27 Hydrogen and Proton Transport Properties of Nanoporous Zeolite Micromembranes

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1 INTRODUCTION

Nanoporous zeolites are ideal material for inorganic membrane. Their uniform molecular-sized pores and large pore volume mean that they can have high permselectivity and permeation flux (Coronas and Santamaria, 1999). Indeed, zeolites are capable of separating molecules by their size, shape and polarity (Brek, 1974; Szostak, 1989). Close boiling compounds, isomers and azeotropes were successfully separated using zeolite membranes. The difference in the valence of silicon and aluminum atoms forming the aluminosilicate framework of the pore wall results in a negatively charged zeolite channel. Cations such as protons can travel through the negatively charge channels making zeolites an attractive material for proton exchange membrane in fuel cell application. The crystalline zeolites also have excellent mechanical strength and thermal stability, and are resistant to most acids, bases and organic solvents. Recently, the authors have reported several strategies for incorporating zeolites in microchemical systems for use in separation and reaction (Wan *et al.*, 2001; Chau *et al.*, 2002; Yeung and Chau, 2002). Gas permeation across silicalite-1 micromembrane has been measured and the results show that the micromembrane outperformed the regular-sized zeolite membrane in both permeability and permselectivity. 1-pentene epoxidation reaction has also been successfully conducted in a titanium silicalite-1 (TS-1) zeolite microreactor (Wan *et al.*, 2001).

Zeolite micromembranes' application is not limited to gas, gas-liquid and liquid-liquid separations. They also find uses as selective barrier for sensors and ion-conducting membrane for electrochemical systems (e.g., microfuel cell). Miniaturization benefits membrane separation by improving mass and heat transfer rates (Franz *et al.*, 2000; Losey *et al.*, 2000). It also allows larger membrane area to be packed in a smaller volume enabling the design of a more efficient and compact separation unit. This work reports the fabrication of HZSM-5 zeolite

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micromembrane and its performance for hydrogen permeation and proton transport. Although there are numerous works that discuss the fabrication of zeolite micromembranes, to our knowledge this is the first successful demonstration of gas permeation and proton transport in the zeolite micromembrane.

2 EXPERIMENTAL

An array of forty-nine freestanding HZSM-5 zeolite micromembranes was fabricated using a new technique developed in our laboratory. A 7 x 7-grid pattern was first etched onto the silicon wafer using conventional photolithography and etching method. Each 300 μm squares were etched to a depth of 250 μm. A large 7 mm x 7 mm square was then etched onto the reverse side of the pattern, such that only a thin layer (~ 50 μm) of silicon separates the two patterns. Localized zeolite growth within the grid patterns was achieved through selective seeding. The grid patterns were functionalized using mercapto-3-propyltrimethoxysilane (50 mM in ethanol) and then seeded five times with colloidal zeolite (120 nm TPA-ZSM-5) to obtain the desired seed population. A five micron thick ZSM-5 film was grown onto the seeded grids from a synthesis solution containing 40 SiO_2: 2 Al_2O_3: 1 TPAOH: 10 NaOH: 20,000 H_2O at 423 K for 48 h. X-ray diffraction analysis (Philips PW1030) indicated that a highly oriented (101) ZSM-5 film was obtained under these synthesis conditions. After inspecting the zeolite film for defects and imperfections, the remaining thin layer of silicon that separates the two patterns was then etched away to create the free standing ZSM-5 film. Leak test of the micromembranes was done using helium, and prior to the removal of the organic templates, the membrane was impermeable to helium (~ 400 kPa). The controlled removal of the organic templates from the zeolite pores was accomplished using a new low temperature template-removal technique based on oxygen plasma treatment (RF = 400 W, 473 K, 20 h). The activated membrane was tested for hydrogen and oxygen permeation at room temperature (i.e., 294 K). The gases were fed to one side of the micromembranes where the pressure was kept at 136 kPa. The flux across the membrane was then monitored and measured at the reverse side at a fixed pressure of 101.3 kPa (i.e., ΔP = 34.5 kPa). The proton transport across the zeolite micromembrane was measured in a homemade cell. One side of the cell contains 50 mL of hydrochloric acid solution while the other side separated by the zeolite micromembrane is filled with 250 mL of distilled, deionized (D.D.I.) water. A pH meter (Orion 420A) was used to monitor the proton transport across the micromembrane. The membrane microstructure was characterized using optical (Olympus BH-2) and scanning electron microscopes (JEOL JSM6300), while its composition was analyzed using x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometer (TOF-SIMS).

