



Highly disordered hard carbon derived from skimmed cotton as a high-performance anode material for potassium-ion batteries

Xiaodong He^a, Jiaying Liao^a, Zhongfeng Tang^a, Lina Xiao^a, Xiang Ding^a, Qiao Hu^a, Zhaoyin Wen^b, Chunhua Chen^{a,*}

^a CAS Key Laboratory of Materials for Energy Conversions, Department of Materials Science and Engineering & Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Anhui Hefei 230026, China

^b Key Laboratory of Energy Conversion Laboratory, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

HIGHLIGHTS

- Acid soaking on skimmed cotton is utilized to achieve disordered porous structure.
- The disordered porous structure is favorable for the high rate potassium storage.
- Various techniques are adopted to elucidate the electrochemical storage mechanism.

ARTICLE INFO

Keywords:

Potassium storage
Rate performance
Anode
Cotton
Full cell

ABSTRACT

Potassium-ion batteries attract tremendous attention for large scale application due to the abundance of K resources. Herein, a highly disordered hard carbon derived from a skimmed cotton is investigated for this purpose. The study shows that a simple soaking treatment in hydrochloric acid for the skimmed cotton before its high-temperature carbonization can critically impact the structure and the electrochemical properties of the obtained hard carbon significantly. This hard carbon exhibits a high initial coulombic efficiency (73%) and superior cycling stability and rate capability (253 mAh g⁻¹ and 165 mAh g⁻¹ at 40 mA g⁻¹ and 4000 mA g⁻¹, respectively) due to its unique porous architecture and large surface area. The full cell by coupling the hard carbon with a cathode material, i.e. potassium-rich iron hexacyanoferrate shows an outstanding electrochemical performance. These promising properties highlight the potentials of such a hard carbon in practical applications.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been developed successfully as power sources for portable electronic devices, electric vehicles and electrical energy storage applications [1–5]. However, the reserves of lithium on the earth is a bottleneck of LIBs, developing metal-ion batteries beyond LIBs is necessary in the long run. Sodium ion batteries (NIBs) and potassium ion batteries (KIBs) have both attracted tremendous interest these years due to their remarkable energy density and abundant resources [6–11]. Particularly, the standard potential of K⁺/K (–2.88 V vs. the SHE) is 0.32 V lower than that of Na⁺/Na (–2.56 V vs. the SHE) [12], which allows KIBs achieve higher voltage operation and energy density than SIBs.

Electrodes play a key role in the KIB technology. For the cathode side, many research groups have studied Prussian blue analogs, organic solids or layered metal oxides (K_xMO₂) [13–15]. As for the anodes,

carbon based materials such as graphite, carbon nanotubes (CNTs), soft carbon and hard carbon get wide range of developments due to their nature abundance and high capacity [16–20]. Graphite in KIBs achieves a high reversible capacity of 270 mAh g⁻¹, which is close to the theoretical value 279 mAh g⁻¹ when KC₈ forms upon potassiation. However, graphite undergoes a huge volume expansion by 61% during the potassiation, resulting in an inferior cycle life and rate capability [16]. CNTs are limited by its poor initial coulombic efficiency (usually less than 20%). Goonetilleke et al. used single-walled and multi-walled carbon nanotubes as anode materials on KIBs, similar to their work on NIBs [21]. The single-walled CNTs delivered an initial discharge capacity of 1000 mAh g⁻¹ but only 196 mAh g⁻¹ is reversible and this capacity rapidly decreases to 110 mAh g⁻¹ after 20 cycles. Multi-walled CNTs also produced a high 1st discharge capacity of 3858 mAh g⁻¹ with a very poor initial coulombic efficiency of only 9%. To address the drawbacks of these KIBs anode, Wang et al. constructed a novel

* Corresponding author.

