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## LOW CATALYST LOADED ETHANOL GAS FUEL CELL SENSOR

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## LOW CATALYST LOADED ETHANOL GAS FUEL CELL SENSOR

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#### ABSTRACT

One of the applications of polymer electrolyte fuel cells is using them as gas concentration measurement sensors. Since various gases can react with air in fuel cells, the concentration of the gas can be determined using the generated current density and calibration curve of the fuel cell sensor. Currently, the most challenging issues regarding fuel cell sensors are their durability and production cost due to their high amount of platinum (Pt) catalyst used to fabricate the sensor. In this study, fuel cell sensors with polymer electrolyte membrane for ethanol gas concentration measurement in human exhaled breath were studied for the purpose of determination of the best electrode Pt catalyst loadings and polymer electrolyte membrane in terms of reducing the sensor production cost and improving the sensor linear response and durability. The results of experiments using a fully automated test system with LabVIEW software package, consisting of a breath simulator, a potentiostat, a highly accurate multimeter, several fastresponse solenoid valves, and a 3D printed sensor housing, have been obtained and presented. The results confirm that the sensor Pt catalyst loading can be reduced by approximately 130 times compared to the catalyst loading in commercial sensors without notably changes on the sensor performance. In addition, the fabrication of sensors with very low Pt loading on the cathode side is possible and can be economically favorable for manufacturing ethanol gas sensors. It also has been shown that the peak current density measurement method, which expedites the sensor recovering time, can be used for low

catalyst loading sensors due to the observation of very good linearity behavior of the sensor with changing the ethanol gas concentration. Finally and after the validation of the sensor performance, a Nafion study and a durability study has been done. It was concluded that Nafion 115, 117, 438 and 1110 have the highest current density and linearity of calibration curve among all tested Nafions. Moreover, during eight weeks of durability study, the linearity of the calibration curve increased. The Nafion 1110 had the most linearity while Nafion 115 and 117 were capable of more current generation.

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## DEDICATION

To my mother, my father, my Ali and my Mehdi and My LOVE

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### CHAPTER I

#### INTRODUCTION

#### 1.1 Fuel cells, Electrochemical Sensors and Breathalyzers

In this chapter, the working principle of PEM fuel cells and their application as an electrochemical sensor will be reviewed briefly. Subsequently, the literature review related to this study is presented which followed by a summary about the purpose of this study.

## 1.1.1 Analysis of volatile compounds in chemical compositions investigation

The analysis of volatile compounds is an efficient method to appraise information about the chemical composition of liquids and solids. This principle is applied to several practical applications, such as food analysis where many important features (e.g. freshness) can be directly inferred from the analysis of volatile compounds [1-3]. The same approach can also be applied to a human body where the volatile compounds, collected from the skin, the breath or in the headspace of fluids, might contain information that could be used to diagnose several kinds of diseases. In particular, breath is widely studied and many diseases can be potentially detected from breath analysis. The most fascinating property of breath analysis is the non-invasiveness of the sample collection. Solid-state sensors are considered the natural complement to breathe analysis, matching the non-invasiveness with typical sensor features such as low-cost, easiness of use, portability, and the integration with the information networks. Sensors based breath analysis is then expected to dramatically extend the diagnostic capabilities enabling the screening of large populations for the early diagnosis of pathologies. In the last years there has been an increased attention to the development of sensors specifically aimed to this purpose. These investigations involve both specific sensors designed to detect individual compounds and non-specific sensors, operated in array configurations, aimed at clustering subjects according to their health conditions.

#### 1.1.2 Electrochemical Solid Polymer Electrolyte Sensors

Chemical sensors are widely used in many branches of industry, traffic, environmental and medical monitoring, for investigation of metabolism and control of biological processes. They are well-established and powerful tools to gain real-time information for process control by in-situ measurements of chemical composition without sampling. They provide direct, real-time information on the contents of certain chemical substance(s) present in their environment [4]. Their practical importance continuously increases as they not only offer an advantageous alternative to time- and cost demanding laboratory analyses but, primarily, feed necessary input information to a great variety of automatic devices, regulating mechanisms and robots; therefore, humans often cease to be direct users of the information provided and can concentrate on the designing and operating larger scientific or technological systems. Sensor signals are handled by electronic circuits and it is advantageous, for financial, spatial and operational reasons, to integrate the sensor and its electronic circuitry into a single block; in this way it is further possible to construct integrated systems with sensor arrays and systems with some degree of artificial intelligence (smart sensors). A significant group of chemical sensors is based on electrochemical principles [5]. The classical electrochemical sensors with liquid electrolytes are usually rather bulky and awkward; moreover, drying or leakage of the electrolyte may corrode various parts of the device and thus limit its lifetime and impair its function. Therefore, the progress in the field is directed towards solid-state sensors, i.e., those that contain no macroscopic liquid phase. Both types of sensors work according to electrochemical measuring principles, e.g. amperometric, potentiometric or impedimetric. As compared to sensors based on liquid electrolytes, solid electrolyte sensors principally exhibit some significant advantages including [6, 7]:

- Higher selectivity for certain components in a broader matrix of other gases;
- Long-term stability for maintenance-free application over months and years;
- Lower limit of detection down to the lower ppb-range;
- Faster response for sensor applications in control loops (<1 s) and
- High operating temperature for applications in combustion control or biotechnology where often sterilization or self-cleaning behavior is required.

There exist several ways for preparation of solid-state electrochemical sensors and one of the important approaches is the replacement of a liquid electrolyte by a solid polymer exhibiting an ionic conductivity, called a solid polymer electrolyte (SPE). In this type of sensor, an indicator electrode is either created directly on the SPE surface, or is in intimate contact with it [8-10]. The SPE provides an electrolytic connection of the indicator electrode with the other electrodes in an electrochemical cell, i.e., with a reference and a counter electrode. Moreover, SPE can serve for separation of the sample (detection) space

to which the indicator electrode is exposed from the reference and counter electrode compartment. The following advantages result from this arrangement [4]:

1. The geometry of the detection space can be designed entirely on the basis of the detection demands, without respect to electrochemical requirements on the cell.

2. It is possible to detect substances even in environments that have properties unsuitable for electrochemical measurements, e.g., in liquids of negligible electrical conductivity and in gases. The possibility of detecting substances in the gaseous phase may actually be considered as the main contribution of SPE-based sensors to electroanalytical chemistry.

3. The indicator electrode can be in direct contact with the test medium, without any additional diffusion barrier.

The transport of the electroactive substance towards the electrode is then rapid which is reflected in favorable static and dynamic properties of the sensor (the response is large and rapid). The electrochemical reactions that determine the sensor signal, i.e., the current obtained in an amperometric circuit or the potential in a potentiometric circuit, occur at the three-phase boundary where the test medium, the indicator electrode and the SPE meet and thus the properties of this boundary exert the decisive influence on the sensor behavior. These properties depend on the kind of SPE and its actual physico-chemical state and on the character of the electrodes, i.e., their material, geometry, pretreatment and their connection with the SPE. In some SPE-based sensor designs, the polymer is wetted with an electrolyte solution or with pure water, other sensors employ no liquid at all. In contrast to most sensors with inorganic solid electrolytes which need an elevated temperature, SPE-based sensor soperate under an ambient temperature.

#### 1.1.2.1 Amperometric vs. Potentiometric Electrochemical Sensors

Amperometric devices are a type of electrochemical sensor, since they continuously measure current resulting from the oxidation or reduction of an electroactive species in a biochemical reaction [11, 12]. Clark oxygen electrodes perhaps represent the basis for the simplest forms of amperometric biosensors, where a current is produced in proportion to the oxygen concentration. This is measured by the reduction of oxygen at a platinum (Pt) working electrode in reference to an Ag/AgCl reference electrode at a given potential [13]. Typically, the current is measured at a constant potential and this is referred to as amperometry. If a current is measured during controlled variations of the potential, this is referred to as voltammetry. Furthermore, the peak value of the current measured over a linear potential range is directly proportional to the bulk concentration of the analyte, i.e. the electroactive species [11, 13, 14]. Despite the disadvantage of this often indirect sensing system, it is claimed that amperometric devices maintain a sensitivity superior to potentiometric devices. An example of an amperometric device is the glucose biosensor, which is based on the amperometric detection of hydrogen peroxide.

Potentiometric devices measure the accumulation of a charge potential at the working electrode compared to the reference electrode in an electrochemical cell when zero or no significant current flows between them [11, 13, 15]. In other words, potentiometry provides information about the ion activity in an electrochemical reaction [16]. For potentiometric measurements, the relationship between the concentration and the potential is governed by the Nernst equation, where  $E_{cell}$  represents the observed cell potential at zero current. This is sometimes referred to as the electromotive force or EMF.

$$E_{cell} = E_{cell}^{0} - \frac{RT}{nF} \ln Q$$
(1)

 $E_{cell}^{0}$  is a constant potential contribution to the cell, R the universal gas constant, T the absolute temperature in degrees Kelvin, n is the charge number of the electrode reaction, F is the Faraday constant and Q is the ratio of ion concentration at the anode to ion concentration at the cathode [17].

