UNIVERSITI TEKNIKAL MALAYSIA MELAKA

CYCLIC VOLTAMMETRY ANALYSIS OF CARBON-BASED ELECTROCHEMICAL CAPACITOR IN 1M H_2SO_4

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

MUHAMAD ARIF BIN AZIZAN

B050910173

900622-06-5137

FACULTY OF MANUFACTURING ENGINEERING

2013

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

TAJUK: **Cyclic Voltammetry Analysis of Carbon - Based Electrochemical Capacitor in 1M H_2SO_4**

SESI PENGAJIAN: 2012/2013 Semester 2

Saya **MUHAMAD ARIF BIN AZIZAN**

mengaku membenarkan Laporan PSM ini disimpan di Perpustakaan Universiti Teknikal Malaysia Melaka (UTeM) dengan syarat-syarat kegunaan seperti berikut:

1. Laporan PSM adalah hak milik Universiti Teknikal Malaysia Melaka dan penulis.
2. Perpustakaan Universiti Teknikal Malaysia Melaka dibenarkan membuat salinan untuk tujuan pengajian sahaja dengan izin penulis.
3. Perpustakaan dibenarkan membuat salinan laporan PSM ini sebagai bahan pertukaran antara institusi pengajian tinggi.

☐ SULIT (Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysiasebagaimana yang termaktub dalam AKTA RAHSIA RASMI 1972)

☐ TERHAD (Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)

☒ TIDAK TERHAD

Disahkan oleh:

________________________ ________________________

Alamat Tetap:

No. 16 (F) LEPAR HILIR O4,

26300 GAMBANG, KUANTAN,

PAHANG DARUL MAKMUR.

Cop Rasmi:

Tarikh:

Tarikh: ________________________

** Jika Laporan PSM ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh laporan PSM ini perlu dikelaskan sebagai SULIT atau TERHAD.

DECLARATION

I hereby, declared this report entitled "Cyclic Voltammetry Analysis Of Carbon - Based Electrochemical Capacitor In 1M H_2SO_4" is the results of my own research except as cited in references.

Signature :………………………………………….

Author's Name : MUHAMAD ARIF BIN AZIZAN

Date :

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The members of the supervisory committee are as follow:

………………………………

(DR. MOHD ASYADI ‘AZAM BIN MOHD ABID)

ABSTRAK

Dengan pembangunan komponen kepada saiz yang lebih kecil, teknologi alat-alat penyimpanan tenaga menjadi penting. Fakta mengatakan bahawa bateri tidak boleh digunakan dalam aplikasi kuasa tinggi kerana ketumpatan kuasanya yang rendah. Kitaran hidup untuk bateri juga pendek. Berlawanan dengannya, kapasitor elektrokimia menpunyai ciri ketumpatan kuasa yang lebih tinggi dan kitaran hidup yang lebih lama berbanding bateri. Masalah wujud apabila kapasitor elektrokimia hanya mempunyai ketumpatan tenaga yang rendah. Untuk menyelesaikan masalah ini, kajian telah dilakukan selama beberapa tahun.

Dalam projek ini, kapasitor elektrokimia telah dihasilkan dengan menggunakan bahan karbon (karbon teraktif + *graphene*) sebagai bahan elektrod. H_2SO_4 merupakan elektrolit yang telah digunakan dan berfungsi sebagai pembawa ion. Sebagai penambahan, *polyvinylidene fluoride* (PVDF) telah digunakan sebagai pengikat manakala polipropilena sebagai pemisah. Sebelum dicirikan, komponen-komponen kapasitor elektrokimia perlu disusun mengikut susunan yang betul dan kemudian diletakkan di dalam jig atau syiling sel. Seterusnya, analisis dijalankan dengan mengunakan sistem *Basic DC Voltammetry*. Hasil kajian yang dibincangkan di dalam laporan ini termasuklah fabrikasi kapasitor elektrokimia dimana faktor yang diambil kira adalah komposisi bahan ketika process penyalutan. Kaedah voltammetri berkitar digunakan untuk menganalisa kapasitor elektrokimia yang dihasilkan. Nilai kapasitor, kriteria caj/pelepasan caj dan jangka hayat juga dibincang di dalam laporan ini. Pengimbas mikroskop elektron juga digunakan untuk mengkaji purata kebesaran liang untuk bahan karbon.

