

# OPTIMAL-CATALYZED POROUS SILICON ELECTRODES FOR SELF-BREATHING MEMS FUEL CELLS

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**Abstract:** Pt nano-particles are deposited on porous silicon surface by electrochemical deposition method to form porous silicon electrodes, which are integrated on the cathode flow-field plate to replace traditional carbon paper for enhancing diffusion-layer capability. The test results show that the peak current increases with increasing the electro-deposited Pt and the peak current reaches its maximum when the loaded Pt gets 0.38mg/cm<sup>2</sup>. Attributed to the high electro-catalytic activity of the porous-silicon electrode, the utilization of Pt is significantly higher than that of the carbon-paper electrode where Pt/C is brushed for loading. The performance of the fuel cell with 350nm porous silicon electrode is much better than that of the cell with 5μm porous silicon.

**Keywords:** Porous silicon electrode, electro-deposition, miniature fuel cell, silicon-based micromachining

## INTRODUCTION

Based on MEMS technology, μPEMFCs (micro proton-exchange-membrane fuel-cells) have been developed rapidly in recent years [1-9]. Conventional μPEMFCs used carbon-paper as electrodes, on which catalyst was manually sprayed [2-4]. The complicated manual operation does not facilitate the integration of PEMFC with MEMS devices, thereby, resulting in high fabrication cost and non-uniformity in performance. Besides, the thick (200~300μm) and big-sized pores (20nm~50μm) in the carbon-paper cause low efficiency in material transfer [10] and, thus, does not facilitate miniaturization of the fuel cells.

Instead of carbon-paper, much thinner porous-silicon diffusion-layer is a good candidate to effectively reduce the diffusion-layer thickness and shorten the diffusion path, thereby, speeding up the transfer of fuel to the catalyst surface. In this way the material transfer is changed from diffusion into liquidity, thereby, reducing the diffusion resistance. Moreover, the porous-silicon process is integratable with the silicon-based flow-field plate that facilitates volume production. Hence, using porous silicon instead of carbon-paper is one of the effective ways for integration of key components and miniaturization of the fuel cells.

## EXPERIMENTS

### Fabrication of porous silicon

Porous-silicon structure is fabricated by using n-type (100) silicon as anode (where the resistivity is 0.04~0.15Ω·cm), Pt as cathode and ethanol+40%HF as aqueous etchant for anodic-oxidization. The formed

porous silicon is with the cross section cut along the longitudinal direction of the pore shown in Fig. 1(a). The porous-silicon structures with various pore-size and depth can be prepared by adjusting the oxidization current and time. Ethanol is herein used for rinsing the porous silicon so as to reduce the residual stress in the pores. Finally, the porous silicon is dried naturally in air.

### Preparation process and characterization of catalytic electrodes

Deposition of Pt nanoparticles on the surface of porous silicon is processes as follows. After sputtering Ti/Au (100nm/100nm) conductive layer, the porous silicon sample is immersed into 5mmol/L H<sub>2</sub>PtCl<sub>6</sub>+0.1mol/L H<sub>2</sub>SO<sub>4</sub> electrolyte for cyclic-voltammetry electro-depositing Pt nanoparticles on the surface, with the resultant SEM-image shown in Fig. 1(b). The deposition amount of Pt can be controlled by accounting the number of the cycles, with the amount measured by an inductively coupled plasma atomic emission spectroscopy system.

Loading Pt/C catalyst on carbon-paper surface is implemented by following steps. Appropriate amount of 60% (wt%) Pt/C catalyst, PTFE (polytetrafluoroethylene, 50%) and Nafion solution (5%) are uniformly dispersed in isopropanol/water solution. Then the ink is brushed on the carbon-paper and dried to constant weight in a vacuum oven (120°C). The Pt loading amount is 0.4mg·cm<sup>-2</sup>.

