



## CHAPTER II

### LITERATURE REVIEW

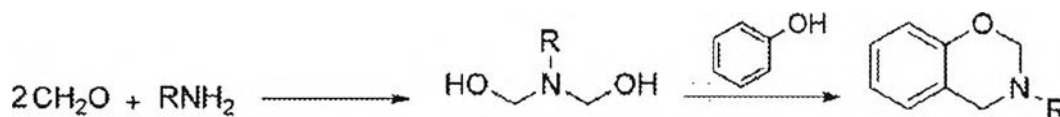
#### 2.1 Polybenzoxazine

Polybenzoxazines as a novel type of phenolic resin offer many advantages in comparison with the traditional phenolic resins. Their precursors can be easily prepared from inexpensive raw materials, and polymerized without using strong acid or basic catalysts and without producing any by-products. Polybenzoxazines also provide unique characteristics like low water absorption and high dimensional stability due to near-zero shrinkage upon curing (Ishida *et al.*, 1995). Therefore, they are widely applied in various fields such as protective coatings for circuits in television studios and computer chips, airplane bodies, materials for airplane interiors, curing agents for other synthetic resins and varnishes which form films with a good resistance to water, alkali and solvents. The major disadvantages of the typical polybenzoxazines are their brittleness and a high temperature needed for the polymerization. Various studies have been reported aiming at performance improvement of polybenzoxazines. Generally, for performance enhancement, the preparation of novel monomers, copolymers, polymer alloys, and fiber reinforced composites have become increasingly attractive to overcome the shortcoming of the typical polybenzoxazines.

##### 2.1.1 Chemical Methodologies for Synthesis of Benzoxazine Monomer

Benzoxazine monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution or solventless methods. Various types of benzoxazine monomer can be synthesized using various phenols and amines with different substitution groups attached. These substituting groups can provide additional polymerizable sites and also affect the curing process. Consequently, polymeric materials with desired properties may be obtained by tailoring the benzoxazine molecular structures. In this section synthesis of different benzoxazine monomers is discussed.

Holly *et al.* (1944) first reported the condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well defined benzoxazine monomers. According to the reported procedure, this reaction was performed in a solvent in two-steps. Later Burke *et al.* (1949) found that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound and forms a Mannich bridge. In 1965, the same group synthesized Mannich condensation for benzoxazine synthesis in a solvent proceeds by adding amine to formaldehyde at lower temperatures at first to form an N,N-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring in Figure 2.1.



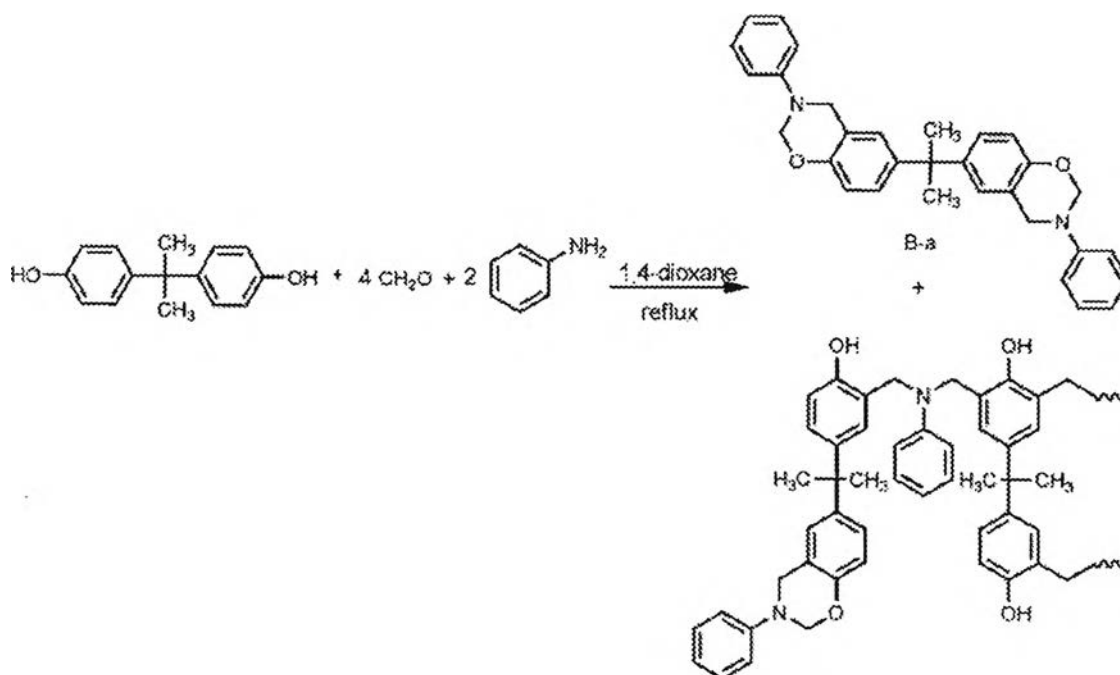
**Figure 2.1** Synthesis of 3,4-dihydro-2H-1,3-benzoxazines.

However, curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with an average molecular weight around 1000 Da. Thus, materials with good performance could not be made from this approach since the thermal dissociation of the monomer competed with chain propagation reaction so that high-molecular weight linear structures were unobtainable (Riess *et al.*, 1985). To overcome this limitation, Ishida and coworkers have developed a new class of difunctional or multifunctional benzoxazine monomers. The precursor was synthesized using bisphenol-A, formaldehyde and aniline using 1,4-dioxane as a solvent and the pure monomer was referred as B-a and oligomers were as oligo-B-a. The structures of oligo-B-a and B-a were analyzed by  $^1\text{H-NMR}$  measurements. The overall synthetic procedure is shown in Figure 2.2 (Ning and Ishida, 1994). The main constituent of the resulting products was a monomer with difunctional benzoxazine ring structures at both ends of the bisphenol A. The rest of the composition consisted of a mixture of dimers and oligomers, with

both benzoxazine rings and free phenol structures, as detected by NMR, FTIR and SEC. It was observed that the composition of the products is, to a large extent, dependent on the polarity of the solvent. This synthetic method consists of a few simple steps and can easily provide different phenolic structures with wide design flexibility. To achieve successful processing, cure kinetics of this material was investigated by using DSC, which indicated that the curing of benzoxazine precursors is an autocatalyzed reaction until vitrification is occurred, and diffusion begins to control the curing process (Ishida *et al.*, 1995).

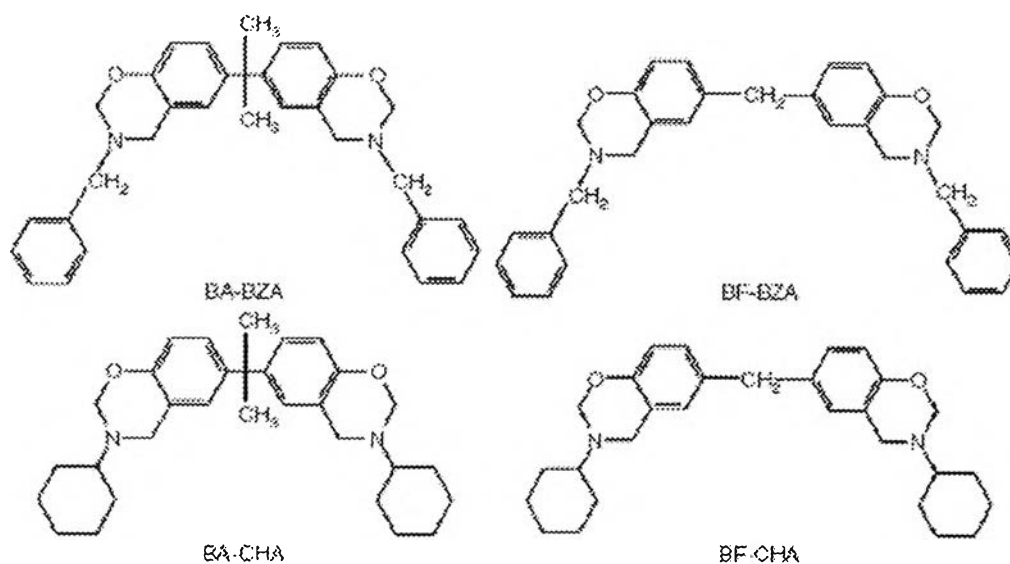
The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors are the major disadvantages associated with this procedure. The use of an organic solvent also increases the cost of the products and causes environmental problems. Furthermore, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins. To overcome these shortcomings, Ishida (U.S. Patent, 1996) developed a solventless synthesis in the melt state.

