

Gas Separation Membranes Containing $\text{Re}_6\text{Se}_8(\text{MeCN})_6^{2+}$ Cluster-Supported Cobalt-Porphyrin Complexes

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Abstract: Cellulose nitrate (CN) composite membranes, containing cobalt porphyrin (CoP) complexes self-assembled within nanometer-sized rhenium clusters (ReCoP), have been prepared and their oxygen and nitrogen gas permeabilities were analyzed. The solubility of ReCoP and the characteristics of the corresponding composite membranes were analyzed using a Cahn microbalance, FT-IR spectroscopy, wide-angle X-ray scattering, and differential scanning calorimetry. The nitrogen permeability through the CN composite membranes decreased upon addition of ReCoP and CoP, which implies that the presence of these oxygen carrier complexes affects the structure of the polymer matrix. The oxygen permeability through the composite membranes containing small quantities of ReCoP decreased, but it increased upon increasing the concentration. The oxygen gas transport was affected by the matrix at low ReCoP concentrations, but higher concentrations of ReCoP increased the oxygen permeability as a result of its reversible and specific interactions with oxygen, effectively realizing ReCoP carrier-mediated oxygen transport.

Keywords: cellulose nitrate, cobalt porphyrin, facilitated transport, membrane.

Introduction

Oxygen transport through polymer membranes containing metalloporphyrin oxygen carriers has been widely investigated, since the addition of these oxygen carriers is known to increase oxygen permeability and oxygen/nitrogen selectivity simultaneously.¹⁻⁵ The oxygen-enriched properties of those polymeric membranes are related to the reversible oxygen-binding behaviors of the metalloporphyrins, where a five-coordinate metalloporphyrin is known to bind molecular oxygen, both rapidly and reversibly:



An oxygen-bound metalloporphyrin complex, or oxygen

adduct, reacts rapidly with a second $\text{M}^{2+}\text{-P}$, forming a binuclear dioxygen-bridged complex, and/or oxidation of metalloporphyrins. Oxidation induced by the loss of a ligand is effectively retarded through the formation of a stable five-coordinate complex. Although metalloporphyrin complexes with axial ligands are thermodynamically stable, the metalloporphyrin is still labile in the ligand complex. A momentary dissociation of the axial ligand in the oxygen-bound complex causes an electron transfer from the M^{2+} ion to the bound oxygen molecule to yield M^{3+} and a superoxide anion. This binuclear complex is then irreversibly converted to an oxo-bridged M^{3+} dimer. Therefore, in order to maintain stable, reversible oxygen binding, it is necessary to modify the metalloporphyrin in order to inhibit dimerization and/or irreversible oxidation.

Much work has been conducted with a view to overcoming these particular issues,⁶⁻¹⁰ and two main approaches have so far been successful. The first is a steric approach, whereby a planar porphyrin is sterically substituted in order to prevent dimerization. A typical example includes the picket fence

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metalloporphyrin, meso- $\alpha,\alpha,\alpha,\alpha$ -tetrakis(o-pivalamidophenyl) porphyrinato metal, which consists of four pivalamido groups on one side of the porphyrin plane which provide a cavity for protecting the bound oxygen from dimerization. A second approach involves attaching metalloporphyrins to a rigid polymer chain to prevent two metalloporphyrins dimerizing.

In this study, a "self-assembling" cyano-rhenium cluster building block has been developed as a support material for the metalloporphyrin to promote five-coordination, and prevent dimerization through steric hindrance. These rhenium clusters contain cobalt (tetraphenylporphyrinato) (CoP) complexes, in which the cobalt porphyrin units are linked to the cyano-rhenium clusters to form discrete metalloporphyrin complexes (Scheme I).¹¹ Since the CoP complexes are attached directly to the bulk Re cluster, the possibility of metalloporphyrin dimerization is significantly reduced. The preparation and characterization of cellulose nitrate (CN) composite membranes, containing both Re cluster supported and unsupported CoP complexes, have been conducted. The unsupported CoP complex has been included in order to ascertain the effects of the rhenium cluster support on the stability of the carrier.