ABSTRACT

With the development of components to miniature sizes, the technology of the energy storage devices become crucial. It is known by fact that batteries cannot be used in high power application due to low power density. The life cycle of the batteries is also short. On the contrary, the electrochemical capacitors (ECs) hold the characteristic of higher power density and longer life cycle compared to batteries. A problem exists when the energy density is low. To solve this problem, researches have been done throughout the years.

In this project, the EC is fabricated by using different ratio of carbon weight (activated carbon + graphene) as the electrode material. The electrolyte that functions as the ion carriers are presented by using H_2SO_4. In addition, the polyvinylidene fluoride (PVDF) is used as a binder while polypropylene (PP) as a separator. Before the EC are characterized, the EC components are assembled in the jig or coin cell according to the arrangements that has been set. Basic DC Voltammetry System is used to conduct the CV analysis. Results discussed in this report include the fabrication of the EC; whereby the parameters that are taken into consideration are the composition of the materials involved in the coating process. CV method is used to analyze the fabricated EC obtained. Parameters including the capacitance value, charge/discharge characteristic and life cycle are included in this report. Scanning Electron Microscope (SEM) is used to analyze the average pore sizes of the carbon materials.

DECLARATION

To my beloved father, Azizan B. Mohd Nawar, my beloved mother, Siti Rauhazani Bt. Yom and all my siblings.

ACKNOWLEDGEMENT

Firstly, I would like to express my utmost gratitude to my supervisor, Dr. Mohd Asyadi ‘Azam Bin Mohd Abid for his guidance, advice, concern, understanding and patience throughout the research period. His supervision has helped a lot in the progression of this final year project. I am indeed very grateful to be under his supervision. In addition, I would like to express my appreciation to his PhD and Master student, Elyas B. Talib and Mohd Shahril Amin B. Bistamam for giving their attention to me to finish this report. Without them, I think it is difficult for me to finish this report alone.

Special thanks to my friend and also my group members, Hazwan Hasif B. Hamdan, Mohamed Fakhruddin B. Abdullah and Aisyah Bt. Hassan for her help in periods of uncertainties and difficulties. Thank for your kindness for helping each other in order to finish this report together. Not to forget Magna Value for providing me guidance, advices and kindness throughout the completion of this report.

Other than that, sincere appreciation is dedicated to my parents and my sisters for their love, encouragement and continuous support particularly when I am facing difficulties.

TABLE OF CONTENT

Abstrak		i
Abstract		ii
Dedication		iii
Acknowledgement		iv
Table of Content		v
List of Tables		vii
List of Figures		viii
List Abbreviations, Symbols and Nomenclatures		ix

CHAPTER 1: INTRODUCTION

1.1	Background	1
1.2	Problem Statement	4
1.3	Objectives	5
1.4	Scope	5

CHAPTER 2: LITERATURE REVIEW

2.1	Electrochemical capacitor (EC)	6
2.1.1	Electrochemical double layer capacitor (EDLC)	6
	2.1.1.1 Mechanism of EDLC	7
	2.1.1.2 Material of high surface area	9
	2.1.1.3 Capacitance and pore size	11
	2.1.1.4 Advantages and disadvantages of EDLC	12
2.1.2	Pseudocapacitor	13
	2.1.2.1 Mechanism of pseudocapacitor	13
	2.1.2.2 Nanostructuring material to increase capacitance	15

2.2 Electrode materials 17
2.2.1 Carbon materials as electrodes 17
2.2.2 Carbon electrode materials of EC 19
2.2.2.1 Activated carbon 19
2.2.2.2 Carbon nanotube (CNT) 20
2.2.2.3 Graphene 20
2.3 Electrolytes 23
2.3.1 Aqueous solution 24
2.4 Cyclic voltammetry 27
2.4.1 CV of non-Faradaic processes 27
2.4.2 CV of Faradaic processes 29

CHAPTER 3: METHODOLOGY
3.1 Construction of carbon based electrochemical capacitor 32
3.2 Electrode material preparation 33
3.3 Fabrication process to produce the EC 37
3.4 Set up for CV analysis 38
3.5 Flow chart 40

CHAPTER 4: RESULTS AND DISCUSSION
4.1 Result of the EC fabrication process 41
4.2 Cyclic Voltammetry Analyses of the fabricated EC 45
4.2.1 Specific Capacitance value 45
4.2.2 Type of the fabricated EC 46
4.2.3 The performance of the EC by varying the value of scan rate 48
4.2.4 Charge/discharge behavior analysis 51
4.2.5 C_{sp} for multiple cycles and its decreasing rate 52
4.3 Pore size analysis by SEM 55

