

# 行政院國家科學委員會專題研究計畫 成果報告

## 碳分子篩薄膜之製備及其應用於二氧化碳氣體分離滲透性 質之研究 研究成果報告(精簡版)

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計畫主持人：曾惠馨

計畫參與人員：博士班研究生-兼任助理：Itta Arun Kumar

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# EFFECT OF MWCNTS ON POLYIMIDE BASED CARBON MEMBRANES

Hui-Hsin Tseng<sup>1</sup>, Itta Arun Kumar<sup>2</sup>

<sup>1</sup>*Department of Occupational Safety and Health, Chung Shan Medical University, Taichung 402, Taiwan*

<sup>2</sup>*Department of Environmental Engineering, National Chung Hsing University, Taichung 402, Taiwan*

\*Corresponding author: Tel.: +886 4 24730022 ext.11823; fax: +886 4 23248194. E-mail: hhtseng@csmu.edu.tw

## Abstract

A novel polyimide (PI) and multiwall carbon nanotubes (MWCNT) composited carbon molecular sieve membrane was prepared by spin-coating technique. The characteristics of the carbon membranes and single gas permeation properties of the carbon molecular sieve membranes (CMSMs) pyrolyzed at 500°C were investigated. The results indicated that modified PI based carbon membrane with MWCNT, the permeability increased 2~4 times with increasing the selectivity also. Further the membranes were extensively characterized by Field Emission Scanning Electron Microscopy (FE-SEM) for surface morphology studies. The addition of MWCNT modifier redounds to the reduction of defect in the carbon membrane and permeation of pure gases. The membrane is obtained in only one coating step, and it is constituted by a thin microporous carbon film of above 3µm in thickness which is supported on a macroporous alumina substrate.

*Keywords:* Carbon molecular sieve membrane; Gas separation; Pyrolysis; Carbon dioxide

## Introduction

Carbon molecular sieve membranes (CMSMs) are very promising materials in the field of gas separation, both in terms of separation properties (permeability and selectivity) and stability (thermal and chemical). CMSMs produced by pyrolysis of different polymeric materials (polyimide based, PVDC, phenolic resin, polyfurfuryl alcohol, etc) are characterized by a very narrow micro porosity (~3-6Å) which allows discrimination between gas molecules of different size. Polymers like polyimides are excellent precursors to obtain carbon molecular sieve films [1] and have been used extensively in the preparation of CMSMs with different configurations, e.g. hollow fibers [2], supported membranes [3-5], capillary tubes [6], and unsupported carbon flat membranes [7].

In the field of carbon membranes, it is not uncommon that a strong trade off relationship exists between the permeability and selectivity, i.e. the permeation flux

through the carbon membranes is considerably reduced as the gas selectivity increases because of the disordered pore structure and diffusion resistance membranes. To tackle this challenging issue, some strategies such as the synthesis of composite membranes by incorporating silica have been envisaged [8], but it is still far from satisfactory. To solve this challenging task, here we proposed a simple strategy to incorporate nanotubes into the membranes that could significantly improve the gas flux without losing the selectivity of membranes.

The main objective of this paper is to evaluate the use of polyimide as a precursor to prepare CMSMs. In this study we reported a preparation of CMSMs by incorporating MWCNT into the polymeric precursor polyimide in order to improve the permeation performance of membranes. Further the membranes performance for CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> gas molecules is compared with polyimide in terms of permeability and selectivity. All these membranes characterized by FE-SEM to evaluate the surface morphology.

## 2. Experiment

### 2.1. Preparation of PI/MWCNT carbon membrane

Porous  $\alpha$ - alumina disks of average pore size: 0.14  $\mu\text{m}$ , diameter: 2.3 mm, porosity: 40-48% were used as the membrane support. A commercially available polyimide (PI) polymer purchased from Alfa Acer (USA) was used as a precursor in this study. The chemical formula of polyimide (PI) is given in Fig. 1.

