Micro Alkaline Fuel Cell supported by MEMS-based Backbone

M Pilaski¹, S-H Sun², G Dura¹, J Wartmann¹, F Letzkus² and A Heinzel¹

¹The hydrogen and fuel cell center, Carl-Benz-Str. 20, 47057 Duisburg, Germany and
²Institut für Mikroelektronik Stuttgart, Allmandring 30a, 70569 Stuttgart, Germany
m.pilaski@zbt-duisburg.de

Abstract. This work presents the application of nitride membranes produced with Si-MEMS-technology as a platform to build up new membrane-electrode assemblies (MEA) for alkaline fuel cells. Active alkaline fuel cell MEAs were combined by integrating hydroxide permeable electrolyte into micro-channels of 1 μm diameter in 5 to 10 μm thick MEMS-based membranes. A platinum catalyst was sprayed onto the surface and an electric conductive layer was applied on top. Taking advance of the small form factor these fuel cells can be applied in small devices with low energy demand.

1. Introduction

On the way to a clean energy supply without fossil fuels, energy conversion systems without CO₂ production and high efficiency are needed. In addition, electricity generated from renewable energy sources must be temporarily stored in form of chemical energy in order to bridge temporal discontinuities. Fuel cells and electrolysers are regarded as key technologies. Due to good availability of Nafion® membrane, the development of acid fuel cells and in particular the corresponding catalyst systems were strongly preferred. However, despite considerable progress, the use of precious metal catalysts is still essential. Additional corrosion processes, e.g. of the carbon carrier material lead to limitation of the service lives. Alkaline fuel cells, on the other hand, have the great advantage that non-precious metals such as Co, Ni or Mn and their alloys can be used as catalysts for the reaction. Due to their better geological availability compared to the precious metals, these catalysts facilitate the sustainable use of fuel cells and enable high saving potential. Since polymer alkaline electrolyte materials for membrane application became available in the last years they have gathered more interests due to easier handling and higher resistance against CO₂ contaminations in air supply than alkaline fuel cells with liquid electrolyte solution [1].

To gain advantage of these new membrane materials in applications of micro-fuel cells we adapt the concept of a Si-stencil matrix to serve as backbone for a self-supporting alkaline fuel cell. Due to the alkaline environment the contact of silicon with the electrolyte has to be avoided. As solution the silicon surface can be covered with a Si₃N₄-layer to prevent etching of the structure. Using these MEMS-based membranes as support for ion-exchange membrane materials the prepared fuel cells could either be applied as energy supply in small devices or as research tool in catalyst research by high-throughput screening. The latter was the first goal within the herein presented work to help identify new potential non-precious metals for the application in alkaline fuel cells.
2. Materials and Methods

2.1. Membrane manufacturing
Nitride membranes have been fabricated by 6 inch Si-MEMS technology using a Si backbone with nitride coverage as so-called Si$_3$N$_4$-stencil mask (Figure 1). It is based on a silicon-on-insulator (SOI) wafer and includes an epitaxy step at the beginning in order to increase the silicon thickness to 5 μm. The wafer backside was covered with silicon nitride by PECVD deposition. The micro channels were formed using optical lithography followed by Si dry etching. The backside membrane frame openings were created using nitride dry etching after contact lithography. Bulk silicon was removed in KOH etchant, followed by an oxide removal. Finally, the membranes were fully covered with silicon nitride in a LPCVD process. The membrane separation was carried out using a wafer dicing method. The quadratic membranes were designed with a frame size of 10x10 mm$^2$ and an inner channel area of 5x5 mm$^2$. The channel diameter was defined as 1 μm with a pitch of 3 μm.

Figure 1. The Si$_3$N$_4$ stencil mask process: (a) silicon epitaxy and backside nitride deposition, (b) front side lithography, silicon dry etching, (c) backside lithography, nitride dry etching, (d) backside wet etching in KOH, (e) oxide etching in buffered HF, (f) Si$_3$N$_4$ deposition with LP CVD