The catalytic electrodes performance is tested by cyclic voltammetry method in 0.5mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. The electrode under test, the Pt electrode and the saturated calomel electrode are used as working electrode,

auxiliary electrode and reference electrode, respectively. Before testing, nitrogen is introduced for 30min to remove the oxygen in the solution. All the experimental procedure is carried out at room temperature and protected with nitrogen gas.

### Fabrication of the anode/cathode plates

Fig. 2 schematically shows the silicon micromachining processes, where (a) is the process for anode fluid-plate structure and (b) is that for cathode. The flow-field patterns of the anode are an array of serpentine pit-matrix plus two square holes as fuel inlet and outlet. The pit-matrix area is  $293\mu\text{m}\times 293\mu\text{m}$  at top and  $300\mu\text{m}$  in depth. The through hole for hydrogen entering is  $1.5\text{mm}\times 1.5\text{mm}$  in area and that for hydrogen out is  $0.5\text{mm}\times 0.5\text{mm}$ , respectively. The front-side of the cathode is porous silicon diffusion layer, with the average pore-size as  $350\text{nm}$  (see Fig. 3). The through holes at the backside of the cathode are with the cross-sectional area as  $300\mu\text{m}\times 300\mu\text{m}$  for air in/out. The dimension of the flow field plate is  $1.6\text{cm}\times 1.8\text{cm}$ , where the central active area is about  $1.2\text{cm}\times 1.2\text{cm}$ .

### Performance test of fuel cell

Fig. 4 shows the cross-sectional configuration and the photograph of the formed MEMS fuel-cell with porous-silicon cathode. The performance is evaluated by using an Arbin FCTs fuel cell instrument (Arbin Instrument Co.). Before testing, the cell is allowed to activate for at least 15min under the current density of  $20\text{mA}\cdot\text{cm}^{-2}$ . The cell is operated at  $20\pm 3^\circ\text{C}$  and  $50\pm 3\%$  relative humidity. High-purity hydrogen is used as the fuel source, which is without any humidification under atmospheric pressure. The flow rate of the hydrogen is regulated at  $20\text{ml}\cdot\text{min}^{-1}$ .

## RESULTS AND DISCUSSION

The SEM in Fig. 1b shows the  $350\text{nm}$ -sized porous silicon that is deposited with  $0.32\text{mg}/\text{cm}^2$  Pt nanoparticles. Being observed clearly, the Pt particles

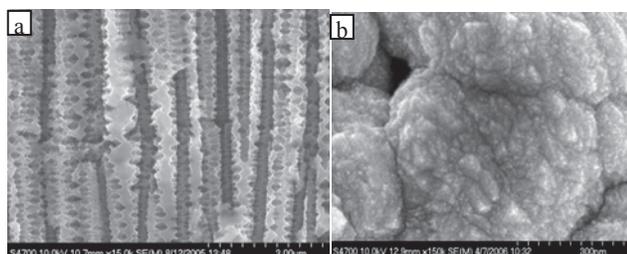


Fig. 1: SEMs of raw porous silicon (a) and that deposited with  $0.32\text{mg}/\text{cm}^2$  Pt nanoparticles (b).

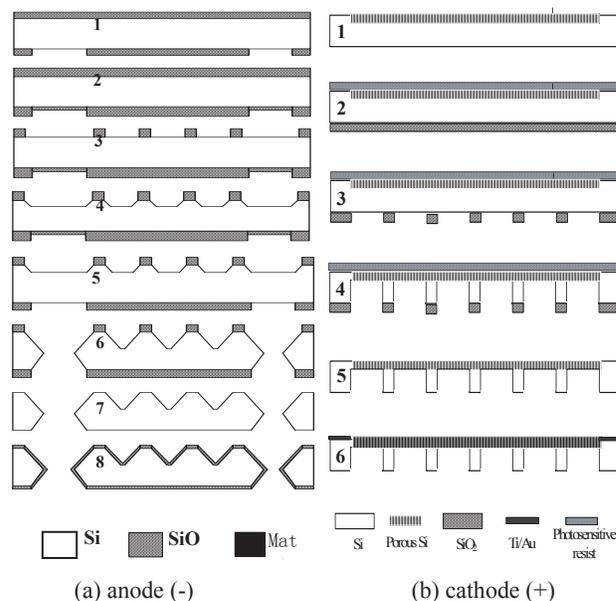


Fig. 2: Fabrication process of silicon fluid-plate at anode (a) and cathode (b).

