

## Book Review

# Carbon Membrane Technology: Fundamentals and Applications

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### ABSTRACT

Carbon membrane has shown great advantages with high separation performance, especially under high temperature and pressure condition with its strong mechanical and chemical stabilities, as well as well-defined pores structures [1]. An overview of the fundamental aspect and industrial application of carbon membrane is thus important to demonstrate the potential development of the membrane. This recent published book summarized both aspects in two parts. For the first part, the formation, state-of-art of the performance, characterization and transport mechanism of carbon membranes were discussed. For the second part, the application of carbon membrane in biogas upgrading, natural gas sweetening, hydrogen purification, micro-, ultra- or nanofiltration and other applications were reported. Subsequently, future perspectives of the carbon membrane were also analysed. In short, the book offers a thorough discussion on the fundamentals and applications of carbon membrane towards a sustainable development, which is a valuable resource for both academic and industrial researchers.

*Keywords:* Carbon membrane, membrane preparation, gas transport mechanism, membrane application

### 1.0 BOOK REVIEW SUMMARY

In this book, Part 1 describes the fundamentals of carbon membranes. There are four chapters in this part. Chapter 1 reports the preparation of carbon membranes. Readers can find a table summarizing the typical precursor materials used to produce carbon membranes, including their configurations and carbonization conditions. Types of precursor materials include cellulose, cellulose acetate, polyacrylonitrile,

polyethyleneimine, polyimide, polyphenylene oxide, and phenol resin. The regeneration methods are also discussed in this chapter to remove the oxygen adsorbed on the membrane surface and water condensed in the pore structure. Factors used to tune the pore structures of the membrane are reported, including H<sub>2</sub>-assisted approaches, oxidative treatment, chemical doping, etc. Several post-treatments are discussed to improve membrane performance. For instance, ideal selectivities of H<sub>2</sub>/CH<sub>4</sub> and

H<sub>2</sub>/CO<sub>2</sub> can reach up to 50.7 and 7.1, respectively, after ozone treatment. Additionally, challenges faced in upscaling the fabrication of carbon membranes are summarized.

Chapter 2 discusses the state-of-the-art performance of carbon membranes. The separation performance for different gases, including He/CH<sub>4</sub>, H<sub>2</sub>/N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/CH<sub>4</sub> for unsupported and supported carbon membranes, is reviewed. Several carbon membranes have surpassed the Robeson upper bound separation performance, including CMS-800°C, CMS-900°C, and CMS-1000°C. Support modification is reported to enhance membrane performance. For example, a TiO<sub>2</sub> intermediate layer has been added to support the formation of a thinner CMS layer with a large d-space, leading to higher permeability and selectivity.

Chapter 3 summarizes the characterization tools required for carbon membranes. Comprehensive characterization analyses on the morphology and microstructures of the membrane are shown, including TGA, SEM, TEM, XRD, and N<sub>2</sub> and CO<sub>2</sub> physisorption. The evolution of chemical structure during carbonization is discussed via TGA-MS analysis. Readers can find comprehensive characterization analysis methods in this chapter. Equations are used to estimate the microstructure of carbon membranes, such as d-spacing based on XRD, as well as micropore volume and

average micropore width based on high-pressure CO<sub>2</sub> adsorption. The schematic diagram for the gas permeation measurement setup and related equations, such as permeability, ideal selectivity, and separation factor, are presented in the chapter. The time-lag method is also shown to estimate the diffusivity and sorption coefficient.

Chapter 4 describes the gas transport mechanisms for carbon membranes. A general gas transport model based on Fick's first law is reported. Transport mechanisms for carbon membranes, including Knudsen diffusion, surface diffusion, and molecular sieving at different pore sizes, are shown. Equations for the respective transport mechanisms enhance the reader's understanding of the topic. For instance, gas flux based on Knudsen diffusion indicates the unsuccessful formation of membranes, as gas transport across membranes depends on pore radius, average velocity, and molecular weight of gas molecules. For selective surface flow, activated diffusion is represented by an Arrhenius-type equation considering the activation energy. For molecular sieving, an activation energy equation for diffusion via molecular sieving is presented. Subsequently, these equations are related to the effects of process parameters, such as pressure and temperature. However, the effect of feed composition is not included in the chapter. Table 1 highlights each chapter for Part 1.

