

SYNTHESIS AND CHARACTERIZATION OF  
ACTIVATED CARBON FROM PALM KERNEL SHELLS FOR  
ELECTROCHEMICAL DOUBLE LAYER CAPACITOR

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Thesis submitted in fulfillment of the requirements  
for the award of the degree of  
Master of Science (Advanced Materials)

Faculty of Industrial Sciences & Technology  
UNIVERSITI MALAYSIA PAHANG

AUGUST 2015

## ABSTRACT

Storage of electrical energy at an electrode–electrolyte interface under supercapacitive mode is intriguing owing to its large power capability compared to batteries. A large electrode surface is required for storing large amount of energy and high electrical conductivity of the electrode and electrolyte enable high rate delivery. Furthermore, primary material supply should be ensured for a research result to be adopted by industry. These requirements make carbons, in all of its allotropes, as a desirable candidate as an electrode material for supercapacitors. Biomass provides as an excellent source of carbon considering the renewability; however, properties of biomass even from similar species strongly vary depending on the geographical location. Malaysia is the largest exporter of palm oil; for each 2.5 kg of crude palm oil over 100 kg of biomass is produced as a byproduct. Palm oil produces six main biomass types such as fronds, trunks, empty fruit bunches, palm kernel shells (PKS), mesocarp fiber and palm oil mill effluent. Among them PKS contribute ~6%. However, use of PKS as a source of carbon for supercapacitors electrode has not been tested so far.

This research thesis aims to evaluate the electrochemical properties of the carbon produced from PKS. Decomposition behavior of cleaned PKS was studied using thermogravimetric analysis and accordingly carbonized by pyrolysis. The as-prepared char was chemically activated using KOH, NaOH, H<sub>2</sub>SO<sub>4</sub>, and ZnCl<sub>2</sub> in four impregnation ratios and optimized for the best surface properties. The structure and microstructure of the activated carbon were studied using X- ray diffraction and scanning electron microscopy, respectively. The electrochemical properties of all the sixteen samples obtained under various activation conditions were studied by cyclic voltammetry, galvanostatic charge-discharge cycling and electrochemical impedance spectroscopy in a three-electrode system configuration using electrodes prepared from the PKS activated carbon (AC) as working electrode, Pt wire as counter electrode, and Hg/HgO as reference electrode in 1 M KOH electrolyte. The electrochemical properties were correlated with the surface properties in detail. Finally, a working supercapacitor is fabricated using the PKS AC electrodes developed on nickel foam substrate, glassy fiber as a separator, and 1 M KOH as electrolyte. The device delivered energy densities 6.6, 6.0, 5.7, 5.2, 4.5, 4.1, 3.5, 3.0 Wh/kg at power densities 60, 180, 310, 600, 1200, 1800, 300, 4000 W/kg, respectively. These values are comparable to the commercially available devices using activated carbon. Owing to the large abundance of carbon and promising results herewith, the present results show huge promise in developing PKS ACs as commercial supercapacitor electrodes.

## ABSTRAK

Penyimpanan tenaga elektrik di antara muka elektrod-elektrolit di bawah mod superkapasitif adalah menarik kerana keupayaan kuasa yang besar berbanding bateri. Permukaan elektrod yang luas diperlukan untuk menyimpan jumlah tenaga yang besar dan kekonduksian elektrik yang tinggi kepada elektrod dan elektrolit bagi membolehkan kadar penghantaran yang tinggi. Tambahan pula, kesediaan bekalan bahan utama adalah perlu untuk mendapatkan hasil kajian yang boleh diguna pakai oleh industri. Keperluan ini membuatkan karbon, dalam semua alotrop, sebagai bahan dikehendaki sebagai bahan elektrod untuk superkapasitor. Biojisim yang sedia ada adalah sumber karbon yang sangat baik; walaubagaimanapun, ciri-ciri biojisim walaupun dari spesies yang sama adalah berbeza-beza bergantung kepada lokasi geografi. Malaysia adalah pengeksport terbesar minyak sawit; bagi setiap 2.5 kg minyak sawit mentah lebih daripada 100 kg biojisim dihasilkan sebagai hasil sampingan. Kelapa sawit menghasilkan enam jenis biojisim utama iaitu; pelepah, batang, tandan buah kosong, tempurung isirong sawit (PKS), gentian mesokarpa dan efluen kilang minyak sawit. 6% daripadanya adalah PKS. Walaubagaimanapun, penggunaan PKS sebagai sumber karbon untuk elektrod superkapasitor belum diuji setakat ini.

Tesis penyelidikan ini bertujuan untuk menilai sifat-sifat elektrokimia karbon yang dihasilkan daripada PKS. Tindakan penguraian daripada PKS bersih dikaji menggunakan analisis termogravimetri dan seterusnya dikarbonkan melalui pirolisis. Arang yang tersedia telah diaktifkan secara kimia dengan menggunakan KOH, NaOH, H<sub>2</sub>SO<sub>4</sub>, dan ZnCl<sub>2</sub> dalam empat nisbah impregnasi dan dioptimumkan untuk sifat-sifat permukaan terbaik. Struktur dan struktur mikro karbon teraktif telah dikaji dengan menggunakan pembelauan x-ray dan mikroskopi pengimbas elektron. Sifat elektrokimia semua enam belas sampel diperoleh di bawah pelbagai keadaan pengaktifan telah dikaji dengan voltametri berkitar, galvanostatik caj-nyahcas dan spektroskopi impedans elektrokimia dalam konfigurasi sistem tiga elektrod menggunakan elektrod disediakan daripada karbon teraktif (AC) PKS sebagai elektrod kerja, dawai Pt sebagai elektrod kaunter, dan Hg/HgO sebagai elektrod rujukan dalam 1 M KOH. Sifat elektrokimia telah dikaitkan dengan sifat-sifat permukaan secara terperinci. Akhir sekali, superkapasitor bekerja difabrikasi menggunakan elektrod PKS AC yang dibangunkan pada substrat busa nikel, gentian kaca sebagai pemisah, dan 1 M KOH sebagai elektrolit. Peranti masing-masing membebaskan kepadatan tenaga 6.6, 6.0, 5.7, 5.2, 4.5, 4.1, 3.5, 3.0 Wh/kg pada kepadatan kuasa 60, 180, 310, 600, 1200, 1800, 300, 4000 W/kg. Nilai-nilai ini boleh dibandingkan dengan peranti yang boleh didapati secara komersial menggunakan karbon teraktif. Oleh kerana karbon didapati dengan banyak dan mempunyai keputusan awal yang berpotensi, keputusan ini menunjukkan potensi besar dalam membangunkan AC PKS sebagai elektrod superkapasitor komersial.

