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Highly Water-Permeable Metal–Organic Framework MOF-303 Membranes for Desalination

Shenzhen Cong, Ye Yuan, Jixiao Wang, Zhi Wang, Freek Kapteijn, Xinlei Liu*

ABSTRACT: New membrane materials with excellent water permeability and high ion rejection are needed. Metal-organic frameworks (MOFs) are promising candidates by virtue of their diversity in chemistry and topology. Here, continuous aluminum MOF-303 membranes are prepared on α -Al₂O₃ substrates *via* an *in-situ* hydrothermal synthesis method. The membranes exhibit satisfying rejection of divalent ions (for example, 93.5% and 96.0% for MgCl₂ and Na₂SO₄, respectively) on the basis of size sieving and electrostatic repulsion mechanism and unprecedented permeability (3.0 L·m⁻²·h⁻¹·bar⁻¹· μ m). The water permeability outperforms typical zirconium MOF, zeolite, commercial polymeric reverse osmosis and nanofiltration membranes. Additionally, the membrane material exhibits good stability and low production costs. These merits recommend MOF-303 as a next-generation membrane material for water softening.

Metal-organic frameworks (MOFs) are a family of porous crystalline materials composed of inorganic metal ions or metal clusters connected by organic ligands *via* coordination bonds.¹⁻⁴ Given by their diversity in chemistry and topology, MOFs have been extensively explored for applications such as gas storage, separation, sensing, catalysis, proton conduction, *etc.*⁵⁻⁷ Significant progresses have been made on fabricating polycrystalline MOF membranes, especially for gas separations.⁸⁻¹³ However, applications of polycrystalline MOF membranes in water treatment were initially obstructed due to the lack of chemical stability. Although highly water-stable zirconium MOF membranes were unveiled in recent years,^{14, 15} the related research is still in its infancy. Highly water-permeable MOF membranes with satisfying rejection had been on demand.

Very recently, a water-stable aluminum MOF named MOF-303 (Al(OH)(HPDC); HPDC, 1H-pyrazole-3,5-dicarboxylate) was reported.^{16, 17} It has the *xhh* topology and is constructed from an infinite, rod-like Al(OH)(-COO)₂ clusters linked through HPDC ligands (**Figure S1**). In the clusters, octahedrally-coordinated Al(III) are corner-shared bound by four bridging carboxyl and two hydroxyl groups. MOF-303 features a 3D framework with 1D rhombic channels (open space around 0.6 nm) along *a*-axis.¹⁶ The clusters and ligands endow the 1D channels with hydrophilic sites. The high pore volume together with the hydrophilic nature of the framework was translated into impressive water capacity. Besides, fast sorption kinetics were observed attributed to the 1D hydrophilic channels which created a favorable situation for the formation of well-defined water cluster structures.^{17, 18} Furthermore, the pore opening size of the 1D channels is around 0.60 nm in diameter, locating between the diameters of water molecules (0.28 nm, **Table S1**) and common hydrated ions (≥ 0.66 nm, **Table S1**).¹⁹ Therefore, water desalination can be realized based on the size exclusion mechanism (**Figure 1**). Additionally, cheap metal and ligand sources are available and water can be used as solvent for the production of MOF-303. The above

merits of MOF-303 satisfy the prerequisites of a high-performance membrane material for water desalination to mitigate the shortage of fresh water. However, to the best of our knowledge, no dense polycrystalline MOF-303 membranes have been unveiled.

In this work, to harness these properties inside energy-efficient membranes, continuous polycrystalline MOF-303 membranes supported on porous alumina disks were fabricated *via* an *in-situ* hydrothermal synthesis method. The as-synthesized membranes exhibited high rejection for divalent ions and unprecedented permeability, recommending MOF-303 as an excellent membrane material for water softening.

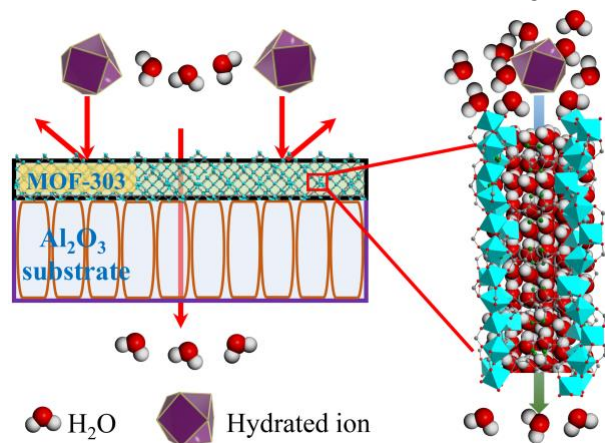


Figure 1. Schematic representation of water desalination with a metal–organic framework MOF-303 membrane.

