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Recent advances in methanol concentration sensor for DMFC

R. Govindarasu[1,*], R. Parthiban[1], P.K. Bhaba[2] and S.Sundar[1]

[1]Department of Chemical Engineering, Sri Venkateswara College of Engineering, Sriperumbudur, India.

[2]Department of Chemical Engineering, FEAT, Annamalai University, Annamalai Nagar- 608 002. India.

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ABSTRACT

Power generation efficiency of a DMFC depends on the concentration of methanol solution, hence analysis on the development of methanol concentration sensor is getting importance. Measurement of methanol concentration using various techniques namely MEMS, Capacitive type, Dielectric constant and piezoelectric crystal are critically analyzed in this paper. Based on the specific requirement, a particular type of methanol concentration sensor is utilized for the defined power output of DMFC.

Introduction

Direct-methanol fuel cells are a subcategory of proton-exchange membrane fuel cells in which methanol is used as the fuel. In comparison with hydrogen-fuelled solid Polymer Electrolyte Membrane Fuel Cells (PEMFCs), DMFCs using methanol directly as a fuel to convert chemical energy to electric power. As electrochemists' dream in the 20th century, DMFC is regarded as one of most promising energy technologies in the 21st century (1). Efficiency is presently quite low for these cells, so they are targeted especially to portable applications, where energy and power density are more important than efficiency(16). Direct methanol fuel cells are the technology of choice for many portable power applications and have advantages like a liquid fuel, quick re-fuelling, low cost of methanol and the compact cell design making it suitable for various potential applications and no parasitic power losses the performance of DMFC that is power generation efficiency of DMFC depends on the concentration of methanol(19,18).

DMFC performance can be impacted by the methanol to water concentration (2). Hence it is necessary to determine this methanol concentration in fuel cell. Various techniques that are available for detecting the methanol concentration is discussed in this paper and the techniques are embedded methanol sensor (microchip) based on MEMS technology, capacitive sensor based on impedance spectrum analyzer, detecting dielectric constant and conductivity of the ethanol solution using shear horizontal surface acoustic wave (SH-SAW) and piezoelectric crystal. The performance of these sensors depends on their sensitivity to concentration, temperature, other impurities and by-products evolved during DMFC operation. Based on the specific requirement, a particular type of methanol concentration sensor is utilized to sense the concentration of methanol to produce optimum performance of DMFC. Basically, the direct methanol fuel cell is a proton exchange membrane fuel cell that is fed with an aqueous solution of methanol. The two catalytic electrodes where the methanol oxidation (anode) and the oxygen reduction (cathode) occur are separated by a membrane which conducts protons from anode to cathode, while other compounds diffusion is blocked. The combination of electrodes and membranes is called Membrane Electrode Assembly (MEA). Each electrode is made of a gas diffusion layer and a catalytic layer. The state of the art in membranes is Nafion. Aqueous methanol is fed at the anode side. It diffuses through the diffusion layer to the catalytic layer where it is electrochemically oxidized into carbon dioxide, protons and electrons. Protons formed during this reaction diffuse through the Nafion membrane to the cathode catalytic layer.

They participate in oxygen reduction to form water at cathode side. Oxygen may be pure or in the form of air. Electrons are collected by graphite bipolar plates which are the two poles of the cell. Water is consumed at the anode in the reaction; pure methanol cannot be used without provision of water via either passive transport such as back diffusion (osmosis), or active transport such as pumping. Currently, platinum is used as a catalyst for both half-reactions (17). This contributes to the loss of cell voltage potential, as any methanol that is present in the cathode chamber will oxidize. At anode, the methanol is oxidized into carbon dioxide and six protons plus six electrons. The six protons formed are react at the cathode with oxygen to form water.

Methanol concentration sensors

The concentration of methanol solution in the direct methanol fuel cell chamber is monitored with a methanol concentration sensor (7). The sensor is placed between the anode and cathode beneath the membrane electrode assembly. Feedback is provided to the control valve of the pre-pressurized methanol and water reservoirs by the sensor. When the concentration is below 3%, the valve is opened, and the pure methanol is injected from the reservoir into the methanol chamber. A uniform concentration of methanol in the fuel cell chamber is maintained by the high diffusivity of methanol and by the mixing driven by the buoyant co_2 bubbles. A basic diagram showing the methanol concentration sensor and the placement of methanol concentration sensor in direct methanol fuel cell is shown in the fig 1.

