

Sago Waste Based Activated Carbon Film as an Electrode Material for Electric Double Layer Capacitor

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Abstract: In this feasibility study a novel prospective electrode material for electric double layer capacitors (EDLC) has been investigated. This promising material is activated carbon (AC) film produced using sago waste as a precursor. Important parameters of the technological process are the KOH to charcoal ratio and the content of the polytetrafluoroethylene (PTFE) binder. The influence of these parameters on the microtexture and pore structure and on the electrochemical characteristics of the AC films has been studied in detail. The measured specific surface area (SSA) of the samples is in the range from 212 to 1498 m²/g. It has been found that the presence of micropores increases the specific capacity while the presence of the mesopores acts in the opposite direction, because these mesopores are too wide in diameter for aqueous electrolyte. The specific capacitance of the studied samples has been found to be in the range from 16 to 64 F/g.

Keywords: Sago waste, activated carbon, KOH ratio, PTFE content, specific surface area, pore structure, specific capacitance.

INTRODUCTION

Carbon, in all its allotropic forms, is one of the most widely used materials and has countless applications in various industrial processes and technical devices [1-3]. Among them are those related to the development of advanced energy storage systems with high energy and power density, e.g. fuel cells, lithium ion batteries and electrochemical capacitors. A promising and actively studied variety of the latter is the electrical/electrochemical double layer capacitor (EDLC) also known as “super-capacitor” or “ultra-capacitor”, which is characterized by energy density in the range of 1-10 Wh/kg and power density of 1000-10000 W/kg. Such advantageous parameters together with many other technological and economical benefits (high number of charge-discharge cycles; faster charge-discharge; absence of disposable parts and environmentally harmful components; high efficiency up to 98%; low thermal load; safety and reliability) substantiate the concept of replacement of the batteries as a storage media by EDLC in many systems where traditionally batteries are used (e.g. hybrid electric vehicles, power back-up systems, UPS *etc.*).

The key components of each EDLC are the electrodes made of carbon with high degree of porosity and, correspondingly, with high specific surface area (SSA). The overall performance of the entire EDLC system depends

strongly on the parameters of the electrode material. Some of the potentially appropriate materials are various grades of activated carbon (AC) [4], carbonized polymers [5, 6], aerogels [7], carbon fibers [8], and nano-tubes [9, 10]. Among them, AC is a natural choice since it is characterized by high SSA (up to 3000 m²/g). The detailed analysis [11-13] of the experimental data however reveals the role of the micro porosity and shows that AC with characteristic sizes of the pores less than 2 nm are not appropriate because the ionic motion in such narrow channels is slower and prohibits the percolation of the electrolyte. Similar adverse effects can be caused also by various irregularities of the pores as well as by the absence of connections between them (isolated pores). Another critical issue is the role of the binder, which holds together the activated carbon particles as a single mechanical unit and ensures a resistance against etching by the electrolyte solution but also tends to block the pores. Most of the problems mentioned above however can be solved selecting an appropriate carbonaceous precursor.

In the present study we consider as such precursor a material that is abundant in Indonesia, namely the industrial waste from the processing of sago (starch from *Metroxylon sagu* also known as sago palm). Indonesia exports between 200000 and 260000 tons of sago flour annually but the residues from its production tend to be discharged to the rivers. These residues, which are largely composed of celluloses and lignin [14], are both a waste and a pollutant. Their chemical composition suggests that they possess some potential as electrochemical materials, because of their porous structure. In this paper we report the results of the research focused on both the preparation of AC films based

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on sago waste and on the investigation of their electrochemical properties. We discuss also the importance of the technological parameters such as the potassium hydroxide (KOH) to charcoal ratio and the concentration of the polytetrafluoroethylene (hereafter *PTFE*) binder and their influence on the capacitance of EDLC.

