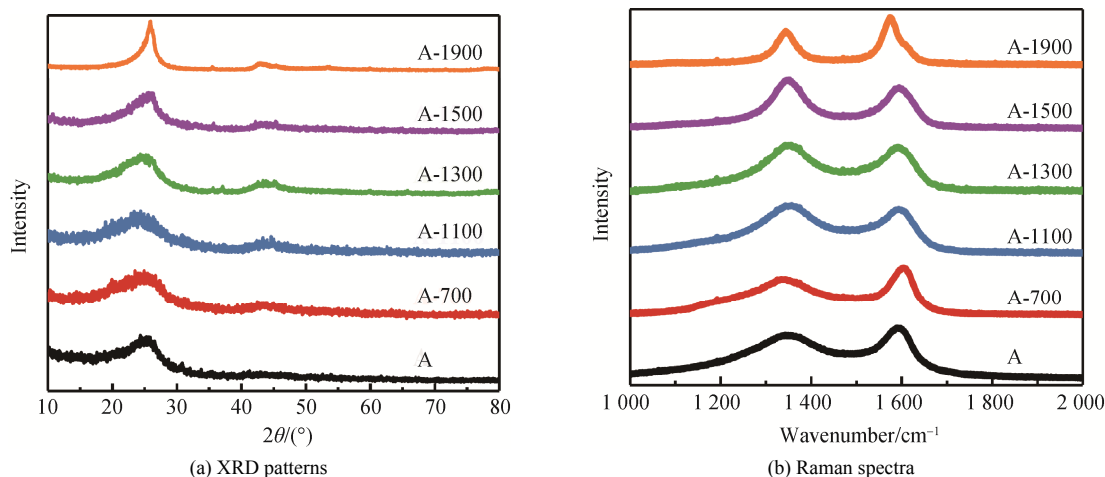


Fig. 1 XRD patterns and Raman spectra of anthracite and anthracites pyrolyzed at different temperatures

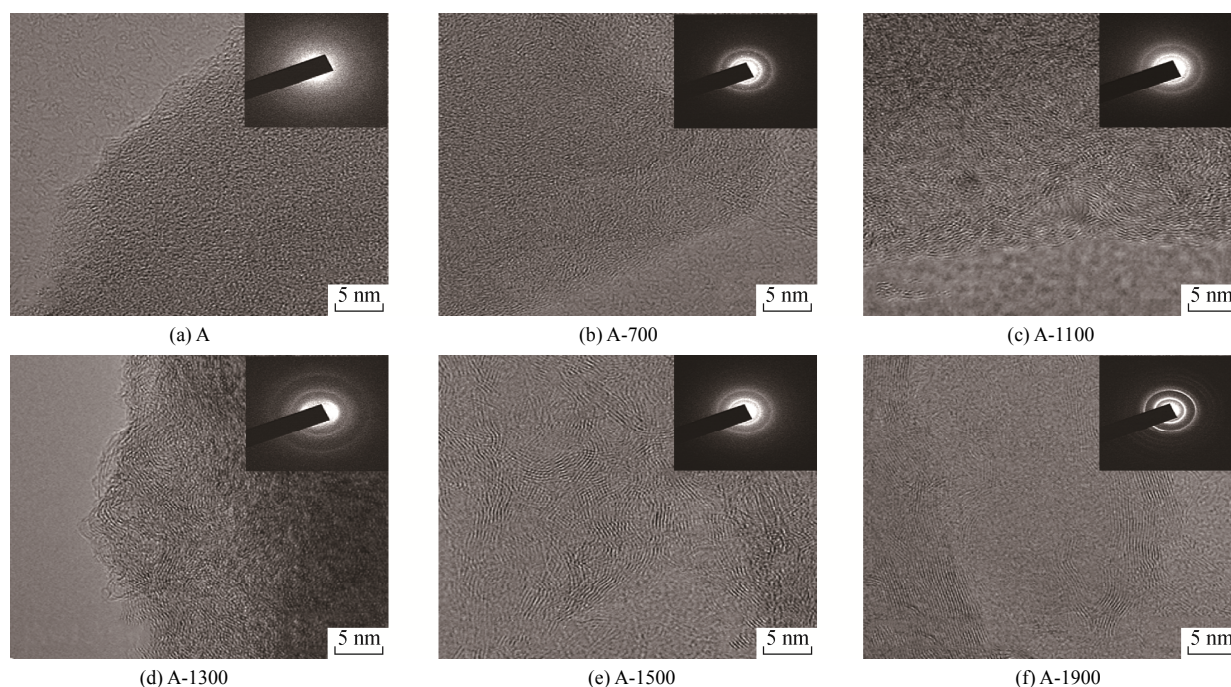


Fig. 2 HRTEM images of anthracite and anthracites pyrolyzed at different temperatures

