Synthesis of ZIF-8 membrane via facile cathodic deposition in aqueous medium for propylene/propane separation

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Heng-Yu Chi

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Committee Chairperson: Prof. Zhiping Lai
Committee Members: Prof. Kuo-Wei Huang and Prof. Vincent Tung
ABSTRACT

Synthesis of ZIF-8 membrane via facile cathodic deposition in aqueous medium for propylene/propane separation

Heng-Yu Chi

Metal-organic frameworks (MOFs) are porous crystalline materials built by metal clusters coordinated to organic ligands. Synthesis of MOFs has attracted considerable attention in recent decades, owing to its potential for a wide range of applications such as gas separation, dye adsorption, and catalysis, etc. The development of MOF membranes further enhances the potential of this type of material in industrial applications. Membrane fabrication methods, including in-situ growth, seeded secondary growth, interfacial growth, and vapor-phase deposition, have been widely studied. However, most of these methods either require a complicated synthesis procedure or are time-consuming. Recently, the electrochemical synthesis has emerged as a highly promising approach to fabricate MOF membranes in a scalable manner, because it allows shorter synthesis time, milder synthesis condition, continuous reaction, and crystal self-healing.

In this thesis, for the first time, an aqueously cathodic deposition (ACD) approach was developed to fabricate ZIF-8 type of MOF membranes without the addition of any supporting electrolyte or modulator. The fabrication process used 100% water as the sole solvent, and a low-defect density membrane was obtained in only 60 min under room temperature without any pre-synthesis treatment. The membrane exhibited superior performance in C₃H₆/C₃H₈ separation with C₃H₆ permeance of 182 GPU and selectivity of
142, making it sit at the upper bound of permeance versus selectivity graph, outperforming the majority of the published data up to 2019. Notably, this approach used an extremely low current density (0.13 mA cm$^{-2}$) operated under a facile apparatus set-up, enabling an attractive method for environmentally friendly, energy-efficient, and scalable MOF membrane fabrications. This work demonstrates the enormous potential of aqueously electrochemical deposition of the MOF membrane in future research.
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I have met numerous warm-hearted colleagues and enthusiastic researchers during my master’s. I am extremely thankful for all kinds of support either in mental or essential sides and also an interesting discussion on scientific research. I have learned a lot from you, and I also appreciate the timely companionship when I felt frustrated.

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<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-MIM</td>
<td>2-methylimidazole</td>
</tr>
<tr>
<td>AAO</td>
<td>anodic aluminum oxide</td>
</tr>
<tr>
<td>ACD</td>
<td>aqueously cathodic deposition</td>
</tr>
<tr>
<td>BE</td>
<td>binding energy</td>
</tr>
<tr>
<td>Bmim</td>
<td>1-butyl-3-methylimidazole</td>
</tr>
<tr>
<td>COF</td>
<td>covalent-organic framework</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>DI water</td>
<td>deionized water</td>
</tr>
<tr>
<td>FID</td>
<td>flame ionization detector</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared</td>
</tr>
<tr>
<td>GPU</td>
<td>gas permeation unit</td>
</tr>
<tr>
<td>H$_2$BDC</td>
<td>1,4-benzenedicarboxylate</td>
</tr>
<tr>
<td>KCl</td>
<td>potassium chloride</td>
</tr>
<tr>
<td>MOF</td>
<td>metal-organic framework</td>
</tr>
<tr>
<td>MTBS</td>
<td>methyltributylammonium methylsulfate</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>sodium sulfate</td>
</tr>
<tr>
<td>NH$_4$F</td>
<td>ammonium fluoride</td>
</tr>
<tr>
<td>OPD</td>
<td>optical path difference</td>
</tr>
<tr>
<td>Pt/Pd</td>
<td>platinum/palladium</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SDA</td>
<td>structure-directing agent</td>
</tr>
<tr>
<td>TBATFB</td>
<td>tetrabutylammonium tetrafluoroborate</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZIF</td>
<td>zeolitic imidazolate framework</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS

θ  An angle
Å  Angstrom
°C  Degree Celsius
%  Percentage
n  Refractive index
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Chapter 1: Introduction and overview

Propylene/propane separation is one of the most energy-intensive processes in the petroleum industry. With the potential for reducing energy consumption by 90%, membrane-based separation comes up as a promising candidate for olefin/paraffin separation. [1, 2] Metal-organic framework (MOF) [3-6] is widely discussed due to the well-defined pore size and high porosity, giving them the strong potential for effective membrane separation. In particular, zeolitic imidazolate framework-8 (ZIF-8) possesses an appropriate aperture size for propylene/propane separation. [7] Inspired by the separation potential of this material, our group firstly demonstrated an impressive capability of ZIF-8 membranes for efficient separation of propylene/propane. [8, 9] Although numerous methods have been developed on the ZIF-8 membrane, the synthesis of defect-free MOF membranes remains a big challenge.

Recently, the electrochemical method has emerged as a promising method. Research on the electrochemical deposition of MOF is still in its infancy, with most of the efforts being focused on thin-film production, [10-12] and only a few works have been published for membrane fabrication. [13-15] The deposition procedure and the set-up are mostly delicately controlled with steps such as careful selection of a electrolyte and a reference electrode, using a double electrochemical cell to eliminate the disturbance of the reactions occurred on the counter electrode, and a prolonged post-synthesis treatment, which makes this approach challenging to be applied for scale-up productions. In addition, few publications have used this approach to achieve satisfactory performance in gas separation with both high permeance and selectivity. In this thesis, the fabrication
of ZIF-8 membranes via aqueously cathodic deposition (ACD) without the addition of any supporting electrolytes or modulators is reported. The fabrication process used pure water as a sole solvent and completed in only 60 min without any post-treatment. The membrane showed the best combination of permeance versus selectivity in the separation of the C₃H₆/C₃H₈ mixture.

