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Aqueously Cathodic Deposition of ZIF-8 membranes for Superior Propylene/propane Separation

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Electrochemical deposition has emerged as a novel approach to fabricate metal-organic framework (MOF) films. Here, for the first time, an aqueously cathodic deposition (ACD) approach is developed to fabricate ZIF-8 type of MOF membranes without addition of any supporting electrolyte or modulator. The fabrication process uses 100% water as the sole solvent and a low-defect density membrane is obtained in only 60 min under room temperature without any pre-synthesis treatment. The membrane exhibits superior performance in C₃H₆/C₃H₈ separation with 182 GPU C₃H₆ permeance and 142 selectivity, making it sit at the upper bound of permeance vs. selectivity graph, outperforming majority of the published data up to 2019. Notably, this approach uses an extremely low current density (0.13 mA cm⁻²) operated under an ultra-facile apparatus set-up, enabling an attractive way for environmentally friendly, energy efficient and easily scalable MOF membrane fabrications. This work demonstrates a great potential of aqueously electrochemical deposition of MOF membrane in the future research.

1. Introduction

Gas separation using membrane technology has attracted numerous attentions in the recent decades due to its high separation performance, energy efficiency and attractive economic feasibility. Efforts in studies on MOF-based membranes have resulted in prolific outcomes owing to the material's ordered crystallized structures, high porosity and unique chemical environment, which can provide either sieving effects or selective adsorption for gas separations.^[1] Among a variety of MOFs developed, ZIF-8 stands out as a promising candidate for the membrane application attributed to its high thermal and chemical stability.^[2] ZIF-8 has a window size of ~0.34 nm (Figure S1a).^[3] However, the structure flexibility allows it to be used in a number of binary gas separations such as H₂/CO₂, CO₂/N₂, H₂/CH₄, C₂/C₃, and C₃H₆/C₃H₈. In particular for C₃H₆/C₃H₈ separations, C₃H₆ and C₃H₈ have kinetic diameters of 0.40 nm and 0.42 nm respectively (Figure S1b and 1c), the slightly size difference enables C₃H₆ to diffuse through ZIF-8 in a speed of 125 times higher than C₃H₈.^[4] This large diffusion disparity allows for an effective C₃H₆/C₃H₈ separation with estimated ideal permselectivity of 130.^[5] Inspired by the separation potential of this material, our group has firstly demonstrated the ability of ZIF-8 membrane for effective C₃H₆/C₃H₈ separation^[6] and a selectivity up to 90 was achieved after careful optimization of the activation process and defect elimination.^[7] However, improving the selectivity is always compensated by a decrease in permeance. Many novel membrane fabrication methods have been developed such as substrate-seeded heteroepitaxy (SSH), spin coating techniques (SCT), liquid-phase epitaxy (LPE), interfacial synthesis, bottom-up modular assembly (BMA), chemical vapor deposition (CVD), and atomic layer deposition (ALD).^[8] Although separation performance has been continuously improved following the intensive efforts being contributed to this field, the same trade-off trend between the selectivity and permeance was observed. The main reason is that defects are developed randomly during the membrane process in all the above mentioned

1 fabrication methods. A relatively thick membrane is required to minimize defects, but thus
2 inevitably decrease the membrane permeance.

