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Insight into the synthesis and electrical properties of alkali-earth-substituted Gd_3GaO_6 oxide-ion and proton conductors

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ARTICLE INFO

Article history:

Received 6 April 2016

Received in revised form

1 June 2016

Accepted 7 June 2016

Available online 15 July 2016

Keywords:

New conductors

SOFC

PCFC

Electrolytes

Stability tests

Mixed conduction

ABSTRACT

Novel ionic conductors were prepared by substituting Ca^{2+} and Sr^{2+} for Gd^{3+} in Gd_3GaO_6 . A microwave-assisted combustion technique was used to synthesize these compounds at 900 °C. SEM observations showed that both substituents promote grain growth during sintering. XRD proved that the $Gd_{3-x}(Ca,Sr)_xGaO_{6-x/2}$ solid solutions are formed up to $x = 0.10$. Below 600 °C, the level of conductivity under wet Ar is higher than that of measured under dry atmospheres, thereby demonstrating the contribution of proton defects to the overall conductivity. The highest level of proton conduction, i.e. $\sigma_{600^\circ C} = 1 \times 10^{-3} \text{ S cm}^{-1}$, was measured for $Gd_{2.9}Sr_{0.1}GaO_{5.95}$ at 600 °C in wet Ar. At higher temperatures, only oxygen ions contribute to the conductivity. At 800 °C, a total oxide-ion conductivity of $\sigma_{800^\circ C} = 1 \times 10^{-2} \text{ S cm}^{-1}$ was measured for the highest substitution level, i.e. $x = 0.10$. In both temperature ranges, activation energy associated with ionic transport decreases with the Me content as a result of an increase in grain size. Stability tests were successfully achieved as the structure of materials remains unchanged after different treatment under severe conditions. Conductivity measurements under varying oxygen partial pressures demonstrated that materials are purely oxide-ion conductors up to $pO_2 = 1 \times 10^{-5} \text{ atm}$. At higher pO_2 , a p-type contribution appears.

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Introduction

Owing to their high operating temperatures (>800 °C), solid oxide fuel cells (SOFCs) would play an important role in producing clean energy in the immediate future as they have the

potential to offer a high chemical to electrical energy conversion efficiency as well as the co-production of high-quality process heat [1,2]. These operating conditions meet with the use of a wide range of fuels including hydrocarbons, coal gas, biomass, hydrogen, and other renewable fuels [3–5]. Nevertheless, the time-to-market for SOFCs is continuously delayed

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<http://dx.doi.org/10.1016/j.ijhydene.2016.06.090>

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as they face with fast-acting deterioration through redox cycling in temperature [6–8], in addition to a manufacturing cost still too high [9,10]. Thus, the objective of researches in this area primarily concerns these last two points, which essentially requires a lowering of the operating temperature. Firstly, this would allow the use of metal alloys as interconnects, until now the cause of a significant additional cost, and would increase the lifetime of SOFCs by reducing the reactivity between materials in contact. For this reason, extensive research works have been continuously carried out in order to develop fully functional and cheaper SOFCs able to operate for longer time by playing on material composition.

Proton-conducting solid electrolytes are in a central position among high temperature ion conductors since the weak molecular weight of protons is associated with a low migration energy and thus to a potentially higher conductivity at intermediate temperature. For the time being, only few proton-conducting materials seem to fulfil the conditions for competing with the best oxygen ion conductors. Acceptor-substituted barium zirconates and cerates [11–13], and solid solutions from both of them [14–16], exhibiting a perovskite structure, are among the best proton-conducting oxide materials [17] known to date. In recent year, there has been a growing interest for next generation of proton-conducting materials containing tetrahedral moieties such as rare-earth ortho-tantalates and ortho-niobates in the series $\text{Ln}_{1-x}\text{Ca}_x\text{REO}_{4-x/2}$ (RE = rare earth; M = Ta, Nb, P) [18–20], lanthanum barium gallates $\text{La}_{1-x}\text{Ba}_{1+x}\text{M}'\text{O}_{4-x/2}$ (M' = Al, Ga) [21–24] and apatite type $\text{La}_{9.33+x}\text{Si}_6\text{O}_{26+3x/2}$ [25,26]. Among the series of materials above-mentioned, the best proton conductivity ($\sim 1 \times 10^{-4} \text{ S cm}^{-1}$ at 600 °C) has been reported in $\text{La}_{0.8}\text{Ba}_{1.2}\text{GaO}_{3.9}$ [21]. The crystal structure of these materials was investigated that led to a better knowledge of oxygen diffusion pathways as well as proton incorporation and migration [24]. Upon removal of an oxygen from a $[\text{GaO}_4]^{5-}$ unit, the oxide-ion vacancy is accommodated by the creation of a $[\text{Ga}_2\text{O}_7]^{8-}$ group with the neighbouring tetrahedral entity so that all the Ga sites maintain their tetrahedral coordination [19,27,28]. The reactivity of the oxygen vacancy with a water molecule leads to the break up of the $[\text{Ga}_2\text{O}_7]^{8-}$ entity to form two $[\text{GaO}_4\text{H}]^{4-}$ groups connected by means of the proton incorporated. The mobility of the proton from one $[\text{GaO}_4]^{5-}$ unit to another is then ensured by a H-bonding-mediated transfer.