2.2. Fuel cell preparation and testing
To integrate the manufactured Si$_3$N$_4$-membranes into working fuel cells different consecutive layers were applied on the surface and into the micro-channels of the Si$_3$N$_4$-membranes shown in Figure 2. As first layer the alkaline fuel cell membrane material was applied, which allows hydroxide-ions to permeate through. Two different materials, purchased from FUMATECH BWT GmbH, were tested. The first one is called FAA3 and could be bought as chopped membrane flakes with bromide as bound counter ion and was dissolved in ethanol to allow a coating. The second material is called FAA2 and was also delivered with bromide as counter-ion, but already dissolved in dimethylacetamide. In both materials the bromide-ion had to be exchanged prior to the application in a fuel cell. While the FAA3-material can be treated with a 1 M aqueous solution of Na$_2$CO$_3$ prior to dissolving in ethanol to allow a coating, the second material is called FAA2 and was also delivered with bromide as counter-ion, but already dissolved in dimethylacetamide. In both materials the bromide-ion had to be exchanged prior to the application in a fuel cell. While the FAA3-material can be treated with a 1 M aqueous solution of Na$_2$CO$_3$ prior to dissolving in ethanol, the FAA2 material has to be treated after deposition on the membrane. The deposition of the ionomer solutions have been performed either by dip-coating or by ultrasonic spray coating (SONO-TEK ExactaCoat, Figure 2.2).

Additionally a catalyst layer is sprayed on top of the ionomer by ultrasonic spray coating (Figure 2.4). The catalyst dispersion was prepared by mixing 40 wt% Pt/C (HiSpec4000, 600 mg), dist. water (21.4 ml), ethanol (6.2 mL) and 2.4 ml of a 10 wt.% solution of FAA3-ionomer after ion-exchange in Na$_2$CO$_3$-solution. On each side 10 layers were sprayed with a spray-rate of 0.5 ml/min. To resemble a bipolar plate and collect the current produced, 20 layers of silver-nanowires (AgNW) were applied on the catalyst layer (Figure 2.5) [3]. These nanowires were purchased at Sigma-Aldrich as 0.5 wt% suspension in isopropyl alcohol with 60 nm diameter and 10 μm in length.

The prepared micro-fuel cells were placed in a holder to connect each side to an electrical load and flush preheated hydrogen and air on anode respectively cathode side (Figure 2.6).
Figure 2. Different stages during manufacturing of the micro-fuel cells: (1) blank Si$_3$N$_4$-membranes before coating; (2) ultrasonic spray coating and pore filling with alkaline electrolyte dispersion; (3) Si$_3$N$_4$-membrane covered with electrolyte; (4) μFC after coating with catalyst layer; (5) complete μFC with conductive AgNW layer on top; (6) testing of the μFC in a custom made reactor.

3. Results and Discussion

The SOI-stencil mask process to fabricate Si$_3$N$_4$-covered membranes could be optimized to high membrane yields with low stress. A complete wafer with 96 single membranes is shown in Figure 3. The desired diameter and spacing could be confirmed by SEM.

For a successful manufacturing of a fuel cell based on Si$_3$N$_4$-Stencil membranes is a complete filling of all micro-channels with ionomer is important. If any pores remain unfilled they might be filled with catalyst or AgNWs resulting in electrical short circuits. The quality of the ionomer-coating and pore-filling was studied by laser confocal scanning microscopy (LCSM) and SEM of a crosscut.

The FAA2-ionomer had to be applied by dip-coating, as ultrasonic-spray deposition was not applicable with this very viscous dispersion. Microscopic images of the coating surface are shown in Figure 4 and after the consecutive ion-exchange in Figure 5.

Figure 3. Wafer with 96 intact membranes. Membranes have a silicon thickness of 5 μm, covered with 250 nm LP-CVD nitride. Insert: High resolution SEM picture to demonstrate the micro channel pattern.

Figure 4. Microscopic image of a scratched FAA2 coating on Si$_3$N$_4$-substrate.

Figure 5. Microscopic image of a FAA2 coating on a Si$_3$N$_4$-SOI-wafer after Na$_2$CO$_3$-ion-exchange.
Before ion-exchange the surface is very uneven. In structured regions defects were observed where micro-channels were not filled sufficiently. After ion-exchange the polymer has swollen and a more even surface has been formed. Nevertheless, defects are still present which might be filled with catalyst- or AgNW-ink in the following steps.

For the FAA3-material ultrasonic spray coating of an ethanolic dispersion could be applied, resulting in a very even coating and exceeding the results observed by dip-coating with this material. The surface resulting from the spray coating shows residues of the formed drops during the coating process (Figure 6 and Figure 7). Even though this coating is not completely uniform and even, only little amount of defects can be found on each side (Figure 7 on the bottom right). As the coating is applied on both sides, it is very unlikely to have matching defects on both sides. After consecutive coating with a Pt/C-catalyst and silver nanowires a broken fuel cell has been studied by SEM (Figure 8). This image proves a successful pore filling over the whole length of each broken micro-channel. The additional catalyst and silver-nanowire layers are easy to be recognized in this image as well.