The thesis is composed of five chapters. The following chapter provides general backgrounds on the issue of alkenes/alkanes separation, membrane technology, MOFs, and ZIF-8. The detailed experimental methods and materials are described in Chapter 3. The results of the ACD-fabricated ZIF-8 membrane and discussions on the high separation performance in C₃H₆/C₃H₈ are summarized in Chapter 4. Finally, the conclusion and perspective are presented in Chapter 5.
Chapter 2: Background

2.1 Separation of alkenes from alkanes

Alkenes are important raw materials for the fabrication of plastics and fine chemicals. Two hundred million tons of ethylene and propylene are consumed annually to produce these products. [1, 2, 16] High-purity alkenes (>99.5%) are required for the production because a little amount of impurity may deactivate the catalysts in the polymerization processes. [17, 18] Thus, alkenes need to be nearly completely separated from alkanes. Unfortunately, the separation of alkene/alkane mixture remains an extremely challenging task due to their similar physicochemical properties (e.g. size and boiling point, see Table 2.1). Nowadays, the industrial separation process mainly depends on the cryogenic high-pressure distillation, which requires cycles of evaporation and condensation. [19] The process consumes a huge amount of energy (Figure 2.1a). [20, 21] For example, around 10-15 % of US annual energy consumption is used in chemical separation (Figure 2.1b). The purification process of ethylene and propylene occupies 0.3 % of global energy use. [1, 2, 16] As one of the major energy-intensive processes, to find alternatives is considered a pressing need. Membrane-based separation is a fabulous candidate due to its size-sieving essence, giving it the potential to reduce energy consumption by 90 % from distillation. [1, 2, 16, 22]
Table 2.1 Comparison of chemical properties between propylene and propane.

<table>
<thead>
<tr>
<th></th>
<th>Molecular structure</th>
<th>Chemical Formula</th>
<th>Molar Mass</th>
<th>Boiling Point</th>
<th>Kinetic Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene</td>
<td><img src="image" alt="Propylene structure" /></td>
<td>C₃H₆</td>
<td>42.081 g·mol⁻¹</td>
<td>−47.6 °C</td>
<td>4.0 Å</td>
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<tr>
<td>Propane</td>
<td><img src="image" alt="Propane structure" /></td>
<td>C₃H₈</td>
<td>44.097 g·mol⁻¹</td>
<td>−42.1 °C</td>
<td>4.2 Å</td>
</tr>
</tbody>
</table>

Figure 2.1 (a) International Energy Agency estimation of the energy consumption (EJ/year) and greenhouse gas (GHG) emissions (in metric tons of carbon dioxide equivalent/year) of the global chemical industry in 2010. [20, 21] (b) Total US energy cost consumption and chemical separation cutting-cost. [1]
2.2 Membrane technology

The separation process using membrane technology has attracted significant attention in recent decades due to its continuous operation, energy efficiency, and attractive economic feasibility. If the membrane can reach $C_3H_6$ permeability higher than one barrer and $C_3H_6/C_3H_8$ selectivity of 35, it can have a high potential to compete with the industrial method. [8, 23, 24]

For an ideal gas-selective membrane, it requires gas selective pores, high porosity, and ultrathin thickness (<1 µm) to achieve high selectivity and permeance (flux normalized by pressure). However, improving selectivity is always accompanied by a decrease in permeability. Lloyd M. Robeson summarized the literature data of polymeric membranes and demonstrated the “upper bound” concept for the trade-off relationship between limits of separation factor and permeability in 1991. [25] Afterwards, he updated the upper bound with much larger polymeric membranes database, specifically including a series of perfluorinated polymers in 2008, as shown in Figure 2.2. [26] However, in most cases, even the membrane performance at the upper bound is still far away from the economically feasible zone. Hence, the development of a membrane with performance surpassing the Robeson’s upper bound has become an essential target in the membrane research field.
In addition to polymers, microporous crystalline materials such as zeolite, [27, 28] MOF, [3-6] and covalent-organic frameworks (COF) [29, 30] have emerged as novel membrane materials due to their large surface area, high pore volume per weight, well-defined pore size, and rigid architecture, making them auspicious for effective membrane separation. [31] Zeolite membranes such as the MFI zeolite membranes were used in the separation of CO₂ from syngas resulting from the gasification of black liquor [32], xylene
isomers, [33, 34] and so on. [27, 28, 35] DDR@CHA hybrid membranes were introduced recently for high CO$_2$ perm-selectivities. [36] However, the thermal activation for removal of the structure-directing agent (SDA) limits its utilization of polymeric substrates, which is considered as a way forward to decrease membrane costs. [35] For COF membranes, LZU1-ACOF-1 bilayer membranes were developed as a highly H$_2$-selective membrane. [37] Nevertheless, the pore size of COFs are too large (0.8-5 nm) [38, 39] to achieve gas-sieving (0.25-0.5 nm). [4, 19, 40] MOF membranes will be discussed in the following section.

2.3 Metal-organic framework (MOF)

MOF was firstly introduced in 1995 by Yaghi et al. [3] It is constructed by metal ions (or clusters) bridged by organic ligand. This has attracted a great deal of attention due to the highly tunable architecture, simple synthesis, and high surface area as well as pore volume. [6] The maximum degree of porosity and pore sizes outdoes zeolites. [41] Taking MOF-5 as an example (Figure 2.3a), it is built up by zinc ions coordinated to 1,4-benzenedicarboxylate (H$_2$BDC) with pore volumes of 0.54-0.61 cm$^3$ cm$^{-3}$, which is much higher than zeolite A (0.18-0.47 cm$^3$ cm$^{-3}$). [5] Also, it can be extended as IRMOF-2~IRMOF-16 for diverse functionalities and pore sizes. [6] HPDC and TPDC were changed as building blocks to form IRMOF-12 and IRMOF-16 (Figure 2.3b and c). The tunability in reticular chemistry makes it possible to target specific characters. The sieving effects or selective adsorption for gas separations can be achieved, owing to the unique properties through crystal engineering. [35]
2.4 Zeolitic imidazolate framework (ZIF)

As a wide discussion addressed on MOF membranes, ZIF, a subgroup of MOF, shines as a rising star for gas separation. ZIF is constructed of transition metal ions (e.g., Zn, Co, Cu, Fe) combined with imidazolate linkers with zeolitic topology (Figure 2.4). ZIF-8, first introduced in 2006 by Chen et al. [45], has been widely discussed in recent decades due to its higher stability, angstrom-scale pores, and simple synthesis nature in aqueous solution.

