



CHAPTER II

LITERATURE REVIEW

2.1 Carbon Aerogels

Carbon aerogels were first developed by Pekala *et al.* in the resorcinol-formaldehyde system at the end of 1980s. Their various characteristics make them attractive as various applications such as electrode materials for supercapacitors, the deionization of ionic solutions, advanced catalyst supports, chromatographic packing, and adsorbents. The physical, chemical, and electrochemical characteristics of carbon aerogels depend strongly on the fabrication method; therefore, different synthesis and processing methods can be used to produce tailored gels for specific applications (Sepehri S. *et al.*, 2009).

2.1.1 Preparation of Carbon Aerogels

Carbon aerogels are obtained by pyrolysis of organic aerogels, which are mostly produced by the polycondensation reaction of resorcinol and formaldehyde in different solvents and using different catalysts. They are generally supercritical dried prior to pyrolysis of the organic aerogels to preserve their pore texture (Fairén-Jiménez *et al.*, 2006).

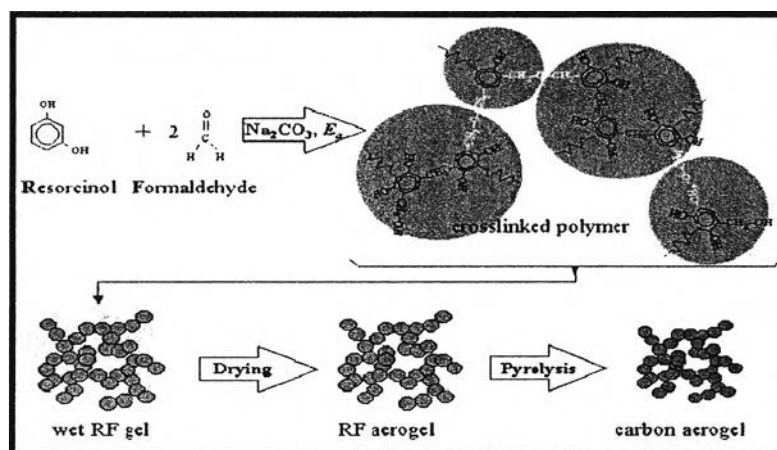


Figure 2.1 Schematic diagram of the reaction of resorcinol with formaldehyde (Berthon-Fabry and Achard, 2003).

In order to expand the source of raw materials and reduce the cost, many alternative materials were used to prepare carbon aerogels.

Li W. and Guo H. (2000) carried out some experiments for the preparation of low density carbon aerogels. In their experimental, a cresol mixture was first used to polycondense with formaldehyde catalyzed by NaOH for the preparation organic aerogels. They concluded that a cresol mixture could be used as a raw material to prepare low density monolithic, crack-free aerogels, and carbon aerogels. Density is an important index to judge the aerogel quality. The lower the carbon aerogel density, the lower the electrical resistivity, hence the preparation of the super-low-density aerogel is important in understanding the physical transport mechanism within these materials. Li W. *et al.* (2002) attempted to make lower cost aerogel by using cresol. A mixture of cresol (Cm), resorcinol, and formaldehyde has been used as an alternative economic route to the classical resorcinol-formaldehyde synthesis. The porous structure of the mixed carbon aerogels (CmRF) was similar to that of RF carbon aerogels.

Fu R. *et al.* (2003) reported the polycondensation reaction of resorcinol and furfural for the synthesis of carbon aerogels. According to the reported procedure, this reaction was performed in isopropyl alcohol with HCl as a catalyst, and the resultant aerogels were then dried directly with supercritical isopropyl alcohol, which was followed by carbonization.

Wu D. and Fu R. (2005) also prepared organic and carbon aerogels by gelation of phenol-furfural using HCl as a catalyst and supercritical drying in ethanol. The experimental results showed that the gelation ability of the phenol-furfural system could be enhanced by increasing the phenol-furfural concentration, the mass ratio of HCl to phenol (HCl/P), the mole ratio of phenol to furfural (P/F), and the gelation temperature. Furthermore, organic and carbon aerogels could be obtained by directly drying phenol-furfural aerogels at ambient pressure under proper preparation conditions.

