



## Full Length Article

# Oxygen separation membrane based on facilitated transport using cobalt tetraphenylporphyrin-coated hollow fiber composites



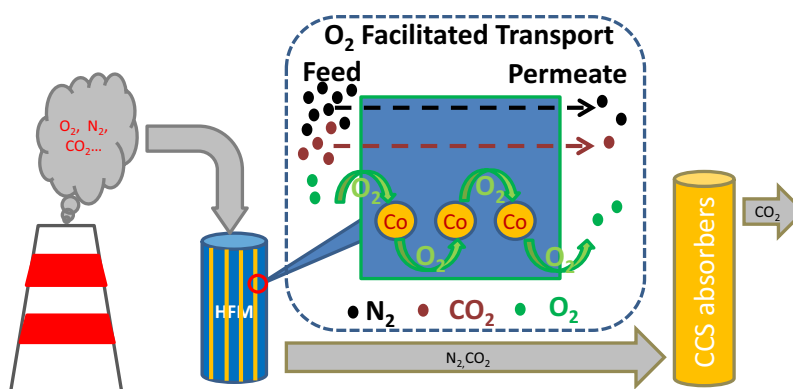
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## HIGHLIGHTS

- Oxygen in flue gas causes degradation of absorbent in carbon capture process.
- Oxygen facilitated transport hollow fiber membrane is proposed for oxygen removal.
- Membrane is characterized by microscopy and spectroscopy and gas permeation.
- Coating layer is a thin dense layer with an increasing packing density.
- Oxygen/carbon dioxide selectivity is reversed by current membrane.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The post-combustion flue gas discharged from coal-fired power plants is a major source of carbon dioxide, which contributes to global warming. Oxygen in post-combustion flue gas causes oxidative degradation of the amine-based solvents used in the carbon capture process. In this study, a cobalt tetraphenylporphyrin mediated facilitated transport membrane is considered for flue gas pretreatment. It is possible to exactly characterize the membrane by various microscopic and spectroscopic techniques. The results show that the hollow fiber is evenly coated as a thin dense layer with an increasing packing density. Gas permeation test shows that the oxygen/nitrogen and oxygen/carbon dioxide selectivity values reach 2.8 and 1.5, respectively, with an oxygen permeance of 53 GPU at 0.05 bar. It is expected that, because of the oxygen facilitated transport behavior, the membrane system will be able to remove oxygen from post-combustion flue gas using the current membrane for flue gas pretreatment, retarding the degradation of the absorbent.

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## 1. Introduction

Most cogeneration power plants all over the world use fossil energy such as coal and natural gas. These fossil fuel power plants are major emitters of CO<sub>2</sub>, a greenhouse gas that is a primary cul-

prit of global warming [1]. To address carbon pollution from coal or natural gas-fueled power plants, governments and stakeholders have shown strong interest in carbon capture and sequestration – a process that traps CO<sub>2</sub> and then stores it underground [2]. The post-combustion flue gas discharged from fuel coal-fired power plants is estimated to contain typically 11.78% (v/v) CO<sub>2</sub>, 5.03% (v/v) O<sub>2</sub>, 70.22% (v/v) N<sub>2</sub>, SO<sub>x</sub>, and NO<sub>x</sub>; the process temperature is around 50–60 °C [3]. O<sub>2</sub>, SO<sub>x</sub> and cause NO<sub>x</sub> cause

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oxidative degradation of amine-based solvents in the CO<sub>2</sub> capture process, which leads to frequent replacement of the absorbent, resulting in financial and operational problems, and secondary pollution [4]. Even though some new solvents have been proposed [5], oxidative degradation still plays an important role in CCS [6–8]. Before the flue gas enters the absorber, suitable measures should be adopted to remove harmful gas components; such removal has the beneficial effect of slowing down the degradation and increasing the process efficiency. There are some techno economic problems in existing techniques to mitigate O<sub>2</sub> content directly in the solvent. O<sub>2</sub> adsorption needs continuously supplying of adsorbent and it results in an additional operating cost. Since most equipment is constructed using anticorrosion materials which is resistant to corrosion with acid gas containing alkanolamine solutions, the use of an O<sub>2</sub> vacuum stripper requires an additional capital cost. Because membrane has some advantages, and can be processed into hollow fibers with high surface areas, it is attractive for flue gas pretreatment in post-combustion [9,10]. Furthermore, the apparatus for membrane separation is very simple, without movable add-ons, compact, and relatively straightforward to run and manage.

The existing commercial oxygen separation technologies are cryogenics, physical adsorption, and membrane technology [11]. These technologies are based on differences in boiling points, adsorption capacities, and molecular kinetic diameters, respectively. In view of separation efficiency, to remove the oxygen alone from the flue gas is cost-effective because the oxygen content is quite low (4–7%, v/v). However, conventional membrane materials cannot deal with this process well, because the kinetic diameter of CO<sub>2</sub> (3.3 Å) is smaller than that of O<sub>2</sub> (3.46 Å) and CO<sub>2</sub> permeability in a membrane is larger than that of O<sub>2</sub>. Thus, CO<sub>2</sub> always goes through the membrane faster than O<sub>2</sub> [12]. O<sub>2</sub>/N<sub>2</sub> separation is also an awkward task for conventional membranes because of the similar kinetic diameter. An ion transport membrane can convey O<sub>2</sub> selectively; however, the severe operation conditions of such membranes (>600 °C, 100–300 psi) and the complicated equipment limit application in post-combustion flue gas pretreatment under low temperature [13]. A high O<sub>2</sub>-selective membrane for oxygen separation using conventional materials is needed. Such a membrane may meet the requirements of highly efficient O<sub>2</sub> removal in the pretreatment of post-combustion flue gas.

