Erzincan Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
2018, (11), 1
ISSN: 1307-9085, e-ISSN: 2149-4584

Erzincan University
Journal of Science and Technology
2018, (11), 1
DOI: 10.18185/erzifbed.374936

The Production of a Silicon-Based Proton-Exchange Membrane with Different Porosity Layers

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Geliş / Received: 04/01/2018, Kabul / Accepted: 05/04/2018

Abctract
The aim of this study, which combines renewable energy and porous silicon – two prominent issues in recent years – was to make a porous proton exchange membrane for a proton exchange membrane fuel cell. To make a membrane of the desired thickness, wet etching was performed on the 4.41 cm2 rear side of a double-sided, polished, p-type silicon wafer with a thickness of 200 µm and a resistivity of 0.001 to 0.005 Ω-cm. Then the silicon wafer was cleaned using the RCA cleaning method and the grid shape on the mask was printed on the front side of the silicon using photolithography. The 3.61 cm2 front face of the silicon was placed in a double-tank electrochemical cell designed by us and was anodized at various current densities for certain periods of time to allow the formation of a porous layer throughout the sample. Finally, the pore formation was completed by passing a high current through the rear surface of the silicon to ensure that the pore tips were opened. The thickness of the porous layer formed was observed by scanning electron microscopy. Electrochemical impedance spectroscopy was performed, with the help of a fuel passage test and with formic acid, to measure the usability of the porous silicon as a membrane. Ion passage was observed as a result of the experiments performed.

Keywords: Porous silicon, Proton exchange membrane, Silicon etching, Electrochemical impedance spectroscopy, Electrolytic polishing

Farklı Gözenekli Tabakalardan Oluşan Silikon Tabanlı Proton Geçiren Membran Üretimi

Öz
Son yıllarda dikkat çeken iki konu olan, yenilenebilir enerji ve gözenekli silikonu birleştiren bu çalışma, proton ileten membran yakıt hücresi için gözenekli silikon proton ileten membran yapmayı amaçlamaktadır. Bu amaçla, öncelikle istenilen kalınlıkta membran yapabilmek için 200µm kalınlık, 0.001-0.005 Ωcm özdirencine sahip çift yüzü parlak p tipi silikon dilimin 4.41 cm2' lik arka yüzüne ıslak aşındırma yapılmıştır. Daha sonra RCA yöntemi ile silikon dilimin temizliği yapılıp silikonun ön yüze fotolitografi yardımı ile maske üzerindeki ızgara şekli basılmıştır. Bizim tarafımızdan tasarlanmış bir çift tanklı elektrokimyasal hücreye yerleştirilen silikonun 3.61 cm2' lik ön yüzüne çeşitli akım yoğunluklarında belirli sürelerde anodizasyon yapılıp gözenekli tabakanın numune boyunca oluşumu sağlanmıştır. Son olarak gözenek uçlarının açıldığından emin olmak için silikonun arka yüzeyinden yüksek akım geçirilmek suretiyle gözenek oluşumu tamamlanmıştır. Oluşturulan gözenekli tabaka kalınlığı taramalı elektron mikroskobu ile gözlemlenmiştir. Gözenekli silikonun membran olarak kullanılabilirliğinin ölçüsü olarakta methanol yardımı ile yakıt geçiş testi ve formik asit yardımı ile elektrokimyasal empedans spektroskopi yapılmıştır. Yapılan deneyler sonucunda iyon geçişi gözlemlenmiştir.

Anahtar Kelimeler: Gözenekli silikon, Proton ileten membran, Silikon aşındırma, Elektrokimyasal empedans spektroskopi, Elektrolitik parlatma

1. Introduction

As energy demand increases rapidly every day, fossil fuel reserves, which are used as a major source of energy, are also rapidly decreasing. In addition, the increase in environmental problems caused by the burning of fossil fuels has led researchers to search for alternative energy sources. Hydrogen fuel cells have recently attracted attention as one of the alternative and renewable energy sources. Fuel cells used to obtain electricity directly from hydrogen

