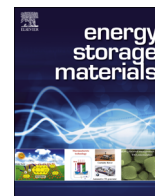




ELSEVIER

Contents lists available at ScienceDirect

Energy Storage Materials

journal homepage: www.elsevier.com/locate/ensm

Commercial carbon molecular sieves as a high performance anode for sodium-ion batteries



Si-Wei Zhang^{a,1}, Wei Lv^{a,1}, Chong Luo^a, Cong-Hui You^a, Jun Zhang^a, Zheng-Ze Pan^a, Fei-Yu Kang^a, Quan-Hong Yang^{a,b,*}

^a Shenzhen Key Laboratory for Graphene-based Materials and Engineering Laboratory for Functionalized Carbon Materials, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

^b School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

ARTICLE INFO

Article history:

Received 23 December 2015

Received in revised form

24 December 2015

Accepted 24 December 2015

Available online 1 January 2016

Keywords:

Carbon molecular sieve

Sodium ion battery

Anode

Ultra-small pore

ABSTRACT

A commercial carbon molecular sieve (CMS) demonstrates excellent Na ion storage performance and is the best among current commercially available materials and much better than most hard carbons reported with complex microstructures. With a very low specific surface area measured by N₂ adsorption, the CMS shows a high reversible capacity of 297 mA h/g at a relatively high current density of 100 mA/g, and, more promising, a very high initial Coulombic efficiency of up to 73.2%, which is the highest among unmodified commercial carbons. Such good performance is mainly the result of its abundant ultra-small (0.3–0.5 nm) pores that only allow the insertion of Na ions while rejecting the electrolyte, thus preventing its contact with the carbon surface, which is a basic principle for the design of a high performance anode material for a sodium-ion battery (SIB). The CMS also exhibits high rate and cyclic performance. Such performance basically meets the demand for commercial anode materials for a SIB, and hopefully, this finding will promote the commercialization of SIBs for practical use as graphite does for lithium-ion batteries.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

With the increasing demand for low cost and large-scale “green” energy storage for power grids and other applications, sodium-ion batteries (SIBs) rather than lithium-ion batteries (LIBs) have attracted great interest due to the worldwide abundance of sodium and the low cost of sodium-precursors [1–3]. However, the practical use of SIBs is not possible at the moment, and one of the most important reasons for this is the lack of a suitable anode for Na ion storage [4–6]. Although Li and Na have many similar properties, graphite, which is used as the anode of commercial LIBs, cannot be used for SIBs and this fact has been known since 1988 [7]. This is mainly because of the larger radius of Na ions for intercalation and the fact that there is no stable position for Na on a graphene layer [8]. Thus, many researchers have investigated Na ion storage in disordered carbons, which relies on a pore-filling mechanism, and high porosity is therefore normally needed to reach a high capacity and rate capability [9–12]. Previous reports

have shown these carbons have a high capacity, but a low initial Coulombic efficiency and poor cyclic stability because the high specific surface area (SSA) induces the formation of a solid electrolyte interphase (SEI) layer making these carbons practically unusable [10]. Although expanded graphite shows promise in avoiding these problems, their low capacity cannot meet the demand of high energy density [13,14].

Recently, several reports have shown that hard carbons with a low SSA (less than 10 m²/g), such as carbons derived from mixtures of pitch and phenolic resin [15], resorcinol and formaldehyde [16], and graphene oxide and sucrose [17], exhibit a high initial Coulombic efficiency of over 80% and good cyclic stability because the contact area between electrode and electrolyte is much lower while still leaving enough interlayer space for the intercalation of Na ions. However, for these carbons, high-temperature graphitization is normally required to eliminate defects and achieve a high Coulombic efficiency [18]. In addition, the low yields of these carbon precursors also restrict their practical applications. Considering that a carbon material is still most promising for the commercialization of SIBs, the finding of a commercially available carbon with a suitable structure for Na ion storage is urgently needed [6]. The basic principle underlying the design for a high performance carbon-based anode for a SIB is that ultra-small pores (0.3–0.5 nm) are required that allow only Na ion insertion while

* Corresponding author at: Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China.

E-mail addresses: yang.quanhong@sz.tsinghua.edu.cn, qhyangcn@tju.edu.cn (Q.-H. Yang).

¹ These authors equally contributed to this work.

rejecting the electrolyte, thus preventing its contact with the carbon surface. Considering that the predicted minimum inter-layer space required for Na ion insertion is 0.37 nm in anode materials [19], we propose that the pore size of a commercial carbon molecular sieve (CMS) for N₂/O₂ separation (0.3–0.5 nm) may fully meet the requirement for Na ion insertion [20–22].

In this study, we carefully investigated the potential of a commercial CMS as the anode for SIBs and demonstrated its excellent Na ion storage performance. Free of any modifications, the commercially obtained CMS shows a much higher reversible capacity than most previously reported porous carbons. The value measured is 297 mA h/g at a current density of 0.1 A/g, and more promisingly, it has a high initial Coulombic efficiency (73.2%). The carbon also shows superior rate capability and good cyclic stability. For comparison, graphite and a commercial active carbon (AC) measured under the same conditions show a lower capacity (50 mA h/g and 180 mA h/g, respectively) and a much lower initial Coulombic efficiency (32.0% and 21.1%, respectively). These results clearly demonstrate that the commercial CMS is a promising anode for SIBs and, due to its commercial availability on a large scale, may promote the commercialization of SIBs as graphite does for LIBs.

