

Nanoengineering of a New Generation Proton Exchange Membrane for Micro Fuel Cells

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ABSTRACT

We report development of a silicon-based proton exchange membrane (PS-PEM). This has been achieved through development of a technique for self-assembly of molecules with functional end groups inside high aspect ratio nanopores within a porous silicon membrane. A membrane electrode assembly (MEA) was built using the developed PS-PEM. The developed MEA delivered an open circuit potential (OCP) of 0.76 V and a power density of 47 mW/cm².

Keywords: fuel cell, proton exchange membrane (PEM), porous silicon, self-assembly, and membrane electrode assembly (MEA)

1 INTRODUCTION

In recent years, creating a thermally and mechanically stable (i.e. non-swelling) PEM for micro fuel cells has garnered intense interest. Early efforts on fabricating silicon-based PEMs have focused on adding perfluorosulfonate ionomers such as Nafion in a silicon membrane with large pores [1]. Unfortunately, the lack of adhesion between the perfluoro polymers and the silicon base structure, along with significant volume change of the polymers, results in failure of the membrane electrode assembly (MEA) over time. One approach to solve these problems is to covalently bond molecules with functional groups inside silicon nanopores. Efforts to do so have been largely unsuccessful due to difficulties in self-assembling molecules in torturous nanopores with extremely high aspect ratios. The common approach has been (e.g. in [2]) to soak a porous membrane in the solution containing the self-assembly molecules. Diffusion is relied upon to deliver molecules through torturous nanopores with aspect ratios in the 1000s. But no evidence of functionalization deep within the pores has been presented; instead proton conductivity (or performance in a MEA) has been evaluated.

A simple estimation suggests that one pore volume of a 1 mM solution contains 3-4 orders of magnitude fewer molecules than necessary for complete coverage of all hydroxylated sites on the wall of a long (several microns) nanopore. Therefore, high aspect ratio nanopores should be filled with the 1 mM solution thousands of times to supply

enough solute molecules to the pores. Increasing the solution concentration to reduce the number of filling times is not an option, since it leads to self-polymerization of the solute molecules. The approach taken in this study has been to extract the depleted solvent from the bottom of the membrane pores continuously while the solute-rich solvent is supplied to the top of the membrane.

An experimental apparatus has been fabricated for this purpose and a set of recipes has been developed to assemble 3-mercaptopropyl-trimethoxysilane (MPTMS) molecules within a silicon membrane. Details of the developed processes and performance of a MEA fabricated using the developed PS-PEM are described in the following sections.

2 FABRICATION PROCESS

A silicon membrane was fabricated through KOH etching of a p-doped silicon wafer. The membrane was anodized in HF electrolyte in a standard two-chamber bath. Details about the apparatus and the process could be found in [3]. Since the primary goal for this effort was to develop a PEM in which a pore size of several nanometers is necessary to maintain a low fuel crossover level, 5-7 nm in diameter pores were produced inside the membrane. This was achieved by varying several parameters including concentration of the HF electrolyte, anodization current density, and silicon doping level. The pores grew through the entire membrane thickness, except through an approximately 50-nm thick layer at the backside of the membrane that was later etched using reactive ion etching process. The anodization process and subsequent back etching of the membrane with SF₆ plasma rendered the porous membrane surface hydrophobic due to high concentration of fluorine on the surface and inside the pores. The surface of the pores was cleaned and hydroxylated. This process left the pores slightly wider (7-10 nm) than their original size (cf. Figure 1).

2.1 Functionalization Apparatus

As mentioned earlier, one pore volume of the solvent contains orders of magnitude less solute molecules necessary for all OH sites inside a long pore. For example, one volume of a 5-nm diameter, 20- μ m long pore only contains 232 MPTMS molecules, when filled with a 1 mM

solution, while the number of potential OH sites on the pore wall is close to 2 million. A relatively dilute solution of 1 mM was selected to avoid self-polymerization of the MPTMS molecules. Therefore, the pores should be filled thousands of times to supply the number of molecules needed in the pores. In order to achieve this goal, a setup was fabricated to allow holding the porous membrane die between top and bottom compartments of a chamber and flow the solution through the pores.

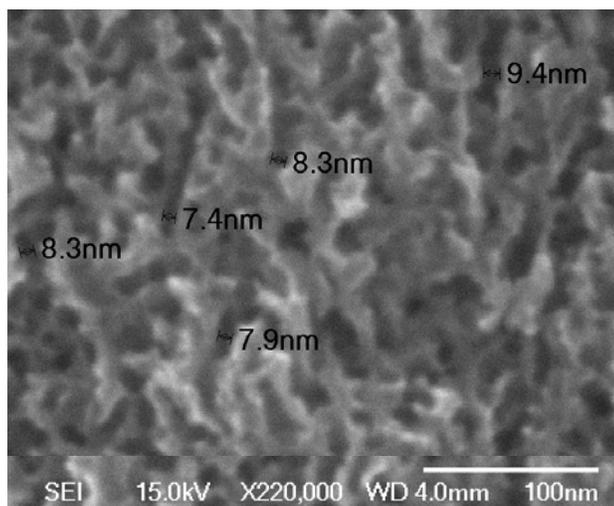


Figure 1: SEM view of the cross section of the membrane after hydroxylation. The cleaning/hydroxylation process was conducted in $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solution. Continuous oxidation of the silicon backbone attacked by OH^- and its subsequent dissolution in aqueous ammonia (NH_3) resulted in under-etching the fluorine terminated Si as well as fluorine compounds on the surface of the pores.