In addition, aerogels from other organic starting materials have been produced such as polyurethanes (Biesman G. *et al.*, 1998), polyureas (Je Kyun Lee, US Pat. 2006), and melamine-formaldehyde (Zhang R. *et al.*, 2002).

2.1.2 Control of Mesoporous Structure of Organic and Carbon Aerogels

Organic aerogels, prepared according to the method proposed by Pekala *et al.*, was elucidated that resorcinol–formaldehyde (RF) aerogels are mesoporous materials with high surface areas and had few micropores (Tamon H. *et al.*, 1997).

Tamon H. *et al.* (1998) studied the mesoporous structure of organic and carbon aerogels by taking into account the synthesis conditions of the RF aquagels. They concluded that the mesoporous radius of the RF aerogel could be controlled in the range of 2.5-9.2 nm by changing the mole ratio of resorcinol to sodium carbonate used as a catalyst and the ratio of resorcinol to distilled water used as a diluent. Shrinkage also played a role in control of the mesopore radius. As the pyrolysis temperature increased, the mesopore volume became small but the peak radius of pore distribution was maintained. It was also noticed that with an increase in the pyrolysis temperature, ethane adsorption became larger than ethylene adsorption on the aerogels. The carbon aerogels prepared by pyrolysis at 1000°C had the same ethane and ethylene adsorption characteristics as activated carbons did.

2.1.3 Properties and Electrochemical Applications of Carbon Aerogels

Carbon aerogels contain a monolithic three-dimensional mesoporous network of carbon nanoparticles, exhibiting high porosity (80-98%), low electrical resistivity, controllable pore structure, high surface area (up to 1100 m²/g), good electrical conductivity (25-100 S cm⁻¹) (Pekala *et al.*, 1992), thermal and mechanical properties. These attractive properties make carbon aerogels very suitable as electrode materials for supercapacitors

Wang *et al.* (2001) studied morphological effects on electrical and electrochemical properties of carbon aerogels. Suitability of carbon aerogel for supercapacitor was explored by Fisher *et al.* (1997), Saliger *et al.* (1998), and Pekala *et al.* (1998)

Meng Q.H. *et al.* (2004), Frackowiak E. (2007), and Azais P. *et al.* (2007) studied factors affecting on the electrochemical performance of supercapacitors, such as specific surface area, pore volume, pore size distribution, as well as the surface groups of the electrode materials. Meng *et al.* (2004) reported that both the

surface area and pore volume of carbon aerogels determined their specific capacitance. High pore volume and wide pore distribution contributed to an increase of capacitance. Frackowiak E. (2007) concluded that micropore played an essential adsorption role in the formation of the electrical double layer, and the presence of mesopore was necessary for efficient charge propagation into the bulk of the electrode material, allowing the so-called frequency response to be fulfilled. Azais P. *et al.* (2007) indicated that the concentration of surface groups and their nature were found to have an important influence on the performance degradation of supercapacitors.

Li J. *et al.* (2008) investigated the structure and electrochemical properties of carbon aerogels, which synthesized at ambient temperature. They concluded that the performance and the structure of carbon aerogels for supercapacitor applications depended strongly on the mole ratio of resorcinol to sodium carbonate used as catalyst (R/C). The carbon aerogels were porous materials with pearly network structure, the particle size increased with an increase of R/C ratio. The total surface areas were in the range of 600-1000 m²/g. The conclusions were also indicated that carbon aerogels electrodes had good electrochemical performance, high reversibility, and high specific capacitance. The higher capacitance of 183.6 F/g was obtained with R/C ratio of 1500. Moreover, carbon aerogels with R/C ratio of 1500 had low resistance, small leakage current, and good electrical conductivity.