**Table 1** Highlights of each chapter for Part 1

Chapters	Aspects of discussion	Some highlights of chapter
1	Membrane formation	- Configurations and carbonization conditions of precursor -Pores tuning approach and post-treatment
2	Membrane performance	- He/CH <sub>4</sub> , H <sub>2</sub> /N <sub>2</sub> , O <sub>2</sub> /N <sub>2</sub> and CO <sub>2</sub> /CH <sub>4</sub> -Support modification
3	Membrane characterization	-TGA, SEM, TEM, XRD, N <sub>2</sub> and CO <sub>2</sub> physisorption -Gas permeation measurement set-up
4	Gas transport mechanism	-Transport mechanisms based on pores sizes -Effects of pressure and temperature

Part 2 of this book describes the applications of carbon membranes. Carbon membranes are applied in industrial processes due to their high chemical, thermal, and mechanical stability, cost-effectiveness, and high selectivity with well-defined pores. There are five chapters in this part. Comprehensive reviews on the wide application of carbon membranes in different areas, like biogas upgrading, natural gas sweetening, hydrogen purification, liquid mixture separation, etc., are performed.

Chapter 5 covers the application of carbon hollow fiber membranes in a biogas upgrading pilot plant. Low-quality carbon hollow fiber membranes are classified in the chapter. Fibers with weak spots and severely curled shapes can easily break during operation. For the actual utilization of biomethane, the process flowsheet is discussed. The technology readiness level is evaluated. Actual photos of the biogas upgrading membrane plant are presented. Permeation data of the biogas upgrading process is shown, with plant operation time up to 190 hours. Challenges and suggestions related to membranes or modules are provided at the end of the chapter, serving as important considerations for membrane application. For instance, shell-side feed configuration might damage membrane fibers due to high-pressure feed flow. Bore-side feed configuration is more efficient for the membrane system.

Chapter 6 presents the application of carbon membranes for natural gas sweetening. Several technologies for natural gas sweetening are introduced, including absorption, adsorption, and membranes. Natural gas production is also discussed in this chapter. A comprehensive comparison of ionic liquids, polymeric, inorganic, and carbon membranes for natural gas sweetening is conducted. Firstly, three

types of polymeric membranes for H<sub>2</sub>S removal are reported, including membranes based on rubbery polymer selective layers, membranes with a selective layer made of block copolymers, and membranes with a selective layer made of glass polymers. Types of polymeric membranes for acid gas removal from natural gas are tabulated with their permeance, selectivity, feed pressure, and gas composition data for CO<sub>2</sub>, H<sub>2</sub>S, and CH<sub>4</sub>. Most importantly, commercialized membranes are shown in the chapter, with the materials used, company, and module. The procedures for preparing carbon membranes using polymer precursors and the schematic diagram for the tubular pyrolysis oven system are also reported. Following that, process design, simulation, and optimization are presented. A schematic diagram of a cascade membrane system with recycles is shown. The financial approach for the process via techno-economic studies is discussed in this chapter based on membrane configuration. A comparison study with the amine absorption process is performed. It is reported that a membrane system is economically feasible compared to an amine-based capture system when the CO<sub>2</sub> feed concentration is higher than 25%. The Joule-Thomson cooling effect related to high CO<sub>2</sub> feed concentrations is also discussed in the chapter. It serves as a guideline for researchers in evaluating the potential of carbon membranes in process applications. Lastly, for effective separation, at least two stages of membrane modules are required.

Chapter 7 summarizes the usage of carbon membranes in hydrogen purification. Precursors of the polymers are tabulated with H<sub>2</sub> permeability (barrer) and selectivities of H<sub>2</sub>/CO<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>, and H<sub>2</sub>/CH<sub>4</sub>. Properties of the precursors are reported, including cellulose derivatives, polyimides,

polyetherimides, phenolic resins and analogous compounds, polyfurfuryl alcohol, polyphenylene oxide, etc. Hydrogen-related carbon molecular sieve membrane reactors are also tabulated in this chapter. Information including the types of precursors, catalysts involved, types of reaction, and temperature is shown in the table. Photos of single tubes and pilot scale membrane reactors are demonstrated to enhance readers' understanding of the application. The information serves as an important guideline for researchers interested in obtaining purified hydrogen as a renewable energy source at high temperatures.

