

Zeolite micro fuel cell

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Microfabricated HZSM-5 micromembranes were successfully employed as a proton-exchange membrane in a micro fuel cell and the energy generation is strongly dependent on the Al-content of the HZSM-5.

Micro fuel cells offer a clean, portable energy source for today's increasingly mobile lifestyle.¹ They have the advantage of high specific and volumetric energy densities, long life cycle, zero-recharging time, greater flexibility and the absence of hazardous waste products at the end of the life cycle. Miniature proton-exchange membrane fuel cells (PEMFC) fuelled by hydrogen stored or produced onboard showed the best promise.² Proton exchange membranes that can tolerate high temperature operation (*i.e.*, 423–483 K) are the subject of intense study,^{3,4} for the electrocatalysts are not only more efficient at these temperatures, but can also better tolerate the CO poison in the reformed fuel. The various strategies used include the modifications of commercial perfluorinated Nafion[®]-type membranes and the use of new proton conducting membranes based on polybenzimidazole (PBI) and polyetherketones (PEEK).⁴

There is also a growing interest in inorganic proton conductors including zeolites and solid acids. The recent review article by Lu and coworkers⁵ shows that the majority of the works in solid acid membranes are on solid acid doped polymer membranes and composites. Layered metal(IV) phosphates containing protogenic functional groups and heteropolyacidic compounds were widely investigated.^{4,5} Zeolites and molecular sieves are mostly added to proton conducting membranes to remedy methanol crossover in direct methanol fuel cells or as a carrier for solid acids and other protogenic materials.⁶ However, many zeolites are ion conductors and can be grown into thin films and membranes. Experiments and model calculations indicate that proton mobility in ZSM-5 is among the highest in zeolites.⁷ ZSM-5 films and membranes are also easier to prepare and are amenable to miniaturization and microfabrication.⁸ This work investigates HZSM-5 as proton conducting membrane for a microfabricated miniature hydrogen PEMFC.

The array of freestanding zeolite micromembranes shown in Fig. 1a was fabricated on a silicon substrate.⁹ The front and back of the Si(100) wafer was simultaneously patterned by traditional photolithography method and etched with a KOH solution (30%, BDH Lab) to create a supporting structure for the deposition and growth of the zeolite membrane. Each of the square recesses measures $600 \times 600 \mu\text{m}^2$ on the surface and

tapered to $250 \times 250 \mu\text{m}^2$ at a depth of $250 \mu\text{m}$ due to the anisotropic etching of silicon. The recesses were selectively seeded with a monolayer of 100 nm TPA-Sil-1 zeolites by grafting aminopropylsilanes on the surfaces of the recesses. ZSM-5 zeolite films of different Si : Al ratios were grown on the seeded surfaces by hydrothermal synthesis at 423 K from solutions with molar compositions of $40 \text{SiO}_2 : z \text{Al}_2\text{O}_3 : 5 - y \text{TPAO}_2\text{O} : y \text{Na}_2\text{O} : 20\,000 \text{H}_2\text{O}$ (where $z \leq 2$ and $0 \leq y \leq 4$) prepared from tetraethyl orthosilicate (TEOS, 98%, Aldrich), aluminium sulfate (98+%, Aldrich), tetrapropylammonium hydroxide (TPAOH, 1 M, Aldrich) and sodium hydroxide (99+%, BDH). After hydrothermal synthesis, the samples were rinsed with excess distilled water and examined under the optical microscope (Olympus BH2-MJLT) for defects. The ZSM-5 films grown on the seeded surface have a preferred (101) crystallographic orientation according to the X-ray diffraction studies