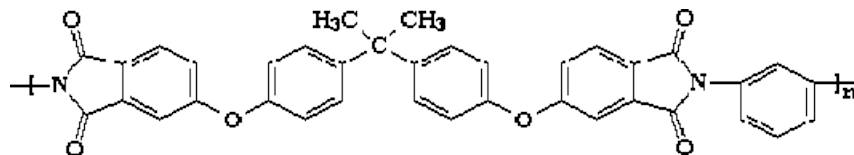


Fig. 1. Structure of polyimide.

A small quantity of dope solution containing 15wt% of polyimide (PI) in N-Methyl-2-pyrrolidone (NMP) was spread on the finely polished surface of alumina support by means of the spin coating technique (spin velocity 5000 rpm, spin time ~15), resulting in a thin film of the polymeric layer on the support. The coated polymeric film was immediately immersed into a coagulant bath consisting of isopropyl alcohol (IPA)-water (1:1 ratio) at room temperature (~25°C) for approximately for 2 h. The gelled polymeric layer was dried in air at room temperature and carbonized under vacuum by heating up to 500°C (heating rate 0.5°C /min) for 1 h. The carbonized samples were cooled slowly in vacuum to room temperature. For preparing the PI/MWCNT mixed matrix coating solution, 1.5g of MWCNT were dispersed in 98.5ml of NMP solvent with ultrasonic dispersion for 2h. 1ml of this nanotube solution was mixed with required amount of 15% PI polymer solution in 1:25 ratio and stirred constantly for 3h at 80°C. Thus the prepared polymer/MWCNT solution was coated on an alumina supported disks by above

procedure. The coated membranes were also kept in IPA-water bath. The membranes obtained by above process were carbonized at the same conditions.

## 2.2. Gas permeation measurement

The permeation characteristics of pure gas through the carbon membranes were measured by the slope of the downstream pressure versus time plots after steady state had been reached using follow equation:

$$P = \frac{dp}{dt} \left( \frac{V \cdot T_0 \cdot L}{p_0 \cdot T \cdot \Delta p \cdot A} \right)$$

where P is the permeability in Barrer (1 Barrer =  $1 \times 10^{-3}$  cm<sup>3</sup> (STP) cm/(cm<sup>2</sup>s cmHg)), dp/dt the rate of pressure rise at the steady state, V(cm<sup>3</sup>) the downstream volume, L (cm) the membrane thickness,  $\Delta p$  (cmHg) the pressure difference between the two sides, T(K) the measurement temperature, A (cm<sup>2</sup>) the effective area of the membrane, and  $p_0$  and  $T_0$  the standard pressure and temperature, respectively. The ideal separation factor of a membrane for gas A to gas B is expressed by:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

## 2.3. Physical characterization of CMSM

The CMSM was characterized with scanning electron microscope (FESEM, Philips XL30 field-emission scanning electron microscope), and N<sub>2</sub> adsorption (Micromeritics ASAP 2010).

# 3. Results and discussion

## 3.1. Membrane structure

Fig. 1 shows the FE-SEM images of surface view and cross-section of CMSM obtained by spin coating of 15% PI solution modified with/without MWCNT. Fig. 1(a) shows the top view of the PI-based carbon membrane. Fig. 1(b) shows the cross-section of supported CMSM obtained after carbonization of a supported PI film. Two different parts can be distinguished, the carbon membrane layer and the macroporous carbon support. This supports that the rapid coagulation of polymer prevents the infiltration of solution into the porous alumina support, and an excellent polymeric film was achieved. The carbon film is a thin layer having a thickness around 3-4  $\mu\text{m}$ . The FE-SEM micrograph with high amplification ratio of Fig. 1(b), see Fig. 1(c), demonstrates that the carbon membrane is a dense film having closed pores. Therefore, even the membrane

prepared by this one coating-time method could be find many pore from the top vies, the gases having different molecular size still can separated by molecular sieving mechanism. SEM picture of the surface of the PI/MWCNT membrane were shown in Fig. 1(d). The MWCNT were difficult to see in the microscope and therefore assumed to be well distributed.

