CHAPTER - I

INTRODUCTION

Electrical energy storage devices are mandatory in many applications viz., telecommunication devices (cell phones, remote communication, walkie-talkies etc), standby power systems, and electric hybrid vehicles in the form of storage components (batteries, supercapacitors and fuel cells). These prompted the need for advanced power sources offering high power density. The electrochemical capacitors (ECs) or supercapacitors represent a new generation of electrochemical energy storage components with very high capacitance for energy storage. Electrochemical capacitors store energy in either capacitive (double layer of electrostatic charges) or pseudocapacitive (a faradic battery-like reaction) nature. Exploiting both the advantages of battery (high energy density) and conventional capacitors (high power density), ECs easily offer higher specific capacitance values up to several thousand Farad for applications requiring pulse power. They can also be cycled several hundred thousand times. Being an entity of ECs, hybrid capacitors incorporating a battery-like anode (+) and a carbon based cathode (-) having non-faradic character have more to render in terms of power and energy [1].

This class of energy storage device is commonly known in many names such as supercapacitor, ultracapacitor or electrochemical double-layer capacitor (EDLC). It is capable of condensing energy, by arraying electrical charges, electrostatically at the electrode/electrolyte interface, known as the helmholtz layer, achieving capacitance in the order of Farads. Penetrating into the current market as a feasible alternative to batteries, ECs are paving ways for researchers to investigate
all possible materials that could deliver enhanced performances in terms of power and energy density, charge discharge characteristics, cycling stability and reversibility.

New materials for electrodes such as activated carbons, nanostructured carbon, carbon nanotubes, activated fibers and graphite of high porosity, nano sized transition metal oxides, conducting polymers etc. provides high specific surface area with good electrical conductivity. Since electrical capacitance of ECs is quite dependent on the number of ions (anions or cations) present at the electrode/electrolyte interface, highly increased specific surface area of these new electrode materials is essential for the ECs to obtain remarkably increased number of ions adsorbed on the surface of electrodes so as to realize the so-called “supercapacitance”. To be specific, the term supercapacitor (SC) is commonly used to describe carbon/carbon symmetrical cells exhibiting “super-capacitance” with several tens of hundreds of farads. SCs in general, are attributed to the purely non-diffusional charge reaction during the polarization. Hence, SCs do not exhibit redox (reduction/oxidation) reaction for electricity storage. Thus, the charge-discharge cycle life of SCs can be over 300,000 cycles (charge/discharge) and the turn around efficiency is up to 96% without significant degradation between the operating temperatures of –25 and +50ºC. In addition, the charge time becomes very rapid up to a few seconds and the specific power density is at least two order higher than the secondary or rechargeable batteries. These are the most distinctive outstanding characteristics as a new type of energy storage power source that any other types of electric storage devices such as advanced lithium-ion and lithium polymer rechargeable batteries cannot offer power density as high as what SCs could offer. However, the specific energy density of the SCs is hitherto one order of magnitude
less than that of rechargeable lithium batteries. Research into ECs is presently classified into two main areas that are based primarily on their mode of energy storage, namely; (i) the electrochemical double layer capacitor also referred to as pseudo capacitors. The former stores energy (electricity in the form of electrostatic means that is typically the same way as a traditional capacitor and secondly (ii), the redox supercapacitor exhibits reversible Faradaic-type charge transfer and the resulting capacitance is not electrostatic in origin and hence the name pseudo capacitors. Invoking the developmental pace of advanced materials such as nanostructured transition metal oxides, carbons and electro-conductive porous polymers, the electrochemical capacitor (EC) and the battery (lithium battery) will soon be rolled in the same area of energy storage in which energy is paramount in the so-called hybrid energy storage device. It is with the above-astounded advantages and applications in mind, the present work was embarked at developing ECs using novel nanostructured metal oxides and inexpensive nanoporous carbonaceous materials as potential electrodes focusing on high power and energy ECs.

1.1. WHAT ARE SUPERCAPACITORS?

A supercapacitor is an electrochemical capacitor that offers very high capacitance in a small package. It consists of two electrodes with electrolyte and separator. They are capable to store a large amount of charge (energy) that can be released very quickly. Supercapacitors hold their stored electric charges in an ionic layer that forms at the interface between each of the two electrodes and a common electrolyte. This means they are superior in short term and high-energy applications, such as when an appliance is switched on or an electric car accelerates.
Supercapacitors offer many benefits; the global market for portable rechargeable batteries is rapidly expanding, with a 17% increase to US$ 4.5 billion in 2003.

- They can be recharged very quickly (in a matter of seconds)
- When fitted alongside a battery can extend battery life by up to five times by 'leveling out' high power demands on the battery (load leveling)
- They can be manufactured in any size and shape
- They can be retrofitted on to existing designs
- The devices are generally made from low-toxicity materials

1.2. BASIC PRINCIPLE OF A CAPACITOR [1]

A capacitor is commonly known as an electrical condenser. The amount of electricity which a capacitor will hold depends on the electrical pressure or voltage applied to the capacitor. The plates are charged with equal amounts of positive and negative electrical charges, respectively. This is a "physical" storage of electricity and is analogous with the "chemical" storage in a battery. A capacitor is said to be charged when there are more electrons on one conductor plate than on the other. If an electric potential (voltage) is applied to the capacitor plates, the plates will become charged, one positively and one negatively. The plate with the larger number of electrons has the negative polarity. The opposite plate then has the positive polarity. When a capacitor is charged, the energy is stored in the dielectric material in the form of electrostatic field. When an electron is added to one plate of a capacitor, one electron is driven away from the opposite plate. This phenomenon is known as the principle of electrostatic induction. Fig.1.1 shows the principle of electrostatic induction in a capacitor.
1.3. BASIC PRINCIPLE OF SUPERCAPACITOR

In a conventional capacitor (condenser), the charge accumulation is achieved electrostatically by positive and negative charges residing on two interfaces separated by a vacuum or a molecular dielectric (a film of mica, a space of air, or an oxide film). Supercapacitors store the electric energy in an electrochemical double layer formed at the interface between the polarizable electrodes and compensate for the electronic charges at the electrode surface, as shown in Fig.1.2. This charge distribution layer is called the electric double layer (or electrochemical double layer). This picture presents the principle of an electrochemical capacitor and function of carbon electrode.

The thickness of double layer depends on the concentration of electrolyte and the size of ionic clusters and it is typically the order of $5 - 10 \, \text{A}^0$ for concentrated electrolytes. When voltage is applied to the wires attached to two conducting surfaces, charges (electrons) are pumped from one surface to the other surface.
leaving one of the surfaces positively charged (+Q) and the other surfaces negatively charged (-Q) as shown in Fig.1.3.

