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Orange Peel-Derived Activated Carbon as a Potential Electrode Material for Supercapacitor Application

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Supercapacitors are emerging as a viable alternative to batteries in a variety of applications. In recent years, extensive research has been carried out on the development of new electrode material to produce supercapacitors with high energy density. In this study, 2 different types of activated carbon (AC) namely commercialized AC (i.e. steam-activated charcoal) and self-prepared phosphoric acid-treated orange peel AC were used to fabricate the supercapacitor electrodes. Prior to the fabrication, the structural properties and surface morphology of both ACs were examined using the Brunaeuer-Emmett-Teller (BET) analysis and Scanning Electron Microscope (SEM). The results revealed that commercialized AC exhibited more pores on its surface and a higher BET surface area of 818.8441 m^2/g than orange peel-derived AC, which had a surface area of 137.9910 m^2/g. The fabricated coil cell supercapacitor in sodium sulfate electrolyte demonstrated specific capacitance of 35.5880 F/g for the commercialized AC and 57.7056 F/g for the orange peel-derived AC. Higher energy density was recorded for supercapacitor fabricated using orange peel-derived AC (8.0147 Wh/kg), compared to the commercialized AC counterpart (4.9428 Wh/kg). Despite its inferior physical properties, the superiority of supercapacitor performance (e.g., specific capacitance and energy density) with orange peel AC suggested that there is a potential for orange peel AC-based supercapacitors to be used in real-world applications, but more research on the optimization of electrode composition, type, and electrolyte concentration is required.

1. Introduction

The world has faced energy shortages and environmental degradation due to the over-exploitation of non-renewable energy sources, such as petroleum, natural gas and fossil fuel. Energy storage devices play a significant role in addressing these global challenges by storing natural energy to eliminate waste and collect extra energy for backup use (Sun et al., 2021). The rapidly expanding market for electronic devices also necessitates the development of more energy storage systems. Supercapacitors, which have a higher specific power, a longer cycle life (>100,000 cycles), and a shorter charge time, will be used more in the future as an alternative energy storage resource for rechargeable batteries (Kamila et al., 2021). Carbon materials derived from fossil fuels, including carbon nanotubes and gprahene, as well as conductive polymers, are the most efficient active materials for supercapacitors (Herou et al., 2018). Graphene is one of the most popular materials in electrochemical studies because of its unique properties such as structure, electrical conductivity, mechanical, and catalytic properties (Smith et al., 2019). Graphene production, however, is a time-consuming and expensive

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process with a low yield. According to Serrano-Luján et al. (2019), chemical reduction is a common graphene production process that is not environmentally friendly because it relies on reducing agents that are hazardous to the environment.

Recently, biomass-derived carbon electrodes have emerged as a potential substitute for graphene due to their mechanical properties, compositions, versatility of morphologies, abundance and low cost. These include cattle bone, bamboo, coconut shell, tea residue, cornhusk, banana peel and etc. (dos Reis et al., 2020). Lignin, cellulose and hemicellulose are naturally abundant in plants and biomass. Ago et al. (2016) reported that lignin can increase the specific surface area of the supercapacitor electrode's activated carbon, which produces sub-micron to nanofibers that increases active sites and specific capacitance. As for the cellulose, it has abundant functional groups and excellent reticular porous structure, making it a suitable raw material for the carbon electrode of supercapacitors (Sun et al., 2021).

In the present work, the activated carbon (AC) derived from orange peel, which contains a high concentration of lignin and cellulose, was investigated as a potential electrode material for supercapacitors. Although research on orange peel-derived AC for supercapacitor electrodes is not new, the literature lacks direct comparisons of supercapacitor performance using the same electrolyte and AC loading on the electrode. The structure of the supercapacitor fabricated for majority of past research was also not clearly revealed. In this study, the energy density and specific capacitance of a coil cell supercapacitor fabricated from phosphoric acid-treated orange peel AC were compared to those made from commercialized AC (i.e. steam-activated charcoal), and the differences were correlated to the structural properties and surface morphology of both ACs, revealing the potential of using orange peel waste as raw materials for supercapacitor carbon electrodes.

