Liquid methanol concentration sensors for direct methanol fuel cells

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Abstract

Liquid-fed direct methanol fuel cells (DMFCs) are one of the most promising candidates for portable power electronics and automotive applications due to their potentially high-energy density, simple storage, and distribution of the fuel. The concentration of methanol in the fuel circulation loop of a DMFC system is an important operating parameter, because it determines the electrical performance and efficiency of the system. The methanol concentration in the circulating fuel stream is usually measured continuously with a suitable sensor for the purpose of maintaining optimal power and efficiency in the DMFC system. Various methods of sensing methanol concentration have been proposed over the past decade. This paper reviews these methanol concentration sensors for DMFCs, which are generally classified into two groups: electrochemical and physical. The construction and operating principles of each sensor, as well as its advantages and disadvantages, are described. The sensorless methods for controlling the methanol concentration are introduced briefly. Finally, the perspective on the future of methanol concentration sensors is discussed.

1. Introduction

New generations of mobile devices offer various advanced features, which require device makers to search for more reliable and longer lasting power sources beyond what are currently available. Micro and small polymer electrolyte membrane fuel cells (PEMFCs) are one of the most favoured options for new mobile devices. In a PEMFC, hydrogen and methanol are the common fuels. Miniaturization of the hydrogen PEMFC, however, suffers significant limitations with respect to hydrogen storage. Liquid-fed direct methanol fuel cells (DMFCs) have higher energy density and, therefore, are considered to be a more promising candidate for mobile power applications. Methanol is a liquid at room temperature and easy to handle; it has a high-energy density ($3800\,\text{kcal}\,\text{l}^{-1}$) compared to hydrogen at 360 atm. ($658\,\text{kcal}\,\text{l}^{-1}$), and it is cheap. Furthermore, the liquid-

fed DMFC system does not require a fuel processor and consists of a small number of components, permitting simple, compact designs. All of these factors make it a promising power source.

The operation of DMFCs is based on the direct oxidation of an aqueous liquid solution of methanol at the anode and concomitant reduction of oxygen at the cathode:

$$CH_3OH + H_2O \rightarrow CO_2 + 6e^- + 6H^+ \quad \text{(anode)}$$

$$1.5O_2 + 6e^- + 6H^+ \rightarrow 3H_2O \quad \text{(cathode)}$$

$$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O \quad \text{(overall cell)}$$
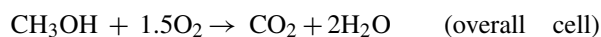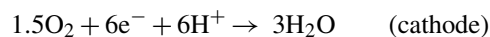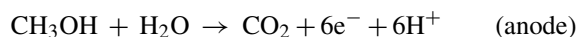
The methanol concentration in the fuel to be fed to the fuel cell plays a significant role in keeping a predetermined power output from the fuel cell [1]. When the methanol concentration is below a predetermined value, the power output is low and unstable, and when the methanol concentration is above that predetermined value the output power may be obtained, but

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crossover is an issue. The crossover of methanol from the anode to the cathode through the membrane electrolyte occurs because of the high solubility of methanol in the membrane electrolyte, electro-osmosis, and diffusion, and results in a significant loss in efficiency. Therefore, the fuel needs to be fed to the fuel cell with its methanol concentration held consistent within a predetermined concentration range.

In all, for liquid-fed DMFC systems with recirculation of the analyte and cathode product water, the closed-loop control of methanol concentration is required for long-term stable operation. This requires a concentration sensor to provide feedback for the controlled injection of makeup methanol into the recirculated stream. The requirements for the methanol concentration sensor can be summarized as follows:

- wide methanol sensing range of up to 5 M,
- high resolution and accuracy around the operating point,
- in-line operation and rapid response (usually a fraction of a second for closed-loop control is acceptable),
- tolerance to metallic ion impurities such as Fe^{3+} and Cu^{2+},
- ideally, tolerance to the dissolved CO_2 and the CO_2 bubbles,
- long-term stability,
- wide range of operating temperatures ($10\,^\circ C$ to $85\,^\circ C$ in most cases), and
- amenable to miniaturization for tight packaging and system integration.

Up to now, several methods of measuring methanol concentration in aqueous solution have been considered. None of these methods have satisfied all of the desired criteria. In this short review paper, all the methods can be divided into two main groups according to their sensing principles: (i) electrochemical methods, in which the methanol oxidation current under a constant applied voltage, or one of the operating characteristics of the sensing fuel cell is measured, and (ii) physical methods, in which physical properties such as density, viscosity, infrared light transmittance, dielectric constant, refractive index, heat capacity, or the speed of sound, are measured. For the reader's convenience, Section 2 introduces various concentration definitions and gives their conversion relationships, since the unit of concentration differs, depending on the publication. The operating principles of electrochemical sensors and physical sensors are described, and their advantages and disadvantages are analyzed in Sections 3 and 4, respectively. Section 5 briefly introduces the sensorless methods for adjusting the methanol concentration.

2. Concentration definition and conversion

There are numerous ways of expressing solution concentrations according to their applicable environments [2]. With respect to the aqueous methanol solution in DMFCs, the three most common concentration units are: molarity, mole fraction, and volume fraction. The two other units, molality and weight percent, are rarely used. It is important to clarify the different definitions of these concentration units and give the relationship to convert from one concentration unit to another. The defini-

tions of different concentration units are given in the expressions (1)–(5).

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}} \tag{1}$$

$$\text{Molality (m)} = \frac{\text{moles of solute}}{\text{kg of solvent}} \tag{2}$$

$$\text{Mole fraction } x_B = \frac{\text{moles of solute B}}{\text{total moles of solution}} \tag{3}$$

$$\text{Weight percent (wt\%)} = \frac{\text{mass of solute}}{\text{total mass of solution}} \times 100 \tag{4}$$

$$\text{Volume fraction (vol\%)} = \frac{\text{volume of solute}}{\text{total volume of all components}} \times 100 \tag{5}$$

