

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

ADEKUNLE MOSHOOD ABIOYE

UNIVERSITI TEKNOLOGI MALAYSIA

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ADEKUNLE MOSHOOD ABIOYE

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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 CO<sub>2</sub> 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 m<sup>2</sup> g<sup>-1</sup>, total pore volume of 0.244 cm<sup>3</sup> g<sup>-1</sup>, micropore volume of 0.198 cm<sup>3</sup> g<sup>-1</sup> 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<sup>-1</sup>, 29.88 – 250.68 W kg<sup>-1</sup> and 3.99 – 9.61 Wh kg<sup>-1</sup>, 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.

## ABSTRAK

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 kedua-dua bahan tersebut dan mengurangkan kelemahan-kelemahannya. Namun begitu, penggunaan elektrod komposit untuk superkapasitor belum dieksploitasi 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 menjimatkan. Karbon teraktif (AC) telah disediakan daripada tempurung kelapa sawit (OPS) melalui pengaktifan  $\text{CO}_2$  menggunakan ketuhar gelombang mikro dengan ketetapan suhu sebagai parameter kawalan. Metodologi sambutan permukaan (RSM) dan reka bentuk Box-Behnken (BBD) digunakan untuk mengoptimumkan parameter-parameter pengendalian dalam proses penyediaan. AC yang disediakan dalam keadaan optimum mempunyai luas permukaan BET sebanyak  $574.37 \text{ m}^2 \text{ g}^{-1}$ , jumlah isi padu liang  $0.244 \text{ cm}^3 \text{ min}^{-1}$  dan isi padu liang mikro  $0.198 \text{ cm}^3 \text{ min}^{-1}$  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 voltammetri, luahan-cas galvanostatik dan spektroskopi impedans elektrokimia. Hasil daripada ujian-ujian elektrokimia tersebut menunjukkan bahawa elektrod komposit nano mempamerkan prestasi berkemampuan tinggi berbanding dengan elektrod AC. Berbanding dengan elektrod AC, kemampuan khusus, ketumpatan kuasa dan ketumpatan tenaga telah meningkat daripada 114.92 kepada  $276.84 \text{ F g}^{-1}$ , 29.88 kepada  $250.68 \text{ W kg}^{-1}$  dan 3.99 kepada  $9.61 \text{ Wh kg}^{-1}$ . Di samping itu, kemampuan khusus serta ketumpatan tenaga telah didapati berkurang dengan kenaikan suhu pengkalsinan daripada  $300 \text{ }^\circ\text{C}$  kepada  $500 \text{ }^\circ\text{C}$  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  $300 \text{ }^\circ\text{C}$  selama 1 jam memberikan peningkatan maksimum sebanyak 205% kepada kedua-dua nilai kemampuan khusus ketumpatan tenaga, manakala pengkalsinan elektrod komposit nano pada  $500 \text{ }^\circ\text{C}$  selama 2 jam memberikan peningkatan kuasa maksimum sebanyak 112%. Tesis ini berjaya mewujudkan kemungkinan untuk menggunakan suhu sebagai parameter proses dalam ketuhar 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 menunjukkannya sebagai elektrod yang berpotensi untuk digunakan di dalam superkapasitor.

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## LIST OF SYMBOLS

|                 |   |  |
|-----------------|---|--|
| $\text{\AA}$    | - | Angstrom                                   |
| $A$             | - | Surface area                               |
| $C$             | - | Capacitance of the supercapacitor          |
| $C_1$           | - | Capacitance of first electrode             |
| $C_2$           | - | Capacitance of second electrode            |
| $C_{cell}$      | - | Cell capacitance                           |
| $C_{dl}$        | - | Double layer capacitance                   |
| $CeO_2$         | - | Cerium dioxide                             |
| $CH_3CN$        | - | Acetonitrile                               |
| $cm$            | - | Centimeter                                 |
| $CO_2$          | - | Carbon dioxide                             |
| $D$             | - | Distance between the electrodes            |
| $E$             | - | Energy                                     |
| $\varepsilon$   | - | Dielectric constant of double layer region |
| $\varepsilon_0$ | - | Dielectric constant of free space          |
| $\varepsilon_r$ | - | Relative dielectric constant               |
| $FeCl_3$        | - | Iron (III) chloride                        |
| $Fe_3O_4$       | - | Iron (II, III) oxide                       |
| $g$             | - | Gram                                       |
| $H_2SO_4$       | - | Sulphuric acid                             |

|                  |   |  |
|------------------|---|--|
| $H_3PO_4$        | - | 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                           |

|          |   |                 |
|----------|---|-----------------|
| $Y_0$    | - | Capacitor layer |
| $ZnCl_2$ | - | Zinc chloride   |
| $ZnO$    | - | Zinc oxide      |

**LIST OF ABBREVIATIONS**

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

|             |   |                              |
|-------------|---|------------------------------|
| <i>OPSC</i> | - | Oil palm shell char          |
| <i>RSM</i>  | - | Response surface methodology |
| <i>SEM</i>  | - | Scanning electron microscopy |
| <i>XRD</i>  | - | X-ray diffraction            |

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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<sub>2</sub>, NiO, IrO<sub>2</sub>, MnO<sub>2</sub>), 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;

Kotz and Carlen, 2000; Pandolfo and Hollenkamp, 2006). 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 been 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 ( $\text{ZnCl}_2$ ), Sodium hydroxide ( $\text{NaOH}$ ), Potassium hydroxide ( $\text{KOH}$ ), Potassium carbonate ( $\text{K}_2\text{CO}_3$ ), Iron (III) chloride ( $\text{FeCl}_3$ ) and Phosphoric acid ( $\text{H}_3\text{PO}_4$ ). 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<sub>2</sub>) 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<sub>2</sub> is very expensive and scarce, as such extensive research into RuO<sub>2</sub> 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<sub>2</sub>. 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).

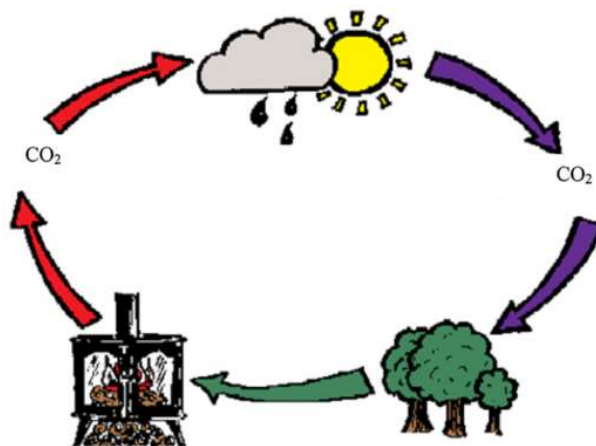
Many researchers have used different experimental techniques to synthesize nanocomposite electrode materials. Among these experimental techniques wet impregnation and electrodeposition are the most widely used synthesis methods, however, good control of morphology and particle size is lacking in wet 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<sub>2</sub> released during combustion of biomass is equivalent to the CO<sub>2</sub> captured from the atmosphere by the plant while growing (photosynthesis) (Muradov and Veziroglu, 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.