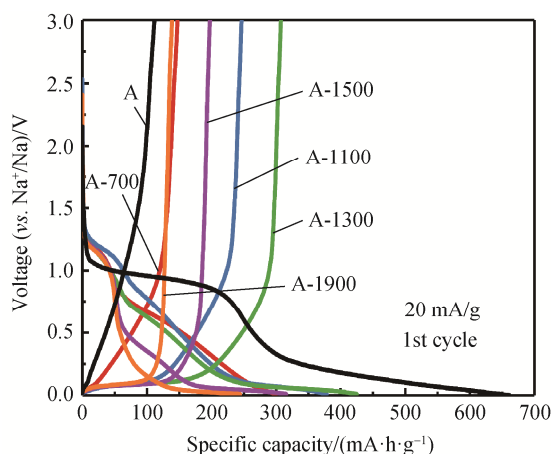
Table 1 Physical parameters of anthracite and anthracites pyrolyzed at different temperatures (from XRD patterns and Raman spectra)

Sample	$2\theta/(\circ)$	d_{002}/nm	I_D/I_G
A	25.30	0.352	3.16
A-700	24.92	0.357	3.22
A-1100	23.46	0.379	2.93
A-1300	24.32	0.366	1.95
A-1500	26.06	0.342	1.62
A-1900	25.88	0.344	0.82
H300-3-700	24.76	0.359	3.38
H300-3-900	23.68	0.375	3.21
H300-3-1100	23.54	0.378	2.82
H300-3-1300	26.14	0.341	2.08

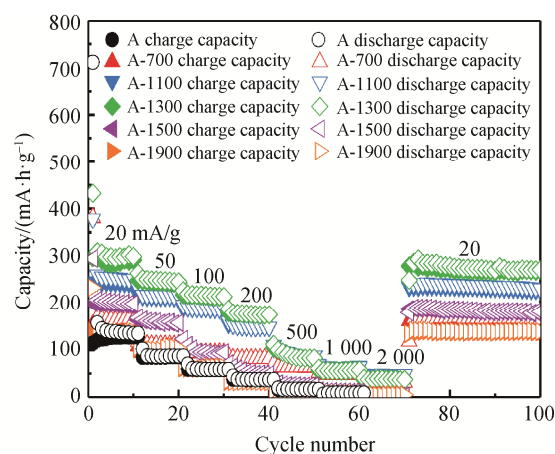
In Fig. 3(a), compared with raw anthracite, the initial reversible capacity and ICE of anthracites pyrolyzed at different temperatures increase, especially the sample A-1300 (*i.e.*, 307 mA·h/g at 20 mA/g, 72.4%). The plateau capacities (*i.e.*, capacity below 0.1 V) of pyrolyzed anthracites have an incipient growth and reach a maximum value at 1 300 °C as the pyrolyzed

temperature increases, while raw anthracite has nearly no plateau capacity. According to some previous studies on the Na storage mechanisms^[15, 17, 23], the low potential plateau region results from the Na⁺ insertion/extraction between the carbon layers, and the high potential sloping region is associated with defects adsorption on the surface.

Nevertheless, the reversible capacity of the sample A-1300 decreases rapidly when the current density increases to a certain value, which is 218 mA·h/g at 100 mA/g, and only 105 mA·h/g at 500 mA/g (see Fig. 3(b) and Table 3). Moreover, the optimum sample A-1300 needs to heat at 1 300 °C, which is relatively high for the ideal operation condition. The results indicate that the poor rate capability and high pyrolyzed temperature both have a serious impact on the SIB application. The presence of hydrogen or the shortage of oxygen in the precursors will form a graphitizing carbon, reflecting that the optimal pyrolyzed temperature based on the reversible capacity can be lower through hydrogenation. In addition, hydrogenated precursors are also more likely a soft carbon after pyrolysis, which mostly have good rate capabilities^[7, 24–28].



(a) Galvanostatic charge/discharge curves



(b) Rate performances

Fig. 3 Electrochemical performances of anthracite and anthracites pyrolyzed at different temperatures

3.2 Pyrolyzed hydrogenated-anthracite

Fig. 4 shows the XRD patterns and Raman spectra of pyrolyzed hydrogenated anthracites. In Fig. 4(a), the diffraction peaks of (002) plane are broad and asymmetric, revealing that the pyrolyzed hydrogenated-anthracites remain an amorphous structure. When the pyrolyzed temperature increases, the values of I_D/I_G (see Table 1) from the Raman spectra [see Fig. 4(b)] decrease, and the (002) plane diffraction rings from the SAED images (see Fig. 5) become sharp and bright gradually, both indicating the increased graphitization degree. Note that the small graphite ribbons appear when the pyrolyzed temperature increases to 1 300 °C [see Fig. 5(d)], which is lower than the pyrolyzed temperature of the sample A-1500. It is indicated that the hydrogenated-anthracite follows the pyrolysis rule like anthracite, which gradually tends to

graphitization when the pyrolyzed temperature increases. Meanwhile, the graphitization of pyrolyzed hydrogenated-anthracite is faster than that of pyrolyzed anthracite, leading to a lower pyrolyzed temperature.

