STUDY OF CARBONACEOUS WASTE AS ELECTROCHEMICAL CAPACITOR

by

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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ABSTRACT

Carbonaceous waste used in this project is obtained from furnace in ethane to ethylene cracking process. Prior to this project, this waste is treated as scheduled waste and sent to Kualiti Alam Sdn Bhd for disposal. This report intended to point out the outcomes of the project entitle "*Study of Carbonaceous Waste as Electrochemical Capacitor*". The main aim of this project is to add value of this carbonaceous waste by utilizing its carbon properties possesses by the material and use it in electrochemical capacitor. In this project, carbonaceous waste has been characterized and preliminary study to use this carbonaceous material as capacitor has been carried out. The carbonaceous waste can be classified as low-crystalline graphite and possess carbon characteristic. After the experimental work, the results show that this waste can be used as capacitor as it has charge-discharge effect and can be used to provide power. Electrochemical performance of capacitor from commercial carbon and from carbonaceous waste is also compared and evaluated. Further studies could be carried out to optimize the charge-discharge capacity and the efficiency of capacitor using this material. As conclusion, this study has proved that this specific carbonaceous waste is able to act as electrode in electrochemical capacitor.

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LIST OF ABBREVIATIONS

XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
$LiClO_4$	Lithium Perchlorate
A	Ampere
V	volt

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CHAPTER 1: INTRODUCTION

The title of this Final Year Project is **Study of Carbonaceous Waste as Electrochemical Capacitor**. This chapter will describe the background of study, problem statement, objectives and scope of work.

1.1 Background of Study

In ethylene production plant, ethylene is produced by cracking of ethane in very high temperature (≈900°C) furnace by using pyrolisis method. By-product produces by this reaction is hydrogen and also solid waste, which deposited onto the furnace tubes. Hydrogen will be used in fuel gas system while the solid by-product will be removed periodically from furnace and being stored before sent to Kualiti Alam for disposal purposes.

Other option of treating this by-product instead of disposing it is to use them in electrochemical capacitor and rechargeable lithium battery since by-product from any petroleum cracking process possesses carbonaceous properties. Available electrochemical capacitor and lithium battery in the market uses commercial carbon, which possesses different characteristic compared to the by-product obtained from ethylene plant.

The study is carried out is to investigate the feasibility of by-product waste as electrochemical capacitor, thus providing alternatives in handling and treating the waste. Certain method of characterization has to be carried out to classify and compare the by-product with other type of commercial carbon available in the market.

1.2 Problem Statement

By-product of ethane to ethylene cracking process possesses carbonaceous properties. In the ethylene production plant, this by-product is treated as scheduled waste; thus not fully utilize the carbonaceous properties possessed.

Disposal process is carried out by local waste management services provider, Kualiti Alam Sdn. Bhd. Certain amount has to be paid to Kualiti Alam for the disposal services.

In year 2008, total by-product that had been produced from ethylene plant is approximately 22 metric tonne [1]. Total disposal cost is approximately MYR 125 000. This carbonaceous waste is produced continuously every year; thus the cost of disposal can be classified as annual maintenance cost to the company.

To add value of the carbonaceous waste, a preliminary study of its ability as capacitor has been carried out. This study will be evaluating the electrochemical performance of capacitor that has been fabricated from the carbonaceous waste. Fabricating electrode may reduced maintenance cost to company, and also might gives extra profit to the company.

1.3 Objectives

This study will be carried out in two parts; the first part is to conduct preliminary study of physical properties of the carbonaceous waste.

Physical properties can be evaluated using two characterization methods; X-Ray Diffraction (XRD) and also Scanning Electron Microscope (SEM). Results of these characterization processes will be further discuss in **Chapter 4: Results and Discussion** section.

The second part of this study is to evaluate the electrochemical capacitor performance of carbonaceous waste. Under certain condition, the capacitor performance will be evaluated, in terms of its specific discharge capacity, charge-discharge capacity, and also its efficiency. Comparison of electrochemical capacitor fabricated using the carbonaceous waste and capacitor using commercial carbon will be carried out to evaluate the capacitor's economic feasibility.

1.4 Scope of Study

The scope of study in this project is:

1. Carbonaceous waste obtained from Ethylene Malaysia Sdn.Bhd (EMSB); an ethylene production plant located in Kerteh, Terengganu.
2. Carbon used throughout the whole study is non-treated carbon
3. Electrochemical capacitor using carbonaceous waste is in electrolyte of 1 M Lithium Perchlorate in Acetonitrile.

The overall framework for this study is first to characterize the carbonaceous waste, then fabricating electrochemical capacitor using the waste. The electrochemical capacitor performance is then being evaluated. It can be summarized into:

Literature search

Identify material, apparatus, equipments needed for experiment

Preparation of sample

Characterization of sample

Preparation of electrode and electrolyte

Preparation of equipments and material testing

Result findings, discussion and conclusion of project.

CHAPTER 2: LITERATURE REVIEW

2.1 Carbonaceous Waste from Ethane Cracking

This by product is usually known as petroleum coke. Petroleum coke by definition is black solid residue, consists mainly of carbon and has low content of ash. It can be used as feedstock in coke ovens in steel industry, for heating purposes, for electrode manufacture and for production of chemicals. The two most important qualities are "green coke" and "calcinated coke" [2] This category also includes "catalyst coke" deposited on the catalyst during refining processes: this coke is not recoverable and is usually burned as refinery fuel.

2.1.1 Removing waste from furnace

In petrochemical plant, maintenance of furnace will be carried out to remove coke from the furnace. This process is known as "decoking" process. Decoking is accomplished when the heater is put on steam only operation, and isolated from the effluent header. Air along with dilution steam is injected into the heater at controlled temperature to burn off the coke. The decoking effluent is sent to firebox and will be burnt. Other method of decoking is through mechanical cleaning. Mechanical cleaning is accomplished by injecting water at high pressure to remove any foulants from the wall. This process is also known as hydroblasting or hydrojetting. The contaminated water is directed to the mobile hydrojetting effluent separator where solid particles are removed. After the decoking process, solid coke will be stored in tanks before disposal purposes. Other option that is available to treat this carbonaceous waste is to utilize its carbonaceous properties as electrode in capacitor.

2.2 Properties of carbon

2.2.1 Type of carbon

Carbon occurs freely in crystalline forms such as in diamond and graphite. Different type of carbon will have different structure. For example, graphite is soft, has a hexagonal structure and carbon atoms arranged in layer planes. The distance between layer planes in graphite is 0.3354nm.

Graphite is also found in nature. Natural graphite is classified as flake, vein or microcrystalline, depending on the crystallite size and particle shape. Other type of carbon is amorphous carbon. Amorphous carbon is carbon with dimensions of layer planes that are small and the separation between the layer planes becomes large. Example of amorphous carbon is charcoal, coke and soot.

2.2.2 Manufacturing and processing of carbon

To produce carbon, any organic-material or carbon-containing gases or liquids is heated virtually in an inert environment, which contains no oxygen (or limited supply of oxygen). Transforming of the solid precursor to solid carbon during carbonization step usually forms hard carbon. Hard carbons are those carbons that are non-graphitized, and are mechanically hard. Soft carbons are mechanically soft and can be graphitized.

When a material is heated to produce carbon, the chemical structure of the materials is destroyed and gases can form that contain carbon, oxygen and hydrogen, depending on the original composition and ambient environment. The remaining solid product is mainly carbon.

Three common precursors of carbon are coke, petroleum coke and coal-tar pitches.

2.2.3 Applications of carbon

The earliest use of carbon may have been for writing anf as coloring agent. The role of carbon in electrochemistry started when charcoal is discovered could be substitute material for metals in galvanic experiment. The role of carbon becomes wider in the electrochemistry application.

Other uses of carbon are:

1. Capacitors
2. Batteries
3. Production of metals and chemicals
4. Fuel cells

Carbonaceous materials have many properties that are favorable in electrode fabrication and also in capacitor. Desirable properties of carbon for electrochemical applications are [5]

1. Good electrical conductivity
2. Acceptable corrosion resistance
3. Availability in high purity
4. Low cost
5. High thermal conductivity
6. Dimensional and mechanical stability
7. Light in weight and ease of handling
8. Availability in a variety of physical structure

2.3 Electrochemical Capacitor

Capacitor is a passive electronic component that stores energy in the electrostatic field that is present at a two-phase interface. Capacitor provides alternative approach to meeting the increasing demand of power-storage systems. Electrochemical storage had attracted much attention due to their high power capability and long life cycle. These properties are due to their high reversible charge-storage process. Capacitors are able to store and deliver power at relatively high rates because the mechanism of energy storage is simple charge-separation.

The vast increase in capacitance achieved by capacitors is due to the combination of[3]:

a. Extremely small distance that separates opposite charges
b. Highly porous electrodes that embody very high surface area

Electrochemical capacitor generally consists of a cathode electrode, anode electrode and electrically conductive electrolyte. A voltage is applied to the capacitor during charging process. The carbon electrodes attract positive or negative charges to form double layers at the interfaces.

The presence of these charged interfaces is the source of stored electrical energy, which when discharge releases electrons through the external circuit that is connected to the carbon electrodes. In discharge state, the positive and negative ions are dissipated in the electrolyte and electrode.

Figure below shows the operating principle of carbon electrode in electrochemical capacitor.