3 Recently, the electrochemical deposition has emerged as a novel approach to fabricate
4 MOF films.^[9] This approach requires relatively minor or non pre-treatment of the substrate,
5 shorter synthesis time, and milder synthesis condition.^[10] It also allows for continuous
6 production which acts as a major advantage compared with other methods for industrial scale-
7 up.^[9] More importantly, this method may provide an error-correction mechanism since the
8 deposition can be controlled by current. In general, anodic dissolution, cathodic deposition
9 and electrophoretic deposition are the three methods being used in this approach for the
10 fabrication. For anodic dissolution, a metal plate is used as anode and the metal source for the
11 MOF formation was dissolved from the metal plate. The dissolved metal ions react with the
12 ligand in the solvent and form a film on the metal plate.^[11] For cathodic deposition, both
13 metal ions and ligand are dissolved in the solvent and probase formed from the reduction
14 reaction near the conductive substrate. The formed probase facilitates the deprotonation of the
15 metal-ligand complex and promotes the nucleation and crystal growth on the substrate.^[12] For
16 electrophoretic deposition, the charged particles are driven by the electrical field towards the
17 conductive substrate and form a film on the substrate. In this method, a secondary growth is
18 normally adopted to allow for further crystallization and defect healing.^[13] Organic solvents
19 have been widely used for the film fabrication across the published works on electrochemical
20 deposition.^[9-10, 12] Electrolyte such as methyltributylammonium methylsulfate (MTBS),
21 tetrabutylammonium tetrafluoroborate (TBATFB), 1-butyl-3-methylimidazolium bromide
22 (BMIN bromine), NH_4F , Na_2SO_4 , and KCl are normally added into the solvent to increase
23 conductivity.^[10] Modulator was also sometimes added to modify the crystal morphology or
24 speed up the crystallization for targeted film deposition.^[14] The addition of the electrolyte or
25 modulator has somewhat added another dimension of complexity into the fabrication process.
26 Little in-depth research was conducted so far 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 much desirable if the addition of the electrolyte can be eliminated for a better control over the synthesis process. Organic solvents also cause a concern for the potential negative impacts on the environment in the large-scale industrial production. In comparison, water would be the best possible choice for an environmentally friendly process.^[15] However, as water is very easily to be electrolyzed in a basic solution, it has remained to be a challenge in this field to adopt 100% water as the sole solvent to anodically/cathodically deposit MOF membrane.

As a promising approach, research on electrochemical deposition of MOF is still at its infant stage with most of the efforts being focused on thin film production,^[9-10] only a few works have been published for membrane fabrication.^[12b, 13] The deposition procedure and set-up are mostly delicately controlled such as careful selection of electrolyte and reference electrode, using double electrolyte cell to eliminate the disturbance of the reactions occurred on the counter electrode, and prolonged post-synthesis treatment, which makes this approach challenging to be used for scale-up production. In addition, little publication has used this approach to achieve satisfactory performance in gas separation with both high permeance and selectivity. Here, we reported the fabrication of ZIF-8 membranes *via* aqueously cathodic deposition (ACD) without addition of any supporting electrolyte or modulator. The fabrication process used pure water as solvent and completed in only 60 min without any post-treatment. The membrane showed the best combination of permeance vs. selectivity in the separation of C₃H₆/C₃H₈ mixture.

2. Results and Discussions

2.1. Membrane Fabrication Set-up

The experimental set-up is very simple. It comprises two electrodes in a single electrolyte cell, as shown in **Figure 1**. AAO coated with a 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 ligand to $\text{Zn}^{\text{(II)}}$ ratio of 60 was used for complete ligand deprotonation and thus to ensure a pure MOF to be formed.^[16] A dilute solution of $\text{Zn}^{\text{(II)}}$ ($\text{Zn}^{\text{(II)}} : \text{H}_2\text{O} = 1:3889$) was used to slow down the crystal growth in the bulk solution and thus help to form an uniform deposition on the substrate. During the deposition process, zinc cations were driven towards the substrate at cathode side and formed zinc-ligand complexes. The probase OH^- released from the reduction of water built up a 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,^[17] facilitated the deprotonation of the zinc-ligand complex near the substrate. The deprotonated zinc-ligand complex then further went to oligomerization, nucleation, crystallization and finally formed a layer of dense crystals on the substrate.

