



## Evaluation of the Actual Working Temperature of A Single-Chamber SOFC

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Single-chamber solid oxide fuel cell (SOFC) experiments have been carried out at temperatures below 900°C with methane-air mixtures. Our study confirms previous results obtained by Hibino and co-workers with conventional materials like  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  for the cathode and a NiO-ytria-stabilized zirconia (YSZ) cermet for the anode. In addition, special attention has been paid both to the gas flow and to the actual operating temperatures. Platinum meshes and wires upon the electrodes would greatly influence their actual operating temperature and they have been systematically avoided for the working cells within this study.  
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Preliminary experimental evidence for the feasibility of a single-chamber solid oxide fuel cell (SOFC) was provided several decades ago.<sup>1</sup> But it has been only recently that the workability of a fuel cell with significant current densities was demonstrated by Hibino and co-workers with Iwahara.<sup>2</sup> Their single-chamber cell is basically a SOFC operating at high temperature directly from a methane/air mixture. By modifying some materials and operating conditions, Hibino and co-workers<sup>3</sup> further improved their cell. Their latter results are concerned with a cell operating down to 450°C with a peak power density approaching 650 mW/cm<sup>2</sup> at 550°C.<sup>4</sup> Despite these remarkable results, at least two points remain to be clarified. One is concerned with the confirmation of Hibino and co-workers' results by other sources; deceptively low outputs were registered by Bay *et al.*,<sup>5</sup> reaching at most 4 mW/cm<sup>2</sup> at 950°C. The other point relates to the actual operating temperature of single-chamber cells. A better knowledge of this temperature is important in that it may largely influence cell performances in an unstable mixture of methane and air.

### Experimental

The double-face single-chamber cell in Fig. 1 is basically the same as that described in Ref. 2. Conventional materials such as in Ref. 3 are used for all main components, *e.g.*, cathode, electrolyte, and anode. The  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  powder for the cathode has been supplied Praxair and alternatively by NexTech. The yttria-stabilized zirconia (YSZ) electrolyte, 8% M in yttria and 0.2 mm thick, has been provided by Performance Ceramics. The cermet slurry consisting of a Tosoh TZ-8Y powder, ballmilled with a fine NiO powder from Baker (nickelous oxide no. 2796-01), is prepared according to a state-of-the-art procedure,<sup>6</sup> the composition in terms of weight ratios being basically 55% nickel oxide/45% YSZ. Coating the electrolyte and firing at 1200 or 1250°C for 3 h results in electrode layers approximately 10-20 μm thick with electrode areas of about 8 × 8 mm in size. As seen in Fig. 2, our experimental setup departs from that of Hibino *et al.* in some details. A sample holder machined out of a Macor block is used to specifically constrain the methane/air mixture around the sample and a nitrogen blanket gas is used around this block. Both concentric tubes are made of fused silica. Platinum meshes and wires are totally avoided for the working cells due to platinum high catalytic activity in regard to methane. The cell is pressed between two gold meshes and the gas mixture allowed to flow on both sides. The cells are operated mainly at a furnace temperature of 800°C with *R*, the methane-to-oxygen ratio, equal to 2. Temperatures between 750 and 900°C are further investigated and the methane-to-oxygen ratio is also varied down to one. Initially, the cell current was simply drawn into an ohmic load and, later, into an active current sink. The sample holder temperature was monitored in two different ways: (i) directly through a thermocouple embedded

into the Macor sample holder and (ii) indirectly by a thermocouple external to the outer silica tube and correspondingly calibrated with the inner chamber temperature.

Because methane/air mixtures are involved which may lead to strongly exothermic reactions within the present experiments, one cannot simply rely on the so-called furnace temperature. To more closely follow up the actual reactions going on, an additional thermocouple was used to monitor the gas temperature exiting from the sample holder. It was made of a fine gauge, 0.003 in. in diameter, type K supported by a thin alumina capillary. The hot junction was lightly coated with an Aremco 570S cement to protect it from any promoting catalytic effect that would result from direct contact with the gas mixture. In a second set of experiments, a fine gauge, 0.003 in. in diameter, type R thermocouple was fixed on an 11 × 11 × 0.2 mm YSZ platelet and totally embedded with a light coating of YSZ-based cement. This thermocouple further exited from the sample holder through a thin alumina capillary also coated with the YSZ-base cement where the thermocouple may contact the methane/air mixture. The other side of the YSZ platelet was either left blank or gold and platinum meshes were added alternatively to the sample to investigate their respective effects upon the platelet temperature. The purpose of the whole setting was to more closely evaluate the actual temperature of the single-chamber cell under various conditions in the absence of an undergoing electrocatalytic process.