Different concentration expressions can be converted based on the molar mass of both solute and solvent and the density of the solutions. The conversion relationships between the molarity of a methanol concentration and the mole fraction, as well as the volume fraction, weight percent and molality of methanol concentration in aqueous solution at $20\,^\circ C$ are calculated and plotted in Fig. 1.
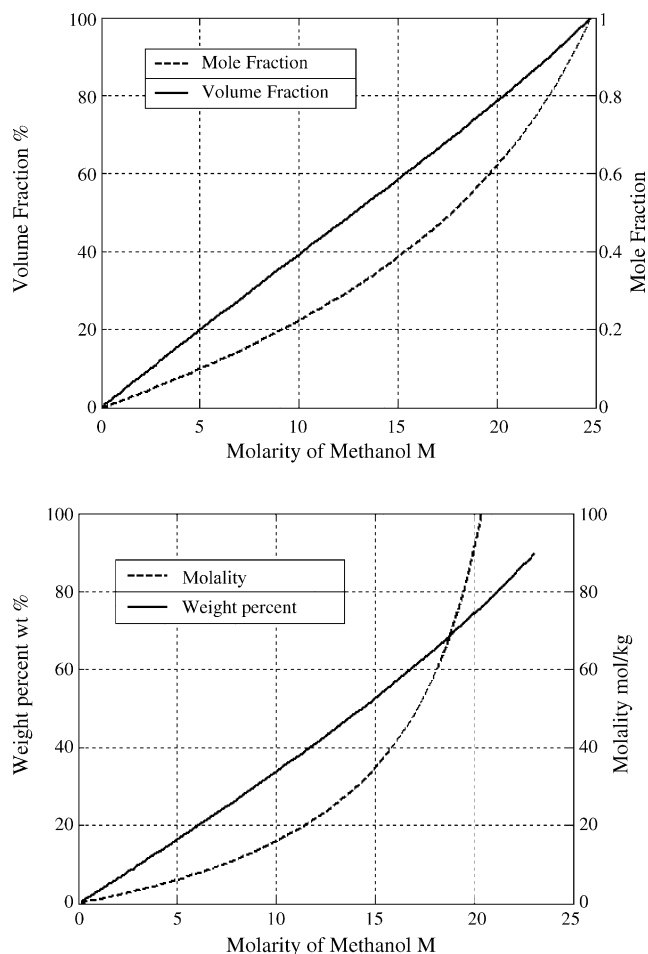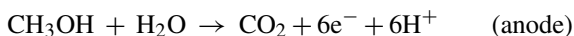

Fig. 1. Methanol concentration expression conversion at $20\,^\circ C$.
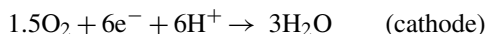
3. Electrochemical sensing methods

The sensing principle of electrochemical methanol sensors is generally based on the electro-oxidation of methanol to carbon dioxide on platinum/ruthenium (Pt/Ru) anode catalysts and the concomitant reduction of oxygen or protons on platinum (Pt) cathode catalysts.

$$CH_3OH + H_2O \rightarrow CO_2 + 6e^- + 6H^+ \qquad \text{(anode)}$$

For the oxidation current type sensor:

$$6H^+ + 6e^- \rightarrow 3H_2 \qquad \text{(cathode)}$$

For the fuel cell-based sensor:

$$1.5O_2 + 6e^- + 6H^+ \rightarrow 3H_2O \qquad \text{(cathode)}$$

The fundamental construction of the electrochemical sensor is the same as a conventional polymer electrolyte membrane-based direct methanol fuel cell, as shown in Fig. 2. The sensing cell consists of a polymer electrolyte membrane (usually Nafion) coated with Pt/Ru (anode) and Pt (cathode) on each side, respectively. A porous electrode backing substrate (diffusion layer) such as porous carbon fibre paper, is hot-pressed onto each side of the coated membrane, forming a membrane electrode assembly (MEA). The anode perforated conductive plate serves as a mechanical support and a current collector, and also acts as a fuel supplier. The cathode perforated conductive plate supports the cathode side of the MEA and is configured for air access to the cathode side or hydrogen by-product exhaust from the cathode, and also serves as a current collector. A dilute aqueous methanol solution is fed into the anode side of the sensor and diffuses through the diffusion layer to oxidize at the anode Pt/Ru–Nafion interface of the MEA. On the cathode side, air diffuses through the perforated plate and diffusion layer to the Pt–Nafion interface of the MEA, where water is produced by
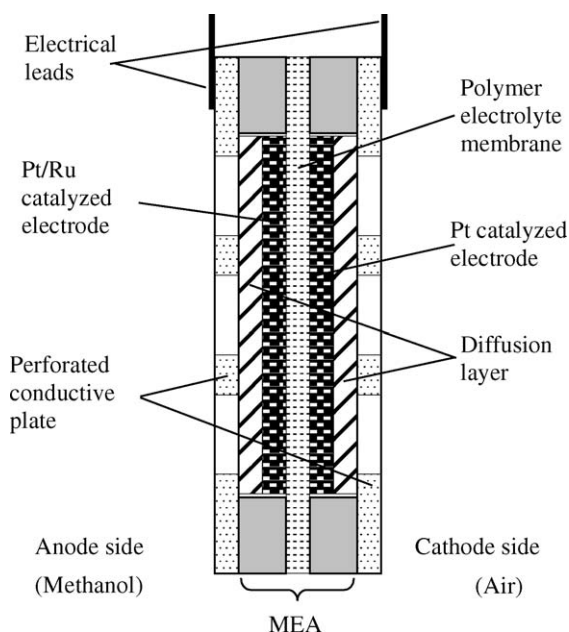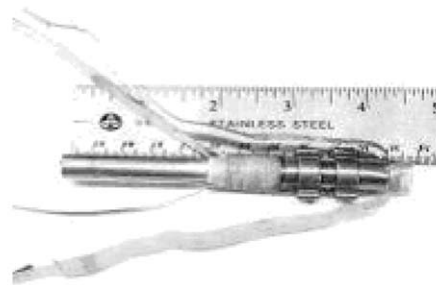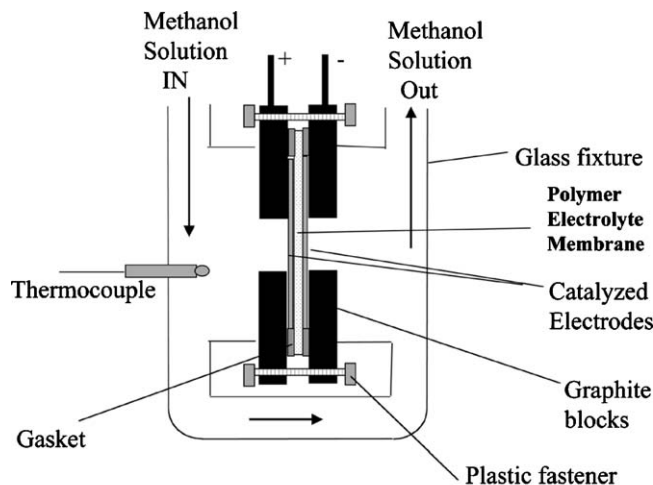

Fig. 3. Details of construction of the methanol sensor, reproduced by permission of The Electrochemical Society, Inc., courtesy of [4,8].

the oxygen reduction reaction for the fuel cell type sensor, or hydrogen is generated by the proton reduction reaction for the oxidation current type sensor.

Depending on the reaction mechanism, the electrochemical sensors function by measuring the methanol oxidation current of a sensing cell under a constant potential (oxidation current type) or by measuring the operating characteristics of a small capacity unit cell such as open-circuit voltage, short-circuit current, or operating voltage under a constant load (fuel cell-based type).

