PROTECTIVE GAS FOR SOFC SYSTEMS 
BASED ON WATER-ALCOHOL MIXTURES 

W. Halliop, A. Tuck 
Fuel Cell Technologies Ltd. 
20 Binnington Court, Kingston, Ontario K7M 8S3, Canada 

W. T. Thompson 
Royal Military College of Canada 
P.O. Box 17000 Stn Forces, Kingston Ontario K7K 7B4, Canada 

ABSTRACT 
Solid oxide fuel cells generally require a purge system to protect the cell anodes from damage during startup and shutdown. A novel “liquid” purge system has been proposed to reduce the complexity, cost and volume of existing purge systems. The proposed system incorporates the use of dilute organic compounds such as a water methanol solution. This is vaporised to produce a protective cover gas by flash evaporation. Thermodynamic calculations are supported by bench testing and finally implementation in a pre-production 5 kW SOFC. Good agreement between theory and testing has shown that dramatic improvements can be made in the target areas, and the system can be successfully incorporated into a commercial product.

INTRODUCTION 
Solid Oxide Fuel Systems based on cathode supported cells of the type developed by Siemens Westinghouse Power Corporation are able to provide a very long operational life. Single cell and bundle life of up to 70,000 hrs and large 100 kW system operating life of above 20,000 hrs have been reported (1, 2). It is upon this technology that Fuel Cell Technologies (FCT) and Siemens Westinghouse have developed two generations of 5 kW CHP (Combined Heat and Power) SOFCs for residential use. The first “Alpha” generation of these units were installed in 2003, and the second “Beta” generation development is ongoing.

The long life that is typical of these systems can only be achieved if proper operating conditions are observed over the whole operating period, and if factors that contribute to degradation of cells, stacks and other system components are kept to the minimum. The cell anodes in this system are composed of Ni-YSZ cermet. The anodes can undergo oxidation if exposed to oxidising conditions at elevated temperatures. The Ni oxide has a larger volume than metallic Ni, and can result in mechanical damage and reduction of the cell life.

Anodes do not undergo oxidation in the presence of fuel; however for the sake of safety the fuel is preferably supplied to the cell stack only above its autoignition temperature, when the formation of explosive gas mixtures is not possible. This temperature is often
substantially higher than the temperature at which Ni oxidation can proceed at a significant rate.

To create the protective atmosphere in the temperature range where the oxidation of Ni is possible but fuel cannot yet be added for safety reasons, a slightly reducing “purge” gas is often used. The reducing agent in the “purge” gas both prevents Ni oxidation and reacts with any air leaking into the anode compartment. However, the concentration of this component has to be sufficiently low so that an explosive mixture cannot be formed with air. The protective gas is most often a diluted mixture of H₂ in N₂, usually at the concentration of about 4 %, which is the lower explosion limit of hydrogen in at ambient temperature. Although the use of a H₂-N₂ mixture is acceptable in a laboratory setting, it is rather impractical for small CHP SOFC units that are installed at residential locations since cylinders of compressed gases are required.

Several means have been proposed to produce the protective “purge” gas mixture without the need to use compressed gases, e.g., by a very well controlled incomplete combustion of fuel that would produce a gas mixture with a low concentration of unburned fuel (3), however they have not been generally adopted. In the following paper, a new method of producing a practical protective gas mixture is presented, and its scientific rationale and experimental testing are discussed.

THEORETICAL BACKGROUND

The new method relies on formation of reducing gas mixtures produced by evaporation/thermal decomposition of diluted aqueous solutions of selected low molecular weight organic compounds (4), such as methanol and ethanol. The temperature above which the protective atmosphere is required is generally 300 – 500°C, which excludes any possibility of condensation of the steam rich gases. The reducing component can be the original alcohols, however it is more probable that at the cell stack temperature, in the presence of a very large excess of steam and the catalytically active cell anodes, the alcohols will undergo thermal decomposition and/or a steam reforming reaction with the formation of hydrogen, carbon dioxide and/or monoxide. For an aqueous solution of methanol, the main reactions are as follows:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3 \text{H}_2 \tag{1}
\]

\[
\text{CH}_3\text{OH} \rightarrow \text{CO} + 2 \text{H}_2 \tag{2}
\]

The following considerations take into account the presence of these reactions and the consequences of the gas composition changes, particularly in respect to safe concentration of the purge gas-air mixtures.

