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Experimental validation of a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ electrode model operated in electrolysis mode: Understanding the reaction pathway under anodic polarization

F. Monaco[a,*], V. Tezyk[b], E. Siebert[b], S. Pylypko[a], B. Morel[a], J. Vulliet[c], T. Le Bihan[c], F. Lefebvre-Joud[a], J. Laurencin[a]

[a] Univ. Grenoble Alpes – CEA/LITEN, 17 rue des Martyrs, 38054, Grenoble, France
[b] Univ. Grenoble Alpes – CNRS, LEPMI, 1130 rue de la Piscine, 38402 Saint Martin d'Hères, France
[c] CEA, DAM, Le Ripault, F-37260 Monts, France

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ABSTRACT

In order to validate the reaction mechanism of porous LSCF oxygen electrodes, a set of experiments has been conducted on two types of symmetrical cells exhibiting different microstructures. In both cases, the polarization curves exhibit a dissymmetry with a transition at low anodic overpotential associated to a modification in the shape of the electrochemical impedance spectra. To interpret the experimental results, a micro-scale electrode model including two reaction pathways has been used. The model considers an oxidation/reduction at TPBs (surface path) in parallel to an oxygen transfer at the gas/LSCF interface (bulk path). Thanks to a 3D electrode reconstruction, the simulations have been performed with a reduced number of unknown parameters. It has been found that the simulated data are in good agreement with the experimental polarization curves and impedance spectra at OCP as well as under anodic polarization. Once validated, the model has been used to unravel the complex electrode operating mechanisms in electrolysis mode. The simulations have shown that the transition detected at low anodic polarization is due to a change in the dominant reaction mechanism passing from the bulk to the surface path. Moreover, the relative contribution of the two pathways has been investigated as a function of temperature.

1. Introduction

Solid Oxide Cells (SOCs) are electrochemical devices that can reach high conversion efficiencies due to their high operating temperature. Nowadays, they appear as a promising technology for the reversible gas to electricity conversion [1,2]. Indeed, thanks to their flexibility, the same electrochemical device can be alternatively used in fuel cell mode for electrical power generation and steam electrolysis mode for hydrogen production [3] (i.e. in Solid Oxide Fuel Cell – SOFC – mode or in Solid Oxide Electrolysis Cell – SOEC – mode). Typical materials for SOCs are dense Yttria Stabilized Zirconia (YSZ) for the electrolyte, porous Ni-YSZ cermet for the H_2 electrode and a porous composite of YSZ and Lanthanum Strontium Manganite (LSM) for the O_2 electrode. In the latter, oxidation/reduction of oxygen occurs at the so-called Triple Phase Boundary (TPB) lines where the electronic, ionic and gas phases meet. Recently, this composite has been advantageously replaced by Mixed Ionic and Electronic Conductors (MIEC) for which the reaction can extend from the vicinity of TPBs to the whole surface area of the porous electrode resulting in a substantial increase of the performances [4]. Among the different compounds, the Lanthanum Strontium Cobalt Ferrite ($La_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ – LSCF) perovskite is the most employed material for SOC application [5–7]. To mitigate LSCF reactivity with the electrolyte, a barrier layer of ionic conductive Ceria doped Gadolinium Oxide ($Ce_{1-x}Gd_xO_{2-\delta}$ – CGO) is usually added between YSZ and the electrode to avoid the direct contact between the two materials [8–10]. Moreover, composite LSCF-CGO electrodes have also been proposed to improve the mechanical compatibility with YSZ.

In fuel cell mode, the reaction pathway for LSCF electrodes has been extensively studied experimentally [11–16] and theoretically [17–26]. Adler et al. [17] have analyzed the impedance of porous LSCF electrodes with a model in which the polarization resistance is dominated by the so-called "chemical impedance" that takes into account the oxygen vacancies diffusion in the bulk of the LSCF and the reaction at the surface of electrode particles. The same mechanism has been used by Deseure et al. [19] to model the ac and dc response of a dense electrode in fuel cell mode. Prestat et al. [23] and Fleig et al. [24] have

* Corresponding author.
E-mail address: federico.monaco@cea.fr (F. Monaco).

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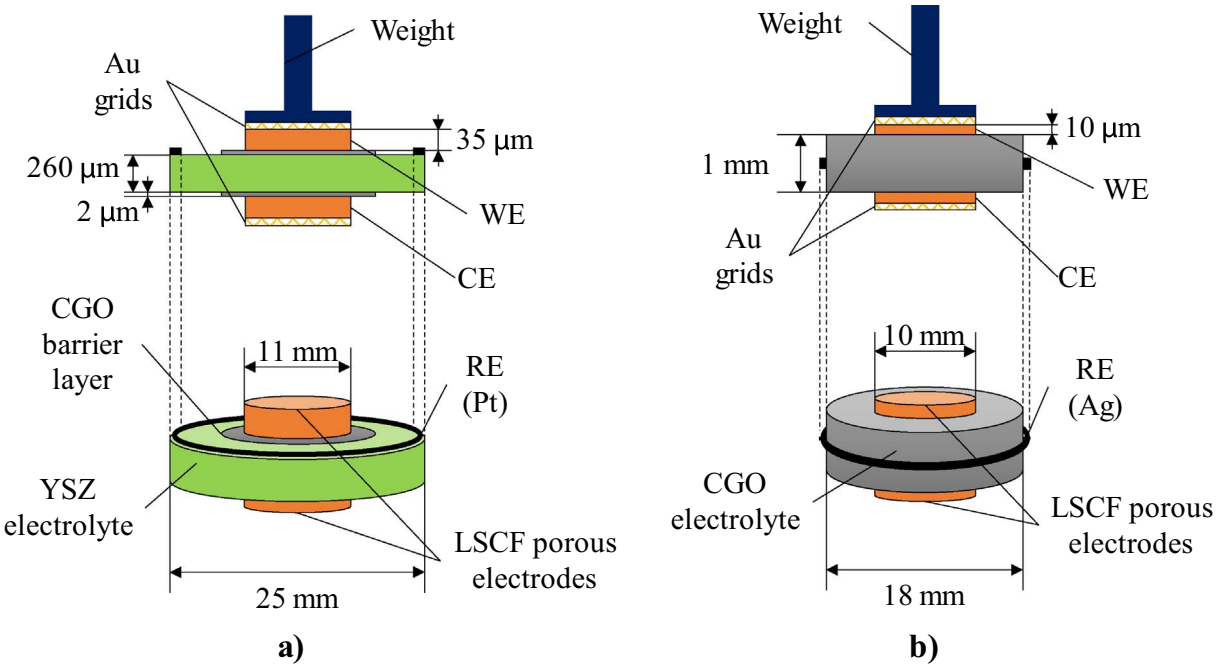