When the capacitor is charged, energy is stored in the dielectric material in the form of electrostatic field. The capacity of an electrical capacitor is the ratio of electricity and the electrical pressure or voltage. In other words, the capacity of a capacitor depends on the amount of electricity it will hold at a certain pressure or voltage. This ratio may be expressed as,

$$V = \frac{Q}{C}$$  \hspace{0.5cm} (1.1)

Fig.1.2. (A) Principle of a single-cell double-layer capacitor and illustration of the potential drop at the electrode/electrolyte interface  
(B) Function of carbon electrode in an electrochemical capacitor

where, "Q" is the quantity of electricity, "V" is the electrical voltage and "C" is called the capacitance and it measured in a unit called Farad, abbreviated as F. This is a
large unit; more common units are microfarad, abbreviated µF (1µF=10^{-6} F) and the pico farad, abbreviated pF (1 pF=10^{-12} F). The capacity of a capacitor depends upon the size, spacing of the conducting plates and the type of insulating or dielectric medium between the plates.

\[ C(F) = \frac{\varepsilon A}{d} \quad (1.2) \]

Where, \( \varepsilon \) = Dielectric constant, \( \varepsilon = \varepsilon_0 \varepsilon_r \)

\( \varepsilon_0 \) = Space permittivity (8.854x10^{-12} C^2Nm^2)

\( \varepsilon_r \) = Relative permittivity (depending on the dielectric used)

A = Area of one plane, (m^2)

D = Distance between the plates, (m)

![Fig.1.3. Capacitor stores energy in the form of separated electrical charge](image)
The capacitance is directly proportional to the surface areas of the plates and is inversely proportional to the separation between the plates. Capacitance also depends on the dielectric constant of the substance separating the plates.

The corresponding electric field in the electrochemical double layer is high and is assumed to be $10^6$ V/cm. Compared to conventional capacitors where a total capacitance is typically on the order of pico-farads and microfarads, the capacitance and energy density stored in the supercapacitor by the electrochemical double layer is higher. To achieve a higher capacitance the surface area of the electrode is additionally enlarged by using porous electrodes, where an extremely large internal surface area is expected. There are several techniques for determining the specific capacitance, such as a unit cell test (two electrode system), a half cell test (three electrode system), and an impedance test. The unit cell and half–cell tests are mainly used to determine the specific capacitance of the supercapacitor. The specific capacitances reported in the literature are not consistent, mainly due to the various experimental methods used. For the sake of consistency, it is worth specifying the electrochemical technique for calculating the specific capacitance between the two electrode and three electrode systems. 

**Fig.1.4 (a)** shows the double layer of electrodes used in the two-electrode system (2E), which represents a real double layer supercapacitor device and its equivalent circuit. 

**Fig.1.4 (b)** shows the double layer of electrodes used in the three–electrode system (3E), which is used in the laboratory cell with a reference electrode and its equivalent circuit. Assuming that the weight of each individual electrode is “m”, then

$$C_1 = C_2 = C$$
The capacitance measured for the two electrode system is

\[ C_{2E} = \frac{1}{2} C \]  

(1.3)

The specific capacitance turns out to be

\[ C_{\text{spec-}2E} = \frac{C_{2E}}{2m} = \frac{1}{4} (C / m) \]  

(1.4)

for the three electrode system, the double layer capacitance is measured as

\[ C_{3E} = C \]

and the specific capacitance is

\[ C_{\text{spec-}3E} = \frac{C_{3E}}{m} = (C / m) \]  

(1.5)

Thus, the relationship between the specific capacitance measured at the two electrode and three electrode techniques is

\[ C_{\text{spec-}3E} = 4C_{\text{spec-}2E} \]

In the double layer of plane electrodes, charge densities of about 16-50 \( \mu F/cm^2 \) are commonly realized. Taking an average value of 30 \( \mu F/cm^2 \), the capacitance of a single polarisable electrode with a typical surface area of 1000 \( m^2/g \) for porous materials leads to a specific capacitance of 300 F/g. At 1 V in an aqueous electrolyte, the maximum storage energy, \( E \), is

\[ E(W/g) = \frac{CV^2}{2} = \frac{(300 \times 1^2)}{2} = 150 \]
150 kJ/kg or 42 Wh/kg theoretically. This value is considerably lower than that obtained for available batteries but higher than that for conventional capacitors. This value depends on the double layer capacitance, the specific surface area of the respective electrode material, the wetting behaviour of the pores and the nominal cell voltage. The maximum power density of supercapacitor is given by,

$$P_{\text{max}} = \frac{V_i^2}{4R}$$

(1.6)

Where, $V_i =$ initial voltage, $R =$ equivalent series resistance (ESR).

Therefore, the key factors determining the power of supercapacitors are the resistivity of the electrode itself, the resistivity of the electrolyte within the porous layer of electrode, and the contact resistance between the electrode and the current collector, as shown in Fig. 1.5.

In evaluating the performance of supercapacitors, the characterization of their energy density and power density are the most important factors of rating electrochemical power devices. In addition, from practical and fundamental points of view, there is a question of how the energy density and power density are related to various types of electrochemical power sources including fuel cells and rechargeable batteries.
Fig. 1.4. Electric double layer and its equivalent circuit in (a) two-electrode system and (b) three-electrode system.

Fig. 1.5. Equivalent circuit of an electrochemical capacitor.
1.4. NEED FOR SUPERCAPACITORS

The most common electrical energy storage device is battery. Batteries have been the technology of choice for most applications because they can store large amounts of energy in a relatively small volume and weight and provide suitable levels of power for many applications. Shelf and cycle life have been a problem with most types of batteries, but users have learned to tolerate this shortcoming due to the lack of an alternative. In recent times, the power requirement in a number of applications has increased markedly and have exceeded the capability of batteries of standard design. This has led to the design of special high power pulse batteries often with the sacrifice of energy density and cycle life. Supercapacitors are being developed as an alternative to pulse batteries. To be an effective alternative, ultracapacitors must have much higher power and longer shelf and cycle life than batteries. Ultracapacitors have much lower energy density than batteries and their low energy density is in most cases the factor that determines the feasibility of their use in a particular high power application. For ultracapacitors, the trade-off between the energy density and the RC (time constant) of the device is an important design consideration. In general, for a particular set of materials, a sacrifice in energy density is required to get a large reduction in the time constant and thus a large increase in power capability.

