Mechanical behavior of $Ce_{0.9}Gd_{0.1}O_{1.95}$-$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ oxygen electrode with a coral microstructure for solid oxide fuel cell and solid oxide electrolyzer cell

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ABSTRACT

The objective of this work is to investigate the mechanical behavior of CGO-LSCF composite developed by electrostatic spray deposition as an oxygen electrode for Solid Oxide Fuel Cell and Solid Oxide Electrolysis Cell. The coating is characterized by a highly porous morphology designated coral microstructure. Its mechanical behavior was studied by scratch and ultramicroindentation tests and a model of material degradation under progressive compressive loading has been proposed. The coral's damage mechanism involves three regimes: at very low loads stresses are concentrated at the tips of individual corals that fracture and fill the spaces between corals (regime I); as load increases, generalized fracture of the corals occurs and the material starts compacting into an increasingly dense layer (regime II); finally, at the highest loads, the material behaves like an almost fully dense (regime III). As load increases during testing porosity decreases from about 60 to about 5 vol% in the compacted material. The transitions between regimes are associated to increases in the contact stress and the same damage mechanism is found during scratching and indentation. Hardness increases from about 2–100 MPa, while the Young's modulus varies in the range 1–18 GPa, as the porosity decreases. Calculations of the real contact pressure during loading allowed estimating a yield stress of 83 MPa that can be considered as a low limit for the materials fracture strength.

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1. Introduction

Fuel cell technologies are currently mainly focused on hydrogen production as a potential fuel (Solid Oxide Electrolyzer Cells) as well as on the production of electricity directly from the electrochemical reaction between the fuel and oxygen (Solid Oxide Fuel Cells). The current research in solid oxide cells focuses on the reduction of the total resistance of the cell, achieved by reducing the electrolyte thickness, since the cell resistance is proportional to the electrolyte thickness (distance for oxygen ions to transfer from one side of the cell to the other). However, requirements for the electrolyte impose limitations to further decreases in thickness and the electrolyte has to be dense to avoid fuel-oxygen mixing. The further decrease of the cell resistance by increasing the oxygen gas diffusivity requires the development of new oxygen electrodes with highly porous microstructures. An example of this is a coral-like microstructure developed by the authors [1] that is characterized by a two-scale porosity level in which macroscopic pores exist between corals and nanoscale pores are present on the corals surface and inside corals, increasing the total available surface area [2]. Such porosity facilitates the adsorption process and provides a high active zone for oxygen reduction reaction. However, a high porosity level decreases the mechanical strength of the electrode.

One of the requirements for the oxygen electrode is a high resistance to the mechanical stresses that occur during cell operation and especially at the electrode/electrolyte interface that may cause degradation of the cell or even compromise its integrity. Stresses depend on material properties but also on process

variables and use conditions. During cell operation, the mechanical stresses on the electrode result from the differences between the components thermal expansion, the mechanical loads applied to ensure a good contact of the cell components and the stack own weight. Research has been done on the assessment of mechanical properties of materials used in SOFC, the stacks and also on their probability of failure [3–14].

Studies have been made on the mechanism of mechanical failure of cell stacks by modeling approaches. Nakajo et al. [8] used a thermo-electrochemical model and Weibull statistics to study the influence of assembly, electrical load shutdown, phases heating-up/cooling down, current-voltage characterization and dynamic operation. The probability of mechanical failure of SOFC stacks has been calculated and procedures to reduce it by controlling the operation conditions have been proposed. The failure of gas diffusion layers, interconnect and other cell components was also estimated [9,10].

Laurencin et al. [5] investigated the risk of failure due to residual stresses and cracks generated during manufacturing. A numerical tool was used to estimate the stress state and cell degradation during operation for the planar cell configuration. Lin et al. [7] used Finite Element Analysis (FEA) to model stresses in planar SOFC stacks including the effect of glass-ceramic seals. Anandakumar et al. [14] used FEA to model thermal stresses and the probability of failure in cells of NiO-YSZ/YSZ with single LSM and NiO-YSZ/YSZ with functionally graded CGO-LSCF. The results have shown that the lowest probability of failure occurs for a functionally graded SOFC.