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**LIST OF SYMBOLS**

$\varepsilon$	Dielectric constant
$A$	Conductor surface area
$C$	Capacitance
$C_{dl}$	Electrical double-layer capacitance
$C_{\phi}$	Pseudocapacitance
$d$	Dielectric thickness
$e$	Electron
$M$	Molarity
$n$	Number of electrons
$O_{ad}$	Adsorbed oxidants
$Q$	Charge
$q_o$	Charge associated with bare surface
$q_1$	Charge associated with adsorbed species
$q_m$	Charge on metal surface
$R_{ad}$	Adsorbed reductants
$t$	Electrical double-layer thickness
$U$	Potential energy
$V$	Electric potential

**LIST OF ABBREVIATIONS**

ACs	Activated carbons
CDCs	Carbide derived carbons
Co(OH) <sub>2</sub>	Cobalt hydroxide
CNTs	Carbon nanotubes
EC	Electrolytic capacitor
EDLC	Electrochemical double layer capacitor
EFB	Empty fruit bunch
Fe <sub>2</sub> O <sub>3</sub>	Iron oxide
HPC-0	Hierarchical porous carbon from dried pig bone without activation agent
HPC-1	Hierarchical porous carbon from dried pig bone with KOH activation at 1:1 weight ratio
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
IrO <sub>2</sub>	Iridium oxide
ISI	Institute for Scientific Information
KOH	Potassium hydroxide
LIB	Lithium ion battery
MF	Mesocarp fiber
MnO <sub>2</sub>	Manganese oxide
NaOH	Sodium hydroxide
NEC	NEC Corporation
NiO	Nickel oxide
OECD	Organization for Economic Co-operation and Development
PC	Pseudocapacitor
PKS	Palm kernel shell

POME	Palm oil mill effluent
$\text{RuO}_2$	Ruthenium oxide
SC	Supercapacitor
SOHIO	Standard Oil of Ohio
$\text{V}_2\text{O}_5$	Vanadium oxide
$\text{ZnCl}_2$	Zinc chloride
ZTCs	Zeolites-templated carbons

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 BACKGROUND**

Energy consumption would increase in the coming years due to growing economies and increasing population. Primary supply of sustainable and clean energy is one of the major challenges of the 21st century. A recent report by British Petroleum points that 1.3 billion more people will become new energy consumers by 2030 with a total population of 8.3 billion (British Petroleum, 2013). Exxon's 2040 Energy Outlook projects 35% increase in global electricity demand during 2010–2040 (Exxon Mobil, 2014). Developing non-OECD countries alone will experience a 150% increase in electricity demand led by India and China (Exxon Mobil, 2014). By the present energy growth of 1.6% per year, 35 years are required to have such magnitude of energy; therefore, a crisis is inevitable (U.S. Energy Information Administration, 2013). This increased energy demand is one part of the scenario; the other part is depleting natural resources, increased production cost, high environmental concerns such as global warming due to excessive use of fossil fuels. Over 85% of the primary supply in the present-day energy mix is contributed by the fossil fuels – the main contributor to the global warming; thereby putting the life sustenance in the planet at an increased risk. All these concerns point out to turn our attention to clean, sustainable, and zero cost sources of energy such as wind, solar, tides, etc.

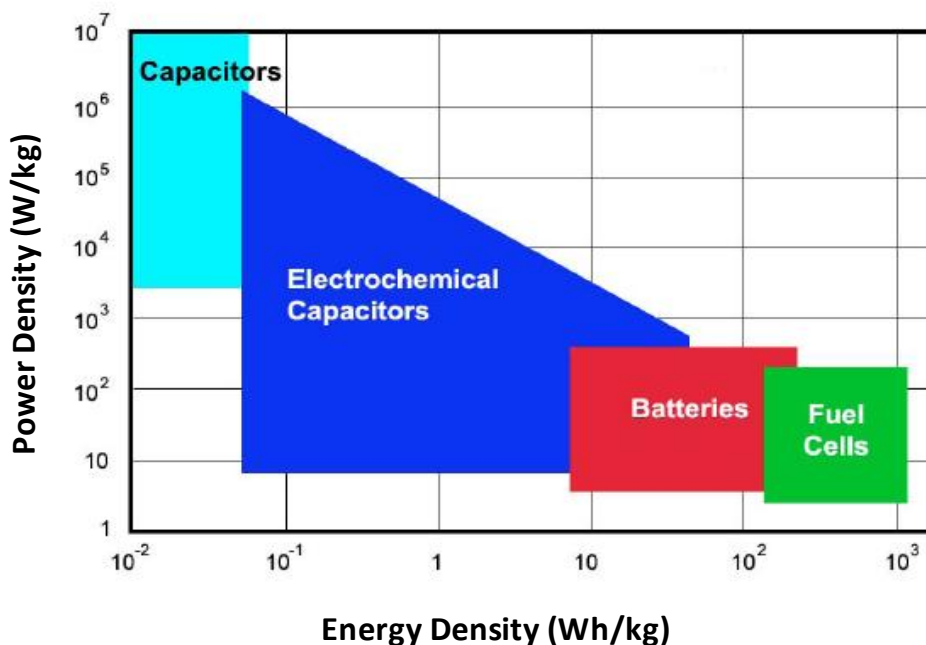
Sustainable energy is a dual topic of energy conversion and storage. Energy is converted into electricity when the renewable resources are available and stored until it is utilized. Secondary lithium ion batteries (LIBs) and supercapacitors (SCs) have become two popular protocols for energy storage devices because they are rechargeable,