Figure 2.4 Linkage of (a) metal-imidazolate linkers in ZIFs and (b) Si-O in the zeolite. [43]
ZIF-8 has a window size of ~0.34 nm (Figure 2.5). However, the structure flexibility allows it to be used in several binary gas separations such as H$_2$/CO$_2$, CO$_2$/N$_2$, H$_2$/CH$_4$, C$_2$/C$_3$, and C$_3$H$_6$/C$_3$H$_8$. [46] The imidazolate linkers are able to rotate during the pressure elevation, opening the small window of ZIF-8 (Figure 2.6a). [47-50] In 2012, Koros et al. proposed the effective aperture size (4.0-4.2 Å) of ZIF-8 (Figure 2.6b). Gas molecules from the size of 2.6 Å (helium) to 5.0 Å (iso-C$_4$H$_{10}$) have the capability to diffuse through ZIF-8. [7] Especially for C$_3$H$_6$/C$_3$H$_8$ separation, C$_3$H$_6$ and C$_3$H$_8$ have kinetic diameters of 0.40 nm and 0.42 nm, respectively. The slight size difference enables C$_3$H$_6$ to diffuse through ZIF-8 at a speed of 125 times higher than C$_3$H$_8$. [51] This large diffusion disparity allows an effective C$_3$H$_6$/C$_3$H$_8$ separation with an estimated ideal permselectivity of 130. [7]

![Figure 2.5 Linkage of Zn$^{II}$ bridged to 2-methylimidazole and the molecular structure of ZIF-8.](image-url)
Figure 2.6 (a) Swing effect in the 2-methylimidazole linkers of ZIF-8: experimental observation and simulation results. [47] (b) Corrected diffusivities in ZIF-8 at 35 °C versus the molecular diameter of probe molecules. [7] (Pink slash region represented as effective aperture size.)

Inspired by the separation potential of this material, our group first demonstrated the ability of ZIF-8 membrane for effective $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation. [8] A selectivity up to 90 was achieved after careful optimization of the activation process and defect elimination. [9]
2.5 Fabrication methods of ZIF-8 membranes

2.5.1 In-situ synthesis

In-situ synthesis is straightforward for heterogeneous nucleation and crystal growth happening directly on the substrate. The approach is simple; however, optimum synthesis for the defect-free membrane is effortful. Surface-modified [52, 53] or metal oxide-coated substrates [54, 55] are frequently required for better nucleation growth affinity to the surface due to the local saturation.

Huang et al. used polydopamine coordinating on the hydroxyl group of alumina surface, promoting ZIF-8 layer growth on the substrate (Figure 2.7a). [52] The resulting ZIF-8 membrane has high H₂ separation selectivity with a thickness of ~20 µm. Tanaka et al. modified the substrate surface by 3-(2-imidazolin-1-yl)propyltriethoxysilane (IPTES), providing a pseudo-surface as active sites for ZIF-8 nucleation (Figure 2.7b). [53] The grain size of the polycrystalline membrane can be easily controlled by the graft density of IPTES, which is also considered as the nucleation density.
Figure 2.7 (a) Schematic illustration of polydopamine-modified alumina substrate as covalent linkers for ZIF-8 growth. [52] (b) IPTES-modified substrates served as active sites with different graft-densities for ZIF-8 nucleation. [53]

Zhang et al. adopted the seed-rubbing method from zeolite, implanting ZnO particles onto substrates via the rubbing process. As an active bridging site, the ZnO layer induced the ZIF-8 membrane growth on the substrates (Figure 2.8a). [54] Wang et al. electrodeposited metal oxide or metal hydroxide and then pressed ligand powder on substrates. [55] After heat-treatment, the solvent-free MOF membranes are easily formed due to the high activity of the metal-oxide layer (Figure 2.8b).
2.5.2 Seeded secondary growth

Seeded secondary growth contains seeding followed by secondary growth, making it better control of defect-free membrane fabrication. Small, high density, and well-dispersed seeds are desirable for the seeding layer, and the secondary growth enhances grain intergrowth. Compared to in-situ growth, seeded secondary growth can have better reproducibility. Most of the MOF membranes are fabricated via this method; however, the synthesis time for a high-quality membrane often takes several hours or days.

Dip-coating, [56, 57] slip-coating, [8, 58] rubbing, [59-61], and microwave-assisted [62, 63] approaches are employed as promising seeding strategies. For the dip-
coating or slip-coating method, well-dispersed ZIF-8 suspension is required for good coverage of seed layers. Substrates were immersed or came into contact with ZIF-8 suspension several times to form a seed layer (Figure 2.9a). Following secondary hydrothermal growth, high-quality membranes were formed (Figure 2.9c and d). The membranes served good H$_2$ selectivity [56] or C$_3$H$_6$/C$_3$H$_8$ separation performance. [8, 57] For a manual rubbing seeded approach, nano-sized seeds were synthesized before the seeding process. After secondary growth, dense ZIF-8 membranes can be formed on flat substrates [60] or ceramic hollow fibers [59, 61] with carefully rubbed ZIF-8 seeds.