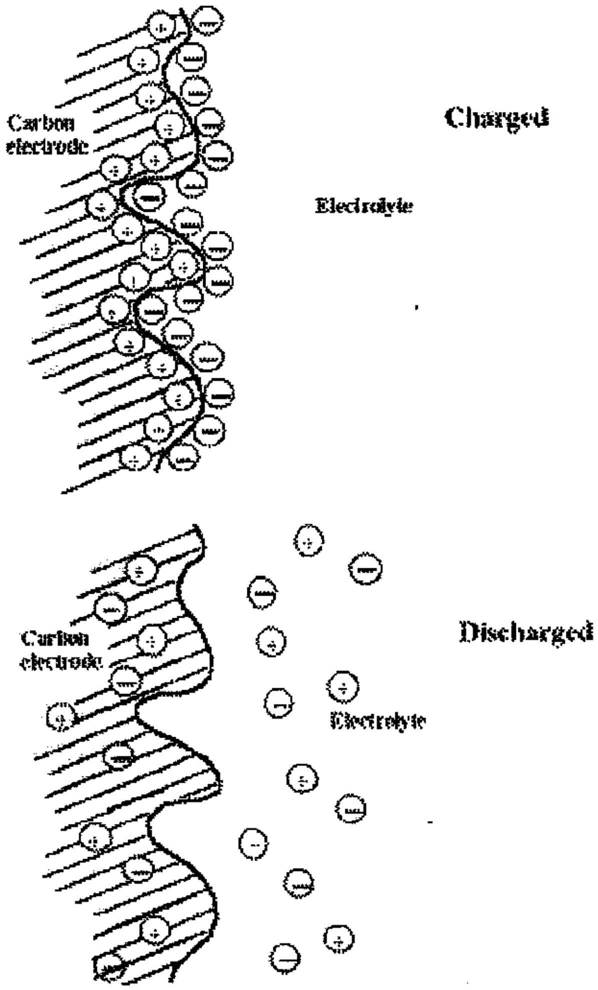


Figure 1: Operating Principle of Carbon Electrode in Capacitor

A variety of porous forms of carbon are currently preferred as the electrode materials because they have exceptionally high surface areas, relatively high electronic conductivity and acceptable cost. The power – storage capabilities are closely linked to the physical and chemical characteristics of the carbon electrodes.

Carbon materials have long been incorporated into the electrodes of energy-storage device as:

a. Electro-conductive additives
b. Supports for active materials
c. Electron transfer catalyst
d. Intercalation hosts
e. Substrates for current leads
f. Agents for the control of heat transfer, porosity, surface area and capacitance.

2.3.1 Electrode material characteristic

Carbon material possesses certain unique combinations of physical and chemical properties that attract it as electrode material; which are:

a. High conductivity
b. High surface-area range
c. High temperature stability
d. Controlled pore structure
e. Processability and compatibility in composite materials

First two of these properties are critical to the construction of capacitor electrodes. Properties of carbon allow both conductivity and surface-area to be manipulated [3]

CHAPTER 3: METHODOLGY

The main part of this study is divided into two; characterization of the carbonaceous waste and to evaluate the electrochemical performance of capacitor.

For characterization of carbonaceous waste, the process flows are as below:

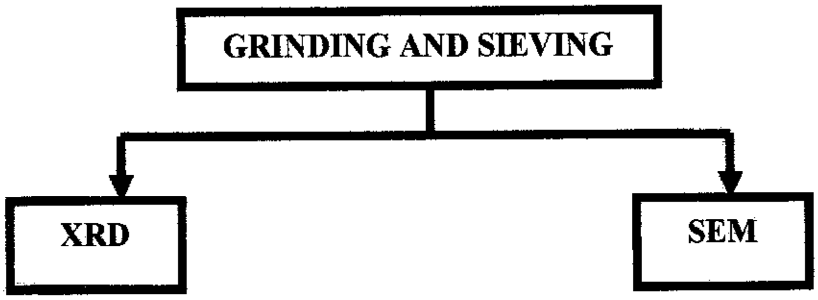


Figure 2: Process Flow for Characterization of Carbonaceous Waste

For electrochemical performance of capacitor, the process flow of experiment are divided into three main parts; electrode preparation, electrolyte preparation and electrochemical evaluation.

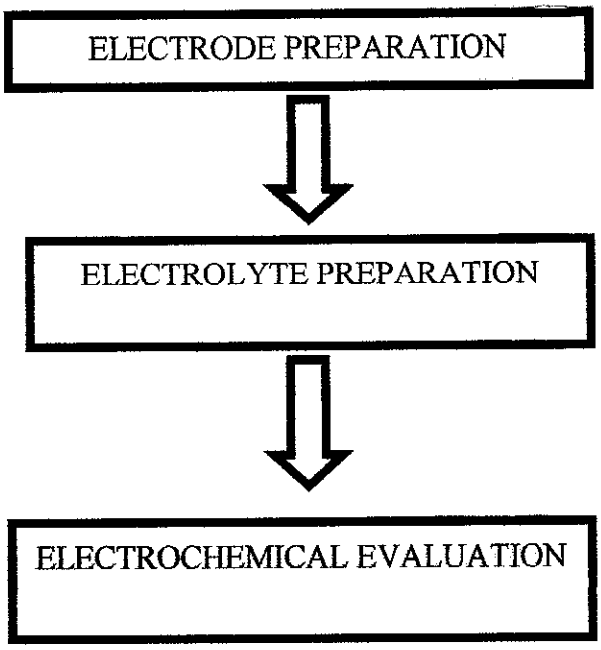


Figure 3: Process Flow of Evaluating Electrochemical Performance of Capacitor

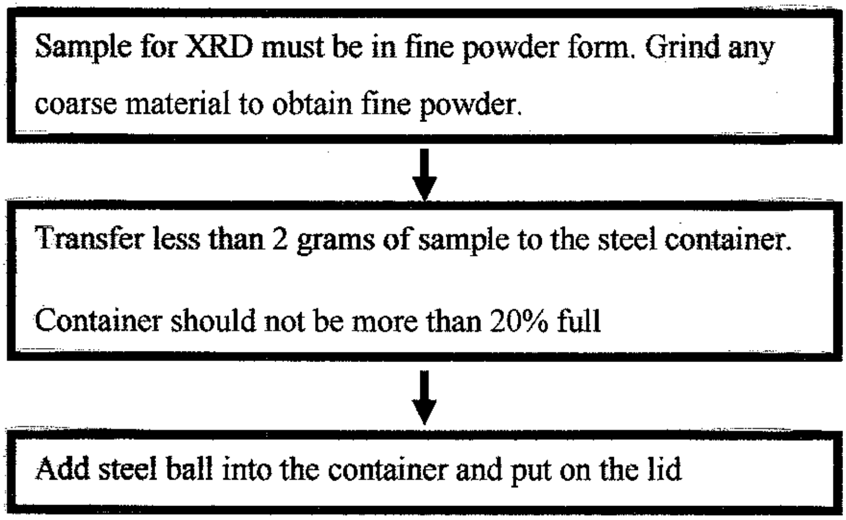
Before proceeding in the electrode fabrication, the carbonaceous waste must first be prepared and characterized. Preparation of the carbonaceous waste can be carried out in grinding and sieving process. These two processes are important to ensure the carbon that will be used in the electrodes are in form of fine powder; thus providing higher surface area for reaction. Finer powder will also ensure more accurate evaluation in future characterization processes. Characterization of carbonaceous waste is carried out using two different processes; X-Ray Diffraction and also Scanning Electron Microscope (SEM).

3.1 Characterization of carbonaceous waste

3.1.1 Grinding and Sieving

High surface area of carbonaceous waste is favorable in the capacitor electrode fabrication. Thus, the carbonaceous waste is preferably in powder form. Since carbonaceous waste has hard physical structure, the press grinder is used to pound it until it became into powder form. After the grinding process, the carbonaceous waste is sieved to separates any big particles or any contaminant that might exist with the sample. Various size of sieve is used; the finest powder is taken to be used throughout the study. Uniform fine grain size will results in optimal XRD analysis results.

The grinding processes are as follows:



Sample for XRD must be in fine powder form. Grind any coarse material to obtain fine powder.

Transfer less than 2 grams of sample to the steel container.

Container should not be more than 20% full

Add steel ball into the container and put on the lid

↓

Put the container in the grinder, fasten snugly, close the lid and turn on the grinder. Hard samples may require longer grinding time

↓

After sieving, transfer the powder to a piece of weighing paper and sieve it through the mesh. Smallest mesh used is 50µm

↓

Sample is ready to be used for further processes.

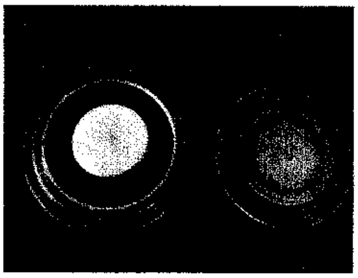


Figure 5: Steel Ball Inside the Container

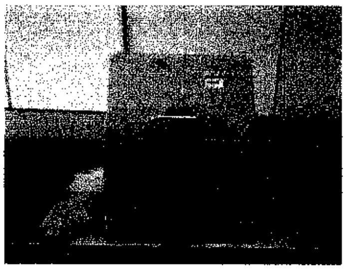


Figure 6: Press Grinder Machine

Figure 4: Mechanical Sieve

3.1.2 Characterization **Process**

X-Ray Diffraction (XRD)

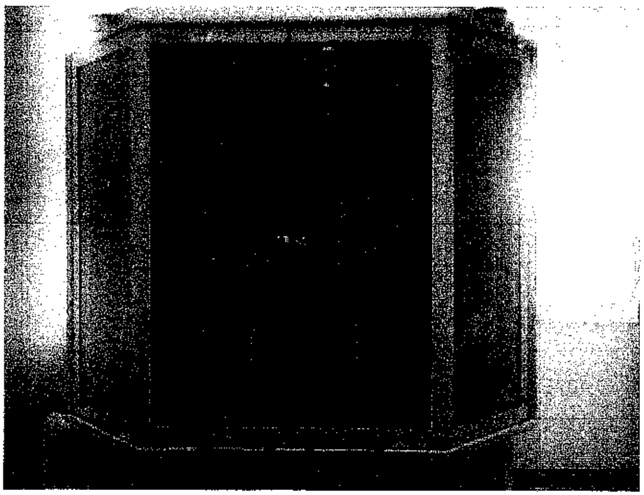


Figure 7: XRD Equipment

Procedures in XRD are as follows:

Load sample onto the tray in front of the XRD.

Sample side is facing up.

↓

Run the sample and print results using software

↓

Identify the most intense peak from the results.

Scanning Electron Microscope (SEM)

The second characterization process used in this study is Scanning Electron Microscope. In this study, SEM is used to investigate the surface morphology of the carbonaceous waste.

