

A new proton-conducting porous silicon membrane for small fuel cells

T. Pichonat*, B. Gauthier-Manuel, D. Hauden

*Laboratoire de Physique et Métrologie des Oscillateurs du C. N.R.S. Associé à l'Université de Franche-Comté;
IMFC FRW 0067, 3 Avenue de l'Observatoire, 25044 Besancon Cedex, France*

Abstract

In this paper, we report the fabrication of a new miniature fuel cell (FC) for portable applications based on a Nafion[®]-filled porous silicon membrane. This technique allows to combine advantages of Nafion[®] such as good proton conduction and silicon such as easy serial and parallel integration. Other advantages are the integration of gas feed and electrical contacts into the membrane etching process thanks to simple KOH wet etching processes and metal sputtering and the possibility of encapsulation. Moreover, with this technique we hope to reduce the lateral water diffusion through the membrane which is a problem with Nafion[®] membranes. All the results have been obtained at room temperature and gas feed (H₂) is provided by the electrolysis of a NaOH solution.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Porous silicon; Membrane; Miniature fuel cell; Nafion[®]

1. Introduction

Miniaturization and development of devices such as cellular phones or portable computers and the desire to increase life time of batteries lead the research beyond common types of batteries like nickel–cadmium (NiCd), nickel metal hydride (NiMH) or lithium ion (Li-ion). Since the last few years, many laboratories have been involved in the conception of fuel cells (FC) for portable applications because of their great energy density within the same dimensions of previously mentioned batteries, their simple use (easily and quickly rechargeable just by refilling in fuel) and the fact that it is theoretically a non-polluting technology. Several types of FC are developed like proton exchange membrane fuel cell (PEMFC) or direct methanol fuel cell (DMFC) which are the most popular solutions for portable applications.

Most of them use ionomeric membranes made of Nafion[®] (for example see [1]) or Nafion[®] based membranes [2]. Nafion[®] is the reference material in proton-conducting membranes but many other types of ionomeric membranes are also reported (see for example [3]). Literature also reports original research axes like hybrid silica/Nafion[®] membranes [4] or a porous silica membrane filled with sulfonated polyelectrolyte [5]. However, this last method requires a thick porous carbon disk as support and is not suitable to obtain miniature cells.

We report here a new way of making miniature fuel cells using silicon substrate with porous silicon membrane filled with Nafion[®] allowing us to take advantage of both Nafion[®] for proton conduction and silicon for mass production, easy etching process, possibility of integration and metallization of electrical contact within the process.

2. Experimental

2.1. Silicon membrane

Membranes are made of phosphorus-doped 0.016–0.024 Ω cm n⁺-type (1 0 0) oriented silicon wafers with standard wet KOH etching process (Fig. 1). This process can be broken up into six steps: thin thermal oxidation of the silicon wafer (1.2 μm thick) (step 1), photoresist deposition (step 3), UV insolation through a photolithography mask and development in an adapted solution (step 4), desoxidation of insolated patterns (step 5) and then KOH etching (step 6). We add to this process a sputtered Cr–Au layer (Cr layer of 15 nm thick and Au layer of 800 nm thick) on the silicon oxide layer (step 2) in order to allow the localization of the porosity during anodization and to collect current in the future fuel cell, each side being electrically isolated by the silicon oxide layer. Membrane thickness is fixed to 40 μm by adjusting processing time and temperature. Sixty-nine square membranes of 3 mm × 3 mm are collectively processed on a 4 in. wafer.

* Corresponding author.

E-mail address: tristan.pichonat@lpmo.edu (T. Pichonat).

