

# Effect of current pulsing and “self-oxidation” on the CO tolerance of a PEM fuel cell

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## Abstract

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 increases in current from the fuel cell to create an anode over-potential that oxidizes CO from the catalyst surface, 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. 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 496 ppm CO in the anode fuel, a pulse of 1.0 A/cm<sup>2</sup>, 0.5 Hz, and a 20% duty cycle proved most effective. When the cell was exposed to approximately 500 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 a constant voltage and power a higher percentage of the time than “self-oxidation”; hence, pulsing was more effective in increasing the CO tolerance of the cell.

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## 1. Introduction

Proton exchange 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 best 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, typi-

cally 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 [1,3]. However, during the start up phase, which typically lasts close to 2 h, CO levels close to 500 ppm can be produced. Furthermore, it has been shown that CO concentrations as small as 5–10 ppm can be detrimental to the performance of a PEMFC [4]. Hence, it appears to be more practical and economical to attempt to make fuel cells 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 at steady-state as well as the CO concentration produced during 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 (CO<sub>2</sub>). Car-

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bon 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  $\text{CO}_2$ , thereby lowering the CO concentration of the anode fuel. 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 surface, the anode becomes increasingly polarized to higher potentials to sustain the current demanded. The high anode 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, “self-oxidation” has only been investigated with limited operating conditions. 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.

The second method used to create an anode over-potential was pulsing. Carrette indicates that pulsing a fuel cell with positive current spikes can be an effective method for creating an anode over-potential by stating: “The electrical pulses increase the anode potential to values at which the CO is oxidized to  $\text{CO}_2$ . In this way, the catalyst surface is continually cleaned and the loss of cell voltage is minimized” [3]. Pulsing is 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. A CO concentration of 500 ppm has not been investigated and the effectiveness of current pulsing as a function frequency, amplitude, and duty cycle has yet to be determined. 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.

The objective of this work was to determine and compare the effect of cell current pulsing and “self-oxidation”, with an anode fuel CO concentration of 500 ppm, 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.

## 2. Experimental

Membrane Electrode Assemblies (MEAs) were purchased from 3M. Each MEA had a surface area of  $50 \text{ cm}^2$ . The cathode catalyst is Pt and has a catalyst loading of  $0.4 \text{ mg/cm}^2$ . The anode has a total catalyst loading of  $0.6 \text{ mg/cm}^2$  and is approximately  $0.4 \text{ mg/cm}^2$  Pt and  $0.2 \text{ mg/cm}^2$  Ru. The proton exchange membrane is  $30 \mu\text{m}$  thick and constructed of cast Nafion<sup>®</sup>. The MEA was placed in a  $50 \text{ cm}^2$  single cell assembly. Ni foam flow fields were used to evenly distribute the gases over their respective electrode. Humidity was supplied to the cell by two stainless steel humidification bottles. The system was controlled via a fuel cell test station that maintains the cell temperature ( $60^\circ\text{C}$ ), gas flow rate, and humidification bottle temperature ( $60^\circ\text{C}$  for each bottle). A dc programmable electronic load was used to maintain the cell voltage or current and display the corresponding value. The electronic load was also programmed to create periodic increases in current, which, in turn created over-potentials in the anode. The current pulse amplitude, frequency, and duty cycle were varied in the investigation. An oscilloscope was also used to display the data. Premixed  $\text{H}_2/50 \text{ ppm CO}$  and  $\text{H}_2/496 \text{ ppm CO}$ , as confirmed by the supplier, were used as anode fuel.

Once the performance of the MEAs were characterized using  $\text{H}_2$  as the anode fuel and air as the cathode reactant, CO was introduced into the anode fuel. CO concentrations of 50 and 496 ppm were used to generate plots of the variation of cell voltage with time, the variation of cell current with time, and the variation of cell current with cell voltage. “Self-oxidation” was observed when the cell current was held constant with 496 ppm CO in the anode fuel. After determining the behavior of the MEAs with 50 and 496 ppm in the anode fuel, the system was subjected to current pulses of various amplitudes, frequencies, and duty cycles with  $\text{H}_2/496 \text{ ppm CO}$  as the anode fuel. The variation of cell voltage with respect to current density and time was collected. An example current pulse is illustrated in Fig. 1.