**Figure 1.1:** The carbon cycle (Saidur *et al.*, 2011)

## 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 suffer 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-induced 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 polymeric 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<sub>2</sub> 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<sub>2</sub> 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

- Abdullah, N. and Gerhauser, H. (2008). Bio-oil derived from empty fruit bunches. *Fuel*. 87: 2606–2613.
- Abdullah, S. S., Yusup, S., Ahmad, M. M., Ramli, A. and Ismail, L. (2010). Thermogravimetry Study on Pyrolysis of Various Lignocellulosic Biomass for Potential Hydrogen Production. *International Journal of Chemical and Biological Engineering*. 3(3): 137-141.
- Abechi, S. E., Gimba, C. E., Uzairu, A. and Dallatu, Y. A. (2013). Preparation and Characterization of Activated Carbon from Palm Kernel Shell by Chemical Activation. *Research Journal of Chemical Sciences*. 3(7): 54-61.
- Adeyi, O. (2010). Proximate composition of some agricultural wastes in Nigeria and their potential use in activated carbon production. *Journal of Applied Sciences and Environmental Management*. 14(1): 55 - 58.
- Adinata, D., Wan Daud, W. M. and Aroua, M. K. (2007). Preparation and characterization of activated carbon from palm shell by chemical activation with  $K_2CO_3$ . *Bioresource Technology*. 98(1): 145-9.
- Agarwala, R. C. and Agarwala, V. (2003). Electroless alloy/composite coatings: A review. *Sadhana*. 28(3): 475-493.
- Amatucci, G. G., Badway, F., Du Pasquier, A. and Zheng, T. (2001). An Asymmetric Hybrid Nonaqueous Energy Storage Cell. *Journal of the Electrochemical Society*. 148(8): A930-A939.
- Andrieu, X. (2000). *Ultracapacitors for Portable Electronics*. In: Osaka, T. and Datta, M. (Ed.) *Energy Storage Systems in Electronics (New Trends in Electrochemical Technology)*. (pp. 521-550). Amsterdam: Gordon and Breach Science Publishers.

- Anik, M., Körpe, E. and Şen, E. (2008). Effect of coating bath composition on the properties of electroless nickel–boron films. *Surface and Coatings Technology*. 202(9): 1718-1727.
- Aravinda, L. S., Nagaraja, K. K., Nagaraja, H. S., Bhat, K. U. and Bhat, B. R. (2013a). ZnO/carbon nanotube nanocomposite for high energy density supercapacitors. *Electrochimica Acta*. 95: 119-124.
- Aravinda, L. S., Udaya Bhat, K. and Ramachandra Bhat, B. (2013b). Nano CeO<sub>2</sub>/activated carbon based composite electrodes for high performance supercapacitor. *Materials Letters*. 112: 158-161.
- Arbizzani, C., Mastragostino, M. and Meneghell, L. (1996). Polymer-Based Redox Supercapacitors: A Comparative Study. *Electrochimica Acta*. 41(1): 21-26.
- Arbizzani, C., Mastragostino, M. and Soavi, F. (2001). New trends in electrochemical supercapacitors. *Journal of Power Sources*. 100(1–2): 164-170.
- Ashassi-Sorkhabi, H. and Rafizadeh, S. H. (2004). Effect of coating time and heat treatment on structures and corrosion characteristics of electroless Ni–P alloy deposits. *Surface and Coatings Technology*. 176(3): 318-326.
- Atieh, M. A., Bakather, O. Y., Al-Tawbini, B., Bukhari, A. A., Abuilawi, F. A. and Fettouhi, M. B. (2010). Effect of carboxylic functional group functionalized on carbon nanotubes surface on the removal of lead from water. *Bioinorganic Chemistry and Applications*. 2010: 603978.
- Aworn, A., Thiravetyan, P. and Nakbanpote, W. (2008). Preparation and characteristics of agricultural waste activated carbon by physical activation having micro- and mesopores. *Journal of Analytical and Applied Pyrolysis*. 82(2): 279-285.
- Balathanigaimani, M. S., Shim, W.-G., Lee, M.-J., Kim, C., Lee, J.-W. and Moon, H. (2008). Highly porous electrodes from novel corn grains-based activated carbons for electrical double layer capacitors. *Electrochemistry Communications*. 10(6): 868-871.
- Basri, N. H., Deraman, M., Suleman, M., Nor, N. S. M., Dolah, B. N. M., Sahri, M. I. and Shamsudin, S. A. (2016). Energy and Power of Supercapacitor Using Carbon Electrode Deposited with Nanoparticles Nickel Oxide. *International Journal of Electrochemical Science*. 11(1): 95-110.



- Basu, P. (2010). *Biomass Characteristics. Biomass Gasification and Pyrolysis*. (pp. 27-63). Boston: Academic Press.
- Bello, A., Fashedemi, O. O., Barzegar, F., Madito, M. J., Momodu, D. Y., Masikhwa, T. M., Dangbegnon, J. K. and Manyala, N. (2016). Microwave synthesis: Characterization and electrochemical properties of amorphous activated carbon-MnO<sub>2</sub> nanocomposite electrodes. *Journal of Alloys and Compounds*. 681: 293-300.
- Bergese, P., Colombo, I., Gervasoni, D. and Depero, L. E. (2003). Microwave generated nanocomposites for making insoluble drugs soluble. *Materials Science and Engineering: C*. 23(6-8): 791-795.
- Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S. and Escaleira, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*. 76(5): 965-77.
- Bhattacharjya, D. and Yu, J.-S. (2014). Activated carbon made from cow dung as electrode material for electrochemical double layer capacitor. *Journal of Power Sources*. 262: 224-231.
- Bouchelta, C., Medjram, M. S., Bertrand, O. and Bellat, J.-P. (2008). Preparation and characterization of activated carbon from date stones by physical activation with steam. *Journal of Analytical and Applied Pyrolysis*. 82(1): 70-77.
- Brenner, A. and Riddell, G. E. (1946). Nickel Plating on Steel by Chemical Reduction. *Journal of Research of the National Bureau of Standards*. 37(31): 31-34.
- Burke, A. (2000). Ultracapacitors: why, how, and where is the technology. *Journal of Power Sources*. 91(1): 37-50.
- Cabal, B., Budinova, T., Ania, C. O., Tsyntsarski, B., Parra, J. B. and Petrova, B. (2009). Adsorption of naphthalene from aqueous solution on activated carbons obtained from bean pods. *Journal Hazardous Materials*. 161(2-3): 1150-6.
- Cagnon, B., Py, X., Guillot, A., Stoeckli, F. and Chabmat, G. (2009). Contributions of hemicellulose, cellulose and lignin to the mass and the porous properties of chars and steam activated carbons from various lignocellulosic precursors. *Bioresource Technology*. 100(1): 292-8.
- Calvo, E. G., Lufrano, F., Staiti, P., Brigandì, A., Arenillas, A. and Menéndez, J. A. (2013). Optimizing the electrochemical performance of aqueous symmetric

