This is the Pre-Published Version. This is the peer reviewed version of the following article: Li, G, Yu, Y, Huang, B, Chen, P, Shao, Z, An, L. Revealing the sodium-storage performance enhancement of adsorption-type carbon materials after ammonia treatment: Active nitrogen dopants or specific surface area? Int J Energy Res. 2021; 45: 7447-7456, which has been published in final form at https://doi.org/10.1002/er.6327. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

Revealing the sodium-storage performance enhancement of adsorption-type

carbon materials after ammonia treatment: active nitrogen dopants or specific surface area?

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Abstract

Adsorption-type carbon materials are promising candidates for fast sodium-ion storage via surface physisorption or chemisorption of sodium ions. Post-treatment of carbon such as ammonia can simultaneously strengthen both adsorption effects by increasing the specific surface area for physisorption, and by introducing active nitrogen dopants for chemisorption. Which factor, however, the increment of specific surface area or the introduction of active nitrogen dopants, predominantly contributes to sodium-storage capacity increment, remains a question. Answering this question is of great importance for understanding the sodium storage mechanism of adsorption-type carbon materials and thereby optimizing their sodium storage capabilities. In this work, pristine carbon is thermally treated in ammonia at temperatures from 600 to 1200 °C, resulting in a simultaneous increase of specific surface area (8.6 - 1155 m² g⁻¹) and active nitrogen dopants (0.75 - 6.47 wt. %). Correlations between sodium storage capacity and specific surface area/active nitrogen dopants are established. It is found that as the post-treatment temperature increases, the capacity increment is contributed first by sodium physisorption on active surface, and then by sodium chemisorption on nitrogen dopants. Our findings enrich the mechanistic understanding of sodium storage in adsorption-type carbon materials, which may guide the rational designs of carbon materials for high-rate sodium-based energy storage systems.

Keywords: Adsorption-type carbon materials; Sodium storage; Specific surface area; Active nitrogen dopants; Physisorption; Chemisorption

1. Introduction

Lithium-ion battery (LIB) technology was awarded by the Nobel prize in Chemistry in 2019, due to its successful and widespread adoption in multiple fields such as communication and transportation, which has brought dramatic improvement to human life.^{1–6} However, modern LIB technology still confronts a major issue toward rate capabilities.^{7,8} For its application in battery electric vehicles, it often consumes plenty of time to achieve a full charge.⁹ A primary reason for this problem is the sluggish lithium-ion diffusion in the interlayer of electrode materials during lithiation.¹⁰ Another reason is the large desolvation energy of lithium ions, leading to sluggish lithium-ion diffusion across the electrolyte/electrode interface.¹¹ Aiming to address these issues, one promising strategy is to use adsorption-type energy storage materials, which avoids interlayer diffusion by achieving metal-ion storage via surface adsorption. Another promising strategy is to use metal ions with low desolvation energy as charge carriers, accelerating the metal-ion diffusion across the electrolyte/electrode interface.

Sodium ions offer a smaller desolvation energy (118.1 - 186.3 kJ mol⁻¹) compared to that of lithium ions (160.7 - 254.1 kJ mol⁻¹),¹² thus facilitating the ion transport across the electrode-electrolyte interface. Therefore, sodium ions show great promises as charge carriers to achieve fast energy storage.^{13–17} Moreover, using adsorption-type sodium storage materials can shorten the ion diffusion path by achieving sodium storage on the surface, precluding the sodium-ion insertion and diffusion in interlayers, thus further enhancing the sodium storage kinetics.

Adsorption-type carbon materials, enabling sodium storage via surface sodium-ion adsorption, are regarded as promising materials for fast sodium storage.¹⁸ This is because sodium ions are stored on the surface instead of interlayers, precluding the sluggish insertion behavior in sodium storage, thus offering fast sodium storage kinetics.