Experimental

Materials. Re, Se, CsI, I₂, (Bu₄N)I, SOCl₂, 4,4-dipyridyl, 5,10,15,20-tetraphenyl-21H,23H-porphine cobalt(II) (CoP), and cellulose nitrate (CN, 11.8-12.2 wt.% nitrogen) were all purchased from Aldrich and used as received.

Preparation. Cs₄Re₆Se₈I₆ and a small amount of CsRe₆Se₈I₆ were obtained when Re, Se, CsI and I₂ (6:8:4:1 mole ratio), were sealed together in a quartz tube and then heated in a furnace at 850°C for 100 hrs. The resulting products were then stirred in a 1 M HI aqueous solution for 2 hrs. The resulting Cs₄Re₆Se₈I₆ solution was filtered to afford insoluble CsRe₆Se₈I₆, which was then added to 50 mL of 0.05 M aqueous (Bu₄N)I and stirred. The obtained brown precipitate was dissolved in 100 mL acetonitrile, and 10 drops of

SOCl₂ were added to the solution. This was then stirred for 15 min. The products obtained by evaporating the solvent, were then re-dissolved in a mixture of acetone and toluene (1:1 mole ratio) and stirred for a further 24 hrs. Removal of the solvent yielded (Bu₄N)₃[Re₆Se₇(SeH)I₆].

AgBF₄ (0.257 g, 1.32 mmol) in 4 mL of acetonitrile was added to a solution of (Bu₄N)₃[Re₆Se₇(SeH)I₆] (0.650 g, 0.200 mmol) in dichloromethane (4 mL). The mixture was then stirred in the absence of light for 12 hrs. The resulting orange-red supernatant was then decanted from the yellow precipitate. Addition of ether to the supernatant resulted in the formation of a light yellow precipitate, which was collected and dissolved in 2 mL of acetonitrile, and finally filtered. Diffusion of ether into the orange filtrate afforded yellow-orange, powders of [Re₆Se₈(MeCN)₆](BF₄)₂ (Re-cluster) (0.31 g, 72 %).

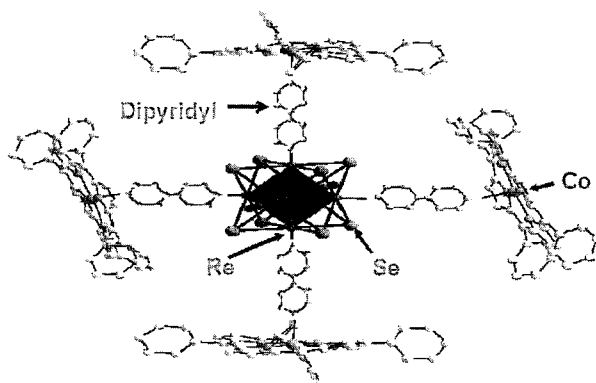
Acetone solutions of [Re₆Se₈(MeCN)₆](BF₄)₂ and 4,4-dipyridyl were combined and then added to a solution of 5,10,15,20-tetraphenyl-21H, 23H-porphine cobalt(II) (CoP) in toluene, and the resulting mixture stirred overnight. The Re-supported CoP (ReCoP) complex were obtained by solvent evaporation and then stored in a vacuum oven prior to use. The ReCoP complex was found to comprise 4 mol of CoP and 1 mol of Re-cluster, as confirmed by elemental analysis.

Acetone solutions of both CoP and ReCoP were mixed with acetone solutions of CN, and the complex was then carefully cast on a glass plate under vacuum to form a transparent, red-colored membrane with a thickness of approximately 100 μ m (CoP and ReCoP concentrations were between 1-15 wt%).

Characterization. Sorption tests for O₂ in CoP and ReCoP were conducted using a Cahn D200 microbalance. Approximately, 100 mg of sample was loaded into the microbalance sample pan and the whole system was evacuated (150 torr) prior to testing. Pure sample gas was then fed into the chamber (at 30°C) and allowed to sorb into the sample until sorption equilibrium was established. The equilibrium sorption values obtained have been corrected for buoyancy forces.

