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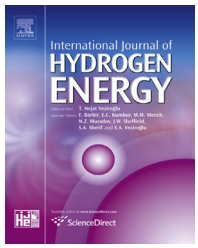

Electrochemical properties of graded and homogeneous $Ce_{0.9}Gd_{0.1}O_{2-\delta}$–$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ composite electrodes for intermediate-temperature solid oxide fuel cells

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ABSTRACT

Graded and homogeneous CGO–LSCF composite electrodes deposited by Electrostatic Spray Deposition on an YSZ substrate have been studied with and without screen-printed LSCF current collector. Impedance spectroscopy measurements have been performed in air at open circuit potential between 450 °C and 700 °C; and during isothermal treatments at 600 °C for 200 h; and at 800 °C for 12 h to estimate the relevance of such oxygen electrodes for intermediate temperature solid oxide fuel cells (IT-SOFCs). A thin and dense CGO layer is firstly deposited to avoid any chemical reaction between LSCF and YSZ. No significant increase of the polarization resistance has been evidenced during isothermal test at 600 °C for 200 h, proving good stability of the electrode. Using a LSCF current collector layer (CCL), the polarization resistance decreases by a 1.5 order of magnitude compared to samples with single cathode functional layer (CFL). The electrochemical results do not conclusively indicate which composition presents lower polarization effects.

Introduction

Global research is focused on finding inexpensive and clean energy. The solid oxide fuel cell (SOFC) is a promising technology for production of pure electric energy with zero CO_2 emissions. However, working at temperature of 1000 °C, yields high costs for the application and decreases its life span. The great opportunity comes with so called intermediate temperature SOFC (IT-SOFC) operating below 700 °C. The most common electrode materials are LSM–YSZ composite and Ni–YSZ cermet which are not compatible at intermediate temperatures range due to increased over potentials and high electrolyte ohmic losses. $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) can successfully replace LSM as a cathode material in IT-SOFCs. Moreover, undesirable reaction between LSCF and YSZ [1–4] can be eliminated by insertion of a dense $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO) barrier diffusion layer [5–7]. CGO is mechanically and chemically compatible with LSCF and YSZ because of its close

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thermal expansion coefficients [8–10] at intermediate temperatures. The electrode based on CGO–LSCF composite, possesses mixed ionic-electronic conductivity together with catalytic properties from LSCF and enlarged ionic conductivity from CGO.

The other issue influencing the SOFC performance is the electrode microstructure. Electrostatic spray deposition (ESD) is an inexpensive and versatile technique to create dense or porous coatings with good adhesion to the substrate. In general, precursor solution is atomized to a spray when the high voltage is set between the nozzle with precursor solution and the heated substrate. Droplets inside the spray dry during the flight and create solid coating on the grounded substrate. Deposition is controlled by process parameters (nozzle-to-substrate distance, deposition time, substrate temperature, solution flow rate) and the precursor solution physico-chemical properties (boiling point, conductivity, surface tension, etc.). Deposition is performed at relatively low temperature (300–400 °C) combined with post-annealing at temperatures lower than 1000 °C.

This work describes preparation and electrochemical characterization of composite electrodes built of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) with a coral microstructure (high porosity for gas access) deposited on 8 mol. % Y_2O_3–ZrO_2 (YSZ) pellet by ESD. A thin and dense CGO layer was firstly deposited by ESD on YSZ in order to separate LSCF and YSZ. Homogeneous and graded compositions of CGO–LSCF mixture throughout composite electrodes were studied in order to see the benefit of CGO insertion on the performances. Moreover, the relevance of screen printed LSCF current collector onto coral microstructure was also investigated.

Experimental

Oxygen electrode preparation

Two types of electrodes were investigated: 1) single-layered – CGO–LSCF composite as a cathode functional layer (CFL) without any current collector layer, 2) double-layered – CGO–LSCF composite as a CFL and a screen-printed LSCF current collector layer (CCL). Samples descriptions of composition, laboratory of screen-printing and configuration during electrochemical measurements are listed in Table 1.

