

# Defect formation and prevention during the preparation of supported carbon membranes

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**Abstract:** Supported carbon membranes were prepared using phenolic resin as the carbon precursor and porous graphite as the support. The support was impregnated with the resin solution, dried, cured and carbonized to obtain a membrane layer. One-time coating cannot effectively reduce the number of defects in the membrane. Repeated impregnation cycles to add more carbon layers, using a slow cooling rate during carbonization, performing carbonization at a low temperature and short time (500 °C and 10 min), and coating the supported membranes with permeable polymers were used simultaneously to reduce the population of defects to a certain extent. As a result, gas separation selectivity of the membranes was significantly increased.

**Key Words:** Gas separation; Carbon membrane; Phenolic resin; Defect formation; Defect prevention

## 1 Introduction

In recent years, carbon membranes have attracted much attention as an alternative for polymeric membranes, owing to their good shape selectivity, high hydrophobicity, high thermal strength and high resistance against corrosion<sup>[1]</sup>. Carbon membranes have shown their advantages for commercial separation of oxygen over nitrogen based on their kinetic characteristic<sup>[2]</sup>. Carbon membranes are generally prepared via two ways. One is to prepare polymeric membranes from selected polymeric materials, and convert it to carbon membrane carbonization at controlled conditions<sup>[1,3]</sup>. Another method is to coat surface of suitable porous supports with polymeric materials and to convert them to carbon membrane by carbonization<sup>[1,3]</sup>. Chemical composition and moiety geometry, chain structure and rigidity, physicochemical properties of polymeric precursors play major roles in determining the properties of the resultant carbon membranes, especially the micropore structure and separation capability<sup>[4,5]</sup>. Phenolic resins have been used to prepare supported carbon membranes for gas separation by some researchers. High carbon yield and low price are the most important benefits of phenolic resin precursors<sup>[3]</sup>.

One of the most important problems to be solved in preparing carbon membranes is to their reproducible separation properties. Several researchers have reported that carbon membranes prepared under the similar pyrolysis conditions do not exhibit the similar separation performance, especially selectivity<sup>[6]</sup>. Cracks are common defects in supported carbon

membranes. These cracks might be in the form of micro-cracks or macro-cracks with width of more than 2 μm. Carbon membranes for gas separation work based on the difference in diffusion coefficient between different species<sup>[7]</sup>. The existence of cracks in carbon layers seriously decreases selectivity of the membranes. Gas molecules diffuse through these cracks with high flux via viscous flow, molecular diffusion or Knudsen diffusion, depending on relative dimensions of gas molecules and cracks. Therefore, the population increase of cracks may decrease the difference of diffusion coefficient of gas species, leading to poor selectivity. Researchers have proposed different ways to prevent crack formation or even to remove them. Acharia et al. coated the polymer in solution over the external surface of the support with a brush<sup>[8]</sup>, changed the geometry of the support and used a flat support, and replaced brush coating with spray coating. Gas permeation results showed the formation of cracks relatively was decreased<sup>[8]</sup>. Many researchers have tried by repeating the coating-carbonizing operations to cover the previous defects and to create uniform carbon layers over the surface of supports. Schiflett attempted to prepare defect-free carbon layers over porous stainless steel by repeating coating-carbonization of polyfurfuryl alcohol for four times<sup>[9]</sup>. Kita et al. coated the external surface of porous alumina tubes with 40% phenolic resin solution via dip coating method. They repeated the coating-carbonizing operations for three to four times in order to form a defect-free carbon layer<sup>[10]</sup>. Rao and Sircar coated porous graphite with latex polyvinylidene chloride. They also repeated coating-carbonizing operations for

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five times<sup>[11]</sup>. Chen and Yang used graphite disk as supports and coated them with polyfurfulyl alcohol solution. They repeated the coating-carbonizing operations for five times in order to form a uniform carbon layer<sup>[12]</sup>.