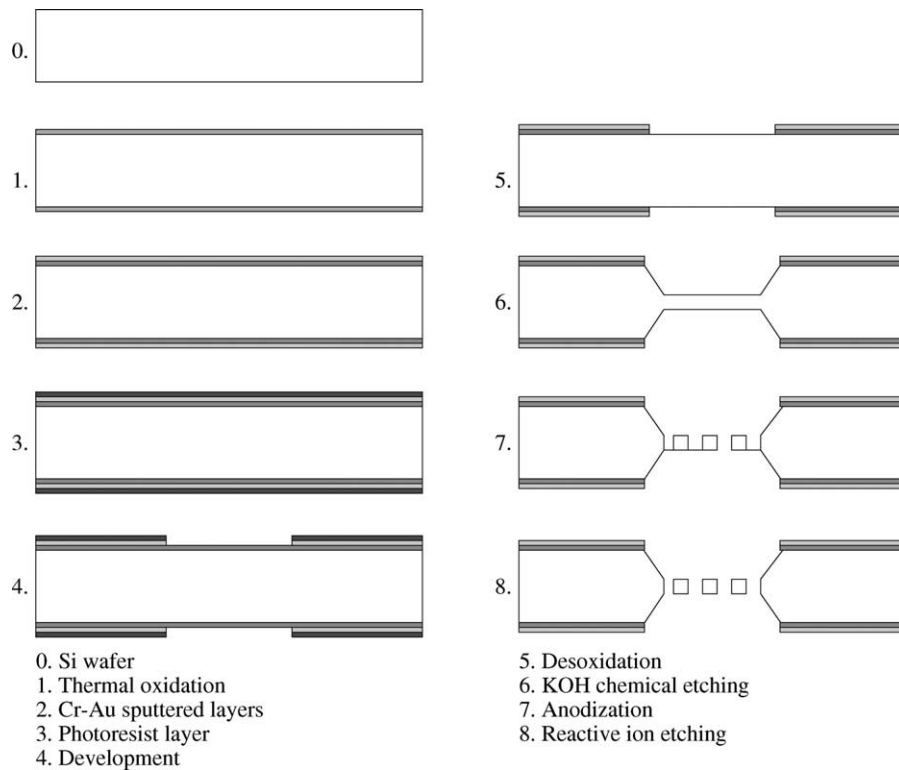


Fig. 1. Porous silicon membrane process.

2.2. Porous silicon

Silicon membranes are made porous by anodization in a double-tank cell (diagram in Fig. 2). The anodization cell used was conceived by AMMT GmbH (AMMT PSB wet etching machine for porous silicon). It consists of two half-cells in which Pt electrodes are immersed and the silicon wafer separates and isolates the two half-cells.

The electrolyte used is an ethanoic–HF solution (50% of pure ethanol and 50% of a 48% HF solution). Anodization is carried out in the dark at constant current, with a current density equal to 250 mA/cm^2 to obtain pores of 30 nm diameter and a porosity of about 50% [7].

Once anodization is achieved, membranes are rinsed into an oxidizing bath (Le Vert decontamination solution from the French company Prevor) neutralizing HF solution. Then several deionized water baths and isopropyl alcohol are

used for rinsing and reducing stress into pores. Membranes are finally dried at ambient air. Porous silicon membranes with a silica surface layer are obtained. The characterization of these porous membranes is made by SEM imaging (Fig. 3).

At this step of the process just a few channels are really opened as proved by conductivity measurements. Indeed due to some discrepancy on the thickness of the silicon membranes all the parts of the membranes can not be etched at the same time. When the first channels emerge process efficiency dramatically decreases: all the current goes through these opened channels making them bigger and bigger and no more holes are created.

We add a short additional thin reactive ion etching (R.I.E.) process using SF_6 and O_2 gases for silicon etching on the back side of the membranes in order to make sure that all the pores are opened. R.I.E. working conditions are a $100 \mu\text{bar}$

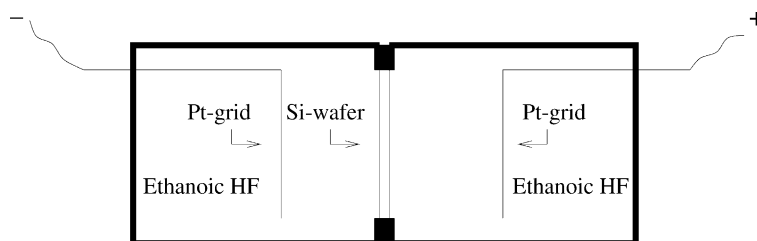


Fig. 2. Schematic view of the double-tank cell used for anodization (from [6]).

