Short Communication

Preparation of High Cycle Performance Carbon-Based Anode Materials Based on Cellulose Aerogels for Lithium-Ion Batteries

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Cellulose aerogels were used as precursors to prepare three-dimensional porous carbon-based anode materials. The structure and morphology of the material were characterized by scanning electron microscope, X-ray diffraction, Raman spectroscopy, and specific surface area tests. The electrochemical properties of the material were investigated by constant current charge-discharge tests. The results showed that the carbonized material had a three-dimensional porous structure, with an initial charging capacity of 803.3mAh/g, a discharge capacity of 836.9mAh/g, and a coulombic efficiency of 95.99%. The reversible capacity of 570.2mAh/g could still be maintained after 100 cycles. This excellent cycling stability was mainly attributed to the high specific surface area of the carbon-based anode material, which facilitated the transport of lithium ions to the electrode/electrolyte interface.

Keywords: Cellulose aerogels; Li-ion battery; Carbon-based anode material; Porous carbon material

1. INTRODUCTION

In response to the increasingly severe energy and environmental crisis, the demand for sustainable development of novel energy materials has become increasingly urgent. Lithium-ion batteries (LIBs) are a novel type of highly efficient and green power supplies and have a wide range of applications in many fields due to a high energy density and good cycle stability [1-3]. Anode materials are important components and parts of LIBs that are attractive subjects of research to scientists. Graphite is a mainstream commercial anode material that has the advantages of a low-voltage platform and stable cycle performance. However, the graphite anodes currently used in commercial lithium-ion batteries have a low theoretical capacity of only 372 mAh/g [4]. The low reversible specific capacity of graphite cannot meet the demand of next generation lithium-ion batteries. Therefore, to develop high-energy and high-power lithium-ion batteries, it is necessary to improve the capacity of the materials used in the cathodes of lithium-ion batteries to solve key problems for the application of lithium-ion batteries. Anode materials with high specific capacities such as porous carbon materials have been reported [5-6]. Porous

carbon materials are widely used as electrode materials because of good electrical conductivities, large specific surface areas and well-developed pore structures [7-8]. Porous carbon materials are typically obtained by carbonization of precursors of natural or synthetic sources, followed by activation [9]. Different synthesis approaches, including templating method [10], etching of metal carbides [11], and sol-gel process [12], have been explored to control the pore structure of porous carbon materials at the micropore and mesopore levels. Carbon aerogels are a class of mesoporous carbon materials prepared by sol-gel polycondensation. Carbon aerogels are a novel porous nanomaterial with a high porosity and low density (up to $0.001 g/cm^3$) [13]. Cellulose aerogels have the advantages of cellulose regeneration, low-carbon and environmentally-friendly [14-15], as well as low density, high porosity, and strong adsorption performance. Cellulose aerogels are among the precursors used to prepare porous carbon materials utilized as negative electrodes with the highest development potential [16-17]. Cellulose aerogels can be used as precursors to promote the mass production of environmentally friendly and low-cost porous carbon-based anode materials. Traditional carbon materials have low theoretical capacities, low energy densities, and few active sites and therefore limited application as anode materials for lithium batteries. Most current research on carbon-based anode materials is focused on carbon materials with good electrical conductivities and high specific surface areas: studies have been performed on the chemical reduction and separation of graphene, carbon nanotubes, and carbon black [18-20]. However, a complex preparation process, high production cost, and nonrenewability severely limit industrial production and large-scale use of these carbon-based anode materials. In this study, a cellulose aerogel was used as a precursor to prepare a carbon-based anode material by high-temperature carbonization. The three-dimensional network structure of the cellulose aerogel resulted in excellent porosity for the prepared material. Carbonization at high temperatures created secondary pores in the cellulose aerogels while maintaining the three-dimensional network skeleton structure. The carbon-based anode material obtained using the cellulose aerogel precursor had the advantages of a good electrical conductivity, a large specific surface area, and a high porosity. The three-dimensional pore structure of the material can shorten the insertion and deintercalation paths of lithium ions and increase the number of active sites for the transmission of lithium ions. A large specific surface area can increase the number of bound lithium ions, thus speeding up electron conduction. The use of a cellulose aerogel to prepare a carbon-based anode material with excellent cycling and rate performance provides a novel strategy for preparing low-cost environmentally friendly lithium batteries.

