

**INCREASING THE CO TOLERANCE OF PEM FUEL CELLS VIA CURRENT
PULSING AND SELF-OXIDATION**

A Thesis

by

ARTHUR H. THOMASON

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2004

Major Subject: Mechanical Engineering

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May 2004

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ABSTRACT

Increasing the CO Tolerance of PEM Fuel Cells via Current Pulsing and Self-Oxidation.

(May 2004)

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An investigation was conducted to determine and compare the effect of cell current pulsing and “self-oxidation” in increasing the CO tolerance of a PEM fuel cell. The most effective pulsing parameter values were also determined. Current pulsing involves periodically demanding positive current pulses from the fuel cell to create an anode over-potential, while “self-oxidation” or sustained potential oscillations is achieved when the anode catalyst becomes so saturated with CO that the anode over-potential increases to a value at which CO is oxidized from the catalyst surface. The CO tolerance of a fuel cell system with a Pt-Ru anode was tested using 50 and 496 ppm CO in the anode fuel. The performance of the system declined with an increase in CO concentration. Current pulses of various amplitude, frequency, and duty cycle were applied to the cell while CO was present in the anode fuel. With 50 ppm CO in the anode fuel, the most effective pulse in increasing CO tolerance while maintaining normal cell operation was 1.0 A/cm², 0.25 Hz, and a 5% duty cycle. A pulse (120 Hz, 50% duty cycle) similar to the ripple current often generated when converting DC to single-phase 60 Hz AC had a positive effect on the CO tolerance of the system, but at frequencies that high, the pulse duration was not long enough to completely oxidize the CO from the catalyst surface. With 496 ppm CO in the anode fuel, a pulse of 1.0 A/cm², 0.5 Hz, and a 20% duty cycle proved most effective.

When the cell was exposed to 496 ppm CO, without employing pulsing, “self-oxidation” occurred and CO was periodically oxidized from the catalyst surface. However, pulsing allowed the cell to operate at the desired voltage and power a higher percentage of the time than “self-oxidation”; hence, pulsing was more effective.

DEDICATION

I dedicate this work to my wife, Kerrie. She is my soul mate and best friend.

I also dedicate this work to my parents, Bill and Jane. Their love and support has been invaluable over the years. The guidance and values that they have instilled in me has played a significant role in getting me where I am today.

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1. INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) are currently on the verge of being implemented as home power generating units. However, there are still many obstacles that prevent fuel cells from playing a major role in electrical power production. One of the problems the fuel cell industry faces is finding a safe, economical, and effective way to supply the unit with hydrogen or hydrogen-rich gas. Until a hydrogen based economy can be implemented, reforming natural gas (which is already supplied to many homes today) appears to be the solution; however, the by-products of the reforming process, namely carbon monoxide (CO), can poison the cell by blocking the Pt electro-catalyst, thus degrading its performance. The most common reforming process is currently autothermal reforming (ATR), which consists of partial oxidation (POX) and steam methane reformation (SMR). After reforming, a gas clean-up system, typically consisting of water gas shift reactions and preferential oxidation (PROX), is employed to reduce the concentration of CO in the reformat [1,2]. Currently, these gas clean-up systems are expensive and bulky [3]. Nevertheless, an adiabatic natural gas reformer followed by the appropriate CO clean up procedures is typically expected to produce between 10 and 100 ppm CO during steady state operation [3,1]. However, during the start up phase, which typically lasts close to 2 hours, CO levels of approximately 500 ppm can be produced. Furthermore, it has been shown that CO concentrations as small as 5 to 10 ppm can be detrimental to the performance of a PEMFC [4]. Hence, it appears to be more practical and economical to attempt to make the cell more tolerant to CO than

attempting to further reduce the amount of CO produced in the reforming process. In doing this, the amount of CO produced by the reformer will be less critical; thus, the CO concentration produced during steady-state as well as start up can be tolerated.

Various methods of increasing the CO tolerance of PEMFCs have been explored and documented in literature. Virtually all of the methods employed to date involve oxidizing the CO on the catalyst surface to carbon dioxide (CO₂). Carbon dioxide does not have an affinity for the catalyst; thus, it is expelled with the excess hydrogen. One method used to stimulate the oxidation of CO on the catalyst is “oxidant bleeding.” Oxidant bleeding entails mixing a small amount ($\approx 1\%$) of oxidant (air, oxygen, or hydrogen peroxide) with the anode fuel [2,3]. This chemically oxidizes some of the CO into CO₂, thus lowers the CO concentration. However, this method involves complicated control systems in order to maintain safe fuel cell operation [3]. Furthermore, oxidant bleeding is not efficient, as only 1 out of every 400 oxygen molecules participate in the oxidation of CO. The remaining oxygen combusts with the anode fuel which could lead to a decline in the fuel cell performance or even cell failure [2].

The oxidation of CO can also occur in the presence of a high anode potential. It has been shown that an anode over-potential can make PEMFCs more tolerant to CO by electrochemically oxidizing CO from the surface of the catalyst [4]. Two different methods for creating anode over-potentials have been discussed in the literature. The first method is referred to as sustained potential oscillations or “self-oxidation.” To employ this method, the cell current must be held constant. In this process, as CO continues to accumulate on the catalyst, the anode becomes increasingly polarized to higher potentials to sustain the current demanded. The high potential, stimulates the

electro-oxidation of CO on the catalyst surface [4]. “Self-oxidation” is a simple way to oxidize CO because no control system or additional equipment is necessary. However, sustained potential oscillations have only been shown to be effective with an anode fuel CO concentration of 108 ppm CO. Thus, further investigation of this technique is imperative to verify that “self-oxidation” is an effective means for increasing the CO tolerance of a PEMFC during the reformer start-up process and steady-state operation. The second method used to create an anode over-potential is called pulsing. Carrette indicates that pulsing the cell with positive current spikes can be an effective method for creating anode over-potentials by stating: “The electrical pulses increase the anode potential to values at which the CO is oxidized to CO₂. In this way, the catalyst surface is continually cleaned and the loss of cell voltage is minimized” [3]. Pulsing is also an efficient way to increase the CO tolerance of a PEMFC because the only energy required to implement this technique is the small amount of energy needed to trigger the temporary increase in cell current. However, to completely characterize the effect of pulsing, more research must be done. In Carrette’s work, the fuel cell was used as a proton pump (hydrogen was applied to the anode and cathode). This technique is useful in establishing an anode reference; however, pulsing must be investigated under normal cell operation (air applied to the cathode) to realize its applications. Furthermore, CO concentrations of 50 and 500 ppm have not been investigated and the effectiveness of current pulsing as a function frequency, amplitude, and duty cycle has yet to be determined. The frequency, amplitude, and duty cycle of a ripple current are of particular of interest. A ripple current is the current variation generated when the DC output of a fuel cell is converted to single-phase, 60 Hz, AC power via an inverter. The switching of

the inverter creates a sinusoidal oscillating ripple current of 120 Hz across the electrodes [5]. The amplitude of this wave can be up to two times the current demanded of the system. A ripple current should be present in any fuel cell used to generate AC power. Thus, by using the ripple current as a pulsing mechanism, the cost and complexity of the pulsing technique would be almost non-existent. Finally, a comparison of pulsing and “self-oxidation” is also necessary to determine the most effective method for increasing the CO tolerance of a PEMFC.

1.1. Objective

The objective of this work was to determine and compare the effect of cell current pulsing (at a variety of pulse amplitudes, frequencies, and duty cycles) and “self-oxidation,” at various anode fuel CO concentrations, on the CO tolerance of a PEMFC. An additional objective was to determine the most effective pulsing parameter values in increasing the CO tolerance of a PEMFC. A secondary objective was to determine the effect that a simulated ripple current has on the CO tolerance of a PEMFC.

1.2. Scope of research and format of thesis

To satisfy the objective, experiments were conducted and the results were evaluated. Each set of experimental parameters were evaluated via the cell performance, as indicated by the variation of voltage with current density, the variation of voltage with time, and the variation of current density with time.

This work is significant for a number of reasons. It has real world applications that can ultimately lead to an overall increase in the performance of the reformer/fuel cell

system. By monitoring the CO output of the reformer, a control system could be created that would vary system parameters, based on the results of this work, so that cell performance is maximized at all times. This work could also lead to a reduction in the cost of the reforming process. By increasing the CO tolerance, the need for the expensive CO clean-up stage of the reforming process could be eliminated. Finally, if ripple currents or “self-oxidation” prove to be an effective method for increasing the CO tolerance of a PEMFC, the cost and complexity of increasing CO tolerance would be non-existent.

This thesis is organized by sections. The Background section includes descriptions of fuel cell principles of operation, the reforming process, CO poisoning, CO oxidation, and ripple current. The test equipment, test parameters, and test procedure are described in the Experimental section. The section titled Results and Discussion is divided into six sections based on the type of experiment conducted. Each section exhibits the data collected and describes the significance of the finding. In the Summary section, all of the key findings are restated. Lastly, a Conclusions and a Recommendations for future work section are provided.

2. BACKGROUND

Before describing the experiment, it is necessary to understand the basic principles of fuel cell operation, the reforming process, CO poisoning, CO oxidation, and ripple currents. Discussions of each of these topics are provided in the following sub-sections. The metric used to evaluate the performance of the PEMFC is also discussed.

2.1. Fuel cell principles of operation

A fuel cell is an electrochemical system that produces electricity via a chemical reaction. The reactants necessary to generate electricity in a PEM fuel cell are hydrogen (fuel) and oxygen (oxidizer). For a stationary power generation unit, the hydrogen will most likely come from reformed natural gas (reformate) and the oxygen will be obtained from air. The reformate is applied to the anode, while the air is sent to the cathode. Each electrode is constructed of a carbon cloth that is both conductive and porous. The anode and cathode are separated by a non-conductive, proton permeable membrane, known as a proton exchange membrane (PEM). A catalyst, typically Platinum (Pt), is applied between the PEM and electrode on each side. The electrodes, catalyst, and PEM are collectively known as the membrane electrode assembly (MEA). An exploded and an assembled view of a MEA are given in Fig. 1. Porous and conductive flow fields are placed against each electrode to insure that the hydrogen-rich reformate and air are evenly dispersed over the anode and cathode, respectively.

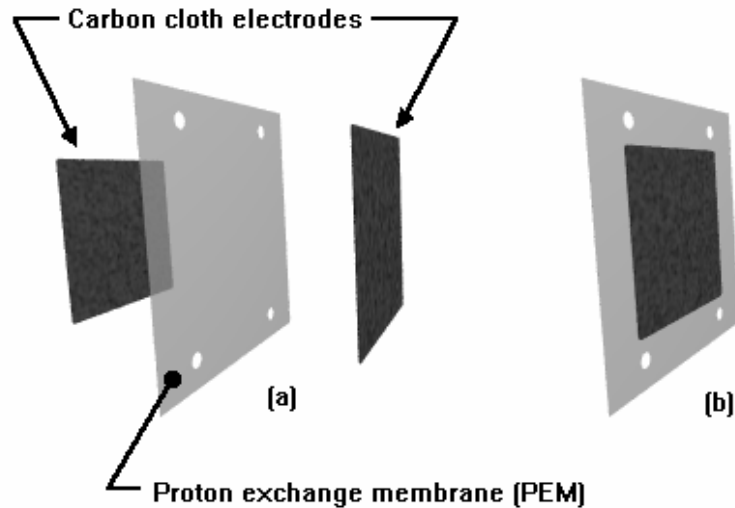
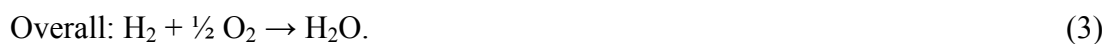


Fig. 1: Membrane electrode assembly (MEA). (a): exploded view of MEA (L to R: anode, PEM, cathode). (b): MEA as an assembled component.

A fuel cell generates electricity when H_2 flows through the porous cloth anode to the Pt catalyst layer, where each H_2 atom is broken down into hydrogen ions (H^+) and electrons (e^-). The hydrogen ions migrate through the PEM to the cathode side. The electrons flow through the electrode and flow field across a load, to the anode. The difference in potential between the anode and cathode allows the electrons to flow across the load and useful energy to be created. Once the hydrogen ions reaches the cathode, the ions, electrons, and oxygen combine to create water via the aid of the Pt catalyst. The basic operation of a PEM fuel cell is illustrated in Fig. 2. As given by Appleby [6], the reactions that take place at each electrode are as follows:



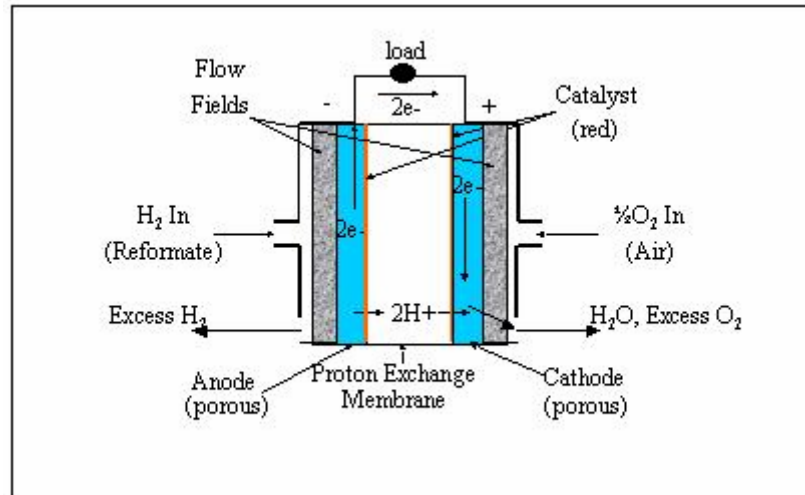
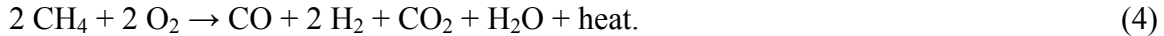


Fig. 2: Illustration of the basic operation of a PEMFC.

2.2. The reforming process

Now that the principles of fuel cell operation have been discussed, the origin of the hydrogen fuel source must be considered. Until a hydrogen based economy can be implemented, reforming natural gas appears to be the most effective way to get hydrogen to fuel cell home power generation units. Natural gas is appealing because it is currently piped to many homes today. Natural gas, which consists mainly of methane (CH_4), can be reformed to create a hydrogen-rich anode fuel for a PEMFC. Unfortunately, even after a thorough series of gas clean-up procedures, small concentrations of CO and other by-products (namely CO_2 and Nitrogen) remain in the reformat. To reduce the amount of CO produced in the reforming process to a low level (on the order of 10 ppm), a number of steps are required. First, the natural gas is sent to the reformer, where partial oxidation (POX) and steam CH_4 reformation (SMR) occurs. In the POX process, some of the CH_4 , reacts with oxygen as shown in the following equation:



However, many CH_4 molecules make it through the POX process without reacting.

After POX, the reformat is sent to the steam methane reformer (SMR). The SMR reacts the remaining CH_4 with water vapor to form H_2 and CO via the following reaction:



The amount of CO produced in the reaction is reduced when the CO and water vapor react to form CO_2 and H_2 :



The combination of the first two processes are often referred to as the auto thermal reforming (ATR) process. At this point, approximately of 40% the reformat is H_2 and 12% (120,000 ppm) is CO . This is far too much CO for a fuel cell to tolerate; hence, further reactions are needed.

In the third phase of the reforming process, water gas shift reactions are often used to further reduce the amount of CO produced. A high temperature shift (HTS) requires a temperature of 370°C (700°F) and uses a Fe^+ catalyst. A low temperature shift (LTS) requires a temperature of 175°C (350°F) and employs a Cu^+ catalyst. With each method CO and water vapor react to form CO_2 and H_2 :



A low temperature shift can reduce the CO concentration of the reformat to 0.5% (5,000 ppm). A subsequent high temperature shift will yield reformat with 50% H_2 , 50 ppm CO , and 3% CH_4 .

The final step of the reforming process is CO polishing. This is carried out via preferential oxidation (PROX). In this phase, the reformat is sent through catalyst beds at temperatures between 220° and 320° F. CO is oxidized in this process via the following reaction:



This reduces the CO concentration to levels around 10 ppm CO. After CO polishing, the reformat is sent to the fuel cell. The anode off gas from the fuel cell is then sent back to the reformer, to recycle the unused fuel. A diagram of this process is presented in Fig. 3. A photograph of an adiabatic natural gas reformer that employs POX, SMR, LTS, CO polish, and AGO is given in Fig. 4.

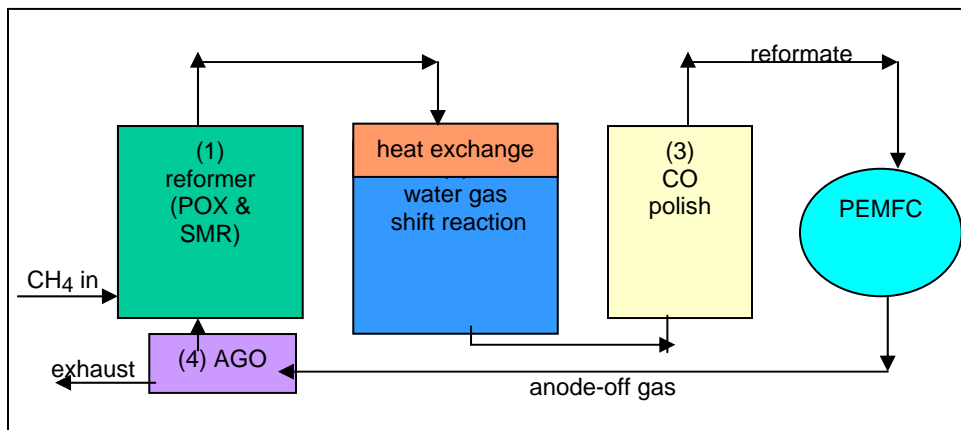


Fig. 3: Schematic of the CH₄ reforming process.



