



Preparation of highly porous binderless activated carbon electrodes from fibres of oil palm empty fruit bunches for application in supercapacitors



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HIGHLIGHTS

- ▶ Oil palm empty fruit bunches have been processed into supercapacitor electrodes.
- ▶ CO₂ and KOH activations can produce highly porous binderless carbon electrodes.
- ▶ Small quantity KOH can reduce CO₂ activation time significantly.
- ▶ Supercapacitors based on these electrodes exhibit excellence performances.
- ▶ Therefore this novel method offers a significant economic advantage.

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ABSTRACT

Fibres from oil palm empty fruit bunches, generated in large quantities by palm oil mills, were processed into self-adhesive carbon grains (SACG). Untreated and KOH-treated SACG were converted without binder into green monolith prior to N₂-carbonisation and CO₂-activation to produce highly porous binderless carbon monolith electrodes for supercapacitor applications. Characterisation of the pore structure of the electrodes revealed a significant advantage from combining the chemical and physical activation processes. The electrochemical measurements of the supercapacitor cells fabricated using these electrodes, using cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge–discharge techniques consistently found that approximately 3 h of activation time, achieved via a multi-step heating profile, produced electrodes with a high surface area of 1704 m² g⁻¹ and a total pore volume of 0.889 cm³ g⁻¹, corresponding to high values for the specific capacitance, specific energy and specific power of 150 F g⁻¹, 4.297 Wh kg⁻¹ and 173 W kg⁻¹, respectively.

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1. Introduction

Supercapacitors are electrochemical devices that primarily consist of electrodes, current collectors, an electrolyte and a spacer and are promising electrical energy storage devices for applications that demand high energy density, high reliability, maximum power, long-cycle life or long-term operation stability, suitable dimensions and weight, low cost, fast discharge/charge time, low level of heating, safety, etc. Its energy capacities allow supercapacitors to fill the gap between batteries and conventional capacitors in term of energy and power requirements. Therefore, applications of supercapacitors include in appliances such as electronic devices, electric vehicles, and military equipment.

Common materials used as supercapacitor electrodes include conducting polymers, metal oxides, and porous materials such as activated carbon, carbon aerogels and carbon nanotubes. Activated carbon is advantageous because of its high surface area and porosity, good thermal and electrical conductivity, good anti-causticity, high stability, low cost and commercial-scale availability (Pandolfo and Hollenkamp, 2006; Obreja, 2008).

Activated carbon electrodes can be produced from biomass precursors (wood, fruit shells, stones and bunches) and fossil-fuel based precursors (petroleum and coal) and have been tested for supercapacitor applications. Biomass precursors are cheaper, readily available, environmentally friendly, renewable, and structurally porous.

The palm oil industry is a major agricultural sector in Malaysia, Indonesia and Thailand, covering 27 million hectares of agricultural land. This industry involves the processing of oil palm fruits

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into cooking oil and generates large quantities of biomass waste that are a pollutant if directly discharged into the environment. This biomass waste includes palm kernel cakes, palm kernel shells, empty fruit bunches (EFB) and mesocarp fibres (Razuan et al., 2010; Fan et al., 2011). In Malaysia, the annual production of EFB is 8.5 million tons and is traditionally used as fertiliser (after burning), mulching material for palm oil plantations and boiler fuel in palm oil mills. Non-traditional uses include bedding material, particleboard and medium density fibreboard. In the present study, EFB has been used as a raw material to produce monolithic nanoporous activated carbon for supercapacitor electrodes. The processing of EFB involves pre-carbonisation, pulverisation, pelletisation, chemical treatment, carbonisation and activation. The amounts of chemical activating agent (KOH) used for the treatment of pre-carbonised EFB were appropriately selected, and the activation time was varied to control development of the electrode pore structure. The symmetrical supercapacitor cells were fabricated using these electrodes and the capacitive behaviour of the electrodes and their supercapacitor performance was evaluated using electrochemical methods including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge (GCD). The objective of this paper is to investigate the relationship of the behaviour and performance of supercapacitor cells to the pore-structure of electrodes especially as it relates to the activation time during electrode preparation.

2. Experimental

2.1. Electrode preparation and cell fabrication

Self-adhesive carbon grains (SACG) were prepared from fibres of EFB using our previously reported method (Deraman et al., 1998). The method begins with the pre-carbonisation of fibres of EFB at low temperature ($\sim 280^\circ\text{C}$), followed by ball milling for approximately 18 h, and sieving to obtain a powder of SACG with a particle size of $< 106\ \mu\text{m}$. The SACG was mixed with KOH at a ratio (by weight) of 5% KOH to 95% SACG. The wet mixing was conducted in distilled water, and the mixture was stirred for $\sim 1\ \text{h}$ to ensure homogeneity, followed by drying and milling for 20 min to produce a fine powder of KOH-treated SACG. Green monoliths (GMs) of the SACG and green monolith (GMK) of the KOH-treated SACG were prepared in a mould (20 mm diameter) using $250\ \text{kg cm}^{-2}$ of compression force. The materials were carbonised at $\sim 800^\circ\text{C}$ under a N_2 atmosphere (with a flow rate of 1.5 litres per minute) to produce the carbon monoliths (CM), carbon monolith of the untreated SACG (CM-U) and carbon monolith of the treated SACG (CM-K). The CM-U and CM-K were activated by CO_2 (with a flow rate of 1 litre per minute) from room temperature to $\sim 800^\circ\text{C}$ at a rate of 5°C per minute to produce the activated carbon monoliths (ACM), ACM-U and ACM-K.

