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CGO as a barrier layer between LSCF electrodes and YSZ electrolyte fabricated by spray pyrolysis for solid oxide fuel cells

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ABSTRACT

Perovskite $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) is often used as a cathode material for solid oxide fuel cells (SOFC) due to high mixed ionic and electronic conductivity and good catalytic activity. Unfortunately, sintering of the LSCF cathode together with the yttria stabilized zirconia (YSZ) electrolyte, leads to formation of the $La_2Zr_2O_7$ and $SrZrO_3$ phases in the interface. These phases increase the resistance of the cell. To avoid creation of the undesirable phases, diffusion barrier layers are often used. In this work 200 nm thick cerium-gadolinium oxide (CGO) layer deposited by spray pyrolysis is used as a diffusion barrier. The impact of sintering temperature on the effectiveness of diffusion barrier was examined. For optimized sintering temperature of 900 °C, the CGO barrier layer leads to lowering polarization loses of almost two orders of magnitude from 477 mΩ cm^2 (when CGO is not used) to 7 mΩ cm^2.

1. Introduction

For solid oxide fuel cells the most popular choice for cathode material was $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) mainly because it is compatible with yttria stabilized zirconia ($Zr_{0.84}Y_{0.16}O_{2-x}$, YSZ) electrolyte [1,2]. However, it is characterized by predominant electronic conductivity and sluggish oxygen reduction reaction [3]. That is why other materials were sought among mix ionic and electronic conductors with high catalytic activity for oxygen reduction [4–6]. The other cathode materials, like $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF) [7], $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) [8] and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [3,9], belong to this group. Unfortunately, these cathodes contain strontium and during sintering with commonly used electrolyte, yttria stabilized zirconia [6], parasitic oxides, like $La_2Zr_2O_7$ and $SrZrO_3$, are formed. Formation of these low conductivity phases cause power loses of the cell [10].

To avoid parasitic phase formation diffusion barrier layers are used [11]. The task of diffusion barrier layer is mainly to prevent the diffusion of the cations to the cathode-electrolyte interface (mainly strontium from cathode and zirconium from the electrolyte). To sufficiently protect, the barrier layer must be dense, continuous, homogeneous and gas-tight [12]. It must be also chemically stable and not react with cell components. Its thickness should be relatively low to avoid the introduction of additional ohmic resistance [13].

Widely known and used materials for diffusion barrier layer are samarium [14–16] and gadolinium doped ceria ($Ce_{0.8}Gd_{0.2}O_{2-x}$, CGO) [11,17], which were mostly elaborated as a protecting interface between zirconia based electrolytes and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ [18,19], $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ [19], $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ [8] or composite of $(La_{0.6}Sr_{0.4})_{0.99}CoO_{3-\delta}$ and CGO [20] cathodes. The right choice of the deposition method is crucial for the effectiveness of such layer. Several methods were investigated for CGO layer formation: pulsed laser deposition (700 nm thick layer) [21], magnetron sputtering (400 nm [21] 1–2.5 μm [22] and 3–5 μm [23] thick layers), screen printing (7 μm thick layer) [21,23], physical vapor deposition (1–3 μm thick layers) [24–26], spin coating (1 μm thick layer) [13], dip-coating (100–700 nm thick mesoporous layers) [27], electrostatic spray (85 nm thick layer) [28], slurry spray (2–3 μm thick layers) [29], screen printing infiltrated by sol-gel (1.5 μm thick layer) [30] and spray pyrolysis (700 nm [21] and 250–300 nm [31] thick layers). Suitable deposition method should take in to account that treatment temperature of CGO should not exceed 1100 °C [11]. Above this temperature a low conductivity solid solution of CGO and YSZ is formed.

It is hard to find suitable method for barrier layer deposition. Most of them have some disadvantages leading to creation of thick, or porous or inhomogeneous layers or they require high sintering temperatures. Methods, which provide barrier layers with satisfying properties are usually very expensive and they are limited to laboratory use. A perspective method is spray pyrolysis, which can be easily used in industry due to cost effectiveness and scalability. After optimization of the deposition parameters it can yield homogenous and relatively thin layers

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with thickness from a few nanometers to a few micrometers. However, the process of optimization should be executed carefully and precisely.