- supercapacitors based on an activated carbon xerogel. *Journal of Power Sources*. 241: 776-782.
- Chang, S.-K., Zainal, Z., Tan, K.-B., Yusof, N. A., Yusoff, W. M. D. W. and Prabakaran, S. R. S. (2012). Nickel–cobalt oxide/activated carbon composite electrodes for electrochemical capacitors. *Current Applied Physics*. 12(6): 1421-1428.
- Chen, T. and Dai, L. (2013). Carbon nanomaterials for high-performance supercapacitors. *Materials Today*. 16(7-8): 272-280.
- Chen, W.-H. and Kuo, P.-C. (2010). A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. *Energy*. 35(6): 2580-2586.
- Chen, X., Chen, K., Wang, H. and Xue, D. (2015). A colloidal pseudocapacitor: Direct use of  $\text{Fe}(\text{NO}_3)_3$  in electrode can lead to a high performance alkaline supercapacitor system. *Journal of Colloid and Interface Science*. 444: 49-57.
- Cheng, L., Guo, P., Wang, R., Ming, L., Leng, F., Li, H. and Zhao, X. S. (2014). Electrocapacitive properties of supercapacitors based on hierarchical porous carbons from chestnut shell. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 446: 127-133.
- Conway, B. E., Birss, V. and Wojtowicz, J. (1997). The role and utilization of pseudocapacitance for energy storage by supercapacitors. *Journal of Power Sources*. 66: 1-14.
- Conway, B. E., Bockris, J. O. M. and Amma, I. A. (1951). The Dielectric Constant of the Solution in the Diffuse and Helmholtz Double Layers at a Charged Interface in Aqueous Solution. *Transactions of the Faraday Society*. 47: 756-766.
- Cruz, G., Pirilä, M., Huuhtanen, M., Carrión, L., Alvarenga, E. and Keiski, R. L. (2012). Production of Activated Carbon from Cocoa (*Theobroma cacao*) Pod Husk. *Journal of Civil & Environment Engineering*. 2(2): 109-115.
- Daud, Z., Kassim, A. S. M., Aripin, A. M., Awang, H. and Hatta, M. Z. M. (2013). Chemical Composition and Morphological of Cocoa Pod Husks and Cassava Peels for Pulp and Paper Production. *Australian Journal of Basic and Applied Sciences*. 7(9): 406-411.

- Davies, A. and Yu, A. (2011). Material advancements in supercapacitors: From activated carbon to carbon nanotube and graphene. *The Canadian Journal of Chemical Engineering*. 89(6): 1342-1357.
- Deng, H., Li, G., Yang, H., Tang, J. and Tang, J. (2010a). Preparation of activated carbons from cotton stalk by microwave assisted KOH and K<sub>2</sub>CO<sub>3</sub> activation. *Chemical Engineering Journal*. 163(3): 373-381.
- Deng, H., Yang, L., Tao, G. and Dai, J. (2009). Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation-application in methylene blue adsorption from aqueous solution. *J Hazard Mater*. 166(2-3): 1514-21.
- Deng, H., Zhang, G., Xu, X., Tao, G. and Dai, J. (2010b). Optimization of preparation of activated carbon from cotton stalk by microwave assisted phosphoric acid-chemical activation. *Journal of Hazardous Materials*. 182(1-3): 217-24.
- Du Pasquier, A., Plitz, I., Menocal, S. and Amatucci, G. (2003). A comparative study of Li-ion battery, supercapacitor and nonaqueous asymmetric hybrid devices for automotive applications. *Journal of Power Sources*. 115(1): 171-178.
- Duku, M. H., Gu, S. and Hagan, E. B. (2011). A comprehensive review of biomass resources and biofuels potential in Ghana. *Renewable and Sustainable Energy Reviews*. 15(1): 404-415.
- Elmouwahidi, A., Zapata-Benabithé, Z., Carrasco-Marin, F. and Moreno-Castilla, C. (2012). Activated carbons from KOH-activation of argan (*Argania spinosa*) seed shells as supercapacitor electrodes. *Bioresource Technology*. 111: 185-90.
- Eskicioglu, C., Terzian, N., Kennedy, K. J., Droste, R. L. and Hamoda, M. (2007). Athermal microwave effects for enhancing digestibility of waste activated sludge. *Water Research*. 41(11): 2457-2466.
- Faraji, S. and Ani, F. N. (2016). Electroless nano zinc oxide-activate carbon composite supercapacitor electrode. *Journal of Electroceramics*. 1-7.
- Faraji, S., Faraji, A. H. and Noori, S. R. (2014). An investigation on electroless Cu-P composite coatings with micro and nano-SiC particles. *Materials & Design*. 54(0): 570-575.

- Faraji, S., Rahim, A., Mohamed, N. and Sipaut, C. (2012). Effect of SiC on the corrosion resistance of electroless Cu–P–SiC composite coating. *Journal of Coatings Technology and Research*. 9(1): 115-124.
- Faraji, S., Rahim, A. A., Mohamed, N., Sipaut, C. S. and Raja, B. (2011). The influence of SiC particles on the corrosion resistance of electroless, Cu–P composite coating in 1M HCl. *Materials Chemistry and Physics*. 129(3): 1063-1070.
- Farma, R., Deraman, M., Awitdrus, A., Talib, I. A., Taer, E., Basri, N. H., Manjunatha, J. G., Ishak, M. M., Dollah, B. N. and Hashmi, S. A. (2013). Preparation of highly porous binderless activated carbon electrodes from fibres of oil palm empty fruit bunches for application in supercapacitors. *Bioresource Technology*. 132: 254-61.
- Foo, K. Y. and Hameed, B. H. (2011a). Microwave-assisted preparation of oil palm fiber activated carbon for methylene blue adsorption. *Chemical Engineering Journal*. 166(2): 792-795.
- Foo, K. Y. and Hameed, B. H. (2011b). Preparation of activated carbon from date stones by microwave induced chemical activation: Application for methylene blue adsorption. *Chemical Engineering Journal*. 170(1): 338-341.
- Foo, K. Y. and Hameed, B. H. (2011c). Preparation of oil palm (*Elaeis*) empty fruit bunch activated carbon by microwave-assisted KOH activation for the adsorption of methylene blue. *Desalination*. 275(1-3): 302-305.
- Foo, K. Y. and Hameed, B. H. (2012a). Adsorption characteristics of industrial solid waste derived activated carbon prepared by microwave heating for methylene blue. *Fuel Processing Technology*. 99: 103-109.
- Foo, K. Y. and Hameed, B. H. (2012b). Mesoporous activated carbon from wood sawdust by  $K_2CO_3$  activation using microwave heating. *Bioresource Technology*. 111: 425-32.
- Foo, K. Y. and Hameed, B. H. (2012c). Microwave-assisted preparation and adsorption performance of activated carbon from biodiesel industry solid residue: influence of operational parameters. *Bioresource Technology*. 103(1): 398-404.