could be produced in diverse design with light weight and flexibility, and are easy to manufacture (Chen et al., 2009). The rate of charging or discharging of energy per unit mass is defined as power density and the total energy stored per unit mass is the energy density (Burke, 2000). The LIBs provide the highest energy density (150 – 200 Wh/kg) but at the expense of cycle life ( $<10^3$  cycles) and power density (0.5 – 1 kW/kg); whereas SCs have higher power density (2 – 5 kW/kg) and longer cycle life ( $10^4$ – $10^6$  cycles) but suffer from inferior energy density ( $>5$  Wh/kg) (Kotz and Carlen, 2000). Nevertheless, SCs are the devices of choice when high power applications are sought.

The comparison of energy storage and power capabilities of a storage device is represented by Ragone plot. Figure 1.1 is a general Ragone plot of energy storage devices including capacitors, SCs, and batteries. Batteries and fuel cells were typical low power density devices whereas conventional capacitors may have high power density of  $>10^6$  W/kg at very low energy density,  $<0.1$  Wh/kg. One would see that the SCs fill the large gap between conventional capacitors and batteries. Still SCs suffer from energy storability when the power capability is increased. Therefore, development of electrode materials of SCs gained tremendous attention to simultaneously provide high energy and power densities which are unavailable in other class of energy storage devices.

The SCs are divided into two categories; viz. electrochemical double layer capacitors (EDLCs) and pseudocapacitors (PCs) which are distinguished by their charge storage mechanism (Shen et al., 2012). The EDLCs arise from the charge accumulation in an electrochemical-double layer formed at the interface between the charged surface of an electrode-electrolyte system (non-faradaic) (Conway, 1999). Meanwhile, PCs undergo faradaic reaction through an electron transfer process that produces a change in chemical or oxidation state in the electroactive material during charge storage process (Conway, 1999 and Shen et al., 2012). Because of the non-faradaic process, EDLCs could be charged and discharged at a faster rate; therefore have high power density. However, they have inferior energy densities. The PCs are in other way around – they have superior energy density but a compromised power density. Beneficial advantages both EDLCs and PCs are combined in asymmetric capacitors in which anode is fabricated using a pseudocapacitor material and cathode using an EDLC material (Ma et

al., 2007 and Liu et al., 2006). There are also materials developed which encloses PC and EDLC combining in a single materials systems, called hybrid materials (Aziz et al., 2013).



**Figure 1.1:** Ragone plot for various energy storage and conversion devices.

Adapted from: Winter and Brodd, 2004.

EDLCs use carbons, which are occurring in various allotropes including graphite, graphene, diamond, nanotubes, fullerene, amorphous carbon, and glassy carbon (Walker, 1972). Activated carbons (ACs) are amorphous and highly porous that offer high surface to volume ratio; and therefore, a popular choice as an electrode material for EDLCs. ACs satisfies basic requirement of electrode material due its high electric conductivity, low cost, large surface area, and porosity (Su and Centi, 2013). There is a new approach in production of ACs by utilizing biomass materials from agricultural and industrial sector byproducts (Wei and Yushin, 2012) such as ginkgo shells (Jiang et al., 2013), celtuce leaves (Wang et al., 2012), banana fibers (Subramanian et al., 2007), argan seed shells (Elmouwahidi et al., 2012), coffee shells (Jisha et al., 2009), and so on. A summary of this sources are given in the next chapter.



Malaysia is playing a big role as one of largest producers and exporters of palm oil. Upon production of 2.5 kg of crude palm oil over 100 kg of biomass is produced; which was 80 million dry tons in 2010 and projected to be 100 million dry tons by 2020 (Lim et al., 2010). Palm oil produces six main biomass types such as fronds, trunks, empty fruit bunches (EFB), palm kernel shells (PKS), mesocarp fiber (MF) and palm oil mill effluent (POME). From this abundant byproducts, 6% of it is in form of PKS (Agensi Inovasi Malaysia, 2013). Without any specific use except as fuel to mill's boilers (Wan Daud et al., 2000), PKS is a suitable candidate as carbon precursors in producing ACs for many industrial products. However, use of PKS as a source of ACs for fabrication of electrode materials for EDLC has not been tested so far.

## **1.2 PROBLEM STATEMENT**

Utilization of biomass to produce value added products would have two simultaneous impact, viz. (i) environmental remediation and (ii) wealth creation. The PKS could be converted into ACs and could be an electrode material for SCs. However, qualities of ACs are affected by many factors including precursors, type of activation, temperature and impregnation ratio. Therefore, there is a dire need to optimize the activation procedure for best performance when the PKS ACs is used as electrodes for supercapacitors.

## **1.3 RESEARCH OBJECTIVES**

This research has the following objectives:

1. To develop activated carbon from PKS through chemical activation for improved surface properties.
2. To evaluate the electrochemical properties of the PKS ACs.
3. To fabricate an electrochemical double layer capacitor using PKS ACs and evaluation of energy storage capabilities.

