CHARACTERIZATION AND SUPERCAPACITIVE PERFORMANCE OF NANOCOMPOSITE ELECTRODES MADE OF NICKEL OXIDE AND ACTIVATED CARBON FROM OIL PALM SHELL

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UNIVERSITI TEKNOLOGI MALAYSIA
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A thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy (Mechanical Engineering)

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To the glory of Almighty Allah

In memory of my late parents

And

To my wife and daughters
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ABSTRACT

Electrochemical capacitors or supercapacitors or ultracapacitors have been identified as a promising technology that has a significant role in the electrical energy storage device revolution. The quality of the electrode material is one of the key factors that determines the performance of supercapacitors. Among the commonly used electrode materials are carbon-based materials, transition metal oxide and conducting polymers. A combination of two or more of these electrode materials in a single electrode has been found to exploit the relative advantages of the two electrode materials and mitigate their relative disadvantages. However, the use of composite electrodes for supercapacitors have not been fully exploited due largely to the divergence in the synthesis technique of which none have been consolidated. This study synthesized nanocomposite electrodes with high power, high energy and long cycle life for supercapacitor applications using a simple, fast and economical technique. Activated carbon (AC) was prepared via microwave-induced CO₂ activation of oil palm shell (OPS) using bed temperature as the control parameter. The response surface methodology (RSM) and Box-Behnken design (BBD) were utilized to optimize the operating parameters of the preparation process. The AC prepared at optimum conditions had a BET surface area of 574.37 m² g⁻¹, total pore volume of 0.244 cm³ min⁻¹, micropore volume of 0.198 cm³ min⁻¹ and yield of 74.06%. A novel green activated carbon-nickel oxide nanocomposite electrode was synthesized using electroless deposition method for supercapacitor applications. Investigation of the electrochemical performance of the nanocomposite electrodes was carried out using cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. The results from electrochemical tests showed that the nanocomposite electrodes exhibit superior capacitive performance compared with the AC electrode. The specific capacitance, power density and energy density were found to increase by 114.92 – 276.84 F g⁻¹, 29.88 – 250.68 W kg⁻¹ and 3.99 – 9.61 Wh kg⁻¹, respectively with respect to the AC electrode. In addition, the specific capacitance as well as the energy density was found to reduce with the increment in the calcination temperature from 300 °C to 500 °C and time from 1 h to 2 h, suggesting that high calcination temperature and long calcination time are detrimental to the electrochemical performance of the nanocomposite electrodes. The nanocomposite electrode calcinated at 300 °C for 1 hour offers the maximum enhancement of 205% in both specific capacitance and energy density, while the nanocomposite electrode calcinated at 500 °C for 2 hours offers the maximum power enhancement of 112%. This thesis has established the possibility of using temperature as a process parameter in microwave heating and proved that electroless plating method is a good synthesis method for organizing nanocomposite electrode materials. Furthermore, the good structure and superb electrochemical performance of the nanocomposite material revealed that it is a promising electrode for supercapacitor applications.
