Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 3327–3335

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Single step reactive sintering and chemical compatibility between $La_9Sr_1Si_6O_{26.5}$ and selected cathode materials

José M. Porras-Vázquez [a,b], Lucía dos Santos-Gómez [a], Isabel Santacruz [a], Miguel A.G. Aranda [a], David Marrero-López [c], Enrique R. Losilla [a,*]

[a] Dpto. de Química Inorgánica, Cristalografía y Mineralogía, Universidad Málaga, 29071 Málaga, Spain
[b] School of Chemistry, University of Birmingham, B15 2TT Birmingham, United Kingdom
[c] Dpto. de Física Aplicada I, Laboratorio de Materiales y Superficies (Unidad Asociada al C.S.I.C.), Universidad de Málaga, 29071 Málaga, Spain

Received 4 October 2011; received in revised form 7 December 2011; accepted 17 December 2011
Available online 27 December 2011

Abstract

Apatite-type silicates are considered as promising electrolytes for solid oxide fuel cells (SOFC). However more studies on the chemical compatibility of these materials with common SOFC electrodes are required. Here, we report the synthesis of single phase $La_9Sr_1Si_6O_{26.5}$ composition by reactive sintering at 1650 °C for 10 h. Fully dense pellets showed very high oxide-anion conductivity, 25 mS cm^{-1} at 700 °C. Furthermore, the chemical compatibility of $La_9Sr_1Si_6O_{26.5}$ with some selected cathode materials has also been investigated. The lowest reaction temperatures were determined to be 1100 °C, 1000 °C and 900 °C for $La_{0.8}Sr_{0.2}MnO_{3-\delta}$, $La_2Ni_{0.8}Cu_{0.2}O_4$ and $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$, respectively. The segregation of minor amounts of SiO_2 seems to be a key limiting factor that must be overcome. Finally, these cathode materials were deposited over dense oxy-apatite pellets and the area specific resistances in symmetrical cells were determined. These values, at 700 °C, were 14.4 and 2.6 Ω cm^2 for $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$, respectively. Furthermore, the area specific resistances are notably improved 0.6 Ω cm^2 when a 50 wt.% composite of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{1.9}$ is used.

Keywords: Apatite-type electrolyte; SOFC; Chemical compatibility; Area-specific resistance

1. Introduction

Solid oxide fuel cells (SOFCs) are one of the most promising types of fuel cell for large scale power generation and combined heat and power applications. SOFCs offer many advantages over classical combustion-based power generation technologies and have been intensively studied for many years [1–4]. Yttria-stabilized zirconia, YSZ, is the oxide-conducting electrolyte used in the commercial systems. One significant disadvantage of ZrO_2-based SOFCs is the temperature of operation at which ionic conductivity is sufficiently high for practical applications, usually 800–1000 °C.

The oxy-silicates with apatite-type structure and composition $La_{10-x}(SiO_4)_6O_{2\pm\delta}$ have been proposed as alternative electrolytes for SOFCs, exhibiting higher ionic conductivity compared to the YSZ in the intermediate temperature range (500–800 °C), combined with moderate thermal expansion coefficients and very low electronic conductivity [5–11]. Numerous works, including theoretical atomistic simulations [12–14] and neutron powder diffraction [15,16], show that the ionic conduction occurs mainly via interstitial oxide migration both parallel and perpendicular to the channels [14] and it increases with the oxygen concentration in the lattice.

One of the limitations for the practical application of apatite-type silicates as solid electrolytes is the high sintering temperature, which usually ranges between 1600 and 1700 °C. Different synthesis routes have been used to obtain dense ceramics, such as hot-pressing [17], sol–gel [18,19] and freeze-dried precursors and spark-plasma sintering [20]. However, the densification route may alter the conducting properties and the relationship between ceramic microstructure and the grain boundary resistance to the oxide ion conductivity remains to be established.

* Corresponding author. Tel.: +34 952134234; fax: +34 952131870.
E-mail address: r_losilla@uma.es (E.R. Losilla).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.12.042