Fig. 6 shows the XPS spectra of the samples A-900 and H300-3-900, respectively. Clearly, the O1s spectra of the sample A-900 and the sample H300-3-900 are fitted into three peaks, representing O=C groups (≈ 531.1 eV), C—OH or C—O—C groups (≈ 532.4 eV), and O=C—OH groups (≈ 533.8 eV), respectively^[31]. As anthracite is reduced through hydrogenation during the early stages of carbonization^[17, 29–30], the content of oxygen in hydrogenated-anthracite is changed. After pyrolysis, the percentage of C=O groups in the sample H300-3-900 increases and the percentages of the other two oxygen functional groups decrease, compared with the sample A-900 (see Table 2).

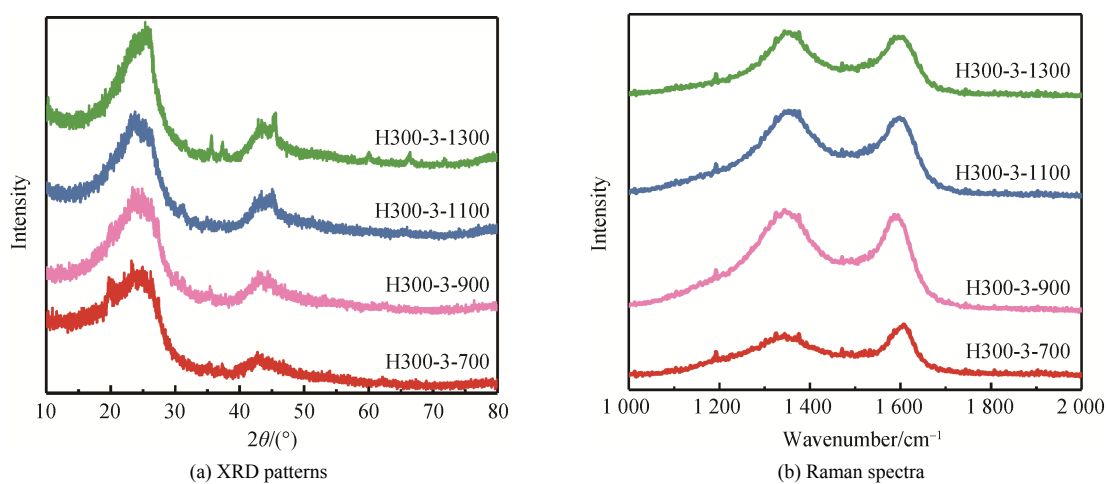


Fig. 4 XRD patterns and Raman spectra of pyrolyzed hydrogenated-anthracites

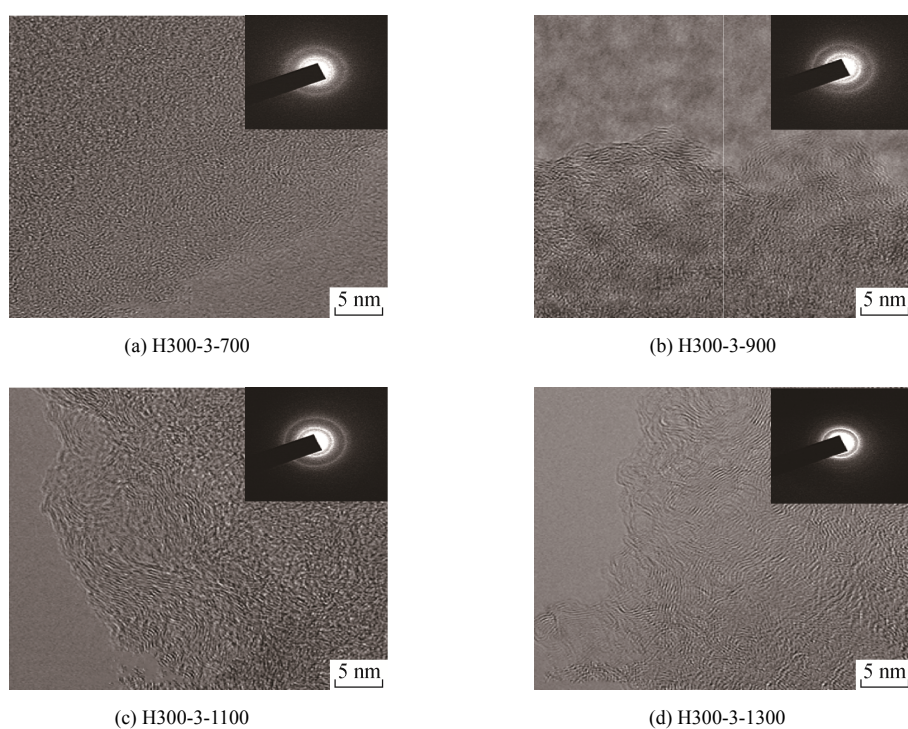


Fig. 5 HRTEM images of pyrolyzed hydrogenated-anthracites

