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The transport properties of sodium-ion in the low potential platform region of oatmeal-derived hard carbon for sodium-ion batteries

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ABSTRACT

Hard carbon is the most common carbon-based material with abundant raw material resources, low cost, high reversible capacity and reliable safety performance, it is the most suitable sodium-ion batteries (SIBs) anode material for commercial production, which attracts the interest of the researchers. Unfortunately, the electrochemical performances of hard carbon are still underestimated in the previous reports. In this research, we use a simple process flow to obtain carbonized oatmeal as a kind of hard carbon. It can deliver initial reversible capacity of 272.4 mAh g⁻¹ at 20 mA g⁻¹, the capacity retention rate is 93.3% after 100 cycles, exhibits a good electrochemical performance. Simultaneously, the transport properties of sodium-ion in carbonized oatmeal material are also characterized by electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT). The measurement results show that the low potential platform region of the oatmeal-derived hard carbon is attributed to the insertion/extraction characteristics of sodium-ion in the graphitic microcrystallites sheets.

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1. Introduction

As a kind of alkali metal ion batteries, SIBs have rich raw material resources, low production cost, no overdischarge characteristics and simple waste recycling process, which made it attracts much attention [1,2]. In the future, SIBs are also expected to be used as a large scale energy storage battery system, and have become an alternative to lithium-ion batteries. For the commercial production of SIBs, the electrode materials with excellent electrochemical performance and low cost are important factors. Fortunately, with the cathode electrode materials currently consisted of transition metal oxides, polyanionic compounds and organic materials, the research and development of the cathode materials have been relatively mature. However, the suitable anode materials with satisfactory electrochemical performances are still unclear, which would limit the development for SIBs [3,4].

Carbon-based materials have the characteristics of wide raw material resources, low cost and diverse structure, which are the preferred research targets for the SIBs anode materials. At this stage, as a kind of carbon-based materials, the better sodium-ion storage property of hard carbon has led to the increasing researches around the world. Compared with the conventional graphite, hard carbon is amorphous carbon, which is mainly composed of graphite-like crystallites with small width and thickness, but the arrangement is more disordered than graphite, and it has a relatively expanded interlayer distance [4].

Among the various hard carbon proposed to the anode applications, biomass-derived hard carbon has received extensive attention. According to the report, the materials that can be used as biomass-derived hard carbon precursors are concentrated on sugars, fruit peels and natural polymers, as well as some precursor materials that are not very obvious, such as phytoplankton blooms [5]. Plant resources, the largest available renewable organic







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resources on earth are inexpensive and easily available, which are also one of the most promising raw materials for the preparation of hard carbon [6-8].

Currently, the biomass-derived carbon is widely used in electrochemical applications as important electrode material, and it is one of the hot topics in the electrochemical field [9]. Cao et al. [6] obtained the lamellar hard carbon (RSS) derived from rape seed shuck by hydrothermal and pyrolysis methods, and researched the effect of carbonization temperature on the material properties. The experimental results show that the degree of graphitization, defect structure and specific surface area of RSS are directly related to the carbonization temperature. As the anode, The interlayer distance of the product obtained by heat treatment at 700 °C is 0.39 nm, and the electrode delivers a reversible capacity of 196 mAh g^{-1} with the best performance. Corn stalk piths have also been proven to be used as a precursor material. Zhu et al. [10] synthesized the corn stalk piths-derived hard carbon through an uncomplicated heat treatment process. The obtained hard carbon material shown a reversible capacity of 310 mAh g^{-1} and a 79% capacity retention after 700 cycles. Furthermore, they also found that hard carbon materials exhibit severe electrochemical polarization at higher current densities, resulting in reduced platform capacity and reduced rate performance. Therefore, they researched the electrochemical properties of loofah sponge-derived hard carbon based on different electrolytes [11]. At 3C, the sample has a plateau capacity of 143 mAh g^{-1} in ether-based electrolytes, much higher than in common ester-based electrolytes, and the high-rate cycle performance has also been greatly improved. Bai et al. also made great contributions to the research of hard carbon materials. By employing the electrostatic spinning method and a further heat treatment process followed, they composited a polyvinylpyrrolidone (PVP) nanofibres of derivative called mille-feuille shaped hard carbon [12]. The optimized sample carbonized at 1000 °C achieved a good capacity of 271 mAh g⁻¹, and after 100 cycles, the capacity retention rate is 94%. In the material modification aspect, they also reported a natural K-doped carbon material with the coconut endocarp as a precursor [13]. The ultra-high potassium content allows the material to have an expanded interlayer distance of 0.4 nm, and it shows the excellent electrochemical performance, the initial reversible capacity is high (314 mAh g^{-1}), the cycle stability is good (289 mAh g^{-1} after 200 cycles). In order to improve the sodium storage capacity for hard carbon, P-doped has also proven to be effective modification [14,15]. These researches have advanced the rapid development for SIBs.

