Chapter 7

Future Prospects

7.1 Conclusions

1. The simple or planar porphyrins and OIm complexes form oxygen adducts reversibly in solution at low temperature. (Chapter 2)

2. The low oxygen affinity (p_{50}) for the CoTPP are attributed to the enormously large oxygen-releasing rate constant (k_{off}= 10^8 s^{-1}). (Chapter 2)

3. A solid membrane of CoTPP-OIm was prepared: The membrane reversibly forms an oxygen adduct not only at low temperature under normal pressure, but also at room temperature under high oxygen pressure. (Chapter 3)

4. The extraordinarily high selectivity (P_{O2} / P_{N2} > 120) was obtained with P_{O2} = 9.6 Barrer. (Chapter 4)

5. The temperature dependency of P_{N2} obeyed Arrhenius-type although that of P_{O2} has a small maximum. (Chapter 4)

6. Above 90% of downstream oxygen concentration was obtained through a one-shot permeation process from air. (Chapter 4)

7. Concentration fluctuation model was applied to this facilitated transport of oxygen. The contribution of the CoTPP to the oxygen facilitated transport is extremely large. (Chapter 5)

8. The I_0/I_{100} values of PtOEP and PdOEP in the poly(TMSP) film is estimated to be 225 and 121 and large Stern-Volmer constants (K_{SB} 6.6%$^{-1}$ for PtOEP and 17.0%$^{-1}$ for PdOEP) are obtained. Especially, the luminescence intensity of PdOEP dispersed in the poly(TMSP) film was drastically changed by the oxygen concentrations. The limits of oxygen detection of PtOEP and PdOEP dispersed in the poly(TMSP) films were less than 0.3%. (Chapter 6)

The author concluded the polymeric simple and planar cobalt tetraphenylporphyrin membrane showed the extraordinary high selectivity (P_{O2} / P_{N2} > 120) with P_{O2} = 9.6 Barrer. This very efficient facilitated oxygen transport in this polymeric CoTPP thin membrane improved both the selectivity and flux of the oxygen shown in Figure 7-1 with the upper limit between permeability vs. permselectivity of relationship for oxygen/nitrogen separation through the polymer membrane without the oxygen carrier.[1] This figure clearly shows that the CoTPP-OIm membrane has the great performance as a oxygen selective membrane. The author concluded again that the membrane consists of the simple and planar porphyrin combined with polyimidazole have a great potential for the practical use as a oxygen facilitated membrane.

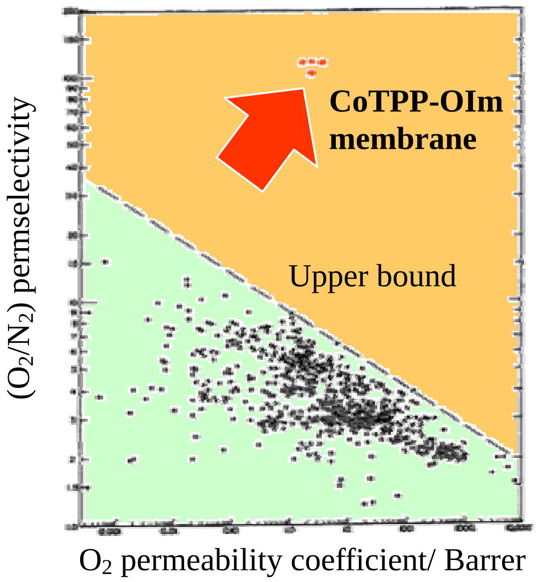
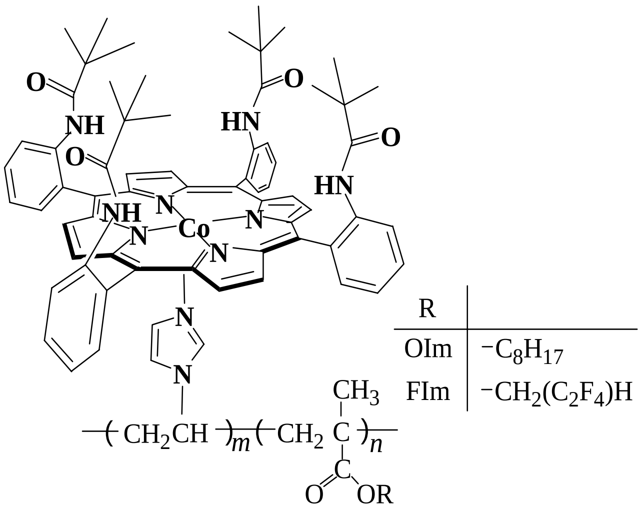


Figure 7-1. Oxygen/nitrogen separation factor versus oxygen permeability.



