

Nanoporous Silicon-Based Direct Hydrochloric Acid Fuel Cells

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Abstract: Fabrication and characterization of Au/Porous silicon/Silicon (Au/PS/Si)-type direct hydrochloric acid fuel cells have been presented in this work. The Au/PS/Si cells were prepared by first creating the nanoporous silicon layer in single-crystalline Si using the anodic etching under illumination and deposition Au catalyst layer onto the porous silicon. The porous silicon filled with hydrochloric acid was developed as a proton conducting membrane. Using HCl:H₂O (1.7 M) solution as fuel the open circuit voltage of 0.65 V was obtained and maximum power density of 3.5 mW/cm² at room temperature was achieved. It is shown that the Au/PS/Si-type direct hydrochloric acid fuel cell with gold catalyst operating at room temperature can be considered as the most promising type of low cost fuel cell for small power-supply units.

Keywords: Porous silicon membrane, HCl electrolyte, gold catalyst, power density, open circuit voltage.

1. INTRODUCTION

Nowadays, the demand for clean and renewable energy sources for the rapidly growing portable electronics market (mobile electronic devices, telecommunication, military equipment, etc.) attracts the attention of many research centers. The direct methanol fuel cell (DMFC) based on proton exchange membrane (PEM) with organic polymer membrane (Nafion®), as proton conductor, which uses liquid methanol is considered as the promising type of fuel cell for small power-supply units [1]. The fabrication of most portable electronic devices is based on standard micro-fabrication technique, but PEM type fuel cells with polymer membrane are not readily integrated with this technique. Taking the above into consideration, it would be desirable to develop a solid state proton conducting membrane and fuel cell technology compatible with standard micro-fabrication techniques. The crystalline structure of porous silicon presents a network of silicon in nano (micro)-sized regions with an extremely large surface-to-volume ratio (up to 800 m²/cm³). The structure of porous silicon is like a sponge or columnar where quantum confinement effects play fundamental role. The pore surfaces are covered by silicon hydrides (Si-H) and silicon oxides (Si-O). Existence of pores, especially the canal-form pores, which determine large ion (proton) conductivity along the pores opens new perspectives for using porous silicon-based structures as hydrogen fuel cells [2].

Chiefly, previous works on fuel cells using the porous silicon have been focused on direct methanol

fuel cell. Traditionally, platinum group metals (Pt, Pt-Ru, Pt-Ir alloy, RuO₂ and Pd) have been employed as the most effective catalysts within most types of low temperature fuel cells including those with polymer electrolytes [3, 4]. The membranes in these fuel cells become highly acidic during operation, demanding the use of corrosion resistant construction materials and platinum group metal catalysts.

Present study demonstrated that the direct fuel cell with nanoporous silicon layer as proton conducting membrane, aqueous hydrochloric acid as fuel and gold catalyst film (Hydrochloric Acid Fuel Cell-HCAFC) is interesting for micro power generation. HCAFC have suggested as an alternative to DMFC. In HCl fuel cell, oxygen is substituted by chlorine as the oxidizing agent. Hence the product from this fuel cell is not water, but hydrogen chloride. The use hydrochloric acid fuel cells in industries where chlorine is produced as a by-product, e.g. in magnesium and sodium electrolysis, can also be beneficial. Only a few papers on hydrogen-chlorine fuel cells with Nafion membrane are available together with a handful of registered patents [5-7]. Data on properties of Au/Porous silicon-based fuel cells with sodium borohydride and hydrogen sulphide solutions as fuel were early published [8, 9].