Glass transition temperatures (T_g) were obtained by differential scanning calorimetry (DSC) using a TA Instruments model 2920 at a speed of 10°C/min, under nitrogen gas. The d -spacing of the composite membranes were investigated by wide angle X-ray diffraction (WAXD) using a MacScience M18XHF22 X-ray diffractometer, operating with CuK α radiation of wavelength (λ) 1.5406 Å, at a scanning speed of 5°/min. The composite membranes were examined using a HITACHI, S-4200 scanning electron microscope (SEM), operating at 5 kV. The permeability coefficients for O₂ and N₂ were measured at different upstream pressures (at 35°C) using the constant volume method. FT-IR measurements were performed on a 6030 Mattson Galaxy Series FT-IR spectrometer; 64-64 scans were signal-averaged at a

Scheme I



resolution of 4 cm^{-1} .

Results and Discussion

When oxygen gas comes into contact with a metalloporphyrin, oxygen molecules become coordinated through the formation of oxygen-porphyrin complexes. Oxygen solubility in the unsupported CoP metalloporphyrin was determined to be $5.99 \times 10^{-3}\text{ mol(O}_2\text{)/mol(CoP)}$, while in the Re-cluster supported cobalt porphyrin (ReCoP) it was found to be $1.17 \times 10^{-1}\text{ mol(O}_2\text{)/mol(CoP)}$, demonstrating a *ca.* 20 fold increase. This result is considered to be due to the enhanced chemically-specific binding of oxygen associated with the Re-cluster supported CoP complex.

SEM images of the cross sections and surface morphologies of the CN composite membranes containing either 7 wt% CoP or 7 wt% ReCoP, are shown in Figure 1. Both CoP- and ReCoP-loaded membrane systems show homogeneity. Similar morphologies were obtained for all samples studied here. The uniformity and lack of defect formation in the two surfaces can be further supported by low gas per-

meances, which will be discussed in the following section.

Figure 2 shows the oxygen and nitrogen gas permeabilities for the CoP- and ReCoP-loaded CN-composite membranes, obtained using increasing upstream pressures. The permeabilities of O_2 through the CN-CoP- and CN-ReCoP-loaded membranes fall within the range 0.4~0.5 and 0.6~1.5 barrer, respectively. In contrast, the N_2 permeability through the composite membranes of CN-CoP and CN-ReCoP are both extremely low, with values of 0.1 barrer or less, irrespective of whether a carrier (CoP or ReCoP) is present.

The N_2 gas permeability through the composite membrane in whole range is typically lower than that for O_2 . The ideal separation ratio values were calculated on the basis of the ratio of the oxygen and nitrogen permeabilities for pure gases. However, this simple ratio is irrelevant since the permeability of N_2 is extremely low. In addition, each gas may affect the permeation of the others, the ideal selectivity values are therefore different from those for mixed gases. This difference is likely to be even more pronounced in facilitated transport membranes, in which the complex formed by the oxygen molecules and the carrier is expected

