Short communication

# Enhancement of the performance and reliability of CO poisoned PEM fuel cells[☆]

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## Abstract

CO poisoning is a major issue when reformate is used as a fuel in PEM fuel cells. Normally, it is necessary to reduce the CO to very low levels (~5 ppm) and to use CO tolerant catalysts, such as Pt–Ru alloys. As an alternative approach, we have studied the use of pulsed oxidation for the regeneration of CO poisoned cells. Results are presented for the regeneration of Pt and Pt–Ru anodes in a PEM fuel cell fed with CO concentrations as high as 10,000 ppm. The results show that periodic removal of CO from the catalyst surface by pulsed oxidation can increase the average cell potential and overall efficiency.

Although use of pulsed techniques has been studied before, the careful control of each cell's voltage that this approach requires has limited its use in large fuel cell stacks. When uniform pulsing is done on a stack of fuel cells in series, the variations in voltage across the cells can limit the usefulness of this approach. A novel method that allows each cell in a stack to be separately pulsed under controlled conditions has been developed to overcome this problem. Weak or defective cells in a fuel cell stack can also be supplemented to enhance the power output and reliability of fuel cells. We present the results of experiments and calculations that quantify these benefits, specifically as they relate to PEM fuel cells operating on impure hydrogen produced by reforming fuels.
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## 1. Introduction

Previously, we described [1] a new technique for enhancing the power output and reliability of fuel cells. This technique is based on a microprocessor-based device that can automatically control the potential of individual cells or small groups of cells in a fuel cell stack by controlling the current through the selected cell or group of cells.

The device, which we have called a Fuel Cell Health Manager[TM] (FCHM[TM]), makes use [1,2] of a bridged connection circuit, as shown in Fig. 1. This enables the voltage and current flowing through the bridged cell to be adjusted without interrupting the normal operation of the fuel cell stack. The device is based on Kirchoff's current law. If $I_1$ is the current to the load, $I_2$ the current through the bridging loop and $I_3$ the current through the treated cell, then, according to Kirchoff's current law, $I_3 = I_1 + I_2$ (i.e. sum of currents at the node is zero). The voltage of the treated cell can thereby be adjusted by changing the current, $I_2$, through the bridging loop.

By controlling the voltage of an individual cell, cell poisons can be removed from an individual cell or group of cells by momentarily changing the potential of the electrodes (decreasing cell voltage). By removing poisons, the average cell voltage can be increased significantly, thereby increasing overall fuel cell efficiency. Additionally, it is possible to supplement or bypass a weak cell in the stack. Supplementing a weak cell is of benefit from an overall fuel cell stack energy/power point of view as it allows use of the energy that the cell is capable of producing and prevents complete loss of cell voltage, and subsequent cell reversal and catastrophic failure.
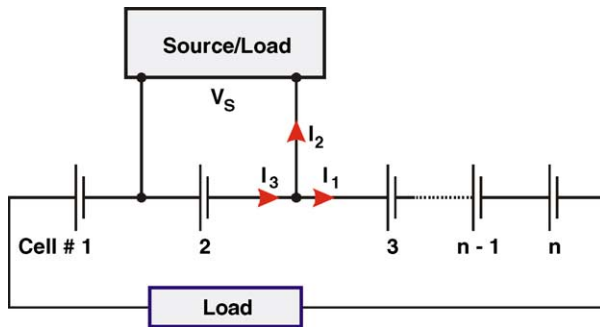
Fig. 1. Principle of operation of the Fuel Cell Health Manager (FCHM$^{TM}$).

In this paper, we present the results of experiments and calculations that we have made to quantify these benefits, specifically as they relate to PEM fuel cells operating on impure hydrogen produced by reforming fuels such as natural gas or methanol. The results of a cost/benefit analysis for the installation of an FCHM$^{TM}$ on a 4 kW residential fuel cell system are presented.