2. EXPERIMENTAL SECTION

2.1 Chemicals

The cellulose powder, urea, sodium hydroxide, polyvinylidene fluoride (PVDF), and N-methyl-2 pyrrolidone (NMP) used in this study were analytically pure. All chemical reagents were purchased from Sinopsin Chemical Reagents Co., Ltd.

2.2 Preparation of porous carbon-based anode materials

Cellulose powder was added to sodium hydroxide, urea, and an aqueous solution, and the mass

fraction of cellulose powder was 5%-8% and the mass ratio of sodium hydroxide, urea, and water was 7:12:81 in the resulting mixture. The mixed solution was evenly stirred with magnetic stirrers to ensure the cellulose was fully swollen, and the gel was then frozen at -18 °C for 24 h. Then, the hydrogel was rinsed repeatedly with distilled water, and the cellulose aerogel was freeze-dried in a vacuum. The obtained cellulose aerogel was placed in a furnace and heated to 800 °C (using a 5 °C/min heating rate under an argon atmosphere). The furnace was maintained at 800 °C for 4 h and then cooled naturally to ambient temperature, yielding a porous carbon-based anode material.

2.3 Characterizations of material structure and morphology

A sample of the prepared material was coated with gold and the morphology was then observed using a scanning electron microscope (SEM, S-570, Hitachi, 7Ibaraki, Japan) with an accelerating voltage of 30 kV.

X-ray diffraction (XRD, XPertPro) patterns were obtained using a PANalytical X'pert diffractometer at 40 kV and 40 mA using Cu Ka radiation. Raman spectroscopy (RM-1000, Renishaw) using a 514.5-nm excitation (with an Ar+-ion laser) was used to characterize the optical properties of the material. The specific surface area was determined using a specific surface-aperture tester (BET, Tri Star II 3020). A temperature of 77 K and a nitrogen adsorption medium were used.

2.4 Electrochemical measurement

An anode was fabricated by mixing the as-produced porous carbon-based anode material, carbon black (super P), and PVDF in weight proportions of 8:1:1. Then, the mixture was stirred with an appropriate quantity of NMP to produce a uniform slurry. The slurry was pasted on a Cu foil to produce an electrode film that was then dried at 65 °C in a vacuum oven for 24 h and washed to produce circular electrode sheets. The average mass content of the electrode was 1.5 mg•cm^{-2}. Cells were assembled in an argon-filled glove box with a water/oxygen content lower than 0.1 ppm. The electrolyte was 1 mol•L^{-1} LiPF$_6$ dissolved in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 by vol.). Electrochemical characterization was performed with CR2032 coin cells (composed of a Celgard 2300 film, lithium foils, and working electrodes) at room temperature. Galvanostatic measurements were conducted between 0.05–2 V on a LAND cycler (CT 2001A, Wuhan Kingnuo Electronic Co., China), where the cells were aged for 6 h for full electrode infiltration before testing.

3. RESULTS AND DISCUSSION

SEM images of the precursor cellulose aerogel and porous carbon-based anode materials are shown in Fig. 1. The figure shows that the carbonized carbon-based anode material retained the porous three-dimensional network structure of the cellulose aerogel. The original three-dimensional network structure of the cellulose aerogel resulted in the formation of secondary pores.
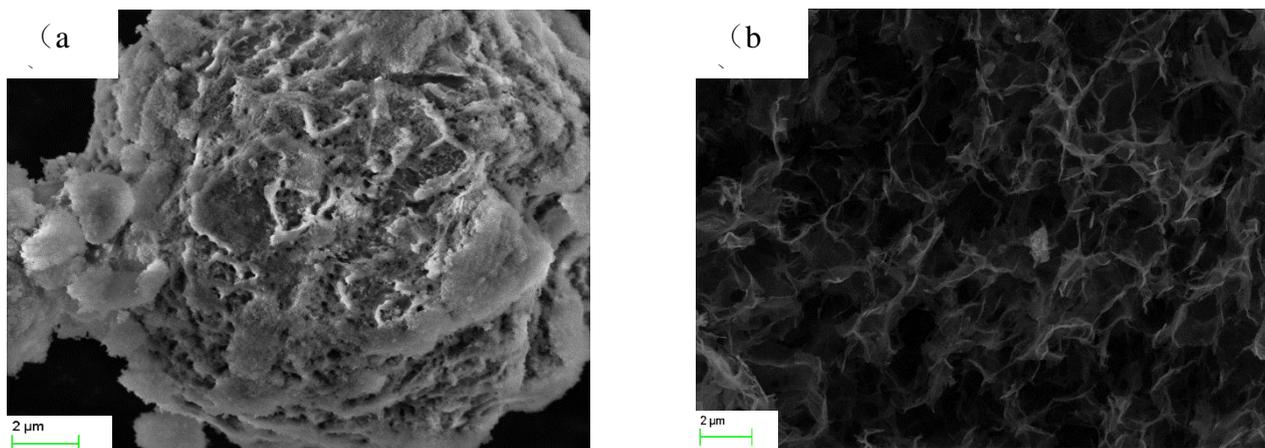
Figure 1. SEM micrographs of the precursor cellulose aerogel (a) and porous carbon-based anode material (b)