Nevertheless, in hard carbon materials, the electrochemical storage behavior of sodium-ion is controversial [16–18]. For the low potential platform region, Dahn et al. [16] believed that it corresponds to the filling and deposition of sodium-ion in the micropores, but Cao et al. [17] thought that it is related to the behavior of sodium-ion insertion/extraction between the graphitic microcrystallites sheets. Although the researchers hold different opinions, they all give support for the corresponding experimental results, which shows that the full understanding of the sodium storage mechanism still needs further research.

How to solve the problems in performance and sodium storage mechanism has become the top priority in the research work of SIBs biomass-derived hard carbon materials. In the present work, a biomass-derived hard carbon was prepared through high-temperature heat treatment and potassium hydroxide solution activation process from oatmeal (COs). The electrochemical performance measurement results show the COs electrode can display an initial reversible capacity of 272.4 mAh g⁻¹ with a capacity retention rate of 93.3% after 100 cycles. Moreover, after different current density cycling (from 20 to 1000 mA g⁻¹), the reversible capacity can recover to 92.1%. The small specific surface area, the

distributed nanoscale mesopores, the presenced oxygen functional groups and the expanded interlayer distance are responsible for the electrochemical performances, which are conducive to sodium-ion diffusion and reversible accumulation. And we also adopted the EIS and GITT measurements to research the sodium-ion diffusion coefficient (D_{Na}) changing trend in different voltage ranges for the COs electrodes. The D_{Na} values are relatively small in the voltage range near the charging/discharging platform, corresponding to the combination of graphite carbon and sodium-ion to form sodiumgraphite intercalation compounds (Na-GICs), which show the COs electrodes are related to the sodiation/desodiation process. In a word, this research has summarized the important factors affecting electrochemica performance of COs and further elaborated the electrochemical sodium storage mechanism, provided new ideas for the future development of biomass-derived hard carbon materials with excellent performance.

2. Experimental section

2.1. Material preparation

COs was prepared by activating the pyrolysis products of oatmeal with KOH solution. First, oatmeal was washed with anhydrous ethanol followed by dring at 100 °C overnight to remove water. Then, oatmeal was transferred to a tubular furnace for carbonizing under Ar flow at 1200 °C for 2 h (the heating rate is $10 \degree C min^{-1}$). Immerse the obtained material first in 30% KOH solution for 6 h and then place it in 3 M HCl solution for 3 h, the product was got by further washing and dring.

2.2. Materials characterization

The NETZSCH STA 449F3 simultaneous thermal analyser (Germany) was carried out to acquire the thermogravimetric analysis information. The species data of the surface functional groups before and after carbonation was obtained by the Bruker TENSOR27 fourier transform infrared spectrometer (Germany). The TESCAN VEGA 3 SBH scanning electron microscope (Czech Republic) investigated the appearance of COs. The Rigaku MiniFlex 600 X-ray powder diffractometer (Japan) examined the structure information. Furthermore, the Raman spectroscopy was obtained on the confocal microprobe Raman system (LabRAM HR Evolution, France) in an ambient air, from which the degree of graphitization of COs can be known. The N2 adsorption/desorption isotherms were acquired by the Micromeritics Tristar 3000 analyser (America), and the specific surface area and pore size distribution information can be calculated. The Tecnai G² TF30 S-Twin microscope (Netherlands) evaluated the high-resolution transmission electron microscopy and selected area electron diffraction images. The PHI5000 Versaprobe-II X-ray photoelectron spectrometry (Japan) was used to record the chemical compositions on the surface of COs.