## 2. Experimental

Experiments were made using a single cell fuel cell having a 25 cm$^2$ active area manufactured by ElectroChem Inc. The measurements were made at room temperature using ElectroChem membrane electrode assemblies (MEAs) with Pt and Pt/Ru anode catalyst. Impure hydrogen (Matheson) containing various levels of CO was fed to the anode. To obtain a stable reference, the cathode was used in a hydrogen evolution mode [3]. To achieve this, humidified hydrogen was supplied to a Pt cathode. In this configuration, hydrogen is consumed at the anode and evolved at the cathode. Since no water is produced or consumed, water balance is easily maintained and the system is stable over long periods of time.

Equipment was used to simulate the functions of the FCHM$^{TM}$ system. As mentioned earlier, in our experiments, a single cell was used. A Kikusui Model PBX 20-10 Bi-Polar Power Supply, connected in parallel with the fuel cell, was used for the source that is used to control the cell voltage. This source can be used to momentarily raise the anode potential to strip off cell poisons. The Kikusui Power Supply can be used in either a controlled current or voltage mode. This power supply is also programmable so that the cell can be cycled through a predetermined voltage (or current) profile. A Fluke Hydra Model Data Logger has been used to monitor cell voltage and current.

## 3. CO poisoning of PEM fuel cells

### 3.1. Mechanism of CO poisoning of platinum and platinum alloys

The mechanism of CO poisoning of a Pt catalyst is well established. As shown below (equations (1)–(3)), CO
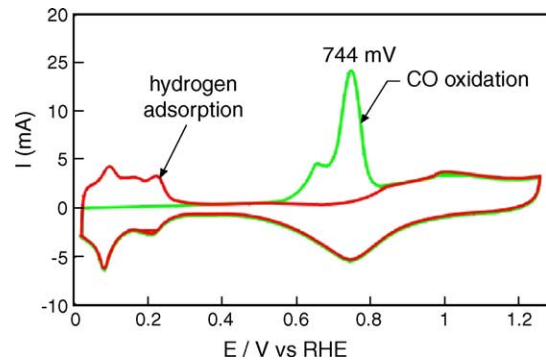


Fig. 2. Cyclic voltammogram showing the blocking of a Pt surface by 1% CO. The red curve shows a clean platinum surface; the green curve, one blocked with CO (adapted from [3]). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) (Source: Reproduced by permission of the Electrochemical Society, Inc.).

competes with hydrogen for the active sites on the platinum at normal anode operating potentials.

$$H_2 + 2[\ ] \leftrightarrow 2[H] \tag{1}$$

$$2[H] \leftrightarrow 2[\ ] + 2H^+ + 2e^- \tag{2}$$

$$CO + [\ ] \leftrightarrow [CO] \tag{3}$$

where [ ] represents a catalytic site on the electrode.

Recent work of Papageorgopoulos and de Bruijn [3] shows that, for a 1% CO/hydrogen mixture, CO blocks 98% of the active sites at 25 °C. This blocking of a platinum catalyst is clearly shown in the cyclic voltammograms shown in Fig. 2.

In this figure, the red curve shows the behaviour of a clean platinum surface, while the green curve shows the behaviour of the platinum blocked by CO when the cell is fed impure hydrogen containing 1% CO. Note that the hydrogen adsorption region peaks that are seen in the 0.0–0.3 V region of the red curve almost completely disappear when the cell is exposed to CO (green curve).

The adsorbed CO on a catalytic site can be removed by raising the anode potential to about 700 mV versus RHE. At this potential, as shown in equations (4) and (5), the CO reacts with hydroxyl species that are formed on the platinum surface to form $CO_2$. Operation of the anode at a potential high enough ($\sim$700 mV) that CO is removed by oxidation to $CO_2$ would result in a serious loss of efficiency and is not practical.