### 1.1.3 Fuel Cell Technology

A fuel cell (FC) is an electrochemical energy converter that converts chemical energy of fuel directly into DC electricity. Typically, a process of electricity generation from fuels involves several energy conversion steps, namely [18]:

1. Combustion of fuel converts chemical energy of fuel into heat.

2. This heat is then used to boil water and generate steam.

3. Steam is used to run a turbine in a process that converts thermal energy into mechanical energy,

4. Finally, mechanical energy is used to run a generator that generates electricity.

A fuel cell circumvents all these processes and generates electricity in a single step without involving any moving parts. It is this simplicity that attracts attention. Such a device must be simpler, thus less expensive and far more efficient than the four-step process previously depicted.

At the heart of a polymer electrolyte membrane (PEM) fuel cell is a polymer membrane that has some unique capabilities. It is impermeable to gases but it conducts protons (hence the name, proton exchange membrane). The membrane that acts as the electrolyte is squeezed between the two porous, electrically conductive electrodes. These electrodes are typically made out of carbon cloth or carbon fiber paper. At the interface between the porous electrode and the polymer membrane there is a layer with catalyst particles, typically platinum supported on carbon. A schematic diagram of cell configuration and basic operating principles is shown in Figure 1.2. Electrochemical reactions happen at the surface of the catalyst at the interface between the electrolyte and the membrane. Hydrogen, which is fed on one side of the membrane, splits into its primary constituentsprotons and electrons. Each hydrogen atom consists of one electron and one proton. Protons travel through the membrane, whereas the electrons travel through electrically conductive electrodes, through current collectors, and through the outside circuit where they perform useful work and come back to the other side of the membrane. At the catalyst sites between the membrane and the other electrode they meet with the protons that went through the membrane and oxygen that is fed on that side of the membrane. Water is created in the electrochemical reaction, and then pushed out of the cell with excess flow of oxygen. The net result of these simultaneous reactions is current of electrons through an external circuit—direct electrical current.



Figure 0.1 A fuel cell is similar to a battery in that it has electrodes and an electrolyte, but it needs a fuel and oxidant supply and it generates waste heat and water [18].

The hydrogen side is negative and it is called the anode, whereas the oxygen side of the fuel cell is positive and it is called the cathode.



0.2: The basic principle of operation of a PEM fuel cell [18].

#### 1.1.3.1 How Fuel Cells Work as a Sensor

The fuel cell sensor can be likened to a battery; whilst a battery constantly delivers a voltage output, a fuel cell sensor only delivers a voltage/current output when alcohol is injected into the sensor. The output voltage/current is minute (in the low millivolts/micro amp) and is linear to the alcohol level present and being measured. The output voltage/current is generated via an electro-chemical reaction that occurs when alcohol is applied to the fuel cell electrolyte solution, this reaction will only last for a short time (and is dependent on alcohol concentration level) upon which the output will then dissipate back to zero voltage. The internal electrode surface area of a fuel cell is coated with high quality Pt material; electrical contacts are also made from Pt material. The electrolyte is an acidic solution. The alcohol fuel cell consists of an acidic electrolyte layer coated on both sides with finely divided Pt oxide. Pt wires are attached to the Pt; these connect to the breathalyzer readout module. When the person taking the breath test expires breathe into the tester unit, any alcohol present initiates a chemical reaction that produces two free electrons from each molecule of alcohol. This reaction takes place on the upper surface of the fuel cell. Positive hydrogen ions are freed in the process, and migrate to the lower surface of the cell, where they combine with atmospheric oxygen to form water, consuming one electron per H+ ion in the process. Thus, the upper surface has an excess of electrons, and the lower surface has a corresponding deficiency of electrons. If you connect the two surfaces electrically, a current flows through this external circuit to neutralize the charge. This current is a direct indication of the amount of alcohol oxidized by the fuel cell. With appropriate signal processing, it is possible to display breath alcohol concentrations directly and with significant accuracy.

#### 1.1.3.2 Why Fuel Cells for Breathalyzer

Fuel cell detection units are inherently accurate and alcohol specific compared to alternatives such as semi-conductors sensors. They also retain this extreme accuracy for extended periods, between 6 and 12 months before they require calibration with frequency of recalibration being far less often than units using lesser technologies. Unlike, for instance, semi-conductor units, they retain their calibration accuracy. A semi-conductor based unit can easily be inaccurate for law enforcement purpose just weeks after calibration. Consequently, fuel cell breath testers are specified by law enforcement agencies worldwide as their preferred measurement technology standard. This standard is conspicuously higher than those for 'consumer' breath testers which are not regarded as sufficient for evidentiary purposes should a drink driving suspect be liable to conviction or legal proceedings.

#### 1.1.4 Alcohol Breathalyzers

Measurements of alcohol blood levels are becoming prevalent in order to enforce drinking and driving laws [19]. While analysis of blood samples is generally required for conviction in a law court, routine analysis requires the use of portable and easy to operate devices which can be used directly in police cars. The measurement of alcohol concentration in the breath is a valid method because the alcohol concentration in exhale air is proportional to the alcohol concentration in blood. Among the electrochemical techniques which can be used for measuring alcohol levels in breath samples, the ethanolair fuel cell based on SPE technology has been more promising so far. The SPE cell consists of two noble metal electrodes deposited on either side of a proton conducting membrane, usually Nafion (Nation is the registered trademark of E.I. du Pont de Nemours, Wilmington, DE, USA, for its perfluorosulfonic acid materials). Noble metal based electrodes have to be used because of the highly acidity of the membrane. The SPE concept can be used in many applications.

Breath analyzers do not directly measure blood alcohol concentration, which requires the analysis of a blood sample. Instead, they estimate BAC indirectly by measuring the amount of alcohol in the subject's breath. There are two prevalent and widely accepted breathalyzer technologies in testing instruments - Hand-held field testing devices are generally based on electrochemical Pt fuel cell analysis while desktop analyzers generally use infrared spectrophotometer technology, and occasionally electrochemical fuel cell technology. Consumer breath analyzers, basically those not used by law-enforcement and industry, are increasingly using a silicon oxide sensor (also called a semiconductor sensor) to determine the blood alcohol concentration. The primary driver for this is lower cost however, semiconductor technology is generally considered unreliable and problematic in providing accurate and reliable BAC.

### 1.2 Literature Review

Accurate, rapid and low-cost alcohol detection and quantification is required for applications such as ethanol gas concentration measurement in human breath, clinical analysis, foods and beverages industries, and agricultural and environmental analyses [20, 21]. The ethanol gas concentration measurement in exhaled breath of vehicle drivers is essential for determination of the blood alcohol concentration in drunk drivers. For this purpose, the electrochemical-based/fuel cell sensors was introduced in 1970s [22, 23].

Although gas chromatography [24, 25], infrared [26–28], and semi-conductor [29–31] techniques are commercially available, the breath ethanol measurements are usually performed by fuel cell sensors [32] due to their acceptable accuracy, linearity, sensitivity and selectivity, portable field-based size, moderate-cost, and rapid response time to expedite the assessment of vehicle drivers [33]. Although the available fuel cell sensor technology is accept-able to measure the ethanol gas concentration, this technology has not been updated for many years. Despite significant progress that has been made in the fields of Nano-technology, catalysts, and fuel cells in the past decade, commercial fuel cell sensors are still based on 1970s technology. At present, the Pt catalyst content in fuel cell sensors is very high (manufacturing cost issue) and liquid phosphoric or sulfuric acid [34, 35] is used as their electrolyte (safety issue). The recent advances in proton exchange membrane fuel cells (PEMFCs) [36–39] can lead researchers to the next generation of fuel cell sensors that are highly accurate, safe and cost-effective [40,41]. Fuel cells are electrochemical devices, which can directly con-vert the chemical energy of some fuels (in this study the fuel is ethanol gas) to electricity [42, 43]. It has been reported that PEM-FCs with solid polymer electrolytes can be successfully used with direct ethanol fuel [44–49]. The PEMFC can be used as the ethanol gas sensor such that the magnitude of generated current determines the feed ethanol gas concentration. PEMFCs are comprised of two electrode catalysts, which usually contain a precious metallic catalyst such as platinum [50], or platinum- ruthenium [51]. The electrodes are separated by an electrolyte membrane such as Nafion [52], or Titania-Nafion composite [53]. A more detail of related recent studies is as following:

Zuba assessed the reliability and performance of two handheld devices, the Alcotest 7410 and the AlcoSensor IV, in view of their use for evidential purposes [54]. The readings of portable instruments were in very good agreement with the results of confirmatory analyses performed by stationary devices. The correlation with the results of blood analysis was weaker, but comparable with the correlation between the readings of stationary devices and the results of blood analyses. The differences in results were independent of alcohol concentration.

Chen and Danao choose ethanol, a potential biomarker of liver function, as a model biomarker to demonstrate the effect of sampling conditions on different phases and how breath sampling could be standardized by developing predictive models [55]. Results showed exhaled breath (EB) samples were affected by breath temperatures and exhaled breath condensate (EBC) samples were affected by condensing temperatures. Flow rate changes did not have a significant influence on both EB and EBC samples.