Pristine carbon, made of one-step polymer carbonization, often possesses limited adsorption sites for sodium storage. As such, the post-treatment of carbon, such as ammonia, is usually required to create more sodium storage sites by simultaneously increasing the specific surface area and introducing active nitrogen dopants. Increasing the specific surface area can expose more accessible surface for sodium storage via physisorption, while introducing active nitrogen dopants can boost sodium storage capacity by binding with sodium ions during sodiation.^{18,19} Hence, it brings out a critical question: which factor, the increase of specific surface area or the introduction of active nitrogen dopants, predominantly contributes to sodium storage capacity increment? To answer this question, we first prepare the adsorption-type pristine carbon by carbonizing organic precursor in Ar. Then, pristine carbon is thermally treated at temperatures ranging from 600 °C to 1200 °C, displaying a simultaneous increase of specific surface area $(8.6 - 1155 \text{ m}^2 \text{ g}^{-1})$ and active nitrogen dopants (0.75 - 6.47 wt. %). Next, the sodium storage behaviors of adsorption-type carbon materials after ammonia treatment are revealed by cyclic voltammetry (CV) curves. An evolution of CV profiles with the temperature, from a quasi-rectangular shape (Stage I, 600 < T < 900 °C) to a bumping shape (Stage II, 900 < T < 1200 °C), is observed. At Stage I, the quasirectangular-shape CV curves indicate a dominant electrochemical double-layer capacitor (EDLC) sodium storage behavior via physisorption. At Stage II, the bumpingshape CV curves indicate a dominant sodium storage behavior with surface redox reactions via chemisorption. In addition, correlations are established between sodium storage capacity and specific surface area/active nitrogen dopants. It is found that with increasing the ammonia treatment temperature, the capacity increment is contributed first by sodium physisorption on active surface, and then contributed by sodium chemisorption on nitrogen dopants.

2. Experimental sections

2.1 Pretreatment, carbonization and post-treatment of materials

Carbon materials were prepared by carbonizing organic precursor, the commercialized polyacrylonitrile (PAN) chopped fiber (Bannor Industrial Co., Ltd), in a tube furnace under an inert atmosphere of Ar. It was first pretreated in air at 250 °C for 2 h in a muffle furnace with a heating rate of 1 °C min⁻¹. Next, it was transferred to a tube furnace, followed by carbonization in Ar for 2 h at various temperatures (650 °C, 1100 °C and 1300 °C), with a heating rate of 5 °C min⁻¹. The Ar gas flow was kept at 100 ml min⁻¹ during carbonization. Carbon material obtained at 1100 °C was used as the pristine carbon for further post-treatment in ammonia. The pristine carbon was transferred to the tube furnace again but thermally treated in ammonia at various temperatures (600 - 1200 °C) for 2 h. The heating rate was 5 °C min⁻¹ and the ammonia gas flow rate was kept at 50 ml min⁻¹. After thermal treatment, the adsorption-type carbon materials were obtained, and they were grinded into carbon powder for further use. The obtained adsorption-type carbon materials are labeled as C-NX, where X represents the ammonia post-treatment temperature.

2.2 Characterizations of materials

The phase of materials was characterized by X-ray diffraction (D/max 2500PC) with a Cu–K α X-ray radiation source at a scan rate of 6° min⁻¹. The structures of materials were characterized by field emission scanning electron microscopy (Tescan MAIA3, Japan) operating at 200 kV and Raman spectra (Renishaw RM-1000, Britain) with 488 nm laser excitation. The X-ray photoelectron spectroscopy (XPS) spectra was recorded by a spectrometer having Mg/Al K α radiation (Thermo VG Scientific, USA) operating at 15 kV. The morphologies of the samples were investigated with transmission electron microscopy (Jeol JEM-2100F) and their crystal structures were revealed by selected

area electron diffraction (SAED) pattern. The pore properties of carbon materials were characterized by nitrogen adsorption/desorption isotherms (ASAP 2020) using Barrett– Joyer–Halenda (BJH) method using the desorption branch of the isotherm curves and specific surface area was calculated by Brunauer-Emmett-Teller (BET) equation.

2.3 Electrochemical measurements

2025-type coin cells were assembled in an Ar-filled glove box (MBRAUN, Germany) to examine the sodium storage properties of carbon materials. For the preparation of working electrode, firstly, a mixture of carbon powder, carbon black and poly(vinyl difluoride) (PVDF) with a weight ratio of 80:10:10 was dispersed in N-Methyl pyrrolidone (NMP) and stirred for 2 h. Then, the resultant slurry was pasted onto the copper foil with a thickness of 9 µm, followed by drying in a vacuum oven at 80 °C for 12 h. Last, the copper foil coated with active materials was cut into circular pieces with a diameter of 10 mm. The mass loading of active materials was in the range of 1.6 - 2.0 mg cm⁻². The sodium foil with a diameter of 12 mm was used as the counter electrode and glass fiber membrane with a diameter of 16 mm was used as the separator. 1.0 M NaClO₄ dissolved in 1:1 (v/v) diethyl carbonate/polycarbonate (Suzhou Fosai New Material Co., Ltd.) was used as the electrolyte. After cells were assembled, they were rested for 12 h before electrochemical measurements. The galvanostatic charge and discharge tests were conducted using Neware battery testing system (CT2001A, China). CV was performed using electrochemical workstation (CHI604E, China) with different scan rates ranging from 0.2 mV s⁻¹ to 2 mV s⁻¹. Galvanostatic intermittent titration technique (GITT) measurement was performed by applying constant current of 50 mA g^{-1} for 20 min followed by 2 hours of open circuit period upon charging and discharging. Electrochemical impedance spectroscopy (EIS) spectra was recorded with an amplitude of 5 mV and frequency ranging from 100 kHz to 0.1 Hz.