The XRD pattern of the porous carbon-based anode material is shown in Fig. 2. The first broad peak (002) at approximately 25.6° was related to the spacing between graphene layers in the turbostratic domains. The weak absorption peak (100) at 43° corresponded to the planar characteristic peak of graphite. These results showed that the carbonized carbon-based anode material was amorphous.
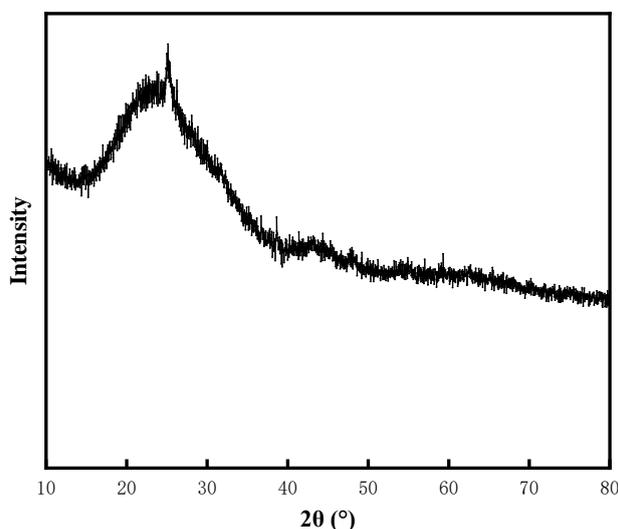

Figure 2. XRD pattern of the porous carbon-based anode material

Fig. 3 shows the Raman spectra of the porous carbon-based anode material. Two characteristic peaks corresponding to the D band (1350 cm^{-1}) and G (1580 cm^{-1}) band were observed. In general, the D band represented defects and disorders in the structure [21], whereas the G band indicated sp^2 hybridization of the carbon network [22]. The ratio of the integrated areas of D and G bands ID/IG was 0.89 and was related to the number of defects in the material [23]. This result showed that the porous carbon-based anode material had a high degree of graphitization and disorder, which facilitated electron conduction and increased the quantity of stored Li$^+$. Therefore, the incorporation of the prepared material enhanced the battery capacity.

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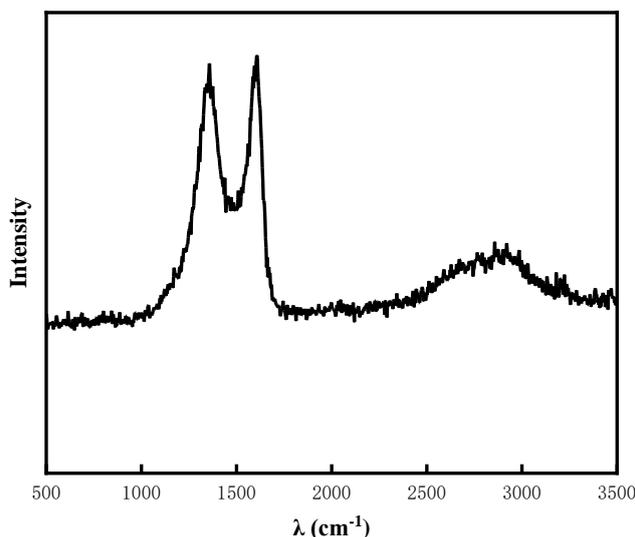
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Figure 3. the Raman spectrum of the porous carbon-based anode materials