An et al. [3] performed a study of $(Pr_{0.7}Sr_{0.3})MnO_{3 \pm \delta}/8YSZ$ oxygen electrode before and after a 1000 h durability test at 1000 °C using indentation, plate tensile tests, four-point bending, ball-on ring and pressure-on-ring tests. Pećanac et al. [11,15] performed a study of the elastic and fracture properties and the sensitivity to subcritical crack growth of porous (up to 46%) and dense BSCF, LSCF and CGO ceramics in order to predict the lifetime limits for application of critical membrane parts at room temperature. However, these studies were made on bulk sintered samples or coated samples tested using conventional macroscale methods that require large volumes of material and machining operations and allow assessing only sample (coating and substrate) properties. The measurement of the mechanical properties of the thin electrode film material requires the use of micro or nanoscale techniques, able to tests small volumes of material and with little or no specific sample preparation. This has been attempted by some authors,

Xiang et al. [13] used nanoindentation to determine the hardness and elastic modulus of a non-reduced NiO-YSZ hydrogen electrode in a half-cell configuration and proposed a method to determine these properties based on a work of indentation approach. Li et al. [7] measured the elastic modulus and nanohardness for a wide range of CGO/LSCF composites for IT-SOFC using indentation. The pellets and bars were produced from a mixture of CGO and LSCF powders by pressing and sintering. Densities, measured by the Archimedes method, were in the range 94–98% of the theoretical value. The values obtained for the elastic modulus were in the range 119–153 GPa and 8.9–10.8 GPa for the hardness. Both properties varied almost linearly with density.

However, most of these studies and model predictions are based on relatively dense materials (porosity levels under 30%) and since porosity has an enormous influence on the mechanical properties, the results cannot be extrapolated to materials with much higher porosity like the coral structures developed by the authors.

The mechanical properties of highly porous materials (above 50 vol% porosity) are controlled by the distribution of the solid phase unlike denser materials (below 50 vol% porosity) where the mechanical properties are controlled by the presence of isolated pores [16]. Structures with very high levels of porosity may be described as cellular materials for which several mechanical behavior models apply. Most of these models are based on the description of the solid phase as an assembly of walls and struts in a periodic microstructure of cells with a known mechanism of deformation under loading: elastic deformation followed by buckling and bending of cell walls, densification and fracture due to rupture of cells [17,18].

Though the internal structure of each coral in the microstructure developed in the present work could be compatible with a cellular material, the overall morphology of the coral structure is more typical of a columnar structure and a periodic nature can hardly be recognized. Since the structure of the coral microstructure films developed in the present study cannot be described as a cellular material a different micromechanical response is to be expected.

The present work aims at studying the mechanical behavior and evaluating the properties of a CGO-LSCF oxygen electrode material with a coral microstructure, developed by Electrostatic Spray Deposition (ESD) using microscratch and ultramicroindentation tests. The mechanisms of material deformation and damage under loading were analyzed and measurements of the hardness and Young's modulus of the coating material and estimates of its strength were obtained.

2. Experimental

2.1. Electrode preparation

A composite CGO-LSCF coating was deposited by electrostatic spray deposition on a homemade YSZ ($Zr_{0.92}Y_{0.08}O_{1.96}$) disk substrate with a diameter of 19 mm and about 1 mm thickness. Deposition was carried out from two precursor solutions: lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$), strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3 - \delta}$ solution and cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and gadolinium nitrate ($Gd(NO_3)_2$) for $Ce_{0.9}Gd_{0.1}O_{1.95}$ solution. Adequate amounts of salts to prepare a total concentration of 0.02 mol L^{-1} were dissolved in distilled water and ethanol in 5:1 vol ratio to create LSCF precursor solution; diethylene glycol monobutyl ether, well known as butyl carbitol ($CH_3(CH_2)_3(OC_2H_2)_2OH$) and ethanol in 4:1 vol ratio for CGO precursor solution.

Graded CGO and LSCF composite coatings were prepared by changing flow rates of the precursor solutions. The deposition was carried out in three steps: deposition of single CGO was done firstly to create a barrier diffusion layer; then, the deposition of graded composition CGO-LSCF and, finally, the deposition of single LSCF. The detailed description of the deposition parameters in every step can be found elsewhere [1]. The substrate temperature was kept at 400 °C monitored by thermocouple. The positive high voltage applied between the nozzle and the grounded substrate ranges from 7 to 11 kV. After deposition, the samples were heat treated at 900 °C for 2 h at a rate of 3 °C min^{-1} in air.

2.2. Mechanical characterization

The characterization of the mechanical behavior and an assessment of the mechanical properties of the coating were carried out using microscratching and microindentation testing methods.

2.2.1. Microscratch tests

The microscratch tests were performed using a MTS XP