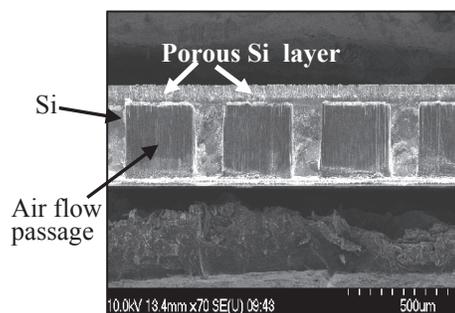


Fig. 3: Close-up cross-section of the cathode.

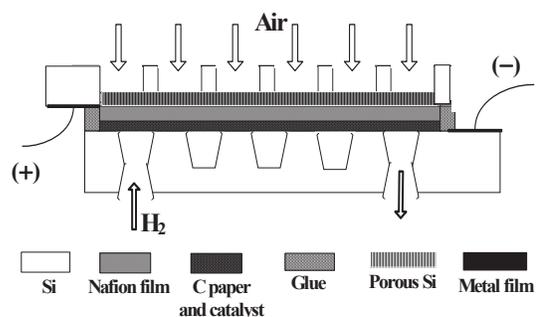


Fig. 4: Cross section and photograph of  $\mu\text{PEMFC}$ .

are uniformly dispersed on the porous silicon surface, with the particle size of around 7nm. Fig. 5 shows the tested cyclic voltammetry results for the porous-silicon electrode, with the loaded Pt from 0.06mg/cm<sup>2</sup> to 0.41mg/cm<sup>2</sup>. The peak current increases with increasing the electrodeposited Pt and reaches its maximum when the loaded Pt gets 0.38mg/cm<sup>2</sup>. With the Pt amount further increasing, the peak current turns to slightly decrease, which is probably due to the aggregation of the over loaded Pt particles.

Compared in Fig. 6, where similar amount of Pt is loaded for both the porous-silicon and the carbon-paper electrodes, the hydrogen absorption-desorption peak area of the porous-silicon electrode is significantly higher than that of the carbon-paper electrode (where Pt/C is brushed for loading). It indicates that the utilization efficiency of the thin-layer catalyst obtained by the electro-deposition method is much higher, thereby, significantly improving the catalytic efficiency and reducing the amount of the scarce Pt resource.

In Figs. 7-8, the battery performance is tested and compared for the two fuel-cells with 350nm-sized and 5μm-sized porous-silicon cathodes. Obviously the 350nm-sized porous-silicon is the optimal design, with 37mA/cm<sup>2</sup> maximum discharge-current-density, 7.5mW/cm<sup>2</sup> peak power-density and 7200s constant current discharge (at 5mA/cm<sup>2</sup>) to drop the output-voltage from 0.8V to 0.2V. The comparing results is explained as follows. The smaller the pore size of porous silicon, the greater the specific surface and the more effective usage of catalyst at the same Pt loading of two porous-silicon electrodes.

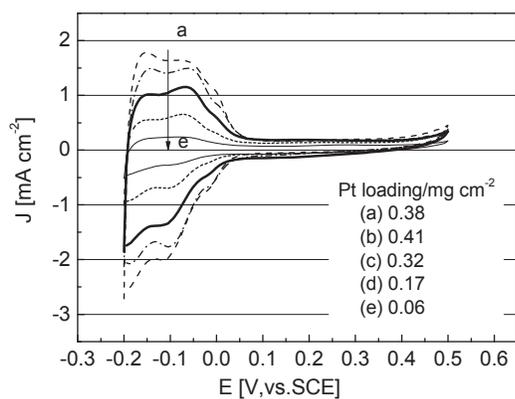


Fig. 5: C-V characterizations of porous-Si electrodes modified with various Pt nanoparticles.