SEM consists of[4]:

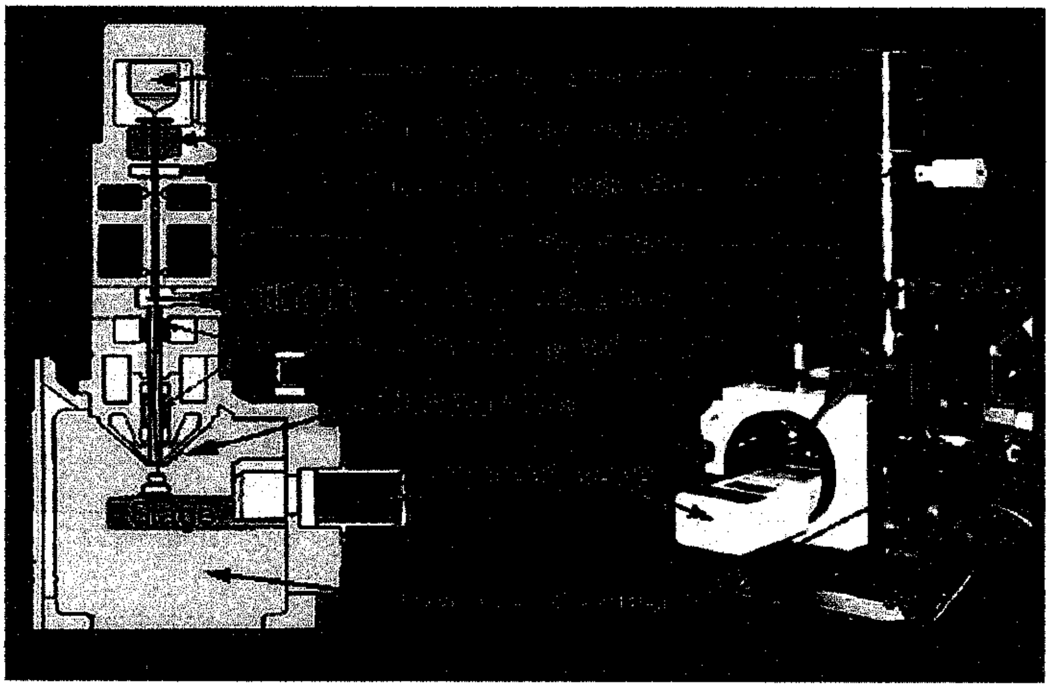
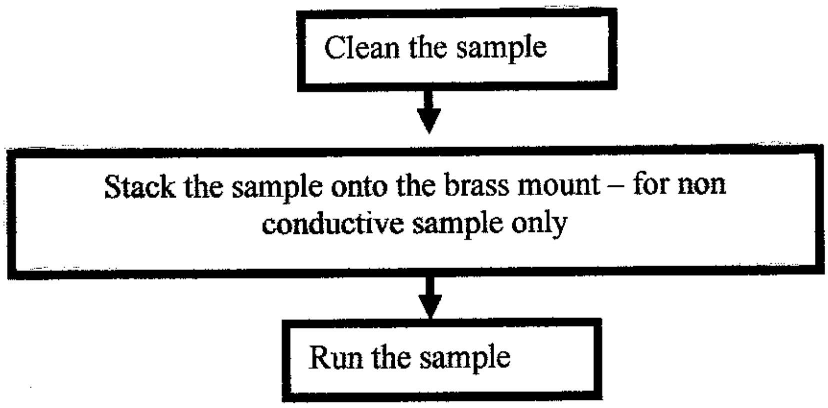


Figure 8: SEM Electron Beams' Path Through the Column

Sample preparation before using SEM is important for non-conductive sample. Since SEM uses electrons to produce images, the conventional SEM requires the sample to be electrically conductive.

The procedures in SEM are as follows:



For all conductive material, there is no preparation required before using SEM.

During the process, a beam of electron is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held in vacuum. The beam travels through the electromagnetic field and lenses, which focus the beam down towards the sample. Once the beam hit the sample, electrons and X-rays are ejected from the sample.

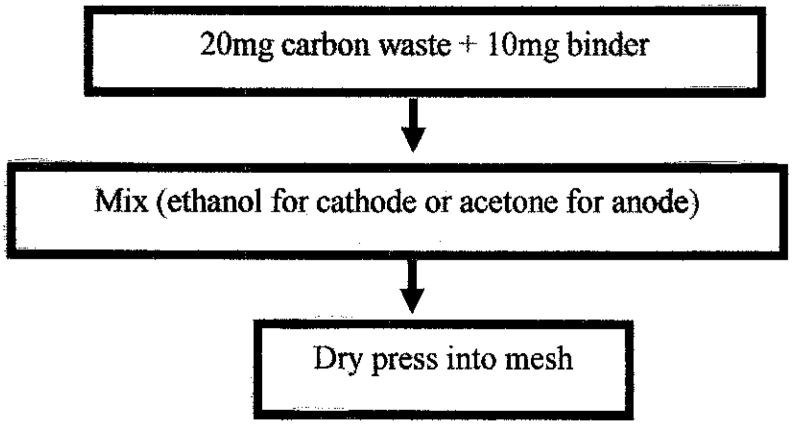
3.2 Electrochemical Performance of Capacitor

3.2.1 Electrode Fabrication

After the sample preparation and characterization process, the sample can be further used in the electrode fabrication. Electrodes in capacitor are identified as anode and cathode. Anode and cathode are typically produced by suspending particulate material and the binder in a solvent to form an electrode paste. 20mg of carbon waste is mixed with 10mg of binder. In this study, type of binder used is Teflon in powder form.

The mixture is then mix with solvent. Different type of solvent is used for cathode and anode. Solvent used usually depends on the desired process parameters. However, since the electrode paste solvent is generally removed by drying, the solvent used is usually volatile. In this study, ethanol is used for cathode while acetone is used as solvent for anode.

After producing the electrode paste, the mixture is transferred to a current collector and will be mashed manually. The mixture is then dried in the drying cabinet for 2hours at 90°C. Purpose of drying is to remove moisture in the mixture.



3.2.2 Electrolyte preparation

- Electrolyte used in this study is lithium perchlorate ($LiClO_4$) in Acetonitrile. Lithium perchlorate exists as white crystalline salt. It is noteworthy for its high solubility in many solvents.
- In capacitor, the electrolyte has to have:

  ➔ High dielectric constant
  ➔ High dielectric strength
  ➔ High resistivity

In this study, 1.0 M of Lithium perchlorate in acetonitrile is used. Due to small size of lithium ions, this electrolyte is the most favorable electrolyte compared to other water-based electrolyte such as sodium chloride or sulphuric acid. To synthesis the electrolyte, 0.254g of lithium perchloride salt is dissolved into 0.25ml of acetonitrile. The solution is stirred to make a well-mix solution.

3.2.3 Capacitor evaluation

After the electrode and electrolyte were completely prepared, the electrodes are assembled in test cell for the electrochemical evaluation.

This test cell is attached to a computer, where special software called Arbin will be used to evaluate the performance of the capacitor. The results obtained from this software are voltage profiles, charge and discharge capacity, charge and discharge energy, and also internal resistance data. These results can be further analysed to evaluate the efficiency of each cycle and specific discharge capacity of the capacitor.

Test Cell Configuration

Configurations in the test cell are as follows:

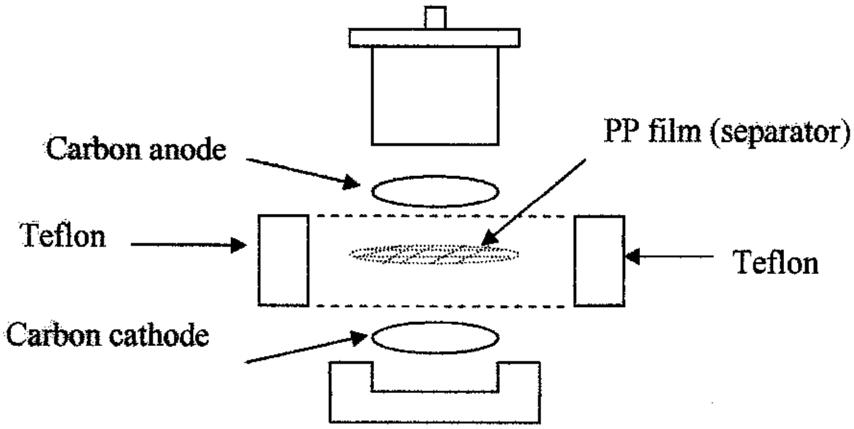


Figure 9: Test Cell Configuration

Carbon anode is separated with carbon cathode using a PP film. This separator acts as electrical insulation between cathode and anode. It also provides an ion passage during the charge-discharge process.

The configuration of test cells have to be in the according sequence, or there might be possibilities of short-circuit occurs in the test cell.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterization of carbonaceous waste

4.1.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is the most widely used for the identification of unknown crystalline materials. Other applications of XRD include characterization of crystalline materials, identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically, determination of unit cell dimensions and also measurement of sample purity.

The X-Ray Diffraction determines the existence of phase in carbonaceous waste. It is a non-destructive method that reveals detailed information about the chemical composition and crystallographic structure of carbonaceous waste.

Diffraction occurs when monochromatic X-ray beam with wavelength lambda is projected onto a crystalline material at angle theta. For this study, angle theta is set to 2-theta. Diffraction only occurs when the distance traveled by the rays reflected from successive planes differs by a complete number n of wavelength[5]

XRD results can be evaluated from patterns that are produced by plotting the angular positions and intensities of the resultant diffracted peaks of radiation. If mixture of different phases is present, the diffractogram is formed by addition of individual patterns.

