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Analysis of the environmental impact on the design of fuel cells

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20060645

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Declaration

I, Petros Mandla Sibiya declare that this research is my own work. It is submitted for the Magister Technologiae: Engineering: Electrical to the Department of Applied Electronics and Electronic Communication at the Vaal University of Technology, Vanderbijlpark. This dissertation has never been submitted before for evaluation to any educational institution.

Petros Mandla Sibiya
18 April 2006

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- Mr Hendrik Detleefs
- Mr Hans Strydom
- Mr Andre Needham

Dedication

This project is dedicated to my parents, Enoch Sibiya and Olpha Buthelezi.

Abstract

The air-breathing Direct Methanol Fuel Cell (DMFC) and Zinc Air Fuel Cell (ZAFC) were experimentally studied in a climate chamber in order to investigate the impact of climatic environmental parameters such as varying temperature and relative humidity conditions on their performance. The experimental results presented in the form of polarization curves and discharge characteristic curves indicated that these parameters have a significant effect on the performance of these fuel cells. The results showed that temperature levels below 0°C are not suitable for the operation of these fuel cells. Instead, it was found that air-breathing DMFC is favored by high temperature conditions while both positive and negative effects were noticed for the air-breathing ZAFC. The results of the varying humidity conditions showed a negative impact on the air-breathing DMFC at a lower temperature level but a performance increase was noticed at a higher temperature level. For air-breathing ZAFC, the effect of humidity on the performance was also found to be influence by the operating temperature.

Furthermore, common atmospheric air pollutants such as N_2O, SO_2, CO and NO_2 were experimentally investigated on the air-breathing DMFC and ZAFC. At the concentration of 20 ppm, these air contaminants showed to have a negative effect on the performance of both air-breathing DMFC and ZAFC. For both air-breathing DMFC and ZAFC, performance degradations were found to be irreversible. It is therefore evident from this research that the performance of the air-breathing fuel cell will be affected in an application situated in a highly air-polluted area such as Vaal Triangle or Southern Durban. It is recommended the air-breathing fuel cell design include air filters to counter the day-to-day variations in concentration of air pollutants.

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GLOSSARY OF ABBREVIATIONS AND SYMBOLS

A

AC – Alternating Current

Ah – Ampere - hours

A – Amperes

C

CO_2 – Carbon dioxide

CO – Carbon monoxide

CH_3OH – Methanol

D

DC – Direct Current

DEAT – Department of Environmental Affairs and Tourism

DMFC – Direct Methanol Fuel Cell

E

e^- – Electron

G

GDL – Gas Diffusion Layer

H

H^+ – Hydrogen proton

H_2 – Hydrogen

H_2O – Water

H_2SO_4 – Sulphuric acid

I

IR – Internal resistance

K

KOH – Potassium hydroxide

K_2CO_3 – Potassium carbonate

K_2SO_3 – Potassium sulphate

M

MEA – Membrane Electrode Assembly

N

N_2 – Nitrogen

NO_2 – Nitrogen dioxide

N_2O – Nitrous oxide

NH_3 – Ammonia

O

O_2 – Oxygen

OCV – Open Circuit Voltage

ORR – Oxidation Reduction Reaction

P

PC – Personal Computer

PAN – Peroxyacetylene

PEMFC – Polymer Electrolyte Membrane Fuel Cell

ppb – Parts per billion

pphm – Parts per hundred million

ppm – Parts per million

Pt – Platinum

Pt-Ru – Platinum - Ruthenium

Pt- B – Platinum - Black

R

RH – Relative Humidity

RWGSR – Reverse Water Gas Shift Reaction

S

SO_2 – Sulphur dioxide

S.A. – South Africa

T

TCoE – Telkom Center of Excellence

U

USB – Universal Serial Bus

V

V – Volts

Z

ZAFC – Zinc Air Fuel Cell

Zn – Zinc

ZnO – Zinc Oxide

Symbols

Acm^{-2} – Current density in amperes per square centimeters

°C – Degrees Celsius

°K – Kelvin

% – Percent

$\mu g\ m^{-3}$ – Micrograms per cubic meter

Definition of terms

Air - breathing: refers to the natural convection by which the oxygen needed by the cell reaction is directly transferred into the cell from ambient air.

Anthropogenic gases: refers to greenhouse gases originating from human actions.

Electrochemistry: is a science of reactions that can take place at the interface of an electronic conductor such as the electrode and an ionic conductor, which is the electrolyte.

Electrokinetics: is the science of electrical charges in a moving substance such as water.

Irreversible loss: refers to a conversion of potential energy into heat as a result of friction and wind resistance. Thus being an irreversible process since the heat cannot be converted back into kinetic or potential energy.

Oxidant: a chemical such as oxygen that consumes electrons in an electrochemical reaction.

Chapter 1 Introduction

1.1 Background

In recent years there has been a growing concern with the degradation of the environment and the effect air pollution has on human health. These strong concerns are the result of burning fossil fuels as the method of acquiring energy, which at the moment is the most widely used method in the South Africa's energy sector. However, the use of clean energy sources such as fuel cells could lead to a viable option for power sources in a wide range of applications which includes vehicular, stationary and portable applications.

Recently, various types of fuel cells such as Polymer Electrolyte Membrane Fuel Cell (PEMFC), Zinc Air Fuel Cell (ZAFC) and Direct Methanol Fuel Cell (DMFC) have been under intensive research and development at Vaal University of Technology. Research on these fuel cells has been focusing on development and increasing the performance in terms of efficiency for wide range of applications.

However, not much research has been done on the impact of air pollution on air-breathing fuel cells. This is very vital for fuel cells since the use of ambient air provides oxygen on the cathode side, as it is required to complete the electrochemical reaction that produces electricity (Kosanovic, 2004). When the oxidant supplied to the fuel cells is not from a contained source such as bottled oxygen, impurities present in the immediate atmosphere may have a negative effect on the air-breathing fuel cell performance and operation (Moore *et al.*, 2000).

Among the three fuel cells mentioned above, PEMFC is the preferred choice for mobile applications. However, there is still little information published on what can happen when a PEMFC powered car gets stuck in a heavily air polluted area such as Vaal Triangle or in a bumper-to-bumper traffic alongside with petrol or diesel vehicles.

Furthermore, the operation of these three types of fuel cells may be required elsewhere around the world to fulfill the power demands of various applications. Therefore, since the operation of passive air-breathing fuel cells is directly linked to the surrounding atmosphere, the effect of widely varying climatic environmental conditions such as temperature and air humidity was investigated. The available information in the literature concerning the impact of these environmental conditions on fuel cells is very limited and specific. The generation of systematic experimental data is very crucial for fuel cell developers to enable optimization of fuel cells operating conditions according to the specific fuel cell design and operation requirements.

1.2 Problem statement

Recently, the Vaal University of Technology became involved in the fuel cell technology research, with research efforts being applied to designing various types of fuel cells for the telecommunication field. However, some of the fuel cells developed at the Telkom Center of Excellence (TCoE) rely strongly on the ambient air to supply the oxygen needed to complete the electrochemical reaction that produces electricity. Therefore, before these products can perform in commercial applications, they must be tested under varying climatic environmental conditions and be exposed to some of the major air pollutants in order to determine if there are any performance shortfalls caused by these conditions.

1.3 Methodology

The first step was a literature survey on fuel cells, specifically on the air-breathing PEMFC, DMFC and on the ZAFC. This part of the theoretical work focused on obtaining information in the existing literature on the effects of temperature and relative humidity on these fuel cells. This also included learning about their method of operation and gathering information about all technical aspects relating to their operation and performance.

The second step was to determine the valid experimental test procedure to be used for each fuel cell type and to organize all the equipment needed to perform temperature and humidity experiments on these fuel cells.

The third step involved the gathering of information on the common types of major air pollutants and the data on their prevalence in the Vaal Triangle area or any other area identified as a major air pollution hotspot in South Africa. This information served as a guide in the determination of the concentration levels of the gas impurities, which were used to perform the air pollution experiments.

The forth step was to design the appropriate polluted atmospheric environment that would not be harmful to people and the equipment. Suitable experimental procedures for the air pollution experiments were developed and all equipment required for each fuel cell type was identified and organized. Finally the experiments were performed and the experimental data was analyzed.

1.4 Delimitations

Detailed information relating to the design of air-breathing DMFC, PEMFC and the design of the ZAFC was not part of this research. Furthermore, in all the experiments performed on air-breathing DMFC and ZAFC, an assumption was made that the air pressure was constant at all times since these fuel cells operate under ambient atmospheric pressure. The work done in this research only concentrated on low power air-breathing fuel cells and high power fuel cell systems were excluded.

1.5 Importance of research

The main objective of this research was to determine if the fuel cells using atmospheric air as the oxidant are to be considered as viable power sources for applications in the highly air polluted areas of South Africa. Another objective was to determine the effects

of ever changing climatic environmental conditions on fuel cell performance and operation.

The appropriate design guidelines for the air-breathing PEMFC, DMFC and the ZAFC were developed from the results obtained from these experiments to prevent technical risks in the early commercial applications.

1.6 Overview of the dissertation

This dissertation consists of five chapters. Chapter one gives the background motivation of the research topic. Chapter two focuses on the air-breathing fuel cell types and discusses information from the existing literature on the effect of climatic environmental parameters that affect fuel cell performance. The findings and the conclusions made about the effect of air pollution on the air-breathing fuel cell performance are also presented based on the views of other fuel cell researchers who did a similar research.

Chapter three focuses on the experimental study on the impact of atmospheric conditions on the performance of the air-breathing ZAFC. In addition, the results obtained from the investigations done on the air-breathing ZAFC were presented.

The results of the investigation on the impact of atmospheric conditions on the performance of the air-breathing DMFC are presented in chapter four.

The conclusions and recommendations are presented in chapter five.

1.7 Summary

In this chapter, an introduction to the research was given. The aims of this research were stated. The importance of the research was emphasized and the scope was outlined. The delimitations were also clearly stated.

In the next chapter, air-breathing fuel cells and their operation are introduced and discussed. Furthermore, environmental factors that are suspected to have an impact on these fuel cells are addressed in detail based on previous related studies reported in the literature.

Chapter 2 Air-breathing fuel cells and the impact of the environment on their performance

2.1 Introduction

A fuel cell is a device that converts chemical energy from a chemical reaction directly into electrical energy with high efficiency as compared to the power devices based on thermal, mechanical and electrical energy conversion processes. For proper operation of a fuel cell, a fuel such as hydrogen or methanol and an oxidant like oxygen must continuously be supplied to it. Some fuel cell designs use pure oxygen supplied from a gas cylinder, but this is expensive. Therefore, ambient air is used as an alternative by some of the fuel cell designs to provide the required oxygen to the cathode side (Li *et al.*, 2003).

According to Bender *et al.* (1995:13.1) the effect of atmospheric oxygen as a depolarizing agent in electrochemical systems was first noted early in the nineteenth century.

Although a blower or fan could be used to feed air to the fuel cell, each of these devices consumes a certain amount of power, but may nevertheless be helpful in large-scale fuel cells and fuel cell stacks. For small power fuel cells or where pumping or fan system is not available, natural convection mass transfer is used to obtain oxygen directly from the ambient air to supply the fuel cell cathode side (Li *et al.*, 2003).

Hottinen *et al.* (2003) mentioned that for a small PEMFC system, power density and simplicity of the system form vital design criteria. The use of free convection for oxygen transport to the cathode might be desirable to eliminate power consuming fans and compressors. Therefore, atmospheric factors relating to the environment in which the air-breathing PEMFC operates should be investigated in order to attain a commercially viable portable-power generating system.

The air-breathing DMFC has also attracted the interest of many researchers as an alternative power source for the next generation power units in portable electronics since air compressors can simply be removed. This reduces the volume, cost and energy consumption of the system. Nevertheless, investigations of this type of DMFC in ambient environment are limited. Therefore, reliability of the air-breathing DMFC as a practical device remains undetermined (Chen & Yang, 2003).

This chapter examines passive air-breathing fuel cells such as PEMFC, ZAFC and DMFC designed for low power applications. The working principle of the above mentioned fuel cells and the influence on their performance caused by the surrounding environment in which they operate will be discussed in detail. This will give insight to the reader about the challenges of the varying climatic conditions and also the impact of common atmospheric air pollutants on air-breathing fuel cell performance as reported by other researchers.

All the work presented in this chapter is based on the literature and the findings of other fuel cell researchers who previously did similar research regarding environmental impact on fuel cell performance.

2.2 Types of passive air-breathing fuel cells

According to (Hottinen, 2004:26) the term air-breathing in fuel cells refer to the natural conversion by which oxygen required in the cell reactions is transferred directly from the ambient air into the cell.

The natural convection of air into the cathode channels is driven by buoyancy that is caused by the temperature and gas deposition and gradients. The temperature gradient is caused by the heat generated in the cell reactions and with possible external heating of the cell. The changes in gas composition are caused by cathode reactions that consume oxygen to produce water (Hottinen, 2004).

2.2.1 The air-breathing DMFC

According to Kho *et al.* (2005:50) the passive air-breathing DMFC operates without the help of external devices for the pumping of methanol and blowing air into the cell. As shown in figure 1, oxygen diffuses into the cathode directly from the ambient air by the air-breathing action of the cell while methanol diffuses into the anode from the built-in feed reservoir driven by concentration gradient between the anode and the reservoir. The configurations of the single cells and stacks of the passive feed DMFC are very different from the active ones into which methanol and air are fed by force.

As it can be seen in figure 1, the most striking feature of the passive air-breathing DMFC is its simpler structure and the compactness of the system design. It consists of membrane electrode assembly (MEA) that comprises two electrodes, the anode and the cathode, separated by a Nafion 115 proton conducting membrane. The MEA is sandwiched between two electrical current collectors made of stainless steel plates. For the simplicity of the system, a 3 ml methanol solution reservoir is built into the anode fixture (Liu *et al.*, 2005).

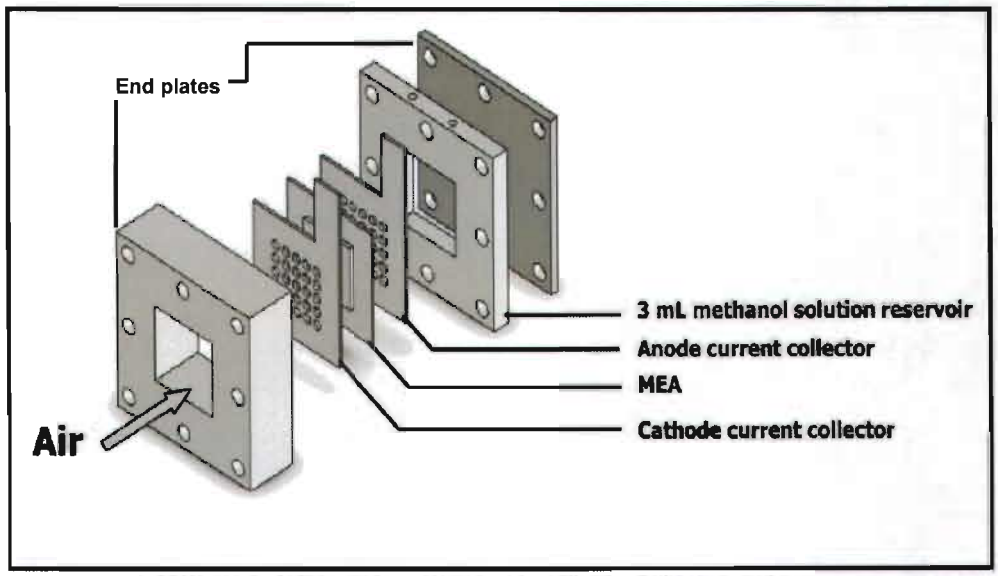

Figure 1 Schematic diagram of an air-breathing DMFC (Liu *et al.* 2005:290).

According to Chen and Yang (2003) an air-breathing DMFC has an anode at which methanol is electrochemically oxidized to carbon dioxide (CO_2) and a cathode at which oxygen is reduced to water (H_2O). The electro-chemical reactions of the air-breathing DMFC are as follows:

$$\text{Anode reaction: } CH_3OH + H_2O \rightarrow 6H^+ + CO_2 + 6e^- \quad (1)$$

$$\text{Cathode reaction: } 1.5O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad (2)$$

$$\text{Overall reaction: } CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O \quad (3)$$

The overall reaction for the air-breathing DMFC is the electro-oxidation of methanol to CO_2 and H_2O along with heat by a combustion reaction as in equation (3). The thermodynamic reversible potential at 298°K of the overall reaction is 1,21 V. In practice this theoretical cell potential is never achieved due to poor oxidation kinetics of methanol and the problem of methanol cross over to the cathode. The normal working cell voltage is around 0,6 to 0,7 V for a single cell (Chen & Yang, 2003).

The passive air-breathing DMFC operates at the temperature of up to 70°C to prevent too high vapor pressures, because the boiling point of methanol at atmospheric pressure is at 65°C (Reeve, 2002).

2.2.2 The air-breathing PEMFC

According to Ying *et al.* (2005:572) for air-breathing PEMFC, the air is introduced into the cathode channels by free convection. When the air-breathing PEMFC is operating, thermal gradients in the solution caused by cell irreversible loss result in density differences that drive the connection. Moreover, density differences are also caused by the consumption of oxygen and production of water in the electro-chemical reaction, which contribute to buoyancy forces that drive the fluids through the channel configuration. Figure 2 presents a schematic structure of the air-breathing PEMFC showing the channel configurations of both anode and the cathode.

The single air-breathing PEMFC shown in figure 2 consists of seven components, which include the electrolyte with a perfluorinated polysulfonate structure developed by Du Pont and two electrodes made of carbon-supported platinum catalyst. These three parts are assembled into a sandwich structure to form MEA.

The cathode bipolar plate is machined into a straight channel and the anode plate is designed as a serpentine groove. These bipolar plates provide a gas path for the cathode and anode reactant into the cell. They also play an important role in the way membrane is hydrated (Ying *et al.*, 2005).

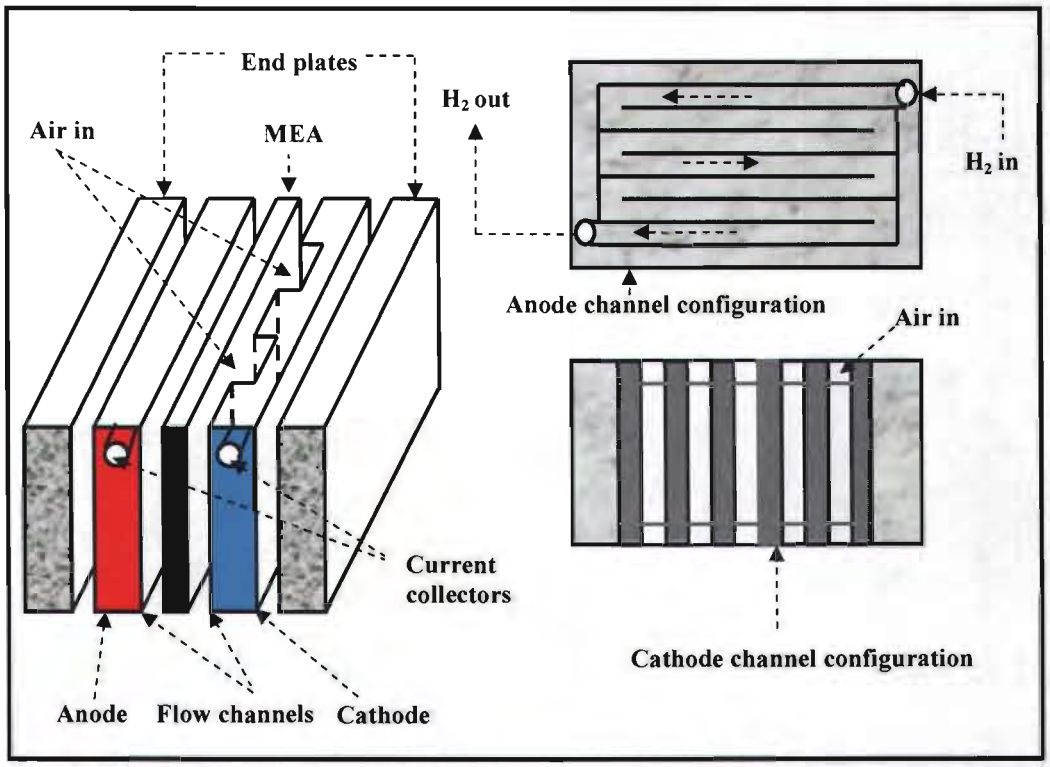

Figure 2 Schematic diagram of channel configuration for the air-breathing PEMFC (Ying *et al.* 2005:565).

According to Chu and Jiang (1999:128) nafion membrane as an electrolyte for PEMFC has shown good ion conductivity and stability in the temperature range of 0°C to 100°C of normal fuel cell operating conditions.

The electrochemical reactions for an air-breathing PEMFC at the anode and the cathode catalyst layer are as follows:

$$\text{Anode reaction: } H_2 \rightarrow 2H^+ + 2e^- \quad (4)$$

$$\text{Cathode reaction: } \tfrac{1}{2} O_2 + 2e^- + 2H^+ \rightarrow H_2O \quad (5)$$

$$\text{Overall cell reaction: } H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \quad (6)$$

The practical working voltage of an air-breathing PEMFC is typically from 0,7 V for a single cell, and many cells may be connected in series in order to produce a higher working voltage (Young, 1960).

2.2.3 The air-breathing ZAFC

The air-breathing ZAFC uses oxygen directly from the atmosphere to produce electrochemical energy. It has some similarities to a number of types of fuel cells as well as some characteristics of batteries (Zhang, 2005).

Bender *et al.* (1995:13.1) stated that oxygen diffuses into the cell directly from the atmosphere and is used as the cathode reactant. The air cathode catalytically promotes the reaction of oxygen with an aqueous alkaline electrolyte, which is not consumed by the reaction. After oxygen has gone through the gas diffusion electrodes, it forms hydroxyl ions. These hydroxyl ions travel through the electrolyte to the zinc anode and react with zinc to form zinc oxide.

Figure 3 depicts a schematic diagram of a typical air-breathing ZAFC, which consist of a central static replaceable anode cassette. The replaceable anode cassette contains an electrochemically generated zinc particles in a potassium hydroxide (KOH) solution acting as an electrolyte. This is then compacted onto a current collection frame and inserted onto a separator envelope, flanked on two sides by high power air or oxygen reduction cathodes (Goldstein *et al.*, 1999).

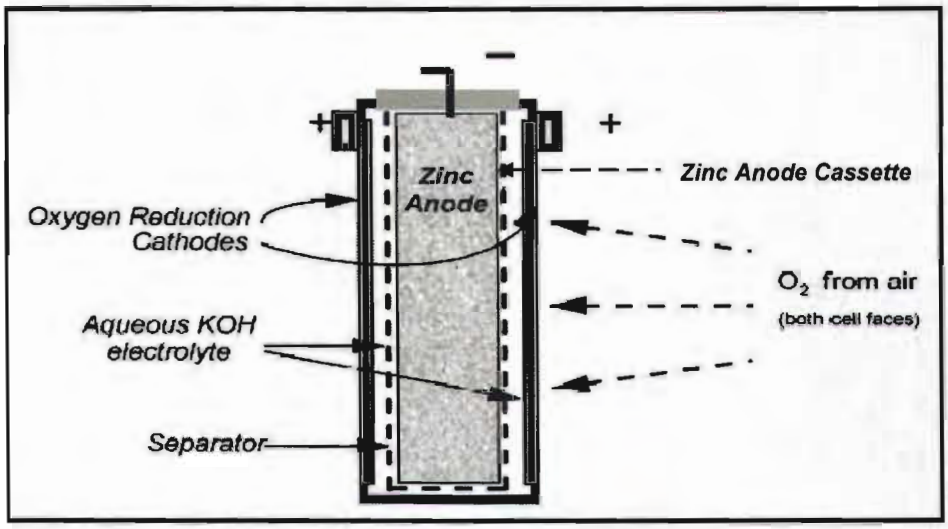

Figure 3 Schematic diagram of an air-breathing ZAFC (Goldstein *et al.* 1999:172).

The electrochemical reactions for the air-breathing ZAFC are as follows:

$$\text{Anode: } Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \quad (7)$$

$$\text{Cathode: } \tfrac{1}{2}\, O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (8)$$

$$\text{Overall reaction: } Zn + \tfrac{1}{2}\, O_2 \rightarrow ZnO \quad (9)$$

After the zinc is used up, the recycling or refuelling system uses electrolysis to convert ZnO back to zinc metal in pellet form using AC electricity (Zhang, 2005).

According to Bender *et al.* (1995:13.6) ZAFC operate at temperatures from 0 to 40°C with the nominal open circuit voltage of 1,45 V. The initial closed circuit voltage at 20 °C ranges from 1,1 to 1,4 V depending on the discharge load. The discharge is relatively flat with a cut-off voltage of 0,8 V.

2.3 Theoretical background for determining the performance of the fuel cell

The characteristic performance of a fuel cell at any given set of operating conditions is expressed in a polarization curve, which is a graph of fuel cell voltage versus current or current density expressed in (Acm^{-2}).

Figure 4 shows a polarization curve that is typical of both air-breathing DMFC and PEMFC. Neither of these fuel cells can achieve the theoretical voltage of 1,23 V. In reality, these fuel cells have highest output voltage at open circuit conditions and this voltage drops with increasing current drawn. The fuel cell efficiency is defined as the percentage ratio of the operating cell voltage relative to the ideal cell voltage (College of Desert, 2001).

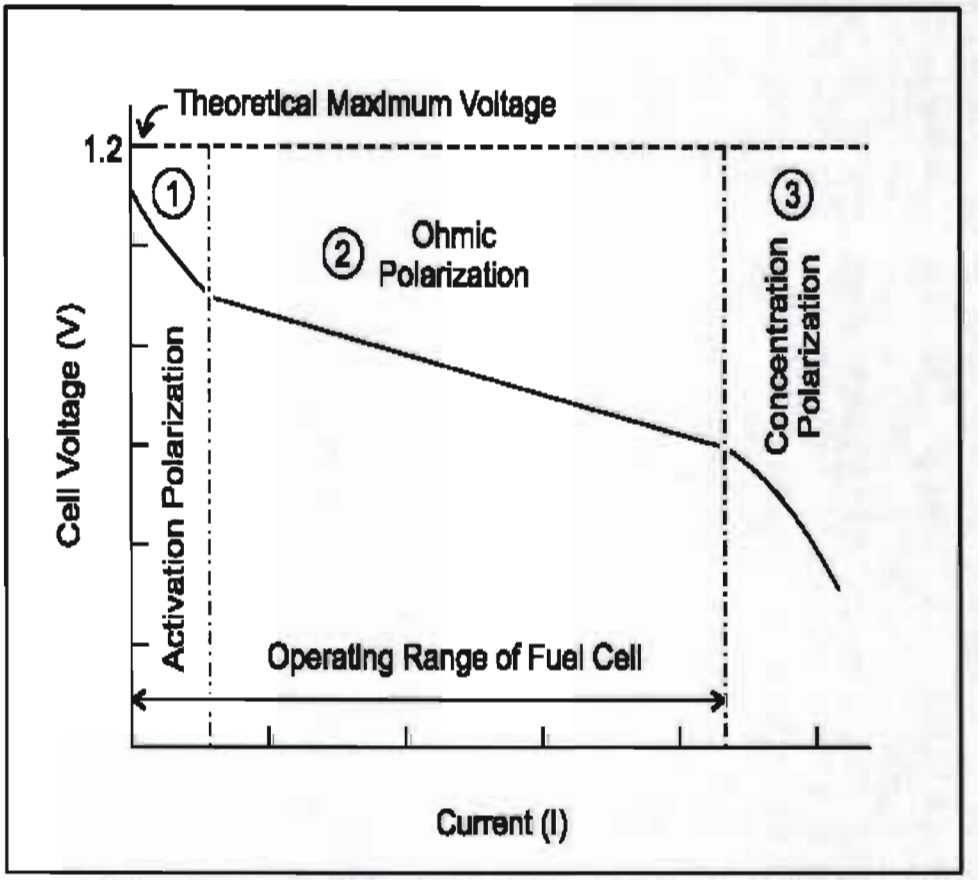

Figure 4 Polarization curve for PEMFC and DMFC (College of Desert, 2001:4:47).

Polarization is caused by chemical and physical factors associated with various elements of the fuel cell. In figure 5, increasing polarization curves are associated with a greater power and higher electrochemical efficiency of the fuel cell. The lower the polarization curve, the lower the electrochemical efficiency and power output of the fuel cell (College of Desert, 2001).

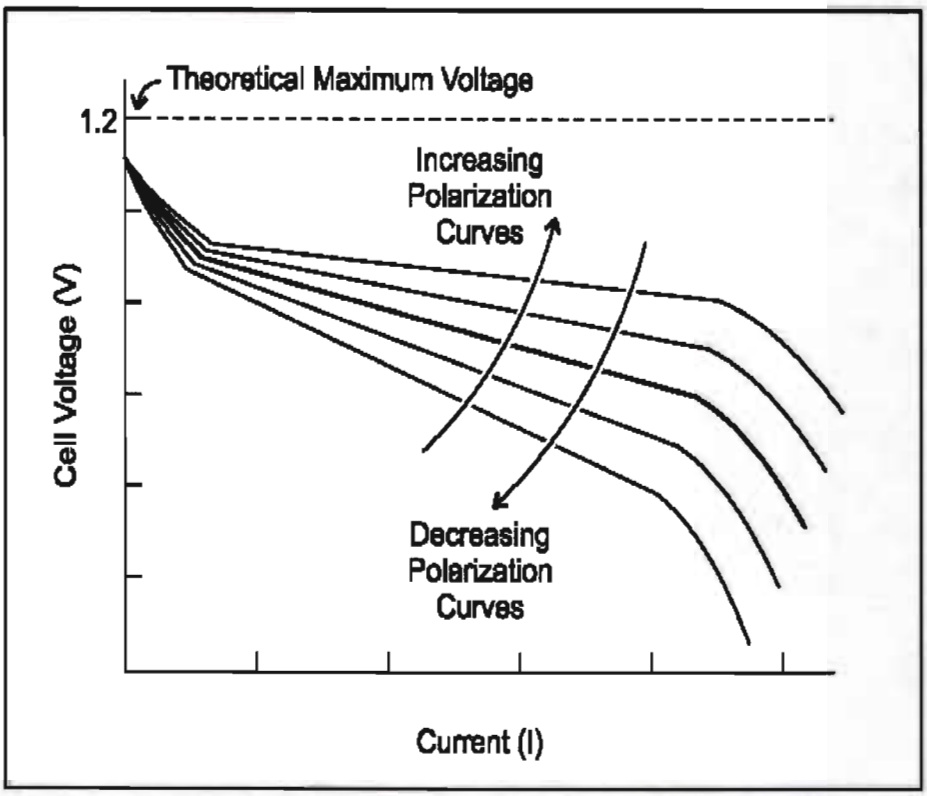

Figure 5 Polarization curve variations (College of Desert, 2001:4:50).

