



# Preparation and characterization of polyimide–silica composite membranes and their derived carbon–silica composite membranes for gas separation

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## HIGHLIGHTS

- Morphology of composite membranes was dependent on surface property of SiO<sub>2</sub> particle.
- Permeability of gas (CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, He) increased with increasing filler volume fraction.
- Composite membranes with modified SiO<sub>2</sub> had comparable selectivity with pure P84.
- Composite membrane using modified SiO<sub>2</sub> had higher selectivity than the pristine SiO<sub>2</sub>.
- Free volume theory provided acceptable predictions with the experimental data.

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## ABSTRACT

Polyimide (PI)–silica composite membranes and their derived carbon–silica composite membranes were prepared for gas separation. The polyimide–silica composite membranes were prepared using the sol–gel technique, in which the polyimide matrix was synthesized by the condensation of pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) while the inorganic phase was prepared by the in situ hydrolysis of tetraethyl orthosilica (TEOS) and a silane coupling agent, (3-aminopropyl)triethoxysilane (APTES). The derived carbon–silica composite membranes were prepared by the pyrolysis of the polyimide–silica composite membranes at 900 °C under vacuum. The structures of the membranes were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, and X-ray diffraction (XRD) technique. The gas (He, CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>) permeabilities of the polyimide–silica composite membranes and carbon–silica composite membranes were investigated. With the introduction of the silica, there was no significant enhancement of the gas separation in the resulting polyimide–silica composite membranes over the polyimide membrane, which still suffered a “trade-off” relationship between permeability and selectivity. However, the derived carbon–silica composite membranes exhibited better gas separation properties. The C–SiO<sub>2</sub> 28% composite membrane produced the highest permeances of 1042.18, 991.21, 296.03 and 155.26 GPU for He, CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>, respectively, which were 21.61, 137.67, 103.15 and 150.74 times, respectively, of those of the pure carbon membrane. The C–SiO<sub>2</sub> 11% composite membrane produced the highest selectivities of 37.57, 36.61 and 7.09 for He/N<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub>, respectively, which had surpassed the Robeson's upper bound for these gas pairs. The agreement between the pure gas selectivity and the mixed gas selectivity for O<sub>2</sub>/N<sub>2</sub> gas pair was reasonable, ranging from –8.30% to +16.61% using the pure gas selectivity as the base except for C–SiO<sub>2</sub> 23% composite membrane which showed +35.81% difference.

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## 1. Introduction

Membrane-based gas separation has been of great interest in several industrial applications [1]. Compared with the traditional

separation technologies such as cryogenic techniques and absorption and pressure swing adsorption technology, membrane-based gas separation possesses many significant advantages, such as lower energy and capital costs and simplicity of the equipment. For a feasible gas separation process, high selectivity and high permeability are the essential requirements of membranes: the higher selectivity results in higher separation efficiency and lower

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