**CHAPTER 6**

**SUPERCAPACITORS: PROSPECTS AND FUTURE DIRECTION**

Electrochemical devices for energy storage play a crucial role in the energy dependent world for meeting the situation of fast depletion of fossil fuels [1-2]. Among various possible electrochemical energy storage devices, supercapacitors have been attracting interest in both academic community and industrial production in the past few decades due to their desirable power density, fast charge/discharge rates and favourable life cycles [3-6]. Supercapacitors and rechargeable batteries are similar devices with negative electrodes, positive electrodes and separators that are present with an electrolyte. Normally, supercapacitors can be considered as the intermediate between the conventional battery and dielectric capacitor. In these days, supercapacitors are employed in many applications like consumer electronics, possibly in transportation, grid balancing and power back-up replacing the use of batteries in these applications. Super capacitors can also be used along with rechargeable batteries in order to provide additional power that is normally required in these applications.

Historically, a capacitor was originally started from a Leyden jar consisting of a glass container whose interior and exterior were coated with metal foils. Those metal foils and the jar function as the electrodes and dielectric, respectively. During the charging process, positive charges gradually accumulate on one plate while negative charges accumulate on the other plate. When two electrodes are connected by means of a conductive wire with or without a load, a discharging process takes place. The dielectric is generally composed of an
electrical insulation material, such as a vacuum, a non-ionized gas, a solid such as a ceramic or polymer, or a liquid (aqueous or non-aqueous electrolyte). Electrolytic dielectrics include metal oxides (aluminum oxide and tantalum pentoxide), aqueous and non-aqueous electrolytes. The first electrochemical Double Layer capacitor (EDLC) was introduced in 1957 for low voltage applications. In 1962, carbon based electrochemical capacitor was introduced by the Standard Oil company of Ohio. In EDLCs, the energy storage is dependent on the adsorption of electrolyte ions on the surface area of the porous electrodes. Energy storage in pseudocapacitors arises due to the reversible surface redox reactions taking place at the interface of electrode and electrolyte. Common electrode materials for pseudocapacitors are transition metal oxides ( RuO2, MnO2, and Fe3O4), transition metal sulfides (MoS2), carbon materials containing oxygen or nitrogen surface functional groups and conducting polymers (mainly, polythiophene (PT), polypyrrole (PPy) and polyaniline (PANi)). It is desirable to fabricate hybrid supercapacitors involving diffusion controlled redox reactions as in a battery-type electrode materials with capacitive materials. The aim in doing all these is to make supercapacitors meet the requirements of all electronic devices and that too in a simple way and almost in perfect fashion. However, the present-day design of supercapacitors with rigid bulky or planar structure instead of meeting the demands of miniature size and capable of large scale production so that the extent of their application can be met in future for powering all electronic devices. Even though carbon materials and metal oxides are presently employed as electrode materials in supercapacitors, the inherent deficiencies in these two materials namely wide pore size distribution in carbon materials and limited electronic conductivity in metal oxides, led to examine alternate materials like metal organic frameworks (MOFs) and COFs which are amenable for porous architecture manipulation or metal nitrides and mixed conductors with improved electrical conductivity. The two types of electrolytes, namely liquid ( aqueous, organic, and ionic liquids) and solid electrolyte ( like Li2S-P2­S­5 systems) and quasi-solid state electrolytes (polymer systems) suffer from low ionic conductivities which will come in the way of fast charge/ discharge capability of the super capacitors. The current research on these materials are based on extending the operating potential window, limit the toxicity and flammable nature of organic electrolytes, and the cost and viscosity of the ionic liquids and these efforts will continue in the near future. Many reviews have focused their attention to these aspects [7-16]. The current research efforts on supercapacitors are focused on materials development (electrode, electrolyte and current collectors) and also device design and fabrication aspects. These efforts are pictorially shown in Fig.6.1. Even though all these aspects are important and essential, this monograph mainly deals with some aspects on the current efforts on materials development, the logistics in searching them and their possible application in supercapacitors from energy storage point of view. The other aspects are covered in many other excellent text books already available in literature [1].

All of us know that Electricity is one of the forms of energy that can be interconverted and made to do the work. It is largely a versatile form of energy but it has its own drawbacks like it is not easy to store it quickly. Capacitors are one of the devices that can store tiny amounts of power instantly but what we need is to store and release large amount of energy at short time intervals. In this sense, supercapacitors (also known as ultracapacitors) are the devices that combine both these conditions of storing large power and store in short time.

Of all the various energy storage systems, supercapacitor can be considered to be a promising alternative to batteries due to its high-power density, long cycle life and fast charge-discharge process. flexible electrochemical supercapacitors with their unique advantages such as flexibility, shape-conformability, and light weight, are attracting ever-increasing attention to meet the current requirement for portable and wearable electric devices [1]. The recent progress of all-solid supercapacitors has been outlined in this monograph. Various electrode materials like carbon nanotubes, graphene, and pseudo capacitive materials are considered and their performance is also compared and analyzed. The latest progress in strategies to improve the energy and power density in these devices is mentioned.