3.1. Oxidation current type sensors

A number of papers discuss the relationship between methanol concentration and the methanol oxidation current [3,4]. These sensors are based on a MEA and frame construction, and the difference in the approach is where the control of the oxidation of methanol takes place. This type of sensor is based on measuring the diffusion-limited concentration-dependent oxidation current for the electro-oxidation of methanol at the Pt/Ru electrode under a constant anodic potential. A number of patents using a similar construction have been issued [5–7]. With the same electrochemical principle a different construction using a flexible, tubular design was reported with a fast response [8]. Some of the different constructions of these methanol sensors are shown in Fig. 3 [4,8]. The sensing cell was dipped into the methanol solution and the current was measured at a given
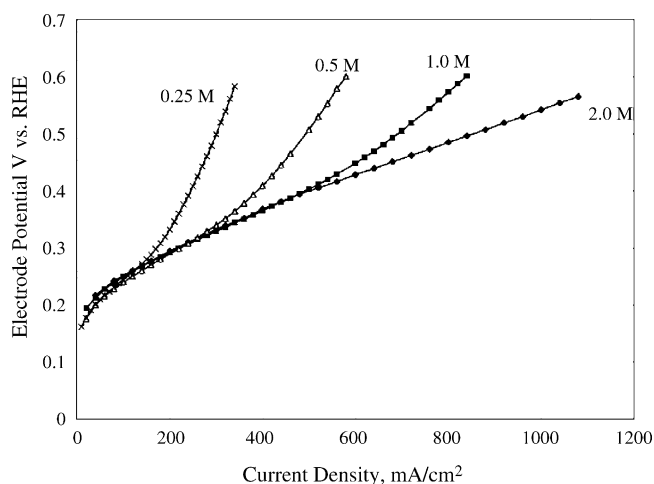

Fig. 2. Schematic of the electrochemical methanol sensor.

Fig. 4. Polarization curve for methanol oxidation, reproduced by permission of The Electrochemical Society, Inc., courtesy of [4].

Fig. 5. Open-circuit voltage of a unit cell vs. methanol concentration, courtesy of [9].

cell voltage to determine methanol concentration. Polarization curves for methanol oxidation at a Pt/Ru–Nafion interface at 90 °C for various concentrations of methanol are shown in Fig. 4 [4]. The potential applied to the electrodes is generally in the range of 0.45–0.65 V. Higher cell potentials may dissolve the ruthenium in the anode catalyst. Cell potentials lower than 0.4 V are not enough to develop a diffusion-limited current at higher methanol concentrations, i.e., greater than 1 M.

This method was alleged to be reliable in the methanol concentration range of 0.01–5 M over a wide temperature range of 0–100 °C. This type of methanol sensor is based on measuring the limited current for methanol oxidation at the anode. Therefore, the sensor only works when the fuel supply is limited by diffusion, and the response of the sensor is relatively slow. For relatively high methanol concentration, this sensor must be operated at higher current densities. Also, an external power source must be applied to the fuel cell to drive the electrode reactions and operate the sensor.

3.2. Fuel cell-based type sensors

The operating characteristics of the DMFC are greatly dependent on the methanol concentration. This fuel cell type of methanol sensor determines the methanol concentration by measuring the open-circuit voltage, short-circuit current, or the operating voltage of a small capacity liquid DMFC loaded with a constant resistor.

In the open-circuit state of a DMFC, the methanol crossover from the anode side to the cathode side is dependent on the methanol concentration. As the methanol concentration increases on the anode side, the methanol crossover rate also increases. It is well known that the output voltage of the fuel cell at open-circuit drops with increasing methanol concentration due to the methanol diffusion through the membrane to the air cathode side, as shown in Fig. 5. For a normal DMFC operation, methanol crossover should be reduced to improve the fuel cell efficiency. However, the fuel cell type of sensor utilizes the methanol crossover and determines the methanol concentration
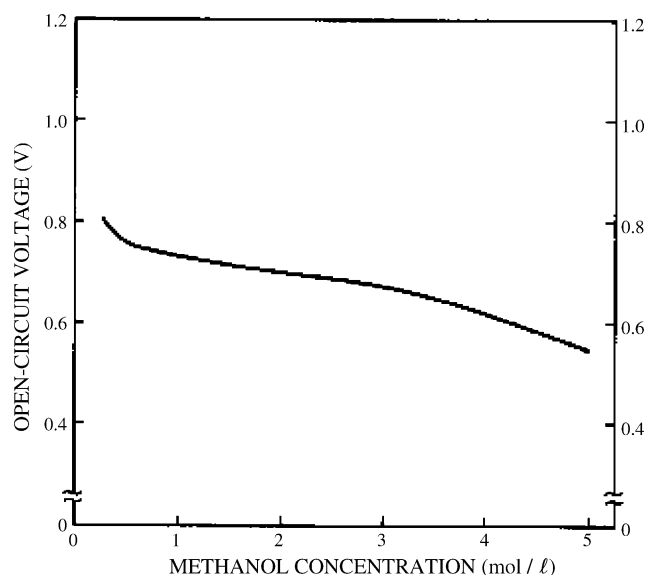
by measuring the reduced open-circuit voltage. In US patent 4,810,597, the open-circuit voltage of a sensing unit cell was measured for determining and controlling the methanol concentration in the range of 0.7–1.2 M with a resolution of 0.1 M at 1 M [9]. A similar patent, US patent 2,003,196,913, also considered sensor application based on methanol crossover [10]. However, the reproducibility of these sensors are not very good.

In US patent 6,488,837 a methanol electro-oxidation anode and an air electro-reduction cathode were shorted together through an external electrical connection [11]. Methanol access from the aqueous solution to the anode catalyst side of the MEA was limited by diffusion through a physical barrier consisting of an aperture opening and a porous medium. In this sensor all the methanol that reaches the anode catalyst is completely consumed at the anode (no cross-over) with concomitant oxygen reduction at the cathode. The measured short-circuit current response shows a good linear relationship with the methanol concentration up to 1 M, as shown in Fig. 6.
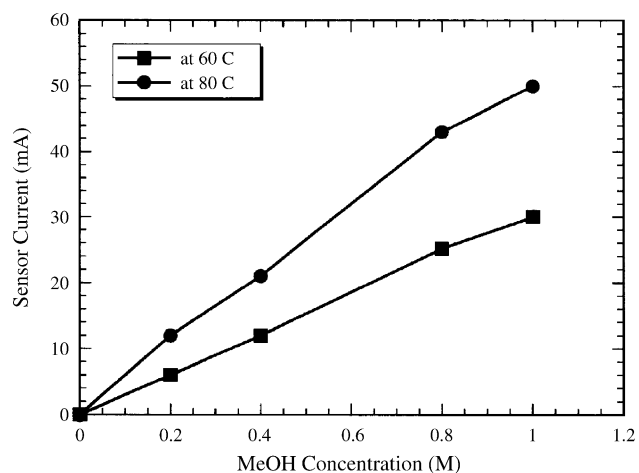

Fig. 6. Short-circuit current vs. methanol concentration, courtesy of [11].
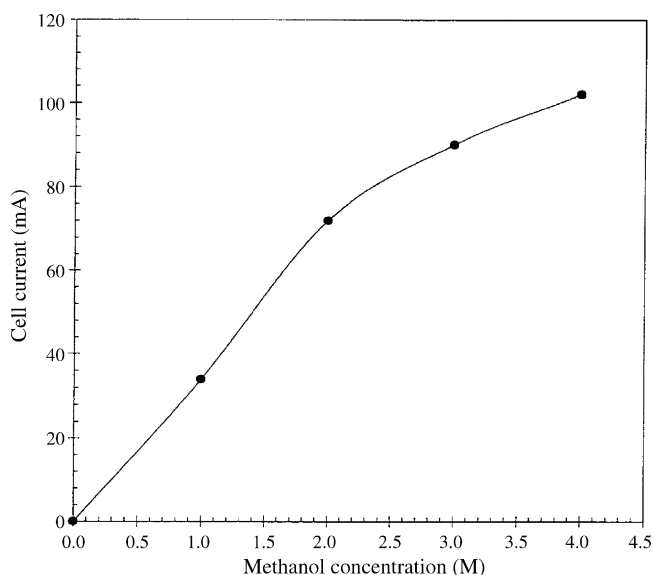
Fig. 7. Fuel cell current vs. methanol concentration, courtesy of [13].

