



An Experimental Evaluation of the Temperature Gradient in Solid Oxide Fuel Cells

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Solid oxide fuel cells (SOFCs) working under direct reforming or catalytic partial oxidation may experience severe thermal gradients due to cooling or overheating at the fuel cell inlet. In this work, we show that the ohmic resistance measurement of thick electrolyte cells composed of smaller cathodes displaced along the opposite side of a full-size anode provides excellent results to evaluate the temperature gradients along cells submitted to such processes. Taking the catalytic partial oxidation of methane in single-chamber SOFC, as an example, we evaluate an overheating of more than 50°C within the first centimeter length of the cell. © 2006 The Electrochemical Society. [DOI: 10.1149/1.2398729] All rights reserved.

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The use of solid oxide fuel cells (SOFCs)^{1,2} as efficient energy-converter devices rests on their high working temperature. These ceramic fuel cells generally operate between 800 and 1000°C, although a major research effort is put forward to reduce their operation below 800°C for reducing manufacturing costs and improving cell lifetime. Depending on the selected range of temperature, a SOFC system would allow for either cogeneration or bottoming cycle, which add significantly to the overall power-generation efficiency. The high operating temperature of SOFC affords, in principle, for the direct use of hydrocarbon fuels by means of their catalytic conversion to carbon monoxide and hydrogen. The most economical way to convert these fuels is to proceed through direct internal reforming (DIR), as it is observed in tubular or planar designs, or through catalytic partial oxidation (CPOX), which is at the basis of the functioning of single-chamber SOFC (SC-SOFC). However, both DIR and CPOX may lead to high temperature variations along the fuel cell.

In the case of direct reforming of methane, a significant cooling at the inlet of the fuel cell is expected due to the fast kinetics of the endothermic reforming reaction, especially over conventional Ni–yttria-stabilized zirconia (YSZ) cermet.³ It then aggravates the temperature gradient that normally exists between the inlet and outlet of operating cells and may induce further thermal stresses and cracking of electrolyte and sealant.⁴ Although this expected cooling effect is frequently mentioned, very little data exists in support of such an assertion, possibly due to the difficulty of measuring exact surface temperature under SOFC conditions.⁵ Various catalytic types of experiments have been performed on Ni–YSZ substrates. For instance, direct measurements with thermocouples gave a slight decrease of $\Delta T \sim 20^\circ\text{C}$ on a 100 mm long Ni–YSZ sample exposed to a molar ratio $\text{H}_2\text{O}/\text{CH}_4$ of 3 at 915°C.⁶ A comparison of the outlet stream composition of a mixture of CH_4 , CO , CO_2 , H_2 , and H_2O to the equilibrium constant of the shift reaction at 950°C implied a $\Delta T \sim 50$ to 60°C.⁷ More recently, Versa Power operated a 121 cm² single-cell stack with 25 thermocouples contacting the backside of an anode interconnect. Dong and Thompson⁸ measured a maximum ΔT of 35°C under the following conditions: furnace temperature, 750°C; current density, 0.661 A/cm²; mixture of fuel representative of high DIR conditions (85%).

The case of SC-SOFC is different because it operates directly in mixtures of air and hydrocarbon fuels via partial-oxidation reactions.^{9–11} Operated between 300 and 800°C,^{12,13} these fuel cells need excellent catalytic activity and selectivity of the electrode materials to reach good performances. The catalytic partial oxidation of methane to CO is exothermic, and even a low conversion to CO_2 generates a large amount of heat, difficult to remove because of the

fast reaction kinetic of the reactions.¹⁴ The importance of measuring the actual working temperature of the SC-SOFC was previously recognized.¹⁵ Indeed, on cells often smaller than 1 cm², overheating superior to 100°C has been recorded according to the considered fuel, the complete cell materials, and the flow rates.^{16–18} The knowledge of the true cell temperature thus becomes essential for a clear comparison of cell performances. Moreover, like in DIR, temperature gradient is also expected along larger cells but this time with an overheating close to the fuel inlet. The ΔT reported before may thus be only mean temperature increases, the true temperature at the fuel cell inlet being even more important. This fact has never been considered before, and may have contributed to the loss of nickel that was observed by Jacques-Bédard et al.¹³ along a Ni–YSZ cermet anode exposed to various mixtures of CH_4/O_2 at 800°C.