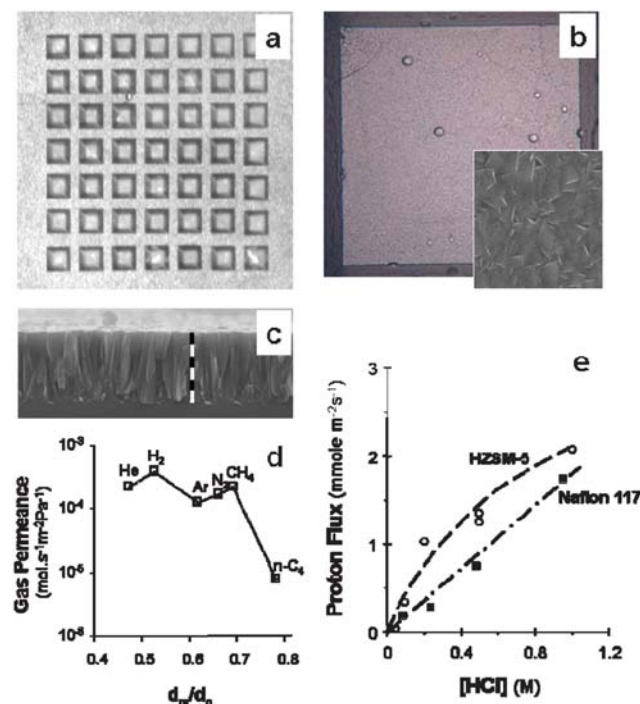


Fig. 1 Scanning electron microscope pictures of (a) the zeolite micromembrane array showing (b) the individual freestanding micromembranes of $250 \times 250 \mu\text{m}^2$ square. A higher magnification image of the zeolite membrane surface is shown in the inset picture in (b). (c) The cross-section of the micromembrane shows a well-intergrown, $6 \mu\text{m}$ thick zeolite layer. The plots of (d) single gas permeance and (e) proton flux indicate that the zeolite micromembrane displays good molecular sieving and proton conducting properties. Note: the proton flux of Nafion[®] 117 at room temperature is included for comparison.

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(XRD, Philips PW1830). The surface and bulk elemental compositions of the zeolites were analyzed by X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5600) and X-ray fluorescent spectroscopy (XRF, JEOL JSX 3201Z).

The final steps in the fabrication of zeolite micromembranes involved etching away the remaining 50 μm Si layer and removing the TPA^+ organic molecules from the zeolite pores. The etching was carried out in a well-stirred, thermostated bath at 353 K using a selective etchant, tetramethylammonium hydroxide (TMAH, 25%, MosesLake). The etching process was monitored with an optical microscope to avoid over- and under-etchings. The resulting freestanding zeolite micromembranes display good mechanical strength and could withstand pressures of up to 0.5 MPa before failure. Leak test was conducted using helium (UHP) at a pressure differential (ΔP) of 40 kPa to check for defects and cracks in the micromembranes before calcining in air to remove the TPA^+ molecules. The micromembranes were calcined at 823 K for 48 h at heating and cooling rates of 0.3 K min^{-1} . Fig. 1a–c are the images of the fabricated zeolite micromembranes taken by the JEOL 6300 scanning electron microscope (SEM). The forty-nine micromembranes arranged in a 7×7 square array occupy a $0.56 \text{ cm} \times 0.56 \text{ cm}$ area. Each micromembrane measures 0.062 mm^2 giving a membrane area of 3.062 mm^2 . The freestanding zeolite is polycrystalline and consists of intergrown zeolite crystals as shown in Fig. 1b. The anisotropic growth responsible for the preferred $\langle 101 \rangle$ zeolite crystal orientation is clearly evident in the membrane cross-section of Fig. 1c. The zeolites are well-intergrown along the entire 6 μm thickness of the membrane.

The single gas permeance of ultrahigh purity gases including helium, hydrogen, nitrogen and argon as well as the hydrocarbons, methane (CH_4 , 99.5%) and *n*-butane (*n*- C_4H_{10} , 99.9%) were measured for the ZSM-5 (Si/Al = 15) micromembrane. The gas permeances are plotted in Fig. 1d as a function of the ratio of the kinetic diameter of diffusing gas molecule (d_m) to the average diameter of the zeolite pore (*i.e.*, $d_p = 0.55 \text{ nm}$). Excellent permeance with high $\text{H}_2/n\text{-C}_4$ and $\text{C}_1/n\text{-C}_4$ permselectivity ratios of 50 and 30 were obtained. Molecular sieving is clearly evident from the plot indicating that the zeolite micromembrane is relatively free of defects and the primary gas transport was through the zeolite pores. Hydrogen fuel crossover is not a problem in the microporous ZSM-5. The ZSM-5 is impermeable to H_2 even at 473 K and 0.3 MPa after it had been hydrated by a stream of humid air.

