# Fabrication and evaluation of a passive alkaline membrane micro direct methanol fuel cell

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R.W. Verjulio [a], J. Santander [a,*], N. Sabaté [a], J.P. Esquivel [a], N. Torres-Herrero [a], A. Habrioux [b], N. Alonso-Vante [b]

[a] Instituto de Microelectrónica de Barcelona, IMB-CNM (CSIC), Campus UAB, 08193, Bellaterra, Barcelona, Spain
[b] IC2MP, UMR-CNRS 7285, University of Poitiers, 4 rue Michel Brunet, 86022 Poitiers, France

## ARTICLE INFO

## ABSTRACT

A passive silicon microfabricated direct methanol fuel cell employing a polymer anion exchange membrane has been identified as a promising integrable power supply for portable devices in the MEMS field. In this work the fabrication steps of the different components: silicon current collectors and membrane-electrode assembly (MEA), as well as the mounting approach and performance evaluation for the whole passive alkaline micro air-breathing direct methanol fuel cell (µADMFC) are shown. This system, with a small active area of 0.25 cm$^2$, was tested near of the real application conditions with totally passive fueling and at room temperature. Different MEA configurations and methanol and KOH concentrations were compared. Best performance was observed for the MEA with a previously sprayed catalytic layer on carbon cloth instead of the MEAs with the catalytic layer deposited directly onto the alkaline membrane. A maximum power density of 2.2 mW cm$^{-2}$ was achieved for 15 µL of 1 M methanol + 4 M KOH fuel solution.

## 1. Introduction

The recent technological advances on the functionalities of the modern portable devices and the increasing presence of micro-electromechanical systems (MEMS) in a wide range of applications like automotive, biomedical instrumentation or radio frequency communications, led to intensive research to obtain small power sources which satisfy the requirements of high power density, long life operation and low cost [1]. Some complementary strategies are presently being pursued to overcome these challenges and regarding their integration in MEMS technology, and micro-fuel cells are one of the most promising of them [2–7].

The micro-fuel cells are efficient and clean energy conversion systems, with no moving parts, which can be considered as low cost systems if produced on a large scale [7–11].
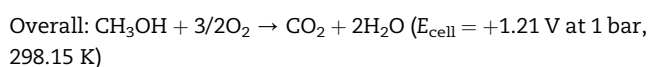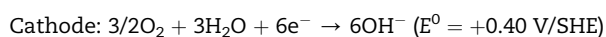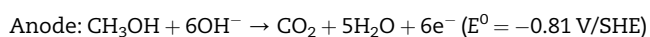
Among the different types of fuel cells, the direct methanol fuel cell (DMFC), a type of polymer electrolyte membrane fuel cell (PEMFC) that used liquid methanol as fuel, is one of the most suitable fuel cells to be focused toward the development of micro-fuel cells. Methanol has a high theoretical energy density (4384 Wh L$^{-1}$), higher than that of gas fuels [8,12], and has only one carbon atom in its molecule and no C–C bonds, being a simple alcohol relatively easy to oxidize. However, the major obstacle that has restrained the more rapid development of DMFCs systems is the methanol crossover through

the membrane from the anode to the cathode. In addition, the high costs of proton exchange membranes (mainly Nafion® from DuPont) and precious metal catalysts (Pt based catalysts), and CO poisoning of Pt catalysts at lower temperature in acidic media, have further hampered development of DMFCs.

Anion exchange membrane fuel cells (AEMFCs) are, in principle, a promising alternative to PEM based fuel cells and are currently garnering renewed attention [13]. In an AEMFC, an anion exchange membrane (AEM) conducts hydroxide anions (as opposed to protons) during current flow, which results in several advantages: (1.) The oxygen reduction reaction (ORR) is much more facile in alkaline environments than in acidic environments [14,15]. This could potentially facilitate the use of less expensive non-noble catalysts with high stability in alkaline environments. (2.) The electro-oxidation kinetics for many liquid fuels is enhanced in an alkaline environment. (3.) The electroosmotic drag associated with ion transport opposes the crossover of liquid fuel in AEMFCs, thereby permitting the use of more concentrated liquid fuels, which is an advantage for portable applications. (4.) The flexibility in terms of fuel and ORR catalyst choice also expands the parameter space for the discovery of highly selective catalysts that are tolerant to crossed over fuel [16]. These potential advantages make AEMFCs an attractive future device [13,17–20]. The fuel cell equations for direct use of methanol with an alkaline electrolyte are [19,20]:

Anode: $CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^-$ ($E^0 = -0.81$ V/SHE)

Cathode: $3/2O_2 + 3H_2O + 6e^- \rightarrow 6OH^-$ ($E^0 = +0.40$ V/SHE)

Overall: $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$ ($E_{cell} = +1.21$ V at 1 bar, 298.15 K)

The main characteristic of the passive microfabricated fuel cells is its capability to work without complex pumping systems, only by capillary pressure [7]. Therefore, passive micro-alkaline membrane direct methanol fuel cells (μADMFC) designed to breathe air without the necessity for ancillary devices such as air pumps or fans can offer several advantages, including the opportunity to eliminate parasitic power loss and to use simpler structures and more compact system designs than in the case of active μDMFCs. In turn, these advantages can lead to a potential low cost alternative for applications in the field of Power-MEMs or lab-on-a-chip.

To proof this concept, in this study, the use of micro-fabrication techniques to elaborate an air-breathing μADMFC able to work under ambient conditions is demonstrated. The effect of methanol and KOH concentrations on the fuel cell electrical performances was investigated.

## 2. Experimental

The device is based on the use of micromachined silicon-based current collectors, prior passivated with silicon nitride to avoid being etched by the alkaline media. For the preparation of the small-scale membrane electrode assemblies (MEAs), A201 Tokuyama anion-exchange membranes and commercial Pt-based catalysts have been used.

### 2.1. Fuel cell's silicon current collectors

The current collector is an important component of the μADMFC. It not only supplies a passage for the transport of reactants, but also provides structural support for the MEA and collects the electrical current [21,22]. The use of micro- and nanotechnologies (MNT) in the fabrication process of micro-fuel cells can provide them with the well known advantage of batch fabrication, which can contribute to reduce the cost per device unit [23].

Fig. 1 schematically shows the main steps in the micro-fabrication process of the Si current collectors. A more detailed description can be found elsewhere [24]. Starting from a silicon wafer 300 μm thick, a deep reactive ion etching (DRIE) process was performed to perforate the channels. A passivation layer of silicon nitride was deposited to insulate around the wafer and protect the silicon from the alkali solutions. The electrodepositable photoresist Eagle 2100 ED (Dow) has been used to define the metallized patterns on a previously sputtered aluminum layer. The electrical conductivity was improved by a subsequent electrodeposited nickel-gold layer. Once fabricated, the silicon current collectors are cut in chips of 10 mm × 14 mm to be used to mount the μADMFC. Current collectors with 25% and 45% open ratios were employed for the anode and the cathode, respectively. Both current collectors have the same channel dimensions of 80 μm × 80 μm (300 μm-deep) and the same active area of 0.25 cm² (5 mm × 5 mm).

### 2.2. Preparation of the alkaline MEAs

To prepare the MEAs, square pieces of 1 cm² of anion exchange membrane A201 (Tokuyama, thickness ~28 μm) were cut. They were then submitted to a 24 h pre-treatment in 1 M KOH solution at room temperature followed by 2 h in 1 M KOH solution at 50 °C and finally washed in ultrapure water (MilliQ). Pt:Ru/C (1:1, 60 wt%, E-tek) and Pt/C (60 wt%, E-tek) were used as anode and cathode catalysts, respectively [25–28]. The inks were prepared according to the following procedure: 10 mg of catalyst powder, 125 μL of alkaline ionomer AS-4 (5 wt %, Tokuyama) and 875 μL of ultrapure water (18 MΩ cm) were mixed. The inks were then homogenized in an ultrasonic bath for 2 h. The geometric active areas of the MEAs were of 0.25 cm².

The airbrush technique was used to deposit the ink on the substrate (A201 membrane or carbon cloth). After being painted, the MEAs were hot-pressed at 2 kN and 110 °C for 3 min.

In order to prove the concept of passive and air-breathing micro alkaline fuel cell at room temperature two different relatively high catalyst loadings respectively fixed to $4 \text{ mg}_{metal} \text{ cm}^{-2}$ (MEA-1) and $8 \text{ mg}_{metal} \text{ cm}^{-2}$ (MEA-2 and MEA-3) were considered. Two different ways were used to prepare MEAs. The first one consists in directly depositing the catalysts onto the membrane by using spray deposition method (MEA-1 and MEA-2). The interest of this kind of MEA lies in