2.3. Electrochemical performance characterization

CR2016 coin cells was assembled to conduct the electrochemical performance. Made the working electrodes, the prepared COs, polyvinylidene fluoride and Super-P were used as the active material binder and conductive agent, which were mixed at a mass ratio of 8:1:1, and added to *N*-methyl-2-pyrrolidone in well. Coat the resulting mixed slurry on a pure Cu foil with a scraper and dried in a vacuum environment overnight, baking temperature was not too high. Then, assembling the battery, the well punched electrodes was transferred to an Argon-filled glove box with precisely control of the moisture and oxygen contents. The electrolyte was prepared by adding 1 M NaClO₄ in a mixed solvent of ethylene carbonate (EC)

and propylene carbonate (PC) (volume ratio = 1:1). The counter electrode was the homemade sodium foil act and the separator was the glass fiber. The galvanostatic charge/discharge measurements and galvanostatic intermittent titration technique (GITT) measurements were employed at various rates on a CT2001A battery measurement system (China). A PGSTAT302 N Autolab electrochemical workstation (Switzerland) was used to test the electrochemical impedance spectroscopy (EIS) information and cyclic voltammetry (CV) performance. For the selection of the measurement environment, all above the electrochemical performance measurements were conducted between 0.01 and 3 V at room temperature.

3. Results and discussion

The effect of carbonization temperature on COs was detected by thermogravimetric analysis (TGA). Fig. 1a shows the TGA, the pyrolysis process of the precursor material can be divided into the following three stages [19]: the first stage is from room temperature to 250 °C, as the temperature increases, the material shows a slight weight loss, water evaporation is the main reason. Secondly, the stage is in the range of 250–500 °C, the pyrolysis process is the main stage, the quantity of the precursor material significantly reduces, expressed as the polymerization of cellulose and hemicellulose and the release of volatile gas [20]. The third stage is above 500 °C, the precursor material enters the process of carbonization. The deep volatile components are transferred to the outer layers and accompanied by a dehydrogenation reaction, the duration is long and the ash and fixed carbon are residues [21]. Oatmeal has a high carbon yield and is very beneficial for commercial production.

Fig. 1b shows the analysis of surface functional groups for COs and the precursor material by using fourier transform infrared spectroscopy (FTIR), the range of 4000–500 cm⁻¹ can be divided into two parts [22,23]. One is the absorption peak of functional groups, such as the [–OH] of alcohol, phenol and carboxylic acid, the [C–H] of aliphatic, the corresponding peak positions are 3416 cm⁻¹ and 2926 cm⁻¹. Another is expressed in the range from 800 to 1800 cm⁻¹, that is interpreted as the [C=O], [C–O] and [C=C] of aromatic. Compared with the precursor material, the absorption peak intensities of the C–O, O–H and C–H bond for the carbonized product become gradually weaker, and the bond contents are decreasing. The integrated TGA data indicates that the C–O, O–H and C–H bond are cleaved during the heat treatment and accompanied by the release of CO₂, CO, CH₄, C₂H₄ and C₂H₆ [8,19].

Scanning electron micrographs (SEM) provided the detailed

morphologies of COs. As shown in Fig. 2a, the surface of the precursor material is an irregular "stone forest" structure, there is no obvious pore distribution. After heat treatment, observing the surface of the material, it find that some small particles are adsorbed on it (Fig. 2b). The energy dispersive spectrometer (EDS) is used to analyze the types and relative contents of the elements on the surface of the carbonized precursor, which is important for the analysis of carbonized products. The C content is high, indicates that the precursor material has been successfully converted to the carbon material. It can also be known that the elements of the fine particles are mainly metallic ions, such as Mg, Ca and K (inset in Fig. 2b), these are the alkali metals contained in the biomass itself. Combined with the data analysis of the TGA, it can be seen that the fine particles are the ash produced by the biomass after carbonization, mainly inorganic salts and oxides. Fig. 2c shows the morphology of the product after activation by the KOH solution. The strong alkali solution would "burn" the product, making the surface produce some pores, which could increase the specific surface area of COs, adds more reactive sites with sodium-ion [24]. Finally, the HCl solution was used to remove the residual ash, that making the pores of the surface distribution obvious, and no impurity adsorption (Fig. 2d). Above all, after a simple process flow, the oatmeal transformed into a unique appearance of carbon materials successfully.