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have numerous advantages, such as high efficiency, and clean and safe operation (Ehteshami and Chan, 2014; Sharma and Ghoshal, 2015; 2016). Fuel cells vary depending on the electrolyte used in their structure. One of them is a proton exchange membrane fuel cell (PEMFC). The membranes, one of the most important parts of the PEMFC, are divided into two groups, organic and inorganic. Organic membranes are produced from natural or synthetic polymers. The most common organic proton exchange membrane on the market is Nafion® (Gold et al., 2004). Although Nafion® has broad chemical stability and compatibility, it is not thermally stable and cannot operate at high temperatures. Inorganic membranes have disadvantages such as high cost and brittleness, although they do have the advantages of long term durability against environmental conditions and high temperatures. There are remarkable recent studies on the use of porous silicon as an inorganic membrane (Torres et al., 2009; Park et al., 2016; Wang et al., 2017). Nanoporous silicon provides proton exchange through nano-sized pores. In addition, nano-sized pores create diffusion barriers within large fuel molecules. Because of these properties, nanoporous silicon is used as a proton conducting membrane in proton exchange membrane fuel cells (Lai et al., 2015). Granitzer and Rumpf (2010) reported that the thickness of the porous silicon layer increased regularly with the increase of the etching time. However, when a certain period of time is exceeded under specified conditions, the electrolyte is consumed at the pore tips and therefore silicon dissolution has not occurred. Therefore, the thickness of the porous silicon layer is reduced while the etching continues. In the studies conducted so far, dry etching techniques have been used to control the pore size in electrochemical etching and membrane layer control. Unlike the techniques used in published literature, electrochemical and chemical etchings, as well as an electrochemical polishing technique, have been used in this study in order to control the pore size and layer thickness from the cell interior. Membrane characterization was performed using an electrochemical impedance analysis method to examine the membrane properties of the samples produced.

2. Materials and Methods

This study consisted of two parts; fabrication and characterization. To provide better pore control during fabrication, a boron doped p-type silicon wafer with a thickness of 200 μm and a resistivity of 0.001 to 0.005 Ω-cm was used. For electrochemical anodic etching, a Teflon double-tank electrochemical cell was employed using a double-tank technique (Gör and Karacalı, 2017). While AFN549 (Wet-Chemical Etching of Silicon, 2011) was used for chemical etching, hydrofluoric acid controlled anodization was used for pore formation. The solution was made up of 1 : 2 (v/ v) of HF (40%)/ETOH (99%), because this ratio has been observed to provide the most controlled and smoothest pore formation (Karacali PhD Thesis, 2003). The fabrication steps are given in Figure 1. Firstly, the silicon wafer was thinned by grinding the rear of the silicon wafer to reduce it to the desired thickness – with AFN 549 there is a 2 μm wear rate per minute for 20 minutes. Secondly, the grid mask designed using a photolithographic method was transferred onto the wafer to prevent disintegration of the sample by preventing pore formation everywhere in the silicon. In our work, while determining the layer thickness parameters depending on current density and time, we observed with the scanning electron microscope that a linear layer thickness was not formed by the linear increase of time, as stated by Granitzer and Rumpf (2010). For this reason, thirdly, the porous layer was formed by electrochemical anodization, periodically repeating this produced two different porous layers by applying a current density of 5 mA/cm2 for 80 minutes and 10 mA/cm2 for 40 minutes in a double-tank electrochemical cell designed by us (Gör and Karacalı, 2017). Finally, the electrochemical polishing was carried out for 1 hour at −10 V to ensure that the pore tips were fully opened (Properties of Porous Silicon).

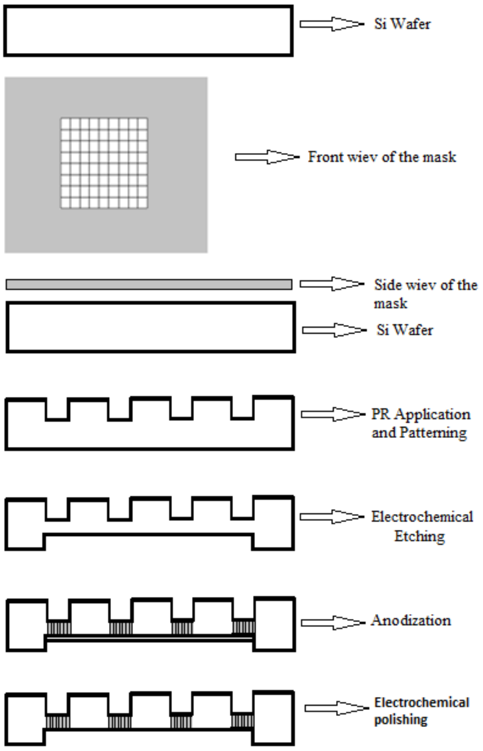


Figure 1. Stages of porous silicon membrane production

Scanning electron microscopy (SEM) images of the porous layers used for structural characterization were obtained after fabrication was completed. After fabrication parameters were determined with the aid of SEM images, electrochemical impedance spectroscopy analysis was performed to determine if the resulting porous silicon showed useful membrane properties.