It was mentioned in the section (2.2.3) that air-breathing ZAFC share some characteristics with the batteries. Therefore, the performance of the air-breathing ZAFC can be determined in terms of its discharge characteristic curve similar to the one used in batteries. This curve is a plot of cell voltage versus the discharge time at which the cell is discharged at a constant current drain expressed in ampere-hours (Ah).

According to Linden (1995: 3.4) as the cell resistance or discharge current increases, the discharge voltage decreases and a discharge curve shows a more sloping profile. This is illustrated in figure 6 where curve 2 is similar to curve 1 except it represents a cell with a higher internal resistance or higher discharge rate as compared to the cell represented by curve 1.

In the idealized case, the discharge of the battery proceeds at the theoretical voltage until the active materials are consumed and the capacity is fully utilized, and then the voltage drops to zero.

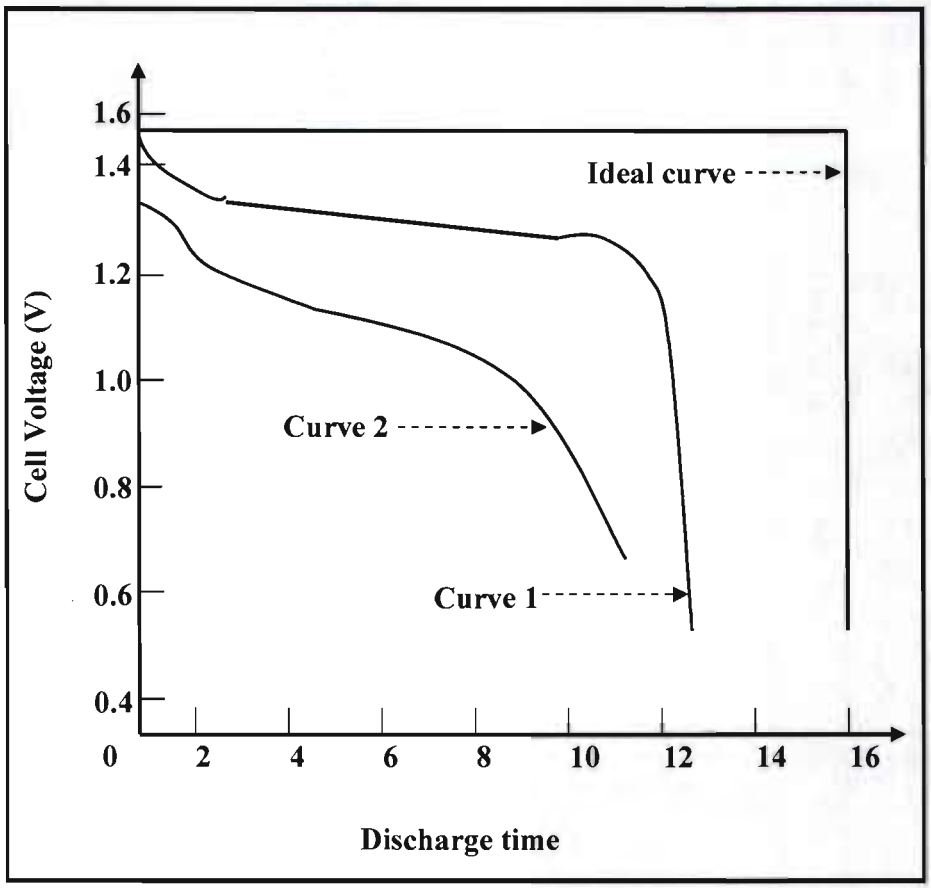

Figure 6 Discharge characteristic curves of a lead-acid battery (Linden, 1995:13.4).

2.4 The impact of the climatic environmental factors on air-breathing fuel cells

Air-breathing fuel cells discussed in the previous sections are designed to operate using oxygen from the surrounding air, which in turn makes them much lighter, simpler and lower in cost than the active types. This is because there is no need for additional auxiliaries for providing oxygen and the necessity of buying expensive oxygen gas cylinder is eliminated.

The main disadvantage is that any variation of climate, which includes parameters such as the surrounding temperature and relative humidity, could pose a serious challenge on the performance of these air-breathing fuel cells. These parameters and their effects on fuel cells are presented on the next sections based on the previous studies.

2.4.1 Effect of humidity on the air-breathing PEMFC

Ying *et al.* (2005) did an experimental study on the air-breathing PEMFC and reported that, when an air-breathing PEMFC operates at low humidity conditions, it is easy for the membrane to dehydrate at the anode side. This is because the water source is only from the water product in the cathode reaction and air humidity. Membrane dehydration results in low proton conductivity of the membrane, thus increasing proton transfer resistance. When considering the reverse situation of air-breathing PEMFC working at high ambient humidity, it was reported that water vapor is condensed into a liquid and then blocks the gas path, which result in a serious oxygen transport limitation.

The effect of ambient humidity in air-breathing PEMFC can be clearly observed from the curves of voltage and power versus current density shown in figure 7. Ambient humidity is reported as relative humidity (RH), which is expressed as a percentage of the water vapour saturation level of air for the ambient temperature.

Figure 7 shows that when the RH is 53%, the performance of the air-breathing PEMFC is low at low current density, but improved when the current load increases. This indicates that at low current density the RH plays an important role in hydrating the membrane, but as the water product at the cathode increases with increasing current density, hydration of membrane is independent of RH. At this humidity level there was no liquid water blockage in the channels and in the back diffusion layer (Ying *et al.*, 2005).

At a RH of 63% and low current density, the PEMFC performance was better than at 53% RH. However, liquid water existed in the diffusion layer and blocked the gas path between the channel and the reaction layer resulting in decreased performance. At a RH of 77%, the liquid water existed in the form of small dew drops at first then later large dew drops in the cathode channels. This resulted in a gas path blockage. At this point the performance suddenly decreased. Therefore, in case of high humidity conditions, the liquid water plays an important role in oxygen transport limitations.

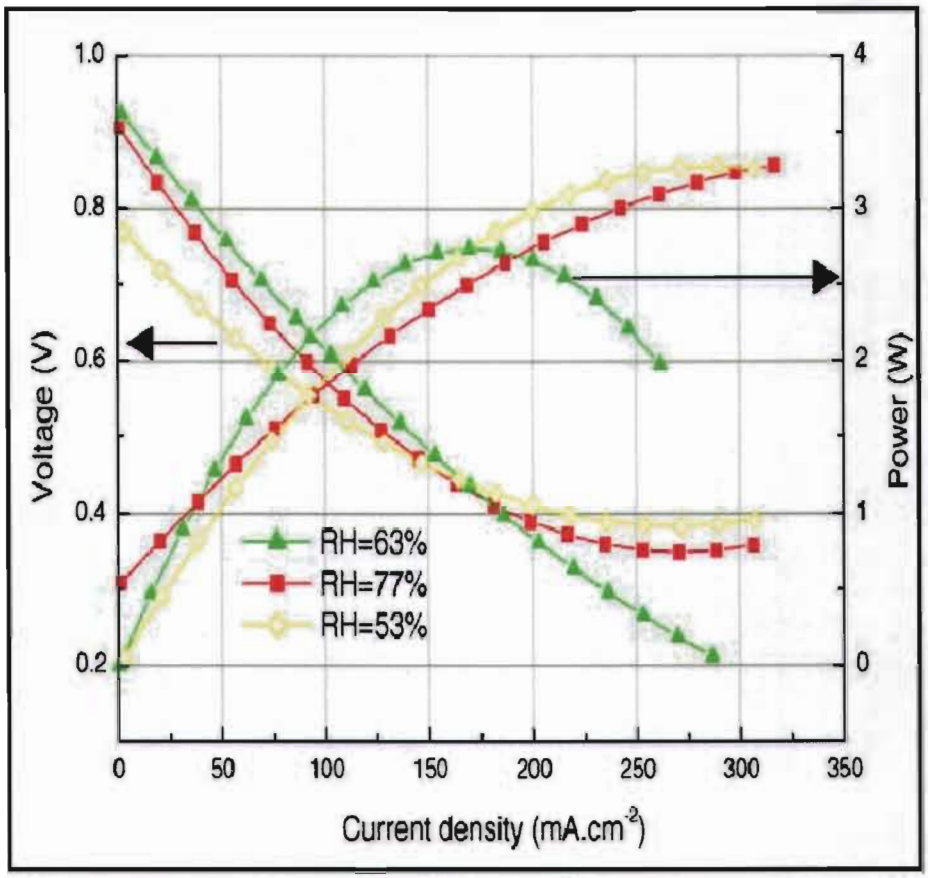

Figure 7 Performance of the air-breathing PEMFC under varying humidity levels (Ying *et al.* 2005:567).

2.4.2 Effect of humidity on the air-breathing ZAFC

The air-breathing ZAFC uses KOH aqueous solution as an electrolyte that functions primarily as an ionic conductor. However, this type of electrolyte has been reported to have a water vapour pressure that has to be balanced by water concentration in the surrounding atmosphere. If this balance is not maintained, the excess water either escapes from the electrolyte by evaporation or is absorbed by the electrolyte. Either way the concentration of the solution changes.

The relationship between KOH concentration and RH is depicted by the curve in figure 8, from which it can be seen that the usual operating KOH concentrations of between 20 and 32% require RH levels in the range of 55 and 77% (Berndt, 1997).

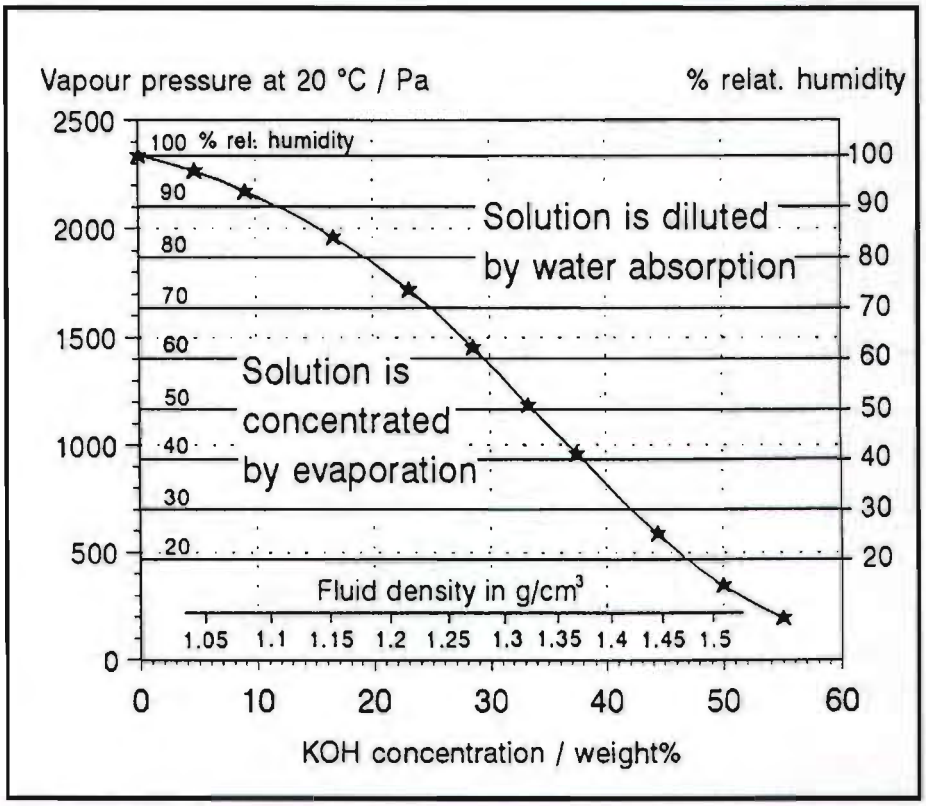

Figure 8 Vapor pressure of the KOH solution (Berndt, 1997:59).

It was reported by (Sieminski, 2000:2) that for a typical ZAFC design, the KOH electrolyte with a concentration of 35% is at equilibrium point when the RH is 50% at room temperature. This implies that there is no water vapor transfer under these conditions.

However, when the ambient RH is below 50% level, water vapor will migrate through the air electrode out of the electrolyte. This condition is referred as the dry out condition and it can reduce the cell power and capacity to a point of failure.

At the RH levels above 50%, the electrolyte can gain water from the air. This condition will result in flooding of the cell, which in turn will block oxygen access and affect the cell capacity and power.

Bender *et al.* (1995:13.5) also presented the same theory and also mentioned the fact that, the gain or loss of water by the ZAFC electrolyte will cause the cell to fail before delivering its full capacity. It was also reported that the instantaneous water transfer rates at the given environment would vary throughout the life of the cell, depending on the length of the exposure.

As the cell gains or loses water, the transfer rates will decrease because the electrolyte concentration will change with the ambient RH to maintain equilibrium according to figure 8. The effect of continued moisture loss or gain from the electrolyte is shown in figure 9.

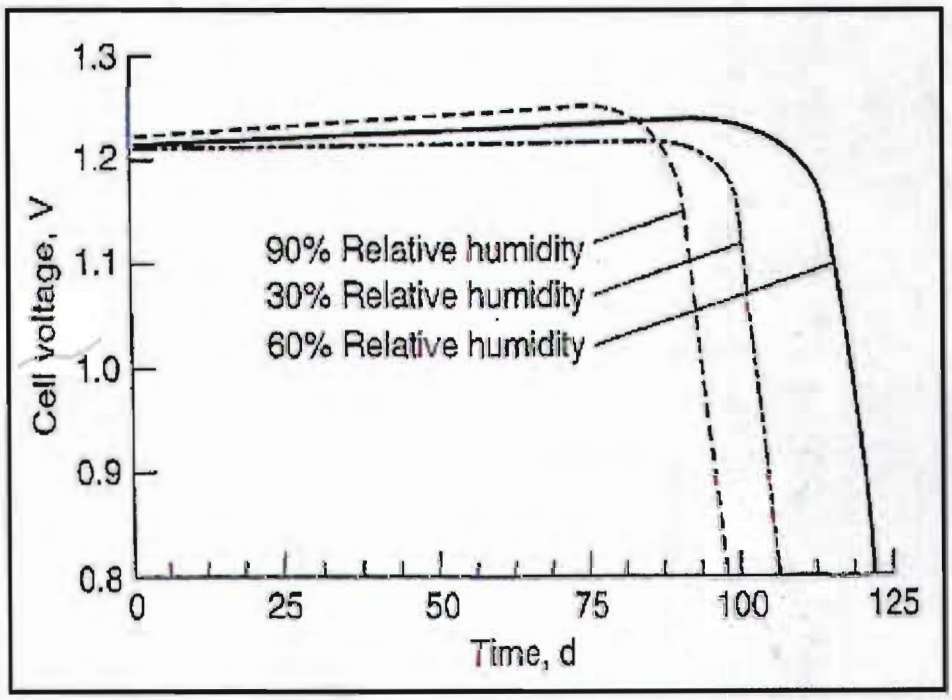

Figure 9 Performance of the zinc air cell discharged at 21°C under various RH levels (Bender *et al.* 1995:13.18).

Figure 9 shows an intermittent discharge of the zinc air cell at 30, 60 and 90% RH. It can be seen that the least amount of water transfer occurs at the 60% RH level and the cell delivers the maximum service. However, the capacity of the cell was minimized when the RH was at 90% level.

2.4.3 Effect of humidity on the air-breathing DMFC

Not many research publications were found that provide data or discuss the effect of humidity on the air-breathing DMFC performance. According to Ge and Liu (2005:59) humidification for DMFC does not have any significant effect, which basically indicates that dehydration of the membrane is not a problem for the operation of DMFC.

2.4.4 Effect of temperature on the air-breathing PEMFC

Hottinen *et al.* (2003) concluded from an experimental study on the air-breathing PEMFC that this type of fuel cell operates at its best when it is exposed at low ambient temperatures when the temperature gradient between the cell and the air is at a maximum. Under these conditions the airflow velocity is also at its maximum resulting in more effective oxygen transport and water removal.

Consequently, the cell performance decreases with an increase in ambient temperature because this decreases the temperature gradient between the cell and air. This results in a decrease in airflow velocity and an increase of mass transfer limitation in the cathode of the cell. At higher temperatures and humidity levels, the airflow rate is not enough to remove water from the cell and hence the cell will be flooded (Hottinen *et al.*, 2003). Similarly, Chu and Jiang (1999) reported that the proper operation temperatures for air-breathing PEMFC are at the lower range of 20 to 40°C.

In figure 5, the performance of the cell improved as the temperature increases from ambient to 60°C. A further increase in temperature to 75°C led to a significant performance loss and it was concluded that the optimum operating temperature for an air-breathing PEMFC without external humidification is near 60°C. Poor cell performance at a temperature of 75°C was reported to be a result of drying proton conducting phases. However, in practical situations even a temperature of 60°C may not be practical for air-breathing PEMFC (Hottinen, 2004).

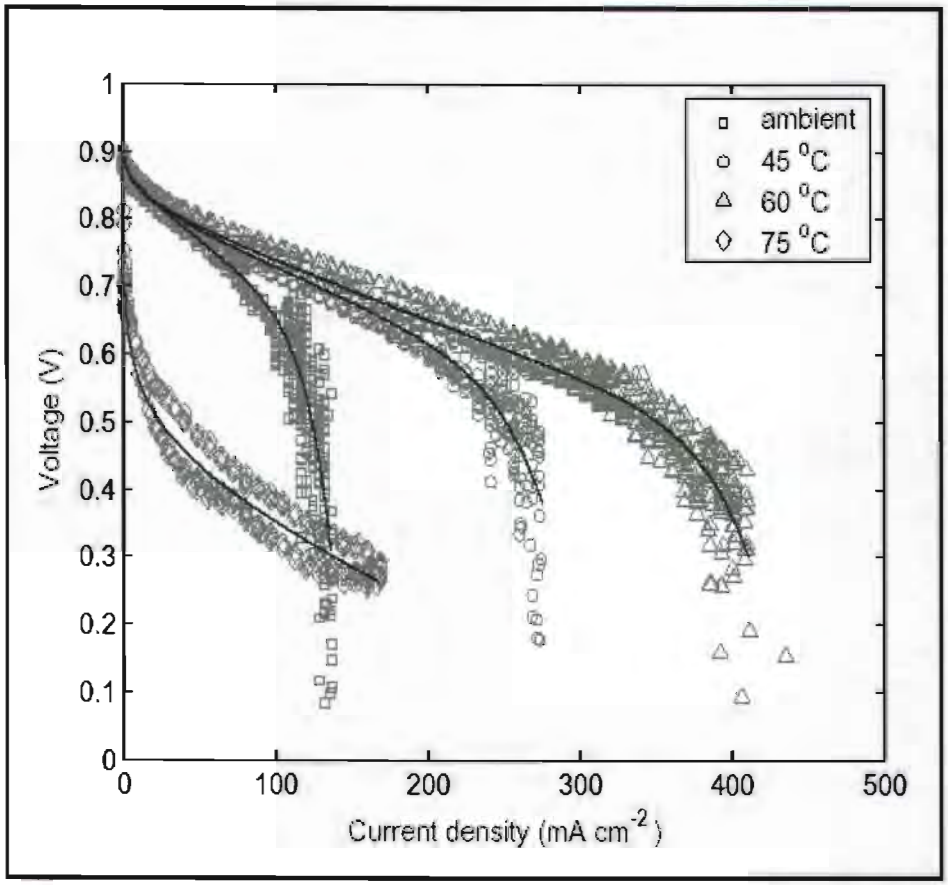

Figure 10 Effect of temperature on the air-breathing PEMFC performance (Hottinen, 2004:27).

2.4.5 Effect of temperature on the air-breathing DMFC

According to Liu *et al.* (2005:289) the operating temperature for a passive air-breathing DMFC is positively correlated to the concentration of methanol solution. Therefore, when a passive air-breathing DMFC is operated under a given ambient environment, a more concentrated methanol solution will lead to a higher operating temperature, which in turn will cause faster electrokinetics of both methanol oxidation and oxygen reduction reaction (ORR). This will automatically result in a higher cell performance.

Ge and Liu (2005:57) reached the same conclusion after conducting an experimental study on the DMFC. The polarization curve in figure 11 shows that current density

increases with a temperature increase. This is expected since methanol oxidation kinetics and cathode kinetics improve as the temperature increases.

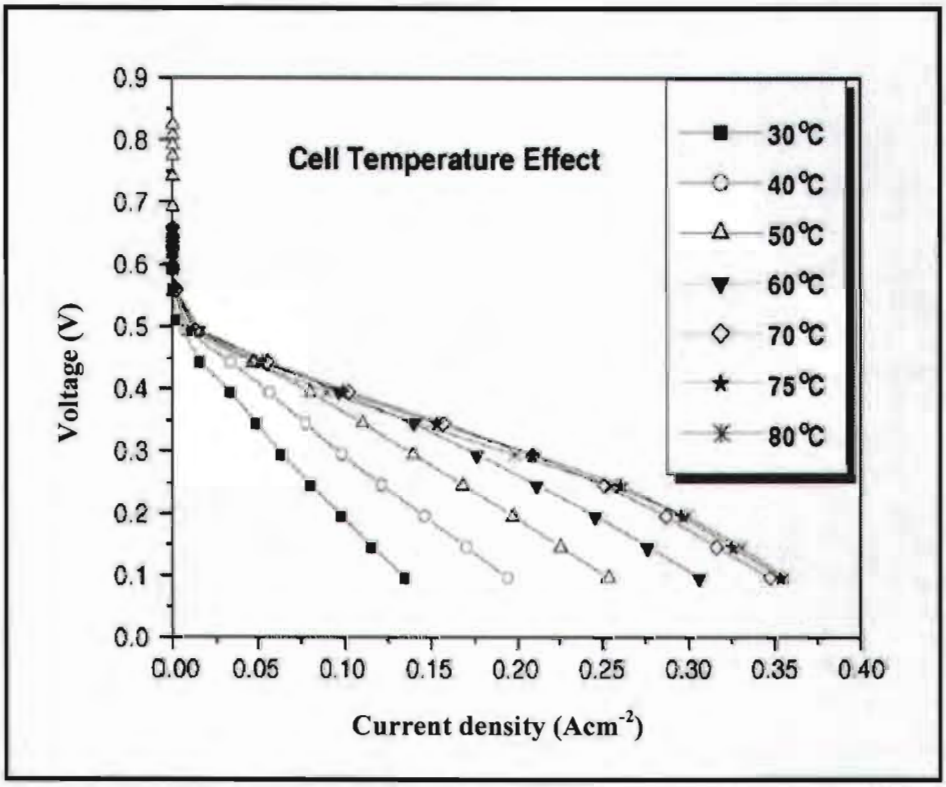

Figure 11 Effect of varying temperature conditions on the air-breathing DMFC performance (Ge & Liu, 2005:57).

The data used to construct figure 11 were reconfigured and represented on a current density versus temperature graph to further examine the effect of operating temperature (figure 12). Figure 12 shows that current density is not a function of temperature but it has a maximum value for each cell voltage at 70 to 75°C. Moreover, current densities are different at different cell voltages, with the current density increasing with decreasing cell voltage. However, the increase in cell operating temperature also has the following negative effects on the DMFC operation:

- The oxygen partial pressure decreases with the temperature due to the increase in vapour partial pressure, which in turn causes both a decrease in open cell voltage and an increase in concentration over potential.

- The rate of methanol crossover increases with temperature, which decreases the cell performance.
- Water transfer from the anode to the cathode through the membrane increases with temperature. Therefore, additional water increases the liquid water fraction in both the cathode catalyst layer and diffusion layer, causing an increase in concentration polarization.

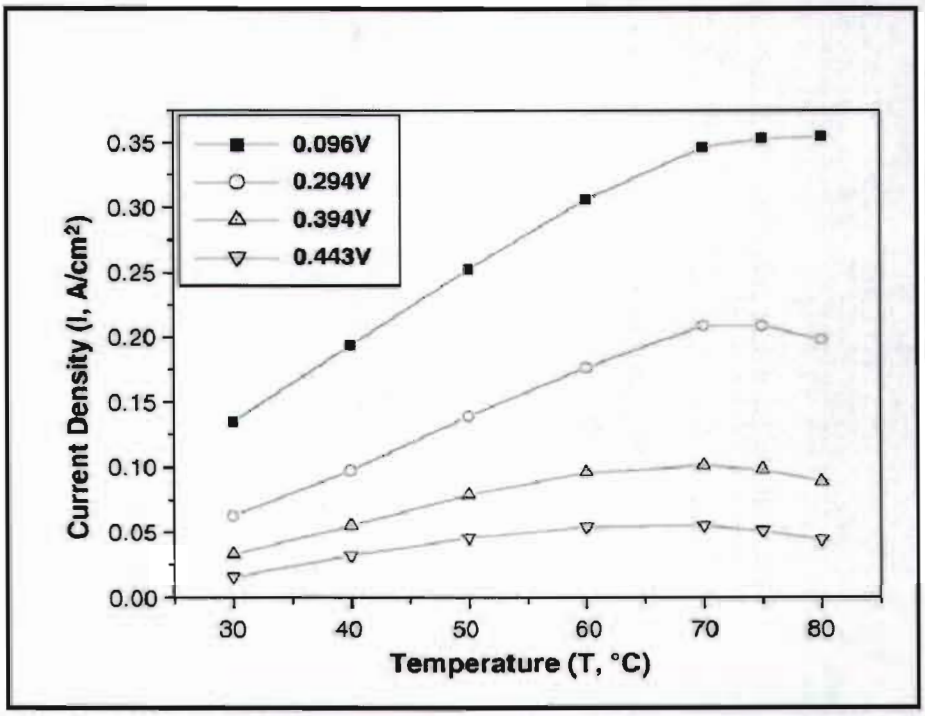

Figure 12 Fuel cell current density as a function of temperature at different cell voltages (Ge & Liu, 2005:57).

Therefore, the total effect of temperature on the DMFC performance is a function of the positive effect of the temperature on kinetics and the combined negative effects mentioned above.

2.4.6 Effect of temperature on the air-breathing ZAFC

According to Linden (1995:3.9) the temperature at which the cell operates has a pronounced effect on both the capacity or service life and the voltage characteristics. Low

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temperatures cause a reduction in chemical activity and increase the cell internal resistance. Figure 13 shows the discharge characteristic curves of a cell being discharge at constant current drain under various temperature conditions. From these curves it can be seen that cell voltage is lower at low temperatures. Although the optimum discharge temperature is between 10 and 40°C, the cell can still operate at the temperature conditions below 10°C.

It can also be seen from these curves that extremely low temperature conditions such as –20°C result in lower cell voltages and delivered capacity.

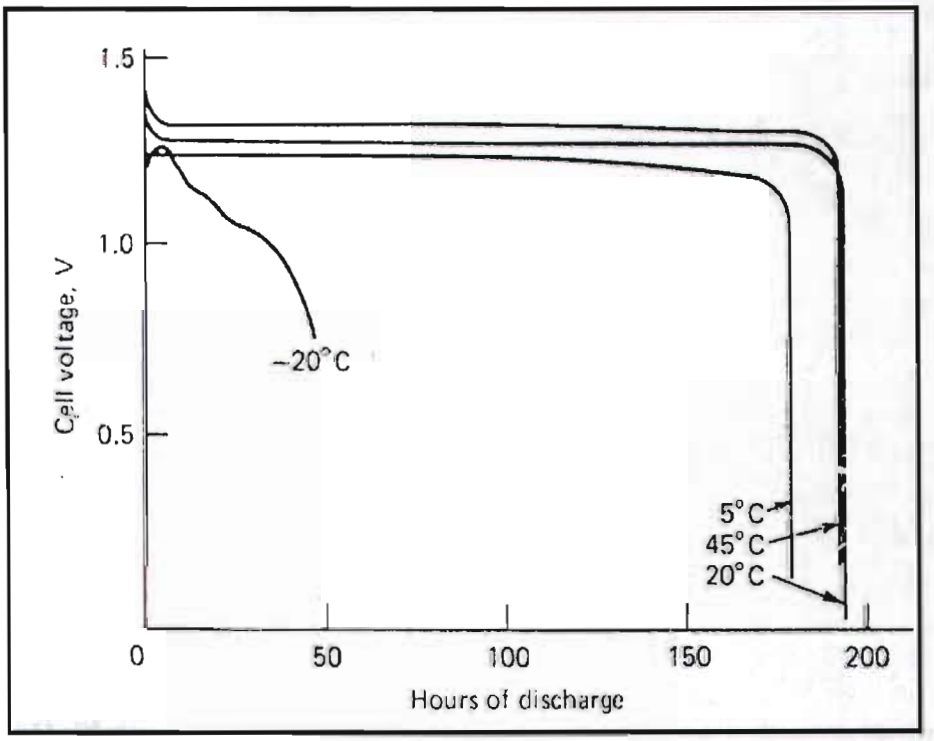


Figure 13 Effect of temperature on the ZAFC discharge curves (Linden, 1995:3.9).