X-ray diffraction (XRD) and Raman spectroscopy collected the microstructure information of COs. The XRD pattern is displayed in Fig. 3a, the diffraction of (002) and (101) planes for the graphite laver structure are shown as the diffraction peaks near 23° and 43°. respectively, which indicates that COs is a typical non-graphitic carbon material [25]. Based on the Scherer equation, with the full width at half-maximum value of the (002) diffraction peak at $2\theta \approx 23^{\circ}$, 1.07 nm is the thickness of the graphitic domains (L_c), which indicating that COs only contains a small amount of graphitic microcrystallites sheets stacking structure [26]. According to the previous researches, the carbon materials for LIBs have low values [27], which equals one for fewer layers. The ideal situation for reversible storage of alkali metals would be the occurrence of large free space between graphitic microcrystallites sheets and low external surface to avoid irreversible reactions with the electrolyte [25]. In addition, the Raman spectroscopy shown in Fig. 3b shows the degree of graphitization for COs, it can be seen that the COs exhibits a broad D-band and G-band. As we know, the D-band at 1340 cm^{-1} is designated as the A_{1g} joint vibration mode of the diamond-like carbon sp³ electron structure, corresponding to the edge carbon of the graphite sheet and the small graphitic microcrystallites, the G-band near 1590 cm^{-1} is referred to as the E_{2g}



Fig. 1. (a) TGA analysis of the precursor material, (b) FTIR spectra of the precursor material and COs.



Fig. 2. The SEM images of COs during processing: (a) the precursor material, (b) after carbonization, (c) after KOH solution treatment, (d) after HCl solution treatment (COs).

joint vibration mode of the sp² electron structure, corresponding to the aromatic ring structure carbon of the graphite sheet [28,29]. I_D/I_G is expressed as the integral intensity ratio of the D–band and G–band, and it is estimated to be 1.03. For hard carbon with a disordered structure, this ratio is common, which is consistent with the XRD analysis. Moreover, the graphitic microcrystallites width in the *a*-axis direction (L_a) can also be calculated to be 3.54 nm by the value of I_D/I_G . The small crystallite size favors the fast sodium-ion diffusion efficiency.

Fig. 3c summarized in the N₂ adsorption/desorption isotherms. A distinct hysteresis loop is shown in the relative pressure ranging, that is characterized by a typical mixed behavior of type II and type IV. According to existing research, this phenomenon indicates that there are a large amounts of mesopores in the COs particles [30,31]. Based on the Brunauer-Emmett-Teller (BET) calculation method, the specific surface area is 69.841 m² g⁻¹. In comparison to the other carbon materials with a higher specific surface, this small surface area of COs can limit the formation of the solid electrolyte interphase (SEI) film, thereby increasing the initial coulomb efficiency. Fig. 3d shows the pore size distribution estimated by the Barrett-Joyner-Halenda (BJH) model, the measured average pore diameter is 3.39 nm. These mesopores can ensure adequate electrolyte penetration, increase the sodium-ion diffusion rate, even alleviate the volume changes at the sodiation/desodiation process

[31]. During the heat treatment stage, the functional groups continue to decrease, the C–C aromatic structures appear poorly stacked, and the stacked graphitic microcrystallites sheets begin to increase, which should lead to the mesopores evolution of COs [32]. Even the activation of KOH solution can also provide more mesopores for COs [24].

To research further the microstructure of COs, high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were collected and the results are shown in Fig. 4a. The HRTEM image exhibits COs made up of graphitic microcrystallites with some stacking regions, observed the disorder structure to further determine the amorphous properties of COs. The SAED patterns can also be found without the presence of crystal diffraction spots. The contour curve of the six stacked layers demonstrated by the arrow is depicted in Fig. 4b, according to the corresponding scale, the interlayer distance of COs is 0.39 nm. Compared with the interlayer distance of 0.335 nm for the graphite material, the obtained expanded interlayer distance of COs is beneficial to the sodiation/desodiation process. The highly disordered structure of COs illustrated by HRTEM, SAED as well as XRD and Raman, which is helpful for the transmission and storage of sodium-ion, making it a suitable carbon-based anode material for SIBs.

