High performance electrode materials for electric double-layer capacitors based on biomass-derived activated carbons

Dabin Wang [a,b], Zhen Geng [a,c], Bing Li [a,b], Cunman Zhang [a,b,*]

[a] Clean Energy Automotive Engineering Center, Tongji University, Shanghai 201804, China
[b] School of Automotive Studies, Tongji University, Shanghai 201804, China
[c] School of Materials Science and Technology, Tongji University, Shanghai 201804, China

ABSTRACT

Activated carbons (ACs) are successfully synthesized from corncob by a simple chemical activation methodology and demonstrated as novel, suitable electrode materials for electric double-layer capacitors (EDLCs). The as-prepared samples were characterized by SEM, TEM, XPS, FT-IR and N_2-sorption followed by further electrochemical characterization. All samples exhibit a high specific surface area, favorable pore size distribution combining good electrical conductivity and excellent capacitive performance. The optimal sample achieved not only high specific capacitance (401.6 F g^{-1} in 0.5 M H_2SO_4 and 328.4 F g^{-1} in 6 M KOH aqueous electrolyte at a current density of 0.5 A g^{-1}), but also showed excellent cycling performance, with 100% and ~91% retention over 10000 cycles at 5 A g^{-1} in the above mentioned electrolytes. Furthermore, the sample also displayed improved rate capability with discharge capacitance retention of ~60% at 20 A g^{-1} in 0.5 M H_2SO_4 and ~75% at 20 A g^{-1} in 6 M KOH. The results indicate surface functional groups associate with high surface area and appropriate microstructure affect the capacitive performance of corncob-based ACs significantly. Herein, ACs prepared from corncobs are presented as a promising substitute to conventional electrode materials for EDLCs.

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1. Introduction

Supercapacitors can bridge the gap between conventional capacitors and rechargeable batteries. As one of the most promising electrochemical energy storage systems, supercapacitors along with lithium-ion battery have attracted much attention due to their wide applications ranging from mobile devices to electric vehicles. Normally, supercapacitors serve as auxiliary power source in electric vehicles since it can offer high power density, however Li-ion battery cannot when the car is about to start and accelerate. Therefore, it is a matter of considerable interest to improve energy density and reduce cost before large-scale industrial applications for supercapacitors.

Basically, there are two kinds of charge storage mechanisms in supercapacitors: double layer capacitance effects – with carbon electrodes or derivates with predominant electrostatic double-layer capacitance and pseudo-capacitance effects – with metal oxide or conducting polymer electrodes with a high amount of electrochemical pseudo-capacitance. Despite the fact that pseudo-

capacitors have relatively high energy densitiy due to the introduction of redox reactions, disadvantages such as inferior cycling stabilities and high cost are barriers to their commercialization. Conversely, EDLCs have advantages like good cycling stabilities, high rate performance, and high power density and disadvantages such as limited energy densities. High surface areas, optimized pore structures, and favorite surface functional groups of the electrode materials have been suggested to be the key issues in improving electrode performance in EDLCs [1–4]. Accordingly, numerous carbon-based materials such as activated carbons (ACs) [5], activated graphene [6], carbon nanotubes [7] and carbon aerogels [8] and the like have been subjected to intensive research in the past decades.

Among the aforementioned carbon materials, activated carbons derived from agricultural wastes (such as corn stover [9], coconut shells [10], coffee beans [11] and cotton stalk [12]) gathered much attention due to their low cost, easy accessibility, non-toxicity and good chemical stability, and turned out to be the most promising candidates for future energy storage. Additionally, activated carbons derived from agricultural wastes tend to be rich in nitrogen and oxygen functional groups [13,14], which are favorable to enhance the capacity. In this paper, activated carbons derived from corncobs are prepared by simple chemical activation process

* Corresponding author. Tel.: +86 21 69589355; Fax: +86 21 69589355.
E-mail address: zhangcunman@tongji.edu.cn (C. Zhang).

and then employed as electrode materials for EDLCs. The as-obtained samples delivered high capacitance and excellent cycling performance in aqueous electrolytes with well-developed microporosity (specific surface area up to 3054 $m^2 g^{-1}$, 49 vol% micropores). Effects of surface chemical properties on the capacitive performance in different aqueous electrolytes are also elaborated here.

2. Experimental

2.1. Synthesis of corncob-based activated carbons

Activated carbons were prepared by the following strategies: (i) pyrolysis/carbonization of corncobs and (ii) chemical activation with KOH as activating agent. Detailed processes were given in our previous report [15]. An additional ball milling process was introduced after activation to obtain finer powders that favored for electrode fabrication. The as-obtained samples are hereafter designated as "Cxxx", xxx is the activation temperature of samples (Table 1).