Before the new purge system was introduced to operating SOFC units, several aspects of this purge method were analysed:

- Safety of the gas mixtures in air with respect to explosion potential
- Effectiveness in preventing Ni oxidation
- Potential formation of unwanted by-products such as CO
- Energy requirements for evaporation
- Conditions of evaporation

Positive results of the preliminary analysis led first to experimental testing and then to a full-scale implementation.

**Safety of the Gas Mixture**

The concentration of the reducing component in the purge gas should be as high as possible to decrease the amount of gas needed to consume all available air; however it must not be so high that the purge gas can form a flammable mixture with air. All potential species involving the elements present in the purge gas and the stack atmosphere (H, O, C, N) need to be considered, and the starting concentration of the reducing agent kept at such a level that no species can exceed the flammability limit.

The lower flammability limits for methanol and ethanol in air at room temperature are 6.72 vol% and 3.28 vol% respectively (5). However since hydrogen can be produced by thermal decomposition or steam reforming of alcohol, the maximum concentration of alcohol in the gas mixture must be limited to that which corresponds to the lower explosion limit of hydrogen in air (4.0 vol% at room temperature (5)). The explosive limits are affected by the change in the gas temperature, however the concentration of the flammable species will decrease on mixing of the purge gas with air to provide a safety margin.

**Effectiveness of the Gas Mixture in Preventing Ni Oxidation**

All of the thermodynamic calculations have been performed by Gibbs energy minimisation using the FACT software (6). The results of these thermodynamic calculations for the cases of diluted solutions of methanol and ethanol are presented in the Table 1 below. These calculations were done with the assumption that the aqueous solutions are considered completely evaporated; to provide a composition of the gas phase that is the same as the composition of the liquid phase.

As seen in Table I, the concentration of alcohols in the solution needed to prevent formation of NiO increases with the increase in temperature, but a concentration of about 0.43 wt% of methanol or 0.31 wt% of ethanol will prevent oxidation of Ni up to the temperature of 900 °C. On the other hand, the upper limit of the safe concentration of alcohols corresponds to that at which the hydrogen produced by the reforming reaction is 4 % (somewhat higher concentrations can be used if the dilution on mixing with air is taken into account). Assuming full reforming of alcohols into H₂ and CO₂, the hydrogen concentration of 4 % in the gas phase corresponds to concentration of 2.41 wt% of methanol (see Figure 1) or 1.75 wt% of ethanol. Therefore, in the concentration range of 0.43 to 2.41 wt% of methanol and 0.31 to 1.75 wt % of ethanol the composition of the gas phase should be both protective for Ni and safe. As there is always some air ingressation into the anode space, and some electrochemical oxidation can take place at the anodes even at the open-circuit condition, it is preferable to use the alcohol concentrations that are at the upper acceptable limits to provide for adequate reduction capacity.
Potential Formation of CO

Decomposition of methanol or ethanol can produce CO (see Reaction [2]). Table I shows the equilibrium concentration of CO formed during the reforming of alcohols at the concentration of 3.1 wt% for methanol and 2.2 wt% for ethanol. These concentrations produce a gas mixture that is about 5 % H2. In the typical cathode-supported tubular SOFC systems, the purge gas exits the stack through the combustion chamber, where this CO can oxidize to CO2 on mixing with air. The maximum concentration of CO allowable in the exhaust of heating furnaces is 400 ppm in most jurisdictions. It appears that the CO concentration could exceed 400 ppm only for the temperatures approaching 700 °C, but since this is higher than the autoignition temperature of CO of 651 °C (7), the CO produced will likely burn to create CO2.

Table I. Minimum concentration of methanol and ethanol in solution to prevent Ni oxidation and concentration of H2 and CO in the gas phase for solutions of 3.1 wt% methanol and 2.2 wt% ethanol.

