A NOVEL HYBRID PLANAR APPROACH FOR MEMS-COMPATIBLE MICRO FUEL CELLS

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Abstract: A novel approach for the obtaining of a compact and MEMS-compatible micro fuel cell is presented. The device consists of a polymeric membrane sandwiched between two electrode-current collector microplates. The membrane consists of a polymer matrix of polydimethylsiloxane (PDMS) filled with a proton conducting polymer. The silicon plates incorporate Ni current collectors and the catalysts in a fine microfabricated mesh by electrodeposition. The advantage of the present approach is based on the capability of PDMS to bond to silicon by plasma oxidation, which would allow the assembly of all components into a highly compact device.

Keywords: microfuel cell, polymeric fuel cell, PDMS

INTRODUCTION

In the recent years, research in micro fuel cells field has been mainly focused on the design and fabrication methods required to miniaturize the different elements that compose these devices. A lot of advances have been reported on the development of new materials that improve catalytic reactions, the reduction of the catalyst contents and the design of novel architectures and packaging solutions to optimize fuel cell performance at a microscale [1-3]. However, the monolithic integration of the fuel cell micro-parts remains still as a technological challenge, given that the incorporation of additional plates, screws or adhesives is usually required to assemble its components together and lower their contact resistance. The origin of this drawback lies on the incompatibility of polymeric electrolytes with the materials typically used in MEMS technology. This work presents a new approach towards a fully integrated micro fuel cell.

Device description

The device is based on the integration of a thin polymeric electrolyte with silicon micromachined structures that act as both current collectors and electrodes. Figure 1 shows an exploded scheme of the proposed micro fuel cell were all parts are identified. It can be seen that unlike other approaches, the electrode layer will be embedded within the current collector structures. These structures consist of silicon microfabricated plates with an array of channels obtained by a Deep Reactive Ion Etching process (DRIE). On top of these plates, a denser grid of silicon is defined in a separate DRIE process and covered with a Pt (cathode) / Pt-Ru (anode) catalytic layer. In this way, the microchannels are used to deliver the reactants from the outer parts of the fuel cell to the catalytic grid, which once the micro fuel cell is assembled, will be in direct contact with the PDMS-electrolyte membrane. The key aspect of the present approach is that the polymeric electrolyte - fabricated with a combination of a porous polydimethylsiloxane (PDMS) membrane impregnated with a proton-conducting polymer – can be easily integrated with the current collector structure by taking advantage of the adhesion capabilities of PDMS to silicon after an oxygen plasma treatment.

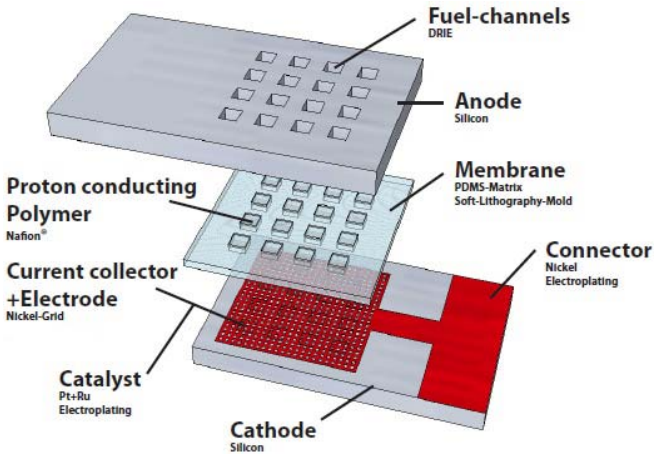

Fig. 1: Exploded view with detail and all parts of the proposed micro fuel cell identified.

MICROFUEL CELL FABRICATION

As it has been shown in Figure 1, the cell has been conceived as a 3-part assembly: a polymeric electrolyte sandwiched between two electrode-current collector structures. In the following, the fabrication process of these both type of components is described in detail.

Current collector fabrication process

Fabrication starts with a 500 μm-thick Silicon-on-Insulator (SOI) wafer that has a 5 μm-thick device layer and a 1μm-thick buried oxide. A dense electrode silicon grid (feature size around 5 microns) is first defined on the top side of the wafer by a DRIE process. This grid is then metalized with a thin Ti-Ni sputtered layer. This metallic film provides the electrical conductivity for electroplating a thicker (5μm) Nickel layer required for the current collection of the cell which is then used as seed layer in the

catalyst electroplating process. After this, a second DRIE process is performed on the wafer back side in order to define an array of microchannels for fuel delivery. Etch process stops automatically when the buried SiO_2 is reached. Then, the buried SiO_2 is removed from the windows with diluted HF. Finally, the metallic grid is electroplated in a Pt-Ru bath in order to provide the electrode grid with catalytic activity. Figure 2 summarizes schematically the main steps of this fabrication process whereas Figure 3 shows two SEM images of two different designs of current collectors.