## 1.4 RESEARCH SCOPE

The study focuses on the production of ACs using PKS as carbon precursor. In order to achieve the above stated objectives, the following scope of research has been identified:

1. The PKS could be converted into ACs through chemical activation using common activation agents, viz. potassium hydroxide (KOH), sodium hydroxide (NaOH), zinc chloride ( $\text{ZnCl}_2$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ). An optimum condition could be developed by controlling the impregnation ratio between the activation agents and the as-prepared charred PKS.
2. Physicochemical properties of the ACs using different activation agents could be studied by thermogravimetric analysis, surface porosity analysis, X-ray diffraction analysis, and field-emission scanning electron microscopy.
3. Evaluation of electrochemical properties of the ACs in the 1 M KOH as electrolyte. A detailed analysis of performance of the electrode under various activation conditions could be undertaken. A correlation could be drawn on the surface properties or activation agents and charge storage properties.
4. A practical EDLC could be fabricated and its performance parameters could be evaluated under various conditions and compared with the other choice of materials such as physically activated carbon and carbon nanotubes.

## 1.5 SIGNIFICANCE OF RESEARCH

Through this research, it is believed that PKS as oil palm biomass can be exploited as a material of choice for energy storage devices thereby simultaneously reducing waste and producing a value added product. There are numerous researchers working on ACs based SCs. A literature survey outlined in the next chapter reveals that no effort has so been reported to use ACs from PKS as an EDLC electrode. It is also expected that PKS ACs could be a promising electrode material for SCs as the minerals

contained in the biomass of diverse source could offer different electrochemical properties.

## **1.6 THESIS OVERVIEW**

This thesis comprises of six chapters. Chapter 1 introduces the research problem, objectives, scopes and significance of this study. Chapter 2 reviews the literature related to energy storage materials, in particular those use in EDLCs. Chapter 3 discusses the methodology, apparatus and experimental equipment used throughout this research. Chapter 4 details experimental results and a comprehensive discussion of the results for materials characterization. Chapter 5 describes the electrochemical performance of activated carbon as a function of activation agents as well as performance of a working EDLC developed in this study. Chapter 6 discusses the overall summary and recommendations for future work. References and appendices are also included for better understanding of the research.

## **CHAPTER 2**

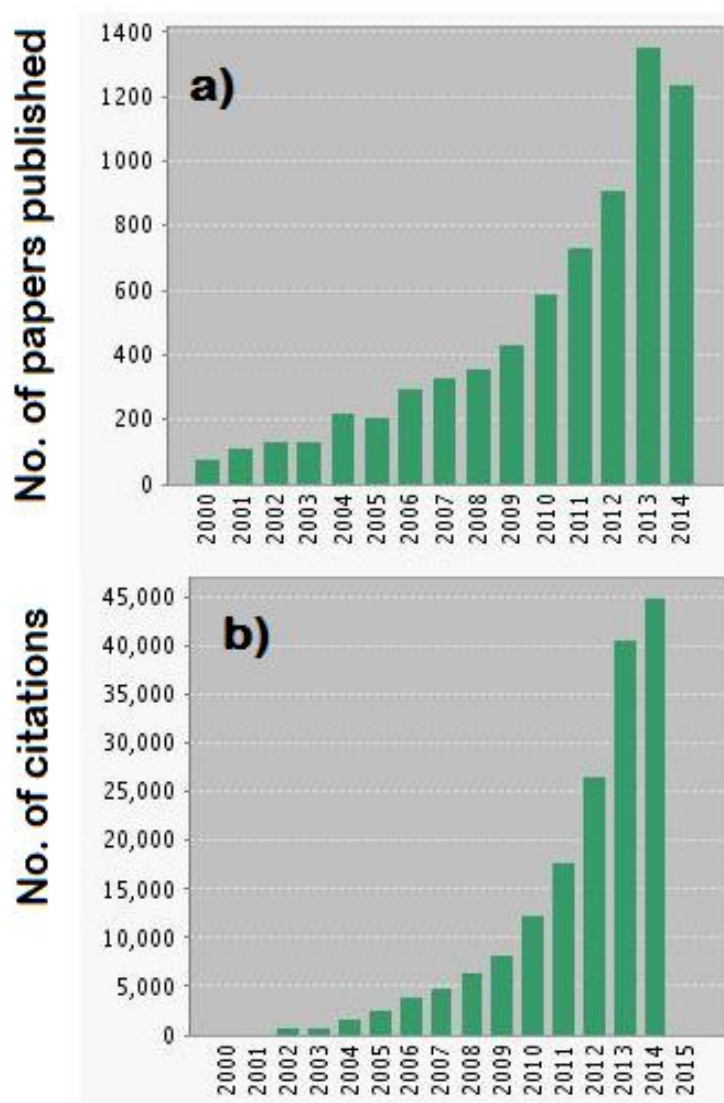
### **LITERATURE REVIEW**

#### **2.1 HISTORY**

Concept of storing electrical charge in the interface between a metal and an electrolytic solution has been studied since nineteenth century; but the practical use of double-layer capacitors only began only in 1957 when a patent was placed by Howard I. Becker (US 2800616 A) of General Electric for an electrolytic capacitor (EC) using porous carbon electrodes (Becker, 1957). Unfortunately, Becker's device was impractical in that, similarity to a flooded battery, both electrodes needed to be immersed in a container of electrolyte, and the device was never commercialized although it had an exceptionally high capacitance  $\sim 10 \text{ F/inch}^3$  (Miller, 2007). The Standard Oil Company, Cleveland, Ohio (SOHIO), patented a disc-shaped capacitor utilizing a carbon paste in an electrolyte in 1970 (US 3536963 A) which can be attributed to the invention of the device in the format commonly used today (Boos, 1970). Following commercial introduction NEC's SuperCapacitor in 1978, under license from SOHIO, ECs have evolved through several generations of design and varied choice of materials (Kötz and Carlen, 2000).

