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Durability test on coral $Ce_{0.9}Gd_{0.1}O_{2-\delta}$-$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ with $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ current collector working in SOFC and SOEC modes

Jaroslaw Sar[a,b,*,1], Josef Schefold[c], Annabelle Brisse[c], Elisabeth Djurado[a,b,1]

[a] Univ. Grenoble Alpes, LEPMI, 1130 rue de la Piscine, F-38402 St Martin d'Hères, France
[b] CNRS, LEPMI, F-38000 Grenoble, France
[c] European Institute for Energy Research (EIFER), Emmy-Noether-Str. 11, D-76131 Karlsruhe, Germany

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A B S T R A C T

This work presents a 790 h durability test performed on a solid oxide cell. An innovative $Ce_{0.9}Gd_{0.1}O_{2-\delta}$-$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ oxygen electrode with coral microstructure was deposited on a solid oxide fuel cell (SOFC) anode supported with 8 mol.% yttria-stabilized zirconia (8YSZ) electrolyte. An initial cell potential was found to be 817 mV at 773 °C under synthetic air on the oxygen electrode side, and pure hydrogen (500 NmL.min^{-1}) on the hydrogen electrode side, under 0.5 A.cm^{-2} current density in SOFC. The initial cell potential in the solid oxide electrolysis cell (SOEC) was 1200 mV at 773 °C under synthetic air on the oxygen electrode side and a mixture of steam/hydrogen (80 %/20 %, respectively) on the hydrogen electrode side under −0.75 and −0.5 A.cm^{-2} current density. The cell resistance progressively increased during the durability test. The increase at the high frequency range was mainly responsible for an increase in total cell resistance. This frequency range was associated with the blocking effect on the oxygen electrode/electrolyte interface. U-j curves showed reversibility of the current loading from −0.75 to 0.5 A.cm^{-2}. SEM observations indicated cracks in the 8YSZ electrolyte and the detachment of the oxygen electrode.

1. Introduction

The great interest in high temperature solid oxide cells (SOC) comes from the reversible operation as solid oxide fuel cell (SOFC) and solid oxide electrolysis cell (SOEC). As a SOFC, electricity is produced directly from the electrochemical reaction between gaseous hydrogen and oxygen. As a SOEC (inversely), hydrogen, or syngas, is produced by splitting H_2O, or a mixture of H_2O with CO_2. Commercialization of SOC is frustrated by high material and fabrication costs. However, the continuously extending lifetime of the cell stack is reaching the acceptable value of 50000 h or around 6 years [1]. Current research in the domain of SOFC and SOEC pursues an increase in durability and performance. Main cell degradation sources are reported to originate from: grain coarsening [2], particle smoothing/coarsening [3,4], kinetic demixing, and formation of Kirkendall voids or micropores [5,6]. Furthermore, cell stability and performance are diminished by phase instability [7], interfacial segregation [8–10], evaporation [1,11], accumulation of impurities in active zones [12],[13], interdiffusion [14], delamination and microstructure degradation of the electrolyte/oxygen electrode interface [15–19]. However, the recent work of Graves et al. [20] has shown that all irreversible processes that lead to cell degradation in SOEC were removed by reversible cycling in SOFC.

Comparison of potential degradation rates is difficult to realize due to variable experimental conditions i.e. no standardized test conditions and specifications have not been established. In addition, the cell itself can also vary due to material variation, design, area, and thickness. Thus a particular comparison between the fuel cell and the electrolysis mode of operation is required. The current density (j) flow in the circuit depends of the operating mode and is generally described as positive in the fuel-cell mode and negative in the electrolysis mode. The cathode and anode reverse their role respective of the working mode. To clarify, the hydrogen electrode is the electrode on which fuel is consumed (SOFC) or produced (SOEC) and the oxygen electrode is the electrode on which oxygen is produced (SOEC) or consumed (SOFC).

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[*] Corresponding author. Tel.: +33 476826574; fax: +33 476826777.
E-mail address: sar.jaroslaw@gmail.com (J. Sar).

[1] Postal address: 1130 rue de la Piscine, F-38402 Saint Martin d'Heres, France.

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Cell based on Ni-YSZ electrode, 8YSZ electrolyte and LSCF oxygen electrode were tested in fuel cell and electrolysis modes. Under fuel cell operation conditions, such cells achieved a potential degradation rate of 0.9–1.5%.1000 h^{-1} at 750 °C under 0.5 A.cm^{-2} over long test duration between 2000 and 5000 h. [21,22]. Potential degradation rates in the electrolysis mode were noticed to be higher than in the SOFC mode, even if the cell was stable in SOFC after switching to electrolysis mode, the cell displayed rapid degradation [23]. Low potential degradation values, as 3.2%.kh^{-1} was found for metal supported cell with an area of 12.5 cm^2 under −0.3 A.cm^{-2} at 800 °C during 2000 h [24]. Potential degradation rates are reported to start from 5 %.kh^{-1} and to stabilize at the final stage of the test at 2 %.kh^{-1} by Hauch et al. [13] for 16.5 cm^2 anode supported cell under current density of −0.5 A.cm^{-2} at 850 °C during 600–700 h. A similar degradation rate of 3%.kh^{-1} was found in 1000 h tests on 45 cm^2 cell [25]. Schefold et al. [26] reported initial low degradation of 2.5%.kh^{-1} up to 5600 h (even 1.7 %.kh^{-1} between 2000 h and 5600 h) and a total degradation of 3.8%.kh^{-1} for 9000 h durability tests for 45 cm^2 anode supported cells at 780 °C and −1 A.cm^{-2} current density.