3. Results and discussion

3.1 Identification of adsorption-type carbon materials

Carbonizing precursor in Ar at different temperatures leads to the formation of completely different surface microstructures of carbon materials. At a low carbonization temperature (650 °C), amorphous carbon with no crystalline structure is obtained (Figs. 1a-b). This is due to insufficient thermal energy during carbonization, precluding the formation of ordered carbon chains. At an elevated temperature (1100 $^{\circ}$ C), the formation of defective graphene sheets with an interlayer spacing of 0.386 nm is observed (Figs. 1d-e). Further elevating the carbonization temperature (1300 °C) leads to the formation of graphitic nanodomains (Figs. 1g-h), with an interlayer spacing of 0.335 nm. All SAED patterns exhibit dispersed diffraction rings, revealing turbostratic carbon structures.^{20,21} The appearance of (110) ring in Fig. 1i indicates an improved crystallization of carbon when carbonizing at a high temperature (1300 °C). The improved crystallization with the temperature is further confirmed by the XRD patterns (Figure S1). (002) peaks become more sharpened and are shifted toward 26°, corresponding to the (002) peak of graphite, indicating the improved crystallization.²² Raman spectra (Figure S2) also shows that as the carbonization temperature increases, D and G peaks become sharpened and Id/Ig ratios are reduced. These results further confirm the improved crystallization of carbon materials and enhanced ordering of local structure.²³

The sodium storage properties of carbon materials with different surface microstructures are first revealed by CV curves (Fig. S3a). Carbon with defective graphene displays a broad cathodic peak in the range of 0 - 1 V (vs. Na/Na⁺), indicating a typical sodium storage behavior via surface adsorption. The galvanostatic charge/discharge curve (Fig. S4b) further confirms such behavior, with no appearance

of voltage plateau but only voltage slope. Kinetic analysis by CV curves (Fig. S3b) and GITT measurements (Fig. S3c-f) also indicates its adsorption behavior, by observing a large *b* value of 0.8 and large ion diffusion coefficients. In sharp contrast, carbon with graphitic nanodomains displays a sharp cathodic peak near 0 V (Fig. S3a) and a discharge voltage plateau near 0 V (Fig. S4c), which is a typical battery-type sodium storage behavior.²⁴

3.2 Physical properties of adsorption-type carbon materials

Carbon with defective graphene is employed as the pristine carbon for further ammonia treatment at various temperatures (600 - 1200 °C). Thermal treatment of pristine carbon in ammonia leads to the formation of more disordered surface microstructures, with abundant pores, defects and cavities (Fig. S5b). Meanwhile, the nitrogen content in carbon materials increases with the temperature (Fig. 2c), since more ammonia molecules (NH₃) will decompose to NH and NH₂ radicals and react with carbon at elevated temperatures²⁵:

$$NH_3 \rightarrow \bullet NH + H_2$$
 (1)

$$NH_3 \rightarrow \bullet NH_2 + \bullet H$$
 (2)

$$C + \bullet NH \rightarrow HCN$$
 (3)

$$C + \bullet NH_2 \rightarrow (CN)_2 + H_2 \tag{4}$$

The composition of nitrogen dopants is evaluated using Gaussian fitting method (Figs. 2a-b), containing three types of nitrogen with different binding energies: pyridinic-N ($398.4 \pm 0.3 \text{ eV}$), pyrrolic-N ($400.4 \pm 0.3 \text{ eV}$), graphitic-N ($401.4 \pm 0.3 \text{ eV}$).²⁶ Pyridinic-N and pyrrolic-N are regarded as active nitrogen dopants for sodium storage since they can bind with sodium ions during sodiation.²⁰ Graphitic-N is inactive for sodium storage since it is inert for sodium chemisorption.²⁰ The concentration of active nitrogen

dopants increases from 0.75 wt.% (pristine carbon) to 6.47 wt.% (C-N1200), as shown in Table S1 and Fig. 2d.

