Gas permeation properties and preparation of carbon membrane by PECVD method using indene as precursor

M Kyaw\textsuperscript{1,3,4}, N P. Dugos\textsuperscript{1}, S Mori\textsuperscript{2}, S A. Roces\textsuperscript{1} and A B. Beltran\textsuperscript{1}, S Suzuki\textsuperscript{2}

\textsuperscript{1}Chemical Engineering Department, De La Salle University, 2401 Taft Ave, Manila 0922, Philippines
\textsuperscript{2}Department of Chemical Engineering, Tokyo Institute of Technology, Tokyo 152-8552, Japan
\textsuperscript{3}Department of Chemical Engineering, Mandalay Technological University, Mandalay, Myanmar

E-mail: myatkyaaw@gmail.com

Abstract. This work could demonstrate a new approach to the fabrication of gas separation membrane using indene as polymeric precursor for low pressure PECVD system. Membrane characterization was done by taking Scanning Electron Microscopy (SEM) and FTIR measurements. For membrane performance testing, permeability and selectivity of the membrane were evaluated with pure gases of H\textsubscript{2}, N\textsubscript{2}, and CO\textsubscript{2} using a differential permeation technique. PECVD-derived polyindene membrane showed selectivities of 8.2 and 4.0 for H\textsubscript{2}/CO\textsubscript{2} and H\textsubscript{2}/N\textsubscript{2}, respectively, at room temperature. Polyindene (PIn) membrane was successfully fabricated onto a zeolite 5A substrate via radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD) at room temperature.

1. Introduction
Membranes in gas separation has been applied because of its advantages such as low energy requirement and low operating cost. In this perspective, the interest on inorganic membranes such carbon membrane for gas separation has also grown for showing higher selectivity and remarkable high thermal and chemical resistances \cite{1}. Generally, a carbon membrane is fabricated by the pyrolysis of an organic precursor and this membrane shows very good molecular sieving effect in gas separation \cite{2}. Normally, membrane fabrication via pyrolysis technique can be done at processing temperature of 500°C and above \cite{1}. For instance, Teixeira et al. fabricated supported carbon membrane using phenolic resin solution by pyrolysis technique with heating up to 900°C under nitrogen atmosphere. In their research work, the resultant membrane showed significant performance in terms of gas separation and selectivity \cite{3}. In this method, it needs high temperature to decompose the polymeric precursor in membrane fabrication process.
Another effective method to manufacture a carbon membrane which is done at low temperature is plasma-enhanced chemical vapor deposition (PECVD) [1]. PECVD is a kind of CVD in which plasma is utilized as the energy source. The use of plasma can increase the reactivity of monomers to deposit thin films and as a consequence of this, varieties of material can be utilized as precursors for membrane fabrication [4]. Therefore, interest on utilizing PECVD in the synthesis of inorganic membrane is increasing since PECVD can be processed at low temperature [1]. For instance, some research groups already did fabrication of carbon membranes at room temperature via PECVD method using hexamethyldisiloxane (HMDSO) [5], hexamethyldisilazane [6] and propylene [1] as precursors. Since the resultant membranes showed remarkable selectivities of gases, PECVD has become an attractive and a promising technique to fabricate carbon membranes for gas separation. However, most of carbon membrane fabrication was done using silicon-based materials as precursors. Therefore, it is also important to explore more precursors as a carbon source in PECVD method to fabricate inorganic membranes for gas separation.

