ABSTRACT

Conventional anode-supported cells have been tested under single-chamber mode of operation. Two humidifying conditions have been studied at various methane-to-oxygen ratios and flow rates, and the results are compared to the case where the inlet gas mixture is kept dry. Maximum power densities of the cells and real-time mass spectrometry analyses of the outlet streams are presented. Humidifying the gas is either detrimental or beneficial depending on the procedure used for the addition of water. Although useful, the mass spectrometry analyses may not explain all of the variations in performance. The chemical reactions inside a single-chamber SOFC are complex and further work would be needed to help find the best operating mode of this new design.

INTRODUCTION

The most interesting fuel for SOFC systems is natural gas consisting mainly of methane, i.e. 80-95% CH₄. SOFCs using methane or hydrocarbons as fuel are subjected to carbon deposition on Ni-based anode materials leading to their deactivation (1,2). Koh et al. (2) studied extensively the carbon deposition on Ni-YSZ anode supported cells fuelled by methane. According to these authors, reversible carbon deposition occurs at or near the three-phase boundaries while the irreversible carbon deposition takes place mostly on the external surface of Ni cermet anode under special conditions like an excess of methane gas. The use of wet fuel is proposed to avoid this phenomenon and also to promote the oxidation of the carbon compounds with an enhancement of the reforming reactions that produce the syngas (3).

Since the first proposal of a single-chamber SOFC, several of its potentialities have been cited. However the reactions that occur in the presence of a mixed gas (fuel and air) in the same reactor are complex and give rise to some challenges.

Although conventional materials such as Ni-YSZ cermet and LSM20 cathode can be used in a single-chamber cell configuration (4-6), no one has ever looked at the effect of adding water to the inlet stream of the gas mixture. Like other parameters that affect the cell performance, for example, the actual cell temperature and the methane-to-oxygen ratio, the water content may certainly influence their behaviour. To further understand the efficient operation of single chamber SOFC, the following preliminary studies are comparing two humidifying modes of water addition to the case where the inlet gas
mixture is kept dry. The performances as well as the exhausted products from the chamber are compared under various methane-to-oxygen ratios.

**EXPERIMENTAL**

Our experimental set-up is similar to the one described in our previous works (5,6). Anode-supported cells, model ASC1 from InDec BV, of which nominal composition is NiO (55%)-YSZ (45%)/YSZ/LSM20, are used as cells. The electrode area measures about 16x20 mm². On each cell, the following steps are performed: (a) reduction of the cermet with CH₄ gas alone, (b) addition of O₂, (c) stabilisation and measurements of the cell performance at various temperatures and in different mixed gas conditions. Furthermore, two modes of water vapour addition are investigated. In the humidified-A process, steps (a) to (c) are performed with humidified gas; in the humidified-B process, the water vapour is introduced only in step (c). Humidified conditions were established by saturating the mixed gas with water at room temperature. The total inlet gas flows at 450 sccm and 350 sccm STP. The methane to oxygen ratio (R_{mix}) was increased from 0.8 to 2 and the operating temperature (oven temperature) was fixed at 700°C. The real temperature of the cell is measured by fixing a thermocouple in contact with the cell along its thickness. Our measurements in ΔT are thus referring to the difference between the temperature of the cell and the controlled temperature of the oven. A mass spectrometer from Balzers (model Prisma) is used on-line to analyze the exhausted gases. Using this equipment, synthetic air was obtained by changing the nitrogen by argon containing 5% Helium. Polarization curves are established using a Solartron 1286 potentiostat-galvanostat in a 4-wires 2-electrodes configuration.

**RESULTS AND DISCUSSION**

Commonly used electrode materials of the type Ni-YSZ anodes and LSM cathodes have shown enough specificity to, respectively, oxidize fuels like methane and reduce oxygen gas so as to be utilized in single chamber SOFC applications. As for the case of the more conventional double chamber planar SOFC, reducing electrolyte thickness and working with an anode-supported cell increase markedly the performance allowing reduction in operating temperature (6). However, the best catalysts for the above mentioned reactions given a high conversion rate of the feeding gas mixture may not have been elaborated yet for the single chamber case. At the anode, the ideal reaction should be the partial oxidation of the fuel. Under methane, such a reaction leads to the production of H₂ and CO according to:

\[
\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad [1]
\]

Further interactions between the incoming reacting species and the reaction products are followed by a series of reactions difficult to evaluate in full details due to the complexity of the system. For example, water should already be formed through at least the direct oxidation of hydrogen, and favour the subsequent steam reforming and water-gas shift reactions. Addition of external water may affect these processes and further the performances of the fuel cells. Figure 1 presents, the characteristic E-j curves of anode supported cells measured at 700°C and 450 sccm flow rate in dry and humidified...
conditions. These results obtained at a methane-to-oxygen ratio $R_{\text{mix}}$ equal to 1.2, show that the humidified-A mode leads to a significant drop in cell performance. On the contrary, dry and humidified-B modes stay close to each other.