A small capacity sensing DMFC was loaded with a constant resistor of 1 Ω and the voltage across the resistor was used as the measurement signal to determine the methanol concentration in US patent 5,624,538 [12]. A linear dependency of the voltage drop across the resistor in the methanol concentration ranging up to 1 M was claimed. Considering the saturation of the electrical output of the fuel cell-based sensor at high methanol concentrations, US patent 6,527,943 provided a method for avoiding the saturation and extending the measurement range of the sensor [13]. This was done by decreasing the resistor loaded on the fuel cell sensor, and by increasing the air supply. With a suitable choice of load and air stoichiometry, a measurement range for the aqueous methanol solution of up to 4 M was claimed. The measured electrical output of the sensing fuel cell has a linear response to the methanol concentration over the range of 0–2 M, as shown in Fig. 7.

For the fuel cell-based sensor, the cathode of the sensor is exposed to the air and the anode side is exposed to the methanol solution. Currently, this type of sensor is the most competitive type of methanol concentration sensor. However, the main issues of this sensor are the reliability due to the degradation of the membrane and catalyst, and the slow response due to the methanol diffusion, especially at a high methanol concentration range.

3.3. Summary of electrochemical sensors

Electrochemical sensors offer many advantages such as a simple structure, the same fabrication process as for a general DMFC, a simple output in the form of voltage or current, and they are easily miniaturized. However, all electrochemical sensors have issues with degradation of the electrolyte membrane and deterioration of catalysts with operation time. These degradation issues have a number of sources including the over-drying of the membrane and the contamination such as the localization of impurity metallic ions at the catalyst–membrane interface

[14–16]. Further, electrochemical sensors have a narrow measurement voltage range and slow response due to diffusion limitations, and some electrochemical sensors must operate at high current densities for high methanol concentration measurement.

4. Physical sensing methods

The absolute physical properties of aqueous methanol solutions have been investigated and measured in different ways by a number of researchers [17–29]. The physical properties of aqueous methanol solutions, such as density, viscosity, relative dielectric constant, heat capacity, and the sound of speed, vary with the concentration of methanol. Therefore, methanol concentration can be measured with a very high resolution using traditional instruments such as a high-accuracy density meter or a gas chromatograph. However, these instruments are very complicated and cumbersome, and not easily miniaturized. The bulk size and the expensive cost of these instruments limit their application in small and/or commercial DMFC systems.

Recently, researchers have been trying to determine methanol concentration by measuring physical properties with miniaturized systems and micro-electro-mechanical systems (MEMS). In the following subsections, the relationships between the methanol concentration and physical properties are given, and various physical sensors are described.

4.1. Measuring density type sensors

The density of an aqueous methanol solution changes greatly with methanol concentration. Therefore, the methanol concentration can be determined by measuring the density through a density sensor. The relationship between the methanol concentration and the density at room temperature is shown in Fig. 8.

Enoksson and Sparks developed a MEMS density sensor based on the resonant vibration of a U-shaped silicon microtube [30,31]. For this type of sensor, the tube etched on a silicon wafer is continuously loaded with the fluid. A change of the liquid density in the tube changes the mass loading of the vibrating
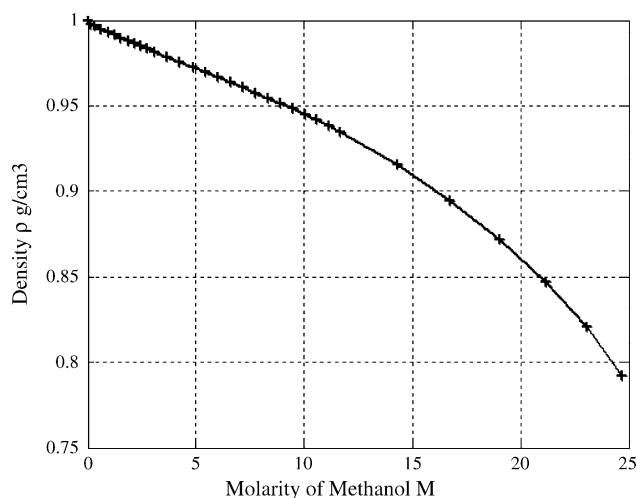

Fig. 8. Density of aqueous methanol solutions vs. molarity of methanol at 20 °C [21].
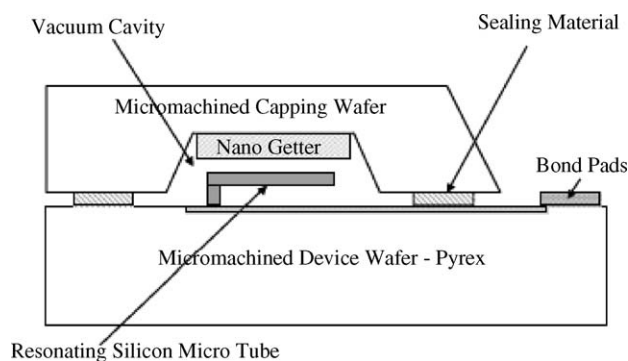
Fig. 9. Cross-sectional illustration of a MEMS density sensor, © 2005 IEEE, courtesy of [30].

tube and thus shifts the resonant frequency of the vibration due to the change in the inertial mass of the vibrating tube system. Variations in the density or concentration of the fluid will be detected through a change in the resonant frequency of the tube. There are two holes in the bottom glass chip that admit fluid into the U-shaped microtube, as shown in Fig. 9. The tube system is excited electrostatically into resonant vibration and its motion can be detected optically using a laser beam focused on the tube, or capacitively using metal electrodes under the tube.

These density/concentration sensors are very effective at monitoring small fluid volumes and low flow rates and can work over the entire concentration range of aqueous methanol solutions. However, the sensitivity of these sensors does not satisfy the requirement of fuel cells, and these sensors are sensitive to CO_2 bubbles in the fuel loop.