The chemical composition and state on the surface of COs were



Fig. 3. (a) XRD pattern, (b) Raman spectrum, (c) N₂ adsorption/desorption isotherms and (d) BJH pore size distributions of COs.



Fig. 4. (a) HRTEM and SAED images of COs, (b) contrast profiles along the arrows indicate interlayer distance of COs.

used to in-depth research by X-ray photoelectron spectroscopy (XPS). As summarized in Fig. 5a, observing the full spectrum of COs, after performing the background correction, the C 1s and O 1s peak can be found at 284.8 and 532.1 eV. Then, using the Gaussian-Lorentzian peak shape to curve fit the C 1s and O 1s spectra. Then, in-depth analyze two spectra, the C 1s spectrum has three components in Fig. 5b, the characteristic of the C–C bond is shown at the main peak of 284.8 eV, the other two peaks near 287.1 and 285.9 eV, which allotted to the C=O and C–OH bond [33]. The allotment of peaks in the O 1s spectrum is meaningful, as the information acquired by the O 1s spectrum. Since the photoelectron kinetic energies of O 1s are lower than those of C 1s, the O 1s

sampling depth is smaller, thus making the O 1 s spectrum are slightly more surface specific [33–35]. As shown in Fig. 5c, when observing the changes of C 1 s spectral region, the O 1s peak near 532.1 eV is considered to stem from the C–OH bond and that at 531 eV to the C=O bond [36]. Meanwhile, As reported in previous research [37], the surface oxygen-containing functional groups can participate in the redox reaction, thereby improving the sodium storage capacity. Even more remarkably, the π – π conjugation was not investigated in the C 1 s spectrum, which confirmed that COs was not stacked by a multi-layered graphitic microcrystallites sheets [31].

The typical CV curves are summarized in Fig. 6a, there are three reduction current peaks are observed near 0.84, 0.32 and 0.01 V



Fig. 5. High-resolution XPS spectra of COs: (a) wide-range XPS spectrum, (b) C 1s, (c) O 1s.



Fig. 6. Electrochemical performance of the COs electrode: (a) CV curves, (b) galvanostatic charge/discharge cycling profiles, (c) cycling performance (at 20 mA g⁻¹), (d) rate performance.

during the first reduction process. The side reaction between the sodium-ion and surface functional groups of COs shows a reduction

peak near 0.84 V, similar to the previously reported behavior of lithium-ion for carbon materials [8]. Based on the previous report,

it is plausible to assign the reduction peak at 0.32 V to the electrolyte component decomposes and formation of the surface SEI film [38,39]. A reduction peak can be observed at 0.01 V, corresponding to the sodiation process. Furthermore, a peak near 0.01 V can be observed during the oxidation process, the feature is interpreted as sodium-ion extraction from the graphitic microcrystallites sheets. In the low potential region, the sodium storage mechanism of the material (Na⁺ + xC + e⁻ \leftrightarrow NaC_x) is consistent with the existing research, which will be illustrated by EIS and GITT measurements below. Noticeably, the CV curves gradually overlaps in the subsequent redox processes, indicating that the attenuation of the reversible capacity of the COs electrode occurs mainly in the first few cycles, then exhibits excellent reversible for the sodium-ion insertion/extraction [40].

Fig. 6b represents galvanostatic charge/discharge curves for the obtained COs electrode, the measured current density is 20 mA g⁻¹. The initial specific discharge and charge capacities are 584 and 272.4 mAh g⁻¹, the initial coulomb efficiency is approximate 46.64%. The irreversible capacity is mainly caused by the formation of SEI film. In addition, the COs electrode shows a significant high potential tilt curve and a platform curve below 0.1 V. The previously reported results have confirmed that the sodium-ion adsorption at the surface or defect sites is in the high potential slope range, the sodium-ion insertion in the graphitic microcrystallites is the low potential platform range [17]. Obviously, the capacity of the COs electrode comes from both. Subsequently, the galvanostatic charge/ discharge curves are gradually overlapped, thereby explaining that the COs electrode has excellent cycle performance, which consistent with the CV observations.