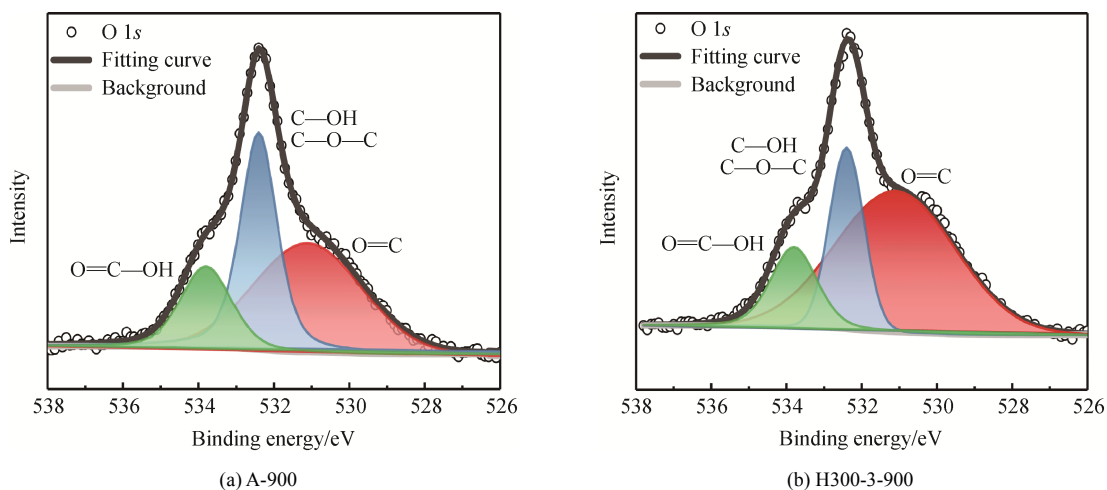


Fig. 6 XPS spectra of the samples A-900 and H300-3-900

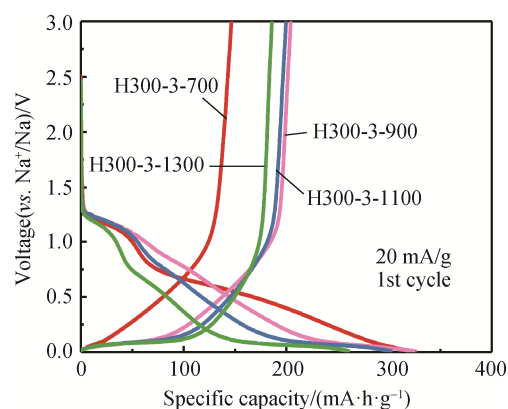
These variations lead to an easy-graphitized carbon. Note that the atomic percents of O1s between the samples A-900 and H300-3-900 are alike. This result is probably because these two samples both remain oxygen functional groups that can be only resolved at higher temperatures^[7, 18, 32–33].

Fig. 7 shows the electrochemical performances of pyrolyzed hydrogenated-anthracites. In Fig. 7(a), the

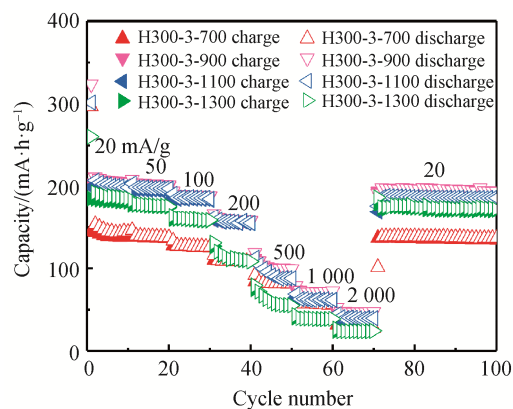
Table 2 Physical parameters of the samples A-900 and H300-3-900 (from XPS)

Sample	at/%		Fitting peak area/%		
	C 1s	O 1s	O=C	C—OH C—O—C	O=C—OH
A-900	93.17	6.83	45.2	37.2	17.6
H300-3-900	93.23	6.77	62.0	23.1	14.9

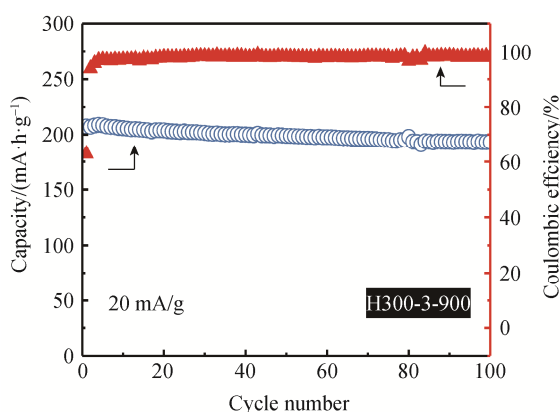
at is atomic percent ratio.



