Dissertation project

A Brief Review
on
Supercapacitor as an Energy Storage Device

By

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Abstract

Supercapacitor, the noble energy storage device, is nowadays attracting the researchers throughout the globe. It has a high specific power contained in a very little volume, so that, its capacitance is very much higher than that of the normal capacitor with the same volume. It can also provide a high peak voltage pulse through the circuit. Therefore, supercapacitors are currently used in many of the industrial sectors. In this dissertation project we have reviewed the structure of supercapacitors, working principles of supercapacitors, types of supercapacitors, different material systems used in supercapacitors and its relative comparisons. The different electrical parameters which are significantly enhanced in comparison with the other energy storing materials, such as, normal capacitors or batteries, is discussed here. In this report we have also presented the current status of supercapacitors and its drawbacks, in order to have an idea about its betterment.

Chapter 1

Introduction

First of all we have to define that what we mean by energy storage. Energy storage means to capture or store the energy that is produced by any manner and utilize it for future purpose, and the materials which possess such kind of behaviour are called energy storage materials. The device that stores energy (for future use) is known as accumulator or battery.

We know that there are various forms of energies, e.g. mechanical, chemical, nuclear etc. The process of storing any sort of energy involves with converting the form of the energy from one to another. The task of storing energy economically in a form that the stored energy can be used in future is really a tedious one.

1.1. A Outline of Various Energy Storages

The various way of the energy storage is discussed below. From here you can get an outline of the energy storage.

Various Energy Storage	Examples
Mechanical	• Compressed air energy storage • Fireless locomotive • Flywheel energy storage • Gravitational energy storage • Hydraulic accumulator • Pumped storage hydroelectricity
Electrical and electromagnetic	• Capacitor • Super capacitor • Superconducting magnetic energy storage
Thermal	• Brick storage heater • Cryogenic energy storage • Liquid nitrogen engine • Eutectic system • Ice storage air conditioning • Molten salt storage • Phase-change material

	• Seasonal thermal energy storage • Solar pond • Steam accumulator
Chemical	• Fossil fuel storage
Biological	
Electrochemical	• Capacitor • Super capacitor

So, these are the examples of various energy storing materials.

Here we will only have an intense discussion about the supercapacitor, viz. how this supercapacitor can be manufactured and what are the advantages of this thing while using as an energy storing component.

1.2. What is a Supercapacitor

*A **supercapacitor** (also called a **ultracapacitor** or **Goldcap**[1]) is a high-capacity capacitor with having a capacitance values much higher than other capacitors (but lower voltage limits) that bridge the gap between electrolytic capacitors and rechargeable batteries.* The energy stored per unit volume (or mass) in a supercapacitor is typically 10 to 100 times more than the electrolytic capacitors. They also can accept and deliver charge much faster than the batteries, and tolerate many more charge and discharge cycles than rechargeable batteries.

Supercapacitors are used in applications requiring many rapid charge/discharge cycles rather than long term compact energy storage: within cars, buses, trains, cranes, elevators, where they are used for regenerative braking, short-term energy storage or burst-mode power delivery.[2] Smaller units are used as memory backup for static random-access memory (SRAM).

In case of ordinary capacitors we generally use solid dielectric, but in case of supercapacitors we do not use the conventional dielectric, instead of that we use electrostatic double-layer capacitance (EDLC) and electrochemical pseudocapacitance.[3] Both of them contribute to the total capacitance of the supercapacitor.

- **Electrostatic double-layer capacitors (EDLCs)** use the carbon electrodes or its derivatives with having much higher electrostatic double-layer capacitance than electrochemical pseudocapacitance, so that the Helmholtz double layer can be formed at the interface between the surface of a conductive electrode and the electrolyte in order to create a separation between the two layers of charges.

This separation is of the order of a few Ångströms (0.3 – 0.8 nm), much smaller than in a conventional capacitor.

- **Electrochemical pseudocapacitors** use the metal oxides or conducting polymers as electrodes. These materials have a high amount of electrochemical pseudocapacitance additional to the double-layer capacitance. Pseudocapacitance is achieved by Faradaic electron charge-transfer with redox reactions, intercalation or electrosorption.

- **Hybrid capacitors,** such as lithium-ion capacitors, use asymmetric electrodes, i.e., electrodes with different characteristics. One of them exhibits mostly electrostatic capacitance and the other one mostly electrochemical capacitance.

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                    ┌─────────────────────────┐
                    │     Supercapacitors     │
                    └─────────────────────────┘
         ┌─────────────────────────┬─────────────────────────┐
┌─────────────────────────┐       │      ┌─────────────────────────┐
│ Double-layer capacitors │       │      │    Pseudocapacitors     │
│ Charges stored          │       │      │    Charges stored       │
│ electrostatically       │       │      │    electrochemically    │
└─────────────────────────┘       │      └─────────────────────────┘
                    ┌─────────────────────────┐
                    │     Hybrid capacitors   │
                    │     Charges stored both │
                    │     electrostatically and│
                    │     electrochemically   │
                    └─────────────────────────┘
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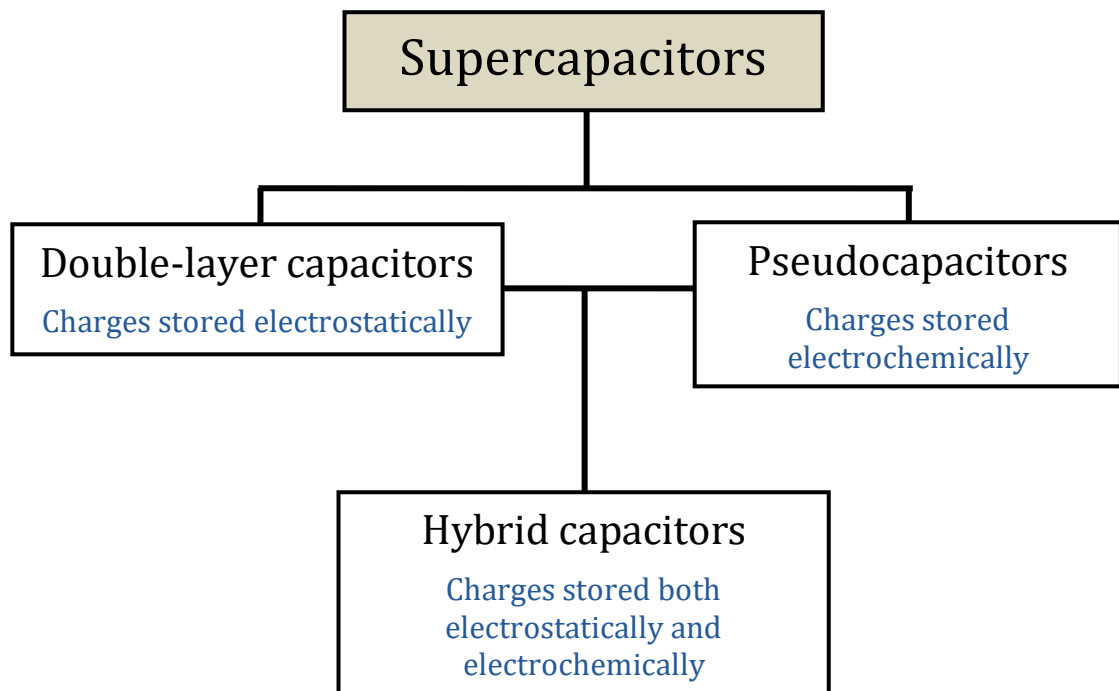
The electrolyte inside the supercapacitors forms an ionic conductive connection between the two electrodes. This phenomena distinguishes the supercapacitors from the conventional electrolytic capacitors, where the dielectric layer always exists, and the so-called electrolyte (e.g., MnO_2 or conducting polymer) is in fact part of the second electrode (the cathode, or more precisely the positive electrode). Supercapacitors are polarized by design with asymmetric electrodes, or, for symmetric electrodes, by a potential applied during manufacture.

▪ Why Supercapacitor

There are lots of topics those deserve to be discussed. One of such topics is what are advantages and disadvantages of using a supercapacitor over the batteries. Here we are excluding the normal capacitor from our analogical discussion since it does not provide any type of compatible data with respect to the other two. In this section we shall discuss about the analogy among this three circuit components. In order to have the judgement that which one is more advantageous than the other one we have to check some of the values of the parameters like specific energy, specific power, operating voltage, temperature limits etc. When we concern about the commercial use then cost per Wh and service life also become a very important factor.

The parameters with their corresponding values are placed in the table below as it will be more convenient to have an analogical discussion.

Performance Comparison	Battery (Lithium – ion)	Supercapacitor
Specific Energy	100 – 200 Wh/kg	5 Wh/kg (typical)
Specific Power	1000 – 3000 W/kg	up to 10000 W/kg
Charge Time	10 – 60 minutes (600 – 3600 seconds)	1 – 10 seconds
Cycle Life	more than 500 (typical)	up to 1 million (or 30000 hours)
Operating Voltage	3.6 – 6 Volt	2.3 – 2.75 Volt
Service Life	5 – 8 years	10 – 15 years
Charge Temperature	0 to 45℃	-40 to 65℃
Discharge Temperature	-20 to 60℃	-40 to 65℃
Cost	30 – 70 INR/Wh (typical)	1400 INR/Wh (typical)

Instead of having a very high cost compared to the batteries, supercapacitors also provide a very high specific power value. Thus, from the table above we can see that supercapacitor will be more useful for commercial purpose compared to the batteries (lithium-ion).