1.5. CLASSIFICATION OF SUPERCAPACITORS

Supercapacitors are able to attain greater energy densities still maintaining the characteristic high power density of conventional capacitors. Supercapacitors, also known as ultracapacitors or electrochemical capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances in several
orders of magnitude larger than conventional capacitors. The supercapacitors have been classified into three major categories as shown in Fig.1.6.

1.5.1. Electrochemical double-layer capacitors

Electrochemical double layer capacitor stores energy using the double layer concept. This double layer is realized when two electrodes immersed in an electrolyte, are polarized. The polarized charges at both the positive and negative electrodes resemble two capacitors connected in series (Fig.1.7).

![Supercapacitors classification diagram]

**Fig.1.6.** Classification of supercapacitors based on electrode materials

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Analyzing the exploded view of the individual electrode, Helmholtz has identified the existence of a 'double layer' in the electrochemical cell in 1879. And it is named after him as Helmholtz layer. There are several theoretical models that describe the structure of the double layer such as the Gouy-Chapman model and the Gouy-Chapman-Stern model. However the most common one would be the Helmholtz model. Helmholtz double layer is a structure of charge accumulation and charge separation that always occurs at the interface when an electrode is immersed into an electrolyte solution. This layer is formed as the solvated ions are blocked and accumulated at the electrode/electrolyte interface. This would create a charge separation between the solvated ions and the electrode material that resembles the charge storage mechanism similar to conventional capacitor, where $d$ is distance between conducting plate and insulating material. In general, positive and negative
charges are arrayed at counter position with an extremely short distance, such as atomic distance (~10 Å), between both at the contact interface of two different phases where, in this case, the two phases would be the solid carbon electrode and the electrolyte. This interfacial charge distribution layer is explained as the Helmholtz layer in Fig.1.8. The excess charge on the electrode surface is compensated by an accumulation of excess ions of the opposite charge in the solution. This structure behaves essentially as a capacitor as it possesses the double layer. The amount of charge is a function of the electrode potential. Fig.1.9 illustrates the electrode potential before and after charging. The charges are polarized at the interface forming the Helmholtz layer. Thus creating a electrical potential which was be observed after the charging [2].

Fig.1.8 Helmholtz double layer
1.5.1.1. Non-Faradaic

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) [2].

1.5.1.2. Faradaic

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. This is known as pseudocapacitance in ECs. The energy storage is indirect and is analogous to that in a battery. In a battery cell, every electron charges is Faradaically neutralized by charge transfer, resulting in a charge of oxidation stage of some redox-electroactive reagent, e.g., $\text{Ni}^{3+} + \text{O}_2^- + \text{OH}^- + e + \text{H}^+ \rightarrow \text{Ni}^{2+} + 2\text{OH}^-$ in the cathode of an Ni-Cd battery.
The electrons involved in a 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 (orbital) of 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., PbO2, some sulfides, RuO2) or else is a well-conducting semiconductor and a productor, e.g., NiOOH.

1.5.1.3. Characteristics of Electrochemical Double Layer Capacitor

Some of the main characteristics of EDLC are

- It employs carbon or metal oxides as the material for the electrodes
- Its capacitance values can be measured as high as several hundreds of Farads
- Fast charge time up to a few seconds
- High specific power density compared to batteries (at least two order of degree) but specific energy density is one order less than batteries.
- It can be charged to any voltage within its voltage rating.
- Stores much more energy than a conventional capacitor of similar size.
- Able to deliver frequent pulses of energy without any detrimental effects unlike batteries which experience reduced life if exposed to frequent high power pulses
- Can be charged extremely fast while batteries are damaged by fast charging.
- Can be cycled hundreds of thousands of times unlike batteries which are cyclable only up to few hundred cycles.
- No charge circuit (Self charge)
- No explosion risk
- It requires no maintenance and is robust to environmental extremities such
arctic temperatures.
Wide temperature range (operation)
Pollution free
No liquid leak (if properly sealed)

1.5.2. Pseudocapacitors

In contrast to EDLCs, which store charge electrostatically, pseudocapacitors store the charges faradaically through the transfer of charge between electrode and electrolyte. This is accomplished through electrosorption, reduction-oxidation reactions and intercalation processes. These faradaic processes may allow pseudocapacitors to achieve greater capacitances and energy densities than EDLCs. There are two electrode materials that are used to store charge in pseudocapacitors, conducting polymers and metal oxides.

Pseudocapacitance arises from reversible faradaic reactions occurring at the electrode and is denoted as ‘pseudo’-capacitance in order to differentiate it from electrostatic capacitance. The charge transfer that takes place in these reactions is voltage dependent, so a capacitive phenomenon occurs. There are two types of reactions that can involve a charge transfer that is voltage dependent.

In a redox reaction involving an oxidant, Ox, and reductant, Red, of the form, Ox+Ze Red the potential, E, is given by the Nernst equation is shown in equation 1.7.

\[ E = E^0 + \frac{RT}{zF} \ln \frac{R'}{1 - R'} \]  

(1.7)
E° is the standard potential, R is the gas constant, T is the absolute temperature, Z is the number electrons, F is the Faraday constant, and R’ is defined as \([\text{ox}] / ([\text{ox}]+[\text{red}])\), (where square brackets denote species concentrations). The amount of charge q (given by the product zF), is therefore a function of the potential E [3].

It is uncertain if the operating potential range of RuO₂ could be substantially extended in nonaqueous electrolytes. Protons have to be available and so some acidic solute in a nonaqueous solvent would be required, e.g., CF₃SO₃H in a polar nonaqueous medium. Use of a Li salt as electrolyte would in principle be possible, but then the system would become equivalent to a Li⁺ ion intercalation battery system with Li⁺ insertion and deinsertion instead of the corresponding protonic processes that take place in aqueous acidic solutions at RuO₂. Such systems are already well known with cathode materials. They are LiCoO₂, MnO₂, or V₆O₁₃ (Fig.1.10), Li⁺ intercalation battery systems which behave as a transitional class of electrochemical power sources as they exhibit pseudocapacitance because their state of charge is dependent on potential. For fundamental thermodynamic reasons, they are commonly regarded as “non-aqueous electrolyte batteries” [2].