Kapasitor elektrokimia atau superkapasitor atau ultrakapasitor telah dikenal pasti sebagai sebuah teknologi yang berpotensi dan mempunyai peranan yang penting dalam revolusi peranti penyimpan tenaga elektrik. Kualiti bahan elektrod merupakan salah satu faktor utama yang menentukan prestasi superkapasitor. Antara bahan-bahan yang biasa digunakan sebagai elektrod adalah bahan-bahan yang berasaskan karbon, logam teroksida dan polimer pengaliran. Gabungan dua atau lebih bahan-bahan ini ke dalam satu elektrod tunggal dapat mengeksploitasi kelebihan-kelebihan relatif kedu-dua bahan tersebut dan mengurangkan kelemahan-kelemahannya. Namun begitu, penggunaan elektrod komposit untuk superkapasitor belum diperkakas sepenuhnya disebabkan terdapat pelbagai perbezaan dalam teknik sintesisnya yang dapat digabungkan. Kajian ini bertujuan untuk mensintesis elektrod komposit nano yang mempunyai kuasa dan tenaga yang tinggi serta kitaran hayat yang panjang melalui satu teknik yang mudah, cepat dan menjaminan. Karbon teraktif (AC) telah disediakan daripada tempurung kelapa sawit (OPS) melalui pengaktifan CO$_2$ menggunakan ketuhar gelombang mikro dengan ketetapan suhu sebagai parameter kawalan. Metodologi sambutan permukaan (RSM) dan reka bentuk Box-Behnken (BBD) digunakan untuk mengoptimunmkan parameter-parameter pengendalian dalam proses penyediaan. AC yang disediakan dalam keadaan optimum mempunyai luas permukaan BET sebanyak 574.37 m$^2$ g$^{-1}$, jumlah isi padu liang 0.244 cm$^3$ min$^{-1}$ dan isi padu liang mikro 0.198 cm$^3$ min$^{-1}$ dengan kadar penghasilan sebanyak 74.06%. Elektrod komposit nano mesra alam baharu yang terdiri daripada karbon teraktif-nikel teroksida telah disintesis menggunakan kaedah pemendapan tanpa-elektrik untuk digunakan di dalam superkapasitor. Kajian terhadap prestasi elektrokimia elektrod komposit nano tersebut telah dijalankan menggunakan ujian kitaran voltametri, luahan-cas galvanostatik dan spektroskopi impedans elektrokimia. Hasil daripada ujian-ujian elektrokimia tersebut menunjukkan bahawa elektrod komposit nano mempamerkan prestasi berkemuanan tinggi berbanding dengan elektrod AC. Berbanding dengan elektrod AC, kemuanan khusus, ketumpatan kuasa dan ketumpatan tenaga telah meningkat daripada 114.92 kepada 276.84 F g$^{-1}$, 29.88 kepada 250.68 W kg$^{-1}$ dan 3.99 kepada 9.61 Wh kg$^{-1}$. Di samping itu, kemuanan khusus serta ketumpatan tenaga telah didapati berkurang dengan kenaikan suhu pengkalsinan daripada 300 $^\circ$C kepada 500 $^\circ$C dan masa daripada 1 jam kepada 2 jam, menunjukkan bahawa suhu pengkalsinan yang tinggi dan masa yang panjang akan menjejaskan prestasi elektrokimia elektrod komposit nano tersebut. Pengkalsinan elektrod komposit nano pada 300 $^\circ$C selama 1 jam memberikan peningkatan maksimum sebanyak 205% kepada kedua-dua nilai kemuanan khusus ketumpatan tenaga, manakala pengkalsinan elektrod komposit nano pada 500 $^\circ$C selama 2 jam memberikan peningkatan kuasa maksimum sebanyak 112%. Tesis ini berjaya mewujudkan kemungkinan untuk menggunakan suhu sebagai parameter proses dalam ketuah pemanas dan membuktikan bahawa kaedah penyaduran tanpa-elektrik adalah kaedah sintesis yang baik bagi menghasilkan bahan-bahan elektrod komposit nano. Selain itu, struktur yang baik dan prestasi elektrokimia yang hebat daripada bahan komposit nano menunjukkan diri sebagai elektrod yang berpotensi untuk digunakan di dalam superkapasitor.
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<tbody>
<tr>
<td>Å</td>
<td>Angstrom</td>
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<tr>
<td>A</td>
<td>Surface area</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance of the supercapacitor</td>
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<tr>
<td>$C_1$</td>
<td>Capacitance of first electrode</td>
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<tr>
<td>$C_2$</td>
<td>Capacitance of second electrode</td>
</tr>
<tr>
<td>$C_{\text{cell}}$</td>
<td>Cell capacitance</td>
</tr>
<tr>
<td>$C_{\text{dl}}$</td>
<td>Double layer capacitance</td>
</tr>
<tr>
<td>$CeO_2$</td>
<td>Cerium dioxide</td>
</tr>
<tr>
<td>$CH_3CN$</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>$cm$</td>
<td>Centimeter</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>$D$</td>
<td>Distance between the electrodes</td>
</tr>
<tr>
<td>$E$</td>
<td>Energy</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Dielectric constant of double layer region</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Dielectric constant of free space</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Relative dielectric constant</td>
</tr>
<tr>
<td>$FeCl_3$</td>
<td>Iron (III) chloride</td>
</tr>
<tr>
<td>$Fe_3O_4$</td>
<td>Iron (II, III) oxide</td>
</tr>
<tr>
<td>$g$</td>
<td>Gram</td>
</tr>
<tr>
<td>$H_2SO_4$</td>
<td>Sulphuric acid</td>
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</table>
$H_3PO_4$ - Phosphoric acid