Tele:
E-mail addresses: govind.nitt@gmail.com

MEMS based sensors

This sensor is based on Micro Electro Mechanical Systems (MEMS) technology. It is a mass based sensor and can be applied to other fuel cells. As the mass of total tube/liquid system increases the vibrational frequency decreases.

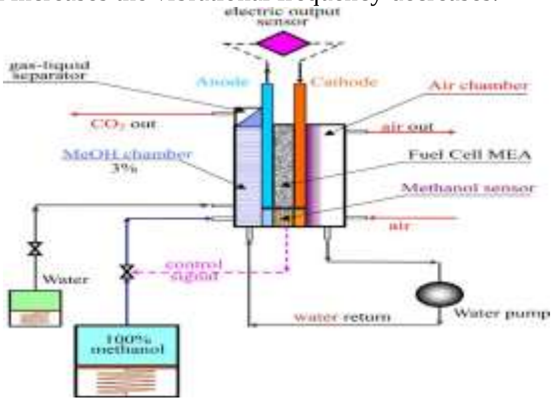

Fig. 1 Methanol concentration sensor in DMFC [3]

This is the basic principle used to determine the concentration of methanol. The resonant output will be higher for higher methanol concentration. It consists of a micro fluidic chip that employs a resonant micro tube and on-chip platinum temperature sensor to measure density of a fluid. The concentration of methanol is determined using density and temperature output. The MEMS fabrication uses a combination of plasma and wet etching, photolithography, along with wafer bonding to form the micro fluidic chips.

Fig 2. Uncapped microtube resonator chip (4)

Fig 2, shows the uncapped micro tube resonator chip. The silicon tube is anodically bonded to glass. This glass wafer has metal electrodes and runners to carry electric signals. A thin film metal layer is used as an on-chip temperature sensor. The resonator is finally vacuum packaged at wafer level using thin film getter to reduce external damping of vibrating micro tube (4). The MEMS chip requires external electronics to amplify the signals and drive the micro tube into resonance. The tube is driven into resonance electrostatically, motion is sensed. The signal is processed to get methanol concentration. Fig 3 shows that a predictable slope in the density value was observed with changing methanol concentration

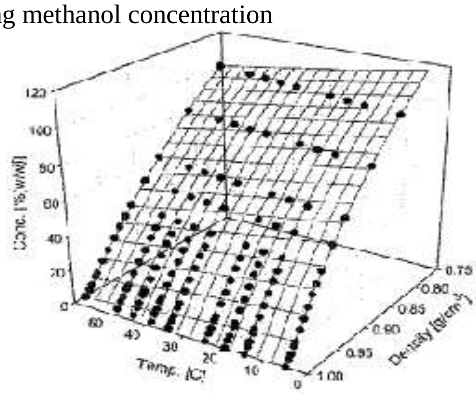

Fig 3 Density-temperature-concentration 3D plot [4]

A basic methanol concentration sensor was calibrated using the above plot. A major benefit of using this technology is the virtual immunity of the technique to low concentration DMFC reaction by products. Fig 3 gives the methanol concentration sensor output as a function of temperature. It shows that the sensor output for fixed concentrations is flat with respect to temperature. A basic methanol concentration sensor was calibrated using density-temperature-concentration plot. Using the density and temperature output the methanol concentration is determined.

A major benefit of using this technology is the virtual immunity of the technique to low concentration DMFC reaction by products. The MEMS chip based density sensor has been used to measure the concentration of sulphuric acid, solvents and petrochemicals with no change in sensor performance (5). Formic acid is a common by product of DMFC and formic acid contaminants below 100ppm does not affect the accuracy of sensor.

Capacitive concentration sensors:

Capacitive concentration sensors are based on impedance spectrum analyzer electronics (impedance spectroscopy) that is suitable for use under process conditions. The measurement approach uses impedance spectrum analyzer electronics and is suitable for use under process conditions. Earlier determining methanol concentration by measuring the permittivity of liquid has been a difficult task. But by introducing impedance analyzer concept compact sensor electronics with high measurement resolution has become available (6) calibration of the measurement system for the required temperature range is done with selected reference liquids. It is relatively inexpensive and less bulk compared to any other sensors and is more suitable for commercial applications. This dielectric impedance spectroscopy can be performed over a wide range of temperatures and requires cheap electronics that is feasible for mass production.

