



Atmospheric-pressure plasma modification to improve RO performance of methyl-functionalized silica membranes in organic aqueous solutions

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Abstract

Various industries discharge water mixed with organic solvents, typically recovering them through energy-intensive methods like distillation or burning. However, as we aim for a circular economy, there is a growing need for energy-efficient recovery technology. Reverse osmosis (RO), a membrane separation technology, stands out as it does not require phase change and is more energy-efficient compared to conventional distillation [1]. For an effective RO concentration of these solvent mixtures, the membrane must exhibit mechanical strength to withstand high osmotic pressure difference and resistance to solvents and water. Organosilica membranes, which integrate organic components into a silica structure, exhibit excellent mechanical strength and resistance to solvents and water [1, 2]. These membranes are promising for use in the concentration of organic aqueous solvents by RO. However, the rejections of organic solvents are moderate compared to that of conventional membranes. It is necessary to increase the rejection properties while maintaining the water permeance. We previously found that adjusting the hydrophilicity and pore size of organosilica membranes through atmospheric-pressure plasma enhances both the permeance and selectivity in the pervaporation dehydration of water/alcohol mixtures [3, 4]. In this study, we investigated the RO properties of plasma-modified organosilica membranes to clarify their potential for use in RO-based concentration of aqueous organic solutions.

The organosilica membranes were prepared by the following procedure. An α - Al_2O_3 particle layer and 1, 2-Bis (triethoxysilyl) ethane-derived intermediate layer [5] were formed on the α - Al_2O_3 porous substrate. Subsequently, Methyltriethoxysilane (MTES)-derived sol was coated and fired at 300°C in N_2 atmosphere to form organosilica separation layer. The MTES-derived sol was obtained by mixing MTES, EtOH, H_2O , and HCl (molar ratio MTES: H_2O : HCl = 1: 30: 0.01, MTES = 5 wt%) and subjected to hydrolysis and polymerization at 50°C. The surface structure of the membranes was controlled by irradiating the membrane surface with atmospheric-pressure plasma at a specified time. The permeation properties were evaluated in aqueous solutions of MeOH, EtOH, IPA, t-BuOH, acetonitrile (ACN), DMF, DMAc, NMP, and acetone ($\text{H}_2\text{O}/\text{solvent} = 95/5$ -85/15 wt%) at 50°C and applied pressures of 6-12.5 MPa.

Gas permeation experiments were conducted to investigate the structure of the membranes with and without plasma modification. As summarized in Table 1, the H_2 permeance slightly decreased from 2.1×10^{-6} to $1.2 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, while the N_2 permeance drastically decreased from 1.3×10^{-7} to $8.3 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, resulting in an increased H_2/N_2 permeance ratio. Because the diameter of H_2 and N_2 are 0.29 nm and 0.36 nm, this change in permeances indicate

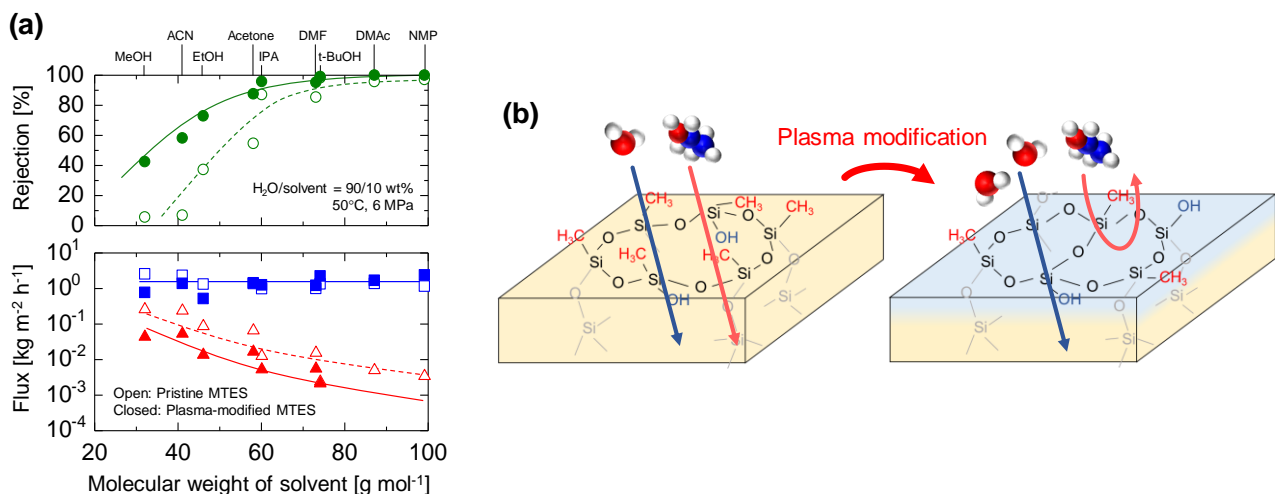


Fig. 1. (a) Molecular weight dependence of flux and rejection in RO separation of $\text{H}_2\text{O}/\text{solvent}$ mixtures. (b) Illustration of the changes in MTES-derived membranes with and without plasma modification.



the pore size was reduced by plasma modification. Table 1 summarizes the C/Si and O/Si ratios measured using XPS for the MTES-derived films with and without plasma modification. Plasma modification reduced the C/Si ratio from 1.12 to 0.36 and increased the O/Si ratio from 1.60 to 1.96 [6]. This indicates the oxidation of methyl groups on the membrane surface and the subsequent formation of Si-O-Si linkages, leading to a reduction in the size of the silica network pores.

Fig. 1 (a) shows the dependence of the molecular weight of the solvent on the permeation flux and rejection rate of the MTES-derived membranes with and without plasma modification. The rejection rate increased with increasing molecular weight for both MTES-derived membranes with and without plasma modification, indicating that separation is based on the size sieving effect. For instance, in the H₂O/Acetone system, the permeation fluxes of the MTES-derived membranes with and without plasma modification were similar, at 1.37 and 1.44 kg m⁻² h⁻¹, respectively, while the rejection rate significantly increased from 54.6% to 87.6%. This enhanced rejection, without substantially reducing the water flux, was achieved in all systems examined. This improvement is likely due to the combined effects of surface hydrophilization and reduced pore size. Surface hydrophilization was confirmed by the water contact angle, which decreased from 103.7° to 48.0°, as listed in table 1.

As illustrated in Fig. 1 (b), hydrophilization caused by the oxidation of methyl groups on the membrane surface and decreased pore size successfully improved the selectivity without significantly decreasing the water permeance.

Table. 1 Membrane performance, chemical compositions measured by XPS, and water contact angles of MTES-derived films with and without plasma modification.

Sample	H ₂ permeance [mol m ⁻² s ⁻¹ Pa ⁻¹]	N ₂ permeance [mol m ⁻² s ⁻¹ Pa ⁻¹]	H ₂ /N ₂ [-]	C/Si [-]	O/Si [-]	C.A. [°]
Pristine MTES	2.1×10 ⁻⁶	130×10 ⁻⁹	16	1.12	1.60	103.7
Plasma-modified MTES	1.2×10 ⁻⁶	8.3×10 ⁻⁹	145	0.36	1.96	48.0

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