In this book some important aspects of the component materials for supercapacitor applications are presented to explicitly understand the functional differences of capacitors with respect to batteries and what are the performance features of these materials and how they can be modified. In this exercise, the material characteristics both composition and texture, have been considered.

Research and development efforts have been many in the deployment of Electrochemical supercapacitors’ (ES) component materials in order to increase the performance characteristics and also to make these devices commercially viable. With considerable progress in the field of material design and development, the technical developments in these devices in the past decades are significant. The two material areas to be addressed for supercapacitor applications are the ES electrode materials and the electrolyte materials. Both these aspects have been considered in this presentation. In the case of electrode materials, the emphasis has been on developing high capacitive materials especially double layer capacitive carbons, pseudocapacitive materials and their composites. From the point of view of energy storage capacity, it is desirable to develop active electrode materials with high capacitance values but at the same time one has to have consideration on cost and cyclability. Electrolyte materials (solvents and ionic species) are also important components of ES devices. Aqueous electrolyte solutions were mostly used because they were nonhazardous and easy to handle in spite of the limitation that the operation potential windows is restricted up to ~1.0V. The energy storage density is proportional to the square of the operating voltage, using alternative electrolyte systems with significantly wider operating voltage windows can improve the energy storage capacity of the device. In this sphere, organic and ionic liquid electrolytes are being examined. However, these electrolytes face material handling issues and technical challenges. The purpose of this presentation is to consider the progress and technical challenges that are faced in the development of electrode and electrolyte for ES devices.

Though the development of Electrochemical Supercapacitor has been reaching the level of device applications, still there are a variety of issues like limited performance capabilities, long term durability, and affordability in terms of cost. It is only a matter of time, that ESs will become important components of future energy systems. The research and development exercises that are being pursued in these days will soon lead ESs to undoubtedly becoming integral components of future energy systems, but still more efforts are required to make these systems economically feasible. Another aspect that must be looked into is to improve the energy density of these devices over the commercially available battery technologies. This appears to be possible that in the near future, active electrode materials will be found with higher capacitance values and the range of operational voltages will also be increased by the deployment of organic and other suitable electrolytes.

The issue that has to be surmounted at present is to close the gap in the energy density between batteries and ESs without losing the large cyclability of the ESs. Another issue in the development of ESs is the stability of the material during charging and discharging cycles since this is connected to the performance of ESs during long periods of operation [17]. Electrolyte decomposition or degradation can also be an issue especially when carbon-based electrodes are employed due to textural changes and increased resistance [18]. Corrosion of the current collectors may also be another challenge but it may become possible by adopting suitable surface treatments which will increase the stability of the current collectors. Cost reduction is another major challenge to be overcome in making ESs as suitable energy conversion devices for large scale deployment.

Identifying appropriate electrolytes electrode materials and current collectors with good performance characteristics at low cost is necessary for these devices to find wide application. An ESs electrode is normally composed of a conductive metallic current collector coated with a psuedocpacitive component like active carbon layer. This interface of the collector and the active material is responsible for the functioning of the current collector. This interface can add charge transfer resistance that will contribute to the internal resistance of the final device and thus affect the overall performance of the device. The internal resistance of these current collectors can be reduced considerably by etching and subsequent carbonaceous coating by chemical vapor deposition or any other procedures that can be adopted and it can reduce the internal resistance to a low value of the order of 0.5 Ώ cm2. However new developments on the materials for current collectors and surface treatment techniques can improve the performance of future current collectors. In this direction, the utilization of a carbon nanotube (CNT)-based current collectors can be expected to show high capacitance value and increased cyclability [19]. The use of these materials will have the advantages of high surface area and electrical conductivity, chemical and electrochemical and mechanical durability and will be comparable to capacitors based on transition metal oxides and conducting polymers. However, further research efforts in the new generation current collectors can significantly contribute to the weight reduction of these devices. The major challenge in development of next generation current collectors is to find suitable materials which will withstand long prolonged periods of operation without much material corrosion.

Carbonaceous materials are mostly used as active components of double-layer electrodes because of their high conductivity, electrochemical stability, and porosity. Activated carbons still are employed as the material for practical devices, due to high surface area, low cost and amenable to prepare from various available precursor sources. Though it is a common belief that pore volume and pore sizes that can accommodate solvated ions are contributing to the capacitance values, recent studies showed that systems with pore sizes (<2nm) [20] are appropriate materials for high capacitance which probably means that some kind of desolvation at the molecular level permits ion transport and adsorption of these ions in the micropores. It may be mean that for any carbonaceous material for capacitor application has to be tunable in their pore sizes so as to be suitable for the adsorption of ionic species.

