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Plasma-Enhanced Chemical Vapor Deposition of Indene for Gas Separation Membrane

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Polyindene (PIn) membrane was fabricated onto a zeolite 5A substrate by using plasma-enhanced chemical vapor deposition (PECVD) at low temperature. Membrane characterization was done by taking Scanning Electron Microscopy (SEM) and FT-IR measurements and the new peak was found in the plasma-derived PIn film. Membrane performance was analyzed by checking permeability of pure gases (H_2, N_2, and CO_2) through the membrane. PECVD-derived PIn membrane showed high gas barrier properties and selectivities of 8.2 and 4.0 for H_2/CO_2 and H_2/N_2, respectively, at room temperature.

Keywords: Indene, Carbon membrane, PECVD, Gas separation

INTRODUCTION

Membrane technology and gas separation membranes have been applied in hydrogen purification (Tseng et al. 2016), carbon dioxide capture (Haider et al. 2018; Wang et al. 2015), oxygen enrichment (Li & Huang 1997), and hydrocarbon separation (Semenova 2004) because of its advantages such as low energy requirement and low operating cost (Ismail & Li, 2008). In this perspective, the interest on inorganic membranes such as carbon membrane for gas separation has also grown for showing higher selectivity and remarkable high thermal and chemical resistances. Generally, a carbon membrane is fabricated by the pyrolysis of an organic precursor and the resultant membrane shows the significant molecular sieving effect in gas separation (Nagasawa et al. 2016). However, the processing temperature of carbonization in the membrane fabrication process via pyrolysis technique is pretty high and it is usually well above 500°C. Another possible effective method to manufacture a carbon membrane is applying plasma-enhanced chemical vapor deposition (PECVD) technique in membrane fabrication. PECVD is a kind of CVD in which plasma is utilized as the energy source and the process can be done at low temperature (Nagasawa et al. 2017). The use of plasma can increase the reactivity of monomers to deposit thin films. As a consequence of this, varieties of material can be utilized as precursors for membrane fabrication (Vasudev et al. 2013). Therefore, interest on utilizing of PECVD in the synthesis of inorganic membrane has been increasing and some research groups already demonstrated fabrication of membrane via PECVD technique (Kafrouni et al. 2009; Nagasawa et al. 2017; Roualdes, Sanchez & Durand 2002).

The attention on polymeric systems which have aromatic backbones has grown since the product membranes demonstrated an improvement in permeability (Yampolskii 2012). Indene (In) is a polycyclic hydrocarbon which includes a benzene ring. It can be smoothly polymerized to give polymer with the aid of acidic catalyst (Brum, Laux, & Forte 2013). Goel et al. reported a simple chemical approach to create one dimensional polyindene (PIn) nanofiber by the use of a single step cationic polymerization reaction (Goel, Mazumdar & Gupta 2010). Moreover, In can also be polymerized in a living fashion to prepare random copolymers with high molecular weight. In 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 (Abdul Karim, Nomura & Masuda 2002). 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 PIn as a gas barrier film. Fabrication of PIn film as a gas barrier layer using PECVD method and studying its gas separation properties will fulfil the desire to generate new candidates for gas separation membrane.

Herein, we report successful fabrication of polyindene (PIn) membrane on zeolite 5A substrate prepared via PECVD at low temperature. Moreover, characterization of deposited film and permeabilities of gases through PIn film and their selectivities are also presented.

MATERIAL AND METHOD

Material

In this work, 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.

Experimental Procedure

Firstly, the substrate was fabricated on glass tube and set up in PECVD system. As shown in Fig. 1, PECVD was organized in a reactor supplied with an RF coil run at 13.56 MHz and power was stable at 20 W. Indene (In) was transported to the reactor at the flow rate of 0.2 sccm. The flow rate of In was controlled by the flow rate of Ar carrier gas (2 sccm). The pressure and temperature of the bubbler were at 1 kPa