1.3. Evolution of Supercapacitors

In the early 1950s, general electric engineers began experimenting with porous carbon electrodes, in the design of capacitors, from the design of fuel cells and rechargeable batteries. Activated charcoal is an electrical conductor material. It is available in an extremely porous "spongy" form of carbon with high specific surface area. In 1957 H. Becker developed a "**low voltage electrolytic capacitor with porous carbon electrodes**".[4][5][6] He believed that the charges in the carbon pores store the energy.

In 1966 a group of researchers at Standard Oil of Ohio (SOHIO) developed another version of the component that stores electrical energy as "**electrical energy storage apparatus**", while working on experimental fuel cell designs.[7][8]

In 1970, the electrochemical capacitor patented by Donald L. Boss was registered as an electrolytic capacitor with activated carbon electrodes.[9]

In the earlier version of the electrochemical capacitors they used two aluminium foils covered with activated carbon – the electrodes – which were soaked in an electrolyte and separated by a thin porous insulator. This design gave a capacitor with a capacitance on the order of one Farad, significantly higher than electrolytic capacitors of the same dimensions. This basic mechanical design remains the basis of most electrochemical capacitors.

SOHIO did not commercialize their invention, licensing the technology to NEC, who finally marketed the results as "supercapacitor" in 1971, to provide backup power for computer memory.[8]

Between 1975 and 1980 Brian Evans Conway conducted extensive fundamental and development work on ruthenium oxide electrochemical capacitors. In 1991 he described the differences between "Supercapacitor" and "Battery" behaviour in electrochemical energy storage.

In 1999 he coined the term "supercapacitor" to explain the increased capacitance by surface redox reactions with Faradaic charge transfer between electrodes and ions.[10][11] His "supercapacitor" stored electrical charge partially in the Helmholtz double-layer and partially as result of Faradaic reactions with "pseudocapacitance" charge transfer of electrons and protons between electrode and electrolyte.

The market expanded slowly. That changed around 1978 as Panasonic marketed its Goldcaps brand.[2] This product became a successful energy source for memory backup applications.[8] Competition started only few years later. In 1978 ELNA "Dynacap"s entered the market.[12]

First generation EDLC's had relatively high internal resistance that limited the discharge current. They were used for low current applications such as powering SRAM chips or for data backup.

At the end of the 1980s, improved electrode materials increased capacitance values. At the same time, the development of electrolytes with better conductivity lowered the equivalent series resistance (ESR) increasing charge/discharge currents. In 1982 the first supercapacitor with low internal resistance was developed for military applications through the Pinnacle Research Institute (PRI), and was marketed under the brand name "PRI Ultracapacitor".

Since capacitors' energy content increases with the square of the voltage, researchers were looking for a way to increase the electrolyte's breakdown voltage. In 1944 using the anode of a 200V high voltage tantalum electrolytic capacitor, David A. Evans developed an "Electrolytic-Hybrid Electrochemical Capacitor".[13][14] These capacitors combine features of electrolytic and electrochemical capacitors. Evans' capacitors, coined Capattery,[15] had an energy content about a factor of 5 higher than a comparable tantalum electrolytic capacitor of the same size.[16]

Recent developments include lithium-ion capacitors. These hybrid capacitors were pioneered by FDK in 2007.[17] They combine an electrostatic carbon electrode with a pre-doped lithium-ion electrochemical electrode. This combination increases the capacitance value. Additionally, the pre-doping process lowers the anode potential and further increasing specific energy.

Research departments active in many companies and universities [18] are working to improve characteristics such as specific energy, specific power, and cycle stability and to reduce production costs.

Chapter 2

Basics of Supercapacitor

2.1. Basic Design

The electrochemical capacitors (supercapacitors) consist of two electrodes. An ion-permeable membrane (separator) separates themselves from each other, and an electrolyte acts as an ionical connection between them.

When a voltage is applied to the electrodes, they become polarized, and as a result of this polarization of electrodes the ions in the electrolyte form electrical double layers of the electrodes with opposite polarity. For instance, if we consider the positively polarized electrode, then it will have a layer of negative ions at the electrolyte/electrode interface along with the charge-balancing layer of positive ions adsorbing onto the negative layer and vice-versa.
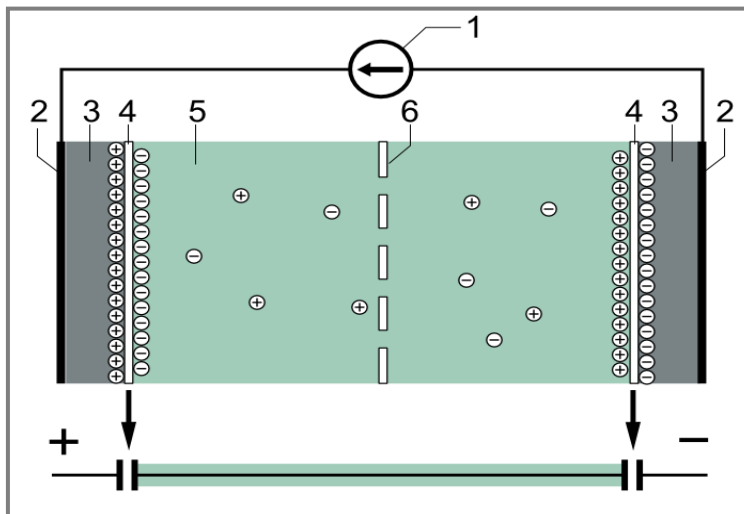

Figure 1 : The schematic diagram of a supercapacitor

1. power source
2. collector
3. polarized electrode
4. Helmholtz double-layer
5. electrolyte having positive and negative ions
6. separator

In addition, due to statistical uncertainty, some ions from the electrodes may permeate the double-layer formed by the ions of the electrolyte (Helmholtz double-layer) and are specifically adsorbed and will have a contribution to the pseudocapacitance causing a significant increase of the total capacitance of the supercapacitor.

2.2. Capacitance Distribution

Here the two electrodes form two double-layers of ions and the electrode acts like the connection between them, so that, we may think this as two capacitors are connected in series through a wire. Let, the capacitances of the two individual capacitors be C_1 and C_2, and the total capacitance be C_{total}, then in a crude approach using the double-layer capacitance model proposed by Helmholtz in 1853[19] we may write,

$$C_{total} = \frac{C_1 C_2}{C_1 + C_2}$$

There may be either symmetric or asymmetric electrodes inside a supercapacitor. Symmetric electrodes mean that both of the electrodes contain the same capacitance values, which makes the total capacitance value half of the each capacitance value, i.e., if $C_1 = C_2 = C$ (say), then $C_{total} = \frac{C}{2}$.

On the other hand, if the electrodes are asymmetric in nature, so that, they are having different capacitance values, then the total capacitance value can be taken as that of the electrode with the smaller capacitance value, i.e., if $C_1 \gg C_2$, then $C_{total} = C_2$.

2.3. Energy Storage Principles

The double-layer effect is responsible for the storing of the electrical energy into an electrochemical capacitor; however, this double-layer does not contain any solid dielectric to separate the charges.

In the electric double-layer of the electrodes, there are mainly two storage principles that contribute to the total capacitance of an electrochemical capacitor:[20]

1. **Double-layer capacitance:** It corresponds to the storing of electrical energy by means of the electrical double layer effect.[21][22][23] This electrical phenomenon appears at the interface between a conductive electrode and an adjacent liquid electrolyte, as observed. If a voltage is applied then two layers of ions with opposing polarity form at this boundary, one at the surface of the electrode, and one in the electrolyte. The two layers of ions are separated by a single layer of solvent molecules that adheres to the surface of the electrode and acts like a dielectric in a conventional capacitor.

   The amount of electric charge stored in double-layer capacitance is linearly proportional to the applied voltage and depends primarily on the electrode surface. The unit of capacitance is the Farad.

2. **Pseudocapacitance:** It corresponds to the storage of electricity in an electrochemical capacitor. This Faradaic charge transfer originates by a very fast sequence of reversible Faradaic redox, electrosorption or intercalation processes on the surface of suitable electrodes.[24][25][26] Pseudocapacitance is accompanied by an electron charge-transfer between electrolyte and electrode coming from a de-solvated and adsorbed ion. One electron per charge unit is involved. The adsorbed ion has no chemical reaction with the atoms of the electrode (no chemical bonds arise[27]) since only a charge-transfer takes place.

Faradaic pseudocapacitance only occurs together with static double-layer capacitance. Pseudocapacitance and double-layer capacitance both contribute inseparably to the total capacitance value.

The amount of pseudocapacitance depends on the surface area, material and structure of the electrodes. Pseudocapacitance may contribute more capacitance than double-layer capacitance for the same surface area by a factor 100.[24]

The amount of electric charge stored in a pseudocapacitance is linearly proportional to the applied voltage. The unit of pseudocapacitance is Farad.

