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Research paper

In-situ polymerization of magnetic biochar – polypyrrole composite: A novel application in supercapacitor

K.R. Thines [a], E.C. Abdullah [a, *], N.M. Mubarak [b, **], M. Ruthiraan [a]

[a] Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia, Jalan Semarak, 54100 Kuala Lumpur, Malaysia
[b] Department of Chemical Engineering, Faculty of Engineering and Science, Curtin University, 98009 Sarawak, Malaysia

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ABSTRACT

This paper focuses on the production of magnetic biochar through a novel vacuum condition in an electrical muffle furnace by employing durian rind as the raw material in the presence of three different metallic salts. A high BET surface area value of 835 m^2 g^{-1} was attained at the pyrolysis temperature and time of 800 °C and 25 min. This magnetic biochar was embedded with polypyrrole (PPY) through an in-situ polymerization process which improved specific capacitance of the polymer composite compared to the pure PPY and magnetic biochar. The MBCP composite exhibited the highest specific capacitance of 572 F g^{-1} and energy density of 71.50 Wh kg^{-1} compared to other existing PPY coated carbon composite. This MBCP composite exhibits a good potential for future low-cost supercapacitor applications with an impressive specific capacitance and energy density value.

1. Introduction

One of the main components which have been gaining wide attention and application in the electronic industry would be supercapacitors. Supercapacitors, or also well known as electrochemical capacitors have been gaining a great interest in various applications in the field of electric power, vehicles, railways, electronic products and telecommunications. The main component which plays a vital factor in determining the performance of supercapacitors would be the electrode material [1,2] which focuses on the energy storage [3,4]. The energy storage ability of a supercapacitor electrode material arises from the ionic and electronic charge separations at the electrode – electrolyte interfaces [5,6]. Among various conductive polymer, PPY exhibited a good energy storage capacity, good electrical conductivity, ease of low-cost synthesis and a good environmental stability [7-9]. Even though PPY consists of a nanostructured fibrous network to provide a rapid ionic transport within the bulk matrix [10,11], the rate capability of this conductive polymer is hindered by the manipulation in the structural conformation with frequent ion exchange and weakening of electrical properties with increasing electrochemical cycles [12].

Therefore, an addition of carbon nanomaterials such as graphene or carbon nanotubes is recommended to introduce an electrically conducting network to improve the electrochemical cyclic stability of the electrode [8]. Hence, research has been focused on the production of low-cost carbon materials which prepared from abundantly available biomass to solve the sustainability issue while this low-cost carbon material is employed to produce a carbon-PPY composite to enhance the electrochemical performance of supercapacitor electrode material. On that note, the largely consumed durian fruit in Malaysia has been generating several environmental related issues due to the poor management of abundant durian rind [13]. These durian rind were employed to synthesize low-cost biochars with an impressive porous structure which enhance the ion diffusion and electrolyte access for a good electrochemical activity [14]. Besides that, durian rind also have been utilized as a supercapacitor electrode material which demonstrated a significant electrochemical performance [15]. These impressive findings provided the much-needed solution for the environmental issues related to the poor management of durian

* Corresponding author.: Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia, Jalan Semarak, 54100 Kuala Lumpur, Malaysia
** Corresponding author.: Department of Chemical Engineering, Faculty of Engineering and Science, Curtin University, 98009 Sarawak, Malaysia
E-mail addresses: thinesraj27@gmail.com (K.R. Thines), ezzatc@utm.my, ezzatchan@gmail.com (E.C. Abdullah), mubarak.mujawar@curtin.edu.my, mubarak.yaseen@gmail.com (N.M. Mubarak).

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rind. In addition, the preparation of activated carbon from vacuum pyrolysis char of teak sawdust studied by S. Ismadji [16] in their study use of steam activation enhanced increase in BET surface area and pore volume. In recent years, the application of metal derived biochar (magnetic biochar) along with PPY as the supercapacitor electrode material has been carried out and it resulted in an impressive electrochemical performance. Magnetic biochar was found to enhance the electrochemical performance of conductive polymer due to its high porosity and impressive conductivity ability which ease the abundant loading of pseudocapacitive materials via serving as nucleation and anchoring sites [17]. A typical muffle furnace consists of a muffle which presents in the shape of hollow cuboid made of special refractory material in which electrical energy will be supplied to heat the muffle rather than fuel fired due to cost constraint. Electrical furnace, which is generally preferred for heat treatment of small segments, has a wide range of advantages such as pollution free chamber, uniformity of temperature and a total control of temperature in the chamber, minimum loss of heat energy, easy working principle and a clean working environment [18]. The novelty of vacuum condition in an electrical muffle furnace indicates the successful production of magnetic biochar in the absence of any inert gas such as nitrogen and helium which is generally used in microwave process.

In this study, the abundantly available durian rind, was employed and converted into hematite and magnetite-loaded magnetic biochar through a novel vacuum condition in an electrical muffle furnace. This magnetic biochar was then used to produced the novel PPY coated hematite and magnetite doped biochar composite by employing an in-situ polymerization process in the presence of magnetic biochar, pyrrole monomer and oxidant. In-situ polymerization process was done in varying weight of pyrrole monomer and magnetic biochar and the composites produced were fabricated as the supercapacitor electrode material. The morphology, electrical conductivity and specific capacitance value of the prepared electrode were determined as well.

