A Methanol Concentration Controller for Fuel Cells

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Abstract— Fuel cells are used for backup power in remote telecommunications sites. This paper focuses on a prototype methanol controller built with an ultrasonic sensor for detecting the density of the methanol/water mixture and a sensor for the temperature of the mixture. The controller was calibrated to determine the amount per volume of water and methanol which enables the controller to control the percentage of methanol in the water. The prototype addresses one of the problems in methanol fuel cells called "Methanol Crossover". Methanol crossover occurs when methanol is not completely used in the process of generating electrons, and a certain percentage of the methanol is wasted. Crossover may damage the proton exchange membrane of the fuel cell and also reduce the efficiency and lifespan of a DMFC.

Index Terms— DMFC: direct methanol fuel cell.

Mole: The amount of a substance that contains as many atoms, molecules, ions, or other elementary units as the number of atoms in 0.012 kilogram of carbon 12. The number is 6.0225×10^{23}, or Avogadro's number.

PEM: Proton exchange membrane

I. INTRODUCTION

A fuel cell is an electrochemical energy conversion device much like a battery except that is easily refueled because the fuel is stored outside the cells. With a fuel cell, fuel constantly flows through the cell and is easily replenished outside the cell, so it never stops providing electrical current. As long as there is a flow of fuel through the cell, the electricity flows out of the cell. A fuel cell is an energy-**producing** device while a battery is an energy-**storing** device. With batteries the fuel is stored inside the battery and cannot easily be replenished. Most fuel cells in use today use hydrogen and oxygen as the chemical fuel. A fuel cell provides a DC voltage that can be used to power motors, lights or other DC electrical appliances. The DC voltage can also be inverted to a more usable AC voltage [1].

The direct methanol fuel cell (DFMC) is best suited for portable electronic systems of low power, running for long times. The DMFC is also a PEM fuel cell except that it uses a slightly thicker membrane and the membrane is not only treated with platinum but also with ruthenium. The operating temperature is between 20-90 ˚C [2].

DMFCs have a number of disadvantages, i.e.:

- Firstly the fuel-anode reactions proceed slower than in the case of pure hydrogen. The oxidation of hydrogen occurs readily – the oxidation of methanol is a much more complex reaction and this results in a fuel cell with far lower power density for a given size.
- The second is that of methanol crossover. There is always a small amount of wasted fuel that migrates through the electrolyte to the cathode and this is called fuel crossover.

In the DMFC with a PEM electrolyte fuel crossover is severe, the reason is that methanol mixes very readily with water, and so spreads into the water that is an essential part of the structure of the PEM electrolyte. The methanol will thus reach the air cathode. This has a platinum catalyst, and although it will not oxidize the fuel as effectively as the Pt/Ru catalyst on the anode, it will do so fairly readily. The reaction of the fuel at the cathode is not only a waste of fuel – it will also reduce the cell voltage.

II. CONCENTRATION CONTROLLER ASSEMBLY

Measurement of methanol concentration in real time, during DMFC system operation, is important for maintaining constant methanol concentration and ensuring uniform system performance. The concentration of methanol is dropped by continuous power generation in the system. Therefore, the system must be capable of detecting the concentration in situ, to calculate the amount of fresh methanol to be added and to supply fresh methanol to the anode sides.

The complete design of a methanol concentration controller evolves around the sensor used to determine the concentration mix of methanol and pure water. The very first step thus was to determine what type of sensor could be used in the design of the controller.

There are several methods developed for measuring the concentration of methanol. Methods that can be used include:

- Methods using a Böhme meter and dielectric constant.
- pH measurement.
- Conductivity measurement.
- Methods adopting infrared absorption and refraction factor.
- Ultrasonic methods.

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The ultrasonic method was found to be suitable for measurement, as this method is non-invasive and offers real-time measurement. Sound velocity in a methanol solution varies with the concentration of the methanol and the temperature of the solution [3].