Both of these capacitances can only be recognized by measurement techniques. The amount of stored energy (or we can also say the stored charge) in unit volume, i.e., the energy density (or the charge density) in an electrochemical capacitor basically depends upon the sizes of the electrodes, though having an extreme variation of the amount of capacitance for each of the storage principles. Practically, these storage principles can form a capacitor with a capacitance value of the order of 1 to 100 Farad which is surprisingly much greater than that of a usual capacitor.

2.3.1. Electrostatic Double-layer Capacitance

Now we shall have an intense discussion on the very first storage principle, i.e., the electrostatic double-layer capacitance. Helmholtz laid the theoretical foundations for understanding the double layer phenomenon. The formation of double layers is exploited in every electrochemical capacitor to store electrical energy. An electrochemical capacitor consists of two electrodes, a separator that mechanically separates these two electrodes. These electrodes are ionically connected to each other through an electrolyte. Now, unlike the ordinary capacitors, this electrolyte is a mixture of positive and negative ions and these ions are dissolved in a solvent (for example, water).

At each of the two electrodes surfaces there originates an area in which the liquid electrolyte can have a contact with the metallic surfaces of the electrodes which are conductive in nature. Here this surface acts as an interface

between the two phases of matter, such as the insoluble solid electrode surface and its adjacent the liquid electrolyte. A very special phenomenon, known as the double-layer effect, occurs next to this interface.[28]
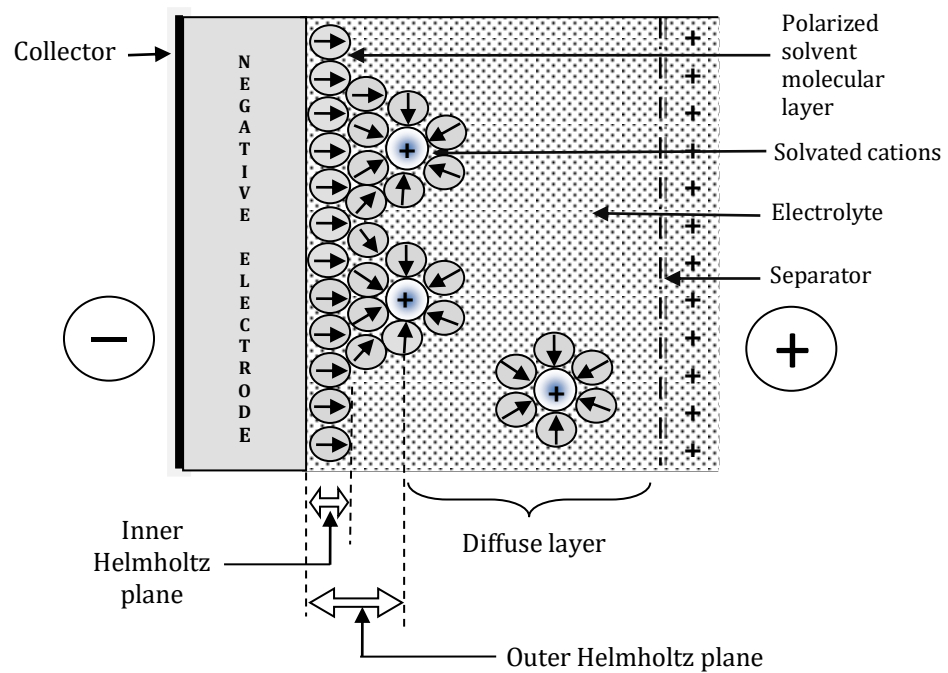

Figure 2 : Simplified view of a double-layer of negative ions in the electrode and solvated positive ions in the liquid electrolyte, separated by a layer of polarized solvent molecules

Now if we apply a voltage across the electrodes of an electrochemical capacitor then both the electrodes become polarized and each of them generates an electrical double-layer. Each double-layer has two layers of charges: one layer is made of electrons and is situated in the surface lattice structure of the electrode, and the other one is with opposite polarity, emerges from the dissolved and solvated ions in the electrolyte. These two layers are separated by a monolayer of the solvent molecules, e.g. if the solvent is water then this monolayer is of water molecules, known as the inner Helmholtz plane (IHP). Solvent molecules adhere by physical adsorption on the surface of the electrode and separate the oppositely polarized ions from each other, and can be idealised as a molecular dielectric. In this process, no transfer of charge takes place there in between the electrode and the electrolyte, so we can say that the force causing the adhesion are not chemical bonds but physical forces (e.g. electrostatic forces). In spite of being polarized the adsorbed molecules suffer no chemical changes due to the lack of charge transfer between the electrode and the electrolyte.

Here the magnitude of the counter-charges in the outer Helmholtz plane (OHP) is matched by the total amount of charges in the electrode. This double-layer phenomenon stores electrical charges very similar to the way it

occurs in a conventional capacitor. The double-layer charge forms a static electric field in the molecular layer of the solvent molecules in the IHP that corresponds to the strength of the applied voltage.
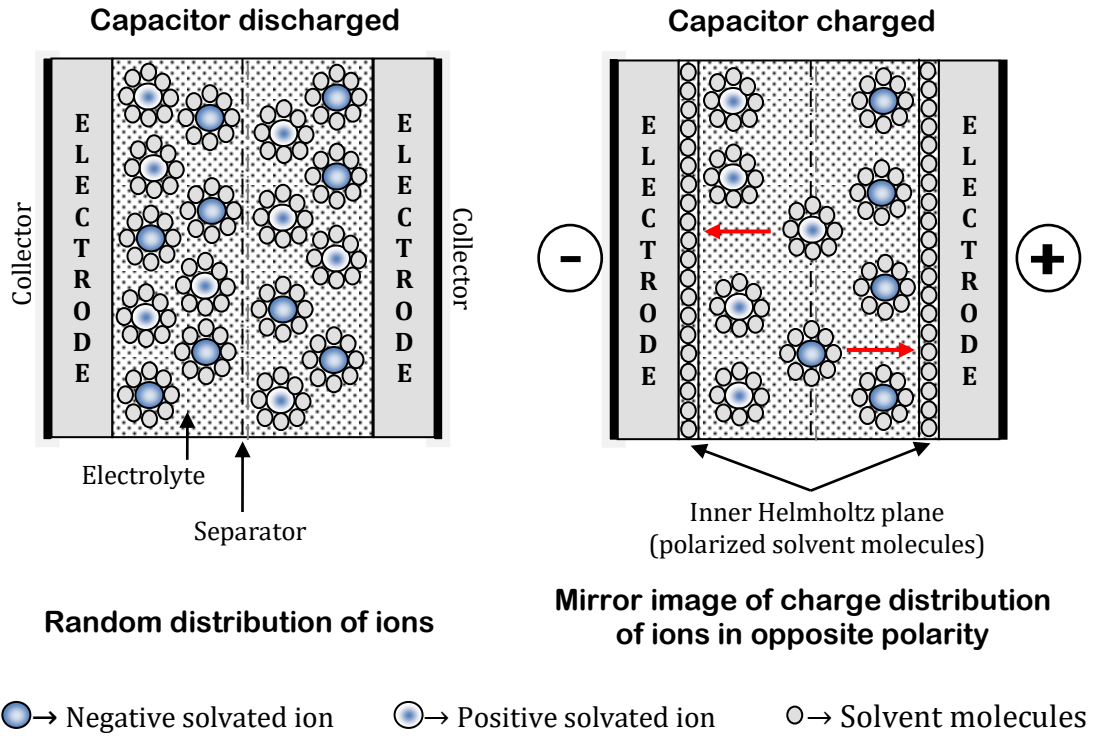
Capacitor discharged **Capacitor charged**

Electrolyte

Separator

Inner Helmholtz plane
(polarized solvent molecules)

Random distribution of ions **Mirror image of charge distribution
of ions in opposite polarity**

◯→ Negative solvated ion   ◉→ Positive solvated ion   ○→ Solvent molecules

Figure 3 : Structure and function of an ideal double-layer capacitor

In a conventional ordinary capacitor the double-layer serves approximately as the dielectric layer, however it is made of a single molecule with a thickness of molecular range. Thus, the standard formula for a conventional parallel plate capacitor can be used to calculate their capacitance:[29]

$$C = \epsilon \frac{A}{d}$$

Here C is the capacitance of the capacitors made form materials with a high permittivity ε, A is the large surface area of the electrode plate and d is the tiny distance between plates. As a result, double-layer capacitors have much higher capacitance values than conventional capacitors, arising from the extremely large surface area of activated carbon electrodes and the extremely thin double-layer distance on the order of few Ångströms (0.3 – 0.8 nm), of the order of the Debye length.[13][21]

Drawbacks: The major drawback of the carbon electrodes while contributing to the double-layer supercapacitors is the small values of quantum

capacitance[30] which act in a series[31] with capacitance of the ionic space charge. Therefore, if the capacitance density further increases in supercapacitors then it causes an increase of quantum capacitance of carbon electrode nanostructure.[30]

The amount of charge stored per unit voltage (or charge density) in an electrochemical capacitor is primarily a function of the electrode size. The electrostatic energy storage in the double-layers is linear with respect to the stored charge, and this corresponds to the concentration of the adsorbed ions too. Also, while charge in conventional capacitors is transferred via electrons, capacitance in double-layer capacitors is related to the limited moving speed of ions in the electrolyte and the resistive porous structure of the electrodes. Since no chemical changes take place within the electrode or electrolyte, charging and discharging electric double-layers in principle is unlimited. Real supercapacitors lifetimes are only limited by electrolyte evaporation effects.