3 RESULTS AND DISCUSSION

The scanning electron micrograph in Figure 1a shows the array of freestanding ZSM-5 micromembranes fabricated onto the silicon substrate. Chemical analysis indicates that the micromembranes have a Si/Al ratio of 11 and contains 8 atomic percent of sodium. Wetting angle experiments show that water spread readily on

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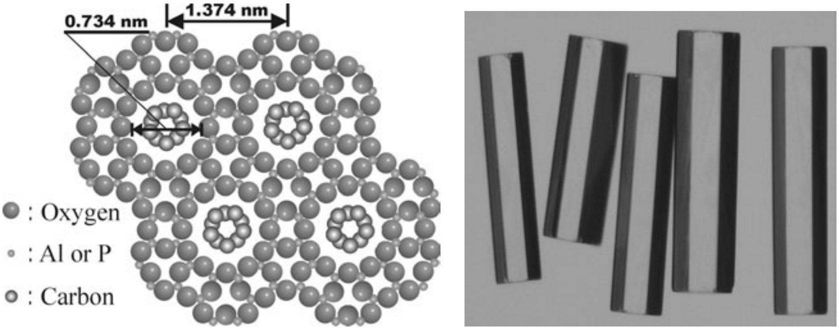

(a) (b)

Figure 1 (a) The framework structure of the crystal viewed along [001] direction. The carbon nanotubes are also schematically shown in the figure. (b) Photograph of as-grown AFI single crystals.

for the light polarized perpendicular to the *c*-axis ($E\perp c$), which is consistent with the one-dimensional character of the nanotubes.

Raman spectra were measured using a Renishaw 3000 Micro-Raman system equipped with a single monochromator and a microscope. Samples were excited using the 514.5 nm line of a Ar^+ laser with a spot size of ~2 μm. Signals were collected in a back scattering configuration at room temperature and detected by an electrical-cooled charge-coupled-device (CCD) camera. The spectra resolution of the optical system is about 1 cm^{-1}.

3. RESULT AND DISCUSSION

3.1. TEM Observation

Fig. 2 is a high-resolution transmission electron microscope (HRTEM) image (JEOL2010 electron microscope, operating at 200 kV) of the nanotubes. The AFI framework was removed using hydrochloric acid before the TEM observation (Wang, 2001). The contrast of the SWNTs is very weak due to their small dimensions compared to the thickness of the supporting amorphous carbon film (~ 10 nm). However, it can be recognized that the typical SWNT contrast consist of paired dark fringes. Such contrast becomes more obvious when the picture is

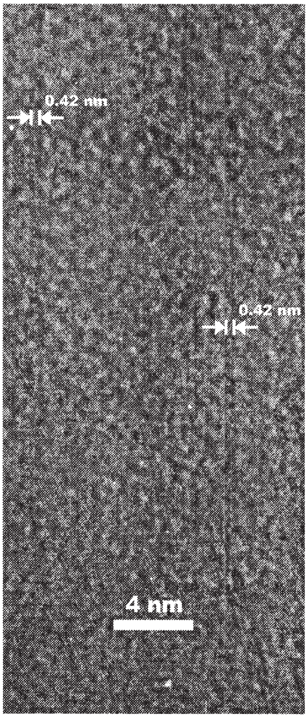

Figure 2 High-resolution TEM image of the SWNTs. The nanotubes were moved out from the AFI channels and dispersed on a carbon lacy film for the TEM observation.

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blocked by water and the micromembrane is impermeable to both hydrogen and oxygen. This latter characteristic is important for fuel cell application where the membrane barrier must prevent the cross diffusion of the fuel (i.e., hydrogen) and oxidizer (i.e., oxygen or air) that could lead to a decrease in efficiency.

Nafion is the most popular proton exchange membrane used in the polymer electrolyte membrane fuel cell (PEMFC). Gierke proposed that cations such as proton are transported through the Nafion by traveling from one isolated clusters of hydrated sulfonate groups to another through water filled nanometer-sized channels (Mauritz *et al.*, 1980). This means that water management is critical for the proper operation of a Nafion membrane. Also, the larger pore sizes (~10 nm) of Nafion means that reactant cross over and diffusion of electrode materials must be carefully considered. Membrane shrinkage due to dehydration and its swelling in the presence of methanol and other organic fuel further exacerbate these problems. The polymer membrane also has poorer mechanical strength and lower operating temperature, which severely restrict the operation of a PEM fuel cell. It is therefore attractive to replace the current PEM with an inorganic analog such as zeolite membrane. The HZSM-5 zeolite is one possible candidate.