Ammonia post-treatment of pristine carbon also leads to more exposure of active surface for sodium physisorption, due to the loss of carbon atoms by ammonia etching. From N₂ adsorption and desorption isotherms, pristine carbon displays a type-II profile with a nonporous feature (Fig. 3a).²⁷ As for C-N600 and C-N700, they display a typical type-I profile with abundant micropores, showing that micropores are first generated on the carbon surface by ammonia etching. At elevated temperatures (800 - 1200 °C), the profiles of adsorption/desorption curves belong to type IV with the observation of hysteresis loops, indicating the presence of mesopores. The adsorption quantity of N₂ constantly increases with the temperature, reaching a highest value of 439.3 cm³ g⁻¹ at 1200 °C. The specific surface area of adsorption-type carbon materials, calculated by BET equation, also constantly increases with the temperature, starting from 8.6 m² g⁻¹ (pristine carbon) to 1155 m² g⁻¹ (C-N1200). The increasing pore volumes of adsorption-type carbon materials as the temperature increases (Figs. 3c-d) is also attributed to the loss of carbon atoms by ammonia etching.

3.3 Electrochemical activity analysis

CV profile of pristine carbon (Fig. 4a) displays a broad cathodic peak in the range of 0 - 1 V, indicating a sodium storage behavior via adsorption. Increasing the post-treatment temperature leads to the evolution of CV profiles, from a quasi-rectangular shape to a bumping shape. A quasi-rectangular shape of CV profile is observed for C-N700, displaying potential-independent current with no distinct anodic/cathodic peaks. This reveals that sodium-ion storage is achieved by a typical EDLC behavior, in which the amounts of adsorbed sodium ions are highly dependent on the specific surface area of adsorption-type carbon materials.²⁸ As the post-treatment temperature further increases, some faint and broad anodic peaks (1.84 V, 2.61 V and 3.00 V) and cathodic peaks (0.01 V and 1.10 V) start to appear (C-N800). These emerging peaks result from surface redox reactions between nitrogen dopants and sodium ions, i.e., chemisorption of sodium ions on active nitrogen dopants.²⁸ Further increasing the temperature leads to enhanced intensities of these redox peaks, indicating that sodium-ion storage via surface redox reactions is enhanced and more sodium ions bind with nitrogen dopants during sodiation. Meanwhile, the rectangular region area of CV curves, contributed by the EDLC behavior, remains basically unchanged from C-N800 to C-N1200. This confirms that additional sodium storage capacity is dominantly contributed by the active nitrogen dopants.

3.4 Correlations between sodium storage capacity and physical properties

As the post-treatment temperature increases, the specific surface area and active nitrogen dopants simultaneously increase, leading to improved sodium storage capacities, as shown in Fig. 5 and Fig. 6a. The galvanostatic charge/discharge curves of adsorption-type carbon materials display diverse profiles, as shown in Figs. 5a-b. C-N600 exhibits a reversible sodium storage capacity of 153 mAh g⁻¹, larger than that of pristine carbon (110 mAh g⁻¹). The charging curve of C-N600 becomes linear, indicating a potential-independent desorption behavior of sodium ions in the voltage range of 0 - 3 V. As for the discharging curve of C-N600, the slope of the curve decreases in the voltage range of 1 - 3 V compared to that of pristine carbon, revealing an enhanced sodium adsorption in this voltage range. Further increasing the posttreatment temperature leads to a depressed charging curve in the voltage of 2.25 - 3 V. This is consistent with the enhanced anodic peaks at around 2.61 V of CV curves (Fig. 3), indicating enhanced sodium chemisorption behaviors. The cyclic performance of adsorption-type carbon materials is shown in Figs. 5c-d and Fig. S8a. C-N1200 displays