3. Results

Initially the silicon wafer was treated using electrochemical anodic etching by applying four different current densities (5, 10, 20 and 30 mA/cm2) over four different time periods (40, 80, 120 and 160 minutes). As a result of the experiments, it was found that when they were produced at 20 to 30 mA/cm2 current densities with increasing periods, the samples started to disintegrate. Therefore, it was decided to use current densities of 5 and 10 mA/cm2 for 80 and 40 minutes, respectively, to form pores along the silicon wafer. The results obtained are given in Table 1.

Table 1. The effect of current density change on pore size and pore diameter (while time is constant) for a 200 µm thick, two-sided, polished, 100-point, p-type silicon wafer with a resistivity of 0.001 to 0.005 Ω-cm

Current density (mA/cm^2)	Duration (min.)	Layer Thickness (µm)	Pore Diameter (nm)	Active surface area (cm^2)
5	40	5	15	4.41
5	80	10	22	3.61
5	120	15	25	3.61
5	160	20	35	3.61
10	40	10	20	4.41
10	80	20	17	4.41
10	120	30	25	4.41
10	160	40	20	3.61
20	40	20	25	4.41
20	80	35	15	3.61

Figure 2 shows the surface SEM image of the structure.

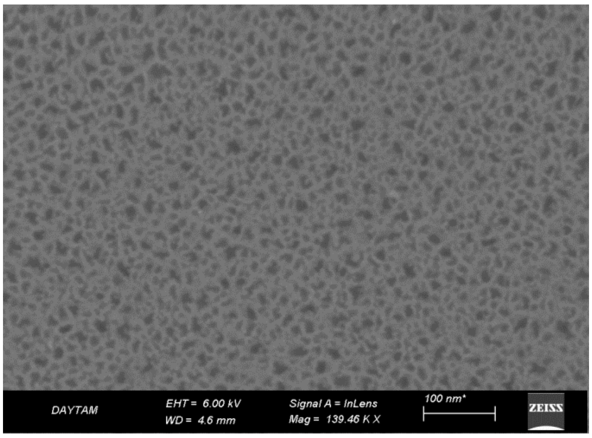


Figure 2. Top view of the porous silicon layer produced by a current density of 5 mA/cm2 for 80 minutes and by 10 mA/cm2 for 40 minutes

The cross-sectional SEM image shown in Figure 3 shows a periodic structure consisting of two different porosities with a total thickness of 160 µm: 10 µm for 5 mA/cm2 and 10 µm for 10 mA/cm2.

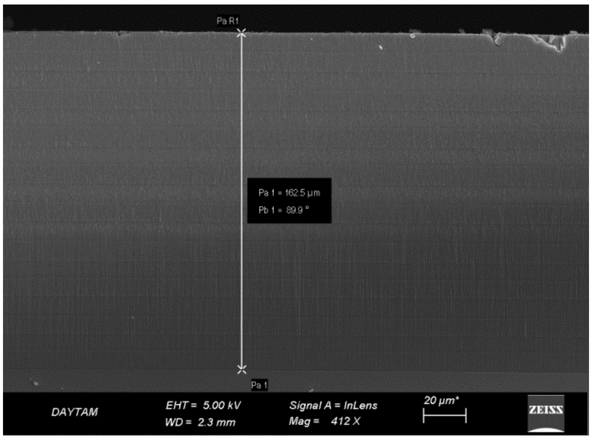


Figure 3. Cross-sectional SEM image of the porous silicon layer layered for 80 minutes at 5 mA/cm2 and 40 minutes at 10 mA/cm2.

