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Influence of gamma irradiation exposure on the performance of supercapacitor electrodes made from oil palm empty fruit bunches

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ABSTRACT

Carbon-monolith electrodes for supercapacitors were prepared from GMs (green monoliths) made from pre-carbonized fibers of oil palm EFB (empty fruit bunches) and GMs of pre-carbonized EFB fibers exposed to gamma radiation at 5 kGy, 15 kGy, and 20 kGy. GMs and irradiated GMs were carbonized and activated to prepare ACM (activated-carbon-monolith) electrodes. The gamma radiation affected the pore structure of the ACM electrodes and the electrochemical performance of the supercapacitors; irradiation doses of 0 kGy, 5 kGy, 15 kGy and 20 kGy produced specific capacitances of 121 F g^{-1}, 196 F g^{-1}, 11 F g^{-1}, and 12 F g^{-1}, respectively. The irradiation dose of 5 kGy appears to be optimum and produces a specific power and specific energy of 236 W kg^{-1} and 5.45 W h kg^{-1}, respectively, representing 34% and 60% increases over ACM electrodes prepared from non-irradiated GMs.

1. Introduction

Supercapacitors, also known as EDLCs (electrochemical double-layer capacitors), operate in the energy range that lies between conventional capacitors and batteries. They have been widely used as an energy storage device that can store and release energy. Their delivery (charge–discharge) performance is better than commercial rechargeable batteries, and they also have a longer cycle life [1]. Supercapacitor applications as high power energy storage devices are mainly found in electronic and military devices, space flight technology, automotive and public transportation, and as low-power energy storage devices; they can be found in, for example, portable media players, game consoles, photographic flash, and printers [2]. Recently, supercapacitors have been critically analyzed for use in public transportation; specifically, they show promise in improving the performance of hybrid bus powertrain systems achieving both optimal size and good energy management [3].

The electrode is one of the major supercapacitor components. The other components are the electrolyte, current collector and separator. The energy storage process that occurs at the electrode–electrolyte interface involves the formation of an electric double layer via the migration of ionic charges in the electrolyte and electronic charges in the electrode. While many materials, such as graphene [4–7], CNTs (carbon nanotubes) [8,9], conducting polymers [10,11], triblock copolymers [12], metal oxides [13–16], carbon aerogels [17], activated carbons [18–21], and composites [22–24] have been widely developed as electrodes materials for supercapacitor, activated carbon is still the best porous electrode material for supercapacitors because of its high surface area, chemical stability, wide availability, and the simple and low cost preparation methods compared to other carbon-based materials, such as carbon nanotubes, carbon aerogels, and graphene. Significant effort has been dedicated to improving the properties of the activated carbon electrodes used in supercapacitors, such as studies on pore structure and surface chemistry because of the electrode's influence on the performance of supercapacitors [25,26].

Various methods, such as modifying the properties of the organic precursors or the pre-carbonized organic precursors used to produce carbon electrodes, have been applied prior to carbonizing the electrodes because the electrode properties, such as the pore structure and surface chemistry, are determined partly

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by the properties of the precursors. This modification can be performed chemically using an activating agent, such as KOH [27], H_2SO_4 [28], H_3PO_4 [29], K_2CO_3 [30], or $ZnCl_2$ [31]; physically using a gas, such as CO_2 [32] or steam [33,34]; by a combination of physical and chemical methods [35–37]; or by microwave irradiation [38]. Additionally, this modification can be performed by mixing the organic precursor or pre-carbonized material with an additive, such as a metal oxide [39], conducting polymer [40], CNTs [41,42], graphene [43], graphene oxide [44], petroleum coke [45], or carbon fibers [46]. The purpose of these modifications is to improve the electrochemical performance of the supercapacitor. In the present study, a gamma irradiation technique is used to modify the properties of the pre-carbonized organic precursor, i.e., SACG (self-adhesive carbon grain) prepared from fibers from oil palm EFB (empty fruit bunches), which contain partially decomposed hemicellulose, cellulose and lignin. These macromolecules were sensitive to the γ-irradiation treatment [47–49], and the effect of the γ-irradiation was found to be strongly dependent on its dosage level. In the present study, the dosage applied to green monoliths of SACG was varied from 5 kGy to 20 kGy. The objective of the present study was to observe the effects of varying the γ-radiation dose on the properties of the carbon monolith electrodes produced from these green monoliths and correlate these effects with the performances of supercapacitors fabricated using these electrodes.

This paper is organized as follows: Section 2 presents the preparation and characterization procedures of electrodes from non-irradiated and γ-irradiated green monoliths of pre-carbonized oil palm fibers. Section 3 reports the results and discussion of physical and electrochemical data characterizing non-irradiated and γ-irradiated electrodes. Section 4 presents the conclusions of this study.