| Temp. (°C) | Methanol | Ethanol |
|------------|----------|---------|
|            | Min. conc. to protect Ni (wt %) | Concentration in the gas phase for 3.1 wt% methanol | Min. conc. to protect Ni (wt %) | Concentration in the gas phase for 2.2 wt% ethanol |
|            | Hydrogen (vol%) | CO (ppm) | Hydrogen (vol%) | CO (ppm) |
| 450        | 0.199    | 5.11    | 120        | 0.143    | 5.15    | 122        |
| 500        | 0.221    | 5.11    | 179        | 0.159    | 5.15    | 182        |
| 550        | 0.245    | 5.10    | 252        | 0.176    | 5.15    | 256        |
| 600        | 0.269    | 5.09    | 339        | 0.193    | 5.14    | 345        |
| 700        | 0.319    | 5.07    | 551        | 0.229    | 5.12    | 560        |
| 800        | 0.372    | 5.05    | 803        | 0.268    | 5.09    | 817        |
| 900        | 0.427    | 5.02    | 1080       | 0.307    | 5.06    | 1100       |

Potential Effect on the Cell Voltage

The effectiveness of the purge can be assessed by monitoring SOFC cell voltages. During the purge (either H2-N2 mix or water/methanol), the specie that is responsible for the removal of oxygen and for keeping the cell voltage up is generally hydrogen. Some of the hydrogen reacts with oxygen in the stack area, keeping its concentration very low. The remaining hydrogen controls the stack voltage according to the reaction:

\[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O \] [3]

To determine the potential change in the stack voltage, the thermodynamic values of the cell voltage were calculated for both a H2-N2 protective gas and a methanol-water derived gas mixture, which was then compared with the thermodynamic cell voltage corresponding to Ni oxidation according to the reaction (6):

194 Electrochemical Society Proceedings Volume 2005-07
Whereas the measured open-circuit cell voltage values are often lower than the thermodynamic values on account of various factors (particularly electronic conductivity of the electrolyte and the fuel or air leakage), in a well working SOFC system the difference is generally small, and it should not be substantially affected by the change in the way the protective atmosphere is provided. The relative concentration of hydrogen will depend on the degree it is oxidised in the cell stack, which in turn can be controlled by the flow of the purge gas. It was assumed here that the flow of the purge gas was such that about half of hydrogen became oxidised, which is likely the highest acceptable value. The concentration of the purge medium was chosen so that the starting hydrogen concentration was 4.0 % (that corresponded to 2.41 wt% of methanol or 1.75% ethanol solution), and the oxygen concentration was that of air (20.8%). The actual gas concentrations of active species in the cell stack were therefore for H2-N2 purge 2 % H2, 2 % H2O and 96% N2, and for methanol purge 2 % H2 and 96.7% H2O.

Figure 2 presents the results of the cell voltage calculations, including the critical conditions associated with formation of NiO.

**Water-Methanol and Water-Ethanol Evaporation**

When implementing a system incorporating a liquid based purge system, attention must be given to the evaporation mechanism used to generate the vapour mixture. Evaporation of alcohol-water solutions at the conditions that allow the gas phase to equilibrate with the liquid phase may result in a very significant enrichment of the gas phase in the more volatile organic species, and create gas mixtures that are potentially explosive on contact with air. It is important to ensure that the gas mixture delivered to the cell stack is at the same composition as the starting solution. This can be achieved for example by a “flash evaporation”, in which the solution is heated at such a high rate that it converts into the gas phase without any significant change in the composition. Another such method can be “plug flow” evaporation, where a “plug” of liquid moves through the evaporator coil, converting into a gas/liquid mixture and then into pure gas, without undergoing a macroscopic shift in the composition.

Figure 1 shows the concentrations of methanol and hydrogen in the gas phase corresponding to the equilibrium (8) and for the “flash” or complete evaporation of the solution. For the 2.41 wt% methanol solution (that on flash evaporation and subsequent reforming produces the gas mixture containing 4 % H2), the equilibrium concentration of methanol in the gas phase is such that after reforming the H2 concentration in the gas mixture is about 22 %, which is much higher than the lower explosion limit.

**Heat Requirement**

Creating the protective gas by evaporation of dilute alcohol solutions requires thermal energy for preheating, evaporating, heating the vapours and reforming the alcohols. Assuming that the starting solution of 2.41 wt% methanol is at the ambient temperature (20 °C), producing the purge gas of the temperature in the 300 to 600 °C range requires the supply of heat of 50 - 60 W per each mL/min of the liquid flow, or per each 1.26
L/min (STP) of the resulting gas flow. Assuming for example that a small 5 kWe residential CHP system requires the purge gas flow of about 20 L/min (STP conditions), the heat requirement will be in the order of 0.9 – 1.1 kW.