There are a number of ways to determine which of the parameters change when water and methanol are mixed. One of the first considerations was to test what happens to the pH of the concentration of water and methanol mixture. A laboratory electronic pH measuring instrument was used. Two tests were conducted. One on pure water where the pH measured was around 7 and in the second with a mixture of 50% methanol. The change was hardly noticeable. This method for testing concentration was then not considered as an option for the control system. The second method used to test the concentration was to test the conductivity of the mixed liquid compared to that of the pure water and again it was not found to be a feasible method for the testing of the liquid because the change in concentration was not clearly noticeable.

The next possible solution was to find a commercial sensor and only two types were found. The first is manufactured by Texas Instruments for Sensata Technologies and the second by Murata Manufacturing Co. Ltd. Sensata Technologies methanol concentration sensor is an optical sensing device for real time methanol concentration analysis. This sensor is a miniaturized, self–contained optical system (shown in Figure 1), which measures the refractive index of aqueous methanol samples rapidly and affordably. The patented sensor design enables inline process control for methanol-based fuel systems.

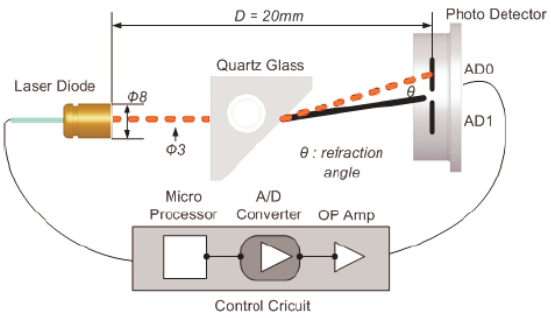

Fig. 1 Experimental set-up for optical sensing system [4]

This sensing system resolves extremely small changes in concentration, in the order of 0,01%, while providing a large dynamic measurement range (0-100% methanol concentration). The above sensor seemed to be ideal but the manufacturer, Texas Instruments, did not want to supply this sensor as it was only manufactured for the exclusive use of Sensata Technologies.

The second manufacturer, Murata Manufacturing Co. Ltd, has introduced an ultrasonic impulse transducer based on a laminated piezoelectric ceramic technology.

This sensor is based on the fact that sound velocity in a methanol solution depends on the concentration of the methanol and the temperature of the solution. In fact, within the thin concentration range of several percent, a change of one percent in the concentration of methanol can be determined according to Takaaki Asada, Chief of the Product Development Section, Murata Manufacturing Co. Ltd. [3]

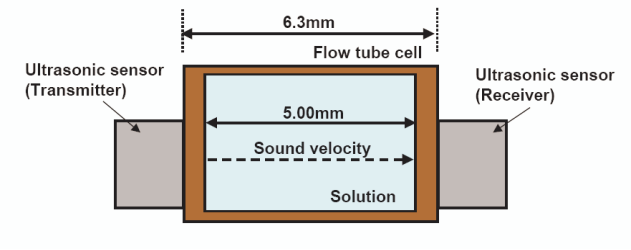

Fig. 2 Acoustic configuration of the sensor [3]

When the methanol has a concentration of 2 to 5 percent at 25 °C, a change of 1 percent in concentration produces a change of 3.4 m/s in sound velocity. Figure 2 illustrates a basic configuration of the acoustic system of the sensor. To be able to measure sound velocity with high precision, the time with which an ultrasonic wave radiated by the ultrasonic transmission transducer takes before reaching the ultrasonic reception transducer located at a specific distance, must be determined precisely.

Figure 3 shows an ultrasonic transmission impulse transducer and an ultrasonic reception impulse transducer which are bonded on both sides of the resin rectangular tube. The transducers are facing each other with a methanol and water solution inside the resin tube. The printed circuit board with the drive control IC and other devices mounted are bonded on the top surface of the tube to constitute a sensor module.