The basic principle involved in measurement of methanol concentration involves application of electric field to pair of sensing electrodes. The liquid feed flows through the electrodes and influences permittivity between these electrodes. The capacitance is then measured from which complex dielectric constant (€) is calculated. The dielectric spectrum can be obtained by sweeping the frequency of electric field. The advancement in sensor design includes usage of PTFE shell as electrode fixture instead of stainless steel which avoids the use of sealant. The schematic diagram of capacitive concentration sensor showing sensing electrodes, guard electrodes and PTFE shell is given in the fig 4

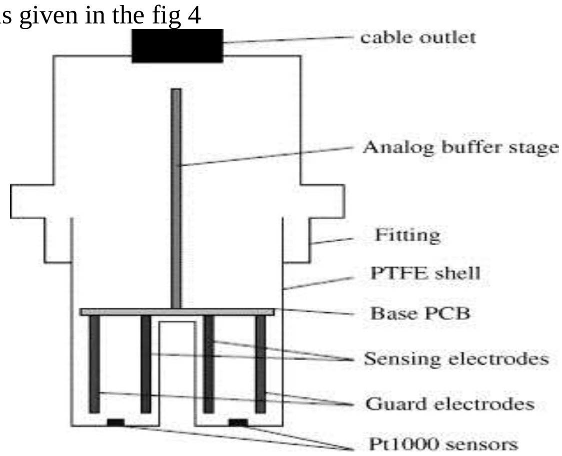

Fig 4. Design principle of capacitive sensor (6)

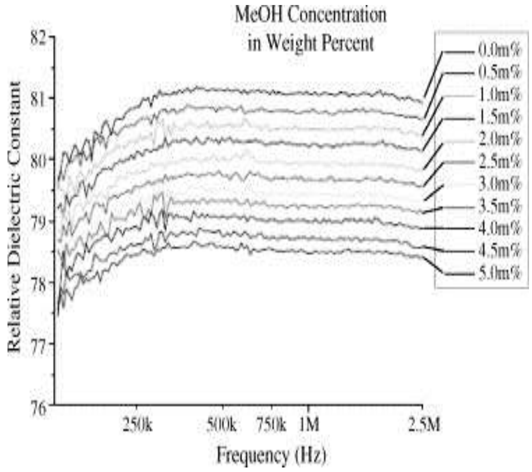

Fig 5. Measured dielectric spectra reflecting methanol concentration (7)

Fig 5 represents the change in dielectric constant with respect to varying frequency of electric fields for different concentrations of methanol in (weight percent). The drop in relative dielectric constants for lower frequencies (approx below 1 mhz) is due to the conductivity of contaminants that are present in feed. Hence for determining the mass of methanol frequency above 1 mhz is chosen. The results show a good reproducibility and accuracy of the acquired dielectric constant. The capacitive sensors can be used for wide range of temperatures and they give results with more accuracy.

SH-SAW concentration sensors

Surface acoustic wave (saw) has wide range of application not only in filters, resonators but also in sensors and actuators (8,14). When liquid phase is realized then shear horizontal surface acoustic sensor must be used. The detection in SH-SAW sensors are based on electrical and mechanical perturbations and therefore SH-SAW sensors are capable of measuring both mechanical and electrical properties of liquid with high sensitivity. The viscosity and density is detected by mechanical perturbation and the dielectric constant and conductivity is detected by electrical perturbation. A 36° y-cut x-propagating litAO_3 substrate is used as SH-SAW sensor substrate. On the substrate, inter-digital transducers and sensing surface are designed and fabricated. The SH-SAW sensor consists of two saw delay line. One of the propagating surfaces of sensor is metallized while other is left free. When sensor is loaded the mechanical perturbations occur at shorted surface, while free surface is perturbed electrically (9)

