Design and Microfabrication of a PEM Fuel Cell with Silicon-Supported Electrodes in a Column Matrix Configuration

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ABSTRACT

The use of silicon microfabrication is evaluated to form micron scale electrode structures for proton exchange membrane fuel cells. The structure of the half cell consists of a perforated; electrically conductive; silicon gas diffusion layer (GDL) on one side. With an etched matrix of high aspect ratio silicon columns covered with platinum catalyst and a thin polymer electrolyte film (Nafion), acting as the electrodes on the other side. Design guidelines are defined through analytical modeling of mass transport, catalytic surface area, and internal ionic and electrical resistance. Progress in developing the microfabrication processes to create the silicon structure, the Pt layer, the Nafion layer and cell assembly are then presented. Work to date suggests that achieving high catalytic surface area and low ionic resistance in the electrodes will be challenging with the proposed approach, but will allow first order modeling and geometric optimization to potentially reduce Pt loading.

Keywords: Micro fuel cell, PEM fuel cell, Deep reactive ion etching, Platinum deposition, Silicon-supported electrodes

1. INTRODUCTION

1.1. Microfabrication applied to PEM Fuel Cells

Silicon microfabrication technology has been used in recent years to miniaturize proton exchange membrane (PEM) fuel cells operating on hydrogen or methanol fuel [1-3], primarily aimed at small-scale, portable power generation. Most research has focused on fabricating smaller scale channels to allow system miniaturization, enhance mass transport, or address water management problems [4]. Recently, entire micro fuel cell structures have also been fabricated in silicon [5]. Instead of relying on standard electrode structures, such as porous inks of carbon-supported platinum, this work aims to evaluate the potential of silicon microfabrication to improve electrode structures, the heart of the PEM fuel cell. Lithography, deep reactive ion etching (DRIE), and thin film deposition techniques commonly used for microelectromechanical system (MEMS) fabrication provide a new degree of freedom in optimizing electrode structures, which could not only enable high performance micro fuel cells, but also benefit large-scale PEM fuel cell markets, such as the automotive industry, by reducing material costs.

1.2. Platinum utilization and stability

By observing the trend of current density as a function of Pt catalyst loading for conventionally fabricated PEM fuel cells (Fig. 1), we notice that the increase is less than linear, indicating that there is a waste of Pt as loading increases. Since noble metals are a significant fraction of a fuel cell's cost, reaching 53-68 $US/kW for automotive applications (0.7 W/cm², total loading 0.6-0.8 mgPt/cm² [6]), improving the Pt utilisation would open markets that require low cost, high density power sources. Another critical aspect is the limited lifespan of PEM fuel cells, attributed to the stability of small Pt nanoparticles on carbon supports. Here, we propose to use silicon as the support structure to leverage the capabilities of microfabrication to maximize Pt utilisation, while potentially increasing catalyst stability.

1.3. A tool for fundamental studies

Additionally, microfabrication of the electrode structure provides an approach to create idealized structures for fundamental electrochemical studies. With a well-defined microstructures instead of ill-defined porous media, we can directly determine the catalytic surface, the mass transport phenomena, as well as ionic and electronics conduction paths. Controlled experiments could provide deeper understanding of these physical and chemical phenomena and guide the design of fuel cell electrodes.

This article presents an approach to create a working microfabricated electrode. Following a description of the proposed geometry, modeling and microfabrication process development to implement the structure will be presented.
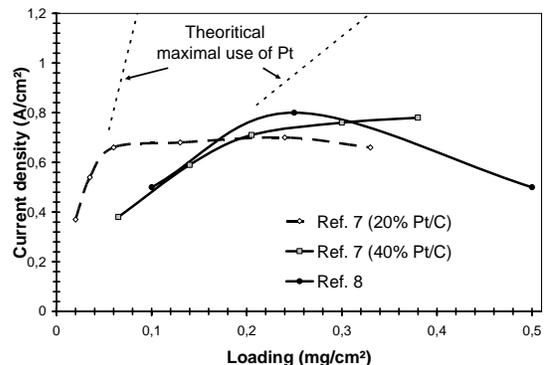

Fig.1 Current density for conventional PEM fuel cells as a function of Pt loading (cathode), showing significant potential for improvement compared to the trend if all Pt in the electrode were active (straight lines).