2. Experimental

Porous silicon layers with thickness of 10-20 μm and average porosity from 40 to 80% were prepared on n-type (111) Si substrates ($\rho = 1 \times 10^{-4} \Omega \cdot \text{m}$) by anodic etching in a HF: H₂O solution under the white light illumination [10]. For some measurements the PS films were then detached from Si substrate by electro-polishing. The free-standing PS films were characterized by porosity, thickness and resistivity

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measurements. The average porosity, i.e. the void fraction in the porous layer was measured by gravimetry technique [2].

$$P(\%) = (m_1 - m_2)/(m_1 - m_3) \quad (1)$$

Here m_1 is Si sample mass before the anodization etching, m_2 just after etching and m_3 after the removal of the porous layer by electro-polishing or after a rapid dissolution of the whole porous layer in a 3% KOH solution. The resistivity and charge carrier concentration measurements were carried out on the free-standing PS layers attached to dielectric substrate (glass) by using Van der Pauw technique. The *In* or *In-Ga* alloy was used as ohmic contact to PS layer. Morphological characterizations of the porous silicon surface were performed by scanning electron microscopy (SEM; JSM-5410LV).

The Au/Porous Silicon/Silicon (Au/PS/Si) structures were fabricated by evaporation of a thin Au film onto the PS surface at room temperature by using the electron-beam technique. The thickness of the deposited Au film was of 150 nm as obtained by the measurements during evaporation with the aid of a deposition controller (Inficon, Leybold). After anodization the porous silicon membrane on silicon substrate was immersed in a HCl solution and was exposed to electro-treatment under *dc* current density (of 40 mA/cm² for 20 min) to partially oxidize the pore surfaces. The current-voltage (*I-V*) characteristics, open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) of the Au/PS/Si cells and PS/Si structures were measured at room ambient (300 K, 40% RH) as well as in HCl electrolyte (300K) in measuring cell. The electrolyte with various concentrations of HCl in water (1.1 – 6.0 M) was made from 37% HCl.

The hydrochloric acid-stimulated generation of the open-circuit voltage (V_{oc}) between the contacts to Au film and PS layer (or Si substrate) was measured directly by a "Thurlby-1503" digital multimeter. The relative humidity (RH) of air was measured with an "Extech-44470" hygro-thermometer. The photosensitive properties of the Au/PS/Si structures were analyzed by measuring of current-voltage characteristics in the dark, daylight and under the tungsten-halogen lamp illumination (about 1.50 kW.m⁻²). All the investigated structures exhibited very weak photosensitivity. The value of the open-circuit photo-voltage in daylight and under tungsten-halogen lamp illumination was of 1-3 mV. Therefore, HCl-stimulated measurements were performed under daylight illumination.

3. RESULTS AND DISCUSSION

SEM micrographs of the porous silicon and Au/porous silicon surfaces are shown in Figure 1. Here bright islands and relatively dark regions are the top of silicon walls and intervals containing no of porous silicon, respectively. In these experiments we used porous silicon layers with porosity of 65%.

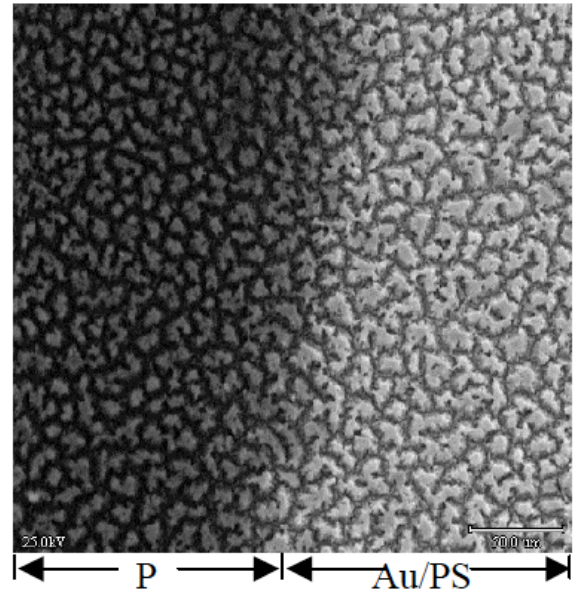


Figure 1: SEM micrograph of porous silicon surface.

The electrical measurements on the free-standing PS layers with 65% porosity ended up with $\rho = 1.8 \times 10^4$ $\Omega \cdot m$ for resistivity, $p = 9.6 \times 10^{18}$ m⁻³ for hole concentration, and $\mu = 3.6 \times 10^{-5}$ m²/(V.s) for hole mobility.