Both the specific characteristics and the discharge profile vary for each battery or cell system but normally the best performance is obtained between 20 and 40°C. At higher temperatures, chemical deterioration may be rapid enough during the discharge to cause loss of capacity (Linden, 1995).

2.5 The impact of the common atmospheric air pollutants on air-breathing fuel cells

Rao (1991:30-34) defined air pollution as the diffusion into the atmosphere of chemical compounds emitted by anthropogenic and natural activities, which have the potential to impact negatively on the environment. The variety of matter emitted into the atmosphere by natural and anthropogenic sources is so diverse that it is difficult to classify air pollutants neatly. However, air pollutants are normally divided into the following two categories:

- Primary air pollutants, which are emitted directly from the sources.
- Secondary air pollutants formed in the atmosphere by chemical interactions between primary pollutants and normal atmospheric constituents.

Typical air pollutants that fall under primary and secondary air pollutants category are given in table 1.

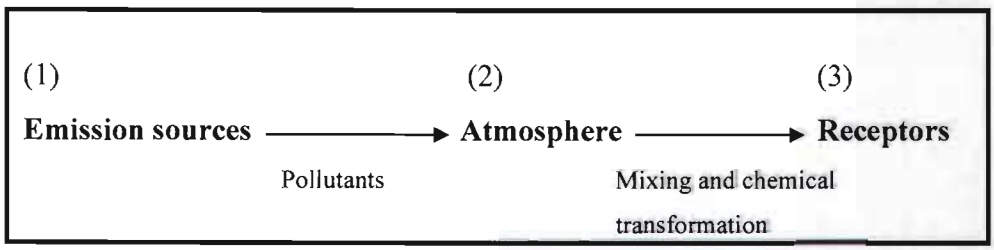
Table 1 Primary and secondary air pollutants.

PRIMARY AIR POLLUTANTS	SECONDARY AIR POLLUTANTS
1. Inorganic gases such as sulphur dioxide, hydrogen sulphide, nitric oxide, ammonia, carbon monoxide, carbon dioxide and hydrogen fluoride	1. Sulphur trioxide
2. Particulate matter such as ash, smoke, dust, fumes, mist and spray	2. Nitrogen dioxide
3. Olefinic and aromatic hydrocarbons	3. PAN (peroxyacetyl nitrate)
4. Radioactive compounds	4. Ozone
	5. Various sulphate and nitrate salts

From the large number of primary air pollutants emitted into the atmosphere, it has been reported that only a few that are present in the atmosphere at sufficient concentrations to be of immediate concern. These include the following five major types:

- Particulate matter
- Sulphur oxides
- Oxides of nitrogen
- Carbon monoxide and carbon dioxide
- Hydrocarbons

According to Seinfeld (1975:3) air pollution is a global problem since air pollutants ultimately disperse throughout the entire atmosphere. This air pollution problem can be depicted as a system, which is made up of three basic components shown in the structure below.



There are five major emission sources:

- Transportation
- Electric power generation
- Refuse burning
- Industrial and domestic fuel burning
- Industrial processes

The atmosphere acts as a medium for transport, dilution, physical and chemical transformation for the emitted pollutants. The final stage is when air pollutants are detected by the receptors such as instruments, human beings, animals, plants, or

materials. Detection by these various receptors is manifested by some response such as an irritation (Seinfeld, 1975).

Therefore, this brings an immense challenge on the fuel cell researchers to investigate if there will be an irritation encountered by various types of air-breathing fuel cells in terms of performance degradation in air polluted areas.

The air pollution levels will vary greatly from one area to another. For example, the variation can be from near zero levels in remote regions to high levels in the city centers or close to industrial and chemical plants (Moore *et al.*, 2000).

There are very few reports of experimental studies on the effect of air pollution on the air-breathing fuel cell performance, particularly on the air-breathing DMFC and ZAFC. Most research done on this topic has concentrated on the poisoning of fuel cell catalyst on the anode side by carbon monoxide (CO) and low molecular weight alcohol such as methanol (CH_3OH).

Table 2 shows typical concentration differences for major air pollutants between clean and polluted air.

Table 2 Comparison of pollutant concentration levels between clean and polluted air (Seinfeld, 1975:8).

COMPONENT	CLEAN AIR	POLLUTED AIR
SO_2	0.001 – 0.01 ppm	0.02 – 2 ppm
CO_2	310 – 330 ppm	350 – 700 ppm
CO	< 1 ppm	5 – 200 ppm
NOx	0.001 – 0.01 ppm	0.01 – 0.5 ppm
Hydrocarbons	1 ppm	1 –20 ppm
Particulate matter	10 – 20 μgm^{-3}	70 – 700 μgm^{-3}

According to Seinfeld (1975:5-8) the concentrations of air pollutants are normally expressed by using the following concentration scales:

- Parts per million (ppm) by volume (volume fraction $\times 10^{6}$) is employed for gaseous air pollutants. Lower concentrations may be expressed in part per hundred million (pphm) or parts per billion (ppb).
- The weight of pollutant per volume of air in micrograms per cubic meter, abbreviated as μgm^{-3}.

The following sections discuss the findings of published studies about the effects of common atmospheric air pollutants on the air-breathing PEMFC. Published studies on the effect of air pollutants on air-breathing DMFC and ZAFC are scarce. Therefore, it is difficult to draw generalized conclusions on the effects of air pollution on air-breathing fuel cells from the literature.

2.5.1 Effect of sulphur dioxide (SO_2) on the air-breathing PEMFC

According Mepsted (2001:2) 66% of atmospheric SO_2 comes principally from power stations as a result of burning coal or oil containing sulphur. Industrial combustion sources constitute 16% of this gas and motor vehicles are not a major contributor of this gas since it is only 2% that comes from diesel vehicles.

Moore *et al.* (2000:258) did an experimental study on the effect of battlefield contaminants and SO_2 at a concentration level of 500 ppb on the PEMFC and concluded that SO_2 did not have any detrimental effect on the fuel cell performance for the time duration of the experiment.

However, Mohtadi *et al.* (2004:1) said the results obtained by Moore *et al.* (2000) were due to the low concentration levels of SO_2. Therefore based on that, Mohtadi *et al.* (2004) also did an experiment on the PEMFC using higher concentrations of SO_2 in the range of 2,5 and 5 ppm. The effect of this gas impurity at these concentrations is shown in figure 14.

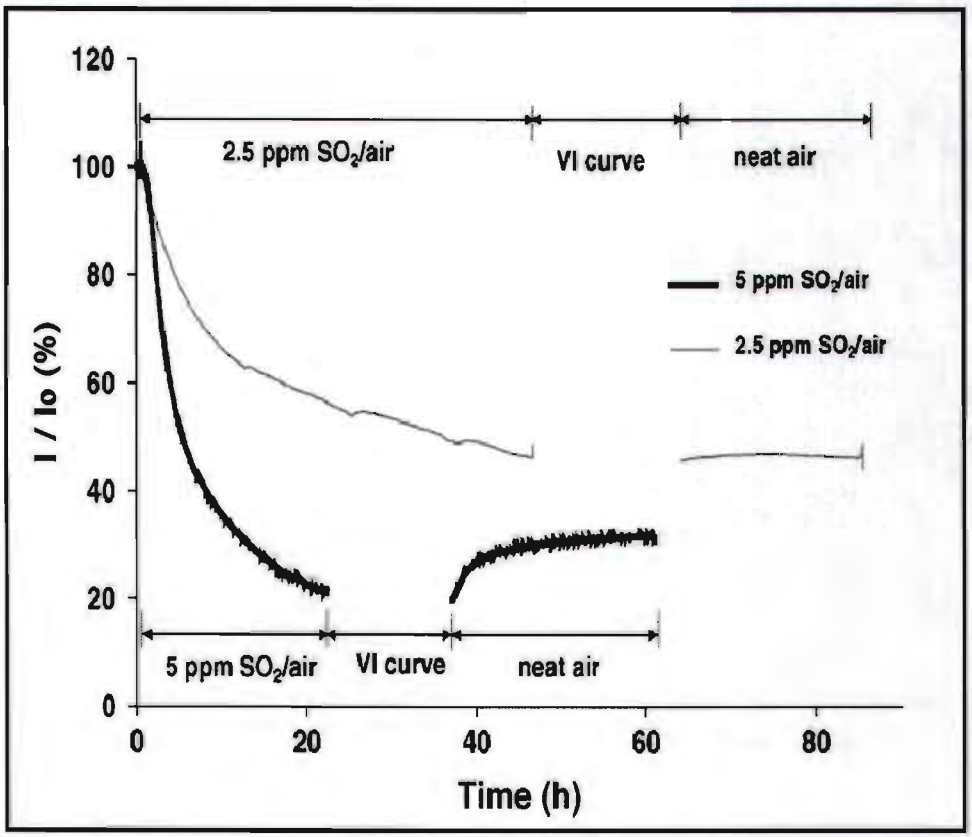


Figure 14 Transient response comparing the fuel cell performance after exposure to 2,5 and 5 ppm of SO_2 (Mohtadi *et al.* 2004:222).

Figure 14 shows that exposure of PEMFC to the increased levels of SO_2 does have an effect, particularly on the cell current. The cell current decreased by approximately 78% when exposed to 5 ppm of SO_2 for 23 hours. The cell current decreased by approximately 53% when exposed to 2,5 ppm SO_2 for the same exposure time.

When comparing the transient data, it appears that the rate of poisoning is a strong function of the SO_2 concentration as higher poisoning is observed at 5 ppm SO_2. However, partial recovery in the performance was obtained when applying neat air for 24 hours after the cathode was exposed to 2,5 and 5 ppm SO_2. The VI curves in the transient response represent the voltage versus current density curves of the PEMFC when exposed to 2,5 and 5 ppm SO_2 before introducing the clean air (Mohtadi *et al.*, 2004).

2.5.2 Effect of nitrogen dioxide (NO_2) on the air-breathing PEMFC

Nitrogen oxides are released into the atmosphere in the form of nitric oxide due to the combustion of fossil fuels, and then oxidized to NO_2. NO_2 at the concentration level of 500 ppb does not affect the performance of PEMFC (Moore *et al.*, 2000).

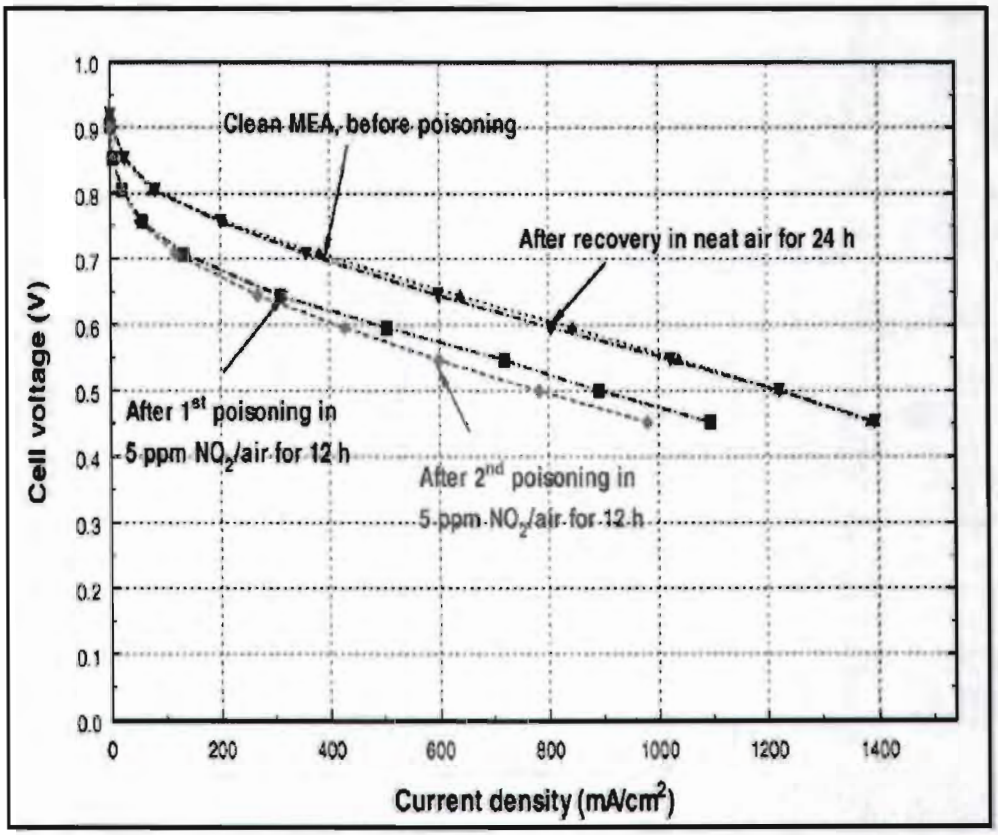


Figure 15 Polarization curves showing the effect of NO_2 at 5 ppm on the cell performance (Mohtadi *et al.* 2004:219).

As shown in the polarization curves in figure 15, experimental study done by Mohtadi *et al.* (2004:218) showed a performance loss in the cell when it was exposed to 5 ppm of NO_2 for 12 hours. However, as neat air was reintroduced afterwards, the cathode recovered the cell performance. This clearly shows that the conclusions made by (Moore *et al.*, 2000) concerning these air contaminants not having an effect on the fuel cell performance were based on low concentrations of the gas impurities.

2.5.3 Effect of carbon monoxide (CO) on the air-breathing fuel cells

CO is generated in the atmosphere by combustion processes and by the oxidation of organic compounds (Mepsted, 2001:20). The largest fraction of this gas impurity is mostly caused by gasoline-fueled motor vehicles. Most emissions of this air pollutant are found in urban areas, where concentrations of about 10 to 15 ppm occur (Perkins, 1974).

According to Colmati Jr. *et al.* (2002) CO has a greater detrimental effect on the PEMFC and the DMFC, as it is strongly adsorbed on the platinum (Pt) catalyst of the fuel cell electrode and inhibits the anodic reaction. The effect of this gas on fuel cell performance has been researched by several fuel cell researches and thus it is well understood.

According to Baschuk and Li (2001:696-700) CO poisoning is found mainly in transportation applications and cannot be avoided because of the use of pure hydrogen as a fuel for PEMFC. One of the major limitations is on-board hydrogen storage, which is difficult to implement. The hydrogen generated on-board by reforming liquid hydrocarbon or alcohol fuels results in 74% of H_2, 25% of CO_2 and 1 to 2% of CO. However, the CO concentration can be reduced to about 2 to 100 ppm by using a selective oxidation processes. Nevertheless, even at such concentration levels, CO poisoning would still plague PEMFC operation and performance.

The electrochemistry of CO and H_2 must be clearly understood in order to understand the behavior of PEMFC in the presence of CO. This is because Pt or its alloys are invariably used and needed in low temperature acidic electrolyte fuel cells in order to facilitate electrochemical reaction for the production of electrical power. The oxidation of CO occurs on the 100 and 110 sites of Pt in an acidic electrolyte. Oxidation of CO takes place within a voltage range of 0,6 to 0,9 V.

Oetjen *et al.* (1996) studied the effects of CO on the PEMFC performance and produced the set of polarization curves shown in figure 16. Each curve represents the performance of the cell at a certain concentration of CO poisoning in the hydrogen (H_2) fuel gas.

The operating cell temperature was at 80°C and the CO concentrations were 25, 50,100 and 250 ppm.

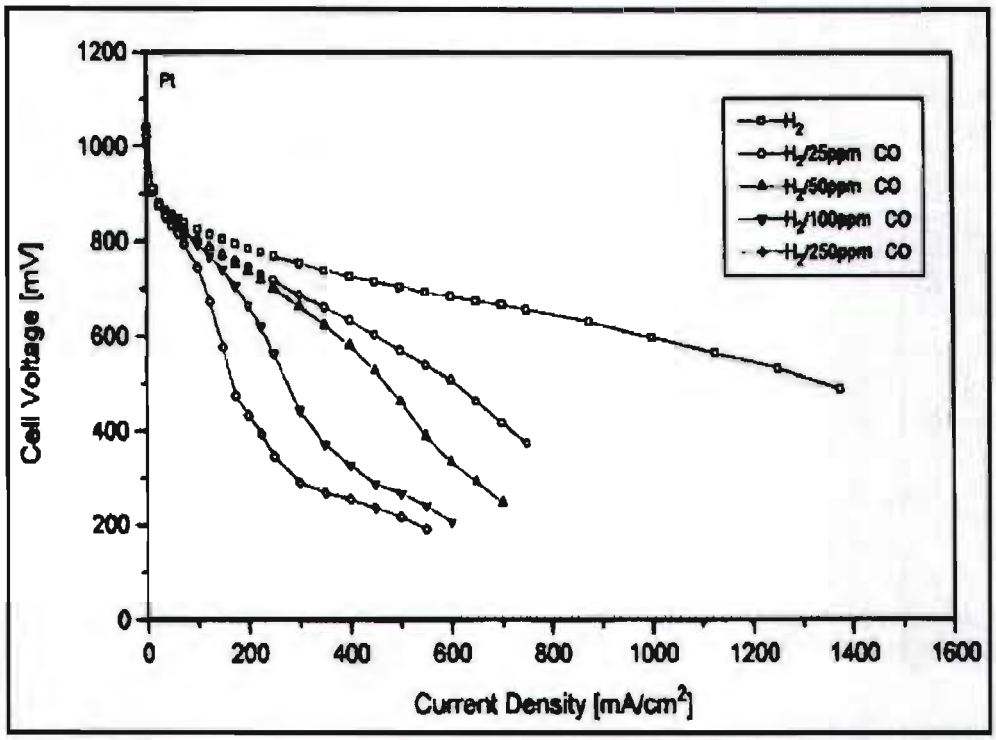


Figure 16 Effect of CO on the PEMFC (Baschuk & Li, 2001:700).

As shown in figure 16, the performance of the cell decreases as the concentration of CO is increased. For CO concentrations greater than 50 ppm, the polarization curve had two distinct slopes. The lower slope is associated with the adsorption and oxidation kinetics of H_2 and CO at the anode. At increasing current densities, the potential of the anode increased to a point where CO could be oxidized to CO_2 and thus resulting to higher reaction rates for H_2 adsorption and oxidation.

It was also found that the poisoning effect takes some time to reach steady state and operating the fuel cell at an open circuit voltage (OCV) with pure hydrogen for two to three hours could reverse the CO poisoning. Therefore, CO poisoning effect must be taken as a transient phenomenon in the operation of PEMFC used in transportation applications (Baschuk & Li, 2001).

Ralph and Hogarth (2002:118) mentioned that in a typical MEA where the temperature is 80°C, CO in the reformate stream binds very strongly to the Pt electrocatalyst sites in the anode layer. Even at low ppm levels of CO, the CO coverage is above 0,98 and thus the adsorbed CO prevents the dissociative electrosorption of hydrogen, which is represented as follows:

$$H_2 + 2Pt \rightarrow 2Pt - H_{ads} \qquad (10)$$

This lowers the cell potential produced by MEA dramatically because a much higher anode potential is needed to sustain the rate of hydrogen electro-oxidation. As illustrated in figure 17, the effect of CO was determined from 10, 40 and 100 ppm on a MEA anode with a Pt loading of 0,25 mg Pt cm^{-2} (Ralph & Hogarth, 2002).

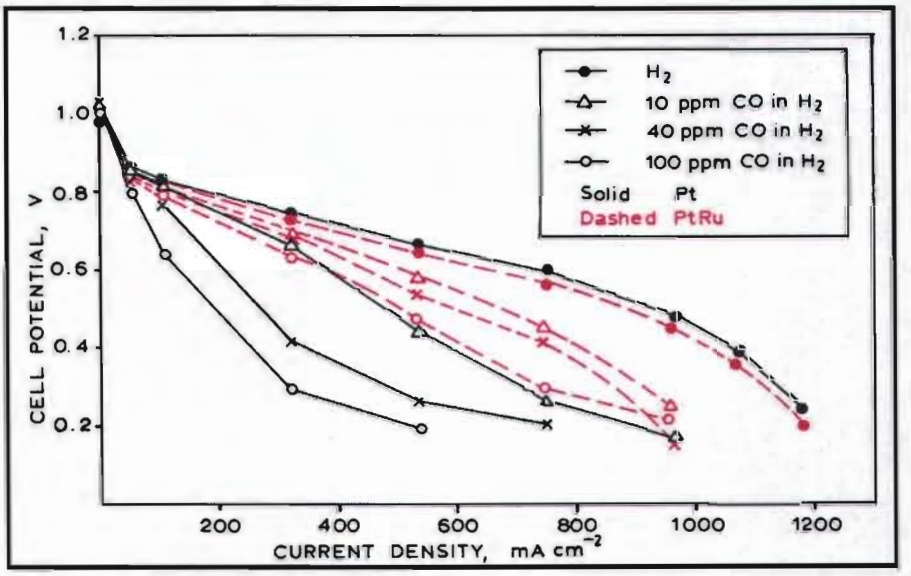


Figure 17 Effect of CO poisoning on the MEA at ppm levels (Ralph & Hogarth 2002:118).

As the CO content is increased from 10 to 100 ppm, there is progressive lowering in the cell potential from that achieved when using pure hydrogen. At such low Pt loading on the anode, the cell potential losses are significant even at low current densities below 200 $mAcm^{-2}$. At higher current densities the cell potential losses are more pronounced.

Eventually, the cell potential is reduced to approximately 0,3 V at which electro-oxidation of CO to CO_2 occurs as follows:

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \quad (11)$$

Under these circumstances the anode potential reaches approximately 0,45 V. This is enough to drive CO electro-oxidation and some of the poisoned Pt sites will be free to take part in hydrogen electrosorption and electro-oxidation reaction (10). Figure 17 also shows the large improvement in CO tolerance for an MEA with an anode based on Pt-Ru electrocatalyst. The cell potentials are significantly higher at all current densities compared with the MEA based on pure Pt, for operation with hydrogen containing 10, 40 and 100 ppm CO.

2.5.4 Effect of atmospheric benzene on the air-breathing PEMFC

According to Mepsted (2001:1) the main source of atmospheric benzene is the combustion and distribution of petrol. Exhaust fumes contains both unburnt benzene and benzene formed from the combustion of other aromatic compounds. The experimental studies done by Mepsted (2001) and Moore *et al.*, (2000) which investigated the effects of atmospheric benzene on the PEMFC both showed that benzene has a significant effect on the performance of the fuel cell. It was also reported that in most cases this effect is permanent.

Benzene is most likely to adsorb onto the Pt catalyst sites within the MEA. Therefore, it takes up the catalytic sites and smothers the fuel cell. It is so strongly bound that thermal energy alone is insufficient to remove it (Mepsted, 2001).

Figure 18 illustrates the fuel cell performance after being exposed to 50 ppm concentration of benzene in the air, and shows that benzene had a marked effect on the cell performance. It can be seen that the cell potential decreased for as long as benzene was present in the air stream (Moore *et al.*, 2000).

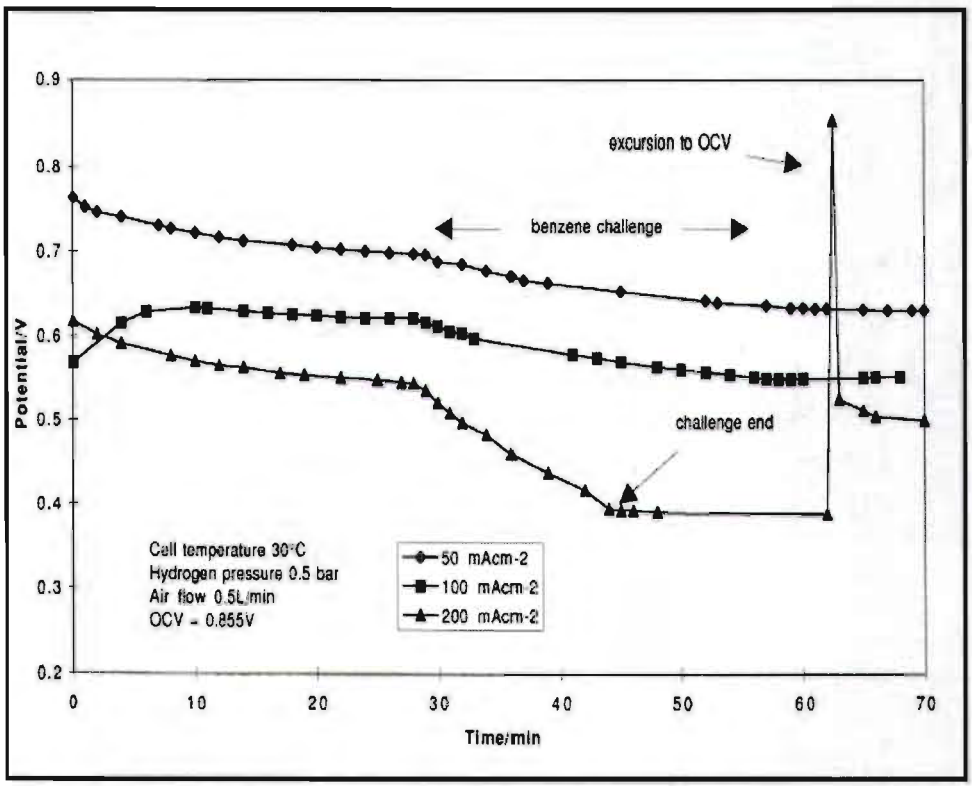


Figure 18 Effect of benzene on the PEMFC performance (Moore *et al.* 2000:258).

2.5.5 Effect of ammonia (NH_3) on the air-breathing PEMFC

NH_3 is not monitored as an atmospheric pollutant. However, it is present in many industrial fertilizers and its exposure to the fuel cell could occur mostly in rural areas. It is produced as a by-product of the reformation of petroleum fuels. Both partial oxidation and auto thermal reformation will produce approximately 10 ppm of NH_3 when operated above 700°C to 800°C from recombination of nitrogen and hydrogen. In an aqueous environment, NH_3 will solubilise and be transported by electro-osmotic drag through the membrane to the cathode of the PEMFC.

In an experimental study that investigated the effect of NH_3 on the PEMFC, the performance of MEA was adversely affected by NH_3, when operated at low temperature and high potential. However, at low cell potential the contaminant effect of NH_3 was eliminated (Mepsted, 2001).

2.5.6 Effect of carbon dioxide (CO_2) on the air-breathing fuel cells

While it has been known for many years that CO poisons Pt-based electrocatalysts, it was discovered recently that CO_2 also poison the PEMFC (Ralph & Hogarth, 2002).

Similarly, De Bruijn *et al.* (2002) reported that the influence of CO_2 on the PEMFC performance could be present at concentrations of up to 25% when a reforming process generates a hydrogen gas or in the cleaning of carbon based fuels. However, this effect is normally neglected and has only been described in a limited number of papers. This is because the influence of CO_2 is thought to be better than that of CO. While CO_2 itself is regarded as an inert, the formation of CO by reverse water gas shift reaction (RWGSR) leads to a negative impact of CO_2 on the performance of the PEMFC anode.

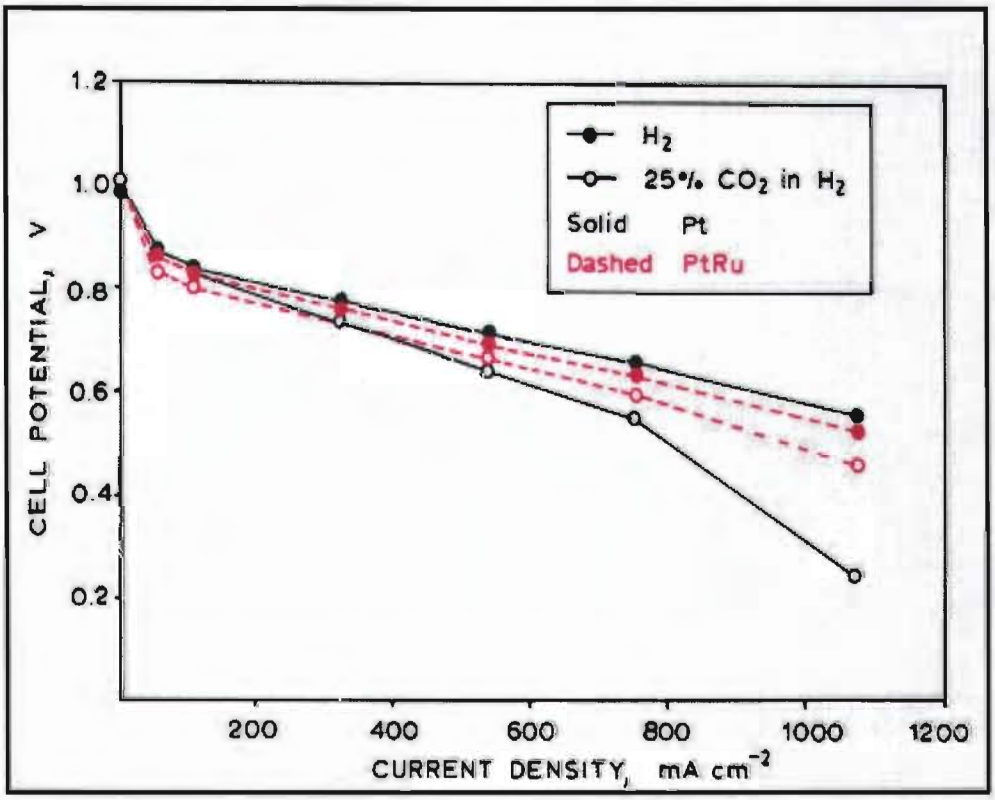


Figure 19 Polarization curves showing the effect of CO_2 on the PEMFC performance (Ralph & Hogarth, 2002:123).

As shown in figure 19, CO_2 at a concentration of 25% which is present in most of the reformate streams has a negative effect on a Pt anode. Cell potential losses become significant at higher current densities. The reformate containing 25% of CO_2 in H_2 at 80°C can generate 100 to 200 ppm of CO by RWGSR given as follow:

$$CO_2 + H_2 \rightarrow H_2O + CO \qquad (12)$$

The exact amount of CO produced by reaction (12) depends on the water concentration. In practice 10 ppm of CO is normally produced by RWGSR (Ralph & Hogarth, 2002).

