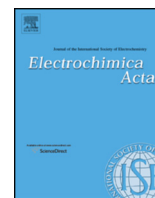




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Electrochimica Acta

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

Hierarchically nanoporous pyropolymer nanofibers for surface-induced sodium-ion storage



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ARTICLE INFO

Article history:

Received 22 February 2017

Received in revised form 12 April 2017

Accepted 2 May 2017

Available online 3 May 2017

Keywords:

carbon nanofiber
pyropolymer
nanoporous carbon
electrode
supercapacitor

ABSTRACT

Surface-driven charge storage materials based on both electrochemical double layer (EDL) formation and pseudocapacitive behavior can deliver high energy and power capabilities with long-lasting cycling performance. On the other hand, the electrochemical performance is strongly dependent on the material properties, requiring sophisticated electrode design with a high active surface area and a large number of redox-active sites. In this study, hierarchically nanoporous pyropolymer nanofibers (HN-PNFs) were fabricated from electrospun polyacrylonitrile nanofibers by simple heating with KOH. The HN-PNFs have a hierarchically nanoporous structure and an exceptionally high specific surface area of $3,950.7 \text{ m}^2 \text{ g}^{-1}$ as well as numerous redox-active heteroatoms (C/O and C/N ratio of 10.6 and 16.8, respectively). These unique material properties of HN-PNFs resulted in high reversible Na-ion capacity of $\sim 292 \text{ mAh g}^{-1}$ as well as rapid kinetics and stable cycling performance in the cathodic potential range (1–4.5 V vs. Na^+/Na). Furthermore, energy storage devices based on HN-PNFs showed a remarkably high specific energy of $\sim 258 \text{ Wh kg}^{-1}$ at $\sim 245 \text{ W kg}^{-1}$ as well as a high specific power of $\sim 21,500 \text{ W kg}^{-1}$ at $\sim 78 \text{ Wh kg}^{-1}$, with long and stable cycling behaviors over 2,000 cycles.

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1. Introduction

The rapid increase in the demand for portable electronic devices and large-scale energy storage systems requires more powerful and long-lasting rechargeable power sources. [1,2] Supercapacitors are one of the best candidates to meet these needs because of their high-power capabilities and long-term cycle life. [3–18] In contrast, the significantly low capacitance and operating voltage of supercapacitors compared to rechargeable batteries limit their potential in extensive applications. [3–5] The capacitance of supercapacitors is strongly dependent on the surface area of electrode materials and the atomic-scale charge separation distance, which is profoundly linked to the pore structure of the electrode materials. [3–5] In addition, the working cell voltage is normally determined by the electrolyte used. While an aqueous electrolyte can be operated in a narrow water splitting potential range ($\sim 1.23 \text{ V}$), the organic/ionic liquid electrolytes can

provide a much larger potential window above 3 V. [6–11] Zhu et al. reported that graphene-based porous carbon with a high surface area of $3,100 \text{ m}^2 \text{ g}^{-1}$ showed a high specific capacitance of 200 F g^{-1} and a working voltage of 3.5 V in ionic liquid electrolytes via physical adsorption and desorption mechanism of the charges forming electrochemical double-layers (EDLs), which reached an energy density of $\sim 20 \text{ Wh kg}_{\text{cell}}^{-1}$. [10] In addition, hierarchically porous carbon with a nanostructure delivered high power capabilities together with further improved energy characteristics in a large working voltage window ($\sim 3.5 \text{ V}$) based on organic/ionic liquid electrolytes. [11–13] Therefore, many studies have focused on realizing the high energy characteristics of supercapacitors without a loss of power capability using well-defined carbon-based electrode materials (CEMs) at large operating voltages. Nevertheless, their increased energy densities are still much lower than those of typical rechargeable batteries ($\sim 150 \text{ Wh kg}_{\text{cell}}^{-1}$), [19] indicating the need for additional strategies to boost them.

The pseudocapacitive charge storage behaviors of CEMs have been reported in aqueous electrolytes, in which nitrogen and oxygen heteroatoms on the surface/near surface of CEMs can store charge by faradic reactions and deliver higher capacity than

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conventional supercapacitors based on EDL formations. [14–18] The surface-induced redox reactions of CEMs can be used in organic electrolytes, including alkali-ions, wherein various and complex redox reactions between alkali-ion and functional groups on the surface of CEMs can occur in large operating voltage ranges. [19–24] Lee et al. reported oxygen functionalized carbon nanotubes for Li-ion storage in the cathodic potential region between 1.5–4.5 V vs. Li⁺/Li, which showed a high reversible capacity of ~200 mAh g⁻¹. [19] The specific capacities were increased further using functionalized graphene nanoplatelets and/or microporous carbon nanosheets, which have more redox-active heteroatoms and larger surface area. [20,21] In addition, nanoporous carbon nanosheets containing oxygen and nitrogen heteroatoms exhibited high rate capabilities and outstanding cycling stability over 2,000 cycles as a cathode for Na-ion storage. [22] These results suggest that by designing active CEMs based on both EDL and pseudocapacitive charge storage behaviors, the desirable energy characteristics can be achieved together with the intrinsic advantages of supercapacitors.

Pyropolymer is an intermediate material between a polymer and carbon, which can be fabricated by low temperature pyrolysis (<1,000 °C) of a polymer precursor including mainly rigid aromatic structures in the backbone and/or side chains forming a network structure by heating. [25–27] The molecular structure induced from the thermo-transition of the polymer is composed basically of a hexagonal carbon structure containing numerous heteroatoms and defect sites that are highly redox-sensitive. [26] Hence, through the nanostructured design and optimization of a porous structure, pyropolymers can be great electrode materials exhibiting high electrochemical performance.