In this study, we are proposing a method to evaluate the local change in temperature and performance on fuel cells exposed to conditions where heterogeneous catalytic reactions are occurring along their length. More specifically, we have examined the case of SC-SOFC made of conventional electrode materials and YSZ electrolyte. We show that the use of thick electrolyte membranes and electrochemical impedance spectroscopy (EIS) to measure the ohmic resistance of cells made of smaller cathodes that face and move along a full-size anode on the other side can be rightfully used for achieving this goal.

Experimental

Electrolyte-supported cells were prepared by conventional screen printing technique. Thick 8YSZ membranes (500 μm) from Marktech, LSM, and Ni cermet were used as electrolyte, cathode, and anode, respectively. Each electrode consisted of two layers: (i) 50 wt % LSM/50 wt % YSZ and (ii) LSM for the cathode, and (i) 45 wt % NiO/55 wt % YSZ and (ii) NiO for the anode. LSM + YSZ powder was prepared by mixing $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (Praxair) with 8YSZ powder (Tosoh). NiO + YSZ powder was prepared by mixing NiO powder (Baker) with the same batch of 8YSZ powder. Subsequently, inks were prepared from these powders with the addition of triton (dispersant), terpineol (solvent), and PVB (binder). In all cases, the inner electrode layer was dried at 150°C after printing. Moreover, the anode layers were deposited and sintered first, followed by the cathode layers. Final sintering of the anode and cathode layers was performed for 3 h at 1375 and 1100°C, respectively.

Cells were prepared with the same anode geometry (14 \times 23 mm²) on an electrolyte membrane measuring 16 \times 25 mm. Cathode geometry and positioning varied as presented in Fig. 1. The surface area of the cathode was either 1.07 cm² when measuring the effect of cathode positioning at the inlet, center, and outlet position

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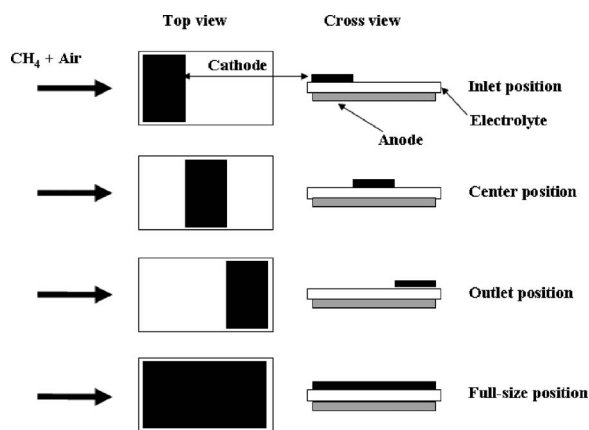


Figure 1. Schematic diagram of the different cathode geometries tested with a full-size anode surface area (14×23 mm) on the opposite side.

against the fuel flow direction or 3.2 cm^2 for a full-size cathode. In the following, all the results are normalized against these geometric cathode areas.

Cells were tested in an experimental setup (Fig. 2), similar to the one described earlier.¹⁰ Previous to the reduction of the nickel oxide, the cell was heated to a nominal temperature of 700°C , controlled by the thermocouple TC#1. Reduction was then performed under atmospheric pressure in an argon/methane mixture according to the procedure we previously developed.¹⁹ The exhausted gas was analyzed in real time with a mass spectrometer from Balzers (model Prisma). A thermocouple (TC#2) was placed in front of the cell and was used to measure the local temperature under operating conditions. Current–voltage curves were obtained using a Solartron 1286 potentiostat. Impedance measurements were carried out in a two-electrode configuration with a Solartron SI 1260 impedance/gain phase analyzer at a frequency range varying from 0.1 Hz to 100 kHz.

Results and Discussion

Because the ohmic drop in SOFCs is essentially governed by the resistance of the electrolyte at high temperatures, the use of a thick membrane should in principle reflect any significant change of temperature resulting from thermal processes occurring over the cell. To verify this and the effect of overheating due to the CPOX reactions along the cell, we first measured the characteristic E - j curves of the three configurations studied here along with the full-size cell. All the measurements were performed at $T = 700^\circ\text{C}$ in a methane– O_2 mixture ($R = 1$) and a total flow rate of 450 sccm. The results are displayed in Fig. 3. In every case, the cells are characterized by large electromotive forces at around 920 mV and the curves are showing relatively linear relation at all current densities. The peak power densities were equal to 199, 116, and 92 mW cm^{-2} , respectively, for the inlet, center, and outlet position. Cells with a cathode located at