Fig. 4: Adiabatic natural gas reformer that employs POX, SMR, LTS, CO polish, and AGO.

2.3. CO poisoning

In the discussion of the reforming process, it was indicated that CO is a by-product of natural gas reformation. Hence, the effect that CO has on the performance of a PEMFC is important. Catalysts, such as platinum (Pt) are added to the anode and cathode of a PEMFC to obtain a high reaction rate at low temperatures. Pt based alloys are an effective catalyst at the anode because hydrogen oxidation occurs abundantly on these surfaces. However, CO (which is inevitably present in reformat) adsorbs on the platinum alloy surface due to its strong affinity to the catalyst, thus halting the hydrogen oxidation reaction by blocking the adsorption site [3]. This phenomena is referred to as CO poisoning. For a PEMFC to operate as desired, the CO must be cleaned from the catalyst surface. This can be carried out via CO oxidation.

2.4. CO oxidation and anode over-potential

One method for removing CO from the catalyst surface is CO oxidation. In this process, CO combines with an oxygen-containing molecule to form CO₂ (i.e., $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$). CO₂ does not have an affinity for the catalyst; thus, it is expelled with the anode off gas. This, in essence, cleans the CO from the surface and allows the hydrogen oxidation to continue. However, for the adsorbed CO to react with oxygen containing molecules (primarily OH), energy is required. Hence, if the anode potential of a PEMFC become great enough, CO can be readily oxidized from the catalyst surface into CO₂.

The useful power that a PEMFC creates is obtained via the potential difference between the anode and cathode; this is known as the cell voltage. By convention, the anode potential is positive and the cathode potential is negative. As the current demanded of the cell increases (i.e., a smaller resistor is applied across the electrodes), the anode potential becomes more positive, while the cell voltage decreases. However, even at cell potentials close to short-circuit, the anode potential is not large enough to completely oxidize CO from the catalyst surface. Fortunately, the anode potential can be increased by creating an anode over-potential.

When the anode potential of a PEMFC is considerably larger than the thermodynamic potential necessary for an electrolytic cell to decompose water, the excess voltage above the decomposition voltage is known as the anode over-potential [7]. An anode over-potential can also be described as the voltage lost to $T\Delta S_{\text{irreversible}}$. When the anode is operating on pure H₂, this loss is negligible, but as the catalyst becomes poisoned by impurities, such as CO, the anode over-potential increases. With an over-potential, the

anode voltage can reach high enough levels to stimulate the electro-oxidation of CO_{ad} on the catalyst surface.

Two methods for creating anode over-potentials were used in this work: “self-oxidation” and pulsing. An anode over-potential can be created via “self-oxidation” by first demanding a constant current from the fuel cell system in the presence of CO. As the CO continues to accumulate on the catalyst and H_2 reaction sites are blocked, the anode over-potential continues to increase in order to sustain the current demanded. “This, in turn, accelerates the electro-oxidation of CO_{ad} on the catalyst surface via the oxygen containing surface species such as OH_{ad} . Hence, the overall reaction that takes place is as follows:



At certain over-potentials, the CO electro-oxidation rate exceeds the rate of CO adsorption and the surface coverage of CO declines” [4]. Once the CO is oxidized from the catalyst surface, the over-potential drops until more CO accumulates on the catalyst surface, at which time the over-potential rises again. This process is known as sustained potential oscillations or “self-oxidation.”

With lower CO concentrations, an equilibrium point is often reached at which the CO adsorption rate is equal to the CO oxidation rate. Hence, the anode over-potential never gets large enough to completely oxidize CO from the catalyst surface and the cell performance suffers. In this case, an anode over-potential can be created artificially by suddenly demanding a high current pulse that brings the cell potential close to zero. This method is called pulsing. Pulsing is effective because the reaction time of a PEMFC is finite; thus, when a current pulse is applied, an anode over-potential is created in order to

meet the current demanded. The amount of current demanded dictates the over-potential voltage. Therefore, the amplitude of the current pulse is key in making sure that all of the CO is oxidized from the catalyst. By periodically applying current pulses, CO is continually cleaned from the catalyst. However, creating an anode over-potential of any kind interferes with the normal operation of the fuel cell. Hence, the amplitude, frequency, and duty cycle of the over-potential should be optimized, while still achieving the desired result.

One way to reduce the amplitude of the over-potential necessary to oxidize CO is to add Ruthenium (Ru) to the anode. This is effective because Ru affects the Pt in the surface to bond CO weaker and the OH species can form more readily on Ru surfaces than on Pt surfaces [8,4]. In other words, Ru helps to bring about the formation of OH from water. Thus, Ru exhibits an extremely high activity for the catalytic oxidation of CO [9]. Furthermore, CO electro-oxidation on Ru enhanced Pt is shown to have two oxidation peaks in the stripping voltammetry, both at an over-potential significantly lower than that found on Pt alone [10]. Thus, in the presence of a Pt-Ru catalyst, CO can be oxidized via a significantly lower anode over-potential than with pure Pt.

To compute the anode over-potential voltage, we must first use the fact that the overall fuel cell voltage (i.e., potential difference between the anode and cathode) with pure hydrogen as the anode fuel can be calculated as follows [4]:

$$V_{H_2} = V_0 - \eta_a + c - I \left(\frac{L}{\sigma} \right) - IR_0 \quad (10)$$

where V_0 (V) is the open circuit voltage, I (A/cm²) is the current density, η_a (V) and η_c (V) are the anode and cathode over-potentials, L is the thickness of the PEM, σ is the

conductivity of the PEM, and R_0 is any interfacial resistance present in the system.

Similarly, the cell potential of a PEMFC with CO in the anode fuel is given by:

$$V_{CO} = V_0 - \eta_{CO} + \eta_c - I \left(\frac{L}{\sigma} \right) - IR_0. \quad (11)$$

Solving in terms of the anode over-potential, the following equation is obtained:

$$\eta_{CO} = -V_{CO} + V_0 + \eta_c - I \left(\frac{L}{\sigma} \right) - IR_0. \quad (12)$$

Expressing equation 12 in terms of equation 10 yields:

$$\eta_{CO} = \eta_{H_2} + V_{H_2} - V_{CO}. \quad (13)$$

Thus, the over-potential of the anode in presence of CO can be determined by the following equation because the over-potential that occurs in the presence of pure hydrogen is negligible:

$$\eta_{CO} \approx V_{H_2} - V_{CO}. \quad (14)$$

This is a useful equation because it can be used to determine the over-potential necessary to completely oxidize CO from the catalyst surface. Furthermore, it illustrates the fundamentals of “self-oxidation;” as the cell voltage drops with CO accumulation, the anode over-potential increases until the CO is oxidized.

The anode over-potential also varies with the current density of the cell. The dependence of the anode over-potential on current density is described via the following relationship:

$$\eta_{CO} = a + b \log I, \quad (15)$$

where a and b are constants and I (A/cm^2) is the current density. This indicates that at higher current densities the anode over-potential obtained will be greater. Hence, CO

oxidation should be achieved more readily at higher current densities. Thus, this equation illustrates the mechanism behind the pulsing technique.

2.5. Ripple current

To apply the pulsing technique, the cell current must be suddenly increased. This requires additional electronics to trigger the pulse. However, with ripple currents, variations in current are already present in the system; thus, it may be possible to use ripple currents as a pulsing mechanism. When DC power is converted to AC via an inverter, the AC current and voltage produced can be expressed respectively as:

$$V_{AC} = V_{DC} \sin \omega t \quad (16)$$

$$I_{AC} = I_{DC} \sin \omega t, \quad (17)$$

Where ω is the AC frequency, t is the time, V_{DC} is the DC voltage, and I_{DC} is the DC current. Thus, the power produced is:

$$P_{AC} = V_{AC} I_{AC} \sin^2 \omega t, \quad (18)$$

$$\text{or } P_{AC} = \frac{1}{2} V_{AC} I_{AC} - \frac{1}{2} V_{AC} I_{AC} \cos 2\omega t. \quad (19)$$

Therefore, the frequency of power oscillation demanded from the DC unit is twice that of the output current of the DC to AC inverter. Hence, when the DC output of a fuel cell is converted to single-phase, 60 Hz, AC power via an inverter, a sinusoidal oscillating ripple current of 120 Hz is generated in the fuel cell. The amplitude of this wave can be up to two times the current demanded of the system. Hence, if 10A is demanded from the fuel cell by the inverter, a ripple current with a peak amplitude of 20A, a frequency of 120 Hz, and a duty cycle of 50% could be generated. An example of this wave is illustrated in Fig. 5. This figure illustrates the variation of cell current with time for a

PEMFC that is connected to an inverter demanding a current of 10 A. Ripple currents are often filtered out because they can increase fuel consumption [5]. However, with CO in the anode fuel of a PEMFC, ripple currents could prove to be very useful. If ripple currents prove to be an effective pulsing mechanism, they can reduce the cost and complexity of the fuel cell power generation system.

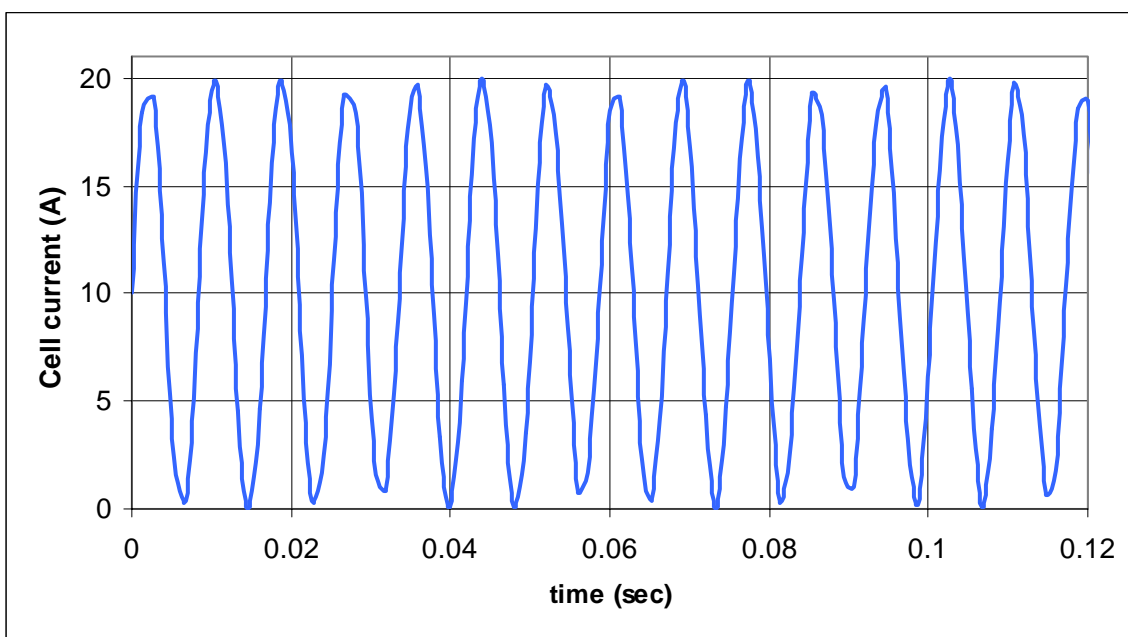


Fig. 5: Variation of cell current with time for a PEMFC; ripple current generated by an inverter with a demand of 10A. Frequency: 120 Hz, duty cycle 50%.

2.6. PEMFC performance metrics

To determine the effect that a particular method or set of parameters has on the CO tolerance of a PEMFC, meaningful metrics must first be established. In the fuel cell industry, cell performance is typically evaluated via a polarization curve, which is the

variation of cell voltage with current density. Hence, this metric was used in this work as well. Fig. 6 illustrates an example of this plot. When operating a fuel cell, it is desirable to maximize the power output of the unit. Therefore, the higher the cell voltage at a specific current density, the better the cell performance is. Hence, in Fig. 6, curve 2 is more desirable than curve 1.

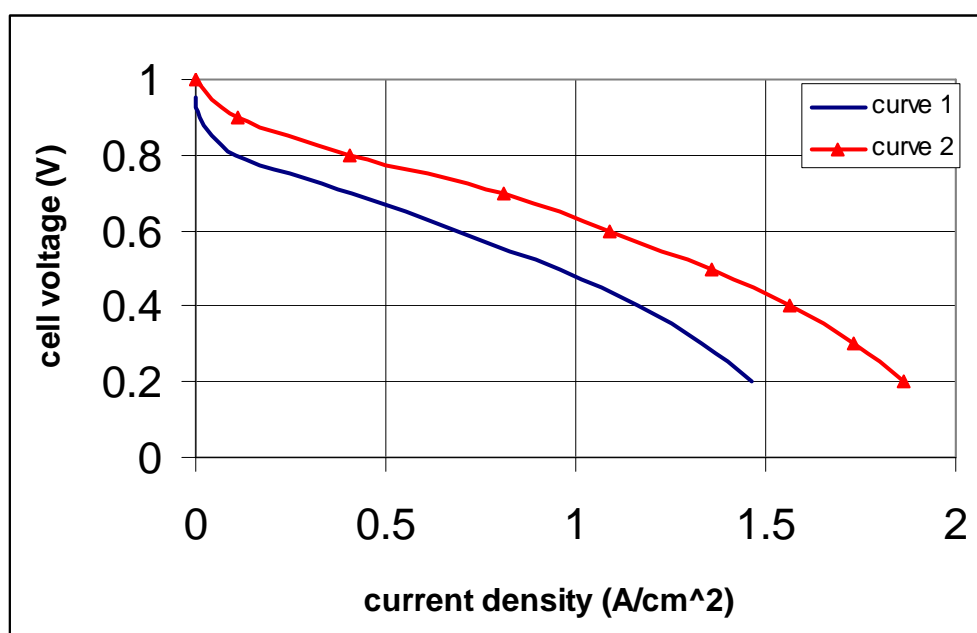


Fig. 6: Typical variation of cell voltage with current density (polarization curve). Curve 2 represents more desirable cell performance.

Although the variation of cell voltage with current density is an important metric, other metrics must be considered when cell poisoning is involved. Because the effect of CO poisoning varies with time, it was also important to investigate the variation of voltage and current density with time. A high current density that remains high over time at a specific voltage is desirable. Similarly, a high voltage that remains relatively constant with time at a specific current density is also desirable. An example of the

variation of cell voltage with time is given in Fig. 7. Note that curve 1 remains at 0.67 V over the time period. Curve 2 is less desirable because the voltage drops over time.

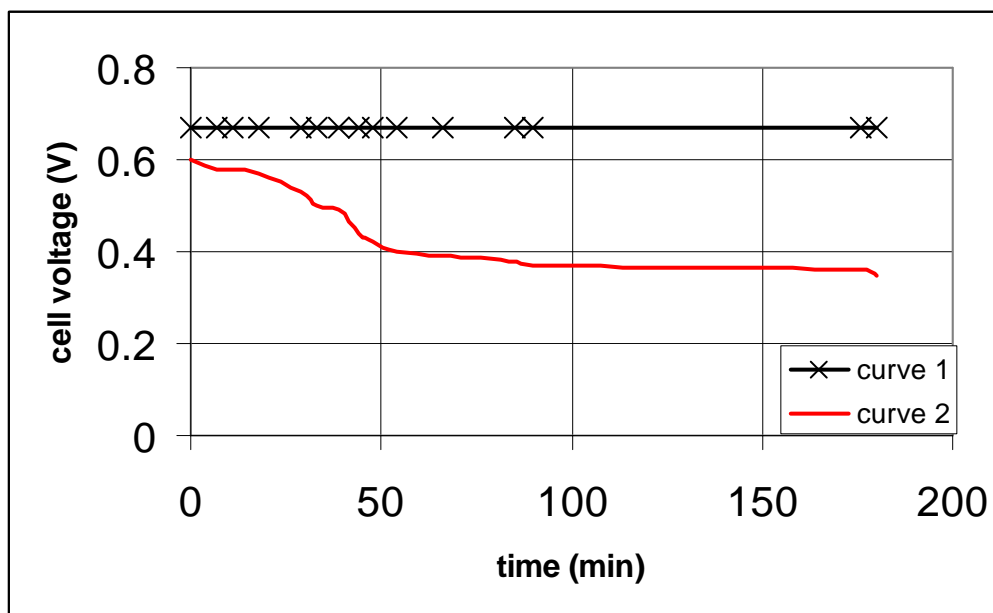


Fig. 7: Example of the variation of cell voltage with time. The cell current density was held constant at 0.4 A/cm^2 . Curve 1 represents more desirable cell performance.

3. EXPERIMENTAL

In the following sections, the equipment and experimental procedures and techniques used to measure fuel cell performance are described. The fuel cell operating conditions at which cell performance was determined is also explained. A description of the current pulsing procedures, parameters, and instrumentation is provided as well.

3.1. Test equipment

Membrane Electrode Assemblies (MEAs) were purchased from 3M Corporation. Each MEA had a surface area of 50 cm^2 . The cathode catalyst is Pt and has a catalyst loading of 0.4 mg/cm^2 . The anode has a total catalyst loading of 0.6 mg/cm^2 and is approximately 0.4 mg/cm^2 Pt and 0.2 mg/cm^2 Ru. The proton exchange membrane is 30 microns thick and constructed of cast Nafion® from Dupont Corporation. The MEA was placed in a 50 cm^2 single cell assembly. Thin Ni foam sheets were used to distribute the reactant gases over each electrode; H_2 is sent to the anode and air is sent to the cathode. These Ni foam sheets are known as flow fields. An exploded view of the fuel cell assembly is given in Fig. 8. Fig. 9 shows a close up of the Ni foam flow field in place on the hydrogen flow plate. Ni foam is an effective flow field because it is porous and conductive. The flow field needs to be porous so that the gas can travel from the inlet in the end plate through the flow field to the respective electrode. The flow field must also be able to conduct the electricity produced at the anode back to the endplate, and then through the load.