Bianchini et.al showed that the oxidation of ethanol to acetic acid can be selectively achieved on Pd-based catalysts in both passive and active direct fuel cells equipped with an anion-exchange polymer membrane [56]. Along with significant mass transformations, unique power densities have been obtained for long working times.

Kamiya and sudoh used a polymer electrolyte membrane, a Nafion membrane, instead of the liquid electrolyte for fabricating fuel cell sensors for ethanol. Platinum-based membrane-electrode assemblies were prepared to do electrochemical measurements of breath alcohol levels [57]. Total amounts of coulomb of transient sensor output were found to be quite linear relative to the ethanol gas concentration. In a thesis by Prest, the physical and electrochemical properties of a commercially available fuel cell-based breath alcohol sensor was characterized [58]. Loss of proton conductivity and Loss of electrochemically active surface area of Pt as a result of membrane dehydration were investigated in the commercial sensors.

Polymer electrolyte membrane were successfully fabricated and tested for the detection of ethanol gas concentration by Kim et.al. Nafion 115 membrane was used for the polymer electrolyte and 10% Pt/C sheets with 0.5 mg/ $cm^2$  Pt loading were used as catalyst electrodes [59]. The peak height of electrical signal obtained from the fuel cells was found to be quite linear with the ethanol gas concentration.

In this study PEMFC was used as a sensor to measure ethanol gas concentration in simulated breath of drunken drivers. The obtained current response of the sensor was measured as a function of blood alcohol concentration (BAC). The BAC is the ethanol content in grams divided by blood volume in deciliters. The permissible legal detection limit of BAC for non-business and business drivers are 0.08% and 0.04%, respectively in most states of the United States, which correspond to 208 and 104 ppm ethanol in human breath [60]. It is noted that the ratio of alcohol concentration in blood to alveolar air is 2100:1[61, 62]

Although some researchers have shown the possibility of using PEMFC sensors with solid polymer electrolyte to measure ethanol gas concentration [40,41,63], no study has been done so far to show the effect of catalyst loading on the performance of these sensors and how much the catalyst loading in commercial sensors can be decreased if their fabrication technology is updated. The objective of this study is to answer these questions.

For this purpose, the solid polymer electrolyte membrane (Nafion) and electrodes containing carbon-supported Pt catalyst were employed to fabricate the PEMFC sensors. These sensors were used to measure ethanol gas concentration in the simulated exhaled human breath. Electrodes with different Pt catalyst loading were examined to investigate the effect of Pt loading on performance of fresh sensors. The fresh sensor in this study denotes a sensor tested in the same day that the membrane electrode assembly (MEA) has been fabricated. It is noted that in addition to the catalyst loading [64] that is the purpose of this study, the type of catalyst [65] and the electrode microstructure [66–70] can play important roles in performance determination of any electrochemical systems, including fuel cell sensors. The type of catalyst, the electrode microstructure, durability and environmental tests, and improvement of polymer electrolytes for fuel cell sensors are ongoing studies in Advanced Energy & Sensor Lab.

## CHAPTER II

#### SENSOR FABRICATION, EXPERIMENTAL SETUP AND TESTING

## 2.1 Sensor working principle

As shown in Figure 2.1 the sensor basically is a direct ethanol PEMFC. Ethanol is catalyzed at the anode catalyst layer surface generating  $H^+$  and  $e^-$ . Electrons go to the external circuit generating electricity and hydrogen ions go through the internal circuit via ionic conductive electrolyte to complete the fuel cell circuit.



Figure 2.1: A schematic of the sensor working principle [18].

Corresponding to the ethanol concentration at the entrance the current would be generated. After fuel cell calibration for different ethanol concentrations, the PEMFC can be utilized as the ethanol sensor based on the generated current from alcohol containing breath.

#### 2.2 Sensor Fabrication

In this section the fabrication and assembly of the electrochemical sensors and their components is explained in detail.

#### 2.2.1 Activation Process of Nafion

**Nafion** is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer discovered in the late 1960s by Walther Grot of DuPont [71]. It is the first of a class of synthetic polymers with ionic properties which are called ionomers. Nafion's unique ionic properties are a result of incorporating perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone. Nafion has received a considerable amount of attention as a proton conductor for PEMFCs because of its excellent thermal and mechanical stability.

The chemical basis of Nafion's superior conductive properties remain a focus of research. Protons on the SO<sub>3</sub>H (sulfonic acid) groups "hop" from one acid site to another. Pores allow movement of cations but the membranes do not conduct anions or electrons. Nafion can be manufactured with various cationic conductivities.

Nafion polymeric sheets are being used as the electrolyte for PEMFC ethanol sensor. The list of different Nafions used in fabrication of sensors in this study is as follows:

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- Nafion 115
- Nafion 117
- Nafion 211
- Nafion 212
- Nafion 438
- Nafion 1110
- Nafion XL

Prior to fabrication, Nafion membrane requires impurity removal (cleaning) by the following steps. Nafion was immersed in boiling 3 wt% H<sub>2</sub>O<sub>2</sub> aqueous solution for 1 h. Then, it was rinsed in DI water several times, followed by boiling in DI water for 1 h. The Nafion membrane cleaning was continued by immersing in boiling 1M H<sub>2</sub>SO<sub>4</sub> aqueous solution for another hour. Finally, the Nafion membrane was rinsed several times with DI water and stored in DI water at room temperature prior to its usage in sensor fabrication. The process is shown in figure 2.2.



Figure 2.2: The Nafion activation process and materials.

### 2.2.2 Electrodes and Current Collectors

The PEMFC sensor contains of two Pt/C electrodes, which are impregnated by Nafion ionomer to be both electrical and ionic conductive. Based on Pt content of electrodes they can be classified as follows:

- 0.03 mg/cm<sup>2</sup> 20% Pt/C on Vulcan Cloth
- 0.20 mg/cm<sup>2</sup> 20% Pt/C on Vulcan Cloth
- 0.30 mg/cm<sup>2</sup> 40% Pt/C on Vulcan Cloth
- 0.50 mg/cm<sup>2</sup> 60% Pt/C on Vulcan Cloth
- 0.50 mg/cm<sup>2</sup> 60% Pt-Ru/C on Vulcan Cloth
- 0.10 mg/cm<sup>2</sup> 10% Pt/C on Vulcan Cloth
- 0.25 mg/cm<sup>2</sup> 30% Pt/C on Vulcan Cloth
- 0.40 mg/cm<sup>2</sup> 50% Pt/C on Vulcan Cloth

The current collectors are highly electronic conductive metals that enhance the electrons transfer from Pt/C electrodes to the external circuit. In order to have more cost-effective material, we use 316 stainless steel mesh.

## 2.2.3 Assembly of Different Components

The electrodes and activated Nafion membranes were cut precisely by laser cutter machine (VLS2.30 Versa Laser) in a circular shape with the diameter of 15 mm (Area  $\approx$  1.8 cm2). It should be noted that Nafion membranes should be cut slightly larger than electrodes to prevent short-circuiting. Nafion 115 was then placed between two electrodes and was compressed using a hot press (MTI Corporation), which applied 10 MPa (or 2.5

kN) of pressure at 100°C for 1.5 min to complete the Membrane Electrode Assembly (MEA) fabrication. The fabricated MEA should be sandwiched between two current collectors (0.01 in. thick stainless steel metal grid, McMaster) to improve the current collection from the sensor's electrodes. The process is shown in figure 2.3.



Figure 2.3: A schematic of the sensor fabrication and assembly process.

#### 2.2.4 Sensor Testing Chamber Design and Fabrication

In order to ensure good contact between current collectors and electrodes and to minimize gas leakage from anode channel to cathode, a sensor chamber was designed and printed by a high resolution 3D printing machine (Objet EDEN260 V). The 3D model of the chamber is shown in figure 2.4. The screw/bolt-fit chamber cap was used to seal the sensor chamber and provide enough pressure on sensor current collectors to maintain perfect connection between sensor layers. Figure 2.5 shows the sensor assembly inside the sensor chamber.





Figure 2.4: 3D design of the sensor chamber for 3D printing process.

## 2.3 Experimental Setup and Testing

In this section, the experimental equipment and set up as well as the working principle of the setup is explained in detal.

## 2.3.1 Solution Preparation

BAC is commonly used as a metric of alcohol intoxication for legal or medical purposes. Blood Alcohol Content is the legal name for BAC but Blood Alcohol Concentration is sometimes used for simpler description.



Figure 2.5: PEMFC ethanol gas sensor assembly inside the sensor chamber.

