Applied Thermal Engineering 72 (2014) 298–303

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Effects of nano/microstructures on performance of Si-based microfuel cells

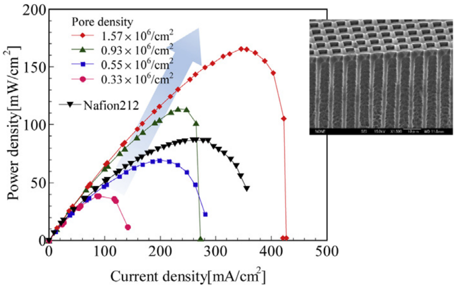
Gyoko Nagayama [a], *, Akihiro Kuromaru [b], Masashi Kaneda [b], Takaharu Tsuruta [a]

[a] *Department of Mechanical Engineering, Kyushu Institute of Technology, Sensui 1-1, Tobata, Kitakyushu, Fukuoka 804-8550, Japan*
[b] *Graduate School of Engineering, Kyushu Institute of Technology, Sensui 1-1, Tobata, Kitakyushu, Fukuoka 804-8550, Japan*

HIGHLIGHTS

- The contact surface structure of porous Si-based MEAs on the cell performance is investigated.
- The porous Si-based MEA show a power density higher than that of the Nafion®-212.
- Densely arranged nano/microstructures reduce the activation and ohmic overvoltages.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 November 2013
Received in revised form
27 April 2014
Accepted 3 July 2014
Available online 17 July 2014

Keywords:
Porous Si
Nano/microstructure
Anodic etching
Membrane electrode assembly
Microfuel cell

ABSTRACT

We investigated the effects of the contact surface structure of porous Si-based membrane electrode assemblies (MEAs) on the performance of microfuel cells, because the contact area of the triple-phase boundary among the MEA components plays an important role in the performance of polymer electrolyte fuel cells (PEFCs). An n-type silicon substrate was first wet-etched with KOH and subsequently anodically etched to fabricate a porous Si substrate. The cross section of the mechanically polished Si wafer showed pores with high aspect ratios. Electrolyte solutions were filled into the pores to prepare a porous Si membrane (PSM), and the MEA was fabricated by hot-pressing the PSM between two conventional catalyst-coated carbon-paper electrodes. The porous Si-based MEA worked well and showed a power density higher than that of the Nafion®-212-based membrane. Further, we examined the effects of the nano/microstructures at the triple-phase boundary and found that the more densely arranged nano/microstructures reduced the magnitudes of the activation overvoltage and ohmic overvoltage, thereby improving the cell performance.

1. Introduction

The increasing demand for portable power supply systems for portable electronic devices such as smart phones, laptop computers, global satellite positioning (GPS) devices, etc. is driving demand for alternative rechargeable power sources. The use of micromachining, miniaturized electrodes, gas diffusion layers, and membranes integrated on Si wafers has recently attracted much attention as a possible method of fabricating Si-based microfuel cells [1–11]. Polymer electrolyte fuel cells (PEFCs) are portable and show high energy efficiency, low emission, and low noise. However, the commercialization of PEFCs has achieved limited success so far because of their high cost and other technical barriers such as low performance, particularly for microfuel cells [8,11].

---

* Corresponding author. Tel./fax: +81 93 884 3139.
E-mail address: nagayama@mech.kyutech.ac.jp (G. Nagayama).

http://dx.doi.org/10.1016/j.applthermaleng.2014.07.006

Nomenclature

a	square orifice of micropores [μm]
b	pitch separating micropores [μm]
h	depth of micropores before anodic etching [μm]
I	current density [mA/cm^2]
$P_{\max}$	maximum power density [mW/cm^2]
s	microstructure size (=$a + b$) [μm]
Greek symbols	
β	Tafel slope [mV/decade]
Φ	surface solid fraction of porous Si-based MEA [−]
η_{act}	activation overvoltage [V]
η_{ir}	ohmic overvoltage [V]

Most microfuel cells developed to date have had active areas in the range of 0.1–2 cm^2 and maximum power densities up to 700 mW/cm^2. Active direct methanol microfuel cells (DMFCs) show power densities approximately one order of magnitude lower than those of hydrogen-fueled micro-PEFCs. Reducing the magnitude of the activation overvoltage is crucial for improving the performance of PEFCs operated at room temperature. Although increasing the amount of catalyst and adjusting the cell operation pressure, reactant concentration, flow rate, etc. are actually effective methods of decreasing activation loss, they also increase production cost, and the latter approach especially render cells non-portable. Thus, alternative fuel cell components should be developed to overcome these problems.