Current-voltage characteristics of Au/PS/Si cell as a function of HCl electrolyte concentration for a hydrochloric acid fuel were presented in Figure 2. Open circuit voltage and short circuit current density as a function of HCl concentration are shown in Figures 3 and 4 respectively. It is seen that the open circuit voltage decreases (from 650 to 180 mV) where as the short circuit current density increases (from 10 to 25 mA/cm²) with increasing HCl electrolyte concentration. The non-linear variation for open circuit voltage and short circuit current density with HCl concentration can be caused with change of proton concentration penetrating from electrolyte across gold catalyst into porous silicon membrane. It is be noted that the successive placing in and removal of Au/PS/Si cell from HCl electrolyte is accompanied by the response and recovery of the open circuit voltage with response time of 20-40 s. The control instrumentations showed that for PS/Si structures without Au layer in HCl

electrolyte formation of V_{oc} and J_{sc} of remarkable value were not observed.

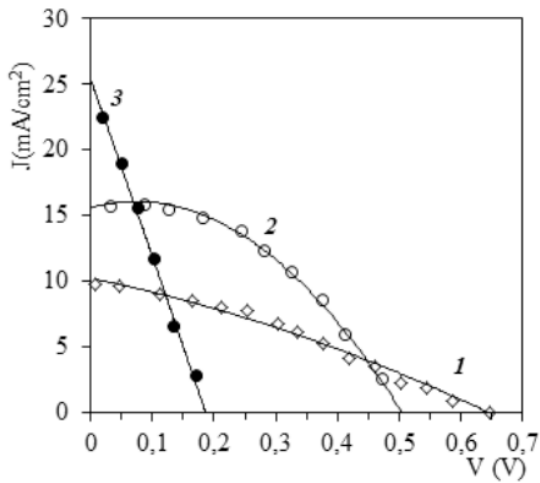


Figure 2: Current-voltage characteristics of Au/PS/Si cell in different HCl+H₂O solution: (1) 1.1 M, (2) 1.7 M, (3) 6M.

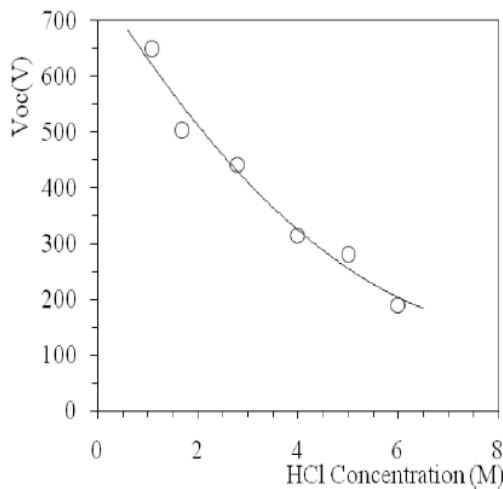


Figure 3: The open circuit voltage of Au/PS/Si cell versus HCl concentration.

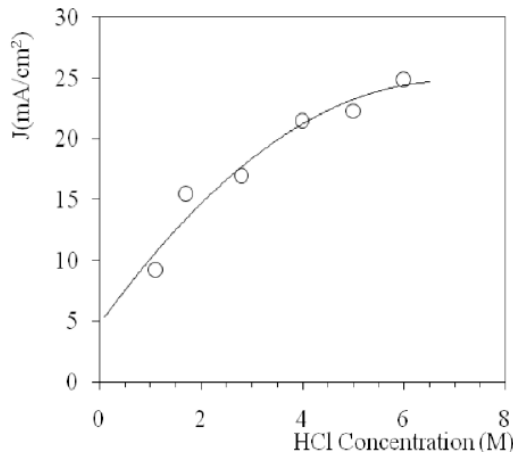


Figure 4: The short circuit current density of Au/PS/Si cell versus HCl concentration.

Figure 5 shows the power output-current density curves of Au/PS/Si cells depending on HCl concentration. Results were gained at room temperature with 1.1 M, 1.7 M and 6 M hydrochloric acid concentration. From the polarization curves we found that maximum of the power density of the single direct hydrochloric acid fuel cell reaches 3.5 mW/cm² for HCl electrolyte of 1.7 M.