For this study, the characterization using XRD was carried out under these conditions:

Scan speed: 2^0/min

2□ range: 10°-80°

The XRD result for this carbonaceous waste is as follows:

Table 1: XRD Result of Carbonaceous Waste

mple ame	Left Angle	Right Angle	Left Int.	Right Int.	Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °
rbon	21.12	29.36	5.29	2.61	25.74	3.45826	299	295	2.093

Dimension of carbon layer can be calculated using Scherrer equation;

$L_a=1.84\lambda/B\cos$□ [7]

Where:

λ is wavelength of x-rays

B=Full Width at Half Maximum (FWHM)

The width of the diffraction peak, in radians, at a height half-way between background and the peak maximum

□ = Angle corresponding to peak

For analysis purposes, diffraction peaks from the results has been converted into d-spacing. This will allows identification of the material in the sample because each material has set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

d-spacing	Intensity (I)	Plane- h	Plane-k	Plane-l	Comments
3.37	100	0	0	2	Strongest line.
2.132	2	1	0	0	
2.036	3	1	0	1	
1.682	8	0	0	4	
1.541	2	1	0	3	
1.232	2	1	1	0	

At highest peak;

2-THETA	CPS (intensity)
20	40.991
20.5	21.995
21	43.99
21.5	52.988
22	55.987
22.5	67.984
23	83.981
23.5	112.97
24	150.97
24.5	177.96
25	286.93
25.5	329.92
26	326.92
26.5	272.94
27	157.96
27.5	111.97
28	64.985
28.5	53.988
29	33.992
29.5	27.994
30	25.994

For this study, the results is as follows:

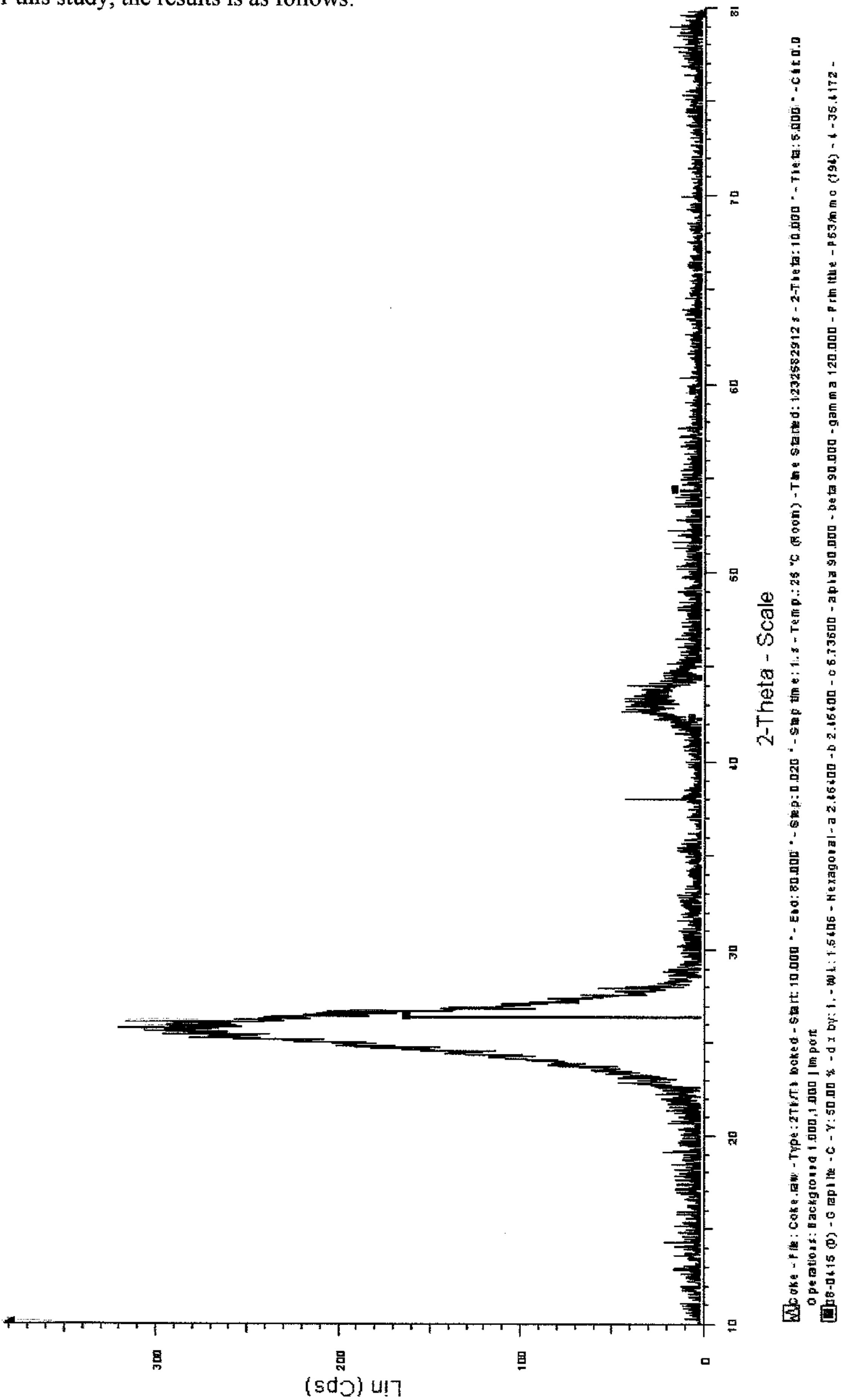


Figure 10: XRD Results

Results are commonly presented as peak positions at 2□ and X-ray counts (intensity) in the form of an x-y plot (as show previously). Intensity (I) is either reported as peak height intensity, or as integrated intensity, which is the area under peak. From the results, the most intense peak is identified. Peak positions occur where the X-Ray beam has been diffracted by the crystal lattice. For this study, the highest peak is shows intensity of 300. According to literature review, high crystalline graphite has intensity of 700, while the sample has intensity lower than 300. The resultant intensity is in the range of high crystallized graphite and amorphous carbon. It can be concluded that this carbonaceous waste is low-crystalline graphite.

It is also observed that there is another one peak existed; indicating there are other material other than carbon might also existed in the sample. This peak is assumed contained impurities, may be resulting from catalyst used in the cracking processes. D-spacing of each peak may be further solved, and automate search/matching routines compare the *d*s of the unknown to those known material can be carried out. Since the information of cracking processes is limited, no existing material other than carbon is known, hence limiting the ability to compare the other peak with other material. Further study on the ethylene cracking furnace is recommended to identify other possibilities of existing compound in the sample. After all the possible material involved in the process are identified, search might be carried out to identify the material existed in the sample; other than carbon.

XRD has its own strengths and limitations. Among the strength of XRD are:

1. powerful and rapid(less than 20minutes) technique for identification of an unknown material
2. in most cases, it provides an unambiguous mineral determination
3. minimal sample preparation is required
4. XRD units are widely available
5. Data interpretation is relatively straight forward

Among the limitations in using XRD for characterization purposes are:

1. Homogeneous and single phase material is best for identification of an unknown
2. Must have access to a standard reference file of inorganic compounds
3. Requires tenths of a gram of material which must be ground into a powder
4. For mixed material, detection limit is ~2% of sample
5. For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated
6. Peak overlay may occur and worsens for high angle 'reflections'

4.1.2 Scanning Electron Microscope (SEM)

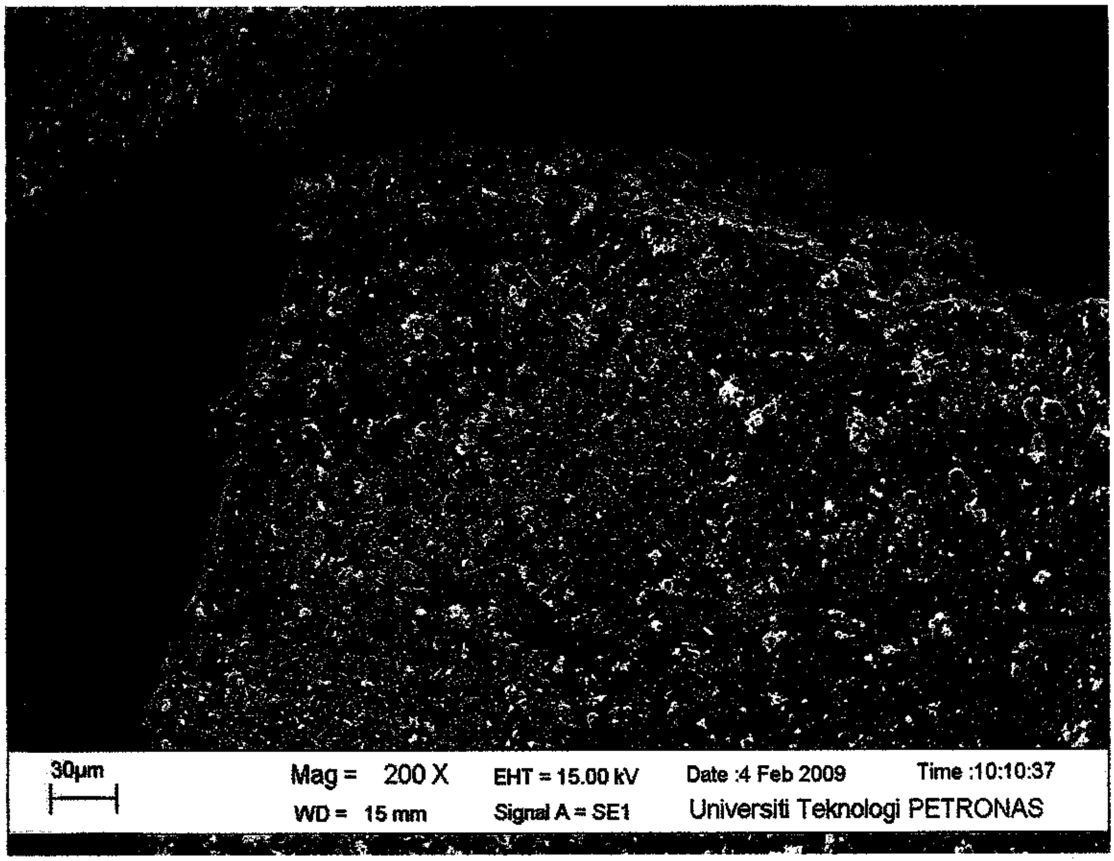
The other characterization that has been carried out is using Scanning Electron Microscope (SEM). SEM can characterize nanomaterials and nanostructure. The SEM creates images by using electrons instead of light waves. In SEM, source of electrons is focused into a beam, with a very fine spot size of~5nm and having energy range from few hundred eV to 50keV. Images are produced by collecting the emitted electrons on a cathode ray tube.