Further characterizations were performed to determine the texture and porosity of the prepared material. Nitrogen adsorption/desorption was used to determine the Brunauer–Emmett–Teller (BET) specific area. The results are presented in Fig. 4. Both the isotherms of the precursor cellulose aerogel and porous carbon-based anode material exhibited distinct hysteresis loops and were therefore classified as type IV plots based on the IUPAC classification [24]. At a low relative pressure (P/P0<0.2), there was no discernible monolayer-to-multimonolayer transition, indicating that there were few micropores in the sample. A lag in the both the isotherms of the precursor cellulose aerogel and carbon-based anode material appeared at a relative pressure of approximately 0.8, whereas prominent adsorption and desorption peaks only appeared under high pressure, indicating that the structures of the precursor cellulose aerogel and carbon-based anode material were mainly mesoporous. The corresponding aperture distribution diagrams showed that the precursor cellulose aerogel and carbon-based anode material were mainly mesoporous. A mesoporous structure can shorten the diffusion path of Li^+ and facilitate volume expansion to increase the rate capability during the charge/discharge process. BET adsorption theory was used to calculate a specific surface area of 52.96 m^2/g for the precursor cellulose aerogel and a considerably higher value of up to 620.63 m^2/g for the carbon-based anode material. A large specific surface area can increase the contact area between the material and an electrolyte, as well as increase the number of active sites for Li^+ transmission, which can improve the specific capacity of the anode material [25].
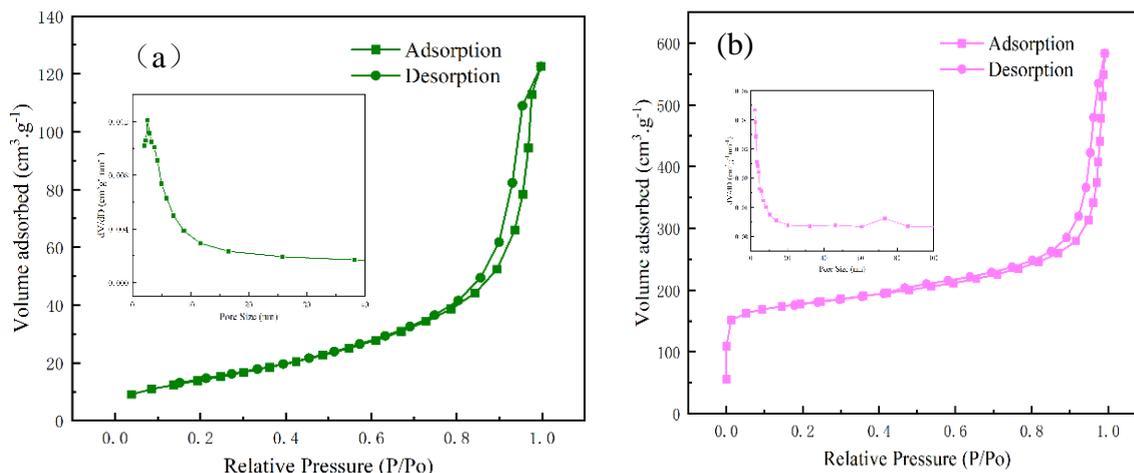
Figure 4. N_2 adsorption/desorption isotherms of the precursor cellulose aerogel (a) and porous carbon-based anode material (b)

Fig. 5 shows the charge–discharge curves of the porous carbon-based anode material at a current density of 100 mA/g f for the first, tenth and fiftieth cycles. The anode material exhibited a high initial discharge capacity of 836.9 mAh/g, a charge capacity of 803.3 mAh/g, and an initial coulombic efficiency up to 95.99. During the tenth cycle, the charge and discharge capacities were 579.3 mAh/g and 589.3 mAh/g, respectively. At the end of 50 cycles, the porous carbon-based anode materials exhibited a specific capacity of 543.5 mAh/g, along with a high capacity retention rate of 99.37%. The discharge process of the lithium battery mainly involved alloying between lithium ions and the anode material, and therefore the specific capacity represented the capacity for the lithium-ion alloying process. As the charging process mainly involved Li^+ stripping, the charging capacity represented the reversible stripping capacity of Li^+. The higher the coulombic efficiency is, the smaller the Li^+ loss and irreversible capacity during the charging and discharging processes are. The carbon-based anode material prepared by carbonization of the cellulose aerogel had a good charge–discharge capacity and Coulombic efficiency. This result indicated that Li^+ exhibited good imbibition behavior in the prepared material, which can be attributed to the enhancement of the Li^+ transmission rate by the three-dimensional porous material structure.

