# “Charging and Discharging of Supercapacitor”

## Major Project Report

*Submitted in Partial Fulfillment of the Requirements for the Degree of*

MASTER OF TECHNOLOGY

IN

ELECTRICAL ENGINEERING

(Electrical Power System)

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I **Komalben Rajubhai Patel**, Roll No. **10MEEE10**, give undertaking that the Major Project entitled **"Charging and Discharging of Supercapacitor"** submitted by me, towards the partial fulfillment of the requirements for the degree of Master of Technology in **Electrical Power System, Electrical Engineering**, under Institute of Technology of Nirma University, Ahmedabad, is the original work carried out by me and I give assurance that no attempt of plagiarism has been made. I understand that in the event of any similarity found subsequently with any published work or any dissertation work elsewhere; it will result in severe disciplinary action.

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This is to certify that the Major Project Report entitled **"Charging and Discharging of Supercapacitor"** submitted by **Ms. Komal R. Patel (10MEEE10)**, towards the partial fulfillment of the requirements for the award of degree in **Master of Technology (Electrical Engineering)** in the field of (**Electrical Power System)** of Nirma University is the record of work carried out by her under our supervision and guidance. The work submitted has in our opinion reached a level required for being accepted for examination. The results embodied in this major project, to the best of my knowledge, have not been submitted to any other University or Institution for award of any degree or diploma.

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**- Komal R. Patel**

# Abstract

A new technology, the supercapacitor, has emerged with the potential to enable major advances in energy storage. Supercapacitors are governed by the same fundamental equations as conventional capacitors, but utilize higher surface area electrodes and thinner dielectrics to achieve greater capacitances. This allows for energy densities greater than those of conventional capacitors and power densities greater than those of batteries. As a result, supercapacitors may become an attractive power solution for an increasing number of applications.

A simple resistive capacitive equivalent circuit is sufficient to characterize its internal behavior. The equivalent model consists of three R-C branches. The internal parameters of supercapacitor is explained by using practical charging and discharging characteristics. With the help of internal parameters of supercapacitor the exact behavior of supercapacitor for charging and discharging characteristics can be obtained. By changing these internal parameters the required charging discharging characteristics can be achieved. To replace the battery with supercapacitor it is required to have charging and discharging characteristics of supercapacitor same as battery. To obtain same characteristics as battery with the help of supercapacitor modification in its internal parameters is required. And to get performance of supercapacitor same as battery it is require to have internal parameters of supercapacitor equivalent to battery. To obtain the desired value of internal parameters of supercapacitor modification in material used in supercapacitor is required. By choosing such material which increase the value of electrical series resistance (ESR) the capacitance value will decreases. So compromise has been done between the desirable characteristics and power density

# Nomenclature

| | |
|---|---|
| Capacitance | C |
| Applied voltage | V |
| Voltage across capacitor | $C_v$ |
| Charge on the capacitor plate | q |
| Resistance | R |
| Differential capacitance | $C_{diff}$ |
| Integral capacitance | $C_k$ |
| Fixed capacitor | $C_0$ |
| Variable capacitor | $C_1$ |
| Immediate branch resistance | $R_i$ |
| Immediate branch capacitance | $C_{i0}$ |
| Voltage dependant immediate branch capacitance | $C_{i1}$ |
| Delayed branch resistance | $R_d$ |
| Delayed branch capacitance | $C_d$ |
| Long term branch resistance | $R_l$ |
| Long term branch capacitance | $C_l$ |
| Leakage resistance | $R_{leak}$ |
| Charging current | $I_{ch}$ |
| Transfer current | $I_{tr}$ |

# List of Figures

# List of Tables

# Contents

# Chapter 1

# Introduction

A capacitor is a device that stores energy in an electric field between two charged "plates" for a short period of time. A capacitor is a passive electronic component consisting of a pair of conductors separated by a dielectric (insulator). When there is a potential difference (voltage) across the conductors, a static electric field develops across the dielectric, causing positive charge to collect on one plate and negative charge on the other plate. Energy is stored in the electrostatic field. An ideal capacitor is characterized by a single constant value, capacitance, measured in farads. This is the ratio of the electric charge on each conductor to the potential difference between them. Capacitors are widely used in electronic circuits for blocking direct current while allowing alternating current to pass, in filter networks, for smoothing the output of power supplies, in the resonant circuits that tune radios to particular frequencies and for many other purposes.

## 1.1 Theory of Operation

A capacitor consists of two conductors separated by a non-conductive region. The non-conductive region is called the dielectric or the dielectric medium. In simpler terms, the dielectric is just an electrical insulator. Examples of dielectric mediums are glass, air, paper, vacuum, and even a semiconductor depletion region chemically identical to the conductors. A capacitor is assumed to be self-contained and isolated, with no net electric charge and no influence from any external electric field. The conductors thus hold equal and opposite charges on their facing surfaces, and the dielectric develops an electric field. In SI units, a capacitance of one farad means that one coulomb of charge on each conductor causes a voltage of one volt across the device. The capacitor is a reasonably general model for electric fields within electric circuits. An ideal capacitor is wholly characterized by a constant capacitance C, defined as the ratio of charge Q on each conductor to the voltage V between them:

$$C = \frac{Q}{V} \tag{1.1}$$

Sometimes charge build-up affects the capacitor mechanically, causing its capacitance to vary. In this case, capacitance is defined in terms of incremental changes:

$$C = \frac{dq}{dv} \tag{1.2}$$

## 1.2 Energy Storage

Work must be done by an external influence to "move" charge between the conductors in a capacitor. When the external influence is removed the charge separation persists in the electric field and energy is stored to be released when the charge is allowed to return to its equilibrium position. The work done in establishing the electric field, and hence the amount of energy stored, is given by:

$$\begin{aligned} W &= \int_{q=0}^{Q} V\,dq \\ &= \int_{q=0}^{Q} \frac{q}{C}\,dq \\ &= \frac{1}{2}\frac{Q^2}{C} = \frac{1}{2}\frac{C}{V^2} = \frac{1}{2}VQ \end{aligned}$$

## 1.3 Charging and Discharging of a Capacitor

The charging and discharging of a capacitor is an important aspect of electrical circuits. Both functions are controlled by the circuit time constant, which is proportional to the value of the capacitance.

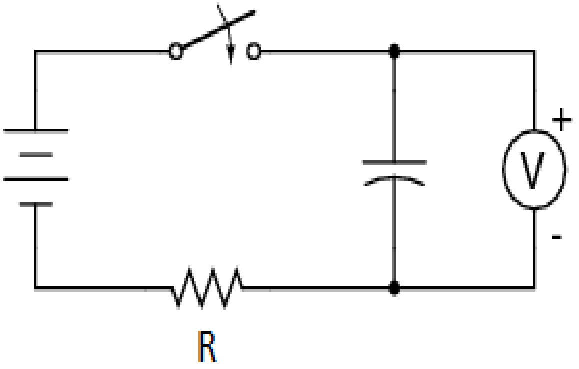


Figure 1.1: Circuit Diagram for Charging a Capacitor

### 1.3.1 Charging of a Capacitor

In order to explain the concept of the charging time constant, a simple RC circuit, shown in Figure 1.1 is used. The capacitor is charged from the battery, when the circuit switch is on. At any instant during the charging, the Kirchhoffs voltage equation is given by:

$$V = v + iR \tag{1.3}$$

$$i = \frac{dq}{dt} = \frac{d}{dt}(Cv) = C\frac{dv}{dt} \tag{1.4}$$

V = Applied voltage,
v = Voltage across the capacitor,
q = Charge on the capacitor plates,
R = Resistance.

$$V = v + RC\frac{dv}{dt} \tag{1.5}$$

Rearranging Equation:

$$\frac{-dv}{(V-v)} = \frac{-dt}{CR} \tag{1.6}$$

Integrating both sides of Equation:

$$log_e(V-v) = -\frac{t}{CR} + K \tag{1.7}$$

where K is the constant of integration. At the start of charging, t=0 and v=0. Then

$$K = log_e V \tag{1.8}$$

. Using this value of K and rearranging Equation:

$$v = V(1 - e^{\frac{-t}{RC}}) = V(1 - e^{\frac{-t}{\tau}}) \tag{1.9}$$

where $\tau$ = RC = time constant

The time constant is defined as the time during which the voltage across the capacitor would have reached its maximum value had it maintained the initial rate of rise.

### 1.3.2 Discharging of a Capacitor

In Figure 1.2 if the switch is open then the source voltage is disconnected, the capacitor circuit is shorted, and it will discharge through the resistance.

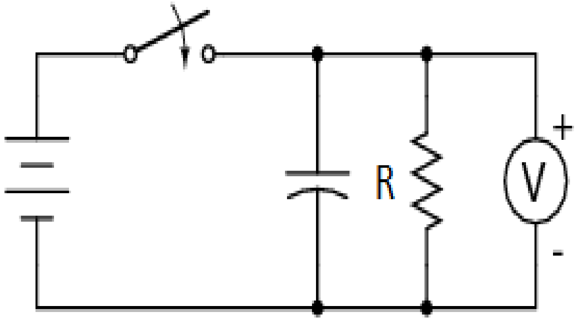


Figure 1.2: Circuit Diagram for Discharging a Capacitor

$$0 = V + RC\frac{dv}{dt}\frac{dv}{v} = -\frac{dt}{RC} \tag{1.10}$$

Integrating both sides of Equation:

$$\int \frac{dv}{v} = \frac{1}{RC} \int dt log_e v = -\frac{t}{RC} + K \tag{1.11}$$

where K is the constant of integration. At the start of discharge, t=0 and v=V. Solving for K and rearranging:

$$v = Ve^{\frac{t}{\tau}} \tag{1.12}$$

The voltage across the capacitor decreases exponentially

**The capacitors can be generally classified as follows:-**

- Electrostatic Capacitor
- Electrolytic Capacitor
- Electro-Chemical Capacitor

1. **Electrostatic Capacitors:-**
   Electrostatic capacitor is typically made of two metal electrodes (parallel plates) separated by a dielectric as shown in Fig. 1.3

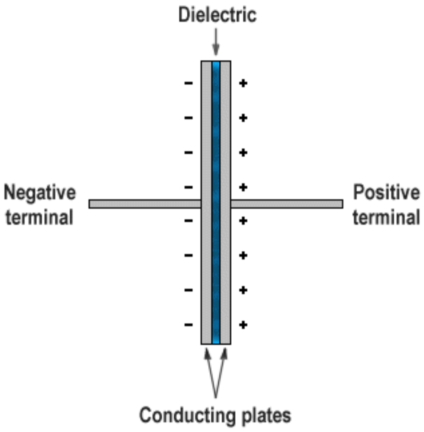


Figure 1.3: Simplified Electrostatic Capacitor

   The dielectric is nothing, but is a non conducting material that is inserted between the parallel plates of the metal electrode material. The operating voltage of the capacitor depends upon the strength of the

$$C = \frac{Q}{V} \tag{1.13}$$

2. **Electrolytic Capacitor:-**
   An electrolytic capacitor is similar in construction to an electrostatic capacitor but has a conductive electrolyte salt in direct contact with the metal electrodes. Aluminum electrolytic capacitors, for example, are made up of two aluminum conducting foils (coated with an insulating oxide layer) and a paper spacer soaked in electrolyte.The oxide layer serves as the dielectric and is very thin, which results in higher capacitance per unit volume than electrostatic capacitors. Electrolytic capacitors have plus and minus polarity due to the oxide layer, which is held in place by the electric field established during charge. If the polarity is reverse-biased, the oxide layer dissolves in the electrolyte and can become shorted and, in extreme cases, the electrolyte can heat up and explode.

3. **Electrochemical Capacitor:-**
   Electrochemical capacitor also use electrolyte solutions but it have greater capacitance per unit volume due to their porous electrode structure compared to electrostatic and electrolytic capacitors. At the macroscopic level, the Electro-chemical capacitor takes the equation:

   $$C = \frac{\epsilon_0 A}{d} \tag{1.14}$$

   to the extreme by having a very high electrode surface-area (A) due to the porous electrodes and very small separation d between the electronic and ionic charge at the electrode surface. The high-energy density of electrochemical capacitor is due to their greater capacitance per unit volume compared to conventional capacitors. Electrochemical capacitors are grouped into two major categories-symmetric and asymmetric.

   - *Symmetric electrochemical capacitor* use the same electrode material (usually carbon) for both the positive and negative electrodes.
   - *Asymmetric electrochemical capacitor* use two different materials for the positive and negative electrodes.

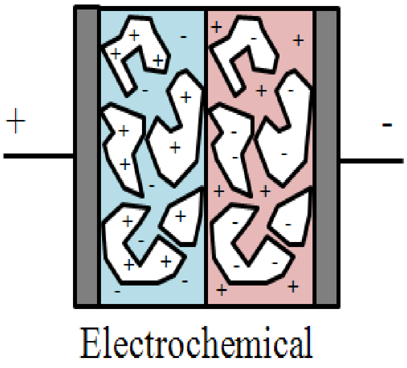


Figure 1.4: Electrochemical Capacitor

## 1.4 Supercapacitor

Supercapacitor is a electro-chemical capacitor. It is also known as a electric double-layer capacitor (EDLC), supercondenser, electrochemical double layer capacitor, or ultracapacitor.

Figure 1.5: Supercapacitor

Compared to conventional electrolytic capacitors the energy density is typically on the order of hundreds of times greater . In comparison with conventional batteries or fuel cells, supercapacitor also have a much higher power density.

Supercapacitors are also able to achieve comparable power densities. Additionally, supercapacitors have several advantages over electrochemical batteries and fuel cells, including higher power density, shorter charging times, and longer cycle life.

## 1.5 Literature Survey

Literature survey play's very important role in the project. Literature survey consists of book referred which gives fundamental knowledge of supercapacitor, its charging and discharging. Paper were taken from IEEE conferences proceeding, journal proceeding and other standard publications. Important information was derived from the major references cited below:

1. **B. E. Conway, "Electrochemical Supercapacitors: Scientific Fundamental and Technological Applications", Kulwar Academic/Plenium Publishers, New York, 1999**[1]
   This book gives the information about the electrochemical supercapacitor, its construction and working principle.

2. **Walter J. Sarjeant,Fellow, IEEE, Jennifer Zirnheld, and Frederick W. MacDougall "Capacitors", IEEE Transaction on plasma science, vol-26, no-5, Octomber 1998**
   The paper[2] represents the background of the capacitors. Over the last decade, significant increases in capacitor performance, especially in reliability and energy/power densities, have been achieved for energy discharge applications. Recent innovations in analysis of aging are introduced for predicting component performance and fault tolerance, especially relevant for very high energy storage applications necessary for next generation simulators, electrically energized fusion research machines, and advanced high power electronics for commercial, industrial, and military applications Emerging power electronics applications in the millisecond and longer time are projected to have a broad application need for electrochemical chemical double layer capacitors, especially for compact sizes as this technology has the potential of achieving energy densities of many 20 kJ/kg for discharge times of tens of seconds. Higher power density prismatic power electronics enables a broad range of applications in the commercial arena in areas such as motor drives, inverters, power quality systems, and mobile power systems.

3. **M Jayalakshmi, K Balasubramanian "Simple Capacitors to Supercapacitors - An Overview", International Journal of Electrochemical Science, 3 (2008)**
   The paper[3] represents review on the renaissance of a conventional capacitor to electrochemical double layer capacitor or super capacitor.The needs of to-days computer world cannot be fulfilled by the conventional capacitors such as electrostatic and electrolytic capacitors as their utility is limited to certain specific applications. Electric double layer capacitor (EDLC) uses carbon as the electrodes and stores charge in the electric field at the interface. It uses either aqueous or nonaqueous electrolyte. It gives high power density but low energy density. So the next generation electrochemical double layer capacitor or super capacitor which uses transition metal oxide as the electrode material along with carbon has been under innovation which is expected to deliver both desirable power and energy densities. In this overview, an attempt to provide information on the chronological order of development of capacitors and the related research work is made.

4. **Alexandru Vasile, Paul Svasta, Andreea Brodeal, Cristina Marghescu, Ciprian Ionescu "EDLC Characterization Platform", IEEE 16th International Symposium for Design and Technology in Electronic Packaging, 2010**
   The Paper [4] shows the Technological improvements have led to the development of low resistivity materials with higher surface which are capable of storing more energy in the form of electrical charge. This technology is a better theoretical understanding of the process of charge transfer, a process that appears in double layer type materials, led to the development of capacitors with high capacitance, known as EDLC(Electrochemical Double-Layer Capacitor). It is helpful for the user to be able to predict the behavior of the EDLC in different conditions. This paper introduces a platform which can be used to obtain the capacitance as a function of voltage, time or temperature.

5. **Donald R. Cahela, Bruce J. Tatarchuk, "Overview of electrochemical double layer capacitor"**
   The paper [5] shows that Electrochemical liquid double layer capacitors (ELCC)are energy storage devices with properties intermediate between batteries and electrolytic capacitors. The commercial success of carbon based ELCC is due to their low cost, extremely high cycle life, and wide range of operating temperatures. They are used mainly for power backup for electronic circuits. ELCC are also used for load lev-

eling applications in electric vehicles and also pulse power applications. Nonaqueous electrolytes, such as organic, solid polymers, and inorganic offer higher energy densities due to the greater decomposition voltages. Advanced ELCC will likely use metal oxides or conductive polymers to provide higher energy and power densities than carbon based ELCC.