Tewari *et al.* (2006) mentioned that CO_2 poisoning is a major problem for the ZAFC's and it limits their use as air-breathing energy sources. The poisoning reaction depletes the KOH electrolyte directly by the following reaction:

$$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O \qquad (13)$$

The reaction in equation (13) has an effect of reducing the number of hydroxyl ions available for reaction at the electrodes. This conversion from hydroxide to carbonate also reduces the ionic conductivity of the electrolyte solution. In a very concentrated electrolyte solution, it may also block the pores of the GDL by the precipitation of K_2CO_3 salt. The conversion of the electrolyte from KOH to K_2CO_3 by the absorption of CO_2 slows down the rate of the oxidation of the fuel at the anode. The sluggish anode kinetics decreases the performance of the fuel cell as a whole, unless the electrolyte is being continuously circulated.

2.6 Air pollution hotspot areas in South Africa

According to Groundwork (2003:4-39) the use of coal by South Africa's industrial sector is the primary source of the country's air pollution. More than 90% of the country's electricity is generated from coal combustion.

The country's main oil refineries are located in the areas shown in figure 20 and the following listed industrial areas have been reported as major air pollution hotspots in South Africa:

- Vaal Triangle area
- Secunda
- Southern Durban
- Joe Slovo and Table View in Cape Town

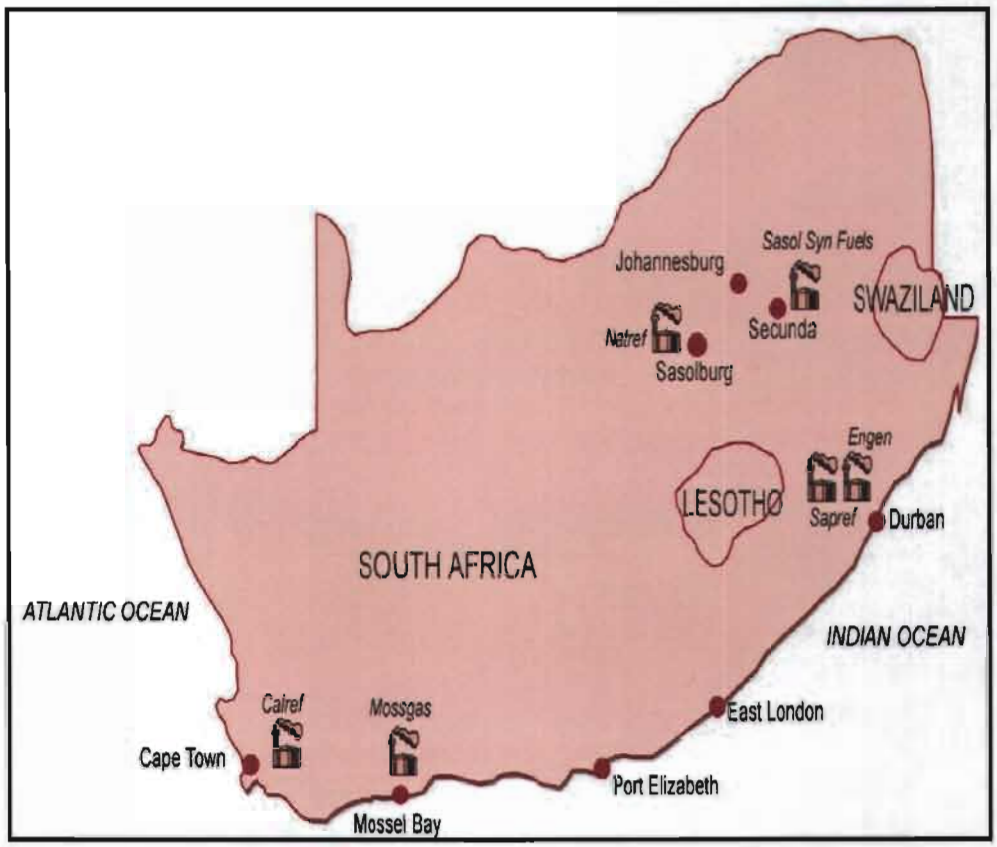


Figure 20 South African map showing industrial areas identified as air pollution hotspot areas (Groundwork, 2003).

From the above-mentioned areas, Vaal Triangle area is known as the industrial giant of South Africa, with Sasolburg as a major centre for the chemical industry. It is accompanied by Lethabo power station, which generates electricity from coal combustion

and other industrial companies such as Mittal Steel producing resources required by heavy industry and the largest markets in South Africa.

2.7 Summary

The surrounding environment will have the most profound effect on fuel cell operation and performance when the required oxygen for the chemical reactions is obtained directly from the ambient air. Therefore, the various types of air-breathing fuel cells that include PEMFC, DMFC and the ZAFC were presented and discussed in this chapter. Fuel cell performance was presented in terms of voltage and current characteristic curves for PEMFC and DMFC and discharge characteristic curves for the ZAFC. The effects of varying climatic environmental conditions such as ambient temperature and air humidity and the effects of common atmospheric air pollutants on the air-breathing fuel cells were presented and discussed in detail based on previous studies. Air pollution hotspot areas in South Africa were mentioned.

In the next chapter, the experimental investigations that were performed on the air-breathing ZAFC to determine the impact of the environment on the performance of this fuel cell are presented and discussed.

Chapter 3 Impact of the environment on the air-breathing ZAFC

3.1 Introduction

In this chapter, the effects of the surrounding environment on the air-breathing ZAFC performance were investigated. The effects of varying temperature and humidity conditions on the performance of the air-breathing ZAFC were experimentally studied in a climate chamber. Furthermore, the air-breathing ZAFC was also exposed to the air-polluted environment in order to investigate the impact of common atmospheric air pollutants on the performance. The air-breathing ZAFC was exposed to air impurities such as SO_2, N_2O, NO_2 and CO at 20 ppm levels. This concentration was chosen by considering the worst case scenario where an air-breathing fuel cell is required for an application situated very close to a chemical or power plant. Furthermore, the aim of choosing this relatively high concentration was to achieve the results and significant signals as quickly as possible. The results obtained from these experiments are presented in the form of discharge characteristic curves.

3.2 Temperature and humidity experiments on the air-breathing ZAFC

The purpose of these experiments was to determine the effect of varying temperature and humidity conditions on the performance of the air-breathing ZAFC. An 80 Ah air-breathing ZAFC that was used for these experiments was obtained from zinc-air energy systems (ZnERGY). As part of the preparation for these experiments, all the technical data relating to this particular fuel cell was obtained from zinc-air energy systems (ZnERGY). The data sheet (ANNEXURE A) indicates that the operating temperature for this particular fuel cell is from –20°C to 60°C. However, the data sheet did not specify the humidity levels suitable for the operation of this fuel cell. Therefore, since this particular ZAFC was operated using 26% aqueous KOH solution as an electrolyte, figure 8 was consulted to determine the RH levels that suit this concentration. It was found that, this KOH concentration is at equilibrium with the ambient room temperature when the RH is approximately at 68%.

The schematic diagram of the experimental test set-up used for the air-breathing ZAFC temperature and humidity experiments is shown in figure 21.

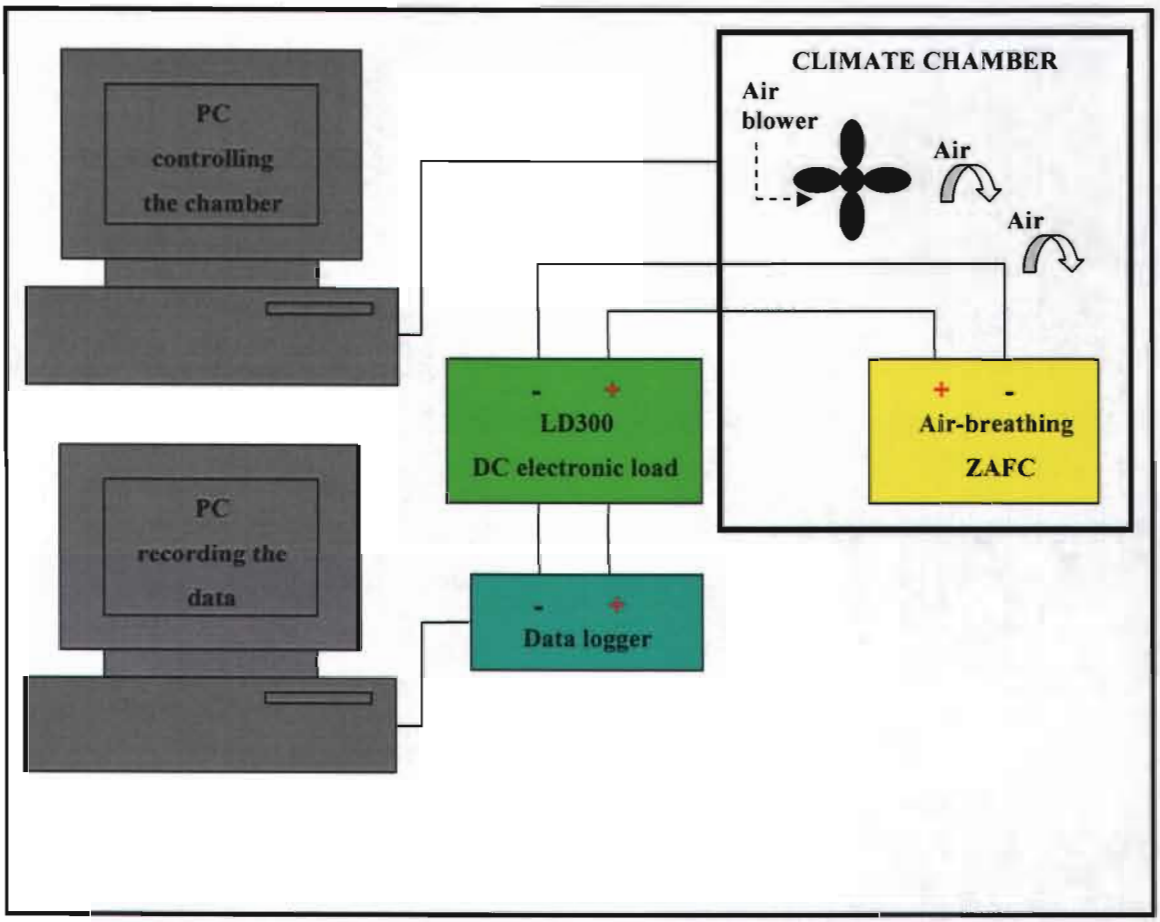


Figure 21 Schematic diagram of the air-breathing ZAFC test set-up for temperature and humidity experiments in a climate chamber.

In the experimental test set-up shown in figures 21 and 22, the equipment used was required to serve the following purposes:

- The climate chamber was used to produce an artificial environment in which the temperature and humidity could be controlled by means of computer software in order to maintain the desired climatic conditions.
- The 4-channel data logger/recorder was interfaced with a computer via a universal serial bus (USB) cable in order to continuously record the voltage readings over the time interval in which the ZAFC was discharged.

- A computer interfaced with a data logger was installed with a software program that incorporates a data logger from Velleman instruments. All the settings of the data logger were made using this computer software program.
- LD300 DC electronic load was used to discharge the air-breathing ZAFC under a constant current mode of discharge.

Figure 22 shows a picture of the experimental test set-up used to perform temperature and humidity experiments of the air-breathing ZAFC.

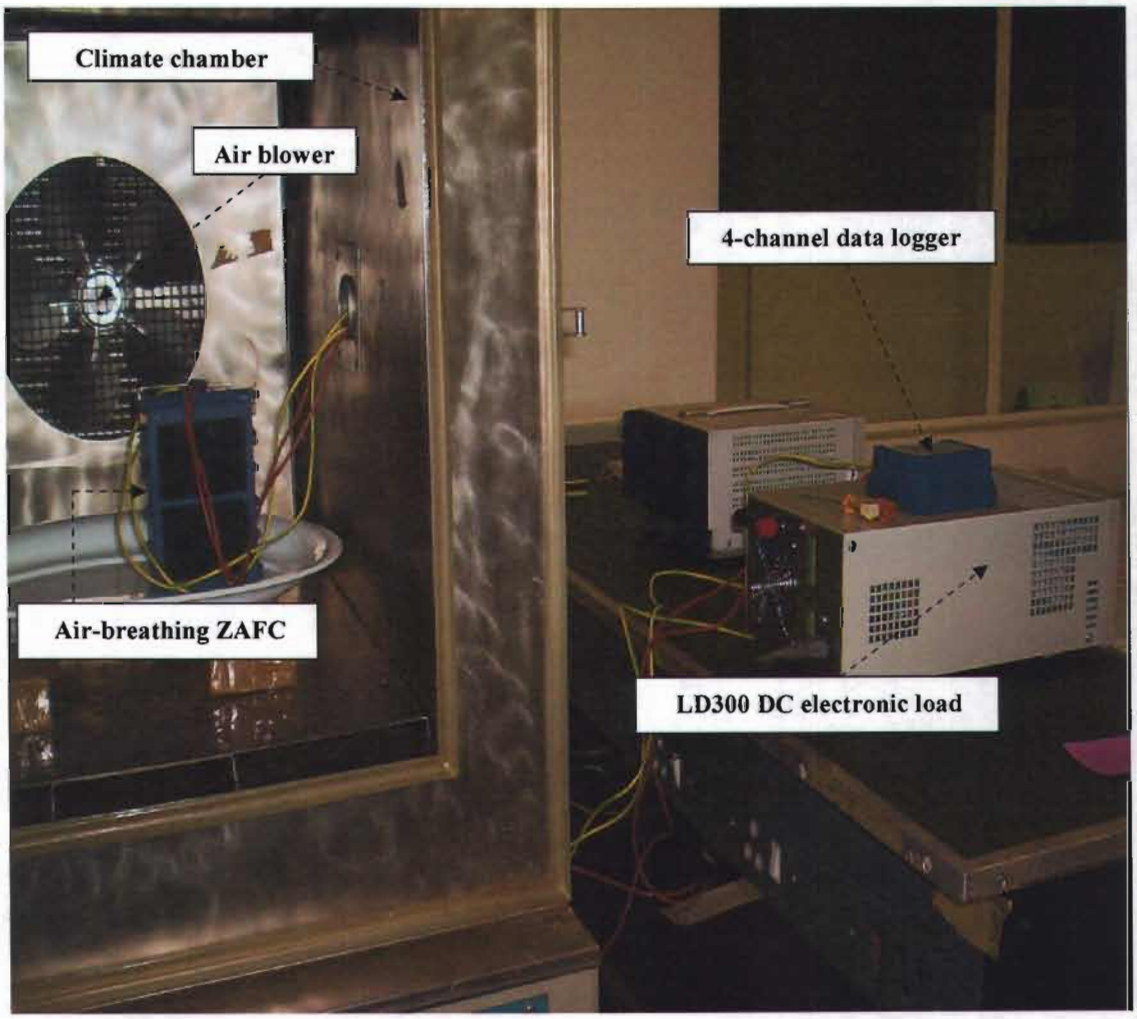


Figure 22 Experimental test set-up for the air-breathing ZAFC temperature and humidity experiments.

3.2.1 Temperature experiments on the air-breathing ZAFC

The first temperature experiment of the air-breathing ZAFC was done under normal ambient room conditions using the experimental test set-up shown in figure 23.

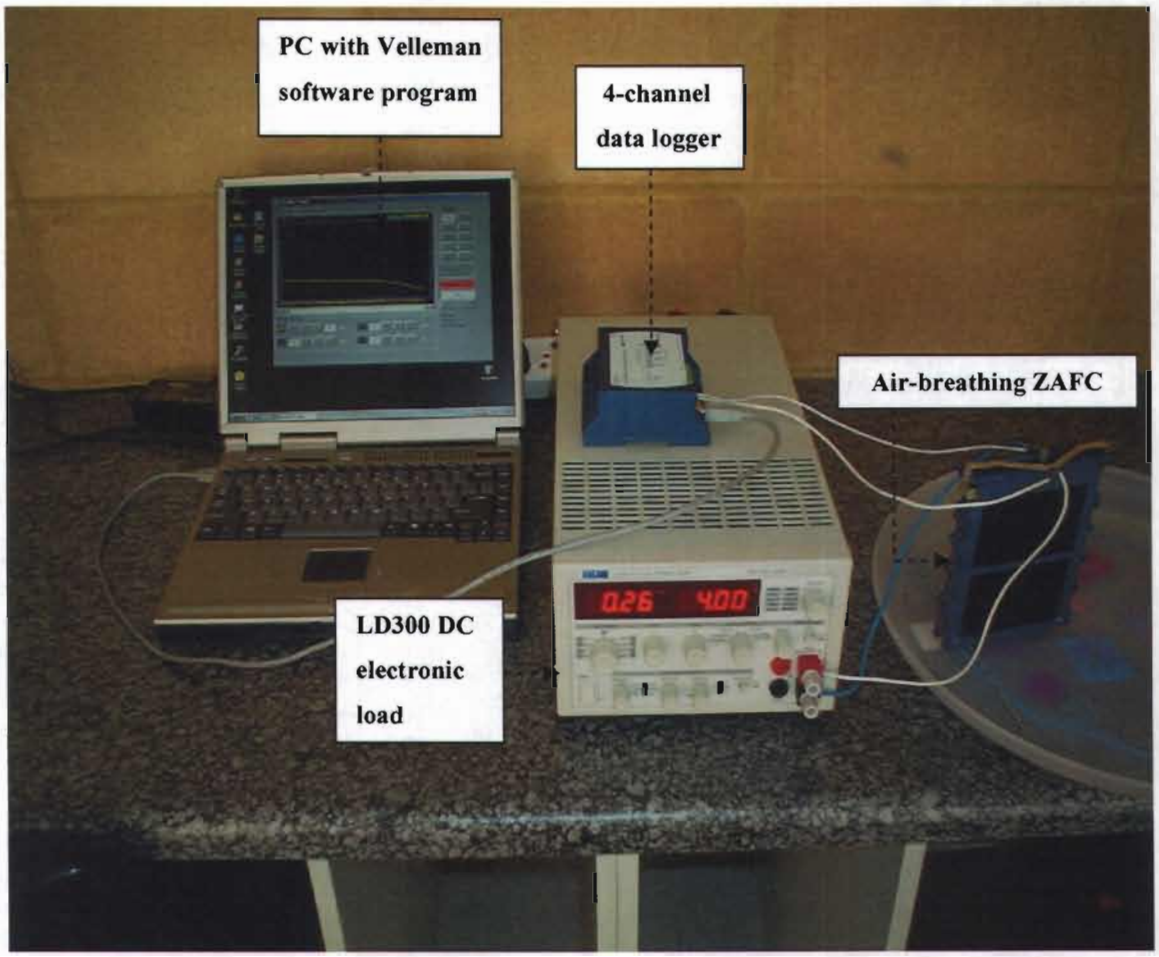


Figure 23 Test set-up for the air-breathing ZAFC temperature experiment at ambient room conditions.

The following experimental procedure was used to perform the temperature experiment on the air-breathing ZAFC at ambient room temperature and humidity conditions:

- Firstly, the air-breathing ZAFC was prepared by putting the zinc anode inside the cell casing and then filling the cell casing with an electrolyte KOH solution which had a concentration of 26%. After doing that, the cell immediately started operating. The

air-breathing ZAFC was given approximately five to ten minutes for it to stabilize to an open circuit voltage of around 1,38 to 1,4 V.

- One air-breathing ZAFC was then connected to the DC electronic load and the constant current mode was selected to discharge the cell at a constant current drain of 2 A while another air-breathing ZAFC was discharged at a constant drain of 1 A.
- The temperature and ambient humidity inside the laboratory was measured by a digital temperature and humidity meter. The room temperature was recorded to be 21,6°C while RH was recorded to be 52,3%.
- The computer was used to make the settings of the data logger. These settings included a working voltage level of 3 V and a time interval of 1000 s for the data logger to take the voltage samples. The record option was selected on a software program in order to start recording the voltage readings for the entire discharge period.
- The air-breathing ZAFC was continuously supplied with the 26% KOH solution for the entire discharge period until the voltage dropped to zero.
- The last step was to select the stop recording option on the Velleman software program when the air-breathing ZAFC was completely discharged.

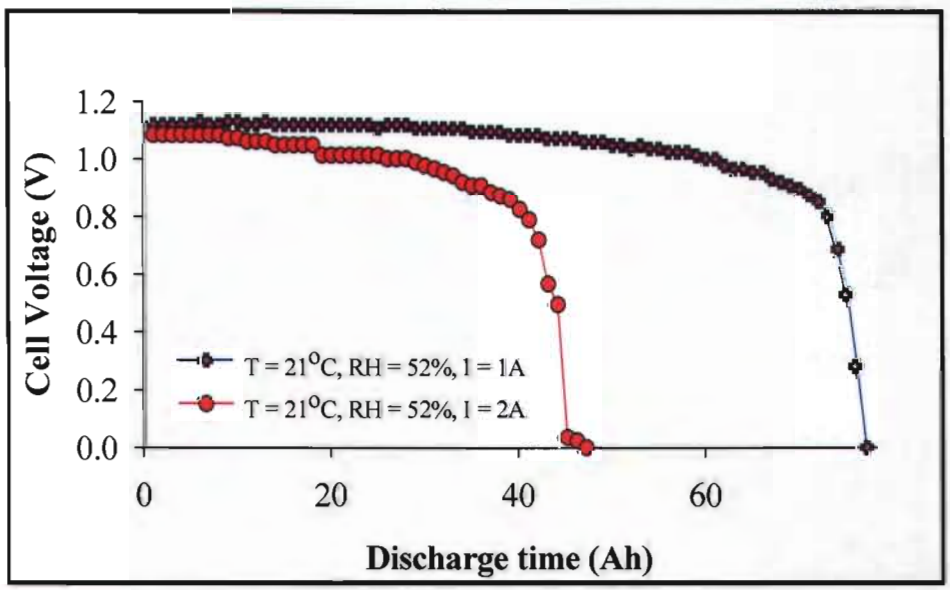


Figure 24 Results of the air-breathing ZAFC discharged at a constant current drain of 1 A and 2 A at ambient room conditions.

Figure 24 shows the performance results obtained when the air-breathing ZAFC was discharged under normal ambient room temperature conditions at current drains of 1 A and 2 A respectively. These results are discussed in chapter 5.

The second temperature experiment performed on the air-breathing ZAFC was done in the climate chamber shown in figure 21 and 22. The purpose of the experiment was to investigate the effect of varying temperature conditions on the performance of an air-breathing ZAFC.

The following experimental procedure was used to perform the air-breathing ZAFC experiment under varying temperature conditions:

- The climate chamber was set to a constant RH level of 50% and the operating temperature levels used when performing this experiment were chosen to be within the limits as given in the data sheet (ANNEXURE A). Therefore, starting at the lower temperature of –20°C, the air-breathing ZAFC was discharged under a constant current mode at a current drain of 2 A.
- When the air-breathing ZAFC was completely discharged at the temperature of –20°C, the humidity of the climate chamber was kept constant at 50% and the temperature of the climate chamber was increased to +20°C for the second experiment. The climate chamber was given one hour to stabilize on the new temperature and humidity settings before recording the data. New fuel supplies were used on the air-breathing ZAFC for each experiment where the temperature of the climate chamber was increased by 20°C. This included inserting the new zinc anode inside the cell casing. For each temperature increment, the air-breathing ZAFC was discharged at a constant current drain of 2 A.
- When the air-breathing ZAFC was completely discharged at the temperature of 40°C under a constant RH level of 50%, the temperature of the climate chamber was increased by 20°C to 60°C while the humidity inside the climate chamber was still maintained at 50% RH. Finally, the temperature of the climate chamber was increased by 10°C to 70°C while the humidity was kept constant at 50% RH.

- The last step was to plot the discharge characteristic curves for all the temperature experiments performed in the climate chamber.

The performance results of the temperature experiment performed in a climate chamber are presented in figure 25 and are discussed in chapter 5.

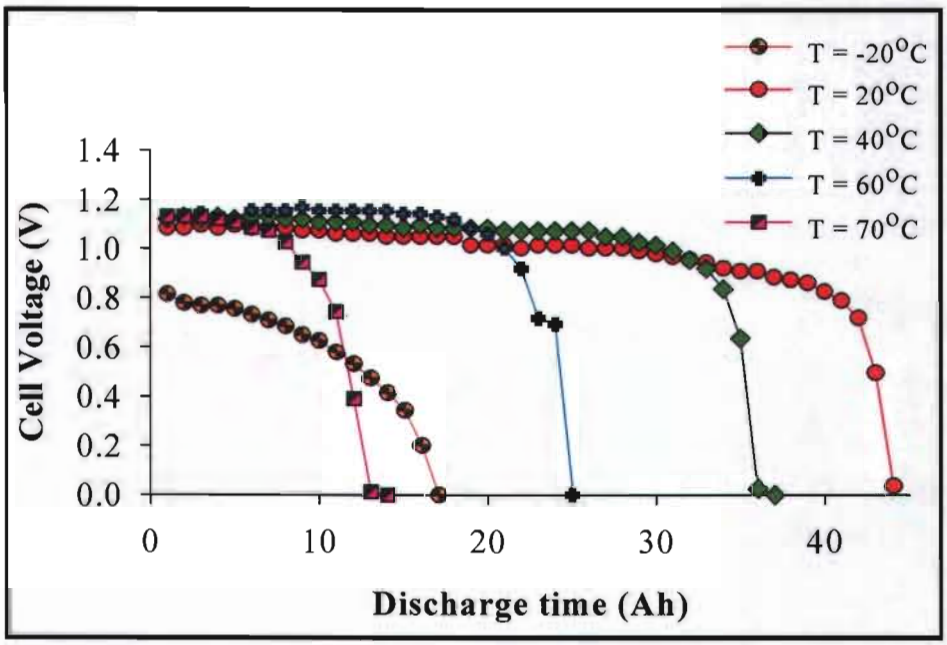


Figure 25 Results of the air-breathing ZAFC under varying temperature conditions at a constant RH of 50%.

3.2.2 Air-breathing ZAFC humidity experiments

The purpose of these experiments was to investigate the effect of varying humidity conditions on the performance of the air-breathing ZAFC. These experiments were done in a climate chamber using the experimental test set-up shown in figure 21 and 22.

The following experimental test procedure was used to perform the humidity experiments on the air-breathing ZAFC:

- The temperature of the climate chamber was first set to a constant level of 20°C and the RH level was increased in steps of 10% starting from 70% up until 90%. The air-

breathing ZAFC was discharged at a constant current drain of 2 A as done in the temperature experiments.

- The last step was to plot the discharge characteristic curves for these three humidity levels.

The discharge characteristic curves obtained from the humidity experiment explained above are shown in figure 26 and are discussed in chapter 5.

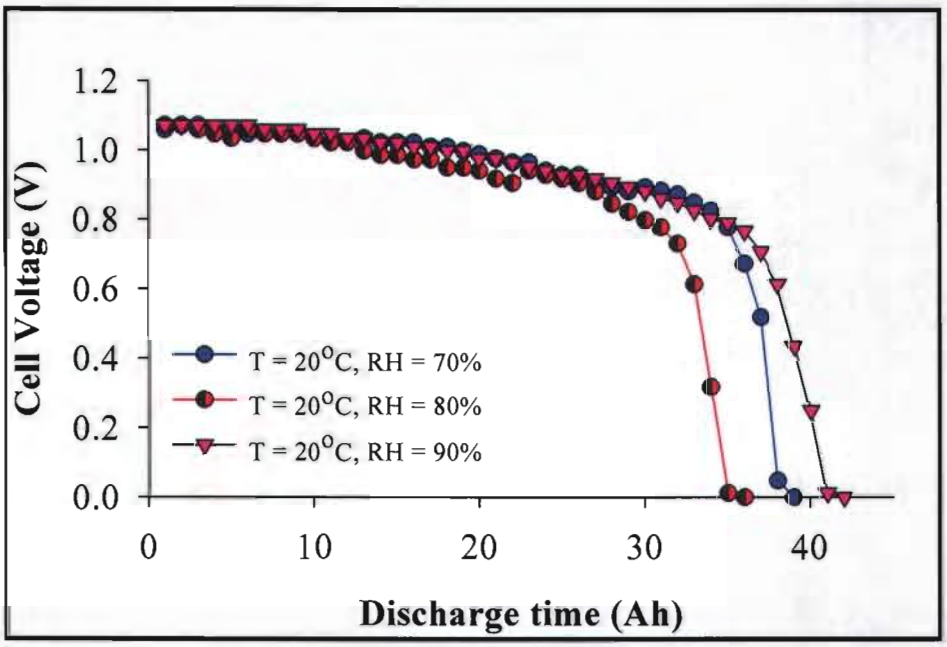


Figure 26 Results of the air-breathing ZAFC under varying RH conditions at a constant temperature of 20°C.

According to Berndt (1997:57) RH changes considerably with the temperature. Therefore, a second set of humidity experiments were performed on the air-breathing ZAFC where the temperature of the climate chamber was increased to 60°C and kept constant at that level. The experimental procedure used for these humidity experiments performed at a temperature of 60°C was as follows:

- The humidity of the climate chamber was increased in steps of 10% for each experiment starting from 70% RH up until 90% RH.

The discharge characteristic curves obtained from the humidity experiments performed at 60°C are presented in figure 27 and are discussed in chapter 5.