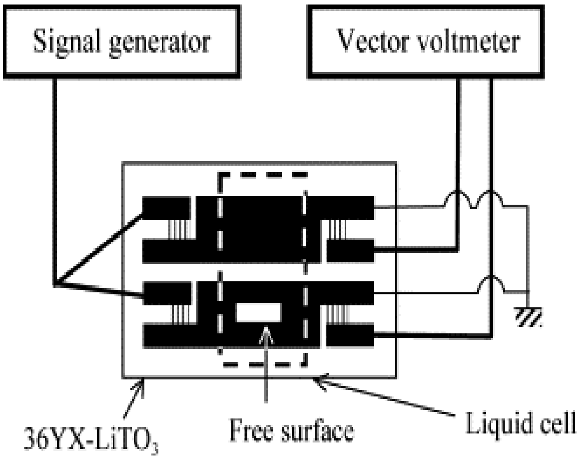

Fig. 6 SH-SAW sensor schematic diagram (10)

The differential signals between the surfaces is detected and digital outputs from the sensor is monitored using voltmeter. The phase difference and the amplitude ratio between channels is measured. The temperature of the set up is varied using high-temperature chamber keeping distilled water at 25°c as reference. The same procedure is carried out for different methanol concentrations. The schematic diagram of SH-SAW is given in fig 6.

The experimental result of methanol concentration measuring phase shift is shown in fig 7. The lines in the plot are best-fit lines. Linear relationship between concentration and phase shift is obtained. The concentration resolution is estimated on the basis of time stability. Fig 8 shows methanol concentration sensor output as a function of temperature. For different concentrations the plot is obtained. It shows that as the methanol concentration increases phase shift increases due to permittivity. it also shows that even at very high temperatures, the SH-SAW sensor measures methanol concentration with high sensitivity.

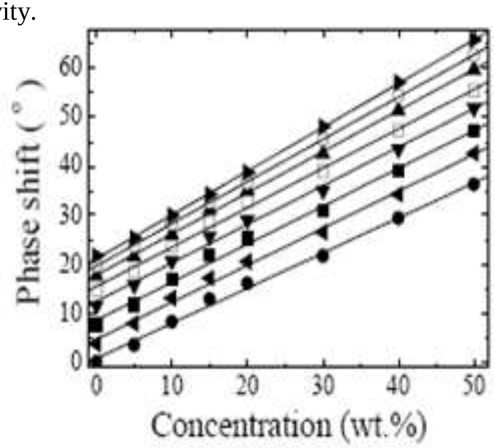

Fig 7 Experimental results of phase shift between reference and samples (9)

SH-SAW sensors are most suitable for high temperature applications and it has excellent potential for liquid characterisation (10). The results indicate that the methanol concentration can be measured when the temperature is lower than 60 °c. If the temperature is higher than 60 °c, bubbles are generated on the sensor surface and the sensor is influenced by them. A liquid flow system was demonstrated to reduce the influence of bubbles (11). SH-SAW sensors are most suitable for high temperature applications and it has excellent potential for liquid characterisation (12). Fig 8 explains the structure of AO-mode lamb wave sensor.

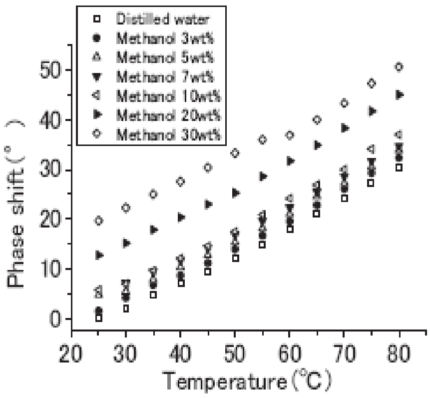

Fig 8. Experimental result of methanol concentration measuring phase shift (8)

Piezoelectric crystal concentration sensors

Piezoelectric crystal sensors are passive solid-state electronic devices, which can respond to changes in temperature, pressure, and most importantly, to changes in physical properties at the interface between the device surface and a foreign fluid or solid. Such changes in physical properties include variations in interfacial mass density, elasticity, viscosity, and layer thickness (13) this type of sensor operates by observation of the propagation of an acoustic wave through the solid-state device. Sensing is achieved by correlating acoustic wave propagation variations to the amount of methanol captured at the surface and then to the amount or concentration of methanol present in the sample exposed to the sensor, or to the changes of physical properties of interfacial thin films.