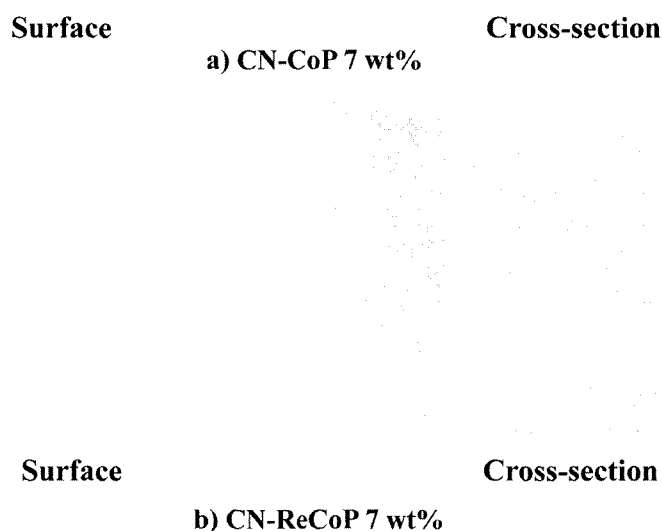
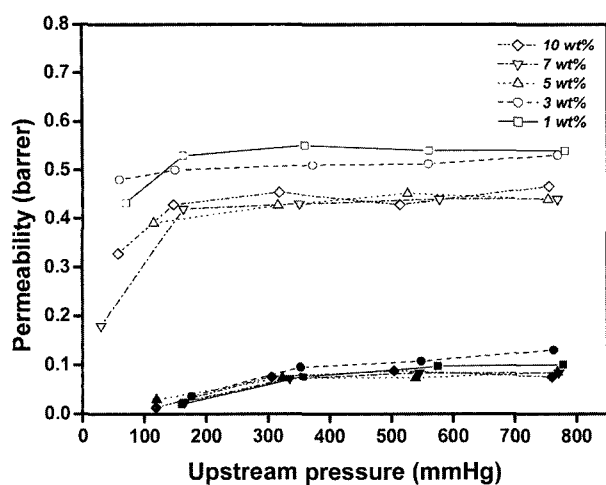
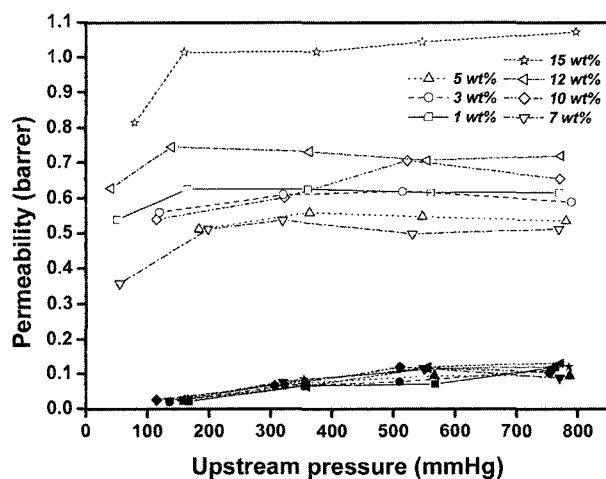


Figure 1. SEM images revealing the surface and cross section morphologies of the composite CN membranes containing 7 wt% (a) CoP and (b) ReCoP, respectively.



(a)



(b)

Figure 2. Gas permeability dependence of upstream pressure for the composite membranes containing (a) CoP and (b) ReCoP, respectively.

to affect nitrogen permeation.

Nitrogen permeability through membrane showed no significant dependence on the upstream pressure. Moreover, increasing pressure appeared not to affect the permeabilities of oxygen, suggesting that the effect of the matrix is too big to show the effect of facilitation in this system.

Figure 3 shows the relationship between the gas permeability and the oxygen carrier concentration for CoP- and ReCoP-loaded CN composite membranes. In general, membranes with enhanced oxygen-enriching properties require a number of oxygen carriers present within the membrane. The addition of an oxygen carrier into a solid polymeric membrane can influence the gas permeation property of the membrane: (1) by incorporating increasing amounts of oxygen carrier; or (2) through the formation of a complex between the carrier and the polymer chain of the membrane

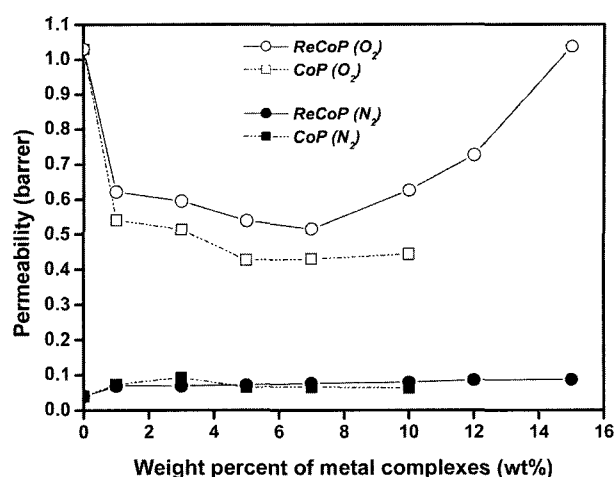


Figure 3. Concentration dependence of gas permeability for the composite membranes containing CoP and ReCoP.

matrix, leading to lower chain flexibility. Therefore the possibility for the composite membrane prepared in this study is that the ReCoP oxygen carrier may occupy some gas permeation channels in the polymer matrix, thereby decreasing the free volume of the membrane. These effects are likely to reduce the oxygen and nitrogen permeabilities.

