EMBEDDED MEMS-BASED CONCENTRATION SENSOR FOR IMPROVED ACTIVE FUEL CELL PERFORMANCE

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Abstract: A MEMS-based methanol concentration sensor for monitoring and controlling the methanol to water ratio in a DMFC system is described. This sensor is based on a microfluidic chip that employs a resonant microtube and on-chip platinum temperature sensor to measure the density of a fluid. Using the density and temperature output the methanol concentration is determined. The performance of the sensor over temperature, concentration and in the presence of formic acid by-products is examined. Test comparisons between this sensing method and refractive index and speed-of-sound methanol concentration sensors are made. Additional biofuel applications for the sensor will be discussed.

Keywords: microfluidics, methanol concentration sensor, density, Direct Methanol Fuel Cell, DMFC, chemical sensor

1. INTRODUCTION

This paper presents a MEMS chemical sensor, shown in Fig. 1, which has been under developed specifically for the fuel cell chemical concentration market for over three years. This microfluidic technology has previously been used to measure fluid density, chemical concentration in a laboratory setting [1] and mass flow rate [2]. It uses a getter assisted, vacuum packaged [3], single crystal silicon resonating tube along with an integrated thin film RTD.

Direct fuel cells do not reform the fuel into hydrogen gas but directly produce electricity using air and fuels such as aqueous solutions of methanol, ethanol or formic acid. One problem that has hampered the use of these fuel cells is membrane crossover. Membrane crossover occurs when the fuel to water concentration gets too high and fuel goes through the membrane to the other side of the fuel cell. A high fuel concentration lowers performance due to crossover and membrane damage while a high water concentration starves the system of fuel, again lowering performance [3]. A fuel to water concentration sensor is often employed in active direct fuel cells to optimize fuel cell performance, but a robust sensor has not been developed. Direct Methanol Fuel Cells (DMFCs) are the most
common direct fuel cells and are being actively
developed for laptop computers, digital cameras,
battery recharging stations and digital assistants
with initial product launches anticipated in 2008.
Methanol is relatively inexpensive, easy to handle
transport and store. It is critical from an
economic standpoint that the sensor work over a
wide temperature range, be relatively small so that
it can be embedded in a portable system and is
capable of being manufactured at a low cost.

2. EXPERIMENTAL

The frequency of the microtube and a thin film
resistor are used to provide a fluid density and
temperature output, which are employed to
produce a chemical or methanol concentration.
Fig. 2 shows the resonant microtube. This tube is

driven electrostatically while the tube’s vibration
frequency is sensed capacitively. In this
photograph the silicon cap which seals the
resonator in vacuum has been removed. This
silicon cap contains a getter to reduce the cavity
pressure. The cap is sealed to the glass wafer via
wafer-to-wafer bonding. Fluid is admitted to the
microtube through holes in the back of the
metalized glass chip [1-3].

Fig. 2. A decapped, MEMS chip, on a finger
tip, showing the microtube and metal
pattern.

Fig. 3. Methanol to water concentration
as a function of density and temperature.

Fig. 3 shows how the methanol to water
concentration varies with both density and
temperature. A comparison with alternate
methanol concentration sensing technologies like
ultrasonic and refractive index measurements is
made in Fig. 4. The refractive index varies very
little as a function of methanol concentration. An
ultrasonic, speed-of-sound sensor does have a
higher sensitivity to methanol concentration
changes at concentrations above 40% than
density, but has a flat portion in the sensitivity
curve and then a reversal in slope at lower
methanol concentration values, where DMFCs
operate. Density measurement appears to be the
best available means of sensing methanol concentration for DMFCs.

Methanol concentration was measured using the MEMS device over the typical consumer electronics temperature range of use, 10°C to 50°C. Different methanol to water concentrations were prepared ranging in concentrations from 0.6 Moles/liter up to 3 Moles/liter and is shown in Fig. 5. For other applications such as testing petrochemicals, this MEMS resonating sensor has been operated at 150°C. To accommodate higher flow rates a compact, by-pass package design has been developed, with a transition to low-cost plastic electro-fluidic packages as the final goal. The novel by-pass package design opens this technology up to many high-flow rate applications [5].

A benefit of using the mass-based density sensor technology over an electrochemical method is the virtual immunity of the technique to low concentrations of DMFC reaction by-products. In addition to low speed, electrochemical methanol concentration sensors will have problems with chemical impurities. The MEMS-chip based density sensor has been used to test the concentration of sulfuric acid solutions, solvents and petrochemicals with no change in sensor performance [1]. Formic acid is a common DMFC by-product. Typical DMFC systems will have formic acid concentrations of up to 100 ppm. Very little impact on formic acid concentration was noted between 50 ppm and 100 ppm. At 1000 ppm the relatively dense (1.222 gm/cc for formic acid versus 0.791 gm/cc for methanol at 20°C). impurity began to introduce a slight error in the mass-based measurement method. Fig. 6 shows another plot of seven methanol concentrations, each with an additional 1000 ppm of formic acid added to the solution. Again the sensor output over temperature is consistent at all concentration levels between 0.6 Moles/liter and 3 Moles/liter with the addition of the formic acid impurity.

Since this sensor is mass-based it can be applied to other fuel cells types and fuels, including active ethanol, ethylene glycol and formic acid [6] direct fuel cells. The technology is also being applied the ethanol and butanol

![Fig. 5. Methanol concentration test output of the sensor over temperature and concentration.](image1)

![Fig. 6. Methanol concentration plot over temperature with 1000ppm of formic acid present.](image2)

Table 1. Fuel monitoring using a density measurement.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Density Range (gm/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>0.725-0.775</td>
</tr>
<tr>
<td>E85</td>
<td>0.775-0.782</td>
</tr>
<tr>
<td>Diesel</td>
<td>0.822-0.860</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>0.860-0.900</td>
</tr>
</tbody>
</table>
quality monitoring as well as biodiesel fuel blending [7,8]. Water absorption is a problem for ethanol distillation and density measurement is an excellent method of checking for water contamination. Table 1 shows how density can be monitor the type of fuel employed. E85 is an 85% ethanol-15% gasoline fuel. The fuel type can clearly be distinguished using a density measurement.

3. CONCLUSIONS

A mass-based methanol concentration sensor for controlling the methanol to water concentration in a DMFC system was described. The sensor is based on a microfluidic chip that employs a resonant microtube and on-chip platinum temperature sensor to measure the density of a fluid. Using the density and temperature output the MEMS methanol concentration is determined. The sensor was found to have a linear output between temperatures of 10°C to 50°C at methanol concentrations of between 0.6M and 3M. In tests with petrochemicals the sensor operated at 150°C. Formic acid contaminants under concentrations of 100 ppm did not affect the accuracy output of the methanol sensor. The mass-based density sensor was found to perform better over temperature than methanol sensors based on refractive index or ultrasonic speed of sound measurements. The density sensing approach meets the performance requirements with respect to methanol concentration, temperature and resistance to chemical impurities required for an embedded DMFC application. A MEMS-based density sensor also has application to petrochemicals and biofuels including ethanol, butanol and biodiesel.

4. REFERENCES