Figure 6 shows the cycling performance of the porous carbon-based anode material obtained at a current density of 100 mA/g. After 100 charge and discharge cycles, the specific charging capacity, discharge capacity, and Coulomb efficiency were 570.2 mAh/g, 570.4 mAh/g, and 99.97%, respectively. This result indicated that the large specific surface area and mesoporous structure of carbon-based anode material provided a large space for Li^+ storage. Li^+ completely reacted at the electrode/electrolyte interface, thus improving the cycling stability of the electrode material. Guan [26] performed a similar study, except that resorcinol and formaldehyde (RF) were used as precursors to prepare carbon aerogels via a sol-gel process. The results showed that carbon aerogels can be considered ideal electrodes for rechargeable batteries due to a high surface area, an electrically conducting network, and chemical inertness.
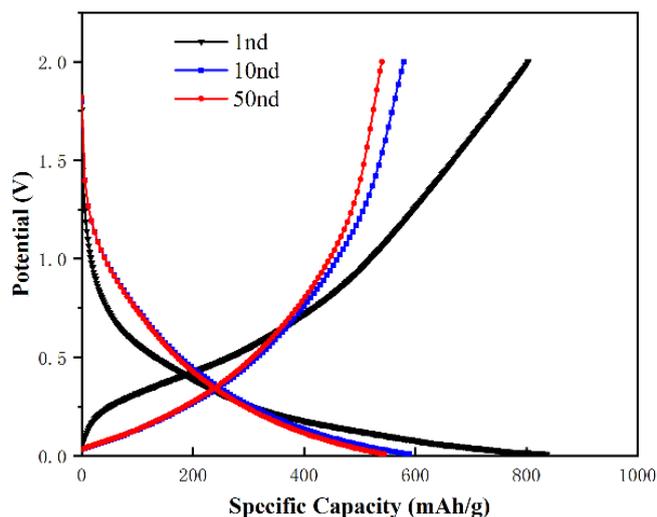
Figure 5. Charge–discharge curves of the porous carbon-based anode material obtained at a current density of 100 mA/g

The initial charge capacity was 958.6 mAh/g. However, the ratio of the rechargeable capacity to the total capacity (first cycle) was in the 30% to 40% range. Unlike the study by Guan, we used a cellulose aerogel as a precursor to prepare carbon electrodes, resulting in a significant improvement in the cycling stability of the electrode material. The microporous structure of the carbonized material can enhance the stability of SEI films, thus preventing solvent molecules from damaging electrode materials.
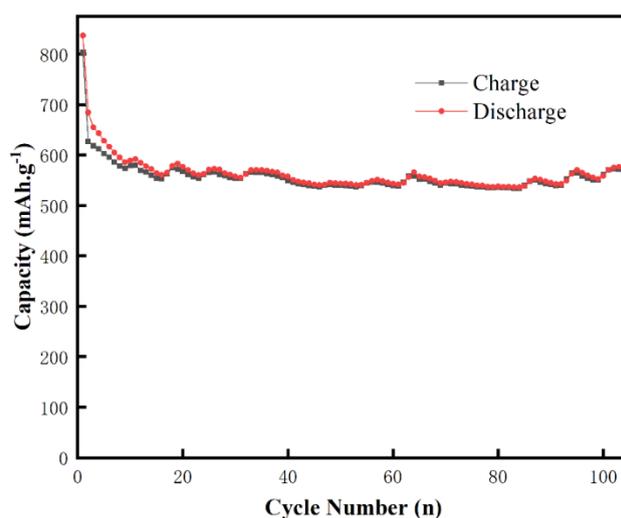

Figure 6. Cycling performance of the porous carbon-based anode material at a current density of 100 mA/g

