Mesoporous activated carbons with enhanced porosity by optimal hydrothermal pre-treatment of biomass for supercapacitor applications

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ABSTRACT

A significant improvement of up to 94% in mesopore area of hydrochar-derived activated carbons (ACs) has been achieved using optimal concentrations of biomass (coconut shell) and chemical activating agent ($ZnCl_2$) during hydrothermal pre-treatment. For the first time, we have demonstrated that stoichiometry can influence hydrochar properties and availability of $ZnCl_2$ for activation which has significant impact on the textural properties of mesoporous activated carbons. Tuning of key process parameters and hydrothermal treatment conditions ($ZnCl_2$:biomass ratios and biomass & $ZnCl_2$ concentrations), together with hydrothermal pre-treatment with H_2O_2, resulted in BET and mesopore areas up to 2440 m^2 g^{-1} and 1121 m^2 g^{-1}, respectively. When the mesoporous carbon was employed as an electrode material in supercapacitors, stable energy density at 7.6 W h kg^{-1} was observed (90% of 8.5 W h kg^{-1} @ 0.22 kW kg^{-1}) at a high power density of ~4.5 kW kg^{-1}, which is one the best performance observed thus far in biomass-derived activated carbons.

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1. Introduction

Hydrothermal treatment for conversion of biomass into valuable carbon materials has received growing attention due to its simplicity and ability to deliver carbon materials (hydrochars) with high concentrations of oxygenated functional groups (OFGs). The presence of OFG on these hydrochar materials makes them suitable for numerous applications such as adsorption [1,2], drug delivery [3], in vivo bio-imaging [3,4], catalyst support [5–7], activated carbon (AC) synthesis [8–10], etc. A variety of catalysts have been used for the hydrothermal treatment of biomass to obtain specific products with desired properties at economically favorable processing conditions (reduced temperature and time) [11–13]. For example, Cui et al. reported that the presence of $Fe(NH_4)_2(SO_4)_2$ and Fe_2O_3 catalyzed the formation of hydrochar from biomass by promoting dehydration and condensation reactions and resulted in the BET surface area of 113 $m^2 g^{-1}$ and 402 $m^2 g^{-1}$, respectively [14]. Likewise, Fechler et al. reported the use of hydrothermal carbonization under hypersaline conditions to develop significant porosity (BET surface area ~ 673 $m^2 g^{-1}$) in hydrochar derived from glucose [15].

However, the absence of chemical activation in the preparation of the hydrochar implies that its porosity is underdeveloped and thus its direct use in various applications has performance limitations compared to synthetic ACs [1,16,17]. Textural porosity should, therefore, be improved for facilitating high mass transfer fluxes and high catalyst loading for enhanced performance in catalytic or energy applications. The synthesis of highly porous carbon materials with the presence of OFG on the hydrochar has been shown to promote chemical activation [8,18–20]. Sevilla et al. have demonstrated the importance of hydrothermally treated precursors for AC synthesis when KOH was added for post hydrothermal treatment to improve activation [8].

Despite these advances in the chemical activation of hydrochars, a fundamental understanding of the specific role of chemical activating agents in the hydrothermal and activation process is currently lacking, especially for designing scale-up operations. We have recently shown that mesopore area in biomass-derived ACs (from coconut shell) can be significantly increased by subjecting

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the raw biomass to ZnCl$_2$-mediated hydrothermal pre-treatment prior to activation [21]. We further investigated the role of hydrothermal temperature on induction of oxygenated functional groups (OFGs) on the hydrochar surface and solubility of ZnCl$_2$ (the chemical activating agent) [22]. Specifically in this work, we have chosen the optimized temperature for different ZnCl$_2$:biomass ratios from the earlier work [22] and optimized the concentrations of both biomass and ZnCl$_2$ to investigate their influence on (i) hydrolysis and dehydration of biomass and the resulting OFG content, (ii) changes in the solution pH due to the presence of ZnCl$_2$ and formation of acids, (iii) the chemical state of Zn^{2+} and (iv) locking of Zn^{2+} in the solid phase [43].

Concentration of ZnCl$_2$ (the chemical activating agent) in a hydrothermal environment affects the amount of OFGs formed on the precursor which in turn influences the affinity of ZnCl$_2$ to the precursor surface. Amarasekara and Ebede have proposed that Zn^{2+} exists as hydration shells in solution and the coordinated water molecules act as nucleophiles [23]. These nucleophiles are expected to be greatly attracted to the free electron pairs of the O atoms in the OFGs, thereby giving Zn^{2+} greater access to the precursor surface which leads to better dehydration of lignocellulosic biomass. Thus, the OFGs promote chemical activation by ZnCl$_2$, leading to higher mesopore area and volume. Although ZnCl$_2$ acts as a catalyst in the hydrothermal process, its high concentration under subcritical conditions could diminish its availability for chemical activation due to its reduced solubility [24]. Therefore, it is vital to optimize the concentrations of the biomass and ZnCl$_2$ in the context of the hydrothermal treatment temperature and ZnCl$_2$:shell ratio employed.