1.5.3. Hybrid Capacitor

A hybrid capacitor is a double layer capacitor fabricated with one electrode purely double layer (carbon based as the negative electrode) and another electrode with pseudocapacitance (e.g., metal oxide based as the positive electrode). The energy density of these devices is found to be significantly higher than that of pure EDLCs. Like the activated carbon cathode in EDLC, an activated carbon in the cathode of the hybrid capacitor absorbs anions at the electric double-layer and linearly polarizes to positive side in the charging process. On the other hand, as
shown in Fig. 1.11, a Li doped graphite in the anode of the hybrid capacitor that intercalates Li$^+$ ions into its interlayer in the charging process and de-intercalates Li$^+$ ions in the discharging process. When the anode is charged, potential of the anode becomes very negative and approaches the deposition potential of Li-metal anode as illustrated in Fig.1.11.

![Diagram of charge/discharge process of redox supercapacitor](image)

**Fig.1.10. Charge/discharge process of redox supercapacitor**

*by metal oxide*

The voltage is largely developed at anode but negligibly at cathode. Voltage developed in the electrolyte is due to a solution resistance the so-called ohmic drop (IR drop). The voltages developed at each electrode are made from resulting charge stored and electrode capacity. Because the cathode capacity is much larger than that of anode, voltage development occurs mostly at anode when a cell is charged.
1.6. ADVANTAGES AND DISADVANTAGES OF SUPERCAPACITORS

1.6.1. Advantages

- Virtually unlimited life cycle - cycles millions of time -10 to 12 year life
- Low impedance
- Charges in seconds; No danger of overcharge
- Very high rates of charge and discharge
- High cycle efficiency (95 % or more)
- Supercapacitors are relative expensive in terms of cost per Watt
- Excellent power density, that is > $10^6$ W/Kg
- Simple principle and mode of construction
1.6.2. Disadvantages

- Linear discharge voltage prevents the use of full energy spectrum
- Low energy density-typically holds one-fifth to one-tenth of the energy of an electrochemical battery
- Cells have low voltages-serial connections are needed to obtain higher voltages. Voltage balancing is required if more than three capacitors are connected in series
- High self-discharge- the rate is considerably higher than that of an electrochemical battery
- Requires sophisticated electronic control and switching equipment
- Poor volume energy density

1.7. DIFFERENCES BETWEEN SUPERCAPACITOR AND BATTERY

The most important difference between supercapacitor and battery is the principle of electrochemical energy storage. Electrochemical energy can be stored in two different fundamental ways. In a battery, the potentially available chemical energy storage requires Faradaic oxidation and reduction of electrochemically active reagents to release charges that can perform electric work when they flow between two electrodes having different potentials; that is, the charge storage is achieved by electron transfer that produces a redox reaction in the electro active material according to Faraday’s law.

With an electric double–layer capacitor (EDLC), the charge storage process is non-faradaic; that is, ideally no electron transfer takes place across the electrode
interface and the storage of electric charge and energy is electrostatic. Electron charges are accumulated on the electrode surface with lateral repulsion and involvement of redox chemical changes. Because the charging and discharging of such EDLCs involve no chemical phase and composition changes, such capacitors have a high degree of cycleability of the order of $10^6$ times and a high specific power density, although the specific energy density is rather small. However, in some cases of the supercapacitor based on pseudocapacitance (redox type of supercapacitor), the essential process is faradaic; that is the charge storage is achieved by an electron transfer that produces a redox reaction (Faradaic reaction) in the electroactive materials according to Faraday’s law. The supercapacitors based on pseudocapacitance have higher specific capacitance than the EDLCs, due to the redox reaction as in a battery, although the redox reaction gives rise to high internal resistance in supercapacitors, resulting in a decrease in specific power density. The typical electrodes of supercapacitors based on pseudocapacitance are metal oxides (i.e., RuO$_2$, IrO$_2$, Co$_3$O$_4$) and conducting polymers (i.e., polypyrrole, polyaniline, polythiophene).

A supercapacitor requires two equivalent electrodes, one of which is charged negatively with respect to the other, the charge storage and separation being electrostatic. At each electrode, the charge storage and separation are established across the electrode interface.

The electrodes of supercapacitors have high surface area and porous matrices. However, batteries have bipolar electrode configuration for high voltage series combinations. For a battery, the maximum Gibbs energy is the product of charge $Q$ and the difference of potential, $\Delta E$, between the Nernstian reversible
potentials of the two electrodes, that is, $G = Q \Delta E$. In the capacitor case, for a given charge $Q$, $G$ is $1/2 \, Q \Delta V$. For a given electrode potential difference, $\Delta E = V$, it is evident that the energy stored by a two-electrode cell accommodating a given faradaic charge $Q$ at voltage $\Delta E = V$, is twice that stored in a capacitor charged with the same $Q$ at the same voltage. In the process of charging, a pure electric double layer capacitor, every additional element of charge has to do electrical work (Gibbs energy) against the charge density already accumulated on the electrodes, progressively increasing the inter electrode potential difference.

In a battery cell being charged, a thermodynamic potential (ideally) exists independent of the extent of charge $Q$ added, as long as two components (reduced and oxidized forms) of the electroactive material remained existing together. Thus, the potential difference (electromotive force) of the battery cell is ideally constant throughout the discharge or recharge half cycles, so that $G = Q \Delta E$ rather than $Q$, $1/2 \, \Delta E$ (or $1/2 \, V$). This difference can be illustrated by the discharge curves shown schematically in Fig.1.12, where the voltage of capacitor declines linearly with the extent of charge, while that for an ideal battery it remains constant as long as two phases remain in equilibrium. The decline in the supercapacitor voltage arises formally since $C = Q/V$ or $V = Q/C$; therefore, $dV/dQ = 1/C$. The ideal battery cell voltages on discharge and recharge, as a function of state of charge, are shown as parallel lines of zero slope in Fig.1.12. There is significant IR drop, depending on the discharging and recharging rates. An overall comparison of electrochemical capacitor and battery characteristics are given in Table 1.1.
Fig. 1.12. Discharge/recharge characteristics of supercapacitor and battery
Table 1.1. Comparison of supercapacitor and battery characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Supercapitor</th>
<th>Battery</th>
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<tbody>
<tr>
<td>Slope of charge and discharge curve</td>
<td>Declining slope</td>
<td>Constant slope</td>
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<td>Intrinsic stage of charge</td>
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<td>Bad</td>
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<tr>
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<td>Good</td>
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<td>Poor</td>
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<tr>
<td>Cyclability and cycle life</td>
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<td>Bad</td>
</tr>
<tr>
<td>Origin of internal IR</td>
<td>High area matrix + electrolyte</td>
<td>Active electrode materials + electrolyte</td>
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<tr>
<td>Life time</td>
<td>Long</td>
<td>Poor</td>
</tr>
<tr>
<td>Cell stacking by bipolar system</td>
<td>Possible</td>
<td>Impossible</td>
</tr>
</tbody>
</table>