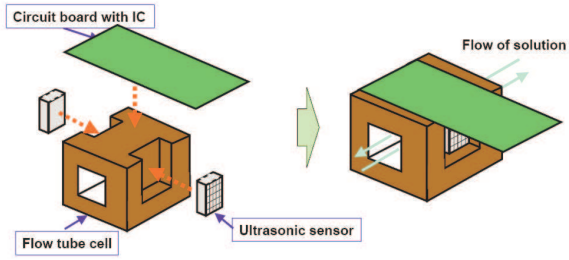

Fig. 3 General view of the sensor [3]

The methanol solution to be measured is fed through the rectangular tube and the delay time between the transducers is measured to determine the sound velocity. The ultrasonic wave pulses radiated by the echo sounder transmitter passes through the resin diaphragm, the measuring methanol solution and the opposite resin diaphragm are received by the echo sounder receiver. The dedicated IC generates pulse signals for driving the echo sounder transmitter and converts the timing difference between the zero-crossing of the transmitted signal and that of the received signal into direct-current signals. These direct-current signals are used to determine the propagation velocity of sound waves in the solution. Rectangular pulses with a pulse width of 83 ns in pulse width and 5 $V_{p\text{-}p}$ are applied to the transmission

transducer.

Figure 4 shows the terminal voltages of the transmission transducer and the reception transducer. An acoustic signal received at the receiver is checked for zero crossing of the first sinusoidal impulse and the measurement range indicates minute changes in the solution concentration (1 percent should be clearly sensed). The change in sound velocity in relation to the methanol concentration depends on the concentration range of methanol and the temperature of the solution. When the methanol has a concentration of two to five percent at 25 °C, a change of one percent in concentration produces a change of 3.4 ms^{-1} in sound velocity.

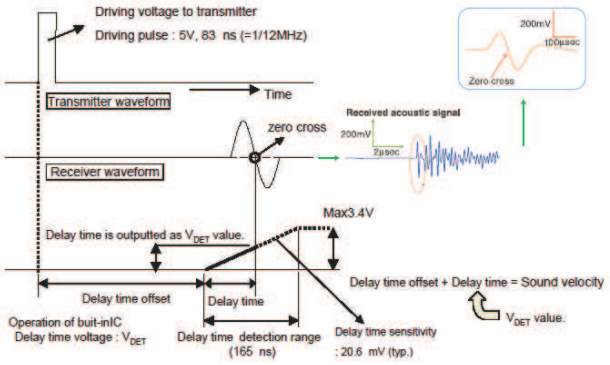

Fig. 4 Measurement of sound velocity [3]

The other main advantage of this sensor is that it has a built-in sensor for temperature measurement. Therefore this sensor was chosen for this design.

III. Electronic Design

The electronic design of the methanol controller was made after selecting all the necessary components needed. A PIC micro controller was used together with the Murata sensor. The design consists out of two parts namely the software design and a hardware design.

Figure 5 shows the basic flow diagram for the micro controller software program used in the methanol controller system.

After the setup and greeting phase it measures and converts the detector voltage and also calculates the correct detector voltage. The temperature is measured and calculated next. Then derived algorithms are applied to determine the volume of methanol in the solution being tested.

The second part, the hardware design was done using the following components: The Murata Sensor with a PIC18F452 micro controller. For the speed control of the pump a L6202 H-Bridge IC was used and a MAX232 Serial controller was used for the data logger.

The second most important device after selecting the sensing device was the micro controller and there were plenty to choose from. The device selected for this design was a PIC18F452 since it was readily available and it contained all the needed functions such as analogue to digital conversion, pulse width control and a built-in serial port.