Stability of MOF-303 powders in saline water was tested before membrane fabrication. MOF-303 powders were suspended in various saline aqueous solutions (0.10

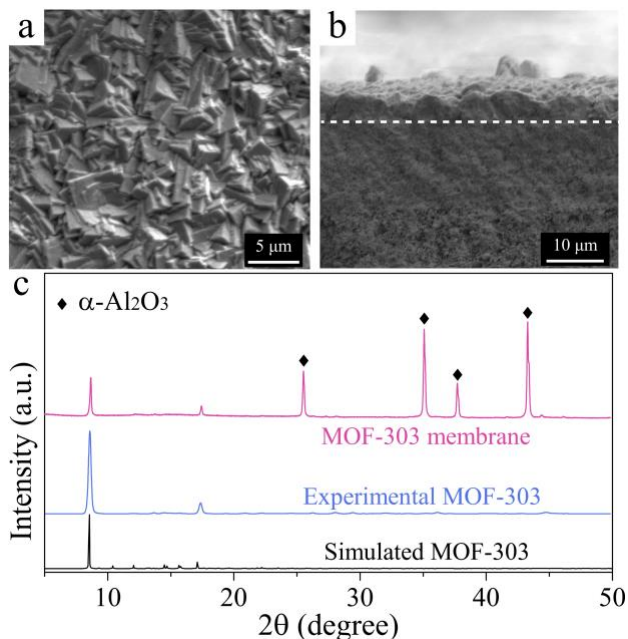


Figure 2. Top view (a) and cross-sectional (b) SEM images of a MOF-303 membrane. A dash line is shown in Figure b to distinct the membrane layer and substrate. (c) XRD patterns of experimental MOF-303 powders and membrane. The simulated one is provided for comparison.

wt. % KCl, NaCl and MgCl₂) at 50 °C. The concentration of MOF-303 in these solutions was relatively low (0.04 wt. %) and adequate water solutions were used in case the stability is concentration-dependent.¹⁸ After 50 days' treatment, both the crystalline structure and morphology of MOF-303 were well retained as evidenced by the XRD patterns and SEM images, respectively (Figures S3 and S4).

Since no recipes for fabricating polycrystalline MOF-303 membranes were disclosed, the amount of metal source, ligand, alkali and solvent, temperature, duration and the type and roughness of substrates were thoroughly studied in this work to yield sufficient growth nuclei and form fairly well-intergrown membrane structures. Finally, an optimal recipe obtained (see details in the Supporting Information): the molar ratio of Al³⁺:H₃PDC:NaOH:H₂O was fixed at 1:1:2:2000; the proper temperature and duration were 100 °C and 48 h, respectively; porous α-Al₂O₃ disks with asymmetric configuration (70 nm average pore size for the top layer) were preferred as substrates. Porous alumina was employed as substrate, which has been widely used in commercial crystalline zeolite membrane modules, because of its low transport resistance, easy scaling up, and good chemical and fantastic thermal stability. In addition, the surface of the alumina substrate can partially dissolve under alkaline conditions and the released Al will coordinate with HPDC ligands, facilitating the nucleation and growth of MOF-303 membranes.

As indicated in Figures 2a and 2b, the surface of the substrate is completely covered with well-intergrown crystals with no visible cracks or pinholes. The crystals have sharp edges with size between 1.0-4.0 μm yielding a membrane thickness of around 4.0 μm. The crystalline structure and random packing of the grains were confirmed by the XRD patterns (Figure 2c).