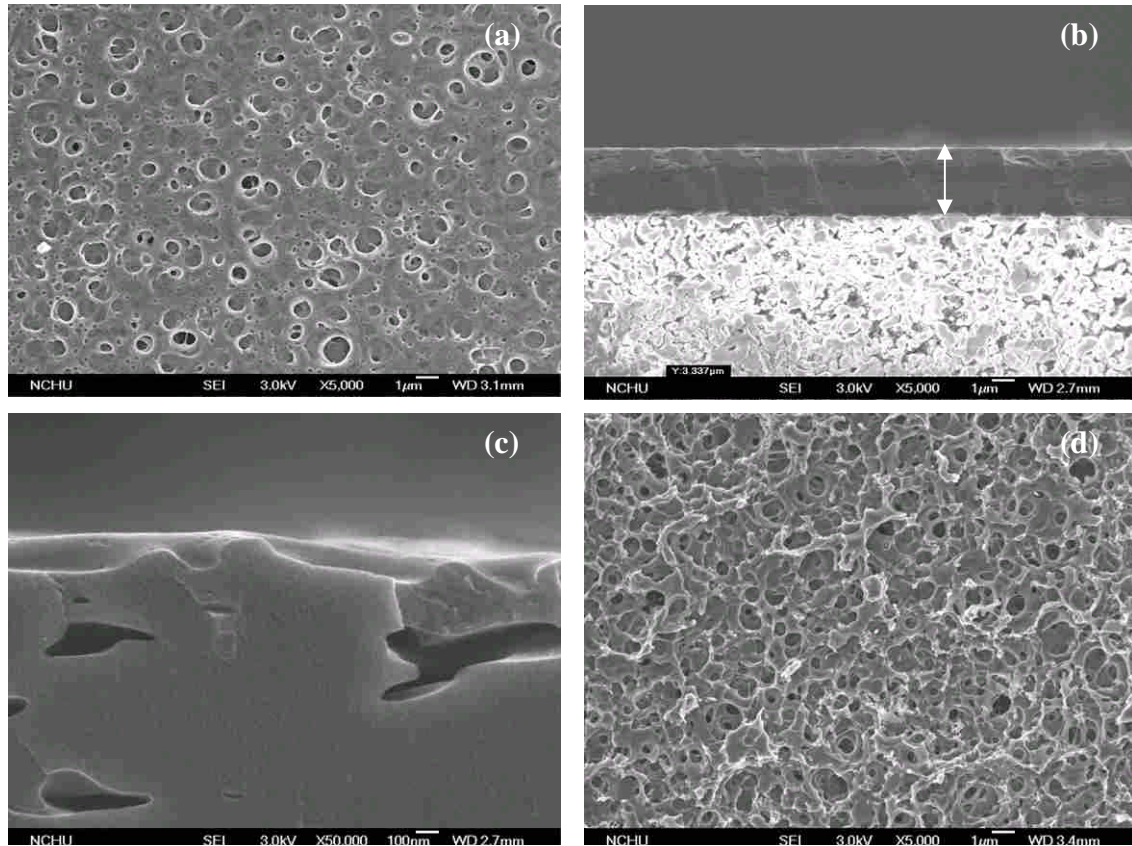


Fig. 1. SEM microphotographs of carbon membrane: (a) top view, and (b) cross-section, (c) magnification part of (b) of PI based CMSM; (d) top view of PI/MWCNT based CMSM.

### 3.2. Permeation measurements

From the results, as shown in Fig. 2, at 500 °C the gas permeability increases as the kinetic diameter of the gas molecule decreases, from N<sub>2</sub> to CO. All these facts indicate that the transport of gas molecules through the carbon film takes place according to a molecular sieve mechanism. This means that the microporosity of the carbon film is very narrow and as a consequence, it can discern between gas molecules depending on their molecular size.