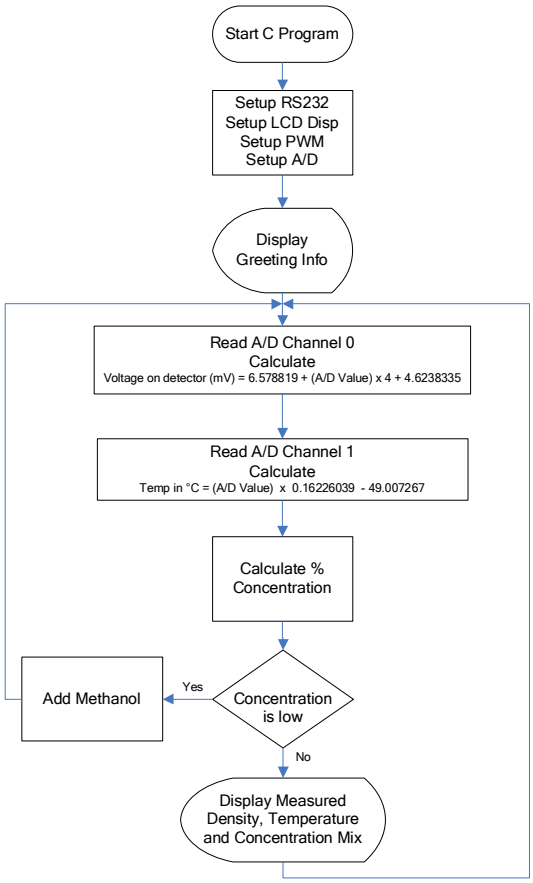

Fig. 5 Flow diagram of the methanol controller software

The circulating pump is used to pump the solution through the sensor and it is connected to an H-Bridge (L6202 situated at the right-hand topside of the circuit) which is used as a voltage driver to the pump. The H-Bridge is connected to an inverter and the output of the pulse width modulator of the PIC micro controller. The pulse width modulator is used to vary the speed of the circulating pump. The aim of this part of the design was to test the influence of changing flow rate, on the sensor.

A four line LCD display is used to display the outputs measured from the ultrasonic detector and the temperature sensor. It shows the calibrated values measured for the detector voltage Det_V in millivolts, temperature of the fuel, the air temperature and the percentage volume mix. It also indicates when methanol is added and whether the temperature is changing too fast for accurate measurement.

To enable data logging on a PC a MAX232 was added to the circuit. This enables recording on a PC of all measured and calculated values. Furthermore, the Murata sensor was added to channel 1 (concentration) and 2 (temperature) of the analogue converter of the micro controller. A push button connected to the microcontroller allows for changing the volume mix of the concentration.

IV. Measurement and Results

Figure 6 shows the liquid path diagram of the concentration tester. The tank that was used was made of high thermal plastic, which could easily be heated up in a warm bath to ensure measurements at different temperatures. An electric heater connected to a thermo controller was used as the heating bath to ensure the gradual heating up of the methanol mixture while circulating the mixture through the sensor.

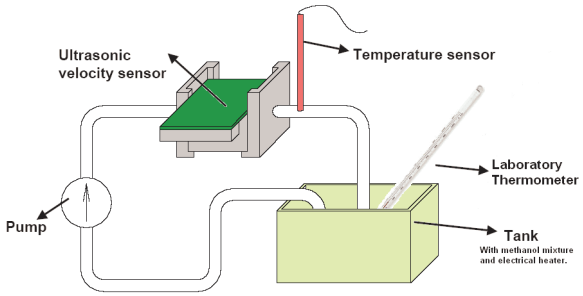

Fig. 6 Basic layout of the sensor liquid circuit

It can be seen in figure 7 that the temperature has an effect on the density. According to Simetric [5] the density of pure water is a constant at a particular temperature and does not depend on the size of the sample. The density of water also varies with temperature and impurities.