The cycling performance measurement of the COs electrode as exhibited in Fig. 6c, the constant current density is also 20 mA g⁻¹. The COs electrode shows excellent reaction reversibility and structural stability, the reversible capacity is 254.1 mAh g⁻¹ after 100 cycles with a 93.3% capacity retention. According to the research by Cao et al. [17], the attenuation of the reversible capacity

in the cycle may be due to the volume "adjustment" during the sodiation/desodiation process in the material. In addition, as the number of cycles increases, the coulombic efficiency of the COs electrode also increases, and stay relatively stable. This result is superior to the biomass-derived hard carbon for SIBs that have been reported.

The rate performance is a key indicator for evaluating the electrode material. As shown in Fig. 6d, when the initial current density is 20 mA g^{-1} , the COs electrode has a reversible capacity of 273.3 mAh g⁻¹, as the current density gradually increases to 50, 100, 200, 500 and 1000 mA g⁻¹, maintain 10 cycles under each condition, the corresponding reversible capacity is 194.7, 124.3, 87.6, 60.3 and 43.5 mAh g⁻¹, respectively. Interestingly, when the current density is restored to the initial state, the reversible capacity can be rapidly recovered to 251.7 mAh g⁻¹. Considering all measurement results, the COs electrode displays a good rate performance, the expanded interlayer distance of the material can be used to explain this. As we know, the expanded interlayer distance is beneficial for the reversible sodiation/desodiation behavior, this is particularly important for the larger diameter sodium-ion [6,8].

Tab. S1 summarizes the performances comparison of the COs electrodes and some carbon-based materials [41–53]. It can be found that the COs electrode exhibits excellent performance, the small specific surface area can make the formed SEI film limited, thereby reducing irreversible capacity. The nanoscale mesopores facilitate the contact of the electrolyte with the material, improve the sodium-ion migration efficiency. The beneficial surface functional groups can provide more defect sites for sodium-ion adsorption. Most importantly, the expanded interlayer distance ensures reversibility of sodium-ion insertion/extraction, and is very effective for improving the cycling performance.

EIS measurements researched the electrochemical reaction kinetics of the COs electrode during cycling. The Nyquist plots of the EIS measured for different voltage ranges of the fourth discharge and charge cycle are depicted in Fig. 7a and b, respectively, all the



Fig. 7. EIS results for the COs electrode: Nyquist plots at various potentials during (a) discharge and (b) charge, (c) Nyquist plot and fitting curve by using the equivalent circuit (inset in Fig. 7c), (d) sodium-ion diffusion coefficients calculated from the EIS measurements of the COs electrode for discharge and charge.

Nyquist plots are composed of a tilt line in the low frequency range and a semicircle in the high-middle frequency range. As we know, a point in the ultra-high frequency region represents ohmic resistance (R_s, the interface contact resistance between the current collector and electrode material, the unique resistance of the electrolyte and electrode material are included). The semicircle corresponds not only to diffusion migration resistance (R_{SFI}) of sodium-ion through the SEI film, but also as charge transfer resistance (R_{ct}), R_{ct} is known as an electrochemical reaction resistance. Diffused Warburg impedance (Z_w) of the solid diffusion process of sodium-ion inside the material is expressed as the tilt line in the low frequency region. CPE1 and CPE2 are the capacitance for the passivation film and electric double layer capacitor, respectively. The electrochemical resistance generally decreases as the polarization potential of the electrode decreases (Fig. 7a), while it increases with continuous charge (Fig. 7b). In the initial stage of discharge, the electrode material has a lower sodium conductivity, larger electrochemical reaction resistance and electrochemical polarization, then the above conditions are improved with the increase of the degree of discharge. The resistance of the charge transfer process through the SEI film and the active material double layer increases during the charge process, thus increasing the impedance [54]. These of all reflect the dependence of the electrochemical resistance on the polarization potential. In addition, the COs electrode during charging at 0.113 V is illustrated in Fig. 7c, and the internal figure also exhibits the equivalent circuit model.

