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


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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 cm², 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 NaFon®
from DuPont) and precious metal catalysts (Pt based cata-
lysts), 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
ions (as opposed to protons) during current flow, which
results in several advantages: (1) The oxygen reduction re-
action (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 se-
lective 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]:

\[
\text{Anode: } \text{CH}_3\text{OH} + 6\text{OH}^- \rightarrow \text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^- \quad (E^0 = -0.81 \text{ V/SHE})
\]

\[
\text{Cathode: } 3/2\text{O}_2 + 3\text{H}_2\text{O} + 6\text{e}^- \rightarrow 6\text{OH}^- \quad (E^0 = +0.40 \text{ V/SHE})
\]

\[
\text{Overall: } \text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (E_{\text{cell}} = +1.21 \text{ V at 1 bar, } 298.15 \text{ K})
\]

The main characteristic of the passive microfabricated fuel
cells is its capability to work without complex pumping sys-
tems, 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 advan-
tages, 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 advan-
tages can lead to a potential low cost alternative for ap-
lications in the field of Power-MEMs or lab-on-a-chip.

To prove 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 assem-
bles (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 so-
lutions. The electrodepositable photore sist Eagle 2100 ED
(Dow) has been used to define the metallized patterns on a
previously sputtered aluminum layer. The electrical conduc-
tivity 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 ex-
change 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 (Mil-
liQ). 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 mgmetal cm⁻² (MEA-1) and 8 mgmetal 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 cata-
lysts onto the membrane by using spray deposition method
(MEA-1 and MEA-2). The interest of this kind of MEA lies in