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$La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ perovskite membrane: Oxygen semi-permeation, thermal expansion coefficient and chemical stability under reducing conditions

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ABSTRACT

The $La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ perovskites are one of the most promising materials for catalytic membrane reactor because of their excellent oxygen semi-permeation, low thermal expansion coefficient and good chemical stability at high temperature (700–1000 °C) under a wide range of oxygen partial pressure (from 0.21 to 10^{-19} atm). In this paper, the thermal expansion coefficient (TEC) and the oxygen semi-permeation of $La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ perovskite in relation with Sr and Ga substitutions have been measured and discussed. The chemical stability of $La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ perovskite formulations under diluted methane atmosphere is tested and discussed.

This study leads to identify the Sr and Ga substitution ratios presenting the best compromise between high oxygen semi-permeation, low thermal expansion coefficient and good chemical stability in working conditions. In this way, one of the best compromises between good oxygen permeation fluxes, dimensional and chemical stabilities are $La_{0.6}Sr_{0.4}Fe_{0.6}Ga_{0.4}O_{3-\delta}$ and $La_{0.6}Sr_{0.4}Fe_{0.7}Ga_{0.3}O_{3-\delta}$.

1. Introduction

The international rising cost of fossil fuels has strongly motivated the research activities about the development of novel energy sources from natural gas [1–3]. The catalytic membrane reactor (CMR) is a promising solution for the production of fuel from natural gas [4–9], via gas to liquid process (GTL). Compare to Autothermal reformer, CMR reactor makes possible the separation of O_2 from air and the production of syngas from natural gas in a single step. The main element of this technology is the dense ceramic membrane which, on one hand separates oxygen from air with an infinite selectivity, and on the other hand allows the partial oxidation of methane from natural gas in hydrogen and carbon monoxide, in according to the following reaction:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$$

During the last decade, numerous materials has been studied and proposed for this application [10]. Teraoka et al. were the first to work on perovskite materials (ABO_3) for CMR application [11–13] because of the mixed ionic and electronic conductivity properties of these materials. These perovskite materials answer to some requirements such as a high oxygen semi-permeation, a good mechanical reliability and a good chemical stability at high temperature (between 700 °C and 1000 °C) and under a wide range of oxygen partial pressure (from 0.21 to 10^{-19} atm) [14,15]. These three properties are often opposite and one of challenges for industrial application is to obtain the best compromise between high oxygen semi-permeation and a good chemical stability. In the past, many researches have focused on the development of materials having high oxygen semi-permeation regardless their chemical stability. Recently, the researchers are focusing on new materials with a particular attention on the chemical stability under low oxygen partial pressure or methane [16]. Unfortunately, few works identify clearly the membrane materials corresponding to the best compromise between the three main parameters for CMR application; (i) high oxygen semi-permeation, (ii) a good dimensional and (iii) chemical stabilities under a large range of pO_2 at high temperature (900 °C). This work proposes a complete and rational approach for the selection and the optimisation of the membrane material for the potential CMR application. The $La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ perovskites represent a good promising material because of its high oxygen semi-permeation resulting of Sr content on A site and its good chemical stability resulting of Ga content on B site [17–20]. Kharton et al. [17] have studied the solubility limit of Ga and Sr in the $La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ perovskite system. The maximum solubility limit of Ga in the perovskite lattice decreases from 0.7 to 0.3 with the increasing of Sr substitution ration from 0.3 to 0.8. Up to this maximum solubility limit, they observe the presence of $LaSrGa_3O_7$ impurity with the $La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ perovskite phase. In order to obtain the single $La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ per-

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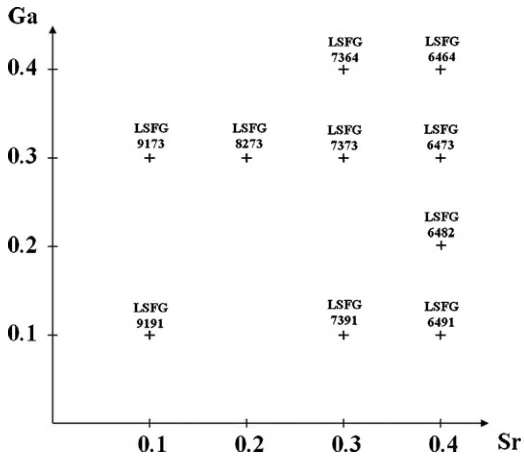

Fig. 1. $La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ studied compositions.

ovskite phase, this work focuses on formulations having Sr and Ga substitution ratios below 0.5 (or maximum solubility limit of Ga or Sr in perovskite lattice).

Besides, Kharton et al. [17] show that the oxygen semi-permeation increases with Sr and Ga substitution ratio from $LaFeO_3$ host perovskite structure, and Ishihara et al. [21] show that the maximum of oxygen semi-permeation corresponds to Ga content close to 0.3 with Sr content of 0.2. The chemical stability and thermal expansion coefficient under reducing atmosphere decrease unfortunately strongly with Sr content at high temperature [17]. In the case of this work, the particular attention is given to identify the eventual interaction effect between Sr and Ga ratios on oxygen semi-permeation and the chemical expansion of $La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ perovskite between air and nitrogen at high temperature (900 °C). Then, the large diagram of oxygen flux performances and of chemical expansion for $La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ materials is clearly presented in this paper. Finally, the best compromise between chemical stability, TEC and oxygen semi-permeation could correspond to the following composition $La_{0.8}Sr_{0.2}Fe_{0.7}Ga_{0.3}O_3$ or $La_{0.7}Sr_{0.3}Fe_{0.7}Ga_{0.3}O_3$, as suggested by Juste et al. [22].