6. **Pawan Sharma, T.S. Bhatti "A review on electrochemical double-layer capacitors"**
   The paper [6] represents that various energy storage technologies have been developed in the market for various applications. The electrochemical double-layer capacitor (EDLC) is an emerging technology, which really plays a key part in fulfilling the demands of electronic devices and systems, for present and future. This paper presents the historical background, classification, construction and voltage balancing of the EDLC technology. The applications of EDLC in electrical vehicles, power quality, and others are also discussed and their advantages over other storages technologies are also discussed.

7. **Kuldeep Sahay, Bharti Dwivedi "Supercapacitors Energy Storage System for Power Quality Improvement: An Overview", Journal of electrical system, 2009**
   The paper [7] shows that Power quality problem causes a misoperation or failure of end user equipments. Distribution network, sensitive industrial loads and critical commercial operations suffer from outages and service interruptions which can cost financial losses to both utility and consumers. In India the use of electronic loads is increasing very fast and the gap between demand and the supply have made the reliability and power quality a critical issue. Further there is continuous thrust on optimal utilization of the non-conventional energy sources along with the central power station. In this paper a critical review have been presented chronologically various work to improve quality of power with the help of energy storage device i.e. Supercapacitors energy storage systems for ASD, elevators, UPS, and power distribution system, ride through capability, real power injection and reactive power injection for stabilization of the system.

8. **Philip P. Barker - IEEE Senior Member "Ultracapacitors for Use in Power Quality and Distributed Resource Applications", IEEE, 2002**
   The paper [8] shows that ultracapacitor an emerging storage technology already being used for applications such as DC motor drives, UPS systems and electric vehicles. The latest EC store enough energy to

rival a lead-acid battery and can outperform batteries in several key performance parameters such as power density, cycle life and temperature sensitivity. As the EC technology improves further, an impressive world of applications should emerge. These applications include intermittent renewable energy storage, bulk power system peak shaving, load leveling, and various other distributed resource possibilities. This paper also provided the list of companies who make the supercapacitor.

9. **Domenico CASADEI, Gabriele GRANDI, Claudio ROSSI "A Supercapacitor-Based Power Conditioning System for Power Quality Improvement and Uninterruptable Power Supply", IEEE, 2002**
   The paper [9] shows that Power Conditioning System(PCS) which uses a supercapacitor bank as energy storage device is proposed as a viable solution for improving the quality and the reliability of the electric energy supply. At the same time some other task cane be performed such as reactive power compensation, current harmonics reduction and smoothing of pulsating loads. here they also says that PCS can operate as Uninterruptable Power Supply(UPS) during short time interruption of the grid supply.

10. **L. Zubieta and R. Bonert "Charactrization of Double Layer Capacitor for Power Electronics Application", IEEE, 1998**
    The paper [10] shows that The Double-Layer Capacitor for power applications is a new device. A simple resistive capacitive equivalent circuit is insufficient to characterize its terminal behaviour. Based on physical reasoning, an equivalent circuit is proposed to provide the power electronics engineer with a model for the terminal behavior of the DLC. The equivalent model consists of three RC branches, one of them with a voltage dependent capacitor. A method to identify the circuit parameters is presented. Measurements of carbon-based DLCs for power applications are presented, analyzed and the equivalent circuit response is compared with experimental results.

11. **Y. Y. Yao, D. L. Zhang, D. G. Xu, "Study of Supercapacitor Parameters and Characteristics", International Conference on Power System Technology, IEEE, 2006**
    The paper [11] shows that the supercapacitor is a high efficient and green energy storage component that offers intensive charging and discharging current and performs a perfect reliability and cycling ability. In this paper three topics are discussed for supercapacitor-based

system research and application. Firstly, a comparison among several parameter models of the supercapacitor is presented. In the same time the characteristics of ESR (Equivalent Series Resistance) and EPR (Equivalent Parallel Resistance) are described and studied. Secondly the methods of voltage sharing and overvoltage protection for series connected supercapacitors are discussed, and their advantages and disadvantages are compared with each other. Thirdly a radiation experiment is taken to examine the supercapacitor in its anti-radiation ability for spaceflight application.

12. **Lingling Du, "Study on Supercapacitor Equivalent Circuit Model for Power Electronics Application", $2^{nd}$ International Conference on Power Electronics and Intelligent Transportation System, IEEE, 2009**
The paper [12] presented that with the development of smart grid, energy storage technology will play an increasingly important role in the power system. As an excellent quick energy storage device, supercapacitors have instantaneous power densities more significant than batteries and energy densities larger than dielectric capacitors, and have been widely applied to power quality conditioning equipment, new energy power generation system, etc. However, for the design of supercapacitor based energy storage systems, more insights are needed to analyze the transient response of supercapacitor for many design aspects, such as the design of the voltage balance circuit, the optimization of the energy management scheme, etc.

13. **Zhao Yang, Sun Jianan, Zhang Yicheng, Liang Haiquan, "A New Equivalent Circuit Model of Hybrid Supercapacitor with Aqueous Electrolyte", IEEE, 2011**
The paper [13] presents a new equivalent circuit model of hybrid supercapacitor with aqueous electrolyte which can describe its dynamic characteristic during the process of charging and discharging. Firstly, each component of hybrid supercapacitor with aqueous electrolyte was modeled separately. Then the whole equivalent circuit model was built by combining each component's model. Subsequently the least squares algorithm was adopted to identify the parameters of the model with the real experiment data, which can overcome the drawbacks of existing methods. Finally the equivalent circuit model was simulated with the help of Matlab/Simulink. The result proves the high precision and validity of the new model.

14. **John R. Miller, Patrice Simon, "Supercapacitors: Fundamen-**

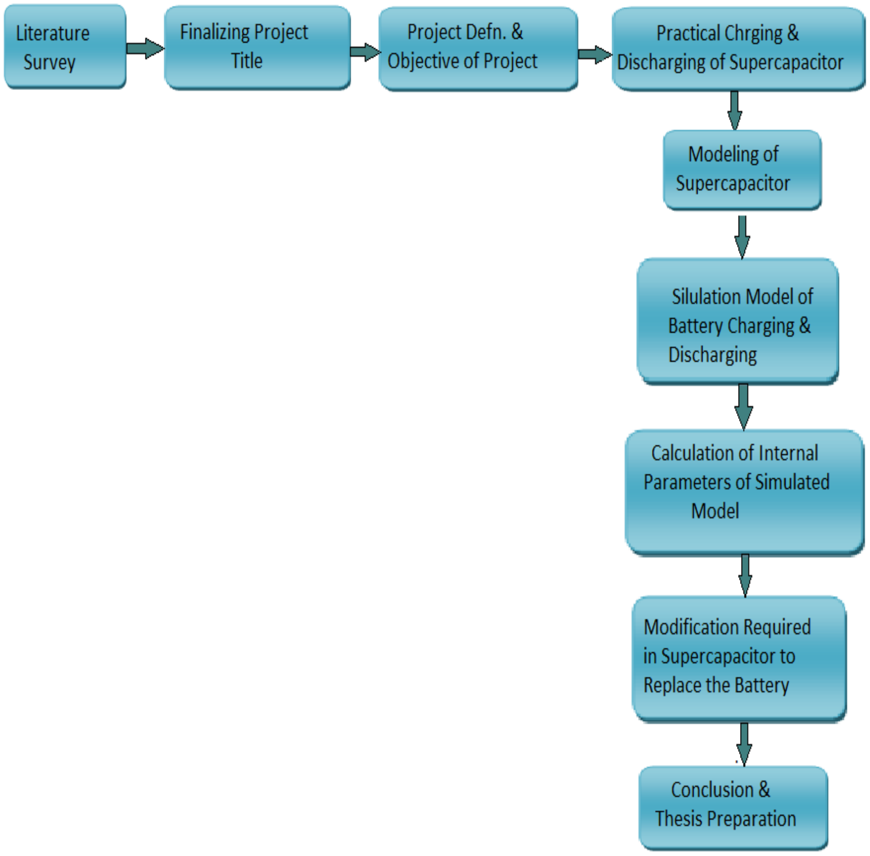
**tals of Electrochemical Capacitor Design and Operation", The Electrochemical Society Interface, Spring, 2008**
The paper [14] shows the basic concept of supercapacitor, history of supercapacitor, technology used in supercapacitor, advantages of supercapacitor, disadvantages of supercapacitor and application of supercapacitor.

15. **V.A. Shah, Jivanadhar A. Joshi, Ranjan Maheshwari, Ranjit Roy, "Review of Ultracapacitor Technology and its Application", Fifteenth National Power Systems Conference (NPSC), IIT Bombay, December 2008**
The paper [15] shows energy storage technologies do not represent energy sources but they provide value added benefits to improve system stability, power quality and reliability of supply. As batteries technologies are low cost ,well established and widely used technology offer disadvantages like volume, weight, poor power density, high internal resistance, poor transient response, they are not suitable for some transient application or where volume and size are an important issue. On the other hand due to advancement in the material and other technology, Ultracapacitors offers high power density, fast transient response, low Wight, low volume and low internal resistance which make them suitable for pulsed load application. In this paper we will review some of the present application of the Ultracapacitor(UC) in the field of low power and high power applications like telecommunication devices, automatic meter reading system, load leveling on the electrical power system, maintaining continuity of power during outages, improving profitability in high energy system, enhance transmission capacity of the transmission grid in high power application, various power quality and backup related uses such as UPS system and power stabilization, to improve reliability of wind turbine pitch system. Simple ultracapcitor and battery model with pulse load is simulated in MATLAB-SIMULINK without and with DC to DC buck boost converter to prove ultracapacitor as a peak power supply device.

## 1.6 Objective of the Project

The objective of this project is to explore the possibility of application of supercapacitor for replacement battery for energy storage. The purpose of the project is to model the supercapacitor for energy storage application and simulate it for battery replacement. This will form basis to redesign the supercapacitor or combination of supercapacitor for energy storage application. In this project how to replace the battery with supercapacitor and which modification is required is proposed.

## 1.7 Project Planning



## 1.8 Thesis Organization

**Chapter 1** is the introduction of the project, main objective of the project done, selecting the problems to be solved, planning of the complete work to be done, shows various papers referred to understand the basics of the topic and develop an application using the idea of the earlier research done in that area.

**Chapter 2** describes about the basic knowledge of supercapacitor, how its working, its construction, advantages, disadvantages and application of supercapacitor.

**Chapter 3** describes the main two characteristics of supercapacitor: charging and discharging. The identification of equivalent model parameters of supercapacitor.

**Chapter 4** gives the experimental results and simulation results of supercapacitor. By using this experimental results calculation parameters of supercapacitor has to be done.

**Chapter 5** includes the problems occurs in the battery, MATLAB simulink model for battery charging and discharging. How to replace the battery with supercapacitor and calculation of internal parameters of battery.

**Chapter 6** shows which parameters affects the performance characteristics of supercapacitor and the modification required to replace the battery with supercapacitor.

# Chapter 2

# Supercapacitor

## 2.1 Introduction

Supercapacitors are also known as ultracapacitors, electro-chemical double layer capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors. In doing so, supercapacitors are able to attain greater energy densities while still maintaining the characteristic high power density of conventional capacitors.

Supercapacitors have the ability to store greater amounts of energy than conventional capacitors, and are able to deliver more power than batteries. The performance improvement for a supercapacitor is shown in Fig 2.1, a graph termed a “Ragon plot”. This graph shows the power density of various energy storage devices, measured along the vertical axis,versus their energy densities, measured along horizontal axis. In Fig 2.1, it is seen that supercapacitors occupy a region between conventional capacitors and batteries. Despite greater capacitances than conventional capacitors, supercapacitors have yet to match the energy densities of mid to high-end batteries and fuel cells.

Besides bridging the gap between capacitors and batteries, supercapacitors also possess a number of desirable qualities that make them an attractive energy storage option. The mechanisms by which supercapacitors store and release charge are completely reversible, so they are extremely efficient and can withstand a large number of charge/discharge cycles. They can store or release energy very quickly, and can operate over a wide range of temperatures.

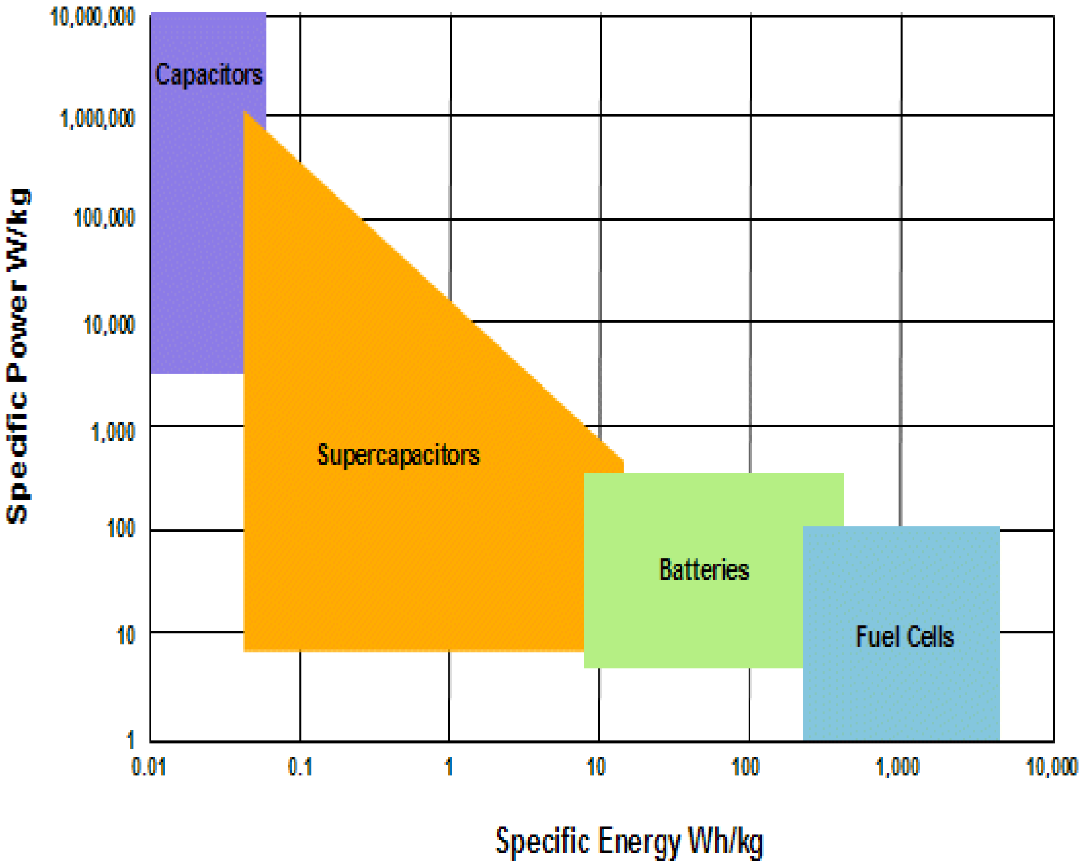


Figure 2.1: Ragone Plot of Various Energy Storage Devices

### 2.1.1 Historical Background

- The first supercapacitor based on a double layer mechanism was developed in 1957 by General Electric using a porous carbon electrode [Becker, H.I., “Low voltage electrolytic capacitor”, U.S. Patent 2800616, 23 July 1957]. It was believed that the energy was stored in the carbon pores and it exhibited ”exceptionally high capacitance”, although the mechanism was unknown at that time.

- It was the Standard Oil Company, Cleveland (SOHIO) in 1966 that patented a device that stored energy in the double layer interface [Rightmire, R.A., “Electrical energy storage apparatus”, U.S. Patent 3288641, 29 Nov 1966.].

- Standard Oil of Ohio gave the licensing to NEC, which in 1978 marketed the product as a supercapacitor.

- The idea of replacing batteries with capacitors in conjunction with novel alternative energy sources became a conceptual umbrella of "Green Electricity" (GEL) Initiative, introduced by Dr. Alexander Bell

- One particular successful implementation of the "GEL Initiative" concept was introduced in the article: "Muscle power drives battery-free electronics" (Alexander Bell, EDN, 11/21/2005), describing muscle-driven autonomous, environmentally-friendly solution, which employs a multi-Farad supercapacitor (hecto- and kilo-Farad range capacitors are now widely available) as intermediate energy storage to power the variety of portable electrical and electronic devices (MP3 players, AM/FM radios, flashlights, cell-phones, emergency kits, etc.).

- As the energy density of supercapacitors (or ultracapacitors - these two terms can be used interchangeably) is bridging the gap with batteries, it could be expected that in the near future the automotive industry will implement ultracapacitors as a replacement for chemical batteries.

### 2.1.2 Current Commercial Activity

A number of companies around the world currently manufacture supercapacitors in a commercial capacity.

- NEC and Panasonic in Japan have been producing supercapacitor components since the 1980s.

- In the U.S.A Epcos, ELNA, AVX, and Cooper produce components, while Evans and Maxwell produce integrated modules that include voltage balancing circuitry.

- Kold Ban International markets a supercapacitor module designed specifically for starting internal combustion engines in cold weather.

- Cap-XX in Australia offers a range of components, as does Ness Capacitor Co. in Korea.

- In Canada, Tavrima manufactures a range of modules.

- ESMA in Russia sells a wide variety of EDLC modules for applications in power quality and for starting internal combustion engines.

## 2.2 Supercapacitor Construction

We clearly shown from Fig 2.2 that there is a major construction difference between conventional capacitor and electrochemical capacitor.In a conventional capacitor, energy is stored by the removal of charge carriers, typically electrons, from one metal plate and depositing them on another. This charge separation creates a potential between the two plates, which can be harnessed in an external circuit. The total energy stored in this fashion increases with both the amount of charge stored and the potential between the plates. The amount of charge stored per unit voltage is essentially a function of the size, the distance, and the material properties of the plates and the material in between the plates (the dielectric), while the potential between the plates is limited by the breakdown field strength of the dielectric. The dielectric controls the capacitor's voltage. Optimizing the material leads to higher energy density for a given size of capacitor.