![Figure 1. Characteristics of single chamber SOFC at 700°C, under 450 sccm flow rate and $R_{\text{mix}}=1.2$, performance of anode-supported cell in dry and humidified modes.](image)

As shown before, cell performance is dependent on the methane to oxygen ratio (5,6). Figure 2 illustrates the maximum power densities measured in dry and humidified conditions under 450 sccm and $R_{\text{mix}}$ values varying from 0.8 to 2.0. Comparing these three conditions, the maximum power densities occur around $R_{\text{mix}}$ values between 1.0 and 1.2. Moreover, humidified-A mode leads to lower cell performance at any $R_{\text{mix}}$ condition. Such decrease in performance when a humidified fuel is used was observed before in conventional double chamber fuel cells (3). Contrary to this, however, when the water vapour is added in step (c) as in the humidified-B mode case, i.e., well after the reduction of the cermet and the introduction of oxygen, it leads to higher power densities at $R_{\text{mix}} >1.2$. Humidified-B mode may thus be the favourable mode in single chamber SOFC for well defined conditions of $R_{\text{mix}}$ and temperature. Similar results are obtained when the total flow rate is decreased to 350 sccm.

In a single chamber SOFC system, it is well demonstrated that the real temperature of the cells plays a key role on their efficiencies (5,6). Our recordings show that a drop in temperature is occurring for both of the humidified modes compared to the dry condition. The values of $\Delta T$ at maximum power densities in various $R_{\text{mix}}$ conditions are summarized in Table 1. At their maximum power densities ($R_{\text{mix}}$ around 1.0 and 1.2), the difference observed varies from at least 10 to 35°C between the cells exposed to dry and wet conditions. Such a decrease in temperature may probably be explained by the endothermic nature of the steam reforming reaction that occurs at the anode surface:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2
\]  

[2]
However referring to Figure 2, the differences in cells temperature may not by themselves explain all of the variations observed in terms of performance. For example, at $R_{\text{mix}} > 1.2$, better performances are obtained for humidified-B mode compared to the dry one despite the similar increases in temperature. Furthermore, on the basis of $\Delta T$ alone, one would expect better performances of the humidified-A mode compared to the humidified-B mode at $R_{\text{mix}}$ values between 1.0 and 1.2. However, the maximum powers recorded do not follow this trend.

Real-time mass spectrometry analyses recorded after the cells had stabilized are shown in figures 3 to 5. At open circuit voltage, they represent the environment that arises from the heterogeneous reactions which occur preferentially at the anode surface. Under these conditions, we found that the conversion of CH$_4$ as well as the production of H$_2$, CO, and CO$_2$ are always at their maximum for the dry mode at any $R_{\text{mix}}$ values (Figure 3 and 4). This is surprising since one would expect that the electrochemical performance of the cells would follow a trend similar to the production of H$_2$ and CO which are the actual fuel feeding the cell under operating conditions. While this is the case for the humidified-A mode which shows the lowest maximum power densities at any $R_{\text{mix}}$ values, the humidified-B mode is invariably displaying better performances at $R_{\text{mix}} > 1.2$ (Figure 2).

### Table 1. Anode supported single chamber SOFC operating at 700°C under total gas flow rate of 450 sccm: $\Delta T$ observed at maximum power density.

| $R_{\text{mix}}$ | Dry | Humidified-A | Humidified-B |
|------------------|-----|--------------|--------------|
| 2                | 44  | 37           | 45           |
| 1.6              | 51  | 44           | 52           |
| 1.2              | 63  | 51           | 42           |
| 1.0              | 71  | 45           | 35           |
| 0.8              | 36  | 12           | 25           |

Real-time mass spectrometry analyses were also performed during the polarization of the cells. Under the present experimental conditions, however, the current densities never
reached high enough values to change any significantly the flow rates of the individual species present in the outlet stream.