### Results and Discussion

After first heating the cell in pure nitrogen to the operating temperature, the methane/air mixture was introduced and the cermet was quickly reduced by the incoming gas. The effectiveness of the reduction was readily observed by the appearance of the cell potential. At the same time, the temperature of the gas exiting the sample chamber rose by at least 35 to 45°C as shown in Fig. 3 for furnace operating temperatures between 800 and 900°C. Cell performance at 900°C was poor compared to that at 800°C. The cells operated at 900°C also rapidly degraded with time. The actual behavior of two different cells is illustrated in Fig. 4. In contradistinction, the cell operated at 800°C behaved well. With a methane-to-oxygen ratio equal to two, a maximum specific power of 85 mW/cm<sup>2</sup> was calculated from the curve in Fig. 4. This largely confirms the results already obtained by Hibino and co-workers<sup>3</sup> at 950°C despite the absence of platinum, the lack of any additive to the lanthanum manganite cathode, and the significantly lower operating temperature in the present study for basically the same cell materials. This thereby confirms the validity of their approach. Furthermore, largely improved performances have been obtained recently by Hibino and co-workers,<sup>4</sup> but on entirely different materials and with a much lower methane-to-oxygen ratio.

Postexamination of the cell operated at a nominal temperature of 900°C led to the observation of extensive degradation of the gold mesh facing the anode. This is most probably due to the formation of a gold-nickel eutectic. This eutectic is known to melt at 955°C.<sup>7</sup>

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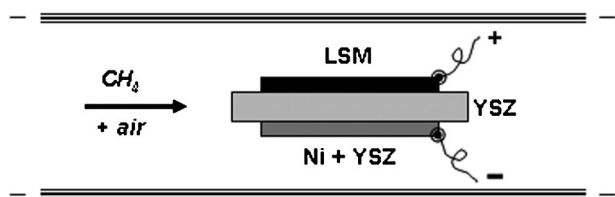


Figure 1. Simplified schematic of a single-chamber cell.

Following our temperature measurements of the gas exiting the sample holder, its formation is thus most likely to happen with the use of gold meshes and wires at too high a temperature.

A complementary picture of the actual cell temperature was given in our second set of experiments with a thermocouple directly cemented upon the YSZ platelet. Within our experimental conditions and in the absence of any chemical reaction, little effect of the incoming gas flow upon the sample temperature was found. Using pure nitrogen or pure methane, the magnitude of this effect is at most equal to 0.5°C. Turning to methane/air mixtures, the temperature rise of a blank YSZ platelet as a function of the gas flow and at different furnace temperatures is given for runs performed, respectively, with a CH<sub>4</sub>:O<sub>2</sub> equal to 1 in Fig. 5 and equal to 2 in Fig. 6. No significant temperature rise was found at either 700 or 750°C. As the furnace temperature was raised to 800°C, a slight overheating of the sample became obvious with a tendency for the temperature to decrease toward higher gas flows. Although the temperature rise was significantly higher at 850°C, the same trend remained with increasing gas flow. More heat also evolved from the methane-rich mixture at this latter temperature. Concerning gold present in different forms

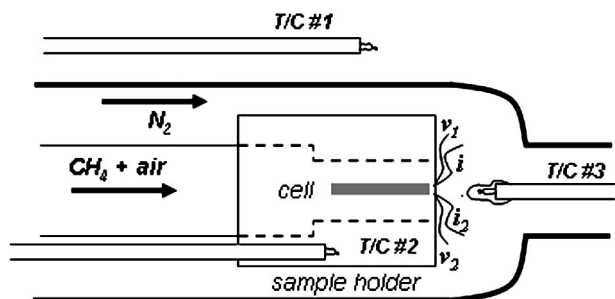


Figure 2. High-temperature setup for the single-chamber cell.

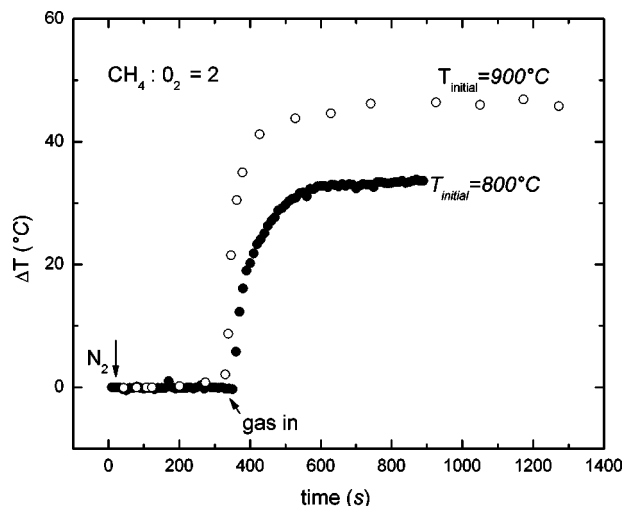


Figure 3. Temperature rise at the beginning of two different cell experiments.

