

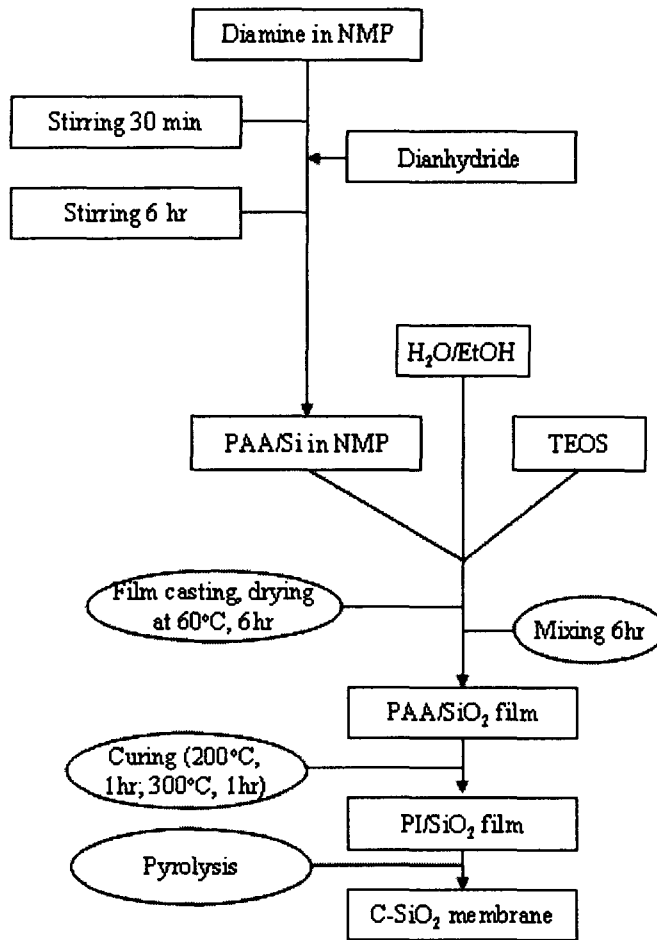
## Preparation and Characterization of Carbon-Silica Membranes Derived from Polyimide-Silica Composites

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Although carbon itself is perhaps the most thermochemically stable material, it is very susceptible to oxidation, which is an obvious drawback in the efficient and reproducible fabrication of carbon membranes. Therefore, the addition of silicon and/or silicon compounds such as silica and silicate seems to be a natural choice for the next generation of membrane materials. In particular, carbon and silica play an important role in material science because of their relevance in the academic field and in practical applications. Although the chemical combination of these two materials has been reported in several papers[1-3], most of the methods used involved the pyrolysis and selective removal of one phase followed by hybridization of polymer and silica sol, resulting in the formation of large mesopores that are not suitable for gas separation. In this study, polyimide/silica composites, based on the products of the hydrolysis of tetraethoxysilane (TEOS) and poly(amic acid) solution, were used to fabricate carbon-silica membranes, which were subsequently evaluated with respect to gas permeation and separation performances. A considerable amount of research has been carried out since the mid-1970s on sol-gel processing of metal oxides to produce ceramics and glasses of high purity [4,5]. Research on polyimide/silica hybrids was first reported in the early 1990s. Nandi et al.[6] have produced polyimide-metal oxide hybrid materials by mixing solutions of pyromellitic anhydride (PMDA), diaminodiphenyl ether(ODA) and either titanium or silicon tetraalkoxides.

In present work, polyimide/silica were prepared at various silica concentration (4.7-32.4 wt%) using sol-gel route and carbon-silica membranes were produced by pyrolysis of the polyimide/silica films under an inert atmosphere. Scheme 1 illustrates the preparation of

polyimide/silica films and carbon-silica membranes.



Scheme 1. The procedure for polyimide/silica composites film and carbon-silica membrane preparation

The permeability coefficient for a permanent gas is determined by multiplying the permeation rate by the membrane thickness and can be expressed by

$$P = dp/dt(VT_0L/p_0T\Delta pA)$$

(1)

where  $P$  is the permeability represented in Barrer;  $dp/dt$  is the rate of

the pressure rise under the steady state;  $V(\text{cm}^3)$  is the downstream volume;  $L(\text{cm})$  is the membrane thickness;  $\Delta P(\text{cmHg})$  is the pressure difference between the two sides;  $T(\text{K})$  is the measurement temperature;  $A(\text{cm}^2)$  is the effective area of the membrane; and  $p_0$  and  $T_0$  are the standard pressure and temperature, respectively. Permselectivity as defined in this study is the ratio of permeability of the selected gases to that of nitrogen. Figure 1 shows a typical graph obtained from present gas permeation experiment.

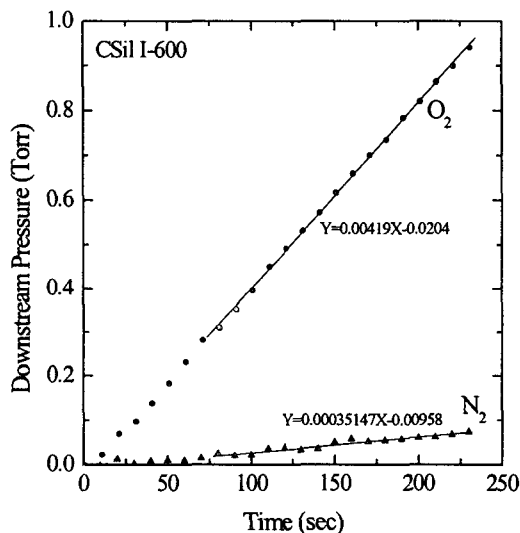


Figure 1. A typical time-lag graph obtained from a constant volume method.

Table 1 lists the gas permeability and selectivity of present C-SiO<sub>2</sub> membranes carbonized at 600 °C. As can be seen it, the gas permeability decreased with silica content from 5 wt% to 19 w%. This indicates that dense silica phase hinder the penetration of small gas molecules such as He, CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>. On the whole, these C-SiO<sub>2</sub> membranes derived from polyimide/silica showed the high gas permeabilities with an appropriate permselectivity. The high gas

permeability might be due to formation of large pores between carbon phase and silica phase.

Table 1. The Gas Permeation Results of C-SiO<sub>2</sub> Membranes Derived from Polyimide/silica Composites at 25 °C.

Sample	Permeability (Barrer)				Selectivity		
	He	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	He/N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>
C-SiO <sub>2</sub> (4.7wt% )	6126	4014	919	86	71.3	46.7	10.7
C-SiO <sub>2</sub> (18.5 wt%)	3744	2597	583	57	66.1	45.8	10.3

## References

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