![Figure 6](image6.png) **Figure 6.** Microscopic image of a FAA3 coating on Si$_3$N$_4$-SOI-membrane.

![Figure 7](image7.png) **Figure 7.** LCSM image of an FAA3 coating on Si$_3$N$_4$-SOI-membrane.

![Figure 8](image8.png) **Figure 8.** SEM-image of a broken micro fuel cell based on a SOI-membrane with FAA3-ionomer, catalyst and AgNW-layer.

The nanowire layer has been studied concerning their electrical resistance. With 20 sprayed layers the electrical resistance was measured at around 10 Ω/cm enabling energy production by fuel cell reaction. Beside the collection of the produced electrons, hydroxide ions have to be transported from cathode to anode. To ensure the ion-conductivity of the deposited ionomer material, electrochemical impedance spectra have been measured. These measurements have been performed at in-plane layers and it was assumed that the corresponding through-plane conductivity is correspondingly consistent. All tested coatings showed evidence for ion-conductivity while FAA2-coatings showed better conductivity than FAA3-coatings. As FAA2 coated membranes had to be treated with an ion-exchange after coating, the applied layer started to detach from the Si-based supporting membrane due to swelling of the polymer. Additionally a high number of membranes broke due to additional stress induced by this swelling. In contrast the FAA3-coated membranes did not need a post treatment as they were ion-exchanged before dissolving, resulting in a higher yield for this material and coating.

Different MEMS-based membranes were coated with FAA2 or FAA3-ionomer, a catalyst layer and silver nanowires. For testing each cell has been placed inside a sealed housing to be able to apply hydrogen and air on the corresponding sides. The cell has been heated with a heat-gun and the gas supply has also been preheated at 80 °C and humidified at 70 %rH.

The tested cells were able to generate electricity by the alkaline fuel cell reaction (Figure 9). Nevertheless, their performance is far lower than that of normal sized fuel cells with proton exchange membranes. Firstly the generated open circuit voltage (OCV) could not reach the in practice possible value of around 1.0 V. This suggests the presence of short circuits through the membrane. This is more pronounced for the FAA2 based cell than for the FAA3-based ones. Secondly the voltage drops rapidly with increased current. Overall this is a systematic problem as only the micro-channels are available for ion-transport from cathode to anode. FAA2-based cells showed a better performance than
all tested FAA3-cells as their voltage reduces not as fast as the compared FAA3-cells. Most likely this can be addressed to the better ion-conductivity of the FAA2-material. Different SOI-membranes have been coated with FAA3-ionomer and are now compared concerning their activity. These SOI-membranes differ in membrane thickness and different Si₃N₄-coating layers. The best results of these cells were achieved with a 5 μm thick membrane with 250 nm thick Si₃N₄-coating. By reducing the Si₃N₄-coating layer to 150 nm, the performance decreased drastically. It could be increased a bit by using a thinner membrane of 2 μm with the same Si₃N₄-layer. These variations effect mainly the performance at higher current-densities leading to the suggestion that the ion-transport is affected. The influence of Si₃N₄-layer-thickness has been studied by goniometric measurements. A thicker layer corresponds to a higher surface polarity than a thinner layer. This leads to a conclusion that a higher surface polarity simplifies the pore filling of the micro-channels with ionomer, which is highly polar as well. Accordingly the thinner Si₃N₄-layer leads to an insufficient pore filling of the micro-cannels and fewer channels are available for ion-transport processes. The thinner membrane thickness on the other hand reduces the length for this ion-transport yielding a higher performance of this cell.

![Figure 9](image-url)

**Figure 9.** Polarization-Curves of MEMS-based μFCs 70 °C, atm. pressure, V_H₂ = 5 ml/min, V_air = 5 ml/min, Prepared either by dip-coating of 10μm SOI-membrane with FAA2-ionomer in DMAc or ultrasonic spray coating of FAA3-solutions on different SOI-Si₃N₄-wafers.

4. Conclusion

It could be successfully shown that MEMS-based Si₃N₄ covered SOI-Stencil matrix membranes could be applied as backbone for alkaline micro fuel cells. The best results could be obtained with FAA2-ionomer by FUMATECH BWT GmbH on a 10 μm thick SOI-membrane with 84 μW/cm² power-output. This is by far not yet applicable for an industrial application but many ways are possible to improve e.g higher porous Si-based membranes and thinner and smoother finished electrolyte layer. For now these cells can be applied for catalyst research in high-throughput experiments where different catalysts activity is compared by their produced heat measured by IR-thermography.

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