Fig. 1. Cell dimensions and experimental setups: a) Cell I – b) Cell II.

also proposed models for dense LSCF film. In their model, Fleig et al. [24] have refined the Adler's approach with intermediate surface reactions of oxygen ionization leading to an electrostatic potential step across the LSCF surface. Besides, Yurkiv et al. [25] and Mortensen et al. [26] have extended this modeling approach based on oxygen bulk diffusion and charge transfer at the LSCF surface to the LSCF-CGO composite electrodes.

For pure LSCF electrodes, several experimental results have confirmed the mechanism proposed by Adler et al. [17] at the Open Circuit Potential (OCP) and under cathodic polarization [4,13,14,27]. However, some authors [18,28–30], have suggested that the direct oxygen oxidation/reduction at TPBs could also participate to the electrode response, especially in anodic polarization for which the oxidation at TPBs could control the reaction mechanism [20,31–33]. Similarly for LSCF-CGO electrodes, Kim et al. [16] have suggested a significant contribution of the TPBs even under cathodic polarization.

Recently, our research group developed a stationary and dynamic model for porous LSCF and LSCF-CGO composite electrodes allowing the simulation of polarization curves [20] as well as Electrochemical Impedance Spectra (EIS) at OCP and under polarization [21]. A special attention was paid to take into account the influence of the electrode microstructure on the transport and electrochemical processes. The model considers two parallel reaction pathways combining the oxygen exchange at the LSCF/gas interface (i.e. “bulk path”) and the direct oxidation/reduction at the TPBs (i.e. “surface path”). As expected for the porous LSCF electrode, the simulations have shown that the reaction pathway is dominated by the bulk path under cathodic polarization and at OCP. Nonetheless, the simulations have highlighted a transition from the bulk to the surface path arising in anodic polarization. The presence of a polarization threshold that depends on the temperature in electrolysis mode is thus theorized but still needs to be fully validated [20].

The main objective of this work is to validate the reaction mechanism for porous LSCF electrodes in anodic polarization. For this purpose, experiments have been conducted at different temperatures on two symmetrical cells exhibiting different microstructures prepared and tested in two independent ways. For one of the two cells, the polarization curves and the impedance spectra at OCP and under anodic polarization have been simulated with the model considering the electrode microstructural properties taken from a 3D reconstruction. For the other cell, electrochemical tests have been performed in order to obtain two sets of independent experimental data to validate the electrode behavior. The goal of the work is first to evidence the presence of a threshold related to the transition from the bulk to the surface path, confirming the modification of the reaction pathway in anodic polarization for the porous LSCF electrode. Then, the impact of temperature on the reaction pathway is investigated and the value of the LSCF/CGO double layer capacitance is discussed.

2. Materials and methods

2.1. Cells description

Two different symmetrical button cells (denoted Cell I and Cell II thereafter) were fabricated with the same $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ material. The manufacturing conditions were not the same for the two cells in order to obtain different electrode microstructures. The main characteristics and conditions of cell fabrication are detailed hereafter:

- For the first cell (Cell I), a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ commercial powder provided by Fuel Cell Materials was used (d_{50} = 0.6 µm). Porous LSCF electrodes with a thickness of ≈35 µm and a surface area of 1 cm^2 were deposited symmetrically by screen printing on both sides of a dense 8YSZ electrolyte (diameter: 25 mm, thickness: 260 µm, provider: Kerafol). A $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ barrier layer of 2 µm was deposited by screen printing to limit the formation of insulating phases ($SrZrO_3$ and $La_2Zr_2O_7$) between LSCF and YSZ (Fig. 1a). CGO powder was provided by Fuel Cell Materials. LSCF and CGO inks were made up by mixing LSCF or CGO powders (nearly 50 wt%) with a mixture of terpineol (Sigma Aldrich) as solvent and PVb (Polyvinyl butyral) as binder. CGO was sintered at 1300 °C for 1 h and LSCF at 1000 °C for 1 h.
- For the second cell (Cell II), a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ commercial powder provided by Marion Technologies (d_{50} = 0.27 µm) was used. X-Ray Diffraction showed that it contained a small amount of $SrCO_3$ impurity. Porous LSCF electrodes with a thickness of ≈10 µm and a surface area of 0.79 cm^2 were deposited symmetrically by screen printing on both sides of a dense $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ electrolyte