



Sodium-ion supercapacitors based on nanoporous pyroproteins containing redox-active heteroatoms



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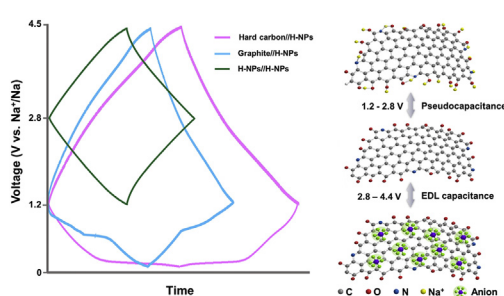
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HIGHLIGHTS

- Nanostructured pyroproteins (H-NPs) are fabricated by a simple pyrolysis with KOH.
- The H-NPs have numerous redox-active heteroatoms for pseudocapacitive charge storage.
- The H-NPs also exhibit a high specific surface area of 3050 m² g⁻¹.
- High capacitance of 348 F g⁻¹, low ESR of ~1.70 Ω and stable 30,000 cycles are achieved.
- High energy (217 Wh kg⁻¹) and high power (1900 W kg⁻¹) are achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanostructured carbon-based materials fabricated via simple methods from renewable bio-resources have great potential in rechargeable energy storage systems. In this study, nanoporous pyroproteins containing a large amount of redox-active heteroatoms (H-NPs) were fabricated from silk fibroin by an *in situ* carbonization/activation method. The H-NPs have a large surface area of ~3050 m² g⁻¹, which is mainly comprised of nanometer-scale pores. Also, these H-NPs have oxygen and nitrogen heteroatoms of 17.4 wt% and 2.9 wt%, respectively. Synergistic sodium ion storage behaviors originate from electrochemical double layer capacitance and pseudocapacitance, leading to very high electrochemical performances of H-NPs in aqueous and non-aqueous electrolyte systems. Sodium-ion supercapacitors (NISs) based on commercial graphite//H-NPs show a high specific power of ~1900 W kg⁻¹ at ~77 Wh kg⁻¹. Also, NISs based on commercial hard carbon//H-NPs exhibit a high specific energy of ~217 Wh kg⁻¹ at ~42 W kg⁻¹. In addition, outstanding cycling performances over 30,000 cycles are achieved for symmetric NISs.

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1. Introduction

Due to their high power capability and long-term cyclic stability, supercapacitors, also known as electrochemical double layer (EDL) capacitors, are promising energy storage devices in several fields, including portable electronics, electric vehicles, and energy storage systems [1,2]. The low energy density of conventional

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supercapacitors ($\sim 5 \text{ Wh kg}^{-1}$), however, limits their practical application [3]. Accordingly, high capacitance and a large operating voltage window are required to achieve high energy densities, because the maximum storage energy of supercapacitors is given by $CV_i^2/2$, where C is the capacitance and V_i is the initial voltage [1–3]. The capacitances are proportional to the active surface area and inversely proportional to the effective thickness of the EDLs, indicating that an advanced electrode design, with high surface area and effective nanopores for the EDLs, plays a key role in achieving high energy densities [4–10]. Meanwhile, nanostructured carbon-based materials (NCMs) that contain redox-active heteroatoms have recently attracted much attention as cathode materials for lithium- and/or sodium-ion storage [11–14]. In the cathodic potential ranges of 1.0–4.5 V vs. Li^+/Li and/or Na^+/Na , the oxygen and nitrogen functional groups on NCMs can be redox hosts for pseudocapacitive charge storage [11–15]. The pseudocapacitive charge storage is fast and highly stable, and it can deliver a large amount of charge [11–15]. Therefore, as one of the most feasible strategies to increase the energy density of supercapacitors, a synergistic charge storage using both EDL capacitance and pseudocapacitance has great potential. Shao et al. reported functionalized high-surface-area nanocellular carbon foams that can deliver a high specific capacity of 152 mAh g^{-1} at a specific current of 0.1 A g^{-1} in the cathodic potential range [16]. The carbon foams also showed good rate capabilities and a stable cycling performance over 1600 cycles. The sodium-ion storage capabilities achieved using the synergistic charge storage behaviors could be improved by introducing more redox-active heteroatoms on their surface and/or by extending their surface area. However, there are few studies on materials using the synergistic charge storage and their energy storage devices.

Silk is one of the most abundant biopolymers in nature, with an annual worldwide production of 480,000 ton [17,18]. In our previous study, the structural transition of silk fibroin into pyroproteins was investigated for the first time [19]. We found that the β -sheet structure of the silk fibroin is transformed into carbon basic-structural-units (BSUs) by simple heating, indicating that silk protein is a good carbon precursor that contains a large amount of heteroatoms [19]. Hou et al. reported hierarchically porous pyroprotein nanosheets fabricated from reformulated silk proteins [20]. The well-defined pyroprotein nanostructure led to superior electrochemical performances as an electrode for supercapacitors and/or as an anode for rechargeable batteries. Nevertheless, the multi-step method *via* a wet process and followed by a drying process and an activation/graphitization process is not suitable for practical application. Alternatively, a conventional activation method composed of two steps, such as carbonization followed by activation, can be used to prepare porous pyroproteins with a high surface area [21,22]. The porous pyroprotein prepared by the two step activation shows good electrochemical performance as an electrode for EDL capacitors [21,22]. Liang et al. reported cocoon-derived porous pyroproteins that show a specific capacitance of 215 F g^{-1} in 6 M KOH aqueous electrolyte solution [21]. In addition, Kim et al. showed that porous pyroproteins can deliver a maximum energy of 19.6 W L^{-1} by using organic electrolytes [22]. However, the electrochemical performances that originated from the EDL capacitance have an intrinsic limitation in their energy character, leading to a common specific capacitance and energy compared with other reports based on highly porous NCMs [23–27].

