論文の要旨

題　目　Development of Organically Bridged Silica Membranes and Application to Water Purification

(橋架けアルコキシドを用いた有機シリカ膜の開発と水処理への応用)

氏　名 Rong Xu

A desired reverse osmosis (RO) membrane should have high water permeability and salt rejection, as well as superior durability. Given the limitations of conventional polyamide-based RO membranes, the development of robust RO membranes which possess high chlorine tolerance and hydrothermal stability, is becoming an especially important task. The present study focuses on the design and development advanced RO membranes using a highly promising class of materials, organically bridged silica. The transport mechanism was discussed for these innovative organosilica membranes.

**Chapter 1** is "*General introduction*". Typical desalination technologies are overviewed and the materials and limitations of conventional RO membranes were summarized. New materials for emerging RO membranes was introduced, and use of organically bridges silica materials was proposed for the development of robust organosilica membranes with superior separation performance and high stability in RO application.

**Chapter 2** is "*Development of chlorine-resistant and hydrothermal stable organosilica membranes for reverse osmosis*". A new type of microporous organosilica membrane derived from bis(triethoxysilyl)ethane (BTESE) has been developed for reverse osmosis (RO). Sol-gel derived BTESE membranes rejected isopropanol with rejection higher than 95%, demonstrating superior molecular sieving ability for neutral solutes of low molecular weight. The BTESE organosilica membranes were resistant to water to at least 90 °C with no obvious changes in filtration performance. Furthermore, the accelerated chlorine-resistance test confirmed excellent chlorine stability in this material, showing great promise as a new type of robust RO membrane materials.

**Chapter 3** is "*Reverse osmosis performance of organosilica membranes and comparison with the pervaporation and gas permeation properties*". A series of factors including the effects of solute species, calcination temperatures and operational variables on membrane performances were systematically investigated. Observed activation energies for permeation were larger for membranes with a smaller pore size, and were considerably larger than the activation energies for water viscosity. The BTESE-derived organosilica membranes exhibited exceptional hydrothermal stability in temperature cycles up to 90 °C. The applicability of the generalized SD model to RO and pervaporation (PV) desalination processes was examined, and the quantitative differences in water permeance were accurately predicted by the application of generalized transport equations.

**Chapter 4** is "*Optimizing water permeability by introducing polarizable ethenylene bridges and aqueous ozone modification*". Bis(triethoxysilyl)ethylene (BTESEthy) was used as a novel precursor to develop a microporous organosilica membrane via the sol-gel technique. Water sorption measurements confirmed that ethenylene-bridged BTESEthy networks had a higher affinity for water than that of ethane-bridged organosilica materials. High permeance of $CO_2$ with high $CO_2/N_2$ selectivity was explained in relation to the strong $CO_2$ adsorption on the network with $\pi$-bond electrons. The introduction of polarizable and rigid ethenylene bridges in the network structure led to improved water permeability and high NaCl rejection (>98.5%) in RO. Moreover, the aqueous ozone modification promoted significant improvement in water permeability of the membrane. After 60 min of ozone exposure, the water permeability reached $1.1 \times 10^{-12}$ $m^3/(m^2$ s Pa), which was close to that of a commercial seawater RO membrane.

**Chapter 5** is "*Comparative study on structure-property of organosilica membranes with ethane, ethylene and acetylene bridging groups*". Acetylene-bridged organosilica membranes were prepared and compared with the previous organosilica membranes with ethane and ethylene bridges. Similar to BTESE and BTESEthy membranes, BTESA membranes were thermally stable up to 300 °C in air. Compared with BTESE and BTESEthy membranes, BTESA membranes exhibited higher permeance and lower selectivity in gas permeation. MWCO measurements suggested that BTESA membranes had the largest effective pore size among the three membranes, resulting in a relatively low level of NaCl rejection. However, BTESA membranes exhibited highest water permeability of up to approximately $8.5 \times 10^{-13}$ $m^3/(m^2$ s Pa) in RO, owing to the introduction of the more polarizable and rigid acetylene bridges in the silica network.

**Chapter 6** is "*Conclusions*". Main conclusions obtained in chapters 2-5 were summarized and recommendations for future work were provided.