2. ELECTRODE GEOMETRY

The proposed silicon fuel cell configuration consists of a matrix of columns supported by a perforated gas diffusion layer (GDL), as illustrated in Fig. 2. This silicon microstructure acts as an electron conduction path, as well as a mechanical structure and support for the catalyst. The fuel or oxidizer diffuses through the perforated GDL and between the columns to reach their surface. Platinum catalyst is coated on the surface of the silicon columns. Ionic transport to these catalytic sites is provided by a thin film of Nafion (the polymer electrolyte typically used in PEM fuel cells) that covers the columns. To complete the fuel cell, two such silicon structures are bonded to a planar Nafion membrane, creating an ionic channel between the catalysts (column surface) on the anode and cathode sides. To achieve good performance, the electrode should maximize the surface area of catalyst while minimizing the resistance to ionic, electronic, and mass transport to and from the catalytic sites. A model of the internal resistances is illustrated in Fig. 3 (for the cathode only), which will be used as a guide for the theoretical analysis.

Prototype configuration - The prototype under development consists of a 1cm^2 array of square columns, each measuring 80μm high and 8μm wide with a spacing of 8 μm.

Cathode +

Silicon GDL

Nafion Membrane

Silicon GDL

Anode -

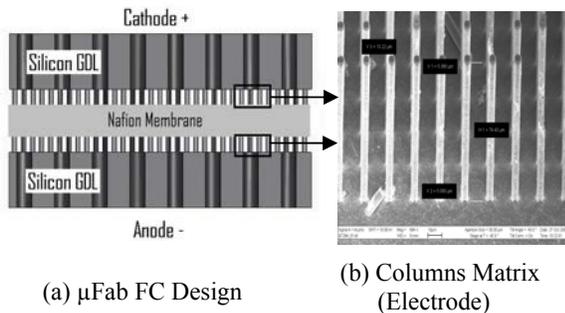(a) μFab FC Design

(b) Columns Matrix (Electrode)

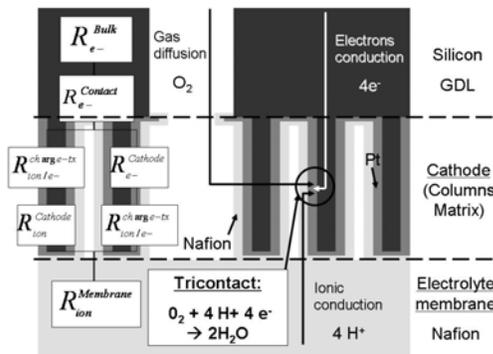**Fig.2** Side view of a μFab fuel cell with SEM images

Fig. 3 – Schematic of a small part of the microfabricated PEM fuel cell cathode, with the equivalent resistance circuit for ion and electron conduction.

The resulting Pt surface is 11 cm^2. The holes in the GDL will be 80μm in diameter and 300-400 μm deep, with a spacing of 300 μm. This configuration was defined from the analysis presented in the following section.

3. MODEL ANALYSIS

3.1. Geometric surface optimization

The column matrix configuration that maximizes the active area can be defined from simple geometry and fabrication constraints. Equation 1 describes the catalytic surface area (S_{3D}) per unit of planar cell area (S_{2D}) as a function of the column perimeter, P, height, h, and half width, R, as well as the maximum aspect ratio use for etching (*RAPF*):

$$\frac{S_{3D}}{S_{2D}} = \frac{P_c h}{\left(\dfrac{h}{RAPF} + 2R\right)^2} + 1 \qquad (1)$$

Figure 4 shows the ratio of catalytic to planar cell area as a function of column height and width for square columns, with *RAPF* of 11. The maximum corresponds to a critical ratio between the width of the columns and the width of the trench of 1:1. This result comes from the balance of two conflicting parameters: the area of a column versus the number of column per unit cell area.

3.2. Mass transport analysis

Mass transport at the cathode typically limits the current density achievable in PEM fuel cells; therefore an analysis was necessary to adequately design the microstructure. Fortunately, it is possible to analyse the mass transport with fundamental relations given the well defined structure. Using the Maxwell-Stefan equations for multicomponents diffusion in gases at low density [4], mass transport of oxygen, nitrogen and water vapour for the cell operating in free convection was calculated, from the external flow field to the surface of the columns on the cathode side. In order to get a first order validation of mass transport inside the structure, equations were simplified: advection movement of particles was neglected and only diffusion was considered.