For this study, SEM had been carried out in different magnitude of magnification. SEM results from:

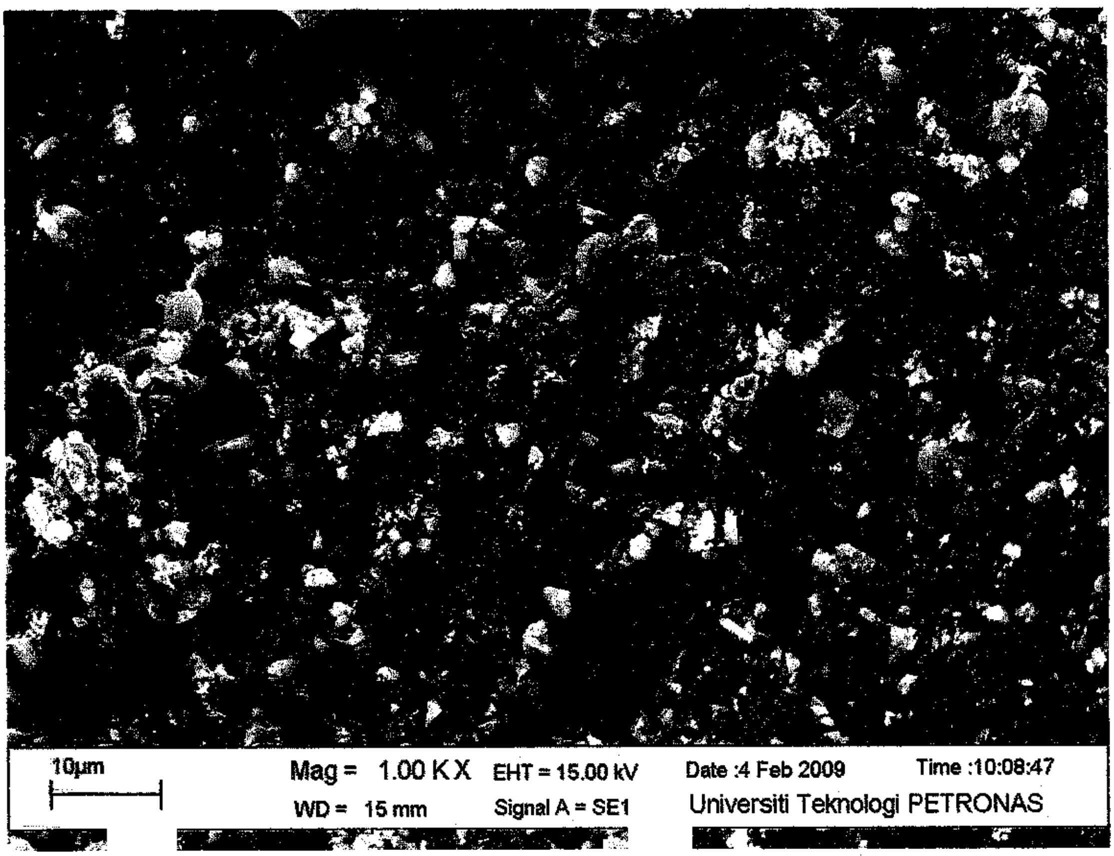
1. 200x magnification
2. 1000x magnification
3. 3000x magnification
4. 5000x magnification
5. 10000x magnification

Result obtained from SEM is as follows:

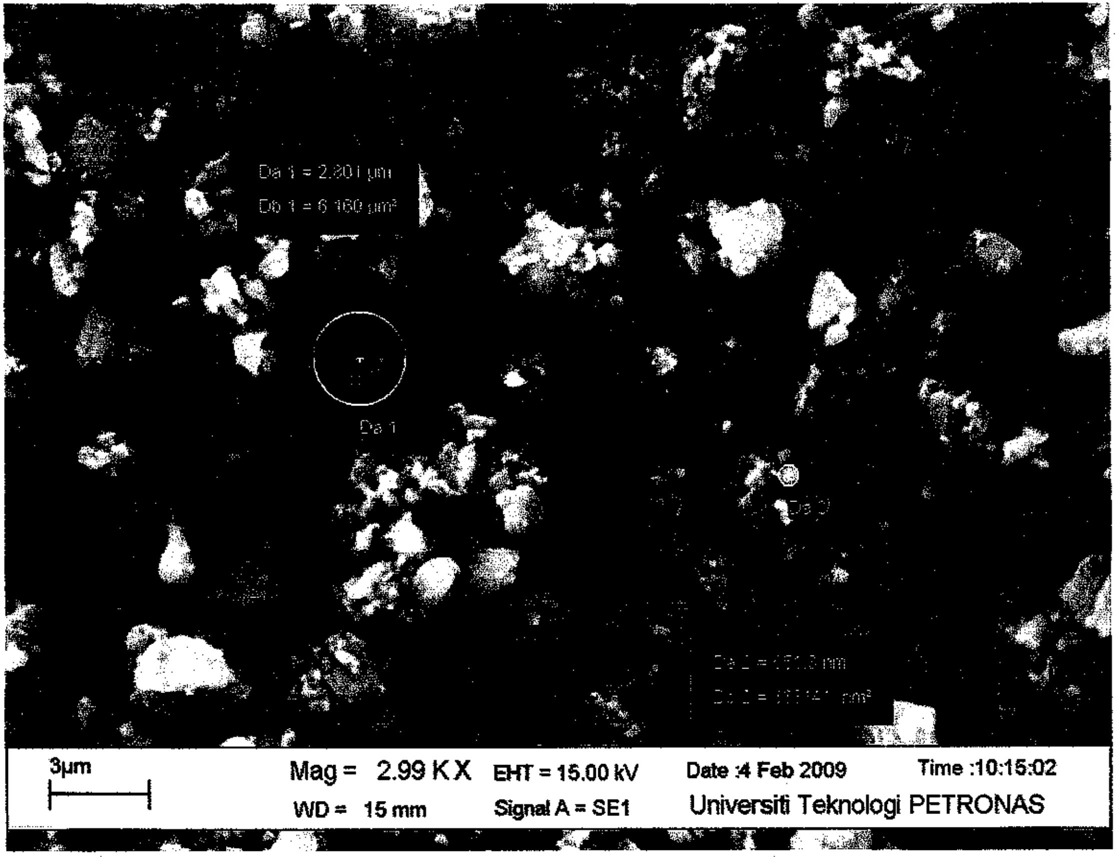
a. Magnification : 200 x



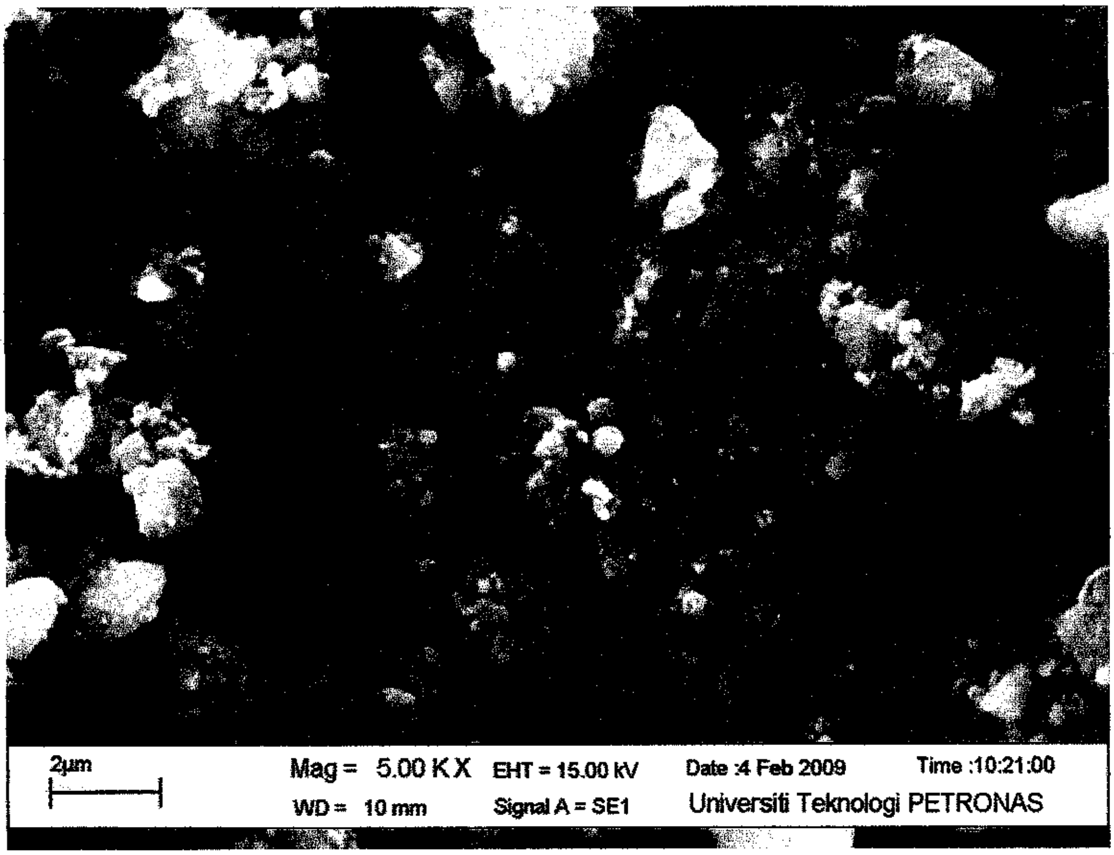
b. Magnification: 1000 x



c. Magnification: 3000 x



d. Magnification: 5000 x



e. Magnification: 10000x

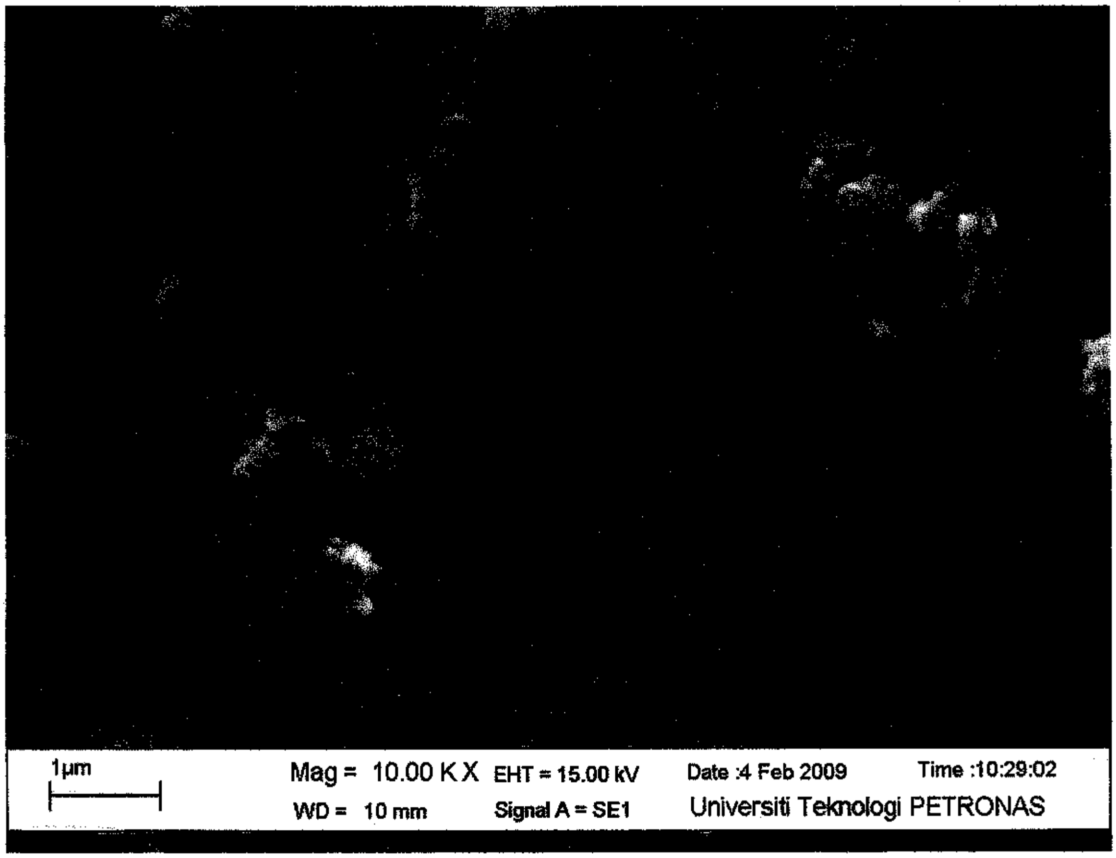


Figure 11: SEM Results for Carbonaceous Waste

From the results, it shows that there are various sizes of carbon particles in the sample. The grain size has a wide range of 0.1ɥm to 10ɥm. Since this is non-pretreated carbon, the particle sizes of carbon are not uniform; thus it might affect the capacitance effect of the electrochemical capacitor.

4.2 Electrochemical Capacitor Performance

Once the electrode and electrolyte has been assembled in the test cell, the performance of capacitor is evaluated. The electrochemical parameters in the experiment are:

1. Capacitor is a carbon-carbon capacitor
2. Electrolyte used is Lithium perchlorate($LiClO_4$) in acetonitrile
3. Current used: 0.005 A, 0.01A, 0.05A.
4. Potential window: 0~2V

The capacitor performance will be evaluated in terms of:

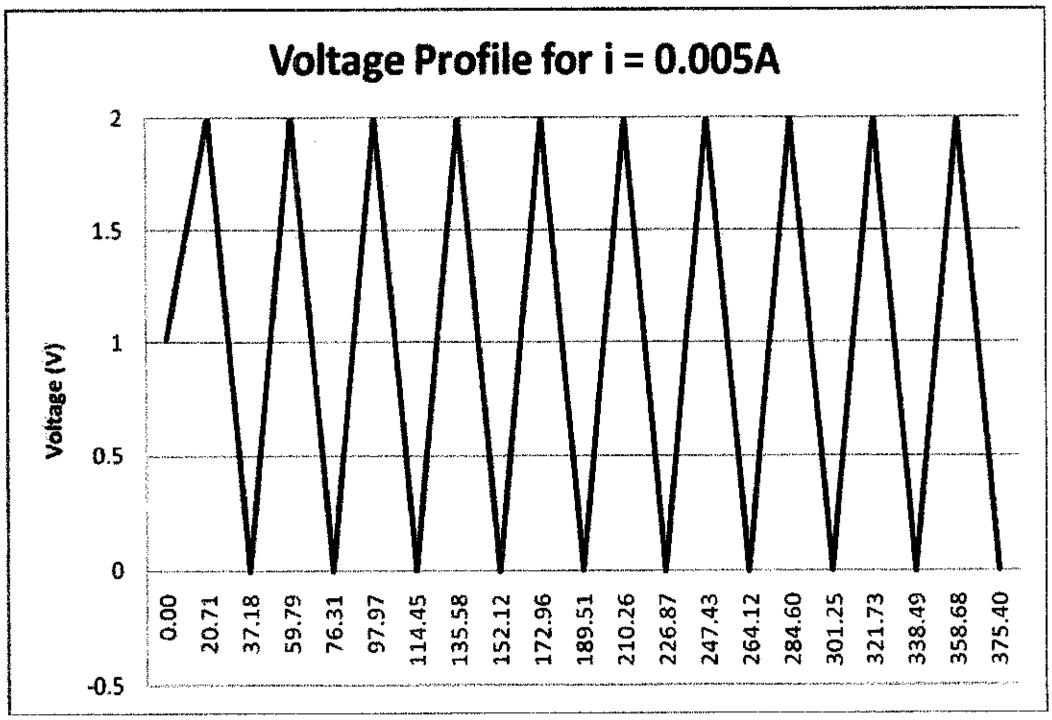
a. Charge-discharge time

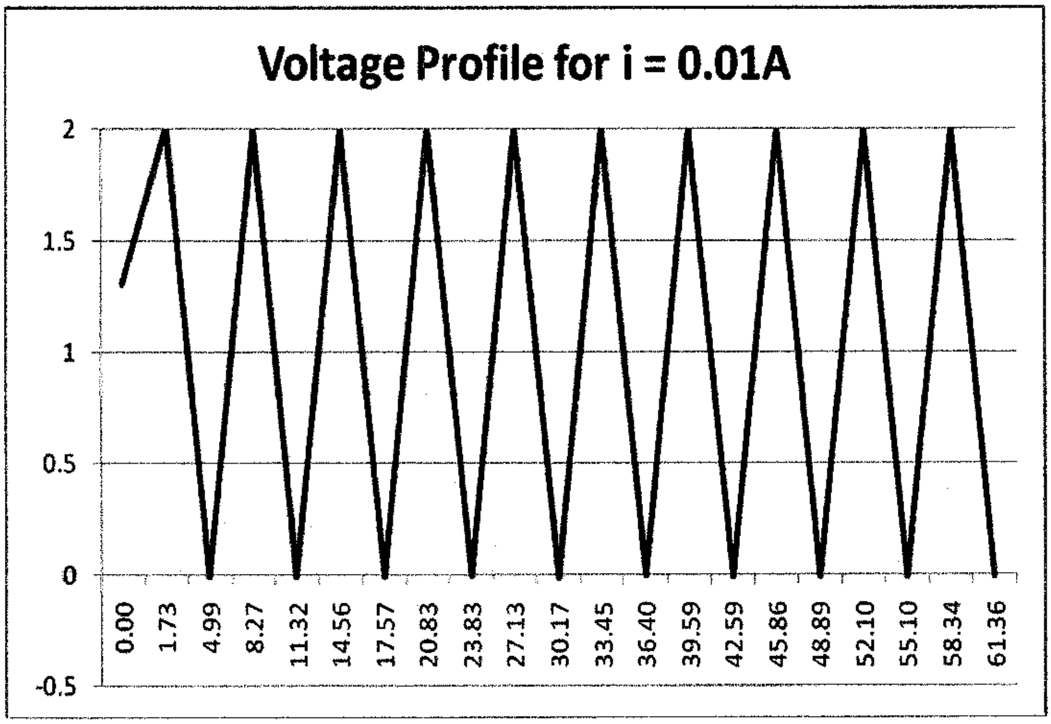
b. Charge-discharge specific capacity

c. Efficiency

d. Comparison between commercial carbon capacitor with carbonaceous waste capacitor