## CONCLUSION

The paper reports silicon-based self-breathing μPEM fuel-cells, where the cathode is constructed

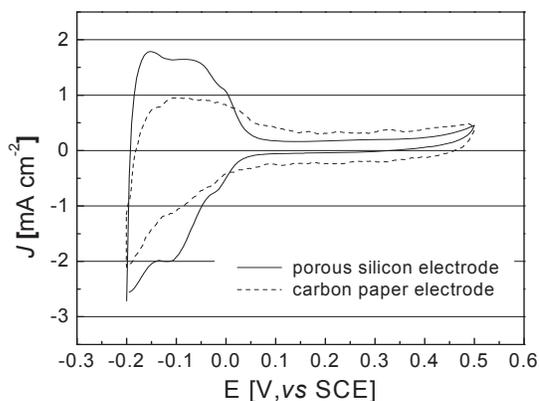


Fig. 6: Comparison in CV characterization between the porous-Si electrode modified with Pt nanoparticles (0.38mg/cm<sup>2</sup>) and the carbon paper with Pt/C catalyst (0.40mg/cm<sup>2</sup>).

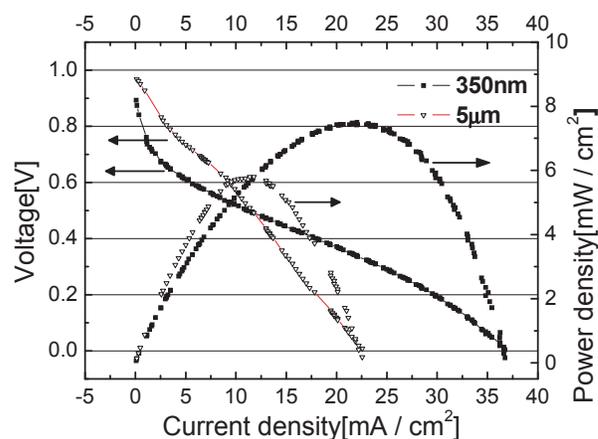


Fig. 7: Performance comparison between two porous-silicon PEMFCs with the pore size as 5μm and 350nm, respectively.

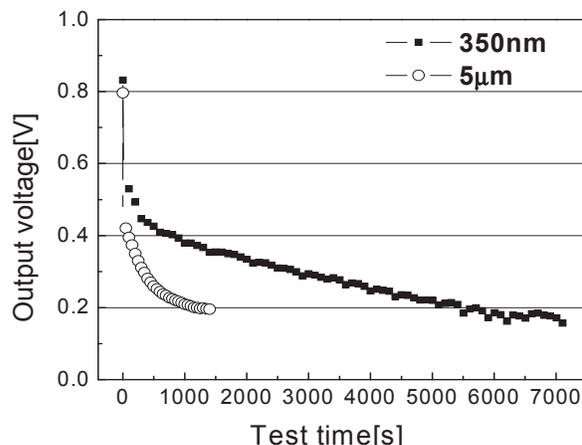


Fig. 8: Discharge curves (current density=5mA/cm<sup>2</sup>) of two fuel-cells, with pore size as 5nm and 350nm.

with catalyst-electrodeposited porous-silicon. Being used to replace the conventional carbon-paper, the developed porous-silicon electrode features larger specific surface-area for better electro-catalytic activity. Besides, the porous silicon structure can be batch-fabricated by anodic-oxidization. The testing results for the fuel-cell indicate that, with similar loading amount of Pt catalyst, the fuel-cell with the porous-silicon electrode performs higher Pt utilization efficiency and stronger electro-catalytic activity than the conventional fuel-cells with carbon-paper cathode.

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