The ZSM-5 micromembrane shown in Figure 1 was converted into an HZSM-5 micromembrane through ion exchange in an acid solution. Figure 2a shows the proton transport across the hydrated HZSM-5 membrane from a 0.1 N HCl solution to D.D.I. water. The pH of the D.D.I. water decreases as the proton diffuses through the micromembrane under the influence of a concentration gradient until equilibrium is established. Both initial (R_0) and average (R_{ave}) proton transport rates across the micromembranes can be calculated from these data. Figure 2b displays the plots of R_0 and R_{ave} as a function of the concentration gradient across the micromembrane. The figure shows that the proton transport rate increases as the concentration gradient increases, but reaches a plateau for $[H_3O^+]$ concentrations greater than 0.2 M. A maximum proton transport rate of 1.3×10^{-3} $mole^1 m^{-2} s^{-1}$ was obtained from the 5-µm thick HZSM-5 micromembrane.

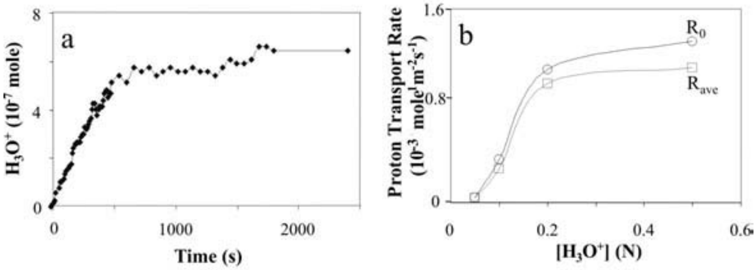

Fig. 2 (a) Moles of proton transported across the zeolite membrane from a 0.1 N HCl solution to deionized water as a function of time. (b) The initial (R_0) and average (R_{ave}) proton transport rates as a function of the concentration of HCl solution.

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Although this is sufficient for microfuel cell application, improvements can be made by decreasing the transport resistance (i.e., membrane thickness, zeolite pore size) and by increasing ion capacity and mobility (i.e., NaA and NaX zeolites) of the zeolite micromembrane.

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REFERENCES

Brek, D. W. 1974, *Zeolite molecular sieves – structure, chemistry and use*, (New York: John Wiley & Sons, Inc).

Chau, J. L. H., Wan, Y. S .S., Gavriilidis, A. and Yeung, K. L., 2002, Incorporating zeolites in microchemical systems, *Chem. Eng. J.*(in press).

Coronas J. and Santamaria J., 1999, Separations using zeolite membranes, *Separation and purification methods*, **28**, pp. 127.

Franz, A. J., Jensen, K. F. and Schmidt, M. A., 1999, Palladium membrane microreactors, In *Microreaction Technology: Industrial prospects*, edited by Ehrfeld, W.(Berlin: Springer-Verlag), pp. 267.

Geus, E. R. and van Bekkum, H., 1995, Calcination of Large MFI-Type single-crystals.2. Crack formation and thermomechanical properties in view of the preparation of zeolite membranes, *Zeolites*, **15**, pp. 333.

Losey, M. W., Isogai, S., Schmidt, M. A. and Jensen, K. F., 2000, Microfabricated devices for multiphase catalytic processes, In *Proceedings of the Fourth International Conference on Microreaction Technology*, Atlanta, USA, 2000, p. 416.

Mauritz, K. A., Hora, C. J. and Hopfinger, A. J., 1980, In *Ions in Polymers*, edited by Eisenberg, A., (New York: American Chemical Society).

Szostak, R., 1989, *Molecular sieves – principles of synthesis and identification*, (New York: Van Nostrand Reinhold).

Wan, Y. S. S., Chau, J. L. H., Gavriilidis, A. and Yeung, K. L., 2001, Design and fabrication of zeolite-based microreactors and membrane microseparators, *Microporous and Mesoporous Materials*, **42**, pp. 157.

Wan, Y. S. S., Chau, J. L. H., Gavriilidis, A. and Yeung, K. L., 2001, Design and fabrication of zeolite-containing microstructures, In *5th International Conference on Microreaction Technology*, Strasbourg, France.

Yeung, K. L. and Chau, J. L. H., Zeolite micromembranes, *U.S. Pat. Application.*

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