4.2.1 Voltage profiles





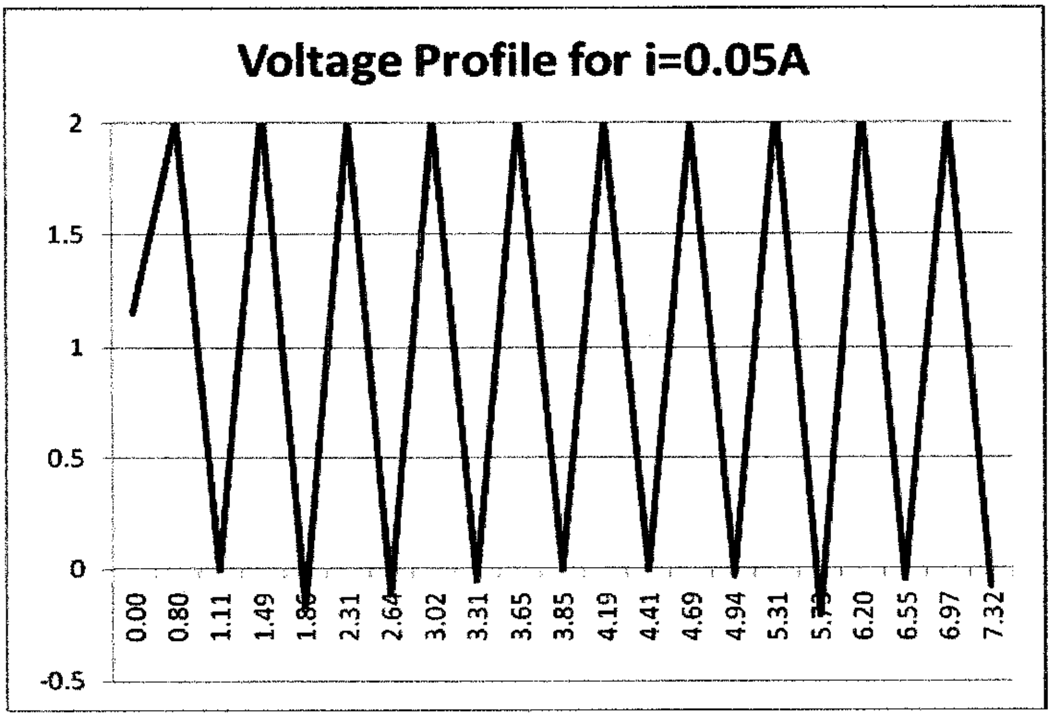


Figure 12: Voltage Profiles for Different Current

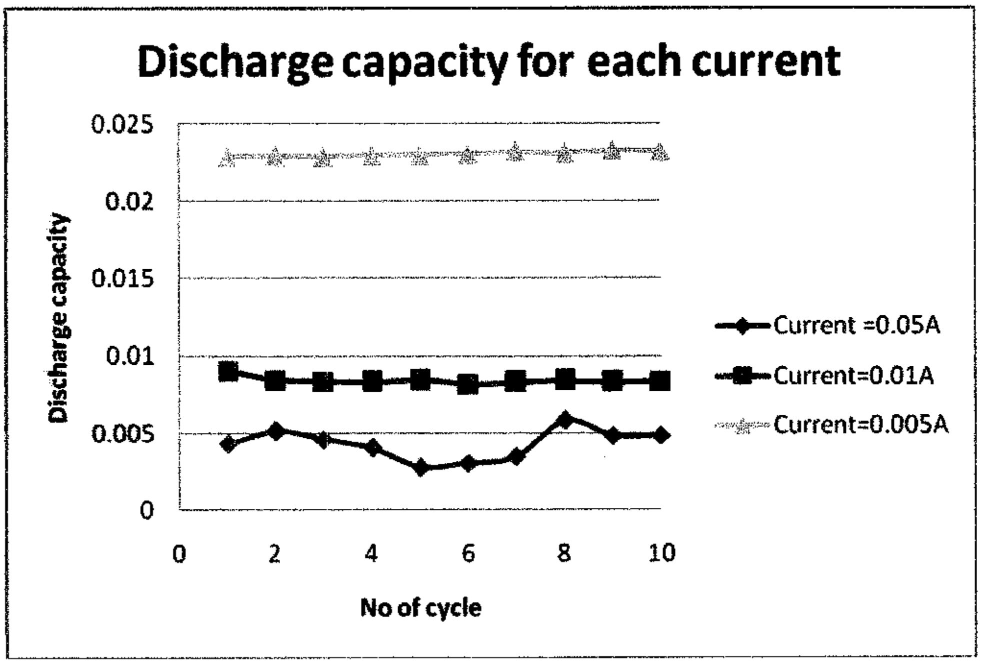
From these voltage profile, charge-discharge time for each cycle can be determined:

Current Applied/ No of cycle	**i=0.005A**		**i=0.01A**		**i=0.05A**	
	Charge time(h)	**Discharge time(h)**	**Charge time(h)**	**Discharge time(h)**	**Charge time(h)**	**Discharge time(h)**
1	0.005753	0.004575	0.00048	0.000906	0.000222	0.00009
2	0.006281	0.004589	0.00091	0.000847	0.000106	0.00010
3	0.006017	0.004578	0.00090	0.000836	0.000125	0.00009
4	0.005869	0.004594	0.00091	0.000833	0.000106	0.00008
5	0.005789	0.004597	0.00092	0.000844	9.44E-05	0.00006
6	0.005764	0.004614	0.00091	0.000819	9.44E-05	0.00006
7	0.005711	0.004636	0.00089	0.000833	7.78E-05	0.00007
8	0.005689	0.004625	0.00091	0.000842	0.000103	0.00012
9	0.005689	0.004656	0.00089	0.000833	0.000131	0.00010
10	0.005608	0.004644	0.00090	0.000839	0.000117	0.00010

Table 2: Charge-Discharge Time for Each Current

4.2.2 Discharge capacity

Discharge capacity for each current at different cycle



Graph 1: Discharge capacity vs. Number of cycle

From the time obtained in voltage profile, discharge capacity of a capacitor could be determined. Discharge capacity is calculated using this formula:

$$\boxed{Q = i \, x \, t}$$

Where Q = discharge capacity (mA.h)

i = current applied (mA)

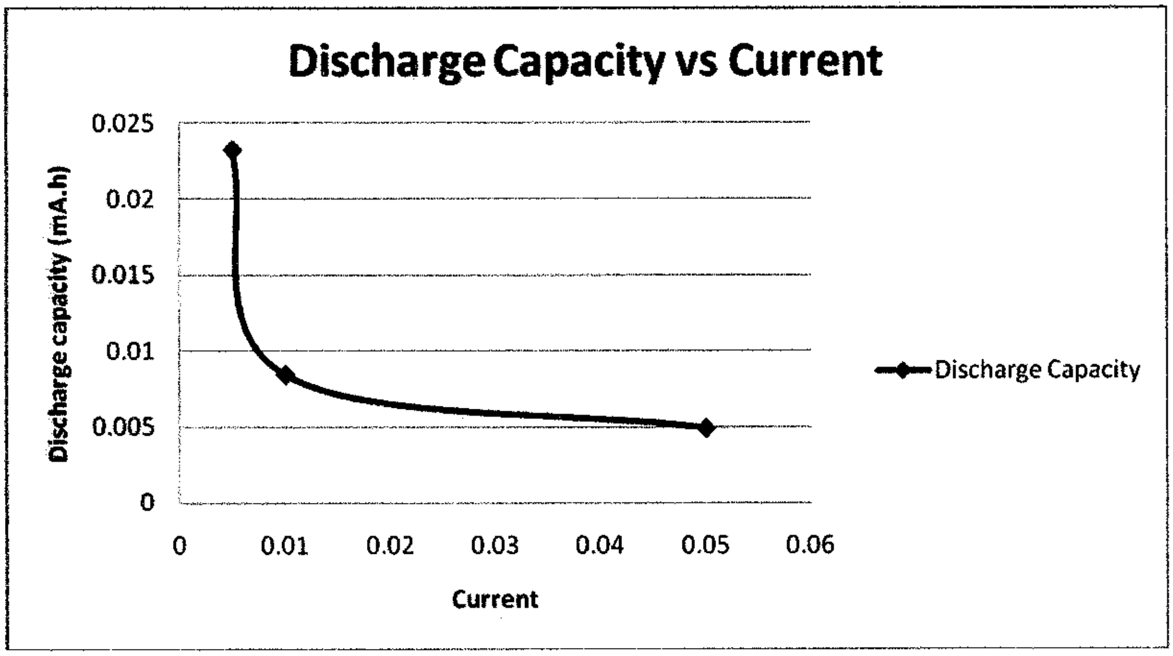
t =discharge time (h)

Capacity can also be known as charge delivered in certain period of time when there's voltage potential difference. Specific capacity is capacity of capacitor with respect to weight of active material in the electrode. To calculate specific discharge capacity (mA.h/g) , the following formula is used:

$$\boxed{= \frac{\text{Discharge capacity}}{\text{Weight of active}}}$$

Where weight of active material is weight of carbonaceous waste used in the electrode =20mg

Overall discharge capacity at each current



Graph 2: Discharge capacity vs. Current

At lower current applied, the discharge capacity is higher. This might be caused by non-uniform carbon particle sizes in the carbonaceous waste. The structure of this carbon waste could not store and deliver the charge when higher current is induced. Higher current might also affect the stability of the electrolyte used; thus interfered the charge-discharge process. Since this is a non-pretreated carbon, lower current should be used to maintain the stability of the structure. For pre-treated carbon, the particle sizes are smaller and more uniform, thus explains the capability of receiving charge at higher current.

Efficiency of capacitor

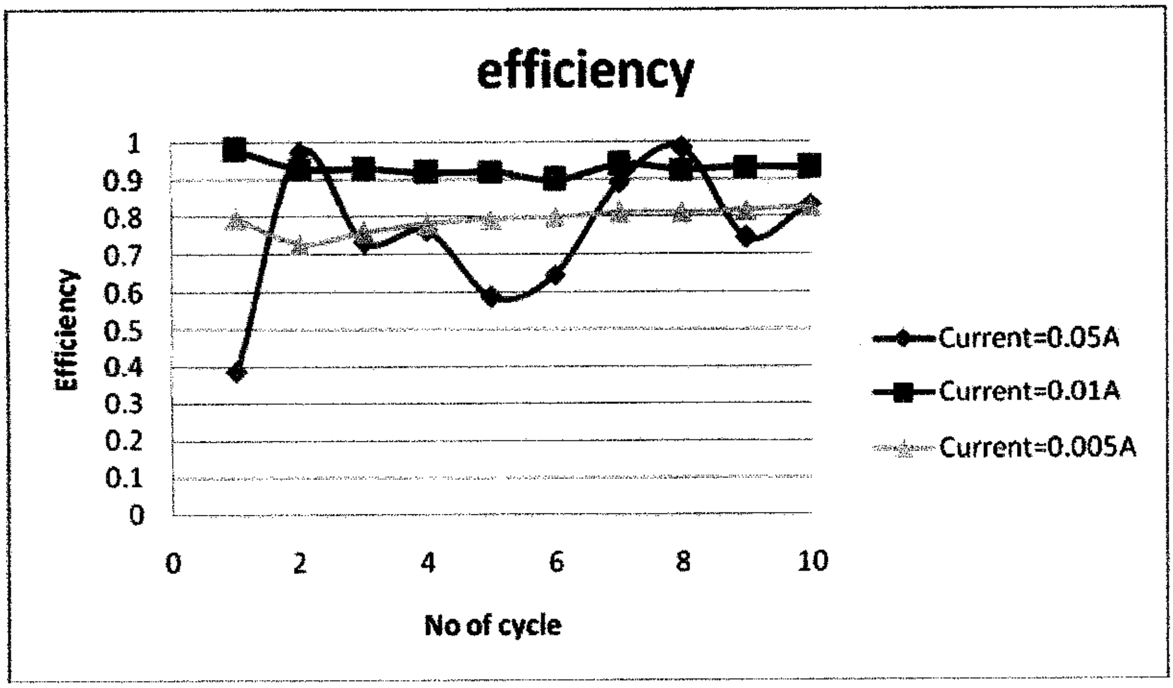
Efficiency of capacitor can be calculated using this formula:

$$\zeta = \frac{\text{discharge capacity}}{\text{Charge capacity}}$$

Efficiency of capacitor is ability for the capacitor to deliver the charge that had been stored. This is one of the most important criteria that electrochemical capacitor should possesses. Some material might capable in receiving the charge when certain amount of current induced, but may fail to deliver the charge when it is needed.