$IrO_2$ - Iridium oxide

$K_2CO_3$ - Potassium carbonate

$KBr$ - Potassium bromide

$KOH$ - Potassium hydroxide

$Li_4Ti_5O_{12}$ - Lithium titanate

$m$ - Mass of electrode

$MnO_2$ - Manganese oxide

$NaOH$ - Sodium hydroxide

$Ni(OH)_2$ - Nickel hydroxide

$NiO$ - Nickel oxide

$P_{max}$ - Maximum power

$R$ - Resistance

$R_u$ - Contact resistance

$RuO_2$ - Ruthenium oxide

$R_p$ - Charge transfer resistance

$SC$ - Specific capacitance

$S_{BET}$ - BET surface area

$t$ - Thickness of the electrical double layer

$TiO_2$ - Titanium dioxide

$V$ - Voltage

$V_{drop}$ - Voltage drop

$V_t$ - Total pore volume

$V_{\mu}$ - Micropore volume

$W_d$ - Warburg diffusion

$wt\%$ - Weight percent
<table>
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<tr>
<td>$Y_0$</td>
<td>Capacitor layer</td>
</tr>
<tr>
<td>$ZnCl_2$</td>
<td>Zinc chloride</td>
</tr>
<tr>
<td>$ZnO$</td>
<td>Zinc oxide</td>
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# LIST OF ABBREVIATIONS

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<th>Description</th>
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<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of variance</td>
</tr>
<tr>
<td>ARTEM</td>
<td>Atomic resolution transmission electron microscopy</td>
</tr>
<tr>
<td>BBD</td>
<td>Box-Behnken design</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CAC</td>
<td>Commercial activated carbon</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>df</td>
<td>Degree of freedom</td>
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<tr>
<td>EC</td>
<td>Electrochemical capacitor</td>
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<tr>
<td>ED</td>
<td>Electroless deposition</td>
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<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
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<tr>
<td>EDLC</td>
<td>Electrochemical double-layer capacitor</td>
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<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
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<tr>
<td>ESR</td>
<td>Equivalent series resistance</td>
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<tr>
<td>FESEM</td>
<td>Field-emission scanning electron microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>GCD</td>
<td>Galvanostatic charge-discharge</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>LPM</td>
<td>Litre per minute</td>
</tr>
<tr>
<td>OPS</td>
<td>Oil palm shell</td>
</tr>
<tr>
<td>OPSAC</td>
<td>Oil palm shell activated carbon</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>OPSC</td>
<td>Oil palm shell char</td>
</tr>
<tr>
<td>RSM</td>
<td>Response surface methodology</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
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<td>XRD</td>
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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Global energy crisis brought about by soaring increase in global energy demand far in excess of energy supply as a result of population growth and industrial development resulted in high cost of energy, depletion of fossil fuel on continuous basis, global warming and climate change. As such, more attention is being paid to clean, efficient, renewable and sustainable energy sources such as solar and wind energy that have high potential of meeting the future energy requirement. However, the electrical energy being generated from these sources is not continuous but rather intermittent hence the needs for efficient energy storage devices to smoothing the supply and at the same time store the excess energy. Electrochemical capacitors popularly called supercapacitors or sometimes ultracapacitors have been identified as a promising technology that has an important role to play in the electrical energy storage device revolution. Supercapacitors are special class of capacitors that use various electrodes such as carbon-based materials (activated carbons, carbon aerogels, carbon fibers, carbon nanotubes), conducting polymers and metal oxides to achieve higher energy densities than the conventional electrolytic capacitors, thus lying between the electrochemical batteries and convention capacitors (Kotz and Carlen, 2000; Halper and Ellenbogen, 2006).
The electrode material is one of the key factors that determine the performance of supercapacitors. And a lot of researches have been carried out in the area of electrode materials for supercapacitors. According to Kavaliauskas et al. (2011), among the commonly used electrode materials are carbon-based materials (activated carbons, carbon nanotubes, carbon blacks and glassy carbons), transition metal oxides (such as RuO$_2$, NiO, IrO$_2$, MnO$_2$), and conducting polymers. Each of these electroactive materials has merits and demerits which are uniquely associated with them and which govern their application in supercapacitors as enumerated below:

i. **Carbon-based materials**: Provide high power density due to high surface area and have long cycle life but small specific capacitance which are mainly double layer capacitance

ii. **Metal oxides/hydroxides**: Have wide potential window and combined pseudocapacitance with double layer capacitance but have poor cycle life and relatively small surface area.

iii. **Conducting polymers**: Have good conductivity, high capacitance, low cost and ease of fabrication but have poor cycle life and relatively low mechanical stability (Yang, 2012).

Based on electrode material used, electrochemical capacitors may be classified into three main groups; namely electrochemical double-layer capacitor (EDLC), pseudocapacitor and hybrid capacitors, each having a unique charge storage mechanism (Halper and Ellenbogen, 2006). The electrochemical double-layer capacitors use carbon based electrodes and employ electrostatic charge mechanism known as a non-Faradaic mechanism for the development of capacitance at the electrode/electrolyte interface. On the other hand, pseudocapacitor use transition metal oxide and conducting polymer and employ fast Faradaic mechanism such as oxidation-reduction reactions for the development of capacitive charges either within the material itself or at the interface and at potentials which are specific to the redox couple of the electrode and electrolyte materials (Conway et al., 1997; Davies and Yu, 2011;
Hybrid capacitors, as the name suggest, are a combination of electrochemical double-layer capacitors and pseudocapacitors. The combination of the two supercapacitors leads to better performance characteristics as a result of exploiting the relative advantages of the two capacitors while at the same time mitigating their relative disadvantages.

Among the carbon-based materials, activated carbon is most widely used as supercapacitor electrodes because of large surface area due to high surface porosity, controlled pore structure, good electrical conductivity, good thermal and chemical stability, ease of processability, low framework density, compatibility in nanocomposite materials, ready abundance and relatively low cost (Kavaliauskas et al., 2011; Pandolfo and Hollenkamp, 2006; Sevilla and Mokaya, 2014). Also, the double-layer capacitance can be modified by decorating porous carbon surfaces with electrochemically active surface functionalities (Elmouwahidi et al., 2012). In the area of energy generation and storage, carbon materials have over the years being playing very crucial roles and this date back to prehistoric era when human being started using charcoal for heat sources; others are graphite moderators of atomic reactors for power plant, the use of cokes in the production of various metals – for melting and reducing natural ores, and graphite anode of lithium-ion batteries (Inagaki et al., 2010). Carbon electrode, though well polarizable (Frackowiak and Beguin, 2001), its electrical conductivity is however sturdily dependent on factors such as the type of thermal treatment, its microstructure, the content of heteroatoms and hybridization. More importantly, carbon materials are environmentally friendly especially when the green method is adopted for the preparation.