2.3.2. Electrochemical Pseudocapacitance

When a voltage is applied at the electrochemical capacitor terminals then it causes a movement of the electrolyte ions towards the opposite polarity electrode and forms a double-layer in which a single layer of solvent molecules acts as separator. Pseudocapacitance can originate when specifically adsorbed ions out of the electrolyte pervade the double-layer. This pseudocapacitance stores electrical energy by means of reversible Faradaic redox reactions on the surface of the suitable electrodes in an electrochemical capacitor with an electric double-layer.[10][20][21][32][33]

An electron charge-transfer between electrolyte and electrode coming from a de-solvated and adsorbed ion accompanies the phenomenon of pseudocapacitance, i.e., only one electron per charge unit is participating. This Faradaic charge transfer originates by a very fast sequence of reversible redox, intercalation or electrosorption processes.

The electrons involved in the Faradaic processes are transferred to or from valance electron states (orbitals) of the redox electrode reagent. They enter the negative electrode and flow through the external circuit to the positive electrode where a second double-layer with an equal number of anions has formed. The electrons reaching the positive electrode are not transferred to the anions forming the double-layer, instead they remain in the strongly ionized and "electron hungry" transition-metal ions of the electrode's surface. As such, the storage capacity of Faradaic pseudocapacitance is limited by the finite quantity of reagent in the available surface.
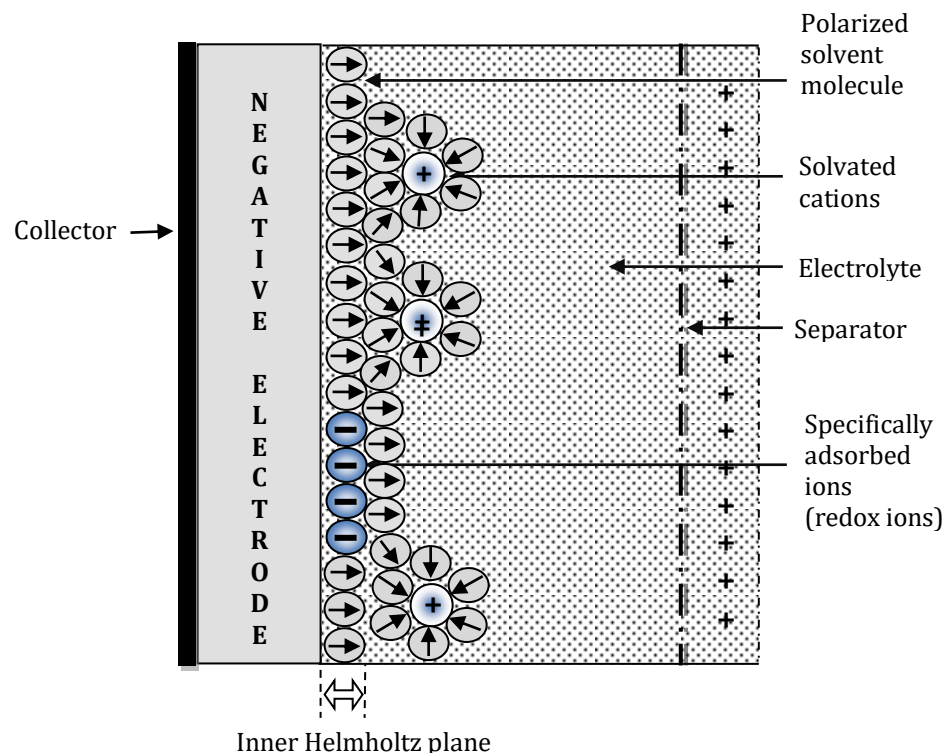
Inner Helmholtz plane

Figure 4 : Simplified view of a double-layer with specifically adsorbed ions which have submitted their charge to the electrode to explain the Faradaic charge-transfer of the pseudocapacitance

A Faradaic pseudocapacitance only occurs together with a static double-layer capacitance, and for the same surface area its magnitude of capacitance may exceed the value of the double-layer capacitance by a factor 100, depending upon the nature and the structure of the electrode because all the pseudocapacitance reactions take place only with de-solvated ions, which are much smaller than solvated ions in terms of their solving shell.[10][32] The amount of pseudocapacitance has a linear function within narrow limits determined by the potential-dependent degree of surface coverage of the adsorbed anions.

Now the electrodes providing pseudocapacitance effects via redox reactions, intercalation or electrosorption has a huge dependence on the chemical affinity to electrode materials to the ions adsorbed on the electrode surface as well as on the structure and dimension of the electrode pores. So, the materials exhibit redox behavior (transition-metal oxides like RuO_2, IrO_2 or MnO_2) we can use them as electrodes injected by doping in the conductive electrode materials (like active carbon, as well as conducting polymers such as polyaniline or derivatives of ploythiophene).

The amount of electric charge stored in a pseudocapacitance is linearly proportional to the applied voltage. The unit of pseudocapacitance is Farad.

2.4. Potential Distribution

The ordinary conventional capacitors (or electrostatic capacitors, such as ceramic capacitors and film capacitors) basically consist of two electrodes and a dielectric material that separates these two electrodes. When the capacitor is charged, then the energy is stored in terms of static electric field that permeates the dielectric between these two electrodes. The total stored energy linearly proportional to the stored charge. It implies that the potential (voltage) between the plates also has a linear dependence on the stored charge. Here the only constraint is that the breakdown field strength of the dielectric limits the potential difference between the two plates (or the maximum applied voltage). The same phenomenon also occurs in the case of the electrolytic capacitors. Actually here most of the potential decreases over the anode's thin oxide layer.

Now the electrochemical capacitors (or supercapacitors) also consist of two electrodes, but in contrary to the electrostatic and electrolytic capacitors these two electrodes are separated by an ion-permeable membrane, termed as the separator, and they are electrically connected by an electrolyte. Energy storage occurs within the double-layer of both the electrodes as a mixture of a double-layer capacitance and pseudocapacitance. When both the electrodes have approximately the same resistance (internal resistance), the potential of the capacitor decreases symmetrically over both the double-layers, whereby a voltage drop across the ESR (or equivalent series resistance) of the electrolyte is achieved. For asymmetric electrodes in the hybrid capacitors the voltage drop between them could be asymmetrical. The maximum potential across the capacitor (the maximum voltage) is limited by the electrolyte decomposition voltage.
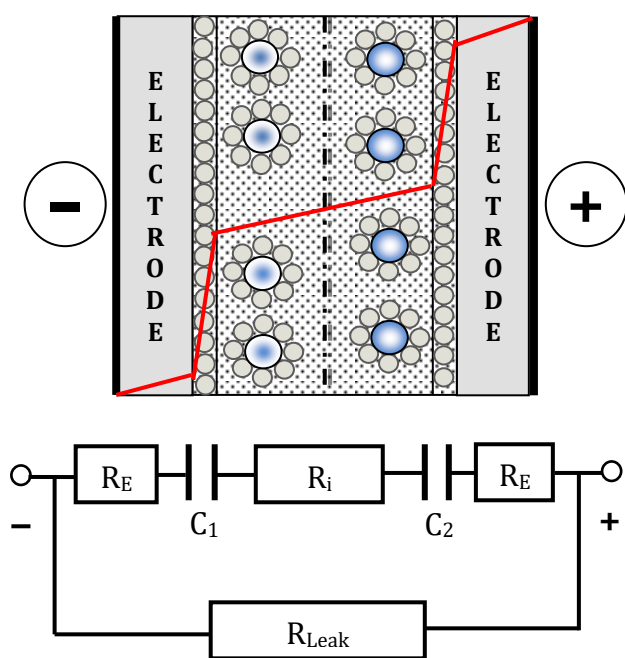

Figure 5 : Basic illustration of the functionality of a supercapacitor, the voltage distribution inside of the capacitor and its simplified equivalent DC circuit

Both the electrostatic and electrochemical energy storage in supercapacitors has linear dependence with the stored charge as like the conventional capacitors. The voltage difference between the capacitor terminals is linear with respect to the amount of energy stored. Such linear voltage gradient differs from the rechargeable electrochemical batteries, in which the voltage between the terminals remains independent of the amount of the stored energy, providing a relatively constant voltage.
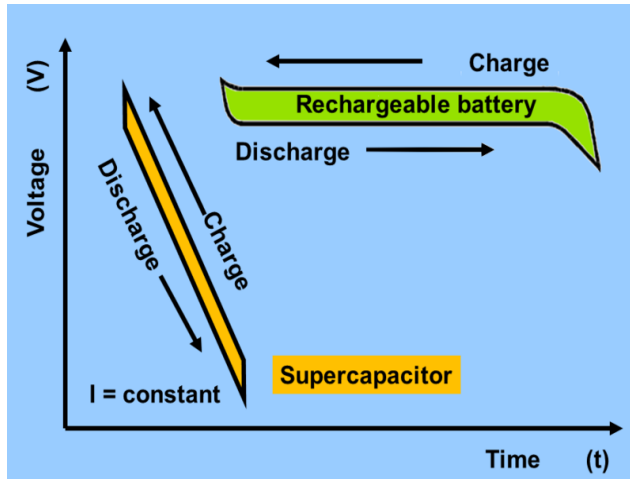
2.5. Electrical Parameters

Here we shall discuss about the electrical parameters, like capacitance, operating voltage, internal resistance, energy capacity, specific power and specific energy, lifetime and self-discharge.