- Foo, K. Y. and Hameed, B. H. (2012d). Preparation of activated carbon by microwave heating of langsat (*Lansium domesticum*) empty fruit bunch waste. *Bioresource Technology*. 116: 522-5.
- Foo, K. Y. and Hameed, B. H. (2012e). Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced  $K_2CO_3$  activation. *Bioresource Technology*. 104: 679-86.
- Foo, K. Y. and Hameed, B. H. (2013). Utilization of oil palm biodiesel solid residue as renewable sources for preparation of granular activated carbon by microwave induced KOH activation. *Bioresource Technology*. 130: 696-702.
- Frackowiak, E. and Beguin, F. (2001). Carbon materials for the electrochemical storage of energy in capacitors. *Carbon*. 39(6): 937-950.
- Frackowiak, E., Khomenko, V., Jurewicz, K., Lota, K. and Beguin, F. (2006). Supercapacitors based on conduction polymers/nanotube composite. *Journal of Power Sources*. 153: 413-418.
- Frakowiak, E., Jurewicz, E., Delpeux, S. and Beguin, F. (2001). Nanotubular materials for supercapacitors. *Journal of Power Sources*. 97-98: 822-825.
- Fu, L. J., Liu, H., Zhang, H. P., Li, C., Zhang, T., Wu, Y. P. and Wu, H. Q. (2006). Novel  $TiO_2/C$  nanocomposites for anode materials of lithium ion batteries. *Journal of Power Sources*. 159(1): 219-222.
- Gamby, J., Taberna, P. L., Simon, P., Fauvarque, J. F. and Chesneau, M. (2001). Studies and characterisations of various activated carbons used for carbon/carbon supercapacitors. *Journal of Power Sources*. 101(1): 109-116.
- Ghosh, A. and Lee, Y. H. (2012). Carbon-based electrochemical capacitors. *ChemSusChem*. 5(3): 480-99.
- Gomez, J. and Kalu, E. E. (2013). High-performance binder-free Co-Mn composite oxide supercapacitor electrode. *Journal of Power Sources*. 230: 218-224.
- González-García, P., Centeno, T. A., Urones-Garrote, E., Ávila-Brandé, D. and Otero-Díaz, L. C. (2013). Microstructure and surface properties of lignocellulosic-based activated carbons. *Applied Surface Science*. 265: 731-737.
- Guo, J. and Lua, A. C. (2000). Preparation of activated carbons from oil-palm-stone chars by microwave-induced carbon dioxide activation. *Carbon*. 38: 1985-1993.

- Halper, M. S. and Ellenbogen, J. C. (2006). Supercapacitors - A Brief Overview. Virginia, USA: MITRE Nanosystems Group.
- Hamza, U. D., Nasri, N. S., Amin, N. S., Mohammed, J. and Zain, H. M. (2015). Characteristics of oil palm shell biochar and activated carbon prepared at different carbonization times. *Desalination and Water Treatment*. 1-8.
- Haque, K. E. (1999). Microwave energy for mineral treatment processes—a brief review. *International Journal of Mineral Processing*. 57(1): 1-24.
- Haykiri-Acma, H., Yaman, S. and Kucukbayrak, S. (2010). Comparison of the thermal reactivities of isolated lignin and holocellulose during pyrolysis. *Fuel Processing Technology*. 91(7): 759-764.
- He, P., Xie, Z., Chen, Y., Dong, F. and Liu, H. (2012). Co<sub>2</sub>SnO<sub>4</sub>/activated carbon composite electrode for supercapacitor. *Materials Chemistry and Physics*. 137(2): 576-579.
- He, X., Geng, Y., Qiu, J., Zheng, M., Long, S. and Zhang, X. (2010). Effect of activation time on the properties of activated carbons prepared by microwave-assisted activation for electric double layer capacitors. *Carbon*. 48(5): 1662-1669.
- He, X., Ling, P., Qiu, J., Yu, M., Zhang, X., Yu, C. and Zheng, M. (2013). Efficient preparation of biomass-based mesoporous carbons for supercapacitors with both high energy density and high power density. *Journal of Power Sources*. 240: 109-113.
- Hesas, R. H., Wan Daud, W. M. A., Sahu, J. N. and Arami-Niya, A. (2013). The effects of a microwave heating method on the production of activated carbon from agricultural waste: A review. *Journal of Analytical and Applied Pyrolysis*. 100: 1-11.
- Hoseinzadeh Hesas, R., Arami-Niya, A., Wan Daud, W. M. A. and Sahu, J. N. (2013a). Comparison of oil palm shell-based activated carbons produced by microwave and conventional heating methods using zinc chloride activation. *Journal of Analytical and Applied Pyrolysis*. 104: 176-184.
- Hoseinzadeh Hesas, R., Arami-Niya, A., Wan Daud, W. M. A. and Sahu, J. N. (2013b). Preparation of granular activated carbon from oil palm shell by microwave-induced chemical activation: Optimisation using surface response