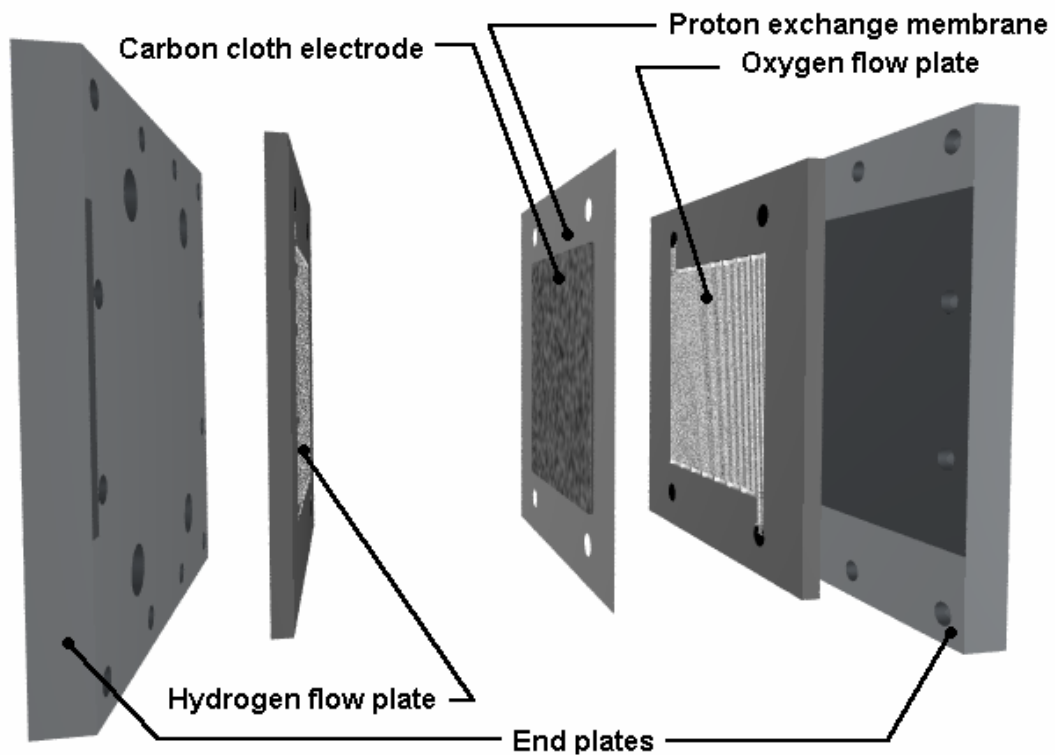


Fig. 8: Exploded view of 50 cm² single fuel cell assembly from Center Point Energy Power Systems, Inc. (L to R: anode end plate, hydrogen flow plate, including Ni foam flow field, MEA, oxygen flow plate, including Ni foam flow field, cathode end plate).

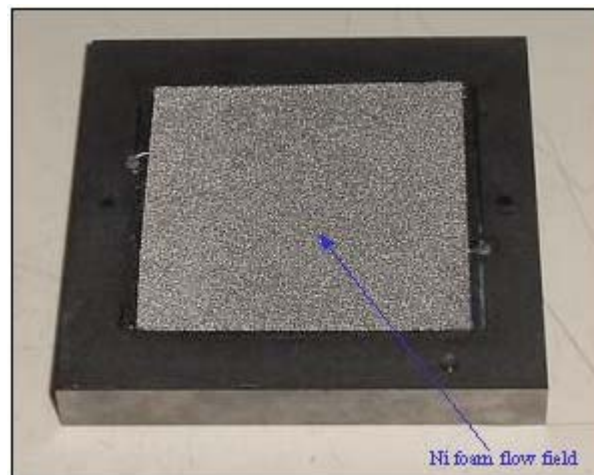


Fig. 9: Close-up view of the hydrogen flow plate with Ni foam flow field in place.

Each reactant gas was bubbled through a stainless steel humidification bottle containing de-ionized water to increase the gas humidity to a level near 100%. Reactant gas humidification is necessary to prevent membrane dehydration, as water is necessary for the hydrogen ions to migrate through the membrane. The system was controlled via a fuel cell test station that maintains cell temperature, gas flow rate, and humidification bottle temperature. A programmable electronic load was used to maintain and display a desired fuel cell voltage or current. By varying the amplitude, frequency, and duty cycle, the electronic load was also programmed to create periodic increases in current, which, in turn created over-potential in the anode. The electronic load allowed the user to control pulse amplitude, frequency, slew rate, and duty cycle. An oscilloscope was also used to record data. Premixed tanks containing H₂/50 ppm CO and H₂/496 ppm CO were used as the anode fuel for the CO tolerance experiments. Finally, a relay was employed to protect the cell from achieving a negative voltage if high current spikes occurred. If the cell voltage went below zero, the load was bypassed. The experimental unit is shown in Fig. 10.

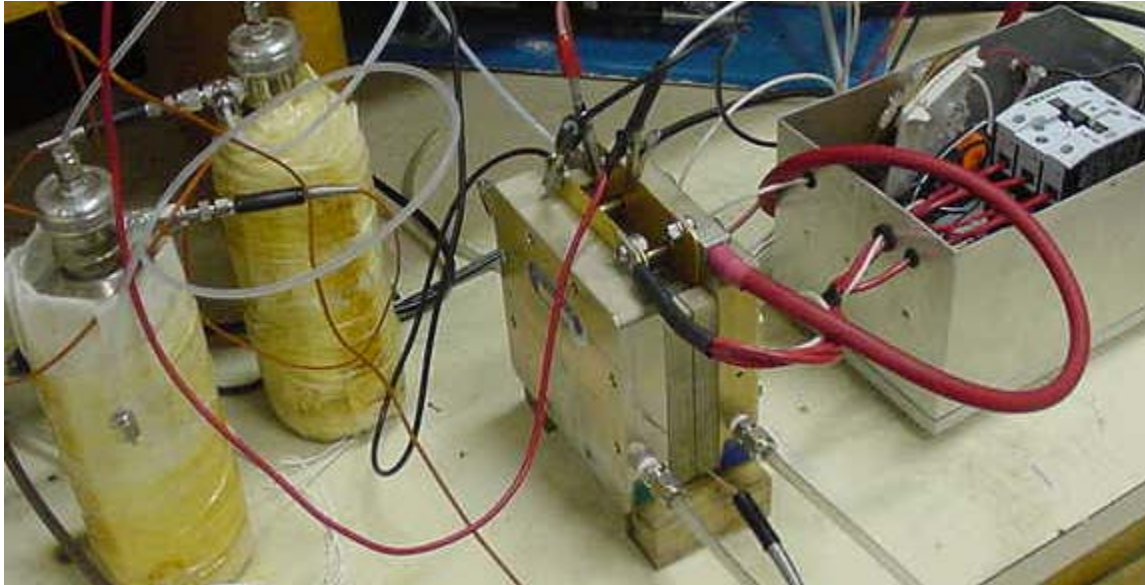


Fig. 10: Experimental unit, items (listed L to R: hydrogen humidification bottle, air humidification bottle, fuel cell, relay).

3.2. Test procedure

In the following sections, a description of the experimental procedures used to determine the effect of CO on MEA performance and the effect of current pulsing on MEA performance in the presence of CO are provided.

3.2.1. Determination of effect of CO on MEA performance

The first step in this experiment was to determine how the MEA performed under normal operation, that is, without the presence of CO in the anode fuel. Pure H₂ was used for the anode side and air was used on the cathode side. Using the programmable electronic load, various loads were applied to the cell. Voltage and power data with respect to current density were collected to create a polarization curve, as shown in Fig. 6. The variation of cell voltage and current density with time, as illustrated in Fig. 7, was

also recorded to further determine the cell behavior under normal operation. In these experiments, a constant current of 19 A (0.38 A/cm^2) or 20 A (0.4 A/cm^2) and a constant voltage of 0.6 V were used as the respective set point.

After determining the fuel cell behavior under these conditions, 50 ppm CO was introduced into the anode fuel, once steady state operation was achieved. The variation of cell voltage and current density with time were documented. Once the MEA had been exposed to 50 ppm CO for 1 hour, various loads were applied and voltage and power data with respect to current density were collected. A polarization curve and plots of the variation of cell voltage and current density with time were created using these results. After each experiment was conducted using CO in the anode fuel, the MEA was replaced. However, before another experiment was conducted, the new MEA performance was evaluated to make sure that the cell voltages at specific current densities on the polarization curve were within 10% of the values obtained using the previous MEAs, for the purpose of comparison.

Using a new MEA, these steps were repeated with 496 ppm CO in the anode fuel. The variation of cell voltage with time at a constant current density was of particular interest, as “self-oxidation” can occur with these experimental conditions. The results of these experiments were compared with the control (no CO present) to characterize the effect of CO concentration on MEAs.

3.2.2. Determining the effect of current pulsing on MEA performance in the presence of CO

Once the behavior of the MEAs were characterized with 0, 50, and 496 ppm CO in the anode fuel, a new MEA was installed in the fuel cell assembly. The system was operated using H₂ and air at a constant current density of 0.38 A/cm² until steady state behavior was obtained. At this time, 50 ppm CO was introduced into the anode fuel. After one hour, while maintaining a base current of 0.38 A/cm², a periodic current pulse with an amplitude of 1.2 A/cm², a frequency of 0.25 Hz, and a duty cycle of 10% was demanded from the fuel cell for one hour. The pulse was produced by the programmable electronic load generator. The variation of cell voltage with time was documented over the 2 hour period. Using various base current densities, pulse frequencies, duty cycles, and amplitudes, voltage and power data with respect to current density were collected to create a polarization curve. The data from each run was compared to determine if frequency, duty cycle, and amplitude affect the performance and if some of these variables have more of an effect than others. The experiment was then repeated using H₂/496 ppm CO as the anode fuel.

3.3. Fuel cell operating conditions

For each experiment conducted, the fuel cell temperature and humidification water temperatures were held constant at 60⁰C. The cathode reactant was air and the anode fuel was a mixture of H₂ and CO. The level of CO concentrations used in the anode fuel were 0, 50, and 496 ppm. The method used to determine the appropriate flow rates for each experiment and the current pulsing parameters are given in the following sections.

A table of each combination of operating and pulsing parameter investigated and its significance is presented in Appendix A.

3.3.1. Determination of reaction rates and stoichiometric ratio

The flow rates of the reactants were dictated by the current demanded from the cell. Fuel cells have been found to be most efficient when nearly 100% of the reactants (H₂ and O₂) are consumed. Therefore, it was necessary to compute the flow rate that allows for 100% utilization for the current demanded. The H₂ flow rate needed to maintain close to 100% utilization (80% or more) for a 50 cm² MEA was computed with the following relationship:

$$\frac{H^2 \text{ flow rate}}{\text{current}} = \left\{ \frac{22.4 \frac{SL}{mol} 60 \frac{s}{min}}{2 \frac{e^-}{mol} 96500 \frac{As}{e^-}} \right\} = \frac{0.00696 SLM}{A}, \quad (20)$$

where, *SL* is standard liters, *mol* stands for moles, *s* is seconds, *min* is minutes, *A* is amperes, *e⁻* stands for an electron, and *SLM* means standard liters per minute. 22.4 is the number of standard liters in a mole, 2 is the number of electrons in a mole of H₂, and 96500 is the number of A•s generated by one electron.

Similarly, the air flow rate needed to maintain close to 100% O₂ utilization for a 50 cm² MEA was computed using the following equation:

$$\frac{\text{Air flow rate}}{\text{current}} = \left\{ \frac{22.4 \frac{\text{SL, air}}{\text{mol, air}} 60 \frac{\text{s}}{\text{min}}}{0.21 \frac{\text{mol, oxygen}}{\text{mol, air}} 4 \frac{e^-}{\text{mol, oxygen}} 96500 \frac{\text{As}}{e^-}} \right\} = \frac{0.01658 \text{ SLM}}{\text{A}}. \quad (21)$$

However, because we are using air, other molecules, besides O₂, are present; thus, not all of the available O₂ will reach the catalyst surface to react. This can cause O₂ starvation.

However, these concentration losses can be minimized by increasing the air stoichiometry to at least 2 [11]. In other words, by increasing the flow rate of air to twice what is given by (21), the losses created by the other molecules present in air can be overcome, as there will be enough available O₂ to react for the current demanded.

Table 1 shows the hydrogen and air flow rates necessary for peak performance. Because pure H₂ (or pure H₂ with very low CO concentration) was used in each experiment, a stoichiometric ratio of 1 was used for H₂, while a stoichiometric ratio of 2 was used for air, as previously discussed. This chart was used to determine the appropriate flow rate for each experiment. When current pulses were applied, the flow rate corresponding to the maximum current achieved was selected. Thus, this value was used as the controller set point.

Table 1: Gas stoichiometry table: current/gas flow rates for 50 cm² single PEMFC

Current (A)	Hydrogen flow rate (SLM) (S=1)	Oxygen flow rate (SLM) (in air, S=2)	Current (A)	Hydrogen flow rate (SLM) (S=1)	Oxygen flow rate (SLM) (in air, S=2)
1	0.00696	0.03316	41	0.28536	1.35956
2	0.01392	0.06632	42	0.29232	1.39272
3	0.02088	0.09948	43	0.29928	1.42588
4	0.02784	0.13264	44	0.30624	1.45904
5	0.0348	0.1658	45	0.3132	1.4922
6	0.04176	0.19896	46	0.32016	1.52536
7	0.04872	0.23212	47	0.32712	1.55852
8	0.05568	0.26528	48	0.33408	1.59168
9	0.06264	0.29844	49	0.34104	1.62484
10	0.0696	0.3316	50	0.348	1.658
11	0.07656	0.36476	51	0.35496	1.69116
12	0.08352	0.39792	52	0.36192	1.72432
13	0.09048	0.43108	53	0.36888	1.75748
14	0.09744	0.46424	54	0.37584	1.79064
15	0.1044	0.4974	55	0.3828	1.8238
16	0.11136	0.53056	56	0.38976	1.85696
17	0.11832	0.56372	57	0.39672	1.89012
18	0.12528	0.59688	58	0.40368	1.92328
19	0.13224	0.63004	59	0.41064	1.95644
20	0.1392	0.6632	60	0.4176	1.9896
21	0.14616	0.69636	61	0.42456	2.02276
22	0.15312	0.72952	62	0.43152	2.05592
23	0.16008	0.76268	63	0.43848	2.08908
24	0.16704	0.79584	64	0.44544	2.12224
25	0.174	0.829	65	0.4524	2.1554
26	0.18096	0.86216	66	0.45936	2.18856
27	0.18792	0.89532	67	0.46632	2.22172
28	0.19488	0.92848	68	0.47328	2.25488
29	0.20184	0.96164	69	0.48024	2.28804
30	0.2088	0.9948	70	0.4872	2.3212
31	0.21576	1.02796	71	0.49416	2.35436
32	0.22272	1.06112	72	0.50112	2.38752
33	0.22968	1.09428	73	0.50808	2.42068
34	0.23664	1.12744	74	0.51504	2.45384
35	0.2436	1.1606	75	0.522	2.487
36	0.25056	1.19376	76	0.52896	2.52016
37	0.25752	1.22692	77	0.53592	2.55332
38	0.26448	1.26008	78	0.54288	2.58648
39	0.27144	1.29324	79	0.54984	2.61964
40	0.2784	1.3264	80	0.5568	2.6528

3.3.2. *Current pulsing parameters*

Each of the current pulses demanded from the cell had an amplitude between 19 A (0.38 A/cm²) and 70A (1.4A/cm²). 19 A (0.38 A/cm²) was selected as the minimum pulse amplitude applied because a constant current density of 19 A (0.38 A/cm²) or 20 A (0.4 A/cm²) was the set point for most of the experiments, as described in section 3.2. Hence, a 19 A (0.38 A/cm²) pulse is effectively no pulse at a base current density of 19 A (0.38 A/cm²). The maximum pulse amplitude used was 70 A (1.4A/cm²) because as the programmable electronic load switches from the base current density to 70 A (1.4A/cm²), cell voltage spikes can drop below 0 V, which can damage the cell.

The frequencies ranged from 0.25 Hz to 240 Hz and the duty cycle was between 5% and 50%. The lower limit for both frequency and duty cycle were determined by the limitations of the programmable electronic load. 240 Hz was chosen as an upper limit because it is twice the frequency of a ripple current. The highest duty cycle tested was 50% because at duty cycles higher than this, the cell produces the desired voltage less than 50% of the time, which would be undesirable for most applications. The slew rate is the rate at which the current changes with time during the transition phase of a pulse. A sudden increase in cell current is needed to create a large over-potential. Therefore, the slew rate was held constant at the maximum value allowed by the programmable electronic load, 10 A/msec, for each experiment. An example square wave pulse is illustrated in Fig. 11.