2.5.1. Capacitance

The capacitance values for commercial capacitors are specified as "rated capacitance C_R". This is the value for which the capacitor has been designed. The value for an actual component must be within the limits given by the specified tolerance. Typical values are in the range of Farads (F), three to six orders of magnitude larger than those of electrolytic capacitors.

If the energy of a loaded capacitor loaded with a DC voltage V_{DC} is W (usually expressed Joules) then we can write

$$W = \frac{1}{2}\, C_{DC.}\, (V_{DC})^2$$

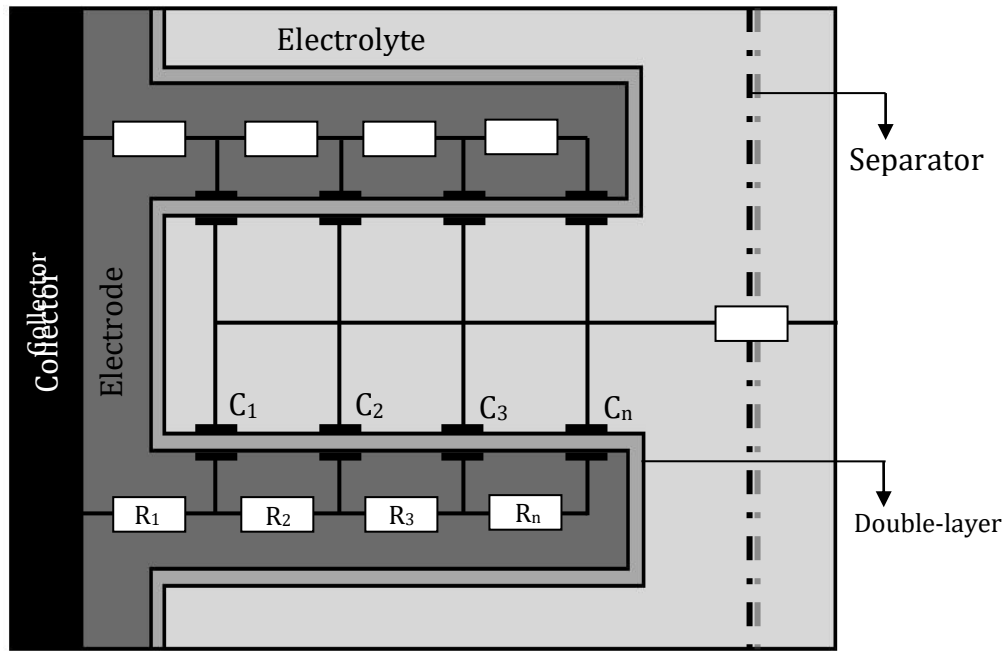This is also called the "DC capacitance".

Figure 8 : Schematic illustration of the capacitance behaviour
resulting out of the porous structure of the electrodes

2.5.2. Operating Voltage

Supercapacitors generally functions over a low voltage value. In order to keep the components safe the voltage should remain within the specified limits. The rated voltage U_R is the maximum DC voltage or peak pulse voltage that can be applied to the supercapacitor continuously and it also has to be mentioned that under this voltage range the supercapacitor will be under the specified temperature range. They are not supposed to be operated with more than the rated voltage.

The rated voltage also tells about the safety margin against the electrolyte's breakdown voltage. At this breakdown voltage the electrolyte decomposes and so does the separating solvent molecules in the Helmholtz double-layer (like water splits into hydrogen and oxide). Then the solvent molecules become unable to separate the electrical charges from each other.

Operating supercapacitors below the rated voltage improves the long-time behavior of the electrical parameters. Capacitance values and the internal resistance during cycling are more stable and lifetime and charge-discharge cycles may be extended.[34]

2.5.3. Internal Resistance

The charging-discharging a supercapacitor is connected to the movement of charge carriers (ions) in the electrolyte across the separator to the electrodes and into their porous structure. Losses occur during this movement that can be measured as the internal DC resistance.

With the electrical model of cascaded, series-connected RC (resistor/capacitor) elements in the electrode pores, the internal resistance increase with the increasing penetration depth of the charge carriers into the pores. The internal RC resistance is time dependent and increases during charging-discharging. In applications often only the switch-on and switch-off range is interesting. If R_i be the internal resistance and ΔV the voltage drop at the time of discharge, starting with a constant discharge current $I_{discharge}$, then we can write,

$$R_i = \frac{\Delta V}{I_{discharge}}$$

Note that, the internal DC resistance should not be confused with the internal AC resistance called the equivalent series resistance (ESR) normally specified for any capacitor. It is measured at 1 kHz frequency. ESR is much smaller than the DC resistance.

This internal resistance R_i determines various properties, such as, the charge and discharge peak currents as well as the charging (or discharging) times. The time constant is given by the following expression,

$$\tau = R_i \cdot C$$

For example, if a 100 F supercapacitor with an internal resistance of 30 mΩ then its time constant is 3 sec. This implies that after 3 sec, charging with a current limited only by internal resistance, the supercapacitor has 63.2% of full charge. Standard supercapacitors have a time constant of about 5τ.

2.5.4. Energy Capacity

Supercapacitors occupy the gap between the high power - low energy electrolytic capacitors and the low power – high energy rechargeable batteries. The maximum energy (W_{max}) stored in it is given by the following formula,

$$W_{max} = \frac{1}{2} \cdot C_{total} \cdot (V_{loaded})^2$$

The above formula describes the amount of the energy stored. However, only a part of this energy is available for applications, the presence of

voltage drop and also the internal resistance means that some of this energy will not be accessible.

The effective usable amount of energy (W_{eff}) is reduced by the difference between V_{max} and V_{min} and is given by,[35]

$$W_{eff} = \frac{1}{2}\, C \cdot [(V_{max})^2 - (V_{min})^2]$$

2.5.5. Specific Energy and Specific Power

The amount of energy stored in a supercapacitor per unit mass is called the specific energy and it is measured in Watt-hours/kg (Wh/kg).

The typical value for the specific energy of a supercapacitor is 0.5 to 15 Wh/kg. It is experimentally proved that the supercapacitors can store energy 10 to 100 times more than the electrolytic capacitors, but one tenth of the batteries.

Since the quantity specific energy alone is not enough to compare the supercapacitors with the batteries and as well as the capacitors, so that, the quantity specific power is introduced. The speed at which energy can be delivered to or absorbed from the load is called the specific power and it is measured generally gravimetrically in Watt-hours/kg (Wh/kg).

The maximum power transferred to the load by a supercapacitor is given by,[35]

$$P_{max} = \frac{1}{4} \cdot \frac{V^2}{R_i}$$

where, V be the applied voltage and R_i be the internal DC resistance of the supercapacitor.

The described maximum power P_{max} specifies the power of a theoretical constant single maximum current peak of an applied voltage. But in the real circuits the current peak is not constant caused by the voltage drop. Later a more realistic formula for the effective power P_{eff} for the supercapacitors is established and it is given by,

$$P_{eff} = \frac{1}{8} \cdot \frac{V^2}{R_i}$$

Supercapacitors can have specific power (typically) 10 to 100 times greater than that of the batteries and can reach up to 15 kW/kg.[36][39]

2.5.6. Lifetime

We know that any type chemical change does not take place in the electrodes (except the electrodes made from polymers). Therefore, the lifetime of a supercapacitor depends on the rate of evaporation of the liquid electrolyte. This evaporation is explicitly dependent on the temperature, current load, current cycle frequency and voltage. Here, the current load and the cycle frequency cause Joule effect, and hence internal heat generation, so that the evaporation-determining temperature is the sum of ambient heat and internal heat. The temperature is often represented as the core temperature in the centre of the supercapacitor body. As the core temperature increases, the evaporation becomes faster and hence the lifetime becomes shorter.

The real application lifetime of supercapacitors, also called "service life" or "load life", can reach up to 10 – 15 years or more at room temperature. Such long time periods cannot be tested by the manufacturers. So, they specify the expected capacitor lifetime at the maximum temperature and voltage conditions. The results are specified using the notation "tested time (hours)/ maximum temperature (℃)", for example 5000 h/ 65℃. Now from here we can estimate that for lower temperature the lifetime will be increased.

The lifetime specification can be used to make an estimation of the expected lifetime for a given design. There is a formula for the temperature dependence of reaction rates. For every 10℃ reduction in operating temperature, the estimated life doubles.

$$L_x = L_0 \cdot 2^{\frac{T_0 - T_x}{10}}$$

where, L_x and L_0 are the estimated lifetime and the specified lifetime respectively and T_0 and T_x are the upper specified capacitor temperature and the actual operating temperature of the capacitor cell respectively. Evaluated by this formula, capacitors specified with 5000 h at 65℃, have an estimated lifetime of 20000 h at 45℃.