- methodology. *Chemical Engineering Research and Design*. 91(12): 2447-2456.
- Hsieh, C.-T. and Teng, H. (2002). Influence of oxygen treatment on electric double-layer capacitance of activated carbon fabrics. *Carbon*. 40(5): 667-674.
- Hu, C.-C. and Chen, W.-C. (2004). Effects of substrates on the capacitive performance of  $\text{RuO}_x \cdot n\text{H}_2\text{O}$  and activated carbon– $\text{RuO}_x$  electrodes for supercapacitors. *Electrochimica Acta*. 49(21): 3469-3477.
- Hu, Q.-H., Wang, X.-T., Chen, H. and Wang, Z.-F. (2012). Synthesis of Ni/graphene sheets by an electroless Ni-plating method. *New Carbon Materials*. 27(1): 35-41.
- Huang, Q., Wang, X., Li, J., Dai, C., Gamboa, S. and Sebastian, P. J. (2007). Nickel hydroxide/activated carbon composite electrodes for electrochemical capacitors. *Journal of Power Sources*. 164(1): 425-429.
- Hung, C. J., Lin, P. and Tseng, T. Y. (2014). High energy density asymmetric pseudocapacitors fabricated by graphene/carbon nanotube/ $\text{MnO}_2$  plus carbon nanotubes nanocomposites electrode. *Journal of Power Sources*. 259: 145-153.
- Inagaki, M., Konno, H. and Tanaike, O. (2010). Carbon materials for electrochemical capacitors. *Journal of Power Sources*. 195(24): 7880-7903.
- Ioannidou, O. and Zabaniotou, A. (2007). Agricultural residues as precursors for activated carbon production—A review. *Renewable and Sustainable Energy Reviews*. 11(9): 1966-2005.
- Ismanto, A. E., Wang, S., Soetaredjo, F. E. and Ismadji, S. (2010). Preparation of capacitor's electrode from cassava peel waste. *Bioresource Technology*. 101(10): 3534-40.
- Jahromi, S. P., Pandikumar, A., Goh, B. T., Lim, Y. S., Basirun, W. J., Lim, H. N. and Huang, N. M. (2015). Influence of particle size on performance of a nickel oxide nanoparticle-based supercapacitor. *RSC Advances*. 5(18): 14010-14019.
- Jain, A. and Tripathi, S. K. (2014). Fabrication and characterization of energy storing supercapacitor devices using coconut shell based activated charcoal electrode. *Materials Science and Engineering: B*. 183: 54-60.
- Jayalakshmi, M. and Balasubramanian, K. (2008). Simple Capacitors to Supercapacitors - An Overview. *International Journal of Electrochemical Science*. 3: 1196 - 1217.

- Jia, B., Su, L., Han, G., Wang, G., Zhang, J. and Wang, L. (2011). Adsorption Properties of Nickel-Based Magnetic Activated Carbon Prepared by Pd-Free Electroless Plating. *BioResources*. 6(1): 70-80.
- Jin, H., Wang, X., Gu, Z. and Polin, J. (2013). Carbon materials from high ash biochar for supercapacitor and improvement of capacitance with HNO<sub>3</sub> surface oxidation. *Journal of Power Sources*. 236: 285-292.
- Jin, X.-J., Yu, Z.-M. and Wu, Y. (2012). Preparation of Activated Carbon from Lignin obtained by Straw Pulp by KOH and K<sub>2</sub>CO<sub>3</sub> Chemical Activation. *Cellulose Chemistry and Technology*. 46(1-2): 79-85.
- Jones, D. A., Lelyveld, T. P., Mavrofidis, S. D., Kingman, S. W. and Miles, N. J. (2002). Microwave heating applications in environmental engineering—a review. *Resources, Conservation and Recycling*. 34(2): 75-90.
- Jurewicz, K., Delpeux, S., Bertagna, V., Béguin, F. and Frackowiak, E. (2001). Supercapacitors from nanotubes/polypyrrole composites. *Chemical Physics Letters*. 347(1–3): 36-40.
- Kalyani, P., Anitha, A. and Darchen, A. (2015). Obtaining Activated Carbon from Papaya Seeds for Energy Storage Devices. *International Journal of Engineering Sciences & Research Technology*. 4(1): 110-122.
- Kavaliauskas, Z., Marcinauskas, L. and Valetkevicius, P. (2011). Formation and Characterization of Carbon and Nickel Oxide/Carbon Composites for Supercapacitors. *Acta Physica Polonica A*. 119(2): 253-255.
- Kim, H. and Popov, B. N. (2002). Characterization of hydrous ruthenium oxide/carbon nanocomposite supercapacitors prepared by a colloidal method. *Journal of Power Sources*. 104: 52-61.
- Kim, J. H., Choi, H. J., Kim, H.-K., Lee, S.-H. and Lee, Y.-H. (2016). A hybrid supercapacitor fabricated with an activated carbon as cathode and an urchin-like TiO<sub>2</sub> as anode. *International Journal of Hydrogen Energy*. 41(31): 13549-13556.
- Kim, M., Hwang, Y., Min, K. and Kim, J. (2013). Introduction of MnO<sub>2</sub> nanoneedles to activated carbon to fabricate high-performance electrodes as electrochemical supercapacitors. *Electrochimica Acta*. 113: 322-331.
- Kotz, R. and Carlen, M. (2000). Principles and applications of electrochemical capacitors. *Electrochimica Acta*. 45: 2483–2498.



- Laforge, A., Simon, P. and Fauvarque, J.-F. (2001). Chemical synthesis and characterization of fluorinated polyphenylthiophenes: application to energy storage. *Synthetic Metals*. 123: 311-319.
- Lam, S. S. and Chase, H. A. (2012). A Review on Waste to Energy Processes Using Microwave Pyrolysis. *Energies*. 5(12): 4209-4232.
- Lee, H.-M., Lee, K. and Kim, C.-K. (2014). Electrodeposition of Manganese-Nickel Oxide Films on a Graphite Sheet for Electrochemical Capacitor Applications. *Materials*. 7: 265-274.
- Lee, H. Y. and Goodenough, J. B. (1999). Supercapacitor Behavior with KCl Electrolyte. *Journal of Solid State Chemistry*. 144: 220—223.
- Lewandowski, A., Olejniczak, A., Galinski, M. and Stepniak, I. (2010). Performance of carbon-carbon supercapacitors based on organic, aqueous and ionic liquid electrolytes. *Journal of Power Sources*. 195(17): 5814-5819.
- Li, M., Feng, C., Zhang, Z., Chen, R., Xue, Q., Gao, C. and Sugiura, N. (2010). Optimization of process parameters for electrochemical nitrate removal using Box-Behnken design. *Electrochimica Acta*. 56(1): 265-270.
- Li, W., Peng, J., Zhang, L., Yang, K., Xia, H., Zhang, S. and Guo, S. H. (2009). Preparation of activated carbon from coconut shell chars in pilot-scale microwave heating equipment at 60 kW. *Waste Management*. 29(2): 756-60.
- Li, W., Zhang, L.-B., Peng, J.-H., Li, N. and Zhu, X.-Y. (2008). Preparation of high surface area activated carbons from tobacco stems with  $K_2CO_3$  activation using microwave radiation. *Industrial Crops and Products*. 27(3): 341-347.
- Li, X., Xing, W., Zhuo, S., Zhou, J., Li, F., Qiao, S. Z. and Lu, G. Q. (2011). Preparation of capacitor's electrode from sunflower seed shell. *Bioresource Technology*. 102(2): 1118-23.
- Liang, H., Chen, F., Li, R., Wang, L. and Deng, Z. (2004). Electrochemical study of activated carbon-semiconducting oxide composites as electrode materials of double-layer capacitors. *Electrochimica Acta*. 49(21): 3463-3467.
- Liu, H., He, P., Li, Z., Liu, Y. and Li, J. (2006). A novel nickel-based mixed rare-earth oxide/activated carbon supercapacitor using room temperature ionic liquid electrolyte. *Electrochimica Acta*. 51(10): 1925-1931.