3 SELF-ASSEMBLY VERIFICATION

Penetration depth of the functional group inside the membrane was verified using Time of Flight-Secondary Ion Mass Spectroscopy (ToF-SIMS) with depth profiling. As can be seen in Figure 2, sulfur penetrated through the entire membrane thickness. Results show a higher count for all elements at both top and bottom of the membrane. This is counterintuitive, considering the fact that the anodization process left the pores larger at the top of the membrane than its middle. Also, the hydroxylation process enlarged the pores at the bottom of the membrane and made it more porous than its middle. Thus, silicon count should have been the lowest at both sides of the membrane. We speculate that higher count at both sides of the membrane is an artifact of the technique employed. Generally, more surface area near the beam results in generation of more secondary ions. Hence, a higher number of counts could result from a more porous surface. If this argument is true, variation of the elements count could also represent a change in the pore size. Interestingly, it appears that the silicon, oxygen, and fluorine count curves, which represent

the initial construct of the porous membrane (i.e. before functionalization), have a relatively similar slope.

Also, the variations in the count curves for sulfur and hydrogen (and to some extent carbon at the first half of the curve) that represent the MPTMS presence in the pores follow a similar slope. These curves have a noticeably steeper slope than that of silicon. This suggests that the higher sulfur count up to a certain depth might not be due only to the surface effect described above, but perhaps suggests sulfur concentration is higher close to the top surface. It is not clear, however, whether this higher concentration is due to the higher surface area of the more porous structure at the top of the membrane or the presence of physisorbed molecules on the monolayer.

Finally, the thiol end group of the MPTMS molecule was oxidized to sulfonate group in nitric acid at room temperature.

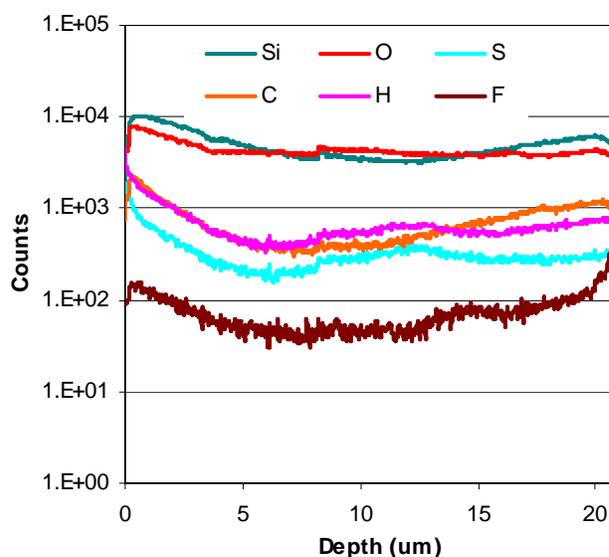


Figure 2: Time of Flight-Secondary Ion Mass Spectroscopy (ToF-SIMS) results (phased depth profile using a 22 kV Au^+ analysis beam and a 2 kV Cs^+ sputtering beam) showing composition of the 20- μm thick membrane. A spot on the membrane was carved in gradually until reached to the bottom of the membrane. Note that the sudden spike in fluorine content at the bottom of the membrane is due the back-etching process used to open up the pores.

4 MEA FABRICATION AND TESTING

A MEA was built by applying Pt-based catalyst on both sides of the PS-PEM and sputter coating of Cr/Au current collectors (i.e. electrodes) outside the membrane area. The edges of the catalyst painted area overlaps with the Cr/Au electrodes. The MEA was tested using Solartron SI 1287 potentiostat. Results are shown in Figure 3. An open circuit potential of 0.76 V and a maximum power density of 47 mW/cm^2 were achieved. Overall, performance of the MEA was better than the performance reported in a recent study. However, the open circuit potential (OCP) is still lower

than the typical OCP achieved using Nafion® membrane. We believe this is due to H₂ cross over. This is primarily due to larger pore diameter in our PS-PEM (~7-10 nm) than in Nafion® (~5 nm). Perhaps, large pore size (~10 nm) in Pichonat and B. Gauthier-Manuel [2] could be the reason for the low OCP of 0.4 V reported in their study.

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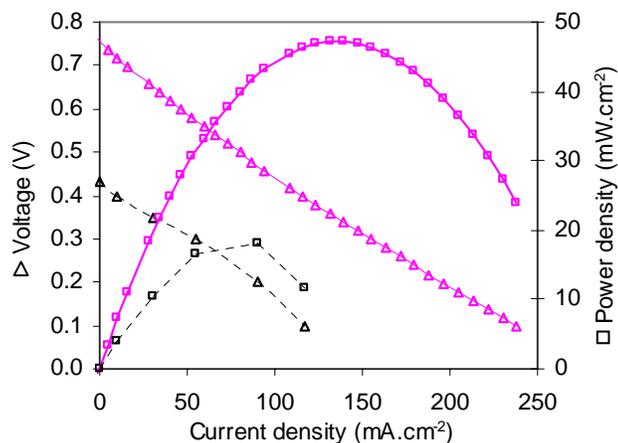


Figure 3. Characteristics of a functionalized membrane (this study (—) & Ref. [2] (----)).

5 CONCLUSIONS

A silicon-based proton exchange membrane was developed through functionalization of a porous silicon membrane with MPTMS molecules using a new method. Penetration of the MPTMS molecules throughout the entire membrane thickness was verified using ToF-SIMS technique. The thiol end group of the MPTMS molecule was later oxidized in nitric acid. A MEA fabricated using the PS-PEM delivered an open circuit potential of 0.76 V and a maximum power density of 47 mW/cm².

ACKNOWLEDGMENTS

The authors would like to acknowledge and appreciate the support provided by DARPA. This work was carried out in part in the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois, which are partially supported by the U.S. Department of Energy under grants DE-FG02-07ER46453 and DE-FG02-07ER46471. The authors would like to thank Drs. Tim Spila and Rick Haasch for their assistance with the ToF-SIMS and XPS analysis.

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