In a typical synthesis, the reactants, i.e., aldehyde, amine and phenolic precursors are physically mixed together, heated to their melting temperature, and thereafter maintained at a temperature sufficient to complete the interaction of the reactants to produce the desired benzoxazine. It should be pointed out that formaldehyde is not typically used as it evaporates easily and loses stoichiometry quickly. Instead, paraformaldehyde is used. The choice for phenols and amines provides the flexibility in designing monomer structure for tailoring the properties of the resulting polybenzoxazine polymer. The main advantages of the solventless synthetic method are improvement of reaction times compared with the traditional synthetic route and formation of fewer intermediates and by-products as contaminants.



**Figure 2.2** Synthesis of bisphenol-A and aniline based benzoxazine (B-a) monomer.

Gârea *et al.* (2006) synthesized four different benzoxazine monomers bis(4-benzyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (BA-BZA), bis(4-ciclohexyl-3,4-dihydro-2H-1,3 benzoxazinyl) isopropane (BA-CHA), bis(4-benzyl-3,4-dihydro-2H-1,3-benzoxazinyl) methane (BF-BZA), bis(4-ciclohexyl-3,4-dihydro-2H-1,3-benzoxazinyl) methane (BF-CHA) led to products in Figure 2.3, which include oligomers revealed by  $^1\text{H-NMR}$  and GPC. The quantity of oligomers mainly depends on the basicity of the oxygen and nitrogen atoms from the oxazine cycles, which influences the possibility of oxazine cycles opening and, thus, the formation of oligomers. Therefore, the benzoxazine monomers obtained from BA exhibit a higher concentration of oligomers than for those based on BF. The effective thermal polymerization of the benzoxazine monomers may be followed by GPC, which shows that there are two main factors which influence the polymerization reaction: the basicity of the N and O atoms from the oxazine cycles and the oligomers already existing in the monomers from their synthesis, which may act as a catalyst through the phenolic groups. FTIR proved the gradual formation of the tetrasubstituted aromatic rings within the polymer, the process depending on time and, again, on the initial concentration of the oligomers in the monomers.



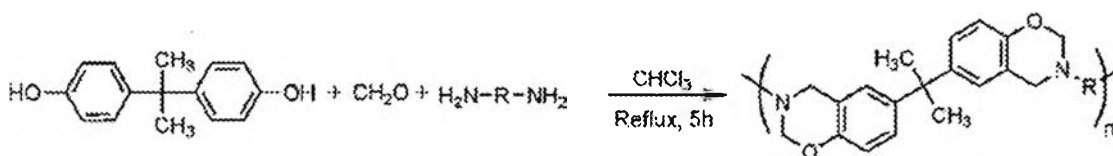
**Figure 2.3** Chemical structures of the synthesized benzoxazine monomers.

The  $T_g$  values of the obtained polybenzoxazines, as determined from  $\tan \delta$ -temperature curves, depend mainly on the nature of the phenolic component and less on the amine component. The dependence of ionic conductivity against time during the polymerization of the benzoxazine monomers gives the value for the gel time and, therefore, the reactivity of each of the benzoxazine monomers. The major difference in the reactivities for monomers based on BA and BF is due to the initial concentration of oligomers in each monomer, while the minor difference in the reactivities of the monomers based on the same phenol but with different amines is explained in terms of the electron density at the nitrogen atom from amine.

### 2.1.2 Preparation of High Molecular Weight Benzoxazine Precursors

Preparation of high molecular weight benzoxazine precursors would result in gel or insoluble solid because of the ring-opening polymerization of the once-formed cyclic ring. If it is possible to obtain soluble high molecular weight polybenzoxazine precursors, processing into thin films should become very easy, and application into the fields for which the low molecular weight cyclic monomer has not been used will be realized.

High molecular weight polybenzoxazine precursors have been synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde in Figure 2.4. The precursors were obtained as soluble white powder. The structure of the precursors was confirmed by IR,  $^1\text{H}$  NMR and elemental analysis, indicating the presence of cyclic benzoxazine structure. The precursor solution was cast on a glass plate, giving transparent and self-standing precursor films, which were thermally cured up to 240 °C to give brown transparent polybenzoxazine films. The toughness of the crosslinked polybenzoxazine films from the high-molecular weight precursors was greatly enhanced compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films revealed that polybenzoxazine from aromatic diamine exhibited the highest strength and modulus, while polybenzoxazine from longer aliphatic diamine had higher elongation at break. The viscoelastic analyses showed that the glass-transition temperature of the polybenzoxazines derived from the high-molecular weight precursors were as high as 238–260 °C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability (Takeichi *et al.*, 2005).