CHAPTER 5: CONCLUSION & FUTURE WORK

5.1	Conclusion	58
5.2	Future work	59

REFERENCES 60

APPENDIX A

Gantt chart

LIST OF TABLES

1.1 Comparison of Capacitor, EC and Battery (Martin, 2004). 3

2.1 Properties of various materials used in electrochemical capacitor electrode materials (Simon, 2008). 22

2.2 The type of the electrolytes and it charge of the ions. 23

2.3 Properties of various electrolytes (Simon, 2008). 25

2.4 The difference between aqueous and organic EDLC 26

3.1 Physical and chemical properties of activated carbon. 33

3.2 Material and its function. 34

3.3 Apparatus and its function. 34

3.4 Materials used and its weight. 36

4.1 The composition of the materials used in the successful coating process. 42

4.2 Specific capacitance value for potential of 1V 50

4.3 C_{sp} for different cycles and it decreasing rate. 52

LIST OF FIGURES

1.1	Plot of specific power versus specific energy for various power/energy sources (kotz, 2000).	1
2.1	Schematic diagram of an EC (Simon, 2008).	7
2.2	Mechanism and charge/discharge of EDLC (Source: <http://www.murata.com>07/12/12).	9
2.3	Schematic diagram of the pore size network of an activated carbon grain (Wei, 2012).	10
2.4	Pseudocapacitance's mechanism (Wei, 2012).	15
2.5	Strategy to increase capacitance (Gogotsi, 2008).	16
2.6	Representation of pore in carbon electrode active layer (Signorelli, 2009).	18
2.7	Example SEM micrograph of porous carbon (Manocha, 2003).	19
2.8	CV diagram for an EDLC cell (Signorelli, 2009).	29
2.9	Voltage as a function of time for CV and shape of a CV for a Nernstian electrochemical reaction (Sugimoto, 2003).	30
3.1	Example of EC construction.	32
3.2	Image of carbon powder.	33
3.3	Material and equipment needed for electrode material.	35
3.4	Arrangement of the electrode, separator and spacer in the coin cell.	37
3.5	Basic DC voltammetry system.	38
3.6	Assembly of cyclic voltammatery characterization.	39
3.7	Flow chart of methodology.	40
4.1	Schematic diagram of the coin cell.	41
4.2	Example of the carbon coating failure.	43
4.3	Example of the successful coating.	43

4.4 CV curve of carbon materials in different scan rate for 2V. 45
4.5 Example of the CV curve of EC with different scan rate (Maher, 2012). 47
4.6 Example of the CV curve of pseudocapacitance (Trasatti, 1971). 47
4.7 Example of the CV curve of lithium battery (Hui, 2013). 48
4.8 Graph of specific capacitance versus scan rate. 50
4.9 Charge/discharge for the fabricated EC. 51
4.10 CV curve for 5 cycles in 1000 mV/s scan rate. 53
4.11 CV curve for 5 cycles in 500 mV/s scan rate. 53
4.12 CV curve for 5 cycles in 10 mV/s scan rate. 54
4.13 CV curve for 5 cycles in 1 mV/s scan rate. 54
4.14 SEM image of carbon materials. 55
4.15 a) SEM image of activated carbon.b) SEM image of activated carbon obtain from the experimental. 56

LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

AC	-	Alternating current
CDC	-	Carbide derive carbon
CNT	-	Carbon nanotube
CMG	-	Chemical modulated graphene
CO_2	-	Carbon dioxide
CV	-	Cyclic voltammetry
EC	-	Electrochemical capacitor
EDLC	-	Electrochemical double layer capacitor
ESR	-	Equivalent series resistance
H_2SO_4	-	Sulfuric acid
KOH	-	Potassium hydroxide
MWNT	-	Multi wall nanotube
PTFE	-	Polytetra fluoroethylene
SEM	-	Scanning electron microscope
SiC	-	Silicon carbide
SS	-	Stainless steel
SSA	-	Specific surface area
TiC	-	Titinium carbide
VN	-	Vanadium nitride

nm	-	nanometer
°C	-	degree Celcius
V	-	Volt
g	-	gram
%	-	percent
mL	-	milliliter
>	-	More than
F	-	Fahrenheit
C	-	Capacitance
Q	-	Charge on capacitor
E	-	Voltage drop
I_p	-	peak current
D	-	Diffusion coefficient
C^0	-	Concentration of bulk solution

CHAPTER 1

INTRODUCTION

1.1 Background

Nowadays, energy storage becomes an important issue that needs to be discussed. This is due to their power and energy storage. Power density means that it is the strength in term of wattage of a given current and voltage combination while energy density is the time duration of the wattage that can be applied. There are many types of energy storage device that had been used today such as batteries, capacitor and electrochemical capacitor (EC). Figure 1.1 shows the different device that was used as energy storage. There are four types of devices that being compared according to their energy and power density.