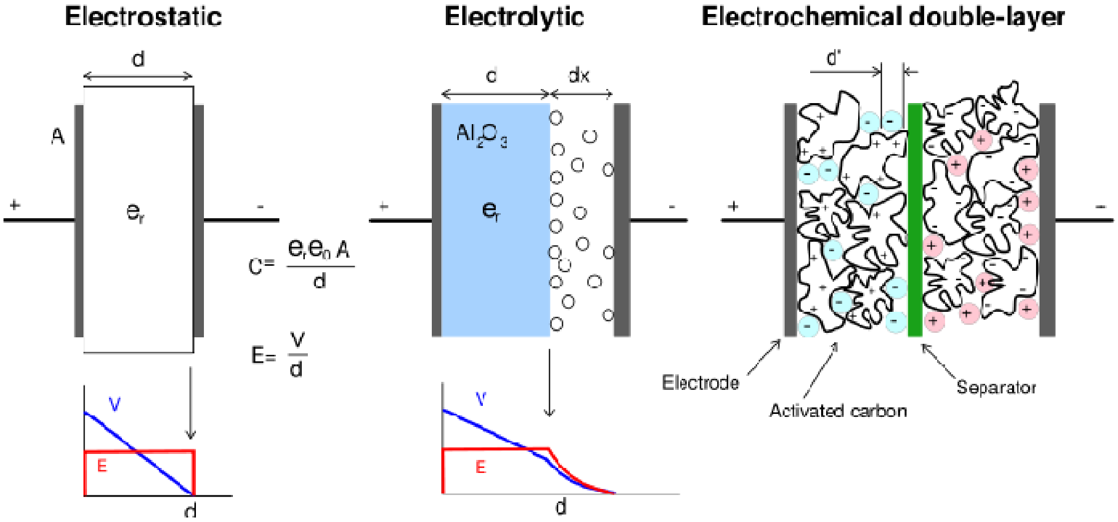


Figure 2.2: Comparison of Construction Diagrams of Three Capacitors

Supercapacitors do not have a conventional dielectric rather than two separate plates separated by an intervening insulator, these capacitors use virtual plates that are in fact two layers of the same substrate. Their electrochemical properties, the so-called "electrical double layer", result in the effective separation of charge despite the vanishingly thin (on the order of nanometers) physical separation of the layers. The lack of need for a bulky layer of dielectric, and the porosity of the material used, permits the packing of plates with much larger surface area into a given volume, resulting in high capacitances in practical-sized packages.

In an electrical double layer, each layer by itself is quite conductive, but the physics at the interface where the layers are effectively in contact means that no significant current can flow between the layers.

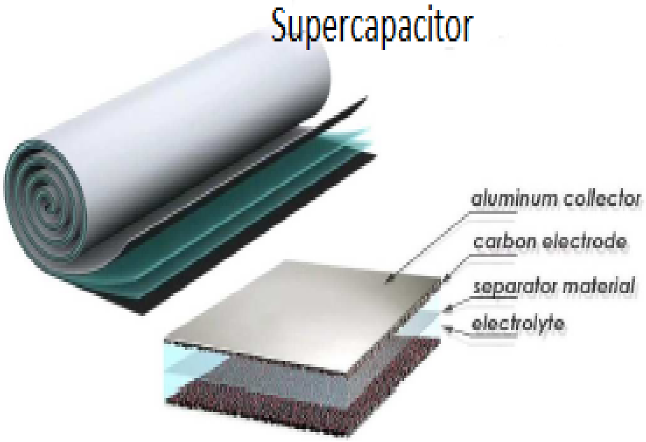


Figure 2.3: Various Parts of Supercapacitor and its Position

However, the double layer can withstand only a low voltage, which means that electric double-layer capacitors rated for higher voltages must be made of matched series-connected individual supercapacitors, much like series-connected cells in higher-voltage batteries.

### 2.2.1 Electrode Material

Selection of electrode materials plays a crucial role in determining the electrical properties of a supercapacitor. Double-layer charge storage is a surface process, and the surface characteristics of the electrode greatly influence the capacitance of the cell. Carbon is the most widely used electrode material, but considerable research is being conducted into metal-oxides and conducting polymers.

- **Carbon:-**Development of the electrochemical capacitor began. Today, it is still an attractive option because of its low cost, availability, and long history of use. Carbon electrodes can take a number of manufactured forms such as foams, fibres, and nanotubes.

- **Conducting Polymers:-**Conducting polymers store and release charge through redox processes. When oxidation occurs, (also referred to as doping), ions are transferred to the polymer backbone. When reduction occurs (dedoping) the ions are released back into the solution. Charging in conducting polymer films therefore takes place throughout the bulk volume of the film, and not just on the surface as is the case with carbon. This offers the opportunity of achieving high levels of specific capacitance.

- **Metal-Oxides:-**Metal-oxides present an attractive alternative as an electrode material because of high specific capacitance and low resistance, possibly making it easier to construct high-energy, high-power supercapacitors. Extensive research into rutheniumoxides has been conducted for military applications, where cost is presumably less of an issue than it is for commercial ventures.

### 2.2.2 Electrolytes

The choice of electrolyte in an supercapacitor is as important as the choice of electrode material. The attainable cell voltage of a supercapacitor will depend on the breakdown voltage of the electrolyte, and hence the possible energy density (which is dependent on voltage) will be limited by the electrolyte. Power density is dependent on the cells ESR, which is strongly dependent on electrolyte conductivity. There are currently two types of electrolyte in use in supercapacitor: *organic and aqueous.*

- Organic electrolytes are the most commonly used in commercial devices, due to their higher dissociation voltage. Cells using an organic electrolyte can usually achieve voltages in the range of 2 2.5 V. The resistivity of organic electrolytes is relatively high, however, limiting cell power.

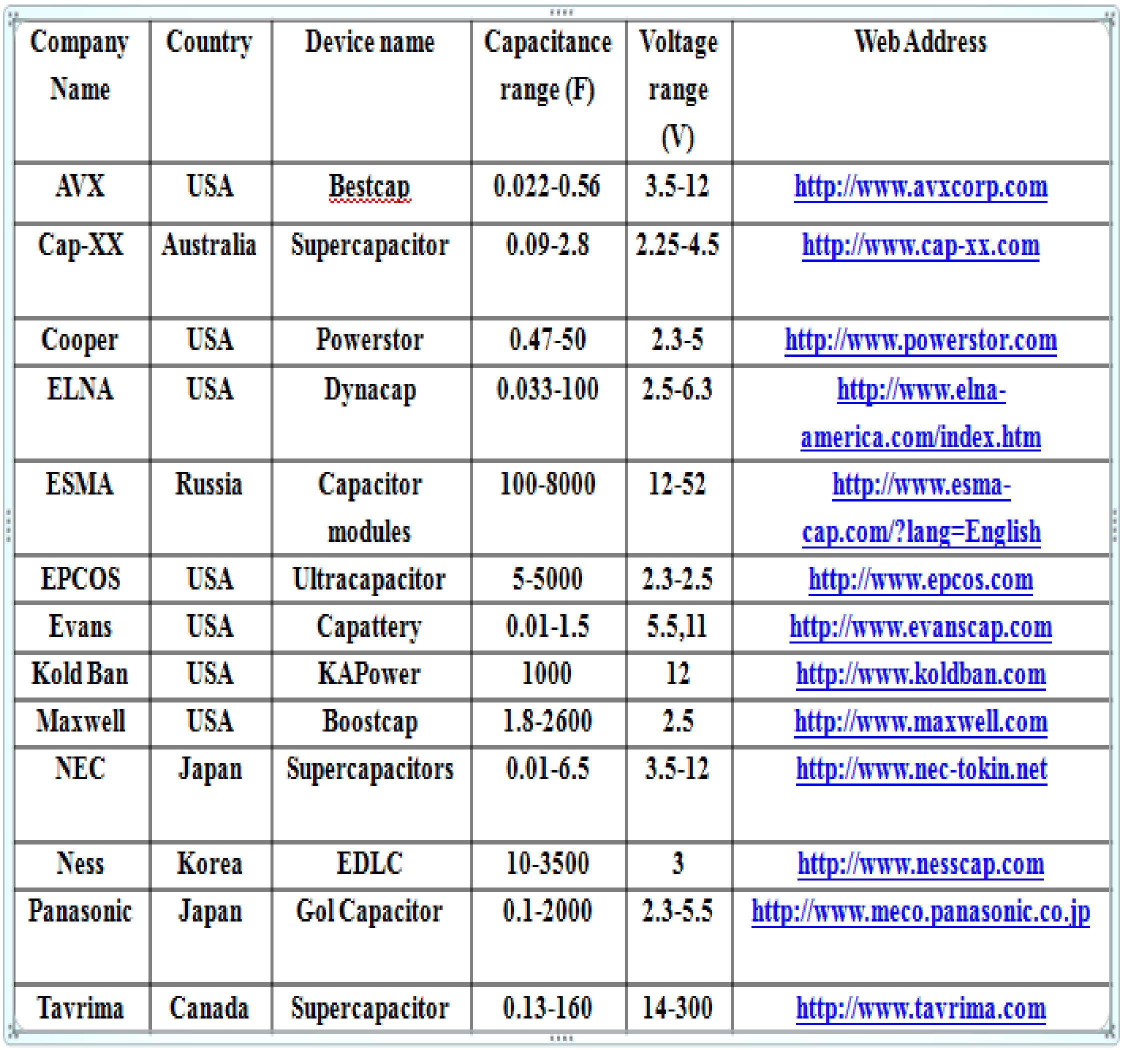
- Aqueous electrolytes have a lower breakdown voltage, typically 1 V, but have better conductivity than organic electrolytes.

The capacitance of an supercapacitor is greatly influenced by the choice of electrolyte. The ability to store charge is dependent on the accessibility of the ions to the porous surface-area, so ion size and pore size must be optimal. The best pore size distribution in the electrode depends upon the size of the ions in the electrolyte, so both electrode and electrolyte must be chosen together.

### 2.2.3 Separator

The separator prevents the occurrence of electrical contact between the two electrodes, but it is ion-permeable, allowing ionic charge transfer to take place. Polymer or paper separators can be used with organic electrolytes, and ceramic or glass fibre separators are often used with aqueous electrolytes. For best supercapacitor performance the separator should have a high electrical resistance, a high ionic conductance, and a low thickness.

### 2.2.4 Summary of Supercapacitor Construction



| Company Name | Country | Device name | Capacitance range (F) | Voltage range (V) | Web Address |
|---|---|---|---|---|---|
| AVX | USA | Bestcap | 0.022-0.56 | 3.5-12 | http://www.avxcorp.com |
| Cap-XX | Australia | Supercapacitor | 0.09-2.8 | 2.25-4.5 | http://www.cap-xx.com |
| Cooper | USA | Powerstor | 0.47-50 | 2.3-5 | http://www.powerstor.com |
| ELNA | USA | Dynacap | 0.033-100 | 2.5-6.3 | http://www.elna-america.com/index.htm |
| ESMA | Russia | Capacitor modules | 100-8000 | 12-52 | http://www.esma-cap.com/?lang=English |
| EPCOS | USA | Ultracapacitor | 5-5000 | 2.3-2.5 | http://www.epcos.com |
| Evans | USA | Capattery | 0.01-1.5 | 5.5,11 | http://www.evanscap.com |
| Kold Ban | USA | KAPower | 1000 | 12 | http://www.koldban.com |
| Maxwell | USA | Boostcap | 1.8-2600 | 2.5 | http://www.maxwell.com |
| NEC | Japan | Supercapacitors | 0.01-6.5 | 3.5-12 | http://www.nec-tokin.net |
| Ness | Korea | EDLC | 10-3500 | 3 | http://www.nesscap.com |
| Panasonic | Japan | Gol Capacitor | 0.1-2000 | 2.3-5.5 | http://www.meco.panasonic.co.jp |
| Tavrima | Canada | Supercapacitor | 0.13-160 | 14-300 | http://www.tavrima.com |

Figure 2.4: Commercially Available Supercapacitors and its Properties

The functional components of a supercapacitor crucial to its operation are the electrodes, electrolyte, and separator. The surface properties of the electrode material have a significant impact on specific capacitance, as do the chemical properties if pseudocapacitance is exhibited. While activated carbon is currently the most commonly used material, conducting polymers present a possible future alternative. Metal-oxides may also become viable one day. The choice of electrolyte has a significant impact on achievable power, as well as influencing specific capacitance. Aqueous electrolytes have better conductivity than organic electrolytes, but have a low breakdown voltage.

## 2.3 Working Principle of Supercapacitor

Supercapacitor devices consist of two electrodes to allow a potential to be applied across the cell, and there are therefore two double-layers present, one at each electrode/electrolyte interface.

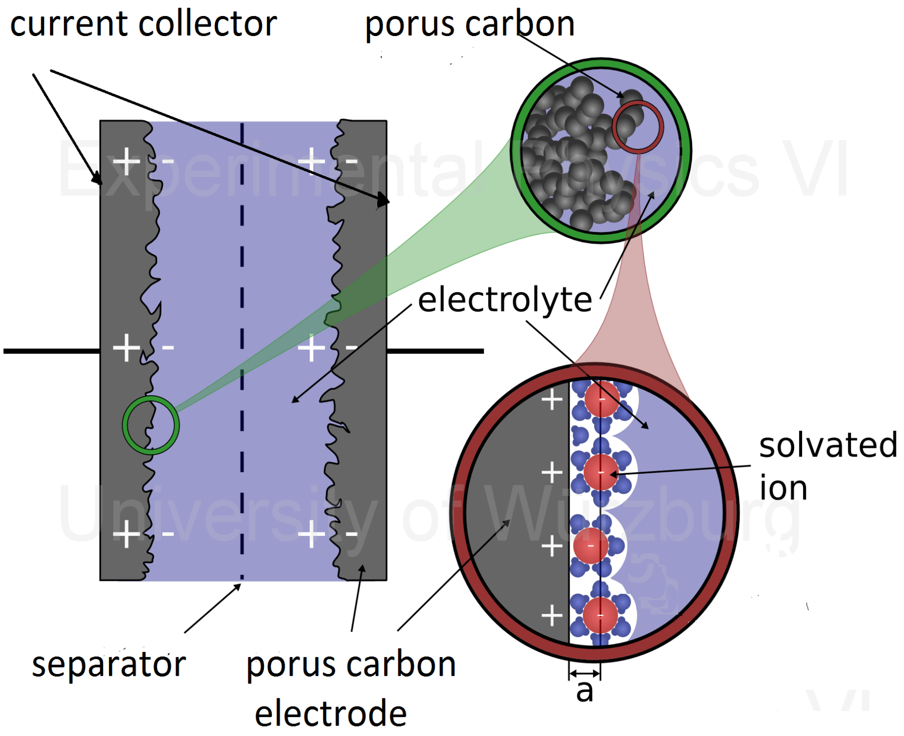


Figure 2.5: Conceptual Diagram of Supercapacitor Construction

An ion-permeable separator is placed between the electrodes in order to prevent electrical contact, but still allows ions from the electrolyte to pass through (Fig. 2.5).The electrodes are made of high effective surface-area materials such as porous carbon or carbon aerogel in order to maximize the surface-area of the double-layer. High energy densities are therefore achievable in supercapacitors due to their high specific capacitance, attained because of a high electrode/electrolyte interface surface-area and a small charge layer separation of atomic dimensions.

Supercapacitors are able to be developed as energy storage devices based on an understanding of the physical processes that take place. supercapacitors operate on principles similar to those of conventional electrostatic capacitors. A conventional capacitor stores energy in the form of electrical charge, and a typical device consists of two conducting materials separated by a dielectric. When an electric potential is applied across the conductors electrons begin to flow and charge accumulates on each conductor. When the potential is removed the conducting plates remain charged until they are brought into contact again, in which case the energy is discharged. The amount of charge that can be stored in relation to the strength of the applied potential is known as the capacitance, and is a measure of a capacitors energy storage capability.

Supercapacitors store electrical charge in a similar manner, but charge does not accumulate on two conductors separated by a dielectric.

Instead the charge accumulates at the interface between the surface of a conductor and an electrolytic solution(Fig 2.3). The accumulated charge hence forms an electric double-layer, the separation of each layer being of the order of a few Angstroms. An estimate of the capacitance can be obtained from the double-layer model, in which the double-layer consisted of two charge mono layers. One layer forms on the charged electrode, and the other layer is comprised of ions in the electrolyte.

Supercapacitors utilize an electrochemical double-layer of charge to store energy. As voltage is applied, charge accumulates on the electrode surfaces. Following the natural of unlike charges, ions in the electrolyte solution diffuse across the separator into the pores of the electrode of opposite charge. However, the electrodes are engineered prevent the recombination of the ions. Thus, a double-layer of charge is produced at each electrode. These double-layers, coupled with an increase in surface area and a decrease in the distance between electrodes, allow supercapacitors to achieve higher energy than conventional capacitors.