In this deposition process, due to the narrow potential window of water reduction (see Figure S2), the current density must be very low to avoid vehemently water electrolysis. Otherwise, the resulted hydrogen evolution will form a layer of bubbles on the substrate. The bubbling process would not only disrupt the deposition process, but also form very high concentration of OH^- ($[\text{OH}^-]$) near the substrate. The high $[\text{OH}^-]$ will corrode the already formed MOF, leading to severe amount of membrane defects. An optimal current density of 0.13 mA cm^{-2} was identified, which ensured both slow water electrolysis and quick deposition rate. After 60 min, a uniform membrane with thickness in visible light wavelength range (See

Figure S3) was obtained. After the cathodic deposition, there was little precipitation obtained in the residual solution, proving that most of MOFs grew directly on the substrate. As a comparison, an in-situ growth of the membrane on AAO was also conducted, but no membrane was formed (See Figure S4c and 4d).

2.2. Membrane Growth

An ex-situ investigation of the deposition process was conducted by SEM analysis (Figure 2 and Figure S5). 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). Looking at the whole process, the crystal size had continuously increased from 10 min to 60 min (Figure 2a-e), resulting in a gradual increase of membrane thickness (Figure 2f-j). Correspondingly, the membrane growth gradually decreased the conductivity of the substrate, which caused the increase of voltage in order to maintain the constant current (Figure S6). In this process, the crystal morphology gradually transformed from cubic (Figure 2a) to rhombic dodecahedra (Figure 2e) with mostly (110) phase exposed. The (110) phase is the most thermodynamically stable face of ZIF-8,^[14b] ensuring the chemical stability of the membrane. Meanwhile, the thickness of the membrane was increased from ~50 nm (Figure 2f) to ~500 nm (Figure 2j).

At 10 min (Figure 2a), cubic crystals have been uniformly deposited on the solid surface around the pores of the substrate (See Figure S4a and 4b for pristine AAO), implying that nucleation happened initially on the conductive surface. This phenomenon suggested that the electric current functioned as a driving force for the nucleation to occur. The corresponding XRD pattern (Figure S7) showed the characteristic peaks at (001), (002), (112), (022), (012), and (222) of ZIF-8 have emerged, suggesting the nucleation and crystallization have been co-happening 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 2b), the cubic

crystals have almost fully covered the substrate. When it went to 30 min (Figure 2c), the crystals have been undergoing a morphological transformation from cubic to rhombic dodecahedra, and intergrown to form a membrane on the substrate. For 30 – 40 min, the crystals continued to crystallize and grew to seal the grain boundary *via* intergrowth (Figure 2d), and finally formed a continuous membrane at 60 min (Figure 2e). The final membrane formed comprised a single layer of crystals with size ~500 nm.

2.3. Gas Separation Test

The membranes deposited from 30 min onwards were tested for C₃H₆/C₃H₈ separation using the Wicke – Kallenbach technique (Figure S8) with both sides of the membrane are maintained at ambient pressure. The feed is a mixture of 50:50 molar ratio of C₃H₆ and C₃H₈, while the permeate is purged with argon as a carrier gas. The results are listed in **Table 1**. As expected, the permeance of C₃H₆ 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 sharply enhanced to 142 with C₃H₆ permeance reached 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 C₃H₆/C₃H₈ separation. The selectivity of 142 has reached to the estimated ideal permselectivity of 130.^[5] The permeance of 182 GPU has outperformed the majority of the published works while remained the selectivity uncompromised. **Figure 3** 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.

The potential of ACD method to be used in real petrochemical industry was also evaluated. In general, the separation of C_3H_6/C_3H_8 is industrially carried out at temperature around 50 °C and pressure from 3 bar up to 18 bar.^[2] Thus, both thermal and mechanical stability of the membrane are crucial for the real commercialization. To test the thermal stability, an online test of gas separation performance at varied temperatures (22 – 130 °C) was conducted (Figure S9). With the increase of temperature, the permeance of C_3H_6 remained relatively stable, but the selectivity decreased and reached the lowest point at 130 °C (Figure S9a). This observation was mainly due to the increased C_3H_8 permeance (Figure S9b). The selectivity gradually returned to its original values after the temperature reduced back to around 22 °C, implying that the membrane obtained by ACD method can withstand high temperatures without damaging its intrinsic crystalline structure. The selectivity at 50 °C and 130 °C are around 130 and 55, both are satisfactory for industrial applications.