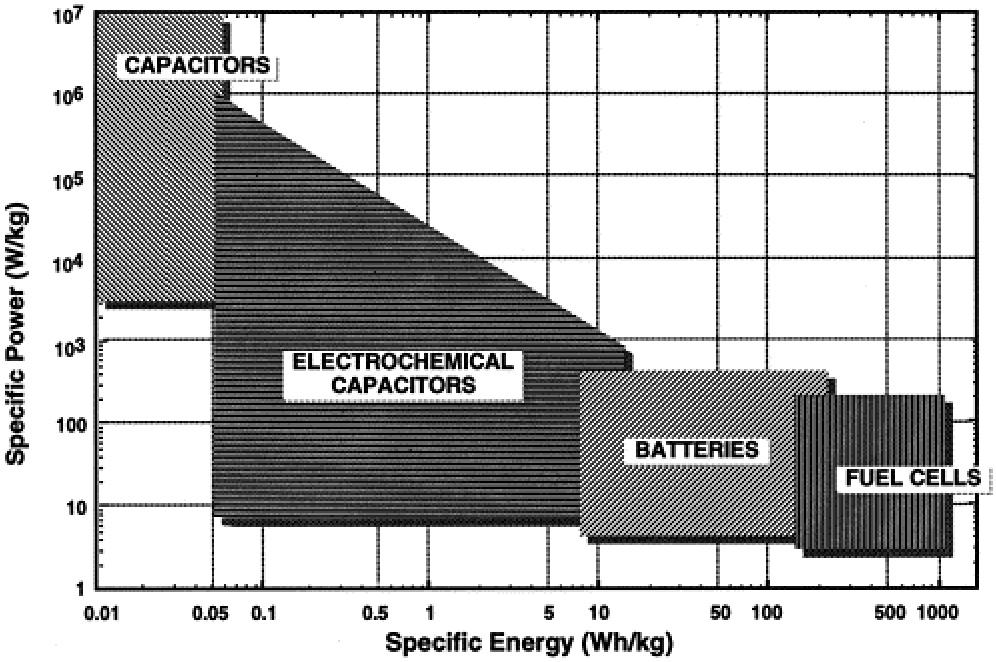

Figure 1.1: Plot of specific power versus specific energy for various power/energy sources (Kötz, 2000).

Recently, batteries are the common form of electrical energy storage that had been used. This is due to their higher energy density compared to EC. Higher energy density means it can store more energy but the limitation of the batteries is it delivers less power compared to the conventional capacitor. So, batteries are not suitable to be used in the applications that need high power supply. Usually non rechargeable batteries can store from 90 to 445 Wh kg^{-3} of energy while rechargeable batteries can achieve 1000 cycles in their lifetime and store 225 Wh kg^{-3} of energy.

Conventional capacitor has more power densities if compared to the batteries. The value of power density of conventional capacitor is between $1.0x10^2$ to $27x10^{10}$ kW kg^{-1}. Its life cycles also 10 times longer compared to batteries. This is the advantage of the capacitor but it also has the drawback which is a small energy density that limit its application especially to those which required a large amount of energy storage.

Electrochemical double layer capacitor (EDLC) is created and is released throughout the interface of the electrolyte/electrolyte resulting in parallel movement of electrons in external wires (Winter, 2004). The EC has properties that are in between of the others two common energy storage devices. It offers high energy density, high power density and long life cycle. Furthermore, this EC does not require a dielectric material like in conventional capacitor that can cause dielectric breakdown. EC can be applied to many applicants like electric vehicles, satellite propulsion and pulse power application.

Usually, the capacitance value of EC is 1000 times higher than dielectric capacitor and its power density is 100 times higher than batteries. Comparisons between dielectric capacitor, EC and battery in term of its properties, performance and efficiency have been shown in Table 1.1.