1.8. COMPONENTS OF SUPERCAPACITORS [4]

1.8.1. ELECTRODE MATERIALS

Selection of electrode materials is more significant as it plays a crucial role in controlling cycle life, long-term stability, high surface area and resistance to electrochemical oxidation/reduction. The choice of electrode material is more precise in obtaining high surface areas with low 'matrix resistivity. Double-layer charge storage is a surface process and the surface characteristics of the electrode greatly influence the capacitance of the cell. As the energy storage capacity is directly
proportional to the surface area of the electrode, electrochemical inert material with high surface area is also considered as a key factor for choosing the electrode material. Accordingly, the electrochemical supercapacitors mainly consist of three types of materials: (i) transition metal oxides (ii) electronically conducting polymers and (iii) carbon nanotubes and related carbonaceous materials. Carbon is the most widely used electrode material but considerable research is being conducted on metal-oxides and conducting polymers.

1.8.1.1. METAL OXIDES

The concept and use of metal oxide as an electrode material in electrochemical capacitors was introduced by Trassatti and Buzzanca based on ruthenium dioxide (RuO₂) as a new interesting electrode material. Some other oxides, such as, IrO₂, Co₃O₄, MoO₃, WO₃ and TiO₂ as electrode materials in electrochemical capacitors have been developed.

The cyclic voltammogram of the metal oxide electrodes has almost rectangular shape and exhibits good capacitor behaviour. However, the shape of the cyclic voltammogram is not a consequence of pure double-layer charging but a consequence of the redox reactions occurring in the metallic oxide giving rise to the redox pseudocapacitance. A very high specific capacitance of up to 750 F/g was reported for RuO₂ prepared at relatively low temperatures. Hydrous ruthenium oxide, RuOₓ(OH)ᵧ that acts as a mixed electronic-protonic conductor has been recognized as one of the promising candidate for electrodes as it can store charge by reversibly accepting and donating protons from an aqueous electrolyte, represented in the following potential-dependent equilibrium as,
\[
\text{RuO}_x(\text{OH})_y + \delta \text{H}^+ + \delta \text{e}^- \rightarrow \text{RuO}_{x-\delta} \text{(OH)}_{y+\delta}
\]

Its electrochemical properties depend on the amount of water incorporated in its structure and change in oxidation state (Ru$^{4+}$/Ru$^{3+}$) of ruthenium, which was actually responsible for the capacitance of 770 F/g for high performance ultra-capacitors. Hydrous ruthenium oxide \(\text{RuO}_x(\text{OH})_y\) has been recognized as one of the most promising candidates for electrodes as it can store charge by reversibility accepting and donating protons from an aqueous electrolyte.

Apart from providing the maximum specific capacitance of 770 F/g, use of ruthenium oxide also allows one to tune the electrochemical and physical properties, morphologies, crystalline structures and proton dynamics in \(\text{RuO}_2.x\text{H}_2\text{O}\) for high performance ultra-capacitors. Hydrous ruthenium oxide is a very expensive material and hence much effort is being made worldwide to replace ruthenium oxide by other nanostructured transition metal oxides. Conducting metal oxides such as \(\text{RuO}_2\) or \(\text{IrO}_2\) were the favored electrode materials in early electrochemical capacitors used for space or military applications. The high specific capacitance in combination with the low resistance resulted in very high specific power. An energy density of 8.3 Wh/kg and a power density of 30 kW/kg were achieved in a prototype 25 V electrochemical capacitor but only with \(\text{RuO}_2.x\text{H}_2\text{O}\) material and electrolyte. These capacitors however turned out to be too expensive.

A rough calculation of the capacitor cost showed that 90% of the cost resides in the electrode material. In addition, these capacitor materials are only suitable for aqueous electrolytes thus limiting the nominal cell voltage to 1.0 V. Several studies have attempted to take advantage of the material properties of such metal oxides at a reduced cost. The dilution of the costly noble metal by the formation of perovskites
was investigated. Other forms of metal compounds such as nitrides were investigated. However, these materials are not yet commercially available in the electrochemical capacitor market. Hence, worldwide effort is being made to replace ruthenium oxide by other nanostructured metal oxides.

1.8.1.2. CONDUCTING POLYMERS

The use of conducting polymers as active materials for supercapacitors such as electrodes made up of polyaniline, polythiophene and polypyrrole, etc., had many advantages including the fast doping-dedoping during charge-discharge, high charge density, easy chemical/electrochemical synthesis and low cost compared to that of the noble metal oxides. There are three possible schemes by which the conducting polymers can be used as electrodes in redox supercapacitors. In type I capacitors, two identical electrodes comprising symmetrical p-doped conducting polymer films are used and two different p-doped conducting polymers are used in type II capacitors. Type II capacitors can be charged to a comparatively higher voltage by virtue of the difference in the potential range over which the polymers can be doped and dedoped. A mixture of both n- and p-doped conducting polymers can be used in type III capacitors and this can achieve the highest possible voltage of 3V in its charged state.

Conducting polymers are permeable to small molecules and hence every volume element of the electrode material at the molecular level is in contact with the electrolyte solution, resulting in an extremely high effective surface area. Due to their low compatibility with the electrolyte phase, the separation of polymer chains in conducting polymers is small relative to the double layer thickness causing a high electrolyte resistance in the polymer matrix and a low effective surface area. This
compatibility can be reduced by the use of dispersions/solutions. Conducting polymers also lack adequate chemical stability due to their high propensity for degradation and consequently the cycle life of supercapacitor electrodes made from them is not high. However, there are many exceptions and one such is the electrochemically deposited polyaniline nanowires on stainless steel electrodes at a potential of 0.75 V vs SCE in 1M H₂SO₄ electrolyte showed 775 F/g at 10 mV/s along with good cycle life, suggesting the potential implications of the use of nanostructured conducting polymers for the fabrication of high performance supercapacitor electrodes. The long-term stability during cycling, however, may be a problem. Swelling and shrinking of electroactive polymers is well known and may lead to degradation during cycling.