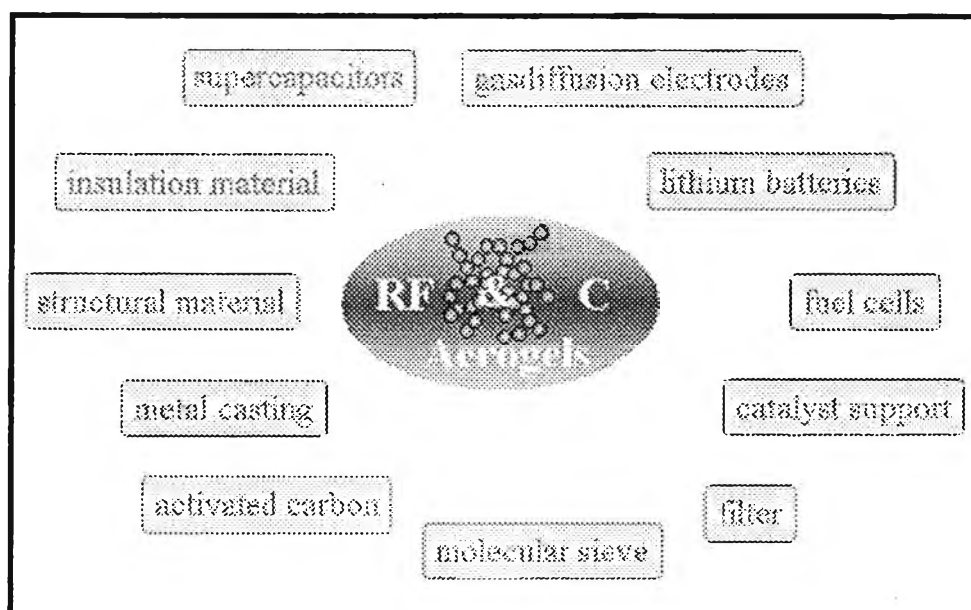
**Figure 2.4** Synthesis of polybenzoxazine precursors.

Agag *et al.* (2007) prepared polybenzoxazine matrix through high molecular weight polybenzoxazine precursors. They have used AB-type aminophenols instead of amines and phenols separately. They have obtained self-standing thin films from the precursors before curing by casting the precursor solutions onto glass plates. After the thermal treatment of the AB polybenzoxazine precursor films up to 250 °C, reddish-brown, transparent polybenzoxazines have been obtained. Both viscoelastic analyses and TGA have indicated that the thermosets derived from these novel AB precursors have excellent

thermomechanical properties as well as high thermal stability. This enhancement in the thermal properties can be attributed to the increase in the crosslinking density and hence suggests that the use of AB precursors is an effective approach for obtaining a novel polybenzoxazine matrix with excellent thermomechanical properties.

## 2.2 Carbon Aerogels

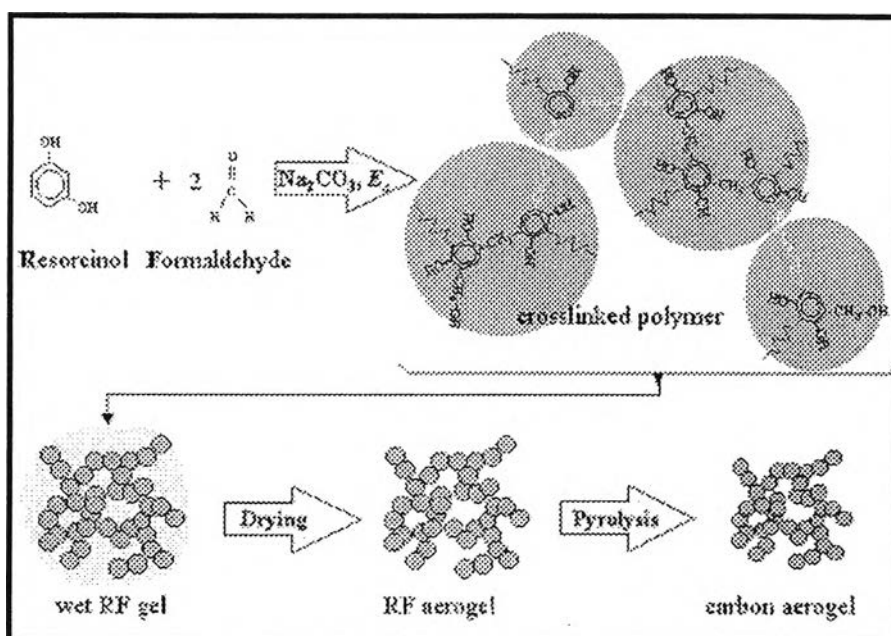
Carbon aerogels, discovered by Pekala *et al.* in 1989, compose of particles with sizes in the nanometer range, covalently bonded together. They are highly porous materials consisting of a continuous rigid solid framework. Carbon aerogels can be used in many applications such as gas adsorption devices, for heavy metals and ions removal, purification of drinking water, electronic capacitors, fuel cell electrodes, parts for inertial confinement fusion targets, catalyst support and chromatographic packing.