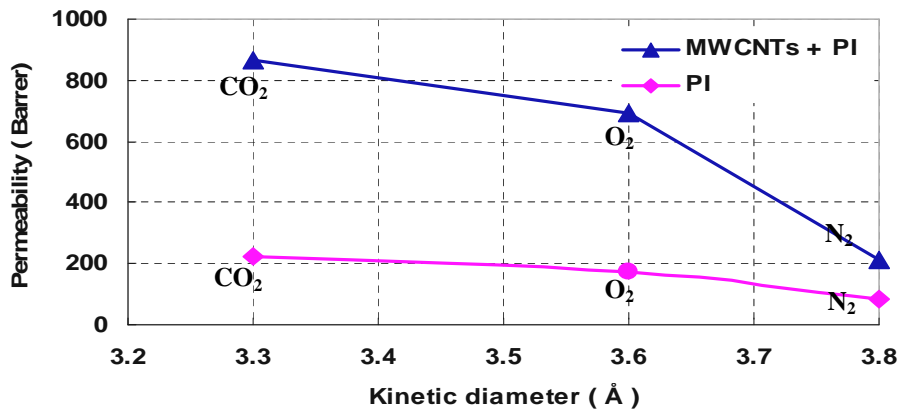


Fig. 2. Comparison of PI and PI/ MWCNTs CMS membranes with different gas molecules sizes

In addition of MWCNTs in PI predicted that the transport of gases inside nanotubes is order of magnitude faster than in any other known materials with nanometer scale. The rapid transport rates exist because the walls of nanotubes are much smoother than the other materials (see Table 1). These experiments show that the carbon nanotube membranes can have spectacularly high fluxes. In the present case PI/nanotube CMS membranes also increases permeability of single gas molecules rapidly compared to the PI based CMS membranes.

Table1. Permselectivity values of PI and PI/MWCNTs of different gases

Sample code	Permeability (Barrer)			Selectivity		
	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /O <sub>2</sub>
PI	222.89	172.66	84.05	2.65	2.05	1.29
PI/MWCNTs	866.64	694	213.47	4.05	3.25	1.27

#### 4. Conclusions

PI/MWCNT composite membranes with excellent gas separation performance were prepared by incorporating MWCNTs into a polymer carbon matrix. The results of these membranes were compared with PI CMS membranes. SEM images of the synthesized membranes suggested that many pores formed on the surface to pass the different gas molecules. Gas permeation tests were conducted with single gas molecules CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> and the efficiency of the CMS membranes were evaluated in terms of permeability and selectivity. The gas permeability increases after adding MWCNTs to the polymer precursor due to the abundant micro channels brought by nanotubes. Therefore the nanotubes offered a favorable effect in increasing gas permeability by decreasing the gas diffusion resistance

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## 研究成果自評

本研究內容與原計畫相符、所有預期目標皆已達成；研究成果因添加奈米碳管對碳分子篩選薄膜作改質，而有效地提升氣體的滲透率與選擇率，因此不論就學術成或應用價值，皆適合在學術期刊發表或申請專利。目前已將研究成果投稿至 DESALINATION 期刊審查中，專利申請亦在準備中。

## 出席國際學術會議心得報告

計畫編號	95-2221-E-040-007-
計畫名稱	碳分子篩薄膜之製備及其應用於二氧化碳氣體分離滲透性質之研究
出國人員姓名	曾惠馨
服務機關及職稱	中山醫學大學/職業安全衛生學系暨碩士班
會議時間地點	September 2-6, 2007; Siófok, Hungary
會議名稱	PERMEA 2007 MEMBRANE SCIENCE AND TECHNOLOGY CONFERENCE OF VISEGRAD COUNTRIES
發表論文題目	Preparation and characterization of carbon molecular sieve membrane for gas separation application- the effects of polymeric precursor

### 一、參加會議經過

研究人員此次前往匈牙利，參加由匈牙利化學協會於 2007 年九月二日至六日所舉辦的「PERMA 2007：薄膜科學與技術研討會」(PERMA 2007: Membrane Science and Technology Conference of Visegrad Countries)。