Fabrications of activated carbon are carried out using either a two-stage thermal/physical process or a single stage chemical process. The two-stage thermal process involves the carbonization (pyrolysis) of the precursor materials at a moderate temperature between 400 °C and 850 °C under an inert atmosphere in order to release the volatile matters and also produce char with undeveloped pore structure; and the activation of the char at elevated temperature between 600 °C and 900 °C using carbon dioxide, air, steam or a mixture of these gases – which are environmentally friendly – as oxidizing agent to produce activated carbons with well-developed porosity. In
single stage chemical process, the carbonization and activation are carried out concurrently usually at temperature between 300 °C and 950 °C after the precursor material have been mixed with activating agents such as Zinc chloride (ZnCl₂), Sodium hydroxide (NaOH), Potassium hydroxide (KOH), Potassium carbonate (K₂CO₃), Iron (III) chloride (FeCl₃) and Phosphoric acid (H₃PO₄). These activating agents also serve as dehydrating agents and oxidants. High energy cost and low yield due to longer activation time and high activation temperature are the main problems of physical activation. While chemical activation has the problem of activated carbon and the environment being contaminated as a result of the chemical agents used during production. However, chemical activation has the advantages of shorter process time and lower activation temperature. The advantages of chemical activation over physical activation were responsible for its preference by commercial activated carbon manufacturers and researchers some years back. However, global concern as regards environmental protection and introduction of modern technologies have recently led the research and scientific communities shifting interest towards the use of microwave heating technology as a viable alternative to conventional activation methods for the production of activated carbons (Xin-hui et al., 2011a; Yuen and Hameed, 2009). Microwave heating is preferred over conventional heating as it offers a number of advantages in addition to the considerable reduction in activation time.

The search and development of green carbon materials have been the focus of research interests in the last decade, during which those with considerable potentials for agro-industrial waste mitigation are given special attention. Activated carbon belongs to the group of carbonaceous materials, as such is predominantly amorphous in nature. Therefore, fabrication and treatment methods are the primary factors responsible for the high porosity development in activated carbon (Abechi et al., 2013). Furthermore, from available literature, memory, chemical polarity, high surface area and pore structure of activated carbon have been found to be dependent on the precursor material as well as the activation process. Most commercial activated carbons are produced from fossil fuel based precursor material (petroleum and coal) which made them expensive and environmentally non-friendly hence, the increasing focus on biomass precursor materials which are cheaper, readily available, renewable, structurally porous and green (Farma et al., 2013). In recent years the use of waste
agricultural biomass such as waste coffee beans (Rufford et al., 2008), cassava peel waste (Ismanto et al., 2010), apricot shell (Xu et al., 2010), sugarcane bagasse (Rufford et al., 2010; Si et al., 2011), rice husk (He et al., 2013), sunflower seed shell (Li et al., 2011), coffee endocarp (Valente Nabais et al., 2011), rubber wood sawdust (Taer et al., 2011a), oil palm empty fruit bunch (Farma et al., 2013), camellia oleifera shell (Zhang et al., 2012), poplar wood (Liu et al., 2012), argan seed shell (Elmouwahidi et al., 2012), bamboo species (González-García et al., 2013), peanut shell (He et al., 2013) as precursor materials to prepare porous carbons for electrochemical double-layer capacitors (EDLCs) have gained much attention due to its abundant availability and low cost. The amount of waste agricultural biomass being generated across the globe has been on the increase with the increase in agricultural activities in various countries. Efforts at diversifying their utilization have, therefore, been a serious challenge since direct discharge of some of these wastes causes environmental problems. The primary usage of some of these bio-wastes remains as feedstock for boilers while the majority are burnt for the purpose of quick disposal.

Recently, researchers have also focused on the advance of alternative electrode materials. Because of high specific capacitance at low resistance, transition metal oxides are attractive alternative electrode materials with which high energy and high power supercapacitors can easily be constructed. Among the metal oxides, ruthenium oxide (RuO$_2$) is the most widely researched and most beneficial; it is known to give very high capacitance up to between 720 to 900 F/g (Jayalakshmi and Balasubramanian, 2008). The capacitance of hydrous ruthenium oxide has been found to surpass that of conducting polymer and carbon-based materials (Zheng et al., 1995). However, RuO$_2$ is very expensive and scarce, as such extensive research into RuO$_2$ is conducted for military application where cost is not an issue. Other metal oxides such as nickel oxide (Basri et al., 2016; Chang et al., 2012; Kavaliauskas et al., 2011), nickel hydroxide (Huang et al., 2007), cobalt oxide (Chang et al., 2012; Gomez and Kalu, 2013; He et al., 2012; Xie et al., 2013), zinc oxide (Faraji and Ani, 2016; Aravinda et al., 2013a; Selvakumar et al., 2010), titanium oxide (Fu et al., 2006; Liang et al., 2004; Selvakumar and Bhat, 2012), cerium oxide (Aravinda et al., 2013b), vanadium oxide (Perera et al., 2013), manganese oxide (Kim et al., 2013; Lee et al., 2014; Malak-Polaczyk et al., 2010; Nakayama et al., 2007; Peng et al., 2011;
Staiti and Lufrano, 2010) have been studied as supercapacitor electrode materials, however, none of these metal oxides are used in commercial production of supercapacitors because they are yet to obtain capacitances comparable to RuO$_2$. Although pseudocapacitors can achieve higher capacitance than EDLCs, however, they often suffer from the poor electrical conductivity of the electroactive materials resulting in low power density and cycling stability (Chen and Dai, 2013).