$$H_2O + [\ ] \leftrightarrow [OH] + H^+ + e^- \tag{4}$$

$$[CO] + [OH] \rightarrow 2[\ ] + CO_2 + H^+ + e^- \tag{5}$$
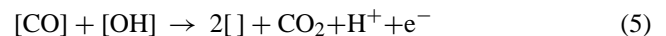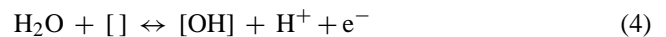
The impact of CO on the anode potential as a function of cell current is illustrated in Fig. 3 for two different fuel pressures. In Fig. 3a (10 psig), we see that, because of the blockage of the active sites on the platinum catalyst, the anode potential rises quickly until it reaches a sufficiently high potential where oxidation of the adsorbed CO can occur ($\sim$700 mV). There is then a region (from $\sim$0.4 to 1.2 A)
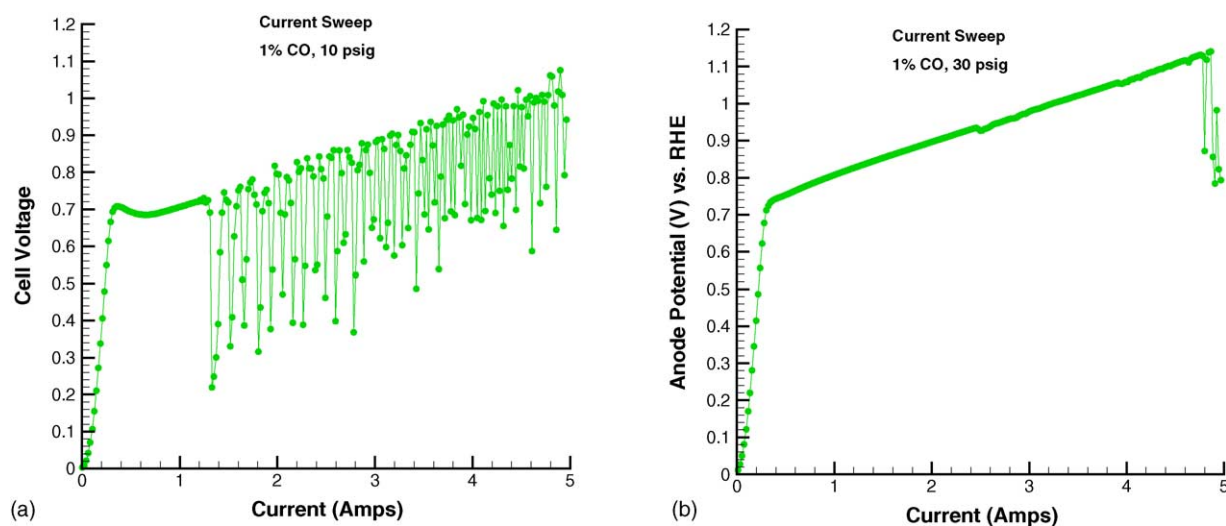
Fig. 3. Effect of pressure on cell voltage during a current sweep at (a) 10 psig and (b) 30 psig fuel pressure.

where the anode stays at the CO oxidation potential. Above a current of ~1.2 A, transport of the CO to the surface appears to become limited and the platinum surface becomes temporarily cleaned allowing the anode potential to fall back into the hydrogen region followed by rapid blocking as CO migrates to the surface. This causes the oscillatory behaviour that is observed. This explanation of Fig. 3a is supported by the data recorded at 30 psig (Fig. 3b). In this figure, it is seen that, because of the more rapid transfer of CO to the surface, oscillatory behaviour does not occur until the cell current is ~4.8 A. Below this current, CO transport is apparently fast enough to keep the surface essentially completely blocked and the anode operates at the CO oxidation potential.

## 3.2. Existing approaches to minimize the effects of CO poisoning

### 3.2.1. Reformer design

To prevent poisoning, CO levels need to be kept very low (~5 ppm). This requires the use of both shift and preferential oxidation (PrOx) reactors following the reformation stage, which add complexity and cost to the fuel cell system. Even when these additional stages are used, it is difficult to maintain low CO levels during startup and transient operation without using an addition air bleed into the fuel stream. The air bleed needed for the fuel cell stack can cause overheating at the anode if the air is not controlled and mixed properly.