2.5.7. Self-discharge

The charge carriers within the pores are separated by the energy stored in the double-layer by a distance of the order of molecules. Over this tiny distance it is very certain that irregularities can occur and this irregularities

leads to a small exchange of charge carriers which causes a gradual discharge. This self-discharge is called leakage current.

This leakage depends on the capacitance, voltage, temperature and the chemical stability of the electrode-electrolyte combination. At room temperature the leakage current is so small that it is specified as time to self-discharge. Generally supercapacitor self-discharge time is specified in hours, days or weeks.

As an example, a 5.5 V/F Panasonic "Goldcapcitor" specifies a voltage drop at 20℃ from 5.5 V to 3 V in 600 hours (25 days or 3.6 weeks) for a double cell capacitor.[38]

Chapter 3

Types of Supercapacitors

In this section we shall discuss on the topic that according to the charge storage procedure the supercapacitors can be categorized in how many kinds.

Types of Supercapacitors

There are two storage principles in which the electrical energy can be stored into a supercapacitor; those are *static double-layer capacitance* and *electrochemical pseudocapacitance.* It is the material and the structure of the electrodes on which the distribution of the two types of capacitance depends. Based on these two energy storage principles there are three types of supercapacitors:[13][21]

1. Electrochemical Double-layer Capacitor (EDLC)

In this type of capacitors the activated carbon or derivatives, with much higher electrostatic double-layer capacitance than electrochemical pseudocapacitance, are used as electrode materials.

2. Pseudocapacitor

The transitional-metal oxide or conducting polymers with high amount of electrochemical pseudocapacitance are used as electrodes in this type of supercapacitors.

3. Hybrid Capacitor

The asymmetric type of electrodes, where one of them exhibits mostly electrostatic while the other one exhibits mostly electrochemical capacitance (such as lithium-ion capacitance), are used in this type of supercapacitors.

The double-layer capacitance and pseudocapacitance both contribute to the total capacitance value of an electrochemical capacitor in a combined manner. So, a correct description of these capacitors only can be given under the generic consideration.
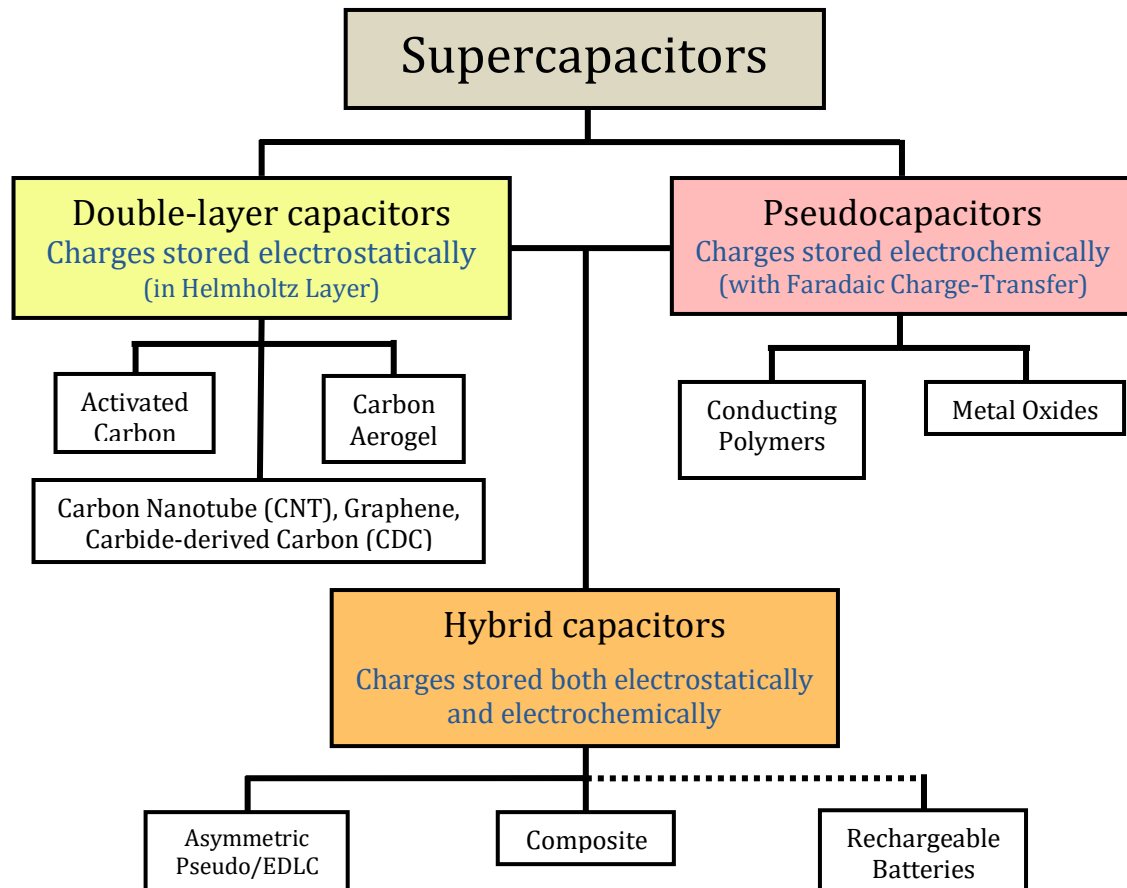
The capacitance value of a supercapacitor is determined by two storage principles:

- **Double-layer Capacitance :** In this procedure the electrical energy is stored as an electrostatic storage and this is because of the tiny separation of the charges in the Helmholtz double-layer. This Helmholtz double-layer is formed at the interface between the electrodes and the electrolyte and the distance created with this separation between this two layer is of the order of few Ångströms (0.3-0.8 nm).

- **Pseudocapacitance :** In this case the electric energy is stored as an electrochemical storage and this is because of the ongoing redox reactions, electrosorption and intercalation on the surface of the electrode by specifically adsorbed ions. This entire phenomenon results in a reversible Faradaic charge-transfer on the electrode.[13]

Although the double-layer capacitance and the pseudocapacitance both contribute to the total capacitance inseparably,[20] the ratio of them can vary greatly. Depending upon the design of the electrodes and the materials been used and the composition of the electrolyte this variation between the capacitance occurs.

Pseudocapacitance can increase the capacitance value by as much as a factor of 10 over that of the double-layer by itself.[11][32]

The concepts of supercapattery and supercabattery have been recently proposed to better represent those hybrid devices that behace more like the supercapacitor and the rechargeable battery, respectively.[39]

The EDLCs are electrochemical capacitors in which energy storage predominantly is achieved by double-layer capacitance. In the past, all electrochemical capacitors were called "double-layer capacitors". Contemporary usage sees double-layer capacitors, together with the pseudocapacitors, as part of a large family of electrochemical capacitors[11][32] called supercapacitors. They are also known as the ultracapacitors.

Chapter 4

Materials

The properties of any supercapacitor can be recognized from the interaction of their internal materials, i.e., the materials used as electrodes, electrolyte, separators and collectors. Especially, the combination of the electrode material and type of electrolyte determine the functionality and thermal and electrical characteristic of the capacitors.

4.1. Electrodes

There are usually a thin coating applied on the electrodes of a supercapacitor and they are electrically connected to a conductive, metallic current collector. Electrodes should be chosen in such a way that they should have the following characteristics:

1. Good conductivity;
2. High temperature stability;
3. Long-term chemical stability (inertness);
4. High corrosion resistance;
5. High surface areas per unit volume or mass.

Other requirements include environmental friendly and low cost.

The amount of the double-layer as well as the pseudocapacitance stored per unit voltage in a supercapacitor is predominantly a function of the electrode surface area. Therefore, if the electrodes typically are made of porous, spongy material with having a surprisingly large amount of surface area, then we can achieve a huge capacitance value between the two electrodes. Additionally, the ability of the electrode material to perform a Faradaic charge transfer in order to get the pseudocapacitance which enhances the total capacitance.

We can understand that the smaller the pores, the larger the surface area which can store more amount of charges, and that increases the capacitance and specific energy. However, smaller pores lead to an increase of the equivalent series resistance (ESR) and decrease the specific power. If we want to apply this with high peak currents then we require larger pores and low internal losses, while applying with high specific energy needs small pores.

4.1.1. Electrodes for Electrochemical Double-layer Capacitors (EDLC)

The material which is most commonly used to construct electrodes for supercapacitors is carbon in various manifestation, for example activated carbon (AC), carbon fibre-cloth (AFC), carbide-derivative carbon (CDC), carbon aerogel, graphene, garphane[40] and carbon nanotubes (CNT).[20][41][42]

It is experimentally checked that the carbon-based electrodes exhibit predominantly static double-layer capacitance, although a small amount of pseudocapacitance also may be present there depending upon the pore size distribution. In this case pore sizes in carbon is typically less than 2nm (micropores) to 2-50nm (mesopores),[43] but the fact is that only the micropores contribute to the pseudocapacitance. If the pore size becomes of the order of the salvation shell size, then the solvent molecules are excluded and only the unsolvated ions fill the pores (even for large ions), increasing ionic packing density and storage capability.[20]

1. Activated Carbon (AC)

Activated was the very first material which was chosen for the EDLC electrodes. Its characteristics are as follows:

- electrical conductivity is around 1250 to 2000 S/m (0.003% of the metals), which suffices the need of a supercapacitor.[22]

- extremely porous with a high specific area, for example, 1 g (a pencil-eraser-sized amount) has a surface area of roughly 1000 to 3000 square meters,[41][43] i.e., about a size of 4 to 12 tennis courts.