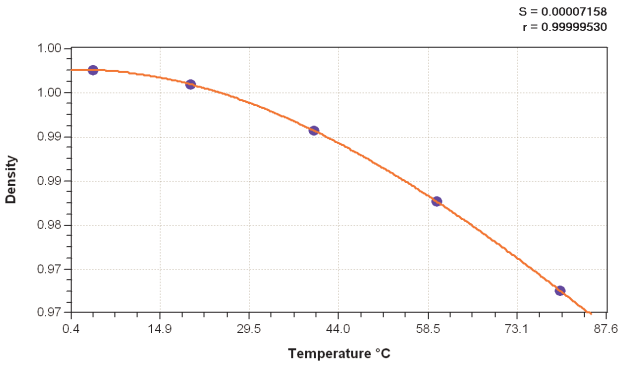

Fig. 7 Density versus temperature of pure water

It was therefore important to test the effects of temperature changes on the detector. Figure 8 shows the heating up and cooling down curves of pure water. The curves $y_{0rc\%n}$ and $y_{0rh\%n}$ shows the effect of a quick cool down and heat up of the water respectively. The curves $y_{0sc\%n}$ and $y_{0sh\%n}$ shows what happens to the detector value if the water is cooled down and heated up slowly. The slow cool down results were obtained by leaving the concentration tank in about 5 litre of water and letting the water cool down by itself to ambient temperature. The slow heating up of the tank was done by heating up the concentration tank in the same 5 litre of water. The temperature was adjusted by 5 °C at a time and the detector values were only recorded after 10 readings of the same temperature, taken 1 second apart. Values were then recorded by the data logger for approximately 1 minute at this time.

From these results it was concluded that the temperature detector built into the sensor is slow to react and care had be taken to ensure correct reading of the ultrasonic detector at the right temperature. This was proven further by looking at the high end of the temperature curve when the rapid heating effect is starting to slow down. It seemed that the best results could be obtained from a slow cool down test since the heat up curve could have minor discrepancies since the stabilisation might not have taken place as needed.

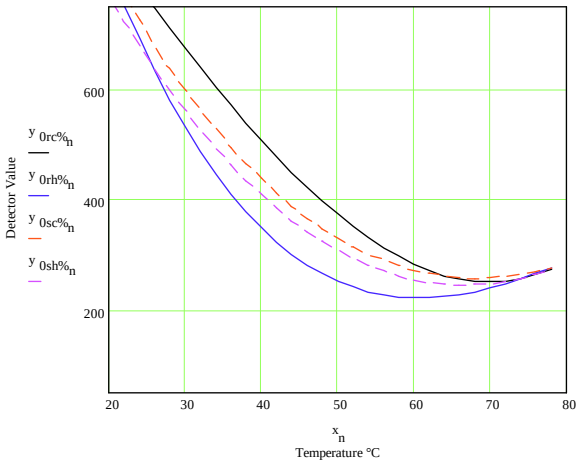

Fig. 8 Detector values versus temperature of pure water

The problem however is that with a methanol mixture, the methanol starts to vaporise at round about 63 °C and therefore all further testing was performed up to a maximum of 60 °C.

An During a slow cool down of a 0% mixture, the thermocouple of the heater tank was set at 40 °C and left in that position for about an hour. Every time the heating element came on the water was heated up to about 43 °C and then cooled down to 40 °C. From Figure 9 it can be seen that the readings obtained from the detector shows a slight change in the density of the curve between 40 °C and 43 °C. This again proves that special care had to be taken to ensure correct temperature readings.

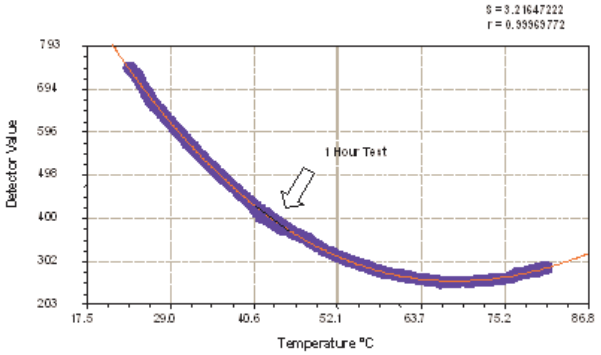

Fig. 9 Detector values versus temperature of pure water on a slow cool down test

To test the stability of the detector a 4% volume mixture of methanol and water was tested using the cool down method and using the same solution 8 hours apart. A fourth

test ($y_{4ss\%n}$) was also done with a new liquid mixture and using a very slow cool down period. See figure 10.

Another test done to ensure the correctness of the values read was to vary the speed of the circulating pump to see if this would have an effect on the values measured. The fluctuations measured were only a few millivolts.