**Figure 2.5** General application of carbon aerogels ([http://www.ep2.physik.uni-wuerzburg.de/ag\\_fricke/textonly/supercaps\\_index.html](http://www.ep2.physik.uni-wuerzburg.de/ag_fricke/textonly/supercaps_index.html) ).

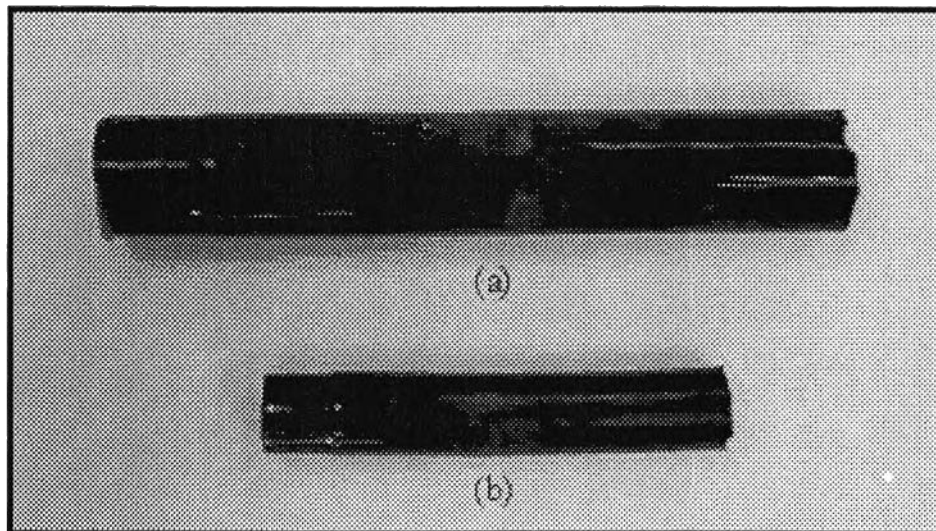
### 2.2.1 Preparation of Carbon Aerogels

Carbon aerogels have been generally synthesized from resorcinol-formaldehyde, phenol resorcinol-formaldehyde and prepared in four steps namely sol-gel formation, solvent exchange, a supercritical drying and pyrolysis, all of these steps affect the structure of carbon aerogels.



**Figure 2.6** Schematic diagram of the reaction of Resorcinol with Formaldehyde [1,2] ([http://www.ep2.physik.uniwuerzburg.de/ag\\_fricke/textonly/supercaps\\_index.html](http://www.ep2.physik.uniwuerzburg.de/ag_fricke/textonly/supercaps_index.html)).





**Figure 2.7** Effect of the pyrolysis on a of resorcinol-formaldehyde aerogel (a) before pyrolysis (b) after pyrolysis ([http://www.ep2.physik.uni-wuerzburg.de/ag\\_fricke/textonly/supercaps\\_index.html](http://www.ep2.physik.uni-wuerzburg.de/ag_fricke/textonly/supercaps_index.html)).

However, the conventional method is not suitable for commercial application because it involve a supercritical drying step which is very complicate, expensive and dangerous and use quite expensive raw material. Researchers have tried to produce carbon aerogels from cheap raw materials — polyurethanes (Bieman *et al.*, 1998), cresol-formaldehyde (Li *et al.*, 2001), melamine-formaldehyde (Zhang *et al.*, 2002) and phenolic-furfural (Wu *et al.*, 2005) — and safety synthesis method — freeze drying (Tamon *et al.*, 1999) and ambient drying (Li *et al.*, 2006).