The new generation carbon materials like carbon nanotubes (CNT) and their composites with dispersion medium like graphene can be one of the possibilities for the device applications with desirable parameters. Other forms of carbon materials like mesoporous carbons, carbon nanofibers and carbon onion nanostructures are the other possible materials that can be examined as materials for ESs applications. Essentially, it appears that the development of active carbon-based materials and also evolving suitable fabrication techniques are the directions in which these devices will become commercially viable.

Transition metal oxides and conductive polymers were two classes of materials that are traditionally examined for pseudocapacitive applications. However even in these two cases, issues regarding technical and cost have to be still addressed.

Ruthenium oxide-based materials have been preferred till now due to their operational stability and desirable capacitance values. However, cost and availability are two points in the ways of exploiting these materials. From these points of view, though various metal oxides and mixed metal oxides have been examined, the conductivity values and cyclability considerations are issues of concern in examining these materials.

As stated above, conductive polymers are another class of materials with good capacitive values. Redox processes-based instability and volumetric changes and irreversibility of these materials are two limiting issues and there are attempts to overcome them by suitable substitution in the backbone of the polymer. A recent review addressed [21] the various aspects of polyaniline and polypyrrole and their composite-based supercapacitor applications. According to these authors the issues to be considered include the following:

(1) The influence of surfactant and of doping of the polymer on the supercapacitor behavior of polymers are yet to be established.

(2) Which of the factors namely the electrolyte or the surface area controls the maximum power density obtainable in conducting polymer-based supercapacitors.

(3) Which of the polymerization process is appropriate for supercapacitor applications

(4) The possibility of exploring other conducting polymers like polyindole has not yet been fully explored.

Though the exercises on development of Pseudocapacitor materials are in progress, compositing carbons with these materials have assumed significance for higher energy storage capability. Though the application of conducting polymer materials may not be appropriate for stand-alone applications, the composites with carbon materials like CNT and graphene are the potential materials that may find wide application and will be investigated deeply in coming days. One of the advantages of the carbon-based composite materials will be the increased mechanical stability. The one dimensional architecture that can be obtained by CNT based materials are amenable for the aligned electrode fabrication which can show enhanced electrolyte transport and charge storage capabilities in addition to suppressing volumetric changes during charging discharging cycles. Another area of importance to supercapacitor applications is the selection of suitable electrolytes. Even though aqueous electrolytes are the preferred ones, the operational window is restricted to ~1 volt and from this point view acetonitrile and propylene carbonate have been employed due to their higher ionic conductivity. However, the toxicity issues and also operational potential window size of the organic electrolytes have led the focus to turn to ionic liquids which can increase the potential window to ~3.5 Volts. The primary concern on the use of ionic liquids is their ionic sizes due to large size and structures of the constituent ionic species. Even though there was some initial hesitation in employing ionic liquids as electrolytes due to their limited conductivity at low temperatures, there appears to be scope to design and material selection which can make the ESs perform over wider temperature range. These aspects especially suitably selected mixtures of anionic and cationic species will make ionic liquid based ESs to be promising in the near future.

**Prospects and Possible Future Research Directions**

As in any scientific endeavor, one can expect vigorous research efforts will also be made on supercapacitor materials with improved performance characteristics in terms of cyclability, potential window, material fabrication capability and cost considerations. The main objective behind these efforts will be to bridge the gap between capacitors and conventional batteries.

1. Various nanoarchitectures and porous nature of the carbon materials will be examined from the point of view of surface area, functional groups effect on ionic adsorption with a view to improve energy storage capability. Active carbon materials with tunable textural properties will be introduced. The advantages of dimensionality in carbon architectures will also be exploited.
2. New system configurations involving new electrode materials, electrolytes and current collectors and other constituents will be examined and new supercapacitor models will come in vogue.
3. The conventional binary, ternary and other combinations of oxide materials will be evaluated for application as supercapacitors for improved energy storage capability.
4. As stated before, new conducting polymers will be examined for supercapacitor applications. These efforts will be to improve the utilization of redox centres and energy storage limits.
5. Composite or hybrid materials will be evolved for possible application as super capacitor applications. Theoretical computational science will be employed to screen a vast variety of hybrid materials for this application with a view to optimize physical properties, temperature tolerance, and electrical conductivity.
6. The increased use of ionic liquids as electrolytes will be taken up in the coming days. These studies will be aimed at extending the applicable potential window and also the stability of the device.
7. Basic understanding of the phenomena occurring in ESs during charging, energy storage, and discharge will be improved.

In essence, the development in supercapacitors are in two directions, namely finding new materials and also designing features of the devices. This situation is pictorially shown in the form of a growing tree in Fig.6.1.



Fig.6.1. Advances on new materials and devices of supercapacitors (SCs). [adopted from ref.7]

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