With the EIS measurements, according to the following equation, the $D_{Na}(EIS)$ can be computed [55–57]:

$$D_{Na}(EIS) = \frac{1}{2} \left[\frac{dE}{dx} \right] \left(\frac{V_m}{FSA_w} \right)^2$$
(1)

where V_m indicates the molar volume, S expresses the effective area of the electrode (can be estimated as the specific surface area

of COs), F represents the Faraday constant, $A_{\rm w}$ represents the Warburg coefficient, and (dE/dx) is the slope of the coulomb titration line.

As shown in Fig. 7d, $D_{Na}(EIS)$ can be calculated using equation (1) equal to 10^{-14} – 10^{-16} cm² s⁻¹. Compared with the value of the lithium-ion diffusion coefficient in the graphite material, this value is smaller, which is mainly caused by the larger diameter sodiumion. Observing the GITT curve between $D_{Na}(EIS)$ and voltage E, it can be seen that the voltage is higher than 0.1 V during discharge, the change of $D_{Na}(EIS)$ value is small, but with the continuous discharge of the COs electrode, the $D_{Na}(EIS)$ value rapidly decreased, indicating that the sodium-ion diffusion has undergone a large change, verifying that the behavior of sodium storage is divided into two processes. As the EIS measurement method for the sodium storage mechanism is similar to that of the GITT measurement, the two results will be analyzed together to explain the transport properties of sodium-ion in the COs electrode.

Measurements of the GITT are carried out, which is also an important method to evaluate the D_{Na} in the COs electrode over different voltage ranges. Fig. 8a shows the GITT curves for the fourth cycle, according to the following equation, the D_{Na} (GITT) can be predicted [58]:

$$D_{Na}(GITT) = \frac{4}{\pi} \left(\frac{m_b V_m}{M_b S}\right)^2 \left[\left(\frac{dE}{d\delta}\right) / \right] \left(\frac{dE}{d\sqrt{\tau}}\right)^2 \quad (\tau < < L^2 / D_{Na})$$
⁽²⁾

where m_b represents the mass of COs, M_b and V_m indicate the molecular weight and molar volume, respectively, S is the effective area of the electrode (can be estimated as the specific surface area of COs), τ is the pulse current time, δ is the stoichiometric parameter, the thickness of the COs electrode is expressed as L. Fig. 8b shows A single GITT titration curve for the COs electrode during discharge, the system is labeled E_0 , E_s , ΔE_τ , ΔE_s , τ in the figure. The



Fig. 8. GITT measurements: (a) GITT potential profiles of the COs electrode for discharge and charge, (b) a single GITT titration curve during discharge, (c) linear fitting of a single GITT titration curve during discharge, (d) sodium-ion diffusion coefficients calculated from the GITT potential profiles of the COs electrode for discharge and charge.

voltage E as a function of $\tau^{1/2}$ shows in Fig. 8c, When the input current is small enough and the time interval is short sufficiently, the instantaneous response of the voltage satisfies the linear function of the square root of time, i.e., $dE/d\tau^{1/2} = \Delta E_{\tau}/\tau^{1/2}$. Simultaneously, the coulometric titration curve is fairly linear within the component range related in this phase, i.e., $dE/d\delta = \Delta E_s/\Delta\delta$, then equation (2) can be further simplified as [58]:

$$D_{Na}(GITT) = \frac{4}{\pi} \left(\frac{m_b V_m}{M_b S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \quad (\tau < < L^2 / D_{Na})$$
(3)

Here ΔE_{τ} is the changes in the electrode potential during passage of the constant current, and ΔE_s is the changes in the electrode potential during passage of the steady-state voltage. Based on equation (3), $D_{Na}(GITT)$ of the COs electrode is calculated, Fig. 8d shows the graphs of $D_{Na}(GITT)$ and voltage E calculated from the GITT curves, it can be observed that the order of $D_{Na}(GITT)$ is $10^{-9} \sim 10^{-10} \, \mathrm{cm^2 \, s^{-1}}$.