PRACTICAL IMPLEMENTATION

Hardware

The hardware involved in the implementation of the liquid purge system consists of several components. These include a method of delivering and metering the correct quantity of liquid, and then providing a method of flash vaporizing it for use in the SOFC.

Delivery

The accurate delivery of the liquid purge can be easily accomplished by the use of many readily available metering pumps. Several options were tested as part of the implementation of the liquid purge system. Special consideration was given to the durability and materials used in the pump design.

It was also desired to have the liquid purge supply be internal to the SOFC unit. Therefore a tank was sourced to hold the required volume of liquid to allow for a safe startup and shutdown of the SOFC. Since a CHP-SOFC is normally run on a continuous basis, a single startup and shutdown was deemed to be sufficient.

Steamer/Evaporator

Early testing was completed with an electrically heated steamer that allowed for the production of superheated steam. This system was used successfully in FCT’s Alpha Unit SOFCs (9). Since the electric heater required large amounts of electricity for operation, this was not considered for further development.

FCT’s Beta Product (9) was designed from the start to incorporate a liquid based purge system. In order to make this possible, it was necessary to develop a delivery system that was reliable, effective, and efficient. Most early testing was concentrated on developing a steamer that would allow for the vaporization of the required volume of liquid while using available heat from the SOFC. This removed the dependence on an external power source to be available for steam production. Several oven tests were completed to show that a coil with sufficient length and conductivity could be placed in close proximity to the cell stack, and would not suffer failure due to the repeated thermal shock of vaporization.

These tests proved that there was sufficient room available for the coil to vaporize the mixture at all operating temperatures. Further durability testing was necessary to show the long-term viability of the coil in the environment. This testing was completed using a spiral configuration since this allowed for the maximum length to be placed in the smallest volume. Particular attention was given to the design of the initial part of the coil.
since it is subjected to the greatest thermal shock loading. Several design iterations were completed before settling on the final design.

**Test Results and Discussion**

Although lab testing had shown promise for the liquid purge system, the final design required testing in the product prior to its availability for use. FCT’s Beta SOFC system was chosen for this purpose. The conventional N$_2$-H$_2$ purge gas was used as a backup system and to provide reference data. To determine the effectiveness of the system, the cell voltage was monitored to ensure that the fuel electrode was not oxidized. The results of this testing are shown in Figure 3.

This testing shows a good agreement of the test results with the thermodynamic calculations. The cell voltage exceeds the minimum cell voltage (this is, the theoretical voltage below which the Ni oxidation can take place) throughout the operating range of the purge system. Further durability testing has been ongoing throughout the development of the Beta units, without a failure of the liquid purge system. Table II shows that when compared to a conventional compressed gas purge system, the cost, complexity and volume of the purge system have all been reduced.

**Table II. Effect of method of purging on the FCT Beta system parameters.**

| Purge System      | Cost per Use ($Can.) | Number of Components | Volume (L) |
|-------------------|----------------------|----------------------|------------|
| Compressed Gas    | 480                  | 20                   | 463        |
| Liquid Purge      | 0.85                 | 5                    | 45         |

**CONCLUSIONS**

The development of a novel purge system for use in SOFCs has enabled FCT to reduce the complexity, cost and size of the necessary purge system used in 5 kW class CHP-SOFCs. Throughout the development there has been good agreement between the theoretical thermodynamic calculations and the test results. The high reliability and ease of use of the liquid purge system has allowed it to become the standard product for use in FCT SOFC systems and will continue to be developed through experience gained during Beta installations.

**REFERENCES**

1. K. Kendall, N. Q. Minh, S. C. Singhal, in *High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications*, S. C. Singhal, K. Kendall Editors, p. 210, Elsevier, New York, (2003).

2. S. C. Singhal, in *SOFC-VI*, S.C. Singhal and M.Dokiya, Editors, PV99-19, p. 39, The Electrochemical Society Proceeding Series, Pennington, NJ, (1999).
Figure 1. Concentrations of methanol and hydrogen after reforming in the gas phase as a function of methanol concentration in the solution for the conditions of equilibrium and flash evaporation.
Figure 2. Thermodynamic cell voltages for the H₂-N₂ and alcohol-water purge gas system of the starting concentration 4% H₂, assuming 50% oxidation, and for the Ni oxidation reaction.

Figure 3. Cell voltage testing in a FCT Beta unit on liquid purge.