The real surface area of the nominal contact area of the membrane electrode assembly (MEA) components should be increased in order to improve cell performance. We previously found that a porous Si-based MEA worked well and that higher cell performances and lower cell resistances could be achieved by using thinner Si substrates [12]. Increasing the membrane thickness lowers proton conductivity, while increasing the thickness increases the fuel crossover; *i.e.*, the reactant leaks from the anode to the cathode. However, the Si substrate is quite fragile, making it difficult to tightly compress fuel cells in order to achieve good seals and lower the contact resistance. Thus, it is difficult to decrease the thickness of the porous Si substrate below 100 μm. On the other hand, nano/microstructures of the porous Si have been shown to decrease the magnitude of the activation overvoltage, because the contact area of the MEA components can be extended in the vicinity of the triple-phase boundary. Hence, the effects of MEA nano/microstructures on cell performance should be clarified.

Therefore, we used Si microfabrication techniques to develop a porous Si-based hierarchical nano/microstructured MEA for a hydrogen-fueled microfuel cell, in order to clarify the effects of the nano/microstructures at the contact surfaces of the porous Si-based MEA on the cell performance.

2. Fabrication of porous SI-based MEA

The porous Si-based MEA is composed of one n-type Si substrate sandwiched between two catalyst-loaded carbon-paper electrodes. The n-type Si substrate was a 350-μm-thick double side polished wafer oriented in the <100> direction, and its resistivity was 21.7 Ω cm. The Si substrate was fabricated using conventional microelectromechanical systems (MEMS) fabrication technology and photo-assisted electrochemical (anodic) etching [13]. Fig. 1 shows the flow of the fabrication process, and the details are as follows.

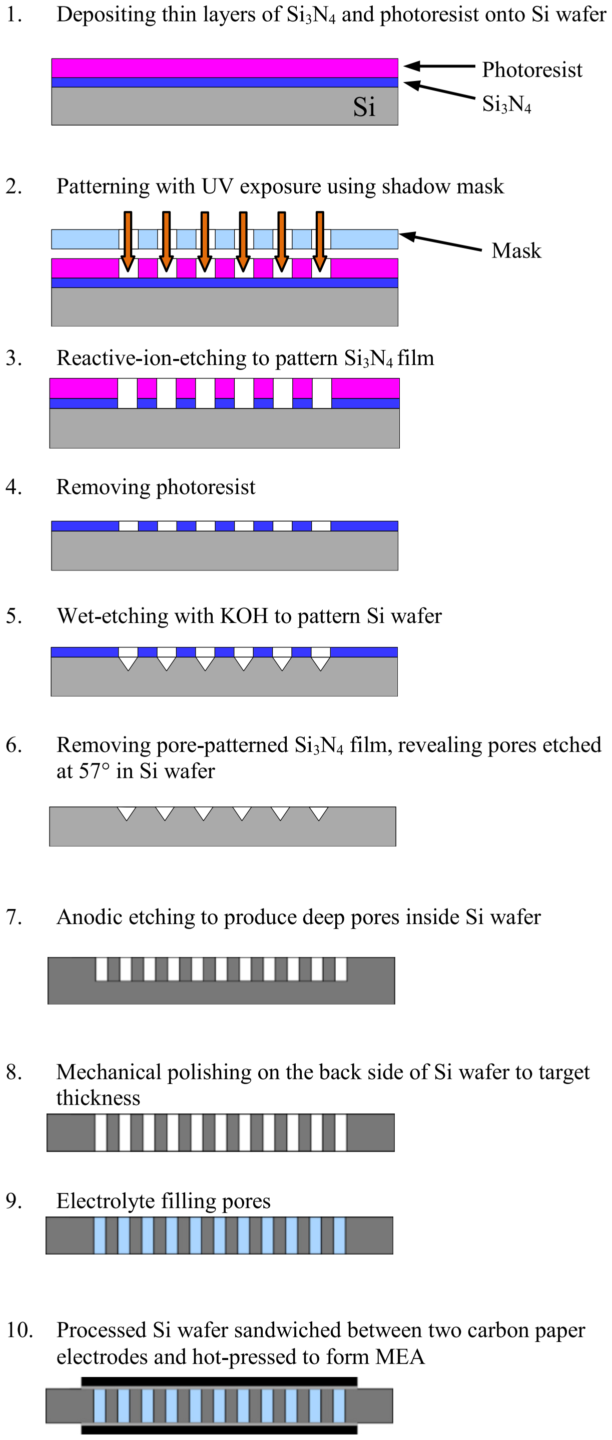


Fig. 1. Schematic illustrating flow of MEA fabrication.

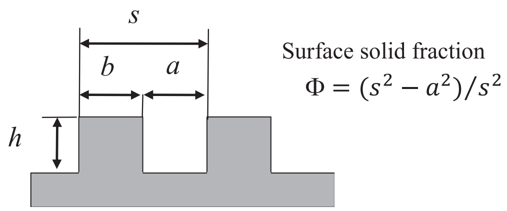


Fig. 2. Microstructure sizes.