Table 1 – Description of sample composition, place of screen-printing and electrochemical configuration during impedance spectroscopy.

Sample	Composition	Current collector	IS configuration
1	Graded	ENSMSE	3-Point electrodes
2	Graded	–	3-Point electrodes
3	Homogeneous	–	3-Point electrodes
4	Graded	KIT	Symmetrical
5	Graded	KIT	Symmetrical
6	Homogeneous	KIT	Symmetrical
7	Homogeneous	KIT	Symmetrical

Cathode functional layer

Coral CGO–LSCF composites were deposited on in-house made YSZ disk shaped substrates; 19 mm in diameter and 1 mm thick. Dense electrolyte pellets were polished to provide a smooth and uniform surface before the deposition. LSCF and CGO solutions were prepared with a total salt concentration of 0.02 mol L^{-1}. The precursor solution of LSCF consisting of lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$, Rectapur Prolabo, 99.5%), strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$, Strem Chemicals, 99%), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Merck, 99%) and iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Sigma Aldrich, 99.99%) were weighted to achieve proper stoichiometry of the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ solution. The precursor solution of $Ce_{0.9}Gd_{0.1}O_{1.95}$ was based on cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, Rectapur Prolabo, 99.5%) and gadolinium nitrate ($Gd(NO_3)_2$, Aldrich, 99.99%). Salts were dissolved in distilled water and ethanol (C_2H_5OH, Sigma–Aldrich, 99.8%) in a 5:1 volume ratio to create the LSCF precursor solution, and in diethylene glycol monobutyl ether (butyl carbitol $(CH_3(CH_2)_3(OC_2H_2)_2OH$, Acros Organics, 99%)) and ethanol in a 4:1 volume ratio to create the CGO precursor solution.

Depositions were carried out in air during 3 h at a 35 mm nozzle-to-substrate distance by using two syringes pumps (Sage M361) with separated pipes to simultaneously provide two separate precursor solutions. Thus, graded and homogeneous CGO–LSCF composite electrodes were prepared. The deposition procedure consisted of two successive steps: 1) deposition of a thin CGO buffer layer, and 2) deposition of CGO and LSCF. A graded composition was deposited by varying the flow rate of the LSCF precursor solution from 0 to 1 mL h^{-1} (Q_{LSCF}), while the flow rate of CGO was varied from 1 to 0 mL h^{-1} (Q_{CGO}). Flow rates were varied with 0.1 mL h^{-1} step every 15 min [11].

A homogeneous composition was deposited by fixing flow rates of CGO and LSCF precursor solutions equal to 0.5 mL h^{-1} e.g. a total flow rate equal to 1 mL h^{-1}. The substrate temperature was kept stable at 400 °C, calibrated before the deposition by a K-type thermocouple. A positive high voltage was applied during the deposition ranging from 7 to 11 kV. The layer was deposited in a disk shape with a diameter of ~17 mm. After the deposition, all CGO–LSCF electrodes were annealed at 900 °C for 2 h with a heating/cooling rate of 3 °C min^{-1} in air.

Current collector layer

Current collector layers were screen printed either at Ecole Nationale Supérieure des Mines de Saint-Étienne (ENSMSE) in France and or at Karlsruhe Institute of Technology (KIT) in Germany, respectively. Samples fabricated in LEPMI consisted of CGO–LSCF coral microstructure without a current collector layer.

The CCLs from ENSMSE were circular with a diameter of ~17 mm accurately matched to the coral structure. For these samples, the screen printing was carried out only on one face of the YSZ pellet. Four successive printings, each dried for 15 min at 115 °C in air, were performed to achieve a total current collector thickness of 75 μm. Then, the CCLs were heated to high temperature in air to sinter the layer and remove binders from the layer. To completely debind organic

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