E-mail address: cchchen@ustc.edu.cn (C. Chen).

polycrystalline semi-hollow microrods-structured soft carbon as a KIB anode, which exhibited a capacity of over 320 mAh g⁻¹ at a current density of 100 mA g⁻¹ and retained 249 mAh g⁻¹ after 100 cycles. However, when the current density was increased to 1 A g⁻¹, this soft carbon only delivered a specific capacity of 110 mAh g⁻¹. Furthermore, the initial coulombic efficiency of this soft carbon was only 58% [18].

Hard carbon (HC) is considered to be a promising anode in both NIBs and KIBs due to its larger interlayer spacing and stable structure. Jian et al. first prepared hard carbon spherules as the anode material in KIBs with a high initial coulombic efficiency of 76% and good cycling stability. Nevertheless, this hard carbon spherules suffers poor rate capability with only 121 mAh g⁻¹ at a current density of 1.4 A g⁻¹ [22]. To enhance the rate capability of hard carbon, Yang et al. synthesized a novel nitrogen/oxygen dual-doped hard carbon which shows an excellent rate performance with 118 mAh g⁻¹ at 4 A g⁻¹. However, a poor initial coulombic efficiency of 25% limits its practical applications in KIBs [23].

To tackle the aforementioned drawbacks, in this work, we prepare hard carbon (HC) materials by using a skimmed cotton as a precursor and studied their K-ion storage performance. After a treatment with hydrochloric acid and following carbonization, the skimmed cotton derived hard carbon exhibits a promising high initial coulombic efficiency, excellent rate capability and cycling stability. Furthermore, a full K-ion cell is realized.

2. Experiments

2.1. Electrode preparations

A skimmed cotton was first immersed into 100 mL deionized water or 100 mL HCl (1.0 M) for 24 h, respectively, and then washed with deionized water and dried at 80 °C overnight in a vacuum oven. The dried treated cottons were first decomposed at 900 °C for 2 h and then carbonized at 1200 °C (heating rate: 5 °C min⁻¹) in a tube furnace with Argon flow of 200 sccm min⁻¹. The fabricated hard carbons were denoted as HC-H₂O and HC-HCl. To construct full cells, a cathode material, i.e. potassium iron hexacyanoferrate (KFe[Fe(CN)₆] or KFeHCF) was synthesized using a typical co-precipitation method according to our previous work [24].

2.2. Characterization

Fourier transform infrared spectroscopy (FT-IR, Magna-IR 750 spectrometer) was performed on both HC-precursors by direct transmittance using KBr pellet. The structures of the as-prepared samples were characterized on an X-ray diffractometer (TTR-III, Cu K α radiation) at a scan rate of 5° min⁻¹. The ex-situ XRD of the electrodes were carried out by disassembling the coin cell at different charging/discharging status. Moreover, the parafilm (Neenan, WI 54956) was used to prevent the electrode from being oxidized during testing. The morphologies of the samples were investigated with field emission scanning electron microscopy (FESEM, Zeiss Supra 40) and the EDS mappings were measured by an energy-dispersive X-ray (EDX) spectrometer (Bruker Quantax, XFlash 6130). The microstructures were investigated with high-resolution transmission electron microscopy (HRTEM, JEM-2100F). Thermal gravimetric analysis (TGA) curves were obtained on a TA Instruments (SDT Q600) under flowing N₂. Raman spectrometer (Renishaw inVia Raman Microscope) were performed to analysis the graphitization of HCs. Their specific surface areas and pore size distribution results were determined by nitrogen adsorption and desorption method (Tristar II 3020 M, Micromeritics).

