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Change of an anode's microstructure morphology during the fuel starvation of an anode-supported solid oxide fuel cell

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ABSTRACT

A RedOx cycle is one of the most dangerous factors of anode degradation due to microstructure changes. In this paper, the evolution of anode microstructure during a RedOx cycle caused by a fuel starvation process was studied using electrochemical measurements. After a power generation experiment, the anode microstructure was reconstructed using a combination of focused ion beam and scanning electron microscopy (FIB–SEM). The microstructure changes were quantified for parameters such as the tortuosity factor, tripe phase boundary density, volume fraction, connectivity and average grain size. The three dimensional microstructure reconstruction indicated that the fuel starvation condition might cause significant changes in microstructure morphology.

Introduction

Solid Oxide Fuel Cells (SOFCs) are electrochemical devices that can convert the chemical potential of fuels directly into electricity. Because of their high working temperature (600 °C–1000 °C), SOFCs have the highest energy conversion rate among all types of fuel cells. A solid oxide fuel cell consists of two porous ceramic electrodes (cathode and anode) separated by a dense solid ceramic electrolyte made of yttria stabilized zirconia phase (YSZ). The electrode microstructure morphology is an important factor determining its electrochemical performance. A typical anode consists of porous Ni/YSZ and a typical cathode is made from porous lanthanum strontium cobalt ferrite (LSCF). Each component plays a unique and important role in the transport process by providing a pathway for different species; a YSZ phase for oxygen ions, Ni and LSCF phases for electrons and a pore phase for gases. While the SOFC slowly reaches its commercialization, it becomes a key issue to guarantee long term and safe operation. It is generally accepted that to satisfy the market, 40 000 h of safe operation is required [1,2]. One of the most dangerous causes of anode degradation is the oxidation of Ni particles. Because NiO occupies more volume than Ni, oxidation results in internal stresses inside an anode. A further reduction of NiO to Ni results in shrinking of the

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particle volume. This expansion and contraction of Ni particles is called in the literature a RedOx cycle and may cause damage to a cell microstructure. There are several possible causes of a RedOx cycle such as i) the thermal cycle of a SOFC system during shut down and start up, ii) the stop of gas supply in the case of an emergency situation, iii) oxidation from steam in the case of SOFC with a reforming system, iv) leakage through the sealing, v) local fuel starvation caused by a load following operation, vi) too high a hydrogen conversion rate and vii) high fuel dilution. From a reaction point of view, they can be classified into two groups. One is the redox by chemical reaction ($Ni + O_2 \rightarrow NiO$) and/or by electrochemical reaction ($Ni + O^{2-} \rightarrow NiO$). The first group, redox by chemical reaction, is often studied in laboratory scale experiments by stopping the fuel supply and blowing air to the anode side. After the oxidation of nickel particles, air is stopped and hydrogen is fed again to the anode to finish the RedOx cycle. This approach was studied for both electrolyte supported cells [3–20] and anode supported cells [21–26]. Conclusions were different from one paper to another. Some authors report massive degradation, other authors report moderate or find no significant degradation. In the second group, the anode is electrochemically oxidized. Electrochemical oxidation will happen rather in the vicinity of the anode-electrolyte interface. For laboratory scale experiments, current is applied to the cell to force oxygen ions to go through the electrolyte and oxidize Ni at the anode-electrolyte interface. In the case of the electrolyte supported cell, Takagi et al. [27] found moderate degradation that was not fatal for the cell. In the case of the anode supported cell, the conclusions are in contradiction with each other. Sarantaridis et al. [28] has reported a catastrophic effect of the redox cycle on the cell whereas Hatae et al. [29] reported no electrolyte crack or OCV drops. An outstanding research to conclude all the above mentioned cases was conducted by Laurencin et al. [20,30,31]. In their research they investigated both anode supported [30] and electrolyte supported [20] cells as well as different types of oxidation: chemical and electrochemical [30]. Impedance spectroscopy was used to estimate the electrochemical degradation. Their results indicated probability of delamination at the anode-electrolyte interface and mechanical damage of the cell as a result of stress [31]. To estimate the probability of the cell failure, the thermo-mechanical model has been proposed [31].

Recent research suggests that fuel starvation might occur during transient operations, if fuel is consumed in the cell faster than it can be supplied [32,33]. When fuel starvation occurs during a real SOFC operation, the cell might be strongly polarized and oxygen ions keep coming out from the cathode side which causes electrochemical oxidation of Ni in the anode. In this study we focus on this electrochemical oxidation of Ni by fuel starvation. Recent results by Fang et al. [34] show the significance of this problem. In their research, a stack of cells was investigated under high current density and high fuel utilization factor. Their research indicates that the upstream part of the anode was oxidized as a result of fuel starvation. At the laboratory scale, this situation was studied recently by different research groups [35,36]. In their research using diluted hydrogen as fuel, it was observed that cell performance drops rapidly at very low hydrogen concentration (below 2%). Further investigation unraveled the oxidation of nickel near the anode-electrolyte interface [35,36]. Chen et al. [36] have reported the fatal failure of an anode-supported cell after exposing the cell to fuel starvation conditions [36]. Throughout the research an explanation of the cell failure by fuel starvation was provided from a macroscopic point of view. However the impact of fuel starvation on the electrode microstructure remains unclear.

The most precise information about cell microstructure can be derived from real structural analysis. Recently, the combination of a focused ion beam and scanning electron microscope (FIB–SEM) as well as the X-ray tomography technique brought a breakthrough in the direct 3D observation of porous structure [37–43]. 3D structure reconstruction was introduced to the field of SOFCs by Wilson et al., in 2006 [44]. The method enables the observation of many sequential 2D images of a porous microstructure and reconstructs it into a 3D structure using advance image processing. From the reconstructed microstructure, it is possible to evaluate the microstructure parameters. These parameters directly obtained from the real electrode structure are the key to considering the relationships between porous microstructures and the cell power generation performance. There were attempts to use the 3D microstructure observation to investigate microstructure evaluation during the RedOx cycle [9,27,45], but to the authors' best knowledge, it has not been applied to the fuel starvation problem.

The literature review clearly unravels the gap in published data that the authors aim to fill by providing detailed information about microstructure morphology change, during the fuel starvation of an anode supported solid oxide fuel cell. The novelty lays in using state-of-the-art techniques such as FIB–SEM, combined with advanced methods of deriving microstructure parameters to report the changes caused in microstructure during the fuel starvation process.

Experiment

Experimental set-up

A conventional double-tube type test apparatus for SOFC button cell evaluation was used (BEL Japan, Inc., BEL-SOFC). The SOFC sample was located between two ceramic tubes in the electric furnace. The ceramic tubes have a double co-axial structure. The fuel/air is supplied through the inner-tube and exhausted through the gap between the inner-tube and the outer-tube. The furnace was heated-up to 800 °C. Fuel was fed to the anode via flow controllers omitting a humidifier. Air was used as an oxidant on the cathode side. The anode and the cathode were connected to the measuring devices with 0.5 mm platinum wires. Platinum meshes were welded with platinum wires and connected with each electrode. An electrochemical Interface (Solartron analytical, model 1287A) was used for the current–voltage characteristic measurements.

Experimental method

In the experiment, three commercial samples provided by SOFC Power were used. The Ni/YSZ–YSZ–GDC/LSCF samples