PROTON TRANSPORT THROUGH SELF-ASSEMBLED FUNCTIONALIZED NANOPOROUS SILICON

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ABSTRACT
In this study, self-assembly of molecules with thiol functional group inside extremely high aspect ratio silicon nanopores is presented. The thiol end group was subsequently oxidized to sulfonate group to enhance proton transport through the pores. Penetration of the assembled molecules down to the bottom of the pores was verified by measuring sulfur variation through the membrane thickness using Time of Flight-Secondary Ion Mass Spectroscopy (ToF-SIMS) technique.

KEYWORDS: Proton exchange membrane (PEM), Power source for portable applications, Micro fuel cell, Self-assembled monolayer (SAM)

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 (cf. Fig. 1). Efforts to do so have been largely unsuccessful due to difficulties in self-assembling molecules in tortuous nanopores with extremely high aspect ratios. The common approach has been (e.g. in [2-4]) 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. Here we present full functionalization of a nanoporous silicon membrane.

EXPERIMENTAL
A 20 µm thick silicon membrane was anodized in HF electrolyte and 5-7 nm diameter pores were produced through the entire membrane thickness. 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 SF6 reactive ion etching process. The anodization process and subsequent back etching of the membrane rendered the porous membrane surface hydrophobic due to high concentration of fluorine on the surface and inside the pores. A recipe was developed for cleaning and hydroxylation of the pores wall. In order to avoid self-polymerization...
of the 3-mercaptopropyl-trimethoxysilane (MPTMS) molecules used for functionalization, a dilute solution of MPTMS in benzene (1 mM) was used. One pore volume of the solution contained 3-4 orders of magnitude less molecules than necessary for complete coverage of all hydroxylated sites within the pores. To supply sufficient molecules to all sites, a setup was fabricated that allows supply of solute-rich solution to the pores and extraction of the depleted solvent from the bottom of the pores. After completion of the self-assembly process, the thiol end of the MPTMS molecule was oxidized to sulfonate in nitric acid.

RESULTS AND DISCUSSION

Penetration of the functional group inside the membrane was verified using Time of Flight-Secondary Ion Mass Spectroscopy (ToF-SIMS) with depth profiling (cf. Figure 2). A spot on the membrane was carved in gradually until reached to the bottom of the membrane. 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.
CONCLUSIONS

A nanoporous silicon membrane with pore aspect ratio of several thousands was successfully functionalized. This was achieved through development of a set of recipes for fabrication of a porous silicon membrane, its hydroxylation, and development of a new technique for supplying the necessary number of molecules deep inside the nanopores. The results were verified using ToF-SIMS with depth profiling.

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REFERENCES


Figure 2. ToF-SIMS results (phased depth profile using a 22 kV Au+ analysis beam and a 2 kV Cs+ sputtering beam) showing composition of the membrane.