Chapter 1

SUPERCAPACITOR : AN INTRODUCTION

1.1 Supercapacitor - An Emerging Electrical Energy Storage Device

Changing climatic patterns, depletion of fossil fuels and uneven distribution of energy sources necessitate opting for alternate, renewable sources to meet the ever growing energy demands of the societies around the globe. To cope up with such transiting energy paradigm, it is inevitable to develop affordable, efficient and reliable energy storage technologies to harvest energy from the unlimited but intermittent renewable energy sources such as wind, tide and sunlight. Electro-chemical supercapacitors gain prominence as electro-chemical energy storage device due to their unmatching superior characteristics such as: high power densities at reasonably high energy densities and long cycle life. A plot of power vs. energy density - known as Ragone plot for the important energy storage systems is shown in Figure 1.1 (Simon and Gogotsi, 2008).

As can be seen, if a supercapacitor is employed as an energy storage device, the specific power indicates that how fast it can deliver energy, and the specific energy indicates that how far it can deliver on a single charging. The time constraints of the devices indicated in the figure are derived by dividing the energy density by the power. The future market for batteries and the supercapacitor is expected to grow exponentially. Owing to the superior characteristics of the supercapacitors which have been mentioned above, they are already employed in spectrum of applications from power electronics, large scale vehicular applications such as buses and subway trains, store energy at intermittent generators in windmills to smart grid applications catering to stability, frequency smoothing and regulation and for peak shifting.

A capacitor, originally termed as a condenser is a passive electrical terminal used to electrostatically store energy in an electric field separated by a dielectric (insulator). A supercapacitor differs from a regular capacitor owing to its very high capacitance. Differential voltage application on the positive and negative plates, charge the capacitor - similar to buildup of electrical charge while walking on a carpet and release of energy through fingers while touching an object. The supercapacitors are rated in farads, which is several orders of magnitude higher than the electrolytic capacitor. Supercapacitors are considered to be ideal energy storage devices due to their ability to undergo frequent charge-discharge cycles at high current and short duration. The charge time of a supercapacitor is nearly 10 sec and the self-discharge of a supercapacitor is substantially higher that of an electrostatic capacitor and little higher than a battery - the main contributor to this phenomenon is organic electrolyte.In general, the energy stored in a supercapacitor falls to nearly 50% in duration of 30 days; while a nickel based battery self discharges 10-15% in a month but Li- ion battery discharges only to an extent of 5% per month.

1.2 Historical Perspective

In the ancient times, the idea of the possibility of storing an electrical charge in surface emerged from the phenomena associated with rubbing of amber. In the mid eighteenth century, the effect of such phenomena was understood when physics of so-called *static electricity* was being investigated and during that period, various *electrical machines* such as the Electrophorus and the Wimshurst machine were being developed. Excellent examples of these, as well as Leyden jars, can be witnessed in the Museum of Science in Florence. Understanding of electricity at the molecular electronic level did not begin until 140 years later, starting indirectly with the work of Michael Faraday and later with that of J. J. Thomson and of Millikan on the electron. The development of the Leyden jar, and the discovery of the principle of charge separation and charge storage on the two surfaces of the Leyden jar, separated by a layer of glass, were considered as milestones in the physics of electricity and later for electrical technology, electronics, and electrochemical engineering.

The discovery of the Leyden jar, referred to in early works and in technological applications up to the middle of the twentieth century as the *condenser* is attributed either to Dean Kleist at Leyden or contemporarily to Musschenbroek at Kamin, Pomerania. In later terminology, the device in var-

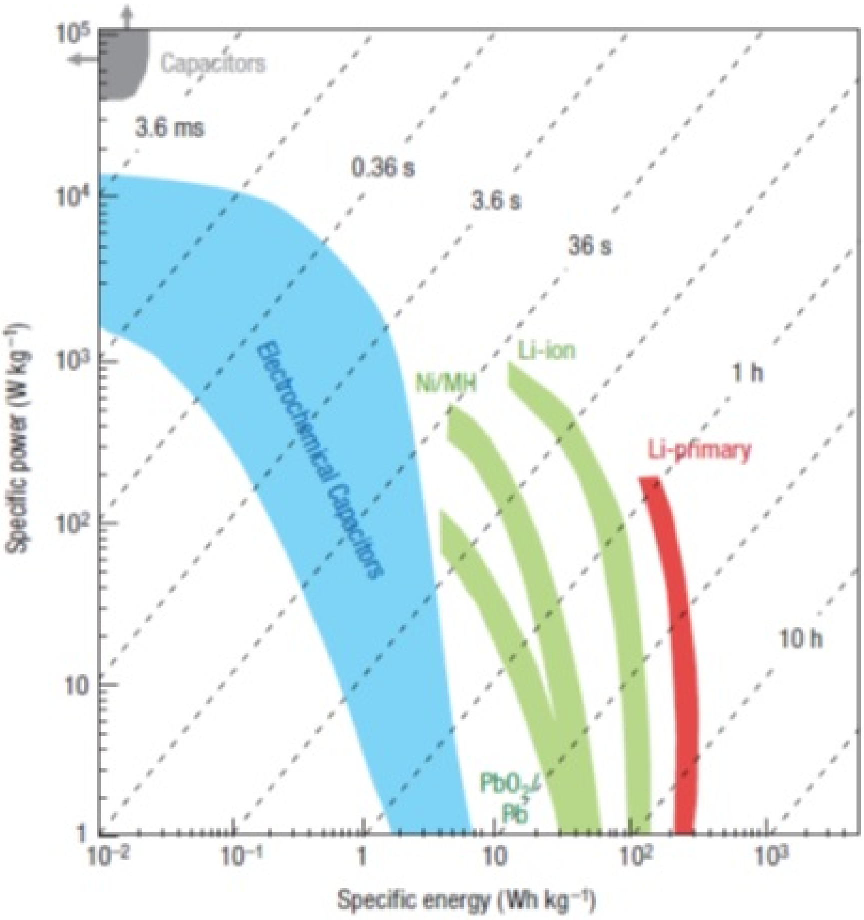

Figure 1.1: Specific power against specific energy, also called a Ragone plot for various energy storage devices. [Reproduced with permission from Ref. [1].

ious embodiments is referred to as a *capacitor* and its capability for charge storage per volt, is referred to as its *capacitance*, C. It has to be mentioned that the word *capacity*, used in battery terminology is to indicate the extent of Faradaic charge storage (in units of coulombs or watt-hours) should not be confused with *capacitance* (given in units of farads), which applies to capacitors.

For several years there existed uncertainty about the nature of electricity after the independent discoveries of *electricity* by Galvani in 1776 and voltaic electricity by Volta in 1800, and it remained poorly understood for a long time, notwithstanding the work by Faraday, including his finding of the chemical equivalence of electrical charge. It was not until the discoveries by J. J. Thomson on the charge-to-mass ratio of the ubiquitously produced negative charge carriers arising in the ionization of low-pressure gases - first investigated by Crookes (*Crookes*, 1879), and the work by Millikan (*Millikan*, 1913) and by Townsend (*Townsend*, 1879) on the absolute value of the charges borne by such particles that a modern view of the nature of electricity could be proposed in terms of accumulation or deficiency of such charges, and the dynamics of their motion. In 1881 Johnstone Stoney (Stoney, 1881 and 1891) coined the name *electron* (from the Greek word eAliKrOV for amber) for such negatively charged particles, which are the natural units of electricity, the electron charge being 4.80 x 10^{-10} electrostatic units (esu) of charge or 1.60 x 10^{-10} absolute electromagnetic units (emu) of charge.

It is of historical interest that Faraday himself has failed to reach the conclusion that his laws relating the extent of a charge's passage (current x time = coulombs) to quantitatively determinable extents of chemical change associated with the electrolysis of aqueous acid and metal-salt solutions, implied an atomic unit of electricity. However, the importance of his laws is in no way diminished by that difficulty because the laws clearly demonstrated in a quantitative way the equivalence of electrical charge to the extent of a generated chemical change that was dependent on the chemical identity of the element concerned and its equivalent weight or oxidation state in solution. It was only much later, von Helmholtz (Von Helmholtz, 1881) in his Faraday Lecture of 1881, arrived at the key conclusion that Faraday's laws implied that a fundamental unit of electrical charge was universally involved. This concept has paved the way for the development of the quantitative and more fundamental science of electrochemistry and for a quantitative science of the electrical nature of matter. This work was further elucidated through spectroscopy and the theoretical advances of Bohr, Sommerfeld, Schroedinger, and Heisenberg on electron energy states in atoms and molecules, and the significance of ionization and its relation to solvolysis in solution and the state of solid salts (*Conway*, 1981).

Although the experimental phenomenology of electrical charging of surfaces, including those of the Leyden jar condenser, was well understood in the mid- and later part of the eighteenth century, the full physical significance of charging or discharging processes at the plates of capacitors could not have been at all fully understood until the atomic nature of electricity, the electron, was characterized and its properties directly determined (J.J. Thomson,1903; Millikan, 1913; Townsend, 1879). Similarly, the charging or discharging of capacitors by a flow of electrical charges in wires could not have been understood until the electron theory of metals had been developed and the mechanism of current flow in metal conductors was understood. Nor for that matter could the physical and chemical significance of the charging of amber be understood until satisfactory ideas about the ionization of molecules and macromolecules (through frictional or triboelectrical effects) had been formulated, partially through the results on spectroscopic ionization limits of electron energy states in molecules or atoms. Thus, the mechanisms of electrical charge storage in capacitors remained incompletely understood at the atomic physical level until some 140 years after the development of the Leyden jar capacitor and related contemporary electrical machines. Nevertheless, it was Faraday who had some of the first (in principle) correct ideas about polarization in dielectrics and the significance of dielectric strain and lines of (electrical) force in the dielectric materials of charged condensers.