The interest on polymeric systems which have aromatic backbones has grown since the product membranes by using aromatic polymers demonstrated an improvement in permeability [7]. Indene (In) is a polycyclic hydrocarbon which is comprised with a benzene ring. Moreover, In is readily polymerized with an acidic catalyst to give polymers. Goel et al. reported a simple chemical approach to create one dimensional polyindene (Pn) nanofiber by the use of a single step cationic polymerization reaction [8]. Kanaoka et al. also showed that In can be polymerized in a living fashion to prepare random copolymers with high molecular weight [9]. Pn became an attractive and significant polymeric material in the previous couple of years because of its cyclic structure and for showing a planar conformation and high glass transition temperature after polymerization [9]. Nevertheless, regardless of its proven exceptional characteristics, the synthesis of In as a gas barrier film is still an unexplored area and no attempt has yet been made to fabricate Pn as a gas barrier film. Fabrication of Pn as a gas barrier film using PECVD method and studying its gas separation properties will fulfil the desire to generate new candidates for gas separation membrane.

In this study, we report the successful fabrication of PIn membrane prepared by using a radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) system. Moreover, characterization and gas barrier properties of deposited film and their selectivities are also presented.

2. Materials and Method

Zeolite 5A was obtained from GL Science Japan and was used as substrate material without any treatment. 1st Grade Indene (In) was purchased from Wako Chemical Company and utilized as precursor for carbon source. For generating plasma source, Dressler Cesar® RF Power Generator was used.

To determine effective pore sizes of membrane, Normalized Knudsen-based permeance (NKP) method was used as given in Equation (1) [1]. In this work, hydrogen (H₂) was utilized as a standard gas and it denotes as “S”.

\[
f_{NKP} = \frac{P_i}{M_i P_S} \sqrt{\frac{M_S}{M_i}}
\]  
(1)

According to the modified gas-translation model [1], the gas permeance for the \(i\)th component, \(P_i\), through the microporous membrane can be expressed by Equation (2).

\[
P_i = \frac{\varepsilon}{3\pi L} \left( \frac{d_p - d_i}{d_p} \right)^2 \sqrt{\frac{8}{\pi M_i RT}} \exp \left( -\frac{E_{P_i}}{RT} \right)
\]  
(2)

By introducing Equation (2), Equation (1) can be simplified as follows:
\[
f_{\text{NKP}} = \frac{P_i}{M_s P_S} \frac{(d_p - d_i)^3}{(d_p - d_S)^3} \exp \left( -\frac{E_{P,i} - E_{P,S}}{RT} \right)
\]

Assuming all of the gases diffuse within uniform pores and neglecting the activation energy differences in gas permeation, Equation (3) can be cut down as follows:

\[
f_{\text{NKP}} = \frac{P_i}{M_s P_S} \frac{(d_p - d_i)^3}{(d_p - d_S)^3}
\]

The effective pore size can, therefore, be calculated approximately fitting the attained \( f_{\text{NKP}} \) with Equation (4).

2.1. Experimental procedure
Firstly, zeolite 5A (3.2 mm \( \oplus \) 2 mm) was fabricated on glass tube and set up in PECVD system. As shown in Figure 1, PECVD was operated in a reactor equipped with an RF coil operated at 13.56 MHz and power was stable at 20W. Indene (In) was supported into the reactor at flow rate of 0.2 sccm. The flow rate of In was controlled by the flow rate of Ar carrier gas (2 sccm) and the pressure and temperature of the bubbler (1 kPa and 20\(^\circ\)C, respectively). The pressure in the reactor was stable at 30 Pa throughout the plasma deposition. The gas separation performance of the plasma-derived polyindene (PI\(_n\)) membrane were evaluated by using a differential permeation technique at room temperature.

3. Results and Discussions
Figure 2 shows the scanning electron microscopy (SEM) images of surface and side view of PI\(_n\) layer growth after 1.5 hr deposition. The plasma-deposited layer was continuous and it has sponge and liquid film structure. Moreover, there was no obvious defect on its layer and the adhesion between zeolite 5A substrate and deposited polyindene layer was also strong. Thickness of finalized 1.5 hr deposited polyindene layer was approximately 20 \( \mu \text{m} \).
Figure 2. SEM images of (a) the surface and (b) the cross-section of a RF-PECVD-derived polyindene membrane deposited onto a zeolite 5A substrate.