In order to simulate alcohol containing breath, 500 mL of water-ethanol solution should be prepared and heated up till 34°C at breath simulator. Below table shows the proper amount of needed water and ethanol for each specific BAC:

BAC	H <sub>2</sub> O (mL)	C2H5OH (µL)	H <sub>2</sub> O (mL)	C <sub>2</sub> H <sub>5</sub> OH (µL)
0	500	0	500	0
0.005	499.9617	38.33905017	500	38
0.01	499.9233	76.67685978	500	77
0.02	499.8467	153.3487575	500	153
0.03	499.77	230.0156938	500	230
0.05	499.6167	383.3346837	500	384
0.07	499.46	536.6338332	500	537
0.08	499.3867	613.2759691	500	614
0.10	499.2335	766.5453654	500	768
0.14	498.927	1073.02467	500	1075
0.18	498.6206	1379.424682	500	1383
0.20	498.4674	1532.594964	500	1537
0.25	498.0846	1915.434	500	1923
0.30	497.7019	2298.149276	500	2309

Table 2.1: The amount of ethanol used for certain BACs

BAC = m / V

m: alcohol weight (g)

V: blood volume (dL)

BAC [=] g / dL

## 2.3.2 Experimental Procedure

Figure 2.6 illustrates the sensor experimental setup. Dry air passes through a normallyclosed solenoid valve (Omega – SV8COIL-24DC), which is controlled by LabVIEW software. The flow rate of dry air is controlled by a rotameter at 5 L min-1, which is sent into a breath simulator. The breath simulator consists of a 500 mL DI water and ethanol mixture held accurately at 34°C to simulate human breath that contains alcohol. The simulated exhaled breath vacates the breath simulator and, through a normally-open solenoid valve (Omega – SV8COIL-24DC), is conducted to the vent in order to wash the outlet tubing with the same mixture that is going to enter the sensor chamber.

Prior to the sensor chamber, a normally-closed solenoid valve (Omega – SV8COIL-24DC) lets the tubing be washed for 10 s, then simultaneously the normally-open vent valve will be closed and the normally-closed sensor valve will be opened for 1 s to feed the sensor. The solenoid valves with 1 ms accuracy can ensure the reproducibility of the sensor feeding system during the entire experiment. Sensor electrodes were connected to a data logger (KEYSIGHT digital multimeter) via cathode and anode wires to measure the current generated by the sensor. In order to draw the current from the MEAs a constant voltage load of 1 mV was applied to all sensors using potensistate (SP-150, Bio-logic). To achieve the highest consistency, all experiments are automated and controlled by an inhouse code developed using LabVIEW software package.

The sensors with different Pt loadings were subjected to 10 different BACs from 0.005 to 0.2% to investigate their electrochemical performance and linearity response versus the change of% BAC. The sensors were kept at room temperature during testing. After each test with certain BAC, the sensor was washed with pure DI water through the testing cycle for several times to remove remaining ethanol gas in tubes and housing. Removing the remaining ethanol from tubing and sensor electrodes is essential since any remaining ethanol can interfere with the next run's current measurement.
# 2.3.2.1 Solenoid Valves Controlling and Multimeter

The solenoid valves are controlled by programming in LabVIEW software through a data acquisition (DAQ) system. The LabVIEW window for controlling of valves is shown in figure 2.7. In this figure, the meaning of red numbers are as following:



Figure 2.6: A schematic of the experimental setup.

Number of cycles: It shows the number of desire injections plus 2. E.g. if you enter
 you will get 3 injections.

2- Off time (min): It shows the rest time between injections.

3- Washing time (s): It shows the time for washing the tubing before each sample injection.

4- Feeding time (s): It shows the time duration that sample is sending to sensor chamber.It is sampling or injection time.



Figure 2.7: LabVIEW program window.

5- Elapsed time (s): It shows the whole 1 cycle time: feeding time + washing time + off time.

6- Finished cycles: It shows the number of completed cycles minus 1.

7- Run bottom: The run will be started by pushing this bottom.

8- Stop bottom: The run will be stopped by pushing this bottom.

The multimeter software including the name of different options is shown in figure 2.8.



Figure 2.8: A view of multimeter software.

# CHAPTER III

# **RESULTS AND DISCUSSION**

# 3.1 Introduction

In this study, the MEA of PEMFC ethanol gas sensor consists of solid polymer electrolyte sandwiched by two electrodes. Electrodes are basically gas diffusion electrodes (GDE, Fuel Cells Etc.) comprised of Vulcan carbon-supported Pt catalyst (HiSpec 3000 and 4000, AlfaAesar/Johnson Matthey) and Nafion ionomer spread on woven car bon cloth (GDL-CT, CeTech) as the gas diffusion layer (GDL). GDEs with 10, 20, 30, and 40% Pt/C with Pt loading of 0.1, 0.2, 0.25, and 0.3 mg/cm<sup>2</sup>, respectively, were used as the sensor electrodes (It should be noted that 10% Pt/C, 0.1 mg/cm<sup>2</sup> Pt and 30% Pt/C, 0.25 mg/cm<sup>2</sup> Pt GDEs were customized with the exact same catalyst and GDL type with the other GDEs). The ratio of Nafion ionomer to Pt was held constant at 3:2 for all GDEs. The characteristics of all GDEs used in this study including their electrochemical active specific surface area (ECSA) are listed in Table 2.1. (The ECSA values were calculated and reported by the catalyst layer provider.) Nafion 115 with the thickness of 127 m (Fuel Cells Etc.) was used as the solid electrolyte membrane for fabrication of MEAs. The SEM micrographs of a typical GDE used is illustrated in Figure 3.1.



Figure 3.1: SEM micro porous structure of a typical sensor electrode (a) surface, (b)

#### cross section view

Table 3.1: Characteristics of different gas diffusion electrodes used in this study
---

	Pt catalyst	ECSA a		Pt in 1.8 $cm^2$			
Catalyst	loadin g (mg/cm <sup>2</sup> )	_	CL <sup>c</sup>	MPL d	GDL e	GDE f	electrode (mg)
10% Pt/C	0.10	105	10	70	310	390	0.18
20% Pt/C	0.20	90	10	70	310	390	0.36
30% Pt/C	0.25	80	9	70	310	389	0.45
40% Pt/C	0.30	60	8	70	310	388	0.54
20% Pt/C	0.03	90	2	70	310	382	0.05
Commerci	3	20h	1	Ele	ectrolyte thic	kness: 1	57.27
al sensor	2	30°	0	mm			g

a) ECSA: electrochemical active specific surface area.

b) The value is the reported surface area for Platinum black by vendor.

c) CL: catalyst layer

d) MPL: micro porous layer

e) GDL: gas diffusion layer

f) GDE: gas diffusion electrode (GDE = CL + MPL + GDL)

g) Commercial sensor electrode area was 1.21 cm2. The amount of Pt loading for electrode area of 1.8 cm2 was extrapolated.

# 3.2 Results and discussion

In this section the result of the study is presented categorized in terms of sensor with identical, non-identical platinum loading in the electrodes as well as the effect of Nafion and time on the durability of the sensors.

#### 3.2.1 Peak and Area Measurements

The peak and the area underneath of each curve can be measured very precisely by using Origin pro software. The area also can be calculated by the following equation:

# 3.2.2 Catalyst Loading Study

The first stage of sensor testing is related to the investigation of the effect of catalyst loading on the current density and linearity of the sensor calibration curve. In this series of testing we used Nafion 115 and catalyst layer based Table 2.2.



Figure 3.2: Calculation procedure of the pick and area under the curve.

Sensor Number	Anode Catalyst loading	Cathode Catalyst loading
Sensor 11	20% Pt/C 0.2 mg/cm <sup>2</sup> Pt	20% Pt/C 0.2 mg/cm <sup>2</sup> Pt
Sensor 12	40% Pt/C 0.3 mg/cm <sup>2</sup> Pt	40% Pt/C 0.3 mg/cm <sup>2</sup> Pt
Sensor 13	60% Pt/C 0.5 mg/cm <sup>2</sup> Pt	60% Pt/C 0.5 mg/cm <sup>2</sup> Pt
Sensor 14a	40% Pt/C 0.3 mg/cm <sup>2</sup> Pt	20% Pt/C 0.2 mg/cm <sup>2</sup> Pt
Sensor 14b	20% Pt/C 0.2 mg/cm <sup>2</sup> Pt	40% Pt/C 0.3 mg/cm <sup>2</sup> Pt
Sensor 15a	60% Pt/C 0.5 mg/cm <sup>2</sup> Pt	20% Pt/C 0.2 mg/cm <sup>2</sup> Pt
Sensor 15b	20% Pt/C 0.2 mg/cm <sup>2</sup> Pt	60% Pt/C 0.5 mg/cm <sup>2</sup> Pt
Sensor 16a	60% Pt/C 0.5 mg/cm <sup>2</sup> Pt	40% Pt/C 0.3 mg/cm <sup>2</sup> Pt
Sensor 16b	40% Pt/C 0.3 mg/cm <sup>2</sup> Pt	60% Pt/C 0.5 mg/cm <sup>2</sup>
Sensor 17a	40% Pt/C 0.3 mg/cm <sup>2</sup> Pt	20% Pt/C 0.03 mg/cm <sup>2</sup>
Sensor 17b	60% Pt/C 0.5 mg/cm <sup>2</sup> Pt	20% Pt/C 0.03 mg/cm <sup>2</sup>
Sensor 18a	20% Pt/C 0.2 mg/cm <sup>2</sup> Pt	20% Pt/C 0.03 mg/cm <sup>2</sup>
Sensor 18b	20% Pt/C 0.2 mg/cm <sup>2</sup> Pt	60% Pt/C 0.5 mg/cm <sup>2</sup>
Sensor 19	60% Pt/C 0.5 mg/cm <sup>2</sup> Pt	20% Pt/C 0.2 mg/cm <sup>2</sup>

Table 3.2: Catalyst study number reference.