The bulk form used in the electrodes is having low-density with many pores, leads to high value of double-layer capacitance. On the other hand, *solid activated carbon* (or *consolidated amorphous carbon*) is the mostly used electrode material, since it is cheaper than any other carbon derivatives.[44] An electrode with a surface area about $1000m^2$/g gives us a typical double-layer capacitance of about 10 $\mu F/cm^2$ and a specific capacitance of 100F/g.

2. Activated Carbon Fibres (ACF)

Activated carbon fibres or ACFs are produced from the activated carbon and have a typical diameter of 10 μm. They can have readily controlled micropores with having a very pore-size distribution.

An ACF made electrode has a typical surface area of about $2500m^2$/g. Advantages of using ACF electrodes are:

- low electrical resistance along the fibre axis,
- good contact to the collector.[41]

The ACF electrodes basically exhibit double-layer capacitance with a small amount of pseudocapacitance due to their specific size, numbers and distribution the micropores.

3. Carbon Aerogel

Carbon aerogel is derived from an organic gel in which the liquid component of the gel has been replaced with a gas. Aerogel electrodes are made via pyrolysis of resorcinol-formaldehyde aerogels.[45] It has some useful characteristics which make this material a more perfect one in constructing EDLC electrodes. These characteristics are:

- highly porous (they enable thin electrodes with a thickness in the range of several hundred micrometers and with uniform pore size),
- highly conductive (more conductive than activated carbon),
- ultralight,
- synthetic,
- significant mechanical and vibration stability of the electrodes in high-vibration environments.

Researchers have become successful in constructing a carbon aerogel electrode with gravimetric densities of about 400 – 1200 m^2/g and volumetric capacitance of around 104 F/cm^3, which yields a specific energy of 325 kJ/kg (90 Wh/kg) and specific power of 20 W/g.[46][47]

A standard aerogel electrode mainly produces double-layer capacitance. But since composite materials are incorporated with the aerogel electrodes, therefore it can add a high amount of pseudocapacitance which also increases the total capacitance.[48]

4. Graphene

Graphene is basically a graphite sheet with a thickness of the order of one-atom. In this lattice structure, the atoms are arranged in a regular hexagonal pattern,[49][50] so this graphene is also called "nanocomposite paper".[51]

The benefits of using graphene are:

- the specific surface area is very much greater than that of the AC, ACF, carbon aerogel and carbide-derived carbons (theoretically 2630 m^2/g which can provide us a capacitance of around 530 F/g);[52][53]
- the electrical conductivity is higher than that of the activated carbon;
- the curved graphene sheets can be operated up to 4 Volt;

- In the case of curved graphene sheets, the obtained specific energy at room temperature is 85.6 Wh/kg (308 kJ/kg) and this is equal to a conventional nickel metal hydride battery, but with 100-1000 times greater specific power.[54][55]

In 2012 scientists have successfully used graphene sheets directly as electrodes without collectors.[52][53]

In one embodiment, a graphene-based supercapacitor uses curved graphene sheets that do not stack face-to-face, forming mesopres that are accessible to and wet-table by ionic electrolytes.

5. Carbide-derived Carbon (CDC)

Carbide-derived carbon or CDC, also known as *tunable nanoporous carbon*, is basically a family of carbon materials derived from carbide precursors (titanium carbide and silicon carbide), that are transformed into pure carbon via physical (e.g., thermal decomposition) or chemical (e.g., halogenations) processes.[56][57]

Carbide-derived carbons can exhibit the following properties:
- high specific surface area;
- tunable pore sizes (more precisely diameters) in order to maximize the ion confinement (this also leads to an increase of pseudocapacitance);
- using the tailored pore design we can have 75% greater specific energy (10.1 Wh/kg, with 3500 F capacitance) than that of the conventional activated carbons with more numbers of times of charge-discharge cycles (over one million times).[58]

As of 2015, a CDC supercapacitor offered a specific energy of 10.1 Wh/kg, 3500 F capacitance and over one million charge-discharge cycles.[58]

6. Carbon Nanotubes (CNT)

Carbon nanotubes or CNTs, also called buckytubes, are carbon molecules having a hollow structure with walls formed be one-atom-thick sheets of graphite. These sheets are rolled at specific and discrete ("chiral") angles, and the combination of chiral angle and radius controls properties such as electrical conductivity, electrolyte wettability and ion access.

There are mainly two types of nanotubes, viz. single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). MWNTs are formed by enveloping one or more than one outer tubes over a SWNT. As SWNTs have diameters in the order of few nanometers (1 to 3 nm), MWNTs have thicker coaxial walls which are separated by spacing (0.34 nm).

Now the benefits of using CNTs are:

- Capable of storing the same amount of charges per unit surface area as AC, but they are also arranged in a regular pattern which offers a greater wettability to the capacitor.[59][60] SWNTs have a high theoretical specific surface area of 1315 m^2/g, while in case of MWNTs is lower and is determined by a diameter of the tubes and degree of nesting.

- CNTs exhibit a large amount of electrical conductivity.

CNT made supercapacitors can deliver us higher capacitance than that of the activated carbon made supercapacitors, e.g. 102 F/g for MWNTs and 180 F/g for SWNTs.[61]
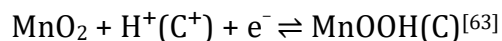
4.1.2. Electrodes for Pseudocapacitors

The materials having the electrochemical signature of a capacitive electrode (i.e., linear voltage dependence on current versus voltage curve) as well as Faradaic redox behaviour can only be used for making the electrodes of the pseudocapacitors. MnO_2 and RuO_2, each of them possesses such behaviours, so that, they are generally used for this purpose. In addition to that, the charge storage occurs due to the electron-transfer mechanisms rather than the accumulation of ions in the electrochemical double-layer.

Nowadays, maximum numbers of researches are focused on transition-metal oxides (like MnO_2) rather than noble metal oxides (like RuO_2), as the former category is available with a lower cost than the latter one. Moreover, the charge storage mechanisms of transitional-metal oxides are based predominantly on pseudocapacitance.

Two mechanisms of MnO_2 charge storage behaviour were introduced.

1. The first mechanism implies the interaction of protons (H^+) or alkali metal cations (C^+) in the bulk of the material upon reduction followed by deintercalation upon oxidation.[62]

$$MnO_2 + H^+(C^+) + e^- \rightleftharpoons MnOOH(C)^{[63]}$$

2. The second mechanism is based on the surface adsorption of electrolyte cations on MnO_2.

$$(MnO_2)_{surface} + C^+ + e^- \rightleftharpoons (MnO_2^- C^+)_{surface}$$
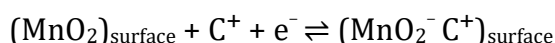
Not every material with Faradaic behavior can be used as an electrode for pseudocapacitors, such as $Ni(OH)_2$ since it is a battery type electrode (non-linear dependence on current versus voltage graph)[64]

1. Metal Oxides

According to the researches, electrodes made of transition metal oxides (such as RuO_2, IrO_2, Fe_3O_4, MnO_2 etc.) or sulfides (such as TiS_2) exhibit greater amount of pseudocapacitance. They, either alone or in combining, generate strong Faradaic electron-transferring reactions with a low resistance.[65] For example, RuO_2 in combination with H_2SO_4 electrolyte provides us a specific capacitance of 720 F/g and also a high specific energy of 26.7 Wh/kg (96.12 kJ/kg).[66] This huge amount of pseudocapacitance is around 100 times higher than the double-layer capacitance using activated carbon electrodes.

In this case, each of the electrodes the charge/discharge process takes place over a window of about 1.2 Volt. The transitional-metal oxides made electrodes also provide us a very good reversibility with a several hundred-thousand cycles while RuO_2 gives us a voltage window of 2.4 Volt. But since RuO_2 is very much expensive so that it has limited applications.

As reported in 2014, a RuO_2 supercapacitor anchored on a graphene foam electrode gave specific capacitance of 502.78 F/g. It also had a specific energy of 39.28 Wh/kg and specific power of 128.01 kW/kg over 8000 cycles with constant performance.[67][68]

2. Conductive Polymers

Although being mechanically weak, conductive polymers are used for the electrodes of pseudocapacitors, as they have usually high conductivity, which provides us a relatively high capacitance with a low ESR. Such conductive polymers are polyaniline, ploythiophene, polypyrrole and polyacetylene. These type of electrodes made from or coated with conductive polymers cost comparably to the carbon electrodes.

