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ScienceDirect

Procedia Engineering 98 (2014) 101 – 104

Procedia Engineering

www.elsevier.com/locate/procedia

11th International Symposium on Systems with Fast Ionic Transport, ISSFIT 11

Interaction of $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ with $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$

Aleksander Chrzan[a]*, Maria Gazda[b], Dagmara Szymczewska[a], Piotr Jasinski[a]

[a]*Faculty of Electronics Telecommunications and Informatics, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdansk, Poland*
[b]*Faculty of Applied Physics and Mathematics, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdansk, Poland*

Abstract

Iron doped strontium titanates $SrTi_{1-x}Fe_xO_{3-\delta}$ are perovskites of versatile properties. They can be used in solid oxide fuel cells or high temperature oxygen sensors. Their reactivity with electrolyte materials, cathode buffer layer materials, other cathode materials or current collector layers has not been fully tested. In this study we use X-ray diffraction to check $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ compatibility with $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (used as electrolyte or cathode-YSZ electrolyte buffer layer), $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (typical current collector) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (typical cathode). It is shown that $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ reactivity with $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ is negligible up to 1400 °C, while reaction with $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ occurs between 1000 °C and 1200 °C leading to the formation of NiO, $SrLaFaO_4$ and possibly $La_4Ni_3O_{10}$.

Peer-review under responsibility of the Gdansk University of Technology

Keywords: strontium titanate; ceria; interface; solid oxide fuel cells;

1. Introduction

Progress in fuel cells and gas sensors resulted in a need for development of various conducting ceramics. As a result, perovskites became materials of high interest as they show versatile properties. The most popular perovskites are recognized by chemical formula ABO_3, where A and B are metal atoms, although there is some interest in layered perovskites, e.g. A_2BO_4 [1]. For many years perovskite $(La,Sr)MnO_3$ had dominated as material for cathodes in solid oxide fuel cells [2], until mixed ionic-electronic conductors were developed [3]. Since then, many different

* Corresponding author. Tel.: +48 58 347 13 23; fax: +48 58 347 17 57.
E-mail address: aleksander.chrzan@eti.pg.gda.pl

Peer-review under responsibility of the Gdansk University of Technology
doi:10.1016/j.proeng.2014.12.494

compound families have been studied, including strontium titanate $SrTiO_3$ doped with iron (STF) [4]. Although STF does not show as high electronic or ionic conductivity as some other perovskites, e.g. $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), it has drawn much attention thanks to promising electrode properties and ability to control magnitude and ratio of ionic and electronic conductivity [4]. However, the STF cathodes may require a separate current collector layer, such as $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (LNF), which exhibits sufficient electronic conductivity and moderate chromium poisoning resistance [5]. On the other hand, $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ shows almost no conductivity temperature dependence between 600 °C and 800 °C and significant oxygen partial pressure dependence which promotes it as a high temperature, resistive oxygen sensor [6]. In both applications potential reactions between STF and other device components can be an issue. In the case of gas sensors, a reaction between STF and alumina substrate leads to the formation of $SrAl_2O_4$ [6]. In the case of fuel cell cathodes STF reacts with yttria stabilized zirconia (YSZ) forming $SrZrO_3$ based phases [7]. B. Bochentyn reported that niobium doped $SrTiO_3$ is stable in the presence of YSZ or ceria in air but reacts with ceria in reducing atmosphere [8], although studies concerning gadolinium doped ceria (CGO) with STF were not carried. In this paper we investigate STF-CGO composite stability at high temperatures in order to determine if CGO electrolyte or buffer layer may be applied in direct contact with STF. Apart of this, we study STF compatibility with LNF (current collector material) and LSCF, which can be used as a dense layer on the cathode/electrolyte interface [9].