#### **2.2 RECENT EMERGENCE OF EDLC**

Figure 2.1 shows the trends in research publications and their citations generated using the keywords "electrochemical capacitors" from ISI web of knowledge published by Thomson Reuters on 30 October 2014.



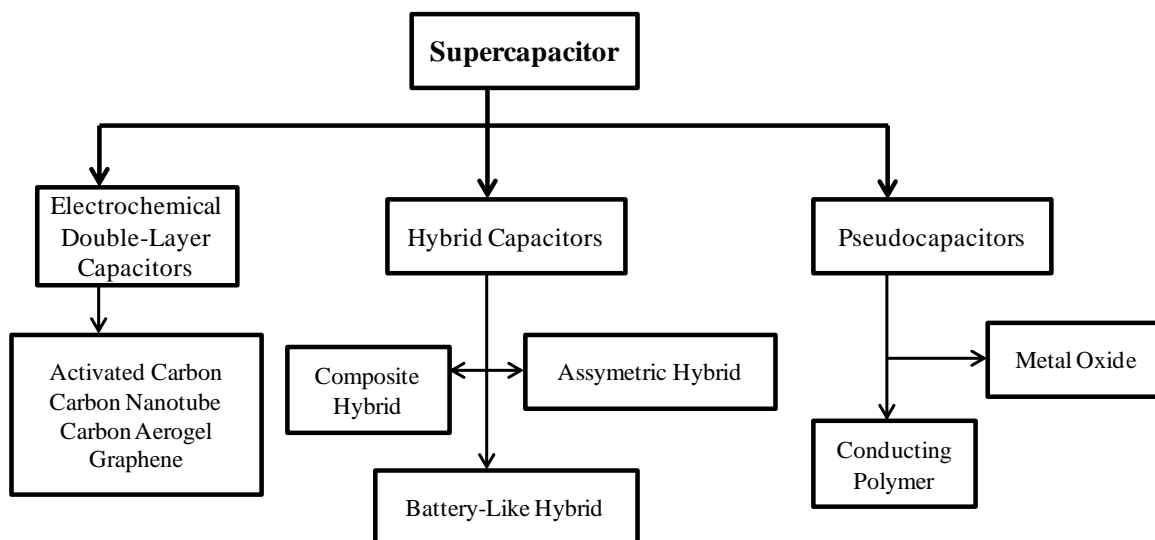
**Figure 2.1:** Trend in research publications and citations in electrochemical capacitors generated from ISI web of knowledge using the keywords “electrochemical capacitors” on 30 October 2014. (a) Number of published articles in each year and (b) Number of citation in each year.

In Figure 2.1(a), there is a large increment in number of published articles starting from 1995 to the recent date. One would see a dramatic increase in the number of publications after 2010. In 2013, it is more than 1300 articles were published throughout the year, marking nearly 30% increase compared to the previous year. The recent emergence in electrochemical capacitors could be related to, as explained in the Chapter 1, the emergence of sustainable energy paradigm. As will be shown subsequently, the simple device structure and higher reliability lead investments in this

area. Figure 2.1(b) illustrates the number of citations in each year for the publications bear the keywords “electrochemical capacitors”. More than 7000 articles published in this area and gained over 170,000 citations in 20 years; averaging ~25 citations per paper. Therefore, interests in electrochemical capacitors are incredible.

## 2.3 CLASSIFICATION OF SUPERCAPACITOR

Supercapacitors are classified into three groups based on the charge storage mechanism; (1) electrochemical double layer capacitors (EDLC), (2) pseudocapacitors (PCs) and (3) hybrid capacitors. Figure 2.2 shows a schematic of this classification along with choice of materials in each group.

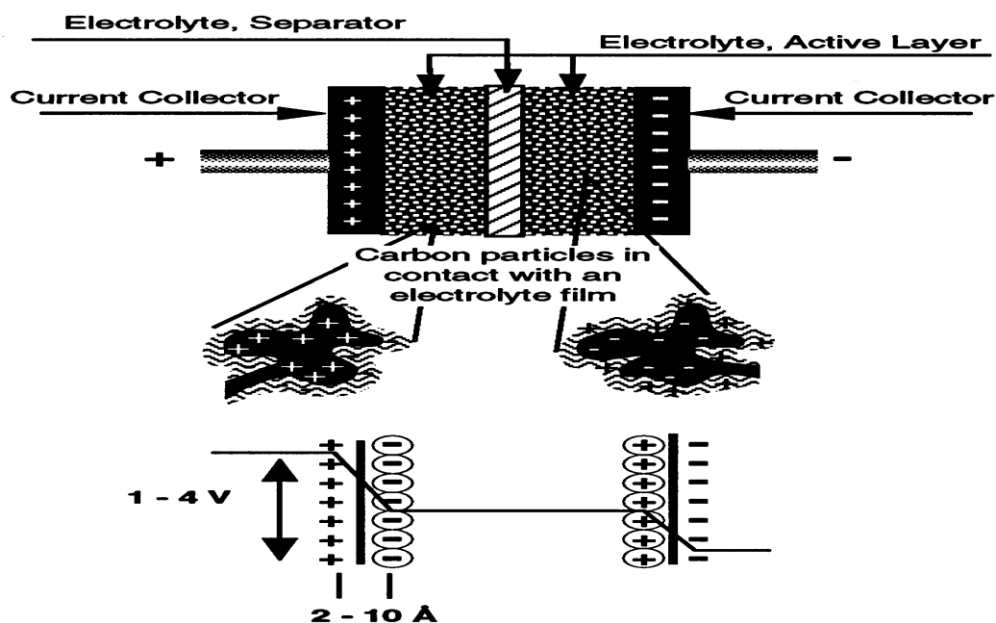


**Figure 2.2:** Classification of supercapacitors.

### 2.3.1 Electrochemical Double-Layer Capacitors (EDLCs)

An electrical double-layer is established when an electronic conductor (electrode) is brought in contact with an ionic conductor (electrolyte) (Figure 2.3) (Kötz and Carlen, 2000). Electrical charges are accumulated electrostatically at the electrode-electrolyte interface; therefore, a porous electrode would increase the active area for charge accumulation. Negative ions accumulate on the surface of positive electrode during charging process, and vice versa (Cericola and Kötz, 2012). Typical width of the