ACM-U and ACM-K were produced by CO_2 activation at several activation times, i.e., 1, 2, 3, 4 and 5 h. To avoid cracks due to excessive heating after activation longer than 2 h, a multi-step activation method which divided the total activation time into several segments of heating steps, previously employed by us (Taer et al., 2010), was used in this study. For convenience, the ACMs produced are labelled as ACM-U1 to ACM-U5 and ACM-K1 to ACM-K5 to denote activation times of 1–5 h, respectively. All ACM electrode, after polished into the required thickness ($\sim 0.4\ \text{mm}$), were washed to remove the activating agent with distilled water until pH 7. The electrodes were found to decrease slightly in weight after washing.

For studying the capacitive properties of the ACMs electrodes, symmetrical supercapacitor cells were fabricated using two ACMs electrodes prepared for each selected activation time. Stainless steel foils (316-L stainless steel foils with a thickness 0.02 mm,

Goodfellow Cambridge Ltd., England) were used as the current collectors and 1 M sulphuric acid was used as an electrolyte. A Teflon spacer ring separated the ACM electrodes by 0.2 mm. The diameter, thickness and weight of the ACM electrodes were $\sim 14.5\ \text{mm}$, $\sim 0.4\ \text{mm}$ and 50–60 mg, respectively.

2.2. Physical characterisation

The dimension and weight of the ACMs were measured to determine the sample density. The porosity parameters of the ACMs (i.e., Brunauer–Emmett–Teller (BET) surface area (S_{BET}), mesopore surface area (S_{Meso}), micropore volume (V_{Micro}), total pore volume (V_{Tot}) and average pore diameter (D)) were determined from nitrogen adsorption–desorption isotherm data recorded at -196°C using an Accelerated Surface Area and Porosimeter system (ASAP 2010, Micromeritics). The calculation of these parameters was done based on the standard method (Sing et al., 1985). The structural features of the ACMs were investigated by X-ray diffraction (XRD). XRD patterns were generated over a diffraction angle (2θ) range from 5° to 85° , using a Bruker AXS D8 advance diffractometer that employed $\text{CuK}\alpha$ radiation. The interlayer spacing (d_{002}) of the ACMs was evaluated by the application of Bragg's Law ($n\lambda = 2d \sin 2\theta$) to the position of the (002) peak, where $n = 1$ and $\lambda = 1.5406\ \text{\AA}$. The microcrystallite dimension (stack height = L_c , stack width = L_a) of the ACMs was calculated from the XRD diffraction pattern using the Debye–Scherrer equations ($L_c = 0.89\lambda/\beta\cos(\theta_{002})$ and $L_a = 1.94\lambda/\beta\cos(\theta_{100})$), where β is equal to the peak width at half height (Carrott et al., 2001; Awitdrus et al., 2010; Valante-Nabais et al., 2011) of the respective peaks. The morphology of the ACMs was investigated using a Field Emission Scanning Electron Microscopy (FESEM) technique (Supra PV 55 model).

2.3. Electrochemical characterisation

An electrochemical instrument (Solartron 1286 electrochemical interface and Solartron 1255 HF frequency response analyser) was used to study the performance of the supercapacitor cells using CV, EIS and GCD methods. All measurements were carried out at room temperature (25°C). From the voltammogram, the specific capacitance (C_{sp}) of the electrodes was determined using equation:

$$C_{\text{sp}} = \frac{2i}{Sm} \quad (1)$$

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

From the EIS data, the specific capacitance (C_{sp}) of the electrodes was determined using equation:

$$C_{\text{sp}} = -\frac{1}{\pi f Z'' m} \quad (2)$$

where f = frequency, and Z'' = imaginary impedance at f . The EIS data as a function of the frequency were analysed using the following equations:

$$C(\omega) = C'(\omega) - jC''(\omega) \quad (3)$$

$$C''(\omega) = -Z'(\omega)/\omega|Z(\omega)|^2 \quad (4)$$

$$C'(\omega) = Z^{\text{prime}}(\omega)/\omega|Z(\omega)|^2 \quad (5)$$

where $Z(\omega) = 1/j\omega C(\omega)$, C' = real capacitance, C'' = imaginary capacitance, Z' = real impedance, and Z'' = imaginary impedance (Portet et al., 2005).

From the GCD data (charge–discharge curve) recorded at a current density of $10\ \text{mA cm}^{-2}$, the specific capacitance (C_{sp}) of the electrodes was determined using equation:

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