2. Experimental

STF, CGO, LNF and LSCF powders were prepared by a modified Pechini method. Following reagents were used during syntheses: $Sr(NO_3)_2$ (99%, *Sigma-Aldrich, USA*), $Fe(NO_3)_3{\times}9H_2O$ (98%, *Sigma-Aldrich, USA*), $Ti[O(CH_2)_3CH_3]_4$ (97%, *Sigma-Aldrich, USA*), $La(NO_3)_3{\times}6H_2O$ (99%, *Fluka, Austria*), $Ni(NO_3)_2{\times}6H_2O$ (97%, *Fluka, Austria*), $Co(NO_3)_2{\times}6H_2O$ (98%, *Sigma-Aldrich, USA*), $Gd(NO_3)_3{\times}6H_2O$ (99.9%, *Sigma-Aldrich, USA*), $Ce(NO_3)_3{\times}6H_2O$ (99%, *Sigma-Aldrich, USA*), $C_2H_6O_2$ (98.5%, *POCH, Poland*), $C_6H_8O_7$ (99%, *Sigma-Aldrich*). To synthesise STF citric acid was dissolved in distilled water. The solution was then stirred and heated on a hot plate to 70 °C. Next, iron nitrate and strontium nitrate were added. After complete dissolution of the nitrates ethylene glycol was added and left on a hot plate for 24 h for water to evaporate. Titanium citrate was prepared separately by mixing ethylene glycol with citric acid and titanium (IV) butoxide. When the solutions became homogenous they were mixed and heated for 24 h at 180 °C on a hot plate and fired for 2h at 500 °C in a furnace. CGO, LNF and LSCF were prepared by a dissolution of appropriate nitrates in water with citric acid. After an addition of ethylene glycol solutions were also stirred, heated and ultimately fired at 500°C in a furnace. In all cases the molar ratio of cations : citric acid : ethylene glycol was 1:2.2:20. After the firing all powders were calcined at 1000 °C for 10 h in an air atmosphere.

The obtained powders were mixed maintaining weight ratio 50:50 in a mortar and pressed uniaxially under a pressure of 100 MPa to form pellets. The pellets were sintered at 1000 °C,1200 °C or 1400 °C for 10 h. Table 1 lists all of the prepared samples.

Table 1. Types of the prepared samples.

Composition	Not sintered	Sintered at 1000 °C	Sintered at 1200 °C	Sintered at 1400 °C
STF-LNF	STF/LNF_0	STF/LNF_1000	STF/LNF_1200	STF/LNF_1400
STF-CGO	STF/CGO_0	STF/CGO_1000	STF/CGO_1200	STF/CGO_1400
STF-LSCF	STF/LSCF_0	STF/LSCF_1000	STF/LSCF_1200	STF/LSCF_1400

Pellets densities were measured using a fluid displacement method with kerosene as a working liquid. Then pellets were ground in mortar. Structural information was obtained using X-ray diffraction (Philips X'Pert Pro) with Cu Kα radiation at room temperature. HighScore Plus (*PANalytical*) software was used in order to match observed peaks with patterns from database.

3. Results and discussion

Pallets open porosities are listed in Table 2. In the case of all three compositions sintering at 1000 °C results in large porosity ranging between 30% and 40%. Obtained samples were fragile. Samples sintered at 1200 °C are far more durable but still exhibit open porosities above 20% with minimal porosity of 22% for the STF-LSCF mixture. Similarly, in the case of the sintering at 1400 °C, the STF-LSCF sample was the densest with almost no open pores. The results show that the addition of LSCF to STF enhances sinterability.

Table 2. Open porosity of sintered samples.

Composition	Sintered at 1000 °C	Sintered at 1200 °C	Sintered at 1400 °C
STF-LNF	36%	26%	7%
STF-CGO	33%	28%	7%
STF-LSCF	39%	22%	1%

X-ray diffraction was carried in order to check the phase composition of the samples. Fig. 1 shows XRD patterns of all STF-CGO and STF-LSCF samples. In Fig. 1 (A) peaks corresponding to the STF and CGO phase are marked with dots and triangles, respectively. Regardless of the applied sintering temperature, no additional peaks were observed. The only effect visible in XRD patterns is a slight narrowing of peaks at 1200 °C which is connected to the grain growth. In Fig. 1 (B) peaks corresponding to STF and LSCF phase are marked only with dots, since these two phases have undistinguishable patterns. There is no evidence of reaction between STF and LSCF. The narrowing of peaks after sintering at 1200 °C is also visible. Therefore it can be deduced that neither CGO nor LSCF create any new phases with different crystal structure at 1400 °C, when in contact with STF.