In our study, two key performance measurements were made, namely the fuel passage and proton conductivity for the fuel cell membranes. In both tests, the anodization unit with a Teflon double-tank structure was used. In the study on fuel passage measurements conducted by Gold et al. (2004) and Rhee et al. (2003), they preferred formic acid and methanol when examining the formation of the membranes. In the same study, it was detailed that the passage of methanol was faster than the passage of formic acid. Therefore, we filled non-ionized water on one side of the double-sided tank and methanol on the other side in order to carry out the fuel passage test of the porous silicon obtained at the completion of the anodization process. The resistance was measured, using a Keithley 2400 sourcemeter controlled by LABVIEW software, by applying a constant ± 10 V for 90 seconds between the two electrodes. In the case of a positive voltage, an increase in the current was observed because of the ions coming from the methane formed by equalization and the catalytic effect of the platinum electrodes, which cause the resistance value to decrease. As a result of a negative voltage application, the concentration difference between the two compartments increases as the resultant ions move to the opposite side and the current is decreased as the resistance value increases. The results obtained are given in Figure 4. Electrochemical impedance spectroscopy was performed to determine the proton exchange across the membrane after the fuel passage measurements. For impedance spectroscopy measurements, a 1 M sulfuric acid solution was placed on the cathode side of the Teflon cell and a 5 M formic acid solution was placed on the anode side. For the membrane test, a 400 mV signal from 10 kHz to 20 kHz was applied between the two electrodes and the Nyquist Z drawing obtained from the resulting measurements from an EDC-1630 digital LCR meter, as shown in Figure 5. A semi-circular structure was observed in the Nyquist Z plot. This shape symbolizes a parallel circuit. As a result of the calculations, the difficulty of proton exchange in the circuit is represented by a resistance (R), while a double layer between the electrolyte and the membrane is represented by a capacitor. There is also a leakage capacitor or a non-ideal capacitor (Q) in the circuit. The angular frequency is ω, and n is the frequency exponential. When $0 < n < 1$, the value of n between the solid electrode and the electrolyte ranges from 0.8 to 1 (Gold et al. 2004; Hecini et al. 2015). The results obtained from the electrochemical impedance spectroscopy are given in Table 2.

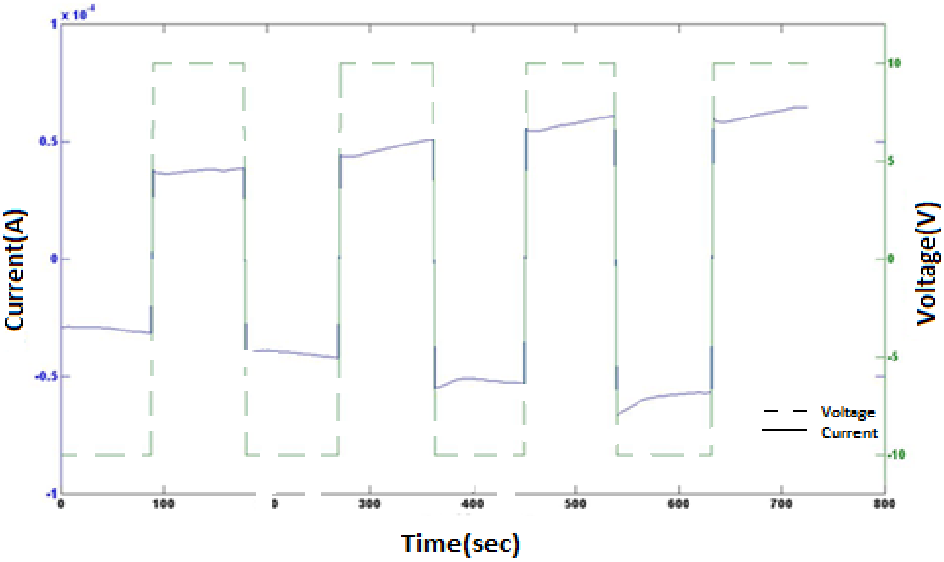


Figure 4. Time dependent change in the current for a porous silicon membrane as a result of 90 seconds of ±10 V application

