



Short Communication

Humic acids-based hierarchical porous carbons as high-rate performance electrodes for symmetric supercapacitors



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HIGHLIGHTS

- HAs are used to prepare HPCs via a simple KOH activation process.
- Though the mass ratio of KOH/HAs is only 1.5, the obtained HPCs possess high SSA.
- The yield of LHA-HPC reaches to 51 wt% which is expected to be commercialized.
- HPCs are successfully applied as electrode materials in supercapacitors.

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ABSTRACT

Two kinds of hierarchical porous carbons (HPCs) with specific surface areas of $2000 \text{ m}^2 \text{ g}^{-1}$ were synthesized using leonardite humic acids (LHA) or biotechnology humic acids (BHA) precursors via a KOH activation process. Humic acids have a high content of oxygen-containing groups which enabled them to dissolve in aqueous KOH and facilitated the homogeneous KOH activation. The LHA-based HPC is made up of abundant micro-, meso-, and macropores and in 6 M KOH it has a specific capacitance of 178 F g^{-1} at 100 A g^{-1} and its capacitance retention on going from 0.05 to 100 A g^{-1} is 64%. In contrast, the BHA-based HPC exhibits a lower capacitance retention of 54% and a specific capacitance of 157 F g^{-1} at 100 A g^{-1} which is due to the excessive micropores in the BHA-HPC. Moreover, LHA-HPC is produced in a higher yield than BHA-HPC (51 vs. 17 wt%).

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1. Introduction

Biomass materials (BM) such as porous starch (Du et al., 2013), banana peels (Lv et al., 2012), animal bone (Huang et al., 2011) and fish scales (Chen et al., 2010) have been used to prepare hierarchical porous carbons (HPCs) and these materials have been successfully applied as electrode materials in supercapacitors. These BM-HPC materials have a number of advantages such as environmentally friendly synthesis processes, and porous structures with interconnected micro-, meso- and macropores. The micropores (pore sizes less than 2 nm) provide large surface areas which ensure high capacitance, the mesopores (2–50 nm) facilitate the diffusion of the electrolyte ions into the available surface area and the macropores (>50 nm) act as ion-buffers to ensure adequate penetration of the electrolyte into the electrode materials.

The most common methods to synthesize HPCs are template methods which require the synthesis and the removal of the templates. Chen et al. (2010) reported that fish scale-based HPCs were achieved by a self-templating method and exhibited a specific capacitance of 130 F g^{-1} at a current density of 40 A g^{-1} in 7 M KOH solution. However, the fish scales only contained 41% organic matter (Ikoma et al., 2003) which resulted in a low HPC yield. Lv et al. (2012) synthesized banana peel-based HPCs using a self-templating and chemical activation method but banana peels have a low residual carbon content (31.6 wt%) and the HPC preparation method was complex. Thus, the commercial viability of HPCs is hindered by the current preparation methods and by starting materials with low organic or residual carbon contents.

Humic acids (HAs) as a green, renewable, inexpensive and amphiphilic biomass material has more than 40 wt% carbon content (Stevenson, 1994). It consists of a skeleton of alkyl/aromatic units inter-molecularly or intra-molecularly cross-linked mainly by carboxylic acid, phenolic and alcoholic hydroxyls, ketone, and quinone groups. In previous work, an amphiphilic precursor could

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well-dispersed in aqueous KOH, which results in a nano-scale contact between the KOH and precursor, facilitating a homogeneous chemical (Guo et al., 2014). The aromatic structure of HAs could construct the carbon skeleton of HPC after activation, while the heteroatoms (including N, S, and O) provide more “active sites” for activation to facilitate the formation of hierarchical porous structure. Therefore, leonardite humic acids (LHA) and biotechnological humic acids (BHA) were respectively employed as the precursor to prepare HPCs via a mild KOH activation (KOH/HAs = 1.5 by weight). The porous structures and electrochemical performances of the two HPCs were characterized and each material was used as the electrode in a symmetric supercapacitor.

2. Experimental

2.1. Preparation of the raw materials

BHA and natural LHA were provided by Beijing Zimingyuan Co., Ltd. Pure BHA and LHA were obtained by three steps: (1) The HA was dissolved in alkaline solution (pH = 11) and then filtrated; (2) the filtrate was acidified to pH = 3 with 0.1 M hydrochloric acid and then a HA gel was formed after 8 h; (3) the HA gel was repeatedly washed with distilled water until the filtrate reached a neutral pH value and then the gel was dried at 60 °C.

2.2. Preparation of the hierarchical porous carbons

Potassium hydroxide and pure LHA (KOH/LHA = 1.5:1, mass ratio) were mixed and dissolved in water, and then dried in air at 80 °C for 24 h. The dried sample was activated in a tube furnace under a N₂ atmosphere at 800 °C for 1 h with a heating/cooling rate of 3 °C min⁻¹. The obtained black solid was then thoroughly washed with 1 M HCl at 80 °C for 6 h. After that, the material was dried at 80 °C for 24 h. The HPC sample was labeled LHA-HPC. The BHA-HPC sample was prepared using the same method except BHA was used in place of LHA.