Figure 3 shows FT-IR spectra characterized for indene (monomer) and the PECVD-derived PIn film. The FT-IR spectra of PECVD-derived PIn film shows broad peaks and C-H stretch are prominent. The additional peak was observed at 1708 cm\(^{-1}\) and it showed poly-indene has conjugated aldehydes and ketones (C=O). Normally, band for aldehydes and ketones can be observed at 1720 cm\(^{-1}\). But, because of the presence of a conjugated bond or an aromatic ring, the band’s frequency may be lower by 20-30 cm\(^{-1}\). In this case, plasma polymerized indene (PIn) contains aromatic rings according to the band at 3016 cm\(^{-1}\). Therefore, band for C=O stretch was observed at the lower frequency of 1708 cm\(^{-1}\). The main CH stretching band of the aromatic ring lies at 3024 cm\(^{-1}\). The band at 3028 cm\(^{-1}\) is combinations of the CH frequencies in the range of 1600-1800 cm\(^{-1}\). The strong 2845 and 2939 cm\(^{-1}\) bands are the characteristic stretching frequencies of the CH\(_2\) group. The larger frequency represents the unsymmetrical mode, and the lower frequency represents the
symmetrical one. The 1456 cm\(^{-1}\) bending mode for aromatic C=C stretch is also strong. The C=C stretching vibration of aromatic ring is represented by a band at 1458 cm\(^{-1}\). Based on FT-1R results, there are sufficient polar sites in the plasma deposited indene film for preferential interaction and sorption of polar CO\(_2\) gas. There is also the strong CH stretch, aromatic out-of-plane bend, lies at 754 cm\(^{-1}\) in fingerprint region.

Table 1 and Figure 4 show the single gas permeance of H\(_2\) (kinetic diameter, d\(_{\text{H}_2}\)=0.289 nm), N\(_2\) (0.36 nm), and CO\(_2\) (0.33 nm) at 25 °C for a RF-PECVD-derived carbon membrane as a function of plasma-deposition time. It is shown (Table 1, Figure 4 and 5) that the permeance with a deposition time of 0 indicates the permeance of zeolite 5A substrate before the plasma-deposition.

Table 1. Permeance of single gases at 25°C with deposition time.

| Deposition time (hr) | Permeance (mol/m\(^2\)/s/Pa) | Separation factor | (H\(_2\)/CO\(_2\)) | (H\(_2\)/N\(_2\)) |
|---------------------|-------------------------------|------------------|------------------|------------------|
|                     | H\(_2\) | N\(_2\) | CO\(_2\) |                     |                  |
| 0                   | 5.02\(\times\)10\(^{-6}\) | 1.62\(\times\)10\(^{-6}\) | 1.32\(\times\)10\(^{-6}\) | 3.8 | 3.1 |
| 0.5                 | 3.25\(\times\)10\(^{-6}\) | 1.03\(\times\)10\(^{-6}\) | 8.56\(\times\)10\(^{-7}\) | 3.8 | 3.2 |
| 1                   | 3.31\(\times\)10\(^{-7}\) | 1.01\(\times\)10\(^{-7}\) | 7.06\(\times\)10\(^{-8}\) | 4.7 | 3.3 |
| 1.5                 | 3.83\(\times\)10\(^{-8}\) | 9.59\(\times\)10\(^{-9}\) | 4.67\(\times\)10\(^{-9}\) | 8.2 | 4.0 |

Figure 5 shows the separation factor for H\(_2\)/CO\(_2\) and H\(_2\)/N\(_2\) systems which were calculated based on permeance ratios of H\(_2\)/CO\(_2\) and H\(_2\)/N\(_2\), respectively. The polyindene (PI\(_n\)) membrane showed lower permeances of gases and higher selectivity as deposition time was prolonged. In the case of 0.5 hr deposited PI\(_n\) membrane, it indicated a H\(_2\) permeance of 3.25\(\times\)10\(^{-6}\) mol/m\(^2\).s.Pa. In the subsequent deposition, the permeance of H\(_2\) decreased from 5.02\(\times\)10\(^{-6}\) mol/m\(^2\).s.Pa to 3.83\(\times\)10\(^{-8}\) mol/m\(^2\).s.Pa after 1.5 hr deposition. Moreover, separation factor for H\(_2\)/CO\(_2\) and H\(_2\)/N\(_2\) increased to 8.2 and 4.0, respectively after 1.5 hr deposition.