Highly reverse-selective gas membrane separation has high separation efficiency enabled by facilitated transport membranes. Facilitated transport membranes contain a distinctive carrier, which combines exclusively and reversibly with one of the blending constituents (reactive molecule) [14]. The reactive molecule is conveyed through another mechanism in addition to the normal sorption-diffusion in these membranes. Since the carrier does not affect the transport of the insensitive molecules, the separation factor also increases independent of the molecular size. Facilitated transport has already been used in the separation of CO<sub>2</sub> from the H<sub>2</sub>-containing gas mixture [15]. Facilitated transports of O<sub>2</sub> in the presence of different oxygen carriers have also been reported [14]. For O<sub>2</sub>/N<sub>2</sub> separation, cobalt(II) complexes such as CoBPC [16], CoFPP [17], CoPc [18], Cosalen [19], and picket-fence cobalt-porphyrin [20,21] have been used as O<sub>2</sub> carriers and have been integrated into flat-sheet polymeric membranes. Obstacles to the application of these membranes are carrier instability, short lifetime, and inferior membrane mechanical strength [21]. Cobalt(I)-tetraphenylporphyrin (CoTPP) has a simple planar molecular structure, with large binding and releasing rate of O<sub>2</sub>; it shows good stability and has been used in membrane separation of O<sub>2</sub>/N<sub>2</sub> gas pairs [22]. Since hollow fiber membranes are mechanically self-sustaining and because the cartridge has a compact design, these materials have been used in various applications [23]. It is expected that O<sub>2</sub>-facilitated transport can be achieved for O<sub>2</sub>

removal in the pretreatment of post-combustion flue gas by using a hollow fiber composite membrane, which is coated using certain kinds of polymer materials with the incorporation of an oxygen carrier, such as CoTPP.

Polyethersulfone (PES) has good selectivity for the industrial important gas pairs [24]. Hollow fiber membranes made of PES have good mechanical strength and have been used widely in commercial gas separation [25]. Polydimethylsiloxane (PDMS) is a rubbery polymer under normal temperature; it has high gas permeance and can be used as a common protective material on membrane support to fill and seal defects and eliminate gas cross-over [26]. In this work, a PES-PDMS-CoTPP hollow fiber composite membrane was fabricated using PES hollow fiber membrane as a substrate support, PDMS, and synthesized CoTPP as coating materials. The composite membranes were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and atomic force microscopy (AFM). Oxygen, nitrogen, and CO<sub>2</sub> permeance performance were also examined for these membranes.

## 2. Materials and methods

### 2.1. Synthesis of tetraphenylporphyrin (TPP)

Into a three neck round bottom flask, 30.3 mL benzaldehyde (approximately 0.67 M) was added to refluxing propionic acid (400 mL, b.p. 141 °C); then, 21 mL fresh distilled pyrrole (in 50 mL propionic acid) was added to the reaction solution over a period of 5 min, followed by refluxing for 1 h. After it had cooled down, the reaction mixture was filtered by means of a Buchner funnel. The filter residue was washed first with methanol until the filtrate was clear; it was then rinsed with deionized water to remove the residue of propionic acid. Finally, the resulting bright purple TPP particles were dried under vacuum for 8 h.

### 2.2. Preparation of cobalt tetraphenylporphyrin (CoTPP)

The metalation reaction was performed with anhydrous cobalt dichloride. TPP (3.5 g) was dissolved in, or mixed with, DMF (150 mL) in a 250 mL round-bottom flask, which was placed in a heating mantle, and; then, the mixture was heated to 140 °C with stirring. Anhydrous cobalt dichloride (3.0 g) was added to the reaction mixture and refluxing was performed for 6 h. When the metalation was complete (as determined by thin-layer chromatography, TLC), the volume of the reaction mixture was reduced to about 50 mL by rotary evaporation of DMF solvent under reduced pressure. After cooling to ambient temperature, the reaction residue was poured into a flask containing 150 mL of absolute ethanol and mixture was stored in a refrigerator overnight for crystallization. After filtration using a Buchner funnel, CoTPP was obtained as a chestnut crystal. The CoTPP solid particles were carefully washed once with small amount of distilled water and absolute ethanol. Finally, the CoTPP particles were dried under vacuum for 8 h.

### 2.3. Fabrication of hollow fiber composite membrane

The PES hollow fiber membrane used in this work was fabricated by the diffusion-induced phase separation method, as mentioned in our previous work [27]. To prepare the PES-PDMS-CoTPP hollow fiber composite membrane, a toluene solution of PDMS prepolymer (2.7%, Dow Corning 184 Sylgard) and CoTPP (0.3%, coordinated with 1-benzylimidazole) was coated on the outer surface of the PES HFM using a continuous coating system.

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