At this point it has to be mentioned that the charging of metallic plates of a capacitor involves production of an excess (negative plate) or deficiency (positive plate) of the density of the delocalized electron plasma of the metal over a short distance (ca. 0.1-0.2 nm, the Thomas-Fermi screening distance) from the formal outer surface of the metal plate. However, each plate has its own electric potential (an equipotential) throughout its material, except very near its surface. Hence, local charge density variation within the so-called *Thomas-Fermi screening distance* has to arise according to the Poisson relation that expresses the field gradient in terms of the local space charge density and the Gauss relation that expresses the field as a function of surface charge density. At an insulator such as amber, the excess charge density that arises upon charging has a different origin that is associated with localized molecular ionization (localized oxidation) of the insulator material at its surface, or in some cases is due to negative ionization by localized uptake of electrons at electron acceptor sites on the surface (localized reduction). These latter phenomena are the subject of triboelectricity. The principle that electrical energy can be stored in a charged capacitor was known since 1745; at a voltage difference, V, established between the plates accommodating charges $+q$ and $-q$, the stored energy, G, is $\frac{1}{2}CV^2$ or $\frac{1}{2}qV$, G being a Gibbs free energy which increases as the square of V. The utilization of this principle to store electrical energy for practical purposes, as in a cell or battery of cells seems to have been first proposed and claimed as an original development in the patent granted to Becker in 1957 (*Becker*, 1957).

The patent described the electrical energy storage by means of the charge held in the interfacial double layer at a porous carbon material perfused with an aqueous electrolyte. The principle involved was charging of the capacitance, C_{dl} of the double layer, which arises at all solid/electrolyte interfaces, such as metal, semiconductor, and colloid surfaces and also at the phase boundary between two immiscible electrolyte solutions (*Samec*, 1979).

In 1957, a team of General Electric Engineers were experimenting with devices using porous carbon electrode and they observed the electric double layer capacitor effect. They have inferred that energy was in store at the carbon pores and it showed an exceptionally high capacitance. Later in 1966, a group of researchers at Standard Oil of Ohio accidently rediscovered the effect while working on fuel cell designs. Their cell design contained two layers of activated charcoal separated by a thin porous insulator, and the mechanical design remained the same for most electric double layer capacitors to date. In 1978 NEC finally introduce the term Supercapacitor and its application was used to provide backup power for maintaining computer memory (*Conway*, 1999). Due to its application, supercapacitor captured the attention of many researchers which led to trying of other composite as electrode material such as Metal Oxides and Conducting Polymer etc.

Among the challenges faced in this century is unquestionably energy storage. Therefore it is important that new, environmentally friendly and low-cost energy storage systems be found, in response to the needs of emerging ecological concerns and modern society (Arico et al., 2005).

Supercapacitors (also called electric double-layer capacitors or ultracapacitors) are energy storage devices with very high capacity and a low internal resistance, that are able to store and deliver energy at relatively higher rates as compared to batteries due to the mechanism of energy storage which involves a simple charge separation at the interface between the electrode and the electrolyte (Stoller, et al., 2008; Wu et al., 2010). A supercapacitor consists of two electrodes, an electrolyte, and a separator which isolates the two electrodes electrically. Electrode material is the most important component of a supercapacitor (Ervina et al., 2012; Pope et al., 2013). Some of the benefits of supercapacitors when compared with other energy storage devices are long life, high power, flexible packaging, wide thermal range (-40°C to 70°C), low maintenance and low weight (Wang et al., 2009). Supercapacitors can best be utilized in areas that require applications with short load cycle and high reliability, for example energy recapture sources such as forklifts, load cranes and electric vehicles, power quality improvement (Miller and Simon, 2008). Among the promising applications of supercapacitors is in fuel cell vehicles and low emission hybrid vehicles (Wu, 2002; Cai et al., 2011). Supercapacitors with its unique qualities when used with batteries or fuel cells they can serve as temporary energy storage devices providing high power capability to store energy from braking (Zhang and Zhou, 2009; Mittal and Kumar, 2011).

Due to its high power capability a bank of supercapacitors, can bridge the short time duration between a power failure and the start up of backup power generators. Even though energy density of supercapacitor is greater than that of conventional capacitors; it is considerably lower than batteries or fuel cells. Electrochemical performances of an electrode material strongly rely on factors like surface area, electrical conductivity, wetting of electrode and permeability of electrolyte solutions (Rajagopalan and Chung, 2014). Passive components are required in all electronic applications to store electrical energy in volume and weigh as small as possible. The power needed by an application as well as the speed of storage process determines the type of energy storage device to be used. Essentially, when it comes to applications the ones that need faster discharge rate go for capacitor while the slower ones go for batteries. From figure 1.1, it can be seen that a batteries are capable of attaining up to 150 Wh/kg of energy density, around 10 times what an electrochemical capacitor is capable of. In terms of power density batteries do not have the capability of reaching the values of electrochemical capacitors. Batteries hardly reach 200 W/kg which is about 20 times less than the expected electrochemical capacitor performance. Batteries experience weaknesses like rapid decrease in performances due to fast charge discharge cycles or cold environmental temperature, they are expensive to maintain and have a limited life time (Schneuwly and Galley, 2000).

One of the frequently asked question is how can the electrochemical supercapacitor technology compare to the battery technology? At the moment, these supercapacitors cannot be used to substitute for the battery technology but could work as a supplement in terms of momentary and temporary power outage by providing instantaneous current required thereby reducing battery current. In large scale battery units, electrochemical supercapacitors can be installed in parallel to compensate for momentary and temporary interruptions. This would greatly repress the undue stress put on batteries from short term interruptions (Smith and Sen, 2008).

1.3 Supercapacitors and Batteries as Electrical Energy Storage Devices: Similarities and Differences

Fundamentally, electrical energy can be stored in two different ways - indirectly or directly. Indirectly, in batteries, potentially available chemical energy requires Faradaic oxidation and reduction of the electrochemically active components to release charges to perform electrical work, when they follow between two electrodes with different electrode potentials. Directly, in an electrostatic way, as negative and positive electric charges on the plates of a capacitor - a process called as non-Faradaic electrical energy storage. Compared to fuel combustion systems, which are limited thermodynamically by Carnot cycle considerations, the efficiencies of the two modes of electrochemical systems - batteries and supercapacitors, usually involve more reversible processes, with direct conversion of potentially available chemical energy to *Gibb's free energy*, G.

An important difference emerges between the reversibility of Faradaic and non-Faradaic systems. In energy storage by capacitors, only an excess and a deficiency of electron charges on the capacitor plates needs to be established on charge and the reverse on discharge; no chemical changes are involved. However, with storage of electrochemical energy in battery cells through Faradaic reactions, chemical interconversions of the anode and cathode materials have to take place, usually associated with phase changes. Although the overall energy change can be conducted in a relatively reversible thermodynamic way, the charge and discharge processes in a battery often involve irreversibility in interconversion of the chemical electrode reagents; thus the cycle life of battery cells is usually restricted to one thousand to several thousand discharge and recharge cycles, depending on the type of battery. By contrast, a hardware capacitor has an almost unlimited cyclability since no chemical and phase changes are involved during its charging and discharging processes.

Ordinary capacitors unless they are large, have a very small amount of charge storage. That is, they have a low energy density for electrical energy storage. However, charged electrode/solution interfaces contain double layers that have capacitances of about 16 to 50 μF cm^{-2}; hence, with the sufficiently large accessible electrode areas that are realizable with high-area carbon powders, felts, and aerogels, very large double-layer capacitances on the order of 10 to 100 F per gram can be achieved. It is the practical realization of this possibility in recent years (but originating in early technological development some 35 years ago at Sohio) that has led to the relatively new field of electrochemical capacitors. These are now actively progressing as energy storage devices to complement batteries.

Because the charging and discharging of such double-layer capacitors involves no chemical phase and composition changes which, in batteries, lead to materials irreversibility, such capacitors have a high degree of recyclability, on the order of 105-106 times. Only electrons need to be moved to and from the electrode surfaces through the external circuit, and cations and anions of the electrolyte transported within the solution to the charged interfaces. It is for these reasons that capacitor charging and discharging processes are highly reversible. In the cyclic voltammetry of such systems, the charging and discharging voltammograms are almost mirror images of one another, while for battery processes they are rarely of this kind. This is a major and characteristic difference between battery and capacitor electrical energy storage systems.

It must be emphasized at the outset that there has never been an aim or projection of a possible substitution of batteries by supercapacitors; rather, opportunities arise for complementary operation of electrochemical capacitors that are electrically coupled in discharge and recharge with batteries, while other kinds of applications especially favor capacitor-type behavior, such as backup power systems. Also, there are stand-alone opportunities for using multiple rechargeable electrochemical capacitors in a variety of independent functions.