Production of chemically activated hydrochars is gaining much popularity because of its simplicity, low cost and suitability for energy applications even though other porous materials exhibit a more controlled porosity, such as templated carbons, carbide-derived carbons or metal organic frameworks [25]. It is of both fundamental and applied interests to develop ACs from biomass, a low-cost feedstock, with suitable properties to deliver high performance in energy related applications. A major limitation of the microporous electrode materials for high power applications is the reduction in rate of energy delivery because of the hindrance to ionic motion in narrow pores [26–28]. It is therefore desirable to employ ACs with high surface area and optimal mesoporosity for the electrochemical double layer capacitors to fully exploit the rate of energy delivery. For enhanced charge storage performance, high surface area coupled with the presence of mesopores of appropriate sizes in the AC plays an important role [25,26]. Deraman reported a binderless AC from self-adhesive pre-carbonized rubber wood sawdust as electrode for supercapacitor that had a specific capacitance and energy density of 138 F g^{-1} and 2.63 W h kg^{-1} [29]. AC derived from cherry stones has been shown to deliver energy density of 1–2 W h kg^{-1} at a power density of 1.5–2 kW kg^{-1} [30]. Li et al. reported the energy density of 4.5 W h kg^{-1} at power density of 2 kW kg^{-1} [31].

In this work, we report the synthesis of biomass-derived ACs with high surface areas obtained by maintaining optimal ZnCl$_2$:biomass ratios and biomass and ZnCl$_2$ concentrations during the course of hydrothermal treatment, and their application for energy storage. The resulting mesoporous carbon, when employed as electrode material, delivered a high specific capacitance of 246 F g^{-1} and good cycleability up to 2000 cycles. Further, tuning of pre-treatment conditions for higher surface area and mesoporosity in the ACs delivered 7.6 W h kg^{-1} at a higher power density of 4.5 kW kg^{-1}. We demonstrate the effectiveness of hydrothermal pre-treatment of waste biomass in improving the properties of the resulting hydrochar and the promising use of the chemically activated carbons for energy storage applications.

2. Materials and experimental procedure

Coconut shells (*Cocos nucifera*) from Malaysia were used as a starting material in this study. ZnCl$_2$ (reagent grade, Scharlab), hydrochloric acid (37%, Panreac), sodium hydroxide (Merck, EMSURE, >99%), poly(vinylidene fluoride) binder (Sigma–Aldrich), N-Methyl-2-pyrrolidone (ACS reagent, ≥99.0%, Sigma–Aldrich), glassy fiber filter paper (GF/B, Whatman) H$_2$SO$_4$ (≥98%, Sigma–Aldrich) and Carbon black (Super P, Sigma–Aldrich) were used as received. The shells were dried at 105 °C for 24 h and crushed using a commercial laboratory blender (Waring) and then ground and isolated to 10–20 mesh granules.

2.1. Hydrothermal treatment

2.1.1. Hydrothermal treatment with H$_2$O$_2$
The coconut shell granules with H$_2$O$_2$ (15 g shell in 90 mL H$_2$O$_2$ (10% w/v)) were kept in a Parr autoclave at 200 °C for 20 min [32]. The autoclave was then cooled to room temperature, and the products were collected and dried at 105 °C.

2.1.2. Hydrothermal treatment with ZnCl$_2$
An aqueous ZnCl$_2$ solution together with coconut shell granules was placed in an autoclave in appropriate quantities so that the desired ZnCl$_2$ concentration and ZnCl$_2$:shell ratios (1:1 and 3:1) were obtained. The contents of the autoclave were held at the desired temperature for 20 min. Subsequently, the autoclave was cooled to room temperature and the products were recovered and dried at 105 °C for 12 h. We have shown earlier that higher hydrothermal temperature (315 °C) for hydrochar preparation at low ZnCl$_2$:shell ratios (1:1) favors mesopore formation, while lower temperatures (275 °C) are preferred when the ZnCl$_2$:shell ratios were increased (3:1) [22]. Based on these results, an appropriate temperature at a particular ZnCl$_2$:shell ratio was chosen in this work to investigate the effect of substrate concentration (biomass, ZnCl$_2$ and water) keeping ZnCl$_2$:shell ratio constant.

2.2. Physico-chemical activation

The hydrochars were activated by using the procedure previously described in literature [21,33–36]. Briefly, the dried hydrochar product was loaded onto alumina boats and positioned inside a quartz tube that was placed in a furnace (Carbolite). The temperature was ramped to 800 °C at a rate of 10 °C/min in the presence of N$_2$ at a flow rate of 50 mL/min. N$_2$ was then replaced by CO$_2$ at a flow rate of 40 mL/min for 2 h. The furnace was cooled to room temperature in the presence of N$_2$ at a flow rate of 50 mL/min. The products were stirred for 30 min in 250 mL hydrochloric acid (about 0.1 mol/L), and washed with abundant distilled water until a pH of 6 was obtained for the rinse. Finally, the AC was dried at 105 °C for 24 h and used for porosity analysis and electrochemical characterizations.

2.3. Hydrothermal pre-treatment classification and nomenclature

Table 1 represents the various experiments that were carried out. The hydrochar precursors from coconut shell were prepared via the following pre-treatments:

1) A – Hydrothermal treatment with ZnCl$_2$:shell = 1:1 @ 315 °C
2) B – Hydrothermal treatment with ZnCl$_2$:shell = 3:1 @ 275 °C
3) C – Successive hydrothermal treatment with H$_2$O$_2$ @ 200 °C followed by ZnCl$_2$:shell = 3:1 @ 275 °C