Recently, acceptor-doped Nd_3GaO_6 compounds have been presented as good oxygen-ion conductors in spite of their very low substituting levels [29]. RE_3GaO_6 (RE = rare-earth) compounds were discovered by Schneider et al. [30] and Caruthers et al. [31] and have been particularly studied for their optical [32–34] and magnetic [35] properties. In the present study, the potentialities of acceptor-doped Gd_3GaO_6 materials as proton conducting electrolytes was evaluated. The Gd_3GaO_6 compound crystallizes in an orthorhombic cell ($a = 8.9928(1) \text{ \AA}$, $b = 11.2809(2) \text{ \AA}$, $c = 5.4812(1) \text{ \AA}$) [36] with a non-centrosymmetrical space group ($Cmc2_1$). Its structure is built up from two kinds of edge-sharing GdO_7 polyhedra forming a three-dimensional framework to which distorted GaO_4 tetrahedra, elongated along the c axis, are bonded via vertexes (Fig. 1).

The Gd^{3+} cations are localised in two different asymmetrical sites of sevenfold coordination and Ga are in distorted

oxygen tetrahedral [32,36]. The Ga–O bond lengths are in the range 1.83(2)–1.89(2) Å and the Gd(1)–O(2) distance is about 2.32 Å, O(2) being the only one oxygen to be linked with gadolinium cation. Given these structural features, that are similar to those of observed in LaBaGaO_4 , attempts were made to apply the above-mentioned approach to the Gd_3GaO_6 compound by substituting Ca^{2+} and Sr^{2+} for Gd^{3+} to form both $\text{Gd}_{3-x}\text{Me}_x\text{GaO}_{6-x/2}$ (Me = Ca, Sr) solid solutions. With regard to this latter chemical formulation, $x/(3-x)$ represents the atomic fraction of Me^{2+} on the gadolinium site. As a result of the large coordination number of gadolinium, only the formation of vacancies on oxygen sites O(2) coordinated to Gd^{3+} cations can be expected. Furthermore, binary or more complex oxides containing rare-earths are, in every case, hydrophilic and then prone to react with water vapour. This would lead to believe that the incorporation of proton defect (OH^*) in the structure of $\text{Gd}_{3-x}\text{Me}_x\text{GaO}_{6-x/2}$ (Me = Ca, Sr) compounds would be then possible.

In the present study, the synthesis, structural characteristics, stability in varying conditions and transport properties of alkali-earth-substituted Gd_3GaO_6 materials are reported. Nanopowders were synthesized using a microwave-assisted combustion (MWAC) technique derived from the Pechini method [37,38]. Since they are likely to affect transport properties of materials, the chemical composition and microstructure of the sintered products were characterised by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Since adjoining materials should be thermo-mechanically compatible in a SOFC or PCFC, their coefficient of thermal expansion were evaluated by high-temperature XRD. Oxide-ion and proton conductivities were measured in both dry and humidified argon atmospheres as a function of the temperature. The influence of the nature and ionic radius of the substituent on the ionic conductivity are discussed and results are compared with those obtained in previous studies [29]. In view of applying these materials for the co-electrolysis of steam and CO_2 to produce syngas, short duration stability ($\sim 50 \text{ h}$) tests were carried out under wet $\text{Ar}-5\% \text{ H}_2$ and wet CO_2 . At last, the temperature-dependences of the total conductivity were investigated by electrochemical impedance spectroscopy as a function of $p\text{O}_2$ while ensuring a constant partial pressure of water of 0.024 atm.

Experimental

Nanopowders of a series of compounds in the $\text{Gd}_{3-x}\text{Me}_x\text{GaO}_{6-x/2}$ (Me = Ca, Sr; $0 \leq x \leq 0.10$) solid solution were synthesized by a soft chemical method based on a microwave-assisted synthesis. In this process, materials are directly heated by radiation leading to a higher temperature homogeneity in the reaction mixture compared with indirect heating using a thermal source. Starting materials were commercial anhydrous $\text{Me}(\text{NO}_3)_2$ (Me = Ca, Sr; Sigma Aldrich, 99.9%), $\text{Ga}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Strem Chemicals, 99.9%). All nitrates were successively dissolved in 150 mL of deionized water and mixed until a transparent solution was obtained. Citric acid (Alfa Aesar, 99%) of chemical formulation $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ was used both as a chelating agent and a fuel; it was dissolved separately in deionized water in a proportion

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