On the other hand, chemical incompatibility between apatite-type silicates and commonly used electrode materials has also been reported. For instance, Tsipis et al., studied the electrochemical stability of $La_{10}Si_5Al_1O_{26.5}$ with several cathode materials: $La_2Ni_{0.8}Cu_{0.2}O_{4+\delta}$, $La_2Ni_{0.8}Cu_{0.2}O_{4+\delta}$–Ag cermet, $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-\delta}$–$Ce_{0.8}Gd_{0.2}O_{2-\delta}$, and $La_{0.7}Sr_{0.3}MnO_{3-\delta}$–$Ce_{0.8}Gd_{0.2}O_{1.9}$ composites [21]. Relatively low performances of these electrodes were achieved in this work, mainly associated with surface diffusion of silica from the electrolyte to the electrodes. Ruddlesden–Popper phases, $LaSr_2Mn_{1.6}Ni_{0.4}O_{7-\delta}$, $La_2Ni_{0.5}Cu_{0.5}O_{4+\delta}$, $LaSr_2Mn_{1.6}Ni_{0.4}O_{7-\delta}$, $La_4Ni_{3-x}Cu_xO_{10-\delta}$ and $La_{3.95}Sr_{0.05}Ni_2CoO_{10-\delta}$; and perovskite phases, $SrMn_{0.6}Nb_{0.4}O_{3-\delta}$, $Sr_{0.7}Ce_{0.3}Mn_{0.9}Cr_{0.1}O_{3-\delta}$ and $Gd_{0.6}Ca_{0.4}Mn_{0.9}Ni_{0.1}O_{3-\delta}$ have also been tested with $La_{10}Si_5Al_1O_{26.5}$. However, a poor electrochemical performance was again observed, partly associated with a strong cation interdiffusion between the materials [22,23]. Bonhomme et al. tested $La_9Sr_1Si_6O_{26.5}$ with $La_{0.75}Sr_{0.25}Mn_{0.8}Co_{0.2}O_{3-\delta}$, and no reactivity between apatite and perovskite materials was observed [24]. However the electrode resistance decreased by increasing the cathode porosity and with the use of a perovskite–apatite composite as a cathode material. The same electrolyte has also been studied with $Nd_{1.95}NiO_{4+\delta}$ cathode and no apparent chemical reactivity was found between both materials [25]. Recently, Marrero-López et al. carried out a compatibility study of $La_{10}Si_{5.5}Al_{0.5}O_{26.75}$ with several electrode materials commonly used in SOFCs, i.e. $La_{0.8}Sr_{0.2}MnO_{3-\delta}$, $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, as cathodes; and NiO–CGO composite, $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ and Sr_2MgMoO_6 as anodes. In general, bulk reactivity between the electrodes and the electrolyte was not observed. However the area-specific polarisation resistance (ASR) of these electrodes increased significantly by increasing the sintering temperature, indicating some reactivity at the electrolyte/electrode interface. This effect was minimised using a ceria buffer layer between the electrolyte and electrode materials, obtaining a SOFC with relatively high performance for 100 h of operation [26].

In this work, fully dense $La_9Sr_1Si_6O_{26.5}$ ceramics were prepared by reactive sintering in a single thermal treatment with the total conductivity of 2.5×10^{-2} S cm^{-1} at 700 °C. Furthermore, its potential use as solid electrolyte for SOFC has been evaluated. Chemical compatibility and area-specific resistance, with several electrode materials, have been investigated by X-ray powder diffraction, energy dispersive spectroscopy and impedance spectroscopy measurements.

2. Experimental

2.1. Synthesis-sintering conditions

$La_9Sr_1Si_6O_{26.5}$ samples were prepared by reaction sintering, RS, using high purity oxides: La_2O_3 (Alfa, 99.999%), $SrCO_3$ (Alfa, 99.99%) and SiO_2 (ABCR, quartz powder, 99.31%). Lanthanum oxide was precalcined at 1000 °C for 2 h in order to achieve decarbonation. Reagents were ground for 30 min in an agate mortar, pelletized (500 MPa, ~10 mm diameter and ~1 mm thickness) and heated in air at 1650 °C for 5, 10 and 20 h at a heating/cooling rate of 5 °C min^{-1}. These samples are hereafter labelled as RS_t^T, where T and t indicate the sintering temperature (°C) and time (h) respectively. Compaction (% theoretical density) was calculated taking into account the mass, volume of the pellets and the crystallographic density obtained from the powder diffraction study.

$La_2Ni_{0.8}Cu_{0.2}O_{3-\delta}$ (LNC) and $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) cathode materials were prepared by sol–gel citrate precursor methods. The synthesis procedure was similar to that previously reported [27–29]. Commercial powders of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (cathode) (LSM, Praxair specialty ceramics) and $Ce_{0.8}Gd_{0.2}O_{1.9}$ (electrolyte) (CGO, Rhodia) were also used. Furthermore, a composite of 60 wt.% of LSCF and CGO was prepared by mixing the corresponding powders in an agate mortar using acetone as grinding/mixing improving agent.

2.2. Powder diffraction

X-ray powder diffraction (XRPD) patterns were recorded with a X'Pert MDP PRO diffractometer (PANalytical) equipped with a Ge(1 1 1) primary monochromator, using monochromatic Cu Kα_1 radiation (λ = 1.54059 Å) and the X'Celerator detector. The overall measurement time was approximately 4 h per pattern to have good statistics over the 10–100° (2θ) angular range, with 0.017° step size. XRPD studies were also performed to evaluate the chemical compatibility of the apatite-type electrolyte with the different electrodes. The electrolyte and electrodes powders were ground in a 1:1 wt.% ratio in an agate mortar and then fired between 700 and 1300 °C for 24 h in air. All Rietveld quantitative phase analyses (RQPA) were carried out using the GSAS suite of programs [30]. Final global optimised parameters were: background coefficients, zero-shift error, cell parameters and peak shape parameters using a pseudo-Voigt function [31] corrected for axial divergence [32]. The atomic parameters were not refined.

2.3. Microstructural characterization

The morphology of the sintered pellets was studied using a JEOL SM 840 scanning electron microscope. The ceramic surfaces were polished with diamond spray from 6 to 1 μm of diameter and then thermally etched at 50 °C below the sintering temperature for 15 min at a heating/cooling rate of 5 °C min^{-1}. Finally, the samples were gold sputtered for better image definition. Average grain size of sintered pellets was estimated from SEM micrographs using the linear intercept method from at least 30 random lines and three different micrographs with the help of image-analysis software. In addition, the microstructure between the electrode and electrolyte layers and/or any evidence of degradation after electrochemical tests were studied using a JEOL SM-6490LV scanning electron microscope combined with energy dispersive spectroscopy (EDS).

2.4. Conductivity and area-specific resistance measurements

Platinum electrodes were made by coating opposite pellet faces of the dense $La_9Sr_1Si_6O_{26.5}$ pellets with METALOR®