A Quartz Crystal Microbalance (QCM) and a shear-horizontal (SH) Surface Acoustic Wave (SAW) device (14) use shear vibration, which does not radiate a bulk wave into liquid in contact, and thus are available for liquid characterization. However, both QCM and SH SAW device are basically fabricated on piezoelectric single crystal wafers of special cuts. This limits integration with Si-based devices. Methanol concentration is measured through the propagation of surface wave at the boundary between a piezoelectric crystal and methanol.

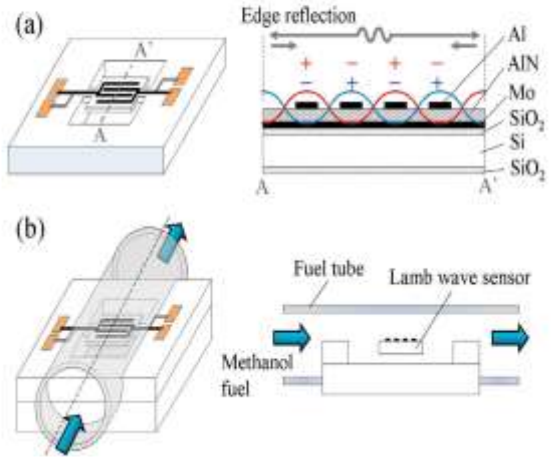

Fig 9. Structure of the AO-mode lamb wave resonator (15)

Recently, lamb wave, an acoustic wave propagating in a thin plate was used to measure methanol concentration. Lamb wave is generated using a suspended piezoelectric thin film such as ALN and pzt deposited on Si wafers. The resonator is composed of a suspended $Si/SiO_2/ALN$ composite membrane with metal electrodes. By applying ac signal to the top IDT (Inter Digital Transducer), lowest anti-symmetric a0-mode lamb wave is generated, and it is confined by the edge reflectors as a standing wave the concentration of methanol is measured by resonant frequency shift, i.e. Phase velocity shift, due to mass loading effect.

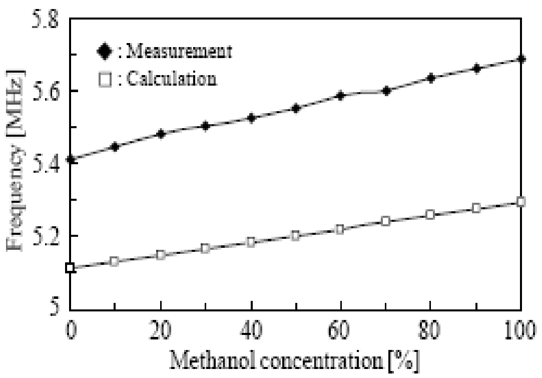

Fig 10. Measured and calculated relationship between methanol concentration and frequency shift (1)

Fig 9 gives the relationship between methanol concentration and frequency shift. The Temperature Coefficient of Frequency (TCF) was found to be –31 ppm/k and might approach zero by leaving a 1 µm thick buried oxide (box) layer.

The fabricated sensor showed an almost constant sensitivity of 510 ppm/% in methanol concentration from 0 % to 100 %,. Additionally, the presence of edge reflectors confines the lamb wave to the anti symmetric AO mode thereby reducing the size of the sensor, hence making the sensor a viable choice for measurement of methanol concentration in DMFCs (15)

Conclusion

Direct methanol fuel cell (DMFC) has been identified as the most promising candidate to replace batteries in micro-power applications. Since power generation efficiency of the DMFC depends on the concentration of methanol solution and hence it is necessary to detect the concentration of methanol in direct methanol fuel cell operation. The MEMS technology based sensors though less bulk and applicable for wide range of temperature, it is insensitive to common impurities. Capacitive sensors on the other hand in addition to being less bulk, employ cheap and feasible electronics resulting in lower costs. SH-SAW sensors are most applicable for high temperature operations and it has excellent potential for liquid characterization. A brief outline on main sensors for detecting methanol concentration in DMFC has been described in this paper. Further research on development of more efficient methanol concentration sensors for dmfcs is in progress and paves way for better performance of dmfcs.