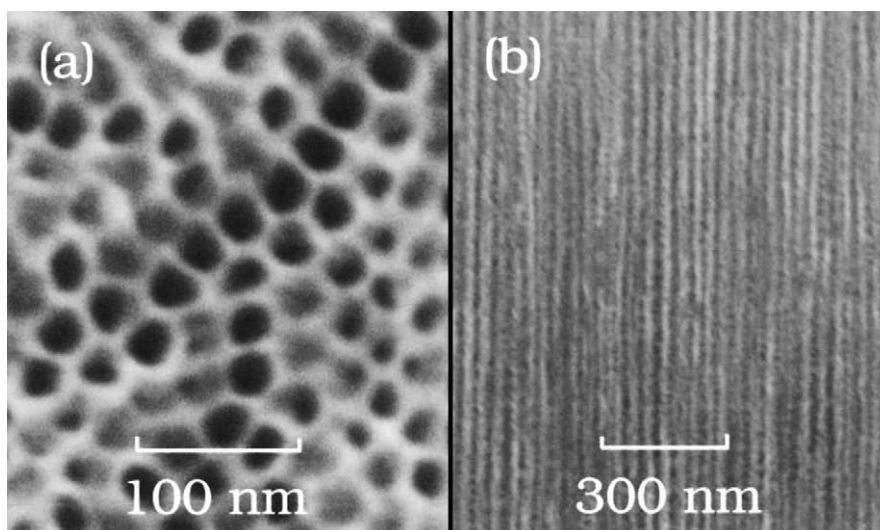


Fig. 3. n^+ -type porous silicon made by anodization at 250 mA/cm^2 in the dark in an ethanoic–HF bath: (a) SEM porous silicon front view; (b) SEM porous silicon cross-section view.

pressure, a 150 W plasma power, 20 sccm of SF_6 and 7 sccm of O_2 which allow to etch $0.6 \mu\text{m}$ thick per minute.

The characterization of opened pores is carried out by conductivity measurements in a 3% hydrochloric acid electrolyte solution (Fig. 4). A study concerning membrane conductivity as a function of R.I.E. processing time has led to determine an optimized processing time of 60 s (corresponding to a membrane etched thickness of $0.6 \mu\text{m}$) when membrane conductivity nearly reaches its top value.

2.3. Proton-conducting porous silicon

Without any further treatment, realized porous silicon membranes do not conduct enough protons (fuel cell tests without pore filling show no generated current). They must artificially be made proton-conducting by filling the pores.

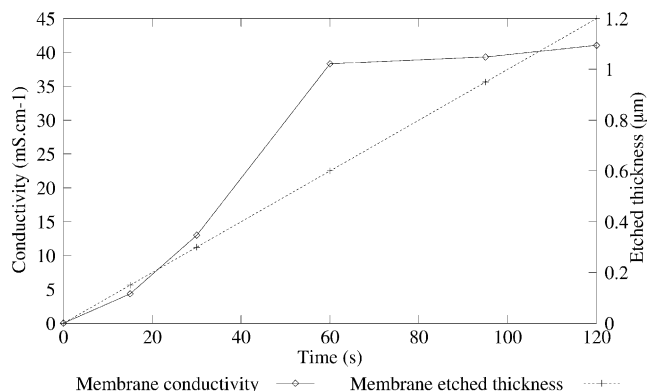


Fig. 4. Porous silicon membrane conductivity values before and after different R.I.E. processing times. We can observe a plateau in conductivity reached after 60 s of R.I.E. processing which means it is not necessary to etch furthermore.

Our solution consists in filling the silicon pores with a Nafion[®] solution and letting the solvents evaporate to leave only Nafion[®] into the pores in order to obtain a membrane with the advantages of Nafion[®] for proton conduction compatible with an integrated silicon mass production technology.