The permeability of oxygen can be represented as follows:

$$P(O_2) = P_{\text{membrane}} + P_{\text{carrier-mediated}}$$

P_{membrane} is dependent on matrix properties such as polymer chain flexibility, free volume, and so on, while P_{membrane} is dependent on the physical diffusion of oxygen in the membrane, but independent of the upstream pressure. In contrast, $P_{\text{carrier-mediated}}$ is dependent on the concentration of oxygen reversibly-bound to a fixed carrier, upstream pressure, and the reversible oxygen-binding equilibrium constant of the carriers within the membrane.^{12,13}

The N_2 permeability of membrane-containing oxygen carriers, on the other hand, depends only on the properties of the membrane matrix. Since the chain flexibility and the free volume of the membrane matrix are expected to change upon addition of an oxygen carrier, it can be assumed that the N_2 permeability corresponds to the permeability of the matrix. Therefore, the variation in N_2 permeability with oxygen carrier concentration reflects the changes in the polymer chain flexibility and the free volume in the membrane as the oxygen carrier number is increased.

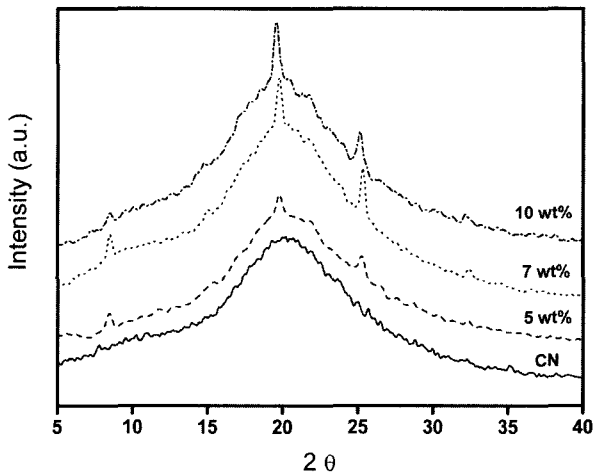
As shown in Figure 3, N_2 permeability through both CoP- and ReCoP-loaded membranes decreases and remains low despite increases in the number of oxygen carriers. This suggests that the oxygen permeability through the membrane matrix also decreases with the number of oxygen carriers. Decreases in the gas permeability through the composite membrane indicate that there is a tortuous pathway effect.

The oxygen permeability decreased by an order of magnitude in the low wt% range, implying that the tortuous pathway effect is significant. The total O₂ permeability was found to increase with the number of oxygen carriers from *ca.* 7 wt% onwards, suggesting this value is significant for oxygen permeability in the high oxygen carrier concentration range. The facilitated transport of oxygen caused by the reversible reaction between the oxygen carrier and molecular oxygen is thus a significant factor.

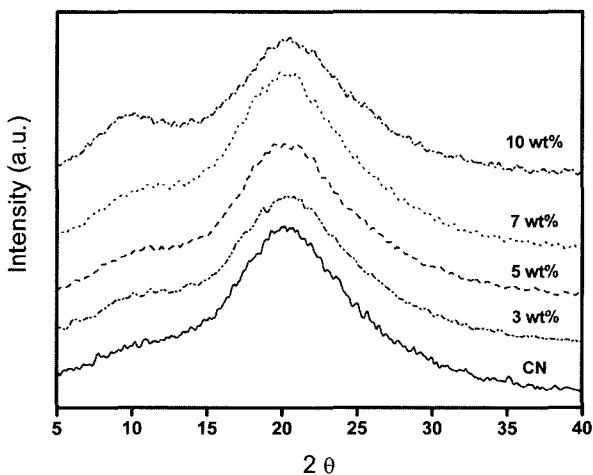
Conformation changes in the oxygen carrier-loaded polymer matrix have been analyzed by WAXS (Figure 4). For CN-composite membranes containing CoP, the observed crystallinity formation with increasing concentration is not apparent in the composite membranes containing ReCoP. The free volume determined from the maximum angle is maintained throughout the range of CoP wt% studied. For the ReCoP-loaded CN-membranes, a second maximum angle

at 9.9° (*d*-spacing is *ca.* 8.9 Å) is observed, which may have formed as a result of the embedded nano-clusters within the polymer chains. The presence of the inorganic metallic clusters is likely to result in the blocking of the gas transport pathways throughout the membrane.

