Journal of Power Sources 195 (2010) 6758–6763

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Rapid synthesis of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ electrolyte by a CO_2 laser and its electric properties for intermediate temperature solid state oxide full cells

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ARTICLE INFO

Article history:
Received 12 January 2010
Received in revised form 30 March 2010
Accepted 30 March 2010
Available online 8 April 2010

Keywords:
Intermediate temperature solid oxide fuel cells
Laser rapid solidification
Solid state reaction
Relative density
Impedance spectra
Activation energy

ABSTRACT

A laser rapid solidification (LRS) method has been developed for the synthesis of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM), an excellent electrolyte for solid oxide fuel cells. It is shown that pure perovskite LSGM phase can be produced within a few seconds with this method under optimized synthetic conditions and it solidified in densely packed and relatively ordered ridge-like blocks with a relative density of 98.5%. The unique microstructures are attributed to the oriented crystalline growth in the molten pool dictated by heat transfer directions. It is found that the samples synthesized by LRS exhibit superior electrical properties for fuel cell applications to those by solid state reactions. The conductivities of 0.027, 0.079 and 0.134 S cm^{-1} measured at 600, 700 and 800 °C, respectively are much higher than those of the samples synthesized by solid state reactions with similar purity and density.

1. Introduction

Solid oxide fuel cells (SOFCs) can directly convert chemical energy of fuels to electrical energy with advantages of high electrical efficiency, fuel versatility, and low pollution emissions [1]. Conventional SOFCs with Y_2O_3-stabilized ZrO_2 (YSZ) electrolytes require high operating temperatures (800–1000 °C) and serious problems may arise such as mechanical stress due to mismatch in thermal expansion, interfacial diffusion and/or reaction between electrolyte and electrode materials and difficulty in sealing. These problems increase manufacturing cost and reduce the reliability of the fuel cells [2]. In order to reduce the operating temperature, many efforts have been devoted to develop novel electrolytes for intermediate temperature (600–800 °C) SOFCs. The perovskite oxide, strontium- and magnesium-doped $LaGaO_3$ (LSGM), exhibits a higher ionic conductivity (~0.10 S cm^{-1} at 800 °C [3,4]) than YSZ over a wide range of oxygen partial pressure. These superior electrical and stable properties make $LaGaO_3$-based oxides the most promising candidates as electrolytes for intermediate temperature SOFCs.

LSGM powders were generally synthesized by solid state reactions [5–9] or wet chemical routes [10–19]. However, the solid state reactions suffer from the chemical in-homogeneity, severe time and energy wasting while the wet chemical methods require expensive metal alkoxide precursors, great care in mixing the precursors to achieve the desired stoichiometry and tedious pretreatment before the final calcinating step. Due to the narrow composition range for the stability of the perovskite phase, small deviations from the ideal composition would result in secondary phases which deteriorate the performance of the electrolyte [19,20]. The synthesis of a pure single phase material of LSGM is a rather difficult task. Therefore, it is necessary to explore new and rapid synthetic methods.

The synthesis of pure bulk materials with laser rapid solidification (LRS) is a relatively new technique [21–25]. In this paper, laser rapid solidification was employed to synthesize LSGM electrolyte and the microstructure and electrical properties of the samples synthesized by laser were studied and compared to the samples synthesized by solid state reactions. It is shown that high purity LSGM electrolyte can be produced within a few seconds with this technique which simplifies the processing procedures and shortens the sintering time greatly. Further investigations on the samples reveal that the LSGM material synthesized by the laser synthetic route exhibits unique microstructure and superior electric properties for SOFCs.

2. Experimental

$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) samples were prepared with starting materials of Ga_2O_3 (99.99%), La_2O_3 (99.99%), MgO (98%)

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doi:10.1016/j.jpowsour.2010.03.092

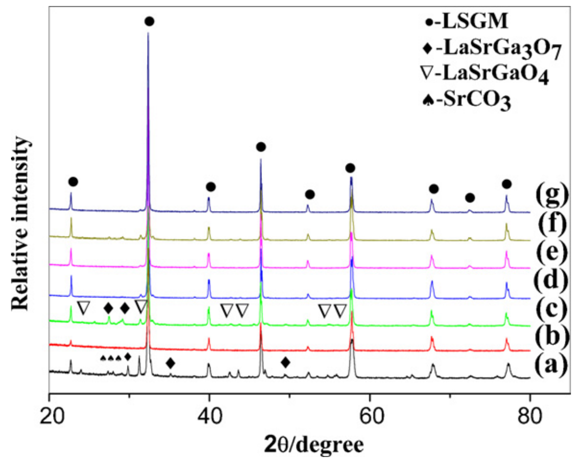

Fig. 1. XRD patterns of LSGM powders synthesized by (a) solid state reaction at respectively 1200 °C for 24 h and at 1400 °C for 6 h (SSR1); (b) solid state reaction at respectively 1250 °C for 10 h, 1500 °C for 6 h and 1600 °C for 2 h (SSR2); (c–g) laser rapid solidification (LRS) with respectively 800, 1000 and 1100 W laser powers at 1 mm s^{-1} scan speed, and 1100 W laser power at 2 and 0.6 mm s^{-1} scan speed.