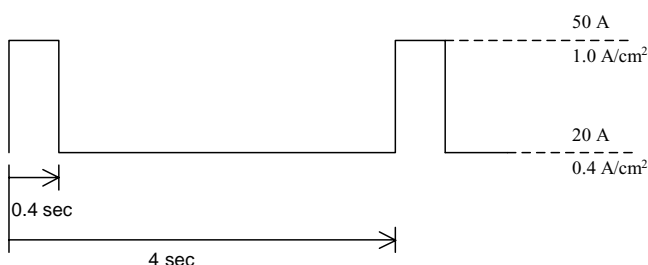


Fig. 1. Variation of cell current with time. An example of a square wave pulse generated by the electronic load, base current =  $0.4 \text{ A/cm}^2$  (20 A), pulse amplitude =  $1 \text{ A/cm}^2$  (50 A), frequency = 0.25 Hz, duty cycle = 10%.

### 3. Results and discussion

The results and significance of each experiment conducted are given in the following sections. 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 optimum pulsing parameters with 496 ppm CO in the anode fuel are presented in Section 2. Section 3 illustrates the effect of “self-oxidation”. In the final section, a comparison of pulsing and “self-oxidation” is presented.

#### 3.1. Effect of CO in the anode fuel on cell performance

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 reformate. Therefore, the effect of CO concentrations of 50 and 496 ppm on the cell performance was investigated. The cell was also operated on pure H<sub>2</sub> to establish a baseline level of performance for the experiment. Fig. 2 shows 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 test was first conducted using pure H<sub>2</sub> as the anode fuel for 19 h. 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 test was then performed a third time using the new MEA and 496 ppm CO in the anode fuel.

As shown in Fig. 2, 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

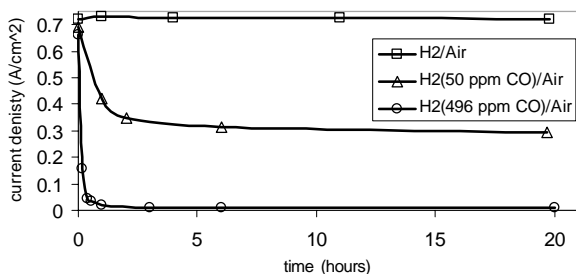


Fig. 2. Variation of current density with time, using various concentrations of CO in the anode fuel. The cell voltage was held constant at 0.60 V.

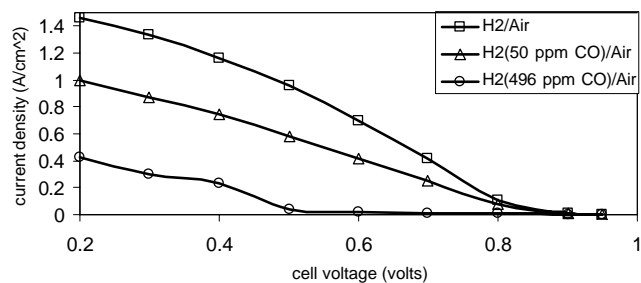


Fig. 3. Variation of current density with cell voltage, using various concentrations of CO in the anode fuel.

declined significantly over the first 6 h. After approximately 7 h the current density remained relatively constant as the rate of CO absorption was close to the rate of CO oxidation. Hence, with 50 ppm CO in the anode fuel, the current density reached an asymptote after approximately 7 h. With higher CO concentrations, the catalyst would become saturated more quickly. As shown in Fig. 2, with 496 ppm CO in the anode fuel, the current density of the cell remains relatively constant after about 2 h.

Higher CO concentrations also create a greater decline in current density. After 19.8 h of 50 ppm CO in the anode fuel, the cell had a current density that was 41% of that obtained with pure H<sub>2</sub>. While, with 496 ppm CO, the cell could only achieve 1% of the current density obtained with pure H<sub>2</sub> after 19.8 h. 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. 2 was repeated at various cell voltages ranging from 0.20 to 0.95 V. However, in this experiment, the cell was only exposed to CO 1 h before data was collected. Fig. 3 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 h of CO exposure. At cell voltage levels between 0.80 and 0.95 V, 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 and 0.60 V (when pure hydrogen is used as the anode fuel). This can be seen in Fig. 4. Hence, to obtain the maximum power output possible, fuel cells are typically operated at current densities between 0.40 and 0.60 V. The cell current densities obtained in this voltage region are significantly less than what is obtained using pure H<sub>2</sub>. With 50 ppm CO in the anode fuel, the current density obtained at 0.4 V is 60%