2. Experimental

2.1. Materials

The carbon molecular sieve is type 1.5GN-H purchased from Kuraray Chemical (Japan), and its specifications can be found in the MSDS data sheet [23]. The active carbon is type XFP06 7440-44-0 purchased from Nanjing XFNANO Materials Tech Co., Ltd (China). Graphite powder is natural flake graphite of 800 mesh purchased from Qingdao Huatai Graphite Co., Ltd (China). All the samples were used without any modifications.

2.2. Materials characterization

The morphologies of the samples were characterized by scanning (SEM, TESCAN, MIRA3, Czech Republic) and transmission electron microscopy (TEM, F30 FEI). The X-ray diffraction (XRD) measurements were obtained at room temperature using a Rigaku D/max 2500 PC diffractometer (Rigaku Corp., Japan) using Cu K α radiation ($\lambda=0.154$ nm). Nitrogen adsorption experiments were conducted using a Micromeritics ASAP 2020 analyzer at 77 K. Carbon dioxide adsorption experiments were conducted using a BELSORP-MAX-12-NVP-DPP (Japan) analyzer at 273 K. The specific surface area and the pore size distribution were obtained from Brunauer–Emmett–Teller (BET) analyses of the adsorption isotherms and density functional theory (DFT) methods, respectively. Fourier transform infrared (FTIR) spectra were collected with a Nicolet iS50 instrument. Raman spectra were recorded with a multi-wavelength micro-Raman spectroscope (JY HR800) using 532.05 nm incident radiation.

2.3. Electrochemical measurements

Electrochemical measurements were carried out using 2032-type coin cells containing electrolyte of 1 M sodium perchlorate (NaClO₄) dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (volume ratio: 1:1). The electrode slurry was prepared by mixing active material (70 wt%), carbon black (15 wt%) and polyvinylidene fluoride (PVDF, 15 wt%) in N-methyl pyrrolidinone (NMP), and then coated on a Cu foil. A sodium foil was used as the counter electrode, and a glass fiber (Whatman GF/D CAT NO. 1823-257) as the separator. All cells were assembled

with 1.2 mg active material per cell inside an Ar-filled glovebox. All of the cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements were obtained using a Solartron 1470E Cell Test electrochemical workstation. The CV tests were conducted between 0.005 and 2.5 V (vs. Na/Na⁺) at a scan rate of 0.1 mV/s. The EIS tests were measured in the frequency range of 100 kHz to 10 mHz at an open-circuit potential and the modulating amplitude was 5 mV. The galvanostatic charge/discharge performance tests and the rate capability tests at different C-rates were performed using a Land 2001A cell test system (Wuhan, China) at room temperature.

3. Results and discussion

As shown in the inset of Fig. 1a, bulk CMS is a black, cylindrical solid with a diameter of 1.4–1.6 mm and a length of 3–6 mm. According to the production data sheet, the carbon content of the CMS is >98% and it has a specific gravity of 0.65–0.70 g/cm³, ensuring its high volumetric energy density and making it more practicable than many nanomaterials with low density. In order to prepare the electrode slurry, a large piece of CMS was ground into powder with a particle size of 1–4 μ m, which can be seen in the scanning electron microscope (SEM) image in Fig. 1a. It is noted that these particles are solid and no pores can be observed. We also used a commercial AC and graphite as reference samples for comparison. The morphology of both samples are shown in Fig. 1b and c with AC having solid particles of about 2 μ m size and graphite having a much larger particle size with a lamellar structure. The microstructures of these three samples are further investigated by transmission electron microscopy (TEM). The CMS shows graphitic-like domains of \sim 4 nm length that are twisted together in a disordered manner and a high resolution TEM image (Fig. S1a and c) shows the distance between the graphitic layers in these domains is about \sim 0.4 nm, which is in agreement with data obtained from the X-ray diffraction (XRD) patterns in Fig. 1e. A broad diffraction peak at 22.7° (2θ) for CMS also suggests its long-range disordered graphitic-like structure, and the interlayer spacing calculated from the Bragg equation is about 0.391 nm, in agreement with the TEM observation (Fig. S1c). In contrast, the AC shows a totally disordered structure as indicated by the absence of peaks in the XRD pattern and further proved by the TEM image in Fig. S1b, while the strong and sharp peak at 26.5° (2θ) in the XRD pattern of graphite indicates its good crystal structure with an interlayer distance of \sim 0.335 nm. In Raman spectra (Fig. 1f), the sharp G-band of graphite suggests its good crystal structure composed of sp² carbons, and the I_D/I_G values of AC and CMS are about 0.85 and 1.05, respectively, indicating their disordered structure and more exposed edges. It is noted that the I_D/I_G of CMS is higher than that of AC, possibly because CMS is more sp³ carbon induced by the large number of functional groups as indicated by FTIR spectroscopy (Fig. S1d). These functional groups result in better wetting quality of the material by the electrolyte, which ensures high rate performance even with a large particle size.

The microstructure of CMS was further investigated by N₂ and CO₂ adsorption measurements. Table 1 summarizes the porous structure of the CMS and reference samples. As shown in Fig. 2a, the N₂ adsorption/desorption isotherm of CMS is of type II, characteristic of a nonporous solid (not accessible for nitrogen adsorption) and the very low adsorption amount suggests a low SSA calculated by the N₂ adsorption (17 m²/g). Graphite also shows a very low adsorption volume and a low SSA (7 m²/g), but it has a type III adsorption isotherm (Fig. 2c), suggesting its surface has a weaker interaction with the N₂ molecules than does CMS. In contrast to these two carbons, AC shows a type I isotherm with micropores centered at 1–2 nm and large SSA of 2164 m²/g. Such a

Download English Version:

<https://daneshyari.com/en/article/1564630>

Download Persian Version:

<https://daneshyari.com/article/1564630>

[Daneshyari.com](https://daneshyari.com)