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Microstructural comparison of solid oxide electrolyser cells operated for 6100 h and 9000 h

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HIGHLIGHTS

- Comparison of long-term operation cells (6100 h and 9000 h) with non-operated cell.
- Investigation of morphological and compositional changes due to diffusion.
- Nickel depletion in cathode identified as main cause for degradation.
- Hypothesis of two driving forces which cause the cell degradation.

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ABSTRACT

Solid oxide electrolyser cells (SOEC) operated for 6100 h and 9000 h with a current density of −0.75 and −1 A/cm^2, respectively, were analyzed and compared with a non-operated cell. The cathode-supported cells consisted of an 8 μm thick Ni/8YSZ cermet as hydrogen cathode, a 10 μm thick 8YSZ electrolyte, a screen-printed $Ce_{0.8}Gd_{0.2}O_{1.9}$ diffusion barrier with a thickness of 5 μm and a 30 μm thick $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ layer as oxygen anode.

The cells were investigated by various electron microscopy as well as microanalytical techniques. The post-test analyses showed several degradation phenomena such as formation of nano-sized pores at grain boundaries, formation of $SrZrO_3$ at the interface electrolyte/anode and agglomeration of nickel particles in the cathode. Comparisons of the operated cells with the non-operated cell indicate that nickel depletion in the cathode is responsible for a loss of performance since this depletion leads to a significant enlargement of electrolyte thickness. Analysis of these cells leads to the conclusion that two mass transport processes in the electrolyte caused by different driving forces are the main reason of the cell performance loss: at the cathode side, the electrical potential gradient appears to govern the formation of pores, while at the anode side, formation of $SrZrO_3$ generates a chemical potential gradient causing the cations to migrate against the direction of the electric field.

1. Introduction

Hydrogen is one of the most promising candidates for clean energy storage. The most common hydrogen sources are hydrocarbons and water. Conventional methods of hydrogen production, such as steam reforming, partial oxidation and coal gasification, rely on non-renewable resources and generate by-products such as carbon dioxide and carbon monoxide.

Alternatively, high temperature solid oxide electrolyser cells (SOECs) can be employed for water splitting, resulting in the production of high purity hydrogen. High temperature electrolysis allows efficient electrical-to-chemical energy conversion [1,2] and is an attractive method for conversion and storage of energy from renewable sources.

In recent years, many efforts have been spent to understand the degradation mechanisms of solid oxide fuel cells (SOFC) which can be regarded as reverse SOECs. Although the structure of SOEC and

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SOFC are identical, different operating conditions lead to diverse degradation phenomena which are not yet fully understood in SOEC mode. Eguchi et al. [3] investigated various electrode materials by impedance spectroscopy in SOEC and SOFC mode. U–I measurements of a planar cell consisting of Ni/YSZ as hydrogen electrode and $La_{0.6}Sr_{0.4}MnO_3$ (LSM) as oxygen electrode resulted in different slopes in SOEC and SOFC mode indicating a smaller resistance in SOFC than in SOEC mode. In addition, low polarization was observed for Ni/YSZ cermet in SOFC mode while high polarization was observed for electrolysis. Furthermore, in SOEC and SOFC mode different conditions are applied. While electrolyser cells operate with a cell voltage of 1.1–1.4 V, a lower cell voltage is obtained in SOFC mode (0.6–1 V) [4]. A high cell voltage leads to a decrease of oxygen partial pressure at the cathode in SOEC mode which causes an increase in the electronic conductivity of the ionic phase.

However, the knowledge of decomposition mechanisms in SOFC mode is still essential for further understanding of degradation phenomena in SOEC mode. Several alterations have been observed in SOEC components. Concerning the electrolyte, 8 mol% yttria-stabilized zirconia (8YSZ), Knibbe et al. [5] already reported pore formation along grain boundaries in an SOEC with LSM-based electrodes. Regarding the cathode Ni/YSZ, it is widely accepted that operation under high steam condition leads to an agglomeration of nickel and formation of nickel hydroxide [6,7] causing a reduction of the length of the triple phase boundary (TPB). In an SOEC based on a lanthanum strontium cobalt ferrite anode, which was also investigated in this paper (cell 2), Tietz et al. [8] observed $SrZrO_3$ formation in pores of the diffusion barrier near the anode analyzed by scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDS). Pores in the electrolyte near the interface electrolyte/anode were interpreted as Kirkendall voids [9,10] due to mass transport of zirconium and yttrium. Other degradation phenomena such as demixing of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) and formation of Co_3O_4 were discussed by Tietz et al. [8]. However, these SEM/EDS analyses must be treated critically since the SEM images showed $SrZrO_3$ particles which are smaller than the excitation volume of the electron beam in SEM/EDS measurements. In addition, a detailed analysis of the origin of the nano-sized pores was not reported.