Chapter 8 discusses the application of carbon membranes for liquid mixture separation, involving microfiltration, ultrafiltration, and nanofiltration. The production process for carbon membranes is reported, starting from precursor selection, membrane formation, pyrolysis, and modification. Chemical vapor deposition and compression technology are also reported as alternative ways of generating carbon membranes for liquid mixture separation. The coating methods for the pyrolysis process are described, including spin-coating, cast-coating, and dip-coating. Additionally, different vital aspects are discussed in this chapter, including pores and surface modification, as well as pores formation using the template method. An antifouling study is also covered, mainly focusing on pore fouling and cake filtration. The application of the membrane in membrane filtration, process integration, membrane

bioreactors, and energy production is discussed. It is reported that carbon membranes can achieve more than 99% removal efficiency and retention of oil from an oil-in-water emulsion.

Chapter 9 discusses other applications of carbon membranes. These applications are essential for the sustainable development of carbon membranes, including CO<sub>2</sub> capture from flue gas, olefin/paraffin separation, artificial photosynthesis, and organic solvent separation. It is reported that the cost can be reduced to \$57/ton CO<sub>2</sub> avoided by improving membrane performance up to 2.5 times. Additionally, carbon membranes made from polyimide have exceeded the upper bound, showing excellent C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivities of 4 and 21, respectively. The schematic diagram for the artificial photosynthesis application is shown in this chapter. It is reported that 555.5 kW of energy is required to produce 100 Nm<sup>3</sup>/h of hydrogen.

Chapter 10, the last section of the book, discusses the future perspective of carbon membranes. Impressive points of view are analyzed, including advanced processes for carbon membrane development and novel carbonization processes. Readers can find the schematic design and detailed procedures for these processes in this chapter. The risks associated with the carbonization procedures are also discussed. The design of carbon membrane modules and operations required for upscaling are summarized. Table 2 highlights each chapter for Part 2.

**Table 2** Highlights of each chapter for Part 2

Chapters	Aspects of discussion	Some highlights of chapter
5	Biogas upgrading	-Classification of bad fibers -Challenges and suggestion related to membrane and membrane module
6	Natural gas sweetening	-Commercialized membranes -Financial approach
7	H <sub>2</sub> purification	-H <sub>2</sub> performance of precursors -H <sub>2</sub> -related carbon molecular sieve membrane reactors
8	Micro-/ultra-/nanofiltration	-Production process -Modification of pores and surfaces
9	Other applications	-CO <sub>2</sub> capture from flue gas, olefin/ paraffin separation, artificial photosynthesis and organic solvent separation
10	Future perspectives	-Advanced process for carbon membrane development -Novel carbonization process

## 2.0 FINAL REMARKS

As discussed in the book, carbon membranes show advantages over polymeric membranes in terms of chemical and thermal stability, allowing them to be applied in harsh conditions. Compared to ceramic membranes, carbon membranes have limitations under extremely harsh conditions. However, they are comparatively cheaper and easier to upscale. Therefore, niche areas for carbon membranes compared to polymeric and ceramic membranes include hydrogen purification, organic solvent separation, and CO<sub>2</sub> capture from natural gas and flue gas. Overall, the book presents a comprehensive review of carbon membrane technology, serving as a vital resource for researchers. It provides the necessary information for studies involving both fundamental and application aspects. There are a few topics not included in the book, such as the potential of carbon membranes in Industry 4.0. The aspects of additive manufacturing in the production of carbon membranes can be further explored. Additionally, detailed studies

on the geometry of membrane modules can be included in the book. The performance of the membrane system is often affected by its design, which influences its stage-cut. Furthermore, the effect of feed composition on the gas transport mechanism of the membrane can be included in the book, as it can trigger the Joule-Thomson effect, significantly impacting membrane performance.

## REFERENCES

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