### 3.2.2. Use of CO tolerant catalysts

To try to overcome the CO poisoning problem, platinum-alloy catalysts such as Pt/Ru have been developed that are more expensive than pure platinum. With these catalysts, the CO oxidation reactions, as per equations (4) and (5), occur at substantially lower potential. The use of CO tolerant catalysts

such as Pt/Ru still results in a substantial loss of cell potential [4] as shown in Table 1. The results show that, while the cell potential is increased by about 250 mV when compared to pure platinum, there is still a loss of about 200 mV (or a loss of 30% in voltage efficiency) when compared with the use of pure hydrogen as a fuel.

### 3.2.3. High temperature membranes

The CO tolerance of PEM fuel cells increases with increasing temperature [5]. From a CO tolerance point of view, it is desirable to operate a PEM fuel cell at as high a temperature as possible. However, increasing temperature decreases membrane life and makes maintaining membrane hydration more difficult. The choice of operating conditions is dependant on application. For high power applications, such as automotive applications, a thin membrane and relatively high operating temperature is usually chosen. These conditions shorten membrane life [6]. When long stack life is required, for example in stationary power applications, lower operating temperatures and thicker membranes are used. Even under these conditions, current membranes do not achieve the 40,000 h life that has been set [7] as a target for stationary systems.

There is considerable interest at the present time in the development of high temperature membranes. The work [8] on phosphoric acid doped polybenzimidazole is an example of this. The long-term chemical and mechanical stability of these membranes still remains to be determined however.

Table 1
Oxidation potentials of CO at Pt and Pt/Ru surfaces [4]

| Fuel | Catalyst | Fuel cell voltage | $\eta_v$ (%) | $\Delta\eta_v$ (%) |
|---|---|---|---|---|
| Hydrogen | Pt | 0.682 | 55.4 | – |
| 100 ppm CO | Pt | 0.231 | 18.8 | −66.1 |
| 100 ppm CO | Pt/Ru | 0.482 | 39.2 | −29.2 |

### 3.3. Removal of CO by periodic pulsed oxidation

To provide an improved method for the removal of CO from fuel cells and to improve overall efficiency, ESTCO has developed and patented [2] a Fuel Cell Health Manager (FCHM[TM]) system. This system provides a method for periodically raising the anode potential to remove the accumulated poisons from the electrocatalyst and for improving cell performance. The FCHM[TM] allows the anode potential of the cells to be raised to any desired level. It has been found that this is required for only a relatively short period (tens of milliseconds) to strip off the CO from the Pt surface. By stripping off the CO, the anode potential can be maintained in the hydrogen oxidation region rather than rising to a potential necessary for CO oxidation. This results in a very significant increase in the voltage efficiency of a fuel cell operating on reformate. As an example, Fig. 4 illustrates the removal of CO from a cell operating on 1000 ppm CO/hydrogen mixture. The measurements were made at room temperature using an MEA with a Pt/Ru anode catalyst and a Pt cathode catalyst. The results show that, with a short duty cycle consisting of a 200 ms regeneration pulse applied every 10 s, the average cell potential can be maintained at about 200 mV versus RHE whereas, without regeneration, the anode potential rises to about 540 mV versus RHE. This 340 mV lowering of the anode potential would almost double the efficiency of a stack operating on 1000 ppm CO/hydrogen under these conditions.