Table 1.1: Comparison of Capacitor, EC and Battery (Winter, 2004).

Parameters	**Dielectric Capacitor**	**EC**	**Battery**
Charge Time	10^{-6}~10^{-3} sec	1-30 sec	3~4 hrs
Discharge Time	10^{-6}~10^{-3} sec	1-30 sec	1 ~ 5 hrs
Energy Density (Wh/kg)	< 0.1	1 ~ 10	20 ~ 100
Power Density (W/kg)	> 10,000	1,000 ~ 2,000	50 ~ 200
Cycle life	> 500,000	> 100,000	500~2000
Charge/Discharge Efficiency	~ 1.0	0.90 ~ 0.95	0.7~ 0.85

Higher energy and higher discharge time make EC more powerful compared to dielectric capacitor while the EC has a longer cycle life than batteries is due to the absence of chemical reaction. Although, batteries are better in term of high energy density compare to others but they have a lower power density and short cycle life.

Although all the above devices have different mechanism but there are also electrochemical similarities of these three systems. The common features are the energy providing processes that take place at the phase boundary of the electrode interface and the separation of electron and ion during the transportation process.

1.2 Problem Statement

There are many types of energy source that can be obtained from the nature such as wind, sun, fossil fuel and many more. These energy sources are usually stored in energy storage devices like batteries, conventional capacitor and EC. These devices have its advantages and also disadvantages and only suited for certain application depending on their energy density and also power density. For batteries, it has higher energy density but low in power density. Nowadays, researchers focus on the EC to improve their energy density since its power density and lifecycle was already higher than batteries. There are many factors that need to be considered in order to improve the energy density of the EC such as type of electrode material and also electrolyte. In this study, carbon material (activated carbon + graphene) was used as an electrode since it's contributed to a high value of capacitance. Carbon materials such as graphite, carbon nanotube (CNT), activated carbon and graphene oxide are becoming popular to be used as its electrode material. This is due to their special characteristic which is a porous material. To measure the value of capacitance, cyclic voltammetry (CV) method will be used. Before this experiment is conducted, the principle of the CV needs to be known first. There are some variable in this method that will vary the result obtained such as scan rate and voltage window. Furthermore, the uses of CV have not been well discussed before. Besides determining the capacitance, CV can also determine whether the fabricated EC is EDLC or pseudocapacitor, charge/discharge and also its life cycle. So, if EC can increase its energy density in the future, then the uses of the battery can be replaced.

1.3 Objectives

The objectives of this research project are:-

1) To fabricate the electrochemical capacitor by using carbon as the electrode material.
2) To characterize the fabricated electrochemical capacitor by using cyclic voltammetry analysis.

1.4 Scope

In order to understand how the EC is working, it is necessary to understand the basic theory of it. Theory will give a brief definition of the EC with the specific mechanism and also the function of each component inside. The study of some diagram about the EC also can help for a better understanding. Then, the experiment was conducted in the Material Laboratory of Manufacturing Faculty, Universiti Teknikal Malaysia Melaka (UTeM) and MAGNA VALUE SDN BHD. Fabrication of the EC was done completely at MAGNA before it is characterized in the material laboratory in UTEM. Then, the CV will be used as a characterization method to obtain the capacitance value, charge/discharge, cycle life and determination of the fabricated EC. Note that, in this experiment, carbon materials used as an electrode are activated carbon and graphene while the electrolyte is 1M H_2SO_4. So, the result obtained will be compared to the previous research to see the differences.

CHAPTER 2

LITERATURE REVIEW

2.1 Electrochemical capacitor (EC)

There are two types of EC that is electrochemical double layer capacitor (EDLC) and Pseudocapacitor. For example, if the electrode used is carbon nanotube that allows intercalation of Li ions, then the electron transfer reaction occurs at the surface of the electrode and this capacitance is called pseudocapacitance. If Faradaic reaction is not allowed to happen, charge only can be absorbed physically into the double layer without any electron transfer.

2.1.1 Electrochemical double layer capacitor (EDLC)

In ‘super’ or ‘ultra’ capacitors, application of a potential to the surface of a conducting electrode in an electrolyte solution produces polarization of the ions in the region of the electrode surface. Applying a negative potential to the surface will produce an increase in cations close to the electrode surface and a depletion of anions. This region near the electrode surface is termed the double layer or the Helmholtz layer; hence the name for the capacitors that use this mechanism is EDLC. Then the higher concentration of ions in the solution, the smaller the distance of ions in solution need to travel to compensate for the charge appearing at each electrode.