In this work the CGO barrier layer was deposited on YSZ surface by two-step spray pyrolysis method optimized during previous investigation described elsewhere [32]. The purpose of this work was evaluation of a relatively thin (200 nm) CGO layer as a diffusion barrier protecting interface between YSZ and LSCF with regard to the cathode sintering temperature. The cathodes were symmetrically deposited on YSZ electrolyte with and without CGO barrier layer and the cells sintering conditions were investigated for their optimal electrical performance. The impact of CGO layers on the cell resistance and parasitic phase formation was examined. To the best of our knowledge, such cells fabricated in varying conditions are investigated for the first time. Results were compared to those obtained using standard cell configuration without CGO and to results obtained using different cathode materials like LSM (often used as a standard, stable cathode material [1]) and LSF (from the same cathode materials group [7]).

2. Experimental

Symmetrical cells were prepared and investigated for this study. As an electrolyte material, a 100 μm YSZ thick tape (ESL Ltd.) was cut into 13 mm in diameter circles and sintered at 1400 °C for 2 h. Symmetrical cells with and without CGO barrier layer were made. For samples with CGO, a 200 nm thick layer was sprayed on both sides of electrolyte surface. A precursor was made of cerium and gadolinium nitrate salts ($Ce(NO_3)_3*6H_2O$ (Sigma-Aldrich, 99%) and $Gd(NO_3)_3*6H_2O$ (Sigma-Aldrich, 99.9%)) dissolved in distilled water, ethylene glycol (Sigma-Aldrich, 99%) and tetraethylene glycol (Sigma-Aldrich, 99%) in volume ratios 1:1:8 respectively. The final concentration of metal cations was 0.05 M, which was proven to yield satisfactory results is similar to the concentration used by others [10,33,34]. The precursors flow rate was maintained at 1 cm^3/h, while spraying pressure at 2 bar. During deposition nozzle of the spraying gun was fixed 600 mm from hot plate set at 400 °C. CGO was deposited using two-step deposition process (optimized and described elsewhere [32]) with intermediate sintering at 900 °C of 100 nm thick layer in order to release stresses accumulated during deposition. On the CGO layer a LSCF cathode was deposited from the paste (ESL 4421-A) and sintered for 2 h at 800, 900, 950 and 1000 °C in order to examine a cathode sintering temperature impact on the effectiveness of diffusion barrier and influence of diffusion barrier on electrical properties. In the case of the symmetrical cells without CGO, LSFC was deposited directly on YSZ surface and sintered at the same temperatures. Ag/YSZ composite paste was deposited on cathode surface as a current collector and sintered for 1 h at 800 °C. Additionally, the symmetrical cells without CGO layer were prepared using $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ sintered at 900 °C (on 1 mm thick electrolyte) and $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (ESL 4420) sintered at 1000 °C for comparison. For these sintering temperatures the lowest polarization resistance was obtained. Electrical measurements were carried using Solartron SI 1260 impedance analyzer combined with Solartron SI 1287 potentiostat/galvanostat. Measurements were performed in the frequency range from 1 MHz to 0.1 Hz with an excitation voltage of 20 mV in the temperature range 600 °C–800 °C. Selected spectra were compared using ADIS method (described in more details in [35]).

The cross section images were obtained by scanning electron microscopy (SEM) FEI Quanta FEG 250 with secondary electron detector operating in a high vacuum mode with the accelerating voltage of 10 kV. The element distribution was collected using the Energy Dispersive X-ray Spectroscopy (EDX) by EDAX Genesis APEX 2i with ApolloX SDD spectrometer under the accelerating voltage of 20 kV with resolution of 100 nm.