Acknowledgements

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References

[1] C. Limy, J.-M. Leger and S. Srinivasan, Direct Methanol Fuel Cells: from a twentieth century electrochemist's dream to a twenty-first century emerging technology, in: J.O.M. Bockris, B.E. Conway, r.e. White (eds.), modern aspects of electrochemistry, kluwer academic publishers/plenum press,new york, pp. 53–118 (2001)

[2] J. Cruickshank, k.Scott, "The degree and effect of methanol crossover in the direct methanol fuel cell, J. Power sources 70 (1998)

[3] Shi-Chune YAO , Xudong Tang , Cheng-Chieh Hsieh , Yousef Alyousef ,Michael Vladimer, Gary K. Fedder, Cristina H. Amon, "Micro-Electro-Mechanical Systems (MEMS)-based micro-scale direct methanol fuel cell development", energy 31 636–649(2006)

[4] D.Sparks,K.Kawaguchi, M.Yasuda , D.Riley, V. Cruz, n. Tran, a. Chimbayo, N.Nafaji, "Embedded MEMS-based concentration sensor for improved active fuel cell performance",14th international conference on solid-state, actuators and microsystems, 1911-1914 (2007)

[5] D.Sparks, S.Smith, R.Schneider, J.Cripe.S.Massoud-ansari, a.Chinmayo, N.Nafaji, "A variable temperature resonant density sensor made using an improved chip level vacuum package", sens actuators. A 107 (2003)

[6] Doerner.S.; Schneider,T; Schroder, J; Hauptmann P.: universal impedance spectrum analyzer for sensor applications, ieee sensors, totonto (canada), proceedings, pp.596-599,(2003)

[7] Doerner, S.; Schultz, T.; Schneider, T.; Sundmacher, K.; Hauptmann, P.; ,Capacitive sensor for methanol concentration measurement in direct methanol fuel cells (DMFC), sensors, proc ieee , 639- 641 (2), (2004)

[8] Hengbing ZhAO, Jun Zhang, Hajijang Wang, David P. Wilkinson, caikang elton gu, journal of power sources volume 159 issue 1, 13 september (2006)
[9] Kondoh, Jun, Tabushi, S0ohei; Matsui Yoshikazu, Shiokawa, Showko, Development of Methanol Sensor using an shear horizontal surface acoustic wave for direct methanol fuel cell, (2008)
[10] Endo, Saburo; Kondoh, Jun; Sato, Katsuhiko; Sawada, NAOmi Japanese journal of applied physics 51(7), 07gc19-07gc19-5 (2012).
[11] Satoru Mikuni, Jun Kondoh, Tomati Morikawa, NAOmi Sawada, and Tohru Ohta, Develpopment of methanol sensor using SH-SAW for direct methanol fuel cells, november (2009).
[12] Jun Kondoh, Yusuke Okiyama, Satoru Mikuni, Yoshikaza matsui, makato nara, tpshimasa mori and hiromi Yatsuda, “development of shear horizontal surface acoustic wave sensor systems for liquids with floating electrode unidirectional transducer”, japanese journal of applied physics,47(5), 4065–4069 (2008)
[13] Sang-mok Chang, Hiroshi Muramatsu, Chikashi Nakamura, Jun Miyake,] “the principle and application of piezoelectric crystal sensors”, materials science and engineering: c 12(1–2),111–123 (2000)
[14] D.S. Ballantine jr.et al., acoustic wave sensors, theory, design and physico-chemical applications, san diego: academic press, (1997)
[15] Hino, r.; Esashi, M.; tanaka, s.; , "antisymmetric-mode lamb wave methanol sensor with edge reflectors for fuel cell applications,", ieee 23rd international conference on micro electro mechanical systems (MEMS),871-874 (2010)
[16] M.Z.F. Kamaruddin, S.J. Kamarudin, w.r.w. Daud, m.s. Masdar, an overview of fuel management in direct methanol fuel cells, renewable and sustainable energy reviews, volume 24, august 2013, pages 557-565
[17] M. Stähler, A. Burdzik, calibration method for carbon dioxide sensors to investigate direct methanol fuel cell efficiency, journal of power sources, volume 262, 15 september 2014, pages 147-161
[18] L. Arun Kumar, P.Karthikeyan, “An experimental investigation of proton exchange membrane (PEM) fuel cellat different operating conditions”, Elixir Renewable Energy Engg. 70 (2014) 24142-24145
[19] D.S. Falcão, Y.B. Oliveira, C.M. Rangel, A.M.F.R. Pinto, review on micro-direct methanol fuel cells, renewable and sustainable energy reviews, volume 34, june 2014, pages 58-70