**1.8.1.3. CARBON MATERIALS**

Nanostructured carbonaceous materials including carbon nanotubes (CNT) represent an interesting class of materials for supercapacitor applications. Carbonaceous materials have been particularly popular for making electrodes for many types of batteries, fuel cells and ultracapacitors owing to their large surface area and high conductivity. Most of these carbonaceous materials are derived from precursors such as coconut shells, wood powders, coal tar, resins, resorcinol-formaldehyde and related polymers which yield active electrode materials with surface areas ranging between 1000 and 2000 m²/g, resulting in capacities as high as 500 F/g in alkaline electrolytes. The surface of these materials can be functionalized by a variety of methods to tailor their properties and some of these surface-functionalized carbon shows surface areas up to even 3000 m²/g.
Carbon nanotubes (CNTs) are attractive materials for electrodes of electrochemical supercapacitors due to their unique characteristics of chemical stability, low mass density, low resistivity and large surface area. CNT electrodes with a surface area of 430 m$^2$/g show a specific capacitance of 110 F/g and a power density of 8 kW/kg in a solution of 38 wt% H$_2$SO$_4$. Heat treatment at high temperature improves the specific capacitance of single-walled CNT to 180 F/g with a larger power density of 20 kW/kg. CNTs are potential candidates for supercapacitor and commercial application is yet to be realized because of difficulties in mass production and purification. Furthermore, the properties of CNTs depend on their prehistory and hence their reproducibility is often questionable with respect to their diameter and conductivity distribution. Other double-layer capacitor materials such as activated carbon, carbon balck, carbon aerogel and carbon nanofibers are, however, inexpensive and some of them provide improved performance as supercapacitor electrodes.

1.8.1.4. CONDUCTING POLYMER-TRANSITION METAL OXIDE COMPOSITES

Recently, many new classes of nanostructured composite electrodes have been developed by the unique combination of organic species with various inorganic materials for supercapacitors. The large capacitances exhibited by these systems, originated form a combination of the double-layer capacitance and pseudocapacitance associated with the participation of adsorbed intermediates in the surface redox-type reactions.

Integration of a nanostructured transition metal oxide into a conducting polymer matrix provides an effective way to harness the electrochemical activity of nanosized oxide clusters. By anchoring the transition metal oxides into conducting
polymers, the reversible redox chemistry of the soluble polyoxometalate clusters can be combined with that of the conducting polymer to bring benefit for energy storage applications. Thus, the resulting composite displays the combined activity of its organic and inorganic components to store and release charge in a solid-state electrochemical capacitor. When PEDOT is intercalated between the layers of MoO$_3$ by microwave irradiation, an unusually enhanced double-layer capacitance of 300 F/g is observed compared to that of pristine MoO$_3$. This could be explained on the basis of higher electronic conductivity, enhanced bi-dimensionality and increased surface area facilitating this improved performance after polymer intercalation.

1.8.1.5. CONDUCTING POLYMER-CARBON NANOTUBE COMPOSITES

At present, three types of electrically conducting polymers such as polyaniline (PANI), polypyrrole (PPy) and PEDOT are widely used as supercapacitor electrode materials in the form of composites with multiwalled carbon nanotubes (MWNTs). The energy storage is due to combination of both Faradaic and pseudocapacitance components and the CNT plays the role of a perfect backbone for a homogeneous distribution of conducting polymers in the composite. CNTs preserve the mechanically weak and pure conducting polymers from mechanical changes such as shrinkage and braking during long cycling and it also improves the charge transfer that enables high charge-discharge rate. These composites can have unique microtextural, mechanical and conducting properties allowing efficient charge propagation leading to the capacitance of 100 to 300 F/g for different asymmetric configurations in the voltage range of 0.6 to 1.8 V. This advanced type of CNT-conducting polymer composite in the doped state allows formation of a three-dimensional supercapacitor using a synergistic effect of complementary properties of
both these components. The operation of these asymmetric capacitors in its optimal potential range with MWNT/PPy and MWNT/PANI as negative and positive electrodes reaches a higher capacitance of 320 F/g, due to the importance of the conducting properties of MWNT and good charge propagation in their available mesoporosity. The open mesoporous network of nanotubes allows quick charge propagation via the electrode/electrolyte interface with an efficient reversible storage of energy during subsequent charge/discharge cycles.

1.8.1.6. TRANSITION METAL OXIDES- CARBON NANOTUBE COMPOSITES

The mixing of fine oxides/hydroxides with MWNTs using various methods like ultrasonic vibration led to the new class of transition metal oxide-carbon nanotube composite materials. A non-aqueous hybrid supercapacitor using manganese oxide/MWNTs composite and pure MWNTS as positive and negative electrodes respectively, shows better capacitance and energy characteristics than those obtained for the symmetric capacitors. The enhancement of capacitance of multiwalled carbon nanotubes functionalized with metal oxides is attributed to the entangled network of nanotubes that forms open mesopores and their chemical stability with a basal geometry makes them suitable for supercapacitor applications.

1.8.2. ELECTROLYTES

The choice of electrolyte in an EDLC is as important as the choice of electrode material. The attainable cell voltage of a supercapacitor depends on the breakdown voltage of the electrolyte and the possible energy density (which is dependent on voltage) will be limited by the electrolyte. Power density is dependent
on the cell’s ESR, which is strongly dependent on electrolyte conductivity. The
supercapacitor makes use of three kinds of electrolytes namely (1) liquid electrolytes
(2) polymer composite electrolytes and (3) ionic liquid electrolytes. The capacitance
of an EDLC is greatly influenced by the choice of electrolyte. The ability to store
charge is dependent on the accessibility of the ions to the porous surface-area and
so ion size and pore size must be optimal. The best pore size distribution in the
electrode depends upon the size of the ions in the electrolyte so both the electrode
and electrolyte must be chosen together.

1.8.2.1. LIQUID ELECTROLYTES

There are currently two types of electrolyte used in electrochemical
supercapacitors: (i) organic and (ii) aqueous. Organic electrolytes are the most
commonly used in commercial devices, due to their higher dissociation voltage. Cells
using an organic electrolyte can usually achieve voltages in the range of 2.0 – 2.5 V.
The resistivity of organic electrolytes is relatively high and limits cell power. Aqueous
electrolytes have a lower break down voltage, typically 1.0 V, but have better
conductivity than organic electrolytes. Organic electrolytes have a very high
dissociation voltage of around 4 V where as aqueous electrolytes (KOH or H₂SO₄)
has a dissociation voltage of around 1 V. Thus for getting an output of 12 V, using
aqueous electrolyte one would require 12 unit cells whereas with organic electrolyte
one would require 3 unit cells. This clearly shows that for high voltage requirement
one should opt for organic electrolyte. There is added requirement for using organic
electrolyte. As ions of organic electrolyte are larger, they require large pore size of
electrode material.
1.8.2.2. POLYMER COMPOSITE ELECTROLYTES

A family of nanostructured organic-inorganic composite polymer electrolytes has been developed which appears to be highly promising in the elimination of cost of preparation, ease of processing and environmental safety for conventional solid polymer electrolytes (SPEs). The structure of these composites was designed at the molecular nanoscale to possess fast proton as well as lithium ion transport, through modified organic ligands with inorganic surfaces. This new family of materials consists of transition metal oxides in a polymer matrix such as nanosize SiO₂/polymer [polyethylene oxide (PEO); polypropylene oxide (PPO); polytetramethylene oxides (PTMO)] composites synthesized by sol-gel method. Another interesting family of solid-state nanocomposite electrolytes using poly (ethylene oxide) (PEO) containing nanoscale fillers of layered double hydroxides (LDHs) acts as electrolytes with high ionic conductivity.