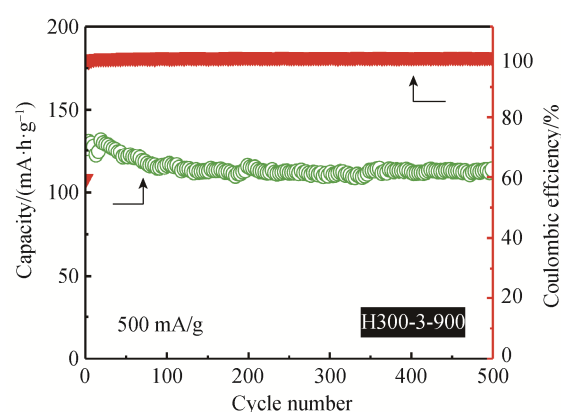
(a) Galvanostatic charge/discharge curves



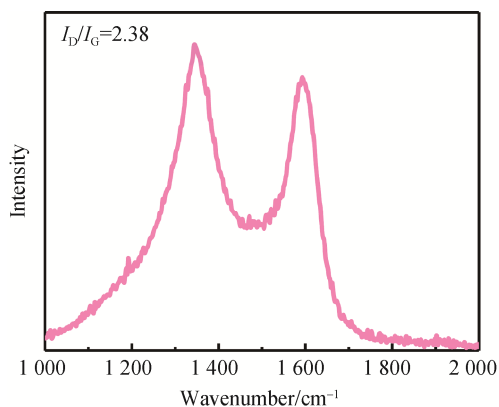
(b) Rate performances



(c) Cycle performances at 20 mA/g



(d) Cycle performances at 500 mA/g



(e) Raman spectra of H300-3-900

Fig. 7 Electrochemical performances of pyrolyzed hydrogenated-anthracites

reversible capacity of pyrolyzed hydrogenated–anthracite reaches a maximum value at 900 °C, and then slowly decreases with the increase of the pyrolyzed temperature. The optimal pyrolyzed temperature based on the reversible capacity after hydrogenation turns into 900 °C, which is lower than 1 300 °C for pyrolyzed anthracite and more suitable for industrial production. In Fig. 7(b) and Table 3、Table 4, the reversible capacity of H300-3-900 at 20 mA/g is inconspicuous. Nevertheless, its reversible capacity maintains 112 mA·h/g when the rate increases to 500 mA/g. Differing from previous reports (see Table 3 and Table 4)^[34–36], we obtained the improved rate performance of pyrolyzed hydrogenated anthracite. For the cycling stability, the reversible capacity of the sample H300-3-900 is 193 mA·h/g at 20 mA/g after 100 cycles (see Fig. 7(c)) and 113 mA·h/g at 500 mA/g after 500 cycles (see Fig. 7(d)), and the corresponding capacity retention ratios are 93% and 90%, respectively. Moreover, the I_p/I_G value of the sample H300-3-900 is 2.38 after 100 cycles at 500 mA/g (see Fig. 7(e)), which is lower than the value before cycle (see Table 1), corresponding to a slight decrease of the reversible capacity of the sample H300-3-900 during the first 100 cycles.

Fig. 8 shows the Na storage kinetics of the sample H300-3-900. In Fig. 8(a), the CV curves of the sample H300-3-900 at various scanning rates show a couple of oxidation and reduction peaks, corresponding to the plateau region and the slope region in the charge/discharge

profiles, respectively. In Fig. 8(b), according to a relationship between the peak current (I) and the scanning rate (v), *i.e.*, $I = av^{b[37–38]}$, the values of b are calculated from the CV curves at different scanning rates (from 0.1 mV/s to 1.0 mV/s). The $\lg(v)$ - $\lg(I)$ plots of oxidation and reduction peaks have a good linear relationship. The fitted b -value of the sharp peak at 0.10 V is 0.38 (close to 0.50), indicating a diffusion-controlled process of the plateau capacity, while the fitted b -value of the hump peak at 0.8 V is 1.07 (close to 1.00), indicating a surface capacitive process of the sloping capacity. Furthermore, the contribution percentages of the two processes can be obtained by $I(V) = k_1v + k_2v^{1/2[39]}$, where k_1v and $k_2v^{1/2}$ are the diffusion and capacitive behavior contributions from the total capacity, respectively. In Fig. 8(c), the percentage of capacitive contributions of the sample H300-3-900 increases from 59.9% to 95.3% when the scanning rate increases from 0.1 mV/s to 1.0 mV/s, illustrating that the capacitive behavior endows a great reversible capacity and a superior rate capability^[40]. Fig. 8(d) shows the potential profile to calculate the Na^+ diffusion coefficient (D_{Na^+}) for the discharge process during the second cycle. In Fig. 8(e), the average D_{Na^+} of H300-3-900 is higher than that of A-900, which further confirms that the kinetics are effectively accelerated in the sample H300-3-900 as an anode^[41].

The results indicate that the pyrolyzed hydrogenated anthracite has a lower pyrolyzed temperature and an improved rate performance.