In the early stages of the development of electrochemical capacitor technology and related fundamental work, there was some confusion in the area of electrochemical engineering and on the differences between the properties and operation of a battery and a supercapacitor, and what advantages one might have over the other. This confusion may have been assisted by some groups calling the capacitor devices *ultracapacitors* and others, *supercapacitors*, the latter as originated by the Ottawa group in 1975. The present preferred name, proposed by Burke, is now more scientific and generic, namely *electrochemical capacitors.*

In this section, we discuss on some of the similarities and differences between electrochemical capacitors and batteries with respect to the electrochemical processes that are involved in their discharge and recharge cycling, and in their potential uses as electrical energy storage devices. In particular, the fundamentally different mechanisms of charge storage that are normally involved will be emphasized, along with the consequent, usually different, relations between the extents of charge accommodated at the electrodes and the electric potential differences (cell voltage) between pairs of electrodes having conjugate,$\pm$, polarities. One of the main and kinetically significant differences between capacitors and batteries is that the electrodes of the latter usually undergo substantial phase changes during discharge and recharge (minimally though for the intercalation systems), which lead to kinetic and thermodynamic irreversibility. On the other hand, capacitors of the double-layer type require only electrostatic charge accommodation with virtually no phase change, though some small but significant reversible electrostriction of the electrolyte can arise upon charging.

1.3.1 Faradaic and Non-Faradaic Processes

A fundamental difference between the operational mechanism of electrochemical capacitors and battery cells is that for the double-layer type of capacitor, the charge storage process is non-Faradaic - ideally no electron transfer takes place across the electrode interface and the storage of electric charge and energy is electrostatic. In battery-type processes, the essential process is Faradaic - electron transfer does take place across the double layers, with a consequent change of oxidation state, and hence the chemistry of the electro active materials. Intermediate situations arise where Faradaic charge transfer occurs, but owing to special thermodynamic conditions that apply, the potential, V, of the electrode is some continuous function of the quantity of charge, q, passed so that a derivative, dq/dV, arises. This is equivalent to and measurable as a capacitance and is designated as a pseudocapacitance. A somewhat different situation arises when chemisorptions of ions or molecules takes place with partial charge transfer (Lorenz and Salie, 1961; Schultze and Koppitz, 1976; Conway and Kozlowska and Sharp, 1975). For example, in a process such as

$$M + A^{-} \leftrightarrow M/A^{(1-\delta)-}(inM) \tag{1.1}$$

Such a reaction at the surface of an electrode M usually gives rise to a potential dependent pseudocapacitance and the quantity δe is related to the so-called *electrosorption valence.* Hence, the important differences in the charge storage processes are as follows:

In non-Faradaic process, the charge accumulation is achieved electrostatically by positive and negative charges residing on two interfaces separated by a vacuum or a molecular dielectric (the double layer or, e.g., a film of mica, a space of air or an oxide film, as in electrolytic capacitors).

In Faradaic process, the charge storage is achieved by an electron transfer that produces chemical or oxidation state changes in the electroactive materials according to Faraday's laws (hence the term) related to electrode potential. Pseudocapacitance can arise in some cases. The energy storage is indirect and is analogous to that in a battery. In a battery cell, every electron charge is Faradaically neutralized by charge transfer, resulting in a change of oxidation stage of some redox electroactive reagent. For example, in the cathode of Ni-Cd battery (*Linden*, 1995), the following reaction takes place.

$$\mathrm{Ni}^{3+}.\mathrm{O}^{2-}.\mathrm{OH}^- + e^- + H^+ \rightarrow \mathrm{Ni}^{2+}.2\,\mathrm{OH}^- \tag{1.2}$$

In a capacitor, actual electron charges, either in excess or deficiency, are accumulated on the electrode plates with lateral repulsion and no involvement of redox chemical changes. However, in some cases of double-layer charging, some partial electron transfer does occur, giving rise to pseudocapacitance, e.g., when chemisorption of electron-donative anions such as Cl^-, Br^-, I^- or CNS^-, takes place as represented in Eq. 1.1.

The electrons involved in double-layer charging are the delocalized conduction-band electrons of the metal or carbon electrode, while the electrons involved in Faradaic battery-type processes are transferred to or from valence-electron states (orbitals) of the redox cathode or anode reagent, although they may arrive in or depart from the conduction-band states of the electronically conducting support material. In certain cases, the Faradaically reactive battery material itself is metallically conducting (e.g., $\mathrm{PbO_2}$, some sulfides, $\mathrm{RuO_2}$), or else is a well-conducting semiconductor and a proton conductor, e.g., Ni·O·OH.

1.3.2 Types of Capacitors and Batteries

Various types of capacitors and their mode of energy storage - electrostatic or Faradaic (when pseudocapacitance arises), are summarized in Table 1.1. Herein we provide only the over view of different kinds of capacitors and it is a matter for detailed discussion in Chapter 2. Normally, capacitors function as elements of electronic circuits or communications equipment, or as ballast for starting electric motors or electric discharge tubes such as fluorescent lights. Also, devices of very large capacitance are now available for storing electric energy in various applications. In Table 1.2, we summarize a few distinguished types of batteries. These are generally classified as primary (non-rechargeable) or secondary (multiply rechargeable) batteries. The discharge or recharge mechanism is mainly Faradaic, although all electrode interfaces exhibit a double-layer capacitance that is reversibly chargeable. For batteries the latter mechanism accommodates about 2-5% of the total charge accepted. In a different class from the battery systems listed in Table 1.2 are fuel cells in which the anode and cathode (oxygen or air) reactants are supplied on a continuous basis from external reservoirs, and the electrode surfaces provide an interface for either electrocatalytic oxidation or reduction

Table 1.1: Types of capacitors and mode of energy storage

Type	Basis of charge or energy storage	Examples
Vacuum	Electrostatic	
Dielectric	Electrostatic	Mica, Mylar, paper
Oxide electrolytic (thin film)	Electrostatic	Ta_2O_5, Al_2O_3
Doulble-layer	Electrostatic (charge separation at double-layer at electrode interface)	Carbon powders, fibres
Colloidal electrolyte	Electrostatic (special double layer system)	
Redox oxide film	Faradaic charge transfer (pseudocapacitance)	RuO_x, IrO_x, Co_3O_4
Redox polymer film	Faradaic charge transfer (pseudocapacitance)	Polyaniline, polythiophene
Soluble redox system	Faradaic charge transfer (pseudocapacitance)	$V^{2+}/V^{3+}/VO^{2+}$, $\mathrm{Fe(CN)}_6^{4-}$ - $\mathrm{Fe(CN)}_6^{4-}$

of the reagents supplied. The primary metal-air cells are operated as semi-fuel cells, but the *fuel* is an easily oxidizable base metal and a gas-diffusion catalyzed air or O_2 cathode is employed. Such cells using Al are not rechargeable except by mechanical replacement of the metal anodes. However, if Zn is used, electrochemical recharging is possible, but requires a bifunctional catalyzed counter electrode capable of evolving H_2 on recharge or reducing O_2 (air) on discharge.

1.3.3 Electrochemical Capacitors and Batteries: Comparative Properties

The behavior and properties of electrochemical capacitors and batteries are summarized in this section in tabular forms. The advantages and disadvantages of employing electrochemical capacitor for electrical energy storage are listed in Table 1.3. Comparative electrical characteristics of battery and electrochemical capacitor behavior are given in Table 1.4, and the essential difference of thermodynamic behavior of ideal battery and electrochemical capacitor materials are given in Table 1.5. The overall comparison of electrochemical capacitor and battery characteristics under charge-recharge conditions is presented in Table 1. 6.

Table 1.2: Types of batteries and mode of energy storage

Type	Basis of charge or energy storage
	Primary
Leclanche, Zinc-MnO_2	Faradaic
Alkaline, Zinc-MnO_2	Faradaic
Mg-AgCl	Faradiac
Mg-PbCl_2	Faradaic
Li-SOCl_2 and other cathodes	Faradiac
Li-CF_x	Faradiac
Al-air (catalyzed)	Faradiac
Mg-AgCl	Faradiac
Mg-PbCl_2	Faradiac
Li-SOCl_2 and other cathodes	Faradiac
Li-CF_x	Faradiac
Al-air (catalyzed)	Faradiac
Zn-air (catalyzed)	Faradiac
	Secondary
Lead-acid, Pb-PbO_2	Faradiac
Nickel-cadmium, Ni·O·OH-C	Faradiac
Nickel-hydrogen, Ni·O·OH-metal hydride	Faradiac
Nickel-zinc, Ni·O·OH-Zn	Faradiac
Mercuric oxide-zinc, HgO-Zn	Faradiac
Silver oxide(s)-zinc, AgO-Zn	Faradiac
Zinc-air (catalyzed)	Faradiac
Li-TiS_2	Faradaic (exhibiting intercalative psuedocapacitance)
Li-MoS_2	Faradaic (exhibiting intercalative psuedocapacitance)
Li-MnO_2	Faradaic (exhibiting intercalative psuedocapacitance)
Li-CoO_2	Faradaic (exhibiting intercalative psuedocapacitance)
Li-C-CoO_2 and other cathodes	Faradaic (exhibiting intercalative psuedocapacitance)
Li-iron sulfides	Faradaic (exhibiting intercalative psuedocapacitance)
Na-S	Faradaic (exhibiting intercalative psuedocapacitance)