Fig. 5 illustrates the effect of periodic regeneration on the current produced in a cell where the anode potential is held at a constant potential of 400 mV versus RHE. The results show that, with periodic regeneration, the average cell current is about 1.5 A s whereas without regeneration, this current falls to less than 35 mA, a decrease by more than a factor
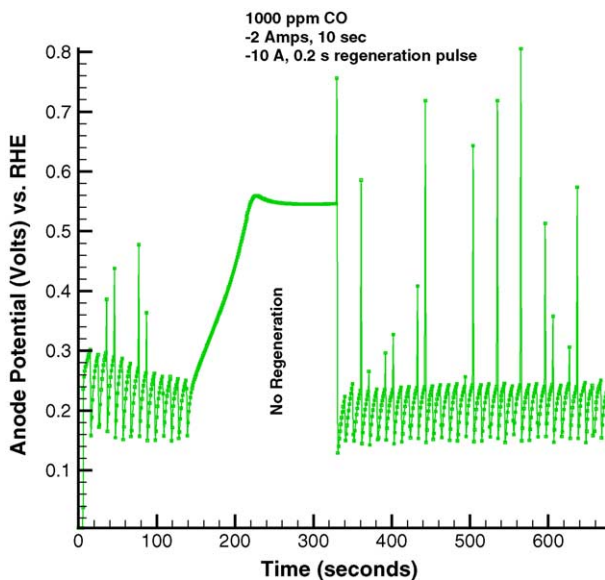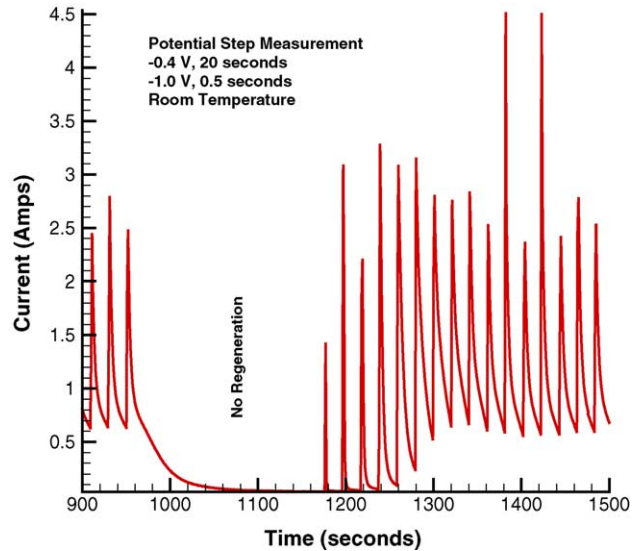


Fig. 5. Effect of periodic regeneration on cell current.

of 40. This large difference is the result of the fact that CO cannot be oxidized at this potential and the surface becomes almost completely blocked. In the example shown, an MEA having a Pt catalyst at both the anode and cathode was used. A hydrogen mixture containing 1000 ppm CO was used as the fuel. Experiments carried out at ESTCO have shown that the FCHM[TM] technique is still effective with CO levels as high as 10,000 ppm (1% CO).

Extended duration experiments (see Fig. 6) have shown that the performance is stable for extended periods (12 h) of cell regeneration. The stability over very long periods (thousands of hours) remains to be measured.

## 4. Impact of the FCHM[TM] on stack reliability

Fuel cell stacks are typically constructed by connecting a relatively large number of cells (perhaps 100 or more) in series to raise the voltage to a useable value. In this configuration, failure of a single cell in the stack can lead to stack failure. One of the more common failures of PEM fuel cell power systems occurs when one of the MEAs becomes less hydrated than other MEAs in the stack. Dehydration of the MEA increases the electrical resistance of the affected cell, generates more waste heat, which, in turn, further dries out the membrane electrode assembly. This situation creates a negative hydration spiral.