該薄膜科學與技術研討會係由捷克共和國、匈牙利、波蘭及斯洛伐克等 Visegrád 國家所舉辦的系列研討會之一，每二年舉辦一次，其組織與委員會如下表所示：

Organizers	Organizing Committee	Scientific Committee
Hungarian Chemical Society	Békássy-Molnár, E. (Hungary) – Chair	Bryjak, M. (Poland)
Czech Society of Chemical Engineers	Bélafi-Bakó, K. (Hungary) -- Co-Chair	
Polish Chemical Society	Bleha, M. (Czech Republic)	
Slovak Society of Chemical Engineers	Bodzek, M. (Poland)	
	Schlosser, S. (Slovakia)	
	Bryjak, M. (Poland)	

近年來，由於薄膜程序於發展綠色技術、水處理及環境保護等領域中，係相當受矚目之工程技術，因此該研討會相當歡迎從事薄膜相關領域之研究學者、學生及業界工程師等共同參與，期望能提供從事薄膜相關之研究人員的國際交流機會。

### 二、與會心得

討論的議題共分為：水及廢水處理 (water and waste water treatment)、薄膜反應器與生物反應器 (membrane reactors and bioreactors)、燃料電池與離子選擇性薄膜 (fuel cells and ion selective membranes)、薄膜接觸器 (pertraction and membrane contactors)、氣體與揮發性有機化合物的分離 (gas and VOC separation)、特殊膜材 (novel membranes)、傳



輸與薄膜積垢 (transport and membrane fouling)、電鍍薄膜程序 (electromembrane processes)、複合程序 (hybrid processes)、滲透蒸發 (pervaporation)、食品與飲料的應用 (food & beverage applications) 等十一個主題，與會者均可全程參與，瞭解各方面的趨勢與發展。以下依據與研究人員較相關之研究領域的各主題討論內容之心得作一綜合性摘要。

1. 燃料電池與離子選擇性薄膜方面：近年來質子交換膜燃料電池，因，而被視為最具發展潛力之燃料電池，然目前仍面臨下列問題：(1)因氫氣儲存技術：一般使用高壓鋼瓶或儲氫合金，但有成本、重量、安全性等不利因素；(2)成本高：其觸媒層所使用的貴金屬-鉑其費用和供貨不確定性增加成本；(3)氫的來源：重組後的燃料內含有一氧化碳和其他污染物；(4)氧還原反應的效率低：受到觸媒載體性質、合成方法等許多因素的影響。而在此次會議發表的論文中，有多篇皆與該主題有關，並提出下列方法，以解決目前質子交換膜燃料電池所面臨的問題：(1)使用雙金屬觸媒如：Pt-Ru、Pt-Sn；(2)金屬觸媒中加入氧化物，如：ZrO<sub>2</sub>、CeO<sub>2</sub>；(3)先行將重組器所產生的燃料，經過附有觸媒及少量 O<sub>2</sub> 或空氣的反應槽；(4)添加少量的氧化劑一起進入陽極，產生氫氧根，把附著在鉑表面的 CO 氧化成 CO<sub>2</sub> 等。因此在薄膜中添加金屬觸媒以提升對 H<sub>2</sub> 的選擇率則為較新穎之研發技術。
2. 氣體與揮發性有機化合物的分離方面：就與會中所發表之論文而言，現今較常應用於氣體與揮發性有機化合物分離的薄膜材料包含有高分子薄膜、及以沸石、金屬為基礎的無機薄膜，而與本人研究相關的碳分子篩選膜則僅見一篇。其應用領域除富氮或富氧之氣體分離外，引發的溫室效應之氣體的分離，或提升替代性能源氣體之純度，亦為日後應用之重點方向。
3. 滲透蒸發方面：近年來由於替代能源之漸受重視，及半導體場所產生的大量有機廢溶劑等問題，因此利用滲透蒸發技術，將有機溶劑與水分離之技術已漸受重視，其因下列特色，而具有取代傳統化工程序中蒸餾分離之潛力，

三. 攜回資料：論文摘要一本、論文全文光碟一片、識別證。