2.3. Characterization

Thermogravimetric analysis (TGA) was carried out on an NETZSCH TG 209 apparatus with a heating rate of 10 °C min⁻¹ under N₂. XPS analysis was carried out on a Perkin Elmer PHI-1600 electron system (America PE Company) using a Mg K X-ray source at 250 W. The surface areas and the porous textures of the HPCs were examined using N₂ sorption at 77 K (ASAP2020). The macropores were measured using the AutoPore IV 9510 mercury porosimetry analyzer from the Micrometrics Company. The morphology of products was observed using a Philips XL30 scanning electron microscopy (SEM).

2.4. Supercapacitors fabrication preparation and electrochemical measurements

The symmetric capacitors were a combination of HPC/acetylene black/polytetrafluoroethylene (mass ratio of 8:1:1) electrodes (13 mm diameter and about 80 μm thick) with a polypropylene membrane as the separator and 6 M KOH aqueous solution as the electrolyte. They were constructed in a vacuum box. Galvanostatic charge/discharge analysis was carried out on an Arbin MSTAT instrument. The specific capacitance of the supercapacitor was calculated based on charger/discharger according to the formula: $C_g = 2I\Delta t / (\Delta V_m)$, where C_g is the gravimetric specific capacitance (F g⁻¹), I is the current (A), Δt is the discharge time (s), m is the mass (g) of the HPC in the signal electrode and ΔV is the potential change during the discharging process (excluding the IR drop).

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were carried out using a PARSTAT 2273 system.

3. Results and discussion

First the LHA and BHA were analyzed to determine their suitability to prepare a BM-HPC material. LHA is a natural humic acids derived from leonardite, while BHA is a regenerated humic acids derived from biodegradation of straws. LHA has more aromatic and cyclic hydrocarbon than BHA, which is identified by the broad band at 1605 cm⁻¹ (aromatic C=C stretching) in FT-IR spectrum (Fig. S1). The bulk and surface compositions of the samples were determined by XPS and the results are listed in Table 1. Both samples have a high oxygen content, which implies the existence of many oxygen-containing groups. TG analysis of the two HA samples after carbonization at 1000 °C was also performed (Fig. S2) and there is a significant mass loss between 180 and 600 °C which is a typical temperature range for the thermal decomposition of oxygen-containing groups. The mass loss between 600 and 1000 °C can be attributed to decomposition of the polyaromatic structures. The residual carbon percentage in LHA was 60.1 wt%, indicating that this precursor is a suitable biomass material for the preparation of porous carbon. The residual carbon content of BHA was only 38.2 wt%.

To further determine the HA surface carbon and oxygen functional components, the XPS carbon and oxygen peaks were deconvoluted and the results are shown in Fig. S3. Most of the oxygen-containing functional groups in the HAs are C(=O)O (carbonyls and carboxyls) and C—O bonds (phenols and ethers). These functional groups are effective at dispersing humic acids in aqueous alkaline solutions. When the two HAs were dispersed in aqueous KOH (with a mass ratio of KOH/HAs = 1.5), colloids were formed. The zeta potentials of the colloids were -59.1 mV for LHA and -62.6 mV for BHA, indicating that both colloids are stable. The stable colloidal solutions visibly elucidate that HAs presented nanometer in aqueous KOH and the nano-scale contact of KOH and HAs facilitate homogeneously KOH activation.

After KOH activation, the structural parameters of the HA-HPC samples were determined and the results are summarized in Table 2. The surface functional groups of the HAs improved the efficiency of the KOH activation which increased the specific surface area (SSA). Both samples have similar SSA, around 2000 m² g⁻¹, but the porous textures of the two HPCs are obviously difference. The V_{tot} , V_{mic} , V_{mes} , V_{mac} and porosity data for BHA-HPCs indicate that the sample possesses many micropores, whereas the data for LHA-HPCs indicates that this sample has higher porosity and abundant meso-, meso- and micropores. In addition, the yield of LHA-HPC was 51 wt% which is much higher than the yield for BHA-HPC (17 wt%). For comparison, the yields of several raw materials for porous carbon production are as follows: ginkgo shells (24 wt%) (Jiang et al., 2013), sugar cane bagasse (34.8 wt%) (Rufford et al., 2010), firwoods (20 wt%) (Wu et al., 2004), bamboo scaffolding waste (22.5 wt%) (Choy et al., 2005).

The pore size and the macropore distributions are shown in Fig. S4(b) and (c) respectively. For LHA-HPC, the pore size distribution is broad and can be divided into three regions: (1) micropores (0.4–2 nm); (2) mesopores (2–50 nm) with a maximum peak at 10 nm; and (3) macropores (>50 nm) with three peaks at 63 nm, 2.1 μm and 33 μm. For BHA-HPC, the pore sizes are primarily centralized in the micropore region between 0.4–2 nm although there are a few exterior pores with mesopores (2–4 nm) and macropores (>1 μm). The SEM images in Fig. S5 show that LHA-HPC has numerous macro-, meso- and micropores, while BHA-HPC possesses excessive micropores and a few macropores. The different porous

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