Table 1.3: Advantages and disadvantages of employing electrochemical capacitor for electrical energy storage

Advantages	Disadvantages
• Long cycle life, $> 100,000$ cycles;some systems up to 10^6	• Limited energy density
• Good power density [under certain conditions, limited by IR or equivalent series resistance (esr) complexity of equivalent circuit]	• Poor volume energy density
• Simple principle and mode of construction (can employ battery construction technology)	• Low working voltages (compared with electrolytics; satisfactory compared with batteries)
• Cheap materials (for aqueous embodiments)	• Aq. voltage range 0 - 1.4 V; non-aq. to 4.5 V. In practice, 3.5 V
• Combines state-of-charge indication, $Q = j(V)$	• Non-aq. embodiments require pure, H_2O-free materials; more expensive
• Can be combined with rechargeable battery for hybrid applications (electric vehicles)	• Requires stacking for high potential operation (electric vehicles)
	• Hence, good matching of cell units is necessary

Table 1.4: Comparative electrical characteristics of battery and electrochemical capacitor behavior

Battery	Electrochemical Capacitor
• Ideally has single-valued free energies of components	• Has continuous variation of free energy with degree of conversion of materials or extent of charge held
• emf is ideally constant with degree of charge and discharge, except for nonthermodynamic incidental effects, or phase changes during discharge	• Potential is thermodynamically related to state of charge through $\log[\frac{X}{1-X}]$ factor, in a continuous manner for a pseudocapacitor, or directly to Q for a double-layer capacitor
• Behavior is not capacitative, except in very general sense	• Behavior is capacitative
• Irreversibility is usual behavior (materials irreversibility and kinetic irreversibility)	• High degree of reversibility is common (10^{-4} -10^{-6} cycles with RuO_2 or C double-layer capacitors)
• Response to linear modulation of potential gives irreversible i vs. V profile with non—constant currents	• Response to linear modulation of potential gives more or less constant charging current profile but with some dependence on materials
• Discharge at constant current arises at a more or less constant potential except for intercalation Li batteries	• Discharge at constant current gives mainly linear decline of potential with time, which is characteristic of a capacitor

Table 1.5: The essential difference of thermodynamic behavior of ideal battery and electrochemical capacitor materials

Battery	Electrochemical Capacitor
• During discharge or recharge has unique, single-valued free energies ΔG of the electroactive phases involved ΔG = constant	• Has continuously changing free energy of electroactive material with extent of charge and discharge. $G = \frac{1}{2}CV^2 \quad or \quad \Delta G = \Delta G^0 + RT\ln[\frac{X}{1-X}] \qquad (1.3)$ for pseudocapacitance
• Has corresponding single-valued potential on discharge	• Has corresponding continuous variation of potential during charge and discharge
• Usually not reversible, in the sense that recharge curve is not mirror image of discharge curve, e.g., in cyclic voltammetry.	• Recharge and discharge curves are mirror images of one another, i.e., in cyclic voltammetry. Highly reversible

1.4 Outlook and Scope of the Monograph

Supercapacitors emerge as promising candidates for power devices for future generations. Apart from niche applications, these devices are expected to find several future applications in hybrid electric vehicles and other larger power devices and systems. For supercapacitors to attain such status, it is important that their energy and power densities be maximized. An important way to address this is to develop advanced electrode materials and methods to fabricate these materials. The recent years have seen enormous interest in the research of numerous materials and methods for their synthesis for applications in supercapacitor electrode technology. In the constantly changing technological scenario, it is relevant to review the various aspects of supercapacitor devices. In order to push the frontiers in this area, it is essential to carefully and critically evaluate the materials that are employed for this purpose, and it is inevitable to identify and develop advanced materials and fabrication methods for these devices, with an eye on recent developments in these areas, and their implications on the future of supercapacitor technology. This monograph also addresses the principal technological challenges facing the development efforts in the future.

The aim of this treatise is to give a comprehensive view, present critical analyses and to examine the principle involved in the choice of materials

Table 1.6: Overall comparison of electrochemical capacitor and battery characteristics

Battery	Capacitor
• Ideally has constant (thermodynamic) discharge or recharge potential, except for Li intercalation systems	• Has intrinsically sloping charge and discharge curve
• Does not have good intrinsic state-of-charge indication except for Li intercalation systems	• Due to above reason, it has good intrinsic stage-of-charge indication
• Has moderate or good energy density, depending on equivalent weights and electrode potentials of active materials	• Has relatively poor energy density
• Has relatively poorer power density, depending on kinetics	• Has good power density
• Has less cycle life by a factor of $\frac{1}{100} \approx \frac{1}{1000}$ due to irreversibility of redox and phase-change processes in three dimensions	• Has excellent cyclability or cycle life due to simple addition or withdrawal of charges $(indouble-layertype)$
• Has internal IR due to electrolyte and active materials	• Has internal IR due to high-area matrix + electrolyte
• Has significant T -dependent activation polarization (Faradaic resistance)	• Has little or no activation polarization but C may be temperature-dependent
• Has poorer lifetime due to degradation or reconstruction of active materials	• Has long lifetime except for corrosion of current collectors, etc.
• Electrolyte conductivity can decrease or increase on charging, depending on chemistry of cell reactions, e.g., with Pb-acid	• Electrolyte conductivity can diminish on charging due to ion adsorption
• Can be constructed in bipolar configuration	• Can be constructed in bipolar

for electrode and electrolyte development and their influence on the overall performance of the supercapacitor, covering both the fundamental science (physics, chemistry and engineering aspects). In order to provide the necessary background in this field to the reader, some fundamental aspects and principles of electrochemistry is presented in Chapter 2. In Chapter 3, the basic principles involved in the selection of materials for electrode fabrication, status report on the various types of materials that are employed will be discussed and analyzed, along with various synthetic strategies adapted for their preparation. Considerable attention is given to the various characterization techniques which have been used to gauge the performance of supercapacitors in Chapter 4. Chapter 5 will present on basic conceptual and theoretical background concerning the improvement of capacitance value of the supercapacitors to advance their applications by maximizing their energy and power densities. Chapter 6, the final chapter of this monograph will present the challenges still remaining in this area and the possible propositions to surmount the difficulties, to realize this technology in practical applications.

1.5 References

1. P. Simon and Y. Gogotsi, Materials for electrochemical capacitors, *Nat. Mater.*, 2008, 7, 845-854.
2. W. Crookes (1879), quoted by S. Glasstone in Textbook of Physical Chemistry, Van Nostrand, New York (1940).
3. R. A. Millikan, *Phys. Rev.*, 2, 143 (1913).
4. J. S. Townsend, Electricity in Gases (1879), quoted by Glasstone as in Ref. 2.
5. G. J. Stoney, Phil. Mag.,ll, 381 (1881); Sci. Trans. Roy. Soc. Dublin, 4,583 (1891).
6. H. Von Helmholtz, 1. *Chern. Soc., Lond.*, 39, 277 (1881).
7. B. E. Conway, Ionic Hydration in Chemistry and Biophysics, Elsevier, Amsterdam (1981).
8. J. Thomson, Phil. Mag., 5,346 (1903); see also J. J. Thomson, The Electron in Chemistry, Franklin Institute Lectures, Chapman and Hall, London (1923).
9. H. E. Becker, U.S. patent 2,800,616 (to General Electric Co.) (1957).
10. Z. Samec, *J. Electroanal. Chern.*, 103, I (1979).
11. B.E. Conway Electrochemical Supercapacitors Scientific Fundamentals and Technological Applications, Plenum Press, New York (1999).
12. A.S. Arico, P. Bruce, B. Scrosati, J.M. Tarascon and W.V. Schalkwijk, *Nat. Mater.*, 4 (2005) 366.

13. M.D. Stoller, S. Park, Y. Zhu, J. An and R.S. Rouf, *Nano Lett.*, 8 (2008) 3498.
14. H.P. Wu, D.W. He, Y.S. Wang, M. Fu, Z.L. Liu, J.G. Wang and H.T. Wang, IEEE, (2010) 465.
15. M.H. Ervina, B.S. Miller, B. Hanrahan, B. Mailly and T. Palacios, *Electrochim. Acta*, 65 (2012) 37.
16. M. A. Pope, S. Korkut, C. Punckt and I.A Aksay, *J. Electrochem. Soc.*, 160 (2013) A1653.
17. Y. Wang, Z. Shi, Y. Huang, Y. Ma, C. Wang, M. Chen and Y. Chen, *J. Phys. Chem. C*, 113 (2009) 13103.
18. J.R. Miller and P. Simon, *Mater. Sci.*, 321 (2008) 651.
19. N.L. Wu, Mater. *Chem. Phys.*, 75 (2002) 6.
20. Y.M. Cai, Z.Y. Qin and L. *Chen, Progress Nat. Sci*: *Mater. Int.*, 21 (2011) 460.
21. L.L. Zhang and X. S. Zhao, *Chem. Soc. Rev.*, 38 (2009) 2520.
22. A.K. Mittal and M.J. Kumar, *Nanosci. and Nanotech.*, 13 (2011) 263.
23. B. Rajagopalan and J.S. Chung, *Nanoscale Research Lett.*, 9 (2014) 1.
24. A. Schneuwly and R. Gallay, PCIM, (2000) 1.
25. S.C. Smith and P.K. Sen, IEEE, (2008).
26. W. Lorenz and G. Salie, Zeit. *Phys. Chern.*, N.F. 29,390,408 (1961).
27. J. W. Schultze and F. D. Koppitz, *Electrochim. Acta*, 21, 327, 337 (1976).
28. B. E. Conway, H. A. Kozlowska, and W. B. A. Sharpe, Zeit. *Phys. Chem.*, N.F., 98, 61 (1975).
29. D. Linden, ed., Handbook of Batteries, 2nd ed., McGraw-Hill, New York (1995).

