



Mesoporous activated carbon materials with ultrahigh mesopore volume and effective specific surface area for high performance supercapacitors



Yanhong Lu^{a,*}, Suling Zhang^a, Jiameng Yin^a, Congcong Bai^a, Junhao Zhang^a, Yingxue Li^a, Yang Yang^b, Zhen Ge^b, Miao Zhang^b, Lei Wei^a, Maixia Ma^a, Yanfeng Ma^b, Yongsheng Chen^{b,**}

^a School of Chemistry & Material Science, Langfang Teachers University, Langfang, 065000, China

^b The Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials, State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin, 300071, China

ARTICLE INFO

Article history:

Received 4 June 2017

Received in revised form

6 August 2017

Accepted 21 August 2017

Available online 23 August 2017

ABSTRACT

High specific surface area (SSA), especially effective specific surface area (E-SSA) of the active electrode materials is required for high performance supercapacitors. In this work, such materials (e.g. AC-KOH) were obtained using a scalable industrial method from biomass waste material, with controlling the pore size distribution and mesopores as the major contribution. Thus, an electrode material, with ultrahigh mesopore volume of $1.85 \text{ cm}^3 \text{ g}^{-1}$, E-SSA up to $1771 \text{ m}^2 \text{ g}^{-1}$ for organic electrolyte ion (TEA^+) and taking 55% of the total SSA of $3237 \text{ m}^2 \text{ g}^{-1}$ with an excellent conductivity of 33 S m^{-1} , was obtained. With these outstanding properties, the materials demonstrate excellent double-layer capacitance with remarkable rate performance and good cycling stability. The material delivers capacitance up to 222, 202 and 188 F g^{-1} at current density of 1 A g^{-1} in aqueous, organic and ionic liquid electrolyte system, respectively. Meanwhile, it exhibits a high energy density of 80 W h kg^{-1} in ionic liquid electrolyte at a power density of 870 W kg^{-1} . Furthermore, these materials can be produced in large scale from various biomass materials, and thus could be an excellent choice of the high performance materials required in the increasing important supercapacitor industry.

© 2017 Published by Elsevier Ltd.

1. Introduction

Supercapacitors (SCs), also named electrochemical capacitors or ultracapacitors, are attracting intense scientific attention as they can bridge the energy-power gap between the commercial batteries and traditional capacitors [1–3]. Due to their high power density and excellent cycle life, SCs power a wide variety of devices, ranging from small and low-power electronics up to the large energy units applied in such as electric vehicles [4,5]. Activated carbons (ACs) with high specific surface area (SSA), optimal pore size distribution (PSD) and high conductivity are highly desired as

advanced electrode materials for electrochemical double-layer capacitors (EDLCs) [6–10]. EDLCs store charge when electrolyte ions form electric double layers at the surface of oppositely charged electrodes under an externally applied voltage, with the amount of charge stored being proportional to the available SSA of electrode materials [4]. Note that this available SSA is actually the effective SSA (E-SSA) [11,12], which is often mixed up with the total SSA obtained directly from the Brunauer-Emmett-Teller (BET) analysis. E-SSA, the accessible portion of the total SSA for electrolyte ions, is determined by both the total SSA, PSD of the electrode materials and the electrolyte ion size. So it is critical to design an electrode material by controlling both the SSA and PSD for better capacitance performance. Previously, various approaches have been made to increase the total SSA [13–16], but much less has been done to design and achieve the more meaningful high E-SSA by controlling the microstructures of the materials. Though some approaches, such as carbide-derived and template approaches, have been

* Corresponding author. School of Chemistry & Material Science, Langfang Teachers University, Langfang, 065000, China.

** Corresponding author.

E-mail addresses: luyanhong_2003@126.com (Y. Lu), yschen99@nankai.edu.cn (Y. Chen).

reported [17–20] and offered some sort of controlling of the pore structures, most of these materials suffer from either complicated synthesis process of high-cost, and/or the use of toxic chemicals/gases, thus hindering their possible scalable production and wide application in industry. Also, previously a linear relationship between the E-SSA of the electrode materials and their capacitance of devices has been found based on a general model [11,21]. So it would be ideal to design the electrode materials with high E-SSA, not merely high SSA, by controlling the PSDs of materials for high performance SCs.

In this work, such materials, mesoporous activated carbons (AC-KOH) with ultrahigh E-SSA and thus high capacitance performance have been obtained using a simple industrial hydrothermal carbonization and activation approach from the biomass corn straw. The high synergy of total BET SSA of 3237 m² g⁻¹ and an ultrahigh E-SSA reaching up to 1771 m² g⁻¹, together with a good conductivity of 33 S m⁻¹ was achieved by controlling the PSDs and having the mesopore volume of 1.85 cm³ g⁻¹ as the major contribution to the total pore volume. Note, different from most of previously reported carbon materials, the pore structure of our materials could be controlled and optimized with the more important mesopores as the dominated contribution to the overall pore structure. This mesopore dominated structure, leading to a high E-SSA percentage in the total SSA, makes these materials show both high capacitance and rate performance. The capacitor based on this electrode material delivers a high specific capacitance (C_p) of 222 F g⁻¹ in aqueous (6 M KOH), 202 F g⁻¹ in organic (1.0 M TEABF₄/AN) and 188 F g⁻¹ in ion liquid electrolyte (EMIMBF₄) at current density of 1 A g⁻¹, much better than that of commercial activated carbon YP50, and also among the highest of the materials prepared from other carbon sources (details in Data in Brief article). Furthermore, in ionic liquid electrolyte system, the AC-KOH materials exhibit energy density of 80 W h kg⁻¹, also significantly higher than that of YP50 (51 W h kg⁻¹). The outstanding electrochemical performance of these materials can be attributed to their better controlled and optimal microstructures, which not only provides a high E-SSA accessible to the electrolyte ions but also offers abundant mesopore channels for faster ion transportation. Thus, the combined properties in terms of high E-SSA, abundant mesoporous structure, good conductivity and low-cost make these materials a viable choice for the truly industry applications much required for the increasing green energy platform.