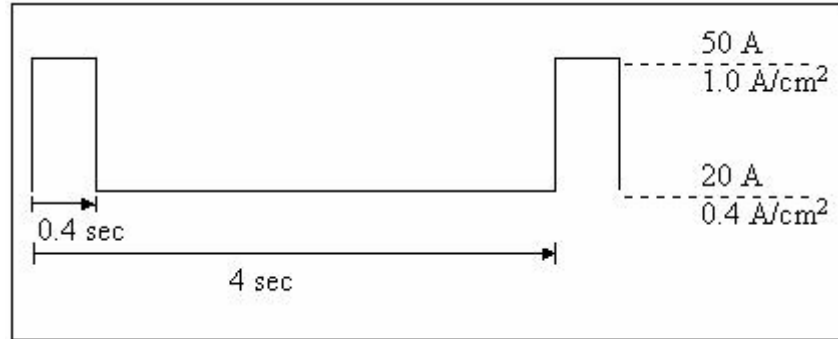


Fig. 11: Variation of current demanded with time. An example of a square wave pulse generated by the electronic load, base current = 0.4 A/cm^2 (20A) pulse amplitude = 1 A/cm^2 (50 A), frequency = 0.25 Hz, duty cycle = 10%, slew rate = 10 A/msec.

4. RESULTS AND DISCUSSION

The results and significance of each experiment conducted are given in the following six sections. As described in section 2.6, the cell performance was determined by the variation of cell voltage with current density, the variation of cell voltage with time, or the variation of current density with time. In the first section, the effect of CO poisoning is illustrated with CO concentrations of 50 and 496 ppm CO. The second section shows the effectiveness of pulsing with 50 ppm CO in the anode fuel on the performance of the fuel cell, while Section 3 discusses the optimum pulsing parameters for this case. The optimum pulsing parameters with 496 ppm CO in the anode fuel are presented in section 4. Section 5 illustrates the effect of “self-oxidation.” In the final section, a comparison of pulsing and “self-oxidation” is presented. A list of each parameter investigated in the experiments described in the following sections is given in Table 2. The number of different parameter values investigated, as well as the range of values tested is also presented in the table. A complete list of each combination of parameter investigated and the significance of each type of experiment is presented in Table 4, in Appendix A.

Table 2: List of the parameters investigated. The number of levels, as well as the range of parameter values tested are listed

parameter	levels investigated	range
base current density	7	0 - 60 A
base voltage	9	0.20 - 0.95 V
CO concentration	3	0, 50, 496 ppm
CO exposure time	10	0 - 20 hours
pulse amplitude	6	19 - 70 A
pulse frequency	7	0.25 - 240 Hz
pulse duty cycle	5	0 - 50%

4.1. Effect of CO in the anode fuel on cell performance with constant cell voltage

During steady-state operation, many of today's reformers produce on the order of 50 ppm CO. However, during start up, approximately 500 ppm CO can be produced. The effect that CO in the anode fuel has on fuel cell performance is of significance because CO is present in natural gas reformat. Therefore, the effect of CO concentrations of 50 and 496 ppm on the cell performance was investigated. The cell was also operated on pure H₂ to establish a baseline level of performance for the experiment. Fig. 12a and 12b show how the CO concentration of the anode fuel affects the current density of the cell with time, while the cell voltage was held constant at 0.6 V (the affect of CO on variation of cell voltage with time is presented in 4.5 with a discussion of "self-oxidation"). The cell voltage was maintained at 0.6 V because maximum cell power output is achieved near this voltage. The test was first performed using pure H₂ as the anode fuel for 19 hours. Using the same MEA the test was repeated with 50 ppm CO in the anode fuel.

After the MEA was exposed to 50 ppm CO, the cell current density significantly decreased due to CO accumulation on the catalyst surface, as illustrated in the plot. Thus, a new MEA was installed before evaluating the 496 ppm CO case. The new MEA was tested to make sure that current density obtained at 0.6 V duplicated (within 10%) the value obtained with the previous MEA on pure H₂ and air. The new MEA had a current density that was 9% lower than the previous unit, while the cell voltage was maintained at 0.60 V. The test was then performed a third time using the new MEA and 496 ppm CO in the anode fuel.

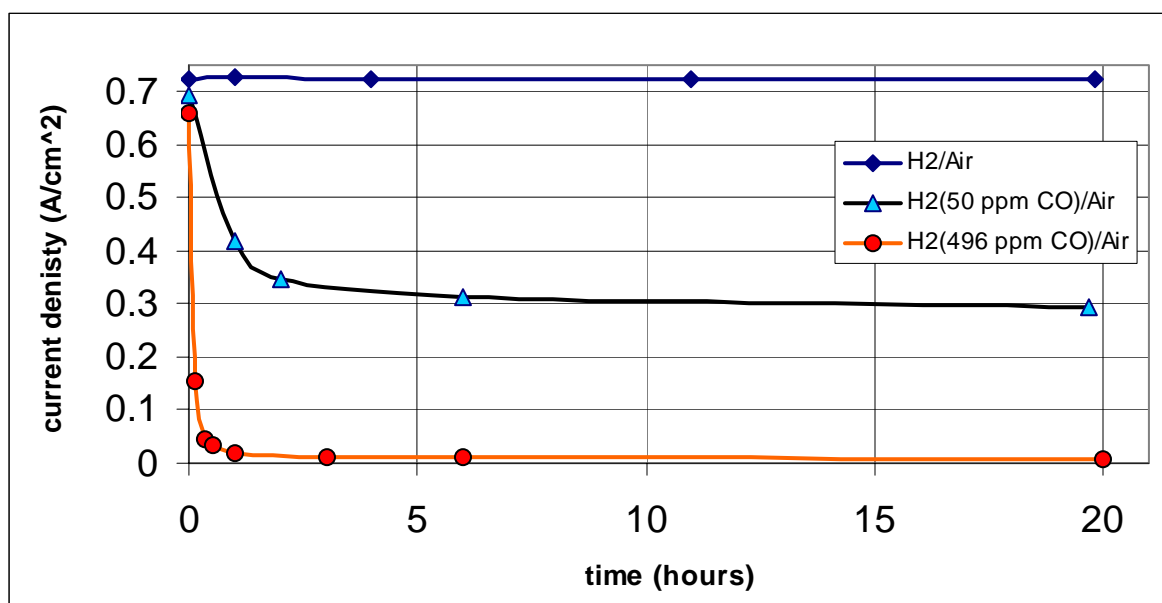


Fig. 12a: Variation of current density with time, using various concentrations of CO in the anode fuel. The cell voltage was held constant at 0.60 V.

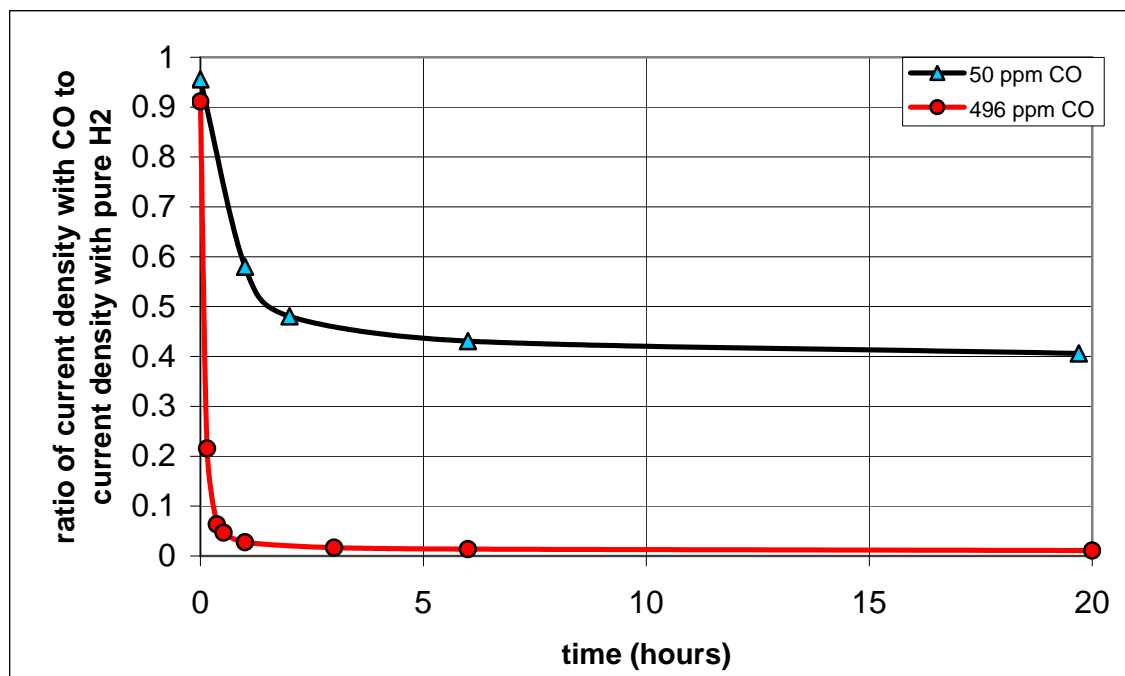


Fig. 12b: Variation with time of the ratio of current density obtained with CO in the anode fuel to the current density obtained with pure H₂ using various concentrations of CO in the anode fuel. The cell voltage was held constant at 0.60 V.

As shown in Fig. 12a, for each of the three cases, the cell performance was very similar before the CO was introduced. However, after CO was introduced into the system, the current density steadily declined until equilibrium was reached. With 50 ppm CO in the anode fuel, the cell current density declined over the first 6 hours. After 7 hours an equilibrium point was reached where the rate of CO absorption equaled the rate of CO oxidation. Hence, with 50 ppm CO in the anode fuel, the current density reached an asymptote at 7 hours. With higher CO concentrations, the catalyst would become saturated more quickly. As shown in Fig. 12a, with 496 ppm CO in the anode fuel, the current density of the cell remains relatively constant after about 2 hours.

Higher CO concentrations also create a greater decline in current density. Fig. 12b gives the current density obtained at a given time with 50 and 496 ppm CO as a ratio of

the current density obtained with pure H₂. This figure shows that after 19.8 hours of 50 ppm CO in the anode fuel, the cell had a current density that was 41% of that obtained with pure H₂. While, with 496 ppm CO, the cell could only achieve 1% of the current density obtained with pure H₂ after 19.8 hours. This demonstrates how detrimental CO is to the performance of PEMFCs. It also illustrates how quickly CO can poison a cell and severely reduce its performance, especially at high concentrations. Most importantly, it indicated that there is a need to find an effective method for increasing the CO tolerance of PEMFCs.

The experiment that produced the results presented in Fig. 12a and 12b was repeated at various cell voltages ranging from 0.20 V to 0.95 V. However, in this experiment, the cell was only exposed to CO 1 hour before data was collected. Fig. 13 shows how the current density of the cell varies with the cell voltage for different concentrations of CO (0, 50, 496 ppm). The experiment was conducted by holding the cell voltage constant at a specific value and recording the corresponding current density, after 1 hour of CO exposure. At cell voltage levels between 0.80v and 0.95v, the cell maintained similar current densities for all three concentrations of CO. However, at cell voltages below 0.60 V, the effect of the CO concentration became more significant and the lower the cell voltage, the more pronounced the effect of CO poisoning became. This is a significant result because the MEAs tested typically produce the most power in the region between 0.40 V and 0.60 V (when pure hydrogen is used as the anode fuel). This can be seen in Fig. 14a. Hence, to obtain the maximum power output possible, fuel cells are typically operated at current densities between 0.40 V and 0.60 V. The cell current densities obtained in this voltage region are significantly less than what is obtained using pure H₂.

With 50 ppm CO in the anode fuel, the current density obtained at 0.4 V is 60% of the value achieved with pure H₂. Only 20% of the current density obtained with pure H₂ at 0.4 V was achieved with 496 ppm CO in the anode fuel. Thus, Fig. 13 illustrates how CO degrades cell performance and the need for finding a way to increase the CO tolerance of PEMFCs. This plot is also consistent with Fig. 12a and 12b in showing that the higher the CO concentration of the anode fuel, the lower the current density, especially for low cell voltage levels.

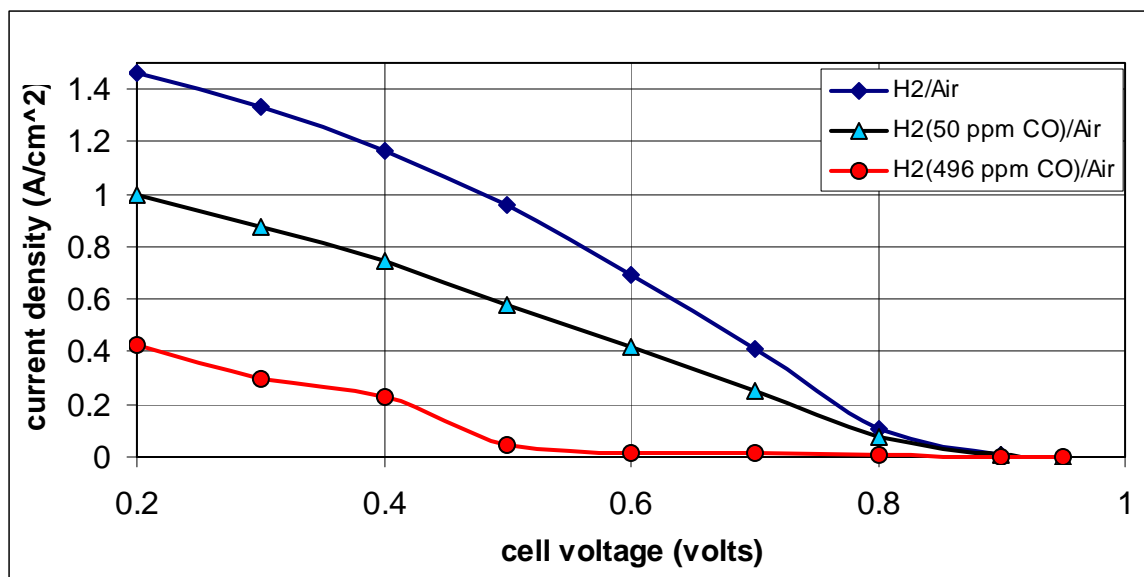


Fig. 13: Variation of current density with cell voltage, using various concentrations of CO in the anode fuel.

In most PEMFC applications, the primary role of the unit is to produce power. Hence, PEMFCs are typically operated at peak power. Thus, the effect of CO poisoning in the cell voltage region where the maximum power occurs warrants further investigation. Fig. 14a displays the variation of power density with cell voltage for various concentrations of CO. As mentioned previously, the peak power for the MEAs tested (operating on pure H₂) is obtained at a cell voltage of approximately 0.50 V.

However, when CO is introduced into the anode fuel, the voltage at which the peak power is obtained decreases to approximately 0.40 V, both for 50 ppm and 496 ppm CO. Fig. 14a also shows that as the CO concentration of the anode fuel increases, the power produced decreases. This shows that CO in the anode fuel significantly reduces the power of a PEMFC in the voltage regions of peak power.

Fig. 14b shows the ratio of power density obtained with CO to the power density obtained with pure H₂ at various cell voltages. This plot shows that the power density decreases the most in the region of peak power. At 0.60 V, with 50 ppm CO in the anode fuel, the power density is 61% of the value obtained with pure H₂. With 496 ppm CO, the power density is only 2% of the value obtained with pure H₂ at 0.60 V. Once again, this illustrates the need for finding an effective method for increasing the CO tolerance of PEMFCs.

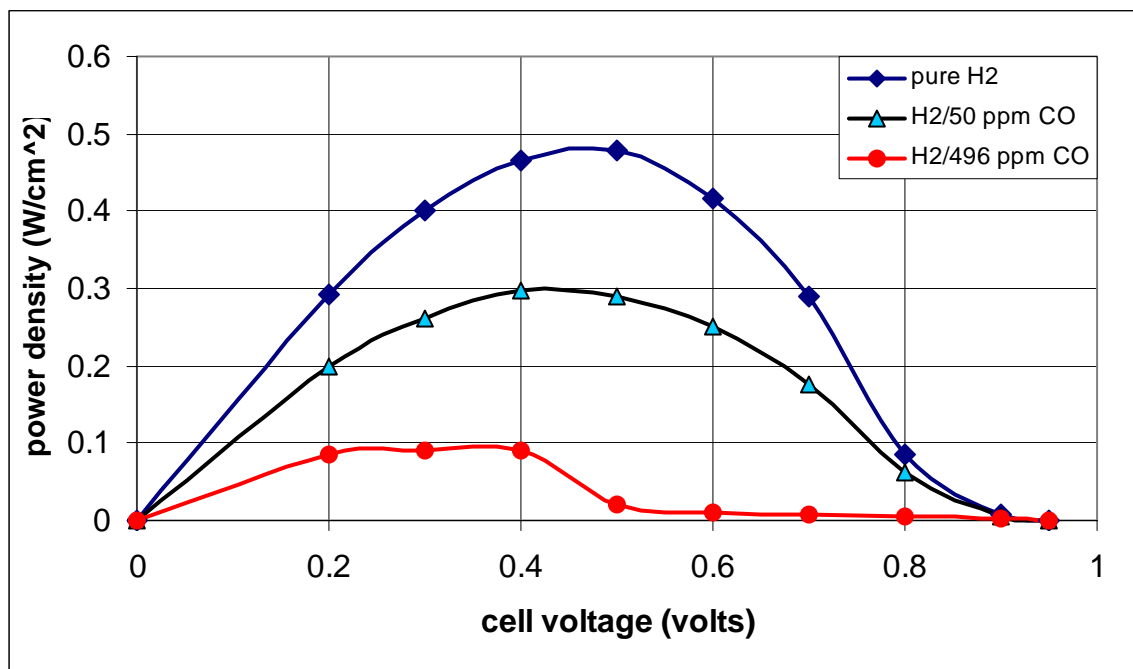


Fig. 14a: Variation of power density with cell voltage, using various concentrations of CO in the anode fuel.