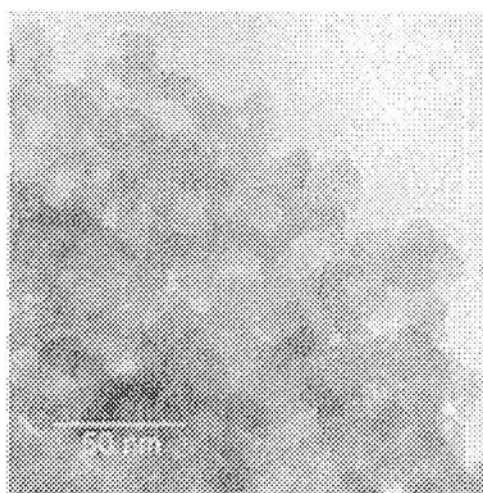
### 2.2.2 Structure and Propreties of Carbon Aerogels

Carbon aerogels, which are highly porous materials consisting of a continuous rigid solid framework and an open, continuous network of pores, represent attractive properties such as:

- A high electrical conductivity (25-100 S/cm)
- Controllable pore structure
- Highly useable surface area (up to 1100 m<sup>2</sup>/g)
- Biocompatibility

- Anti-corrosion by acid or base etc (Li *et al.*, 2006 and 2008).

Transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM), Nuclear Magnetic Resonance (NMR), N<sub>2</sub> adsorption, Small-angle X-ray scattering (SAXS), Mechanical testing, Electrochemical testing etc. have been used to characterize organic and carbon aerogels especially, the analysis of mesoporous and microporous structures of the aerogels is very important for their application.



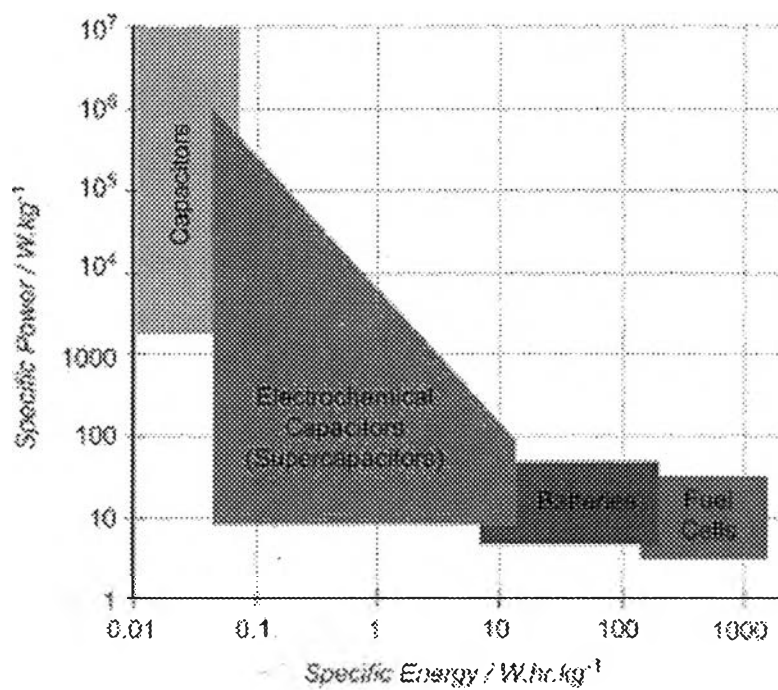
**Figure 2.8** Transmission Electronic Microscopic (TEM) of the carbon aerogel ([http://unit.aist.go.jp/energy/outline/theme02\\_e.htm](http://unit.aist.go.jp/energy/outline/theme02_e.htm)).

## 2.3 Supercapacitors

### 2.3.1 General Properties of Supercapacitors

Supercapacitors, ultracapacitors are generally used names for a category of electrochemical energy-storage devices which can store much more energy than conventional capacitors and offer much higher power density than batteries. The unique combination of high specific power and energy capabilities fills up the gap between the batteries and the conventional capacitors (Figure 2.9 and Table 2.1.) and allows to use in applications for various power and energy requirements, i.e., backup power sources for electronic devices, load-leveling, engine

start or acceleration for hybrid electric vehicles, pulse power technique and electricity storage generated from solar or wind energy.