Figure 7 shows the rate capability of the porous carbon-based anode material within a range of current densities 100−2000 mA/g. The discharge capacity of the battery remained above 800 mAh/g after 10 cycles at a current density of 100 mA/g. After 10 charge–discharge cycles at a current density

of 200 mA/g, the discharge capacity of the battery was 748.65 mAh/g. After 10 charge–discharge cycles at a current density of 500 mA/g, the discharge capacity of the battery was maintained at 682 mAh/g. The discharge capacity of the battery after 10 charge–discharge cycles at a current density of 1000 mA/g was 661 mAh/g. After 10 charge–discharge cycles at a current density of 2000 mA/g, the discharge capacity was maintained at 614 mAh/g. After restoring the current density to 100 mA/g, the discharge capacity quickly recovered to 818.8 mAh/g and was 731 mAh/g after 10 cycles. This result showed the excellent rate performance of the anode material. This excellent performance was ascribed to the three-dimensional structure of the porous carbon-based anode material, which resulted in a decrease in the diffusion distance of the Li ions during charging/discharging and facilitated fast Li-ion storage.
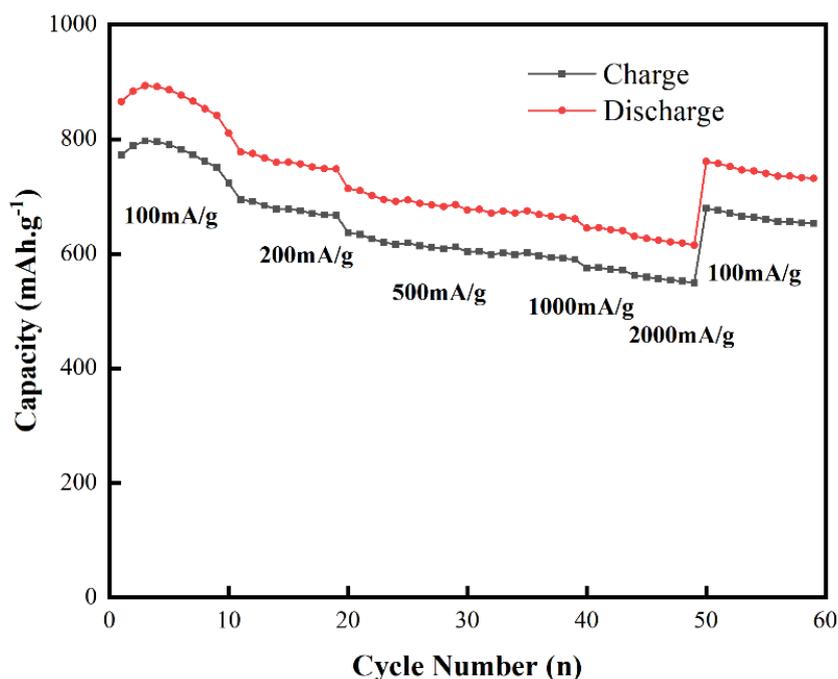

Figure 7. Rate capability at different current densities of the porous carbon-based anode material

The comparison of the electrochemical lithium-storage performance of electrode materials presented in this work other anode materials were added in table 1. In this work, cellulose aerogel as a green and renewable carbon material, was used to prepare porous carbon-based anode materials. As can be seen from table 1, the porous carbon-based anode materials in this work exhibits a higher capacity. This anode material displayed improved electrochemical performance, which could be attributed to its large surface area, abundant porosity, and conductive networks facilitate the lithium reactions.

Table 1. Comparison of the electrochemical lithium-storage performance of electrode materials presented in this work with reported by previous researchers.

Electrode materials	Methods	Specific discharge capacity (mAh/g)	Cycle number	Current density (mA/g)	Reference
Porous carbon materials	cellulose aerogel carbonization	570.4	100	100	This work
NGA	Graphene oxide reduction	230	100	100	27
Sn/C	Composite calcination method	373.5	100	100	28
Petroleum carbon	Direct pyrolysis	264	50	100	29
bamboo shoot carbon	Carbonization	575	50	100	30

4. CONCLUSION

Cellulose aerogels were used as a precursor to prepare a three-dimensional porous carbon-based anode material with a high charge–discharge capacity and coulombic efficiency, as well as an excellent rate performance. After 100 charge–discharge cycles at a current density of 100 mA/g, the specific charging capacity of the carbon-based anode material remains at 570.2 mAh/g and the coulombic efficiency is 99.97%. This result was mainly obtained because the prepared material has a high specific surface area, which can provide a large number of active sites for the transmission of Li^+, and the three-dimensional porous structure can shorten the diffusion path of Li^+ and prolong the service life of a battery. Using a three-dimensional cellulose aerogel as a precursor produces a carbon-based anode material with an excellent electrochemical performance and should be further considered and experimented upon as a promising anode material for lithium-ion batteries with a high power density and energy.

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