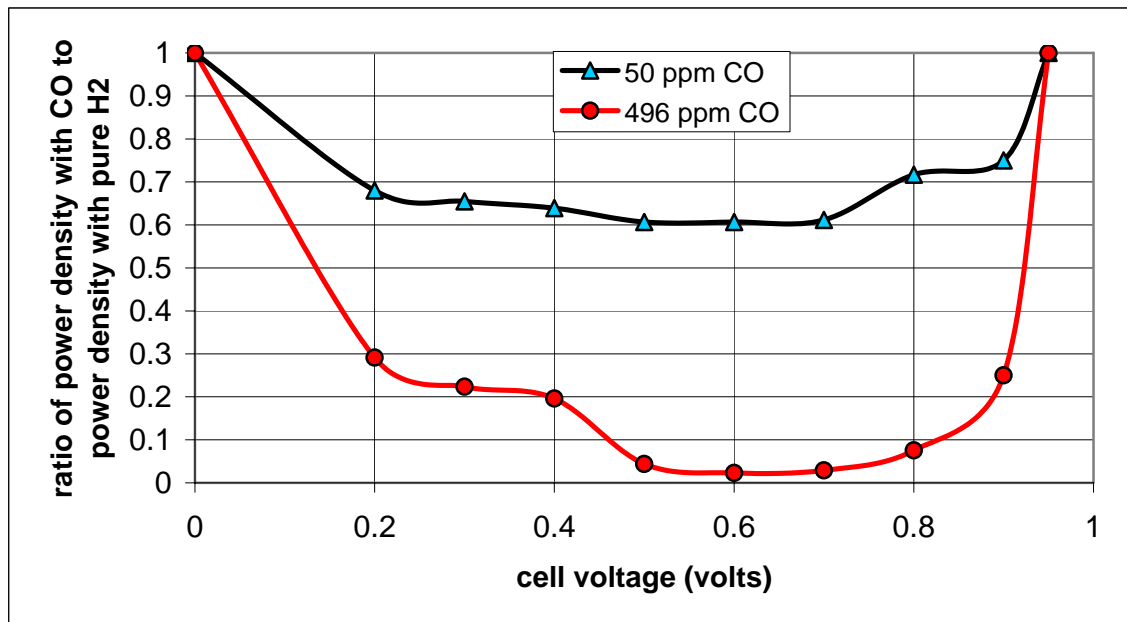


Fig. 14b: Variation with cell voltage of the ratio of power density obtained with various CO concentrations to the power density obtained using pure H₂.

4.2. Effect of current pulsing on cell performance with 50 ppm CO present in the anode fuel

Before determining the most effective pulsing parameters, it was necessary to verify that current pulsing could increase the CO tolerance of a PEMFC. This experiment was conducted using 50 ppm CO because many reformers can maintain this CO concentration during steady state operation. Also, 50 ppm CO is less damaging to the cell performance than 496 ppm CO and it was necessary to first make sure that pulsing was effective in the best-case scenario. In this work, the three pulsing parameters varied were pulse amplitude, frequency, and duty cycle. The values of the current pulsing parameter used in this experiment were based on the results given by Carrette [3]. Fig. 15 shows how pulsing affects the variation of voltage with time using 50 ppm CO in the anode fuel. In

order to create current pulses, the electronic load must be operated in the constant current mode. Thus, after establishing steady-state cell performance on hydrogen and air, the cell was held at a constant current of 19A (0.38 A/cm^2) and 50 ppm CO was introduced into the anode fuel. Cell voltage was recorded for one hour. One hour into the experiment, a current pulse of 60A (1.2 A/cm^2), 0.25 Hz and a duty cycle of 10% was applied to the cell. The cell voltage was then monitored for an additional hour. This pulse corresponds to a 60A pulse that lasts 0.4 sec. every 3.6 seconds. During the 3.6 seconds when the pulse was off, the current was held at 19 A (0.38 A/cm^2).

Fig. 15 illustrates that pulsing was very effective. With 50 ppm CO in the anode fuel, no pulse, and an output current of 19 A (0.38 A/cm^2), the cell voltage dropped from 0.68 V to 0.41 V (a drop of 40%) in one hour. When pulsing began, the cell voltage immediately increased to 0.68 V (the value obtained with pure H_2) and remained within 3% (0.66 V) of the voltage obtained with pure H_2 , over the course of the next hour. Thus, after one hour of CO poisoning, a pulse of a 60 A (1.2 A/cm^2) and 0.25 Hz, with a 10% duty cycle immediately increased the cell voltage by 66% (0.41 V to 0.68 V). Furthermore, these pulsing parameters allow the cell to maintain a voltage that is at least 97% of the voltage obtained on pure H_2 over the course of an hour. Hence, the results of this experiment show that pulsing is effective in increasing the CO tolerance of a PEMFC at a constant current of 19 A (0.38 A/cm^2).

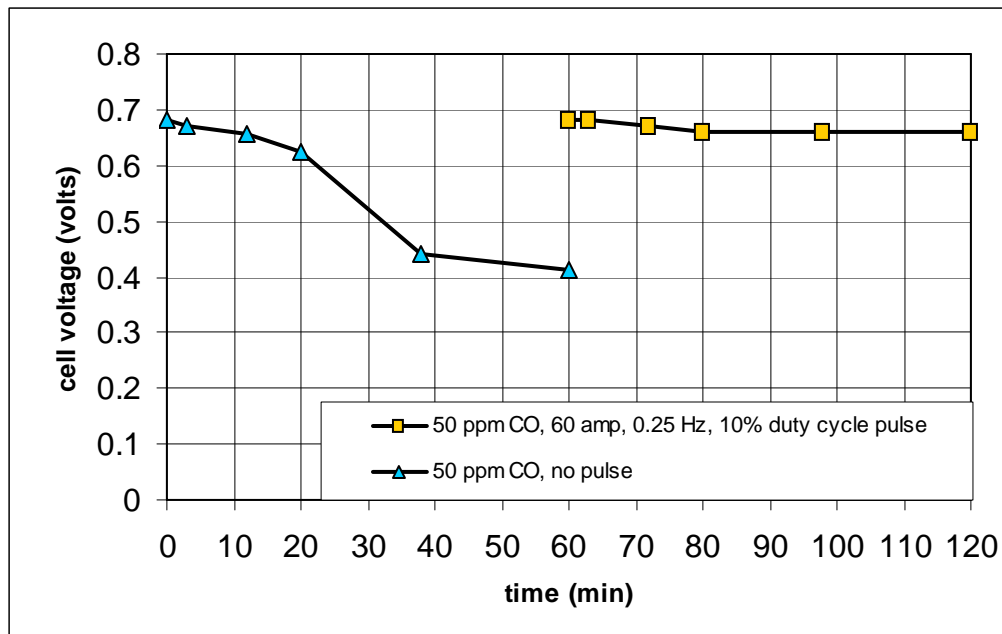


Fig. 15: Variation of cell voltage with time, with 50 ppm CO in the anode fuel for one hour. The base current was held constant at 0.38 A/cm^2 (19A). After one hour with no pulse, a pulse was applied for an hour. Pulse amplitude, 1.2 A/cm^2 (60 A); frequency, 0.25 Hz; duty cycle 10%; slew rate, 10 A/msec. (i.e. pulse duration = 0.4 sec every 3.6 sec).

The results presented in Fig. 15 show that pulsing is effective in increasing the CO tolerance of the cell for a constant current of 19 A (0.38 A/cm^2). However, it is also important to see how pulsing effects the cell at different current densities and how the cell voltages obtained with pulsing in the presence of CO compare to those obtained with pure H_2 . To evaluate the effect of pulsing at a variety of current densities, the variation of cell voltage with current density was investigated. The cell behavior using pure hydrogen was characterized first. 50 ppm CO was then introduced into the anode fuel. After one hour of CO poisoning, data was collected. A pulse of 60 A, 0.25 Hz, and 10% duty cycle was applied and data was recorded. Fig. 16 shows the variation of the ratio of cell voltage to the cell voltage obtained using pure hydrogen with current density. The plot indicates that 50 ppm CO in the anode fuel does not significantly degrade cell performance at low current densities (0 to 0.20 A/cm^2), as 85% of the cell voltage

obtained with pure H₂ is still achieved. However, at higher current densities (0.40 to 1.20 A/cm²) the 50 ppm CO in the anode fuel has a larger effect. For example, at 1.20 A/cm², the cell voltage is only 58% of that obtained with pure H₂. When pulsing is applied, we see that 97% of the voltage obtained with pure H₂ is achieved at 0.2 A/cm², while only 85% of the value obtained with pure H₂ was obtained without pulsing. Even at a current density of 1.00 A/cm² the cell performs at 77% of the value achieved on pure hydrogen, while only 58% is obtained without pulsing. On average, pulsing increased the cell voltage by 25% between 0.20 and 1.00 A/cm². Thus, this plot shows that pulsing is effective in increasing CO tolerance until the base current reaches the pulse current at 1.2 A/cm² (hence, at this point, there is actually no pulse). For pulsing to be effective at a current density of 1.2 A/cm² the pulse amplitude must be increased to a larger value.

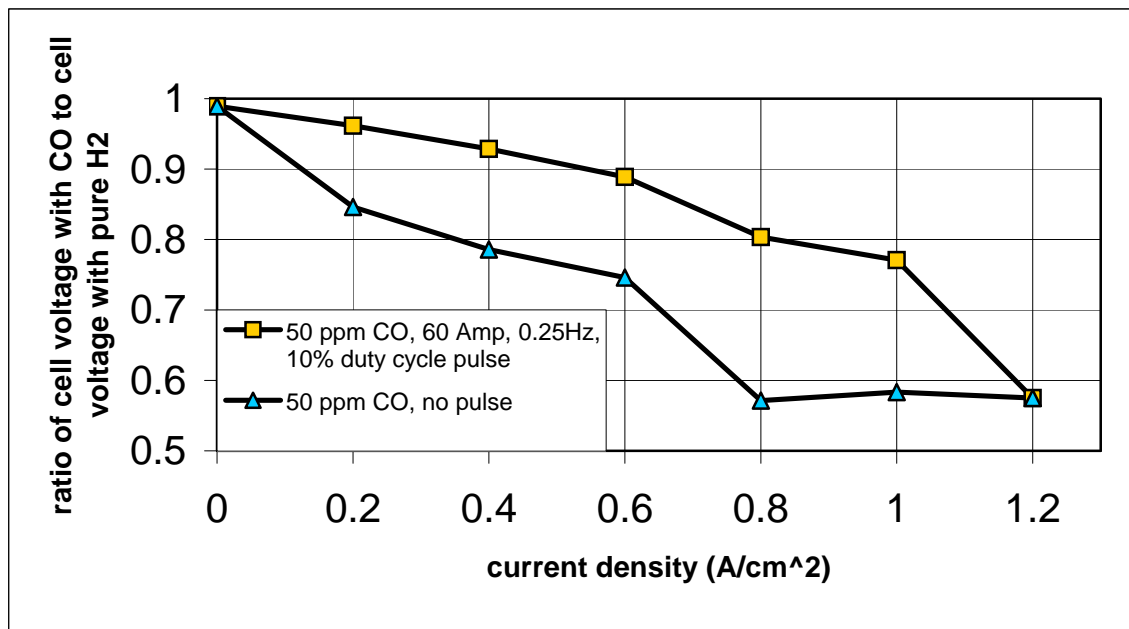


Fig. 16: Variation with current density of the ratio of cell voltage to the voltage obtained using pure H₂. 50 ppm CO was introduced into the anode fuel. Data was taken with no pulse and with a pulse amplitude, 1.2 A/cm² (60 A); frequency, 0.25 Hz; duty cycle 10%; slew rate, 10 A/msec.

4.3. Effect of pulse amplitude, frequency, and duty cycle on cell performance with 50 ppm CO present in the anode fuel

After verifying that pulsing can be an effective means for increasing the CO tolerance of a PEMFC, the effect of pulse amplitude, frequency, and duty cycle were investigated to determine their effect on CO tolerance and to attempt to identify the optimal pulsing parameters. The effect of pulse amplitude is discussed in the first section. In the second section, the effect of frequency and duty cycle is presented.

4.3.1. Effect of pulse amplitude, at a constant frequency and duty cycle, on cell performance with 50 ppm CO present in the anode fuel

The significance and effectiveness of pulse amplitude were evaluated first, while frequency and duty cycle were held constant. The measure of cell performance used for this test was the cell voltage at a particular current density. In this work, pulse amplitude is defined as the cell current (or current density) at the peak of the pulse, regardless of the base current. Fig. 17 shows the variation of cell voltage with pulse amplitude using 50 ppm CO in the anode fuel and a base current of 19A (0.38 A/cm²). A relatively low base current (approximately 20 A, 0.40 A/cm²) was selected to allow a large range of pulse amplitudes to be investigated, as the pulse amplitude must be higher than the base current for pulsing to have an effect. By looking at a large range of pulse amplitudes, trends in pulsing effectiveness could be identified more easily. The pulse frequency and duty cycle were held constant at 0.25 Hz and 10%, respectively. The plot illustrates that the pulse amplitude does affect the CO tolerance of the unit (that is, cell voltage increases) and the effect increases with an increase in pulse amplitude. A pulse amplitude of 70A

(1.4 A/cm²) yields the highest cell voltage, as it was the highest amplitude investigated.

With a 70A pulse, a cell voltage of 0.71 V was obtained. Thus, the higher the pulse amplitude, the more CO is electro-oxidized into CO₂.

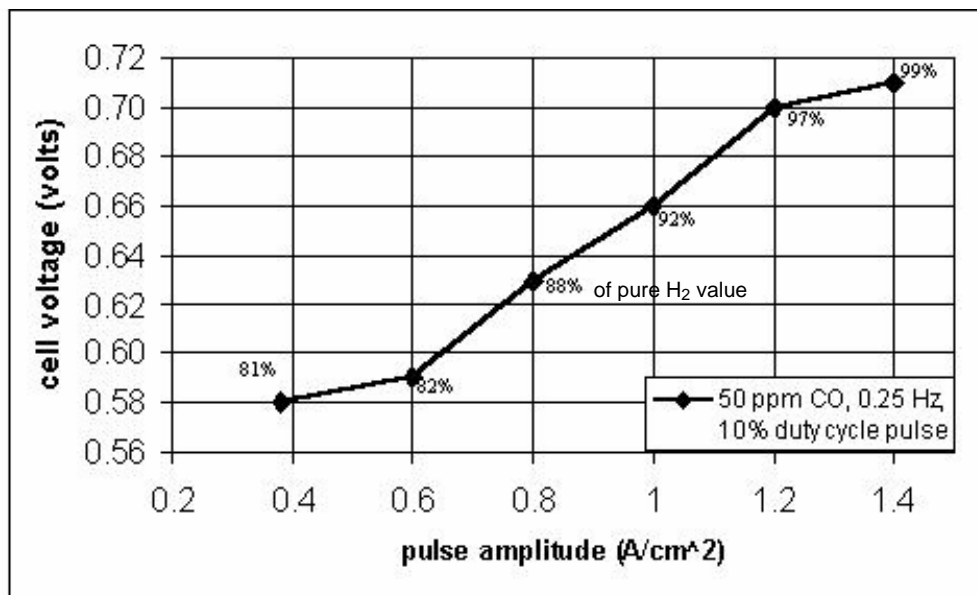


Fig. 17: Variation of cell voltage with pulse amplitude, with 50 ppm CO in the anode fuel and base current held constant at 0.38 A/cm² (19 A). Frequency, 0.25 Hz; duty cycle 10%; slew rate, 10 A/msec. The percentage of the cell voltage obtained as compared with the value obtained using pure H₂, is given for each pulse amplitude.

Fig. 17 also gives the percentage of the cell voltage obtained as compared with the value obtained using pure H₂, for each pulse amplitude investigated. This plot shows that with a pulse of 70A, 99% of the pure H₂ voltage was obtained with this MEA. However, a pulse of 60A (1.2 A/cm²) or higher is capable of shorting the cell and possibly creating a negative cell voltage spike if the catalyst is already heavily poisoned when the pulse is first applied. A 50A pulse produced a cell voltage of 0.66 V, which is still 92% of the voltage obtained using pure H₂. Hence, in this case, a pulse of 50A (1.0 A/cm²) was considered to be the most effective pulse amplitude because it resulted in the highest cell voltage without posing the threat of damaging the cell.

4.3.2. Effect of pulse frequency and duty cycle, at a constant pulse amplitude, on cell performance with 50 ppm CO present in the anode fuel

Once the most effective current pulse amplitude was determined (50 A or 1.0 A/cm²), the next step was to investigate the effect and significance of pulse frequency and duty cycle on cell performance. In the first section, the effect of pulse frequency and duty cycle was determined to see which combination of parameters resulted in the best cell performance. In the second section a discussion of the effect that a simulated ripple current had on cell performance is given.

4.3.2.1. General effect of pulse frequency and duty cycle

In this section the effect of pulse frequency and duty cycle was investigated and the optimum values for these parameters were determined. Fig. 18 shows the variation of cell voltage with duty cycle at various pulse frequencies. The base current was held constant at 20A (0.4 A/cm²) and the pulse amplitude applied was 50 A (1.0 A/cm²). The base current was selected to maintain consistency with section 4.3.1. A pulse amplitude of 50 A (1.0 A/cm²) was determined to be the most effective in the previous section; therefore, it was used as the pulse amplitude in this experiment. Since the cell voltage could slightly decrease between pulses, the minimum value was recorded and plotted in Fig. 18. This decrease in cell potential resulted from CO poisoning and could be considerable if the length of time between pulses was too great. For the case of 50 ppm, the voltage drop between pulses was not significant because of the low rate of CO accumulation on the catalyst surface at this concentration. The greatest voltage decrease occurred for the low frequency cases (0.5 and 0.25 Hz) because the time between pulses

was the greatest at these frequencies. Even for these cases the difference between the maximum and minimum cell voltage was only 0.01V, which is less than the uncertainty associated with this measurement ($\omega_v = 0.012$ V). The drop in voltage between pulses was more significant at the higher concentration of 496 ppm CO as will be shown in section 4.4.