- Liu, M.-C., Kong, L.-B., Zhang, P., Luo, Y.-C. and Kang, L. (2012). Porous wood carbon monolith for high-performance supercapacitors. *Electrochimica Acta*. 60: 443-448.
- Liu, Q.-S., Zheng, T., Wang, P. and Guo, L. (2010). Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation. *Industrial Crops and Products*. 31(2): 233-238.
- Lu, A., Zhang, S., Shan, X.-Q., Wang, S. and Wang, Z. (2003). Application of microwave extraction for the evaluation of bioavailability of rare earth elements in soils. *Chemosphere*. 53(9): 1067-1075.
- Madhu, R., Veeramani, V., Chen, S.-M., Veerakumar, P. and Liu, S.-B. (2015). Functional Porous Carbon/Nickel Oxide Nanocomposites as Binder-Free Electrodes for Supercapacitors. *Chemistry – A European Journal*. 21(22): 8200-8206.
- Malak-Polaczyk, A., Matei-Ghimbeu, C., Vix-Guterl, C. and Frackowiak, E. (2010). Carbon/ $\lambda$ -MnO<sub>2</sub> composites for supercapacitor electrodes. *Journal of Solid State Chemistry*. 183: 969-974.
- Mallory, G. O. (1990a). *The Electroless Nickel Plating Bath: Effect of Variables on the Process*. In: Mallory, G. O. and Hajdu, J. B. (Ed.) *Electroless plating - Fundamentals & Applications*. (pp. 57-99). USA: Noyes Publications/William Andrew Publishing, LLC.
- Mallory, G. O. (1990b). *The Fundamental Aspects of Electroless Nickel Plating*. In: Mallory, G. O. and Hajdu, J. B. (Ed.) *Electroless plating - Fundamentals & Applications*. (pp. 1-56). Orlando, Florida: American Electroplaters and Surface Finishers Society.
- Mallory, G. O. and Hajdu, J. B. (eds.) 1990. *Electroless plating - Fundamentals & Applications*, Orlando, Florida: American Electroplaters and Surface Finishers Society.
- Martyak, N. M. and Lou, J. (2001). Limitations of Nickel Hypophosphite Electroless Nickel Processes. *Process Safety and Environmental Protection*. 79(5): 278-282.
- Mastragostino, M., Arbizzani, C. and Soavi, F. (2001). Polymer-based supercapacitors. *Journal of Power Sources*. 97–98(0): 812-815.

- Mastragostino, M., Arbizzani, C. and Soavi, F. (2002). Conducting polymers as electrode materials in supercapacitors. *Solid State Ionics*. 148: 493–498.
- Menéndez, J. A., Arenillas, A., Fidalgo, B., Fernández, Y., Zubizarreta, L., Calvo, E. G. and Bermúdez, J. M. (2010). Microwave heating processes involving carbon materials. *Fuel Processing Technology*. 91(1): 1-8.
- Metaxas, A. C. (1991). Microwave Heating. *Power Engineering Journal*. 5(5): 237-247.
- Misnon, I. I., Zain, N. K. M., Aziz, R. A., Vidyadharan, B. and Jose, R. (2015). Electrochemical properties of carbon from oil palm kernel shell for high performance supercapacitors. *Electrochimica Acta*. 174: 78-86.
- Muradov, N. Z. and Vezirog̃Lu, T. N. (2008). “Green” path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies. *International Journal of Hydrogen Energy*. 33: 6804-6839.
- Nabais, J. M. V., Nunes, P., Carrott, P. J. M., Ribeiro Carrott, M. M. L., García, A. M. and Díaz-Díez, M. A. (2008a). Production of activated carbons from coffee endocarp by CO<sub>2</sub> and steam activation. *Fuel Processing Technology*. 89(3): 262-268.
- Nabais, J. V., Carrott, P., Ribeiro Carrott, M. M., Luz, V. and Ortiz, A. L. (2008b). Influence of preparation conditions in the textural and chemical properties of activated carbons from a novel biomass precursor: the coffee endocarp. *Bioresource Technology*. 99(15): 7224-31.
- Nakayama, M., Kanaya, T. and Inoue, R. (2007). Anodic deposition of layered manganese oxide into a colloidal crystal template for electrochemical supercapacitor. *Electrochemistry Communications*. 9: 1154–1158.
- Naoi, K. and Simon, P. (2008). New Materials and New Configurations for Advanced Electrochemical Capacitors. *Electrochemical Society Interface*. 17(1): 34-37.
- Ninduangdee, P., Kuprianov, V. I., Cha, E. Y., Kaewrath, R., Youngyuen, P. and Atthawethworawuth, W. (2015). Thermogravimetric Studies of Oil Palm Empty Fruit Bunch and Palm Kernel Shell: TG/DTG Analysis and Modeling. *Energy Procedia*. 79: 453-458.
- Noorden, Z. A., Sugawara, S. and Matsumoto, S. (2014). Noncorrosive separator materials for electric double layer capacitor. *IEEEJ Transactions on Electrical and Electronic Engineering*. 9(3): 235-240.

- Nor, N. S. M., Deraman, M., Omar, R., Awitdrus, Farma, R., Basri, N. H., Dolah, B. N. M., Mamat, N. F., Yatim, B. and Daud, M. N. M. (2015). Influence of gamma irradiation exposure on the performance of supercapacitor electrodes made from oil palm empty fruit bunches. *Energy*. 79: 183-194.
- Oghbaei, M. and Mirzaee, O. (2010). Microwave versus conventional sintering: A review of fundamentals, advantages and applications. *Journal of Alloys and Compounds*. 494(1-2): 175-189.
- Pandolfo, A. G. and Hollenkamp, A. F. (2006). Carbon properties and their role in supercapacitors. *Journal of Power Sources*. 157(1): 11-27.
- Panić, V., Vidaković, T., Gojković, S., Dekanski, A., Milonjić, S. and Nikolić, B. (2003). The properties of carbon-supported hydrous ruthenium oxide obtained from RuOxHy sol. *Electrochimica Acta*. 48(25–26): 3805-3813.
- Pell, W. G. and Conway, B. E. (2004). Peculiarities and requirements of asymmetric capacitor devices based on combination of capacitor and battery-type electrodes. *Journal of Power Sources*. 136(2): 334-345.
- Peng, C., Yan, X.-B., Wang, R.-T., Lang, J.-W., Ou, Y.-J. and Xue, Q.-J. (2013). Promising activated carbons derived from waste tea-leaves and their application in high performance supercapacitors electrodes. *Electrochimica Acta*. 87: 401-408.
- Peng, Y., Chen, Z., Wen, J., Xiao, Q., Weng, D., He, S., Geng, H. and Lu, Y. (2011). Hierarchical Manganese Oxide/Carbon Nanocomposites for Supercapacitor Electrodes. *Nano Research*. 4(2): 216–225.
- Perera, S. D., Liyanage, A. D., Nijem, N., Ferraris, J. P., Chabal, Y. J. and Balkus, K. J. (2013). Vanadium oxide nanowire – Graphene binder free nanocomposite paper electrodes for supercapacitors: A facile green approach. *Journal of Power Sources*. 230: 130-137.
- Prauchner, M. J. and Rodríguez-Reinoso, F. (2012). Chemical versus physical activation of coconut shell: A comparative study. *Microporous and Mesoporous Materials*. 152(0): 163-171.
- Qu, D. and Shi, H. (1998). Studies of activated carbons used in double-layer capacitors. *Journal of Power Sources*. 74(1): 99-107.