Table 3 Comparison of the rate capability (capacity) for different treatment anthracites anodes in SIB

Capacity/(mA·h·g ⁻¹)							Ref.
20 mA/g	30 mA/g	50 mA/g	100 mA/g	200 mA/g	500 mA/g	1 000 mA/g	
252.2		191.2	172.5	149.2	106.2	76.2	[34]
		199	141	127	109	90	[35]
	250	170	140	100	80	50	[36] ^{a)}
307		249	218	180	105	57	This work
204		202	189	162	112	74	This work

a) No precise capacity value is given. The data in the table are from the estimation of the figure.

Table 4 Comparison of the rate capability (capacity retention ratio) for different treatment anthracites anodes in SIB

Capacity retention ratio/%							Ref.
20 mA/g	30 mA/g	50 mA/g	100 mA/g	200 mA/g	500 mA/g	1 000 mA/g	
100		76	68	59	42	30	[34]
		100	71	64	55	45	[35]
	100	68	56	40	32	20	[36]
100		81	71	58	34	19	This work
100		99	93	79	55	36	This work

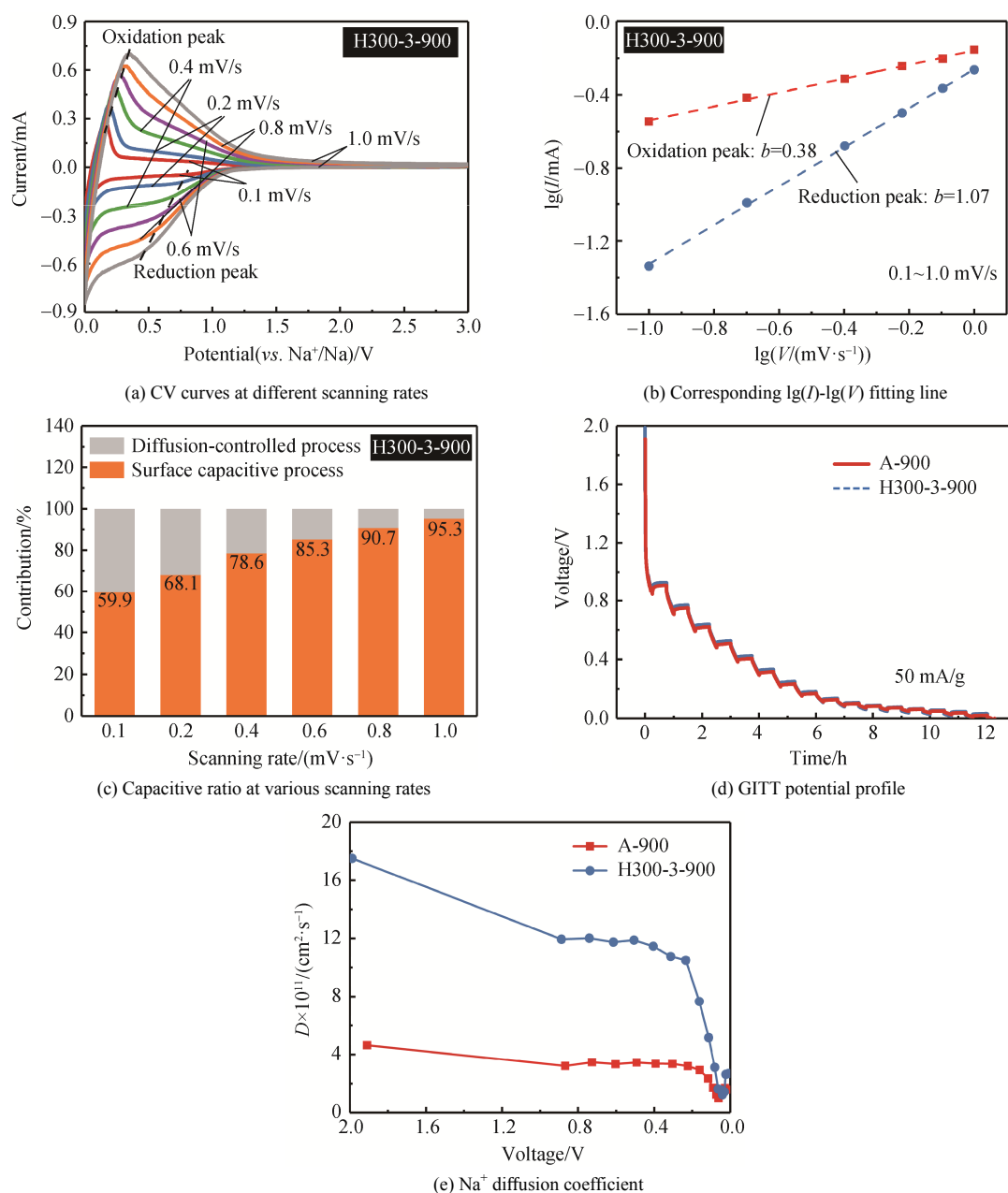


Fig. 8 Na storage kinetics of the sample H300-3-900

4 Conclusions

The electrochemical performances of raw anthracite were inefficient and not appropriate to the SIB. Anthracite through pyrolysis could improve the electrochemical performances. The pyrolyzed anthracite A-1300 had a superior reversible capacity at a low current density, and the initial reversible capacity was 307 $\text{mA}\cdot\text{h/g}$ at 20 mA/g . However, its poor rate capability and high pyrolyzed temperature were still far from the ideal operating conditions for the commercial SIB. Based on some previous studies, pyrolyzed hydrogenated-anthracite could be synthesized. The hydrogenated-anthracite could maintain the pyrolysis rule like anthracite, which gradually tended to graphitization when the pyrolyzed temperature

increased. Also, anthracite could be reduced through hydrogenation, leading to a faster graphitization and a lower pyrolyzed temperature after pyrolysis, which was more suitable for industrial production. Furthermore, the optimal pyrolyzed hydrogenated-anthracite H300-3-900 had an improved rate performance, and the corresponding reversible capacity retained 113 $\text{mA}\cdot\text{h/g}$ at 500 mA/g after 500 cycles.

References:

- [1] LARCHER D, TARASCON J M. Towards greener and more sustainable batteries for electrical energy storage[J]. Nat Chem, 2015, 7(1): 19–29.
- [2] ARMAND M, TARASCON J M. Building better batteries[J]. Nature, 2008, 451(7179): 652–657.
- [3] DUNN B, KAMATH H, TARASCON J M. Electrical energy storage