The main drawback of using such conductive polymers is that they generally provide us a very limited cycling stability.[69] But the ployacene made electrodes have charge/discharge cycles up to 10000 cycles, which is far better than batteries.[70]

4.1.3. Electrodes for Hybrid Supercapacitors

Any type of hybrid capacitors used for commercial purpose generally consists of asymmetric electrodes. In this type capacitor one electrode is with high amount pseudocapacitance whereas the other one is with high amount of double-layer capacitance. In such cases the Faradaic pseudocapacitance

electrode with higher capacitance value provides high specific energy while the EDLC electrode provides high specific power.

The advantage of using the hybrid supercapacitors in comparison with using the symmetrical EDLC's is that they do have higher specific capacitance value as well as they also have a higher rated voltage which corresponds to higher specific energy.[71]

1. Composite Electrodes

Generally by incorporating or depositing pseudocapacitive active materials (such as transitional-metal oxides or conductive polymers) in the carbon-based materials the composite electrodes for hybrid supercapacitors are constructed.

The carbon nanaotubes (CNT's) provide us a homogeneous distribution of the pseudocapacitive active materials, producing a very significant amount of pseudocapacitance as well as double-layer capacitance. These type electrodes are capable of having higher capacitance values than that of the pure carbon or pure metal oxide or polymer-based electrodes.

Another way to fabricate CNT electrodes is by doping with a pseudocapacitive dopant as in lithium-ion capacitors. This gives in a larger voltage of 3.8-4 Volt that prevents electrolyte oxidation.

As reported in 2007, they successfully had a capacitance of 550 F/g[8] and reach a specific energy up to 14 Wh/kg (50.4 kJ/kg).[72]

2. Battery-type Electrodes

The development of the electrodes for new hybrid-type supercapacitors as for lithium-ion capacitors has been influenced by the rechargeable battery electrodes.[73] In combination with a carbon EDLC electrode the special type of configuration made of via asymmetric construction provides higher specific energy than a typical supercapacitor with higher specific power and longer cycle life does. It also has a faster charging and discharging times than batteries.

3. Asymmetric Electrodes (Pseudo/EDLC)

According to the very recent researches, a type asymmetric supercapacitor has been developed whose positive electrode is based on a real pseudocapacitive metal oxide electrode, whereas the negative electrode is based on an EDLC activated carbon electrode.

The advantage of using such type of supercapacitors is that they have higher voltage and correspondingly higher specific energy up to 10-20 Wh/kg (36-72 kJ/kg).[74]

4.2. Electrolytes

An electrolyte is a substance that produces an electrically conducting solution when dissolved in a polar solvent (such as water). The dissolved electrolyte separates into cations and anions, which are distributed uniformly through the solvent. Although being electrically neutral, if an electrical potential is applied to such a solution, the cations of the solution are drawn to the electrode that has an abundance of electrons, while the anions are drawn to the electrode that has a deficit of electrons. The movement of anions and cations in opposite directions within the solution amounts to a current. This includes most soluble salts, acids, and bases. Thus, the electrolytes consist of a solvent and dissolved chemical that dissociated into positive cations and negative anions, making the electrolyte electrically conductive. The more ions the electrolyte contains, the better conductivity.

In case of supercapacitors, electrolytes function as an electrically conductive connection between the two electrodes. In addition to that, the electrolyte offers the molecules for the separating of monolayer in the Helmholtz double-layer and delivers the ions for pseudocapacitance in supercapacitors.

In a way or the other the electrolyte determines the characteristics of a supercapacitor, such as the operating voltage, the temperature range, the equivalent series resistance (ESR), and finally the capacitance. For instance, for the same activated carbon electrode an aqueous electrolyte gives capacitance values of 160 F/g, whereas an organic electrolyte gives only 100 F/g.[75]

An electrolyte must possess the following properties:

1. they should be chemically inert as they are not supposed to attack the other materials inside the capacitor ensuring a long term stability of the capacitor's electrical parameters;

2. they should have a significant low viscosity as they can wet the porous, sponge-like structure of the electrodes.

4.2.1. Aqueous Electrolytes

Water is a relatively good solvent for the inorganic chemical. Water provides a very amount of conductivity (about 100 to 1000 mS/cm) in case of

acids such as sulfuric acid (H_2SO_4), alkalis such as potassium hydroxide (KOH), or salts such as quaternary phosphonium salts, sodium perchlorate ($NaClO_4$), lithium perchlorate ($LiClO_4$) or lithium hexafluoride arsenate ($LiAsF_6$).

The advantage of using an aqueous electrolyte is that it provides a dissociation voltage of 1.15 Volt per electrode (2.3 Volt capacitor voltage) and a relatively low operating temperature range. In the supercapacitor they work under a low specific energy and high specific power.

4.2.2. Organic Electrolytes

When organic solvents such as acetonitrile, propylene carbonate, tetrahydrofuran, diethyl carbonate, γ-butyrolactone and solutions with quaternary ammonium salts or alkyl ammonium salts such as tetraethylammonium tetrafluoroborate ($N(Et)_4BF_4$[76]) or triethyl (methyl) tetrafluoroborate ($NMe(Et)_3BF_4$) are used as electrolytes, they can achieve a higher dissociation voltage of typically 1.35 Volt per electrode (2.7 Volt capacitor voltage), and a higher temperature range.

But the main disadvantage is that these all materials are expensive than aqueous electrolytes. Also the organic solvents have less electrical conductivity (10 to 60 mS/cm) which leads to a lower specific power. But since the specific energy increases with the square of the voltage, a higher specific energy is obtained ultimately.

4.3. Separators

The main task of the separator is to physically separate the two electrodes in order to prevent a short circuit by direct current. The very obvious characteristics that the separator should possess are:

1. it should be very thin (a few hundredth of a millimeter);
2. it must be very porous to the conducting ions in order to minimize the ESR;
3. it should also be chemically inert to protect the electrolyte's stability and as well as the conductivity.

The open capacitor papers are generally used as the inexpensive components. But the sophisticated designs mostly use nonwoven porous polymeric films (like polyacrylonitrile or Kapton, woven glass fibres or porous woven ceramic fibres).[77][78]

4.4. Collectors

The main of the current collectors is to connect the electrodes to the capacitor terminals. The collector is either a metal foil or sprayed onto the electrode surface. They have to be capable of distributing peak currents up to 100 A to the outer circuit.

Chapter 5

Colnclusion and Future Work Needs for Betterment

Supercapacitors, or electrochemical capacitors, are electric devices that store energy electrochemically in conductive materials, in the presence of a suitable electrolyte, by two different mechanisms, namely, the electrostatic adsorption of ions (charges) on a polarized surface and the reversible redox reactions of surface electroactive species.[79] The first mechanism (pure capacitive) is predominant in the so called electrochemical double-layer capacitors (EDLCs) and it is characteristic of high surface area carbon materials.

The second one (based on pseudocapacitance) prevails in the so called active or redox electrodes (also called the pseudocapacitors), like metal oxides/hydroxides (RuO_2, MnO_2, VO_x, Co_3O_4, Fe_3O_4, $Ni(OH)_2$, $Co(OH)_2$, etc.) and conductive polymers (polyaniline, polypyrrole etc.). Both mechanisms involve highly reversible and fast charge and discharge processes that make these materials distinct from the battery-like electrodes. Nevertheless, carbon materials usually contain electroactive surface functionalities that can participate in pseudocapacitive processes, and active materials usually display high surface areas to adsorb electrolyte ions, so they contribute to their total specific capacitance. The third type of electrode for supercapacitors is then the combination of previous ones in the form of composites, typically, a redox material finely dispersed on the large surface of a carbon.

As previously mentioned, the characteristic features of supercapacitors involve that they can be charged and discharged very quickly (within few seconds to milliseconds) and several times (usually more than 100000 cycles) without significant capacitance loss. Hence, these devices can complement or replace batteries when high power delivery or uptake, intermittent energy with variable power demands, and/or long cycling stability are required. This is mainly the case of electric vehicles, when accelerating and braking, and modern multifunctional portable electronic devices (laptops, mobile phones, tablet PCs, cameras etc.), which require different power profiles depending on the function. In addition, supercapacitors exhibit excellent low temperature performance and improve efficiencies in supply systems (such as internal combustion engines, renewable energy systems, batteries and fuel cells) by storing energy when in excess or not needed. As a consequence, apart from automotive and portable electronic devices, supercapacitors find potential application in energy harvesting, renewable energy, electrical grids, wireless sensors and Radio Frequency Identification (RFID).[80]

Interestingly, new trends on future consumer electronics and portable devices (with $86 billion market by 2023 [80]) point out they are becoming increasingly thinner and more power-demanding.[81] In this case, the utilization of supercapacitors for a more efficient use of batteries will allow the effective reduction of their capacity and, therefore, size and weight, as well as an enhanced power performance and the extension of their useful time. Because of all these interesting properties and their potential usage for an increasing number of purposes and applications, supercapacitors market is roaring up to over $11 billion by 2024 with considerable upside potential.[82]

However, despite this significance and promising perspectives, the widespread utilization of supercapacitors has not been attained yet. According to manufacturers, developers and suppliers of supercapacitors, this is assigned to their current high cost to performance ratio and low energy density[83]. As a result, great efforts and multiple research activities are currently driven towards the development of advanced materials and configurations for enhanced energy densities, as well as cheaper preparation and processing methods. Some of these currently most important research lines are analysed in the following sections.

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