electric double layer (EDL) is 2-10 Å (Frackowiak and Béguin, 2001). This charge separation is equivalent to an electric dipole; and therefore, offers an electric potential as shown in the bottom panel of Figure 2.3. There is no charge transfer take place across the interface; the current observed during this process is purely a displacement current due to rearrangement of charges. The schematic double layer capacitor is shown in Figure 2.3. The ions forming double layers in the pores are transferred between electrodes by diffusion through electrolyte ( Kötzt and Carlen, 2000). As there is no charge transfer between electrolyte and electrode, no chemical or composition changes occur in the system. Such process is called non-faradaic process. This superior chemical stability of the system offers complete electrochemical reversibility of the device and allows very high cycling stability ( $>10^6$  cycles).



**Figure 2.3:** Principle of a double layer capacitor and illustration of the potential drop at electrode/electrolyte interface.

Adapted from: Kotz and Carlen (2000).

Carbons are most widely used in EDLCs owing to their high surface area, and high conductivity. Research shows great interest in carbon as materials for supercapacitor because of the accessibility, easy processability and relatively low cost. Wide range of carbon is used in supercapacitor such as activated carbons (ACs) (Jisha et

al., 2009 and Zhang et al., 2013), carbon nanotubes (CNTs) (Barisci et al., 2000 and Fedorovskaya et al., 2014), carbide derived carbons (CDCs) (Oschatz et al., 2010 and Chmiola et al., 2006), carbon onions (Portet et al., 2007 and McDonough et al., 2012) zeolites-templated carbons (ZTCs) (Kim et al., 2013 and H. Xu et al., 2010), carbon aerogel (Zapata-Benabithé et al., 2012 and J. Li et al., 2006) and graphene (El-Kady and Kaner, 2013 and Z. Huang et al., 2013). Carbon-based materials for EDLCs greatly rely on the reversibility of ion adsorption/desorption as the charge-storage mechanism (Naoi and Simon, 2008).

### 2.3.2 Pseudocapacitors (PCs)

PCs stores charges through faradaic process; i.e., charge is transferred between the surfaces or in the bulk near the surface of the solid electroactive materials and the electrolyte (Cericola and Kötz, 2012). Three types of electrochemical processes have been used in the development of supercapacitor using pseudocapacitance. These are surface adsorption of ions from the electrolytes, redox reactions involving the electrolyte, and doping and de-doping of active conducting polymer material in the electrode.

Metal oxides are one of the available choice of materials to increase the capacitance and energy density of SCs at low resistance (Shukla et al., 2000). Most attractive metal oxides known are  $\text{RuO}_2$  and  $\text{IrO}_2$ ; they exhibit ideal pseudocapacitive characteristic that possess high capacitance ranging from 720 to 790 F/g. These values are several folds higher than that can be achieved using EDLCs. Modification of  $\text{RuO}_2$ , such as hydrated  $\text{RuO}_2$  ( $\text{RuO}_x\text{H}_y$ ) is a mixed electron-proton conductor with remarkable specific capacitance from 720 to 900 F/g (Jayalakshmi and Balasubramanian, 2008). However, the high cost, rarity and toxicity of these materials limit the prospect for large-scale commercialization. Many other transition metal oxide materials are explored as a replacement for  $\text{RuO}_2$  with lower cost and no constraint on resources. Promising metal oxides that under extensive study are  $\text{NiO}$  (Vidhyadharan et al., 2014),  $\text{MnO}_2$  (Misonn et al., 2014),  $\text{V}_2\text{O}_5$  (Reddy and Reddy, 2006),  $\text{Co(OH)}_2$  (Kong et al., 2009), and  $\text{Fe}_2\text{O}_3$  (Huang et al., 2014).



## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 BACKGROUND**

Energy consumption would increase in the coming years due to growing economies and increasing population. Primary supply of sustainable and clean energy is one of the major challenges of the 21st century. A recent report by British Petroleum points that 1.3 billion more people will become new energy consumers by 2030 with a total population of 8.3 billion (British Petroleum, 2013). Exxon's 2040 Energy Outlook projects 35% increase in global electricity demand during 2010–2040 (Exxon Mobil, 2014). Developing non-OECD countries alone will experience a 150% increase in electricity demand led by India and China (Exxon Mobil, 2014). By the present energy growth of 1.6% per year, 35 years are required to have such magnitude of energy; therefore, a crisis is inevitable (U.S. Energy Information Administration, 2013). This increased energy demand is one part of the scenario; the other part is depleting natural resources, increased production cost, high environmental concerns such as global warming due to excessive use of fossil fuels. Over 85% of the primary supply in the present-day energy mix is contributed by the fossil fuels – the main contributor to the global warming; thereby putting the life sustenance in the planet at an increased risk. All these concerns point out to turn our attention to clean, sustainable, and zero cost sources of energy such as wind, solar, tides, etc.