Interactions between the oxygen carriers and the membrane also affect the structure of the matrix, and subsequently the gas permeabilities through them. These interactions can be detected using FT-IR (Figure 5). The peak observed at 1252 cm⁻¹, developed as a result of increasing oxygen carrier concentration, infers a new interaction between the polymer matrix and the oxygen carriers. This interaction reduces the flexibility of the polymer chains, resulting in a reduction in the gas permeance. This gradual increase in carrier-matrix interaction is consistent with increases in the glass transition temperature (*T_g*), which changed from 51 to 67°C as the carrier concentration increased.

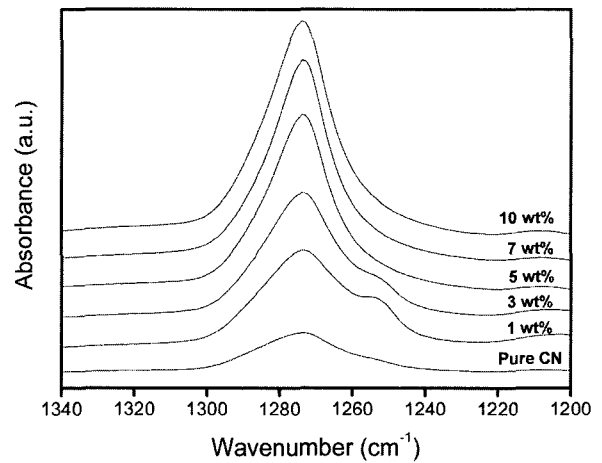


(a)

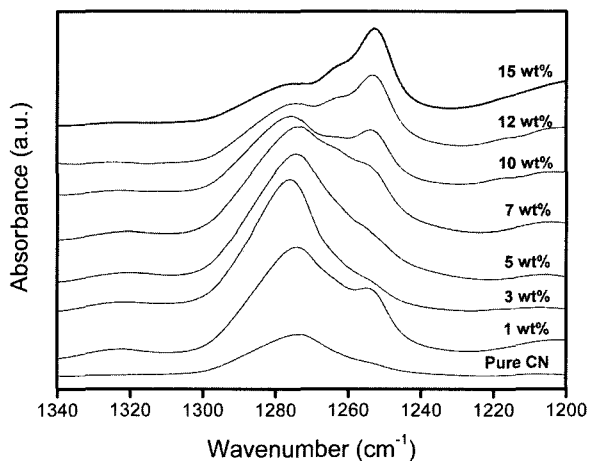


(b)

Figure 4. Wide angle X-ray scattering data for the CoP- and ReCoP-loaded composite membranes, containing varying amounts of (a) CoP and (b) ReCoP, respectively.



(a)



(b)

Figure 5. FT-IR spectra for the CoP- and ReCoP-loaded composite membranes containing varying amounts of (a) CoP and (b) ReCoP, respectively.

CoP carrier, supported by the inorganic nano-clustered play important roles in gas permeabilities: by improving the selectivity of the membranes; and by reducing the permeability through interactions with the matrix and its own intrinsic properties. Facilitated oxygen transport through ReCoP leads to a distinct increase in oxygen permeability as the number of carriers is increased.

Conclusions

Discrete molecules of rhenium cluster-supported cobalt(II) porphyrin complexes (ReCoP), and cellulose nitrate composite membranes containing ReCoP oxygen carriers have been prepared. Oxygen permeability through these membranes was found to increase with increasing number of incorporated oxygen carriers. It has been determined that the oxygen carrier in the membrane not only facilitates oxygen transport, but also affects the polymer chain flexibility and free volume of the membrane.

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