4.2. Capacitance type sensors

The dielectric properties of aqueous methanol solutions have been well investigated by Bao, Mashimo, Sato and Bolund [17–20]. The static dielectric constant of these solutions varies in accordance with the methanol concentration, as shown in Fig. 10. The dielectric constant (or the methanol concentra-
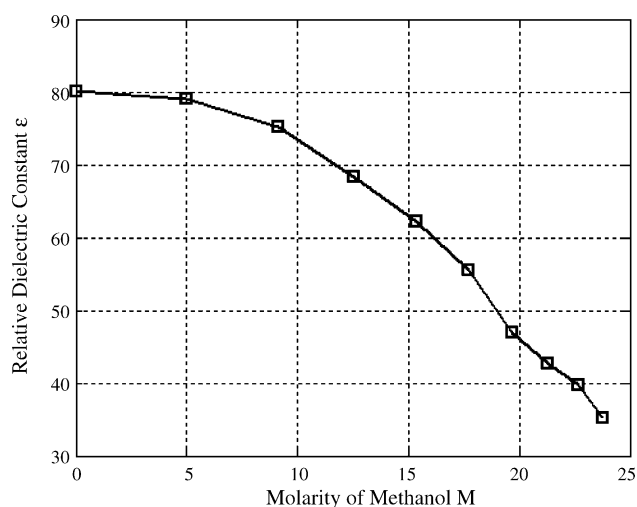

Fig. 10. Relative dielectric constant of aqueous methanol solutions vs. molarity of methanol in aqueous solution at 23 °C [21].
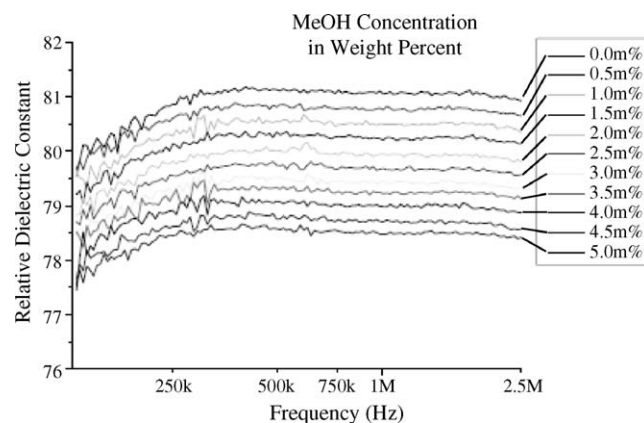

Fig. 11. Measured dielectric spectra of aqueous methanol solution at 20 °C, © 2005 IEEE, courtesy of [37].

tion) can be determined by measuring the frequency-dependent capacitance. This kind of sensor consists of a capacitor that comprises a pair of spaced electrode plates or coaxial electrode cylinders submerged in the solution. The solution passes through the two electrodes of the formed capacitor and the dielectric constant of the solution is detected by measuring the capacitance established between the electrodes.

In the early 1980s, this type of sensor was proposed to measure the methanol concentration in mixed fuels, such as a mixture of gasoline and methanol. A plate capacitor methanol sensor dipped in the fuel tank was disclosed in Japanese patent JP56138431 [32], and a coaxial cylinder capacitor was disclosed in Japanese patent JP4343062 [33]. The capacitance methanol concentration sensor has the drawbacks of electro-corrosion of the electrode plates/cylinders, and dissolution of metallic ions in the fuel due to the application of DC voltage. In order to avoid the above drawbacks and increase the measurement accuracy of the methanol concentration in the mixed fuel, an electrically insulating film was formed on the cylindrical or plate electrodes of the sensing capacitor as disclosed in US patents 4,939,467 and 5,196,801, and WO0113451 [34–36].

Doerner et al. measured the dielectric spectra for a methanol concentration range from 0 wt% to 5 wt%, as shown in Fig. 11 [37]. When the frequency is above 1 MHz, the dielectric spectra become flat and stable due to the less influence of contaminants in the solution. They used a capacitive probe with a pair of planar sensing electrodes in a PTFE shell, shown in Fig. 12, which was used to calculate the complex dielectric constant and determine the methanol concentration in aqueous solution.

The construction of the capacitance sensor is simple, and due to the large difference in dielectric constants between methanol and gasoline, the capacitance sensor works well in this mixed fuel. However, the change in dielectric constants of aqueous methanol solution in the low methanol concentration range is very small, and therefore it is hard to get a satisfactory measurement resolution. Furthermore, this type of methanol concentration determination is extremely sensitive to metallic ions and dissolved CO_2 in the fuel loop, which is always present.
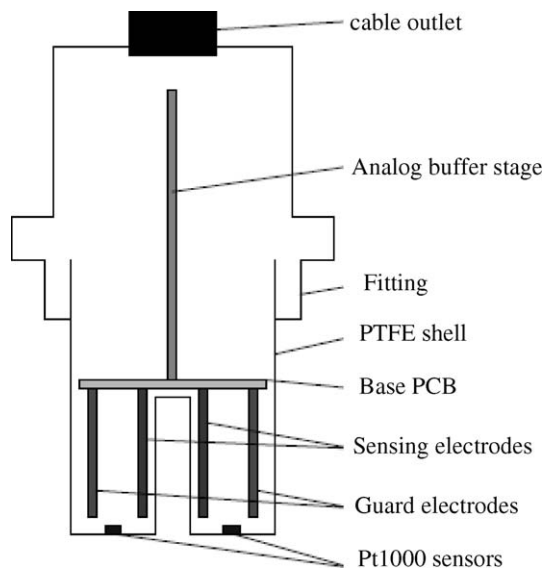
Fig. 12. Structure of the capacitive methanol sensor, © 2005 IEEE, courtesy of [37].

4.3. Viscosity type sensors

Viscosity is a measurement of the resistance to flow for a fluid. When methanol is mixed with water at different ratios, the viscosity of the solution is highly dependent on the methanol concentration, as shown in Fig. 13 [21]. The viscosity first increases and then decreases with increasing methanol concentration, which is dramatically different from the linear relationship expected for an ideal solution of randomly mixed molecules. This viscosity behaviour may be attributed to incomplete mixing of the two components at the microscopic level due to strong O−H hydrogen bonding of the two components and different molecular configurations between water clusters and methanol chains in this binary system [38,39]. Due to the large change in viscosity with the methanol concentration in aqueous solutions, the methanol concentration can be determined by measuring
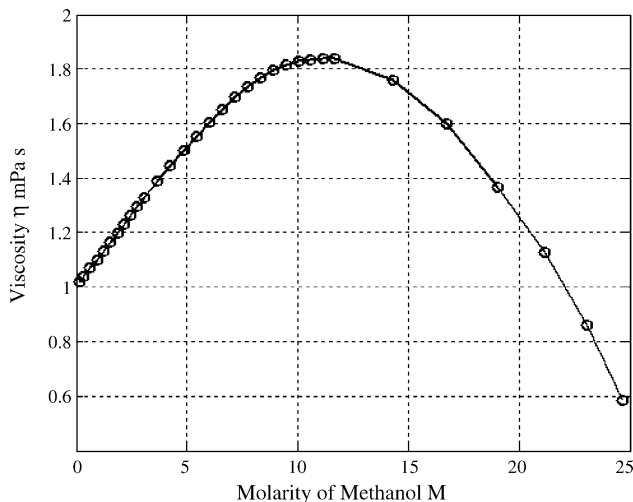