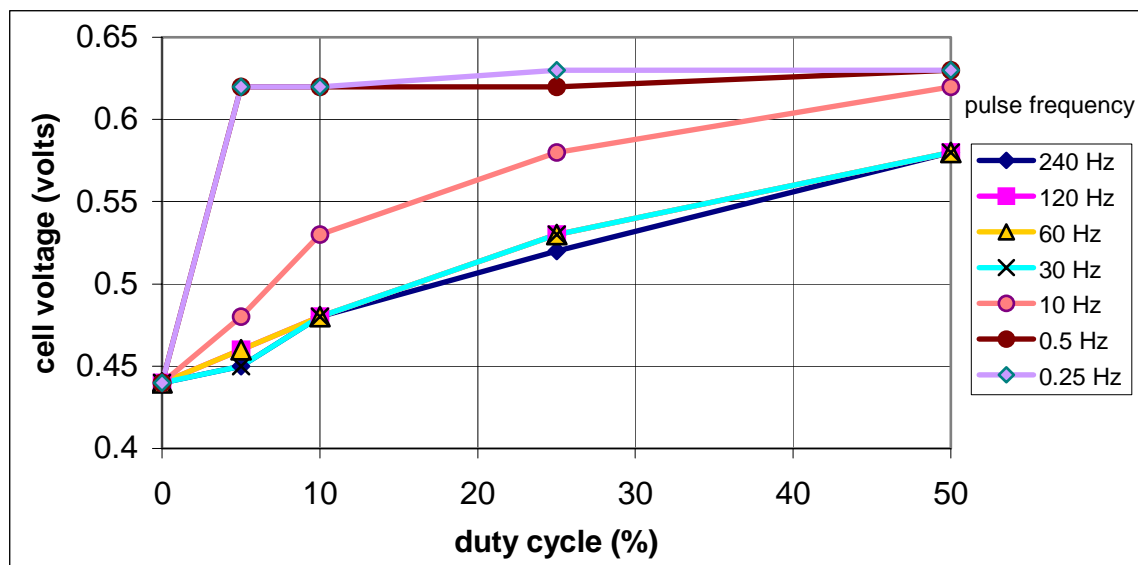


Fig. 18: Variation of cell voltage with duty cycle for different pulse frequencies. The base current was held constant at 0.4 A/cm^2 (20 A). Pulse amplitude, 1 A/cm^2 (50 A); slew rate, 10 A/msec. With no pulse, the cell voltage is 0.44V.

This plot indicated that all pulsing frequencies and duty cycles investigated have a positive effect on cell performance in the presence of 50 ppm CO. However, it also shows that high frequencies are less effective than lower frequencies because the pulse duration is not long enough to completely oxidize the CO from the catalyst. Thus, at the highest frequencies from 30 Hz to 240 Hz the results are almost identical, showing a small effect. However, all frequencies did result in an increased CO tolerance of the system, especially at a duty cycle of 50%. This is due to the fact that a 50% duty cycle creates the longest pulse duration for a given frequency, of any of the duty cycles tested.

Thus, within the parameters tested, pulsing becomes more effective as frequency decreases and duty cycle increases. Therefore, a 50A, 0.25 Hz pulse with a 50% duty cycle proves to be the most effective in increasing the CO tolerance of the fuel cell. A frequency of 0.25 Hz and a 50% duty cycle corresponds to a pulse every 4 seconds that lasts 2 seconds.

When exposed to 50 ppm CO, without pulsing, the cell voltage was 0.44 V at 20 A (0.4 A/cm^2) after one hour. When the cell was operated using pure H_2 , the cell voltage was 0.70 V at 20A (0.4 A/cm^2). By using these parameters (50A pulse, 0.25 Hz, 50% duty cycle), the cell voltage obtained was increased from 0.44 V to 0.63 V (an increase of 43%). Furthermore, the cell voltage obtained, when operating with these values for the parameters, is 90% the value achieved with pure H_2 .

Although these parameters (0.25 Hz and 50% duty cycle) yield the highest CO tolerance, the 50% duty cycle only allows the cell to operate at the desired voltage and current 50% of the time. At 0.25 Hz, a 5% duty cycle cuts the pulse duration to only 0.2 seconds every 3.8 seconds. Hence, the cell can produce the desired current and voltage 95% of the time. Furthermore, employing a 5% duty cycle only causes the cell voltage to decrease 0.01 V from the value obtained with a 50% duty cycle. Therefore, a 50A, 0.25 Hz pulse with a 5% duty cycle appears to be the most effective pulse because it allows the system to maintain the desired voltage and current for a higher percentage of the time with negligible loss of performance, as compared with higher pulse frequencies and duty cycles.

4.3.2.2. Effect of ripple current pulse frequency and duty cycle

A typical ripple current that results from converting DC to single phase 60 Hz, AC power via an inverter, has a frequency of 120 Hz and a 50% duty cycle. As previously mentioned, the frequency and duty cycle of a ripple current are of particular interest because they could be present in a fuel cell system used to generate AC power. Therefore, if ripple currents are effective in increasing CO tolerance, no pulse triggering or additional electronics would be needed. Thus, the cost and complexity of the system could be reduced. While the most effective value of the parameters have been determined, it is still necessary to investigate the parameters similar to those commonly seen in a ripple current.

As illustrated in Fig. 18, with a base current of 20 A and 50 ppm CO in the anode fuel, applying a 50 A, 120 Hz pulse with a 50% duty cycle produces a cell voltage of 0.58V. This increases the cell voltage by 32% over the value obtained without pulsing, but the desired power is only obtained 50% of the time. This means that the ripple current duty cycle and frequency is less effective than the optimal parameters previously discussed (0.25 Hz, 5% duty cycle), when considering the cell voltage obtained and the percentage of time the desired cell power is obtained. That is, a 0.25 Hz pulse with a 5% duty cycle can improve the cell performance by 43% and maintain the desired voltage and current 95% of the time, whereas a ripple current results in 32% of the desired power, 50% of the time.

Fig. 19 further illustrates the difference between a ripple current and 0.25 Hz, 5% duty cycle current pulse. Due to limitations in resolution, the ripple current cannot be displayed accurately using this time scale, but this plot is still useful in showing the

difference between a ripple current and low frequency, low duty cycle current pulse. A typical ripple current is given in Fig. 5 on a smaller time scale. In Fig. 19 we see that with a pulse of 0.25 Hz and a 5% duty cycle, the pulse is only on for a small fraction of the time. With the ripple current, the cell current is always in transition, which makes the power produced by the cell more difficult to condition into useful power. Hence, a ripple current can increase the CO tolerance of a PEMFC, but it is not the most effective method.

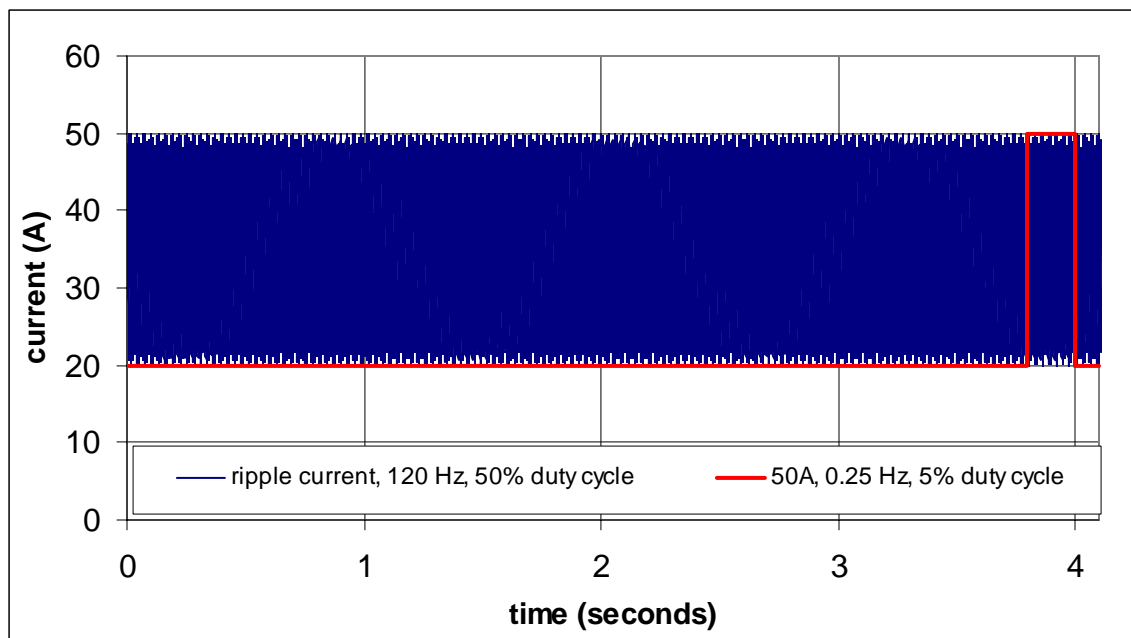


Fig. 19: Variation of current with time: comparison of a 50A, 0.25 Hz, 5% duty cycle with a ripple current (a 50A, 120 Hz, 50% duty cycle). The base current was held constant at 20 A (0.4 A/cm^2).

4.4. Effect of pulsing and variation of pulsing parameters with 496 ppm CO in the anode fuel

In section 4.3.2.1, the optimum pulsing parameters were determined for a PEMFC with 50 ppm CO in the anode fuel because most of the reformers currently available are

capable of producing 50 ppm CO or less after a warm up period of up to 2 hours. However, during this warm up period, many reformers produce CO concentrations near 500 ppm CO. Therefore, it is important to find a way to increase the CO tolerance of the cell during this period, as 500 ppm can quickly poison the cell. Pulsing is a possible solution. Hence, the effect of pulsing with approximately 500 ppm (496 to be exact) CO in the anode fuel is investigated and the optimum values for the parameters are determined in this section.

As shown in section 4.3, the most important variables in determining the effectiveness of a current pulse are amplitude, pulse duration, and time between pulses. A pulse amplitude of 50 A was chosen once again because, as shown in section 4.3.1, it is large enough to effectively oxidize CO, but small enough not to short out the cell. The pulse duration and the time between pulses can both be varied by maintaining a constant duty cycle and varying the pulse frequency. Thus, by employing this method, the most effective pulsing cycle was determined.

Fig. 20 shows the variation of cell voltage with pulsing frequency. The duty cycle was fixed at 20% and the current was held at 20 A (0.4 A/cm^2). A 20% duty cycle was selected after evaluating the results of preliminary experiments. The base current was once again held at 20 A to be consistent with the previous experiments. After each 50 A (1.0 A/cm^2) pulse, the cell voltage immediately increased to 0.65 V. However, as discussed in section 4.3.2.1, the cell voltage decreased between pulses as the catalyst became poisoned. As before, the lowest cell voltage obtained between pulses was recorded.

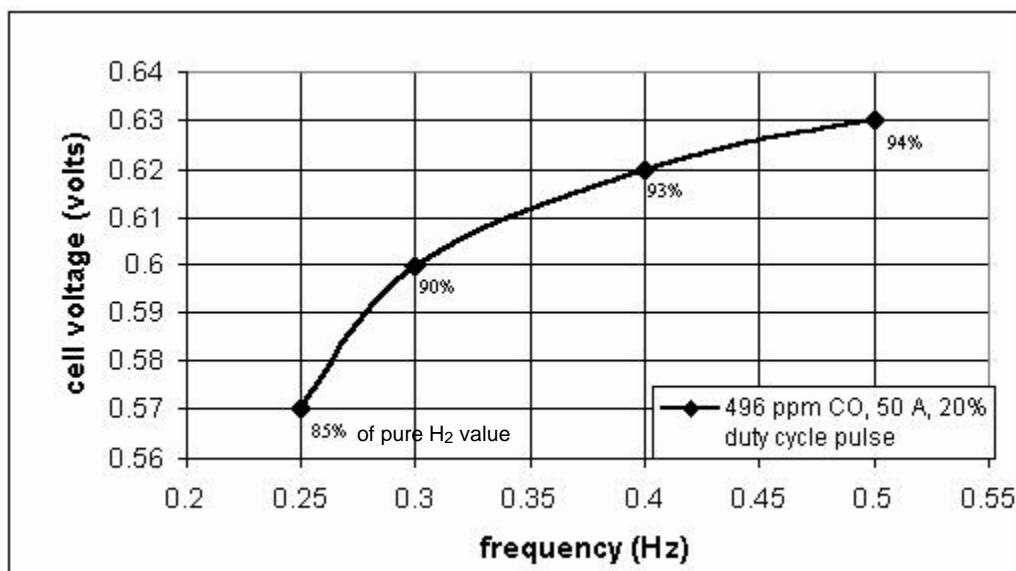


Fig. 20: Variation of cell voltage achieved with pulse frequency. 496 ppm CO is present in the anode fuel. The cell current was held constant at 0.4 A/cm^2 (20 A) and the pulse amplitude was 50 A. In each case, the maximum voltage obtained was 0.65 V. The duty cycle was set at 20%.

The lowest frequency used was 0.25 Hz, which corresponds to a 50A pulse that lasts 0.8 seconds every 4 seconds. The pulse was long enough to completely oxidize CO from the catalyst surface (that is, immediately after each pulse, the cell voltage reached 0.65 V), but, as shown in the plot, the time between pulses was so long that the cell voltage dropped to 0.57 V before the next pulse. As shown in Fig. 20, 0.57 V is only 85% of the value obtained with pure H₂. The minimum cell voltage obtained between pulses increased as the frequency increased. The most effective frequency investigated was 0.5 Hz, which corresponds to a pulse duration of 0.4 seconds every 2 seconds. The 0.4 second pulse was long enough to bring the cell voltage up to 0.65 V and the 1.6 seconds between pulses allowed the voltage to only drop to 0.63 V before the next pulse began. With pure H₂, this MEA obtained 0.67 V at 20 A (0.4 A/cm^2). Thus, for a pulse of 50 A, 0.5 Hz and a 20% duty cycle, the lowest voltage obtained between pulses (0.63 V) is still 94% of that obtain using pure H₂. The cell maintains the desired voltage 80% of the

time, due to the 20% duty cycle. The variation of cell current with time that occurs using a pulse of 50 A, 0.5 Hz, and a 20% duty is presented in Fig. 21a. This plot shows that the base current of 20 A is obtained approximately 80% of the time. Fig. 21b shows how the corresponding cell voltage varies with time for the same pulsing parameter values. In this plot the voltage drop from 0.65 V to 0.63 V between pulses can be seen.

Based on the results of this experiment, a 50 A (1.0 A/cm^2), 0.5 Hz, 20% duty cycle pulse is the most effective in increasing the CO tolerance of a PEMFC with 496 ppm CO in the anode fuel. Comparing this finding with the results obtained in 4.3 illustrates that for the cell to maintain a voltage between 0.63 V and 0.65 V, the time between pulses decreases as the CO concentration increases. However, the time needed to oxidize CO does not appear to depend on the CO concentration as heavily.

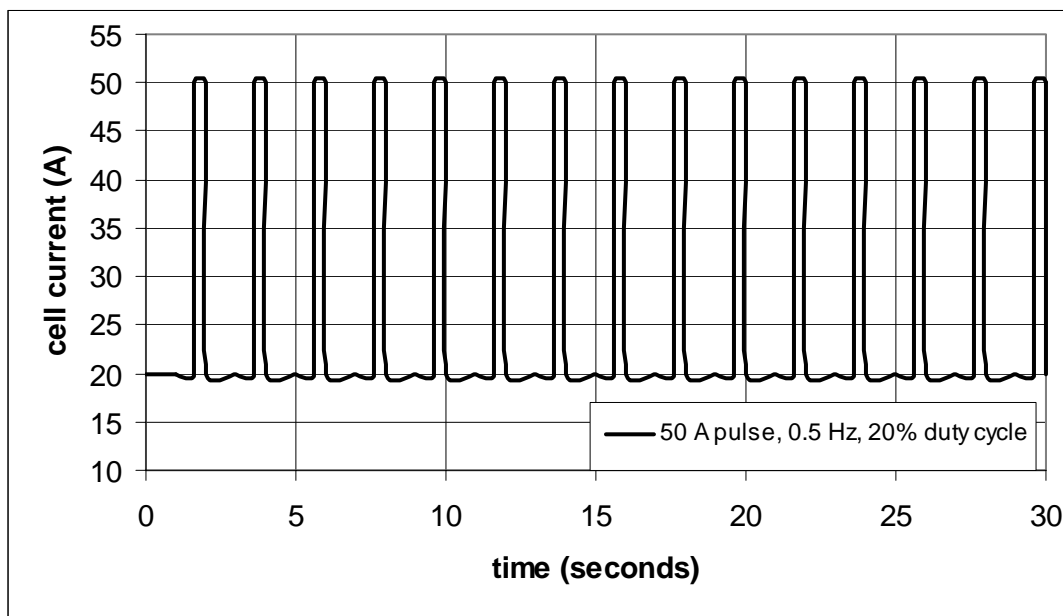


Fig. 21a: Variation of cell current with time created by the “most effective” pulsing parameter values for the 496 ppm CO case. The base cell current was held constant at 20 A (0.4 A/cm^2) and the pulse amplitude was 50 A. The frequency was 0.5 Hz and the duty cycle was set at 20%.