This paper reports hierarchically nanoporous pyropolymer nanofibers (HN-PNFs) by the simple heating of an electrospun nanofiber/KOH mixture as an electrode for Na-ion storage. The HP-PNFs have a high specific surface area of 3,950.7 m² g⁻¹ and numerous redox-active heteroatoms, such as 9.2 wt. % oxygen and 4.3 wt. % nitrogen. In addition, HN-PNFs have a hierarchically nanoporous structure composed of a large number of pores below ~3 nm. These superior material properties of HN-PNFs have great potential as an electrode material for Na-ion storage. In the cathodic voltage range between 1–4.5 V, HN-PNFs exhibited high capacities and power capabilities with a long-term cycle life. Furthermore, energy storage devices based on HN-PNFs deliver a remarkably high specific energy of ~258 Wh kg⁻¹ at ~245 W kg⁻¹ and a specific power of ~21,500 W kg⁻¹ at ~78 Wh kg⁻¹, as well as long and stable cycling performance over 2,000 repetitive cycles.

2. Experimental

2.1. Preparation of HN-PNFs

A high concentration solution (~10 wt. %) of polyacrylonitrile (PAN, Mw = 150,000, Sigma-Aldrich, USA) was prepared in *N,N*-dimethylformamide (99.8%, Sigma-Aldrich, USA). The solution was placed in a syringe attached to a syringe pump in a vertical mount and ejected under ~20 kV between the syringe needle and rotating collector. The distance between the needle and rotating drum collector was ~12 cm. The as-electrospun PAN nanofibers (e-PAN) were peeled off from the collector and the sample was then transferred to an alumina tube furnace for stabilization. Stabilization was conducted at 280 °C for 2 h under a nitrogen atmosphere. The stabilized nanofibers were then soaked in a 1 M KOH solution containing the same KOH weight to the nanofibers. The mixture solution was then dried in a convection oven at 80 °C for 24 h. The dried mixtures were heat-treated in an alumina tube furnace at 850 °C for 2 h under a nitrogen flow of 200 ml min⁻¹. A heating rate of 5 °C min⁻¹ was applied. The resulting HN-PNFs were washed

with distilled water and ethanol (99.9%, OCI Co., USA) and stored in a vacuum oven at 30 °C. The pyropolymer nanofibers (PNFs) were also prepared using a similar process without the soaking step in a KOH solution.

2.2. Characterization

The morphology of the PNFs and HN-PNFs were examined by field-emission scanning electron microscopy (FE-SEM, S-4300SE, Hitachi, Japan) and field-emission transmission electron microscopy (FE-TEM, JEM2100F, JEOL, Japan). The Raman spectra were recorded using a continuous-wave linearly polarized laser (514.5 nm, 2.41 eV, and 16 mW). The laser beam was focused by a 100 × objective lens, resulting in a spot with a ~1 μm diameter. The acquisition time and number of cycles to collect each spectrum were 10 and 3 s, respectively. X-ray diffraction (XRD, Rigaku DMAX 2500) was performed using Cu-K_α radiation (λ = 0.154 nm) at 40 kV and 100 mA. The chemical composition of the samples was examined by X-ray photoelectron spectroscopy (XPS, PHI 5700 ESCA, USA) using monochromatic Al K_α radiation (hν = 1,486.6 eV). Elemental analysis (EA) was performed with an EA1112 instrument (CE Instrument, Italy). The porous properties of the samples were analyzed using the nitrogen adsorption and desorption isotherms obtained using a surface area and porosimetry analyzer (ASAP 2020, Micromeritics, USA) at –196 °C.

2.3. Electrochemical characterization

The electrochemical properties of the PNFs and HN-PNFs were characterized using a Wonatech automatic battery cycler, potentiostat (PGSTAT302N, Metrohm Autolab, Utrecht, The Netherlands) and CR2032-type coin cells. For the half-cells, coin cells were assembled in a glove box filled with argon using PNFs or HN-PNFs as the working electrode and metallic Na foil as both the reference and counter electrodes. NaPF₆ (Aldrich, 98%) was dissolved in a solution of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v) to a concentration of 1 M and used as the electrolyte for Na-ion storage. A glass microfiber filter (GF/F, Whatman) was used as a separator. The working electrodes were prepared by mixing the active material (80 wt. %) with conducting carbon (10 wt. %) and polyvinylidene difluoride (10 wt. %) in *N*-methyl-2-pyrrolidone. The resulting slurries were cast uniformly on Al foil, and the resulting electrodes were dried at 120 °C for 2 h and roll-pressed. The active material mass loading was ~1 mg cm⁻², and the total electrode weight was approximately 2 ~ 3 mg. For asymmetric full cells, coin cells were assembled in a glove box filled with argon using PNFs and HN-PNFs as the anode and cathode, respectively. The same electrolyte and separator for the half-cell tests were used, and the total electrode weight (both anode and cathode) was 4 ~ 5 mg. In addition, asymmetric Na-ion storage devices were cycled galvanostatically between 0.5 and 4.5 V. To assemble the devices, PNFs and HN-PNFs were pre-cycled with Na metal for 10 cycles, and the onset potential of both electrodes was controlled to 1.2 V vs. Na⁺/Na. Electrochemical impedance spectroscopy (EIS) tests were performed at room temperature in the frequency range of 100 kHz to 0.1 Hz using an impedance analyzer (ZIVE SP2, WonATech). The specific capacitance (*C*) was determined from the galvanostatic measurements using the following equation.

$$C = \frac{4I_{cons}}{m dV/dt} \quad (1)$$

where *I*_{cons} is the discharge (constant) current, *m* is the total mass of active materials, and *dV/dt* was calculated from the slope of the discharge curve over the range from *V* = *V*_{max} (the voltage at the beginning of discharge) to *V* = 1/2 *V*_{max}. The energy density (*E*) and

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