2. Materials and methods

2.1. Electrode preparation and cell fabrication

EFB fibers were supplied by Sabutek Sdn. Bhd. SACGs with an average particle size less than 106 μm were prepared from EFB fibers by pre-carbonization (Furnace CTMSB46), milling for 36 h (ball mill AC Motor BS 500-110) and sieving (Matest 24030 Brembate Sopra (BG)) [50]. A 30 g sample of SACG powder was poured into 300 ml of boiling water, stirred for 1 h, and dried in an oven at 100 °C for 48 h. Approximately 10 g of the dried mixture was milled for 20 min to obtain a homogeneous SACG powder. Following this step, 0.75 g of the mixture was placed inside a mold with a diameter of 20 mm and converted into GMs (green monoliths) using a press pelletizing machine (VISITEC 2009-Malaysia).

The GMs were sent for γ-irradiation treatment at dosages of 5, 15, and 20 kGy to produce the irradiated samples GM-5, GM-15 and GM-20, respectively, using a ^{60}Co γ-irradiation source (Gammacell 220 Excel). The non-irradiated and irradiated GMs were carbonized in a carbonization furnace (Vulcan Box Furnace 3-1750) under a 1.5 L min^{-1} flow of N_2 gas, at 800 °C using our previous multi-step heating profile [51] to produce CMs (carbon monoliths). These carbon monoliths were activated using CO_2 (1.0 L min^{-1}) at 800 °C with a multi-step heating profile [45,52,53] for 3 h at a heating rate of 5 °C min^{-1} to produce ACMs (activated carbon monoliths), labeled ACM-0, ACM-5, ACM-15 and ACM-20, respectively. After being polished to a thickness of 0.4 mm, the polished ACM-0 and other ACMs were used as electrodes in symmetrical supercapacitor cells using 316 L stainless steel (0.02 mm thick) as the current collector, 1 M H_2SO_4 as the electrolyte and a Celgard separator (25 μm thick).

2.2. Physical characterizations

The dimensions (Mitutoyo 193-253) and masses (Mettler Toledo AB204) of the monoliths were measured to determine the density of the GMs, CMs and ACMs. Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer Spectrum 400 FT-IR) was used to study the chemical structures of the ACMs. A field emission scanning electron microscope (FESEM, Zeiss SUPRA 55 VP) was used to study the microstructures of the ACMs. An X-ray diffractometer (Bruker AXS: model D8 Advance, wavelength of 1.5406 Å for CuK_α line from Copper X-ray sources) was used to record the XRD (X-ray diffraction) patterns of the ACMs. The liquid nitrogen (77 K) adsorption–desorption isotherm experiments were conducted to characterize the porosity of the ACMs using an instrument (Micromeretic ASAP 2010) equipped with software that can calculate the pore structure parameters of the samples, i.e., the BET surface area (S_{BET}), micropore surface area (S_{micro}), mesopore surface area (S_{meso}), micropore volume (V_{micro}), mesopore volume (V_{meso}) and average pore diameter (D). Raman spectra were recorded over a 200 cm^{-1} to 3200 cm^{-1} Raman shift range from the ACMs using a Renishaw inVia Raman Microscope (Raman microscope enclosure RE 04) employing a 514 nm laser beam.

2.3. Electrochemical characterization

The performances of the supercapacitor cells with ACMs as their electrodes were studied using EIS (electrochemical impedance spectroscopy), CV (cyclic voltammetry) and GCD (galvanostatic charge–discharge) methods on an electrochemical instrument-interface (Solartron SI 1286 and Solartron 1255HF Frequency Response Analyzer). All of the measurements were carried out at room temperature (25 °C).

Using the EIS data, the C_{sp} of the electrodes was determined using equation (1):

$$C_{sp} = -\frac{1}{\pi f_l Z_l'' m} \tag{1}$$

where f_l is the lowest frequency, Z_l'' is the imaginary impedance at f_l and m is the weight of electrode. The EIS data as functions of the frequency were analyzed using equations (2)–(4):

$$C(\omega) = C'(\omega) - jC''(\omega) \tag{2}$$

$$C''(\omega) = Z'(\omega) \Big/ \omega |Z(\omega)|^2 \tag{3}$$

$$C'(\omega) = -Z''(\omega) \Big/ \omega |Z(\omega)|^2 \tag{4}$$

where $Z(\omega)$ is equal to $1/j\omega C(\omega)$, $C'(\omega)$ is the real capacitance, $C''(\omega)$ is the imaginary capacitance, $Z'(\omega)$ is the real impedance and $Z''(\omega)$ is the imaginary impedance [54].

From the voltammograms, the C_{sp} of the electrodes was determined using equation (5):

$$C_{sp} = \frac{2i}{Sm} \tag{5}$$

where i is the electric current, S is the scan rate and m is the weight of electrode.

From the GCD data (charge–discharge curve) recorded at a selected current density, the C_{sp} of the electrode was determined using equation (6):

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