To be an effective means of storing charge, clearly, high surface areas are required. Modern capacitors generally utilize extremely high surface area carbons, typically 1000 m^2 g^{-1} or higher, in contact with an electrolyte solution of high ionic strength. The energy stored is proportional to the square of the voltage, and so higher voltages are particularly attractive as they increase the energy stored (Bakker *et al*, 2011). Figure 2.1 shows the schematic diagram of the EC that consist of an electrolyte, porous electrode and also separator.

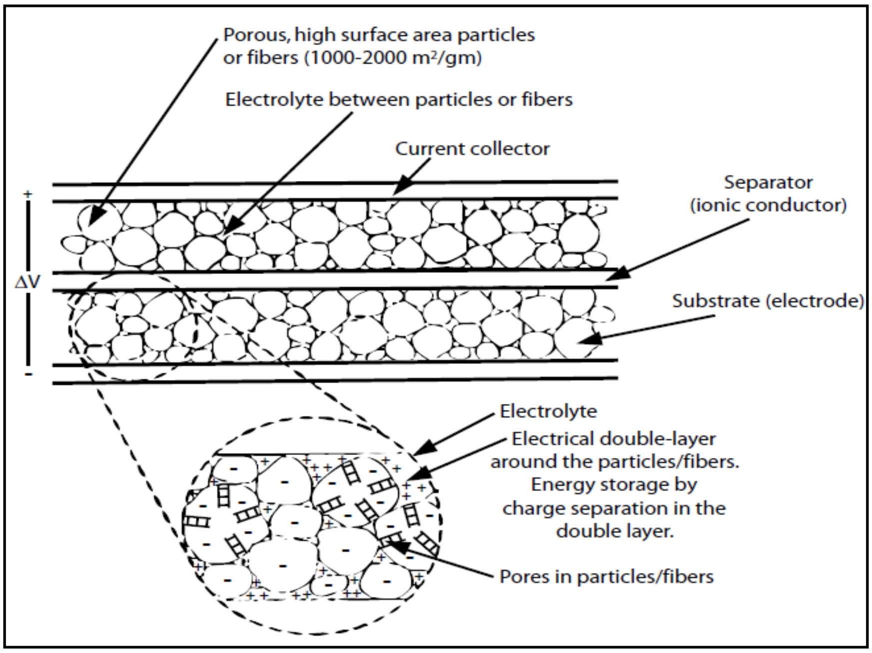

Figure 2.1: Schematic diagram of an EC (Simon, 2008).

2.1.1.1 Mechanism of EDLC

EC store charge electrostatically by using reversible adsorption of electrolyte ions onto active materials that are electrochemically stable and have a high specific surface area (SSA). As mentioned above, the charge separation occurs on polarization at the electrode-electrolyte interface is called double layer. Helmholtz also described that double layer capacitance C:

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d}$$

Eq. (2.1)

Where ε_r is the electrolyte dielectric constant, ε_0 is the dielectric constant of the vacuum, *d* is the effective thickness of the double layer (charge separation distance) and *A* is the electrode surface area.

Then this model was refined by Gouy and Chapman, and stern and Geary. They were suggested to make a present of the diffuse layer because the accumulation of ions is close to the electrode surface. However, the specific capacitance can be increased by using aqueous acid or alkaline solution than using organic electrolyte. But there is one advantage why organic electrolyte is wider used that is they can sustain in a high operating voltage due to their energy store is directly proportional to the voltage square and was proved according to:

$$E = \frac{1}{2}CV^2$$

Eq. (2.2)

Where, if the voltage, V is increase the energy stored, E also increases. As a result of electrostatic charge storage, there is no faradic reaction at EDLC electrode. They can be considered as a blocking electrode from an electrochemical point of view. This major difference from batteries means that there is no limitation by the electrochemical kinetic through a polarization resistance.

The absence of faradic reaction eliminates the swelling in the active material that batteries show during charge/discharge cycles. EDLC can sustain millions of cycles whereas batteries survive a few thousand at best. Finally, the solvent of the electrolyte is not involved in the charge storage mechanism, unlike Li-ion batteries where it contributes to the solid-electrolyte interphase when graphite anodes or high-potential cathode are used. This does not limit the choice of solvents and electrolytes with high power performances at low temperatures can be designed for EDLC.