3. Results and discussion

In Fig. 1 SEM micrographs of symmetrical cells cross-sections sintered at 900 (Fig. 1a), 950 (Fig. 1b) and 1000 °C (Fig. 1c) are presented. One can observe dense YSZ electrolyte (bottom), 200 nm thick CGO barrier layer visible as a bright layer at the interface and LSCF cathode. It is clearly visible that the increase of sintering temperature leads to cathode morphological changes. Grains of LSCF become larger and the porosity is reduced. Moreover, the cathode material is better attached to the substrate surface in the case of the sintering temperature of 1000 °C (Fig. 1c) in contrast to point-type contact for the sintering temperature of 900 °C (Fig. 1a). On the other hand, the perovskite cathode with the smaller grain size has a higher active surface for oxygen reduction.

Fig. 2 shows the Arrhenius plots of the area specific resistance (ASR) of the cells based on impedance spectroscopy measurements. Closed symbols are assigned to results obtained for samples with CGO barrier layer, while open symbols for samples without. The plot visible in Fig. 2a presents a polarization resistance, while in Fig. 2b an ohmic resistance of the symmetrical cells with LSCF cathode sintered at temperatures 800, 900, 950 and 1000 °C is shown. It is clearly visible that the cells without CGO layer have two orders of magnitude higher polarization resistance than the cells with CGO. The results for the samples without CGO show that the polarization resistance is higher when sintering temperature is higher. The higher temperature promotes more intense diffusion of atoms from both the cathode and the electrolyte, and parasitic phase creation. Introduction of CGO prevents the diffusion and, in consequence, below 1000 °C influence of the parasitic phase is not visible and polarization resistance is almost the same. The sintering temperature of 1000 °C reveals that some parasitic phase can be created, because resistance suddenly increases. However, it is still lower by two orders of magnitude than the resistance of the cell without CGO sintered at 1000 °C. Polarization loses can be introduced also by decrease of triple phase boundary (TPB) length because of cathode densification. In the literature reports, the introduction of 110 nm thick CGO

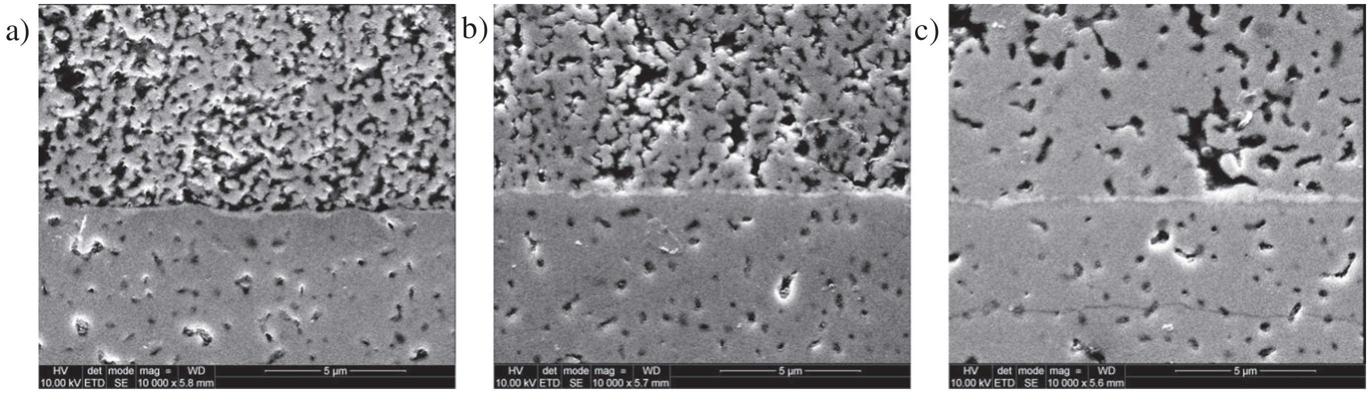

Fig. 1. SEM micrographs of YSZ-CGO-LSCF layers cross-section with LSCF sintered at a) 900 °C, b) 950 °C, c) 1000 °C.

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