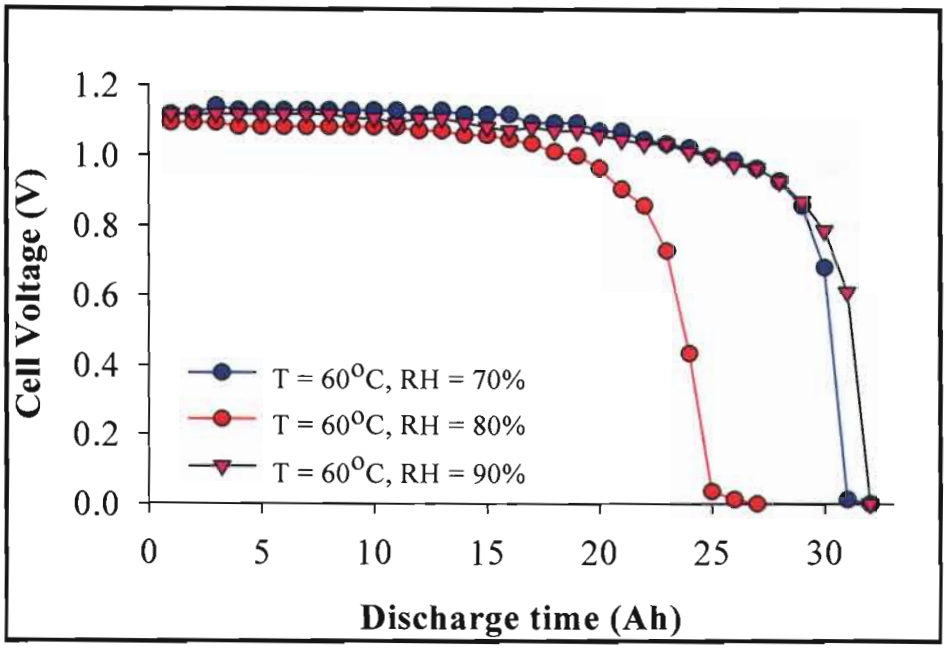


Figure 27 Results of the air-breathing ZAFC under varying RH conditions at 60°C.

3.3 Air pollution experiments on the air-breathing ZAFC

The purpose of these experiments was to investigate the impact of common atmospheric air pollutants such as SO_2, N_2O, NO_2 and CO on the performance of the air-breathing ZAFC.

The schematic diagram of the experimental test set-up used for the air pollution experiments is shown in figure 28. The test apparatus shown in figures 28 and 29 were used to serve the following purposes:

- Vaal Triangle Instrumentation Wholesalers-Eng constructed the air pollution test chamber. The test chamber was constructed with 10 mm thick perspex plastic. The purpose of the air pollution test chamber was to seal the supplied gas impurities while the air-breathing ZAFC was operating inside. A pressure gauge was installed on the lid of the air pollution test chamber to monitor the air pressure inside the test

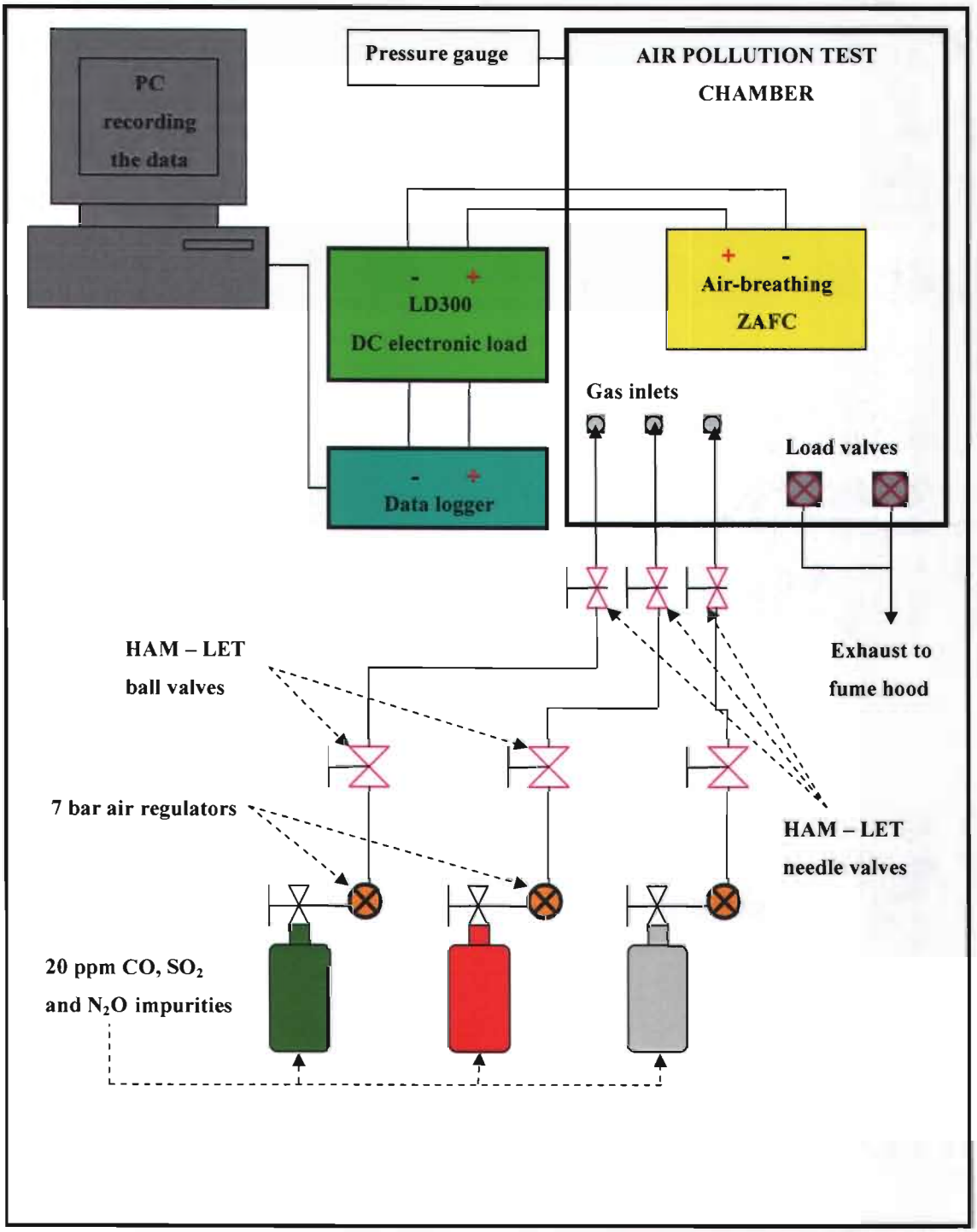


Figure 28 Schematic diagram of the air pollution experimental test set-up for the air-breathing ZAFC.

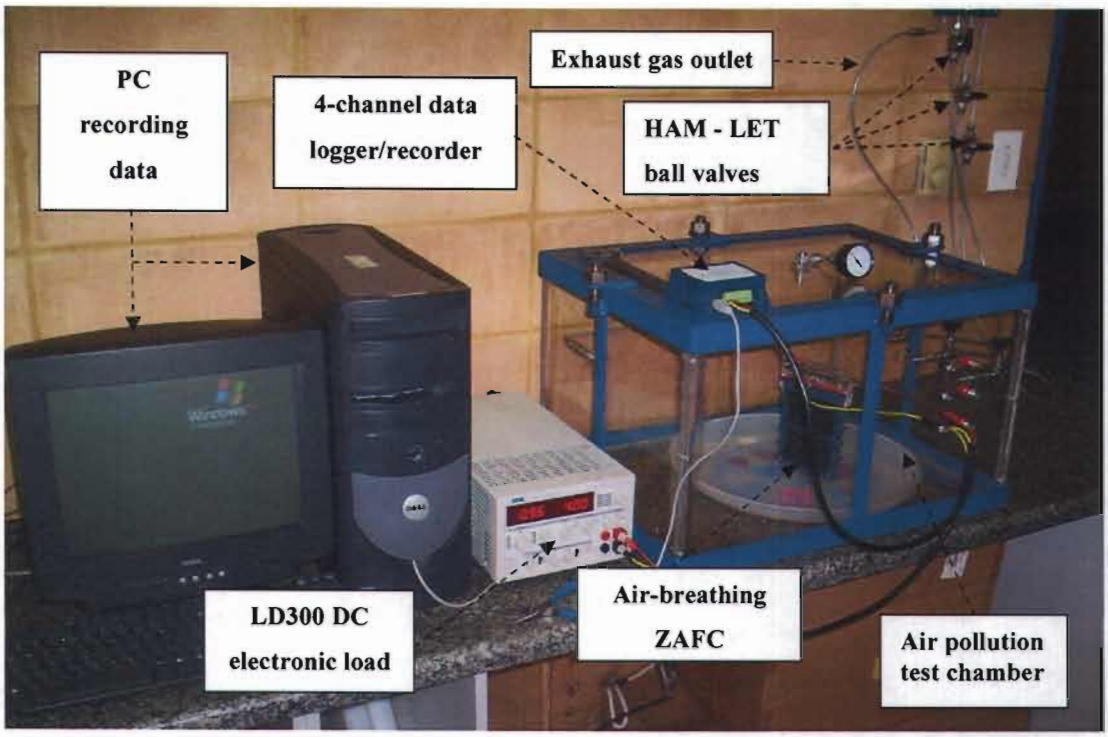


Figure 29 Experimental test set-up for the air-breathing ZAFC air pollution experiments.

The following experimental test procedure was used to determine the effect of air pollution on the air-breathing ZAFC performance:

- The first thing was to establish the baseline performance for the air-breathing ZAFC by first running it on a clean air. The constant current mode of discharge was used in this experiment and the cell was discharged at a constant current drain of 4 A for the entire discharge period.
- After the baseline performance was established, a polluted air containing 20 ppm SO_2 gas impurity was introduced into the air pollution test chamber and the fuel cell was discharged at a constant current drain of 4 A up until the cell was completely discharged.

The same experimental test procedure was used to determine the effect of 20 ppm CO, N_2O and NO_2 on the air-breathing ZAFC performance. The results obtained from these experiments are presented in the following figures and are discussed in chapter 5.

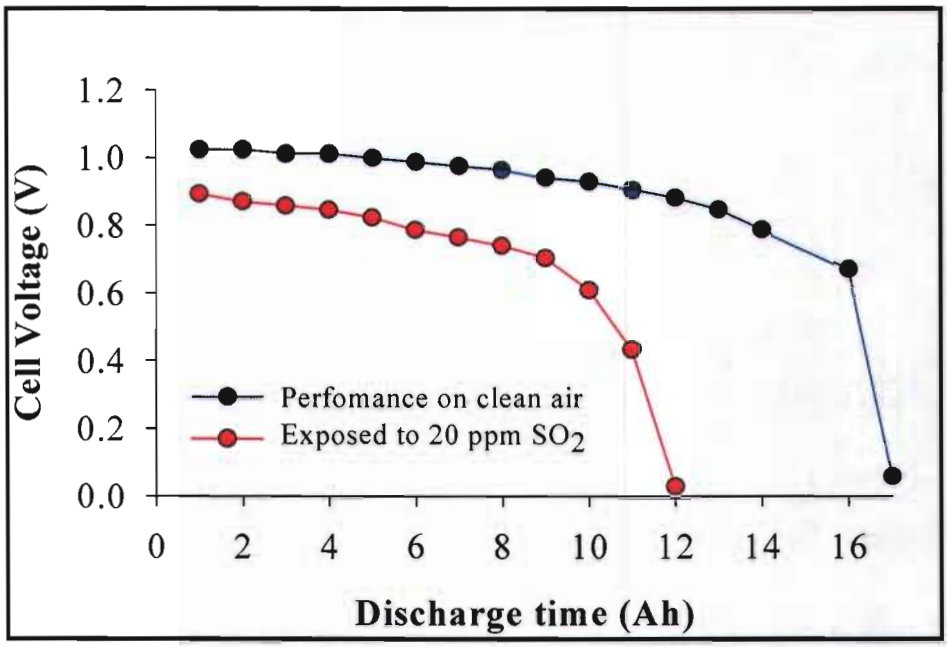


Figure 30 Results of the air-breathing ZAFC before and after being exposed to 20 ppm SO_2.

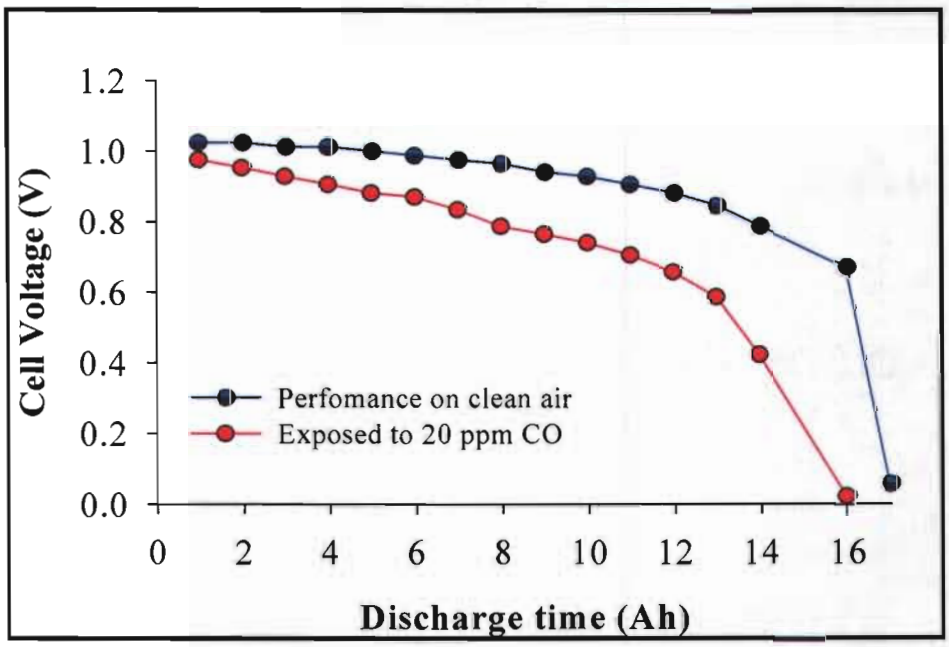


Figure 31 Results of the air-breathing ZAFC before and after being exposed to 20 ppm CO.

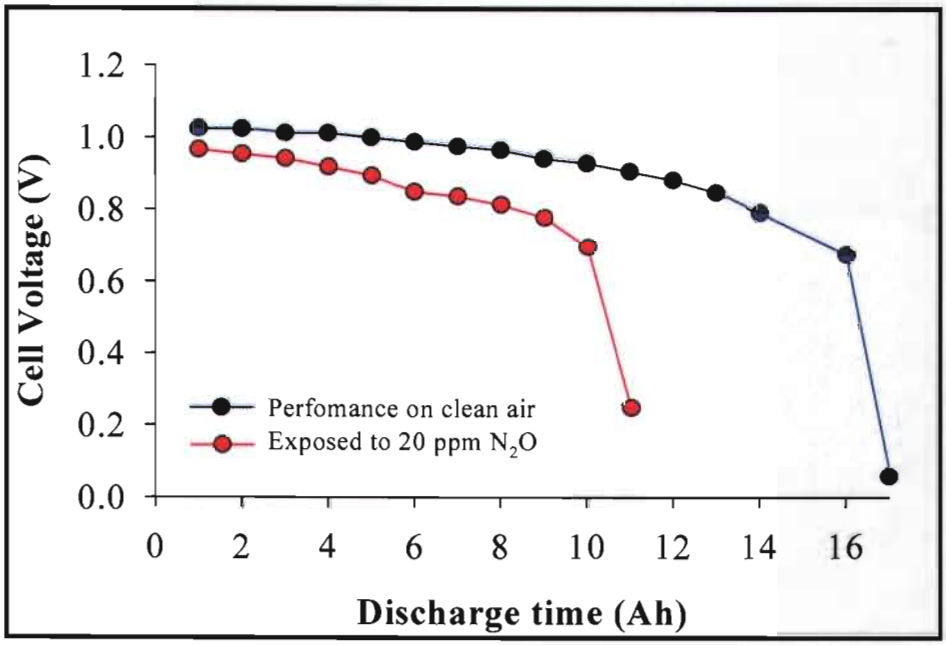


Figure 32 Results of the air-breathing ZAFC before and after being exposed to 20 ppm N_2O.

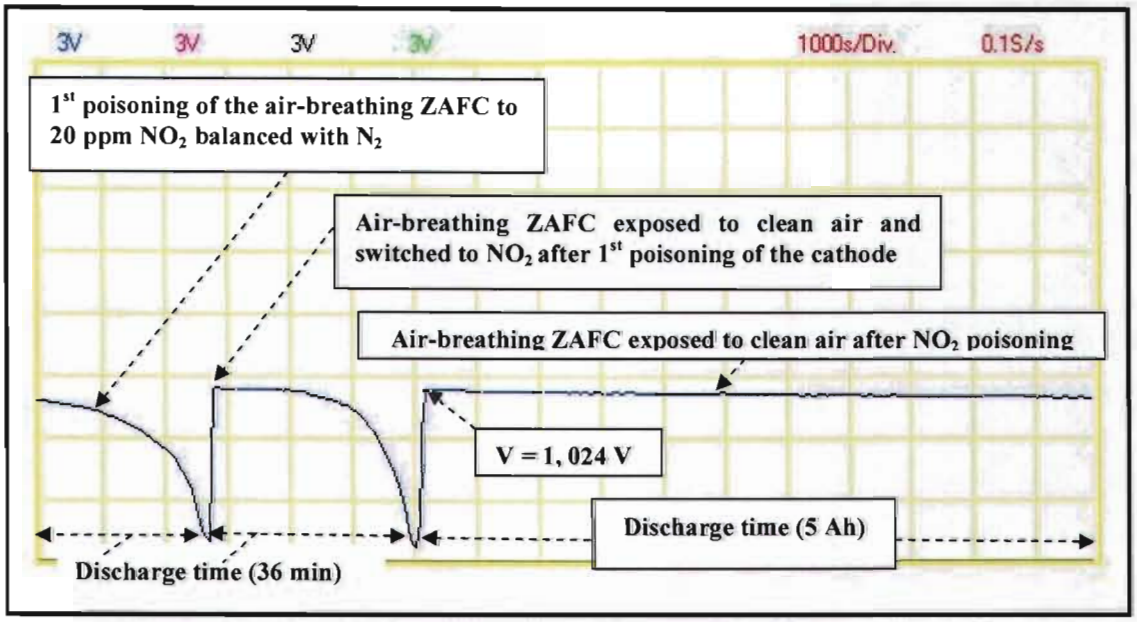


Figure 33 Results of the air-breathing ZAFC exposed to 20 ppm NO_2 balanced with N_2.

Figure 34 shows the air-breathing ZAFC components after the fuel cell was poisoned with 20 ppm CO, SO_2 and N_2O impurities respectively.

Figure 34 Air-breathing ZAFC components after being exposed to 20 ppm CO, SO_2 and N_2O impurities.

3.4 Summary

In this chapter, the air-breathing ZAFC was experimentally studied in a climate chamber to determine the influence of environmental parameters such as varying temperature and humidity conditions on the performance of the fuel cell. In addition, another experimental study was done to investigate the impact of the air pollution on the air-breathing ZAFC performance. For this experimental study, the air-breathing ZAFC was studied in an air pollution test chamber supplied with contaminated air containing 20 ppm CO, SO_2 and N_2O impurities respectively. Furthermore, the air-breathing ZAFC was also exposed to 20 ppm NO_2 balanced with N_2. The results of all the experiments performed in this chapter were presented in the form of discharge characteristic curves.

In the next chapter, similar experimental investigations performed on the air-breathing DMFC are reported and the findings presented in the form of polarization curves.

Chapter 4 Impact of the environment on the air-breathing DMFC

4.1 Introduction

In this chapter, the impact of the surrounding environment on the air-breathing DMFC performance was experimentally investigated to determine the influence of the varying temperature and humidity conditions on the fuel cell performance. This was done in a climate chamber where these environmental parameters were controlled.

The air-breathing DMFC was also experimentally studied in the air pollution test chamber to determine the impact of common atmospheric air pollutants such as CO, SO_2, N_2O and NO_2 on the fuel cell performance.

The results obtained from these investigations are presented in the form of polarization curves.

4.2 Temperature and humidity experiments on the air-breathing DMFC

The air-breathing DMFC used for these experiments was designed and constructed at the Vaal University of Technology. The tested air-breathing DMFC was made up of a two-cell stack with a fan for blowing air into cathode side to achieve a better performance.

The membrane used in the air-breathing DMFC stack was Nafion 117 with the following specifications:

- The catalysts were Pt-Ru on the anode side and Pt-B on the cathode side, both with a loading of 4 mg cm^{-2}. The membrane active area was 100 cm^2.
- The GDL's were carbon cloth on the anode and elat on the cathode side.

The air-breathing DMFC stack was fueled with a 2% methanol solution in all the experiments performed.

4.2.1 Temperature experiments on the air-breathing DMFC

The purpose of these experiments was to determine the effect of varying temperature conditions on the air-breathing DMFC performance.

The first temperature experiment performed on the air-breathing DMFC was done under normal ambient room conditions. The measured room temperature was 22,4°C and the ambient RH was 53,7%. The test set-up for this experiment is shown in figure 35.

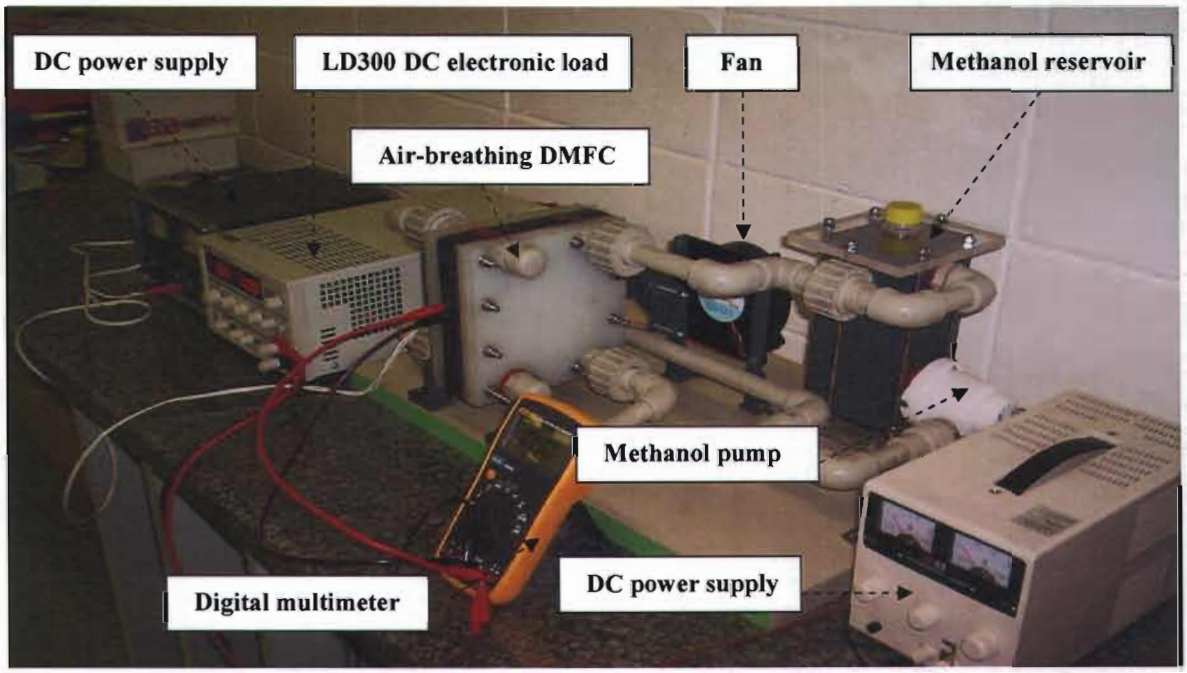


Figure 35 Experimental test set-up used to determine the air-breathing DMFC performance at normal ambient room conditions.

The equipment shown in figure 35 had the following purposes:

- One DC power supply unit was used to power the fan while another was used to power and to control the speed of the methanol pump.
- The LD300 DC electronic load was used to control the electrical load on the air-breathing DMFC as well as to measure the voltage versus current responses.

Subsequent temperature experiments on the air-breathing DMFC were performed in a climate chamber where temperature and humidity conditions were controlled by means of a computer software program. Figure 36 shows the experimental test set-up used to determine the performance of the air-breathing DMFC under varying temperature conditions.

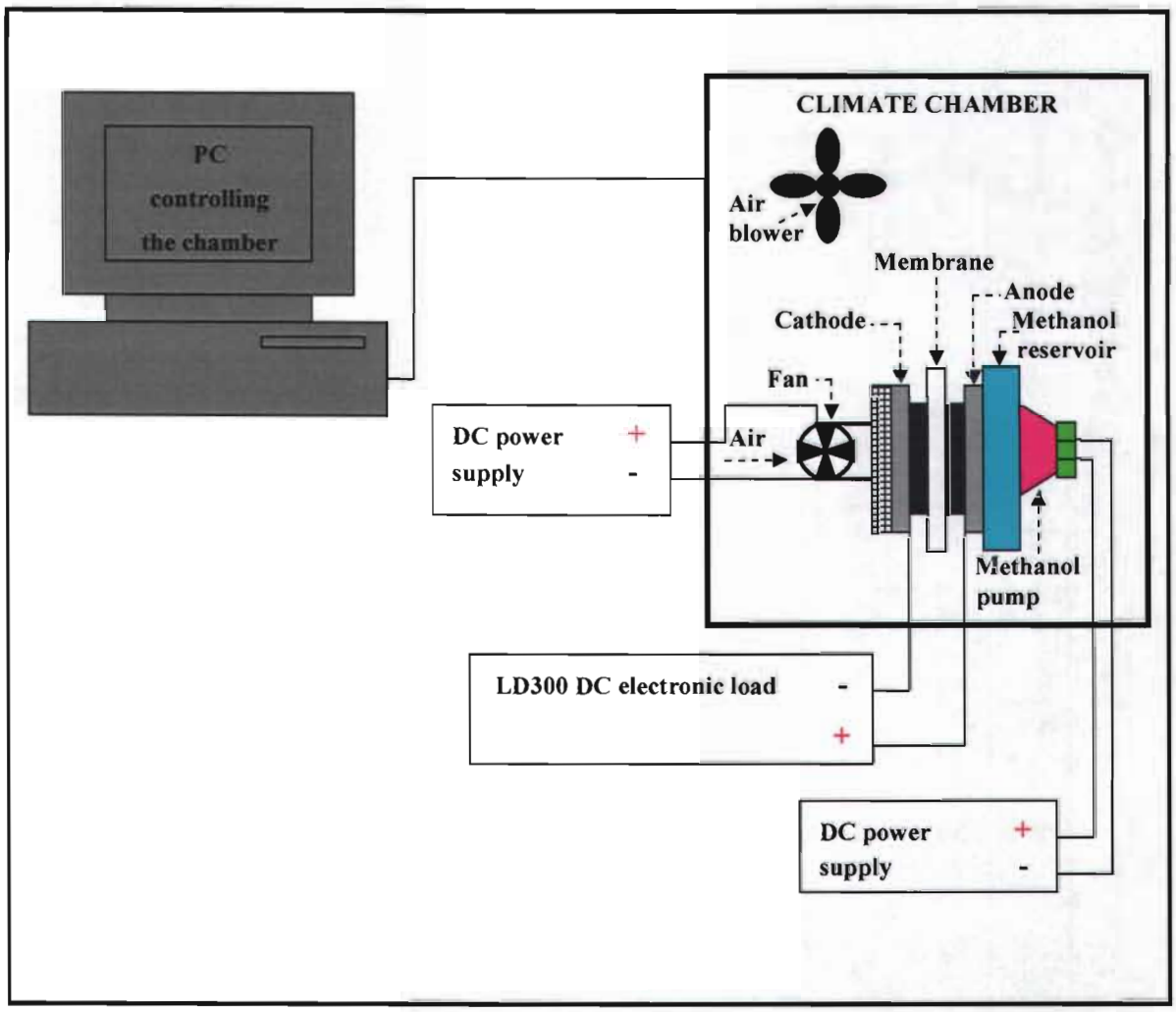


Figure 36 Schematic diagram of the experimental test set-up for the air-breathing DMFC temperature and humidity experiments.

The set of experiments carried out to study the effect of varying temperature conditions on the air-breathing DMFC performance was in the range of 30 to 90°C and measurements of cell performance were made at –10, 30, 60 and 90°C.

The experimental test procedure was as follows:

- As the temperature of the climate chamber was increased in steps of –10, 30, 60 and 90°C, the RH inside the climate chamber was kept constant at 50%. This was accomplished by using a computer software program that controlled the settings of the climate chamber. For each temperature increment, the climate chamber was given one hour to stabilize at the new temperature setting before polarization curve measurements were recorded.

The results of these temperature experiments are shown in figure 37 in the form of polarization curves and are discussed in chapter 5.

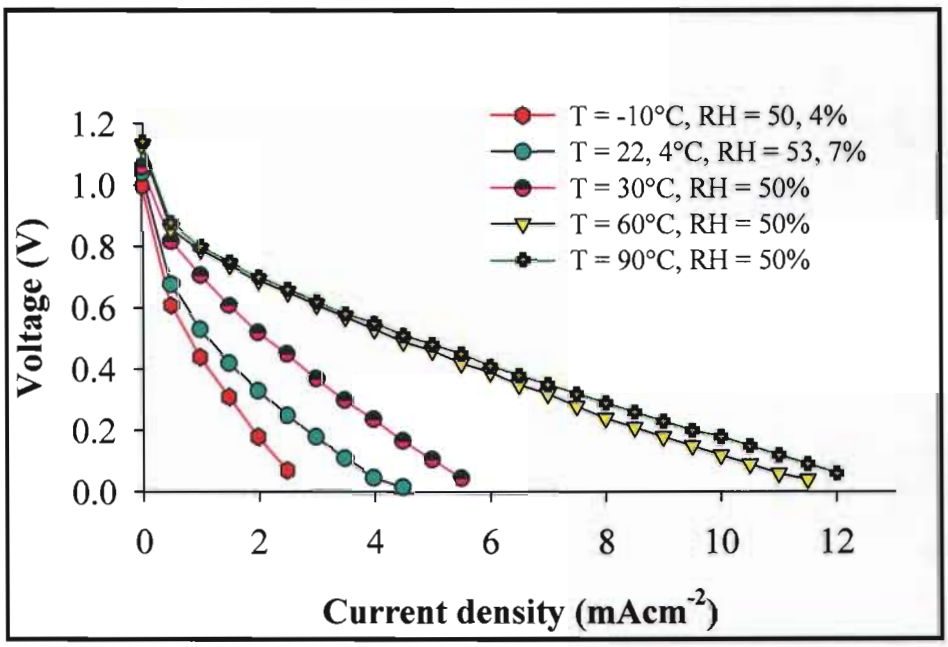


Figure 37 Performance of the air-breathing DMFC under varying temperature conditions at a constant RH of 50%.

