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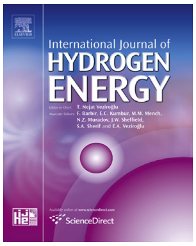

Reformer faults in SOFC systems: Experimental and modeling analysis, and simulated fault maps

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ABSTRACT

The effects of fuel processor faults in an solid oxide fuel cell (SOFC) system are analyzed. Focusing on a laboratory-size SOFC system, a reformer fault is investigated both experimentally and through a model; comparison between experimental and modeling results is presented and discussed. The results show that some types of reformer faults can be dangerous, because they can give rise to local thermal gradients as large as $10–20 \cdot 10^2$ K/m or more in the SOFC stack. Simulation results show that SOFC stacks employing metallic interconnects are expected to withstand faults of larger magnitude than SOFC stacks employing ceramic interconnects. Fault maps are presented and discussed, which can be the basis for the development of a fault detection and isolation (FDI) tool.

Introduction

Natural gas is currently considered the state-of-the-art fuel for solid oxide fuel cell (SOFC) systems for distributed power generation of any size [1], from 5 kW domestic plants [2,3] to 1 MW systems [4,5]. This is mainly due to its availability, capillary distribution system, cleanness, and ease of conversion into hydrogen. Indeed, hydrogen is the ideal fuel of the SOFC stack, which is the core of the system. Natural gas is a mixture without definite composition; methane is the major component, with a typical molar fraction around 90% [6,7]. Other components are nitrogen and higher hydrocarbons, typically ethane, propane, butane, pentane and hexane [6,7]. Among contaminants, the most serious is sulfur, present as H_2S, COS or other organic sulfur compounds. Sulfur is a poison for nickel catalysts, largely present in SOFC systems (in particular in the SOFC stack anode and also in the fuel processor). Typically, the level of sulfur compounds needs to be reduced to 1 ppm or lower [1,8], prior to feeding into the SOFC system. SOFC systems are often equipped with an external fuel pre-processor which desulfurizes the natural gas and also removes higher hydrocarbons [9]. Conversion of methane into hydrogen can then follow different reaction pathways: (i) steam reforming (if the fuel is mixed with steam); (ii) partial oxidation (if the fuel is mixed with air) and (iii) autothermic reforming (if the fuel is mixed with both steam and air) [10]. Among these, methane steam reforming (MSR) is the more

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widely employed process, since the hydrogen percentage in the products is the highest (while it is the lowest with partial oxidation) [11]. In SOFC systems, conversion of methane into hydrogen is typically carried out in a fuel processor, typically an MSR reactor. The possibility of feeding the desulfurized methane-rich gas directly to the anode of an SOFC stack has been investigated as well [12–16]. Upon suitable mixing of the feeding fuel with steam, the MSR reaction can occur directly into the SOFC stack, with the advantage of (i) eliminating the need of a separate fuel processor, leading to simpler operation, higher reliability and lower cost; and (ii) increasing the system efficiency [17]. However, several problems limit its feasibility. Indeed, the steam addition involves a reduction in the open circuit voltage. Moreover, the cooling effect due to the endothermic reaction can engage thermal stress into the ceramic anode which can lead to anode destruction and eventually break-down of the SOFC stack. Finally, the problem of carbon deposition is not still resolved [18]. Thus, as an alternative, also internal partial oxidation has been investigated both experimentally and theoretically [19], as well as internal autothermal reforming [20,21].

Nevertheless, at present, the most widely adopted solution in SOFC systems is a reforming reactor prior to the SOFC stack, so that the reformate fuel fed into the SOFC stack contains a limited amount of unreacted methane. Obviously, in presence of a fault of the reformer, high percentages of unreacted methane are expected to be released into the SOFC stack, and the typical problems encountered in internal steam reforming, in particular temperature gradients, can arise again. Faults of the reformer reactor can be summarized as: (i) catalyst deactivation, which can be due to carbon deposition on the catalyst surface, sulphur poisoning, and/or catalyst degradation due to aging; (ii) reformate fuel leakage, due to leaks in the MSR reactor; (iii) water leakage, due to leaks in the water feeding circuit prior to the MSR reactor.