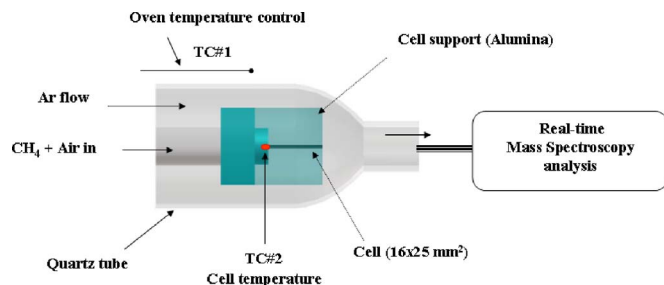


Figure 2. (Color online) Schematic illustration of the experimental setup used for testing the 16×25 mm cells.

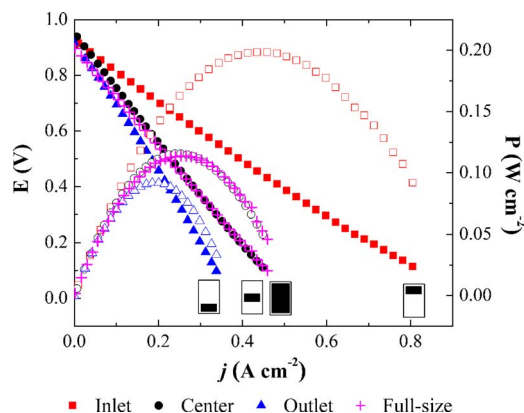


Figure 3. (Color online) (Closed symbols) Cell voltage and (open symbols) power density vs current density for the inlet, center, and outlet position of the cathode at $R = 1$ compared to the full-size cell. $T_{\text{oven}} = 700^\circ\text{C}$, $Q_{\text{tot}} = 450$ sccm, $Q_{\text{CH}_4} = 75$ sccm. The thickness of the YSZ electrolyte is $500 \mu\text{m}$.

the fuel inlet thus showed twice the performance of cells with a cathode lying at the fuel outlet. In comparison, the full-size cell shows a maximum power density of 114 mW cm^{-2} , and its voltage and power density curves are more or less overlapping the curves measured for the center-position cathode. The result seems to indicate that the mean cell temperature of the full-size cell resembles the temperature that may be developing at the middle of its length. To verify that the drop in performance was not due to a depletion of the fuel along the anode side, we measured the outlet gas composition of cells fed with a mixture of $\text{CH}_4/\text{O}_2/\text{Ar} = 75:75:300$ sccm. A typical result is shown in Table I for a cathode located at the outlet position. It is seen that large amounts of H_2 and CO are still present in the outlet stream, indicating that fuel availability on the last third of the cell cannot be questioned for its lower performance. It may thus be concluded from the previous results that a larger increase in cell temperature is probably prevailing at the inlet of the cell due to the CPOX of methane, which mostly occurs at the Ni sites of the anode. As a consequence, the ohmic resistance of the thick ($500 \mu\text{m}$) YSZ electrolyte at the inlet of the cell should also be lowered, which leads to better cell performance in this position.

To further examine the ohmic resistance contribution to the cell performances and the temperature gradient that is expected along the SC-SOFC, EIS was carried out on the above cell configurations. The impedance spectra in the complex plane are displayed in Fig. 4. The data for the inlet-, center-, and outlet-position cells point out that both the high-frequency intercept (R_{HF}) and the area-specific resistance (ASR) are dependent on the cathode position. While the last term is linked to the reactions that are taking place at the electrodes, the high-frequency intercept values are, in our case, typically related to the electrolyte resistance and to its dependency on temperature. Here, we found that R_{HF} goes from $0.96 \Omega \text{ cm}^2$ for the inlet position to $1.56 \Omega \text{ cm}^2$ for the outlet position. From our independent measurements of the ionic conductivity of YSZ electrolyte with temperature ($E_a = 0.81 \text{ eV}$ and $\sigma_0 = 297 \text{ S cm}^{-1}$) and the high-frequency resistance measured by EIS, we calculate a span of 59°C between the temperature at the inlet of the cell (813°C) and the

Table I. Outlet stream composition (sccm) measured by mass spectrometry for a cell where the cathode is located at the outlet position. The cell was fed with a mixture of $\text{CH}_4/\text{O}_2/\text{Ar} = 75:75:300$ sccm at 700°C .