4.2.2 Humidity experiments on the air-breathing DMFC

The purpose of these experiments was to determine the effect of varying humidity conditions on the air-breathing DMFC performance.

The performance of the air-breathing DMFC under varying humidity conditions was determined by using the experimental test set-up shown in figure 38.

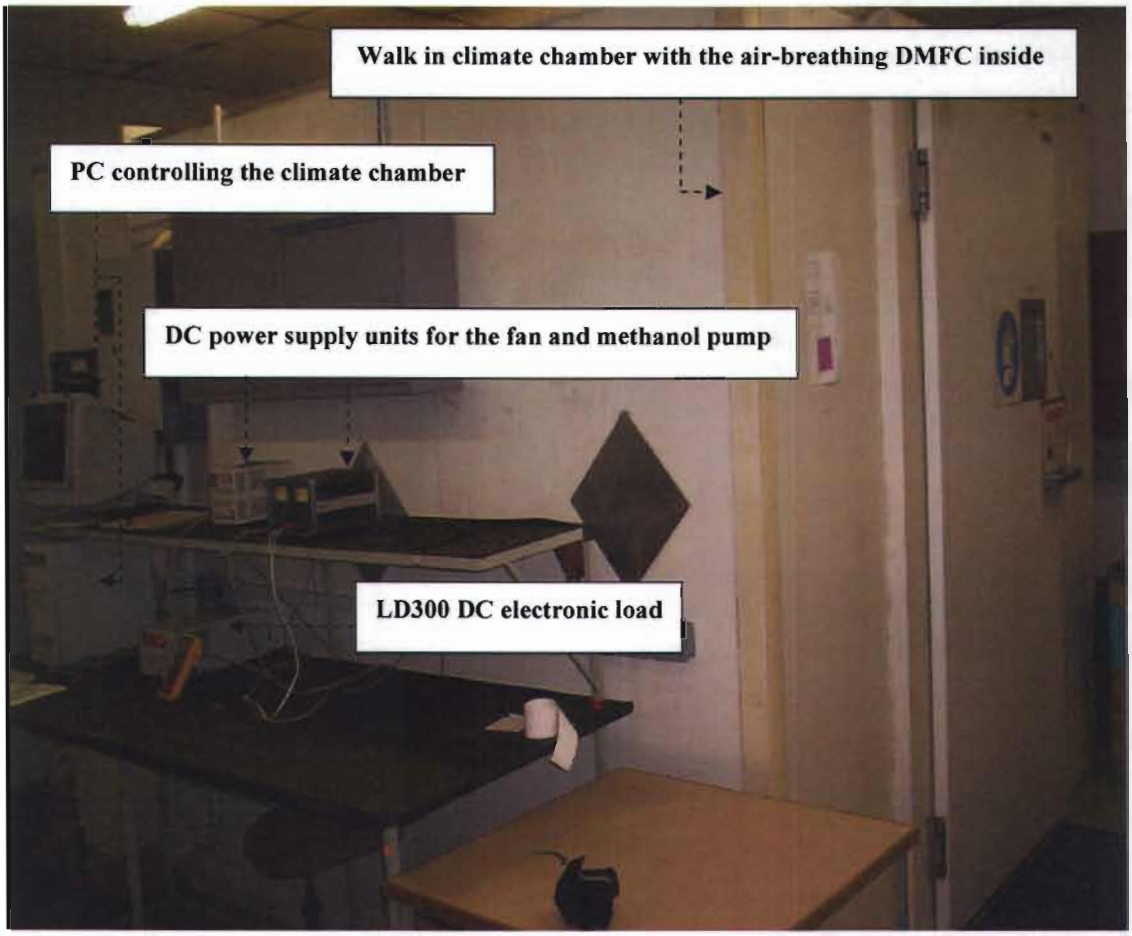


Figure 38 Experimental test set-up for temperature and humidity experiments on the air-breathing DMFC.

The following experimental test procedure was used to determine the effects of varying the humidity conditions on the air-breathing DMFC performance:

- Firstly, the temperature of the climate chamber was set to 25°C and kept constant at that level while RH was set to 70%. Before the air-breathing DMFC was put inside the climate chamber, the climate chamber was given one hour to stabilize at these temperature and humidity settings.

- After putting the air-breathing DMFC inside the walk in climate chamber, the LD300 DC electronic load was used to measure voltage versus current under constant current load conditions. The current was increased in steps of 0,1 A and the corresponding voltage readings were recorded.
- This was followed by increasing the RH by 10% from 70% to 80% while the temperature was kept constant at 25°C. Before measurements were taken, the climate chamber was given one hour to stabilize at each RH setting.

The humidity levels were increased from 70 to 90% with an increment of 10% and the results obtained are presented in figure 39 below. These results are discussed in chapter 5.

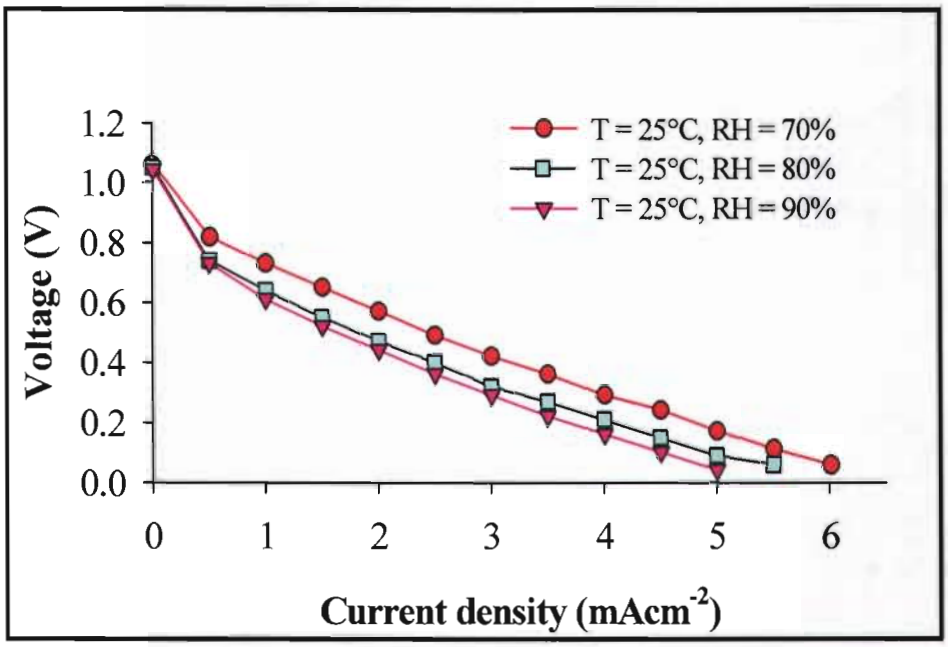


Figure 39 Performance of the air-breathing DMFC under varying RH levels at a temperature of 25°C.

A second set of humidity experiments were performed when the temperature of the climate chamber was increased to 60°C and kept constant at that level while varying the humidity of the climate chamber in steps of 10% from 70 to 90%. The responses of voltage versus current for these experiments were plotted on a Sigma Plot and are presented in figure 40.

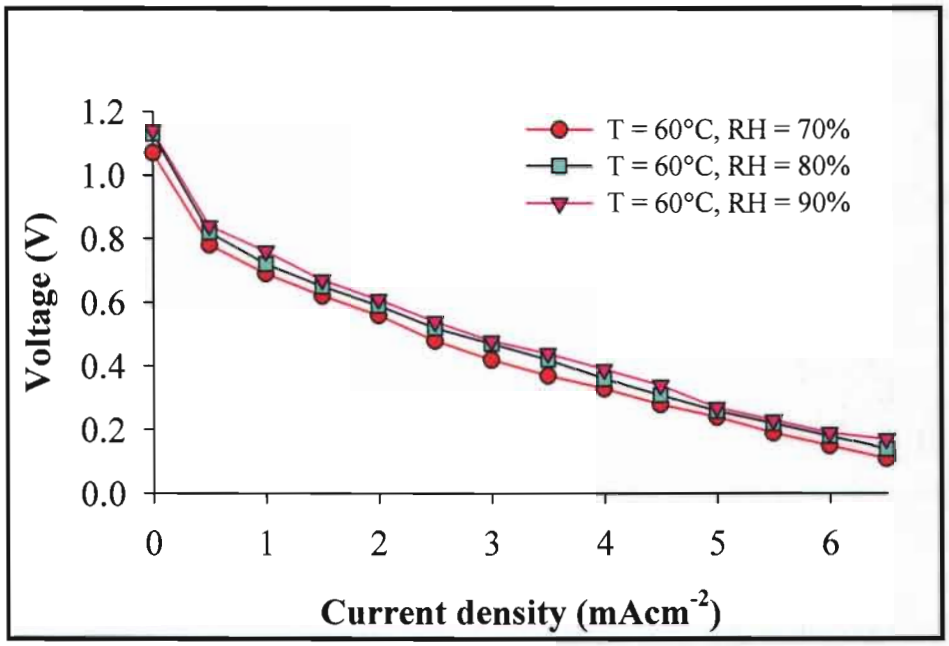


Figure 40 Performance of the air-breathing DMFC under varying RH levels at a temperature of 60°C.

4.3 Air pollution experiments on the air-breathing DMFC

The purpose of these experiments was to investigate the effect of SO_2, CO, N_2O and NO_2 on the performance of the air-breathing DMFC.

A schematic diagram of the experimental test set-up used to perform these experiments is shown in figure 41. The experimental test procedure used to perform air pollution experiments on the air-breathing DMFC was as follows:

- First, the baseline performance was established in a clean air environment by measuring voltage against current on the air-breathing DMFC stack under constant current load conditions.
- After the baseline performance, air containing 20 ppm SO_2 impurity was introduced into the air pollution test chamber for one hour before recording the data. The measurements of voltage versus current were recorded under constant current load conditions using an LD300 DC electronic load. The current increment was 0,1 A.

- After poisoning the air-breathing DMFC cathode with 20 ppm SO_2, the fuel cell was exposed to clean air again and another polarization curve was recorded.

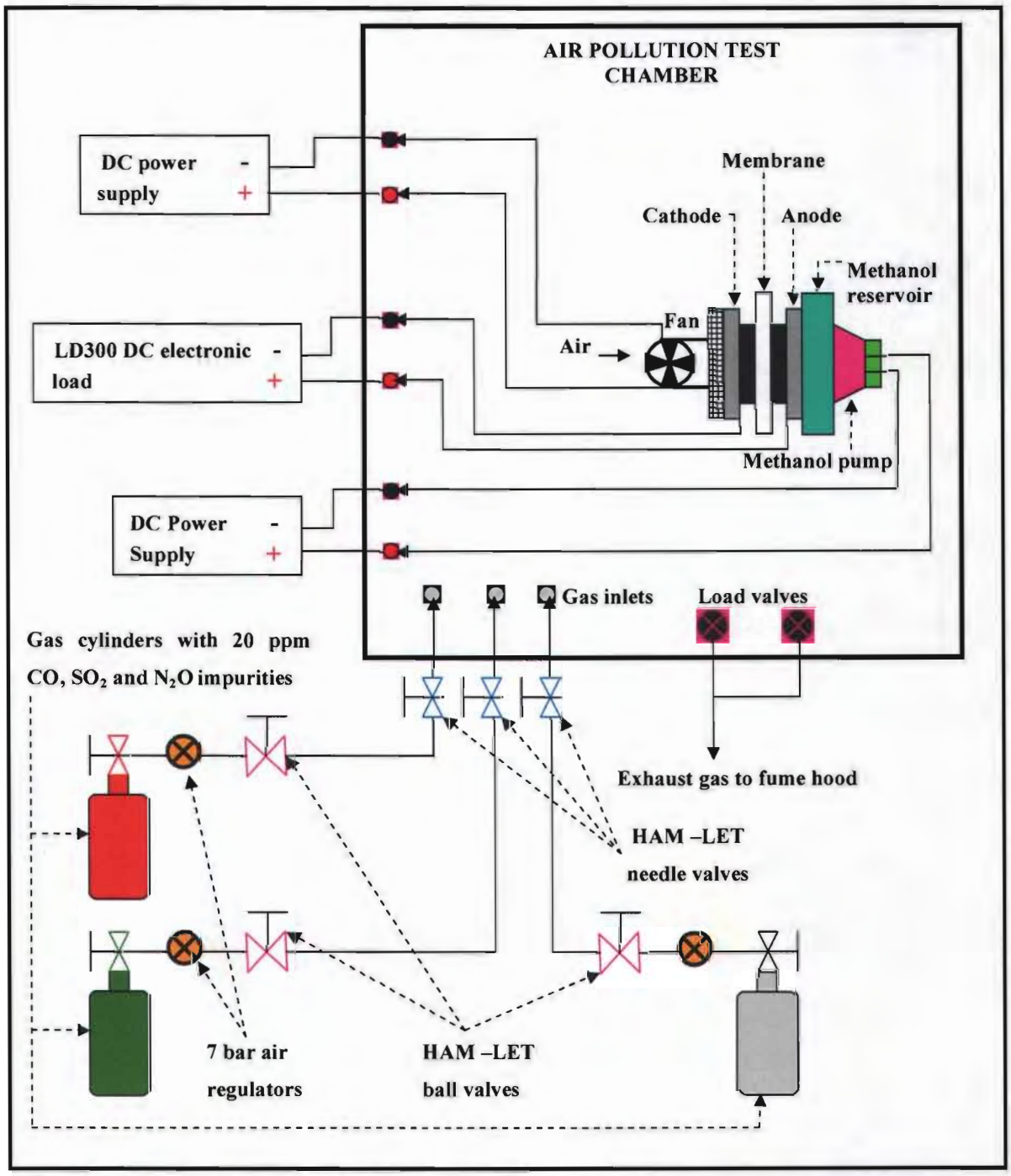


Figure 41 Schematic diagram of the test set-up used for air-breathing DMFC air pollution experiments.

The same experimental test procedure was used to test the performance of the air-breathing DMFC on 20 ppm CO, NO_2 and N_2O respectively. The results obtained when the cathode of the air-breathing DMFC was poisoned with 20 ppm N_2O, CO, SO_2, and NO_2 impurities are presented in the figures below and are discussed in chapter 5.

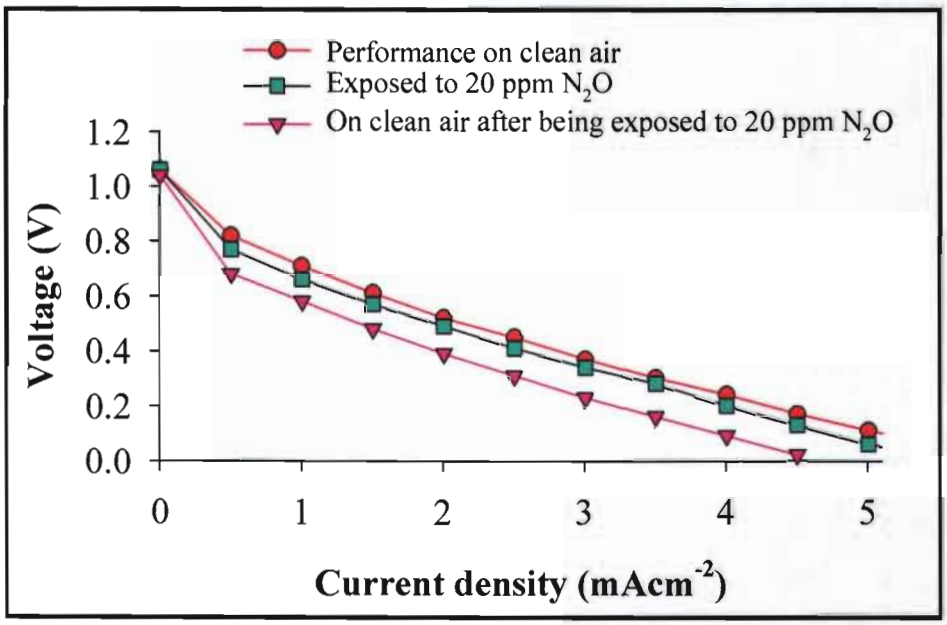


Figure 42 Performance of the air-breathing DMFC before and after being exposed to 20 ppm N_2O.

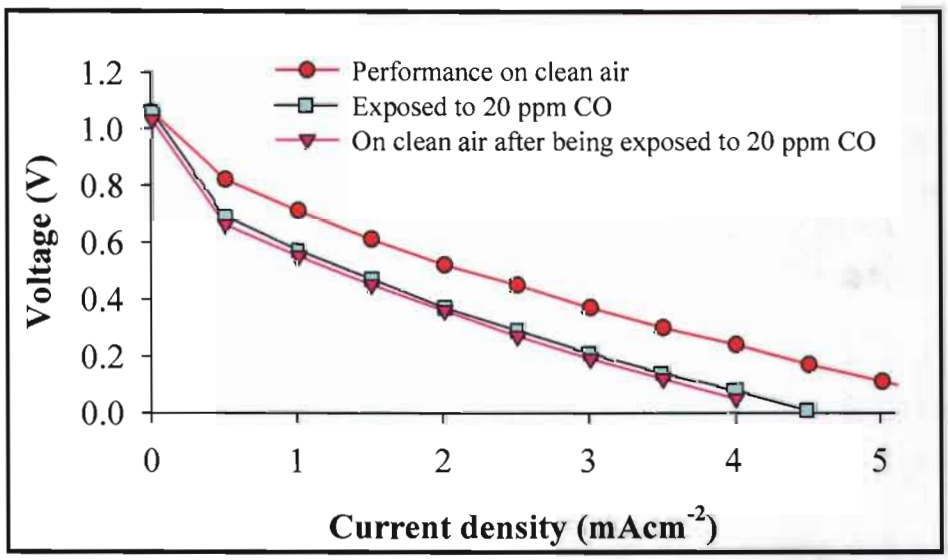


Figure 43 Performance of the air-breathing DMFC before and after being exposed to 20 ppm CO.

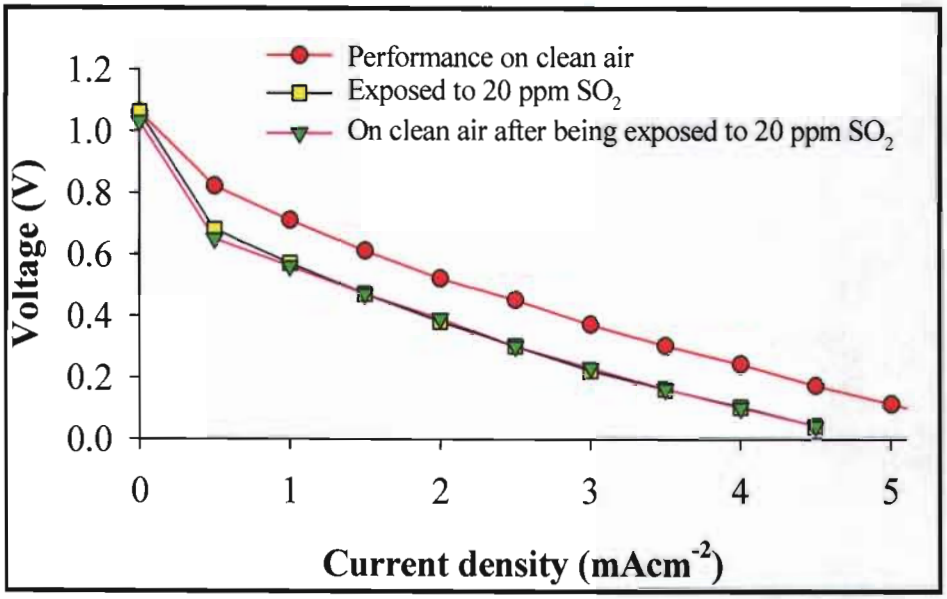


Figure 44 Performance of the air-breathing DMFC before and after being exposed to 20 ppm SO_2.

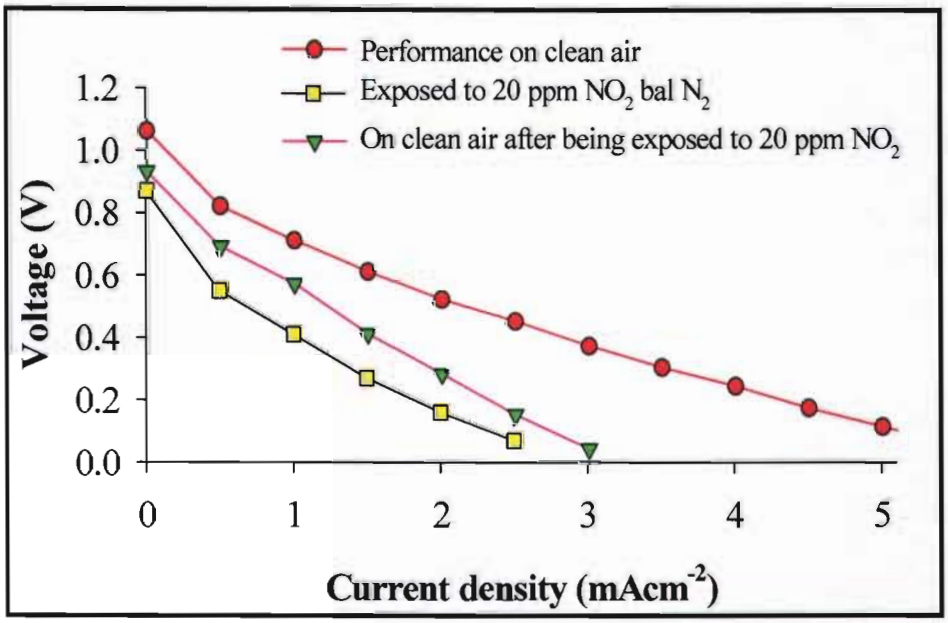


Figure 45 Performance of the air-breathing DMFC before and after being exposed to 20 ppm NO_2 balanced with N_2.

4.4 Summary

In this chapter, the impact of the environment on the air-breathing DMFC performance was investigated. This included the determination of the influence of climatic environmental parameters such as varying temperature and humidity conditions on the fuel cell performance, as well as the impact of air containing CO, N_2O, SO_2 and NO_2 on cell performance. The results obtained from all the experiments performed on the air-breathing DMFC were also presented in this chapter and will be discussed in chapter 5.

In the next chapter, the experimental results are discussed and conclusions are drawn. Recommendations based on the results presented in chapter three and four are given along with recommendations for future research on this topic.

Chapter 5 Conclusions and recommendations

5.1 Introduction

In this final chapter the conclusions and recommendations drawn from the results of the experimental investigations performed to determine the impact of the environment on the air-breathing DMFC and ZAFC performance are presented. These conclusions are based on all the results given in the previous chapters. In addition, recommendations for further research regarding the subject of environmental impact on the design of fuel cells are also presented in this chapter.

5.2 Conclusions

5.2.1 Conclusions for the air-breathing ZAFC

The results presented in chapter three showed that ambient atmospheric temperature and humidity has a significant effect on the performance of air-breathing ZAFC's. Figure 24 shows that the higher the current drawn from the cell under normal ambient room temperature conditions the lower the capacity that can be delivered by an air-breathing ZAFC. When comparing the discharge characteristic curves shown in figure 24, it can be clearly seen that increasing the current drain from 1 A to 2 A did not only decrease the capacity of the fuel cell but it also decreased the discharge voltage. These results support (Linden, 1995:3.5) who reported that higher current drain increases the internal resistance (IR) losses and hence the discharge is at lower voltage and reduced capacity.

The results shown in figure 25 indicate that the surrounding temperature at which an air-breathing ZAFC operates has an effect on the fuel cell performance in terms of discharge voltage and the delivered capacity. At –20°C the air-breathing ZAFC performance was found to be extremely poor. Discharging the air-breathing ZAFC at a constant current of 2 A at –20°C delivered the reduced capacity of 10 Ah and the slope of the discharge curve was steeper. Therefore, operating the air-breathing ZAFC at temperatures below

0°C is not practical for a remote application since this resulted in lower discharge cell voltages at a reduced capacity.

Figure 25 shows that an ambient temperature of 20°C in the climate chamber at 50% RH resulted in the maximum delivered capacity of 42 Ah at reasonable discharge cell voltages. The air-breathing ZAFC discharged at the temperature level of 40°C at 50% RH resulted in an increased cell performance in terms of discharge cell voltages as compared to when the cell was operating at 20°C. However, the delivered capacity at 40°C was reduced to 35 Ah, which is lower than the capacity obtained at 20°C.

As the ambient temperature was increased to 60 and 70°C at a constant RH of 50%, the air-breathing ZAFC delivered a reduced capacity of 24 Ah and 11 Ah respectively. These results are supported by (Linden, 1995:3.9) who suggested that at higher temperatures chemical deterioration might be rapid enough during the discharge to cause loss of capacity. However, it was noticed that when discharging the air-breathing ZAFC at higher temperatures there was an increase in the discharge cell voltages. Therefore, it can be concluded that the reliable operating temperatures for this particular air-breathing ZAFC are between 20 and 40°C.

As seen in figures 26 and 27, RH also plays an important role on the air-breathing ZAFC performance. The effect of humidity on the air-breathing ZAFC is better explained with an aid of the table below.

Table 3 Summary of humidity results for the air-breathing ZAFC.

RH (%)	70	80	90
Delivered capacity at 20°C	36 Ah	33 Ah	38 Ah
Delivered capacity at 60°C	30 Ah	23 Ah	31 Ah

It can be seen in figure 26 that varying humidity conditions had a significant effect on the delivered capacity and less effect on the discharge cell voltage. It can be clearly seen in table 3 that the capacity decreased as the humidity increased from 70% to 80%, but then

increased again at 90% RH. The cell was not expected to have an increased capacity at 90% RH because theoretically high humidity conditions would result in excessive water gain thus flooding the cell to a point of failure. A possible explanation for this maybe that the length of exposure during the experiment was not long enough to cause dilution of the electrolyte.

At higher ambient temperatures of 60°C the effect of humidity on the air-breathing ZAFC performance was more pronounced on both discharge cell voltage and on the delivered capacity (figure 27). When comparing the humidity results of figure 26 and 27 in table 3, it can be seen that increasing the RH at 60°C resulted in a decrease in capacity. As it can be seen in table 3, at 70% RH the capacity was decreased from 36 Ah to 30 Ah. At 80% RH the capacity was decreased from 33 Ah to 23 Ah and at 90% RH the capacity was decreased from 38 Ah to 31 Ah. However, discharge cell voltages at 60°C were higher than at 20°C. At a temperature of 60°C the amount of heat inside the climate chamber was too much in such a way that it started to rain in the form of droplets at 80% and 90% RH levels. Therefore, in this case the loss of capacity can be related to the increased temperature or the electrolyte gaining water from the surroundings of the climate chamber, which in turn diluted the electrolyte. These results more or less support what was reported in the literature (Berndt, 1997; Linden, 1995).

When the ambient air is the source of oxygen for the air-breathing fuel cells such as the air-breathing ZAFC, it has been found to be true that the fuel cell performance depend also on the quality of the intake air (Moore *et al.*, 2000; Mohtadi *et al.*, 2004). This can be clearly seen in the air pollution results of the air-breathing ZAFC (chapter 3). When looking at the baseline performance of the air-breathing ZAFC in figure 30, the fuel cell was discharged at a constant current drain of 4 A in a clean air environment and the cell delivered a capacity of 15 Ah. The discharge cell voltage was around 1 V during the first five hours of discharge. Discharging the air-breathing ZAFC under the exposure to 20 ppm SO_2 was found to have a greatest effect on the air-breathing ZAFC performance. When the cell was operated in the presence of SO_2, the discharged cell voltage decreased to about 0,8 V during the first five hours of discharge. The cell delivered a reduced

capacity of 10 Ah. It can be seen in figure 34 that due to the chemical reactions that took place in the air pollution test chamber when the air-breathing ZAFC was exposed to 20 ppm SO_2, the separator covering the zinc anode changed to a dark brown color and the zinc anode was severely damaged.

Theoretical explanation for the performance degradation on the air-breathing ZAFC due to SO_2 can be given with an aid of the work done by Lee *et al.* (2002) where the following reaction was given:

$$KOH + SO_2 \rightarrow K_2SO_3 + H_2O \qquad (14)$$

As the air mixed with 20 ppm SO_2 contaminant was continuously introduced into the air pollution test chamber, H_2O already present in the pores of the electrodes in equation (8) and the remaining H_2O from equation (14) on the reaction surfaces of the air-breathing ZAFC was converted into H_2SO_4. Therefore, when looking at figure 34, the logical explanation for the condition of the zinc anode is related to the formation of H_2SO_4.

The air with 20 ppm CO impurity also had a negative effect on the performance of the air-breathing ZAFC with a reduced capacity of 12 Ah at lower discharge cell voltages (figure 31), but not as low as with SO_2 contaminated air (figure 30). It has been reported by Tewari *et al.* (2006) that the main problem of the air-breathing ZAFC is CO_2 poisoning by the conversion of KOH to K_2CO_3 that slows down the rate of oxidation of the fuel at the anode. Therefore, the decrease of the air-breathing ZAFC performance by 20 ppm CO is suspected to have been caused by CO_2 poisoning and not CO directly. This is because air-breathing ZAFC doesn't have Pt catalysts that are easily poisoned by CO, as it is the case with PEMFC's. However, it is believed that the following reaction took place when air with 20 ppm CO was introduced into the air pollution test chamber:

$$2CO + O_2 \rightarrow 2CO_2 \qquad (15)$$

In equation (15), CO comes from the 20 ppm CO that was balanced with air. The air supplied into the air pollution chamber contained 19,69% of O_2. Therefore, from equation (15), the following reaction occurred:

$$4CO_2 + 8KOH \rightarrow 4K_2CO_3 + 4H_2O \qquad (16)$$

As a result of equation (16) more K_2CO_3 precipitate was formed from CO polluted air because of the CO concentration. Therefore, the performance decrease is associated with the formation of K_2CO_3.