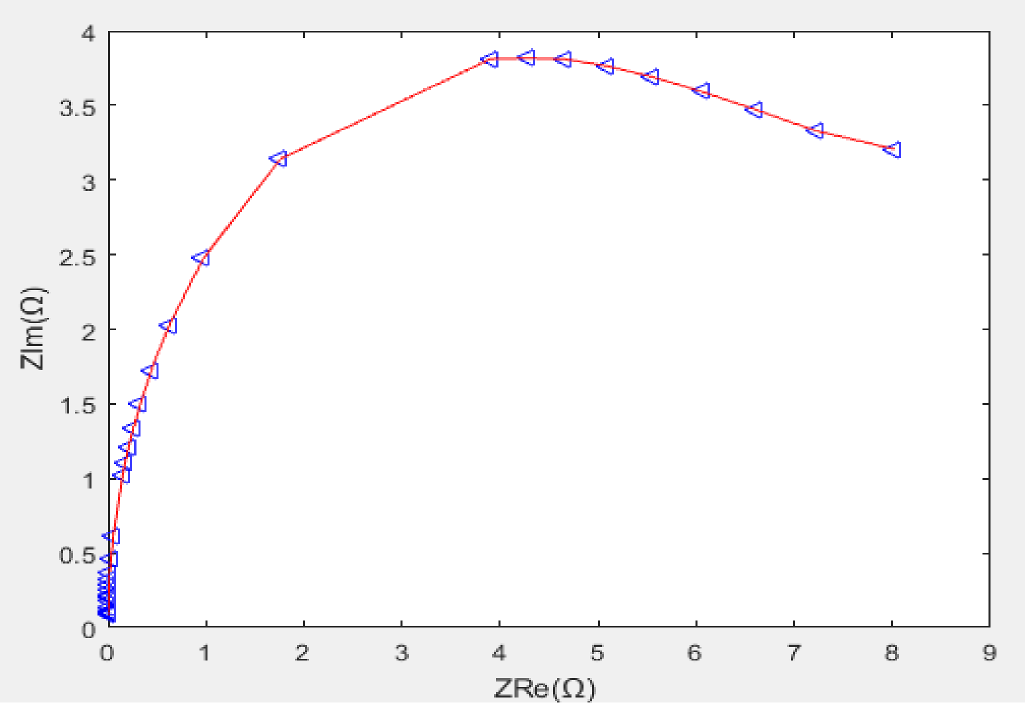


Figure 5. Nyquist Z drawing for the porous silicon membrane

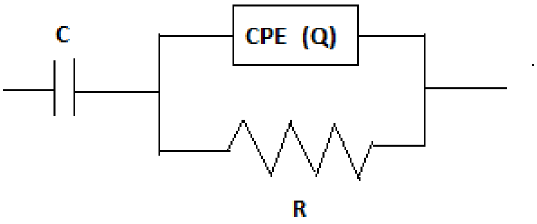
R (Ω)	C (mF)	Q (F)	n	Equivalent Circuit
10	8	0.17×10^{-4}	0.98	

Table 2. Equivalent circuit for the nanoporous silicon membrane

In the impedance spectroscopy analysis, the capacitance and resistance were measured for different frequencies with the EDC-1630 digital LCR meter. The porous silicon membrane, as known from the literature, is defined by a parallel RC equivalent circuit. For this reason, the impedance of the parallel RC circuit is calculated by the MATLAB using the values from the EDC-1630 digital LCR meter. The real values of the calculated impedances form the x-axis, while the imaginary values form the y-axis. The curve obtained was in accordance with the literature. Impedance results that provide the frequency distribution cannot be modeled by simple circuit elements. Generally, it is modeled by the capacitive phase element expressed by the CPE term (Hecini et al. 2015). The total impedance in the parallel circuit (Zoltowski 1998; Hsu and Mansfeld 2001; Hiltz and Lasia 2001; Hecini et al. 2015) is shown by the following:

If, $Z = (1/R+1/ZCPE)-1$,

then the impedance of the CPE (Zoltowski 1998; Hecini et al. 2015) is;

$ZCPE = 1/Q(i\omega)n$

4. Conclusions

From the experimental data obtained, it was observed that when the current density is increased the thickness of the porous layer increases linearly with the current density. Degradation in the pores was observed when more than 40 minutes of anodization was applied at current densities of 20 and 30 mA/cm2. Since this period is insufficient to ensure porosity throughout the sample for both these current densities, they cannot be studied. It has been seen that the most suitable current densities to form regular and controlled porosity are 5 and 10 mA/cm2. In addition, a layered anodization process is applied to form a controlled porous layer and to increase its thickness. The low operating temperature characteristic, which is a major disadvantage of PEM (proton exchange membrane) fuel batteries used as a hydrogen fuel cell – a renewable energy source requiring a continuous source of fuel – was overcome by the prepared membrane. Unlike in published literature, our study used wet etching, anodization and pore formation together as a simple, low-cost method to obtain the desired thickness for the production of silicon that is porous to protons. And unlike the published literature, the pore tips were opened with a high current density by applying a constant voltage to the electrochemical cell, which is much easier and less costly than the normal reactive ion etching (RIE) used to make sure that the pore tips are opened. A fuel passage test was performed to ensure that the pore tips were fully opened, and the results were consistent with published literature. Electrochemical impedance spectroscopy was also performed to control the expected proton exchange across the proton exchange membrane. The results from the electrochemical impedance spectroscopy proved that proton exchange occurred.

5. Acknowledgements

This study is supported by TUBITAK and Atatürk University 2016/209 BAP.