Fig. 13. Viscosity of aqueous methanol solutions vs. molarity of methanol at 20 °C [21].
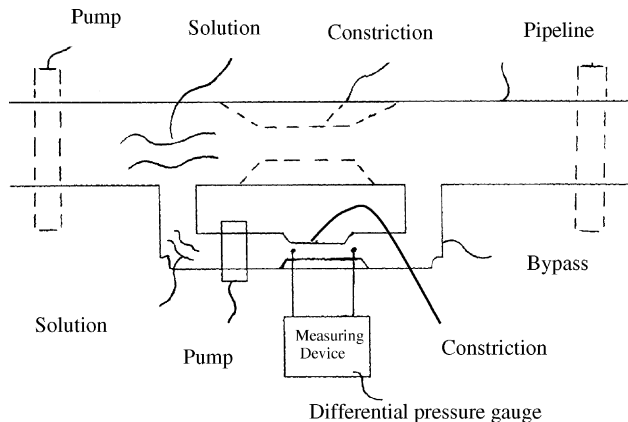

Fig. 14. Methanol concentration sensor by measuring the viscosity, courtesy of [41].

the viscosity according to the Hagen–Poiseuille law. That is, for laminar, non-pulsatile fluid flow through a uniform straight tube, the flow rate is proportional to the pressure drop across the tube and inversely proportional to the viscosity of the fluid:

$$\frac{dV}{dt} = \pi r^4 \frac{\Delta P}{8\eta L}, \tag{6}$$

where dV/dt is the volume flow rate; r and L are the radius and the length of the tube, respectively; ΔP the pressure drop across the channel; η viscosity.

US patent 5,315,863 discloses a device to measure the viscosity of the fluid in a tube by measuring the pressure drop under a controlled flow rate [40]. US patent 6,536,262 gives a different method for determining the methanol concentration based on the change of viscosity with the methanol concentration [41]. The solution was pumped through a constriction with a delivery pump, and the pressure drop across the constriction was measured using a differential pressure sensor, as shown in Fig. 14. The differential pressure across the constriction under a constant laminar flow rate was measured to determine the methanol concentration.

This type of methanol concentration determination is insensitive to the dissolved CO_2 and the metallic ion contamination introduced by fuel recirculation. However, a potential issue is that the viscosity changes with temperature and therefore accurate temperature monitoring is required.

4.4. Speed of sound type sensor

The speed of sound in liquids is related to their density and elastic properties. Due to the strong O−H hydrogen bonding and the different molecular configurations between water clusters and methanol chains in aqueous methanol solutions, the actual sound velocity in aqueous methanol solutions changes from $1150\ \mathrm{m\,s^{-1}}$ to $1580\ \mathrm{m\,s^{-1}}$ over the entire methanol concentration range at room temperature. A couple of papers disclose the relationship between the speed of sound and the methanol concentration at different temperatures, as shown in Fig. 15 [22,23]. The speed of sound increases as the methanol concentration increases in the low concentration region due to the
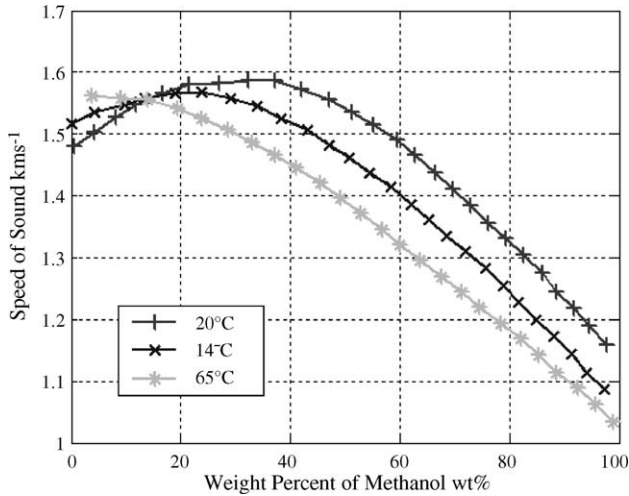
Fig. 15. The speed of sound in aqueous methanol solutions vs. methanol concentration in weight percent [22].

Fig. 16. Methanol sensor based on the speed of sound, courtesy of [42].

strong water–water hydrogen bonds and the increasing chain length of the methanol. As the concentration of methanol is further increased, the speed of sound in the high methanol concentration region decreases due to the replacement of the strong water–water hydrogen bonds with the weaker water–methanol and methanol–methanol hydrogen bonds. Also, as the temperature increases, the maximum sound speed shifts to a lower value of the methanol concentration due to changes in the hydrogen bond length.

US patent 6,748,793 [42] discloses a method for ultrasound sensing of the methanol concentration in aqueous solution based on observed sound velocity. Changes of methanol concentration in the range of 0.1–5% by weight, and a resolution of up to 0.1% were reported. In this patent a piezoelectric transducer was used, working as a transmitter to emit ultrasound waves, as well as a receiver to detect the reflected ultrasound waves from the opposite side, as shown in Fig. 16. Using similar reference and sample chambers, the differential propagation time $\Delta t(x_m)$ of the ultrasound pulses was measured in response to the change of methanol concentration.

$$\Delta t(x_m) = \frac{L}{v(x_m)} - \frac{L}{v_r} \qquad (7)$$

where L is the propagation length of the ultrasound pulses; v_r and $v(x_m)$ are the speed of sound in the reference chamber and the sample chamber, respectively. For a propagation length L of 0.5 M, a time difference Δt of 0.111 μs corresponded to a methanol concentration change of 0.1 wt%.

This method of methanol concentration determination is insensitive to the dissolved CO_2 and the metallic ion contamination introduced by fuel recirculation. However, CO_2 bubbles in the fuel will affect the propagation of the ultrasound wave. The resolution of such a sensing system depends on the length of the propagation path. This device is complicated and not easily miniaturized, and the measurement method is intermittent. Furthermore, a higher temperature will decrease the measurement resolution.
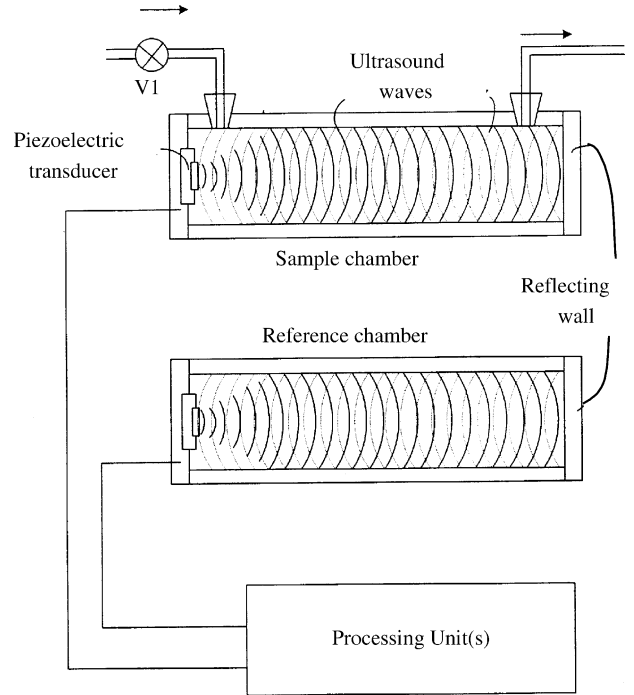
4.5. Infrared spectrum type sensor

Usually, photon energies in the infrared region, ranging in wavelength from 2.5 μm to 16 μm, can induce vibrational excitation of covalently bonded atoms and groups. The exact frequency at which a given vibration occurs is determined by the strength of the bonds involved and the mass of the component atoms. Infrared absorption spectra of compounds are unique reflections of their molecular structure and configuration.