EXPERIMENTAL SET-UP

Preparation of the Studied Samples

Sago wastes that consist of fine and coarse "hampas" (solid residue which is left behind after the starch has been washed out) were obtained from the sago processing plant in Kendari, Indonesia. The material for the samples was selected manually, cleaned and dried in an oven at temperature of 105°C for 24 hours. Afterwards, the samples were placed into a porcelain container and carbonized at 350°C for one hour in a muffle furnace. The obtained charcoal (CS) was cooled down to room temperature and ground using a jar mill to pass through a 70 - 150 µm sieve. Two different activation methods were applied. The first one was a *chemical activation* process consisting of *KOH* impregnation followed by carbonization at high temperature (500–900°C) for several hours. The second one was a two-step physical activation process. In the first step a carbonization of the raw material at temperature less than 700 °C was carried out. The second step converts the carbonized product to a porous AC having high SSA by heating to higher temperature (800-1000 °C). In the case of the chemical activation the charcoals were suspended in a concentrated solution of *KOH* and four types of samples were prepared by varying the weight ratio of *KOH* and charcoal. They correspond to ratios equal to 1:1, 2:1, 3:1 and 4:1 respectively. Then the samples were heated at the activation temperature of 800°C for one hour in a horizontal furnace using nitrogen flow at a speed of 800 ml/min. Each ACs sample was labeled as SCK1, SCK2, SCK3 and SCK4, respectively. The samples were washed by de-ionized water, dried at 110°C for 3 hours and then stored in a desiccator for further studies.

For preparing an electrode of EDLC, 0.95 g of the SC sample was mixed with 5% of *PTFE* powder following the procedures described elsewhere [15]. *PTFE* powder was used as a binder and was mixed with a solution of isopropanol and deionised water with a weight ratio of 1:5. Acetone, in a weight ratio of 2:1 with respect to the SC sample, was added to this solution to allow a good homogenization of the binder suspension. The mixture was then rolled to form flexible film. The SC film was mounted on an aluminum foil using hot hydraulic press at pressure of 5 tons and temperature of 321°C, then cooled down using cool hydraulic press at speed of cooling of 15 degree per minute. The obtained thickness and area of the SC film of the sample SC5 was 400 µm and 10 x 10 cm², respectively. The same procedure was carried out for SCK1, SCK2, SCK3 and SCK4 and each of the samples was labeled as CP51, CP52, CP53 and CP54, respectively. Further, a compound corresponding to SCK4 sample (i.e. with *KOH* to charcoal ratio 4:1) was mixed with varying content of the *PTFE* powder. The samples with *PTFE* content of 10%, 20%, 30% and 40% were labeled accordingly as CP104, CP204, CP304 and CP404.

Apparatus, Method and Procedures used in the Measurements

The porosity and the surface properties of SC, SCK and CP samples were investigated by the nitrogen adsorption-desorption method using an automatic volumetric sorption analyzer, namely Quantachrome, Nova-1000. The SC and SCK samples were measured in the form of powder while the CP samples were measured as AC films. Prior to the measurements, the samples were degassed at 200°C for 5 hours. The SSA values were calculated by applying the Brunauer-Emmett-Teller (BET) model [16, 17]. The total pore volume was obtained from the volume of the adsorbed nitrogen. On the other hand, the micropore volume was calculated using the Dubinin-Radushkevich (DR) equation [18]. The surface morphology of the CP sample was then examined by a scanning electron microscope (SEM) JOEL JSM-6400. The images were taken at a magnification of 2000 x at 10 kV. The Fourier transformed infra-red (IR) spectra were recorded using IRPrestige-21 in the 400 – 3900 cm⁻¹ wave number range by the KBr method.

In the electrochemical experiments, a two-electrode cell was used to measure the capacitance. Both the charging and the discharging capacity of the capacitor were obtained by means of a two-terminal measurement [19]. In the experiment, aluminum foil plates were attached as current collectors to the sheet-shaped film samples with dimensions 2 x 2 cm². The test cell was fabricated using two square electrodes of the same type and size separated by a porous polypropylene membrane inserted between them. A 30 wt.% H₂SO₄/H₂O or 1 M of LiClO₄/PC was used as an aqueous and as an organic electrolyte, respectively. The cell was charged at a constant voltage of 0.9 V for 10 minutes and the capacitance was obtained from the variation of the discharge current density up to 200 mA/cm².

EXPERIMENTAL RESULTS AND DISCUSSION

Fig. (1) shows the Fourier Transform Infra-Red (FTIR) spectra of the activated carbon (SCK) prepared at different *KOH* ratios. They were recorded from 400 to 3900 cm⁻¹. The FTIR analysis was carried out on powder samples in order to investigate the chemical reactivity of functional groups at the surface of SCK that occurred at different *KOH* ratios. The FTIR spectrum of the sago hampas was similar to that of baggase [20], which is a type of lignocellulosic material. The absorption band observed at about 3536 cm⁻¹ was attributed to the O-H stretching vibrations in hydroxyl groups. The strong characteristic peak of oxygen-rich SCK at 1709 cm⁻¹ is attributed to the stretching vibration of the carboxyl group C=O bond in carboxylic acid for all values of the *KOH* ratio [12, 21]. The oxygenated group concentration increases with increasing the *KOH* ratio from 1 to 4. The band at 1392 cm⁻¹ could be attributed to O-H bending of carboxylic acid. The C-O stretching of carboxylic acid at 1223 cm⁻¹ disappeared for SCK when compared to SC.