Chapter 2

FUNDAMENTALS AND ENERGY STORAGE MECHANISMS

2.1 Introduction

Fundamentals in electrodics and electrochemistry of supercapacitors, basic principles governing the overall performance of supercapacitors and their unique characteristics, especially in aspects of charge transfer at interfaces involving electrode with special emphasis on kinetics and energetics are presented and discussed in this chapter, considering the needs of the diversified class of researchers in this filed - electrochemical engineers and technologists, material scientists, physicists and specialists in electrochemistry.

The charging and discharging of a capacitor involve only electrostatic processes and not any type of Faradaic electrode processes. Therefore, the effect of electrode kinetics will arise practically only while a capacitor electrode ceases, and thereby it can no longer be an ideally polarizable one. [1] This situation sets in during an overcharge owing either to decomposition of solution or the occurrence of Faradaic self-discharges due to the presence

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[1] **Ideally polarizable electrode*: It is an electrode characterized by the absence of net current between the two sides of the Electrical double layer. i.e., no Faradic current between the electrode surface and the electrolyte. No direct current flows between the electrode and the surrounding electrolyte. In this sense the electrode/electrolyte interface behaves like a capacitor. This is contrasted with Ideally non-polarizable electrode in which Faradic current freely pass. The equilibrium potential does not change with the passage of current and in this sense the interface behaves as a resistor. Typical examples of these two types are the platinum electrodes (polarizable) and the silver/silver chloride (non-polarizable).

of oxidizable or reducible impurities or even due to the presence of reactive functional groups on the carbon surfaces. Therefore, even in case with electrochemical capacitors either indirect or direct contribution from Faradaic electrode processes can happen due to:

1. During the decomposition of electrolyte, inevitable occurrence of overcharge or over-discharge of the double-layer capacitors occurs;
2. In carbon-based double-layer capacitors, charge or discharge of though small but significant component of pseudo-capacitance occurs;
3. During the self-discharge processes in electrochemical capacitors, open circuit followed by charging takes place;
4. While the governance of the Faradaic mechanisms of charging or discharging of oxide based or conducting polymer based pseudo-capacitors or due to adsorption, the kinetics and energetic of the processes are directly involved.

2.2 Fundamentals

In conventional capacitors, two conducting electrodes are separated by a dielectric, insulating material. When a voltage is applied to a capacitor, opposite charges kept accumulating at the surface of each electrode. The charges are kept separated by the insulator, thereby the electric field produced let the capacitor to store the energy. This concept is pictorially represented in Figure 2.1.

Capacitance $\boldsymbol{C}$ is defined as the ratio of stored (positive) charge Q to the applied voltage $\boldsymbol{V}$:

$$C = \frac{Q}{V} \tag{2.1}$$

For a conventional capacitor, $\boldsymbol{C}$ is directly proportional to the surface area $\boldsymbol{A}$ of each electrode and inversely proportional to the distance $\boldsymbol{D}$ between the electrodes. This can be expressed as in Eq. 2.2.

$$C = \epsilon_0 \epsilon_r . (\frac{A}{D}) \tag{2.2}$$

where, ϵ_0 is the dielectric constant, that is the so called *permittivity* of free space and ϵ_r is the dielectric constant of the insulating material between the electrodes, and the product of these two factors is proportionality constant.

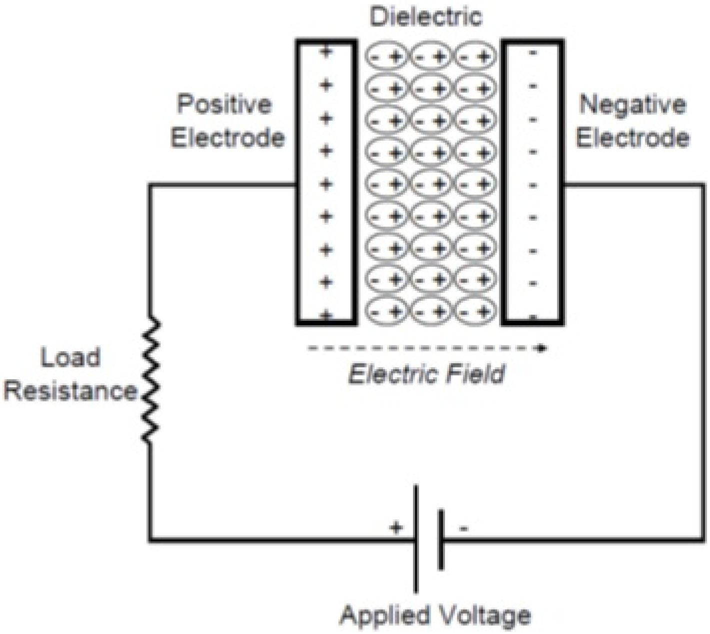


Figure 2.1: Diagrammatic representation of a conventional capacitor

The main attributes of a capacitor are its energy density and power density. In order to measure either of these, the density has to be calculated as a quantity per unit mass or per unit volume. The energy ***E*** stored in a capacitor is directly proportional to its capacitance:

$$E = \frac{1}{2}CV^2 \tag{2.3}$$

It is generally known that the power ***P*** is the energy expended per unit time. To determine ***P*** for a capacitor, one must consider that capacitors are generally represented as a circuit in series with an external *load* resistance ***R***, as is shown in Figure 2. 1. The internal components of the capacitor such as electrodes, current collectors and dielectric material also contribute to the resistance, which is measured cumulatively by a quantity termed as the equivalent series resistance (ESR). The voltage during discharge is determined by these resistances. When measured in terms of impedance (R = ESR), the maximum power $\boldsymbol{P_{max}}$ for a capacitor [1-3] is given by equation (2.4), showing that how ESR can limit the maximum power of a capacitor.

$$P_{\max} = \frac{V^2}{4} \times ESR \tag{2.4}$$

Conventional capacitors have relatively high-power densities, but relatively low energy densities compared to electrochemical batteries and fuel cells (two other energy conversion devices), and hence a battery can store more total energy than a capacitor, but it cannot deliver it faster, implying that its power density is low. Capacitors, on the other hand, store relatively less energy per unit mass or volume, but the stored electrical energy can be discharged rapidly to produce significant power, so their power density is usually high. Supercapacitors are governed by the same basic principles as conventional capacitors, but they incorporate electrodes with higher surface area ***(A)*** and thinner dielectrics that decrease the distance ***D*** between the electrodes. Thus, from equations (2.2) and (2.3), it can be seen that this leads to an increase in both capacitance and energy. By maintaining the low ESR characteristic of conventional capacitors, supercapacitors also are capable of attaining comparable power densities. Further, supercapacitors have several advantages over batteries and fuel cells, including higher power density, shorter charging times, and longer cycle life and shelf life. A schematic of a supercapacitor illustrating some of the physical features described is shown in Figure 2.2.

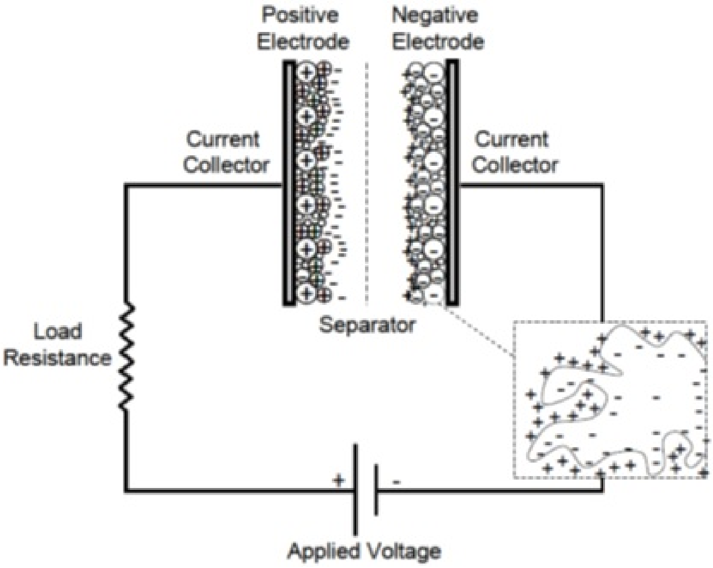
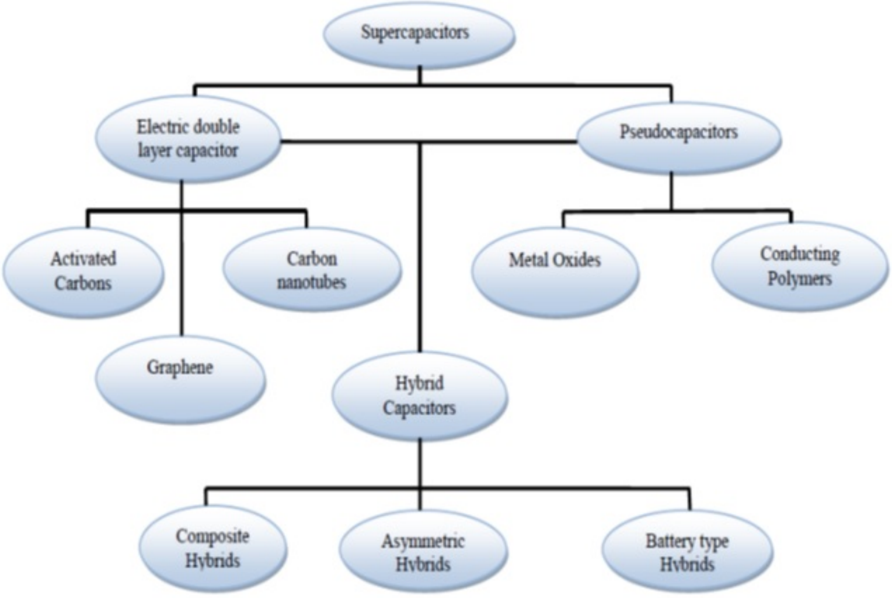