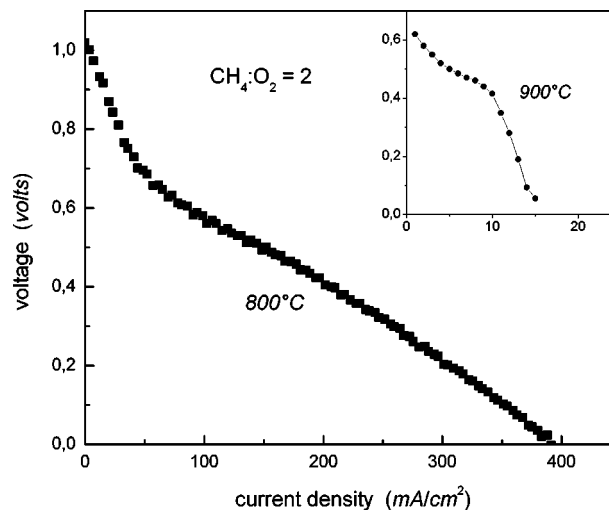


Figure 4. Potential of a cell vs. current density after reduction of the cermet for two different cells operated at  $T_{\text{initial}} = 800$  and  $900^\circ\text{C}$ .

in our cells, little catalytic effect is normally expected from this metal. This was confirmed at 800°C by a gold mesh placed on a blank sample which led to essentially the same temperature rise as those found in Fig. 5 and 6 for a blank sample alone.

The picture became entirely different as platinum meshes were applied on both sides of a blank sample. Even at 700°C, the lowest furnace temperature in this study, temperature rises departed drastically from all preceding observations. At all operating temperatures, the temperature rise was almost linearly related to the magnitude of the gas flow. The heat so evolved should thus be proportional to the gas flow suggesting that the gas mixture reached a constant degree of reaction within the whole range of gas flows and temperatures under consideration. The highest temperature rise obtained at 700°C may be explained by radiative heat losses being somewhat smaller at that lower temperature. In addition, sample overheating is somewhat greater at CH<sub>4</sub>:O<sub>2</sub> equal to 1 in comparison to runs at CH<sub>4</sub>:O<sub>2</sub> equal to 2. In all cases with platinum, the temperature rise at  $R = 1$  is somewhat higher than at  $R = 2$  (Fig. 7 and 8). This is entirely compatible with the higher potential heat available from the air-rich mixture.

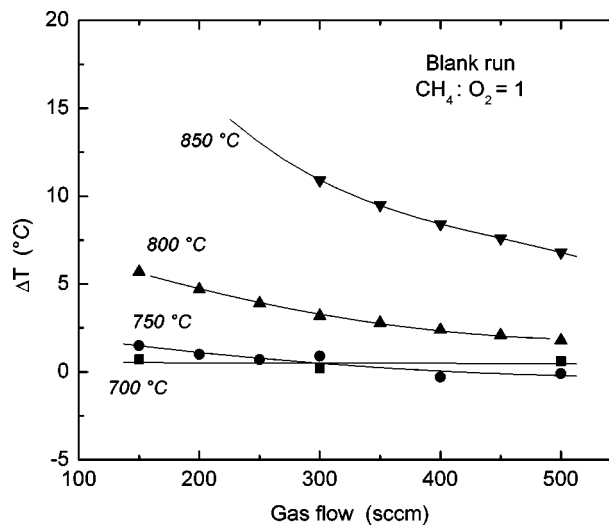
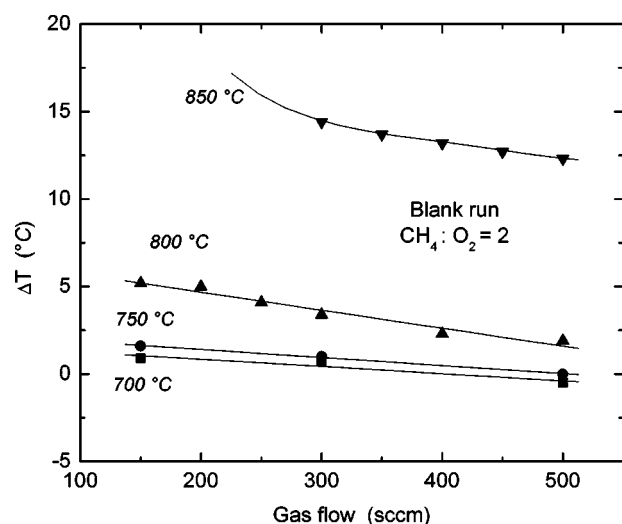