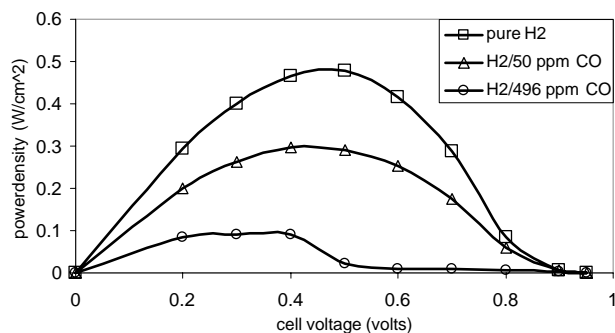


Fig. 4. Variation of power density with cell voltage, using various concentrations of CO in the anode fuel.

of the value achieved with pure H<sub>2</sub>. Only 20% of the current density obtained with pure H<sub>2</sub> at 0.4 V was achieved with 496 ppm CO in the anode fuel. Thus, Fig. 3 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. 2 in showing that the higher the CO concentration of the anode fuel, the lower the current density, especially for low cell voltage levels.

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. 4 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 H<sub>2</sub>) 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 and 496 ppm CO. Fig. 4 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 where peak power occurs.

This plot also shows that the presence of CO causes the power density to decrease 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 H<sub>2</sub>. With 496 ppm CO, the power density is only 2% of the value obtained with pure H<sub>2</sub> at 0.60 V. Once again, this illustrates the need for finding an effective method for increasing the CO tolerance of PEMFCs.

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

Most of the reformers currently available are capable of producing 50 ppm CO or less after a warm up period of up to 2 h. 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

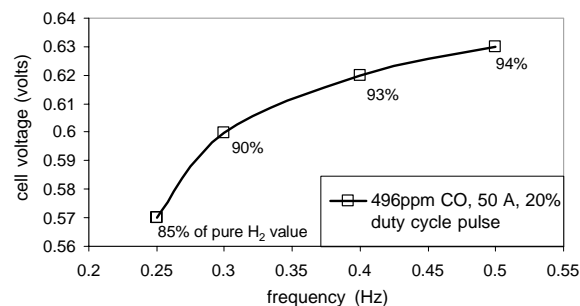


Fig. 5. Variation of cell voltage achieved with pulse frequency. Four hundred and ninety six ppm CO is present in the anode fuel. The cell current was held constant at 0.4 A/cm<sup>2</sup> (20 A) and the pulse amplitude was 50 A. In each case, the maximum voltage obtained was 0.65 V. The duty cycle was set at 20%.

the 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.

The most important variables in determining the effectiveness of a current pulse are amplitude, pulse duration, and time between pulses [3,5]. A pulse amplitude of 50 A was chosen because it is large enough to effectively oxidize CO, but small enough not to short out the cell [5]. 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. 5 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<sup>2</sup>). A 20% duty cycle was selected after evaluating the results of preliminary experiments [5]. The base current was held at 20 A to maintain consistency with previous experiments. After each 50 A (1.0 A/cm<sup>2</sup>) pulse, the cell voltage immediately increased to 0.65 V. However, the cell voltage decreased between pulses as the catalyst became poisoned. Thus, the lowest cell voltage obtained between pulses was recorded.

The lowest frequency used was 0.25 Hz, which corresponds to a 50 A pulse that lasts 0.8 s every 4 s. 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. 5, 0.57 V is only 85% of the value obtained with pure H<sub>2</sub>. 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 s every 2 s. The 0.4 s pulse was long enough to bring the cell voltage up to 0.65 V and the 1.6 s between pulses allowed the voltage to only drop to 0.63 V before the next pulse began. With pure H<sub>2</sub>, this MEA obtained 0.67 V at 20 A (0.4 A/cm<sup>2</sup>). Thus, for a pulse of 50 A, 0.5 Hz and a 20% duty cycle, the lowest voltage obtained between pulses