A first step consists in making porous silicon surface hydrophilic to improve the filling process. It is realized by immersing membranes into “Piranha” solution, consisting in a mixture of a 80% solution of pure sulfuric acid with 20% of a 33% aqueous solution of hydrogen peroxide, for 10 min.

Pore filling with Nafion[®] solution is then realized by simple capillarity. We use a 5% Nafion[®]-117 solution from Fluka GmbH (Sigma–Aldrich group). The volume of Nafion[®] solution used in order to completely fill a porous membrane is calculated according to estimated volume of the pores. Considering a membrane surface of 9 mm^2 and a thickness of $40 \mu\text{m}$, with a porosity of 50%, we can assume that a volume of $3.6 \mu\text{l}$ of Nafion[®] solution fills every pore. The control of pore filling is observed by SEM imaging of the membrane cross section (Fig. 5). The backside of the membrane shows a stalactite profile due to the drying of the Nafion[®] solution.

2.4. Electrodes

We use E-tek electrodes composed of a carbon conducting cloth filled with platinum (20% Pt on Vulcan XC-72) used as H_2/O_2 catalyst. They are fixed to the membrane with Nafion[®]-117 solution playing the role of a glue with proton-conducting properties. As the membrane borders are covered with a Cr–Au layer to collect current, we just have to make sure that the electrodes and the membrane plated borders are in contact.

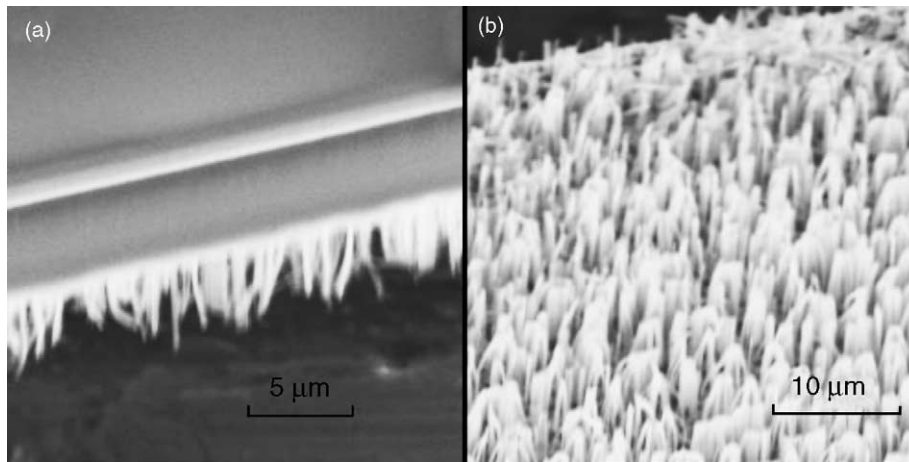


Fig. 5. (a) SEM cross-section view of a Nafion[®] filled porous silicon membrane. We clearly see Nafion[®] going through membrane; (b) SEM image of the back of the membrane after filling with Nafion[®].

3. Discussion and results

All results presented here have been measured with a single membrane electrode assembly. Measurements are carried out at room temperature. H₂ feeding is provided by a 20% NaOH solution electrolysis and O₂ directly by ambient air. In order to bring the gas to the membrane, we use a home-made test cell in which the membrane electrode assembly is mounted. Moreover, it allows us to take electrical contacts on each side of the membrane and to evacuate gas exhausts. Before testing membranes, Nafion[®] filling pores must be acidified to conduct protons in an optimal way. Acidification is realized by immersing the membrane in a 20% sulfuric acid solution during 1 day. Membrane is then rinsed in deionized water.

It is well known that the hydration of Nafion[®] is accompanied with swelling. It seems that it could be a real problem when Nafion[®] is surrounded by narrow channels and does not have room to swell. Although porous silicon structure is rigid and cannot stretch out with Nafion[®], no damage on the pores was observed. We can very likely assume that Nafion[®] cannot swell as much as it should and as a consequence may not give performances comparable to a common Nafion[®]-117 membrane.