Because there is no transfer of charge between electrolyte and electrode, there are no chemical or composition changes associated with non-Faradaic processes. For this reason, charge storage in supercapacitors is highly reversible, which allows them to achieve very high cycling stabilities. Superca-

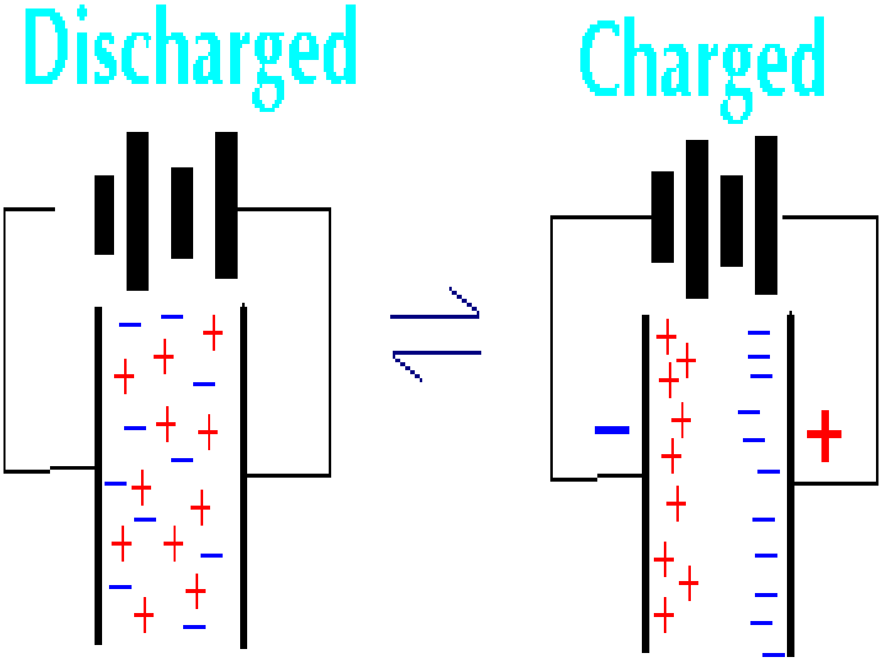


Figure 2.6: Supercapacitor Charge Storage Mechanism

pacitors generally operate with stable performance characteristics for a great many charge-discharge cycles, sometimes as many as 106 cycles. On the other hand, electrochemical batteries are generally limited to only about 103 cycles. Because of their cycling stability, supercapacitors are well suited for applications that involve non-user serviceable locations, such as deep sea or mountain environments.

### 2.3.1 Charge Separation in Supercapacitor

The charging/discharging occurs in an ion adsorption layer formed on the electrodes of activated carbon. The activated carbon fiber electrode are impregnated with an electrolyte where positive and negative charges are formed between the electrode and impregnant. The electric double layer formed become and insulator until a large enough voltage is applied and current begins to flow. The magnitude of voltage where charges begins to flow. The magnitude of voltage where charges begin to flow is where the electrolyte begins to break down. This is called decomposition voltage. Figure 2.7 shows the charge separation in activated carbon electrode material.

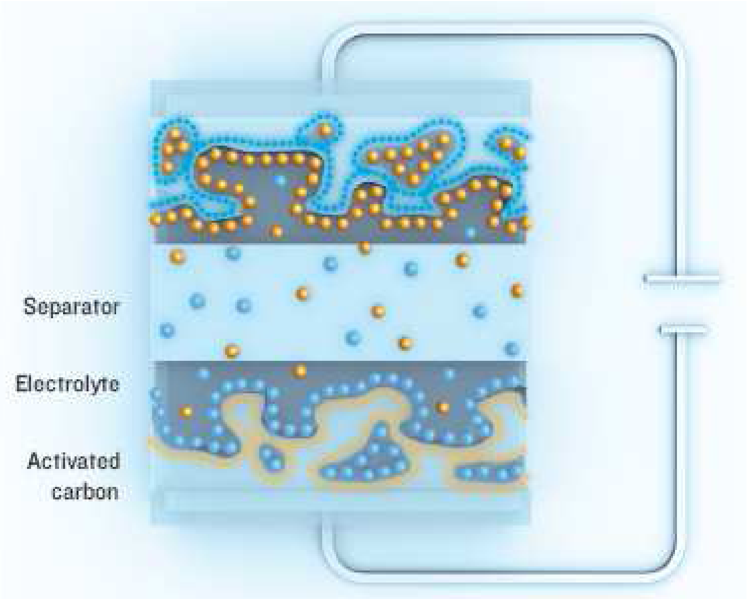


Figure 2.7: Charge Collection on Activated Carbon Electrode Material

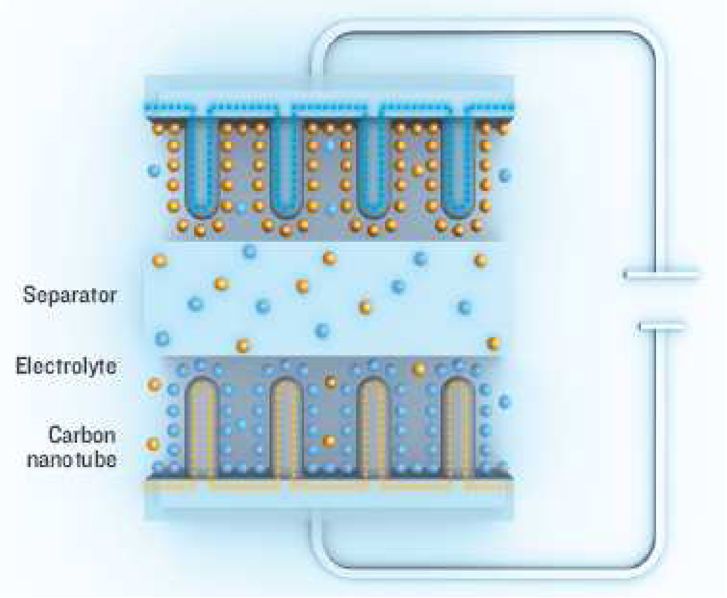


Figure 2.8: Charge Collection on Carbon Nano Tubes Electrode Material

Fig 2.8 shows the charge separation in carbon nano tubes electrode material.

## 2.4 Advantages of Supercapacitor

- High power density.
- Simple charging methods. No special charging or voltage detection circuits required.
- Very fast charge time in seconds.
- Cannot be overcharged.
- Extermely low internal resistance (ESR) and consequent high cycle efficiency (95% or more ) and extremely low heating levels.
- Long cycle life of more than 500,000 cycles.
- No chemical actions.
- 10 to12 year life.
- Small physical size

## 2.5 Disadvantages of Supercapacitor

- Linear discharge voltage characteristic. Fig 2.9 shows the linear dis-

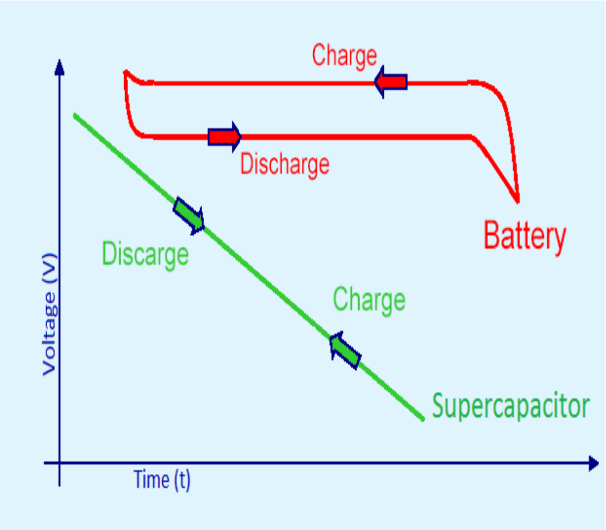


Figure 2.9: Linear Discharge Voltage Characteristics of Supercapacitor

charge voltage characteristic of supercapacitor, which shows that voltage decreases as time increases for supercapacitor and for battery voltage remains constant as time increases.

- Prevents use of all the available energy in some applications.
- High self discharge rate. Much higher than batteries.
- Low energy density-typically holds one-fifth to one-tenth the energy of an electrochemical battery.
- Very low internal resistance allows extremely rapid discharge when shorted, resulting in a shock hazard similar to any other capacitor of similar voltage and capacitance.

## 2.6 Application of Supercapacitor

- Energy smoothing
- Peak power saving
- Power quality improvement
- Momentary load device
- Motor startup capacitors for large engines in tanks and Submarines.
- Regenerative braking
- Automated meter reading

# Chapter 3

# Modeling of Supercapacitor

## 3.1 Supercapacitor Characteristics

### 3.1.1 Charging

The supercapacitors can be charged by either the constant current method or the constant power method.

- **Constant Current Charging:-** The supercapacitor is charged by a constant current input from the converter. The converter chosen can be either a buck or a boost converter. In most of the applications a buck converter is preferred because of the continuous output charge current.

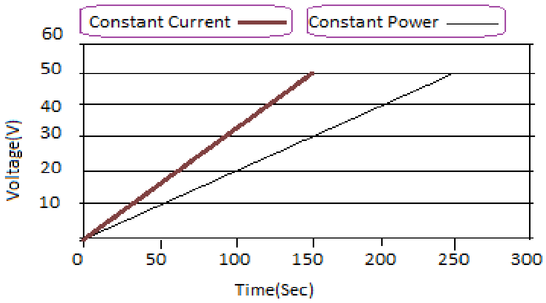


Figure 3.1: Comparison Between the Charging Times for Constant Current and Constant Power

- **Constant Power Charging:-** In this method current from the source is drawn at a constant voltage and used for charging the supercapacitors. This method transfers all the available charge from the source to the supercapacitors quickly. When compared to a constant current charging method, the time taken for charging in a constant power method is much higher. Figure 3.1 shows the time taken to charge the supercapacitor by constant current as well as constant power charging.

### 3.1.2 Discharging

Figure 3.2 gives the discharge profile of the supercapacitor at a constant current. In the graph, $V_t$ represents the terminal voltage of the supercapacitor and $T_d$ represents the discharge time. The figure shows the impact of the capacitive as well as the resistive components on the discharge voltage curve of the supercapacitor. The operating voltage drops steeply initially, due to the equivalent series resistance after which the decrease in the voltage is gradual as a result of the capacitive element in the circuit. The time taken by the voltage to reach a minimum operating voltage is said to be the discharge time of the supercapacitor.

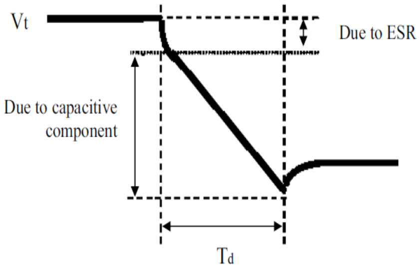


Figure 3.2: Discharge Curve of an Ultracapacitor

## 3.2 Modeling of Supercapacitor

Modeling the supercapacitors using a single resistance and a single capacitance is insufficient to represent adequately the electrical behavior of the devices. In this experiment a constant current of two amperes was used to charge the supercapacitor; then, one hundred seconds pass without current application, and finally, the capacitor was discharged using a constant current of two amperes.

Main objective of this experiment is the development of an equivalent model for the supercapacitor that should be based on two criteria: First, the mode1 should be as simple as possible but describing the terminal behavior, over a time span of 30 minutes, accurately enough for design and application purposes. Second, the model parameters should be calculated based on the results of a series of measurements at the device terminals in a repeatable and clear procedure.

The selection of the equivalent model is based on two criteria : physical reasons related to the double-layer and the supercapacitor construction and practical considerations resulting from the terminal model objective[10].

## 3.3 Physical Facts Leading to the Model

### 3.3.1 Time Behavior of the Supercapacitor

The fact that charge is stored in the double-layer when external voltage is applied. The flow of charges across the interface is not an instantaneous process. It depends on the ion mobility, environmental conditions and several other factors. In addition, the cross of electrical charges is followed by a series of charge distribution processes, and dipole orientation which take a considerably long time .

Based on the last factor, the capacitance of the physically represented by a model which consists of an of parallel branches each one composed of a resistor in series. The time constant of each branch is longer double-layer is in finite number and a capacitor with respect to the previous one producing a general device with a complicate internal behavior.

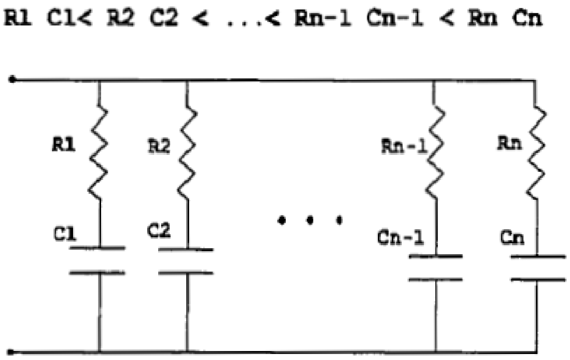


Figure 3.3: General Supercapacitor Model

This model as a representation of the double-layer has several factors favorable to the objective of this research:

- Use of simple electrical components to describe the double layer ( Resistors and Capacitors ) .
- Representation of the double-layer as a terminal device.

But this representation of the supercapacitor is not adequate for the characterization due to the following reasons:

- The presence of an infinite number or even a very large number of branches makes the model too complex for practical use and excessive effort is necessary to represent the model mathematically.

Based on the previous considerations, the selected model will use the RC structure of the model in Figure 3.3 but with a finite number of branches. The number of branches should be the smallest number possible keeping a good level of accuracy when the capacitor performance is simulated.

### 3.3.2 Dependance of the Capacitance on the Potential Difference

The physics of the double-layer showed that the capacitance of the double-layer is not a constant but depends on the potential difference. This has to be included in the equivalent model in order to get accurate results. The physical study of the double-layer is that the differential capacitance is linearly dependent on the potential. Therefore, the capacitance of the supercapacitor model will include a fixed capacitor $C_0$ in parallel with a variable capacitor ($C_1$) linearly dependant on the voltage.

$$C_{diff}(V) = C_0 + C_1 * V \tag{3.1}$$

Based on the differential capacitance, an integral capacitance $C_k$,may be defined as the ratio between the total charge delivered to the capacitor to the voltage across the capacitor terminals.

$$C_k = \frac{Q_{total}}{V_c} \tag{3.2}$$

The integral capacitance may be calculated from the differential capacitance by following equation:

$$C_k = \frac{1}{2}\int_0^V C_{diff} dV \tag{3.3}$$

In terms of $C_0$ and $C_1$ the integral capacitance can be expressed as:

$$C_k = C_0 + \frac{C_1}{2}V \tag{3.4}$$

Although the integral capacitance appears to be the definition used in the specification of the capacitor value for the supercapacitor, the differential capacitance ($C_{diff}$) of the supercapacitor will be the definition used in the modeling of the supercapacitors. That is because the differential capacitance defines the "instantaneous" capacitance of the supercapacitor during any charge action independently of the previous charge cycles applied.

### 3.3.3 Double-layer Leakage

Another characteristic of the double-layer is the self discharge process present in the capacitor as a result of electrochemical reactions occurring across the interface when charge separation is present. This self-discharge or leakage means that part of the charge stored in the double-layer is lost internally and may not be recovered. The leakage effect is represented in the equivalent model by a resistance in parallel with the resistance-capacitance branches. This resistance from now will be called $R_{leak}$.

### 3.3.4 Inductive Effect in the Capacitor

Although specific details of the supercapacitor construction are not available, the general construction process explained in chapter one mentioned that the aluminum foils are wound in spiral. Thus, it is possible to have some inductance inside the device which may affect the slew rate performance of the device. Therefore, a series inductance is included in the equivalent model. Based on the previous physical reasoning, the general structure of the equivalent model as shown in Figure 3.4 is now proposed. Further properties of the proposed model are based on extensive experimentation and the conclusions of this experimentation will be presented in the next section.

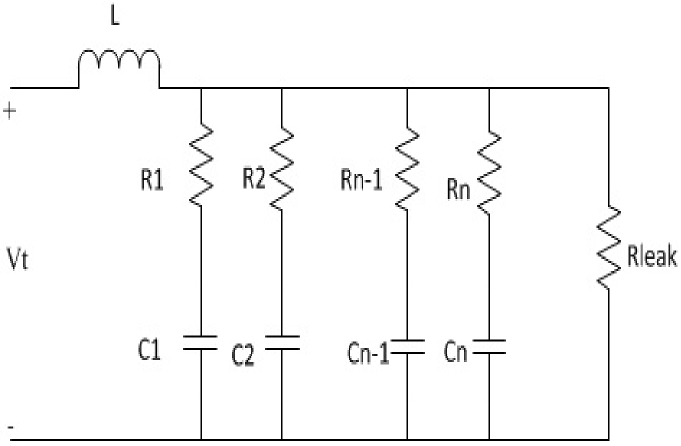


Figure 3.4: Proposed Model Structure

## 3.4 Practical Consideration

With the general structure of the equivalent model selected, the question about the number of branches needed to represent accurately the supercapacitor should be answered. For a practical model, the number of branches should be limited to the smallest number possible. The use of three branches to represent the supercapacitor behavior is proposed. Extensive experimental observations have influenced the selection of the number of branches of the equivalent model and in the model structure; these observations are commented on next:

1. Charging a fully discharged capacitor (all the equivalent internal capacitances with zero voltage) with controlled constant current up to the rated voltage and measuring the time required to this charge allow to calculate an integral capacitance of the device. The integral capacitance measured hardly changes if currents in the ratio of 1 to 10 are used for charging. This result indicates that the fastest branch may be assumed to have a very short time constant compared to further branches. The selection of a much bigger time constant for one branch in respect to the previous one makes the identification and calculation of the parameters simpler.

2. Although the internal time behavior of the supercapacitor may include processes with time constants of hours, the interest in power electronics is restricted to relatively short time or high power applications; so that

the model selected should follow with greater accuracy the capacitor response thirty minutes after the start of a charge or discharge process.