![Figure 2.9 SEM images](image)

**Figure 2.9** SEM images of (a) top-view of ZIF-8 seed layer via slip-coating; (b) top-view and (c) cross-section of ZIF-8 membrane after secondary hydrothermal growth. [58]

The microwave-assisted rapid seeding method was first developed by Jeong *et al.*, applying to both flat substrates [62] and hollow fibers. [63] The process can be divided into three steps. Firstly, the substrates are saturated with metal ions and immersed in the ligand solution. Secondly, the surface of the metal ion-saturated substrate can strongly absorb microwave radiation and react with the ligand. Finally, the rapid and uniform nano-sized seed crystal layer is formed on porous substrates. (Figure 2.10).
2.5.3 Counter-diffusion method

The counter-diffusion method is a fast and straightforward method to control the crystallization happening at the interface. Ligand solution and metal ion precursor diffuse through the substrate from both sides and meet at the interface to form a crystal layer. The thickness of the membrane can be tuned by the concentration of precursor and temperature.

Wang et al. first introduced the counter-diffusion synthesis of ZIF-8 membrane on a flexible nylon substrate. [64] The zinc nitrate and 2-methylimidazole solutions were prepared in methanol separately in a diffusion cell (Figure 2.11a). After 72 h, a continuous ZIF-8 membrane was formed with a thickness of 16 µm (Figure 2.11b). Hara et al. used the concept of counter diffusion on the immiscible and miscible liquid-liquid interfaces of
α-alumina hollow fibers. [65] A Zn\textsuperscript{II} solution in water and a 2-methylimidazole solution in 1-octanol and methanol were prepared for immiscible (water/1-octanol) and miscible (water/methanol) interfaces to form ZIF-8 membranes.

![Figure 2.11](image)

**Figure 2.11** (a) The set-up of the diffusion cell and the scheme of ZIF-8 layer formation via counter-diffusion. (b) The thickness of the ZIF-8 membrane after 72 h reaction. [64]

Nair *et al.* combined the microfluidic processing with the counter-diffusion method, enabling a scalable procedure of ZIF-8 membrane fabrication (Figure 2.12). [66] The reactants were recycled and replenished simultaneously by a microfluidic condition in hollow fiber modules. Furthermore, the position of ZIF-8 membrane formation was guided to the predictable sites (at the inner and outer surfaces, and inside the bulk) by changing two immiscible or miscible solvents via counter-diffusion.
2.5.4 Vapor-phase deposition

In addition to the solution-based synthesis, the vapor-phase deposition has recently been developed due to inevitable liquid contamination potential. Vapor-phase synthesis is scalable and environmentally friendly, preventing pollution from toxic solvents.

Chemical vapor deposition (CVD) of ZIF-8 thin film on a titanium oxide substrate was carried out by Ameloot et al. in 2015. [67] The zinc oxide layer was first fabricated by atomic layer deposition (ALD), following by 2-methylimidazole vapor treatment to form a ZIF-8 layer on the substrate (Figure 2.13a). The CVD-MOF method was also applied to high-aspect-ratio silicon pillar arrays (Figure 2.13b), enabling the integration of MOF in microelectronics.
Recently, Tsapatsis et al. fabricated a ZIF-8 membrane on an alumina substrate via all vapor-phase method (Figure 2.14a). [68] The ALD-deposited impermeable ZnO layer first blocked the pores of the porous substrate. After treating the ZnO layer with ligand vapor, a ZIF-8 selective layer was formed. The ligand-induced permselectivation ZIF-8 membranes showed both high selectivity and permeance under high-pressure tests from 1 to 7 atm (Figure 2.14b and c), which is quite promising for industrial scale-up.

**Figure 2.13** (a) The scheme of CVD-ZIF-8 fabrication procedure. (b) SEM images of ZIF-8-coated silicon pillar array. [67]
2.5.5 Electrochemical deposition

Electrochemical deposition benefits from relatively minor or no pre-treatment of the substrate, shorter synthesis time, and milder synthesis condition. [11] It also allows for continuous production, which is a significant advantage compared with other methods for industrial scale-up. [10] More importantly, this method may provide a defect-correction mechanism since the deposition can be controlled by the current.
In general, anodic dissolution, cathodic deposition, and electrophoretic deposition are the three main methods used in this approach (Figure 2.15). For anodic dissolution, a metal plate is used as an anode, and the metal source for the MOF formation is dissolved from the metal plate. The dissolved metal ions react with the ligand in the solvent and form a film on the metal plate. [69] For cathodic deposition, both metal ions and ligands are dissolved in the solvent, and probase is formed from the reduction reaction near the cathode. The formed probase facilitates the deprotonation of the metal-ligand complex and promotes the nucleation and crystal growth on the substrate. [14, 70] For electrophoretic deposition, the charged particles are driven by the electrical field towards the cathode and form a film on the substrate. In this method, secondary growth is normally adopted to allow for further crystallization and defect healing. However, most effort on electrochemical deposition is mainly focused on thin-film production. [12] Only a few works have concentrated on membrane fabrication. [13-15]
Figure 2.15  Illustration of electrochemical fabrication methods: anodic dissolution, cathodic deposition, and electrophoretic deposition.
Agrawal et al. first introduced the electrophoretic nuclei deposition for a ZIF-8 membrane (Figure 2.16). [13, 71] The porous substrates were fixed onto copper foil, and Zn\textsuperscript{II} and 2-methylimidazole were premixed to form a ZIF-8 nuclei solution. The ZIF-8 nuclei with positive charges was driven onto the substrate in 4 min under 1 V, forming a ZIF-8 nuclei layer (Figure 2.16b and 2.12c). After secondary growth, the ZIF-8 membrane was formed with good gas separation performance.