For low concentrations of aqueous methanol solutions, the change of the absorption frequency or wavenumber is not observable in the specific band of the IR spectrum. However, changes in the amplitude of absorption can be observed and related to small changes in the methanol concentration, as shown in Fig. 17. This can be used to analyze the methanol concentration. The transmittance of IR radiation was detected by an infrared sensor and used for analysis of the methanol
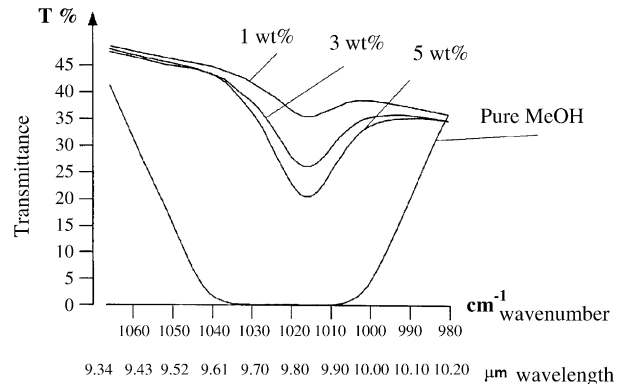

Fig. 17. Peak absorption of IR spectra for aqueous methanol solutions, courtesy of [43].
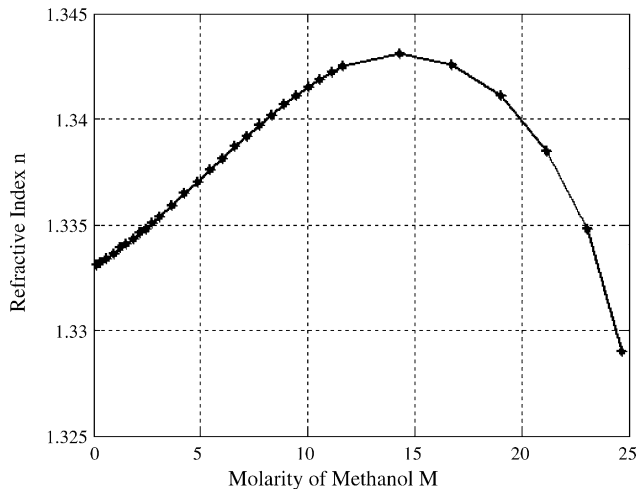
Fig. 18. Refractive index vs. methanol concentration [21].

Fig. 19. Optical methanol concentration sensor, courtesy of [45].

concentration in aqueous methanol solutions in US patent 6,815,682 [43]. The patent reported effective measurement of the methanol concentration in the range of 0–5 wt% with a resolution of 0.1 wt%.

This method has a high measurement resolution at low methanol concentrations of less than 1 M. However, the dissolved CO_2 and CO_2 bubbles will shift the frequency at which the peak absorption occurs, affecting the measurement resolution.

4.6. Refractive index type sensor

The ratio of light speed in a vacuum to its speed in the medium is the refractive index. Light travels slower in any medium than in a vacuum. When light travels at an angle between two different materials, their refractive indices determine the angle of transmission (or refraction) of the light beam. Fig. 18 shows the change of the refractive index in an aqueous methanol solution up to a methanol concentration of 25 M [21].

During the past decade, a variety of techniques have been developed to measure the refractive index for determining the concentration of a binary solution. Longtin and Fan [44] proposed a HeNe laser system-based technique to determine the concentration of a methanol aqueous solution with a high precision on the order of 0.01 wt% over the entire concentration range. Japanese patent JP3251745 discloses a methanol concentration sensor based on the transmission of light through a fibre in the mixed fuel, as shown in Fig. 19 [45]. A U-shaped optical fibre is immersed in the fuel channel and has direct contact with the mixed fuel of methanol and gasoline. A transmitter such as a LED, is applied at one end of the fibre to generate light according to the applied electrical signal. A receiver such as a photocoupler is positioned at the other end of the fibre to receive and convert the transmitted light back to the electrical signal.

For a general LED, the relationship between luminous flux intensity z and input voltage e_i can be approximately expressed as:
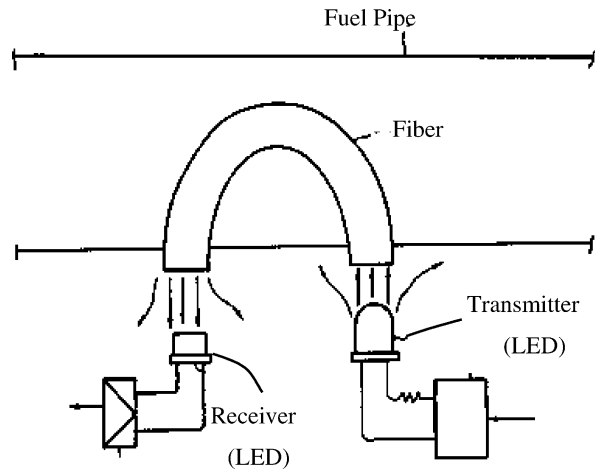
$$z = \alpha_i e_i + \beta_i \tag{8}$$

Assume that all the transmitted light $\lambda(n)z$ is received by the photocoupler and the transition loss of light $(1-\lambda)z$ is introduced by refraction at the fibre/solution interface. The output voltage of the receiver can be expressed as:

$$e_o = \alpha_o \lambda(n)z + \beta_o \tag{9}$$

Changing the applied voltage on the LED from e_{i1} to e_{i2} and detecting the output of the photocoupler e_{o1} and e_{o2}, the transmittance of the fibre $\lambda(n)$, which is the function of the refractive index n, can be calculated from:

$$\lambda(n) = \frac{e_{o1} - e_{o2}}{\alpha_o \alpha_i (e_{i2} - e_{i1})} \tag{10}$$

where n is the refractive index at the fibre/solution interface; λ is the transmittance of light through the fibre; α_i, β_i and α_o, β_o are the constants related to the LED and the photocoupler.

The optical transmission characteristics of the fibre immersed in an aqueous methanol solution are very much dependent upon the refractive indices of the fibre and the solution, and especially on the variation in the solution's index of refraction. The transmittance of light through the fibre, which depends on the methanol concentration, can be calculated based on the applied electrical signal to the transmitter and the electrical output of the receiver.

This methanol concentration sensor is robust. However, due to the small variation of the refractive index with the methanol concentration in an aqueous solution, the measurement resolution is low.