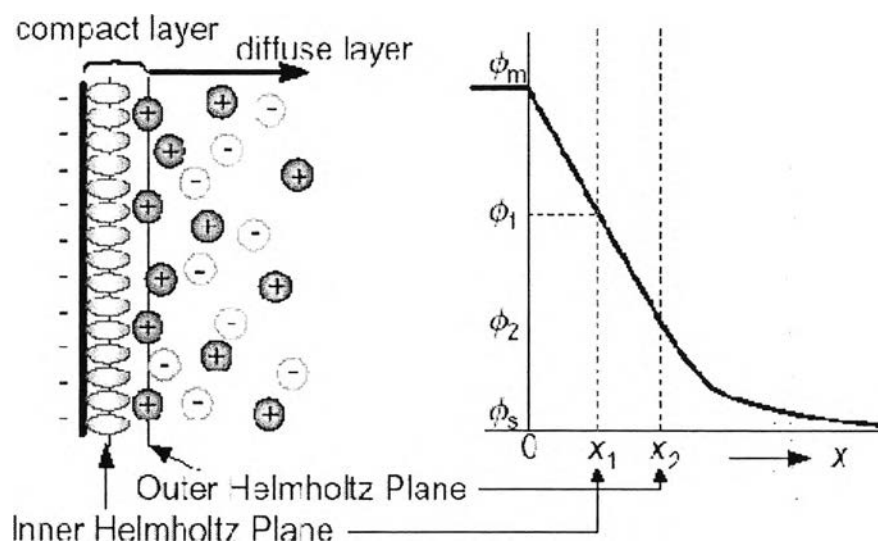


**Figure 2.9** Energy storage Ragone plot (Hall and Bain, 2008).

**Table 2.1** Comparison of typical capacitor and battery characteristics (Pandolfo and Hollenkamp *et al.*, 2006)

<b>Characteristics</b>	<b>Dielectric capacitor</b>	<b>Carbon supercapacitor</b>	<b>Battery</b>
Specific energy (Wh.kg <sup>-1</sup> )	< 0.1	1-10	10-100
Specific energy (W.kg <sup>-1</sup> )	>> 10000	500-10000	< 1000
Discharge time	10 <sup>-6</sup> to 10 <sup>-3</sup> s	s to min	0.3-3 h
Charge time	10 <sup>-6</sup> to 10 <sup>-3</sup> s	s to min	1-5 h
Charge/discharge efficiency (%)	~100	85-98	70-85
Cycle-life (cycles)	Infinite	>500000	~1000
Max. Voltage (V <sub>max</sub> ) determinants	Dielectric thickness and strength	Electrode and electrolyte stability window	Thermodynamics of phase reactions
Charge stored determinants	Electrode area and dielectric	Electrode microstructure and electrolyte	Active mass and thermodynamics

The potential of typical supercapacitors is based on the accumulation of charges at the surface of electrode in the electrolyte, also called electrical double layer, mainly by electrostatic attraction, without faradic reaction, as shown in Fig 2.10.



**Figure 2.10** The electrical double layer ([http://www.chemistry.nmsu.edu/studntres/chem435/Lab14/double\\_layer.html](http://www.chemistry.nmsu.edu/studntres/chem435/Lab14/double_layer.html)).

The capacitance ( $C$ ), which is expressed farad (F), of one electrode due to a pure electrostatic force of ions is proportional to the surface  $S$  of the electrode/electrolyte interface by following the equation (1):

$$C = \frac{\epsilon S}{d} \quad (1)$$

where  $\epsilon$  is the permittivity or dielectric constant of the solution and  $d$  represents the thickness of the electrical double layer (which is generally less than one nanometer), i.e., the distance where the maximal charge density is located in the electrode-electrolyte interface.

The overall capacitance ( $C$ ) is evaluated by the series of two electrodes which are connected, according to equation (2):

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (2)$$

Where  $C_1$  and  $C_2$  are the capacitance of electrode 1 and electrode 2, respectively.

The specific capacitance can be related to the surface of electrode ( $F/cm^2$ ), the volume of electrode ( $F/cm^3$ ) or the mass of electrode ( $F/g$ ). The amount of electrical energy ( $W$ ) that collected in supercapacitor is corresponded to the capacitance ( $C$ ) and the square of volatage ( $V$ ) by following equation (3):

$$W = \frac{1}{2} CV^2 \quad (3)$$

The cell voltage of the supercapacitors is depended on the type of electrolyte. The organic electrolytes operate in range of 2.5 V, whearas in the aqueous electrolytes it is used voltage around 1 V (Frackowiak *et al.*, 2001).