![Figure 2.16](image)

**Figure 2.16** (a) Schematic illustration of electrophoretic nuclei assembly deposition. SEM images of deposited nuclei layer: (b) top-view and (c) cross-section. [13]

Organic solvents have been widely used for film fabrication across the published works on the electrochemical deposition. [10, 11, 14, 15, 70] Electrolytes such as
methyltributylammonium methylsulfate (MTBS), [72, 73] tetrabutylammonium tetrafluoroborate (TBATFB), [74] 1-butyl-3-methylimidazole (Bmim) bromide, [75] NH₄F, [76] Na₂SO₄, [77] and KCl [73] are normally added into the solvent to increase conductivity. A modulator is also sometimes added to modify the crystal morphology or speed up the crystallization for targeted film deposition. [78, 79]

The addition of an electrolyte or modulator has somewhat added another dimension of complexity into the fabrication process. So far, little in-depth research has been conducted to investigate the effects of the electrolyte or modulator on the film fabrication. Considering the nature of the complicated reactions happening during the deposition process, it would be quite desirable if the addition of the electrolyte can be eliminated for better control over the synthesis process. Organic solvents also cause concern for the potential negative impacts on the environment in large-scale industrial production. By comparison, water would be the best possible choice for an environmentally friendly process. [80] However, as water electrolyzes easily in a basic solution, it remains a challenge in this field to adopt 100% water as the sole solvent to anodically/cathodically deposit an MOF membrane.
3.1 Chemicals and materials

Zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, > 99%) and potassium chloride (KCl, > 99%) were purchased from Sigma-Aldrich. 2-Methylimidazole (C₄H₆N₂, 99%) was purchased from Acros Organics. All chemicals were used without further purification. The deionized water (DI water) used for synthesis was purified using a Milli-Q® academic ultrapure water system. Anodic aluminum oxide (AAO) substrates (Anodisc™ 13) with a pore size of 200 nm and thickness of 60 µm were purchased from Whatman®.

3.2 Preparation of precursor solution for electrodeposition of ZIF-8 membranes

2-Methylimidazole (4.105 g, 50 mmol) was dissolved in DI water (50 mL). In a separate container, Zn(CH₃COO)₂·2H₂O (0.183 g, 0.83 mmol) was dissolved in DI water (10 mL). The two solutions were mixed and stirred for 5 seconds to form a ZIF-8 precursor solution for cathodic deposition.

3.3 Cathodic deposition of ZIF-8 membranes on AAO substrates

AAO substrates were coated with platinum/palladium (Pt/Pd) via sputtering deposition at 20 mA for 20 seconds. The Pt/Pd-coated AAO substrate and a graphite paper were parallelly separated 1.5 cm apart and immersed in the ZIF-8 precursor solution. The reactions were conducted for 10 min, 20 min, 30 min, 40 min, and 60 min, respectively, under a current density of 0.13 mA cm⁻². The resultant ZIF-8 membrane synthesized was thus named as M-10, M-20, M-30, M-40, and M-60 accordingly. The membranes obtained...
were substantially rinsed with DI water and methanol after the reaction. The fabricated membranes were activated in methanol for gas permeation test.

3.4 Mixed-gas permeation test

The permeation test was performed by the Wicke-Kallenbach technique, as shown in Figure 3.1. At the feed side, the equal molar ratio of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ with a flow rate of 50 cc min$^{-1}$ was introduced into the permeation cell. At the permeation side, argon was used as the sweep gas with a flow rate of 50 cc min$^{-1}$. Both sides were maintained at 1 bar using a pressure regulator. The composition of the permeate stream was analyzed on-line by an Agilent 7890A gas chromatograph equipped with a flame ionization detector (FID).

![Figure 3.1 Illustration of gas permeation setup.](image-url)
3.5 Mix-gas permeation test at varied temperatures

The permeation cell was heated with a heating mantle from 22 °C to 130 °C. The temperature sensor was equipped to record the temperature. The Wicke-Kallenbach technique was performed under ambient pressure.

3.6 Material Characterization

3.6.1 Scanning electron microscope (SEM)

A Magellan™ XHR scanning electron microscope (SEM) was used to characterize the morphology of the membrane samples. The samples were coated with Pt/Pd via sputtering deposition at 20 mA for 12 seconds. SEM imaging was conducted at an acceleration voltage of 3 kV.

3.6.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns were obtained using a D8 ADVANCE Twin X-ray diffractometer (40 kV, 40 mA) with Cu Kα radiation. The scanning was set to be 0.8 s per step from 5 to 40° 2θ with a step size of 0.0085° 2θ.

3.6.3 Krypton physisorption measurement

Krypton physisorption isotherms were obtained at 77 K using a Micromeritics ASAP 2020 analyzer. Before taking the physisorption measurement, the membrane samples were placed in an analysis tube and degassed in a vacuum at 110 °C for 12 hours. The
membrane BET surface area was measured by subtracting the BET surface area of the substrate.

3.6.4 Fourier-transform infrared (FT-IR) spectroscopy

A Nicolet 6700 Fourier-transform infrared (FT-IR) spectrometer with a KBr beam splitter and CaF₂ window was used to obtain the IR spectra of the membranes. The membrane samples were degassed in a vacuum at 110 °C for 12 hours before taking the measurements. The samples were analyzed with 32 scans at a resolution of 0.964 cm⁻¹.

3.6.5 Cyclic voltammetry (CV) measurement

A cyclic voltammetry (CV) measurement was done using a CHI660D electrochemical workstation. A Pt/Pd-coated AAO substrate, graphite paper, and an Ag/AgCl (in 3 M KCl aqueous solution) electrode were used as a working electrode, a counter electrode, and a reference electrode, respectively. KCl (100 mM) was used as a supporting electrolyte for all CV measurements. CV scans were measured at 100 mV min⁻¹ from -1.0 V to 1.2 V.