The Knudsen ratio of gases compared to experimental permeance ratios of gases can be seen in Table 2. The permeance ratio and Knudsen ratio of H\(_2\)/N\(_2\) showed a small difference and it was nearly the same at 4.0 and 3.73, respectively. Based on the comparison, it proposes that the diameter of the pores in the membrane surface is larger than the kinetics diameter of H\(_2\) (0.289 nm) or N\(_2\) (0.36 nm). Therefore, for H\(_2\)/N\(_2\), it can be assumed that Knudsen diffusion dominates over permeance for the permeation of these gases through the membrane. In the case of the permeance of CO\(_2\), even though the kinetic diameter of CO\(_2\) is smaller than that of N\(_2\), the permeance of CO\(_2\) was lower than that of N\(_2\). This suggests that the permeation of CO\(_2\) is governed by molecular sieving effect or gas translation model in which an interaction of CO\(_2\) molecules with the polyindene layer can also be expected.

Table 2. Permeance ratio of gases of 1.5 hr deposited membrane and ideal Knudsen ratios of gases.

| Gas pair | Knudsen ratio of gases | Permeance ratio of gases (Experimental) |
|----------|------------------------|---------------------------------------|
| H\(_2\)/N\(_2\) | 3.73                  | 4.0                                   |
| H\(_2\)/CO\(_2\) | 4.67                  | 8.2                                   |
In Figure 6, the single gas permeances of the polyindene membrane at its respective deposition times are marked with the kinetic diameter of gases and permeances of gases decreased as deposition time was prolonged.
Figure 6. Single gas permeance at 25°C for a PECVD-derived polyindene membrane as a function of the kinetic diameter of gases.

Since the permeance of the evaluated gases follow the order of CO$_2$ (0.33) < N$_2$ (0.364) < H$_2$ (0.289), this shows that the effective pore size of polyindene layer was larger than the kinetic diameter of H$_2$. Based on the normalized Knudsen-based permeance (NKP), the effective pore size of the plasma-deposited polyindene membrane was about 0.35 nm. Thus, the permeation of H$_2$ and CO$_2$ happened mainly through the membrane matrix while the permeation of N$_2$ was through the grain boundaries.

Diffusivities and permeabilities of gases through finalized membrane (1.5 hr deposited membrane) are summarized in Table 3. As shown in Table 3, CO$_2$ has the smallest diffusion coefficient while H$_2$ has the highest diffusion coefficient.

Table 3. Diffusion coefficients and permeabilities of gases relate to the finalized plasma-derived PIn membrane.

| Parameter       | Symbol | Unit         | Diffusion coefficient |
|-----------------|--------|--------------|-----------------------|
| Diffusion       | D      | m$^2$/s      | H$_2$ 5.05×10$^{-9}$  |
|                 | D      |              | CO$_2$ 6.14×10$^{-10}$ |
|                 | D      |              | N$_2$ 1.26×10$^{-9}$  |

|            | P      | Barrer       | Permeability |
|------------|--------|--------------|--------------|
| H$_2$      | P      |              | 2,293        |
| CO$_2$     | P      |              | 279          |
| N$_2$      | P      |              | 573          |