4.7. Heat capacity type sensor

Heat capacity is the ability of matter to store heat. The heat capacity of a given amount of matter is the quantity of heat required to raise its temperature by 1 K. Molar heat capacity is usually used in chemistry and defined as heat capacity per unit mole of a substance, that is, the amount of heat energy required to raise the temperature of 6.022×10^{23} molecules of the substance by 1 K. The molar isobaric heat capacities of pure water and methanol at 15 °C are 75.4 JK^{-1} mol^{-1} (C_{p1}^*) and
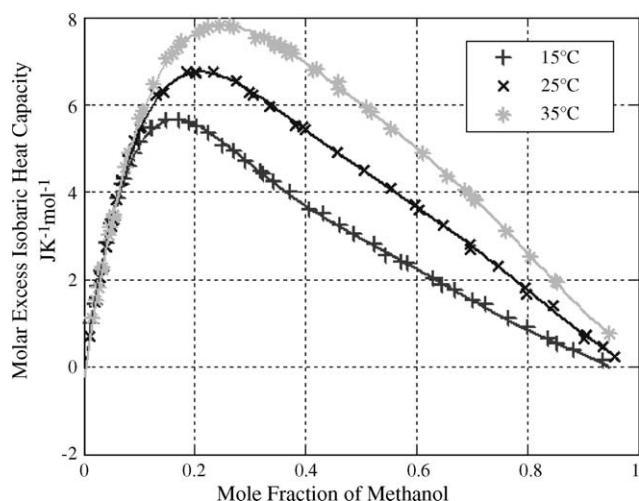
Fig. 20. Molar excess isobaric heat capacity of aqueous methanol solutions vs. mole fraction of methanol [24,25].

78.7 JK^{-1} mol^{-1} ($C^*_{p_2}$), respectively. For an aqueous methanol solution the molar heat capacity has an unexpected change related to the methanol concentration. Benson et al. [24,25] and Simonosn et al. [46] obtained the molar isobaric heat capacities ($C_{p,m}$) of aqueous methanol solutions at different temperatures through experiments and calculated the molar excess isobaric heat capacities ($C^E_{p,m}$) from the relation:

$$C^E_{p,m} = C_{p,m} - (1 - x)C^*_{p_1} - xC^*_{p_2} \qquad (11)$$

where x is the mole fraction of methanol in the aqueous solution; $C^E_{p,m}$ the molar excess isobaric heat capacity; $C_{p,m}$ the molar isobaric heat capacity from the experiment; and $C^*_{p_1}$, $C^*_{p_2}$ are the molar isobaric heat capacities of pure water and methanol, respectively.

The molar excess isobaric heat capacities of aqueous methanol solutions obtained by Benson are plotted in Fig. 20. $C^E_{p,m}$ is positive and increases with temperature at all mole fractions due to an increasing net disruption of hydrogen bonds with increasing temperature. The maximum of $C^E_{p,m}$ shifts to higher values of x with increasing temperature. The molar excess heat capacity rises steeply in the range from $x=0$ to $x=0.2$ before decreasing. The increasing chain length of the methanol in aqueous solution is believed to be responsible for the unexpected decrease of the molar heat capacity.

US patent 20,020,148,284 [47] provides a method for measuring the methanol concentration in aqueous solution, using the fact that the specific heat capacity of an aqueous methanol solution is greatly dependent on the methanol concentration. A known quantity of heat, Q, was supplied to the solution, by pumping it through a heating cell at a constant flow rate, and the resulting increase in temperature or temperature difference was recorded. The temperature difference is proportional to the specific heat capacity which changes as a function of the methanol concentration. A temperature difference of approximately 2 °C was reported for a change of methanol concentration from 0.5 M to 1 M with a flow rate of 100 ml min^{-1}.

This method is insensitive to the pH and metallic ion contamination of the methanol solution. However, a pump is necessary to maintain a constant flow rate in the solution and a constant heating power source is required.

4.8. Summary of physical sensors

Physical methanol concentration sensors measure the changes in physical properties of the solution and then determine the methanol concentration of the solution based on the relationship between the physical properties and the methanol concentration. Most of these sensors are relatively reliable and robust. However, auxiliary driving devices and other sensors are required, such as a pump for a constant flow rate and a pressure sensor for measuring the pressure drop, make the sensing system complex. The complexity of physical sensors makes it difficult to miniaturize this type of sensor. Furthermore, physical sensors are temperature-dependent and may require a temperature sensor as well for temperature compensation.

5. Other measurement methods

Compared to the conventional methods of employing a methanol concentration sensor, a couple of sensorless approaches have been disclosed to decrease the cost and complexity of the fuel cell system and improve the stability of fuel cell operation by monitoring one or more of the fuel cell's operating characteristics. The sensorless method increases or decreases the concentration of methanol supplied to the anode according to the preferred choice of an operating characteristic and a known relationship between the characteristic and the methanol concentration. In US patent 6,589,679 [48], a change of methanol concentration is introduced by periodically reducing or interrupting the amount of methanol supplied to fuel cell and the rate of the potential drop can be used; or the potential difference between the inlet and outlet of the methanol flow can be used; or the load is periodically disconnected from the fuel cell and the open-circuit potential can be used to adjust the methanol concentration. US patent 6,698,278 [49] calculates methanol concentration in the fuel stream based on the measurement of the temperature of the fuel stream entering the fuel cell stack, the fuel cell stack temperature indicating the operating temperature, and the load current.

The sensorless methods do simplify the design of the fuel cell system. However, the sensorless methods are based on the predetermined calibration of the fuel cell system and on empirical models. The monitoring and control of the methanol concentration are inexact due to the complexity of fuel cell operation and fuel cell degradation.

6. Conclusions

Electrochemical sensors offer many advantages over physical method sensors despite issues with degradation of the electrolyte membrane and catalyst performance over long-term operation. They are still used extensively in small fuel cells due to their simple structure, which is compatible with the fabrication process of

DMFCs, and their simple output in the form of electrical signals, i.e., voltage or current. With the improvement of membrane and catalyst degradation and the development of new materials, the electrochemical sensor will prevail for a long time. However, it is difficult to overcome the narrow sensing range and slow response due to the diffusion limitation with electrochemical sensors. This diffusion limitation is more pronounced at higher methanol concentrations. With the development of new membranes for DMFCs working at higher methanol concentration with reduced crossover, this electrochemical sensor will face an increasing challenge from the physical sensor which is not diffusion limited.

Physical methanol concentration sensors are reliable and robust, and have a wide measurement range, but they are complex and not easily miniaturized. With the application of MEMS technology, physical sensors will be more attractive for small fuel cells. The development of higher power density DMFCs running at higher methanol concentration will help to accelerate the application of physical methanol concentration sensors in small DMFCs.

It is well known that the molecular interactions present in different binary liquid mixtures contributes to many of the physical properties of liquid system such as density, viscosity, dielectric constant, refractive index. Due to the similar molecular structure and intermolecular interactions, other aqueous solutions of alcohols such as ethanol and propanol have similar physical properties varying with alcohol concentrations as aqueous methanol solution. Therefore, most of physical sensors for detecting the methanol concentration can be used for other alcohols.

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