We thank DAYTAM for providing the appropriate environment for our work.

6. References

Aslan M., 2016. Membran Teknolojileri, T.C. Çevre ve Şehircilik Bakanlığı.

Bisi, O., Ossicini, S., & Pavesi, L., 2000. Porous silicon: a quantum sponge structure for silicon based optoelectronics. Surface science reports, 38(1), 1-126.

Burham N., Hamzah A. A., Majlis B. Y. 2014. Mechanical characteristics of porous silicon membrane for filtration in artificial kidney. IEEE-ICSE2014. Kuala Lumpur, Malaysia.

Canham L. T., 1990. Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers, Appl. Phys. Lett. 57, 1046.

Canham L. T., 2014. Handbook of Porous Silicone.

Ehteshami, S., M., M., & Chan, S., H., 2014. The role of hydrogen and fuel cells to store renewable energy in the future energy network–potentials and challenges. Energy Policy, 73, 103-109.

Granitzer, P., & Rumpf, K. 2010. Porous silicon—a versatile host material. Materials, 3(2), 943-998.

Gold, S., Chu, K., Lu, C., Shannon, M.A., Masel, R., I., 2004. Acid loaded porous silicon as a proton exchange membrane for micro-fuel cells. Journal of Power Sources 135, 198–203. USA.

Gör, M., ve Karacalı, T., 2017. Porous Silicon Based Membrane Fabrication for Proton Transportation. 13. Nanobilim & Nanoteknoloji konferansı.

Hecini, M., Khelifa, A., Palahouane, B., Aoudj, S., & Hamitouche, H. 2015. A new advance in the study of p-type silicon/electrolyte interface by electrochemical impedance spectroscopy. Research on Chemical Intermediates, 41(1), 327-341.

Karacali T., 2003. Darbeli anodizasyon tekniği ile gözenekli ve Si tabanlı fabry-perot yapılarının üretimi: Yapısal ve optik özelliklerinin incelenmesi. Doktora Tezi, Atatürk Üniversitesi. Fen Bilimleri Enstitüsü, Erzurum.

Lai C., Xiang Z., Liu C., Zhu C., Wang H., Zhu H., 2015. Study on corrosion of macroporous silicon in sodium hydroxide solution by electrochemical methods and scanning electron microscopy, International Journal of Corrosion.

Lim, B. H., Majlan, E. H., Daud, W. R. W., Husaini, T., & Rosli, M. I. 2016. Effects of flow field design on water management and reactant distribution in PEMFC: a review. Ionics, 22(3), 301-316.Nayak, A. P., Islam, M. S., & Logeeswaran, V. J. 2012. Wet Etching. Encyclopedia of Nanotechnology, 2829-2830.

Park, J.; Yanagida, Y.; Hatsuzawa, T., 2016. Fabrication of p-type porous silicon using double tank electrochemical cell with halogen and LED light sources, Sens. Actuators B Chem., 233, 136–143.

Pichonat, T., Gauthier-Manuel, B., 2006. Realization of porous silicon based miniature fuel cells. Journal of power sources 154, 198-201.

Sharma, S., & Ghoshal, S. K. 2015. Hydrogen the future transportation fuel: from production to applications. Renewable and sustainable energy reviews, 43, 1151-1158.

Torres, N., Duch, M., Santander, J., Sabaté, N., Esquivel, J. P., Tarancón, A., & Cané, C. 2009. Porous silicon membrane for micro fuel cell applications. Journal of New Materials for Electrochemical Systems, 12(2–3), 93-96.

Uhlir A., 1956. Electrolytic shaping of germanium and silicon, Bell Syst. Tech. J. 35,333.

Wang, M., Liu, L., & Wang, X. 2017. A novel proton exchange membrane based on sulfo functionalized porous silicon for monolithic integrated micro direct methanol fuel cells. Sensors and Actuators B: Chemical, 253, 621-629.

Westra K., 2010. KOH and TMAH etching of bulk silicon recipes, tricks, what is possible and what is impossible.

Xiang Z., Liu C., Lai C., 2014. Corrosion of Fresh Porous Silicon in Potassium Hydroxide Solution Int. J. Electrıchem Sci., 3935-3948.

Zoltowski P., 1998. On the electrical capacitance of interfaces exhibiting constant phase element behaviour. Journal of Electroanalytical Chemistry, 443(1), 149-154.

URL1:www.microchemicals.eu/technical_information, “Wet-Chemical Etching of Silicon” 2011-01-17.