The main objective of this paper is to identify clearly the Sr and Ga substitution ratios presenting the best compromise between high oxygen semi-permeation, low thermal expansion coefficient and good chemical stability for possible industrial application as catalytic membrane reactor. For the identification of optimal Sr and Ga contents, a methodical approach is privileged using the Asby's diagrams [23] elaborated from experimental results obtained in this work.

2. Experimental part

2.1. Powder synthesis

The perovskite powder compositions are synthesized using a classic solid state reaction (Fig. 1). Ultra-pure precursors of carbonates and metal oxides, i.e. $SrCO_3$ (99.9+%, Sigma–Aldrich Chemistry), La_2O_3 (99.99%, Sigma–Aldrich Chemistry), Fe_2O_3 (99%, Fisher Scientific) and Ga_2O_3 (99.99+%, Sigma–Aldrich Chemistry) are weighed to obtain the desired stoichiometry [24]. The powder is attrition-milled during 3 h to obtain a homogeneous mixture of precursors, separated from milling-beads and dried. The dried powders are calcined at 1100 °C during 8 h for synthesize the final perovskite phase. Then, the powders are attrition-milled a second time to obtain a monomodal grain size distribution, with a mean particles size down to 0.6 μm and a specific surface area of about $7\,m^2\,g^{-1}$.

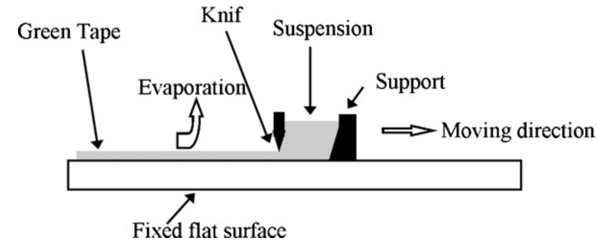

Fig. 2. Tape casting process.

For writing convenience, the perovskite formulations are designated by the abbreviations LSFG$(1-X)X(1-Y)Y$, for example LSFG8273 refer to $La_{0.8}Sr_{0.2}Fe_{0.7}Ga_{0.3}O_{3-\delta}$.

2.2. Membranes preparation

Dense $La_{(1-x)}Sr_xFe_{(1-y)}Ga_yO_{3-\delta}$ membranes used to measure oxygen permeation flux were shaped by tape casting process [25] (Fig. 2). A slurry having a specific rheological behaviour was elaborated from attrition-milled powder. A binder and a plasticizer were added to obtain a suitable cohesive and flexible green tape. The green tape was cut using a laser into disk shape pieces (Ø = 30 mm), which were stacked via heat-lamination to ensure a good planarity of the membrane. Stacks were sintered at high temperature (1250–1350 °C) to obtain membranes with a thickness of 1 mm, an apparent density higher than 95% and a grains size of 1 μm (Fig. 3). The obtained membranes are unpolished to avoid any modifications of the surface properties.

2.3. Characterizations

During attrition-milled process step, grain size distribution is controlled with a laser granulometer (Malvern Instruments Mastersizer 2000). The perovskite phase synthesis by heat treatment is qualitatively analysed using X-ray diffraction (XRD). After powder calcination and attrition-milling, the specific surface area of the perovskite powder is about $7–10\,m^2\,g^{-1}$, which is a proper value for sintering. Densities rate of sintered samples are measured by the Archimedes method. Grains size and overall microstructure obser-

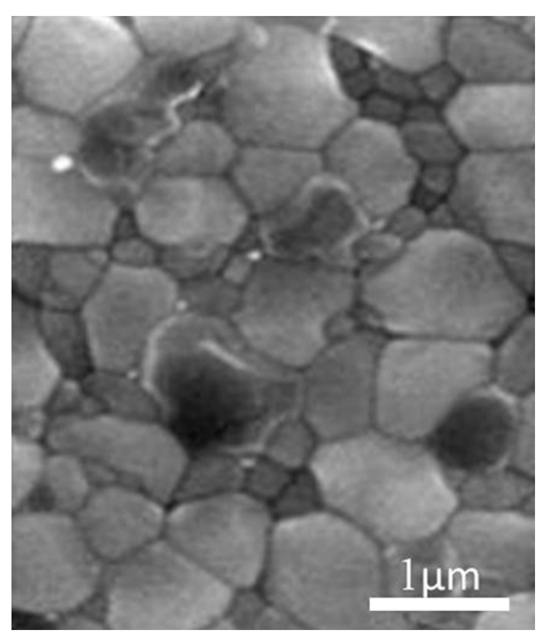

Fig. 3. Microstructure of $La_{0.8}Sr_{0.2}Fe_{0.7}Ga_{0.3}O_{3-\delta}$ dense membrane.