To confirm the integrity of the as-synthesized membrane, single-gas permeation measurements were performed with a

soap-film flowmeter at room temperature (25 ± 2 °C) under a transmembrane pressure of 1.0 bar (see details in the Supporting Information). As shown in Figure 3, the H₂ permeance is about 1.2 × 10⁻⁶ mol · m⁻² · s⁻¹ · Pa⁻¹ and the ideal selectivity for light gas pairs (6.3, 3.9 and 2.9 for H₂/CO₂, H₂/N₂ and H₂/CH₄, respectively.) is close to the corresponding Knudsen diffusion ratio (4.7, 3.7 and 2.8). Size sieving effect is illustrated by the H₂/C₃H₈ and H₂/i-butane pairs with ideal selectivity of 21.8 and 49.6 and Knudsen diffusion ratio of 4.7 and 5.4, respectively. These results verify that the polycrystalline membrane is continuous, highlighting its integrity. No sharp cut-off between H₂ and other gases was observed probably because the pore size of MOF-303 (~ 0.60 nm) is larger than their kinetic diameters (H₂, CO₂, N₂, CH₄, C₃H₈ and i-butane are ~ 0.29, 0.33, 0.36, 0.38, 0.42 and 0.50 nm, respectively).²⁰ The fluctuation of gas permeance with kinetic diameter can be rationalized on the interplay of adsorption and diffusion effects.

The continuous MOF-303 membrane was applied for water desalination. Five different salt solutions (containing KCl, NaCl, CaCl₂, MgCl₂ and Na₂SO₄) with the same concentration (0.10 wt. %) were prepared as feed. The measurements were carried out in a dead-end system (Figure S7) at room temperature (25 ± 2 °C) with a transmembrane pressure of 5.0 bar. Each salt passed through the membrane in a manner of ion pair to conserve electroneutrality. The membrane rejection for different salts was determined by testing the ion conductivity in the retentate and permeate with a conductivity meter. The permeance was obtained based on the permeated volume, membrane area, duration of permeate collection and transmembrane pressure (See details in the Supporting Information).

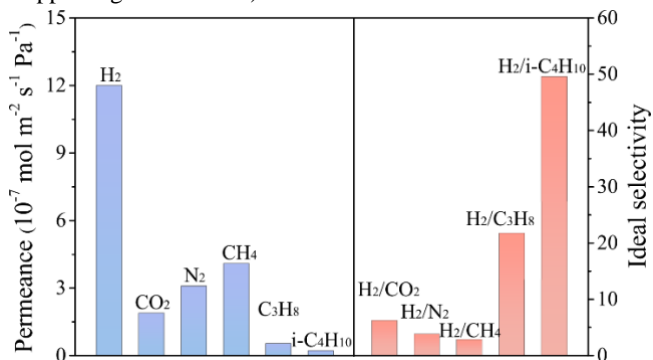


Figure 3. Single gas permeance and ideal selectivity of a MOF-303 membrane. The operation temperature was 25 ± 2 °C under a pressure difference of 1.0 bar. The pressure of the permeate side was kept under ambient condition.

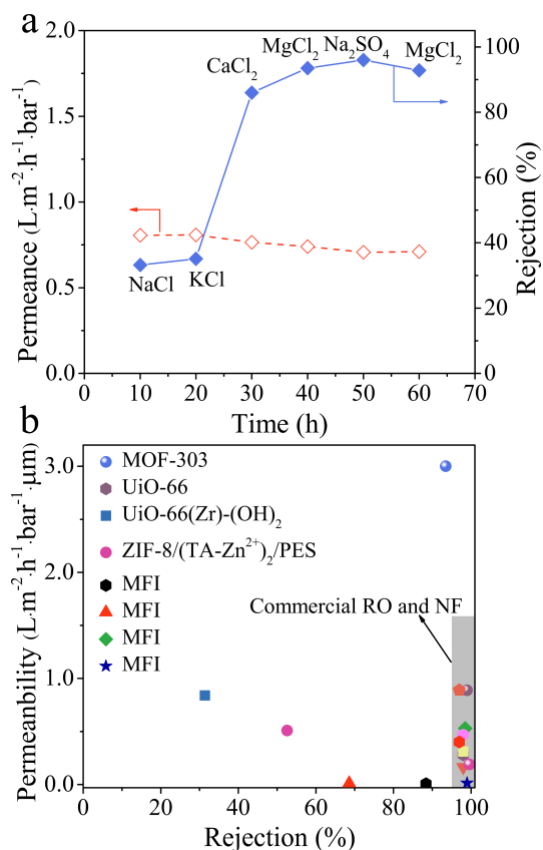


Figure 4. (a) MOF-303 membrane separation performance for water desalination. The feed concentration of each solution (KCl, NaCl, CaCl₂, MgCl₂ and Na₂SO₄) was 0.1 wt. %. The operation temperature and transmembrane pressure were 25±2 °C and 5.0 bar, respectively. The system was flushed with DI water and dried when feed was changed. (b) Desalination (Mg²⁺ retention) performance of MOF-303, zeolite, commercial polymeric reverse osmosis (RO) and nanofiltration (NF) and other MOF membranes. The Figure b was plotted using the data in Table S3.

