

FUEL CELLS

Engineering the next generation

A silicon-based membrane for fuel cells offers significant advantages over Nafion-based membranes.

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Proton-exchange membrane (PEM) fuel cells, which convert chemical energy into electricity using an electrochemical cell (Fig. 1a), could be used as efficient power sources, offering high power density and low environmental impact. An essential component of such fuel cells is the membrane. This is a quintessential nanomaterial, with hydrophilic pores of around 10 nm in size through which protons are transported (Fig. 1b). The most common PEM material is the polymer electrolyte Nafion, which is composed of a hydrophobic Teflon backbone and side chains terminated with hydrophilic sulphonic acid (SO_3H) groups. In a Nafion film, the hydrophilic pores form by phase separation of the side chains from the polymer backbone. The performance of the proton-conducting channels in these films is strongly dependent on the environmental conditions. At high temperature and low relative humidity, the proton-conducting channels shrink and the conductivity decreases markedly. This means that under high-temperature conditions — where the catalysts in the electrodes perform at their best — the membrane performs at its worst. Therefore, to optimize the performance of fuel cells it is useful to design a membrane with high conductivity at high temperature and low humidity.

Writing in *Nature Nanotechnology*, Saeed Moghaddam, Mark Shannon and colleagues¹ at the University of Illinois at Urbana-Champaign, Sandia National Laboratories, Surface Measurement Systems Ltd and the University of New Mexico report a new silicon-based proton-exchange membrane with high proton conductivity over a wide range of relative humidity and temperature. The PEM is constructed by first preparing a bulk silicon membrane using standard processing techniques. The pore structure is then formed by etching the silicon membrane using hydrofluoric acid, resulting in ordered pores with sizes in the range 7–10 nm. Once the pore structure is produced, the surface inside the pores is rendered acidic using three chemical processing steps: the hydrogen-terminated surface is hydroxylated by exposing the membrane

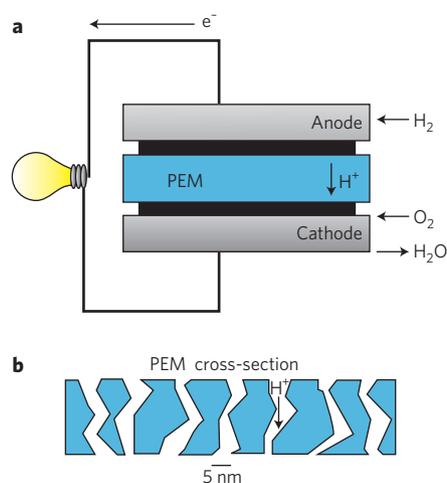


Figure 1 | Proton-exchange membranes.

a, Schematic of a PEM fuel cell. At the anode, the fuel (hydrogen gas, methanol or formic acid) is broken down to produce protons, which are then transported through the membrane to the cathode where they react with oxygen to produce water. The electrons transferred in the reaction carry the electric current and drive the load, represented here by a light bulb. **b**, Schematic cross-section of a PEM. The proton-conducting channels are depicted in white.

to O_2 and washing in deionized water; the hydroxylated surface is then treated with $\text{HS}-(\text{CH}_2)_3-\text{Si}-(\text{OCH}_3)_3$ to produce a self-assembled monolayer; and finally the terminal $-\text{SH}$ groups are oxidized to $-\text{SO}_3\text{H}$ groups. To ensure high proton conductivity at low humidity, the researchers encapsulate each side of the membrane with a thin (2 nm) layer of hydrophilic silica. The silica layer effectively shrinks the size of the pores at the membrane surface and keeps the larger pores from drying out as the humidity drops. The resulting membrane is mechanically robust, the pore volume is independent of temperature and relative humidity, and the proton conductivity remains constant over a wide range of temperature and relative humidity.

The preparation of proton-exchange membranes from inorganic materials has been demonstrated before^{2–4}, but Moghaddam and colleagues are the first

to fabricate a fuel cell incorporating an inorganic membrane with performance superior to that of a Nafion-based PEM fuel cell over the entire range of relative humidity. The porous silicon-based membrane showed proton conductivity three times higher than that of Nafion at high relative humidity (where the conductivity of Nafion is highest), and conductivity an astounding 100 times higher at 20% relative humidity.

The fabrication of these silicon membranes can also be readily integrated into silicon-processing infrastructure, which can be easily scaled up with the potential to lower the overall cost of production. Furthermore, nearly every processing step can be tuned. The pore size and structure can be controlled by adjusting the etching conditions, such as current density or etchant concentration. The acidity of the pores can be controlled by changing the composition of the self-assembled monolayer. For example, by introducing electron-withdrawing groups such as fluorine, it should be possible to increase the overall acidity of the $-\text{SO}_3\text{H}$ groups and further enhance the conductivity.

Finally, it is worth noting that Nafion materials have been used in fuel cells for over 40 years (ref. 5). They have been optimized and re-optimized many times, which has led to considerable improvements in the performance of Nafion-based devices. It is thus conceivable that optimization of the porous silicon membrane will lead to similar enhancements in performance of this next-generation PEM for fuel cells. □

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