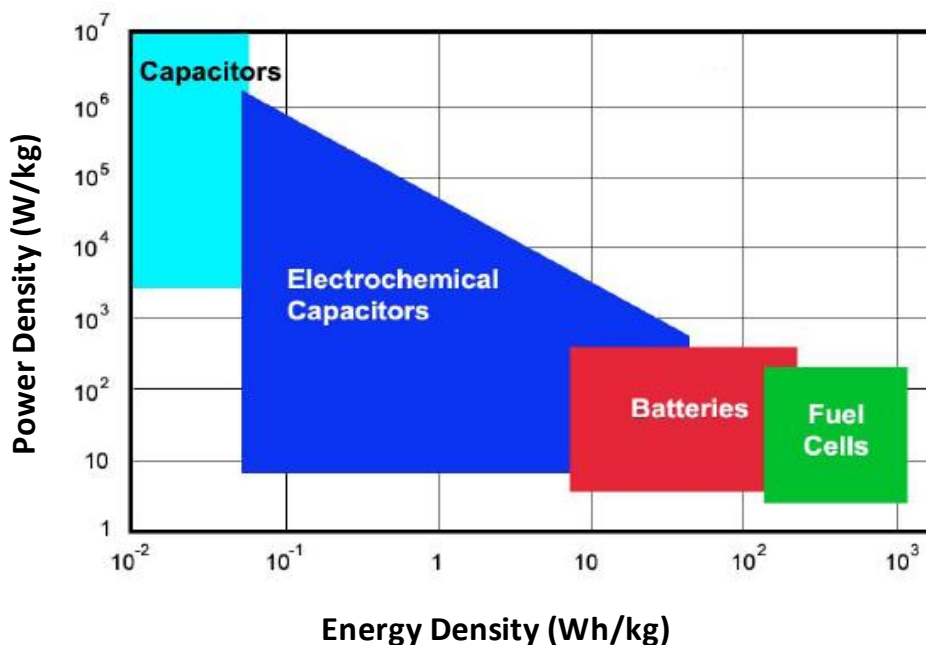
Sustainable energy is a dual topic of energy conversion and storage. Energy is converted into electricity when the renewable resources are available and stored until it is utilized. Secondary lithium ion batteries (LIBs) and supercapacitors (SCs) have become two popular protocols for energy storage devices because they are rechargeable,

could be produced in diverse design with light weight and flexibility, and are easy to manufacture (Chen et al., 2009). The rate of charging or discharging of energy per unit mass is defined as power density and the total energy stored per unit mass is the energy density (Burke, 2000). The LIBs provide the highest energy density (150 – 200 Wh/kg) but at the expense of cycle life ( $<10^3$  cycles) and power density (0.5 – 1 kW/kg); whereas SCs have higher power density (2 – 5 kW/kg) and longer cycle life ( $10^4$ – $10^6$  cycles) but suffer from inferior energy density ( $>5$  Wh/kg) (Kotz and Carlen, 2000). Nevertheless, SCs are the devices of choice when high power applications are sought.

The comparison of energy storage and power capabilities of a storage device is represented by Ragone plot. Figure 1.1 is a general Ragone plot of energy storage devices including capacitors, SCs, and batteries. Batteries and fuel cells were typical low power density devices whereas conventional capacitors may have high power density of  $>10^6$  W/kg at very low energy density,  $<0.1$  Wh/kg. One would see that the SCs fill the large gap between conventional capacitors and batteries. Still SCs suffer from energy storability when the power capability is increased. Therefore, development of electrode materials of SCs gained tremendous attention to simultaneously provide high energy and power densities which are unavailable in other class of energy storage devices.

The SCs are divided into two categories; viz. electrochemical double layer capacitors (EDLCs) and pseudocapacitors (PCs) which are distinguished by their charge storage mechanism (Shen et al., 2012). The EDLCs arise from the charge accumulation in an electrochemical-double layer formed at the interface between the charged surface of an electrode-electrolyte system (non-faradaic) (Conway, 1999). Meanwhile, PCs undergo faradaic reaction through an electron transfer process that produces a change in chemical or oxidation state in the electroactive material during charge storage process (Conway, 1999 and Shen et al., 2012). Because of the non-faradaic process, EDLCs could be charged and discharged at a faster rate; therefore have high power density. However, they have inferior energy densities. The PCs are in other way around – they have superior energy density but a compromised power density. Beneficial advantages both EDLCs and PCs are combined in asymmetric capacitors in which anode is fabricated using a pseudocapacitor material and cathode using an EDLC material (Ma et

al., 2007 and Liu et al., 2006). There are also materials developed which encloses PC and EDLC combining in a single materials systems, called hybrid materials (Aziz et al., 2013).



**Figure 1.1:** Ragone plot for various energy storage and conversion devices.

Adapted from: Winter and Brodd, 2004.

EDLCs use carbons, which are occurring in various allotropes including graphite, graphene, diamond, nanotubes, fullerene, amorphous carbon, and glassy carbon (Walker, 1972). Activated carbons (ACs) are amorphous and highly porous that offer high surface to volume ratio; and therefore, a popular choice as an electrode material for EDLCs. ACs satisfies basic requirement of electrode material due its high electric conductivity, low cost, large surface area, and porosity (Su and Centi, 2013). There is a new approach in production of ACs by utilizing biomass materials from agricultural and industrial sector byproducts (Wei and Yushin, 2012) such as ginkgo shells (Jiang et al., 2013), celtuce leaves (Wang et al., 2012), banana fibers (Subramanian et al., 2007), argan seed shells (Elmouwahidi et al., 2012), coffee shells (Jisha et al., 2009), and so on. A summary of this sources are given in the next chapter.