2. Materials and methodology

2.1 Materials and chemicals

Orange peel waste was collected from the fruit stall at ground floor of D6 in Xiamen University Malaysia. Commercialized AC (i.e. steam-activated charcoal)(Merck), Phosphoric acid, H_3PO_4 (R&M Chemicals), sodium sulfate, Na_2SO_4 (R&M Chemicals), N-Methyl-2-pyrrolidone, NMP (Sigma-Aldrich), polyvinylidene fluoride, PVDF (Sigma-Aldrich) and acetylene black (100 % compressed, 99.9+ %, Thermo Scientific) were used as received without any further purification or modification.

2.2 Preparation of AC from orange peel

The collected orange peel waste was washed and dried overnight at 80 °C in an oven. The dried orange peel was grinded and sieved to obtain powder with uniform size of 0.2 mm. The orange peel powder was then immersed in 1.69 g/mL of aqueous H_3PO_4 at the powder to acid ratio of 1:6 (wt/v) for chemical activation. The mixture was stirred for 18 h at room temperature. It was then carbonized in a tubular furnace (Lenton LTF) for 2 h at 700 °C with the presence of nitrogen gas flowing at the rate 150 cm^3/min. The orange peel AC obtained was then washed with deionized water until the pH was neutral. Finally, the AC was dried for 4 h at 100 °C in an oven, and kept in an airtight container for further usage.

2.3 Characterization of orange peel AC

The surface morphology of phosphoric acid-treated orange peel AC and commercialized AC was examined using Scanning Electron Microscope (SEM) (JEOL-JSM-6701F). The surface area and pore volume of both ACs were determined using the Brunaeuer-Emmett-Teller (BET) analysis in which Micrometritics ASAP 2020 was used to conduct adsorption-desorption of nitrogen gas at 77 K.

2.4 Fabrication of coil cell supercapacitor

The procedures to fabricate the coil cell supercapacitor were performed as descried by Zhuo (2021) with slight modifications. The binder (PVDF): acetylene black: commercialized AC mass composition used in this study was 8:1:1, with NMP serving as the organic solvent. PVDF was first dissolved in NMP before gradually adding acetylene black and AC to prepare the carbon slurry. The carbon slurry was then coated onto aluminium foil, which served as the current collector. The coating was performed with a doctor blade of a thickness of 35 mm to achieve consistent thickness across the aluminium foil surface. The coated film was dried overnight at 120 °C in an oven. The aluminium foil was subsequently cut into pieces of 12 mm-circles with a hydraulic press to be used as the coil cell electrodes. The mass loading of the AC was determined from the mass difference between the uncoated and coated 12 mm-aluminium foil circles. The coil cell supercapacitor fabricated in this study was illustrated in Figure 1 which consisted of coil cell casings (positive and negative cases), current collector – anode and cathode (aluminium foil coated with carbon slurry), separator (glass fiber), spacer and spring. Na_2SO_4 with a concentration of 2 mol/dm^3 was used as the liquid electrolyte.

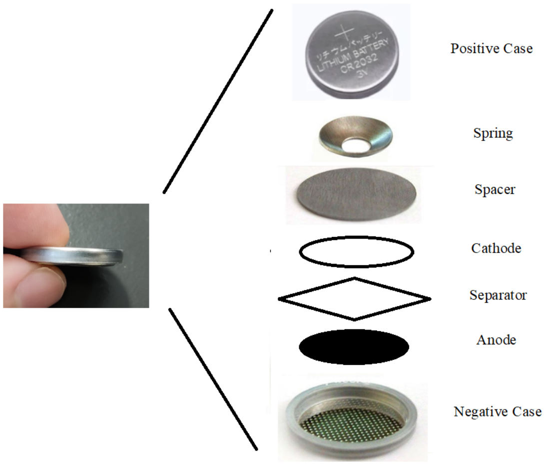


Figure 1: The components of coil cell supercapacitor fabricated in this study

The fabrication was repeated with nylon as the separator. The electrochemical property, namely specific capacitance of the supercapacitors were compared to determine the better material to be used as the separator in this work.