When a fuel cell stack consists of a large number of cells connected in series, the availability of the stack is the product of the individual cell availabilities. The impact of stack size on the impact of system availability is illustrated in Fig. 7 as the stack size increases from 1 to 75 cells. In this calculation, a normal distribution of cell life has been assumed with a mean life of 10,000 h and a standard deviation of 2000 h. The results illustrate the dramatic drop in stack availability
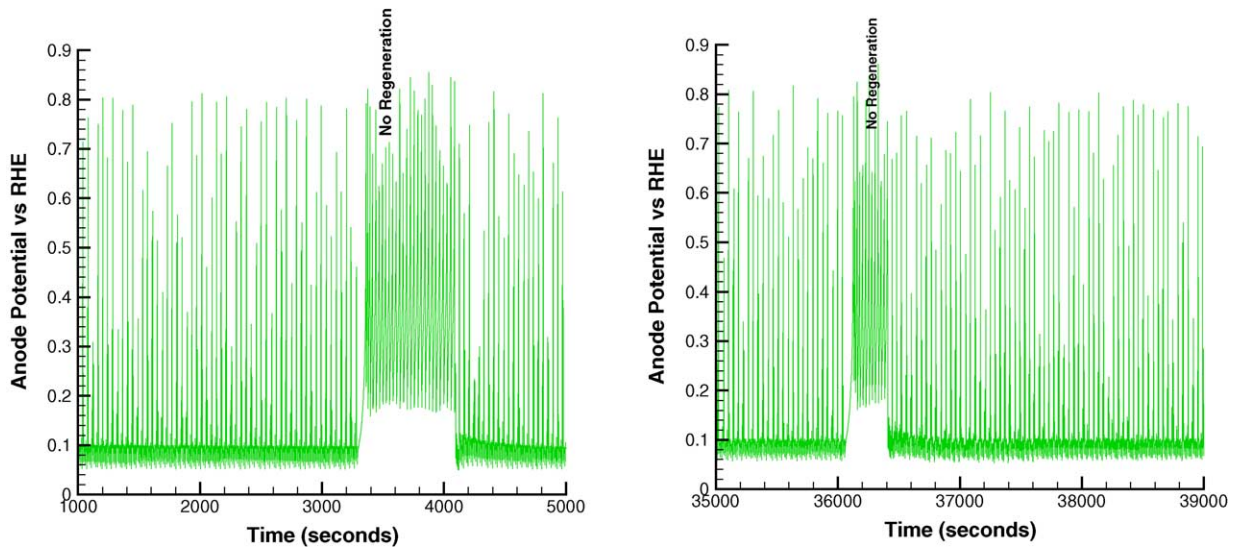


Fig. 4. Effect of periodic regeneration on anode potential.

Fig. 6. Long-term test data showing start and end of test.

as string length increases.

$$P\langle X \geq n_1 | n, p \rangle = 1 - [P(0) + P(1) + \cdots + P(n_1)]$$

A major benefit of the FCHM$^{TM}$ system is that it provides a redundant means to supplement or replace a defective cell in the stack. This redundancy greatly enhances the overall availability of a fuel cell stack fitted with an FCHM$^{TM}$. In a typical FCHM$^{TM}$ design, a number of sources (say $n_1$) are available for cell supplementation or replacement, which means that the stack can remain operational even if $n_1$ cells have failed in the stack. If it is assumed that cell failure follows a binomial distribution, then the improvement in stack reliability can be calculated using binomial probability theory [9]. This theory assumes that the reliability of each cell is independent of the other cells in a stack. According to this theory, the probability of more than $n_1$ cells failing is given by the following.



Fig. 7. Impact on stack size of availability.

In this expression, $n$ is the number of cells in the stack and $p$ the individual cell reliability. $P(0)$ represents the probability that there are no failed cells in the stack, $P(1)$, the probability that there is one failed cell and so on. These probabilities are calculated from the expression:

$$P\langle X = x \rangle = \frac{n!}{x!(n-x)!} p^x (1-p)^{n-x}$$

In Section 5, we illustrate the effect that the installation of an FCHM$^{TM}$ has on the reliability of a 4 kW fuel cell system containing 75 cells.