3. The physical model composed by an infinite number of branches with different time constants gives a clear impression that reactions with time constants between a few seconds and several hours occur inside the device. Observing the terminal voltage after a charge cycle confirms the previous impression and indicate that the charge is redistributed among the different branches. This distribution over the time of interest (30 minutes) should be represented in the model by the response of additional branches. One branch is insufficient to match the capacitor behavior in this wide time span; therefore, two branches with different time constant are proposed to represent the internal charge distribution. The second branch has a time constant in the order of few minutes and the third branch has a time constant in the order of tens of minutes.

4. The selection of the three voltage dependant branches increases the complexity of the parameter identification. In addition, extensive measurements of the internal charge distribution process at different voltages indicate that the assumption of only one branch voltage dependant does not introduces an appreciable error if the capacitor voltage is kept over 1.5 volts. As in the power applications the supercapacitors will not be discharged to very low voltages the dependence of the capacitance with the voltage is assigned to the first branch only.

Based on the previous physical and experimental observations, the proposed model consists of three branches in parallel each one composed of the connection in series of a resistor and a capacitor. In addition, the model includes a leakage resistor in parallel with the three branches and a series inductor in the input. The capacitance of the first branch is divided in a fixed part and a voltage dependant part. The first branch has the smallest time constant. The time constant will be given by the capacitor response to a fast charge process, in other words a charge action with high current. Using the rated values, the time constant expected for this branch is in the order of few seconds. From this point the first branch and its components (R and C) will be named ”immediate” and denoted with the letter ’i’. The name ”immediate” is given because this branch will respond immediately to the charge action. The second branch has a medium time constant, The time constant selected for this branch is between one and two minutes. That means that the time constant for the second branch is at least ten times larger than the time constant for the immediate branch. From this point the second branch will be named "delayed" branch and its elements denoted with the letter 'd'. The third branch will be named "long term" branch and denoted with the letter 'i'. This branch has a time constant of more than 10 minutes which makes it much s lower than the delayed branch. Figure 3.5 presents the detailed proposed model of the carbon based double layer capacitor.

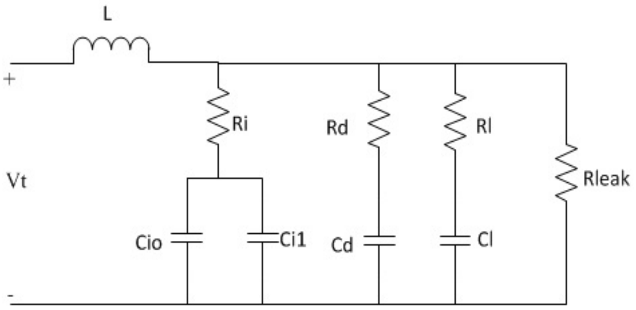


Figure 3.5: Detailed Proposed Model

## 3.5 Identification of Equivalent Model Parameters

The parameter measurement procedure is consists of a controlled current source and a voltage measurement system. However, it is convenient to indicate now that the current source has a very short maximum rise time compared with the typical charge times for the supercapacitors. Furthermore, the current source can be turned on or off at precise intervals in time, by mean of the controller board timing, or by the instant at which the supercapacitor terminals reach some pre-fixed value. However, based on the justified assumption of three branches with distinct time constants the principles of the parameter identification process are now proposed:

- The supercapacitor to be modeled should be in a fully discharged state; that is, all the equivalent internal capacitances have zero voltage.
- The capacitances to be as signed to the equivalent model are given by the differential definition. This definition gives the possibility to know the instantaneous capacitance of the device at any moment.

- The identification of the immediate branch equivalent model parameters is based on the charge of the capacitor up to the rated voltage with high current and the continuous measurement of the terminal voltage. The use of high current reduces the effect of the other two branches in the measurements.
- When the terminal voltage reaches the rated value, the current source is turned off and an internal charge distribution process among the different branches begins. Continuous voltage measurement during that charge distribution is used to identify the delayed and long term equivalent circuit parameters.
- The leakage resistance is identified using a capacitor whose voltage is equal across all the internal equivalent capacitances. In other words, no charge distribution process is distribution process is occurring inside the device. Under this condition, the change in terminal voltage is only a result of the equivalent model leakage resistance.
- The supercapacitor input inductance is calculated using the slope of the current transient the instant that a fully charged capacitor is suddenly short-circuited.

### 3.5.1 Identification of Immediate Branch Parameter

The immediate branch parameters are measured by applying a fast charge to the capacitor. The higher the value of current the lower the charge introduced into the delayed and long term branches; therefore, the current should be as high as possible. The rated short circuit current is defined as the ratio between the rated voltage and the rated internal resistance of the capacitor. The resistance of the immediate branch is determined from the voltage drop produced at the terminals when the current is applied to the capacitor. The supercapacitor terminal voltage is measured at the time $t_0$ before the application of the current. At some time $t_1$ after the turn on of the current source, the terminal voltage is measured again. The time $t_1$ is equal to the maximum rise time of the current source, which is also greater than the $di/dt$ of the device; at his time, the current has reached the desired value but the energy stored in the equivalent capacitance is very low. Therefore, the measured voltage step ($\Delta V$) is due to the equivalent resistance of the immediate branch and the value of the resistance is calculated using equation 3.5. In equation 3.5, I is the controlled current applied, $R_i$ is the immediate branch resistance and $\Delta V$ is the difference between the voltage measured at $t_1$ and the voltage measured at $t_0$ :

$$R_i = \frac{\Delta V}{I} \tag{3.5}$$

The voltage measured at the the $t_1$ is used as a starting point for the capacitance calculation. The fixed part of the immediate capacitance $C_{io}$ is measured based on the defined differential capacitance at the start of the charge action according to the following equation:

$$C_{io} = \frac{dQ}{dV} = \frac{I * dt}{dV} = \frac{I}{dV/dt} \tag{3.6}$$

As the current magnitude is constant, the voltage drop across the immediate resistance is constant; therefore, the dv/dt of the terminal voltage curve as a function of the time is equal to the dv/dt of the voltage curve at the immediate branch capacitance. The slope of the terminal voltage versus time curve is measured at the first instants after the current has been established. This value is used in conjunction with the known value of the current and $C_{io}$, is determined.

The slope of the curve (dV/dt) is measured in the following form: The terminal voltage is measured continuously. When the terminal voltage has increased a value $\Delta V$ with respect to the voltage measured at $t_1$, the time $t_2$ is measured. The time change At corresponding to this $\Delta V$ is equal to $t_2 - t_l$. In this form the dv/dt of the terminal voltage curve in time is measured and its value is used in equation 3.6. The size of the voltage step $\Delta V$ is selected to provide good resolution in the calculation.

The voltage dependant immediate capacitance ($C_{i1}$) may be calculated using the definition of differential capacitance or integral capacitance. As the integral capacitance definition does not need to measure the slope of the terminal voltage curve, this method is more accurate and will be implemented. The time $t_3$ at which the capacitor reaches the rated value is measured. At this time the equivalent integral capacitance of the immediate branch is given by the following relation:

$$C_k = \frac{Q_{total}}{\Delta V} = \frac{I(t_3 - t_1)}{V_{(t_3)} - V_{(t_1)}} \tag{3.7}$$

Where $t_l$ is the time at the start of the charge already mentioned in the calculations of $R_i$ and $C_i$, and $V_{tn}$ represents the terminal voltage at the time $t_n$.

With the value of the integral capacitance calculated, equation 3.4 is used to relate the integral capacitance with the differential capacitance. Using equation 3.4 the value of $C_{i1}$ is calculated:

$$C_{i1} = \frac{2(C_k - C_{io})}{V_{(t_3)} - V_{(t_1)}} \tag{3.8}$$

### 3.5.2 Identification of Delayed Branch Parameter

When the terminal voltage reaches the rated value, the current source is turned off and the redistribution of charge between the immediate and the delayed branch is the predominant action inside the capacitor. At this point the calculation of the delayed branch parameters begins.

The assumption made for the calculation is that the voltage at the delayed branch is zero volts when the current is removed; in other words, the time constant of the delayed branch is much higher than the charge time of the immediate branch,

The equivalent circuit in Figure 3.6 represents the capacitor during that redistribution process.

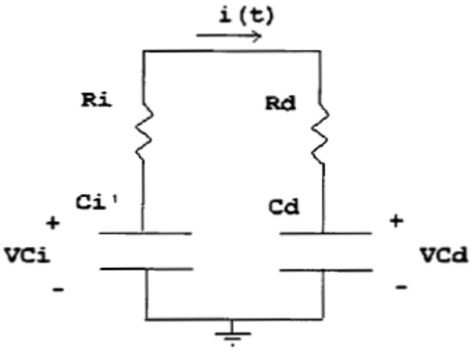


Figure 3.6: Charge Redistribution of Equivalent Circuit

In this figure, $C_i$ is the value of the immediate branch capacitance at the corresponding voltage, and $R_i$ is the immediate branch resistance. The initial current flowing through the circuit when the current falls to zero and $V_{cd}$ is zero ($t_4$), is given by:

$$i_{(t_4)} = \frac{V_{ci}}{R_i + R_d} \tag{3.9}$$

In addition, the following relation between the capacitor current and its voltage is valid at this instant:

$$i_{(t_4)} = C' \frac{dV_{ci}}{dt} \tag{3.10}$$

The time $t_4$, accordingly to the current source characteristics, is equal to the the during which the current source was turned off plus the maximum fall time of the current.The terminal voltage at $t_4$ is measured, and then the voltage is continuously measured until it has dropped a fixed value $\Delta V$. This point determines the instant $t_5$. With these two points of time and voltage the value of $dV/dt = \Delta V/\Delta t$ is determined.
Assuming $R_d \geqslant R_i$ , $V_{ci}$ is approximately equal to the terminal voltage, Therefore, measuring the terminal voltage and $dV_{ci}/dt$, $R_d$ can be calculated through the following equation deduced from 3.9 and 3.10:

$$R_d = \frac{V_{ci}}{C' dV_{ci}/dt} \tag{3.11}$$

The value of $V_{ci}$ and C' used in the calculation of $R_d$ is the terminal voltage and the immediate branch capacitance at the medium point of the dV/dt calculation.

Using the same equivalent circuit shown in Figure 3.2 at some instant ($t_6$) where $V_{cd}$ is different from zero, the value of $C_d$ can be calculated . As the delayed branch was selected to represent the capacitor behavior up to five minutes after the charge action, the calculation of the delayed branch capacitance is done three minutes after the end of the charge action ($t_6 = 180sec + t_3$).

At this instant the current flowing from the immediate to the delayed branch is given by:

$$i(t_6) = C' \frac{dV_{ci}}{dt} \tag{3.12}$$

Further more, the total charge equilibrium equation that represents the interchange of charge between $C_i$ and $C_d$ is given by:

$$\Delta Q = V_{ci}(t_4) * C_k(t_4) - V_{ci}(t_6) * C_k(t_6) = V_d(t_6) * C_d \tag{3.13}$$

The integral capacitance value, needed in the previous equation, may be easily calculated from the differential capacitance. The value of $V_{cd}$ at $t = t_6$ is calculated from Figure 3.6 as:

$$V_{ci}(t_6) = i(R_d + R_i) + V_{cd} + (t_6) \tag{3.14}$$

Using above equation $C_d$ can be calculated:

$$C_d = \frac{\Delta Q}{V_{ci}(t_6) - C' * \frac{dV_{ci}}{dt} * (R_i + R_d)} \tag{3.15}$$

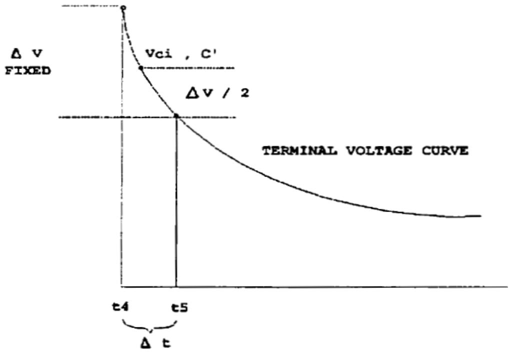


Figure 3.7: dV/dt Calculation

A second proposal for the delayed branch capacitance calculation based only in the charge equilibrium is now presented. In this second possible identification, the time constant for the delayed branch is previously assumed. After three time constant for the delayed branch, the voltages across the immediate and delayed branches are practically equal, and the equation 3.13 for the charge equilibrium is applied with $V_{cd} = V_{ci}$. This procedure has the advantage to Save the calculation of dv/dt which is in general inaccurate. On the other hand, this second proposal needs more time for the computation of the parameter $C_d$ because the calculation is done when the voltages in both branches are considered equal.

### 3.5.3 Identification of Long Term Branch Parameter

The long term branch parameters calculation follows similar steps to those for the delayed branch. In this case, the delayed capacitance is assumed with equal voltage to the immediate branch and the long term capacitance is assumed fully discharged. To make these assumptions valid, the start time for the calculation of the long term branch should be at least three times the delayed branch time constant. This criterion assures that the delayed voltage is within 95% of the immediate branch voltage.

The equivalent circuit for the charge transfer to the long term branch is shown in Figure 3.8

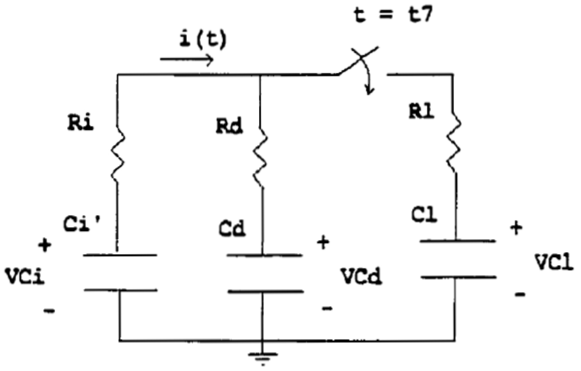


Figure 3.8: Equivalent Circuit for Charge Distribution to $C_l$

The switch $S_1$ is closed at the instant $t_7$ in which the voltages at the immediate and delayed branches are almost equal. In this instant most of the charge transference occurs between the immediate branch and the long term branch because the value of $R_i$ is much lower than $R_d$. Therefore, $R_l$ is calculated using equation 3.11 three delayed branch time constants after the instant which the current was turned off. The calculation of the dV/dt used in equation 3.11 is done in the same form explained for the delayed branch.

The capacitance $C_l$ is calculated using the same procedure explained for the delayed branch but now the capacitance C' in equations 3.11 to 3.15 is equal to the capacitance of the immediate branch in parallel with the capacitance of the delayed branch. The instant of calculation for $C_l$ is thirty minutes after the termination of the current source.

As was done for the delayed branch, the dv/dt of the terminal voltage versus time curve is measured and the equation mentioned for the case of the delayed branch are applied are applied to the results.

In the calculation of the long term branch capacitance it is also possible to use a second identification procedure. In this method, the time constant for the long term branch is previously assumed and the equation for the charge equilibrium is applied after three times the selected time constant. This method save the calculation of dV/dt that for this case is very difficult because the transient is very slow. However, the time needed to calculate the parameter is longer.

### 3.5.4 Identification of Leakage Resistance

The leakage resistance is identified by measuring the decrease in the capacitor terminal voltage over a period of 24 hours. The capacitor used for the leakage resistance determination was previously normalized to 2 volts. After the normalization, it is expected that all the internal capacitances in the equivalent model are charged to the same voltage and the voltage decrease as function of time can be attributed to the equivalent leakage resistance. The duration of the test (24 hours) is much greater than the time constants of the three equivalent model branches; therefore, the capacitor is assumed as the parallel equivalent of the three branches and the resultant circuit is an RC circuit. The analysis of a simple RC circuit gives:

$$V_c(t) = V_0 e^{(\frac{-t}{R_{leak} C_t})} \tag{3.16}$$

Where $C_t$ is the parallel equivalent capacitance, $V_c$ is the supercapacitor terminal voltage and $V_0$ is the initial voltage for the discharge, or in other words the terminal voltage after the normalization. In the previous equation the value of the leakage resistance is assumed to be much larger than the resistance of the three branches. Using the series approximation for the previous equation with $t << R_{leak} * C_t$ gives:

$$V_c(t) = V_0(1 - \frac{t}{R_{leak} C_t}) \tag{3.17}$$

Defining $\Delta V_c$ as the decrease in terminal voltage after the 24 hours test, the following relation is produced

$$R_{leak} = \frac{V_o \; \Delta t}{\Delta V_c \; C_t} \tag{3.18}$$

In the previous relation $V_o$ is two volts, $\Delta V_c$ is measured after 24 hours, $C_t$ is known from the previous identification of the internal capacitances and $\Delta t$ is equal to 24 hours.By this method we can modeling the parameters of supercapacitor.

# Chapter 4

# Experimental Results and Simulation

The parameters of this supercapacitor model with three RC branches that have distinct time constant can be identified carrying out a single fast current controlled charge. It is proposed that the parameters are identified by charging the supercapacitor from zero to rated voltage and by observing the terminal voltage during the internal charge redistribution.

It is necessary to use a precisely timed and controlled current source to control exactly the provided charge. In addition, the supercapacitor must be in a state where all the model equivalent capacitances have zero voltage, that means any internal charge distribution has ceased and the initial charge stored is known.

The test to identify the parameters assumes that the capacitor holds no charge at the beginning and that the charge current is about 5% of the specified short circuit current. The short circuit current is the rated voltage divided by the inner resistance. This current is applied to the supercapacitor under test until the terminal voltage reaches the rated value.