![Graph showing CH₄ conversion at open circuit voltage before polarization at various Rₘᵢₓ.](image)

**Figure 3.** CH₄ conversion at open circuit voltage before polarization at various Rₘᵢₓ.

A further observation from Figure 3 and 4 is the very similar rates of conversion of CH₄ and production of H₂ and CO between the two humidified modes. This may be totally accidental however considering the number of reactions that may utilize these species. As already mentioned above, one would be the reforming reaction that converts the methane into more CO and H₂; another, still related to the presence of water, would be the gas-shift reaction:

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2. \tag{3}
\]

The mass spectrometry data recorded during the step (a) procedure of reducing the Ni cermet under dry and humidified-A modes, already give some indications that these reaction mechanisms are operating at least in the absence of O₂. As shown in Table 2, and although the conversion rate of CH₄ is low, an important increase in the H₂ concentration is observed when the methane gas is humidified. A more significant amount in CO₂ content is also observed in the presence of water. A later observation that suggests an involvement of the reforming reaction is the decrease by 5 to 10°C of the cell temperature in the humidified-A mode compared to the dry one. The water reforming reaction is indeed known to be endothermic.

**Table 2. Reduction of the cermet with CH₄ at 700°C: percentage of CH₄ converted, and products formed.**

| Mode            | CH₄ conv.(%) | H₂ prod.(%) | CO₂ prod.(%) | CO₂ prod.(%) |
|-----------------|-------------|-------------|--------------|--------------|
| Humidified-A    | 18          | 12          | 9.5          | 2            |
| Dry             | 14          | 6.7         | 6.5          | 0.6          |

When the cells are exposed to oxygen as in step (b) and after, the level of CO₂ measured, is found consistently at higher concentrations under dry mode at every Rₘᵢₓ values. This is shown in Figure 5.
Figure 4. Production of H2 (a) and CO (b) at open circuit voltage before the polarization at various Rmix.

Although the addition of water should favour the shift reaction, our results under humidified modes seem to indicate that it is not a dominating mechanism in the presence of oxygen. Ni-based SOFC anodes were already found not to be effective catalysts for the shift reaction whose equilibrium state may also depend on the fuel utilization factors (7). When oxygen is introduced, competition between the adsorbed species might favour a change in mechanisms. Indeed, according to Figure 5, increasing the amount of oxygen seems to favour the production of CO2 instead, until partial re-oxidation of the nickel surface occurs at Rmix<1.0. The production of CO2 in our conditions may thus come from the direct oxidation of CO.

Figure 5. Production of CO2 open circuit voltage before polarization at various Rmix.

Although the present results cannot totally explain the differences in cell performance observed under the 3 conditions studied here, some hypotheses may be put forward. Overall it seems very difficult to explain all of the differences in cell performance from the mass spectrometry analyses alone. However, pursuing with the scheme of heterogeneous catalysis and electrocatalysis processes, some other hypotheses may still be drawn. These processes are occurring at the external surface of the anode or through its thickness around the three-phase boundaries. The reduce conversion rates of methane onto the nickel surface under humidified modes may certainly be explained by the competition between the adsorbed CH4 and H2O molecules. Without water, a maximum
amount in CH₄ species may be adsorbed and favours its high conversion rates. For explaining the much lower electrochemical performance of the humidified-A mode at Rₘᵢₓ ≥ 1.0, it could also be argued that the Ni cermet may not have been as reduced as for the dry and humidified-B modes. If this is the case, measurements of series resistance of the cells by impedance might shed some light into this behaviour. Finally, to explain the better performance of the humidified-B mode when the methane-to-oxygen ratio increase as for Rₘᵢₓ ≥ 1.2, it is reasonable to believe that the extraneous water molecules diffusing inside the anode might lead to a further increase in the oxidation rates of the CH₄, H₂ or CO species. However, the gas flow rates of the individual species were not affected enough by such processes and stayed undetected through real-time mass spectrometry.

CONCLUSIONS

Our preliminary investigations of the effect of humidifying the inlet gas mixture of a single-chamber SOFC have shown that it might be beneficial to the cell performance when the methane to oxygen ratio Rₘᵢₓ is equal or greater than 1.6. However, maximum power densities are found close to Rₘᵢₓ = 1.2 both for the dry and the humidified-B modes. One can say that the necessary amount of water needed for best operation of the system under dry condition could be internally produced by one of the various reactions available. For simplicity of design and operation of single-chamber SOFCs, this observation might lead to the suggestion that it is better to operate such system on dry conditions alone. However, our findings that a significant decrease in the production of CO₂ is also occurring in both of the humidifying modes are of interest and need further investigations. Much more studies are required in the areas of heterogeneous and electrocatalytic reactions and future work would have to take into account the production of water as well as the deposition of carbon on the anode materials.

ACKNOWLEDGMENTS

The authors thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and Hydro-Québec Research Institute (IREQ) for financial support.

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