Figure 5 presents water vapour and oxygen molar fraction through the cell at a current intensity of 320 mA/cm² and a
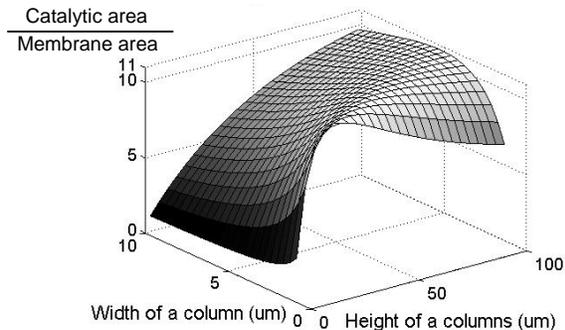

Fig. 4 Ratio of catalytic-to-membrane surface for different width and height of column for the matrix configuration.
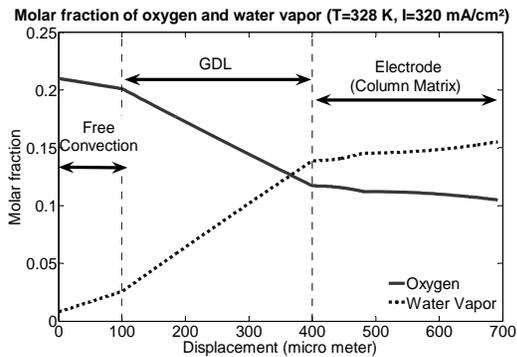
Fig. 5 Calculated concentration distribution from the air stream to the electrode post surfaces.

temperature of 328 K, with a GDL opening ratio of 4.4%. The main mass transport resistance is diffusion through the microfabricated GDL. It can be seen that water vapour molar fraction is about 0.155, which is close to condensation point of 0.154 at atmospheric pressure and a temperature of 328K. Thus, water accumulation could occur on the catalyst surface, which will dramatically lower the diffusion coefficient of oxygen and eventually stop the reduction reaction. This analysis reveals that if the distance between two holes in the GDL gets higher than 300 μm and if the opening ratio in the GDL becomes less than 4%, diffusion problems should start to occur in the catalyst domain of the cathode, for the operating conditions above. Also, Fick's law suggests that the Nafion thickness should be less than 2.8 μm in order to avoid starving the reaction by lack of oxygen at the catalyst surface, for a diffusion coefficient of O_2 in wet Nafion of 5.96×10^{-6} cm²/s [9], an the above conditions.

3.3. Internal resistance analysis

The internal resistance calculation includes ohmic losses through the doped silicon structure, the contact between the doped silicon structure and the platinum, the platinum structure, as well as ionic losses through the Nafion structure. The resistance of those different parts evaluated and summarized in Table 1. For the current configuration, it appears that the ionic resistance of the Nafion structure in the microfabricated fuel cell dominates, and is a significantly larger than typically expected in a conventional fuel cell.

Table 1 Summary of electronic and ionic resistance values predicted for the baseline configuration.

Component	Resistance (mΩ)
Silicon GDL structure	0.15
Silicon columns	0.16
Pt-Si contact (measured)	11
Pt layer	Negligible
Nafion layer on the columns*	600
Membrane*	50

* For a resistivity of Nafion = 5 Ω·cm

4. MICROFABRICATION PROCESS DEVELOPMENT

The techniques and tools used for the microfabrication of a PEM fuel cell electrode came from the different techniques use in MEMS fabrication. The silicon structure is first created by deep reactive ion etching (DRIE). Then, we deposit Pt in nanoscale layer on the entire column surface. The last step is the deposition of liquid Nafion over the columns and bonding to the solid Nafion membrane. The development for each of these processes to build the microfabricated electrode is presented next.

4.1. Deep Reactive Ion Etching (DRIE)

The high aspect ratio columns and holes for gas permeation (Fig. 2) are formed into crystalline substrates by lithography and deep reactive ion plasma etching (STS ASE). This process creates high aspects ratio (>1:10), extruded-like structures, but with scallops on the side walls (Fig. 6a). Since we need a good conductor for the structure we use highly doped p-type silicon (Boron, 10^{18} atoms/cm³), which corresponds to a resistivity of 0.005 Ω·cm.

4.2. Platinum deposition

After etching the silicon structure, Pt is deposited on the electron side using an electron beam evaporator. This deposition technique allows nanometer thick films to be deposited with good adhesion and low resistance ohmic contacts. Although sintering of the deposited Pt film at 866 K is suggested [10], experimental tests on a 2D surface have shown good omhic contact even without a sintering (Table 2). An ohmic contact is critical because the electron current will not be in the same direction for the anode and cathode.