Figure 2.2: Schematics of an electrochemical double layer capacitor

2.3 Supercapacitor Types

The operational principle of a supercapacitor is based on energy storage and the distribution of the ions coming from the electrolyte with respect to surface area of the electrodes. Based on the energy storage mechanism, supercapaci-



Scheme 2.1: Different classes and subclasses of supercapacitors

tors are classified into three classes: Electrochemical double-layer capacitors, pseudo-capacitors, and hybrid supercapacitors as shown in Scheme 2.1, and depicted in Figure 2.3.

2.3.1 Electrochemical double layer capacitors (EDLCs)

EDLCs consist of two carbon-based materials as electrodes, an electrolyte and a separator. EDLCs can store charge either electrostatically or through non-Faradic process, which involves no transfer of charge between electrode and the electrolyte [5, 6]. The principle of energy storage involved by EDLCs is of the electrochemical double layer. When the voltage is applied, there is an accumulation of charge on electrode surfaces, due difference in potential there is an attraction of opposite charges, these result to ions in electrolyte diffusing over the separator and onto pores of the opposite charged electrode. To avoid recombination of ions at electrode, a double layer of charge is formed. The double layer, combined with the increase in specific surface area and decreased distances between electrodes allow EDLCs to attain higher energy density [7].

The storage mechanism in EDLCs permits highly fast energy uptake, delivery and better power performance. There is no chemical reaction due to non-Faradic process, thereby eliminates swelling observed in active material which batteries demonstrate during charging and discharging processes. The

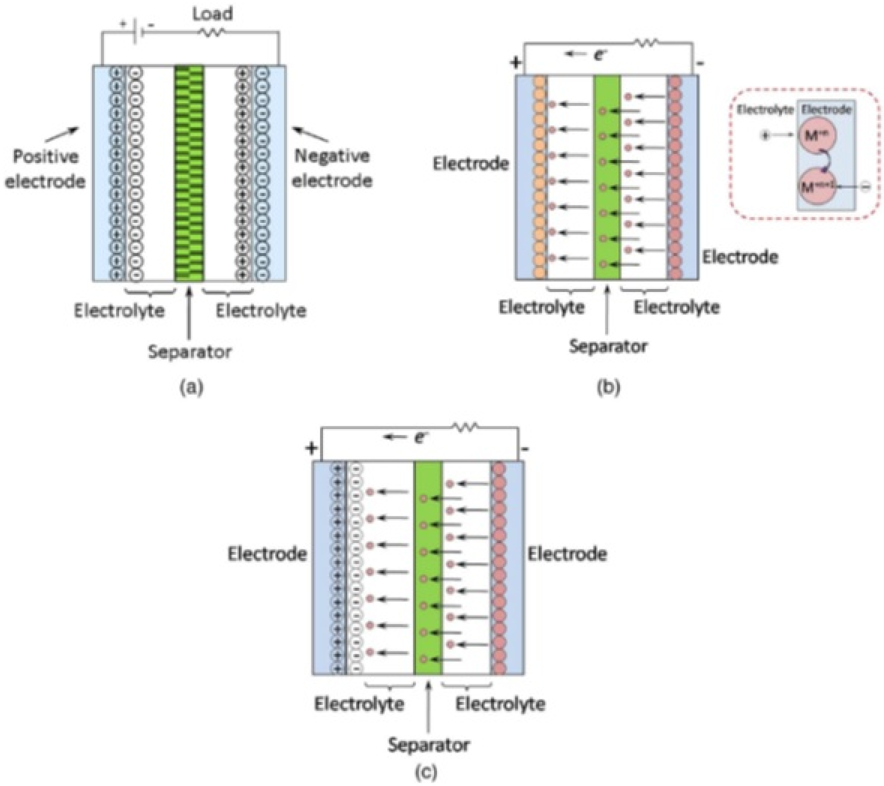


Figure 2.3: Supercapacitor types: (a) EDLC (b) pseudo-capacitor (c) hybrid capacitor [4].

notable differences between EDLCs and batteries are:

1. EDLCs can withstand millions of cycles unlike batteries that can withstand only a few thousands at best.
2. Charge storage mechanism does not involve solvent of the electrolyte; while in Li-ion batteries it contributes to solid electrolyte inter phase when high-potential cathodes are employed or with graphite anodes [8, 9].

However, due to the electrostatic surface charging mechanism, EDLC devices experience a limited energy density, and this is the reason for present focus of research in to increase energy performance and to enhance the temperature range where batteries cannot function. Performance of EDLC can be modulated depending on the choice of the electrolyte.

2.3.2 Pseudo-capacitors

Compared to EDLCs which store charge electro-statically, pseudo-capacitors store charge via Faradic process which involves the transfer of charge between electrode and electrolyte [10]. When a potential is applied to a pseudo-capacitor reduction and oxidation takes place on the electrode material, which involves the passage of charge across the double layer, resulting in Faradic current passing through the supercapacitor cell. The Faradic process involved in pseudo-capacitors aids them to attain greater specific capacitance and energy densities than EDLCs. Examples are metal oxides, conducting polymers, etc., which lead to interest in these materials but due the Faradic nature, it involves reduction-oxidation reaction just like in the case of batteries; hence they also suffer lack of stability during cycling and low power density [11-13].

2.3.3 Hybrid Capacitors

EDLCs offer good cyclic stability and good power performance, while pseudo-capacitors offer greater specific capacitance. The hybrid system offers a combination of both, that is by combining the energy source of battery-like electrode, with a power source of capacitor-like electrode in the same cell [14, 15]. With appropriate electrode combination it is possible to increase the cell voltage, which in turn leads to an improvement in energy and power densities.

Various combinations have been tested in the past with both positive and negative electrodes in aqueous and inorganic electrolytes. Generally, the Faradic electrode results in an increase of energy density at the cost of cyclic stability, which is the main drawback of hybrid devices compared to EDLCs, it is imperative to avoid turning a good supercapacitor into an ordinary battery [16]. Currently, researchers focus on the three different types of hybrid supercapacitors, which can be distinguished by their electrode configurations namely, Composite, Asymmetric and Battery-type.

Composite supercapacitors

Composite electrodes combine carbon based materials with either metal oxides or conducting polymer in a single electrode - that is, a single electrode will possess both physical and chemical charge storage mechanisms. Carbon based materials offer capacitive double-layer of charge and high specific surface area which increases the contact between pseudocapacitive materials and electrolyte. Through Faradaic reaction, pseudocapacitive material increases capacitance in composite electrode [6]. Presently, there are two different types of composites: Binary and Ternary composites. Binary composites involve the use of two different electrode materials, while in the case of ternary it uses three different electrode materials to form single electrode.

Asymmetric supercapacitors

Asymmetric hybrids combine non-Faradic and Faradic processes by coupling and EDLC with a pseudo-capacitor electrode. They are set up in a way that the carbon material is used as a negative electrode while either metal oxide or conducting polymer as positive electrode [6].

Battery-type supercapacitors

Battery type hybrid combines two different electrodes, like in the case of asymmetric hybrids but in these cases they are made up by combining a supercapacitor electrode with battery electrode. This configuration was set up so as to utilize both properties of supercapacitors and batteries in one cell [6].