The ZSM-5 micromembrane was converted to HZSM-5 by ion-exchange and the proton transport was measured in a membrane diffusion cell. The membrane separated two compartments containing an acid solution and deionized distilled water. The pH and conductivity in both chambers were monitored with time. The proton flux was measured from the initial rate data and plotted in Fig. 1e as a function of the HCl acid concentration. Similar measurements were done for Nafion 117 and the data are included for comparison. The figure shows that a 6 μm thick ZSM-5 (Si/Al = 15) micromembrane displays comparable proton flux as the commercial Nafion 117 membrane. A separate study confirmed that the prepared HZSM-5 micromembranes are stable against Al-leaching under acidic conditions (*i.e.*, pH 5 and 10 days).

A conventional membrane-electrode assembly (MEA) with an active area of 1.33 cm^2 was fabricated using a commercial

Nafion 117 membrane and Pt/C catalyst from E-Tek by the hot press method. The MEA performance was measured by CHI 660C electrochemical station. The tests were carried out at room temperature (294 K) using equal flow rates of humidified UHP H_2 (100% R.H.) and dry UHP O_2 . Fig. 2a plots the maximum power density for the conventional Nafion-MEA (\blacksquare) as a function of H_2 flow rate. The fuel cell performance reported in literature is typically obtained at high feed flow rates.^{1a} Fig. 2a shows the Nafion-MEA performs well and delivers 100 mW cm^{-2} under comparable test conditions (*i.e.*, $\geq 50 \text{ sccm}$). MEA using thinner Nafion 112 membrane reports higher performance.¹⁰ Fig. 2a shows the Nafion-MEA performance decreases when the feed flow rate is slower than 10 sccm due to the increased external mass transfer resistance. Flow rates in miniature and micro fuel cells are expected to be low. Indeed, the recent survey by Kundu *et al.*^{2a} shows that the majority of hydrogen-fed micro fuel cells operate at flow rates of less than 10 sccm to accommodate for the design structures imposed by the MEA and hydrogen delivery infrastructure. The MEA performance data in this work were obtained at hydrogen and oxygen feed flow rates of 2.5 sccm.

The hot press method is not suitable for the zeolite micromembrane and Zhao *et al.*'s approach¹¹ of using a Nafion solution to glue together the MEA was modified and adopted for this study. A Nafion-Si MEA was assembled using the new method. The Nafion 117 was supported on a prefabricated silicon grid containing forty-nine etched square windows of $250 \times 250 \mu\text{m}^2$. The Pt/C catalyst coated anode and cathode electrodes were glued to the membrane using 5% Nafion solution (E-Tek). Fig. 2a shows that Nafion-Si (Δ) has a similar performance as the Nafion-MEA. Power densities of 10.5 and 82 mW cm^{-2} were obtained for feed flow rates of 2.5 and 10 sccm, respectively. Sil-1 and HZSM-5 micromembranes were assembled into MEA using the same procedure as Nafion-Si. The thickness of the micromembranes varied from 5.5 to 6.5 μm due to the slight differences in their syntheses. Fig. 2b plots the maximum power density as a function of aluminium content of the zeolite micromembrane. Sil-1 and HZSM-5 with Si/Al ratio > 30 have no measurable current flow. The zeolite MEA (*i.e.*, Si/Al < 30) delivers increasing power in proportion to the aluminium content of the HZSM-5 micromembrane. Also, the open current voltage (OCV) increases from 0.60 to 0.85 V. Power density of 12.8 mW cm^{-2} and OCV of 0.85 V were recorded for HZSM-5 of Si/Al = 15. The results are consistent with the reports that the activation energy for proton intersite hopping in HZSM-5 decreases with the increasing aluminium content of the zeolite.¹²