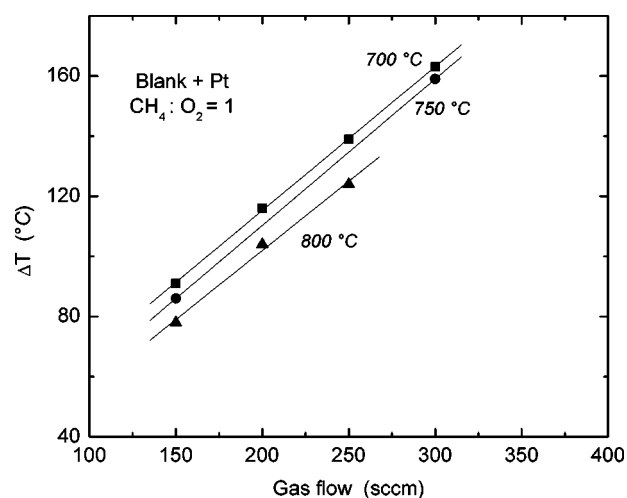
Figure 5. Sample overheating for blank runs at various furnace temperatures with CH<sub>4</sub>:O<sub>2</sub> ratio equal to 1.



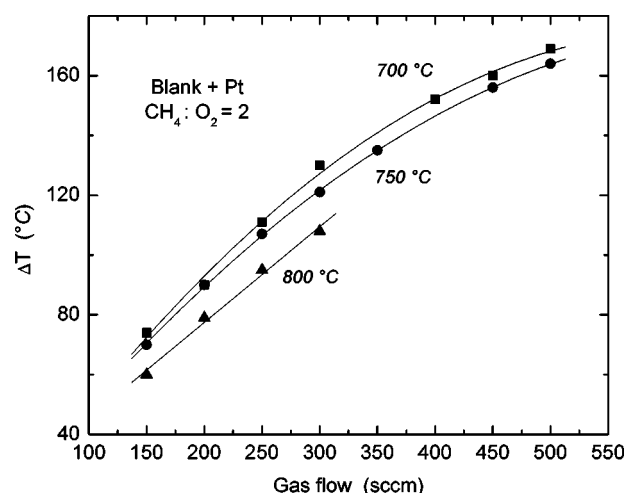
**Figure 6.** Sample overheating for blank runs at various furnace temperatures with  $\text{CH}_4:\text{O}_2$  ratio equal to 2.

There is little information if none on what the actual operating temperature of the cells was in Hibino *et al.* former papers dealing with methane. One is limited to assume that their operating temperature could be the heating temperature of the furnace. However, these authors started more recently to address this problem with various hydrocarbon-air mixtures at heating temperatures of 800°C and below.<sup>8,9</sup> Although little information was provided therein regarding methane, overtemperatures are clearly evidenced regarding higher hydrocarbons with higher molecular weights reacting upon anodes. The whole question still deserves further investigation to fully control the overall reactions upon single-chamber cells.

In operating a single-chamber cell, the gas mixture is provided in excess to the high-temperature compartment so that only a minor



**Figure 7.** Sample overheating for blank runs with platinum meshes at various furnace temperatures.  $\text{CH}_4:\text{O}_2$  ratio equal to 1.



**Figure 8.** Sample overheating for blank runs with platinum meshes at various furnace temperatures.  $\text{CH}_4:\text{O}_2$  ratio equal to 2.

amount of it is expected to react before reaching the cell. This in turn depends considerably on the nature of the materials either preceding or surrounding the cell. A greater flow would also let the mixture react less before reaching the cell. In the absence of platinum, this condition seems to be fulfilled within the present study. To optimize the single-chamber cell efficiency, as much of the gas mixture as possible should be made available to the cell electrodes. Thus, considerable work remains to be done to optimize all parameters related to single-chamber cell design and efficiency.

### Conclusions

Significant currents are obtained from our single-chamber cells thereby confirming previous results by Hibino and co-workers. With equivalent conventional materials,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  for the cathode, YSZ as the electrolyte, and a NiO-YSZ cermet for the anode, comparable performances were obtained at temperatures lower by about 150°C. As shown in this work, a more precise evaluation of the true cell temperature is important in measuring cell performances. Further work is in progress regarding operating conditions and other cell designs.

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