1.8.2.3. IONIC LIQUID ELECTROLYTES

Ionic liquids are a new type of solvents which are actually molten salts at relatively low temperatures consisting of entirely ionic species with wide electrochemical stability windows and possess high chemical stability at high temperatures. Due to its good conductive nature, they can be used as solvent-free “green” electrolytes for high voltage supercapacitors. Some of the commonly used ionic liquids used for supercapacitors include 1-ethyl-3-methyl imidazolium (EMImp), 1-butyl-3-methyl imidazolium (BMImp) and 1-methyl-1-propyl pyrrolidinium (BMPyp) cations, as well as tetrafluoroborate, hexafluoro phosphate and bis((trifluoromethyl)sulfonyl) imide anions. Until now, ionic liquids are used in capacitors as solutions of molecular liquids (cyclic carbonates). The energy stored in
the capacitor containing ionic liquid is high due to an improved electrochemical stability window. The use of ionic liquids in system containing no volatile component, make the devices more environmentally friendly.

1.8.3. SEPARATOR

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

The crucial functional components of a supercapacitor to its operation are the electrodes, electrolyte, and separator. The surface properties of the electrode material have a significant impact on specific capacitance, and do the chemical properties if pseudocapacitance is exhibited. While activated carbon is currently the most commonly used material, conducting polymers present a possible future alternative. Metal-oxides may also become viable one day. The choice of electrolyte has a significant impact on achievable power, as well as influencing specific capacitance. Aqueous electrolytes have better conductivity than organic electrolytes, but have a low breakdown voltage. The properties of the separator also have an impact on cell performance. The type of separator depends upon the type of electrolyte used. If the electrolyte is organic then polymer or paper separator will be used. If the electrolyte is aqueous then ceramic separators are used.
1.9. VARIOUS METHODS FOR THE SYNTHESIS OF METAL OXIDES

Various types of chemical reaction have been used for the synthesis of metal oxides which are used as cathode materials for supercapacitor applications.

1.9.1 Solid State Method/Ceramic Method [5]

The most common method of preparing metal oxides is by allowing the reaction of the component materials in the solid state at elevated temperature. This method is used for the synthesis of new materials because of the ease with which modifications can be effected by incorporating various cations at different sites in various concentrations. Diffusion distances for the reacting cations are markedly reduced by incorporating the cations in the same solid precursor. Carbonate solid solution are ideal precursors for the synthesis of monoxide solid solution and can be used as precursors for preparing spinels and other complex oxides. Besides monoxides solid solution a number of ternary and quaternary oxides of novel structure can be prepared by decomposing carbonate precursors containing different cations in required proportions. Several Oxides, Sulphides, Phosphides etc. have been prepared by this method. If all the components are solids, the method is called as “Solid state thermal method.

1.9.2 Combustion Method [6,7]

Combustion synthesis or self-propagating high temperature (SPHT) synthesis is a versatile method used for the synthesis of a variety of solids. This SPHT method which makes use of exothermic reaction between the reactants to produce a flame due to spontaneous combustion which then yields the desired product or its precursor in finely divided form. Borides, carbides, oxides, chalcogenites and other metal derivatives have been prepared by this method. For example, one may add a
fuel and an oxidizer when preparing oxides by the combustion method both these additives being removed during combustion to yield only the product. or its precursor. Thus one can take a mixture of nitrates (Oxidizer) of the desired metals along with a fuel (e.g. Hydrazine (NH₂–NH₂), glycine (H₂N – CH₂ – COOH) or Urea (NH₂ – CO – NH₂) in solution.

Solution is evaporated to dryness and then the dried sample was heated heated at around 423K for spontaneous combustion to yielding an oxide product in fine particulate form. Even if the desired product is not formed immediately after combustion, the fine particulate nature of the product facilitie its formation on further heating. Use of the combustion in an atmosphere of air or oxygen to prepare complex metal Oxides seems obvious. A variety of oxides have been prepared using nitrate mixtures with a fuel such as glycine or Urea. It seems that almost any ternary or quaternery oxide can be prepared by this method. All the super conducting cuprates have been prepared by this method. Although the resulting products in fine particulate from have to be heated to an appropriate high temperature in a desired atmosphere to obtain the final product.

1.9.3 Sol – Gel Method [8-11]

The Sol-get method has emerged to become an important means of preparing inorganic oxides in recent years. It is a wet chemical method and a multistep process involving both chemical and physical processes such as hydrolysis, Polymersisation, drying and densification. The name sol-gel is given to the process because of the distinctive increase in viscosity, which occurs at a particular point in the sequence of steps. A sudden increase in viscosity is the common feature in sol-gel processing indicating the onset of gel formation.
In the sol-gel process, synthesis of inorganic oxides is achieved from inorganic or organometallic precursors. The important features of the sol-gel literature deals with synthesis from alkoxides.

The important features of the sol-gel techniques are;

- Better homogeneity compared with the traditional ceramic method.
- High purity.
- Lower processing temperature.
- More Uniform phase distribution in multi component systems.
- Better size a morphological control.
- The possibility of preparing new crystalline and non-crystalline materials.
- Easy preparation of thin films and coatings.