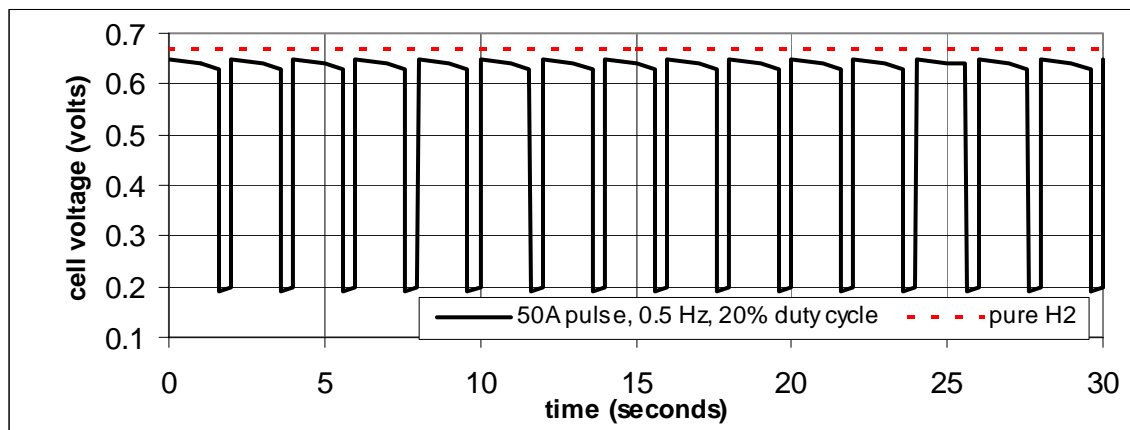


Fig. 21b: Variation of cell voltage with time obtained by employing the “most effective” pulsing parameter values for the 496 ppm CO case. The base cell current was held constant at 20 A (0.4 A/cm^2) and the pulse amplitude was 50 A. The frequency was 0.5 Hz and the duty cycle was set at 20%. The cell voltage obtained using pure H_2 is also shown (0.67 V).

4.5. Effect of CO on cell performance with constant current density: “self-oxidation”

The results given in section 4.1 (showing the effects of 50 and 496 ppm CO on the cell performance) were obtained by demanding a constant cell voltage and recording the corresponding current density. However, it is also important to determine system performance in the presence of CO when the current density is held constant and the voltage is allowed to vary because as CO accumulates on the catalyst surface, the anode over-potential increases to meet the current demanded, and “self-oxidation” can occur. This process is described in greater detail in section 2.4.

Fig. 22 shows the variation of cell voltage with time, both with pure H_2 and with 50 ppm CO in the anode fuel. The cell current was held constant at 20 A (0.4 A/cm^2) and the corresponding voltage was recorded for 3 hours. With pure H_2 as the anode fuel, the cell voltage remained constant at 0.67 V. With 50 ppm CO in the anode fuel, the cell

voltage dropped steadily for about 1 hour. After 1 hour, the voltage remained constant because the rate of CO oxidation was equivalent to the rate of CO adsorption; hence, an equilibrium point is reached and the cell voltage remains constant at 0.37 V. “Self-oxidation” did not occur because the over-potential never reached a large enough value to completely oxidize the adsorbed CO.

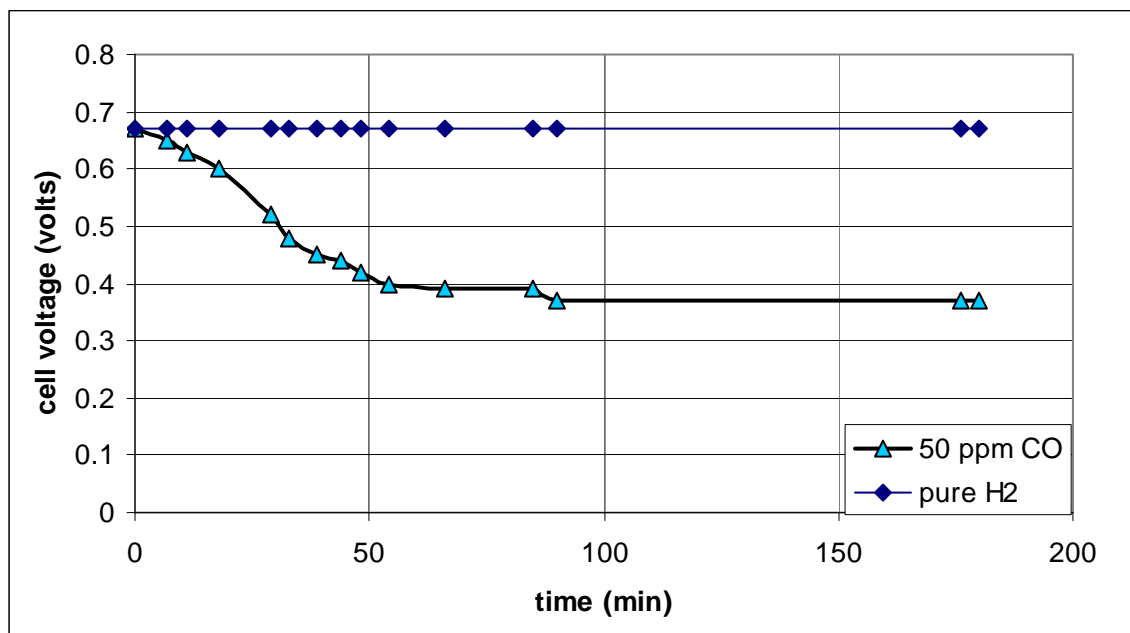


Fig. 22: Variation of cell voltage with time, with pure H₂ and with 50 ppm CO in the anode fuel. The cell current was held constant at 0.4 A/cm² (20 A).

The experiment shown in Fig. 22 was repeated using 496 ppm CO. However, the results were quite different. Fig. 23 shows the variation of cell voltage with time, with 496 ppm CO in the anode fuel. The cell current was held constant at 20A (0.4 A/cm²). This Fig. show that when 496 ppm CO is introduced into the anode fuel and as CO accumulates on the catalyst surface, the cell voltage continues to drop for approximately 5 seconds until it reaches 0.20 V and the anode over-potential becomes large enough to

completely oxidize CO from the catalyst surface. At that time, the voltage increased rapidly back to its original level (0.63 V). This phenomenon is known as sustained potential oscillations or “self-oxidation” [4]. After running the cell with 496 ppm CO in the anode fuel for 10 minutes, “self-oxidation” occurred approximately every 5 seconds. Thus, as explained in section 2.4, with the aid of the low CO oxidation potential created by the Ru catalyst, CO poisoning is automatically controlled when the cell is held at a constant current with 496 ppm CO in the anode fuel. This finding is significant because it indicates that CO tolerance can be increased without the use of additional electronics to provide a current pulse to the system or employing the ripple current. Thus, with “self-oxidation” the CO tolerance is increased and the cost and complexity of the fuel cell power generation system can be reduced because pulsing does not have to be employed. The results presented in this work have shown that both pulsing and “self-oxidation” are effective in increasing the CO tolerance of a PEMFC, but a comparison of these methods must be made to determine which method is most effective.

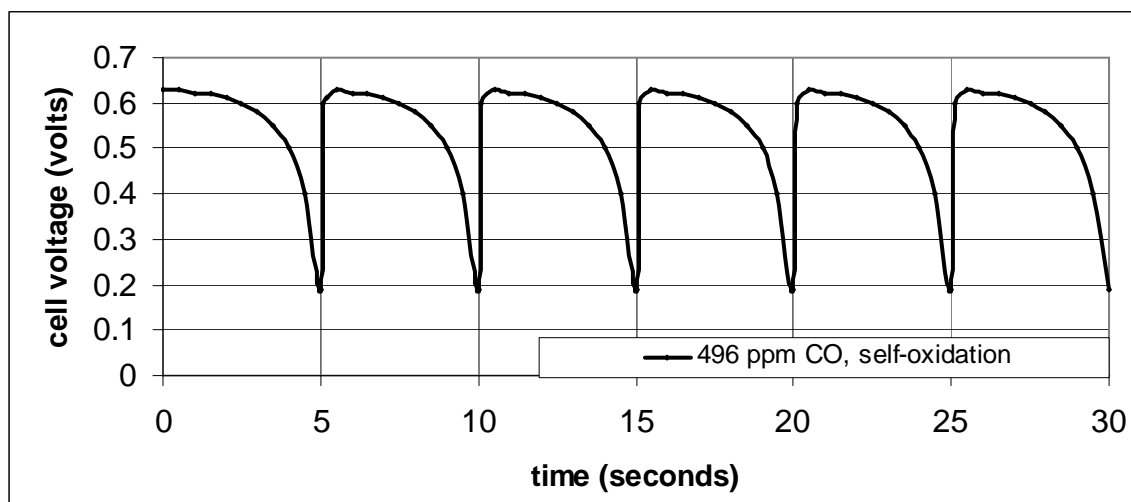


Fig. 23: Variation of cell voltage with time, with 496 ppm CO in the anode fuel. The cell current was held constant at 0.4 A/cm^2 (20 A). After 10 min. of 496 ppm CO in the anode fuel, this pattern remains consistent.

4.6. Comparison of pulsing and “self-oxidation” with 496 ppm CO in the anode fuel

The results presented in this work have shown that both pulsing and “self-oxidation” are effective in increasing the CO tolerance of a PEMFC. Although pulsing has been shown to be a simple and effective means for increasing CO tolerance, the pulse must still be triggered, which involves introducing additional electronics into the system. With 496 ppm CO in the anode fuel, the “self-oxidation” method presents a simple alternative, since no auxiliaries are required. The only thing needed is for the cell to be run at a constant current with an anode having an approximate catalyst loading of 0.4 mg/cm^2 Pt and 0.2 mg/cm^2 Ru. Thus, it is important to compare the effectiveness of pulsing with “self-oxidation.” Five different performance measures for comparison will be discussed in this section. For a technique to be considered effective in increasing CO tolerance, it must successfully increase CO tolerance with minimal interference of normal cell operation. Hence, the measures used to compare pulsing with “self-oxidation” were: percentage of time under normal operation; total energy output; average power; and maximum voltage. These are discussed in the following sections.

4.6.1. Percentage of time under normal operation

In order to be an effective power generation unit, a fuel cell must produce the desired voltage for a large percentage of the time. In this work, the desired voltage is defined as 90% or greater of the voltage obtained using pure H_2 as the anode fuel. The percentage of time that each method allows the cell to produce the desired voltage is of interest because the goal is to determine the most effect method of increasing CO tolerance. Fig.

24 shows the variation of cell voltage with time using 496 ppm CO in the anode fuel, both with pulsing and “self-oxidation.” The pulsing parameters determined to be most effective (50 A, 0.5 Hz, 20% duty cycle), as discussed in section 4.5, were used. As, previously discussed, “self-oxidation” occurs when no pulsing is applied. As shown in Fig. 24 (dashed lines), when “self-oxidation” occurs the cell voltage is continuously varying, which makes the power output by the cell more difficult to condition into useful power. With pulsing, the cell voltage is relatively constant except during the quick transition periods when the pulse is turned on or off.

This plot indicates that pulsing allows the system to maintain normal operation (that is, behave in a manner similar to that obtained using pure H₂) for a higher percentage of the time than “self-oxidation.” In this case normal operation is defined as any cell voltage of 0.60 V or above because 0.60 V is 90% of the value obtained with pure H₂ (0.67V). “Self-oxidation” only maintains a voltage above 0.60 V about 50% of the time, while with pulsing, 0.60V or greater is maintained 80% of the time. Thus, when considering percentage of time at normal operation (a cell voltage of 0.60V or above), pulsing is more effective than “self-oxidation.”

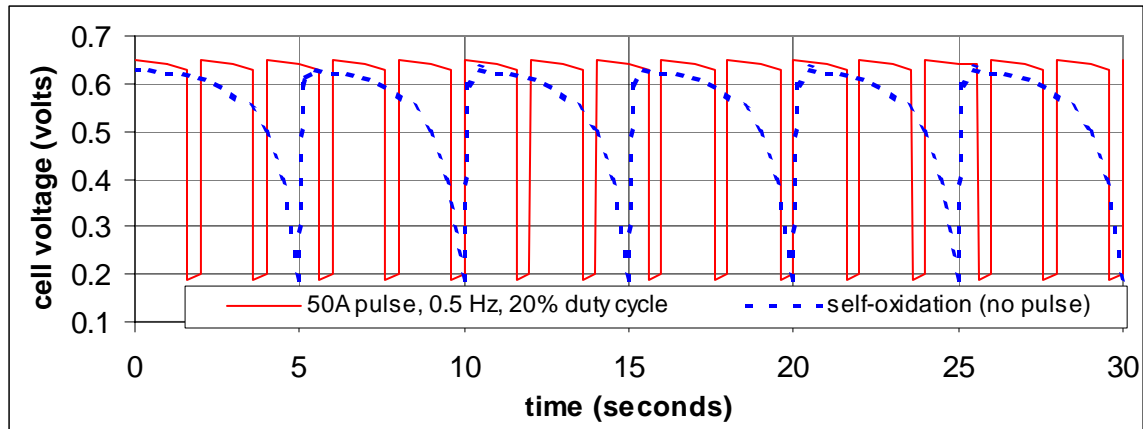


Fig. 24: Variation of cell voltage with time using 496 ppm CO in the anode fuel. Data was collected with and without a pulse. Base cell current was held constant at 20A (0.4 A/cm²). The pulse was 1.0 A/cm² (50A), 0.5 Hz, with a 20% duty cycle.

4.6.2. Energy and average power

Another way to compare the effectiveness of the two methods is to compare the Energy and average power produced in each case. The performance of a fuel cell is often characterized by the power it can produce. Thus, both energy and average power output are useful metrics in evaluating the two methods of increasing CO tolerance.

Energy can be determined with the following equation:

$$E = \int I(t) v(t) dt . \quad (22)$$

The integral was evaluated from 0 to 20 seconds, as both methods have completed an even number of cycles at this point. The variation of cell voltage with time, used to evaluate the integral is given in Fig. 24, while the corresponding cell current is given in Fig. 25. Fig. 25 shows the variation of cell current with time for pulsing and “self-oxidation.” With “self-oxidation,” no current pulses are applied; thus, the cell current is constant with time and the integral becomes:

$$E = I \int_0^{20} v(t) dt . \quad (23)$$

Therefore, by determining the area under the “self-oxidation” curve (dashed line) in Fig. 24 over a period of 20 seconds and multiplying by the corresponding current (20 A) given in Fig. 25, we find that with “self-oxidation,” we get $E = 218 J$.

With pulsing the cell current is not constant with time. Thus, (22) was evaluated numerically. This calculating showed that with pulsing we get $E = 246 J$, over an interval of 20 seconds. This shows that with pulsing, you can obtain 28 J more energy every 20 seconds than with “self-oxidation”. This means that over a 20 second period, 13% more energy is produced with pulsing than with “self-oxidation.”

Similarly, average power was computed by evaluating the following relationship:

$$\bar{P} = \frac{\int_0^{20} I(t) v(t) dt}{\int_0^{20} dt} = \frac{E}{20 \text{ sec}} . \quad (24)$$

Hence, with pulsing, $\bar{P} = 12.3 W$, while with “self-oxidation” $\bar{P} = 10.9 W$. This shows that 13% more power is obtained with pulsing. Although the area under the pulsing and

“self-oxidation” curves ($\int_0^{20} v dt$) in Fig. 24 are identical after 20 seconds, when

considering the uncertainty involved with the measurement ($\omega_{v-t} = 0.24 V \cdot s$, $Area_{pulse} = 11.12 V \cdot s$, $Area_{self-oxidation} = 10.92 V \cdot s$), the energy and average power differ significantly because pulsing increases the cell current to 50 A ($1.0 A/cm^2$) during the pulse. With “self-oxidation,” the current remains constant with time at 20 A ($0.4 A/cm^2$). This is illustrated in Fig. 25. Hence, when evaluating the two methods via energy and average power, pulsing is more effective than “self-oxidation.”

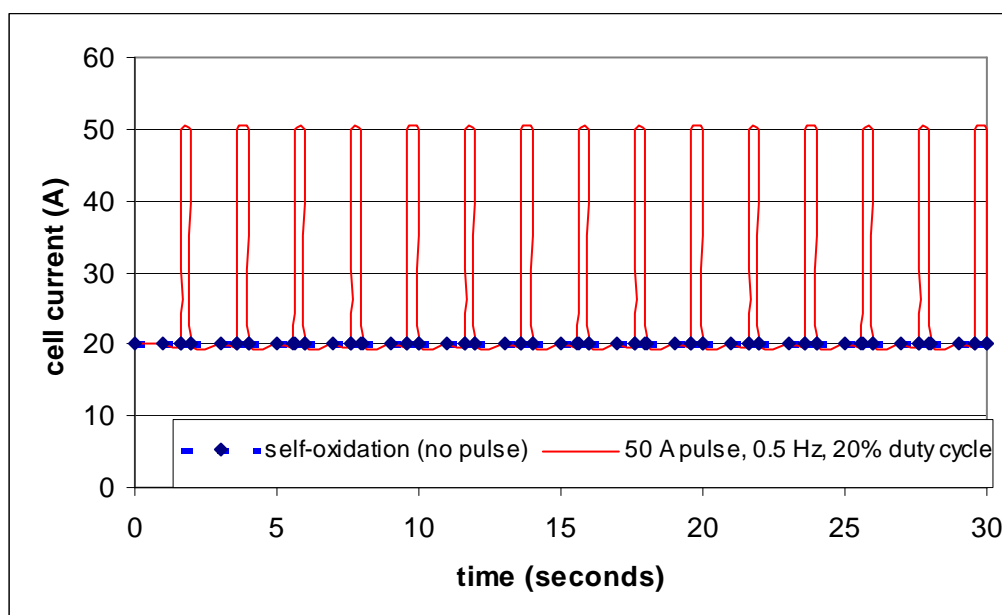


Fig. 25: Variation of cell current with time using 496 ppm CO in the anode fuel. Data was collected with and without a pulse. Base cell current was held constant at 20A (0.4 A/cm^2). The pulse was 1.0 A/cm^2 (50A), 0.5 Hz, with a 20% duty cycle.