2.5 Measurement of electrochemical performance of the coil cell supercapacitor

The fabricated coil cell was placed inside a coil cell holder and the electrochemical properties were analyzed using a potentiostat (Ametek VersaSTAT 4 Potentiostat Galvanostat) with the software (Ametek VersaStudio). Figure 2 shows the connection of the positive and negative terminals of the potentiostat to the coil cell holder.

Figure 2: Connection of coil cell holder and the potentiostat

The cyclic voltammetry (CV) was measured in a potential window of 1 V at scan rate of 50 mV/s for 5 cycles. The specific capacitance and energy density of the supercapacitor was calculated using Eq(1) and Eq(2) (Zhu et al., 2016):

$$C_s = \frac{\int I\, dV}{v m \Delta V} \qquad (1)$$

where C_s was the specific capacitance (F/g), $\int I\, dV$ was the area enclosed by the curve of CV (VA), v was the scan rate of CV (V/s), m was the mass loading of AC (g), and ΔV was the potential window of the CV (V).

$$E = \frac{1}{2} C_s V^2 \qquad (2)$$

where E was the energy density (Wh/kg) and V was the potential window of the CV (V).

2.6 Comparison of orange peel AC and commercialized AC as electrode material

The procedures described in Section 2.4 were repeated, except that orange peel AC was used in the carbon slurry mixture and the coating was performed with a doctor blade of a thickness of 40 mm. The separator (between glass fiber and nylon) with a higher specific capacitance was used. The specific capacitance and energy density of the orange peel AC-fabricated coil cell supercapacitor were compared to that of commercialized AC.

3. Result and discussion

3.1 Surface morphology and structural properties of ACs

The surface morphology of commercialized AC and phosphoric acid-treated orange peel AC is shown in Figure 3. More pores were clearly visible on the surface of commercialized AC. Although the orange peel AC had more developed pores (circled in red in Figure 2(b)), the presence of pores was not consistent across the entire surface of the AC. According to Luo et al. (2020), weight ratio of chemical activator and the nitrogen flow rate were the significant parameters that could affect surface area and porosity of the AC produced. The surface morphology of the orange peel AC prepared in this study could be attributed to the process conditions used for the chemical activation and carbonization processes, which require further investigation or optimization.

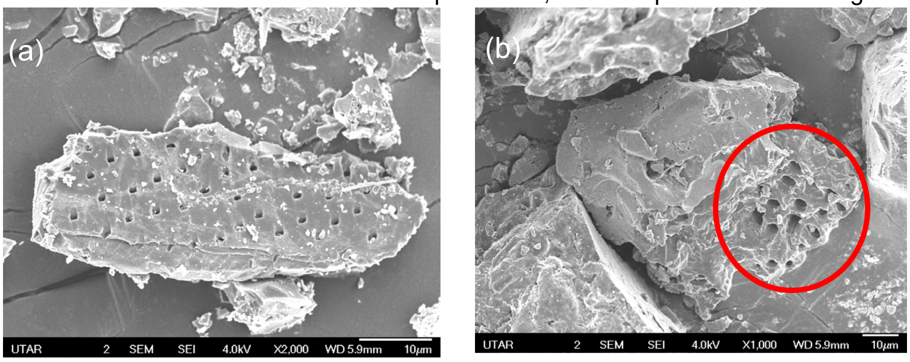


Figure 3: The surface morphology of (a) commercialized AC; and (b) phosphoric acid-treated orange peel AC

The BET surface area and total pore volume of the commercialised AC were significantly higher than the orange peel-derived AC, which was consistent with the surface morphology. Higher values may have resulted from the presence of more pores on the surface of commercialised AC compared to the latter.