In the present study, a non-operated cell of the same type has been used as reference for comparisons to the two operated cells with a degradation rate of 11 mV/kh (cell 1) and 40 mV/kh (cell 2), respectively. The corresponding, frequently quoted, degradation values are 0.98%/kh and 3.80%/kh, respectively (referred to the starting cell voltage). To clarify degradation mechanisms such as pore formation, nickel agglomeration and $SrZrO_3$ formation, high-resolution techniques such as transmission electron microscopy (TEM) and selected area electron diffraction (SAED), were applied. Based on these results a hypothesis of degradation mechanisms of SOECs is introduced.

Table 1
Operating conditions for cell 1 and cell 2.

	Cell 1	Cell 2
Current density [A/cm^2]	−0.75	−1
Temperature [°C]	777–780	775–782
H_2O supply [NmL/min]	581	871
Absolute feed humidity [%]	80	80
Steam conversion [%]	41	36
H_2 supply [NmL/min]	100	100
H_2 supply [%]	13.8	9.2
N_2 supply [NmL/min]	45	118
Duration [h]	6100	9000
Starting voltage [mv]	1017	1060
Degradation rate [%/kh]	0.98	3.80

2. Experimental

The cells were fabricated at Forschungszentrum Jülich. The circular cathode-supported cells consist of a Ni/8YSZ cermet as hydrogen cathode (8 μm), an 8YSZ electrolyte with a thickness of 10 μm, a barrier composed of $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO) and a $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ oxygen anode (30 μm). All layers were deposited by screen printing on a Ni/8YSZ substrate. The cells had an active cell area of 45 cm^2 [8].

Long-term SOEC operation of the cells is reported in Refs. [11–13]. The operating conditions are summarized in Table 1.

For detailed analysis of non-operated and operated cells, the cells were broken to study the fracture surfaces that represent cross sections through the ceramic and composite layers of the SOECs. Other parts of the cells were embedded in epoxy resin under vacuum and polished with diamond paste. For electron microscopy investigations, lamellas were prepared by the focused ion beam (FIB) technique (FEI STRATA FIB 205, Eindhoven, Netherlands) using a gallium source. The lamellas were thinned to a thickness of approximately 100 nm and analyzed by transmission electron microscopy (TEM, FEI Tecnai F20, Eindhoven, Netherlands). The TEM measurements were carried out at 200 kV using a Gatan imaging filter (GIF 2000, Pleasanton, USA). EDS measurements (Oxford INCA EDS system, Abingdon, United Kingdom) were performed to obtain detailed information of chemical composition with a high lateral resolution up to 1 nm. Furthermore, selected area electron diffraction (SAED) was employed for investigation of local crystallographic structures. In addition, electron probe micro analysis (EPMA, JEOL JXA-8530F, Tokyo, Japan) and SEM (LEO/Zeiss 1450VP, Jena, Germany) with an Oxford INCA EDS system were applied.

3. Results and discussions

3.1. SEM analysis

SEM analysis was performed for cell 1, cell 2, and the non-operated cell. Fig. 1 shows an SEM image of the non-operated cell. It is noted that the electrolyte contains voids that originate from the production process. Size and number of these voids do not change during SOEC operation (Figs. 2 and 3). Thus, it is assumed that the voids do not have a significant impact on the degradation.

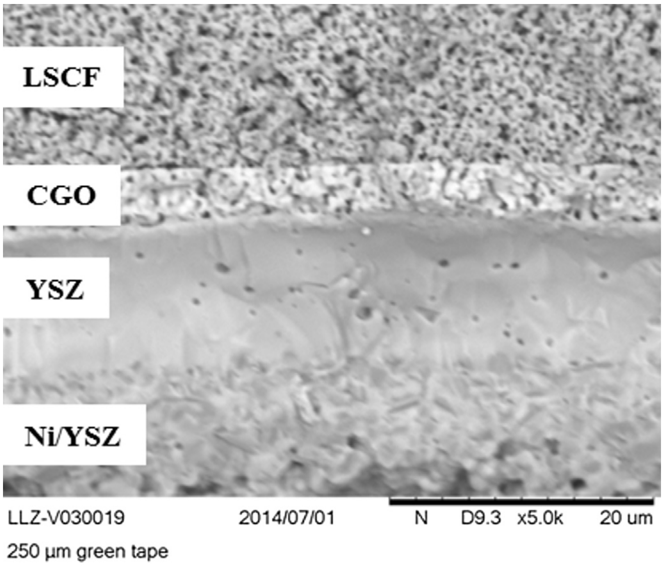

Fig. 1. SEM image of non-operated cell; fracture surface.