The approach to determine the different parameters is based on the fact that the three equivalent branches have distinctly different time constants. Therefore, the transient process of each branch can be observed independently by measuring the terminal voltage as function of time. It is assumed, and this is justified by the results, that the response to the fast controlled charging process is determined only by the parameters of the first or immediate branch. After the external charging stops, all charge is in the capacitors of the immediate branch. Then, the charge redistributes itself to the delayed branch without effecting the third or long time branch, which has a much higher time constant. After the voltages in the immediate and delayed capacitors are equalized, the charges start to redistribute to the capacitor of the long term branch.

## 4.1 Test Procedure

The following test procedure is used to calculate the parameters of the previously introduced supercapacitor model. The procedure is described by a series of events n, at which the supercapacitor terminal voltage $V_n$ and the time $t_n$ are measured[10].

### 4.1.1 Immediate Branch Calculation

The immediate branch parameters are identified charging a fully discharged supercapacitor with constant current. As the time constant of the immediate branch is small compared with the time constant of the other two branches, it is assumed that all the charge is initially stored in the immediate branch.

- **n=0:**
  At that time $V_0 = 0\ V$.
  $Q_0 = 0$.
  Current source is switched on$(I = I_{ch})$.
- **n=1:**
  $t_1 = 9\ sec.$
  $t_1$ is given at the at which current source is rises to the set value $I_{ch}$ in 9 sec.
  At that time measure $V_1$.
  $V_1 = 1.29\ V$.
  After small time $t_1$ the supercapacitor terminal voltage is mainly determined by the voltage drop at $R_i$.

$$R_i = \frac{V_i}{I_{ch}} = \mathbf{0.645}\ \Omega \tag{4.1}$$

- **n=2:**
  At when $V_2 = V_1 + \Delta V$.
  $\Delta V$ chosen to be 500 mV.
  Measure $t_2$.
  $t_2 = 62\ sec.$
  $\Delta t = t_2 - t_1 = 53\ sec.$ Now we calculate $C_{i0}$.

$$C_{i0} = I_{ch} * \frac{\Delta t}{\Delta V} = \mathbf{212\ F} \tag{4.2}$$

- **n=3:**
  Reached when $V_3 = Vrated.V_3 = 2.4\ V.$
  Measure $t_3$.
  $t_3 = 210\ sec.$
  Now current source is turned off($I_{ch} = 0.$)

- **n=4:**
  $t_4 = t_3 + 9\ sec.$
  9 sec is given by fall time of the current.
  At that time measure $V_4$. $V_4 = 1.828\ V.$
  Total charge supplied to the supercapacitor: $Q_{tot} = I_{ch} * (t_4 - t_1) =$ 420 coulomb.
  Now we calculate $C_q = \frac{Q_{tot}}{V_4} = 229.75\ F.$
  Voltage dependant capacitance can be calculated by following equation:

$$C_{i1} = \frac{2}{V_4} * [\frac{i_{ch} * (t_4 - t_1)}{V_4} - C_{i0}] = \mathbf{19.43\ F} \tag{4.3}$$

### 4.1.2 Delayed Branch Calculation

After event 4, and due to the assumption of distinct time constants, the immediate branch is charged to $V_4$, and the other two branches are discharged. Then, the charge redistribution from the immediate to the delayed branch takes place. The time constant of the long term branch is much longer than the time for the charge redistribution to $C_d$, so that it is assumed that during the charge distribution to $C_d$ no charge redistributes to $C_l$. The equivalent circuit from Fig.4.1 represents the situation.

- **n=5:**
  At when $V_5 = V_4 - \Delta V.$
  $\Delta V is chosen to be 500\ mV.\ \therefore V_5 = 1.328\ V.$
  Measure $t_5$. $t_5 = 303\ sec.$
  $\Delta t = t_5 - t_4 = 84\ sec.$
  As $\Delta V$ is small and $C_d$ is assumed dischrage, $I_{tr} = \frac{V_4 - \frac{\Delta V}{2}}{R_d}.(R_i neglected because R_i << R_d).$

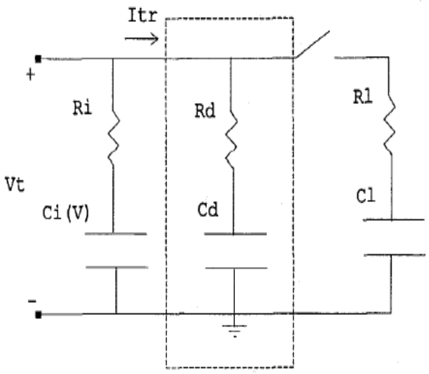


Figure 4.1: Delayed Branch Identification of Equivalent Circuit

Relating the transfer current $I_{tr} = \frac{C_{diff} * \Delta V}{\Delta t}$.
Here, $C_{diff} = C_{i0} + (C_{i1} * V) = 258.63\ F$
Now,

$$R_d = \frac{V_4 - \frac{\Delta V}{2} * \Delta t}{C_{diff} * (\Delta V)} = \mathbf{1.025}\ \Omega \tag{4.4}$$

- **n=6:**
  $t_6 = t_5 + 3(R_d * C_d)$.
  Typically $R_d * C_d = 20\ sec. \therefore t_6 = 303\ sec.$
  Measure $V_6$. $V_6 = 1.164\ V$.

$$C_d = \frac{Q_{tot}}{V_6} - [C_{i0} + \frac{C_{i1}}{2} * V_6] = \mathbf{137.51\ F} \tag{4.5}$$

### 4.1.3 Long Term Branch Calculation

After event 6, the immediate and delayed capacitors are charged to $V_6$ and the long term capacitor is fully discharged. After $t_6$, the charge redistribution from the immediate and delayed branches to the long term branch takes place. The equivalent circuit from Fig.4.2 represents the situation.

- **n=7:**
  At when $V_7 = V_6 - \Delta V. V_7 = 0.664\ V$.
  Measure $\Delta t = 73\ sec.$

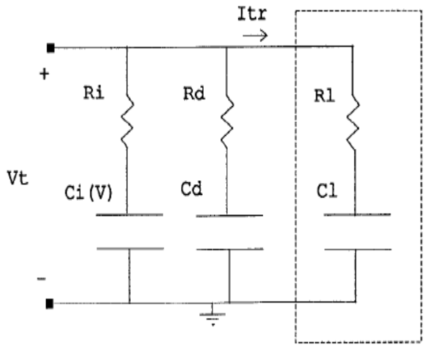


Figure 4.2: Long Term Branch Identification of Equivalent Circuit

As $\Delta V$ is small and $C_l$ is assumed discharge, $I_{tr}$ is virtually constant and given by:$I_{tr} = \frac{(V_6 - \frac{\Delta V}{2})}{R_l}$.
$(R_i and R_d neglected because R_i << R_d << R_l)$.
Because $R_d$ is much larger than $R_i$, the transfer current I, at this initial instant is supplied mainly from the immediate branch:$I_{tr} = C_{diff} * \frac{\Delta V}{\Delta t}$.

$$R_l = \frac{[(V_6 - \frac{\Delta V}{2} * \Delta t]}{C_{diff} * (\Delta V)} = \mathbf{5.9}\ \Omega \tag{4.6}$$

- **n=8:**
  $t_8 = 30\ min.$
  At t, it is assumed that the charge redistribution to the long term branch has ended and the three equivalent capacitors have the same voltage.
  Measure $V_8 . V_8 = 0.60\ V.$
  The long term capacitor $(C_l)$ is calculated using the charge balance:

$$C_l = \frac{Q_{total}}{V_6} - [C_{i0} + (\frac{C_{i1}}{2} * V_8)] - C_d = \mathbf{344.66\ F.} \tag{4.7}$$

## 4.2 Measurement Parameters from Experimental Result

With the clear definition of the procedure for the parameter calculation, the parameters values may now be measured. The following table summarizes the results of the parameters measurements:

| **Parameters** | **Capacitor of 560 F** |
|---|---|
| $R_i$ | 0.645 $\Omega$ |
| $C_{i0}$ | 212 F |
| $C_{i1}$ | 19.43 F |
| $R_d$ | 1.025 $\Omega$ |
| $C_d$ | 137.51 F |
| $R_l$ | 5.9 $\Omega$ |
| $C_l$ | 344.66 F |
| $R_{leak}$ | 1.6 $K\Omega$ |

Table 4.1: Internal Parameters of Supercapacitor

## 4.3 Experimental Data

The experimental graph voltage verses time for Charging and discharging (at constant current applying 2 amp) are given below. Which is clearly mention that voltage is increasing with time and capacitor is charge and voltage is decreasing with time when capacitor is discharge.

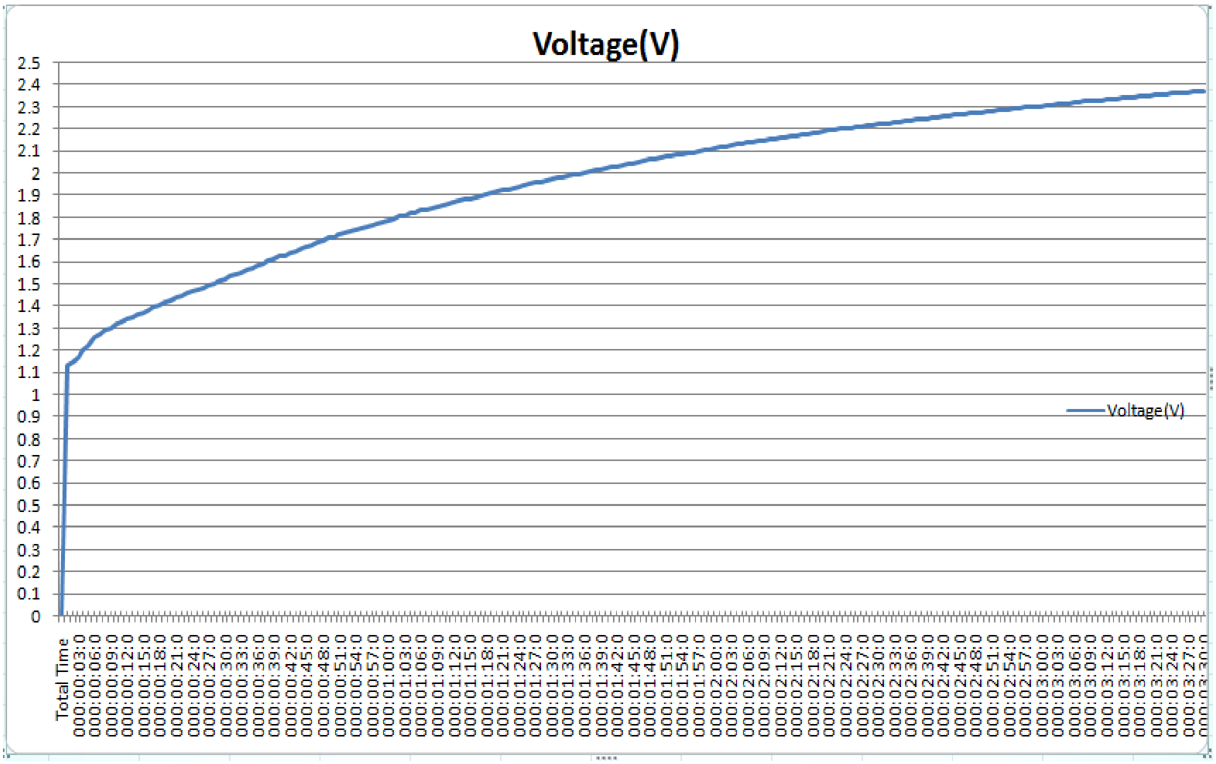


Figure 4.3: Charging of Supercapacitor With Constant Current 2 Amp

Figure 4.3 shows the terminal voltage during the charge action with constant current and the first minutes of the internal charge distribution process. This graphic presents the first three minutes of the capacitor response to a charge action. In other words, the figure compares the experimental results with the simulation during the time that the immediate and delayed branches predominate in the capacitor behavior.

Figure 4.4 shows terminal voltage during recharge action with constant current.After that, the capacitor is discharged until the voltage across the immediate and delayed branches are at approximately equal. Finally, the current is turned off again and the change in terminal voltage there after is very low since that change is given only by the long term branch.

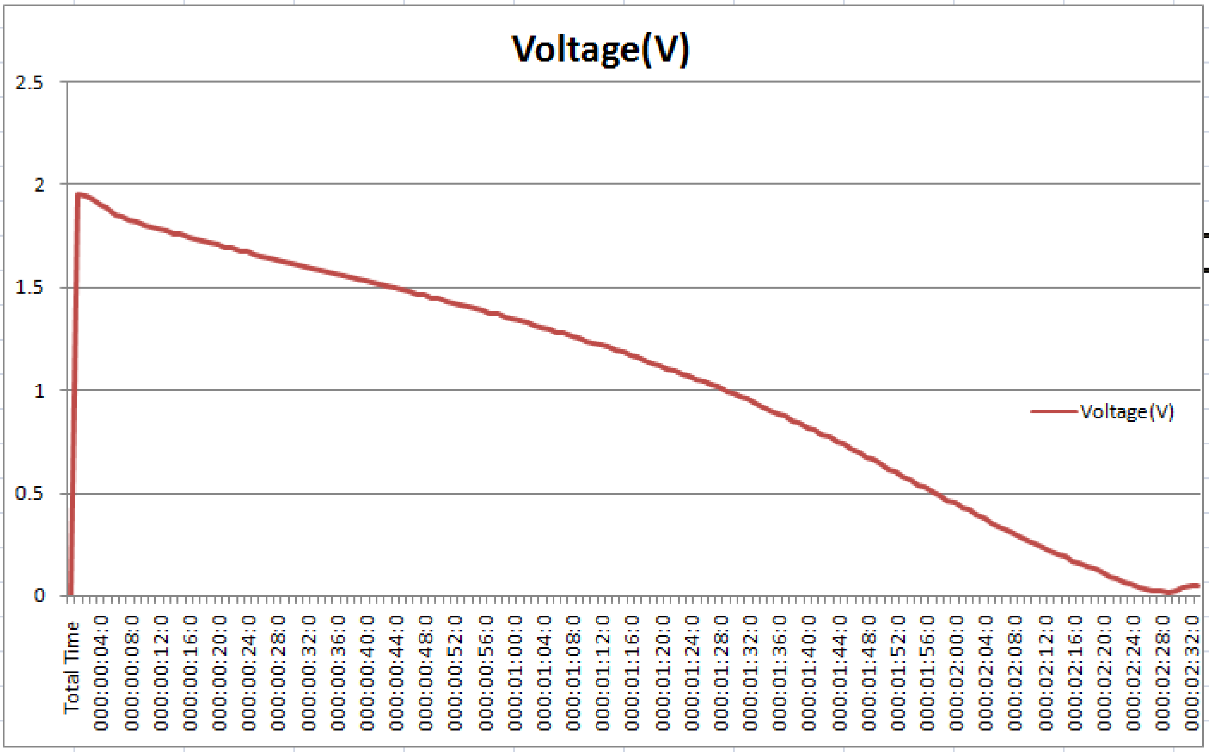


Figure 4.4: Discharging of Supercapacitor With Constant Current 2 Amp

## 4.4 Simulation of Supercapacitor

The software to be used for simulation is MATLAB. Simulink tool is used for getting charging and discharging characteristics.

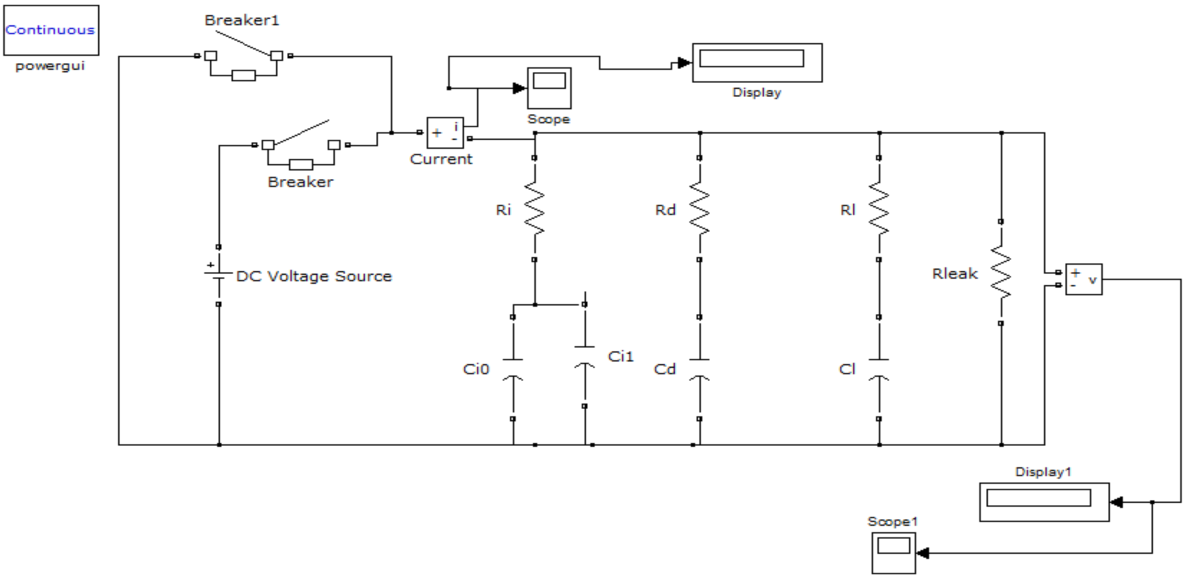


Figure 4.5: Simulation Model of Supercapacitor

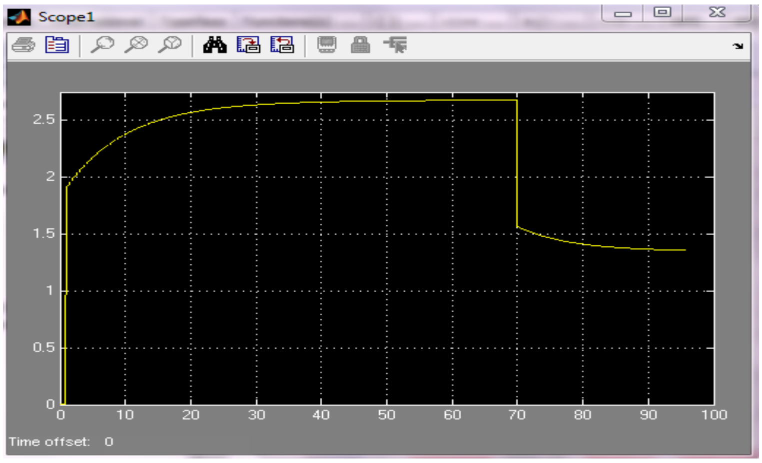


Figure 4.6: Charging Graph of Simulated Model

Fig 4.5 represents the simulation model of charging and discharging of supercapacitor. Fig 4.6 shows the charging graph of simulated model. That gives comparison of experimental graph and simulated graph. This graph represents the capacitor response to a charge action. Fig 4.7 shows the discharging graph of simulated model. In other words, the figure compares the experimental results with the simulation during the time that the immediate and delayed branches predominate in the capacitor behavior.