- for the grid: A battery of choices[J]. *Science*, 2011, 334(6058): 928–935.
- [4] PALOMARES V, SERRAS P, VILLALUENGA I, et al. Na-ion batteries, recent advances and present challenges to become low cost energy storage systems[J]. *Energ Environ Sci*, 2012, 5(3): 5884–5901.
 - [5] PAN H L, HU Y S, CHEN L Q. Room-temperature stationary sodium-ion batteries for large-scale electric energy storage[J]. *Energ Environ Sci*, 2013, 6(8): 2338–2360.
 - [6] YANG Z G, ZHANG J L, KINTNER-MEYER M C W, et al. Electrochemical energy storage for green grid[J]. *Chem Rev*, 2011, 111(5): 3577–3613.
 - [7] SAUREL D, ORAYECH B, XIAO B W, et al. From charge storage mechanism to performance: a roadmap toward high specific energy sodium-ion batteries through carbon anode optimization[J]. *Adv Energy Mater*, 2018, 8: 1703268.
 - [8] DOEFF M M, MA Y P, VISCO S J, et al. Electrochemical insertion of sodium into carbon[J]. *J Electrochem Soc*, 1993, 140(12): L169–L170.
 - [9] STEVENS D A, DAHN J R. High capacity anode materials for rechargeable sodium-ion batteries[J]. *J Electrochem Soc*, 2000, 147(4): 1271–1273.
 - [10] THOMAS P, BILLAUD D. Electrochemical insertion of sodium into hard carbons[J]. *Electrochim Acta*, 2002, 47(2): 3303–3307.
 - [11] ALVIN S, YOON D, CHANDRA C, et al. Revealing sodium ion storage mechanism in hard carbon[J]. *Carbon*, 2019, 145: 67–81.
 - [12] HOU H S, QIU X Q, WEI W F, et al. Carbon anode materials for advanced sodium-ion batteries[J]. *Adv Energy Mater*, 2017, 7: 1602898.
 - [13] GE P, FOULETIER M. Electrochemical intercalation of sodium in graphite[J]. *Solid State Ionics*, 1988, 30: 1172–1175.
 - [14] STEVENS D A, DAHN J R. The mechanisms of lithium and sodium insertion in carbon materials[J]. *J Electrochem Soc*, 2001, 148(8): A803–A811.
 - [15] LI Y M, HU Y S, QI X G, et al. Advanced sodium-ion batteries using superior low cost pyrolyzed anthracite anode: Towards practical applications[J]. *Energy Storage Mater*, 2016, 5: 191–197.
 - [16] KIPLING J J, SHERWOOD J N, SHOOTER P V, et al. Factors influencing the graphitization of polymer carbons[J]. *Carbon*, 1964, 1(3): 315–318.
 - [17] FRANKLIN R E. Crystallite growth in graphitizing and non-graphitizing carbons[J]. *Proc R Soc Lon Ser-A*, 1951, 209(1097): 196–218.
 - [18] GILBERT J B, KIPLING J J, MCENANEY B, et al. Carbonization of polymers I-thermogravimetric analysis[J]. *Polymer*, 1962, 3(1): 1–10.
 - [19] HONDA H, KOBAYASHI K, SUGAWARA S. X-ray characteristics of non-graphitizing-type carbon[J]. *Carbon*, 1968, 6(4): 517–523.
 - [20] MORINOBU E, AGNÈS O, TSUNEO K. High resolution electron microscopy of graphitizable carbon fiber prepared by benzene decomposition[J]. *Jpn J Appl Phys*, 1977, 16(9): 1519–1523.
 - [21] LU Y X, ZHAO C L, QI X G, et al. Pre-oxidation-tuned microstructures of carbon anodes derived from pitch for enhancing Na storage performance[J]. *Adv Energy Mater*, 2018, 8: 1800108.
 - [22] QI Y R, LU Y X, LIU L L, et al. Retarding graphitization of soft carbon precursor: from fusion-state to solid-state carbonization[J]. *Energy Storage Mater*, 2020, 26: 577–584.
 - [23] SUN N, GUAN Z R X, LIU Y W, et al. Extended “adsorption-insertion” model: A new insight into the sodium storage mechanism of hard carbons[J]. *Adv Energy Mater*, 2019, 9: 1901351.