The sol-gel method is widely used in ceramic technology. The sol-gel techniques has been used to prepare sub-micrometer metal oxide powders with a narrow particle size distribution and unique particle shapes (e.g. Al₂O₃, TiO₂, Fe₂O₃), uniform SiO₂. Small metal clusters (e.g. Nickel, coppers, gold) have been prepared by in-situ chemical reduction of metal salts. Metal-ceramic composites (e.g. Ni – Al₂O₃, Pt – ZnO₂) can also be prepared in this manner. By employing several variants of the basic sol-gel techniques, a number of multi composite oxide systems have been prepared. Typical of these are, SiO₂ - B₂O₃, TiO₂, SiO₂ - Al₂O₃. A variety of ternary and still more complex oxides such as PbTiO₃, Pb Ti₁₋ₓSrₓO₃ and NASICON have been prepared by this technique.
1.9.4 Hydrothermal Synthesis [12,13]

In hydrothermal process, starting chemicals are dissolved in water or other solvents with a proper mineralizer. Then the solution is placed in a high pressure reactor and heated at an elevated temperature to induce chemical reactions. Since high pressure is applied in the hydrothermal process, the solubility of reactants is increased and the desired compounds can be synthesized at lower temperature. The low temperature is advantageous for suppressing particle grain growth and reducing energy consumption. Then the product is washed repeatedly with distilled water, filtered and dried at 100° to eliminate residual alkali and salts from the products.

Major features of hydrothermal process are given below:

1. Powders are formed directly from solution
2. Powders are anhydrous, crystalline or amorphous depends on hydrothermal temperature
3. It is possible to control the particle size by hydrothermal temperature.
4. It is possible to control the particle size, shape from the starting materials.
5. Powders are highly reactive on sintering
6. In many cases powders do not need calcination
7. In many cases powders do not need milling process.

One of the disadvantages in this process is the requirement of high – pressure reactor with high temperature control.
1.9.5 Microwave Oven Synthesis [14]

In this method, the high purity reactants are grounded well and exposed to microwaves irradiation for about 5-10 minutes in silica crucibles kept inside a domestic microwave oven operating at highest power level.

The peculiar characteristics of this method are:

- This method has very short reactions times and energy economy.
- Microwave reaction one occurs at lower temperature than conventional method.
- The rapidity of the reactions offers excellent condition for retention of meta stable phases.
- In fine better product yield and better structural uniformity of products than conventional ceramic method.

Microwaves synthesis methods used for the synthesis of spinals and other oxides materials of any type of structure have so far been successfully synthesis by this method.

1.9.6 Solution precipitation method [15, 16]

This method provides an alternative route for the synthesis of finely dispersed oxide powders at lower reaction temperature and offers better control over the morphology and texture of solid particles. In this method stoichiometric ratio of metallic salts are dissolved in n- butanol and at moderate temperature (< 600°C), the pH of the resulting solution is adjusted to the desired value by adding dilute HNO₃ / NH₄OH solution. The resultant solution is allowed to evaporate the solvent, to obtain a slurry residue, which is first dried at 80°C and then transferred to an alumina boat
and heated at 450°C for 12hrs. It is interesting to note that LiCoO₂, LiNiVO₄ and LiCo₀.₅Ni₀.₅O₂ cathode materials are prepared by using this solution precipitation method. The advantage of this method is to synthesize ultrafine cathode materials which show higher reversible capacity than the samples prepared by solid state thermal method.

1.10. APPLICATIONS OF SUPERCAPACITORS

Significant advances have been made in improving both energy and power density and new applications for electrochemical supercapacitors are being developed at an increasing rate. Some of the supercapacitor applications are given below:

1.10.1. MEMORY BACKUP

Supercapacitors have been long in use as short-term backup supplies in consumer appliances. Many appliances now incorporate digital components with memory, and even a very brief interruption in the power supply would otherwise cause a loss of stored information. In such situations a supercapacitor can act as the power supply for a short period, thereby retaining data. The common alternative to the supercapacitor in this application is the battery. Batteries do not generally have a long product lifetime, and therefore need to be replaced regularly. Today consumer appliances are also cheap to the extent that a battery could cost upto 20 % of the price of the appliance. Supercapacitors are a good choice as backup power supply due to their long life time.
1.10.2. ELECTRIC VEHICLES

The prospect of the use of supercapacitors in electric vehicles has drawn much attention to the technology appealing to the energy-conscious because of their energy efficiency and the possibility of recuperating energy lost during braking. Many of the current power sources being considered for use in electric vehicles (EVs) do not meet the power requirements of vehicle acceleration. Fuel cells are promising due to their extremely high energy density but they are currently limited in their power specifications. Both the power and energy requirements of an EV can therefore be satisfied with a combination of fuel cell and supercapacitor technology. A combined power source configuration allows the high-energy density device such as a fuel cell to provide the average load requirements. Peak load requirements that result from accelerating or climbing up hills can be met by the high-power device such as a supercapacitor bank. The utilization of supercapacitors also makes regenerative braking possible. As the EDLC bank can be recharged, it is possible to store some of the energy of an already moving vehicle and therefore increase the fuel efficiency of the EV.

1.10.3. POWER QUALITY

Supercapacitors can be used as the energy storage device for systems designed to improve the reliability and quality of power distribution. Static condensers (Statcons) and dynamic voltage restorers (DVRs) are systems that aim to inject or absorb power from a distribution line in order to compensate for voltage fluctuations. As a result, such systems require a DC energy storage device of some sort from which energy can be drawn and in which energy can be stored. The vast majority of voltage perturbations on the distribution bus are short-lived, most not
lasting more than ten cycles [17]. The limited storage capability of the supercapacitor is therefore not a problem. The storage device must also be able to respond quickly to voltage disturbances, so the supercapacitors have the advantage of possessing a fast discharge time. Batteries are not generally suitable for short-duration, fast response applications such as the Statcon or DVR.

1.10.4. BATTERY IMPROVEMENT

An increasing number of portable electronic devices such as laptops and mobile phones incorporate batteries as power supplies. Many such devices draw high power, pulsed currents, and current profiles consisting of short, high current bursts result in a reduction of battery performance. Using supercapacitors in combination with a battery is therefore an optimal solution. A supercapacitor can relieve the battery of the most severe load demands by meeting the peak power requirements, and allowing the battery to supply the average load. The reduction in pulsed current drawn from the battery resulted in extended lifetime of battery.

1.10.5. ELECTROMECHANICAL ACTUATORS

Electromechanical actuators can perform thrust vector control for the launch of space vehicles, or can act as flood-control actuators on submarines. Most actuation systems demand pulsed currents with high peak power requirements but fairly moderate average power requirements. While a supercapacitor bank on its own is unlikely to be able to store enough energy, a battery combined with a supercapacitor can be designed to meet both average and peak load requirements. Trying to meet both requirements with a battery alone results in an oversized configuration, which is undesirable in space applications in which weight must be
kept to a minimum. By designing a hybrid power source consisting of a battery and an EDLC bank, weight savings of 60% can be made over using a battery alone.
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