and $SrCO_3$ (99%). MgO and La_2O_3 were fired at 1000 °C for 7 h before weighting to decompose carbonate and hydroxide impurities. The absence of impurities in the reagents was checked by X-ray diffraction (XRD). The mixtures were ground in a mortar for 2 h and then pressed into cuboid bars (40 mm × 5 mm × 5 mm) by uni-axial cold press with a steel mould at a pressure of 10 MPa and dried for 2 h at 100 °C in a baking oven before sintering. The synthesis was performed by using a 5 kW continuous-wave CO_2 laser. The laser beam was striking onto a bar placed at a distance where the defocus length was set to 120 mm. The beam spot on the sample was approximately 12 mm in diameter. As the laser beam moves ahead along the length direction, the synthesized sample behind cools naturally and rapidly to room temperature. Such cooling process can be regarded as rapid solidification. In order to optimize the synthesis conditions, we changed the scan speed from 0.6 to 3 mm s^{-1} at a fixed laser power and altered the laser power from 700 to 1100 W at a fixed scan speed. For comparison, two series of samples were prepared by conventional solid state reactions with pressed bars or pellets, one by calcinating at 1200 °C for 24 h and then sintering at 1400 °C for 6 h with intermediate grinding (denoted as SSR1) and another by calcinating at 1250 °C for 10 h and then sintering at 1500 °C for 6 h and at 1600 °C for 2 h with intermediate

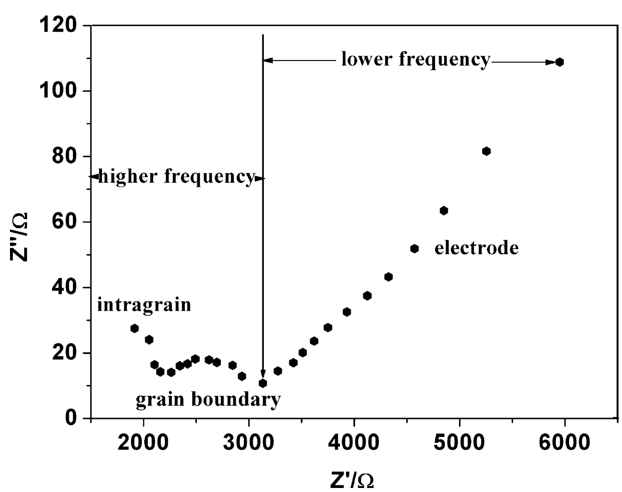

Fig. 2. Representative AC impedance spectra at 250 °C of the LSGM prepared by solid state reaction (SSR2).

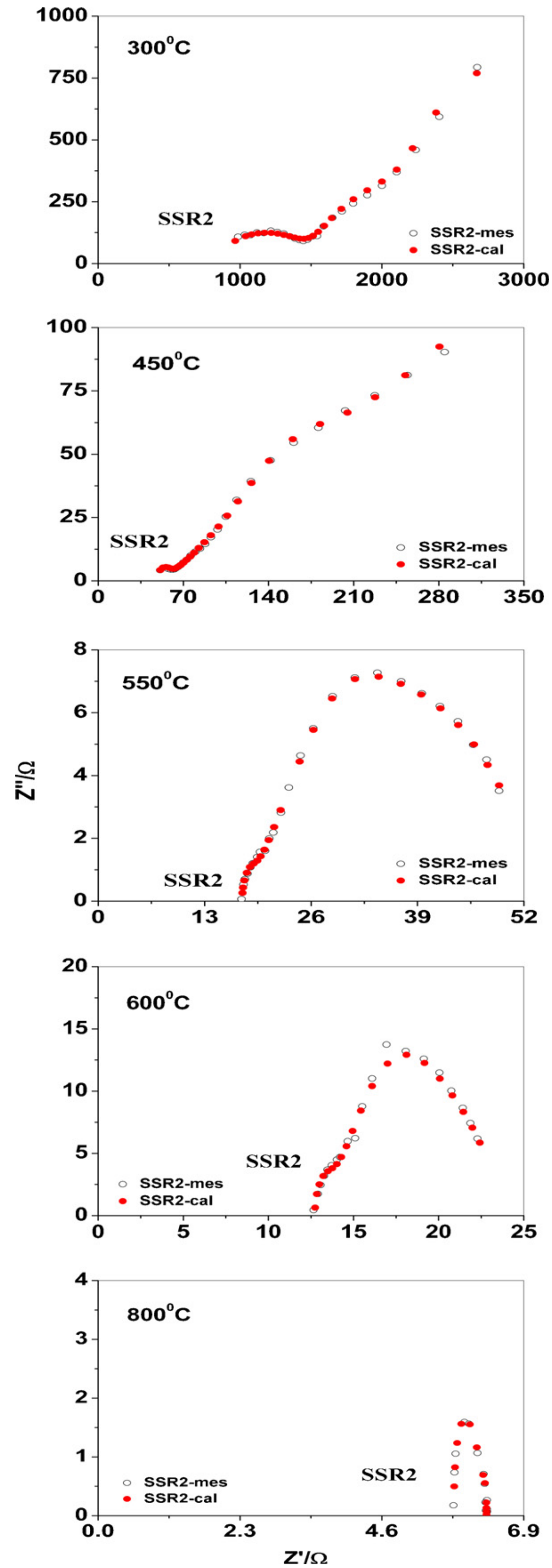

Fig. 3. Representative AC impedance spectra from 250 to 900 °C of the LSGM prepared by solid state reaction (SSR2).