2. Experimental

2.1. Materials synthesis

All chemicals used in this study are analytical grade and used directly without further treatment unless otherwise indicated. Distilled water was used in all experiments. The commercially landmark available AC, YP50 was obtained from Tianjin Plannano Energy Technologies Co., Ltd with BET SSA of 1493 m² g⁻¹. The biomass material, air-dry corn straw was collected from local place, and was shattered and sieved through 100 mesh sieve. The collected powders under 150 μm were dried at 120 °C for 24 h under vacuum. The corn straw derived ACs were synthesized through a hydrothermal carbonization and followed by an activation step following our previous procedures [12,22]. Typically, corn straw powders (8.00 g) were added into distilled water (60 mL) and stirred for 2 h. The as-prepared suspension was then transferred to a sealed 100 mL Teflon-lined autoclave, heated to 180 °C and maintained at this temperature for 12 h. After the autoclave was cooled to room temperature, the hydrothermal product was filtered, washed with distilled water and finally dried in vacuum at 120 °C for 24 h. For the optimal process, the hydrothermal product

was mixed with different activation agents at the weight ratio of 1–4, placed into a nickel boat in a horizontal tube furnace and heated to 900 °C for 1 h at 5 °C min⁻¹ under Ar. After cooling to room temperature, the products were thoroughly washed with 0.1 M HCl and distilled water until the pH value reached 7. Finally, the collected sample was dried in a vacuum oven at 120 °C for 12 h. KOH, ZnCl₂, K₂CO₃ and Na₂CO₃ were used as the activation agents, and the corresponding final products were labeled as AC-KOH, AC-ZnCl₂, AC-K₂CO₃ and AC-Na₂CO₃, respectively. Note other ratios other than 4:1 such as 2:1 and 5:1 with activation agents have been tested for the activation step, including the case of KOH, where the corresponding products are named as AC-KOH-2:1 and AC-KOH-5:1, respectively. The activation production yield (η) was calculated with the weight ratio of the activation product to the hydrothermal product.

2.2. Characterization

X-ray diffraction (XRD) was carried out using a Rigaku D/Max-2500 diffractometer with Cu K_α radiation. The interlayer spacing (d_{002}) was calculated from the Bragg peaks using the Bragg law: $n\lambda = 2d\sin\theta$, where λ is the wave length of the X-ray radiation and θ is the Bragg angle. The height (L_c) of stacking carbon domains was calculated from (002) peak using Scherrer's equation: $L_c = K\lambda/(\beta_c \times \cos\theta)$, where K is the shape factor (0.89), λ is the wave length of the X-ray radiation, β_c is the full widths at half maximum (FWHM) of the diffraction peaks and θ is the Bragg angle. Raman spectra were examined with a LabRAM HR Raman spectrometer using laser excitation at 514.5 nm. Lorentzian fitting was carried out to confirm the positions and FWHM of the D and G bands. The size (L_a) of carbon domains can be carried out by L_a (nm) = $(560/E^4)(I_D/I_G)^{-1}$, where E is the laser energy (2.41 eV), I_D and I_G are the intensities of the D and G bands, respectively. X-ray photoelectron spectroscopy (XPS) analysis was obtained using AXIS HIS 165 spectrometer (Kratos Analytical) with a monochromatized Al K_α X-ray source (1486.71 eV photons). The nitrogen adsorption/desorption analysis was done at 77 K on a Micromeritics ASAP 2020 apparatus. The BET method was employed for the SSA, and the density functional theory (DFT) method was used for the PSD analysis. Scanning electron microscopy (SEM) images were obtained on a Phenom Pro SEM. High resolution transmission electron microscopy (HR-TEM) was conducted in a FEI Tecnai G2 F20 electron microscope using an acceleration voltage of 200 kV.

2.3. Fabrication of supercapacitors

The supercapacitor test cells were fabricated by a symmetrical two-electrode system [23,24]. The electrode materials, mixed with carbon black (Super P, Timcal) and polytetrafluoroethylene (PTFE, solid powder, Dupont) at the weight ratio of 85:5:10, was rolled into 80–100 μm thickness sheets and punched into 12 mm diameter electrodes. After dried at 120 °C for 6 h under vacuum, the electrodes were weighted and hot pressed onto Al foils with conducting carbon coating (or foam Ni) and then dried at 180 °C for 6 h under high vacuum. The dry electrodes were transferred into a glove box filled with Ar to assemble the coin-type supercapacitors which consisted of two current collectors, electrolyte, two electrodes with identical weight and a separator sandwiched. 6 M KOH, 1.0 M TEABF₄/AN and EMIMBF₄ electrolytes were investigated respectively.

2.4. Electrochemical measurements

All the electrochemical tests were performed at room temperature. Cyclic voltammetry (CV) measurements were carried out using

Download English Version:

<https://daneshyari.com/en/article/5431740>

Download Persian Version:

<https://daneshyari.com/article/5431740>

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