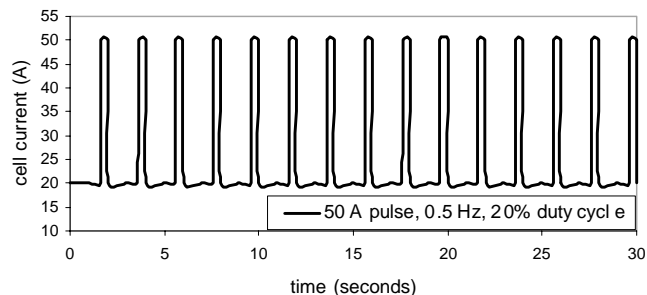


Fig. 6. Variation of cell current with time created by the “most effective” pulsing parameter values for the 496 ppm CO case. The base cell current was held constant at 20 A ( $0.4 \text{ A/cm}^2$ ) and the pulse amplitude was 50 A. The frequency was 0.5 Hz and the duty cycle was set at 20%.

(0.63 V) is still 94% of that obtain using pure  $\text{H}_2$ . 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. 6. This plot shows that the base current of 20 A is obtained approximately 80% of the time. Fig. 7 shows how the corresponding cell voltage varies with time for the same pulsing parameter values. In this plot the voltage drop from 0.65 to 0.63 V between pulses can be seen. Based on the results of this experiment, a 50 A ( $1.0 \text{ A/cm}^2$ ), 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.

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

The results given in Section 3.1 (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.

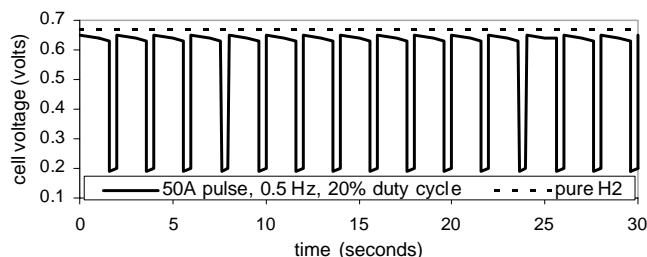


Fig. 7. Variation of cell voltage with time obtained by employing the “most effective” pulsing parameter values for the 496 ppm CO case. The base cell current was held constant at 20 A ( $0.4 \text{ A/cm}^2$ ) and the pulse amplitude was 50 A. The frequency was 0.5 Hz and the duty cycle was set at 20%. The cell voltage obtained using pure  $\text{H}_2$  is also shown (0.67 V).

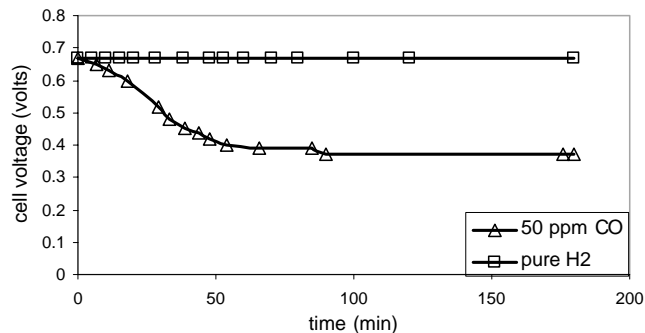


Fig. 8. Variation of cell voltage with time, with pure  $\text{H}_2$  and with 50 ppm CO in the anode fuel. The cell current was held constant at  $0.4 \text{ A/cm}^2$  (20 A).

Fig. 8 shows the variation of cell voltage with time, both with pure  $\text{H}_2$  and with 50 ppm CO in the anode fuel. The cell current was held constant at 20 A ( $0.4 \text{ A/cm}^2$ ) and the corresponding voltage was recorded for 3 h. With pure  $\text{H}_2$  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 h. After 1 h, the voltage remained constant because the rate of CO oxidation was equivalent to the rate of CO adsorption; hence, an equilibrium point was 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.