## **CHAPTER 3**

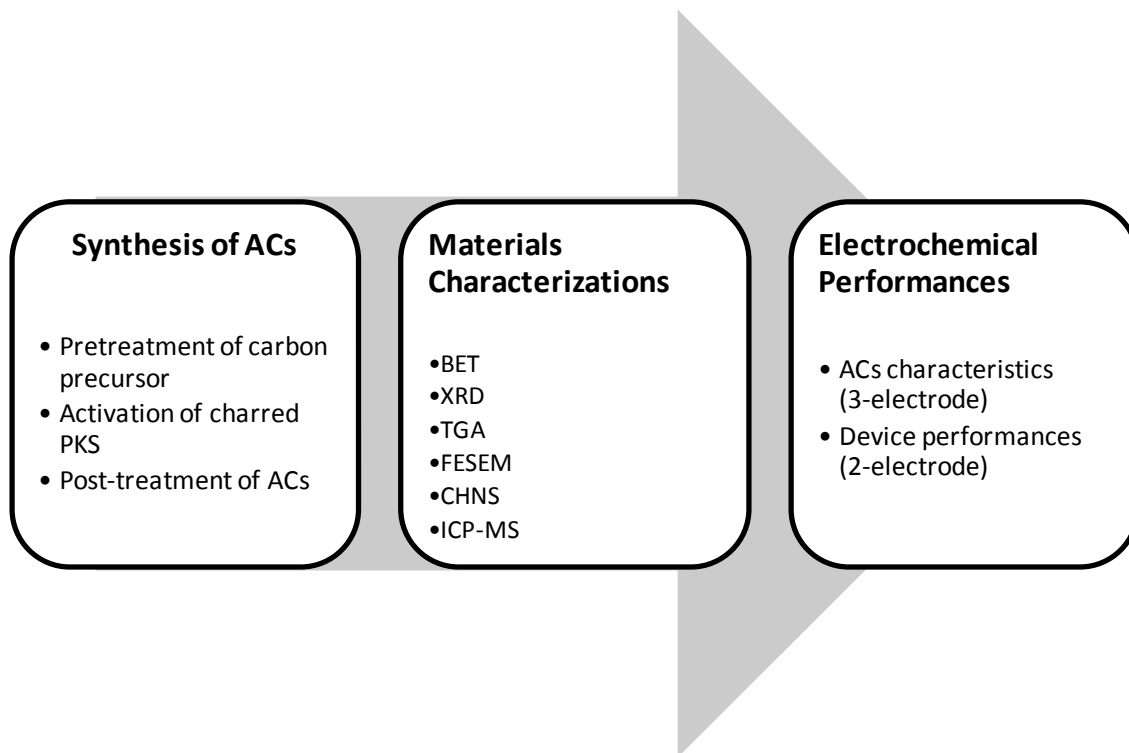
### **MATERIALS AND METHODS**

#### **3.1 INTRODUCTION**

In this chapter, the methodology of the research as well as the materials used will be explained in detail. These include the preparation of ACs using different activation agents, step by step procedures of material characterizations using different techniques. The performance of ACs was then evaluated using electrochemical procedures. Figure 3.1 displayed the flow of the procedure taken in completing this work.

#### **3.2 MATERIALS**

The PKS were charred in a electrical furnace. Chemical used as activating agents were sodium hydroxide (NaOH), potassium hydroxide (KOH), sulfuric acid 98% (H<sub>2</sub>SO<sub>4</sub>) and zinc chloride (ZnCl<sub>2</sub>). Hydrochloric acid (HCl) was used in post-treatment of ACs. In electrode preparation process polyvinylidene fluoride (PVDF) used as binder N-methyl-2-pyrrolidone (NMP) as solvent and Super-P (carbon black) was use as conductive carbon. All the solutions in this work were prepared using deionized (DI) water.



**Figure 3.1:** Flow chart of this work.

### 3.3 PREPARATION OF ACTIVATED CARBON

#### 3.3.1 Pre-Treatment of Carbon Precursor

The PKS waste was collected from oil mill factory. The PKS was washed thoroughly with distilled water to remove soil and dirt by sonication process and then dried at 105 °C to remove moisture. PKS was charred at 500 °C for 1 hour at heating rate 10 °C/min and the resultant charred PKS was separated from impurities before proceed into activation step. Charred PKS was store in airtight container to prevent moisture absorption.

#### 3.3.2 Activation of Charred PKS using Different Activation Agents

In this study, four activation agents were used to activate PKS char that is (1) KOH (2) NaOH (3) H<sub>2</sub>SO<sub>4</sub> and (4) ZnCl<sub>2</sub>. Activation agents used were commonly used as activation agents to produce ACs. As-prepared charred PKS produced from previous

work was treated with different impregnation ratio (0.5, 1.0 1.5 and 2.0). Impregnation ratio is defined as the ratio of mass activation agents to mass of charred PKS. Charred PKS was introduced into 50% m/v solution of activation agent for 24 h by sonication process. The impregnated charred PKS was then dried at 105 °C in an electrical oven to remove moisture then carbonized in an electric furnace at heating rate of 10 °C/min and the final temperature of 500 °C with holding time of 2 hours. The summary of carbonization condition was illustrated in Table 3.1. The resultant ACs were washed repeatedly with 1 M HCl and then rinsed with hot deionized water until pH 8-7 was obtained then dried at 105 °C. The ACs were then stored in airtight bottle samples to prevent moisture absorption. Resultant ACs then named X-Y where X was the activation agent used and Y was the impregnation ratio of the activation agent used. The example of activation condition was shown in Table 3.2.

**Table 3.1:** Synthesis condition of ACs.

Start Material	Activation agent	Impregnation time	Activation temperature	Activation time
Charred PKS	KOH NaOH H <sub>2</sub> SO <sub>4</sub> ZnCl <sub>2</sub>	24 hours	500 °C	2 hours

**Table 3.2:** Example of activation condition in different impregnation ratio.

Mass of charred PKS (g)	Impregnation ratios	Mass of activation agent (g)	Volume of deionized water (ml)	Designated name
15	0.5	7.5	7.5	KOH-0.5
	1.0	15.0	15.0	KOH-1.0
	1.5	22.5	22.5	KOH-1.5
	2.0	30.0	30.0	KOH-2.0