## 5. An FCHM$^{TM}$ example—a 4 kW residential fuel cell system

As an example, in this section, we illustrate the effect of installing an FCHM$^{TM}$ system on a 4 kW residential PEM fuel cell system on stack reliability as well as capital and operating costs. For the purpose of these calculations, we have assumed that the stack has 75 cells each capable of providing 75 A s with a total stack voltage of 52 V. For the FCHM$^{TM}$, we have assumed that the cells are divided into 15 groups each containing 5 cells. The FCHM$^{TM}$ system has three supplementation/bypass converters each capable of accessing five groups of cells in the stack. We have also assumed that the control logic and cell voltage monitoring resides in the existing fuel cell controller.

### 5.1. Impact of the FCHM$^{TM}$ on fuel cell system reliability

To illustrate the effect of the installation of an FCHM$^{TM}$ on the reliability of this 75 cell stack, consider a system that has been built using individual cells that have a reliability of 0.99 (i.e. a 1% chance of failure) in 40,000 h of operation. Without
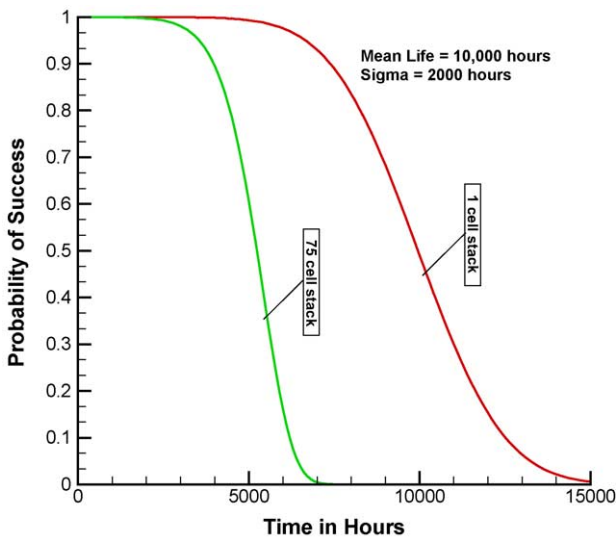
an FCHM$^{TM}$, failure of any cell leads to stack failure and the reliability (see Section 4) is $P(0) = 0.4706$. Thus, for a 75-cell stack built with individual cells having a reliability of 0.99, the probability of failure is greater than 50% over the 40,000-h period. With the FCHM$^{TM}$, however, the probability of stack failure becomes:

$$P\langle X > 1|25, 0.99\rangle = 1 - P\langle 0\rangle - P\langle 1\rangle$$
$$= 1 - 0.7778 - 0.1969$$
$$= 0.0258$$

With the FCHM$^{TM}$, the probability of failure decreases from about 53% to about 2.6%.

If the design were modified to allow each of the converters to access all of the cells in the stack, then the probability of stack failure would reduced to:

$$P\langle X > 3|75, 0.99\rangle = 1 - P\langle 0\rangle - P\langle 1\rangle - P\langle 2\rangle - P\langle 3\rangle$$
$$= 1 - 0.4706 - 0.3565 - 0.1330$$
$$-0.0327 = 0.0072.$$

In this case, the probability of stack failure decreases to less than 1%.

### 5.2. Cost/benefit analysis for a 4 kW

Based on these assumptions, we have made a preliminary analysis of the cost of the FCHM$^{TM}$, in relatively small lots. This estimate ranges from US$ 240 for a system capable of cell regeneration (CO removal) to US$ 1335 for a system capable of regeneration plus supplementation and by-pass to the full load value of 75 A s. The difference in these costs reflects the use of DC/DC converters and the current rating of the components that must be used.