The experiment presented in Fig. 8 was repeated using 496 ppm CO. However, the results were quite different. Fig. 9 shows the variation of cell voltage with time, with 496 ppm CO in the anode fuel. The cell current was held constant at 20 A ( $0.4 \text{ A/cm}^2$ ). This figure shows 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 s 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” [4,5]. After running the cell with 496 ppm CO in the anode fuel for 10 min, “self-oxidation” occurred approximately every 5 s. Thus, with the aid of the low CO

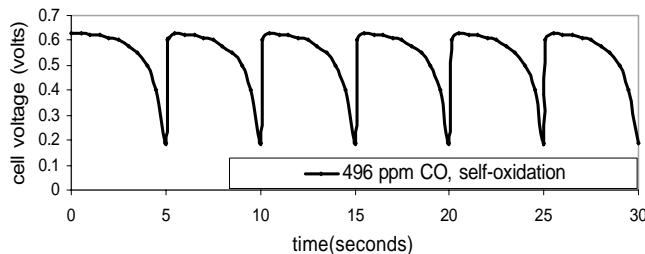


Fig. 9. Variation of cell voltage with time, with 496 ppm CO in the anode fuel. The cell current was held constant at  $0.4 \text{ A/cm}^2$  (20 A). After 10 min of 496 ppm CO in the anode fuel, this pattern remains consistent.

oxidation potential created by the Ru catalyst, CO poisoning is automatically controlled when the cell is held at a constant current of 20 A ( $0.4 \text{ A/cm}^2$ ) with 496 ppm CO in the anode fuel. This finding is significant because it indicates that the CO tolerance of a PEMFC can be increased without the use of additional electronics to provide a current pulse to the system. 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.

### 3.4. 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, as 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  $0.4 \text{ mg/cm}^2$  Pt and  $0.2 \text{ mg/cm}^2$  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.

#### 3.4.1. Percentage of time under normal operation

In order to be an effective power generation unit, a fuel cell must produce the desired output 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  $\text{H}_2$  as the anode fuel at a given current density. Fig. 10 shows the variation of cell voltage with time using 496 ppm CO in the anode fuel. The results of both the pulsing and “self-oxidation” method are presented. The pulsing parameters determined to be most effective (50 A, 0.5 Hz, 20% duty cycle) were used. As, previously discussed, “self-oxidation” occurs when no pulsing is applied. As shown in Fig. 10 (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

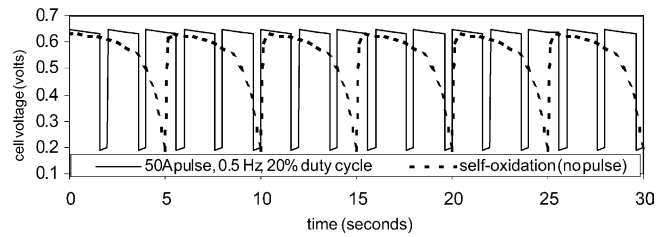


Fig. 10. Variation of cell voltage with time using 496 ppm CO in the anode fuel. Data was collected with and without a pulse. Base cell current was held constant at 20 A ( $0.4 \text{ A/cm}^2$ ). The pulse was  $1.0 \text{ A/cm}^2$  (50 A), 0.5 Hz, with a 20% duty cycle.

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  $\text{H}_2$ ) 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  $\text{H}_2$  (0.67 V). “Self-oxidation” only maintains a voltage above 0.60 V about 50% of the time, while with pulsing, 0.60 V or greater is maintained 80% of the time. Thus, when considering percentage of time at normal operation (a cell voltage of 0.60 V or above), pulsing is more effective than “self-oxidation”.

#### 3.4.2. 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:

$$E = \int I(t)v(t) dt \quad (1)$$

The integral was evaluated from 0 to 20 s, 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. 10, while the corresponding cell current is given in Fig. 11. Fig. 11 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:

$$E = I \int_0^{20} v(t) dt \quad (2)$$

Therefore, by determining the area under the “self-oxidation” curve (dashed line) in Fig. 10 over a period of 20 s and multiplying by the corresponding current (20 A) given in Fig. 11, we find that with “self-oxidation”, we get  $E = 218 \text{ J}$ .