2.4 Electric double layer

An electric double layer is a structure appearing when a charged object is placed into a liquid (electrolyte). The balancing counter charge for this charged surface will form on the liquid (electrolyte), mainly concentrating near to the surface. There are several theories or models for this interface

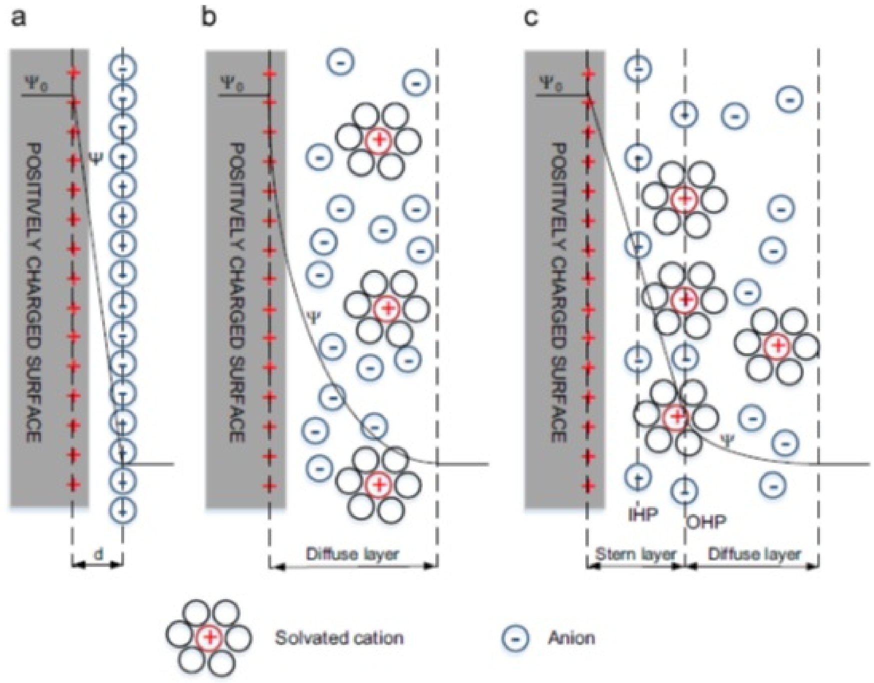


Figure 2.4: EDL Models (a) Helmholtz model (b) Gouy-Chapman model (c) Stern model

between a solid and a liquid. In Fig. 2.4 the Helmholtz model, the Gouy-Chapman model and the Stern model are pictorially illustrated, where ψ is the potential, ψ_0 is the electrode potential, IHP refers to the inner Helmholtz plane, and OHP refers to the outer Helmholtz plane as applicable to the Stern model.

2.4.1 Helmholtz Model

This theory is the simplest approximation for modeling the spatial charge distribution at double layer interfaces. The charge of the solid electronic conductor is neutralized by opposite sign ions at a distance from the solid. This is the distance from the surface to the center of the ions. This theory considers rigid layers counter balancing the charges from the solid. As of today, this is taken as the simplest theory, which does not adequately explain what occurs in nature [17, 18].

2.4.2 Gouy-Chapman or Diffuse Model

Gouy suggests that the same amount of opposite ionic charge appears in a liquid surrounding a charged solid, but the ions are not rigidly attached to the surface [17]. These ions in the solution tend to diffuse into the liquid phase until the counter potential set up by their departure restricts this tendency. The kinetic energy of the ions in the solution will partially determine the thickness of the diffuse layer. Gouy and Chapman developed theories of this diffuse layer in which the ion concentration in the solution near the surface follows the Boltzmann distribution. This model fails for highly charged double layers [18]. Experimentally, the measured thickness of double layers is greater than the calculated.

2.4.3 Stern Modification of the Diffuse Double Layer

The Gouy?Chapman model makes a better approach to the reality than the Helmholtz model, but still has limited quantitative applications. It assumes that the ions are point charges and that they can approach the surface with no limits, which is not true. Stern modified the Gouy-Chapman model stating that the ions have a finite size, so limiting their approach to the surface. The first ions in the Gouy-Chapman model are at the ? distance away from the surface, but the Stern model assumes that there can be specifically surface-adsorbed ions in plane ?, this is known as the Stern layer. Ions are strongly adsorbed by the electrode within this so-called compact layer. In the compact layer there are specifically adsorbed ions (forming the inner Helmholtz plane), and non- specifically adsorbed counter-ions (forming the outer Helmholtz plane) [19]. Summarizing, in order to resolve the shortcomings of the Gouy-Chapman model for the diffuse layer, Stern suggested the combination of both previous models, giving an internal Stern layer (e.g. the Helmholtz layer) and an outer diffuse layer (e.g. the Gouy-Chapman layer).

2.4.4 Electric Double Layer in Supercapacitors

Although the above models give a satisfactory description of the electrical double layer on plane surfaces, they fall short of describing the real charge distribution in nano porous electrodes employed in supercapacitors. The peculiarities of ion electrosorption in porous media make the process of charge storage extremely difficult, and there is still a lack of complete understanding of the behavior of ions in nanopores. When a supercapacitor is charged, electrons are forced to go from the positive electrode to the negative electrode through an external circuit. As a consequence, cations within the electrolyte concentrate in the negative electrode and anions in the positive electrode forming an EDL that compensates the external charge unbalance. During the discharge, electrons travel from the negative electrode to the positive electrode through an external circuit, and both kinds of ions in the pores become mixed again until the cell is discharged. Ions do not move in the bulk electrolyte the same way as they do within the pores of an electrode material. The mobility of ions into the pores is greatly influenced by the pore size, which if too small makes the pores inaccessible, not contributing to double layer capacitance [20]. Since not all the pores are accessible to the ions, there is no linear relation between the capacitance exhibited by a material and its specific surface area [21-24] measured with a small gas molecule probe such as N2 or Ar. Various studies suggest that pore size below 0.5 nm is not accessible to hydrated ions [24, 25], and pores smaller than1nm can be too small for organic electrolytes [26]. Generally, there is a controversy regarding the effect of pore size on capacitance. Chmiola et al. claimed that pores with sizes below 1nm greatly contribute to the capacitance [27]. This increase was explained with the distortion of the salvation shell, thus reducing the distance between charges and enhancing the capacitance [28, 29]. On the other hand, constant capacitance in the micropores was measured in organic electrolyte on the basis of a detailed assessment of pore size using complementary adsorption techniques. The decrease in the distance between the electronic and ionic charges is counter balanced by the corresponding decrease in the effective dielectric permittivity inside the pores, which occus due to gradual ion de-solvation [30-32]. Leaving the controversy of capacitance vs. pore size behind, it is worth mentioning that industrially important values are also calculated on a volumetric basis. It then becomes clear that too wide pores contain free space, which is not used for capacitive charge storage, but decreases the density of electrodes. This effect is detrimental to volume-based capacitance as well as the existence of narrow electrolyte-inaccessible pores. Thus, tuning pore size is anyway needed to have carbon materials with narrow, short and electrolyte-accessible pores [27]. Apart from it, there is a general agreement that the power capability of a supercapacitor can be enhanced by the presence of a small amount of mesopores (pores wider than 2 nm) for a rapid supply of electrolyte to the micropore surface where main charge storage takes place [33]. There have been numerous attempts to properly describe the capacitance of carbon materials depending on the pore shape and size and the specific character of their interaction with electrolytes. For mesoporous carbons with cylindrical pores, the traditional model is used [34]:

$$\frac{C}{A} = \frac{\epsilon_r \cdot \epsilon_0}{b \cdot \ln(\frac{b}{b-d})} \tag{2.5}$$

where b is the pore radius and d the distance between the ion and the carbon surface. For micropores, it is assumed that the ions line up in the center of a cylindrical pore, so the capacitance is calculated from [34]:

$$\frac{C}{A} = \frac{\epsilon_r \cdot \epsilon_0}{b \cdot \ln(\frac{b}{a_0})} \tag{2.6}$$

where a_0 is the effective size of the ion. This ionic radius was found to be close to the bare ion size, which means that the ions could be completely desolvated. However, more realistic approximation to the pore shape in carbon is a slit, not a cylinder, a sandwich capacitance model was later proposed [35].

$$\frac{C_{tot}}{2A} = \frac{C_S}{A} = \frac{\epsilon_r \cdot \epsilon_0}{b - a_0} \tag{2.7}$$

2.4.5 Pseudo-capacitance

Pseudo-capacitance is a Faradaic charge storage mechanism based on fast and highly reversible surface or near-surface redox reactions. Importantly, the electrical response of a pseudocapacitive material is ideally the same as the one of a double-layer capacitor. That is, the state of charge changes continuously with the potential, leading to proportionality constant that can be formally considered as capacitance. Some materials can also store significant charge in a double layer such as functionalized porous carbon, combining thus both capacitive and pseudo-capacitive storage mechanisms.

The significance of the term and phenomenon referred to as *pseudo-capacitance* has not been well understood in the fields of electrochemical capacitor and batteries. Let us therefore first discuss on its origin and significance. Regular double-layer capacitance arises from the potential-dependence of the surface density of charges stored electrostatically (i.e., non-Faradaically) at the interfaces of the capacitor electrodes. On the capacitor electrodes (metals or carbon surfaces), the accumulated charge is a combination of an excess or a deficit of conduction-band electrons at or in the near-surface region of the interface, together with counterbalancing charge densities of accumulated cations or anions of the electrolyte on the solution side of the double layers at the electrode interfaces. However, a double-layer capacitor device must employ two such double layers, one at each electrode interface, working one against the other on charge or discharge. Pseudo-capacitance arises at electrode surfaces where a completely different charge storage mechanism applies. It is Faradaic in origin, involving the passage of charge across the double layer, as in battery charging or discharging, but capacitance arises on account of the special relation that can originate for thermodynamic reasons between the extent of charge acceptance (Δq) and the change of potential (ΔV), so that a derivative d(Δq)/d(ΔV) or dq/dV, which is equivalent to a capacitance, can be formulated and experimentally measured by dc, ac, or transient techniques.

The capacitance exhibited by such systems is referred to as pseudo-capacitance since it originates in a quite different way from that corresponding to classical electrostatic capacitance of the type exhibited (mainly) by double-layer capacitors. It is now known that double-layer carbon capacitors exhibit perhaps 1-5% of their capacitance as pseudo-capacitance due to the Faradaic reactivity of surface (edge) oxygen-functionalities (depending on the conditions of preparation or pretreatment of the carbon material). On the other hand, pseudo-capacitor devices, like batteries, always exhibit some electrostatic double-layer capacitance component proportional to their electrochemically accessible interfacial areas, probably about 5 to 10%.