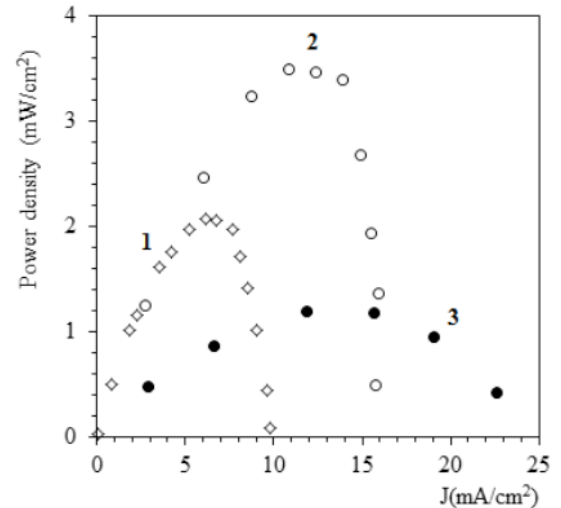


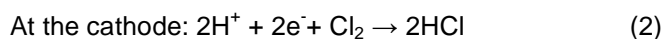
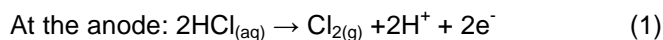
Figure 5: The power density-current density characteristics of Au/PS/Si cell with HCl+H₂O electrolyte of 1.1 M, (2) 1.7 M and (3) 6 M.

As a whole, the following experimental facts related with the change of the electrical characteristics of Au/PS/Si fuel cells with hydrochloric electrolyte were solidly established:

- (1) Formation of the open-circuit voltage (up to 650 mV) under exposition by HCl solution was observed for Au/PS/Si structures. At the same time, in the PS/Si structures (without Au film) placed in HCl electrolyte the electricity generation was not observed.
- (2) The values of the open-circuit voltage and maximum of power density depend on the concentration of HCl electrolyte.
- (3) This phenomenon (formation of electricity) is reversible, i.e. for Au/PS/Si cells, placing in and removal from the HCl solution is accompanied by the response and recovery of V_{oc} respectively.
- (4) These results allow supposing that the Au/PS/Si structures can be used as direct miniature hydrochloric acid fuel cells.

The mechanism of the generation of the electricity in the metal/PS/Si cells under hydrogen-containing

ambient has already been proposed [10]. We suggest that in Au/PS/Si cell, similar to direct ethanol fuel cell [11], the Au film and PS layer filled with hydrochloric acid play the role of the catalytic anode and electrolyte respectively. The interface region between the porous and crystalline silicon (PS/Si), which is very imperfect and stressed, plays the role of the cathode. In the case of Au/PS/Si direct hydrochloric acid fuel cell, when HCl-based fuel is supplied at the Au anode the following reactions take place [12]



The overall reaction can be expressed as



Electrons and protons formed in the Au catalyst film after hydrogen splitting ($\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$), pass through the external circuit and PS layer, respectively and reach the cathode (PS/Si interface) region. Here the hydrogen and electron is recombined producing hydrogen molecule and then hydrogen reacts with chlorine to produce HCl molecules. Stability of operation for Au/PS/Si cells as a function of storage time in the presence of the hydrochloric acid (1.1 M) was observed for about 140 h. More long-time tests of operation stability of the direct hydrochloric acid fuel cells are currently under investigation.

CONCLUSIONS

In this study, fabrication and characterization of Au/PS/Si type direct hydrochloric acid fuel cell has been presented. The performance of the fuel cell was measured at room temperature by supplying hydrochloric acid electrolyte. The test results confirm that the cell generated the open-circuit voltage of 650 mV and maximum power density of 3.5 mW/cm² using HCl solution (1.7 M) as fuel. These results demonstrate the feasibility of development of low-cost small Au/PS-based fuel cells for portable electronic and medical applications

ACKNOWLEDGEMENT

This work was supported by STCU Grant no: 1585

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