The correlation diagram known as the Robeson plot [10] is frequently used to compare the permeability and selectivity of a new membrane. Figure 7 and 8 show the combined the Robeson upper bound data with the experimental data of H$_2$/CO$_2$ and H$_2$/N$_2$ separation, respectively.
As shown in Figure 7, permeability of H$_2$ (2,293 Barrer) and selectivity (8.2) of H$_2$/CO$_2$ in PIn film are well comparable to the permeability and selectivity of the best polymeric membranes. The polyindene film shows trade-off between membrane permeability and
selectivity for H₂/CO₂ separation. Hence, it offers upper bound properties at the high permeability end of the upper bound. But, in case of H₂/N₂ separation as shown in Figure 8, although the permeability of H₂ (2.293 Barrer) in PIn is high enough, selectivity (4.0) of H₂/N₂ is situated below the upper bound line. It means PIn film has no trade-off between permeability and selectivity for H₂/N₂ separation.

4. Conclusion
Polyindene carbon membranes were fabricated onto a zeolite 5A substrate using a radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD) system at room temperature. The plasma-deposited PIn layer was continuous and there was no significant defect on its layer. Moreover, the additional stretch of conjugated aldehydes and ketones which is favorable for the interaction of CO₂ and the membrane matrix was observed in plasma deposited PIn layer. The resultant membrane showed ideal selectivities of 4.0 and 8.2 for H₂/N₂ and H₂/CO₂, respectively at 25 °C. According to the Robeson plot, this membrane shows trade-off between membrane permeability and selectivity and offers upper bound properties at the high permeability end of the upper bound. This work revealed a unique approach to the fabrication of gas separation membrane at low temperature.

References
[1] Nagasawa H, Kanezashi M, Yoshioka T and Tsuru T 2016 Plasma-enhanced chemical vapor deposition of amorphous carbon molecular sieve membranes for gas separation RSC Adv. 6 59045–9
[2] Hamm J B S, Ambrosi A, Griebeler J G, Marcilio N R, Tessaro I C and Pollo L D 2017 Recent advances in the development of supported carbon membranes for gas separation Int. J. Hydrogen Energy 42 24830–45
[3] Teixeira M, Rodrigues S C, Campo M, Pacheco Tanaka D A, Llosa Tanco M A, Madeira L M, Sousa J M and Mendes A 2014 Boehmite-phenolic resin carbon molecular sieve membranes-Permeation and adsorption studies Chem. Eng. Res. Des. 92 2668–80
[4] Vasudev M C, Anderson K D, Bunning T J, Tsukruk V V and Naik R R 2013 Exploration of plasma-enhanced chemical vapor deposition as a method for thin-film fabrication with biological applications ACS Appl. Mater. Interfaces 5 3983–94
[5] Roualdes S, Sanchez J and Durand J 2002 Gas diffusion and sorption properties of polysiloxane membranes prepared by PECVD J. Memb. Sci. 198 299–310
[6] Kafrouni W, Rouessac V, Julbe A and Durand J 2009 Synthesis of PECVD a-SiCXNY:H membranes as molecular sieves for small gas separation J. Memb. Sci. 329 130–7
[7] Yampolskii Y 2012 Polymeric Gas Separation Membranes Macromolecules 45 3298–311
[8] Goel S, Mazumdar N A and Gupta A 2010 One-dimensional nanofibers of polyindene: Synthesis and characterization J. Polym. Res. 17 639–45
[9] Abdul Karim S M, Nomura R and Masuda T 2002 Cationic copolymerization of indene with styrene derivatives: Synthesis of random copolymers of indene with high molecular weight J. Polym. Sci. Part A Polym. Chem. 40 2449–57
[10] Robeson L M 2008 The upper bound revisited J. Memb. Sci. 320 390–400

Acknowledgments
The authors gratefully acknowledge the financial support of the Japan International
Cooperation Agency (JICA) through the ASEAN University Network/Southeast Asia Engineering Education Development Network (AUN/SEED-Net), De La Salle University and Tokyo Institute of Technology.