Figure 3.3: Sensor catalyst loading study.



Figure 3.4: Sensor catalyst loading study. (Cont'd).



Figure 3.5: Sensor catalyst loading study. (Cont'd).



Figure 3.6: Sensor catalyst loading study. (Cont'd).

Regarding the figure 3.3 of various catalyst loading sensors, it was found that, it is possible to fabricate sensors with non-identical catalyst loading since the reduction of

catalyst on the cathode side does not affect the current and charge densities significantly and the result would still be reliable. The term "identical electrode sensor" means the Pt loading for the anode and cathode of sensors are exactly the same. However, the anode side catalyst loading reduction would affect the current density and linearity of the calibration curve. A more detail of this issue is discussed in the following figures.

#### 3.2.2.1 Comparison of the Sensors with Nafion 115 and Different Catalyst Loadings

Figure 3.4 shows the electrical current response of the sensors with various electrode Pt loadings at the BAC of 0.05%. Figure 3.4(a) demonstrates responses of identical electrode sensors. Figure 3.4(b) shares the same concept of Figure 3.4(a) but for non-identical electrode sensors, where the cathode Pt loading is kept as low as 0.03 mg/cm2 (20% Pt/C with 0.03 mg/ cm2 Pt). It should be noted that the same current test was accomplished for ten %BAC values but only the results of BAC = 0.05% are demonstrated in this figure. As shown in Figure 3.4(c), for all case studies when the ethanol-containing gas was injected into the sensor's anode compartment, the current across the external circuit was increased sharply in very short time (peak time). It fell rapidly down after reaching a peak and exhibited a sluggish decline towards the end of the cycle (decay/recovery time). The recovery curve exhibited exponential behavior as a exp(-bt). This equation can be applied to all fabricated sensors, where only (a) and (b) are changing by catalyst loading and %BAC. The peak current and the area underneath the current response curve are also dependent on the Pt loading for the sensor electrodes and %BAC. Three different steps could be considered for current generation in a fuel cell sensor including (i) diffusion of C2H5OH and O2 into the electrodes catalysts, (ii) electrochemical reaction of C2H5OH

and  $O_2$  on the anode and cathode active sites, and (iii) H<sup>+</sup> diffusion in solid electrolyte polymer (Nafion 115) [38].



Figure 3.7: Current density measurement at BAC = 0.05% using different Pt loading on sensor electrodes for (a) identical electrodes and (b) non-identical electrodes with low Pt loading on cathode (cathode Pt loading for all sensors was kept at 20% Pt/C—0.03 mg cm-2). The Pt catalyst loading shown for each graph is related to the anode. (c) Concepts of peak time, decay/recover time, peak current and charge density (area underneath of

## current curve).

Ethanol gas is oxidized over the Pt catalyst at the anode (reaction 1) but Pt loading on the cathode side also plays an important role in sensor current generation since oxygen reduction (reaction 2) takes place on the cathode side. By the same anode Pt loadings, the sensors with low Pt loading on their cathode exhibit lower current densities than the sensors with high Pt cathode loading. Nevertheless, our investigations for current peaks obtained from identical sensors and non-identical sensors with very low Pt loading confirm that the value of peak current is reduced by less than 2 times on average if the catalyst loading reduces significantly in cathode.

Anodic reaction: 
$$C_2H_5OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$$
 (1)

Cathodic reaction: 
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 (2)

#### 3.2.2.2 Identical electrode sensors

Figure 3.5 demonstrates the sensor performances with identical Pt loading on their electrodes as the function of %BAC and examines the linearity response of different sensors by altering the electrode's catalyst loading. The peak current density of different catalyst loaded sensors is shown in Figure 3.5(a). The increase of Pt/C loading from 10% to 40% raised the peak current densities, which was expected due to an increase in the catalyst loading on electrodes. Increasing the catalyst loading increases the active sites resulting inactivation polarizations reduction leading to an increasing in generated current densities. In addition to the output current density magnitude and sensors response linearity, the sensitivity of sensors is another important factor for MEAs characterization. The sensor sensitivity would be obtained by the slope of calibration curves shown in Figure 3.5(a). The current density sensitivity factors (slope of calibration curves) of identical electrode sensors were calculated with respect to total mass of Pt loaded in each sensors GDEs. Table 3.2 listed the sensitivity values for identical sensors. The trend of sensitivity

factors can be explained by total amount of Pt loading in each sensor; the higher the Pt loading in grams, the higher sensitivity. Although, it is reported (and also shown in Table 3.1) that catalysts made from HiSpec 3000 (20% Pt/C) has higher electrochemical specific surface area (ECSA) than catalyst made from HiSpec 4000 (40% Pt/C) [26] but higher Pt loading in 40% Pt/C than other GDE catalysts led to the highest sensitivity for 40% Pt/C catalyst. Based on the study shown in Table 3.3, although the ECSA is very important but the key factor effecting on sensor performance and its sensitivity is the sensor total Pt loading; e.g. although the sensor with 30% Pt/C loading has the highest surface area (0.072  $m^2$ ) but the highest sensitivity goes to 40% Pt/C sensor with highest total Pt loading (1.08) mg). Figure 3.5(b) demonstrates the changes in the area under the current response curves, which represents the charge density. The charge density sensitivity factors of identical sensors with 10%, 20%, 30% and 40% Pt/C loaded electrodes are also calculated and listed in Table 3.3. It is believed that the area under the curve could represent the ethanol concentration in the feed more accurately than by using the peak current value [38]. In this study, the sensitivity, peak current and charge densities follow the same trend, which shows the highest sensitivity, current and charge densities for 40% Pt/C and the lowest ones for 10% Pt/C loading. The regression least square coefficient ( $R^2$ ) shown in Figure 3.5(c) and (d) revealed that all of the sensors with different Pt loadings had acceptable linear response toward changing ethanol concentration from BAC 0.005 to 0.2%. The sensor with 20% Pt/C and 0.2 mg/cm<sup>2</sup> loading only showed poor linearity at BACs between 0.005 to 0.1% and could not perform as good as other sensors across the full range of BACs. The best linearity was obtained from the sensor with 30% Pt/C and 0.25 mg/cm<sup>2</sup> loading, revealing more than 99% linearity. Since obtaining the peak current density is faster than the charge

density, employing the peak current density method for these sensors to measure the ethanol concentration is preferred. Thus, the sensor can be recovered for the next use faster. It was discovered that the measurement accuracy would not be changed if the peak current method is used instead of charge density to measure the ethanol gas concentration for a fresh sensor operating at room temperature.

#### 3.2.2.3 Non-identical electrode sensors

Ethanol oxidation and hydrogen ion generation take place on the anode side of the sensor. Since the ethanol concentration in the feed gas is in the range of ppm, the catalyst loading on the anode should be high enough to guarantee the occurrence of ethanol oxidation and sensor functioning. On the other hand, the oxygen concentration in air is 21 Vol%, which is significantly higher than the ethanol concentration in the anode.

sensors.							
Anod	Cathod Senso		Electrochemica	Electrochemica Curren		Charg	Charg
e Catalyst	e Catalyst r total		l active surface area	t density	t density	e density	e density
		loading	$(m^2)$	slope $(\mu A/$	sensitivity	slope ( $\mu C$ /	sensitivity
		(mg)		<i>cm</i> <sup>2</sup> )	(mA/g)	<i>cm</i> <sup>2</sup> )	(C/g)
10 %	10 %	0.36	0.038	8.51	85.10	1143.6	11.44
Pt/C	Pt/C						
20%	20%	0.72	0.064	28.22	141.10	3611.4	18.06
Pt/C	Pt/C						
30%	30%	0.90	0.072	41.36	165.44	4740.6	18.96
Pt/C	Pt/C						
40%	40%	1.08	0.064	67.64	225.47	7057.8	23.53
Pt/C	Pt/C						
Anode and Cathode Pt loading is $0.2 mg/cm^2$							

Table 3.3: Electrochemical active surface area and sensitivity of identical electrode

Therefore, the Pt loading on the cathode can be potentially lower than the anode. Thus, fabrication of sensors with lower Pt loading on cathode can be economically favorable, especially in mass production, without having any crucial effect on the sensor's performance. Figure 3.6 demonstrates the sensors performances with non-identical electrode Pt loadings (low Pt loading: 20% Pt/C 0.03 mg/cm<sup>2</sup> on the cathode) as the

function of %BAC and examines the current response and linearity of different sensors by altering the anode catalyst loading. The peak current densities shown in Figure 3.6(a) revealed that the trend of current generation of sensors with non-identical anode loading is similar to identical electrode sensors. The current density sensitivity factor of non-identical electrode sensors were calculated respect to total mass Pt loading in sensor for 10%, 20%, 30% and40% Pt/C anode loadings. Table 3.4 listed the sensitivity values for non-identical sensors. The sensors with 40% Pt/C and 0.3 mg/cm<sup>2</sup> loading on the anode side showed the highest sensitivity and peak current density. Figure 3.6(b) shows the charge density also follows the linear behavior by increasing the ethanol concentration (%BAC). The charge density sensitivity factors of this kind of sensors were also calculated for 10%, 20%, 30% and 40% Pt/C anode loadings. The calculated least square coefficient (R<sup>2</sup>) demonstrated in Figs.15(c) and 15(d) shows that the sensors with low Pt loading on the cathode have a good linearity response. Only the sensor with 20%Pt/C and 0.2 mg/cm2anode loading deviated from linear behavior. The R<sup>2</sup> values for both peak current and charge densities are high.