The test cell is electrically connected to an ammeter and a voltmeter. When the membrane electrode assembly is supplied with H₂ and O₂ from electrolysis, it becomes a fuel cell whose performances can be measured. We obtain a current density of about 101 mA/cm² in minimal charge and 796 mV for open circuit tension (Fig. 6). We achieve a power density of 20 mW/cm².

These performances are preserved as long as the assembly is supplied with H₂ and O₂. We have observed this constant behavior for a week long.

These results are not yet optimized and should be improved to obtain a lower resistance as observed with Nafion[®] membranes.

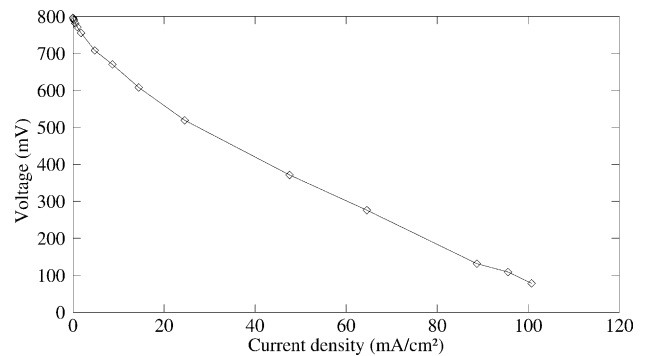


Fig. 6. *I*-*V* curve of a porous silicon membrane filled with Nafion[®].

4. Conclusion

We have demonstrated a new way of making miniaturized fuel cells using a porous silicon membrane filled with Nafion[®]-117. Its main advantage is the total compatibility with silicon micromachining which allows cell miniaturization. The silicon mineral structure of the membrane cancels the transverse conduction of water that dehydrates the organic membranes and limits the functionality of miniature fuel cells.

First tests are encouraging and allow hope for even better performances in the future.

Acknowledgements

The submitted paper is the subject of a patent pending (deposit number US 10/407069). This work is financially supported by the French Industry Agency within the framework of MicroPAC program. One of the authors (T.P.) benefits by a grant from Sagem SA. We would like to thank P. Blind of Centre de transfert des microtechniques de

Franche-Comté (C.T.M.) for the KOH wet etching, A. Mesnier for the Nafion[®] filling, L. Petrini for the anodization process and conductivity measurements and J. Scortesse for his helpful assistance.

References

- [1] X. Ren, T.E. Springer, S. Gottesfeld, Water and methanol uptakes in Nafion membranes and membrane effects on direct methanol cell performance, *J. Electrochem. Soc.* 147 (1) (2000) 92–98.
- [2] P. Dimitrova, K.A. Friedrich, U. Stimming, B. Vogt, Modified Nafion[®] based membranes for use in direct methanol fuel cells, *Solid State Ionics* 150 (2002) 115–122.
- [3] N. Caretta, V. Tricoli, F. Picchioni, Ionomeric membranes based on partially sulfonated poly(styrene): synthesis, proton conduction and methanol permeation, *J. Membr. Sci.* 166 (2000) 189–197.
- [4] D.H. Jung, S.Y. Cho, D.H. Peck, D.R. Skin, J.S. Kim, Performance evaluation of a Nafion/silicon oxide hybrid membrane for direct methanol fuel cell, *J. Power Sources* 106 (2002) 173–177.
- [5] T. Yamaguchi, M. Ibe, B.N. Nair, S. Nakao, A pore-filling electrolyte membrane-electrode integrated system for a direct methanol fuel cell application, *J. Electrochem. Soc.* 149 (11) (2002) A1448–A1453.
- [6] A. Halimaoui, in: L. Canham (Ed.), *Properties of Porous Silicon*, vol. 18, INSPEC, 1997.
- [7] V. Lehmann, *Electrochemistry of Silicon*, Wiley-VCH, 2002.