 - [24] LUO W, JIAN Z L, XING Z Y, et al. Electrochemically expandable soft carbon as anodes for Na-ion batteries[J]. *ACS Cent Sci*, 2015, 1(9): 516–522.
 - [25] WENZEL S, HARA T, JANEK J, et al. Room-temperature sodium-ion batteries: Improving the rate capability of carbon anode materials by templating strategies[J]. *Energ Environ Sci*, 2011, 4(9): 3342–3345.
 - [26] FAN L, LIU Q, CHEN S H, et al. Soft carbon as anode for high-performance sodium-based dual ion full battery[J]. *Adv Energy Mater*, 2017, 7: 1602778.
 - [27] TANG K, FU L J, WHITE R J, et al. Hollow carbon nanospheres with superior rate capability for sodium-based batteries[J]. *Adv Energy Mater*, 2012, 2(7): 873–877.
 - [28] YU L Q, SONG H H, LI Y T, et al. Rod-like ordered mesoporous carbons with various lengths as anode materials for sodium ion battery[J]. *Electrochim Acta*, 2016, 218: 285–293.
 - [29] DASOG M, KEHRLE J, RIEGER B, et al. Silicon nanocrystals and silicon-polymer hybrids: synthesis, surface engineering, and applications[J]. *Angew Chem Int Ed*, 2016, 55(7): 2322–2339.
 - [30] HESSEL C M, REID D, PANTHANI M G. Synthesis of ligand-stabilized silicon nanocrystals with size-dependent photoluminescence spanning visible to near-infrared wavelengths[J]. *Chem Mater*, 2012, 24(2): 393–401.
 - [31] ZHAO H Q, YE J Q, SONG W, et al. Insights into the surface oxygen functional group-driven fast and stable sodium adsorption on carbon[J]. *ACS Appl Mater Inter*, 2020, 12(6): 6991–7000.
 - [32] EMMERICH F G. Evolution with heat treatment of crystallinity in carbons[J]. *Carbon*, 1995, 33(12): 1709–1715.
 - [33] KIPLING J J, SHERWOOD J N, SHOOTER P V, et al. Factors influencing the graphitization of polymer carbons[J]. *Carbon*, 1964, 1(3): 315–318.
 - [34] WANG Boyang. Preparation of coal-based carbon anode materials and its electrochemical performance in sodium ion batteries[D]. Dalian: Dalian University of Technology, 2021.
 - [35] ZHUANG Z H, CUI Y L, ZHU H G, et al. Coal-based amorphous carbon as economical anode material for sodium-ion battery[J]. *J Electrochem Soc*, 2018, 165(10): A2225–A2232.
 - [36] ZHAO Dan. Investigation of sodium storage performance in oxygen-functionalized coal-based carbon materials[D]. Taiyuan: Taiyuan University of Technology, 2020.
 - [37] SHAO M, CHENG Y Y, ZHANG T, et al. Designing MOFs-derived FeS₂@carbon composites for high-rate sodium ion storage with capacitive contributions[J]. *ACS Appl Mater Inter*, 2018, 10(39): 33097–33104.
 - [38] LI S, XUE P, LAI C, et al. Pseudocapacitance of amorphous TiO₂@nitrogen doped graphene composite for high rate lithium storage[J]. *Electrochim Acta*, 2015, 180: 112–119.
 - [39] WANG J, POLLEUX J L, LIM J, et al. Pseudocapacitive contributions to electrochemical energy storage in TiO₂ (anatase) nanoparticles[J]. *J Phys Chem C*, 2007, 111(40): 14925–14931.
 - [40] CAO B, LIU H, XU B, et al. Mesoporous soft carbon as an anode material for sodium ion batteries with superior rate and cycling performance[J]. *J Mater Chem A*, 2016, 4(17): 6472–6478.
 - [41] DONG R Q, ZHENG L M, BAI Y, et al. Elucidating the mechanism of fast Na storage kinetics in ether electrolytes for hard carbon anodes[J]. *Adv Mater*, 2021, 33: 2008810.