Figure 3.8: The performance of PEMFC ethanol sensors with identical Pt loading on electrodes as a function of %BAC and their linearity response. (a) Peak current density of sensors with different Pt loading. (b) Charge density of sensors with different Pt loading.

(c) Regression coefficient of peak current densities for sensors operating from

BAC0.005–0.1% and 0.005–0.2%. (d) Regression coefficient of charge densities for

sensors operating from BAC 0.005–0.1% and 0.005–0.2%.



Figure 3.9: The performance of PEMFC ethanol sensors with low Pt loaded cathode (20% Pt/C—0.03 mg cm-2) as a function of %BAC and their linearity response. (a) Peak currentdensity of sensors with different anode Pt loading. (b) Charge density of sensors with different anode Pt loading (c) Regression coefficient of peak current densities for sensorsoperating from BAC 0.005–0.1% and 0.005–0.2%. (d) Regression coefficient of charge densities for sensors operating from BAC 0.005–0.1% and 0.005–0.1% and 0.005–0.2%.

			electione se	115015.			
Anode	Cathode	Sens	Electroche	Current	Current	Charge	Cha
Catalyst	Catalyst	or total	mical active	density	density	density	rge
		Pt	surface area	slope	sensitivity	slope	density
		loading					sensitivi
		(mg)					ty
10%	20 %	0.23	0.025	3.36	52.59	711	11.1
Pt/C	Pt/C						3
20%	20 %	0.41	0.037	2.17	19.05	181.8	1.60
Pt/C	Pt/C						
30%	20 %	0.50	0.041	18.04	129.89	1959.6	14.1
Pt/C	Pt/C						1
40%	20 %	0.59	0.037	27.51	167.86	3087.0	18.8
Pt/C	Pt/C						4

Table 3.4. Electrochemical active surface area and sensitivity of non-identical electrode sensors.

<sup>a</sup> The cathode catalyst loading is  $0.03 \text{ mg/}cm^2$ 

#### 3.2.3 The Commercial Sensor

Figure 3.7 illustrates a commercial ethanol gas sensor's performance as a function of %BAC. The commercial sensor employs very thick porous polyvinyl chloride (PVC) membrane that is loaded with liquid acid electrolyte with two thin (10  $\mu$ m) identical Pt electrodes ( $32 \text{ mg/cm}^2 \text{Pt}$ ). The commercial sensor was tested in the same cell hardware with the fabricated sensors in this study. Figure 3.7(a) and (b) demonstrates the peak current density and charge density generated by this sensor, respectively. The slope of calibration curve of commercial sensor for current density and charge density were calculated by 213.85  $\mu$ A/cm<sup>2</sup> and 27814.2  $\mu$ C/cm<sup>2</sup>, which are correspond to sensor sensitivity of 8.09 mA/g and 1.05 C/g, respectively. Comparison of the magnitude of sensitivity factors, peak current and charge densities of the commercial sensor and the fabricated sensors in the lab revealed that the commercial sensor generates up to one order of magnitude higher current and charge densities than the sensors developed in lab. High current and charge densities of the commercial sensor are expected due to extremely high loading of Pt catalyst on its electrodes, which causes very lower Pt mass-based sensitivity for commercial sensor. Although the generated current density of the commercial sensor is

greater than the fabricated sensors in lab, the majority of the fabricated sensors exhibited slightly better linearity with changing %BAC, especially in BAC range of 0.005–0.1%, and all of them exhibited larger Pt mass-based sensitivity factor (see Table 3.5). Figure 3.7(c) shows the SEM micrograph of the commercial sensor with the same magnification as the fabricated sensors in lab. The energy dispersive x-ray spectroscopy (EDS) analysis of the commercial sensor electrode illustrated in Figure 3.7(d) confirms that almost 100 wt% of the electrode is Pt catalyst. In order to compare the developed sensors with the commercial one, the best performing sensor from each category (i.e. identical electrode and non-identical electrode) was selected and listed in Table 3.3 along with the commercial sensor characteristics. The criteria to select the best sensor were combination of the amount of Pt loading, linearity, sensitivity and magnitude of the current density generation of the sensor. Table 3.5 indicates that the best sensor is the one with 40% Pt/C 0.30 mg/cm<sup>2</sup> anode and 20% Pt/C 0.03 mg/cm<sup>2</sup> cathode, since it has the highest linearity response, the lowest Pt loading and high Pt mass-based sensitivity. The amount of Pt used in the commercial sensor is more than 130 times higher than that in this sensor. In addition, this sensor has 67% less Pt catalyst compared to a PEMFC sensor fabricated and tested by Kim, et al. [38]. The advantages of the commercial sensor over fabricated sensors are its higher current and charge density generation plus probably its stability. Figure 3.8 illustrates a preliminary study for durability and repeatability of the best developed sensor. The durability runs were completed after 2 months of the sensor sitting idle in a lab environment. Getting almost similar results from the sensor after 2 months shows that the sensor was durable and its Nafion membrane was still active and could preserve its moisture. Rerunning the sensor for 2 extra times indicated that results are repeatable, and the sensor could keep its accuracy

for all repeated runs. A more detail durability study is discussed in section 3.4.2. A recent study using power-generating fuel cell electrode material as breath alcohol sensor with 20% Pt/C and Pt loading of 0.4 mg/cm<sup>2</sup> showed 97% less Pt usage compared to the commercial sensor [46]. However, in our study we developed the sensor with non-identical Pt loading electrodes which lead to the use of 100–130 times less Pt loading than commercial sensor due to applying cathodes with extremely low amount of Pt loading. Subsequently, we depict that with this lower amount of Pt loading, sensitivity and linearity of the results are still reliable as a breath alcohol sensor.

Table 3.5: Comparison of best fabricated sensors in lab with a commercial sensor.

Sensor category	Pt loading (mg/cm <sup>2</sup> )		Peak current density at BAC	Peak current Current lensity at density BAC		Regression coefficient (R <sup>2</sup> ) for peak current density at BAC ranges of	
	Anode	Cathode	0.05% (µA/cm <sup>2</sup> )	sensitivity	0.005 - 0.1%	0.005 - 0.2%	(mg)
Identical electrode	0.25	0.25	2.2	165.44	0.98	0.99	0.90
Non-identical electrode	0.30	0.03	1.7	167.86	0.99	0.99	0.60
Commercial	32	32	13.7	8.09	0.93	0.99	77



Figure 3.10. Performance of the commercial alcohol sensor as a function of %BAC and its linearity response, (a) Peak current density, (b) Charge density, (c) SEM micrograph, magnification: ×500), (d) EDS analysis.



Figure 3.11: The repeatability analysis of the best developed sensor in catalyst loading study (i.e. 40% Pt/C–0.30 mg cm<sup>2</sup> anode and 20% Pt/C–0.03 mg cm<sup>2</sup> cathode). Solid line is the fresh sensor run, and dash lines are the sensor repeatability runs after 2 months in lab and idle condition.

# 3.2.4 Studies on Polymer Electrolyte Membranes (Nafions)

In this section sensors with various Nafions are tested through different BACs from 0.01 to 0.2. Four kinds of catalyst layers of 40% for both sides, 30% for both sides, 40% and 20% for anode and cathode sides and 30% and 20% for anode and cathode sides are selected based on the results of catalyst loading studies. The results for different Nafions are shown in Figure 3.9. A list of the best sensors regarding the pick current densities and linearity of the calibration curve from this study is shown in Table 3.6.





Figure 3.12: Sensor Catalyst loading study





Figure 3.13: Sensor Catalyst loading study (Cont'd.)

# 3.2.5 Durability and Stability study

An eight-week durability analysis was performed for the selected sensors with best Nafion and catalyst loading combinations. The tests has been done every two weeks for each sensor and the results are shown in Figure 3.10. As can be seen from these figures, the current density of the sensor become stable after the second test and the linearity of the calibration curve increases during the time. Among all sensors, Nafion 1110 has the most linearity while Nafion 115 and 117 are capable of more current generation.

Sensor Type (Pt	Current density Peak $(\mu \Lambda)$	Linearity
Cathode Respectively)	Current density reak $(\mu R)$	(Regression)
Nafion 117 with 30%-20% Pt	0.34-3.15	0.959
Nafion 1110 with 30%-20% Pt	0.84-2.40	0.962
Nafion 115 with 30%-20% Pt	0.29-4.00	0.940
Nafion 438 with 30%-20% Pt	0.89-3.59	0.977
Nafion 117 with 40%-20% Pt	0.54-3.73	0.938

 Table 3.6: The best sensors of Nafion study regarding the pick current densities and linearity of the calibration curve.



Figure 3.14: Results of durability study





Figure 3.15: Results of durability study (Cont'd.)



Figure 3.16: Results of durability study. (Cont'd.)