In this study, nanoporous pyroproteins that contained a large amount of redox-active heteroatoms (H-NPs) were fabricated from silk fibroin by a simple one-step carbonization/activation process with potassium hydroxide. The *in situ* method induced a poor stacking ordering of the produced carbon BSUs in pyroproteins, which resulted in huge differences in the pore structure and surface

properties of H-NPs. The H-NPs had a high surface area of $\sim 3050 \text{ m}^2 \text{ g}^{-1}$ and numerous oxygen and nitrogen atoms of 17.4 wt % and 2.9 wt%, respectively, which lead to very high sodium-ion storage performances in both aqueous and organic electrolytes. In addition, different types of H-NP-based sodium-ion supercapacitors (NISs) delivered a specific energy of $\sim 217 \text{ Wh kg}^{-1}$ at 42 W kg^{-1} for commercial hard carbon//H-NPs and a specific power of $\sim 1900 \text{ W kg}^{-1}$ at 77 Wh kg^{-1} for commercial graphite//H-NPs with stable cycles. Furthermore, significant cycling performance over 30,000 cycles was achieved for symmetric NISs. The following are the main points of the current study: 1. highly porous and functionalized pyroproteins (H-NPs) can be fabricated by the practically useful *in situ* carbonization/activation method; 2. the H-NPs can store charges in both aqueous and organic solvents through a mechanism based on both EDL capacitance and pseudocapacitance; and 3. asymmetric NISs and symmetric NISs based on H-NPs show competitive energy and power densities, good rate capabilities, and stable cycling performances. This paper also reports the versatile sodium-ion storage characteristics of H-NPs, which exhibit potential for usage as cathode materials in sodium-ion batteries.

2. Experimental

Preparation of H-NPs: Cocoons of *B. mori* silkworm silk were boiled for 30 min in an aqueous solution of Na_2CO_3 (OCI Co., 99%, 0.02 M, USA) and rinsed thoroughly with water to remove the glue-like sericin proteins. The extracted silk fibroin was dried in a vacuum oven at 30°C for 48 h. The silk fibroin (5 g) was mixed with 5 g of KOH in a mortar, and the mixture was heated to 800°C for 2 h at a heating rate of $5^\circ \text{C min}^{-1}$. The resulting products (H-NPs) were washed using distilled water and ethanol (OCI Co., 99.9%, USA), and were then dried in a vacuum oven at 30°C . As a control sample, the silk fibroin was heated to 800°C for 2 h at a heating rate of $5^\circ \text{C min}^{-1}$ (SF-800). The SF-800 was also mixed with KOH and heated to 800°C for 2 h at a heating rate of $5^\circ \text{C min}^{-1}$ (A-SF-800).

Characterization: Sample morphology was examined using field-emission scanning electron microscopy (FE-SEM, S-4300, Hitachi, Tokyo, Japan) and field-emission transmission electron microscopy (FE-TEM, JEM2100F, JEOL, Tokyo, Japan). The Raman spectra were recorded using a continuous-wave linearly polarized laser (wavelength: 514.5 nm; 2.41 eV; power: 16 mW). The laser beam was focused by a $100\times$ objective lens, resulting in a spot diameter of approximately $1 \mu\text{m}$. A 10 s acquisition time and three circulations were used to collect each spectrum. X-ray diffraction (XRD, Rigaku DMAX 2500) was performed using $\text{Cu-K}\alpha$ radiation (wavelength $\lambda = 0.154 \text{ nm}$) operated at 40 kV and 100 mA. The chemical composition of the samples was examined using X-ray photoelectron spectroscopy (XPS, PHI 5700 ESCA, Chanhassen, MN, USA) with monochromatic $\text{Al-K}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) and by elemental analysis (EA) with an EA1112 instrument (CE Instrument, Italy). The porous properties of the samples were analyzed using nitrogen adsorption and desorption isotherms that were obtained using a surface area and a porosimetry analyzer (ASAP 2020, Micromeritics, USA) at -196°C .

Electrochemical characterization: The electrochemical properties of H-NPs, SF-800, A-SF-800, commercial graphite (Sigma-Aldrich, $<150 \mu\text{m}$, 99.99%, USA), commercial hard carbon (Kureha co., Carbotron[®] P S(F), Japan), and symmetric and asymmetric NISs were characterized using a Wonatec automatic battery cycler and CR2032-type coin cells in an organic electrolyte. For the half-cell, the coin cells were assembled in a glove box filled with argon, using the samples as the working electrodes and metallic Na foils (Sigma-Aldrich, 99.9%, USA) as both the reference and counter electrodes. NaClO_4 (1 M; Sigma-Aldrich, purity: 99.99%, USA) was

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