3.6.6 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were taken using a Kratos Amicus spectrometer with monochromatic Al-Kα radiation. A wide scan was acquired to calibrate the spectra before elemental scans. The binding energy (BE) was referenced at 284.6 eV with C 1s peak.
Chapter 4: Results and discussions

4.1 Membrane fabrication set-up

The experimental set-up is straightforward. It comprises two electrodes in a single electrolyte cell, as shown in Figure 4.1. AAO coated with a Pt/Pd conductive layer was used as the working electrode, while graphite paper without any pre-treatment was used as the counter electrode. In the deposition precursor solution, a relatively high imidazole ligand to Zn\(^{II}\) ratio of 60 was used for complete ligand deprotonation, thus ensuring a pure MOF to be formed. [80] A dilute solution of Zn\(^{III}\) (Zn\(^{III}\): H\(_2\)O = 1:3889) was used to slow down the crystal growth in the bulk solution, helping to form a uniform deposition on the substrate. During the deposition process, zinc cations were driven towards the substrate on the cathode side and formed zinc-ligand complexes. The probase OH\(^-\) released from the reduction of water built up an OH\(^-\) concentration gradient near the cathode. Thus, we hypothesized that the formed OH\(^-\), due to its higher pKa value compared with other species in the precursor, [81] facilitated the deprotonation of the zinc-ligand complex near the substrate. The deprotonated zinc-ligand complex then further went on to oligomerize, nucleate, crystallize, and finally form a layer of dense crystals on the substrate.
In the deposition process, due to the narrow potential window of water reduction (Figure 4.2), the current density must be very low to prevent water from electrolyzing vehemently. Otherwise, the resulting hydrogen evolution would form a layer of bubbles on the substrate. The bubbling process would not only disrupt the deposition process but also form a very high concentration of OH⁻ ([OH⁻]) near the substrate. The high [OH⁻] would corrode the already formed MOF, leading to a severe amount of membrane defects. An optimal current density of 0.13 mA cm⁻² was identified, which ensured both slow water electrolysis and a quick deposition rate. After 60 min, a uniform membrane with thickness in the visible light wavelength range (Figure 4.3) was obtained. The color
of the membrane could be observed due to the interference of the thin film. After the cathodic deposition, there was little precipitation in the residual solution, proving that most of the MOFs grew directly on the substrate. The electric field indeed drove the growth of the MOF membrane. As a comparison, an in-situ growth of the membrane on AAO was also conducted, but no membrane and only a few crystals formed on the surface of the substrate (Figure 4.4a and b).

Figure 4.2 Cyclic voltammetry curve (CV) of ZIF-8 synthesis precursor compared with CV curves of pure water, 2-MIM aqueous solution, and zinc acetate aqueous solution.
Figure 4.3 (a) Photo image of the ZIF-8 membrane on the AAO substrate. (b) Schematic demonstration of the color of the membrane. The color on the top surface of the membrane was caused by thin-film interference. The optical path difference (OPD) is in the range of visible light.

Figure 4.4 (a, b) AAO after immersing in ZIF-8 synthesis precursor for 60 min and (c, d) pristine AAO.
4.2 Membrane growth

An ex-situ investigation of the deposition process was conducted by SEM analysis (Figure 4.5 and Figure 4.6). The investigation was conducted at 10 min (M-10), 20 min (M-20), 30 min (M-30), 40 min (M-40), and 60 min (M-60) intervals. Looking at the whole process, the resulting crystal size had continuously increased from 10 min to 60 min (Figure 4.5a-e), resulting in a gradual increase in membrane thickness (Figure 4.5f-j). Correspondingly, the membrane growth gradually decreased the conductivity of the substrate, which caused an increase of voltage to maintain the constant current (Figure 4.7). In this process, the crystal morphology gradually transformed from cubic (Figure 4.5a) to rhombic dodecahedra (Figure 4.5e), with most of the (110) phase exposed. The (110) phase is the most thermodynamically stable face of ZIF-8, [79], ensuring the chemical stability of the membrane. Meanwhile, the thickness of the membrane was increased from ~50 nm (Figure 4.5f) to ~500 nm (Figure 4.5j). The uniformity of the ZIF-8 membrane obtained at different times can be observed in Figure 4.6.
Figure 4.5 SEM images of front and cross-section of membranes synthesized at: (a,f) 10 min, (b,g) 20 min, (c,h) 30 min, (d,i) 40 min, and (e,j) 60 min.
Figure 4.6 Low magnification SEM images of ZIF-8 membranes obtained at: (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, and (e) 60 min.
At 10 min (Figure 4.5a), cubic crystals were uniformly deposited on the solid surface around the pores of the substrate (Figure 4.4c and d for pristine AAO), implying that nucleation happened initially on the conductive surface of the AAO substrate. This phenomenon suggested that the electric current functioned as a driving force for the nucleation to occur. The corresponding XRD pattern (Figure 4.8) showed the characteristic peaks at (001), (002), (112), (022), (012), and (222) of ZIF-8 emerged, suggesting the nucleation and crystallization were happening at the same time within 10 min of the deposition. In addition, no foreign peaks were observed, suggesting a pure ZIF-8 phase was obtained. At 20 min (Figure 4.5b), the cubic crystals almost entirely covered
the substrate. When it went to 30 min (Figure 4.5c), the crystals underwent a morphological transformation from cubic to rhombic dodecahedra and intergrown to form a membrane on the substrate. For 30 min and 40 min, the crystals continued to crystallize and grew to seal the grain boundary via intergrowth (Figure 4.5d), and finally formed a continuous membrane at 60 min (Figure 4.5e). The final membrane formed comprising a uniform layer of crystals with size ~500 nm.