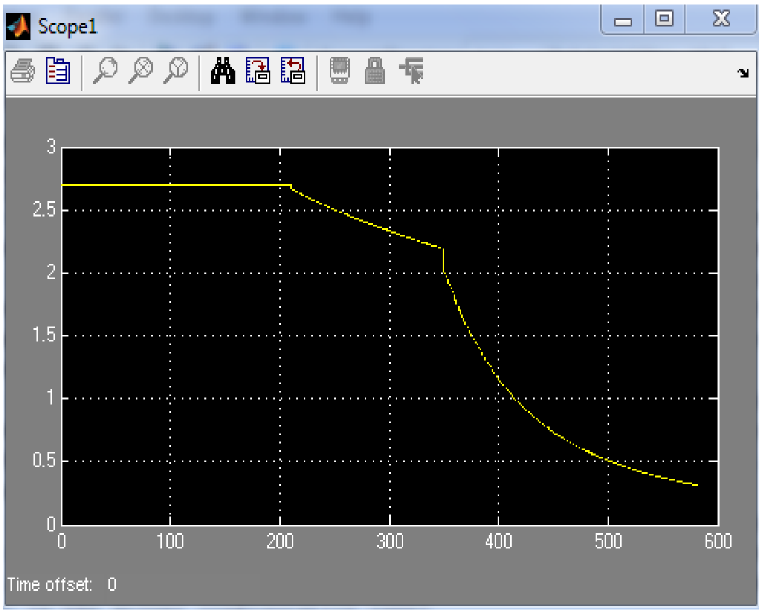


Figure 4.7: Discharging Graph of Simulated Model

The experimental and simulated results are in a very good agreement with each other. This graph shows the time constant of immediate branch is few seconds and delayed and long term branch is very high in minutes.

# Chapter 5

# Replacement of Battery With Supercapacitor

An electrical battery is one or more electrochemical cells that convert stored chemical energy into electrical energy. Like a battery, a supercapacitor has an electrolyte (electrically active chemical) inside it, separating its plates, which is more like the electrolyte in a battery than the dielectric in a conventional capacitor (which might just be a piece of plastic or air). In a conventional capacitor, positive charges form on one plate and negative charges on the other with the dielectric sitting in between them, keeping the charges safely apart. In a supercapacitor, the electrolyte is electrically active and adds another dimension: the charged plates polarize the electrolyte, making positive ions inside it move one way and negative ions the other, and causing a second set of charges to form. That is why supercapacitor also called electric double layer capacitor or EDLC. Unlike in a battery, the positive and negative charges in a supercapacitor are produced entirely by static electricity; no chemical reactions are involved.

Batteries store electricity using chemical reactions happening between an electrolyte (orange), a positive electrode (blue), and a negative electrode (red). Capacitors store static electricity by building up opposite charges on two metal plates (blue and red) separated by an insulating material called a dielectric (orange). Supercapacitors store more energy than ordinary capacitors by creating a double layer of separated charges between two plates made from porous, typically carbon-based materials. The plates create the double-layer by polarizing the electrolyte (yellow) in between them (Fig 5.1). The basic unit of electric charge is called the farad (F). Typical capacitors used in electronic circuits store only mini scale amounts of electricity (usually rated in units called microfarads or picofarads, which are millionths and billionths of a farad). In other side supercapacitor can store a charge thou-

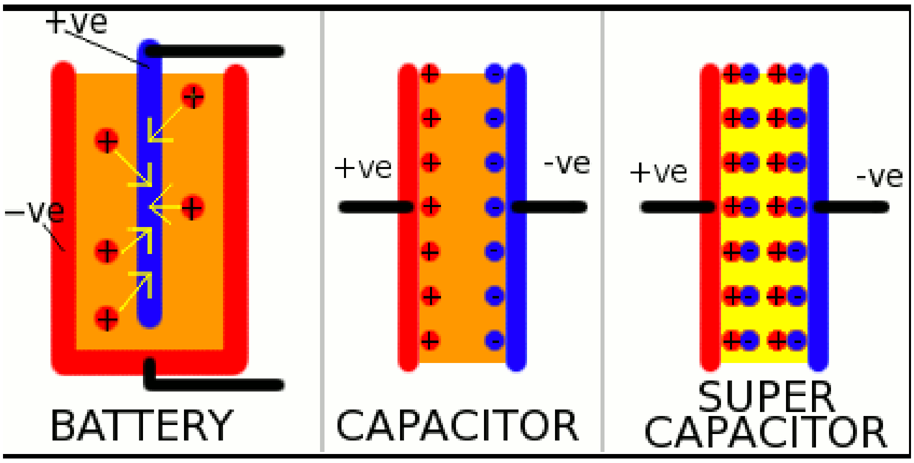


Figure 5.1: Construction comparison between battery, capacitor and supercapacitor

sands, millions, or even billions of times bigger (rated in farads). The big advantage of a supercapacitor is that it can store and release energy almost instantly much more quickly than a battery. That is because a supercapacitor works by building up static electric charges on solids, while a battery relies on charges being produced slowly through chemical reactions, often involving liquids.

Batteries and supercapacitors compared in terms of their energy and power. Batteries have a higher energy density (they store more energy per unit mass) but supercapacitors have a higher power density (they can release energy more quickly). That makes supercapacitors particularly suitable for storing and releasing large amounts of power relatively quickly, but batteries are still king for storing large amounts of energy over long periods of time. Supercapacitors work at relatively low voltages (maybe 2-3 volts), they can be connected in series (like batteries) to produce bigger voltages for use in more powerful equipment. Since supercapacitors work electrostatically, rather than through reversible chemical reactions, they can theoretically be charged and discharged any number of times. They have little or no internal resistance, which means they store and release energy without using much energy and work at very close to 100 percent efficiency (97-98 percent is typical).

There are two types of batteries:

1. **Primary Batteries** (disposable batteries), which are designed to be used once and discarded.

2. **Secondary Batteries** (rechargeable batteries), which are designed to

be recharged and used multiple times.

Generally rechargeable batteries are classified as follows:-

1. Nickel cadmium battery.
2. Nickel metal hydride battery.
3. Lithium ion battery.
4. Lead acid battery.

Batteries have many advantages like high self-discharge rate, long life nearly 5 years, good reversibility, easily available, low cost, simple charging method. Over several advantages batteries have many disadvantages like bulky, non eco-friendly, failure rate is high, charging time is high, lead-acid batteries requires acid which is harmful to the human beings etc. So, it is require to overcome these disadvantages and find the better replacement of batteries. The relative energy storage device is capacitor but the main disadvantage of capacitors are low energy storage capacity. This disadvantage can be overcome with the help of supercapacitors. In order to obtain the same characteristics of battery with the help of supercapacitor the modification in internal parameters is required. The internal parameters require to obtain the same characteristics of battery the following procedure has been adopted.

- Obtain the charging and discharging characteristics of battery by using MATLAB Simulink,
- Use these charging and discharging characteristics as the characteristics of supercapacitor,
- Calculate the internal parameters for obtained characteristics,
- State the require modification to be done in supercapacitor in order to obtain the require internal parameters.

## 5.1 MATLAB Simulink Model for Battery Charging

For getting charging characteristics of battery MATLAB Simulink tool is used. Here 6.5 Ah, 2.7 V Lithium-Ion battery is used. Its initial state of charge is 0% in the starting. For charging this battery 2 A constant current is applied.

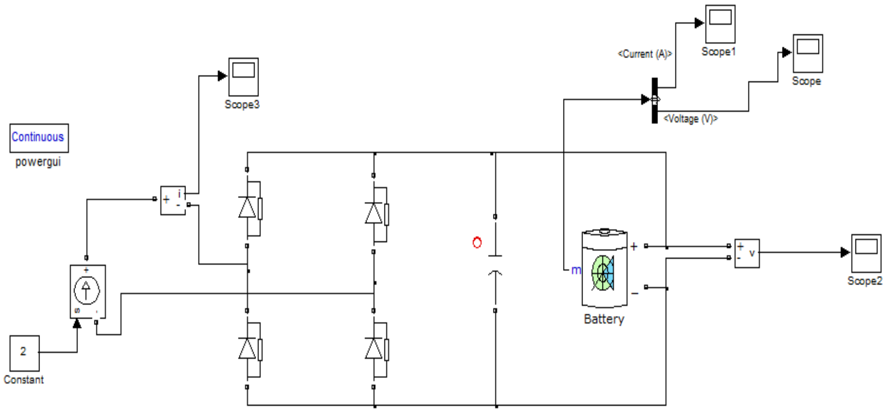


Figure 5.2: MATLAB Simulink Model for Battery Charging

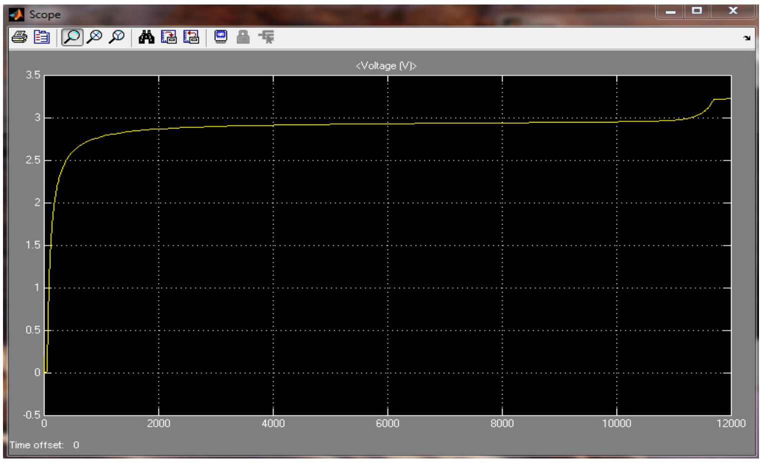


Figure 5.3: Charging Characteristic of Battery

Following charging characteristic is obtained from the MATLAB Simulink model for battery charging.

The total charging time of the battery can be found from its charging characteristics. This charging time is used for calculating of internal parameters of supercapacitor.

## 5.2 MATLAB Simulink Model for Battery Discharging

For getting discharging characteristics of battery, MATLAB Simulation tool is used. Its initial state of charge is 100% in the starting. For getting discharging characteristics constant current of 2 A is applied.

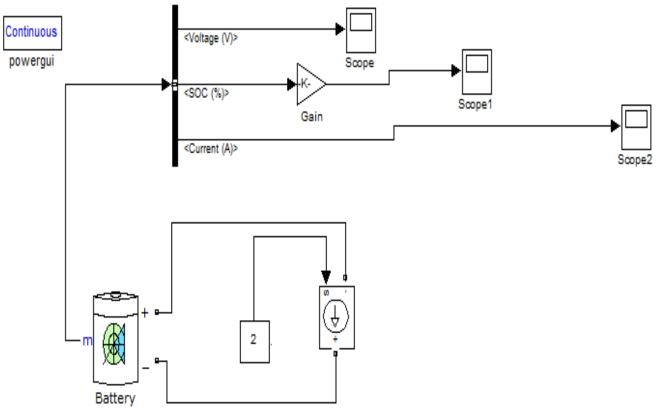


Figure 5.4: MATLAB Simulink Model for Battery Discharging

Following discharging characteristics is obtained from the MATLAB Simulink model for battery discharging. The total discharging time of the battery can be found from its discharging characteristics. This discharging time is used for calculating of internal parameters.

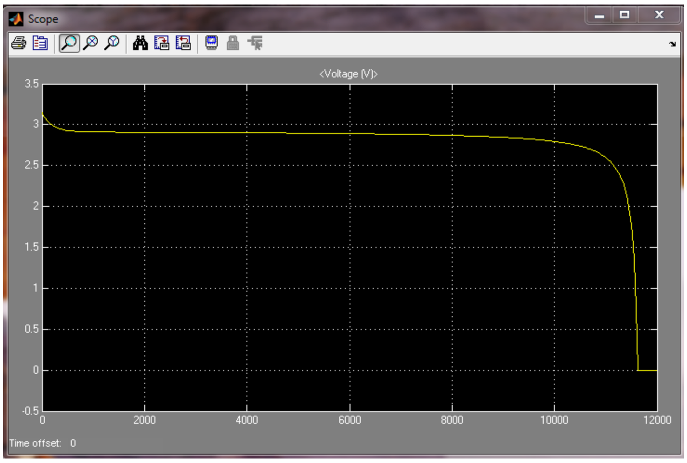


Figure 5.5: Discharging Characteristics of Battery

## 5.3 Internal Parameter Calculation Using Charging and Discharging Characteristics

In order to obtained same characteristics with the help of supercapacitor modification in internal parameters have to be done and it is explained below.

Use above charging and discharging characteristics as an supercapacitor characteristics and calculate its internal parameters. The following test procedure is used to calculate the parameters of the previously introduced supercapacitor model. The procedure is described by a series of events n, at which the battery terminal voltage $V_n$ and the time $t_n$ are measured.

### 5.3.1 Immediate Branch Calculation

The immediate branch parameters are identified charging a fully discharged battery with constant current. As the time constant of the immediate branch is small compared with the time constant of the other two branches, it is assumed that all the charge is initially stored in the immediate branch.

- **n=0:**
  At that time $V_0 = 0\ V$.
  $Q_0 = 0$.
  Current source is switched on($I = I_{ch}$.)

- **n=1:**
  $t_1 = 139\ sec.$
  $t_1$ is given at the at which current source is rises to the set value $I_{ch}$ in 139 sec.
  At that time measure $V_1$.
  $V_1 = 1.67\ V.$
  After small time $t_1$ the supercapacitor terminal voltage is mainly determined by the voltage drop at $R_i$

$$R_i = \frac{V_i}{I_{ch}} = \mathbf{0.835}\ \Omega \tag{5.1}$$

- **n=2:**
  At when $V_2 = V_1 + \Delta V$.
  $\Delta V$ chosen to be 500 mV (0.5 V).

Measure $t_2$.
$t_2 = 228\ sec.$
$\Delta t = t_2 - t_1 = 89\ sec.$ Now we calculate $C_{i0}$.

$$C_{i0} = I_{ch} * \frac{\Delta t}{\Delta V} = \mathbf{356\ F} \tag{5.2}$$

- **n=3:**
  Reached when $V_3 = Vrated.V_3 = 2.7\ V.$
  Measure $t_3$.
  $t_3 = 724.82\ sec.$
  Now current source is turned off($I_{ch} = 0$.)

- **n=4:**
  $t_4 = t_3 + 139\ sec.$
  139 sec is given by fall time of the current.
  At that time measure $V_4$. $V_4 = 2.9\ V.$
  Total charge supplied to the supercapacitor: $Q_{tot} = I_{ch} * (t_4 - t_1) =$ 1449.64 coulomb.
  Now we calculate $C_q = \frac{Q_{tot}}{V_4} = 499.87\ F.$
  Voltage dependant capacitance can be calculated by following equation:

$$C_{i1} = \frac{2}{V_4} * [\frac{i_{ch} * (t_4 - t_1)}{V_4} - C_{i0}] = \mathbf{99.22\ F} \tag{5.3}$$

### 5.3.2 Delayed Branch Calculation

After event 4, and due to the assumption of distinct time constants, the immediate branch is charged to $V_4$.Then after delayed branch parameters are calculated.

- **n=5:**
  At when $V_5 = V_4 - \Delta V.$
  $\Delta V ischosentobe 500\ mV(0.5\ V).$
  $\therefore V_5 = 2.4\ V.$
  Measure $t_5$. $t_5 = 11182\ sec.$
  $\Delta t = t_5 - t_4 = 10318\ sec.$
  As $\Delta V$ is small and $C_d$ is assumed dischrage, $I_{tr} =$

$\frac{V_4 - \frac{\Delta V}{2}}{R_d} . (R_i neglected because R_i << R_d)$.
Relating the transfer current $I_{tr} = \frac{C_{diff} * \Delta V}{\Delta t}$.
Here, $C_{diff} = C_{i0} + (C_{i1} * V) = 623.89\ F$
Now,

$$R_d = \frac{V_4 - \frac{\Delta V}{2} * \Delta t}{C_{diff} * (\Delta V)} = \mathbf{87.659}\ \Omega \tag{5.4}$$

- **n=6:**
  $t_6 = t_5 + 3(R_d * C_d)$.
  Typically $R_d * C_d = 300\ sec$.
  $\therefore t_6 = 12000\ sec$
  Measure $V_6$. $V_6 = 2\ V$.

$$C_d = \frac{Q_{tot}}{V_6} - [C_{i0} + \frac{C_{i1}}{2} * V_6] = \mathbf{209.93\ F} \tag{5.5}$$

### 5.3.3 Long Term Branch Calculation

After event 6, the immediate and delayed capacitors are charged to $V_6$ and the long term capacitor is fully discharged. After $t_6$, the charge redistribution from the immediate and delayed branches to the long term branch takes place.