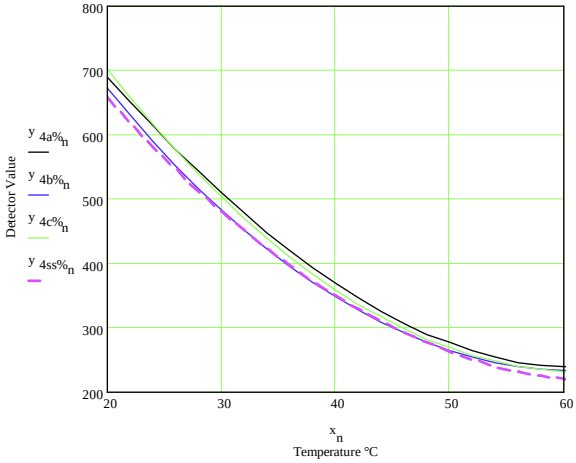

Figure 10: 4% by volume methanol mixture on a slow cool down test repeated 3 times

The temperature was held as constant as possible over this period and the minor changes in detector voltage could have been caused by minor temperature changes. The maximum deviation measured here was not more than 14 mV and this will have little effect on the control of the methanol concentration as the difference between 3% to 4% concentration at 20 °C is in the order of 230 mV.

After the micro controller was reprogrammed with the parabolic formulas derived, the controller was tested with different samples of methanol/water mixtures while slowly changing the temperature from 20 to about 60 °C. The tests were done in a closed system with 100 ml of fluid to avoid the loss of methanol when the fluid is heated up. The controller successfully tested the different samples but great care had to be taken with fast changing temperature values.

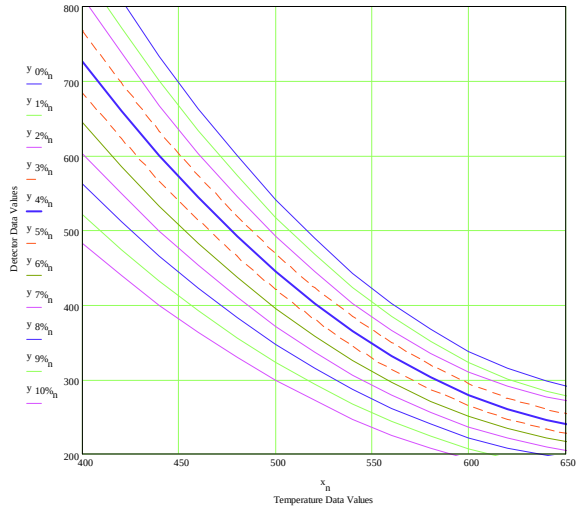

Fig. 11: Comparison of different water methanol mix samples changing temperature over time

Comparing the Analogue to Digital Conversion Value with the derived value gave an indication if replenishment of methanol is needed and this function was also added to the control system. This means that methanol can automatically be replenished with a dosing pump controlled from the micro controller, if needed. The level per volume of methanol needed can also be changed by just pushing and holding the button down.

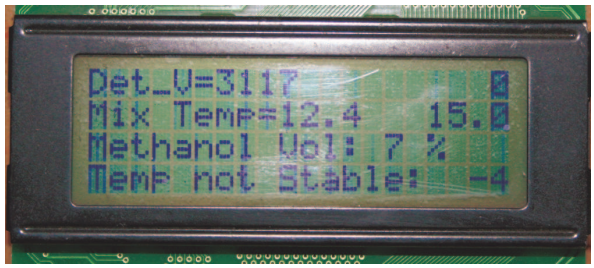

Fig. 12 LCD display of the prototype

Figure 12 shows the display of the prototype indicating on the first line the detector voltage measured in millivolts. The second line shows firstly the temperature of the methanol mixture and secondly the ambient temperature. The third line indicates the percentage of the methanol mixture and the fourth line shows different error messages that may be needed to display any errors.

The algorithm written to determine the correct percentage mixture starts with testing for a 10% mixture first applying the equation for a 10% mixture given below. If the result is lower a next test is done to see if the value might be 9%. The test is repeated every time for a lower value until the result obtained is higher than the equation which will then be taken as the correct volume mixture.

To methanol and water mixture should ideally be kept at between 3 and 4% methanol in the mixture to obtain the 1 Mole ideal value. In this controller this value can be altered for experimental purposes but is set to keep the solution a 4% by default when the unit is restarted.