The aim of this paper is to analyze the behavior of a natural gas fueled SOFC system during a fault of the reformer. The behavior of a planar SOFC stack in presence of a fault of the reformer is expected to be greatly influenced by the type of interconnector employed. At present, there are two types of interconnect materials available for SOFCs, i.e. ceramics and metallic alloys [22]. Ceramics are the traditional option, in particular lanthanum chromite ($LaCrO_3$), which shows satisfactory electrical conductivity, high chemical stability, and a thermal expansion coefficient (TEC) very close to that of the other SOFC ceramic components. Among metallic alloys, Cr-containing ferritic steels are the most widely used interconnects [23]. Their main issue is the compatibility with the other SOFC ceramic components, since at typical SOFC operating temperature chromium evaporates and subsequently gets deposited (i) at the triple phase boundaries, leading to degradation of the SOFC stack performance, and (ii) in the sealing glasses, with loss of hermetic seals. Also, formation of interfacial insulating compounds has been experimentally identified [24]. On the other hand, if compared to ceramic lanthanum chromite, Cr-containing ferritic steels show superior mechanical strength, electronic conductivity, and ease of fabrication. In addition, they exhibit lower cost, and a TEC close to that of the other SOFC components. Furthermore, metallic interconnects feature a thermal conductivity one order of magnitude higher than that of ceramics, and this is expected to reduce thermal gradients [22] and the associated risks, i.e. increased mechanical stresses and possible formation of cracks. A quantitative estimate of the threshold temperature gradient which can be tolerated by an SOFC is not an easy task. This tolerable threshold depends on the geometry, materials, manufacturing process and operating conditions [25–27]. Literature works report that temperature gradients in the order of $2 \cdot 10^2$ K/m are considered not to be dangerous for SOFCs of any type [25]. On the other hand, in-plane solid temperature gradients of the order of $5 \cdot 10^2$ K/m are reported to be non-critical in the case of tubular SOFCs [27], and are expected to be relatively critical in the case of planar SOFCs [28]. $10–20 \cdot 10^2$ K/m seems a reasonable order of magnitude for the threshold in-plane temperature gradient tolerable by a planar SOFC, as proposed in Ref. [29].

The present paper follows a previous work, where we presented a model for the simulation of a system based on a planar SOFC stack deploying a metallic interconnector [30]. The model was validated under steady-state and transient non-faulty operating conditions. In the present work, we validate our system simulation model with experimental data obtained under transient operating conditions which mimic a fault of the fuel processor. Also in this case, experimental data are collected from a system based on a planar SOFC stack employing a metallic interconnector; simulations of the performance of an analogous system based on an SOFC stack deploying a ceramic interconnector are presented as well for comparison.

In the last section of the present paper, we use the validated model to perform a fault analysis, i.e. an analysis of the behavior of the system in presence of a fault of the reformer, with results collected in fault maps which show the behavior of some monitored system variables in presence of a fault. Fault maps are presented for systems based on an SOFC stack employing either metallic or ceramic interconnects. The differences between the two options are discussed.

The rationale for drawing fault maps is that these are the basis for the development of a fault detection and isolation (FDI) tool. According to the definitions given in Ref. [31], fault detection is the determination that a fault is present in a system, and is followed by fault isolation, which is the determination of the kind, location and time of detection of a fault. A wide number of FDI methods have been proposed in the literature and applied to a variety of systems in the field of chemical or mechanical engineering [32–34], where they have been classified into three main groups: quantitative model-based methods; qualitative model-based methods, and process history based methods. We focus on the development of a quantitative model-based FDI tool [35], involving: i) development of a system simulation model; ii) model validation though the available experimental data; iii) collection of fault data, which can be in the form of fault maps; iv) development of a diagnostic tool, trained through the fault data in order to be able to detect and isolate faults; v) application to the real system. In the real system (Fig. 1), the validated model runs in parallel with the real plant, simulating a non-faulty plant operating with the same inputs. At the same time, sensors make appropriate measurements onto the real system: the differences between simulated and measured values of the

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