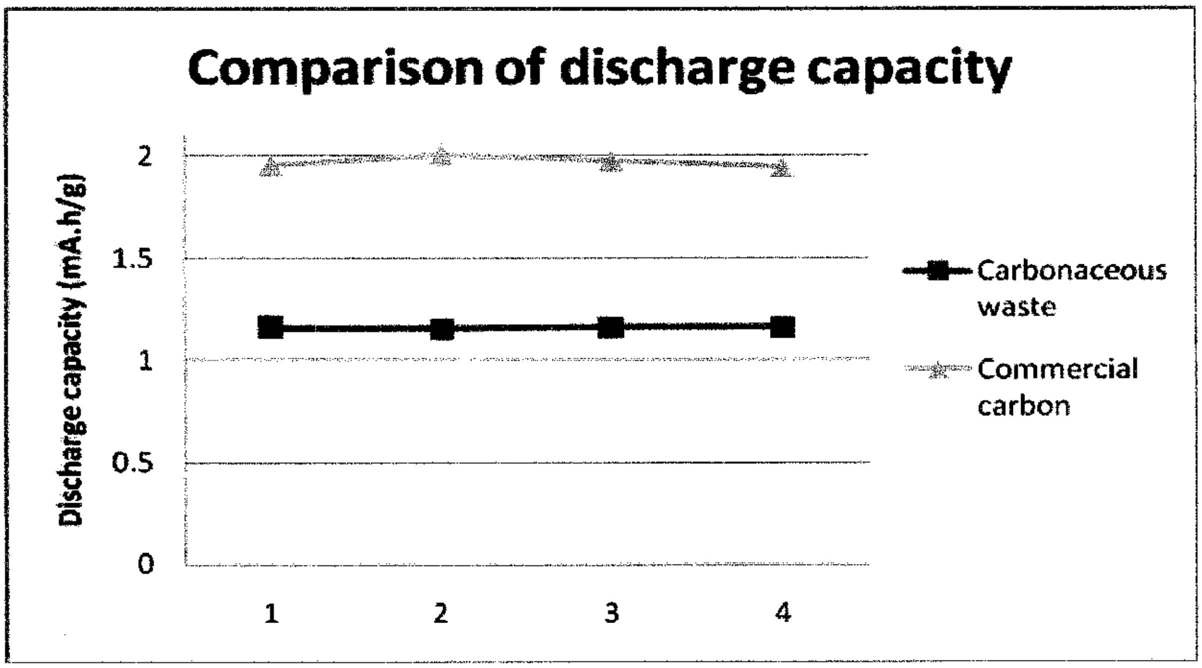
From the experimental results, average efficiency of the capacitor at any current is more than 75%, thus proving that this material is able to discharge the charge that had been stored.

Efficiency for capacitor when 0.05A current is induced is in non-linear form. This might be caused by non-uniform carbon structure and also because of impurity existed in the carbonaceous waste. Impurity in the carbonaceous waste might have metal elements, which can affect the charge-discharge performance of the capacitor.



Graph 3: Efficiency vs. Number of cycle

4.3 Economical Comparison



Graph 4:Comparison of discharge capacity between commercial carbon and carbonaceous waste

No of cycle	**Commercial Carbon (mA.h/g)**	**Carbonaceous Waste (mA.h/g)**
1	1.952	1.159
2	2.006	1.156
3	1.975	1.164
4	1.947	1.161

Table 3:Discharge capacity of commercial carbon and carbonaceous waste

Discharge capacity of electrochemical capacitor from carbonaceous waste is compared to electrochemical from commercial carbon. This experiment is carried out in the same condition; current of 0.005mA with voltage limited to 2V. 4 cycles of charge-discharge process are evaluated.

Properties of these two carbon are different since commercial carbon has undergoes pre-treatment processes beforehand. This pre-treatment process has change the structure of the carbon; they posses higher surface-area, smaller carbon size and more porous compared to the non-treated carbon. These properties had affected the discharge capabilities of these two carbons.

Even though the carbonaceous waste is non-treated carbon, its discharge capacity is approaching the discharge capacity by the commercial carbon. This shows that this carbonaceous waste has a promising future in capacitor field.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the XRD results, structure of carbonaceous waste used in the study can be determined. The structure lies between high crystalline graphite and amorphous carbon. It shows that carbonaceous waste used in this study is low-crystalline graphite, not petroleum coke.

After evaluating the electrochemical capacitor performance of the carbonaceous waste, the results shows that this specific material is able to hold charge and deliver charge; thus proves that this material is capable in acting as electrode in capacitor. The discharge capacity by carbonaceous waste capacitor is 1.161mAh/g while the efficiency is ~99%.

From comparison of electrochemical capacitor between commercial carbon and carbonaceous waste, it shows that there is potential of using this waste as capacitor since the discharge capacity of both capacitor do not have much different.

5.2 Recommendations

Since it is proved that this specific material can act as electrode in electrochemical capacitor, several improvements can be made to increase the capability of delivering charge in the capacitor. The improvement can be made in terms of:

a. To use cyclic voltmetry to investigate electrochemical redox reaction in carbonaceous waste

b. To investigate pre-treatment effect on electrochemical performance of carbonaceous waste.

c. To use pre-treated carbon before the evaluation process.

REFERENCES

[1] Health, Safety and Environment Department, Ethylene Polyethylene (M) Sdn.Bhd, Kerteh, Terengganu

[2] www. iea . org

[3] A.G Pandolfo, 'Carbon Properties and Their Role in Supercapacitors' , Journal of Power Sources, 157(2006),pp 11-27

[4] Chola V Alluri, www.mos.org

[5] http://electrochem.cwru.edu

[6] www.panalytical.com

[7] Hang Shi, "Coke vs. Graphite as Anodes for Lithium-Ion Batteries, Journal of Power Sciences, 75(1998), pp. 64-72

APPENDICES

1. Example of discharge capacity calculation

At the 10th cycle of charge-discharge process when I = 0.005A

Discharge time = 0.004644 h

I = 0.005A≈ 5Ma

Discharge capacity , Q = 0.004644 (5)

= 0.02322Ma.h

2. Specific discharge capacity calculation

At the 10th cycle (i=0.005A), discharge capacity = 0.02322Ma.h

Specific discharge capacity = 0.02322/20$x10^{-3}$

= 1.161 Ma.h/g

3. Efficiency calculation

At 10th cycle(i=0.005A);

Charge capacity = 0.028042

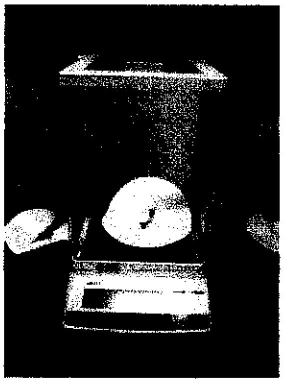
Discharge capacity = 0.02322

Efficiency = 0.02322/0.028042

= 0.83

Preparation of capacitor

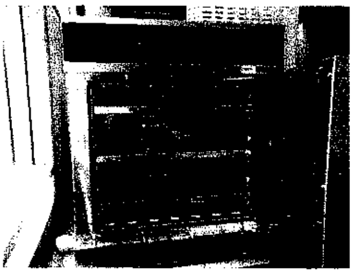
1. Weigh the carbonaceous waste and binder



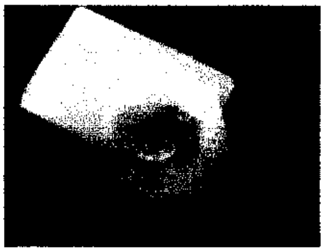
2. Mix carbonaceous waste with binder and solvent

3. Press onto mesh

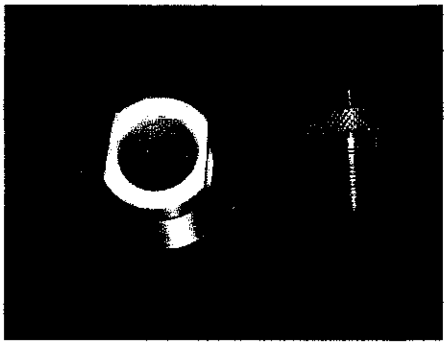
4. Dry the electrodes in drying cabinet



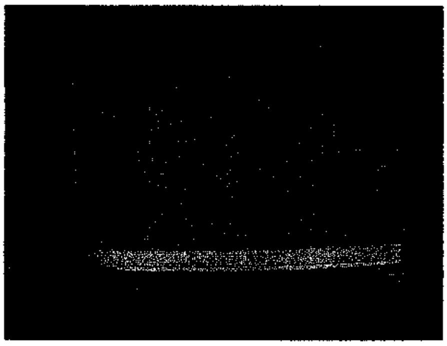
5. Immersed in electrolyte



6. Arranged in test cell



7. Evaluate the performance



Charge-discharge capacity for different current:

For I=0.005A;

Charge capacity (mAh)	**Discharge capacity(mAh)**	**Efficiency**
0.028763889	0.022875	0.795268
0.031402778	0.022944444	0.73065
0.030083333	0.022888889	0.760849
0.029347222	0.022972222	0.782773
0.028944444	0.022986111	0.794146
0.028819444	0.023069444	0.800482
0.028555556	0.023180556	0.81177
0.028444444	0.023125	0.812988
0.028444444	0.023277778	0.818359
0.028041667	0.023222222	0.828133

I=0.05A

Charge capacity (mAh)	**Discharge capacity(mAh)**	**Efficiency**
0.011111111	0.004305556	0.39
0.005277778	0.005138889	0.97
0.00625	0.004583333	0.73
0.005277778	0.004027778	0.76
0.004722222	0.002777778	0.59
0.004722222	0.003055556	0.65
0.003888889	0.003472222	0.89
0.005138889	0.005833333	0.98
0.006527778	0.004861111	0.74
0.005833333	0.004861111	0.83

I= 0.0.1A

Charge capacity(mAh)	**Discharge capacity(mAh)**	**Efficiency**
0.0048	0.0091	0.9800
0.0091	0.0085	0.9299
0.0090	0.0084	0.9290
0.0091	0.0083	0.9202
0.0092	0.0084	0.9212
0.0091	0.0082	0.8994
0.0089	0.0083	0.9404
0.0091	0.0084	0.9266
0.0089	0.0083	0.9346
0.0090	0.0084	0.9321

Specific Discharge capacity for each current applied:

I =0.005A

i=0.005A	**i=0.01A**	**i=0.005A**
1.14375	0.452778	0.215278
1.147222	0.423611	0.256944
1.144444	0.418056	0.229167
1.148611	0.416667	0.201389
1.149306	0.422222	0.138889
1.153472	0.409722	0.152778
1.159028	0.416667	0.173611
1.15625	0.420833	0.291667
1.163889	0.416667	0.243056
1.161111	0.419444	0.243056

Example of Current (A), Voltage (V), vs. Test Time (T) graph. Graph is obtained from battery cycler, ARBIN software.