The combination of these disparate capacitive materials to form a nanocomposite electroactive material constitutes an important approach to the development, control and optimization of the structure and properties of the electrode material to augment their performance for supercapacitors. For example, supercapacitors with high specific capacitance and rate capability could be obtained when a small amount of transition metal oxide is uniformly dispersed on the high surface area, porous and conductive carbon materials carbon materials (Tai and Teng, 2004; Wang and Hu, 2004; Yuan et al., 2005). The properties of nanocomposite electrodes are dependent on the individual components and the morphology and interfacial characteristics of the nanocomposites. In the last decade there has been an increase in research interest towards the development of nanocomposite electrode materials. As a result researchers have come up with all kind of nanocomposite materials such as activated carbon mixed with either metal oxides or conducting polymers, metal oxides mixed with conducting polymers, graphene mixed with metal oxides or conducting polymers and carbon nanotube with metal oxides or conducting polymers. Material selection, surface area, particle size, synthesis method, fabrication process parameters and electrical conductivity are some of the factors to be considered during design and fabrication of nanocomposite electrode materials (Yang, 2012).

Many researchers have used different experimental techniques to synthesize nanocomposite electrode materials. Among these experimental techniques wet impregnation and electrodeposition are the most widely used synthesis methods, however, good control of morphology and particle size is lacking in wet impregnation while in electrodeposition additional electricity and electrodes are needed. In recent times, electroless deposition is gaining more ground among researchers as an effective synthesis method of depositing metal nanoparticles (Ramani et al., 2001; Selvakumar
et al., 2010) due to its low cost, simple process, high reproducibility and simple equipment requirement (Faraji et al., 2014; Faraji et al., 2012; Faraji et al., 2011). Despite the fact that a lot of progress has been made in the development of nanocomposite electrode materials for supercapacitor applications, there are still more hurdles to cross and challenges to overcome if supercapacitors are to replace batteries.

1.1.1 Why Green?

The renewable energy source is one of the three top options for sustainable production of carbon-free energy; others are nuclear energy system and decarbonization of fossil energy. Renewable energy sources include solar, wind, geothermal, hydropower, biomass, municipal solid waste. The use of biomass as precursor material for the production of activated carbons is considered as a zero or neutral greenhouse gas emission because CO$_2$ released during combustion of biomass is equivalent to the CO$_2$ captured from the atmosphere by the plant while growing (photosynthesis) (Muradov and Vezirog˘lu, 2008). Thus, it is referred to as zero carbon emissions or the carbon cycle and is depicted in Figure 1.1. Solar energy is converted to chemical energy through the process of photosynthesis and stored in biomass.

Furthermore, since microwave heating equipment does not emit greenhouse gasses, there is no need for air quality monitoring. Hence, malfunctioning or outdated microwave system does not incur any fine or penalty.
1.2 Research Problem and Hypotheses