Table 1: The structural properties of both ACs

Type of AC	BET surface area (m^2/g)	Total Pore Volume (cm^3/g)
Commercialized	818.8441	0.4472
Orange peel	137.9910	0.1465

3.2 Selection of separator for coil cell supercapacitor

A separator acts as a sandwich between two electrodes in a supercapacitor, allowing ions to diffuse through during the charging and discharging processes, while also preventing short circuits. The material of the separator imposes significant effect on the supercapacitor's electrical performance or properties. Polyolefin was proposed by Verma et al. (2020) as the most commonly used separator material in supercapacitor applications. In this study, the effect of using glass fiber and nylon as the separator was investigated using supercapacitor fabricated with commercialized AC. Figure 4 shows the CV results when different separators were used.

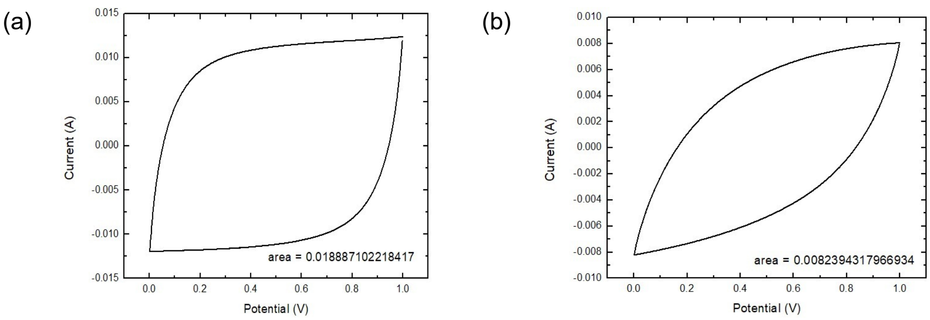


Figure 4: Area enclosed by CV curve of supercapacitor with (a) glass fibre; and (b) nylon separator

The enclosed area of a supercapacitor with a glass fibre separator was 0.0189 VA, while that of a supercapacitor with a nylon separator was 0.0082 VA. The specific capacitance of a given supercapacitor could be calculated using the value of the enclosed area. Based on the correlation shown in Eq(1), the area enclosed by the CV curve and the specific capacitance are positively related. A larger enclosed area is therefore expected to result in a higher specific capacitance of the supercapacitor. According to the results in Figure 3, glass fibre is the better separator material, which could lead to a higher specific capacitance and energy density (Eq(2)) of the commercialised AC-derived supercapacitor. In a recent work by Hubert et al. (2022), the authors demonstrated that glass fibres are used as separator in supercapacitors not only for their insulation properties but also to reinforce the supercapacitor structure. It is also worth noting that the supercapacitor with glass fibre separator had a higher current flow during the charge and discharge process, with a current magnitude of 0.0124 A near 1 V and -0.0119 A near 0 V, compared to the nylon-based supercapacitor, which had a current magnitude of 0.0807 A near 1 V and -0.0082 A nearby 0 V. Glass fibres was chosen as the separator for coil cell supercapacitor in this study.

3.3 Comparison of orange peel AC and commercialized AC as electrode material

In order to compare the electrical properties of the supercapacitor fabricated using different types of AC, various thicknesses (trial and error) of coated carbon slurry were applied to the current collector so that the average mass loading of the AC on the coated current collector was similar. Figure 5 shows the appearance of the coated aluminum foil as the current collector in this study. The thickness of the coated carbon slurry and the average AC mass loading on the 12 mm-aluminium foil circles using commercialized and orange peel-derived ACs are shown in Table 2.