- **n=7:**
  At when $V_7 = V_6 - \Delta V . V_7 = 2.7\ V$.
  Measure $\Delta t = 1316\ sec$.
  As $\Delta V$ is small and $C_l$ is assumed discharge, $I_{tr}$ is virtually constant and given by:$I_{tr} = \frac{(V_6 - \frac{\Delta V}{2})}{R_l}$.
  $(R_i and R_d neglected because R_i << R_d << R_l)$.
  Because $R_d$ is much larger than $R_i$, the transfer current I, at this initial instant is supplied mainly from the immediate branch:$I_{tr} = C_{diff} * \frac{\Delta V}{\Delta t}$.

$$R_l = \frac{[(V_6 - \frac{\Delta V}{2} * \Delta t]}{C_{diff} * (\Delta V)} = \mathbf{12.44}\ \Omega \tag{5.6}$$

- **n=8:**
  $t_8 = 180\ min.$
  At t, it is assumed that the charge redistribution to the long term branch has ended and the three equivalent capacitors have the same voltage.
  Measure $V_8.V_8 = 2\ V.$
  The long term capacitor $(C_l)$ is calculated using the charge balance:

$$C_l = \frac{Q_{total}}{V_6} - [C_{i0} + (\frac{C_{i1}}{2} * V_8)] - C_d = 60\ F. \tag{5.7}$$

### 5.3.4 Measurement Parameters from Experimental Result

With the clear definition of the procedure for the parameter calculation, the parameters values can be calculated. The following table summarize the results of the parameters measurements:

| **Parameters** | **Battery (6.5 Ah, 2.7 V)** | **Supercapacitor (560 F, 2.7 V)** |
|---|---|---|
| $R_i$ | 0.835 Ω | 0.645 Ω |
| $C_{i0}$ | 356 F | 212 F |
| $C_{i1}$ | 99.22 F | 19.43 F |
| $R_d$ | 87.659 Ω | 1.025 Ω |
| $C_d$ | 209.93 F | 137.51 F |
| $R_l$ | 12.44 Ω | 5.9 Ω |
| $C_l$ | 60 F | 344.66 F |

Table 5.1: Internal Parameters Required to Replace Battery with Supercapacitor

From the obtained results, in order to replace battery with supercapacitor internal parameters required for supercapacitor is shown in table 5.1. By implementing the internal parameters of battery in supercapacitor, charging and discharging characteristics of battery can be obtained with the help of supercapacitor. And hence by varying the internal parameters of supercapacitor the required characteristics can be obtained. To change the internal parameters of supercapacitor some modification in design and material is required. By changing the material used in supercapacitor the internal parameters variation is to be found.

# Chapter 6

# Modification Required in Supercapacitor to Replace Battery

Supercapacitor contains several internal parameters which decides the charging and discharging behavior of the supercapacitor. These parameters are dependent on various materials used as electrode material, separator material and electrolyte material. By changing these parameters the desired charging and discharging characteristics can be obtained. In order to replace the battery it is require to have the charging and discharging characteristics of supercapacitor same as battery. And to obtain the same characteristics as battery from the supercapacitor, modification in internal parameters of

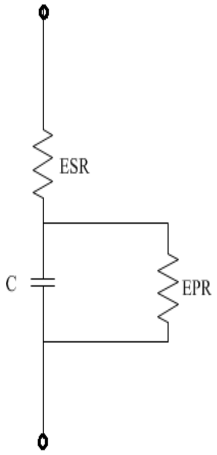


Figure 6.1: Classical Equivalent Circuit of Supercapacitor Consists of ESR and EPR

supercapacitor is to be done. Supercapacitor primarily classified by two resistances namely electrical series resistance (ESR) and electrical parallel resistance (EPR).

To change the charging and discharging characteristics of supercapacitor it is require to change the value of ESR and EPR. And it can be change by changing the various material used for anode, cathode and separator. The main advantage to replace the battery with supercapacitor is to have the high energy density compared to conventional capacitor and higher power density compared to battery.

## 6.1 Electrical Series Resistance (ESR)

The ESR models power losses that may result from internal heating, which will be important during charging and discharging. The maximum possible power that can be supplied by a supercapacitor dependent on voltage and ESR given by following equation:

$$P = \frac{V^2}{(4 * ESR)} \tag{6.1}$$

The ESR consists of parallel combination of three resistances. These three resistances are immediate branch resistance $R_i$, delayed branch resistance $R_d$ and long term branch resistance $R_l$.
ESR calculation for supercapacitor (560 F, 2.7 V):-

$$\begin{aligned} ESR &= \frac{R_i * R_d * R_l}{(R_i * R_d)\ (R_d * R_l)\ (R_l * R_i)} \\ &= \frac{0.645 * 1.025 * 5.9}{(0.645 * 1.025)\ (1.025 * 5.9)\ (5.9 * 0.645)} \\ &= 0.37099\ \Omega \end{aligned}$$

ESR calculation for replacement of battery with supercapacitor (6.5 Ah, 2.7 V):-

$$ESR = \frac{R_i * R_d * R_l}{(R_i * R_d)\ (R_d * R_l)\ (R_l * R_i)}$$

$$
\begin{aligned}
&= \frac{0.835 * 87.659 * 12.44}{(0.835 * 87.659)\ (87.659 * 12.44)\ (12.44 * 0.835)} \\
&= 0.7755\ \Omega
\end{aligned}
$$

Above calculation shows that the ESR of battery with replacement of supercapacitor is higher than the simple supercapacitor. To replace the battery with ESR of supercapacitor must be equal to the ESR of battery.

The ESR is primarily responsible for charging time and load discharging time. Greater the value of ESR greater will be the charging time and it will discharge quickly. In order to change the ESR of supercapacitor it is require to change the materials used in conventional supercapacitor. To obtain the charging and discharging characteristics same as battery the ESR of supercapacitor should be equivalent to battery ESR. Usually ESR is consists of electrode resistance, electrolyte resistance and contact resistance that wastes power for internal heating when charging or discharging in supercapacitors. ESR is almost less than one million but influences the energy efficiency and power density. ESR depends on various factors which are classified as under.

### 6.1.1 Factors Affecting ESR

- Electrode material
- Electrolyte

⇒ **Electrode Material**

ESR primarily depends on electrode material used for electrodes i.e. anode and cathode. In supercapacitor various electrode materials can be used depending upon the application of supercapacitor. There are various electrode material like activated carbon, carbon aerogel, carbon nanotubes.

- **Activated Carbon:-** Because it is less expensive and possesses a higher surface area than other carbon based materials, activated carbon is the most commonly used electrode material in supercapacitor. Although capacitance is directly proportional to surface area, empirical evidence suggests that, for activated carbons, not all of the high surface area contributes to the capacitance of the device.This discrepancy is believed to be caused by electrolyte ions that are too large to diffuse into smaller micro pores, thus preventing some pores from contributing to charge storage. Larger pore sizes correlate with higher power densities and smaller pore sizes correlate with higher energy densities.

- **Carbon Aerogel:-** Carbon aerogel can also be used as electrode material in supercapacitor. Carbon aerogel are formed from a continuous network of conductive carbon nano particles with interspersed mesopores. Due to this continuous structure and their ability to bond chemically to the current collector, carbon aerogel do not require the application of an additional adhesive binding agent. As a binder-less electrode, carbon aerogel have been shown to have a lower ESR than activated carbons.

- **Carbon Nanotubes:-** Recent research trends suggest that there is an increasing interest in the use of carbon nanotubes as an supercapacitor electrode material. Electrodes made from this material commonly are grown as an entangled mat of carbon nanotubes, with an open and accessible network of mesopores. Unlike other carbon based electrodes, the mesopores in carbon nanotubes electrodes are interconnected, allowing a continuous charge distribution that uses almost all of the available surface area. Thus, the surface area is utilized more efficiently to achieve capacitances comparable to those in activated-carbon-based supercapacitors, even though carbon nanotubes electrodes have a modest surface area compared to activated carbon electrodes. Because the electrolyte ions can more easily diffuse into the mesoporous network, carbon nanotubes electrodes also have a lower ESR than activated carbon. Especially, carbon nanotubes can be grown directly onto the current collectors, subjected to heat-treatment, or cast into colloidal suspension thin films. The efficiency of the entangled mat structure allows energy densities comparable to other carbon-based materials and the reduced ESR allows higher power densities.

- **Hybrid and Composite Material:-** Hybrid supercapacitor is a new highly reliable energy storage device. It is a combination of supercapacitor and battery (eg.C and Li-ion). Hence it is known as capattery (**capa**citor ba**ttery**). Below Graph shows the relation of specific energy and specific power for battery, supercapacitor and hybrid capacitor which is clearly shows that hybrid supercapacitor full fill the requirement of battery as well as supercapacitor.

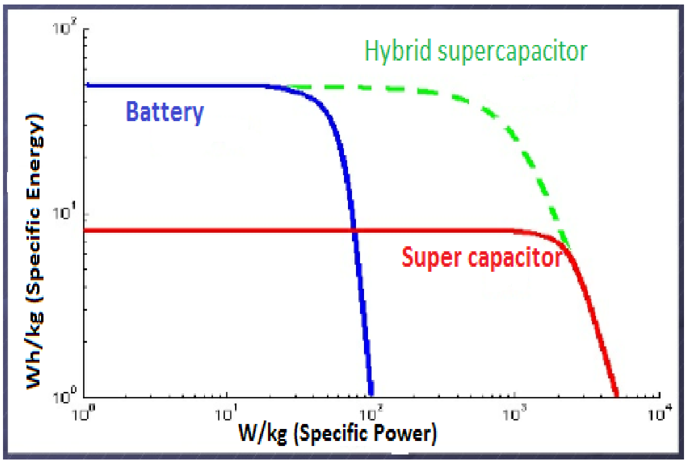


Figure 6.2: Comparison Characteristics of Battery, Supercapacitor and Hybrid Supercapacitor

✓ **Why we use the hybrid supercapacitor?**

In supercapacitor two symmetric capacitors are connected in series and the total capacitance is halved.

$$\frac{1}{C_{total}} = \frac{1}{C} + \frac{1}{C}$$

$$C_{total} = \frac{C}{2}$$

But in a hybrid supercapacitor one of the electrodes is replaced by a battery electrode. So we can get the total replaced by a battery electrode. So we can get the total capacitance of the single capacitor electrode with the added capacitance of the single capacitor electrode with the added advantage of battery electrode.

Hybrid electrode configurations show considerable potential consisting of two different electrodes made of different materials. The polymer is used as the positive electrode and an activated carbon or carbon nano tubes used as the negative electrode.

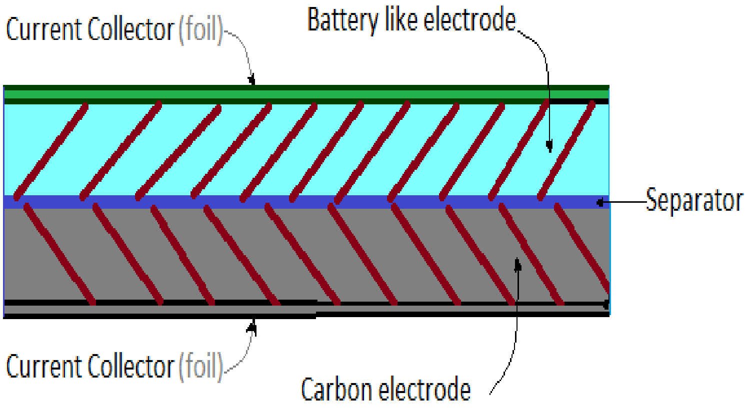


Figure 6.3: Schematic of Hybrid Supercapacitor

Fig 6.3 shows the schematic of hybrid supercapacitor.Composite electrodes integrate carbon-based materials with either conducting polymer or metal oxide materials and incorporate both physical and chemical charge storage mechanisms together in a single electrode. The carbon-based materials facilitate a capacitive double-layer of charge and also provide a high-surface-area backbone that increases the contact between the deposited capacitive materials and electrolyte. The polymer materials are able to further increase the capacitance of the composite electrode through faradaic reactions. This electrode is able to achieve higher capacitances than either a pure carbon nanotubes or pure polymer-based electrode. Hybrid supercapacitor can achieve very high energy density and power density without sacrifices in cycling stability and affordability. Now a days various cathode material like $LiMn_2O_4$, $LiCoO_2$, $LiFeP_2O_7$ etc. are proposed for hybrid supercapacitor. Research has been going on $LiMn_2O_4$ material because of high voltage, low cost and low toxicity. For anode material carbon based material carbon nano tubes are used.
Carbon nano foam is having the following positive properties compared to other carbon.

- High surface area
- Low electrical resistance
- No participation in faradic reactions at the applied voltage
- High capacity (100-200 F/g)
- Unlike activated carbon, carbon nano foam combine high surface

area with high bulk density to give large capacitance values

⇒ **Electrolytes**

The choice of electrolyte in an supercapacitor is as important as the choice of electrode material. The attainable cell voltage of a supercapacitor will depend on the breakdown voltage of the electrolyte, and hence the possible energy density (which is dependent on voltage) will be limited by the electrolyte. Resistance of an electrolyte can limit power density, its ion concentration and operating voltage can limit the energy density of a supercapacitor. Power density is dependent on the cells ESR which is strongly dependent on electrolyte conductivity. There are currently two types of electrolyte in use in supercapacitor: organic and aqueous.

- **Organic:-** Organic electrolytes are the most commonly used in commercial devices, due to their higher dissociation voltage. Cells using an organic electrolyte can usually achieve voltages in the range of 2 2.5 V. The resistivity of organic electrolytes is relatively high however limiting cell power.

- **Aqueous:-** Aqueous electrolytes, such as $H_2SO_4$ and $KOH$, generally have lower ESR and lower minimum pore size requirements compared to organic electrolytes. Aqueous electrolytes have a lower breakdown voltage typically 1 V but have better conductivity than organic electrolytes. The capacitance of an supercapacitor is greatly influenced by the choice of electrolyte. The ability to store charge is dependent on the accessibility of the ions to the porous surface-area, so ion size and pore size must be optimal. The best pore size distribution in the electrode depends upon the size of the ions in the electrolyte, so both electrode and electrolyte must be chosen together.

## 6.2 Electrical Parallel Resistance (EPR)

The EPR models current leakage,and influences long-term energy storage. EPR is an inner equivalent parallel resistance usually hundreds of kilo-ohms and decides the leakage current when the supercapacitor is in a stand by mode.

EPR involved slowly charging the supercapacitor to its rated voltage and then allowing a significant amount of time to pass before measuring the supercapacitor's terminal voltage. The EPR can be calculated from below equation:

$$EPR = \frac{-t}{ln\frac{V_2}{V_1}C} \tag{6.2}$$

where t is the time, $V_1$ is the initial voltage, $V_2$ is the final voltage, and C is assumed to be equal to the rated capacitance. The time constant of C and EPR is usually quite large, so the EPR can be ignored in the case of a short discharge up to the order of a few minutes.

To determine the ESR the EPR is ignored and the equivalent circuit is assumed to consist only of the ESR and the capacitance.

# Conclusion

The supercapacitor has higher power density than battery and higher energy density than conventional capacitor. The charging time of supercapacitor is quite less compare to battery. The experiment of charging and discharging of 560 F, 2.7 V supercapacitor is done at constant current of 2 A. From this experiment charging and discharging time of supercapacitor is known. By using these charging and discharging characteristics internal parameters of supercapacitor has been calculated. From these parameters the exact behavior of supercapacitor is obtained.

In order to replace battery with supercapacitor it is require to change the internal parameters of supercapacitor. Simulation has been done on battery having the rating of 6.5 Ah, 2.7 V in MATLAB Simulink software. To charge the battery constant current of 2 A is applied, and charging and discharging characteristics of battery is obtained from the simulation.

By using these charging and discharging characteristics as a supercapacitor characteristic the calculation has been done to find its internal parameters. From these parameters the electrical series resistance (ESR) of battery and electrical series resistance (ESR) of supercapacitor are calculated.

To replace battery with supercapacitor ESR value of supercapacitor should be equal to battery, i.e. the value of ESR of supercapacitor is to be increased. By increasing the value of electrical series resistance (ESR), the value of capacitance (C) is going to decreased. To overcome this difficulty compromise has been done between the value of electrical series resistance (ESR) and the value of capacitance (C). For this difficulty hybrid supercapacitor is used.

This hybrid supercapacitor fulfills the gap between the battery and supercapacitor. In this hybrid supercapacitor one electrode made of battery electrode and another electrode made of carbon electrode. Battery electrode increases the value of electrical series resistance (ESR) and carbon electrode increases the value of capacitance (C). So hybrid supercapacitor can be used for replacement of battery.

# Publication

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# Future Scope

- To replace the battery with supercapacitor the hybrid supercapacitor concept can be used in which the advantages of battery and supercapacitor are implemented.
- Model the hybrid supercapacitor and obtained charging and discharging characteristics same as battery.

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