Supercapacitors have been identified as electrochemical energy storage devices capable of replacing the batteries as the number one choice energy storage device. However, substantial improvement is required through the development of new materials before supercapacitors can meet the energy demand of the future systems such as large scale industrial equipment, hybrid electric vehicles and portable electronics. For this reason, production of high surface area carbon electrodes from biomass and the development of composite electrodes have been on the increase in recent years. Physical activation (Misnon et al., 2015; Taer et al., 2011b; Valente Nabais et al., 2011), chemical activation (Bhattacharjya and Yu, 2014; Kalyani et al., 2015; Misnon et al., 2015; Rufford et al., 2008) and combined physical and chemical activation (Farma et al., 2013; Ismanto et al., 2010) are the most widely used activation processes. However, there are issues and concerns emanating from the use of these conventional heating methods such as thermal gradient, long process time, additional cost of washing the activated carbon and danger posed to human being and the environment by the chemicals being use as activating agents. In an attempt to solve the problem of associated with the conventional heating method, microwave-induced activation was developed. A major concern in microwave heating is the inability to monitor and control the temperature inside the microwave leading to the adoption of
microwave power as process parameter. Furthermore, microwave-induced chemical activation was the choice of the majority of the researchers probably due to the short process time. Thus, the issue of safety with the chemical activating agents and additional cost of washing the activated carbons came up. As far as my knowledge there are few works on the production of activated carbon via microwave-induced activation. And none of the activated carbons produced have been evaluated as supercapacitor electrode. Therefore there no available information on the effect of the preparation condition. From available literature on microwave-induced physical activation, use of high microwave power and long process time are the main issues (Li et al., 2009; Xin-hui et al., 2011a; Yang et al., 2010)

The development of nanocomposite electrode material constitutes an important approach towards the improvement in the performance of supercapacitors. Fabrication of nanocomposite electrodes have been on the increase in recent years, as such, different types of synthesis techniques have been employed. Wet impregnation method is the most widely use technique, however, the method lacks good control of the morphology and particles size. Aravinda et al. (2013b) and Selvakumar et al. (2010) used mechanical mixing to organize nanocomposite electrodes but the method surfer from inability to coat intricate shape. Other synthesis methods such as magnetron sputtering (Kavaliauskas et al., 2011) require cutting-edge equipment. Extended process time is the major concern of the hydrothermal process (Madhu et al., 2015). Fabrication of nanocomposite electrodes by electroless deposition is gaining more ground amount researchers (e.g. Faraji and Ani (2016)), however, the effect of heat treatment on the electrochemical performance has not been study.

1.2.1 Statement of the Research Problem

How does activated carbon prepared by microwave-induced activation of waste agricultural biomass and decorated with nickel oxide lead to improve performance of supercapacitor?
1.2.2 Research Questions

i. Of what significance are the preparation conditions of activated carbons on their properties?

ii. How does the use of activated carbons from waste agricultural biomass coated with nickel oxide contribute to the capacity of the supercapacitor?

iii. How does one configure supercapacitor for better performance?

1.2.3 Research Hypotheses

Unlike physical and chemical activation processes using convention heating method microwave-induce activation process is expected to take a shorter time due to the interior and volume heating of microwave irradiation. Many reported works on microwave-induced activation process are carried out by chemical activation with only a few reports on physical activation. Among the published works on microwave-induced physical activation, none had used microwave heating for the pyrolysis/carbonization. Instead, they all used convention heating method for the carbonization. As such, there is no information on the pyrolysis conditions for obtaining good char suitable for activation. Also, longer pyrolysis time could lower the carbon yield; no information yet because most microwave induced pyrolysis were optimized for optimum liquid yield, for example, Salema and Ani (2012).

Activated carbon if well prepare is expected to have a large surface area and porosity, good electrical and thermal conductivity needed to enhance the capacities of the supercapacitor. The features could be improved upon through optimization of the activation process and surface modification of the activated carbon that may invariably lead to better performance. One purpose of surface modification of activated carbons is to either improve or introduce oxygen functional groups on the surface of activated carbons. It have been reported by many researchers e.g. Ismanto et al. (2010); Liu et
al. (2012); Jin et al. (2013) that surface modification of activated carbons leads to improvement in electrochemical capacitive behavior of the activated carbons despite the fact that no significant effect was noticed on the surface area of the modified activated carbons. Presently, research into the coating of the surface of activated carbon with transition metal oxides is being pursued by researchers because of the observed improvement in the electrochemical capacitive behavior in the reported works. However, information on the electroless deposition of metal oxides on activated carbons is limited since the area is relatively new. Till date, there is no study reported on the electroless deposition of metal oxides on activated carbon from oil palm shell. As such there is the need for investigation so as to establish the optimum conditions.