This work presents durability tests on a full cell working in the SOFC and SOEC modes for a total time of 790 h. Impedance spectroscopy was used to examine cell kinetics. The ohmic resistance, electrochemical and gas polarization resistance were de-convoluted and compared with the post-mortem microstructural and chemical analysis.

2. Experimental

2.1. Oxygen electrode preparation

A circular anode-supported SOFC with an area of 45 cm^2 was secured from Forschungszentrum Jülich on which the up-scaled oxygen electrode was deposited by electrostatic spray deposition (ESD) in LEPMI (Electrochimie et Physicochimie des Matériaux et des Interfaces). On the 1.5 mm thick Ni/YSZ substrate, an approximately 8 μm thick Ni/YSZ cermet served as the hydrogen electrode. The role of the substrate is to provide mechanical strength to the whole cell, while the Ni/YSZ hydrogen electrode plays the electrochemically active functional layer role, where the electrochemical reaction takes place. Eight mol.% yttria-stabilized zirconia (8YSZ) was used as a dense electrolyte with a thickness of 10 μm. Processing details of Ni/YSZ electrode with 8YSZ electrolyte can be found elsewhere [27,28]. The oxygen electrode comprised of a coral functional layer (CFL) deposited by ESD and the current collector layer (CCL) was screen-printing. A homogeneous composition of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (CGO-LSCF) for CFL and CGO as a barrier diffusion layer was deposited prior to printing LSCF as CCL. The parameters for ESD were chosen to create a highly porous microstructure called coral microstructure [29] adjusted to the large scale of the substrate. As an initial part of deposition, a dense and thin CGO barrier diffusion layer was deposited by ESD for 45 min [30]. The next step was the deposition of CGO and LSCF with 1:1 molar ratio for 405 min. The last step was a coating of pure LSCF for 90 min. An x-y moving substrate holder was used during the process to cover the full surface and guarantee good homogeneity in the coating thickness. A precise description of CGO-LSCF composite production was presented in [30] and a 3D analysis of CGO-LSCF oxygen electrode with coral microstructure in [31]. A post-annealing treatment was performed at 900 °C for 2 h in air to ensure crystallization. LSCF CCL was screen-printed onto sintered coral microstructure in two cycles. The sample was kept for 1 h drying at 60 °C between printings. Subsequently, the sample was heated to 600 °C with a rate of 0.5 °C.min^{-1} to burn off the binder and then sintered at 900 °C for 2 h with a heating/cooling rate of 3 °C.min^{-1}.

2.2. Durability test in the SOFC and the SOEC modes

The durability test and other electrochemical tests were performed on the SOFC test bench from Energy research Centre of the Netherlands (ECN) adapted for both SOFC and SOEC testing at the European Institute for Energy Research (EIFER). The experimental setup with the cell is presented in Fig. 1.

The cell was placed in between two alumina plates which also served as gas distributers. Pt-grids were used to provide current collecting for the electrodes. The cell potential was measured with Pt sense wires welded to the grids. Moreover, 2 kg weight load was used to ensure good grid-electrode contact. The sweep gas was synthetic air (O_2 and N_2) on the oxygen electrode side. The total gas flow was kept stable at 1500 NmL.min^{-1}. The hydrogen electrode was supported in H_2, N_2 and H_2O. The exact gas flows varied with the experiments (see Results section). Steam was produced from de-ionized water preheated by upstream tubing. In addition, external heating was guaranteed by a ceramic heating element. It should be kept in mind that the setup was operating in an open housing, H_2 was burned off at the rim of the cell. This may increase the cell temperature if the gas flow is not adjusted. Three thermocouples were set in the setup; one in the cell center (corresponding to the cell temperature) and two on the cell edge. The Solartron 1287 potentiostat was used to measure cell potential. The over-potential protection was installed to cut current density in case of a lack of steam. The impedance spectroscopy spectra were measured using a Solartron frequency response analyzer (SI 1255) within the frequency range of 0.1 Hz to 40 kHz. The frequency limit for IS measurements was

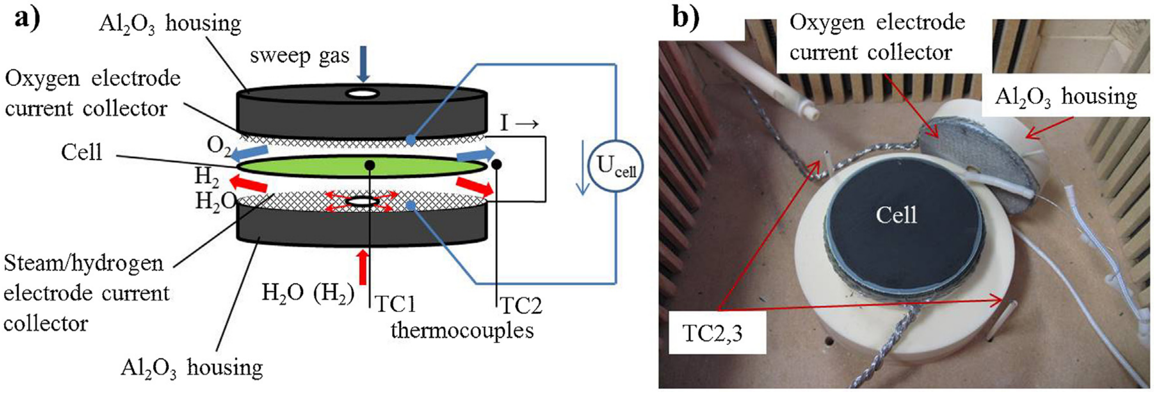

Fig. 1. The test bench, a) schema of the experimental test setup, b) mounted cell.