- Rahim, Y. A., Aqmar, S. N. and Dewi, D. R. S. (2010). ESR Study of Electron Trapped on Activated Carbon by KOH and ZnCl<sub>2</sub> Activation. *Journal of Materials Science and Engineering*. 4(3): 22-26.
- Ramani, M., Haran, B. S., White, R. E., Popov, B. N. and Arsov, L. (2001). Studies on activated carbon capacitor materials loaded with different amounts of ruthenium oxide. *Journal of Power Sources*. 93(1–2): 209-214.
- Ramasamy, C., Del Val, J. P. and Anderson, M. (2014). An electrochemical cell study on polyvinylpyrrolidone aqueous gel with glycol addition for capacitor applications. *Electrochimica Acta*. 135: 181-186.
- Raymundo-Piñero, E., Leroux, F. and Béguin, F. (2006). A High-Performance Carbon for Supercapacitors Obtained by Carbonization of a Seaweed Biopolymer. *Advanced Materials*. 18(14): 1877-1882.
- Rouquerol, J., Avnir, D., Fairbridge, C. W., Everett, D. H., Haynes, J. H., Pernicone, N., Ramsay, J. D. F., Sing, K. S. W. and Unger, K. K. (1994). Recommendations for the Characterization of Porous Solids (Technical Report). *Pure & Applied Chemistry*. 66(8): 1739-1758.
- Rufford, T. E., Hulicova-Jurcakova, D., Fiset, E., Zhu, Z. and Lu, G. Q. (2009). Double-layer capacitance of waste coffee ground activated carbons in an organic electrolyte. *Electrochemistry Communications*. 11(5): 974-977.
- Rufford, T. E., Hulicova-Jurcakova, D., Khosla, K., Zhu, Z. and Lu, G. Q. (2010). Microstructure and electrochemical double-layer capacitance of carbon electrodes prepared by zinc chloride activation of sugar cane bagasse. *Journal of Power Sources*. 195(3): 912-918.
- Rufford, T. E., Hulicova-Jurcakova, D., Zhu, Z. and Lu, G. Q. (2008). Nanoporous carbon electrode from waste coffee beans for high performance supercapacitors. *Electrochemistry Communications*. 10: 1594-1597.
- Rugayah, A. F., Astimar, A. A. and Norzita, N. (2014). Preparation and Characterisation of Activated Carbon from Palm Kernel Shell by Physical Activation with Steam. *Journal of Oil Palm Research*. 26(3): 251-264.
- Sahoo, P. and Das, S. K. (2011). Tribology of electroless nickel coatings – A review. *Materials & Design*. 32(4): 1760-1775.

- Saidur, R., Abdelaziz, E. A., Demirbas, A., Hossain, M. S. and Mekhilef, S. (2011). A review on biomass as a fuel for boilers. *Renewable and Sustainable Energy Reviews*. 15(5): 2262-2289.
- Salema, A. A. and Ani, F. N. (2012). Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer. *Journal of Analytical and Applied Pyrolysis*. 96: 162-172.
- Schlesinger, M. (2010). *Electroless Deposition of Nickel*. In: Schlesinger, M. and Paunovic, M. (Ed.) *Modern Electroplating*. (pp. 447-458) Fifth ed.: John Wiley & Sons, Inc.
- Selvakumar, M. and Bhat, D. K. (2012). Microwave synthesized nanostructured TiO<sub>2</sub>-activated carbon composite electrodes for supercapacitor. *Applied Surface Science*. 263: 236-241.
- Selvakumar, M., Krishna Bhat, D., Manish Aggarwal, A., Prahladh Iyer, S. and Sravani, G. (2010). Nano ZnO-activated carbon composite electrodes for supercapacitors. *Physica B: Condensed Matter*. 405(9): 2286-2289.
- Sevilla, M. and Mokaya, R. (2014). Energy storage applications of activated carbons: supercapacitors and hydrogen storage. *Energy & Environmental Science*. 7(4): 1250-1280.
- Shibata, M., Varman, M., Tono, Y., Miyafuji, H. and Saka, S. (2008). Characterization in Chemical Composition of the Oil Palm (*Elaeis guineensis*). *Journal of the Japan Institute of Energy*. 87(5): 383-388.
- Si, W.-J., Wu, X.-Z., Xing, W., Zhou, J. and Zhuo, S.-P. (2011). Bagasse-based Nanoporous Carbon for Supercapacitor Application. *Journal of Inorganic Materials*. 26(1): 107-112.
- Simon, P. and Gogotsi, Y. (2008). Materials for electrochemical capacitors. *Nature Materials*. 7: 845-854.
- Sonia, T. S., Mini, P. A., Nandhini, R., Sujith, K., Avinash, B., Nair, S. V. and Subramanian, K. R. V. (2013). Composite supercapacitor electrodes made of activated carbon/PEDOT:PSS and activated carbon/doped PEDOT. *Bulletin of Materials Science*. 36(4): 547-551.
- Staiti, P. and Lufrano, F. (2010). Investigation of polymer electrolyte hybrid supercapacitor based on manganese oxide-carbon electrodes. *Electrochimica Acta*. 55: 7436-7442.