However, 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), the first requirement is to use stronger substrates. The ACD approach is feasible to prepare high quality ZIF-8 membranes on strong substrates such as α -alumina and metal flat plate or hollow fiber, as illustrated in Figure S10. The non-conductive α -alumina substrates can be rendered conductive using the same way as we did for AAO substrates. The ACD approach also has potential to prepare ZIF-8 membrane on packed membrane modules since this approach only requires conductivity and are not sensitive to the substrate geometry. In particular, the defect ‘self-healing’ property of this approach will be very helpful to minimize the defect formation caused by substrate geometry, which is very beneficial for membrane assembly in different packed columns. Nevertheless, while the method can be potentially applied to stronger substrates, applying MOF membranes under high pressure is still a big

challenge that requires substantial future studies as demonstrate in many previous work in this field.

2.4. Discussion on Gas Separation Results

The high permeance of our membrane can be attributed by 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 ligand existed in the structure which can block the pores of the crystal. Factor (a) has been proved in the SEM analysis (Figure 2j), showing the single layer of crystals of ~500 nm solely contributed the thickness of the membrane. To prove factor (b), we conducted a krypton adsorption to measure the surface area of the membrane. This measurement has followed the previous published works.^[18] The Brunauer-Emmett-Teller (BET) specific surface area of M-60, expressed as per membrane area per 100 nm thickness was $177 \text{ m}^2 \text{ m}^{-2} 100 \text{ nm}^{-1}$. This result was comparable with the published data using krypton adsorption (See Table S1). 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 $1.05 - 1.19 \text{ g cm}^{-3}$ depending on the synthesis and activation methods,^[19] coupled with the obtained membrane thickness ~500 nm, the calculated BET surface area is $1485 - 1698 \text{ m}^2 \text{ g}^{-1}$. It is noticeable that some crystals have grown into the pore of the AAO substrate (Figure 2), but no continuous growth of such crystals were observed along the near surface pores after careful analysis of a collection of SEM images. This didn't allow these 'in-pore' crystals to be accountable for the thickness of the membrane. It is aware that these crystals might affect the surface area calculated here. However, it was 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 ($1485 - 1698 \text{ m}^2 \text{ g}^{-1}$). Comparing the values with a broad range of published data,^[3, 17, 20] this result was considered to be within a reasonable range, which proves factor (b) that the membrane exhibits high porosity.

To prove factor (c), FTIR measurement was conducted as shown in **Figure 4**. Membrane obtained at 60 min, and 2-methylimidazole (2-MIM) were plotted together for comparison. Overall, C-H 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 has been deprotonated and incorporated into the crystal structure, no FTIR detectable uncoordinated 2-MIM existed in the membrane.

The high selectivity of our membrane directly proves that our membrane has little defects. This can be further confirmed by the XPS studies as shown in **Figure 5**. Figure 5a and 5b 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.^[21] Clearly, M-60 displays two narrow peaks at 1022.1 eV and 1045.2 eV respectively, which implies the majority of Zn are 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,^[22] which would shift the peak towards lower BE.^[23] Similar observations were observed for N 1s spectra (Figure 5b), systematic peak shift and broadening towards lower BE were observed from sample M-60, M-40 and M-30. We didn't observe any peak above 400 eV which is normally associated with -NH- of 2-MIM,^[24] implying that little non-deprotonated

2-MIM was existed in our samples. This is also consistent with the FTIR results (Figure 4). For M-60, a sharp peak was observed at 398.9 eV which is assigned to N-Zn coordination, suggesting that majority of N are in the similar chemical environment. For M-40 and M-30, the peak shifted and broadened towards lower BE, we believe this phenomenon are also mainly due to unsaturated Zn-N bonds as the number (x) of Zn-N_x coordination is positively correlated with BE.^[24b] The unsaturated Zn is widely accepted as the point defects in the framework and could significantly affect molecule diffusion.^[25] As the XPS results demonstrated, M-30 exhibited the largest quantity of these defects. The defects were continuously healed with the deposition time, which ended up with a low-defect density membrane (M-60). This is in good agreement with the C₃H₆/C₃H₈ separation performance discussed earlier.