The nitrogen adsorption-desorption method was employed to measure the surface properties of the SC and SCK samples. Fig. (2) shows N₂ adsorption isotherms of the SC and SCK samples at 77 K. According to the classification of the International Union of Pure and Applied Chemistry (IUPAC) [22], these adsorption isotherms for all samples

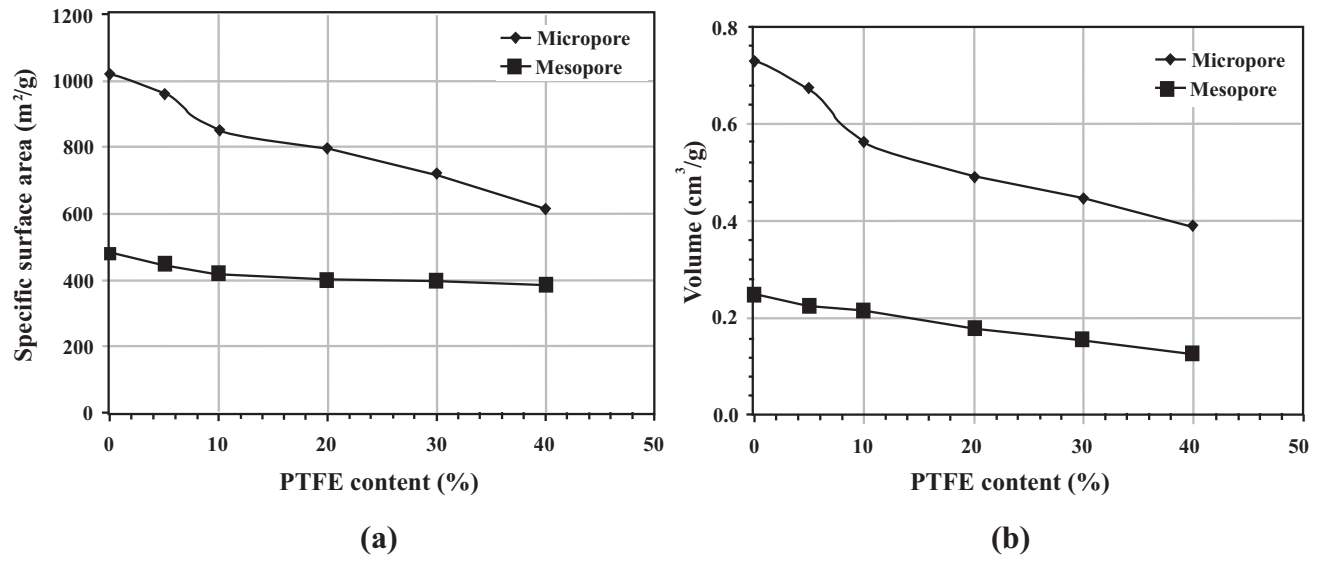


Fig. (5). The variation of SSA and the total volume of micropores and mesopores with PTFE content.