2.2 Polybenzoxazine

Polybenzoxazine as a novel type of phenolic resin offers many advantages in comparison with traditional phenolic resins. Benzoxazine monomers can be prepared simply from inexpensive raw materials and polymerized without using strong acid or basic catalysts and without generating any by products. Polybenzoxazines possess typical characteristics of traditional phenolic resins such as heat resistance, good flame retardance, and electronic properties. In addition, they provide unique characteristics like low water adsorption and also excellent dimensional stability due to the near-zero volumetric shrinkage upon cure (Ishida 1996). Various applications as electronic materials, matrix resin for fiber-reinforced plastics, and adhesives are expected. The cured materials, however, are brittle and relatively high temperature is

needed for the ring opening polymerization. Therefore, further performance enhancement of polybenzoxazine is also strongly expected.

2.2.1 Chemical Methodologies for Synthesis of Benzoxazine Monomers

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 (Ghosh *et al.*, 2007).

2.2.1.1 *Mono-Functional Benzoxazine Monomers*

Holly and Cope (1944) first reported the polycondensation reaction of primary amine 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 (1949) found that the benzoxazine ring reacted preferentially with free ortho positions of the phenolic compound and formed a Mannich bridge. The procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeded by first adding amine to formaldehyde at lower temperatures to form *N,N*-dihydroxymethylamine derivative, which then reacted with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring (Burke *et al.*, 1965).

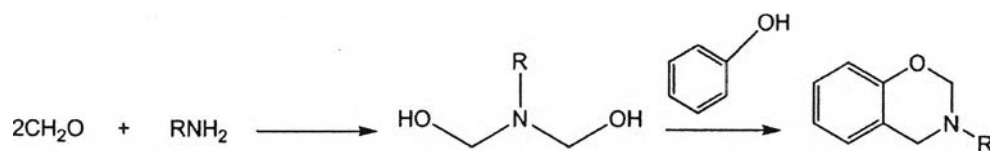


Figure 2.2 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines (Ghosh *et al.*, 2007).

The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors was the disadvantages of Mannich condensation process. The use of an organic solvent also increased the cost of products and created the environmental problems. Furthermore, the solvent residue in the precursors led to problems during processing of the ben-

zoxazine resins (Brunovska *et al.*, 1998). To overcome these shortcomings, Ishida *et al.* (1996) developed a solventless synthesis in a melt state. The reaction mechanism and kinetics of solventless synthesis were proposed by Liu (1995) in order to use this procedure to prepare a large quantity of benzoxazine monomers.

2.2.1.2 Di-Functional and Multifunctional Benzoxazine Monomers

Ishida and coworkers (1994 and 2002) have developed a new class of difunctional and multifunctional benzoxazine monomers and their curing into phenolic materials with the ring opening reaction being initiated by dimers and higher oligomers in the resin composition. The precursor was synthesized using bisphenol-A, formaldehyde and methylamine in different solvents and referred to as B-m, as a reference to two of its original ingredients: bisphenol-A and methylamine. 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.

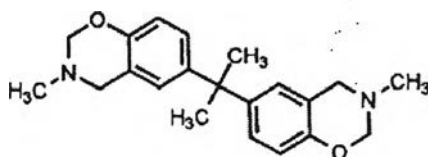


Figure 2.3 Chemical structure of benzoxazine (B-m) monomer (Ghosh *et al.*, 2007).

2.2.2 Preparation of High Molecular Weight Benzoxazine Precursors

High molecular weight polybenzoxazine precursors containing cyclic benzoxazine groups in the backbone were prepared from bisphenol-A, various diamines, and paraformaldehyde. Partially ring-opened structure was observed, but the ratio of the ring-closed structure in the precursor was high enough to be used as benzoxazine precursors (Takeichi *et al.*, 2005). Takeishi *et al.* also found that after the cure of benzoxazine groups, tough film with much improve thermomechanical property.

Several methods were applied to prepare high molecular weight benzoxazines, namely AB-type polybenzoxazine prepolymer, based on the reaction of primary amine-containing phenols such as tryamine and *p*-aminophenol with para-

formaldehyde (Agag and Takeishi, 2006). Agag and Takeishi (2006) proposed a new approach for a preparation of benzoxazine matrix through high molecular weight benzoxazine precursors. They used AB-type aminophenol instead of amine and phenol separately and found that the precursors gave self-standing thin films when their solutions were cast in dioxane over glass plates and dried. Then, upon a gradual thermal cure up to 250°C, they afforded polybenzoxazine films. 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.