3. Conclusion

In conclusion, we have developed an aqueously cathodic deposition (ACD) approach for ultra-facile fabrication of MOF membrane on AAO substrates without addition of any supporting electrolyte or modulator. This approach enables to fabricate ultra-thin membrane consisted of a single layer of crystals. A low-defect density membrane can be obtained within 60 min without any post-synthesis treatment. The membrane exhibited superior performance in C₃H₆/C₃H₈ separation with 182 GPU C₃H₆ permeance and 142 selectivity at room temperature, making it outperform most of the published data. Notably, for the first time, this approach uses water as the sole solvent, adopts an extremely low current density, and employs a very simple apparatus set-up, enabling an attractive way for environmentally friendly, energy efficient and easily scalable MOF membrane fabrications. The membrane showed good thermal stability that well 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 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-sheet or hollow fiber. To apply the membranes on high pressure gas separation, which is still a big challenge up to date, further substantial research efforts will be needed.

4. Experimental Section

Chemicals and Materials: Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, > 99%) and potassium chloride (KCl, > 99%) were purchased from Sigma-Aldrich. 2-Methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 99%) was purchased from Acros Organics. All chemicals were used without further purification. The deionized water (DI water) used for synthesis was purified using Milli-Q® Academic ultrapure water system. Anodic aluminum oxide (AAO) substrates (Anodisc™ 13) with pore size of 200 nm and thickness of 60 μm were purchased from Whatman®.

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, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.183 g, 0.83 mmol) was dissolved in DI water (10 mL). The two solutions were mixed together and stirred for 5 seconds to form the ZIF-8 precursor solution for the cathodic deposition.

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 by 1.5 cm and immersed in the ZIF-8 precursor solution. The reaction was taken 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 by DI water and methanol after the reaction. The fabricated membranes were activated in methanol for gas permeation test.

Mixed-gas Permeation Test: The permeation test was performed by the Wicke-Kallenbach technique as shown in Figure S8. At the feed side, the equal molar ratio of C_3H_6/C_3H_8 with 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 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 online by Agilent 7890A gas chromatograph equipped with flame ionization detector (FID).

Material Characterization: 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.

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

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

A Nicolet 6700 Fourier-transform infrared (FT-IR) spectrometer with a KBr beam splitter and CaF_2 window was used to obtain the IR spectra of the membranes. The membrane samples were degassed under vacuum at 110°C for 12 hours before measurements. The samples were analyzed with 32 scans at a resolution of 0.964 cm^{-1} .

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

X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Kratos Amicus spectrometer with monochromatic Al-K α 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.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

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Figure 1. Illustration of experimental setup used for aqueously cathodic deposition (ACD) of ZIF-8 membrane.

Figure 2. 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 3. Comparison of C_3H_6/C_3H_8 separation performance with membranes reported up to 2019.

Figure 4. Comparison of FTIR spectra of M-60 with 2-MIM.

Figure 5. XPS spectra of (a) Zn 2p and (b) N 1s.

Table 1. Permeance and selectivity of C₃H₆ in C₃H₆/C₃H₈ separation test.

Sample	C ₃ H ₆ Permeance (GPU)	C ₃ H ₆ /C ₃ H ₈ Selectivity
M-30	1618 ± 22	3 ± 0.03
M-40	692 ± 17	11 ± 0.39
M-60	182 ± 9	142 ± 4

Table of Content

An ultrathin ZIF-8 membrane with ~500 nm thickness is fabricated via a novel aqueously cathodic deposition (ACD) method. The membrane shows superior C_3H_6/C_3H_8 separation performance with the permeance of C_3H_6 up to 182 GPU and the selectivity of C_3H_6 over C_3H_8 up to 142, which surpass all the reported membrane performances prepared by conventional methods.

Metal-Organic Frameworks

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Aqueously Cathodic Deposition of ZIF-8 membranes for Superior Propylene/propane Separation