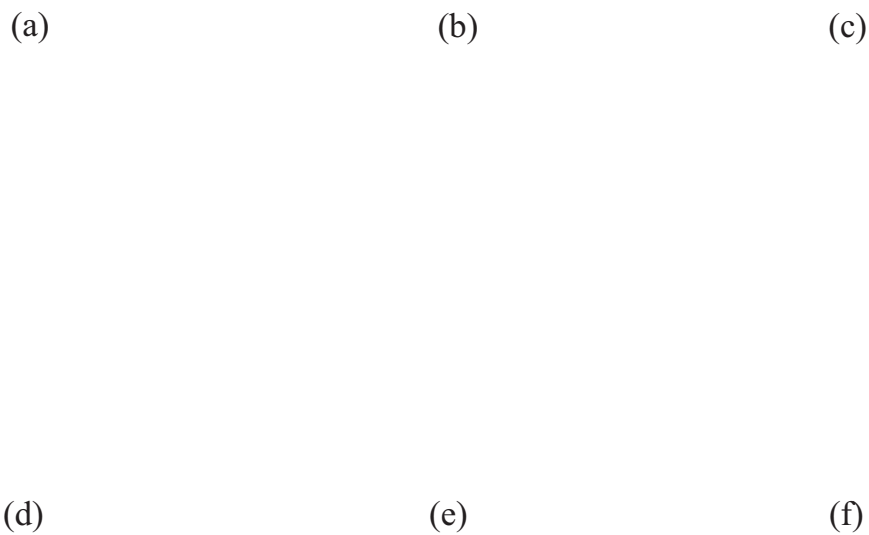


Fig. (6). SEM images of the samples: (a) SCK4, (b) CP54, (c) CP104, (d) CP204, (e) CP304 and (f) CP404. The samples CP104, CP204, CP304 and CP404 were prepared using SCK4 compound and PTFE content of 10%, 20%, 30% and 40%, respectively.

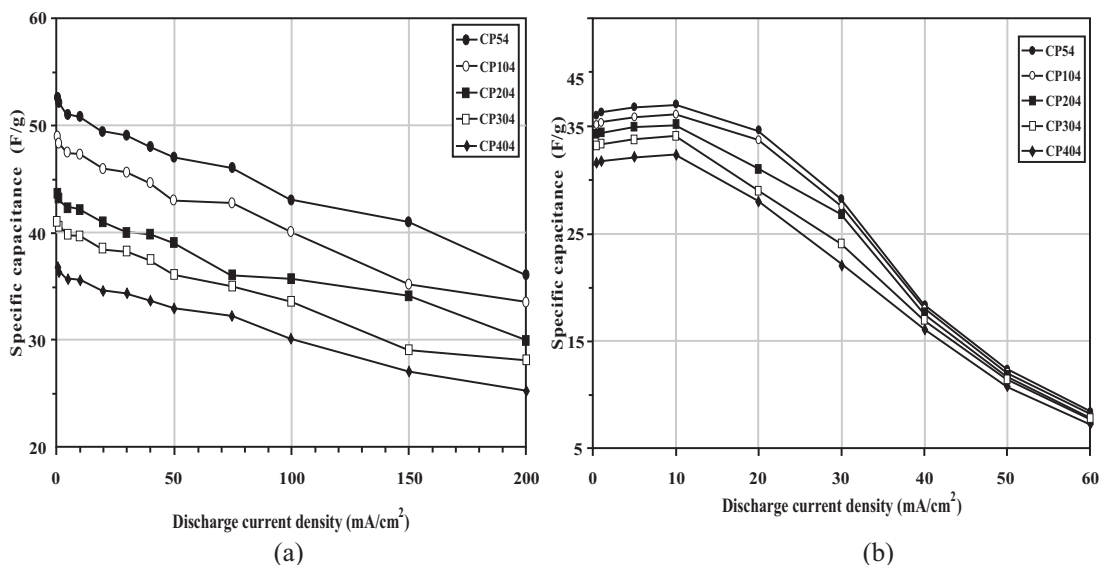


Fig. (7). The specific capacitance of the CP samples in: (a) aqueous electrolyte (30 wt.% H₂SO₄/H₂O) and (b) organic electrolyte (1 M LiClO₄/PC), as a function of the discharge current density and different content of the PTFE binder. The labels CP104, CP204, CP304 and CP404 correspond to samples produced using SCK4 compound and PTFE content of 10%, 20%, 30% and 40%, respectively.

CONCLUSIONS

In this feasibility study we presented a novel and very promising electrode material for EDLC. It is based on the sago waste, which is abundant in Indonesia.

The AC films prepared from this material have a micro-porous structure with a relatively high percentage of small mesopores that depends on the KOH to charcoal ratio. An increase of the latter leads to the formation of bigger number of small mesopores than the number of micropores and eventually causes an increase of the total SSA. In the studied samples the SSA was in the range from 212 to 1498 m²/g.

Another important technological parameter is the content of the PTFE binder. The experimental results show that the SSA of the SCK4 samples decreases when the content of the PTFE increases due to the reduction of the number of micropores. Such explanation is confirmed by the micro-textural SEM images of the CP samples. The specific capacitance of the samples was in the range from 16 to 64 F/g. The role of mesopores and micropores is important for controlling the value of the capacitance in EDLCs. Therefore, for realization of an electrode material made from the CP samples, the amount of the binder must be minimized in order to maximize the specific capacitance.

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