Nevertheless, some researchers have reported that only one-time coating could be successful in formation of defect-free carbon layers over the surface of supports. Centeno and Fuertes prepared carbon membranes via coating thin layers of phenolic resin over the internal surface of porous alumina tubes. Their investigations showed that only one-time coating is sufficient for preparation of defect-free carbon membranes<sup>[13]</sup>. Wei et al. used a tube support made of novolac resin particles and coated it by a 60% resin solution in alcohol. They showed that only one-time coating-carbonizing operation is enough for the formation of a defect-free carbon layer. They concluded that high concentration of the resin solution leads to the formation of a thick carbon layer over the support surface<sup>[14]</sup>. Some researchers have concluded that carbon layer thickness plays an important role in defect formation and separation properties. In dip coating, they claimed that concentration of resin solution is the main effective parameter on resin layer thickness and therefore carbon layer thickness<sup>[14]</sup>. Duke et al. dip coated the surface of supports made from alpha-alumina and silica molecular sieves with the phenolic resin solutions of resole and novolac type to prepare carbon membranes. They concluded that an optimized concentration was needed to prepare selective carbon layers<sup>[15]</sup>. Shiflett showed that for every combined system of support and thin layer, there is a critical thickness, beyond which cracks are formed. Shiflett showed that for the supported carbon membrane over the surface of vicor glass, this thickness is  $22 \pm 1 \mu\text{m}$ <sup>[9]</sup>. Controlling the cooling rate of the membrane after carbonization was used by some researchers to reduce the thermal stress on carbon layer. For example Li and Chung used a cooling rate of 1 °C/min from 550 °C or 800 °C to 500 °C, then a rate of 2 °C/min to 200 °C and finally a rate of 5 °C/min to 50 °C<sup>[16]</sup>.

One of the main reasons for crack formation in carbon membranes is the mass and volume reduction of carbon layers during carbonization. It should be mentioned that the support structure is generally rigid, and therefore surface layer has a stress that leads to the crack formation<sup>[6]</sup>. Many researchers have pointed out that supports play an important role in synthesis of carbon membranes because every defect in supports could be transferred to the upper coating layers. Furthermore, the difference in physico-mechanical properties between support and thin layer (polymer and ultimately carbon) can lead to crack formation during curing and carbonization. As a result, some researchers have tried to choose the support whose properties are as close as possible to the properties of carbon thin layer<sup>[14]</sup>. Centeno<sup>[17]</sup>, Rao<sup>[11]</sup> and Chen<sup>[12]</sup> used graphite supports as its property similarities with the coated carbon layer to prevent crack formation. Along with all the attempts that were employed to prevent the defect formation in carbon membranes, some researchers used different coating techniques to repair the membrane defects. Peterson et al.<sup>[18]</sup>

used polydimethyl siloxane (PDMS), and Jones<sup>[19]</sup> used poly-4-methyl pentene and Teflon to cover the defects in carbon membrane. Some other materials were used for coating the inorganic membranes. For example, Zhang et al.<sup>[20]</sup> used beta-cyclodextrin for zeolite membrane coating. It was possible that such a material could be useful for carbon membrane coating.

The aim of this investigation is to determine factors that are related to crack formation and examine possible methods for preventing defect formation and/or repairing the defects in the preparation of supported carbon membranes using phenolic resin as precursor and porous graphite as support. Furthermore, some new ideas such as partial carbonization and using new materials for membrane coating were also examined.

## 2 Experimental

### 2.1 Materials

Phenolic resin was used in the form of novolac type (IP 500 from Rezitan Company, Iran). Methanol and N-methyl pyrrolidone (NMP) from Merck Company were used to dissolve the resin.

Graphite was selected as the support in order to have the highest similarity with the carbon layer. Graphite was in the form of slab and obtained from Carbon Industrie-Produkte GmbH, Germany. The graphite support was formed by hot pressing graphite particles. This slab was machined in the form of the tube with an external diameter of 10 mm and internal diameter of 6 mm and was used as the support. Nitrogen and methane gases with a purity of 99.999 % and carbon dioxide with a purity of 99.99 % was supplied by Roham Gas Company (Tehran, Iran).

### 2.2 Membrane preparation

Phenolic resin was dissolved in methanol to prepare a 60 mass% solution. Then the solution was diluted with NMP in order to prepare a solution with a required concentration. Such a mixed solvent was used for a better dissolution of phenolic resin by some researchers<sup>[12]</sup>. This solution was used to coat the internal surface of the support via dip coating. Since the support was symmetric, both inner and outer surface could be coated. Inner surface was chosen to protect the sensitive carbon layer against the mechanical damages such as abrasion. Different concentrations of resin in solvent were used. After coating, the coated support was dried for one day at ambient conditions, and then completely dried in an atmospheric oven for 12 h at 50 °C and finally in a vacuum oven ( $\approx 2 \text{ mmHg}$ ) for 12 h at 50 °C. Then the dried coated support was kept in the oven with a specified heating program up to 150 °C for 2 h in order to complete the curing reactions. The curing operations were performed slowly based on the program shown in Fig. 1 to avoid possible remnant of the solvents.

The coated support was placed in a quartz tube, transferred to a tube furnace and carbonized in a nitrogen flow

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