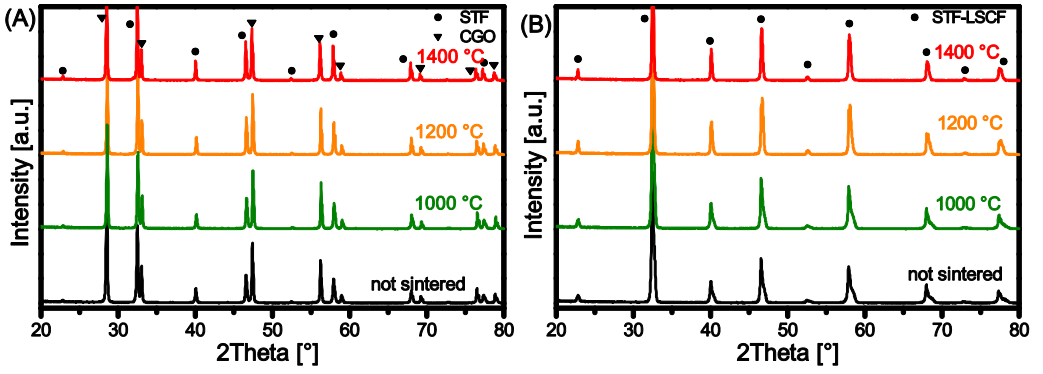

Fig. 1. XRD patterns of the STF-CGO mixture (A) and the STF-LSCF mixture (B). None of them shows additional phases.

Fig. 2 shows XRD patterns of STF-LNF samples after sintering at different temperatures. Sample sintered at 1000 °C exhibits no additional peaks in comparison to raw powders. After sintering at 1200 °C and 1400 °C the peaks corresponding to $SrLaFeO_4$ and NiO occurred. Additionally, it can be seen that the peak at 47.0° corresponding to LNF exclusively, disappeared or overlapped with STF peak at 46.6°. This indicates that the LNF stoichiometry changed towards the higher iron content. It was shown by Niwa et al. [10] that LNF can be unstable at 1200 °C leading to the formation of NiO and $La_4Ni_3O_{10}$. $La_4Ni_3O_{10}$ exhibits the XRD pattern similar to that of $SrLaFeO_4$ thus it can also be present in the sample. On the other hand, a pure LNF sample sintered at 1200 °C was prepared and no additional phases were visible in the measured XRD pattern (not shown in this paper). Thus, it can be concluded that STF reacts with LNF at 1200 °C or causes its decomposition.

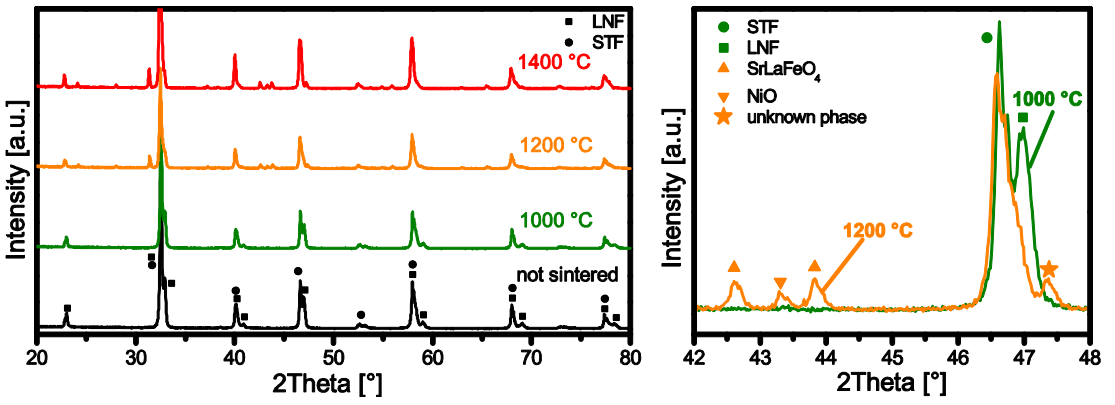

Fig. 2. XRD patterns of the STF-LNF mixture.

4. Conclusions

STF-LNF, STF-CGO and STF-LSCF composites were obtained from powders prepared by a modified Pechini method and sintered at 1000, 1200 or 1400 °C. Obtained pellets porosities were measured using fluid displacement method and characterized by X-ray diffraction. The XRD analysis revealed that STF-CGO and STF-LSCF samples remained as separate phases after sintering at up to 1400 °C, which indicates that these materials can be used simultaneously. In the case of STF-LNF composite the reactions between phases occurred between 1000 °C and 1200 °C leading to the formation of NiO, $SrLaFeO_4$, possibly $La_4Ni_3O_{10}$ and other, unidentified phases. Based on obtained samples porosities, STF mixed with LSCF has the best sintering properties of all three compositions.

Acknowledgements

This work is partly supported by project founded by National Science Centre Poland based on decision DEC-2012/05/B/ST7/02153.

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