- Sudagar, J., Lian, J. and Sha, W. (2013). Electroless nickel, alloy, composite and nano coatings – A critical review. *Journal of Alloys and Compounds*. 571(0): 183-204.
- Sun, F., Gao, J., Liu, X., Wang, L., Yang, Y., Pi, X., Wu, S. and Qin, Y. (2016). High-energy Li-ion hybrid supercapacitor enabled by a long life N-rich carbon based anode. *Electrochimica Acta*. 213: 626-632.
- Taer, E., Deraman, M., Talib, I. A., Awitdrus, A., Hashmi, S. A. and Umar, A. A. (2011a). Preparation of a Highly Porous Binderless Activated Carbon Monolith from Rubber Wood Sawdust by a Multi-Step Activation Process for Application in Supercapacitors. *International Journal of Electrochemical Science*. 6: 3301 - 3315.
- Taer, E., Deraman, M., Talib, I. A., Awitdrus, A., Hashmi, S. A. and Umar, A. A. (2011b). Preparation of a Highly Porous Binderless Activated Carbon Monolith from Rubber Wood Sawdust by a Multi-Step Activation Process for Application in Supercapacitors. *International Journal of Electrochemical Science*. 6(8): 3301 - 3315.
- Tai, Y.-L. and Teng, H. (2004). Modification of porous carbon with nickel oxide impregnation to enhance the electrochemical capacitance and conductivity. *Carbon*. 42(11): 2335-2338.
- Tang, S.-Y., Xia, Z.-N., Fu, Y.-J. and Gou, Q. (2008). Advances and Applications of Microwave Spectroscopy. *Chinese Journal of Analytical Chemistry*. 36(8): 1145-1151.
- Tay, T., Ucar, S. and Karagoz, S. (2009). Preparation and characterization of activated carbon from waste biomass. *Journal of Hazardous Materials*. 165(1-3): 481-5.
- Theydan, S. K. and Ahmed, M. J. (2012). Optimization of preparation conditions for activated carbons from date stones using response surface methodology. *Powder Technology*. 224: 101-108.
- Valente Nabais, J. M., Teixeira, J. G. and Almeida, I. (2011). Development of easy made low cost bindless monolithic electrodes from biomass with controlled properties to be used as electrochemical capacitors. *Bioresource Technology*. 102(3): 2781-2787.

- Vargas, A. M. M., Garcia, C. A., Reis, E. M., Lenzi, E., Costa, W. F. and Almeida, V. C. (2010). NaOH-activated carbon from flamboyant (*Delonix regia*) pods: Optimization of preparation conditions using central composite rotatable design. *Chemical Engineering Journal*. 162(1): 43-50.
- Wang, C.-C. and Hu, C.-C. (2004). The capacitive performance of activated carbon–ruthenium oxide composites for supercapacitors: effects of ultrasonic treatment in NaOH and annealing in air. *Materials Chemistry and Physics*. 83(2-3): 289-297.
- Wang, K., Li, L. and Zhang, H. (2013). Synthesis of Nickel Oxide/Active Carbon and Electrochemical Performance. *International Journal Electrochemical Science*. 8: 5036 - 5041.
- Wang, T., Tan, S. and Liang, C. (2009). Preparation and characterization of activated carbon from wood via microwave-induced  $ZnCl_2$  activation. *Carbon*. 47(7): 1880-1883.
- Wu, T.-N. (2008). Environmental Perspectives of Microwave Applications as Remedial Alternatives: Review. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*. 12(2): 102-115.
- Wu, X., Xing, W., Florek, J., Zhou, J., Wang, G., Zhuo, S., Xue, Q., Yan, Z. and Kleitz, F. (2014). On the origin of the high capacitance of carbon derived from seaweed with an apparently low surface area. *Journal Materials Chemistry A*. 2(44): 18998-19004.
- Xie, L.-J., Wu, J.-F., Chen, C.-M., Zhang, C.-M., Wan, L., Wang, J.-L., Kong, Q.-Q., Lv, C.-X., Li, K.-X. and Sun, G.-H. (2013). A novel asymmetric supercapacitor with an activated carbon cathode and a reduced graphene oxide–cobalt oxide nanocomposite anode. *Journal of Power Sources*. 242: 148-156.
- Xin-Hui, D., Srinivasakannan, C., Jin-Hui, P., Li-Bo, Z. and Zheng-Yong, Z. (2011a). Comparison of activated carbon prepared from *Jatropha* hull by conventional heating and microwave heating. *Biomass and Bioenergy*. 35(9): 3920-3926.
- Xin-Hui, D., Srinivasakannan, C., Jin-Hui, P., Li-Bo, Z. and Zheng-Yong, Z. (2011b). Preparation of activated carbon from *Jatropha* hull with microwave heating: Optimization using response surface methodology. *Fuel Processing Technology*. 92(3): 394-400.



- Xu, B., Chen, Y., Wei, G., Cao, G., Zhang, H. and Yang, Y. (2010). Activated carbon with high capacitance prepared by NaOH activation for supercapacitors. *Materials Chemistry and Physics*. 124(1): 504-509.
- Yagmur, E., Ozmak, M. and Aktas, Z. (2008). A novel method for production of activated carbon from waste tea by chemical activation with microwave energy. *Fuel*. 87(15-16): 3278-3285.
- Yang, D. (2012). Application of Nanocomposites for Supercapacitors: Characteristics and Properties. In: Ebrahimi, F. (ed.) *Nanocomposites - New Trends and Developments*. Croatia: InTech.
- Yang, H., Yan, R., Chin, T., Liang, D. T., Chen, H. and Zheng, C. (2004). Thermogravimetric Analysis–Fourier Transform Infrared Analysis of Palm Oil Waste Pyrolysis. *Energy & Fuels*. 18(6): 1814-1821.
- Yang, K., Peng, J., Srinivasakannan, C., Zhang, L., Xia, H. and Duan, X. (2010). Preparation of high surface area activated carbon from coconut shells using microwave heating. *Bioresource Technology*. 101(15): 6163-9.
- Yuan, G.-H., Jiang, Z.-H., Aramata, A. and Gao, Y.-Z. (2005). Electrochemical behavior of activated-carbon capacitor material loaded with nickel oxide. *Carbon*. 43(14): 2913-2917.
- Yuen, F. K. and Hameed, B. H. (2009). Recent developments in the preparation and regeneration of activated carbons by microwaves. *Advances Colloid and Interface Science*. 149(1-2): 19-27.
- Zhang, J., Gong, L., Sun, K., Jiang, J. and Zhang, X. (2012). Preparation of activated carbon from waste *Camellia oleifera* shell for supercapacitor application. *Journal of Solid State Electrochemistry*. 16: 2179–2186.
- Zhang, L., Xu, C. and Champagne, P. (2010). Overview of recent advances in thermochemical conversion of biomass. *Energy Conversion and Management*. 51: 969–982.
- Zheng, J. P., Cygan, P. J. and Jow, T. R. (1995). Hydrous Ruthenium Oxide as an Electrode Material for Electrochemical Capacitors. *Journal of Electrochemical Society*. 142(8): 2699-2703.
- Zong, L., Zhou, S., Sgriccia, N., Hawley, M. C. and Kempel, L. C. (2003). A Review of Microwave-Assisted Polymer Chemistry (MAPC). *Journal of Microwave Power & Electromagnetic Energy*. 38(1): 49-74.