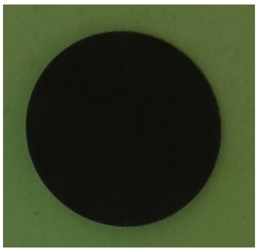
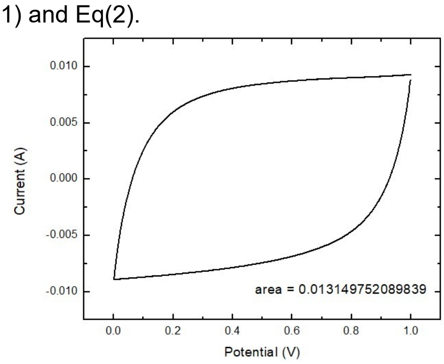
(a)  (b) 

Figure 5: The appearance of (a) aluminum coil coated with carbon slurry; and (b) coated 12 mm-aluminium foil circle used as carbon electrode for coil cell supercapacitor

Table 2: The thickness and AC mass loading of the carbon electrode, and specific capacitance and energy density of the supercapacitor

Types of AC	Thickness (mm)	Average AC mass loading (mg)	Specific capacitance (F/g)	Energy density (Wh/kg)
Commercialized	35	7.39	35.5880	4.9428
Orange peel	40	7.90	57.7056	8.0147

Figure 6 depicts the CV curve of the supercapacitors, with the supercapacitor fabricated using orange peel-derived AC showing a higher enclosed area of 0.0228 VA compared to commercialized AC at 0.0131 VA. As for the current flow, it was also observed that the former had a higher current flow during the charge and discharge process, with a current magnitude of 0.0153 A near 1 V and -0.0154 A near 0 V, compared to the commercialized AC counterpart, which had a current magnitude of 0.0093 A near 1 V and -0.0089 A nearby 0 V. The specific capacitance and energy density (Table 3) of the supercapacitor fabricated using orange peel-derived AC were also higher since both of these properties are linearly correlated to the enclosed area as shown in Eq(1) and Eq(2).

(a) 

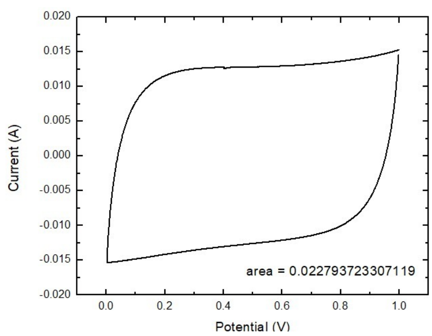
(b) 

Figure 6: Area enclosed by CV curve of supercapacitor fabricated with electrodes using (a) commercialized AC; and (b) orange peel-derived AC

The results in Table 2 showed that the electrical performance of the coil cell supercapacitor with orange peel-derived AC as the electrodes was superior to commercialized AC, despite the latter's higher BET surface area and total pore volume. According to Surawan and Priambodo (2019), the surface area and pore volume of the electrodes influence the energy storage capacity of a supercapacitor. Despite the fact that the findings of this study contradict it, Decaux et al. (2014) explained that the suitability of carbon pore size for the electrode is also determined by the solvent-ion couple used as the electrolyte. Shaker et al. (2021) also reported that the sources and composition of the biomass used for AC preparation (e.g. carbon, oxygen, hydrogen, nitrogen, and sulphur), activation agent and method, and electrolyte types all affect the electrical performance of the supercapacitor.

4. Conclusions

Supercapacitors were fabricated successfully using commercialized AC and orange peel-derived AC as the carbon electrode materials. With a similar average mass loading of AC on the electrodes (7.39–7.9 mg), the supercapacitor fabricated using orange peel-derived AC demonstrated higher specific capacitance and energy density, despite having a smaller specific surface area and total pore volume than commercialized AC. The findings of this study revealed the possibility of using orange peel waste as a potential carbon electrode material for supercapacitors with comparable performance to commercialized AC, with further research into other potential factors (e.g. electrode composition, type, and electrolyte concentration) contributing to its electrochemical properties required.

Acknowledgments

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