a highly stable cyclic performance in 500 cycles at 1 A g⁻¹, due to the highly reversible sodium adsorption on the carbon surface. The rate performance of C-N1200 is shown in Fig. S8b, showing a much-improved rate capabilities compared to the pristine carbon. The correlations between sodium storage capacity and physical properties of carbon materials are constructed, as shown in Fig. 6. There is a strong correlation ($R^2 \sim$ 0.97) between sodium storage capacity and specific surface area when the specific surface area is below 1016 m² g⁻¹, but a weak correlation ($R^2 \sim 0.58$) above 1016 m² g⁻¹ ¹. This reveals that the sodium storage capacity increment is dominantly contributed by the specific surface area when carbon materials are thermally treated at low temperatures (600 - 900 °C). In addition, there is a strong correlation ($R^2 \sim 0.94$) between sodium storage capacity and active nitrogen dopants when the active nitrogen dopants are in the range of 1.76 - 6.47 wt.%, but a weak correlation ($R^2 \sim 0.73$) below 1.76 wt.%. This reveals that the sodium storage capacity increment is dominantly contributed by the active nitrogen dopants when carbon materials are thermally treated at high temperatures (900 - 1200 °C). The sodium storage mechanism on the adsorptiontype carbon materials is illustrated, as shown in Fig. 7. Pristine carbon possesses sparse active sites for sodium storage (Fig. 7a). By thermal treatment in ammonia at 600 - 900 °C, abundant micropores are generated on the carbon surface by ammonia etching, exposing more active surface for sodium physisorption. Resultantly, they provide additional capacity in the sloping region above 0.1 V, as evidenced by the galvanostatic charge/discharge curves (Fig. 5a).²⁹ Therefore, the capacity increment of carbon materials is dominantly contributed by sodium physisorption on the active surface (Fig. 7b). In addition, the uptake of nitrogen adsorption at the relative pressure of 0.96 - 1.0 (Fig. 3a) indicates the generation of macropores on the carbon surface,³⁰ which facilitates the infiltration of electrolyte and further enhances the sodium-ion adsorption.

By thermal treatment in ammonia at 900 - 1200 °C, active nitrogen dopants are introduced into carbon materials, serving as effective sodium storage sites. The intensities of redox peaks are gradually enhanced with the concentration of active nitrogen dopants. Hence, the capacity increment is dominantly contributed by sodium chemisorption on active nitrogen dopants (Fig. 7c).

4. Concluding remarks

In summary, sodium storage performance enhancement of adsorption-type carbon materials after ammonia treatment is revealed. As ammonia post-treatment temperature increases from 600 °C to 1200 °C, a simultaneous increase of specific surface area (8.6 - 1155 m² g⁻¹) and active nitrogen dopants (0.75 - 6.47 wt. %) is observed. This results in a transition of sodium storage behavior from EDLC dominant behavior via physisorption to dominant surface redox behavior via chemisorption. Correlations between sodium storage capacity and specific surface area/active nitrogen dopants are established. It is found that as the post-treatment temperature increases, the capacity increment is contributed first by sodium physisorption on active surface, and then contributed by sodium chemisorption on nitrogen dopants. These findings enrich the sodium storage mechanism in adsorption-type carbon materials and may guide the rational designs of adsorption-type carbon materials for high-rate sodium-based energy storage systems.

Conflict of interest:

The authors declare no competing interests.

Acknowledgement:

This work was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. 15222018).

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Figures:



Fig. 1 Carbon materials with different surface microstructures and their SAED patterns. (a-b) Amorphous carbon showing no periodic structural arrangement. (d-e) Defective carbon with disordered surface graphene sheets. (g-h) Carbon with graphitic nanodomains with an interlayer spacing of 0.335 nm.



Fig. 2 a) N1s spectra of pristine carbon and carbon thermally treated at low temperatures (600 - 800 °C). b) N1s spectra of carbon thermally treated at high temperatures (900 - 1200 °C). c) The evolution of concentrations of elements with the post-treatment temperature. d) Concentrations of different nitrogen dopants in carbon thermally treated at different temperatures. Nitrogen composition contains three types: pyridinic-N (N-6), pyrrolic-N (N-5) and graphitic-N (N-Q).



Fig. 3 (a,b) Nitrogen isotherm adsorption/desorption curve of adsorption-type carbon materials and (c,d) their pore size distribution.



Fig. 4 (a,b) Electrochemical activity analysis of adsorption-type carbon materials.



Fig. 5 (a-b) Galvanostatic charge/discharge curves of adsorption-type carbon materials and (c-d) cyclic performance of adsorption-type carbon materials.



Fig. 6 (a) The active nitrogen dopants, specific surface area, and sodium storage capacities of adsorption-type carbon materials at various post-treatment temperatures.(b) Correlation between sodium storage capacity and specific surface area. (c) Correlation between sodium storage capacity and active nitrogen dopants.



Fig. 7 Sodium storage mechanisms via physisorption and chemisorption. (a) Pristine carbon possesses sparse active sites for sodium storage. (b) Thermal treatment at 600 - 900 °C displays an enhanced physisorption by more exposed surface. (c) Thermal treatment at 900 - 1200 °C displays an enhanced chemisorption by active nitrogen dopants.