The configuration of the supercapacitor would start from the electrode’s preparation. Classic electrodes can be fabricated by co-precipitation and cathodic deposition with the use of additives and polymer binders. The polymer binder fuses active materials and permits the electrode to adhere to a current collector (Sonia et al., 2013). However, the polymetric binder material leads to increased resistance and reduced capacitance in the supercapacitor. Other experimental techniques in use to organize the carbon nanocomposite electrodes are wet impregnation, electrodeposition, sputtering, pulse laser, thermal evaporation and plasma reduction. Among these techniques wet impregnation is the most widely used, but good control of morphology and particle size are missing. Electrodeposition requires additional electricity and electrodes. Moreover, some of these techniques involve lengthy processing, sophisticated equipment and may make demolition of the carbon structure possible. On the other hand, electroless deposition is an effective route to deposit metal nanoparticles (Ramani et al., 2001; Selvakumar et al., 2010) and polymers (Sonia et al., 2013). The use of activated carbon-metal oxide nanocomposite electrode either as the positive electrode or negative electrode or both is a function of electrolyte and is expected to have an impact on the performance of the supercapacitor.
1.2.4 Objectives of the Work

The primary aim of this research was to prepare nanocomposite materials by electroless deposition of nickel oxide nanoparticles on oil palm shell-based activated carbons and investigate their performance as supercapacitor electrodes. The specific objectives of the study are:

i. To characterize activated carbons from oil palm shells prepared by microwave-induced CO$_2$ physical activation using bed temperature as control parameter in order to establish the critical parameters of the activated carbons.

ii. To synthesize activated carbon-nickel oxide nanocomposite electrodes using the electroless deposition (plating) method.

iii. To evaluate the performance of activated carbon-nickel oxide nanocomposite electrodes for supercapacitor.

1.3 Scope of Work

This research covers the preparation of powder activated carbons from oil palm shells via microwave-induced CO$_2$ physical activation. The response surface methodology (RSM) and Box-Behnken design (BBD) features of the Desert Expert software (version 7.1.6, Stat-Ease, Inc. Minneapolis) was employed to design the experimental runs to reduce the number of experiments. The preparation of the activated carbon was tailored towards electrode for supercapacitor. For improve performance, the activated carbon was modified by electroless deposition of nickel oxide, which is a transition metal oxide, onto the activated carbon to obtain activated carbon-nickel oxide nanocomposite electrode. The performance of the activated
carbon-nickel oxide nanocomposite was investigated via a typical two-electrode test cell using Gamry Instrument (Interface1000).

1.4 **Significance of Study**

The research proposes the use of microwave for the pyrolysis and activation processes and electroless plating for the synthesis of AC-nickel oxide nanocomposite electrode. The benefit of microwave heating is that it can be used for other biomass materials. The activated carbons from this research can be used as electrodes for different types of supercapacitor. The use of waste agricultural biomass as precursor materials will serve as waste management and promote environmental pollution mitigation considering the vast amount of biomass waste being generated by oil palm mills in Malaysia.

1.5 **Organization of the Thesis**

This thesis comprises of five chapters with each chapter discussing specific areas of the research. Introductory background of the study is covered in Chapter 1. The aim and objective of the research study are highlighted in this chapter. Also, the chapter outlines the scope and significance of the study.

Review of works relevant to the study is the focus of Chapter 2. The production processes of AC and synthesis of AC-metal oxide nanocomposite electrode for supercapacitor applications were adequately covered. Also, the use of microwave heating technology and RSM for optimization of activated carbon production was covered.
Chapter 3 gives a detail explanation of the raw materials selection, equipment employed for the research, experimental conditions and procedures followed in carrying out the research.

Detail description and analysis of the experimental results obtained from the production of activated carbon and the optimization of production process, synthesis of activated carbon-nickel oxide nanocomposite electrodes and evaluation of the electrochemical performance of the nanocomposite electrodes are presented in Chapter 4.

The general conclusion from the experimental findings and recommendations for future research are presented in Chapter 5.
REFERENCES