Fig. 2c and d plot the cell voltage (E) and power density (P) of Nafion-MEA, Nafion-Si and Zeolite (*i.e.*, HZSM-5 Si/Al = 15) single-cell, micro fuel cells as a function of current flux (j). The tests were conducted using 2.5 sccm humidified H_2 (100% R.H.) and 2.5 sccm dry O_2 at 294 K and at an ambient pressure of 101.3 kPa. Fig. 2c shows that the cell voltages are lower than the ideal potential voltage of 1.19 V for the H_2/O_2 fuel cell. This is attributed to the irreversible losses due to activation, ohmic and concentration polarizations in the fuel cells. Hot pressing could alter the activity of the catalyst and the transport property of the porous electrode, and may explain the higher activation and concentration polarizations of Nafion-MEA compared to

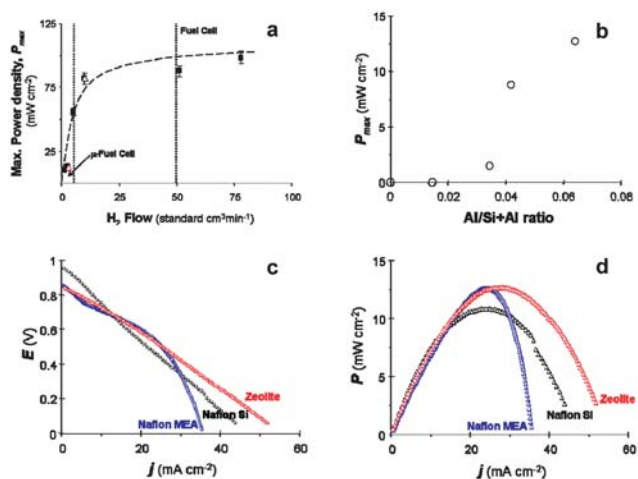


Fig. 2 (a) Plots of the maximum power density obtained from a Nafion 117 MEA prepared by hot press (■) and glue (△) methods for different H₂ feed flow rates. (b) The effects of the aluminium content of the HZSM-5 micromembrane on the P_{\max} generated by the zeolite micro fuel cell (2.5 sccm H₂ (100% R.H.), 2.5 sccm dry O₂, $T = 294$ K). (c) & (d) performance comparison between Nafion MEA prepared by the hot press method, Nafion Si assembled by the glue technique and a HZSM-5 zeolite micro fuel cell (2.5 sccm H₂ (100% R.H.), 2.5 sccm dry O₂, $T = 294$ K).

Nafion-Si. The lower ohmic losses of Nafion-MEA are expected, because of the better contact between the membrane, catalyst and electrode in the hot pressed MEA. The zeolite micro fuel cell displays similar activation and ohmic losses, but not the severe concentration polarization seen in the Nafion-MEA. The higher activation polarization compared to Nafion-Si is due to the activated transport of protons in the zeolites.

The residual water in the zeolites dramatically reduces the barrier for intersite proton hopping.¹³ A Grotthus-like mechanism had been proposed, where protons diffuse between neighbouring aluminium sites in the “hydrated” zeolites *via* a chain of water molecules in the pores.¹⁴ This suggests that water and therefore humidification plays an important role in the proton conductivity in zeolite. Indeed, it was observed that the “dehydrated” zeolite micro fuel cell performed poorly with a nearly zero current flow. The measured OCV and current increased with time as the zeolite became hydrated with water formed by the fuel cell reaction. The steady-state OCV of 0.48 V and j_{\max} of 8 mA cm⁻² were obtained only after a prolonged operation of 6 h. Replacing the dry H₂ with a humidified H₂ feed, an OCV of 0.84 V and j_{\max} of 55 mA cm⁻² were obtained as shown in Fig. 2c. Once hydrated, ZSM-5 zeolite can retain water molecules up to a desorption temperature of 600 K. Fig. 2d shows the Nafion-MEA, Nafion-Si and Zeolite micro fuel cells deliver P_{\max} of 12.6, 10.8 and 12.8 mW cm⁻² at 0.52, 0.45 and 0.48 V, respectively. The results clearly show that the Zeolite micro fuel cell can achieve the same performance as the Nafion-based PEMFCs. Further improvements in membrane transport by decreasing the diffusion pathways through the zeolite (*i.e.*, thinner membrane and b-oriented HZSM-5) are expected to yield higher fuel cell performance.

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