As depicted in **Figure 4a**, the membrane rejection roughly increases with hydrated ion diameter (in nm, K⁺ (0.66) = Cl⁻ (0.66) < Na⁺ (0.72) < SO₄²⁻ (0.76) < Ca²⁺ (0.82) < Mg²⁺ (0.86)), demonstrating a size sieving mechanism. The rejection of monovalent ions (33.2% and 35.1% for NaCl and KCl, respectively.) is lower than expected. This can be interpreted by the structural flexibility of MOF-303. Although the pore size of MOF-303 is around 0.60 nm estimated from crystallographic data,¹⁶ an average pore size of 0.80 nm was derived from our Ar adsorption experiment (Figure S5).²¹ Hence, good rejection was achieved in the case of divalent ions (93.5% and 96.0% for MgCl₂ and Na₂SO₄, respectively.) when their hydrated ion diameters are close to 0.80 nm. These results further prove the membrane integrity. As rearrangement and dehydration of the water shell surrounding ions could take place during transport, reducing their effective size, a small amount of divalent ions were present in the permeate. Moreover, the flexibility of MOF-303 framework also account for this phenomenon. Although the hydrated ion diameter of SO₄²⁻ is smaller than Ca²⁺ and Mg²⁺, the rejection for Na₂SO₄ is higher than CaCl₂ and MgCl₂. This can be rationalized on the electrostatic repulsion effect. Carboxyl groups in the ligands of MOF-303 can be ionized thus endows the membrane surface with negative charges (**Figure S7**). The membrane exhibited a moderate permeance (0.74

L·m⁻²·h⁻¹·bar⁻¹). Over the 60 h's evaluation, the permeance was well maintained. Furthermore, a constant ion rejection can be recognized from the repeated tests using MgCl₂ solutions (**Figure 3a**). These indicate that the crystalline structure and grain boundaries of the membrane, the interfaces between the membrane and substrate and the substrate were not damaged during the test. Direct evidences can be found from the invariable SEM images (**Figure S8**) and XRD pattern (**Figure S9**). An outstanding stability and qualified mechanical strength were proved.

In order to benchmark and compare the intrinsic performance of membrane materials, membrane thickness was normalized and permeability was calculated. As anticipated, the MOF-303 membrane delivers the highest permeability (3.0 L·m⁻²·h⁻¹·bar⁻¹·μm) combined with satisfying rejection (for Mg²⁺) (**Figure 4b** and **Table S2**). The exceptional water permeability is 3.6, 5.7, 1.9, 3.4 times of the reported typical zirconium MOF UiO-66,¹⁵ zeolite MFI,²² commercial polymeric reverse osmosis²³⁻²⁵ and nanofiltration membranes,^{23, 25-27} respectively. This can be attributed to the high water capacity and fast water sorption kinetics of MOF-303.¹⁷ The hydrophilic 1D channels in MOF-303 could create a favorable situation for the formation of well-defined water cluster structures facilitating water transport.¹⁸ The high water permeability, satisfying rejection for divalent ions, low material cost together with good stability and reproducibility (**Table S2**) point that MOF-303 is a promising next-generation membrane material for water softening.

In conclusion, continuous polycrystalline MOF-303 membranes were fabricated on porous α-Al₂O₃ substrates via an *in-situ* hydrothermal synthesis approach. The as-synthesized membranes exhibited a high rejection of divalent ions (93.5% and 96.0% for MgCl₂ and Na₂SO₄, respectively.) and an unprecedented water permeability (3.0 L·m⁻²·h⁻¹·bar⁻¹·μm). The high water capacity and fast water sorption kinetics played an important role in this exceptional water permeability. Furthermore, the membranes feature excellent stability, good stability and low material cost. These properties indicate that MOF-303 is a promising membrane material for water softening. Since MOF membranes with thickness down to a few tens of nanometers were successfully produced via a scalable route, it can be envisaged that, after this earliest report, there will be some optimal preparation conditions for fabricating supported high-flux MOF-303 membranes with thinner selective layer for practical applications.

ASSOCIATED CONTENT

Supporting Information.

Experimental and characterization details; structure of MOF-303; N₂ adsorption-desorption isotherms, SEM images and XRD patterns of MOF-303 powders and membranes, gas separation performance, water desalination performance. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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