2.2. Characterization

The scanning electron microscopy (SEM, FEI SIRION 200/INCA, OXFORD) and transmission electron microscopy (TEM, JEM-2100F, JEOL) were used to determine the morphology and texture of the samples. Elemental analysis (Elementar, vario EL III), X-ray photoelectron spectroscopy (XPS, UIVAC-PHI PHI 5000 VersaProbe) and Fourier Transform Infrared Spectrometer (FT-IR, BRUKER, EQUINOXSS/HYPERION 2000) were employed to determine the element content and surface functional groups. A high accuracy balance (METTLER TOLEDO with 0.00001 g accuracy) was used to diminish the experimental error.

Nitrogen sorption isotherms and textural properties of all samples were determined at −196 °C using nitrogen in a conventional volumetric technique by a Micromeritics ASAP 2020 sorptometer over a wide relative pressure range from about 10^{-6} to 0.995. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation based on adsorption data in the partial pressure (P/P$_0$) ranging from 0.02 to 0.25 and the total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of 0.98. Pore size distributions (PSDs) were calculated by using the Density Functional Theory (DFT) Plus Software (provided by Micromeritics Instrument Corporation), which is based on calculated adsorption isotherms for pores of different sizes. All of the samples were degassed at 300 °C for 600 min prior to the measurements.

2.3. Electrochemical measurements

Electrochemical measurements for different as-prepared samples along with the commercial activated carbon (NORIT® A SUPRA) which was ordered from Sigma–Aldrich and used as reference materials in this work, were carried out in a three-electrode system: The working electrode was prepared by mixing 80 wt.% active material, 15 wt.% Super-P carbon black and 5 wt.% polytetrafluoroethylene (PTFE) binder in de-ionized water. The

slurry of the mixture was dried at 80 °C for two hours and then rolled into sheet and pressed onto the nickel foam under a pressure of 10 MPa. The mass loading of the active materials is about 2~4 mg. A platinum plate electrode served as counter electrode and an Hg/HgO or Ag/AgCl electrode served as reference electrode in 6 M KOH or 0.5 M H_2SO_4 aqueous electrolyte, respectively. Electrochemical performance was measured at room temperature.

Symmetric supercapacitor was also fabricated to investigate the practical performance of the samples. In two-electrode system measurements, the preparation process of the electrodes were almost the same with three-electrode system except that circular electrodes were employed to match the testing configuration. The cathode and anode electrodes were pressed together and separated by polypropylene membrane. The electrochemical measurements of the symmetric supercapacitor were carried out in both alkaline and acidic electrolytes using the electrochemical working station in a two-electrode cell at room temperature.

Cyclic voltammetry (CV) was carried out by six repeated cycles at a scan rate ranging from 5 to 100 mV s^{-1}. Galvanostatic charge/discharge (GCD) was tested at a current density load ranging from 0.5 to 20 A g^{-1} and electrochemical impedance spectroscopy (EIS, frequency ranging from 0.1 Hz to 100,000 Hz with potential amplitude of 10 mV) was performed on a CHI 760E electrochemical workstation.

3. Results and discussion

Fig. 1 shows the SEM and TEM images of a typical as-prepared sample-C850 (The SEM and TEM images of sample C650 and C750 are not shown here since they are similar with C850). It mainly composed of vast irregular granules which results from the introduction of ball milling process after activation, and demonstrates uniform pore size distribution which confirmed the well-developed microporosity of the sample. Apparently, finer granularity and well-developed microstructure may be favorable to fast charge transfer and large charge storage capacity, and this will be discussed later.

The N_2-sorption isotherms and pore size distributions (PSDs) of all samples are schematically shown in Fig. 2. The isotherm of samples C650, C750, C850 and Norit A Supra belong to typical type I according to the IUPAC classification, a characteristic of microporous materials. The PSDs of all samples are similar, ranging from 0.5 nm to 4 nm. Combined with the morphology and microstructure demonstrated in Fig. 1, the hierarchical microstructure is concluded since the sample comprises certain external pores and great amount of internal micro- as well as meso-pores in the carbon granules. It has been proved that the micropores between 0.8 and 1.4 nm, would be fully accessible to the hydronium ions (0.36–0.42 nm) [16], and hydrated bisulfate ions (0.53 nm) [17,18] produced by dissociation of the electrolyte (0.5 M H_2SO_4), which indicates that the methodology in this paper is favorable for massively producing ACs for electrochemical energy storage.

Normally, carbons derived from biomass materials mainly consist of organics are rich in nitrogen and oxygen functional groups [14,19]. However, the as-prepared samples derived from corncobs are rich in oxygen contents (as high as 14.53%) but have

Table 1
Different Prepared Conditions for Different Corncob Activated Carbon Samples.

Sample	Heating Rate	Activation Temperature	Activation Time	Ball Milling Time	KOH/Carbon Ratio	Yield
C650	5 °C /min	650 °C	3 h	120 min	4	45.2%
C750	5 °C /min	750 °C	3 h	120 min	4	38.6%
C850	5 °C /min	850 °C	3 h	120 min	4	27.5%
Norit A Supra	Commercial activated carbon					