N_2O at 20 ppm also had a negative effect on the delivered cell voltage and on the capacity (figure 32). Under the influence of N_2O, the delivered capacity decreased to about 10 Ah at a lower discharge cell voltages as compared to the performance obtained in a clean air environment.

The performance of the air-breathing ZAFC was greatly affected by 20 ppm NO_2 impurity introduced into the air pollution test chamber (figure 33). Every time this air contaminant was introduced into the air pollution test chamber, the cell was discharged so quickly that it would be impossible for it to be utilized in any application under those conditions. The delivered capacity was found to be less than 1 Ah every time NO_2 was introduced.

However, the air-breathing ZAFC performance recovered immediately when the fuel cell was exposed to clean air afterwards. The poor performance of the air-breathing ZAFC in the presence of NO_2 is suspected to have caused by a lack of oxygen. This is due to the fact that 20 ppm NO_2 introduced into the air pollution test chamber was balanced with N_2 and not with oxygenated air because of the NO_2 instability in air. For this reason NO_2 would never be a problem when air-breathing fuel cells are used in natural air.

5.2.2 Conclusions for the air-breathing DMFC

The data of the air-breathing DMFC temperature experiments plotted in figure 37 showed that varying temperature conditions have a significant effect on the fuel cell performance. At –10°C, the stack performance was poor compared to performance at temperatures above 0°C (figure 37). This poor stack performance is suspected to have resulted from an increase in a cell resistance. This was most probably due to the decrease in proton conductivity of the membrane. The other contributing factor to the poor performance of the air-breathing DMFC stack at –10°C was an ice formation of the methanol solution and on the other active areas of the fuel cell stack. Therefore, ambient temperatures of –10°C are not suitable for any application of the DMFC.

However, it can be clearly observed in figure 37 that as the temperature of the climate chamber was increased under a constant RH of 50% the stack performance increased. The measured performance at 30°C was better than at ambient room temperature conditions and the highest performance in terms of voltage and current density was obtained at temperatures of 60 and 90°C. These results support the reports of (Ge & Liu, 2005) who mentioned that the electrochemical kinetics on the cathode and anode of the DMFC improves with an increase in operating temperature. Therefore, it can be concluded that the higher the surrounding temperature, the better the performance of the air-breathing DMFC.

In figure 39, it can be seen that the performance of the air-breathing DMFC decreased with an increase in RH at 25°C. However in figure 40, as RH of the climate chamber was increased, the stack performance also increased. The highest performance at 60°C was found to be at 90% RH. Therefore, it can be concluded that varying humidity conditions have an impact on the air-breathing DMFC performance but this impact on the performance is highly dependent on temperature.

The results of the experimental investigations performed on the air-breathing DMFC to determine the impact of air pollution on the fuel cell performance showed that air

pollutants have a negative impact on the fuel cell performance. The results in figure 42 showed a decrease in the stack performance when air containing 20 ppm N_2O was supplied to the cathode. The effect of this gas impurity on the air-breathing DMFC performance was found be irreversible. The stack performance did not recover after 20 ppm N_2O balanced with air was shut off and the fuel cell was operated with a clean air for about an hour. Instead of recovering the performance when the fuel cell was operated on a clean air again, the air-breathing DMFC stack performance decreased even more. Nevertheless, the effect of 20 ppm N_2O on the air-breathing DMFC performance was less detrimental than the effects of 20 ppm CO and SO_2 impurities.

Figure 43 shows a decrease in performance of the air-breathing DMFC after introducing 20 ppm CO dissolved in air into the air pollution test chamber. The stack performance could not be recovered afterwards when the fuel cell was supplied with a clean air again. The effect of this gas in PEMFC's has been researched and published in many papers and it has been reported in theory that CO adsorbs strongly on the Pt catalysts of the fuel cell electrodes and thus inhibits the anodic reaction. The results obtained showed that air-breathing DMFC is also not free from this problem. When comparing the effect of the air impurities such as SO_2 and N_2O that were balanced with air, the worst performance was obtained when the air-breathing DMFC was operated on air with CO impurity.

In figure 44, 20 ppm SO_2 was also found to have a negative effect on the air-breathing DMFC performance. The performance of the air-breathing DMFC could not pick up when the fuel cell was operated on a clean air again, which basically means the effects were permanent. However, the decrease in the stack performance was found to be less detrimental than when the fuel cell was exposed to 20 ppm CO. According to Mepsted (2001:17), the permanent effect of SO_2 simply means that the SO_2 species binds strongly with the catalytic sites and therefore blocks the fuel cell reactions. In addition, it was also reported that SO_2 is a polar molecule with a lone pair electron that enable it to adsorb strongly to a variety of metals.

Figure 45 shows that the air-breathing DMFC stack performance was very poor due to the NO_2 impurity introduced into the air pollution test chamber. The reason for this poor performance is associated with the lack of oxygen in this gas mixture. The stack performance improved when the fuel cell was operated on clean air afterwards but the actual performance before the contaminated air was introduced could not be recovered.

In conclusion, all the results obtained from the air pollution experiments performed on the air-breathing DMFC and ZAFC showed a negative effect on the performance of these fuel cells. At this stage, there is still no concrete evidence of the mechanism by which some of these impurities degrade the performance. However, the results of this research has shown and made it clear that the quality of the air stream entering the fuel cell is as important as the quality of the fuel itself. Therefore, quality of the air stream must also be of reasonably high purity in order to guarantee the performance stability found in a clean air environment. It is clear from the results that these fuel cells are not reliable for applications situated in areas such as those mentioned in section 2.6 where 20 ppm levels of gaseous air pollutants could be found. It was reported in literature that fuel cell performance is affected by air pollutants even at lower concentration levels such as those used by Mohtadi *et al.* 2004. This means that even if the concentration levels found in industrial areas mentioned in section 2.6 are lower than 20 ppm, air-breathing DMFC and ZAFC performance would still be affected depending on the length of exposure.

Furthermore, the presented results have also shown that climatic environmental parameters such as varying temperature and humidity have an impact on the performance of the air-breathing DMFC and ZAFC. This impact may be positive or negative. It all depends on the severity of these environmental parameters. Therefore, this suggests that air-breathing DMFC and ZAFC must be designed by first considering the environment at which they are going to operate.

However, there is still more work to be done on the subject of the environment and fuel cell designs in order to assist fuel cell developers and designers with the technical barriers posed by the environment on fuel cells.

5.3 Recommendations

The biggest problem associated with operating the air-breathing ZAFC at higher temperatures lies in the rapid evaporation of the electrolyte. Therefore, if this particular air-breathing ZAFC was to be operated at higher temperatures for remote applications purposes, it is recommended that a bigger storage tank for the electrolyte be included in the air-breathing ZAFC design. As for air-breathing DMFC, it has been proven that higher temperature conditions are favorable for better performances. Therefore, if this particular type of fuel cell is required in the area where it is very cold, it is recommended that an external heating system or a heat jacket be included in the air-breathing DMFC system in order to make sure the performance is optimum at all times.

It has been proven that using atmospheric air as an oxidant introduces a plethora of air contamination into the cathode side of the fuel cell. It has also been reported before that to compound matters the contamination rate will vary from hour to hour, day to day and from one season to the next. This makes it impossible to account for the effect of air pollution on fuel cell performance. Therefore, it is suggested that air filters must be implemented in the air-breathing fuel cells such as DMFC and ZAFC in order to eliminate the effect of atmospheric air pollutants. For air-breathing ZAFC, CO_2 air filters are necessary in the air-breathing ZAFC system. According to Kosanovic (2004), a team of researchers at the Los Alamos National Laboratory and also at Donaldson has been working on the problem of air-contamination for years and has developed prototype air filters for fuel cells. Therefore, it is recommended that local researchers must also look at the development of air filters for air-breathing fuel cells in order to avoid the high costs of importing these air filters.

5.4 Fields for future research

In future, experimental work must be done to investigate the methods to mitigate the effect of SO_2, N_2O and CO on the performance of air-breathing DMFC and ZAFC. The physical reasons for the performance decrease in air-breathing ZAFC due to the SO_2,

N_2O and CO influence must still be investigated. The effects of other potential ambient air impurities such as benzene and ammonia must also be investigated on the air-breathing DMFC and ZAFC. The effect of SO_2, N_2O and CO has to be investigated again on these fuel cells with air filters implemented in the fuel cell design. This will determine if the problem of air pollution on air-breathing fuel cells can be easily solved by the use of air filters. If not other methods to counter air pollution must be found.

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ANNEXURE A

Data sheet of an air-breathing ZAFC

ZnERGY
ZINC-AIR ENERGY SYSTEMS

Data Sheet
ZnErgy Zn 60 E

Physical characteristics

Height	191mm
Length	130mm
Width	19mm
Volume	472cm³
Weight of cell	380 g
Weight of electrolyte	150 g
Quantity of electrolyte	120 ml
Total weight of cell	530 g

Electrical characteristics

Nominal voltage at 8 A/+20°C	1.0 V
Open circuit voltage	1,4 V
Peak current (<60 sec)	40 A
Final discharging voltage	0,6 V
Nominal capacity (C_{10})	60 Ah
Energy (C_{10})	60 Wh
Energy density gravimetric; 1=8A	113 Wh/kg
Energy density volumetric; 1=8A	127 Wh/l

Discharge Current [A]	Guaranteed Capacity [Ah]
2.5 A	90 Ah
4 A	80 Ah
8 A	60 Ah

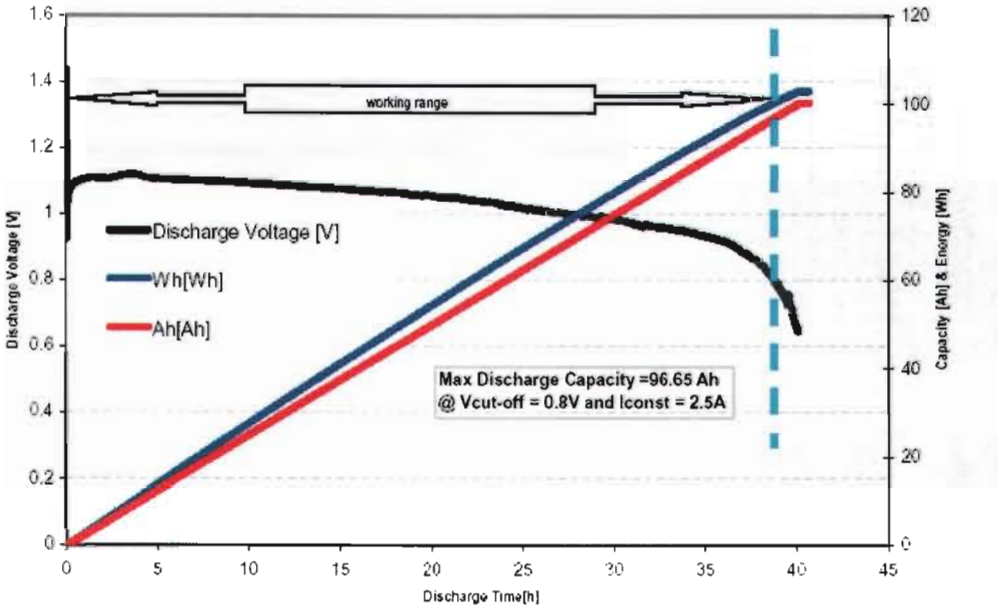
Thermal characteristics

Operating temperature	-20°C to +60°C

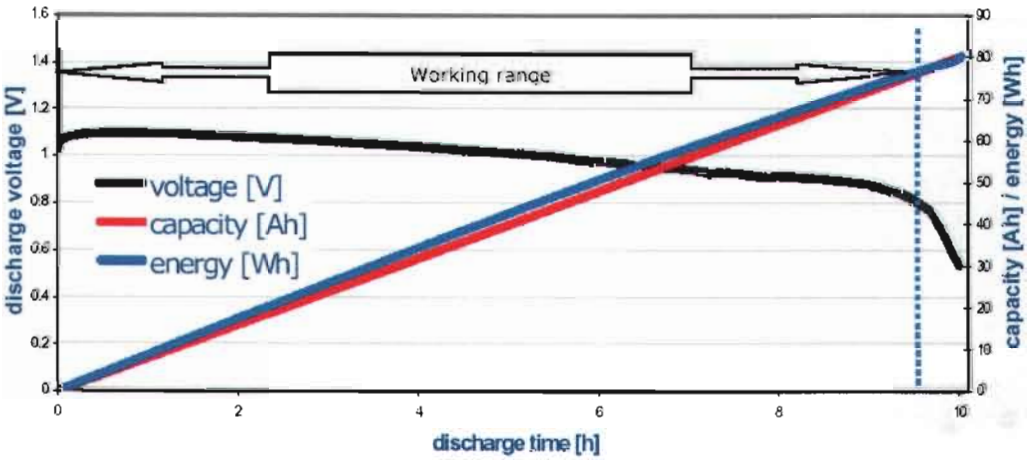
ZnERGY
ZINC-AIR ENERGY SYSTEMS

Data Sheet
ZnErgy Zn 60 E

Discharge curve (C_{40}) with I_{const} = 2.5A



Discharge curve (C_{10}) with I_{const} = 8A



ZnERGY
ZINC-AIR ENERGY SYSTEMS

Data Sheet
ZnErgy Zn 60 E

Cell casing

The casing and the lid of the cell consist of Polystorol (PS).

Ventilation

For the optimum operation of the zinc-air cell an effectual supply of the reactant oxygen is necessary. With low currents, free ventilation (surrounding air) is sufficient, while with higher currents an additional ventilation system is helpful, e.g. a fan.

Storage

The inactive ZOXY cells (without electrolyte) can be stored up to 10 years.

Electrolyte and activation

The electrolyte is a 6M KOH solution. Only after filling, the electrolyte in the cell the system is activated and performs as indicated.

Recharge

The discharged cell can be electrically charged using a charger ZnERGY special charger. For the optimal use of the cell in the electrical recharge modus, it is recommended to discharge the cell up to max. 65% DOD.

ZnERGY
ZINC-AIR ENERGY SYSTEMS

Data Sheet
ZnErgy Zn 60 E

Application

Fields of application are the stationary and mobile power supply with long operating time and medium energy demand.

Figure 1: Typical DC Power Back-Up System (e.g. TRIATHLONZ2/3/8 SERIE)

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ZnERGY Zinc-Air Energy Systems
21 Roger Dysan Road
Pretoria West, 0183
www.znergy.co.za

ANNEXURE B

Data sheet of carbon monoxide (CO)

AFROX

MATERIAL SAFETY DATA SHEET

CARBON MONOXIDE

DATE: April 2001

1 PRODUCT AND COMPANY IDENTIFICATION

PRODUCT IDENTIFICATION

Product Name	CARBON MONOXIDE
Chemical Formula	CO
Trade Name	Carbon Monoxide (N3.7)
Colour coding	Signal Red (A.11) body with a Yellow (C.61) shoulder.
Valve	Neriki Brass 5/8 inch BSP left hand female.
Company Identification	African Oxygen Limited 23 Webber Street Johannesburg, 2001 Tel. No: (011) 490-0400 Fax. No: (011) 490-0506

2 COMPOSITION/INFORMATION ON INGREDIENTS

Chemical Name	Carbon Monoxide
Chemical Family	Flammable, toxic, reactive gas
CAS No.	630-08-0
UN No.	1016
ERG No.	119
Hazchem Warning	Toxic gas

3 HAZARDS IDENTIFICATION

Main Hazards. All cylinders are portable gas containers, and must be regarded as pressure vessels at all times. Carbon monoxide is a toxic, flammable gas. The flammability limits in the air are between 12.5% and 74.2% by volume. Inhaled carbon monoxide binds to the blood haemoglobin, greatly reducing the red blood cells ability to transport oxygen to body tissues. Effects may include headaches, dizziness, convulsions, loss of consciousness and death.

Adverse Health effects. Carbon monoxide is a chemical asphyxiant, and the inhalation of concentrations as low as 400 ppm in air could result in headache and discomfort within 2 - 3 hours. Inhalation of concentrations of 4000 ppm in air could prove fatal in less than one hour.

Chemical Hazards. Carbon monoxide containing moisture and sulphur-containing impurities can cause corrosion of steel at any pressure. Dry, sulphur-free carbon monoxide is safe for use with steel and other common metals at pressures up to 13790 kPa.

Biological Hazards. Carbon monoxide in excess of 50 ppm will produce symptoms of poisoning if breathed in for a sufficiently long time. As little as 200 ppm will produce slight symptoms (slight headache, discomfort) in several hours. A concentration of 400 ppm will produce headache and discomfort within two to three hours. With moderate exercise, 1000 - 2000 ppm will produce slight palpitation of the heart in 30 minutes, a tendency to stagger in 1,5 hours, and confusion of the mind, headache, and nausea in 2 hours. A concentration of 2000 - 2500 ppm will usually produce unconsciousness in about 30 minutes. Its effects at higher concentrations may be so sudden that a man has little or no warning before he collapses. These effects are summarised in the following table.

Effect	Concentration (ppm)
Permissible for an exposure of 8 hours	50
Concentration which can be inhaled for 1 hour without appreciable effect	400 - 500
Concentration causing a just appreciable effect after 1 hour of exposure	600 - 700
Concentration causing unpleasant but not dangerous symptoms after 1 hour of exposure	1000 - 2000
Dangerous for exposure of 1 hour	1500 - 2000
Fatal in exposures of less than 1 hour	4000 & above

Vapour Inhalation. The concentration, exposure time and physical activity of the individual will determine the percentage conversion of haemoglobin to carboxyhaemoglobin. The effects produced depend on the degree and duration of saturation of blood with carbon monoxide. The symptoms caused by various amounts of carboxyhaemoglobin in the blood are given in the following table.

Blood Saturation % Carboxyhaemoglobin	Symptoms
10 - 20	No symptoms.
10 - 20	Tightness across forehead, possibly slight headache.
20 - 30	Headache and throbbing in temples.
30 - 40	Severe headache, weakness, dizziness, dimness of vision, nausea, vomiting, collapse.
40 - 50	Same as previous item but with more possibility of collapse and syncope, increased respiration and pulse.
50 - 60	Syncope, increased respiration and pulse, coma with intermittent convulsions.
60 - 70	Coma with intermittent convulsions, depressed heart action and respiration, possibly death.
70 -80	Weak pulse and slow respiration, respiratory failure and death

Eye Contact No known effect.
Skin Contact No known effect.
Ingestion No known effect.

4 FIRST AID MEASURES

Conscious persons should be assisted to an uncontaminated area and be treated with supplemental oxygen. Quick removal from the contaminated area is most important. Unconscious persons should be removed to an uncontaminated area, and given artificial respiration and oxygen at the same time. The administering of the oxygen at an elevated pressure (up to 2 to 2.5 atmospheres) has shown to be beneficial as has treatment in a hyperbaric chamber. The physician should be informed that the patient has inhaled toxic quantities of carbon monoxide. Prompt medical attention is mandatory in all cases of overexposure to carbon monoxide. Rescue personnel should be equipped with self-contained breathing apparatus and be cognisant of extreme fire and explosion hazard.

5 FIRE FIGHTING MEASURES

Extinguishing media. Dry powder. Carbon dioxide. Fog-water spray. (In the absence of fog equipment a fine spray of water may be used.)

Specific hazards. Highly flammable. May form explosive gas mixtures with air. Is a chemical asphyxiant.

Emergency actions. Evacuate area. Post warnings to prevent persons from approaching with lit cigarettes or open flames. Using water, keep all cylinders in the vicinity of the fire cool. Remove cylinders from the vicinity of the fire if possible. Remove all cylinders with signs of overheating to a safe area. Keep cool. CONTACT THE NEAREST AFROX BRANCH.

Protective Clothing. Exposed fire fighters should wear approved self-contained breathing apparatus with full face mask. Safety gloves and shoes, or boots, should be worn when handling cylinders.

Environmental precautions. As carbon monoxide is only slightly lighter than air it will not diffuse rapidly. Caution should be taken when entering confined spaces as pockets of high concentrations may occur. Ventilate all confined spaces using forced draught if necessary. Ensure that all electrically powered equipment is flameproof.

6 ACCIDENTAL RELEASE MEASURES

Personal Precautions. As carbon monoxide is a chemical asphyxiant, self-contained breathing apparatus should be used when entering confined spaces where leaks have occurred. Do not enter any potentially hazardous area with any source of ignition such as a lit cigarette or match.

Environmental precautions. Carbon monoxide does not pose a hazard to the environment. An explosive gas-air mixture could be formed when leaks occur, so eliminate all forms of ignition.

Small spills. Small leaks should be extinguished by shutting off the source of supply, e.g. closing the valve on the cylinder, or tightening the gland nut. If unable to stop small leaks the cylinder should be moved into the open, well away from any source of ignition. Should a small leak have ignited, use a multi-purpose dry powder or carbon dioxide extinguisher. Should there be no extinguisher available, a welders glove or heavy cloth, soaked in water may be used to extinguish the flame.

Large spills. Stop the source if it can be done without risk. Eliminate all sources of ignition and static discharges. Restrict access to the area until completion of the clean-up procedure. Post relevant warning signs. Wear adequate protective clothing when working near the source of the leak. Ventilate the area using forced-draught if necessary. Ensure that all equipment is flameproof.

7 HANDLING AND STORAGE

Do not allow cylinders to slide or come into contact with sharp edges. Carbon monoxide cylinders may be stacked horizontally provided that they are firmly secured at each end to prevent rolling. Ensure that equipment is adequately earthed. Conspicuous signs should be posted in the storage area forbidding smoking or the use of naked lights. Do not store reserve stocks of carbon monoxide with cylinders containing oxygen, or other highly oxidising or flammable materials. Use the "first-in first-out" inventory system to prevent full cylinders from being stored for excessive periods of time. Compliance with all relevant legislation is essential. Keep out of reach of children.

8 EXPOSURE CONTROLS/PERSONAL PROTECTION

Occupational exposure hazards. Lacking odour and colour, carbon monoxide gives no warning of its presence, and inhalation of high concentrations can cause sudden, unexpected collapse. The eight-hour time-weighted average threshold limit value (TLV) adopted by the American Conference of Governmental Industrial Hygienists is 50 ppm (55 mg/m^3) for exposure to carbon monoxide. Occupational Safety & Health Administration has adopted an eight-hour time-weighted average exposure limit of 35 ppm (40 mg/m^3) and a ceiling limit of 200 ppm (229 mg/m^3) for carbon monoxide.

Engineering control measures. Engineering control measures are preferred to reduce exposures. General methods include mechanical ventilation, process or personal enclosure, and control of process conditions. Administrative controls and personal protective equipment may also be required. Use a suitable flameproof ventilation system separate from other exhaust ventilation systems. Exhaust direct to outside. Supply sufficient replacement air to make up for air removed by exhaust system.

Personal protection. Use self-contained breathing apparatus when fighting large fires.

Eyes Use safety glasses when working with cylinders.

Hands Use suitable protective gloves when working with cylinders.

Skin No known effect.

9 PHYSICAL AND CHEMICAL PROPERTIES

PYSICAL DATA

Chemical Symbol	CO
Molecular Weight	28.01
Specific volume @ 20°C & 101.325 kPa	850 ml/g
Density gas @ 20°C & 101.325 kPa	1.165 kg/m^3
Auto-ignition temperature	652°C
Relative density (Air=1) @ 101.325 kPa	0.967
Flammability limits in air	12.5 - 74.2% (by vol)
Colour	None
Taste	None
Odour	None

10 STABILITY AND REACTIVITY

Conditions to avoid. Overheating of cylinders. Never test for leaks with a flame. Use soapy water when testing for leaks. Never use cylinders as rollers or supports, or for any other purposes other than the storing of carbon monoxide. Do not use carbon monoxide cylinders for the storage of any other gas.

Incompatible materials. Steel and other common metals are satisfactory for use with dry, sulphur-free carbon monoxide at pressures up to 13790 kPa. The presence of moisture and sulphur-compounds appreciably increases the corrosive action on steel at any pressures.

Hazardous decomposition products. Only carbon dioxide is formed when carbon monoxide burns in air.

11 TOXICOLOGICAL INFORMATION

Acute Toxicity	Exposure to concentrations of more than 4000 ppm could be fatal in less than one hour. (See Table in Section 3)
Skin & eye contact	No known effect
Chronic Toxicity	The effects of prolonged exposure to low concentrations of carbon monoxide are similar to the acute effects (see above)
Carcinogenicity	No known effect
Mutagenicity	No known effect
Reproductive Hazards	No known effect

12 ECOLOGICAL INFORMATION

As carbon monoxide is only slightly lighter than air it will not disperse rapidly. However, it does not pose a hazard to the ecology.

13 DISPOSAL CONSIDERATIONS

Disposal Methods Small amounts may be blown to the atmosphere under controlled conditions. No sources of ignition should be in the vicinity. Large amounts should only be handled by the gas supplier.

Disposal of packaging The disposal of containers must only be handled by the gas supplier.

14 TRANSPORT INFORMATION

ROAD TRANSPORTATION

UN No.	1016
Class	2.3
Subsidiary risk	Chemical asphyxiant
ERG No.	119
Hazchem warning	Toxic gas

SEA TRANSPORTATION

IMDG	1016
Class	2.3
Packaging group	
Label	

AIR TRANSPORTATION

ICAO/IATA Code	1016
Class	2.3
Subsidiary risk	Chemical asphyxiant
Packaging group	
Packaging instructions	
- Cargo	200
- Passenger	Forbidden
Maximum quantity allowed	
- Cargo	25 kg
- Passenger	Nil

15 REGULATORY INFORMATION

EEC Hazard class	Toxic gas
Risk phrases	R11 Highly flammable R18 In use may form flammable explosive vapour-air mixture R 20 Harmful by inhalation R 23 Toxic by inhalation R 44 Risk of explosion if heated under confinement R48 Danger of serious damage to health by prolonged exposure
Safety phrases	S2 Keep out of reach of children S9 Keep container in a well-ventilated place S16 Keep away from sources of ignition S33 Take precautionary measures against static discharges S36 Wear suitable protective clothing S38 In case of insufficient ventilation, wear suitable respiratory equipment S44 If you feel unwell, seek medical advice (show the label where possible) S51 Use only in well ventilated areas
National legislation	None

Refer to SABS 0265 for explanation of the above.

16 OTHER INFORMATION

Bibliography

Compressed Gas Association, Arlington, Virginia
Handbook of Compressed Gases - 3rd Edition
Matheson, Matheson Gas Data Book - 6th Edition
SABS 0265 - Labelling of Dangerous Substances

17 EXCLUSION OF LIABILITY

Information contained in this publication is accurate at the date of publication. The company does not accept liability arising from the use of this information, or the use, application, adaptation or process of any products described herein.

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For product and safety enquiries please phone

EMERGENCY No: 0860020202 (24 hr)

ANNEXURE C

Data sheet of nitrous oxide (N_2O)

AFROX

MATERIAL SAFETY DATA SHEET

NITROUS OXIDE

DATE: April 2001

1 PRODUCT AND COMPANY IDENTIFICATION

PRODUCT IDENTIFICATION

Product Name	Nitrous Oxide
Chemical Formula	N_2O
Trade Names	Medical Nitrous Oxide, Compressed Nitrous Oxide, Instrument Grade NitroBoost
Colour Coding	Medical Nitrous Oxide French Blue (F 09) body with White stenciling. Nitrous Oxide, Instrument Grade French Blue (F 09) body with the "Instrument Grade" logo affixed centrally to the body of the cylinder. Nitroboost French Blue (F 09) body with a yellow shoulder, and "Nitroboost" Label stating "Toxic not for Medical use"
Valves	Medical & Instrument Grades 3SN – Brass 11/16 inch - 20t p.i. male. Nitroboost Neriki – Brass 5/8 inch left hand female, positive pressure.
Company Identification	African Oxygen Limited 23 Webber Street Johannesburg, 2001 Tel. No: (011) 490-0400 Fax. No: (011) 490-0506

2 COMPOSITION/INFORMATION ON INGREDIENTS

Chemical Name	Nitrous Oxide
Chemical Family	Oxidant
CAS No.	10024-97-2
UN No.	1070
ERG No	122
Hazchem Warning	5 A Non-flammable Compressed Gas

3 HAZARDS IDENTIFICATION

Main Hazards All cylinders are portable gas containers, and must be regarded as pressure vessels at all times. Nitrous oxide is non-flammable, but readily supports combustion. Never permit oil, grease or other readily combustible substance to come into contact with high concentrations of nitrous oxide.

Adverse Health Effects. Nitrous oxide should not be used with any condition where air is entrapped within the body, and where its expansion might be dangerous such as : Head injuries with impairment of consciousness; Artificial, traumatic or spontaneous pneumothorax air embolism; Decompression sickness; Following a recent dive; Following air encephelography; Severe bullous emphysema; During myringoplasty; Gross abdominal distension; Intoxication; Maxillofacial injuries.

Chemical Hazards Nitrous oxide is non-flammable, but strongly supports combustion (including some materials which do not normally burn in air). Since dry nitrous oxide is non-corrosive, most materials of construction are suitable. Avoid all combustible materials.

Biological Hazards Administration of nitrous oxide, more frequently than every 4 days should be accompanied by routine blood cell counts for evidence of megaloblastic change in red cells and hypersegmentation of neutrophils.

Vapour Inhalation The use of nitrous oxide causes inactivation of vitamin B12 which is a co-factor of methionine synthase. Folate metabolism is consequently interfered with, and DNA synthesis is impaired following prolonged nitrous oxide administration. These disturbances result in megaloblastic bone marrow changes. Exceptionally heavy occupational exposure and addiction have resulted in myeloneuropathy and subacute combined degeneration.

Eye Contact No known effect.

Skin Contact No known effect.