2. Materials and methods

2.1. Collection and grinding of durian rind

Durian rind was collected from a durian stall located in Taman Megah Cheras (Latitude:N 3° 3′ 19.926″, Longitude:E 101° 46′ 5.9484) Kuala Lumpur. The collected locally grown fruits at Selangor were mainly mixed type of D160 and D190 cultivator were bought from the orchard owner. These durian rinds were made sure not to be contaminated with fungus and in it was available in a dry condition when it was collected. This collected durian rind was then chopped into smaller pieces to ease the cleaning process. These durian rind were then washed thoroughly to remove all the dirt from the rind and leftover durian on the inner part of rind while any durian rind spotted with fungus were discarded. The washed durian rind was then dried in vacuum oven for 5 days continuously at 105 °C. The grinding process was carried out at Forest Research Institute of Malaysia (FRIM) by employing a two-stage grinding process. The initial grinding process was done to obtain a particle with a size of less than 1 mm and the second grinding process was carried out to obtain particles with size less than 20 μm by employing the ball mill grinder through a continuous grinding and sieving process. The ground durian rind particles were sieved to obtain a particle size of less than 20 μm and the grinding process is repeated until the required particle size is obtained. High yield of durian rind's particles was obtained by employing this two-stage grinding process due to the less lost in mass during the grinding. The ground durian rind particles were then stored tightly in a sealed bag and it was placed in a desiccator.

The fruiting period of Durian differ according to the different geographical area and the weather condition at these areas leading to off-season fruting. Generally, Peninsular Malaysia undergoes a main fruiting season from June to August [19] while East Malaysia consisting of Sabah and Sarawak straddles across June through August and Sabah has a minor one in November and December [19,20]. Generally, durians are only available for short period in a year. As the demand for the Durians has been increasing annually, few attempts have been made to modify the flowering period to extent the fruiting season. Exploiting differences in fruiting seasons and experimenting the cloning process were the few methods embraced to extend the fruiting season. Application of ethephone, daminozide, NAA (a-napthalene acetic acid), GA3 or fertilizer were found to be unsuccessful in inducing early flowering period [21]. Futhermore, paclobutrazol (Cultar®), a suppressor of gibberellin (GA) production, were used as the foliar sprays for early flowering and fruit production and it was found that the increase in concentrations of paclobutrazol resulted in higher production of number of flowers produced per tree [22] but provided a negative impact on the average weight of fruits produced. Up to the year 1990, there were more than 100 different Malaysian clones of Durian which were registered and all of it were differed by fruit characteristics [23]. All Durian accessories were given the prefix “D” to distinct from other fruits such as rambutan which were given the prefix “R” [24]. Durian clones are differentiated by certain aspects such as tree form, vigor and leaf size, frequency and intensity of flowering, the size and shape of fruits, the thickness and color of rinds; aril volume, color, aroma, texture and flavor; seed number and size. The process of cloning Durian requires a high degree of self incompatibility and flowers have to be cross-pollinated to determine the fruit [25]. Besides that, hybridization of different *Durio* species were initiated as well to improve the quality and the yield of the fruits. As an example, artificial hybridization of *D. zibenthinus* with several wild species such as *D. graveolens, D. oxleyanus* and *D. kutejensis* were attempted to improve the fruit quality while the interspecific crosses done between *D. zibenthinus* and *D. graveolens* provided viable seeds [26]. Besides that, durian is generally classified as a food which has a high tonic value. Research also indicates that the indigestibility of the aril causes the food to be aphrodisiac [27] [28]. The strong odour generated by Durian is probably due to the sulphuric compound present together with some base [29]. Another study done reported that there were 63 volatile constituents (including 30 esters, 5 ketones and 16 sulphurous compounds) which would have contributed to the odour of the Durian [30]. Durian stands out to be the best sell among the seasonal fruits in South East Asia, especially Malaysia due to its high market price. Durians are generally produced in villages, orchards or foothills which are located far from the market or the cities. This distance generally increases the prices of Durians at the town, but not at the villages due to the high competition of abundant availability of Durian.

2.2. Preparation of metal ion – durian rind biomass

Analytical grade metal salt of iron (III) oxide, Fe_2O_3, iron (II) sulphate heptahydrate, $FeSO_4.7H_2O$ and iron (III) chloride hexahydrate, $FeCl_{3.}6H_2O$ along with ground durian rind particles were used for the oxidization process to achieve a better porous structure at the surface of durian rind particles together with the attachment of carboxylic and carbonyl group on the surface of durian particles prior the pyrolysis process [31].

Initially, 200 cm^{-3} of 1.0 mol L^{-1} respective metal's ion salt solution were transferred into a 1 L Pyrex laboratory bottle, followed by the addition of 150 cm^{-3} of nitric acid, HNO_3 and 50 cm^{-3} of potassium permanganate, $KMnO_4$ in the ratio of 3:1 as suggested