### 2.3.2 Types of Supercapacitors

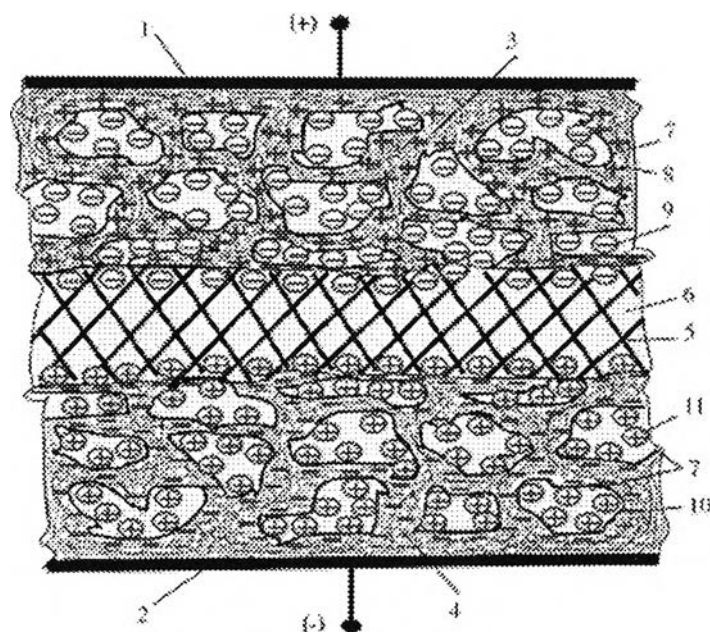
Supercapacitors can be categorized into two types according to their charge/discharge mechanisms (Frackowiak *et al.*, 2001; Burke 2000; Conway 1999).

#### 2.3.1.1 *Electric Double Layer Capacitors (EDLC)*

Electric Double Layers Capacitors (EDLC) store energy by charge separation in the double layer formed at the interface between the surface of the solid material electrodes and liquid electrolyte.

As shown in Figure. 2.11, on the metallic substrates (1, 2), called current collectors, porous material electrodes (3, 4) are provided. The electrical contact between them is prevented by a separator layer which is a porous material such as porous polyethylene, polypropylene, cellulose etc. that makes liquid electrolyte (6) can diffuse into its pores. (5). The porous separation layer (5) and the pores (7) from porous electric conductive electrodes are impregnated with liquid electrolyte. When applied voltage between the two electrodes, positive charge (8) at the exposed pore surface of one electrode attracts the negative ions (9) from the electrolyte and the negative charge (10) at the exposed pore surface of the other

electrode attracts the positive ions (11) from the electrolyte existing in the pores (Obreja. 2008).



**Figure 2.11** Schematics for a charged supercapacitor: 1 and 2—current collectors; 3 and 4—electrodes; 5—separator; 6—electrolyte; 7—pores in the electrode material; 8—positive charge; 9—negative ion; 10—negative charge (electrons); 11—positive ion (Obreja. 2008).

In particular, porous carbon materials especially carbon aerogels, are the most promising materials as an electrode for EDLCs, as they allow an interconnected three-dimensional network structure, a high specific surface-area, good electrical conductivity and a suitable pore size for common electrolytes (2-5 nm) (Kim *et al.*, 2005 and Hwang *et al.*, 2003, Frackowiak *et al.*, 2001).

### 2.3.1.2 Pseudocapacitors

Pseudocapacitors can store energy via surface faradaic redox reactions, which in most instances can be described as charge transfer reactions at the surface or in the bulk near the surface of the solid electrode. These reactions are voltage-dependent. The pseudocapacitors are made possible by electrode material that can be reversibly oxidized and reduced over a wide potential range. Therefore, transition metal oxides ( $\text{RuO}_2$ ,  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{SnO}_2$ ) and conducting polymers (aniline,

pyrrole) with various oxidation states are considered as promising materials for pseudocapacitors (Hwang *et al.*, 2007). Table 2.2 shows the specific capacitance of various materials. The specific capacitance of pseudocapacitors is higher when compare with EDLCs (carbon materials).

**Table 2.2** The specific capacitance of selected electrode materials (Burke 2000)

Material	Density (g/cm <sup>3</sup> )	Electrolyte	F/g	F/cm <sup>3</sup>
Carbon cloth	0.35	KOH	200	70
		organic	100	35
Carbon black	1	KOH	95	95
Carbon aerogel	0.6	KOH	140	84
Particulate from SiC	0.7	KOH	175	126
		organic	100	72
Particulate from TiC	0.5	KOH	220	110
		organic	120	60
Anhydrous RuO <sub>2</sub>	2.7	H <sub>2</sub> SO <sub>4</sub>	150	405
Hydrous RuO <sub>2</sub>	2.0	H <sub>2</sub> SO <sub>5</sub>	650	1300
Doped conducting polymers	0.7	organic	450	315