# CHAPTER IV

# CONCLUSIONS AND RECOMMENDATIONS

# 4.1 Conclusions

Solid polymer electrolyte fuel cell sensors with different Pt catalyst loading on electrodes were fabricated to measure the ethanol gas concentration in exhaled human breath. The sensitivity, peak current density and charge density for two types of sensors including (i) identical electrode sensors, and (ii) non-identical electrode sensors were measured. The results revealed that the GDE with 40% Pt/C - 0.3 mg/cm<sup>2</sup> loading has the highest sensitivity factor, peak current and charge densities of all types of the sensors studied. The least square coefficient  $(R^2)$  for almost all of the two types of sensors were found to be acceptable for detecting ethanol concentration with very good accuracy in the BAC range of 0.005–0.2%. The  $R^2$  values for peak current densities were as high as the charge densities. Thus, using the peak current density measurement method will be preferable over the charge density measurement method since the latter takes more time for completion of the sensor reading. Utilizing a low Pt containing cathode did not have crucial adverse effect on the sensor performance, indicating that this type of sensor can be more cost-effective than other types without losing accuracy. Comparison of the performance of the commercial sensor with the fabricated low catalyst loading sensors indicates that these sensors are significantly cheaper and more linear in a wider range of

%BAC. Considering all merits of a fuel cell sensor (i.e. sensitivity, high current generation, high linearity response in wide range of %BAC, and low production cost), the sensor with anode loading of 40% Pt/C - 0.3 mg/cm<sup>2</sup> and cathode loading of 20% Pt/C - 0.03 mg/cm<sup>2</sup> is the winner. This sensor requires 130 times lower Pt loading compared to the commercial sensor and 67% less Pt loading compared to the PEMFC sensor studied by other researchers for ethanol gas measurement. Regarding the Nafion study, as it was expected the sensor with Nafion 115 and 40% Pt/C - 0.3 mg/cm<sup>2</sup> on both anode and cathode sides and the sensor with Nafion 1110 and 30% Pt/C - 0.3 mg/cm<sup>2</sup> on both anode and cathode sides generate the most current density among all other sensors. The most linearity of the calibration curve is related to the sensor with Nafion 115 and 30% Pt/C - 0.3 mg/cm<sup>2</sup> on both anode and cathode sides as well as the sensors with Nafion 117 and 1110 with 30% Pt/C - 0.3 mg/cm<sup>2</sup> on anode side and 20% Pt/C - 0.3 mg/cm<sup>2</sup> on cathode sides. Regarding the durability study the current density of the sensor become stable after the second test and the linearity of the calibration curve increases during the time. Among all sensors, Nafion 1110 has the most linearity while Nafion 115 and 117 are capable of more current generation.

#### 4.2 Recommendations

For the next step of this research the following suggestions may be considered:

- 1- Functionalization of different Nafion and MEA to increase the durability of the sensors and reduce the sensitivity of the sensor to dehydration
- 2- Improvement of the current density generation using the new technologies of Nafion and GDL

- 3- Design and fabrication of a sensor housing to ensure enough pressure of the sensor and eliminate leakage of the gas from anode side to cathode and to the out of the housing
- 4- Modification of the new housing to come up with the breathalyzer with interchangeable sensors (removing the old sensor after several months and inserting the fresh sensor)
- 5- Improvement of the fabrication method of the sensor to ensure the efficient contact between the catalyst on the GDL and MEA
- 6- Fabrication of a stand-alone system using the best sensors of this study and required
   Micro controller programming and a current amplifier

# REFERENCES

- 1. Di Natale, Corrado, Roberto Paolesse, Eugenio Martinelli, and Rosamaria Capuano. "Solid-state gas sensors for breath analysis: a review." Analytica chimica acta 824 (2014): 1-17.
- 2. Ibanez, Elena, Sara Lopez-Sebastian, Elena Ramos, Javier Tabera, and Guillermo Reglero. "Analysis of volatile fruit components by headspace solid-phase microextraction." Food Chemistry 63, no. 2 (1998): 281-286.
- 3. Borjesson, T., U. Stollman, P. Adamek, and A. Kaspersson. "Analysis of volatile compounds for detection of molds in stored cereals." Cereal Chem66, no. 4 (1989): 300-304.
- 4. Opekar, František, and Karel Štulík. "Electrochemical sensors with solid polymer electrolytes." Analytica Chimica Acta 385, no. 1 (1999): 151-162.
- 5. Janata, Jiri, Mira Josowicz, and D. Michael DeVaney. "Chemical sensors." Analytical Chemistry 66, no. 12 (1994): 207R-228R.
- 6. Moos, Ralf, Kathy Sahner, Maximilian Fleischer, Ulrich Guth, Nicolae Barsan, and Udo Weimar. "Solid state gas sensor research in Germany–a status report." Sensors 9, no. 6 (2009): 4323-4365.
- 7. Guth, Ulrich, Winfried Vonau, and Jens Zosel. "Recent developments in electrochemical sensor application and technology—a review." Measurement Science and Technology 20, no. 4 (2009): 042002.
- 8. Opekar, F. "Amperometric detectors based on solid polymer electrolytes."CHEMICKE LISTY 90, no. 12 (1996): 916-926.
- 9. Alber, Kathryn S., James A. Cox, and Pawel J. Kulesza. "Solid-state amperometric sensors for gas phase analytes: A review of recent advances." Electroanalysis 9, no. 2 (1997): 97-101.
- Bontempelli, Gino, Nicola Comisso, Rosanna Toniolo, and Gilberto Schiavon. "Electroanalytical sensors for nonconducting media based on electrodes supported on perfluorinated ion-exchange membranes." Electroanalysis 9, no. 6 (1997): 433-443.

- 11. Eggins, Brian R. Chemical sensors and biosensors. Vol. 28. John Wiley & Sons, 2008.
- 12. Luppa, Peter B., Lori J. Sokoll, and Daniel W. Chan. "Immunosensors—principles and applications to clinical chemistry." Clinica Chimica Acta 314, no. 1 (2001): 1-26.
- 13. Chaubey, Asha, and B. D. Malhotra. "Mediated biosensors." Biosensors and bioelectronics 17, no. 6 (2002): 441-456.
- 14. Thévenot, Daniel R., Klara Toth, Richard A. Durst, and George S. Wilson. "Electrochemical biosensors: recommended definitions and classification."Biosensors and Bioelectronics 16, no. 1 (2001): 121-131.
- 15. D'Orazio, Paul. "Biosensors in clinical chemistry." Clinica Chimica Acta 334, no 1 (2003): 41-69.
- 16. Bakker, Eric, and Ernö Pretsch. "Potentiometric sensors for trace-level analysis." TrAC Trends in Analytical Chemistry 24, no. 3 (2005): 199-207.
- 17. Buerk, D. G. "Biosensors. Theory and applications, Technomic Publish. Co."Inc., Lancaster (1993).
- 18. Barbir, Frano. PEM fuel cells: theory and practice. Academic Press, 2013.
- 19. Millet, P., A. Michas, and R. Durand. "A solid polymer electrolyte-based ethanol gas sensor."Journal of applied electrochemistry 26, no. 9 (1996): 933-937.
- 20. Azevedo, A.M., et al., Ethanol biosensors based on alcohol oxidase. Biosensors and Bioelectronics, 2005. **21**(2): p. 235-247.
- 21. Zhao, H., et al., Liquid methanol concentration sensors for direct methanol fuel cells. Journal of Power Sources, 2006. **159**(1): p. 626-636.
- 22. Jones, A., Measuring Alcohol in Blood and Breath for Forensic Purposes-A Historical Review. Forensic science review, 1996. **8**(1): p. 13-44.
- 23. Zuba, D., Accuracy and reliability of breath alcohol testing by handheld electrochemical analysers. Forensic Science International, 2008. **178**(2–3): p. e29-e33.
- 24. Jones, A.W., G. Mårdh, and E. Änggård, Determination of endogenous ethanol in blood and breath by gas chromatography-mass spectrometry. Pharmacology Biochemistry and Behavior, 1983. **18, Supplement 1**: p. 267-272.
- 25. Curry, A., G. Walker, and G. Simpson, Determination of ethanol in blood by gas chromatography. Analyst, 1966. **91**(1088): p. 742-743.