The parabolic formulas for the different methanol/water mixtures were derived as:

$$Det\_V_{0\%_n} = 3742.54 - 10.041 \times temp\_val + 0.00728 \times temp\_val^2$$

$$Det\_V_{1\%_n} = 3546.59 - 9.485 \times temp\_val + 0.00685 \times temp\_val^2$$

$$Det\_V_{2\%_n} = 3494.70 - 9.497 \times temp\_val + 0.00698 \times temp\_val^2$$

$$Det\_V_{3\%_n} = 3209.02 - 8.596 \times temp\_val + 0.00623 \times temp\_val^2$$

$$Det\_V_{4\%_n} = 3010.98 - 8.029 \times temp\_val + 0.00579 \times temp\_val^2$$

$$Det\_V_{5\%_n} = 2839.96 - 7.578 \times temp\_val + 0.00548 \times temp\_val^2$$

$$Det\_V_{6\%_n} = 2672.96 - 7.142 \times temp\_val + 0.00518 \times temp\_val^2$$

$$Det\_V_{7\%_n} = 2495.81 - 6.664 \times temp\_val + 0.00483 \times temp\_val^2$$

$$Det\_V_{8\%_n} = 2318.65 - 6.182 \times temp\_val + 0.00448 \times temp\_val^2$$

$$Det\_V_{9\%_n} = 2136.39 - 5.685 \times temp\_val + 0.00412 \times temp\_val^2$$

$$Det\_V_{10\%_n} = 1979.36 - 5.268 \times temp\_val + 0.00382 \times temp\_val^2$$

V. Conclusion

The theoretical study was completed and the most appropriate commercial sensor available for testing density

of the concentration mix was found to be the Murata sensor. The Murata sensor makes use of ultrasonic pulses which are propagated through the liquid and the time taken to receive the signal is then converted into a voltage output. This voltage level can then be used as an indication of the density of the fluid. The sensor could easily establish 1% changes in the concentration mix. The sensor also included a temperature sensor which could be utilized for the measurement of the fluid temperature in order to determine the correct concentration level, since temperature plays a major role on the measurements that were taken.

The development and the design of the variable concentration controller system were done using a Microchip PIC18F452 to control all the functions. The device was programmed using a PICStart Plus Programmer together with using MPLab programming software. The code was written using the C programming language. The code is provided in Annexure A of this document. The device also has the built-in feature to change the flow rate of the liquid being tested.

A practical design and prototype product of a micro controlled system was built and various measurements were taken to calibrate and to accomplish the design specifications.

Testing the device proved to be successful but great care had to be taken when the temperature changed quickly and it is recommended that the container with the fuel cell fuel should be isolated to prevent fast temperature changes. Temperature had a major effect on the calibration of the unit and measurements had to be taken very carefully. It will also be advisable to place the detector as close as possible to the container tank to avoid changing temperatures in the transport system. It was found that when the temperature rises rapidly the detector read higher values than the actual values and if it cooled down rapidly the opposite is also true as can be seen from Figure 8. Normally this should not happen since rapid temperature changes should not take place in normal operating conditions.

Methanol can be replenished easily from a methanol tank and a dosing pump connected to the controller. Small spurts of methanol can be added to fuel the fuel cell a couple of seconds apart to ensure replenishment as needed. This should ensure that the methanol is not wasted by crossover. Methanol crossover studies will now be possible with the DMFC control system.

Other tests done with the methanol controller where higher volumes of methanol were used showed some interesting phenomena with regards to the methanol density. Between 20% and 30% volume mix the density became inversely affected by the increase in volume.

The use of an optical detector system should also be investigated as it might produce more rapid and accurate measurements. A more sensitive temperature measuring method can also be considered. This might improve the quality of measurements when the temperature is changing and during startup of the system produce accurate readings sooner.

Another option would be to control the concentration of the methanol in the water to adjust for higher or lower currents. In order to do this, the methanol feed should be controlled proportional to the load current of the fuel cell. This means that methanol should only be added when the load increases. A fuel cell in the regenerative mode can also be considered as a sensor for determining the amount of methanol to be added.

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