2.5 Summary and Outlook

The demand for clean and sustainable energy have made electrochemical capacitors as a possible device for energy storage and power supply. However, the development of these devices depends on the ways of fine tuning the characteristics of these materials. After the introduction of supercapacitors, many modifications have been incorporated from the point of view of commercialization. Not only the design but also emphasis has been given on the development of active electrode materials for better charge storage [41].

The supercapacitor types and materials can be summarized as follows: In short, there are three kinds of capacitors and they are classified according to the capacitance value as follows:
Types of Capacitor

1. Electrostatic capacitor (pico farads to low microfarad)
2. Electrolytic capacitor (microfarad)
3. Super capacitor (farad)

Materials for capacitor applications:

1. Energy storage processes in carbons:
    - Double layer capacitance- microporous, activated carbon
    - Intercalation —graphitic carbons with planar atomic microstructure

Table 2.1: Comparison between supercapacitor and Li-ion [42]

Function	Supercapacitor	General Li-ion
Charging Time	10 Second	Upto 60 mins
Cycle Life	1 million or 30,000 h	500 or higher
Cell Voltage	2.3 to 2,75 V	3.6 V
Specific Energy (Wh/kg)	5 (typical value)	120-240
Specific (Power W/Kg)	Upto 10,000	1000-3000
Service Life (industrial)	10-15 years	5-10 years
Charge Temperature	-40 to 650 C	0 to 450C

   - Surface adsorption processes

2. Pseudo-capacitance
   - Conducting polymers (redox)
   - Metal oxides (intercalation)

3. Hybrid capacitors (one electrode carbon and the other electrode battery-like)
   - Carbon/PbO_2/sulfuric acid
   - Carbon/NiOOH/KOH
   - Carbon/metal oxide/organic
   - Carbon/conducting polymer/organic

A comparison of supercapacitor with a typical battery like lithium ion is given in Table.2.1. The advantages and disadvantages of supercapacitor are summarized in Table 2.2

This research in this area has to be focused towards development of suitable materials (like transition metal oxides in the nano-state) with high capacity at the same time showing minimum electronic and electrolytic resistance in a cost-effective manner.

Table 2.2: Advantages and limitations of supercapacitors[42]

Advantages	• Nearly unlimited cycle life can be cycled millions of times • High specific power low resistance facilities high load currents • Charges in seconds, no end of charge termination required • Simple charging draws only what it needs not subject to overcharge • Safe and allows abuse • Excellent low temperature charge-discharge performance
Disadvantages	• Low specific energy, only a fraction of a regular battery • Linear discharge voltage prevents using the full energy spectrum • High self-discharge higher than most of the batteries • Low cell voltage requires series connections with voltage balancing • High cost per watt

References

1. Conway, B. E. (1999). Electrochemical Supercapacitors : Scientific Fundamentals and Technological Applications. New York, Kluwer-Plenum.
2. Burke, A. (2000). & quot;Ultracapacitors: why, how, and where is the technology." Journal of Power Sources 91(1): 37-50.
3. Chu, A. and P. Braatz (2002). & quot;Comparison of commercial supercapacitors and high power lithium-ion batteries for power—assist applications in hybrid electric vehicles I. Initial characterization & quot; Journal of Power Sources 112(1): 236-246.
4. Vangari. M, Pryor. T and Jiang. L. J. Energy Eng., 2013, 139 (2) 72-79.
5. M.V. Kiamahalleh, S.H.S. Zein, G. Najafpour, S.A Sata and S. Buniran, Nano, 7 (2012) 1.
6. M.S. Halper and J. C.Ellenbogen, Mitre Nanosystems Group, (2006).
7. H. Choi and H. Yoon, Nanomaterials, 5 (2015) 906.
8. P. Simon and Y. Gogotsi, Nature Mater., 7 (2008) 845.
9. M.S. Ata, McMaster University, (2012).
10. S. Mohapatra, A. Acharya and G. S. Roy, Lat. Am. J. Phys. Educ., 6 (2012) 380.
11. S.M. Chen, R. Ramachandran, V. Mani and R. Saraswathi, Int. J. Electrochem. Sci., 9 (2014) 4072.
12. M. Beidaghi, Florida International univeristy, (2012).
13. T. Chen and L. Dai, Materials Today, 16 (2013) 272.
14. A. Burke, Z. Liu and H. Zhao, Institute of transportation studies, (2014).
15. A. Burke, Electochim. Acta, 53 (2007) 1083.
16. P. Simon and K. Naoi, Electrochem. Soc., (2008) 34.

17. Endo M, Takeda T, Kim Y, Koshiba K, Ishii K. High power electric double layer capacitor (EDLC & # 39;s); from operating principle to pore size control in advanced activated carbons. Carbon Sci 2001; 1(3): 117–28
18. Bagotsky V. Fundamentals of electrochemistry. Hoboken, New Jersey: John Wiley & amp; Sons, Inc.; 2005.
19. Zhang L L, Zhao X S. Carbon-based materials as supercapacitor electrodes. Chem Soc Rev. 2009;38(9): 2520-31.
20. Sharma P, Bhatti T.A review on electrochemical double-layer capacitors. Energy Convers Manag. 2010; 51(12): 2901-12.
21. Barbieri O, Hahn M, Herzog A, Kötz R., Capacitance limits of high surface area activated carbons for double layer capacitors. Carbon 2005; 43(6): 1303-10.
22. Qu D, Shi H. Studies of activated carbons used in double-layer capacitors. J Power Sources 1998; 74(1): 99-107.
23. Gamby J, Taberna P, Simon P, Fauvarque J, Chesneau M., Studies and characterizations of various activated carbons used for carbon/carbon supercapacitors. J Power Sources, 2001; 101(1):109-16.
24. Shi H. Activated carbons and double layer capacitance. Electrochim Acta 1996; 41(10): 1633-9.
25. Qu D. Studies of the activated carbons used in double-layer supercapacitors. J Power Sources 2002; 109(2): 403–11.
26. Kim Y, Horie Y, Ozaki S, Matsuzawa Y, Suezaki H, Kim C, et al. Correlation between the pore and solvated ion size on capacitance uptake of PVDC-based carbons. Carbon 2004; 42(8–9): 1491–500.
27. Chmiola J, Yushin G, Gogotsi Y, Portet C, Simon P, Taberna P L. Anomalous increase in carbon capacitance at pore sizes less than 1nanometer. Science (New York, N.Y.)2006; 313(5794):1760–3.
28. Simon P, Burke A. Nanostructured carbons: double-layer capacitance and more. Electrochem. Soc. Interface 2008; 17(1): 38-44.
29. Largeot C, Portet C. Relation between the ion size and pore size for an electric double- layer capacitor. J Am Chem Soc 2008; 130(9): 2730–1.
30. García-Gómez A, Moreno-Fernández G, Lobato B,Centeno T. Constant capacitance in nanopores of carbon monoliths. Phys Chem Chem Phys 2015; 17(24): 15687–90.
31. Stoeckli F, Centeno T A. Pore size distribution and capacitance in microporous carbons. Phys Chem Chem Phys 2012; 14(33): 11589–91.
32. Centeno T, Stoeckli F. The volumetric capacitance of microporous carbons in organic electrolyte. Electrochem Commun 2012; 16(1): 34–6.
33. Vix-Guterl C, Frackowiak E, Jurewicz K, Friebe M, Parmentier J, Béguin F. Electrochemical energy storage in ordered porous carbon materials. Carbon 2005; 43(6): 1293–302.

34. Huang J, Sumpter B, Meunier V. Theoretical model for nanoporous carbon supercapacitors. Angew Chem 2008; 120(3): 530–4.
35. Feng G, Qiao R, Huang J, Sumpter B G, Meunier V. Ion distribution in electrified micropores and its role in the anomalous enhancement of capacitance. ACS Nano 2010; 4(4): 2382–90
36. Augustyn V, Simon P, Dunn B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. Energy Environ Sci 2014; 7(5): 1597–614.
37. Conway B E, Pell W G. Double-layer and pseudo-capacitance types of electrochemical capacitors and their applications to the development of hybrid devices. J Solid State Electrochem., 2003; 7(9): 637–44.
38. Naoi K, Simon P. New materials and new configurations for advanced electrochemical capacitors. Electrochem. Soc. Interface 2008; 17(1): 34–7.
39. Chuang C-M, Huang C-W, Teng H, Ting J-M. Effects of carbon nanotube grafting on the performance of electric double layer capacitors. Energy Fuels 2010; 24(12): 6476–82.
40. Zhu Z Z, Wang G C, Sun M Q, Li X W, Li C Z. Fabrication and electrochemical characterization of polyaniline nanorods modified with sulfonated carbon nanotubes for supercapacitor applications. Electrochim. Acta, 2011; 56 (3): 1366–72.
41. Samantara A.K., Ratha S. (2018) Historical Background and Present Status of the Supercapacitors. In: Materials Development for Active/Passive Components of a Supercapacitor. SpringerBriefs in Materials. Springer, Singapore.
42.How does a Supercapacitor Work? `http://batteryuniversity.com/learn/article/whats_the_role_of_the_supercapacitor`