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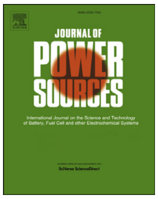

Current and temperature distributions in-situ acquired by electrode-segmentation along a microtubular solid oxide fuel cell operating with syngas

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HIGHLIGHTS

- Current/temperature distribution analyzed along microtubular SOFC fed with syngas.
- Local currents and temperatures were in-situ measured by electrode-segmentation.
- Fuel depletion increases with internal reforming, thus, causes performance-loss.
- Maximum temperature difference along the cell decreases with internal reforming.
- Methane conversion is dominantly affected by hydrogen partial pressure.

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ABSTRACT

Addressing the fuel distribution and endothermic cooling by the internal reforming, we have measured longitudinal current/temperature variations by “Electrode-segmentation” in a microtubular solid oxide fuel cell operated with syngas (50% pre-reformed methane) and equivalent H_2/N_2 (100% conversion of syngas to H_2) at three different flow rates. Regardless of the syngas flow rates, currents and temperatures show irregular fluctuations with varying amplitudes from upstream to downstream segment. Analysis of the fluctuations suggests that the methane steam reforming reaction is highly affected by the H_2 partial pressure. Current-voltage curves plotted for the syngas and equivalent H_2/N_2 flow rates reveal that the fuel depletion is enhanced toward the downstream during the syngas operation, resulting in a larger performance degradation. All the segments exhibit temperature drops with the syngas flow compared with the equivalent H_2/N_2 flow due to the endothermic cooling by the methane steam reforming reaction. Despite the drops, the segment temperatures remain above the furnace temperature; besides, the maximum temperature difference along the cell diminishes. The MSR reaction rate does not consistently increase with the decreasing gas inlet velocity (increasing residence time on the catalyst); which we ascribe to the dominating impact of the local temperatures.

1. Introduction

In combination with its storage and transport issues, the insufficient distribution infrastructure of the most appropriate energy carrier hydrogen has been postponing the commercialization of various fuel cell systems. In regard of the recent demands for the use of conventional fuels, such as methane and other higher hydrocarbons owing to their widespread distribution lines accompanied with easy-to-store characteristics [1–3], Solid Oxide Fuel Cells (SOFCs) have been relatively promising for various applications, ranging from mega-scale power plants to micro-scale portable applications. SOFCs with their rather high energy conversion efficiencies attaining to 65% [4] at high operation temperatures (600–1000 °C) release high quality waste heat allowing for various cogeneration processes [5,6].

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SOFCs are designed in various concepts, such as anode-, cathode-, or electrolyte-supported. Anode-supported SOFCs with smaller ohmic and concentration overpotentials have been superior to the cathode- and electrolyte-supported concepts [7,8].

Owing to their geometry, tubular SOFCs have mitigated the thermo-mechanical stresses arising due to the thermal expansion coefficient mismatch of the cell components, residual stresses, and spatial temperature variations during the operation. However, tubular SOFCs in large diameters show low integration ability for bundle configuration, and they yield relatively poor power densities because of the long current conduction pathways. In comparison, microtubular SOFCs (mt-SOFC) exhibit considerably enhanced power densities as well as start-up characteristics [9,10]. We thus aim to improve the performance and durability of anode-supported mt-SOFCs.

Referring to the fuel tolerance of SOFCs, though the electrochemical oxidation of CH_4 in SOFCs is quite slow [11–13], the rate of electrochemical CO oxidation has been reported to be comparable to that of hydrogen oxidation reaction (HOR) [12,13]. Since SOFCs operate with Ni-based catalysts at high temperatures resembling to the catalytic steam reformers (CSR), usually employed to produce H_2 from hydrocarbons [4,5,7], H_2 and CO can be synthesized through reforming processes. The operational and structural analogy between CSRs and anodes of SOFCs inspires to unify the regarding fuel reforming and energy conversion processes, respectively. This concept has been referred to as the direct internal reforming (DIR) and investigated extensively with various approaches numerically as well as experimentally [1,2,4,5,7,11,12,14–21].

In CSRs, CH_4 is reformed through so-called methane steam reforming (MSR) and water gas shift reactions as given in Eqs. (1) and (2), respectively. However, the water gas shift reaction has been frequently reported to remain in the thermodynamic equilibrium during the DIR process, thus, the MSR reaction has been the focus of researches [3,11,18].