Outlet gas composition (sccm)				
CH_4	O_2	H_2	CO	CO_2
47.8	42.4	22.3	11.6	17.3

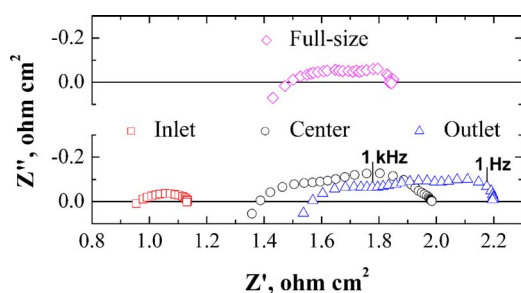


Figure 4. (Color online) Impedance spectra of Ni-YSZ//YSZ//LSM (Inlet, Center, Outlet, and Full-size positions) at 700°C and $R = 1$ obtained under open-circuit conditions.

temperature at its outlet (754°C). Such a variation is much more important than the maximum deviation in temperature ($\pm 3^\circ\text{C}$) that is sensed by the thermocouple on each third of cells. This suggests that the recorded temperature represents solely the mean catalytic activity occurring at the anode. All the results and the calculated temperature are shown in Table II. With an R_{HF} value of 1.48 $\Omega \text{ cm}^2$ the full-size cell is showing a mean temperature of 762°C. In fact, R_{HF} of the full-size cell is comparable within experimental errors and uncertainties (high-frequency inductive effects, exact electrode surface areas after processing, and current distribution between both electrodes) to the sum of the individual components forming a parallel circuit

$$\frac{1}{R_{F\text{-size}}} = \frac{1}{R_{\text{Inlet}}} + \frac{1}{R_{\text{Center}}} + \frac{1}{R_{\text{Outlet}}} \quad [1]$$

This shows that dividing the cell into three parts is representative, from an electrical point of view, of what is happening at this position in a complete cell.

A similar rise in temperature in SC-SOFC has been recorded before with thermocouples placed close to the cells. However, such a gradient along the cell has never been accurately quantified before. The results reveal that a steep decrease in temperature is taking place within less than 1 cm length along the fuel cell.

It may thus be confirmed that R_{HF} turns out to be a useful measurement to estimate the local temperature along a fuel cell exposed to heterogeneous catalytic reactions. Indeed, the use of a thick YSZ electrolyte allows for the large variation of R_{HF} observed and, hence,

Table II. Calculated temperature based on the high-frequency resistance (R_{HF}) measured by EIS, along with the temperature sensed by the thermocouple at the cell inlet on the four different cell configurations at $\text{CH}_4/\text{O}_2 = 1$ and 700°C.

	Inlet	Center	Outlet	Full-size
R_{HF} ($\Omega \text{ cm}^2$)	0.96	1.39	1.56	1.48
T_{calc} ($^\circ\text{C}$)	813	768	754	762
$T_{\text{cell inlet}}$ ($^\circ\text{C}$)	766	770	764	770

for the accurate evaluation of the local temperature. The gradient of performance obtained on each third of cells (Fig. 3) is a consequence of the gradient of temperature that comes from the high catalytic activity of Ni towards the partial oxidation of CH_4 . Such a gradient of performance is particularly exacerbated in this experiment due to the use of a thick YSZ electrolyte. In the case of thin electrolyte the performances would not change quite as much, but the large gradient of temperature would still be present.

Conclusion

In SC-SOFC, a large increase in temperature at the cell inlet is caused by partial and complete oxidation of methane on the anode. This implies a nonhomogeneous performance in electrolyte-supported cells. In situ evaluation of the temperature gradient along the cell was developed via impedance spectroscopy. This was allowed by using a thick YSZ electrolyte (500 μm) and by moving a smaller cathode that faced a full-size anode on the other side. We evaluated a temperature gradient of more than 50°C within the first 1 cm length of the fuel cell. The proposed method may be used, at least under open-circuit conditions, as a screening tool for the local temperature change of cells fed with fuel mixtures that lead to exothermic or endothermic reactions. It may be useful to evaluate the thermal conditions that exist within interconnectors and along the gas channels of unit-cell stacks.

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