4.6.3. Maximum voltage

The maximum voltage obtained in a cycle is an important parameter because it can indicate whether the CO is getting completely oxidized from the catalyst. If the maximum voltage is close to the value obtained with pure H_2 , it means that almost all of the CO that accumulates on the catalyst is oxidized with each over-potential cycle. Fig. 26 shows the variation of maximum cell voltage with current density using 496 ppm CO in the anode fuel. Data was collected with a pulse and with “self-oxidation” (no pulse). The pulse applied was 50A and 0.5 Hz with a 20% duty cycle. The highest voltage achieved in a cycle (both for the applied pulse and the “self-oxidation”) is shown. This plot shows that the maximum cell voltage obtained with pulsing is almost identical to the maximum cell voltage obtained with “self-oxidation.” The only noticeable difference

occurs at the lower current densities of 0.2 A/cm^2 and 0.4 A/cm^2 ; however, these discrepancies are insignificant when considering the uncertainty involved with the measurement. At a constant current of 0.4 A/cm^2 (20 A), pulsing produces a maximum cell voltage of 0.67 V and “self-oxidation” yields 0.62 V. When operating the unit on pure H_2 at 0.4 A/cm^2 (20 A), the cell produces a corresponding voltage of 0.70 V. This indicates that pulsing and “self-oxidation” are basically equally effective, in terms of maximum voltage produced, in increasing CO tolerance.

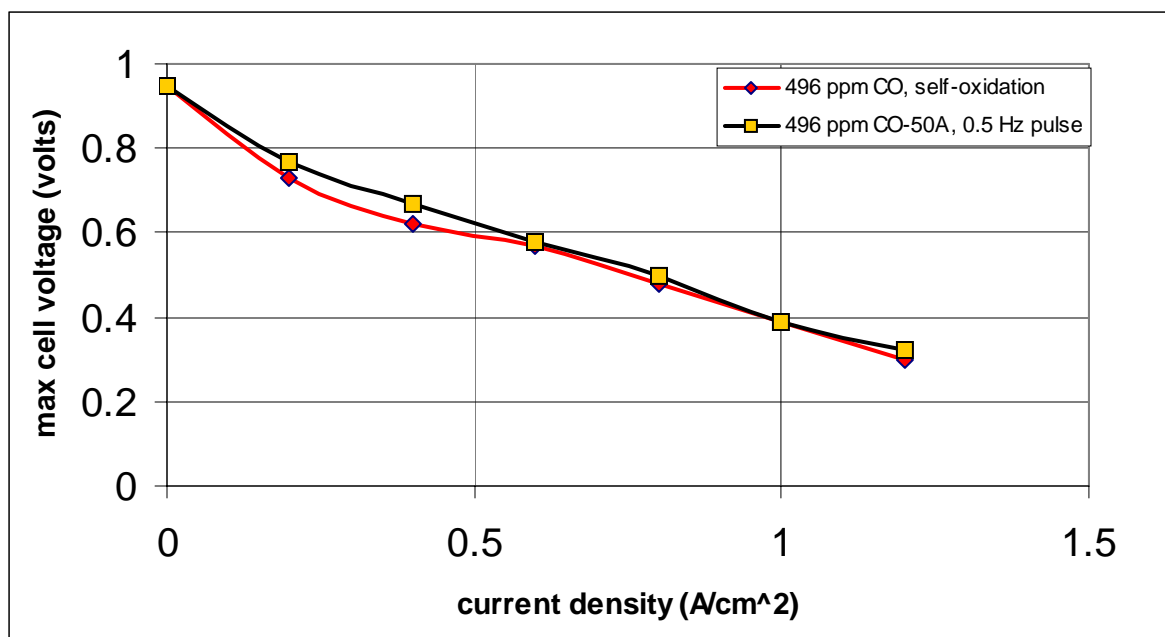


Fig. 26: Variation of maximum cell voltage with current density using 496 ppm CO in the anode fuel. A 1.0 A/cm^2 (50A), 0.5 Hz, 20% duty cycle current pulse was applied. The highest voltage achieved in a pulsing cycle is shown.

Table 3 summarizes the results of this section. The table shows that pulsing is more effective or as effective in every category except for “additional equipment required,” because with pulsing, the pulse must be triggered via an electronic device, while with

“self-oxidation,” no additional equipment is required. Therefore, this comparison indicates that pulsing is more effective than “self-oxidation,” but if the pulsing mechanism fails or cannot be employed, “self-oxidation” would be a good back-up solution, as it will still significantly increase the CO tolerance of the cell.

Table 3: Comparison of pulsing with “self-oxidation,” the cell current was held constant at 20 A (0.4 A/cm²)

	pulsing, 50A, 0.5 Hz, 20 % duty cycle	self- oxidation
% time voltage above 0.6v	80	50
energy (J), over 20 seconds	246	218
average power (W)	12	11
max voltage obtained in cycle	0.67	0.62
additional equipment required	electronics to trigger pulse	none

5. SUMMARY

In this section, a summary of the results found in this work are presented. In the first sections, the results are summarized in paragraph form. In the second section, the major findings are bulleted.

5.1. Summary discussion

The CO tolerance of a Pt-Ru anode was evaluated using 50 ppm and 496 ppm CO in the anode fuel. The effect of current pulses on the CO tolerance of the system was investigated. Current pulses proved to be an effective means for increasing the CO tolerance of PEMFCs. Furthermore, the pulse amplitude, frequency, and duty cycle determined the effectiveness of the pulse. Under our experimental conditions, with 50 ppm CO in the anode fuel, the most effective pulse in increasing the anode CO tolerance and maintaining normal operation of the cell is 50 A (1.0 A/cm^2), 0.25 Hz, and a 5% duty cycle. The frequency and duty cycle of a ripple current (120 Hz and 50%) proved to be effective in increasing the CO tolerance of the cell with 50 ppm CO in the anode fuel. This is an attractive pulse source because a ripple current would already be present in units designed for home power generation. Hence, no additional electronics or triggering are required. However, it was not as effective in increasing CO tolerance as the 0.25 Hz, and a 5% duty cycle pulse.

With 496 ppm CO in the anode fuel, the most effective pulse in increasing anode CO tolerance and maintaining normal operation of the cell is 50A (1.0 A/cm^2), 0.5 Hz, and a 20% duty cycle. When the cell is operating on constant current with 496 ppm CO in the

anode fuel, the anode over-potential gets high enough to oxidize CO from the catalyst. Thus, “self-oxidation” occurs. “Self-oxidation” and pulsing are both effective means of making a PEMFC more tolerant to CO. However, pulsing produces a greater energy, and average power and maintains a cell voltage close to what is obtained with pure H₂ for a larger percentage of the time. The advantage of “self-oxidation” is that it does not require any additional electronics or triggering. Thus, the application should dictate which method is employed.

5.2. Major findings

The important findings of this investigation are shown below:

- With 50 ppm CO in the anode fuel, the most effective pulse in increasing the anode CO tolerance and maintaining normal operation of the cell is 50 A (1.0 A/cm²), 0.25 Hz, and a 5% duty cycle.
- The frequency and duty cycle of a ripple current, 120 Hz and 50%, proved to be effective in increasing the CO tolerance of the cell with 50 ppm CO in the anode fuel. However, it was not as effective in increasing CO tolerance as the 0.25 Hz, and a 5% duty cycle pulse
- With 496 ppm CO in the anode fuel, the most effective pulse in increasing anode CO tolerance and maintaining normal operation of the cell is 50A (1.0 A/cm²), 0.5 Hz, and a 20% duty cycle.

- When the cell is operating on constant current, with 496 ppm CO in the anode fuel, “self-oxidation” occurs.
- Pulsing produces a greater energy and average power, and maintains a cell voltage close to what is obtained with pure H₂ for a larger percentage of the time than “self-oxidation.”

6. CONCLUSIONS

The following conclusions were drawn from the experiments presented in this work:

- Current pulses are an effective means for increasing the CO tolerance of a PEMFC.
- Varying the current pulsing parameters of amplitude, frequency, and duty cycle will alter the effect of the pulsing technique.
- There should be a combination of pulse amplitude, frequency, and duty cycle that will allow an optimum level of CO tolerance to be obtained.
- To maintain a consistent cell voltage between pulses in the presence of CO, the current pulsing frequency must be increased as the concentration level of CO in the anode fuel increases.
- A ripple current (typically created by inverters) can increase the CO tolerance of a PEMFC; however, this method is not as effective as current pulsing.
- “Self-oxidation” is an effective method for increasing the CO tolerance of a PEMFC with a Pt-Ru Anode at certain CO concentrations
- Current pulsing is more effective than “self-oxidation” in increasing CO tolerance.

7. RECOMMENDATIONS FOR FUTURE WORK

The following recommendations for future work were based on the finding and conclusions presented in this work:

1. In order to insure that pulsing and “self-oxidation” are practical solutions for increasing the CO tolerance of PEMFCs for home power generation, long term experiments on fuel cell stacks should be conducted.
2. Although the effectiveness of a simulated ripple current was evaluated, an actual ripple current, generated by an inverter, should also be investigated to insure that it is an effective means for increasing CO tolerance.
3. More combinations of pulsing parameters for 496 ppm CO should be considered to verify the findings given in this paper.
4. A more comprehensive investigation of combinations of parameters should be conducted, including an investigation of the interaction between parameters.
5. In this study, CO concentrations of 50 ppm and 496 ppm were studied. However, to further characterize the effect of CO, pulsing, and “self-oxidation” on PEMFCs, experiments with other CO concentrations should be conducted.

6. Once the behavior of PEMFCs has been evaluated with a large number of CO concentrations and the optimum pulsing parameters have been determined for each, a relationship should be derived so that the optimum pulsing parameters can be computed for any CO concentration.
7. After a relationship is derived to compute the optimum pulsing parameters for a given CO concentration, a system that monitors the reformer CO output and adjusts the pulsing parameters accordingly should be created.
8. New methods and techniques for increasing CO tolerance in PEMFCs should be explored.

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APPENDIX A

COMBINATION OF PARAMETERS INVESTIGATED

Table 4: List of each combination of parameters investigated and its significance

CO Concentration (ppm)	current (A)	voltage (V)	pulse frequency (Hz)	pulse amplitude (A)	pulse duty cycle (%)	time (min)	comments		
0	73.1	0.2	No	Pulse	Applied	N/A	characterizing cell behavior on pure hydrogen, constant voltage Section 4.1		
	66.6	0.3							
	58.2	0.4							
	47.8	0.5							
	34.6	0.6							
	20.6	0.7							
	5.3	0.8							
	0.4	0.9							
0	0.95	50					49.7	0.2	characterizing cell behavior with 50 ppm CO in anode fuel, constant voltage Section 4.1
43.6	0.3								
37.2	0.4								
29	0.5								
21	0.6								
12.6	0.7								
3.8	0.8								
0.3	0.9								
0	0.95	496					21.3	0.2	characterizing cell behavior with 496 ppm CO in anode fuel, constant voltage Section 4.1
14.9	0.3								
11.4	0.4								
2.1	0.5								
0.8	0.6								
0.6	0.7								
0.4	0.8								
0.1	0.9								
0	0.95	0	36.1	0.6	characterizing cell behavior with time on pure hydrogen, constant voltage Section 4.1				
36.4	0								
36.2			60						
36.2			240						
		660							

Table 4: Continued

CO Concentration (ppm)	current (A)	voltage (V)	pulse frequency (Hz)	pulse amplitude (A)	pulse duty cycle (%)	time (min)	comments
	36.1					1140	
50	34.6	0.6	No	Pulse	Applied	0	characterizing cell behavior with time using 50 ppm CO in the anode fuel, constant voltage Section 4.1
	21					60	
	17.4					120	
	15.6					360	
	14.7					1182	
	496					33	
7.8	9						
2.3	22.2						
1.7	31.2						
1	60						
0.6	180						
	0.5	360					
	0.4	1200					
0	70	0.28	No	Pulse	Applied	N/A	characterizing cell behavior on pure hydrogen, constant current Section 4.2
	60	0.4					
	50	0.48					
	40	0.56					
	30	0.63					
	20	0.7					
	10	0.78					
	0	0.94					
	10	0.76					
	20	0.68					
	30	0.6					
	40	0.53					
	50	0.45					
	60	0.37					
70	0.27						
50	60	0.23	0.25	60	10		verifying that pulsing works in the presence of 50 ppm CO, constant current Section 4.2
	50	0.37					
	40	0.45					

Table 4: Continued

CO Concentration (ppm)	current (A)	voltage (V)	pulse frequency (Hz)	pulse amplitude (A)	pulse duty cycle (%)	time (min)	comments
50	30	0.56	0.25	60	10	N/A	characterizing cell behavior with 50 ppm CO in the anode fuel, constant current Section 4.2
	20	0.65					
	10	0.75					
	0	0.93					
	10	0.76					
	20	0.66					
	30	0.58					
	40	0.48					
	50	0.37					
	60	0.25					
	60	0.23	No	Pulse	Applied		
	50	0.28					
	40	0.32					
	30	0.47					
	20	0.55					
	10	0.66					
	0	0.93					
	10	0.65					
	20	0.53					
	30	0.42					
40	0.3						
50	0.27						
60	0.23						
19	0.68	0.25	60	10	0	characterizing effect of pulsing over time with 50 ppm CO in the anode fuel, constant current Section 4.2	
	0.67				3		
	0.658				12		
	0.623				20		
	0.44				38		
	0.411				60		
	0.68	No	Pulse	Applied	0		
	0.68				3		
	0.67				12		
	0.66				20		
	0.66				38		
	0.66				60		

Table 4: Continued

CO Concentration (ppm)	current (A)	voltage (V)	pulse frequency (Hz)	pulse amplitude (A)	pulse duty cycle (%)	time (min)	comments
50	19	0.58	0.25	19	10	N/A	characterizing effect of pulse amplitude with 50 ppm CO in the anode fuel, constant current Section 4.3.1
		0.59		30			
		0.63		40			
		0.66		50			
		0.7		60			
50	20	0.58	120	50	50	N/A	characterizing effect of pulse frequency and duty cycle Section 4.3.2.1
		0.58	60	50	50		
		0.58	30	50	50		
		0.62	10	50	50		
		0.63	0.5	50	50		
		0.63	0.25	50	50		
		0.52	240	50	25		
		0.53	120	50	25		
		0.53	60	50	25		
		0.53	30	50	25		
		0.58	10	50	25		
		0.62	0.5	50	25		
		0.63	0.25	50	25		
		0.48	240	50	10		
		0.48	120	50	10		
		0.48	60	50	10		characterizing effect of pulse frequency and duty cycle Section 4.3.2.1
		0.48	30	50	10		
		0.53	10	50	10		
		0.62	0.5	50	10		
		0.62	0.25	50	10		
		0.45	240	50	5		
		0.46	120	50	5		
		0.45	60	50	5		
		0.45	30	50	5		
		0.48	10	50	5		
		0.62	0.5	50	5		
		0.62	0.25	50	5		
0.44	No Pulse Applied				0	characterizing cell behavior over time with 50 ppm CO in the anode fuel, constant current	
0.67					7	Section 4.5	
0.65					7		
0.63					11		

Table 4: Continued

CO Concentration (ppm)	current (A)	voltage (V)	pulse frequency (Hz)	pulse amplitude (A)	pulse duty cycle (%)	time (min)	comments
50		0.6	No	Pulse	Applied	18	
		0.52				29	
		0.48				33	
		0.45				39	
		0.44				44	
		0.42				48	
		0.4				54	
		0.39				85	
		0.37				90	
		0.37				176	
		0.37				180	
496	20			50	20		characterizing effect of frequency with 496 ppm CO in the anode fuel, constant current, minimum voltage recorded Section 4.4
		0.57	0.25			N/A	
		0.6	0.3				
		0.62	0.4				
		0.63	0.5				characterizing cell behavior with time using 496 ppm CO in the anode fuel, constant current Section 4.5
	0.63				0		
	0.63				0.008		
	0.62				0.017		
	0.62				0.025		
	0.61				0.033		
	0.6				0.042	Self-oxidation is observed	
	0.58				0.051		
	0.55				0.058		
	0.5				0.067		
	0.4					0.075	

VITA

Arthur H. Thomason was born on November 20, 1974 in Zachary, Louisiana. He was raised in Ponca City, Oklahoma, until moving to Conway, Arkansas, to attend Hendrix College. In June of 1997, Arthur graduated with distinction from Hendrix College with a Bachelor of Arts degree in physics and received the honor of cum laude. He then worked as a professional bicycle stunt rider, maintaining a world ranking in the top 20 from 1999 through the present. While maintaining his career as a professional athlete, he moved to College Station, Texas, in August of 2000 to begin graduate work at Texas A&M University, where he received a Master of Science in mechanical engineering in December of 2003.

His work experience includes a summer research position at The Center for Laser and Photonics Research at Oklahoma State University where he studied transverse effects in semiconductor ring lasers via computer modeling. The results of his work were presented at the 1997 National Conference for Undergraduate Research in Austin, Texas. Currently, he works as a Research Assistant for the Center for Electrochemical Systems and Hydrogen Research (CESHR) at Texas A&M University in College Station, Texas, where he has been actively involved with PEM fuel cell research since the winter of 2002.

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