- 26. Perez-Ponce, A., S. Garrigues, and M. de la Guardia, Vapour generation-Fourier transform infrared direct determination of ethanol in alcoholic beverages. Analyst, 1996. **121**(7): p. 923-928.
- 27. Gallignani, M., S. Garrigues, and M. de la Guardia, Direct determination of ethanol in all types of alcoholic beverages by near-infrared derivative spectrometry. Analyst, 1993. **118**(9): p. 1167-1173.
- 28. Buchanan, B.R., et al., Detection of Ethanol in Wines Using Optical-Fiber Measurements and Near-Infrared Analysis. Applied Spectroscopy, 1988. **42**(6): p. 1106-1111.
- 29. Wang, X., S. Yee, and P. Carey, An integrated array of multiple thin-film metal oxide sensors for quantification of individual components in organic vapor mixtures. Sensors and Actuators B: Chemical, 1993. **13**(1–3): p. 458-461.
- 30. Maekawa, T., et al., Development of SnO2-based ethanol gas sensor. Sensors and Actuators B: Chemical, 1992. **9**(1): p. 63-69.
- 31. Chen, Z. and K. Colbow, MgO-doped Cr2O3: solubility limit and the effect of doping on the resistivity and ethanol sensitivity. Sensors and Actuators B: Chemical, 1992. **9**(1): p. 49-53.
- 32. Park, J.-K., et al., Determination of breath alcohol using a differential-type amperometric biosensor based on alcohol dehydrogenase. Analytica Chimica Acta, 1999. **390**(1–3): p. 83-91.
- Wang, Y., et al., Electrochemical sensors for clinic analysis. Sensors, 2008. 8(4): p. 2043-2081.
- Shao, Y., G. Yin, and Y. Gao, Understanding and approaches for the durability issues of Pt-based catalysts for PEM fuel cell. Journal of Power Sources, 2007. 171(2): p. 558-566.
- 35. Aragane, J., H. Urushibata, and T. Murahashi, Effect of operational potential on performance decay rate in a phosphoric acid fuel cell. Journal of Applied Electrochemistry, 1996. **26**(2): p. 147-152.
- 36. Negro, E., et al., Pt electrodeposited over carbon nano-networks grown on carbon paper as durable catalyst for PEM fuel cells. Applied Catalysis B: Environmental, 2015. **166–167**: p. 155-165.
- 37. Andersen, S.M., et al., Durability of carbon nanofiber (CNF) & amp; carbon nanotube (CNT) as catalyst support for Proton Exchange Membrane Fuel Cells. Solid State Ionics, 2013. **231**: p. 94-101.

- 38. Lin, R., et al., Electro-catalytic activity of enhanced CO tolerant cerium-promoted Pt/C catalyst for PEM fuel cell anode. International Journal of Hydrogen Energy, 2012. **37**(5): p. 4648-4656.
- 39. Seger, B. and P.V. Kamat, Electrocatalytically Active Graphene-Platinum Nanocomposites. Role of 2-D Carbon Support in PEM Fuel Cells. The Journal of Physical Chemistry C, 2009. **113**(19): p. 7990-7995.
- 40. Allan, J.T. and E.B. Easton. The Investigation and Characterization of Next Generation Proton Exchange Membranes for Fuel Cell-Based Ethanol Sensors. in 223rd ECS Meeting (May 12-17, 2013). 2013. Ecs.
- 41. Zhu, C., et al., Electrochemical Sensors and Biosensors Based on Nanomaterials and Nanostructures. Analytical Chemistry, 2015. **87**(1): p. 230-249.
- 42. Modjtahedi, A., N. Hedayat, and S.S.C. Chuang, The direct carbon solid oxide fuel cell with H2 and H2O feeds. Solid State Ionics, 2014. **268, Part A**(0): p. 15-22.
- 43. Amirfazli, A., S. Asghari, and M. Koosha, Mathematical modeling and simulation of thermal management in polymer electrolyte membrane fuel cell stacks. Journal of Power Sources, 2014. **268**: p. 533-545.
- 44. Andreadis, G.M., A.K.M. Podias, and P.E. Tsiakaras, The effect of the parasitic current on the Direct Ethanol PEM Fuel Cell Operation. Journal of Power Sources, 2008. **181**(2): p. 214-227.
- 45. Bianchini, C., et al., Selective oxidation of ethanol to acetic acid in highly efficient polymer electrolyte membrane-direct ethanol fuel cells. Electrochemistry Communications, 2009. **11**(5): p. 1077-1080.
- 46. Saleh, F.S. and E.B. Easton, Assessment of the ethanol oxidation activity and durability of Pt catalysts with or without a carbon support using Electrochemical Impedance Spectroscopy. Journal of Power Sources, 2014. **246**: p. 392-401.
- 47. Andreadis, G.M., A.K.M. Podias, and P.E. Tsiakaras, A model-based parametric analysis of a direct ethanol polymer electrolyte membrane fuel cell performance. Journal of Power Sources, 2009. **194**(1): p. 397-407.
- 48. Francesconi, J.A., et al., Analysis of the energy efficiency of an integrated ethanol processor for PEM fuel cell systems. Journal of Power Sources, 2007. **167**(1): p. 151-161.
- 49. Song, S., S. Douvartzides, and P. Tsiakaras, Exergy analysis of an ethanol fuelled proton exchange membrane (PEM) fuel cell system for automobile applications. Journal of Power Sources, 2005. **145**(2): p. 502-514.
- 50. Kamiya, K. and M. Sudoh, Response Characteristics of Fuel Cell Type Alcohol Sensor Using Nafion Membrane. ECS Transactions, 2014. **58**(21): p. 1-10.
- 51. Ioroi, T. and K. Yasuda, Platinum-Iridium Alloys as Oxygen Reduction Electrocatalysts for Polymer Electrolyte Fuel Cells. Journal of The Electrochemical Society, 2005. **152**(10): p. A1917-A1924.
- 52. Opekar, F. and K. Štulík, Electrochemical sensors with solid polymer electrolytes. Analytica Chimica Acta, 1999. **385**(1–3): p. 151-162.
- 53. Satterfield, M.B., et al., Mechanical properties of Nafion and titania/Nafion composite membranes for polymer electrolyte membrane fuel cells. Journal of Polymer Science Part B: Polymer Physics, 2006. **44**(16): p. 2327-2345.
- 54. Zuba, Dariusz. "Accuracy and reliability of breath alcohol testing by handheld electrochemical analysers." Forensic science international 178, no. 2 (2008): e29-e33.
- 55. Chen, Shih-Fang, and Mary-Grace C. Danao. "Predictive models of ethanol concentrations in simulated exhaled breath and exhaled breath condensate under varied sampling conditions." Journal of Biomedical Science and Engineering 2013 (2013).
- 56. Bianchini, Claudio, Valentina Bambagioni, Jonathan Filippi, Andrea Marchionni, Francesco Vizza, Paolo Bert, and Alessandro Tampucci. "Selective oxidation of ethanol to acetic acid in highly efficient polymer electrolyte membrane-direct ethanol fuel cells." Electrochemistry Communications 11, no. 5 (2009): 1077-1080.
- 57. Kamiya, Kazuhiro, and Masao Sudoh. "Response characteristics of fuel cell type alcohol sensor using nafion membrane." ECS Transactions 58, no. 21 (2014): 1-10.
- 58. Prest, Laura. "Fundamental investigation of fuel cell-based breath alcohol sensors and the cause of sensor degradation in low-humidity conditions." PhD diss., University of Ontario Institute of Technology, 2011.
- 59. Kim, Ki-Chul, Sung M. Cho, and Hoo-Gon Choi. "Detection of ethanol gas concentration by fuel cell sensors fabricated using a solid polymer electrolyte." Sensors and Actuators B: Chemical 67, no. 1 (2000): 194-198.
- 60. Liewhiran, C., et al. High Performance Ethanol Sensor for Control Drunken Driving Based on Flame-made ZnO Nanoparticles. in Nano/Micro Engineered and Molecular Systems, 2007. NEMS'07. 2nd IEEE International Conference on. 2007. IEEE.
- 61. Millet, P., A. Michas, and R. Durand, A solid polymer electrolyte-based ethanol gas sensor. Journal of Applied Electrochemistry, 1996. **26**(9): p. 933-937.
- 62. Paixão, T.R.L.C. and M. Bertotti, Development of a breath alcohol sensor using a copper electrode in an alkaline medium. Journal of Electroanalytical Chemistry, 2004. **571**(1): p. 101-109.

- 63. Kim, K.-C., S.M. Cho, and H.-G. Choi, Detection of ethanol gas concentration by fuel cell sensors fabricated using a solid polymer electrolyte. Sensors and Actuators B: Chemical, 2000. **67**(1–2): p. 194-198.
- 64. Zhang, Y., et al., Design of a proton exchange membrane (PEM) fuel cell with variable catalyst loading. Journal of Power Sources, 2015. **291**: p. 46-57.
- Chabot, V., et al., Effect of electrode physical and chemical properties on lithiumion battery performance. International Journal of Energy Research, 2013. 37(14): p. 1723-1736.
- 66. Farhad, S., A.S. Fung, and F. Hamdullahpur, Effect of composite electrode microstructure on temperature distribution in solid oxide fuel cells. Electrochimica Acta, 2013. **99**: p. 9-14.
- 67. Farhad, S. and F. Hamdullahpur, Minimization of polarization resistance in solid oxide fuel cells by proper design of micro-/nano-structure of porous composite electrodes. Electrochimica Acta, 2012. **61**: p. 1-12.
- 68. Farhad, S. and F. Hamdullahpur, Optimization of the microstructure of porous composite cathodes in solid oxide fuel cells. AIChE Journal, 2012. **58**(4): p. 1248-1261.
- 69. Farhad, S. and F. Hamdullahpur, Micro-modeling of porous composite anodes for solid oxide fuel cells. AIChE Journal, 2012. **58**(6): p. 1893-1906.
- 70. Rahman, M.R., et al., The application of power-generating fuel cell electrode materials and monitoring methods to breath alcohol sensors. Sensors and Actuators B: Chemical, 2016.
- 71. Church, Steven. "Del. firm installs fuel cell, The News Journal, p." B7, January 6 (2006).