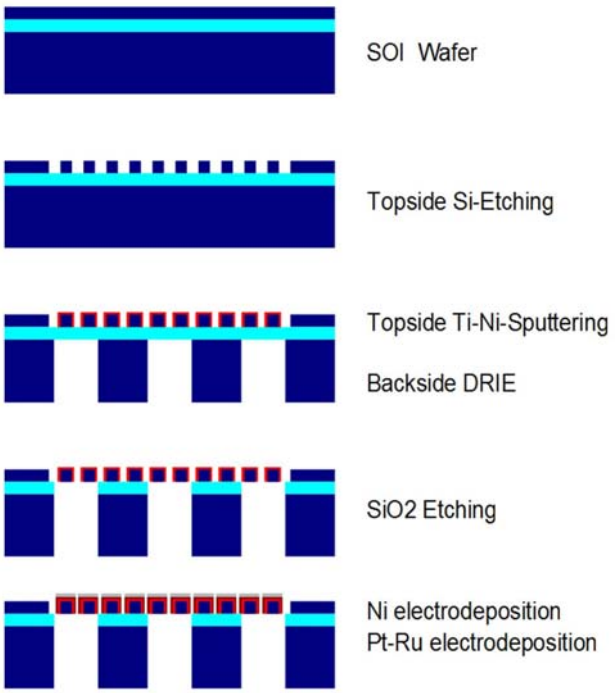

Fig. 2: Main steps of the fabrication process of electrode-current collector structure.

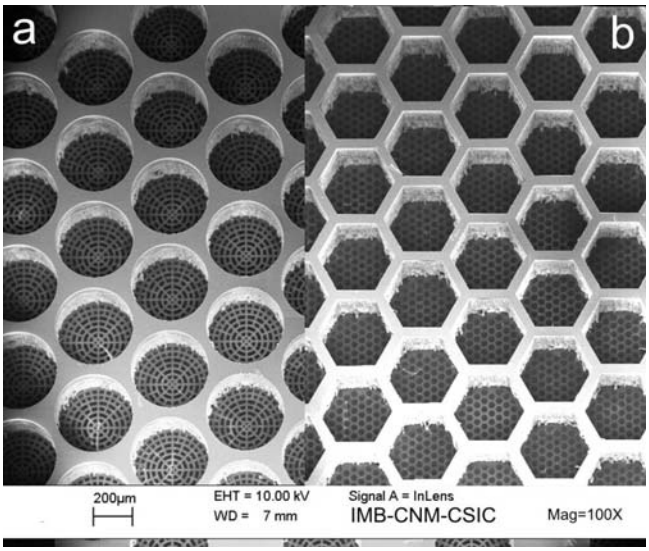

Fig. 3: SEM image of two designs (a-circular and b-hexagonal) of the microfabricated current collectors. Image has been taken from the back side of the silicon chips.

Fabrication of the PDMS-Nafion® membrane

The proposed hybrid polymer electrolyte membrane consists of a PDMS thin film provided with an array of through-holes that are filled with a solution of polymer electrolyte [4]. The fabrication of the hybrid membrane departs from a silicon master that is microfabricated using a SOI wafer. The handle side of the wafer was used for master patterning, which was performed by DRIE process. Each membrane mould consisted of a 10x10 mm cavity with an array of squared microcolumns covering an area of 5x5 mm placed in the center of the cavity. Membranes are then obtained by pouring a volume of 30 µl of PDMS (Sylgard 184, Dow Corning Inc.) prepolymer mixture onto the mould, curing it in an oven and peeling the resulting structure off. This procedure allowed obtaining 10 x 10 mm and 300 µm-thick films with an array of microperforations with a section of 500x500 µm in its central 5x5 mm area.

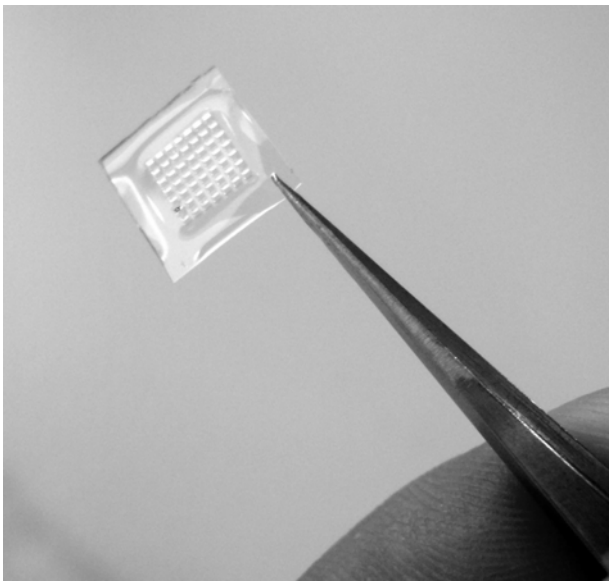

Fig. 4: Picture of one of the microfabricated PDMS membranes.