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_{1273K} = 227 \mathrm{kJ/mol} \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{1273K} = -31.8 \mathrm{kJ/mol} \tag{2}$$

Despite CSR systems operate with the external supply of heat and H_2O, the DIR allows for replacing the external sources by the products of the exothermic electrochemical hydrogen oxidation reaction (HOR) in SOFCs, expressed as

$$H_2 + \tfrac{1}{2} O_2 \leftrightarrow H_2O \quad \Delta H_{1273K} = -250 \mathrm{kJ/mol} \tag{3}$$

Depending on the conditions, 40–70% of heat released from SOFCs is sufficient to maintain their operation through the MSR reaction [3,7,15]. In practice, the surplus heat generated during the operation of an SOFC system is removed by an excess flow of oxidant air in the cathode flow channel based on the convective heat transfer. This surplus heat can be internally consumed by the DIR, so that the air flow rate and the size of the air blower can be reduced.

During the cell operation with H_2, the partial pressure of H_2 decreases while that of the product H_2O increases toward the fuel outlet. As a result, the Nernst loss, based on Eq. (4), included in the concentration loss develops toward the downstream and this causes a remarkable performance deterioration [22,23].

$$U_{cell} = U_0 + \frac{RT}{zF} \ln \left\{ \frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} \right\} \tag{4}$$

where U_{cell} [V] represents the open circuit voltage (OCV), U_0 [V], the standard cell potential, R [J mol^{-1} K^{-1}], the universal gas constant, T [K], the temperature, z, the number of electrons exchanged per molecule of H_2, F [C mol^{-1}], the Faraday constant. Here, p_i [Pa] stands for the partial pressures of H_2, O_2 and H_2O exist on the triple phase boundary (TPB), respectively.

On the other hand, a continuous consumption of the product H_2O along the anode flow channel by the MSR reaction could increase the H_2 partial pressure in the downstream and thus lead to a more homogeneous current distribution. A careful control of the MSR reaction rate can increase the fuel partial pressure toward the fuel outlet [5,13].

Despite its benefits, the DIR introduces particular drawbacks into SOFC systems. At low steam/carbon (S/C) ratios, the elemental carbon deposition occurs in various ways [2–5,7,9,13,15,17,24]. The deposited carbon eventually causes the deactivation of the Ni catalysts [7]. In fact, higher S/C ratios can hinder the carbon deposition, however, this reduces the H_2 partial pressure and thus results in the Nernst-loss.

While the endothermic MSR reaction is frequently pronounced for the removal of the surplus heat released by the HOR, previous papers stated that the heat absorption rate of the MSR reaction is remarkably higher than the heat production rate of the HOR and, thus, resulting in notable local temperature drops [5,7,11,13,15,17,18]. Taking the sensitivity of SOFCs to the thermo-mechanical stresses into account, the control of the MSR reaction rate is substantial in terms of the durability of SOFCs [2,5,14,15,18].

With the electrode-segmentation method, local currents along mt-SOFCs can be in-situ measured [22,25]. Relying on the relation between the local currents and H_2 partial pressures on the regarding parts of the cell, the fuel distribution during the DIR can be evaluated by the longitudinal current variations. The electrode-segmentation method also enables the in-situ acquisition of local temperatures along mt-SOFCs, so that the temperature gradients among the segments can be determined. Thereby, the impact of the endothermic cooling associated with the DIR on the overall temperature distribution along the cells can be analyzed. Furthermore, a comparison of the temperature distributions obtained from the operations of a mt-SOFC with syngas and its equivalent H_2/N_2 provides particular insights into the MSR reaction rate from its endothermic property.

In spite of its advantages, the implementation of the DIR concept is pronounced with difficulties [2–5,7,11,13–15,17]. Due to the complexity of the DIR, researchers have been experimentally investigating the kinetics for the MSR reaction in CSRs for numerical simulations [1–3,7,11,12,14,15]. Although CSRs operate at the similar temperatures on the Ni-based catalysts, the characteristics of operating SOFCs remarkably differ from CSRs because of the HOR. Moreover, particular structural differences among them have been reported [1,5,15]. Thereby, very few research groups have explored the DIR in the operating SOFCs [15,18]. However, these researchers have addressed neither the current nor the temperature distribution along the cell. We have thus in-situ measured the local currents and temperatures by the electrode-segmentation method along a mt-SOFC operated with 50% pre-reformed methane, which provides moderate conditions than the DIR as a starting point. In addition, we have measured the local currents and temperatures for equivalent (100% conversion of syngas to H_2) mixture of H_2/N_2. In this paper, we present spatial current–voltage (I–V) and current-temperature (I-T) curves for both types of the fuels; with them we analyze the fuel distribution, endothermic cooling and MSR reaction rate.

2. Experimental

2.1. Electrode-segmentation method

“Segmentation” is the division of the electrochemical active surface area of a cell into a number of electrically isolated