Scheme

Table 7-1. Half-life Time (τ) of the CoTpivPP Complex in the Membranes under a Humid Atmosphere.

Polymer-ligand	Humidity /%	τ /days
FIm	10	83_5
FIm	50	60_3
FIm	95	25_6
OIm	50	48

7.2 Future prospects for the oxygen facilitated transport membranes

Above 90% of oxygen concentration of downstream was obtained only a small different pressure between upstream and downstream. However, to get more suitable for practical membrane, life extension of the carrier is indispensable. The cobaltporphyrin complex slowly loses its oxygen-binding ability due to irreversible oxidation reactions. It has been known[2] that a water molecule (proton) attacks the cobaltporphyrin-bound dioxygen to yield a hydrodioxy radical and cobalt(III)porphyrin which diminishes the oxygen-binding ability of cobaltporphyrin and that of the membrane.

Fluorine-containing polymers possess unique properties such as high gas solubility, high thermal and chemical stability, oloephobicity, and hydrophobicity.[3,4] This hydrophobic properties of the fluorine-containing polymer is consider to suppress the irreversible oxidation of the active cobaltporphyrin carrier caused by a water molecule and to significantly prolong the operational lifetime of the cobaltporphyrin membrane.[5]

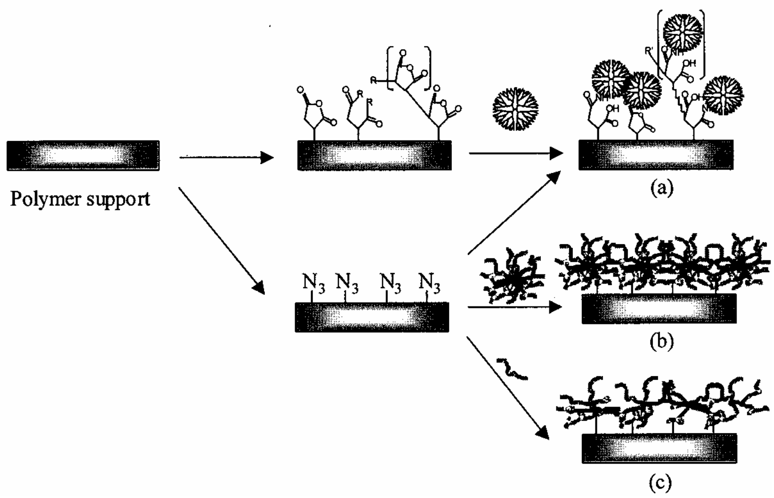


Figure 7-2. Schematic methods for the preparation of nano-thickness selective layer membranes.

Membrane performance also depends on the thickness of the selective layers of a silver-polymer complex, that is, the thinner the selective layer, the better the transport performance of the membrane. A thickness of several micrometers for the selective layer was the limitation in conventional methods used to prepare composite membranes. Based on the exciting developments in the field of nanostructure science and technology, there have been several attempts to reduce the thickness of the selective layer onto a nano-meter length scale.[6-8] Schematic methods for preparing nano-thin selective layer membranes are generalized in Figure 7-2, based on the use of nanometer-sized dendrimers, star polymers, and the preparation of polymer brushes. A several nanometer-thin selective layer in a facilitated transport membrane has been found to produce an improved performance. Although the range and nature of functionalities that can be accessed through nanostructuring is just beginning to unfold, its tremendous potential for revolutionizing the way in which materials and products are created is already clear. And, it will have a great impact on future scientific and commercial applications.

Oxygen and nitrogen are the top three commodity chemicals. Oxygen is used for combustion, chemical oxidation, respiratory therapy, refreshment, aquaculture, and wastewater treatment, while nitrogen is used for purging gases in explosion protection, food storage, and the manufacture of fine electronics and pharmaceuticals. While air is separated to produce oxygen and nitrogen using mainly energy-intensive cryogenic processes, gas separation membranes are very attractive as they are a simple compact device with low initial capital and running costs. To surpass the competitive cryogenic process, the requisites for a next generation air-separation membrane are a high permeability and high selectivity (for example, oxygen permeability of more than 10^2 Barrer and oxygen/nitrogen selectivity of more than 10). As such, facilitated transport membranes containing oxygen-binding cobalt porphyrins, as discussed in this section, are expected to be a candidate for such next generation air-separation membranes. Since air is free and abundant and has the same composition worldwide everywhere, and its efficient usage is an important issue for near-future technology.

Reference

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