Installation of an FCHM$^{TM}$ has a substantial impact on reducing both the capital and operating cost of a residential fuel cell system. A summary of the estimated impact on the capital cost of the fuel cell system is given in Table 2. These figures are based on an estimated cost for a 4 kW system US$

Table 2
Impact of the FCHM$^{TM}$ on fuel cell system costs

| Impact of FCHM$^{TM}$ on system design | Estimated savings (US$) | |
|---|---|---|
| | Current technology | Future technology |
| Smaller stack size (30% increase in stack efficiency) | 3000 | 1200 |
| Relaxed standards for cell voltage deviation | 1000 | 400 |
| No anode bleed control valve | 100 | 100 |
| Relaxed fuel processor requirement (increased CO tolerance) | 3000 | 1200 |
| Estimated total savings | 7100 | 2900 |

Table 3
Impact of the FCHM$^{TM}$ on operating costs

| Operating cost reduction (five years) | Cost savings (US$) | |
|---|---|---|
| | Present technology | Future technology |
| Reduction in fuel costs (reformed natural gas at US$ 3.20 per kg hydrogen equivalent) | 12,815 | 12,815 |
| Stack replacement costs | 10,000 | 4,000 |
| Estimated savings | 22,815 | 16,815 |

20,000 at the present time and reducing to US$ 8000 in the future. We have assumed that the stack cost represents 50% of the total system cost and that, without an FCHM$^{TM}$, the stack needs to be replaced once during the five-year period.

The FCHM$^{TM}$ is also expected to have a major impact on the operating cost of the fuel cell system principally through reduction in fuel cost as a result of the increase in stack efficiency and through a reduction in stack replacement costs as a result of cell supplementation or replacement which allows the stack to continue to run with one or more defective cells. The cost of hydrogen produced by reforming natural gas has been estimated [10] to be US$ 3.20 per kg. We have used this value in our calculations. Assuming a continuous 4 kW output, the estimated savings in operating costs over a five-year period are shown in Table 3.

The results presented illustrate that the FCHM$^{TM}$ will result in substantial capital and operating cost savings. The estimated payback period for the FCHM$^{TM}$ is extremely short—less than one year based on fuel savings alone.

## 6. Conclusions

A technique for enhancing the power output and reliability of fuel cells has been developed [1]. This technique is based on a microprocessor-based device that can automatically control the potential of individual cells or small groups of cells in a fuel cell stack by controlling the current through the selected cell or group of cells.

The use of periodic pulsed oxidation of CO poisons can increase fuel cell efficiency. Savings result from increased fuel efficiency, decreased stack size and a reduction in fuel processing requirements. In addition, cell supplementation and bypass can increase stack reliability. Savings result from extended stack life and less stringent cell matching.

## References

[1] C.L. Gardner, W.A. Adams, J. Blair, A new fuel cell management technique for optimizing power output and fuel use efficiency, in: Proceedings of the Hydrogen and Fuel Cells Conference, Vancouver BC, Canada, June 8–11, 2003.
[2] W. Adams, C.L. Gardner, J.H. Dunn, US Patents #6,339,313 and 6,541,941,2002.
[3] D.C. Papageorgopoulos, F.A. de Bruijn, JECS 149 (2003) A140.

[4] T. Iorio, K. Yasuda, Z. Siroma, N. Fujiwara, Y. Miyazaki, J. Electrochem. Soc. 150 (2003) A1225.

[5] T.E. Springer, T. Rockward, T.A. Zawodzinski, S. Gottesfeld, JECS 148 (2001) A11.

[6] S.J.C. Cleghorn, A portfolio of cost effective MEA products, in: Eighth Grove Fuel Cell Symposium, London, September, 2003.

[7] S. Chalk, P. Davis, P. Devlin, S. Gronich, J. Milliken, Freedom-CAR and hydrogen fuel cell initiatives, in: Eighth Grove Fuel Cell Symposium, London, September, 2003.

[8] B.C. Benicewicz, Advances in Materials for PEM Fuel Cell Systems, ACS Polymer Chemistry Workshop, 2003.

[9] B. Smith, G. Zabowski, Statistics 1 and 2 Course Notes, McGill University.

[10] K. Roberts, Hydrogen production from steam methane reforming and electrolysis as part of a near-term hydrogen infrastructure, in: Proceedings of the Hydrogen and Fuel Cells 2003 Conference and Trade Show, Vancouver, Canada, June 8–11, 2003, pp. 34–44.