In order to provide the PDMS film with the required proton conductivity, its microperforations were then filled with liquid Nafion® (in this case, Nafion® 5% in aliphatic alcohols). After solvent evaporation, cavity filling was confirmed by optical inspection. A top-view detail of a hybrid polymer electrolyte membrane is shown in Figure 4. In this figure, a well-defined pattern of microcavities on the PDMS membrane can be observed, indicating an optimum transfer process from the silicon master to the polymer matrix. Besides, excellent filling of PDMS microcavities with Nafion® is shown, validating the proton conducting electrolyte impregnation process (see Figure 5).

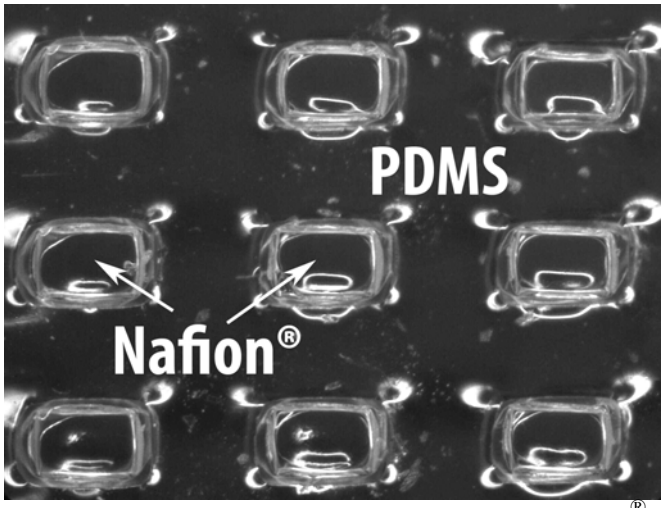

Fig. 5: Detail of the hybrid PDMS-Nafion® membrane.

RESULTS

The proton conductivity of the membrane has been preliminary evaluated by electrochemical impedance spectroscopy (EIS) measurements. For that purpose, symmetrical electrochemical cells consisting of the fabricated hybrid membranes working as electrolyte and two Au thin plates attached to the both sides of the electrolyte acting as electrodes were used. EIS measurements were performed using an Impedance/Gain-Phase Analyzer (SI 1260, Solartron Analytical) with an Electrochemical Interface (SI 1287, Solartron Analytical). The measurements were carried out at room temperature in ambient air. The obtained conductivity of the hybrid membranes was found to be 6.0 ± 0.5 $mScm^{-1}$. This value – obtained from the characterization of 4 different membranes - was obtained by considering an effective membrane area of 5 x 5 mm that is, including the contribution of the non-active PDMS part of the membrane. However, the actual area provided with proton conducting capabilities corresponded to a 25% of the total membrane area. Taking into account only the area filled by Nafion® polymer, values of conductivity associated to the electrolyte resulted to be 24 ± 3 $mScm^{-1}$. These results confirmed the correct operation of the proton conductive polymer once embedded in the PDMS matrix and proved the viability of using the PDMS-Nafion® hybrid membrane as a polymer exchange membrane.

CONCLUSIONS AND FURTHER WORK

This paper reports the ongoing work towards the obtaining of a fully integrated micro fuel cell. The idea is based on the combination of a hybrid polymer membrane (PDMS and Nafion®) as a straight-forward integrable electrolyte for MEMS-based fuel cells together with two electrode-current collector microstructures.

The compatibility of this membrane with MEMS fabrication processes lies in the acknowledged bonding capabilities of PDMS polymer to materials typically used in microsystems technologies – such as silicon, silicon dioxide and glass – as well as its ability to withstand variations of the Nafion® volume. The membrane was fabricated and characterized, yielding a proton conductivity value within the range of values typically reported for Nafion® polymers.

The microfabricated current collectors have been successfully fabricated with a double-side DRIE process. Future work involves catalyst electroplating onto the electrode grids. Then, fuel cell assembly will be performed by taking advantage of the capability of PDMS to bond to silicon by plasma oxidation, which would allow the assembly of all components into a highly compact microdevice.

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