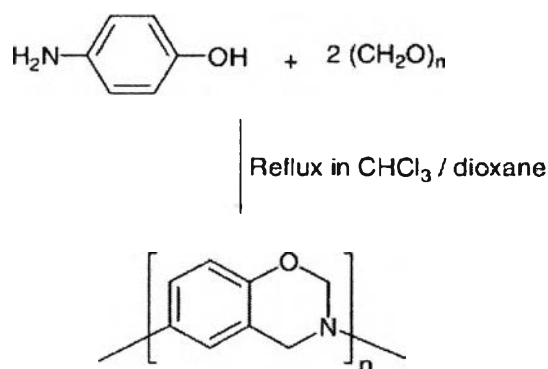


Figure 2.4 Preparation of AB-*p*-aminophenol (AB-PAP) as a benzoxazine prepolymer (Agag and Takeishi, 2006).

2.3 Electrochemical Capacitors

Electrochemical capacitors are energy storage devices, similar to batteries, but offer much higher power density. The main advantage of this storage device is the ability of high dynamic of charge propagation (short-term pulse) that can be useful in the hybrid power sources for electrical vehicles, digital telecommunication systems, UPS (uninterruptible power supply) for computers, and pulse laser technique. The other profits of electrochemical capacitor system is a possibility of full discharge, and a short-circuit between the two electrodes is also not harmful (Frackowiak and Béguin, 2001).

Electrochemical capacitors from carbon are of two types depending on the kind of accumulate energy; the electrical double layer capacitors (EDLCs) and pseudocapacitors (Conway 1991).

2.3.1 Electrical Double-Layer Capacitors (EDLCs)

This capacitor stores energy by charge separation at the electrode/electrolyte interface, mainly focus on carbon materials. The capacitance of EDLCs is strongly dependent upon the surface area of the electrode materials. Among carbon materials, Carbon aerogels are promising materials as electrodes for EDLCs due to their high performance and low cost (Pekala *et al.*, 1992)

2.3.2 Pseudocapacitors

This capacitor can store energy via faradaic redox reactions on the interface of the electroactive material and the electrolyte. The pseudocapacitor with a large capacitance is made possibly by electrode material with can be reversibly oxidized and reduced over wide potential range. Consequently, transition metal oxide and conducting polymers with various oxidation states are considered as promising materials for pseudocapacitors (Prasad and Miura, 2004).

In order to improve the electrochemical performance, a combination of pseudocapacitive materials and carbonaceous materials suitable for EDLCs has been conducted.

Generally, the enhancement of specific capacitance for the carbon materials by quick faradaic reactions can be realized by the following modifications (Frackowiak and Béguin, 2001):

- (1) a special oxidation of carbon for increasing the surface functionality (through chemical treatment (Jurewicz and Frackowiak, 2000), electrochemical polarization (Momma *et al.*, 1996), plasma treatment (Ishikawa *et al.*, 1996))
- (2) the formation of carbon/conducting polymer composites by electropolymerization of a suitable monomer (aniline, pyrrole) on the carbon surface (Ingram *et al.*, 1998) or using a chemical method for polymerization
- (3) insertion of electroactive particles of transition metals oxides such as RuO₂, ZnO, NiO, MnO₂, SnO₂, etc into the carbon material.

Capacitance enhancement of carbon materials by electroactive species is extremely attractive, for example, ruthenium oxides are widely used in electro-

chemical capacitors due to its high specific capacitance and prominent electrochemical properties (Zheng *et al.*, 1975), but it is too expensive to use widely in commercialization. Therefore, other inexpensive metal oxides exhibit capacitive behavior similar to that of ruthenium oxide has been explore for supercapacitors such as ZnO (Kalpana *et al.*, 2006), NiO, MnO₂ (Prasad and Miura, 2004), and SnO₂ (Hwang and Hyun, 2007), etc.