**Figure 4.8** XRD patterns of ZIF-8 membranes under different synthesis times.
4.3 Gas separation test

The formed membranes deposited from 30 min onwards were tested for C$_3$H$_6$/C$_3$H$_8$ separation using the Wicke-Kallenbach technique (Figure 3.1) with both sides of the membrane being maintained at ambient pressure. The feed was a mixture of 50:50 molar ratio of C$_3$H$_6$ and C$_3$H$_8$, while the permeate was purged with argon as a sweep gas. The results are listed in Table 4.1. As expected, the permeance of C$_3$H$_6$ decreased from 1618 GPU (1 GPU= 3.35× 10$^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$) to 692 GPU, while the selectivity slightly increased from 3 to 11 as the deposition went from 30 min to 40 min. However, when it went from 40 min to 60 min, the selectivity was sharply enhanced to 142 with C$_3$H$_6$ permeance reducing to 182 GPU. This observation suggests that the membrane had undergone an intense process of both crystal defect healing and grain boundary sealing in the last 20 min of deposition, which resulted in a continuous membrane exhibiting exceptional performance in C$_3$H$_6$/C$_3$H$_8$ separation. The selectivity of 142 reached the estimated ideal permselectivity of 130. [7] The permeance of 182 GPU outperformed the majority of the published works while the selectivity remained uncompromised. Figure 4.9 shows the position of our work as compared with the published data. It is clear our results sit at the upper-right corner of the graph, highlighting the superior performance of our membrane. This also implies that the ACD developed in this work can be a promising approach for low-defect density MOF membrane fabrication.
Table 4.1 Permeance and selectivity of C\textsubscript{3}H\textsubscript{6} in the C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} separation test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C\textsubscript{3}H\textsubscript{6} Permeance (GPU)</th>
<th>C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-30</td>
<td>1618 ± 22</td>
<td>3 ± 0.03</td>
</tr>
<tr>
<td>M-40</td>
<td>692 ± 17</td>
<td>11 ± 0.39</td>
</tr>
<tr>
<td>M-60</td>
<td>182 ± 9</td>
<td>142 ± 4</td>
</tr>
</tbody>
</table>

Figure 4.9 Comparison of C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} separation performance with membranes reported up to 2019.

The separation of C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} in the petrochemical industry is carried out at pressure up to 18 bar and temperature around 50 °C. [2] To test the thermal stability of the
membrane, we conducted an online test of gas separation performance at varying temperatures (22-130 °C) (Figure 4.10). With the increase of temperature, the permeance of C₃H₆ remained relatively stable, but the selectivity decreased and reached the lowest point at 130 °C (Figure 4.10a). This observation was mainly due to the increased C₃H₈ permeance (Figure 4.10b). The selectivity gradually returned to its original values after the temperature reduced back to ~22 °C, implying that the membrane obtained by the ACD method can withstand high temperatures without damaging its intrinsic crystalline structure. The selectivity at 50 °C and 130 °C was around 130 and 55. Both were satisfactory for industrial applications.

![Figure 4.10](image) Gas separation performance at varied temperatures.
Due to the weak mechanical strength of the AAO substrate, the membrane was tested at low pressure (~1 bar). To apply the membrane under higher pressures (e.g. 2-18 bar), stronger substrates are preliminarily required. The detailed discussion on the potential in extending the ACD method to stronger substrates will be introduced in Chapter 5.2.

4.4 Discussion on gas separation results

The high permeance of our membrane can be attributed to three factors: (a) the membrane is ultra-thin (~500 nm), allowing a short path for the gas to diffuse through; (b) the membrane has high porosity that can accommodate more gas molecules; (c) no detectable residual ligands, which can block the pores of the crystal, existed in the structure. Factor (a) has been proved in the SEM analysis (Figure 2j), showing the uniform layer of crystals of ~500 nm solely contributed to the thickness of the membrane. To prove factor (b), we conducted krypton adsorption to measure the surface area of the membrane. This measurement followed published protocols. [67, 82] The Brunauer-Emmett-Teller (BET) specific surface area of M-60, expressed as per membrane area per 100 nm thickness, was 177 m² m⁻² 100 nm⁻¹. This result was comparable with the published data using krypton adsorption (Table 4.2). Considering the uncertainty of the data, the physisorption data was further evaluated by comparing the calculated surface area (expressed as per gram of the membrane weight) with the typical ZIF-8 surface area. The crystal density of ZIF-8 is 1.05-1.19 g cm⁻³ depending on the synthesis and activation methods. [83] Coupled with the obtained membrane thickness ~500 nm, the calculated
BET surface area was 1485-1698 m² g⁻¹. It was noticeable that some crystals grew into the pore of the AAO substrate (Figure 4.5j), but no continuous growth of such crystals was observed along the near-surface pores after careful analysis of a collection of SEM images. This did not allow these “in-pore” crystals to be accountable for the thickness of the membrane. These crystals might affect the surface area calculated. However, we were unable to quantify these crystals due to the limitation of the analysis technique. With this in mind, we suggest that the real BET surface area of the membrane would be slightly lower than the calculated ideal surface area (1485-1698 m² g⁻¹). Comparing the values with a broad range of published data, [43, 81, 84, 85] this result was considered to be within a reasonable range, which proves factor (b) that the membrane exhibits high porosity.

Table 4.2 Published data of the BET surface of ZIF-8 using krypton adsorption.

<table>
<thead>
<tr>
<th>BET surface area a (m² m⁻² 100 nm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>175-191</td>
<td>[82]</td>
</tr>
<tr>
<td>125-128</td>
<td>[67]</td>
</tr>
<tr>
<td>177</td>
<td>This work</td>
</tr>
</tbody>
</table>

BET surface area was expressed as surface area per area of membrane per 100 nm membrane thickness.