2.3. Electrochemical evaluation

The electrochemical performances of HC-H₂O and HC-HCl were carried out using coin-type half-cells (CR2032 size). The hard carbon

electrodes were comprised of the active materials (80 wt%), Super-P (10 wt%) and sodium carboxymethyl cellulose (CMC, 10 wt%) as the binder. They were mixed in deionized water and the obtained homogeneous slurries were pasted on a copper foil. After drying at 80 °C overnight in a vacuum oven, the electrode disk was fabricated with a diameter of 12 mm. The mass loading of the hard carbon was about 1.0 mg cm⁻². For the fabrication of potassium half-cells, a potassium metal foil was used as the counter electrode. Moreover, KFeHCF was used as the active cathode material for the full-cells. The cathode electrode was prepared by casting a slurry of KFeHCF (70% wt%), acetylene black (20 wt%) and polyvinylidene fluoride (PVDF) (10 wt%) onto an aluminum foil. The mass loading of KFeHCF was about 3.0 mg cm⁻². In order to preferably reveal the full cell properties, the hard carbon electrodes were first discharged and then charged to remove the irreversible capacity. 1.0 M KPF₆ dissolved in DME was used as the electrolyte and a Whatman glass-fiber was used as a separator. CR2032 coin cells were assembled in an argon filled glove box (MBRAUN LABMASTER 130) and then aged for 10 h to ensure full infiltration of electrolyte into the electrodes. The cyclic voltammetry (CV) of the cells was conducted on a CHI 660C electrochemical workstation at a scan rate of 0.2 mV s⁻¹–10 mV s⁻¹ between 0 and 2.5 V. The electrochemical cycling was performed on a multi-channel battery test system (Neware BTS-2300, Shenzhen) in the voltage ranges 0.01–2 V (for HC-H₂O and HC-HCl half-cells) and 1.5–4.1 V (for full-cells) at 25 °C. The specific capacity of half-cells and full-cells were both based on the mass of hard carbon materials.

3. Results and discussion

Fig. 1 shows the SEM images of the initial skimmed cotton precursors and the resultant hard carbons. The precursors are composed of cellulose fibers with diameters around 10–15 μ m. After the carbonization at 1200 °C under Ar, the hollow tubular structure and braided fibrous morphology is observed in both carbonized samples. The fiber diameter of the as-obtained hard carbon has a reduced to 4–10 μ m. These structures promote the infiltration of the electrolyte and shorten the diffusion distance for K⁺ ions, improving the electrochemical performance of the hard carbons.

In order to better understand the effect of HCl treatment on the microstructure of the derived HC-precursors, the FT-IR spectra of these two precursors are also measured (Fig. S1). A broad band around 3432 cm⁻¹ on the spectra of both samples indicates the stretching vibration of free O-H, which exhibits more significant absorption after the infiltration of HCl. The C-C band at 1163 cm⁻¹ and the C-O-C glycosidic ether band at 1112 cm⁻¹ arising from the polysaccharide component become weakened significantly after the acid treatment [25–27]. This result indicates that the highly polymerized cellulose chain is destroyed and the cellulose skeleton structure become more disordered, which ultimately impact the disordered structure of the final product. The acid catalytic hydrolysis process can be divided into three steps as shown in Fig. S2. TGA results in Fig. S3 also confirm this catalytic hydrolysis process. HC-HCl-precursor shows more weight loss than original skimmed cotton and HC-H₂O-precursor from the temperature range of 200–400 °C, which is attributed by the raising content of the H and O in HC-HCl precursor after catalytic hydrolysis of acid. The high-resolution transmission electron microscopy (HRTEM) images in Fig. 2 show the microstructure of HCs. A more disordered structure in HC-HCl is observed. Furthermore, the amount of nanopores stacked by hexagonal carbon layers is increased simultaneously. These results are well supported by Raman spectroscopy analyses and the pore size distribution from N₂ adsorption and desorption.

The XRD patterns of HC-H₂O and HC-HCl are displayed in Fig. 3a. Two broad peaks at 23.08° and 43.66° for HC-H₂O, which can be assigned to the crystallographic planes of (002) and (100) in amorphous carbon. Moreover, these two peaks, which are 22.88° and 43.64° for HC-HCl, show tiny shift to low angles. The (002) peak indicates a large

Download English Version:

<https://daneshyari.com/en/article/7724910>

Download Persian Version:

<https://daneshyari.com/article/7724910>

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