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Laser induced densification of cerium gadolinium oxide: Application to single-chamber solid oxide fuel cells

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ABSTRACT

In single-chamber solid oxide fuel cells (SC-SOFC), anode and cathode are placed in a gas chamber where they are exposed to a fuel/air mixture. Similarly to conventional dual-chamber SOFC, the anode and the cathode are separated by an electrolyte. However, as in the SC-SOFC configuration the electrolyte does not play tightness role between compartments, this one can be a porous layer. Nevertheless, it is necessary to have a diffusion barrier to prevent the transportation of hydrogen produced locally at the anode to the cathode that reduces fuel cell performances. This study aims to obtain directly a diffusion barrier through the surface densification of the electrolyte $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) by a laser treatment. KrF excimer laser and Yb fiber laser irradiations were used at different fluences and number of pulses to modify the density of the electrolyte coating. Microstructural characterizations confirmed the modifications on the surface of the electrolyte for appropriate experimental conditions showing either grain growth or densified but cracked surfaces. Gas permeation and electrical conductivities of the modified electrolyte were evaluated. Finally SC-SOFC performances were improved for the cells presenting grain growth at the electrolyte surface.

1. Introduction

Conventional Solid Oxide Fuel Cells (SOFC) are composed of two chambers separated by a dense electrolyte. The difference in oxygen partial pressure between the two separated electrode compartments leads to the establishment of an open circuit voltage (OCV). Contrary to conventional cells, in Single Chamber SOFC (SC-SOFC), the cell is located in a single gas chamber where it is exposed to a gas mixture of fuel and oxidant (air). The working principle is based on the selectivity of the electrodes; the anode must be selective and active for fuel oxidation, whereas the cathode must be selective for reduction of oxygen. Hydrocarbons are generally used to decrease the risk of explosion; hydrogen is therefore obtained by the partial oxidation of the hydrocarbons. Methane was chosen for this study, the most common fuel used in SC-SOFC. Principal reactions are described in reactions 1, 2 and 3 [1].

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \quad (1)$$

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (2)$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (3)$$

As the generation of the OCV depends only on the electrocatalytic activity and selectivity of the electrodes, and not on a dense electrolyte as in conventional SOFC, it is possible to operate without a gastight electrolyte [1,2]. This fact allows to use simple and conventional processing methods to prepare the electrolyte. For example, screen-printing, a simple and low-cost deposition technique can be used to prepare a thin and porous layer, because in such a case a dense electrolyte is not required [2–4]. However, some authors [2,3] have indicated that the porosity related to the electrolyte may allow the transport of the hydrogen produced locally at the anode (reaction 1) to the cathode, which can generate an OCV drop and a decrease of cell performances. To prevent hydrogen transportation, it is thus necessary to have a dense electrolyte or at least a diffusion barrier layer but at the same time preserving the porosity of the electrodes.

Solid oxide electrolytes based on cerium gadolinium oxide (CGO) materials are considered to be the most promising candidate materials for use in single-chamber solid oxide fuel cells, because they offer considerably high ionic conductivity at intermediate operating temperatures (450–700 °C). Moreover as SC-SOFC operates in hydrocarbon/air mixture and not in pure hydrogen, CGO

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Table 1
Summary of the laser processed samples.

Laser	Range of fluence ($J\,cm^{-2}$)	Range of number of pulses	Results
UV	0.05–0.3	10–60	No effect
	0.05–0.2	1000–6000	No effect
	0.3	3000–6000	Grain growth
	1.3	10	Densification + cracks
IR	2–3.6	5–10	Densification + cracks

stability is not a problem [5,6]. Nevertheless, the achievement of full density materials requires sintering temperatures above 1400 °C [7–9]. Various techniques have been used to densify a CGO electrolyte at 1400 °C; however in the configuration of anode supported SC-SOFC selected in this study, it is difficult to achieve a dense electrolyte deposited by screen-printing by conventional thermal annealing techniques maintaining porous electrodes.

By laser treatment it is possible to induce modifications on materials with localized thermal annealing at high temperatures minimizing heating of the underlying substrate [10,11]. Lasers have been employed successfully to treat ceramic materials with an increasing interest in their densification [12–18]. Most of researches are about carbide, bromides and refractory ceramics densification, showing most of the time positive results with continuous lasers [12,15,19]. However, it has been demonstrated that pulsed laser irradiation offers an attractive alternative to conventional thermal annealing to oxides densifications [17,18]. Sandu et al. [17] have densified and crystallized SnO_2:Sb sol–gel films using excimer laser annealing. Tsagarakis et al. [18] have also used an excimer laser to obtain nanocrystallized $BaTiO_3$. The high intensity of pulsed laser may induce high heating rates and well-defined localization of the energy input within the irradiated material [20].