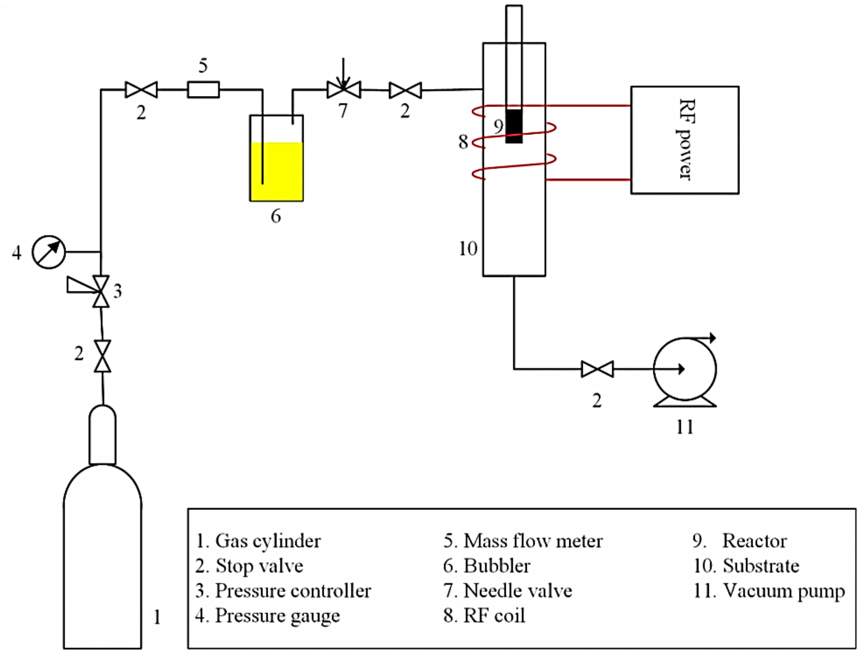
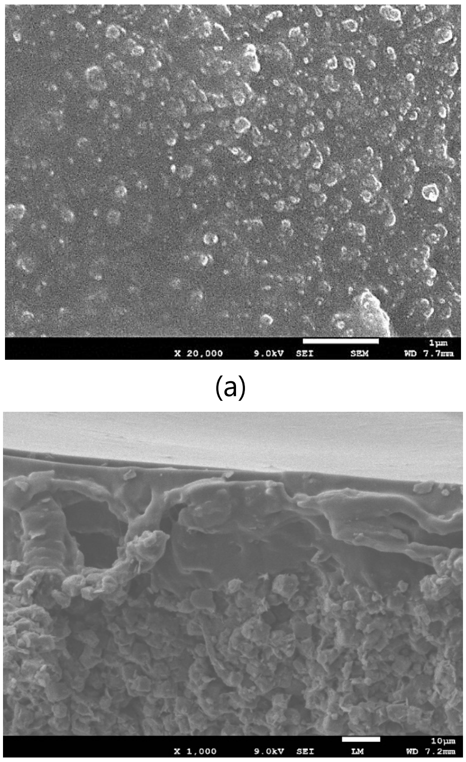


Fig. 1: Schematic diagram of the PECVD equipment

and 20°C, respectively. The pressure in the reactor was maintained at around 30 Pa throughout the deposition process. Pure gas permeation through the PIn membrane was done at room temperature by using custom gas filtration equipment.



(a)

(b)

Fig. 2: SEM image of (a) the surface view (scale bar is 1µm) and (b) the cross-sectional view (scale bar is 10µm) of an indene deposited film

RESULTS AND DISCUSSION

Fig. 2 shows the scanning electron microscopy (SEM) images of surface and side view of PIn layer growth after 1.5 hr deposition. Scanning electron microscope (SEM) revealed that the plasma-derived PIn layer was continuous and showed a liquid film structure. The PIn layer coated the whole surface of substrate layer with no obvious cracks. The thickness of the PIn layer was about 20 µm after 1.5 hr of deposition.