Table 2 Experimental results for the resistivity of contact between Pt and doped silicon

Temperature of sintering (K)	Resistivity of contact (Ω·cm²)
376	0,13
576	0.12

A problem related to this method of deposition is the anisotropic projection of the Pt particles. This problem was alleviated by rotating the holding plate during the deposition (Fig. 6a). The thickness of Pt ranged from 20-50 as a function of depth in the electrode structure. Some scallops (from DRIE) may cut the link in the Pt sheet but it is not necessarily a problem since the conduction medium is the supporting silicon.

4.3. Nafion deposition

To allow transport of H^+ to the catalytic sites, the Pt electrodes are covered with a thin electrolyte film by spin coating liquid Nafion (Liquion, Ion Power). This deposition can be made with the photoresist spin coating system at a variety of speed depending on the thickness wanted.
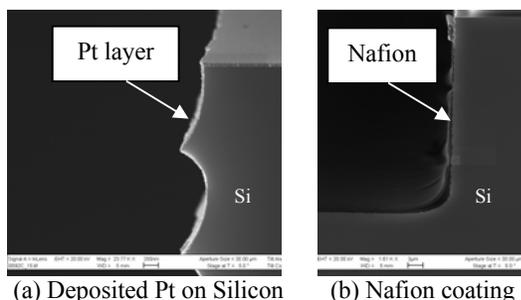
(a) Deposited Pt on Silicon   (b) Nafion coating

Fig. 6 SEM image of Pt deposited on a vertical surface with the electron beam evaporator (a) and Nafion deposited by spin coating over the 3D structure.

For a planar deposition, the thickness can be controlled between 150 nm to 2 μm. Tests where also done to spin coat a layer of Liquion on a 3D surface and the results are shown on Fig. 6b. Achieving uniform coating on the column side wall remains challenging.

4.4. Cell assembly

The final step will require bonding of a Nafion membrane with two electrodes, previously coated with Liquion. Very high strength bonds were achieved by hot pressing Nafion membranes with silicon wafers (down to 200 psi, 400 K). Important characteristics must still be evaluated, such as the quality of the ionic contact between the membrane and the electrode and the mechanical robustness of the assembly as the Nafion expands due to water uptake.

5. DISCUSSION

5.1. Model analysis

Optimization of the catalytic surface available for the reaction in the electrodes suggests a ratio of 1:1 for the width of the columns to that of the trenches. Since this optimum is not a function of scale, the columns do not need to be small to maximize the Pt surface. This raises the question: is it useful to microfabricate a PEM fuel cell electrode? Considering the high resistivity of Nafion however, protons will not conduct over long channels; hence the column height should not extend beyond 10's of μm to prevent wasting Pt. The thickness of Nafion deposited on the columns is not only important for the internal resistivity but also for the diffusion of fuel or oxidizer to the catalysis surface. This pushes the design to smaller Nafion thicknesses, and consequently shorter columns.

It should be noted that the current microfabricated column matrix configuration has 20 to 30 times less area of catalysis than the value normally accepted for conventional PEM fuel cell (200-300 cm²) [6]. However, there is a lot of room for improvement since the etching technique has not been pushed to its limit, both in aspect ratio and in making different column shapes. Furthermore, surface texturing of the columns could dramatically improve the active area.

5.2. Process development

The main difficulties are related to the deposition of films over three dimensional topologies. Here, the goal is uniformity and thickness control of the Pt and Nafion layers. More conformal deposition techniques need to be experimentally tested, such as sputtering or electro-plating of the Pt catalyst and vapour deposition of the Nafion film.

Finally, to achieve the goal of reducing the Pt loading, deposited thicknesses will need to be reduced to a few nm. Films greater that 10 nm were deposited in this initial phase of development for robustness.

6. CONCLUSION

Two main objectives are addressed in this work: microfabrication of a PEM fuel cell electrode and design of a novel column matrix configuration. Common MEMS processes and materials are used and evaluated for PEM fuel cell fabrication, including deep reactive ion etching, evaporation, and spin casting. Also, the importance of the dimensions of the electrode structure were defined, based on mass transport and resistance circuit analyses, the most critical part being the Nafion layer deposited over the columns. We are currently working to complete the fabrication of a cell to experimentally investigate the viability and performance of the approach proposed herein.

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