With pulsing the cell current is not constant with time. Thus, (1) was evaluated numerically. This calculating

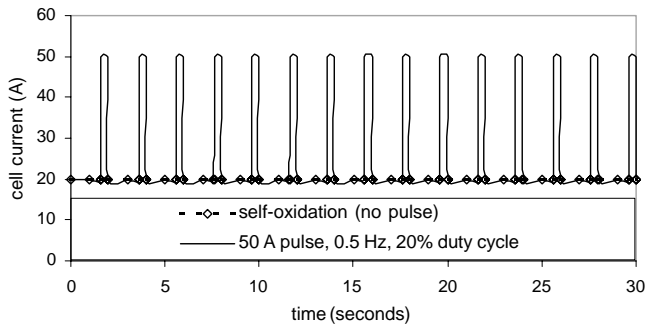


Fig. 11. Variation of cell current with time using 496 ppm CO in the anode fuel. Data was collected with and without a pulse. Base cell current was held constant at 20 A ( $0.4 \text{ A/cm}^2$ ). The pulse was  $1.0 \text{ A/cm}^2$  (50 A), 0.5 Hz, with a 20% duty cycle.

showed that with pulsing we get  $E = 246 \text{ J}$ , over an interval of 20 s. This shows that with pulsing, you can obtain 28 J more energy every 20 s than with “self-oxidation”. This means that over a 20 s period, 13% more energy is produced with pulsing than with “self-oxidation”.

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

$$\bar{p} = \frac{\int_0^{20} I(t)v(t) dt}{\int_0^{20} dt} = \frac{E}{20 \text{ s}} \quad (3)$$

Hence, with pulsing,  $\bar{p} = 12.3 \text{ W}$ , while with “self-oxidation”  $\bar{p} = 10.9 \text{ W}$ . 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. 10 are identical after 20 s, when considering the uncertainty involved with the measurement ( $\omega_{v-t} = 0.24 \text{ V s}$ ,  $\text{Area}_{\text{pulse}} = 11.04 \text{ V s}$ ,  $\text{Area}_{\text{self-oxidation}} = 10.92 \text{ V s}$ ), the energy and average power differ significantly because pulsing increases the cell current to 50 A ( $1.0 \text{ A/cm}^2$ ) during the pulse. With “self-oxidation”, the current remains constant with time at 20 A ( $0.4 \text{ A/cm}^2$ ). This is illustrated in Fig. 11. Hence, when evaluating the two methods via energy and average power, pulsing is more effective than “self-oxidation”.

### 3.4.3. 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  $\text{H}_2$ , it means that almost all of the CO that accumulates on the catalyst is oxidized with each over-potential cycle. Fig. 12 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 50 A 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”.

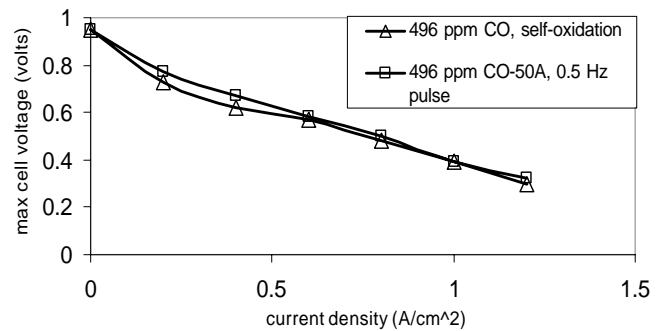


Fig. 12. Variation of maximum cell voltage with current density using 496 ppm CO in the anode fuel. A  $1.0 \text{ A/cm}^2$  (50 A), 0.5 Hz, 20% duty cycle current pulse was applied. The highest voltage achieved in a pulsing cycle is shown.

Table 1

Comparison of pulsing with “self-oxidation”, the cell current was held constant at 20 A ( $0.4 \text{ A/cm}^2$ )

	Pulsing, 50 A, 0.5 Hz, 20% duty cycle	Self-oxidation
Percentage of time voltage above 0.6 V	80	50
Energy (J), over 20 s	246	218
Average power (W)	12	11
Maximum voltage obtained in cycle	0.67	0.62
Additional equipment required	Auxiliaries to trigger pulse	None

The only noticeable difference occurs at the lower current densities of 0.2 and  $0.4 \text{ A/cm}^2$ ; however, these discrepancies are insignificant when considering the uncertainty involved with the measurement. At a constant current of  $0.4 \text{ A/cm}^2$  (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  $\text{H}_2$  at  $0.4 \text{ A/cm}^2$  (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.

Table 1 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.

## 4. Conclusions

- Current pulsing is 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.
- “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.

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