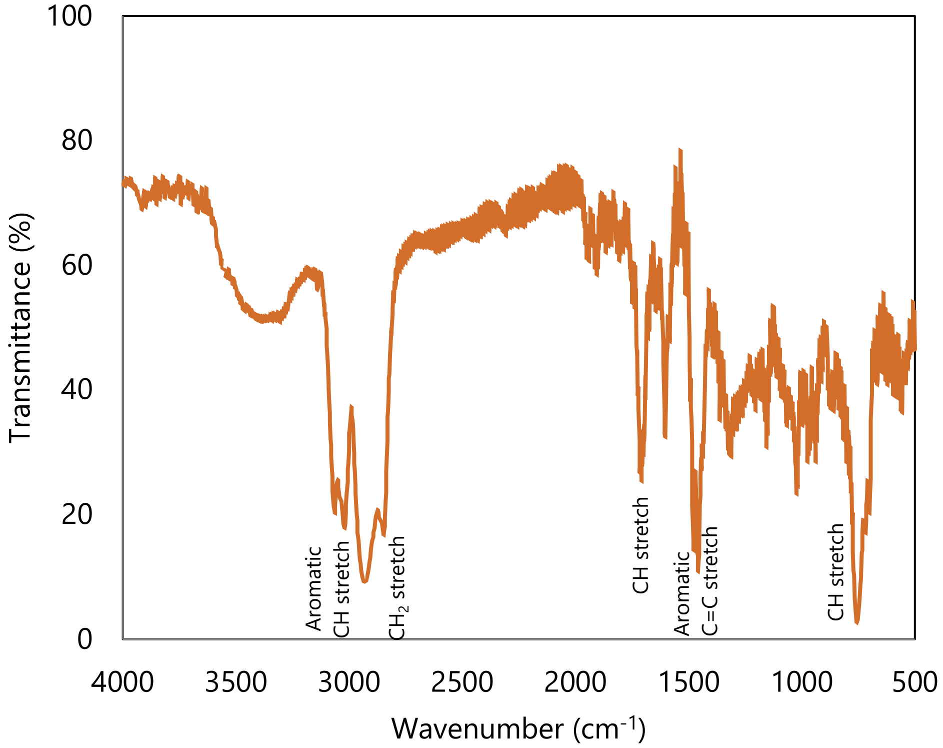


Fig. 3: FT-IR of PECVD-deposited PIn film

Fig. 3 shows FTIR spectra characterized for the PECVD-derived PIn film. The FT-IR spectra of PIn film shows broad peaks and C-H stretch are prominent. The additional peak was observed at 1708 cm^{-1} and it showed polyindene has conjugated aldehydes and ketones (C=O). Normally, band for aldehydes and ketones can be observed at 1720 cm^{-1}. However, because of the presence of a conjugated π bond or an aromatic ring, the band's frequency may be lower by 20-30 cm^{-1}. In this case, PIn layer 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-IR results, there are sufficient polar sites in the plasma-derived PIn 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.

Fig. 4 shows the pure gas permeance of H$_2$, CO$_2$ and N$_2$ through PIn membrane as a function of deposition time at room temperature. Herein, the permeances of deposition time "0" shows the permeances of pure gases through the substrate before the plasma-deposition.

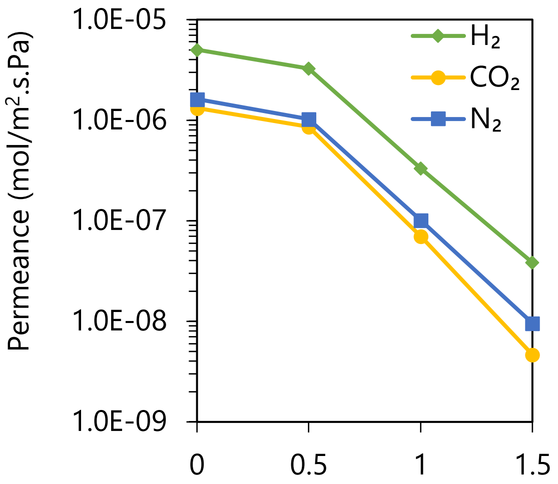


Fig. 4: Pure gas permeance of H_2, CO_2 and N_2 through PIn membrane as a function of deposition time at room temperature

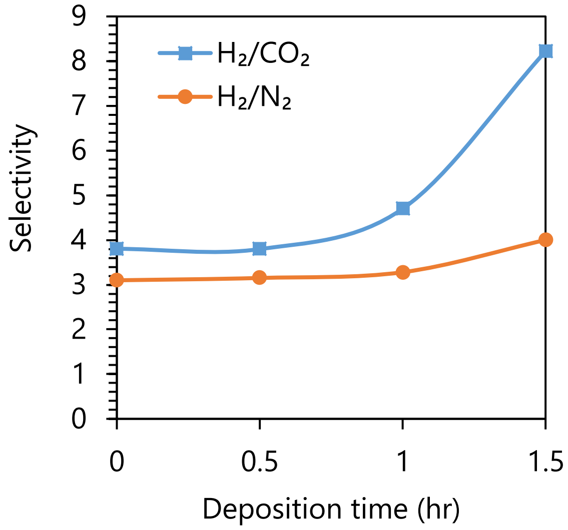


Fig. 5: Separation factor of H_2/CO_2 and H_2/N_2 through PIn membrane as a function of deposition time at room temperature

Fig. 5 shows separation factor for H_2/CO_2 and H_2/N_2 systemes evaluated by the the permeance ratios of H_2/CO_2 and H_2/N_2, respectively. The PIn membrane exhibited higher selectivity and lower permeance increasing deposition time. After 0.5 hr (30 min) of deposition, the PIn membrane displayed a H_2 permeance of 3.25×10^{-6} mol/m^2.s.Pa. The permeance of H_2 sharply declined in the succeeding deposition increasing the permeance ratio. For example, the permeance of H_2 decreased from 5.02×10^{-6} mol/m^2.s.Pa of the original substrate to 3.83×10^{-8} mol/m^2.s.Pa after 1.5 hr deposition. Moreover, separation factor for H_2/CO_2 and H_2/N_2 also increased to 8.2 and 4.0, respectively, after 1.5 hr deposition.

CONCLUSION

Polyindene (PIn) membrane was fabricated onto a Zeolite 5A substrate via radio frequency plasma-enhanced chemical vapor deposition (PECVD) technique at low temperature. The plasma-derived Polyindene (PIn) film was continuous and there was no significant defect on the layer. The additional peak was observed in the PIn film and it is the feature of plasma-derived polymer film. The resultant membrane showed very low permeance of gases and high selectivity for H_2/CO_2 and H_2/N_2 system at room temperature. This study revealed that Indene (In) can be utilized as a new polymeric precursor to the fabrication of a carbon membrane for low pressure PECVD system at low temperature.

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