This study aims to obtain a diffusion barrier of the CGO electrolyte. For this, laser treatments are proposed onto the CGO surface. The influence of laser parameters (wavelength, fluence and number of pulses) has been examined on the laser induced densification of the electrolyte. Microstructural characterizations, permeation tests, electrochemical measurements and fuel cell characterizations were used to determine the effects of laser parameters.

2. Experimental procedure

All the materials used for the cells preparation were commercial powders acquired from Fuel Cell Materials. The experimental procedure used to prepare the SC-SOFC was previously described [3]. Anode support was prepared by uniaxial pressing at 250 MPa to obtain a sample of 22 mm in diameter. The powder mixture was composed of NiO (60 wt%) and CGO (40 wt%). CGO refers to $Ce_{0.9}Gd_{0.1}O_{1.95}$ composition. Then, the electrolyte was deposited by screen printing. The ink was prepared by mixing 63 wt% of CGO powder and 33 wt% of a binder (ESL^{TM} V400). 8 drops per gram of powder of a solvent was added (ESL T404). Two layers of electrolyte ink were deposited with a drying step at 120 °C for each layer, providing a porous electrolyte around 20 μm thick. The assembly was annealed at 1200 °C during 3 h. Finally, surface of the electrolyte was irradiated by the laser.

Two types of pulsed laser were used: a KrF Lambda Physics (λ = 248 nm, τ = 20 ns, frequency = 10 Hz, $4 \times 2.5\,mm^2$ laser spot size) and an ytterbium doped fiber YLIA M20EG (λ = 1064 nm, τ = 100 ns, frequency = 25 kHz, 190 μm diameter of laser spot size). The laser processing of the overall electrolyte surfaces was carried out with the assistance of linear stages. Overlapping of the successive laser spots was used to ensure the treatment of the whole surface. Irradiations of the electrolyte surface were performed in air, with series of pulses between 1 and 10^4 at various fluences. The experimental processing conditions are summarized in Table 1. The surface microstructure was studied by scanning electron microscopy (FEG-SEM, Jeol JSM 6500 F).

A permeation test was developed to measure gas permeation through CGO layer. The device (Fig. 1a) consists of two cavities where the sample is placed in between. A flow rate of $10\,L\,h^{-1}$ of helium was sent to the lower cavity. This gas was chosen to simulate hydrogen diffusion through the electrolyte. Same flow rate of nitrogen was simultaneously sent to the upper cavity. Helium percentage which passes through the electrolyte is recovered at the nitrogen outlet and analyzed by gas chromatography (SRA instruments).

The electrical conductivity of the electrolytes as a function of temperature was measured by electrochemical impedance spectroscopy (EIS). Two parallel platinum electrodes were deposited on the surface of the electrolyte by screen-printing to create a coplanar

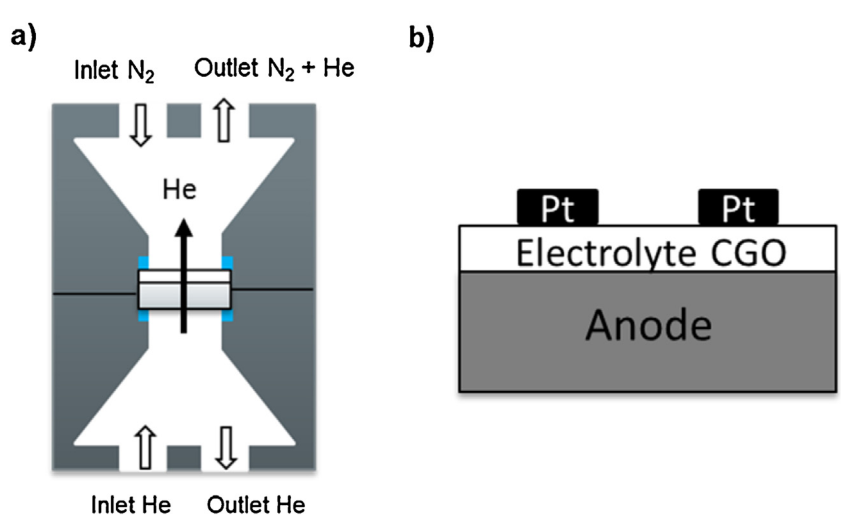

Fig. 1. (a) Permeation test device, (b) Schematic of electrodes configuration for electrical conductivity measurements.