Ingestion Depletion of methienine has been implicated in the neurological deficit seen in chronic abusers of nitrous oxide.

4 FIRST AID MEASURES

Prompt medical attention is mandatory in all cases of overexposure to nitrous oxide. Rescue personnel should be cognisant of extreme fire hazard associated with nitrous oxide-rich atmospheres. Inapplicable, unwitting or deliberate inhalation of nitrous oxide will result in unconsciousness, passing through stages of increasing light-headedness and intoxication, and, if the victim were to be within a confined space, death from anoxia could result. The treatment is removal to fresh air, and if necessary, the use of an oxygen resuscitator.

Eye Contact No known effect.

Skin Contact No known effect.

Ingestion Inapplicable, unwitting or deliberate inhalation of nitrous oxide will result in unconsciousness, passing through stages of increasing light-headedness and intoxication, and, if the victim were to be within a confined space, death from anoxia could result. The treatment is removal to fresh air, and if necessary, the use of an oxygen resuscitator.

5 FIRE FIGHTING MEASURES

Extinguishing media As nitrous oxide is non-flammable but strongly supports combustion, the correct type of extinguishing media should be used depending on the combustible material involved.

Specific Hazards Nitrous oxide vigorously accelerates combustion. Materials that would not normally burn in air could combust vigorously in atmospheres having high concentrations of nitrous oxide.

Emergency Actions If possible, shut off the source of escaping Nitrous oxide. Evacuate area. All cylinders should be removed from the vicinity of the fire. Cylinders that cannot be removed should be cooled with water from a safe distance. Cylinders which have been exposed to excessive heat should be clearly identified and returned to supplier. CONTACT THE NEAREST AFROX BRANCH.

Protective Clothing Safety goggles, gloves and safety shoes should be worn when handling cylinders.

Environmental precautions. As the gas is heavier than air, pockets of nitrous oxide-enriched air could occur. These could lead to the fire spreading rapidly. If possible, ventilate the affected area.

6 ACCIDENTAL RELEASE MEASURES

Personal Precautions Although nitrous oxide is not itself combustible, it supports and accelerates combustion. Clothes and other materials, not normally considered flammable, will burn fiercely in the presence of nitrous oxide, and can be set alight by a single spark, or even hot cigarette ash.

Environmental precautions. Nitrous oxide is known to have an ozone depleting potential. It is a "greenhouse gas" and may contribute to global warming. Beware of nitrous oxide-enriched atmospheres coming into contact with readily combustible materials.

Small spills Shut off the source of escaping nitrous oxide. Ventilate the area.

Large spills Evacuate the area. Shut off the source of the spill if this can be done without risk. Ventilate the area using forced-draught if necessary.

7 HANDLING AND STORAGE

Do not allow cylinders to slide or come into contact with sharp edges. Cylinders of nitrous oxide should not be stored near cylinders of acetylene or other combustible gases. Nitrous oxide cylinders should only be stacked vertically and be firmly secured. Prevent dirt, grit of any sort, oil or any other lubricant from entering the cylinder valves, and store cylinders well clear of any corrosive influence, e.g. battery acid. Compliance with all relevant legislation is essential. Use a "first in - first out" inventory system to prevent full cylinders from being stored for excessive periods of time. Keep out of reach of children.

8 EXPOSURE CONTROLS/PERSONAL PROTECTION

Occupational Exposure Hazards. Scavenging of waste nitrous oxide gas should be used to reduce operating theatre and equivalent treatment room levels to a level below 200vpm of ambient nitrous oxide.

Engineering control measures. Engineering control measures are preferred to reduce exposure to nitrous oxide-enriched atmospheres. General methods include forced-draught ventilation, separate from other exhaust ventilation systems. Ensure that sufficient fresh air enters at, or near, floor level.

Personal protection Safety goggles, gloves and shoes should be worn when handling cylinders.

Skin No known effect.

9 PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL DATA

Chemical Symbol	N_2O
Molecular Weight	44,01
Specific Volume @ 20°C & 101,325 kPa	543,1 ml/g
Boiling point @ 101,325 kPa	-88,5°C
Density, gas @ 101,325 kPa and 20°C	1,8432 kg/m^3
Relative density (Air = 1) @ 101,325 kPa	1,5297
Colour	None
Taste	Sweet
Odour	Sweet

10 STABILITY AND REACTIVITY

Conditions to avoid The build up of nitrous oxide-enriched atmospheres. Never use cylinders as rollers or supports, or for any other purpose than the storage of Nitrous oxide. Never expose cylinders to excessive heat, as this may cause sufficient build-up of pressure to rupture the cylinders.

Incompatible Materials. Since dry nitrous oxide is non-corrosive, most materials of construction are suitable. Avoid all flammable materials.

Hazardous Decomposition Products. When involved in a fire the higher oxides of nitrogen can be formed. Both nitric oxide and nitrogen dioxide are highly toxic.

11 TOXICOLOGICAL INFORMATION

Acute Toxicity	See section 3
Skin & eye contact	No known effect.
Chronic Toxicity	See section 3
Carcinogenicity	No known effect.
Mutagenicity	No known effect.
Reproductive Hazards	See section 3

(For further information see Section 3. Adverse Health Effects).

12 ECOLOGICAL INFORMATION

Nitrous oxide is heavier than air and care should be taken to avoid the formation of nitrous oxide-enriched pockets. It does not pose a hazard to the ecology.

13 DISPOSAL CONSIDERATIONS

Disposal Methods Small amounts may be blown to the atmosphere under controlled conditions. Large amounts should only be handled by the gas supplier.

Disposal of packaging The disposal of cylinders must only be handled by the gas supplier.

14 TRANSPORT INFORMATION

ROAD TRANSPORTATION	
UN No.	1070
ERG No	122
Hazchem warning	5A Non-flammable gas
SEA TRANSPORTATION	
IMDG	1070
Label	Non-flammable gas
AIR TRANSPORTATION	
ICAO/IATA Code	1070
Class	2.2
Packaging group	
Packaging instructions	
- Cargo	200
- Passenger	200
Maximum quantity allowed	
- Cargo	150kg
- Passenger	75kg

15 REGULATORY INFORMATION

EEC Hazard class	Non-flammable
Risk phrases	R8 Contact with combustible material may cause fire R20 Harmful by inhalation R33 Danger of cumulative effects R44 Risk of explosion if heated under confinement R48 Danger of serious damage to health by prolonged exposure.
Safety phrases	S2 Keep out of reach of children S3 Keep in a cool place S9 Keep container in a well-ventilated place S21 When using do not smoke S44 If you feel unwell, seek medical advice (show the label where possible)
National Legislation:	None

Refer to SABS 0265 for explanation of the above.

16 OTHER INFORMATION

Bibliography

Compressed Gas Association, Arlington, Virginia
Handbook of Compressed Gases - 3rd Edition
Matheson. Matheson Gas Data Book - 6th Edition

17 EXCLUSION OF LIABILITY

Information contained in this publication is accurate at the date of publication. The company does not accept liability arising from the use of this information, or the use, application, adaptation or process of any products described herein.

ANNEXURE D

Data sheet of sulphur dioxide (SO_2)

AFROX

MATERIAL SAFETY DATA SHEET

SULPHUR DIOXIDE

DATE April 2001

1 PRODUCT AND COMPANY IDENTIFICATION

PRODUCT IDENTIFICATION

Product Names	SULPHUR DIOXIDE
Chemical Formula	SO2
Trade Name	Sulphur Dioxide
Colour coding	Brunswick green (H 07) body with a Golden yellow (B40) shoulder
Valve	CGA 240 – Steel 3/8 inch 18 NGT right hand female
Company Identification	African Oxygen Limited 23 Webber Street Johannesburg, 2001 Tel No (011) 490-0400 Fax No (011) 490-0506

2 COMPOSITION/INFORMATION ON INGREDIENTS

Chemical Name	Sulphur Dioxide
Chemical Family	Inorgame, acidic gas
CAS No	7446-09-5
UN No	1079
ERG No	125
Hazchem Warning	Toxic and corrosive gas

3 HAZARDS IDENTIFICATION

Main Hazards All cylinders are portable gas containers, and must be regarded as pressure vessels at all times. Sulphur dioxide is a highly irritating gas, it readily elicits respiratory reflexes. It is intensely irritating to the eyes, throat, and respiratory tract.

Adverse Health effects. Inhalation of this gas in concentrations of 8-12ppm in air causes throat irritation, coughing, constriction of the chest, lachrimation, and smarting of the eyes. A concentration of 150 ppm can be endured only a few minutes, because of eye irritation and the effect on the membranes of the nose, throat and lungs. Exposure to a concentration of 500 ppm by volume in air for a few minutes is very dangerous.

Chemical hazards Sulphur dioxide dissolves in water forming sulphurous acid, which is unstable toward heat. In many of its reactions, sulphur dioxide behaves as a reducing agent.

Biological hazards Liquid sulphur dioxide may cause skin and eye burns upon contact with these tissues, which results from the freezing effect of the liquid on the skin or eyes. Low (1%) concentrations of the vapour are irritating to moist skin within a period of 3 minutes.

Vapour inhalation Acute exposure through inhalation may result in dryness and irritation of the nose and throat, choking, sneezing, coughing, and bronchospasm. Severe overexposure may cause death through systemic acidosis, from pulmonary oedema, or from respiratory arrest.

Eye Contact Corneal burns, opacification of the cornea, and blindness may result if liquid sulphur dioxide is splashed in the eyes. Sulphur dioxide can penetrate the intact cornea and cause iritis.

Skin Contact Liquid sulphur dioxide can cause frostbite and skin burns, and it converts to sulphurous acid in moist environments, which may cause skin irritation.

Ingestion Severe burns to the mouth, throat, and gastrointestinal system may occur.

4 FIRST AID MEASURES

Move victims of sulphur dioxide inhalation to fresh air. If breathing has ceased, begin artificial respiration immediately. Administer oxygen if exposure has been severe and breathing is difficult. Skin exposure first aid treatment includes flushing the contaminated skin with copious amounts of water, and continuing as required in order to control burning sensation. Medical attention should be sought if irritation persists, or if skin is broken or blistered. In the event of eye contact, flush eyes immediately with copious amounts of water for at least 15 minutes. Eyelids should be held apart to ensure complete irrigation. Seek medical attention immediately.

5 FIRE FIGHTING MEASURES

Extinguishing media As sulphur dioxide is non-flammable, the correct extinguishing media should be used for the surrounding fire.

Specific hazards Water should never be sprayed at or into a tank or system which is leaking sulphur dioxide. The presence of water causes sulphur dioxide to be very corrosive, and water directed into a tank would also increase the venting rate.

Emergency actions A sulphur dioxide container exposed to a fire should be removed. If for any reason it cannot be removed, the container should be kept cool with a water spray until well after the fire is out. Fire fighting personnel should be equipped with protective clothing and respiratory equipment. CONTACT THE NEAREST AFROX BRANCH.

Protective clothing Exposed fire fighters should wear approved self-contained breathing apparatus with full face mask.

Environmental precautions When sulphur dioxide is released to the environment, the appropriate regulatory agency should be notified. In the event of a release however, provincial, municipal, and/or local reporting regulations must be complied with. It is most important that the response groups in the area affected be notified as quickly as possible.

6 ACCIDENTAL RELEASE MEASURES

Personal Precautions It is essential that every facility handling sulphur dioxide has an emergency plan outlining the actions that employees should take in case of specific emergencies. These actions should include alerting fellow employees and area emergency control groups of the nature and extent of the emergency. The plan should also include co-ordination procedures with area emergency control groups in the event of a major release. If, despite all precautions, persons should become trapped in a sulphur dioxide atmosphere, they should breathe as little as possible and open their eyes only when necessary. Partial protection may be gained by holding a wet cloth over the nose and mouth.

Environmental precautions Only personnel trained for and designated to handle emergencies should attempt to stop a leak. Respiratory equipment of a type suitable for sulphur dioxide must be worn. All persons not so equipped must leave the affected area until the leak has been stopped.

Small spills If sulphur dioxide is released, the irritating effect of the vapour will force personnel to leave the area long before they have been exposed to dangerous concentrations. Sulphur dioxide is fairly soluble in cool water and therefore the vapour concentration can be reduced by the use of spray or fog nozzles. If disposal of sulphur dioxide becomes necessary, such as from a leaking container or vessel, it can be vented into a lime or caustic soda solution. The resulting salt solution should be taken to a plant treating unit for neutralisation and disposal.

Large spills See "Personal Precautions" above.

7 HANDLING AND STORAGE

Sulphur dioxide should be handled only in a well-ventilated area, preferably a hood with forced ventilation. Personnel handling sulphur dioxide should wear chemical safety goggles and/or plastic face shields, approved safety shoes, and rubber gloves. Additional gas masks, air-line gas masks, and self-contained breathing apparatus should be conveniently located for use in emergencies. Instant-acting

safety showers should be available in convenient locations. Cylinders should always be transported in the upright position, with the valve uppermost, and be firmly secured. Use the "first in - first out" inventory system to prevent full cylinders from being stored for excessive periods of time. Compliance with all relevant legislation is essential. Keep away from children.

8 EXPOSURE CONTROLS/PERSONAL PROTECTION

Occupational exposure hazards Prolonged or repeated exposure may cause impaired lung function, bronchitis, hacking cough, nasal irritation and discharge, increased fatigue, alteration in the sense of taste and smell, and longer duration of common colds.

TLV	2 ppm
STEL (15 mins)	5 ppm
IDLH	100 ppm

Engineering control measures. Engineering control measures are preferred to reduce exposures. General methods include: mechanical ventilation, process or personal enclosure, and control of process conditions. Administrative controls and personal protective equipment may also be required.

Personal protection Use an approved gas mask or self contained breathing apparatus when entering a sulphur dioxide contaminated area.

Eyes Wear a chemical safety goggle or full face shield when handling cylinders.

Hands Wear suitable protective gloves when handling cylinders.

Feet Wear protective foot wear when working with cylinders.

Skin Wear suitable protective clothing to prevent the gas from coming into direct contact with skin.

9 PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL DATA

Chemical Symbol	SO_2
Molecular Weight	64,063
Specific volume @ 20°C & 101,325 kPa	366,9 ml/g
Relative density of gas @ 101,325 kPa (Air = 1)	2,263
Boiling point @ 101,325 kPa	- 10°C
Colour	None
Taste	Acidic
Odour	Pungent, Sulphurous

10 STABILITY AND REACTIVITY

Conditions to avoid Overheating of cylinders. Never use cylinders as rollers or supports, or for any other purpose than the storage of sulphur dioxide.

Incompatible materials Moist sulphur dioxide is corrosive to carbon steel; therefore, other materials of construction have to be considered in this case.

Hazardous Decomposition Products. Sulphur dioxide is not flammable, or explosive, in either the gaseous or liquid state. It is a relatively stable chemical. Temperatures above 2000°C are required to bring about detectable decomposition of sulphur dioxide.

11 TOXICOLOGICAL INFORMATION

Acute Toxicity	In extreme cases, dental cavities, loss of fillings, gum disorders, and the rapid and painless destruction of teeth may result from repeated overexposure. See section 3.
Skin & eye contact	See Section 3
Chronic Toxicity	See Section 3
Carcinogenicity	No known effect
Mutagenicity	No known effect
Reproductive Hazards	No known effect

12 ECOLOGICAL INFORMATION

Poses a severe hazard to the ecology in the form of "acid rain".

13 DISPOSAL CONSIDERATIONS

Disposal Methods Due to the complexity and scope of sulphur dioxide disposal procedures, care must be taken to ensure that all existing regulations are complied with. For more detailed information or guidance CONTACT THE NEAREST AFROX BRANCH.

14 TRANSPORT INFORMATION

ROAD TRANSPORTATION	
UN No.	1079
Class	2.3
Subsidiary risk	Toxic and corrosive gas
ERG No	125
Hazchem warning	Toxic and corrosive gas
SEA TRANSPORTATION	
IMDG	1079
Class	2.3
Label	Toxic gas
AIR TRANSPORTATION	
ICAO/IATA Code	1079
Class	2.3
Subsidiary risk	Toxic and corrosive gas
Packaging instructions	
- Cargo	200
- Passenger	Forbidden
Maximum quantity allowed	
- Cargo	25 kg
- Passenger	Forbidden

15 REGULATORY INFORMATION

EEC Hazard class: Toxic, corrosive gas

Risk phrases:
- R20 Harmful by inhalation
- R21 Harmful in contact with skin
- R34 Causes burns
- R37 Irritating to respiratory system
- R38 Irritating to skin
- R41 Risk of serious damage to eyes
- R44 Risk of explosion if heated under confinement
- R53 May cause long-term adverse effects in the aquatic environment
- R58 May cause long-term adverse effects in the environment

Safety phrases:
- S2 Keep out of reach of children
- S3 Keep in a cool place
- S9 Keep container in a well-ventilated place
- S24 Avoid contact with skin
- S25 Avoid contact with eyes
- S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
- S29 Do not empty in drains
- S30 Never add water to this product
- S36 Wear suitable protective clothing
- S38 In case of insufficient ventilation, wear suitable respiratory equipment
- S39 Wear eye / face protection
- S51 Use only in well ventilated areas
- S57 Use appropriate containment to avoid environmental contamination

National legislation: None

Refer to SABS 0265 for explanation of the above.

16 OTHER INFORMATION

Bibliography

Compressed Gas Association, Arlington, Virginia
Handbook of Compressed Gases - 3rd Edition
Matheson. Matheson Gas Data Book - 6th Edition
SABS 0265 - Labelling of Dangerous Substances

17 EXCLUSION OF LIABILITY

Information contained in this publication is accurate at the date of publication. The company does not accept liability arising from the use of this information, or the use, application, adaptation or process of any products described herein.

ANNEXURE E

Temperature results of the air-breathing ZAFC

Table 4 Results of temperature experiments for the air-breathing ZAFC at 50% RH.

Discharge time (Ah)	Voltage (V)				
	-20°C	20°C	40°C	60°C	70°C
1	0.812	1.082	1.118	1.118	1.129
2	0.776	1.082	1.129	1.129	1.129
3	0.765	1.094	1.118	1.141	1.129
4	0.765	1.082	1.129	1.118	1.118
5	0.753	1.094	1.118	1.118	1.106
6	0.729	1.082	1.129	1.153	1.082
7	0.706	1.082	1.129	1.153	1.071
8	0.682	1.082	1.118	1.153	1.024
9	0.647	1.071	1.118	1.165	0.941
10	0.624	1.071	1.106	1.153	0.871
11	0.576	1.059	1.106	1.153	0.741
12	0.529	1.059	1.106	1.153	0.388
13	0.471	1.059	1.094	1.153	0.012
14	0.412	1.047	1.094	1.153	0
15	0.341	1.047	1.082	1.141	
16	0.2	1.047	1.094	1.141	
17	0	1.047	1.082	1.129	
18		1.047	1.082	1.118	
19		1.012	1.082	1.082	
20		1.012	1.082	1.059	
21		1.012	1.071	1	
22		1	1.071	0.918	
23		1.012	1.071	0.718	
24		1.012	1.071	0.694	
25		1.012	1.071	0	
26		1	1.071		
27		1	1.047		
28		1	1.047		
29		0.988	1.024		
30		0.976	1.012		
31		0.965	0.988		
32		0.953	0.953		
33		0.941	0.918		

34		0.918	0.835		
35		0.906	0.635		
36		0.906	0.024		
37		0.882	0		
38		0.871			
39		0.859			
40		0.824			
41		0.788			
42		0.718			
43		0.494			
44		0.035			
45		0			

ANNEXURE F

Temperature results of the air-breathing DMFC

Table 5 Results of temperature experiments for the air-breathing DMFC at 50% RH.

Current density ($mAcm^{-2}$)	Voltage (V) at -10°C	Voltage (V) at 22, 4°C	Voltage (V) at 30°C	Voltage (V) at 60°C	Voltage (V) at 90°C
0	0.998	1.04	1.06	1.13	1.14
0.5	0.61	0.68	0.82	0.86	0.88
1	0.44	0.53	0.71	0.79	0.8
1.5	0.31	0.42	0.61	0.74	0.75
2	0.18	0.33	0.52	0.69	0.7
2.5	0.07	0.25	0.45	0.65	0.66
3		0.18	0.37	0.61	0.62
3.5		0.11	0.3	0.57	0.58
4		0.05	0.24	0.53	0.55
4.5		0.02	0.17	0.49	0.51
5			0.11	0.46	0.48
5.5			0.05	0.42	0.45
6				0.39	0.41
6.5				0.35	0.38
7				0.32	0.35
7.5				0.28	0.32
8				0.24	0.29
8.5				0.21	0.26
9				0.18	0.23
9.5				0.15	0.2
10				0.12	0.18
10.5				0.09	0.15
11				0.06	0.12
11.5				0.04	0.09
12					0.06

ANNEXURE G

Humidity results for the air-breathing ZAFC

Table 6 Results of the air-breathing ZAFC discharged at 20°C under varying humidity conditions.

Discharge time (Ah)	Cell Voltage (V)		
	70% RH	80% RH	90% RH
1	1.059	1.071	1.071
2	1.071	1.071	1.071
3	1.071	1.059	1.071
4	1.059	1.047	1.071
5	1.059	1.035	1.071
6	1.047	1.059	1.071
7	1.047	1.047	1.059
8	1.047	1.047	1.059
9	1.047	1.047	1.059
10	1.035	1.035	1.047
11	1.024	1.024	1.047
12	1.024	1.024	1.035
13	1.035	1	1.035
14	1.024	0.988	1.024
15	1.024	0.988	1.024
16	1.024	0.976	1.012
17	1.012	0.976	1.012
18	1.012	0.953	1
19	1	0.953	1
20	0.988	0.941	0.976
21	0.976	0.918	0.976
22	0.965	0.906	0.965
23	0.965	0.941	0.953
24	0.941	0.929	0.941
25	0.929	0.918	0.929
26	0.929	0.906	0.929
27	0.906	0.882	0.918
28	0.894	0.847	0.906
29	0.882	0.824	0.894
30	0.894	0.8	0.882
31	0.882	0.776	0.859
32	0.871	0.729	0.847
33	0.847	0.612	0.824
34	0.824	0.318	0.8

35	0.776	0.012	0.788
36	0.671	0	0.765
37	0.518		0.706
38	0.047		0.612
39	0		0.435
40			0.247
41			0.012
42			0

Table 7 Results of the air-breathing ZAFC discharged at 60°C under varying humidity conditions.

Discharge time (Ah)	Voltage (V)		
	70% RH	80% RH	90% RH
1	1.118	1.094	1.118
2	1.118	1.094	1.118
3	1.141	1.094	1.118
4	1.129	1.082	1.118
5	1.129	1.082	1.118
6	1.129	1.082	1.118
7	1.129	1.082	1.118
8	1.129	1.082	1.118
9	1.129	1.082	1.106
10	1.129	1.082	1.106
11	1.129	1.082	1.094
12	1.118	1.071	1.106
13	1.129	1.071	1.106
14	1.118	1.059	1.094
15	1.118	1.059	1.082
16	1.118	1.047	1.071
17	1.094	1.035	1.082
18	1.094	1.012	1.071
19	1.094	1	1.071
20	1.071	0.965	1.059
21	1.071	0.906	1.047
22	1.047	0.859	1.035
23	1.035	0.729	1.035
24	1.024	0.435	1.012
25	1	0.035	1
26	0.988	0.012	0.976
27	0.965	0	0.965
28	0.929		0.929

29	0.859		0.871
30	0.682		0.788
31	0.012		0.612
32	0		0

ANNEXURE H

Humidity results for the air-breathing DMFC

Table 8 Results of the air-breathing DMFC under varying humidity conditions at 25°C.

Current density ($mAcm^{-2}$)	Voltage (V)		
	RH = 70%	RH = 80%	RH = 90%
0	1.06	1.05	1.04
0.5	0.82	0.74	0.73
1	0.73	0.64	0.61
1.5	0.65	0.55	0.52
2	0.57	0.47	0.44
2.5	0.49	0.4	0.36
3	0.42	0.32	0.29
3.5	0.36	0.27	0.22
4	0.29	0.21	0.16
4.5	0.24	0.15	0.1
5	0.17	0.09	0.04
5.5	0.11	0.06	
6	0.06		

Table 9 Results of the air-breathing DMFC under varying humidity conditions at 60°C.

Current density ($mAcm^{-2}$)	Voltage (V)		
	RH = 70%	RH = 80%	RH = 90%
0	1.07	1.13	1.14
0.5	0.78	0.82	0.84
1	0.69	0.72	0.76
1.5	0.62	0.65	0.67
2	0.56	0.59	0.61
2.5	0.48	0.52	0.54
3	0.42	0.47	0.48
3.5	0.37	0.42	0.44
4	0.33	0.36	0.39
4.5	0.28	0.31	0.34
5	0.24	0.26	0.27
5.5	0.19	0.22	0.23
6	0.15	0.18	0.19
6.5	0.11	0.14	0.17
7	0.07	0.09	0.105

7.5		0.05	0.06

ANNEXURE I

Air pollution results of the air-breathing ZAFC

Table 10 Results of the air pollution experiments for the air-breathing ZAFC.

Discharge time (Ah)	Cell Voltage (V)			
	On clean air	Exposed to 20 ppm N_2O	Exposed to 20 ppm SO_2	Exposed to 20 ppm CO
1	1.024	0.965	0.894	0.976
2	1.024	0.953	0.871	0.953
3	1.012	0.941	0.859	0.929
4	1.012	0.918	0.847	0.906
5	1	0.894	0.824	0.882
6	0.988	0.847	0.788	0.871
7	0.976	0.835	0.766	0.835
8	0.965	0.812	0.741	0.788
9	0.941	0.776	0.706	0.765
10	0.929	0.694	0.612	0.741
11	0.906	0.247	0.435	0.706
12	0.882		0.035	0.659
13	0.847			0.588
14	0.788			0.424
16	0.671			0.024
17	0.059			

ANNEXURE J

Air pollution results of the air-breathing DMFC

Table 11 Results of the air-breathing DMFC before and after being exposed to 20 ppm NO_2, CO, SO_2 and N_2O impurities respectively.

Current density ($mAcm^{-2}$)	Voltage (V), on clean air	Voltage (V), 20 ppm NO_2	Voltage (V), after exposure
0	1.06	0.87	0.93
0.5	0.82	0.55	0.69
1	0.71	0.41	0.57
1.5	0.61	0.27	0.41
2	0.52	0.16	0.28
2.5	0.45	0.07	0.15
3	0.37		0.04
3.5	0.3		
4	0.24		
4.5	0.17		
5	0.11		
5.5	0.05		
Current density ($mAcm^{-2}$)	**Voltage (V), on a clean air**	**Voltage (V), 20 ppm CO**	**Voltage (V), after exposure**
0	1.06	1.06	1.03
0.5	0.82	0.69	0.66
1	0.71	0.57	0.55
1.5	0.61	0.47	0.45
2	0.52	0.37	0.36
2.5	0.45	0.29	0.27
3	0.37	0.21	0.19
3.5	0.3	0.14	0.12
4	0.24	0.08	0.05
4.5	0.17	0.01	
5	0.11		
5.5	0.05		
Current density ($mAcm^{-2}$)	**Voltage (V), on clean air**	**Voltage (V), 20 ppm SO_2**	**Voltage (V), after exposure**
0	1.06	1.06	1.03
0.5	0.82	0.68	0.65
1	0.71	0.57	0.56
1.5	0.61	0.47	0.47
2	0.52	0.38	0.39
2.5	0.45	0.3	0.3

4.5	0.17	0.04	0.04
5	0.11		
5.5	0.05		
Current density ($mAcm^{-2}$)	**Voltage (V), on clean air**	**Voltage (V), 20 ppm N_2O**	**Voltage (V), after exposure**
0	1.06	1.06	1.04
0.5	0.82	0.77	0.68
1	0.71	0.66	0.58
1.5	0.61	0.57	0.48
2	0.52	0.49	0.39
2.5	0.45	0.41	0.31
3	0.37	0.34	0.23
3.5	0.3	0.28	0.16
4	0.24	0.2	0.09
4.5	0.17	0.13	0.02
5	0.11	0.06	
5.5	0.05	0.02	

ANNEXURE K

Results of the air-breathing ZAFC at ambient room conditions

Table 12 Results of the air-breathing ZAFC discharged at ambient room conditions at a constant rate of 1 A and 2 A.

Discharge time (Ah)	Cell Voltage (V) at 1 A	Cell Voltage (V) at 2 A
1	1.118	1.082
2	1.118	1.082
3	1.118	1.082
4	1.118	1.082
5	1.118	1.082
6	1.129	1.082
7	1.118	1.082
8	1.118	1.082
9	1.129	1.071
10	1.129	1.071
11	1.118	1.059
12	1.118	1.059
13	1.129	1.059
14	1.118	1.047
15	1.118	1.047
16	1.118	1.047
17	1.118	1.047
18	1.118	1.047
19	1.118	1.012
20	1.118	1.012
21	1.118	1.012
22	1.118	1.012
23	1.118	1.012
24	1.118	1.012
25	1.106	1.012
26	1.118	1
27	1.118	1
28	1.118	1
29	1.106	0.988
30	1.106	0.976
31	1.106	0.965
32	1.106	0.953
33	1.106	0.941
34	1.106	0.918
35	1.094	0.906

36	1.094	0.906
37	1.094	0.882
38	1.094	0.871
39	1.082	0.859
40	1.082	0.824
41	1.082	0.788
42	1.082	0.718
43	1.071	0.565
44	1.071	0.494
45	1.071	0.035
46	1.071	0.024
47	1.059	0
48	1.059	
49	1.059	
50	1.047	
51	1.047	
52	1.035	
53	1.047	
54	1.035	
55	1.035	
56	1.024	
57	1.024	
58	1.024	
59	1.012	
60	1	
61	1	
62	0.976	
63	0.965	
64	0.965	
65	0.953	
66	0.953	
67	0.929	
68	0.918	
69	0.906	
70	0.894	
71	0.871	
72	0.847	
73	0.8	
74	0.682	
75	0.529	
76	0.282	
77	0	