Combining with Figs. 7d and 8d, it can find that the trends of D_{Na}(EIS) and D_{Na}(GITT) in different voltage ranges are similar. When the voltage is lower than 0.1 V, $D_{Na}(EIS)$ and $D_{Na}(GITT)$ both appear a sharp decrease, indicating that the sodium-ion diffusion has changed, and the sodium storage mechanism is not unique. According to our earlier research [8], for the hard carbon materials, the sodium storage behavior divides into two types under the different potentials, sodium-ion insertion in the graphitic microcrystallites is in the low potential platform range, sodium-ion adsorption at the surface is in the high potential slope range. Arguably, the interlayer space in the COs electrode is less approachable than the surface sites of the COs electrode. As the surface sites are gradually sodiated, sodium-ion should continue diffuse inside the COs electrode. But, this process wants to be implemented, sodium-ion has to overcome the repulsive charge gradient from the previously bound sodium-ion at the surface locations for diffuse inside the COs electrode, which can further explain the sharp decrease of D_{Na} in the low potential platform region. In combination with the previous reports of lithium-ion diffusion in graphite research, the curves are very similar, indicating that less than 0.1 V low voltage range, the graphite carbon and sodium-ion combine to form Na-GICs, which is a reversible structural phase transition [54,59,60]. It agrees well with the data from EIS and GITT, and further verify the sodium storage mechanism of hard carbon in the low potential platform region.

It is noteworthy that the D_{Na} measured by EIS and GITT are different, which is normal, similar differences in the diffusion coefficient of lithium-ion measured for the same material by different methods are also reported in the literature [59–61]. According to the GITT measurement method, when calculating the $D_{Na}(GITT)$ based on equation (2), the slope $dE/d\tau^{1/2}$ and the factor $dE/d\delta$ are assumed to be constant during each small current pulse, and also unaffected by the voltage drop (IR_b), which in the electrolyte between the counter electrode and sample. Thus, the ohmic effect in the electrolyte and interface can be removed, thereby showing more realistic sodium-ion diffusion information [62]. In EIS, τ depends on the Warburg coefficient, due to the ohmic effects, the Warburg coefficient will increase, which will result in a larger deviation of τ [62]. Summarily, when provided the current pulse height for GITT measurements and the amplitude of the alternating current for EIS, GITT may can provide a more accurate data on D_{Na}. Certainly, the trends of D_{Na} in different voltage ranges measured by GITT and EIS are similar, thus two methods have been used for the related research.

4. Conclusions

Interestingly, we have prepared a hard carbon that was derived from oatmeal. When COs is used as a SIBs anode, it demonstrates an excellent sodium storage performance. The COs electrode can deliver the initial reversible capacity of 272.4 mAh g⁻¹, and the capacity retention can be up to 93.3% after 100 cycles. Simultaneously, for the rate performance measurement, the reversible capacity of the COs electrode can recover to 92.1% after different current density cycles. The excellent electrochemical performances owing to the formation of SEI film is limited by the small specific surface area. The nanoscale mesopores can provide more transport channels for sodium-ion, ensuring that the COs electrode fully contact with the electrolyte, which can also shorten the sodium-ion diffusion pathway and improve the transmission efficiency as well. The presenced surface functional groups can participate in redox reactions. Importantly, the expanded interlayer distance has positive effect on the sodium-ion insertion/extraction process. Furthermore, the D_{Na} of the COs electrode obtained by EIS and GITT measurements are 10^{-14} – 10^{-16} and 10^{-9} – 10^{-10} cm² s⁻¹, respectively. Observing the D_{Na} vs. voltage E curve, it can be found that there is a minimum near 0.1 V, which corresponds to the reversible structural phase transition of Na-GICs formed by the graphite carbon and sodium-ion. Thus, it is verified that the COs electrode has the sodium-ion insertion/extraction behavior between the graphitic microcrystallites sheets in the low potential platform region. Finally, we believe that this hard carbon, obtained from simple processing with green raw materials with exceptional electrochemical performances, is one of the most commercially available anode materials for building the green, safe and low cost SIBs.

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Appendix A. Supplementary data

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