To prove factor (c), FTIR measurement was conducted, as shown in Figure 4.11. The membrane obtained at 60 min, and 2-methylimidazole (2-MIM) were plotted together for comparison. Overall, C-H3 stretching mode at 2855 cm⁻¹, 2925 cm⁻¹, and 2955 cm⁻¹, and C-H aromatic stretching mode at 3135 cm⁻¹ were observed for both samples. A particular
finding was that the N-H stretching band was observed in 2-MIM but disappeared in the membrane. This observation proves that almost all 2-MIM was deprotonated and incorporated into the crystal structure; no FTIR detectable uncoordinated 2-MIM existed in the membrane.

![FTIR spectra comparison](image)

**Figure 4.11** Comparison of FTIR spectra of M-60 with 2-MIM.

The high selectivity of our membrane may directly prove that our membrane has few defects. This can be further confirmed by the XPS studies, as shown in Figure 4.12a and b, which show Zn 2p and N 1s spectra of M-60, M-40, and M-30, respectively. For Zn 2p spectra, two peaks were observed for all the samples and assigned to Zn 2p$_{3/2}$ for lower
binding energy (BE) and Zn 2p$_{1/2}$ for the higher BE. [86] Clearly, M-60 displayed two narrow peaks at 1022.1 eV and 1045.2 eV, respectively, which implies the majority of Zn were in the tetrahedral coordination. For the other two samples, a systematic peak shift and broadening towards lower BE, especially M-30, were observed. This could be closely correlated to the number of unsaturated Zn sites in the framework. It has been established that coordinately unsaturated sites interact more strongly with the adsorbed molecules (e.g. ZnO) than the saturated metal sites, [87], which would shift the peak towards lower BE. [88, 89] Similar observations were observed for N 1s spectra (Figure 4.12b), where systematic peak shift and broadening towards lower BE were observed from samples M-60, M-40, and M-30. We did not observe any peak above 400 eV, which usually is associated with -NH- of 2-MIM, [90-92], implying that little non-deprotonated 2-MIM existed in our samples. This is also consistent with the FTIR results (Figure 4.11). For M-60, a sharp peak was observed at 398.9 eV, which is assigned to N-Zn coordination, suggesting that the majority of N are in a similar chemical environment. For M-40 and M-30, the peak shifted and broadened towards lower BE; we believe this phenomenon is also mainly due to unsaturated Zn-N bonds as the number (x) of Zn-N$_x$ coordination is positively correlated with BE. [91] The unsaturated Zn is widely accepted as the point defects in the framework and could significantly affect molecule diffusion. [93, 94] As the XPS results demonstrated, M-30 exhibited the highest quantity of these defects. The defects were continuously healed with the deposition time, which resulted in a low-defect density membrane (M-60).
Figure 4.12 XPS spectra of (a) Zn 2p and (b) N 1s.
Chapter 5: Conclusion and perspective

5.1 Conclusion

In conclusion, an aqueously cathodic deposition (ACD) approach for ultra-facile fabrication of the MOF membrane on AAO substrates without the addition of any supporting electrolytes or modulators was developed. This approach allows the synthesis of an ultra-thin membrane consisting of a uniform layer of crystals. A nearly defect-free polycrystalline membrane can be obtained within 60 min without any post-synthesis treatment. The membrane achieved superior performance in C₃H₆/C₃H₈ separation with C₃H₆ permeance of 182 GPU and selectivity of 142 at room temperature, outperforming most of the membranes previously reported. Notably, for the first time, this approach used water as the sole solvent, adopted an extremely low current density, and employed a simple set-up, paving an attractive way for environmentally friendly, energy-efficient, and scalable MOF membrane fabrication. The membrane showed excellent thermal stability that substantially meets industrial application requirements. The selectivity decreased with temperature mainly due to the increase in propane permeance but fully recovered when the temperature reduced back to room temperature. The membrane could only be tested under low pressure due to the weak mechanical strength of the AAO substrate. However, the ACD approach has the potential to fabricate high-quality MOF membranes on strong substrates such as α-alumina and metal flat-sheets or hollow fiber. To apply the membranes on high-pressure gas separation is still a big challenge, and substantial research efforts are necessary.
5.2 Perspective

The ACD approach is capable of preparing high-quality ZIF-8 membranes on robust substrates such as α-alumina and metal flat plate or hollow fiber, as illustrated in Figure 5.1. In particular, α-alumina hollow fiber has been commercialized for NaA zeolite membrane production. [95, 96] This type of support is known to be made by sintering alumina particles at elevated temperatures, with the reported surface roughness ranging 80-130 nm. [97] The non-conductive α-alumina substrates can be rendered conductive using the same method that we did for AAO substrates. A coated conductive layer of 20-50 nm could be sufficient to meet the conductivity requirement for the ACD method considering the required current density is only 0.13 mA cm$^{-2}$.

The ACD approach also has the potential to prepare the ZIF-8 membrane on packed membrane modules since this approach only requires conductivity and is not sensitive to the substrate geometry. In particular, the defect “self-healing” property of this approach could be extremely helpful to minimize the defect formation caused by substrate geometry, which is highly beneficial for membrane assembly in different packed columns. In brief, the ACD method is a promising method that could be easily transformed into other supports. Applying MOF membranes under high pressure remains a serious challenge due to the brittle feature of MOF membranes. In the future, more studies should be directed to address this issue. Promising methods include tuning the interfacial interactions between the MOF layer and the support, improving the morphology of the porous support, synthesis of MOF hybrid membranes, etc. The superior separation
performance combined with the high mechanical stability from the MOF membranes could push membrane technology significantly closer to the industry application for propylene/propane separation, which can change the chemical industry.

Figure 5.1 Illustration of ceramic support for membrane deposition using the ACD method.
BIBLIOGRAPHY


APPENDICES


This work forms the majority of basis for Chapters 3, 4, and 5.